EFFECT OF INORGANICS ON THE PYROLYSIS BEHAVIOUR OF AGRICULTURE RESIDUES

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RESUMO

As actuais condições ambientais tornaram necessário procurar e utilizar novas fontes de energia, dando origem a alternativas energéticas modernas, tais como a biomassa. A biomassa é uma fonte de energia renovável com muitas vantagens em relação a outras fontes de energia, tais como alta flexibilidade e disponibilidade. A energia pode ser obtida a partir da biomassa através de diferentes processos termoquímicos ou termofísicos. No presente estudo, foram investigados os efeitos da inorgânica sobre a pirólise da biomassa. Para este efeito, foi comparado o comportamento de quatro amostras de estrume de cavalo, estrume desmineralizado de cavalo, uma mistura de estrume de cavalo e cascas de nozes (50:50) e cascas de nozes em pirólise, numa análise termogravimétrica (TGA) e num reactor horizontal. O estrume de cavalo foi desmineralizado por um processo de lixiviação com água ionizada durante 24 h a 30 °C e com uma proporção de 140 biomassa:água devido ao elevado teor de cinzas presentes neste tipo de biomassa. Uma vez preparadas as amostras, estas foram submetidas a diferentes testes, análises próximas e orgânicas a fim de estudar as diferenças entre elas, concluindo-se que a biomassa desmineralizada tem um maior conteúdo volátil e um menor conteúdo de cinzas, como era de esperar. Após o estudo da biomassa seleccionada, as amostras estudadas anteriormente e as cascas de nozes foram submetidas a pirólise por análise termogravimétrica com um fluxo N2 de 200 ml/min, numa gama de temperaturas de 30-700°C e com uma taxa de aquecimento de 10°C/min. Nesta experiência, os efeitos catalíticos dos inorgânicos sobre a pirólise puderam ser observados reduzindo a diferença de temperatura entre o início e o fim da pirólise de 128°C no estrume desmineralizado de cavalos para 94,5°C no estrume bruto de cavalos, bem como provando que a mistura foi bem sucedida ao permitir que os inorgânicos presentes no estrume de cavalos afectassem a reacção de pirólise quando misturados com cascas de nozes. Estas amostras foram também sujeitas à pirólise num reactor horizontal nas mesmas condições de fronteira que na TGA, onde se verificou através do cálculo da diferença de massa antes e depois da pirólise em cada experiência realizada no reactor horizontal e na TGA, que a pirólise no reactor horizontal foi bem sucedida e, além disso, os gases de escape da experiência de pirólise no reactor horizontal foram analisados pela cromotografia de gás.

Palavras-chave:
Biomassa, pirólise, termogravimetria, reator horizontal, inorgânicos, efeitos catalíticos

ABSTRACT

Current environmental conditions have made it necessary to seek and use new energy sources, giving rise to modern energy alternatives such as biomass. Biomass is a renewable energy source with many advantages over other energy sources such as high flexibility and availability. Energy can be obtained from biomass by different thermochemical or thermophysical processes. In the present study, the effects of inorganics on the pyrolysis of biomass were investigated. For this purpose, the behaviour of four samples horse manure, demineralised horse manure, a mixture of horse manure and walnut shells (50:50) and walnut shells in pyrolysis was compared in a thermogravimetric (TGA) analysis and in a horizontal reactor. Horse manure was demineralised by a leaching process with ionised water for 24 h at 30 °C and with a ratio of 140 biomass:water due to the high content of ash present in this type of biomass. Once the samples were prepared, they were subjected to different tests, proximate and organic analysis in order to study the differences between them, concluding that the demineralised biomass has a higher volatile content and lower ash content as it was expected. After the study of the selected biomass, the previous studied samples and walnut shells underwent pyrolysis by thermogravimetric analysis with a N_2 flow of 200 ml/min, in a temperature range of 30-700°C and with a heating rate of 10°C/min. In this experiment, the catalytic effects of the inorganics on the pyrolysis could be observed by reducing the temperature difference between the beginning and end of pyrolysis from 128°C in demineralised horse manure to 94.5°C in raw horse manure, as well as proving that the mixing was successful in allowing the inorganics present in horse manure to affect the pyrolysis reaction when mixed with walnut shells. These samples were also subjected to pyrolysis in a horizontal reactor under the same boundary conditions as in the TGA, where it was verified by calculating the mass difference before and after pyrolysis in each experiment performed in the horizontal reactor and the TGA, that the pyrolysis in the horizontal reactor was successful and furthermore, the exhaust syngases from the pyrolysis experiment in the horizontal reactor were analysed by the gas chromotograph.

Keywords:
Biomass, pyrolysis, thermogravimetry, horizontal reactor, inorganics, catalytic effects

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NOMENCLATURE

Symbols

E	Activation energy (KJ. Mol^{-1})
H	Hydrogen
O	Oxygen
R	Ideal gas constant (KJ. K $^{-1}$.mol^{-1})
T	Temperature (°C)
VM	Volatile matter
M	Moisture
FC	Fixed Carbon

Acronyms

daf	dry, ash free
db	dry basis
DTG	Differential thermogravimetric
PB	Pine bark
RH	Rice husk
TG	Thermogravimetric
TGA	Thermogravimetric analysis
WS	Wheat straw
HM	Horse Manure

1. INTRODUCTION

1.1. MOTIVATION

1.1.1. ENERGY CURRENT SITUATION

Energy is the world’s engine; energy is what makes it possible for us to live the way we live, and it is a fact that technological progress goes hand in hand with energy and therefore with its increase. Consequently, the development of society is linked to technology, which is why we began to see an abysmal change in energy consumption after the industrial revolution. However, energy consumption does not only affect society and technological progress, but also the economy. Thus, “it can be said that energy consumption, technological innovation and the development of a society are positively related to each other” [2].

Nevertheless, energy consumption is going out of control, this is due to the lack of awareness of the consequences which has led to unthinkable energy consumption levels. Globally, final energy consumption in 2018 was 9.9 million tonnes of oil equivalent (Mtoe), double the consumption recorded in 1973 [3].

Figure 1 clearly shows the exponential increase in primary energy consumption worldwide between 1800 and 2019 [4].

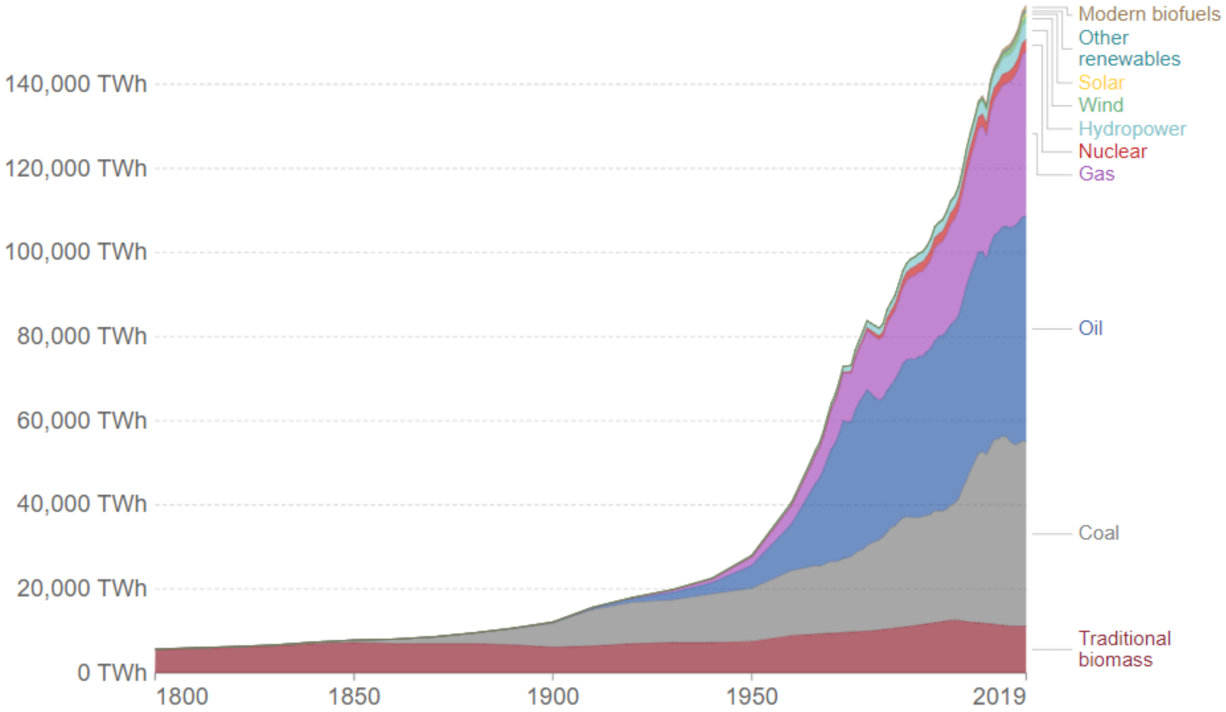


Figure 1. Global Primary energy consumption since 1800 [4].

Such high levels of energy consumption have major repercussions, since the majority is supplied by fossil fuels, which present several problems, such as:

- Deterioration of the environment - the production of energy with fossil fuels is one of the main causes of greenhouse gas emissions, causing climate change, which translates into an increase in the temperature of the planet with all the consequences that this entails.

- Resource depletion - fossil fuels are limited energy sources.

- Energy dependence - many countries are dependent on energy imports from other countries, which is reflected in an unstable economy of the country.

- Harmful effects on people's health - the polluting gases generated by fossil fuels deteriorate air quality.

In order to make the world a more sustainable place, the European Union has produced a series of goals for 2030, among them are [5]:

- A binding target for the EU in 2030 of at least 55% less greenhouse gas emissions compared to 1990.

- A binding EU target of at least 32% renewable energy in energy consumption by 2030.

This therefore, added an immediate need for countries to look for alternatives to fossil fuels.

1.1.2. RENEWABLE ENERGIES

It could be said that renewable energies are the hope for the world, they solve most of the problems that we are currently facing, climate change, energy dependence, etc. They are clean, inexhaustible, and increasingly competitive sources of energy [6]. In fact, renewable energies have evolved very prosperously. Global growth in primary energy consumption from renewable sources was 7.1% in 2018. Renewables increased their contribution to primary energy consumption by 3.7% to 10.8% of the total. As in recent years, renewables remain the fourth largest source of primary energy consumption in the world [7].

There are different types of renewable energies, the most widely used being wind and solar energy. However, despite being less exploited, energy from biomass has some very important advantages over energy from wind and sun, as these two types of energy are characterised by being intermittent, which presents a problem when it comes to energy storage. On the other hand, energy from biomass is easily storable, which is an advantage as it is similar in this aspect to fossil fuels, since we are faced with a global energy supply system that has been designed for the use of fossil fuels. In this way, energy from biomass can be adjusted to supply and demand in contrast to energy from wind and sun. For this reason, biomass is one of the energies with the greatest potential to contribute to the world's basic needs, due to its flexibility and availability [32].

In addition to the availability and flexibility of biomass, this energy source has many other advantages, such as its low price compared to oil or coal, its great abundance, and its presence in a wide variety of regions around the world. Another characteristic of this energy source is that it has zero emissions, i.e., the CO2 emissions produced during the energy conversion of biomass, as they come from carbon removed from the atmosphere in the same biological cycle, do not alter the balance of atmospheric carbon concentration and therefore do not increase the greenhouse effect. In fact, their use contributes to reducing CO2 emissions into the atmosphere when they replace a fossil fuel.

Both electricity and heat can be obtained from biomass. To do this, biomass undergoes processes that can be biological, thermochemical, or mechanical, among these processes are burning, digestion, fermentation or gasification depending on the desired result.

1.1.3. BIOMASS

Biomass is a renewable energy source based on the utilisation of organic matter formed biologically in the immediate past or the products derived from it. It is considered renewable energy because its energy content comes from the solar energy fixed by plants in the photosynthetic process [33].

Analysing biomass from an energy point of view, it is characterized by low levels of carbon and high levels of oxygen and volatiles. The calorific value of biomass lies mainly on these volatiles however, the calorific value is very variable because it depends on the type of biomass and its humidity.

Biomass is a very attractive source of energy to use partly due to its calorific value, the calorific value of lignocellulose wastes ranges from 3000-3500 kcal/kg, 2000-2500 kcal/kg for municipal waste and 10000 kcal/kg for liquid fuels from energy crops [10].

As previously mentioned, for the energy conversion of biomass to take place, it must undergo different processes that can be physicochemical or thermochemical, as shown in figure 2. Thermochemical processes include combustion, gasification, and pyrolysis. Combustion is one of the classic methods for recovering heat from biomass as its product is hot gases suitable for heat production. In this process there is a presence of a lot of air being 20-40% higher than the stoichiometric air needed and a necessary temperature of between 600 and 1300°C [11].

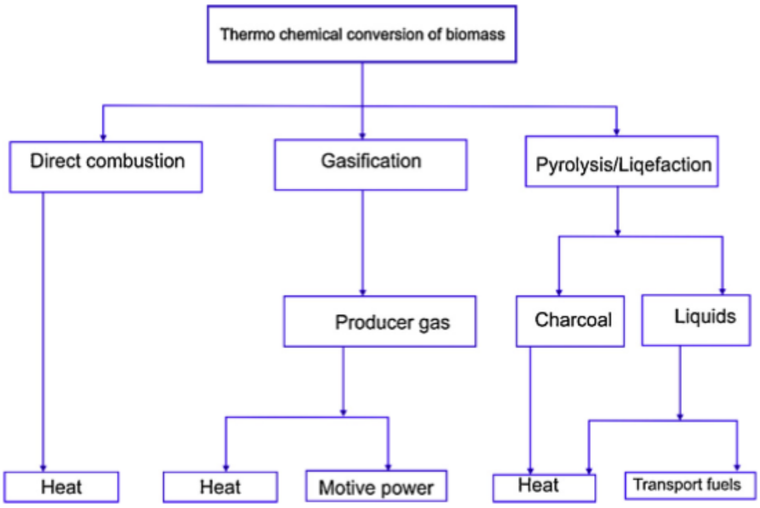


Figure 2. Thermochemical conversion route of biomass [34].

Gasification consists of heating biomass in the presence of oxygen in a controlled manner, with the aim of producing a combustible gas. This process must be carried out in a closed container with a smaller amount of air than is necessary for complete combustion to take place. The objective of the fuel gas is to burn it either in a burner to obtain thermal energy, in a boiler to produce steam or it can be cooled and used in an internal combustion engine to produce mechanical energy.

Pyrolysis is a process similar to gasification, in this process a partial and controlled oxygenation of the biomass is carried out, to obtain as a product a combination of variable fuels, solid fuels (charcoal), liquids (pyrolysis effluents) and gases (lean gas) [11] at maximum temperature, known as the pyrolysis temperature. Pyrolysis is an essential pre-step in a gasifier, which can be faster or slower depending on the type of reactor [26].

1.2. OBJETIVES

Biomass can be easily upgraded through thermochemical conversion processes, such as gasification and pyrolysis, to produce biofuel. These processes are greatly influenced by the feedstock's physical and chemical properties, namely the presence of inorganics. The main objective of this work is to assess experimentally the effect of inorganics on the pyrolysis behaviour of biomass. For this, several agricultural residues were demineralized, mixed, and completely characterized. These residues were pyrolyzed in different reactors to assess the effect of their inorganic composition on this process. Raw, demineralised, and doped samples were analysed in order to compare the different results between samples with higher and lower inorganic content in order to draw conclusions about the influence of inorganics on the pyrolysis process. The experiments carried out were a thermogravimetric analysis and pyrolysis in a horizontal reactor in order to analyse the mass loss that occurs during the pyrolysis in each of the different samples and on the one hand, it is carried out in a horizontal reactor in order to analyse the non-condensable gases of the selected samples and to study the influence of the ashes on the elements present in them.

1.3. THESIS OUTLINE

The general objectives of this work is to study the effect of inorganics on the pyrolysis behaviour of horse manure and walnut shells. The specific objectives are as follows:

- Demineralize horse manure and walnut shells to remove some of the inorganics present in the biomass.
- Characterise the raw and demineralised samples to study the difference between them.
- Mix walnut shells and horse manure to evaluate the effects of adding ashes on pyrolysis.
- Subject the raw and demineralised horse manure, the mixture and the walnut shells to a thermogravimetric experiment in order to analyse the differences in the pyrolysis of each.
- Perform a pyrolysis experiment in a horizontal reactor of raw and demineralised horse manure, the mixture and the walnut shells to analyse the exhaust gases and confirm the correct functioning of the reactor by comparing the difference in mass loss that occurs in the pyrolysis in the horizontal reactor and in the thermogravimetric analysis.

2. THEORETICAL FOUNDATIONS

2.1 BIOMASS CHARACTERIZATION

Biomass can be classified into a variety of groups, for example by origin, waste, natural and produced biomass. Residual biomass comes from domestic or industrial waste, natural biomass is all that which is found in nature without human intervention and finally, produced biomass is that which comes from crop fields whose only purpose is to be used for energy. Another way to classify biomass can be by relating the biofuel produced according to the origin of the biomass as shown in Table 1.

Table 1. Classification of biofuels according to their origin [9].

Origin		Species	
Types	Energy crops	Agriculture	Thistle, sorghum, sunflower, soybean, corn, etc.
		Forestry	Poplars, willows, eucalyptus, etc.
	Remains of silvicultural treatments	Pruning, thinning, thinning, final cuttings, etc.	Forest species in forests
	Municipal solid waste	Originated in population centres as a consequence of the usual and daily activity of the human being.	
	Industrial forestry residues	Industries of first transformation of wood	Imported timber species used by the industry
		Secondary wood processing industries	Imported timber species used by industries

Biomass is any material of present or near-present animal or plant origin. This also includes agricultural, industrial organic and human waste. It is difficult to find a good definition that encompasses all that this term means, however the definition used by the United Nations Framework Convention on Climate Change (UNFCC, 2005) it is useful in this context [1]:

“Non-fossilize and biodegradable organic material originating from plants, animals, and micro-organisms. This shall also include products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and biodegradable organic fractions of industrial and municipal wastes”

To effectively produce fuels and chemicals from biomass as well as to assess technical and economic feasibility, it is of high importance to understand the organic and chemical composition of the feedstock material.

The structural organic composition of the biomass is mainly composed of five components: cellulose, hemicellulose, lignin, extractives and ash. The first, cellulose is the most abundant biopolymer on earth, consequently also in biomass. Hemicellulose, the second most abundant component in biomass, is an heteropolymer composed of several different carbohydrates, such as xylose, mannose and glucose, among others. Cellulose and hemicellulose, combined with the third main component of biomass, lignin, constitute more than 90% of lignocellulosic biomass and 80% of herbaceous biomass. Lignin is an assemblage of aromatic alcohols and is intertwined with the cellulose and hemicellulose fraction of the biomass structure.

It is also important to know that the major components are interrelated as shown in Figure 3 where cellulose is found in the form of elongated fibres, surrounded by hemicellulose which forms a kind of network around it. The lignin is located between the 'strings' formed by the association of cellulose and hemicellulose [9].

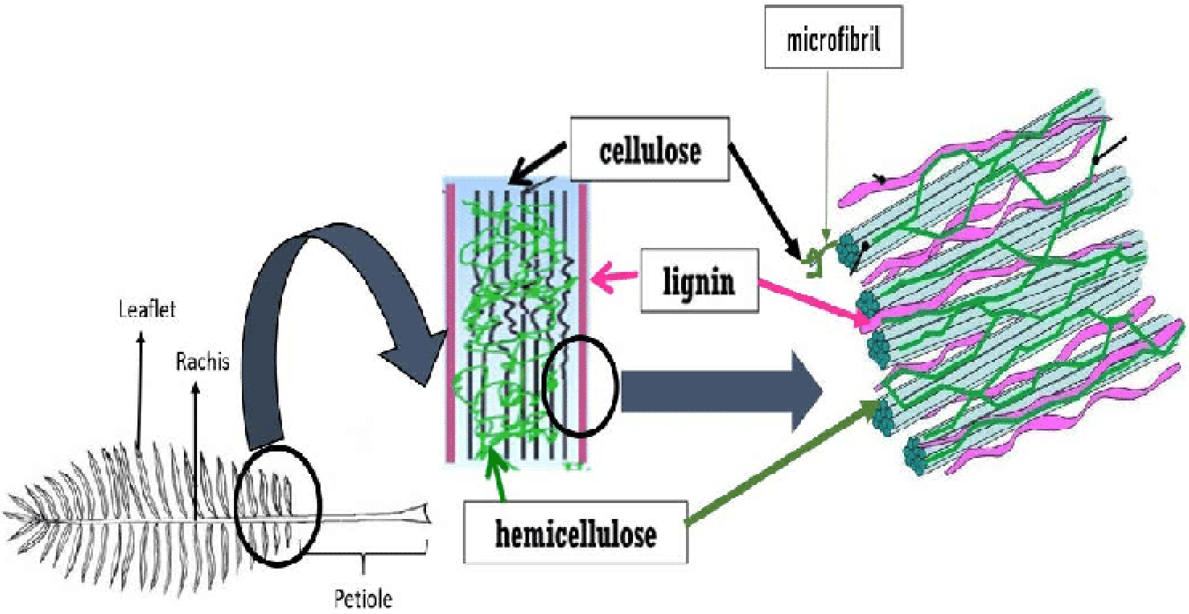


Figure 3. Biomass internal structure [35].

Moreover, the other minority components present in the biomass are extractives and ash. Although these components represent a very small portion of the biomass mass, they have a great influence on the biomass conversion process. The components comprising the extractives include, aliphatic and aromatic hydrocarbons, alcohols, phenols, aldehydes, ketones, aliphatic acids, waxes, glycerides, nitrogenous, water and ethanol. Water-soluble compounds include non-structural sugars and proteins, and ethanol-soluble components are typically represented by chlorophyll and waxes.The extractives contribute to properties such as, colour, odour, durability, adhesion, drying and discolouration. On the other hand, ash is the inorganic part of biomass, can be intrinsic to the biomass or added anthropogenically. Intrinsic ash includes material-like calcium and potassium ions, while anthropogenic ash is mostly silica (dirt) collected during harvest. [8]

The composition of biomass is made up of a large number of elements, but only 20 are indispensable, and of these 20, not all are found in the same proportion. In fact, those that make up 96% of the dry biomass are called macroelements because of their high proportion. These macroelements are carbon (C), hydrogen (H), nitrogen (N), phosphorus (P) and sulphur (S). Among these, carbon and oxygen are the most present elements with 43 and 48 wt.% db, followed by hydrogen with 5.5-6.5% and finally nitrogen with a proportion of between 1.5 and 5%.

Other elements that are also essential in the biomass but are found in smaller quantities are calcium (Ca), sodium (Na), potassium (K), chlorine (Cl), iodine (I), magnesium (Mg) and iron (Fe), which have an abundance of approximately 3.9 wt. %db [12].

It should be added that each element has an influence on the energy characteristics and therefore on the processes that act on it, be it combustion, corrosion, etc. As in the case of carbon (C), hydrogen (H) and oxygen (O), the first two release energy when oxidised, while oxygen contributes to combustion by reducing the amount of air required for complete combustion.

2.2 BIOMASS EXPERIMENTAL CHARACTERISATION

The objective of biomass characterization is to determine the composition and main properties of biomass. This is of great importance since the complexity of using biomass as an energy source lies in the great variability of existing species from a structural, physical, chemical and energy point of view. Therefore, it is essential to characterise biomass in order to assess its behaviour as a fuel. In fact, the transformation conditions are as important as the characteristics of the fuel itself. Consequently, biomass characterisation, apart from providing information on the chemical, physical and energy particularities of biomass, also provides knowledge on the optimal way to transport, store or introduce it in the energy conversion equipment, as well as to estimate the amount of fuel to be generated. In conclusion, it is necessary to know all these parameters in order to achieve the goal of transforming biomass into fuel [13].

Figure 4 shows the different experiments that can be done to the biomass in order to analyse its composition with different objectives.

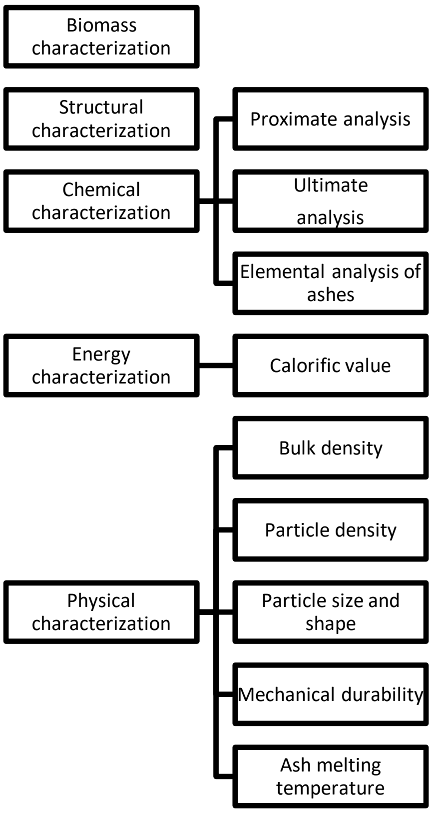


Figure 4. Biomass analysis.

Of all the analyses shown in the figure above, the ultimate analysis is highlighted as it is one of the most widely used for the type of study carried out in this paper and the proximate analysis as it is the one used. Furthermore, in this study, an analysis not shown in the figure was also carried out, which is the thermogravimetric.

Ultimate analysis is an analytical technique that allows to obtain the total content of carbon (C), hydrogen (H), nitrogen (N) and sulphur present in a biomass sample, either solid or liquid. This process is carried out by volatilising the sample through combustion in pure oxygen conditions. This can be done with a reactor, which will determine the four chemical elements: carbon, hydrogen, nitrogen and sulphur. Oxygen, on the other hand, is obtained by difference.

The aim of the proximate analysis is to obtain the content of moisture, ash, volatile materials, and fixed carbon contained in a biomass sample based on standard EN 18122.
This process follows different steps in order to extract the desired values. These values are: the moisture which is the water present in the sample, the ashes which are the inorganic residues produced during the complete combustion of the biomass, and the volatiles which correspond to the organic compounds that degrade during the combustion of the material, generating liquid and gaseous products. Finally, the fixed carbon can be calculated once the values of the other sample parameters have been obtained, as this is the solid residue resulting after the separation of moisture, ash and volatiles at a given temperature.

Thermogravimetric analysis is a technique whose objective is to measure the physical and chemical changes that a sample undergoes as a function of temperature or time under controlled conditions. Thermogravimetry itself encompasses a set of analyses. Dynamic analysis consists of continuously recording the variation of the mass affected by a linear change in temperature, isothermal analysis consists of keeping the temperature constant over a period of time.
This technique has a wide range of applications because it represents very valuable information for research as it allows studies of evaporation of volatiles, decompositions in inert or oxidising atmospheres, as well as oxidation and ferromagnetism studies. [14]

“TGA allows the collection of hundreds or even thousands of data for a single experiment, but it is necessary to filter them in order to select a representative number of data and eliminate noise in the measurements; too little data would cause loss of information and too much data would cause unnecessary high computational expense.” [16]

From this analysis, neither the chemical composition nor the thermal variations related to changes in mass are obtained, but rather the variation of mass with respect to temperature or time is obtained, all of which is represented in a graph called a thermogram.

Figure 5 shows a typical representation of a thermogram.

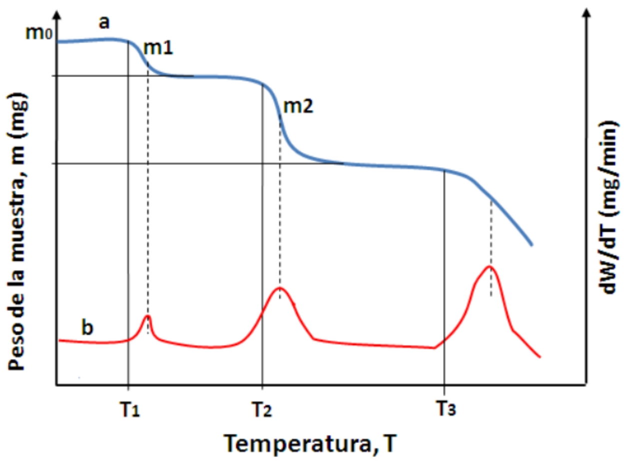


Figure 5. Thermogram a) conventional (blue curve and left axis), b) differential (red curve and right axis) [15].

"For this type of analysis a modern instrumentation is needed whose main parts are: a) an analytical balance, responsible for providing quantitative information on the mass of the sample, usually ranging from 5 to 20 mg b) an oven where the sample holder is located, its temperature can be increased from ambient to 1000 °C, c) a purge gas system, usually nitrogen or argon, which is used to displace the air in the sample chamber and prevent oxidation of the sample. And d) a microprocessor to prevent instrument control and data processing." [15]

2.3. PYROLYSIS

Pyrolysis is a thermochemical decomposition of biomass into a variety of different useful products with many applications. During pyrolysis a variety of complex hydrocarbon molecules from biomass are broken down into small molecules of gas, liquid, or char. This process can occur in the complete absence of oxidising agents or with a small amount of oxidising agents that do not allow gasification to take place [26].

Condensable gases and solid char are the initial products of pyrolysis. Condensable gas can be decomposed into non-condensable gases such as CO, CO_2, H_2 and CH_4, liquids and char. This decomposition occurs on the one hand in a homogeneous gaseous reaction and on the other hand in a heterogeneous thermal solid-gas reaction. [26]

Pyrolysis can be represented by such a reaction:

$$C_nH_mO_p(biomass) \rightarrow \sum\nolimits_{liquid} C_xH_yO_z + \sum\nolimits_{gas} C_aH_bO_c + H_20 + C\ (char)$$

Equation 1. Pyrolysis reaction.

Pyrolysis is carried out in a temperature range of 300-650 °C [26]. This temperature must be obtained in such a way that the biomass is heated rapidly in the absence of oxygen to a maximum temperature, which is called the pyrolysis temperature and must be maintained for a specified period of time to produce the non-condensable gases, solid char and the liquid product. The solid product of pyrolysis is biochar, which makes it a great alternative to burning agricultural products or forest residues emitting carbon into the atmosphere, as biochar would retain a large part of this carbon in its stable solid form in the earth for many years, which is why biomass pyrolysis is becoming of great environmental interest. The liquid product is of great importance and its characteristics depend on different factors including pyrolysis temperature and heating rate.

As previously mentioned, the products obtained from pyrolysis are liquid (tars, heavy hydrocarbons, and water), solid (mostly coal) and gas (CO_2, H_2O, CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6) and the proportion of each product depends on the operating conditions.

The liquid product of pyrolysis, also called tar, bio-oil or biocrude, is mainly composed of homologous phenolic compounds, a mixture of complete hydrocarbons with a large amount of oxygen and water. This liquid is formed from a rapid and simultaneous depolymerisation and fragmentation of cellulose, hemicellulose, and lignin compounds. In a typical operation, the biomass is subjected to a rapid increase in temperature followed by an immediate quenching to "freeze" the intermediate pyrolysis products. Rapid quenching is important, as it prevents further degradation, cleavage, or reaction with other molecules. [26]

The solid product of pyrolysis, also called biochar, is composed mainly of carbon but also contains some oxygen and hydrogen.

The gaseous product of pyrolysis is decomposed into condensable gases (vapour) and non-condensable gases. The condensable gases after cooling in a condenser will become part of the liquid product and the primary non-condensable gases are formed by a mixture of low molecular weight gases such as CO, CO_2, CH_4 and C_2H_6 which do not condense on cooling. In addition, non-condensable gases are added through secondary cracking of the vapour at a higher temperature, these are called secondary gases and the set of primary and secondary gases form the total of non-condensable gases. [26]

In order to understand the pyrolysis process, it is important to keep in mind the reactions that take place in the transformation of cellulose, hemicellulose and lignin.

The thermal composition of cellulose is a complex process, currently according to Anca Couce [27], it is understood that the pyrolysis of cellulose is divided into two processes, which are primary pyrolysis and secondary reactions. In primary pyrolysis, depolymerisation and formation of a liquid intermediate compound (active cellulose) takes place, which is where fragmentation occurs, producing carbonyl groups and transgycosylation, which produces the majority of LGA (levoglucosan). The products of these primary reactions can lead to secondary reactions in a condensation phase or already outside the cellulose matrix. Carbon formation is one of the secondary reactions, another reaction that takes place is the cracking of volatiles that can occur inside or outside the cellulose matrix.

In relation to hemicellulose, there is not as much information as for cellulose, however, there are many similarities between the processes that give rise to cellulose and hemicellulose.

Finally, lignin has a more complex structure than cellulose and hemicellulose and its reaction is also more complex. In a simplified form, it consists of a first phase where the compound liquid is formed, which will react giving rise to pyrolytic lignin, permanent gases and condensable light species (water, carbonyls and alcohols). Then, there are also secondary reactions which occur inside or outside the lignin matrix and can result in phenolic monomers, carbon, gases, and condensable light species.

A diagram of the reactions that take place in the pyrolysis process with their respective products can be seen in Figure 6.

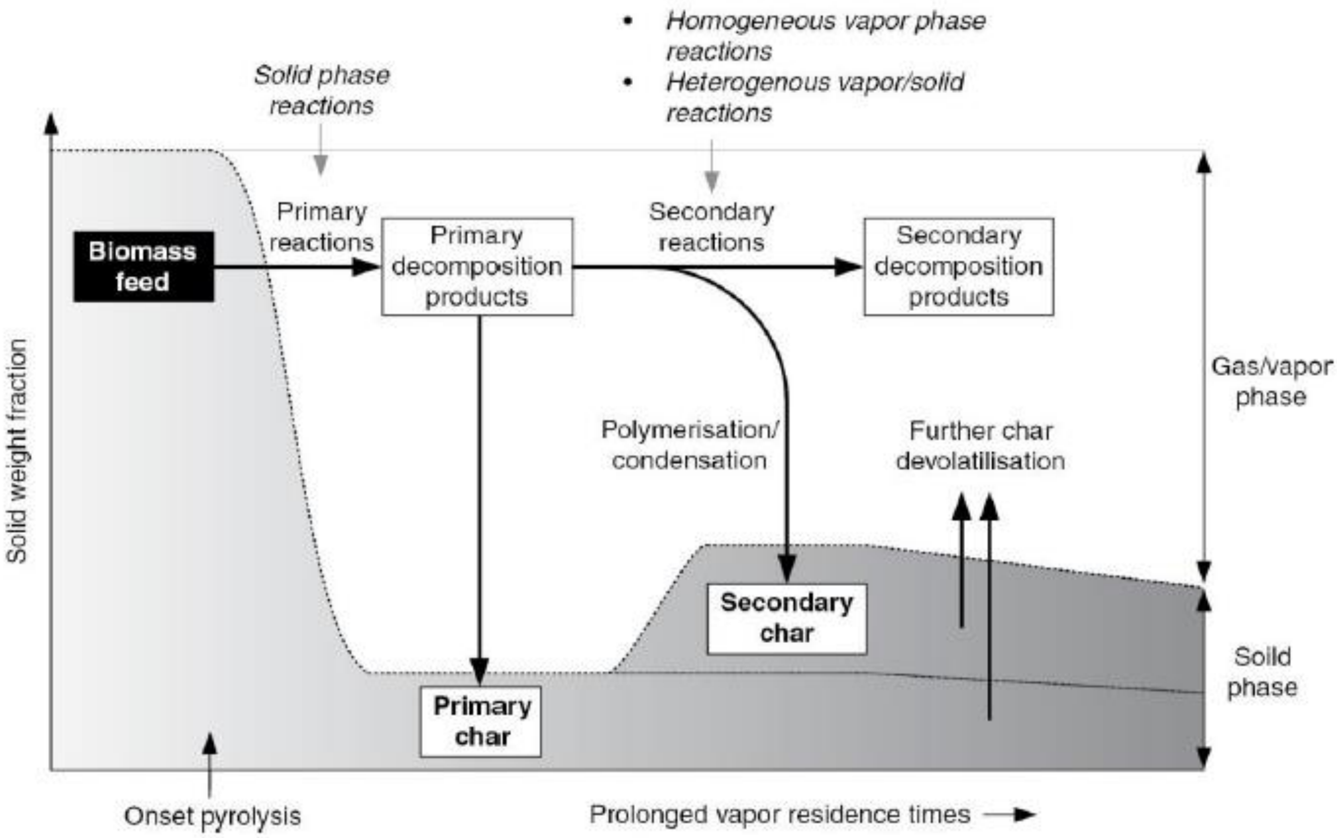


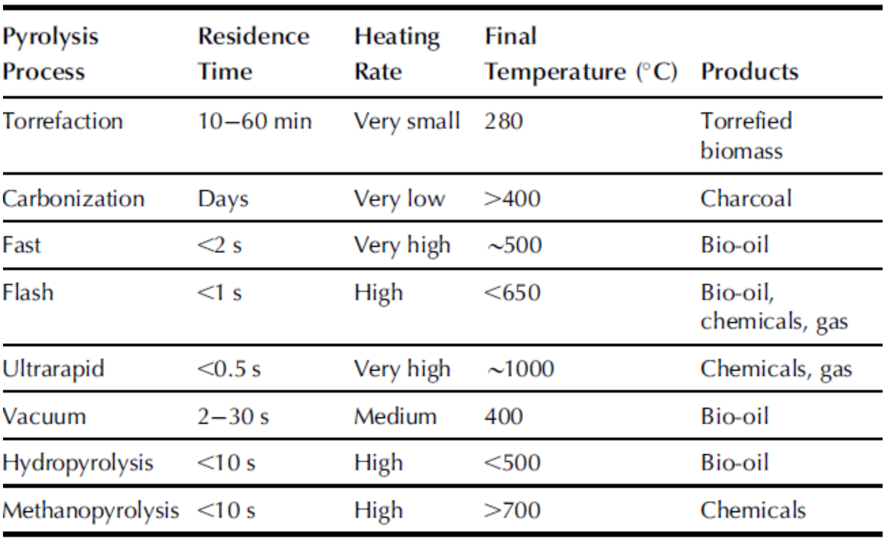
Figure 6. Pyrolysis process [28].

There are different types of thermal decomposition processes, depending on the medium, pressure, and operating conditions, each has its own characteristic products and applications. Slow and fast pyrolysis are based on the heating rate as they usually occur in the absence of medium while hydrous pyrolysis and hydrous pyrolysis are based on the medium where the pyrolysis takes place being H_2O in the first case and H_2 for the second, these two types are mainly used for the production of chemicals. [28]
As just explained, slow and fast pyrolysis are based on the heating rate, slow pyrolysis can be considered when the t_heating, heating time, needed to heat the fuel to the pyrolysis temperature is much longer than the time of the pyrolysis reactions, tr and for fast pyrolysis vice versa, that is: [26]

- Slow pyrolysis: $t_{\_heating} >> t_r$
- Fast pyrolysis: $t_{\_heating} << t_r$

In slow pyrolysis, the residence time of the vapour in the pyrolysis zone is quantified in terms of minutes. Moreover, it is not used for traditional pyrolysis, where the main objective is to obtain the liquid, but is mainly used to obtain carbon and is broken down into two types: carbonisation and torrefaction [26].

Table 2. Characteristics of some decomposition processes [26].



Pyrolysis Process	Residence Time	Heating Rate	Final Temperature (°C)	Products
Torrefaction	10–60 min	Very small	280	Torrefied biomass
Carbonization	Days	Very low	>400	Charcoal
Fast	<2 s	Very high	~500	Bio-oil
Flash	<1 s	High	<650	Bio-oil, chemicals, gas
Ultrarapid	<0.5 s	Very high	~1000	Chemicals, gas
Vacuum	2–30 s	Medium	400	Bio-oil
Hydropyrolysis	<10 s	High	<500	Bio-oil
Methanopyrolysis	<10 s	High	>700	Chemicals

As it is shown in Table 2 in fast pyrolysis, the vapour residence time is given in terms of seconds or milliseconds. This type of pyrolysis is mainly used for bio-oil and gas production, and there are two main types: flash and ultra-fast.

The main objective of this fast pyrolysis is to maximise bio-oil production. The biomass is heated so rapidly that it reaches the pyrolysis temperature before decomposition, this temperature should be 650 °C if the objective is to obtain bio-oil, but can be as high as 100°C if the objective is to obtain gas. However, the heating rate can be as high as 1000-10000 °C /s. [26]

There are 4 characteristics that improve fluid production, which are [26]:

- a high heating rate
- a reaction temperature ranges between 425-600 °C
- a short vapour residence time (<3s)
- rapid cooling of the product gas

Another important characteristic to take into account is the size of the biomass particles,

In this type of pyrolysis, the most commonly used reactor is the fluidised bed reactor, as they are able to obtain better heat transfer and mixing conditions. However, transported bed, circulating bed, rotating cone ablative, screw and microwave reactors are also used. [28] Van del Velden et at. [29] showed that theoretically the particle size of biomass should be less than 200um, however, the range used in practice is between 100 and 3000um.

2.3.1 OPERATION CONDITIONS

Pyrolysis is an endothermic process, i.e., it needs an external heat source to reach the activation energy and is composed of a complex set of reactions that can take place sequentially (one after the other), or simultaneously (at the same time). [16]
Figure 7 shows schematically the materials supplied, the products obtained and the variables that affect the process of pyrolysis. [16]

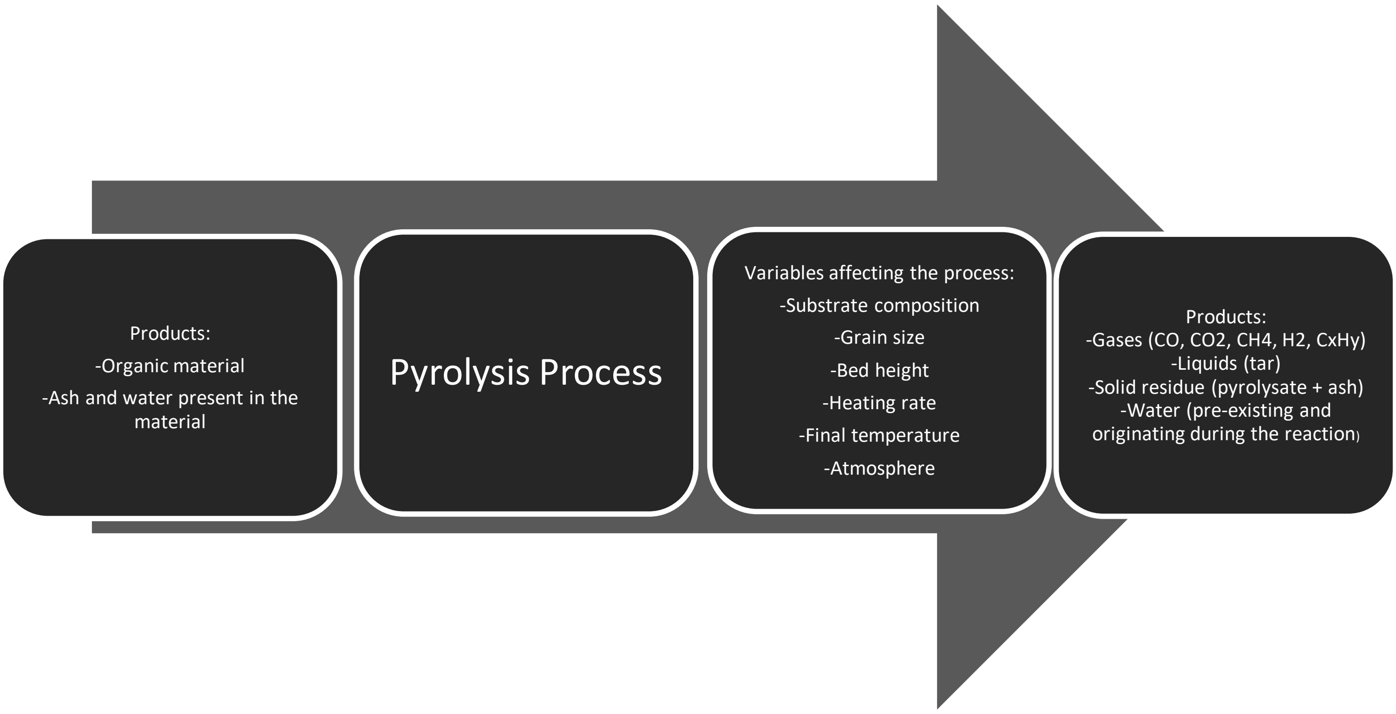


Figure 7. Pyrolysis operation conditions [16].

The different variables that affect the pyrolysis process are:

- Biomass composition, in studies conducted in [16] it has been found that the effects of the materials on pyrolysis can be described as a superposition of the individual effects suffered by the constituent elements of the same under this process. Also, a relationship is obtained with the presence of impurities represented in the ash content of the biomass, these affect the temperature at which decomposition of the biomass begins and the relative amounts of char and tars produced [16] page 51 of ref [33].

- Grain size, the larger the particle size, the longer it takes for the products to leave the particle, promoting secondary reactions, the presence of thermal gradients and the condensation of the volatile phase on the particle surface, increasing the production of solid residues. On the other hand, if the particle has a small grain size the reactions are homogeneous, in a single phase. [16]

- Reaction atmosphere, the influence of which is reflected in the secondary reactions. When carried out under vacuum atmospheres, the development of side reactions is prevented, while increasing the pressure causes the opposite effect. [16]

- Final process temperature, this for a pyrolysis process with a given heating rate is linked to the residence time, which is the length of time during which the solid material or biomass degrades under the influence of temperature, since the temperature increases as a function of time.

In addition, as in this study it is carried out a fast pyrolysis, the different operating conditions that influence this type of process will be explained below [30].

- Influence of reaction temperature, in fast pyrolysis it is known that the reaction temperature has a great influence on the reaction products, the role of this temperature in this type of pyrolysis is to provide sufficient heat for the decomposition of the biomass bonds. The efficiency of biomass conversion increases with increasing reaction temperature, this temperature increase has a positive effect on the yield of the pyrolysis liquid, but at higher temperatures the opposite effect has been found.

The quality of the pyrolysis liquid is an important parameter depending on the application. In general, high temperatures increase the carbon content in the pyrolysis liquid and reduce the oxygenation concentration due to decarboxylation and dehydration reactions. Moreover, the trend of oxygen content with reaction temperatures has the same shape as the ratio of water content to reaction temperature. That is, increasing water content leads to higher oxygen content.

Therefore, as the reaction temperature in the reactor increases, the water content of the pyrolysis liquid first decreases and then increases while the higher heating value (HHV) has the opposite behaviour.

- Influence of inlet gas velocity, in fast pyrolysis the residence time of the steam produced by the reactions in the reactor is a very important factor influencing the yield of the pyrolysis gas and pyrolysis oil products. Fast pyrolysis is characterised by a very short vapour residence time which results in a good yield of pyrolysis oil. When longer residence times occur, side reactions such as recondensation, repolymerisation and carbon formation can occur, leading to a reduction of the pyrolysis oil yield. This residence time can be controlled by the fluidisation gas flow rate, however, variation of the gas flow rate can also change the fluidisation regime, therefore it is important to know the effects of the inlet gas velocity on the product yield and the physicochemical properties of the pyrolysis oil.

According to a study, as the inlet gas velocity increases, the particle jet becomes more vigorous, which improves the mixing between the bed materials and the biomass particles. At the same time, the vapour residence time is shorter, which leads to a lower probability of secondary cracking reaction of the tar. However, at very high gas inlet velocities, it reduces the pyrolysis oil yield due to incomplete condensation of volatiles, which increases the gas yield in fast pyrolysis.

- Influence of biomass feeding rate, this has a great effect on the performance of fast pyrolysis products, as it influences the fluidisation pattern, gas flow rate, solid particle mixing, heat transfer, etc. A higher feed rate increases the gas flow rate, which leads to a shortening of the steam residence time and avoids secondary steam cracking, resulting in improved pyrolysis performance. However, it should not be forgotten that a higher feed rate requires more heat and more space in the reactor than a lower feed rate. Therefore, when the pyrolysis capacity of the reactor cannot adapt to the higher feed rate, the pyrolysis oil yield decreases slightly. In addition, if the feed rate is too high, the gas volume increases and results in a low partial pressure of the condensable vapours, which reduces the amount of pyrolysis oil.

- Influence of biomass particle size, biomass is a poor conductor of heat. Therefore, the size of the biomass particles has an influence on the performance and is of great importance to improve heat transfer problems in the fast pyrolysis process. Large biomass particles take longer to heat up, which can lead to an incomplete fast pyrolysis process and therefore to low pyrolysis oil yields and high carbon yields. This is explained by the fact that as the particle size increases, the heat residence distance from the particle surface to the centre of the particle increases. This slows down the rapid heat transfer from the hot bed materials to the cold biomass particle. As a result, the fast pyrolysis reaction is not completed, and the amounts of generated volatiles and pyrolysis oil decrease.

Thus, smaller particles are preferred for fast pyrolysis due to faster and more uniform heating. However, if the particles are too small, they can be removed from the reaction zone following the flow before the pyrolysis is completed. Therefore, it can be concluded that the particle size can vary depending on the type of pyrolysis.

3. PREVIOUS STUDIES

3.1 BIOMASS CHARACTERIZATION

There are different types of biomass in the research carried out by Laura Camila Buitrago, a study of some of these was carried out in order to characterise different biomasses with high energy potential, this study was a step towards carrying out the kinetic analysis of the pyrolysis of the biomass. In the study of the biomasses, the proximate and elemental analysis was carried out, as well as the content of the characteristic compounds of the biomass corresponding to cellulose, hemicellulose, and lignin. After these analyses, a thermogravimetric analysis was carried out to identify the loss of mass as a function of temperature, in order to establish the relationship between the variation in mass and the reaction rate of the process [17].

This research demonstrates the importance of knowing the physical-chemical characteristics of the biomass in the energy transformation process. Table 3 shows the hemicellulose, cellulose and lignin contents for the coffee husks collected from the literature.

Table 3. Lignocellulosic content of coffee husks [17].

	Hemicelullose (%)	Celullose (%)	Lignin (%)
Arias Ortiz Angelica and Meneses Cruz, Juan Daniel	47,37	36,7	15,93
Murthy, Pushpa and Naidu, Madha	7	43	9
Reinhardt, Hans-Wolf	29,7	24,5	23,7

As can be seen from Table 3, the composition of the biomasses is relative and dependent on the origin of the study sample. Since, all samples belong to the same type of biomass, however, they have different contents of hemicellulose, cellulose and lignin.

On the other hand, as it is shown in table 4. Laura Camila's research also provides literature data of proximate and elemental analysis of the above-mentioned biomass, coffee husks.

Table 4. Proximate and elemental analysis of coffee husks [17].

	Proximate analysis (%)			Elemental analysis (%)			
	Moisture	Volatile Matter	Ash	C	H	O	N
Gomez, A	10,1	82	1,2	50,3	5,3	41,7	<1
Fonseca, Felix	13,1	73,2	3,7	47,5	6,4	43,7	
Becerra, Javier	8,7	90,24	0,76	47,6	6,54	45,33	0,38

Table 4. presents the values obtained from different bibliographic searches, and also explains how it is considered normal for the values obtained between the different samples to be different due to their different origin and the characteristics of each seed. However, it informs us about the values around which the ash, moisture and volatile matter content should oscillate since, despite having a wide range of values, it provides an idea of the characteristic limits of the coffee husk. As for the elemental analysis, there is a greater similarity between them, so it is concluded that as long as the biomass belongs to the same origin, its values can be approximated to those found in this table.

Furthermore, valuable information can also be obtained from the thesis of Jose Penedos [18], where the influence of ash on wheat straw biomass in the pyrolysis and gasification process was analysed by characterising the biomass samples and subjecting them to different thermochemical processes. The biomass samples consisted of Wheat Straw demineralised in different ways as shown in Table 5. A sample A demineralised at a 1:20 ratio of water:biomass at 30°C for 1h, a sample B demineralised at a 1:40 ratio of water:biomass at 30°C a sample C demineralised at a 1:20 ratio of water:biomass for 24h at 30°C and a last sample, D, demineralised at a 1:40 ratio for 24 h at 30°C. From this analysis, it was possible to draw conclusions about the demineralisation processes, concluding that the longer the leaching time, the greater the efficiency in removing ash from the sample. Furthermore, of the samples that were leached for 24 h, it was found that the lower the water/biomass ratio, the greater the efficiency of ash removal. Therefore, process C was selected as the most efficient process for ash removal.

Table 5. Proximate analysis of wheat straw performed in a previous work [29].

Demineralization Process	Leaching Time (h)	Temperature (°C)	Water/Biomass Ratio (mL/g)	Ash Relative Variation (wt. % db)
A	1	30	1:20	-30.6
B	1	30	1:40	-31.9
C	24	30	1:20	-59.9
D	24	30	1:40	-58.9

Regarding the proximate analysis carried out on the demineralised samples under different conditions, the results obtained are shown in Figure 8. It can be observed from the values of the volatiles, ashes and fixed carbon present in the samples that besides showing the evident reduction of ashes in the demineralised biomass, it also presents a higher percentage of volatiles and a decrease of fixed carbon as the leaching time increases and the water/biomass ratio decreases. Furthermore, the analysis of the results shows that the demineralised biomass is significantly less dense than the non-demineralised biomass.

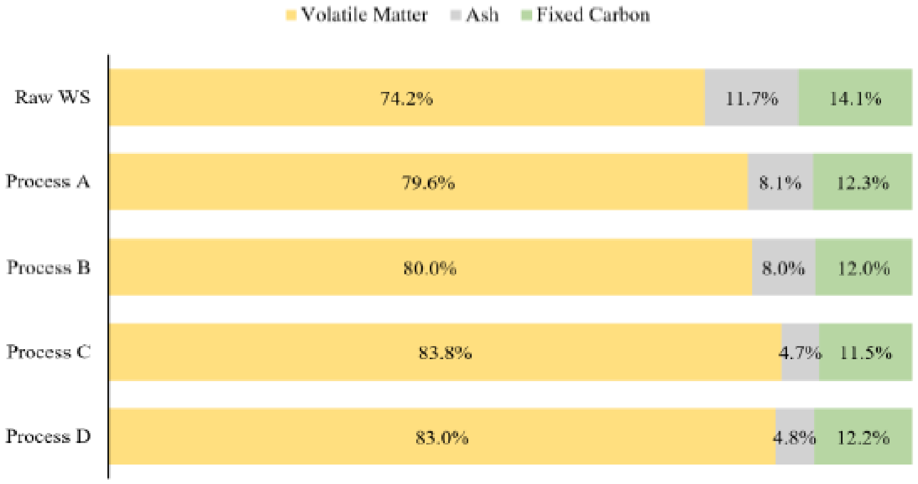


Figure 8. Proximate analysis of wheat straw performed in a previous work [18].

Moreover, in this thesis a chemical characterisation was also carried out to study the composition of the demineralised and non-demineralised biomass, Table 6 shows the results of the analysis [18].

Table 6. Organic analysis from Jose's Penado's thesis [18].

Sample	**Lignin (wt. % daf)**	**Hemicellulose (wt. % daf)**	**Cellulose (wt. % daf)**	**Extractives (wt. % db)**
Raw WS	46.2	11.5	42.3	17.7
Demineralized WS	43.9	10.6	45.5	10.4
Literature	18 - 30	18 - 35	29 - 43	-

In his study it can be observed that there is a 7.3 wt.% db difference in extractives, between raw and demineralised Straw wheat. Contrasting it with the proximate analysis it can be concluded that an absolute reduction of 7% wt.% db was achieved in ash content, this reduction in extractives can be attributed to the pre-treatment deashing.

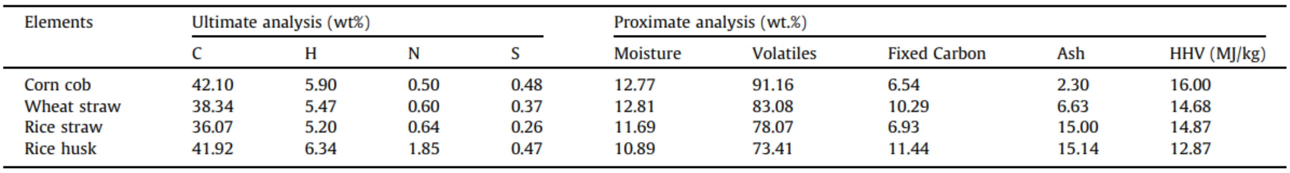
3.2 PYROLYSIS

In the research conducted by Bjoy Biswas, Nidhi [31] the behaviour of four agricultural biomasses in the pyrolysis process were studied. The pyrolysis processes were carried out in fixed bed reactors at different temperatures 300, 350, 400 and 450°C. The biomasses studied were corn cob, wheat Straw, rice Straw and rice husks which showed optimum temperatures of 450, 400, 400 and 450°C respectively. The process was carried out in a glass reactor at atmospheric nitrogen pressure starting at an ambient temperature of 25°C and a heating rate of 20 °C /min, once the pyrolysis temperature was reached, the reactor was kept at the required temperature for 1h to ensure that all condensable vapours were collected. The products obtained from the pyrolysis were gas, oil and coal.

The maximum pyrolysis oil yields were 47.3, 36.7, 28.4 and 38.1 wt.% for corn cob, wheat straw, rice star and rice husks respectively. With the increase in temperature from 300 to 400°C, the pyrolysis oil increased in the case of wheat straw and rice straw, with further increase in temperature the yield of the liquid decreased. However, in the case of corn cob and rice husk, with increasing temperature from 300 to 450°C, the oil yield increased. The char yield for corn cob, wheat star rice Straw and rice husks decreased as the temperature increased from 300 to 450°C and the gas yield increased steadily from 350 to 450°C. It could be concluded that the distribution of the products obtained at different temperatures from the different types of biomass suggested that it had a significant effect on the product distribution due to the structural differences of the different biomasses, as shown by their thermogravimetric analysis.

Prior to pyrolysis, a characterisation of each biomass was carried out as it is shown in table 7, where according to the values obtained shown in the graph below, it can be seen from the proximate analysis that the carbon and hydrogen content in rice husks and corn cob were higher than in rice Straw and wheat Straw. On the other hand, sulphur and nitrogen were found in low proportions in all samples except rice husks which had the highest nitrogen content and corn cob which had the highest sulphur content. As for moisture content, all samples showed different values from each other. The lowest volatile content was found in rice husks with a value of 73.41 wt.% and the highest content in corn cob with a value of 91.16 wt.%. Regarding the ash content, the corn cob and wheat straw samples showed values lower than 7 wt.% while in the case of rice star and rice husks they had a substantially higher content being higher than 15 wt.%. This is beneficial since agricultural residues with higher ash content have the potential to be used as catalysts in different thermal conversion technologies, such as gasification and pyrolysis.

Table 7.Ultimate and proximate analysis of Corn cob, Wheat straw, Rice straw and Rice husks [31].



Elements	Ultimate analysis (wt%)				Proximate analysis (wt.%)				
	C	H	N	S	Moisture	Volatiles	Fixed Carbon	Ash	HHV (MJ/kg)
Corn cob	42.10	5.90	0.50	0.48	12.77	91.16	6.54	2.30	16.00
Wheat straw	38.34	5.47	0.60	0.37	12.81	83.08	10.29	6.63	14.68
Rice straw	36.07	5.20	0.64	0.26	11.69	78.07	6.93	15.00	14.87
Rice husk	41.92	6.34	1.85	0.47	10.89	73.41	11.44	15.14	12.87

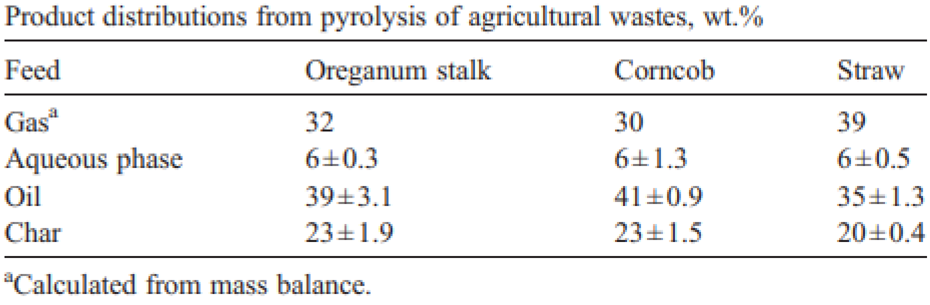
The thermal decomposition of the four residues was determined by thermogravimetric analysis in a nitrogen atmosphere. Thermal decomposition consists mainly of three stages: moisture loss at a temperature of about 100°C, a primary pyrolysis in a temperature range of 200-500°C and a secondary decomposition at high temperatures above 700°C.

For the lignocellulosic biomasses analysed, the main thermally degradable biopolymer classes are cellulose, hemicelluloses and lignin. Hemicellulose decomposes in the temperature range 220-315 °C. Pyrolysis of cellulose occurs in a higher temperature range (315-400 °C). Among the three components, lignin is the most difficult to decompose, covering a wider temperature range of up to 900 °C. The DTG showed the maximum weight loss in four agricultural residues was between 310 and 342 °C. The highest decomposition of agricultural residues occurred slowly over a wide range (300-450 °C) of temperatures with maximum mass loss rate at 312, 310, 302 and 342°C for corn cob, wheat straw, rice straw and rice husk because the final, proximate and chemical composition was different in different agricultural residues.

In another research by Jale Yanik and Cristoph Kornmayer [32] the performance of different pyrolysis products, char, liquid and gas from different agricultural residues (corn cob, corn star and oreganum stalks) was analysed. The pyrolysis process was carried out in a fluidised bed reactor at a temperature of 500°C. The liquid yield was between 35 and 41 % depending on the type of biomass. The chemical composition of the gases and char were also determined.

The fluidised bed reactor had an internal diameter of 40 mm and a length of 300 mm. The bed material was 450 µm silica sand with a bed depth of 37 mm. The feeding system consisted of a hopper and a screw feeder. The nitrogen was split into two streams, one to the reactor as a fluidising gas and the other (b10%) to the feeder to entrain the biomass. The gas velocities were determined by preliminary experiments and were between 0.25 and 0.3 m/s at operating temperatures. The residence time of the gas in the reactor was around 1-2 seconds. In each experiment, after the system reached steady state at 500 °C, the screw conveyor was started, and 100 g biomass was uniformly fed into the reactor. All system components were weighed separately before and after each run to determine the total weight of coke and pyrolytic oil. The amount of gas was determined by difference. As I have already mentioned in different sections, temperature plays an important role in the pyrolysis of biomass. In this case, the pyrolysis temperature was chosen on the basis of the literature to investigate the effect of temperature on the pyrolysis experiment. The experiments ended up showing that the maximum oil yield was in the temperature range of 450-550 °C, because at higher temperatures, the secondary reactions of volatiles cause a significantly lower oil yield. Table 8 shows the obtained yields of oil, coal and gas where it can be seen that the pyrolysis yield did not change significantly with the biomass species.

Table 8. Products of pyrolysis [31].



Product distributions from pyrolysis of agricultural wastes, wt.%

Feed	Oreganum stalk	Corncob	Straw
Gas[a]	32	30	39
Aqueous phase	6±0.3	6±1.3	6±0.5
Oil	39±3.1	41±0.9	35±1.3
Char	23±1.9	23±1.5	20±0.4

[a] Calculated from mass balance.

The biomass that provided the most gas was Straw. The gas was analysed in a two-column GC, as well as with thermal conductivity and flame ionisation detectors connected in series, the thermal conductivity and flame ionisation detectors were connected in series. In addition, a 60 m × 0,25 mm film (chrompack DB 1701) with 0,25 µm film was used. The injector and detector temperatures were maintained at 250 °C and 280 °C, respectively. The oven programme was 4 min isothermal at 45 °C, then 3 °C/min up to 280 °C and finally 15 min at 280 °C. The compounds were quantified by the internal standard method with fluoranthene as internal.

On the other hand, José Penado's thesis has also analysed the pyrolysis process with raw, demineralised and doped wheat straw with ashes. The TG and DTG curves were obtained in the temperature range of 30 °C and 900 °C, in a model DTA 7200 of the Hitachi brand, under atmosphere of nitrogen with 100 ML/min, heating rate of 5 °C /min, using a platinum crucible containing 5mg for raw wheat straw, 3 mg for demineralize wheat straw and 6 mg for doper wheat straw. Figure 9 shows the TG and DTG od TGA curves of the wheat straw analysis.

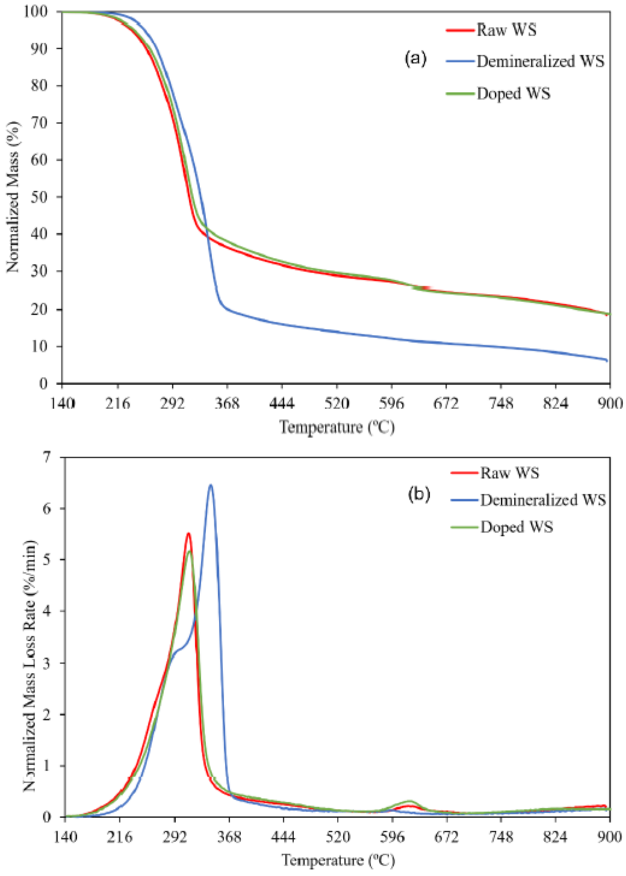


Figure 9. TGA experiment from Jose Penados's thesis [18].

The figures adobe show that the TG curves of the raw and doped Wheat Straw are practically united in one, which means at first sight that dry impregnation of the dry and ashy Wheat Straw has not produced any relevant effect. Furthermore, in the DTG curves, the raw and doped wheat straw show a board and featureless peak with similar values at almost identical temperatures at the DTG peak. Hemicellulose and cellulose are associated with the peak of the DTG curves which means that the rate curves of these two components overlap each other during the decomposition process. However, in demineralised Wheat Straw another trend can be observed, in addition to having a higher peak than raw and doped what Straw, there seems to be a shift in the peak of the DTG curve at higher temperatures as well as the existence of a 'shoulder' near the decomposition temperature of raw and doped wheat Straw. The following phenomenon, explained in the thesis of Jose Penedos [18], which consists of the washing of the straw, causes the splitting of the main DTG peak into the low temperature peak due to the decomposition of cellulose and the high temperature peak which was associated with the decomposition of cellulose [18]. From this, the shoulder and peak decomposition temperatures of the demineralised wheat straw- 310°C and 340°C -suggest that the decomposition of the cellulose was associated with the decomposition of the cellulose. That their overlapping decomposition was partially split by the demineralisation

process, as these temperatures are consistent with the characteristic decomposition temperatures of hemicellulose and cellulose reported in the literature.
In table 9. Are shown the main results from the TGA analysis carried out by Jose Penados.

Table 9. TGA Experiment from Jose Penedos's Thesis [18].

Sample	T_i **(°C)**	T_{peak} **(°C)**	T_f **(°C)**	DTG_{peak} **(%/min)**	TG_{end} **(%)**
Raw WS	217	311	357	5.5	18.4
Doped WS	218	312	365	5.2	18.3
Demineralized WS	236	342	369	6.5	6.0

After performing all the pyrolysis analysis, it can be stated that the highest volatiles extractions occur between 200°C and 370°C in all samples, with primary pyrolysis occurring up to 600°C. At 620°C, a smaller peak can be seen in the DTG curves for the raw and doped Straw wheat. This mass loss appears to increase as the ash content increases and is not present in the demineralised Wheat Straw curve. [18]

After the study, where Jose analysed the different samples in depth, studying their organic and chemical composition and subjecting them to different thermochemical processes in order to analyse the influence of the ashes on them, several conclusions were obtained. On the one hand, it is concluded that the best conditions for demineralising samples and thus eliminating inorganics in the sample are found, which are higher leaching times and smaller ratios water/biomass, and that a demineralised sample is more resistant to thermal degradation than a raw sample, as well as the perception of a partial separation of the thermal decomposition of the hemicellulose and cellulose that occurs in demineralised samples, as opposed to the raw sample, which does not have this separation. Finally, it is concluded that adding ash to a raw sample does not influence pyrolysis in the case of wheat straw.

3.3 EFFECT OF INORGANICS IN THE PYROLISIS OF BIOMASS

Ash is the inorganic part of biomass that does not enter into combustion during energy conversion and remains as ash. It consists mainly of Al, Ca, Fe, K, Mg, Na, P, Si, Ti and minor elements such as As, Ba, Cd, Co, Cr, Hg, Mn, Mo, Ni, Pb, Sb, Tl, V and Zn. [20]. "Major inorganic elements are highly responsible for ash melting, deposit slag formation, and corrosion in the conversion equipment while minor elements are responsible for particulate emission" (Baernthaler et al. 2006).

From an investigation on the effects of ashes on the fast catalytic pyrolysis of pine wood some essential information has been extracted to be able to draw conclusions.

Fast pyrolysis is the thermal decomposition of the natural polymeric constituents of biomass in an oxygen-free atmosphere at temperatures around 500 ◦C. At optimal conditions, including high heating rates of the biomass particles, short vapour residence times and fast condensation of pyrolysis vapours, high yields of pyrolysis liquid (usually in the range of 60 to 70 wt.%, dry-feed basis) can be achieved. (Güray Yildiz., 2014, p. 1)

However, this liquid created in pyrolysis has a number of drawbacks that limit its use in chemical production or fuel applications. These include its high-water content (15-30%), oxygen content (35-40 wt.%), corrosiveness (pH of 2-3), relatively low heating value compared to fossil fuels (ca. 17 MJ/kg), poor volatility and high viscosity, data that I have also found in the research by Güray Yildiz., 2014, p. 1. [19].

For this reason, catalytic fast pyrolysis (CFP), which is based on the use of heterogeneous catalysts in the fast pyrolysis process, aims to improve the quality of the liquid by directing the reactions in the vapour phase with respect to rates and selectivity. The aim of treating this liquid is to be used optimally in the production of heat, electricity, transport fuels and chemicals. [30]

In fast catalytic pyrolysis, the inert heat transfer material is (partially) replaced by a solid catalyst. The composition of this produced liquid is influenced by different factors such as the type of biomass, the type of catalyst, the optimum catalyst temperature, and the catalyst-to-feed ratio. In addition, and not least the interactions between the volatiles generated in fast pyrolysis and the bed content (ash and char) is an important factor in the pyrolysis of the reactor. By interactions I mean the reactions of the reactive species found in the volatiles with the ash/coal particles [19].

In pyrolysis, the production of valuable components is promoted and the production of undesirable oxygenated compounds (acids, sugars, polyaromatic hydrocarbons, etc.) must be reduced, and for this purpose a hydrogen/carbon ratio of decarboxylation must be maintained.

After having superficially explained the process, we will now see the influence that ashes have on the process, since in the catalytic fast pyrolysis process we find a series of problems. The following information also found in the research carried out by Güray Yildiz., 2014.

One problem is the deactivation of the catalyst, which is responsible for the physical, chemical, thermal and mechanical degradation of the catalysts, resulting in reduced activity and selectivity. This catalyst deactivation can be caused by coke and metal deposition on the catalyst or by ash accumulation in or on the catalyst [19].

All biomasses contain ash-forming nutrients in the form of cations that bind to the organic matrix of the biomass in carboxylic and/or phenolic groups, or in the form of precipitates, such as a salt. These minerals (Ca, K, Mg and Na...) are catalytically active and catalyse the cracking and various thrombolysis reactions in the vapour phase and reshape the chemical composition of the resulting pyrolysis liquid and change the distribution of the product generated in the pyrolysis [19].

For this reason, in order to prevent adverse effects on the quality and distribution of pyrolysis products, attempts are made to remove ash-producing elements. These elements can be removed either by washing the biomass with water or more thoroughly by washing it with an acid. However, leaching affects the chemical composition of the biomass and the composition of the pyrolysis liquid, as strong leaching can cause degradation of the hemicellulose, but very small amounts of “alkali metals or alkaline earth metals in their chloride forms have been shown to significantly alter the pyrolysis products. The presence of as little as 0.5 wt.% ash resulted in a strikingly different chemical speciation: in terms of levoglucosan yield, the order of influence from strong to modest K influence was found to be K+ > Na+ > Ca2+ > Mg2+.” [20].

In order to understand the consequences of indigenous or added ashes in fast pyrolysis with catalyst and the possible interactions that can occur in fast pyrolysis with catalyst, it is first necessary to examine the influence of ashes on the distribution and composition of the products resulting from the primary and secondary fast pyrolysis reactions. Different parameters are relevant for the decomposition of the biomass and consequently its pyrolysis liquid production, such as the type and state of the catalyst and the presence of ash in the biomass.

Figure 10 shows the possible effects of the presence of ash (whether or not it has accumulated during the process) on the catalyst activity in fast pyrolysis with catalyst.

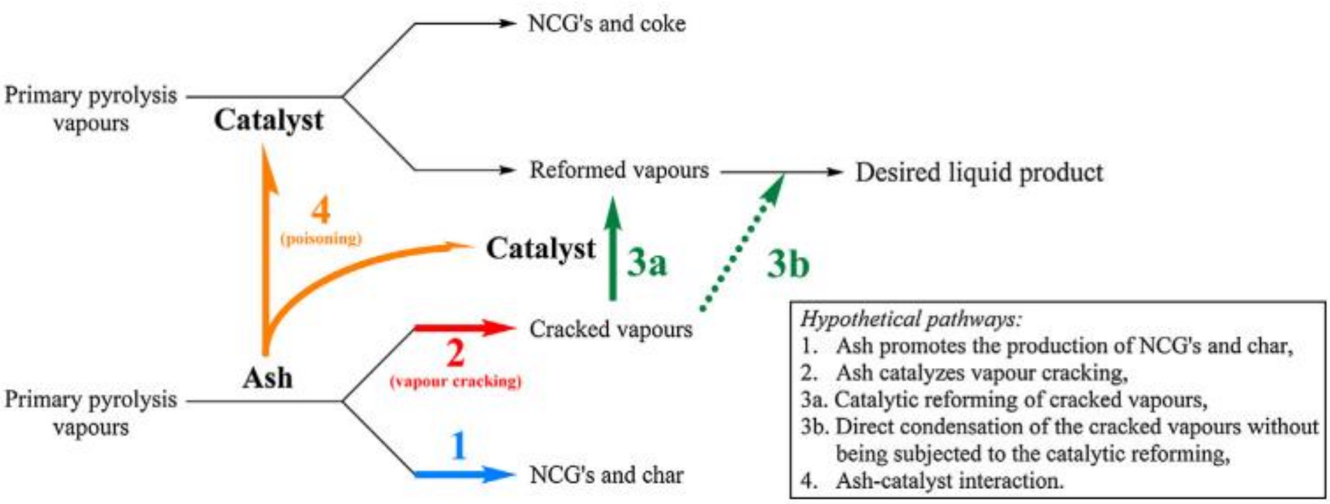


Figure 10. Possible impact of ash on the catalyst and on the products in catalytic fast pyrolysis of biomass [19].

Hypothetically, four pathways can be distinguished in how ash influences chemical phase vapour and catalyst activity (combined effects can also occur) [20]:

1. The catalytic effect of ash itself on the primary pyrolysis vapours results in the increased production of non-condensable gases (NCGs) and char.
2. Ash may crack some larger vapour phase molecules inaccessible to the catalyst’s interior, to smaller ones which are capable of entering the catalyst pores.
3. Cracked vapours may then either be further reformed by the catalyst (a) or not (b).
4. Ash particles poison the catalyst and (negatively) affect the vapour conversion and the reaction chemistry.

In the experiment studied in which they worked with non-catalytic and catalytic fast pyrolysis of pine wood, the different combinations included in each experiment were compared, either:

- A non-catalytic pyrolysis reference experiment (denoted as “NC”).
- Non-catalytic pyrolysis after addition of biomass ash (denoted as “NC + ash”).
- Catalytic pyrolysis with fresh catalyst as a reference experiment (denoted as “R0”).
- Catalytic pyrolysis with fresh catalyst and added biomass ash (denoted as “R0 + ash”), and finally
- Catalytic pyrolysis with catalysts obtained after eight successive reaction/regeneration cycles (denoted as “R8”).”

In Figure 11. taken from the research on pine wood, it can be seen graphically how the operating conditions in the different experiments influence the product yields.

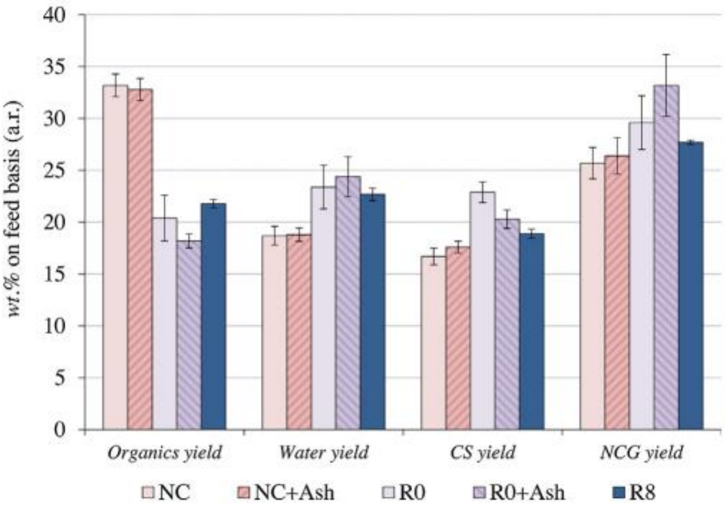


Figure 11.Product yields obtained from ash addition experiments compared to those of the reference, non-catalytic (NC), the catalytic with fresh catalyst (R0), and the 8th cycle of catalyst regeneration (R8) experiments. Fast pyrolysis of pine wood at 500 °C [19].

Figure 11. gives a more visual way to see the differences between the different experiments in order to draw conclusions.

Analysing the graph above it can be could concluded that ash affects the efficiency of the catalyst by influencing the composition of the primary pyrolysis vapours to be modified by the catalyst. In fact, "ash concentrations as low as ca. 3 wt.% relative to the amount of pine wood fed, and ca. 0.002 wt.% relative to the amount of bed material, were found sufficient to have a direct effect on the yield and composition of the catalytic fast pyrolysis product" (Güray Yildiz., 2014, p. 3).

The effects of ash can be compared to the effects caused by selective catalyst loss and/or catalyst deactivation although they are different. To solve the problem caused by ash in catalytic fast pyrolysis, the coal (which contains a large amount of ash) has to be physically removed from the catalyst before the regeneration stage. [19]

Although pine wood, which does not have a high ash content, has been used in this study, the conclusions obtained serve to affirm that with a biomass with a higher ash content the consequences caused by ash will be even more dramatic. [19]

Continuing with the research on the influence of ash in biomass pyrolysis, from a master thesis in which a study was carried out to study physical treatments to reduce the ash content in biomass and the effects caused by ash in biomass products some conclusions can be obtained [20].

It follows that ash is detrimental to the energy conversion process and that ash content has direct effects on the calorific value of biomass, as it reduces the combustible compounds in the biomass. The increase of inorganic compounds limits the combustible components and thus the calorific potential of the biomass decreases. [20]

Ash is detrimental to biomass conversion as during combustion, biomass ash forms slag and fouling. A high content of Si, K, and Na decreases the ash melting temperature and the content of K, Si and Mg increases the tendency to produce more slag. As biomass has a complex composition due to its great variability leading to different fuel properties and in turn to slag formation, fouling and corrosion in combustion installations therefore these physical problems have consequences in boilers and bioreactors impairing the energy conversion process [20].

However, it cannot be concluded that ashes have detrimental effects on pyrolysis because its composition its very wide and various. It is clear that ash has a dominant effect on pyrolysis yields, but it depends on the compositions of the ashes. Alkali metals such sodium, potassium, calcium, and magnesium produce a catalytic effect in pyrolysis by effects on temperature of maximum degradation, rate of degradation, chemical degradation mechanisms and yields of products, the effects caused are lower yields, reduce degradation temperatures and change the reaction pathways and decomposition mechanisms [21].

Furthermore, in another research on the effects of alkali metals on pyrolysis by Qing Xu, Xiaoqian Ma, Zhaosheng Yu and Zilian Cai came to conclusions in their study which stated that ‘ Under the end pyrolysis temperature (1000 C), the rate of solid residue follows the order of no additive > MgO > CaO > BaCO3 > K2CO3 > Na2CO3, indicating that alkaline earth and alkali metal compounds may accelerate the degradation rate of organic matters’ they also affirm that ‘ Under the end pyrolysis temperature (1000 C), the rate of solid residue follows the order of no additive > MgO > CaO > BaCO3 > K2CO3 > Na2CO3, indicating that alkaline earth and alkali metal compounds may accelerate the degradation rate of organic matters.’ [22]

4. MATERIALS AND METHODS

4.1 BIOMASS CHARACTERIZATION

For this research the biomass used was wheat straw, rice husk, walnut shells and horse manure. In order to work with the horse manure, the biomass had to be prepared by grind and sieve to a size of 200µm. After drying, the samples were subjected to proximate analysis where the ash, volatile, moisture and fixed carbon content of each raw and demineralised biomass was obtained under standard conditions, using the precision balance and crucible shown in figures 12 and 14. Wheat Straw, Rice husks and walnut shells samples were demineralised and subjected to a leaching process with deionized water with a water biomass ratio of 20:1 for 60 minutes at 30°C in a magnetic stirrer, however, horse manure, with a high content of alkaline metals, could not be demineralised in the same way and was demineralised following the same procedure but with a water biomass ratio of 10:1, with the demineralisation in water leaching ensuring that the ashes are removed efficiently without altering the chemical properties of the biomass. This was checked by subjecting the raw and demineralised samples to a proximate analysis and then comparing the ash content of each sample.
The aim of the proximate analysis is to obtain the content of moisture, ash, volatile materials, and fixed carbon contained in a biomass sample based on standard EN 18122.

The procedure is the following:

Moisture of the fuel can be determined by drying the sample under standard conditions in the oven shown in Figure 15. Moisture was determined accordingly to standard EN 14774-3 for solid biofuels. The analysis sample of solid biofuel is dried at a temperature of 105ºC until constancy in mass is achieved. Moisture content is then calculated from the loss of mass of the test sample (Equation 2). Constancy in mass is defined as a change not exceeding 1 mg in mass during a further period of heating at (105 ± 2) °C over a period of 60 min [18].

$$M = \frac{m_2 - m_3}{m_2 - m_1} \times 100$$

Equation 2. Moisture calculation,

- m_1 is the mass, in g, of the empty crucible and lid;
- m_2 is the mass, in g, of the crucible and lid plus test sample before drying;
- m_3 is the mass, in g, of the crucible and lid plus test sample after drying.

Volatile matter of a fuel is the condensable and non-condensable vapour released when the fuel is heated. Its amount depends on the heating rate and the temperature to which it is heated. Volatile matter was determined accordingly to standard EN 15148:2009 for solid biofuels. A test portion of the general analysis sample is heated out of contact with ambient air at (900 ± 10) °C for 7 min. This is achieved by closing air intake of muffle furnace (shown in Figure 13.) and heating the sample in the crucible with the lid placed on top. The percentage of volatile matter is calculated from the loss in mass of the dried test portion after deducting the loss in mass due to moisture (Equation 3) [18].

$$VM = \frac{m_2 - m_3}{m_2 - m_1} \times 100 - M$$

Equation 3. Volatile matter calculation.

- m_1 is the mass, in g, of the empty crucible plus lid;
- m_2 is the mass, in g, of the crucible and lid plus test sample before heating;
- m_3 is the mass, in g, of the crucible and lid plus contents after heating;
- M is the moisture, as a percentage by mass, determined according to EN 14774-3.

Ash is the inorganic solid residue left after the fuel is completely burned and is majorly composed of the inorganic matter in biomass. Ash was determined accordingly to standard EN 18122 for solid biofuels. The ash content is determined by calculation from the mass of the residue remaining after the sample is heated in air under rigidly controlled conditions of time, sample weight and equipment specifications to a controlled temperature of (550 ± 10) °C (Equation 4) [18]. The following heating routine was followed (heating performed with muffle furnace (shown in Figure 13.) air intake opened and without crucible lid):

- Increase furnace temperature to 250°C over a period of 30min and maintain at this temperature for 60min to allow the volatiles to leave the sample before ignition.
- Increase furnace temperature to 550°C over a period of 30min and maintain at this temperature level for 120 min. Reheat for further 30 min periods until the change in mass is lower than 0,5 mg.

$$ASH = \frac{m_3 - m_1}{m_2 - m_1} \times 100$$

Equation 4. Ash content calculation.

- m_1 is the mass, in g, of the empty crucible;
- m_2 is the mass, in g, of the crucible plus the test sample before heating;
- m_3 is the mass, in g, of crucible plus remaining solid residue.

Fixed carbon is the solid carbon in the fuel that remains in the char after devolatilization. Since FC depends on the amount of VM, it is determined by difference (Equation 5).

$$FC = 100 - M - VM - ASH$$

Equation 5. Fixed carbon content calculation.

Figure 13. Precision Scale used for weigh measurements [18].

Figure 12.Precision Scale used for weigh measurements [18].

Figure 15. Crucible and lid used for proximate analysis [18].

Figure 14. Drying Oven used for moisture content determination [18].

The chemical characterisation of the raw biomass been constituted by four different sequential analyses, obtaining extractives, lignin, hemicellulose, and cellulose all following procedures obtained from [23]- [25].

The extraction of extractives consists of preparing a 200 ml solution of the pure extraction solvent, deionized water, ethanol and hexane and transferring it to the boiling flask, placing the flask on the heating mantle, then placing the extraction thimble in the extraction chamber and after assembling the extraction equipment as shown in the Figure 18, recirculating a cooling liquid and turning on the heating mantle at the required temperature for each solvent which will be 100 °C, 80 °C and 70 °C for deionized water, ethanol and hexane consecutively for a given time which also depends on each solvent being 11h for deionized water and 6h for ethanol and hexane. After the experiment using deionized water, it is weighed to calculate the hydrophilic content and after the ethanol and hexane process it is weighed again to calculate the hydrophobic content, the total sum of the hydrophilic and hydrophobic will correspond to the extractives [23].

The lignin content is obtained from the biomass without extractives by the following procedure shown in Figure 17. the sample is placed in a flask where a mixture of demineralised water, acetic acid and sodium chlorite is added and the mixture is heated to 70 °C , after 1 h, acetic acid and sodium chlorite are added and mixed, after each following hour, new portions of acetic acid and sodium chlorite are added and mixed again, This step is repeated until the sample is completely separated from the lignin, i.e. until the solid becomes white in colour, which normally takes between 6-8 h. Special care must be taken with the addition of chlorite in excess, because if the reaction is continued, hemicellulose can also be removed in addition to lignin [24].

After this, without adding more acetic acid or sodium chlorite, the flask is left for 24 h of reaction, and after cooling the sample, the holocellulose is filtered until the yellow colour and the smell of chlorine dioxide is removed. It is then dried and weighed, the difference in weight being the lignin content [25]. The hemicellulose content of the holocellulose is determined by the lignin content of the holocellulose.

The hemicellulose content present in the biomasses is obtained by transferring the dried sample, free of extractives and lignin (process shown in Figure 17), to a beaker and adding 150 ml of NaOH solution to the beaker, heating it at 80 °C in a water bath for 3.5 h. After this time, the sample is washed with deionised water until no more Na^+ is detected and allowed to dry, the weight of the residue lost is the hemicellulose content [25].

The cellulose content in the sample is determined by weighing the solid residue after completion of the hemicellulose extraction process.

All the material used for the realization of these experiments is shown in the figures below.

Figure 16.Perkin Elmer Spectrum Spectrometer [18].

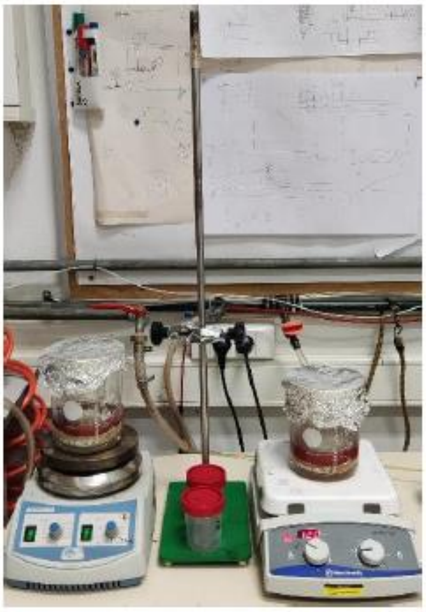


Figure 17. Setup for lignin and hemicellulose determination [18].

Figure 18. Setup for extractive determination [18].

4.2 HORIZONTAL REACTOR

The pyrolysis process was carried out in a horizontal reactor as shown in Figure 19 .

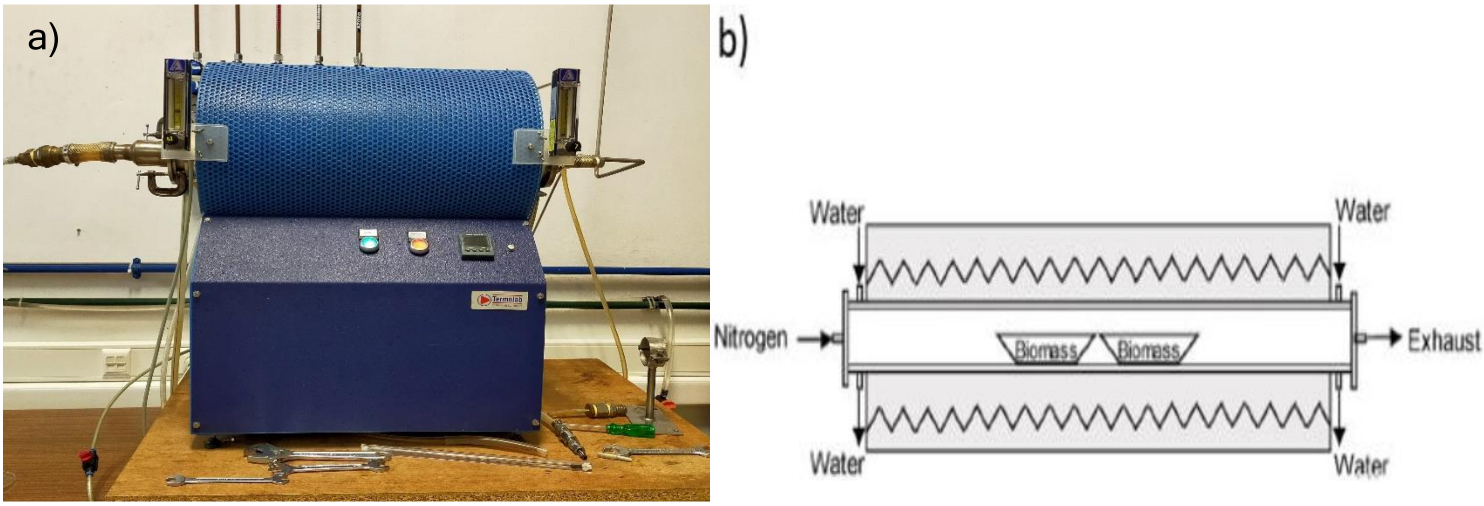


Figure 19. a) tubular reactor furnace; b) reactor scheme.

This reactor has a controlled atmosphere with a constant volume, an aluminium inner tube, an inner diameter of 4 cm and a length of 55 cm. The inner tube is also insulated with fibreglass. Heating is done by an electrical resistance, being controlled by the Eurotherm 3216 controller (a PID temperature controller) and the wall temperature is constantly monitored by means of an s-type thermocouple. The reactor also has a water-cooling system which has the function of cooling the flanges, made of steel, located at the ends. Therefore, at the beginning there is the inlet which is responsible for the inlet of the desired gas into the reactor atmosphere, and on the opposite side the outlet of the exhaust gases. The system also has two rotameters, since it is possible to introduce a mixture of gases into the reactor atmosphere, allowing control of the flow rate. There is a tube connecting the gas source to the rotameter near the reactor inlet, this tube is T-shaped and has one side connecting to the other rotameter in order to introduce another gas into the system. The biomass is introduced into a ceramic crucible, containing about 1-2 grams, placed symmetrically in the centre of the reactor, since according to the temperature profile, the desired temperature remains constant in that position.

The procedure is carried out as follows, the biomass is placed in the crucible in the centre of the tube which is then purged with the carrier N_2 gas for about 10 minutes at a flow rate of 1 L/min, to ensure that there is no oxygen in the reactor atmosphere and that the flow rate is maintained. The heating rate used is 10°C /min and the residence time is one hour. The biomass used in this process has been walnut shells and horse manure in a temperature range between 300°C and 700°C, since the offset in surface area occurs around 500°C.

The aim of this study was to analyse the mass loss of the samples during pyrolysis in the horizontal reactor in order to compare it with the mass loss during thermogravimetric analysis and to capture the non-condensable gases from the pyrolysis and analyse them in a gas chromatograph.

In order to be able to use the gas chromatograph it must first be calibrated. Calibration is done in the following way. Start by opening the helium and hydrogen cylinders, switching on the GC and the computer next to it. The computer is configured in such a way that the calibration method is introduced with the aim of setting values to the parameters in order to be able to see all the interesting peaks of the work being carried out. The most difficult to configure are the N_2 peak because it is very large and the H_2 peak because it is very small. Next, sampling bags are taken from the calibration bottles, these bottles must contain the gases to be calibrated. It is necessary to know the residence time of each component and, for each calibration bottle, at least 3 sampling bags are needed. Once everything is ready, a chromatograph is made for each sampling bag and all the areas of the peaks corresponding to the calibration gases are manually integrated. Finally, the GC is switched off and all the valves necessary for its operation are closed.

Once the GC has been calibrated, the operation process is similar to calibration.

The hydrogen and helium bottles are opened, the GC and the computer are switched on and the computer is programmed by going to setup in the method button and in the method menu, in our case which is biomass, enter ricardo28, and name the experiment. The first experiment should be a cleaning experiment. Let the GC stabilise the temperature of the detectors, the columns and the flow rate of the carrier gas. Then, open the synthetic air bottle and when the GC is ready, the computer screen should be green, turn on the pump until it reaches a pressure below 0.180 atm. This should be sufficient to ensure that the previous gas leaves the GC column. You can now press 'run' on the computer, this will ensure that there is no gas in the column, after the GC emits the noise of a valve closing, turn the pump off. Again, follow the same method and name the experiment, insert the bag of gas into the GC valve, turn on the pump and open the valve that connects the bag to the GC, squeeze the bag and press the 'run' button on the computer. Next, turn off the pump when you hear the sound of a valve closing, then let the test run for 21 minutes, when finished, turn off the GC and all the valves necessary to make it work. The test results are in the test results file.

4.3 TGA

The thermogravimetric analysis was carried out on the different biomasses, this type of analysis allows the measurement of a wide variety of parameters such as moisture loss, decarboxylation, pyrolysis, solvent loss, oxidation, etc. It is a very useful tool to determine the carbon content, and also to compare different products, which is the application that will be given in this study [26].

The operation of this analysis consists of measuring the variation of mass in the sample as a function of temperature or time. Its instrumentation consists of a pan that rests on a sensitive analytical balance. The test sample is placed on the pan and is heated externally. A purge gas that may be reactive or inert (depending on test requirements) is passed over the sample and exits through the exhaust. The heating rate of the sample can be controlled, and the mass change over the entire period is monitored continuously [26].

For this study, the thermogravimetric analysis was carried out in a model STA 7200 of the Hitachi Brand, with a flow rate of 200 mL/min and a heating rate of 10°C /min in a temperature range of 30-700 °C. An alumina crucible was used, this material was used to withstand the high temperatures. Each crucible contained approximately 5 mg of each sample, the samples analysed were horse manure (HM), demineralized horse manure (DHM) at the mixture (50:50) between horse manure and walnut shells (MIX) and walnut shells (NUTS).

After the analysis, TG curves and DTG curves are obtained in order to obtain characteristic values of the process, the second derivative of the TG curve is performed. Having carried out the second derivative, the initial, final and peak temperature and the temperature difference between the initial and final temperatures can be known. The initial temperature of the pyrolysis corresponds to the temperature of the first peak upwards of the second derivative curve, the final temperature corresponds to the temperature of the last peak downwards that is under the large undulation that occurs in the DTG curve, the peak temperature corresponds to the temperature that occurs when the second derivative is at zero. On the other hand, the temperature difference between the initial and final temperature is calculated by subtracting these.

5. RESULTS

5.1 BIOMASS COMPOSITION

Before analysing the composition of each biomass, the samples were previously demineralised as it is explained in the ‘materials and methods’ section in order to compare both compositions.
Figure 20 shows the results of the values obtained for the composition of each biomass and its demineralisation.

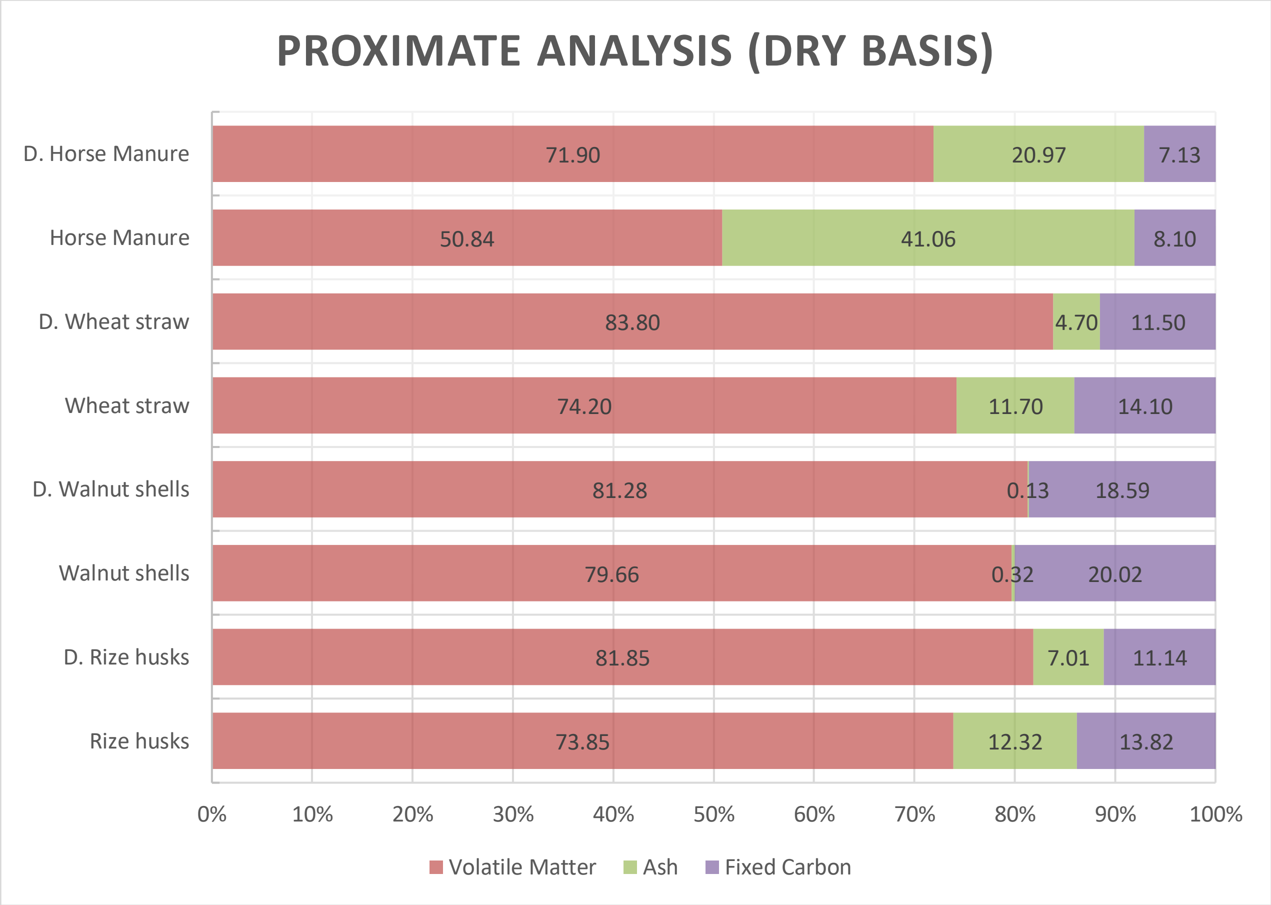


Figure 20. Proximate Analysis of raw and demineralized samples.

The moisture content in wheat straw, walnut shells, rice husks and horse manure was 9.6%, 8.09%, 8.47% and 1.87% respectively. As can be seen in the results of the proximate analysis, there is a large variation between the composition of each biomass, with the composition of the horse manure standing out due to its very high ash content. Moreover, due to this level of inorganics in the sample, which was a problem because the method that had been followed for the demineralisation of each biomass could not reduce the level of inorganics, so the biomass-solution ratio had to be doubled in order to dissolve the large amount of inorganics and not become saturated. This large amount of ash was used to study the influence of inorganics on the pyrolysis of the biomass.

One way to check that the analysis has been carried out correctly is to compare the results with previous studies. In the figures below, it can be seen the comparisons and confirm the validity of the results obtained.

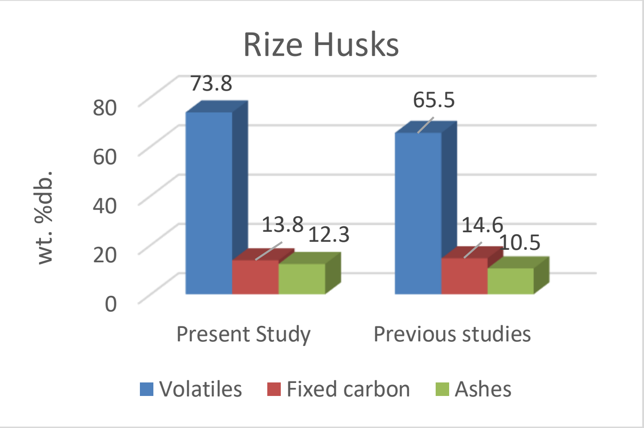


Figure 21. Comparison between Rize husk's proximate analysis carried out and previous studies. [36]

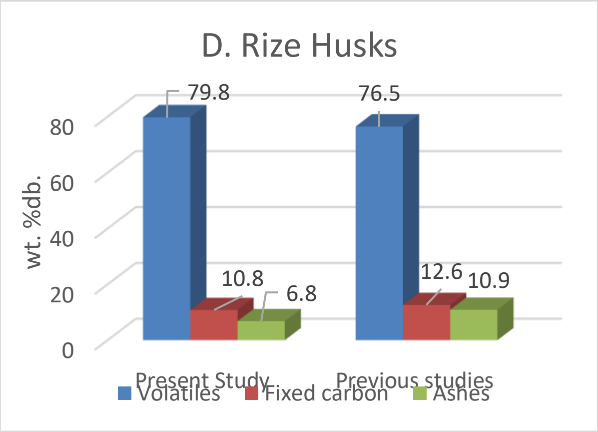


Figure 22. Comparison between D. Rize husk's proximate analysis carried out and previous studies [36].

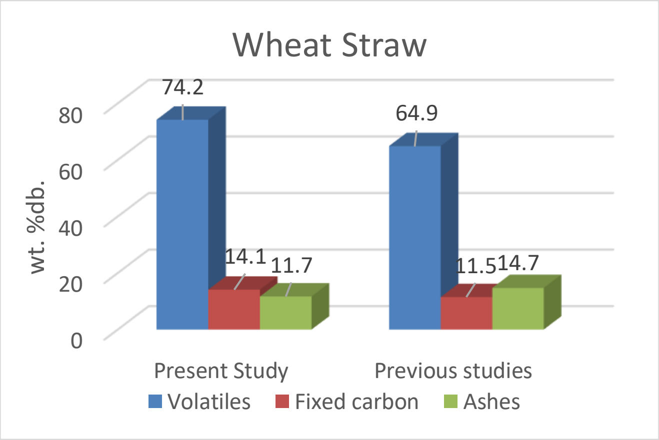


Figure 23. Comparison between Wheat straw's proximate analysis carried out and previous studies [36].

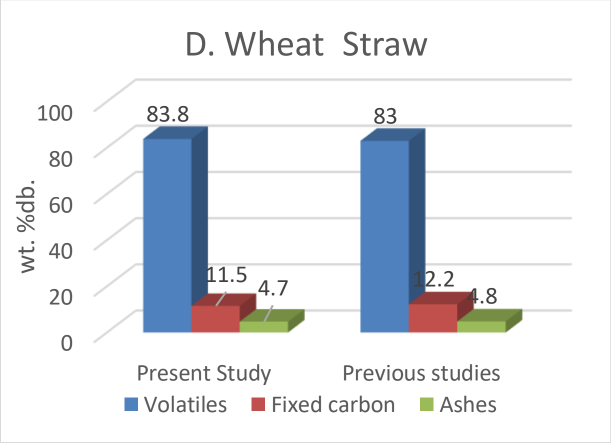
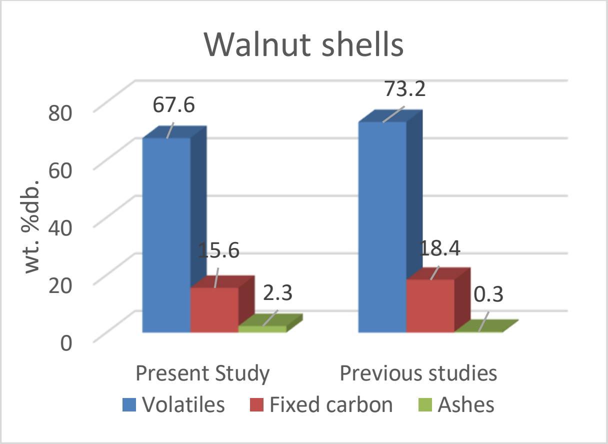


Figure 24. Comparison between D. Wheat straw's proximate analysis carried out and previous studies [18].



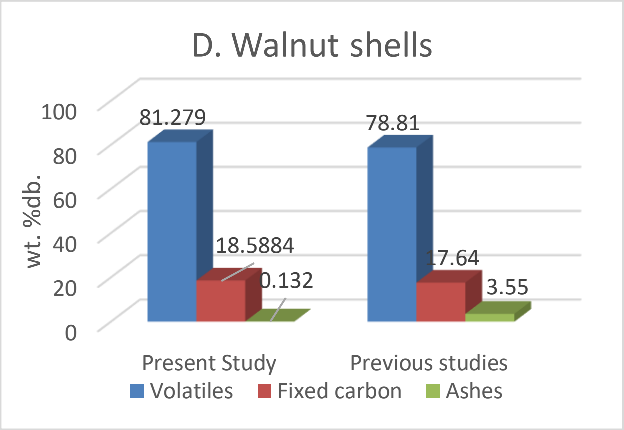


Figure 25. Comparison between Walnut shells's proximate analysis carried out and previous studies.[37].

Figure 26. Comparison between D.Wheat straw's proximate analysis carried out and previous studies[38].

It can be affirmed that the results obtained from the ultimate analysis for each biomass are valid as they have very similar values to those found in previous studies. For each biomass the values are not exactly the same as the ones compared, this can be due to many factors as although they are the same biomass they come from different sources, they have different grain size among other things and this makes that each biomass sample has similar but not exact proportions of ash, volatiles and fixed carbon.

It has also been analysed the extractives present in the samples of raw Wheat straw, walnut shells, and Rice husks, extracting the following values shown in figure 27:

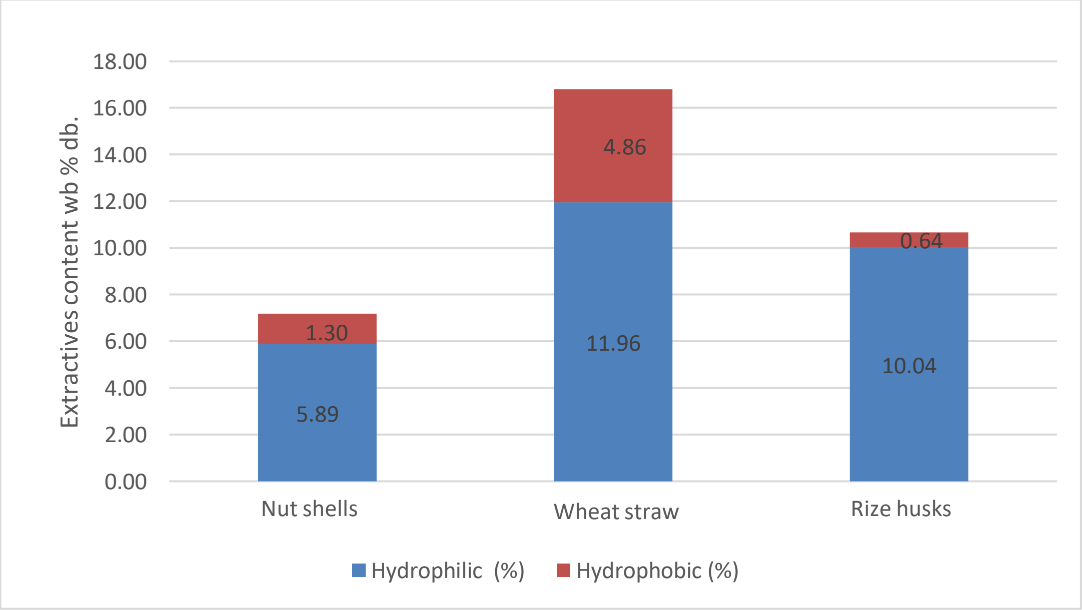


Figure 27. Extractives from Wheat Straw, walnut shells and Rice husks samples.

This analysis was not carried out on the horse manure sample because the type of biomass it is is not considered to be an analysis that will provide relevant information for my study.

Analysing the values shown in Figure 27, it is worth noting that the value of the extractives corresponds to the sum of the hydrophilic and hydrophobic extractives. Furthermore, a tendency can be found that the value of the hydrophilic extractives is higher than that of the hydrophobic extractives in all the samples with a considerable difference, highlighting the Rice husks sample where the value of the hydrophobic extractives is practically close to 0%. This is because the content of extractives is related to the type of biomass, woody plants can be classified into angiosperms, which are plants that produce flowers and fruits, and gymnosperms, which are plants that produce naked seeds. Generally, cellulose, hemicellulose and lignin account for more than 90% of all biomass, therefore extractives <10% and in the case of angiosperms the content of hydrophobic extractives can reach up to 15%, and in the case of gymnosperms, such as rice, they can normally have a hydrophobic extractives content of up to <2%. Hydrophobic extractives are usually triglycerides and hydrophilic extractives are usually phenolic compounds, which have a protective function in plants [39]. For this reason, the proportion and type of extractives is related to the type of biomass.

5.2 TGA

From the thermogravimetric analysis performed on horse manure (HM), demineralised horse manure (DHM), the mixture (50:50) between horse manure and walnut shells (MIX) and walnut shells (NUTS), figures 28 and 29 show the TG and DTG curves obtained and table 10 shows the main results of this analysis.

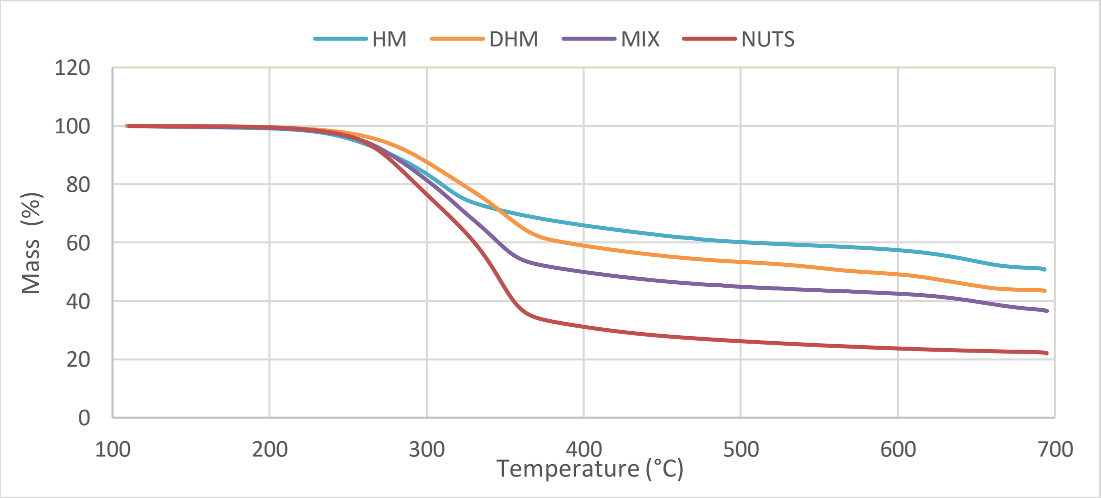


Figure 28. TG curves of TGA of Horse manure, demineralize horse manure, mixture (50:50) between horse manure and walnut shells and walnut shells.

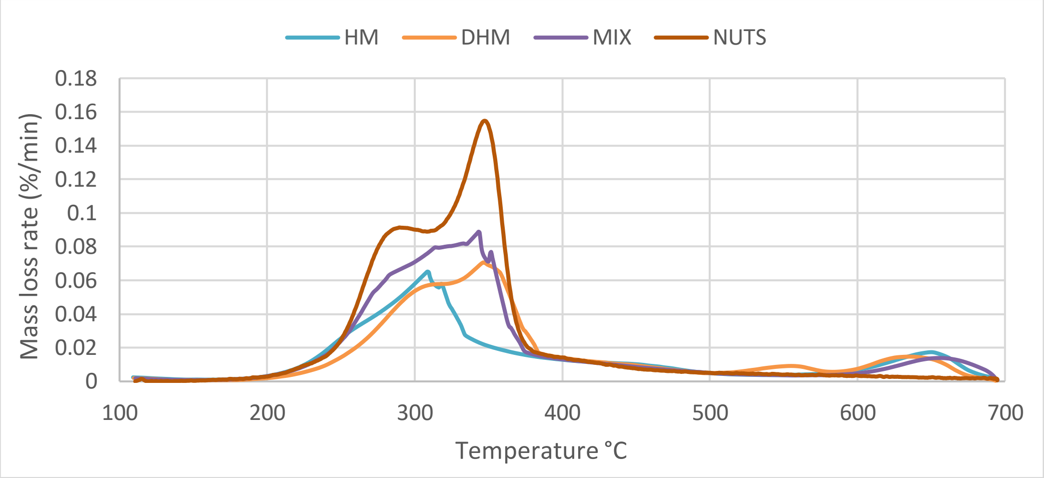


Figure 29. DTG curves of TGA of horse manure, demineralize horse manure, mixture (50:50) between horse manure and walnut shells and walnut shells.

Table 10. Main results of TGA of horse manure, demineralize horse manure, mixture (50:50) between horse manure and walnut shells and walnut shells.

	Ti (°C)	Tpeak (°C)	Tf (°C)	ΔT
HM	239,3	309,5	333,8	94,5
DHM	254,6	347,6	382,6	128
MIX	243,7	344,6	378,5	134,8
NUTS	240,3	347,4	391,3	151,1

In the obtained TG shown in Figure 28, typical TG curves are shown, where the temperature range between 250-400 °C corresponds to an intense process of volatile extraction, which causes a slope in the curve that implies a mass loss. Looking at the figure, focusing on the HM and DHM curves, it can be seen how the mass loss step occurs at lower temperatures in the case of HM, which may be due to the catalytic effects that the inorganics present in HM have on thermal degradation. Since, as can be observed in the values shown in Table 10, where some values of the second derivative of the TG were obtained, the initial and final temperatures of the HM samples are lower than those of DHM, being the initial temperatures 239.34 °C and 254.66 °C and the final temperatures 333.8 °C and 382.6 °C for HM and DHM respectively, which justifies the catalytic effects of the inorganic compounds in HM, by accelerating the pyrolysis reaction making it occur at lower temperatures. In addition, the final residual mass corresponds to some extent to the ash, so the difference in final mass between HM and DHM is due to this, that HM has a higher ash content than DHM and, for this reason, HM has a higher final residual mass than DHM.

Figure 29 shows the DTG curves of each sample as a function of temperature, in the range of temperatures of 250-350 °C of the decomposition, referred to as such due to the overlap of the first and second stage of decomposition, corresponding to hemicellulose and cellulose, respectively. The DTG curve shows that the decomposition of hemicellulose (first stage) normally appears as a more or less 'shoulder' rather than a distinct peak, as is the case for cellulose. As the distinct peaks associated with the different constituents cannot be distinguished, it indicates that the thermal decomposition components occur simultaneously, overlapping each other in the DTG profiles. The second region (third stage) corresponds to the decomposition of lignin occurring over a wide temperature range up to 500 °C. After a stabilization of the curves up to approx. 650 °C a small peak can be observed, this peak increases with the ash content, for this reason it is more accentuated in the HM curve, it can be observed at these temperatures as the ashes are to some extent, reactive and this is more evident at higher temperatures. In this Figure 29. the thermal degradation rates are represented and it can be observed how all the curves follow the same trend, being the HM curve shifted to the left, with respect to the DHM, because the catalytic effects of the ashes affect the pyrolysis causing it to accelerate starting and finishing at lower temperatures with respect to the demineralized sample.

Furthermore, looking at the values in Table 10 where the main values of the second derivative of the TG curve are represented: initial, final, peak temperature and temperature difference between initial and final: T_i, T_{peak}, T_f and ΔT. The previous explanations can be justified since all the temperature values of HM are lower than those of DHM and in fact the ΔT between T_i and T_f of HM is notably lower than that of DHM being, 94.5 and 128.01 respectively, showing that, besides starting at lower temperatures, the reactions take place faster, justifying that the inorganics present in HM have catalytic effects that accelerate the reaction.

On the other hand, with respect to the information provided by Figure 28 and 29 on MIX, NUTS and HM, it can be stated that the physical process of mixing walnut shells with horse manure was successful since, the objective of mixing walnut shells with horse manure was to evaluate the inorganic effects on pyrolysis, by adding horse manure, which has a high ash content, to walnut shells with a lower ash content, it was possible to study these effects. Since the mass loss in the NUTS sample is by far higher than the others with a total of 79.69%, for HM it is 50.41% and MIX it is 65.39%, which is an intermediate value between the two, confirming their correct mixing. The residual mass of NUTS was the lowest; this is to be expected as it is the sample with the lowest ash content and, as mentioned above, the final residual mass corresponds to some extent with the ash content. In contrast, the residual mass of MIX is higher than NUTS due to its higher ash content as it has been mixed.

Finally, in figure 29, in the NUTS curve it can clearly observe the difference between the "shoulder" and then the large pronounced peak corresponding to the decomposition of hemicellulose and cellulose respectively, unlike in HM where it is difficult to differentiate both decompositions and yet in MIX it is easier to see the difference. In addition, around the temperature of 650°C a small peak can be observed in Figure 29. which, as previously mentioned, corresponds to the inorganics present, and in the NUTS's curve this small peak is not visible, evidencing the lower content of inorganics with respect to the other samples. On the other hand, and supported by the data shown in Table 10. which as previously mentioned are data obtained from the second derivative of the TG curve, it can be observed that the T_i and T_f of NUTS are 240.31°C and 347.42 °C respectively and the difference between them is 151.1, being the sample with the longest process, however, MIX has difference between temperatures of 134.8 °C, decreasing this difference a lot, confirming once again, that the mixture has been successful by observing that the difference between temperatures of horse manure is 94.5 °C therefore, the inorganics added when mixing HM with NUTS have had catalytic effects during the pyrolysis of MIX accelerating the process, resulting in a lower temperature difference and thus a faster process with respect to raw walnut shells.

5.3 COMPARISON BETWEEN METHODS

The pyrolysis has been carried out in two different experiments, on the one hand by means of a thermogravimetric analysis and on the other hand in a horizontal reactor, both processes under the same boundary conditions. To confirm the correct performance of both experiments, the mass loss suffered by each sample was compared by measuring the weight of the sample before and after pyrolysis in the different methodologies, (Figure 30). It can be seen the sample before and after the pyrolysis in the horizontal reactor. Figure 31 shows the difference in mass loss between both experiments, it can be seen that the mass loss in the pyrolysis performed in the horizontal reactor is slightly lower in each sample than the pyrolysis performed in the thermogravimetric analysis, this difference may be due to the fact that in the thermogravimetric analysis the amount of sample used is much smaller than the amount used for the horizontal reactor, being in the horizontal reactor of amounts in grams and in the TGA of milligrams. Therefore, this difference between the initial mass quantities may alter the final results despite the fact that they have been carried out under the same conditions because experiments performed with too small masses are not as accurate as those performed with more mass. However, as it is a small difference, it does not affect the conclusion obtained, which is that the pyrolysis performed by both technologies and for each sample has been successful and with reasonable results.

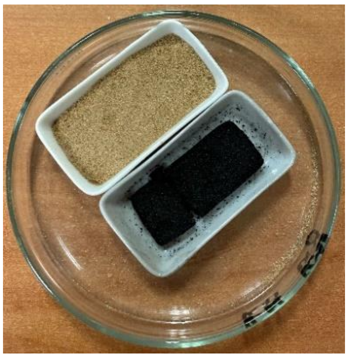


Figure 30. Sample before and after pyrolysis in the horizontal reactor.

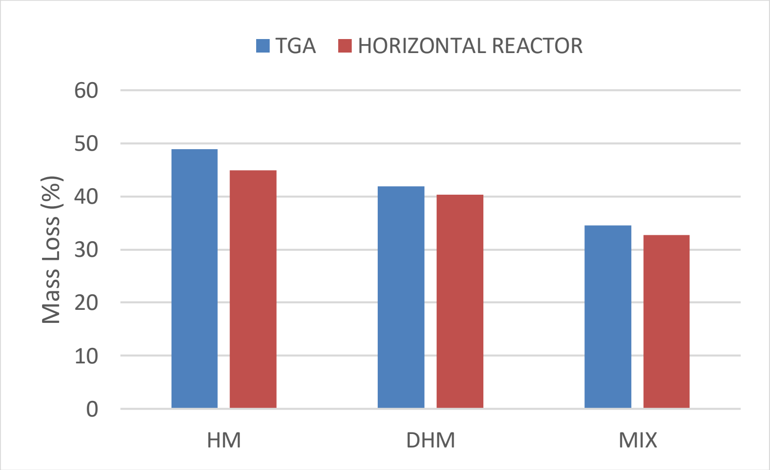


Figure 31. Mass loss of HM, DHM and MIX in the pyrolysis processes.

6. CONCLUSIONS

6.1 WORK SUMMARY

The proposed objectives have been achieved. The demineralization process of horse manure has been successful in removing inorganics without affecting the chemical structure, only influence on the thermal stability has been perceived. The effects of inorganics on pyrolysis have been studied by thermogravimetric analysis and in a horizontal reactor where different conclusions have been drawn. In addition, the mass loss of each sample between the beginning and the end of the pyrolysis in the horizontal reactor has been calculated and compared with the mass loss in each TGA experiment.

6.2 MAIN CONCLUSIONS

The main conclusions of this work are the following:

1. Horse manure being a biomass with high ash content cannot follow the same demineralization procedure as other biomasses such as wheat straw but the water:biomass ratio must be doubled in order to successfully reduce the ash content.
2. Demineralised horse manure is more resistant to thermal degradation, as the final pyrolysis temperature in the TG and DTG analyses is higher than in raw horse manure because of the lower ash content, which consequently does not have the strong catalytic effect of ash in pyrolysis that accelerates and causes the reaction to occur at lower temperatures.
3. The catalytic effects of the inorganics accelerate the pyrolysis process causing pyrolysis to occur at lower temperatures and in a narrower temperature range as the difference between the final and initial temperatures is smaller for raw horse manure than for demineralised horse manure.
4. Pyrolysis performed in a horizontal reactor under the same conditions as a thermogravimetric analysis results in almost identical mass loss. Thus, the results obtained from the thermogravimetric analysis, in terms of temperature, can be used to better understand the process and thus make better use of the reactor, since by knowing at what temperature each decomposition stage in the pyrolysis takes place, the desired products can be extracted from the horizontal reactor.

Therefore, applying the findings to the practical field, biomasses with high ash content, such as horse manure, will be demineralised by doubling the water:biomass ratio and if certain catalytic effects are desired in the pyrolysis of a biomass such as walnut shells, it can be physically mixed with horse manure to obtain these effects, as the high ash content of horse manure determines the catalytic effect of the reaction.

6.3 RECOMMENDATIONS FOR FUTURE WORK

For future work, more experiments should be carried out with the horizontal reactor to analyse the non-condensable gases in the gas chromatograph in order to study the relationship between the elements present in the non-condensable gases from the pyrolysis of biomass and the inorganic matter present in the biomass. With the result of these experiments, information could have been obtained on the differences between the proportions of elements in the non-condensable gases produced in the horizontal reactor pyrolysis of raw horse manure, demineralize horse manure, the mixture of horse manure and walnut shells and walnut shells and with this, it could have been possible to study the influence of the ashes in this distribution.

REFERENCES

[1] UN, “United Nations Framework Convention on Climate Change.” 2005.

[2] https://www.energyavm.es

[3] Jeanette Sanchez, “Situacion del consume energético a nivel mundial y para America Latina y el Caribe (ALC) y sus perspectivas”, 2017.

[4] Hannah Ritchie, Max Roser and Pablo Rosado,"Energy", Our World in Data, 2020.

[5] https://www.miteco.gob.es

[6] ‘La importancia de las energias renovables.” https://www.acciona.com

[7] “Renovables en el mundo y en Europa.” https://www.appa.es

[8] Williams, C. L., Emerson, R. M., & Tumuluru, J. S. “Biomass Compositional Analysis for Conversion to Renewable Fuels and Chemicals”, Biomass Volume Estimation and Valorization for Energy, 2017.

[9] Ana Alvarez Rodriguez, Consuelo Pizarro Garcia, Maria Belen Folgueras Diaz. “Caracterizacion química de biomasa y su relación con el poder calorífico”, 2012-13.

[10] Mateo Moron, “Procesos de conversión de la biomasa en energía.” 2021.

[11] https://www.gimanpro.com/

[12] Fernandez Gonzalez, Jesus gutierreznMartin, Fernando del Rio Gonzalez, Pablo San Miguel Alfaro, Guillermo Bahillo Ruiz, Alberto Sanchez Hervas & Jose Rodriguez Anton, “Tecnologías para el uso y transformación de biomasa energética.” Ediciones Paraninfo, SA., 2015.

[13] Nogués, F. S. “Energía de la Biomasa”,volumen I, Vol. 173.2010.

[14] “Analizador termogravimetrico”. https://www.upct.es/

[15] Emilio Moron. “Analisi termogravimetrico (TGA). Aplicación al estudio del acio tungstofosforico”, 2018. https://steemit.com/

[16] Peña, C. A. M. “Modelación Cinética de Pirolisis de Biomasa “.Doctoral dissertation, Tesis, Universidad Nacional de Colombia, Ingeniería Química y Ambiental, Bogotá., 2013.

[17] Laura Camila Buitrago Fajardo, Yudy Alejandra Ovalle Melo. “Analisis Cinetico de la pirolisis de biomasa.” 2018.

[18] Jose Miguel da Vinha Pereira Penedos, ”Effect of inorganics on the thermal decomposition behaviour of wheat straw.”2021

[19] Güray Yildiz, Frederik Ronsse, Robbie Venderboschb, Ruben van Durenc, Sascha R.A. Kerstend, Wolter , 2014. “Applied Catalysis B: Environmental.” ELSEVIER, 2017.

[20] Ujjain Pradhan. “Physical treatments for reducing biomass ash and effect of ash content on pyrolysis products. “ Master thesis_Ujjain, 2015.

[21] R. Fahmi, A.V. Bridgwater, L.I. Darvell, J.M. Jones, N. Yates, S. Thain, I.S. Donnison. “The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switchgrass and willow”, Fuel, Volume 86, Pages 1560-1569, 2007.

[22] Qing Xu, Xiaoqian Ma, Zhaosheng Yu, Zilin Cai. “A kinetic study on the effects of alkaline earth and alkali metal compounds for catalytic pyrolysis of microalgae using thermogravimetry” Applied Thermal Engineering, Volume 73, Pages 357-361, 2014.

[23] Sluiter, A., Ruiz, R., Scarlata, C., Sluiter, J., & Templeton, D. J. L. A. P. “Determination of extractives in biomass”, Laboratory analytical procedure (LAP), 1617, 1-9, 2005.

[24] Damay, J., Boboescu, I. Z., Beigbeder, J. B., Duret, X., Beauchemin, S., Lalonde, O., & Lavoie, J. M. “Single-stage extraction of whole sorghum extractives and hemicelluloses followed by their conversion to ethanol.” Industrial Crops and Products, 137, 636-645, 2019.

[25] Haiping Yang, Rong Yan, Hanping Chen, Dong Ho Lee, Chuguang Zheng,
“Characteristics of hemicellulose, cellulose and lignin pyrolysis,” Fuel, Volume 86, Pages 1781-1788, 2007.

[26] Basu, P. Biomass gasification, pyrolysis and torrefaction: practical design and theory. Academic press., 2018.

[27] A. Anca-couce, “Reacyion mechanisms and multi-scale modelling of lignocellulosic biomass pyrolysis,” Prog. Energy Combust. Sci., vol. 53, no.2016, pp. 41-79, 2020.

[28] Rodrigo Vieira Santos. “Assessment of biomass and biochar as a porous medium for water retention in soils.”, 2021.

[29] M. Van de Velden, J. Baeyens, A. Brems, B. Janssens, and R. Dewil, “Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction”, Renew. Energy, vol. 35, no. 1, pp. 232-242, 2010.

[30] Hoon Chae Park, Byeong-Kyu Lee, Ho Seong Yoo, Hang Seok Choi. “Influence of Operating Conditions for Fast Pyrolysis and Pyrolysis Oil Production in a Conical Spouted-Bed Reactor.” Special Issue: Experiment and CFD Investigations of Biomass Thermochemical Conversion, Volume 43, Issue 12, Pages 2493-2504, 2019.

[31] Bijoy Biswas, Nidhi Pandey, Yashasvi Bisht, Rawel Singh, Jitendra Kumar, Thallada Bhaskar, ‘Pyrolysis of agricultural biomass residues: Comparative study of corn cob, wheat straw, rice straw and rice husk’, Bioresource Technology, Volume 237, 2017, Pages 57-63, 2017.

[32] R. Segurado, S. Pereira, D. Correia, M. Costa, “Techno-economic analysis of a trigeneration system based on biomass gasification”, Renewable and Sustainable Energy Reviews, Volume 103, Pages 501-514, 2019.

[33] Fernández, J. “Energía de la biomasa. Energías renovables para el desarrollo”. Thomson-Paraninfo. 2003.

[34] N.L. Panwar, Richa Kothari, V.V. Tyagi, “Thermo chemical conversion of biomass – Eco friendly energy routes”, Renewable and Sustainable Energy Reviews, Volume 16, Issue 4, Pages 1801-1816, ISSN 1364-0321,2012.

[35] https://www.researchgate.net

[36] Shannan Xu, Benjamin Bernard Uzoejinwa, Shuan Wang, Yamin Hu, Lili Qian, Lu Liu, Zhixia He, Qian Wang, Abd El-Fatah Abomohra, Chunhou Li, Bo Zhang, “ Study on Co-pyrolysis synergistic mechanism of seaweed and rice husk by investigation of the characteristics of char/coke.” Renewable Energy, Volume 132, Pages 527-542, 2019.

[37] Ana Isabel Marques Ferreiro, “ Pyrolysis of Pine Bark, Wheat Straw and Rice Husk: Thermogravimetric Analysis and Kinetic Study” Thesis, 2015.

[38] Ayhan Demirbas, “Demineralization of Agricultal Residuesby water leaching”, Energy Sources, Volume 25, 2003.

[39] Paulo Eduardo Amara Debiagi, Chiara Pecchi, Giancarlo Gentile, Alessio Frassoldati,Karafas S. Emmanouil, Spyros Apostolos & Guillaume Dayma, “ Identification and quatification of Aromatic Hydrocarbons absorbed on soot from Premixed Flames of Kerosene, Synthetic Kerosene, and Kerosene-Synthetic Bioefuels” energy&fuels,Pagues 6556-6564, 2015.