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Multi-technique characterization of biochar formation

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MULTI-TECHNIQUE CHARACTERIZATION OF BIOCHAR FORMATION

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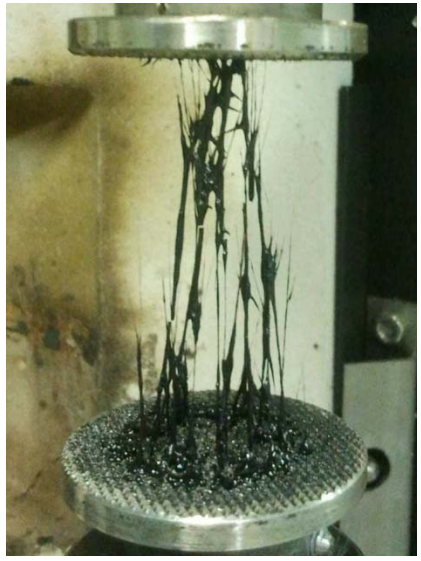
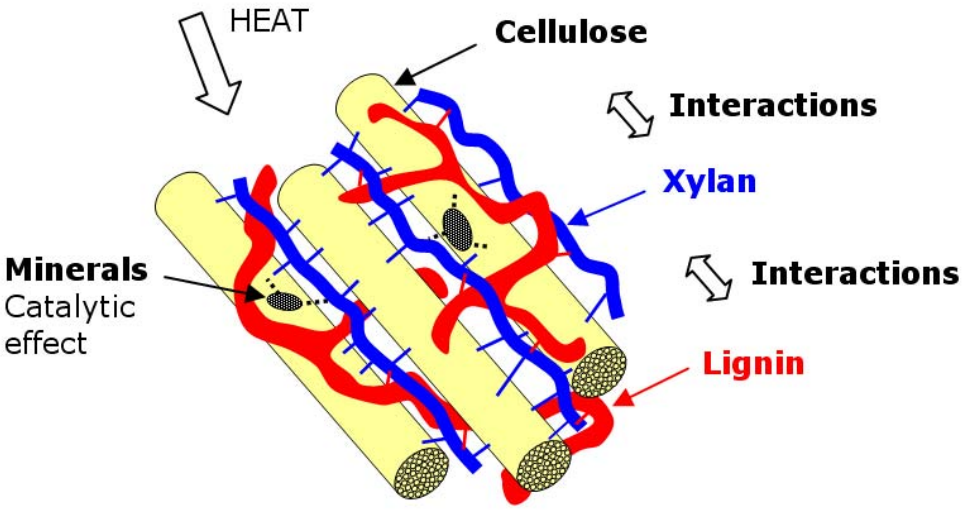
Alba, ECI Biochar, 22/08/2017

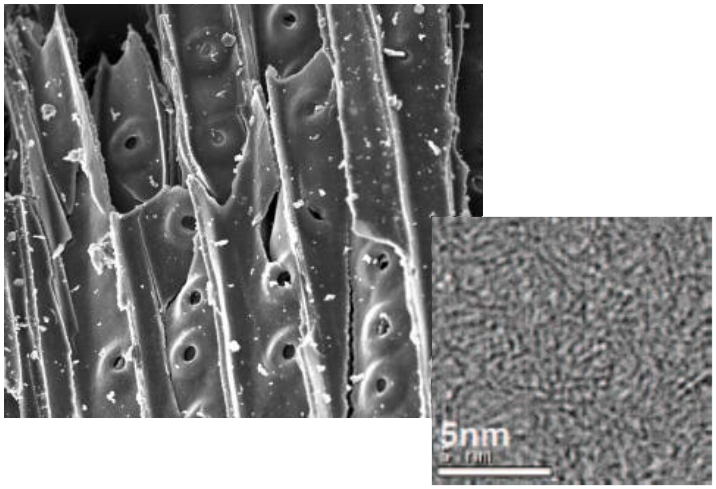


The physical and chemical mechanisms of char formation are complex…

Molecular network of polymers and minerals ⇒ **Intermediate material** ⇗ **Hundreds of volatiles**

Intermediate material ⇘ **Char**



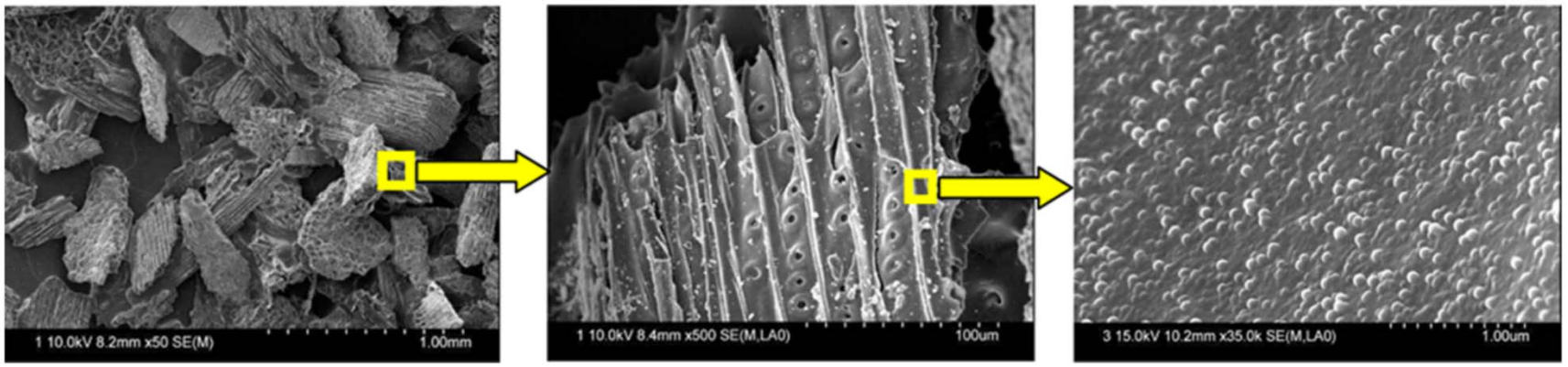


Prof. Manuel Garcia-Perez has pointed out an important question during his Key Note of this conference:

« We need to adress the question why biochar conserves the macro-structure of biomass while many components soften? »

This talk deals with this question.

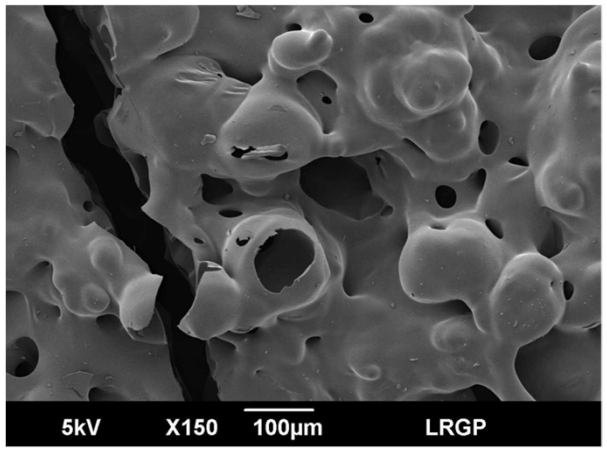
Biochar is formed through an intermediate soft material.



Wood char particles, slow pyrolysis, from mm to µm: bubbles formation at µm length scale (Chem. Eng. Res. Des., 89 (10), 2136, 2011)

Biomass components (notably lignin and hemicelluloses) soften.

Klason, 1901; Göring, 1963; Sharma, 2014



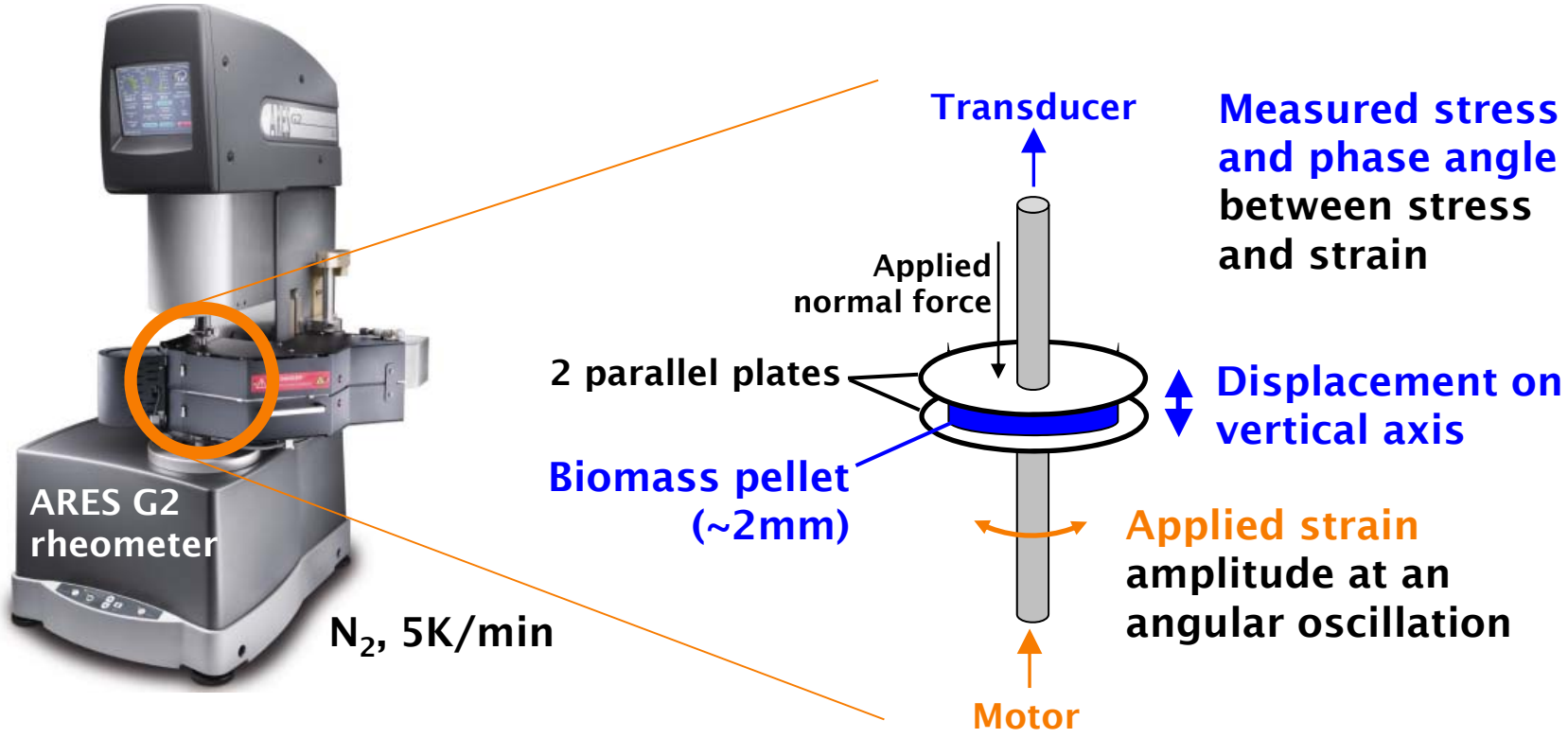
Important to understand how the soft material impacts char formation.

⇒ In-situ analysis of interest to understand the intermediate, labile and soft material

In-situ ^{1}H NMR and rheology have been extensively used for understanding "metaplast" during coal pyrolysis (Sato, 1979, Lynch, 1988, Castro-Diaz, 2005) but <u>not yet for biomass</u>.

Basics of in-situ rheology

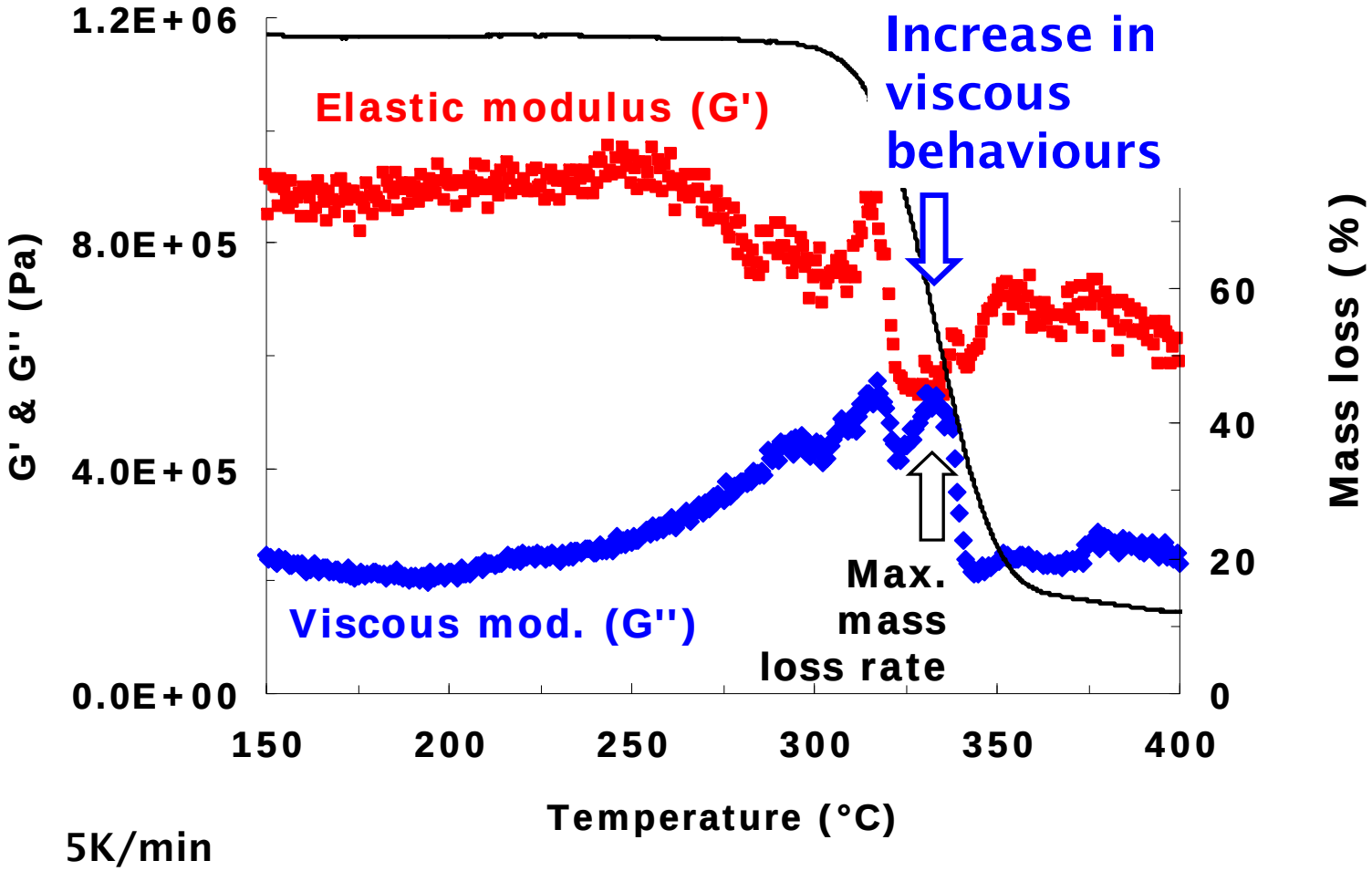
Pyrolysis is conducted inside the rheometer.



Determination of viscous and elastic moduli based on phase angle

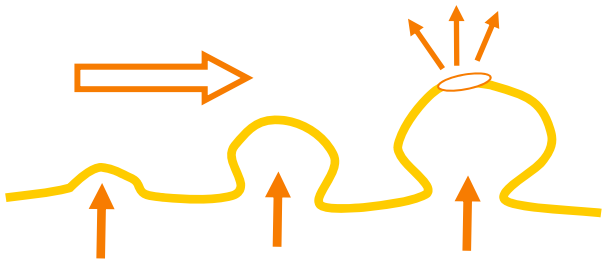
Swelling and shrinking of particles based on the displacement between plates (results not shown)

In-situ rheology during cellulose pyrolysis: it stays mainly hard & elastic (under slow cond.)

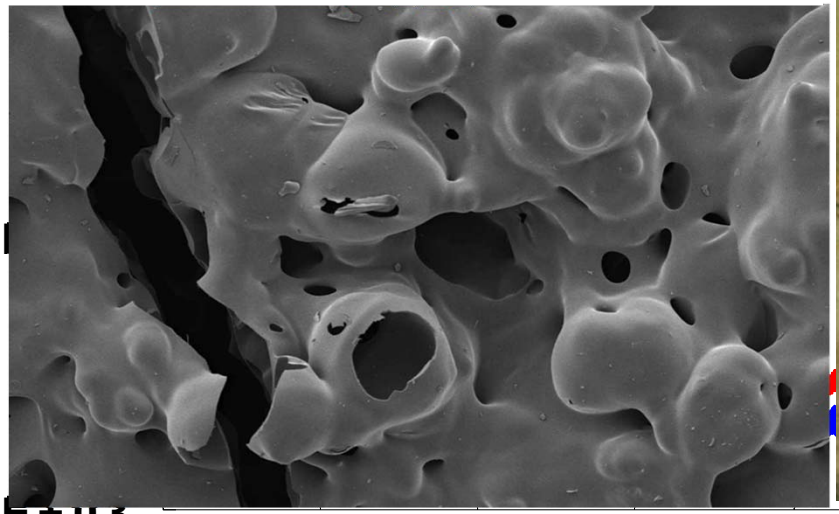


Energy & Fuels, 26 (10), 6432, 2012.

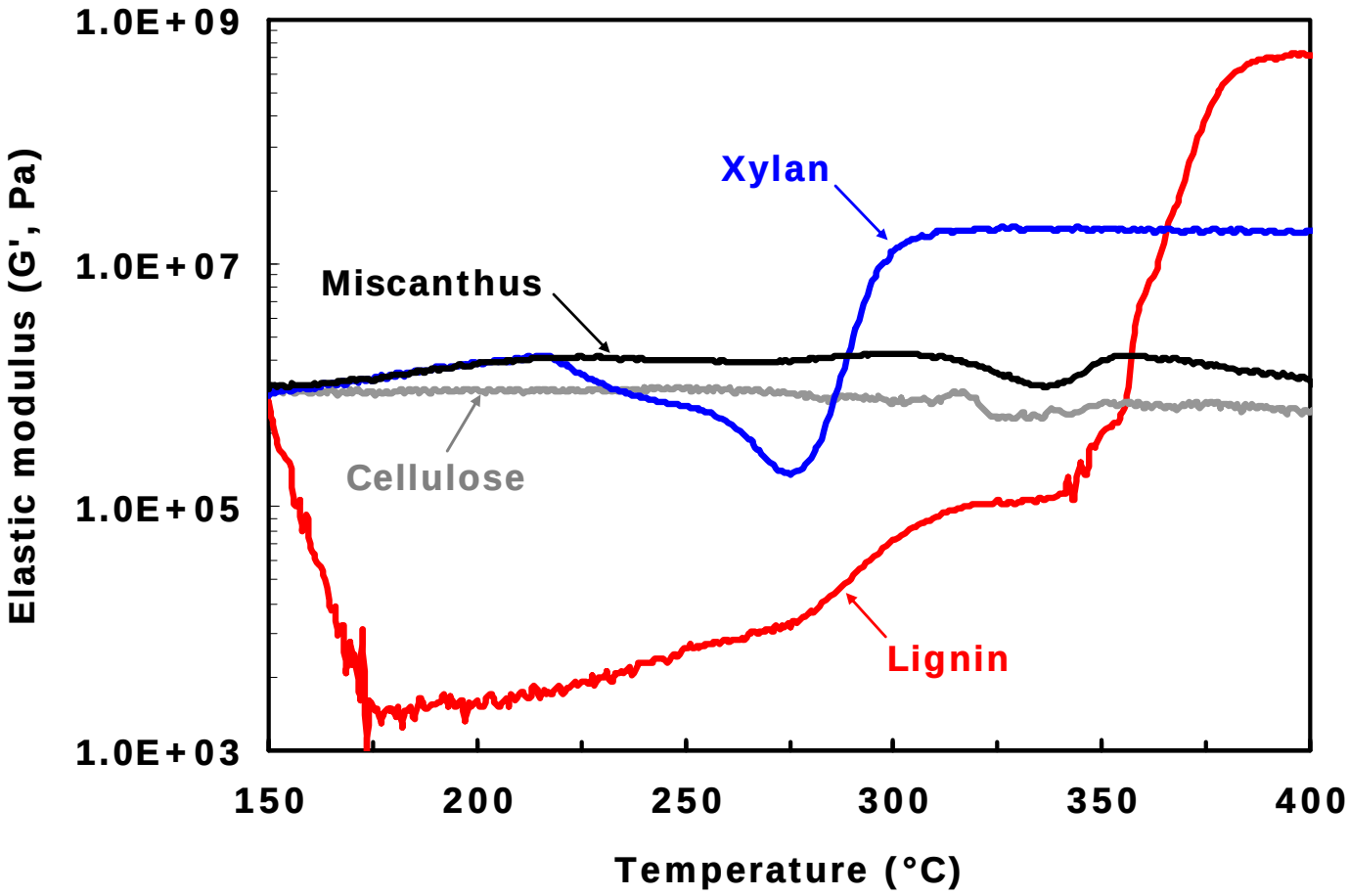
Lignin presents very different behaviours than cellulose.



Formation of a "carbon foam" by volatiles pushing the visco-elastic material.

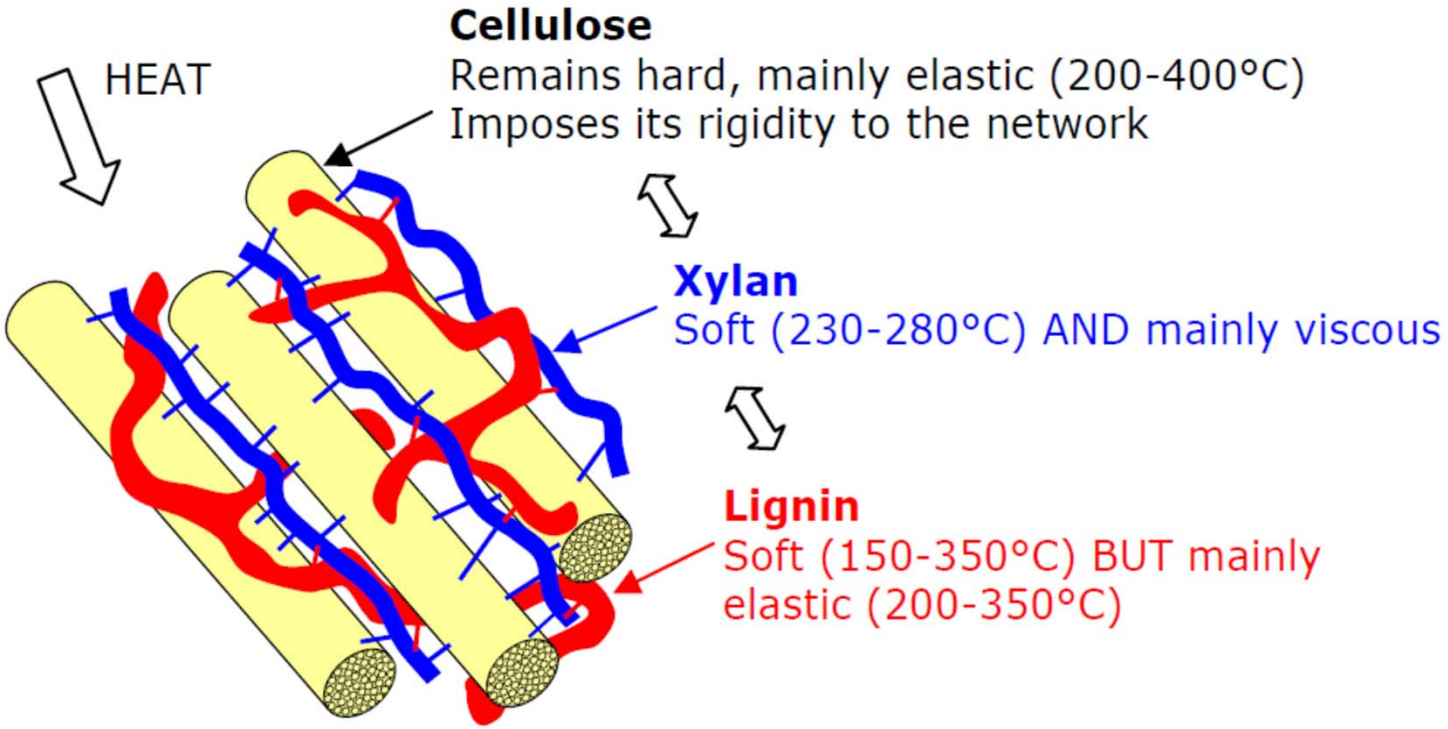


Comparison between cellulose, xylan, lignin and miscanthus for elastic modulus evolution



Lignin softening is not seen in the native network of biomass while G' is 3 orders of magnitude lower & then higher than cellulose.

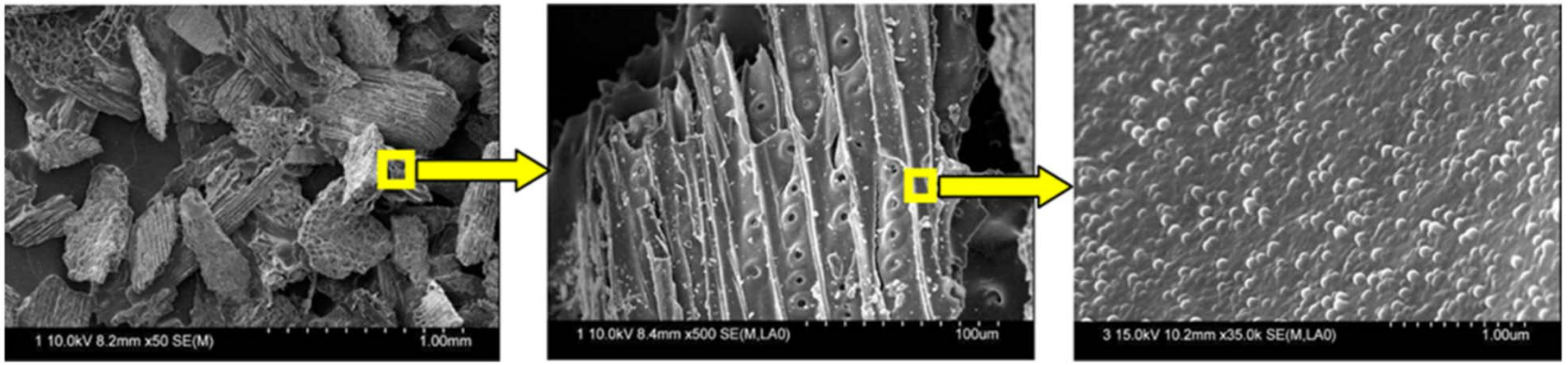
Simplified scheme of visco-elastic properties of fractionated polymers and native biomass

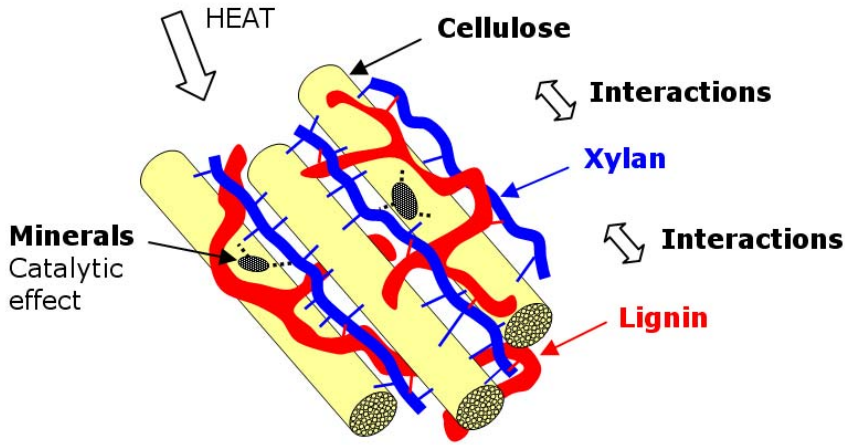


Native network of polymers in miscanthus
Remains hard and mainly elastic (150-400°C)
despite soft xylan and lignin

Energy & Fuels, 26 (10), 6432, 2012.

This finding explains why char globally keeps the same macro-structure of biomass cells (at slow pyrolysis) although forming an intermediate soft material.





Cellulose maintains the overall structure of macro-pores under slow conditions.

Basics of in-situ ^{1}H NMR

Pyrolysis is conducted inside a specific NMR probe (heated up to 500°C).

In-situ ^{1}H NMR analyses protons transverse relaxation (T_2) signal as a function of temperature

= "Proton magnetic resonance thermal analysis" (PMRTA)

(Lynch, 1988, Sakurov, 1993, 2004, Castro-Diaz, 2005)

Protons in rigid structures

= strong magnetic coupling

= short relaxation time

Protons in mobile structures like liquids

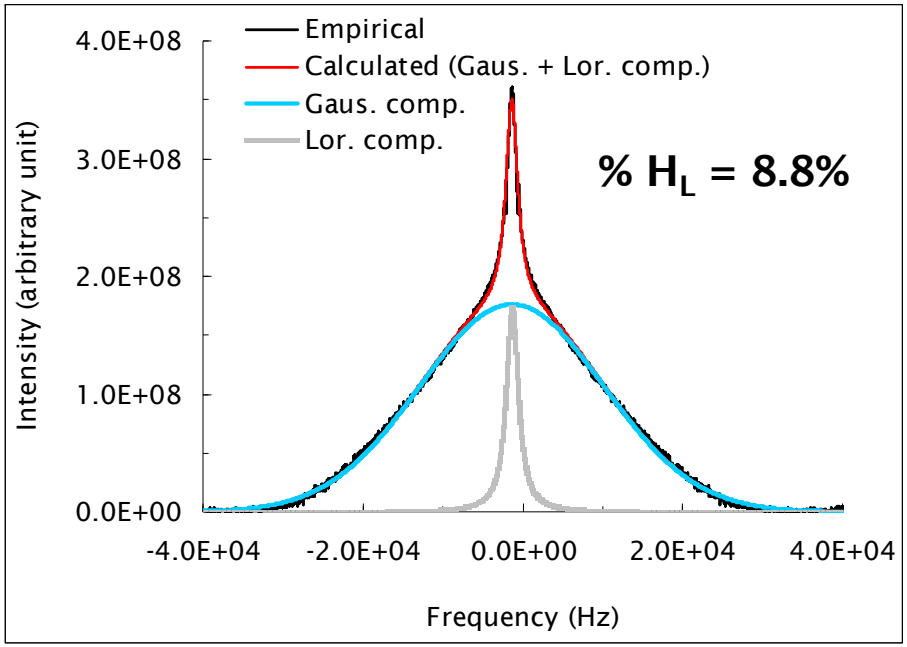
= weaker magnetic interactions

= long relaxation time

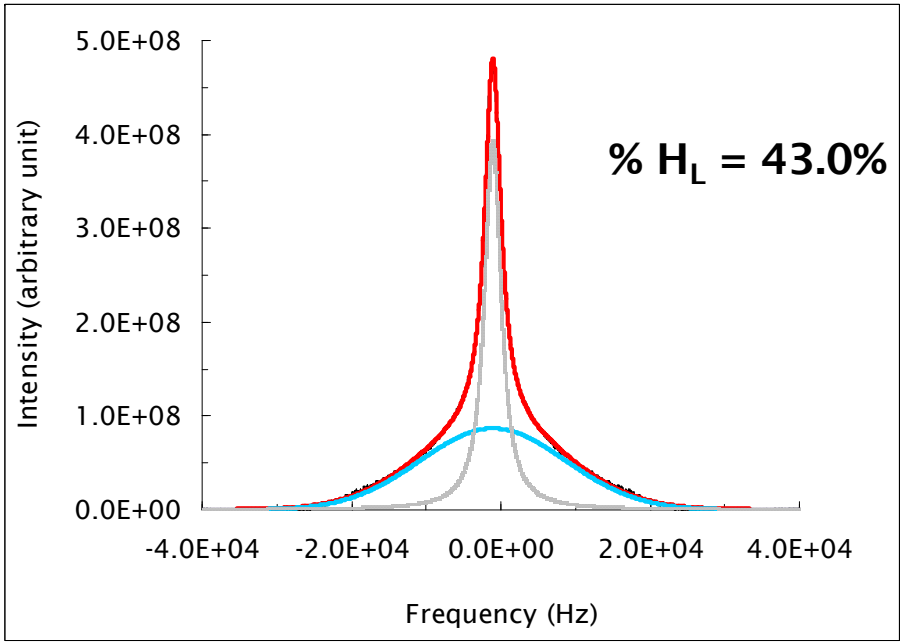
^{1}H NMR spectra were deconvoluted into Gaussian (solid-like) and Lorentzian (liquid-like) distribution functions

Fraction of mobile protons (% H_L) (or of "fluid phase") calculated as:

$$\% H_L = \frac{\text{Lorentzian area}}{\text{Lorentzian + Gaussian areas}}$$



Miscanthus at 200˚C

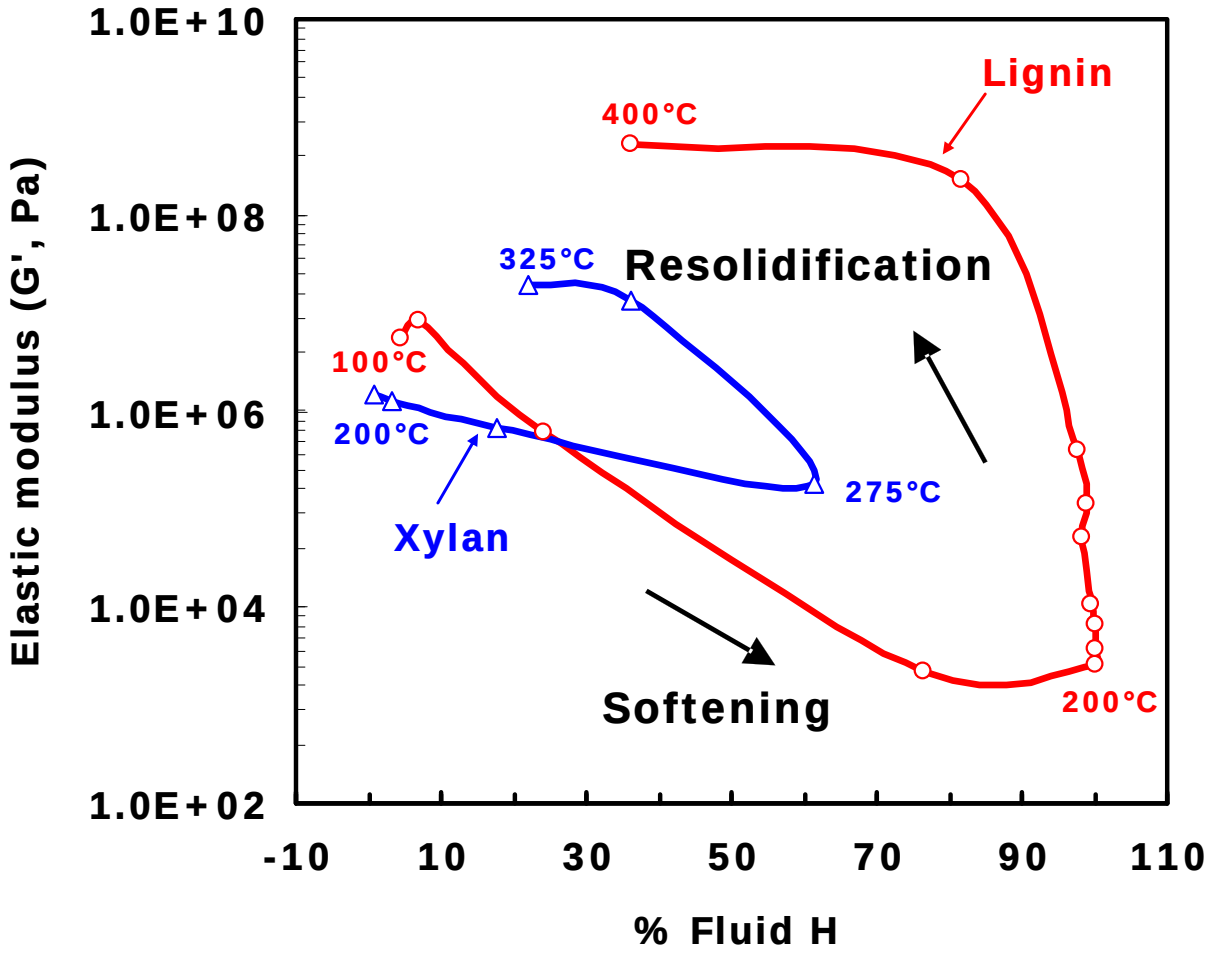


Miscanthus at 300˚C

Fluid phase increases from 200 to 300˚C

ChemSusChem, 5, 1258, 2012

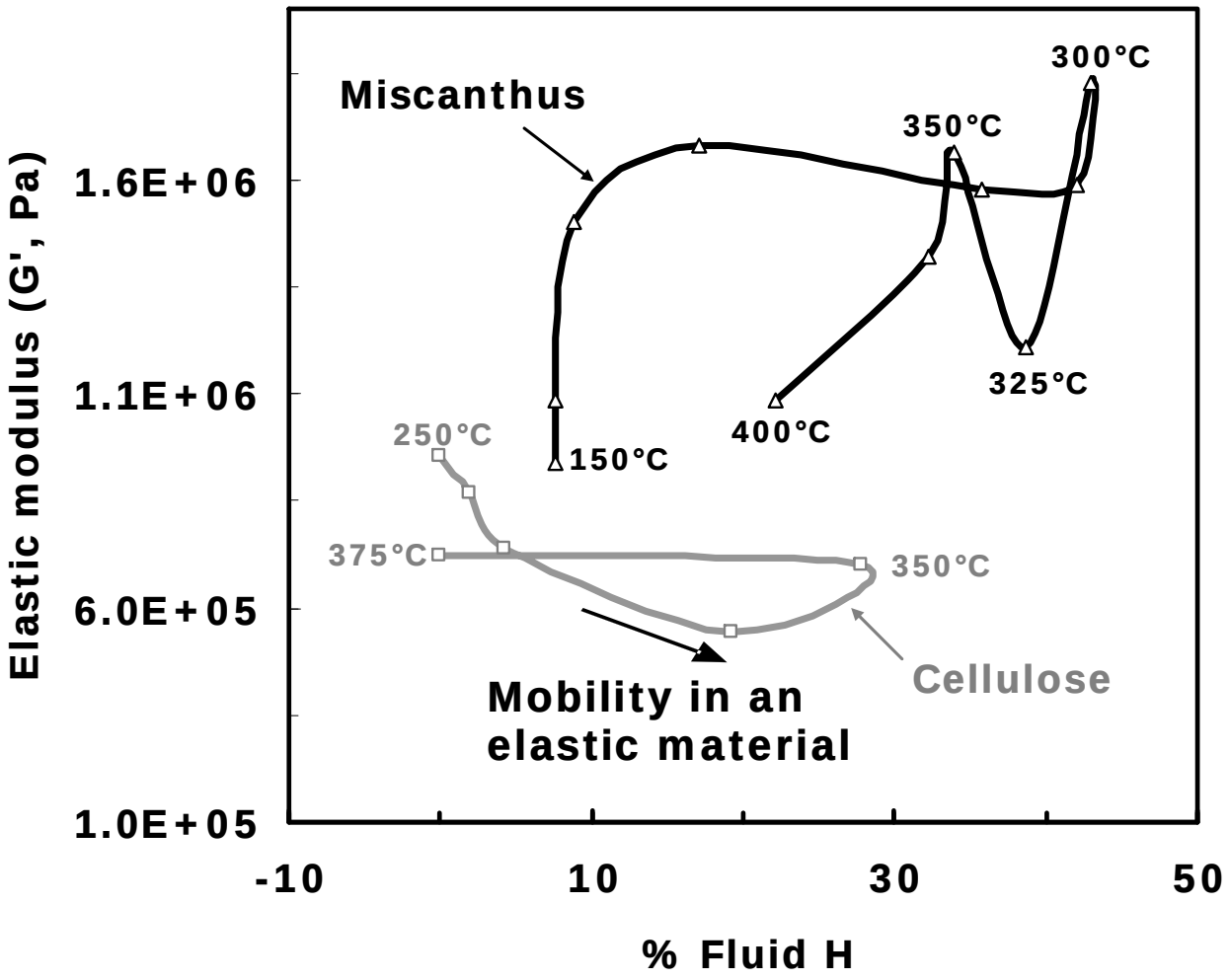
Comparison between ^{1}H NMR (% of mobile protons) and rheology (elastic modulus)



During resolidification, molecular mobility is still present in a solid-like material (inside cages).

Energy & Fuels, 26 (10), 6432, 2012.

Comparison between ^{1}H NMR (% of mobile protons) and rheology (elastic modulus)



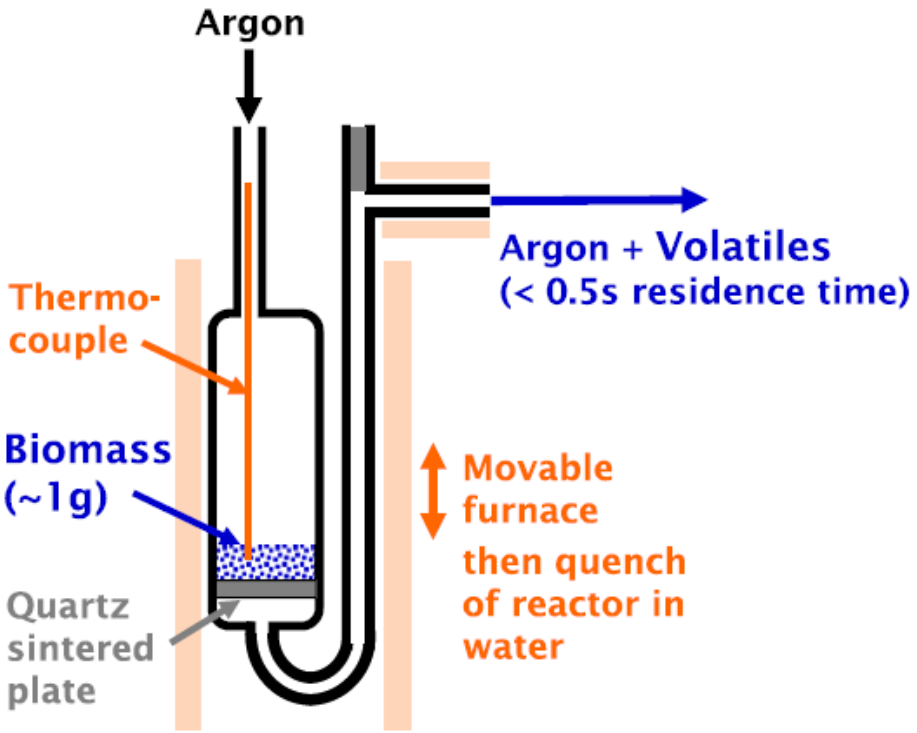
Mobility of cellulose is developed in an elastic solid-like material ("cavities" Mamleev, JAAP, 2009**).**

Miscanthus very complex

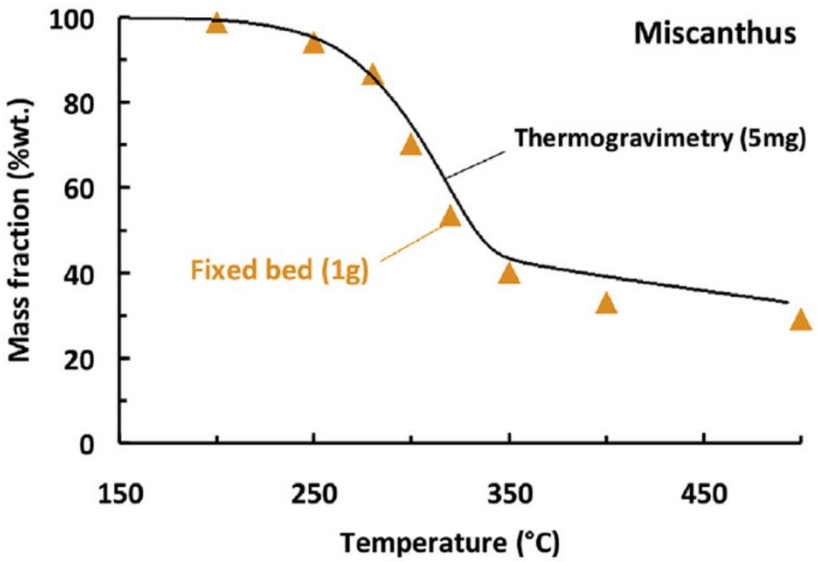
Other complementary methods need to be used.

In-situ analysis were completed by ex-situ ^{13}C NMR analysis of char for characterization of the chemical moieties in char.

Same biomass pyrolyzed in an analytical fixed bed reactor



Good control of mass transfers, similar mass loss than in TGA (mg) = chemical regime

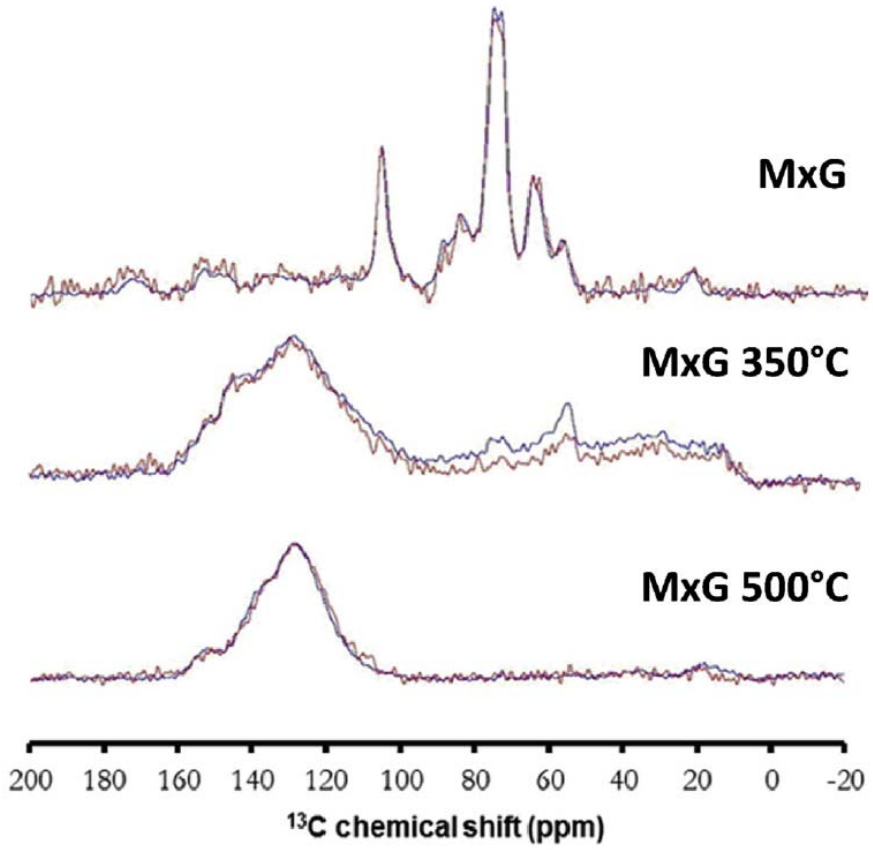


Cross Polarisation/Magic Angle Spinning (CP/MAS) method is fast but not quantitative because of different magnetisation transfer rates from ^{1}H to ^{13}C depending on ^{13}C nuclei environments.

Direct polarisation (DP) is quantitative but very long (~ 10 days for one spectrum).

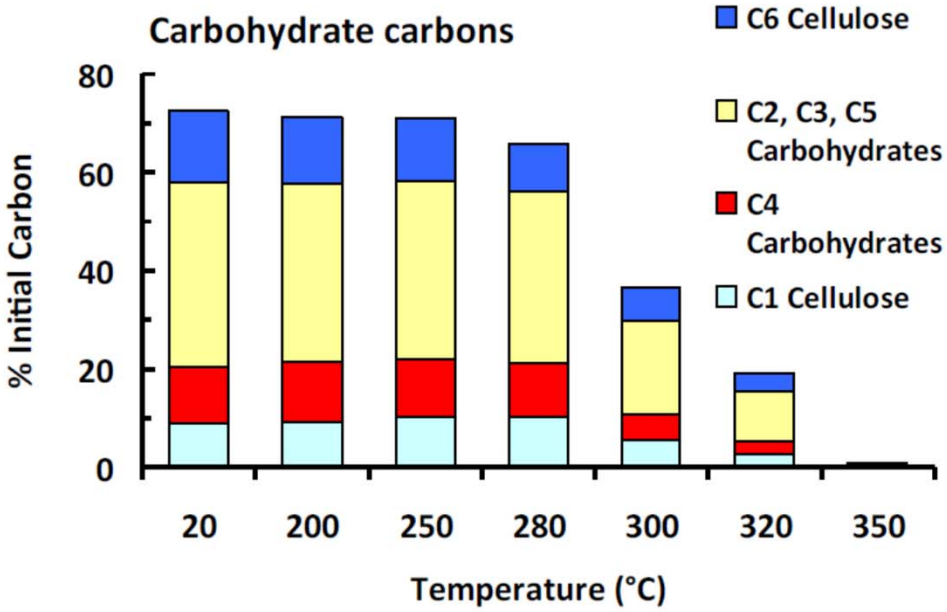
A specific CP/MAS method has been found to give similar spectra than DP/MAS but 50 times faster.

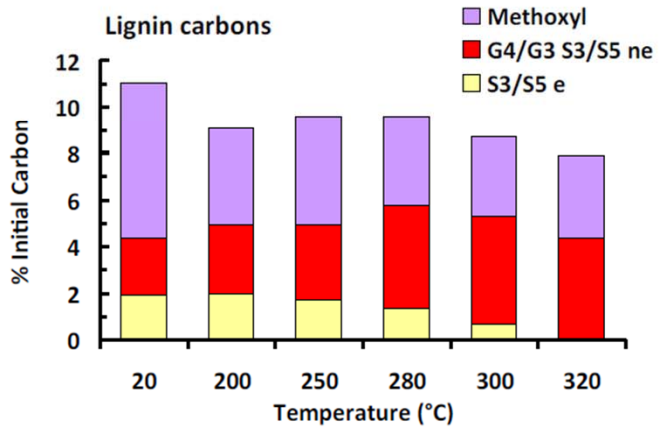
+ 2D ^{1}H-^{13}C solid state NMR at 750MHz



Anal. Chem., 87 (2), 843, 2015
Carbon, 108, 165, 2016

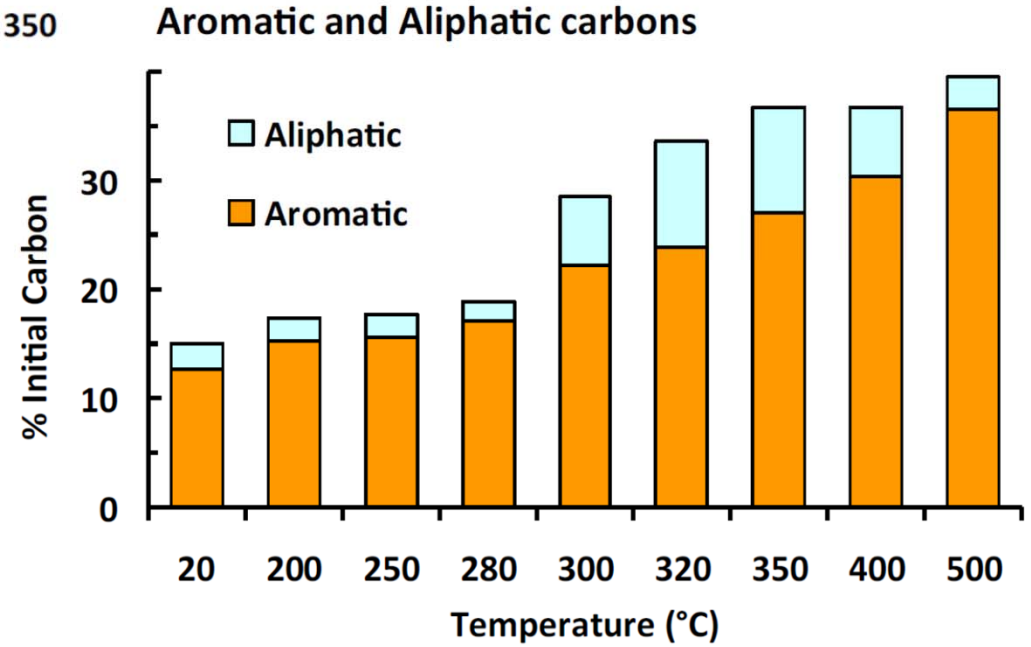
Quantitative evolution of main chemical moieties in Miscanthus chars (C molar balance)





Carbon, 108, 165, 2016

<u>Formation</u> of aromatic carbons mainly from holocellulose (for this biomass)

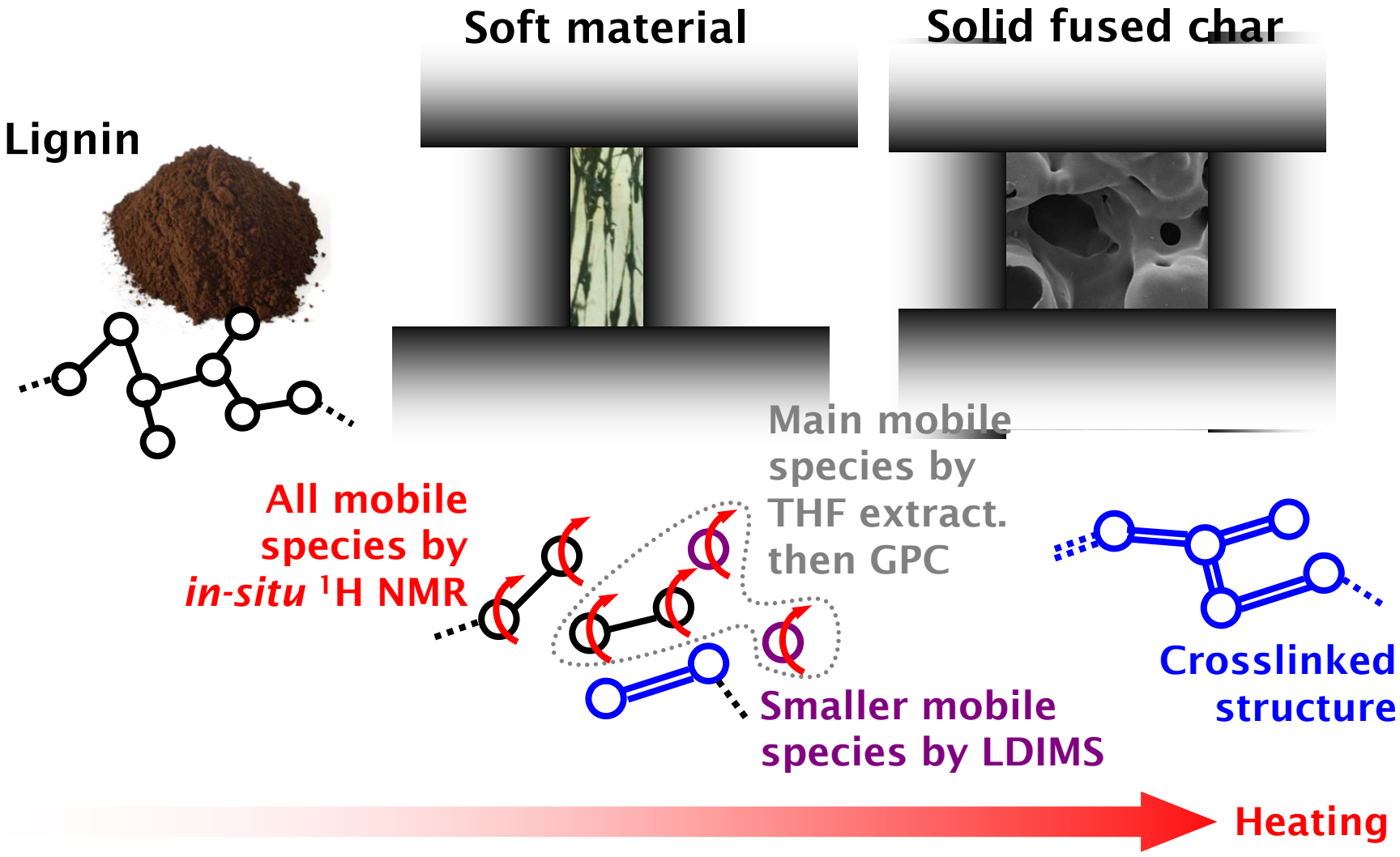


An exemple on the combination of various analytical methods for lignin char formation

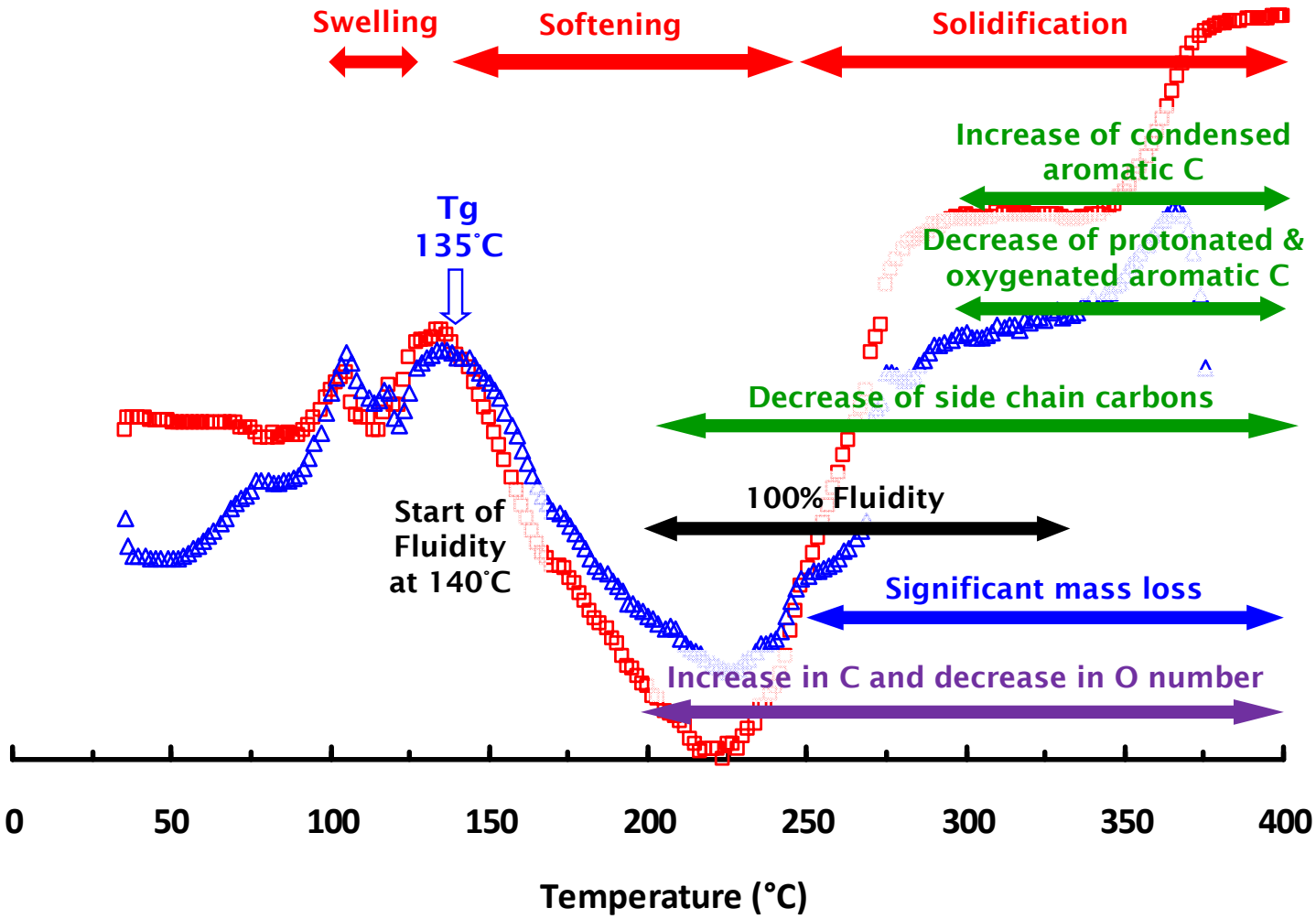
TG	→	Mass loss
DSC	→	Glass transition, heats of reactions
^{13}C and ^{31}P NMR	→	Evolution of chemical moieties
In-situ rheology	→	Swelling/shrinking, softening/solidification
In-situ ^{1}H NMR	→	Mobility
GPC-UV	→	Molecular weight distribution of major mobile species
LDI FT ICR MS	→	Analysis of some mobile species

ACS Sust. Chem. Eng. 5 (8), 6940, 2017

An exemple on the combination of various analytical methods on lignin char



Physical-chemical mechanism of lignin char formation proposed based on these methods



ACS Sust. Chem. Eng. 5 (8), 6940, 2017

To conclude, various techniques are needed to understand char formation.

We want to share our devices…

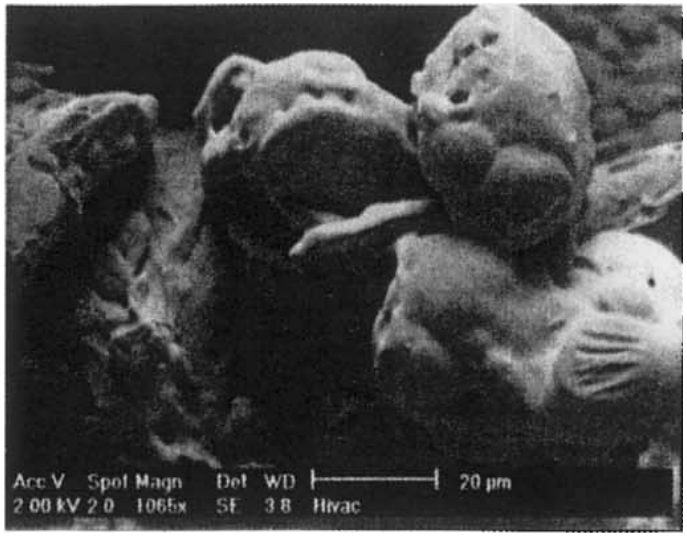
You are welcome in Nancy!

Our coffee break

The Stanislas square

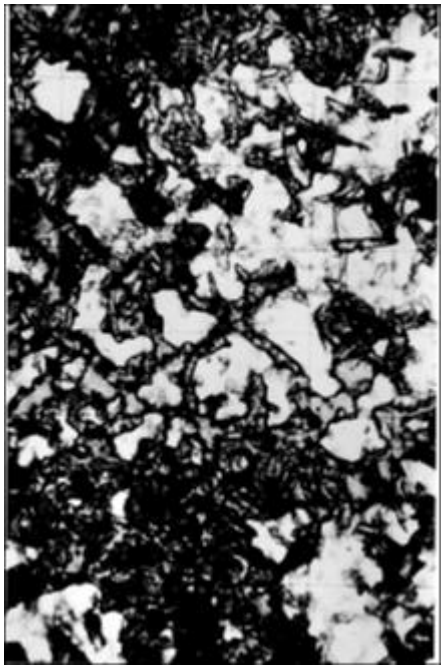
Supplementary slides

Biomass pyrolysis produces an intermediate visco-elastic material evidenced by microscopic analysis



Xylan and lignin form a visco-elastic material at slow and fast heating rates (Fisher et al., 2002)

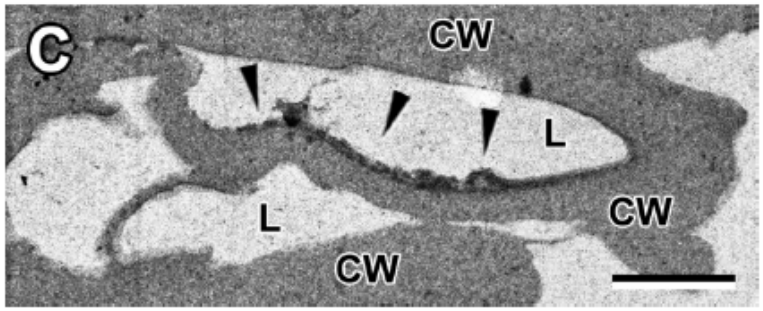
Cellulose before pyrolysis



After pyrolysis

Cellulose produces a viscous material at high heating rates (Boutin et al., 1998)

Structural evolution of biomass material undergoing pyrolysis analysed by microscopic analysis.



Arrows show pyrolysis product coating the internal cell wall of a wood fiber (Haas et al., En&Fuels, 2009)

The mechanisms of the visco-elastic material formation from biomass are not yet understood

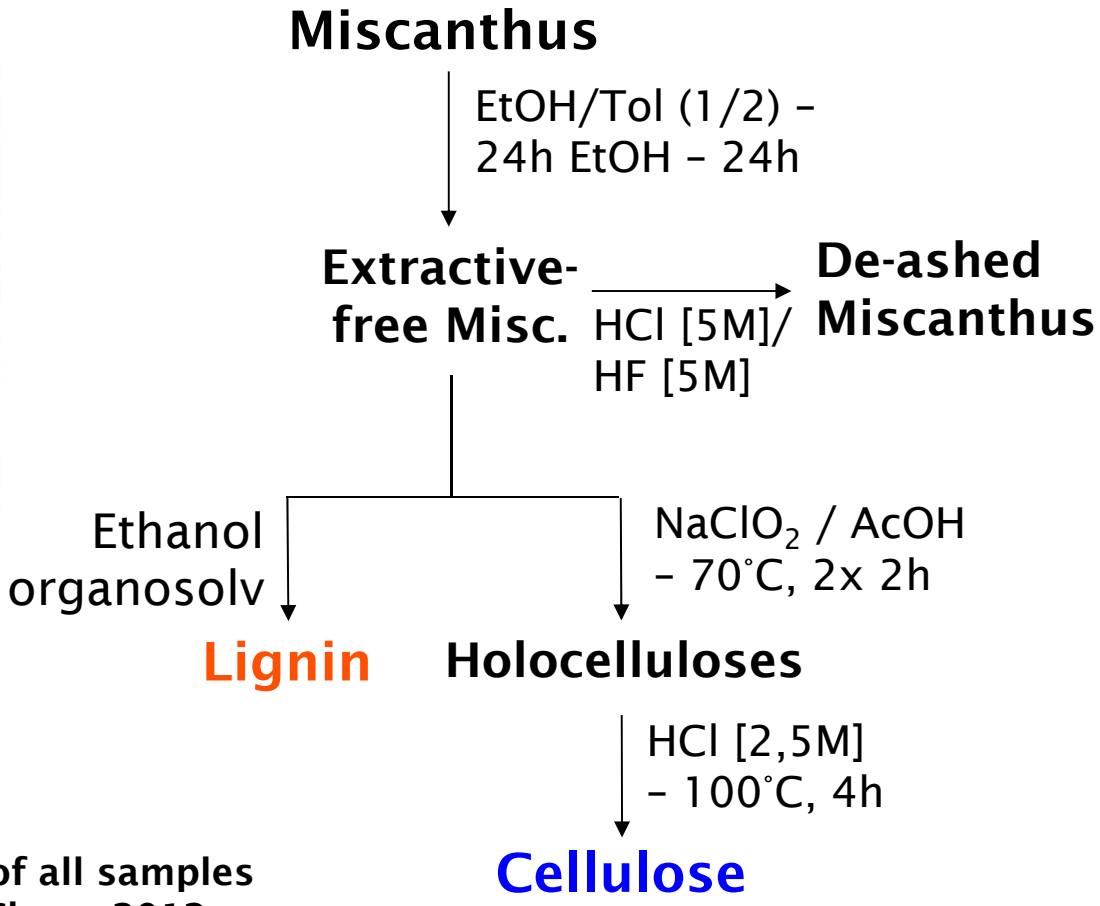
This intermediate visco-elastic material is very important for:

mass transfer mechanisms (Jarvis, 2011, Dufour, 2011)
chemical mechanisms (Lédé, 2002, Castro-Diaz, 2005)
and the selectivity of thermo-chemical processes

⇨ **In-situ ^{1}H NMR and rheology have been extensively used for understanding "metaplast" formation in coal** (Sato, 1979, Lynch, 1988, Castro-Diaz, 2005) **but not yet for biomass**

Experiments was conducted on polymers carefully extracted from biomass (miscanthus)

Miscanthus



Elemental and mineral analysis of all samples given in Dufour et al., ChemSusChem, 2012

It is important to extensively analyse:

cellulose composition and structure: cristallinity index (by XRD), degree of polymerization (DP by GPC), ash content

(Dufour et al. ChemSusChem, in press)

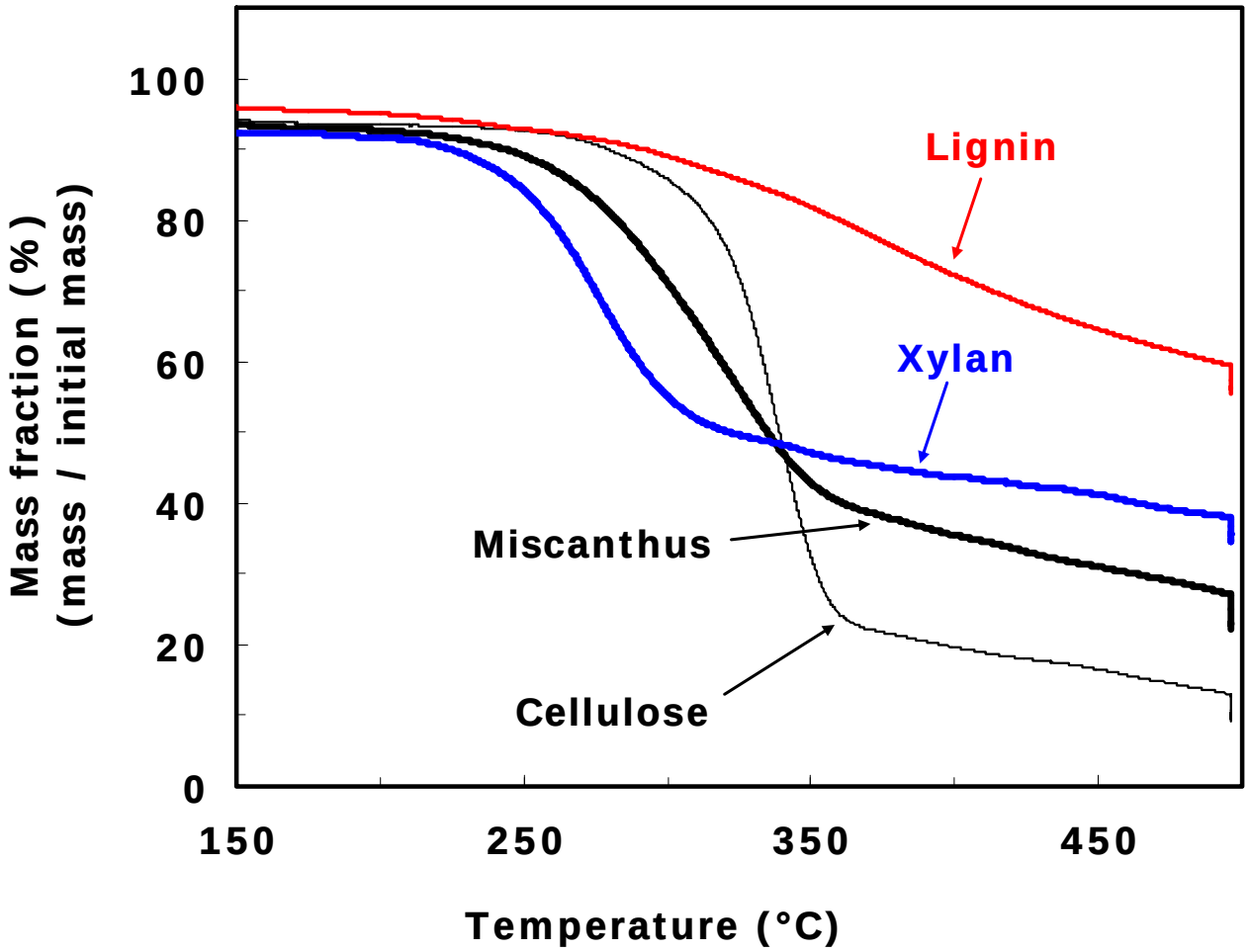
lignin structural compositions by ^{13}C, ^{31}P NMR, FT-IR spectroscopies and GPC, ashes, etc.

(El Hage, 2010)

Lignin extracted by the organosolv process is close to the native one (El Hage, 2010)

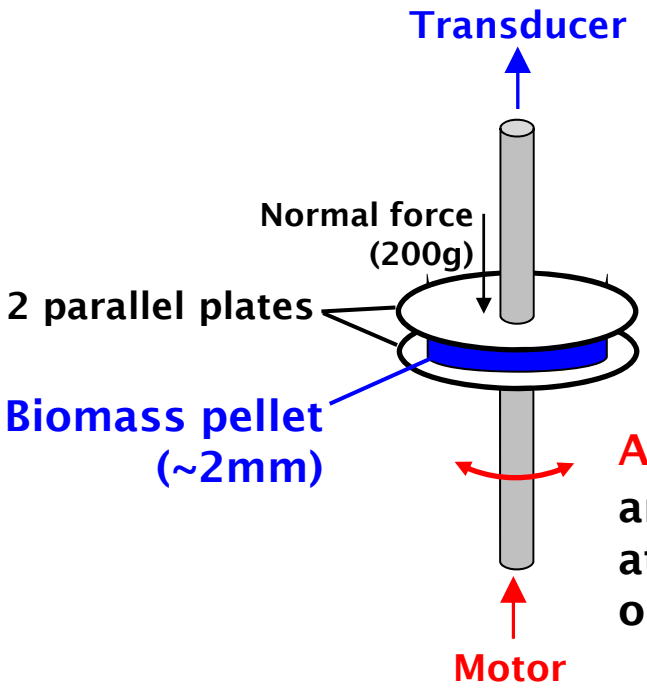
Mass loss of samples

(5K/min, ~1mg of sample, TG-DSC 111, Setaram France)



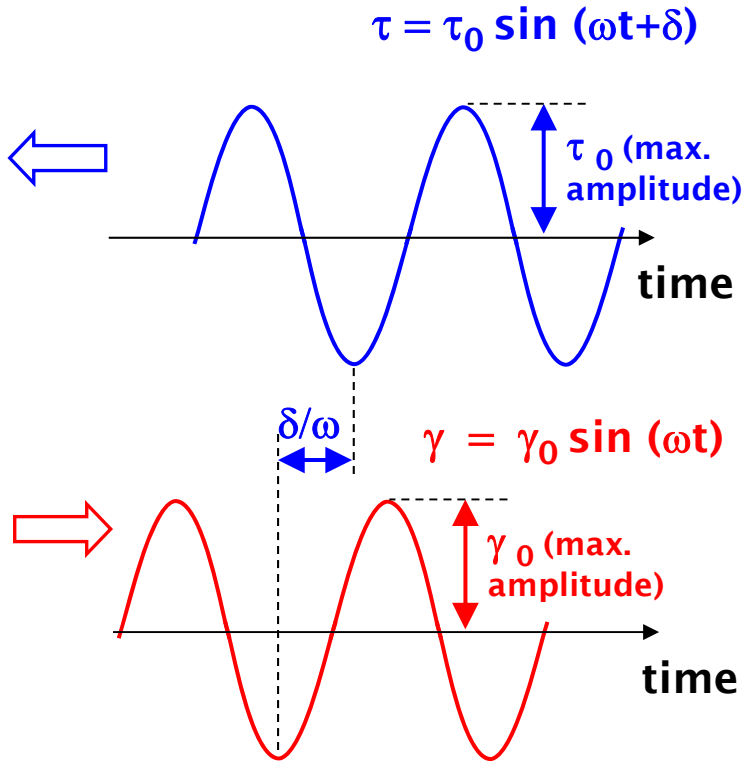
Temperature of maximum mass loss rate: xylan – 275° C, cellulose – 340° C, lignin - 380° C.

Basics of mechanical spectroscopy



Measured stress (τ) and phase angle (δ) between stress and strain

Applied strain amplitude (γ=0.1%) at an angular oscillation (ω=1Hz)

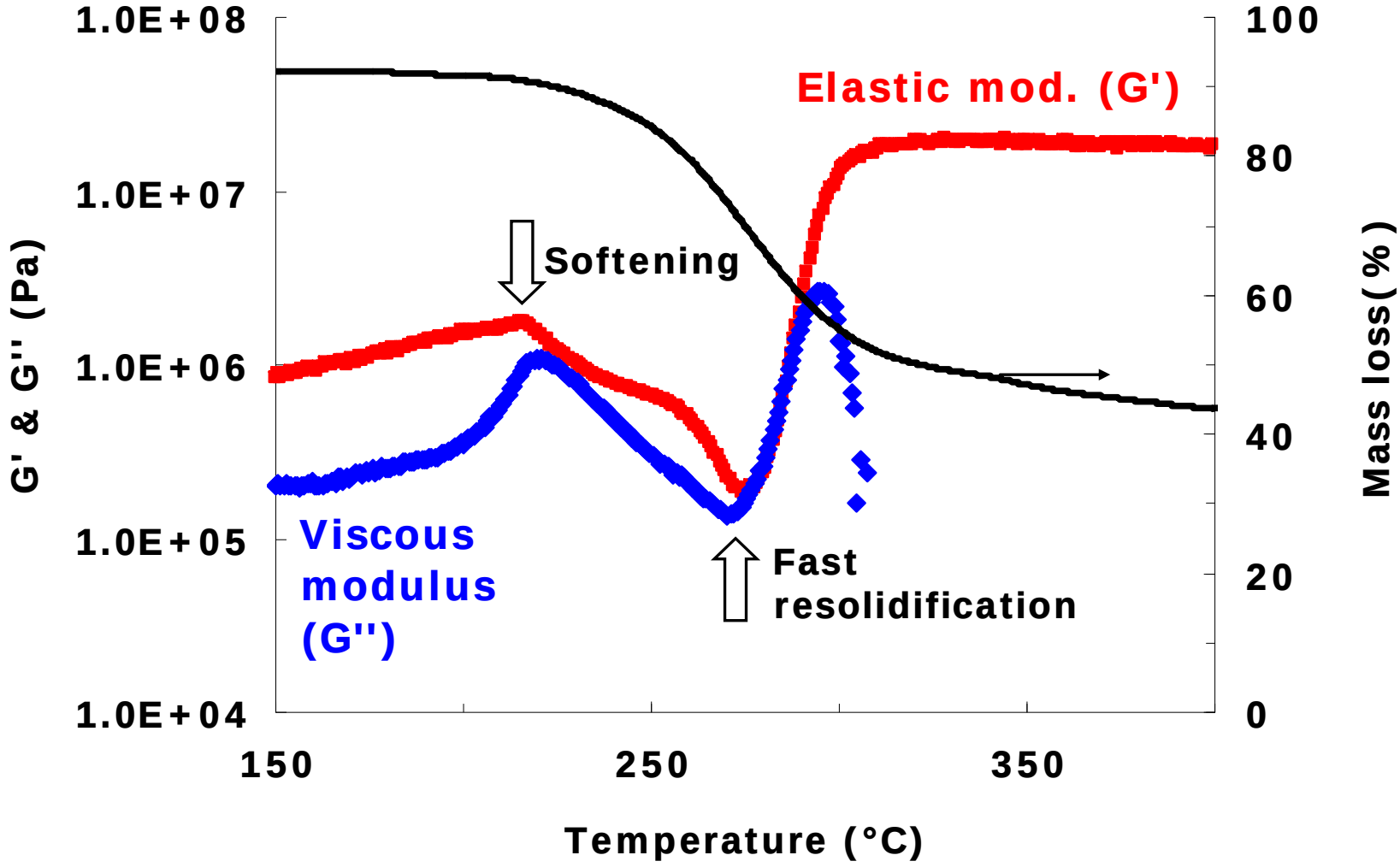


$G' = \cos(\delta)\ \tau_0 / \gamma_0$ — **G' (Pa) = elastic modulus** proportional to the mechanical elastic energy stored and reversibly recovered

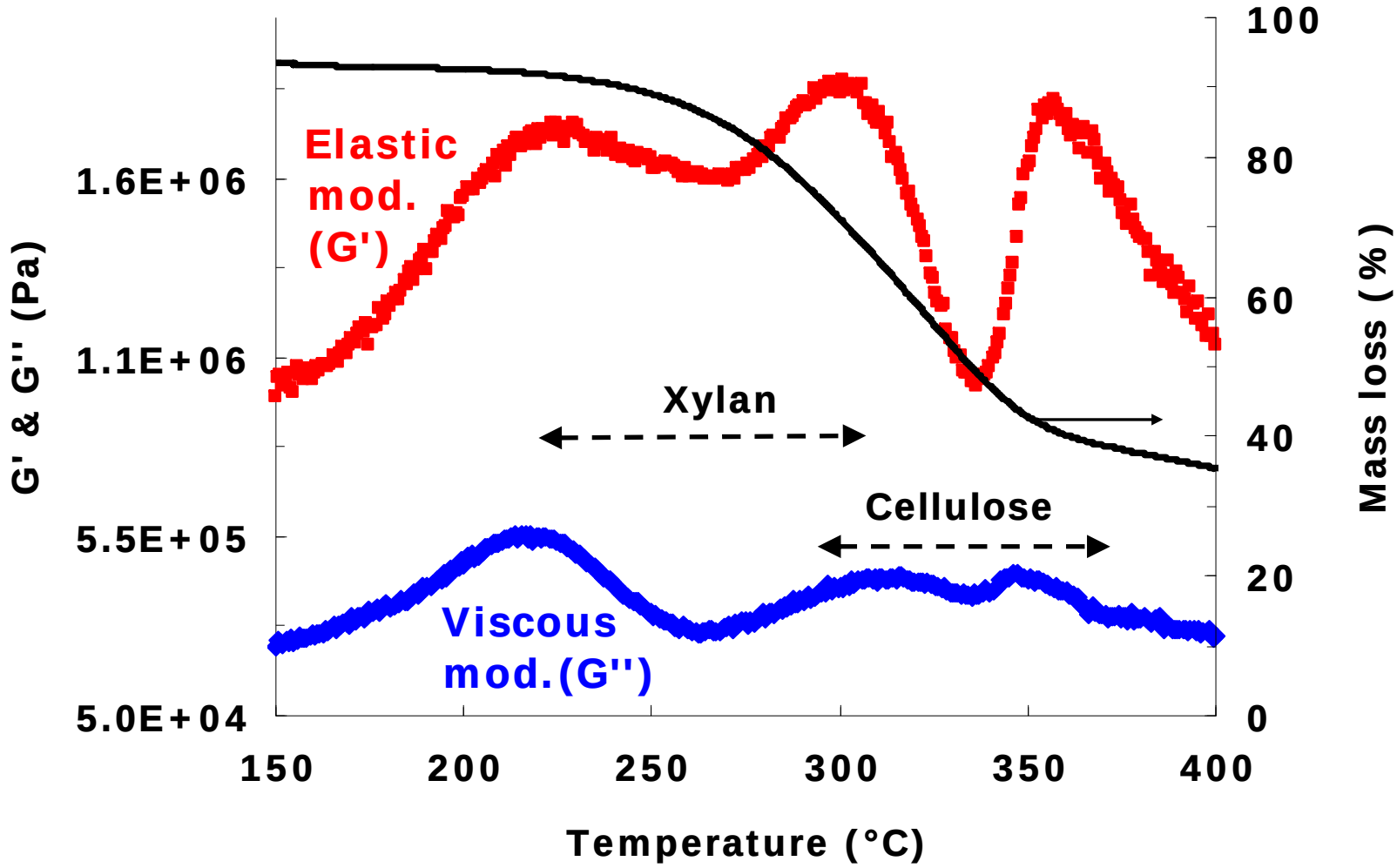
$G'' = \sin(\delta)\ \tau_0 / \gamma_0$ — **G" (Pa) = viscous modulus** proportional to the mechanical energy irreversibly lose through viscous dissipation

$\tan(\delta) = G''/G'$ — tan δ > 1, mainly viscous; tan δ < 1, mainly elastic

Rheological signature of xylan

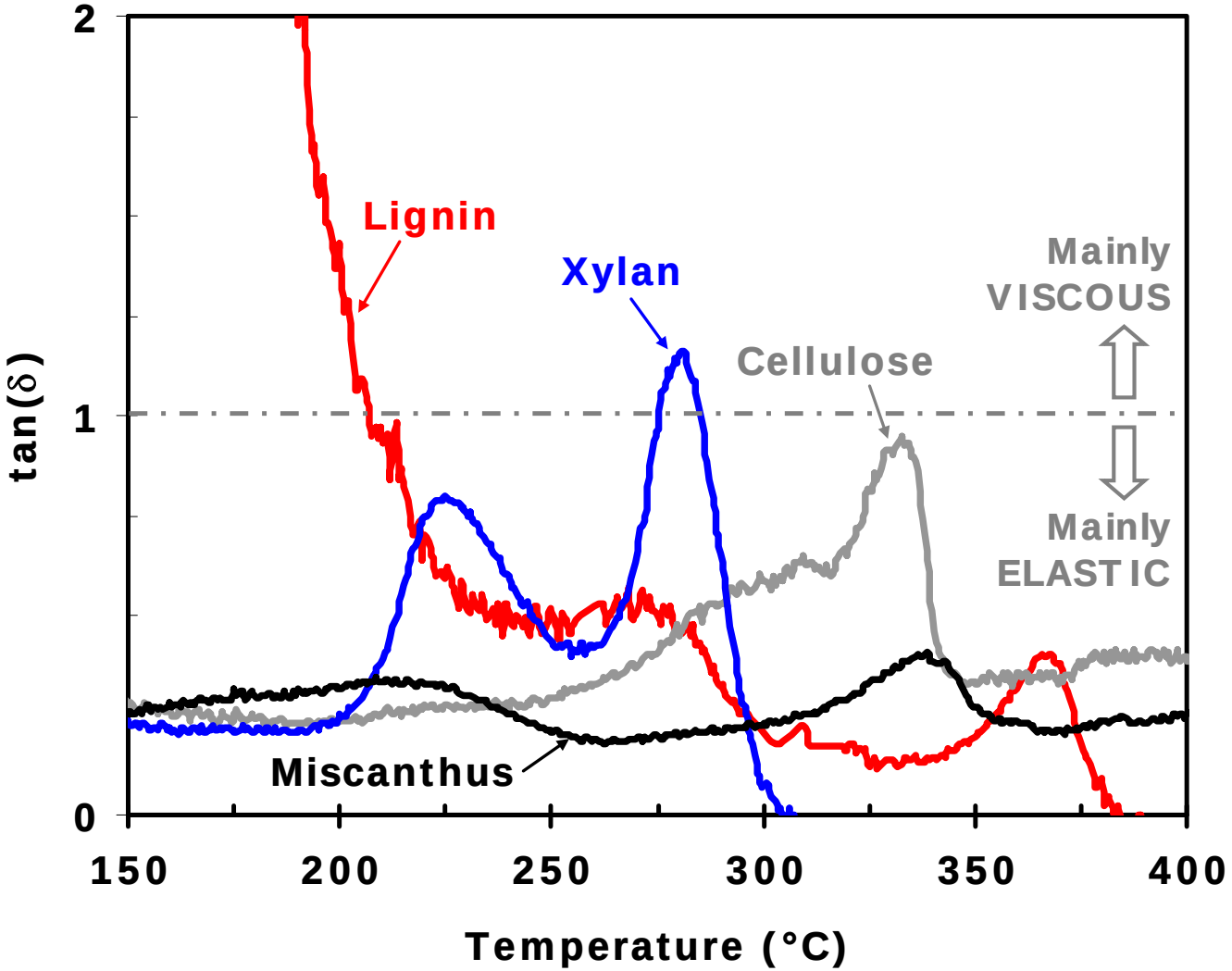


Rheological signature of miscanthus

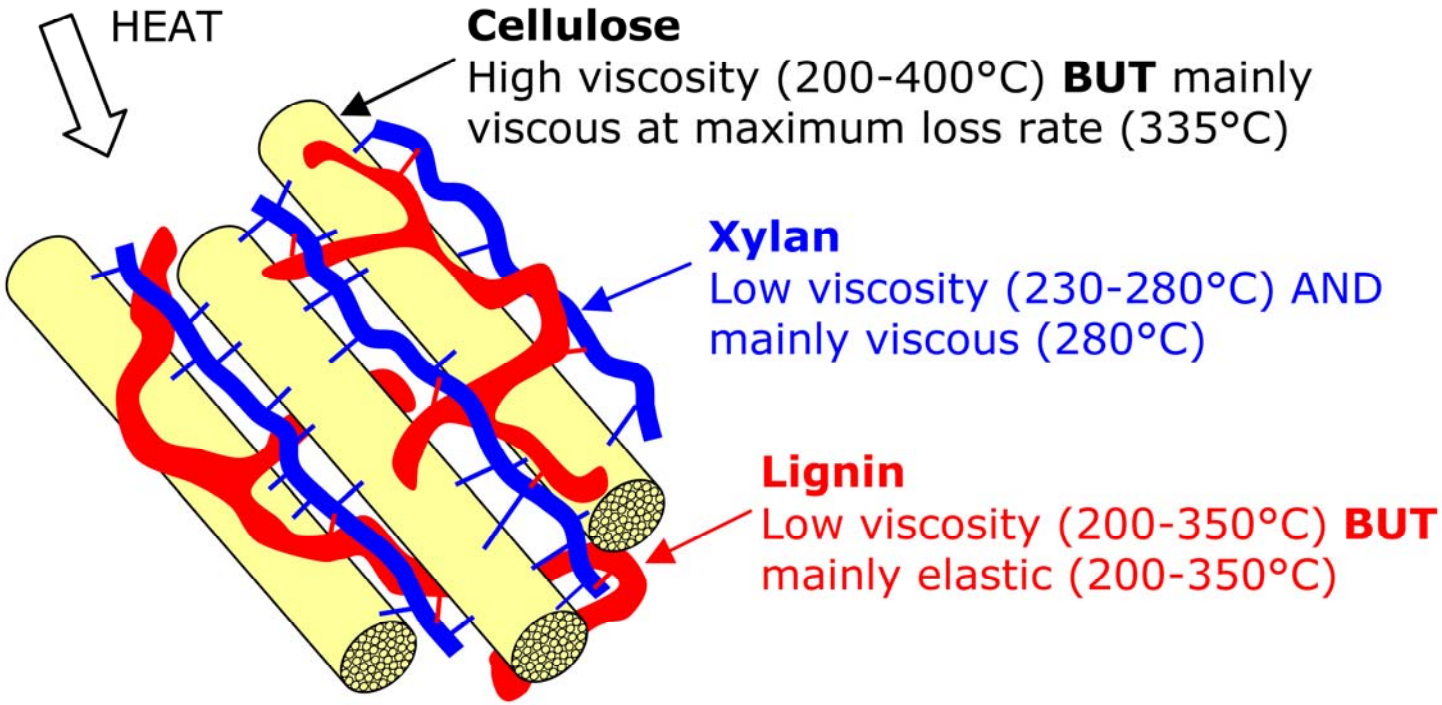


Lignin softening is not seen in the native network consistent with ^{1}H NMR

Comparison between cellulose, xylan, lignin and miscanthus for tan(δ) evolution



Simplified scheme of visco-elastic properties of fractionated polymers and native biomass



Native network of miscanthus
High viscosity and **REMAINS** mainly elastic (150-400°C)

Contents

- Background: importance of pyrolysis and intermediate liquid phase
- Polymers extractions and composition
- **Basics and new insights from in-situ high temperature ^{1}H NMR**
- Basics and new insights from in-situ high temperature rheometry
- Comparison of ^{1}H NMR and rheometry results

In-situ ^{1}H NMR analyses protons transverse relaxation signal as a function of temperature

= "Proton magnetic resonance thermal analysis" (PMRTA)

(Lynch, 1988, Sakurov, 1993, 2004, Castro-Diaz, 2005)

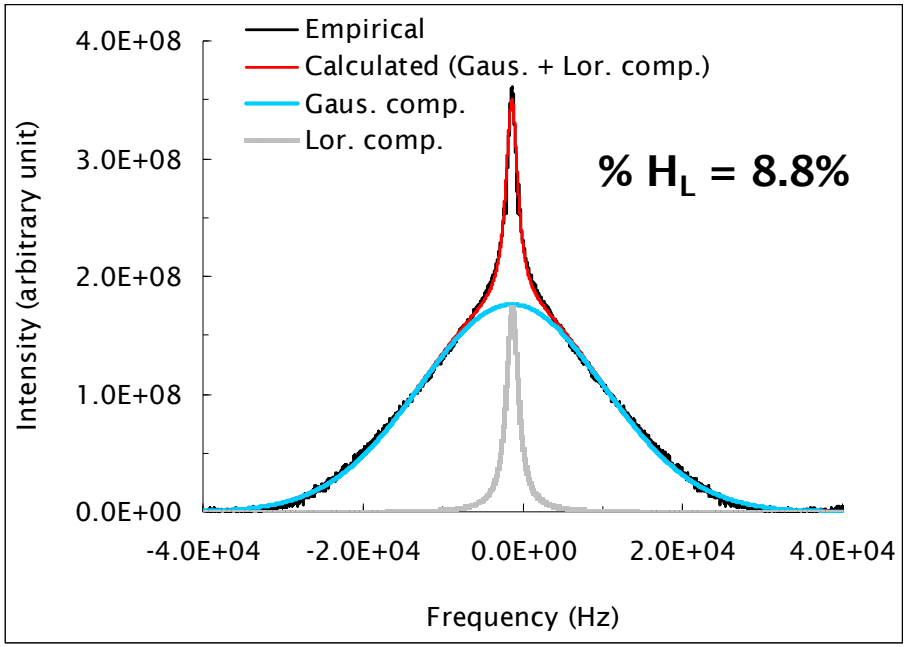
Protons in rigid structures
= strong magnetic coupling
= short relaxation time

Protons in mobile structures like liquids
= weaker magnetic interactions
= long relaxation time

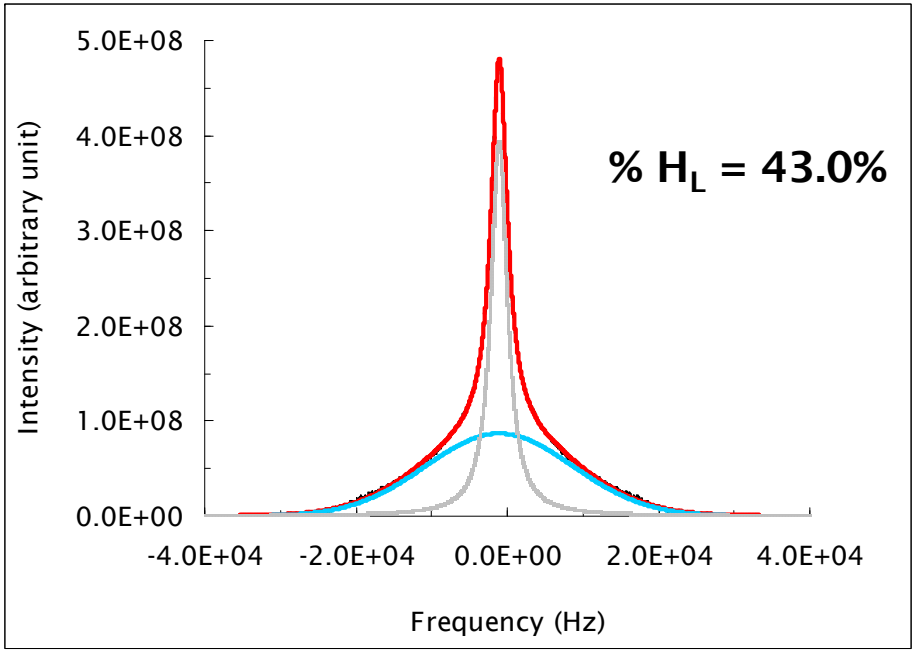
^{1}H NMR spectra were deconvoluted into Gaussian (solid-like) and Lorentzian (liquid-like) distribution functions

Fraction of mobile protons (% H_L) (or of "fluid phase") calculated as:

$$\% H_L = \frac{\text{Lorentzian area}}{\text{Lorentzian + Gaussian areas}}$$



Miscanthus at 200˚C



Miscanthus at 300˚C

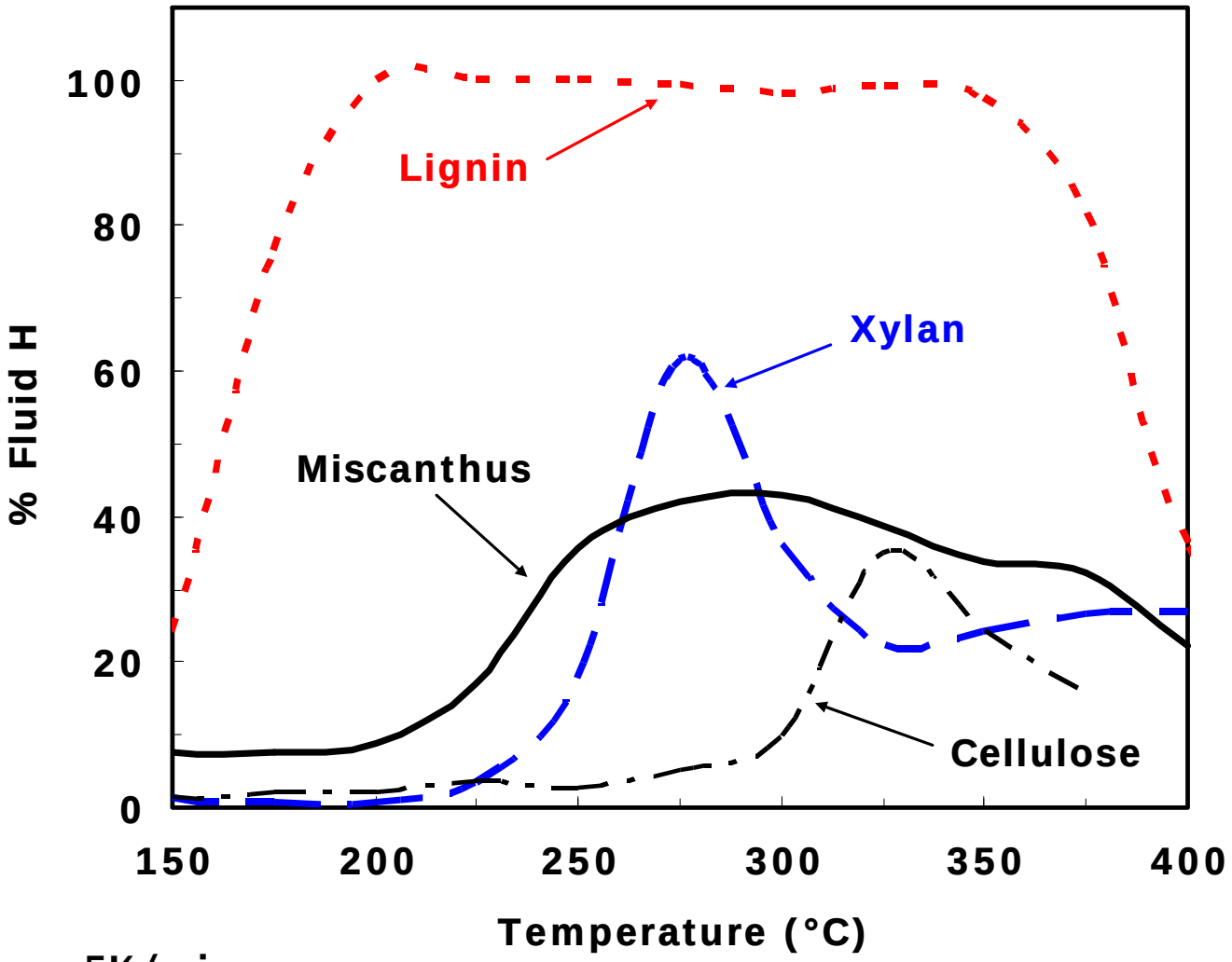
Fluid phase increases from 200 to 300˚C

Mobile protons are very important for pyrolysis mechanisms

Mobile protons stabilise the free radicals formed when bridges break and can control the composition of the pyrolysis products as tars (Solomon, 1993)

Interactions between cellulose and lignin (Hosoya, 2009) could act through the mobile H transfer from H donors' intermediate products to H acceptors

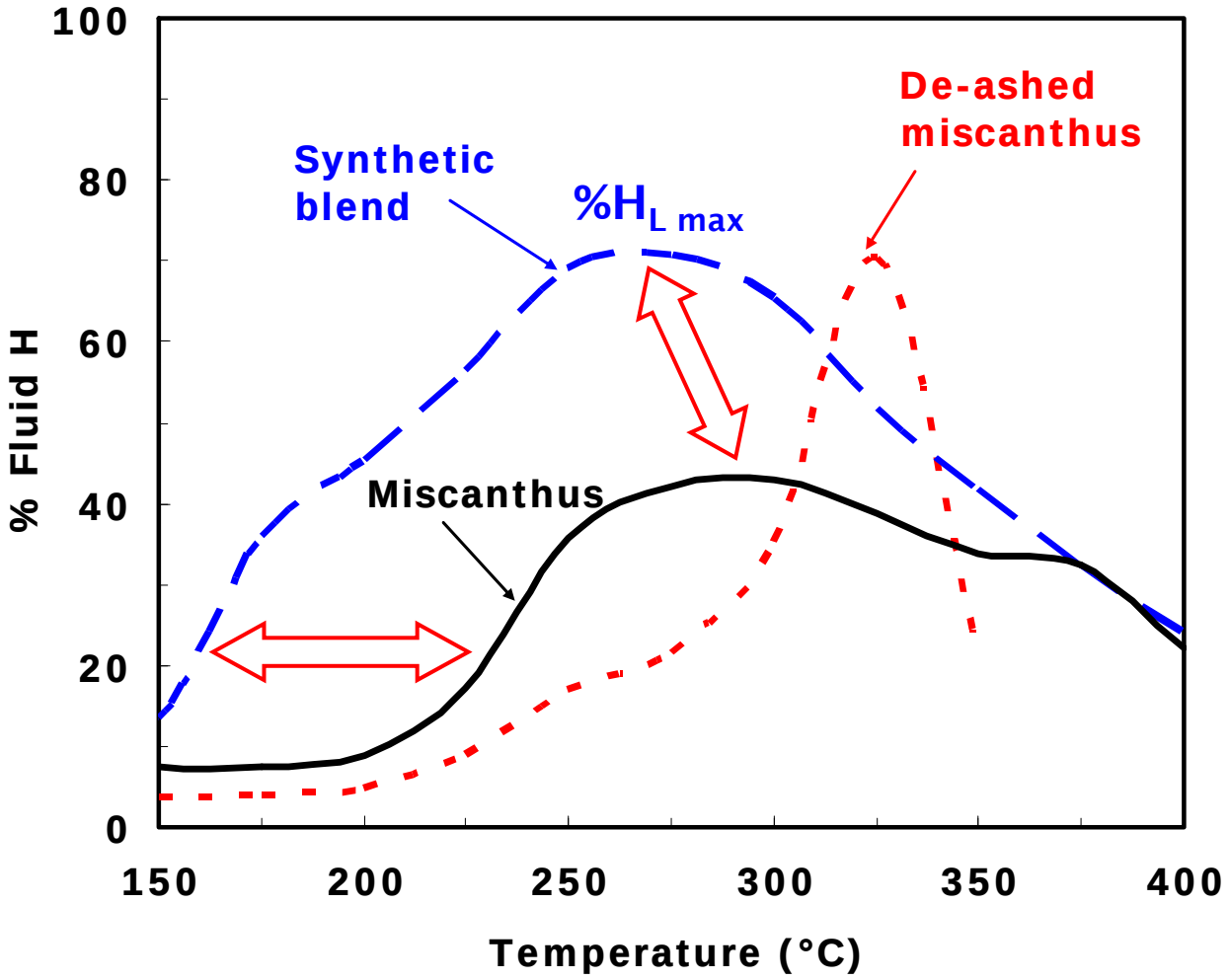
Very different fluid phase development is analysed between cellulose, lignin, xylan and miscanthus



Dufour et al., ChemSusChem, 2012

50mg, 5K/min

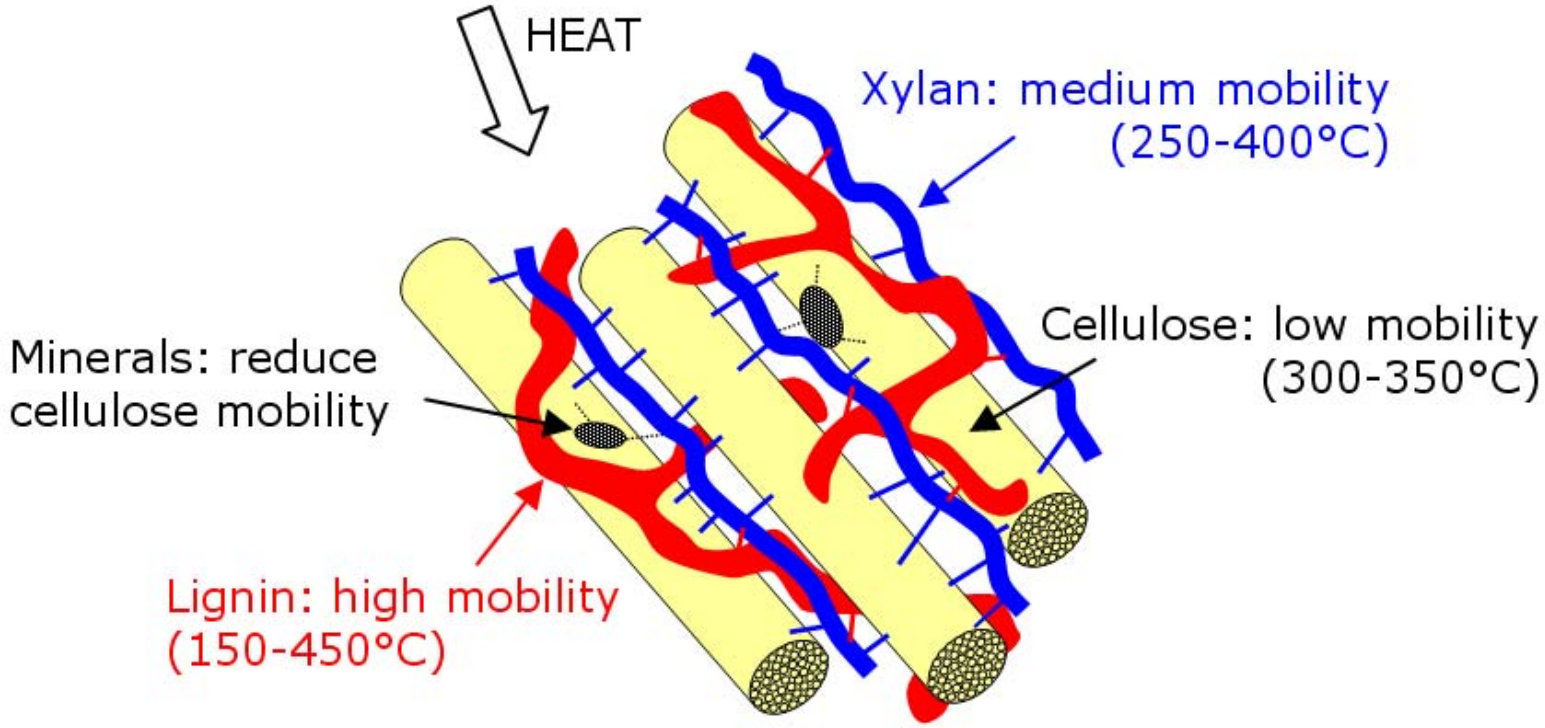
In synthetic blend, fluid phase is developed at a lower temperature (150˚C) than in miscanthus (200˚C) and to a higher max. fluid H fraction.



Dufour et al., ChemSusChem, 2012

Same finding for synthetic holocelluloses and true holocelluloses (not shown).

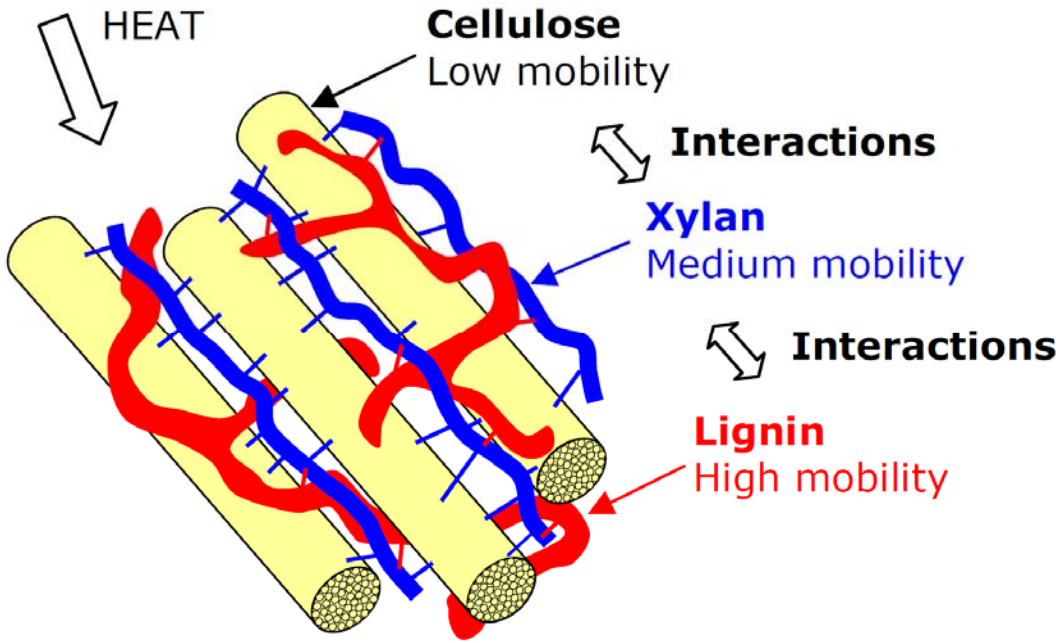
Simplified scheme of fractionated polymers mobility upon pyrolysis



Dufour et al.,
ChemSusChem, 2012

Mobility of the native network is shifted and reduced due to links between lignin/xylan and xylan/cellulose

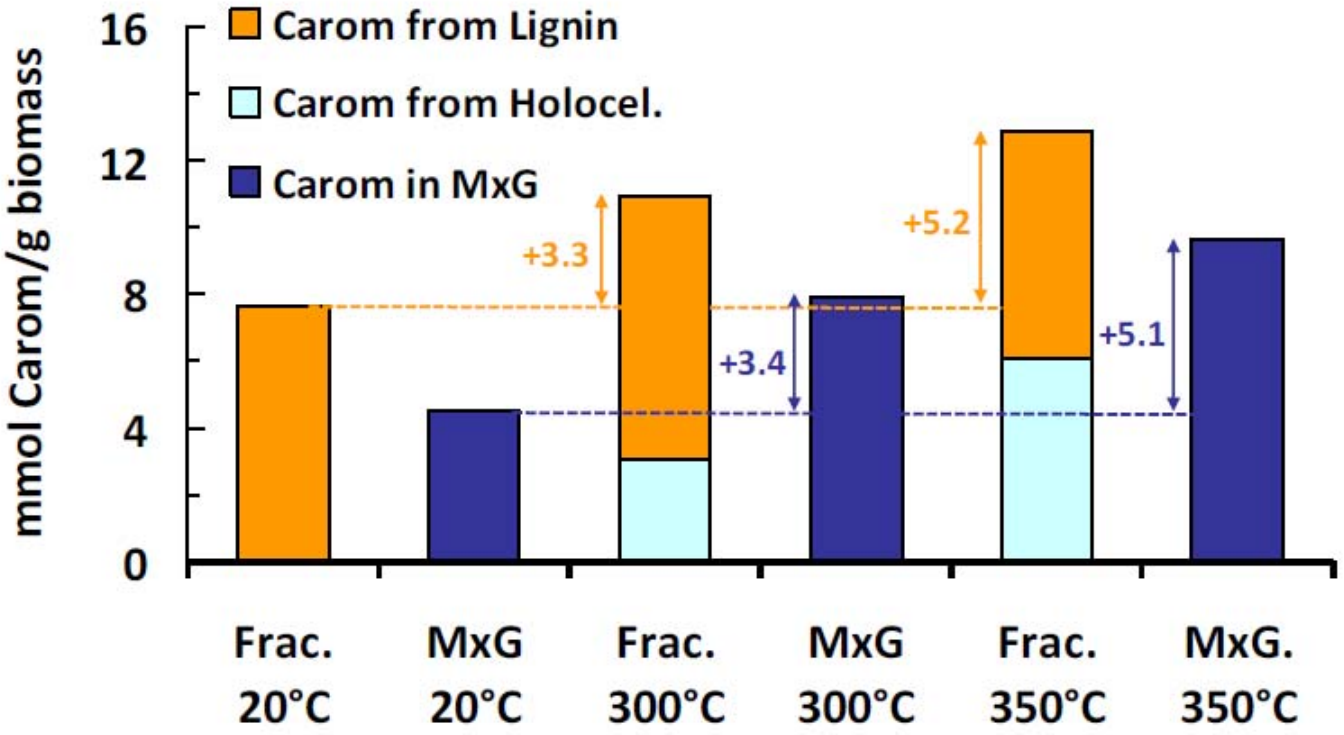
Cellulose maintains the rigidity of the native network



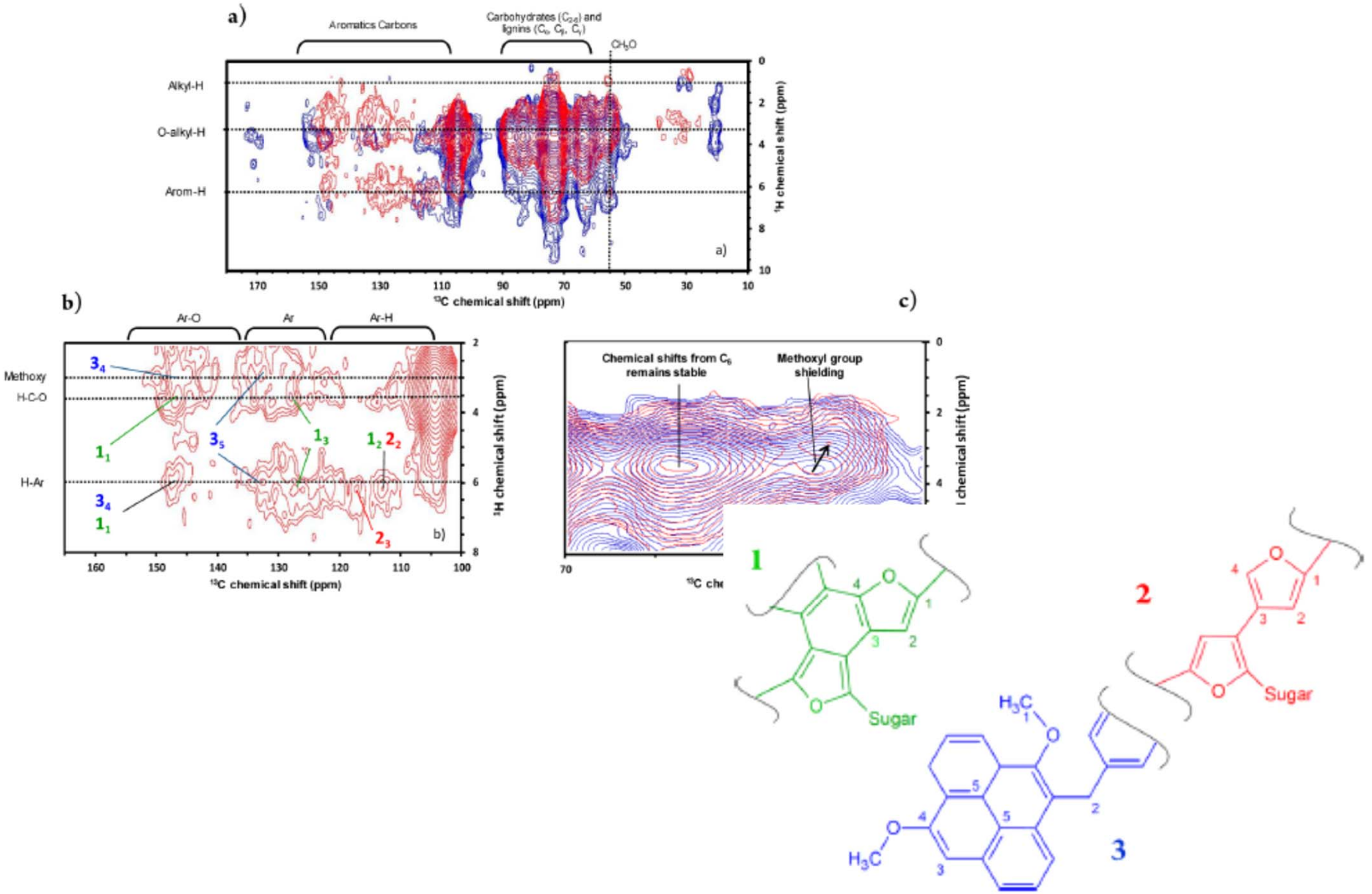
Extraction of lignin, holocellulose and cellulose from Miscanthus

Aromatic clusters mainly formed from holocellulose (stable C yield in aromatics from lignin).

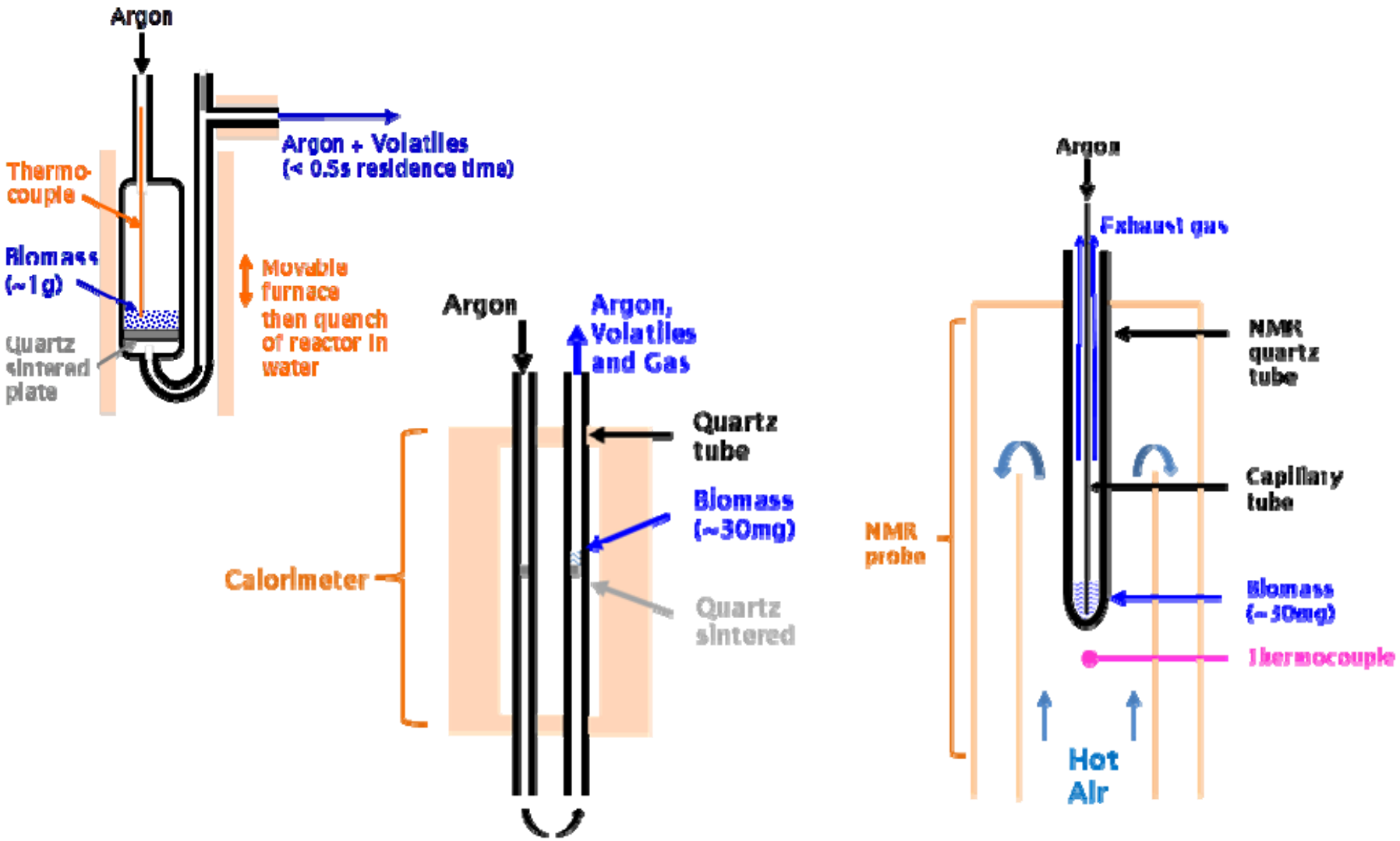
No apparent interaction on the formation of aromatic C yields between native network and separated polymers.



2D HETCOR 1H-13C NMR of intermediate chars



Fixed bed, ^{1}H NMR and DSC under same mass transfer conditions (fixed bed, same carrier gas velocity)



^{1}H NMR in-situ method

1H NMR transverse relaxation signal was stimulated by a solid echo pulse sequence (90˚-T-90˚). The rate of decrease in intensity of 1H NMR signal depends on the strength of the magnetic coupling.

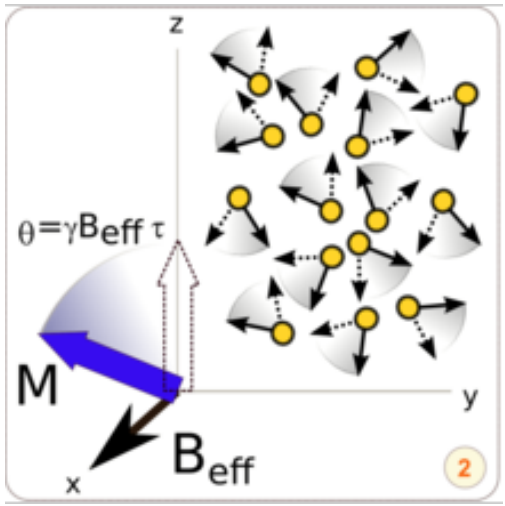
1H in solid/rigid > strong static coupling > short life 1H NMR signal (Gaussian)

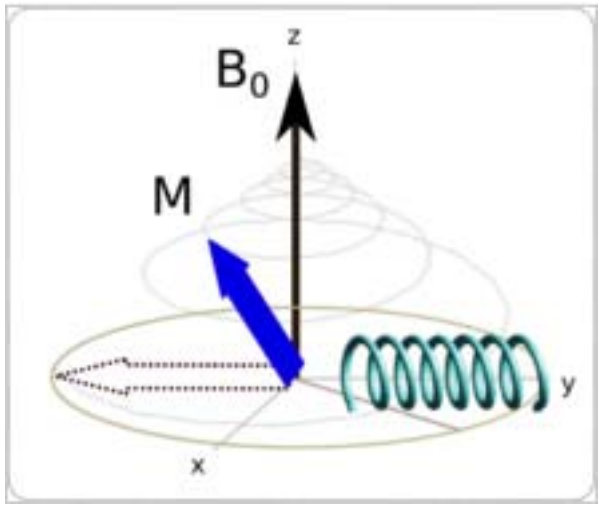
1H in mobile/liquid-like > weaker static magnetic interactions > longer life signal (Lorentzian)

The Fourier-transformed time domain decay of the solid echo pulse deconvoluted in Gaussian and Lorentzian.

Principe de l'analyse RMN H

- Molécules placées sous un haut champ magnétique continu (300Mhz=7 Tesla)
- Quelques spins (ppm) "s'orientent le long du champ magnétique"
- Sans champ, les spins sont dans des positions plus aléatoires
- On applique une onde radio (impulsion de ~µs à 300MHz si 7 Tesla de champ)
- Les protons passent à un niveau de plus haute d'énergie





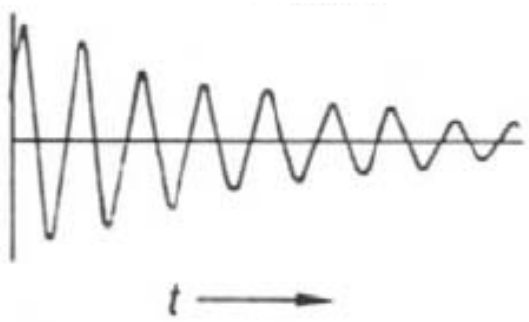
Une bobine (perpendiculaire au champ) mesure le "retour à l'équilibre" des protons.

Relaxation : dissipation de l'énergie (envoyée par l'onde radio) dans les autres atomes environnants les protons.

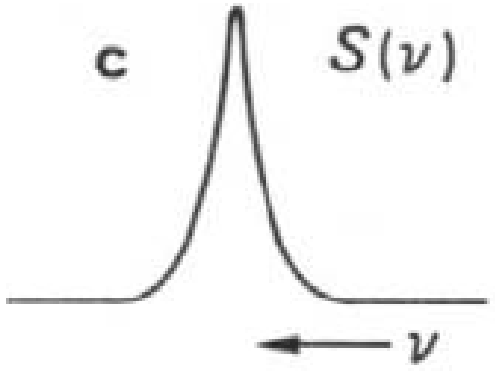
Principe de l'analyse RMN H

Mesure de la relaxation par la bobine

"Field Induction Decay"

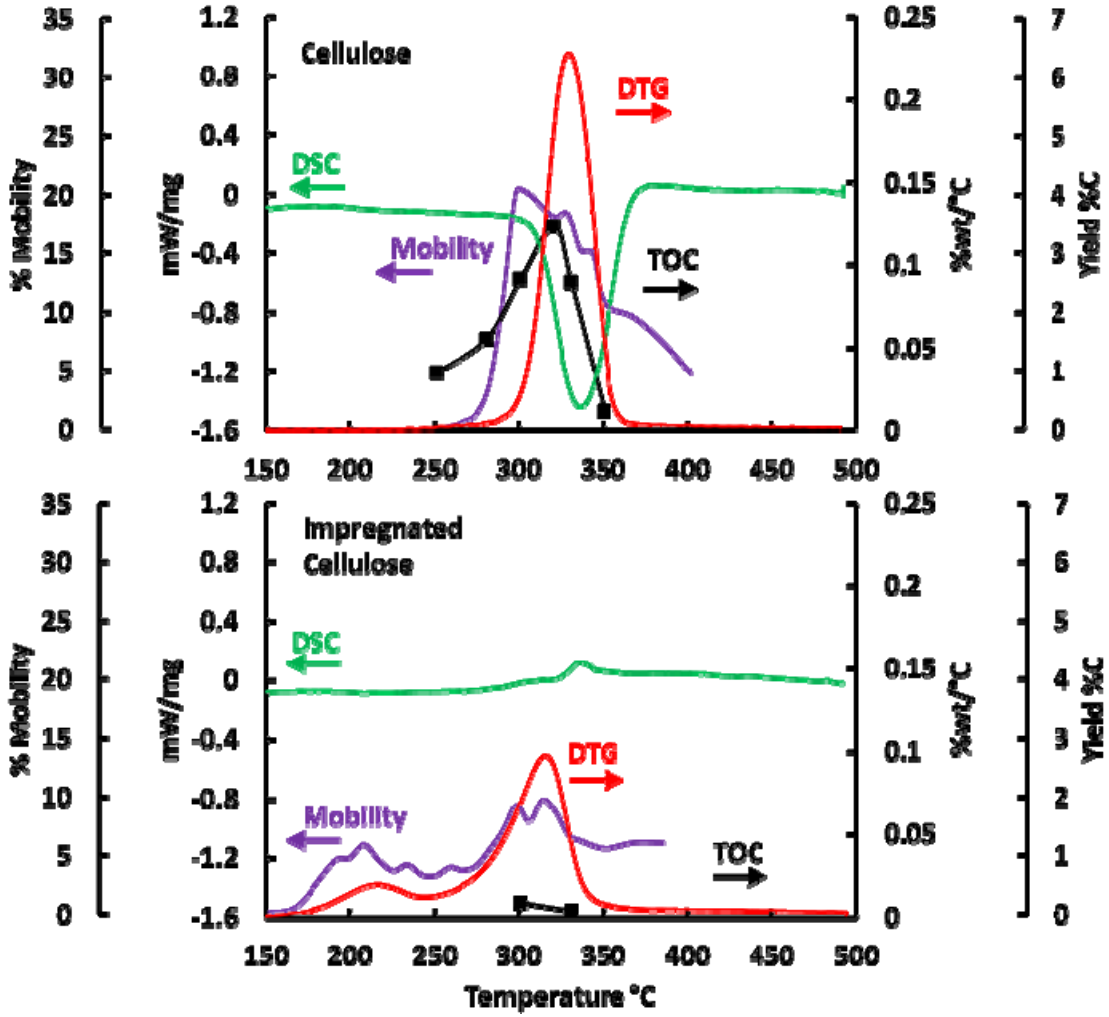


Transformée de Fourier



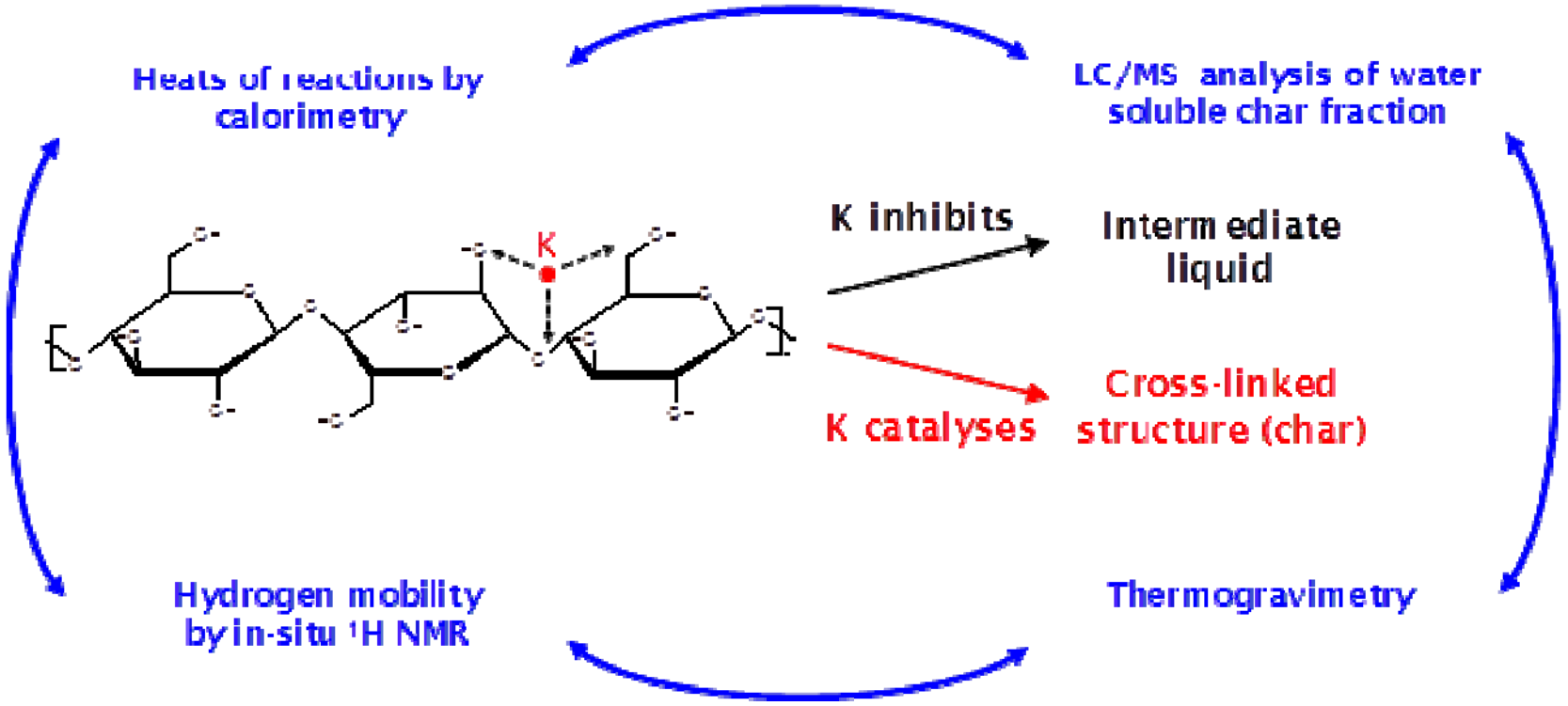
- Un solide "absorbe plus vite" l'énergie qu'un liquide
- Les noyaux des protons dans un solide auront donc un temps de relaxation plus court que les protons dans un liquide.
- Le pic sera donc plus "éfilé" pour les liquides.

Effect of minerals (K) on mobility, DSC, TGA, etc.



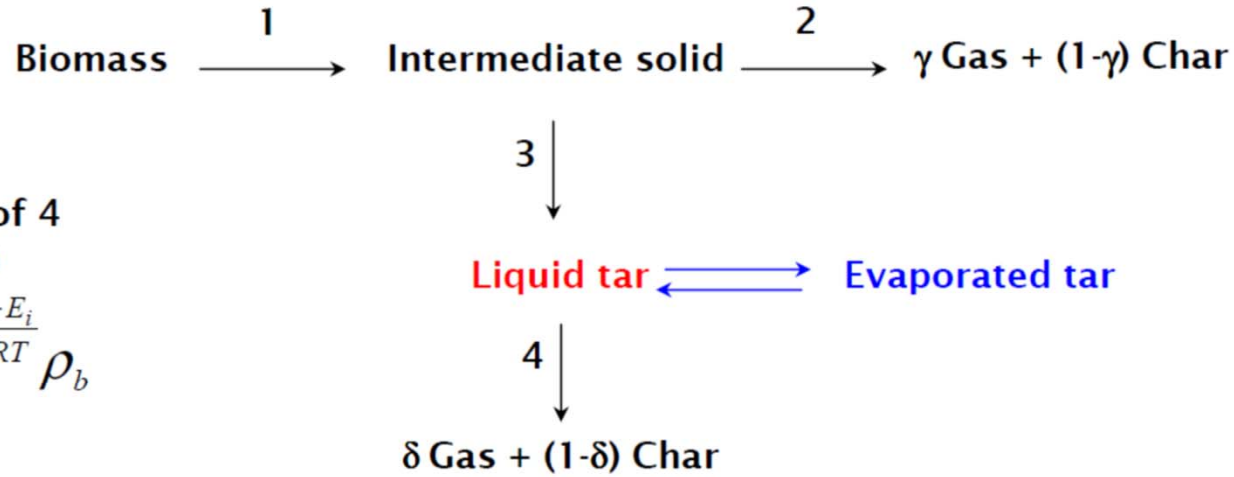
ChemSusChem, 2016

Effect of minerals (K) on mobility, DSC, TGA, etc.



ChemSusChem, 2016

A new model has been developped based on the calculation of characteristic times



Kinetics of 4 reactions

$$r_i = A_i e^{\frac{-E_i}{RT}} \rho_b$$

Internal mass transfer by convection (Darcy law)

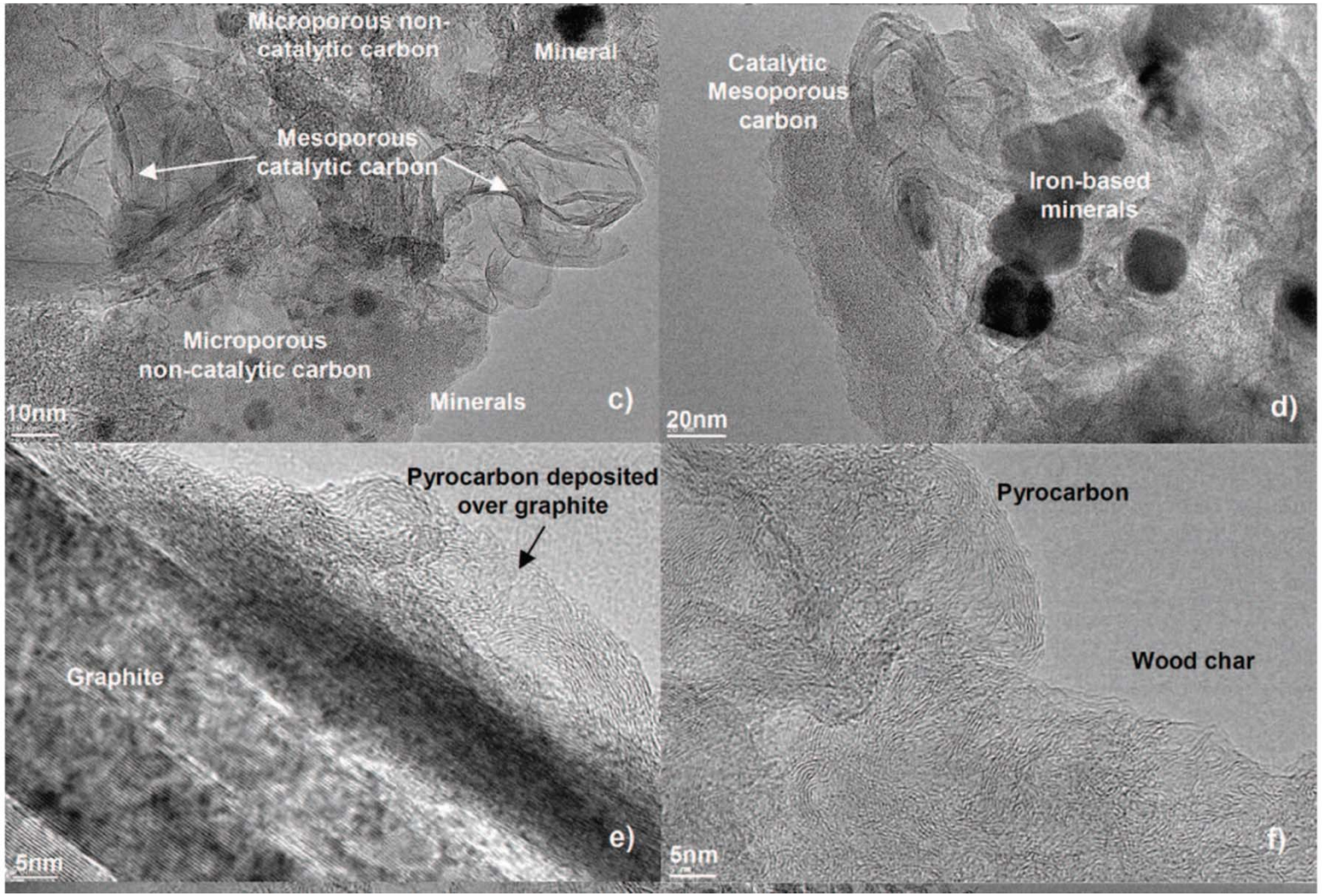
$$Q = \frac{K}{\mu_G} S \frac{\Delta P}{L}$$

Intra-particle tar evaporation
(thermodynamic equilibrium)

$$P_{TG} = A \exp\left(\frac{-B * M_T^{0.59}}{T}\right)$$

Chem. Eng. Res. Des. 2011.

TEM of various carbon structures in char



App. Catal. 2015