Master of Science in *Energy Engineering* *Renewables for Environmental Sustainability*

http://beep.metid.polimi.it/

POLITECNICO DI MILANO

School of Industrial and Information Engineering
Academic Year 2017-18

Lecture notes for:
Bioenergy and Waste-to-Energy Technologies

Biomass characterization

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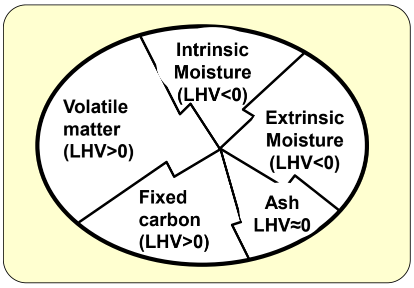
Lecture outline

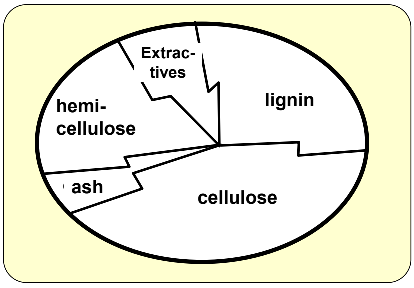
- *Types of characterization*
- *Chemical-physical composition*
- *Proximate composition*
- *Ultimate composition*
- *Heating values*
- *Different bases*
- *The case of waste*

Types of characterization

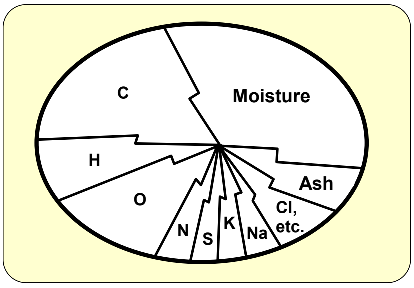
Based on volatility



Based on chemical – physical structure



Based on atoms content



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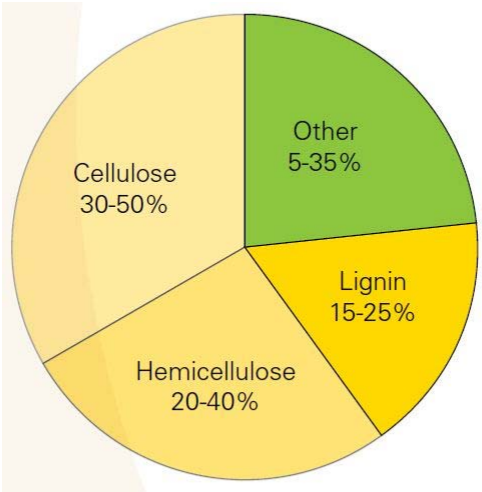
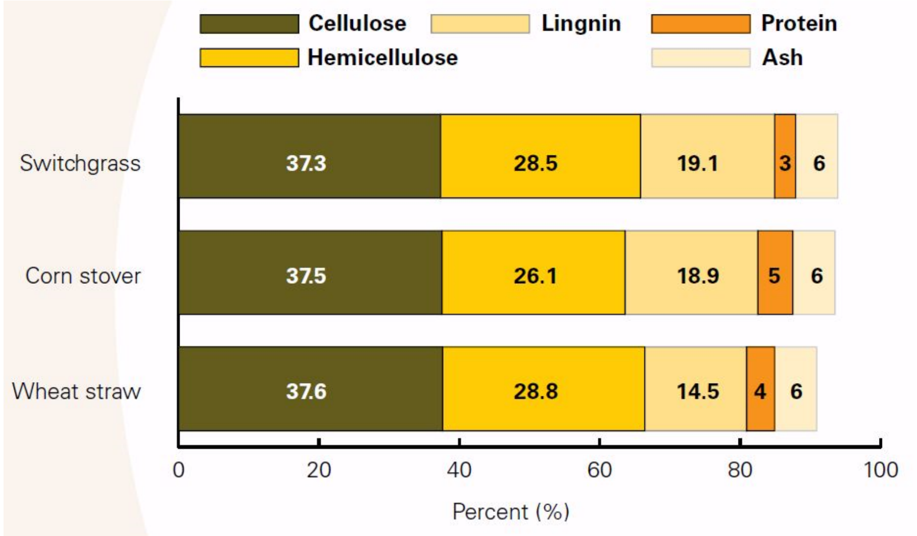
Lignocellulosic biomass



Lignocellulose is the term used to describe the three-dimensional polymeric composites formed by plants as structural material. It consists of variable amounts of cellulose, hemicellulose, and lignin.

Source: http://agbiopubs.sdstate.edu/articles/SGINC1-07.pdf

Some examples

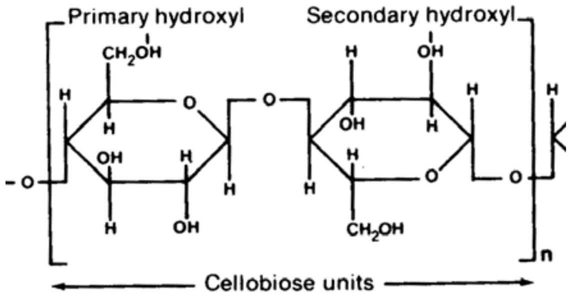


Source: http://agbiopubs.sdstate.edu/articles/SGINC1-07.pdf

Cellulose

(30-40% of total feedstock dry matter)
Cellulose is a glucose polymer linked by ß-1,4 glycosidic bonds. The basic building block of this linear polymer is cellubiose, a glucose-glucose dimer (dimer: two simpler molecules-monomers-combined to form a polymer). Hydrolysis of cellulose results in individual glucose monomers. This process is also known as saccharification.

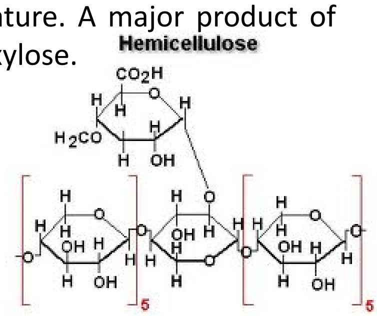
$(C_6H_{10}O_5)_n$



Hemicellulose

(20-40% of total feedstock dry matter)
Hemicellulose is a short, highgly branched polymer of five-carbon (C5) and six-carbon (C6) sugars. Specifically, hemicellulose contains xylose and arabinose (C5 sugars) and galactose, glucose, and mannose (C6 sugars).
Hemicellulose is more readily hydrolyzed compared to cellulose because of its branched, amorphous nature. A major product of hemicellulose hydrolysis is the C5 sugar xylose.

In the figure the brut formula is:
$(C_{62}H_{97}O_{49})_n$
But it can change greatly

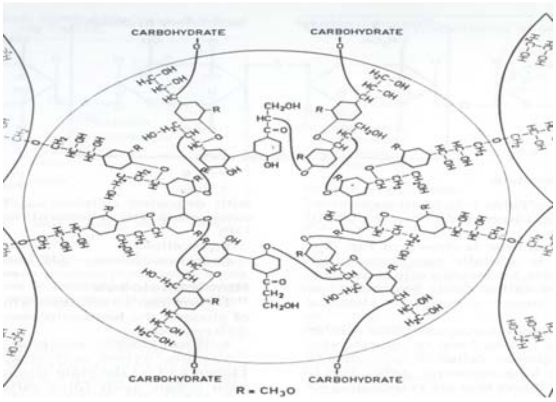


Lignin

(15-25% of total feedstock dry matter)

Lignin is a polyphenolic structural constituent of plants, is the largest non-carbohydrate fraction of lignocellulose. Unlike cellulose and hemicellulose, lignin cannot be utilized in fermentation processes.

$(C_{178}H_{200}O_{62})_n$



Other constituents

Ash (3-10% of total feedstock dry matter in herbaceous biomass) is the residue remaining after ignition (for herbaceous or woody biomass: dry oxidation at 575 ± 25°C). It is composed of minerals such as silicon, aluminum, calcium, magnesium, potassium, and sodium.

Other compounds present in lignocellulosic biomass are known as extractives. These include resins, fats and fatty acids, phenolics, salts, minerals, and other compounds.

Variability in constituents contents

	Minimum	Maximum	Mean	SD
	% of dry matter			
Corn Stover				
Cellulose[b]	31.3	41	37.5	2.8
Structural glucan	33.8	41	37.5	2.2
Hemicellulose	20	34.4	26.1	4.8
Xylan	19.8	25.8	21.7	2.1
Arabinan	1.7	6.1	2.7	1.6
Galactan	0.7	3	1.6	1
Mannan	0.3	1.8	0.6	1.1
Total lignin	15.8	23.1	18.9	2.6
Acid soluble lignin	1.9	3.6	2.9	0.9
Acid insoluble lignin	13.6	19.8	16.4	3.1
Acid detergent lignin	3.1	5	4.1	1.3
Crude protein	3.5	8.7	4.7	2.2
Ash	4.2	7.5	6.3	1.2
Soil	-	-	1.3	-

Source: http://agbiopubs.sdstate.edu/articles/SGINC1-07.pdf

Changes in biomass properties during storage

	Harvest 1 (Oct. 1991)			Harvest 2 (Aug. 1992)		
	Time zero	26 weeks storage		Time Zero	26 weeks storage	
		Inside	Outside		Inside	Outside
	% of dry matter	% change		% of dry matter	% change	
Composition on whole biomass basis						
Extractives	17.0	-7.7	-10.5	14.2	<0.6	-1.8
Ash	5.8	+0.3	+0.2	4.8	<1.0	<1.0
Protein	3.2	+0.6	+0.6	2.8	-0.8	-0.9
Composition on extractive-free basis						
Lignin	21.4	+0.8	+1.5	20.6	-0.5	-0.4
Arabinan	3.4	-0.4	-0.4	3.2	<0.2	<0.2
Xylan	24.9	-1.5	-1.6	25.5	<1.3	<1.3
Mannan	0.4	<0.1	+1.4	0.3	<0.2	<0.2
Galactan	1.1	<0.1	<0.1	1.0	+0.1	<0.1
Glucan	37.8	-2.1	-2.2	40.8	<2.5	<2.5

Source: http://agbiopubs.sdstate.edu/articles/SGINC1-07.pdf

Remarks on chemical-physical composition

- Chemical-physical composition of biomass is relevant to certain conversion processes (i.e. fermentation for ethanol production, oil extraction for biodiesel production), in which such a structure is partly preserved.
- It is relevant also to anaerobic digestion, where hydrolysis is an important step.
- To thermochemical processes, where this structure is completely destroyed, this composition is not relevant.
- Nevertheless, chemical-physical composition can vary greatly, not only with biomass variety, but also with the age and the development phase of the plant, the season, the climatic conditions experienced during the growth and also after harvesting, during storage, etc.

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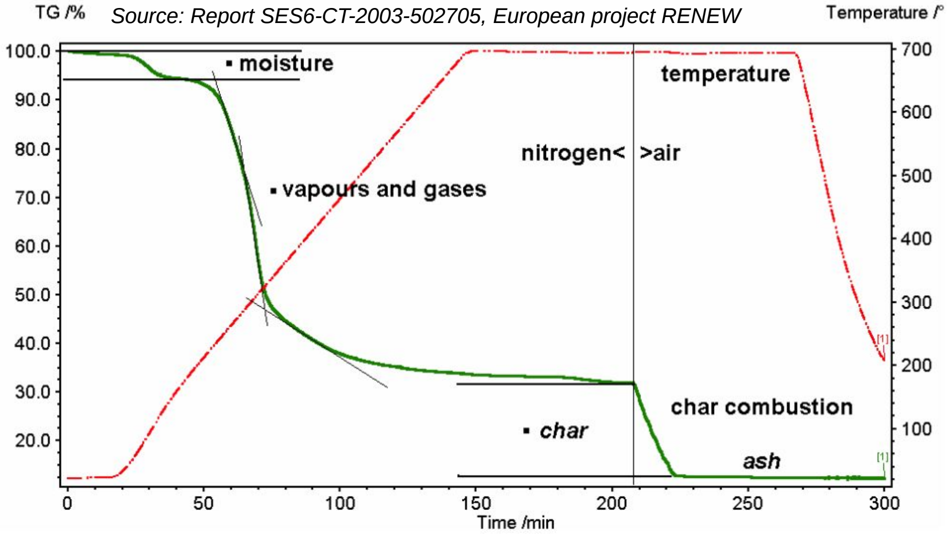
Thermogravimetric analysis (TGA)



1st phase: pyrolysis in nitrogen; 2nd phase: combustion in air.

Examples of proximate analyses

Source: Report SES6-CT-2003-502705, European project RENEW

dry	Wheat straw	Wheat bran	Rice straw	Rice husks	Hay	Cotton stalks	Wood
Volatiles	69 (71,3)	70	59 (69)	66 (64)	65	72	84 (83)
Fixed Carbon	23 (19,8)	22	19 (17)	17 (16)	21	24	16 (17)
Ash	8 (8,9]	8	21 (13)	18 (21)	14	4	0,3 (0,5)

Proximate analysis results are influenced by the way in which the analysis is carried out.

For example, with a faster pyrolysis (i.e. higher K/min ratio) heavier volatile compounds are formed (i.e. with lower H/C ratio). In this way volatiles contain more carbon, thus volatiles content increases while that of fixed carbon diminishes.

References: DIN 51004/5/6/7

Moisture

The conventional determination of moisture is drying in an oven in air to constant weight at 105°C (Ref. DIN 51718). Prolonged drying in the oven can result in loss of volatile constituents due to decomposition, distillation or oxidation.

The moisture content of biomass can change during handling. Typically, after harvesting, moisture content of biomass decreases form the initial value (that for woody biomass can be higher than 50% by mass) to a lower equilibrium value, which can be as low as 5-25%. This equilibrium value depends not only on the biomass variety, but also on ambient conditions (mainly temperature and humidity).

Very dry biomass materials are hygroscopic. When put in contact with humid air, they show a very rapid uptake of moisture.

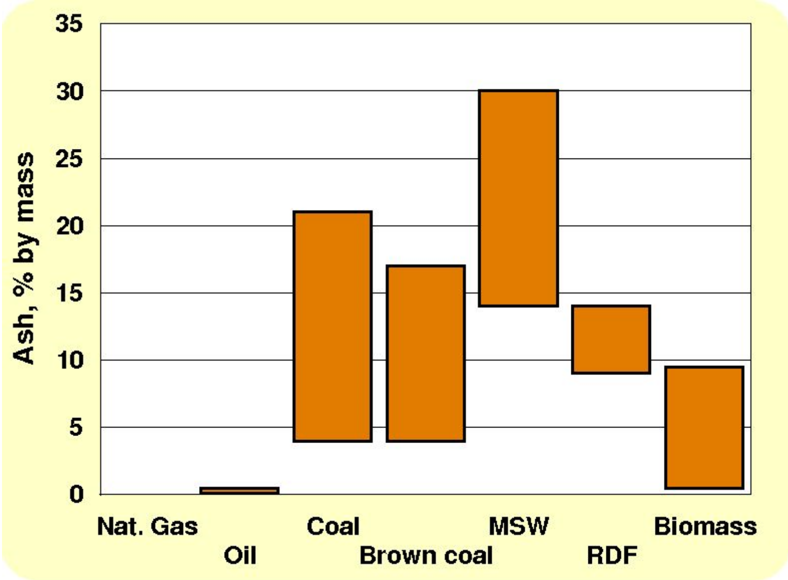
Ash

The ash content of woody biomass without bark is in general below 1%. In contrast, fast growing biomass has an ash content up to 20% (e.g. in some types of rice straw). All fast growing herbaceous biomass like straw, hay or leafs etc. contain about an order of magnitude more ash and heteroatoms than wood. Typical ash contents of straw or hay are 5 to 10%.

Higher ash and heteroatom concentrations are also an indication of higher fertiliser requirements for the faster growing species. Nature recovers the valuable inorganic constituents after fast growth e.g. from the older wood parts. In some cases soil impurities can considerably contribute to the ash content.

Ash composition may be relevant to some particular valorization paths, for example all the termo-chemical routes.

Ash content range for different fuels



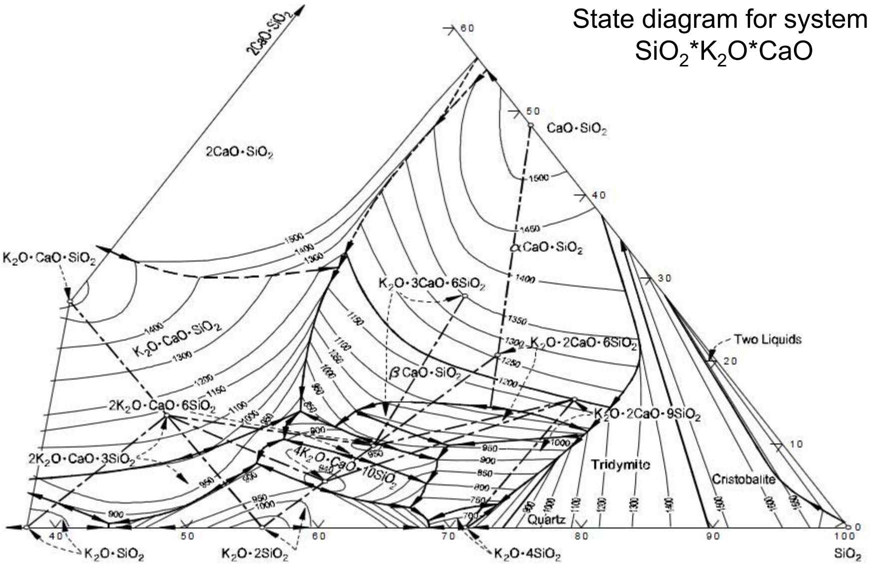
Ash content of biomass feedstock

	Wheat straw	Wheat bran	Rice straw	Hay	Cotton stalks	Wood
K_2O	2,2	1,0	6,2	4,0	0,5	0,04
CaO	0,3	0,1	0,5	0,4	1,7	(0,13)
SiO_2	3,6	<0,1	9,9	0,6	0,4	(0,08)
Cl	0,7	<0,1	1,0	1,0	0,5	(<0,001)
P_2O_5	0,2	0,5	< 0,1	0,7	< 0,1	0,02
Fe_2O_3	< 0.1	< 0,1	0,6	< 0,1	1,0	(0,004)
MgO	0,1	<0,1	0,2	<0,1	0,2	0,02

Source: Report SES6-CT-2003-502705, European project RENEW

Ash melting behaviour

State diagram for system: SiO_2*K_2O*CaO



Ash melting behaviour

Before melting, other critical phenomena can occur.

Temperature /°C	Wheat straw	Wood
Estimated		
Flow	1100,0	
Experimental		
Densification	770,0	1140,00
Distortion	830,0	1240,00
Hemisperical	1100,0	
Flow	1300,0	

Source: Report SES6-CT-2003-502705, European project RENEW

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Ultimate composition

- The ultimate analysis generally reports the elemental carbon (C), hydrogen (H), nitrogen (N), sulphur (S) composition and oxygen (O) very often by difference in the solid fuel. In order to avoid confusion and to give a good representation of the fuel itself, an ultimate analysis is performed and reported on a dry basis, because otherwise moisture is indicated as additional hydrogen and oxygen.
- In some cases, other species may be relevant, for example chlorine. It can represent a possible pollutant and corrosive agent in pyrolysis, gasification and combustion systems.
- A number of instruments have been developed to determine the elemental C, H, N, S and O composition. In some cases C, H, N and S can be determined simultaneously.

Procedure for the ultimate analysis

- Most of the measurement systems employ catalytic combustion with pure oxygen to decompose the biomass sample to nitrogen, water, carbon dioxide and sulphur dioxide, which are then determined quantitatively by chromatography using flame ionization or thermal conductivity detectors.
- Oxygen may be determined directly (not by difference) by catalytic conversion to carbon monoxide.
- The determination of chlorine content, when done, is carried out separately after combustion to HCl in a separate analyser.

Example of ultimate analyses

Source: Report SES6-CT-2003-502705, European project RENEW

	Wheat straw	Wheat bran	Rice straw	Rice husks	Hay	Cotton stalks	Wood
C	45,7 (43,2)	47,7	39,2 (41,8)	44,5 (41)	45,9	46,6 (39,5)	48,6 (50)
H	5,7 (5,0)	6,4	4,8 (4,6)	6,3 (4,3)	6,0	5,6 (5,1)	6,1 (6)
O	43,3 (39,4)	42,0	36,4 (36,5)	36,9 (36)	39,4	42,8 (39,1)	45,0 (43)
N	0,5 (0,6)	2,8	0,4 (0,7)	0,9 (0,4)	2,3	0,7 (0,4)	0,2
S	0,3 (0,1)	0,3	0,2 (0,1)	0,6 (0,01)	0,3		
Cl	0,7 (0,3)		1,9 (0,3)	(0,1)	1,0	0,5 (0,1)	< 0,1

The organics CHO composition of lignocellulose like wood or straw is not much different and approximately represented by $C_6H_9O_4$. For quick estimates a more simplified formula is useful: $C_3(H_2O)_2$. It may be viewed at as a mixture of 50% by mass carbon, with 50 wt% water.

Lecture outline

Heating values

- **Heating values** are meant to represent the energy content of a fuel.
- The heating value may be reported on two bases. The Higher Heating Value (HHV, gross heating value) represents the heat of combustion relative to liquid water as the product. The Lower Heating Value (LHV) is based on gaseous water. The difference in the heating value is the latent heat of the product water.
- For many kinds of coal the gross heating value ranges from 20 to 30 MJ/kg. However, nearly all kinds of lignocellulosic biomass feedstocks fall in the range 15-19 MJ/kg.
- The values for most woody materials are 17-19 MJ/kg; for most agricultural residues, the heating values are about 15 – 17 MJ/kg. All heats reported here are HHV on a dry basis.
- The heating value of carbon feedstock is determined employing an adiabatic bomb calorimeter that measures the reaction heat at 25°C, 1 atm.

HHVs of dry lignocellulosic biomass

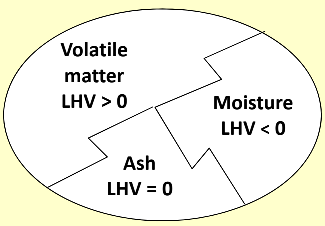
Source: *Report SES6-CT-2003-502705, European project RENEW*

HHV (kJ/kg)	Wheat straw	Wheat bran	Rice straw	Rice husks	Hay	Cotton stalks	Wood
Experimental	17100				17100		
Calculated [1)]	17200	19000	14700	18600	18200	17400	18400
Calculated [2)]	19300	20300	15300	17600	18800	19300	20400
Literature [3)]	17100		15400	15700	16500	15200	19000

1) HHV= 339 C+1214(H-O/8)+226 H+105 S
2) HHV = 20490 – 271 Ash
3) http://www.ecn.nl/phyllis/ http://www.vt.tuwien.ac.at/biobib/

1) Dulong-Bertholot equation (kJ/kg – all contents are by mass).
2) Considering biomass as $C_6H(H_2O)_3$ with different ash contents, the HHV can be calculated according to Ebeling and Jenkins from the dry ash free heating value: HHV (kJ/kg) = K – 271 A where K is the HHV of lignocelluose daf (20490 kJ/kg) and A is the percent ash by mass on a dry basis.

Contributions to Heating Value



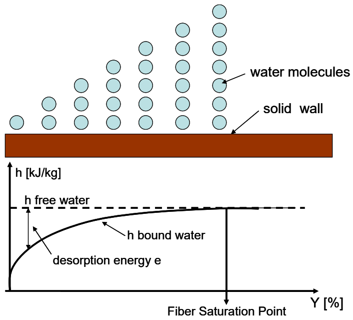
Typically three contributions are considered for most fuels:

- The contribution of Volatile Matter (VM), which is typically positive and depends on the nature of the fuel.
- The contribution of Ash, which is zero, as a result of the conventional behavior of ash as an inert material.
- The contribution of Moisture, considered as liquid water, thus:

$$LHV_{Moisture} = -\Delta H_{eva,H2O} = -2.442 \, MJ/kg \qquad HHV_{Moisture} = 0$$

$$LHV_{biomass} = LHV_{VM} \cdot y_{VM} + LHV_{ASH} \cdot y_{ASH} + LHV_{Moisture} \cdot y_{Moisture}$$
$$HHV_{biomass} = HHV_{VM} \cdot y_{VM} + HHV_{ASH} \cdot y_{ASH} + HHV_{Moisture} \cdot y_{Moisture}$$

Bond energy of moisture – actual behavior



$$Q = \int_{drying-process} \delta Q = \int_{drying-process} dm_{eva}(\Delta h_{eva} + e_b)$$

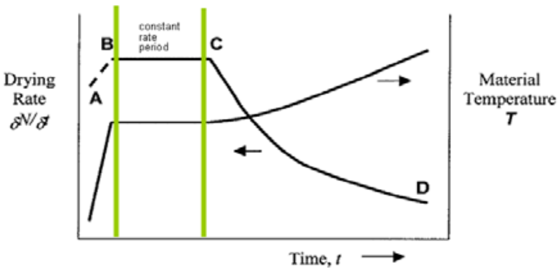
$$E = Q - \Delta h_{eva} m_{eva};$$

$$\Lambda = \frac{E}{m_{eva}} = \frac{\Delta h_{eva}(T)}{\psi_i - \psi_f} \int_{\psi f}^{\psi i} \frac{e_b(\psi, T)}{\Delta h_{eva}} d\psi$$

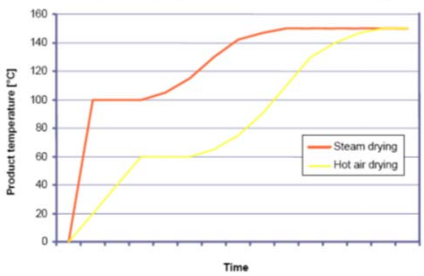
$\Lambda/\Delta h_{eva}$ [%] for wood @ 25°C

Yout \ Yin	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%
0%	35.53	26.05	20.02	15.50	11.88	9.24	7.35	5.94	4.84	3.96
5%	22.66	17.51	13.43	10.15	7.45	5.56	4.30	3.40	2.73	2.21
10%	---	12.36	9.78	7.06	4.80	3.36	2.49	1.92	1.51	1.20
15%	---	---	7.21	4.63	2.72	1.69	1.18	0.87	0.66	0.52
20%	---	---	---	2.06	1.03	0.48	0.30	0.21	0.15	0.11
25%	---	---	---	---	0.00	0.00	0.00	0.00	0.00	0.00
30%	---	---	---	---	---	0.00	0.00	0.00	0.00	0.00
35%	---	---	---	---	---	---	0.00	0.00	0.00	0.00
40%	---	---	---	---	---	---	---	0.00	0.00	0.00

Drying rate



Temperature progress during air and steam drying



Notes:

- Point C corresponds to the Fiber Saturation Point
- Wood does not feature segment BC
- This graphs refer to artificial drying (with hot air or steam), but the behavior is similar for ambient conditions

LHV – HHV connection

The difference between the two heating values on dry basis is determined by heat of evaporation of the water produced during combustion.

$$LHV_{DRY} = HHV_{DRY} - \Delta H_{EV,H_2O} \cdot P_{H_2O} = HHV_{DRY} - 2.442\frac{MJ}{kg} \cdot P_{H_2O}$$

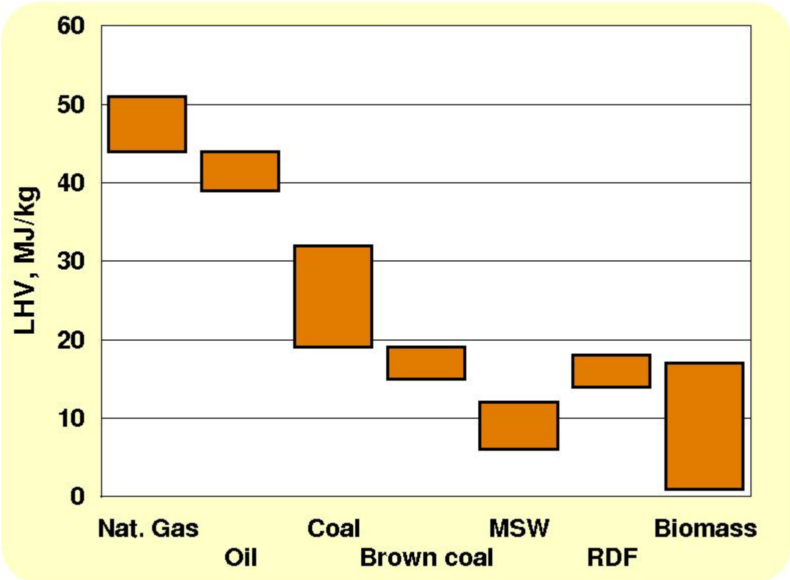
Water production during combustion depends on the hydrogen content. In the presence of halogens (Cl, F, etc), they reduce the amount of hydrogen that produces water (some hydrogen is used in the production of acids).

$$P_{H_2O} = MM_{H_2O} \cdot \frac{1}{2}\left(\frac{y_H}{MM_H} - \frac{y_{Cl}}{MM_{Cl}}\right) = 8.94 \cdot y_H - 0.254 \cdot y_{Cl}$$

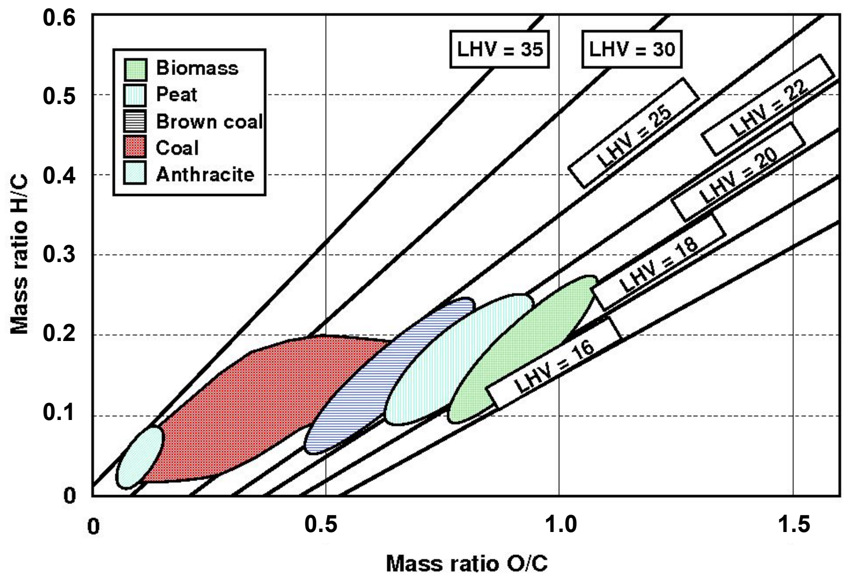
Moisture behaves as liquid water. Thus, it contributes to the difference between LHV and HHV:

$$LHV = HHV - 2.442\frac{MJ}{kg} \cdot \left(P_{H_2O} + y_{Moisture}\right)$$

LHVs of different fuels



LHVs as function of chemical composition



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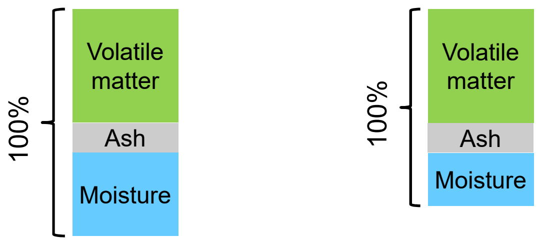
Several bases …

- Composition and properties of biomass feedstock when it is harvested or received to a plant / facility are usually referred as “**As Received basis**” (AR). This basis is typically characterized by a very high moisture content.
- After a certain storage time, moisture content decreases down to a quite stable value, which is the equilibrium value with the environment. Composition and properties of biomass in this condition are referred as “**Air Dried basis**” (AD).
- Mainly for calculation or analytic purposes, it is very useful to refer to dry biomass, i.e. biomass that has been artificially dried as described before. In this case, it is usual to talk about “**dry basis**” (DRY).
- These three bases differ only by the moisture content.
- In many cases it can be interesting to consider only the part of the dry biomass that during oxidation volatilizes, i.e. the volatile matter (which is different from the volatiles of the proximate analysis). In this case the reference is called “**Dry-Ash-Free basis**” (DAF).

What happens when moisture changes?

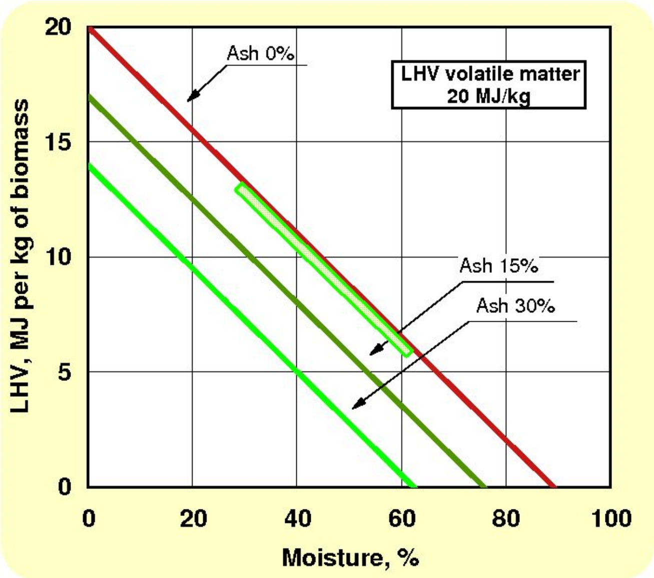
Basis 1: Basis 2:



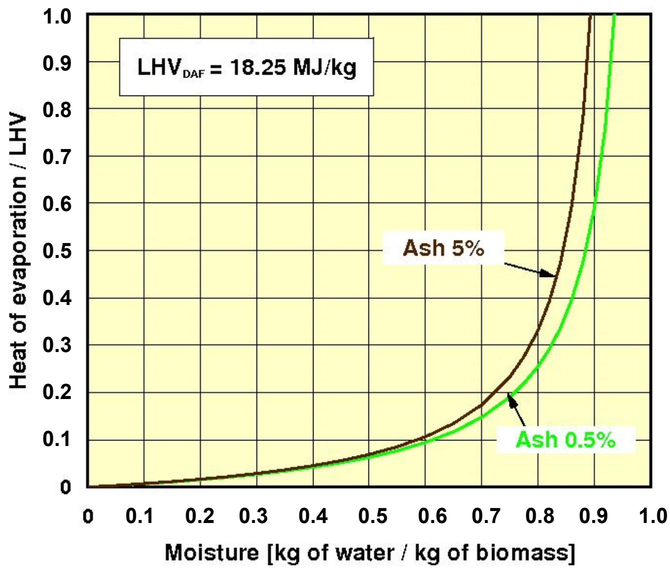
$$y_{Ash}^{(2)} = y_{Ash}^{(1)} \cdot \frac{1 - y_{Moisture}^{(2)}}{1 - y_{Moisture}^{(1)}} \qquad y_{C}^{(2)} = y_{C}^{(1)} \cdot \frac{1 - y_{Moisture}^{(2)}}{1 - y_{Moisture}^{(1)}} \quad \ldots$$

For LHVs and HHVs is better to refer to the most general case …

Connection among LHV, moisture and ash



Weight of the latent heat of evaporation of moisture on the LHV



General case

Conventionally, to ash is assigned a zero energy content (both in LHV and HHV bases). To moisture the energy content of liquid water, thus:

$LHV_{Moisture}$ = -2.442 *MJ/kg*

$HHV_{Moisture}$ = 0

LHV and HHV in the general case are expressed as weighted averages of the corresponding values for the three constituents of the feedstock:

$$LHV_{(X)} = LHV_{VM} \cdot y_{VM,(X)} + LHV_{ASH} \cdot y_{ASH,(X)} + LHV_{Moisture} \cdot y_{Moisture,(X)} =$$
$$= LHV_{VM} \cdot y_{VM,(X)} - 2.442 \frac{MJ}{kg} \cdot y_{Moisture,(X)}$$

$$HHV_{(X)} = HHV_{VM} \cdot y_{VM,(X)} + HHV_{ASH} \cdot y_{ASH,(X)} + HHV_{Moisture} \cdot y_{Moisture,(X)} =$$
$$= HHV_{VM} \cdot y_{VM,(X)}$$

The reference to the common basis (X) is crucial!

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The case of waste

- The waste is a mixture of diverse materials.
- Waste can include some biomass (e.g. wood) or biomass derived material (e.g. paper and cardboard).
- It can include also materials of fossil nature, typically many types of plastics.
- Some materials can be in part derived from biomass (the biogenic share) and in part derived from fossil resources (the fossil share).
- From the point of view of the ultimate composition, the characteristics of waste can be expressed as weighted averages of those of the constituents

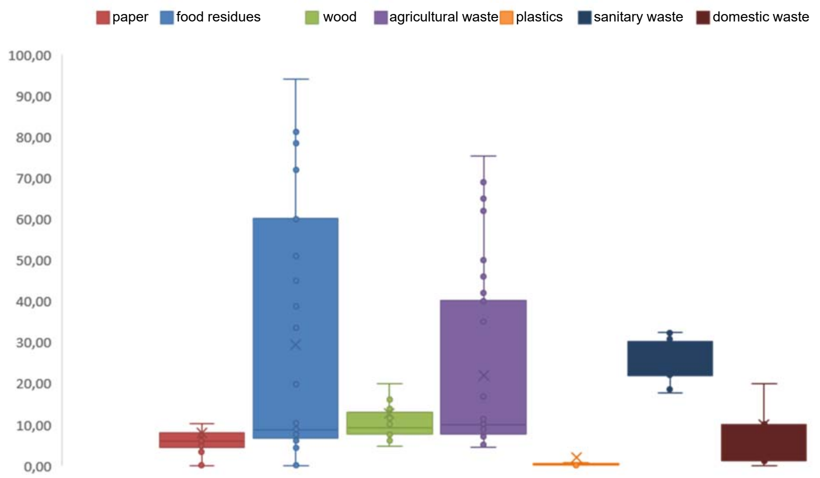
Literature survey of the combustive properties of various materials

10 sources of data:

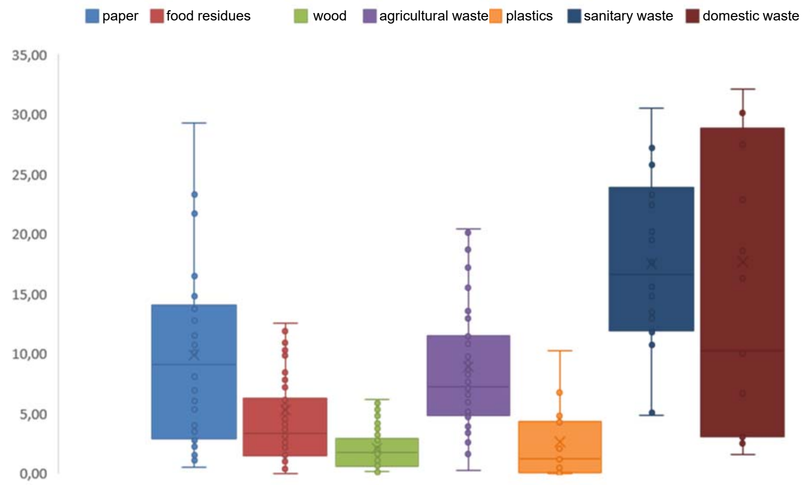
- 1 paper from the scientific journal "Waste Management" → Primary data.
- 6 paper from the scientific journal "Fuel" → 1 source with primary data.
- 1 book "Combustion and incineration processes" by Niessen
  → All secondary data.
- 1 data collection from the "Solar Energy Research Institute"
  → All secondary data.
- 1 data collection from RSE "Ricerca Sistema Energetico"
  → All secondary data.

- Total: 350 data collected

Moisture content, % by mass

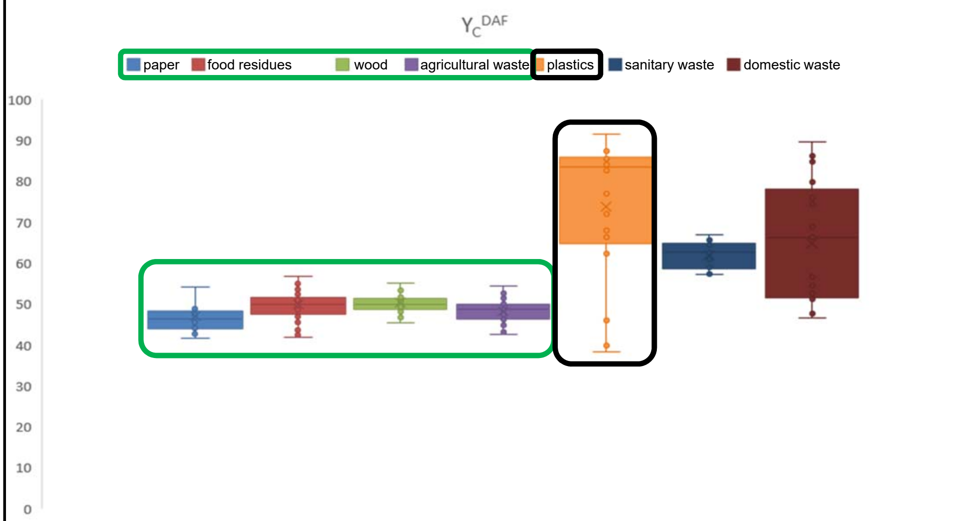


Ash content, % by mass



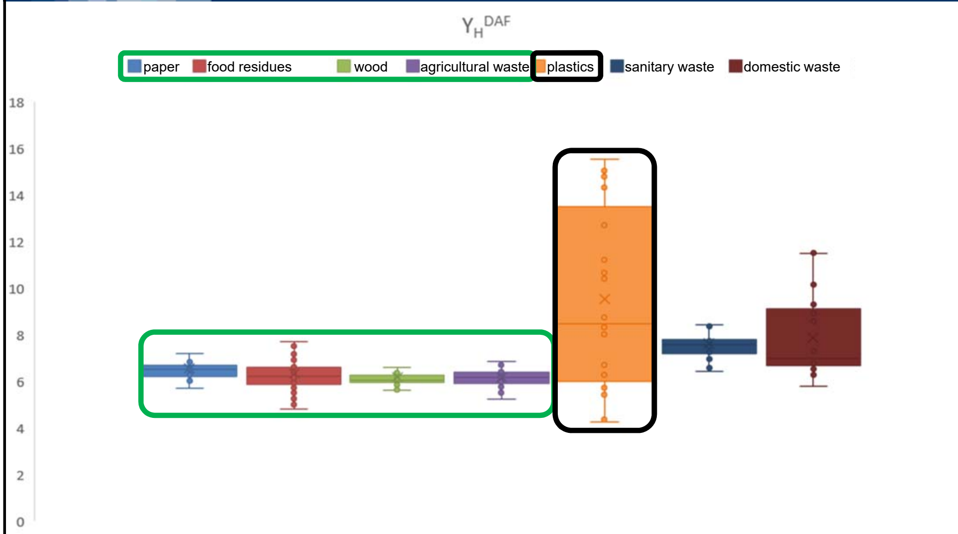
Content of carbon (C), % by mass on DAF basis

47

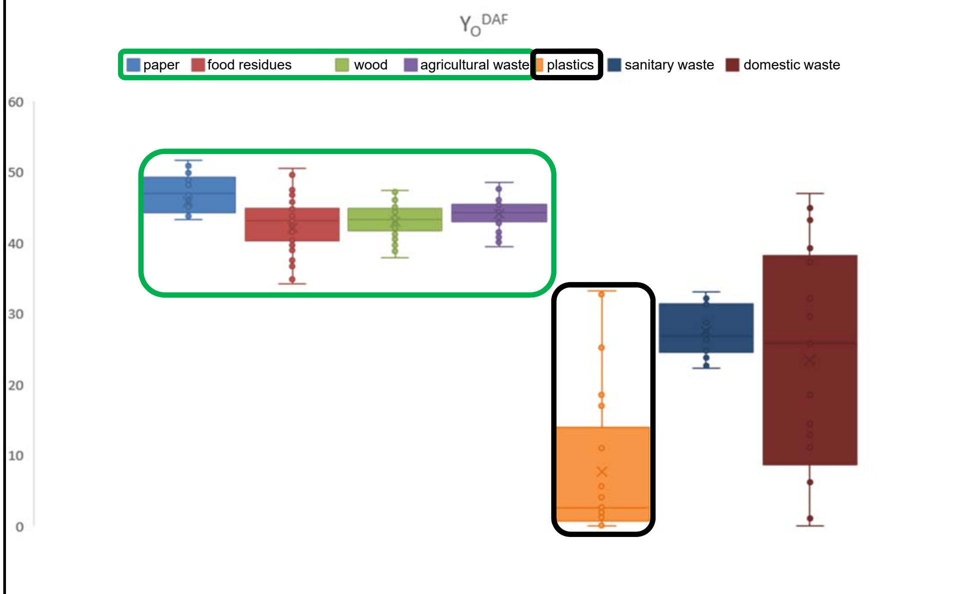


Content of hydrogen (H), % by mass on DAF basis

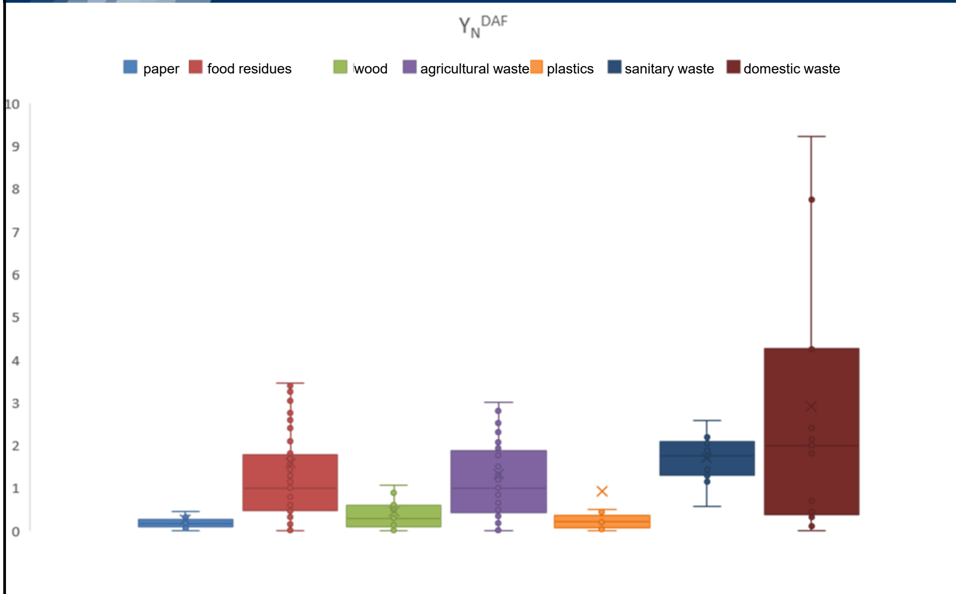
48



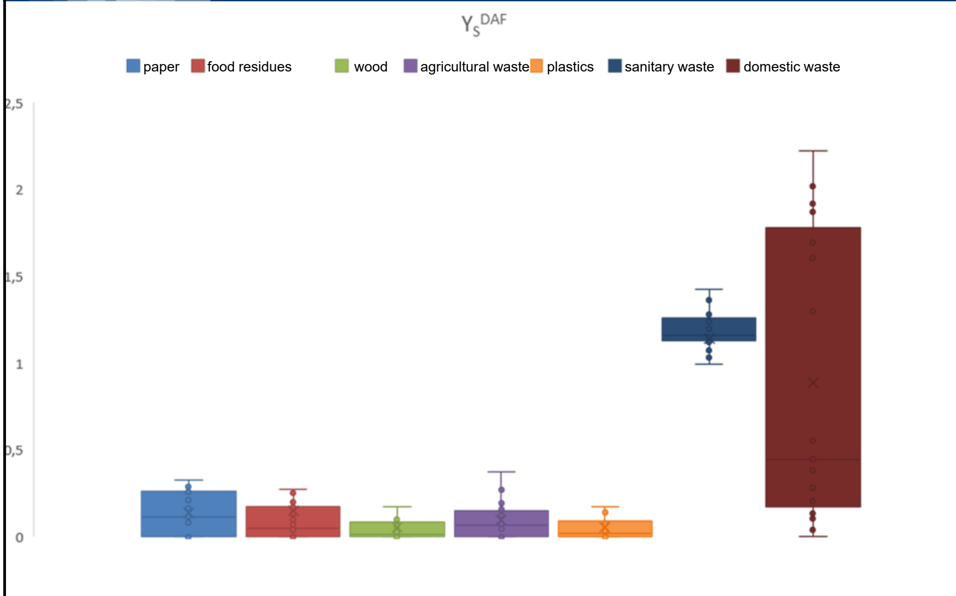
Content of oxygen (O), % by mass on DAF basis



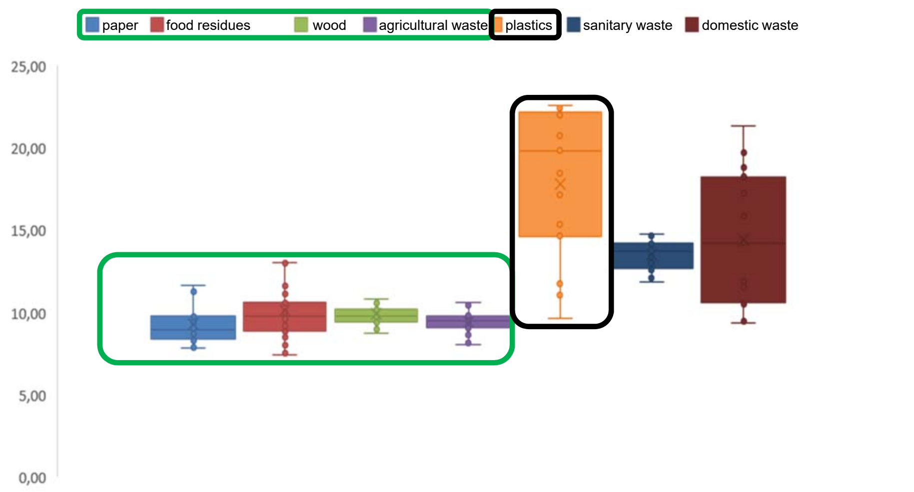
Content of nitrogen (N), % by mass on DAF basis



Content of sulphur (S), % by mass on DAF basis

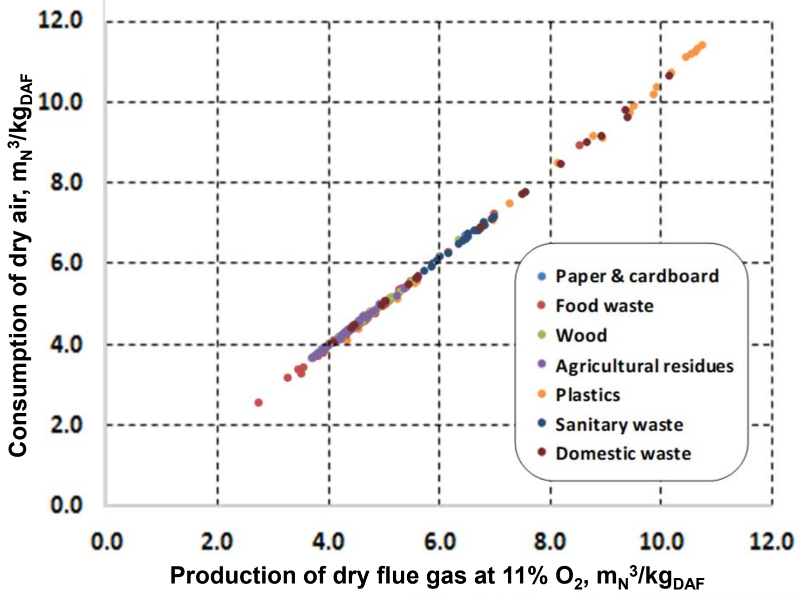


Production of dry flue gas at 11% O_2, m_N^3/kg_{DAF}



“Dry flue gas production” vs. “Dry air consumption”

53



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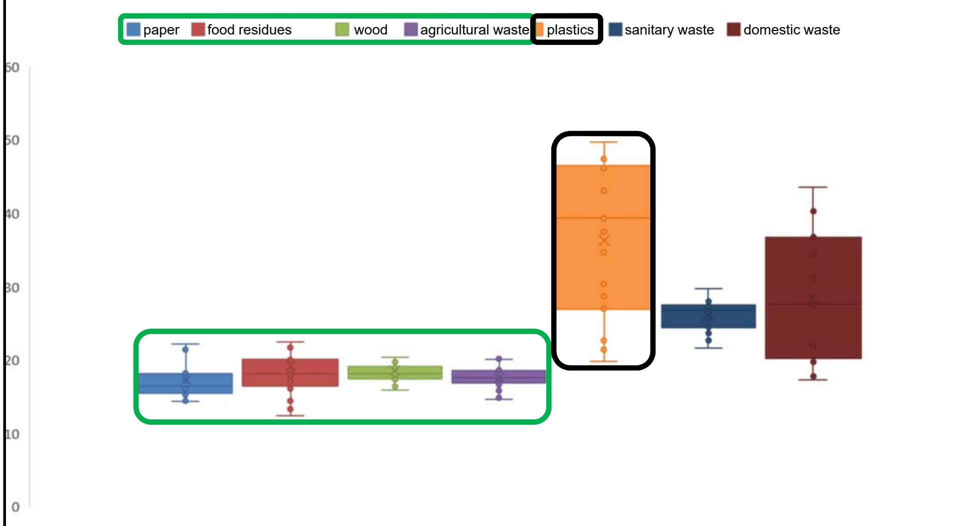
Lower Heating Value (LHV) on DAF basis, MJ/kg_{DAF}

54



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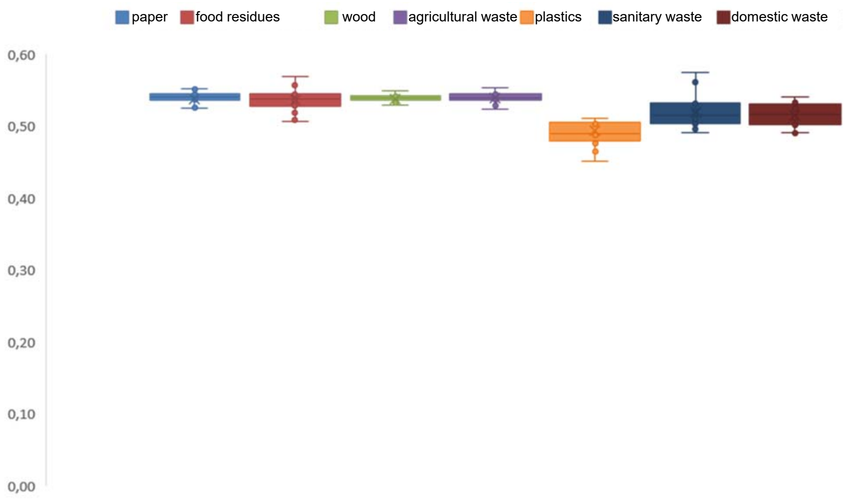
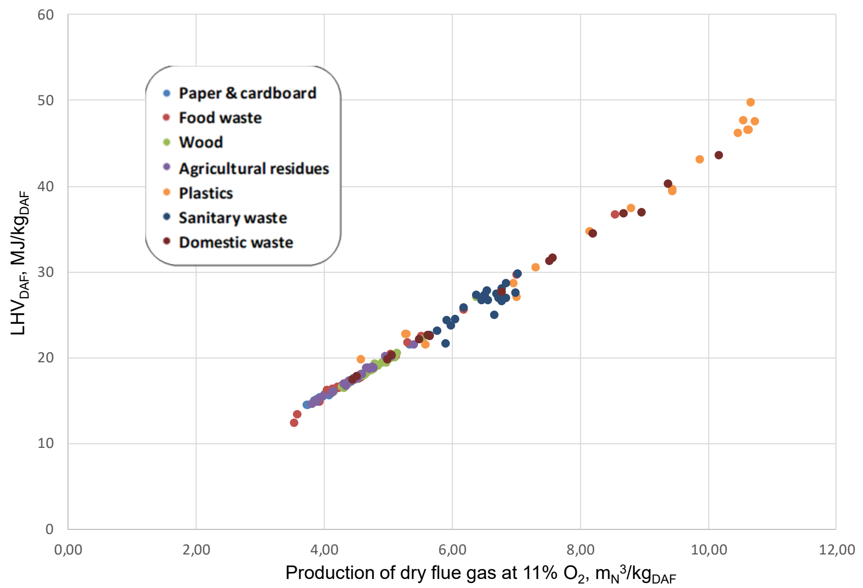
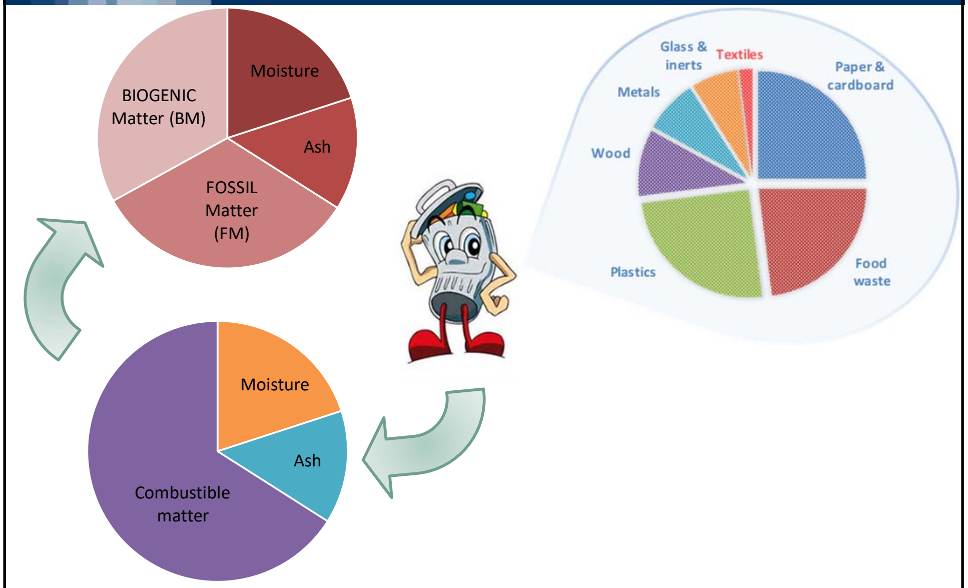
“Dry flue gas production / LHV” on DAF basis



“Dry flue gas production” vs. “LHV” on DAF basis



Waste model: from many to 3 and to 4 components



Some remarks on the case of waste

- The waste is a mixture of diverse materials.
- Its moisture and ash contents can vary greatly and almost independently from its constituents.
- From the point of view of its combustive properties:
  - DAF matter can easily be clustered into “Biogenic Matter (BM)” and “Fossil Matter (FM)”, at least regarding C, H and O contents (→ hence dry flue gas production and the corresponding air consumption), as well as LHV_{DAF}.
  - From the complex model encompassing several constituents, it is possible to derive a simplified model based on four components.
  - Anyway, the dry flue gas production and the air consumption are always roughly proportional to the LHV_{DAF}.