Università di Roma Tor Vergata

UNIVERSITÀ DEGLI STUDI DI ROMA TOR VERGATA

Biomass Polymeric Analysis: Methodological Description And Experimental Results

Relatore

Prof. Stefano Cordiner

Prof. Vincenzo Mulone

Correlatore

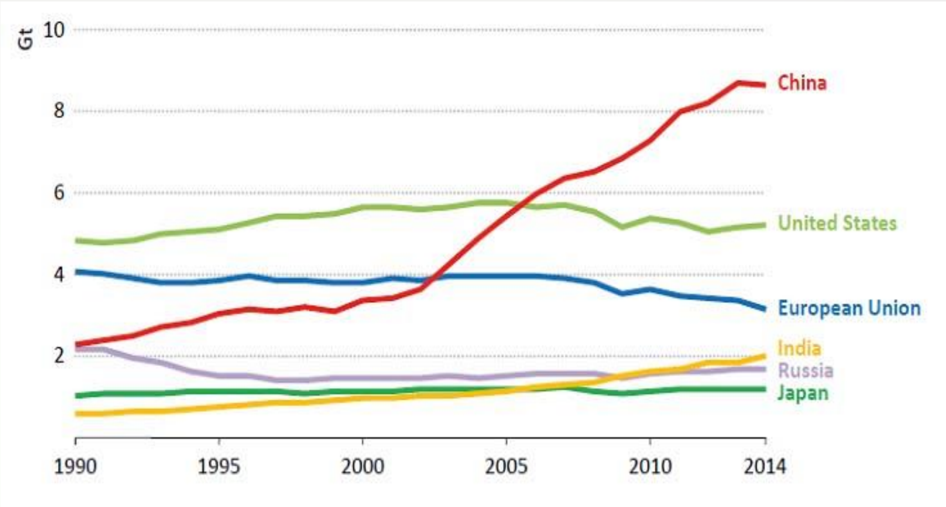
Ing. Alessandro Manni

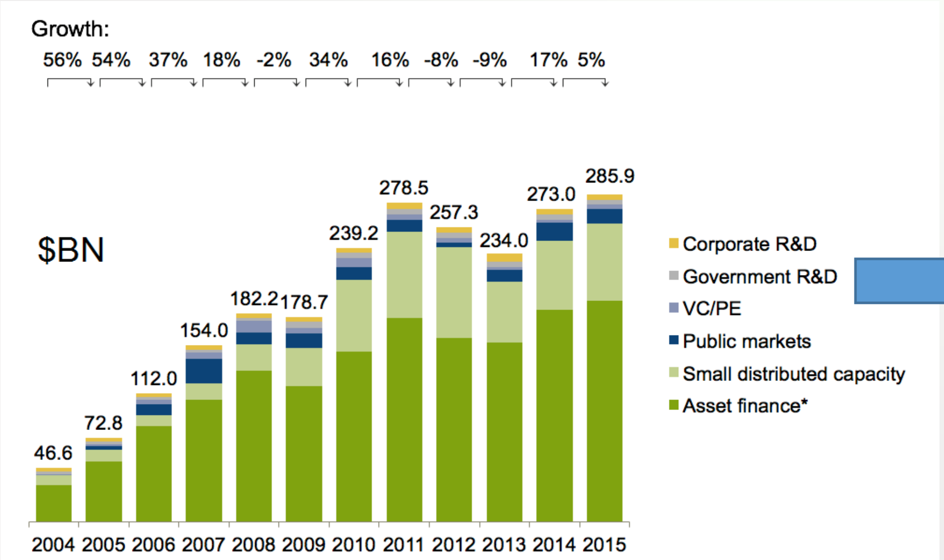
Candidato

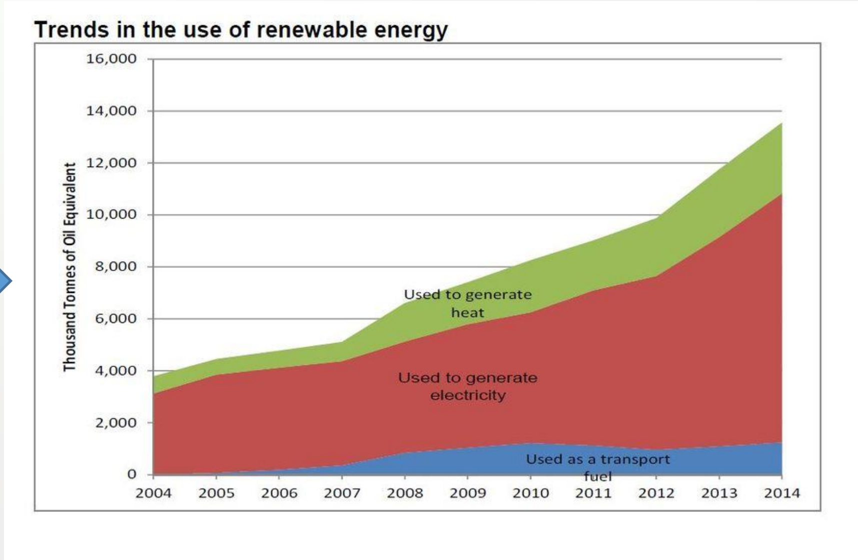
Mohamad El Bachir

Background

- Increase of GHG emissions
- Reducing energy dependence from areas with high geopolitical risk
- Continuous investments and consequent increase in the green energy converted.

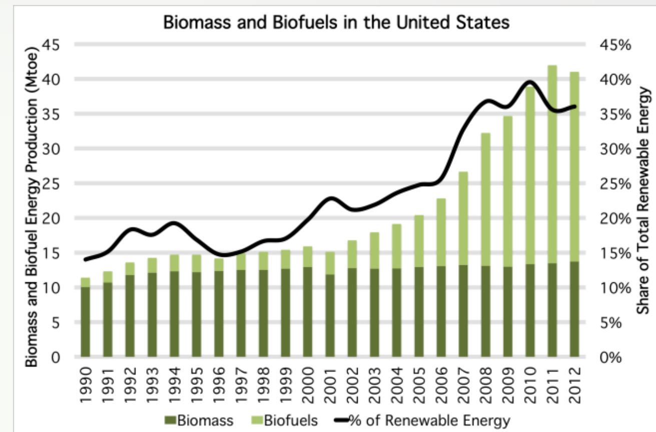


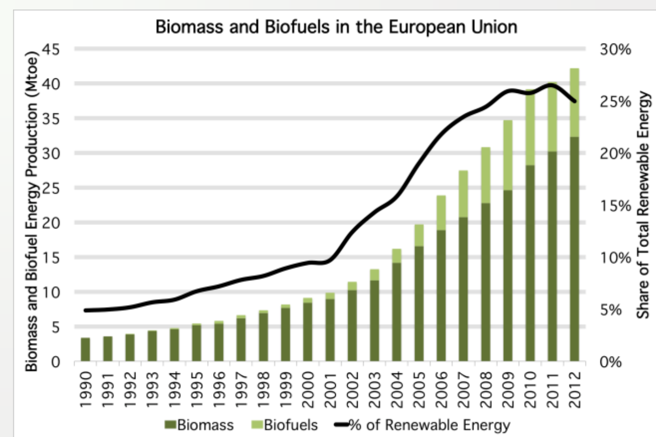




Motivation for Biomass Conversion

- Renewability benefits
  - Grows continuously and hence is renewable
  - Biomass-based energy, fuel, or chemicals reduce reliance on imported fossil
  - Can be provided as a solid, gaseous or liquid fuel: is a unique source of renewable energy.
- Environmental benefits
  - Environmental protection is considered a major issue today, and has been a major driver for biomass energy production use.
  - It makes no net contribution of carbon dioxide to the atmosphere.
- Socio-political benefits
  - Development of new economical and productive systems
  - Positive impact on economical growth





Biomass as an alternative

Biomass is organic matter derived from living species or recently living organism, such as animals and plants, that can be used as a green source of energy.

VIRGIN

- **Terrestrial biomass:** *Forest biomass, Grasses, Energy crops, Cultivated crops*
- **Acquatic biomass:** *Algae, Water plants*

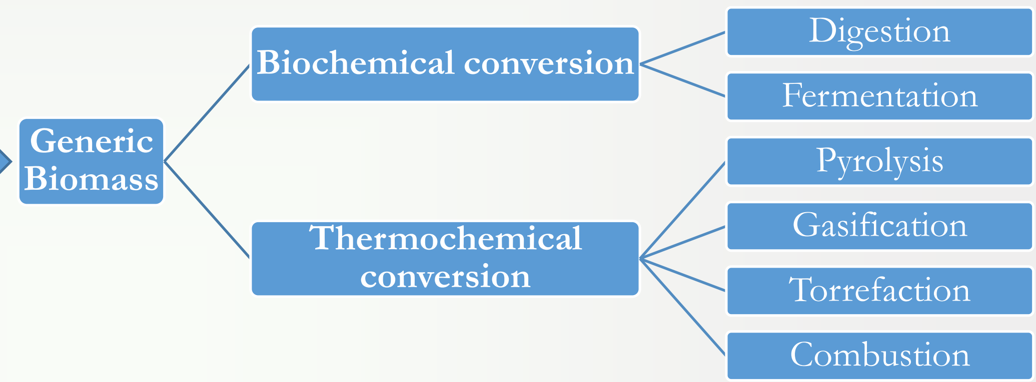
WASTE

- **Municipal Waste and industrial waste:** *MSW, Bosolids, Landfill gas, livestock, waste oil/fat, Sawdust*
- **Agricultural solid waste and Forestry residues:** *Agricultural crop residues, Bark, Leaves, floor residue*

- Only 5% (13.5 billion metric tons) of the earth biomass total amount, can be potentially converted into useful energy.
- This amount, which is equivalent to 6 billion tons of oil, is big enough to provide about 26% of the world’s energy consumption

Biomass as an alternative source

Direct use through combustion or indirect via UPGRADING processes



To understand the best conversion process, is necessary to create a sort of biomass **identity card**.

This can be done through a series of analyses:

- **Polymeric**
- **Proximate**
- **Ultimate**

Target of the Thesis

This project is focused on the analysis of polymeric components of biomass specially the following two biomass kinds:

1) **Ampelodesmos Mauritanicus (AM) herbaceous**
2) **Exhaust Grape Marc (EGM) from the wine-making process**

- AM has been chosen for its phytoremediation capability.
- Toxic metal pollution of waters and soils is a major environmental problem
- The use of specially selected and engineered metal-accumulating plants as the AM for environmental clean-up, is an emerging technology

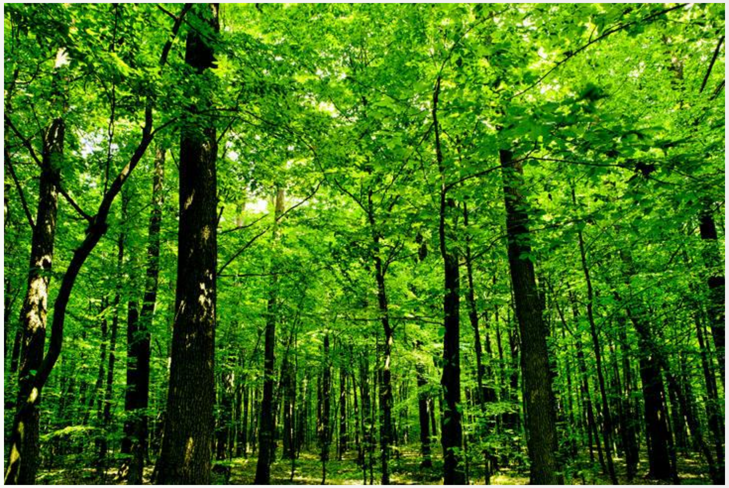
- The exhaust grape marc (GM) is an organic matter derived from grapes production process and/or distillation process; it consists of a mixture of several components such as peels, grape seeds and stalks.
- The usefulness of such product is represented by the feasibility of closing a production process with the maximum energy recovery.

Biomass Composition

Biomass characteristics determine both the choice of conversion process and any subsequent processing difficulties that may arise.

The main parameters of interest are:

- moisture content
- proportions of fixed carbon and volatiles
- alkali metal content
- ash content
- cellulose/lignin ratio



Volatile matter: During the fuel heating up, a release of condensable or noncondensable vapor ,called volatile matter, occurs.

Cellulose/Lignin ratio: This ratio, between two polymers, is very important both in biochemical and thermochemical conversion processes.

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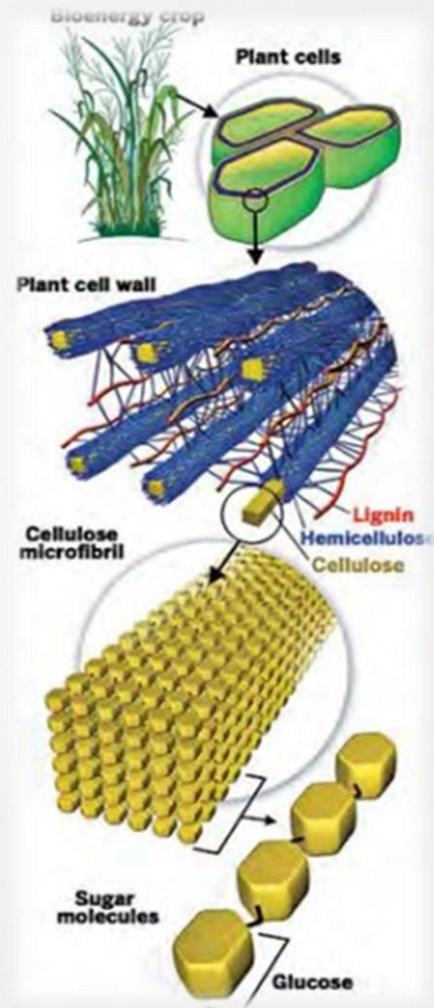
Polymeric Analysis: Biomass Structure

Biomass is a complex mixture of organic materials such as carbohydrates, fats, and proteins, along with small amounts of minerals such as sodium, phosphorus, calcium, and iron.

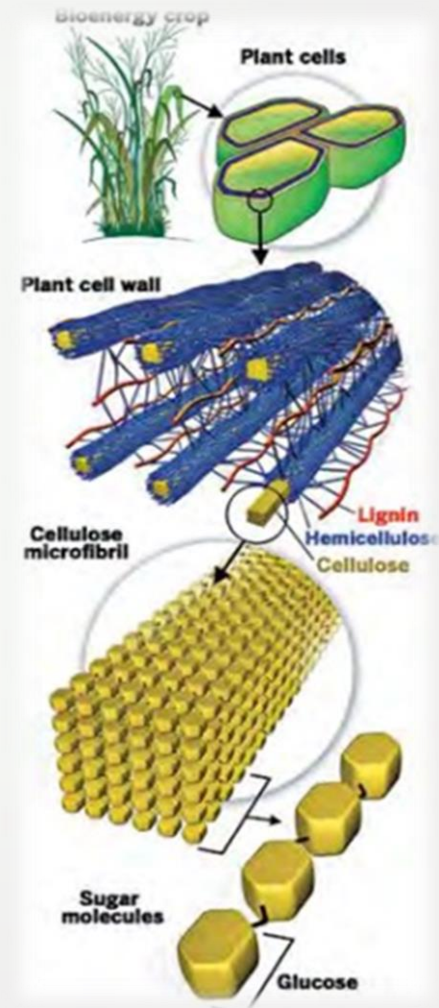
- components of woody biomass
  - extractives
  - cell wall components
    - cellulose
    - hemicellulose
    - lignin
  - moisture
  - ash



Polymeric Analysis: Biomass Structure

Lignocellulosic tissues are biologically-derived natural resources containing some of the main constituents of the natural world:

- Holocellulose: it is the carbohydrate fraction of lignocellulose biomasses that includes cellulose as well as hemicellulose.
- Lignin: it is a class of complex organic polymers crucial for the vascular plants support tissues, holding together adjacent cellulose fibers



- components of woody biomass
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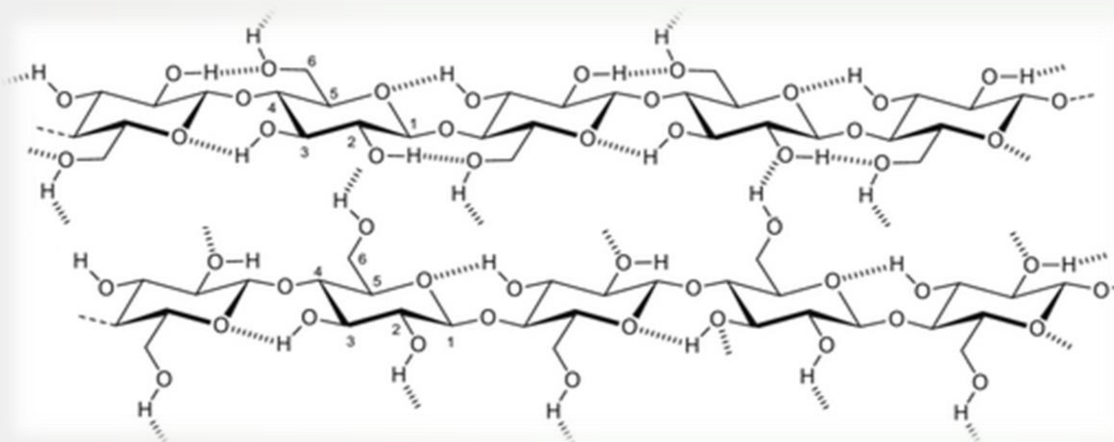
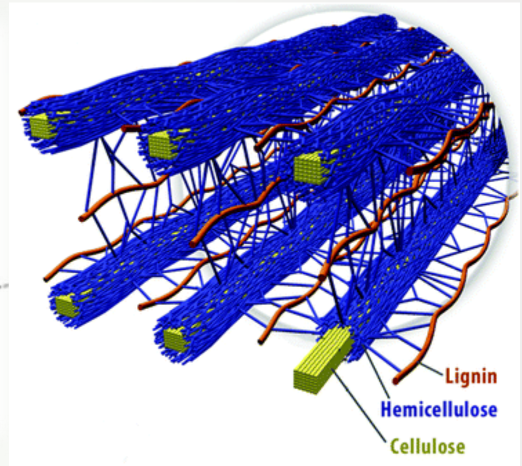
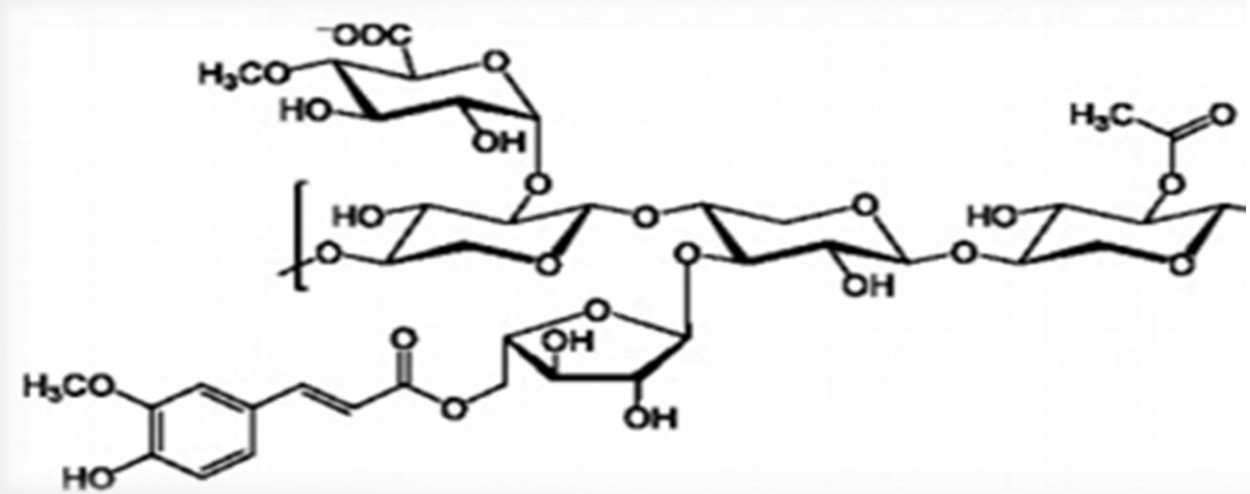
Cellulose structure

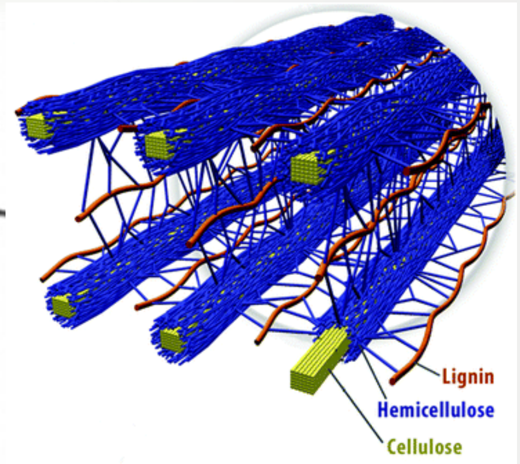




- It is the most common organic compound on earth and the main biomass cell wall component
- It makes 15-30% of the dry mass of primary cell wall and up to 40% of secondary cell wall, where it is found in the form of microfibers.
- It can be represented by the generic formula $(C_6H_{10}O_5)n$, cellulose is a polysaccharide consisting of a linear chain of several hundred to over thousands β(1→4) linked D-glucose units.
- It has a degree of polymerization of about 1200.

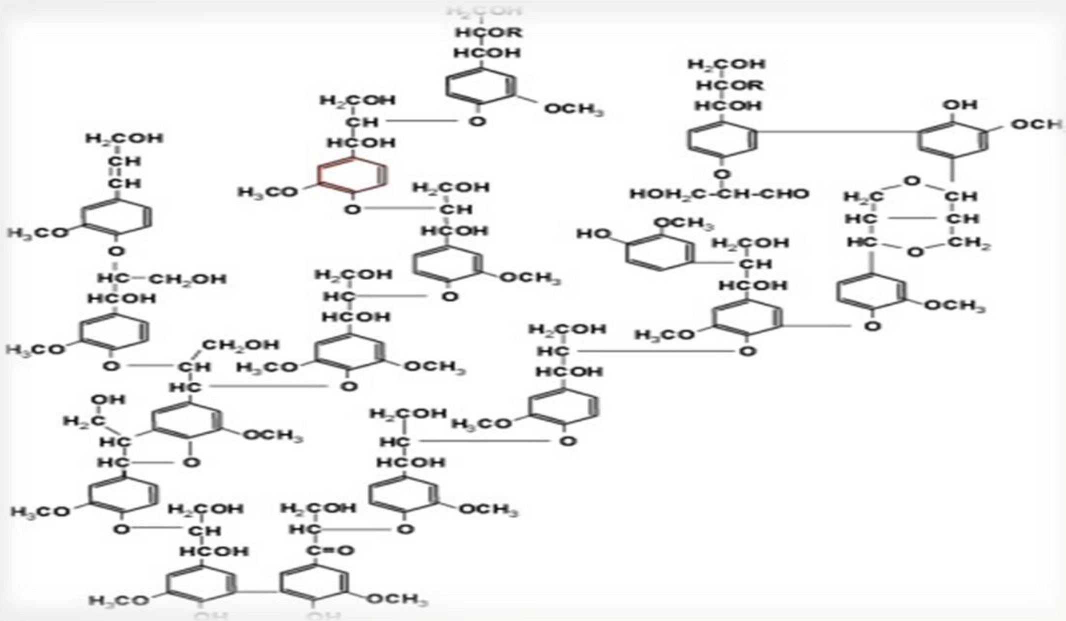
Hemicellulose structure

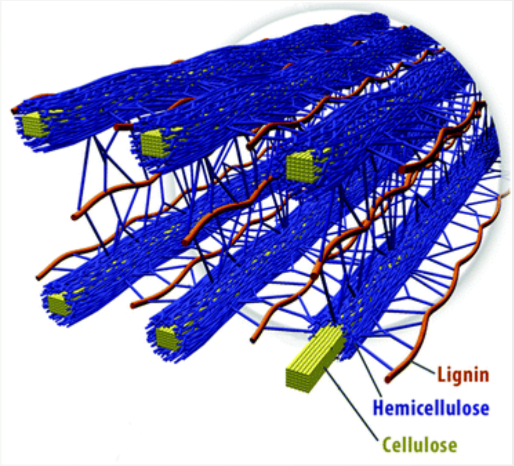




- Composite by short-chain branched substituted sugars polymers with a polymerization degree of 70 to 200.
- It is usually characterized as the heterogeneous polysaccharides soluble in strong alkali.
- Hemicellulose can be represented by the generic formula $(C_5H_8O_4)n$.

lignin structure





- Lignin is a complex natural molecule which is composed by several blocks of phenylpropane, and p-coumaryl, conyferyl, synapyl alcohols.
- It is one of the most abundant organic polymers (exceeded only by the cellulose)
- The presence of lignin in lignocellulosic biomass is the main obstacle of biomass recalcitrance during separation process

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Polymeric Component Composition: Sample preparation

The whole following protocols (NREL and Rowell) have been followed for three biomass samples :

- Generic wood pellet
- Ampelodesmos Mauritanicus
- Exhaust grape marc

Sample preparation: the biomass sample should be taken such that it truly represents the stock it is taken from.
EN14780:2011 (or equivalently ASTM standard, E 1757) describes a standard method for the preparation of a sample for the analysis.

The sample is dried at 105°C for 24 hours to free it from moisture and is then ground down to below 40 mesh size (0.5 mm)

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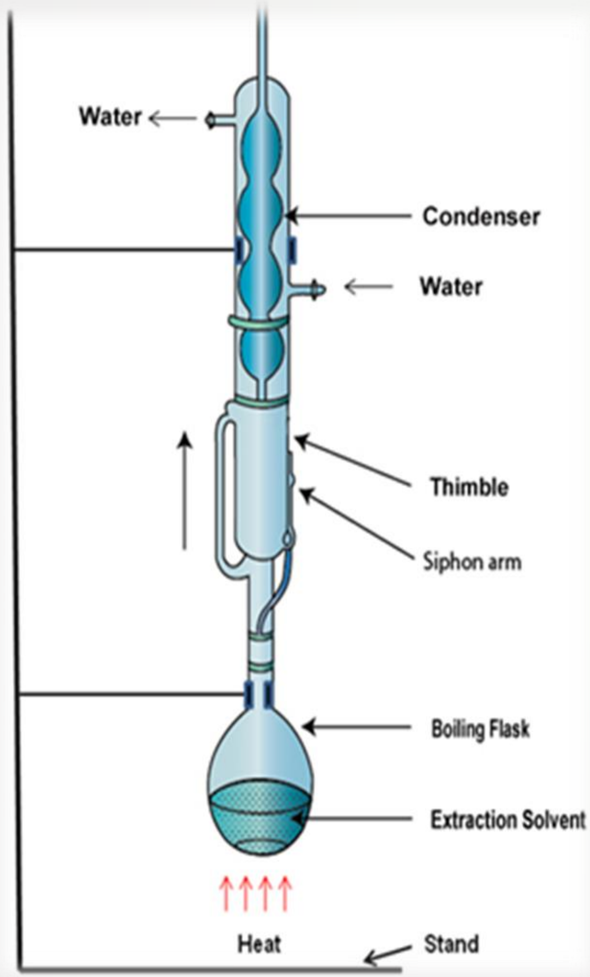
Biomass Extractive Components



Extractives are nonstructural nonpolymer and could affect the analysis of polymer compositions. Therefore, it needs to be removed prior to downstream analysis of the biomass sample (NREL, 2008).

Extractives are the natural chemical products of biomass that are capable of being extracted by some solvents. Based on the solvent used in extraction process, extractives can be classified as water soluble, toluene/ethanol, and ether soluble extractives (Rowell, 2005).

The major apparatus in extraction process is the Soxhlet extraction tube (250ml with a 500 ml flask)

Biomass Extractive Components

- First the sample with thimbles is dried in vacum oven to a constant weight.
- Then the thimbles are kept inside the Soxhlet extraction units.
- The extraction is carried out with ethanol-toluene mixture (1:1 basis) with no less than 8 siphoning
- After the extraction, the thimbles with residues and excess of solvent are drained.
- The samples are washed using ethanol (3 times) and dried in a vacuum oven 105°C.
- Extractive-free sample are finally weighed

Lignin determination

Holocellulose is a water-insoluble carbohydrate fraction of wood materials (is the sum of hemicellulose and cellulose). It can be extracted by the chlorination method by getting rid of the lignin.

ASTM D-1166-84 and ASTM E 1721 gives different methods for determination of acid soluble lignin, with analogue results.

- An extractive-free dry sample has been mixed with hot distilled water, acetone and sodium chloride.
- Every hour, acetone and sodium chloride are added. This process is repeated 8 times until lignin is completely removed.
- The mixture is left for 24 h and then filtered in vacuum conditions.
- The residue is washed three times with acetone and left in an oven

The solid whitish residue left on the filter gives the weight of the lignin free holocellulose

Hemicellulose and cellulose from holocellulose

The whitish residue obtained before, is used for hemicellulose determination

The sample is treated with sodium hydroxide (NaOH) and acetic acid to get cellulose as a solid residue and hemicellulose as the filtrate.

The procedure requires to:

- The holocellulose is stirred with a NaOH (17,5%) solution in a flask and kept in a water bath at 20°C
- Every 5 min NaOH(17,5%) is added for 3 times.
- The solid residue containing cellulose is filtered, washed with NaOH solution and then subjected to acetic acid treatment .
- Thereafter, has been washed three times with distilled water and acetone.
- The solid cellulose residue is dried at 125°C overnight before weighing it.

Results Of The Analysis

Extractives step

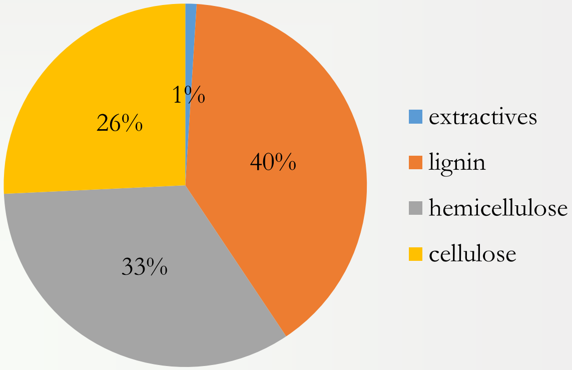
Sample	Pellet [g]	Ampelodesmos Mauritanicus [g]	Exhausted grape marc [g]
Initial	10	10	10
Thimble	2.467	2.412	2.8
Total initial	12.467	12.412	12.8
Final	12.3801	9.9183	12.3224
Extractive free sample	9.9131	7.5063	9.5224
Extractive	0.0869	2.4937	0.4776

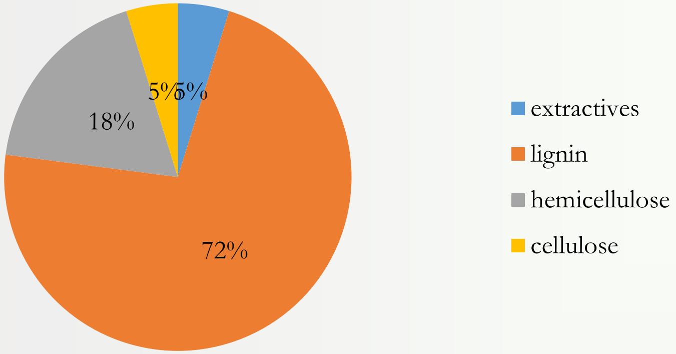
Hemicellulose And Cellulose Step

Sample	Pellet [g]	Ampelodesmos Mauritanicus [g]	Exhausted grape marc [g]
Initial	3.5	3.5	6
Lignin	2.099	2.039	1.45
Hemicellulose	0.9101	0.9222	0.302
Cellulose	0.4909	0.5388	4.248

Analysis Of The Results

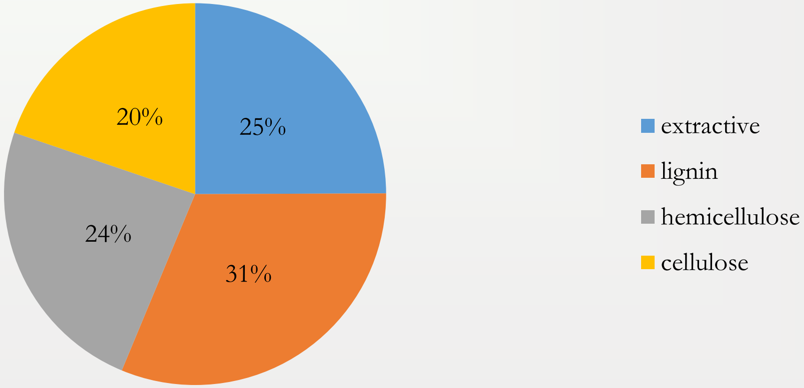
The composition of generic wood pellet is not differ from the standard one





Exhausted grape marc Polymeric composition

Ampelodesmos Mauritanicus Polymeric composition



Conclusions

- This study describes some methodologies used to measure the biomass properties toward energy conversion processes
- In particular, reports result from two biomass analyses, the Ampelodesmos Mauritanicus and the Exhaust Grape marc, used as a case study.
- High lignin content of the Exhaust Grape marc (72%) has been measured with respect to that of the Ampelodesmos Mauritanicus (31%)
- Exhaust Grape marc should be used with direct combustion rather than through an upgrading procedure (such as gasification or pyrolysis).
- The Ampelodesmos Mauritanicus, characterized by a low lignin content, seems to be promising for fast pyrolysis applications.

Thank you for the attention