Aristotle University of Thessaloniki
Department of Chemistry

Centre for Research and Technology-Hellas
Chemical Process & Energy Resources Institute

Valorization of hemicellulose-biomass side streams via catalytic hydrogenation into value added chemicals and fuels

E. Mitsiakou [1], A. Margellou [1], K. Rekos[1] and Konstantinos Triantafyllidis[1,2*]

[1] *Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece*

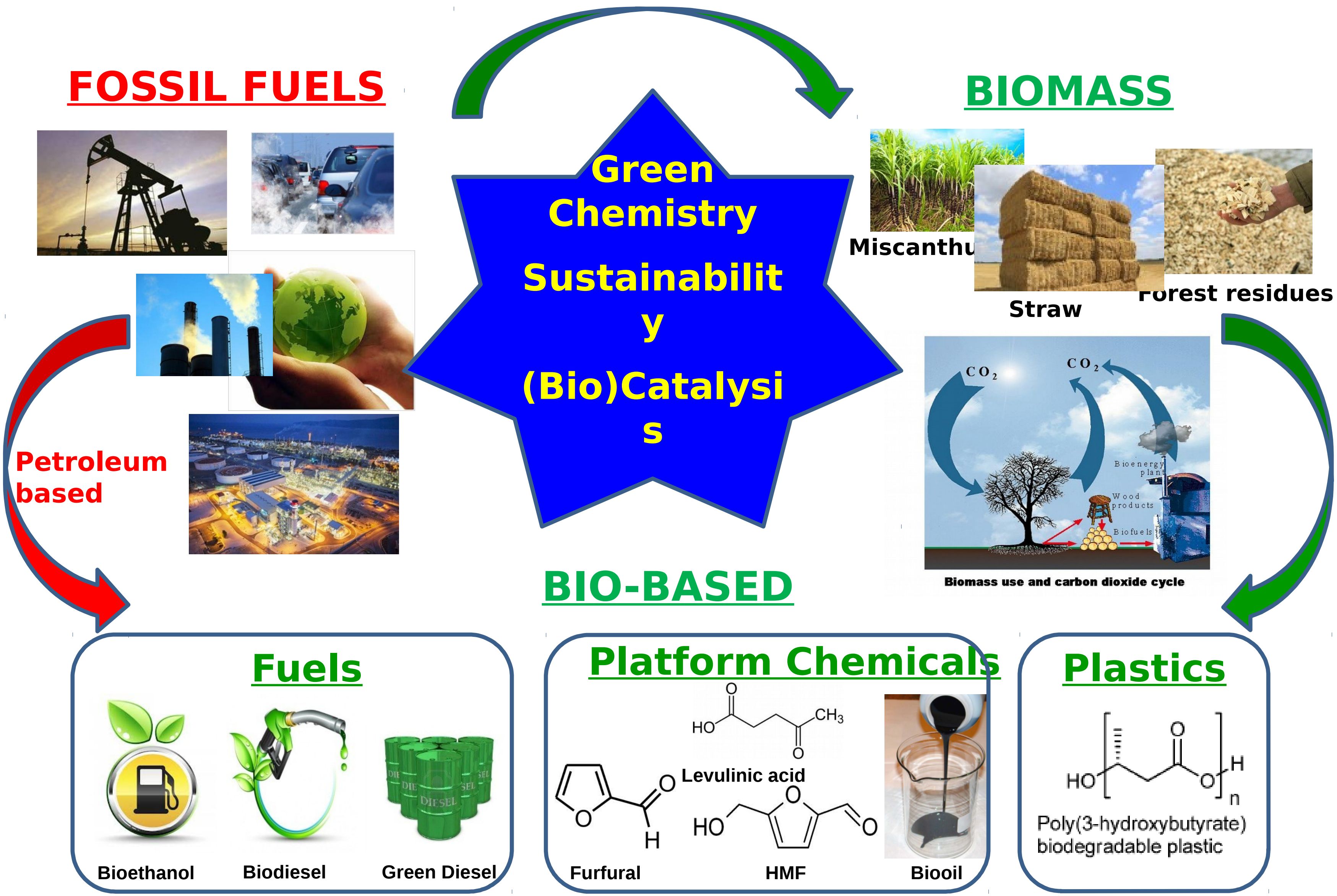
[2] *Chemical Process and Energy Resources Institute, CERTH, 57001 Thessaloniki, Greece*

7th International Conference on Sustainable Solid Waste Management

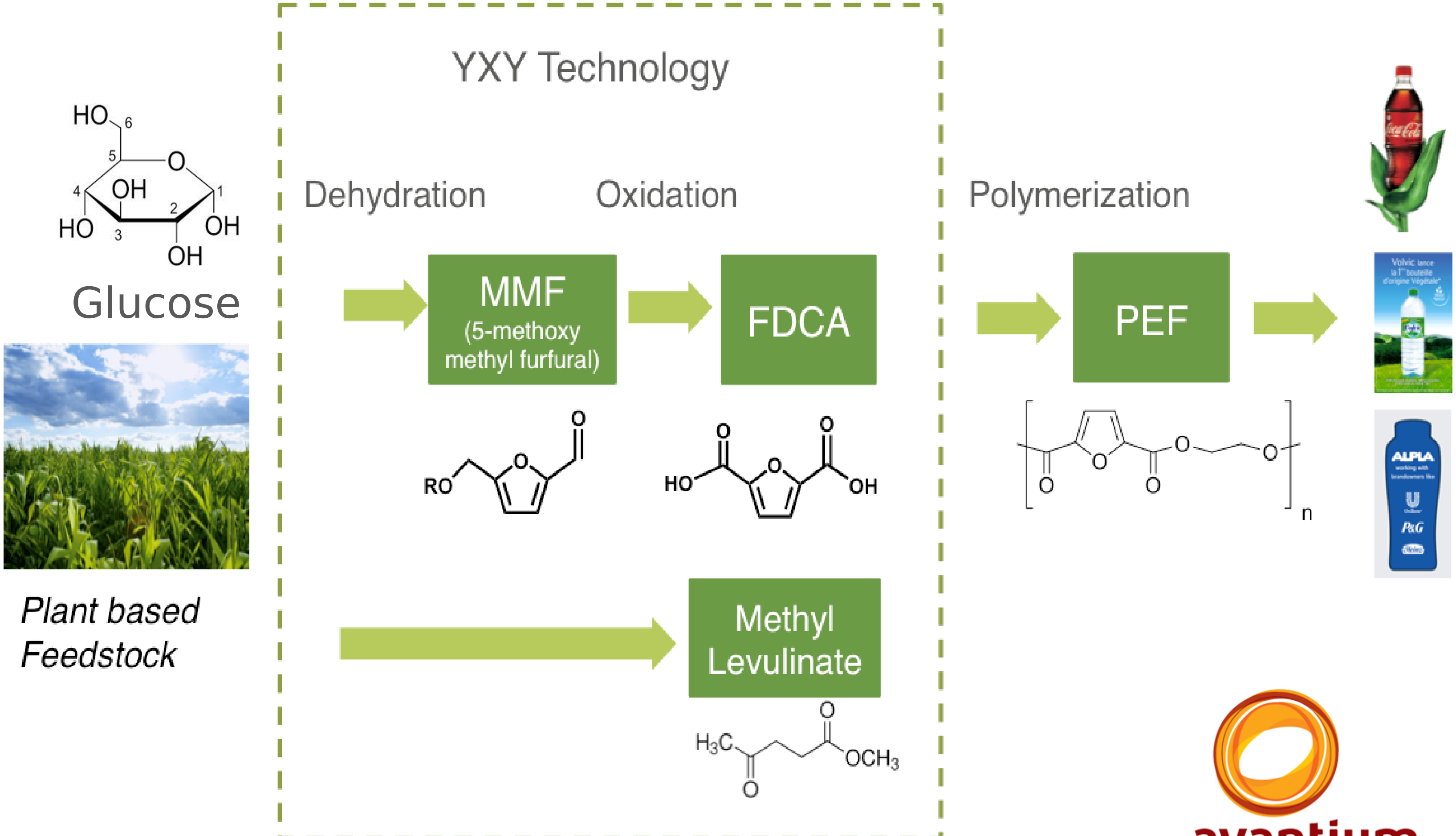
AQUILA ATLANTIS HOTEL Heraklion, Crete Island, Greece

26 – 29 June 2019

Utilization of Biomass



A successful commercial example of biomass derived plastic replacing PET

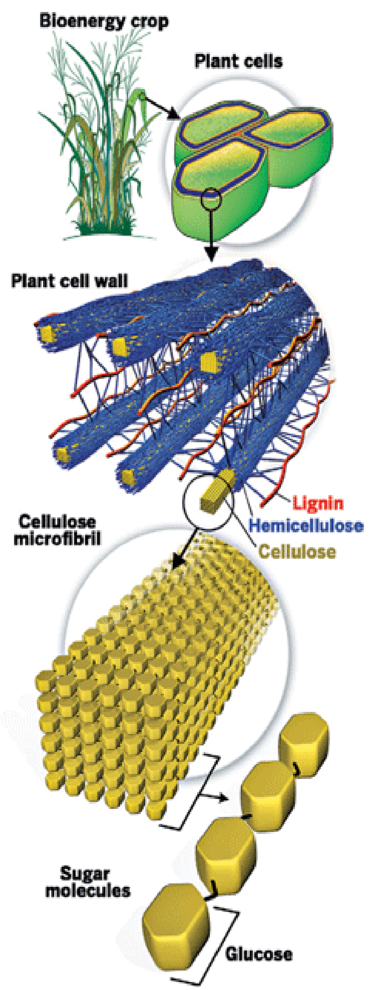


avantium

https://www.avantium.com/yxy/yxy-technology/

Lignocellulosic Biomass

Structure

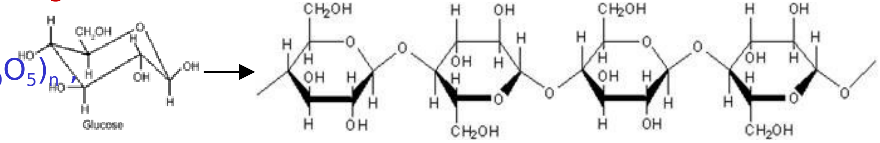


Source: Ritter S.K., Lignocellulose: A Complex Biomaterial, Plant Biochemistry, 86(49) (2008) 15

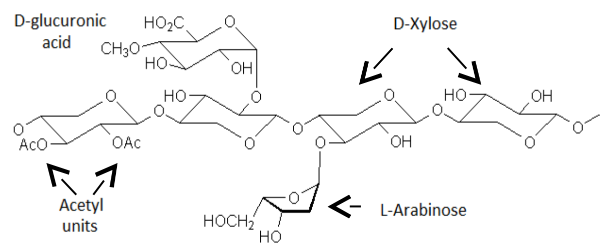
Composition

- **Cellulose:**
  general formula $(C_6H_{10}O_5)_n$
  MW: 300.000-500.000

glucose

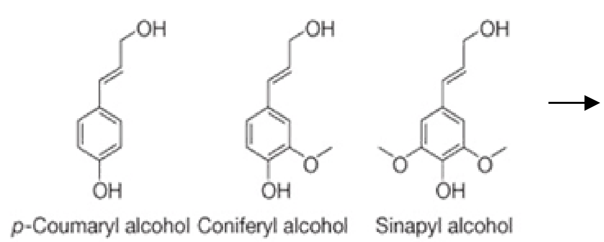


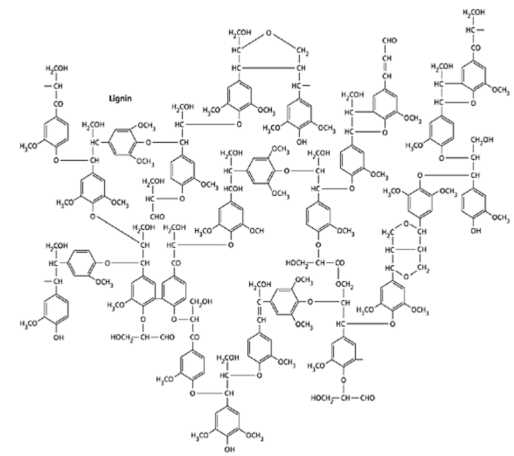
- **Hemicellulose:** general formula$(C_5H_8O_4)_n$



C_5 & C_6 sugars, uronic acids, acetyl units

- **Lignin:**





Phenolic monomers

Cellulose: 30-50%, Hemicellulose: 20-40%, Lignin: 15-25%
Others, 5-35% - Ash 3-10% (Si,Al,Ca,Mg,K.Na), Extractives: Resins, Phenols, Sterols, etc

Lignocellulosic biomass raw materials

- Agricultural and forestry residues/waste (wheat straw, trimmings, tree branches)
- Industrial wood processing residues (e.g. sawdust)
- Food industry waste (e.g. kernels, shells)
- Municipal solid waste (e.g. waste paper)
- Perennial or annual crops with high yield 1-4 ton/1000m^2 year (e.g. eucalyptus, pseudoacacia, willow, miscanthus, switch grass, cellulosic sorghum,..)

Olive kernels

Almond shells

Agricultural & forestry Residues/wastes

Miscanthus

Robinia pseudoacacia

Biomass (agricultural) residues in EU-28 (2006-2015)

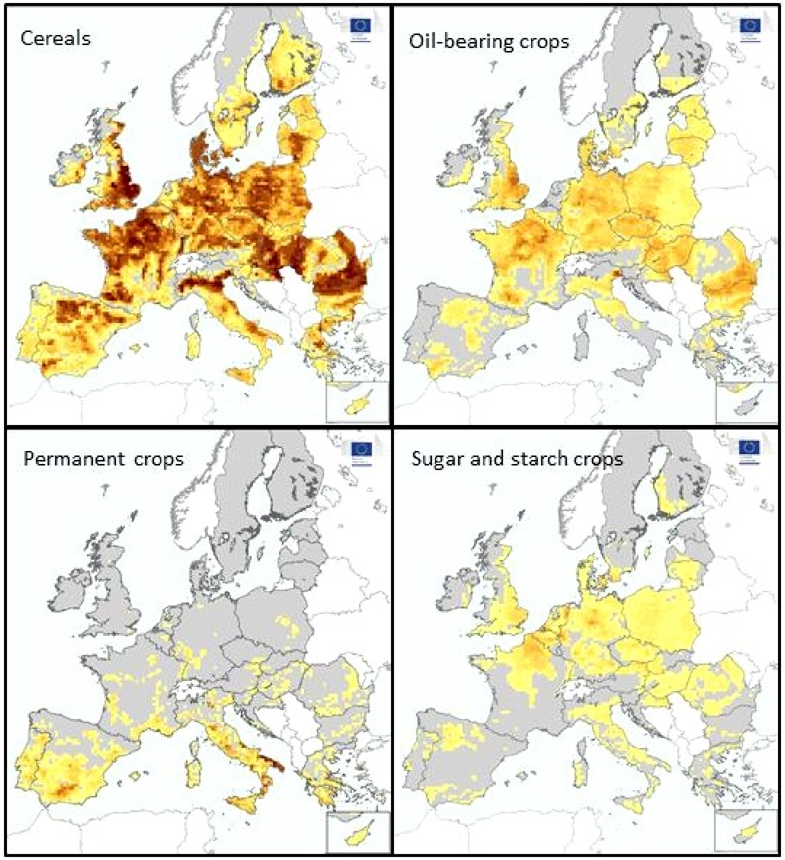
Cereals (328.52Mt)

Wheat *(148.83Mt)*

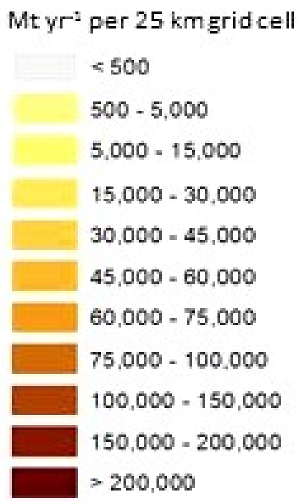
Maize *(80.37Mt)*

Barley *(50.10Mt)*

+ others (49.22 Mt)



European Commission Report, 2018



Oil-bearing crops (73.10Mt)

Rapeseed *(53.99Mt)*

Sunflower *(14.63Mt)*

+ others (4.48 Mt)

Permanent Crops (21.86Mt)

Olive trees *(17.11Mt)*

Vineyards *(4.08Mt)*

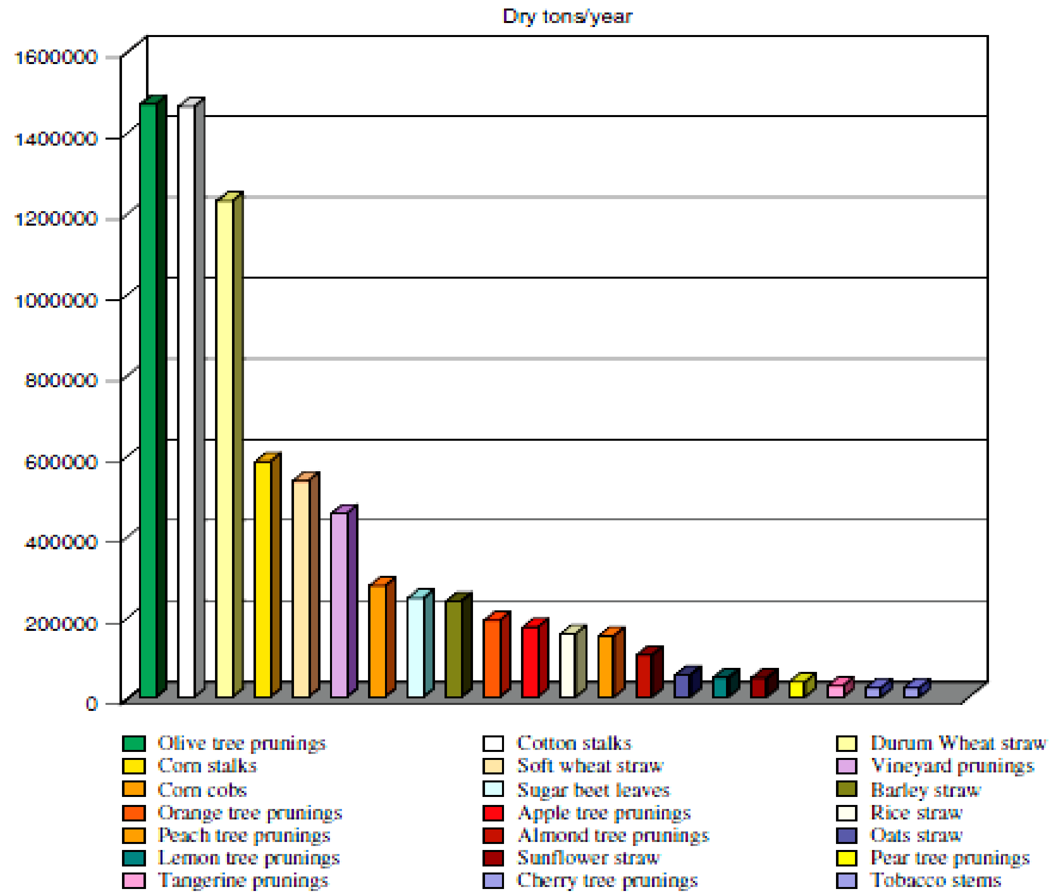
+ others (0.68 Mt)

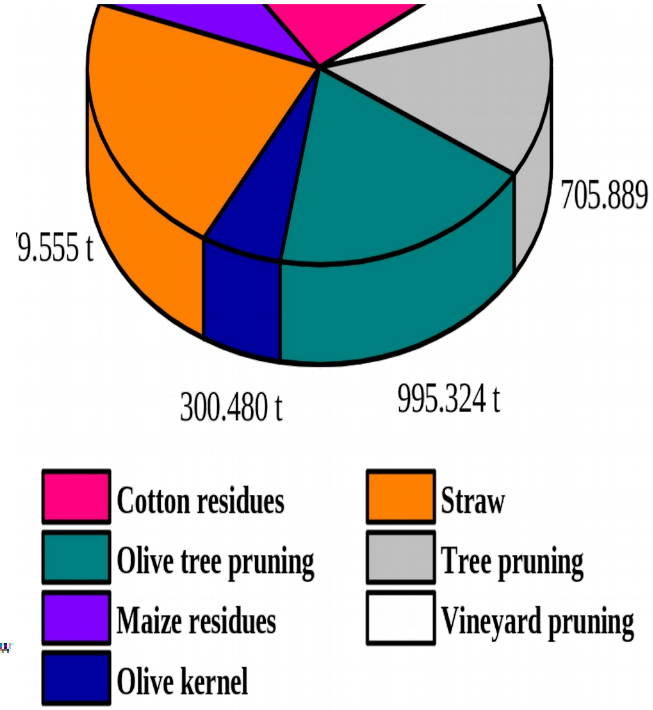
Sugar-starchy crops (13.41Mt)

Sugar beet *(9.23Mt)*

Potatoes *(4.18Mt)*

Biomass (agricultural) residues in Greece





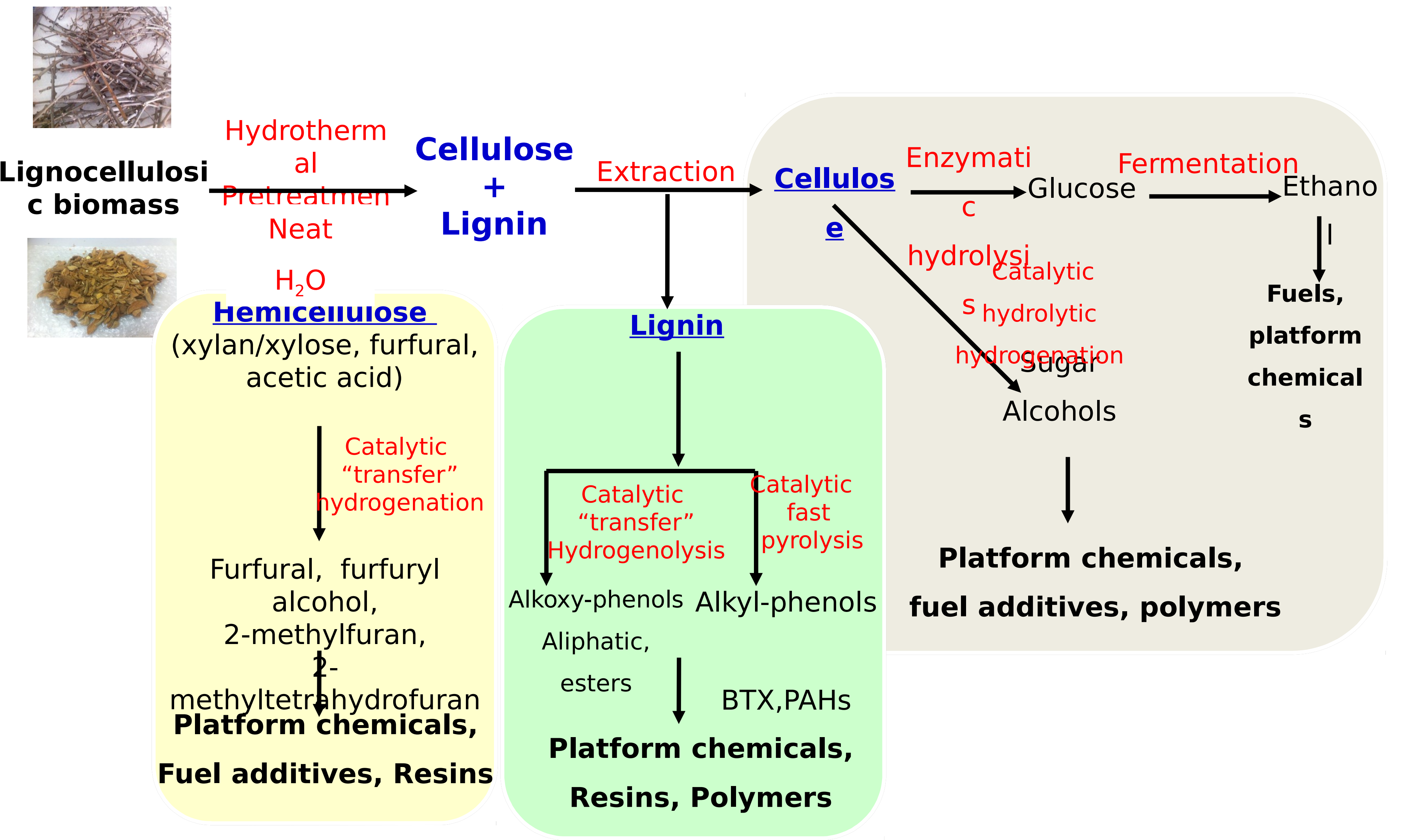
non, Eurobionet-biomass survey in Europe, Country report of Greece, 2003

Center for Renewable Energy Sources & Saving, Greece, 2





Integrated lignocellulosic biomass valorization (Bio-refinery)



Hydrothermal pre-treatment (in pure H_2O)

Biomass

Autoclave reactor

Solid product

Cellulose + Lignin

Enzymatic Hydrolysis

Glucose

Liquid product

Hemicellulose monomers and oligomers, xylose, furfural, acetic, formic acid, etc.

Severity factor (logRo)

$$R_0 = t \cdot \exp\frac{(T-100)}{14.75}$$

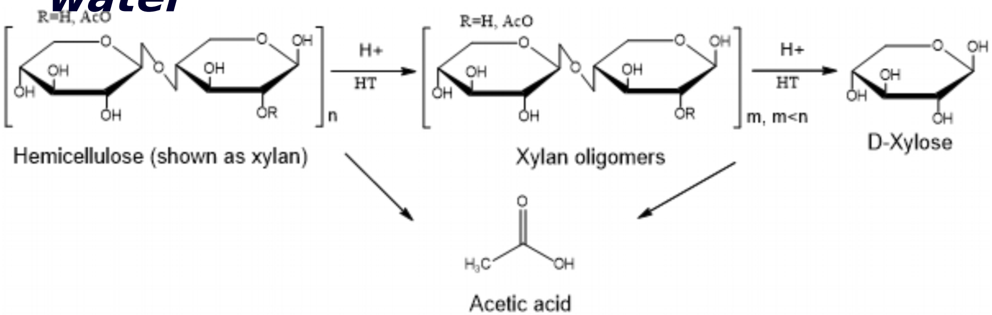
Experimental conditions:

- Temperature : 130-220°C
- Time : 15-180 min
- LSR: 15
- Stirring: 400 rpm

C.K. Nitsos, K.A. Matis, K.S. Triantafyllidis, ChemSusChem, 6 (2013) 110 – 122
C.K. Nitsos, T. Choli-Papadopoulou, K.A. Matis, K.S. Triantafyllidis, ACS Sust. Chem. & Engin. 4 (2016) 4529-4544
C. K. Nitsos, P. A. Lazaridis, A. Mach-Aigner, K. A. Matis, & K. S. Triantafyllidis, ChemSusChem (2019) 12 (6): 1179

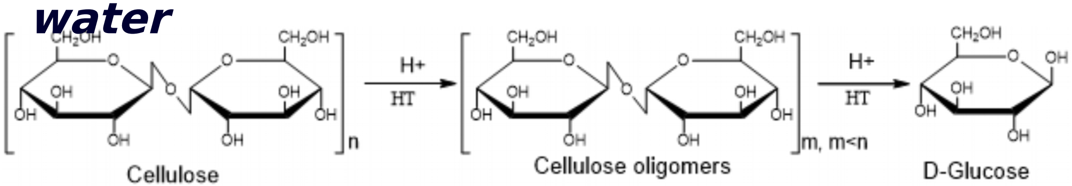
Generalized reaction scheme

Hemicellulose hydrolysis at subcritical water

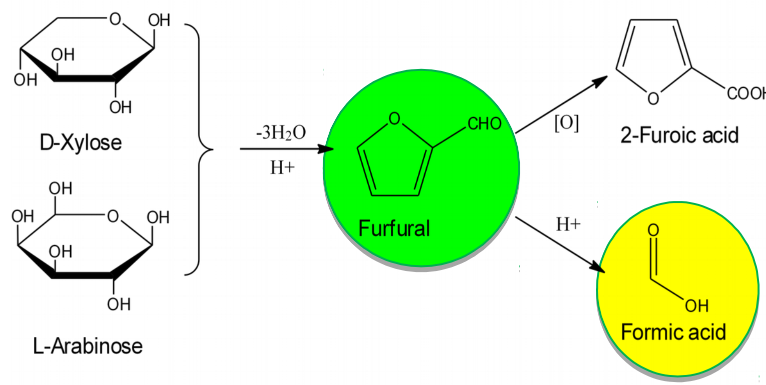


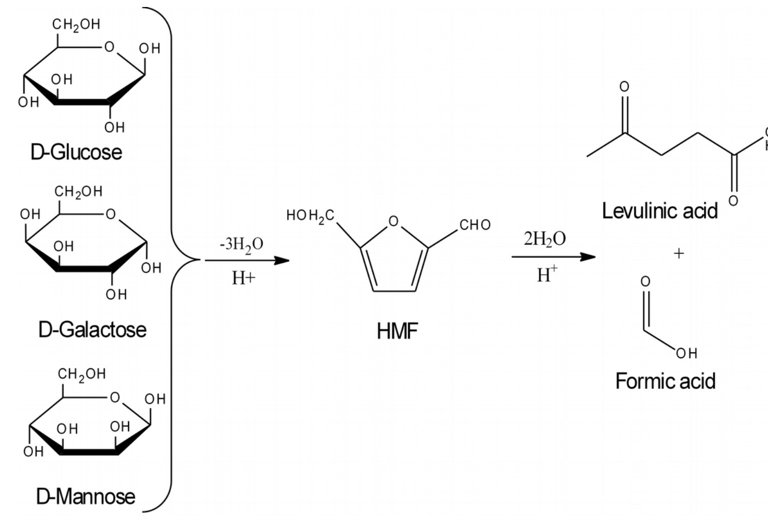
- Self-catalyzed hydrolysis (pH 5 □ 2.5)
- The catalyst (acetic acid) is a biomass component

Cellulose hydrolysis at subcritical water

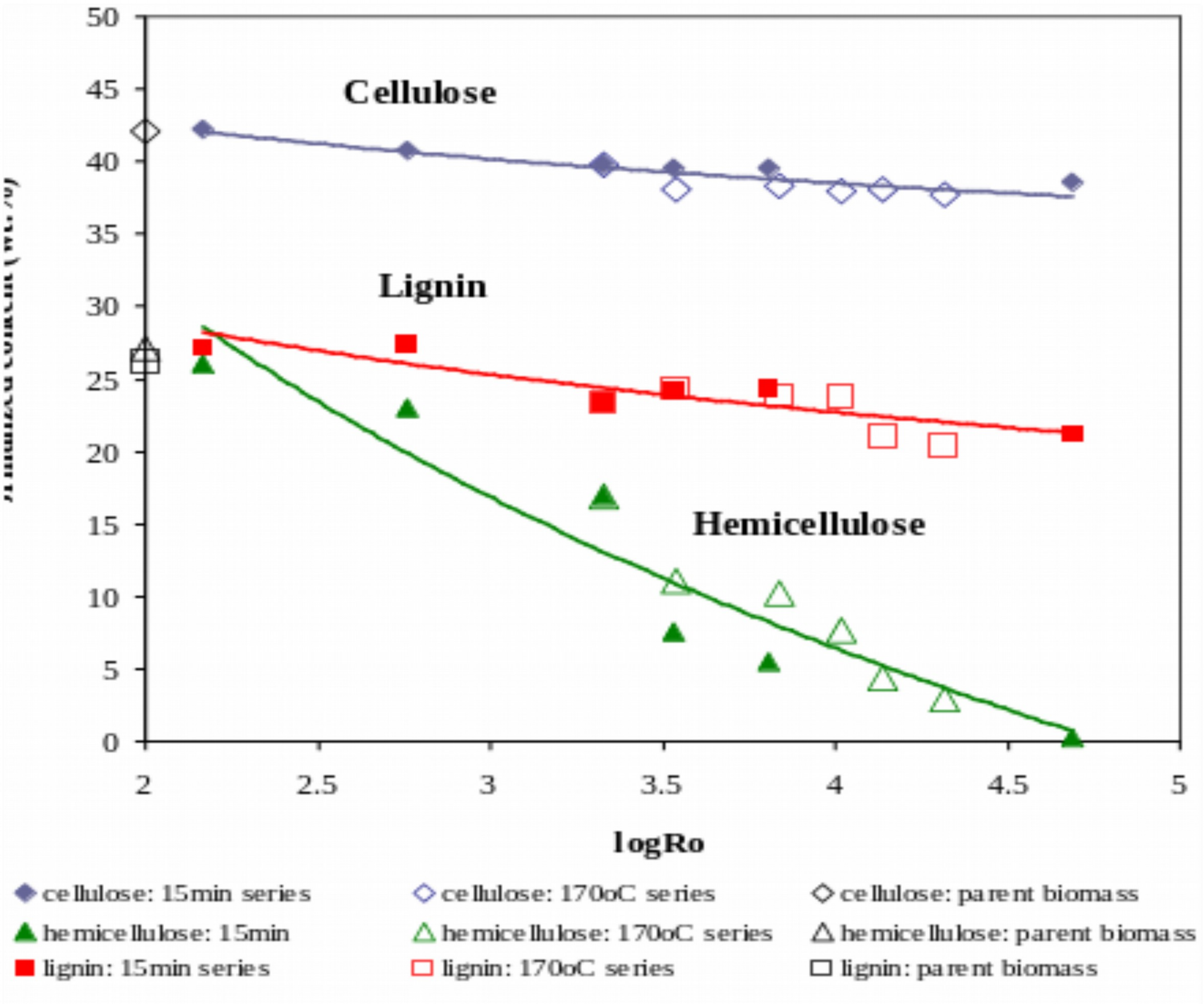


Sugars dehydration products

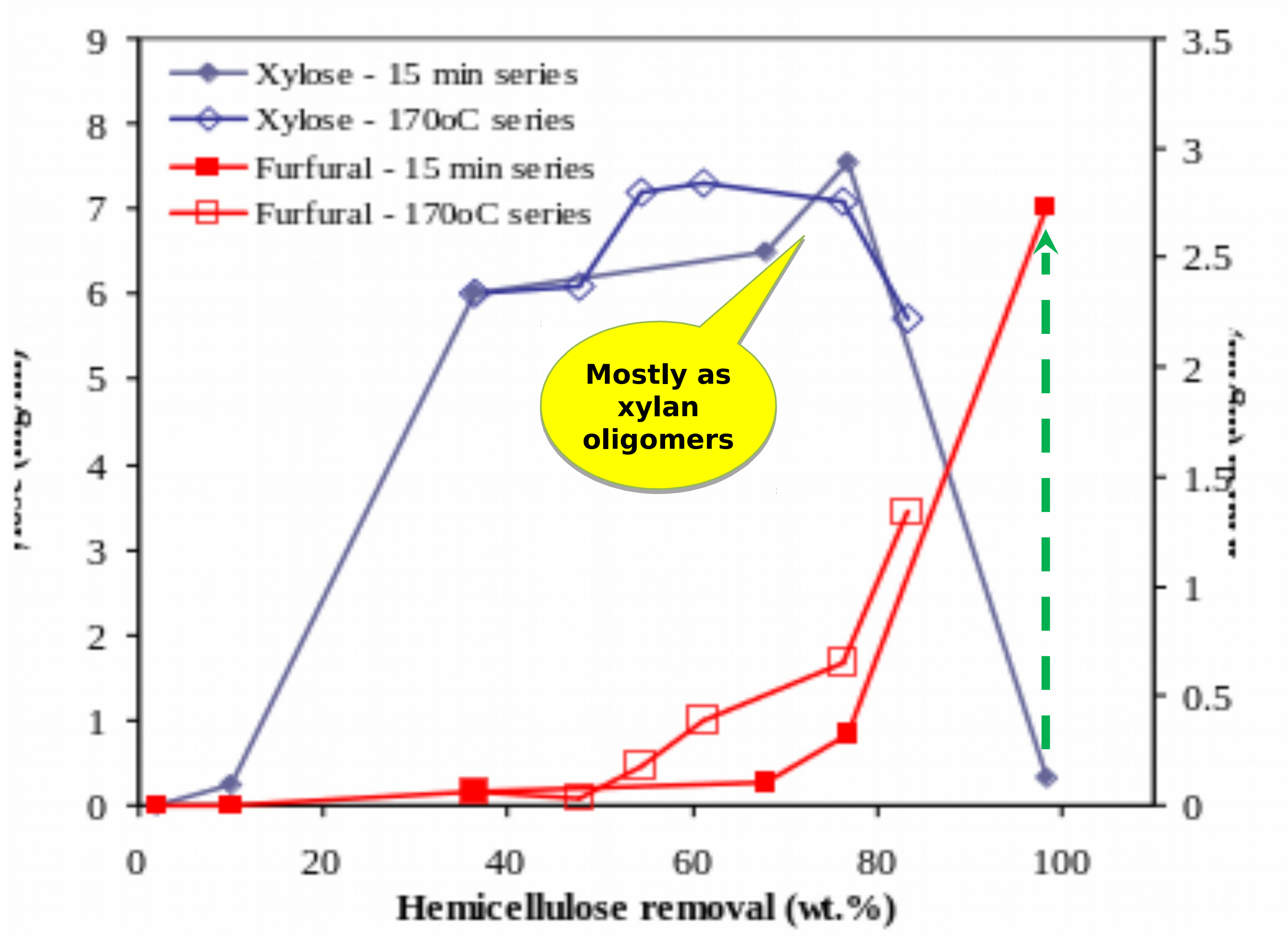




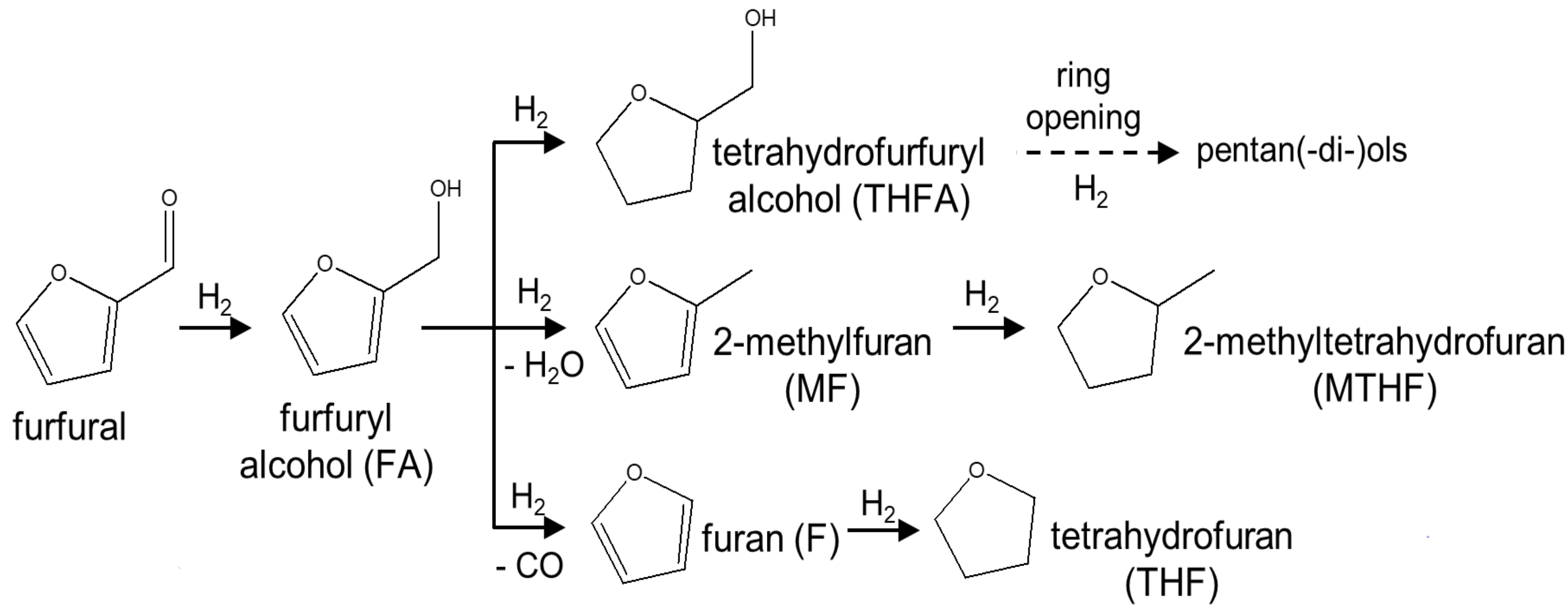
Evolution of main structural components in hydrothermally treated solids



Xylose and furfural concentration vs. % hemicellulose removal



Catalytic hydrogenation of furfural: General reaction mechanism-possible routes

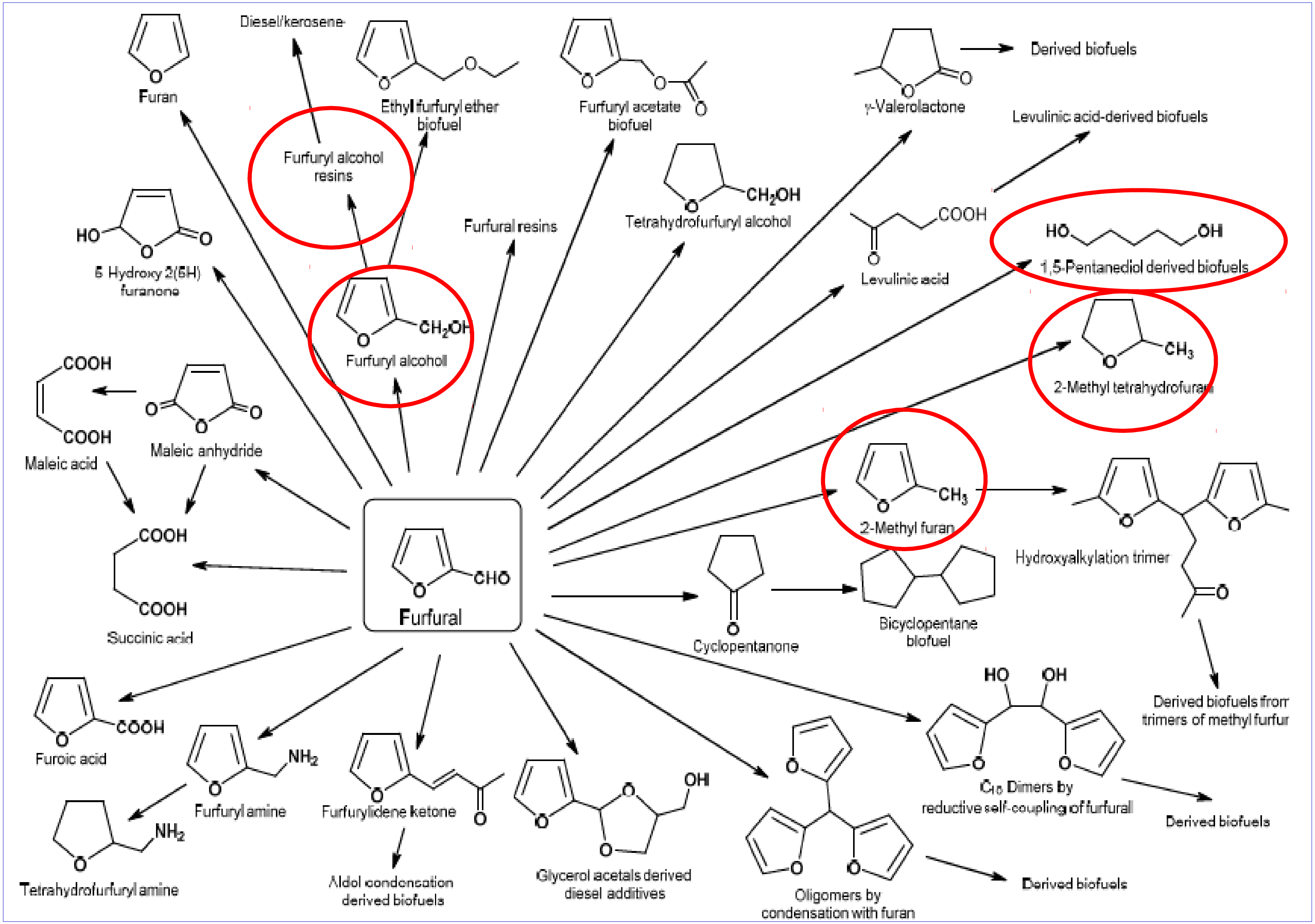


- **Dominant pathways/products depend on catalyst type, reaction parameters and solvent (acting or not as H-donor for inducing transfer hydrogenation)**

Y. Wang, P. Prinsen, K.S. Triantafyllidis, S.A. Karakoulia, A. Yepez, C. Len, R. Luque, ChemCatChem 2018, 10, 3459– 34

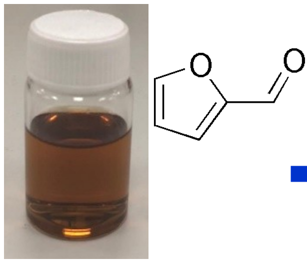
Wang, Y., Prinsen, P., Triantafyllidis, K. S., Karakoulia, S. A., Trikalitis, P. N., Yepez, A., Christophe Len, Luque, R. . ACS Sustainable Chemistry & Engineering, 2018, 6(8), 9831-9844

Furfural derived chemicals and fuels



R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba, M. López Granados, Energy Environ. Sci., 2016,9, 1144-1189

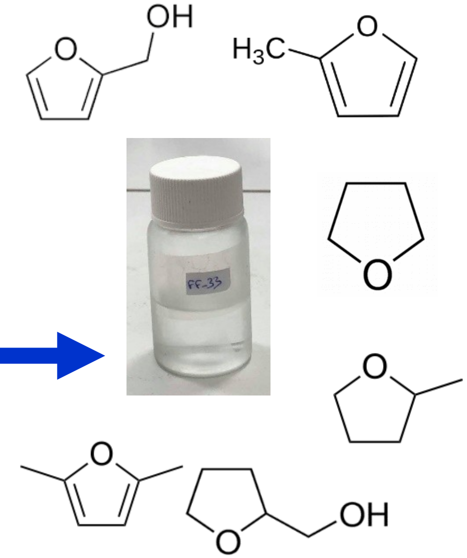
Catalytic hydrogenation experiments of hemicellulose stream



Furfural+Solvent

Solvent,
H_2 source

T, Catalyst

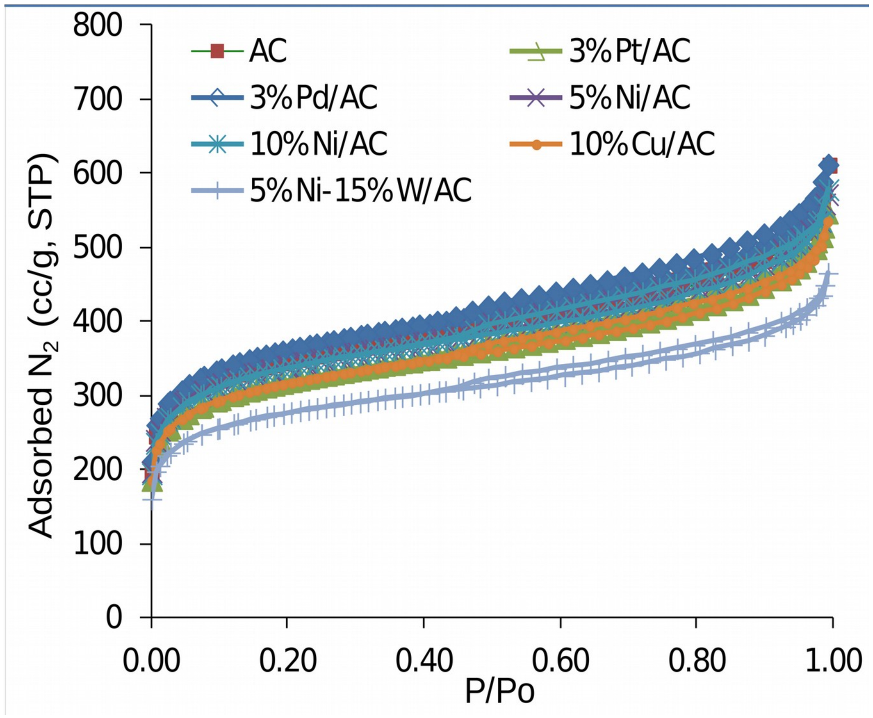


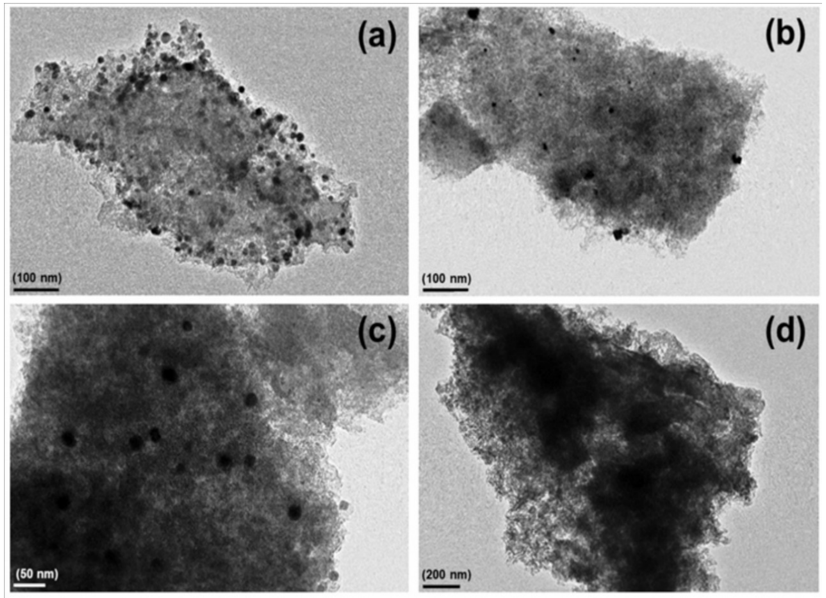
Furanic compounds: Furfuryl alcohol, 2-MF, 2-MTHF, etc.

- **Solvent:** Ethyl acetate, H_2O, **EtOH & IPA (as H_2 donor – transfer hydrogenation)**
- **H_2 gas**: 30 bar at room temp.
- **Temperature:** 180 °C
- **Catalyst:** Ru, Pd, Pt, Cu, Ni supported on Micro/mesoporous Activated Carbon

Catalysts for furfural hydrogenation

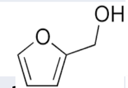
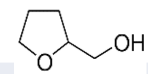
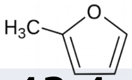
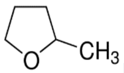
Catalyst	Total SSA (m^2/g)	Total pore volume (cc/g)	Micropore area (m^2/g) / volume (cc/g)	Meso/macro- pore & external area (m^2/g) / volume (cc/g)	Crystal size (nm)
Activated carbon (AC)	1281	0.946	841 / 0.343	440 / 0.603	-
3%Pt/AC	1180	0.847	759 / 0.309	421 / 0.538	13.6
3%/Pd/AC	1338	0.947	886 / 0.362	452 / 0.585	16.6
5%Ni/AC	1251	0.884	831 / 0.343	420 / 0.541	6.8
10%Ni/AC	1246	0.895	806 / 0.329	440 / 0.566	Ni(0) 23.5- NiO 6.1
10%Cu/AC	1172	0.828	768 / 0.313	403 / 0.515	Cu(0) 23.2 - Cu_2O 16.6
5%Ni-15%W/AC	1025	0.720	678 / 0.276	347 / 0.444	Ni(0) 7.8 - WO_2 9.9 - $NiWO_4$ 15.5

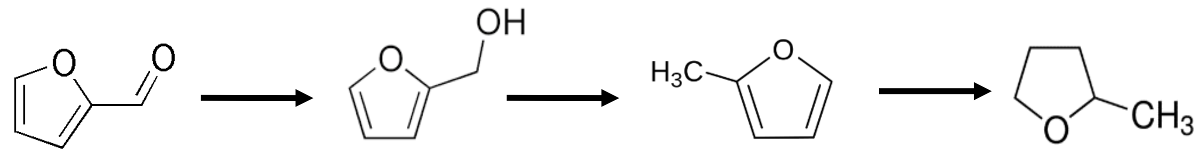




(a) 5%Ni/AC, (b) 3%Pt/AC, (c) 3%Pd/AC, (d) 10%Cu/AC

Effect of reaction time & temperature

Catalyst	Solvent	Time (h)	T (ºC)	H_2 (bars)	*X* (%)	FAL	THFAL	2-MF	2-MTHF
									
3%Pd/AC	EtOAc	1	180	30	15.6	10.1	0.0	43.4	0.0
3%Pd/AC	EtOAc	3	180	30	19.6	6.0	0.0	58.4	0.0
3%Pd/AC	EtOAc	6	180	30	29.3	3.6	0.0	58.6	0.0
3%Pd/AC	EtOAc	9	180	30	34.8	5.8	1.1	74.6	11.5
3%Pd/AC	EtOAc	6	180	30	19.6	6.0	0.0	58.4	0.0
3%Pd/AC	EtOAc	6	220	30	43.4	4.4	3.8	69.4	13.2



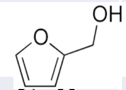
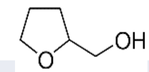
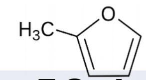
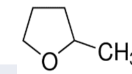
Furfural

Furfuryl alcohol

2-MF

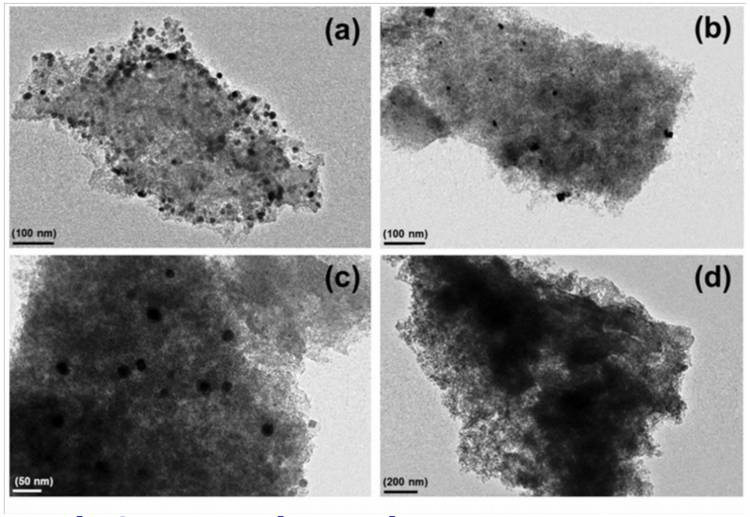
2-MTHF

Effect of catalyst type

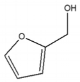
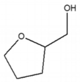
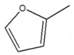
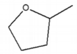
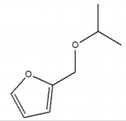
Catalyst	Solvent	Time (h)	T (ºC)	H_2 (bars)	*X* (%)	FAL	THFAL	2-MF	2-MTHF
									
3%Pd/AC	EtOAc	3	180	30	19.6	6.0	0.0	58.4	0.0
3%Pt/AC	EtOAc	3	180	30	72.9	3.5	1.5	74.3	0.0
10% Ni/AC	EtOAc	3	180	30	19.3	21.7	1.3	75.9	0.0
10%Ni/15%W-AC	EtOAc	3	180	30	53.7	18.0	5.4	42.1	0.0

- Pt based catalyst were very reactive and selective towards 2-MF (polar, aprotic solvent)
- Ni based catalysts exhibit also high selectivity to 2-MF but activity improvement is needed

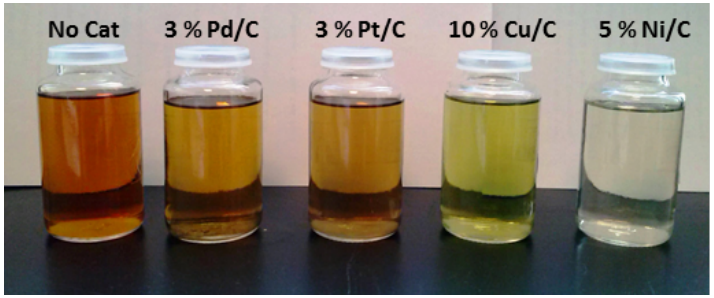
Catalytic transfer hydrogenation of furfural (solvent acting as hydrogen donor)



Ni, Cu, Pt, Pd on micro/mesoporous carbon

Entry	Catalyst	Conversion (%)	Yield (%) FA 	THFA 	MF 	MTHF 	iPrOMF 	Mass balance (%)
1	-	2	6	0	0	0	0	104
2	10%Cu/AC	24	22	0	2	1	1	103
3	3%Pd/AC	47	21	1	5	2	5	87
4	3%Pt/AC	93	47	1	24	3	5	87
5	5%Ni/AC	85	6	1	66	2	3	93
6	5%Ni/AC[b]	10	10	1	1	0	0	102
7	5%Ni/AC[c]	95	20	1	50	1	1	78
8	5%Ni/AC[d]	87	13	1	9	2	0	38[e]
9	5% Ni/AC[f]	67	38	1	17	1	13	103

[a] 200 °C, 5 h, 0.35 M furfural in 60 mL isopropanol, 30 bars H_2, [b] 0 bar H_2/200 ºC, [c] 0 bar H_2/260 ºC, [d] In methanol, [e] Unknown compound eluting at 3.8 min in GC analysis, not included (48 % of total peak area), [f] Spent catalyst recovered after the experiment in entry 5



An example of the successful collaboration between Greece, France and Spain, involving training/exchange of young scientists within the frame of European COST Action "LIGNOVAL"

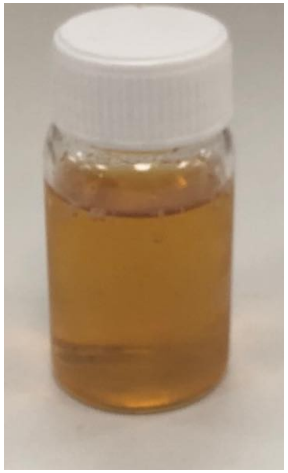
COST
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

LIGNOVAL

Y. Wang, P. Prinsen, K.S. Triantafyllidis, S.A. Karakoulia, P.N. Trikalitis, A. Yepez, C. Len, R. Luque, ACS Sustainable Chem. Eng. 2018, 9831−9844

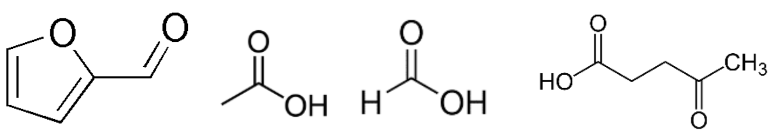
Y. Wang, P. Prinsen, K.S. Triantafyllidis, S.A. Karakoulia, A. Yepez, C. Len, R. Luque, ChemCatChem 2018, 10, 3459– 3468

Catalytic hydrogenation experiments of “real” hemicellulose stream



H_2 (30 bar)

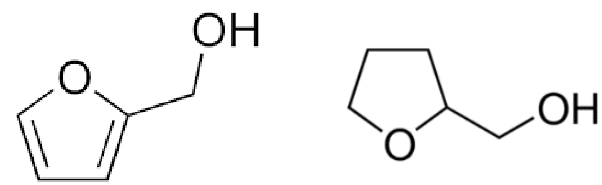
3%Pd/AC



Aqueous side-stream from Hydrothermal Pretreatment of biomass (beech wood)

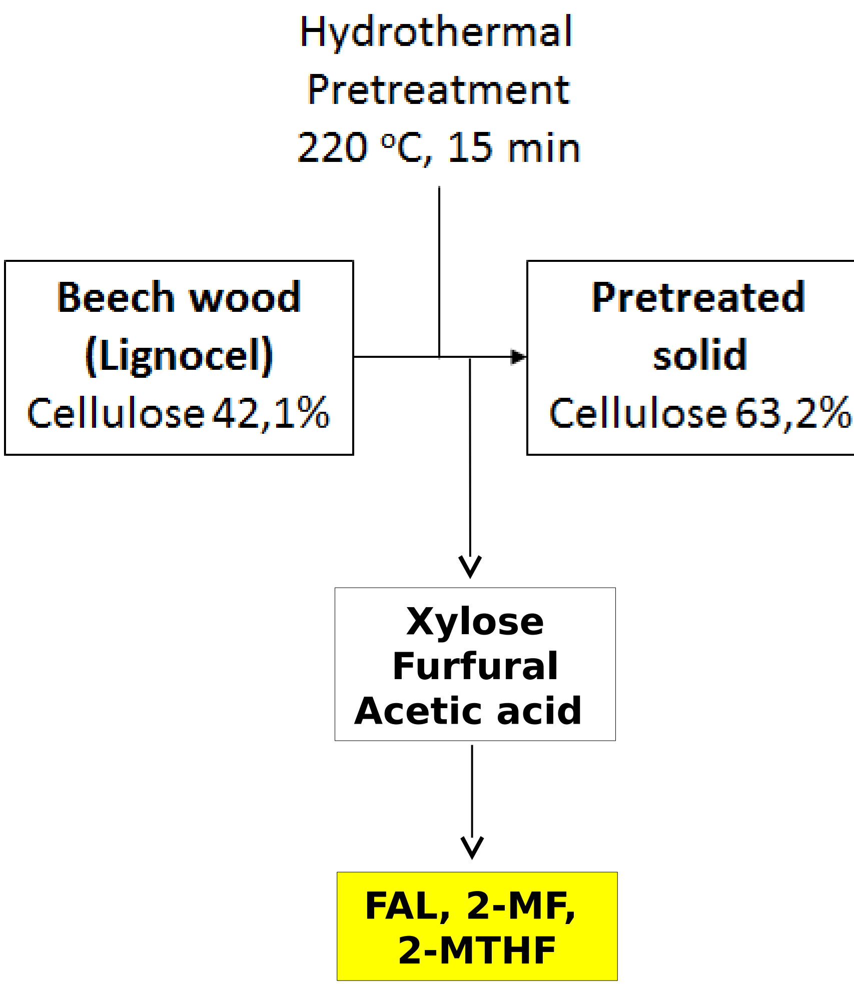
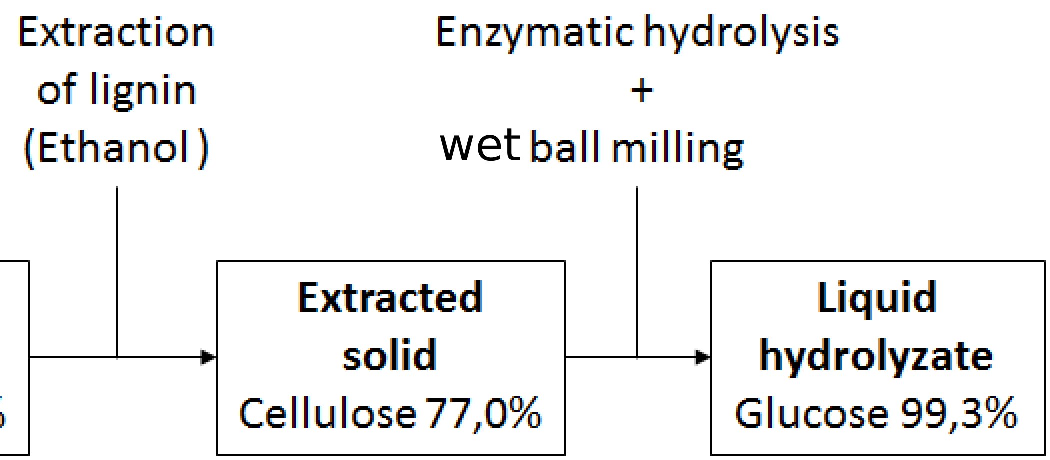
80% FF conversion

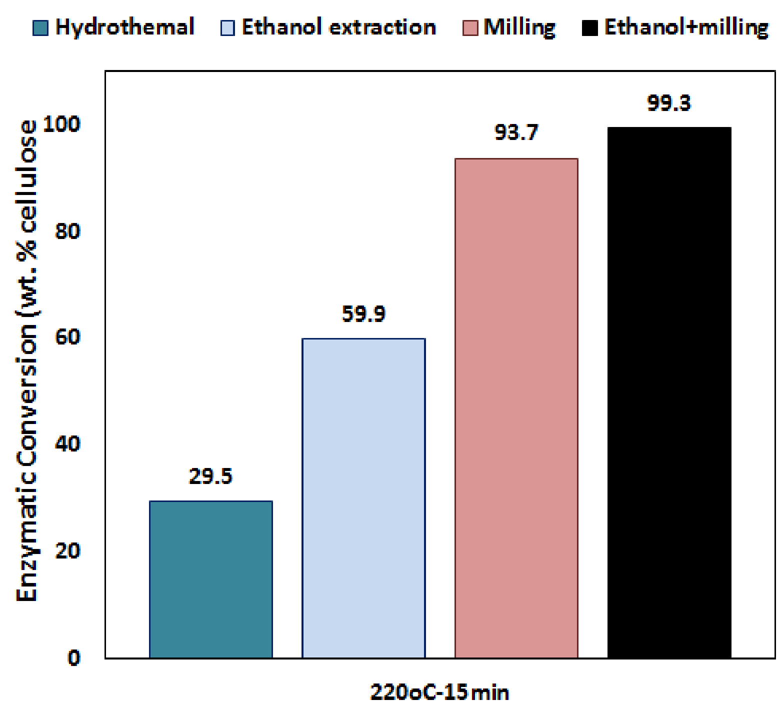
> 95 % selectivity to:



Furfuryl alcohol ***Tetrahydrofurfuryl alcohol***

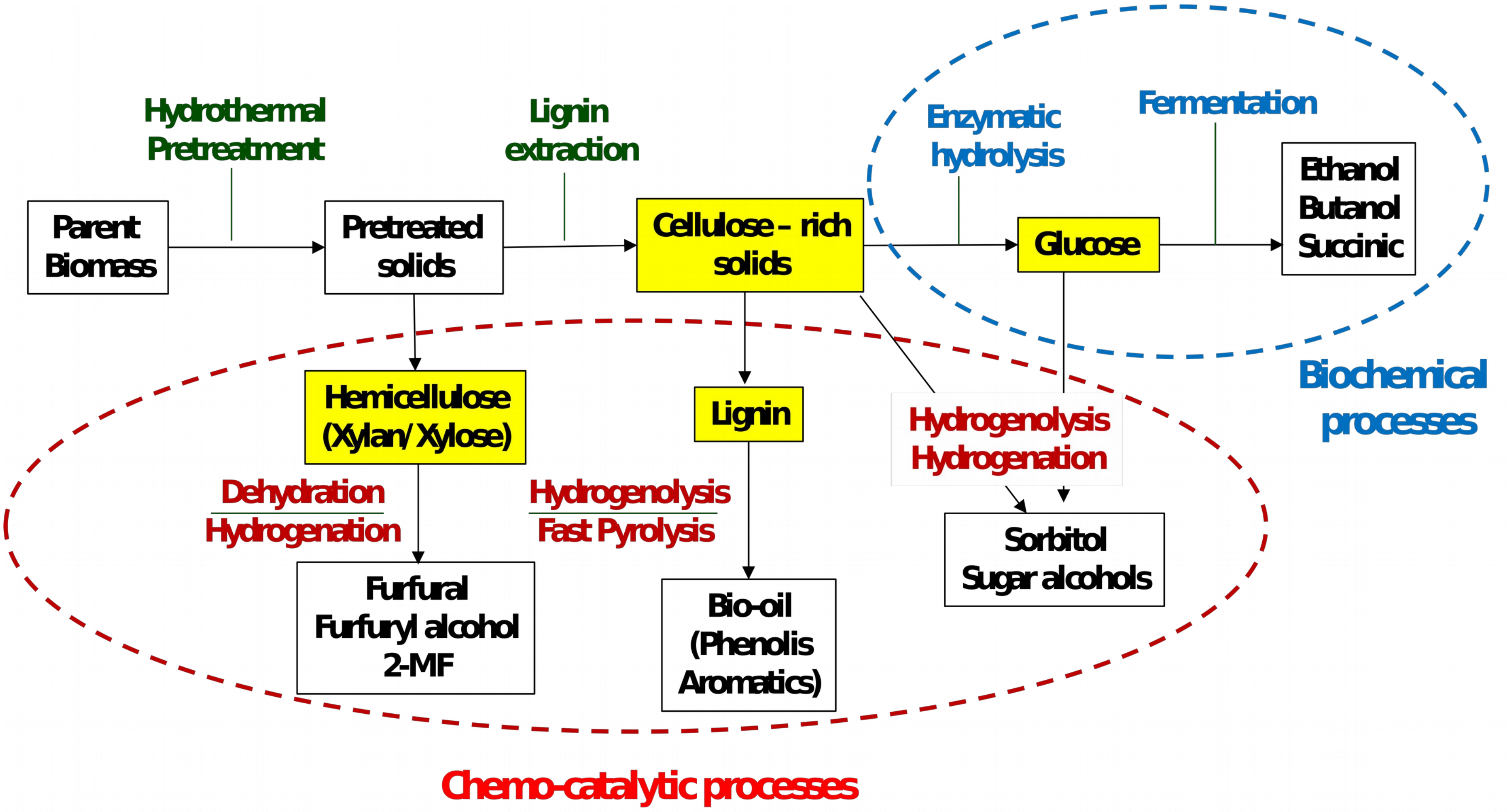
Enzymatic hydrolysis optimization (beech sawdust)



C. K. Nitsos, P. A. Lazaridis, A. Mach-Aigner, K. A. Matis, K. S. Triantafyllidis, ChemSusChem (2019) 12 (6): 1179

"Whole biomass" valorization scheme at AUTH



A synergy between thermochemical pretreatment, chemo- and bio-catalysis is necessary for more efficient biomass valorization

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Group

Prof. K. Triantafyllidis
Dr. Polykarpos Lazaridis
Dr. Ioannis Charisteidis
Dr. Christos Nitsos
Dr. Apostolos Fotopoulos
Dr. Antigoni Margellou
Dr. Dimitrios Giliopoulos
Dr. George Giannopoulos
Christina Pappa, MSc

Collaborators

Prof. Paul Christakopoulos, Prof. Ulrika Rova, Dr. L. Matsakas (LTU, Sweden)

Prof. Rafael Luque (University of Cordoba)

Prof. Christophe Len (Chimie ParisTech, PSL University)

Prof. Vasile Parvulescu, Prof. Simona Coman (U. Bucharest)

Prof. Dimitrios Argyropoulos, North Carolina State University, USA

Dr. Angelos Lappas, Dr. Stylianos Stefanidis, Dr. Eleni Iliopoulou, Dr. Kostas Kalogiannis, Dr. Cryssoula Michailof, Dr. Stamatia Karakoulia (CPERI/CERTH)

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