

Experimental study of shrinkage of wood during pyrolysis

Semester project in Chemical Engineering

Dept. of Chemical Engineering

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Submitted on 15 June 2019

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Abstract

This project explores the use of biomass as a valuable source for renewable energy and biomaterials. The project focuses on the thermal treatment of biomass in pyrolysis. Pyrolysis of biomass involves chemical transformations of the materials. The process starts with dry solid biomass, and converts it to solid char, vapours and gaseous products. The goal of the project is the study of the mass and volume loss of the material, a phenomenon known as shrinkage. The experiments are conducted in an analytical TGA apparatus to characterize the shrinkage of centimeter sized wood spheres and olive stones under slow pyrolysis conditions, realized a heating rate of 25 K/min. The parameters analysed in the project are the size of the biomass and the type of biomass, comparing the effect of pyrolysis of wood samples to olive stone samples.

To my mom and dad. You are the best.

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1. Introduction

1.1 Energy and biomaterials from biomass

Feedstock, olive's stones, biochar and uses, energy diagram of biomass in Europe

Biomass is a valuable source for renewable energy and biomaterials such as biochar. It also has a high potential for application in waste processing, the calorific value of the product gas is dependent on the gasifying agent.

The biomass feedstock also influences the calorific value and the biomaterials obtained from biomass. The fact that the biomass is wet also affects the process. The feedstock is usually classified in timbered biomass, herbaceous biomass, marine plants and manures.

Other characteristics of the feedstock taken into consideration are the moisture (intrinsic and extrinsic), the particle size and density, the operating conditions (partial pressure, temperature and heating gas), the steam to biomass ratio, air equivalence ratio, and the catalyst.

Biomass energy is one of the most widely explored research fields in energy and environmental science right now, the main attractive of the biomass over other sources of energy such as coal or oil is that it is evenly and extensively spread over the nations, which is to say that it is more readily available and can be equally as useful as low-cost fuel.

Biomass as a process also presents the interest of not only the energy, in the form of heat, it can produce, but the products as well, some of them being methane, syngas, H₂, CO, CO₂ and chemical feedstocks. The presence of sulphurs and inorganics can account for H₂S and ash, depending on the treatment method, it can also contain NH₃.

Syngas converted from non-edible biomass has many households application once it's synthesized into biofuels, these applications range from heating, cooking and lighting.

While the production of biochar as an output is not a priority, biochar has become an interesting product of biomass because of multiple uses, some examples being carbon sink, soil amendment, slash-and-char, water retention and energy production (Bio-oil and biogas). Carbon sink is the act of storing carbon in the ground, in the form of biochar, reducing the growth in greenhouse gas levels. Biochar is also found to be very effective at retaining water and water-soluble nutrients, this is understood as soil amendment.

The most interesting and industry focused of these uses is the energy production of char into bio-oil and syngas. Bio-oil and syngas can become the most cost-effective way of generating electricity form biomaterial.

The use of biomass energy in European countries is on the rise in recent years, being most significant in France and Scandinavia. In 2000 the EU15 had a primary energy use

of 41% oil, 23% gas, 15% nuclear, 6% renewables, of which 3.7% was form biomass
(International Energy Agency, 2016).

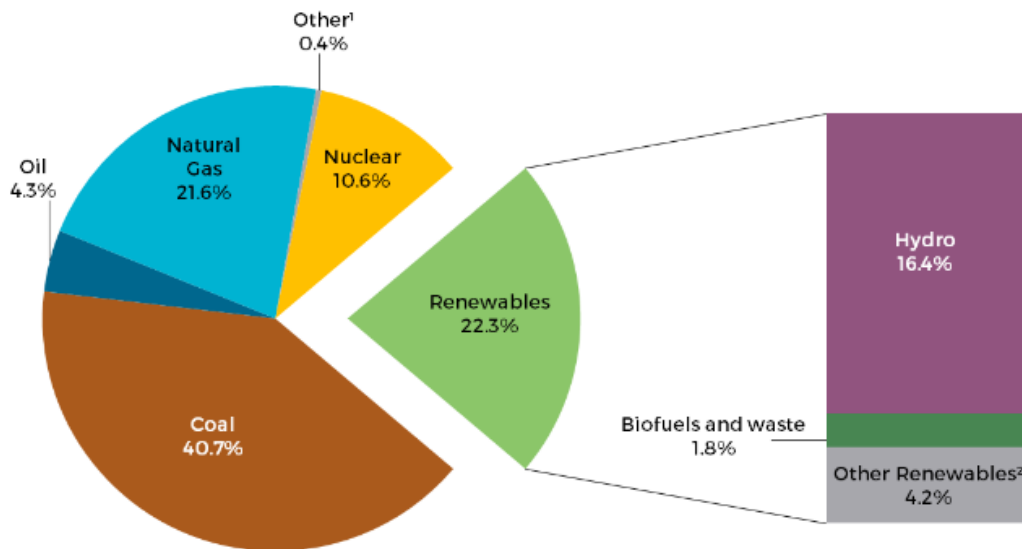


Figure 1. 2014 fuel shares in Europe total primary energy supply (International Energy Agency, 2016)

As *Figure 1* shows, the use of Biofuels as energy sources in Europe consist of a 1.8% of the total primary energy use; the percentage grows larger in northern Europe. In general, of all the biomass consumed in Europe, two thirds of biomass are forestry residues (e.g. Wood industry by-products, wood from Silviculture, waste wood etc...) and the rest of biomass consists mostly of agricultural by products like olive stones **(European Bioenergy Day (EBD))**. This means there's place to grow for the agricultural industry in it's by products as a source of biomass.

1.2 Conversion of biomass

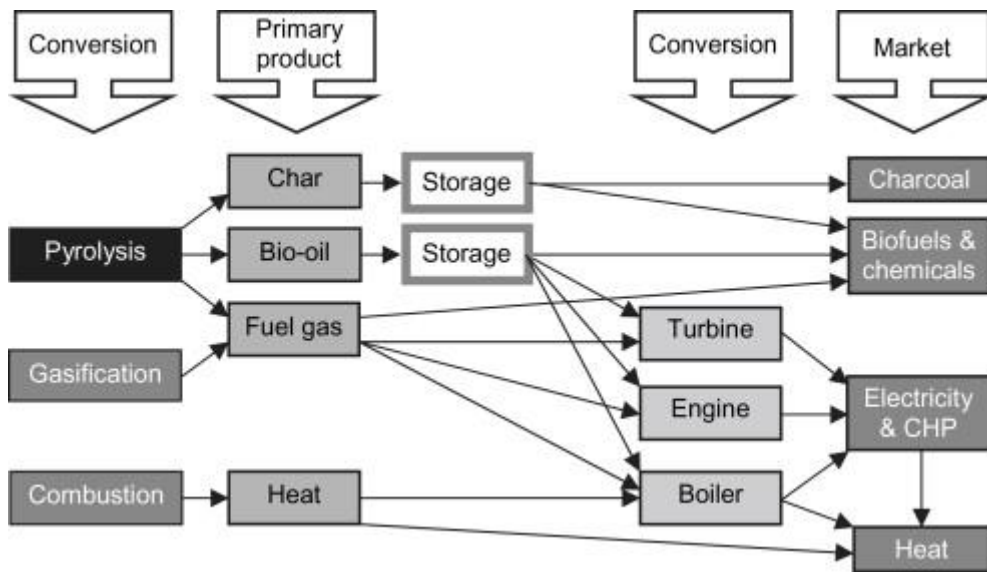


Figure 2. Products from thermal biomass conversion (Bridgwater, 2012)

The diagram in Figure 2 presents the three main conversion methods of biomass, their primary products, and the systems necessary for their conversion into a commercial energy product. Along with fermentation, the three conversion methods will be presented here before focusing on the pyrolysis process.

The conversion of biomass to energy has a wide range of processes, and types of biomass in order to achieve it. The industrial applications, the conversion options and the parameters are also diverse. It should also be noted that the production of energy with biomass is an efficient and currently viable form of renewable energy to help the environment.

The conversion of biomass to energy produces three main products: the energy in form of heat, fuels and the rest is chemical feedstock. The biomass conversion processes that produce the most fuel, and that is of most interest in this project are either gasification or pyrolysis processes.

The four-biomass conversion processes that will be discussed next will be combustion, gasification, pyrolysis and fermentation.

Combustion

The process of combustion consists in the burning of biomass in air, this produces hot gases and heat, which then can be transformed into mechanical power or stored into electricity using stoves, boilers, steam turbines etc.

The combustion of biomass is viable under any type of biomass, but in practice, combustion in industrial environments is used for biomass whose moisture content is below 50%, for this reason, the biomass used for combustion usually has low levels of moisture, if the biomass has a higher level of moisture is pre-dried.

The conversion efficiency of the plants ranges from 20% to 40%, a better conversion efficiency can be found in coal plants. Combustion of biomass can go from a small scale to industrial plants, in coal power plants, the combustion of biomass is an attractive option, because of the high conversion efficiency of the plants.

Gasification

The process of gasification consists in the conversion of biomass into a combustible gas. This is done by the oxidation of biomass with air, steam, or CO₂ at high temperatures, ranging between 800-900°C (**Peter McKendry, 2002**). The product gas consisting mainly of H₂, CO, CH₄, CO₂ and H₂O is named syngas (or producer gas) and can be stored and used in the production of chemicals.

One of the most promising aspects of syngas is the integrated gasification, where turbines convert the gaseous fuel (syngas) to electricity, with a good conversion efficiency. The integrated gasification processes clean the gas fuel before being combusted in the turbine, allowing for a better gas cleaning equipment. This use of gasification is still in demonstration stage (**Mitsui Babcock, 1997**).

The production of syngas allows for the production of methanol and hydrogen, both of which may have a future as fuels. The production of methanol favours hydrogen or oxygen gasification, this is because of the high value of CV gas. Just like integrated gasification processes, this scheme is currently in demonstration stage (**Mitsui Babcock, 1997**).

Pyrolysis

Pyrolysis is the conversion of biomass into bio-oil (up to 80% yield), charcoal (up to 40% yield) and ash (up to 80% yield) (**Peter McKendry, 1993**) by heating the biomass in absence of air, to complete the pyrolysis process the temperature goes around 500°C. The use of pyrolysis presents interests as an integrated process for production of a liquid fuel, that can be used directly, and as an intermediate step to convert biomass into a higher energy content, which can later be processed for heat power and biofuel.

The biofuel conversion when pyrolysis is used, is at its higher efficiency if the process used is flash pyrolysis. The conversion of biomass to biofuel can go up to 80% (**Peter McKendry, 1993**). The biofuel produced in pyrolysis can be used to obtain electricity and heat in engines and turbines, as well as feedstock for refineries.

Problems related to the process of pyrolysis are the fuel oil as a product. The oil presents poor thermal stability and corrosivity. In order to overcome these problems, the bio-oils can be treated by lowering the oxygen content and removing alkalis, this can be done by means of hydrogenation and catalytic cracking (**Qi Zhang et al., 2006**). The adequate treatment of bio-oils is still being developed.

Fermentation

Aside from combustion, pyrolysis and gasification, the final process for conversion of biomass is bio-chemical conversion, this can be divided in two processes, fermentation

and anaerobic digestion. The main process used industrially is fermentation. Fermentation is used commercially at international level in order to produce ethanol from sugar cane, maize, wheat etc.

In fermentation process, the biomass is ground down and the starch is converted by enzymes to sugars. Yeast then converts the sugars to ethanol. The next step is the purification of ethanol by distillation, which requires energy. The conversion of biomass into ethanol is low, this leaves the solid residue to be used as cattle-feed, fuel or biomass for gasification (**Coombs J., 1996**).

As for which compounds are more adequate to use for fermentation, high moisture content biomass is better suited to biological conversion processes. The case of lignocellulosic biomass like wood, is more complex, due to the presence of longer-chain polysaccharide molecules, it requires acid or enzymatic hydrolysis before the resulting sugars can be fermented to ethanol. This is the reason why lignocellulosic biomass is not used in industrial fermentation processes.

1.3 Gasification and pyrolysis comparison

A quick rundown on the basic processes, uses, products, and level of technology of gasification and pyrolysis can help understand when to use the most suitable of the process for energy production.

The processes of gasification and pyrolysis differ in the amount of temperature necessary. Gasification typically employs temperatures in the range from 800° C to 1200° C, while pyrolysis ranges from 350° C to 600° C (**Carolyn J. Roos, 2010**). Since pyrolysis occurs at lower temperatures than gasification, pyrolysis can have longer lifetimes and lower maintenance costs. Also, air emissions are lower since some gas compounds are created at higher temperatures (**Carolyn J. Roos, 2010**).

Since the principal products of gasification is heat and combustible gas (up to 85%), and the principal product of pyrolysis is bio-oil (up to 60%) and syngas (up to 20%), the main uses of pyrolysis and gasification would differ. Both gasification and pyrolysis produce char, but the amount obtained in pyrolysis is larger than gasification.

Since gas is the main product of gasification, it can be used to produce electricity by turbines, or integrated gasification. Gaseous fuels can be also transported via pipeline, and used as heat, power or converted into chemicals.

Bio-oils obtained from pyrolysis can be used as fuel in combustion processes, refined into transportation fuels or also converted into chemicals. Bio-oil is easier to transport than synthesis gas, but difficult to store for long terms due to its corrosiveness (**Carolyn J. Roos, 2010**).

As for the level of technology, biomass gasification is a mature technology and it's been widely used. However, its uses in generating electricity from gas turbines is been

developed recently, the main difficulty lies in the removal of tar from gas. This method has been proven effectively and it's already commercialized.

Pyrolysis technologies are newer and not as widely used as gasification. There is some industrialization around it but the manufacturing of pyrolysis reactors is not as extended as gasification.

1.4 Biochar

As it has been noted before, biochar is the solid product of pyrolysis. At moderate high temperatures in inert atmosphere, pyrolysis decomposes the carbohydrate structure of biomass into carbonaceous solid residue (biochar). Since biochar is highly carbonaceous it contains a high energy content, which makes for a good fuel for heat production in combustion. It can also be used for filtration and adsorption of pollutants once it has been chemically activated.

The application of biochar to soil quality improvement has received attention recently as a way of reducing carbon emissions and other greenhouse gases such as N₂O and CH₄ (**L. Van Zweiten et al., 2009**). The study of the effects of biochar as soil quality improvement is in development due to the numerous parameters like biomass type, pyrolysis conditions and soil properties.

As it has been said in the pyrolysis part of the conversion of biomass point, the detailed structure of biochar is influenced by the parameters of the pyrolysis, temperature, heating rate pressure, purge gas and particle size. These conditions influence the yield, carbon content, surface area, pore volumes and other properties of biochar.

At a pyrolysis analysis of wood similar to this project's, biochar produced at 500°C (**Yongwoon Lee et al., 2013**) presents a decrease in ratio of 0.26. Out of those results, the carbon yield resulted in 43%.

The pH in biochar is an important parameter when the biochar is used for soil improvement treatment. Biochar obtained from wood pyrolysis tends to be highly alkaline. As a result of higher pyrolysis temperatures, the pH in biochar increases (**K.A. Spokas et al., 2012**).

Another parameter to take into account about biochar when is used for soil improvement is the microscopic surface area, which depends on the type of wood used. The microscopic surface area is different between types of wood because of the vascular structure of the wood.

2. Samples and equipment

2.1 Samples

Now as for the samples being used, the samples are spherical wood pieces. The samples are made from beech (*Fagus sylvatica*). Since the parameters, the project will be focusing on, are the size of the samples during pyrolysis, the samples for the project are of 4 different diameters, namely 10 mm, 12 mm, 15 mm, and 18 mm samples as the ones shown in *Figure 3*. The powder necessary to do the proximate analysis is obtained by grinding one of the wood spheres.



Figure 3. Different sizes of wood samples

In order to study the effects of pyrolysis in other types of materials, the pyrolysis experiments were also conducted for olive stones of similar size and weight, like the samples in *Figure 4*. Before conducting the experiments, the olive stones were previously cleaned and dried. As well as the powder necessary for the proximate analysis of wood, it was obtained by grinding some olive stones.



Figure 4. Olive stones samples

2.2 Thermogravimetric analyser (TGA)

The thermogravimetric analyser (TGA) is an instrument that continuously measures the sample weight while the temperature of the sample is modified over time. In the case of this project, the thermal reactions conducted would be under a nitrogen flow (also air flow in the case of proximate analysis).

The TGA system consist of a precision balance with a sample located inside the furnace. The temperature can be modified by heating the flow of gas at a constant rate, this is controlled by the computer connected to the TGA apparatus, and measured by a thermometer next to the sample.

The TGA apparatus at laboratory is also connected to external heaters that can help bring the TGA to higher temperatures at a faster rate, but since the temperature necessary for the project was not too high, there was no necessity to use it. The TGA use in the project is shown in *Figure 5*.

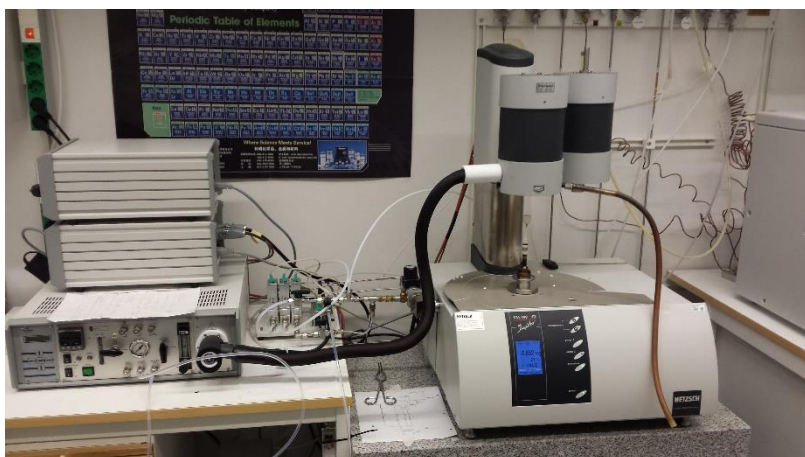


Figure 5. Thermogravimetric analyser (TGA) used to conduct the experiments

The data collected from the thermal reaction is compiled into a plot of mass percentage of the initial mass and is plotted along the temperature in function of time. Once the data analysis is finished, it can be plotted against other parameters to characterize the sample.

3. Experiments results

3.1 Pyrolysis conditions

The pyrolysis test conducted at the TGA were done up to 500°C and with a heating rate of 25K/min. The temperature of the experiment started at ambient temperature and stopped at 120°C, the sample stayed at that temperature for 5 minutes before resuming the 25K/min heating rate up to 500°C where it remained constant for 30 minutes before finishing the experiment. The flow rate of the experiments was nitrogen at 50 ml/min. The following *Figure 6* is a model recreating the conditions the samples underwent during the TGA experiments.

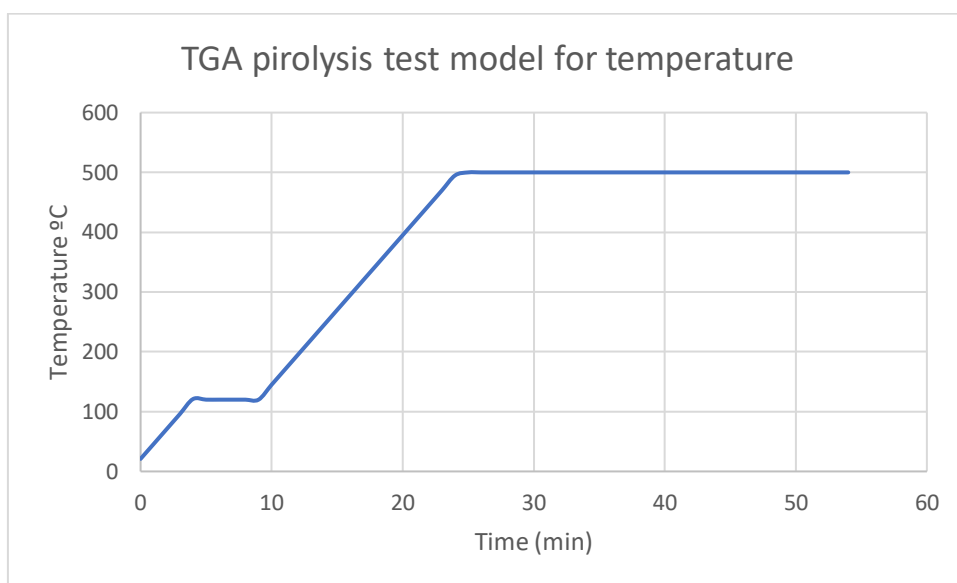


Figure 6. Temperature set up of the TGA pyrolysis experiments

The tests were conducted with balls of wood of different sizes. Before the experiments the shape of the samples was completely spherical, but after the pyrolysis, all the samples adopted a more cylindrical form, with the narrowest part of the sample being the part where the wood rings are formed.

The particle size investigated were of four different diameters, 10 mm, 12 mm, 15 mm and 18 mm diameters for the balls of wood. The 12 mm diameter samples were the first to be tested, 22 repetitions in total, once the repetition were proven to have similar results, the number of experiments conducted for the other samples was reduced. 10 mm samples had 3 repetitions, 15 mm samples had 3 repetitions and 18 mm samples had 2 repetitions.

The experiments were also conducted with powder for the proximate analysis. The powder was obtained by grinding some of the extra wood samples. Proximate analysis is a very accurate experiment, but in order to make sure, the experiment was repeated twice.

Test experiments were also conducted with other material for comparison. Olive stones were chosen for the experiment for the recent interest in the use of agricultural waste as a source of energy using pyrolysis.

The olive stones were cleaned before the experiment, for their selection similar size samples were chosen. The pyrolysis experiments were conducted twice. As with the wood samples, olive stones were also grinded to obtain powder for a proximate analysis of the olive stones, the proximate analysis was conducted twice.

3.2 Mass loss

In order to make the comparison of the accuracy of the samples in the same conditions, the next figures present the different repetitions for two different sample sizes.

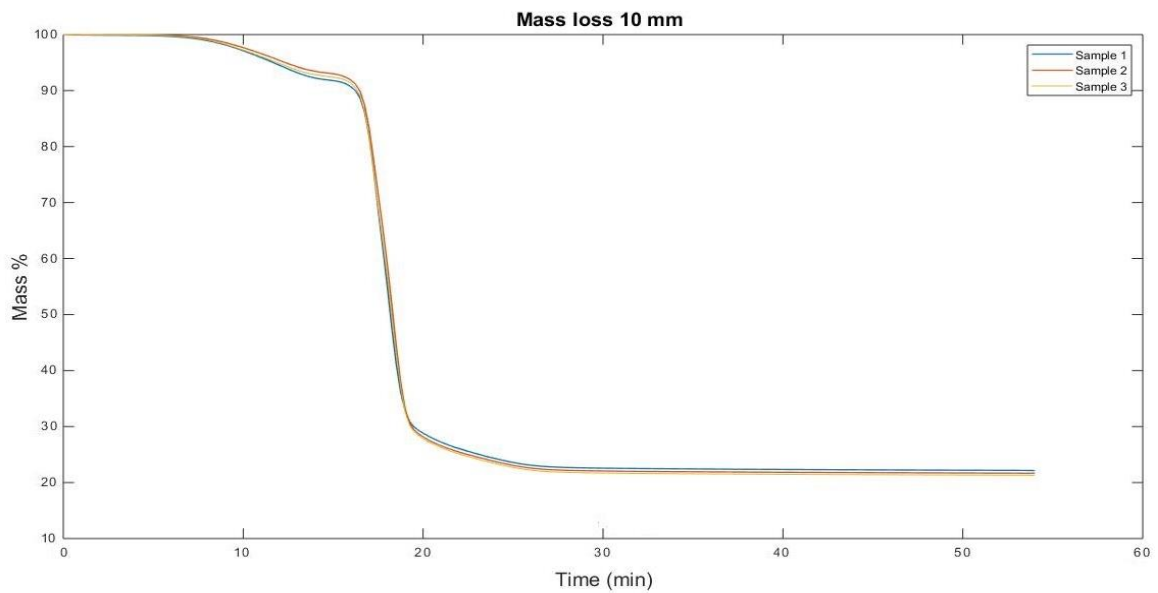


Figure 7. Mass loss comparison for the different 10 mm samples

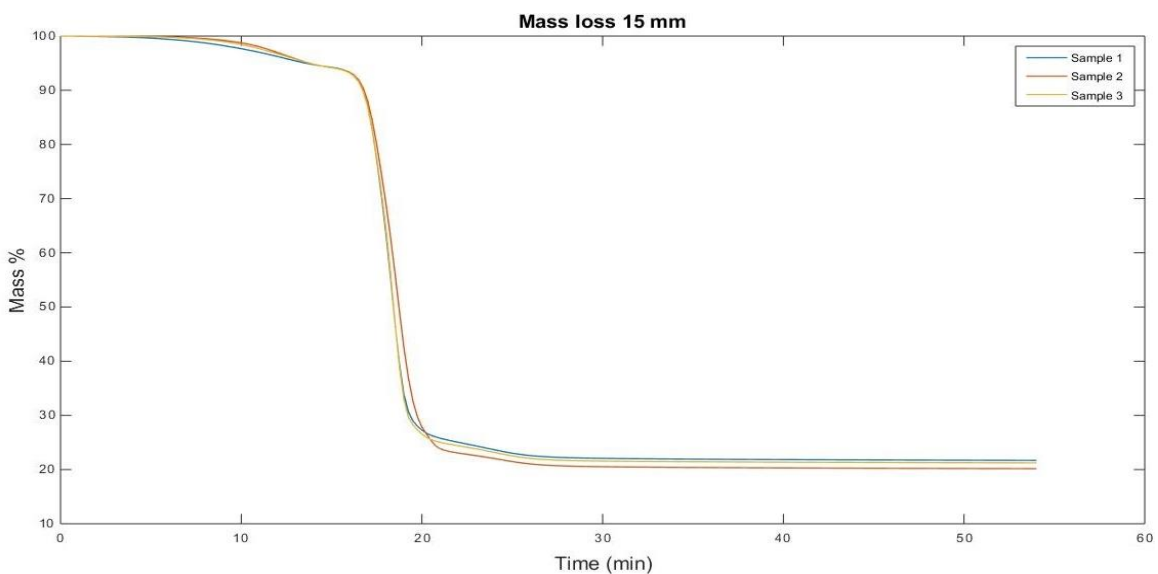


Figure 8. Mass loss comparison for the different 15 mm samples

Figure 7 and Figure 8 show the mass loss over time for the 10 mm samples and 15 mm samples, respectively. The differences in the different repetitions are small, and can be explained by the size of the particle, since the differences are more notable on the 15 mm sample.

In the Figures 7 and Figure 8 the first mass drop occurs around 10 minutes, where the humidity of the sample is evaporated. Then the second mass loss occurs around the 18-minute mark for both samples and it drops at a constant speed until it arrives to the 20-minute mark, when the experiment is about to reach the 500°C. There the mass loss reduces its speed until it remains constant at a 21% of the original sample mass. The second mass drop accounts for the degradation of cellulose, hemicellulose and lignin, leaving the 21% as the content of char in the sample.

In order to characterize the shrinkage of wood particles during pyrolysis, the parameters to modify can be the sample of wood (different size and weight), the heating rate and the final temperature.

The next step in the set of experiments will be choosing one of the three parameters to modify, since the Figure 7 and Figure 8 show that the reduction of mass stops at 350°C, we can discard the final temperature as an interesting parameter to modify. Just as (Haiping Yang et al., 2007) justifies, the temperature at which cellulose degrades is around 315°C, hemicellulose 220 °C and lignin 160 °C. The parameters to modify left are the heating rate and the samples of wood. We chose to do experiments with different size of samples of wood.

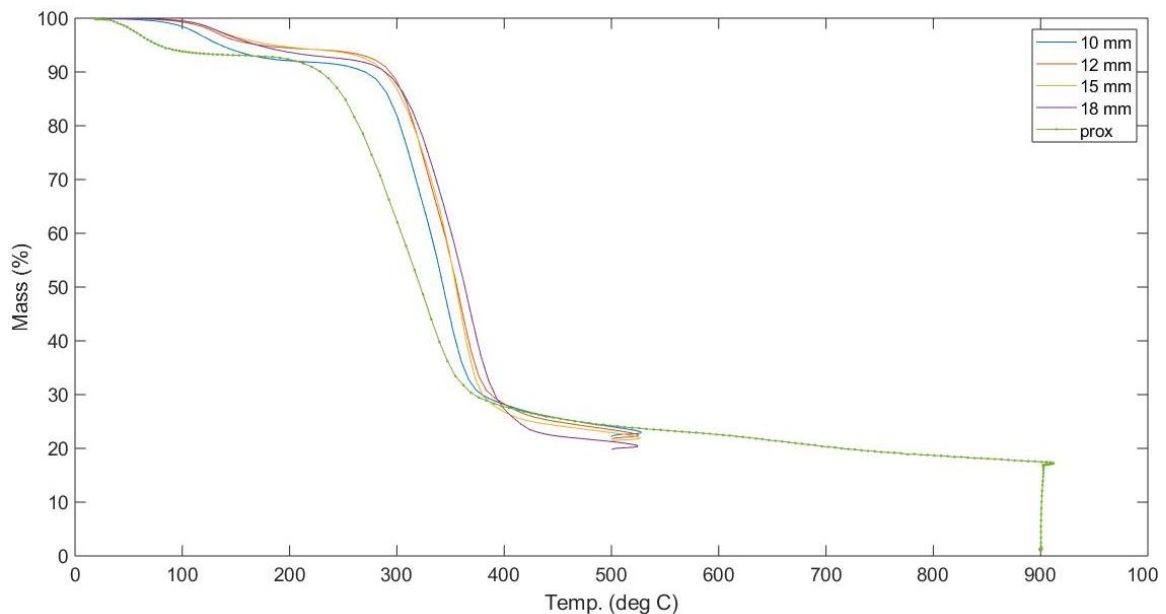


Figure 9. Mass loss of different size samples compared against temperature

The mass loss comparison for different particle sizes is better understood when compared to the temperature of the experiments. *Figure 9* shows the mass loss for the different particle sizes and the proximate analysis.

Starting at 100°C to 200°C the different samples in *Figure 9* suffer a mass drop correspondent to the humidity of the samples. After that, the second mass drop occurs when the degradation of cellulose, hemicellulose and lignin occur at 350°C. Finally, the mass is reduced to 21% when it arrives to 500°C. The proximate analysis follows the same path, although it is heated up to 900°C, arriving at a mass of 19% before entering in contact with air. The difference in the remaining of mass can be due to the last remaining of lignin in the sample needing a higher temperature.

Something important to take into account when discussing the difference in temperature when measuring the samples is that the pyrolysis occurs faster with smaller samples, that is why the powder sample (named “prox” in *Figure 9*) has a reduction in mass at lower temperature than the rest of the samples, the same can be said when following the pattern of mass reduction vs temperature in the *Figure 9*. After the first mass drop of proximate analysis, the next one to follow is the 10 mm sample, followed by the 12 mm sample, closely followed by the 15 mm sample and lastly by the 18 mm sample.

The analysis of these results can be enough to conclude that the size of the sample influences the temperature at which the degradation will take place, since the bigger volume of the sample will slow down the heating.

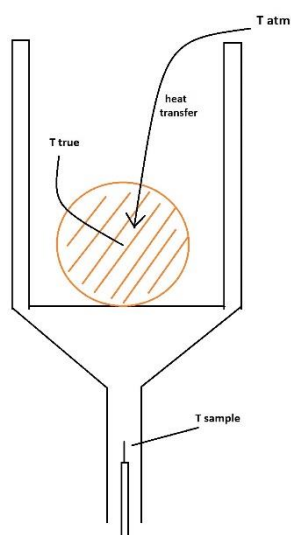


Figure 10. Explanation of the obtention of T. sample data in the TGA

However, the temperature at which the TGA is measuring the reaction might not be the same as the temperature of the sample at that time. As *Figure 10* shows, the thermometer feeding the data of the TGA is close to the sample, but strictly speaking, it does not have the same temperature as the sample. This is not taken into account when

the samples are small, since at smaller samples the true temperature is fairly similar to the measured temperature. But when the particles reach a larger size the veracity of the temperature registered can be dubious. This is not an issue with the TGA apparatus, since it is made to work on smaller samples, but it is important to be careful around 15 mm and 18 mm samples.

A comparison of the different samples from the dry sample point, disregarding the humidity of the sample, could have a more precise relation between mass loss and temperature. Once the dry point has been established as the total amount of the sample, this is what the *Figure 11* shows.

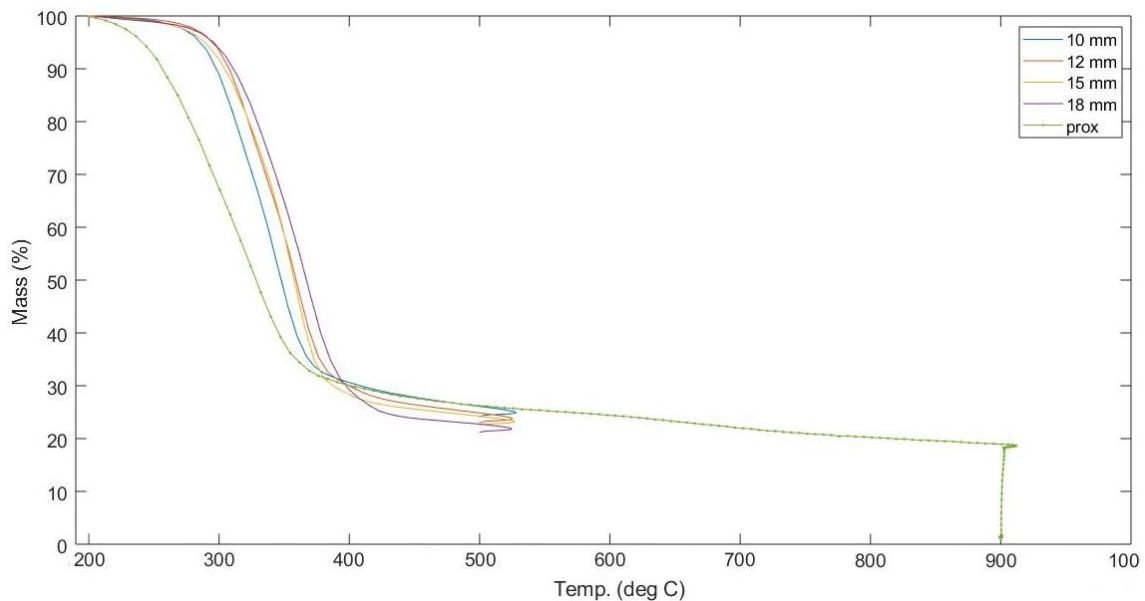


Figure 11. Mass loss of different wood balls based on dry sample mass against temperature

Since the mass loss of the samples has been graphed starting from the dry sample point, the results that *Figure 11* show are a unique mass drop due to the degradation of cellulose, hemicellulose and lignin. The samples arrive at a slightly higher point of remaining mass once the humidity has been taken out of the percentage, and the point at which the different particle sizes start degrading can be appreciated more clearly.

The disregard of humidity in the samples presented in *Figure 11*, shows a more reasonable behaviour of the 18 mm sample, since now the 18 mm sample has its mass loss at the highest temperature.

3.3 Shrinkage

In total, 22 experiments of 12 mm and 0.7 g samples were conducted. The shrinkage of the samples from their spherical form to a spheroid resulted in the measurements of the three principal dimensions with an average of 9.15 mm, 8.3 mm and 6.8 mm, each with a standard deviation of 0.26 mm, 0.28 mm, 0.544 mm respectively. The weight differences is more noticeable, from 0.7 g to an average of 0.156 g. These results translate into a volume loss of 36.2% and a weight loss of 77.5%.

These results of shrinkage are consistent with what is expected. Since the experimental samples have shown a good consistency in the data, and in order to save cost, the next set of experiments conducted would not be requiring so many samples.

The next set of experiments are the pyrolysis of balls of wood of 10 mm, since the previous experience have proven the TGA and sample consistent the samples done to characterize the 10 mm balls were three.

The shrinkage of the 10 mm samples from their spherical form to a spheroid form resulted in three measurements with an average of 8.25 mm, 7 mm and 6.1 mm, each with a standard deviation of 0.12 mm, 0.07 mm, 0.32 mm respectively. The weight differences are more noticeable, from 0.4 g to an average of 0.089 g. These results translate into a volume loss of 34.0% and a weight loss of 77.8%, very similar results with the 12 mm samples.

The shrinkage of the 15 mm samples were conducted in the same parameters, the three measurements of the spheroid were an average of 12.6 mm, 10.6 mm and 9.3 mm, each with a standard deviation of 0.2 mm, 0.56 mm and 0.5 mm respectively. The weight differences went from 1.36 g to 0.28 g. These results translate into a volume loss of 30.7% and a weight loss of 78.4%.

Finally, the shrinkage of the 18 mm samples conducted with the same parameters resulted in the following measurements of the spheroid form were an average of 15.1 mm, 12.3 mm and 10.45 mm, each with a standard deviation of 0 mm, 0.49 mm and 0.21 mm respectively. The weight differences went from 2.18 g to 0.44 gr. These results translate into a volume loss of 36.7% and a weight loss of 79.8%.

The volume of the samples after pyrolysis was calculated as if it was a spherical particle despite not been completely spherical. For the diameter of the particle, an average of the three measurements done after pyrolysis was considered. Therefore, the volume of the samples before and after pyrolysis was considerate spherical.

$$r = \frac{Height+Lenght+Width}{6}$$

$$V = \frac{4}{3}\pi r^3$$

In order to gain a better understanding of the importance of the size and mass of the sample and its effect on the shrinkage in the pyrolysis experiments, the results of the data are shown below.

Table 1. Mass loss and volume shrinkage comparison for different size samples

Diameter (mm)	Mass %	Volume%	Height/Diameter	Length/Diameter	Width/Diameter
10	22,1 ±0,54	66 ±4,17	0,82 ±0,02	0,61 ±0,03	0,70 ±0,01
12	22,5 ±0,58	73 ±4,77	0,82 ±0,01	0,62 ±0,03	0,74 ±0,006
15	21,6 ±0,69	69 ±4,93	0,84 ±0,01	0,62 ±0,03	0,70 ±0,03
18	20,19 ±0,06	63,2 ±0,9	0,83 ±0,06	0,58 ±0,06	0,68 ±0,02

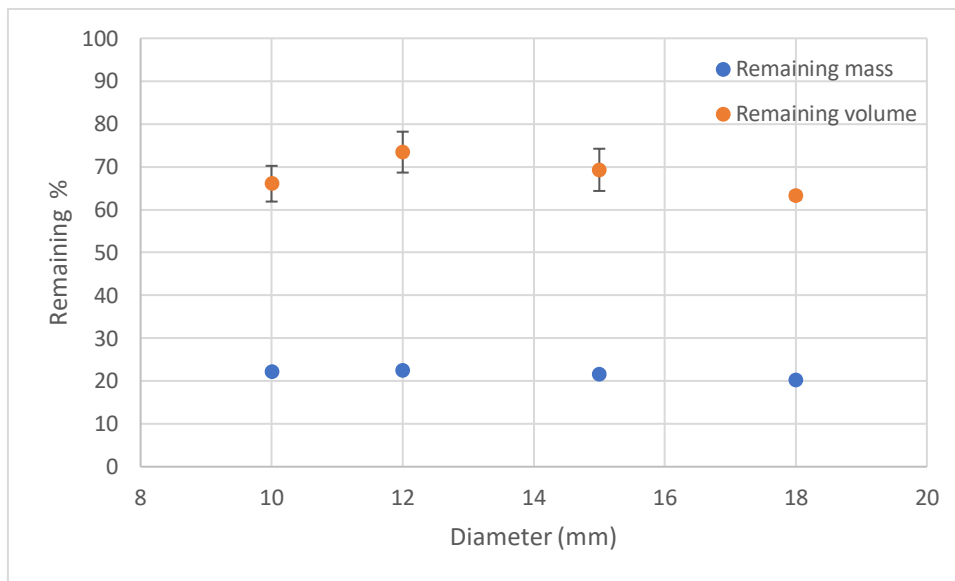


Figure 12. Mass and volume shrinkage comparison of different size samples

Figure 12 shows the comparison of the remaining mass and volume for the different particle sizes. It can be appreciated a consistent mass remaining value for all the different particles, the error bars in remaining mass cannot be appreciated in *Figure 12* because the error is very small. The volume data shows a slightly less consistent data, but it is still considerate adequate values.

Since the samples were not spherical after the pyrolysis experiments, the volume loss may not be an exact estimate, but the Height/Diameter, Length/Diameter and Width/Diameter values offer a consistent relation of the volume loss between samples in *Figure 13*.

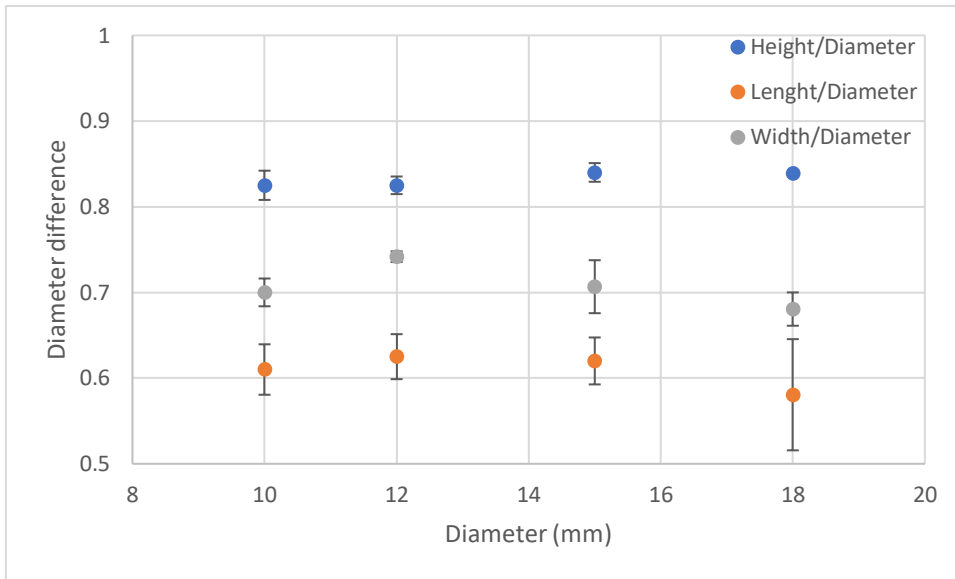


Figure 13. Volume measurements shrinkage comparison of different size samples

The data presented in *Figure 13* indicates similar measurement values for different particle sizes. One thing to highlight of the figure, is the fact that the error seems to be higher on higher particles, this seems to be consistent with the mass loss results previously mentioned.

Despite the smaller variations in diameter difference, the figures show consistent data in the different samples. The mass loss and the volume shrinkage keep consistent, almost reaching the 80% of mass loss predicted in other pyrolysis of biomass projects **(Peter McKendry, 1993)**.

3.4 Olive stones

For the next set of experiments, the samples changes from beech wood to olive stones, without changing the rest of the parameters. The heating rate and the final temperature remain at 25 K/min and 500°C. For the experiments, the three olive stone samples are chosen with similar dimensions and weight.

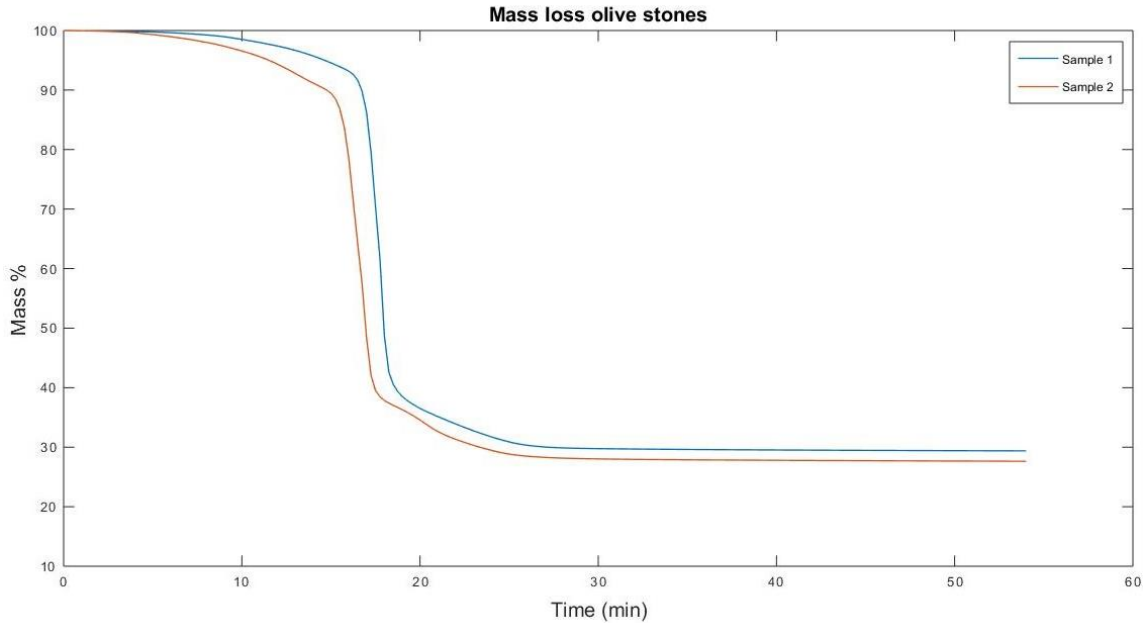


Figure 14. Mass loss comparison for the different olive stone samples

Just as with the mass loss for wood samples, Figure 14 shows the mass loss of olive stones. The first mass drop at around 10-15 min is caused by the evaporation of humidity while the sharp mass loss that follows is the degradation of cellulose, hemicellulose and lignin. The time at which the second mass drop occur in Figure 14, correspond with the temperature of the degradation of cellulose, at 350°C.

There the mass loss in Figure 14 reduces its speed until it remains constant at a 27% of mass loss, the 27% of remaining mass is the content of char in pyrolysis in the olive stone. This is the main difference with the wood pyrolysis, whose char content is 21%.

Before the pyrolysis, the two samples measured an average of 18,45 mm, 9,7 mm and 8,38 mm, each with a standard deviation of 0.25 mm, 0.4 mm, 0.42 mm respectively and a weight of 0.88 g on average. The shrinkage resulted in three measurements with an average of 15.12 mm, 7.57 mm and 6.9 mm, each with a standard deviation of 0.27 mm, 0.42 mm, 0.1 mm respectively. The weight differences are more noticeable, from 0.8 g to an average of 0.246g.

In order to obtain the volume loss in the example, we have to define the shape of the olive stone, either as a rectangle, a cylinder or a double conical form. Since its shape isn't a perfect representation of neither of them, its calculated in three different ways. In the end, the three different ways converge into a similar volume difference.

$$V_{rectangle} = Height \cdot Length \cdot Width$$

$$V_{cylinder} = \pi r^2 \cdot Height \quad r = \frac{Length+Width}{4}$$

$$V_{double\ conical} = 2 \cdot \frac{\pi r^2}{3} \cdot Height \quad r = \frac{Length+Width}{4}$$

Since a more accurate form of the volume would be the double conical formula, that is the one that is used to obtain the volume of the native and pyrolyzed olive stones. These results translate into a volume loss of 47.3% and a weight loss of 72.3%. The change in material and shape of the sample reported an increase in volume difference while maintaining only a small decrease in mass reduction.

In order to have a clearer understanding of the result of the experiment, the compiled data is shown in the table below.

Table 2. Mass loss and volume shrinkage in olive stones

	Height (mm)	Width (mm)	Length (mm)	Mass %	Volume %
Before pyrolysis	18,4 ±0,25	9,7 ±0,4	8,3 ±0,43	100	100
After pyrolysis	15,1 ±0,28	7,5 ±0,43	6,9 ±0,1	27,7 ±0,39	53 ±1,23

The result compiled on the *Table 2* show a higher percentage of remaining of mass compared to the results observed for the wood samples. This result is consistent with the literature findings on the composition of olive stones (**Ayşe E. Pütun et al., 2005**). The study on the composition of olive stones is expanded below in **4.4**.

Despite a higher percentage on the remaining of mass, *Table 2* shows a smaller percentage of the remaining volume, when compared to the wood samples. This can be due to the humidity and porosity of the olive stone samples before pyrolysis. The aspects of the shrinkage of olive stones after pyrolysis is expanded below in **4.1**.

4. Observations of samples after pyrolysis

4.1 Samples after pyrolysis

After the pyrolysis experiments, the samples suffer a shrinkage in volume. Since the remaining of the sample is char, which is to say that the wood has suffered a process of carbonization, the remaining of the sample has a carbon like look. The sample has a black colour and a more fragile structure.

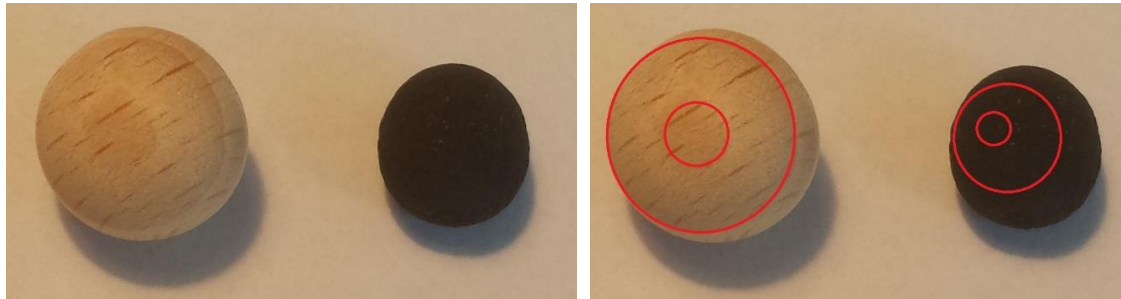


Figure 15. Wood samples before and after pyrolysis

The sample after pyrolysis is not spherical, like it was before the experiment. All the samples after pyrolysis present a greater shrinkage in the part of the wood sample were the rings form. The reason for this is explored in more detail later.

The samples of olive stones after pyrolysis experiment similar result of shrinkage and carbonization. The shrinkage and remaining mass of the sample are similar to the wood sample.



Figure 16. Inside of the samples before and after pyrolysis

Another comparative of the samples before and after pyrolysis is the inside look of the samples. Once the samples have been sliced, it can be appreciated that the lines going through the wood samples are still present after pyrolysis, although more compact and more fragile.

The same can be said for the olive stones samples. Before the experiment, the layers of the olive stone were less attached, but after pyrolysis the sample became more compact and fragile.

4.2 Difference in size shrinkage

Even though this number of experiments is not conclusive, there is enough data to start arriving to some conclusions, and to form hypothesis of why the shrinkage is happening the way that it is.

We can think of two ways of explaining why the shrinkage is greater in the part were the rings form:

1- The heartwood (the middle of the tree trunk) is the main way the water and sap are conducted from the roots to the leaves. since the new rings are meant to widen the trunk, but the new rings increase in diameter by the formation, between the existing wood and the inner bark. The result of this process is the cell division. These cells then go on to form thickened secondary cell walls, composed mainly of cellulose, hemicellulose and lignin.

This hypothesis is discarded right away, since the formation of the new rings occurs in the exterior of the existing wood. Plus, the amount of water and sap in the wood isn't a convincing enough explanation. Which means that if the amount of water and other compounds isn't the reason, the reason must be the structure of the wood cells that transport the sap in the centre of the trunk.

2- Once the difference in humidity and compounds have been discarded the explanation is, that the centre of the rings is made of wider elements. Which is to say that the centre is more porous. This is explained with the presence of the xylem.

The xylem is the tissue in vascular plants whose basic function is to transport water and nutrients (**White, A. Toby et al., 2010**). Wood in plants acts as xylem, and despite the flow not being solely in the centre of the trunk, it is were primary xylem forms a single cylinder, the rest is developed from the centre outwards. This is called centrarch.

Xylem cells are structured in tracheids and vessels. Tracheids are elongated cells, these cells develop a thick lignified cell wall, and once tracheids reach maturity, its protoplast disappear (**White, A. Toby et al., 2010**).

Since xylem cells are structured in tracheids and vessels, the empty space that these elements occupy explains why the experiment samples have shrunk more on the side where the wood rings are.

4.3 Composition of wood samples

After the experiments, the amount of volume loss is 28%, in comparison, the amount of mass loss is 77%. The tar, the compounds that have been separated during pyrolysis have a higher density than the carbon remaining.

The process subjected the samples to high heat, removing water vapor and volatile compounds, syngas. The solid remaining is char, the particles around the crucible were the ash. Since the pyrolysis in wood removes the volatile products, the solid remaining is composed primarily of carbon, char.

The char remaining from this experiments, although it is not carbon completely, can be used for gasification combustion, as a source of energy.

Since the company where the samples were obtained informs about the kind of wood used in the experiments, the composition of the samples is known and can be used to have a better knowledge of the syngas and the char after the experiments:

The samples are made from *Fagus sylvatica*. The species of Wood is a factor in the result of converting wood into char, tar and volatile compounds, as it is the temperature of treatment, the pressure, the dimension of the sample, and the use of catalyst. The main constituents in all types of wood are cellulose, hemicelluloses, lignin and extractives.

Once the sample has undergone the process of pyrolysis, volatile organic compounds (VOC) are released from wood, formed by the degradation of lignin and extractives during the thermal treatment. Hemicelluloses starts degrading at temperatures below 200 °C, its degradation forms organic acids like acetic acid, that end up forming part of the tar. In comparison with hemicelluloses, celluloses resist better to thermal treatment, the degradation starts at 300°C (**María D. Guillén et al., 1999**).

The compounds resulting from the pyrolysis of wood (in this case *Fagus sylvatica*) differ because of its heterogeneous structure and content, still, formaldehyde for example, is one of the main degradation products.

In order to have an idea of the composition of the tar and volatile organic compounds (VOC) in the experiments, the investigation of pyrolysis on *Fagus sylvatica* in a different investigation can provide an approximate idea of the compounds formed.

An analysis of the evolved gas with a single-shot analysis (SSA) and heart-cut analysis (EGA) (**A. Heigenmoser et al., 2012**) were performed after a pyrolysis treatment of *Fagus sylvatica* at 450°C. The results identified 53 compounds, those were 72.82% of the total area examined, the ones with a larger percentage were carbon oxide, acetic acid,

Hydroxy acetaldehyde, 1-Hydroxy-2-propanone, 2-Oxo-propanoic acid methyl, 2-Furaldehyde (furfural), 2,6-Dimethoxy-4-vinylphenol (4-vinylsyringol), 6-Anhydro-β-D-glucopyranose (laevoglucose) among others.

Even though there's a similarity in the compounds, the differences in the degradation of carbohydrates, degradation of lignin and the release of secondary products changes with the pyrolysis experiment set at different temperatures, for example, dihydroxy propiophenone and dihydroxy benzaldehyde were formed at 600 °C from demethylation, but not at 450 °C (A. Heigenmoser et al., 2012).

4.4 Composition of olive stones

The olive stone consists of the wood shell and the seed. Just as the wood from trees, the main component of the olive stone is cellulose, hemicellulose and lignin, unlike wood, olive stones also contain important amounts of fat and protein, studied in the table below (Guillermo Rodriguez et al., 2007). Olive stones also contain free sugars and polyols, and phenols.

Table 3. Chemical composition of olive stones and seed husks as % of dry weight (Heredia et al., 2008)

Component	Whole stones	Seed husk
Moisture	9,79	9,98
Fat	5,53	1,01
Proteins	3,2	1,29
Free sugars	0,48	0,36
Neutral detergent fiber (NDF)	80,1	89,4
Acid detergent fiber (ADF)	58,2	62,6
Cellulose	31,9	36,4
Hemicellulose	21,9	26,8
Lignin	26,5	26

The analysis of the compounds after the pyrolysis takes place have been done by many different articles, just as with the wood samples, we choose one with similar characteristics to ours. In (Ayse E. Pütun et al., 2005), olive stones samples subjected to pyrolysis, with final temperatures ranging from 400°C to 700°C resulted in a 28% weight of char, a 32% weight of bio oil, and a 20% weight of gas, even though the heating rate and the mass in (Ayse E. Pütun et al., 2005) do not match with the experiments conducted in this project, however, the results help prove that they are consistent with the literature.

5. Proximate analysis

Finally, to conclude the experimental analysis, a biomass proximate analysis will be conducted using wood powder. The powder is obtained by grinding some of the wood particles until a sufficient amount of powder is reached.

The proximate analysis consists in determining moisture, ash, volatile matter and fixed carbon contents of the raw biofuel. In the case of this project, the determination of the compounds is determined solely by the weight difference of the raw biofuel when subjected to a controlled temperature program.

The method conducted in this project has a heating rate of 25K/min to 120°C where it stays for 5 minutes, then it resumes the 25K/min up to 900°C, where it stays for 5 minutes, after five minutes oxidative atmosphere is added to the experiment, and it stays this way for 30 minutes. The flow of both nitrogen and air is set at 50 ml/min. This proposal of proximate analysis is made following the guide of other works (**Roberto Garcia et al., 2013**).

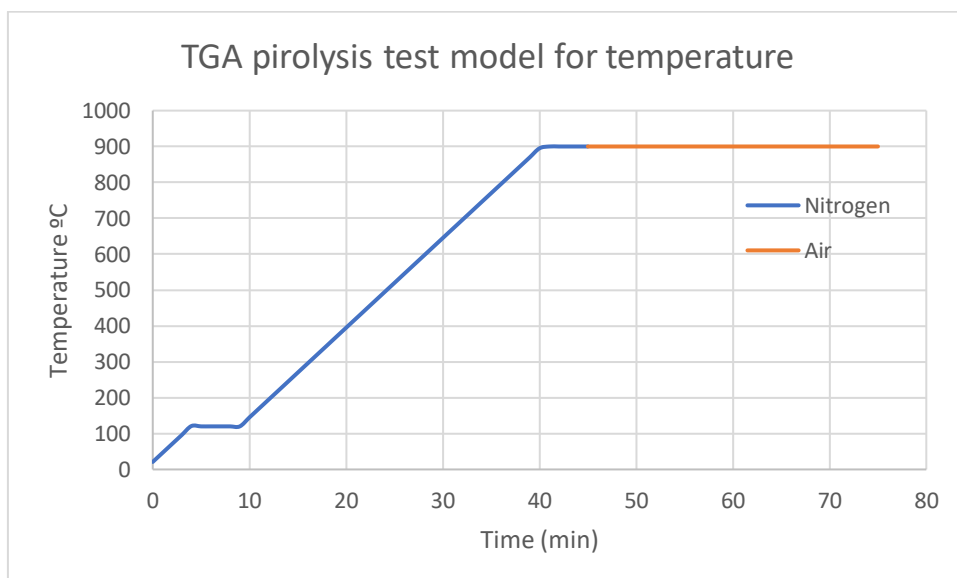


Figure 17. Temperature set up of the TGA proximate analysis experiments

The model presented in *Figure 16* represents the temperature set for the proximate analysis experiments and the type of flow conducted during the experiment.

The next figure shows the results of the proximate analysis of the mass loss in the proximate analysis of wood and the proximate analysis of olive stones.

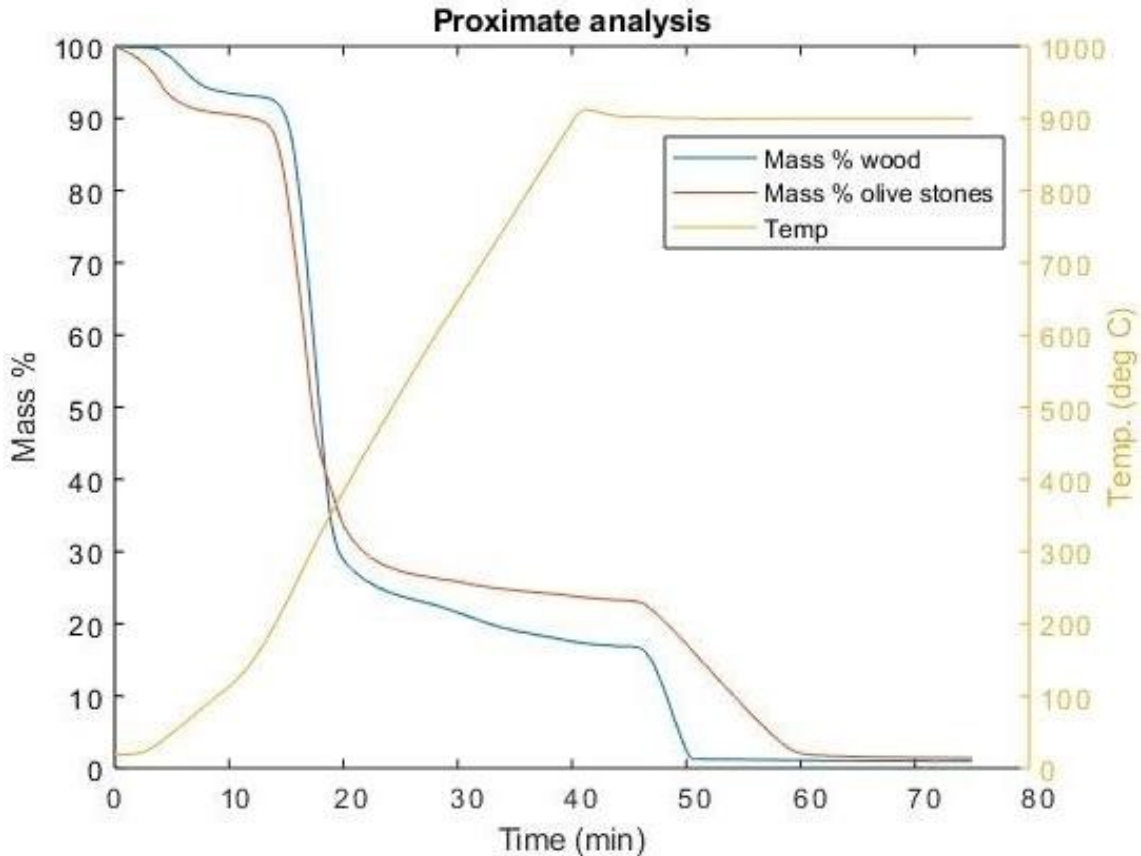


Figure 18. Mass shrinkage comparison for wood and olive stones in the proximate analysis experiments

The results of the experiment in *Figure 18* show three different mass drops at different points of the experiment. Just like with pyrolysis, the first two mass drops correspond to the loss of humidity in the samples from 100°C to 200°C, and the degradation of cellulose, hemicellulose and lignin immediately after, until 500°C. After that, the degradation of cellulose continues a little more, although not enough to make a big difference over the pyrolysis analysis.

Once the TGA changes from a nitrogen flow to an air flow at 900°C, *Figure 18* shows the third mass drop. This occurs due to the combustion of the char with the oxygen in air, leaving only the ash.

Figure 18 also shows the humidity content in the wood sample being lower and taking longer to evaporate. The second mass drop occurs at the same time for both proximate analyses, but the degradation of wood is higher. Lastly, the third mass drop starts at the same time for both samples; the starting time of the third drop represents the time when the atmosphere in the TGA apparatus was changed from nitrogen to air. As can be seen from *Figure 18*, the third mass drop finishes earlier for the wood sample, leaving a lower amount of ash for the wood sample.

Once the proximate analysis is done, we can obtain the percentage of mass left and that will correspond to the percentage of ash in the sample. The wood sample had a 1.28% of ash, and the olive stone sample had a 2.75% ash.

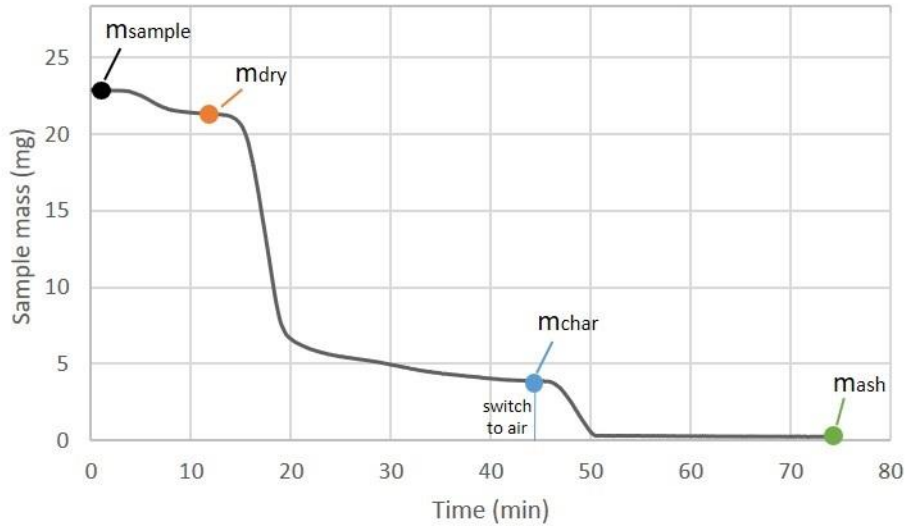


Figure 19. Proximate analysis mass shrinkage to determinate the composition of the samples.

The model conducted in the Figure 19 shows the points where the different particle masses were selected in the TGA proximate analyses data.

Finally, with the proximate analysis, we can calculate the percentage of volatile matter, fixed carbon and ash, using the masses highlighted in the Figure 19. The values are obtained without taking into account the humidity in the sample, this is done by considering the dry sample mass as the total amount of mass in the sample.

$$VM = \frac{m_{dry} - m_{char}}{m_{dry}} \cdot 100 \quad FC = \frac{m_{char} - m_{ash}}{m_{dry}} \cdot 100 \quad Ash = \frac{m_{ash}}{m_{dry}} \cdot 100$$

The proximate analyses were done twice for each compound, with closely similar results. The composition resulting of the pyrolysis experiments for wood and olive stones are presented in the following table.

Table 4. Composition resultant of the pyrolysis in wood and olive stones

	Volatile matter %	Fixed carbon %	Ash %
Wood	79.33	19.27	1.40
Olive stones	72.59	24.45	2.96

The results obtained in Table 4 are compared with similar experiments in other projects to check the legitimacy of the results. In the case of wood, the ash percentage tends to vary around 1%-2%, in the case of beech wood, the one used in the experiments, the ash content is 0.4% (Daya Ram Nhuchhen et al. 2012), an acceptable parameter to the proximate analysis result of 1.4%. The ash percentage in olive stones after proximate analysis is 2.2% (Daya Ram Nhuchhen et al. 2012), since the percentage can vary around 1.5%, for a 2.96% ash content in the proximate analysis, this value is considered correct.

6. Conclusion

The comparison of the mass loss for different particle sizes has shown the velocity of the heating of the inside of the particle being directly influenced by the size of the particle. Despite that, the value for humidity, and char have remained virtually the same despite the change in size, the mass loss and volume shrinkage stayed the same for different sizes. The large sizes of the experiment proved to be more difficult to measure its heating correctly.

The final point of temperature selected for the experiments was enough for almost the complete degradation of the cellulose. The proximate analysis was heated up to 900°C, and the difference of char remaining between it and the pyrolysis experiments was around 1%, not a significant amount.

The results of pyrolysis for wood samples and olive stones samples revealed a 20% of char in wood samples compared to a 27% of char in olive stones samples. Furthermore, the remaining volume of the wood samples was a 67%, compared to the remaining volume of olive stones samples which was a 53%. With a larger content of char and a higher reduction of volume, olive stones could be considered an attractive source of biomass for pyrolysis.

Finally, the proximate analyses obtained the composition of the samples offering a comparative on the possible use of fixed carbon, volatile matter and the content of ash between the wood samples and olive stone samples.

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