Webinar: New trends in catalysis for biomass valorization – 22th July 2020

Catalytic Valorization of Lignocellulosic Biomass

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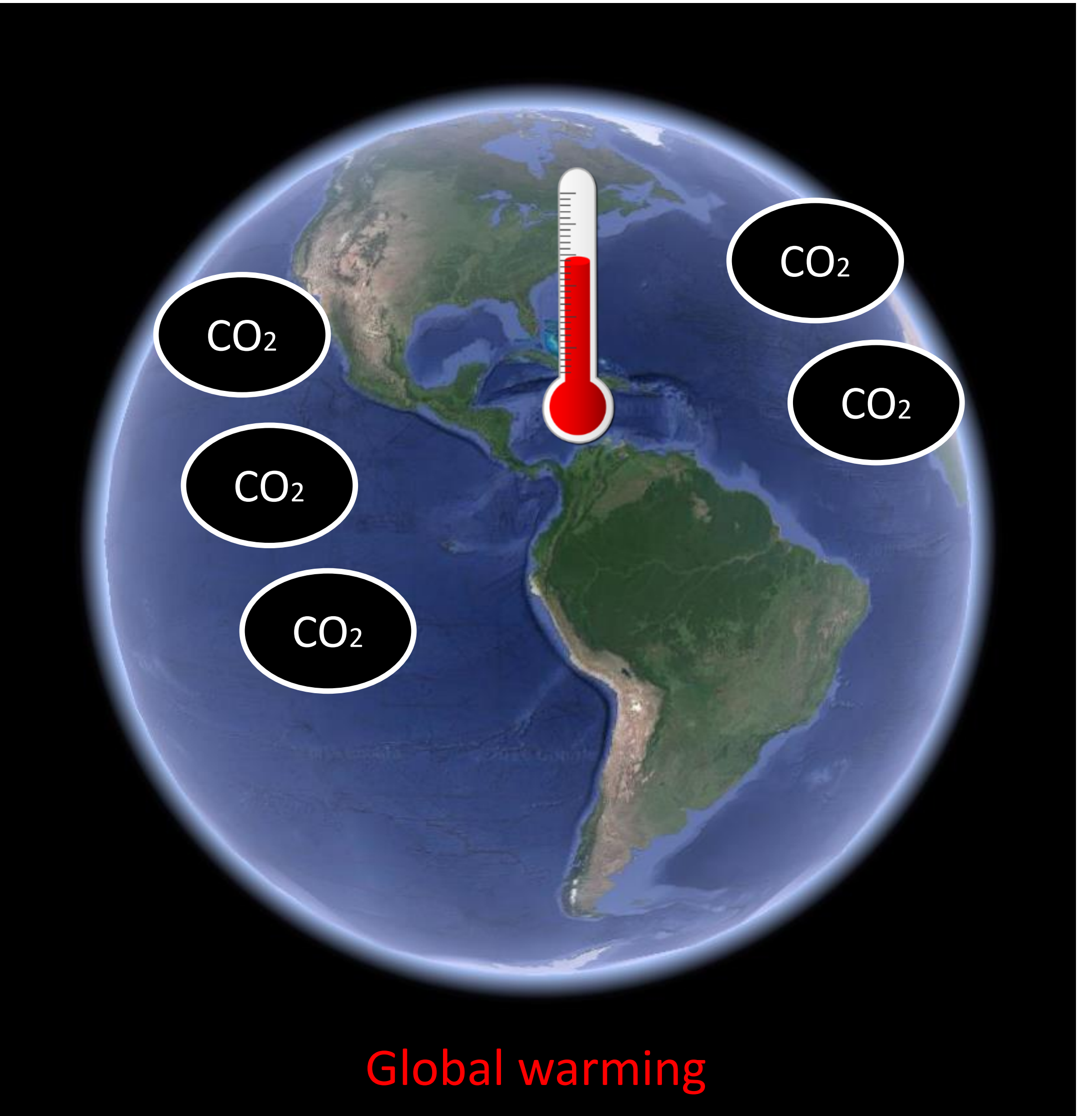
The Earth is suffering…



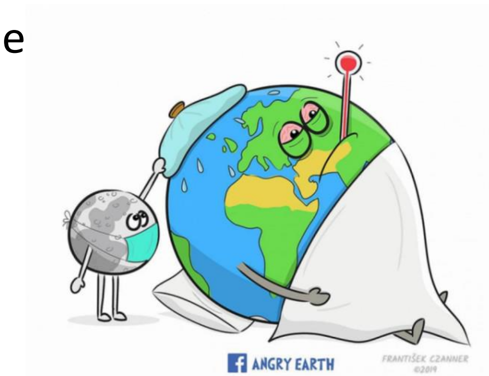
Petroleum a non renewable source of carbon

« The End » of fossil ressources

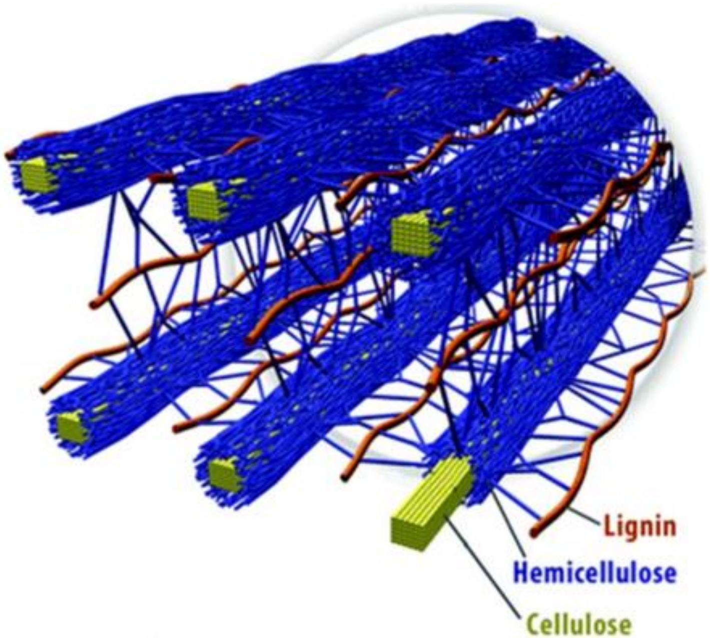
- Extraction becomes more difficult
- Process of heavier fractions
- Fluctuation of the prices
- Political use

Sustainability

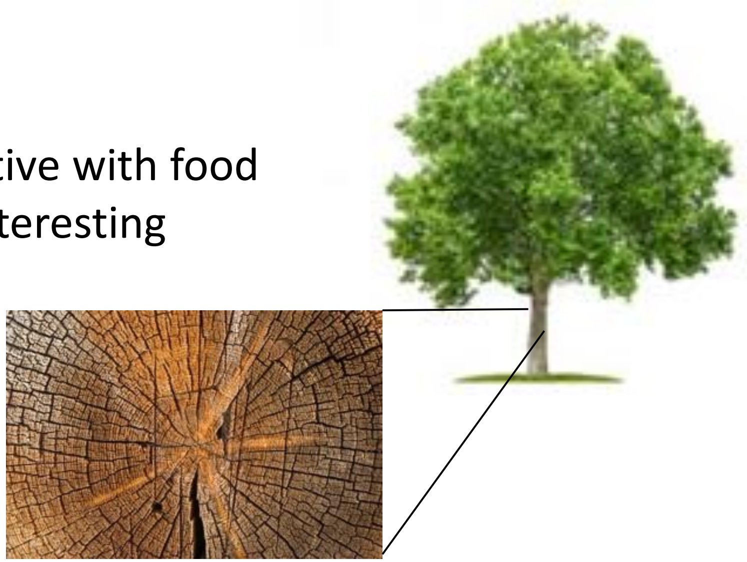
- Neutral Carbon
- Renewable energy sources as an alternative for chemicals and fossil fue



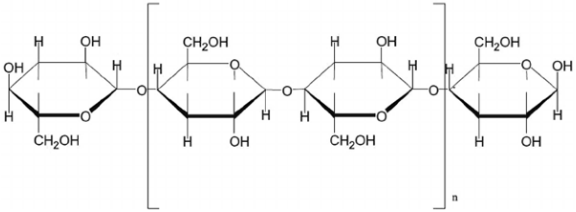
Lignocellulosic biomass



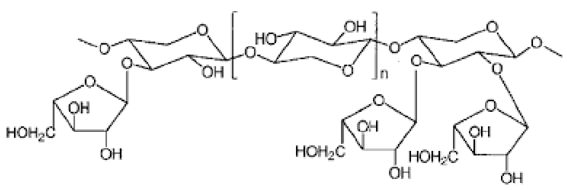
- ✓ Abundant
- ✓ Non competitive with food
- ✓ Chemically interesting



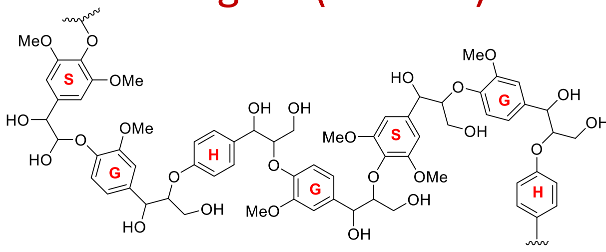
Cellulose (30-45%)



Hemicellulose (20-30%)



Lignin (15-30%)



Sugars, Acids

Aromatics, phenolics

Challenges of the biorefinery

Compared to fossil ressources, biomass feedstocks are:

- More complex, highly functionalized, unstable,
- Containing more contaminants like O, S, N, but also Cl, P, Na, Ca, K, Mg, Si, Fe, Cr…
- Requiring polar/aqueous conditions

Switchgrass

Tulip Poplar

Corn Stover

LIGNOCELLULOSIC BIOMASS DIVERSITY

Pine

Wheat Straw

Beech

Challenges of the biorefinery

Compared to fossil ressources, biomass feedstocks are:

- More complex, highly functionalized, unstable,
- Containing more contaminants like O, S, N, but also Cl, P, Na, Ca, K, Mg, Si, Fe, Cr…
- Requiring polar/aqueous conditions

Lignocellulosic biomass diversity

Composition (C, H, L and others) variation
Feedstock storage and pretreatment
Increase infrastructures costs

Abundant but still limited…

Wastes must be valorized
Targets have to be well identified

From the Refinery to the Biorefinery

Traditional Refinery

Gas

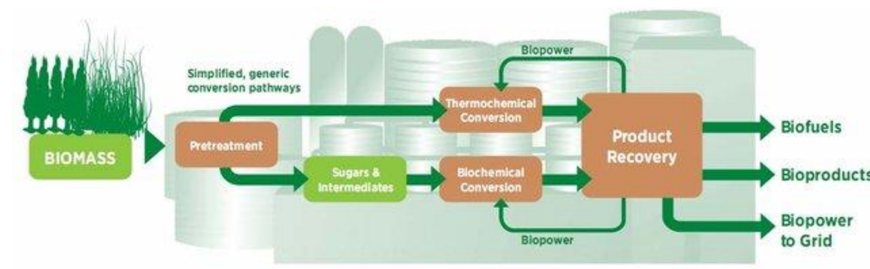
Oils (Fuels)

Petrochemicals
(15-20%)

From the Refinery to the Biorefinery

Traditional Refinery

Biorefinery



Biofuels and Biochemicals






Catalysts for biomass conversion

« Catalysts are needed to improve yields and quality of bio-oils and decrease char/solid formation»

- Metals (Ru, Ni, Fe…)
- Metal Sulfides (Mo, W…)
- Metal Carbides
- Metal Nitrides
- Metal Phosphides
- Metal Oxides
- Zeolites/ordered porous solids

Bi-functionality

Acidic catalysts

Basic catalysts

Deactivation

Poisoning

Degradation

Leaching

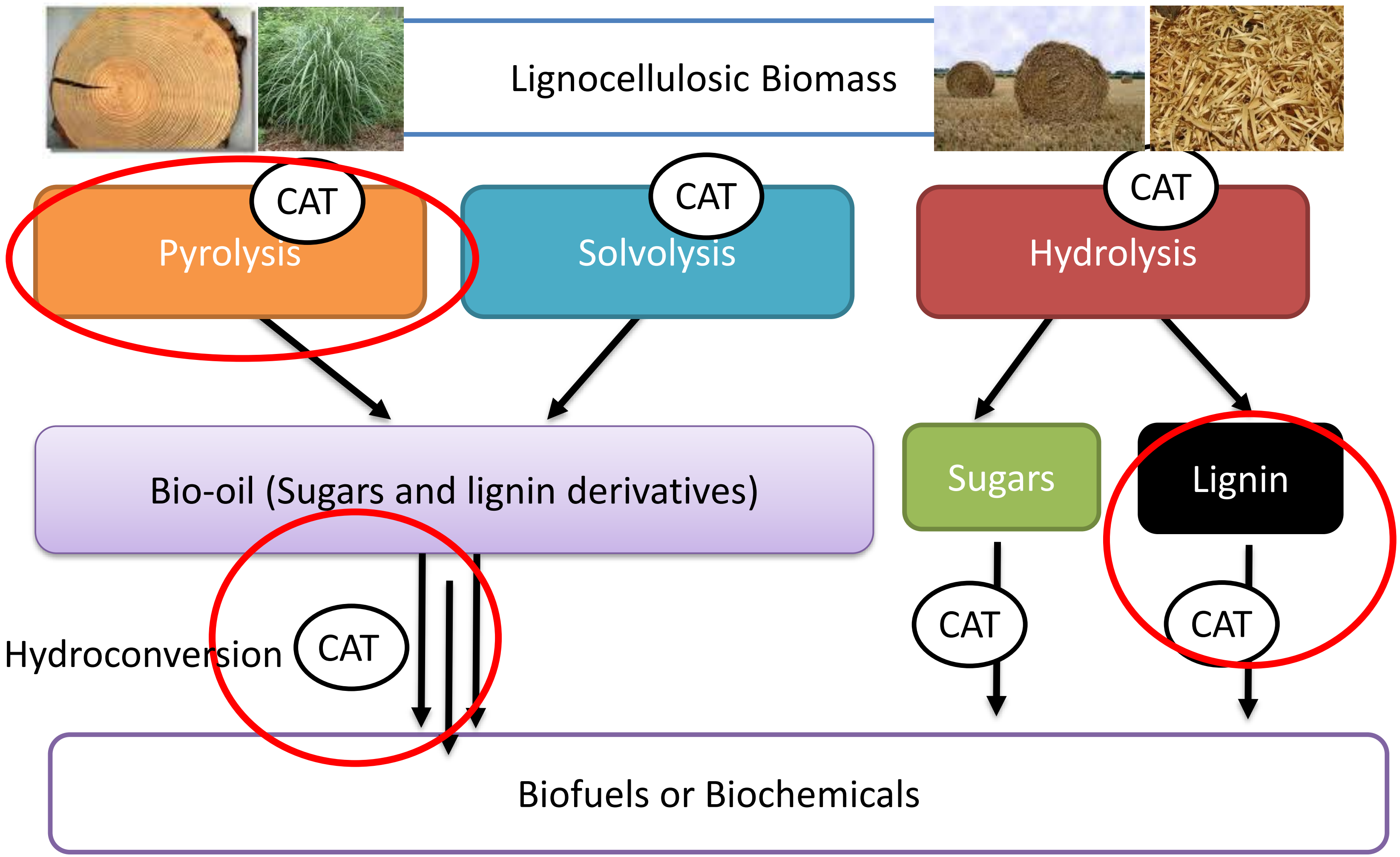
Recyclability

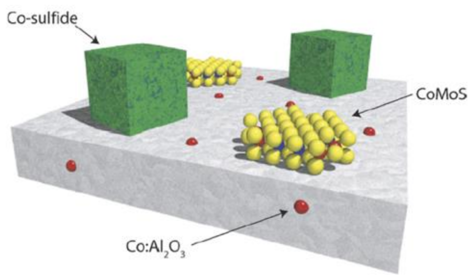
Cleaning

Reduction

Oxidation

Liquefaction of lignocellulosic biomass

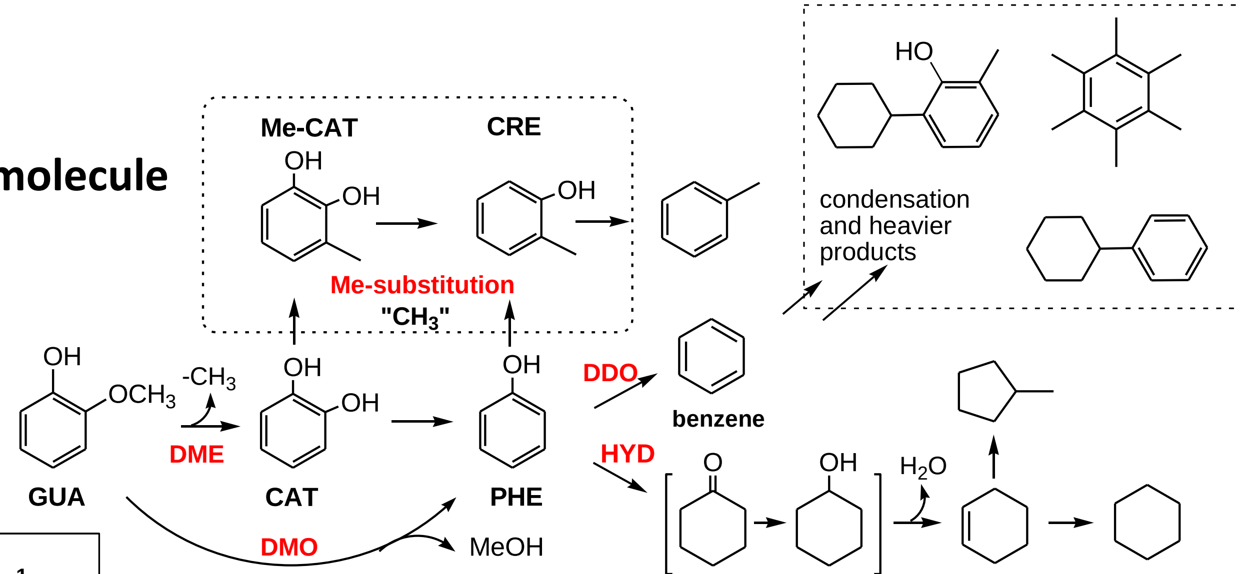


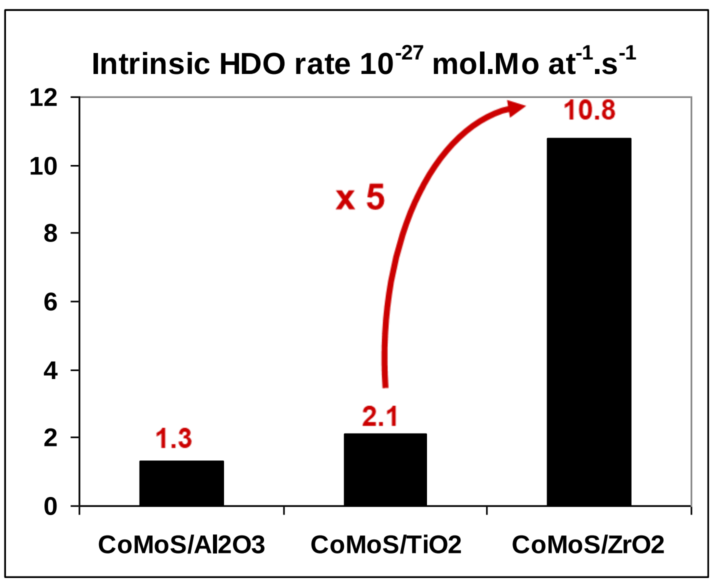


HDO of pyrolytic bio-oils

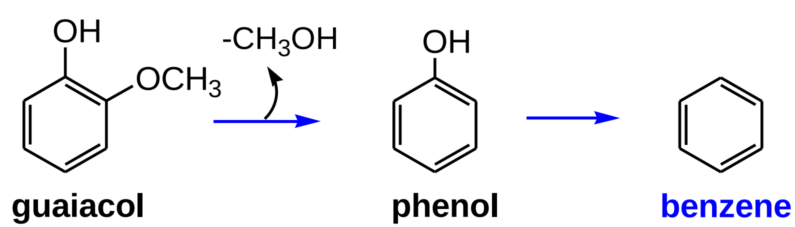
HDO with Guaiacol as model molecule

- Metal sulfide catalysts
- Support effect





CoMoS/ZrO$_2$ Direct deoxygenation reactions



V. N. Bui et al., Appl. Catal. B: Environ., 101 (**2011**) 239 (Part I) and 246 (Part II)

HDO of Guaiacol in liquid phase

HDO of Guaiacol in dodecane
Hydroconversion of lignin in tetralin

$CoMoS/ZrO_2 \approx CoMoS/Al_2O_3 \approx CoMoS/TiO_2$

Analogy between gas-phase and liquid phase can be very limited

- Interaction with Solvent
  Competition, solvating species, mass-transport limitations, structural changes in catalysts….
- Interaction with other components (lignin)

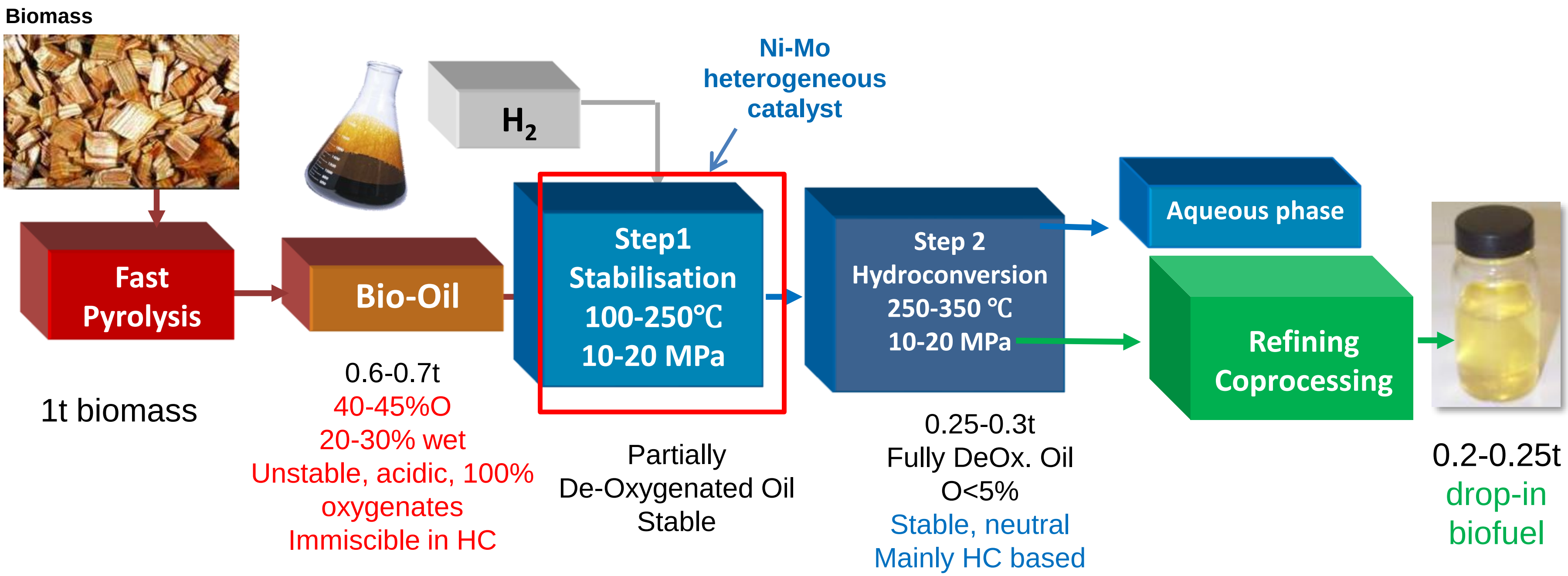
Mixture of molecules for representative reaction

C. Sievers et al. ACS Catal., 2016, 6, 8286

Bio-oil hydroconversion/stabilization

M. Ozagac PhD

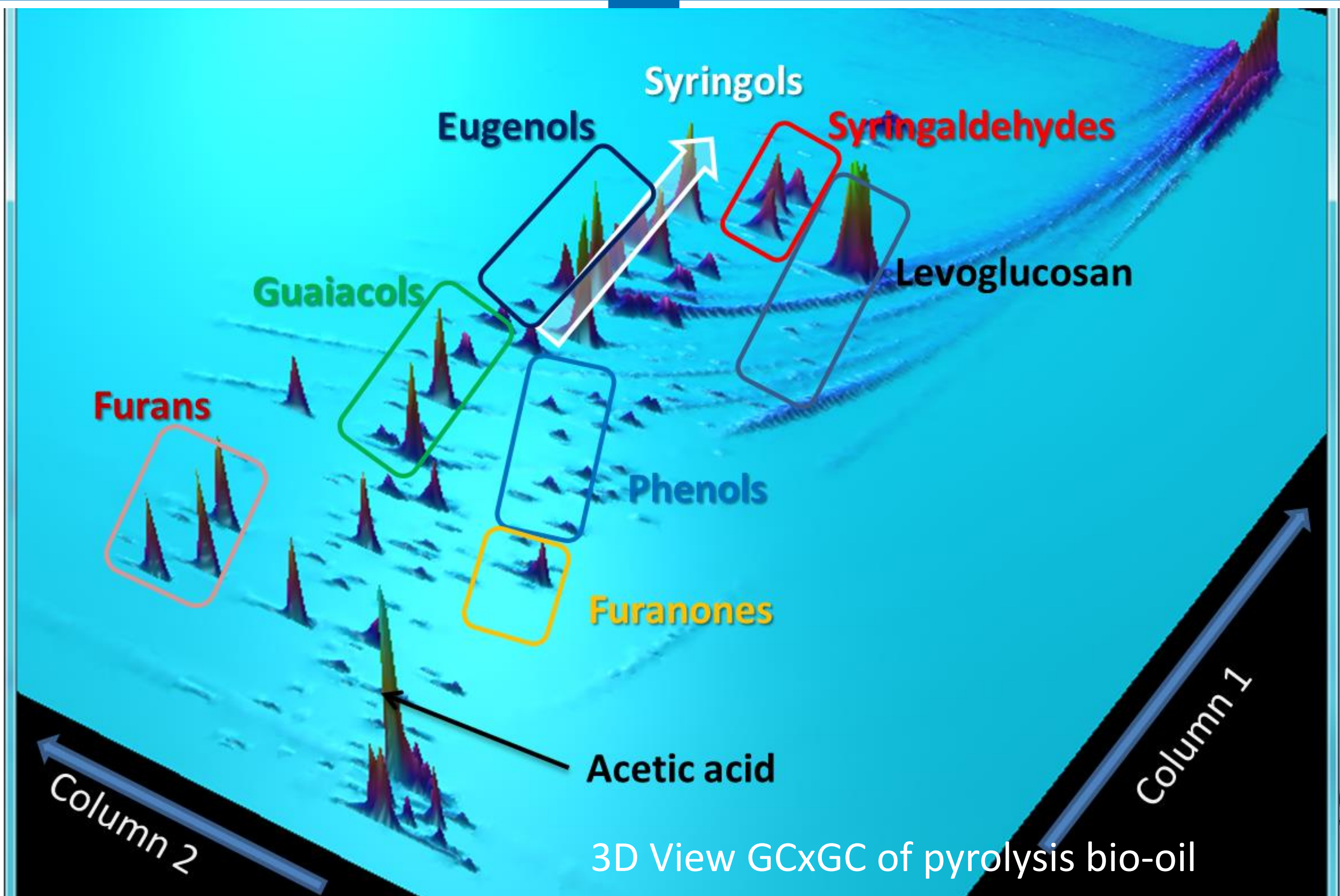
Main Issue: thermal instability during the catalytic hydroconversion process



Catalyst used: reduced $NiMo/Al_2O_3$

Choosing representative model mixture

Pyrolysis Bio-oil Chemical Composition		
Cellulose	Hemicellulose	Lignin
Sugars, acids, alcohols	Furans, acids, alcohols	Phenols, methoxy-phenols



Choosing representative model mixture

Pyrolysis Bio-oil Chemical Composition		
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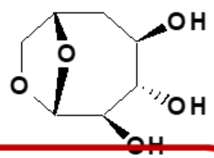
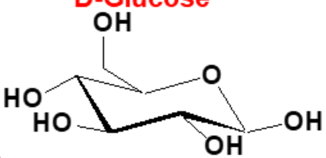
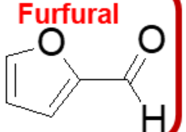
Levoglucosan



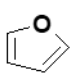
D-Glucose



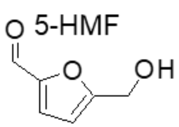
Furfural

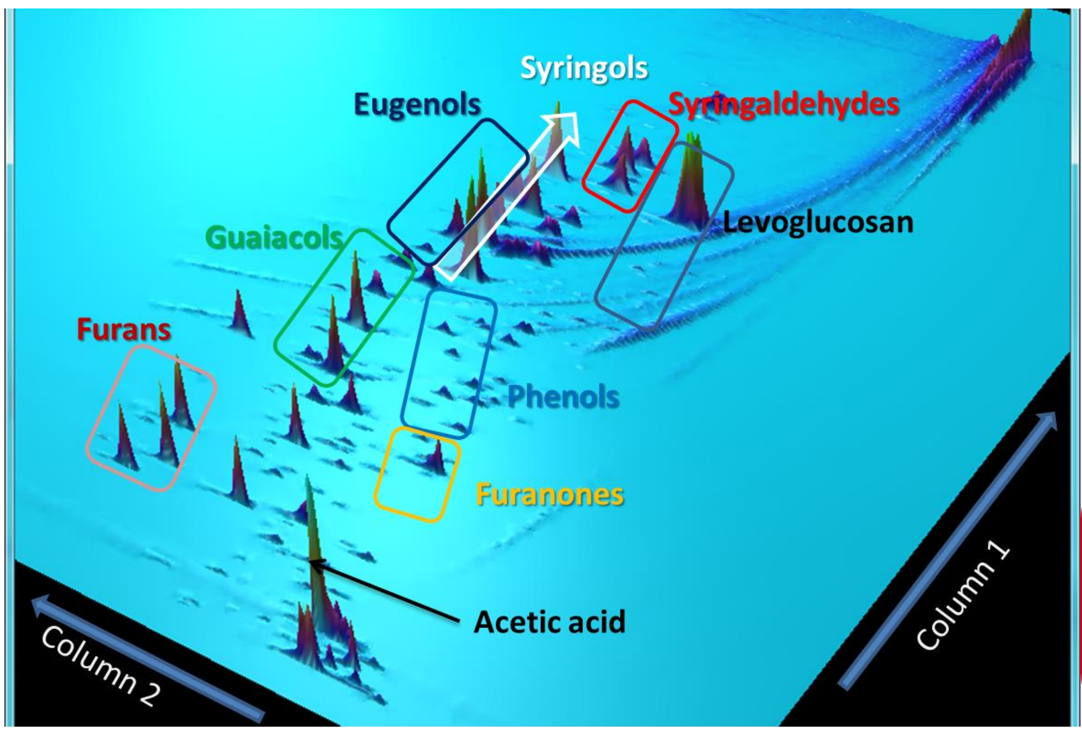


Furan

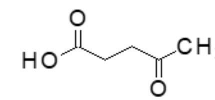


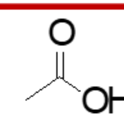
5-HMF



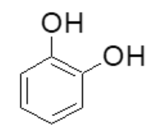


Levulinic Acid

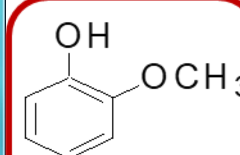




Acetic Acid



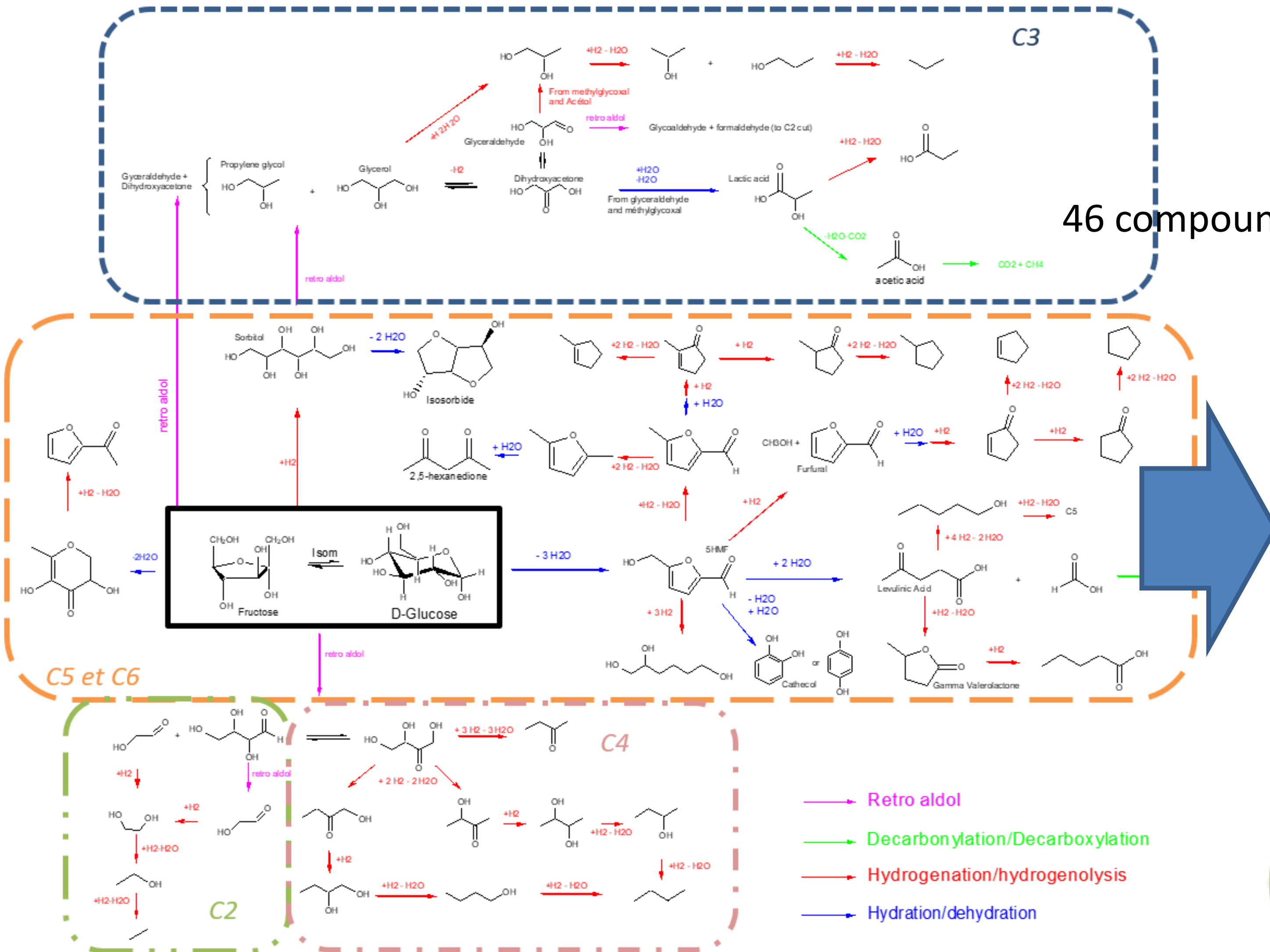
1,2-benzenediol



Guaiacol

Reaction scheme for glucose hydroconversion

Reduced NiMo/Al_2O_3 under H_2 pressure, 250°C

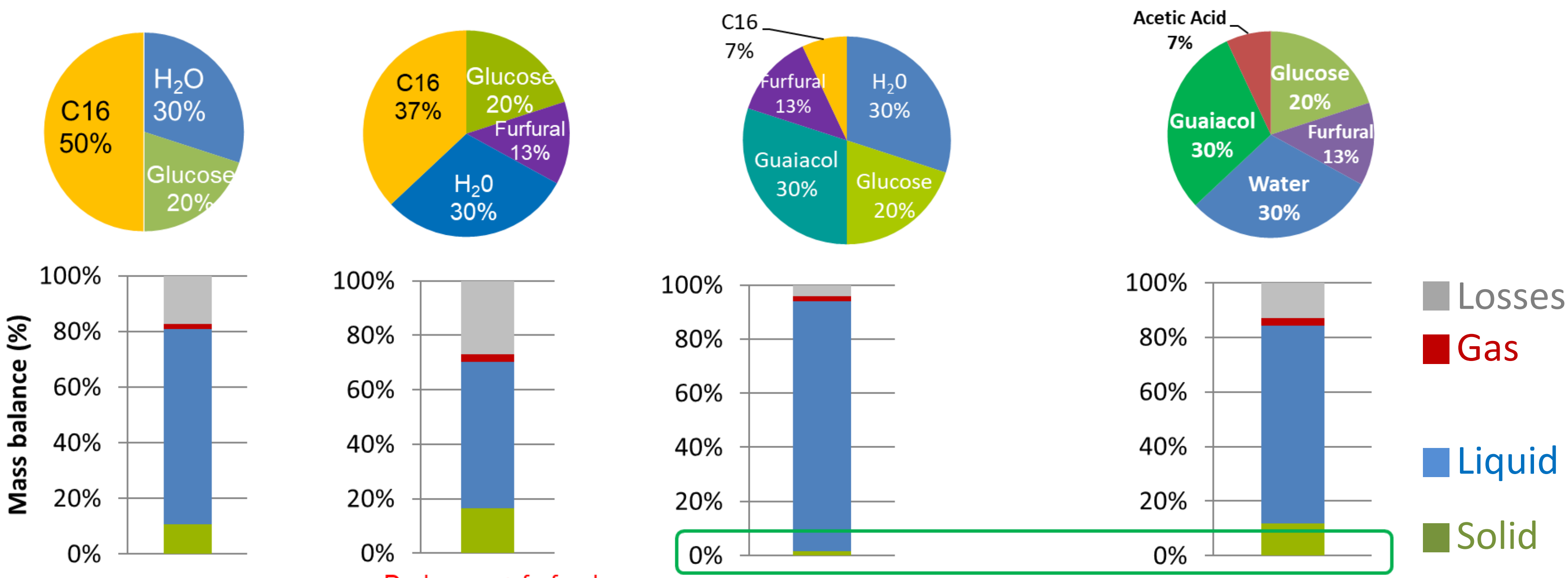


46 compounds identified

Macromolecules

Model Mixtures HDT

C16 as solvent



D-glucose + furfural = High solid production

Guaiacol (one organic phase) → Limiting residue production

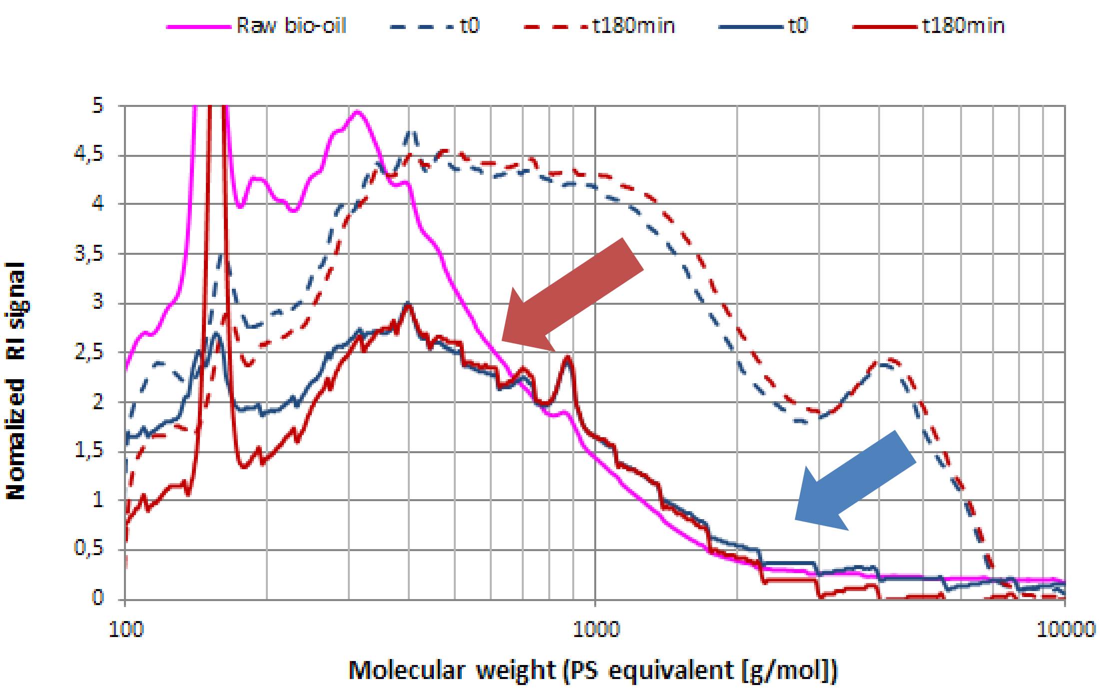
The presence of guaiacol minimized residues production and increased liquid

M. Ozagac et al., Biomass & Bioenergy 95 (**2016**) 182 and 194

Hydroconversion of Bio-oil and guaiacol

HDT of bio-oil without and with guaiacol (50/50wt%) at 250°C on $NiMo_{red}/Al_2O_3$

Size-Exclusion Chromatography SEC-RI detector



Without guaiacol : macromolecules formation

Doted lines: Bio-oil   Solid lines : Bio-oil/guaiacol mixture

M. Ozagac et al., Biomass & Bioenergy 108 (**2018**) 501

Conclusion on guaiacol effect in HDT of bio-oils

Hydroconversion of model compounds

D-Glucose + Furfural + Acetic acid with water

- Production of Macromolecules/solids

Blend with Guaiacol

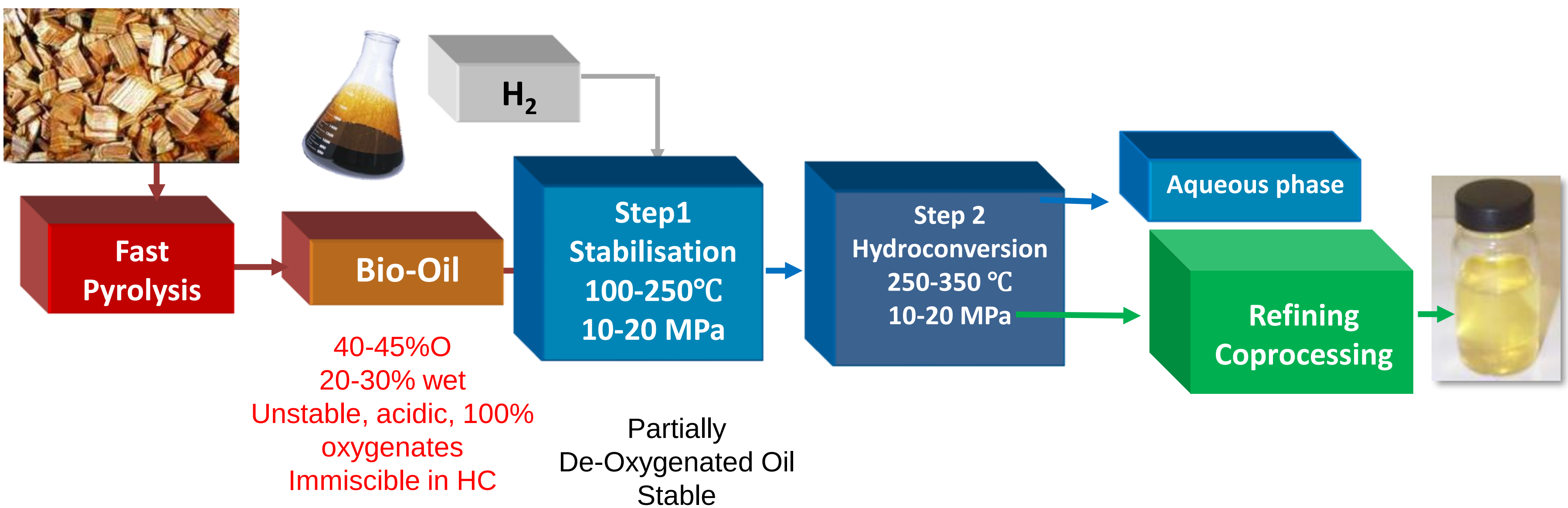
- Solid residues production limited
- Guaiacol is stabilizig reactive compounds precursors of solids

Hydroconversion of Pyrolysis Bio-oil

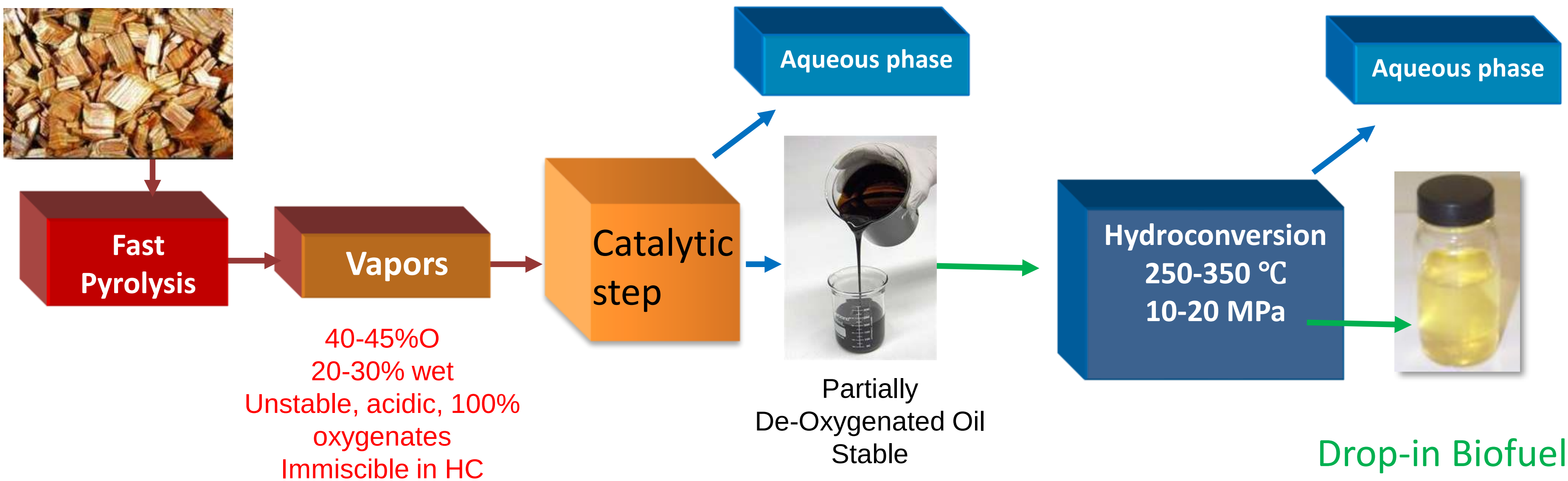
- Same trends !
- Representative

M. Ozagac et al., Biomass & Bioenergy 95 (**2016**) 182
M. Ozagac et al., Biomass & Bioenergy 95 (**2016**) 194
M. Ozagac et al., Biomass & Bioenergy 108 (**2018**) 501

Catalytic conversion of Pyrolytic Vapors



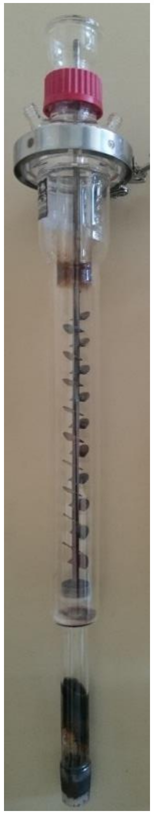
Catalytic conversion of Pyrolytic Vapors



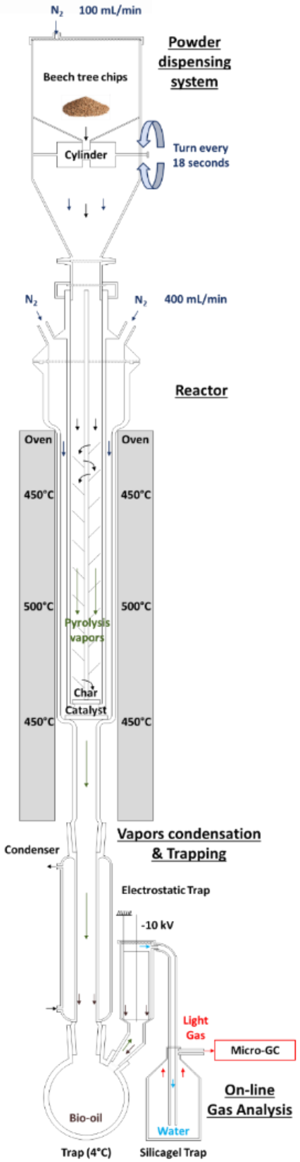
ANR project CATAPULT: CATAlytic **P**yrolysis to **U**pgraded bio-oi**L**s for a join**T** production of chemicals and fuels

📖 C. Torri et al., *J. Anal. Appl. Pyrolysis*, 88, 2010, 7.
📖 P. T. Williams et al., *Energy*, 25, 2000, 493.

Semi-continuous pyrolysis set-up



Picture of the pyrolysis reactor

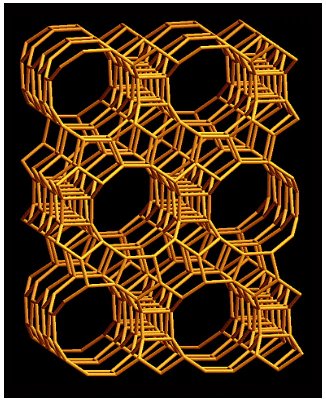


- The reactor, heated at 500°C, quartz tube containing two porous frits
- The first frit stops char and protects the catalyst supported on the second one
- A nitrogen flow of 6 $L.h^{-1}$ inerts the biomass injector and 24 $L.h^{-1}$ added in the reactor
  (Possibility to add H_2 flow during pyrolysis)
- A condensing system collects the bio oil at 4°C
- An electrostatic trap captures very fine oil droplets
- A last trap with silica gel protects the micro GC used for on-line gas analysis

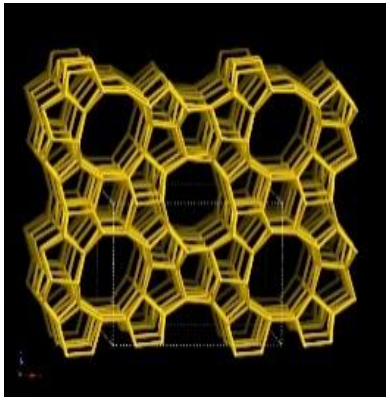
A. Margeriat et al., J. Appl. Anal. Pyrol. 130 (**2018**) 149

Zeolites catalysts

Catalysts	BET (m^2/g)	ICP-OES analysis (wt%)
HBeta	713	
HMFI-90 (ZSM-5)	422	
5%Ni/HMFI-90	392	(Ni) 4.7
5% Zn/HMFI-90	375	(ZnO) 4.9
5% Pt/HFMFI-90	406	(Pt) 4.8
5% Ce/HMFI-90	400	(CeO_2) 4.7



H-Beta BEA Structure



MFI (ZSM-5) Structure

Preparation of catalyst 5%M/HMFI-90 by incipient wetness impregnation

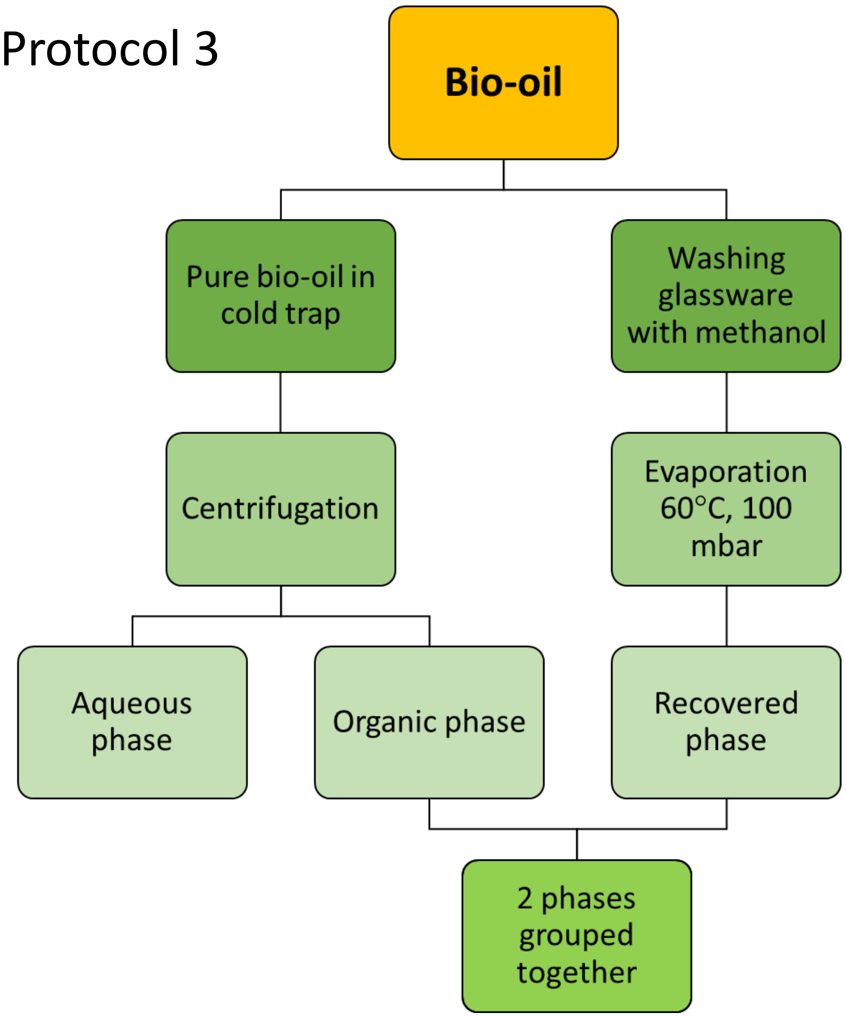
- Precursor used : $M(NO_3)_2$, $6H_2O$
- Dry in air (25°C) then in oven (100°C)
- Calcination at 550°C during 5h
- *In situ* reduction at 500°C under 10% H_2/N_2 (500 mL/min) during 1h

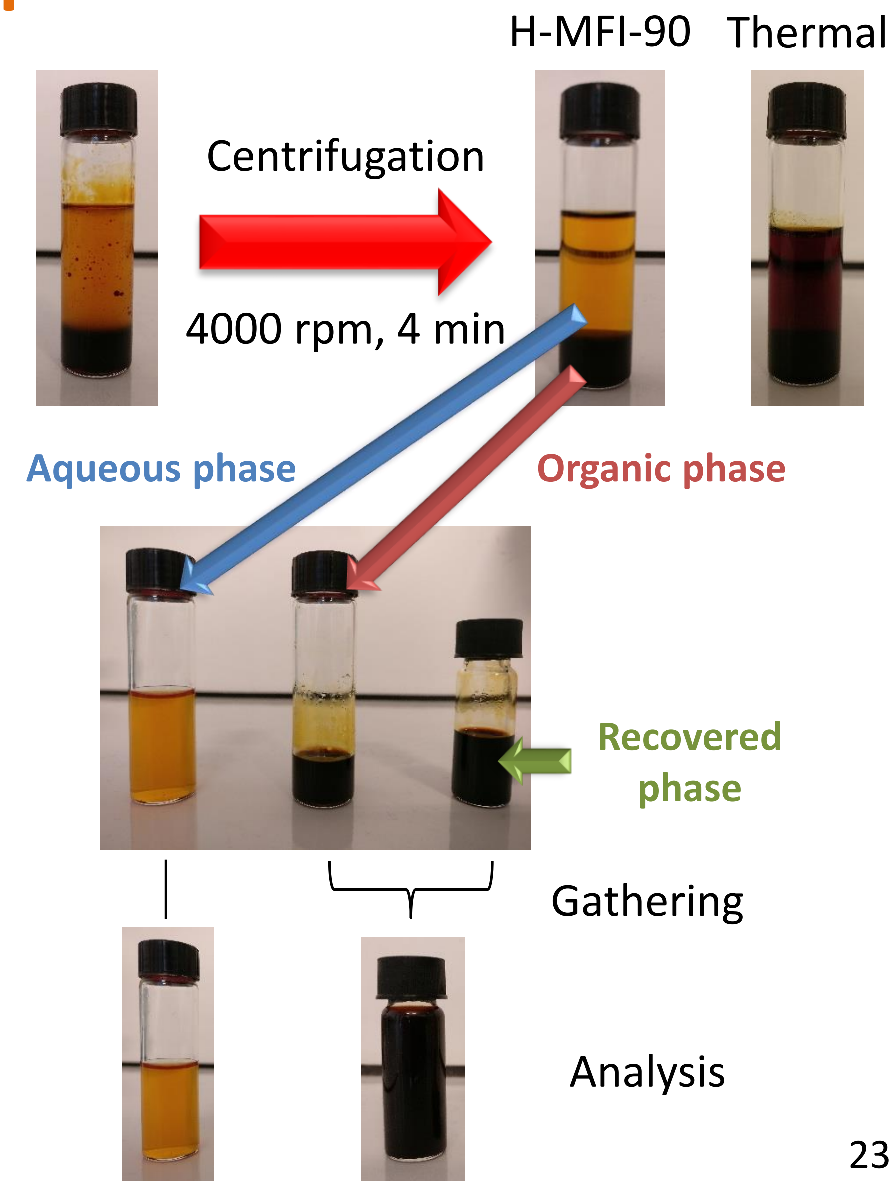
➢ catalyst-to-biomass ratio of 1:10

A. Margeriat et al., J. Appl. Anal. Pyrol. 130 (**2018**) 149

Bio-oil recovery protocol

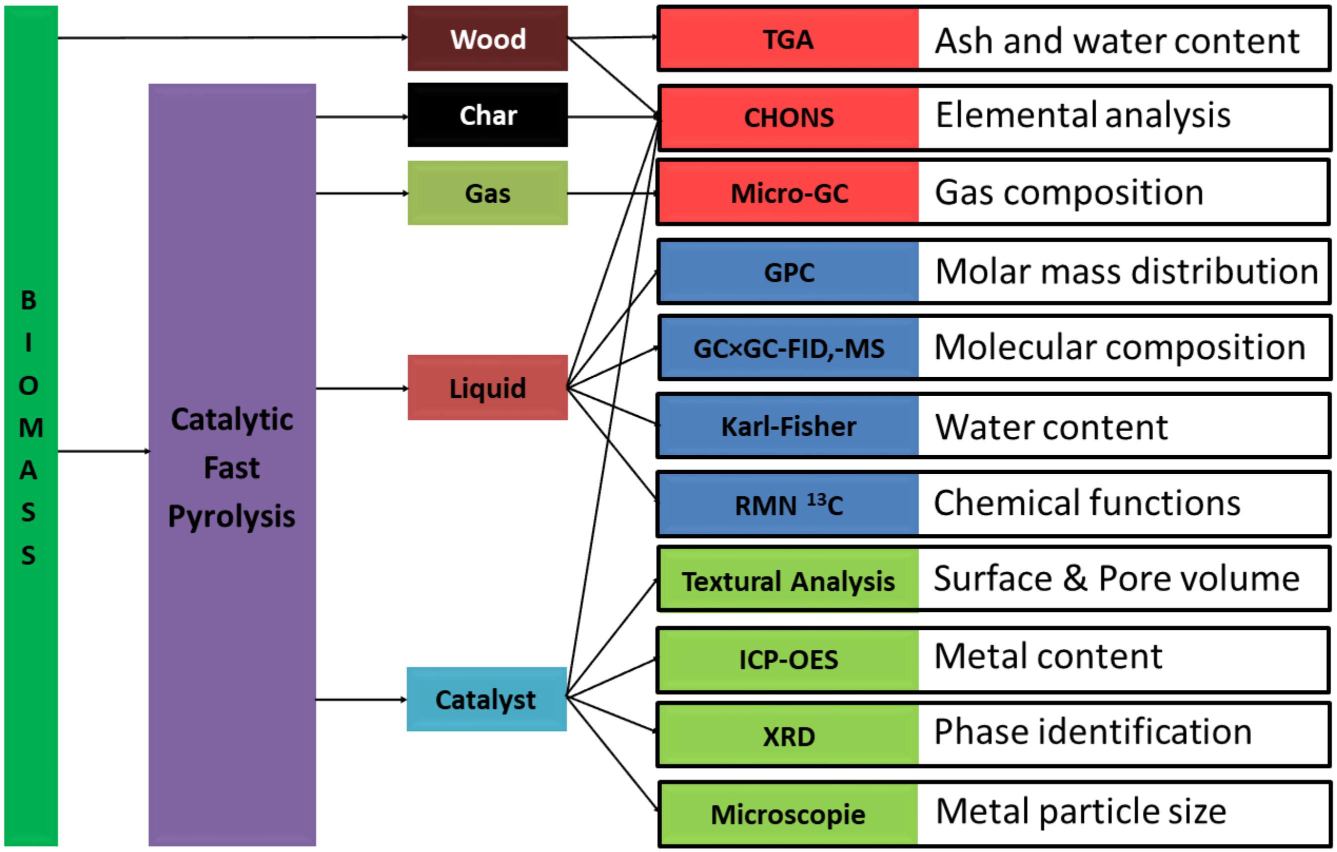
Protocol 3





A. Margeriat et al., J. Appl. Anal. Pyrol. 130 (**2018**) 149

Analytical strategy



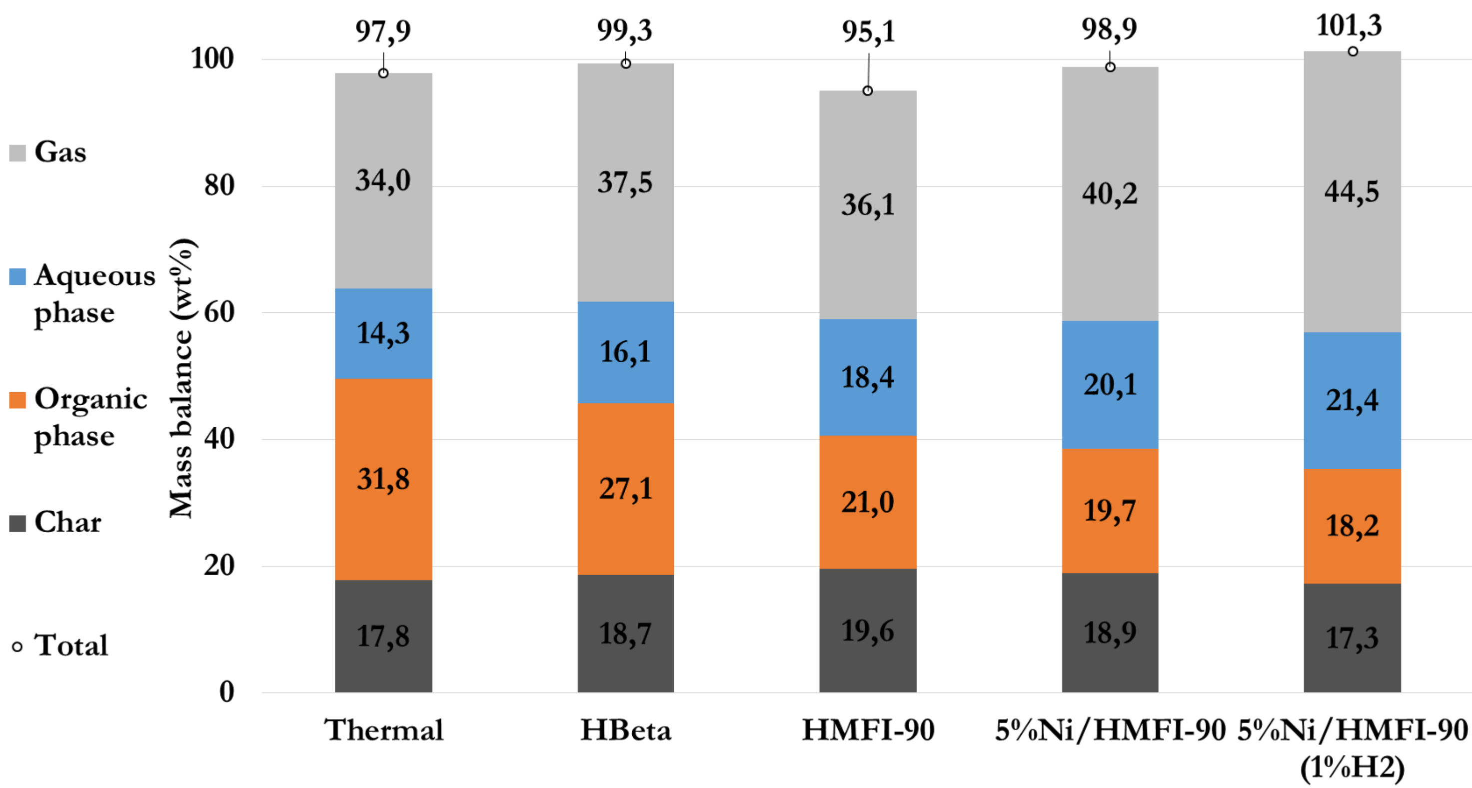
- Multi-techniques analysis of the fractions and catalyst
- screening of catalysts is time-consuming !!!

A. Margeriat et al., J. Appl. Anal. Pyrol. 130 (**2018**) 149

Catalytic results *vs* thermal

Catalyst-to-biomass ratio : 1/10
T: 500°C (pyrolyse); catalyse (470°C)

Mass balance ≥ 95(wt%)



In the presence of catalyst

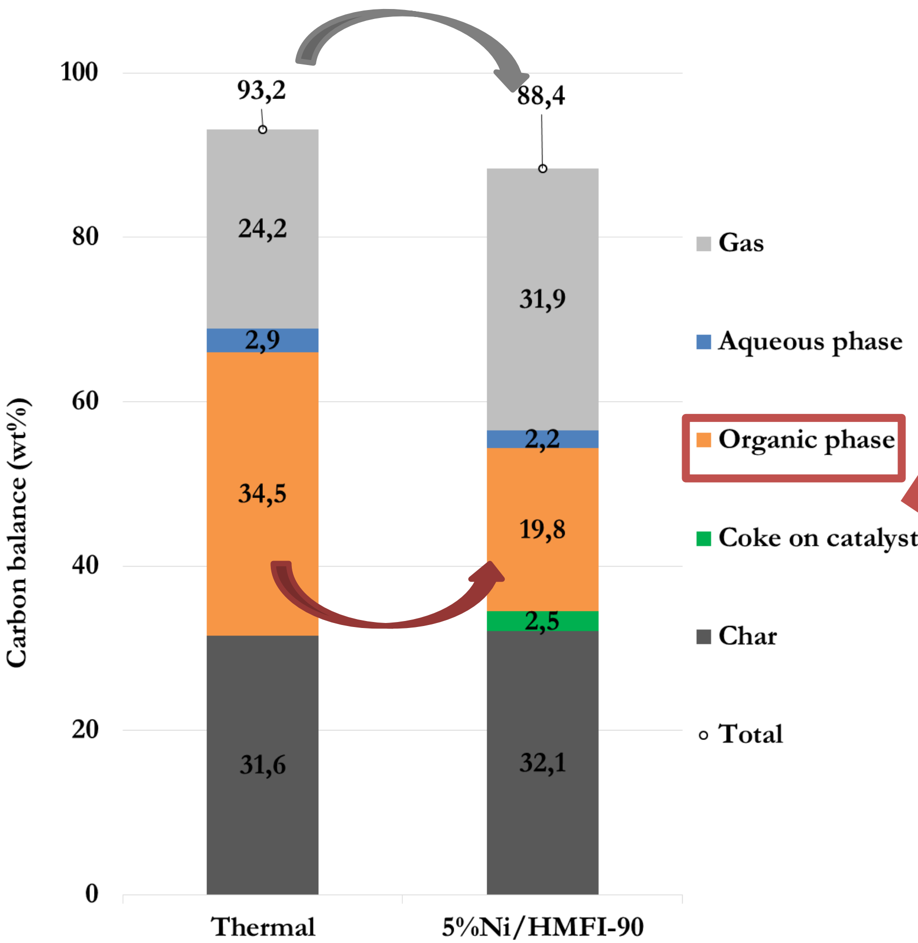
Increase of gas fraction with catalysis

Increase of aqueous fraction

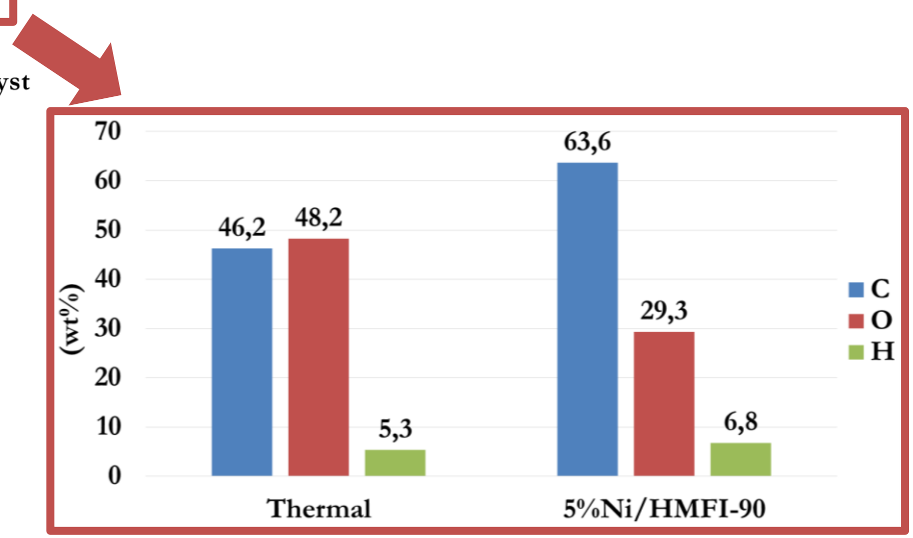
Decrease of organic fraction

A. Margeriat et al., J. Appl. Anal. Pyrol. 130 (**2018**) 149

Carbon balance thermal *vs* catalytic

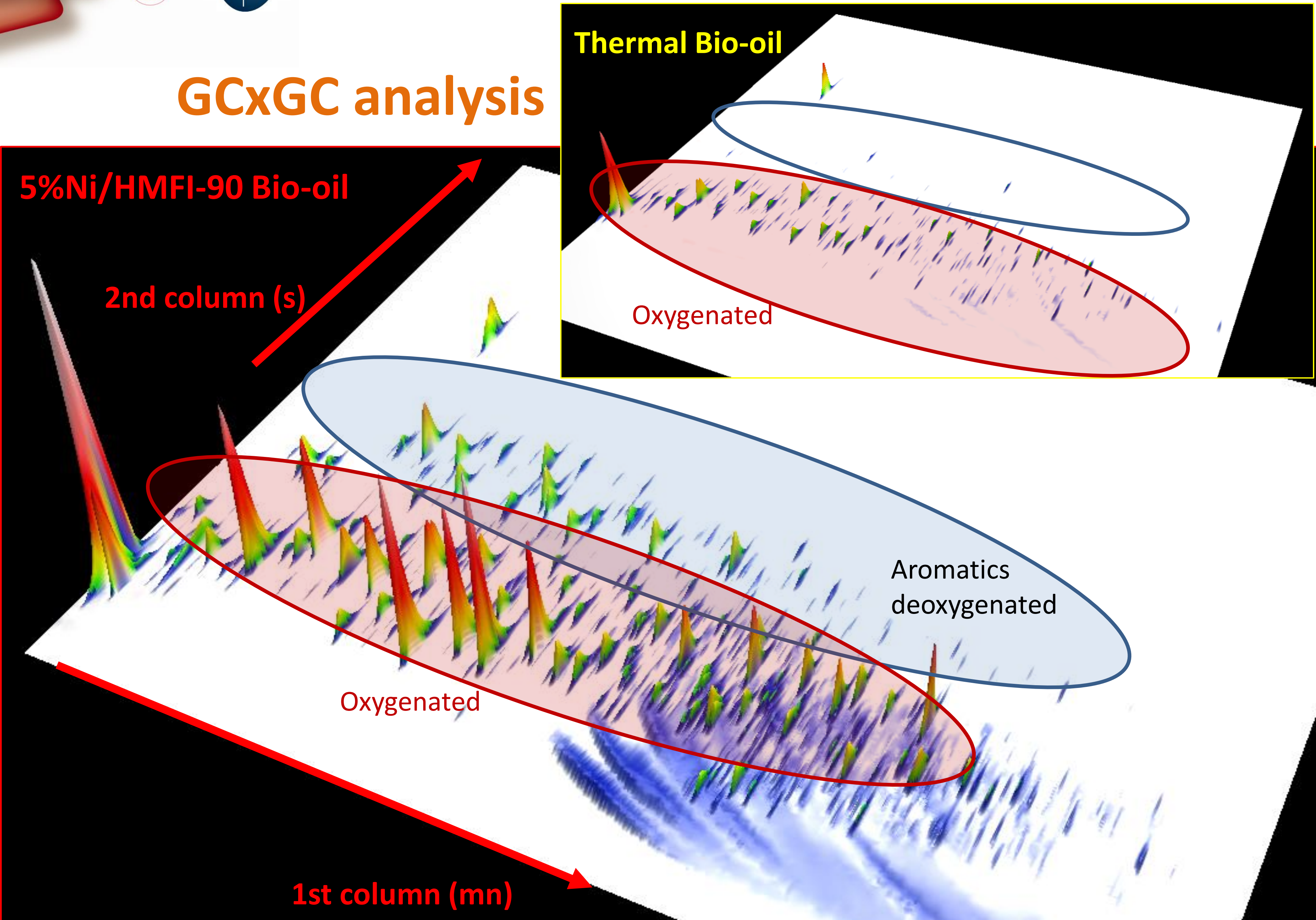


- With a catalyst, gas phase is carbon enriched

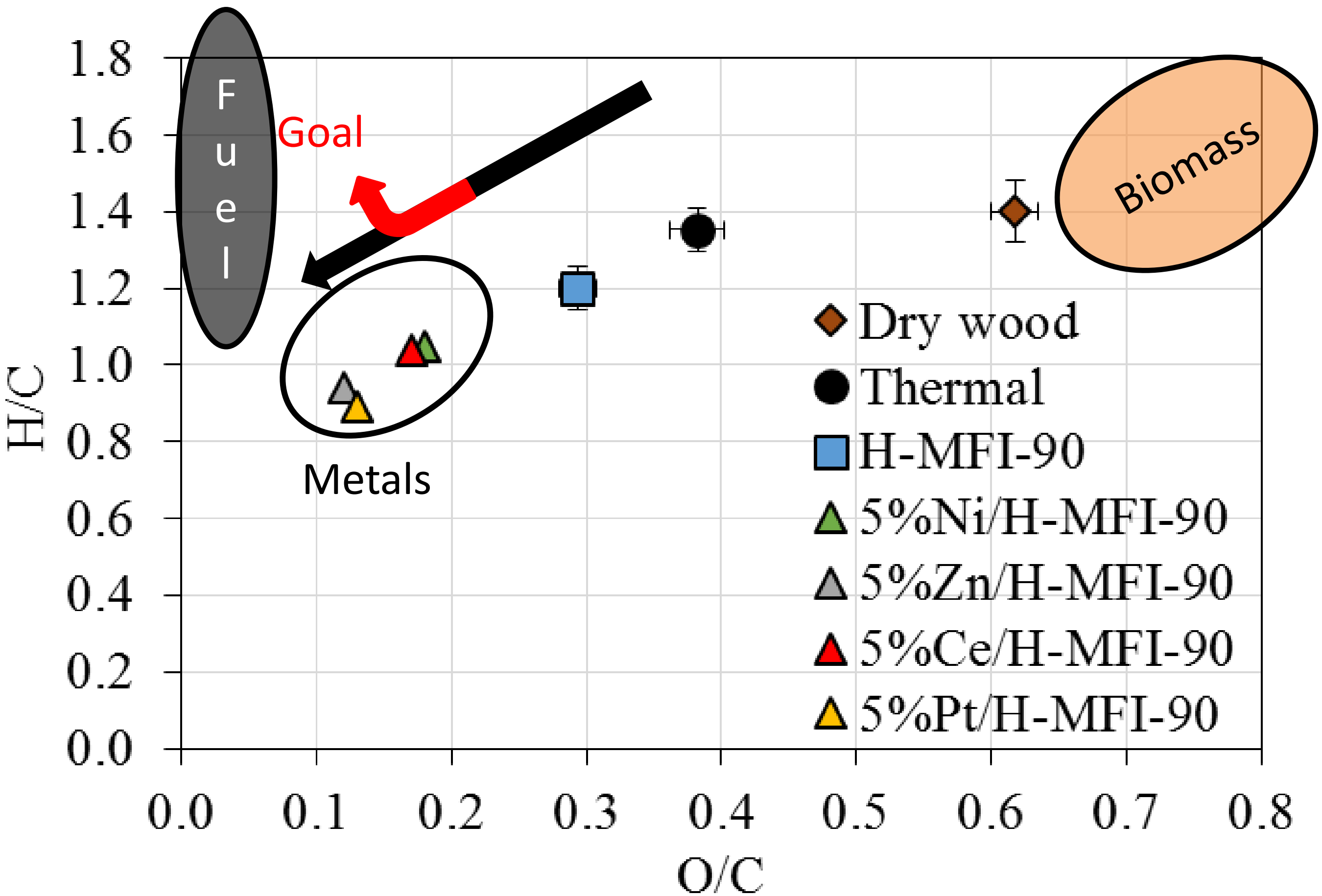


A. Margeriat et al., J. Appl. Anal. Pyrol. 130 (**2018**) 149

GCxGC analysis



Van Krevelen diagram of organic phase



- Presence of metals on H-MFI-90 decreases O/C and H/C ratios
- H_2 addition is necessary to upgrade bio oil

A. Margeriat et al., J. Appl. Anal. Pyrol. 130 (**2018**) 149

Conclusion on catalytic conversion of pyrolytic vapors

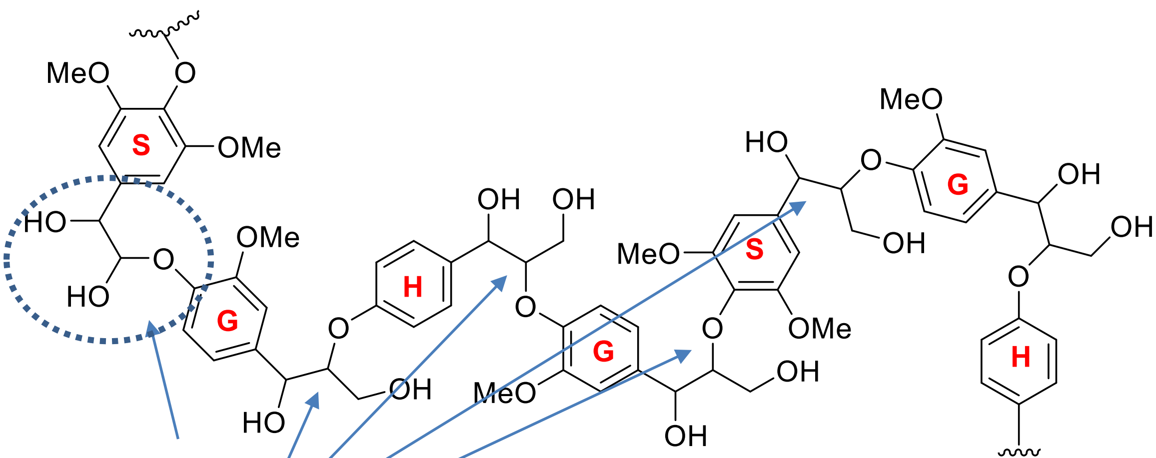
- Catalysis plays a role in the composition and stabilization of the bio-oil
- Metal/HMFI catalysts are good candidates to convert pyrolytic vapors
- Catalyzed bio-oil is more stable (conversion of small acids, aldehyde and ketones)
- Characterization of bio-oil needs improvement (25-33 wt% quantified by GC×GC-FID)

S. Eibner et al., Appl. Catal. B: Env., 219 (**2017**) 517
A. Margeriat et al., J. Appl. Anal. Pyrol. 130 (**2018**) 149

Catalytic Lignin conversion

Lignarocat project
Funded by ANR

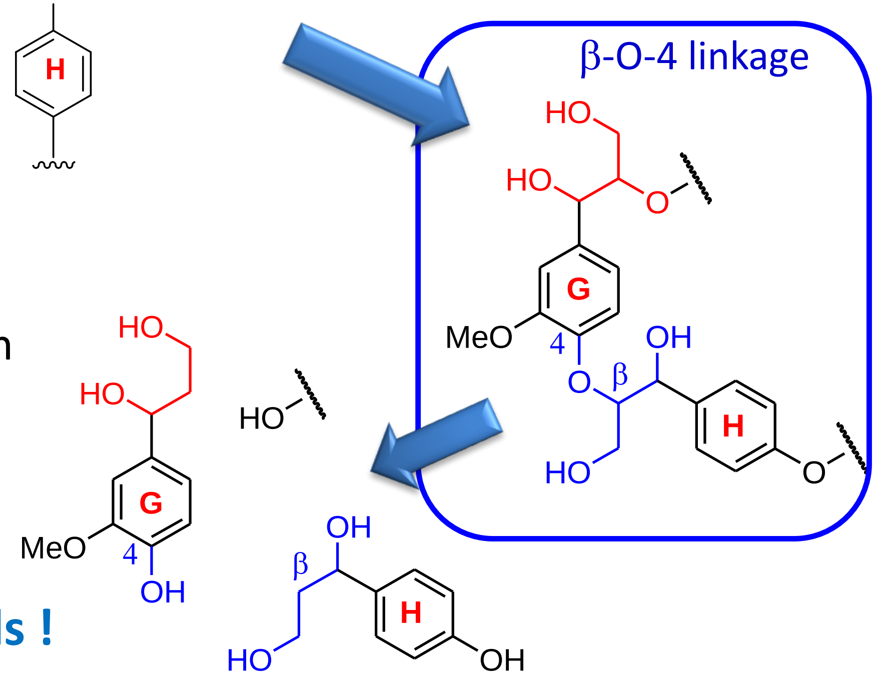
The only natural abundant precursor for aromatics: what is native lignin ?



β-O-4 Ether linkages

50–80% or more of the measurable inter-unit linkage types

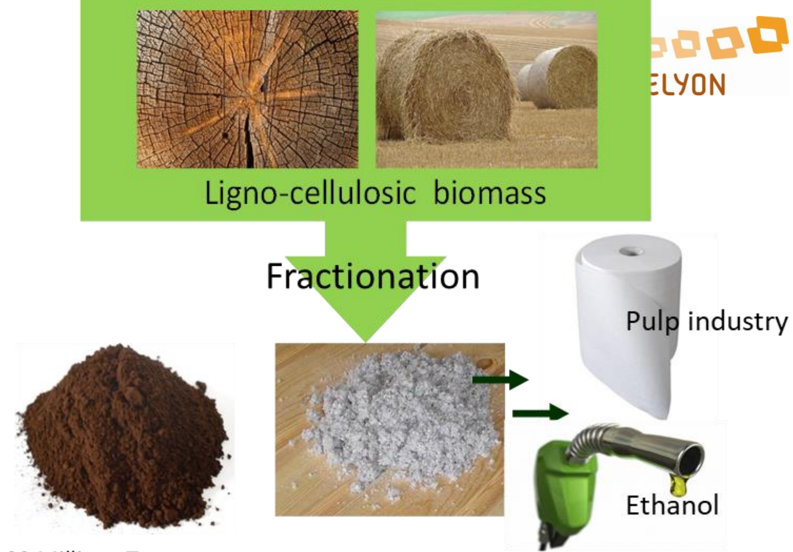
Early-stage Catalytic Conversion of Lignin (ECCL) in LC or “lignin-first” approach



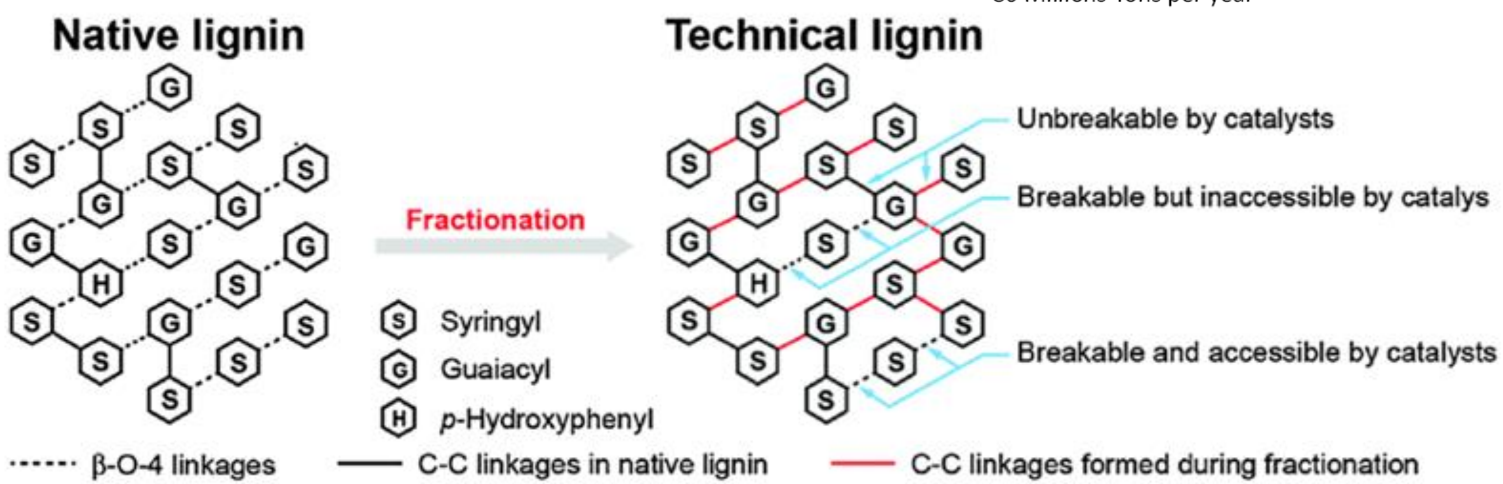
High phenolic monomers yields !

R. Rinaldi *et al.,* Angew. Chem. Int. Ed. 55 (2016) 8164
W. Schutyser et al., Green Chem., 17 (2015) 5035
T. Parsell et al., *Green Chem.*, 17 (2015), 1492

What is (technical) lignin ?



80 Millions Tons per year



Highly branched structure
Strong intramolecular force
Low solubility in solvents

+

Low accessibility

=

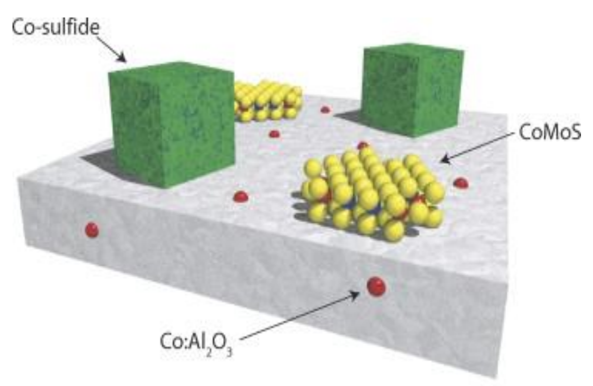
Low conversion and low reaction efficiency

L. Shuai, B. Saha, Green Chem. 19(2017) 3752

Which catalysts ?

- Robust (S-, N-resistant,….)
- Not expensive
- Hydrogenolysis of C-O bonds
- Weak hydrogenating behaviour

Hydrotreating sulfide catalysts
Based on Mo or W
With Ni or Co as promoters

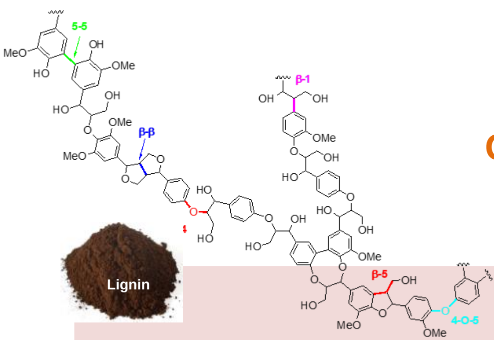


« CoMoS » Active phase

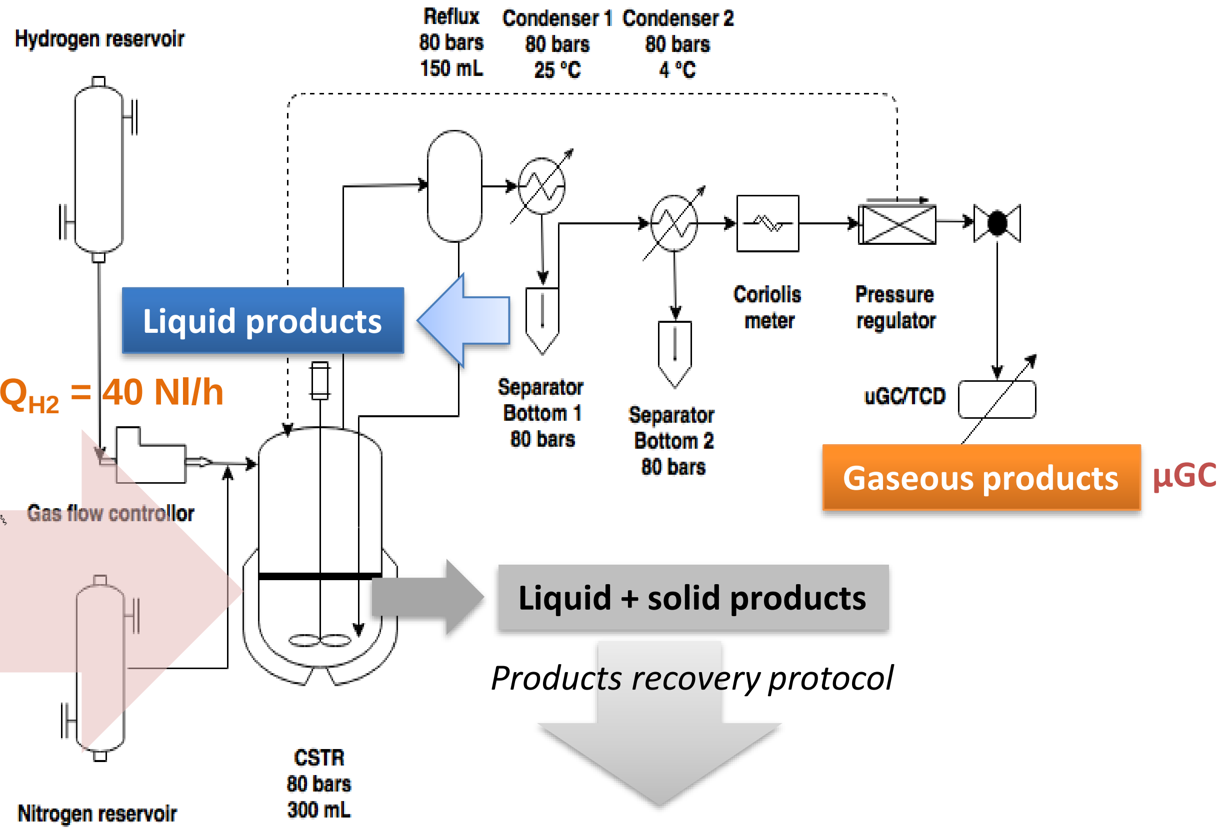
<u>In literature:</u>
Ru, Pd, Cu, Fe and Ni catalysts
Phosphides (Ni, W, Mo)
Carbides (Ru, Mo)

H. Topsoe et al., J. Catal. 68 (1981) 433.

Lignin Catalytic Hydroconversion



Lignin: 30 g
CoMoS/Al_2O_3 10 wt%
Tetralin (70 g)
350 °C P_T = 80 bar



Products recovery protocol

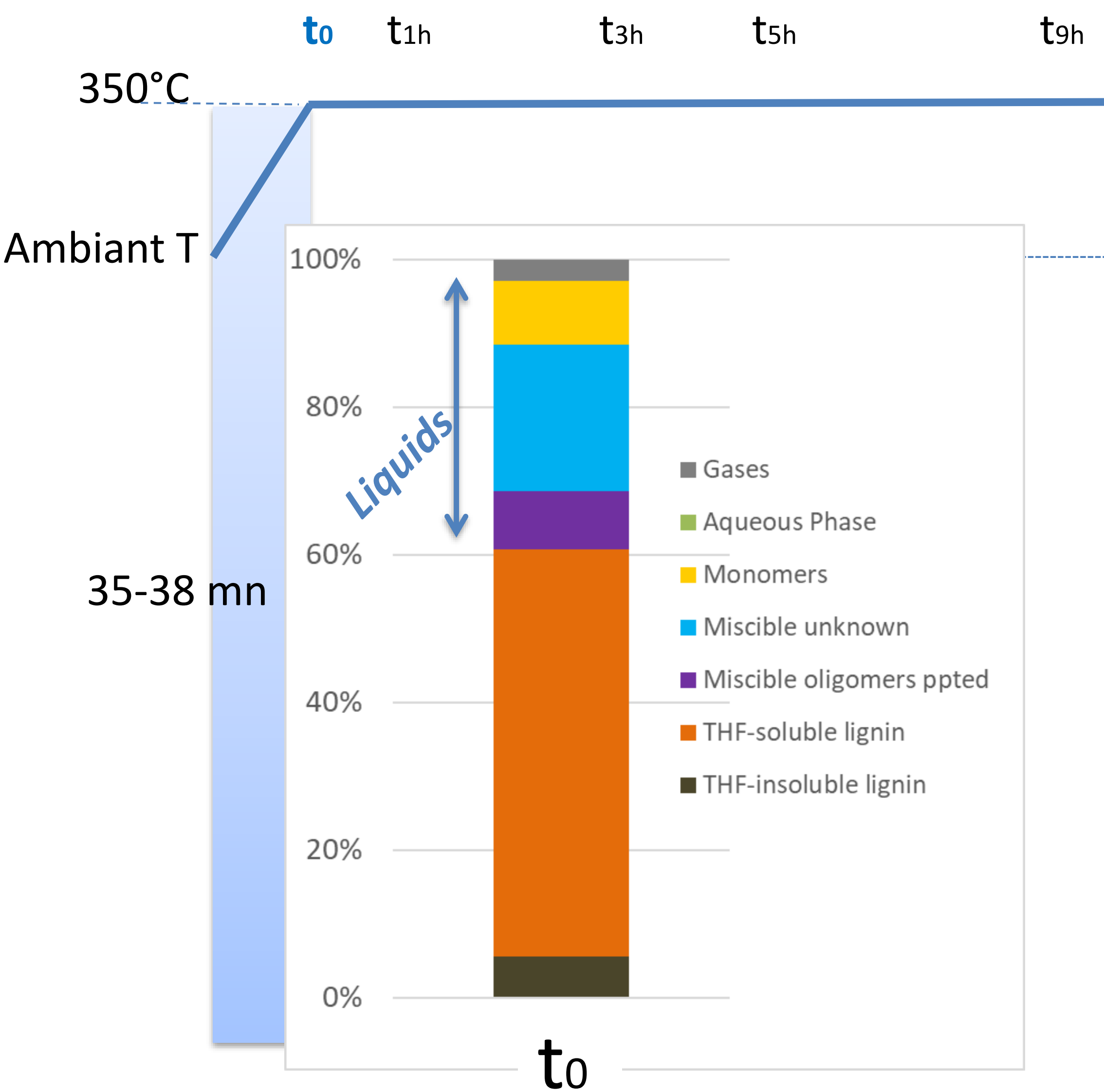
Liquids	THF-Soluble Solids	Insoluble Solids
GPC	CHONS	CHONS
^{13}C NMR	GPC	
GCXGC	NMR (1D and 2D)	

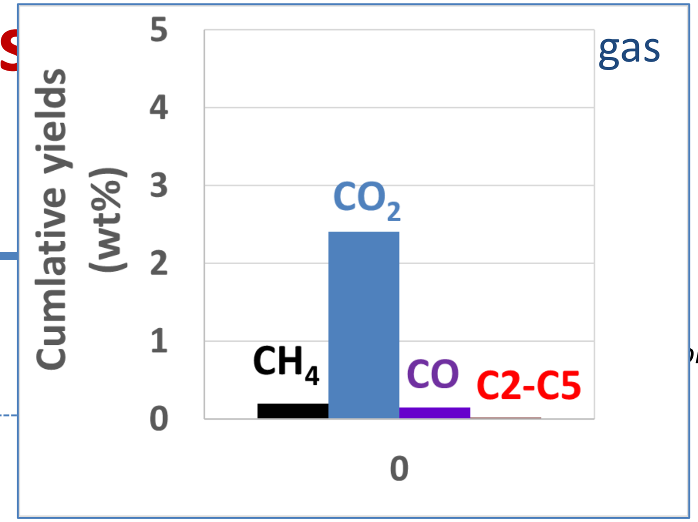
J. Pu et al., Appl. Catal. B: Env. 256 (**2019**) 117769

During the heating stage :

structural changes already occured

Catalytic hydroconvers

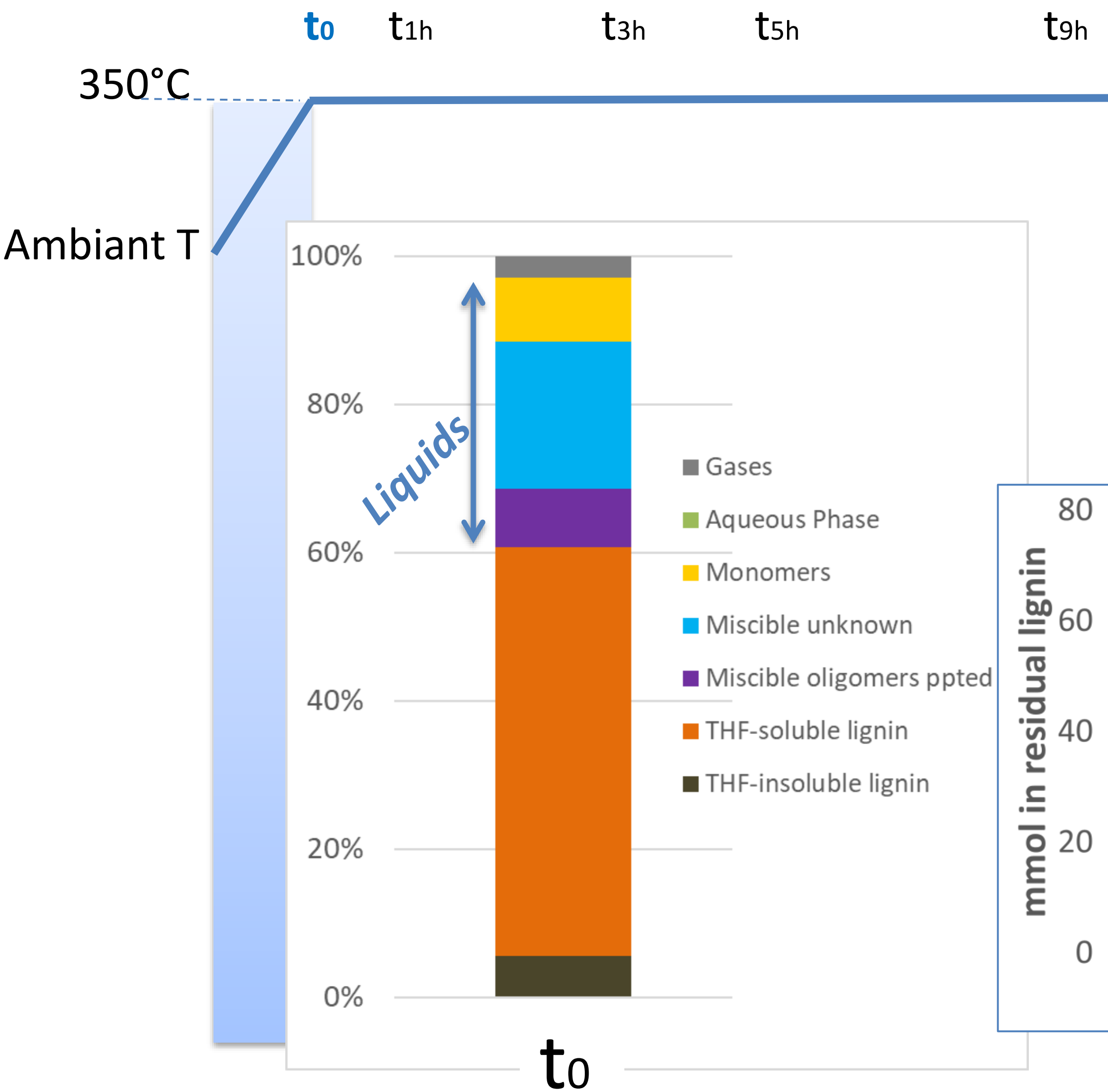




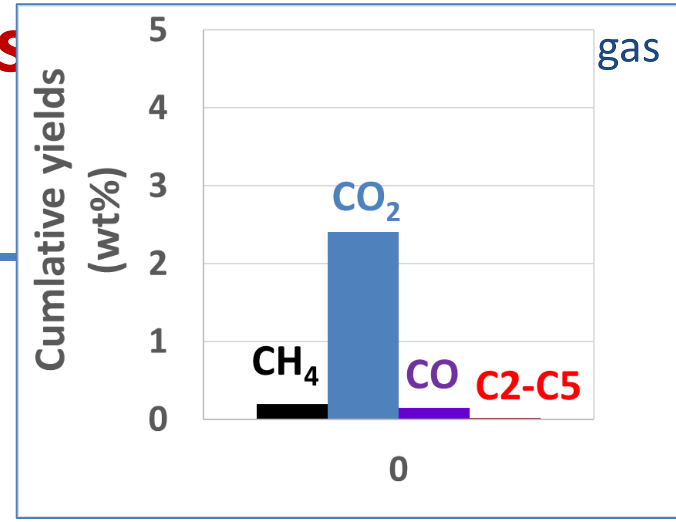
Mass balance: 96-98 wt% for all experiments

Liquids = Miscible oligomers precipitated
+ monomers + aqueous + unknown fraction
THF-soluble lignin = Lignin residue
THF-unsoluble lignin = solids (ash)

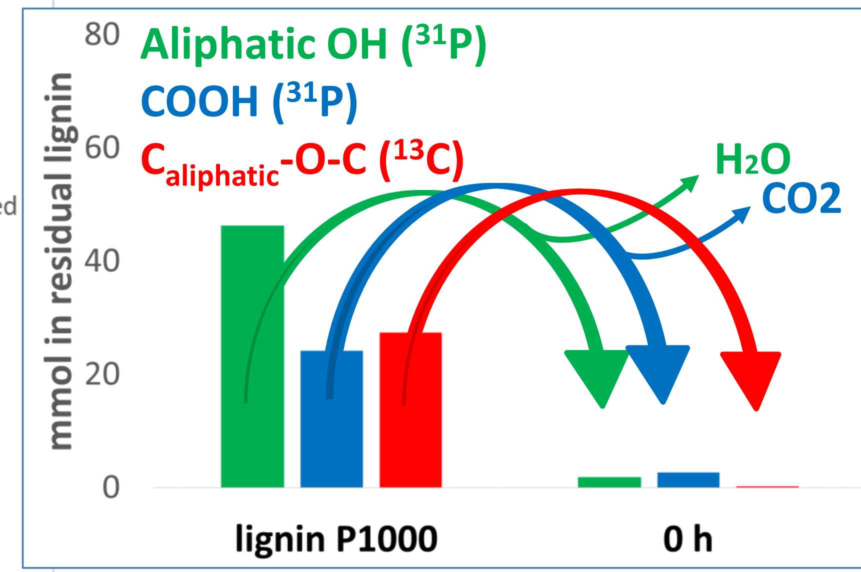
Catalytic hydroconvers



gas



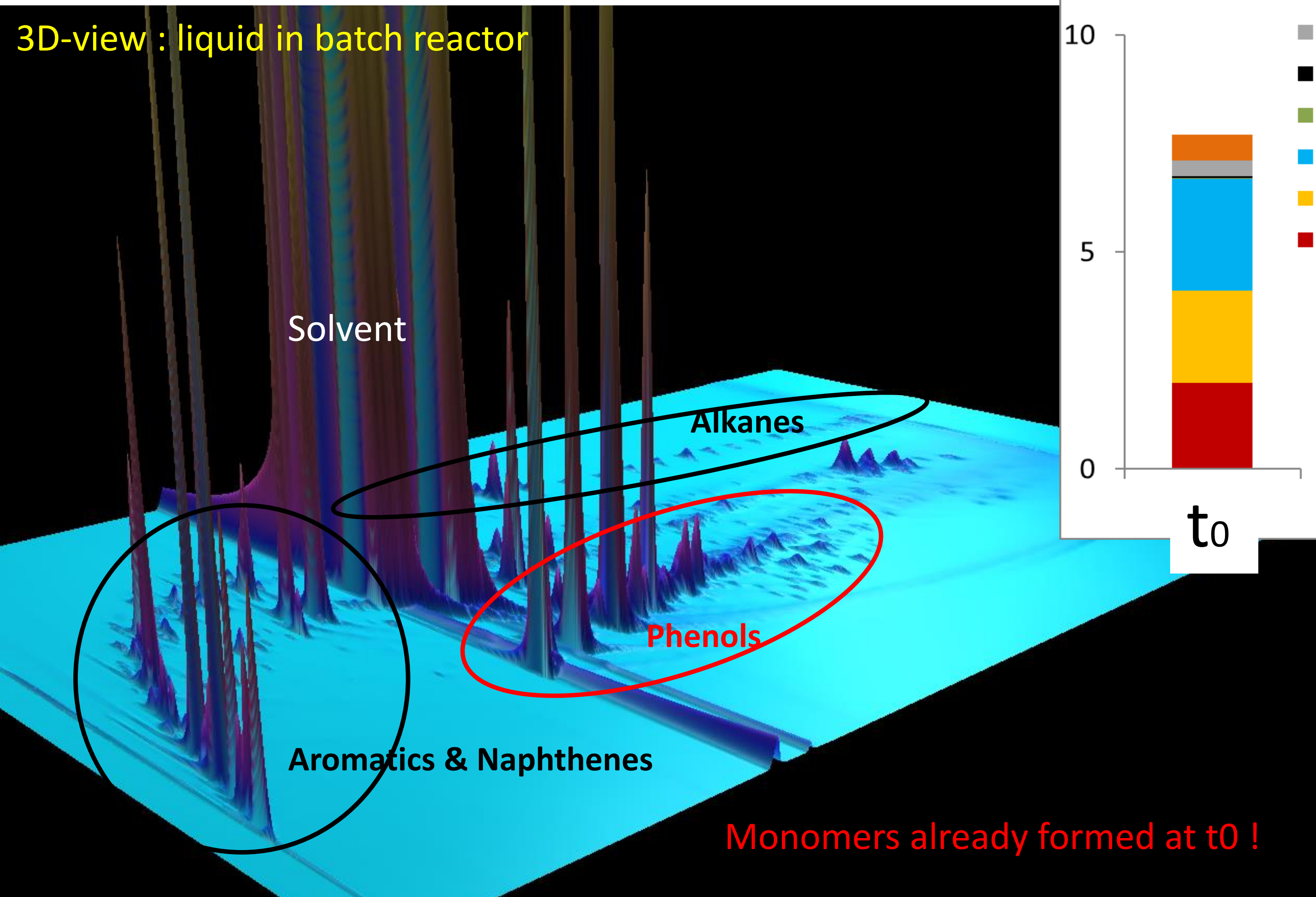
Decarboxylation of -COOH

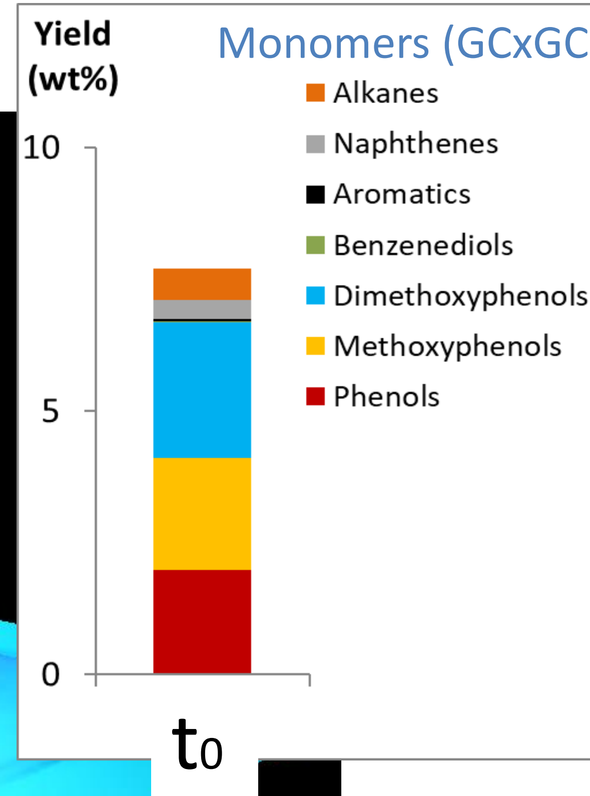


Depolymerization

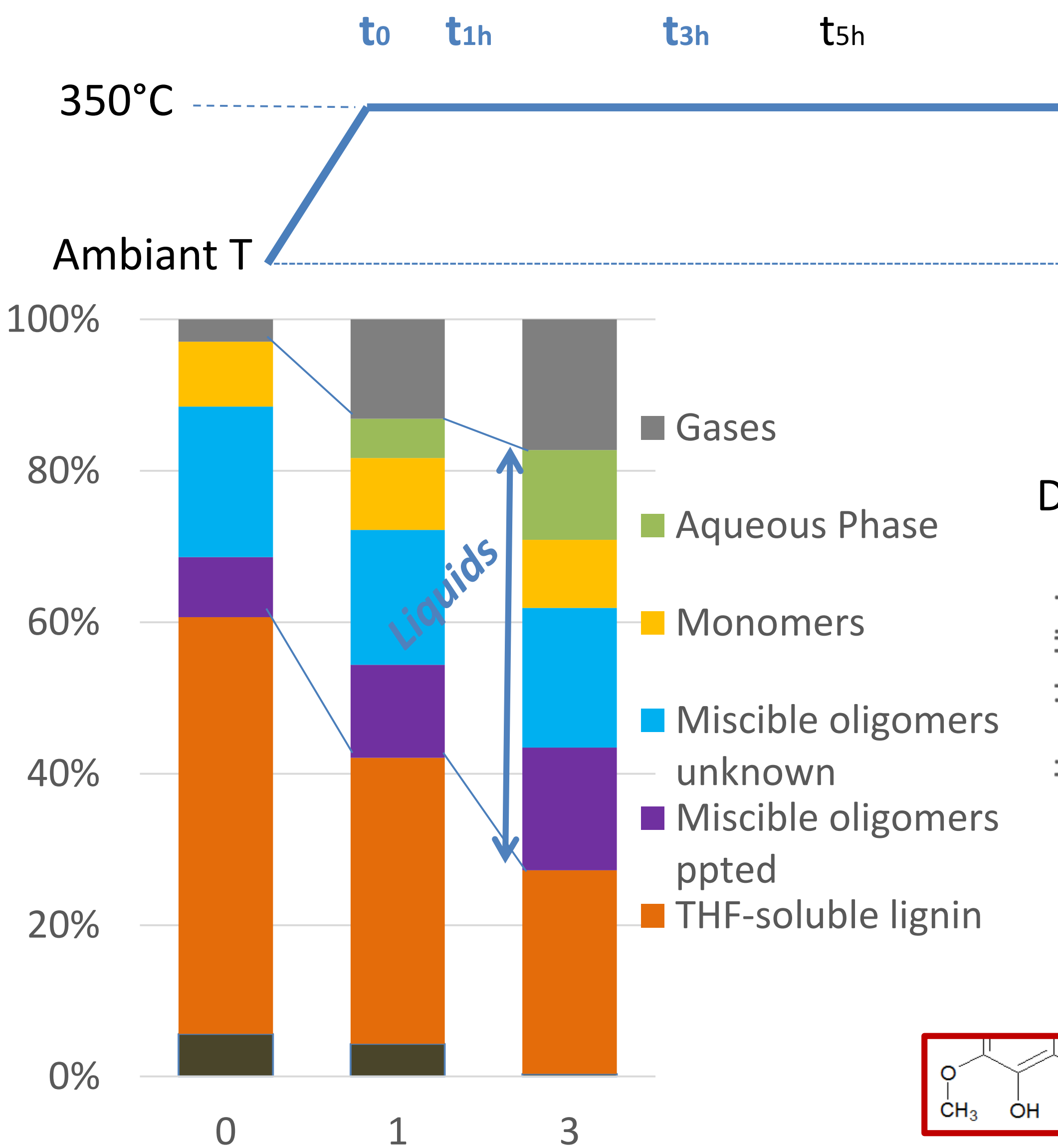
Catalytic hydroconversion results

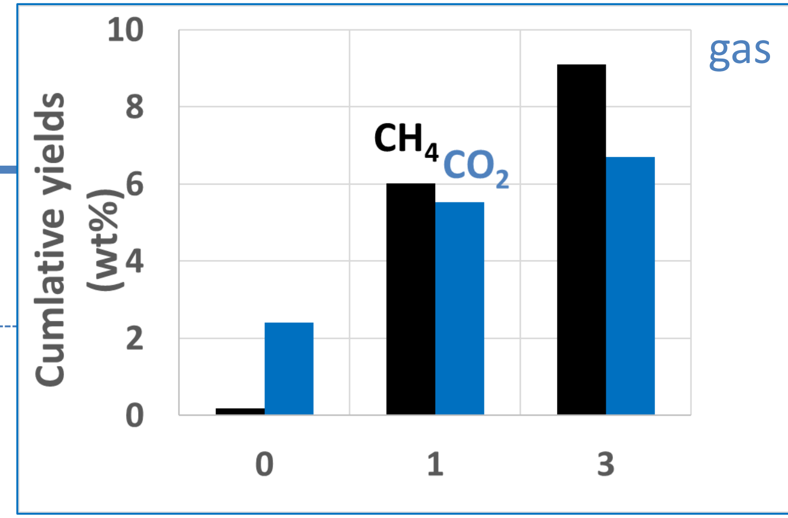
Monomers identification and quantification



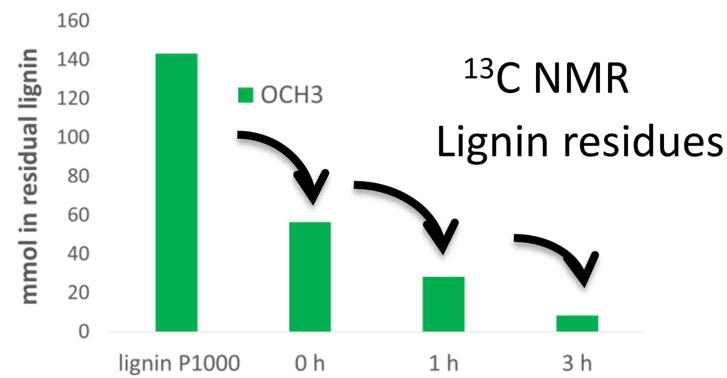


Catalytic hydroconversion results

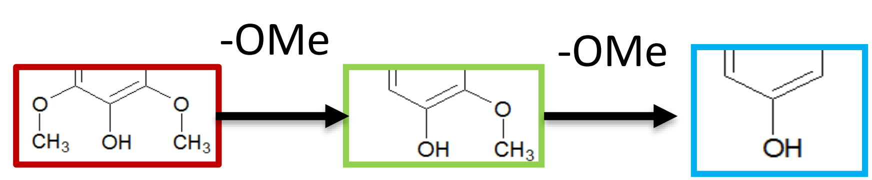




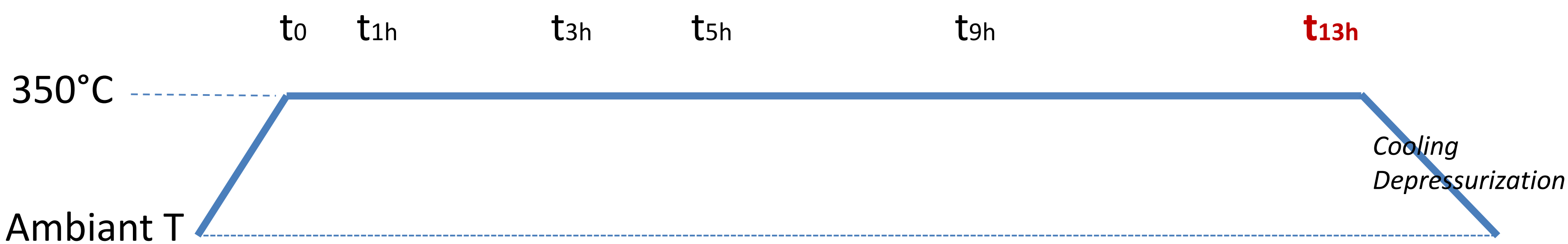
Demethylation or demethoxylation

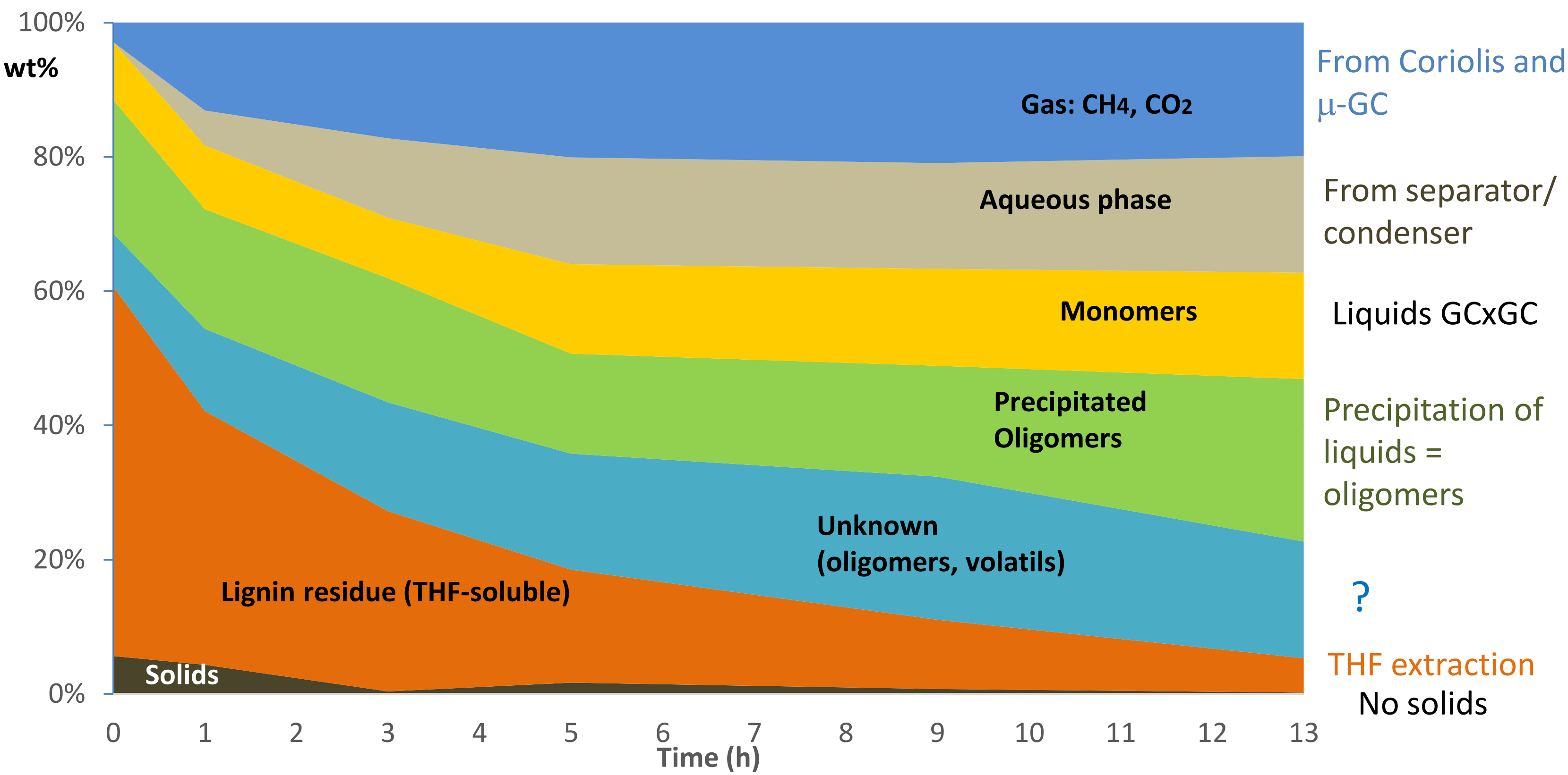


^{31}P NMR



Catalytic hydroconversion results

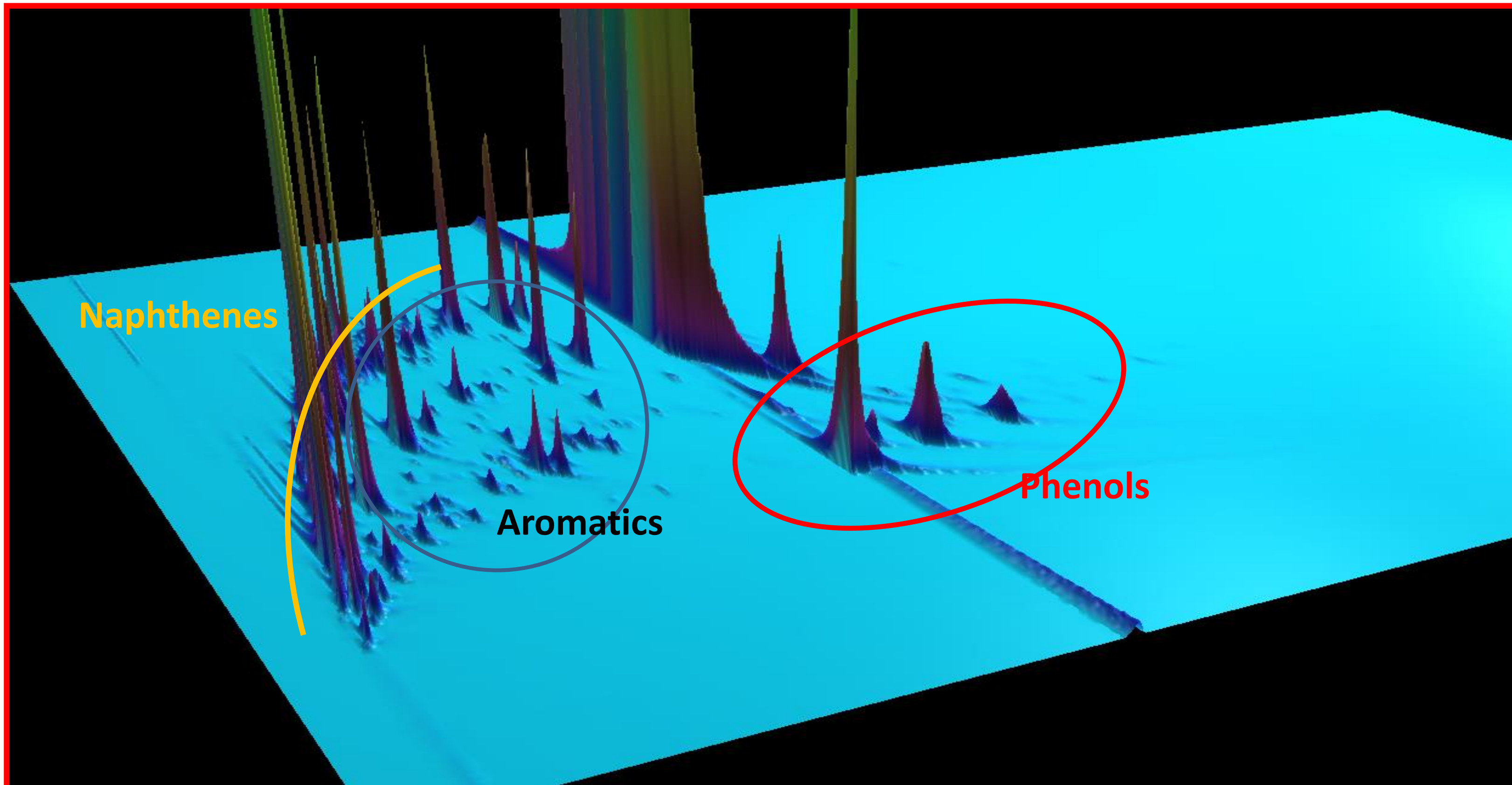




Catalytic hydroconversion results

Evolution of monomers (GCxGC)

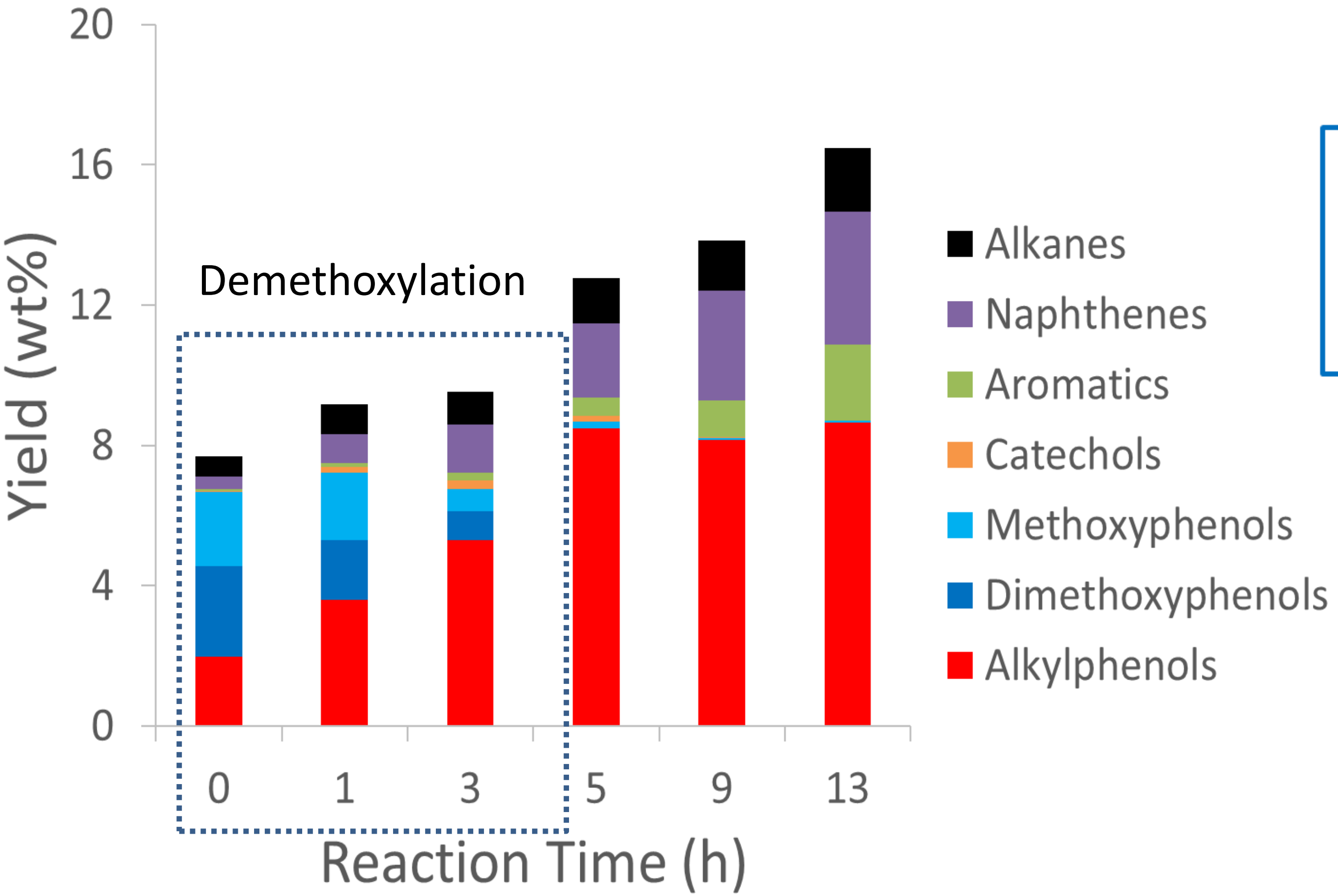
GCxGC-MS: identification **GCxGC-FID: quantification with internal standard**

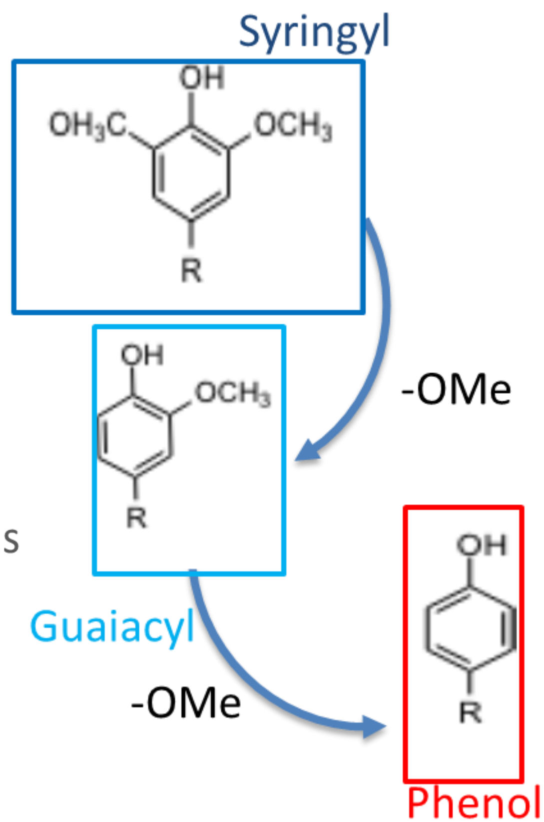


Liquid in condenser

Catalytic hydroconversion results

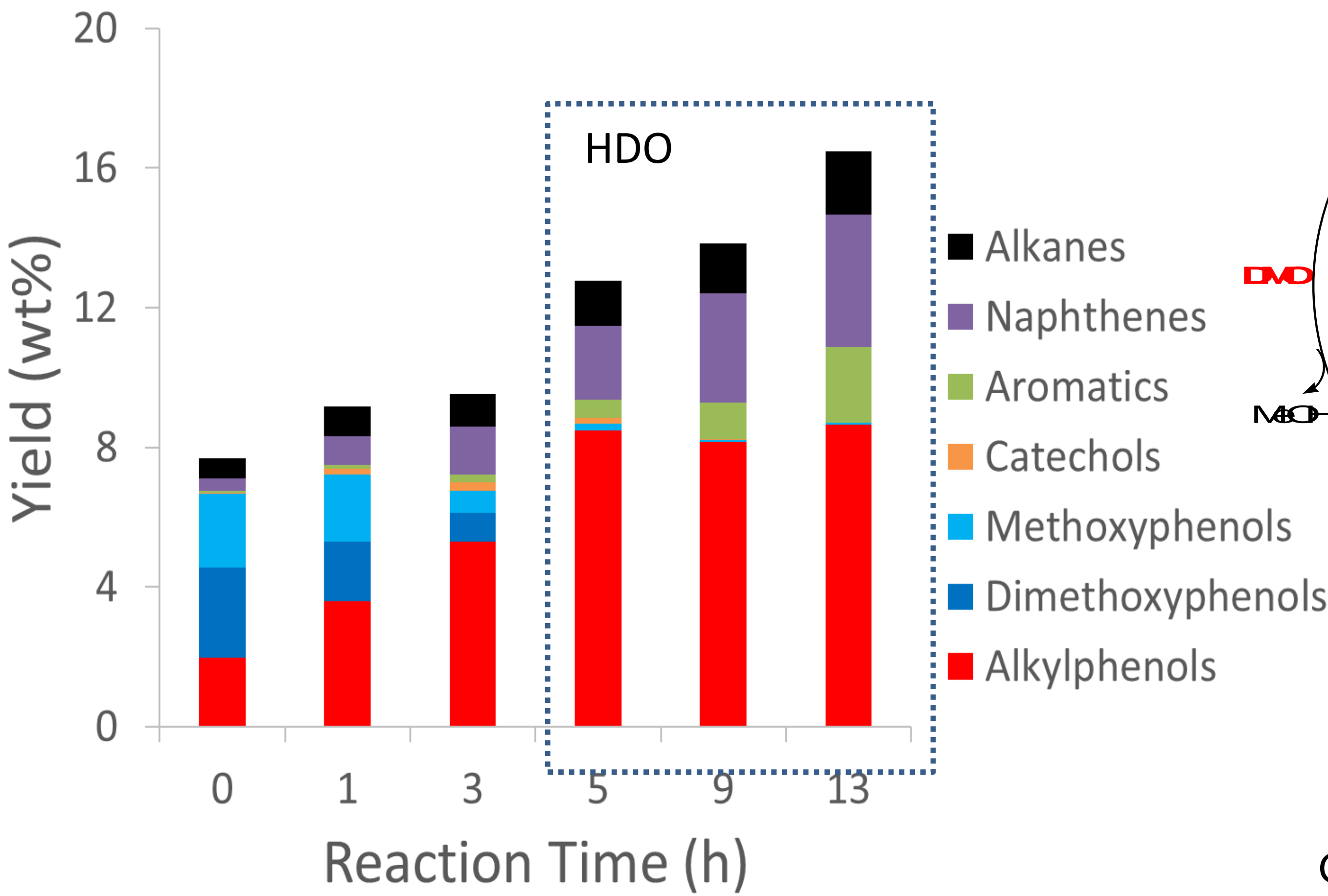
GCxGC Liquids

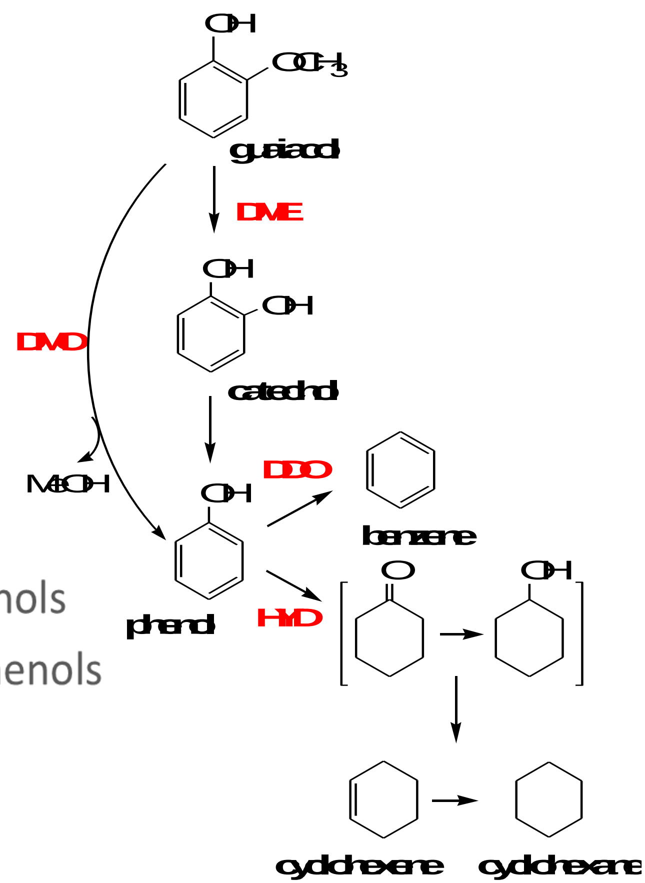




Catalytic hydroconversion results

GCxGC Liquids



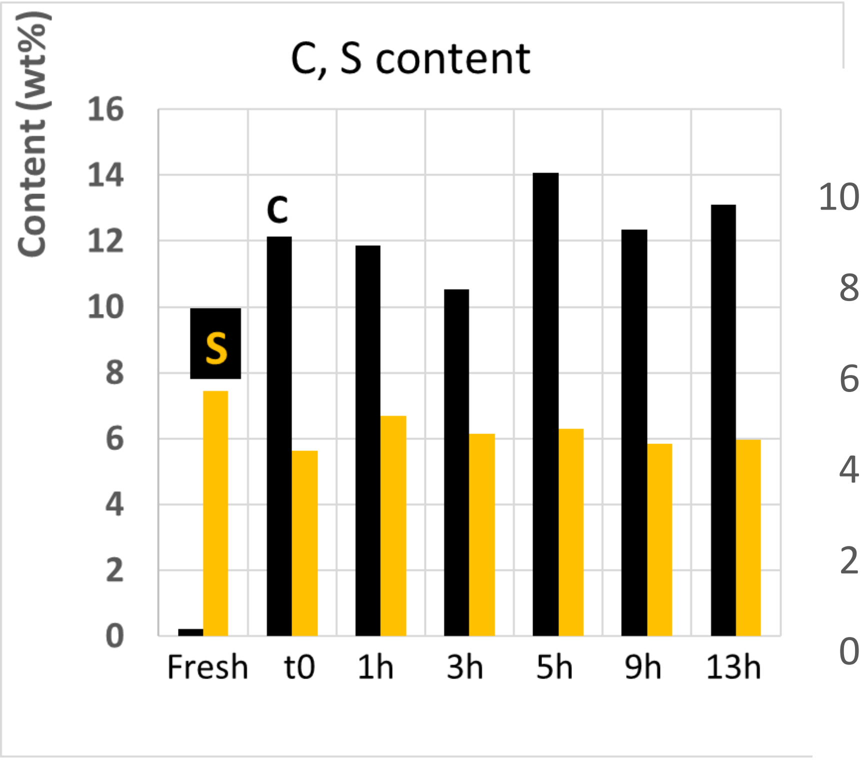


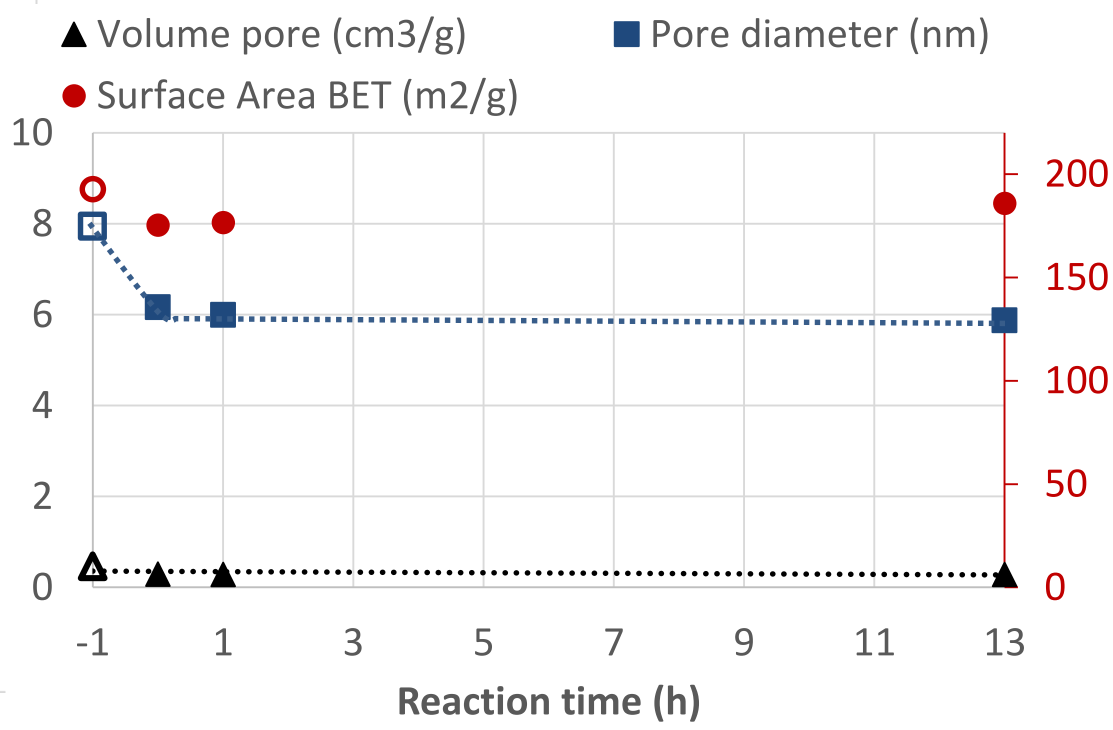
Guaiacol HDO studies

- After 13h, aromatic, phenols and alkanes represent 17 wt% of the starting lignin

Bui et al., *Applied Catalysis B: Environmental,* 101 (2011) 239

CoMoS/Al_2O_3 catalyst evolution





- Low impact on catalyst properties after the heating step
- Still sulfided after 13h reaction
- HDO Catalytic activity until 13h

Conclusion on lignin catalytic hydroconversion to monomers

After 13h hydroconversion 4.4 g of monomers coming from aromatics were formed over 30 g initial lignin (15.4 wt%)

Initially:

- 2 mmol/g of ether inter-units linkages (β-O-4 and 4-O-5)
- Aromatics units quantified in lignin: **44 wt%** of potential « C_6H_6 » units,

After 13h on catalyst:

- No more ether bonds !
- **15.4 wt%** aromatics units are obtained : thus 29 wt% still remain in oligomeric fraction (and lignin residue)
- Not released as monomers because of **C-C bonds**

Message

Technical lignins will not allow to obtain high quantity of monomers but worth to be valorized. Catalysts for selective C-C bonds cleavages are required

General Conclusion

- ✓ Development of characterization techniques
- ✓ Still need of selective and resistant catalysts for lignocellulosic biomass conversion
- ✓ Valorization of the wastes to reach circular economy

Thank You !

Christophe Geantet	Alexandre Margeriat
Chantal Lorentz	Mathieu Ozagac
Nolven Guilhaume	Junjie Pu
Yves Schurmann	Van Ngoc Bui