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Techno-Economic Analysis of Acorn Waste Gasification

Dissertação para obtenção do grau de mestre em Tecnologias de Valorização Ambiental e Produção de Energia

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Resumo

Apesar da sua relevância num contexto histórico, a bolota é um fruto esquecido pela maior parte das pessoas no mundo Occidental. Não obstante, tem estado a haver tentativas nos últimos anos para reintroduzir este fruto à dieta popular, embora tenha sido dificultado por causa dos custos altos deste género de produtos, acrescentando a isto a falta de conhecimentos da população geral. Ao mesmo tempo, estudos científicos exploram o potencial nutricional e culinário desta noz, mas não costumam desviar-se deste âmbito. Como consequência, tem havido poucos estudos feitos da bolota e os seus derivados num contexto de produção energética.

O objetivo do presente trabalho é explorar o potencial energético e tecno-económico dos resíduos da bolota, particularmente pelo meio da gaseificação térmica. O facto de a bolota ter propriedades que permitem o seu consumo pelos humanos significa que deve de dar-se preferência à sua utilização para fins alimentares. Contudo, os resíduos derivados da bolota ainda podem ser utilizados com fins energéticos. No presente estudo, uma amostra dos resíduos da bolota é analisada para determinar as suas propriedades químicas como o seu poder calorífico, a sua composição elementar, e o seu teor de humidade, cinzas, carvões e voláteis. A seguir, uma quantidade maior dos resíduos de bolota é gaseificada, e o *syngas* produzido é analisado para determinar a sua composição. Finalmente, uma avaliação económica é simulada com a ajuda dos dados recolhidos e com base na literatura. Os resultados demonstram propriedades muito interessantes tanto nos aspetos energéticos, tanto nos económicos.

Palavras-Chave: Gaseificação, Bolota, Resíduos da Bolota, Avaliação Económica

Abstract

Despite its relevance historically, acorns are forgotten by the majority of people in the Western world. Nevertheless, there has been attempts in the last few years to reintroduce this fruit into the popular diet, albeit to it's been made difficult due to the prohibitively high prices of these types of products, alongside the general population's lack of knowledge. At the same time, scientific research has explored the nutritional and culinary potential of this nut, however this same research does not tend to deviate from this field. Consequently, there's very little research conducted on acorns and their by-products within an energy-producing context.

The objective of the present study is to explore acorn waste's energetic and techno-economic potential, particularly through the means of thermal gasification. The mere fact that acorns can be consumed by humans means that it should be given priority as a food product. Nevertheless, acorn waste can still be used for energetic purposes. In the present study, a sample of acorn waste is analyzed to determine its chemical properties, which include its heating value, elemental composition, and its moisture, ash, fixed carbon, and volatile content. Next, a larger amount of acorn waste was gasified, and the produced syngas was analyzed to determine its composition. Finally, an economic analysis was simulated with the acquired data and with reference to literature. Results demonstrate very interesting properties both in the energetic and the economic aspects.

Keywords: Gasification, Acorn, Acorn Waste, Economic Evaluation

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List of abbreviations, acronyms, and symbols

€ - Euro

3R – Reduce-reuse-recycle

A – Amperes

CFC – chlorofluorocarbons

CGE – Cold gas efficiency

CHNS-O – Elemental Analysis

CHP – Combined heat power

dB – Decibels

db – Dry basis

DF – Dual-fuel

DME – Dimethyl Ether

E (Wt) – Energy

ER – Equivalence Ratio

EU – European Union

FTS – Fischer-Tropsch Synthesis

g – Gram

GR – Gasifying ratio

h – Hour

ha – Hectare

HHV – Higher Heating Value

HPDI – High Pressure Direct Injection

Hz – Hertz

IRR – Internal Rate of Return

kg- Kilogram

km^2 – Square kilometer

kW – Kilowatt

LHV – Lower Heating Value

LPG – Liquefied Petroleum Gas

$\dot{m}$ - Mass flow

m^2 – Square meter

m^3 – Cubic meter

MAS – Mixed Alcohol Synthesis

MJ – Megajoules

mm – Millimeters

MTBE – Methyl Tertiary-Butyl Ether

MW – Megawatt

MWh – Megawatt-hour

η - Yield

NDIR – Non-Dispersive Infra-Red

NG – Natural gas

Nm^3 – Normal cubic meters

NPV – Net Present Value

ºC – Degrees Celsius

P_e – Power

RH – Relative humidity

S/B – Steam-to-biomass ratio

t(h) – Time

TGA – Thermogravimetric Analysis

V – Volt

$\dot{V}$ - Volume flow

wt% – Percentage by weight

1. General introduction

The technologies developed during the Industrial Revolution and onward until our present times have improved drastically our quality of life in various aspects such as commodity and time, however it's also had negative consequences such as air & water pollution and creating for us a huge co-dependence on fossil fuels. Alongside this co-dependence, fossil fuels per se have become a sort of "weapon" for oil countries to use against countries lacking this resource, thus relying on the importation of fossil fuels. Portugal is an example of the latter, relying on the importation of fossil fuels from countries such as Brazil, Angola, Saudi Arabia, and Nigeria. Add to this the fact that Portugal is the 11th country most dependent on energy imports in the European Union (EU) with a reliance of 65.3% as of 2020, and it's possible to see that Portugal is in a delicate position regarding energy politics [1], [2]. At the same time, while we refuse to act or make changes in our lives to reduce our co-dependence on fossil fuels, the planet's fossil fuel sources are depleting at an alarming rate, since it also doesn't help that the world's population is only increasing and therefore our energy demands are doing the same. If nothing is done right now, this problem will reach a point where it'll be impossible to maintain the lifestyles we have created over the course of the last few decades.

On the bright side, there are to our disposal alternative sources of energy which, contrary to fossil fuels, are considered cleaner, and additionally, can be regenerated in a very short period - for example, biomass - or are considered unlimited - for example, wind and solar energy. While Portugal's energy dependence is still high for EU standards - and above that of the EU's average of 57.5% as of 2020 - it has drastically reduced from 85.3% in 2000. This can be attributed to renewable energy, as Portugal has more than half of its electrical energy produced from renewable sources [3] and is third place in contributions of renewable energy proportional to the primary production of energy [4], both as of 2020. Portugal's main sources of renewable energy are hydric, wind, and biomass [5], nevertheless other sources are being explored such as solar energy and geothermal energy in the Azores.

Portugal's biomass panorama is mostly painted by the use of forest biomass, such as maritime pine and eucalyptus [6]. There are currently eight biomass plants across Portugal, and many of them either are owned by big companies in the cellulose industry or have some sort of cooperation with them. For example, Navigator, the biggest paper and paste company in Portugal, was the biggest electricity producer from biomass in 2019. Another example is that of Altri, the second largest paper and cellulose business in Portugal: through the means of their subsidiary Greenvolt, they operate 5 power plants with a total power of 98 MW, equivalent to 50% of the industry's market share and producing even more energy than Navigator, thus earning the title of largest producer of energy resulting from burning biomass [7].

While Portugal is familiar with the concept and use of renewable energy, there's many more natural resources that go to waste because people often ignore their potential. Despite occupying nearly 24% of continental Portugal's territory, agriculture is an industry that has much more potential than we tend to imagine. The agriculture sector has attracted the EU's attention to what's known as "green growth" and, consequently, is attracted to the cultivation of energy crops to produce biodiesel and ethanol. However, the EU has also agreed that this should not interfere with food production and encourages the use of agricultural residues originating from these food sources, instead of competing for land to dedicate it for a specific crop, or even from having to plant energy crops from scratch. The previously mentioned paper and cellulose industry often works with black licor, eucalyptus waste, and forest biomass to produce its energy, yet the same cannot be said for agricultural wastes. In fact, there's no clear information from official Portuguese sources on the number of by-products and organic wastes originating from agriculture, or even on the prediction on agricultural biomass' energy production potential [8]. While there are accounts on the wastes from olive trees, vineyards, dry fruits, and olive pits being combusted for heat production, these accounts are not officially recorded and cannot be accounted for properly.

1.1. Framework and topic justification

Despite the EU being a big supporter of the expansion of the gasification technology, its use and development is still concentrated mostly within Central and Northern Europe [9]. As seen in literature, most operating large-scale gasification plants (>3 MW) are

within Germany, Finland, and the Netherlands. Sweden and Denmark are also involved in the use of gasification technologies, however many of their plants are either on hold or have been halted or cancelled due to lack of funding. What most of these gasifiers have in common is the feedstock used: most plants (whether currently operating or halted) use different types of woody biomass such as pellets or waste, and occasionally biomass is also listed as an input feedstock for these larger scale gasifiers. However, there are no specifications as to the origin or type of biomass used. The cheapness of this technology, combined with the agricultural influence of the Alentejo region make for an interesting case study where other outlets are explored for the valorization of agro-industrial waste, while also contributing to the development of rural regions.

1.2. General and specific objectives

The general objective of this dissertation is to determine the technological and economic viability of using agricultural waste to produce electric energy and gaseous fuels for a dual-fuel diesel engine. For this dissertation, acorn waste was chosen as the raw material for the gasification trials given that literature shows that acorns and their by-products have a great potential that's often overlooked by people. In addition to this, acorns are not currently considered as part of the human diet and while they're mostly used as animal feed, a large fraction still goes to waste. There are attempts to revive its culinary usage, and while acorns have not become mainstream, this study will use acorn waste, so as to not interfere with their role as a food for humans.
The general structure of this dissertation will follow an order like that observed in the methodology:

- Bibliographic research pertaining to gasification's current state-of-the-art, and the frequency of acorn and their by-products usage in gasification.
- Chemical characterization of a selected sample of acorns, available at the Polytechnic Institute of Portalegre. The sample of acorns underwent heating value, approximate, and ultimate analyses to understand better the biomass' composition.
- Gasification trials of a batch of acorn waste, with a sample of syngas taken during the gasification trial for further analysis of its chemical composition.

- Using the data collected throughout the entire experiment, an economic evaluation was done to determine whether this project would be plausible and profitable at a larger scale.

2. State-of-the-art

2.1 Agricultural waste

The nuanced nature of gasification is reflected especially when working with biomass as feedstock, as its best to adjust the reactor to work with a specific feedstock or a specific group of feedstocks. Subtle factors such as the geographical location or even the composition of the soil can have an impact on the characteristics of the feedstock [10], [11]. Evidently this can prove to be very useful, since this means that the reactor can be configured to work with whichever locally available biomass there is. The use of local sources not only is the most economical choice compared to using sources from outside, but this also has added environmental benefits such as reducing unnecessary long-distance transportation [12].

Working with biomass in the scope of gasification does not only involve the use of forest or woody biomass but also crops. While there are certain energy crops cultivated with the sole purpose of energy production and are not suited for human consumption, other energy sources are primarily used for human consumption, such as corn, soybeans, and palm oil. Within the scope of the EU, however, these types of crops are prioritized for human consumption and are not that deeply explored [13]. A solution to this, which does not interfere with food sources, is the use of agriculture waste that often goes to waste despite its huge biomass potential.

2.1.1. Framework

Our transition from hunter-gatherer communities to agricultural communities took place approximately 12,000 years ago – that is, according to most sources, as there are sources that state that the transition could've take place as early as 23.000 years ago [14]. This transition from a nomadic lifestyle to permanent settlements changed every aspect of our lives and has resulted in consequences that affect us to this present day: the creation of permanent settlements was the result of food security, meaning that humans no longer had to spend the majority of their days scouting for food, which meant that there was more leisure time available to dedicate to other activities and result in the progress and development of new technologies. At the same time, the food

security made available by agriculture resulted in a constant population growth. As of the current date of this paper, there are over 8 billion people on planet Earth, and this population growth is not foreseen to be stopping any time soon: it is estimated that the global population will exceed 10 billion by 2050 [15]. Evidently this population growth has been a result of the ever-growing food demand and given the growth prospects over the next two decades, it's not going to slow down any time soon.

Given its importance, the agriculture sector is deemed to be one of the most effective tools to raise incomes amongst the poor and a powerful key to end extreme poverty [16]. Nevertheless this industry comes with its own set of issues, as is the generation of agricultural solid waste, which include the following categories: animal production solid wastes (some examples include bedding/litter, animal carcasses, damaged feeders, and water-trough), food and meat processing solid wastes (hoof, bones, feathers, banana peels), crop production solid wastes (crop residues, husks), on-farm medical solid wastes (vaccine wrappers and containers, disposable needles, syringes), horticultural production solid wastes (pruning and grass cuttings), and chemical wastes (these mainly consist of the solid wastes generated from the use of pesticides, insecticides, and herbicides (such as pesticide containers and/or bottles).

Often, especially in developing countries, these wastes are not adequately disposed of: Usually agricultural waste is either disposed of indiscriminately or they're burned together in an uncontrolled environment, such as an open field. The inadequate disposal of agricultural wastes results consequently in several environmental and health problems such as pollution and the spread of pathogens. Despite the widespread activity of burning agricultural waste indiscriminately, air pollution only represents a small fraction of agricultural-originated pollution. Agriculture is mostly a source of water pollution – nearly 70% of all surface water supplies on Earth go towards agriculture – and also a source of contempt regarding land resources: the ever-increasing land demands result in the destruction of habitats and contributes to the endangerment of flora and fauna – as is the case with palm oil farms and orangutans, Sumatran elephants, Bornean pygmy elephants, Sumatran rhinos, and Sumatran tigers, for example [17]. In addition to the environmental and health threats, improper agricultural waste management can result in the loss of human lives and infrastructure, and hindering the progress in education and employment prospects in developing

countries [18]. The only solution to combat these issues is the correct management of agricultural wastes, which do not only consist of throwing out these materials. On the contrary, the aim of correct waste management is to find other ways to take advantage of this waste and turn it into useful by-products. For example, by composting agricultural waste or by turning it into substrate for edible fungi cultivation, agricultural waste can be repurposed to "give back to the land". Another example of correct waste management is their use as alternative energy sources and bio-fuel productions, which is the focus of this paper, particularly in the case of gasification.

2.1.2 Agriculture in the EU

Europe is no exception to the rule: with an ever-growing population, more resources and more food is necessary to sustain this growth. As of 2016, 2.535.130.000 tons of waste were generated in the EU, of which 20.690.000 tons came from the agricultural sector. However, this number is interesting as this fraction of waste is equal to only 0,82% of all waste generated in the EU – compared to other industry and compared to its own importance, agriculture generates relatively small amounts of waste [19].

While that percentage of 0,82% may not seem very significant, all those tons of agricultural waste are also equivalent to huge supplies of biomass energy ready to be tapped into. This is where the concept of circular economy comes into. The aim of a circular economy comprises of several points, which include extending the life cycle of products, reducing waste to a minimum, and refurbishing and recycling existing materials for as long as possible [20]. Having both a circular economy can be considered both a necessity and an advantage. For example, despite the ever-increasing need for more raw materials, they are not infinite and there's only so much that can go around. With a circular economy in place, not only will more resources be available to go around equally, but also smart reusing can lower CO_2 emissions [21]. In addition to this, a circular economy can reduce the EU's reliance on outside sources, since one would be using pre-existing resources that are already within EU borders.

In the case of agriculture (or at least agricultural wastes), the circular economy can be approached in several ways: composting, animal feed, using agricultural wastes for other industries, bioenergy, and the reduce-reuse-recycle (3R) approach, the latter

being the most common approach in research: The 3R's method can be seen applied far more many times than all the other methods suggested combined. While bioenergy is still not a common method used within the EU, it does not mean that it does not exist and that there aren't countries getting their energy from these resources. Most EU countries that explore the use of bioenergy are in Central Europe, with a few outliers in Eastern and Southern Europe, like Latvia and Italy.

Given that the EU is comprised of 27 countries with vastly different cultures, languages, customs, landscapes, and even land sizes, it should not come as a surprise that even within the EU there are disparities regarding agriculture. 2016 statistics show that the largest generators of agricultural waste were just four countries: Spain, the Netherlands, France, and Germany. Within this group of four countries, Spain and the Netherlands produced more than half (54,9%) of all agricultural waste in the EU, and adding France and Germany bumps this number up to two thirds. What all these countries share in common (except the Netherlands) are large populations, total area, and arable land, in addition to a long history of agricultural tradition which the Netherlands does share in common with the other three countries [19].

The results change slightly when looking at other parameters such as volume of agricultural waste per capita and volume of generated waste from the agricultural sector per unit area of agricultural land. The average volume of agricultural waste per capita in the EU is of 40 kilograms, and only six countries produce more than 100 kg of agricultural waste per capita: the Netherlands with 299 kg, Latvia with 185 kg, Slovakia with 145 kg, Spain with 135 kg, and Croatia with 119 kg. The average volume of generated agricultural waste per unit area of agricultural land is of 119,6 kilograms per hectare, and only 6 countries exceeded the 200 kg mark established by the study: the Netherlands with 2831 kg/ha, Malta with 944,8 kg/ha, Slovakia with 417,3 kg/ha, Croatia with 317,4 kg/ha, Spain with 270 kg/ha, and Sweden with 266,2 kg/ha [19].

While this information shows the interesting disparities between EU countries, it also shows the little impact Portugal has, and how little waste its generates per capita: Portugal hasn't even contributed one percent of the total agricultural waste generated in the EU, in addition to generating approximately 5 kg of agricultural waste per capita, and 15,2 kg of waste per hectare of arable land. If considering only vegetable and

animal waste, however, the statistics slightly change: 36,7% of all vegetable and animal agricultural waste came from PT, but this stat is still relatively low compared to that of other countries. 5,6 kg of waste generated per ha of arable land, and 2 kg per capita of waste [19]. Despite Portugal's minimal influence in the bigger EU picture, it does not mean that Portugal should exempt itself from being involved in a circular economy and finding ways to make use of its locally available resources: Portugal's small size does not mean that there's no diversity in its agricultural activity.

2.2. Acorn

Acorns are a starchy brown, oval shaped fruit composed mainly of the stem, cupule, and the nut itself, which is the only edible part of the acorn. They can be found from the Mediterranean Basin and North Africa to North America and even Eastern Asia. In fact, acorns are widely consumed in Korean cuisine and in some Native American tribes.

Although not widely consumed in the Western world, acorns have been a part of the human diet for centuries, some even claiming that this relationship transcends the beginning of our existence as *Homo sapiens* [22]. Undeniably so, acorns have contributed to the existence of humanity: evidence has been found of human consumption of acorns since the Paleolithic, when humans mostly led a hunter-gatherer lifestyle. This would eventually lead the acorn to play an important role in the folklore, mythology, and religion of human groups in contact with the fruit. Even when humans transitioned to having a more sedentary lifestyle, acorns were still an important part of the human diet. In fact, it could've even been considered a staple. Even though humans tended to only associate the consumption of acorns to times of famine, this was more common than what we would've wanted as a species throughout history, given the frequency of wars, upheavals, and disasters. Acorn consumption in the West has been recorded even as recently as the 20th century, with bakers in World War II Germany using acorn flour in bakeries, and with lower-income Spaniards making it a significant part of their diet [22][23].

What made acorns the go-to choice during difficult times – and what helped it stay so relevant during most of human history – is its high nutritional value. Compared to other nuts, acorns are low in protein, and have a high fat content – the only nuts with a higher fat content than acorns are pine nuts and almonds – and, most importantly, are

extremely high in carbohydrates. Acorns also have a high content of minerals such as phosphorus, magnesium, calcium, and potassium, and mostly vitamins A and E [24]. Starch is the most significant component of acorns, consisting nearly half of its chemical make-up.

2.2.1. Acorn in Portugal

Portugal is a country located in Southwestern Europe which is characterized for having a Mediterranean climate, with mild wet winters and hot dry summers. More specifically, Portugal is classified as having a type C climate on the Köppen classification, with subcategories of Cs, Csa, Csb, and BSk [25]. Even though Portugal's climate and geography makes it ideal for a wide array of crops, little attention is mustered towards exploring this because of the importance that's given to other sectors such as tourism. Most of the Portuguese territory has a climate suitable for the growth of oaks, except for areas with a high altitude and areas with very low temperatures during the winter. Most of them can be found either in the northern part of the country or in Alentejo region, with a significant portion of them are concentrated in the *Montado* region.

The *Montado* is a man-made ecosystem mostly south of the Tagus river in the Alentejo region that covers around 1.063.000 hectares of land [26]. The dominating species are the cork oak and the holm oak, which collectively can also be referred to as *montado*, hence its name. Not only are they the predominant species in the Alentejo region, but the *montados* are also the dominating forest species within continental Portugal. To have a better notion, the *montados* cover nearly a third of all forest areas in the country [27].

Acorns are still somewhat relevant in Portugal, just not for human consumption. Despite their irrelevance in the average modern Portuguese diet, they're still being widely used for animal consumption, mainly of *Alentejano* breed pigs, and to a lesser extent to feed other species. Acorns are also processed into flour in attempts to reintroduce it to the human diet; however, this amount is very symbolic. All these activities are considered active usage of acorns. Passive usage, on the other hand, entails wild fauna feeding off from the acorns that aren't used for human activity. Despite their potential, more acorns end up being wasted compared to the total

consumed by pigs, other animals, and wild animals combined: 55% of all acorns produced are wasted, and altogether the other activities make up 45% of acorn's current uses [28]. To paint a better picture of the number of acorns wasted in Portugal, about 83.640 tons of acorns are used for pig farming. This is equal to 21% of all acorns produced being used for this specific purpose. This would mean that around 219.057,143 tons are wasted yearly. Figure 1 shows the usage of acorns in Portugal.

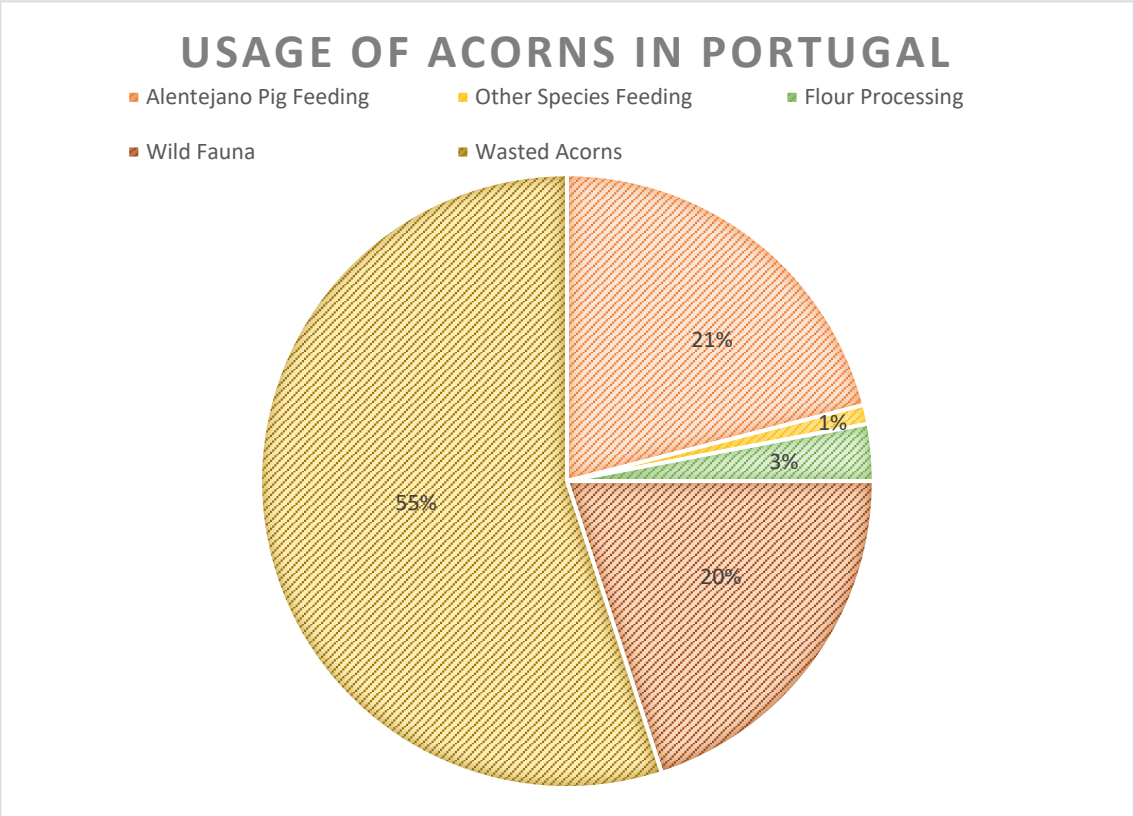

Figure 1. Usage of acorns in Portugal [28].

The most important oak species in Portugal are the Portuguese oak, mostly found in northern Portugal, and the holm oak (or evergreen oak) and the cork oak which are mostly found in the Alentejo region. More than three-quarters of all acorns originate from holm oaks and cork oaks. Figure 2 demonstrates the annual acorn production in Portugal.

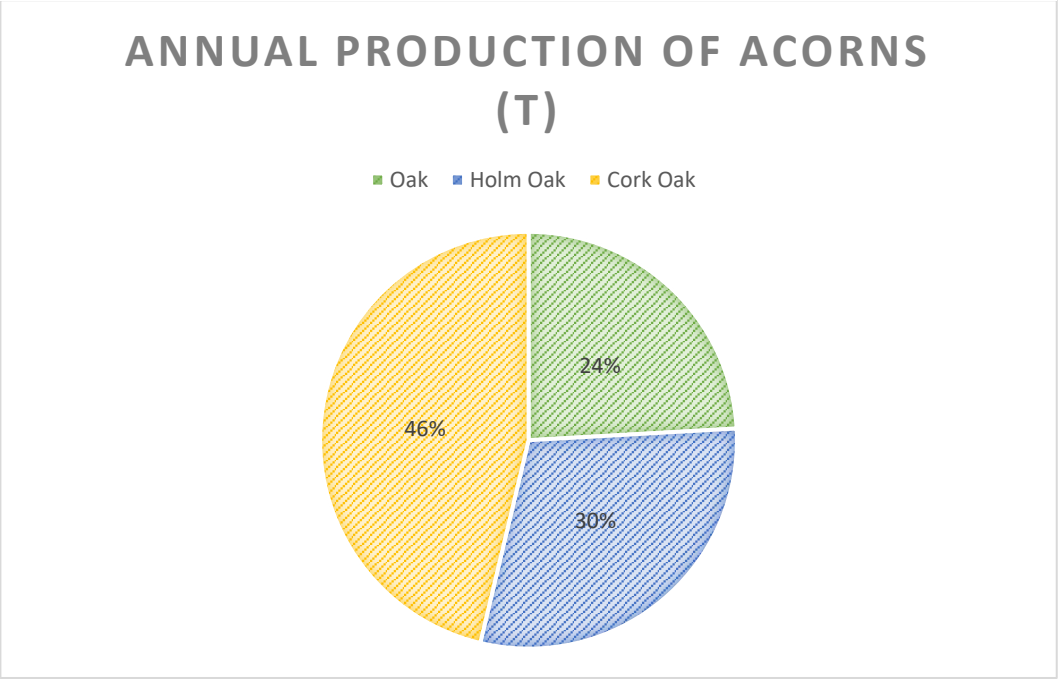

Figure 2. Annual acorns produced per species in Portugal [28].

The abundance of wasted acorns is an issue that many people take to heart and are doing something to change the general population's mindset. The efforts most seen are those where acorns are promoted as a food product since that was its primordial use historically. Oftentimes, scientific papers focus on the nutritional value and the culinary applications of acorns, such as baking [24], [29]–[31].

These suggestions and applications are great since acorns are a widely available food source and can help combat potential future problems with food shortages. At the same time, the waste produced from these same acorns can also be used for energetic purposes. In general, using biomass to produce energy – be it electric or thermal – can be seen as an interesting approach to contributing to the development of a region, and

Portugal is no exception to this. In fact, Alentejo is a primordial agrarian region, and with the majority of the Portuguese *montado* located within Alentejo, the prospect of tapping into the region's biomass reserves seems like a lucrative choice and the region is often viewed as the first choice for projects of this nature [32].

Despite Portugal's agricultural diversity, little attention is paid to the energy potential of agricultural biomass and its derivatives to produce energy. Most of the attention goes to forest biomass because of the large potential there is: Portuguese forests occupy approximately 3,5 million hectares, which is equivalent to 38,4% of all Portuguese territory. Not only does this makes the seventh country in the EU with the largest absolute forest area, but Portugal is also one of the countries with largest forest coverage in relation to its territory size [33].

Besides the large amount of forest biomass available, application of forest biomass can help solve several issues which are very much relevant to the Portuguese context, such as the decrease and control of forest fires, the removal of invasive species like the eucalyptus, and the country's large energy dependency. Nevertheless, one must be careful with the improper use of these forest biomass resources, as an excessive usage may deem it "non-renewable", in addition to contributing to soil erosion, water pollution, and the loss of wild habitats. To mitigate these negative effects, forest biomass waste is preferred.

In addition to all the prior negative effects mentioned, the emission of harmful gases such as NO_x is another one that must be contributed to the list. While NO_x gases are not commonly seen in gasification, the reason for this is because biomass is mostly treated using traditional forest biomass combustion systems, which were approved by the Portuguese government after the 2017 forest fires as a measure to prevent forest fires and increase forest maintenance and cleaning [34]. There is little information regarding gasification plants in Portugal. As of 2010, there are two gasification plants registered in Portugal in the Worldwide Gasification database, and the remaining gasifiers are mostly found in different Portuguese universities, including the Polytechnic Institute of Portalegre [8].

2.3. Thermal gasification

Gasification is the thermo-chemical process used to convert any organic material, whether it be of renewable or non-renewable sources, into syngas. The only criteria necessary for any material to be gasified is for it to contain carbon within its composition, meaning that a wide variety of materials can be used ranging from coal to biomass, to even plastic.

The produced syngas is composed mainly of carbon monoxide, hydrogen, nitrogen, methane, carbon monoxide, and small traces of hydrocarbons and some tars that are usually filtered out during the process [35]. The range of applications for syngas is wide, ranging from power generation, chemical production as is the case with fertilizers, to being used even in the refinery industry and for newer technologies such as fuel cells.

While gasification and pyrolysis are seen as two different processes, one can consider gasification as an "extension" of pyrolysis. Pyrolysis involves complete lack of oxygen, whereas gasification requires the presence of oxygen, albeit in limited amounts. Both processes produce syngas, however gasification focuses more on yielding the maximum amount of syngas compared to pyrolysis. While in pyrolysis syngas the main products sought after are bio-oil and biochar, a limited amount of syngas is also produced, which is why gasification is seen as an extension of pyrolysis. Nevertheless, biochar and bio-oil can also be used to produce syngas if needed. [36]

The process of gasification can be summarized in 5 “sub-processes”: drying, pyrolysis, combustion, cracking, and reduction [37].

1. Drying: This step drives off any moisture present in the feedstock, resulting in water vapor and dry feedstock. While this process is aimed at removing moisture, it is advisable to remove as much moisture as possible prior to gasifying to reduce the need of unnecessary energy consumption, given this step’s endothermic nature. Drying occurs between the range of 100ºC and 150ºC.
2. Pyrolysis: Further heat is applied to the resulting dry feedstock in the absence of (the) oxidant to break it down. This step separates the fixed carbons and volatiles present into charcoal and tars respectively. Pyrolysis takes place

between 200ºC and 500ºC, but feedstock begins to quickly break down at the 240ºC mark.

3. Combustion: Out of the 5 steps that compose gasification, combustion is the only exothermic reaction, as this thermo-chemical reaction involves rapid reactions between the fuel and oxygen, provided by an oxidizing agent. The other endothermic reactions either derive the heat they need from combustion or through recovery by other heat exchange processes in the gasifier. Combustion is fueled either by the tar gases or chars produced during pyrolysis, however this is a nuance that has more to do with the reactor type. Besides heat, other byproducts of combustion include water vapor and carbon dioxide, which are considered "waste products" and are reused in the final step of reduction.
4. Cracking: Once the feedstock is turned and separated into charcoal and tars, this step aims at grabbing these complex compounds and "cracking" them into simpler molecules such as lighter gases. Like drying and pyrolysis, cracking is an endothermic reaction, necessary to ensure proper combustion as complete combustion is only possible when all the components are converted into simpler compounds that have the capacity to react with oxygen. Another reason for its importance is that breaking down these complex compounds (such as tars) prevents them from further condensing and forming sticky tars in liquid form. Besides being very difficult to clean, the presence of tars will reduce a gasifier and engine's lifespan and efficiency. Cracking happens between the 800ºC and 1200ºC mark.
5. Reduction: This final step can be summarized as the "opposite of combustion": while combustion can be summarized as a reaction where oxygen is "added" to a feedstock, reduction does the opposite by removing oxygen from the so-called "waste products" produced during combustion. The removal of oxygen from water vapor and carbon dioxide results in the formation of carbon monoxide and hydrogen, which are the main components of syngas. Reduction happens within the temperature range of 650ºC to 900ºC.

Despite the standard steps and the extensive studies done on the gasification of different feedstocks, ranging from coal to a wide range of biomasses, there's a countless number of factors that influence the gasification process and its end-products. These

can be influenced by the feedstock's properties - for example the type of feedstock and its physical and chemical properties - or these influences can come from the reactor's end: the extent of conversion of feedstock and the chemical reactions that take place during the gasification process, which are affected by temperature, pressure, and the reactor's configuration, among others. Despite all these factors, the most noticeable influences in the chemistry of gasification come from the chemical characteristics and the physical composition of the feedstock [38]. This is the reason why most feedstocks usually go through some sort of pre-treatment to a greater or lesser extent.

2.3.1 Why gasification?

While there are several other thermochemical technologies available in the market, gasification presents a series of environmental and economic advantages that most of these other technologies do not present. For starters, gasification can work with a wide array of materials, with the only condition that they have carbon in its chemical make-up. This means feedstock ranging from mixed waste to even plastic. Other technologies working with the same feedstock would be more likely to emit harmful pollutants, which is another point in favor of gasification since this technology is known to emit much less air pollutants compared to its counterparts [39]. In fact, gasification can even make several other processes less environmentally harmful, as is the case once again with mixed wastes. However, it does not have to be limited to urban waste – agricultural and forest wastes are other examples that can be used to reduce their carbon footprint in their respective industries.

In addition to the environmental benefits, gasification also presents several economic benefits that deems this technology a worthy competitor against other more expensive thermal technologies. Gasification's flexibility means that it can convert feedstock deemed to have "low value" into syngas, a higher quality product with a wide array of valuable and interesting applications, like thermal & electric energy production, chemicals, and fuel additives, among others. Additionally, a gasifier's operation and maintenance costs are lower than that of other conventional technologies, and less pollution control equipment is necessary [39]. Given their affordability, gasification can also be a key in further enhancing the development of rural regions, since often

these places have an abundance of feedstock compatible with gasifiers, ergo, a large source of untapped energy.

2.3.2. Types of gasification reactors

There are different ways gasification processes can be classified. The most common is based on the calorific content of syngas, but other ways depend on the type of reactor used, whether the system reacts under pressure or not, and according to the bed types of the reactors [40]. Main differences in the gasifiers encompass the method which feedstock is introduced into the reactor and whether this feedstock moves around the reactor with the help of air flows or gravity, the type of oxidant used, the temperature range of the reactor, how heat is provided for the gasifier – some gasifiers take advantage of the feedstock, while others use outside sources like steam or an inert material – and the pressure at which the gasifier is operated, among others that will be further discussed.

2.3.2.1 Entrained Flow Reactors

With entrained flow reactors, feedstock, alongside an oxidant are fed simultaneously into the reactor from the top. Feedstock can be in the form of pulverized solids, atomized liquid, or fuel slurry, and the oxidant of choice can consist either of air, steam, oxygen or a mixture of steam and oxygen. With entrained flow reactors, it's most common to see oxygen used as an agent [40], [41].

Both the oxidant and the feedstock flow through the gasifier in a co-current fashion passing through all the stages of gasification and allowing a more complete combustion and taking advantage of the energy stored in the tars, which are nearly negligible due to the high temperatures that are worked with. The high temperatures of entrained flow reactors means that they're well also equipped to remove most ash in the form of slag, as they work with temperatures well above the ash fusion temperature.

Given the very high temperatures worked within this gasifier design and the fact that the temperatures are uniform within the reactor, entrained flow reactors require large amounts of oxidants to operate. Entrained flow reactors have a very high carbon conversion rate; however, the gas efficiency is not the highest.

2.3.2.2. Moving Bed Reactors

Moving bed reactors are one of the oldest reactors invented, first appearing in the early 19th century. When these first appeared, the main source of fuel was biomass, meaning that this technology has had a long time to evolve and adapt to the use of biomass. Such were the importance of these reactors that they were even used to power cars: during the 1940s gasifiers were used to produce gas for cars given the scarcity of petrol during World War II, and consequently several companies produced gasifiers for transportation applications. However, they fell out of favor once the war ended and fossil fuels were readily available once again [42], [43].

Within the moving bed reactor category there are two different models, those consisting of updraft and downdraft gasifiers. Despite their differences, they both share characteristics common to moving bed gasifiers, including the simplicity of the gasifier, its operation, and configuration, their high efficiency, the low oxidant requirements, and the feedstock flexibility – as mentioned before, moving bed gasifiers have an ease to work with biomass.

Updraft reactors are one of the simplest and most common designs, as they have been the standard of coal gasification for the past 150 years. Feedstock is fed into the reactor from the top, whereas the oxidant (air, steam, oxygen, or any other of choice) is fed from the bottom, going in counter-current direction to the feedstock to the top where the produced syngas exits. While its functioning is relatively simple, its thermal efficiency is high as the produced syngas dries whatever feedstock is entering from the top of the reactor, and its high temperatures dry the incoming feedstock, thus transferring its heat and allowing the syngas to leave the unit at a cooler temperature. In updraft reactors, tar and methane production is high at what would be considered typical operating temperatures, given the design of the reactor and the “uneven” temperature distribution, as different regions within the unit have different temperatures and different thermochemical processes take place in them [44].

Downdraft reactors are very similar in design to updraft reactors, with the temperature regions being in the same places as in an updraft reactor (for example, drying takes place at the top of the reactor and combustion takes place at the bottom). However, the main difference is that both the feedstock and the oxidant enter from the

top of the gasifier. This results in lower tar formation compared to updraft gasifiers, which is desirable when working with turbines and gas engines. However, this reactor design is more extensive and is more picky with the particle size of the feedstock, as smaller particle sizes are not well-converted in downdraft gasifiers [45].

2.3.2.3. Fluidized Bed Reactors

Fluidized bed reactors are one of the most popular reactor designs, employed from laboratory to commercial scale, also often used within the petroleum and chemical processing industry [46]. To understand further their popularity, it's best to understand their function.

Feedstock is inserted at the top of the reactor, like how it's done in other reactor models, however the oxidant is introduced from the bottom of the reactor with enough velocity to suspend the feedstock particles within the reactor in such a way that the feedstock will "act" like a fluid. This allows for heat to be distributed in a more uniform fashion and for a high carbon conversion rate (90-95%) and to reduce the formation of tars, since most particles undergo pyrolysis and combustion [47].

Compared to other designs, fluidized bed reactors have a lot of perks which can attribute to their popularity: fluidized bed reactors are very flexible when it comes to the feedstock type and the load being worked with and the oxidant requirements are relatively moderate compared to other designs. The only requirement is for the feedstock to be finely ground, preferably to be less than 6 mm in size, so the feedstock can behave more adequately as a fluid within the gasifier. In addition to its flexibility and excelling solid mixing capacities, fluidized bed reactors have the property of "self-cleaning": by-product char exits the reactor with syngas. This is due to feedstock being of a relatively narrow particle size distribution. Similar to other gasifiers, cyclones are used to separate the dirty particles (chars, tars) from the syngas prior to vapor condensation [46], [48].

2.3.3. Other gasification technologies

Besides the more widely known gasification technologies there are yet other some other ones that are being studied, such as plasma gasification technology and supercritical water gasification.

As the name implies, plasma gasification uses plasma torches to apply energy to carbon-based materials in a controlled environment. Other gasification technologies work with very high temperatures that can reach up to 1000ºC, but plasma gasification takes it to a whole new level: the temperature of plasma can reach 10.000ºC, or even go up as high as 14.000ºC [49]. Just like other gasification technologies, the material fed is carbon-based, and the process of gasification also occurs in the presence of either air, oxygen, steam, or carbon dioxide.

Compared to combustion, plasma gasification has a major advantage, which is its ability to generate slag in the form of vitrified glass. This slag is formed when the plasma torches are applied to the feedstock, resulting in the simultaneous evaporation of the organic and carbonaceous components, and melting of the inorganic components. This melted vitrified gas pours out at the bottom of the gasifier and converts itself into a safe and stable material once cooled down. Besides being easier to collect, this prevents the formation of fly ash which is present in combustion [50].

However, its high temperature of operation also presents disadvantages. Such high temperatures have strain effects on the heat exchange materials which are used to recover the heat from the hot gases to generate steam at operating temperatures of just 1500ºC. Despite its potential, plasma gasification is still a relatively new technology and therefore most companies are still reluctant to invest in it as of present times.

Supercritical Water Gasification is a hydrothermal process best suited for feedstock with a high moisture content. Per se, there are few options available for the treatment of such high-moisture feedstock, such as anaerobic digestion and hydrothermal treatments. While anaerobic digestion is the better-known of the two, it's also a very inconvenient and disadvantageous process given its long treatment time and "wet by-products with low economic value". Hydrothermal processes involve an aqueous system "at temperatures and pressures near or above the critical point of water” [50].

Hydrothermal process is an umbrella term for different processes that can be done using this conditioning, such as carbonization, oxidation, liquefaction, and gasification. While all of these can fall under the same "hydrothermal" category, the operating condition is what determines which of these four processes is done, in addition to which by-products will be yielded.

In the case of hydrothermal gasification, operating conditions are different to those usually observed in regular gasification processes. For example, hydrothermal gasification is best for treating feedstocks with a moisture content above 30%, something that would be very detrimental with a regular gasifier. While an usual technology compared to its other counterparts, it doesn't mean that this technology generates low quality gases: on the contrary, hydrothermal gasification can generate higher gas yields with less tar and char compared to other technologies, even while using a feedstock with an 80% moisture content.

The reason which water is above what's known as its "critical point" is due to the unique properties that supercritical fluids present, compared to liquid or gases. For example, supercritical fluids can dissolve materials that are not soluble either in liquid (water) or steam, under regular conditions [50].

Hydrothermal processes, particularly gasification, under these supercritical water conditions present great advantages, including a high energy value of the gas product due to lower concentrations of CO_2, high pressure of the gas facilitating its transportation, usage, and cleaning, and lower amounts of tars generated. Nevertheless, this does not mean that hydrothermal gasification does not come with its own set of disadvantages, such as the huge "energy input required to heat up the water in a high moisture content feedstock". "The heat provided and the efficiency of the heat exchanger both play an important role in the overall efficiency of the system because sometimes the energy "value" within the biomass is not enough to heat up the water contained (within the biomass)".

2.3.4. Oxidants

As observed in previous sections, there are different option of oxidants depending on the reactor model being used and the user's end goal [51]. Air, oxygen, steam, carbon dioxide, or a mixture of these gases are the most studied oxidants. Each of them comes

with their own set of perks and drawbacks, as these inevitably have different effects on the formation of tars and the syngas's heating value, as an example.

Out of these agents, the most used is air since it's the cheapest option out of the other and consequently is the most popular. However, air's high nitrogen content "dilutes" the syngas and does not provide any significant contribution to the syngas's heating value, resulting in a heating value on the lower range compared to others, ranging from 4 - 7 MJ/Nm^3 [52][53]. Steam and oxygen, on the other hand, produce syngas that would fall in a medium range, with heating values ranging from 10 – 20 MJ/Nm^3. Besides the lack of nitrogen, the presence of oxygen presents itself in a cleaner gas, and the use of steam encouraged higher concentrations of H_2 and CO in the syngas. A significant drawback, however, is the difficulty in extracting, storing, and using oxygen as this is very energy intensive [52]. Oftentimes, oxygen is seen mixed with steam rather than as an agent alone. Lastly, carbon dioxide is an option that's still being studied, as it is a difficult oxidant to work with given its energy demand. However, finding a viable way to harness carbon dioxide as an oxidant would be a significant breakthrough, as this would allow for a new innovative way to use one of the most found pollutants on this planet.

Each oxidant has their own set of parameters that must be considered and are not interchangeable. The list is as follows:

- Air: Equivalence ratio (ER = ratio of air used to stoichiometric air)
- Steam: Steam-to-biomass ratio (S/B)
- Steam-oxygen: Gasifying ratio (GR = (steam + O2)-to-biomass ratio)
- CO2: CO2-to-biomass ratio

2.3.4.1 Equivalence Ratio

Research suggests that equivalence ratio (ER) is determined to be one of the most important parameters related to the improvement of gas quality yield, even more so than bed height and fluidization velocity [52]. Despite its importance, having an ER value that's too high is not ideal, since according to Salaudeen et al. it means:

- More air is introduced in the reactor, improving oxidation rates and resulting in more CO_2, H_2O, and N_2 being formed. In the meantime, less cracking takes place

resulting in less CO and H_2 formed. While this might not affect other feedstock like plastic, this can be an issue in the case of biomass.

- A decrease in methane, as is the example shown when the ER was increased from 0.21 to 0.61 and the methane was reduced from 15.7% to 3.64%.
- The decrease of the syngas's high heating value.

On the other hand, an excessively low ER value can enhance the production of H_2, CO, CH_4, and other hydrocarbons, but it also increases the formation of tars due to the decrease in the reactor's bed temperature. Generally, ER values range between 0,2 and 0,4 when working with biomass [54].

2.3.4.2. Steam-to-Biomass & Gasifying Ratio

Steam gasification, as the name suggests, involves the gasification of fuel with steam as an oxidant. While it's more expensive than air gasification, steam gasification has several desirable properties such as a more concentrated syngas with a higher heating value ranging from 12-14 MJ/m_n^3 [55] due to the lack of nitrogen in steam, and lower tar formations. Steam syngas presents itself as a very attractive option for synthesis and fermentation.

As mentioned before, S/B is a parameter exclusive to steam gasification. There are studies that suggest hydrogen production is also a result of temperature increase, however there are others that do not agree with this statement, nevertheless the same studies agree that an increase in the S/B ratio increases hydrogen production and carbon conversion and decreases CO and CH_4 concentrations [55][56]. Generally, an S/B ratio range between 0,5 and 2,5 has shown to reduce tars and produce a richer syngas, and further reduction is possible with the help of catalysts that encourage tar-reforming reactions. The most used catalysts in these cases are dolomite, alkali metals, and nickel [57].

Adding oxygen also helps in the reduction of tars when working with steam. Besides further helping the reduction of tars, having oxygen mixed with the oxidant can also encourage the gasification process to become autothermal, meaning that syngas would be produced by exclusively using the heat produced by the reaction in itself. Despite steam being included in the oxidant mixture, S/B is not used, instead this being substituted by gasifying ratio (GR). Lower GR values encourage the production of light

tars, whereas the higher the GR value, the lower the tar yield. An example is an 85% reduction in tars when the GR was increased from 0,7 to 1,2, according to a study performed by Aznar et al. [57].

2.3.4.3 CO_2-to-Biomass Ratio

While the term has been coined in literature, as is the case with Basu in his *Biomass Gasification Design Handbook* [57], very limited amount of studies exist on the matter, since the role of carbon dioxide has been explored in a very small amount of studies [58].

Using carbon dioxide as an oxidant seems like a very attractive solution for the mere reason that by using it, it would serve a double purpose: create syngas and reduce pollution. However, the use of carbon dioxide as a gasification oxidant comes with a huge draw back, which is that a constant source of external heat would be necessary to maintain gasification temperatures because heat would not be supplied by partial combustion as is the case with other oxidants. Consequently, carbon dioxide gasification is an energy intensive process with little appeal for gasification studies, and much less for commercial use [59][58].

2.3.5. Tars

Just like the reactor design, chemical composition of the feedstock and the oxidant have an impact on the syngas's heating value, they'll also have effects on the formation of tars. Tar can be defined as a mixture of different hydrocarbons, with the addition of oxygen-containing compounds, derivatives of phenol, guaiacol, veratol, syringol, free fatty acids, and esters of fatty acids. Like many other aspects and parameters of gasification, the yield and composition of tars relies on the feedstock composition, gasifier design, and the temperature of the reaction [57]. To further understand the way tars are formed, it's necessary to make the distinction between primary, secondary, and tertiary tars:

- Primary tar: A mixture of condensable hydrocarbons that undergo molecular rearrangement between 700-900ºC. Primary tar is produced between 200-500ºC, which coincide with the pyrolysis stage of gasification. While chars are

also formed during the pyrolysis stage, these are the solid residues that are left over from gasification and do not have such a great impact in the efficiency of equipment compared to tar. When pyrolyzing cellulose and hemicellulose, primary tars are mostly composed of oxygenated organic compounds (alcohols, carbon-acids, ketones, aldehydes). When pyrolyzing lignin, primary tars are made up of aromatic compounds, bi- and tri-functional substituted phenols. Examples include cresol and xylenol [50].

- Secondary tar: These can also be considered pyrolysis products. When primary tars are rearranged, they produce non-condensable gases and secondary tar, which mainly consist of phenols and olefins that are formed after the 500ºC mark. While no tar is ideal in syngas, secondary tar is "preferred" compared to primary tar, since primary tar is the same one that will quickly condense if given the chance, alongside with still containing certain energy content that could still be used during combustion. Secondary tars are mostly composed of phenols, olephins, and alkylated mono- and diaromatics like hetero-aromatics. Examples include pyridine, furan, dioxin, and thiophene [50].
- Tertiary tar: Tertiary tars are mostly composed of aromatic and poly-nuclear-aromatic-hydrocarbons (PAHs) like benzene, naphthalene, phenantherene, pyrene, and benzopyrene. These only appear when all primary tar has been broken down given the high temperatures at which tertiary tars are formed [50][57]. Secondary and tertiary tars are often lumped together in literature, as the distinction does not always present itself clearly [60].

2.3.5.1. Oxidant influence on tar formation

Literature argues that one of the biggest, if not the most important, influences in tar formation, is linked to temperature [60]. Other factors like feedstock chemical make-up, moisture content, ash, among others pertaining to the feedstock itself, do not seem to have a significant impact on the formation of tar as one would initially think. However, this does not mean that there aren't other factors that influence tar formation: oxidant choice and reactor design can determine the temperature range being worked with. In the case of oxidants, tar formation has been shown to be greatest

with air, and least with steam-oxygen combination. Further sources can be used alongside oxidants, like the addition of catalysts.

- Gasification in air: As a rule of thumb, an increase in ER reduces the concentration of tars in syngas, but also reduces the yield of syngas *and* its quality: heating value is reduced due to nitrogen dilution from air, for example.
- Gasification in steam: An S/B ratio range of 0,5 to 2,5 has shown to produce a large reduction in tar yield, and further reduction is possible with the help of catalysts that encourage tar-reforming reactions. The most used catalysts in these cases are dolomite, alkali metals, and nickel. Adding oxygen also helps in the reduction of tars when working with steam, which is also discussed further ahead.
- Gasification in a steam-oxygen mixture: Besides helping further the reduction of tars, the presence of oxygen also helps the gasification reaction autothermal, meaning that syngas would be produced using only the heat produced by the reaction in itself. Like the other types of gasification, steam-oxygen uses GR. Lower GR values encourage the production of light tars, whereas the higher the GR value, the lower the tar yield. An example is an 85% reduction in tar when the GR was increased from 0,7 to 1,2, according to a study performed by Aznar et al. [57]

2.3.5.2. Reactor design influence on tar formation

Just like oxidants, the design of a reactor can have a huge influence in the formation of tar and the quantity present in syngas. Besides determining the temperature range that can be worked with, the reactor design also has an influence on the types of tar formed. Updraft reactors mostly produce primary tars, downdraft reactors mostly produce tertiary, and fluidized bed reactors produce a mixture of secondary and tertiary tars [60]. Understanding the design and the way each reactor works will paint a clear picture as to why each reactor design produces different types of tar.

- **Updraft Gasifiers:** This reactor design tends to generate the highest amount of tar, ranging from 10-20% by weight of the feed. The reason for this is because of the general upward flow of gas. While feedstock is fed from the top, the gasifying medium is fed from the bottom, and the resulting syngas also leaves

from the top. While primary tar is formed during the pyrolysis stage, it does not have the opportunity to go through higher temperatures since combustion takes place below the pyrolysis region, thus having no opportunity for further conversion into the so-mentioned secondary tar and gases.

- **Downdraft Gasifiers:** Contrary to updraft gasifiers, both gas and feedstock travel downward. The primary tars are formed in the pyrolysis region as expected, and given the downward flow nature of the gasifier, this gives tars the opportunity to pass through reduction and combustion, therefore allowing the formation of secondary tar and non-combustible gases once the primary tars enter in contact with the oxygen present in the combustion zone. This gives downdraft gasifiers the lowest tar production, at less than 1 g/Nm3.
- **Fluidized-Bed Gasifier:** This gasifier is in the "middle" between updraft and downdraft gasifiers when it comes to tar production. Like downdraft gasifiers, the oxidant enters from the bottom, however, the feedstock enters either from the top or the side. Either way, the feedstock is mixed thoroughly, and this allows the oxygen in the oxidant to come in direct contact with biomass particles undergoing pyrolysis at that moment. The direct contact of these oxygen particles with these freshly-pyrolyzed particles burn the primary tars formed.

  Nevertheless, since the combustion and pyrolysis are not taking place in a specific place, this results in the tar also not being formed in a specific location. As a result, while some of the tars are combusted, there are also other tar particles that are not, meaning that whatever tar particles that didn't have the chance to be combusted will be released and leave the gasifier alongside (the syngas).
- **Entrained-flow Gasifiers:** With this gasifier design, tar production is negligible due to the very high temperatures being worked with (over 1000ºC). This results in nearly all tars being converted into noncombustible gases.
-

2.3.5.3. Treatment options for tar removal

Despite tars originating from the gasification of coal having a good commercial value, tars originating from the gasification of biomass is mostly oxygenated and has little

commercial use. This results in not only an added headache when gasifying biomass, but the difficulty in commercializing, or even getting rid of these tars, results in a huge drawback from biomass gasification being used at a greater scale [57]. As a result, a lot of focus has been placed on developing techniques and technologies apt for the removal of tars, and while a lot of progress has been made over the years, this remains an issue. Few factors have such an impact on tar formation to the same extent temperature does. Simply increasing the temperatures worked with will make a difference in the amount of tar formed, and besides design, temperature is one of, if not the, main factor that separates an updraft gasifier from a fluidized bed [60]. Thermal cracking is done at extremely high temperatures, such as the case with entrained flow gasifiers that work with temperatures beyond the 1000ºC marking. To aid in obtaining the desired temperature range, either oxygen or air may be added to allow the partial combustion of tars and hence thermal cracking.

In addition to increasing the temperature worked with, catalytic cracking is a common method used in many plants to remove tar and other undesired substances, which consists of adding the catalyst(s) to the gasifier bed. Dolomite and olivine are some examples of these such catalysts. Evidently, each of these catalysts has its own set of pros and cons: Dolomite is inexpensive and can prevent or decrease agglomeration in fluidized-bed gasifiers when feedstock (particularly biomass) with a high alkali content is used, however dolomite also can increase the particulate content in syngas since it erodes easily when calcined within the gasifier, and in addition is difficult to obtain a tar content of less than 2 grams per m^3_n, which is the limit required to prevent the deactivation of nickel-based catalysts provoked by coke, making it a not-so-ideal catalyst to gasify biomass with. Olivine seems to be more effective than dolomite, however it's difficult to determine performance of olivine in air gasification of biomass because there are no studies yet [61]. Also, olivine is not as abundant as dolomite, and the fact that some countries do not even have olivine deposits makes this catalyst an expensive choice due to the transportation costs that would be attributed to it.

Plasma tar cracking is another method of tar removal being studied because of plasma's properties that have been observed during plasma gasification, so it's been assumed that similar principals could be applied for tars. With plasma gasification, there's nearly no tar present because of the extremely high temperatures being worked

with. Despite the promising properties plasma has shown during plasma gasification, studies have shown disappointing results, with less than 50% of the total tar content being removed [60]. Nevertheless, plasma gasification in itself can also be considered as a tar removal tool with a high success rate.

Most of the methods mentioned above, while very successful, are much more expensive and complicated compared to other methods. Cracking and all its subvariants, along with plasma gasification are what's known as primary methods and overall show a high tar removal rate. There are other cheaper and simpler methods known as secondary methods which are popular because they're easier to commercialize. These secondary methods include scrubbing, the use of a filter, and centrifuge. Because these methods are not as efficient as primary methods by themselves, they're often used in combination with each other.

Scrubbing is usually done with either water or oil. Water scrubbing is cheap and is easy to perform, however because most tar is not soluble in water, the rate of tar removal showcased by water scrubbing is quite low, and the separation of polar tar components from the water is expensive and difficult. Oil scrubbing is another option with a higher tar removal performance compared to water, thanks to its non-polar properties like tar. Studies performed using different types of oils and liquids has shown vegetable oil to be the most efficient at removing tar, with waste-cooking oil following it in a close second place for performance, and engine oil in third place [62]. These studies lay out an interesting base for future studies, where different types of used oils from other industries and waste-cooking oils can be explored for valorization.

Filters are another low-cost method available, with different variants to it including baffle filters, ceramic filters, fabric filters, and electrostatic filters [63]. In addition to these filter types, straw or other types of biomass waste can be used to filter out particles, with some examples including wood shavings [64]. When choosing a filter, both efficiency and resource consumption must be considered: efficiency relies on the fraction of incoming particles which would be retained by the filter and depends on the particle size being worked with, whereas resource consumption depends on initial, operation, and maintenance costs. Filters can be separated into surface or depth-collection type.

Centrifugal separation is the third low-cost method mentioned used for the removal of tars with a pretty self-explanatory name: centrifugal force is used to remove as much tar as possible from syngas on its way out of the gasifier, usually done with the help of a cyclone [65]. Besides tar, centrifugal separation is effective for removing ash, dust, water, and soot. Overall centrifugal separation for tar removal has shown to have good results with coal gasification, but no studies regarding biomass gasification are available as of yet [62].

2.3.6. Syngas applications

2.3.6.1 Electric and thermal energy production

Electric and thermal energy production are some of the most common ways in which syngas can be used, particularly through combined heat power (CHP). What sets CHP apart from conventional methods of electricity production is its efficiency. The lower efficiency observed in traditional power plants is due to the large quantities of heat gone to waste through the atmosphere, and the fact that conventional power plants distribute electricity through the national grid, with energy losses between 7-9% due to transmission and distribution. CHP, on the other hand, aims at repurposing heat that would otherwise be wasted for applications like hot water and boilers, and the power is generated locally which means less opportunities for losses to take place. Overall, conventional power plants have shown an efficiency 30-50% less than that of modern CHP plants, which have shown to have efficiency levels in the 80th percentile [66].

2.3.6.2. Dual Fuel (DF) Engines

DF diesel engines are essentially conventional engines that have been slightly modified to be able to work with both gaseous and liquid fuels. While oftentimes diesel engines can be made by modifying an already existing conventional diesel engine, there are other types of diesel engines made from scratch like high pressure direct injection (HPDI) engines. However, these do not have the capacity of working solely with diesel whenever there's no gaseous fuel available [67], [68]. DF engines essentially work by using mostly a gaseous fuel and a negligible amount of diesel fuel or another liquid fuel of choice to help ignite the gaseous fuel. Oftentimes, these gaseous fuels have

exceedingly high ignition temperatures that cannot be attained without the help of this pilot fuel. It must also be said, that DF engines are frequently mixed up between other types of engines that have similar functions, like bi-fuel engines and gas-diesel engines [69].

While it's most common to find the use of natural gas (NG) in DF engines in literature, there's an array of several other gases that have been studied, such as liquefied petroleum gas (LPG), biomethane, ethanol, methanol, and hydrogen. Syngas is not exception to this: in fact, scientific literature provides considerable materials on the success of using syngas in DF diesel engines, from both an economical and environmental perspective [70]. Most articles, however, focus more on studying the parameters of dual-fuel engines using syngas, rather than focusing on real-life application examples using syngas. Generally, these have to do with engine performance, exploring with different syngas mixtures, studying the effects syngas and its composition have on engines, flow rate, pollutant removal, among others [71]–[75]. While real-world examples using syngas are yet to be found in literature, there are sources citing the use of dual fuel engines in large-scale vehicles such as buses and garbage trucks, and smaller-scale applications in commercial vehicles [76].

2.3.6.3. Fischer-Tropsch synthesis (FTS)

Simply put, FTS converts gaseous fuels into liquid fuels with the help of metal-based catalysts [50]. With this process, syngas can be used to produce diesel and gasoline. A catalytic chemical reaction takes place where CO and H_2 are converted into hydrocarbons with different weights, following Eq. 1:

$$(2n+1)H_2 + n(CO) \rightarrow C_nH_{(2n+2)} + nH_2O \quad \text{(Eq.1)}$$

Depending on the catalyst used, temperature, and type of process employed, different hydrocarbons can be obtained, ranging from methane to higher molecular paraffins and olefins. The catalysts that can be employed for FTS are based on transition metals of iron, cobalt, nickel, and ruthenium. Although it's an option, nickel catalysts are not very desirable because it promotes methane formation. On the other hand, iron is a relatively low-cost catalyst more suitable for a lower H_2/CO ratio syngas such as those

from coal gasification. Ruthenium is extremely expensive, hence rarely used, and cobalt is more active and preferred over ruthenium, however it's still on the more expensive side compared to iron and has a lower water-gas-shift activity [77].
Given the requirements and conditions necessary for FTS to be successful, this is considered a complicated process by nature.

2.3.6.4. Methanol synthesis

Methanol is another product that can be created from syngas. While it can be left at that and be used as a fuel supplement, methanol can also be further converted into ethanol and several other chemical products such as acetic acid, formaldehyde, methyl methacrylate, and methyl tertiary-butyl ether (MTBE). While methanol synthesis is mostly done with natural gas-derived syngas, other feedstock can be used: for example, coal/solid feedstock is used to make approximately 9% of the worldwide output of methanol [78], [79].
The most important reactions pertaining to methanol synthesis are shown below in Eq. 2, 3 and 4.

$$2H_2 + CO \rightarrow CH_3OH \text{ (Eq. 2)}$$
$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \text{ (Eq. 3)}$$
$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (Eq. 4)}$$

Like FTS, methanol synthesis requires the use of catalysts, these mostly being metal-based in nature. Copper, zine oxide, alumina, magnesia, or a mixture such as copper-alumina and nickel-alumina are some examples. However, in recent times there has been advances in creating a new catalyst made of carbon, nitrogen, and platinum.
In the case that methanol undergoes the path of conversion to gasoline, it must then undergo MTG (methanol to gasoline). The end result is very close to the final fuel specifications of gasoline, requiring minimal end processing [80].

2.3.6.5 Mixed alcohols/higher alcohol synthesis (MAS)

A process described to be like FTS and methanol synthesis, MAS is described as a series of exothermic reactions where short alcohols are formed from syngas with the help of

catalysts. MAS can produce C_1-C_5 alkanols, however when the main objective is the production of mixed alcohols, C_3 and above are preferred, as C_1 is methanol and C_2 is ethanol – When ethanol is obtained through MAS it's usually separated from the other alcohols with the use of distillation columns, and methanol can also be produced with methanol synthesis. As some of the previously mentioned syntheses were developed (FT and methanol synthesis), mixed alcohols were recognized as byproducts of these processes when the catalysts used, and the conditions were not optimized [81].
The major reaction in MAS is the formation of alcohol (Eq. 5), with hydrocarbon and water-gas-shift reactions as secondary ones [82].

$$n\mathrm{CO} + 2n\mathrm{H}_{2n+1} = \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\mathrm{H}_2\mathrm{O} \text{ (Eq. 5)}$$

No tests have been done beyond pilot plants or bench-scale reactors since MAS is not applied on an industrial scale as of this present moment. Based on literature, a wide variety of heterogeneous catalysts have been developed and tested at a laboratory scale for the conversion of syngas into mixed alcohols. These catalysts can be broadly divided into noble-metal-based and non-noble-metal-based. The noble-metal-based catalysts exhibit high ethanol selectivity for syngas conversion compared to their non-noble counterparts, however they are not a very attractive choice because within this category there's a limit of choices, with the addition of the high costs of noble metals. On the other hand, non-noble-based catalysts are more efficient at converting syngas into ethanol or other C_{2+} oxygenates and are usually modified methanol and FTS catalysts.

2.3.6.6. Dimethyl ether synthesis

Dimethyl ether (DME) is the simplest ether with several positive properties. For example, it's non-corrosive, non-carcinogenic, has a high oxygen content, and most important, it's environmentally friendly. Like methanol, DME has a lot of application outlets like fuel, production of chemicals such as ethylene and propylene, and also as a replacement for chlorofluorocarbons (CFCs) in aerosols [83]. DME production is divided between indirect and direct synthesis routes. Regardless of the route, DME production is based on the catalytic dehydration of methanol, thus the chemical

reactions that take place are nearly identical to those for methanol synthesis, with the added methanol dehydration reaction (Eq. 6).

$$2CH_3OH \rightarrow CH_3OH + H_2O \text{ (Eq. 6)}$$

What sets them apart is the place where the relevant chemical reactions take place. For example, in the indirect synthesis route, methanol synthesis first takes place in an assigned reactor, and then in a separate reactor DME synthesis takes place with the readily formed methanol. On the other hand, the direct synthesis route involves the same reactions pertaining to methanol and DME synthesis, however instead of being confined in separate reactors, both happen simultaneously over a bi-functional catalyst [83].

2.3.6.7. Fermentation

Different to all the prior mentioned syntheses, fermentation is not a catalytic process, instead it being classified as a biochemical process. Syngas fermentation uses the help of prokaryotic single cell organisms known as acetogens, which can be divided between rods, cocci, and spirochetes, and classified between Gram-positive and Gram-negative motile bacteria that forms spores [84]. In essence, acetogens convert CO, H_2, and CO_2 into acetic acid, which is essential to produce ethanol. Despite the fact that acetones have been thoroughly studied for nearly a century, it's been only since recent times that syngas fermentation is being deployed at a near commercial scale, but studies are yet to determine a standardized methodology to generate high ethanol production levels with a stable culture [84].

2.4. Acorn gasification

As mentioned in Section 2.1, acorns are a great example of an agricultural biomass that mostly goes to waste. Nevertheless, it's very difficult to come across literature pertaining to the gasification of acorns. Most of the time, when acorns are mentioned in literature, the objective is to determine its nutritional potential and composition [24], [85], [86], as there are different movements to bring acorns back into mainstream

diet. The few studies found pertaining to *any* thermo-chemical treatment were either related to the torrefaction or the combustion of acorns [87], [88]. The only study that discusses the gasification of acorns is a 2011 study by Madenoğlu et al. [89]. This study mostly worked with a variety of biomasses, including cauliflower residue, tomato residue, hazelnut shells, and acorns using supercritical water gasification and K_2CO_3 and Trona catalyzers. Within this study, all acorn-pertaining biomass was separated into two different categories: acorns and extracted acorns. While acorns consisted of regular acorns with a tannin content of 75% wt.%, extracted acorns is what was obtained from the former "acorns" through extraction at 80ºC. This study focused mostly on the influence of catalysts within the gasification process, particularly in the gas composition and the product yield, with the results showing particularly interesting results regarding the acorn and acorn extract samples: both acorn and extracted acorn have shown different gasification tendencies compared to the rest of the feedstocks used, and between these 2 acorn-derived feedstocks, extracted acorns had a higher yield due to its higher lignin content and lower tannin content. Additionally, while all biomasses analyzed showed improved gasification yields when catalysts were added both in the case of K_2CO_3 and Trona, the highest hydrogen yield was obtained with acorns when using Trona.

Even though fixed bed gasification is a mature and developed technology, to the best of the student's knowledge, no research has been done using acorns or any form of its by-products. Nevertheless, there's a wide array of examples of agricultural and forest biomass gasified using this technology, that demonstrate viable results with good quality syngas. Kumar et al. performed fixed bed gasification of corncobs and eucalyptus residues, with eucalyptus residues having a higher hydrogen content and a greater heating value compared to corncobs (5,3 MJ/Nm^3 versus 3,7 MJ/Nm^3) [90]. Skoulou et al. gasified both olive tree cuttings and olive kernels, with olive tree cuttings having a greater heating value compared to olive kernels (9,41 MJ/Nm^3 and 8,60 MJ/Nm^3 respectively). Both syngas samples display a calorific content above average, with the addition that olive kernels display a higher char content, making it an attractive source for carbonaceous material production [91]. Dafiqurrohman et al. explored different gasification studies performed using rice husks, with results for syngas heating value ranging from 3,13 MJ/Nm^3 up to 5,4 MJ/Nm^3, with the 3,13

MJ/Nm^3 rice husk syngas having a cold gas efficiency (CGE) of 72,3% and the 5,4 MJ/Nm^3 being capable of a stable power generation of 10 kW [92]. Dogru et al. gasified hazelnuts and obtained a gross calorific value of 5 MJ/Nm^3, suggesting that this technology would be ideal for rural economies with a lot of agricultural residues, particularly nuts [93]. Tavasoli et al. compared the results between the gasification of corn and wheat dry distiller grains and concluded that corn dry distiller grain syngas showcased a higher hydrogen and carbon monoxide content in comparison to wheat dry distiller grain syngas (11% & 56,6%, and 10,5% & 51,5%, respectively), alongside with having a higher lower heating value (LHV) and carbon conversion efficiency [94]. González et al. explored with the gasification of different almond residues (almond shell, almond shell peel, and almond tree pruning). Carbon conversions ranged between 81% and 90%, with LHV of 6,5 MJ/Nm^3, 5,8 MJ/Nm^3, and 6,4 MJ/Nm^3 for almond shell, almond shell peel, and almond tree pruning. The designing of a gasification plant for energy generation is deemed possible with the results obtained in this study [95].

Considering the wide range of biomass successfully tested to this day, using fixed bed gasification, the application of this technology seems to be a promising method to repurpose acorn waste.

2.5. Synopsis

The purpose of this research is to determine the viability of acorn waste gasification using a fixed bed reactor. The success of this technology implementation would mean a new use for all unused acorns, particularly their wastes, as thousands of tons go to waste every year.

The experimental part of this work consists of three main sections: Prior to gasification, a sample of acorn waste is analyzed to determine its chemical properties and predict its behavior during the gasification process. Gasification is then performed using a larger batch of acorn waste, with syngas samples taken to determine its composition, and most importantly, to determine whether acorn waste is a viable feedstock similar to the studies cited in the previous section [90]–[95].

After gasification, an economic analysis was performed to determine whether the installation of a gasification unit would be a viable option. This unit could produce

electricity and could be beneficial for rural communities, which are often where acorns are most present in Portugal.

3. Materials and methods

The present study on acorn waste can be divided into three parts: chemical analyses, gasification, and economic analysis. Chemical analyses and gasification are the practical components of this study, whereas the economic analysis is solely based on calculations.

The first part of this study consists of the chemical characterization of a given acorn waste sample to perform proximate and ultimate analyses, and to determine its higher heating value (HHV). These proximate and ultimate analyses determine different parameters such as moisture, ash content, fixed carbon, volatiles (in the case of proximate analyses), and the elemental make-up of the sample: in other words, how much carbon/oxygen/nitrogen/hydrogen/sulfur make up the sample (in the case of ultimate analyses). The purpose of these analyses is to better understand the chemical behavior of the biomass, alongside predicting the behavior of the feedstock during gasification and whether the feedstock needs any pre-treatments prior to gasification.

The second part of this study is gasification. A larger batch of acorn waste is gasified using a fixed bed gasifier (the fixed bed gasifier used for the experiment is available in the Polytechnic Institute of Portalegre). During gasification, samples of syngas were taken for analysis to determine its chemical composition, LHV, CGE, among other parameters. These, alongside other parameters, were compared to literature to determine whether acorn waste was behaving like other biomass sources gasified using fixed bed reactors. At the same time, other parameters such as the feedstock mass flow and syngas mass flow were observed, as these are necessary for the third part of this study.

The third and final part of this study is the economic study of a hypothetical gasification plant, aimed at generating electricity. As mentioned in the previous paragraph, parameters pertaining to the mass flow of syngas and feedstock, in addition to parameters pertaining to the volume flow of air, char, and tar, are relevant to this final phase, as they are used to model the mass and energy balances. Prior to designing the unit, a mass and energy balance is done for the gasification tests performed in the second part of the study. Having this completed, calculations are done to determine the amount of energy consumed and produced by a unit with total power of 1 MW. In

addition to this, the total biomass required to keep the unit running over the course of a year is calculated, given that the unit has a total power of 1 MW and operates 8000 hours per year. Further calculations are done to determine the total electric energy consumed by the equipment in the gasification unit, along with the profit from the sale of electricity to the national grid, installation & maintenance of equipment, and the total spent on workers needed to keep running the unit. These results aid in calculating the net present value (NPV), internal rate of return (IRR), and payback period of the project, determining whether the project would be viable or not.

3.1. Feedstock

For the following procedures, a sample of acorn wastes was taken from a larger sample stored at BioBIP. These acorn wastes are a mixture of acorns originating from different species of oak from the Northern and Alentejo regions of Portugal (Figure 3 and 4).

Figure 3. A batch of rotting acorn cups and nuts.

Figure 4. Another example from the same batch. This nut is in an advanced stage of decomposition, as it can be seen by its soft structure and strong presence of mold.

At first sight, it can be observed that the acorns are moldy and soft, immediately indicating a high moisture content. This acorn waste was harvested during the late winter period, which is often characterized by rain in Portugal. In addition, this acorn waste was stored in big plastic bags, without any exposure to sunlight. This contributed with the raw material coming with an exceedingly high moisture content of nearly 60%. The moisture content of this raw material was measured using a digital moisture meter (Figure 5).

Figure 5. Digital Moisture Meter (Dr. Meter, MD812 model).

The raw material's moisture content was enough to need a pretreatment before any procedures were done. According to the PowerPallet manual available on the All Power Labs website, the PowerPallet gasifier works best with biomass that doesn't have a moisture content greater than 30%. Otherwise, excess water vapor formed during the

gasification process can result in a less clean gas since the gasifier wouldn't be able to maintain the proper temperatures for producing clean gas [96]. To reduce the acorn waste's moisture content, they were first sifted through hardware cloth mesh screens to separate any particles and debris smaller than a centimeter and were then left out to dry in the sun. As a result of this, the acorn waste's moisture content went down to 10%. Once the acorn waste was dried, a sample was taken for analysis. This sample was too tough to be broken down manually, which is why the help of a food processor was needed to pulverize the nuts to make the sample's analyses easier. Figure 6 shows the dried acorn sample and the pulverized acorn sample.

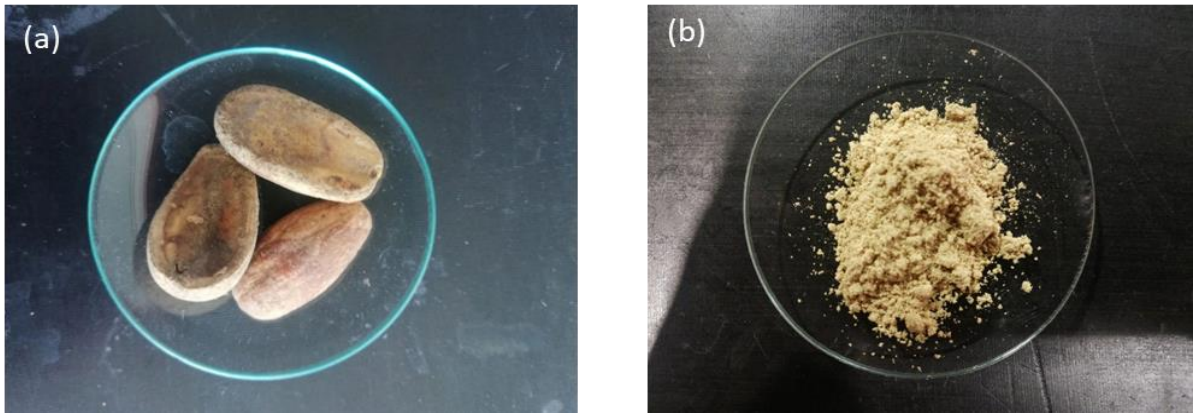

Figure 6. (a) Dried acorn sample; (b) Pulverized acorn sample.

3.2. Feedstock characterization

Prior to any gasification trials, several characterization analyses were conducted, namely:

- Proximate analyses, to determine acorn waste's moisture, volatile matter, fixed carbon, and ash contents;
- Ultimate analyses, or CHNS-O, to determine the elemental composition of the feedstock;
- The determination of the feedstock higher heating value (HHV).

3.2.1. Proximate analysis

The proximate analysis of the acorn waste sample was done using a process called thermogravimetric analysis (TGA), using a PerkinElmer Simultaneous Thermal Analyzer, available at the Biochemical Lab at the Polytechnic Institute of Portalegre. This device was used alongside the Pyris Manager software, where all the tests' parameters were established:

- Initial temperature of 30ºC;
- Maximum temperature of 950ºC;
- The heating rate was established as 30ºC/min;
- Normal atmospheric conditions without air injection;
- Every test lasted approximately 42 min;
- Sample mass = 5 mg per test;

As stated before, yet highlighting its importance, the nature of the acorns used for these analyses is atypical to that of acorns commonly found in scientific literature. The analyzed acorns were in advanced states of decomposition and thus were impossible to label as "healthy", as done by the articles referenced.

Data on the proximate analysis results of acorns are hard to come by in scientific literature, and that which is available is pertaining to other species of Quercus that are not found in the Iberian Peninsula. Therefore, data pertaining to other Quercus species will be used for comparison purposes (see section 4. Results and discussion).

3.2.2. Ultimate analysis

The purpose of an ultimate analysis, also known as elemental analysis, is to determine the main chemical components of a given biomass sample. Usually these elements are carbon, hydrogen, nitrogen, sulfur, and oxygen.
Besides allowing us to determine the elemental composition of a given biomass, CHNS-O analyses allow us to perform a quality control of the biomass, and additionally we can better predict the number of emissions, and more importantly what kind of emissions can be expected during the gasification process.

The ultimate analysis was done using a Thermo Scientific Flash 2000 Organic Elemental Analyzer available in the Biochemical Lab. The acorn waste sample's mass was of 2,985 g and the test had a total duration of 30 minutes.

3.2.3. High heating value (HHV)

Also known as calorific value, heating value is the parameter that determines the energy value found in a fuel. This parameter is very important for the design and control of biomass thermal conversion. Heating value can be divided between lower and higher heating values. The difference between them is that lower heating values doesn't take into the account the heat of vaporization of the biomass' moisture, whereas with higher heating values it is considered, alongside other products and results of the combustion process. It's most common for the results of higher heating values to be shown in literature, however, lower heating values are preferred when designing the combustion chamber [97], [98]. Nevertheless, in this case the objective was to determine the acorn waste's HHV.

The HHV analyses were done using an IKA C200 Calorimeter available at the Biochemical lab in the Polytechnic Institute of Portalegre. The acorn waste's HHV was determined using a 0,528-gram sample, with the test lasting 16 minutes.

3.3. Gasification tests

The gasification tests were done using a PowerPallet PP20 by ALL Power Labs gasifier available in the Polytechnic Campus. The PowerPallet PP20 is currently discontinued, with its closest substitute being the PowerPallet PP30. Despite its discontinued status, all technical information pertaining to the PowerPallet PP20 can be found on the company's website [99]. Table 1 details the gasifier's technical information, obtained from the PowerPallet PP20's datasheet [100].

Table 1. Technical information regarding the gasifier Power Pallet PP20.

Reactor	**Categories**	**Parameters**
PowerPallet PP20	Performance	Continous Power Rating: 15 kW @ 50Hz/18 kW @ 60 Hz
		Sound level at 30 feet: 85 dB(A)
		Biomass Consumption: 1,2 kg/kWh
		Run Time per Hopper fill: 10h @ 5 kW; 5h @ 10 kW; 3h @ 15 kW
		Maximum Continouss Operation: >12 hours

		Start Up Time: 10-20 minutes
	Operating Conditions	Ambient Temperature: 5-40ºC
		Humidity: 5-95% relative humidity (RH)
		Site Requirement: Well-ventilated, protected from rain and direct sun
		Installed Footprint: 1,36 x 1,36 m^2
	Feedstock Biomass	Size: 12-40 mm
		Moisture content: 5-30% dry basis
	Gasifier	Type: APL v5 Patented Thermally Integrated Downdraft
		Materials: 304 SS/310 SS/321 SS/mild steel
		Hearth: Coated Ceramic
		Ash Removal: Automated 12 hour batch vessel
		Fuel Feed: Automated
		Hopper Capacity: 0,33 m^3
		Hopper Filling: Batch
		Minimum Maintenance Cycle: ~12 hours
		Control System: On-Board Automation

The conversion process in this gasifier can be separated into three main stages, with several steps within each stage: Flow of Solids, Flow of Gases, and Flow of Exhaust. The flow of solids involves all the steps that make up the process of gasification, as this first stage's objective is the conversion of feedstock into syngas. Within the PowerPallet PP20, the gasification takes place between the hopper, drying bucket, PyroReactor, and the gasifier. Within the PyroReactor, both pyrolysis and cracking take place, whereas gasification and the further reduction take place within the gasifier. Next to the gasifier there's a smaller unit for the collection of ash.

The flow of gases aims at cooling down and preparing the gas for its application in the engine & generator set. After leaving the gasifier, whatever particles remain in the syngas must be separated to prevent any damage, or at least reduces the amount of damage done as much as possible. This is done with the help of a cyclone, where dust and ash are separated from the syngas with the help of centrifugal force. After leaving the cyclonic dust separator, the syngas is still too hot to be safely filtered. Having a lot of thermal energy, its routed into the spaces between the double walls of the drying bucket. This "recycling" is what allows the gasifier to process higher moisture content – The Power Pallet can work with feedstock with moisture contents as high as 30%, but it's always best to dry your biomass as well as possible – and at the same time it

allows the syngas to cool down enough before moving on to the final step, which is gas filtration. The syngas is cleansed once again from any residual tars, this time with the help of sifted biomass to prevent further tar build-ups in the engine. The flow of exhaust is the final stage, much shorter than the other two stages prior to it. The cleansed syngas is then mixed with air, fed into the engine & generator set to produce electrical energy, and the exhaust gases leave the engine and generator for waste heat recovery, where its heat is passed through the walls of the PyroReactor to help pyrolyze the feedstock. Figure 7 shows a diagram detailing the system used to perform the above-described work.

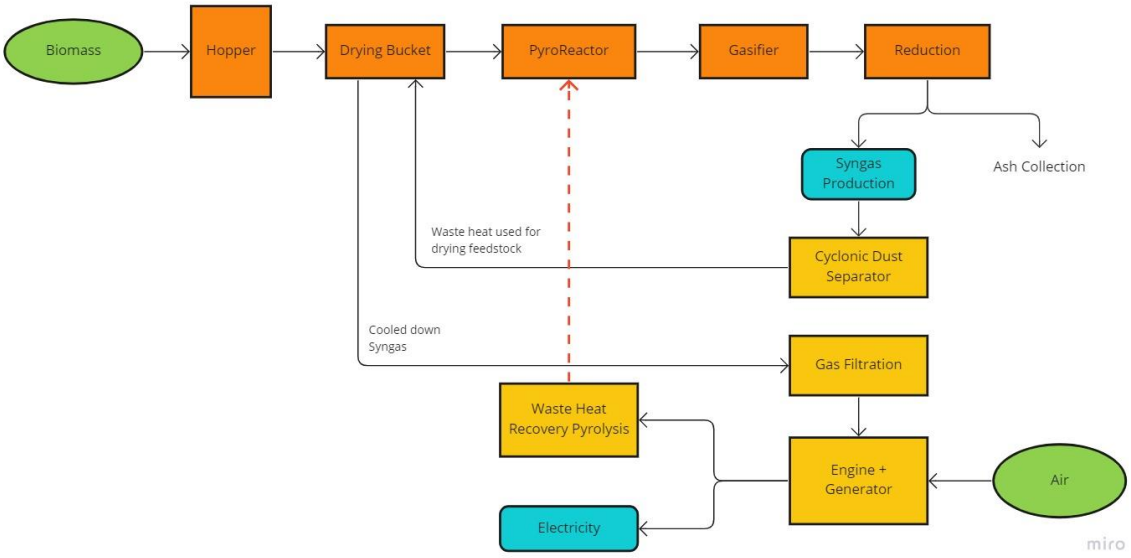

Figure 7. Overall schematics of the system used in this work.

Prior to gasification, the acorn waste was manually sorted into buckets (Figure 8) and then sieved to separate the feedstock from any debris that might damage the gasifier (Figure 9). Once this cleansing and separation was done, the acorn waste was laid out to dry on a piece of cardboard until the next day when the gasification would take place (Figure 10).

The gasification tests were done using 21 kg of acorn waste for 4 hours and 13 minutes. During the gasification tests, three samples of syngas were taken using Tedlar bags for analysis purposes. These samples were analyzed using a non-dispersive infra-red (NDIR) gas analyzer (MCA 100 Syn 2 Portable) to determine the CO, O_2, H_2, CH_4, CO_2 e N_2 percentage in the syngas.

Figure 8. Manual sorting of acorn waste.

Figure 9. Sieving of the acorn waste to filter out any particles and materials that may damage the gasifier, such as rocks.

Figure 10. The filtered-out acorn waste was then laid out on a piece of carboard and left to dry under the sun until the next day.

With the composition of syngas determined, one can use this information to determine syngas's LHV and its density. Density of syngas was calculated with the help of Olanrewaju et al. [101], whereas LHV can be calculated using the following Eq.7 [66]:

$$LHV = 12{,}74\ (H_2) + 12{,}63(CO) + 39{,}84(CH_4) \text{ (Eq.7)}$$

Finally, with the information obtained from the gasification tests, a mass and energy balance in correspondence to the values observed in the unit can be made. All data was converted to kg/h, in the case of it being presented in m^3/h or ml/h, by multiplying the data with its corresponding density (for example, syngas's volume flow multiplied by its density). In the case of the energy balance, it was a matter of multiplying the corresponding mass flows (acorn waste and syngas) by their corresponding heating values, as seen in Eq. 8 and Eq. 9.

$$P_e(W) = \dot{m}(\frac{kg}{h}) \times HHV(\frac{MJ}{kg}) \text{ (Eq. 8)}$$

$$P_e(W) = \dot{m}(\frac{kg}{h}) \times LHV(\frac{MJ}{kg}) \text{ (Eq. 9)}$$

Having the power for acorn waste and syngas, the total energy inserted and coming out of the unit can be calculated, when known the total time the unit will work daily (Eq. 10).

$$E(Wt) = P_e(W) \times t(h) \text{ (Eq. 10)}$$

To ensure both the mass and energy balances were done correctly, both their inputs had to be equal to their corresponding outputs.

4. Results and discussion

4.1. Feedstock characterization

4.1.1. Proximate analysis

While it's difficult to find data pertaining to the moisture content of acorns per se, there's more data available pertaining to the moisture content of acorn starch. The only exception to this is "Oak acorn, polyphenols and antioxidant activity in functional food" by Rakić et al, which actively analyzes moisture content in acorn samples. The analyzed sample's moisture content was observed to contain nearly double that of the mean of the results found in Rakić et al, which is 4.523% of the acorns' mass, as per the samples analyzed [110]. Table 2 shows the proximate analysis results for the acorn waste sample used in this work.

Table 2. Proximate analysis results for the acorn waste sample used in this work.

Parameters	**Units**	**Acorn waste sample**
Moisture	wt.%, as received	10.58
Volatile matter		61.59
Fixed carbon		22.20
Ash		5.63

Besides this scientific paper, most other scientific papers focus on the moisture content of acorn starch. Despite the abundance of these papers, this data is not the best representation of an acorn's chemical makeup because it only focuses on the starches found in acorns: despite starches being the largest component of acorns at 55%, they are not a proper representation of the entire acorn make-up. Nevertheless, it can still give an idea on the moisture content.

The results shown in Taib et al.'s work (Table 3) display a large variation and a broad range in the starch's moisture content, ranging from only 2.20% to 15.90%. These moisture contents were obtained from analyzing four different *Q. ilex subsp. ballota* starch samples. Despite *Q. suber* being mentioned and displayed, there's no data available pertaining to the moisture content found in its starches.

Table 3. Moisture content analysis for four samples of *Q. ilex* subsp. *ballota* acorn starch [24].

Origin of acorn starch	Moisture Content (wt.%)
Q. ilex *subsp. ballota*	2.20
	10.20
	12.44
	15.90

The energy present in biomass feedstock is stored in two different forms: volatile matter and fixed carbon matter. Volatiles are the components of fuel which are readily burned in the presence of oxygen. These mostly consist of combustible gases such as hydrocarbons, hydrogen, oxygen, and carbon monoxide. To determine their numerical value, the biomass feedstock is burned in an inert atmosphere at a temperature of 900 ^{o}C for 7 minutes [111], [112].

While volatiles are partially responsible for the energetic content of feedstock, one must be mindful and pay attention to the percentage of volatiles present in biomass. Biomass feedstock contains much higher volatile matter in comparison to coal, with up to 87% volatile matter compared to up to 44% that can be found in coal. This is also one of the factors that complicates biomass usage in gasification: higher volatile matter content is linked with higher particulate matter emissions, poorer gasification performances, lower thermal outputs, high ash clinks & tar formation, and higher carbon dioxide emissions. Using feedstock with high amounts of volatiles is deemed unfavorable since this would mean having to use extra resources to clean up any tars that would be found within the syngas, in addition to triggering complications in the engine [113].

The volatile matter portion of the sampled acorn waste is quite high, meaning that as an untreated biomass feedstock, they would bring about several issues during the gasification process. The percentage of volatiles found in the acorn waste would make it ideal for a process like combustion, where materials with higher volatile matter burn quickly, at least compared to materials with a high fixed carbon content [114]. Nevertheless, the objective is to use this biomass feedstock in gasification, and for this context in specific its volatility is not favorable for gasification.

The overall content of ash found in the sample has not shown a result out of the ordinary, although it is on the higher end of the spectrum. Data used to compare these

results tended to be closer to 2% of the biomass, however it's not unexpected to find higher or lower ash contents.

Because of its abrasive properties and its lack of contribution to a biomass' energetic content, ash is deemed an undesirable property in biomass While it's inevitable to find ash in any other biomass, their percentage vary drastically depending on the biomass being worked with. In the fortunate case of working with a biomass with a low ash content, this would mean having to spend less resources on cleaning out the ash content from syngas, and additionally the equipment would last longer [115].

Ash is the mineral residue that's left after thermal processes. It can be separated in two parts: inorganic components used for biological processes and structural integrity, and mineral matter that comes from the soil collected with the feedstock [116]. Ash can be divided into three main categories [117]:

6. Rich in calcium and potassium but lean in silica. More often found in woody biomass.
7. Rich in silica but lean in calcium and potassium. Some examples include agriculture residues like rice husk, straw, and bagasse.
8. Rich in phosphorous, calcium, and potassium.

Compared to coal, biomass has smaller ash content, which also varies based on the feedstock that's being used – herbaceous feedstock tends to have a much higher ash content compared to woody biomass. Nevertheless, biomass ash has differing properties from coal ash: biomass ash tends to be finer, constituting mostly of silica, alkaline earth metals and alkali metals, and is also much more corrosive and aggressive, making it easier to damage equipment and shortening their life span. Alkali metal vapors, together with silica and alumina in ash, can mix to form a eutectic mixture which has the additional property of having a lower melting point than that of any of its constituting elements. This mixture could then deposit on surfaces and become sticky, promoting deposit formations as particulate matter adheres and accumulates on it [116].

There are no specific guidelines as to how to categorize different types of ashes, so different examples and methods have been found in literature. Nevertheless, the most common way to divide different types of ash is based on their acidity: S, C, K, and CK. Like most of the data pertaining to acorns in scientific literature, proximate analyses

are not widely available. This is not to mean that data pertaining to acorn's mineral content and composition does not exist, for the contrary has been shown [86], [110], [118] (Table 4). What all three studies have shown is that the most common minerals found in acorns are calcium, phosphorus, and potassium. Sodium and chlorine are also relatively common minerals found in acorns yet are not as significant as the others. Given the data available, the selected acorn waste can be classified as producing K type ashes, more specifically K-LA because acorns – and much less oaks – are not considered herbaceous biomass [119], [120].

Table 4. Ash content of different Quercus species.

Species	**Ash Content (wt.%)**		**Reference**
Not specified	5.0		[121]
	4.8		
	1.3		
	3.7		
	6.9		
	2.0		
	1.5		
	2.0		
	2.4		
	3.1		
Q. robus	2.1		[110]
	3.3		
	8.4		
Q. aegilops	1.5		[118]
Q. callipinus	1.8		
Q. infectoria	1.7		
Q. ithaburensis	Coat	2.9	[86]
	Cup	2.6	
	cotyledon	3.2	
Q. callipinus	Coat	1.8	
	Cup	2.1	
	cotyledon	1.8	

While volatile matter is the gaseous portion of the fuel that's released when the biomass feedstock is heated up, fixed carbon is the solid combustible residue that's left after the biomass feedstock is heated. As the name may suggest, fixed carbon essentially consist of carbon, with light traces of other elements such as hydrogen,

oxygen, nitrogen, and sulfur that were not driven off by the gases. Fixed carbon is not the same as total carbon, given that fixed carbon is what is left after heating the fuel to 900ºC in the absence of air, and total carbon is the total carbon present in the biomass feedstock in normal condition – in other words, when the biomass is not being burned. Total carbon includes volatile matter, since total carbons also encompasses hydrocarbons [122]. Fixed carbon is not a fixed parameter because of its close ties to volatile matter. The quantity of volatiles present in the biomass feedstock directly impacts the quantity of fixed carbons, and even then the total amount of volatiles can vary with the rate of heating [117].

Fixed carbon is an important parameter to know, because not only does it help us determine the parameters of the equipment that'll be used, but also the amount of gas that'll be produced, its ignition temperature, and its efficiency [117], [123]. Fixed carbons can help us determine the size of the gasifier that'll be used, since in most gasifiers the rate at which fixed carbons are converted into gases determines the rate of gasification and its yield; the conversion reaction also happens to be the slowest. Additionally, knowing the form and hardness of the fixed carbons can give us an insight on the caking properties of a fuel, which also aid in choosing the proper combustion equipment.

The fixed carbon content of the acorn waste sample shows a meager 22.2% compared to the 61.58% of volatile matter. Despite volatiles contributing to the energetic content of biomass feedstock in a similar fashion to fixed carbons and there being a correlation between higher volatile matter content and higher gaseous production, large amounts of fixed carbons are a highly preferred and desired property [124]. The acorn waste's lower fixed carbon content means that it has a lower ignition temperature compared to other biomasses, and that when combusting this biomass in specific there's a lower production of charcoal and a higher production of tars.

4.1.2. Ultimate analysis

Research pertaining to the chemical properties and composition of acorns mostly focus on its mineral and nutritional value (carbohydrates, fiber, protein, and fats) [86]. Table 5 shows the results for the acorn waste's ultimate analysis.

Table 5. Ultimate composition of the studied acorn waste sample.

Sample	Ultimate composition (wt.%, db)				
	C	H	N	S	O
Acorn waste sample	39.88	5.65	12.33	n.d.	42,14

n.d. Not detected.

Overall, the studied acorn wastes presented a low carbon content, when compared to other biomass wastes typically used as feedstock in gasification processes [114], [125], [126]. This value can be related to the fact that this sample was composed of acorns already in an advanced state of decomposition. Nitrogen concentration is significant [114], [125], [126], meaning that NO_x emissions were to be expected if submitting this sample directly into combustion processes. One approach that could enhance this sample's fuel properties could be the torrefaction process as a pre-treatment. This process could eliminate moisture, leaving the sample dry enough not to have further microbiological decomposition. Furthermore, this process is known for increasing energy density in biomass samples, simply by volatilization of smaller molecules associated with water removal [87].

4.1.3. High Heating Value (HHV)

Also known as calorific value, heating value is the parameter that determines the energy value found in a fuel. This parameter is very important for the design and control of biomass combustion. Heating value can be divided between lower and higher heating values. Table 6 shows the HHV of the acorn waste sample used in this work.

Table 6. HHV value and sample mass used for acorn waste sample.

Sample	HHV (MJ/kg, db)
Acorn waste	14.74

Given that acorns are not a widely studied biomass, especially within the scope of thermochemical processes, there's few scientific papers available that explore acorns'

HHV. Nevertheless, there's a paper that cites the higher heating value of two different acorn species: the first variant was labeled as American Oak Acorn and was recorded as having a higher heating value of 17,37 MJ/kg, and the second variant was labeled simply as Oak Acorn and was recorded as having a higher heating value of 16,17 MJ/kg [125].

As observed, the HHV obtained for the analyzed sample has a lower HHV value when compared to the cited examples. While we could attribute this in part to the fact that we're dealing with different acorn species from different continents, a huge contributing factor to the sample's lower HHV could be attributed to humidity: several of the cups and nuts in the collected sample had signs of rotting, which is related with the lower carbon content discussed in the previous section. This means that the acorns did not have their humidity removed for storage, allowing bacteria to consume at least part of the acorns, and reducing the acorns' HHV. Even though it's been said that in the cited study it's not specified whether the authors were dealing with decaying acorns or not, it's plausible to assume that the acorns they used were either those that fell recently, or those that haven't shown any signs of rotting as of the time the samples were taken.

When looking at the overall results of the acorn waste characterization, we can observe the following:

1. The HHV of the analyzed sample is lower than that of other acorn samples found in other studies, but this most likely can be attributed to the excess moisture and consequent rotting that could be observed in several acorns. Additionally, the sample's moisture content can also be explained by its advanced stage of decomposition.
2. The high volatile matter content indicates potential issues that could arise in the case the biomass does not undergo any kind of treatment beforehand. Issues that could arise include higher particulate emissions, poorer gasification performance, higher tar formation, higher carbon dioxide emissions, and lower thermal output. The acorn's lower fixed carbon percentage means that it has a lower ignition temperature compared to other biomasses and has more of a tendency to produce tars rather than charcoal.

3. Given that acorns are considered biomass, their ashes are naturally finer and much more corrosive and aggressive compared to coal ash, having negative consequences for equipment such as shorter life spans and more resources spent on maintenance. Nevertheless, we must accept that all biomass has differing degrees of ash content, and this sample has demonstrated acceptable levels of ash content.
4. The elemental analysis has showcased that acorns have a typical biomass composition. Despite having a high oxygen content, the sample's carbon content is still high enough to allow for a worthwhile gasification.
5. Overall, the acorns showcase a potential in terms of its heating value, however there are several issues that might arise if this biomass is used without any prior treatment.
6. Before any gasification trials are performed, the acorns should be sorted out and left to dry to remove any excess moisture that it's collected during its storage.
7. For future use of this sample in gasification trials, the produced syngas should be filtered out to prevent any potential issues with the diesel engine on the long run, and the gasifier should undergo regular maintenance. This consideration is mostly due to the determined values for this sample volatile matter and fixed carbon.

4.2. Gasification tests

During the gasification trial, the best way to determine whether the gasification was effectively taking place was by looking at the flame at the exit of the gasifier. The presence of smoke indicated a poor gasification, which could be attributed to an array of problems, whereas a flame indicated a cleaner combustion. While sometimes the flame had its typical orange color, the flame would also display some blue undertones which was even better than the typical orange. An example of flame color is shown in Figure 11.

Figure 11. Flame color during gasification test.

From the gasification trial, three gas samples were taken for analysis, at the different testing temperatures. The results for gas composition in each sample is shown in Table 7.

Table 7. Syngas composition of the gasified acorn waste.

Parameters	**Units**	**Gasification temperature**		
		600 °C	**650 °C**	**700 °C**
$\dot{m}_{biomass}$	kg/h	5.2		
$HHV_{biomass}$	MJ/kg	14.7		
Air Temperature	° C	13.5	18.7	12.0
Air Volume	m^3/h	6.2	5.8	5.6
Pyrolisis Temperature	° C	505.0	562.0	576.0
Oxidation Temperature	° C	604.0	661.0	705.0
N_2	%	52.0	49.7	46.9
CO_2	%	11.2	11.2	11.4
H_2	%	15.5	17.1	17,0
CH_4	%	4.0	3.1	3.4
CO	%	17.3	18.9	20.8
LHV_{syngas}	MJ/Nm^3	5.3	5.3	5.7
$\dot{V}_{tars}$	ml/h	146.8	128.0	111.5
$\dot{V}_{chars}$	kg/h	0.2	0.1	0.1
Equivalence ratio (ER)	-	0.3	0.2	0.2
$\dot{m}_{syngas}$	kg/h	10.3	10.5	10.4
Cold Gas Efficiency (CGE)	%	62.6	64.4	68.5
η_{syngas}	m^3/kg	2.0	2.0	2.0

The effects of temperature changes during the gasification process can be observed in the composition of the three syngas samples taken at 600, 650, and 700 ºC. Literature corroborates the fact that hydrogen concentrations increase as a result of temperature increase [127]. This can be explained due to thermal cracking, which encourages the formation of hydrogen and carbon monoxide from heavier hydrocarbons, and a decrease in tar concentrations.

Carbon monoxide and methane, on the other hand, are a bit more complicated to corroborate using literature since there doesn't seem to be an agreement: there is literature that demonstrates carbon monoxide concentrations increasing while methane concentrations decrease, while there is also literature supporting the opposite [127]. Overall, it seems to depend on more factors besides temperature alone, such as feedstock chemical composition and reactor design.

The values observed for ER coincide with those observed in literature, particularly regarding biomass gasification [54]. Nitrogen concentrations in syngas are the largest compared to that of other gases, and this is inevitable when working with air as oxidizing agent and one of the biggest reasons for the low heating value content found in air-syngas. Despite all of this, having an excessively high ER value would equate to a decrease in gases with a higher heating value content such as hydrogen, methane, and heavier hydrocarbons, and an increase in nitrogen concentration [52]. As observed above, with an increase in temperature the ER, the lower are the concentrations of nitrogen.

All further calculations will be performed using the characteristics observed in the third syngas sample, taken at 700ºC. Despite not having the highest hydrogen content, the third syngas sample has the lowest nitrogen content, the highest carbon monoxide fraction, the lowest tar volume flow, the highest CGE, and most important, the highest LHV.

4.2.1. Mass balance

Mass balance can be defined as "A consideration of the input, output, and distribution of a substance between streams in a process or stage". For this specific case, the purpose of a mass balance is to understand how much of each substance is introduced

in the gasifier, and how much comes out and in what form. In an ideal mass balance, both the input and the output are equal.

The following mass balance (Figure 12) was done in kilograms per hour. In the case of syngas and air, their mass flow was found by multiplying their volume by their corresponding density. Air's density was determined as 1.222 kg/m^3 (air density at sea level), and syngas's density was calculated using data from Olanrewaju et al., 1.037 kg/m^3 [101], [128].

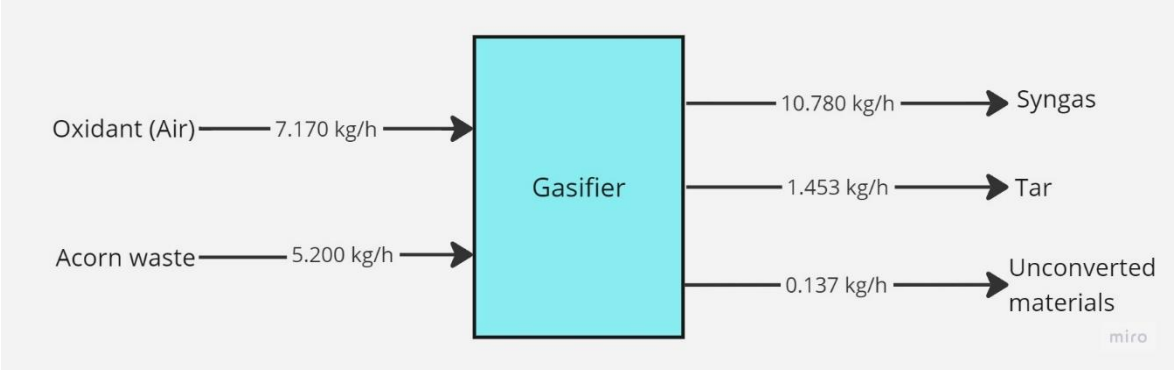

Figure 12. Pilot-scale mass balance for this work.

Table 8 illustrates the steps taken to determine the density of syngas. Following the same procedure as Olanrewaju et al., all compounds that make up syngas were converted to mol% to then calculate the mass fraction of each compound. The mass fractions were then multiplied by the respective density of each compound, to then obtain the density as per the syngas composition. Syngas' density is equal to the sum of the densities of all compounds, as per syngas' composition.

Table 8. Calculations for syngas density.

Gas component	**Composition**		**Mass (kg)**	**Mass fraction**	**Density (kg/m^3)**	**Density as per composition, mol% (kg/m^3)**
	mol%	**kg/kgmol**				
N_2	46.91%	28.010	13.139	0.020	1.165	0.547
CO_2	11.36%	44.010	5.000	0.008	1.842	0.209
H_2	17.55%	2.016	0.354	0.001	0.090	0.016
CH_4	3.36%	16.040	0.539	0.001	0.668	0.022
CO	20.82%	28.010	5.832	0.009	1.165	0.243
Total	100.00%	118.086	24.863	0.038	4.930	1.037

4.2.2.. Energy Balance

Like a mass balance, an energy balance is meant to illustrate how does energy enter and exit the unit, with the input and output being equal. Both the energy inputs and outputs were calculated using Eq. 11 [129]:

$$P = \dot{m} \times LHV \text{ (Eq. 11)}$$

Where ṁ stands for the mass of the fuel and LHV stands for the heating value be it of the biomass or of syngas. Figure 13 illustrates the energy balance observed for this experimental set-up.

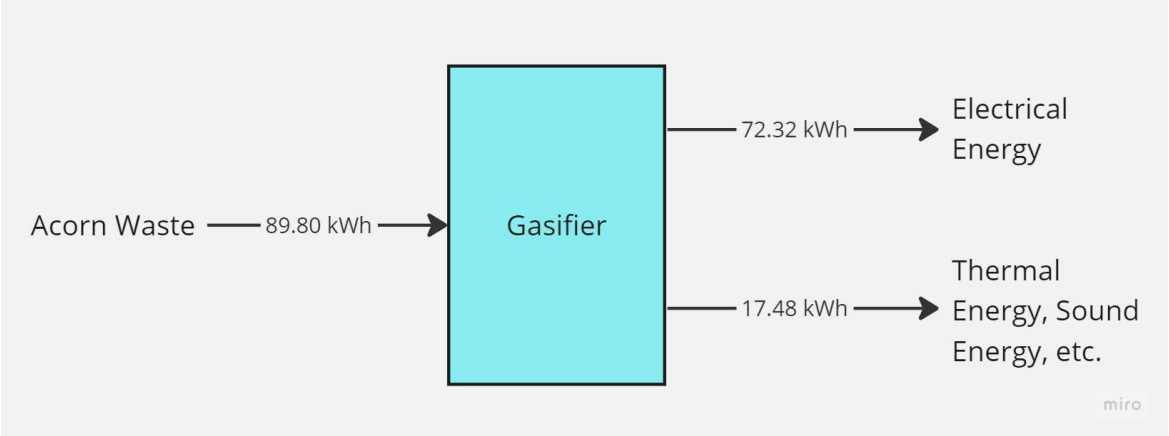

Figure 13. Pilot-scale energy balance for this work.

While it's technically not true that energy losses can be observed, what can be said is that a significant part of the energy coming out of the unit is wasted because it comes out in several forms, such as thermal and sound energy. This, however, does not mean that it all goes to waste, as part of this energy could be recovered: for example, thermal energy can be recovered to heat up and dry biomass prior to gasification.

5. Economic Analysis

In addition to its technological potential, the purpose of this study is to determine the economic viability of a large-scale unit to produce electrical energy. While it's important to know the dimensions of the unit that'll be worked with, it is equally as important to determine how much biomass there is available for correct dimension. Thus, both the sizing of the unit as well as the calculation of available biomass is done simultaneously. After this, an energy balance is done using information such as the unit's capacity (power), and the total amount of time it would be working. From this energy balance, one can then create a mass balance for the entire unit and determine the total amount of biomass that would be required. Having all this information established, further information and calculations regarding other aspects of the project such as equipment' electricity consumption, and the purchase and transportation of biomass can be calculated and researched further.

Most of the results pertaining to the economic analysis are displayed in the Excel provided by IAPMEI, with the objective of creating a financial model for business plans. This Excel program was used to calculate more complex equations and parameters that were already automated within itself, however most calculations had to be performed prior to the use of the IAPMEI Excel, with most of the data coming from the gasification tests, the chemical analyses performed on acorn waste, and under the following assumptions:

- The gasification unit's total power is 1 MW.
- The unit will work 8000 hours per year, divided between 365 days.
- The unit will work using the acorn waste found within the municipality of Portalegre.
- The unit will be autonomous and make profit by selling the remaining generated electric energy to the grid.
- Up to 50% of the unit's fundings will come from community funds.

5.1. Biomass availability

The Alto Alentejo region is much larger than the Municipality of Portalegre, with a total area of 6,084 km^2. According to Ferreira et al, the Alto Alentejo is covered by a total of 2,941.525 km^2, or 294,152.50 ha, of forest. 24,2% of this covered area consisting of cork oak, and 12,8% covered in holm oak, making it a total of of 1,922.6 km^2 or 192,260.5 ha [102]. These parameters will be adapted to the Municipality of Portalegre, which has a total area of 446.20 km^2, and would mean that in total, the municipality is covered by 80.08 km^2 or 8007.06 ha of the territory covered in oaks.

While it is impossible to determine the exact number of acorn by-products that will be used during a given time, we can estimate an approximate amount considering several parameters. On average, for every hectare of land there are 80 cork oaks, although this number can go up to 120 or even 150 cork oaks per hectare [103]. Additionally, every tree can produce between 7 to 40 kilograms of acorns, but on average these numbers go from 10 to 20 kilograms. For the sake of simplicity, it will be said that each tree will produce approximately 15 kilograms. In addition to cork oaks, another prevalent species of oak that's also often found in the Alto Alentejo region and the Municipality of Portalegre with no exceptions is the holm oak, oftentimes having approximately 200 trees per acre. Contrary to cork oaks, holm oaks are not used for other industrial purposes, as holm oaks are protected under Portuguese law. Cork oaks are also protected under the same law (*Decreto-Lei n.º 169/2001, de 25 de maio* [104]) however they are used for cork production which is strictly regulated. In addition to the density per acre of both oak species, it's necessary to know how much each tree produces. This information is not easily available, and much less for these oak species. Therefore, it'll be assumed that both oak species produce an average of 15 kg/tree, according to the magazine *Jornal Vida* [105].

With this information, one can conclude that a hectare of cork trees with an average density of 135 trees would produce nearly 2,025 kilograms of acorns per hectare. Holm oaks would produce more acorns given the higher density of trees per hectare, totalling 3,000 kg/ha. Thus, within the Municipality of Portalegre, cork oaks would produce 10,605,025 kg of acorn waste, and holm oaks would produce 8,310,029 kg of acorns. The total amount of acorn waste is equal to 55% of the total acorns produced by both

oak species. Therefore, the total amount of biomass available for gasification would be equal to 10,403,280 kg.

5.2. Biomass purchase

When researching for information on the cost of acorns per kilogram, little to no information was available. Acorns are not a biomass that's often purchased, and much less does it fall under any regulations controlling its prices. The sale and purchase of acorns depends on the seller and the conditions they wish to establish, which may not often be expressed in a clear manner. For example, a seller from the website *Reforma Agrária* was claiming to sell their acorns at 0.50 €/kg, however in the product description the seller stated that they would sell the product at 2 €/kg [106]. Another seller on the website claims to sell their acorns starting at 5 €/kg [107], which is a completely different price from the former mentioned. A third example available was an article written by Andreas Papadopoulos on valonia oak acorns, and in it acorns were cited to be sold at a 0.50 €/kg [108]. Overall, the prices are set independently by each entity, and this is also influenced by other factors like transportation, quality of the acorns, among others.

5.3. Transportation

Transportation is a parameter that's oftentimes very nuanced, especially in the case of biomass and bioenergy logistics. While there are several ways to transport goods from a given point A to a given point B, there are many more factors to consider that directly affect the costs of transportation, such as the duration of the harvest season, the amount of biomass available, the total amount of days available for collection, the number of workers, technology, among others. In this case, all acorns ripen during the fall, especially during the months of October and November, which means that there is a very short window of time for collecting all the biomass that'll be used for the remainder of the year until the next fall. While initially the total number of days available for transporting supplies seems to be 61 days, when considering weekends, this number of days goes down to 45. These challenges are not exclusive to this scenario. In fact, most biomass is seasonal and available for a limited amount of time.

For this case study, the gasification unit will be located near a food production factory, focusing mainly on acorn products using acorns found within the Municipality of Portalegre. The factory and the gasification unit are two separate entities, meaning that the gasification unit would purchase the feedstock from the food production factory. Given that the feedstock dealing with is considered waste, the feedstock would be purchased at a cheaper price compared to the habitual price of acorns, at 5 €/ton. Additionally, the proximity of the gasification plant would allow for great reductions in transportation costs, which are usually one of the most expensive aspects of an economic plan. The feedstock would be transported from the factory to the gasification unit silo with the help of a conveyor belt.

5.4. Unit set-up

Setting up the unit entails a lot of aspects such as equipment selection, proper dimensioning, feedstock selection, among others.

Prior to setting up the unit, a mass and energy balance are done to better understand the amount of biomass that'll be needed to keep the unit running, alongside the amount of syngas and energy exiting the unit. Both the mass and energy balances would be done proportional to the mass and energy balances done for the pilot-scale gasification tests.

Selection of the equipment is then done based on the mass balance and ensuring that the equipment's total energy consumption does not exceed the total energy generated by the gasification unit. Installation and maintenance of the unit is then calculated based on what's observed in literature.

This project will work with a gasification unit with a power of 1 MW, for a total of 8000 hours per day, divided between 365 days per year. For the sake of simplicity, both the energy and mass balances will be measured daily.

Given that the unit works 21.918 hours per day on average, the daily energy input can be calculated using the following equation, which gives us a total of 21.918 MW of energy being inserted to the gasification unit:

$$E(Wt) = P_e(W) \times t(h) \text{ (Eq. 12)}$$

Knowing that the gasification unit's power is of 1 MW, a mass balance can also be illustrated, with the following equation:

$$P_e(W) = \dot{m}_{acorn\ waste}(\frac{kg}{h}) \times HHV_{acorn\ waste}(\frac{MJ}{kg}) \text{ (Eq. 13)}$$

Given that both the unit's power and acorn waste's HHV are known (see section 4.1.3), a mass flow of 244.898 kg/h was calculated. Multiplying this number by 8000 hours of annual functioning of the gasification plant results in a total of 1,959,184 kg of acorn waste being used in a year, or approximately 10.4% of the total biomass found within the Municipality of Portalegre. Given that approximately 55% of this biomass (equal to 10,403,280 kg) goes to waste, there is an abundant supply of acorn waste that can be readily used for this purpose.

Knowing the total amount of acorn waste biomass that'll be used for this project, a mass balance can be created, for the purpose of better understanding this process. The following mass balance (Figure 14) was designed based on the mass balance observed from the pilot-scale gasification tests, thus the dimensions being proportional.

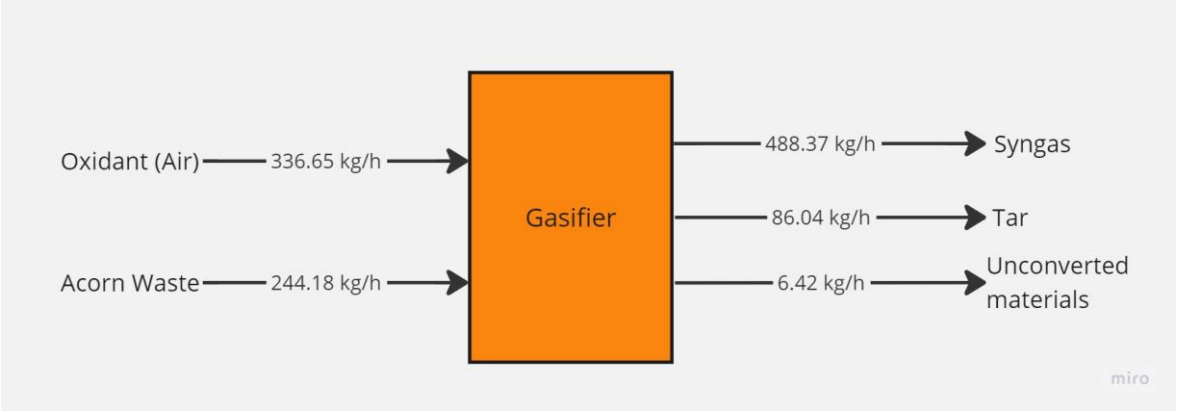

Figure 14. Mass balance for the studied scenario, based on the mass balance from Figure 12.

Having a complete mass balance, in addition to knowing the dimensions of the gasification unit being worked with, a complete energy balance can be created. Like how the energy input was calculated, the energy output can be determined by first determining its power, with the help of syngas's mass flow and lower heating value:

$$P_e(W) = \dot{m}_{syngas}(\frac{kg}{h}) \times LHV_{syngas}(\frac{MJ}{kg}) \text{ (Eq. 14)}$$

Once the power is calculated, the total energy produced by the system is calculated by multiplying the output power by the total amount of hours the unit will work per day, which was previously determined as 21,918 hours.

$$E(Wt) = P_e(W) \times t(h) \text{ (Eq. 15)}$$

Looking at Figure 15, one can see that the resulting energy output is much less than the energy input. Given that energy cannot be created nor destroyed, the explanation for this occurrence is the fact that most of the energy inserted into the unit is lost in the form of thermal, kinetic, sound, and other forms of energy that may not be considered. Nevertheless, this "lost" energy - especially thermal energy - can be repurposed in the gasification unit for several processes, such as biomass drying. Regardless, electrical energy is the only form of energy that'll be eventually sold off to the grid for profit.

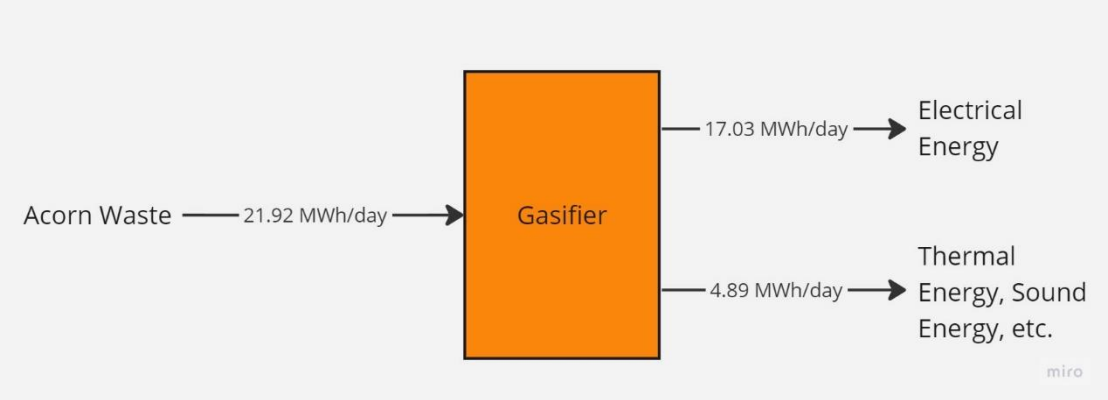

Figure 15. Energy balance balance for the studied scenario.

5.4.1. Equipment installation and maintenance of the unit

With the flows of biomass, syngas, and overall energy having been established, equipment is an essential part of a gasification unit, helping the entire process run smoothly from start to finish. The gasification unit consists of several components, which include a covered silo on-site, a hammer, a vibrating sifter, a pelletizer, and most importantly, the reactor where the actual gasification process takes place.

Table 9 shows each equipment's power, alongside the total amount of hours each of them would work daily. The sum of each equipment's daily energy consumption determines how much electricity is required.

Table 9. Equipment details from the studied unit.

Input	Engine (kW)	Capacity (kg/h)	Hours working (h)	Energy (kWh)	References
Hammer	55	5000.0	1.000	44.058	[130]
Sifter	3	6151.4	0.651	1.953	[131]
Pelletizer	220	3000.0	1.335	293.720	[132]
Reactor	1	183.0	21.918	1.000	[100]

The cost of installation is proportional to the unit's power, which is 1 MW as mentioned prior. For this unit, the installment costs were set as 1320 €/kW [133], making the unit have a total cost of €1,320,000. Additional maintenance costs were also considered in the case of any necessary repairs that would have to be made. For this unit, an additional 7% of the total installation cost was set apart for this purpose [133].

Figure *16* shows a general overview of the unit's flowchart and Table 10 shows a summary of the unit's characteristics.

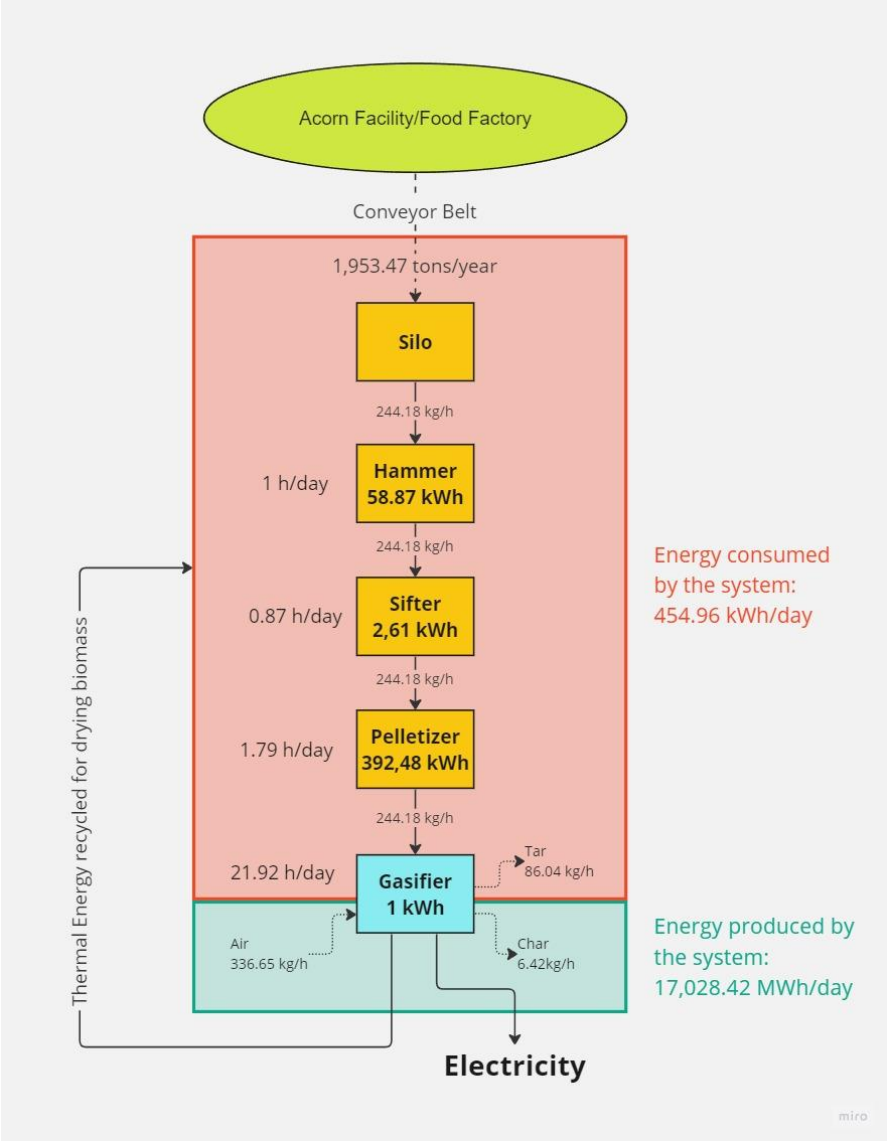

Figure 16. General unit flowchart.

Table 10. Unit characteristics summary.

Location	Portalegre, Portalegre, Portugal
Target Location	Municipality of Portalegre
Feedstock	Acorn Waste
Unit Power (MW)	1
Hours working (h)	8000 hours per year, divided between 365 days
Nº of workers	5; 4 operators and 1 administrator
Main components	Silo, Hammer, Sifter, Pelletizer, Reactor
Feedstock consumption	244,18 kg/h; 1,953,469 kg/year

5.4.1. Profit

Profit is equal to the product of total electric energy available and the corresponding tariff in place. This tariff can be determined through the *Portaria n.º 15/2015, de 23 de janeiro* [109], which establishes the tariffs that can be charged based on the energy's origin. For this case study, a tariff of 121.34 €/MWh is charged.

Profits are made through the sale of electrical energy produced by the gasification unit. The total energy available for sale is equal to the difference between the total electrical energy produced by the system, and the electricity consumption of all equipment (hammer, sifter, pelletizer, and the reactor per se). When sold to the grid, a total profit of €1,103,615 per year is made (Table 11).

Table 11. Energy consumed, produced, profitable and total profit from the studied unit.

Energy (kWh/year)			**Tarif (€/MWh)**	**Profit (€)**
Consumed	**Produced**	**Profitable**		
166,060	6,215,374	6,049,314	121.34	1,103,615

The NPV, IRR, and the payback period are parameters that are calculated to determine whether a project is economically viable. When all three parameters coincide in favor of the project, it means that the project is considered economically viable. In addition, NPV, IRR, and the payback period are analyzed from three different perspectives: from a pre-financing perspective, a post-financing perspective, and from the perspective of the actual investor. The IAPMEI Excel sheet allows for all these values to be calculated automatically with the given information that was calculated in this economic analysis. Results for the IAPMEI excel sheets are presented in Tables 12, 13 and 14.

Table 12. NPV, IRR and payback time from the perspective of 100% project pre-financing (IAPMEI excel sheet, available online at iapmei.pt)

Na perspectiva do Projecto Pré-Financiamento = 100% CP	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033
Free Cash Flow to Firm	**-1 964 833**	**527 527**	**467 152**	**484 133**	**501 624**	**453 639**	**472 195**	**491 308**	**510 994**	**531 270**	**615 943**
Taxa de atualização Ru = RF+Bu*(Rm-Rf)	5,25%	5,26%	5,27%	5,27%	5,28%	5,29%	5,29%	5,29%	5,29%	5,29%	5,30%
Factor de actualização	1,00	1,053	1,108	1,166	1,228	1,293	1,361	1,433	1,509	1,589	-
Fluxos actualizados	**-1 964 833**	**501 178**	**421 619**	**415 058**	**408 480**	**350 847**	**346 850**	**342 758**	**338 581**	**334 331**	**387 616**
Fuxos atualizados acumulados	**-1 964 833**	**-1 463 655**	**-1 042 036**	**-626 978**	**-218 498**	**132 349**	**479 199**	**821 957**	**1 160 538**	**1 494 869**	**1 882 485**

Valor Actual Líquido (VAL)	**1 882 485**	
Taxa Interna de Rentibilidade	**21,76%**	
Pay Back period (arred ano inteiro)	**6**	**Anos**

Table 13. NPV, IRR and payback time from the perspective of the investor (IAPMEI excel sheet, available online at iapmei.pt).

Na perspectiva do Investidor	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033
Free Cash Flow do Equity	**-1 966 748**	**527 527**	**467 152**	**484 133**	**501 624**	**453 639**	**472 195**	**491 308**	**510 994**	**531 270**	**3 088 586**
Taxa de juro de activos sem risco	0,25%	0,26%	0,27%	0,27%	0,28%	0,29%	0,29%	0,29%	0,29%	0,29%	0,30%
Prémio de risco de mercado	5,00%	5,00%	5,00%	5,00%	5,00%	5,00%	5,00%	5,00%	5,00%	5,00%	5,00%
Taxa de Actualização R = Rf + Bu*(Rm-Rf)	5,25%	5,26%	5,27%	5,27%	5,28%	5,29%	5,29%	5,29%	5,29%	5,29%	5,30%
Factor actualização	1	1,053	1,108	1,166	1,228	1,293	1,361	1,433	1,509	1,589	-
Fluxos Actualizados	**-1 966 748**	**501 178**	**421 619**	**415 058**	**408 480**	**350 847**	**346 850**	**342 758**	**338 581**	**334 331**	**1 943 661**
Fuxos atualizados acumulados	**-1 966 748**	**-1 465 570**	**-1 043 951**	**-628 893**	**-220 412**	**130 434**	**477 284**	**820 042**	**1 158 623**	**1 492 954**	**3 436 615**

Valor Actual Líquido (VAL)	**3 436 615**	
Taxa Interna de Rentibilidade	**25,98%**	
Pay Back period	**6**	**Anos**

Table 14. NPV, IRR and payback time from the perspective of post-financing (IAPMEI excel sheet, available online at iapmei.pt).

Na perspectiva do Projecto Pós-Financiamento	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033
Free Cash Flow to Firm	**-1 964 833**	**527 527**	**467 152**	**484 133**	**501 624**	**453 639**	**472 195**	**491 308**	**510 994**	**531 270**	**5**
WACC	5,34%	5,42%	5,43%	5,43%	5,44%	5,45%	5,45%	5,45%	5,45%	5,45%	5,45%
Factor de actualização	1	1,054	1,111	1,172	1,236	1,303	1,374	1,449	1,528	1,611	-
Fluxos actualizados	**-1 964 833**	**500 416**	**420 338**	**413 169**	**406 002**	**348 188**	**343 699**	**339 128**	**334 486**	**329 786**	**3**
Fuxos atualizados acumulados	**-1 964 833**	**-1 464 417**	**-1 044 079**	**-630 910**	**-224 908**	**123 281**	**466 980**	**806 107**	**1 140 594**	**1 470 379**	**1 470 383**

Valor Actual Líquido (VAL)	**1 470 383**	
Taxa Interna de Rentibilidade	**20,33%**	
Pay Back period	**6**	**Anos**

5.4.2. Labor

For the operation and surveillance of the gasification unit, four operators and one administrator are to be hired, with the operators earning a monthly salary of 1000 euros, and the administrator earning a monthly salary of 1300 euros. All five members of the personnel would earn their salaries on a 14-month basis to count bonuses (Table 15).

Table 15. Staff for the operation and surveillance of the gasification unit.

Position	**Nº of people**	**Monthly salary per person (€)**	**Yearly income per person (€)**	**Total earnings of personnel (€)**
Administration	1	1300	18,200	18,200
Operation	4	1000	14,000	56,000

5.5. Economic Analysis Summary Table

Table 16. Summary of technical and chemical characteristics pertaining to the gasification unit economic analysis

Mass Balance	**INPUT (kg/h)** Acorn Waste: 244.18 Air: 336.65	**OUTPUT (kg/h)** Syngas: 448.37 Tar: 86.04 Char: 6.42
Energy Balance	**INPUT (MWh/day)** Acorn Waste: 21.92	**OUTPUT (MWh/day)** Electric Energy: 17.03 Thermal Energy, Sound Energy, etc.: 4.89
Feedstock	Target Location: Municipality of Portalegre Availability (kg): 10,403,280 Amount Used (kg): 1,959,184 Cost (€/ton): 5	
Equipment	Composition: Silo, Hammer, Sifter, Pelletizer, Reactor Installation (€): 1,320,000 Maintenance (€): 92,400	
Electric Energy	Consumed (kWh/year): 166,060 Profitable (kWh/year): 6,049,314 Profit (€): 1,103,615 • Tariff (€/MWh): 121.34	
Labor	Personnel: 5; 4 operators and 1 administrator Salaries (€/month): Operators: 1,000; Administrator: 1,300	

6. Conclusions

The conclusion of this work demonstrates the potential energy and economic viability of acorn waste: despite being undervalued and seldom studied for energy production, acorn waste has proven to have interesting energetic and chemical properties. Gasification of acorn waste at higher temperatures has shown to be more promising and efficient compared to gasification at lower temperatures: gasification at 700ºC resulted in a syngas with LHV of 5.7 MJ/NM^3, a CGE of 68.5%, and a hydrogen content of 17%, compared to syngas samples obtained at 600 and 650ºC (5.3 MJ/NM^3, 62.6%, & 15.5%, and 5.3 MJ/NM^3, 64.4%, & 17.1% respectively). While hydrogen content is higher at 650ºC than at 700ºC, the remaining parameters compensate and result in a higher quality syngas. The overall increase in hydrogen content is a result of thermal cracking, which at the same time explains the decrease in tar formations as temperatures rise. The present work demonstrates that the gasification of acorn waste using a fixed bed reactor is possible, as it yields a good-quality syngas with interesting applications. An economic analysis demonstrated that acorn waste syngas can be used to produce electricity, which if applied in a real-life scenario, can be beneficial for rural communities.

Inevitably, there were some shortcomings that came along with the experimental trials, as often happens with work of this nature. For example, while not directly reflected in this work, the chemical analyses at the Biochemical Laboratory had to be halted temporarily because of the lack of gas used for the analyses. The analyses were performed at around the time the Ukraine/Russia conflict began, which evidently had dire consequences worldwide particularly in the transportation of several materials. While this was an issue that eventually resolved itself with time, other issues such as the gasifier were more difficult to solve: The gasifier used for the trials did not have a proper filter to clear out the impurities, and additionally the syngas analyzer available at the Polytechnic Institute of Portalegre had technical issues of its own.

Despite these limitations, this work demonstrates the great potential that acorn waste has, in addition to exploring a new method of utilizing an often-ignored biomass.

6.1. Future research prospects

Given the lack of studies performed on acorns and their derivatives (such as acorn waste, in this case), further studies and experimentation are encouraged to explore and determine its properties and other potential applications. Further gasification tests are encouraged, with fixed bed reactors and other types of reactors to explore acorn waste's behavior in different

reactors. In addition to this, experimenting with different mixtures containing acorn waste and other types of calorific-dense biomass would be another interesting approach to determine which combinations are best for enhancing syngas quality.

While in terms of economic analysis, relying exclusively on a single biomass source can come with a lot of limitations, which is why the diversification of biomass types, and their sources is encouraged when working with larger-scale projects, as smaller-scale projects may not need the same measures.

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