Evaluation of biomass quality for the production of second-generation biofuels: process requirements x analytical techniques

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Context

- **Oil reserves** : **1 to 1.2 billion barrels** (40-50 years of production at current consumption levels)
- **Vegetal biomass** : main candidate for remplacing of oil : **2,6 x 10^{11} tons, renewable,** potentiel for **greenhouses gazes reduction**
- Low biofuel yield of first biofuel generation per hectare: **1 to 4 TEP / ha**.
- **1,8 M ha** de lands needed in France to fulfill the EU objectives of 5,75 % of biofuels by 2010 (ADEME)
- French ambitions : 5,75 % of biofuels in 2008, 7% in 2010 and 10 % en 2015 : **3,5 M ha of land** needed by 2015

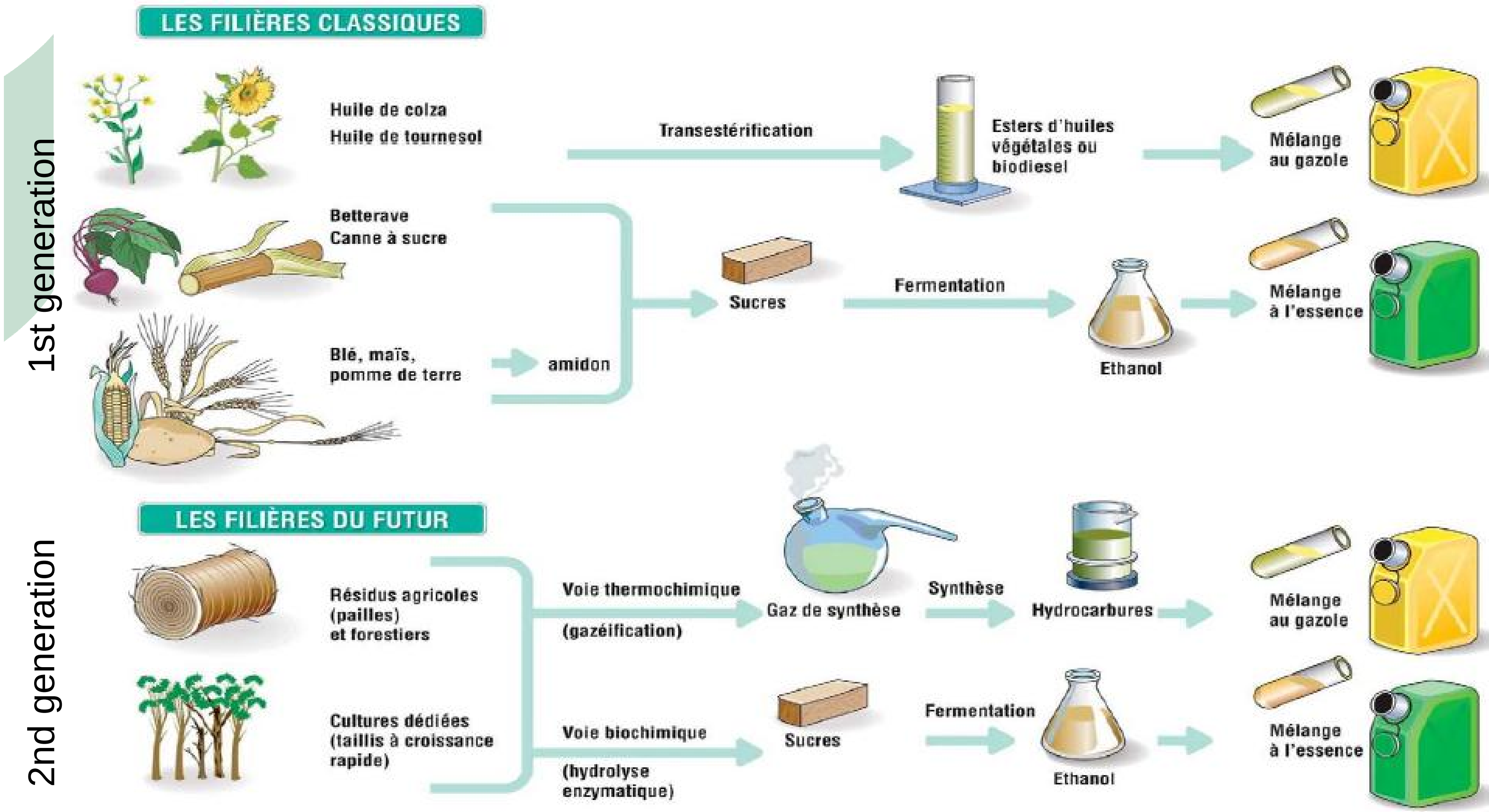
Total cultivable land surface in France : 18,4 M ha

Currently available lands: 1,5 M ha (but only 1.2 to 1.3 M ha really cultivalbe)

Context

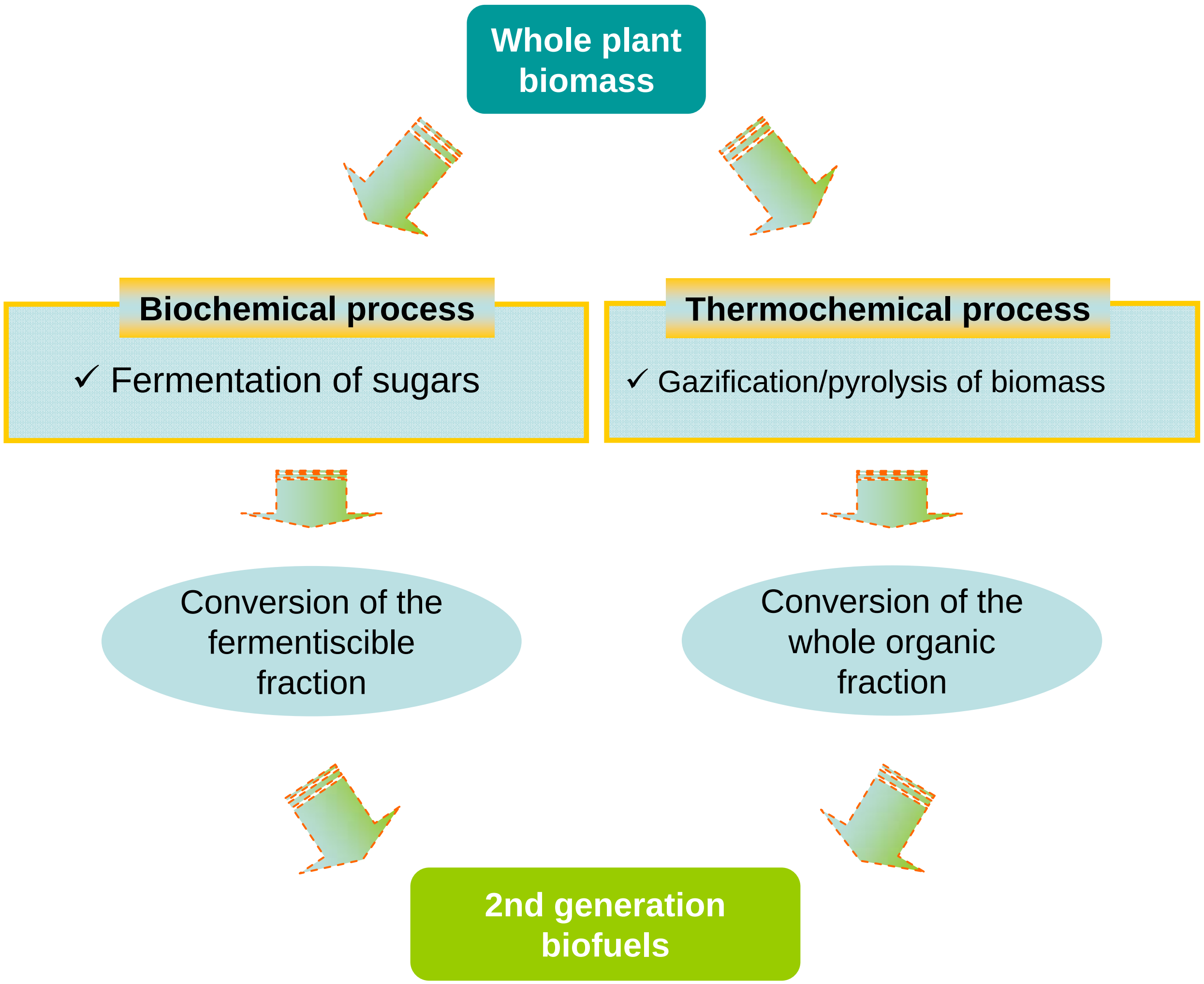
- **2nd generation biofuels**: mandatory choice to respect the Fr/EU commitments while avoiding competition with food production
- Biomass supply will be composed of multi-ressources (agriculture and forestry)
- Is there **adequacy** between **biomass quality** and **biofuel process requirements** ?
- Which **quality criteria** to be considered for the biomass ?
- What is the state of the art in **quality data** and **analytical techniques** for the **biomass characterization ?**

1st and 2nd generation biofuels

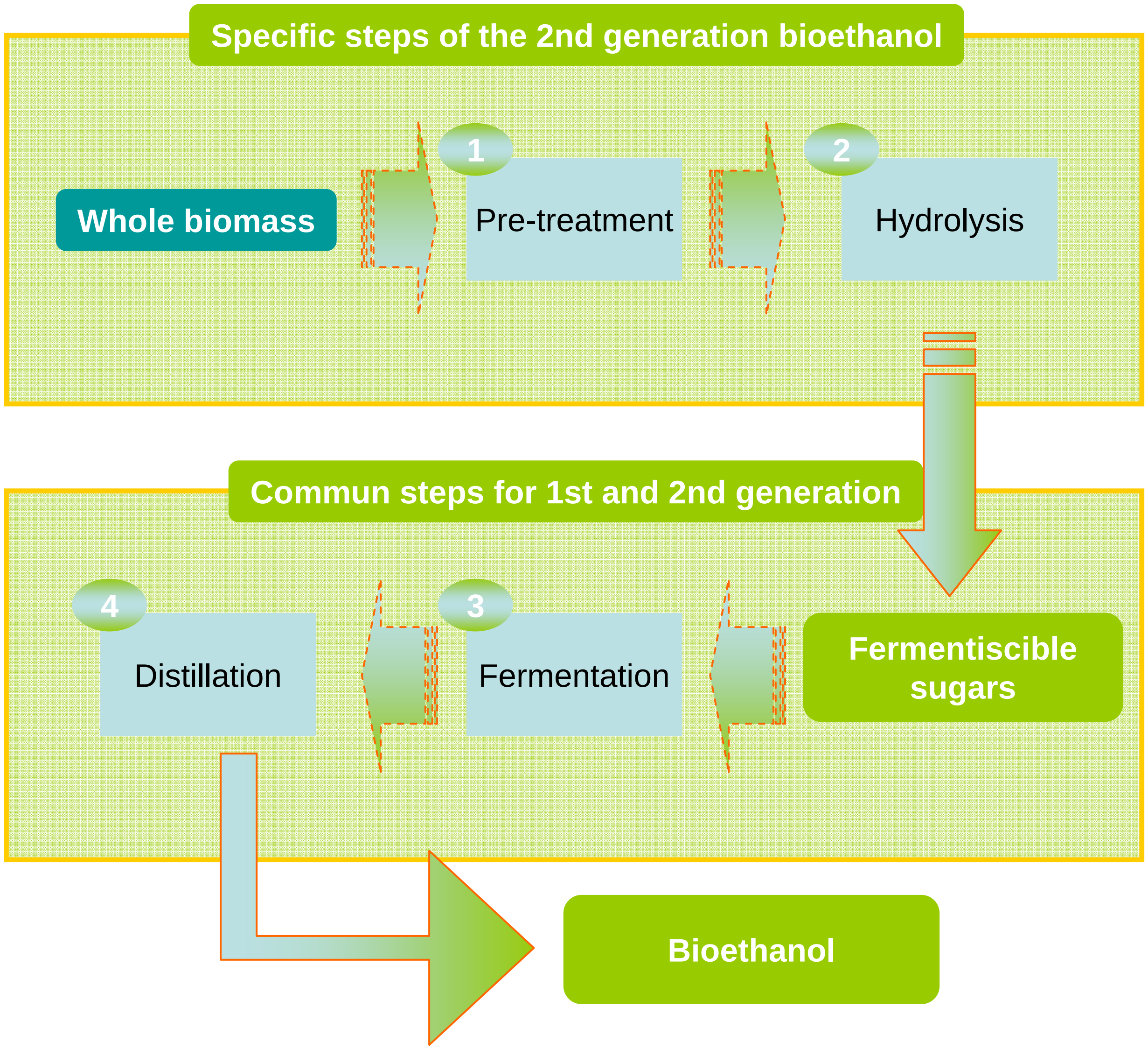


Source : IFP

2nd generation biofuels : 2 production processes

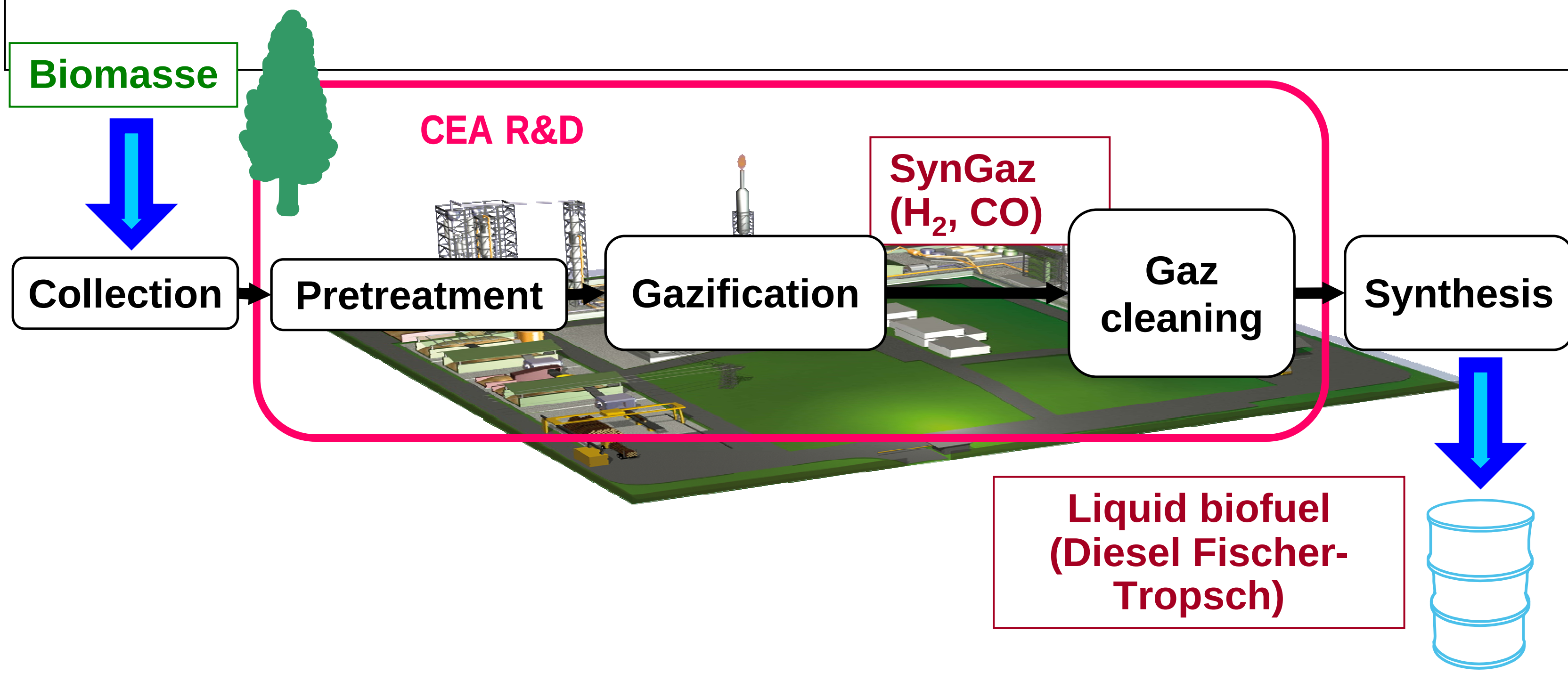


2nd generation bioethanol

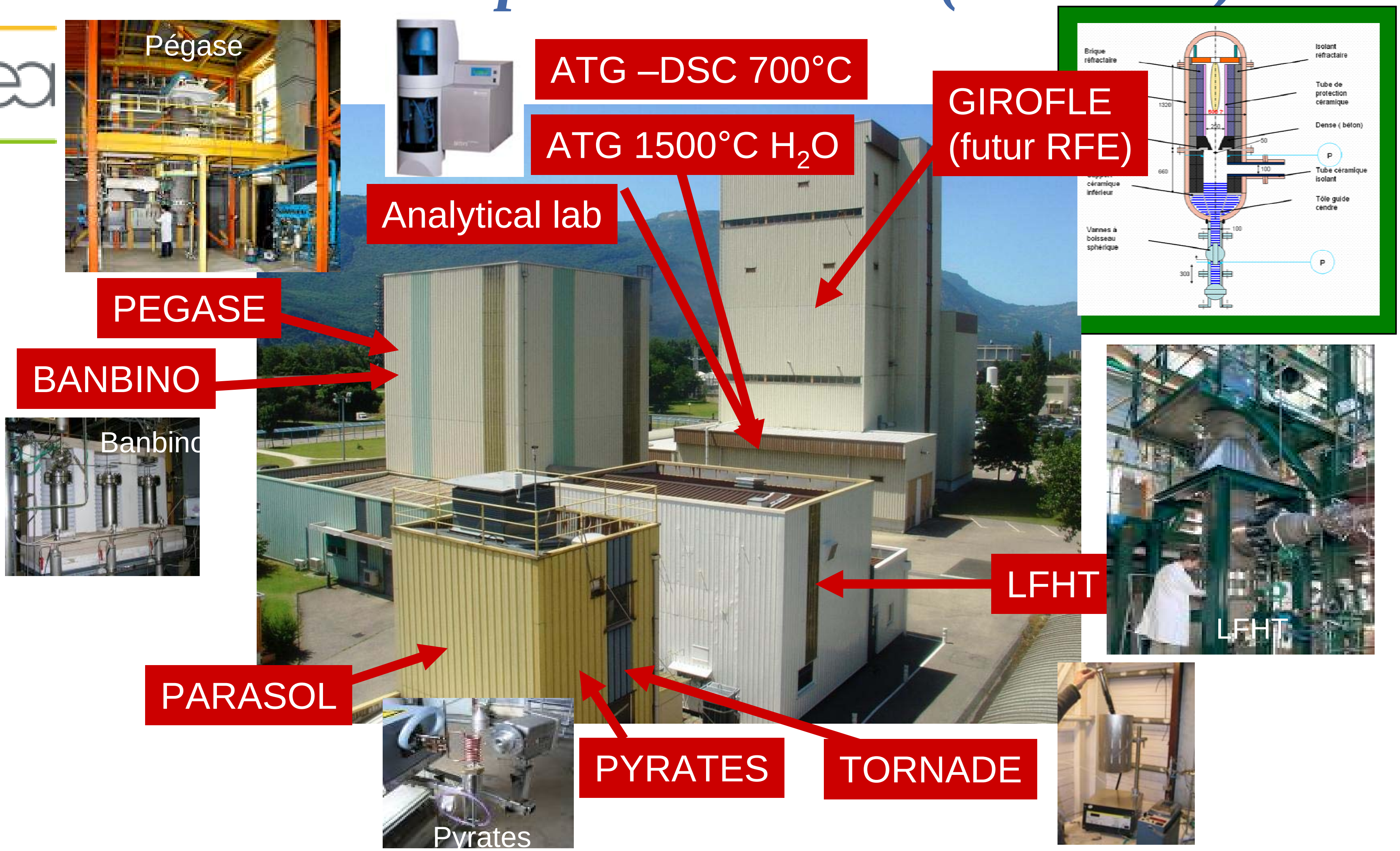


Thermochemical process (CEA)

- **Objectif :** Development of production process of **Liquid biofuel**(Diesel Fischer-Tropsch) from syngaz (H_2, CO) through lignocellulosic biomass **gazification**.

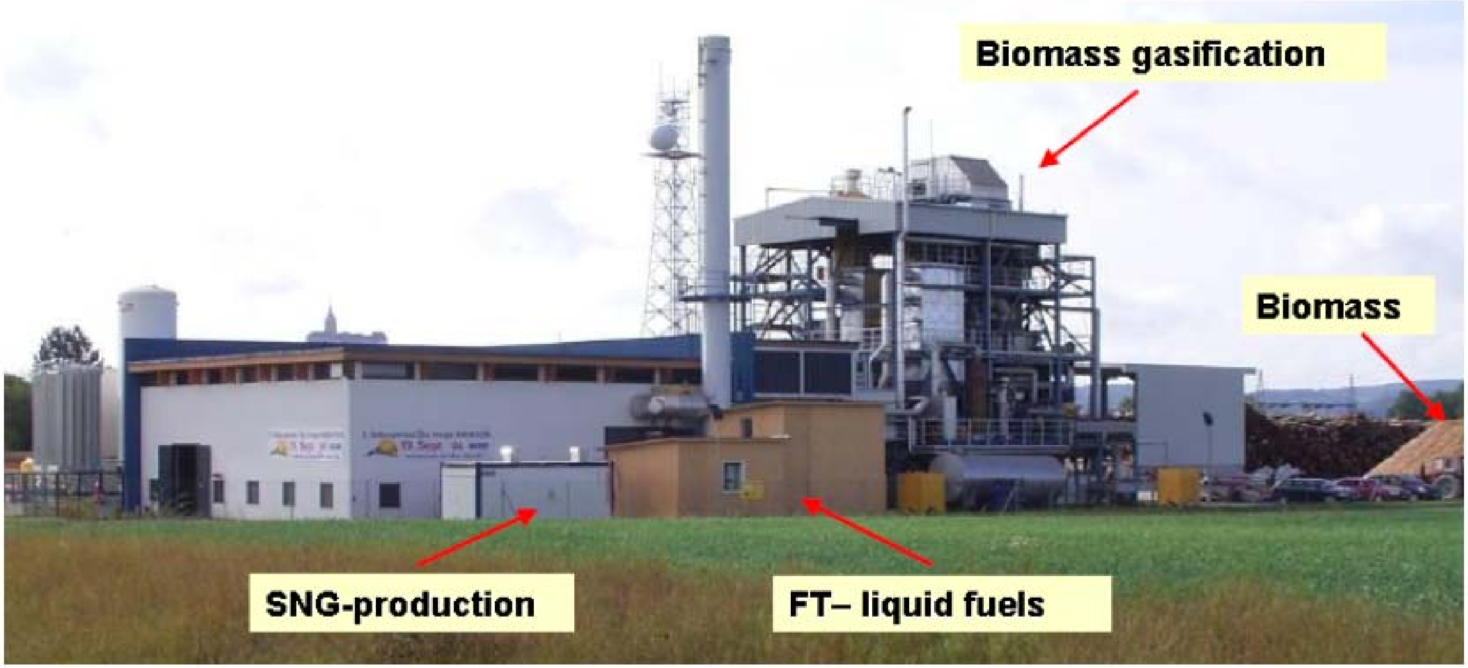


CEA Experimental unit (Grenoble)



Demonstrator unit (Güssing)

depuis 2001 : suivi de l'installation de Güssing



National programme REGIX (2006 – 2009)

- Creation of a workgroup **biomass ressources - process**
- **Elaboration of biomass quality criteria with specifications for processes**
- **State of the art of public biomass quality database and internal data of the projects partners**
  - *Collection of data*
  - *Creation of a compiled database*
  - *Critical analysis of existing and missing data*
- **Confrontation of data and analytical methods**
- **Adoption of common protocols for analysis**
- **Complementary analysis (2 campaigns, 234 samples analysed)**

National programme REGIX (2006 – 2009)

WorkGroup :
Ressources and Process

- FCBA (forestry)
- GIE ARVALIS&ONIDOL (agriculture)
- INRA (agriculture and forest)
- UCFF (forestry)
- CEA (thermochemical process)
- EDF (thermochemical process)
- IFP (thermochemical and biochemical processes)

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Biomass quality criteria
Specification and limits processes

Composition
- C,H,O,N,S, Cl (T, B)
- Monosscharides (hydrolysed sugars, soluble sugars); (B)
- Pölysaccharides (cellulose, hémicellulose, starch) (B)
- Lignin (T, B)
- Extractives (B)
- Ash content (T)
- Ash composition (Cl, K, Na, F, P, Si, Ca, Mg …)(T)
- Ash fusibility (T)
- Moisture content (T, B)

Morphology
- Density (T, B)
- Size distribution (T, B)
- Specific surface (T, B)
- Porosity (T, B)
- Fines content (T, B)

Propriétés physiques
- Thermodynamical (HHV/LHV, heat capacity) (T)

↓

Variability of the quality criteria:
species x origin x pratices

Very Short Rotation Copices (VSRC)

- 8 000 à 15 000 stems/ha,
- Rotation 2 to 3 years
- Production of lots of small stems (D = 3 to 4 cm, H = 4 to 6 m)
- Productivity (experimental stands) up to10 ts/ha/year of biomasse, but variable and very dependent on soil quality

Very Short Rotation Copices (VSRC)

- Agriculture-like plantation and harvesting
- Single product:

→ *VSRC chips*

- **Advantages TTCR :**
  - Short cycles
  - Easy integration in farm exploitations
  - Agricultural-like
  - Cleaning contaminated soils
- **Drawbacks TTCR :**
  - Installation costs
  - Monoproduct
  - Needs of water and fertilizers
  - Quality of chips (high bark/wood ratio, young stems…)

Short Rotation Copices (SRC)

- 1 000 à 2 000 stems/ha,
- Rotations 7 to 10 years
- Production of small trees (D = 15 cm, H = 15 to 20 m)
- 1 or 2 rotation harvestings
- Productivity confirmed at large scale (10 to 12 ts/ha/year of biomass)

Short Rotation Copices (SRC)

- **Advantages SRC :**
  - Low maintenance needed
  - Good biomass quality
  - multiproducts : logs or chips

- **Drawbacks SRC :**
  - Long cycles duration
  - concentration of costs at the installation
  - Forest-like harvesting
  - Rooting

Forest chips

Chips obtained by grinding :

- Different forest residues
- Low diameter trees or stems
- Low value forests

« Typical » dimensions : 2 x 2 x 5 cm

1 m³ of wood produces 2.5 to 3 apparent cubic meters of forest chips

Agricultural biomass


Paille de blé – GIE A&O


Miscanthus– GIE A&O


Triticale – GIE A&O


Noyaux d'açaï – UFPA

Comparison between forest and agricultural biomass

Ai : immature annual cereal crops (sorghum, maize, triticale)

Am : mature annual cereal crops (sorghum, maize, triticale)

Gf : Forage grasses (fescue, brome)

Pv : perennials plants harvested green/autumn (miscanthus, switchgrass et giant cane)

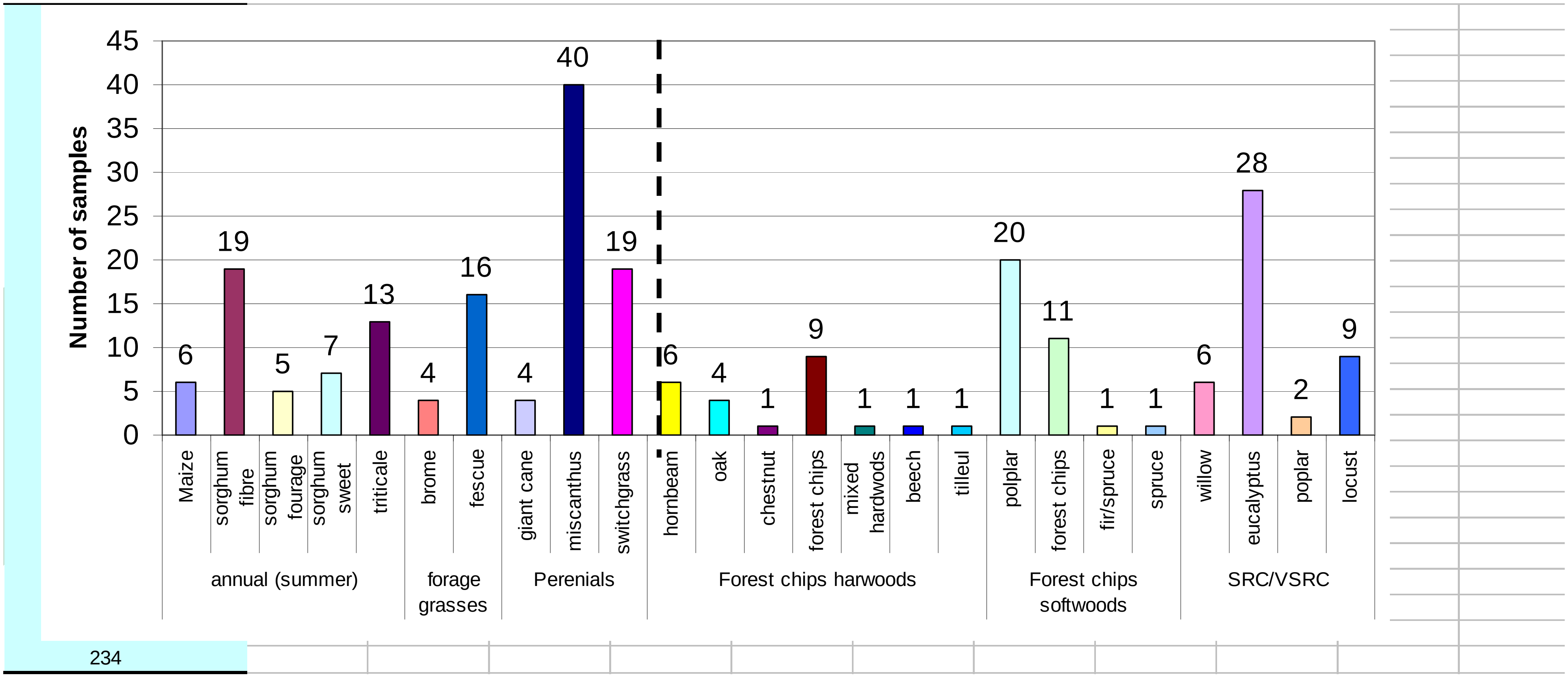
Ps : perennials plants harvested green/winter (miscanthus, switchgrass et giant cane)

Pf : Forest chips of hardwoods

Pr: Forest chips of softwoods

SRC (*TCR*): Short rotation coppices (age at harvesting : 7 to 13 y/o)

VSRC (*TTCR*): Very short rotation coppices (age at harvesting : less than 3 y/o)

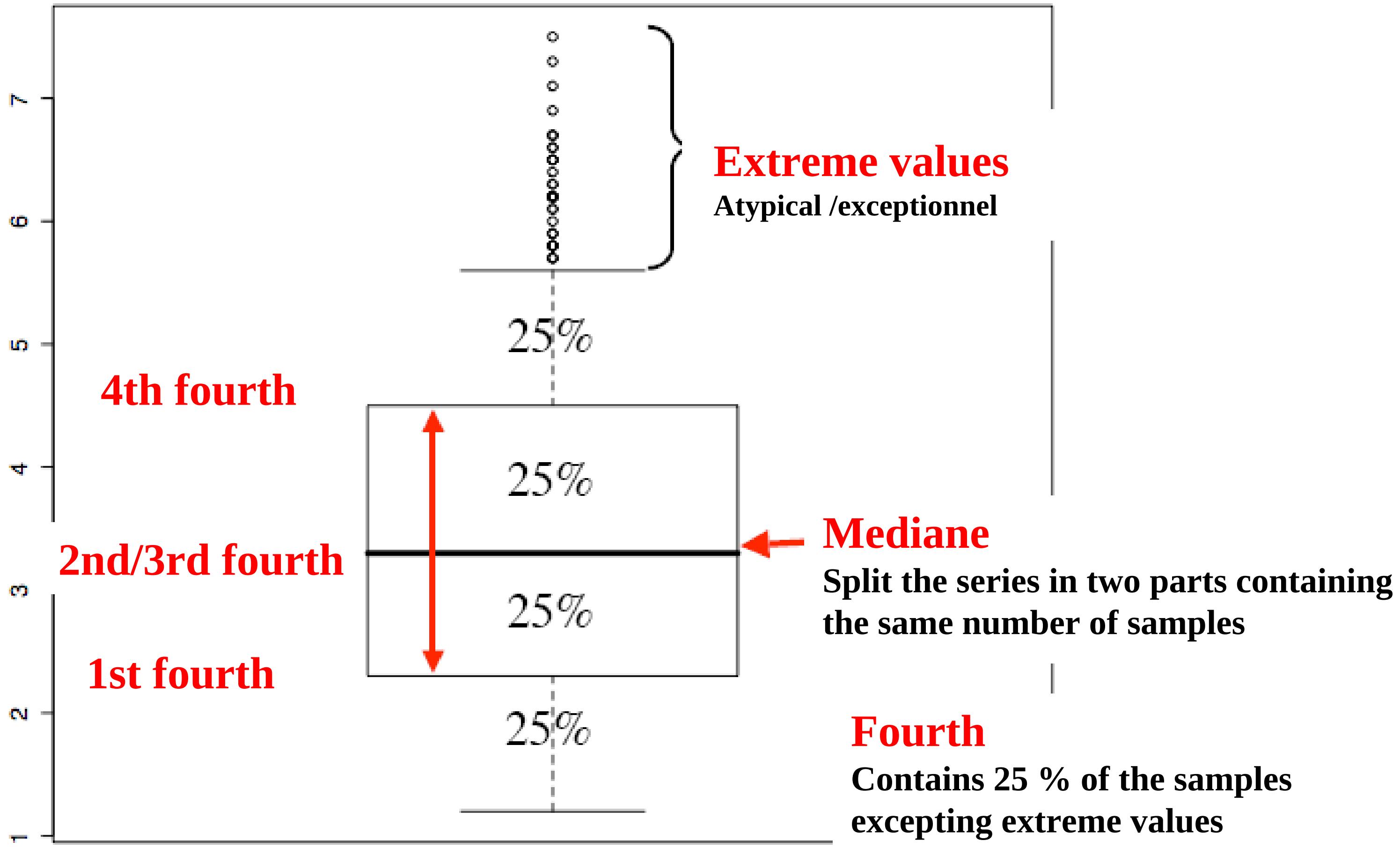


Modalité	Effectif	%
Ai	27	11.54
Am	23	9.83
Gf	20	8.55
Pf	26	11.11
Pr	9	3.85
Ps	40	17.09
Pv	23	9.83
TCR	18	7.69
TTCR	48	20.51
Total	234	100.00

- ✓ 133 agricultural samples
- ✓ 101 forestry samples

=> 234 samples in two campaigns (2007-2008 et 2008 2009)

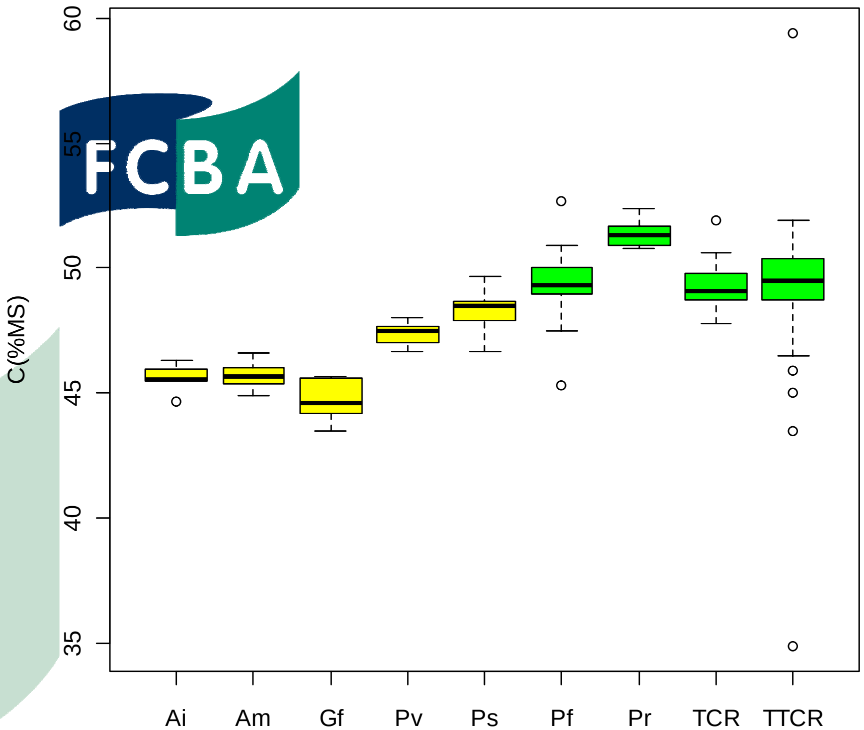
Graphical representation of quality criteria

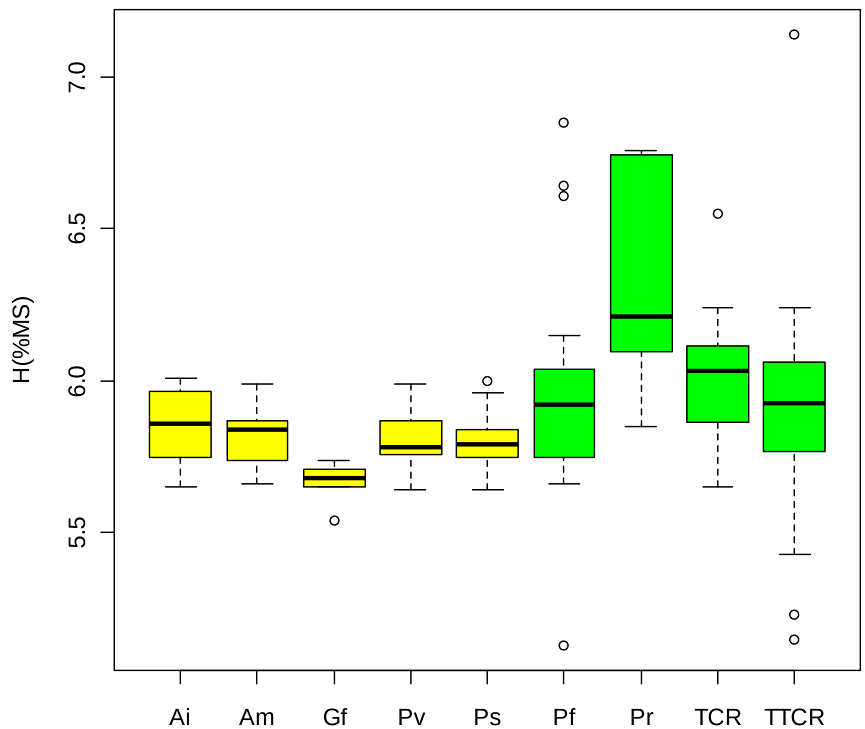


Process specifications x biomass quality

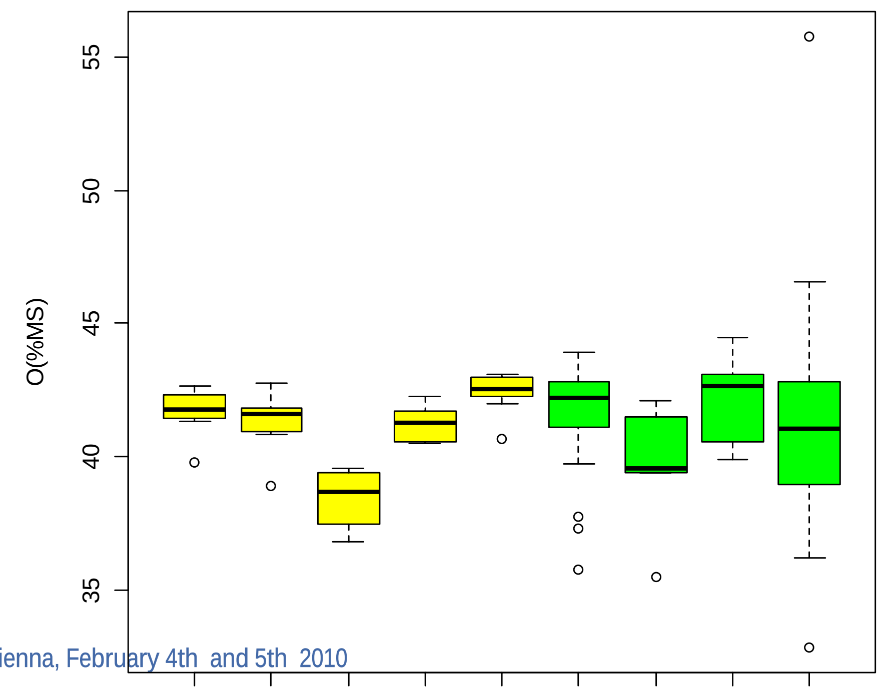
- **Thermochemical processes :**

	EDF		CEA
	Gazification	**Combustion**	**Gazification (Entrained flow reactor)**
C			46 to 52 %DM
H			5 to 7 %DM
O			40 to 46 %DM





Elemental analysis C, H, O



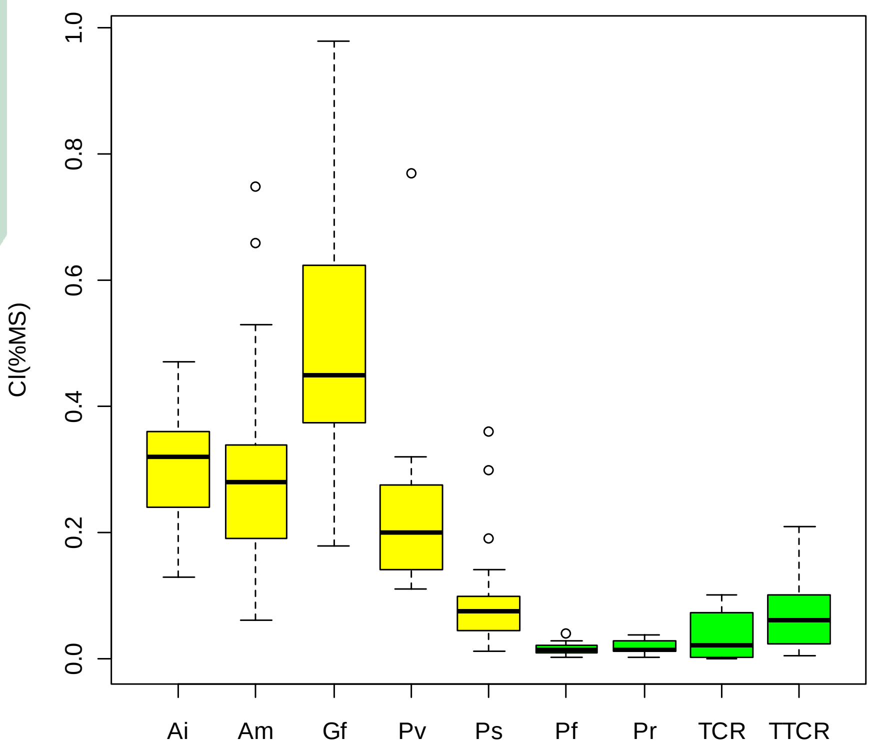
Process specifications x biomass quality

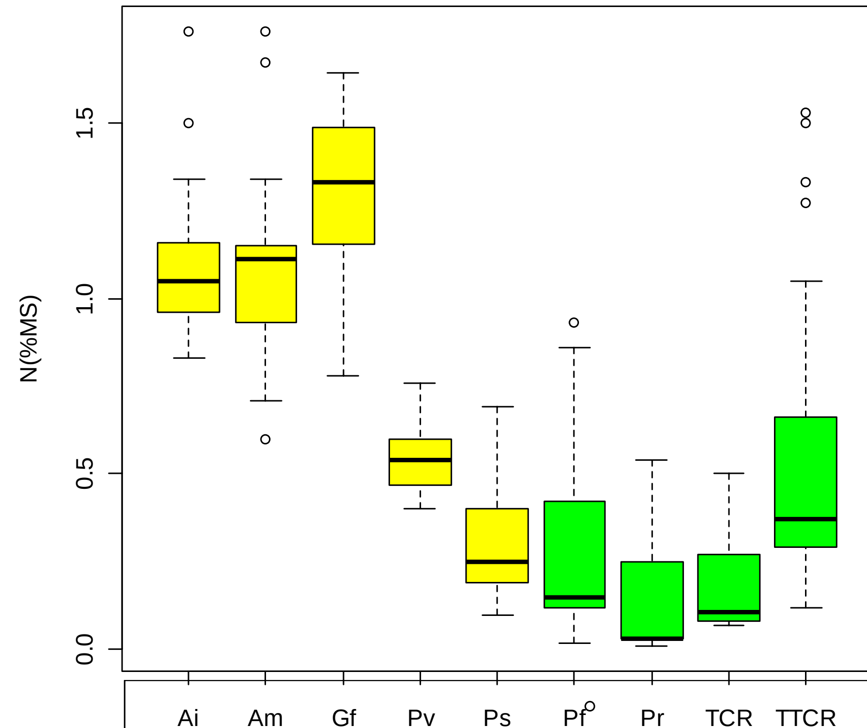
- Specifications for thermochemical processes :

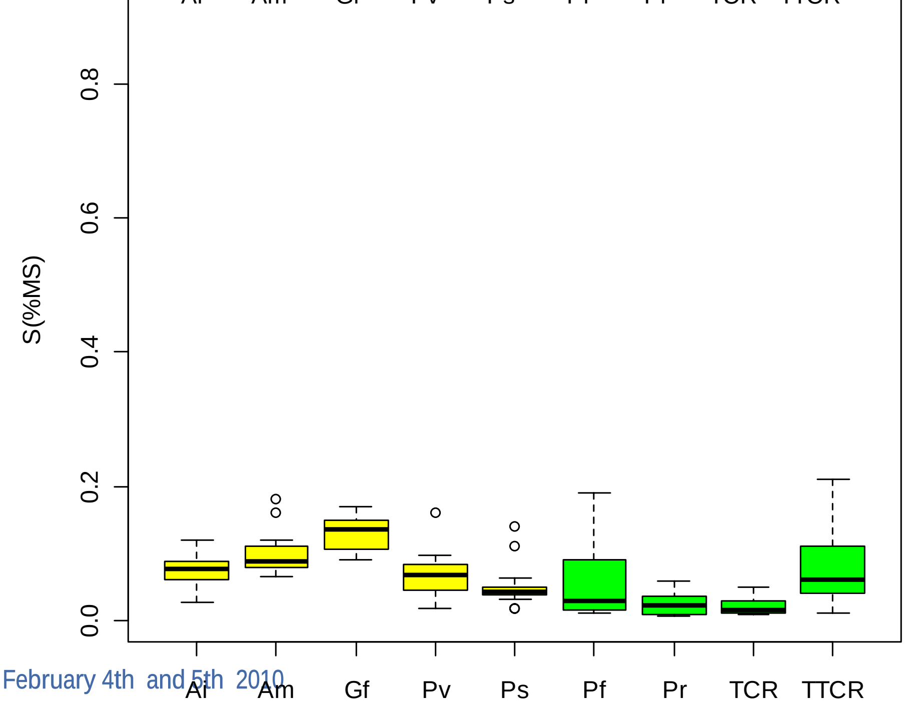
	EDF		CEA
	Gazification	**Combustion**	**Gazification (Entrained flow reactor)**
	% DM	**% DM**	
N	0.2	0.6	
Cl		0.1	< 200 mg/kg
S	0.1 % DM	0.2 % DM	< 0.06 % DM

- Chlore : corrosion; emissions of chlorinated volatiles
- Nitrogen : NOx emissions
- Sulfur : SO2 emissions; corrosion; catalyst desactivation, contribution to ash melting behaviour

N,Cl and S


Cl(%MS)
0.0
0.2
0.4
0.6
0.8
1.0
Ai Am Gf Pv Ps Pf Pr TCR TTCR


N(%MS)
0.0
0.5
1.0
1.5
Ai Am Gf Pv Ps Pf Pr TCR TTCR


S(%MS)
0.0
0.2
0.4
0.6
0.8
Ai Am Gf Pv Ps Pf Pr TCR TTCR

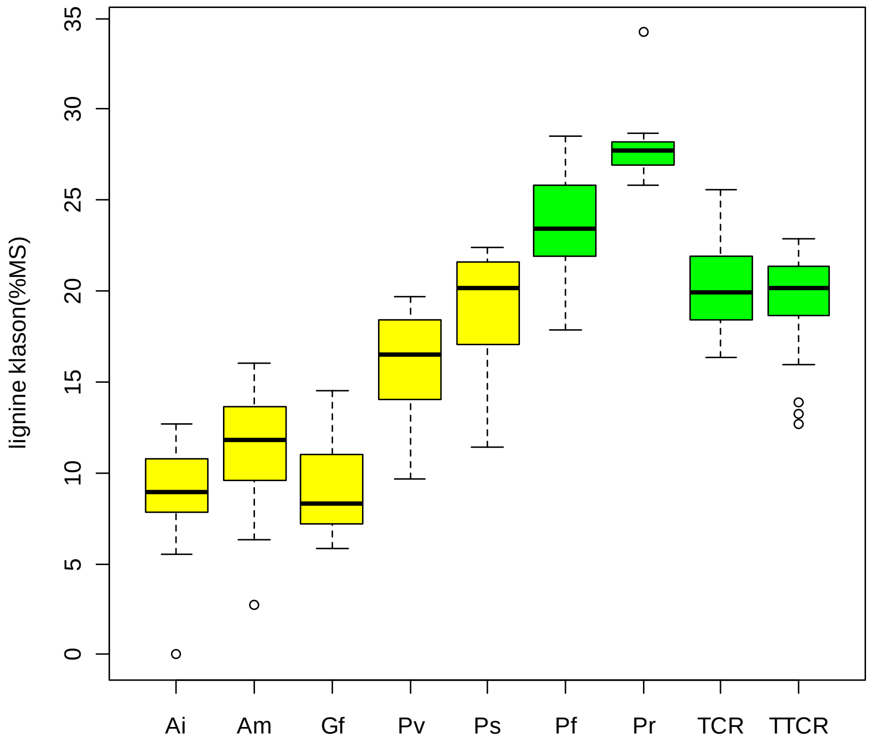
Analytical-related questions

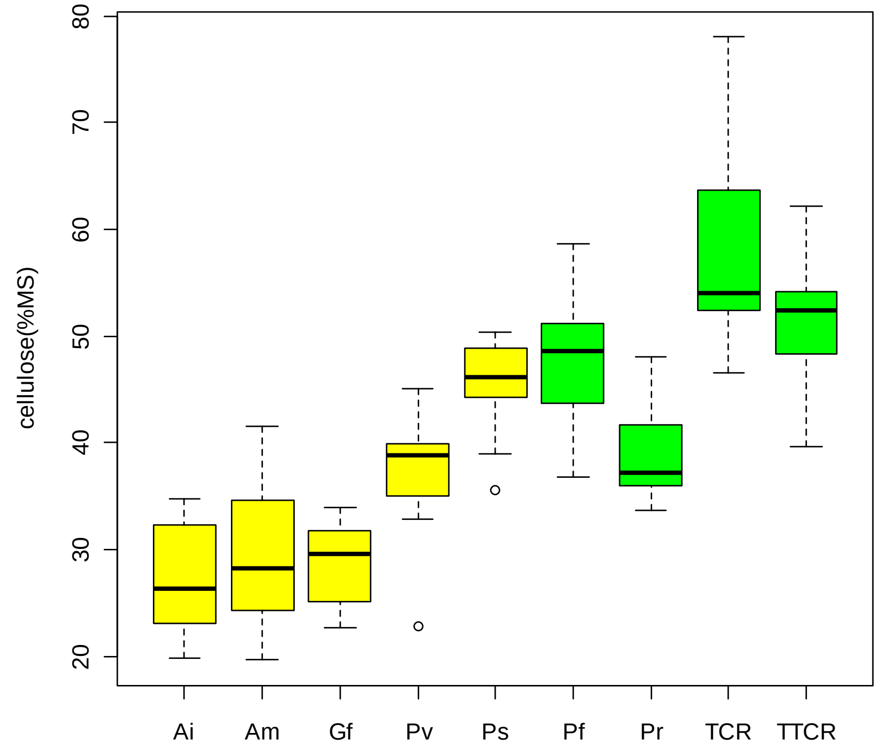
- Traditional elemental analysis not sensitive enough for nitrogen content, especially for forestry samples
- Samples preparation very important to avoid volatilisation of chlorine

Process specifications x biomass quality

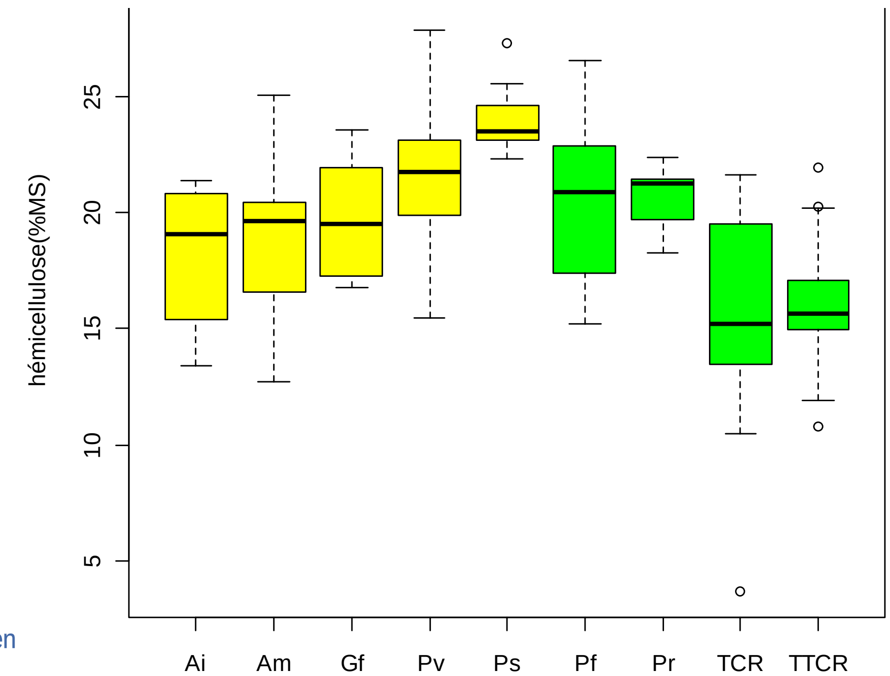
- Specifications for thermochemical processes :

Criteria	Bioethanol process specifications
C6	**As high as possible**
C5	**As low as possible**
Lignin	**Low content, but enough energy for EtOH concentration**





Chemical composition
cellulose, hemicellulose and lignin



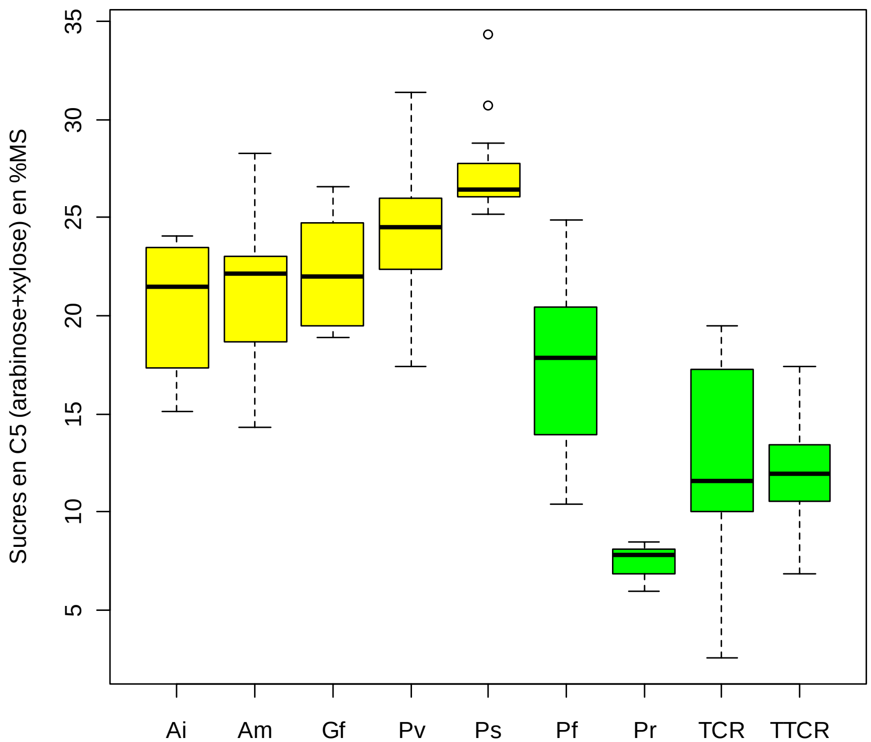
Analytical-related questions

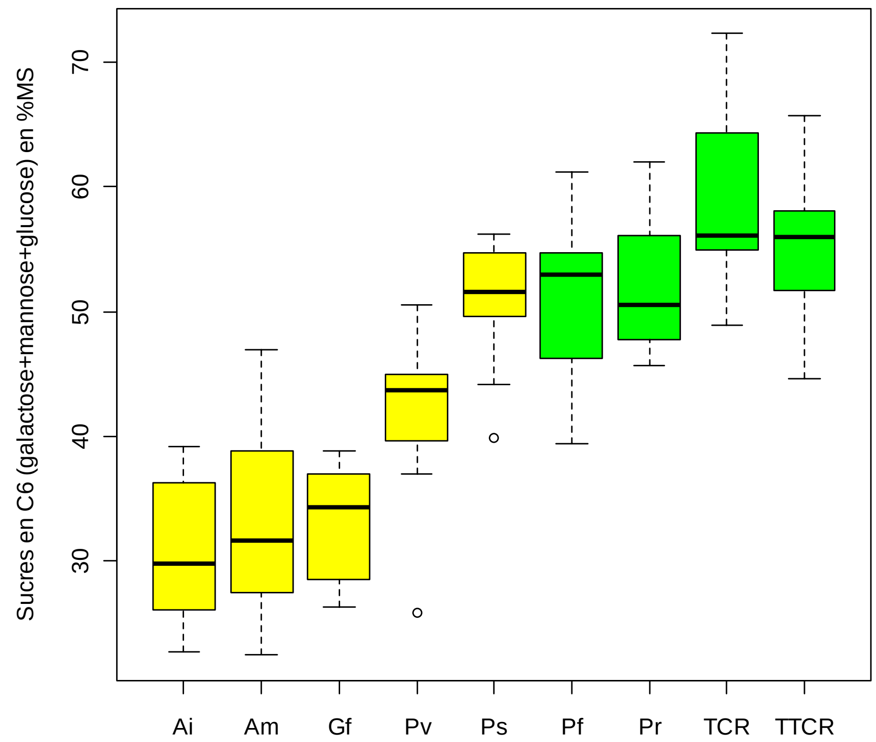
- Huge difference between traditional method used for agricultural and forestry samples
  - Agricultural uses Van Soest animal digestibility tests as indication of chemical composition : neutral detergent fiber (NDF), the acid detergent fiber (ADF) and the lignin (ADL)
  - Forestry analysis : extraction, Klason lignin (+ soluble), hydrolysis of polysaccharides and sugar analysis

Problem : Under- and/or overestimation by a factor up to 3 !!!!

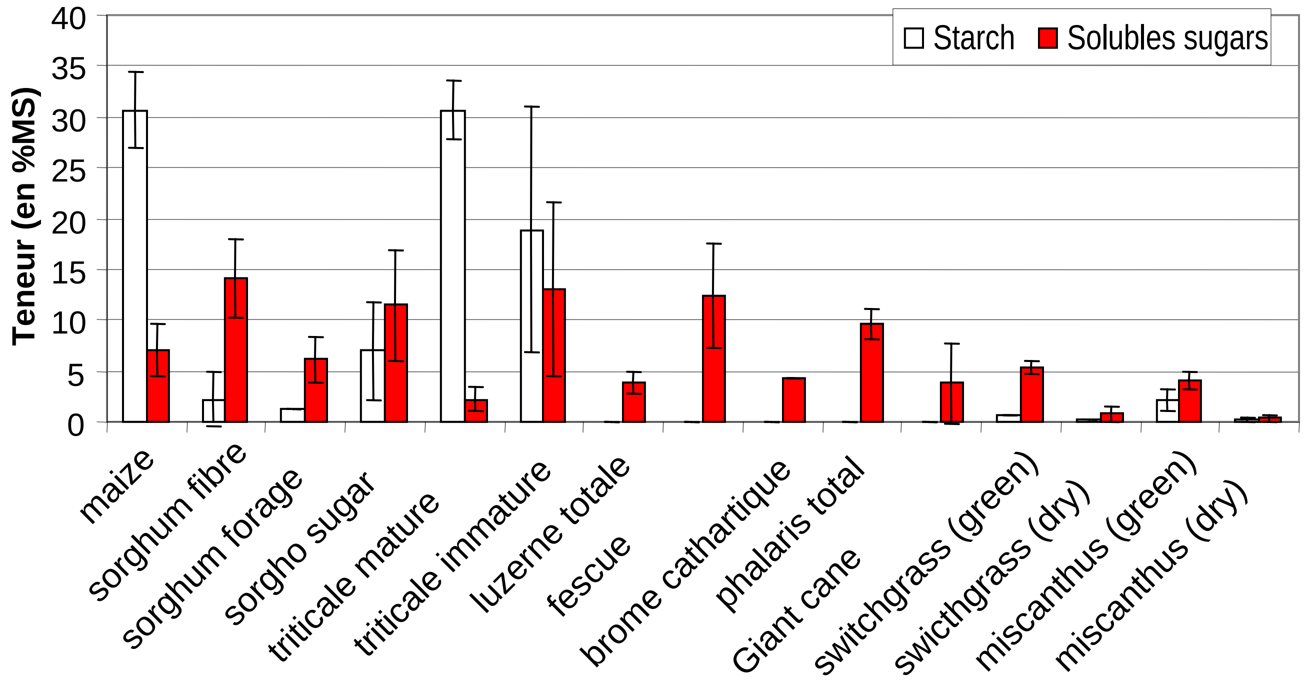
- Combination of both approaches needed
  - Neutral detergent fiber (NDF) for agricultural samples and VSRC
  - “Traditional” extraction for forestry samples
  - Klason lignin (+ soluble), hydrolysis of polysaccharides and sugar analysis for all samples

Composition : monosugars C5 and C6





Water-soluble sugars and starch



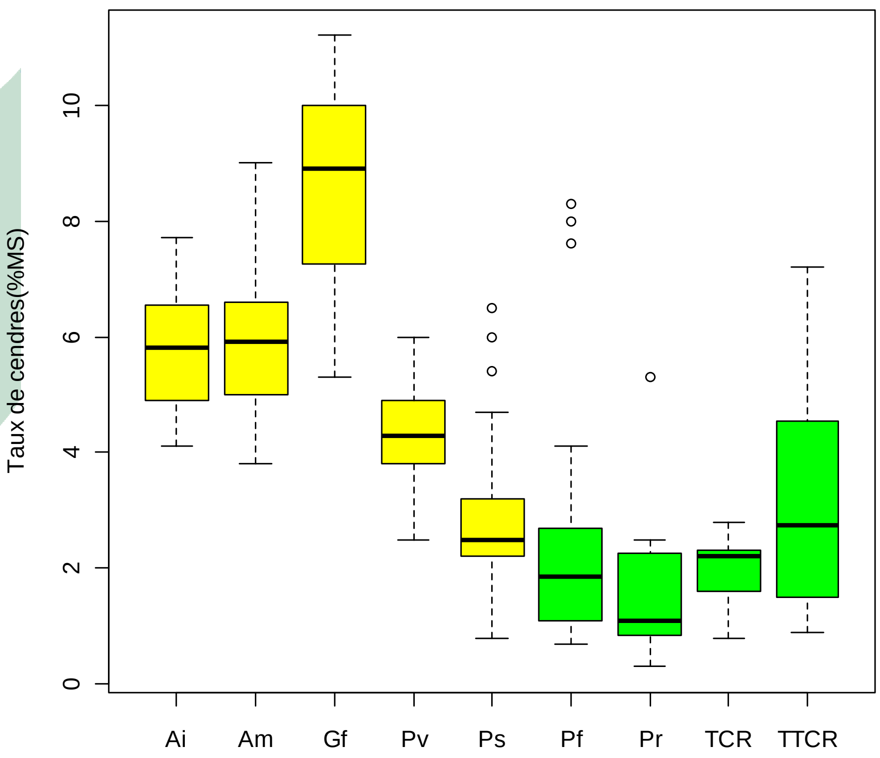
Ash composition

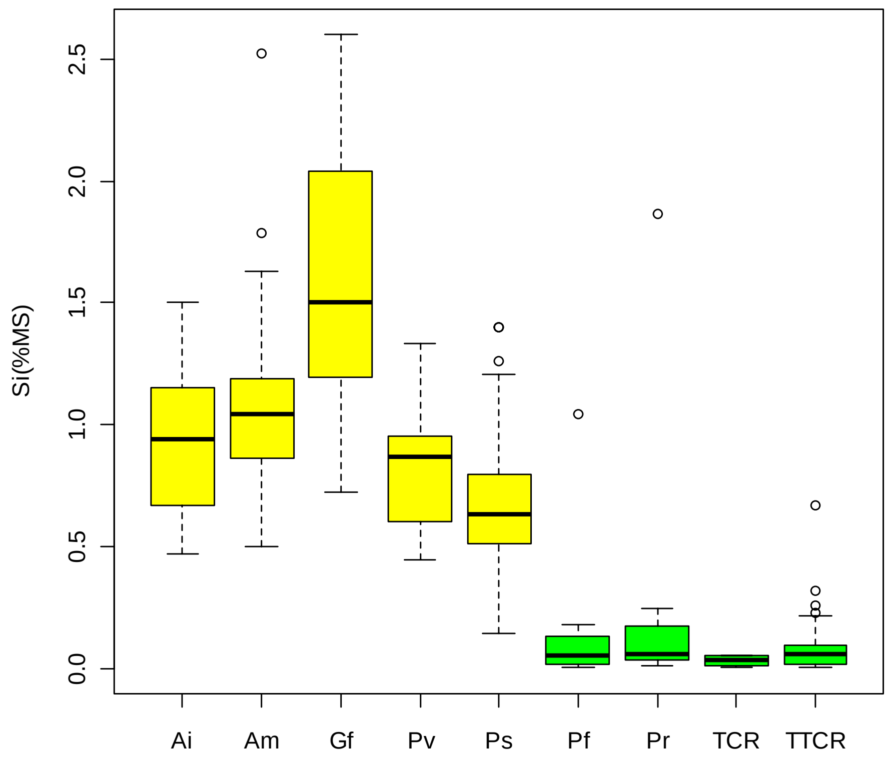
- Thermochemical process

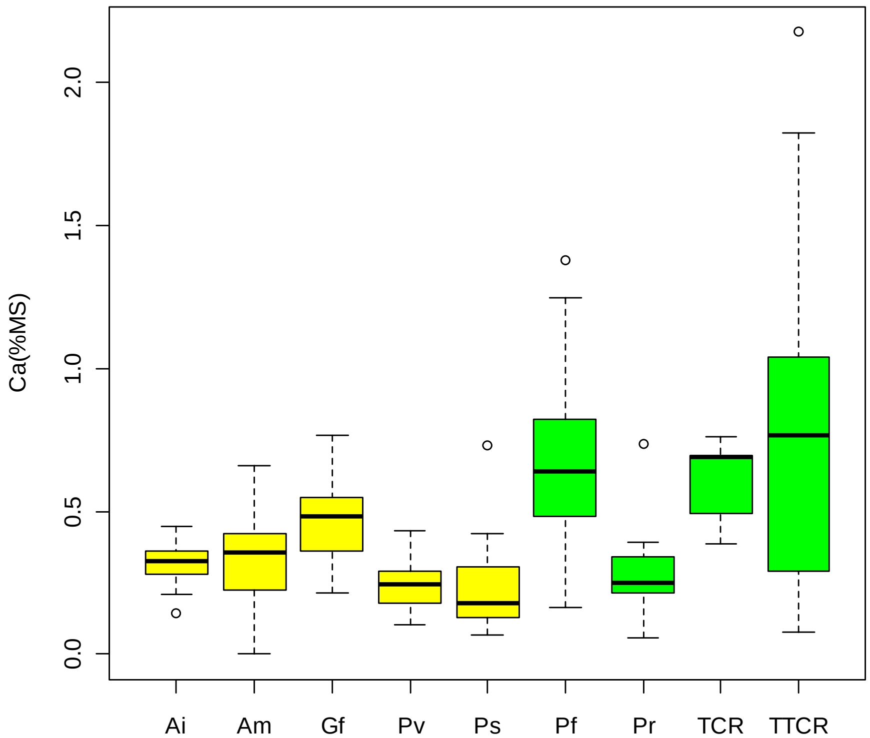
	EDF
	Combustion
CaO	> 15 % of ash composition
MgO	> 2,5 % of ash composition
Na2O	< 0,6 % of ash composition
K2O	< 7 % of ash composition
Si_2O	Not defined

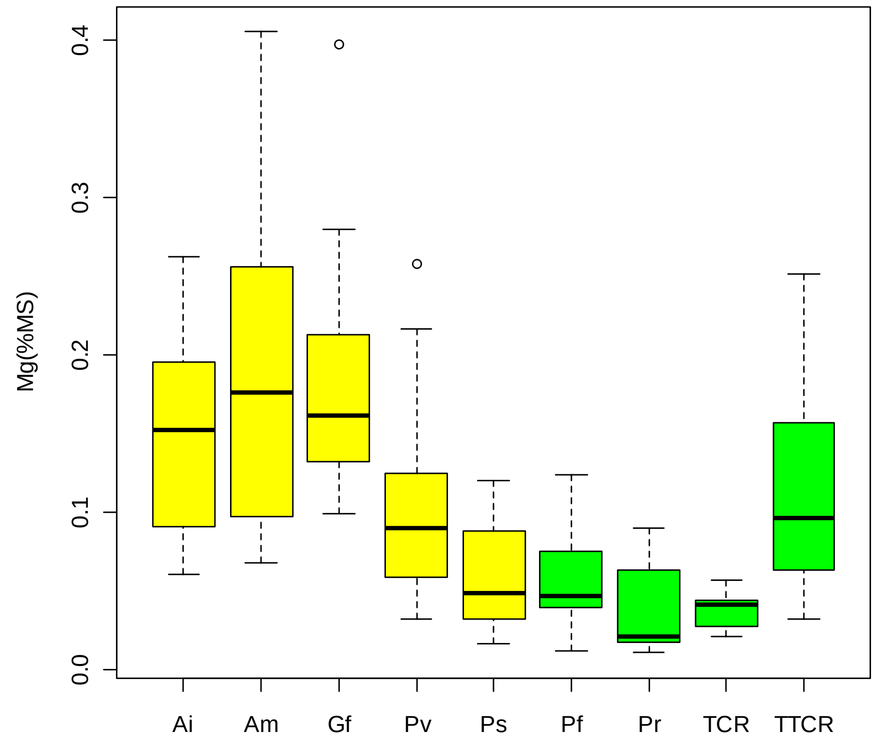
- MAIN ISSUE: Ash must melt during gazification to protect the reactor
- Fusibility of the ashes extremely dependent on composition
- Very high ash content : Evacuation and cleaning costs
- **High Si** => vitrification of ahses and premature corrosion of equipments
- **K** et **Na** decreases the meilting temperature and strongly contribute to corrosion especially if combined to Cl
- **K** forms **silicates** having low fusion temperature => deposit on equipments
- **Ca** et **Mg** increase rapidly ash melting temperature

Ash composition: content and Si content

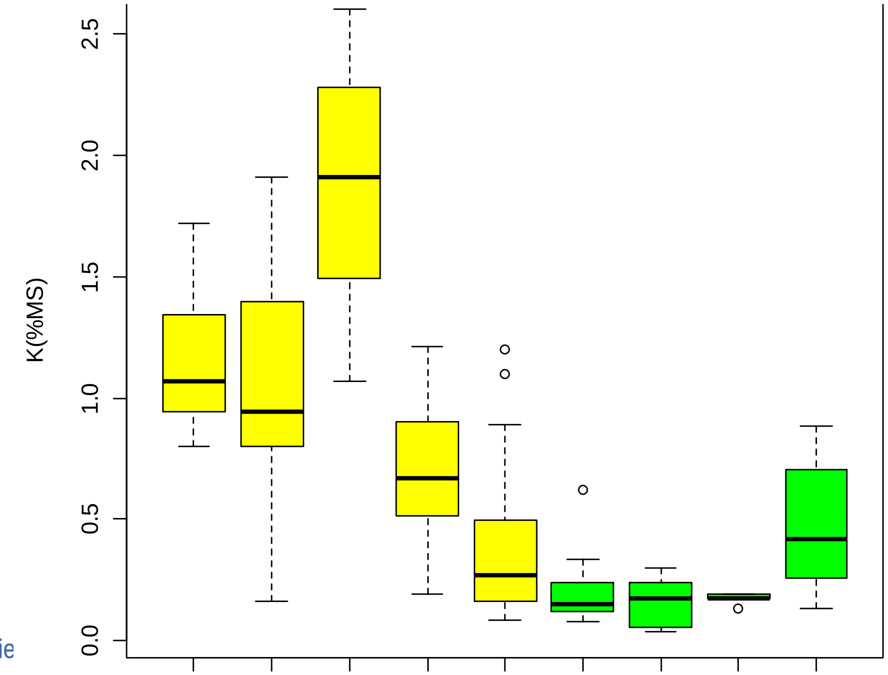


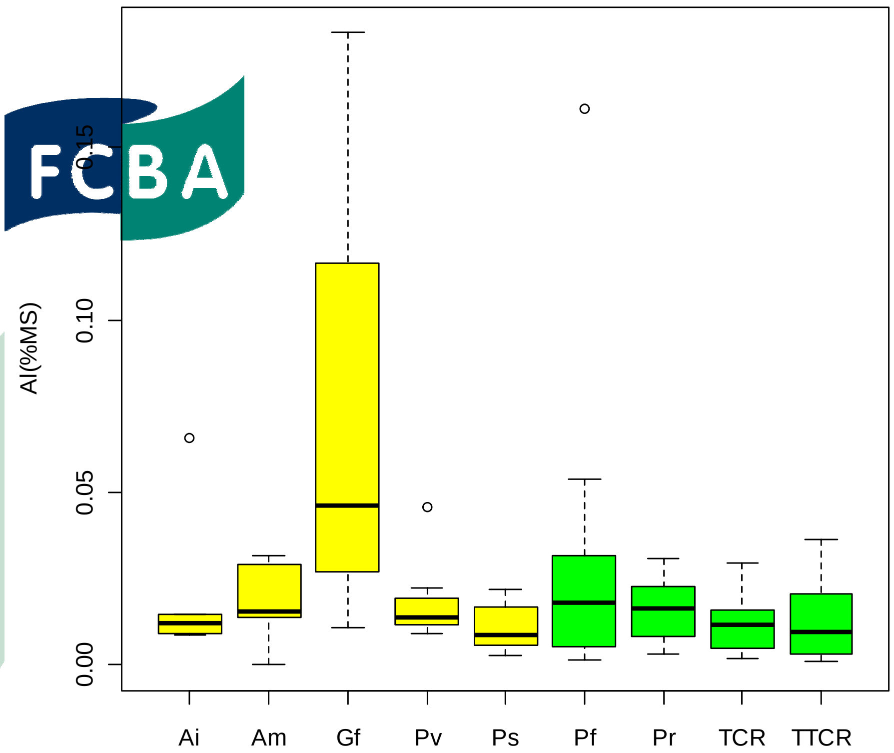


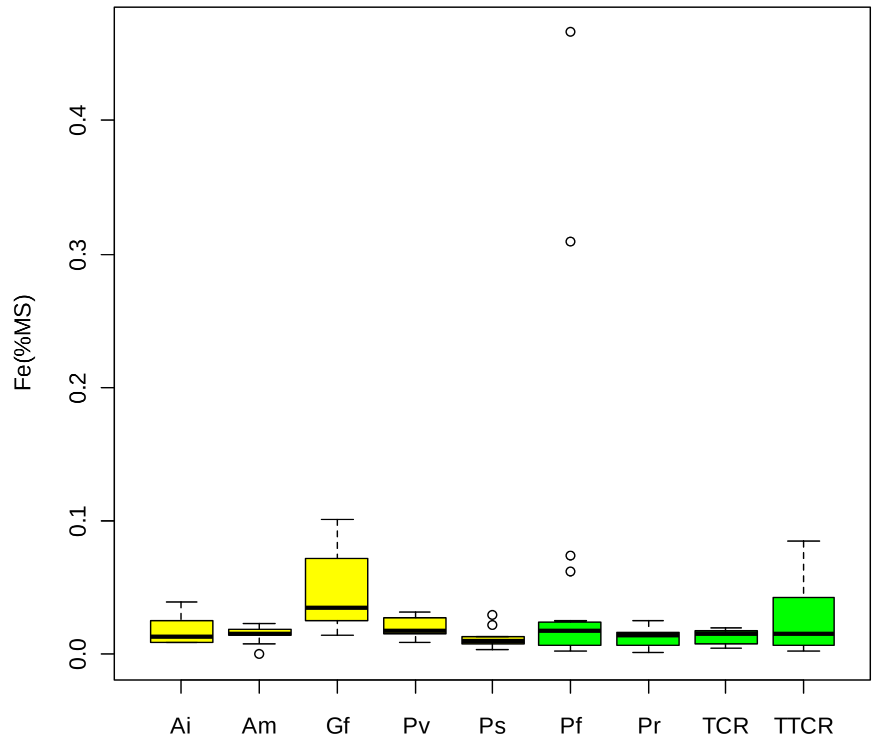


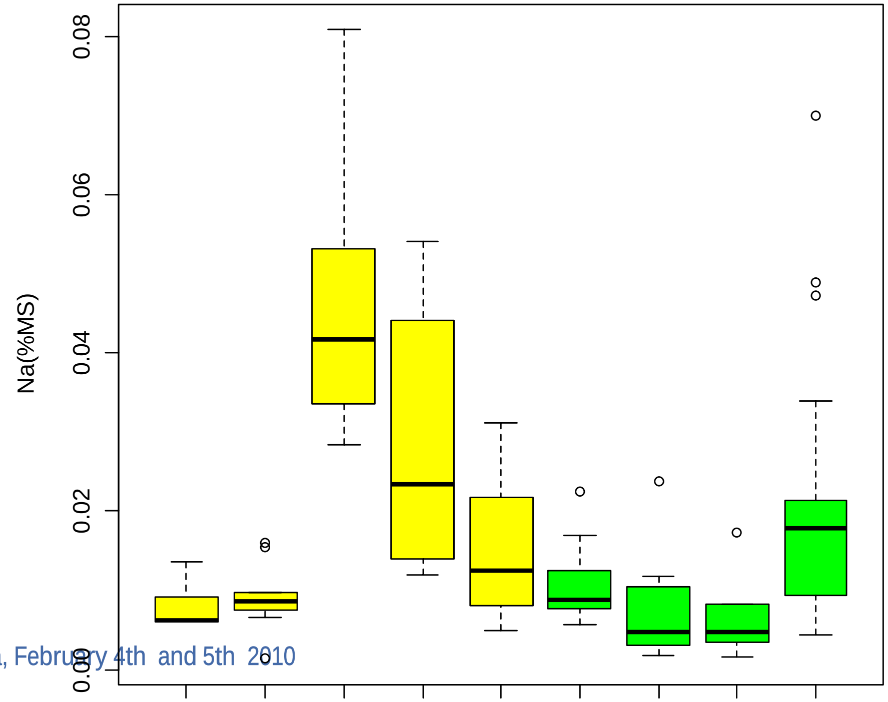


Ash composition: Ca, Mg et K

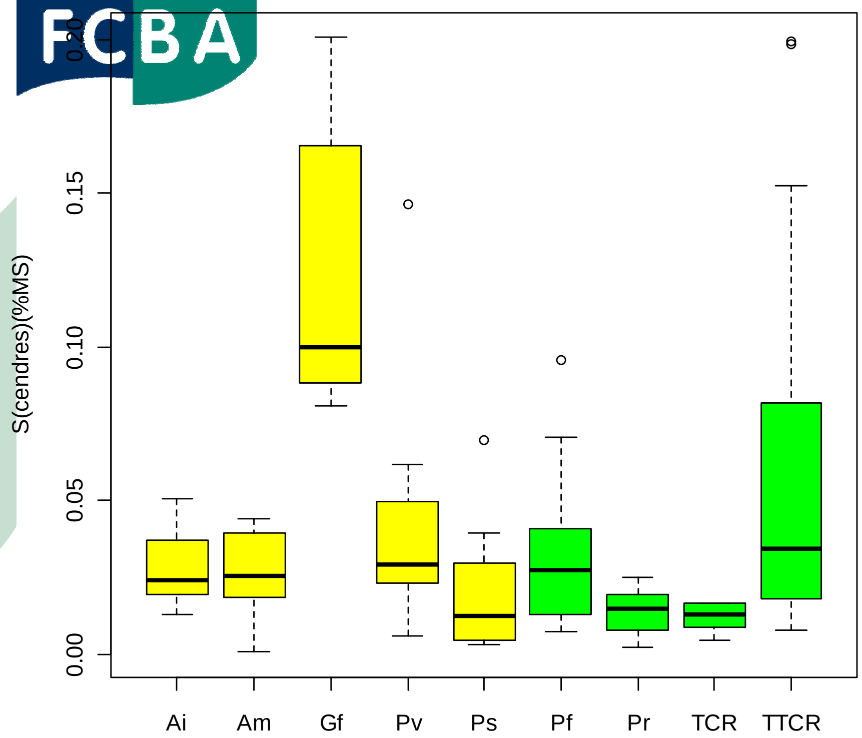


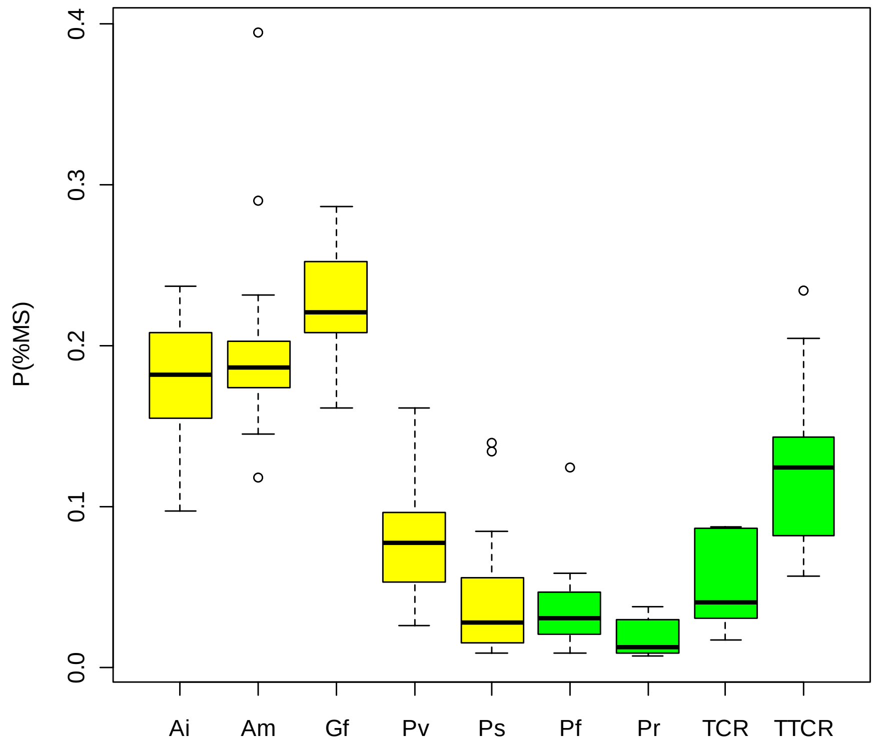






Chemical composition : Al, Fe et Na





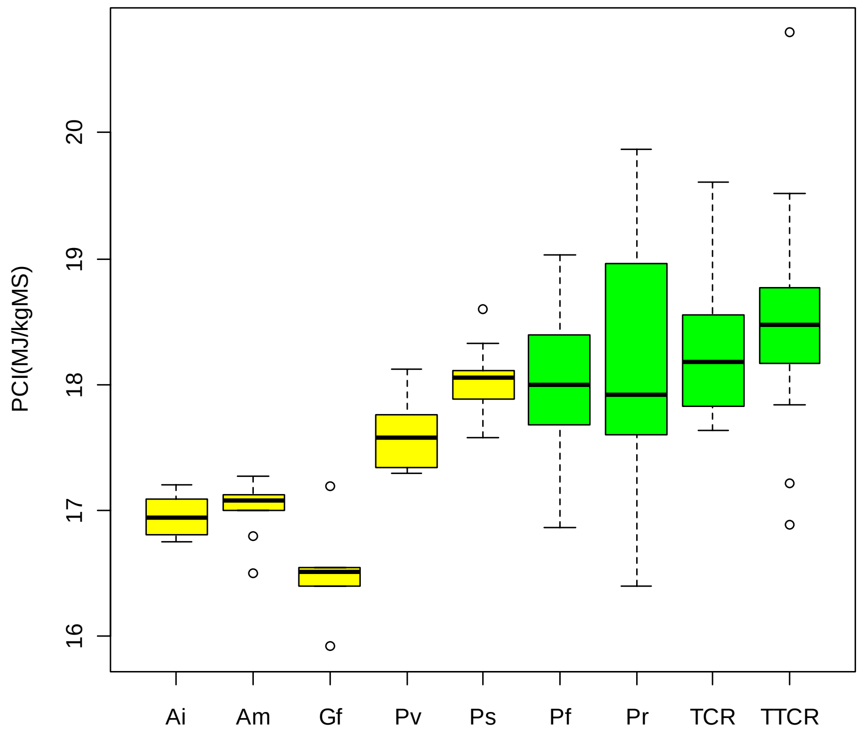
Ash composition :
S and P

Analytical-related questions

- How to measure the melting temperature of ash ?
  - Existing method : visual observation of 4 stages of solid to liquid transformation :
    - fusion
    - softening
    - hemisphere formation
    - fluidisation

- Problem : For the same sample, variations up to 500°C in some températures !!!!

- New analytical method setup by CEA in test
    - "Liquidus" temperature



LHV

Synthesis

- None is perfect !!!! Even biomass !!!! All biomass present advantages and drawbacks depending on the applications for 2nd generation biofuels. The quality can be in same cases adapted or modulated.
- Forestry-biomass present interesting behaviour for both thermochemical and biochemical process, but ash quality could be a problem for gazification.
- N and S : high content for agricultural samples and forestry samples with leaves or very young (VSRC)
- Cl : High levels for agricultural samples and in some specific case also for forestry samples
- Ash composition : agricultural samples rich in Si : forest rich in Ca et K
- Starch and soluble sugars present in some agricultural samples very interesting for biochemical processes; However, higher potential of polysaccharides for forest samples.
- Small variability of LHV, but slightly higher for forestry samples. .

Analytical techniques related issues

- **Nitrogen content**
- **Chemical composition**
- **Ash fusibility temperature and the relation with composition**
- **Different biomass component fine analysis in relation to inhbition during fermentation**
- **Lignin fine structure in relation to tar formation**
- **Analysis of pre-treated biomass**
  - *After torrefaction and/or pyrolyis, char, bio oil, etc*
  - *After pre-treatments prior hydrolysis and fermentation*
- **Repeatability and reproducibility**

- *Round-robin analysis of biomass within this COST action ?*