Chemical conversion of lignocellulosic biomass

Deconstruction game

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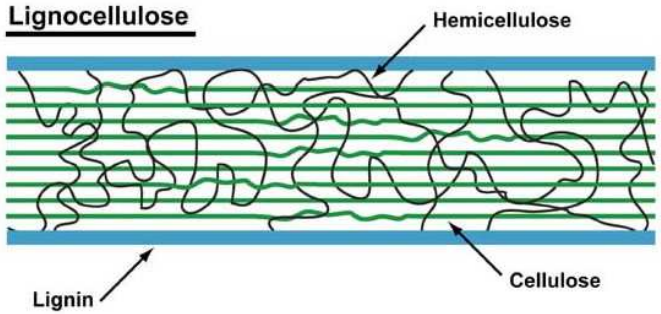
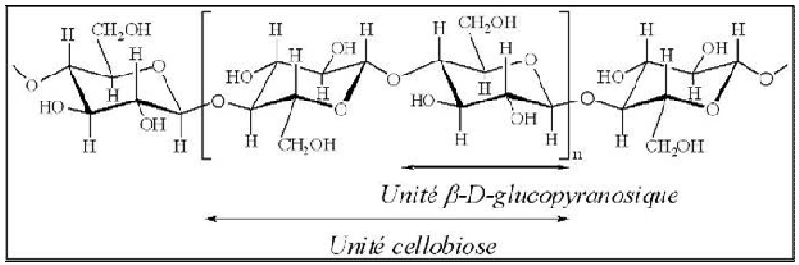
Journées Promotion Procédés Produits
Journée scientifique
NANCY - ENSIC Jeudi 9 juillet 2015

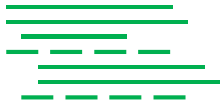
Utilization of lignocellulose : current business model



~ 40% of biomass



cellulose

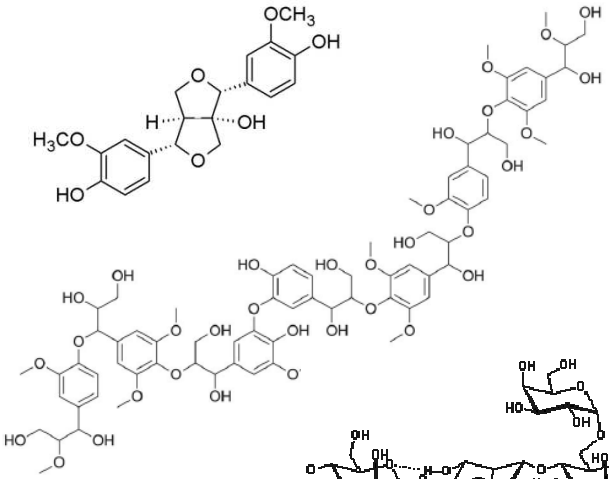


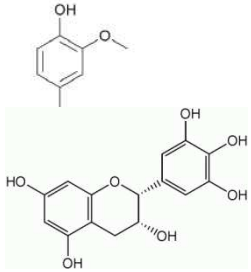
Paper
Bioethanol

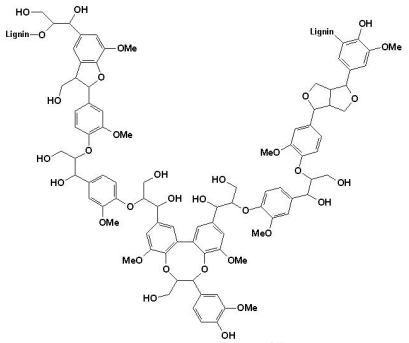
Lignin
hemicelluloses

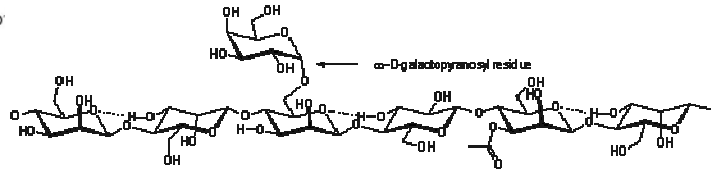
Waste & energy

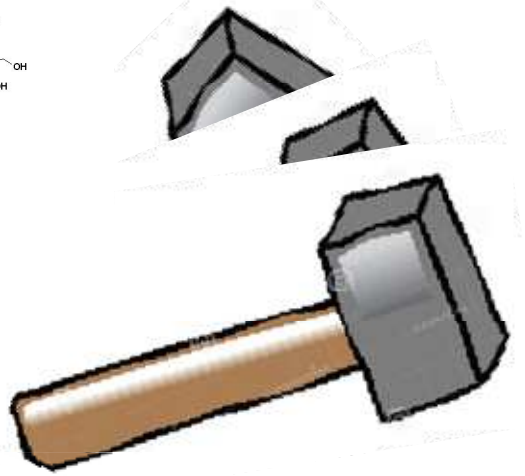
Utilization of lignocellulose : toward a new model

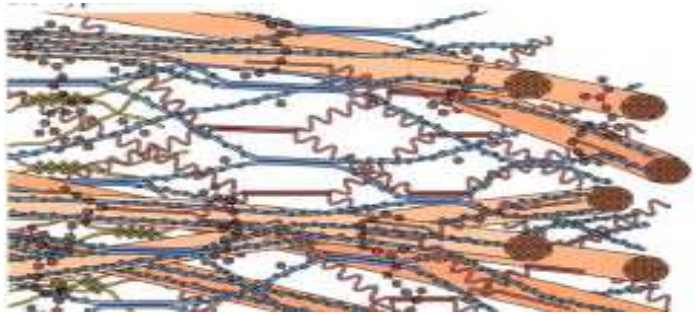








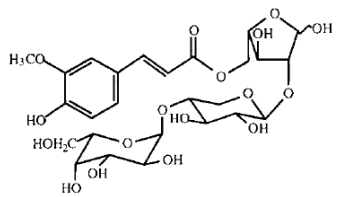


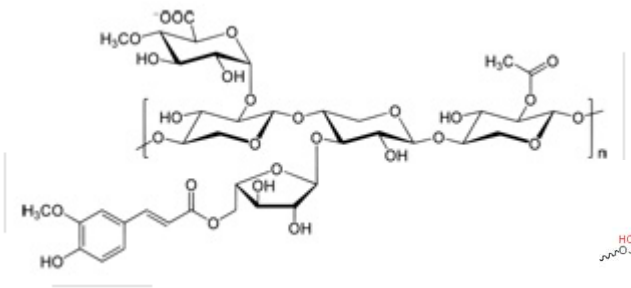


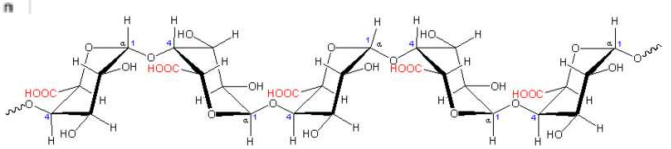
Carpita et McCann (2000)

(BIO)PROCESS CHEMISTRY

- Paper
- Bioethanol
- Nanocelluloses
- Antioxidant
- Food & Feed
- Nutraceutic
- Materials (adhesives, film, polymers..)
- Drugs
- Fibers





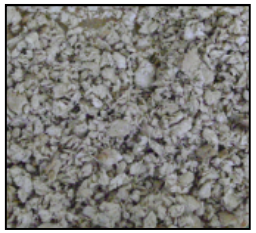


1- Organosolv pulping

Empty Fruit palm Bunch

Organosolv pretreatment

Ethanol-water
H_2SO_4, catal.
170-190°C



Cellulose-rich pulp

enzyme

glucose

+ H_2O

lignin

Hemicelluloses (mono & oligosaccharides)

<u>High quality lignin</u> :
- S free
- Low molecular mass
- Solubility in org solvent
- High C-O-C linkages
- Low C-C linkages

~ 100% green material without formaldehyde

Biomass Bioenergy ***2011****, 35, 4025-4033*

J Adhesion Sci Technol **2011**, *25,* 1549–1560

Bio-organosolv pulping : a two-step deconstruction

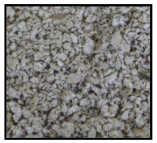
Miscanthus straw

Enzymatic treatment

Cellulases + hemicellulases

Organosolv treatment

pulp

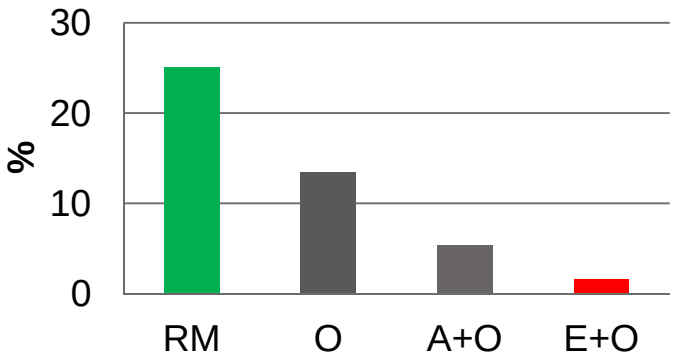


enzyme

gucose

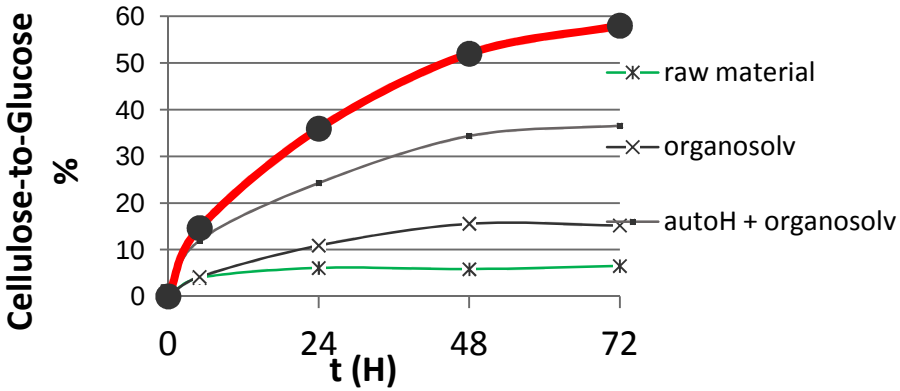
Lignin

Lignin content in solid residues



After enzyme + organosolv : very low lignin content...

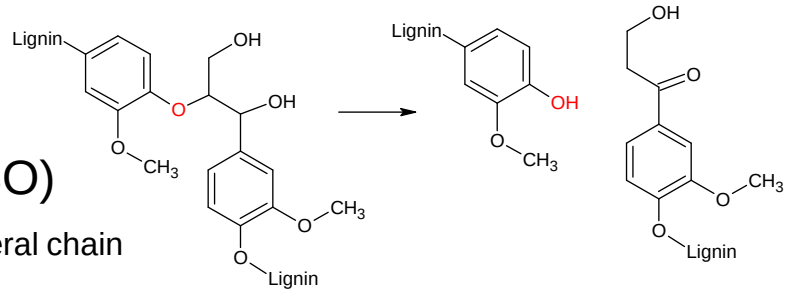
Cellulose hydrolysability



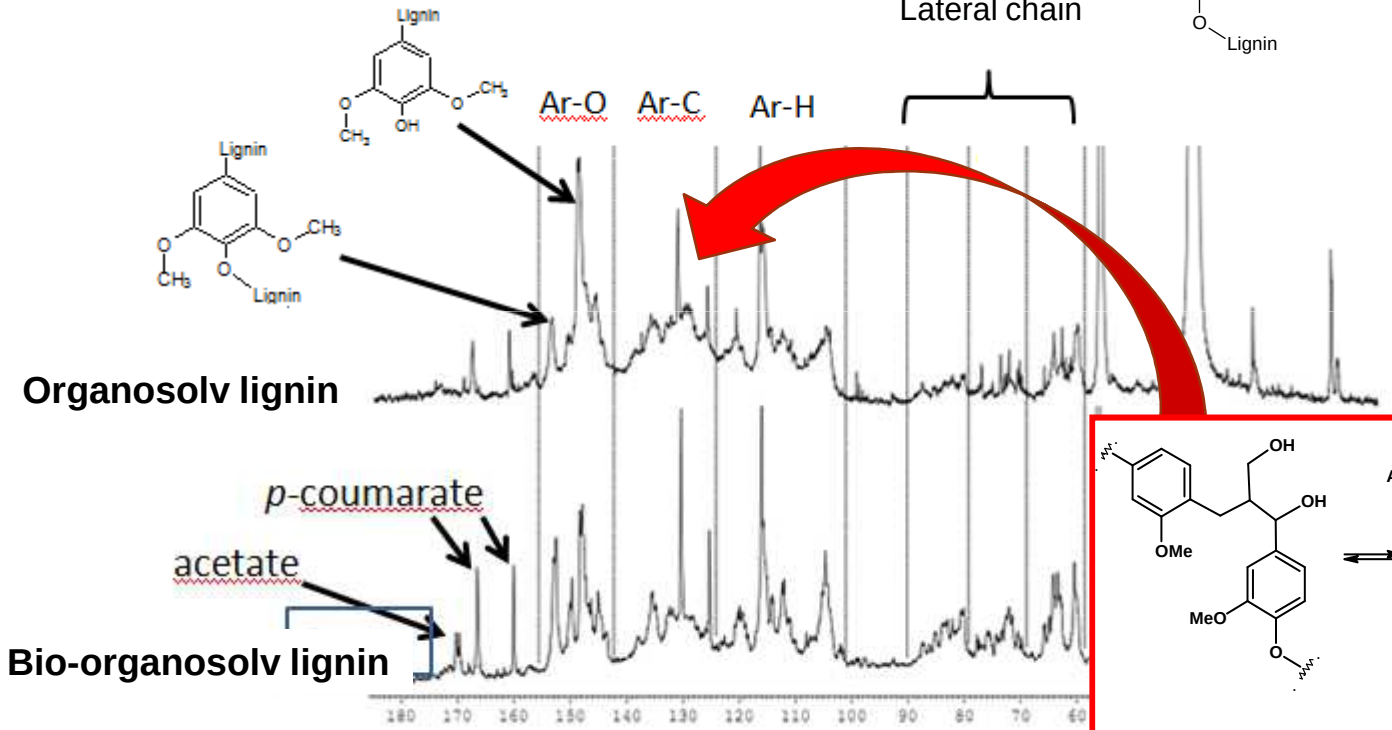
... and very good cellulose-to- glucose conversions

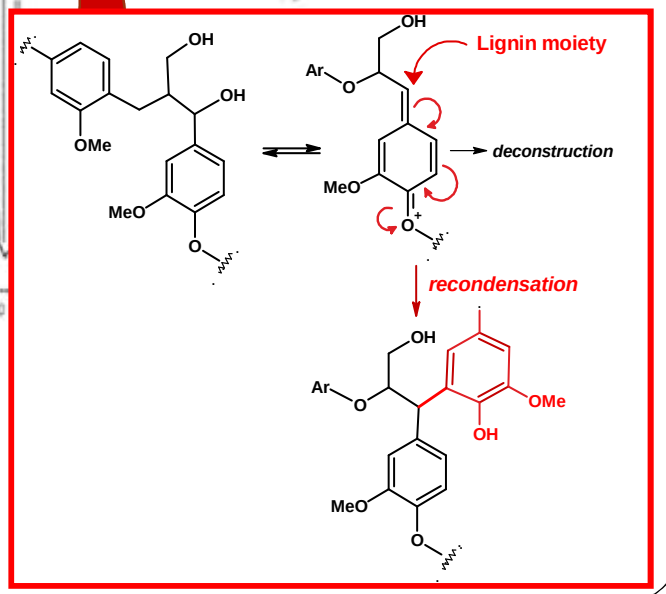
Bioressource Technology **2012**, *112*, 156–163

Bio-organosolv pulping : impact on the lignin structure



^{13}C NMR (in DMSO)





With enzymes :
milder pulping conditions
a smooth lignin depolymerization
Low C-C bonds formation

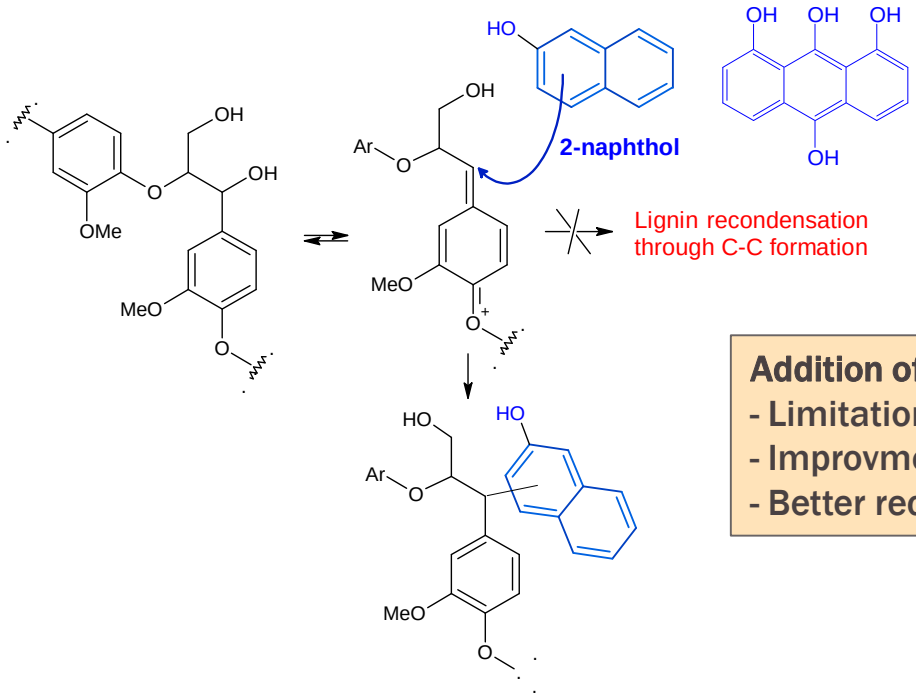
Lignin chemistry

organosolv

pulping

Lignin

Lignin extraction in presence of a nucleophilic aromatic agent (naphthol)



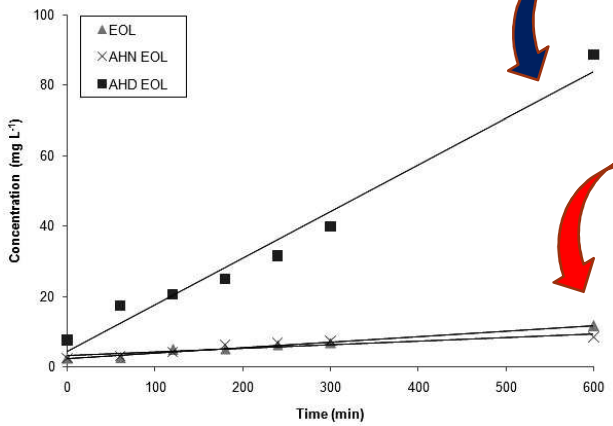
Addition of a catalytic amount of naphthol :
- **Limitation of lignin recondensation**
- **Improvment of lignin extractability**
- **Better recovery of sugars**

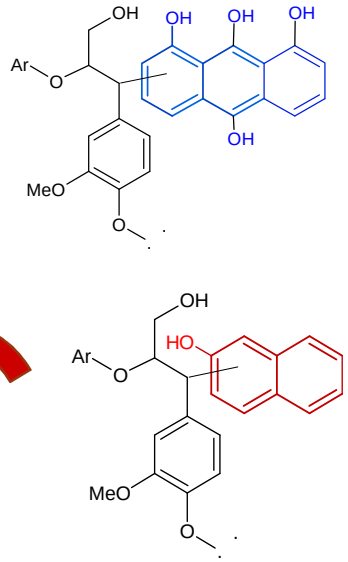
Polymer Degradation and Stability, **2014** *109*, 33-39
Bioressource Technology **2010** *101*, 9321-9329

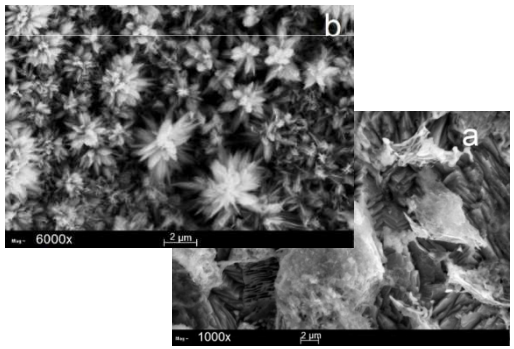
Green corrosion inhibitors from modified lignin

Water solubility of modified lignins

Water dissolution curve







Better water solubility of lignin was obtained when dihydroxyanthraquinone was incorporated into the lignin structure

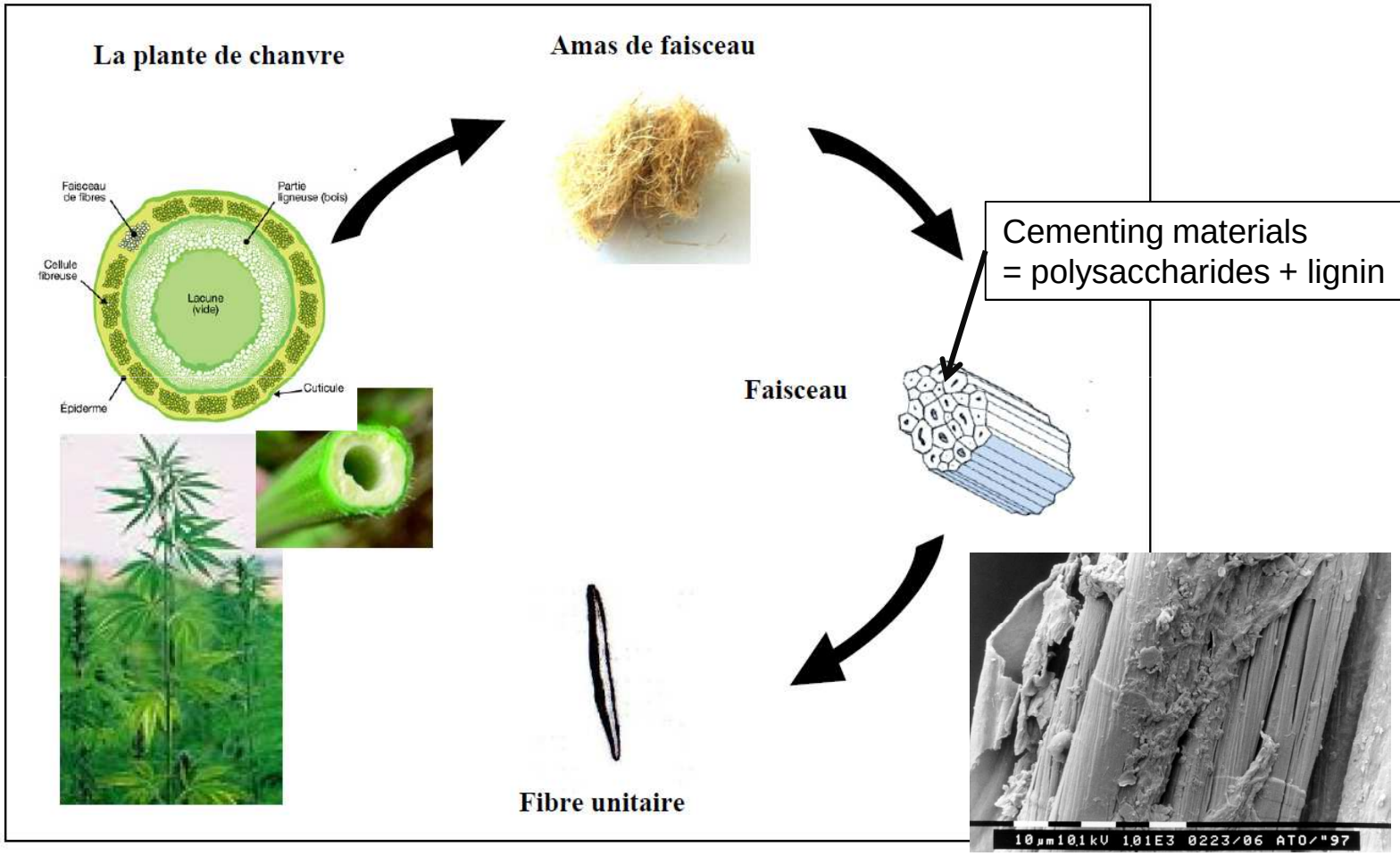
→ Increased of the antioxidant activity

→ Increased hydrogen donating ability (better reducing power)

Ind crops prod, **2015**, *66*, 1-10 ; *Ann. Forest Sc.,72* (1) 17-26, **2015**

2- Fibers extraction

Production of elementary fibers for textile & composite applications



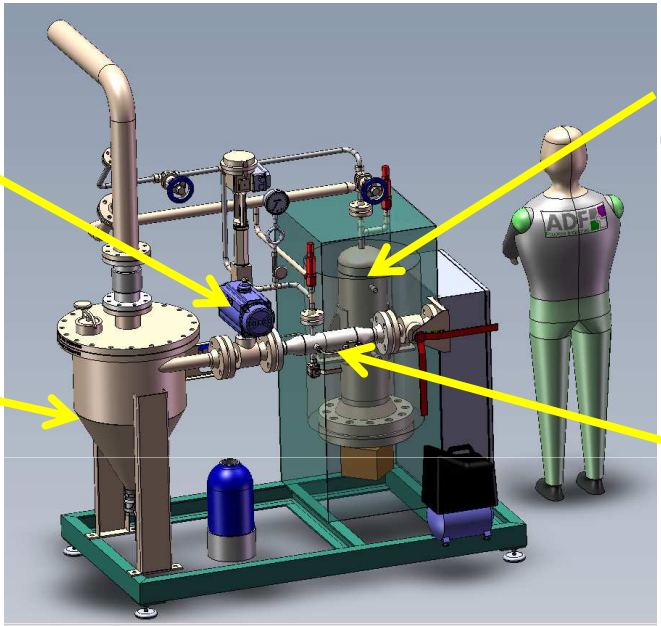
Deconstruction :

Degradation of the cementing materials without affecting the fiber

Steam explosion for the production of hemp fibers

Pneumatic valve

Cyclone



Boiler (steam)

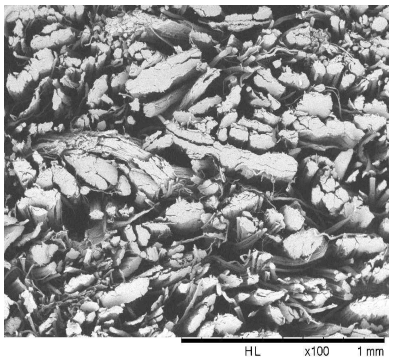
reactor

Steam high pressures and temperatures for a short duration

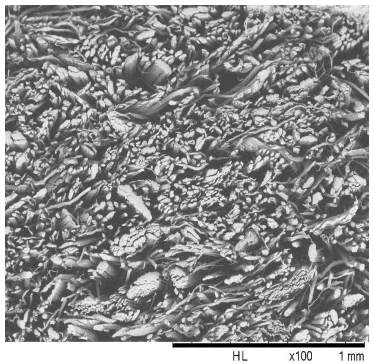
Quick depressurization

Disruption / deconstruction

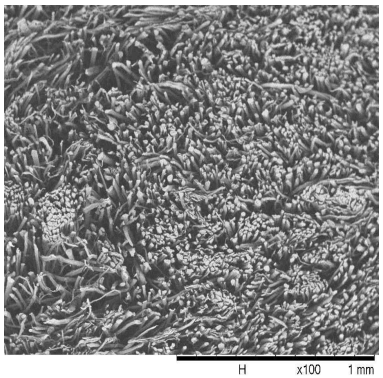
SEM pictures of the cross-sections of three different samples



untreated fibers



condition 1



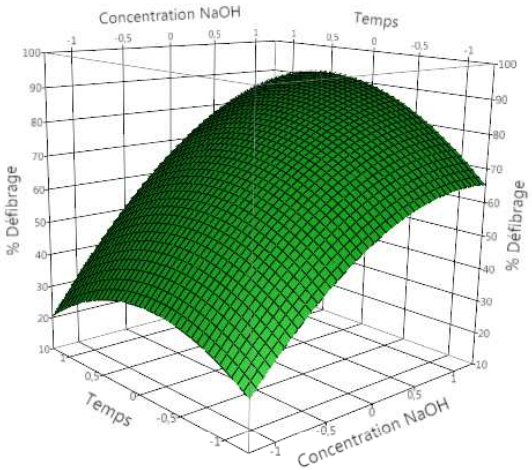
condition2

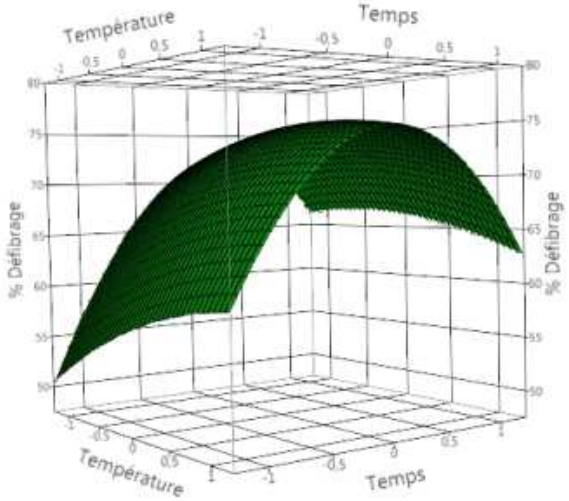
Elementary fibers / bundles

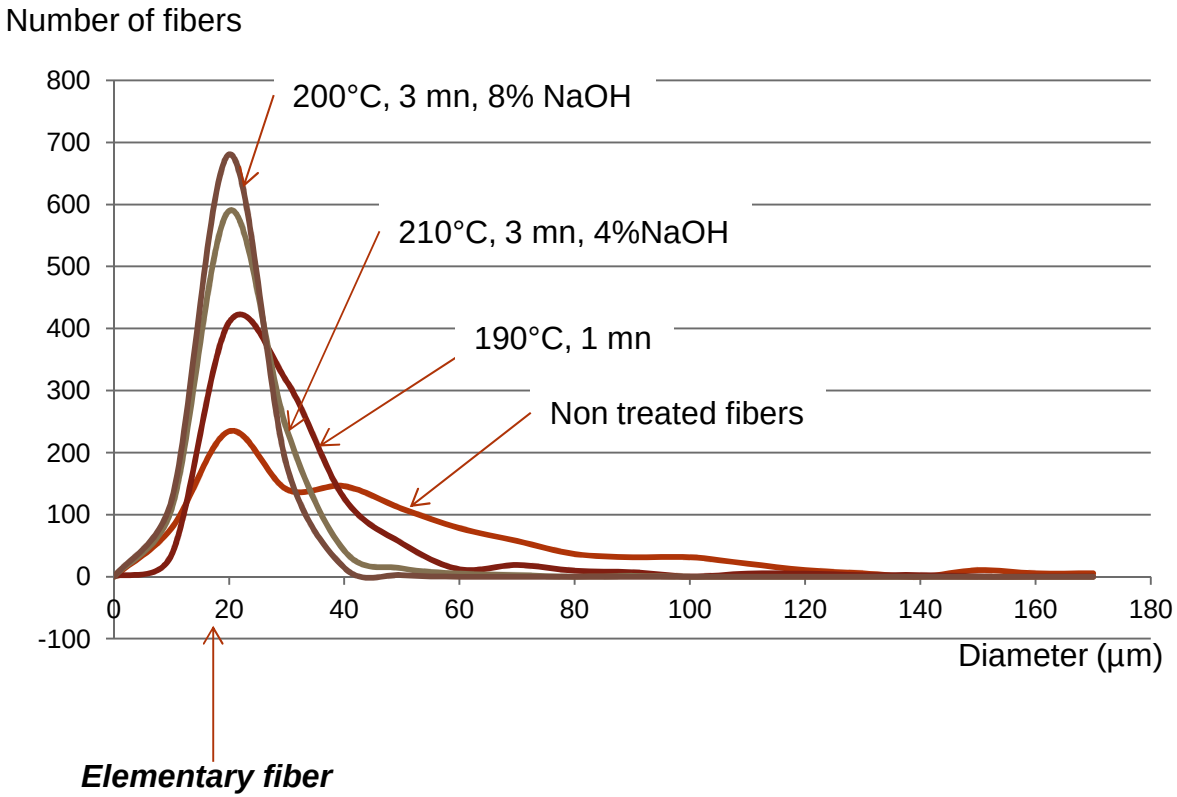
Image processing

To be published

Process optimization



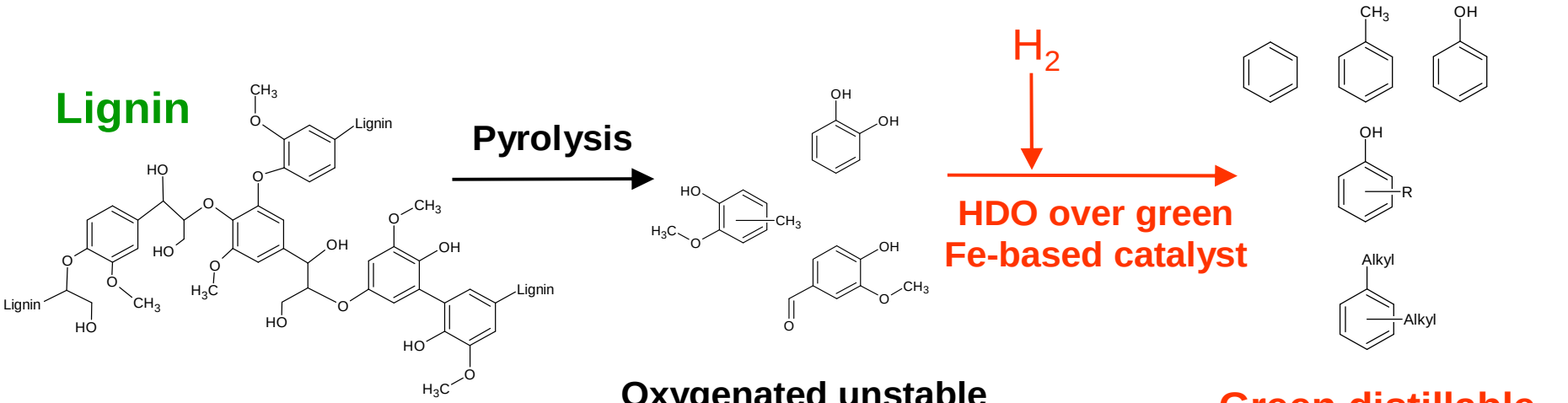




3- Thermal deconstruction

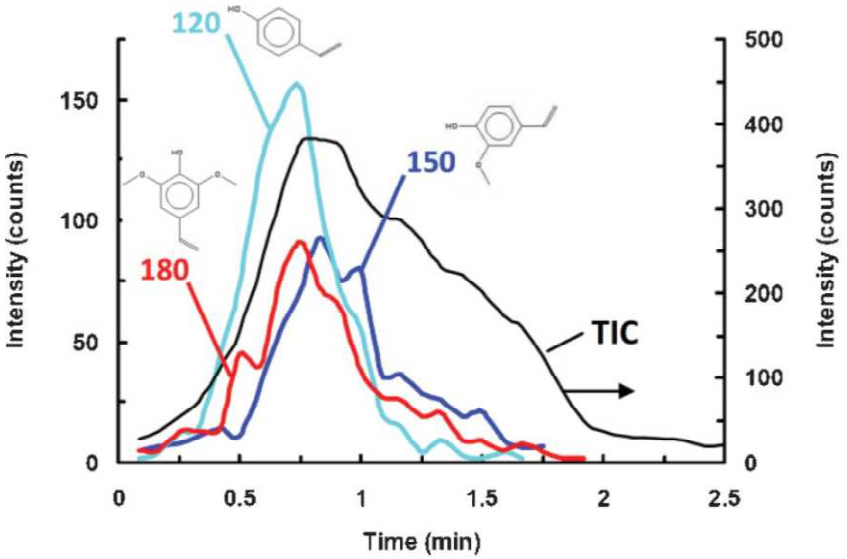
production de composés aromatiques à partir de la lignine

Pyrolyse puis hydrotraitement catalytique des vapeurs sur un catalyseur à base de fer

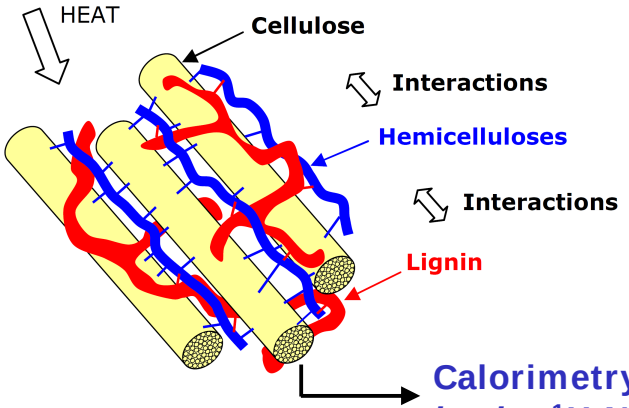


A l'échelle moléculaire, les mécanismes de pyrolyse de la lignine et de catalyse sont étudiés.

Exemple d'étude sur la pyrolyse de la lignine : Analyse en ligne des produits volatiles par spectrométrie de masse à ionisation douce (PI-TOFMS)



De nombreuses méthodes analytiques sont développées.



Gas → **Micro-GC**

Condensables (carbohydrates, furans, aromatics, carbonyls) → **GC*GC/ MS-FID, SEC/ MS, on-line PI-TOF-MS**

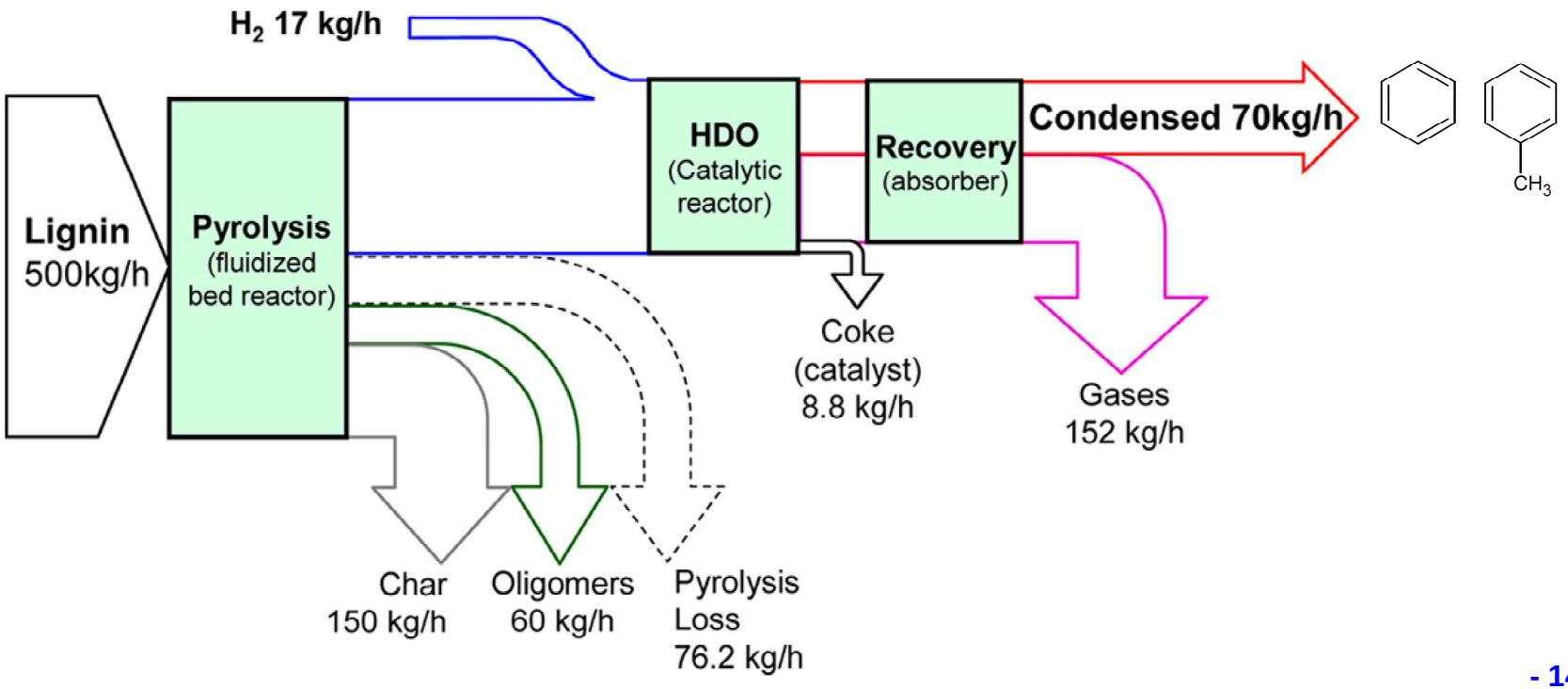
Char → **2D ^{1}H-^{13}C solid state NMR, 1D quantitative ^{13}C NMR, FTIR**

Calorimetry, Thermogravimetry *in-situ* ^{1}H NMR et rheology

Méthodologie : couplage essais/modélisation

Bilan matière du procédé : modélisation sous Aspen Plus® à partir d'essais et de données de la littérature

Pyrolyse en lit fluidisé puis lit catalytique à base de fer



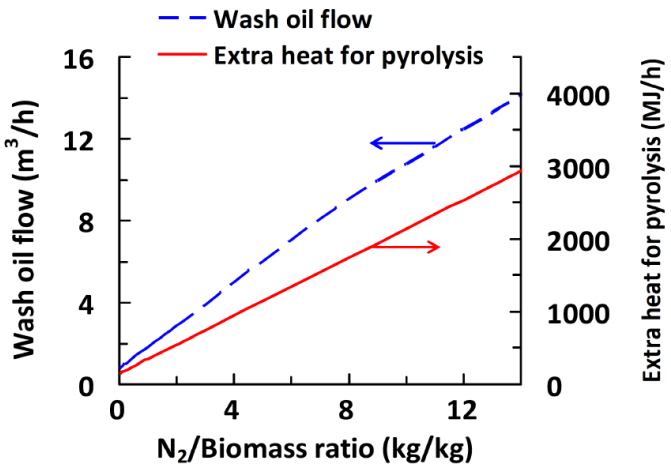
Exemple d'une étude intégrée sur la conversion de la lignine en composés aromatique

Modélisation du procédé : fort impact du débit de gaz de fluidisation sur « l'intensification » du procédé

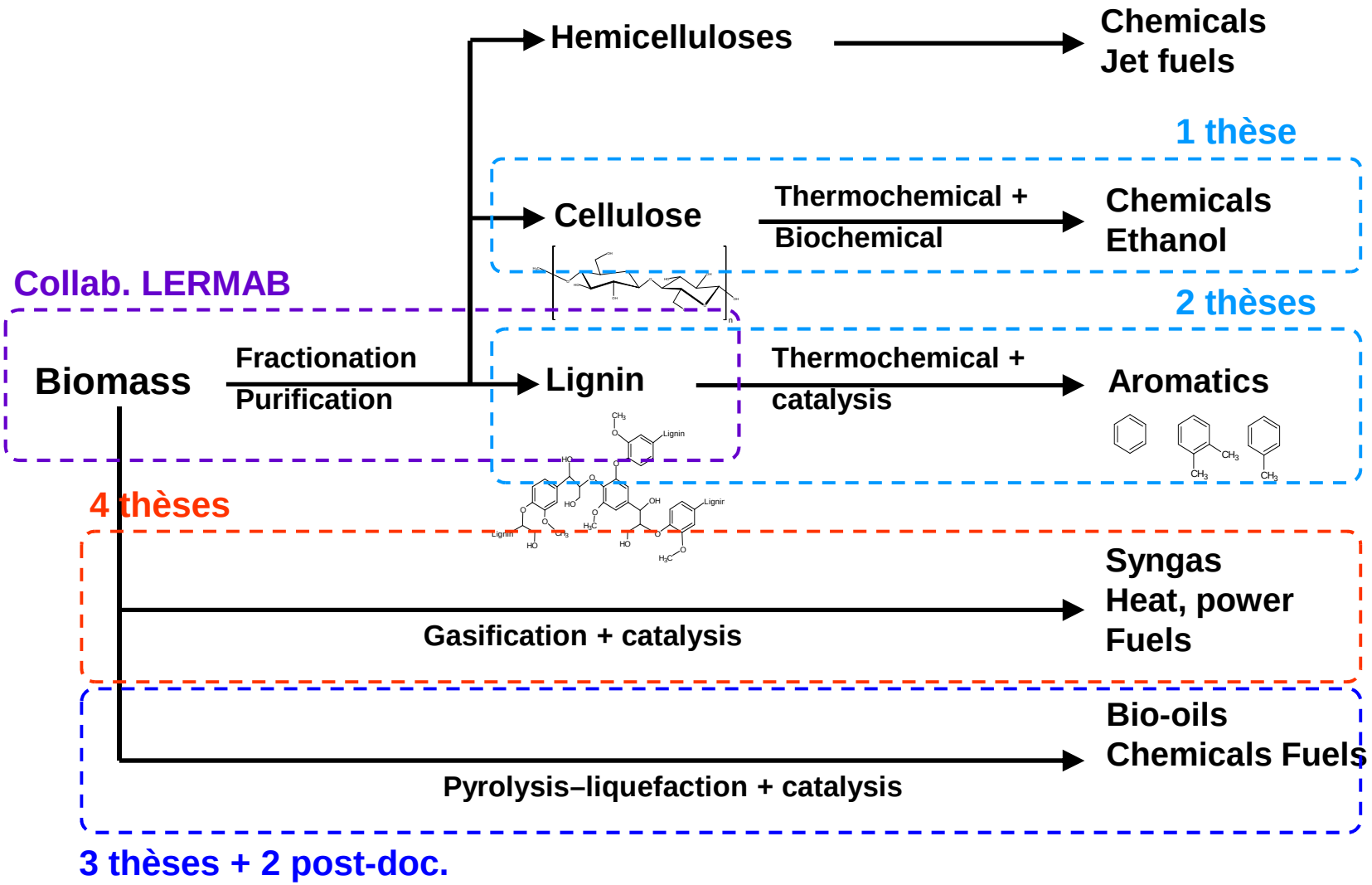
Lit fluidisé : réacteur pas optimal pour la pyrolyse de la lignine

Développement d'un nouveau réacteur

Analyse par rhéologie in-situ : la lignine forme un matériau collant qui agglomère les lits fluidisés.



Activités récentes (2013-2015) du LRGP sur la bioraffinerie à partir de biomasse lignocellulosique



Essais à l'échelle laboratoire et pilote

Laboratoire Hydrotraitement (réseau H_2 150Bar)

Pilote pyrolyse/gazéification (5kg/h biomasse)

Laboratoires à haut niveau de sureté

Plus de 25 personnes travaillent à Nancy sur la conversion (thermo) chimique de la biomasse.

Acknowledgements

- Oil palm tree (USM, Malaysia)

Haswan Hussin, Chun Shen Goh Keat Teong Lee, Mohamad Nasir Mohamad Ibrahim, Afidah Abdul Rahim

- Bio-organosolv treatment (LiBio, ENSAIA)

Patrick Obama, Guillaume Ricochon, Lionel Muniglia

- Steam explosion (Sherbrooke, Canada; CETELOR)

Thibaud Sauvageon, Jean Michel Lavoie, César Cégovia

- Thermal conversions (LRGP, ENSIC)

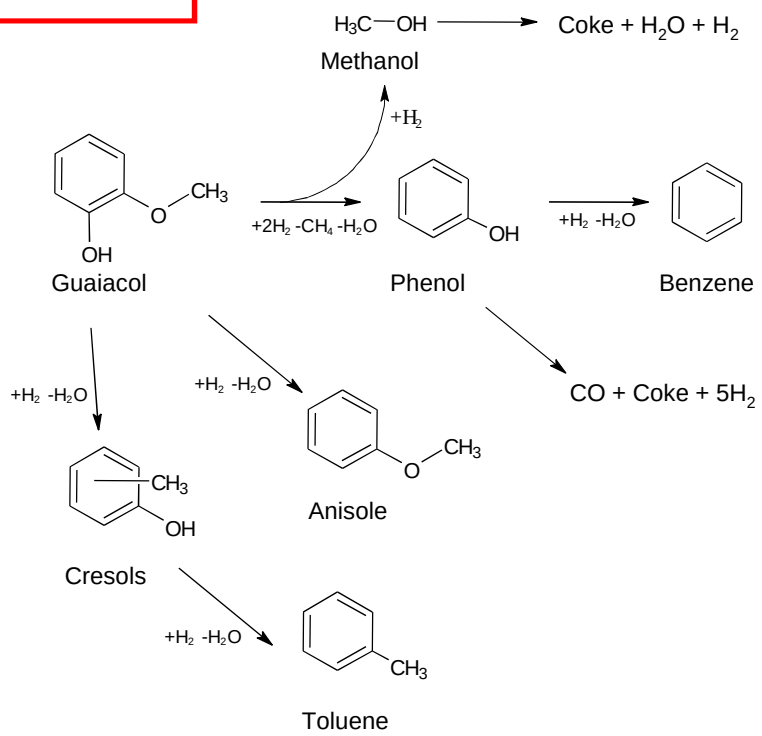
Anthony Dufour, Guillain Mauviel,Yann LeBrech, Binod Shrestha

Méthodologie : couplage essais/modélisation

Essais labo./pilote

Bilan matière
Modèle cinétique

Modélisations réacteur & procédé
Bilan masse/ énergie



Design réacteur & procédé