UNIVERSIDAD CARLOS III DE MADRID
GRADO EN INGENIERÍA MECÁNICA
ESCUELA POLITÉCNICA SUPERIOR

SOLID FUELS CHARACTERIZATION. BIOMASS vs COAL

FINAL PROJECT

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Because only people who are so crazy as to think they can change the world...
are those that do

Abstract ad "Think different" issued by Apple in 1997

Acknowledgment

A research project like this is never the work of anyone alone. The contributions of many different people, in their different ways, have made this possible. I would like to extend my appreciation especially to the following.

In the first place, I would like to express my gratitude to my supervisor, Luis Miguel García, I appreciate his vast knowledge and skill in this area and I would like to thank the assistance He provided at all levels of the research project and taking time out from his busy schedule to serve as my external reader.

I would also like to thank my family for the support they provided me through my entire life and in particular, I must acknowledge my sister and best friend, Tania, without whose encouragement and editing assistance, I would not have finished this project.

I must also acknowledge *Carbones Saiz* for his provision of the materials evaluated in this study. Appreciation also goes out to Department of Thermal and fluids mechanics, for all of their computers, equipment and technical assistance throughout my graduate project.

I would also like to thank my Erasmus friends, for our exchanges of knowledge, skills, and venting of frustration during my Erasmus program, which helped to enrich the experience.

Lastly, and most importantly, I wish to thank **my Grand Mother**. She taught me, helped me and loved me. **To her I dedicate my project.**

Abstract

The use of renewable energy sources is becoming important to reduce global warming and to provide fuel supply. Biomass fuels have to be used in a clean and more efficient way; so, it's important to know their chemical and physical characteristics, in order to choose the best energetic conversion process.

In this project I have done solid fuel characterization, to create a database in compliance with Standard UNE, European CEN/TS. The parameters determined have been: moisture, carbon, hydrogen, nitrogen, oxygen and sulfur (elemental analysis) and high and low heating value, present in the biomass and coal.

The main samples analyzed are residual and forestry biomass, solid biofuels such as pellets and coals.

In this project has been studied the different analyses, equipment behavior and standards for solid fuels with the aim of determining better fuel properties and thus achieve more efficient combustion conditions, minimizing the emission of gases and particles.

Equipment and material required to carry out these analyses, have been provided by UC3M BIOLAB, 202 - Testing Laboratory of Biomass Fuels.

General Index

1 INTRODUCTION

The current energy model is untenable because, apart from the greenhouse, pollution and climate change, there is a limiting factor: dependence of a resource "non-renewable" is becoming scarce.

Biomass is a type of renewable energy that will be basic in our society in the short term, in terms of energy and environmental, for socio-economic development of rural areas, because they can give work in areas preventing migration of rural population to towns to big cities, through forest conservation or energy crops for the production of biomass as fuel. Biomass has a neutral CO_2 balance, it means, does not increase the greenhouse effect, because the carbon is released as part of the current atmosphere (plants, absorb and continuously release CO_2 during their growth) and no subsurface captured in ancient times, just as coal. If the number of goals that have been raised under the Energy Plan Renewables 2011-2020 are reached, biomass will generate revenue close to 725 million euros.

Finally, beyond these quantifiable benefits, there are others like the generation of 15,000 jobs in rural areas, or forest industrially investment of 3,000 million euros.

1.1 Objectives of the research

The energy use of coal and biomass at international level has driven the creation and adaptation of standardized methods that facilitate the characterization of solid fuels. On the road to global standardization, some of these methods have been published as UNE.

1.1.1 Main objective

- Perform physical-chemical analysis of biomass and coal for thermal and/or electrical applications. The parameters determined are moisture, high and low heating value, carbon, hydrogen, nitrogen and sulfur, present in the solid fuels. All parameters are determined following the guidelines of standardized procedures and standardized by European and national technical committees (AENOR CTN 164: Solid Biofuels)

1.1.2 Secondary objectives

- Write a practical guide on how to use the equipment required in this project.
- Design a methodology to calculate moisture, elemental analysis and heating value.

1.2 Project Structure

This Project is divided into 9 Chapters. The contain of each one is described below:

- Chapter 1: INTRODUCTION

This chapter is a presentation of my project, explaining objectives, structure and motivation of this one.

- Chapter 2: INTRODUCTION TO SOLID FUELS.

Here, we can find a brief introduction to solid combustibles, biomass and coal, giving a technical description of each one, describing different resources and analyzing their uses, advantages and disadvantages, and emissions according to Green House Protocol. The most important of this chapter is the initial comparison between solid biomass and coal. Finally I have studied Global, European Union and Spanish situation and I have done a socioeconomic balance of biomass.

- Chapter 3: EXPERIMENTAL WORK. FUEL SAMPLING AND ANALYSIS.

This is a key chapter of this project. In the first place I give a brief description of the analyzed fuels, then we will find sample preparation, in this part, I describe required analysis to prepare samples and results. Next we can find a description of thermal properties analyzed in this project and finally I describe the equipment needed to perform analysis done during this project and I give guidelines of their operation.

- Chapter 4: RESULTS

Here we can find results of the moisture calculation and elemental and heating value analysis. Also, I give a discussion of these results.

- Chapter 5: BUDGET

To develop this project, has been needed the collaboration of my supervisor and the use of different equipment and material. All of these costs have been described in this chapter.

- Chapter 6: CONCLUSIONS

In this section, I explain my conclusions after performing required analysis and discussing obtained results.

- Chapter 7: OTHER POSSIBLE RESEARCH

This chapter has been elaborated in order to have the possibility to continue with the research opened with this project. Here I describe other possible lines of research related to my project.

- Chapter 8: ANNEXES

Here, we can find the list of the tables and figures of the project.

- Chapter 9: REFERENCES

In the last chapter is collected the bibliography, web pages and reference standards consulted, that have done possible carrying out this project.

1.3 Motivation

Coal and biomass are the most representative of solid energy use for electricity production fuel. In the case of coal, is characterized by their diversity and abundance of resources and in the case of biomass, its clean and inexhaustible production.

However, at present, is not just enough to ensure energy supply, also in order to remain being competitive with other energy resources, it is necessary to provide a diverse energy supply, safe, environmentally friendly and a very cost-efficiency.

For these reasons, I decided to carry out this project. To perform different analysis, for solid fuels with the aim of determining better fuel properties, and thus achieve more efficient combustion conditions, minimizing the emission of gases and particles.

2 INTRODUCTION TO SOLID FUELS

According to the RAE, biomass is defined as "Organic matter originated in a biological or miscarriage process, usable energy source."

According AENOR (Spanish Association for Standardization and Certification) biomass is "Material of biological origin excluding those who have been encompassed in geological formations suffering a process of mineralization."

The second description is more accurate because it excludes coal, oil and gas, due to in contrast to Biomass, coal, oil and gas does not fulfill the neutral balance of CO_2.

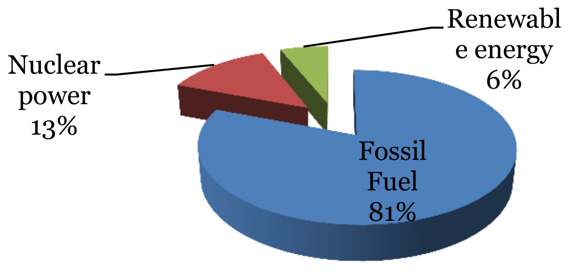
2.1 Biomass as fuel

2.1.1 Technical description

Renewable energy is the use of products obtained from organic matter to produce energy. These products make up what is called "biomass", a definition that encompasses a large set of materials from diverse backgrounds and with very different characteristics.

This definition includes, forest harvesting residues and agricultural crops, garden pruning residues, agro- industrial residues, energy crops, liquid fuels derived from agricultural products, waste of animal or human origin, etc. .

Currently, over 81% of energy supply in Spain comes from fossil fuels, 13% nuclear power, and about 6% Renewable Energy .



Graphic 1. Energy supply in Spain. *(Source Idae)*

This non-renewable 94% has important environmental implications and a strong dependence on foreign supply.

Biomass energy production facilities are supplied with a wide range of biofuels from wood chips and straw to thistles, through olive stones and almond shells. The energy produced by biomass can be used for heating and hot water production in the domestic sector, industrial heating processes and electricity generation.

Among the main solid Spanish biofuels, we can highlights grape, olive pits, almond shells, nuts and of course waste of our forests and forest industries (from bark to splinters, through coastal and sawdust).

The combustion of biomass does not contribute to the greenhouse effect because the carbon is released as part of the current atmosphere (It is absorbed and continuously released by plants during growth) and no subsurface captured in ancient times, just as the coal. The energy contained in the biomass is solar energy stored due to photosynthesis, process by which some organisms, like plants, use solar energy to convert inorganic compounds assimilated (such as CO_2) into organic compounds.

The use of biomass as an energy resource involves various environmental benefits which include:

- Reduced emissions of sulfur and particulate
- Reduced emissions of pollutants such as CO, HC and NOx.
- CO_2 neutral cycle, no greenhouse effect.
- Reduced maintenance and hazards of toxic exhaust gases and fuels in homes.
- Reduced risk of forest fires and insect pests.
- Use of agricultural waste, avoiding burning on the ground.
- Possibility of using fallow land with energy crops.
- Independence of fluctuations in fuel prices from abroad (not imported fuels).
- Improved socioeconomic rural areas.

All this makes the biomass in one of the potential sources of future employment.

2.1.2 Biomass resources

Biomass resources can be classified according to the supply sector, as shown in the table.

SUPPLY SECTOR	TYPE	EXAMPLE
Forestry	Dedicated forestry	Short rotation plantations
	Forestry by-products	Wood blocks, wood chips from thinning
	Dry lignocellulose energy crops	Herbaceous crops
		Oil seeds for methyl esters
Agriculture	Oil, sugar and starch energy crops	Sugar crops for
		Starch crops for ethanol
	Agricultural residues	Straw, pruning from vineyards and fruit trees
	Livestock waste	Wet and dry manure
Industry	Industrial residues	Industrial waste wood, sawdust from sawmills
		Fibrous vegetable waste from paper industries
	Dry lignocellulosic	Residues from parks and
		Demolition wood
Waste	Contaminated waste	Organic fraction of municipal solid waste
		Biodegradable landfilled waste, landfill gas
		Sewage sludge

Chart 1. Classification according to the biomass supply sector. ***(Source Idae)***

2.1.3 How we use the biomass

Biomass can be used for fuels, power production, and products that would otherwise be made from fossil fuels. In such scenarios, biomass can provide an array of benefits.

- **<u>Biofuels basics</u>**

Unlike other renewable energy sources, biomass can be converted directly into liquid fuels, called "biofuels," to help meet transportation fuel needs. The two most common types of biofuels in use today are ethanol and biodiesel.

- **Ethanol** is an alcohol, the same as in beer and wine (although ethanol used as a fuel is modified to make it undrinkable). It is most commonly made by fermenting any biomass high in carbohydrates through a process similar to beer brewing. Today, ethanol is made from starches and sugars, but scientists are developing technology to allow it to be made from cellulose and hemicellulose, the fibrous material that makes up the bulk of most plant matter.

Ethanol can also be produced by a process called gasification. Gasification systems use high temperatures and a low-oxygen environment to convert biomass into synthesis gas, a mixture of hydrogen and carbon monoxide. The synthesis gas, or "syngas," can then be chemically converted into ethanol and other fuels.

Ethanol is mostly used as blending agent with gasoline to increase octane and cut down carbon monoxide and other smog-causing emissions. Some vehicles, called Flexible Fuel Vehicles, are designed to run on E85, an alternative fuel with much higher ethanol content than regular gasoline.

- **Biodiesel** is made by combining alcohol (usually methanol) with vegetable oil, animal fat, or recycled cooking grease. It can be used as an additive (typically 20%) to reduce vehicle emissions or in its pure form as a renewable alternative fuel for diesel engines.

- **Biopower**

Biopower, or biomass power, is the use of biomass to generate electricity. Biopower system technologies include direct-firing, cofiring, gasification, pyrolysis, and anaerobic digestion.

Most biopower plants use **direct-fired systems**. They burn bioenergy feedstock directly to produce steam. This steam drives a turbine, which turns a generator that converts the power into electricity. In some biomass industries, the spent steam from the power plant is also used for manufacturing processes or to heat buildings. Such combined heat and power systems greatly increase overall energy efficiency. Paper mills, the largest current producers of biomass power, generate electricity or process heat as part of the process for recovering pulping chemicals.

Co-firing refers to mixing biomass with fossil fuels in conventional power plants. Coal-fired power plants can use co-firing systems to significantly reduce emissions, especially sulfur dioxide emissions.

Gasification systems use high temperatures and an oxygen-starved environment to convert biomass into synthesis gas, a mixture of hydrogen and carbon monoxide. The synthesis gas, or "syngas," can then be chemically converted into other fuels or products, burned in a conventional boiler, or used instead of natural gas in a gas turbine. Gas turbines are very much like jet engines, only they turn electric generators instead of propelling a jet. High-efficiency to begin with, they can be made to operate in a "combined cycle," in which their exhaust gases are used to boil water for steam, a second round of power generation, and even higher efficiency.

Using a similar thermochemical process but different conditions (totally excluding rather than limiting oxygen, in a simplified sense) will **pyrolyze** biomass to a liquid rather than gasify it. As with syngas, pyrolysis oil can be burned to generate electricity or used as a chemical source for making fuels, plastics, adhesives, or other bioproducts.

The natural decay of biomass under anaerobic conditions produces methane, which can be captured and used for power production. In landfills, wells can be drilled to release the methane from decaying organic matter. Then pipes from each well carry the methane to a central point, where it is filtered and cleaned before burning. This produces electricity and reduces the release of methane (a very potent greenhouse gas) into the atmosphere.

Methane can also be produced from biomass through a process called **anaerobic digestion**. Natural consortia of bacteria are used to decompose organic matter in the absence of oxygen in closed reactors. Gas suitable for power production is produced, and possibly troublesome wastes (such as those at sewage treatment plants or feedlots) are turned to usable compost.

Gasification, anaerobic digestion, and other biomass power technologies can be used in small, modular systems with internal combustion or other generators. These could be helpful for providing electrical power to villages remote from the electrical grid—particularly if they can use the waste heat for crop drying or other local industries. Small, modular systems can also fit well with distributed energy generation systems.

- **Bioproducts**

The petrochemical industry makes a myriad of products from fossil fuels. These plastics, chemicals, and other products are integral to modern life. The same or similar products can, for the most part, be made from biomass.

Fossil fuels are hydrocarbons, which are various combinations of carbon and hydrogen. Biomass components are carbohydrates, which are various combinations of carbon, hydrogen, and oxygen. The presence of oxygen makes it more challenging to create some products and easier to create others. In addition, the wide range of types of biomass should make it possible to make new and valuable products not made from petrochemicals.

The processes are similar. The petrochemical industry breaks oil and natural gas down to base chemicals and then builds desired products from them. Biochemical conversion technology breaks biomass down to component sugars, and thermochemical conversion technology breaks biomass down to carbon monoxide and hydrogen. Fermentation, chemical catalysis, and other processes can then be used to create new products.

2.1.4 Advantages and disadvantages

As our society experiences high and volatile energy prices as well as issues of national security, power generated from biomass material is becoming increasingly important.

Biomass power facilities benefit:

- Local communities
- The national economy
- The environment, including significant climate change benefits.

- Economic Benefits of Biomass Energy

Biomass energy plants make a substantial, positive impact on local and regional economies by generating well-paying jobs in:

- Construction and operation of the plant and
- Collection and transportation of biomass material.

Biomass energy plants support local industry and businesses and encourage new investment in rural communities.

Biomass energy facilities can help stabilize the local timber and forestry industry by providing stable demand for biomass material, which allows loggers, harvesters, processors and transporters to make capital investments.

- Social Benefits of Biomass Energy

As demand for power increases, many regions face potential supply shortfalls. These shortfalls could result in significantly higher electric prices and potential blackouts. Biomass power generation can help address this issue by providing a source of electricity that is:

- Reliable,
- Domestically-produced
- Dispatchable
- Economically-competitive
- Environmentally sustainable

Unlike other forms of renewable energy such as wind and solar energy, biomass energy plants are able to provide crucial, reliable base load generation. In addition to providing base load generation, biomass plants provide fuel diversity, which protects communities from volatile fossil fuels.

Besides these economic developments benefits, biomass plants help ensure a sustainable market for forest products. The jobs created as a result of these facilities help to protect and preserve the unique culture of many rural communities.

- Environmental Benefits of Biomass Energy

Biomass power facilities have numerous attributes, which benefit the environment and world climate change.

Environmental benefits include:

- Cleaner air
- Better forestry management

Biomass plants produce far less particulate matter than the alternative method of open burning wood wastes.

Beyond providing cleaner air, biomass energy plants:

- Encourage better forestry practices which in turn lead to increased protection of critical wildlife habitats
- Produce ash which can be used for soil enhancement in farmland
- Reduce the impact of invasive species
- Reduce wildfire risk
- Improve solid waste management by providing an outlet for land-clearing debris, diseased/infected trees and other wood wastes rather than open burning or depositing in already crowded landfills
- Reduce the impact of natural disasters by providing an outlet for storm debris.

- Climate Change Benefits of Biomass Energy

Unlike energy derived from fossil fuels such as coal, biomass energy does not contribute to climate change. The carbon, which is stored in biomass material as it grows, is already part of the atmosphere. Biomass energy does not add new carbon to the active carbon cycle, whereas fossil fuels remove carbon from geologic storage.

Carbon emissions from biomass facilities would have been released back into the atmosphere through natural decay or disposal through open-burning. The advanced emissions controls on a biomass energy facility significantly reduce the amount of carbon dioxide emitted into the atmosphere along with other emissions such as particulate matter.

Biomass energy is considered a "zero-greenhouse-gas-emitting technology"

In addition to not emitting new carbon into the active carbon cycle, biomass energy has additional climate change benefits.

Like all renewable energy technologies, biomass energy displaces the production of an equivalent amount of energy from fossil fuels. However, biomass energy is not just carbon neutral but actually carbon negative.

In the absence of biomass energy, a large portion of biomass material would be left to decompose naturally, be open-burned or landfilled. Landfilled or naturally decaying biomass material releases carbon in the form of methane as well as carbon dioxide. Methane is 20 to 25 times more potent as a greenhouse-gas than carbon dioxide.

Biomass energy contributes to forest health and fire resiliency, which increases the amount of carbon stored on a sustainable basis.

- **Risks from using Biomass**

There are a number of risks concerning the impact of large-scale biomass production on the environment and society. Some of these can be managed through current mechanisms. Others will require new legislation and setting new industry standards if they are to be managed and mitigated. Indirect land use change poses an important challenge that could potentially be addressed though certification schemes similar to those used in the forestry industry, such as the Reduced Emissions from Deforestation and Forest Degradation (REDD) scheme, or the Land Use, Land Use Change, and Forestry (LULUCF) carbon accounting principles.

- Land use change

Biomass should not be used if it entails harvesting old forests and other types of direct land use change. This is because the felling of old, pristine forests releases large amounts of carbon dioxide that have been stored for centuries in vegetation and the surrounding soil. The ‘carbon debt’ created may take decades to repay, even if the cleared land is planted with highly-productive energy crops that are continuously harvested to replace fossil fuels.

Moreover, it is rarely acceptable to cut down old, unmanaged forests from a biodiversity point of view.

Ultimately, it is better to harvest biomass from land that is already under management, no additional “carbon debt” will be created, and sustainable management can encourage higher net forest growth. The same land use change issues apply to all virgin land types such as rainforests, boreal pristine forests, or grasslands. In general, land use change needs careful consideration in order to avoid creating heavy carbon debt.

Large-scale use of biomass for heat and power can also cause indirect land-use change. Indirect land-use effects occur when the production of biomass feedstock displaces certain activities to other areas where they may cause negative land use changes such as deforestation. For example, if a significant share of the harvested woody biomass used at the moment by the forest industry is diverted to the bioenergy sector and demand for the original products does not decrease, procurement of the raw material could be displaced to other parts of the world, potentially leading to unwanted negative impacts on biodiversity and carbon stocks.

The carbon impact of indirect land use change is difficult to gauge. At present, there is no consensus as to how the impact should be measured.

- Environmental aspects

There are three main environmental concerns associated with the production of biomass feedstock: biodiversity, soil quality, and water habitats.

- Biodiversity can be affected by the conversion of natural habitat, transforming a natural forest to a plantation monoculture, for example and degradation by removing deadwood, for example. The former poses the bigger environmental threat, though both can reduce the number of plants and animal species.
- Soil quality can deteriorate through acidification, land erosion, the release of chemicals, or a change in the balance of nutrients. Emissions to soil may also pollute groundwater.
- Water habitats can be degraded by emissions of nutrients, soil particles, acidic compounds, and chemicals, and by damage to the shorelines that protect them.
- The conclusion for bio-energy is that forest and agriculture management practices need to be developed to protect biodiversity and to fit the specific local or regional conditions.
- Of the types of feedstock considered, waste and agricultural residues carry the least environmental risks from "production" since they are by definition by-products, while traditional forest production and energy crop or forest plantations can cause greater damage to the ecosystem if production is not well-managed.

- Social aspects

The production of biomass for heat and power can have positive and negative social effects. It can create new employment opportunities, increase national income from exports, and encourage the building of infrastructure. But it can also raise concerns about labor conditions, about whether local people will still have access to forests and be able to use them for traditional purposes such as fuel-gathering and hunting, and about increased income differences in local communities. Also, the infrastructure build-out that is typically associated with large-scale biomass harvesting is sometimes problematic, as it increases practical access to new areas of virgin land.

- Possible solutions

To manage and mitigate the risks associated with land use change and the environmental and social aspects of biomass production, most companies, scientists, agree that carefully evaluated sustainability criteria are needed.

These should be applied through a combination of legally binding regulations and other schemes and standards similar to those in place for forest-based products. Without adequate legislation, certification schemes alone will not suffice as they mainly regulate at stand level. Strong governance is also needed to ensure adherence to national and international sustainability agreements.

One issue that requires specifically careful attention is land use change, both direct and indirect:

Direct land use change, where biomass production replaces some other type of vegetation, should be possible to limit through the implementation of sustainability criteria. The criteria should specify which types of direct land use change are acceptable and which are not. Since cause and effect are clear in the case of direct land use change, the criteria can be designed in an analytical and clear way.

Limiting indirect land use change is more difficult, as cause and effect relationships are much more complex.

2.1.5 Emissions

2.1.5.1 Greenhouse Protocol

The Greenhouse Gas Protocol (GHG Protocol) is the most widely used international accounting tool for government and business leaders to understand, quantify, and manage greenhouse gas emissions. The GHG Protocol, a decade-long partnership between the World Resources Institute and the World Business Council for Sustainable Development, is working with businesses, governments, and environmental groups around the world to build a new generation of credible and effective programs for tackling climate change.

It provides the accounting framework for nearly every GHG standard and program in the world - from the International Standards Organization to The Climate Registry - as well as hundreds of GHG inventories prepared by individual companies.

2.1.5.2 Greenhouse Gases

Gases that trap heat in the atmosphere are called greenhouse gases. Here I provide information on emissions and removals of the main greenhouse gases to and from the atmosphere.

- Carbon dioxide (CO_2) : Carbon dioxide enters the atmosphere through burning fossil fuels (coal, natural gas and oil), solid waste, trees and wood products, and also as a result of certain chemical reactions. Carbon dioxide is removed from the atmosphere (or "sequestered") when it is absorbed by plants as part of the biological carbon cycle.
- Methane (CH_4): Methane is emitted during the production and transport of coal, natural gas, and oil. Methane emissions also result from livestock and other agricultural practices and by the decay of organic waste in municipal solid waste landfills.
- Nitrous oxide (N_2O): Nitrous oxide is emitted during agricultural and industrial activities, as well as during combustion of fossil fuels and solid waste.
- Fluorinated gases: Hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride are synthetic, powerful greenhouse gases that are emitted from a variety of industrial processes. Fluorinated gases are sometimes used as substitutes for stratospheric ozone-depleting substances. These gases are typically emitted in smaller quantities, but because they are potent greenhouse gases, they are sometimes referred to as High Global Warming Potential gases ("High GWP gases").

Each gas's effect on climate change depends on three main factors:

- **How much** of these gases are in the atmosphere?

  Concentration, or abundance, is the amount of a particular gas in the air. Larger emissions of greenhouse gases lead to higher concentrations in the atmosphere. Greenhouse gas concentrations are measured in parts per million, parts per billion, and even parts per trillion.

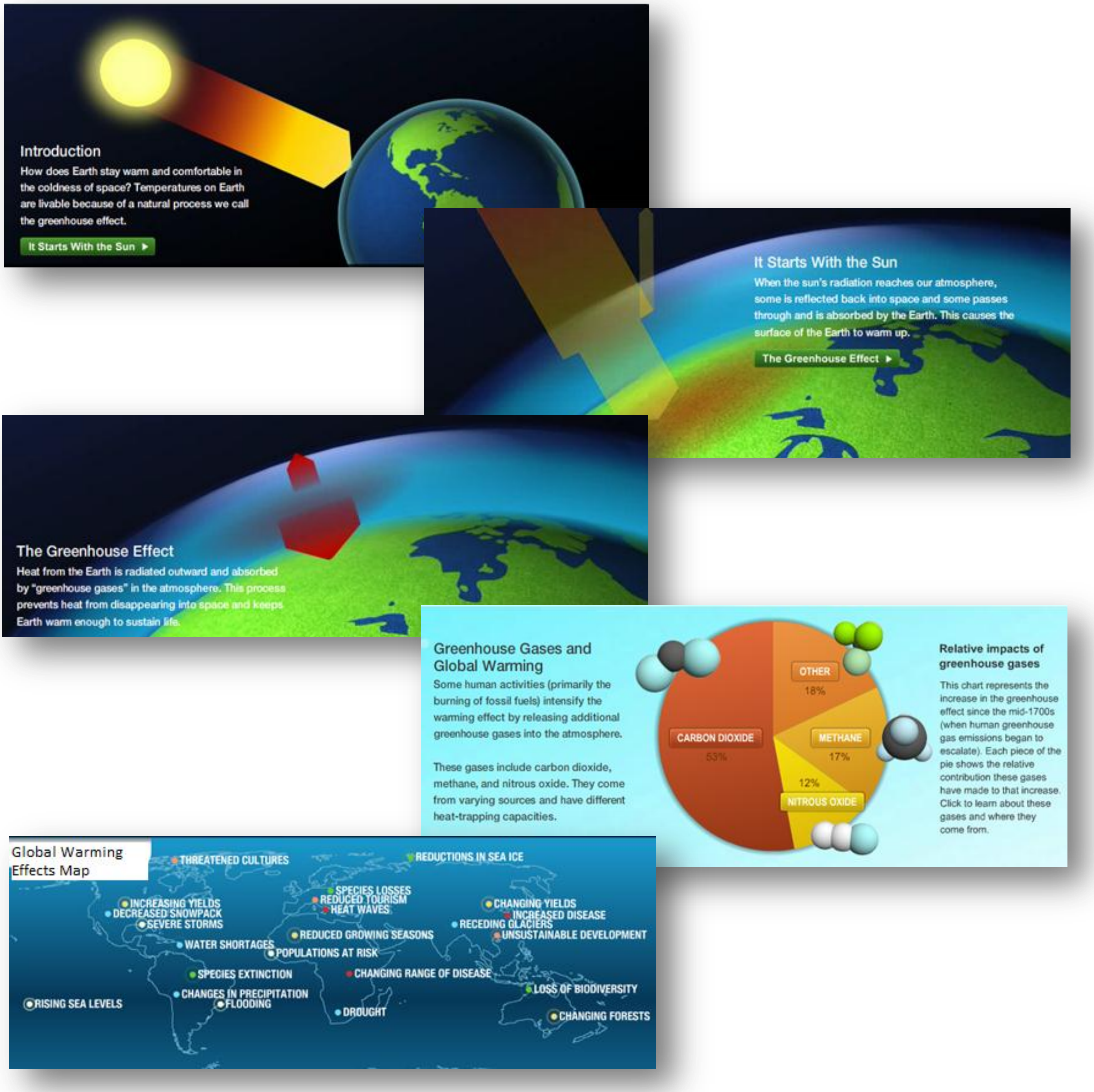
- **How long** do they stay in the atmosphere?

  Each of these gases can remain in the atmosphere for different amounts of time, ranging from a few years to thousands of years. All of these gases remain in the atmosphere long enough to become well mixed, meaning that the amount that is measured in the atmosphere is roughly the same all over the world, regardless of the source of the emissions.

- **How strongly** do they impact global temperatures?

  Some gases are more effective than others at making the planet warmer and "thickening the Earth's blanket."

- **Images below, describe Global warming and Greenhouse effect**:



Introduction

How does Earth stay warm and comfortable in the coldness of space? Temperatures on Earth are livable because of a natural process we call the greenhouse effect.

It Starts With the Sun

When the sun's radiation reaches our atmosphere, some is reflected back into space and some passes through and is absorbed by the Earth. This causes the surface of the Earth to warm up.

The Greenhouse Effect

Heat from the Earth is radiated outward and absorbed by "greenhouse gases" in the atmosphere. This process prevents heat from disappearing into space and keeps Earth warm enough to sustain life.

Greenhouse Gases and Global Warming

Some human activities (primarily the burning of fossil fuels) intensify the warming effect by releasing additional greenhouse gases into the atmosphere.

These gases include carbon dioxide, methane, and nitrous oxide. They come from varying sources and have different heat-trapping capacities.

Relative impacts of greenhouse gases

This chart represents the increase in the greenhouse effect since the mid-1700s (when human greenhouse gas emissions began to escalate). Each piece of the pie shows the relative contribution these gases have made to that increase. Click to learn about these gases and where they come from.

Global Warming Effects Map

Artwork 1. Global Warming explanation. *(Source National Geographic)*

2.1.5.3 Balance of CO_2 emissions

Carbon dioxide (CO_2) is the primary greenhouse gas emitted through human activities. Following table shows us the carbon dioxide properties:

PROPERTIES OF CARBON DIOXIDE	
Chemical Formula	CO_2
Lifetime in Atmosphere	50-200 years
Global Warming Potential (100-year)	1

Chart 2. Properties of carbon dioxide. *(Source National Geographic)*

At this point the contribution of renewable energy to limiting CO_2 emissions will be evaluated. Power generation accounts for 80% of greenhouse gas emissions, so that the incorporation of renewable energy in this sector will help reduce emissions.

To estimate the CO_2 avoided, it is assumed that the renewable electricity generated can not have been generated from non-renewable energy sources such as fossil, in a combined cycle natural gas with 50% rate of return.

The three areas studied to estimate the CO_2 avoided are:

- Electrical Area
- Thermal Area
- Transport Area

AVOIDED EMISSIONS BETWEEN 2011-2020 (tCO2)	
Renewable Energies - Electricity generation	
Hydroelectric	592.172
Wind power	62.712.996
Marine wind power	1.554.616
Thermoelectrical Solar	32.569.924
Photovoltaic Solar	12.934.085
Biomass	**10.587.673**
Biogas	3.093.316
Domestic waste renewable	1.586.777
Sea power	235.108
Geothermal energy	217.767
Total electric Area	126.084.435

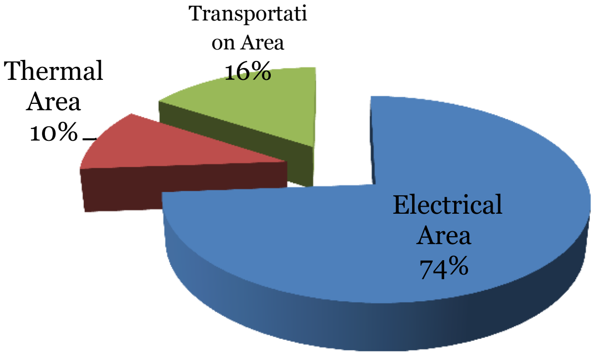
Renewable Energies - Heating and cooling	
Biomass	**11.280.173**
Biogas	975.152
Geothermal energy	65.412
Solar panels	4.969.922
Heating pump	486.308
Total thermal Area	17.776.967
Renewable Energies - Biofuels and transport	
Biodiesel	24.516.882
Bioethanol	2.543.943
Total transport Area	27.060.825
CO2 Avoided between 2011-2020 (tCO2)	**170.922.226**

Chart 3. Avoided emissions 2011-2020. *(Source Idae)*

The implementation of renewable energy between 2011 and 2020 will prevent 170 million tons of carbon dioxide, of which 12.8% are avoided by the use of biomass (excluding biofuels), about 22 million tons of carbon dioxide.

The percentage of CO_2 avoided by the use of renewable energy is different in each area:

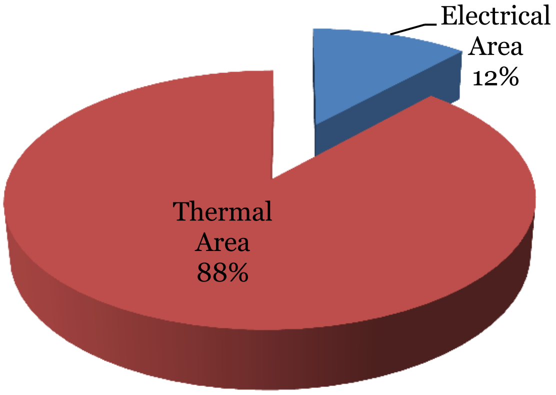
- Electrical Area	73.8%
- Thermal Area	10.4%
- Transportation Area	15.8%



Graphic 2. CO2 avoided by the use of renewable energy. *(Source Idae)*

CO_2 percentage avoided by the use of biomass is different in each area:

Electrical Area	8.4%
Thermal Area	63.4%
Area Transportation	0%



Graphic 3. CO2 avoided by the use of biomass. *(Source Idae)*

Biomass is the principal renewable energy CO_2 avoided in the thermal area and fourth in power generation.

2.1.6 Biomass situation

Now I will give a brief description of Global, Union European and Spanish situation.

2.1.6.1 Global situation

According to the United Nations Food and Agriculture Organization (FAO), some poor countries get 90% of their energy from wood and other biofuels.

This energy source is one-third of energy consumption in Africa, Asia and Latin America being the main source of energy in 2,000 million homes.

The disadvantage of biomass is its lack of technological development and energy efficiency, standing outside of a sustainable planning.

More than 10% (1.5 Gha) of the global area is currently used for crops and 25% (3.54 Gha) for grazing livestock and other animal products. Annually, about 7 or 8 Mha forest become agricultural.

Further development of the technology and proper planning of the use of biomass, would be a boost to the international market for biomass, environmental improvement and rural development in degraded areas.

The estimates established by the Intergovernmental Panel on Climate Change, states that by 2100 the percentage share of biomass in global energy production should be between 25.

2.1.6.2 Situation in the European Union

In the European Union, five countries contribute 56.7% of primary energy produced from biomass, France, Sweden, Germany, Finland and Poland. The main consumers of biomass (per capita consumption) are the Nordic and Baltic countries, Austria and Finland.

It is worth noting that applications for heating supplied by hot pellets are usual practice in many European countries. In some countries, growth in the installation of biomass boilers has been significant since 2004.

In Austria, for example, went from 28,000 installations with a power below 100 kW in 2004 to 47,000 in 2006.

All these developments together with increasing pellet production have built a European market for biomass; where countries with surplus production of this type of biomass supply to countries that consume pellet .

On the other hand, electricity production with biomass is around 60 TWh in the EU, representing around 2% of European electricity production.

2.1.6.3 Situation in Spain

In Spain , as in much of the developed countries, most of the consumption, based biomass, has been replaced, first by coal in the late nineteenth century and then by petroleum fuels or electrical applications during the twentieth century.

In fact this consumption was relegated to some sectors directly related to biomass, such as forestry and in some cases the food or ceramics. Apart from these sectors, the highest consumption of biomass was focused on traditional systems of heating.

Most of the biomass comes from the forestry sector, which has traditionally been used in the domestic sector by inefficient systems (use of firewood), but also boilers forest industries.

In the graph below we can see the great contribution in biomass consumption of traditional domestic uses, is established the high participation of forest industries (around 40%) and by-products from the production of oil and nuts set (8%).

The period between 2005 and 2009 has been a transition period where basis has been established for push-off the biomass sector.

Electricity generation plants that exist in Spain are scarce and most of the installed power plants come from industries that have secured their own fuel production. For example, the paper industry and forestry and food processing industries.

2.1.7 Biomass market

- Market analysis of biomass in Spain

The Renewable Energy Plan includes Spain targets for renewable energy under the European energy policy and establishes the contribution of different renewable energy in 2010 at a rate higher than 12% of primary energy.

Biomass accounts for about 50% of the objectives of the Renewable Energy Plan, however are developing well below the level required to achieve the objectives of PER rhythm. To support these objectives defined for Spain a regulatory framework that allows the further development of renewable energy, the RD 661/2007. This RD is characterized by extending the range and type of hybridization of biomass fuels. This new situation will allow biomass sector companies look more profitable use and the targets set in the PER are actually feasible.

The current situation in Spain has changed from a few years ago because of the crisis and the new PER (Renewable Energy Plan) which replaces the PER 2005-2010 to implement the new PER 2011-2020. This new energy scenario sets the objective to achieve a minimum 20% share of energy from renewable sources in gross final energy consumption in the European Union, the same target for Spain, and a minimum 10% share of energy from renewable sources in energy consumption in the transport sector in each member state by 2020.

The potential of biomass available in Spain, under conservative assumptions, is around 88 million tons of primary biomass in green, including remnants of forests, agricultural residues, existing undeveloped mass and energy to implement crops. In this potential more than 12 million tons of dry biomass from secondary residues added agroforestry industries.

According to the PER 2011-2020 are expected in the coming years, a major expansion of biomass. Therefore, in addition to advance further quantitative contribution of biomass, a qualitative change will occur in technology and efficiency.

2.1.8 Socioeconomic balance

The implementation of the 2011-2020 PER generate a series of direct economic effects that are quantified and susceptible to be added and subtracted as part of an economic balance, and involves assumptions, the result of the estimation may vary.

These effects are avoid increasing imported energy, of special relevance the natural gas and diesel fuel and reduced CO_2 emissions.

Below the balance sheet is detailed out the various effects:

ECONOMIC BALANCE-DIRECT EFFECTS			
Benefits (Millions €)		Costs (Millions €)	
Less importation of Natural gas	17.412	Public investment aid	1.037
Less importation of gasoil	7.125	Financing costs	155
Savings by reducing gasoline consumption	981	Other costs	67
Savings by reducing CO2 emissions	3.587	Premium equivalent special regime	23.235
		Incentive system for renewable heat	191
		Less collection IH*	99
Total	**29.105**	Total	**24.784**

Chart 4. Economic balance. *(Source Idae)*

(*) Less tax revenue corresponding to hydrocarbon biofuels.

As we can see in the balance, the costs are lower than the benefits of the PER, about 15% lower, mainly due to savings in fossil fuels.

Finally, there are other benefits that are harder to quantify, which are detailed below

OTHER BENEFITS	
Accumulated building wealth (Increments contribution to PIB) during 2011-2020 (million €)	33.607
Estimate of total employment linked to renewable energy by 2020	302.865

Chart 5. Other benefits. *(Source Idae)*

2.2 Coal as fuel

2.2.1 Definition

Coal is a black or brownish-black sedimentary rock that can be burned for fuel and used to generate electricity. It is composed mostly of carbon and hydrocarbons, which contain energy that can be released through combustion (burning).

Coal is the largest source of energy for generating electricity in the world, and the most abundant fossil fuel in the United States. Fossil fuels are formed from the remains of ancient organisms. Because coal takes millions of years to develop and there is a limited amount of it, it is a nonrenewable resource.

2.2.2 Types

Coal is very different from mineral rocks, which are made of inorganic material. Coal is made of fragile plant matter, and undergoes many changes before it becomes the familiar black and shiny substance burned as fuel. Coal goes through different phases of carbonization over millions of years, and can be found at all stages of development in different parts of the world. Coal is ranked according to how much it has changed over time. Hilt's Law states that the deeper the coal seam, the higher its rank. At deeper depths, the material encounters greater temperatures and pressure, and more plant debris is transformed into carbon.

2.2.2.1 Anthracite

Anthracite is the highest rank of coal. It has the most amount of carbon, up to 97%, and therefore contains the most energy. It is harder, more dense, and more lustrous than other types of coal. Almost all the water and carbon dioxide have been expelled, and it does not contain the soft or fibrous sections found in bituminous coal or lignite.

Because anthracite is a high-quality coal, it burns cleanly, with very little soot. It is more expensive than other coals, and is rarely used in power plants. Instead, anthracite is mainly used in stoves and furnaces. Anthracite is also used in water-filtration systems. It has tinier pores than sand, so more harmful particles are trapped. This makes water safer for drinking, sanitation, and industry. Anthracite can typically be found in geographical areas that have undergone particularly stressful geologic activity.

China dominates the mining of anthracite, accounting for almost three-quarters of anthracite coal production. Other anthracite-mining countries include Russia, Ukraine, Vietnam, and the United States (mostly Pennsylvania).

2.2.2.2 Hard coal

Coal is an organic sedimentary rock, a type of coal that contains between 45 and 85 percent carbon. It is hard and brittle, laminated, black, and matte or oily shine. It was formed by compressing of lignite, mainly in the Primary Era, during the Carboniferous Permian periods. Arises as a result of the decomposition of vegetable matter from the primeval forests, a process that has required millions of years. It is the most abundant type of coal.

Presents greater proportion of carbon, lower humidity and higher calorific value than lignite.

Regardless of its state is distinguished four varieties of coal carbonization:

Bright coal (conchoidal fracture, with many cracks perpendicular to bedding, is decomposed into fragments in block form, not dyed black, in primarily continuous layers, rarely as lentejón), matte coal (rough surfaces, form coarse fragments, not dyed black color, form coal strata up oily sheen and matte gray to black to several decimeters thick) coal fribrosa (colored black to dark gray, silky luster and fibrous porous texture, easily crushable , dyed in black color, shape and thin strata lentejón) coal and semi-gloss (not dyed, form alternating layers of thin stripes located between bright and dull coal thickness less than 3mm).

The coal used in power plants and in the production of coke, creosote (used as protective wood exposed to the outside) and cresol (used as an antiseptic and disinfectant)

2.2.2.3 Charcoal

Charcoal is a solid fuel with a heating power higher than wood.

When wood is subjected to an incomplete combustion process, the resulting product is charcoal. But coal is clearly distinguishable from the wood, not only by its blackish color, but also because having higher carbon content, calorific value is higher, making it better fuel. Furthermore charcoal contains less oxygen, making it inert, hardly alterable by external conditions or by the attack of biological agents such as fungi, which can attack the wood. Its main use is as fuel, not only for domestic use but also industrial. Its use is widespread in industrialized countries. Do not forget that charcoal is a renewable energy source, increasing interest as a fuel.

Charcoal is made about 80% carbon. Is achieved by heating to temperatures of 400-700°C, wood and other plant residues in the absence of air. The calorific value of the charcoal can be up to 35,000 KJ/kg, greater than that of wood, showing values between 12,000 to 21,000 KJ/kg.

- Shape, color and appearance.

The pieces of charcoal have many forms, if the wood is carbonized without slicing its shape is cylindrical, if it is not sliced, It looks like wooden bark. Its color is black shining due to pyroligneous liquids are deposited on the surface of the wood. The high specific surface area that the original wood have, is maintained in charcoal, because in the carbonization process a change in the chemical composition happen, but not change in the physical structure is produced.

- Specific surface .

The specific surface area of the charcoal is too high, that is, the surface of coal per unit volume is high. This is due to the large number of pores that charcoal has. Specific surface of charcoal is 160-436 m2/g.

- Humidity

The charcoal that is sold has a relative humidity of 6-10% dry basis. Charcoal increases very little moisture. Charcoal is called air drying charcoal when coal humidity is between 4 and 9.5% wet basis and if We say It is humid coal if It is between 10 and 15% and coal wet if humidity is greater than 15%. In the most usual processes are often unable to work at temperatures above 1500°C, so that the dry coal is 3-4% moisture.

- Chemical composition

The charcoal is mainly composed of carbon, also hydrogen, nitrogen and traces of oxygen. A higher carbon content of the original wood, is a higher carbon content charcoal, then a higher calorific value.

One problem is to select the temperature of carbonization, because at higher temperature we can find two opposite effects: increase the C percentage, it means, calorific power increases, but efficiency decreases, that means, the quantity of carbon by kg of original wood decreases. We must find an optimum temperatures interval where we have a high calorific power and enough efficiency.

- Charcoal market in Spain

Charcoal is demanded for domestic use, industrial use and as active carbon. The firewood can be obtain from different resources, for this reason price varies. It is a complex market and uncontrolled.

- Active coals market

Active coals are very expensive. Raw material of this kind of coal is charcoal. Main use of these coals is as a high quality filter.

2.2.3 How to use coal

People all over the world have been using coal to heat their homes and cook their food for thousands of years.

Today, coal continues to be used directly (heating) and indirectly (producing electricity). Coal is also essential to the steel industry.

- Fuel

Around the world, coal is primarily used to produce heat. It is the leading energy choice for most developing countries, and worldwide consumption increased by more than 30% in 2011. Coal can be burned by individual households or in enormous industrial furnaces. It produces heat for comfort and stability, as well as heating water for sanitation and health.

- Electricity

Coal-fired power plants are one of the most popular ways to produce and distribute electricity. In coal-fired power plants, coal is combusted and heats water in enormous boilers. The boiling water creates steam, which turns a turbine and activates a generator to produce electricity.

Almost all the electricity in South Africa (about 93%) is generated by coal. Poland, China, Australia, and Kazakhstan are other nations that rely on coal for electricity. In the United States, about 45% of the nation’s electricity is driven by coal.

- Coke

Coal plays a vital role in the steel industry. In order to produce steel, iron ore must be heated to separate the iron from other minerals in the rock. In the past, coal itself was used to heat and separate the ore. However, coal releases impurities such as sulfur when it is heated, which can make the resulting metal weak.

Many of the biggest coal producers in the world (the United States, China, Russia, India) are also among the biggest steel producers. Japan, another leader in the steel industry, does not have significant coal reserves. It is one of the world’s largest coal importers.

- Synthetic Products

The gases that are released during the coking process can be used as a source of power. Coal gas can be used for heat and light. Coal can also be used to produce syngas, a combination of hydrogen and carbon monoxide. Syngas can be used as a transportation fuel similar to petroleum or diesel.

In addition, coal and coke byproducts can be used to make synthetic materials such as tar, fertilizers, and plastics.

2.2.4 Advantages and disadvantages

- Advantages

Coal is an important part of the world energy budget. It is relatively inexpensive to locate and extract, and can be found all over the world. Unlike many renewable resources, coal production is not dependent on the weather. It is a baseload fuel, meaning it can be produced 24 hours a day, 7 days a week, 365 days a year.

We use and depend on many things that coal provides, such as heat and electricity to power our homes, schools, hospitals, and industries. Steel, vital for constructing bridges and other buildings, relies on coke for almost all production.

Coal byproducts, such as syngas, can be used to make transportation fuels.

Coal mining also provides economic stability for millions of people worldwide. The coal industry relies on people with a wide range of knowledge, skills, and abilities. Jobs associated with coal include geologists, miners, engineers, chemists, geographers, and executives. Coal is an industry that is critical to countries in both the developed and developing world.

- Disadvantages

Coal is a nonrenewable source of energy. It took millions of years to form, and a finite amount of it exists on our planet. Although it is a consistent and reliable source of energy at this point in time, it will not be available forever.

Mining is one of the most dangerous jobs in the world. The health hazards to underground miners include respiratory illnesses, such as “black lung,” in which coal dust builds up in the lungs. In addition to disease, thousands of miners die every year in mine explosions, collapses, and other accidents.

Burning coal for energy releases toxins and greenhouse gases, such as carbon dioxide. These have an immediate impact on the local air quality, and contribute to global warming, the current period of climate change.

Surface mining permanently alters the landscape. In mountaintop removal, the landscape itself is obliterated and ecosystems are destroyed. This increases erosion in the area. Floods and other natural hazards put these areas at great risk.

Coal mining can impact local water supplies in several ways. Streams may be blocked, increasing the chances for flooding. Toxins often leach into groundwater, streams, and aquifers.

Coal is one of the most controversial energy sources in the world. The advantages of coal mining are economically and socially significant. However, mining devastates the environment: air, land, and water.

2.2.5 Coal and carbon emissions

Burning coal releases gases and particulates that are harmful to the environment. Carbon dioxide is the primary emission.

Carbon dioxide is an essential part of our planet's atmosphere. It is called a greenhouse gas because it absorbs and retains heat in the atmosphere, and keeps our planet at a livable temperature. In the natural carbon cycle, carbon and carbon dioxide are constantly cycled between the land, ocean, atmosphere, and all living and decomposing organisms. Carbon is also sequestered, or stored underground. This keeps the carbon cycle in balance.

However, when coal and other fossil fuels are extracted and burned, they release sequestered carbon into the atmosphere, which leads to a build-up of greenhouse gases and adversely affects climates and ecosystems.

- Other Toxic Emissions

Sulfur dioxide and nitrogen oxides are also released when coal is burned. These contribute to acid rain, smog, and respiratory illnesses.

Mercury is emitted when coal is burned. In the atmosphere, mercury is usually not a hazard. In water, however, mercury transforms into methyl mercury, which is toxic and can accumulate in fish and organisms that consume fish, including people.

Fly ash and bottom ash are also released when coal is combusted. Depending on the composition of the coal, these particulates can contain toxic elements and irritants such as cadmium, silicon dioxide, arsenic, and calcium oxide.

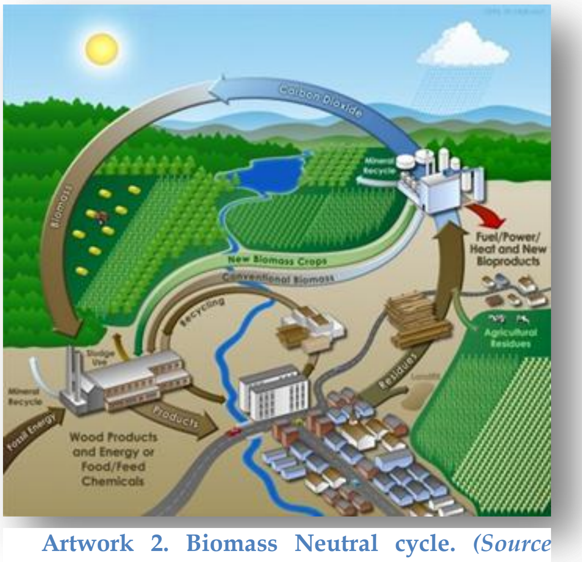
- Coal Fires

Under the right conditions of heat, pressure, and ventilation, coal seams can self-ignite and burn underground. Lightning and wildfires can also ignite an exposed section of the coal seam, and smoldering fire can spread along the seam.

Coal fires emit tons of greenhouse gases into the atmosphere. Even if the surface fire is extinguished, the coal can smolder for years before flaring up and potentially starting a wildfire again. Once coal catches fire and begins smoldering, it is extremely difficult to extinguish.

2.3 Comparison. Biomass vs. Coal

- The difference between biomass and fossil fuels.



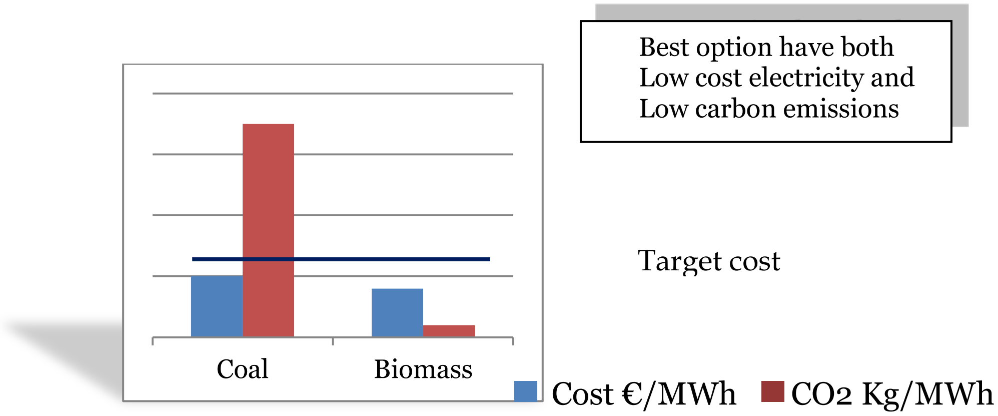
Artwork 2. Biomass Neutral cycle. *(Source National geographic)*

Biomass takes carbon out of the atmosphere while it is growing, and returns it as it is burned. If it is managed on a sustainable basis, biomass is harvested as part of a constantly replenished crop. This is either during woodland or arboricultural management or coppicing or as part of a continuous program of replanting with the new growth taking up CO_2 from the atmosphere at the same time as it is released by combustion of the previous harvest. This maintains a closed carbon cycle with no net increase in atmospheric CO_2 levels. Carbon dioxide (CO_2) from the atmosphere and water absorbed by the plants roots are combined in the photosynthetic process to produce carbohydrates (or sugars) that form the biomass. The solar energy that drives photosynthesis is stored in the chemical bonds of the biomass structural components. During biomass combustion, oxygen from the atmosphere combines with the carbon in biomass to produce CO_2 and water. The process is therefore cyclic because the carbon dioxide is then available to produce new biomass. This is also the reason why bio-energy is potentially considered as carbon-neutral, although some CO_2 emissions occur due to the use of fossil fuels during the production and transport of biofuels. Fossil fuels, like coal or oil, cannot recycle carbon dioxide in this manner. They take millions of years to form through geological processes in the earth's crust and hence millions of years for the GHG emissions released by burning these fuels to be recaptured.

- Biomass vs. Fossil Fuels: Low Cost

In addition to being renewable, biomass emissions and local access relative to fossil fuels are important considerations. While coal may be 20% less costly than biomass right now, coal is also responsible for producing the most carbon emissions and other pollutants than any other fuel source. Other fossil fuels are significantly more costly and also produce high levels of pollution.

Biomass is available in many areas throughout the world and can be cultivated or produced domestically-locally or regionally-with little or no supply or logistical risk. In contrast, reserves of oil and natural gas are located in limited areas throughout the world and are a depleting resource. Furthermore, the majority of known and accessible reserves are located in foreign countries, and supplies are controlled by foreign entities. In addition, finding and developing new reserves are relatively costly and risky. This general lack of access, compared to rising demand for energy, is causing the usual political, economic and widening range of environmental problems to worsen each year.



Graphic 4. Electricity cost and carbon dioxide emissions per kilowatt hour.

To summarize these ideas, I have developed following table, comparing biomass and coal, describing advantages and disadvantages of each one, and commenting it.

FUEL	ADVANTAGES	DISADVANTAGES	COMMENTS
Coal	Low cost	Not sustainable	Coal has an 'unfair' advantage over 'cleaner' forms of power generation in that the power station operators do not have to pay for the damage that they are doing to the atmosphere.
	Apparently plentiful: we will probably not run out of easily mined coal in the next few decades. It has been believed that the world's coal reserves would last a century or more, but some recent research has indicated that this was optimistic.	Requires around 1.7 million litres of fresh water for each gigawatt-hour of electricity generated.	A coal-fired power station generates a large amount of energy in a relatively small area compared to most renewable methods. However, when all the land required for mining and disposal of ash is taken into account coal does not have any space advantage over several sustainable methods.
		Produces more carbon dioxide (CO2) per Watt-hour of energy than any other generation method.	The misleading term 'clean coal' is sometimes used to refer to coal-fired power stations that efficiently extract substances like sulfur from the coal, either before or after burning. It is impossible to burn coal without producing carbon dioxide, so all coal-fired power stations are dirty in this sense. However, it is possible to dispose of (sequestrate) the carbon dioxide so that it is not released into the atmosphere for a long time.
		The methods of mining coal can be very destructive, although responsible coal miners do a remarkably good job of restoring the land after the coal has been mined out.	It seems that some coal-fired power stations that are not economically viable are being kept in operation because decommissioning and cleaning up would be more expensive than keeping them going.

		Very large quantities of ash have to be disposed of and a lot of smoke is produced, although in modern power stations most of the latter is separated from the waste gas stream and disposed of with the ash.	
		Coal contains substances such as sulfur, arsenic, selenium, mercury and the radioactive elements uranium, thorium, radium and radon . When the coal is mined and burned these substances can be released into the environment. Burned sulfur is one of the main causes of acid rain, but most modern coal-fired power stations remove most of the sulfur oxides from the released gasses.	
		War time – For maximum efficiency coal fired power stations must be big. They therefore present a desirable target for enemy attack.	
Biomass	Uses a renewable fuel.	A large area of land is required for the production of the fuel (per MW of power generated.	
	No net addition of carbon to the atmosphere (the CO2 released into the atmosphere by burning one crop is taken out by growing the next).	Because of the above point, this method can never generate enough power to satisfy a major part of current demands.	The sustainability of the production and replacement of the biomass is of critical importance to the ethics of using biomass as a source of energy.
		Burns organic matter that might be better returned to the land for soil improvement.	

Chart 6. Biomass and carbon comparison.

3 EXPERIMENTAL WORK. FUEL SAMPLING AND ANALYSIS

3.1 Analyzed fuel description.

Coal and biomass are the most representative of solid energy use for electricity production fuel. In the case of coal are characterized by their diversity and abundance of resources and in the case of biomass, its clean and inexhaustible production.

This project has studied ten different solid fuels with the aim of determining better fuel properties and thus achieve more efficient combustion conditions, minimizing the emission of gases and particles.

3.1.1 Description of the seven chosen biomass samples.

To undertake this project, I have chosen seven different samples of biomass to analyze.

In the case of almonds, olives and grapes, these samples have been collected from trees. Others like thistle, sludge and pellets have been provided by university and finally corn was bought.

- Thistle
- Sludge
- Pellets
- Olive pits
- Almond shells
- Corn
- Grapes

Below I will give a brief description of each one.

Artwork 3. Solid biomass samples

- **Thistle** 

Thistle is a perennial herbaceous specie, which appears in all seasons, with a good level of annual production. Thistle has excellent production conditions and adaptation of most of Spanish drylands. Its production is much higher than any type of energy crops.

- <u>Thistle Efficiency</u>

The distribution of such biomass varies from one plant to another depending on their development. Thistle production depends heavily on the availability of water in the ground, especially in the active growth phase, in the spring, and the proper fermentation of the crop. There is a strong relationship between rainfalls the agricultural year and overall production of biomass thistle, being mainly incident the amount of rainfall in Spring.

- **Sludge** 

Most sewage treatment plants, have a treatment system sludge generated during wastewater treatment. There are two types of sludge: primary and secondary, according to step debug the generated. These sludges are high in organic matter, so are ideal for obtaining biogas through a process of digestion.

For this reason there are many wastewater treatment plants, which have their own digester to produce methane. In addition to biogas energy can be obtained often exploit for any stage of water purification. The digested manure has several advantages when compared with untreated manure.

The fraction of nitrogen (N) that is absorbed by plants increases. The organic components present in the manure are readily degradable in the digestion, making it possible to save 10-20% of chemical fertilizers.

Organic compounds degrade very slowly (humus, lignin) are not degraded in the process, and improve soil conditions where the manure is applied . The digested manure produces fewer odors than not been treated. Manure produced after digestion is a more homogeneous product. The amount of seed pathogens and agents in the digested manure is digested due to the high operating temperatures.

- **Pellets**

The wood pellet, biomass is a renewable fuel generated or retrieval or use of products derived from wood (sawdust) and listed as a CO2 neutral fuel, so we can determine which cause no environmental impact.

- Pellets power calorific

The pellets have a high calorific value and can reach 4.9 kWh / kg. What comparison is the calorific value of the pellets with diesel and natural gas?

The calorific value of 1Lt. Heating oil is estimated to 10kWh per liter, as the 1 m^3 of natural gas. Therefore: Pellets 2 kg ~ 1 liter heating oil ~ 1m ^{3} natural gas. In comparison, the pellets represent a cost savings of around 45% on the heating bill. They are designed to neighboring communities boilers or for companies boilers, but are starting to be placed on the market for domestic use. Pellets can have different shapes, although they use to be used as a cylindrical shape.

- Density

It depends on the raw material used. If It comes from leafy species, It has higher density than conifers.Density also depends on pressure done by the press during the manufacturing and production process. Real density is the division between real mass divided by real volume of the pellet.

- Humidity

To manufacture pellets, we start from a raw material with less than 12% on humidity weigh, and in pelleting process, it is dryers more, the humidity is 8-10 % approximately.

- Chemical composition

It is a main factor to determine the calorific power. It depends on the raw material we started from. We must know the percentage of wood weight, humidity and used additives to manufacture pellets. With these data we can approximately know their chemical composition.

- Pellets market

Pellets price depends on the raw material price, the humidity percentage, electric power cost, and cost labor. In general, a pellet factory is profitable, when it has economic raw material and humidity less than 25% dry basis. The pellets are sold in bulk or orders although packaged in shrink plastic is the most common form of sale.

- **Olive pits** 

Olives are one of the most extensively cultivated fruit crops in the world. In 2011 there were about 9.6 million hectares planted with olive trees, which is more than twice the amount of land devoted to apples, bananas or mangoes. Only coconut trees and oil palms command more space. Cultivation area tripled from 2,600,000 to 7,950,000 hectares between 1960 and 1998 and reached a 10 million ha peak in 2008. The ten largest producing countries, according to the Food and Agriculture Organization, are all located in the Mediterranean region and produce 95% of the world's olives.

The olive biomass is a recycled natural waste so no trees are cut down to create our product. All raw materials are sourced from sustainable sources. Moreover olive biomass sourcing does not take up agricultural land that could be utilized for food production unlike many of the other agricultural biomass fuels. The use of olive biomass causes no net increase in the CO2 emissions to the atmosphere therefore olive biomass is a suitable alternative to fossil fuels. It is a readily available, reliable, renewable energy source with high calorific value.

Olive biomass is a premium quality agricultural biomass fuel that is sourced for recycling from the olive oil industry. The biomass is the dryed, solid by-product remaining after the olives have been pressed and the olive oil is extracted. The solid residue is composed of olive pits and dried olive cake/husk. This biomass releases considerable energy during it's combustion and its calorific value exceeds that of wood waste biomass.

Olive biomass is used in coal fired power stations where part of the fossil fuel supplied to the boilers are replaced by this carbon clean alternative. Other uses are in biomass power stations where it is burned together with other biomass materials to produce electricity and useful heat. It can be used as an efficient heating fuel also in smaller, direct combustion heating system.

- **Almond shells** 

Almond production generates millions of tons of residues in addition to almond nuts. Almond residues, including shells, hulls, pruning, leaves, skin and inedible kernel disposition, are good feedstocks for production of bioenergy and other valuable compounds.

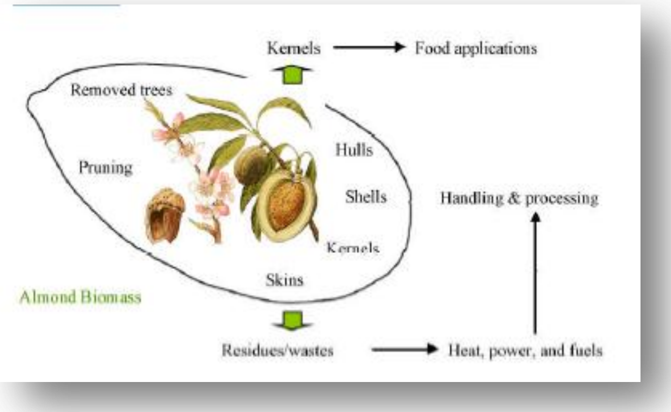
Almond (Prunus dulcis) is a mid-size tree of rose family. Almond fruit consists of the hull, shell, and kernel (nut). The almond tree can grow to a height of seven to ten meters.

The edible kernel or nut is separated and collected for commercial uses. The world produces about 1.8 million tons of almond nuts.

Due to orchard age and knock-down by wind, it's estimated that each year 20,000 acres of almond orchards may be removed. Based on 90 trees per acre and 200 kg mass per tree, by distributing over the total bearing acreage of 660,000 acres, each 1,000 acre of bearing orchard would generate tree mass of 545 tons annually. By estimation, each 1,000 acres of bearing almond orchard can generate more than 4,800 dry tons of biomass annually at hulling and shelling level including prunings and tree removal.

These residues, if processed and used wisely and efficiently, could provide substantial amount of heat and power needed for almond handling and processing (Figure 4).

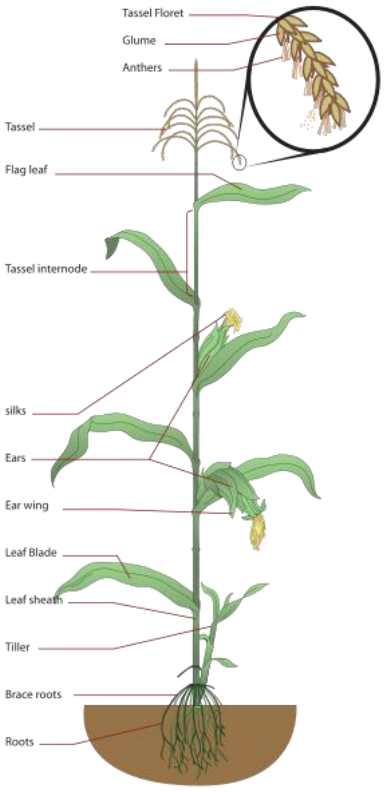
Additionally, advanced conversion technologies may produce liquid and solid fuels and high value materials and chemicals from these residues, bringing extra income to producers and processors. Utilization of these almond residues will certainly enhance the economic viability and sustainability of almond production and processing industries.



Artwork 4. Utilization of almond residues and wastes

- **Corn**

Maize known in some English-speaking countries as corn, is a large grain plant domesticated by indigenous peoples in Mesoamerica in prehistoric times. The leafy stalk produces ears which contain the grain, which are seeds called kernels. Maize kernels are often used in cooking as a starch.



Artwork 5. Maize plant

Maize is widely cultivated throughout the world, and a greater weight of maize is produced each year than any other grain. The United States produces 40% of the world's harvest; other top producing countries include China, Brazil, Mexico, Indonesia, India, France and Argentina. Worldwide production was 817 million tonnes in 2009—more than rice (678 million tonnes) or wheat (682 million tonnes).In 2009, over 159 million hectares (390 million acres) of maize were planted worldwide, with a yield of over 5 tonnes/hectare (80 bu/acre). Production can be significantly higher in certain regions of the world; 2009 forecasts for production in Iowa were 11614 kg/ha (185 bu/acre)There is conflicting evidence to support the hypothesis that maize yield potential has increased over the past few decades. This suggests that changes in yield potential are associated with leaf angle, lodging resistance, tolerance of high plant density, disease/pest tolerance, and other agronomic traits rather than increase of yield potential per individual plant.

"Feed maize" is being used increasingly for heating; specialized corn stoves (similar to wood stoves) are available and use either feed maize or wood pellets to generate heat. Maize cobs are also used as a biomass fuel source. Maize is relatively cheap and home-heating furnaces have been developed which use maize kernels as a fuel. They feature a large hopper that feeds the uniformly sized maize kernels into the fire.

Maize is increasingly used as a feedstock for the production of ethanol fuel. Ethanol is mixed with gasoline to decrease the amount of pollutants emitted when used to fuel motor vehicles. High fuel prices in mid-2007 led to higher demand for ethanol, which in turn lead to higher prices paid to farmers for maize. This led to the 2007 harvest being one of the most profitable maize crops in modern history for farmers. Because of the relationship between fuel and maize, prices paid for the crop now tend to track the price of oil.

Maize is widely used in Germany as a feedstock for biogas plants. Here the maize is harvested, shredded then placed in silage clamps from which it is fed into the biogas plants. This process makes use of the whole plant rather than simply using the kernels as in the production of fuel ethanol.

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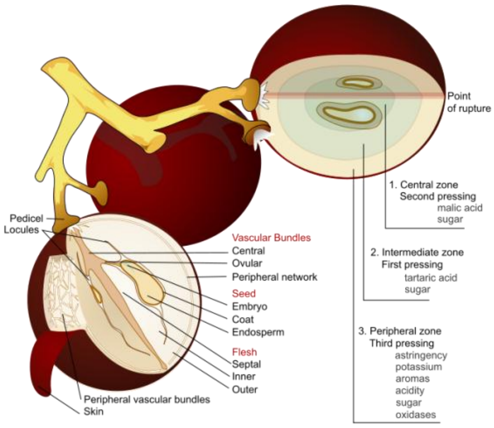
- **Grape** 

A grape is a fruiting berry of the deciduous woody vines of the botanical genus Vitis. Grapes can be eaten raw or they can be used for making wine, jam, juice, jelly, grape seed extract, raisins, vinegar, and grape seed oil. Grapes are a non-climacteric type of fruit, generally occurring in clusters.

According to the Food and Agriculture Organization (FAO), 75,866 square kilometers of the world are dedicated to grapes. Approximately 71% of world grape production is used for wine, 27% as fresh fruit, and 2% as dried fruit. A portion of grape production goes to producing grape juice to be reconstituted for fruits canned "with no added sugar" and "100% natural". The area dedicated to vineyards is increasing by about 2% per year.

There are no reliable statistics that break down grape production by variety. It is believed that the most widely planted variety is Sultana, also known as Thompson Seedless, with at least 3,600 km2. (880,000 acres) dedicated to it.



Artwork 6. Grape description

3.1.2 Brief description of the three chosen coal samples.

One of the objectives of this project is to compare biomass properties with coal ones with the aim of determining which one has better fuel properties and thus achieve more efficient combustion conditions, minimizing the emission of gases and particles.

For this reason I have also analyzed three different types of coal:

- Anthracite, hard coal and charcoal.

I will give a brief description of these types of coal, because the main one is described in section 2.2.2.

Anthracite: is the highest rank of coal. It has the most amount of carbon, up to 97%, and therefore contains the most energy. It is harder, denser, and more lustrous than other types of coal and it burns cleanly, with very little soot.

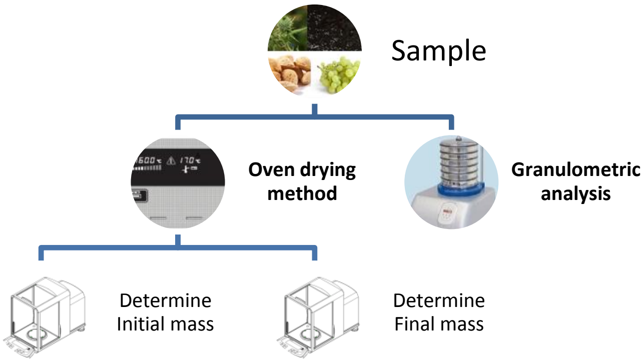
Charcoal: is a solid fuel with a heating power higher than wood. When wood is subjected to an incomplete combustion process, the resulting product is charcoal.

It contains less oxygen, making it inert, hardly alterable by external conditions or by the attack of biological agents such as fungi, which can attack the wood.

Hard Coal: is an organic sedimentary rock, a type of coal that contains between 45 and 85 percent carbon. It is hard and brittle, laminated, black, and matte or oily shine. It was formed by compressing of lignite. Arises as a result of the decomposition of vegetable matter from the primeval forests. It is the most abundant type of coal.

3.2 Samples preparation

The objective of this step is to convert samples into very fine particles without moisture. The first thing to do, was placing on trays in an oven at 105 ° C to dry the samples in order to remove the moisture content. Before introducing the sample into the oven must be weight in a precision balance, obtaining a measure (Initial weight). After drying we must weight it again (Final weight), and it is then sieved to get the ready sample for analysis.



Artwork 7. Process sketch

3.2.1 Granulometric analysis

The granulometric reduction is part of the process of preparation of the solid fuel and is to achieve optimum particle size for burning.

In general, the choice of the final particle size, must be a balance between obtaining small particle sizes favoring their combustion (as there will be more useful on the surface that may occur oxidation reactions) and power consumption. Improper choice of the particle size can generate unburned fuel if the selected size is quite large and does not allow complete combustion, or may unnecessarily increase the power consumption if the size is too small.

- **Granulometric Standards** :

- <u>Solid mineral fuels</u>:
  ASTM D4749/87 (2007)- Standard Test Method for performing the sieve analysis of coal and designation coal size.
- <u>Solid biofuels</u>:
  CEN / TS 15149-1, Methods for determination of particle size distribution. Part 1: Method of oscillating screen with mesh opening of 3.15mm or more.
  CEN / TS 15149-2, Methods for determination of particle size distribution. Part 2: Method of oscillating sieve with mesh size equal to or equal to 3.15mm.
  CEN / TS 15149-3, Methods for determination of particle size distribution. Part 3: Method of rotary screen.

- **Equipment required to perform the analysis**

To perform this test the most used equipment is a **sieve.** This device has several strainers with different sizes in decreasing order. Once the sample fed into the top sieve, the sample is moved in a horizontal plane, classifying the particles in different strainers according size.

Sieve model chosen to performance this analysis is JEL 200/80.

The basic unit consists of a machine base with cast in handles and standing on rubber buffers and an oscillating plate. The base accommodates the direct drive geared motor and electrical wiring for the control panel on which is mounted a 1-30 minute adjustable timer.

This unit can be used with 1-9 sieve frames, each of 25mm net height, plus cover and retaining dish. Standard sieve frames have worldwide 200mm, respectively 203mm diameter. As frames with 220 mm diameter have a recess, these can also be used.

Artwork 8. Sieve JEL 200/80

Operating Instructions

1. Place machine on a vibration free surface.
2. Place retaining dish and sieve frames in position, with largest mesh opening on top.
3. Feed sample, generally 100gr or smaller amounts which can be divided by 100.
4. Switch on by timer.Sieving time generally between 3-10 minutes.
5. Guard movement range – as far as is necessary.
6. The unit was started with the timer, It will switch itself off.

3.2.2 Oven drying method

The objective of this step is to convert the sample without moisture. The first thing to do, is placing samples on trays in an oven at 105 ° C to dry the samples in order to remove the moisture content. Before introducing the sample into the oven must be weight in a precision balance, obtaining a measure (Initial weight). After drying we must weight it again (Final weight).

To perform this process I have needed a total of 8 hours and ambient conditions were temperature of 20°C to 30°C and less than 50% relative humidity. Oven drying method is performance in order to achieve final sample mass without moisture.

Process to reach this result is described below:

1. Determination of the initial mass.

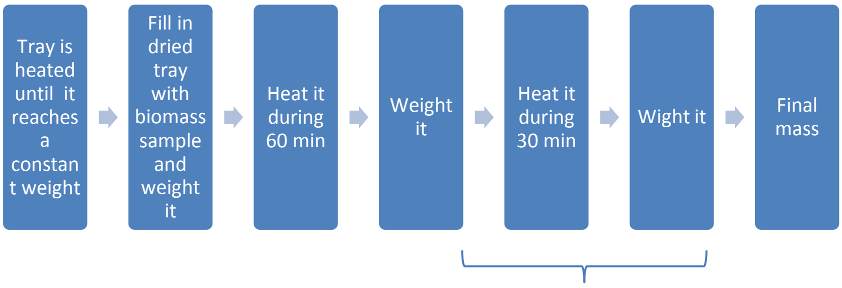
Before the laboratory sample is subjected to any manipulation or treatment that may allow the loss of moisture or dust, the mass of the sample is determined by weighing on a balance with an accuracy of 0.1% of the mass of the sample.

2. Determination of the final mass.

To obtain final mass, biomass has been subjected to a drying process.

Biomass sample is dried until, mass is constant. Steps of drying process are described below:

1. Tray is heated until it reaches a constant weight.
2. Fill in dried tray with biomass sample and weight it.
3. Heat it during 60 min, weight it and repeat the process each 30 min until it reaches a constant weight. When mass is constant we have obtained final mass.



Repeat it until sample reaches a constant

Artwork 9. Drying process

- **Standards used:**

- Solid biofuels. Sampling.Part 1: Methods for sampling. CEN/TS 14778-1
- ASTM Standard Practice E 1757 – 01.

- **Equipment needed to perform oven drying method**

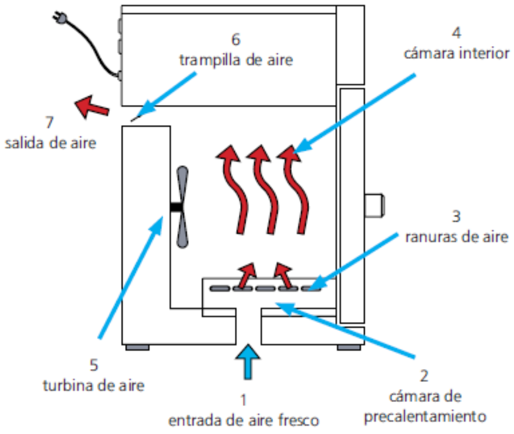
Apparatus required for oven drying method are:

- Analytical balance, accurate to 0.1 mg
- Convection drying oven with temperature control, 105 +- 3 ºC

- **Convection drying oven**

To perform oven drying method, I have chosen the model: MEMMERT convection drying oven. Procedure will be placing samples on trays in the oven at 105 ° C to dry the samples in order to remove the moisture content.

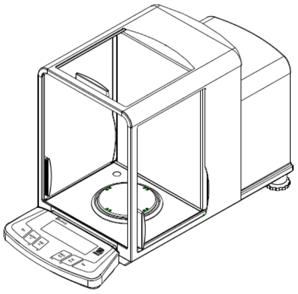
I need to dry 10 different samples, and due to the oven dimensions, is impossible to dry them at the same time. So firstly I will place 5 samples, and then the others five.



Artwork 10. Oven operation

The equipment operates on natural air convection as is shown in the following figure. The fresh air entering (1) is heated in the preheating chamber (2). The preheated air enters through the air slots (3) of the side wall of the chamber (4). The air turbine (5) in the rear wall of the inner chamber produces, compared to the natural convection, a greater exchange of air and increased horizontal forced circulation. By air trap (6) on the back wall of the computer the amount of air that enters and leaves (air change) (7) is set.

- **Analytical balance**


Artwork 11. Ohaus balance

Analytical balance Model chosen to perform test is: Balanaza Ohaus. This balance is a precision weighing instrument

Operation:

For a precise use of the balance, we must follow the following steps:

1. Setting the balance to zero

Remove the load from the pan and press the Zero button to set the display to zero.

2. Tare

Tare refers to the action of discounting the weight of a container so that it only shows the weight of the objects in the container (net weight). To do it correctly, place the empty container on the weighing pan and press the Tare button, then add material to the container and finally sample net weight is shown. To clear the tare value, remove container from the pan and press the Tare button.

3. Weighing

This mode is used to determine the weight of samples in the selected measurement unit. Balance is shipped with grams enabled. Press and hold Mode until "WEIGH" regret on the screen, and release the button. Press Zero to set the balance to zero and then place the sample to be weighed on the plate for the weight display.

3.2.3 Oven drying method Results

The objective of oven drying method is to convert samples into particles without moisture. According to the procedure described before these are the results.

In this table we can see the final weight of our samples obtained by the drying process described above.

Sample	Initial sample Weight (g)	Dryed Conteiner weight (g)	Total Weight (g)	After 60 min	After 30 min	After 30 min	After 30 min	After 30 min	After 30 min
Pellet	6,97	247,89	254,86	254,43	254,38	**254,37**			
Thistle	20,29	244,26	264,55	263,63	263,57	**263,57**			
Almond shell	18,74	54,27	73,01	70,25	70,2	**70,2**			
Hard coal	26,71	247,78	274,49	273,81	273,78	**273,78**			
Charcoal	11,53	41,37	52,9	52,71	52,69	**52,69**			
Grape bones	17,98	54,27	72,25	61,49	61,41	61,39	**61,39**		
Anthracite	38,13	62,31	100,44	99,92	99,87	99,86	**99,86**		
Olive pits	25,43	244,26	269,69	263,38	261,42	261,19	261,12	**261,12**	
Corn	36,17	45,46	81,63	77,87	77,53	77,36	77,26	77,19	**77,19**
Sludge	We have used dry sample			-	-	-	-	-	-

Chart 7. Final weight

To performance oven drying method I have spent a total of 15 hours. As we can see, to reach a constant weight (final weight):

- Pellets, thistle, almond shell, hard coal and charcoal, process had to be repeated twice (120 min).Grapes and anthracite, process had to be repeated 3 times (150min).Olive pits, process had to be repeated 4 times (180min). Corn process had to be repeated 5 times (210 min).

Following table shows us, the percentage of how has varied the weight.

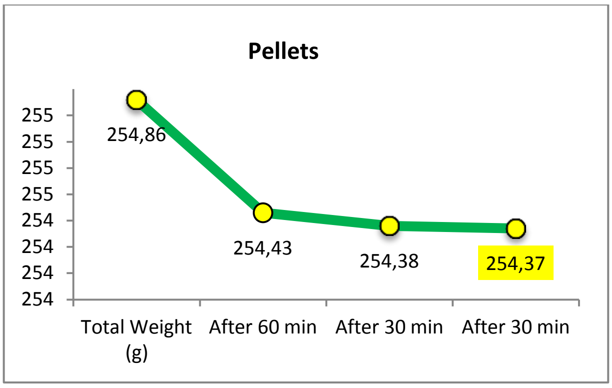
Sample	**% After 60 min**	**% After 30 min**	**% After 30 min**	**% After 30 min**	**% After 30 min**	**% After 30 min**	**Total Variance**
Grape bones	-14,89%	-0,13%	-0,03%	0,00%			**-15,06%**
Corn	-4,61%	-0,44%	-0,22%	-0,13%	-0,09%	0,00%	**-5,48%**
Almond	-3,78%	-0,07%	0,00%				**-3,85%**
Olive pits	-2,34%	-0,74%	-0,09%	-0,03%	0,00%		**-3,20%**
Anthracite	-0,52%	-0,05%	-0,01%	0,00%			**-0,58%**
Charcoal	-0,36%	-0,04%	0,00%				**-0,40%**
Thistle	-0,35%	-0,02%	0,00%				**-0,37%**
Hard coal	-0,25%	-0,01%	0,00%				**-0,26%**
Pellet	-0,17%	-0,02%	0,00%				**-0,19%**
Sludge	-	-	-	-	-	-	**-**

Chart 8. Variance weight

As we can see, grape bones have the highest moisture content, whereas thistle, pellets and coals have the lowest one.

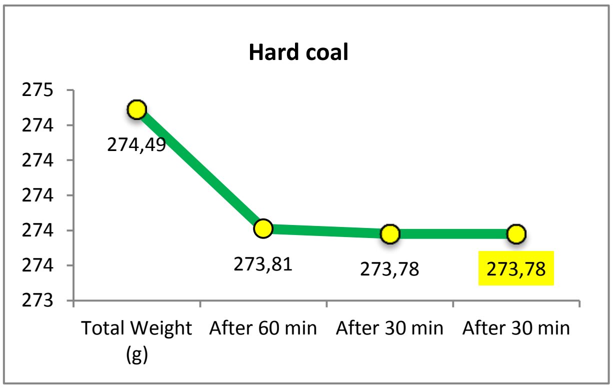
- **Biomass Plots samples:**

Following plots shows us a function of how sample weight has been decreasing over time until It has reached a constant weight. As we can see, all samples have something in common: the main peak occurs in the first phase of drying.



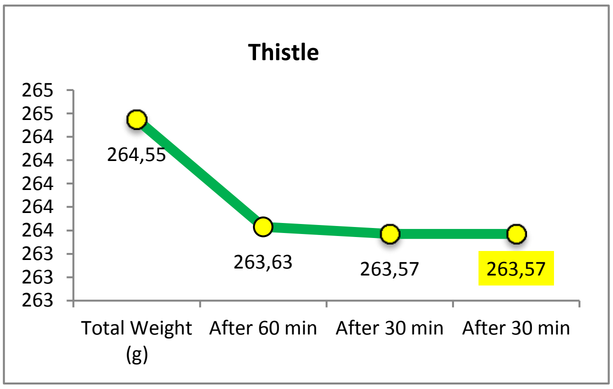
Graphic 5. Pellets

Its weigh has decreased 0,19% in 120 min.

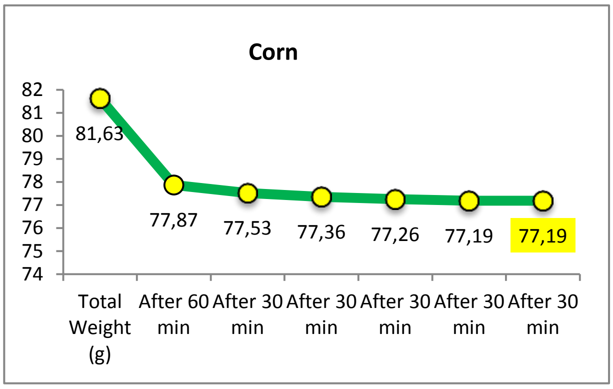


Graphic 6. Hard coal

Its weigh has decreased 0,26% in 120 min.

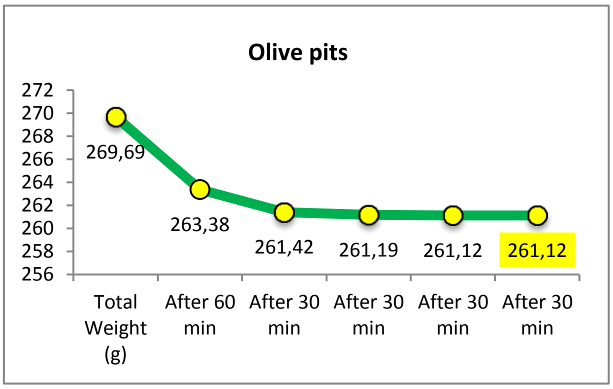


Graphic 7. Thistle



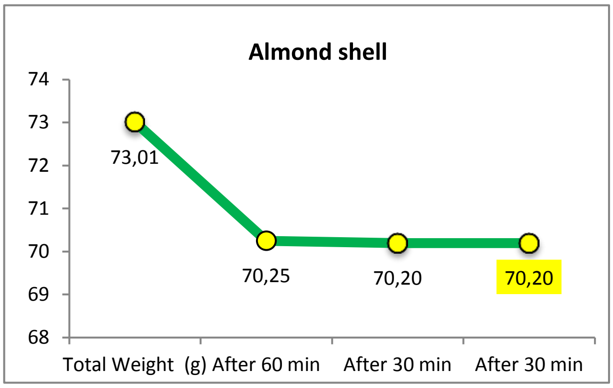
Graphic 8. Corn

Its weigh has decreased 5,48% in 120 min.



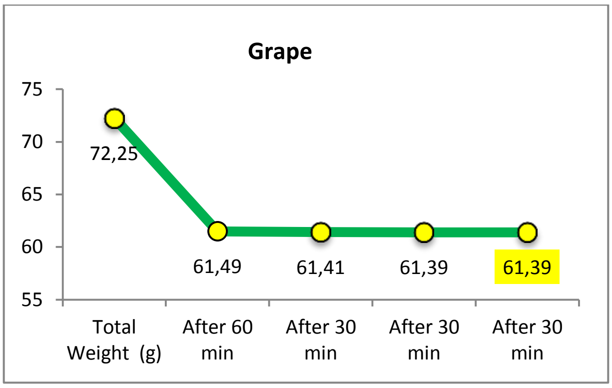
Graphic 9. Olive pits

Its weigh has decreased 3,20% in 180 min.



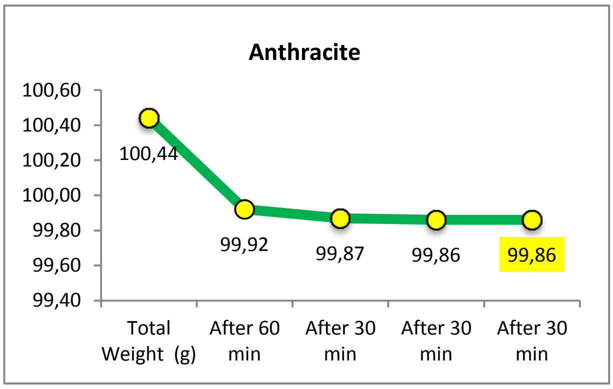
Graphic 10. Almond shell

Its weigh has decreased 3,85% in 120 min.



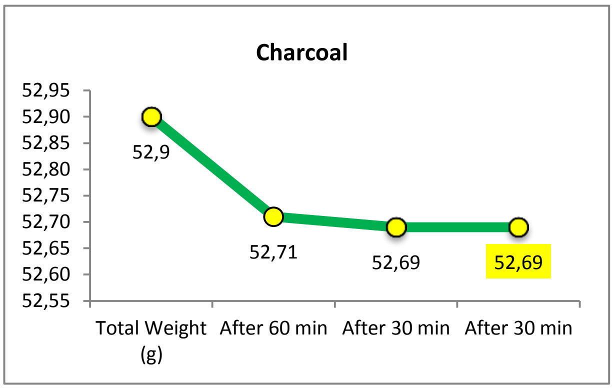
Graphic 11. Grape

Its weigh has decreased 15,06% in 150 min.



Graphic 12. Anthracite

Its weigh has decreased 0,58% in 150 min.



Graphic 13. Charcoal

Its weigh has decreased 0,40% in 120 min.

3.3 Thermal Properties

- Each type of biomass has its specific properties which determine its performance as a fuel in combustion. Most important properties regarding thermal conversion of fuels is as follows.

- ***Moisture content***
- ***Elemental composition***
- ***Calorific value***

3.3.1 Moisture Content

The moisture content of biomass is the quantity of water in the material, expressed as a percentage of the material's weight. This weight can be referred to on wet basis and on dry ash free basis. If the moisture content is determined on a 'wet' basis, the water's weight is expressed as a percentage of the sum of the weight of the water, ash, and dry-and-ash-free matter. Similarly, when calculating the moisture content on a 'dry' basis (however contradictory that may seem), the water's weight is expressed as a percentage of the weight of the ash and dry-and-ash-free matter. Finally, the moisture content can be expressed as a percentage of the "dry and-ash-free" matter content. In that last case, the water's weight is related to the weight of the dry biomass. Because the moisture content affects the value of biomass as a fuel, the basis on which the moisture content is measured must always be mentioned. This is particularly important because biomass materials exhibit a wide range of moisture content (on a wet basis), ranging from less than 10 percent for cereal grain straw up to 50 to 70 percent for forest residues.

- **Moisture method Standards**
  - <u>Solid biofuels:</u>
    UNE-CEN (TS_14774-1 = 2007_EX Solid biofuels. Methods for determination of moisture content Pt1.
    UNE-CEN (TS_14774-2 = 2007_EX Solid biofuels. Methods for determination of moisture content Pt2.
    UNE-CEN (TS_14774-3 = 2007_EX Solid biofuels. Methods for determination of moisture content Pt3.
  - <u>Solid mineral fuels</u>:
    UNE_32002 = 1995 Solid mineral fuels. Determination of moisture from the sample for analysis.

Moisture analysis

To determine moisture content is necessary to performance oven drying method. It has been described in section 3.2.2 of this project. Here I will give a brief description to refresh it. Conditions: 105ºC Temperature and 1atm pressure

Data we need to know are: Initial mass and final mass.

- Determination of the initial mass.
  Before the laboratory sample is subjected to any manipulation or treatment that may allow the loss of moisture or dust, the mass of the sample is determined by weighing on a balance with an accuracy of 0.1% of the mass of the sample.

- Determination of the final mass.
  To obtain final mass, biomass has been subjected to a drying process. Biomass sample is dried until, mass is constant.

Moisture percentage is calculated according to the diminution of the mass weight.

Calculation of moisture content

To calculate it, following equation is required:

$$M_{ad}=\frac{m2-m3}{m2-m1}\cdot 100$$

Where: m_1: mass of empty vessel [g], m_2: mass of vessel and sample before heating [g], m_3: mass of vessel and sample after heating [g]

3.3.2 Elemental Composition

The composition of the ash-free organic component of biomass is relatively uniform. The major components are carbon, oxygen, and hydrogen. Most biomass also contains a small proportion of nitrogen and sulphur.

The carbon (C), hydrogen (H), oxygen (O), sulphur(S) and nitrogen (N) determination in biomass represents the so called elementary analysis. These elements are detected by an elemental analyzer .In this project we perform this analysis with TruSpec LECO.

About 0.05-1.5 g of sample are burned at 900 ° C in an oxygen atmosphere, so the C is converted into CO2, H in H20, S into SO2 and the N in N2. The first three compounds are detected quantitatively by an IR detector, while N2 is determined by a thermal conductivity detector.

To determine C, H, N, S percentage, the Standard required is

BSI_CENTS 15104_Solid biofuels_Content of carbon,hydrogen and nitrogen. AFNOR_CENTS 15289_Solid Biofuels_ Content of sulphur and chlorine.

Elemental analysis

Before to perform elemental analysis, firstly we need to prepare samples, and with samples I include EDTA samples. In this project we prepared 20 EDTA samples and 50 solid biomass and solid mineral samples. This process is described in section 3.4.1.4. After that, we need to calibrate the apparatus. When It is done, we analyze blanks (30 repetitions approximately) until, Nitrogen area is under 1. When the equipment is stabilized, we check it logging EDTA samples. LECO EDTA has 41+- 0.13 C%, 5.56 +- 0.03 H% and 9.57+- 0.03 N%, when we reach these results, we can start logging our samples to analyze them.

3.3.3 Heating value

The calorific value is one of the most important characteristics of a fuel, and it is useful for planning and control of the combustion plants. It indicates the amount of heat that developed from the mass (weight) in its complete combustion with oxygen in a calorimeter standardize. It is defined as the amount heat energy released during the complete combustion of unit mass of biomass.

To determine heating value we consulted these standards:

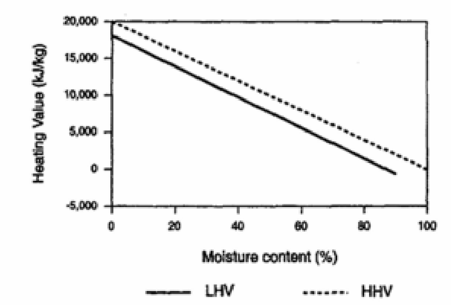
- Solid biofuels: UNE_164001 = 2005_EX Solid biofuels. Method for determining the calorific value.
- Solid mineral fuels: UNE_32006 = 1995 Solid mineral fuels. Calorific value determination by automatic calorimeter.

- There are two types of calorific value (usually expressed in kcal/kg or MJ/kg) might be considered:

1. Higher heating value (HHV): it is the amount of heat released by a complete combustion of a mass unit of a sample at constant volume in an oxygen atmosphere and at the standard conditions (101.3 kPa, 25°C). The HHV takes

into account the latent heat of vaporization of water, and it assumes that the water component is in liquid state at the end of combustion.

2. Lower heating value (LHV), doesn't include the water condensation heat. The high heating value can be determined experimentally in the laboratory with adiabatic calorimeter.



Artwork 12. Heating value as a function of moisture content

- **Graphical interpretation**

  - **Lower heating value (LHV)**

To obtain the Calorific Value of fuel is necessary that all the carbon (C) is completely oxidized becoming into carbon dioxide (CO2)

$$\underset{\text{FUEL}}{CH_2} + \underset{\text{AIR}}{O_2 N_2} \longrightarrow \underset{\text{COMBUSTION GASES}}{CO_2\ H_2O\ N_2} + \underset{\text{OXIDATION FUEL HEAT}}{\text{HEAT}}$$

↓

LHV

WATER VAPOR CONTENT OF GAS COMBUSTION DOES NOT CONDENSE

  - **Higher heating value (HHV)**

To obtain the Calorific Value of fuel is necessary that all the carbon (C) is completely oxidized becoming into carbon dioxide (CO2)

$$\underset{\text{FUEL}}{CH_2} + \underset{\text{AIR}}{O_2 N_2} \longrightarrow \underset{\text{COMBUSTION GASES}}{CO_2\ H_2O\ N_2} + \underset{\text{OXIDATION FUEL HEAT}}{\text{HEAT}} + \underset{\text{HEAT OF VAPOR CONDENSATION}}{\text{heat}}$$

↓

$$\underbrace{\text{LHV} \qquad\qquad\qquad\qquad}_{\text{HLV}}$$

WATER VAPOR CONTENT OF GAS COMBUSTION CONDENSE

- **Heading values relationship**

LHV= HLV - 597 · G

Where: LHV: Lower heating value [kcal / kg comb], HHV: Higher heating value [kcal / kg comb], 597: Heat of water condensation at 0ºC [kcal / kg water], G:Water formed by the combustion of H_2 $\%_{weight}$ plus the own combustible [kg water/ kg comb]. $G = 9H + H\ _20$ Where: 9 : Water kilograms formed after oxidize 1Kg of hydrogen, H: Hydrogen percentage no contained in the combustible, H2O: Combustible moisture percentage.

Final formula:

$$LHV = HHV – 597 \cdot (9H + H_2O)$$

- **Calorific power calculations**

There are two ways to calculate it:

- Analytic method.
- Practical method.

1. **Analytic method.**

This method is based on the energy conservation principle that states:

"The calorific value of a composite is equal to the sum of the calorific values of the single elements that make it up, multiplied by the centesimal amount involved, less the total amount of hydrogen fuel which is already combined with oxygen. "

To be able to use this principle, firstly we have to do the **elemental analysis** of the biomass sample.

- **Carbon heating value**

If C is combined with enough O quantity, It completely burns resulting carbonic anhydride beaming heat.

Chemical reaction:

$$C + 0_2 \longrightarrow CO_2 + 8.140\ [kcal/kg\ ]$$

If there were not enough Oxygen for the combustion, Carbon would oxidize, giving monoxide carbon as a result, and beaming less heat.

Chemical reaction:

$C + ½\ 0_2 \longrightarrow CO + 2.440$ [kcal/kg]

- **Hydrogen heating value**

  - High heating value

$H_2 + ½\ 0_2 \longrightarrow H_2O + 34.400$ [kcal/kg]

This value includes heat of vapor condensation.

Hydrogen HHV = 34.400 [kcal/kg]

  - Low heating value

To calculate it, We use Heating values relationship formula:

$LHV = HHV - 597 \times (9H + H_2O)$

Where: H_2O= 0 because we consider there is no combustible humidity, H= 1Kg

LHV = 34.400 - 597 x 9

LHV = 34.400 - 5.400

Hydrogen LHV= 29.000 [kcal/kg]

- **Sulfur heating value**

Sulfur fuel is a pollutant, and their presence is undesirable, however, when this element is present and is oxidized it releases heat according to the following chemical reaction:

$S + 0_2 \longrightarrow SO_2 + 2.220$ [kcal/kg]

- **Dulong formula**

- **HHV Dry combustible:**

$HHV_D = 8.140 \times C + 34.400 \times (H - O/8) + 2.220 \times S$

Where:

C: centesimal quantity of carbon (weight) by kg of combustible
H: centesimal quantity of hydrogen (weight) by kg of combustible
O: centesimal quantity of oxygen (weight) by kg of combustible
S: centesimal quantity of sulfur (weight) by kg of combustible

- **LHV Dry combustible:**

$LHV_D = 8.140 \text{ x } C + 29.000 \text{ x } (H - O/ 8) + 2.220 \text{ x } S$

2. Practical method

In this method we will use Parr 6300 calorimeter, to determine in a direct way the heating value. Calorimetric method burns a fuel quantity and measure the quantity of heat produced through thermic energy gained by a known liquid, water.

In order to determine the superior calorific dry basis we need moisture value (h) calculated in section 4.1, following the technical specification UNE- EN 14774-3 "Solid biofuels. Determination of moisture content. Method oven. Part 3: Humidity sample for analysis in general."

HHV at constant volume is determined on a dry basis HHV, from the HHV_{bh} wet basis, determined experimentally by bomb calorimeter, and moisture of the sample assay h

$HHV = (HHV_{bh})/ (1-h/100)$

LHV is determined from higher calorific value at constant volume on a dry basis and content of hydrogen determined from the elemental analysis:

$LHV = HHV – 206 \cdot H$

3.4 Required equipment to perform analysis.

Characterization of biomass it is essential to know applications that have in the industry and other sectors. To characterize it , is necessary to evaluate the composition and behavior in different environments, and understand the environment that surrounds it. A useful characterization tool is the elemental analysis, which tries to find the concentration of some key elements such as carbon, hydrogen, nitrogen, oxygen and sulfur. To perform this analysis we will use **CHN(S).**

Heating value is the most important feature in the selection and use of a fuel because it indicates the amount of heat that is released when the amount of mass is burned under standardized conditions. Is a fundamental characterization in the combustion of solid fuel phase. The device that is generally used to determine the calorific value is the **calorimeter.**

Analyses have been performed in UC3M BIOLAB, 202 - Testing Laboratory of Biomass Fuels.

Artwork 13. UC3M BIOLAB, 202

3.4.1 CHN(S)

To perform elemental analysis a measuring instrument named CHN(S) is required, which gives a direct result of the composition of the sample in weight percent.

In addition to the measuring instrument an input of oxygen, helium, and synthetic air is required and precision balance to enter the weight of the sample.

Model chosen to perform this analysis is: TruSpec LECO CHN/CHNS

Artwork 14. CHNS equiment

3.4.1.1 Description

The TruSpec LECO is an instrument that determines the Carbon, Hydrogen, Nitrogen and Sulfur content in homogeneous organic materials. The nominal sample weight is 2 milligrams. The instrument is connected to an external PC, and uses a Windows®-based software program to control the system operation and data management.

Standard: Due to the increased use of experimental methods for the determination of carbon, hydrogen and nitrogen, standardization of these experiments were performed under standard European character, UNE-CEN/TS 15104 Determination of Total Carbon, Hydrogen and Nitrogen. Instrumental methods. In which the steps and the appropriate tools to perform the experiment are indicated.

3.4.1.2 Theory of Operation

The TruSpec LECO Series is used to determine nitrogen, carbon/nitrogen, or carbon/hydrogen/nitrogen and sulfur in many organic matrices. The system is based on the Dumas method of combustion, and provides a result within four minutes for all elements.

There are three phases during an analysis cycle: purge, burn, and analyze. In the sample-drop purge phase, the encapsulated sample is placed in the loading head, sealed, and purged of any atmospheric gases that have entered during sample loading. The ballast volume (zero volume at this point) and gas lines are also purged.

During the burn phase, the sample is dropped into the primary furnace (950 C) and flushed with pure oxygen for very rapid combustion. The products of combustion are passed through the after-burner furnace, furnace filter, pre-cooler, and thermoelectric cooler before collecting in the ballast volume.

In the analyze phase, the combustion gases in the ballast become homogeneous by means of passive mixing. A series of infrared detectors then measure the evolved gases for carbon and hydrogen. In addition, a 3 cc aliquot is captured in a loop before the ballast piston is forced down to evacuate the ballast. The sample aliquot gases are swept through hot copper to remove oxygen and change NOx to N , Lecosorb and Anhydrone to remove carbon dioxide and water, and a thermal conductivity detector to determine nitrogen. An optimized detector is used for each element—ensuring a total analysis time of less than four minutes.

The final result is displayed as weight percentage or in parts per million as determined by the operator. Results can be corrected on a moisture basis.

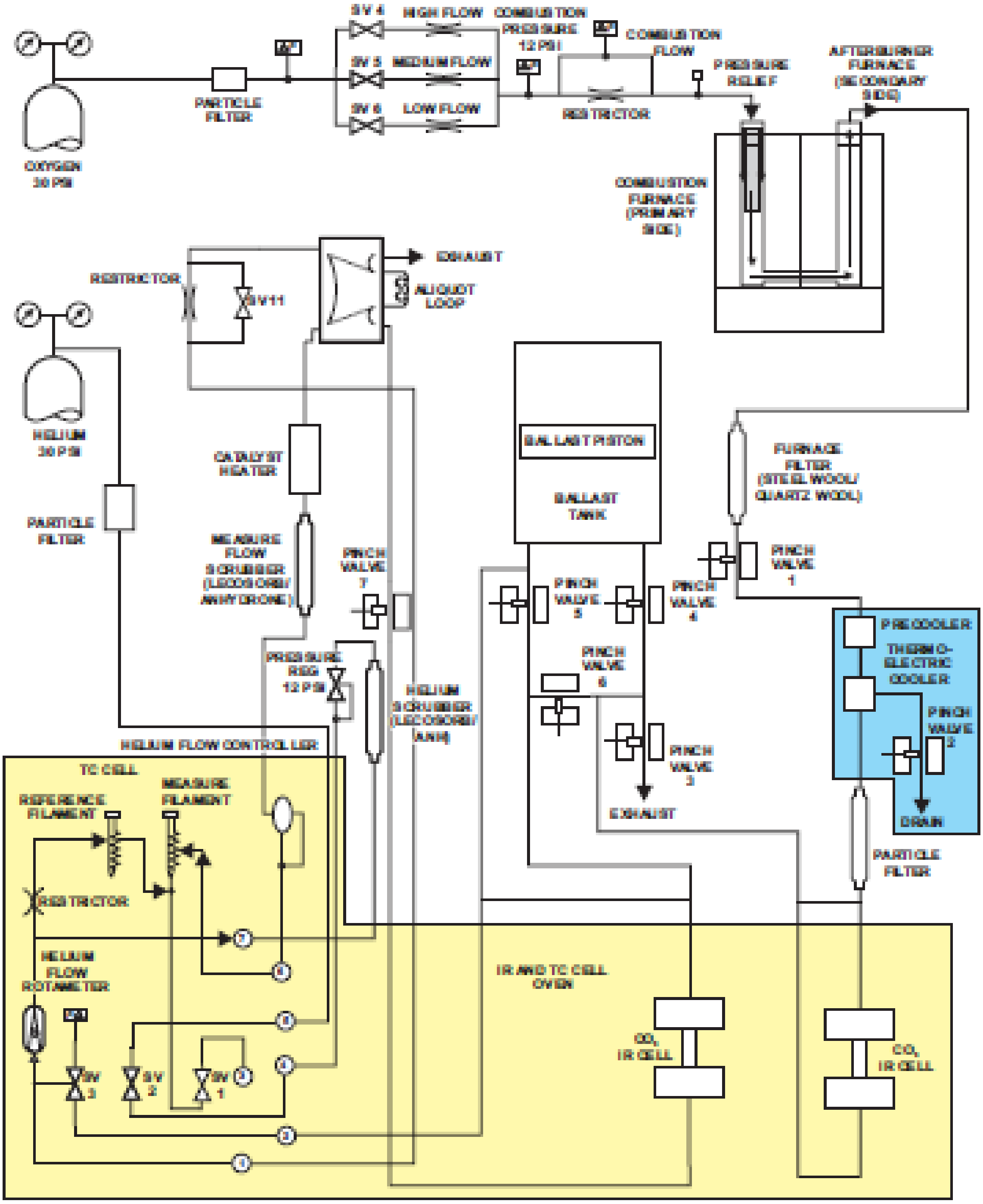
Flow diagram

The following figure shows the flow diagram of the equipment. At first, after purging the circuit and checking of the various components, combustion occurs. As mentioned the combustion occurs in two phases, a first stage in the main burner, and in a second stage in the secondary burner. At such times, it is producing high- flow oxygen for complete combustion. Also while combustion is occurring, is filling the ballast valve while 4 and 8 are opened. If monitoring is observed, a decrease in the pressure is produced that gradually stabilizes as the ballast is filling. Just when combustion ends ballast is full, but still continues entering flow from the combustion gases. This causes the pressure in the ballast will gradually increase, while the flow of oxygen decreases gradually until 6 does not fit anything. At that moment the input ballast valve 4, closes. Pressure inside the ballast is kept constant while the combustion gases are homogenizing. While the stabilizing ballast is entering oxygen flow through the circuit of the combustors and as the valve 8 is open and the valve 4 closed, the oxygen is expelled through the valve 3. This is occurring to clean the debris that have been left after combustion, in burners and on the circuit.

After the gases are stabilized in the ballast, the outlet valve 5 is opened and the gases begin filling the aliquot crossing the infrared cell and crossing the valve 7 is open. The monitoring is observed as the pressure decreases. Once the 3 cubic centimeters of the aliquot are filled, valve 7 is closed while the valve 5 is open and stabilizing the flow, and is when measurement occurs in the infrared cell. Once closed the valve 5 and for a period of time the ballast remains at constant pressure, after that, valve 4 is opened and drive gases away , resulting a second descent of pressure.

The gases that remain in the aliquot are carried by the helium and after passing through the filters to remove any residual water vapor and carbon dioxide, as well as through the copper filter to transform NOx into N_2 pass through the cell of thermal conductivity for the measurement of nitrogen.

Below , we can see the flow diagram.



Artwork 15. Flow diagram

Up to now, we have seen, how CHN is analyzed; now I will describe how S is analyzed.

To analyze Sulfur, we use the other module for the TruSpec LECO Series of Elemental Determinators. A weighed sample is placed in a combustion boat and manually directed into a concentric, horizontal combustion tube. The evolved gases are swept through moisture removers of the module, and transferred to the detection area of the TruSpec.

As I said before, there are three phases during an analysis cycle: purge, combust, and analyze. In the purge phase, the encapsulated sample is placed in the loading head, sealed, and purged of any atmospheric gases that have entered during sample loading. During the combust phase, the sample is dropped into a hot furnace (1100oC) and dosed with oxygen for very rapid and complete combustion. The products of combustion are passed through a secondary furnace (Afterburner, 850oC) for further oxidation, reduction and particulate removal.

In the analyze phase, the combustion gases pass from the furnace through a heated manifold to the H2O infrared detector for water analysis. After moisture is removed by the anhydrone, the combustion gasses pass through the CO2 detector for carbon measurement and the SO2 detector for sulfur measurement. From the CO2 detector the combustion gasses continue through Lecosorb and anhydrone to remove CO2 and H2O after which Nitrogen is measured by thermal conductivity.

- **Equipment components**

The equipment consists of a few major components as the infrared cell, the thermal conductivity cell, the removal filters water vapor and carbon dioxide, the catalyst filter, the particle filter and the filter afterburner.

3.4.1.3 Sample preparation and analysis

To perform this test I have analyzed ten different samples. Before start to analyze, I needed to prepare these samples. Procedure is described below:

1) Place the Sample Cup Holder on the balance.
2) Place foil into the Sample Cup Holder and tare the balance.
3) Remove the foil and the sample cup holder from balance and add sample to foil.
4) Place the sample cup holder and foil on balance and weigh.
5) Remove the foil from the sample cup holder and twist to seal.
6) Enter the mass in the spreadsheet or automatically by pressing print on the balance.

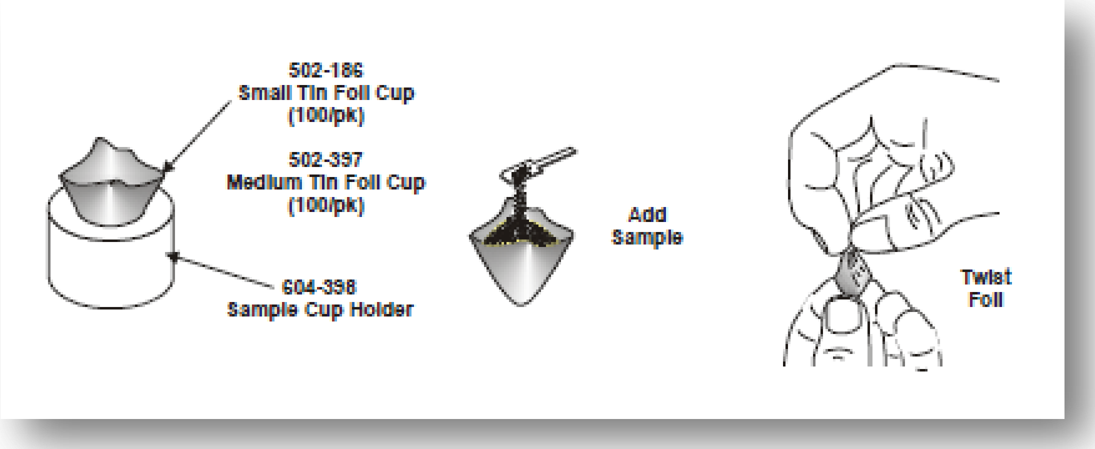
In the following artwork, we can find the required material to prepare samples.

Artwork 16. Material required to prepare samples

We have prepared around 40 EDTA samples and 80 solid biomass and coals samples.

Actually, just 50 biomass and coals samples were necessary, however, as I had to repeat the analysis due to unexpected problems, I had to prepare some more; and the same for EDTA samples.

The way to prepare these samples is shown in this artwork,



Artwork 17. Sample preparation

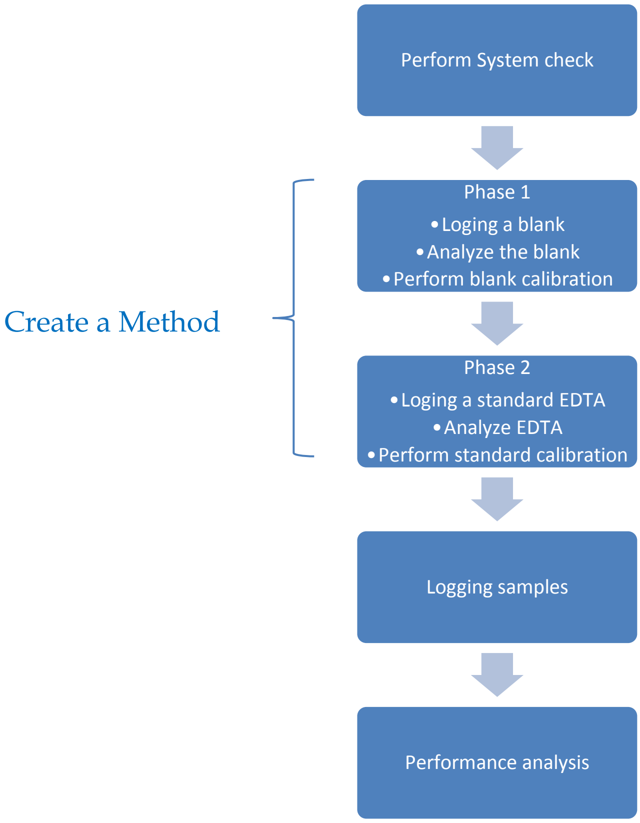
- **Sample analysis**

Sample analysis is used for quick determination of CHNS, of the samples measured in percentage of the weight.

Due to the increased use of experimental methods for the determination of carbon, hydrogen and nitrogen, standardization of these experiments were performed under standard European character, UNE-CEN/TS 15104 Determination of Total Carbon, Hydrogen and Nitrogen. Instrumental methods.

Sample analysis procedure

The first time the instrument is operated, and any time the software is updated, these steps must be performed in the order in which they appear



Artwork 18. Operation plan

- **Perform a System check**

  This is necessary to determine if the instrument is operating properly. Let the instrument warm up and stabilize. Check the results of all systems. It is recommended switch on the equipment 12 hours before starting test to reach a better stabilization when we analyze blanks. Burn temperature needs to be 950º and afterburner temperature 850º. To pass system check, we have to open gases, Oxygen 5.0 (2.4bar), Helium (2.4bar) and synthetic air (2.7 bar).

Artwork 19. Pressure gauges

- **Create a method.**

  - **Login a blank.**

To stabilize equipment we have to analyze blanks until nitrogen area is approximately 1. Before analyze them, we need logging blanks. Information required: Enter Blank for sample name, 1.000 for sample mass.

  - **Analyze a blank.**

Analyze Blank permit to run an analysis without burning a sample. This is done in order to obtain data to set the blank area. Analysis will automatically start with the first blank. We had to analyze more than 40 blanks to reach stabilize the equipment. Table below shows us data reached in our last blank analysis. The blank results started higher, drop slowly, and then stabilize. I focused in the last few blanks analyzed to check the precision, when Nitrogen area was approximately 1, I view statistics. The SD of the blank was 0.0010% at 1.0 g. So, as SD precision is acceptable, we can proceed to the next step.

Name	Mass	C %	H %	N %	Nitrogen Area	Method
Blank	1	0.0001	0.0051	0.00203	1.0804	LECO

Chart 9. Blank analysis

- **Perform blank calibration**

Calibration is the process that adjusts the instrument to produce the correct result when a calibration standard is analyzed. Blank calibration calculates the instrument blank area and adjusts the analysis area accordingly.

- **Login a standard.**

When we have reached stabilize the equipment, It is necessary to check it. I have logged 10 EDTA. These samples firstly had to be prepared as is described in above paragraphs. Required information: Sample name of the standard: EDTA. When entering EDTA, it is only necessary to enter the mass.

- **Analyze a standard.**

Analyze a Standard is used to analyze standard samples for calibration. Analysis will automatically start with the first standard. LECO EDTA have 41.02 C%, 5, 56 H%, and 9, 57 N%. When we analyze EDTA sample, we need to reach these results.

Table below shows us result of the last EDTA analyzed sample.

Name	Mass	C %	H %	N %	Method
EDTA	0,18194	40,87	6,368	9,442	LECO ST

Chart 10. EDTA analysis

This result is precise and statistics indicates the RSD is <0.035.

- **Perform Calibration**

Standard Calibration is a process that adjusts the response of the instrument to that of known standards. The instrument Blank is calibrated before performing standard calibration. Analyzed Standard Samples for Calibration are the same standard samples used in the previous steps. The curve type selected is Single Standard Calibration.

- **Logging samples**

In my project I have analyzed 10 different samples. Seven of these ones are different types of biomass and the other three are different coals.

The measuring range of the sample that can be analyzed with the equipment is between 50 mg and 1.5 g. The resolution of the device is 0.0001 ppm and accuracy of the equipment is shown below:

Carbon .... 25 ppm or 0.5% RSD

Hydrogen............................. 100 ppm or 1.0% RSD

Nitrogen .... 40 ppm or 0.5% RSD

To analyze properly the content of carbon, hydrogen and nitrogen in the sample is necessary to calibrate the equipment.

In order to reach a proper result I have logged:

- 5 samples of corn
- 5 samples of olive pits
- 5 samples of grapes
- 5 samples of thistle
- 5 samples of sludge
- 5 samples of pellets
- 5 samples of almond shell
- 5 samples of charcoal
- 5 samples of hard coal
- 5 samples of anthracite

- **Perform analysis**

After performing system check, create a method (logging and analyzing 20 blanks, performing a blank calibration, logging and analyzing 10 standards and performing a standard calibration), and logging samples, finally we can perform analysis.

This analysis was based on the ASTM D 5373 standard made by LECO. The mass of the samples was between 0.05 and 0.09 grams. Main burner temperature was 950 ° C and the secondary burner 850 ° C. Results of this analysis will be described in section 4 of this project.

3.4.2 Calorimeter

The calorific value is one of the most important characteristics of a fuel. It indicates the amount of heat that developed from the mass (weight) in its complete combustion with oxygen in a calorimeter standardize.

Artwork 20. Parr 6300 Calorimeter

3.4.2.1 Description

Parr 6300 calorimeter is the one, which I have used to perform this analysis. It determines in a direct way the heating value. Calorimetric method burns a fuel quantity and measure the quantity of heat produced through thermic energy gained by a known liquid, water.

Standards consulted to perform this analysis have been:

- Solid biofuels:
- UNE_164001 = 2005_EX Solid biofuels. Method for determining the calorific value.
- Solid mineral fuels:
  UNE_32006 = 1995 Solid mineral fuels. Calorific value determination by automatic calorimeter.

3.4.2.2 Theory of operation

Bomb cylinder and bucket are mounted in the calorimeter. The bomb is completely surrounded by a bucket chamber, sealed co-axially with the bomb head. After the bomb and bucket are closed and sealed, the bomb is filled with oxygen, the bucket chamber is filled with water, initial equilibrium is established, the bomb is fired and the temperature rise is monitored and recorded - all under automatic microprocessor control.

Then, at the completion of a test, automatic control releases the residual pressure in the bomb, rinses the bomb, cools the system and empties the bucket. Water circulates around the bomb to bring all inner parts of the calorimeter to a uniform temperature rapidly, while true isoperibol operating conditions are maintained by an outer water jacket.

Microprocessor based, real time heat leak corrections are applied to implement the isoperibol jacketing method and to support the Parr rapid dynamic method for predicting the final temperature rise. Precise temperature measurements are made with thermistor thermometry providing 0.0001°C resolution over the operating range of the calorimeter.

The calorimeter uses a sophisticated curve matching technique to compare the temperature rise with a known thermal curve to extrapolate the final temperature rise without actually waiting for it to develop.

3.4.2.3 Sample preparation and analysis

Before performing analysis we need to prepare sample and equipment.

- Sample and equipment preparation.

  We need to prepare it according to UNE 32 102 Standard. Sample preparation is described in section 3.2 of this project.

  Then, we need to calibrate the calorimeter. To do that, we use Benzoic Acid. Combustion heat of Benzoic acid is required to determine the effective heating capacity of the calorimeter.

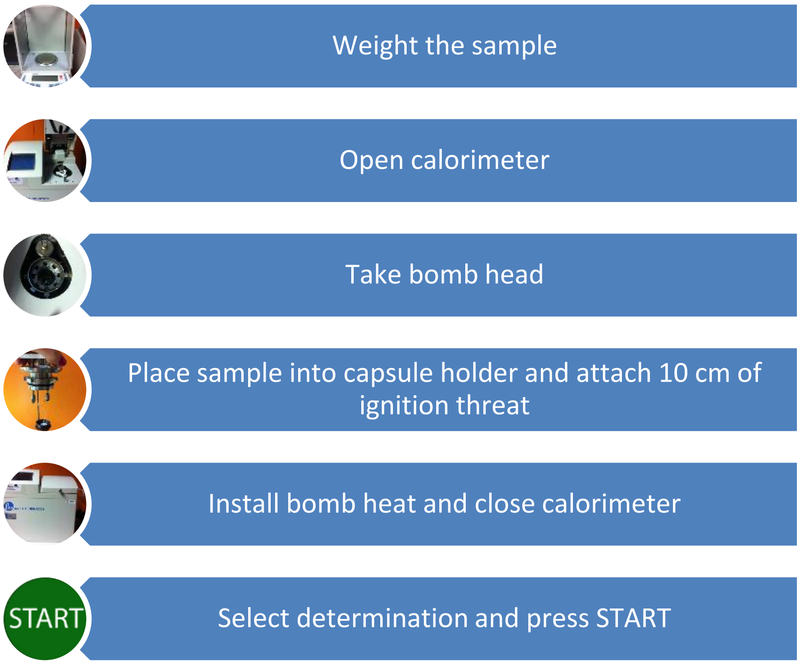
Benzoic heating value is 26.454 MJ/kg. I had to repeat the analyses for 5 times until I reached a value very similar to the indicated by benzoic acid. I got 26. 51 MJ/kg.

Artwork 21. Benzoic Acid

- **Analysis process:**

To analyze a sample, we need to weigh the sample(0.1 mg aprox) then, carefully place the sample into the capsule holder, next attach 10 cm of ignition thread after that , install bomb head in calorimeter and close calorimeter cover making certain the latch is engaged. When we have done it, we select determination and Press START to begin the test.

Required data: Sample ID and weight.



Artwork 22. Calorimeter analysis process

4 RESULTS

The objective of this project was to obtain **moisture**, performing an **elemental analysis** and calculate the **heating value** of different samples of solid fuels. These analyses have been performanced according to the standards described during the project.

4.1 Moisture

Moisture content is a quantity that expresses the amount of water in a solid material and can be expressed on dry weight basis or wet weight basis. Although both terms represent the moisture content, their numerical values are different, so that for the moisture content, have to be indicated the basis we are using. In our project, all calculations have been done on a dry basis. The moisture content on a dry basis, compares the water mass contained in the sample with the dry mass.

To determine moisture content was necessary to performance oven drying method. It has been described in section 3.2.2 of this project.

Calculation of moisture content

Moisture percentage is calculated according to the diminution of the mass weight, expressed in next equation:

$$M_{ad}=\frac{m2-m3}{m2-m1}\cdot 100$$

Where: m_1: mass of empty vessel [g], m_2: mass of vessel and sample before heating [g], m_3: mass of vessel and sample after heating [g]

Following table will show us results of these calculations for each sample,

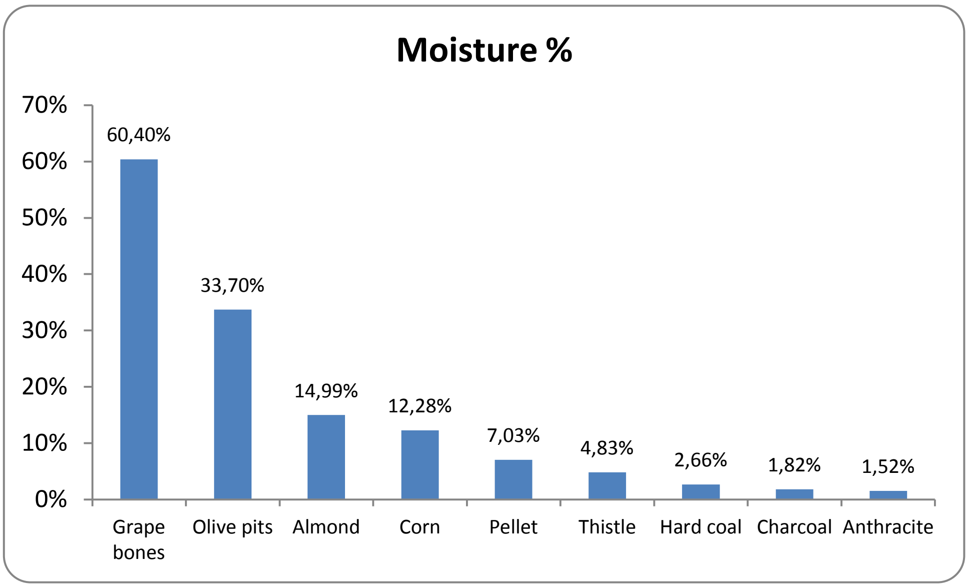
Sample	m_1	m_2	m_3	M_{ad}
Pellet	247,89	254,86	254,37	7,03%
Thistle	244,26	264,55	263,57	4,83%
Almond	54,27	73,01	70,2	14,99%
Hard coal	247,78	274,49	273,78	2,66%
Charcoal	41,37	52,9	52,69	1,82%
Grape bones	54,27	72,25	61,39	60,40%
Anthracite	62,31	100,44	99,86	1,52%
Olive pits	244,26	269,69	261,12	33,70%
Corn	45,46	81,63	77,19	12,28%

Chart 11. Moisture content results.

According to these results, we will discuss them.

Discussion

To start this discussion, this graphic shows us, in a decreasing way, the moisture percentage of the samples analyzed in this project.



Graphic 14. Moisture percentage

As we can see, grape bones have the highest moisture content and olive pits have the second one. Almond shell and corn, have similar moisture content. Pellets have low moisture content; however is not the lowest one. Thistle is the biomass sample with the lowest one. To conclude we can assume that coal has less moisture content than solid biomass.

4.2 Elemental analysis C H N S

Elemental analysis tries to find the concentration of some key elements such as carbon, hydrogen, nitrogen, oxygen and sulfur. Model chosen to perform this analysis is: TruSpec LECO CHN/CHNS. This analysis has been performance according to the standards described during the project.

After calibration, have been performed 50 analyses of different solid fuels. I have analyzed 10 samples, and each one, has been tested for 5 times.

The following table shows the data obtained from the observed concentration of carbon, hydrogen , nitrogen , oxygen and sulfur as well as its initial mass. Oxygen is obtained following this expression: O%= 100- C%- H%- N%- S%.

Name	mass (g)	C %	H %	N %	S %	O%
Pellet	0,1308	47,11	6,99	0,13	0,04	45,73
Sludge	0,1215	30,54	5,95	4,81	1,50	57,20
Corn	0,1319	44,80	7,51	1,13	0,15	46,41
Thistle	0,1402	55,64	9,05	0,97	0,18	34,16
Almond Shell	0,1132	46,53	7,40	0,40	0,03	45,64
Olive pits	0,1047	51,07	5,96	0,90	0,07	42,00
Grapes	0,1140	50,20	7,25	2,37	0,16	40,02
Anthracite	-	95,27	2,42	0,56	1,6	0,15
Hard coal	0,1238	90,21	3,74	1,24	3,11	1,7
Charcoal	0,0756	89,21	3,78	0,35	2,84	3,83

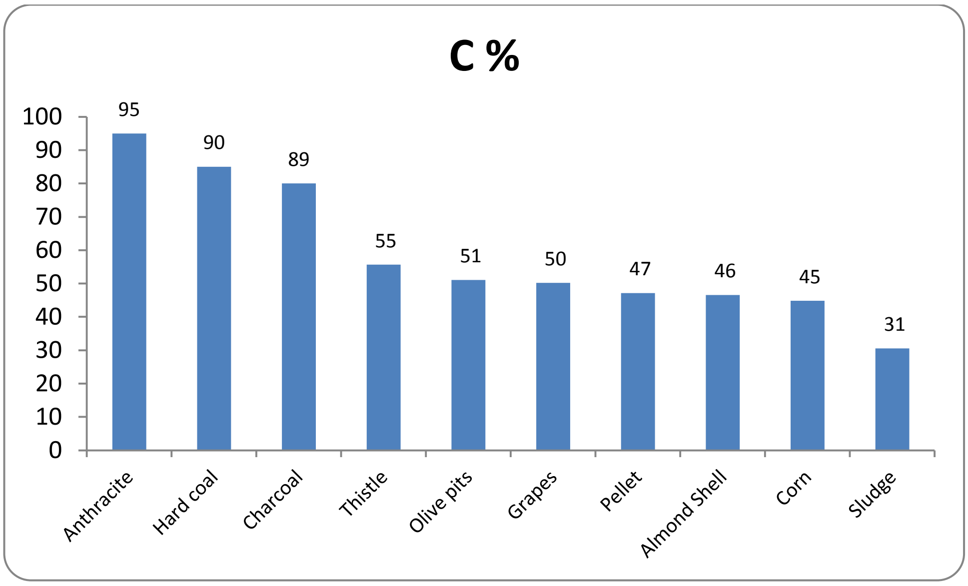
Chart 12. CHNS results

Anthracite values has been collected from Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan because equipment broke down and I couldn´t analyze this sample.

This problem also affected to S% of hard coal and Charcoal. I couldn´t perform these analyses, so, that values are estimated. In order to obtain accurate coal results, I had to increase delay time, minimum analysis time, IR baseline time and TC baseline time.

To have a general view of these result, I have create different plots, to analyze them.

Firstly we will see, in a graphical way, percentage of carbon of the analyzed samples



Graphic 15. Results of Carbon percentage

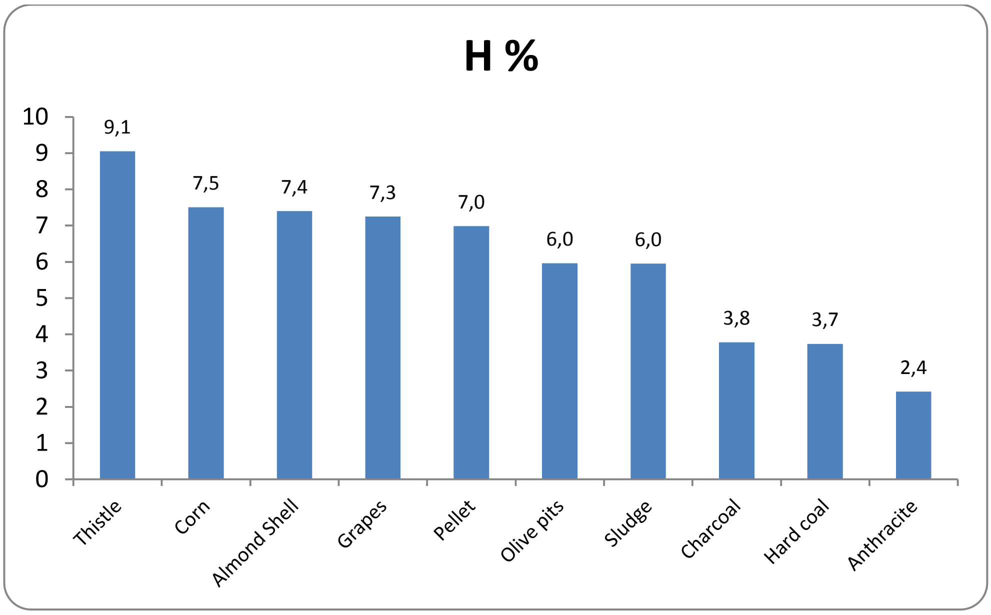
As we can see, coals have the highest percentage of C, as a consequence, they have the highest heating value. If we compare %C with HHV, we can conclude that, carbon is the main factor to determine heating value. We can check it out in the table below:

Sample	C %	Samples	Calorimeter HHV MJ/kg
Anthracite	95,27	Anthracite	33,04
Hard coal	90,21	Hard coal	32,35
Charcoal	89,21	Charcoal	28,85
Thistle	55,636	Thistle	24,98
Olive pits	51,07	Pellet	18,7
Grapes	50,198	Grapes	18,39
Pellet	47,11	Olive pits	17,62
Almond Shell	46,528	Corn	17,56
Corn	44,802	Almond Shell	17,28
Sludge	30,538	Sludge	10,69

Graphic 16. Comparison between Carbon and HHV results

Samples with highest %C have the highest heating value, and sample with lowest %C have the lowest heating value. In the case of Olive pits, grapes, pellets, almond shells and corn, as they have similar %C ,their heating values don´t correspond with %C, because there are also, another elements that influence the heating value calculation.

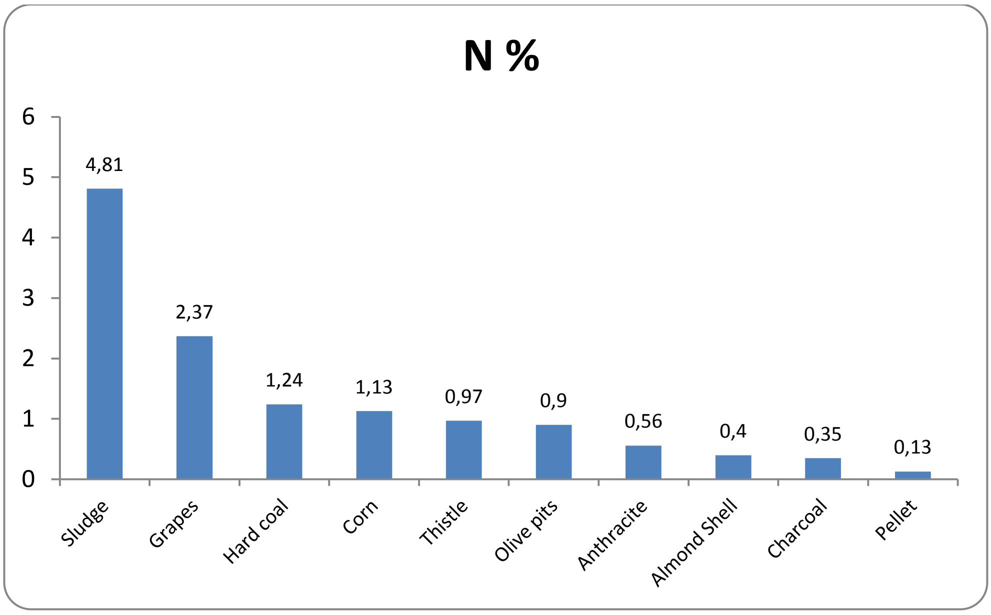
After carbon percentage analysis, I am going to continue analyzing %H



Graphic 17. Results of Hydrogen percentage

As we can see, in general, coals have less H% content than solid biomass.

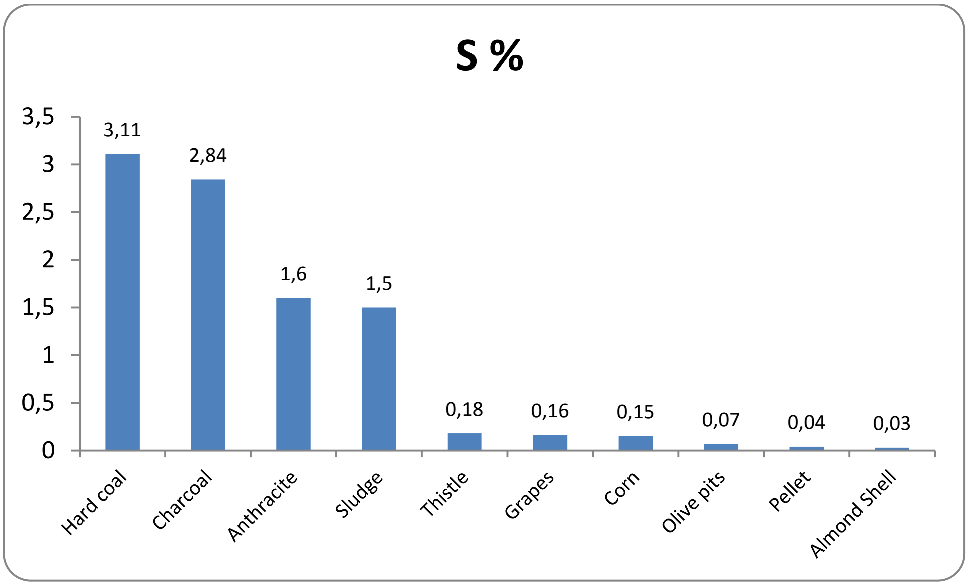
Now we are going to analyze Nitrogen results,



Graphic 18. Results of Nitrogen percentage

N% doesn´t vary a lot. As we can see, there is a unique valor out of the order; it is sludge due to its heterogeneous composition. Nitrogen content in coals varies between 1 and 2.5%, however its content is not of great importance (it is just important because Nitrogen, is the cause of NO_x emissions).

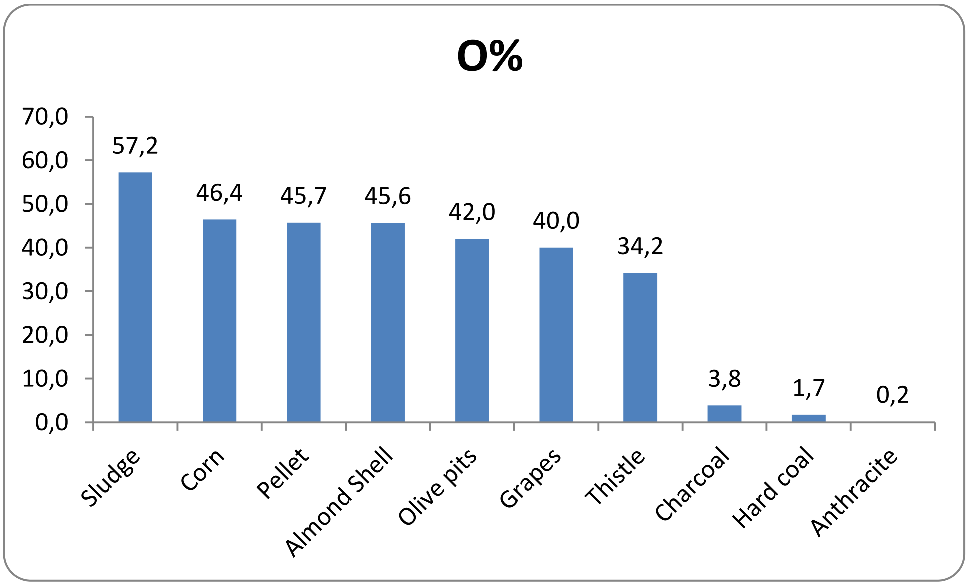
Here we have the sulfur percentage analysis,



Graphic 19. Results of Sulfur percentage

As we can verify, if we compare sludge with solid fuels, it is again, out of order, due to its heterogenic composition. If we don´t take in account this value, we can check that solid fuel that contains higher %S is coal, sulfur rarely exceeds 5% and is often below 0.5%.

Finally I will check %O of solid fuel samples studied in this project. Oxygen has been calculated following this expression: O%= 100- C%- H%- N%- S%.



Graphic 20. Results of Oxygen percentage

As we can see, coals have a less of %O than solid biomass fuel. Samples with higher O% have less heating value as we can check in the following table.

The table below compare %O with HHV

Sample	Calorimeter HHV MJ/kg	Sample	O%
Anhtracite	33,04	Anthracite	0,2
Hard coal	32,35	Hard coal	1,7
Charcoal	28,85	Charcoal	3,8
Thistle	24,98	Thistle	34,2
Pellets	18,7	Grapes	40,0
Grape	18,39	Olive pits	42,0
Olive pits	17,62	Almond Shell	45,6
Corn	17,56	Pellet	45,7
Almond Shell	17,28	Corn	46,4
Sludge	10,69	Sludge	57,2

Graphic 21. Comparison between Oxygen and HHV results.

As we can see heating value values, varies with the O%. Samples with less O% have higher HHV than samples with a greater O%. To conclude we assume, that Coals have less O% as a consequence, they have greater HHV.

4.3 Heating value

The calorific value is one of the most important characteristics of a fuel. It indicates the amount of heat that develops from the mass (weight) in its complete combustion with oxygen in a calorimeter standardize. It is defined as the amount heat energy released during the complete combustion of unit mass of sample.

There are two types of calorific value (usually expressed in kcal/kg or MJ/kg) might be considered:

1. Higher heating value (HHV): it is the amount of heat released by a complete combustion of a mass unit of a sample at constant volume in an oxygen atmosphere and at the standard conditions (101.3 kPa, 25°C). It has been determined experimentally in the laboratory with adiabatic calorimeter.

2. Lower heating value (LHV), doesn't include the water condensation heat.

To perform this analysis we have analyze 10 different solid fuels , and we have repeated the process 3 times for each one. We have reached these results using 2 methods: Analytic method and practical method.

Analytic method

To obtain heating value we have used DULONG FORMULA. All the results are expressed in a dry basis as is described in section 3.3.1.

- HHV Dry combustible:

$HHV_D = 8.140 \text{ X } C + 34.400 \text{ x } (H - O/8) + 2.220 \text{ x } S$

Where:

C: centesimal quantity of carbon (weight) by kg of combustible
H: centesimal quantity of hydrogen (weight) by kg of combustible
O: centesimal quantity of oxygen (weight) by kg of combustible
S: centesimal quantity of sulfur (weight) by kg of combustible

- LHV Dry combustible:

$LHV_D = 8.140 \text{ x } C + 29.000 \text{ x } (H - O/ 8) + 2.220 \text{ x } S$

These expressions are in Kcal/kg, to change units from Kcal to MJ/kg, I have multiplied by $4{,}19\times10^{-3}$.

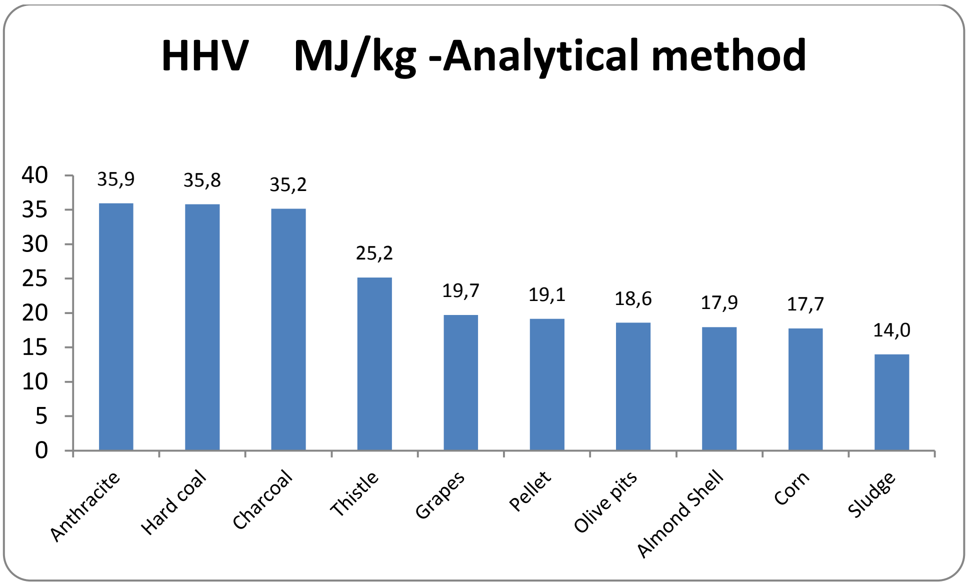
Results are shown in the table below:

Sample	HHV MJ/kg	LHV MJ/kg
Pellet	19,129	18,649
Sludge	13,982	13,444
Corn	17,736	17,359
Thistle	25,169	24,200
Almond Shell	17,948	17,622
Olive pits	18,574	18,394
Grapes	19,709	19,305
Anthracite	35,929	35,383
Hard coal	35,821	35,027
Charcoal	35,152	34,411

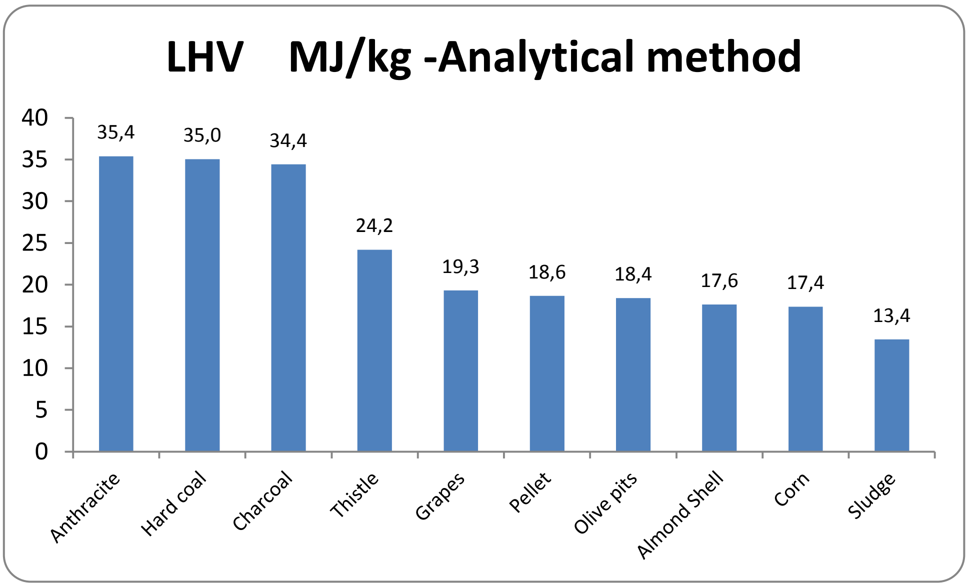
Chart 13. Analytic method heating value results.

As we can see, coals have higher heating value than solid biomass fuel.

In the following plots, we can see in a decreasing way, heating values for the samples analyzed in this project.



Graphic 22. HHV analytic method results



Graphic 23. LHV analytic method results.

Anthracite is the solid fuel with highest heating value whereas; sludge is the sample with the lowest one.

Practical method

The 6300 Calorimeter will automatically make all of the calculations necessary to produce a high heating value of combustion for the sample. However, it is important to understand these calculations to ensure the instrument is set up so the calculations match the procedures and the units are consistent throughout the process.

High heating value

The sample is subjected to combustion with excess oxygen in a pump calorimeter , model 6300 PARR . From the increase in temperature experienced by the water bath in which the pump is submerged in which combustion occurs , the calorimeter determine the HHV test on wet basis , b.h , at constant volume. In order to determine the superior calorific dry basis we need moisture value (h) calculated before, following the technical specification UNE- EN 14774-3 " Solid biofuels . Determination of moisture content. Method oven . Part 3: Humidity sample for analysis in general.

HHV at constant volume is determined on a dry basis HHV, from the HHV wet basis , bh , determined experimentally bomb calorimeter , and moisture of the sample assay h.

HHV is calculated using the following equation:

$$HHV = \frac{HHV\ bh}{1 - \frac{h}{100}}$$

Low heating value

LHV is determined from bs higher calorific value at constant volume on a dry basis and content of hydrogen, oxygen and nitrogen on a dry basis, expressed in percent mass (H, O and N, respectively, determined from the elemental analysis):

LHV= HHV – 2,06·H

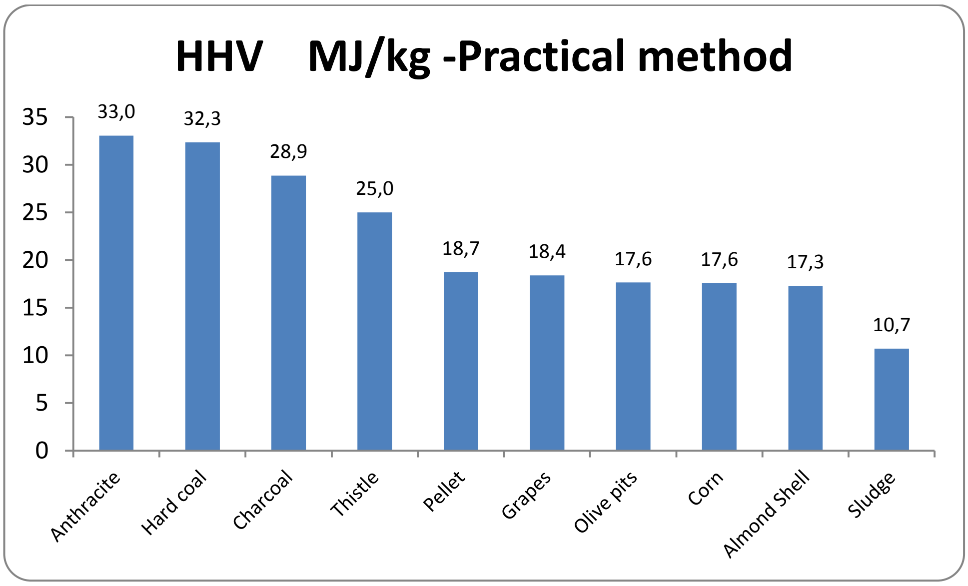
Results are shown in the table below,

Sample	HHV MJ/kg	LHV MJ/kg
Almond Shell	17,28	17,13
Anthracite	33,037	32,99
Charcoal	28,851	28,77
Corn	17,558	17,40
Grapes	18,393	18,24
Hard coal	32,347	32,27
Olive pits	17,624	17,50
Pellet	18,704	18,56
Sludge	10,692	10,57
Thistle	24,978	24,79

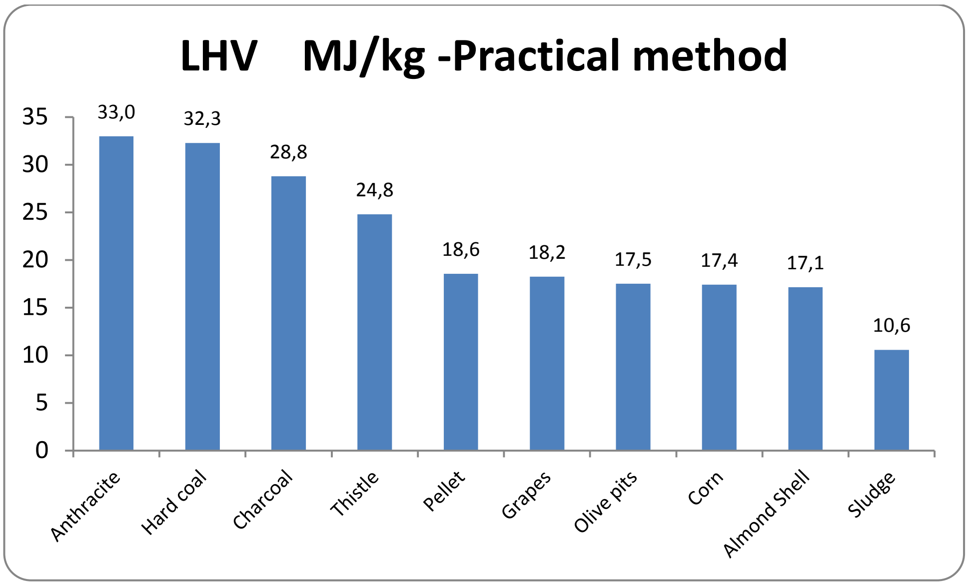
Chart 14. Heating value results. Practical method

As I expected, coals have higher heating value than solid biomass fuel.

In the following plots, we can see in a decreasing way, heating values for the samples analyzed in this project



Graphic 24. HHV Practical method.



Graphic 25. LHV Practical method.

According to analytical results, Anthracite is the solid fuel with highest heating value whereas; sludge is the sample with the lowest one.

Now, in the table below, I am going to compare results from analytical and practical method.

			MJ/kg			
Samples	mass	Calorimeter	Practical method		Analytical method	
	g	HHV bh	HHV	LHV	HHV	LHV
Almond Shell	1,509	17,25	17,28	17,13	17,95	17,62
Anhtracite	1,530	33,03	33,04	32,99	35,92	35,38
Charcoal	1,609	28,85	28,85	28,77	35,15	34,41
Corn	1,530	17,54	17,56	17,40	17,74	17,36
Grape	1,606	18,28	18,39	18,24	19,71	19,30
Hard coal	1,552	32,34	32,35	32,27	35,85	35,02
Olive pits	1,628	17,57	17,62	17,50	18,57	18,39
Pellets	1,552	18,69	18,70	18,56	19,13	18,65
Sludge	1,524	10,69	10,69	10,57	13,98	13,44
Thistle	1,546	24,98	24,98	24,79	25,17	24,20

Chart 15. Comparison between analytical and practical method heating value results

In general, there is not great differences between different methods.

Following table shows us, an exhaustive comparison of heating values calculated by different methods.

Samples	HHV [MJ/kg]		Relative error
	M.Practical	M.Analytical	
Almond Shell	17,28	17,948	0,04
Anhtracite	33,037	35,929	0,08
Charcoal	**28,851**	**35,152**	**0,18**
Corn	17,558	17,736	0,01
Grape	18,393	19,709	0,07
Hard coal	32,347	35,821	0,10
Olive pits	17,624	18,574	0,05
Pellets	18,704	19,129	0,02
Sludge	**10,692**	**13,982**	**0,24**
Thistle	24,978	25,169	0,01

Chart 16. Comparison between analytical and practical method. HHV results.

As I expected, results are very similar, most of them have a relative error under 10%. We can find the highest difference in coals, maybe it could be, due to not accurate estimation in Carbon %values analyzed by LECO. We mustn´t take in account sludges due to its heterogenic composition.

Now we will see what is going on with LHV,

Samples	LHV [MJ/kg]		Relative error
	M.Practical	M.Analytical	
Almond Shell	17,13	17,62	0,03
Anhtracite	32,95	35,38	0,07
Charcoal	**28,77**	**34,41**	**0,16**
Corn	17,4	17,36	0,00
Grape	18,24	19,3	0,05
Hard coal	32,3	35,02	0,08
Olive pits	17,5	18,39	0,05
Pellets	18,56	18,65	0,00
Sludge	**10,57**	**13,44**	**0,21**
Thistle	24,79	24,2	0,02

Graphic 26. Comparison between analytical and practical method.LHV results.

As we can see, is happening something similar to HHV comparison. Relative error is under 10% in most cases. There is one exception, sludges, but as I comment before, It is due its heterogenic composition.

If we compare all the samples analyzed in this project, we can state 1Ton of Anthracite has the same heating value than:

1 Ton Anthracite	1021	kg of	Hard coal
	1145	kg of	Charcoal
	1323	kg of	Thistle
	1767	kg of	Pellets
	1795	kg of	Grape
	1876	kg of	Olive pits
	1883	kg of	Corn
	1912	kg of	Almond Shell
	3086	kg of	Sludge

Chart 17. Anthracite equivalence.

So, the solid biomass fuel with a highest heating value is **thistle**.

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5 BUDGET

To develop this project, has been needed the collaboration of my supervisor and the use of different equipment and material. Analysis has been performed in UC3M BIOLAB, 202 - Testing Laboratory of Biomass Fuels.

Costs have been classified into personal, equipment, material and general cost.

5.1 Personal cost

To develop this Project, I have needed the collaboration of my project manager, Luis Miguel García. To determine this cost, I will take in account how many hours we have spent and the salary. In the table below, different amounts are explained.

Personal	Hours	€/Hours	Amount
Project Manager	80	90	7.200
Graduate	260	45	11.700
Total	340	-	**18.900€**

Chart 18. Personal cost

5.2 Equipment cost

Equipment cost is the total amount of the equipment required to carry out analyses. These tests have been performed in UC3M BIOLAB, 202 - Testing Laboratory of Biomass Fuels. Table below shows equipment unit cost and number of working hours.

Equipment	€/unit	Nº Working hours
CHN(S)	50000	80
Calorimeter	20000	45
Oven	7000	15
Sieve	9000	5
Balance	8000	4
TOTAL	**94.000 €**	149

Chart 19. Equipment cost

5.3 Material cost

Throughout the performance of this Project, there has been a large quantity of material needed. Next table describes different materials and their cost.

GAS	Price	Capacity	Required	Total price
Helium 5.0	12,95 €/m3.	9,1 m3	9,1 m3	117,84
Synthetic air UL	7,46 €/m3.	10 m3	20 m3	149,20
Oxygen 5.0	17,45 €/m3.	10,5 m3	10,5 m3	183,22
Oxygen 3.5	6,90 €/m3.	10,6 m3	10,6 m3	73,14
Total				**523 €**

Chart 20. Material cost

Standards	€/100g	g	Total price
EDTA	32	100	32
Benzoic Acid	29	100	29
Total		-	**61 €**

Chart 21. Standards cost

5.4 General cost

General cost is the sum of the cost detailed before.

Concept	Importe
Personal cost	18.900
Equipment cost	94.000
Material cost	584
Total cost	**113.484 €**

Chart 22. General cost

6 CONCLUSIONS

Coal and biomass are the most representative of solid energy use for electricity production fuel. In the case of coal, is characterized by their diversity and abundance of resources and in the case of biomass, its clean and inexhaustible production.

However, at present, is not just enough to ensure energy supply, also in order to remain being competitive with other energy resources, it is necessary to provide a diverse energy supply, safe, environmentally friendly and a very cost-efficiency.

To reach it, political, socio-economic, business and technological conditions must be appropriate in the market.

This has caused in the energy industry a boost in improving the properties of solid fuels and their efficiency during the combustion process and gas and particles cleaning equipment. Have as a pretext to ensure a further development of the facility, reducing emissions and costs. To achieve this we must take into account that the properties of a fuel can be highly variable and therefore also the equipment and processes for energy use. At the same time, you should know that many of these properties not only influence the combustion process, but also in other activities related to the preparation of the combustible and waste treatment operations and generated emissions. For this reason before feeding a solid fuel in a plant is necessary to determine their physicochemical properties by performing some tests to characterize their properties as combustible, and determine necessary pretreatment and optimal conditions to give reliable information and qualitative adequacy of fuel to equipment and operating conditions of a given combustion plant.

For this reason, this project has studied the different tests, equipment and standards for solid fuels with the aim of determining better fuel properties and thus achieve more efficient combustion conditions, minimizing the emission of gases and particles.

The general conclusions drawn from the work performed are:

- ✓ Characterization tests are needed, allowing us to determine the optimal physicochemical properties of solid fuels.
- ✓ A bad characterization of the fuel may be a contributing factor to damage equipment and the environment.

As is described in the beginning of this project, my objective was performing physical-chemical analysis of biomass and coal and compare both results. All parameters are determined following the guidelines of standardized procedures and standardized by European and national technical committees (AENOR CTN 164: Solid Biofuels).

According to the results obtained after performing moisture analysis, these are conclusions I have reached. The moisture content of the fuel has an important effect on the pretreatments and the combustion process:

- ✓ High moisture contents make more difficult the milling process.
- ✓ Higher moisture contents, increases costs on drying.
- ✓ Decreases combustion efficiency.
- ✓ Coal (~2 %) has less moisture content than solid biomass (~15 %).

Next analysis I performed was the elemental analysis, here I explain conclusions drawn.

Elemental analysis is done in order to find the concentration of some elements such as carbon, hydrogen, nitrogen, oxygen and sulfur. Components more incidents in solid fuels characteristics and final values are: oxygen, nitrogen, and sulfur gases.

Carbon lets estimate the amount of CO_2 and H_2O be formed as a result of combustion. CO2 emissions estimation has become necessary in order to comply with new environmental guidelines that impose a fee for emissions or installation to reduce or capture CO2 emissions . First conclusions of my study are:

- ✓ Carbon is the main factor to determine heating value.
- ✓ Heating value is bigger when %C is greater.
- ✓ Coals have higher percentage of C than solid biomass, as a consequence, coal contaminate more than solid biomass.

Now let's see what happens with the nitrogen. Nitrogen percentage doesn´t vary a lot, its content is not of great importance.

- ✓ Nitrogen content in coals varies between 1 and 2.5%

Nitrogen, is the cause of NO_x emissions and contributes to the greenhouse effect, destroy the ozone layer and causes acid rain . The measures required to control levels, can be very costly to implement.

On the other hand, according to the sulfur, these are my conclusions. It is in responsible of the formation of SO_2 SO_3 , is highly polluting to the atmosphere because is responsible of acid rain and can cause corrosion and fouling problems.

- ✓ Solid fuel that contains higher %S is coal.
- ✓ Sulfur rarely exceeds 5% and is often below 0.5%.

Finally, Oxygen discussion results are follows:

- ✓ Coals have less high difference of %O than solid biomass fuel.
- ✓ Samples with higher O% have less heating value.

Now, I will continue describing conclusions about heating value.

The heating value is one of the most important characteristics of a solid fuel. It is defined as the amount of heat energy released during the complete combustion of unit mass of the solid fuel. As I explained during this project, there are two types of calorific value might be considered: Higher heating value (HHV): it is the amount of heat released by a complete combustion of a mass unit of a sample at constant volume in an oxygen atmosphere and at the standard conditions and lower heating value (LHV), doesn't include the water condensation heat. I have calculated them using two different methods (analytical and practical), and results has been very similar.

- ✓ Coal have higher heating value than solid biomass.
- ✓ Anthracite has the highest heating value (HHV = 33,037 MJ/kg).

After comparing all the samples analyzed in this project, we can state 1Ton of Anthracite has the same heating value than 1323 kg **Thistle**. We should consider the idea of using biomass thistle because of its heating value, furthermore, it is an autochthonous plant that is well adapted to arid areas (requires little labor to cultivate) and you can get 15 to 25 ton per hectare per year. Another advantage is that the thistle contains fewer nitrogen and sulfur than coals, as a consequence, generates less acid rain during combustion.

To conclude and complying the main target of this project, comparing coal with solid biomass fuel:

Coal	Biomass
↓ Moisture content (~2 %)	↑ Moisture content (~15 %)
↑ C (~80 %)	↓ C (~45 %)
↑ N	↓ N
↑ S	↓ S
↑ Heating value (~30 MJ/kg)	↓ Heating value (~17 MJ/kg)

We can assume than the environmental benefits of using biomass instead of fossil fuels as an energy resource are:

- They reduce sulfur emissions, particulates, CO, NO_x and hydrocarbons.
- CO_2 neutral cycle does not contribute to the greenhouse effect.
- Reduction of forest fires and insect pests by clearing forests for these recyclable wastes energy.
- Use of fallow (unused) for crop production energy.
- Independence fuel imports.
- Improving the economy.

7 OTHER POSSIBLE RESEARCH

In order to continue with the research opened in this project, I introduce some ideas that could be interesting to analyze.

- Ash Content.

It is the inorganic matter left out after complete combustion of the fuel .The inorganic component can be expressed as same as the moisture content on a wet, dry and ash free basis. In general it is expressed on dry basis. Generally contains mainly Calcium, Potassium, Magnesium and Phosphorus elements that affect the ash fusion.

The ash value is an integral part of the plant structure that consists of a wide range of elements that represents less than 0.5 % in wood and 10 % in diverse agricultural crop material and up to 30-40 % in rice husks and milfoil. The total ash content in the fuel and the chemical composition of the ash are important.

The composition of the ash affects its behavior under the high temperatures of combustion and gasification. For example, melted ash may cause problems in both combustion and gasification reactors. These problems may vary from clogged ash-removal caused by slagging ash to severe operating problems in fluidized-bed systems

- Volatile Matter Content

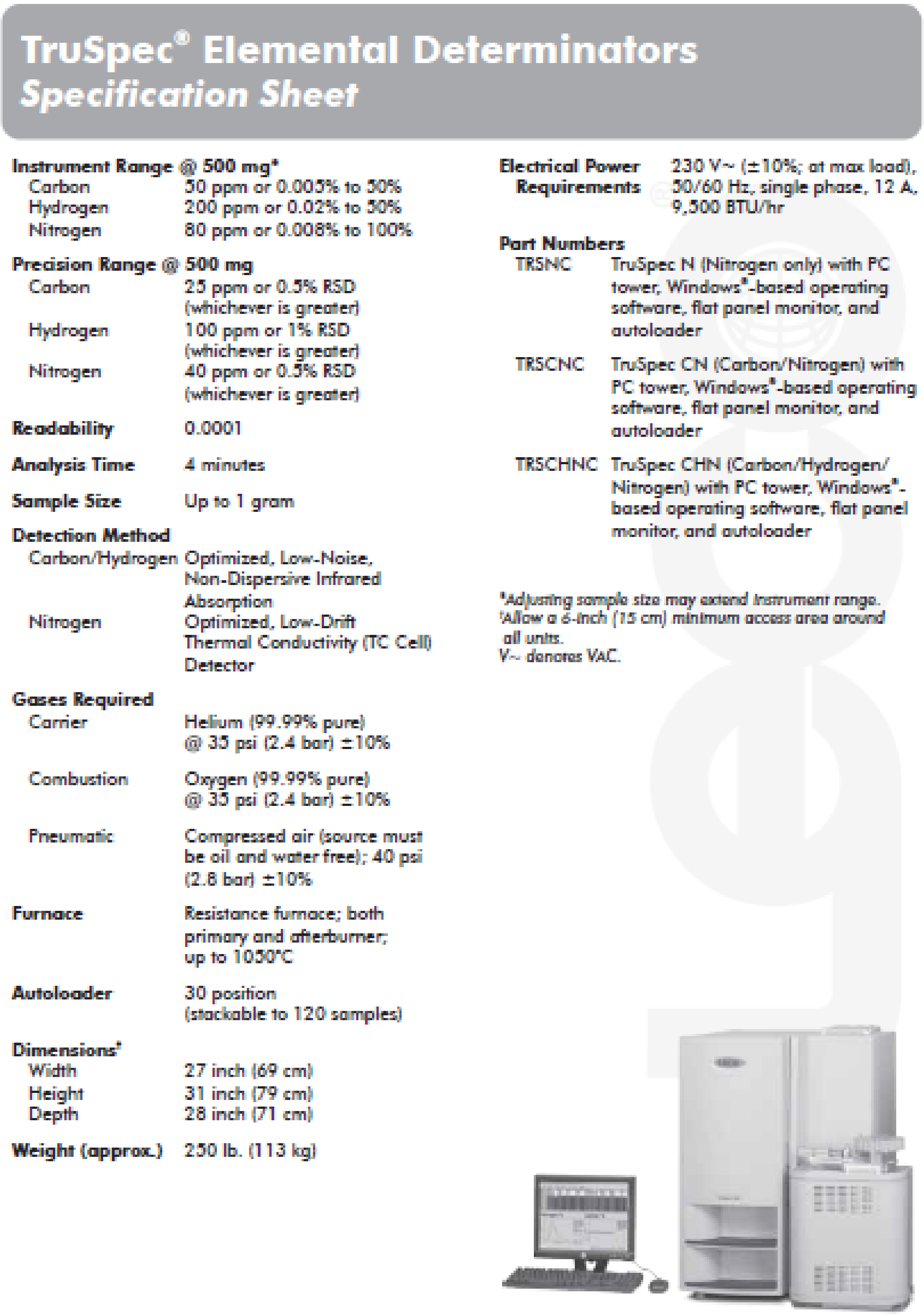
Volatile matter refers to the part of the fuel that is released when the fuel is heated (up to 400 to 500°C). During this heating process the fuel decomposes into volatile gases and solid char. Fuel typically has a high volatile matter content (up to 80 percent), whereas coal has a low volatile matter content (less than 20 percent) or, in the case of anthracite coal, a negligible one.

- Bulk Density

Bulk density refers to the weight of material per unit of volume. For fuel it is generally expressed on an oven-dry-weight basis (zero moisture content) with a corresponding indication of moisture content. Similar to fuel moisture contents, fuel bulk densities show extreme variation, from lows of 150 to 200 kg/m3 for cereal grain straws and shavings to highs of 600 to 900 kg/m3 for solid wood. Together, heating value and bulk density determine the energy density-that is, the potential energy available per unit volume of the fuel. In general, fuel energy densities are approximately one-tenth that of fossil fuel such as petroleum or high quality coal.

8 ANNEXES

8.1 Annex 1. CHNS specifications



TruSpec® Elemental Determinators
Specification Sheet

Instrument Range @ 500 mg*	
Carbon	50 ppm or 0.005% to 50%
Hydrogen	200 ppm or 0.02% to 50%
Nitrogen	80 ppm or 0.008% to 100%
Precision Range @ 500 mg	
Carbon	25 ppm or 0.5% RSD (whichever is greater)
Hydrogen	100 ppm or 1% RSD (whichever is greater)
Nitrogen	40 ppm or 0.5% RSD (whichever is greater)
Readability	0.0001
Analysis Time	4 minutes
Sample Size	Up to 1 gram
Detection Method	
Carbon/Hydrogen	Optimized, Low-Noise, Non-Dispersive Infrared Absorption
Nitrogen	Optimized, Low-Drift Thermal Conductivity (TC Cell) Detector
Gases Required	
Carrier	Helium (99.99% pure) @ 35 psi (2.4 bar) ±10%
Combustion	Oxygen (99.99% pure) @ 35 psi (2.4 bar) ±10%
Pneumatic	Compressed air (source must be oil and water free); 40 psi (2.8 bar) ±10%
Furnace	Resistance furnace; both primary and afterburner; up to 1050°C
Autoloader	30 position (stackable to 120 samples)
Dimensions†	
Width	27 inch (69 cm)
Height	31 inch (79 cm)
Depth	28 inch (71 cm)
Weight (approx.)	250 lb. (113 kg)

Electrical Power Requirements	230 V~ (±10%; at max load), 50/60 Hz, single phase, 12 A, 9,500 BTU/hr
Part Numbers	
TRSNC	TruSpec N (Nitrogen only) with PC tower, Windows®-based operating software, flat panel monitor, and autoloader
TRSCNC	TruSpec CN (Carbon/Nitrogen) with PC tower, Windows®-based operating software, flat panel monitor, and autoloader
TRSCHNC	TruSpec CHN (Carbon/Hydrogen/Nitrogen) with PC tower, Windows®-based operating software, flat panel monitor, and autoloader

*Adjusting sample size may extend instrument range.
†Allow a 6-inch (15 cm) minimum access area around all units.
V~ denotes VAC.

Artwork 23. TruSpec LECO specifications

8.2 Annex 2. CHNS RESULTS

Name	Mass	C %	H %	N %	S %	Method
Pellet	0,09623	46,790	7,024	0,120	0,050	LECO ST
Pellet	0,11459	47,230	7,009	0,130	0,020	LECO ST
Pellet	0,13034	47,190	7,004	0,130	0,040	LECO ST
Pellet	0,17074	47,120	6,947	0,140	0,060	LECO ST
Pellet	0,14215	47,220	6,975	0,130	0,020	LECO ST
Sludge	0,10649	30,340	5,951	4,793	1,580	LECO ST
Sludge	0,16341	30,770	5,919	4,806	1,460	LECO ST
Sludge	0,12135	30,560	5,954	4,804	1,510	LECO ST
Sludge	0,09741	30,570	5,980	4,806	1,620	LECO ST
Sludge	0,11866	30,450	5,954	4,836	1,350	LECO ST
Corn	0,13532	44,460	7,820	1,200	0,560	LECO ST
Corn	0,13123	44,840	7,977	1,258	0,570	LECO ST
Corn	0,14340	44,910	7,993	1,269	0,680	LECO ST
Corn	0,13024	44,940	7,959	1,294	0,690	LECO ST
Corn	0,11909	44,860	5,810	0,630	0,660	LECO ST
Thistle	0,11965	56,270	9,285	1,200	0,120	LECO ST
Thistle	0,16693	55,040	8,906	1,220	0,180	LECO ST
Thistle	0,14123	55,990	9,099	0,870	0,210	LECO ST
Thistle	0,14491	55,360	8,987	0,760	0,240	LECO ST
Thistle	0,12807	55,520	8,952	0,810	0,130	LECO ST
Almond Shell	0,10974	46,860	7,482	0,441	0,030	LECO ST
Almond Shell	0,13589	47,280	7,403	0,467	0,030	LECO ST
Almond Shell	0,11321	46,970	7,471	0,303	0,020	LECO ST
Almond Shell	0,10448	46,760	7,521	0,336	0,040	LECO ST
Almond Shell	0,10275	44,770	7,100	0,430	0,050	LECO ST
Olive pits	0,10422	54,650	5,930	1,040	0,090	LECO ST
Olive pits	0,10145	48,990	7,744	0,290	0,030	LECO ST
Olive pits	0,09874	50,300	5,710	1,040	0,080	LECO ST
Olive pits	0,10753	52,650	5,390	1,170	0,080	LECO ST
Olive pits	0,11158	48,760	5,010	0,980	0,090	LECO ST
Grapes	0,11677	50,480	7,329	2,370	0,140	LECO ST
Grapes	0,10624	50,150	7,198	2,980	0,190	LECO ST
Grapes	0,12795	50,170	7,212	3,150	0,190	LECO ST
Grapes	0,09874	50,110	7,338	3,065	0,170	LECO ST
Grapes	0,12029	50,080	7,190	2,600	0,120	LECO ST
Charcoal	0.07602	89,720	3,706	0,335	0,335	LECO ST
Charcoal	0,07446	89,210	3,778	0,349	2,836	LECO ST
Charcoal	0,19852	89,040	3,110	0,249	2,790	LECO ST
Hard coal	0,12381	90,210	4,943	1,738	1,110	LECO ST
Hard coal	0,19874	90,610	3,810	0,738	1,340	LECO ST
Hard coal	0,09769	91,210	3,260	1,417	0,110	LECO ST

Anthracite values aren´t accurate, so I rejected them. Reason: Equipment broke down.

8.3 Annex 3. Parr 6300 calorimeter Heating values

Sample	mass [g]	Heating Value [MJ/Kg]	Heating Value medio [MJ/Kg]
Almond Shell	0,509	15,83	**17,2542**
	0,50031	18,6768	
	0,50017	17,2583	
Thistle	0,51519	24,989	**24,9782**
	0,49708	24,9579	
	0,53413	24,9876	
Corn	0,53219	17,3845	**17,5367**
	0,51487	17,8672	
	0,48326	17,3584	
Sludge	0,50698	12,0956	**10,6872**
	0,49725	11,581	
	0,51962	8,3851	
Anhtracite	0,49987	33,3133	**33,0316**
	0,52159	32,7499	
	0,50901	18,5554	
Hulla	0,52624	32,997	**32,3380**
	0,52169	33,7054	
	0,50368	30,3115	
Charcoal	0,51198	28,4075	**28,8459**
	0,49875	29,0147	
	0,59874	29,1154	
Pellets	0,58742	19,57117	**18,6909**
	0,48887	18,3159	
	0,47599	18,1857	
Grape	0,51987	19,089	**18,2818**
	0,53216	18,0654	
	0,55421	17,691	
Olive pits	0,506321	17,807	**17,5647**
	0,580141	17,9001	
	0,541172	16,987	

8.4 Annex 4. Artwork index

8.5 Annex 5. Chart index

8.6 Annex 6. Graphic index

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- Instituto Nacional de Estadística. Equivalent CO2 emissions and percentage structure / percentage structure, economic sectors and period. http://www.ine.es/

- Instituto para la Diversificación y Ahorro de la Energía. http://www.idae.es

- IEA - International Energy Agency. http://www.iea.org

- Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas. http://www.ciemat.es

- National Geographic. http://www.nationalgeographic.com.es/

- LECO Corporation. http://www.leco.com/

9.3 Reference standards

- **Granulometric Standards** :
- Solid mineral fuels:
  ASTM D4749/87 (2007)- Standard Test Method for performing the sieve analysis of coal and designation coal size.
- Solid biofuels:
  CEN / TS 15149-1, Methods for determination of particle size distribution. Part 1: Method of oscillating screen with mesh opening of 3.15mm or more.
  CEN / TS 15149-2, Methods for determination of particle size distribution. Part 2: Method of oscillating sieve with mesh size equal to or equal to 3.15mm.
  CEN / TS 15149-3, Methods for determination of particle size distribution. Part 3: Method of rotary screen.

- **Moisture method Standards**
  - Solid biofuels:
    UNE-CEN (TS_14774-1 = 2007_EX Solid biofuels. Methods for determination of moisture content Pt1.
    UNE-CEN (TS_14774-2 = 2007_EX Solid biofuels. Methods for determination of moisture content Pt2.
    UNE-CEN (TS_14774-3 = 2007_EX Solid biofuels. Methods for determination of moisture content Pt3.
  - Solid mineral fuels:
    UNE_32002 = 1995 Solid mineral fuels. Determination of moisture from the sample for analysis.

- **CHNS analysis standards:**
  - Solid biofuels & solid mineral fuels:
    AFNOR_CENTS 15289_Solid Biofuels_ Content of sulphur and chlorine.
    BSI_CENTS 15104_Solid biofuels_Content of carbon,hydrogen and nitrogen.

- **Calorimeter Analysis standards:**
  - Solid biofuels:
    UNE_164001 = 2005_EX Solid biofuels. Method for determining the calorific value.
  - Solid mineral fuels:
    UNE_32006 = 1995 Solid mineral fuels. Calorific value determination by automatic calorimeter.