Valorisation of olive and wine industry co-products techno-economic analysis and life cycle assessment

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Abstract

In this work, a valorisation of olive and wine industry co-products (olive pomace and grape marc, respectively) through different thermochemical processes is studied. First, a characterization of olive pomace and grape marc is made in order to evaluate which thermochemical process is more suitable for each type of biomass. Then a life cycle assessment (LCA) of olive pomace valorisation is made in order to assess the environmental impacts. Several scenarios of biomass conversion process were considered: combustion, gasification and hydrothermal carbonization (HTC) followed by gasification to generate electricity; and pyrolysis to produce biochar, bio-oil and syngas. Finally, a techno-economic analysis was performed for each mentioned scenario in order to evaluate the feasibility and to conclude which scenario is more economically advantageous.

Results suggest that the valorisation of olive pomace might be more suitable through the gasification process and grape marc through the pyrolysis process. From the LCA was possible to conclude that combustion scenario has the biggest environmental impact. In comparison, gasification, HTC and pyrolysis presented a lower impact with a value of 69.45%, 50.96% and 40.97% respectively, considering combustion as 100% impact. Regarding the techno-economic analysis, several scenarios have promising results with some scenarios with payback periods inferior to 5 years. The only exception is HTC followed by gasification which in current days is not competitive with other technologies. Overall gasification and pyrolysis are better alternative to the valorisation of olive pomace and grape marc. Also drying has an important role in terms of environmental impact and economic viability.

Keywords:

Grape Marc; Olive Pomace; Thermochemical Processes; LCA; Techno-Economic Analysis

Resumo

Neste trabalho, a valorização de produtos residuais da produção de azeite e vinho (bagaço da azeitona e bagaço da uva, respectivamente) através de diferentes processos termoquimicos é analisado. Em primeiro lugar, é feita uma caracterização dos produtos residuais de modo a que se possa concluir qual dos processos termoquimicos é mais adequado para cada tipo de biomassa. De seguida, uma análise de ciclo de vida (ACV) da valorização bagaço da azeitona é feita para medir os seus impactos ambientais. Vários cenários são considerados: combustão, gaseificação, carbonização hidrotérmica (HTC) seguida de gaseificação para gerar eletricidade; e pirólise para produzir biochar, bio-óleo e 'syngas'. Por fim, uma análise técnico-económica é realizada para os mesmos cenários mencionados de modo a determinar a viabilidade dos mesmos e concluir qual cenário é mais vantajoso economicamente.

Os resultados indicam que a gaseificação será mais adequada para a valorização do bagaço da azeitona e que a pirólise será mais adequada para o bagaço da uva. Através da ACV pode-se concluir que a combustão tem o maior impacto ambiental. Comparativamente, gaseificação, HTC e pirólise tem um impacto menor com um valor de 69.45%, 50.96% and 40.97% respectivamente, considerando impacto da combustão como 100%. Relativamente à análise técnico-económica, vários cenários apresentaram resultados promisores, apresentando períodos de retorno inferior a 5 anos. A única exceção foi HTC seguida de gaseificação que nos tempos atuais não é competitivo com as restantes tecnologias. Deste modo, a gaseificação e a pirólise apresentam-se como as melhores alternativas para a valorização destes resíduos. O processo de secagem mostrou ter um impacto importante em termos ambientais e económicos

Palavras Chave:

Bagaço da uva; Bagaço da azeitona, Processos Termoquimicos, ACV; Análise Técnico Económica

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Glossary

2PEOP	Two-Phase Exhausted Olive Pomace
2POP	Two-Phase Olive Pomace
3PEOP	Three-Phase Exhausted Olive Pomace
3POP	Three-Phase Olive Pomace
C	Carbon
C_2H_4	Ethylene
C_2H_6	Ethane
Ca	Calcium
CCS	Carbon Storage Technology
CH_4	Methane
CHP	Combined Heat and Power
Cl	Chlorine
CO_2	Carbon Dioxide
DOP	Dry Olive Pomace
EGM	Exhausted Grape Marc
EOP	Exhausted Olive Pomace
ER	Equivalence Ratio
EU	European Union
FC	Fixed Carbon
GHG	Greenhouse Gases
GM	Grape marc
H	Hydrogen
H_2	Hydrogen
H_2O	Water
HHV	Higher Heating Value
IGCC	Integrated Gasification Combined Cycle
K	Potassium
LCA	Life Cycle Assessment
LHV	Lower Heating Value
Mg	Magnesium
N	Nitrogen
N_2O	Nitrous Gases
NO_x	Nitric Oxide
O	Oxygen
OMWW	Olive Mill Wastewater

OP	Olive Pomace
OTB	Olive Tree Pruning
OTPB	Olive Tree Biomass from Pruning
P	Phosphorus
S	Sulphur
SO_x	Sulphur Oxide
VM	Volatile Matter

1 Introduction

Access to energy is a key pillar for human economic development and poverty alleviation. Ensuring everyone has sufficient access is an ongoing and pressing challenge for global development. Thanks to significant efforts across the world, electrification rate reached 89% in 2017 (from 83% in 2010). The progress amounts to an average annual electrification rate of 0.8 percentage points, and newly gained access for more than 920 million people since 2016 [1]. This has resulted in an abrupt increase in consumption of energy over the last decades (Figure 1). Tanger et al [2] predicts from 2010 until 2035 energy consumption is expected to increase by 53%.

However, our energy systems also have important impacts, and with the increase of energy consumption these impacts will tend to increase. More than 80 % of the world's energy comes from fossil fuels (coal, oil and gas) which produce greenhouse gases (GHG) such as CO_2, CH_4, N_2O and fluorinated gases, which are the fundamental driver of global climate change. In order meet our global climate targets and avoid dangerous climate change, the world needs a significant and concerted transition in its energy sources [3].

Balancing the challenge between development and environment therefore provide us with an ultimate goal of ensuring everyone has access to enough sustainable energy to maintain a high standard of living [3].

In order to reduce our global GHG emissions, the world has to transition from an energy system dominated by fossil fuels to a low- carbon one (this is what most countries have set long term targets to achieve within the Paris Climate Agreement). With the exception of carbon capture and storage technology (CCS), there are are two options to achieve this: renewable technologies (including bioenergy, hydropower, solar, wind, geothermal and marine energy) and nuclear energy. Both of these options produce very low CO_2 emission per unit of energy compared with fossil fuels. This process of transitioning from fossil fuel to low- carbon energy sources is designated by 'decarbonization' [3].

'Decarbonization' has already started in many countries, the share of renewable in total final energy consumption increased at the fastest rate since 2012 and reached almost 17.8% in 2016. Concerning electricity production, 26% of the global energy production came from renewable energy resources. In Portugal for instance in 2019, the electricity generated from renewable technologies was 27.828 TWh which accounts for 55.2% of the total electricity generation in Portugal (50.401 TWh) [1,4].

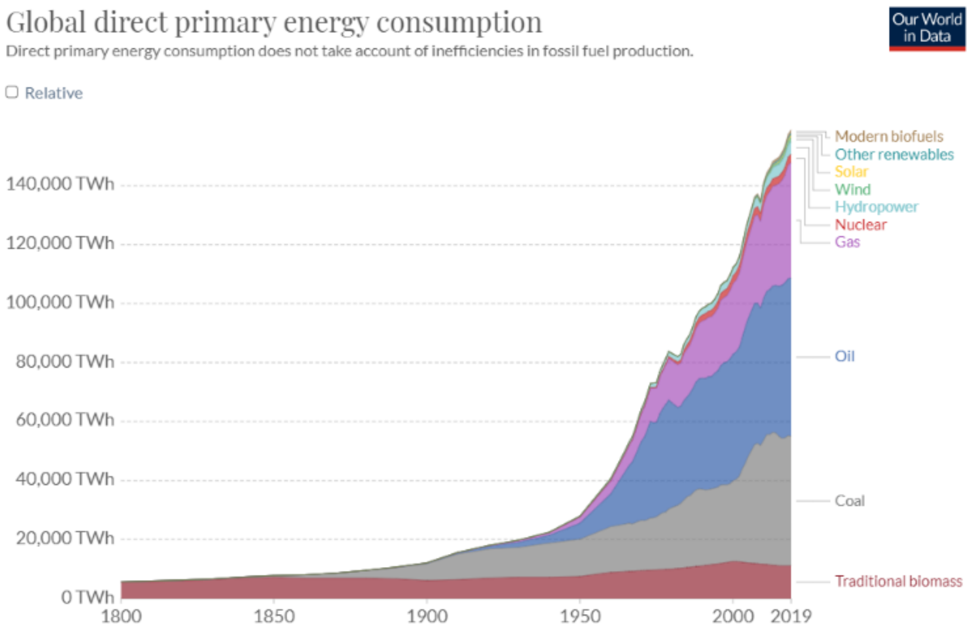

Figure 1- Evolution of global direct primary energy consumption over the decades [3]

1.1- Bioenergy

In 2017, the gross final energy consumption was 370 EJ – an increase of 2% over the past year. The share of renewable energy in the gross final energy was 17.8 % as stated before. Among renewable energy sources, bioenergy (energy from bio-based sources) is the largest. In 2017, bioenergy accounted for 70% of the renewable energy consumption (Figure 2). The contribution of bioenergy share has been decreasing by a few percentage points (approximately 0.5%- 1%) annually partly due to decreasing use of traditional biomass sources. Traditional use of biomass (e.g for cooking) is linked to significant negative health impacts and it is widely used in underdeveloped countries but has had a reduction in the last years [1,5].

Renewable energy technologies have made considerable progress in decarbonizing the electricity sector. In 2017, renewable electricity covered about 26% of the electricity generated globally. In 2017, electricity from biomass based sources was the 3rd largest renewable electricity source after hydropower and wind, 596 TWh of biopower was generated globally, which is an increase of 25 TWh (+4%) over the previous year [5].

Almost half of energy consumption is in the form of heat, which includes space heating for residential and commercial establishments, heating demand for industrial processes and heat for cooking. One of the most widely use renewable energy source for derived heating is biomass which has a 96% share in the renewable heat market globally (24% share of the total). From biomass, in 2017 42.92 EJ of heat was generated globally which is a decrease of about 0.58 EJ over the previous year, this decrease is mainly caused by a reduction of traditional uses of biomass [5].

Regarding transports, biomass-based fuels such as bioethanol and biodiesel are a sustainable and renewable option for replacing fossil oil in the transport sector. The share of renewable remains the lowest in this sector: It has increased year on year to reach 3.3% in 2016. Biofuels constitute the majority of renewable energy used for transport. The share of biofuels in the transport sector in 2017 was about 3% with a total contribution of 3.5 EJ [1,5].

In terms of sources of biomass, there are three major groups [5]:

- **Forestry sector-** It is the largest contributor to the bioenergy mix globally. Forestry products including charcoal, fuelwood, pellets and woodchips account for more than 85% of all the biomass used energy purposes.
- **Municipal and Industrial Waste-** It is utilized for energy predominantly in urban areas. In 2017, domestic supply of waste to bioenergy was 2.51 EJ, 58% was in the form of municipal waste while the remaining was industrial waste to energy.
- **Agriculture Sector –** This is one of the most promising sectors for growth in the bioenergy production in the form of residues from agriculture sector. Currently, the sector contributes less than 3% to the total bioenergy production. Data shows that utilizing the residues from all major crops for energy can generate approx. 4.3 billion tonnes (low estimate) to 9.4 billion tonnes (high estimate) annually around the world. Utilizing standard energy conversion factors, the theoretical energy potential from residues can be in the range of 17.8 EJ to 82.3 EJ. Energy generation from agricultural residues could meet about 3-14% of the total energy supply globally.

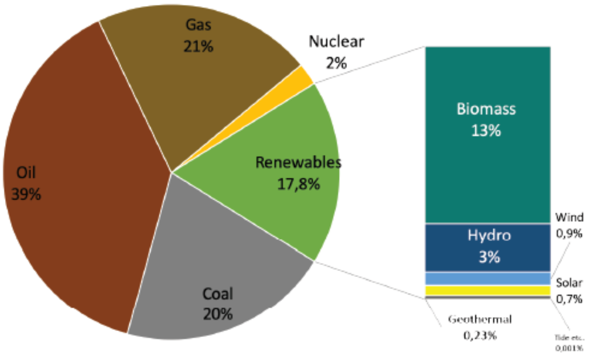

Figure 2- Global direct primary energy consumption [5]

For instance, in Portugal in a previous study was estimated that in current year (2020) from the total energy consumption from biomass 12.69% would be to generate electricity, 70.76% for heating and cooling and 16.55% related to the transport sector (Table 1). Concerning electricity 5.7% of the total energy produced in 2019 came from biomass, the total of this cut corresponded to 2.9 TWh [4,6].

The current status of biomass resources in Portugal shows that the potential estimated for various sectors of the country is 42,489.7 GWh/year. However all the energy is coming almost from the same type of biomass, resulting in a overexploited biomass resource such as forest biomass, which if all the predicted biomass power plants enter in running phase will result in a deficit of forest biomass around 4.0 Mtonne/year. One alternative that could solve this problem is turning our efforts to new sources of biomass, such as the ones coming from the agricultural sector that has a potential of over 4528 GWh/ year [6].

Table 1- Bioenergy production by sector estimation for 2020 [6]

Energy sector	Energy (GWh)
Electricity	4719
Heating and cooling	26302.5
Transportation	6150,9

1.1.1- Agricultural Biomass

In Portugal, the biomass is defined by Decree-Law nº 127/2013 as the set of products consisting in whole or in part of vegetable matter derived from agriculture or forestry, which can be used as fuel for the purpose of recovering its energy content, as well as certain forms of waste when used as fuel. The agricultural biomass mainly comes from agricultural production by-products and the agro-food industry: wine, horticulture, olive oil production, dried fruit, cereals and forage. Some examples of this type of biomass are straw cereals, olive pits/stones and remaining pomace resultant from olive oil extraction, solid wastes generated during the pruning of olive trees and vineyards (leaves and small branches), dried fruits shell. Some of those wastes generated are already used for heat production by direct combustion, but with no records of such use, which weigh down their accounting [6,7].

In developing countries most of biomass residues are not utilized or treated but left in the field to decompose naturally or be openly burned. These waste residues generated from crops such as sugarcane, rice, ground and coffee nuts could be used as a fuel source. Agriculture biomass is lignocellulosic, which means is constituted by cellulose, hemicelluloses and lignin rich residues which can be used for the production of chemicals resins and enzymes. Sugar bagasse and less commonly rice husk and wheat chaff also have uses, but despite this, there is little valorisation of this biomass waste and this important resource remains significantly under-utilized. Thus, as only a small amount of the biomass waste generated becomes for industrial applications and electricity generation the remaining adversely impacts the atmosphere, surface and ground water quality and causes pestilence. The increasing production of agricultural biomass waste also is a risk to human health. Unregulated land disposal pollutes surface and ground waters, inducing eutrophication, and when incorporated into soil, biomass-induced microflora stimulate the production and emissions of NO and N_2O which have considerably greater global impact than CO_2 [7].

In the leading countries in the agricultural sector the production of agricultural waste amount to 3.3 Gt/ year (Table 2) and this number will tend to increase has agricultural productivity in 2050 is projected to be 60 % higher than in 2005/2007, so it necessary to do something to use or treat these valuables feedstock materials [7].

Table 2- Cumulative generation potential of agricultural residues in the leading countries in the agricultural sector [7]

Country of origin	Amount of residue (Mt fresh weight)
China	716
United States of America	682
India	605
Europe	580
Brasil	451
Argentina	148
Canada	105
Total	3287

However, agricultural biomass has some disadvantages associated [8,9]:

- Low energy density due to its reduced lower calorific value
- Biomass production, collection, transport and pre- treatment may involve high costs.
- Larger spatial distribution of the raw material, leading to greater logistics
- Variability in the composition of residual biomass or mixtures of biomass can also be problematic in terms of operation

On the other side, it has also several advantages associated [8,9]:

- Avoidance of emission of N_2O by natural fermentation
- Co-production of fertilizer
- High abundance
- When compared to coal, biomass usually contains lower levels of ash, N and S, thus contributing to the mitigation of CH_4, CO_2, NO_x and SO_x emissions but may also present higher O and H content, as well as increased levels of Ca, Mg, K and Cl
- Lower acquisition cost than fossil fuels

The agricultural sector, just like other sectors, has attracted the attention of EU, to green growth. In the European Parliament resolution on the future of the Common Agricultural Policy after 2013, it is believed that thanks to improvements in production factors linked to advances in knowledge, farmers are well placed to contribute to green growth and respond to the energy crisis through the development of green energy in such forms of biomass, bio-waste, biogas, second generation biofuels and small scale wind solar and hydro energy, which also help create new green job opportunities [6].

In Portugal there is a high abundance of agricultural land and production. Table 3 allows verifying that the main crops produced in Portugal are forage, crops for industry and cereal grain. However, in terms of agriculture area the major one is olive followed by cereal grain, forage and vineyard [6].

Portugal has two agricultural industries that have huge potential in terms of biomass residues which are the wine and olive industry. Wine has a production of over 6 million hectolitres per year and the production of around 179 thousand tonnes of solid waste and 1.34 million tonnes of wine wastewater [10]. Olive oil industry produce around 800 thousand tonnes of olives annually which produce around 1.25 million tonnes of solid waste and 374 thousand tonnes of olive mill wastewater [11].

Table 3- Main crops in Portugal 2014 [6]

Species	Area (ha)	Production (tonnes)
Cereal Grain	30195	1333256
Dried leguminous vegetables	4040	2333
Potato	27214	539872
Major crops for industry	33230	1340361
Fresh vegetables	36667	988650
Main forage crops	233747	6197582
Main fresh fruits	43293	574936
Berry fruit	1385	6934
Main subtropical fruits	3340	43464
Citrus fruits	19804	304016
Main nuts	67561	31982
Vineyard	178986	818871
Olive grove	352350	455374

1.2 Wine Industry

Grape wine represents one of the most important alcoholic beverages in the world. While traditionally wine production and consumption was concentrated in the European continent currently over 67 nations produce, export, import and consume wine. In 2018, the total worldwide wine production was around 279 MhL. Figure 3 shows that the world production of wine has been quite steady in the last two decades. The major producers of wine are Italy, France and Spain with 17.1%, 14.8% and 13.1% respectively of market share in 2018 [10].

Portugal produced 6.1 MhL of wine in 2018 which is 2.2% of the total wine production in the world. The country has been producing around the same amount of wine in the last two decades, with slight decrease in the last years as Table 4 highlights. Therefore, it is possible to conclude that Portugal has been and is one of the major players in this industry [10].

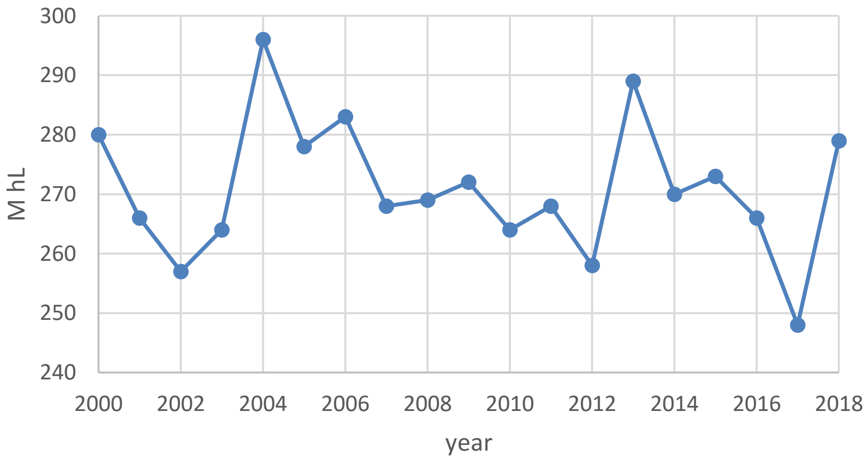

Figure 3- Wine production worldwide in the last two decades [10]

Table 4- Wine production in Portugal in the last two decades [10]

Year	Wine production Portugal (MhL)	Market share (%)
2000	6.7	2.4%
2001	7.8	2.9%
2002	6.7	2.6%
2003	7.3	2.8%
2004	7.5	2.5%
2005	7.3	2.6%
2006	7.5	2.7%
2007	6.1	2.3%
2008	5.7	2.1%
2009	5.9	2.2%
2010	7.1	2.7%
2011	5.6	2.1%
2012	6.3	2.5%
2013	6.2	2.2%
2014	6.2	2.3%
2015	7	2.6%
2016	6	2.3%
2017	6.7	2.7%
2018	6.1	2.2%

1.2.1 Wine Making Process and Wastes

The winemaking process involves the generation of a significant amount of waste and wastewater. These residues should be addressed for recycling or treatment before being returned to the environment [12].

The main environmental impacts associated with wineries include water pollution, soil degradation, damage to vegetation and air emissions, noise from vehicles and equipment. The wine sector, like others needs to minimize its environmental impact using technologies adapted to environmental constraints, allowing the reduction of water consumption, the recovery of by-products and the reduction of waste as foreseen in ISO 14000. ISO 14001 addresses various aspects of environmental management and pollution prevention. It provides fundamental principles for the implementation of Environmental Management System, reducing the environmental risks and remain accessible to all companies. The application of best available techniques and best environmental practices are also fostered by IPPC Directive 2008/1/EC as it ensures a high level of protection for the environment as a whole, balancing out the costs to the operator and the benefits to the environment. Furthermore, it is also essential to implement efficient wastewater treatment systems adapted to each wineries specificities particularly with regard to its size and skilled labour [12].

In brief, wine making follows a multiple step process including destemming, crushing and fermentation, pumping over and pressing [13].

The grapes are normally delivered to the winery during autumn (August- October) in the north hemisphere. The process of partial or total removal of stems from the grapes, destemming, is applied for white and rose wines. Then the grapes are separated depending on whether they can or cannot be crashed, so pulp and juice are released. Crushing is done mechanically, since former manual process may spit the skin or simply crack it. The grapes come through a pneumatic press and produce must and solid residues. The produced amount of must is about 80 L per 100 kg of grapes. The fermentation stage of red wine is done on solid parts; the fermenting must is in contact with the seeds, skins and sometimes even stems, while for white wine the solid parts are not that much involved and the decanting stages must be different. The conversion of grapes into alcohol and CO_2 by yeasts takes place in a stainless steel, cement or wooden fermentation tanks after pressing since the solid parts should be in contact with the must to impart colour, odour and texture [13].

After fermentation decanting takes place. During this process, the wine is separated from the produced wine lees and is fed by pumps to empty tanks that are filled completely for further stabilization. The next stage is maturation where decanted wine is kept in maximum capacity filled vessels. After maturation and stabilization, wine is clarified using chemical agents (fining) for quality improvement and then is decanted into empty thanks. After the desired timed period for settling has elapsed wine is bottled on transportation tanks and distributed to the contact points. Figure 4 shows schematically the wine making process, where is possible to see the major differences between the production of red and white wine and also the type of waste produced by each process [13].

Solid winery waste can be divided into two main categories: solid and liquid waste. Solid winery waste, namely grape stalks, grape marc and grape seeds varies in chemical composition and texture. Grape stalks are obtained the destemming process. They are rich in lignin, cellulose, N and K, having a high agronomic value and are used for composting. Grape stalks have been found to highly effective for soils, as they have low organic matter content. Grape seeds are very rich in linoleic acid and omega 6 fatty acids, with up to 6% phenolics. Grape marc consists of grape skin, stalks, seeds and moisture collected after grape juiced extraction (pressing). It is characterized by high organic content, low nitrogen and phosphorus concentrations and its rich in carbohydrates and phenolic compounds [13].

Winery waste, however, is not limited to waste generated at the first stages of grape harvesting and initial stages of wine formulation. Waste known as lees composed of solid and liquid fractions is generated during fermentation and maturation stages. The solid part is comprised of the remains precipitated at the bottom of the tanks, mainly consisting of bacterial biomass, undissolved carbohydrates of hemi-or cellulosic nature, phenolic compounds, lignin proteins, metals, inorganic salts, organic acid salts and other materials such as pips, fruit skins and grape seeds. The liquid phase is represented mainly by the spent fermentation broth, often rich in organic acids and ethanol. Vinasses, a by-product of the wine lees are defined as liquid fraction waste deriving from the distillation process of the wine lees, which is carried out to recover ethanol and elaborate distilled beverages [13].

Finally, a vast amount of waste, in the form of wastewater (liquid waste) is generated during the further stages of processing, including fermentation, storage and maturation, clarification, decanting and bottling. It contains remains of grape pulp, skin and seeds and different compounds used in the filtration, precipitation and cleaning processes. The main problem of all these organic materials is their disposal and treatment due to their seasonal character and some characteristics which difficult their management[13].

Oliveira and Duarte [12] states that solid waste and wastewater are mainly produced during the harvest period, corresponding to 74% and 87% respectively and one tonne of processed grape approximately produce 0.13 t marc, 0.06 t lees, 0.03 t of stalks and 1.65 m^3 of wastewater.

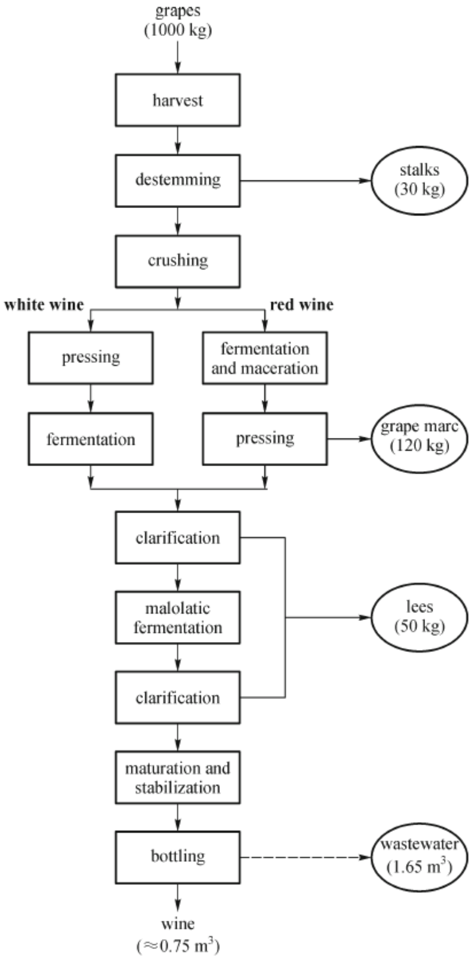

Figure 4- Wine making process [12]

Therefore, as mentioned before in Portugal last year with a production of 6.1 Miohl of wine, approximately were produced 179 thousand tonnes of solid waste and 1.34 million tonnes of wine wastewater., the management of these wastes has become an environmental concern and thus different strategies have been developed in order to reduce its environmental impact and recycle these waste products.

The current applications used nowadays are summarized in Table 5 excepted for grape marc which is going to be detailed on the next section.

Table 5- Wine waste valorisation applications

Waste	Applications	Ref
Grape seeds	Extraction of oil Pharmaceutical/cosmetic products with phenolic content Composting	[13,14]
Grape stalks	Lyphilization and extraction- polyphenol production Composting	[12]
Wine lees	Solubilization and precipitation- tartaric acid production Production of ethanol and distilled beverages Co-composting	[12,13,15]
Wine wastewater	Anaerobic digestion- biogas production Treatment in a conventional municipal activated sludge	[12,16]

1.2.1.1- Grape Marc Current Uses and Applications

Grape marc is major solid residue from the wine making process and it contains unfermented sugar, alcohol, polyphenols, tannins, pigments and other valuable products. Being a natural plant rich in lignocellulosic compounds, grape marc is also a promising feedstock for renewable energy production. However, despite having such a great potential, advanced technologies to exploit this have not been widely adopted in wineries and allied industries [17].

In terms of current and future applications, it is possible to identify the following categories [17]:

1. **Extraction of useful chemical components-** Grapes contain an abundance of different component that are extracted during winemaking. The remaining grape marc serves as a good source of phytochemicals including an array of phenolics, pigments and antioxidants. Also, the recovery of tartaric acid and lignocelluloses is a well-established process.
2. **Biological treatment of grape marc for value added products-** This includes the alcoholic fermentation for beverage spirit, production of bioethanol and biogas and of alternative fermentation by- products.
3. **Agricultural and environmental applications of grape marc-** This includes composting and soil amendment, animal feed and biosorbent for environmental remediation.
4. **Thermochemical conversion technology-** Grape marc has a significant potential as bioenergy feedstock. Several thermochemical process options are available to undertake this conversion, but as with any biomass, the optimal conversion technology will be chiefly influenced by the technical and economic considerations relating the fuel properties of the feedstock being evaluated. Figure 5 shows the scheme of different type of pathways for thermal conversion of biomass, including combustion, gasification and pyrolysis. Depending on the technology used different outputs may be produced: heat energy, shaft work and electricity, or biofuels products such as syngas, biochar and bioliquids.

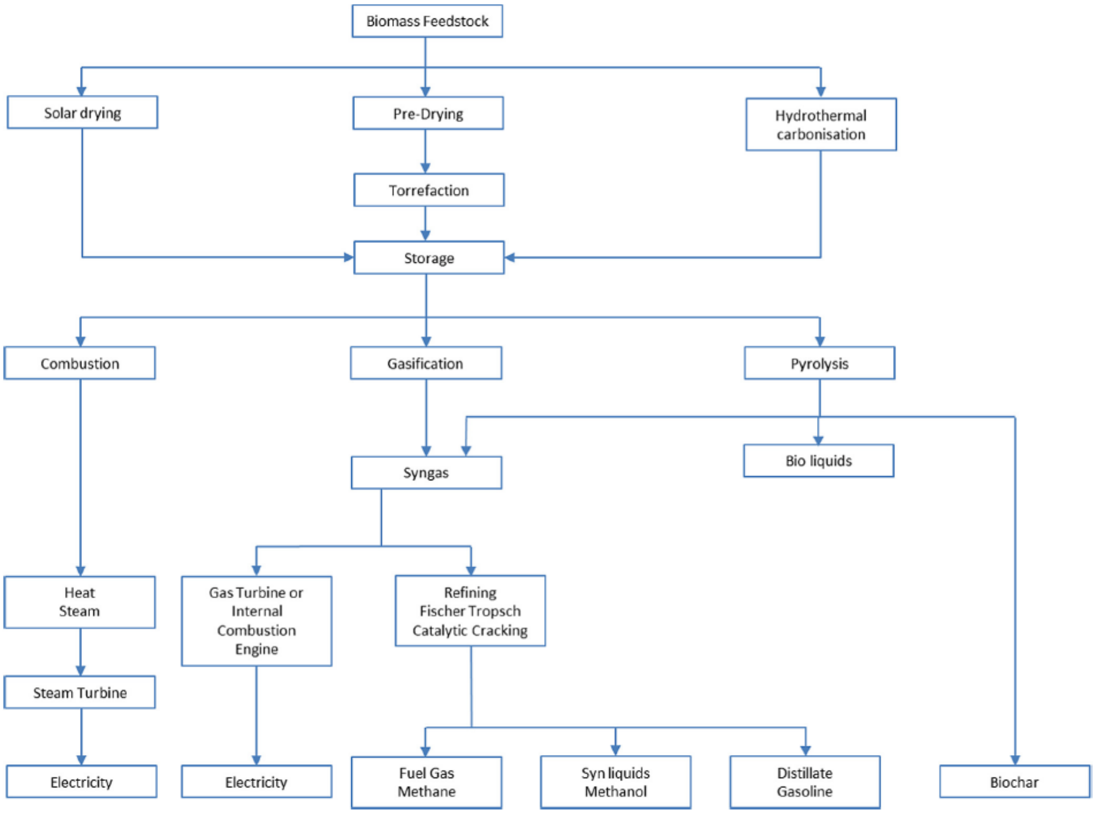

Figure 5- Thermochemical paths of biomass [17]

In Portugal grape marc is used to produced distillate beverages, use for composting or animal feeding [18]. One alternative to the current uses of the biomass could be turning into thermochemical conversion technologies that could be a solution to the deficit of forest biomass that the country is currently facing.

1.3 Olive Industry

Olive oil is one of the main food products in Mediterranean countries. Regular consumption of olive oil in an equilibrated diet that has been recognized as a positive factor for a healthier life and also attracted interest of many researchers. As a consequence, olive trees have spread to other parts of the world and currently, more than 40 countries produce olive oil. In 2019 were produced 21 million tonnes of olives. Nevertheless, Mediterranean countries still represent more than 95% of olive oil production worldwide. Spain is the leading country, both in terms of land devoted to olive tree cultivation and olive oil production, with 2.5 million hectares and 9.18 million tonnes of olives produced which represent 43.54% of the worldwide production [11,19].

Portugal with over 360 000 hectares under cultivation in 2019 produced 791 410 tonnes of olives which accounts of 3.75% of the total production and is a market share substantially higher than wine (2.2%). This value is having a steady growth since the early 20s (Figure 6) and consequently Portugal is the eight major producer of olive in the world [11,20].

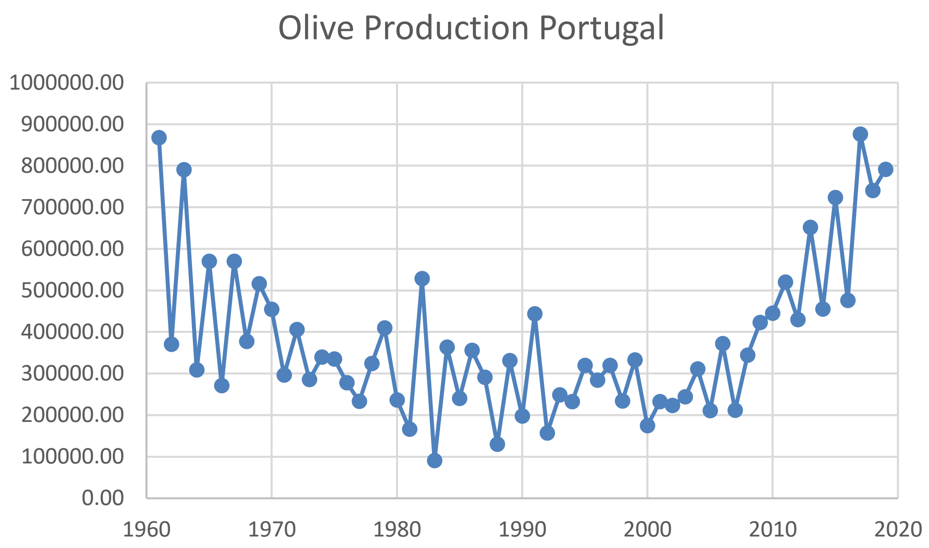

Figure 6- Evolution of olive production in Portugal since de 60s [11]

1.3.1 Olive Oil Processing and Wastes

In addition to the main product, cultivation of olive trees and olive oil processes generate a large amount of different types of lignocellulosic materials, which in general do not have industrial applications and must be eliminated. Olive orchards, olive mills and pomace olive oil extracting industries are the three locations in which olive derived biomass is found [19].

The olive oil production process starts on the olive orchards where pruning of olive trees is performed every two years (annual pruning is also practiced) to eliminate unproductive, old branches as well as to improve olive production, resulting in a large amount of biomass. A wide range of 1.5-3 annual tonnes of pruning biomass per hectare has been reported, or in terms of olive weight 600 kg of pruning biomass are produced by tonne of olive processed [19,21].

The next stage is the harvesting where olives are picked and brought to the second location, the olive mills, where other types of biomass are produced. When olives are collected, many leaves from the trees are picked and separated by a fan in an early separating step. Olive leaves represent approximately 4-7% of olives by weight [19].

The next steps occur at the olive mills and include milling, mixing, or malaxation, and separation in a horizontal centrifuge or decanter. The olives are washed and are ground into a pulp using a revolving mill, usually constructed with stainless steel or granite. The entire olive, including the pit, is pressed until it becomes a paste, which is then whipped, adding water. Next come the phase to separate solid from liquid, either by traditional process, or by continuous system (centrifuge): 3-phase process or 2- phase process [19,22]. (17,18) The differences between the processes are the following ones:

- Two phase process where two fractions are obtained in the decanter and then olive oil is further treated in a vertical centrifuge to eliminate the remaining crushed olives as well as the olive pomace (2POP); used in Spain and Portugal [19].

- Three phase process used in the majority of other countries in which water is added and olive paste is separated into three fractions: oil, olive pomace and wastewater containing a high contaminant charge of sugars, phenols and other soluble [19].
- The traditional process where the ground paste is place between pressing mats and is subjected to pressure, to expel the oil mix (mixture of oil and water). The mixture is then poured into a vat or holding tank. This allowed to rest so that gravity and different densities come into play, separating the oil from the water. This method has been abandoned by most of countries and producers and nowadays just some small production facilities might use this method [22].

The main differences between the extracted raw materials are due to water content. Two-phase pomace has a moisture approximately 50-70% and contains a certain amount of sugars as a result of the presence of vegetation water, while traditional pomace of between 25-30% in the pressing system, and 40-60% in three-phase centrifugal systems [19,22].

Finally, in the pomace olive oil extracting industries, pomace is usually treated to extract the residual oil it contains, including the removal of crushed stones. The olive oil production process is represented schematically in Figure 7 [19].

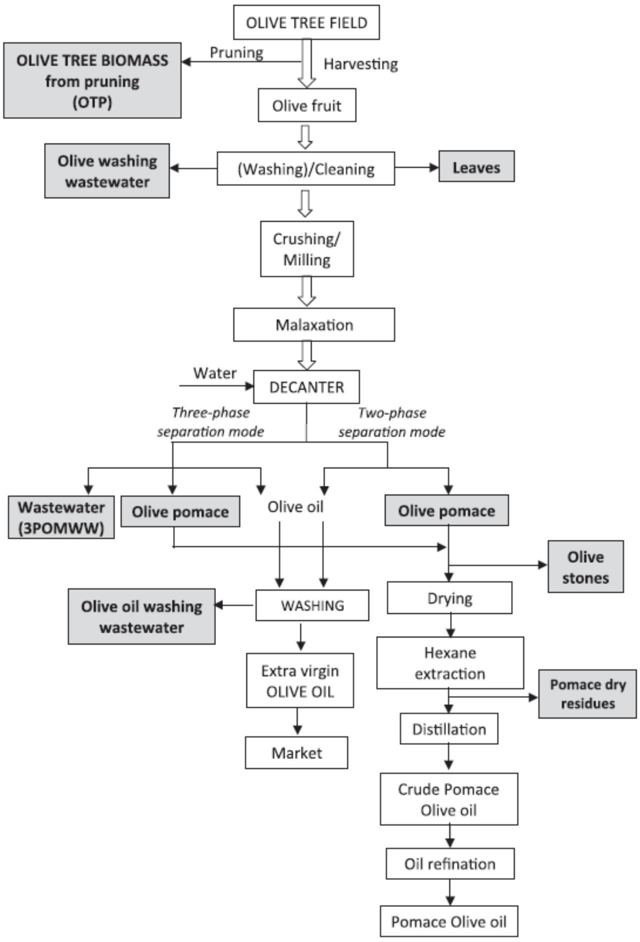

Figure 7- Olive oil making process [19]

The residual biomass of olive processing with potential energy use is classified in two groups. The first group is constituted by residual biomass produced during olive tree culture (pruning and harvest residues). The second group is constituted by residual biomass during the various stages of olive oil extraction [21].

From the first group, there are [19,21]:

- **Olive tree biomass from pruning (OTPB)** which includes leaves (approximately 25% by weight), thin branches (approximately 50 % by weight) and thick branches or wood (approximately 25% by weight), although the proportions may vary depending on the culture conditions, tree age, production and/ or local pruning practice. OTPB, like other biomasses of lignocellulosic composition is a complex mixture of cellulose, hemicellulose and lignin, the three main components, as well as a significant amount of soluble compounds (extractives) and ash.
- **Olive leaves** which are lignocellulosic residues mainly found in two different process points from the process of olive production. They are first found during olive tree pruning (OTP), in which they contribute 25% of the pruning but are usually burned or ground together with the remainder of the OTP by-products, ie branches. The second point is in the olive oil production facility, where leaves are separated from the fruits using a blower machine in the early steps of olive cleaning

From the second group [19,21]:

- **Olive pomace** is constituted of crushed olive stones, together with vegetation water, process water and all materials coming from the fruit except the olive oil, which represents the main residues of the olive oil extraction process by weight, 450-800 kg for each tonne of olive processed. It is important to note that the composition of the olive pomace may differ depending on the production process. Besides water, olive pomace contains carbohydrates lipids (remaining oil), polyphenols, and a number of metals and salts with an average pH of 4.8-5.2. Furthermore, it possesses a high chemical and biological oxygen demand due to its high organic charge
- **Olive Stones** are recovered in the olive oil extraction process after oil separation and represent approximately 8-16% by weight of olive fruit
- **Olive mill wastewater (OMWW)** is generated at three different points: during olive fruits cleaning; from the horizontal centrifuge (decanter during the three-phase separation step; and during the washing process from the secondary centrifuge of virgin olive oil. OMWW contains sugars (1.6-4%) and phenolic compounds responsible for difficulty of proper treatment. This causes environmental concerns as OMWW has a high biological and chemical oxygen demand namely in the range 35-110 and 45-179 g/L respectively.
- **Exhausted olive pomace (EOP)** is generated when olive pomace is subjected to solvent extraction of residual oil. This process consists of drying and solid liquid extraction with hexane. The final solid by-product generated is described in the literature with different names, such as orujillo, extracted or exhausted olive pomace, or dry olive cake.

Table 6 quantifies the number of residues produced in the production of olive oil worldwide and in Portugal. On the other hand, Table 7 it is possible to identify the current applications more common of the wastes produced, except for olive pomace and EOP which are going to be more detailed in the next section.

Table 6- Amount of residues from olive oil production

Type of product	Worldwide (MT)	Portugal (KT)	Ref
Olives	21	791.41	[19,21]
OTPB	12.6-25.2	474.85-949.69	[19]
Olive leaves	0.84-1.47	31.66-55.40	[19,21]
Olive pomace	9.45-16.8	356.13-633.13	[19,21]
Olive stones	1.68-3.36	63.31-126,63	[19,21]
OMWW	8.4-10.5	351.56-395.71	[19]
EOP	3.78-5.25	142.45-197.85	[19]

Table 7- Olive oil waste valorisation applications

Waste	Applications	Ref
OTPB	Burning in the fields Firewood Combustion in powerplants	[19]
Olive leaves	Burning Animal feed Composting	[19]
Olive stones	Thermal use in domestic boilers or in cogeneration plants Extraction of antioxidants Production of ethanol Production of bio absorbents	[19,21]
OMWW	Extraction of antioxidants Additives for cosmetics Production of biogas	[19,22]

1.3.1.1 Olive Pomace and EOP Current Uses and Applications

Olive pomace is the main solid residue coming from extraction of olive oil itself, as mentioned before, olive pomace is produced either by a two or three phase separation system. The corresponding pomaces are usually referred as two or three phase olive pomaces (2POP and 3POP respectively), with the amount of water being the main difference. Currently pomace is used to recover residual olive oil, which is estimated at 2% of the pomace weight. This process consists of drying and solid liquid extraction with hexane. Then, pomace oil is separated by distillation, because of the large difference in volatility between oil and hexane. Pomace- derived olive oil usually sent to a refining process to produce edible oil (different from the virgin olive oil obtained in the decanter). After oil extraction, the exhausted solid obtained is called EOP accounting for 18-25% of the pomace dry weight [19].

EOP has similar composition as olive pomace, except regarding the water and oil that have been removed. Therefore, the potentials applications which have been the object of research for olive pomace may also be considered for EOP [19].

Therefore, using the four categories mentioned on the section 1.2.1.1 it is possible to consider the following applications for these types of biomasses mentioned in Table 8

Table 8- Applications of olive pomace and EOP

Categories	Applications	Ref
Extraction of useful chemicals	Production of antioxidants Extraction of ingredients to use in ceramic materials	[19]
Biological treatment	Bioethanol and hydrogen production Anaerobic digestion to produce biogas	[19]
Agricultural and environmental applications	Composting Animal feed	[19]
Thermochemical applications	Torrefaction or hydrothermal carbonization Combustion or combustion or pyrolysis	[19]

As stated, there are several options for the treatment of these by products, however most of the producers use the pomace to recover residual oil and the EOP is normally used as fuel in drying oven or steam boilers due to its thermal capacity.

In Portugal the production process used is the Two-phase extraction method, the extracted olive pomace is used to recover the residual oil and the EOP is used as biomass to recover energy. Once again thermochemical processes could be the solution to the imbalance of forestry biomass happening in the country and also to have cleaner and more efficient ways of producing energy [18].

1.4 Life Cycle Assessment (LCA) and Techno-Economic Analysis

In order to assess and compare different processes of valorisation of residual biomass it is possible to use different approaches and criterias. Two possible approaches that gives us important insights are the LCA approach and techno-economic analysis.

LCA is a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and materials used and releases to the environment; and to identify and evaluate opportunities which lead to environmental improvements [23].

The main components linked to the LCA are: goal and scope (which identify the purpose of the LCA and the expected results of the study, and determining the limits and assumptions based on the definition of the objective), the life cycle inventory (which quantifies the material and the relevant energy employees and the produced emissions), impact analysis (which allows to evaluate the possible environmental impacts associated with the system's inputs and outputs) and improvement analysis (which also allows to help in the decision-making process, thus leading to choose the best option and find solution to reduce environmental impacts) [24].

Techno-economic assessment is a cost benefit comparison using different methods. It intends to evaluate the likelihood of different technology scales and applications; evaluate the economic feasibility of a specific project; investigate cash flows over the lifetime; and also to compare the economic quality of different technology applications providing the same service. Using this type of analysis is possible to make a sustained decision about a project [25].

1.5 Objective

The main goal of this dissertation is to evaluate if the valorisation of grape marc and olive pomace or EOP using thermochemical processes could be a viable alternative to the current practices. Also if could be a solution for the deficit of forestry biomass in Portugal, as being an alternative feedstock. For that, two approaches will be used: LCA of the different thermochemical processes to assess which has a lower environmental impact and also a techno-economic analysis to evaluate the feasibility of each alternative.

Thus, the intermediate objectives needed to be accomplished in order to fulfil the purpose above are:

- Characterization of the grape marc and olive pomace based on a literature review and gathering of data. Ultimate and proximate analysis are important to assess which thermochemical process is more suitable.
- Elaborate a literature review with state of art different thermochemical processes as an alternative to combustion, which includes HTC, gasification and pyrolysis
- Elaborate a literature review with state of art of LCA and techno-economic analysis of combustion, gasification, HTC and pyrolysis.
- Identify base on the literature review for each by-product and thermochemical processes which are the best operating conditions.
- LCA analysis of different thermochemical processes based on data from previous studies. The software used is called SimaPro and the processes compared are: Combustion, gasification, HTC followed by gasification and pyrolysis
- Techno-economic analysis of the same processes compared in LCA analysis

In the end, the other objective is to identify which process is the more suitable alternative for grape marc and olive pomace current uses both in terms of environmental impacts and techno-economic feasibility.

1.6 Structure

The dissertation is structure in 5 chapters:

1. **Introduction:** Background and contextualization of the problem, the objectives to be achieved and the structure of this document are presented
2. **State of Art:** The literature review is focused on studies of grape marc and olive pomace subjected to different thermochemical processes, including combustion, gasification, HTC and pyrolysis. A literature review of LCA and techno-economic analysis of the different thermochemical processes was considered.

3. **Methodology:** The methods used in the dissertation in order to achieve the goals proposed are presented in this chapter. This is divided in 3 sections, the first related to grape marc and olive pomace characterization, then the LCA methodology implemented and finally the techno-economic analysis methods used.
4. **Results and Discussion:** The results of grape marc and olive pomace characterization, life cycle impact assessment and techno-economic analysis are reported, analysed and commented.
5. **Conclusion and Future Work:** The main conclusions of the thesis and its final remarks are discussed, and the future work to be developed.

2. State of Art

This chapter is devoted to reviewing the tools considered fit to accomplish the objectives of this dissertation.

The chapter is divided in six sections. The first four are relative to the thermochemical processes considered: gasification, HTC, pyrolysis and HTC followed by gasification.

The fifth and sixth sections are relative to the LCA studies and techno-economic analysis regarding grape marc and olive pomace

Figure 8 highlights the range of temperatures used for the different experiences found in the literature for grape marc and olive pomace.

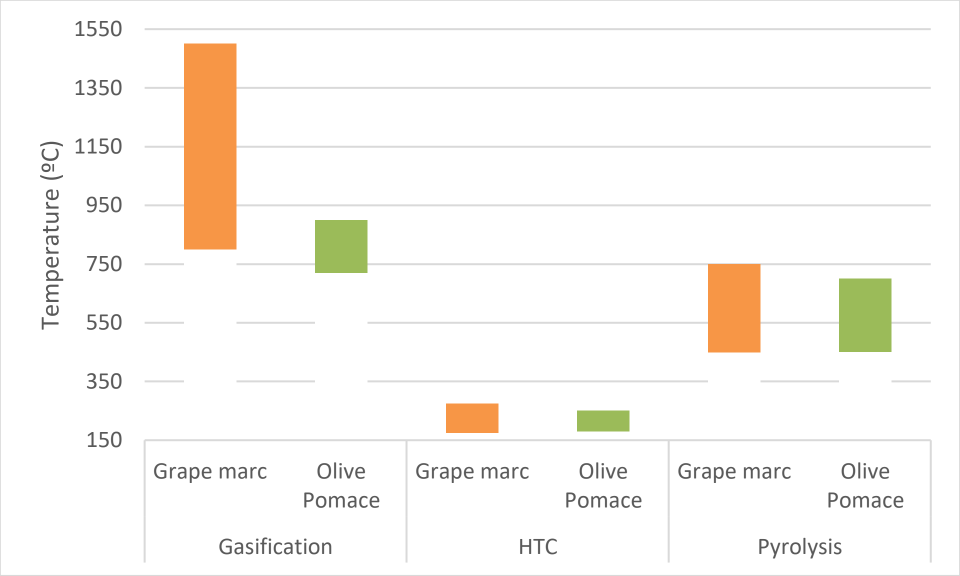

Figure 8- Range of temperatures for different thermochemical processes regarding grape marc and olive pomace

2.1 Gasification

Gasification is the partial oxidation of biomass fuel at high temperatures (typically in the range of 800-1000 ºC) to form a low caloric value combustible mixture together with char and ash. The produced gas is called syngas and it is composed by CO, H_2, CH_4, CO_2, H_2O, N_2 and other hydrocarbon such as C_2H_4 and C_2H_6. The other substances produced apart from the gas are ash, coal particles, tar and oils. Syngas can be combusted to generate heat or electricity (via shaft work in a gas turbine or internal combustion gas engine) or refined to produce hydrogen gas or liquid transport fuels via Ficher-Tropsch synthesis. In this respect, biomass gasification is more attractive final biomass conversion option for grape marc and olive pomace than combustion, as the conversion products are more versatile and cost effective when coupled to an internal combustion engine for electricity production [17,26].

The gasification process takes place within a reactor and can be divided into two main stages. In the first stage occur the pyrolysis process, as a consequence of the thermochemical decomposition of biomass at temperatures above 350 ºC, the volatiles components of the fuel are released. These vapours contain gaseous such as hydrocarbons, H, CO, CO_2, H_2O and tar. The solid fraction from the pyrolysis process (char) is an agglomerate of complex nature consisting of carbon, ash, sulphur compounds and volatile hydrocarbons. In the second stage, the gasification of the pyrolysis products is achieved, and the reaction with the gasifying agent (air, steam oxygen or a mixture of these) leads to an increase of fuel concentration, and to the conversion of char. This last stage is the most important, it is the slower phase, hence it affects the kinetics of the whole process and, consequently, both the sizing and the performance of the reactor [17,26]. The Key equilibrium reaction which occur in the gasification units are [17]:

Partial oxidation: $C+\frac{1}{2}\mathrm{O}_2 \rightleftarrows \mathrm{CO} \quad \Delta\mathrm{H}=-268\,\mathrm{kJ/mol}$ (1)

Complete oxidation: $C+\ \mathrm{O}_2 \rightleftarrows CO_2 \quad \Delta\mathrm{H}=-406\,\mathrm{kJ/mol}$ (2)

Water gas reaction: $C+\ \mathrm{H_2O} \rightleftarrows CO+H_2 \quad \Delta\mathrm{H}=+118\,\mathrm{kJ/mol}$ (3)

Energy release comes from both partial and complete oxidation (combustion), which then drives the gasification and water gas reactions. Further useful reactions involving carbon monoxide, hydrogen and steam can then ensue [17]:

Water gas shift reaction: $C+\ \mathrm{H_2O} \rightleftarrows CO_2+H_2 \quad \Delta\mathrm{H}=-42\,\mathrm{kJ/mol}$ (4)

Methane formation: $Co+\ 3\mathrm{H}_2 \rightleftarrows CH_4+H_2\mathrm{o} \quad \Delta\mathrm{H}=-88\,\mathrm{kJ/mol}$ (5)

The composition of syngas that is produced can be optimized by the selection of the gasifier operation mode, gasifying agent and modulating of operating conditions such as gas flowrate temperature. The choice of the gasifying agent is very important, because it highly affects the characteristics of the syngas. Both the composition and calorific value varies greatly with the gasifying agent; air gasification presents a lower heating value (LHV) of the syngas in the order of 4-5 MJ/ N-m^3, and a large volume of N_2, while pure oxygen gasification allows LHV ranging between 12 and 18 MJ/ N-m^3 [17,26].

Gasification of Grape Marc

In the literature there were not found many relevant studies of gasification of grape marc. The state of art of this section is the following:

1. Experimental tests in entrained flow gasifier has been carried out by Hernández et al [27] in order to evaluate the effect of the biomass particle size and the space residence time on the gasifier performance and the produced gas quality. Three types of biomass fuels were assessed including grape marc after ethanol extraction, known as exhausted grape marc (EGM), and a coal coke blend. Gasification was performed with air at 1050 ºC. The results highlight that a reduction in the fuel particle size leads to an improvement in the gas quality and thus to a higher producer gas heating value, cold gas efficiency, H_2/CO ratio and fuel conversion are also enhanced. Longer space residence times (defined as the reactor volume divided by the air volumetric flow) inside the reactor cause a significant benefit for the gasification process, since all the parameters (CO and H_2 content, gas LHV, cold gas efficiency, and fuel conversion) are improved. The combined effect of higher temperature and residence time has a positive effect on the gasification process, leading to an upgrade of the gas composition and higher gasification efficiencies. All the biomass fuels tested

showed a better behaviour as compared to coal-coke, since they led to higher quality producer gas and higher gasification efficiencies, due to their higher reactivity.

2. Link et al [28] focused on the effect of leaching a pre-treatment on the gasification of wine and grape marc residue. The results of the untreated grape marc are reported on Table 9.

The studies referred used air as gasifying agent and the syngas LHV obtained was in the range expected (Table 9).

Table 9- Result of different studies of gasification of grape marc

Sample	Conditions	Syngas yield	Syngas LHV	Ref
EGM dried to 7.79% moisture	Gas: air T: 1050 ºC	2.5-2.8 (kg gas/kg EGM)	3.5-5.1 (MJ/kg)	[27]
Grape marc dried to 8.5% moisture	Gas: air T: 800 ºC		5.92 (MJ/m^3)	[28]

Gasification of Olive Pomace

Concerning olive pomace there were found more relevant studies. The first worth mentioning was performed by Ducom et al [29] which the purpose of the research was to analyse and compare three different olive mill solid residues by complementary techniques such as Fourier transform infrared spectroscopy and thermochemical methods, in order to characterize these residues as potential fuels for gasification.

The three samples use were: dried 3POP from Tunisia; dried 3POP from France; and 2POP from Spain.

The report provides the following requirements and specifications for fuels feeding a circulating fluidized bed gasifier:

- Moisture content ≤ 35% w/w
- LHV in order of 10-20 MJ/kg
- ash content ≤ 25%
- sulphur ≤ 1% w/w, chlorine ≤ 2% w/w, mercury ≤ 1.5 mg/kg
- ash melting ≥ 960 ºC
- VM in the range of 76-86 %

The typical humidity of solid olive mill waste is usually higher than recommended, ranging between 40-45% w/w for three phase processes and 55-70 % w/w for two-phase olive mill waste. Therefore, a drying step would be necessary. Ultimate and proximate analysis performed in this study showed that the samples considered in this study matched with the requirements. Ash content, sulphur, chlorine and mercury met the requirements. The LHV between 18 and 21 MJ/kg, was in the high range of requirements. The ash melting point was not measured in this study. Finally, volatile matter (VM) contents were also in the favourable range for 3POP samples and slightly below in 2POP with 73.5%.

Regarding biochemical composition, several authors reported that thermochemical decomposition of biomass with a higher content in cellulose and hemicelluloses was faster and produced a larger fraction of gaseous products than that of a biomass with higher lignin content, which leads to a larger fraction of solids products. Moreover, biomass with higher percentage of cellulose and hemicelluloses were reported to produce more CO and CH_4 and less H_2 and CO_2 than lignin. Biomass with high lignin content produces more H_2 than others. The high content of benzene rings in lignin explains the high char yield. Therefore, the use of biomass with high lignin content is recommended for the production of char for energy or other industrial or agronomic applications. The samples studied from this work were found to have moderate lignin content of 13-16% w/w.

In terms of experimental gasification studies, this work highlights the three following ones:

1. Puig-Gamero et al [30] assessed the gasification performance of olive pomace, coal, petcoke and their binary and ternary blends was carried out by means of TGA (thermogravimetric analysis) coupled with mass spectrometry. The thermochemical behaviour of the raw materials was function of their composition and inorganic content. Olive pomace had a low ash content, high volatile content and low moisture (after pre-drying process). Moreover, olive pomace presented the highest reactivity. On the other hand, olive pomace presented the highest H_2, CO, CO_2 and CH_4.
2. A thermodynamic model of combined heat and power (CHP) plant, fed by syngas produced by gasification of dry olive pomace is study by Borello et al [26]. Olive pomace is dried using an air flow having a temperature of 45 ºC and heated by the exhaust gases until it reaches a moisture of 17 %. The gasification was performed with an equivalent ratio (ER) of 0.2 and the LHV of the gas obtained is about 4.5 MJ/kg that is in the range of typical values of air gasification. Tar was 0.07 % of the final composition
3. Tamošiunas et al [31] investigated the potential of olive biomass waste for energy recovery in terms of syngas production using thermal arc plasma gasification method. The sample was EOP. The experiments were carried out at various operational parameters and the syngas obtain was mainly composed of CO, H_2 and CO_2 with the highest concentrations of 41.17%, 13.06% and 13.48% respectively. The produced synthesis gas had a LHV of 6.09 MJ/nm^3.
4. Paulo Brito et al [32] studied the gasification of different biomass resources, including olive pomace. The sample was gasified at temperature near 800 ºC with an ER of 0.25. Results demonstrated that the syngas formed with highest higher heating value (HHV) was obtained for forest residues and olive pomace.

Once again, the results of different experiences are represented in Table 10.

Table 10- Results of different studies of gasification of olive pomace

Sample	Conditions	Syngas yield	Syngas LHV	Ref
Olive pomace dried to 17% moisture	Gas: Air T: 900 ºC ER: 0.2		4.5 (MJ/kg)	[26]
EOP at 8.5% moisture	Gas: steam T: 800 ºC		5.92(MJ/nm^3)	[31]
Olive pomace	Gas: Air ER: 0.25	2.27 (nm^3 gas/kg OP)	4.3 (MJ/nm^3) 3.4 (MJ/kg)	[32]
Olive pomace dried to 9.4% moisture	Gas: Air T: 720 ºC ER: 0.27	3.03 (m^3/kg OP)	5.3 (MJ/m^3)	[33]

2.2 HTC

Pre-treatment technologies are needed to convert the biomass into a solid fuel, which provides a more suitable feedstock for further thermochemical conversion processes, such as combustion/co-combustion and gasification [34].

HTC is a process that involves low temperature heating of the raw biomass to achieve a more energy dense, hydrophobic product. Heating takes place in a water suspension at saturated pressures, making the process well suited to high moisture biomass such as grape marc and olive pomace. HTC is an exothermic process that lowers the O:C and H:C ratios of the biomass to increase the heating value. In the case of HTC, this is achieved via the following successive reaction mechanisms: hydrolysis, decarboxylation, dehydration, aromatization and recondensation. Following processing, the upgraded hydrophilic biomass (referred as hydrochar) comprises 75-80% of the input carbon, while the process water contains 15-20% of the input carbon, with the remaining carbon exiting the process as gas. In this respect, HTC provides a significant advantage over other processes because intensive pre-drying is not required as the hydrochar may easily be separated from the process water, significantly reducing the ash content of the upgraded biomass and the likelihood of downstream reactor fouling if the hydrochar is to be used as a feedstock for gasification for final bioenergy conversion [17].

Hydrochar is a solid carbonaceous material, with physical and chemical characteristics very similar to those of fossil fuel peat and lignite, depending on the applied HTC process conditions. HTC is performed in a hot pressurized water at pressure between 10-50 bars, temperature in range of 180-250 ºC and residence times between 10 minutes to several hours. Although this process can be applied to almost every biodegradable organic material and although it seems possible to give the hydrochar specific physical and chemical characteristics by controlling the process conditions, interactions between the feedstock constituents in each phase are still not know in deep at present [35]. On the other side, process water from HTC process is comprised mostly of source related organic acids and other intermediate products such as furfurals, phenols and monomeric sugar. Various nutrients from biomass may also be present. However, subsequent usage of process water is questionable because it may as well contain potentially genotoxic and/or cytotoxic substances [36].

HTC of Grape Marc

HTC of grape marc has already been study by some authors. Some conclusions were similar to all the works. Hydrochar yield followed a decreasing trend with increasing the temperature. This is consistent with the enhancement of decomposition of grape marc and/or secondary decomposition of hydrochar which leads to gasification and liquefication. HTC led to decrease in H:C and O:C ratios of char with the increase of reaction temperature. Therefore, led to increase in the HHV of the original feedstock. Residence time also had an effect on elemental composition, increasing the holding time provided a hydrochar with higher carbon content, presumably the result of decarboxylation reactions that occur during the treatment and possibly re-combination reactions. HTC also decreased VM and increased fixed carbon (FC). Finally, due to dissolution of inorganics under hydrothermal conditions, a significant decrease in ash content of chars was obtained [34–37].

However, these studies had different goals and were performed with different types of grape marc and different operating conditions, so they reached to some different conclusions. Some of the more relevant studies and conclusions are listed below.

1. HTC of grape marc was examined in an experimental study by Pala et al [34], in which biomass was mixed with water in a 1:4 (biomass/water) ratio and heated to various temperatures ranging from 175-275 ºC with reaction times from 10-60 mins. For comparison purpose, dry torrefaction of grape marc was also carried out. The main objective was to assess the influence of temperature and time on yield and properties of the char. Temperature appeared to have a stronger effect on the reduction of char yield than residence time with a reduction of 61.1-46% and 60-57% respectively, however in this study residence times used are not very high (10-60 mins). HTC showed a higher energy densification and higher energy yield than torrefaction. Torrefaction produced pyrolytic chars having more aromatic nature than hydrochars. Due to dissolution of inorganics under hydrothermal conditions, a significant decrease in ash content of chars was obtained. HTC produced the char having higher combustion reactivity compared to torrefaction. Another advantage of HTC is the fact that aqueous phase showed antioxidant activity.
2. Basso et al [35] implemented a severity factor in order to validate the possibility of predicting the mass yield of the three phase obtained downstream of the HTC process (hydrochar, liquid and gas): the severity factor condenses both temperature and residence time of the carbonization process.

   Grape marc was freshly collected at wine producer in Trentino province in northeast Italy. It was rapidly transported to the laboratory where it was dried for at least 8 h at 105 ºC. Hydrochar was produced at different process conditions, combining three temperatures (180, 220 and 250 ºC) and four residences times (0.5,1,3 and 8 h). As expected, increasing the severity of the process, the energy content of the hydrochar is enhanced. In contrast with Pala et al [34], the authors did not manage to conclude which two process parameters (temperature and residence time) were more effective to enhance the heating value of the hydrochar, the average tendency is that at higher temperatures the marginal increase of HHV is higher than at lower temperatures. One of the differences of the two studies is the amount of residence time which is much higher in this case (from 30 mins to 8 hours). In terms of inorganics, higher temperatures tend to lower its presence, but above 1 hour residence time there is little or no reduction in terms of inorganics. As expected, the longer the residence time and the higher temperature the lower is the hydrochar yield. Moreover, the mass loss by the feedstock during the process tended in proportion to move more to the gaseous phase than the liquid phase.
3. Petrovic et al [36] studied in detailed the physico-chemical and fuel properties of HTC products stream of grape marc in relation to different HTC temperatures.

   Red grape marc from Serbia air dried with a water ratio of 5:1. The HTC temperatures were 180, 200 and 220 ºC with 60 mins residence time. The major difference in this study was the detailed analysis in the inorganics compounds. It stated, that since hemicellulose contains most of inorganics compounds in lignocellulosic biomass its degradation started at 180 ºC leading to leaching of inorganics from biomass into the liquid phase. Accordingly, the results showed that the hydrochar produced at 200 ºC had the lowest content of inorganics. However, at temperatures above 200 ºC some of the removed inorganics were subsequently reabsorbed on a porous hydrochar surface, which was confirmed through the increased of ash content. In contrast to this, the content of sulphur in hydrochar decreased with temperature and thereby preventing the emission of harmful sulphur oxides. This is a highly beneficial aspect of HTC during potential large-scale biomass conversion processes. Amounts of Pb, Cu, Cd and Ni remain unchanged. The remaining results were quite similar to the ones stated in previous studies.

4. Mäkelä et al [37] studied the effects of treatment temperature and liquid pH on grape marc char and liquid properties were determined based on laboratory experiments and the combustion characteristics of char were assessed through thermogravimetric analysis and fuel ash classification.

   Red grape marc from Australia with 75% moisture was dried at 105 ºC overnight. The results showed that HTC increased the energy and carbon contents and decreased the ash content. The effect of liquid pH was statistically significant only for the determined carbon yield of liquid samples. The principal factor of influence was temperature that explained 73% of data variation. Higher treatment temperatures decreased grape marc solid, carbon and energy yields and led to an increase in thermally labile compounds compared to lower temperatures likely due to the condensation of liquid compounds or volatiles trapped in the pores of char particles. The alkali metal contents of char ash were reduced coupled with an increase in respective phosphorous. Overall, the results support the use of hydrothermally treated grape marc in solid fuel applications, if elevated levels of ash phosphorus can be tolerated.

Table 11 summarizes the most important results obtained in the different studies. The results are quite similar being major differences associated with different operating conditions (temperature, residence time and biomass/water ratio). In terms of biomass sample one thing that was unexpected is that all the studies opted for drying of the biomass prior to HTC, which came a bit as surprise because one of the advantages of the HTC process is that intensive pre-drying is not required.

Other important conclusion is that to maximize energy yield which is probably the most viable option in order to apply further thermochemical processes as gasification for example, the operating conditions are normally intermediate ones. This happens because when applying more severe operating conditions (temperature higher than 230 ºC and residence time higher than 1 hour) there will be an energy densification due to the increase of HHV however in terms of energy yield there will be a point where there is a reduction due to a high loss of char yield attribute to dehydration and decarboxylation of lignocellulosic biomass.

Table 11- Results of different studies of grape marc HTC

Sample	Conditions	Char yield (%)	HHV (MJ/kg)	Energy yield (%)	Ref
Grape marc dried at 105 ºC for 8 hours	T: 175-275 ºC Time: 0.5-8h	48-72	21.51-26.19		[35]
Grape marc dried at 25 ºC for 24 hours	T: 175-275 ºC Time:10-60 mins Ratio: 1:4	46.5-61.1	24.32-28.32	66.03-77.40	[34]
Grape marc air dried to 0.74% moisture	T: 180-220 ºC Time: 60 mins Ratio: 1:5	66-86	24.43-26.13	79.69-97.08	[36]
Grape marc dried at 105 ºC overnight to 1.4% moisture	T: 180-260 ºC Time: 30 mins Ratio: 1:3	52-75	24-28	82.91	[37]

HTC of Olive Pomace

Studies performed of HTC of olive pomace had similar results to ones obtain for grape marc. In all studies there are some results that were also very similar. A char reduction with the increase of temperature, decrease in H:C and O:C ratios with the increase of reaction temperature which led to increase of the HHV, increase of the carbon content with holding time and also a decrease in VM and increase in FC. Nevertheless, in terms of inorganics, the studies reached to different conditions. Some stated that ash content remains constant while others state the HTC reduces ash content as reported in the case of grape marc [38,39] .

The more relevant studies on HTC of olive pomace are listed below:

1. Surup et al [38] compared torrefaction and HTC conversion of olive pomace into metallurgical reducing agent. The dependence of yield, CO_2 reactivity, and mechanical properties to reaction time, and heat temperature was investigated.

   Olive pomace dried previously from Tunisia was obtained as feedstock. HTC was performed in a temperature range from 190-250 ºC with a residence time of 30 mins, 2, 6 or 15 h. Hydrochar yield obtain with 30 mins residence time were 10% greater than those obtained for 2 hours residence time, emphasizing the effect on residence time on hydrochar yield for olive pomace. Increasing the residence time for 15 h increased the hydrochar yield about 8% (compared to 6 hours), an observation attributable to formation of secondary char by polymerization of small molecules in the liquid phase and recondensation into the char phase. The FC content produced after 15 hours treatment was nearly twice that reported for values of 5 mins HTC treatment and up to 20% greater compared with HTC treatment for 30 mins. In contrast to other studies, ash content remains nearly constant. Previous studies (other biomasses) reported that HTC significantly decreases ash content and residual alkali metals contain with hydrochar, leading to increase reactivity of hydrochar product. This suggests that the mineral content of olive pulp may be more thermally stable and water insoluble than other types of biomasses.
2. HTC of dried olive pomace (DOP) (three-phase extraction process) was performed by Missaoui et al [40] with temperature between 180-250 ºC and residence time in range from 0-120 mins, to

access the potential of generated hydrochar to produce energy. The effects of process parameters (holding time, temperature and DOP/water weight ratio) on the yield and the quality of the hydrochar were examined.

The results revealed that 30 mins treatment at 215 ºC with a DOP/water weight ratio of 1:6 maximized the energy yield (83%) of HTC process. Both DOP and the hydrochar were characterized by ultimate, proximate and thermogravimetric analyses. These showed that the hydrochar is more carbonaceous and more thermally stable than untreated DOP. Hydrochar contained lower ash and VM content when compared to the raw DOP.

3. Benavente et al [41] focused in the application of the HTC technology as a possible moist agro-industrial waste management treatment. Through this technique, olive mill, canned artichoke and orange waste were carbonized in a lab-scale high pressure reactor at different temperatures (200–250 ºC) and durations (2, 4, 8 and 24 h) in order to obtain useful bioenergy feedstocks. The major difference of this study to the previous ones is that the wet biomass was not previous dried before the HTC process.

   It was found that the moisture content of HTC hydrochars decreases as the temperature and duration increase, which implies that wet biomass can be upgraded and, at the same time, dewatered through HTC. The best results are found for the olive pomace, whose moisture content decreases from over 70% to less than 30% for the experiments carried out under the more severe conditions. Consequently, it was possible to reach energy savings over 50% by using HTC instead of torrefaction technologies. Regarding the hydrochar properties, the HTC of the three organic wastes treated, leaded to hydrochars that present carbon contents and heating values close to those of brown coal and great energy densifications, depending on the type of waste. Accordingly, it can be concluded that it is feasible to manage moist agro-industrial wastes via HTC, which is ostensibly more efficient than torrefaction in terms of energy consumption. Furthermore, high temperatures compensate the long residence time needed at lower temperatures, since the elemental composition of the hydrochar prepared at 250 ºC during 2h matches the hydrochar prepared at 200 ºC during 24h. The ash content did not vary a lot with residence time, but it is lower than initial. As the temperature rises the ash decreases. Alkali index, above 0.17/Gj fouling is probable to occur and above 0.34 foulling is theoretically certain to occur. Olive pomace had 0.66 alkali index initially and after treatment lower than 0.17.

Table 12 summarizes the most important results considered from previous works of HTC of olive pomace. The major difference between the results is due to fact that in one of them olive pomace was not previously dried and so HTC was performed with a sample of more than 70% moisture. However, the results were quite similar in terms of energy densification, but energy yield was significant lower. Moreover, after the pre-treatment process the hydrochar still has a moisture of 30% so to perform a further thermochemical process it will be probably needed a drying process but less energy intensive. The remaining conclusions are quite similar to ones obtained in the previous section.

Table 12- Results of different studies of olive pomace HTC

Sample	Conditions	Char yield (%)	HHV (MJ/kg)	Energy yield (%)	Ref
Olive pomace dried to 10% moisture	T: 190-250 ºC Time: 2-15 h Ratio: 6:19	31-65.3	24-29.5		[38]
Olive pomace dried to 7% moisture	T: 180-250 ºC Time: 0-120 mins Ratio: 1:10 and 1:2	56-71	24.1-27.6	67-83	[40]
Olive pomace wet with 70% moisture	T: 200-250 ºC Time: 2-24 h	13.2-18.4	25.54-31.38	55.67	[41]

2.3 Pyrolysis

Pyrolysis is the thermal decomposition of biomass fuel in the absence of oxygen at temperatures of around 400-700 ºC, the process is endothermic. These thermochemical biomass conversion process produces a mix of gas, liquid (tar or bio-oil) and solid (char) products depending on the pyrolysis conditions applied [17]. Pyrolysis is differentiated between slow pyrolysis, with residence times ranging from minutes to days and optimized for the production of char whereas fast pyrolysis, with residence times on the order of seconds or minutes, it is optimized for the production of bio-oil. On the engineering front, research is focused on optimizing the process variables (temperature, heating rate and oxidation environment) and product upgrading via catalytic and thermal processes to produce infrastructure-compatible liquid transportation fuels [2].

This reaction can be represented by the equation:

$$\mathrm{C_aH_bO_c} \rightarrow \sum\nolimits_{\mathrm{liquid}} \mathrm{C_lH_mO_n} + \sum\nolimits_{\mathrm{gas}} \mathrm{C_xH_yO_z} + \mathrm{H_2O} + \mathrm{C} \qquad (6)$$

This technique is well adapted to heterogenous feedstock or substrates with high mineral content, such as grape marc and olive pomace. Furthermore, it has the advantages to produce three different fraction that could be valorised separately. The gaseous and liquid fractions could be used as biofuels in the pyrolysis plant for heating or electricity production. The solid fraction (char) could be used directly for agricultural soils amendment (called biochar) or activated in order to produce efficient adsorbents for pollutant removal from aqueous and gaseous effluents. Biochars recovery for soil amendment has received widespread attention since it contributes to carbon sequestration, therefore decreasing the CO_2 emissions into the atmosphere. Furthermore, benefits from soil amendment with biochars were not only limited to climate change mitigation, but also to agronomic soil's physical chemical, hydrodynamic and biological properties improvements. Indeed, biochars are highly rich in C, but also contain also significant amounts of O, H, S, N and non-negligible concentrations of various inorganics elements such as Ca, K and P that are very useful for plants growth [42]. Bio-oil contains numerous organic compounds including aromatic hydrocarbons, alkanes, phenols, ethers and alcohols, which may be used as chemical feedstocks or fuel oils for stationary heat energy and electricity generation. Direct use of bio-oils may be problematic due to their viscosity, corrosiveness, thermal stability and LHV, however further processing via hydrogeneration and catalytic cracking to produce fuel products analogous to refine petroleum, such as diesel and high octane gasoline is possible [17].

Regarding the heat of pyrolysis for biomass, works published range from significantly endothermic (750 kJ/kg) to significantly exothermic (-1700 kJ/kg). This large range is caused by a mixture of both exothermic and endothermic reactions that occur during pyrolysis. Typically, hemicellulose and lignin pyrolysis are exothermic reactions whereas cellulose pyrolysis is endothermic. The small amount of cellulose in grape marc and olive pomace suggest that grape marc pyrolysis is not significantly endothermic and hence would not require significantly energy input. Moreover, the pyrolytic gases can provide the power require for the endothermic pyrolysis process, ensuring self-sufficient operating system [43,44].

Pyrolysis of Grape Marc

The more relevant studies found in the literature are listed below:

1. Ibn Ferjani et al [42] examined the potential of grape marc as feedstock for biochar production. Therefore, slow pyrolysis was performed at different temperatures ranging between 300-700 ºC. Then, the produced chars physicochemical properties including their surface chemistry, as well as their textural and structural properties were analysed using different analytical techniques.

   The sample pyrolyzed was grape marc from France after ethanol extraction by distillation process, known as EGM. The experimental results showed that the biochar yields production decreased with the increasing the pyrolysis temperature and reach a plateau above 500 ºC. Results suggest that pyrolysis temperature of 500 ºC may be suitable for biochar production at large scale since the devolatilization step is finished and no significant EGM loss occurs above. The EGM char yield (33%) obtained in the present study are higher than those reported in the literature, for pyrolysis in similar conditions. This observation could be related to high lignin content in grape marc. There is an increase in C and a reduction in H and O with temperature, at least until 500º C. The biochar with better textural temperatures was obtained at 600 ºC because higher temperatures led to volatilization and consequently the biochar obtained is more porous, due to the creation of empty spaces into the carbon matrix. However, the maximum nutrient contents, namely K, N and P were registered at 500 ºC. Based on the biochar yields and characteristics, EGM biochar produced through slow pyrolysis at 500 ºC could be considered as a promising biofertilizer for agricultural proposes.
2. Zhang et al [43] investigated the options of combustion and pyrolysis of wine production residues for their economic and environmental viability. The authors reached to the conclusion that pyrolysis of grape marc is an endothermic process with an energy input of 365 kJ/kg.
3. Khiari and Jeguirim [44] focused on optimization of the pyrolysis process from grape marc potential and to achieve high product yields. Therefore, physic-chemical and energy characteristics of grape marc issued from a Tunisian wine cooperative were determined according to international standards.

   The sample studied was fresh grape marc with 60% moisture, which was dried to 10%. The sample had high ash content and carbon content which confirms that slow pyrolysis is the suitable thermochemical conversion process for grape marc recovery. Particularly, the char yield (FC and ash contents) was about 44%, which was never met in the literature for agricultural biomass under pyrolysis. After pyrolysis, the biochar yield was about 40% which again was never met in literature for agricultural biomass in slow pyrolysis. Such behaviour may be attributed to high lignin content in grape marc. Minerals, which can be an obstacle in combustion operations, become a major asset in pyrolysis. Furthermore, their presence played a catalytic role and shifted the cracking temperatures to lower values, thus reducing the operation cost.

4. Casazza et al [45] evaluated the efficiency of grape marc after the recovery of phenolic compounds. Grape marc and grape marc obtained after the polyphenols extractions were used as raw material for pyrolysis, both of the samples were dried to values close to 5% moisture. The operating temperature was between 350-550 ºC.
   No important changes in the yield were obtained when the temperature increased from 450 ºC to 500 ºC. Most of the compound volatize at temperatures under 450ºC. As stated in previous studies the pyrolysis is just finished at 500 ºC. In terms of the gas composition, the major components are CO_2, CO, CH_4, C_2H_4 and C_2H_6. The presence of CO_2 in gas at lower temperatures is mainly due to the decomposition of free sugars, cellulose and hemicellulose, and a minor contribution of lignin degradation. The increase of temperature leads to a decrease of CO_2 concentration, produced by carboxyl release at relative low temperatures. At higher temperatures, the secondary reactions of volatile compounds produce mostly CO and CH_4 rather than CO_2, as expected for lignin decomposition. The results showed that the increasing the treatment temperature resulted in a significant increment in production of pyrolysis gas.

From the different studies stated, it seems that due to high content of FC and ash slow pyrolysis is more suitable than fast pyrolysis. The best operating temperatures should be around the 500 ºC since the devolatilization step is finished and no significant char loss occurs above. The yields obtain were quite similar (Table 13), the major difference was obtained by Khiari and Jeguirim [44] where char yield was close to 40% because of higher lignin content in this sample of grape marc. Moreover, It was confirmed that pyrolysis of grape marc is not a very endothermic process and that syngas obtained from the process can provide the necessary power and maybe can be used as an energy source if a pre-treatment process (drying) is required.

Table 13- Result of different studies of pyrolysis of grape marc

Sample	Conditions	Char	Bio-oil	Gas	Ref
EGM with 7.55% moisture	Slow pyrolysis T: 500-700 ºC	Yield: 33.8-30.9%			[42]
Grape marc dried to 10% moisture	Slow pyrolysis T: 500 ºC	Yield: 34% HHV: 27 MJ/kg	Yield: 31.5% HHV: 23 MJ/kg	Yield: 34.5% HHV: 9 MJ/kg	[43]
Grape marc dried to 10% moisture	Slow pyrolysis T: 500-750 ºC	Yield: 39.68%			[44]
Grape marc dried to 5.3 % moisture	Slow pyrolysis T: 450-550 ºC	Yield- 31.86-32.57 % HHV: 25-28 MJ/kg	Yield: 29.03-37.40%	Yield: 30.56-39.40%	[45]

Pyrolysis of Olive Pomace

In general, when pyrolysis is performed on olive pomace the percentage mass of char decreases while gas increases when temperature is raised, and that the bio-oils increases up to 500º C, decreasing at higher temperatures. On the other hand, the use of high heating rates reduces the amount of bio-oils obtained. If the solid is the target product, high temperatures (above 700 ºC) and slow heating rates have to be use (slow pyrolysis); in these conditions large proportions of gases are also generated while low yields of low value liquid are produced. These bio-oils consist on a mixture of an aqueous phase and a tarry phase, both phases containing complex oxygenated hydrocarbons that limit their usefulness, turning them to be non-desired products [46].

From the literature review the most important studies worth mentioning were:

1. Caballero et al [46] studied the potential of slow pyrolysis to produce rich gases from 2POP. The effect of pyrolysis temperature and different alternatives for post pyrolysis vapours treatments were used, with the aim to increase the yield and composition of gases

   Concerning the pyrolysis without special treatment, two experiments were performed one at 500 ºC and the other at 700 ºC. In terms of solid yield there was almost no effect with the increase of temperature. On the contrary, there are some studies in the literature about pyrolysis of olive solid waste that have concluded a decrease in the solid yield from 500 to 700 ºC. This difference can be attributed to the fact that in former research heating of the sample can be considered instantaneous while in the pyrolysis experiments carried out in the present work sample was pyrolyzed at 500 and 700 ºC gradually.

   Concerning the liquid yield, it has decreased from 45 to 41.6 % with temperature raise. The gas behaviour is exactly the opposite of the liquid. The decrease of liquid yield with temperature is due to increase in thermal cracking reactions, which reduce the molecular weight of the organic compounds that would give rise to liquids once condensed, turning them into gases. The fact that liquid yield reach their maximum at 500 ºC could be explained as follows: up to this temperature the maximum degradation of lignin and cellulose of biomass takes place yielding liquids and gases, while over 500º C gas yield increased at the expense of liquids, which are cracked over at such temperatures. The liquids consist of a mixture of an aqueous phase that represents 98 % and a tarry organic phase (less than 2 %). The aqueous phase is composed by oxygenated, corrosive, unstable and chemically very complex compounds, which cannot be used as a fuel or chemical source, separation and upgrading operations would be required to get any use of them.

   Solids composition variation was slight with temperature, they had a HHV comparable to those of conventional charcoals and higher than those of fossil coal, with the advantage that pyrolysis solids do not contain polluting elements such as sulphur, but its ash content was very high, they seem a better alternative as a soil amendment than as fuel. Concerning the gases, it was seen that the main components were H_2, CO, CO_2 and CH_4, there were also very low quantities of C_2H_4 and C_2H_6. HHV obtained was much lower compared to natural gas due to the fact that pyrolysis gases had significant amounts of CO_2, which contribute nothing to the calorific value.

2. Slow pyrolysis of olive cake has been carried out by Martín-Lara et al [47] under nitrogen atmosphere at different temperatures to obtain carbonaceous materials with possible applications as solid fuels and absorbents of solid fuels. The content of VM was reduced and FC was increased. The ash content also increased from 10% to 23%. HHV increased from 17 to 28.40 MJ/kg. Although it is not mentioned in the study the high ash content of the char obtained would invalidate the use of these as a fuel for further thermochemical processes.
3. Dinc and Yel [48] studied the catalytic effect of intrinsic inorganics by comparing pyrolysis end products obtained from pyrolysis of olive pomace in three different initial weights (30, 100 and 200 g). The results were very different from the previous ones as shown in Table 14. This is related to the fact that the sample used is two phase wet olive pomace without drying process. The high moisture justifies the low value of char yield obtain and high quantities of liquid and gas yields.
4. Hani and Hailat [49] stated that numerous studies regarding liquid fuel production from various sources of biomass demonstrated that bio-oil product can be obtained from EOP in significant yields. The authors affirmed that their direct use as conventional fuels may present some difficulties due to their high viscosity, poor heating value, corrosiveness and instability. They added that upgrading bio-oil is a necessary process before using them as a regular fuel, essentially involves removal of oxygen. Currently two methods have been proposed for this process. The first method is a typical catalytic hydrotreatment with H_2 and CO under high pressure and/ or in the presence of H_2 donor solvents. The second method utilizes cracking catalysts under atmospheric pressure without H_2. In this study olive cake dried was pyrolyzed using different catalytic ratios on the products yields. The composition of the fuel obtained was investigated and its usability as a potential source of renewable fuel was also investigated. The results without catalyst are presented in Table 14. The catalytic treatment caused removal of oxygen, increased HHV and stability. The chemical characterization showed that the bio-oil obtained from olive oil might be potentially valuable fuel and chemical feedstock.

Like grape marc, for olive pomace slow pyrolysis seems the more suitable thermochemical process in comparison to fast pyrolysis. The char obtained has high ash content, so it is not appropriate for further thermochemical processes such as combustion and gasification, so the soil amendment application could the best alternative. According to the literature, the best operating temperature should be around 500 ºC since it is less energy demanding and the results are quite similar to the ones obtain at higher temperatures and lower temperatures are not an option since the pyrolysis process is not over. Once again gas, can be used as an energy source for the pyrolysis and drying process if needed. The bio-oil has several problems associated, but studies indicate that if treated correctly might be a potentially valuable fuel.

Table 14 summarizes the obtained results.

Table 14- Results obtained for pyrolysis of olive pomace

Sample	Conditions	Char	Bio-oil	Gas	Ref
EOP dried to 12.2% moisture	Slow pyrolysis T: 500-700 ºC	Yield: 32.3-32.5 % HHV: 26-26.5 MJ/kg	Yield: 41.6-45%	Yield: 22.7-25.9% HHV: 12.1-13.2 MJ/kg	[46]
EOP dried to 6.65% moisture	Slow pyrolysis T: 500-550 ºC	Yield: 30.48-31.78% HHV: 26.47-28.40 MJ/kg			[47]
Olive pomace wet	Slow pyrolysis T: 450-600 ºC	Yield: 7.7-10.7 %	Yield: 45.7-61.6%	Yield: 28.1-45.6%	[48]
Olive pomace dried to 5.3% moisture	T: 500 ºC	Yield: 34.5%	Yield: 42.9% HHV: 32.16 MJ/kg	Yield: 22.6%	[49]

2.4 HTC Followed by Gasification

When solid biomass is processed into syngas, it faces several challenges that reduce the effectiveness of energy conversion including high moisture content, low energy content, low bulk density, and lack of fuel uniformity. Drying and pelletization have been the most common and widely used upgrading technologies in recent decades. Furthermore, thermochemical pre-treatment technologies generate much more effective solid fuels for energy conversion technologies, such as gasification [50].

As mentioned before HTC is one such technology that serves as ideal treatment for energy technology such as gasification. This process facilitates mechanical dewatering, which reduces requirement for thermal drying. An improved grindability of hydrochar is another important mechanical property for fuel processing. Increasing the C:O ratio results in high heating value and energy density which are advantageous in logistics. HTC has been applied to various feedstocks such as lignocellulosic biomass, agricultural waste, sewage sludge, grass, biologically treated residues and microalgae. However, there are still little studies related to air gasification of hydrothermal carbonized biomass [50].

There were not found studies of HTC followed by gasification in grape marc and olive pomace, but were found some relevant experiments on other types of lignocellulosic biomasses:

1. Gunarathne et al [50] studied the performance of the air gasification of hydrothermal carbonized biomass pellets (biocoal) in a high temperature agent updraft gasifier.

   The feedstock for producing biocoal consisted of spent grains from a brewery. The biocoal was produced through an HTC procedure at a temperature of 210-215 ºC and residence time of around 4 hours. The solid yield was around 67% of dry input. The raw biomass contained 80 % moisture, while biocoal possesses only 10%. The carbon content increased from 46 to 66% and the oxygen content decreased from 38 to 16%. The H content remained almost constant, and the N content decreased. The HHV on a dry basis improved from 19 to 29 MJ/kg because of a significant increase on the carbon content and a significant decrease in the oxygen content.

   Char gasification demonstrated an optimal ER of operation of 0.2. Syngas with 7.9 MJ N/m^3 LHV was obtained from gasification experiments performed in the pilot scale gasifier. The maximum cold gas efficiency was 80 % at the lowest ER and also resulted in a high purity syngas. The LHV and cold gas efficiency were higher than that of the previously studied unpretreated biomass pellets (6

MJ N/m^3 and 76% efficiency). The fuel conversion positively correlated with residence time in bed, and almost 99% conversion could be achieved for a residence time of 2 hours.

2. Erlach et al [51] compared HTC followed by entrained flow gasification of the biocoal with fluidized bed gasification of raw wood, both with CCS. Simulation studies were undertaken with Aspen Plus and were interpreted using exergy analysis. Syngas production is more efficient from biocoal than from raw wood but the conversion losses in the HTC process outweigh the efficiencies gains in the gasification, energetic efficiency of the biocoal integrated gasification combined cycle (IGCC) is 33.7%, 4.7 percentage points higher than of raw wood. Carbon gaseous and dissolved by-products in the HTC also limit the capture rate. A CCS-IGCC with fluidized bed gasification using raw wood results in an electrical efficiency of 28.6 % (HHV) and carbon capture of 84.5%, while the conversion chain of HTC and a CCS-IGCC with entrained flow gasification yields an electrical efficiency of 27.7% and a capture rate of 72.7%.

There were no specific studies for olive and wine biomasses. Nevertheless, literature suggests that behaviour must be similar for different type of lignocellulosic biomasses. Char gasification efficiency is higher than the raw material, being this efficiency increase significant (around 5%). Nevertheless, this gain is outweighed by the conversion losses in HTC, during this process the char goes through a process of energy densification, but also a mass losses (char yield between 50-70%) and that this losses are higher than the energy densification process and the gain in the gasification efficiency. However, the overall electric efficiency is not very different (around 1% lower) and this process has other advantages associated like is advantageous related to logistics due to hydrochar being more energy dense. Therefore, the pros and cons must be measured, and further studies must be made to assess if this procedure is a good alternative to the current ones.

2.5 LCA

In the literature there are several studies of LCA applied on the wine and olive sector. However, most of the studies are focused on cradle to grave approach where the LCA is done since the cultivation of the grapes and olives until their disposal.

This work focus on the valorisation of the by-products grape marc and olive pomace, therefore it was decided to search for gate-to-grave or gate-to-gate studies where the impacts just are considered from one determined point along the life cycle until their end use and disposal or until another determined point in the life cycle respectively [52].

The most common studies on LCA of thermochemical processes of grape marc or olive pomace are focused in pellets combustion. Benetto et al [53] analysed the production of grape marc pellets and evaluated through an LCA based on primary data from field experiments, the overall environmental performance of using grape marc for heat production, as well as its comparison with alternative fossil and renewable energy sources. Overall, results showed that the production of pellets from grape marc for heat production purposes is a promising technology from an environmental perspective, which is always superior to alternative fuels at endpoint impact levels. Compared to fossil fuels, its main advantage lies in the reduced contribution to climate change. When compared to mixed wood chips, has an advantage regarding the contribution of agricultural land application. Also, Duman et al [54] performed gate-to grave LCA approach of five different scenarios involving the treatment and utilization of olive pomace. Three of these scenarios included the production of biofuel pellets from the olive pomace; the other two are producing fodder additives from olive pomace and composting the olive pomace. The functional unit chosen was the olive pomace produced as a result of the production of 1 kg of olive oil. The pellets were observed to have significantly lower impacts, and in many cases even impact credits for the system, mainly due to the fact that utilizing the biofuel pellet eliminates the consumption of natural gas, which has especially high environmental impacts in case of Turkey. Composting the olive pomace has very high impact score compared to other scenarios, mainly because of raw materials used and hazardous chemical emitted in the process. Finally, Cossu et al [55] performed an LCA study of olive pomace aiming at facilitation Life Cycle Management of this biomass. The authors considered three scenarios: combustion for domestic heat; generation of electric power; and composting. Composting was of 2 to 4 orders of magnitude less impacting than domestic heating and power generation.

Concerning gasification, it was just found one relevant study done by Parascanu et al [56]. The authors compared olive pomace combustion and gasification though LCA in order to point out the environmental performance of these processes to electrical energy production. The FU was 1 MJ of energy production and the environmental impact of each equipment involved in the thermochemical processes such as crusher, combustor/gasifier, cyclone and Rankine cycle were analysed. Rankine cycle was the major contributor to all impact categories due to gases released and to the energy required for the operation of the water pumps. Gasification scenario exhibited higher impact values at mid points level, than the combustion scenario. This occurred mainly due to the fact that higher amount of olive pomace was used in the gasification process to obtain 1 MJ of energy compared to that required by combustion one. The results indicate that combustion process is two times more efficient than the gasification process for electricity generation. Nevertheless, this is against several studies which showed that gasification performance of olive pomace is comparable to combustion [26,33].

Regarding HTC, Benavente et al [39] studied the environmental impacts associated with using HTC to treat olive mill wastes were evaluated and compared to aerobic composting, anaerobic digestion, and incineration using LCA. The FU of this study is defined as the treatment of 1 kg of 2POP. Results indicated that HTC coupled with subsequent energy recovery from the combustion of the generated hydrochar results in net environmental benefits. In addition, results indicate that HTC process water discharge significantly influences system environmental impacts, indicating that research investigating treatment alternatives is needed. In comparison with current management approaches, alternatives using HTC are more environmental advantageous than composting and anaerobic digestion. However, the use of HTC is not as environmentally advantageous as incineration with energy recovery because 35 to 45 % of the energy contained in the olive pomace is lost during HTC, and so the energy produced from the combustion of the hydrochar is lower than that produced from the direct combustion of 2POP. Research focusing on maximizing solid yields and hydrochar energy content is needed to potentially reduce this difference. Moreover, if the electricity recovery efficiency from incineration increases to values greater than 30% the environmental impacts associated with HTC and subsequent energy generation are equal or better than direct 2POP incineration with energy recovery. The authors also recommended that future research effort focus on the evaluation of appropriate and environmentally beneficial HTC process water treatment approaches and methods to improve energetic retention efficiencies of hydrochar. More recently, Mendecka et al [57] stated that Benavente et al [39] used a simplified HTC process layout, without any heat recovery scheme. Therefore, the authors applied a LCA study to evaluate and compare several scenarios of HTC process for olive pomace treatment with energy recovery. Different process conditions by means of temperature (260, 280 and 305 ºC), subsequent combustion of the generated solid product, as well as different scenarios of energy recovery, including heat recovery and self-sufficiency by integrating boiler fired by produced HTC hydrochars were considered. Results indicate that the environmental performance of HTC is mainly dependent on its energy consumption. By implementation of energy recovery scheme in the HTC process it was possible to save up to 53% of energy consumed and as a consequence to obtain values of Climate Change, Acidification end Eutrophication Potentials Impacts 1.4 to 2.0 times lower with respect to the process without heat recovery. For Freshwater Ecotoxicity impact no substantial differences were observed between the cases involving different feeding and heat recovery scenarios. Such an impact is depending on the liquid phase emission during HTC reaction, that depends only on the liquid yield, thus on the process temperature. From the two studies is possible to state that the major impacts of HTC come from energy requirements and from the wastewater.

Concerning pyrolysis Parascanu et al [24] performed a LCA of the olive pomace valorisation by means of a pyrolysis system. The environmental impacts associated with three different stages were evaluated. The first stage is the olive production, the second stage is the olive extraction, where the by-product olive pomace is used as a raw material for the pyrolysis system. The pyrolysis system yields char, gases and tar involving the following stages: biomass drying and grinding, pyrolysis, separation of gases and char, gas cooling by consecutively using an air heat exchanger followed of a water one, and the separation of gases and tar. For this study, 14 midpoint and 3 endpoint impact categories were selected. The functional unit (FU) of 100 kg olive pomace was considered as an overall bench-mark approach. The midpoint and endpoint methodologies for pyrolysis system showed that the main affecting factors for all impact categories are related to the consumption of energy required to perform biomass conversion. The total energy required for the pyrolysis system of 100 kg olive pomace is 481.5 MJ/h. Therefore, the results showed that pyrolysis system can be considered an ecological tool for the valorisation of olive pomace, using energy efficient together with water and air reutilization. Other study performed by El Hanandeh et al [58] uses life cycle methodology to analyse the carbon emission reduction potential of olive pomace as feedstock in a mobile pyrolysis unit. The FU is 1 kg of olive pomace and four scenarios, based on different combinations of pyrolysis technologies (slow versus fast) and end-use of products (land application versus energy utilization) are constructed. The results showed that all the scenarios result in significant GHG emission savings. The authors concluded that energy utilization of fast pyrolysis products reduces more the GHG emissions than slow pyrolysis and using the biochar as soil amendment. However, this last study has some limitations because it does not take in account the various problems associated with the burning of bio-oil which must go through a heavy treatment before usage.

Summing up the literature review suggests that the thermochemical treatment of this by-products in terms of environmental impacts looks a good alternative compared to current practices such as composting. However, the works mentioned focus solely on one or two thermochemical processes and sometimes compare them to other waste valorisation methods. The innovation of these work is that is going to evaluate the environmental impact of four different thermochemical processes (combustion, gasification, HTC followed by gasification and pyrolysis) for the valorisation of olive pomace at the same time.

2.6 Techno-Economic Analysis

Techno-economic analysis, as mentioned before, is a way of assessing the feasibility of a project. Concerning grape marc and olive pomace valorisation there were found some previous studies in the literature.

Zhang et al [43] focuses on the valorisation of grape marc, two methods were designed and compared: combustion to generate electricity, and the pyrolysis for the production of biochar, bio-oil, and biogas. Each of these processes was analysed to determine their economic and environmental viability. Pyrolysis was found to be a superior method of utilizing grape marc from both economic and environmental perspectives. Mainly due to lower capital costs associated and to a lower emission of GHG. Both pyrolysis and combustion exploit the energy content of the waste, which is not recovered by the traditional methods, composting or distillation. In addition to the production of energy, pyrolysis yielded 151 kg of biochar and 140 kg of bio-oil per tonne of grape marc. The authors stated that these products could be used in place of fossil fuels, resulting in a net reduction of CO_2 emissions. It was found that investment in either pyrolysis or combustion had a negligible impact on the price of wine produced for wineries with annual grape crush larger than 1000 tonnes. However, for wineries with small grape crush of less than 50 tonnes composting has significant economic advantages. One possible limitation of the study is that the authors did not take in account the costs associated with the treatment of the bio-oil and assumed that the bio-oil could be sold in market right away after the pyrolysis process.

Concerning gasification, it was found out two relevant works. Borello et al [26] presented a thermodynamic model of CHP plant, fed by syngas produced by dry olive pomace gasification. The plant is designed to produce electric power and hot water by using a cogeneration micro gas turbine (micro GT). Before being released, exhausts are used to dry the biomass from 50% to 17% wb. The paper analyses the whole conversion process from wet biomass to heat and power production, reporting energy balances and cost analysis. The thermodynamic analysis demonstrated that, starting from a gasifier with thermal input size of 800 kW and electric output power of 200 kW could be obtained, with a gross electric efficiency 25%, while the cogeneration section is able to provide 250 kW of thermal energy for low grade heat demand (90 ºC) with 30% thermal efficiency. In terms of profitability cogeneration model had better results compared to case studies with just electricity demand. Other work performed by Hermoso-Orzáez et al [33] focused on obtaining energy from the recovery of obsolete materials through thermochemical conversion processes of the plastic waste in different proportions with biomass of crop residues (olive pomace). The gasification tests of these mixtures were carried out in a downstream fixed bed drown daft reactor, at temperatures of approximately 800 ºC. The results demonstrate the applied technical and economic feasibility of the technology by thermal gasification, for the production of LHV syngas with highest power energy (more than 5 MJ/m^3) produced in mixtures of 100% to 80% of olive pomace with overall electric efficiencies close to 30%. This study was complemented with economic-financial analysis. All the mixtures had a payback period inferior to 10 years.

Finally, an HTC process was designed and modelled by Lucian and Fiori [59] on the basis of experimental data previously obtained for two representative organic waste materials including grape marc. The process accounts for all steps and equipment necessary to convert raw wet biomass into dry and pelletized hydrochar. By means of mass and thermal balances and based on common equations specific to the various equipment, thermal energy and power consumption were calculated. When operating the HTC plant with grape marc (65% moisture content) at optimized process conditions (T= 220 ºC; 1 hour residence time; dry biomass to water ratio= 0.19); thermal energy and power consumption were equal to 1170 kWh per tonne of hydrochar produced, respectively. The overall plant efficiency was 78%. In addition, the techno economical aspects of the HTC process were analysed in detail, considering both investment and production costs. The production cost of pelletized hydrochar and its break-even point were determined to be 157 €/tonne and 200 €/tonne, respectively. The authors concluded that such values make the use of hydrochar as a CO_2 neutral biofuel attractive.

As in the case of LCA studies, the innovation of this work is making a techno-economic analysis for four different thermochemical processes for the valorisation of olive pomace. There are a few studies that have done this work in the literature and is way of evaluating which one is more economically advantageous.

3. Methodologies

Following the literature review this chapter will present the methodologies used in this work in order to achieve the goals of this study. Firstly, section 3.1 focus on methods used to characterize grape marc and olive pomace. Afterwards in section 3.2 is explained the methods used to perform an LCA assessment of olive pomace valorisation through different thermochemical processes (combustion, gasification, HTC followed by gasification and pyrolysis), in order to compare and assess the environmental impacts of each one. Finally, in section 3.3 the same thermochemical conversion pathways are evaluated through a techno-economic analysis to assess the feasibility of this type approach and to conclude which one is more economically advantageous.

3.1 Feedstock Characterization

The performance of different thermochemical conversion pathways relies on the use of appropriate biomass feedstocks. The biomass characterization is fundamental and is commonly conceptualized in three different ways, via either biochemical, proximate, or ultimate analysis. Biochemical analysis refers to the relative abundance of various biopolymers (cellulose, hemicellulose and lignin) in biomass, whereas ultimate analysis refers to the relative abundance of individual elements (C, H, O, N and S). Proximate analysis separates the feedstock into four categories of importance to thermal conversion: moisture, VM (gases and vapours driven of during pyrolysis), FC (non-volatile carbon) and ash (inorganic residue remaining after combustion) [2].

Another important factor is the calorific value of the biomass, which is the energy available in the feedstock as estimated from the heat released during complete combustion to CO_2, H_2O (gaseous H_2O for LHV, or liquid H_2O for HHV) and other minor products (N_2, ash etc), and is a primary measure for quality of feedstock [2].

3.1.1 Data Gathering

The sample used in the present work will be grape marc and olive pomace based on empirical data. All the studies mentioned on the literature review and with relevant data regarding grape marc and olive pomace were considered and data was collected in a excel document.

The data selected included biomass calorific value, ultimate analysis and proximate analysis.

3.1.2 Data Treatment

Data was categorized during the next sections, to evaluate if it is possible to see differences between the different types of biomasses. Afterwards it was applied the mean and standard deviation. With the mean is possible to know which is the average value of a certain characteristic and with the standard deviation to assess how scattered the values are. The formulas used are represented below:

$$\text{Mean: } \bar{X} = \frac{\sum X}{N} \tag{7}$$

$$\text{Standard deviation: } \sigma = \sqrt{\frac{\sum (X - \bar{X})^2}{N-1}} \tag{8}$$

The expected content of each category will be defined as:

$$\mathrm{EC} = \overline{\mathrm{X}} \pm \sigma \tag{9}$$

The range will be defined as:

$$\mathrm{Range:}\ (\mathrm{Min(X)}; \mathrm{Max(X)}) \tag{10}$$

The expected content will be a way of predicting more closely which value should be expected to find in each type of biomass and category, and the range to state which spectrum of values where found in the literature.

3.1.3 Grape marc data

Samples were categorized in two categories. Grape marc (GM) and EGM. The difference between the two samples is that EGM is grape marc after ethanol extraction by a distillation process.

Table 15 represents all the data gathered in the literature regarding calorific value, proximate analysis and ultimate analysis

3.1.4 Olive Pomace Data

The olive pomace samples were divided in six categories. Olive pomace (OP) and EOP, where EOP is olive pomace dried and without the residual oil after a hexane extraction. The other two categories are related to extraction method, if it is an olive pomace obtain by a two-phase extraction method or three-phase extraction method, which were defined as 2POP and 3POP respectively. Therefore, the possible samples obtained were: OP, EOP, 2POP, 3POP, 2PEOP, 3PEOP. Only the first two categories are used because sometimes the extraction method is not mentioned in the literature.

Table 16 contains all the data gathered for olive pomace regarding calorific values, proximate analysis and ultimate analysis

Table 15- Calorific value, proximate analysis and ultimate of different samples of GM

Sample	Calorific value (MJ/kg)		Proximate analysis (%)				Ultimate analysis (%)					Ref
	HHV	LHV	Moisture^{wb}	FC^{db}	VM^{db}	Ash^{db}	C	H	O	N	S	
GM	-		-	25.90	69.00	5.10	53.70	6.20	-	1.76	0.11	[17]
GM	-		-	25.80	67.70	6.50	54.10	6.10	-	2.59	0.16	[17]
GM	-		-	25.30	67.90	6.80	54.80	6.30	-	2.43	0.14	[17]
GM	-		-	28.20	63.60	8.20	53.90	5.70	-	2.39	0.16	[17]
GM	-	19.50	-	26.40	65.80	7.90	49.70	5.56	-	2.23	0.14	[17]
GM	20.10	19.70	-	24.50	72.00	3.50	43.20	5.94	-	0.65	1.24	[17]
GM	19.50	-	-	24.30	67.80	7.50	43.00	9.28	-	2.05	0.17	[17]
GM	-	20.20	-	27.30	65.70	7.00	51.20	5.52	-	2.48	0.17	[17]
GM	21.80	-	-	-	-	4.20	54.90	5.83	-	2.09	0.17	[17]
GM	21.30	-	-	-	-	8.10	48.60	5.73	-	2.48	0.21	[17]
GM	-		-	-	-	2.18	52.97	5.94	34.22	0.54	-	[13]
GM	-		-	-	-	3.46	41.21	5.93	45.50	0.66	-	[13]
EGM	-		7.55	24.35	72.40	3.25	50.75	6.40	38.40	1.18	0.02	[42]
GM	-		-	-	-	3.30	49.70	6.20	35.50	2.40	-	[35]
GM	-	18.02	10.00	31.10	55.60	13.30	42.20	3.50	37.70	3.00	0.30	[44]
GM	20.04		-	21.90	72.60	5.40	49.10	6.30	42.31	2.29	-	[34]
GM	21.64		0.74	17.29	75.49	6.48	49.48	6.86	34.24	2.84	0.24	[36]
GM	19.60		-	-	-	8.23	48.70	5.57	35.90	1.66	-	[37]
GM	-	19.54	7.49	24.73	67.80	7.47	42.97	9.28	-	2.05	0.17	[44]
GM	-	18.70	-	19.7	67.60	12.70	45.50	5.10	34.70	1.80	0.17	[44]
GM	-	19.60	-	-	-	8.23	48.70	5.57	35.90	1.66	-	[44]
EGM	-	18.93	7.79	27.28	65.70	7.00	51.20	5.53	33.62	2.48	0.17	[27]

Table 16- Calorific value, proximate analysis and ultimate of different samples of OP

Sample	Calorific value (MJ/kg)		Proximate analysis (%)				Ultimate analysis (%)					Ref
	HHV	LHV	Moisture^{wb}	FC^{db}	VM^{db}	Ash^{db}	C	H	O	N	S	
EOP	20.70		6.80	21.60	67.20	4.40	53.40	7.50	37.40	1.70	-	[20]
OP	-	-	2.12	11.04	81.75	7.21	52.49	6.65	31.88	1.51	0.26	[24]
3POP	22.00	20.40	52.00	17.60	80.00	2.50	55.10	7.00	33.90	1.30	-	[29]
3POP	22.70	21.10	63.00	17.90	79.00	3.10	53.30	7.20	35.20	1.00	-	[29]
2PEOP	19.70	18.30	-	17.60	73.50	8.90	48.40	6.00	34.90	1.50	-	[29]
2POP	-	-	2.12	11.50	80.73	7.77	52.49	6.66	31.31	1.51	0.26	[30]
2PEOP	19.90	-	12.20	13.70	65.40	8.70	60.40	8.20	-	3.00		[46]
2PEOP	17.10	-	6.65	22.15	60.83	10.37	44.80	7.10	37.30	0.43	-	[47]
OP	16.70	-	10.00	24.20	72.00	3.80	44.60	6.10	44.30	1.10	0.10	[48]
3POP	22.50	-	7.40	16.10	74.20	2.30	53.50	6.80	38.60	1.10	-	[40]
EOP	-	-	-	-	-	-	47.04	5.73	-	0.87	0.06	[31]
2POP	-	-	70.00	-	-	-	56.11	7.39	30.24	0.75	0.10	[41]
2PEOP	20.50	-	9.40	19.70	66.50	4.40	53.40	7.50	32.50	0.46	-	[33]
OP	21.83	-	-	-	-	-	52.47	6.25	36.75	1.53	-	[57]

3.2 LCA Methodology- Olive Pomace Valorisation

In this work, the LCA was carried out using the software SimaPro and it is applied by using general methodological framework and standards for LCA defined by ISO 10040 and ISO 14044 [24]. All the data used was based on empirical works or in justified assumptions.

3.2.1 Goal and Scope Definitions

The aim of this study is to compare olive pomace valorisation through four different thermochemical processes (combustion, gasification, HTC followed by gasification and pyrolysis) in terms of environmental performance. In this regard an LCA methodology is used to identify the environmental impact associated with each studied thermochemical conversion process. The LCA was carried out in accordance with gate-to-cradle approach, taking in account just the moment olive pomace enters in facility and its valorisation. Downstream processes, such as olive production, olive oil extraction and the possible transport of olive pomace are not considered in this study because it is assumed that these values are the same for all management alternatives. The functional unit of this study is defined as 1 kg of 2POP (extraction method used in Portugal) with 60% moisture.

3.2.2 Scenarios, System Boundaries and Assumptions

As mentioned before four treatment approaches were modelled and evaluated. Although, being four thermochemical processes assessed, in total seven scenarios were evaluated (Figure 8,9, 10 and 11) because different drying processes were considered. The scenarios considered are shortly described below:

1. C.A- Combustion of olive pomace to produce electricity. Drying of olive pomace using natural gas.
2. C.B- Combustion of olive pomace to produce electricity. Drying of olive pomace with recirculation of the heat of exhausted gases.
3. G.A- Gasification of olive pomace to produce electricity. Drying of olive pomace using natural gas.
4. G.B- Gasification of olive pomace to produce electricity. Drying of olive pomace with recirculation of the heat of exhausted gases.
5. HTC.A- HTC of olive pomace followed by gasification to produce electricity. Drying of olive pomace using natural gas.
6. HTC.B- HTC of olive pomace followed by gasification to produce electricity. Drying of olive pomace with recirculation of the heat of exhausted gases.
7. P.A- Slow pyrolysis of olive pomace and use of by-products. Biochar used as soil amendment, syngas as thermal input and bio-oil directed to a treatment facility.

Several hypotheses and assumptions were made in order to perform the study:

- The mass and energy balances are modelled assuming the same quantity and uniform properties of olive pomace.

- The acquisition and the maintenance of the equipment required were excluded from the assessment.
- In the drying process were assumed 60% losses based on Jurendic [60] and Kemp [61] and the amount of heat necessary for the process calculated was 2.608 MJ/kg (see appendix A).
- The distance of transport of biochar and bio-oil was assumed to be the same and equal to 50 Kms.
- The end use and end life of pyrolysis bio-oil was not taken into account.
- In the HTC scenario the wastewater treatment is not included within the system boundary and wastewaters with simplified composition of phenols and furfurals are assumed to be discharged into the environment.

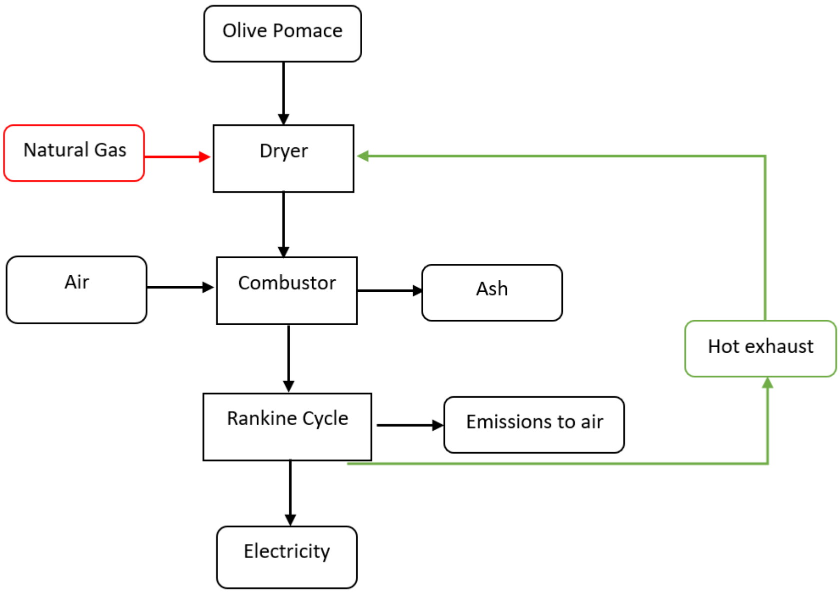

Figure 9- Combustion scenarios C.A (red) and C.B (green)

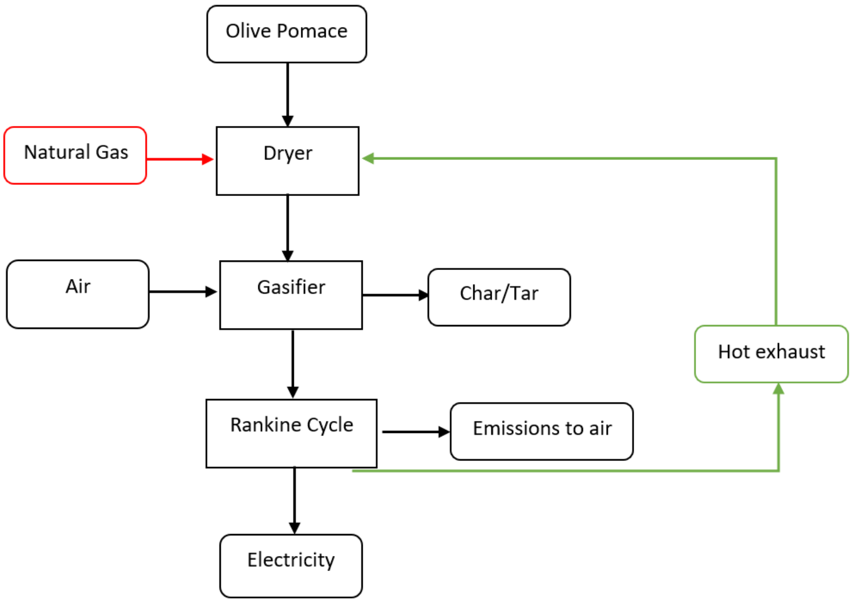

Figure 10- Gasification scenarios G.A (red) and G.B (green)

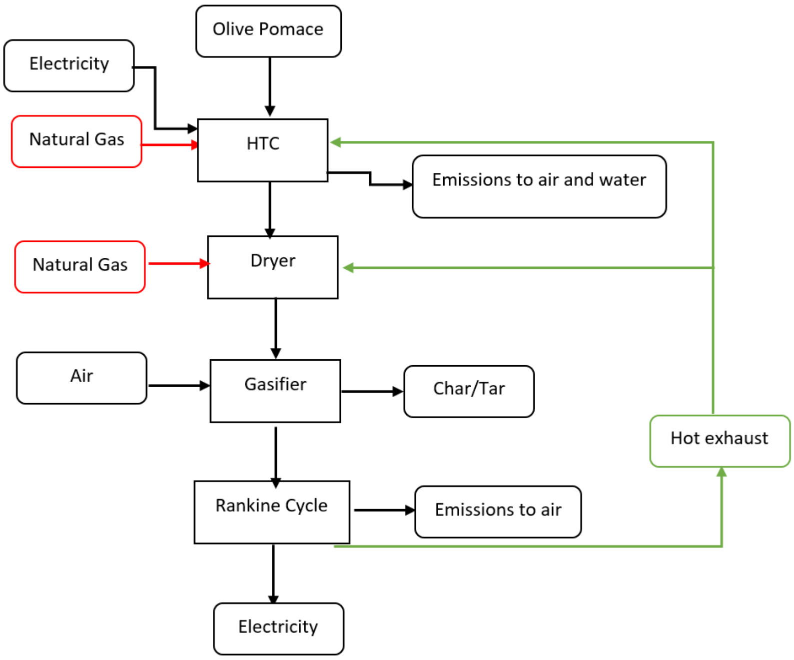

Figure 11- HTC followed by gasification scenarios HTC.A (red) HTC.B 6 (green)

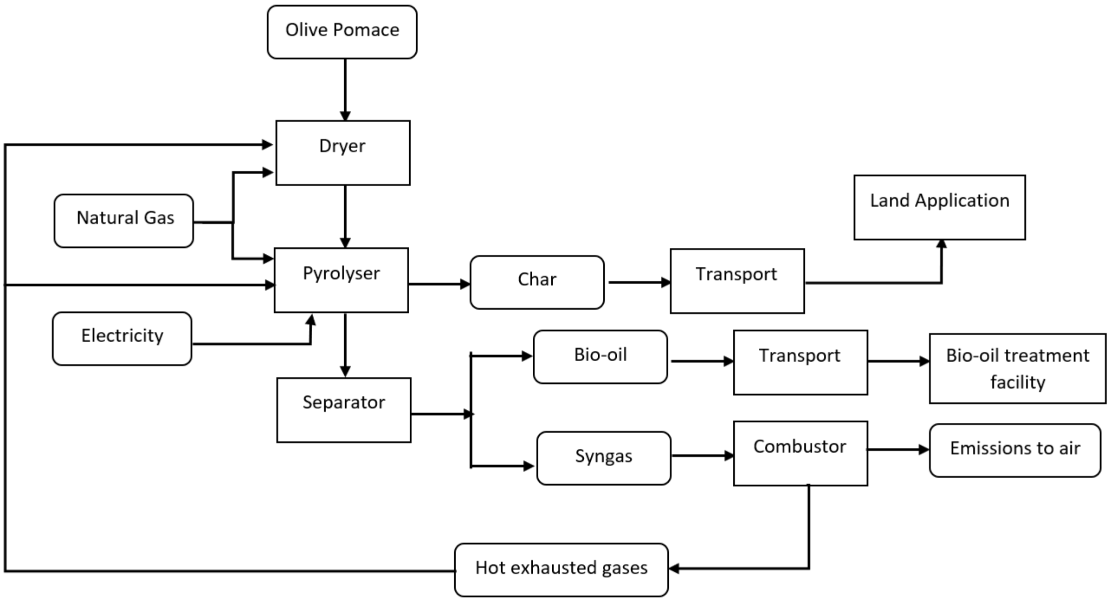

Figure 12- Pyrolysis scenario P.A

Energy requirements

In order to perform the LCA and the correct assessment of the life cycle inventory analysis is necessary to understand the energy requirement of each system.

In general terms all scenarios start with an input of 2POP olive pomace with a moisture of 60% which is going to be dried to moisture of 10%, the HHV of the olive pomace used is based on the results obtain in section 4.1. The thermal energy required for that processed is 2.608 MJ/kg which is detailed in the appendix A. The dryer efficiency is considered 40 % [60,61] which means that 60% of the input heat is lost. The only scenario where the drying process is less intensive is in the HTC scenarios (HTC.A and HTC.B) which prior to drying HTC reduces the moisture to 40% [57].

After the Rankine cycle in some cases there are recirculation of the exhaust gases and in the other scenarios were assumed the use of natural gas for thermal necessities. Regarding pyrolysis process the thermal requirements were met by burning syngas and natural gas, because the thermal input of the syngas did not meet the thermal requirements. All the data used was based on previous empirical work.

The energy balance includes electric and thermal efficiencies which is schematically represented for each process in Table 17. For each layout the best-case scenario was considered (higher thermal and electric efficiencies) since the purpose of this part of the work is to compare which scenario has lower environmental impacts.

The formulas used for the energy balances are also represented below:

$$n_{el} = \frac{E_{el}\times 3.6}{m_{fuel}\times HHV_{fuel}} \tag{11}$$

$$n_{rec} = \frac{Q_{rec}}{Q_{total}} \tag{12}$$

$$n_{burn} = \frac{Q_{em}}{HHV_{fuel}\times m_{fuel}} \tag{13}$$

$$n_{gas} = \frac{m_{syngas}\times HHV_{syngas}}{m_{fuel}\times HHV_{fuel}} \tag{14}$$

$$Energy\ Yield = \frac{m_{hydrochar}\times HHV_{hydrochar}}{m_{fuel}\times HHV_{fuel}} \tag{15}$$

Where: n_{el} is the electric efficiency of the process; E_{el} [kWh] is the electrical energy generated; HHV_{fuel} is the HHV of the fuel in MJ/kg; m_{fuel} is the mass of the fuel in kg; n_{rec} is the heat recovery efficiency of the exhausted gases (0.5); Q_{rec} is the quantity of heat recovered from the exhausted gases in MJ; Q_{total} is the total heat emited from the exhausted gases in MJ; n_{burn} is the efficiency of the burned natural gas or syngas coming from pyrolysis, Q_{em} is the heat emitted from the burning of the respective fuel in MJ; n_{gas} is the cold gas efficiency; m_{syngas} is the mass of gas formed during gasification in kg; HHV_{syngas} is the HHV of the syngas formed during gasification in MJ/kg; $m_{hydrochar}$ is the mass obtain after the HTC in kg; $HHV_{hydrochar}$ is the HHV of the fuel after the HTC process in MJ/kg.

Table 17- Energy balance for each scenario

Energy balance	With heat recovery			Without heat recovery				Ref
Scenario	C.B	G.B	HTC.B	C.A	G.A	HTC.A	P.A	
Input OP at 60% moisture (kg)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	-
Output dry OP at 10% moisture (kg)	0.500	0.500	-	0.500	0.500	-	0.500	-
HHV dry OP at 10% moisture (MJ/kg)	21.150	21.150	-	21.150	21.150	-	21.150	-
Energy yield (%)	-	-	83.000	-	-	83.000	-	[40]
n_{el} (%)	35.000	33.000	32.000	35.000	33.000	32.000	-	[33,51,62,63]
Electricity consumption (kWh)	0.000	0.000	0.020	0.000	0.000	0.020	0.179	[39,57,64]
Net electricity (kWh)	1.028	0.969	0.920	1.028	0.969	0.920	-0.179	
n_{rec} (%)	50.000	50.000	50.000	50.000	50.000	50.000	-	[65]
n_{gas} (%)	-	78.000	82.800	-	78.000	82.800	-	[33,50,65]
n_{burn} (%)	-	-	-	90.000	90.000	90.000	90.000	[65]
Thermal consumption	2.608	2.608	1.470	2.608	2.608	1.470	2.791	[39,60,65]
HHV natural gas	52.000	52.000	52.000	52.000	52.000	52.000	52.000	[66]
HHV syngas (MJ/kg)/ Yield (%)	-	-	-	-	-	-	13.2/25.9	[46]
Net heat production	2.680	1.516	2.164	-2.608	-2.608	-1.470	-1.253	-
Quantity of natural gas (kg)	0.000	0.000	0.000	0.056	0.056	0.031	0.027	-

3.2.3 Life Cycle Inventory Analysis

To perform the environmental assessment, a data collection from the inputs and products related to the analysed processes is required. The Life Cycle Inventory is the compilation and quantification phase of all flows (raw materials, energy and other goods and services, emissions, waste and products) related to the production system during its entire life cycle (ISO4040, 2006 and ISO14041, 1998) [52]. The inventory data associated with the scenarios mentioned before were either collected from previously published data sources, including life cycle inventory studies, scientific literature describing experimental studies, and/or Ecoinvent data bases.

The Life Cycle Inventory data for all the scenarios are presented in Tables 18-21.

Table 18- Inventory data combustion scenario

Stage	Inputs/Outputs	Amount	Ref
Drying	Olive pomace	1 Kg	
C.A	Natural gas	0.056 kg	
C.B	Natural gas	0 kg	
Combustor	DOP	0.5 kg	
	Ash	22 g	
Rankine cycle	Emissions to air		[56,57]
	N_2	2.153 kg	
	H_2O	0.300 kg	
	O_2	0.009 kg	
	NO	0.004 kg	
	SO_2	0.003 kg	
	H_2	0.001 kg	
	CO	0.057 kg	
	CO_2	0.857 kg	
	Particulates; <2.5 μm	7.4*10-3 g	
	Particulates; <10 μm	0.037 g	
	Energy saving	1.028 kWh	

Table 19- Inventory data gasification scenario

Stage	Inputs/Outputs	Amount	Ref
Drying	Olive pomace	1 kg	
C.A	Natural gas	0.056 kg	
C.B	Natural gas	0 kg	
Combustor	DOP	0.5 kg	
	Ash/Tars/Chars	12 g	[56]
Rankine cycle	Emissions to air		[67]
	N_2	1.824 kg	
	H_2O	0.198 kg	
	O_2	0.032 kg	
	SO_2	0.004 kg	
	CO	0.024 kg	
	CO_2	0.462 kg	
	NO	0.008 kg	
	Energy Saving	0.969 kWh	

Table 20- Inventory data HTC followed by gasification scenario

Stage	Inputs/Outputs	Amount	Ref
HTC	Olive pomace	1 kg	
	Emissions to air		[57]
	CO_2	46.536 g	
	H_2	0.014 g	
	CO	1.784 g	
	CH_4	1.255 g	
	O_2	19.638 g	
	Emissions to water		[57]
	Phenols	142.432 g	
	Furfurals	190.89 g	
	Inorganic, N compounds	8.635 g	
HTC and drying			
HTC.A	Natural gas	0.031 kg	
HTC.B	Natural gas	0 kg	
Gasifier	Dry hydrochar	0.313 kg	[53]
	Ash	7.67 g	[56]
Rankine cycle	Emissions to air		[56]
	N_2	1.142 kg	
	H_2O	0.124 kg	
	O_2	0.020 kg	
	SO_2	0.003 kg	
	CO	0.015 kg	
	CO_2	0.289 kg	
	NO	0.005 kg	
	Energy saving	0.920 kWh	

Table 21- Inventory data pyrolysis scenario

Stage	Inputs/Outputs	Amount	Ref
Dryer	Olive pomace	1 kg	
Dryer and pyrolysis	Natural gas	0.027 kg	
Pyrolysis	DOP	0.5 kg	
	Char	32.50%	[46]
	Syngas	25.90%	[46]
	Bio-oil	41.60%	[46]
	Electricity consumption	0.179 kWh	
Transport small truck	Biochar	0.163 kg	
	Distance	50 km	
	Bio-oil	0.208 kg	
	Distance	50 km	
Land application	Fertilizer Saving	0.163 kg	
	N	2.57%	
	Ca	1.34%	
	K	2.17%	
	Mg	0.29%	
	P	0.62%	
Combustor	Emissions to air (burning of)		[46]
	N_2	0.401 kg	
	H_2O	0.070 kg	
	O_2	0.006 kg	
	CO	0.003 kg	
	CO_2	0.181 kg	
	NO	0.001 kg	

3.2.4 Impact Assessment Methodology

SimaPro software is a professional tool to evaluate the environmental impacts of products, processes and services through their life cycle. It allows to model and analyse the life cycle of a product or service in a systematic and transparent way, following the recommendations of the ISO 14040 series (ISO14040, 2006). The midpoints impacts are considered a point in the chain of cause and effect, focusing on unique environmental problems (e.g. climate change). The endpoint method analyses the environmental impact at the end of this chain of cause and effect. In the ReCiPe methodology, eighteen midpoint indicators and three more uncertain endpoint indicators are calculated. The conversion of midpoints into endpoints simplifies the interpretation of the LCA results, partly because there are too many impact categories and have a very abstract meaning. In this way, the endpoint approach provides results with a higher degree of interpretation but greater uncertainty. On the other hand, the midpoint approach is more reliable but does not provide damage information [56].

Due to the advantages and disadvantages of the midpoint and endpoint indicators, both methodologies have been combined in this study. In this way, on the one hand, decisions can be made using midpoint indicators, which are more certain but, in some cases, may have less relevance for decision support.

On the other hand, endpoint indicators are used, which have been shown to be more relevant and decisions can be made more easily but have less certainty [56].

Nine midpoint impacts were screened for all scenarios: climate change (CC), ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (POF), particulate matter formation (PMF) and fossil depletion (FD) [56].

In addition, for a better understanding, the final point indicators were addressed. The following endpoint impacts were examined: damage to human health (HH), damage to ecosystem diversity (ED) and damage to resource availability (RA).

Finally, all the results were normalised, which facilitates the comparison between impact scores of different impact categories. Using the normalisation value, it is possible to identify easily and faster the impact categories with highest and lowest contributions that affect the environment, simplifying the final decision making. As defined in ISO 14044, the normalisation is a process to calculate the magnitude of the results of impact category indicators, in relation to a certain reference information. In this case, the results for each category are normalised with respect to average European emissions [56].

3.3 Techno-Economic Analysis

In the previous chapter were explained the methods used to compare four different thermochemical processes (combustion, gasification, HTC followed by gasification and pyrolysis). This chapter is focused on comparing the same four different thermochemical conversion methods but through a techno-economic analysis in order to assess the feasibility of a project regarding valorisation of olive pomace. For this assessment the scenarios considered were the same of the LCA analysis and the energy requirements are exactly the same as the ones calculated in section 3.2.2. The data required to this part of the thesis is all based on previous works.

3.3.1 Plant Characteristics

For this section four biomass plants will be considered, three of them designed to generate electricity through combustion, gasification and HTC followed by gasification; the fourth of them designed to produce biochar, bio-oil and syngas through pyrolysis. All the facilities receive olive pomace with 60% moisture and it is assumed that all the stages of the process (Figure 9,10,11,12) occur on site. Since the ultimate goal is to compare technologies, the results were normalized considering an input of 1 kg/h of olive pomace, but all the data is based on facilities with large capacity of more than 1 ton/h.

Capacity factor is defined as the ratio between the energy generated in a period and the total energy that could be generated if the facility runs at maximum output during the same period and without interruption [68]. Therefore, if the factory works without stoppage 24 hours every single day of the year the capacity factor would be 100%. In this work it was assumed for all plants a capacity factor between 60-85%.

Another important factor is the lifetime of the biomass plants. Literature reports values between 15 to 25 years, being the majority of the values reported equal or superior to 20 years [63]. Consequently, it is going to be assumed a lifetime of 20 years for all the biomass plants.

3.3.2 Cost Structure

The analysis of costs can be very detailed, but for comparison purposes and transparency, the approach used here is a simplified one. This allows greater scrutiny of the underlying data and assumptions, improved transparency and confidence in the analysis, as well as facilitating the comparison of costs for different technologies in order to identify what are key drivers in any differences.

The three indicators that have been selected are (Figure 12):

- Equipment cost (factory gate and delivery at site)
- Total installed project cost
- Levelized cost of 1 kg/h input of olive pomace, which is in certain way similar to the levelized cost of electricity but need to be adapted because in the pyrolysis scenario there is no electricity produced.

The analysis excludes the impact of government incentives or subsides system balancing costs associated with variable renewables and any system wide cost saving from the merit order effect. Further, the analysis does not take into account any CO_2 pricing, nor the benefits of renewables in reducing other externalities such as reduced local air pollution and contamination of the natural environment.

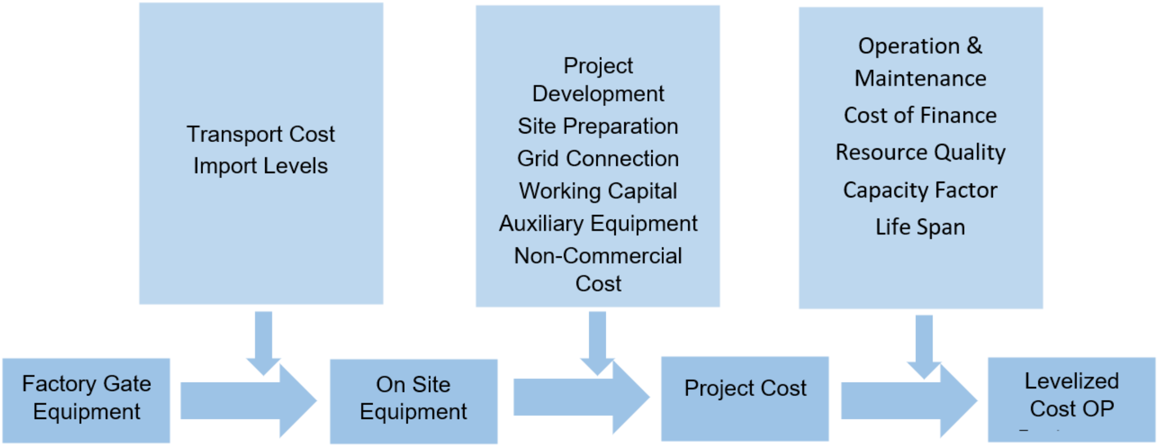

Figure 13- Biomass power generation and cost indicators and boundaries

3.3.2.1 Feedstock Cost

Feedstocks cost can represent 40-50% of the total cost of operating a biomass plant. Nevertheless, a lower cost feedstock is typically associated with agricultural residues like olive pomace [63]. Literature has reported values ranging from 15-30 €/ton [26,33,56].

In Portugal it has been reported in the end of 2019 an excess of olive pomace in treatment facilities which resulted in the selling price of olive pomace to drop to 0 and even to the producers to have to pay for the transport of olive pomace to treatment facilities [69,70]. Therefore, the price of this feedstock is very volatile in Portugal and for this study it will be assumed a price of 15 €/ton including transport, even though the current market price is lower.

3.3.2.2 Total Investment Cost- Capital expenditure (CAPEX)

The CAPEX consists of the costs associated with equipment (prime mover and fuel conversion system), fuel handling and preparation machinery, engineering and construction cost and planning. It can also include grid connection, roads and any kind of new infrastructure or improvements required for the project [63].

3.3.2.3 Operation and Maintenance Expenditure (OPEX)

Operation and maintenance (O&M) refer to the fixed and variable costs associated with the operation of the biomass plant. Fixed O&M can be expressed as a percentage of capital costs. For biomass plants, they typically range from 1-6% of the initial CAPEX per year. Fixed O&M costs consist of labour, schedule maintenance, routine component/equipment replacement and insurance. Variable O&M cost depend on the output of the fuel and are usually express as a value per unit of output (€/kWh). They include non-biomass fuel costs as unplanned maintenance, equipment replacement and incremental service costs [63].

3.3.2.4 Other costs

In the biomass plants analysed most of the costs are included in three categories mentioned before. Other costs that will be taken into account in the study will be ash handling, natural gas and the electricity consumption of the biomass plants. The ash disposal costs are assumed to be 110.9 €/ton of ash [39,63], the price natural gas and electricity consumption was based on the price of 2020 Portuguese market.

3.3.3 Revenues

In terms of revenues, the plants that generate electricity (combustion, gasification and HTC followed by gasification scenarios) generate revenue by selling the electricity produced. In this part, for simplification purposes it is assumed that all electricity generated is sold to the grid and that the selling price is between 0.102-0.109 €/kWh [71]. Another important factor of the revenues generated by selling electricity is the electric efficiency of each power plant which is detailed on section 3.3.5.

The pyrolysis plant generates revenues by selling biochar and bio-oil. In this part of the study it is taken into account the cost of treatment of bio-oil (in the LCA was not taken into account). The selling price of biochar as soil amendment is assumed to be between 0.084-0.21 €/ton and the bio-oil after the treatment between 0.269-0.391 €/ton [43,72].

3.3.4 Economic Model

The economic-financial analysis for the four installations studied was made based on net present value (NPV), evaluation of the period of return on investment (payback period) (PBP) and the internal rate of return (IRR). The evaluation will be done for entire lifetime of the project (20 years), N=20

3.3.4.1 Net Present Value (NPV)

NPV consists of updating the cash-flow "Ct" (the difference between income and expenses for each period analysed) of the project for the different periods to an estimated discounted rate "i". Assuming the same interest rate for all periods, generally the first time period is the first year of amortization, designated as year 1. So "t" takes values between 1 and N. The study considers t=0 is related to the investment during the design and construction phase of the biomass plant. NPV can be equated as [33] :

$$NPV\ (i, N) = -K + \sum_{t=1}^{N} \frac{Ct}{(1+i)^t} \tag{16}$$

Where "i" is the financial discount rate, "Ct" is the annual cash flow (Income minus expenses) each year, and "N" is the total number of years. The time period t=0 is related to the investment during the design and construction phase of the gasifier.

The NPV represent the net profit generated by the project, obtained by financial equivalence at time zero. If the NPV is greater than zero, the project is viable for that interest rate. Consequently, it is a necessary condition although it does not have to be sufficient [33] .

The discounted rate used for this project was based on report of previous biomass projects across Europe, and the values found for the discount rate were between 6-9 %, consequently the value used in this work was 7.5 % [73]. The cash flows will be assumed to be the same for every year.

3.3.4.2 Payback Period- PBP

The recovery period is the number of periods it will take for the investment to recover with the cash flows generated by the project. If K is the investment made and Ct the cash flows in each period, the recovery period, t, will be translated by the following expression [33]:

$$K = \sum_{t=1}^{N} \frac{Ct}{(1+i)^t} \tag{17}$$

3.3.4.2 Internal Rate of Return (IRR)

The internal rate of return (IRR) is the type of update or discount that nullifies the NPV. The rate is internal because it does not depend on factor exogeneous to the investment [33].

In this way, the IRR is calculated by obtaining the rate, IRR, which meets the following equation:

$$NPV\ (IRR, N) = -K + \sum_{t=1}^{N} \frac{Ct}{(1+IRR)^{t}} = 0 \qquad (18)$$

Only those projects that meet “feasibility” condition will be viable: IRR>i, where i is the interest rate that corresponds to the “cost of capital”. The higher the IRR, the better the investment.

Since the values of the discount rate found in literature were between 6-9% for biomass plants, it is considered for all projects that IRR should be higher than 9%.

3.3.5 Best, Average and Worst-Case Scenarios?

To perform this analysis using the economic model mentioned above the seven scenarios previous explained in section 3.2.2, it was considered a worst-case, an average and a best-case scenario for each one of them. Consequently, the total number of scenarios considered were 21 as it is summarized in Table 22.

Table 22- Scenarios considered for the techno-economic analysis

Scenario	Description
S1	Combustion worst-case scenario without heat recovery
S2	Combustion average scenario without heat recovery
S3	Combustion best-case scenario without heat recovery
S4	Combustion worst-case scenario with heat recovery
S5	Combustion average scenario with heat recovery
S6	Combustion best-case scenario with heat recovery
S7	Gasification worst-case scenario without heat recovery
S8	Gasification average scenario without heat recovery
S9	Gasification best-case scenario without heat recovery
S10	Gasification worst-case scenario with heat recovery
S11	Gasification average scenario with heat recovery
S12	Gasification best-case scenario with heat recovery
S13	HTC followed by gasification worst-case scenario without heat recovery
S14	HTC followed by gasification average scenario without heat recovery
S15	HTC followed by gasification best-case scenario without heat recovery
S16	HTC followed by gasification worst-case scenario with heat recovery
S17	HTC followed by gasification average scenario with heat recovery
S18	HTC followed by gasification best-case scenario with heat recovery
S19	Pyrolysis worst-case scenario
S20	Pyrolysis average case scenario
S21	Pyrolysis best-case scenario

The range of values used for this analysis is detailed on Table 23. Some values are detailed for one type of biomass plant (eg:CAPEX), as others are not detailed because they apply for all the biomass plants (eg: feedstock price).

Table 23- Data for worst, average and best-case scenarios in techno-economic analysis

Cost Structure	Description	Worst scenario	Average scenario	Best scenario	Ref
Feedstock price					
	Olive pomace cost (€/ton)	15	15	15	
CAPEX					
	Combustion plant (€/kW)	3780	2646	1512	[63]
	Gasification plant (€/kW)	4872	3360	1848	[63]
	HTC plant (€/(kg/h))	709.52	709.52	709.52	[59]
	Pyrolysis plant (€/ (dry kg/h))	2594.29	1973.25	1324.80	[64]
	Bio-oil treatment facility (% pyrolysis plant cost)	39	39	39	[74]
OPEX					
Fixed	Combustion plant (% Investment Cost)	4.2	3.7	3.2	[33,63]
	Gasification plant (% Investment Cost)	5	4	3	[33,63]
Variable	Combustion plant (€/kWh)	0.0039	0.0036	0.0032	[63]
	Gasification plant (€/kWh)	0.0031	0.0031	0.0031	[63]
Fixed and variable	HTC plant (€/kg)	0.0416	0.0333	0.0250	[59]
	Pyrolysis Plant (%Investment Cost)	5	4.5	4	[43,64,72]
Other Costs					
Ash handling	Price (€/kg)	0.1109	0.1109	0.1109	[63]
Natural gas	Price (€/kWh)	0.0609	0.0590	0.0571	[75]
Electricity	Price (€/kWh)	0.1485	0.1435	0.1385	[75]
Revenues					
Capacity factor	All plants (%)	60	72.5	80	[62,63]
Electric efficiency	Combustion plant (%)	25	30	35	[33,62,63]
	Gasification plant (%)	17	25	33	[33,62,63]
	HTC followed by gasification plant (%)	16	24	32	[33,51,62,63]
Electricity	Selling price ((€/kWh)	0.1020	0.1055	0.1090	[71]
Biochar	Selling price (€/kg)	0.084	0.168	0.210	[43,72]
Bio-oil	Selling price (€/kg)	0.269	0.391	0.330	[43,72]

4 Results and Discussion

In this chapter, the results obtained after applying the methodologies enumerated in chapter 3 are presented and discussed. Results are divided in three sections: grape marc and olive pomace characterization; life cycle impact assessment; and techno-economic analysis.

4.1 Grape Marc and Olive Pomace Characterization

Table 24 and 25 displays the calorific values, proximate analysis and ultimate analysis of different samples of grape marc and olive pomace. From the tables mentioned each category has an expected content and a range, with the expected content it is possible to predict a priori which values are more likely to be obtain for each type of sample. The range represents the spectrum of values stated in the literature.

Firstly, comparing grape marc and EGM the results are very similar. The ultimate analysis shows that the carbon content expected content is around 2% higher in EGM than in grape marc. In addition, the FC content is also 1% greater, which can be explained by the exhaustion of sugars in the ethanol production, remaining a residue with higher content of lignin. However, it was just found two samples of EGM in literature, so it is needed further analysis of samples to confirm the trend.

Overall grape marc has a calorific value near 20 MJ/kg which is comparable to soft coal. Its initial moisture is quite high between 55-75% which requires pre drying to further thermochemical processes. FC content and ash content together are expected to be higher than 30%, which can be an advantage to achieve high yields of char in pyrolysis and HTC. In one case FC and ash were as high as 44%. VM was lower than 70% (expected content), which is lower than the 80% desirable for a gasification.

Regarding olive by-products, comparing olive pomace and EOP were found the major differences. These differences were attributed to the stage of hexane extraction in the EOP, which by removing the residual oil, decreased the VM content, as it is possible to see in Table 24 where the difference in VM content between olive pomace and EOP is more than 10%. This reduction in VM in terms of percentage resulted in an increase of FC and ash in EOP compared to olive pomace. Moreover, it was expected to obtain a lower C and H content in EOP which was very slight (H remain constant), since fatty acids in the oils are mostly composed of C and H. Finally, these observations were consistent with a lower calorific value for EOP (19.58 MJ/kg) as compared to olive pomace (21.15 MJ/kg). Concerning two-phase and three-phase extraction methods there were not found any significant differences. The main difference between 2POP and 3POP it is the higher initial moisture in 2POP, but after the drying process the feedstocks have very similar composition. There is lack of information in 2POP proximate analysis so it is not possible to perform that comparison, but in terms of ultimate analysis the C and H quantities were almost equal which confirms that is not expected a significant variation of the OP with the extraction method.

Overall olive pomace has a calorific value around 20 MJ/kg once again comparable to low types of coal, it has also an initial moisture between 40-70% which indicates that a previous drying process is necessary. VM was near 80% in the case of olive pomace and less than 70% in EOP which indicates that the first might be more suitable for gasification and the second for pyrolysis or HTC.

In general terms, it is possible to state that ash composition is the component which has the biggest spectrum of values, these probably due to the fact that the amount of inorganics in the feedstock varies a lot from place to place where grape and olives are cultivated. For instance, based on literature analysis samples from Turkey have higher quantity of inorganics than from Spain for example. This variation is also valid for other properties but in smaller terms. Additionally, the EGM and EOP initial moisture values are not referred because this type of biomass goes through a treatment which already includes a drying process, where the moisture content varies on the intensity of the drying process.

Finally, comparing grape marc and olive pomace these two by-products are much more similar than initially expected. Calorific value, in both biomass is close to 20 MJ/kg and initial moistures quite high which require a drying process. Excluding the EOP the VM in the olive pomace is around 10% higher than in the grape marc samples, consequently apparently olive pomace should be more appropriate to be gasified. On the other hand, FC and ash content of grape marc are around 7-8% and 2% respectively higher than olive pomace which indicates that grape marc might be more fit to HTC pre-treatment (which is expected to reduce ash content and obtain high char yields) or recovery via pyrolysis. In terms of ultimate analysis, they are quite similar, the major differences are in the C and O content which is around 3% higher and 3% lower respectively in the case of olive pomace compared to grape marc.

Concluding, besides slight differences in general they are comparable types of biomass, that is why on the further section for an LCA and Techno-Economic approach it was just considered an olive pomace sample and extrapolated some of the conclusions for the grape marc samples.

Table 24- Calorific value and proximate analysis of different samples (N= Number of samples) of GM and OP expected content and range

Sample	Result	Calorific value (MJ/kg)		Proximate analysis (%)				N
		HHV	LHV	Moisture^{wb}	FC^{db}	VM^{db}	Ash^{db}	
GM	EC	20.57±0.98	19.42±0.73	-	24.80±3.58	67.58±4.79	6.78±2.85	20
	Range	19.50-21.80	18.02-20.20	60.00-75.00	17.29-31.10	55.60-75.49	2.18-13.30	
EGM	EC	-	18.93	-	25.82±2.07	69.05±4.74	5.13±2.65	2
	Range	-	-	-	24.35-27.28	65.70-72.40	3.24-7.00	
Overall GM	EC	20.57±0.98	19.37±0.70	-	24.94 ±3.38	67.78±4.64	6.63±2.82	22
	Range	19.50-21.80	18.02-20.20	-	17.29-31.10	55.60-74.49	2.18-13.30	
OP	EC	21.15±2.15	20.75±0.49	-	16.39±4.84	77.95±3.92	4.45±2.42	8
	Range	16.70-22.70	20.40-21.10	40.00-70.00	11.04-24.20	72.00-81.75	2.30-7.77	
EOP	EC	19.58±1.45	18.30	-	18.95±3.44	66.69±4.55	7.35±2.77	6
	Range	17.10-20.70	-	-	13.70-22.15	60.83-73.50	4.40-10.37	
2POP	EC	-	-	-	11.50	80.73	7.77	2
	Range	-	-	50.00-70.00	-	-	-	
3POP	EC	22.40±0.36	20.75±0.49	-	17.20±0.96	77.73±3.10	2.63±0.42	3
	Range	22.00-22.70	20.40-21.10	40.00-60.00	16.10-17.90	74.20-80.00	2.30-3.10	
Overall OP	EC	20.36±2.10	19.93±1.46	-	17.55±4,27	72.83±7.11	5.77±2.88	14
	Range	16.70-22.70	18.30-21.10	-	11.04-24.20	60.83-81.75	2.30-10.37	

Table 25- Ultimate analysis of different samples of GM and OP expected content and range

Sample	Result	Ultimate Analysis (%)					N
		C	H	O	N	S	
GM	EC	48.88±4.52	6.12±1.26	37.33±3.96	2.00±0.70	0.25±0.29	20
	Range	41.21-54.90	3.50-9.28	34.22-45.50	0.54-3.00	0.11-1.24	
EGM	EC	50.98±0.32	5.97±0.62	36.01±3.38	1.83±0.92	0.10±0.11	2
	Range	50.75-51.20	5.53-6.40	33.62-38.40	1.18-2.48	0.02-0.17	
Overall GM	EC	49.07 ±4.34	6.11 ±1.21	37.09 ±3.74	1.99 ±0.69	0.23 ±0.27	22
	Range	41.21-54.90	3.50-9.28	33.62-45.50	0.54-3.00	0.02-1.24	
OP	EC	52.51±3.46	6.76±0.44	35.27±4.62	1.23±0.29	0.18±0.09	8
	Range	44.60-56.11	6.10-7.39	30.24-44.30	0.75-1.53	0.10-0.26	
EOP	EC	51.25±5.66	7.01±0.96	35.53±2.32	1.33±0.97	0.06	6
	Range	44.80-60.40	5.73-8.20	32.50-37.40	0.43-3.00	-	
2POP	EC	54.30±2.56	7.03±0.52	30.78±0.76	1.13±0.54	0.18±0.11	2
	Range	52.49-56.11	6.66-7.39	30.24-31.31	0.43-3.00	0.10-0.26	
3POP	EC	53.97±0.99	7.00±0.20	35.90±2.43	1.13±0.15	-	3
	Range	53.30-55.10	6.80-7.20	33.90-38.60	1.00-1.30	-	
Overall OP	EC	51.96±4.38	6.86±0.69	35.36±3.88	1.27±0.64	0.16±0.10	14
	Range	44.60-60.40	5.73-8.20	30.24-44.30	0.43-3.00	0.06-0.26	

4.2 Life Cycle Impact Assessment

LCA results for each evaluated impact category associated with the scenario considered are reported in this section. A positive impact potential indicates a burden to the environment (negative environmental effect), while a negative potential indicates environmental emissions savings (positive environmental effect).

This part is divided in five sub-sections, the first four are related to environmental impacts associated with each thermochemical process (combustion, gasification, HTC followed by gasification and pyrolysis), and the last one concerns the comparison between all the scenarios.

4.2.1 Combustion Scenario

Figure 13 presents schematically the impact of each process of the combustion scenario. The single score (without categories) results are shown, which were obtained using the endpoint method.

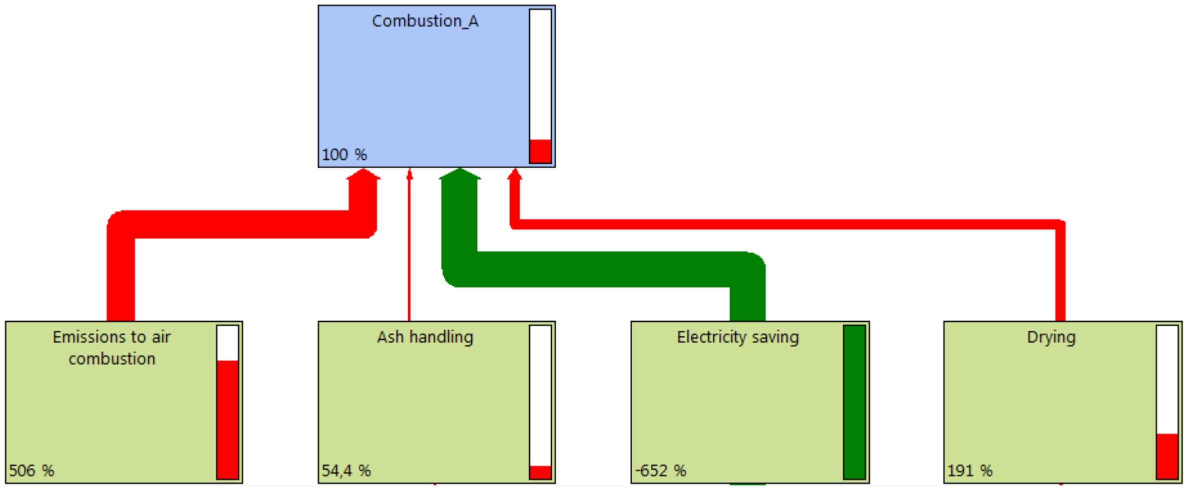

Figure 14- Contribution of each process in the combustion scenario using the endpoint method

The red arrows mean a negative environmental impact, as the green arrow means a positive environmental impact. From the results is possible to note that emissions to air from the combustion process have the higher negative environmental impact which accounts for 67.34% from the total negative impact. The drying process accounts for 25.42% and the ash handling 7.24%.

The saving considered was the electricity generated when handling 1 kg of olive pomace in the combustion plant and accounts for 86.77% of the total negative impacts. This value was obtained considering an electric efficiency of 35 % (Table 17) which is the best-case scenario.

The endpoint results for the combustion scenario according to the ReCIPe methodology is shown on Figure 14.

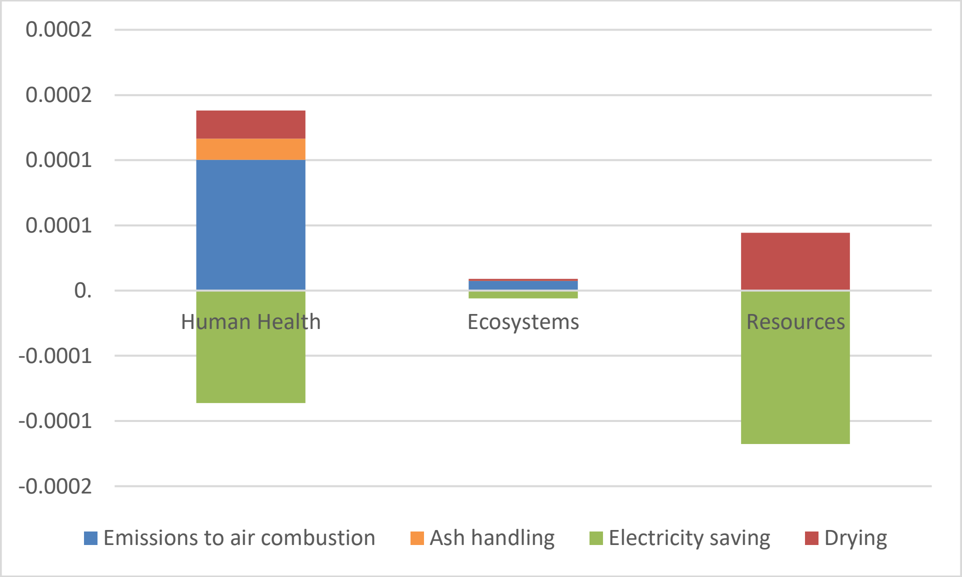

Figure 15- Normalised results using endpoint analysis of the combustion scenario

From Figure 14 it is possible to state that the main damage is on human health (72.09%) mainly caused by air emissions after the combustion process which are detailed on Table 18. Damage to ecosystems has the smallest impact (4.71%) and is dominated by air emissions from combustion. Damage to resources accounts for 23.20% and is related to the consumption of natural gas for the drying process. Regarding the savings, the main saving is related to the avoided consumption of resources which accounts for 56.04% followed by human health (41.06) and ecosystems (2.90%).

Accordingly with results is possible to conclude that the main impact is caused by the air emissions from the combustion process and that this process has the biggest impact on human health. Also, if it was considered the scenario with heat recovery the drying process would have no environmental impact and this would result in a 25.72% reduction of the overall results.

In the next three sections the structure presented is going to be similar to the one presented here.

4.2.2 Gasification Scenario

The results obtained for the gasification scenario are shown in Figure 15 and 16.

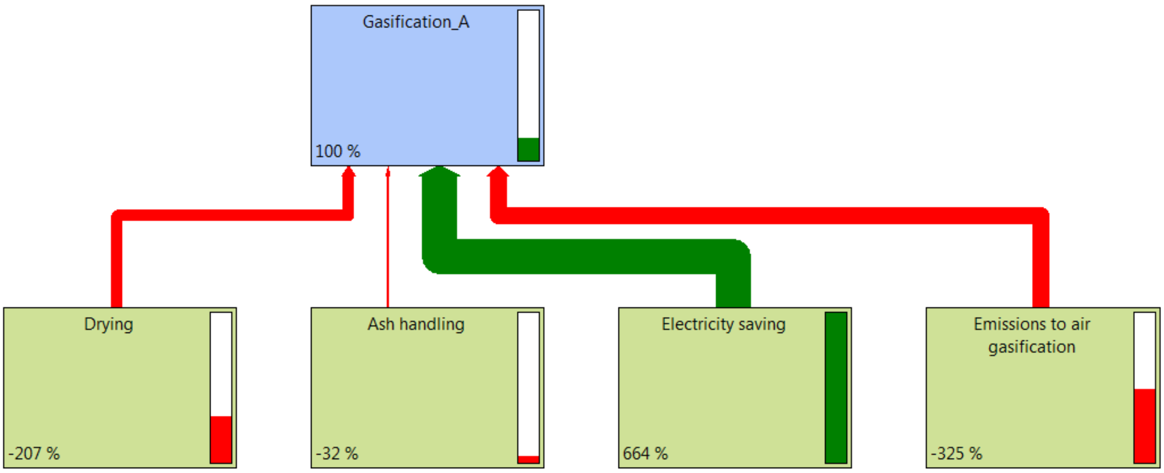

Figure 16- Contribution of each process in the gasification scenario using the endpoint method

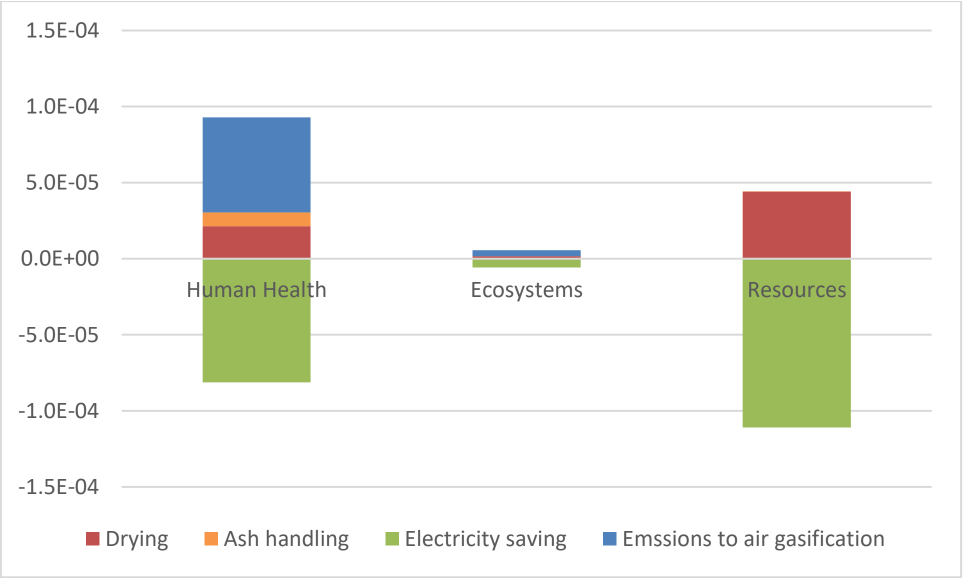

Figure 17- Normalised results using endpoint analysis of the gasification scenario

Figure 15 highlights that the major negative impact is related to air emissions from the burning of syngas obtained in the gasification process and accounts for 57.62% of the overall negative impacts. Drying accounts for 36.70% and the ash handling for 5.67%. Since the drying is the same considered in the combustion scenario, this means that air emissions for gasification are lower than combustion since the overall impact of drying was much higher in this case. The comparison between processes will be further detailed on section 4.2.5.

The savings accounts for 117.73% of the total negative impacts. This value was obtained considering an electric efficiency of 33% (Table 17).

Once again human health is the category with the biggest environmental impacts (65.12%) followed by resources and ecosystems which account for 30.97% and 3.91% respectively. The savings distribution is exactly the same, the only variation is on the quantity of the saving which is lower due to a lower electric efficiency considered.

Consequently, the conclusions obtained were quite similar to the combustion scenario. The emissions from burning the syngas had the biggest overall impact and human health was the category with higher negative impact. However, since quantitively the air emissions are lower compared to the combustion (approximately 38% lower) the drying process has a major overall impact and if it was considered the scenario with heat recovery this would result in 36.70% reduction of the overall negative environmental impacts.

4.2.3 HTC followed by Gasification Scenario

Figure 17 and 18 presents the results obtained for the HTC followed by gasification scenario.

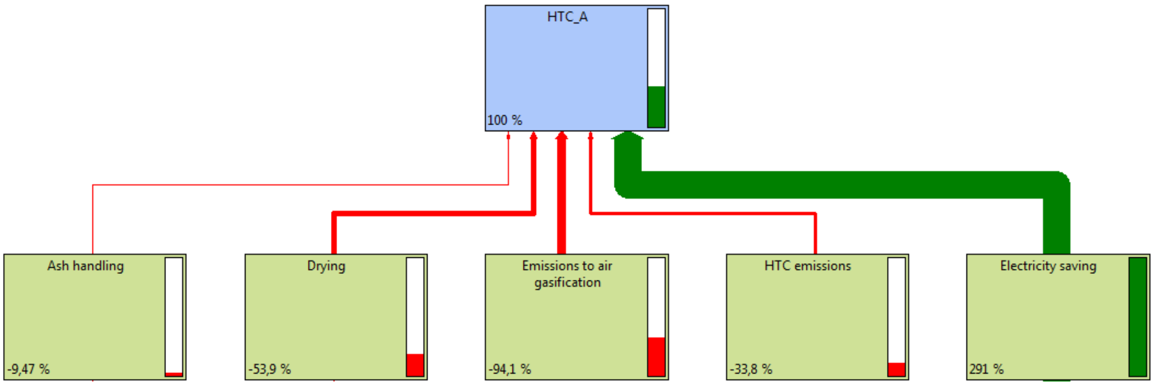

Figure 18- Contribution of each process in HTC followed by gasification scenario using the endpoint method

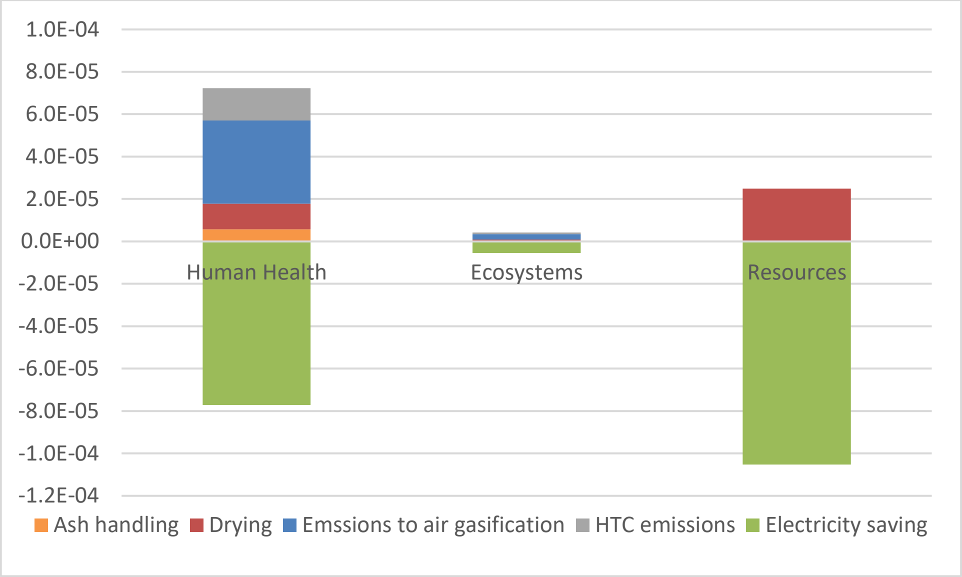

Figure 19- Normalised results using endpoint analysis of HTC followed by gasification scenario

Regarding the single score impacts (Figure 17), once again air emissions has the major negative impact which accounts for 49.20%. Then drying, HTC emissions and ash handling contribute with 28.18%, 17.67% and 4.95% respectively. Savings accounts for 152.14% relative to the negative impact, which was the higher obtained so far, which suggest that the quantitively the negative impacts are lower, since the electric efficiency of this scenario is lower compared to the other ones (32%).

In terms of categories, human health has the biggest impact associated (71.24%) since the processes are similar to the mentioned in the previous scenarios analysed, besides HTC emissions where all the impacts are related to human health. Ecosystems accounts for 4.09% and resources for 24.62%. The savings conclusions are the same mentioned for the gasification scenario.

In this scenario air emissions for burning syngas still has the major impact, however this impact is lower than in the previous scenarios. Also, as expected HTC prior to gasification lower the overall impact of drying comparing to the gasification scenario (approximately by 44%). Nevertheless, there was a new impact related to the emissions generated during the HTC process, but this value was lower than 20%. Finally, as in the previous scenarios drying with heat recovery would result in a lower overall impact, but in this case this reduction would be lower and also the category which has a biggest negative impact associated is human health.

4.2.4 Pyrolysis Scenario

In this section are presented the obtained results for the pyrolysis scenario (Figure 19 and 20).

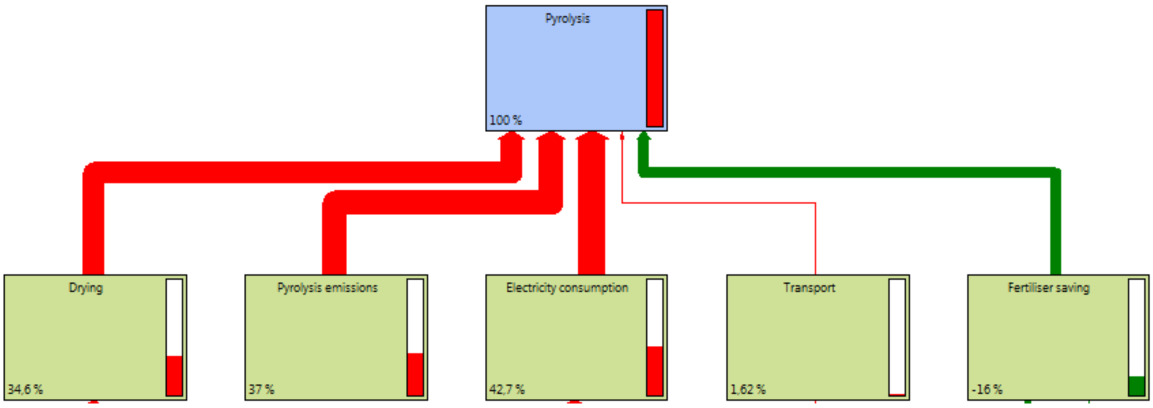

Figure 20- Contribution of each process in pyrolysis scenario using endpoint method

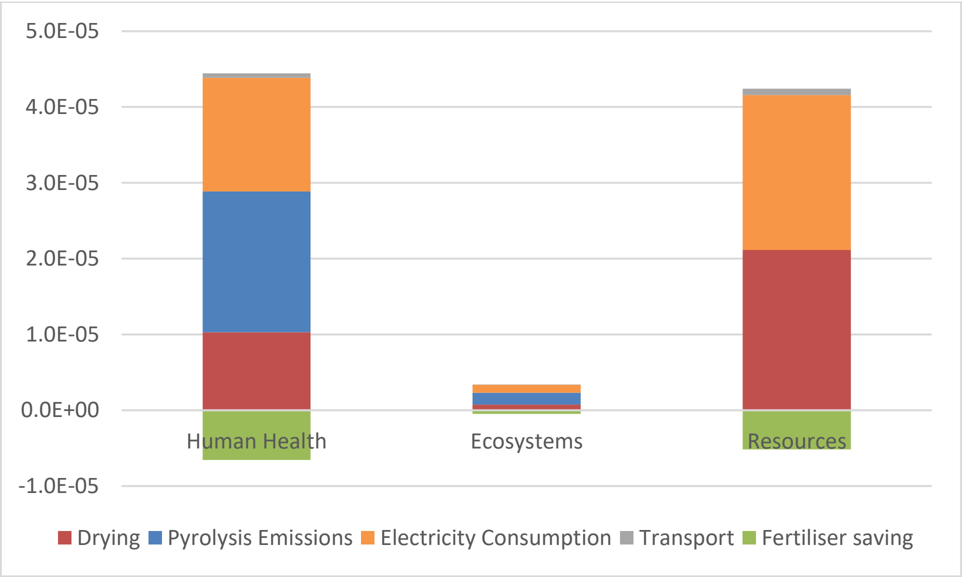

Figure 21- Normalised results using endpoint analysis of pyrolysis scenario

Figure 19 shows that in contrast to the other scenarios, in pyrolysis scenario there is not one process, air emissions previously, which has a much higher impact than the others. In fact, there are three processes which have a major impact that are electricity consumption, pyrolysis emissions (burning of syngas) and drying which account for 36.84%, 31.92% and 29.85% respectively. On the contrary the transport of the bio-oil and biochar have a very low impact with a contribution of 1.40%.

Concerning the savings, the results indicate a saving of 13.80% relative to the total negative environmental impacts which is much lower in comparison to the previous scenarios mentioned. Nevertheless, as mentioned in the 'methodologies chapter' in this study was not considered the end-use of bio-oil which could be used as a fuel after a correct treatment.

In terms of categories the two major impacts are associated with human health (49.22%) and resources (47%). Ecosystems has a lower impact with 3.82% from the overall impact.

Pyrolysis scenario is the only scenario from the ones studied which the end goal is not to produce electricity. Therefore, the results obtained were the most different in comparison to other scenarios. One limitation of the pyrolysis scenario is not having in account the end-use of bio-oil, which might have an important impact in terms of savings.

4.2.5 Scenarios Comparison

The previous sections presented the results regarding different scenarios of recovery of olive pomace. However, the results showed in the previous sections do not allow a direct comparison between scenarios.

In this section a comparison between the different thermochemical processes is will be made. A midpoint and endpoint analysis will be used. Also, two different analysis will be done. First a comparison analysis where is going to be exclude the savings from the generated electricity and fertilizer saving in order to assess the real impacts of each scenario. Afterwards, an analysis where the savings are considered was made.

Figure 21 and 22 show the results obtained for the different thermochemical processes without considering the savings.

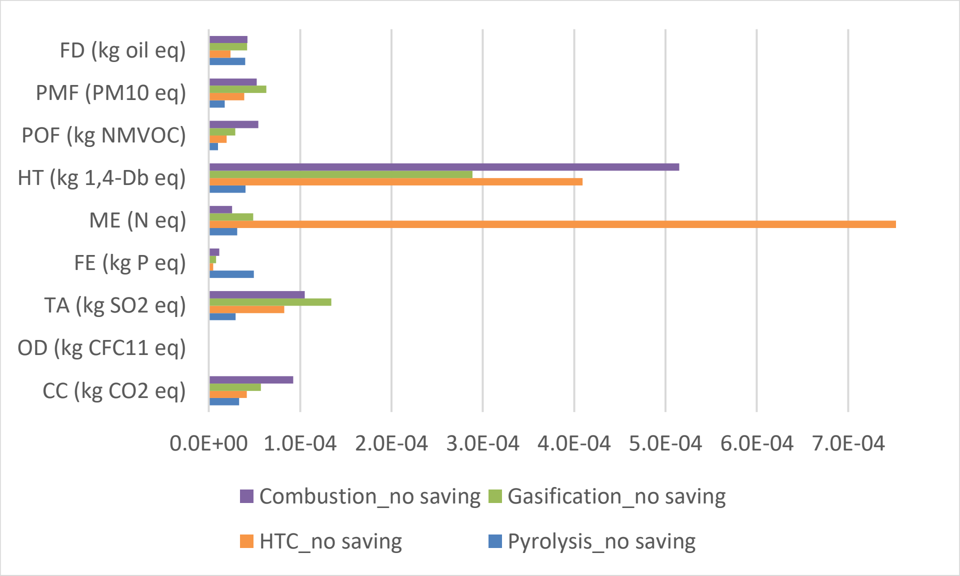

Figure 22- Normalised comparison between different thermochemical processes using a midpoint analysis

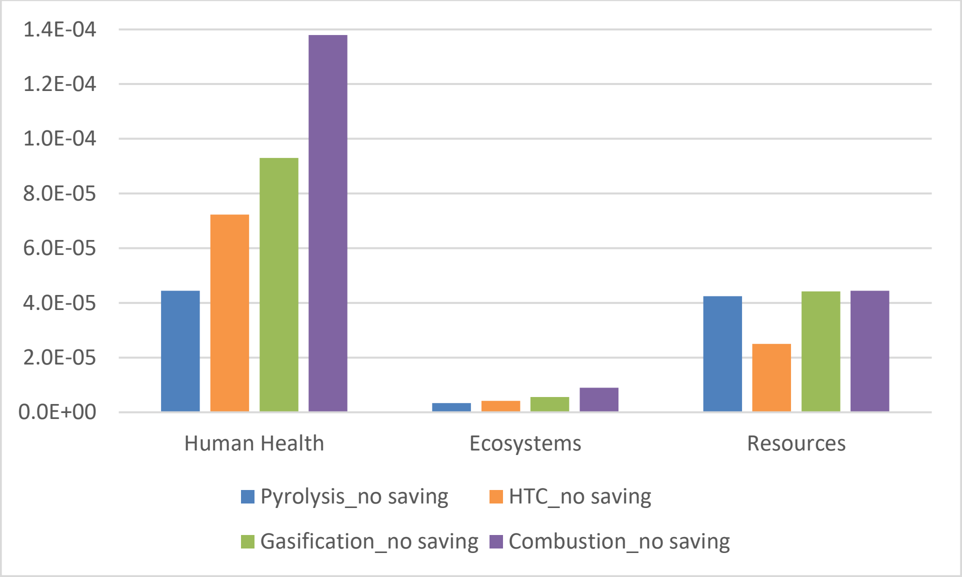

Figure 23- Normalised comparison between different thermochemical processes using an endpoint analysis

As mentioned before the midpoint analysis focus on unique environmental problems. Consequently, this method does not provide any information on damage information but allows to understand which scenario has bigger impact on each category.

Figure 21 highlights the results obtain using the midpoint analysis. Combustion has the major impact on four categories which are: climate change due to a higher emission of GHG; human toxicity due to a higher emissions of dichlorobenzene equivalents; photochemical oxidant formation caused by a higher emission of non-methane volatile organic compounds; and fossil depletion due to higher use of fossil fuels. Then gasification leads in two categories: terrestrial acidification related to higher transformation of air pollutants (SO_2) into acids which cause a higher acidification of soils; and particulate matter formation which is given in PM_{10} equivalents. Furthermore, HTC scenario has a higher contribution in one category which is marine eutrophication, cause by high emissions of nitrate equivalents into water. Finally, pyrolysis has the major impact in two categories: ozone depletion caused by emissions of CFC and NO_x which are quite low and that's why this value is the lower one compared to all categories; and freshwater eutrophication caused by the emissions of phosphate equivalents.

The conversion of midpoint into endpoint impacts simplifies the interpretation of the LCA results and simplifies the comparison between scenarios. Therefore, from Figure 22 is possible to make a direct comparison between the different thermochemical processes impacts. Regarding human health and ecosystems, the trend is similar from the higher to the lowest impact following the order: combustion, gasification, HTC followed by gasification and pyrolysis. Regarding resources impacts, all have similar impacts with the exception of HTC which is around 40% lower. Consequently, the overall impact from the highest to the lowest is: combustion, gasification, HTC followed by gasification and pyrolysis. Based on the single score impacts (see appendix B), considering combustion as 100% impact the comparative value of gasification, HTC and pyrolysis are 69.45%, 50.96% and 40.97% respectively.

The second analysis was done considering the savings obtained for each scenario. In this part of the study results were presented using just the endpoint method without categories (single score) which facilitates the interpretation of results (Figure 23)

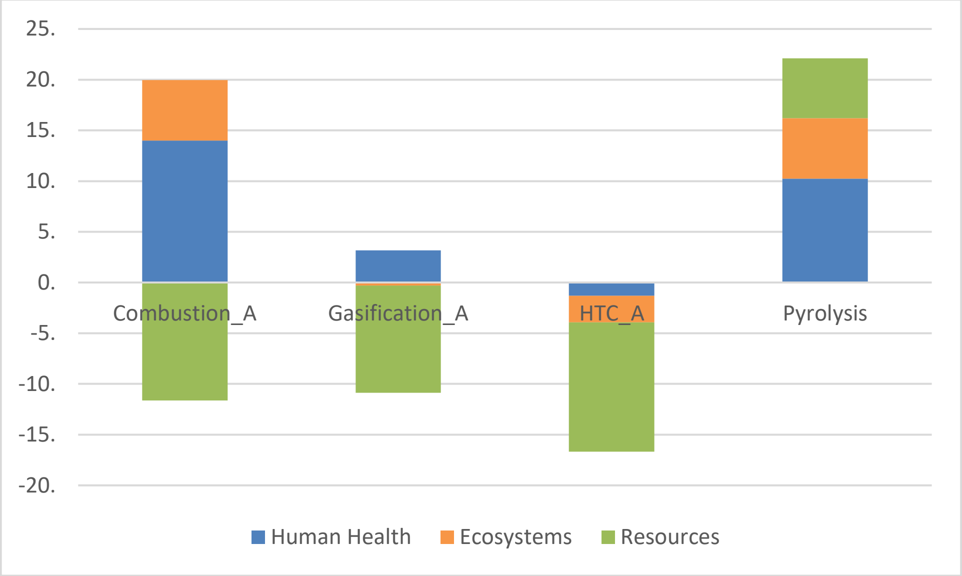

Figure 24- Single score impact of different scenarios (considering savings) using the endpoint method

From Figure 23 it is possible to state that although the saving of electricity in combustion scenario was higher than in the other scenarios, due to a higher electric efficiency (Table 17), it presents the worst results compared to other scenarios that generate electricity. Between gasification and HTC prior to gasification, HTC presents the best results overall, having savings in all categories. Pyrolysis has the worst results from all scenarios but mainly because the end-use of bio-oil was not assessed and is something that would be interesting to be explored in the future. Therefore, the conclusions of this work will just take into account the comparison between scenarios which do not take into account the savings.

Concluding this section, from an environmental point of view pyrolysis presented the best results being its impact 60% lower than the combustion scenario. Gasification and HTC followed by gasification also had promising results with 30 and 50% lower impact compared to combustion.

4.3 Techno-Economic Analysis Discussion

In this section are presented and discussed the results from the techno-economic analysis, which is divided in four sub-sections. The first three sections focus on specific results of each scenario (CAPEX, annual cost breakdown and revenues) while the last section presents the overall results, which takes into account all factors presented in the previous sections, based on the economic model explained on section 3.3.4.

4.3.1 CAPEX

Figure 24 shows the CAPEX costs associated for each scenario. There was not made any distinction between the systems with heat recovery or without heat recovery since it was considered that this factor would not have a significant impact on the total investment costs. As mentioned before all results are normalized for an input of 1 kg/h.

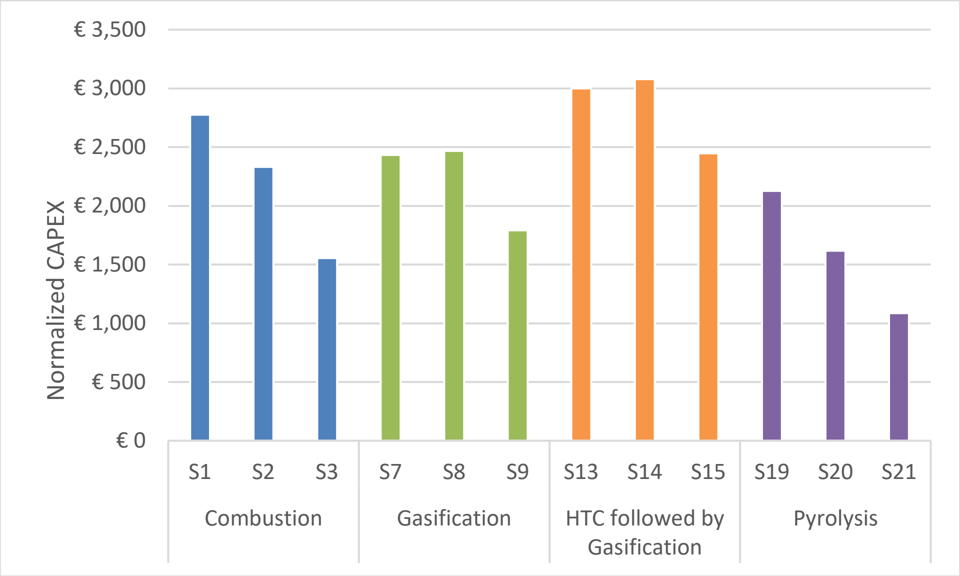

Figure 25- Total Investment cost normalized for 1 kg/h for each scenario

First of all, comparing technologies is possible to note that HTC followed by gasification shows the higher initial investment, because in this scenario are used two technologies, HTC for pre-treatment and gasification to generate electricity. Combustion and gasification are very comparable, however it is possible to say that combustion has a lower CAPEX since the average and best-case scenario have lower initial investment cost associated, and in the worst-case scenario the CAPEX is higher but only because the total power installed in combustion scenario is much higher than in the gasification scenario due to the fact that it was considered a electric efficiency of 25 % in S1 and of 17% in S7 (combustion technology is more developed in terms of electric efficiencies than gasification). Consequently, the difference in the CAPEX between S1 and S7 is not caused by a difference in technology cost but in a difference in total power installed. Finally, pyrolysis is associated with a lower initial investment, worst, average and best-case scenario CAPEX is lower in the pyrolysis scenarios compared to the other technologies.

For instance, comparing worst, average and best-case scenario it is possible to note different evolution of the CAPEX. In the case of pyrolysis, the evolution is quite linear since clearly S19 is associated with a higher cost and S21 with a lower one. Unlike pyrolysis the other 3 thermochemical processes do not have a linear evolution of the cost. In some cases, the average scenario has a higher cost than the worst-case (S8 and S14 compared to S9 and S15). This is related once again with the total installed power which is higher in the average scenario compared to the worst-case scenario due to a higher electric efficiency considered. This increase in power is higher than the reduction cost on the CAPEX (€/kW) in some cases and that is why the evolution of CAPEX is not linear in these cases.

4.3.2 Annual Cost Breakdown

After the initial investment all plants have annual costs from operating the plant. The cost breakdown for combustion, gasification, HTC followed by gasification and pyrolysis is presented in Figure 25, Figure 26, Figure 27 and Figure 28 respectively.

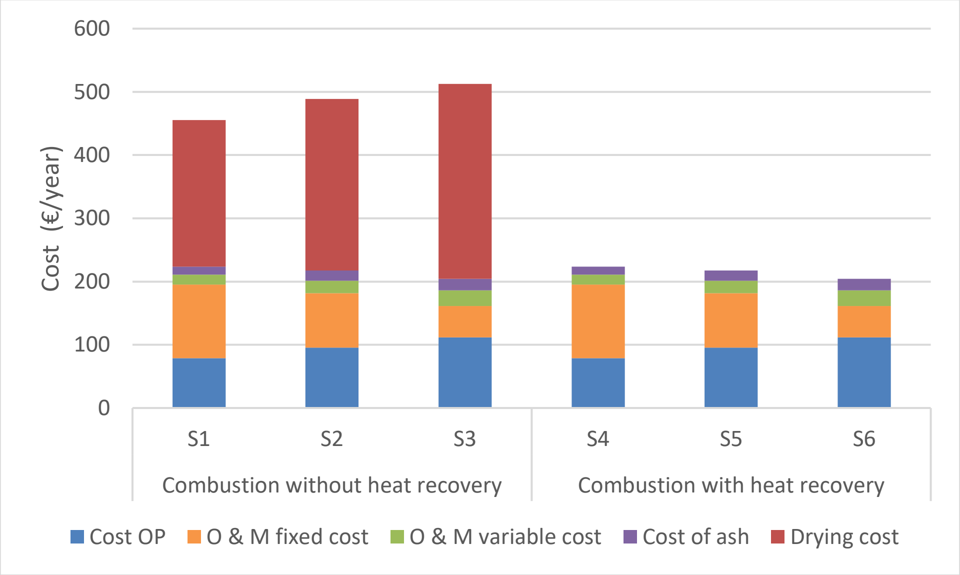

Figure 26- Combustion annual cost breakdown

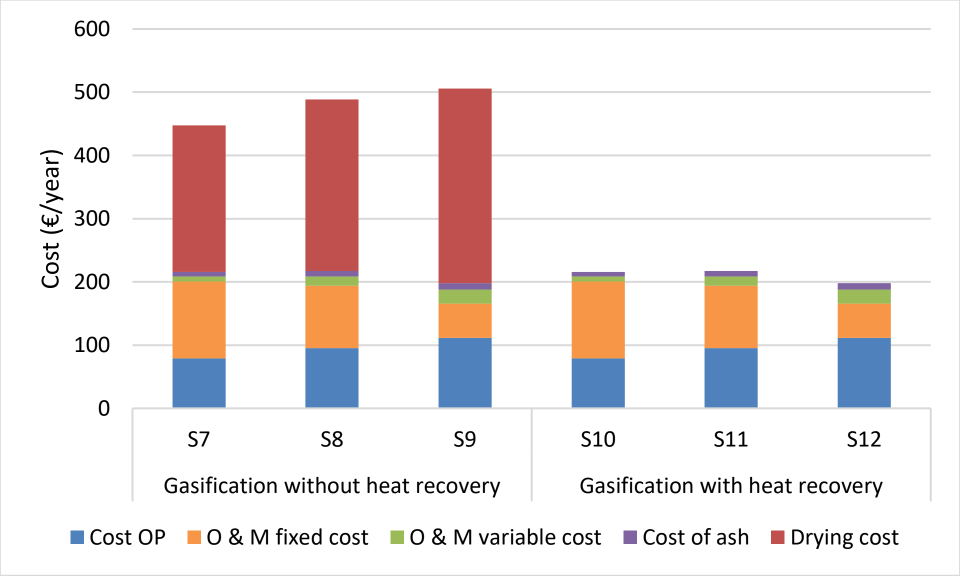

Figure 27- Gasification annual cost breakdown

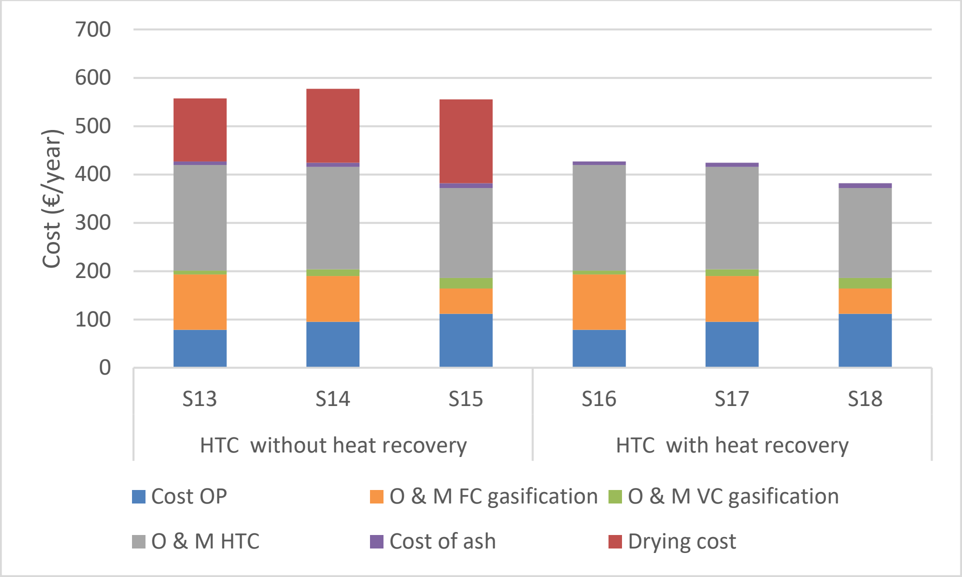

Figure 28- HTC followed by gasification annual cost breakdown

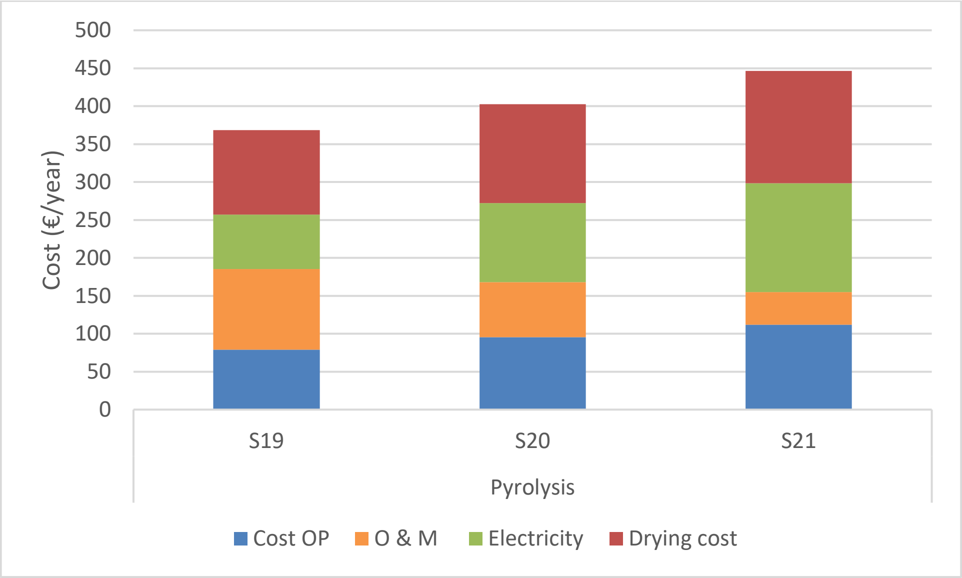

Figure 29- Pyrolysis annual cost breakdown

In terms of cost breakdown, it is possible to see that combustion and gasification patterns (Figure 25 and 26) are the same, the values and the cost distribution are very similar. In the cases without heat recovery drying cost represents more than 50% of the costs, associated with cost of purchasing natural gas. This cost is even higher in the best-case scenarios because in these cases the biomasses plants works with higher capacity factor (85%) compared to worst (60%) and average scenario (72.5%), which means that the plants will have a higher input of olive pomace and therefore more energy is necessary for the drying process. The other two important factor in combustion and gasification scenario are the O & M fixed costs and the olive pomace buying cost which is higher in the best-case scenario for the same reason as the drying cost. Finally, variable cost and ash cost handling seem to have a very low impact in overall cost distribution. Expectedly, the overall costs drop to more than half in the systems with heat recovery, because in these cases there is no cost associated with the drying process (Table17). The other factors have the same distribution has stated before.

In the case of HTC followed by gasification (Figure 27) the distribution of costs is different. The drying cost is still high but a bit lower than in combustion and gasification plants (between 23-31% in the scenarios with no heat recovery), since the thermal energy required for this process is lower as seen in section 3.2.2 O & M fixed costs of gasification and cost of olive pomace have significant impacts as in the other plants, nevertheless the biggest cost is associated with the O & M of HTC (between 39-51%) possibly because it is a recent technology and has less commercial experience as the other solutions. Once again O & M variable cost of gasification and ash disposal costs have the lower impact in the overall costs for every scenario. In the systems with heat recovery there is a drop in overall cost due to the fact that there is no cost associated with drying process, once again this reduction is lower compared to combustion and gasification scenarios for the reason stated above.

Finally, the pyrolysis system (Figure 28) has a more uniform distribution of costs. The drying cost is the higher one with a cost distribution between 30-33%. Olive pomace cost, O & M and electricity consumption have a very similar cost distribution with a range of values between 21-25%, 10-29% and 19-32% respectively.

For instance, comparing the overall cost of the different scenarios it is possible to make the following conclusions. In the systems without heat recovery the overall cost is higher in the HTC followed by gasification, between 555.43-557. 50 €/year compared to combustion and gasification scenarios which have a very similar overall cost of 455.67-512.46 €/year and 447.67-505.99 €/year. Once again these happens because HTC followed by gasification uses two technologies and HTC has mentioned before has no wide usage in the market nowadays. Whereas pyrolysis has a lower overall cost compared to these scenarios with a range of values between 368.32-446.45 €/year, due to fact that the pyrolysis scenarios have a lower drying cost associated since the external thermal input is lower because syngas produced from pyrolysis is burned together with natural gas. Finally, the systems with heat recovery have a lower overall cost because of the reduction of drying cost and as mentioned before this reduction is higher in the combustion and gasification scenarios compared to HTC followed by gasification. The overall operating expenses range from 204.45-223.78 €/year, 197.98-217.09 and 381.82-426.80 €/year for combustion, gasification and HTC followed by gasification scenarios. Which means that combustion and gasification scenarios with heat recovery have the lower overall cost of all the scenarios and that HTC with heat recovery has overall values comparable with pyrolysis.

4.3.3 Annual Revenues

The ultimate goal of all plants is to reach profitability. Figure 29 shows the revenues for each scenario considered. In the same way as in the CAPEX there was not made any distinction in the scenarios with or without heat recovery since that it was considered that the differences in the systems do not have any impact in the revenues generated.

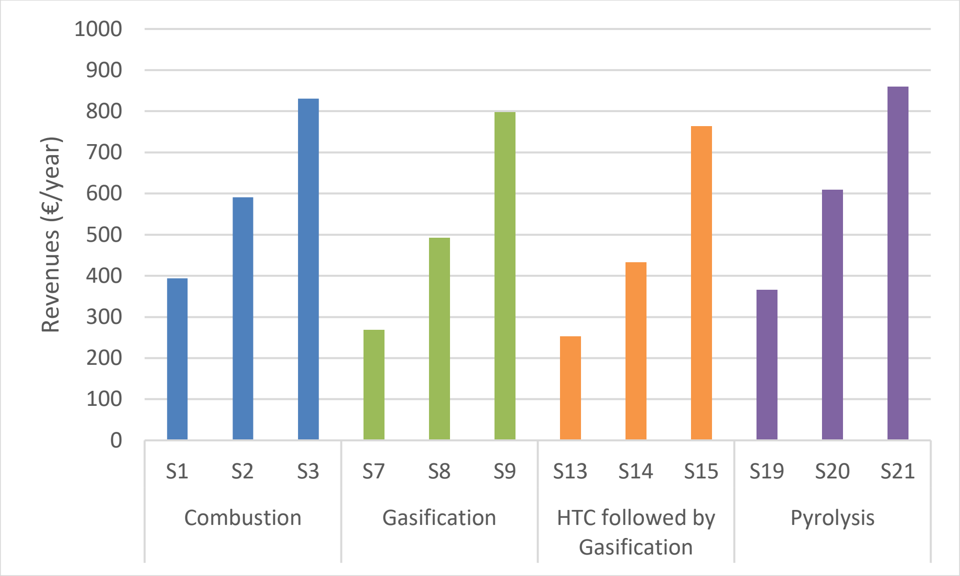

Figure 30- Annual revenues for each scenario

In first place, Figure 29 shows a positive evolution in the revenues from worst, average and best-case scenario for all the plants considered. In the case of the power plants which generate electricity (combustion, gasification and HTC followed by gasification), this increase in revenues is caused mainly because of a higher electric efficiency being considered and also a higher capacity factor. In the pyrolysis plants scenarios, the increase is mainly caused by the increase selling price of biochar and bio-oil and also an increase in the capacity factor (see Table 23).

Comparing technologies pyrolysis and combustion scenarios generate the higher revenues (between 365.61-859.04 and 393.71-834.44 €/year respectively), followed by gasification (267.72-786.76 €/year) and HTC (251.97-762.97). Combustion has higher revenues compared to other plants that generate electricity due to the fact that higher electric efficiencies were considered. Finally, HTC followed by gasification has the lowest income because the overall electric efficiencies are lower mainly because of the losses in olive pomace solid yield during the HTC process, which are expected to be lower in the future.

4.3.4 Overall Results

The previous section presents the specific results of each scenario considered. In this section all the previous results are put together based on the methodology described on section 3.3.4. Also, all the scenarios which have a negative cash flow and/or NPV negative (N=20) will be considered unviable.

Table 26 shows the results obtained for each scenario.

Table 26- Economic model results

Plant type	Scenario	Cash flow	NPV (N=20)	PBP	IRR (%)
Combustion	S1	-61.96	-	-	-
	S2	101.64	-1295.62	-	-
	S3	321.98	1727.901	7	20.1
	S4	169.93	-1043.59	-	-
	S5	373.1	1471.78	9	15
	S6	629.99	4867.91	3	40.4
Gasification	S7	-179.95	-	-	-
	S8	3.51	-2431.72	-	-
	S9	280.77	1070.90	10	14.6
	S10	51.94	-1903.46	-	-
	S11	274.97	335.676	16	9.2
	S12	588.78	4210.91	4	32.7
HTC followed by gasification	S13	-305.53	-	-	-
	S14	-104.68	-	-	-
	S15	180.24	-609.19	-	-
	S16	-174.83	-	-	-
	S17	48.32	-2585.72	-	-
	S18	353.85	1160.68	11	13.2
Pyrolysis	S19	-0.82	-	-	-
	S20	206.33	486.01	13	11.2
	S21	412.59	3120.24	4	37.9

In general terms 9 scenarios had positive results. Beginning with a distinction between worst, average and best-case scenarios it is possible to make the following conclusions. All the worst-case scenarios have negative cash flows and/or negative NPV which is expected since the worst estimative were used in every parameter. Regarding the average scenarios it was obtained 3 positive results; combustion with heat recovery, gasification with heat recovery and pyrolysis; the PBP was 9, 16 and 13 years; and the IRR 15, 9.2 and 11.2 % respectively which suggests that combustion plant has a higher performance than pyrolysis and gasification plants. Finally, all the best-case scenarios had positive results with the exception of HTC followed by gasification with no heat recovery.

Comparing technologies, combustion presented the best results with 3 positive results (S3, S5 and S6) all with payback periods inferior to 10 years and IRR superior to 15. It was also obtained the higher value of NPV, lower PBP and higher IRR from all the scenarios with a value of 4867.91, 3 years and 40.4% for S6 respectively. Gasification had similar results to combustion with 3 positive results but with superior payback periods and lower IRR and NPV. This difference to combustion is mostly caused by a lower amount of revenues in gasification scenarios which results in a lower cash flow. Nevertheless, S12 had the second highest NPV and second lowest PBP with a value of 4210.91 and 4 year respectively. Then HTC followed by gasification presented the worst results with just one positive scenario (S8), as a result of having a higher CAPEX and annual overall cost and a lower revenue generation as seen in the previous sections. Regarding pyrolysis it has 2 positive scenarios from 3, relatively to the best-case scenario (S21), it has the second highest IRR and second lowest PBP with a value of 37.9% and 4 years.

Overall, the results show that as expected, the scenarios with heat recovery have better results that the ones without, which indicates that the drying cost is a major factor for the operating plants with this type of biomass with high moisture. In addition, pyrolysis looks competitive with the systems with heat recovery. Also, that combustion presented the best results in terms of economic analysis, probably due to the fact that more than 90% biomass plants are combustion ones (61), which means it is a more developed technology with higher efficiencies and lower costs associated. HTC followed by gasification is not competitive with the other technologies and does not seem a viable solution to the present days. In the future with a reduction of HTC costs and a higher HTC performance (higher energy yield, lower moisture after HTC and better hydrochar properties) this combination of processes may be a competitive solution economically.

However, there is some uncertainty in this biomass plants which needs to be taken in account before an investment is made. First the price of olive pomace which is very volatile as mentioned before, right now in Portugal the price is below 0 € (producers had to pay transport to the treatment facilities), which can change in the future but since it was considered a 15 €/ton price for olive pomace in this work, suggests that the results may be even better than the presented ones. The major uncertainty factor is the selling price of electricity which was based on previous agreements, and that in future might change to lower values, closer to current prices practiced by other technologies such as wind and solar energy which have become much more competitive in the last years. If the electricity selling price drops to lower values in the future, pyrolysis may be the solution since the revenues generated do not depend on the electricity selling price.

On the contrary, in the future there will be an improvement of most of these technologies which will result in a higher electric efficiency, better properties of products (plant pyrolysis and HTC) and also a lower cost associated with technologies which will make these projects more attractive in terms of investment.

To conclude based on the current data combustion, gasification and pyrolysis plant seem viable project for valorisation of olive pomace and grape marc (which have similar properties as seen in section 4.1). The major problem is the drying process which can be solved by using a heat recovery solution. Another possible solution is instead of using olive pomace as input is using EOP, which is already dried and has no current usage after the extraction of the residual oil. Finally, HTC followed by gasification does not seem a viable solution for the valorisation of this type biomass in current days.

4.4 LCA and Techno-Economic Analysis

In section 4.2 and 4.3 were discussed the results obtained of the LCA and techno-economic analysis independently. In this section both results will be assessed in order to evaluate which scenario(s) have best results in terms of conciliating environmental impact and economic results.

From section 4.2 it was possible to conclude that combustion have the higher environmental impact being pyrolysis the scenario which presented the best results with an overall impact 60% lower. Also, gasification and HTC prior to gasification had promising results with an overall impact 30 and 50% lower than combustion. Regarding the scenarios with heat or no heat recovery, the drying process has a significant environmental impact and using a system with heat recovery could reduce the overall impact by 25.42-36.70%.

From section 4.3 it was possible to conclude that economically combustion presented the best results. Nevertheless, gasification and pyrolysis also presented promising results. On the other hand, HTC is not competitive in the current days. Concerning the drying process, drying had a major impact on the overall costs and if it is just considered the scenarios without heat recovery pyrolysis scenario presented the best results.

As a result of the stated above, combustion and HTC followed by gasification are worst alternatives for the valorisation of olive pomace, the first due to the fact that has around two times higher environmental impacts than the other scenarios and the second because it is not an economically viable. On the other hand, gasification and pyrolysis could be better alternatives with environmental impacts around 30-56% and 60% respectively lower than combustion and also with payback period of an investment of 4 years for the best-case scenario. Another important conclusion is that due to high moisture of this type of biomass drying has an important role in terms of environmental impact and economic viability

5 Conclusions and Future Work

This work focuses on the valorisation of olive and wine industry co-products (olive pomace and grape marc respectively) through different thermochemical processes. These two industries produce more than 1.4 million tonnes of solid waste per year in Portugal which must be handled.

First a characterization of olive pomace and grape marc was made in order to evaluate which thermochemical process is more suitable for each type of biomass. Then, a Life Cycle Analysis (LCA) of olive pomace valorisation is made in order to assess the environmental impacts. Several scenarios of biomass conversion process were considered: combustion, gasification and hydrothermal carbonization (HTC) followed by gasification to generate electricity; and pyrolysis to produce biochar, bio-oil and syngas. Finally, a techno-economic analysis was performed for each mentioned scenario in order to evaluate the feasibility and to conclude which scenario is more economically advantageous. The novelty of this work compared to the ones found in the literature is that compares more than two thermochemical processes for valorisation of olive pomace simultaneously and also puts together an LCA and techno-economic analysis in the same study.

From the characterization of olive pomace and grape marc was found that these two by-products were very similar. Calorific value in both biomass is close to 20 MJ/kg and initial moistures quite high (40-75%) which require a drying process. VM of olive pomace is around 10% higher than in the grape marc samples, consequently apparently olive pomace should be more appropriate to be gasified. On the other hand, FC and ash content of grape marc are around 7-8% and 2% respectively higher than olive pomace which indicates that GM might be more suitable to an HTC pre-treatment (which is expected to reduce ash content and obtain high char yields) or recovery via pyrolysis. In terms of ultimate analysis, they are quite similar, the major differences are in the C and O content which is around 3% higher and 3% lower respectively in the case of olive pomace compared to grape marc. Both samples of biomass are very comparable and probably could be valorised in the same type of facility and for that reason the LCA and techno-economic analysis was only made based on the literature of olive pomace sample.

Subsequently, from life cycle impact assessment (not considering the savings) was possible to conclude that the overall impact of combustion was the highest of all and if combustion was considered as 100% impact the comparative value of gasification, HTC and pyrolysis were 69.45%, 50.96% and 40.97 respectively. However, if it was considered the savings (generation of electricity and use of by-products of pyrolysis) pyrolysis had the worst results from all scenarios but mainly because the end-use of bio-oil was not assessed and is something that would be interesting to be explored in the future. Finally drying had a relevant impact and a scenario with heat recovery would reduce the overall impact of combustion, gasification and HTC followed by gasification by 25.42%, 36.70% and 28.18% respectively.

Regarding the techno-economic analysis, combustion plant presented the best results with payback as short as 3 years. Gasification (with heat recovery) and pyrolysis plant also presented promising results with payback period inferior to 4 years to the best-case scenario. On the other hand, HTC followed by gasification it is not competitive with the other technologies in the current days due to higher initial investment cost and also to due to a higher operational cost associated. Also was possible to conclude that the scenarios with heat recovery have better results that the ones without, which indicates that the drying cost is a major factor for the operating plants with this type of biomass with high moisture. In addition, pyrolysis looks competitive with the systems with heat recovery.

Finally, joining the LCA and techno-economic analysis was possible to state that gasification and pyrolysis plant are better alternatives to the valorisation of olive pomace compared to combustion which has a higher environmental impact and HTC prior to gasification which is not economically viable. Another important conclusion is that due to high moisture of this type of biomass drying has an important role in terms of environmental impact and economic viability. Therefore, two possible solutions, could be using a system of heat recovery which reduces significantly thermal input needed or instead of using olive pomace, using EOP which is already dried.

In the future further work could be developed. This work was based on previous experimental studies and none of them assessed the valorisation of the four thermochemical processes evaluated in this dissertation at the same time. Therefore, an experimental work valorising olive pomace or grape marc through the four different thermochemical processes would be very important to consolidate some of the results of this thesis. Also, some uncertainties could be also analysed in the future. In terms of LCA it would be important to assess the impact of the equipment’s used for each thermochemical process which were excluded from the boundaries of the study and also the impact and the savings of the end-use of the bio-oil. Regarding techno-economic analysis it would be useful to understand better the fluctuation of price of the olive pomace and grape marc which have relevant impact in the operational expenses and also to have a better understanding of the revenues which might be outdated for the current days.

References

[1] IEA, International Renewable Energy Agency, United Nations Statistics Division, The World Bank, World Health Organization. The Energy Progress Report. IEA, IRENA, UNSD, WB, WHO (2019), Track SDG 7 Energy Prog Rep 2019, Washingt DC 2019:176.

[2] Tanger P, Field JL, Jahn CE, DeFoort MW, Leach JE. Biomass for thermochemical conversion: Targets and challenges. Front Plant Sci 2013;4. https://doi.org/10.3389/fpls.2013.00218.

[3] Ritchie H. Energy. Our World Data 2014.

[4] Tahfidzul P, An QUR. 2020 YearBook. APREN, 2020, p. 2020.

[5] GLOBAL BIOENERGY STATISTICS 2019 World Bioenergy Association. n.d.

[6] Ferreira S, Monteiro E, Brito P, Vilarinho C. Biomass resources in Portugal: Current status and prospects. Renew Sustain Energy Rev 2017;78:1221–35. https://doi.org/10.1016/j.rser.2017.03.140.

[7] Tripathi N, Hills CD, Singh RS, Atkinson CJ. Biomass waste utilisation in low-carbon products: harnessing a major potential resource. Npj Clim Atmos Sci 2019;2. https://doi.org/10.1038/s41612-019-0093-5.

[8] Loução PO, Ribau JP, Ferreira AF. Life cycle and decision analysis of electricity production from biomass – Portugal case study. Renew Sustain Energy Rev 2019;108:452–80. https://doi.org/10.1016/j.rser.2019.03.063.

[9] Nunes LJR, Matias JCO, Catalão JPS. Biomass in the generation of electricity in Portugal: a review. 2016.

[10] Vinho I da V e. Evolução da Produção Nacional por Região 2019.

[11] Master N. TOP Countries in Olive Production 2020.

[12] Oliveira M, Duarte E. Integrated approach to winery waste: waste generation and data consolidation. Front Environ Sci Eng 2016;10:168–76. https://doi.org/10.1007/s11783-014-0693-6.

[13] Zacharof MP. Grape Winery Waste as Feedstock for Bioconversions: Applying the Biorefinery Concept. Waste and Biomass Valorization 2017;8:1011–25. https://doi.org/10.1007/s12649-016-9674-2.

[14] Afonso IM;, Ferraz A;, Rodrigues AS;, Vale AP;, Mendes S;, Alonso J;, et al. AFONSO ET AL,CIRCULAR ECONOMY IN THE WINE SECTOR: ASSESSMENT OF THE POTENTIAL OF SEEDS OF PORTUGUESE GRAPE VARIETIES FOR OIL PRODUCTION AND BY-PRODUCTS DEVELOPMENT WWW.INFOWINE.COM, INTERNET JOURNAL OF VITICULTURE AND ENOLOGY, 2018, n. 12/2 CIRCULAR ECONOMY IN THE WINE SECTOR: ASSESSMENT OF THE POTENTIAL OF SEEDS OF PORTUGUESE GRAPE VARIETIES FOR OIL PRODUCTION AND BY-PRODUCTS DEVELOPMENT. n.d.

[15] Eleutheria N, Maria I, Vasiliki T, Alexandros E, Alexandros A, Vasileios D. Energy Recovery and Treatment of Winery Wastes by a Compact Anaerobic Digester. Waste and Biomass Valorization 2016;7:799–805. https://doi.org/10.1007/s12649-016-9541-1.

[16] Espinosa PA. WINERY AND DISTILLERY WASTE MANAGEMENT: PERSPECTIVE AND POTENTIAL FUTURE USES. n.d.

[17] Muhlack RA, Potumarthi R, Jeffery DW. Sustainable wineries through waste valorisation: A review of grape marc utilisation for value-added products. Waste Manag 2018;72:99–118. https://doi.org/10.1016/j.wasman.2017.11.011.

[18] Magalhães B, Cruz VF da, Ascenço C. E2. RELATÓRIO DE BOAS PRÁTICAS DE UTILIZAÇÃO EFICIENTE DE RECURSOS E VALORIZAÇÃO DE RESÍDUOS E SUBPRODUTOS. 2017.

[19] Ruiz E, Romero-García JM, Romero I, Manzanares P, Negro MJ, Castro E. Olive-derived biomass as a source of energy and chemicals. Biofuels, Bioprod Biorefining 2017;11:1077–94. https://doi.org/10.1002/bbb.1812.

[20] Oktay Z. Olive cake as a biomass fuel for energy production. Energy Sources, Part A Recover Util Environ Eff 2006;28:329–39. https://doi.org/10.1080/009083190890067.

[21] Pattara C, Salomone R, Cichelli A. Carbon footprint of extra virgin olive oil: a comparative and driver analysis of different production processes in Centre Italy. J Clean Prod 2016;127:533–47. https://doi.org/10.1016/j.jclepro.2016.03.152.

[22] Macedonia REA of C. Market of Olive Residues for Energy. 2008.

[23] Ramos- J. Life Cycle Assessment of a Coffee Machine. 2018.

[24] Parascanu MM, Puig Gamero M, Sánchez P, Soreanu G, Valverde JL, Sanchez-Silva L. Life cycle assessment of olive pomace valorisation through pyrolysis. Renew Energy 2018;122:589–601. https://doi.org/10.1016/j.renene.2018.02.027.

[25] Lauer M. Methodology guideline on techno economic assessment (TEA). Intell Energy Eur 2008:25.

[26] Borello D, Pantaleo AM, Caucci M, De Caprariis B, De Filippis P, Shah N. Modeling and experimental study of a small scale olive pomace gasifier for cogeneration: Energy and profitability analysis. Energies 2017;10. https://doi.org/10.3390/en10121930.

[27] Hernández JJ, Aranda-Almansa G, Bula A. Gasification of biomass wastes in an entrained flow gasifier: Effect of the particle size and the residence time. Fuel Process Technol 2010;91:681–92. https://doi.org/10.1016/j.fuproc.2010.01.018.

[28] Link S, Arvelakis S, Paist A, Liliedahl T, Rosén C. Effect of leaching pretreatment on the gasification of wine and vine (residue) biomass. Renew Energy 2018;115:1–5. https://doi.org/10.1016/j.renene.2017.08.028.

[29] Ducom G, Gautier M, Pietraccini M, Tagutchou JP, Lebouil D, Gourdon R. Comparative analyses of three olive mill solid residues from different countries and processes for energy recovery by gasification. Renew Energy 2020;145:180–9. https://doi.org/10.1016/j.renene.2019.05.116.

[30] Puig-Gamero M, Lara-Díaz J, Valverde JL, Sánchez P, Sanchez-Silva L. Synergestic effect in the steam co-gasification of olive pomace, coal and petcoke: Thermogravimetric-mass spectrometric analysis. Energy Convers Manag 2018;159:140–50. https://doi.org/10.1016/j.enconman.2018.01.011.

[31] Tamošiunas A, Chouchène A, Valatkevičius P, Gimžauskaite D, Aikas M, Uscila R, et al. The

potential of thermal plasma gasification of olive pomace charcoal. Energies 2017;10. https://doi.org/10.3390/en10050710.

[32] Brito P. 2018 - ENERGY PRODUCTION FROM WASTES BY THERMAL GASIFICATION PROCESSES. Appl Res Tech Technol Educ 2018.

[33] Hermoso-Orzáez MJ, Mota-Panizio R, Carmo-Calado L, Brito P. Thermochemical and economic analysis for energy recovery by the gasification of WEEE plastic waste from the disassembly of large-scale outdoor obsolete luminaires by LEDs in the alto alentejo region (Portugal). Appl Sci 2020;10. https://doi.org/10.3390/app10134601.

[34] Pala M, Kantarli IC, Buyukisik HB, Yanik J. Hydrothermal carbonization and torrefaction of grape pomace: A comparative evaluation. Bioresour Technol 2014;161:255–62. https://doi.org/10.1016/j.biortech.2014.03.052.

[35] Basso D, Weiss-Hortala E, Patuzzi F, Baratieri M, Fiori L. In Deep Analysis on the Behavior of Grape Marc Constituents during Hydrothermal Carbonization. Energies 2018;11. https://doi.org/10.3390/en11061379.

[36] Petrović J, Perišić N, Maksimović JD, Maksimović V, Kragović M, Stojanović M, et al. Hydrothermal conversion of grape pomace: Detailed characterization of obtained hydrochar and liquid phase. J Anal Appl Pyrolysis 2016;118:267–77. https://doi.org/10.1016/j.jaap.2016.02.010.

[37] Mäkelä M, Kwong CW, Broström M, Yoshikawa K. Hydrothermal treatment of grape marc for solid fuel applications. Energy Convers Manag 2017;145:371–7. https://doi.org/10.1016/j.enconman.2017.05.015.

[38] Surup GR, Leahy JJ, Timko MT, Trubetskaya A. Hydrothermal carbonization of olive wastes to produce renewable, binder-free pellets for use as metallurgical reducing agents. Renew Energy 2020;155:347–57. https://doi.org/10.1016/j.renene.2020.03.112.

[39] Benavente V, Fullana A, Berge ND. Life cycle analysis of hydrothermal carbonization of olive mill waste: Comparison with current management approaches. J Clean Prod 2017;142:2637–48. https://doi.org/10.1016/j.jclepro.2016.11.013.

[40] Missaoui A, Bostyn S, Belandria V, Cagnon B, Sarh B, Gökalp I. Hydrothermal carbonization of dried olive pomace: Energy potential and process performances. J Anal Appl Pyrolysis 2017;128:281–90. https://doi.org/10.1016/j.jaap.2017.09.022.

[41] Benavente V, Calabuig E, Fullana A. Upgrading of moist agro-industrial wastes by hydrothermal carbonization. J Anal Appl Pyrolysis 2015;113:89–98. https://doi.org/10.1016/j.jaap.2014.11.004.

[42] Ibn Ferjani A, Jeguirim M, Jellali S, Limousy L, Courson C, Akrout H, et al. The use of exhausted grape marc to produce biofuels and biofertilizers: Effect of pyrolysis temperatures on biochars properties. Renew Sustain Energy Rev 2019;107:425–33. https://doi.org/10.1016/j.rser.2019.03.034.

[43] Zhang N, Hoadley A, Patel J, Lim S, Li C. Sustainable options for the utilization of solid residues from wine production. Waste Manag 2017;60:173–83. https://doi.org/10.1016/j.wasman.2017.01.006.

[44] Khiari B, Jeguirim M. Pyrolysis of grape marc from Tunisian wine industry: Feedstock characterization, thermal degradation and kinetic analysis. Energies 2018;11. https://doi.org/10.3390/en11040730.

[45] Casazza AA, Aliakbarian B, Lagazzo A, Garbarino G, Carnasciali MM, Perego P, et al. Pyrolysis of grape marc before and after the recovery of polyphenol fraction. Fuel Process Technol 2016;153:121–8. https://doi.org/10.1016/j.fuproc.2016.07.014.

[46] Caballero BM, López-Urionabarrenechea A, Pérez B, Solar J, Acha E, de Marco I. Potentiality of “orujillo” (olive oil solid waste) to produce hydrogen by means of pyrolysis. Int J Hydrogen Energy 2020. https://doi.org/10.1016/j.ijhydene.2020.02.220.

[47] Martín-Lara MA, Pérez A, Vico-Pérez MA, Calero M, Blázquez G. The role of temperature on slow pyrolysis of olive cake for the production of solid fuels and adsorbents. Process Saf Environ Prot 2019;121:209–20. https://doi.org/10.1016/j.psep.2018.10.028.

[48] Dinc G, Yel E. Self-catalyzing pyrolysis of olive pomace. J Anal Appl Pyrolysis 2018;134:641–6. https://doi.org/10.1016/j.jaap.2018.08.018.

[49] Hani FFB, Hailat MM. Production of Bio-Oil from Pyrolysis of Olive Biomass with/without Catalyst. Adv Chem Eng Sci 2016;06:488–99. https://doi.org/10.4236/aces.2016.64043.

[50] Gunarathne DS, Mueller A, Fleck S, Kolb T, Chmielewski JK, Yang W, et al. Gasification characteristics of hydrothermal carbonized biomass in an updraft pilot-scale gasifier. Energy and Fuels, vol. 28, 2014, p. 1992–2002. https://doi.org/10.1021/ef402342e.

[51] Erlach B, Harder B, Tsatsaronis G. Combined hydrothermal carbonization and gasification of biomass with carbon capture. Energy 2012;45:329–38. https://doi.org/10.1016/j.energy.2012.01.057.

[52] International Council of Chemical Associations. How to Know If and When it ’ s Time to Commission a Life Cycle Assessment 2019.

[53] Benetto E, Jury C, Kneip G, Vázquez-Rowe I, Huck V, Minette F. Life cycle assessment of heat production from grape marc pellets. J Clean Prod 2015;87:149–58. https://doi.org/10.1016/j.jclepro.2014.10.028.

[54] Duman AK, Özgen GÖ, Üçtuğ FG. Environmental life cycle assessment of olive pomace utilization in Turkey. Sustain Prod Consum 2020;22:126–37. https://doi.org/10.1016/j.spc.2020.02.008.

[55] Cossu A, Degl’innocenti S, Agnolucci M, Cristani C, Bedini S, Nuti M. Send Orders for Reprints to reprints@benthamscience.net Assessment of the Life Cycle Environmental Impact of the Olive Oil Extraction Solid Wastes in the European Union. 2013.

[56] Parascanu MM, Sánchez P, Soreanu G, Valverde JL, Sanchez-Silva L. Environmental assessment of olive pomace valorization through two different thermochemical processes for energy production. J Clean Prod 2018;186:771–81. https://doi.org/10.1016/j.jclepro.2018.03.169.

[57] Mendecka B, Lombardi L, Micali F, De Risi A. Energy Recovery from Olive Pomace by Hydrothermal Carbonization on Hypothetical Industrial Scale: a LCA Perspective. Waste and

Biomass Valorization 2020;11:5503–19. https://doi.org/10.1007/s12649-020-01212-0.

[58] El Hanandeh A. Carbon abatement via treating the solid waste from the Australian olive industry in mobile pyrolysis units: LCA with uncertainty analysis. Waste Manag. Res., vol. 31, 2013, p. 341–52. https://doi.org/10.1177/0734242X12465317.

[59] Lucian M, Fiori L. Hydrothermal carbonization of waste biomass: Process design, modeling, energy efficiency and cost analysis. Energies 2017;10. https://doi.org/10.3390/en10020211.

[60] Jurendić T. Applicability of Simple Mass and Energy Balances in Food Drum Drying. J Basic Appl Sci Res 2014;4:128–33.

[61] Kemp IC. Fundamentals of Energy Analysis of Dryers. vol. 4. n.d.

[62] Luz FC, Rocha MH, Lora EES, Venturini OJ, Andrade RV, Leme MMV, et al. Techno-economic analysis of municipal solid waste gasification for electricity generation in Brazil. Energy Convers Manag 2015;103:321–37. https://doi.org/10.1016/j.enconman.2015.06.074.

[63] Renewable Energy Agency I. RENEWABLE ENERGY TECHNOLOGIES: COST ANALYSIS SERIES Biomass for Power Generation Acknowledgement. 2012.

[64] Rogers JG, Brammer JG. Estimation of the production cost of fast pyrolysis bio-oil. Biomass and Bioenergy 2012;36:208–17. https://doi.org/10.1016/j.biombioe.2011.10.028.

[65] Lund H, ConnolLy D. EnergyPLAN 2014.

[66] TollBox E. Fuels- Higher and Lower Calorific Value 2003.

[67] Doodwin DG, L.Speth R, Moffat HK, W.Weber B. Cantera: An object oriented software toolkit for chemical kinetics, thermodinamics, and transport processes 2018.

[68] Morató T, Vaezi M, Kumar A. Techno-economic assessment of biomass combustion technologies to generate electricity in South America: A case study for Bolivia. Renew Sustain Energy Rev 2020;134. https://doi.org/10.1016/j.rser.2020.110154.

[69] Observador. Produção de azeite pode parar Alentejo por falta de capacidade de armazenar bagaço 2019.

[70] TSF. Olive Pomace puts olive sector “boiling” Trás-os montes 2019.

[71] Marques A. Utilização Energética da Biomassa em Portugal - Caso de estudo da Tratolixo. Diss (Mestre Em Eng e Gestão Ind - Técnico Lisboa 2015:1–123.

[72] Shabangu S, Woolf D, Fisher EM, Angenent LT, Lehmann J. Techno-economic assessment of biomass slow pyrolysis into different biochar and methanol concepts. Fuel 2014;117:742–8. https://doi.org/10.1016/j.fuel.2013.08.053.

[73] Thornton LLP GU. Renewable energy discount rate survey results-2018. 2019.

[74] Shemfe MB, Gu S, Ranganathan P. Techno-economic performance analysis of biofuel production and miniature electric power generation from biomass fast pyrolysis and bio-oil upgrading. Fuel 2015;143:361–72. https://doi.org/10.1016/j.fuel.2014.11.078.

[75] Seletra. Natural Gas and Electricity Prices 2020.

Appendix

A. Drying Methodology

In this appendix is presented the method and the results obtained used in this work for calculating the amount of energy for the drying process based on [60].

Figure A1 shows a schematic sketch of a feedstock input and steam flow in a dryer requested for properly defining of overall mass and energy balance. Liquid or semiliquid material of mass flow m_i (kg/s dry basis), moisture content X_i (kg/kg dry basis) and temperature T_i (K) is dried and scrapped of the drier with a mass flow m_0 (kg/s dry basis), moisture content X_0 (kg/kg dry basis) and temperature T_0(K). Moisture (water) is removed from the material by heating with a mass flow m_w.

Hence, the steam (mass flow m_s (kg/s), temperature T_s (ºC) and the heat quantity Q (kW) is entering the dryer transferring the heat to the wall, cooling and condensing itself outputting the system as a liquid (condensate).

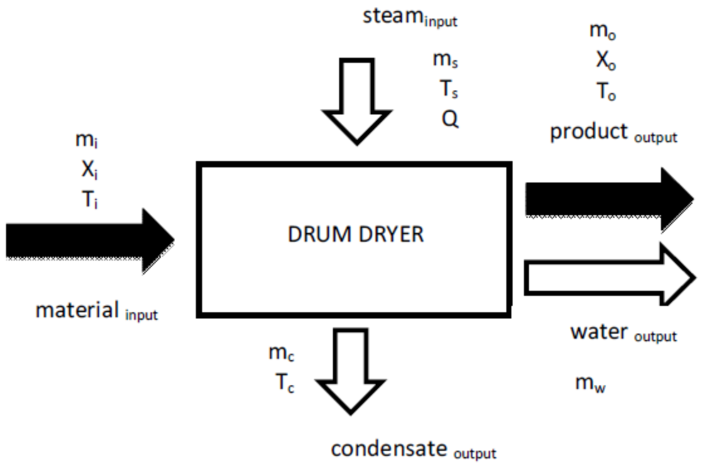

Figure A. 1- Schematic sketch of feedstock input and steam flow in a conventional dryer

To perform the calculations is necessary first to do a mass balance:

$$m_i = m_0 + m_w \tag{1}$$

Where m_i is the mass input; m_0 the mass output and m_w the mass of evaporated water all in kg/h.

Then is necessary to perform an energy balance which is given by the following equations:

$$Q = Q_m + Q_w \tag{2}$$

Thus,

$$Q_m = m_i(C_{pm} + X_i C_{pw})(T_0 - T_i) \tag{3}$$

$$Q_w = m_i(X_i - X_0)(\Delta H_0 - (C_{pw} - C_{ps})T_0) \tag{4}$$

Whereas,

Q, Q_m, Q_w – overall thermal input of dryer, thermal input used to heat the solid material and to evaporate water (kW)

C_{pm}, C_{pw}, C_{ps} – specific heat of material, water and steam (kj/kg k)

ΔH_0- latent heat of condensation (kj/kg)

X_i, X_o – initial and final material moisture content

Using this methodology and assuming a 40% drying efficiency [61] was calculated a necessary thermal input of Q= 2.608 MJ/kg for drying of olive pomace from 60% to 10% moisture.

B. Tables Life Cycle Impact Assessment

This section shows the tables used to present the figure on section 4.2

Table B. 1- Normalised results of combustion scenario using endpoint analysis

Label	Emissions to air combustion	Ash handling	Electricity saving	Drying
Human Health	0.0001	1.63E-05	-8.61E-05	2.15E-05
Ecosystems	7.43E-06	3.38E-08	-6.08E-06	1.55E-06
Resources	0	3.8E-07	-.000118	4.4E-05

Table B. 2- Normalised results of gasification scenario using endpoint analysis

Label	Drying	Ash handling	Electricity saving	Emssions to air gasification
Human Health	2.15E-05	8.87E-06	-8.12E-05	6.27E-05
Ecosystems	1.55E-06	1.84E-08	-5.74E-06	4.02E-06
Resources	4.4E-05	2.07E-07	-.000111	0

Table B. 3- Normalised results of HTC followed by gasification scenario using endpoint analysis

Label	Ash handling	Drying	Emssions to air gasification	HTC emissions
Human Health	5.68E-06	1.21E-05	3.92E-05	1.53E-05
Ecosystems	1.18E-08	8.75E-07	2.52E-06	7.45E-07
Resources	1.33E-07	2.48E-05	0	0

Table B. 4- Normalised results of pyrolysis scenario using endpoint analysis

Drying	Pyrolysis emissions	Electricity consumption	Transport	Fertiliser saving
1.03E-05	1.86E-05	1.5E-05	5.5E-07	-6.55E-06
7.45E-07	1.56E-06	1.06E-06	3.83E-08	-4.65E-07
2.11E-05	0	2.05E-05	8.28E-07	-5.17E-06

Table B. 5- Comparison scenarios using midpoint analysis

Label	Pyrolysis	HTC	Gasification	Combustion
CC	3.32E-05	4.18E-05	5.72E-05	9.25E-05
OD	5.56E-07	2.44E-07	4.3E-07	4.46E-07
TA	2.93E-05	8.28E-05	0.0001	0.0001
FE	4.95E-05	4.83E-06	7.96E-06	1.17E-05
ME	3.1E-05	0.0008	4.88E-05	2.55E-05
HT	4.03E-05	0.0004	0.0003	0.0005
POF	9.98E-06	1.95E-05	2.9E-05	5.41E-05
PMF	1.74E-05	3.88E-05	6.29E-05	5.26E-05
FD	3.99E-05	2.38E-05	4.21E-05	4.23E-05

Table B. 6- Comparison scenario using endpoint analysis

Label	Pyrolysis	HTC	Gasification	Combustion
Human Health	4.44E-05	7.23E-05	9.3E-05	0.0001
Ecosystems	3.41E-06	4.15E-06	5.59E-06	9.01E-06
Resources	4.24E-05	2.5E-05	4.42E-05	4.44E-05

Table B. 7- Single score impact for all scenario using endpoint analysis

Label	Human Health	Ecosystems	Resources
Combustion	37.27	18.2882	7.0515
Gasification	25.1205	11.341	7.024
HTC	19.5251	8.4173	3.964
Pyrolysis	12.0009	6.9138	6.7383

Table B. 8- Single score impact considering savings for all scenarios using endpoint analysis

Label	Human Health	Ecosystems	Resources
Combustion	14.0024	5.9408	-12
Gasification	3.1791	0	-11
HTC	-1	-3	-13
Pyrolysis	10.2324	5.9699	5.917

C. Tables Economic Analysis

This section shows the tables which were used to present the figures in section 4.3.

Table C. 1- CAPEX in €/kg for each scenario

Type of plant	Scenarios	CAPEX
Combustion	S1	€ 2,776
	S2	€ 2,332
	S3	€ 1,555
Gasification	S7	€ 2,433
	S8	€ 2,468
	S9	€ 1,791
HTC followed by gasification	S13	€ 2,999
	S14	€ 3,078
	S15	€ 2,447
Pyrolysis	S19	€ 2,127
	S20	€ 1,617
	S21	€ 1,086

Table C. 2- Annual cost breakdown for each combustion scenario

Cost breakdown	Combustion without heat recovery			Combustion with heat recovery		
	S1	S2	S3	S4	S5	S6
Cost OP	78.84 €	95.27 €	111.69 €	78.84 €	95.27 €	111.69 €
O & M fixed cost	116.59 €	86.28 €	49.74 €	116.59 €	86.28 €	49.74 €
O & M variable cost	15.24 €	19.98 €	24.44 €	15.24 €	19.98 €	24.44 €
Cost of ash	13.11 €	15.84 €	18.58 €	13.11 €	15.84 €	18.58 €
Drying cost	231.89 €	271.46 €	308.01 €	0	0	0
Total	455.67 €	488.82 €	512.46 €	223.78 €	217.37 €	204.45 €

Table C. 3- Annual cost breakdown for each gasification scenario

Cost breakdown	Gasification without heat recovery			Gasification with heat recovery		
	S7	S8	S9	S10	S11	S12
Cost OP	78.84 €	95.27 €	111.69 €	78.84 €	95.27 €	111.69 €
O & M fixed cost	121.65 €	98.70 €	53.74 €	121.65 €	98.70 €	53.74 €
O & M variable cost	8.16 €	14.50 €	22.43 €	8.16 €	14.50 €	22.43 €
Cost of ash	7.14 €	8.63 €	10.11 €	7.14 €	8.63 €	10.11 €
Drying cost	231.89 €	271.46 €	308.01 €	0	0	0
Total	447.67 €	488.54 €	505.99 €	215.78 €	217.09 €	197.98 €

Table C. 4- Annual cost breakdown for each HTC followed by gasification scenario

Cost breakdown	HTC without heat recovery			HTC with heat recovery		
	S13	S14	S15	S16	S17	S18
Cost OP	78.84 €	95.27 €	111.69 €	78.84 €	95.27 €	111.69 €
O & M FC gasification	114.49 €	94.75 €	52.11 €	114.49 €	94.75 €	52.11 €
O & M VC gasification	7.68 €	13.92 €	21.75 €	7.68 €	13.92 €	21.75 €
O & M HTC	218.65 €	211.49 €	186.15 €	218.65 €	211.49 €	186.15 €
Cost of ash	7.14 €	8.63 €	10.11 €	7.14 €	8.63 €	10.11 €
Drying cost	130.70 €	153.01 €	173.61 €	0	0	0
Total	557.50 €	577.05 €	555.43 €	426.80 €	424.05 €	381.82 €

Table C. 5- Annual cost break for each pyrolysis scenario

Cost breakdown	Pyrolysis		
	S19	S20	S21
Cost OP	78.84 €	95.27 €	111.69 €
O & M	106.32 €	72.78 €	43.44 €
Electricity	71.74 €	104.12 €	143.35 €
Drying cost	111.41 €	130.42 €	147.98 €
Total	368.32 €	402.59 €	446.45 €

Table C6- Revenues generated for each scenario

Type of plant		Revenues
Combustion	S1	393.71 €
	S2	590.56 €
	S3	830.44 €
Gasification	S7	267.72 €
	S8	492.05 €
	S9	796.76 €
HTC followed by gasification	S13	251.97 €
	S14	432.37 €
	S15	762.92 €
Pyrolysis	S19	365.61 €
	S20	608.92 €
	S21	859.04 €