UNIVERSITY OF ROMA TOR VERGATA

BIOMASS ULTIMATE AND PROXIMATE ANALYSES: METHODOLOGICAL DESCRIPTION AND EXPERIMENTAL RESULTS

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Target of the Thesis

- Biomass has come up as a **major alternative source**, presenting wide availability and lower environmental impact than fossil fuels.
- In this research, results from the laboratory analyses of biomasses used in a fast pyrolysis lab scale experiment are reported
- This study is devoted to the analysis and **evaluation thermophisical properties of two biomasses:** Ampelodesmos Mauritanicus, chosen due to its phytoremediation capability and the Exhaust Grape Marc coming from the wine-making process.
- A **wide range of analytical tools and methodologies** are here presented and used to give an overview on biomasses thermophysical properties.

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THERMOGRAVIMETRIC ANALYSIS

1. THERMOGRAVIMETRIC ANALYZER (TGA)

- It mainly consists of a **multiple sample furnace** that allows simultaneous analyses.
- **Replaces ovens, desiccators,** and **analytical balances**
- It measures **weight loss as a function of temperature** in a controlled environment.
- The weight loss of each sample is monitored and the furnace temperature is controlled according to the **selected analysis method**.
- An **integrated balance** provides weight measurement during the analysis process.

Sample preparation → Methods → Experimental results

The behavior of agricultural residues known as **Exhaust Grape Marc** and herbaceous biomass known as **Ampelodesmos Mauritanicus** are investigated.

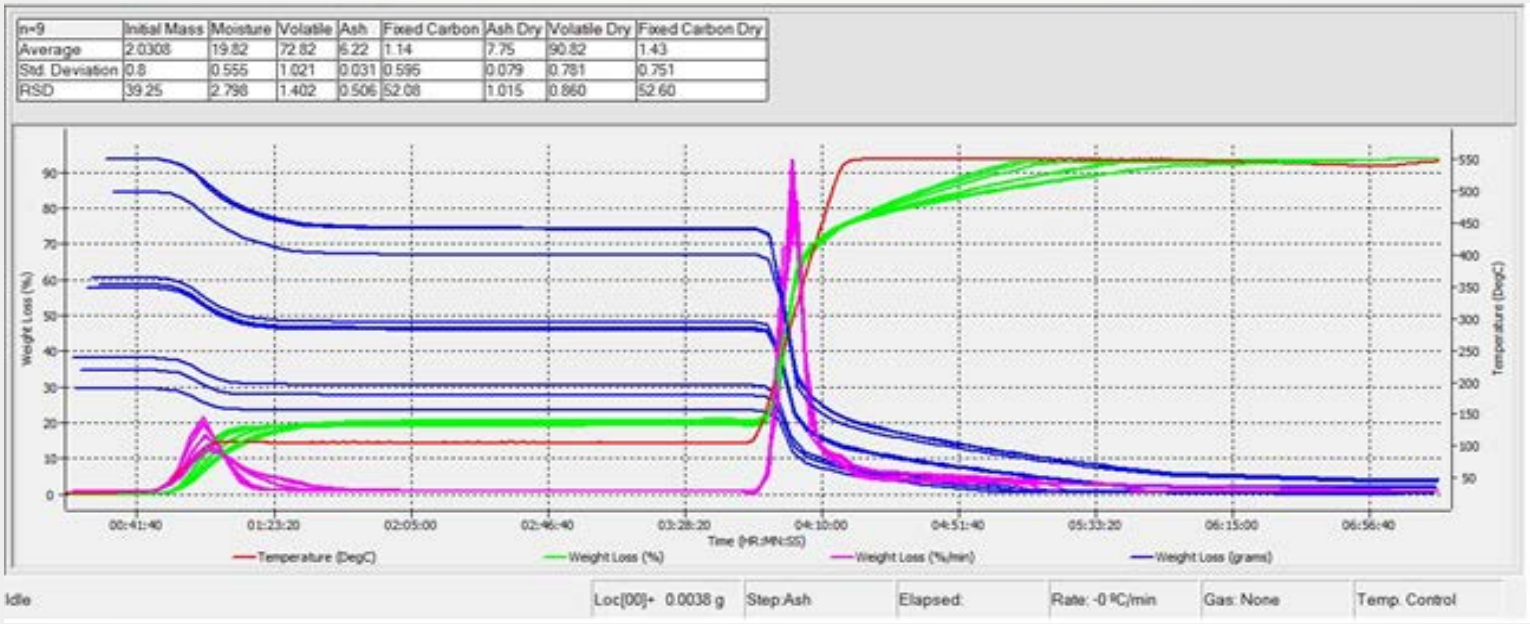
I. Sample Preparation

- Test samples have been prepared according to EN 14778 and EN 14780.
- A **cutting mill** has been used for reducing the nominal max size (**5 mm to 10 mm down to about 1mm**).
- Further decrease of nominal max size through a **wire-mesh sieve** (aperture size of **0.850 mm**).
- 9 Powdered samples of about 5 grams (max) for both the biomass kinds

II. Experimental results and methodology

- **Content determination of ash, volatile matter and moisture** referred to the standards ISO 18122, ISO 18123 and ISO 18134 respectively.

n=9	Initial Mass	Moisture	Volatile	Ash	Fixed Carbon	Ash Dry	Volatile Dry	Fixed Carbon Dry
Average	2.0308	19.82	72.82	6.22	1.14	7.75	90.82	1.43
Std. Deviation	0.8	0.555	1.021	0.031	0.595	0.079	0.781	0.751
RSD	39.25	2.798	1.402	0.506	52.08	1.015	0.860	52.60



Temperature (DegC) Weight loss (%) Weight Loss (%/min) Weight loss (grams)

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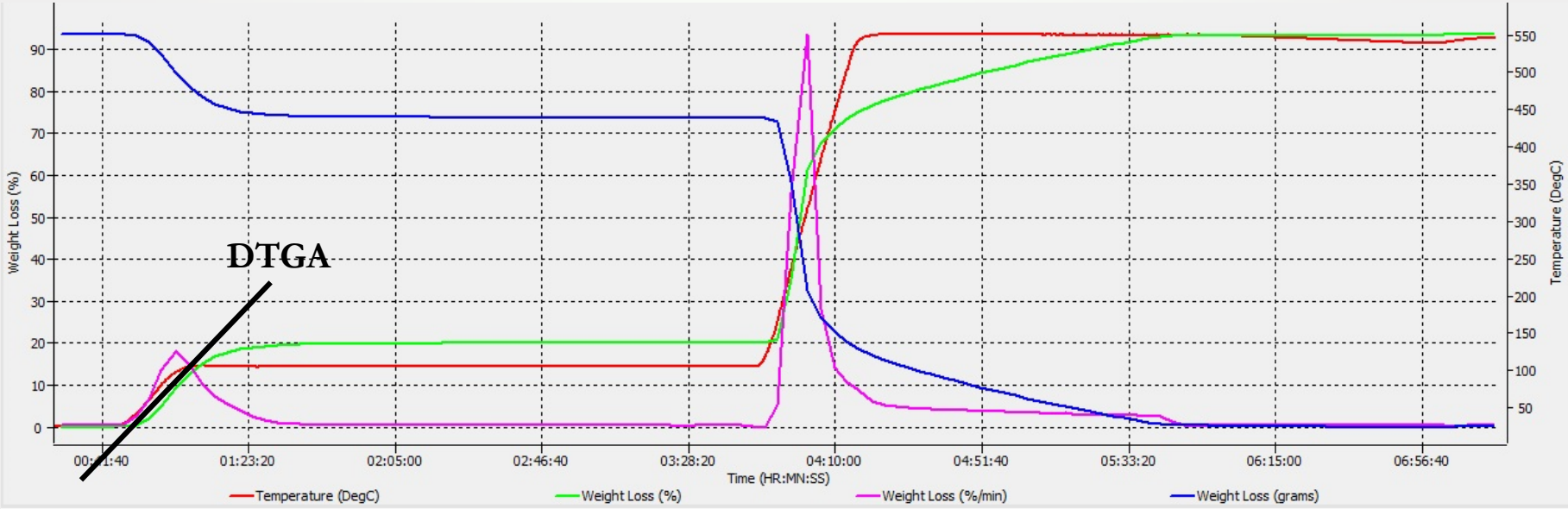
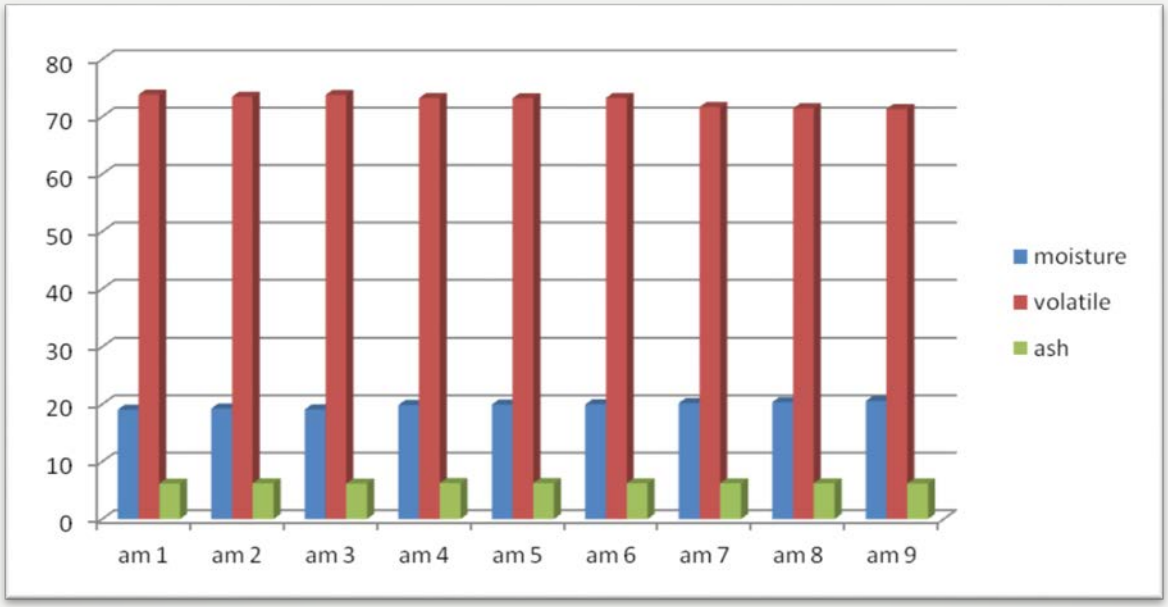
Ampelodesmos Mauritanicus

1. The sample **(inert gas nitrogen)** is heated-up to **105°C** following a **6°C/min ramp**; this temperature is kept constant until the DTGA becomes equal to zero, meaning a zero **moisture residue**
2. The sample is then heated-up to **550°C** following a **15°C/min ramp**, and kept at this temperature until the DTGA becomes again zero, meaning zero **volatile matter**.
3. The nitrogen is then **substituted by oxygen**, which allows for the combustion process of the **fixed carbon** to measure the **unburnt ashes**.
4. The oven is cooled-down at a rate of **100 °C/min** to room temperature.



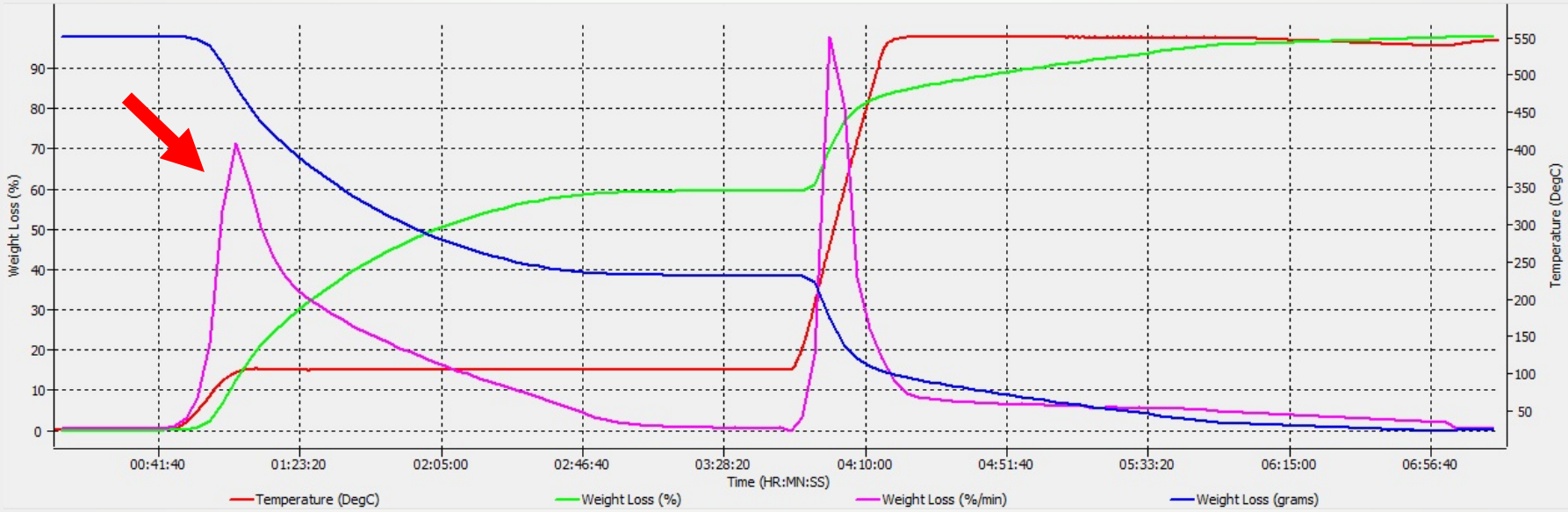
Temperature (DegC) Weight loss (%) Weight Loss (%/min) Weight loss (grams)

Ampelodesmos Mauritanicus



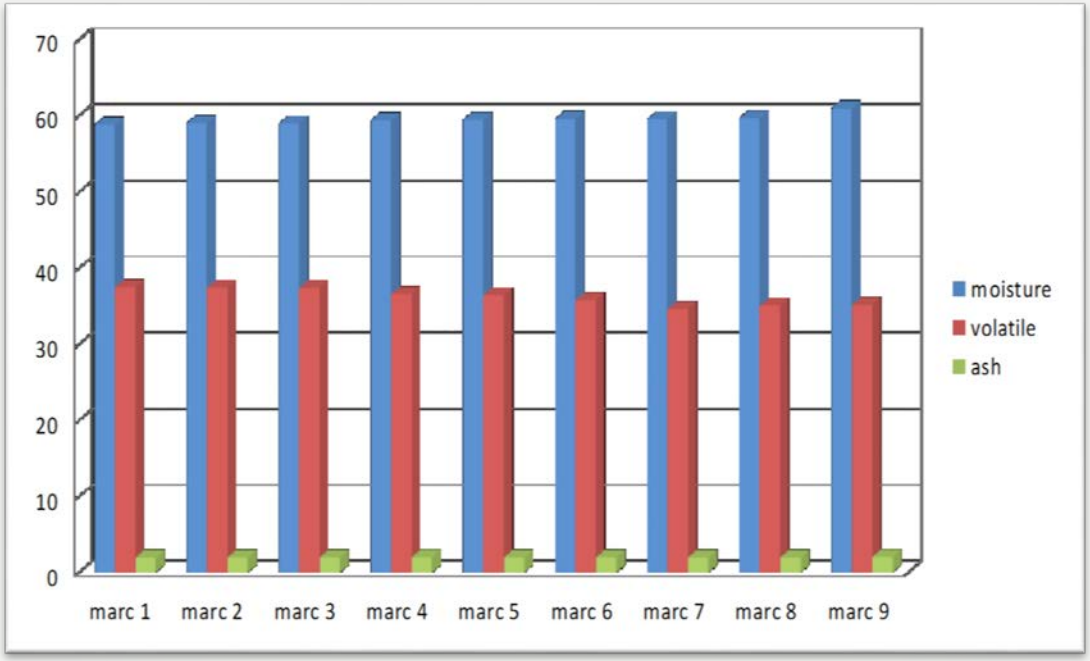
N=9	Initial mass	Moisture	Volatile	Ash	Fixed carbon	Ash dry	Vd	FC
Avg	2.0308	19.82	72.82	6.22	1.14	7.75	90.82	1.43
SD	0.8	0.555	1.021	0.031	0.595	0.079	0.781	0.751
RSD	39.25	2.798	1.402	0.506	52.08	1.015	0.860	52.60

Exhaust Grape Marc



Temperature (DegC) Weight loss (%) Weight Loss (%/min) Weight loss (grams)

Exhaust Grape Marc



N=9	Intial mass	Moisture	Volatile	Ash	Fc	Ad	Vd	FC dry
Avg	3.046	59.51	36.25	2.02	2.22	4.99	89.51	5.50
Sd	0.9	0.629	1.110	0.025	0.792	0.139	1.993	1.970
Rsd	28.92	1.058	3.061	1.228	35.60	2.787	2.226	35.84

CALORIMETRIC ANALYSIS

2. CALORIMETRY

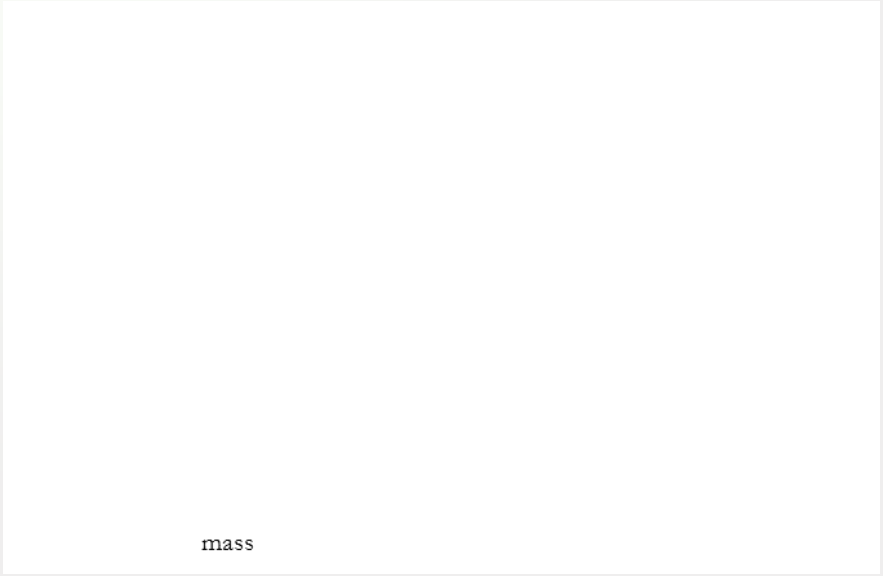
- **Used for measuring HHV.**
- It is composed essentially by four sub-systems: **(1)** a **bomb** or vessel, **(2)** a **bucket** or container for holding the bomb in a measured quantity of water, **(3)** an **insulating jacket** to protect the bucket from transient thermal stresses, and **(4)** a **thermometer** for measuring temperature changes within the bucket.

I. Experimental results and methodology

- The **fluctuation in HHV** among the experiments can be associated to their moisture content, which may vary with respect to the pressure applied during the sample preparation.
- The **quantities have been rearranged** referring to a visual analysis of the combustion residues (difficulties in preparing samples-heterogeneous materials).
- The **greater is the pressure and the higher the mass of the test sample,** but the **lower is the combustion efficiency** and the **quality** of the measurement results

Ampelodesmos Mauritanicus

Exhaust Grape Marc



Ampelodesmos mauritanicus

- The mean Higher Heating Value (**HHV**) is about **14 MJ/Kg.**
- Two samples **,"am1"** and **"am4"**, are considerably far from the average value.
- The Average **LHV** for the Ampelodesmos Mauritanicus: **LHV = 13.20 MJ/Kg**.

Exhaust Grape Marc

- The mean Higher Heating Value (**HHV**) is about **9.35 MJ/Kg.**
- Two samples **,"marc1", "marc3"** and **"marc4"**,are considerably far from this average value.
- The Average **LHV** for the Exhaust Grape marc: **LHV = 7.50 MJ/Kg**.

$$LHV = HHV - h_g\left(\frac{9H}{100} + \frac{M}{100}\right)$$

LHV is determined by **subtracting** the heat of vaporization of the water vapor from the HHV. The energy required to vaporize the water therefore is not released as heat.

CHNS ELEMENTAR ANALYSIS

3. CHNS ELEMENTAR ANALYZER

- Based on a rapid and complete combustion (flash) of the sample within a furnace, at a temperature of **1150 °C**
- The sample is burnt in an **oxygen/carrier gas** and converted into ash and gaseous products: **carbon dioxide, water vapor, elemental nitrogen and/or oxides of nitrogen, sulfur.**
- Gas chromatograph consists in comparing analyzed product with calibration substances **:**

  Sulfanilamide (C6H8N2O2S - 41.8%C, 4.7%H, 16.3%N) – for fuels with a medium carbon content

  Diphenylamine (C12H11N – 85.2%C, 6.6%H, 8.3%N) – for fuels with an high carbon content

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I. Sample Preparation

- Test samples with a **nominal max size of 1 mm** or less have been prepared according to the standard ISO 14780.
- In the CHNS **sample preparation**, following the standard ISO 16948:2015, the sample is directly weighed into capsules filled with a mixture of **biomass and tungsten oxide**.
- Tests have been done with different sample mass (**20 mg, 40 mg, 60 mg, 80 mg and 100 mg**) and different number of samples (**5 tests**) for both Ampelodesmos mauritanicus and Exhaust Grape Marc.

II. Experimental results

Ampelodesmos mauritanicus

	N [%]	C [%]	H [%]	S [%]
AM 1	1.80	45.16	3.861	0.294
AM 2	0.66	44.85	4.101	0.144
AM 3	0.62	44.86	4.710	0.088
AM 4	-	-	-	-
AM 5	0.63	45.21	5.205	0.096

Exhaust Grape Marc

	N [%]	C [%]	H [%]	S [%]
MARC 1	2.52	51.12	2.723	0.544
MARC 2	1.88	50.87	2.641	0.271
MARC 3	-	-	-	-
MARC 4	1.95	50.08	2.522	0.201
MARC 5	1.96	50.06	1.939	0.178

- The values of the CHNS content have been averaged for both biomass kinds:

	N [%]	C [%]	H [%]	S [%]
Avg AM	0.92	45.02	4.469	0.155
Avg MARC	2.07	50.53	2.456	0.298

- **Carbon (C):** During combustion, it is mainly transformed back into CO2, which is again released in the atmosphere. The **low lignin** content like in the AM leads to a lower carbon content as compared to Exhaust Grape Marc.
- **Hydrogen (H):** During combustion, hydrogen is **converted to H2O**. As mentioned in the calorimetric analysis, the hydrogen content affects the calculation of the **lower heating value** from the experimentally measured higher heating value
- **Nitrogen (N)**: It is **absorbed via the soil**. During combustion nitrogen does not oxidize in any significant quantities and is released in the gas phase as N2.
- **Sulphur (S):** It is incorporated in several organic structures like amino-acids, proteins and enzymes. It is an important nutrient for plant growth. (**corrosion**)

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Conclusions

- Research activities have been done related to the utilization of biomass sources for energy conversion purposes
- The analysis of biomass samples is important to understand the energy yield for conversion or toward a biofuel.
- To ensure the validity of the experiments and to determine the heating values, the thermogravimetric behaviour and elemental composition, the **international rules reported by the standards** have been used
- The Heating values measured are in line with the literature available data.
- In particular, the mean **LHV** for the Ampelodesmos Mauritanicus and for the Exhaust Grape Marc is 13.20 MJ/Kg and 7.50 MJ/Kg respectively while the mean values of the **CHNS** content are 0.92, 45.02, 4.469, 0.155 (%) and 2.07, 50.53, 2.456, 0.298 (%) respectively for the ampelodesmos mauritanicus and the exhaust grape marc

Thank you for the attention