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Wallonie

UCL
Université catholique de Louvain

PhD presentation

Chemical composition and biofuel potential of plant biomasses

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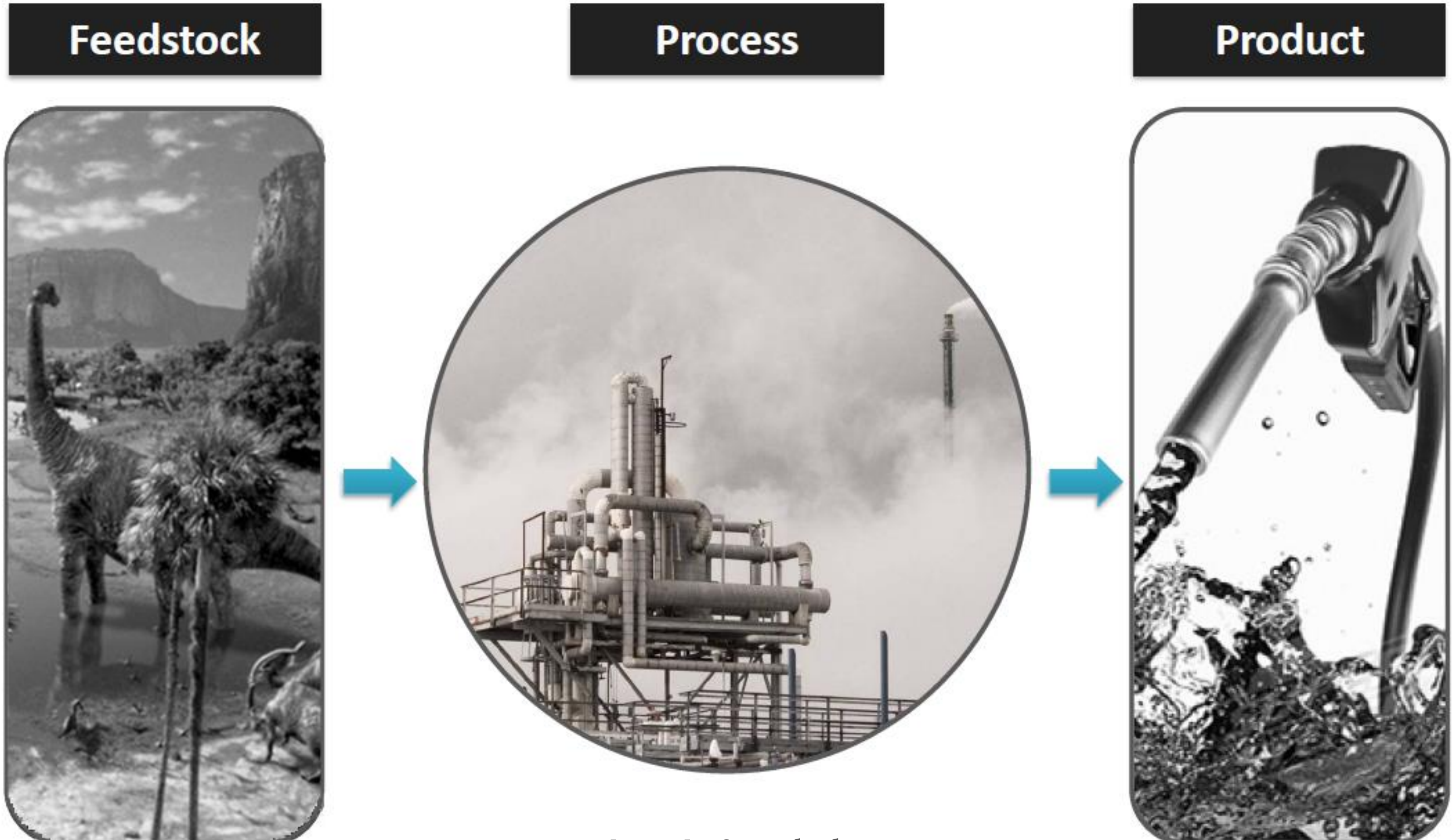
13/02/2013

1. Context

- Production of plant biomasses
  - Conversion into biofuels
  - Chemical composition and suitabilities to be converted into biofuel
  - Fibrous plant biomasses



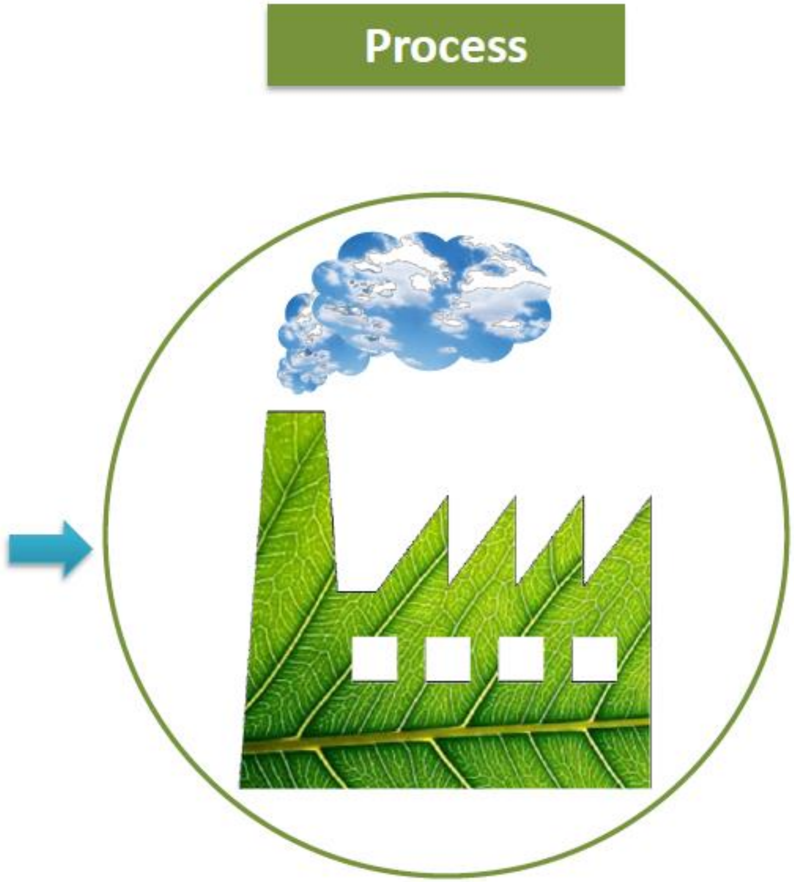
Fossil energy

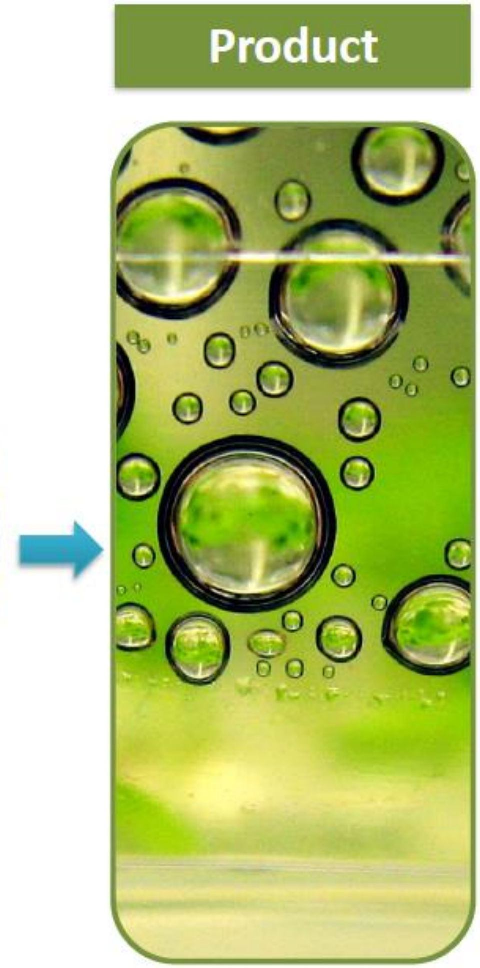


Adapted of Vanholme, 2012

- High production of greenhouse gas → Climate change
- High dependence on fossil fuels → Volatile prices and uncertain availability

Renewable energy from biomasses





Adapted of Vanholme, 2012

Biofuel production from biomasses requires an accurate knowledge of the characteristics of the used resource

Biomass conversion to bioenergy

- Biomass
  - Annual crop / Perennial crop / Algae / Wood/ Residues / Waste
- Bioenergy
  - Thermal / Electric / Mechanical
- Conversion pathways
  - Thermochemical → Combustion
  - Biological → Anaerobic digestion / Ethanolic fermentation

Fibrous plant biomasses

- Non-food
- Acceptable biomass yield par hectare
  - In less favorable soil and climatic conditions
  - Need less input

Perennial

Miscanthus

Switchgrass

Tall fescue

Annual

Hemp

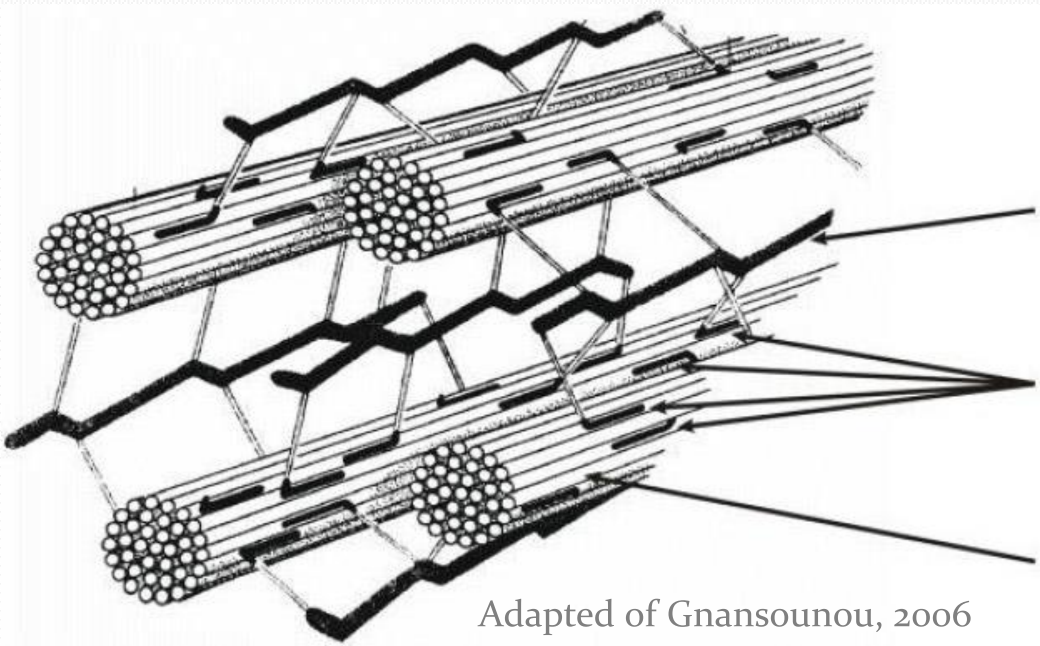
Residues

Spelt straw

Adapted of ENERBIOM, 2012

Chemical composition of plant cell walls

Plant cell wall polymers

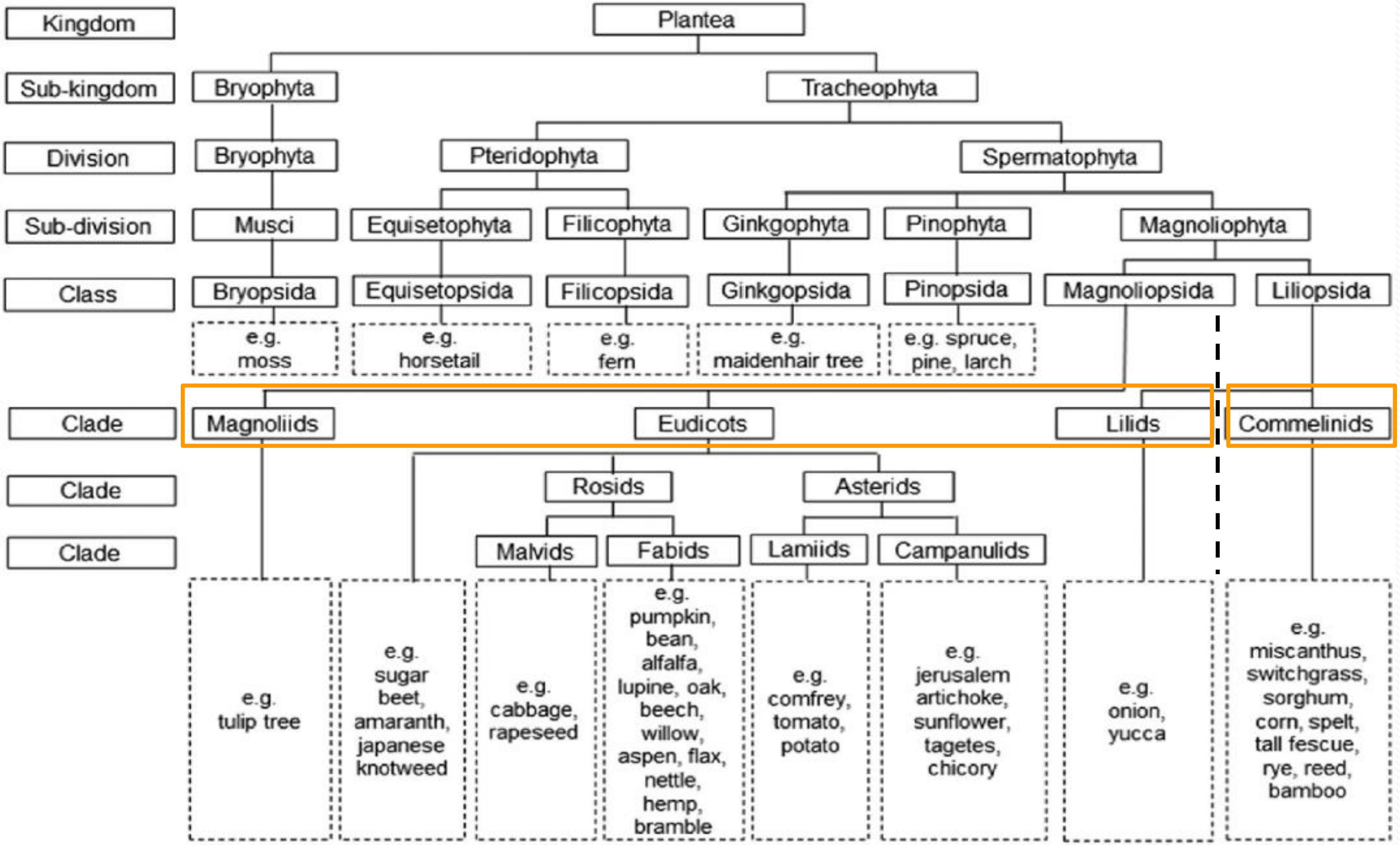


Adapted of Gnansounou, 2006

- Cellulose → Homogeneous and linear polysaccharide made of glucose units
- Hemicelluloses → Heterogeneous and ramified polysaccharides mainly made of xylose units
- Lignin → Phenylpropan polymer
- Other compounds → Pectins, proteins

Chemical composition of plant cell walls

Commelinids species differ in the composition of their wall



Outline

1. Context

2. **Objectives**

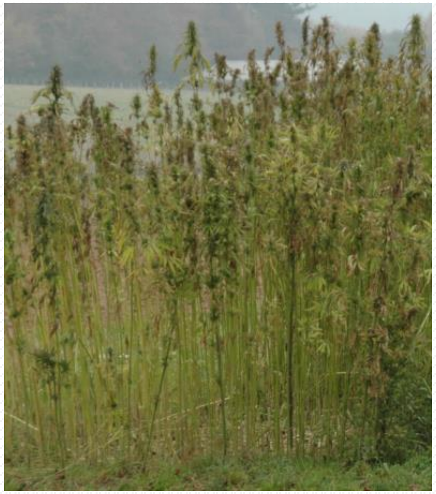
3. Results and discussion

4. Conclusions and prospects

1. What are the key parameters to be used to assess the gross energy productivity?

- Gross energy productivity per hectare
  - Relative chemical characteristics of the biomass → Unknown impact
  - Dry matter yield per hectare
  - Dry matter content

What are the key parameters to classify fibrous plant species in order to maximize the gross energy productivity?



2. What are the relevant parameters to be used to assess the suitabilities to be converted into biofuel?

- Suitabilities to be converted into biofuel
  - Identification of joint relevant parameters of the chemical composition
  - Optimization of the analytical investment

What are the relevant parameters of the chemical composition of plant biomasses to be used to assess their suitabilities to be converted into biofuel?

3. What are the chemical characteristics of plant biomasses?

- Optimizing biomass conversion requires a good knowledge of the chemical characteristics
  - Chemical composition
  - Hemicelluloses composition
  - Suitabilities to be converted into biofuel

What is the chemical composition of the considered biomasses?

- **Sort these biomasses into groups with similar characteristics?**

4. How to quantify correctly cellulose and hemicelluloses?

- Abundance of the cellulose and hemicelluloses
  - Assess available resources for biofuel production
- Van Soest method
  - Reference
  - Bias ?

What is the appropriate method for the quantification of cellulose and hemicelluloses in the context of biofuel production?

Outline

1. Context

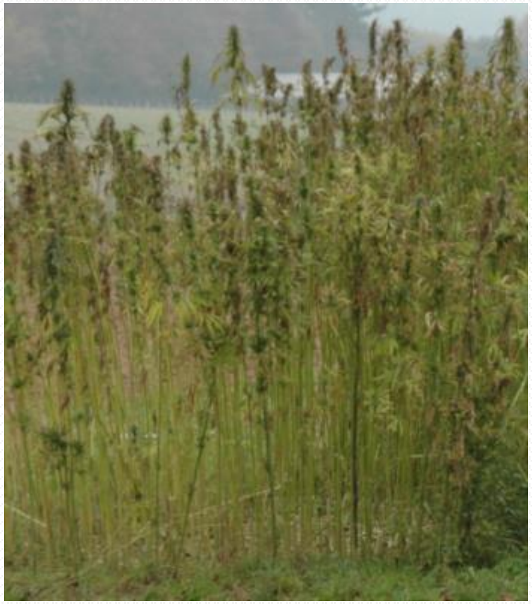
2. Objectives

3. Results and discussion

4. Conclusions and prospects

3.1. Key parameters to assess the gross energy productivity

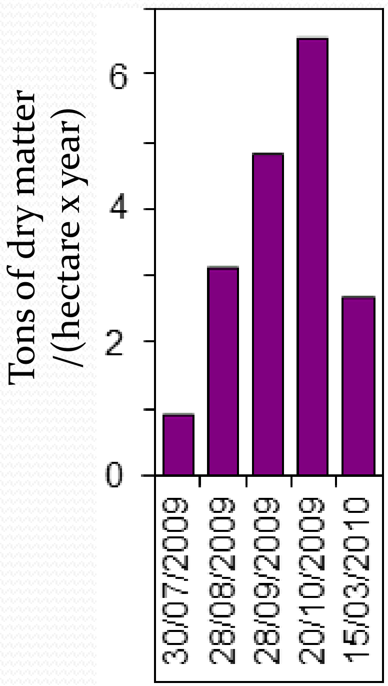
- Relative chemical characteristics of the biomass
- Dry matter yield per hectare
- Dry matter content



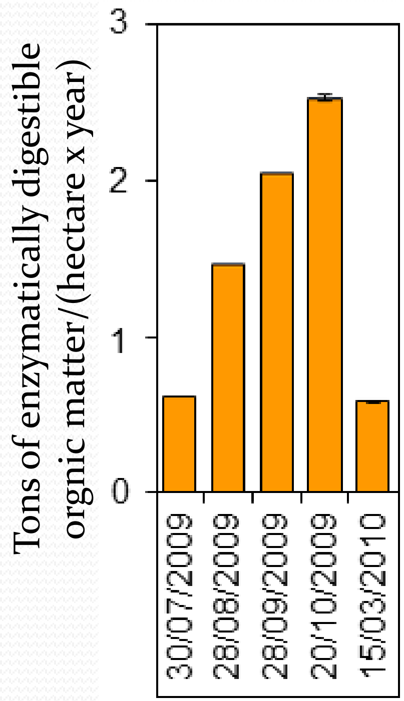
Key parameters to assess the gross energy productivity

- Dry matter yield per hectare
  - Plant maturity → Autumn / (example of fiber sorghum)

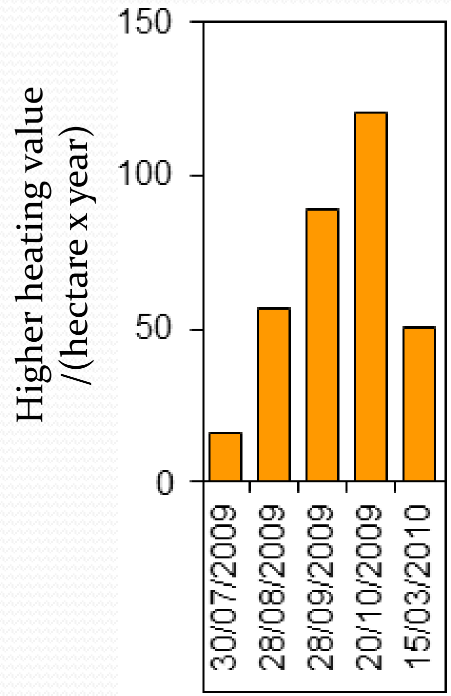
Dry matter yield per hectare



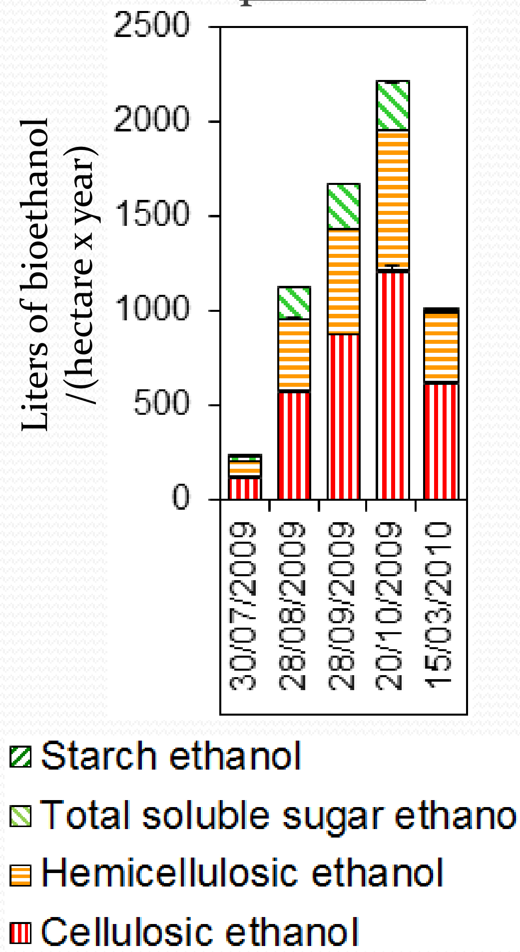
Indicator for the anaerobic digestion



Indicator for the combustion



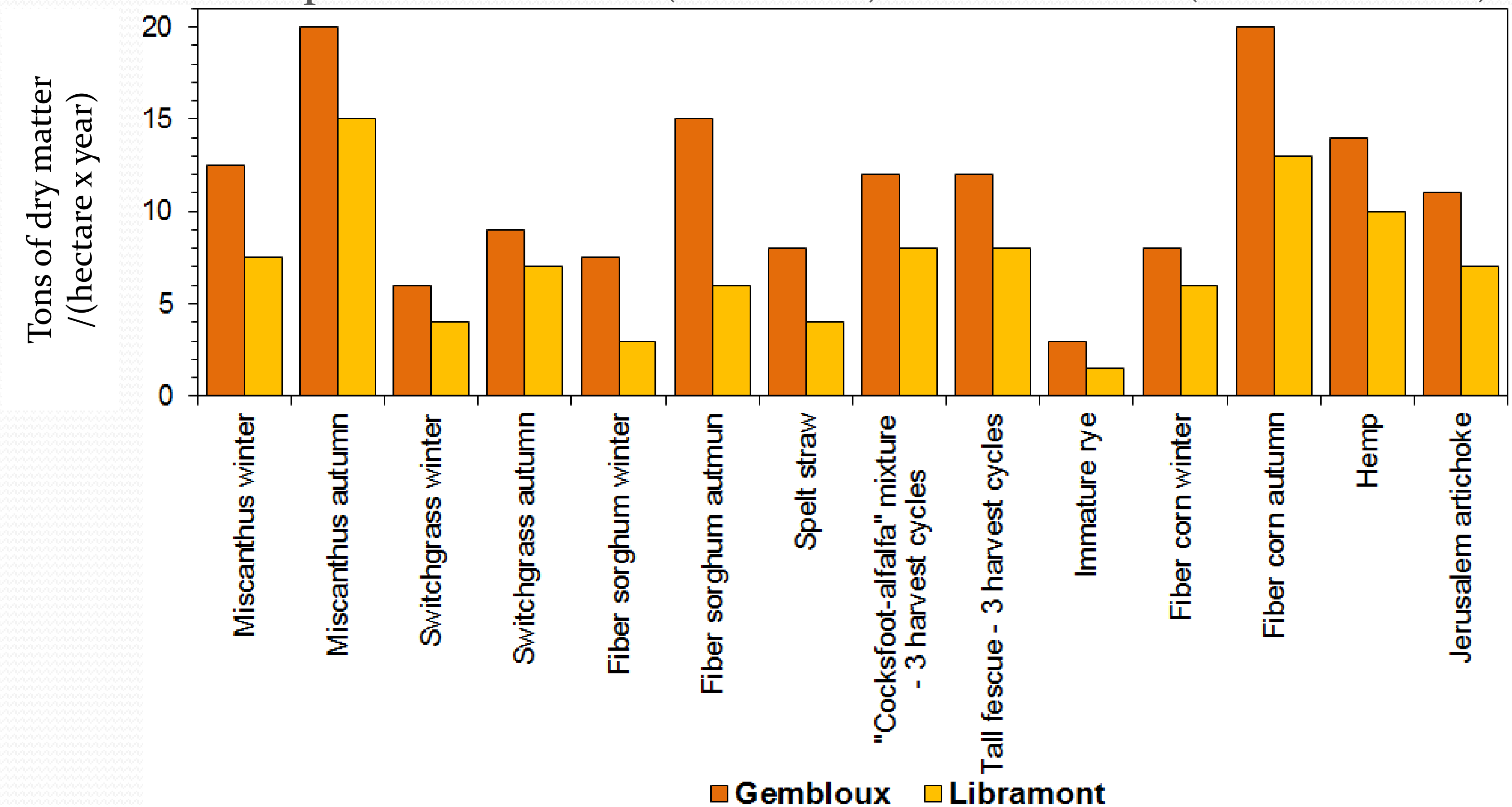
Bioethanol potential



Key parameters to assess the gross energy productivity

- Dry matter yield per hectare
  - Plant species
  - Soil and climate conditions

  → Example of Gembloux (favorable) vs Libramont (less favorable)



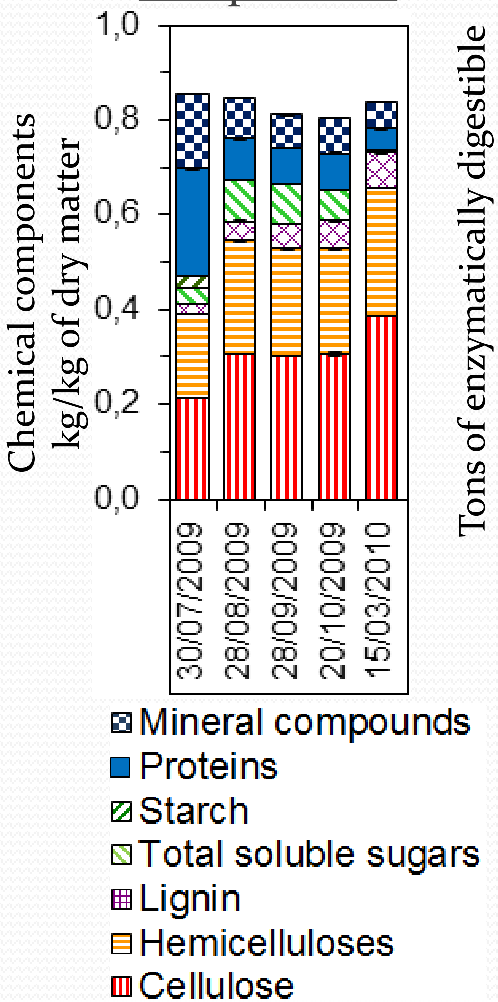
Key parameters to assess the gross energy productivity

- Dry matter content
  - Combustion
  - Bioethanol

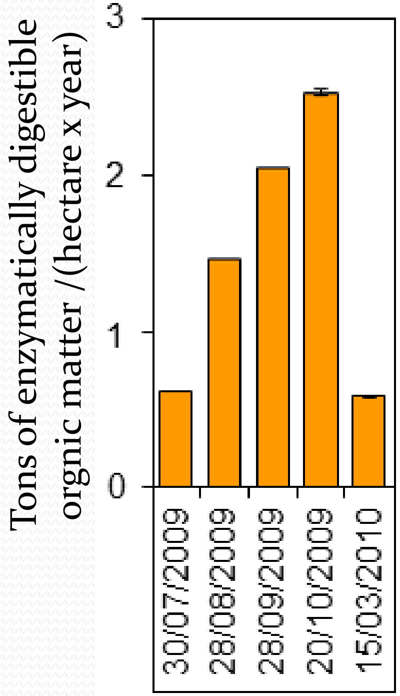
Key parameters to assess the gross energy productivity

- Chemical characteristics of the biomass → Unimportant / (example of fiber sorghum)
  - Not unimportant for the biofuel conversion process

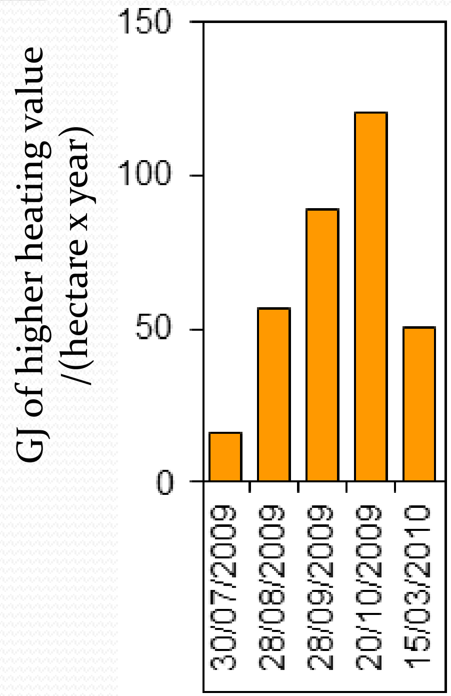
Chemical composition



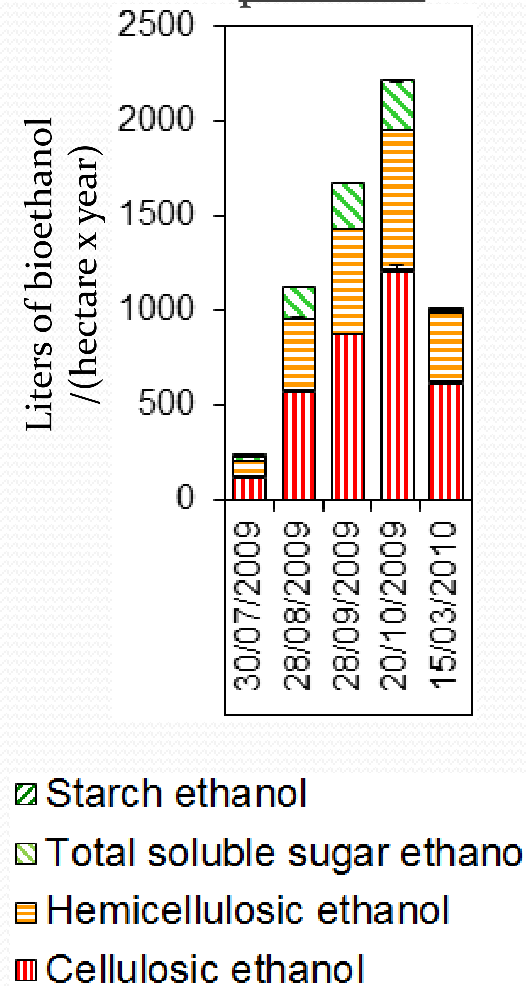
Indicator for the anaerobic digestion



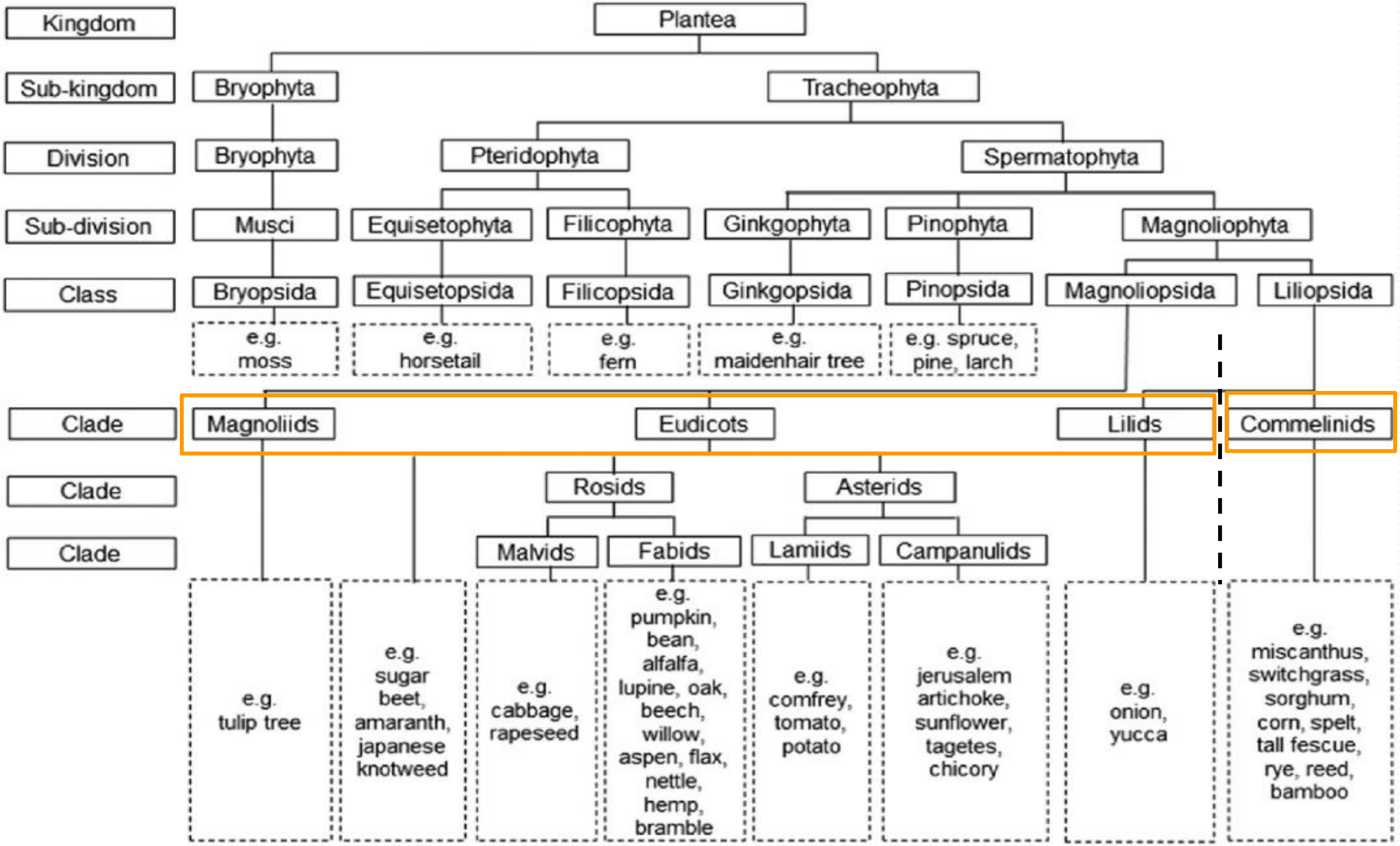
Indicator for the combustion



Bioethanol potential

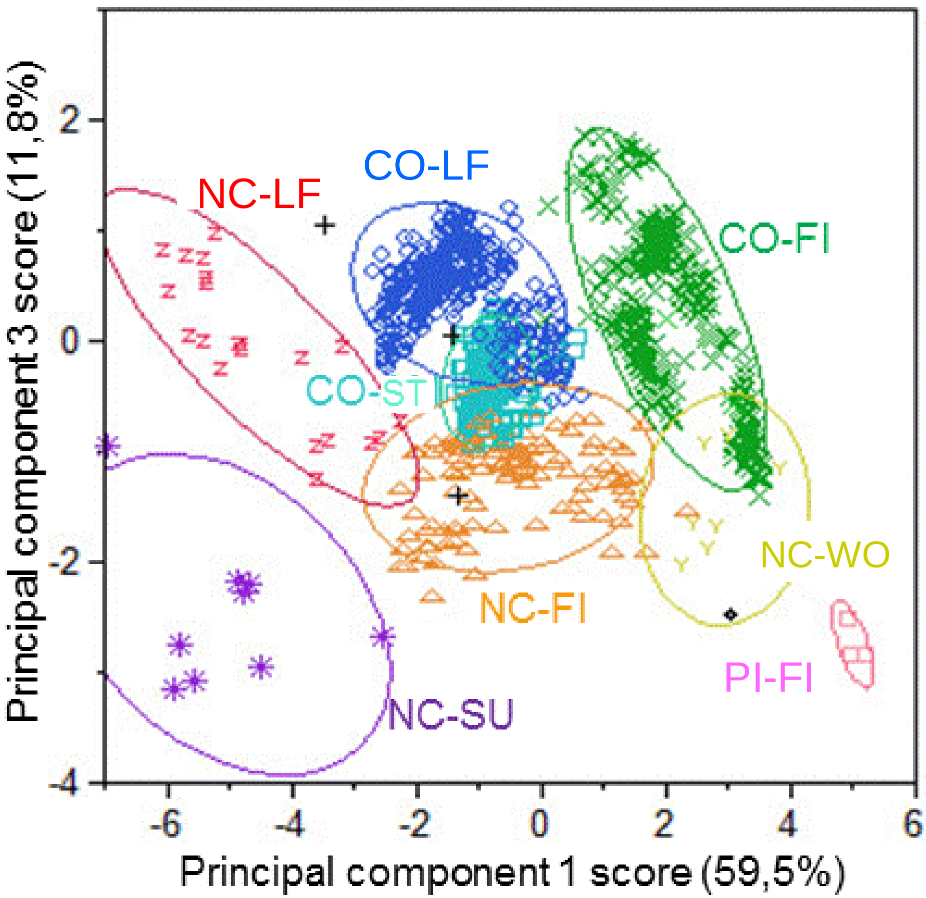


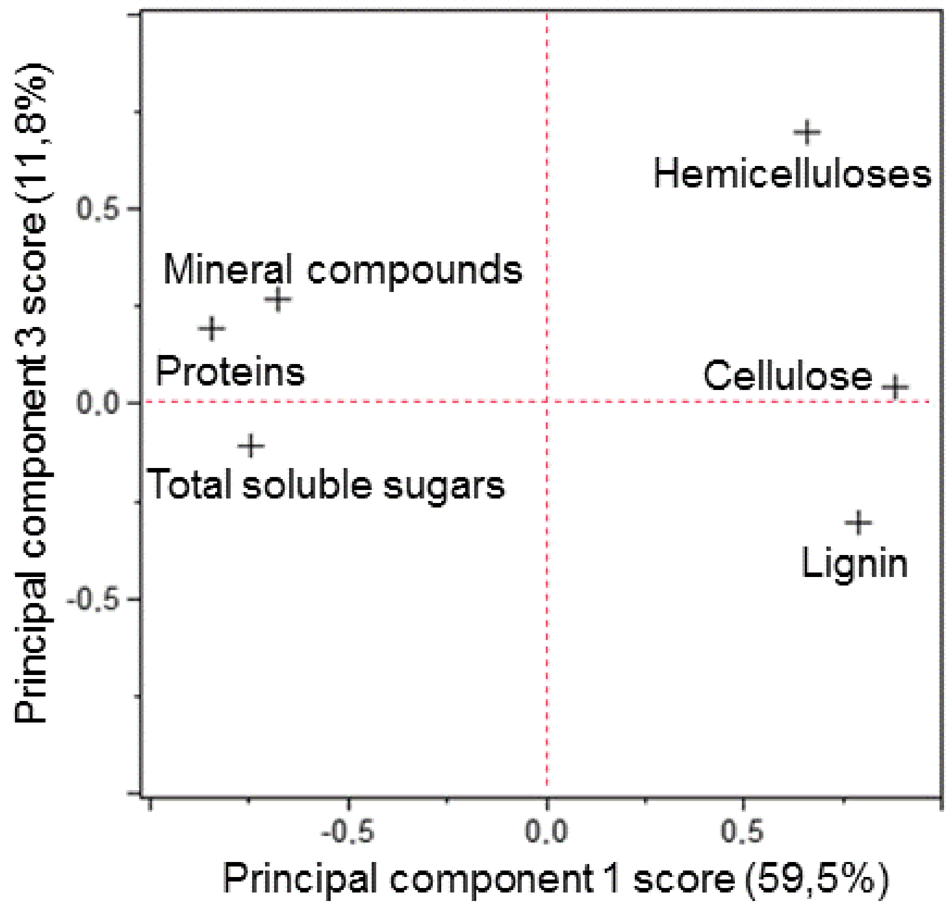
3.2. Chemical composition and suitabilities to be converted into biofuel



Chemical composition and suitabilities to be converted into biofuel

- Plant species diversity structured into groups with similar chemical characteristics



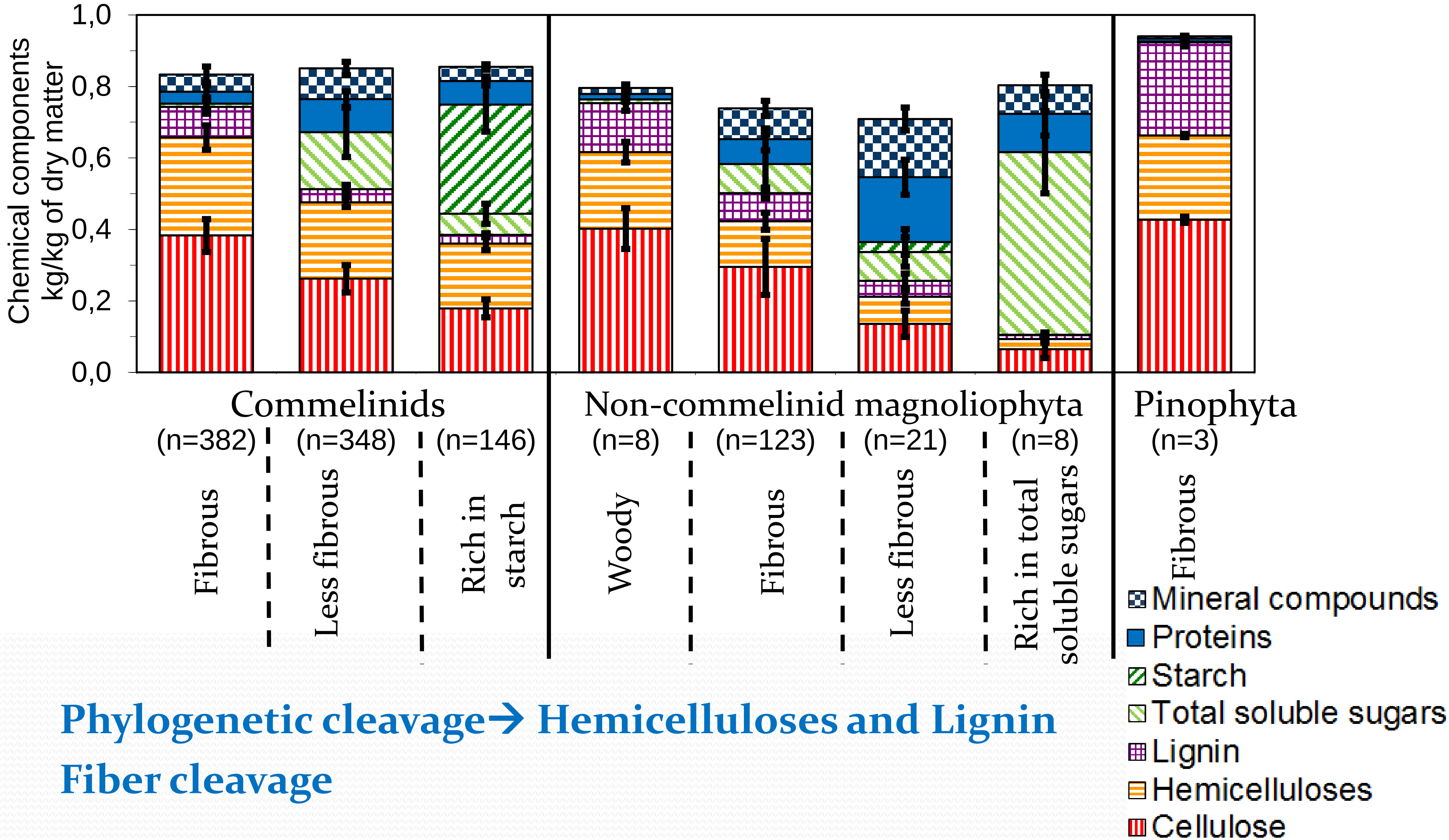


CO : Commelinids   NC : Non-commelinid magnoliophyta   PI : Pinophyta

Godin B., Lamaudière S., Agneessens R., , Schmit T., Goffart J.-P., Stilmant D., Gerin P. & Delcarte J., 2013. *Energy and Fuels*, 27, 2588-2598.

Chemical composition and suitabilities to be converted into biofuel

- Chemical composition of the groups with similar chemical characteristics

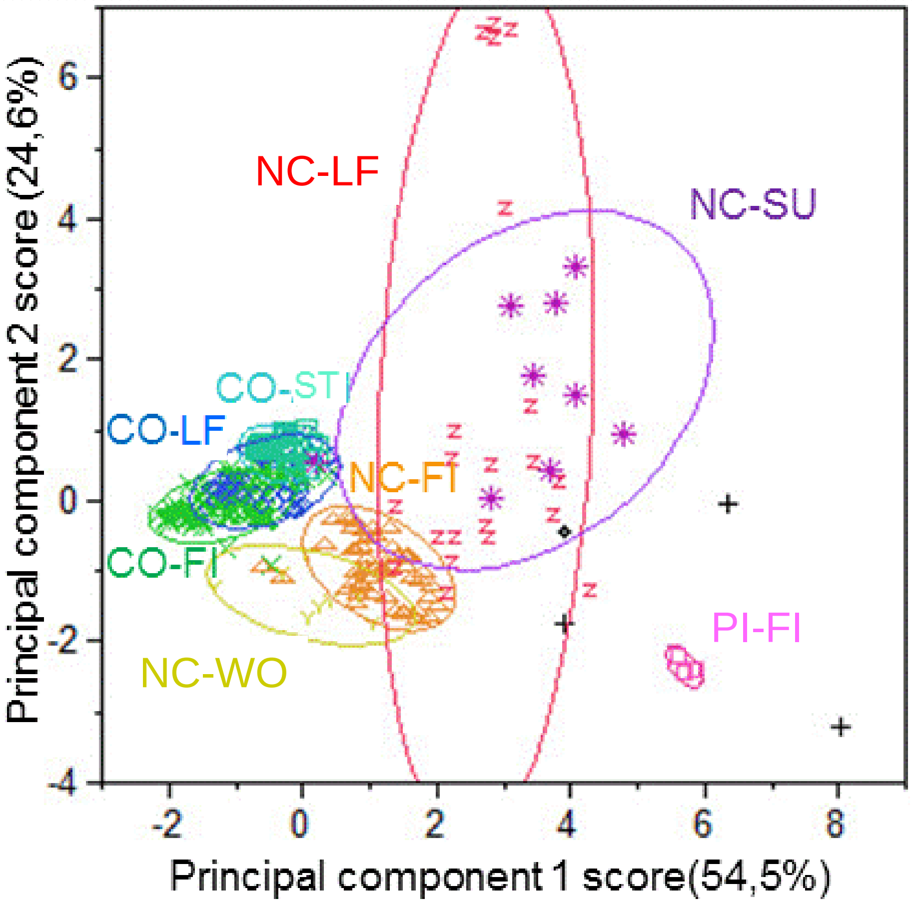


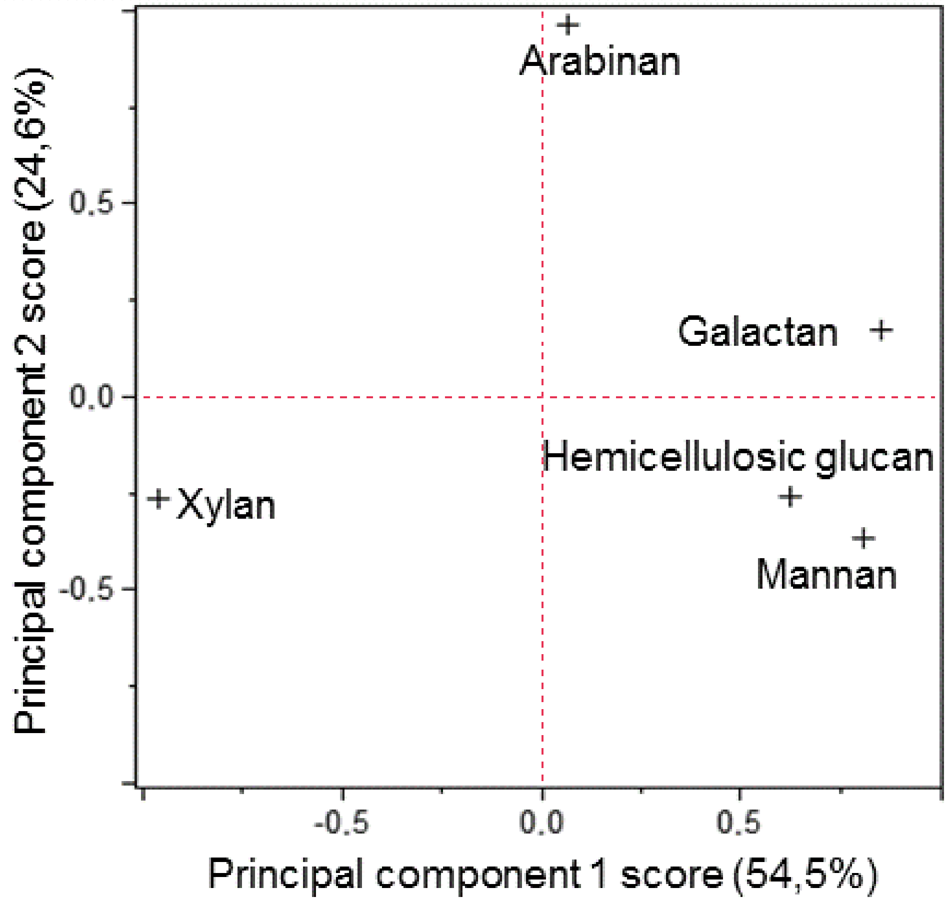
Phylogenetic cleavage→ Hemicelluloses and Lignin

Fiber cleavage

Chemical composition and suitabilities to be converted into biofuel

- Plant species diversity structured into groups with similar chemical characteristics



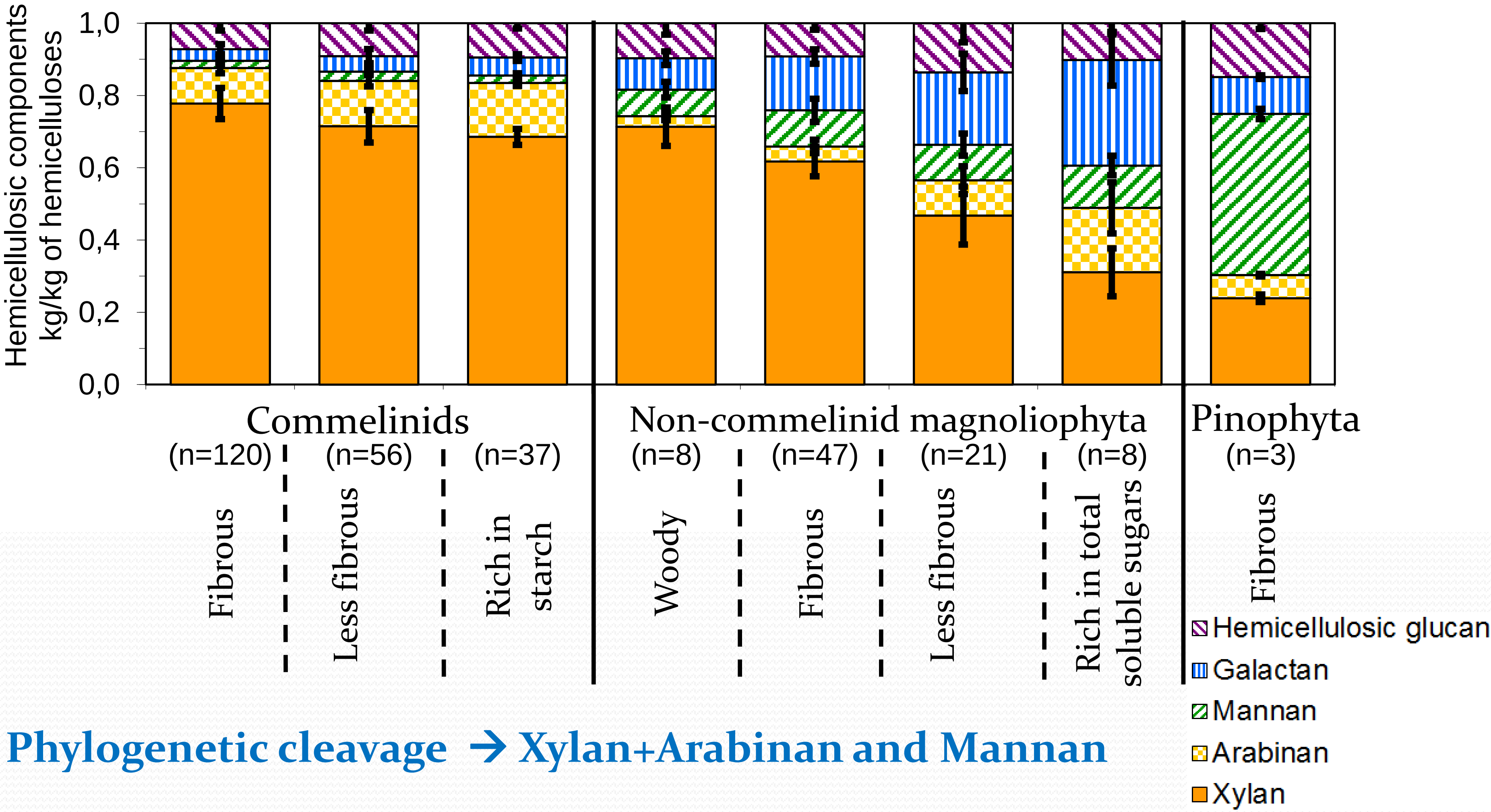


CO : Commelinids ***NC : Non-commelinid magnoliophyta*** ***PI : Pinophyta***

Godin B., Lamaudière S., Agneessens R., , Schmit T., Goffart J.-P., Stilmant D., Gerin P. & Delcarte J., 2013. *Energy and Fuels*, 27, 2588-2598.

Chemical composition and suitabilities to be converted into biofuel

- Hemicelluloses composition of the groups with similar chemical characteristics



Phylogenetic cleavage → Xylan+Arabinan and Mannan

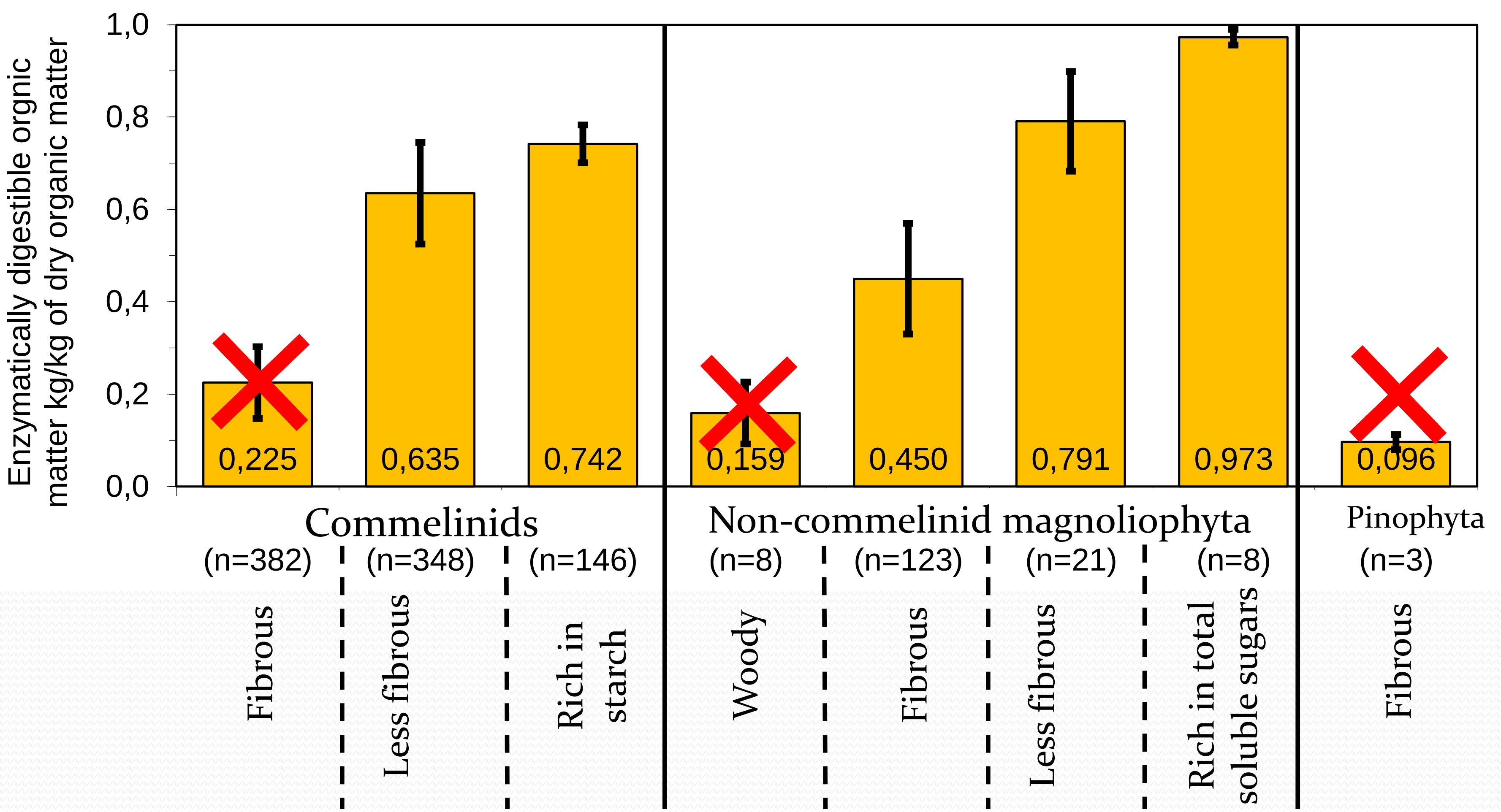
Link between chemical composition and suitabilities to be converted into biofuel

- Indicator for the anaerobic digestion potential without pretreatment of the biomass
  → Enzymatically digestible organic matter
- Indicator for the combustion potential after drying of the biomass
  → Higher heating value
- Bioethanol potential
  → Theoretical model

Godin B., Lamaudière S., Agneessens R., , Schmit T., Goffart J.-P., Stilmant D., Gerin P. & Delcarte J., 2013. *Energy and Fuels*, 27, 2588-2598.

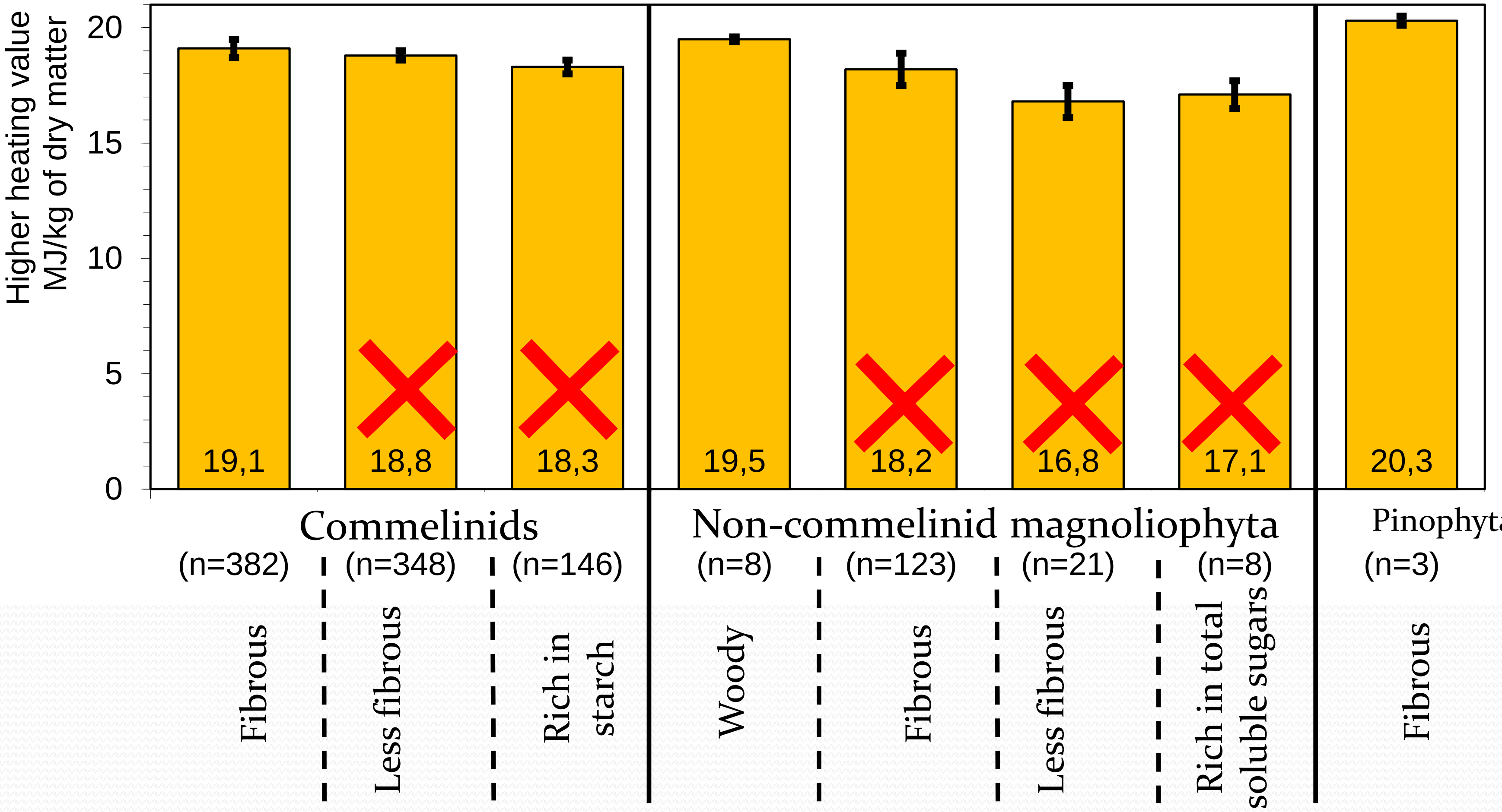
Link between chemical composition and suitabilities to be converted into biofuel

- Indicator for the anaerobic digestion potential
  - Favorable for biomasses with cytoplasm-rich metabolically active cell



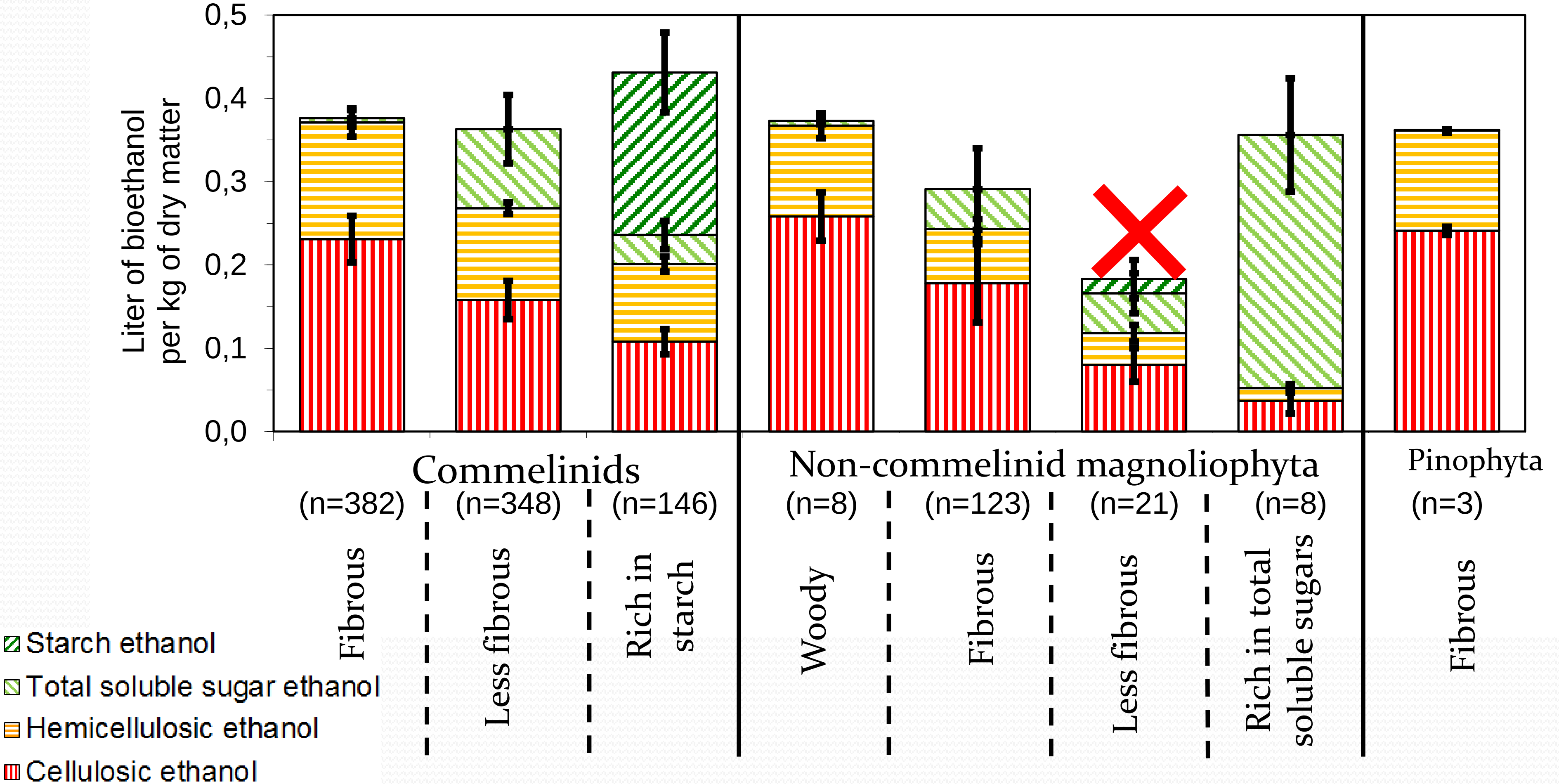
Link between chemical composition and suitabilities to be converted into biofuel

- Indicator for the combustion potential
  - Favorable for biomasses with a high organic matter content



Link between chemical composition and suitabilities to be converted into biofuel

- Bioethanol potential
  - Favorable for all the biomass groups
    → Except for non-commelinid less fibrous magnoliophyta biomasses



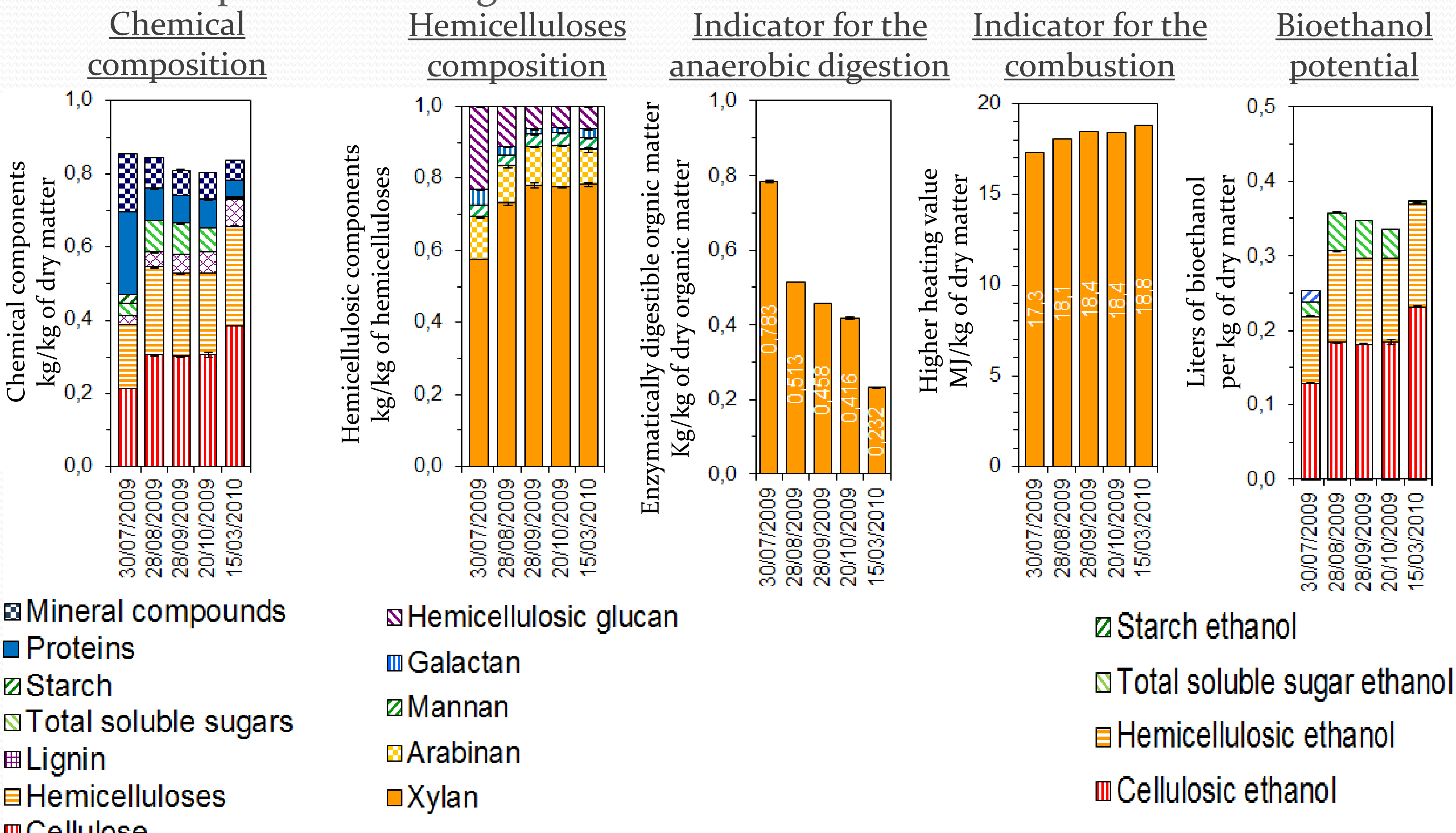
Impact of the crop husbandry on the chemical composition and the suitabilities to be converted into biofuel

- Impact of the plant maturity
- Impact of other crop husbandry factors
  - Location, Year, Cultivar and Level of nitrogen fertilization

Godin B., Lamaudière S., Agneessens R., , Schmit T., Goffart J.-P., Stilmant D., Gerin P. & Delcarte J., 2013. *J. of the Sci. of Food and Agri.*, Accepted.

Impact of the crop husbandry on the chemical composition and the suitabilities to be converted into biofuel

- Chemical characteristics → Dependent on the plant maturity
  - Example of fiber sorghum



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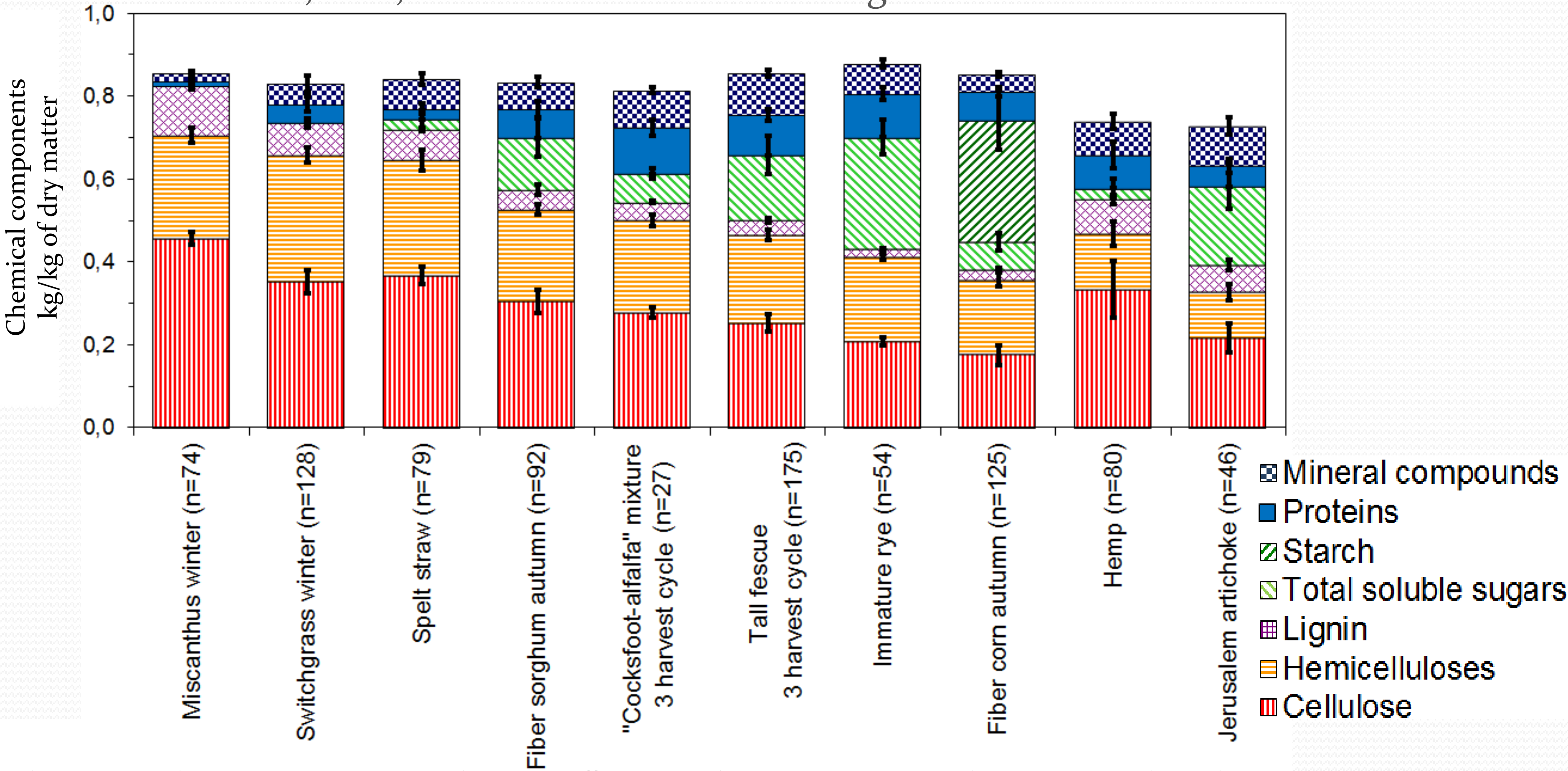
Impact of the crop husbandry on the chemical composition and the suitabilities to be converted into biofuel

- Chemical characteristics → Do not dependent on the other crop husbandry factors
  - Location, Year, Cultivar and Level of nitrogen fertilization



Godin B., Lamaudière S., Agneessens R., , Schmit T., Goffart J.-P., Stilmant D., Gerin P. & Delcarte J., 2013. *Industrial Crops and Products*, 48, 1-12.

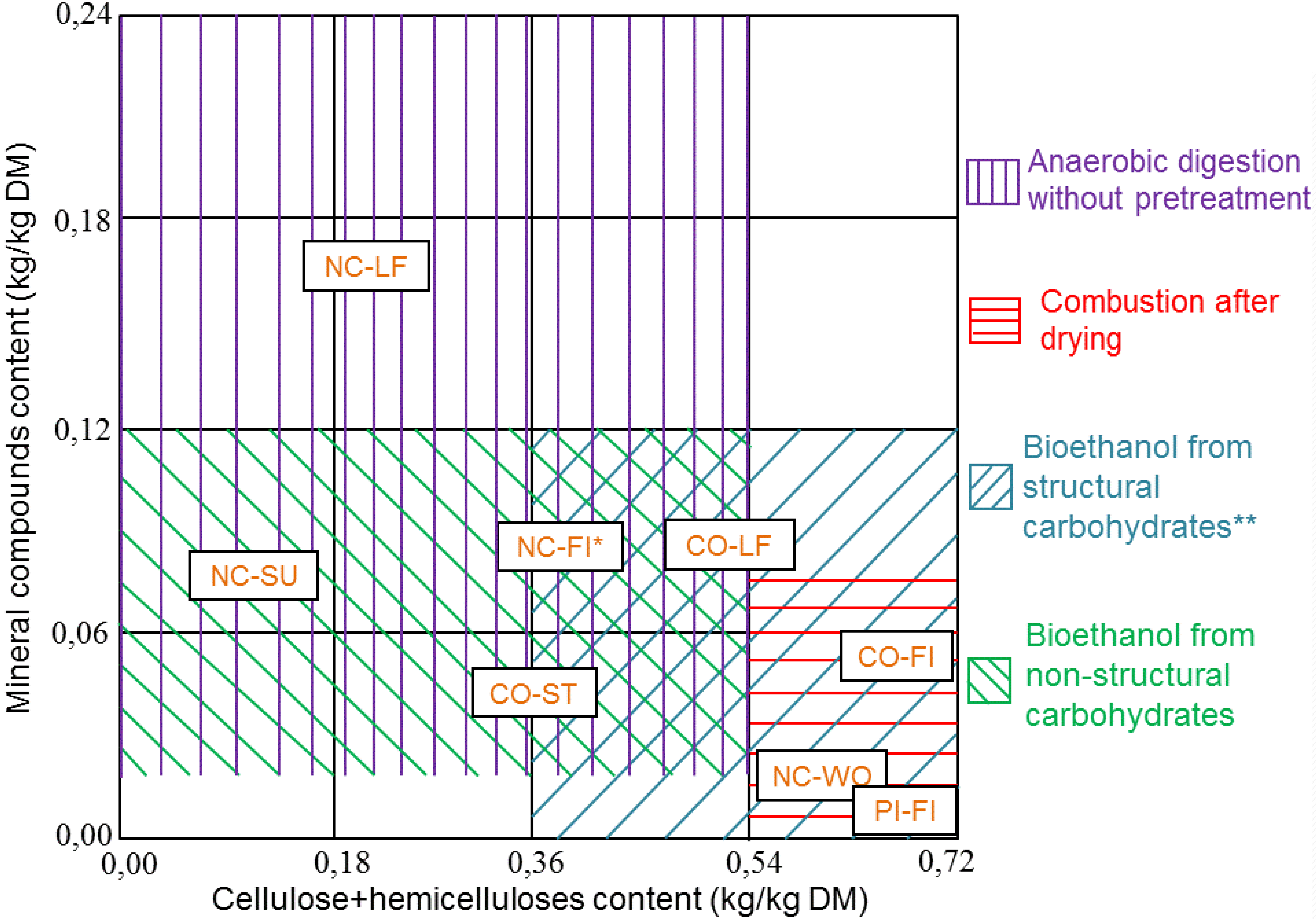
3.3. Relevant parameters to assess the suitabilities to be converted into biofuel

- Identification of joint relevant parameters of the chemical composition

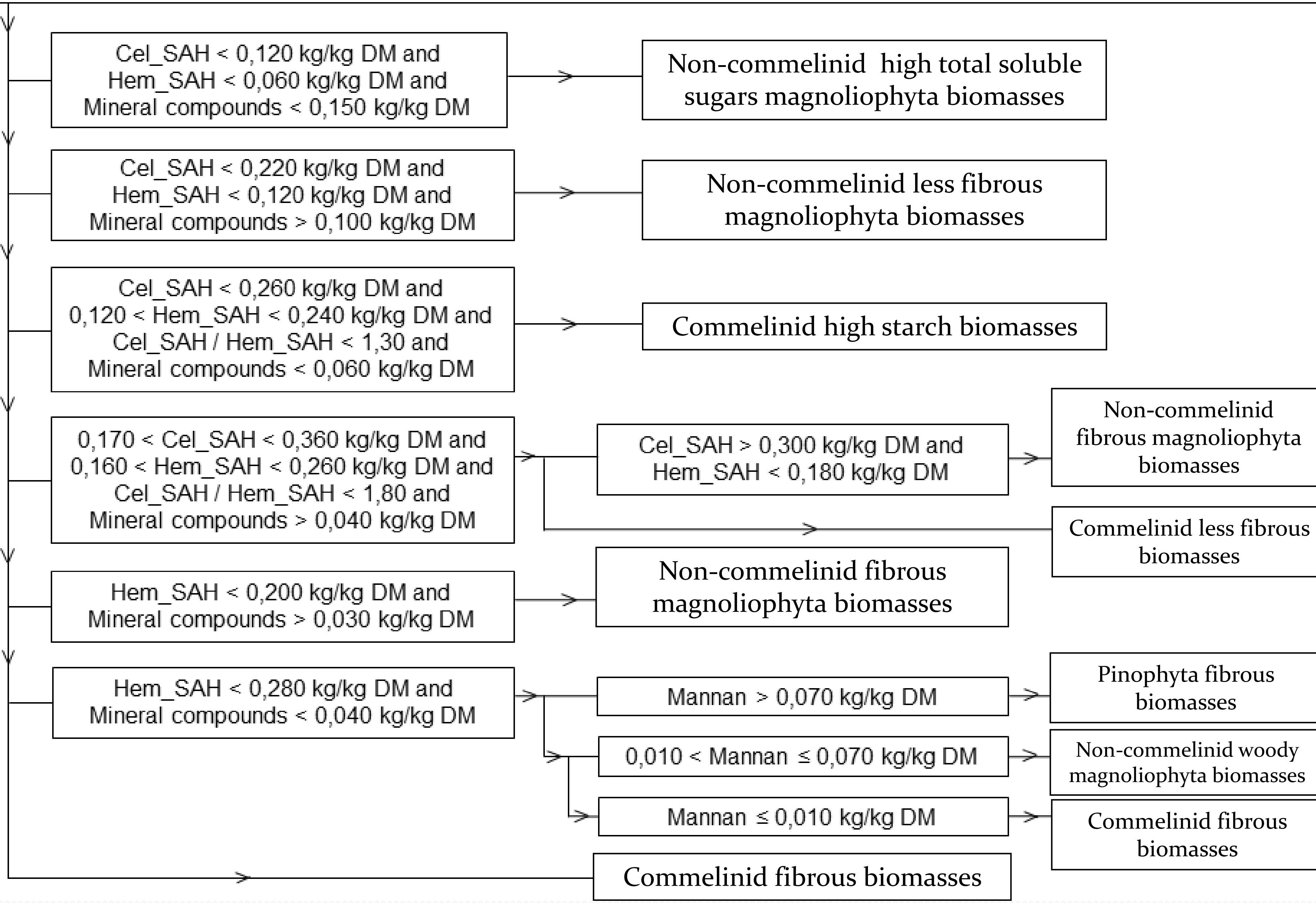
Relevant parameters to assess the suitabilities to be converted into biofuel

- Cellulose, hemicelluloses and mineral compounds content
  - Indicator for the anaerobic digestion (Enzymatically digestible organic matter)
  - Indicator for the combustion (Higher heating value)
  - Bioethanol potential
- Decision tools
- Classification key of plant biomasses

- Decision tool



Classification key of plant biomasses



3.4. Van Soest method : reference to quantify cellulose and hemicelluloses

- The Van Soest method
  - Fiber fractionation by successive chemical extractions and gravimetric quantification
  - Contamination of the fractions by non-cellulosic and non-hemicellulosic components
    - Bias

NDE-SAH-LC-CAD method : appropriate to quantify cellulose et hemicelluloses

- The NDE-SAH-LC-CAD method

1. Extraction with a pH 7 phosphate buffer containing α-amylase and with Van Soest neutral detergent **(NDE)**
2. Solubilization and hydrolysis of cellulose and hemicelluloses with sulfuric acid **(SAH)**
3. Separation of the monosaccharides released by the acid hydrolysis by a classic chromatographic system **(LC)**
4. Quantification of the monosaccharides released by the acid hydrolysis by the charged aerosol detector **(CAD)**

NDE-SAH-LC-CAD method : appropriate to quantify cellulose et hemicelluloses

- Extraction of non-lignocellulosic components with a phosphate buffer containing α-amylase and with Van Soest neutral detergent (NDE)
  - Eliminating interference

Godin B., Agneessens R., Gerin P., Delcarte J., 2011. *Talanta*, 85, 2014-2026.

NDE-SAH-LC-CAD method : appropriate to quantify cellulose et hemicelluloses

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(LC)

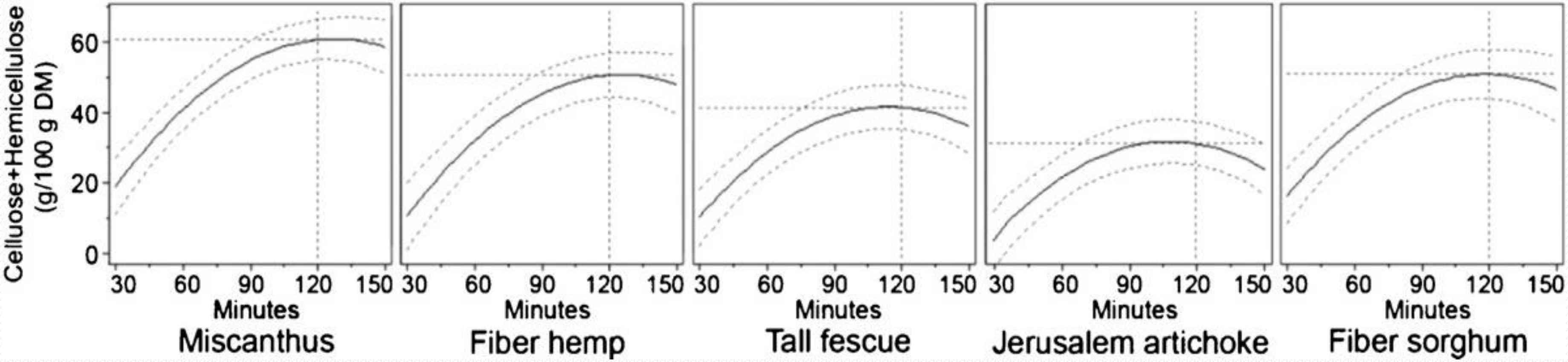
4. Quantification of the monosaccharides released by the acid hydrolysis with the charged aerosol detector **(CAD)**

NDE-SAH-LC-CAD method : appropriate to quantify cellulose et hemicelluloses

- Solubilization and hydrolysis of cellulose and hemicelluloses to monosaccharides with sulfuric acid (SAH)

  Design of experiments (Box-Behnken)

  → Step 2 : Hydrolysis time (120 min) → Most significant



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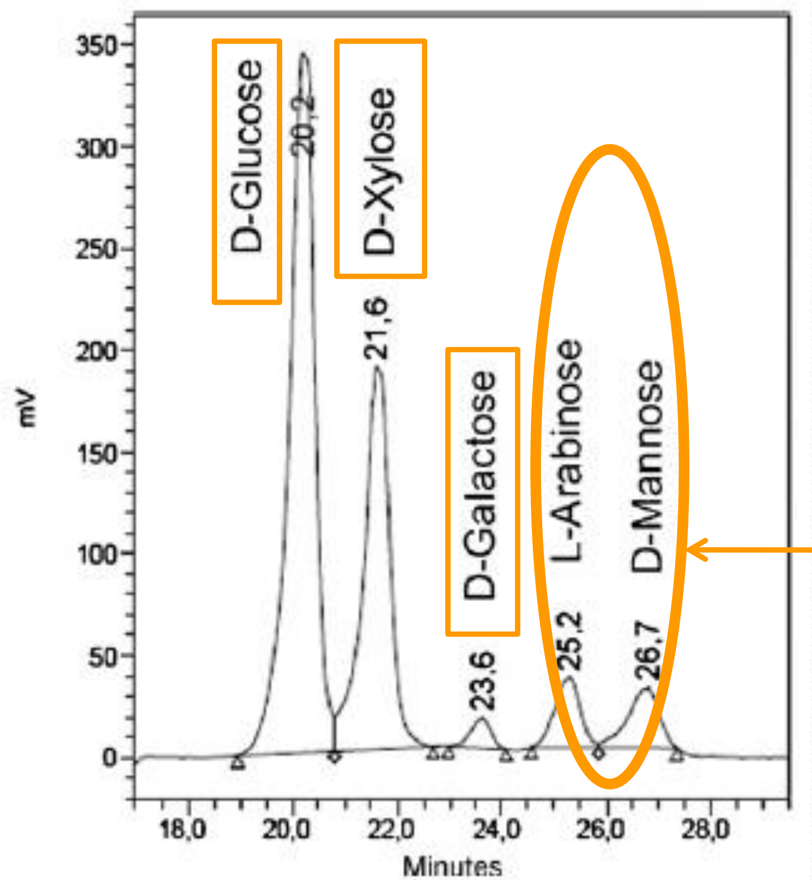
NDE-SAH-LC-CAD method : appropriate to quantify cellulose et hemicelluloses

- Separation of the monosaccharides released by the acid hydrolysis with a classic chromatographic system (LC)

Resolution between chromatographic peaks is higher than 1,50



LC column made of a sulfonate divinylbenzene-styrene copolymer substituted with lead

Critical separation

Godin B., Agneessens R., Gerin P. A., Delcarte J., 2011. *Talanta*, 85, 2014-2026.

NDE-SAH-LC-CAD method : appropriate to quantify cellulose et hemicelluloses

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NDE-SAH-LC-CAD method : appropriate to quantify cellulose et hemicelluloses

- Quantification of the monosaccharides released by the acid hydrolysis with the charged aerosol detector (CAD)

- Charged aerosol detector
  - Step 1 : Nebulization and drying
  - Step 2 : Transfer of positive charges to the particles
  - Step 3 : Measurement of the charge by an electrometer

Godin B., Agneessens R., Gerin P., Delcarte J., 2011. *Talanta*, 85, 2014-2026.

NDE-SAH-LC-CAD method : appropriate to quantify cellulose et hemicelluloses

- High accuracy of the NDE-SAH-LC-CAD method
  - Monosaccharidic composition of cellulose and hemicelluloses
  - Precise

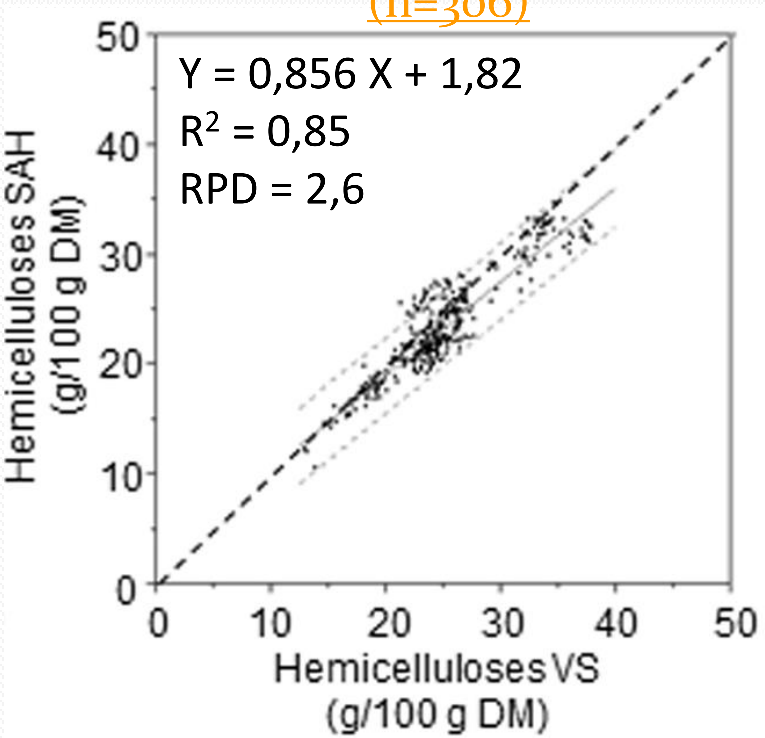
Godin B., Agneessens R., Gerin P., Delcarte J., 2011. *Talanta*, 85, 2014-2026.

NDE-SAH-LC-CAD method compared to Van Soest method

- Van Soest method is biased compared to the NDE-SAH-LC-CAD method
→ Importance to know which method is used

Commelinid biomasses (n=306)

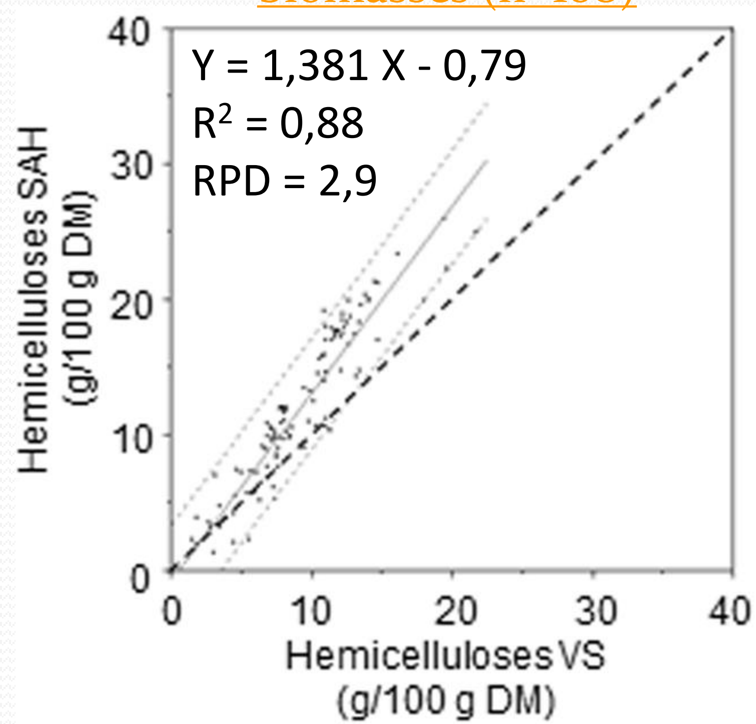
NDE-SAH-LC-CAD method



Van Soest method

Non-commelinid magnoliophyta biomasses (n=108)

NDE-SAH-LC-CAD method



Van Soest method

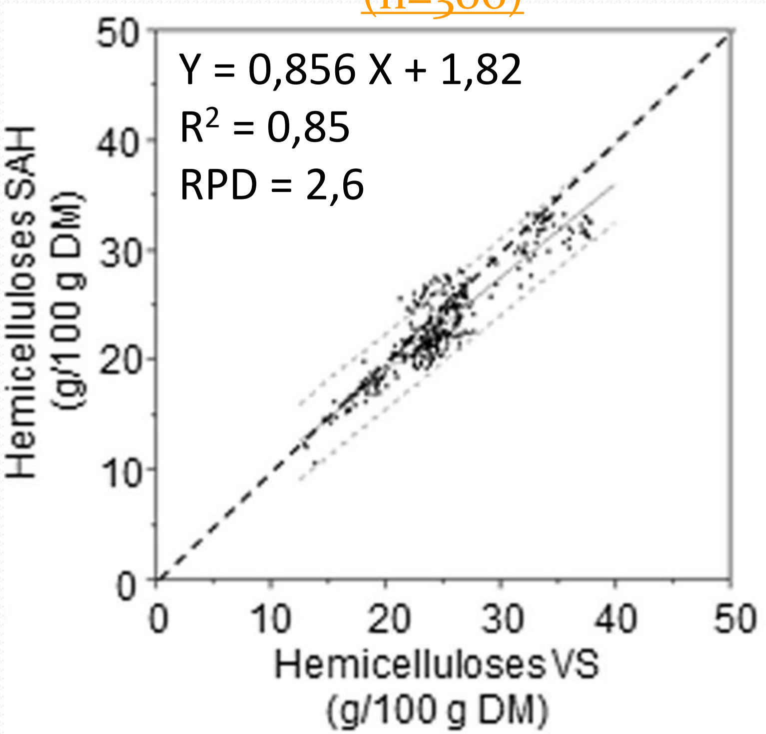
Godin B., Agneessens R., Gerin P., Delcarte J., 2013. *Biomass and Bioenergy*. Submitted.

NDE-SAH-LC-CAD method compared to Van Soest method

- The results of the NDE-SAH-LC-CAD method can be predicted by those of the Van Soest method
  - NDE-SAH-LC-CAD method → Gives hemicelluloses monosaccharidic composition

Commelinid biomasses (n=306)

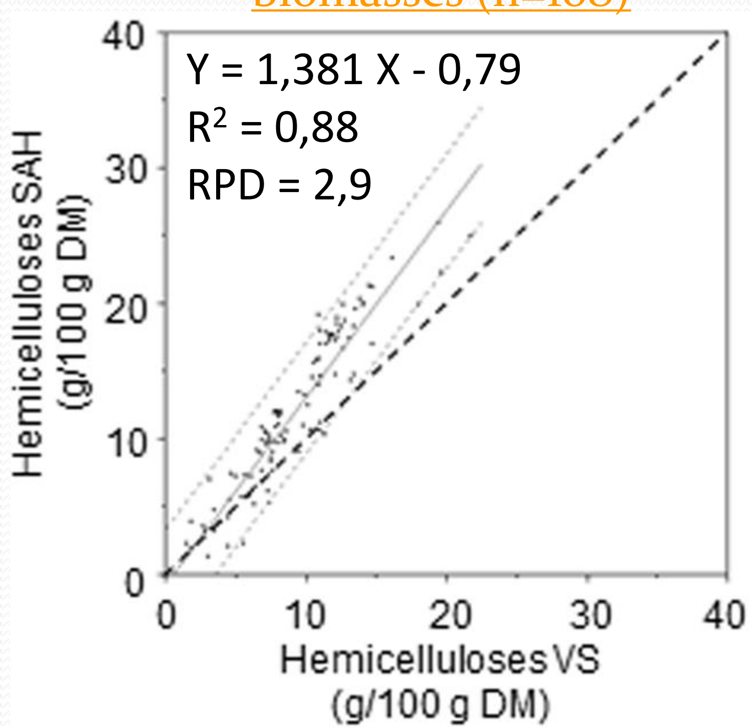
NDE-SAH-LC-CAD method



Van Soest method

Non-commelinid magnoliophyta biomasses (n=108)

NDE-SAH-LC-CAD method



Van Soest method

Godin B., Agneessens R., Gerin P., Delcarte J., 2013. *Biomass and Bioenergy*. Submitted.

Outline

1. Context

2. Objectives

3. Results and discussion

4. Conclusions and prospects

Key parameters to assess the gross energy productivity

- Dry matter yield per hectare
  - Plant species
  - Soil and climatic conditions
  - Plant maturity → Autumn
- Dry matter content
  - Combustion
- Relative chemical characteristics of the biomass → Unimportant
  - Important for the biofuel conversion process → Plant maturity

Relevant parameters to assess the suitabilities to be converted into biofuel

- Cellulose, hemicelluloses and mineral compounds content
  - Decision tools
  - Classification key of plant biomasses



Chemical composition and suitabilities to be converted into biofuel

- Suitabilities to be converted into biofuel
  - The indicator for the anaerobic digestion is favorable for cytoplasm-rich metabolically active cell biomasses
  - The indicator for the combustion is favorable for biomasses with a high organic matter content
  - Bioethanol potential is favorable for all the biomass groups
    → Except for non-commelinid less fibrous magnoliophyta biomasses

Chemical composition and suitabilities to be converted into biofuel

- The diversity of biomasses is structured in groups with similar chemical characteristics
  - Phylogenetic cleavage
    → Hemicelluloses and Lignin / Xylan+Arabinan and Mannan
  - Fiber cleavage
    → Mineral compounds

NDE-SAH-LC-CAD method : appropriate to quantify cellulose et hemicelluloses

- Important to know which method is used to assess the available amounts of cellulose and hemicelluloses
  - NDE-SAH-LC-CAD method → High accuracy
  - Van Soest method → Biased
- The results of the NDE-SAH-LC-CAD method can be predicted by those of the Van Soest method
  - NDE-SAH-LC-CAD method → Gives hemicelluloses monosaccharidic composition

Prospects

- Near infrared spectroscopy
  - Calibration equations for the measured chemical parameters
  - Prediction of the suitabilities to be converted into biofuel

Prospects

- Pilot unit
  - Conversion into energy of the biomasses with the best suitabilities to be converted into biofuel
- Bioproducts
  - Biorefinery → Biomass sequential fractionation of its main chemical components

Thank you for your attention

Main PhD publications

- **Godin B., Lamaudière S., Agneessens R., Schmit T., Goffart J.-P., Stilmant D., Gerin P. A. & Delcarte J., 2013.** Chemical characteristics and biofuel potential of several vegetal biomasses grown under a wide range of environmental conditions. *Industrial Crops and Products*, **46**, 1-12.
- **Godin B., Lamaudière S., Agneessens R., Schmit T., Goffart J.-P., Stilmant D., Gerin P. A. & Delcarte J., 2013.** Chemical characteristics and biofuels potentials of various plant biomasses: influence of the harvesting date. *Journal of the Science of Food and Agriculture*, DOI 10.1002/jsfa.6159.
- **Godin B., Lamaudière S., Agneessens R., Schmit T., Goffart J.-P., Stilmant D., Gerin P. A. & Delcarte J., 2013.** Chemical composition and biofuel potentials of a wide diversity of plant biomasses. *Energy and Fuels*, **27**, 2588-2598.
- **Godin B., Agneessens R., Gerin P. A. & Delcarte J., 2013.** Structural carbohydrates in plant biomasses: correlations between the detergent fiber and the dietary fiber methods. *Biomass and Bioenergy*, Submitted.
- **Godin B., Agneessens R., Gerin P. A. & Delcarte J., 2011.** Composition of structural carbohydrates in biomass: Precision of a method using a neutral detergent extraction and a charged aerosol detector. *Talanta*, **85**, 2014-2026
- **Godin B., Agneessens R., Gofflot S., Lamaudière S., Sinnaeve G., Gerin P. A. & Delcarte J., 2011.** Revue sur les méthodes de caractérisation des polysaccharides structuraux des biomasses lignocellulosiques. *Biotechnol. Agron. Soc. Environ.*, **15**, 165-182.