“La biomasse : source de matière première pour l’industrie chimique"

Francois Jérôme (DR CNRS)
Institut de Chimie des Milieux et Matériaux de Poitiers

Sources de carbone, Fondation maison de la chimie, 03 Octobre 2022

A global picture of the chemical industry

Chemical industry consumes
- 10% of fossil carbon as feedstock
- 7% as energy

Olefins

Aromatics

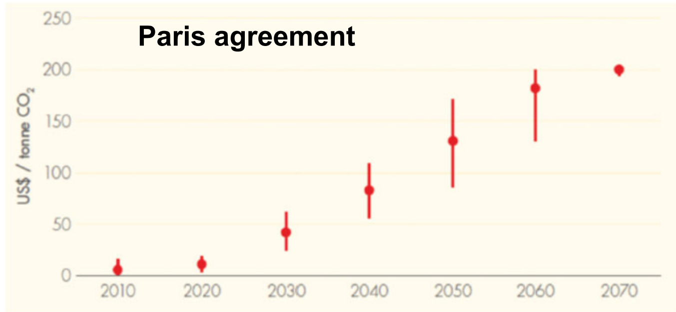
Base chemicals
~ 400 Mt per year

90% → **Polymers**

10% → **Intermediates**

5 % global CO_2 emissions (~ 1,5 Gt/year)
Average : 1-2.5 Kg_{CO2} / $Kg_{product}$

Annual growth of the Chemical industry ~ 3% / year



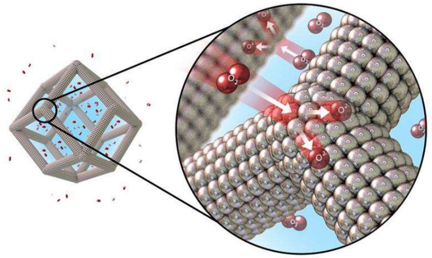
Cost increase
Oil by about $42 per bbl
Gas by about $5.5 per GJ
Fossil H_2 by about $900 per ton

Increase in product prices
~ $200-1000 per ton by 2050

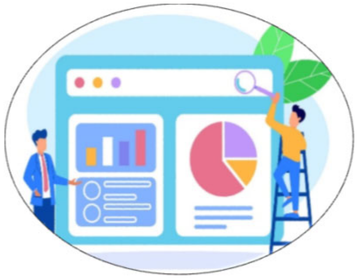
What next…

CO_2 capture and storage (or utilization)

- **Becomes cost-efficient ($40 per ton of CO_2 in 2020-2025)**



New technologies, optimization in catalyst performance, process design and operation, energy and chemical consumption, etc…



How to optimize the chemical industry ?

Electrification (renewable energy)

Shell's chemical complex (solar park of 27 MW)

- **Limited to low-temperature applications**
- **Intermittency**

Reuse

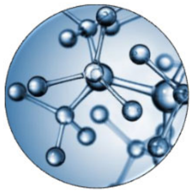
Renewable feedstocks

- **Waste**

Biobased feedstocks

Sugars

Vegetable oils



Chemicals

Production for food and feed
= 3-4 Gt/year

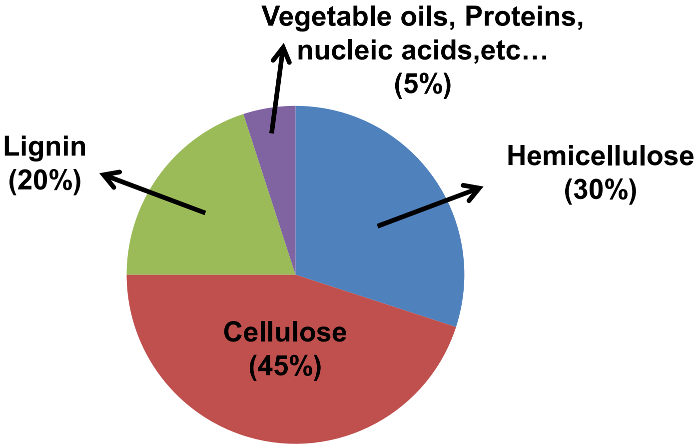
~ 2% could be diverted to chemicals (60-80 Mt/year)

Will take 20-25 years

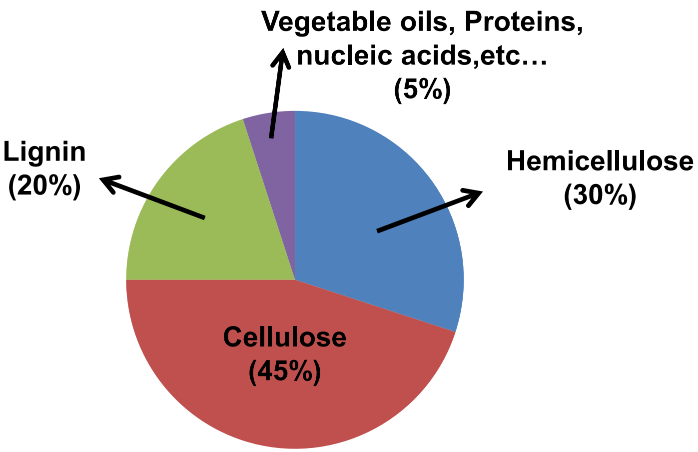
Current volume : 7 Mt/year at a growth rate of 10%

What about biomass waste?

Lignocellulosic biomass waste



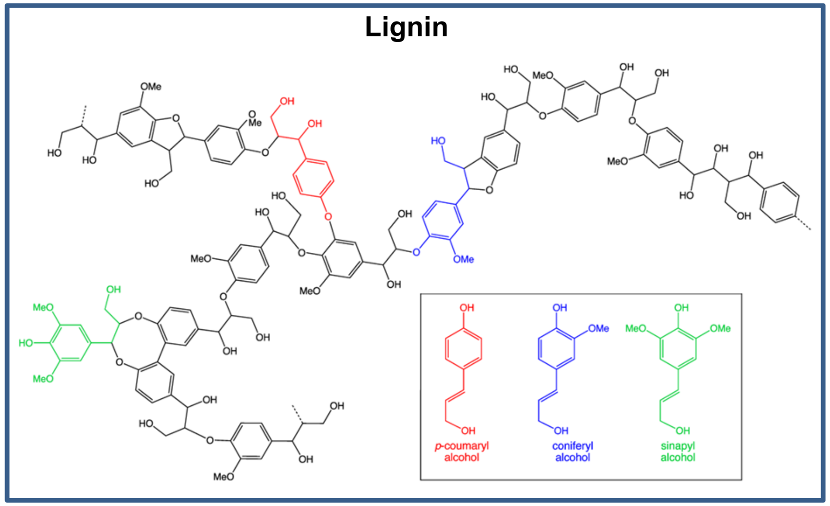
Lignocellulosic biomass waste

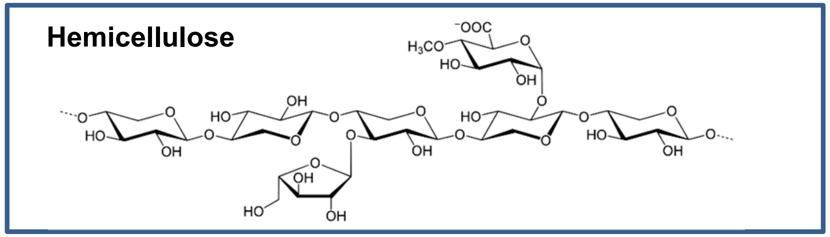


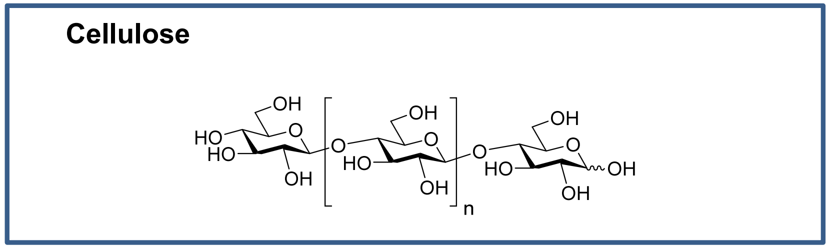
75 % of sugars

Potential stock of biomass (excluding food) = 6-18 Gt/year

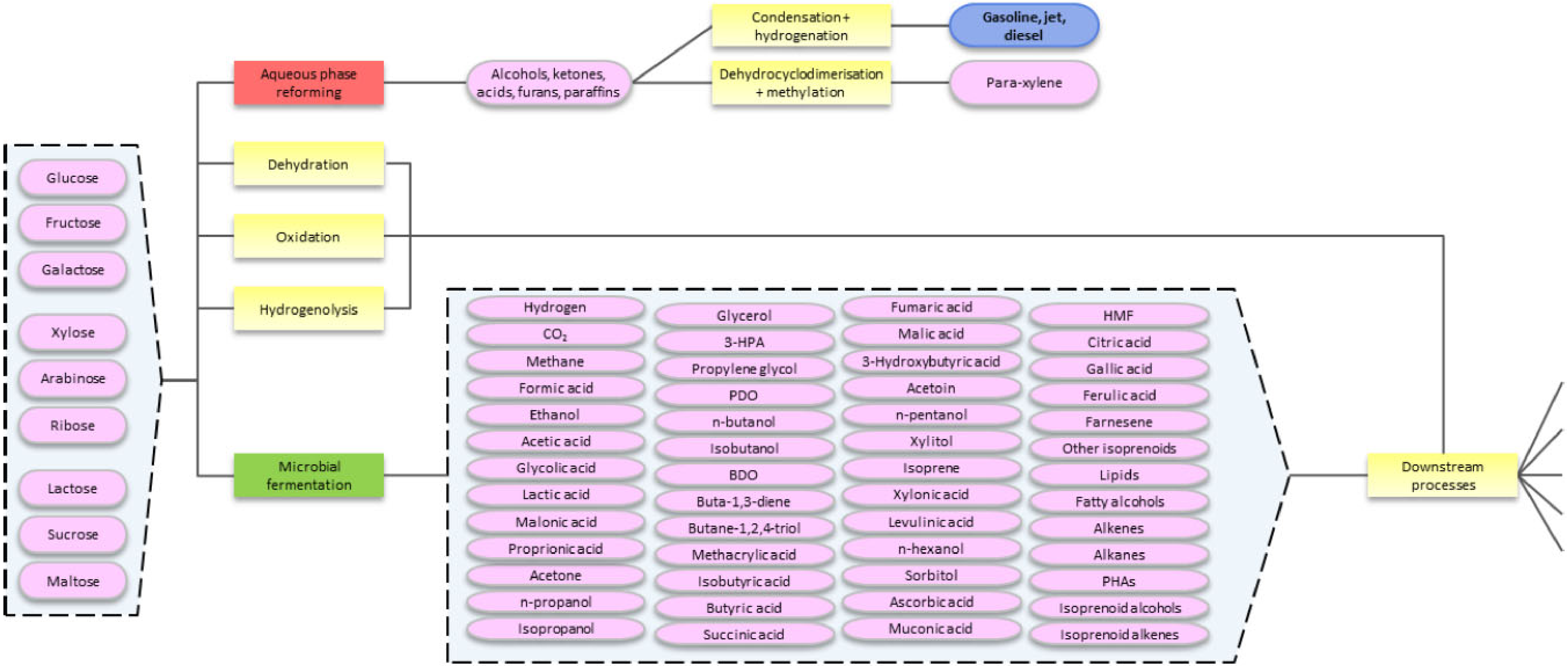
Estimation of biobased chemicals : ~ 400-550Mt/year by 2080



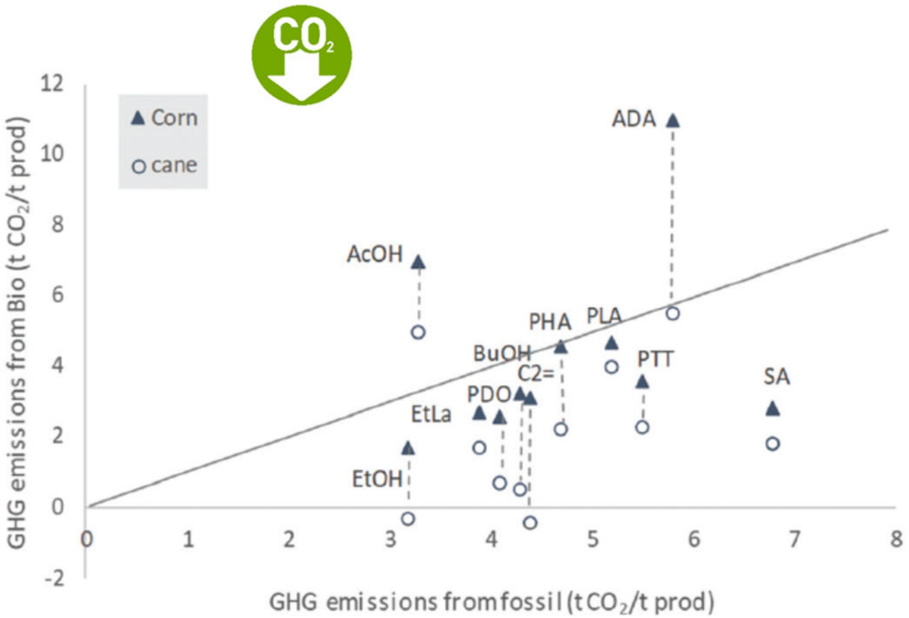




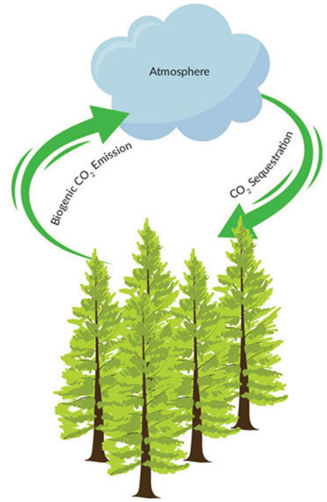
The sugar platform



CO_2 emissions



AcOH	acetic acid
ADA	adipic acid
BuOH	n-butanol
EtOH	ethanol
EtLa	ethyl lactate
PDO	1,3-propanediol
PHA	polyhydroxyalkanoate
PLA	polylactide
PTT	polytrimethyleneterephthalate
SA	succinic acid



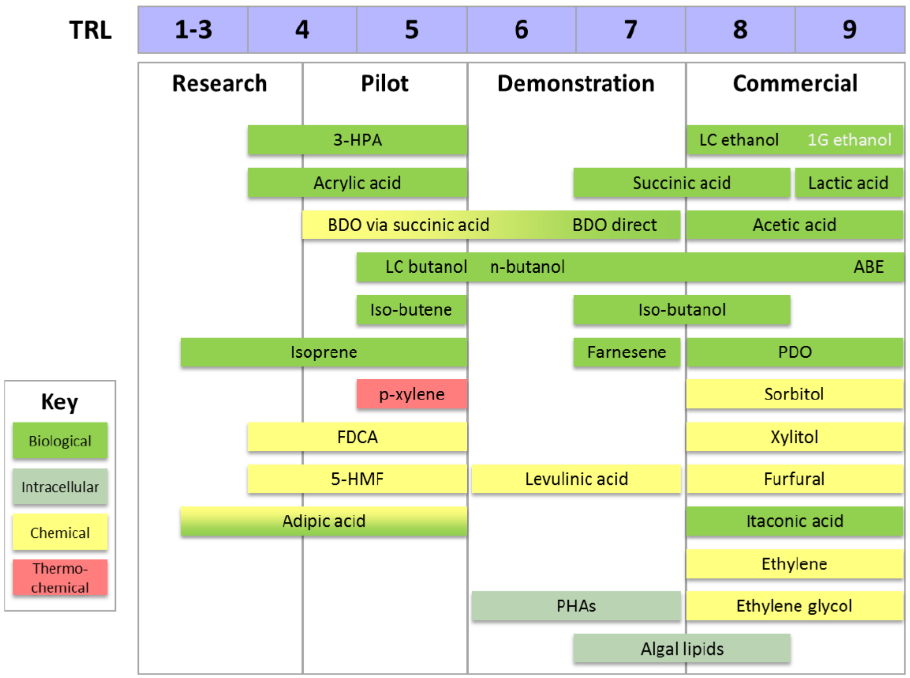
Biobased products are generally produced with lower CO_2 emission

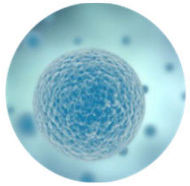
Biobased ≠ Sustainable !!

- **Quality of air and water**
- **Water and land usage**
- **Biodiversity**
- **Deforestation**
- **Soil depletion**
- **Agricultural practice**
- **Etc…**

J. P. Lange, *Energy Environ. Sci.*, **2021**, *14*, 4358–4376

Scale up





Industrial requirements

Selectivity : 70-100%

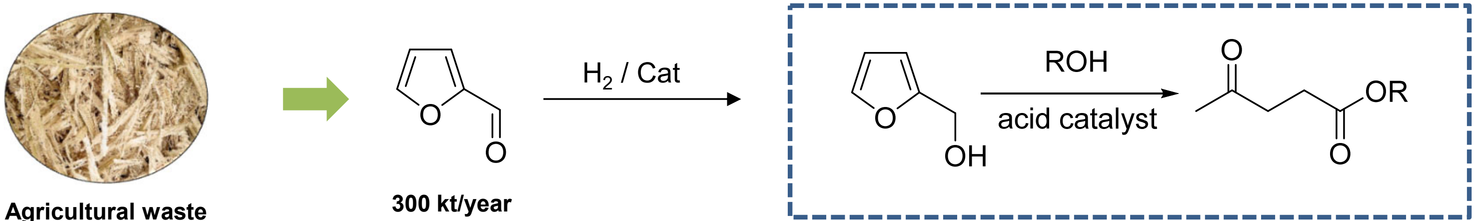
Productivity : 0.1-10 $t_{prod}/m^3/h$

Catalyst consumption: 1-100t_{prod}/kg_{cat}

Product concentration > 15 wt% (*except for highly exothermic reactions*)

J. P. Lange et al, Angew. Chem .Int. Ed. **2015**, *54* ,13186-13197
J. P. Lange et al. Catal. Sci. Technol. **2016**, *6*, 4759-4767

Impact of dilution



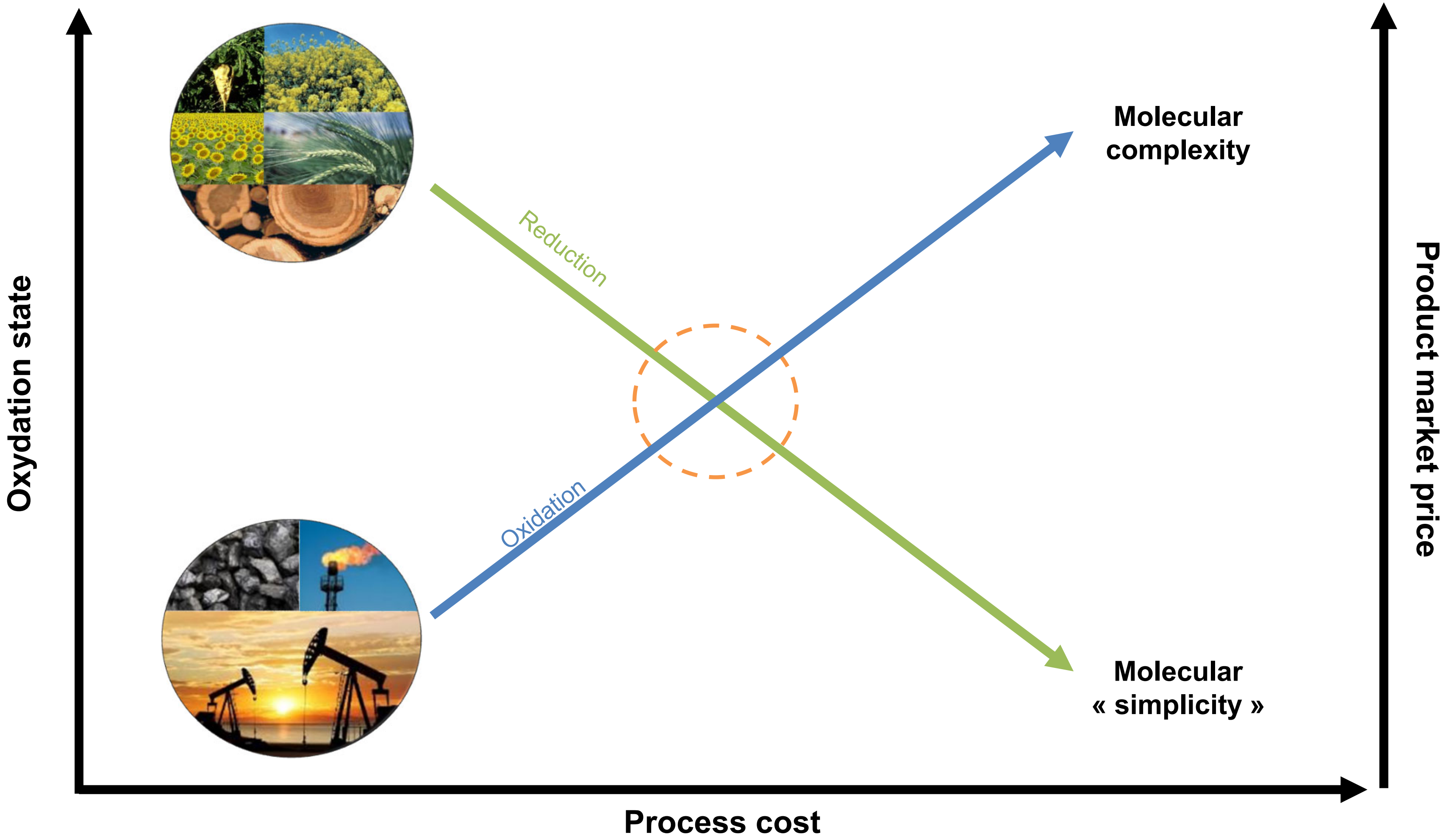
Agricultural waste

300 kt/year
1-3 €/kg

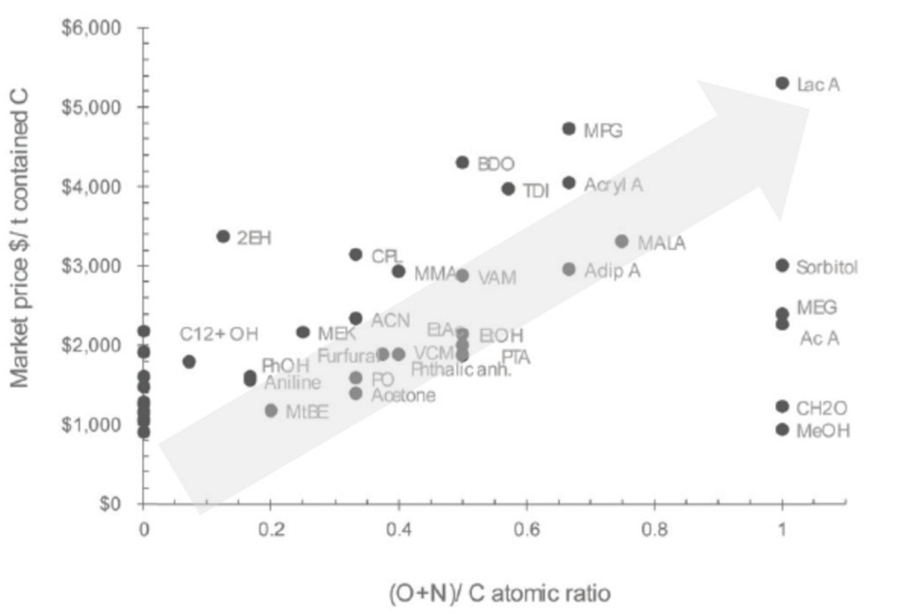
Catalyst	[FA] wt%	Cat amount[a]	Yield (%)	Space Time Yield (kg/m^3/h)
SBA-SO_3H	2.8	25 wt%	96	12
Arylsulfonic acid functionalized mesoporous carbon spheres	2.8	1.5 wt%	80	17
Al-TUD-1	3	30 wt%	80	< 1
Amberlyst-15	1	50 wt%	94	4
Sulphated oxides	5	2.5 wt%	75	60
HZMS-5	2.8	25 wt%	40	3
Al_2O_3/SBA-15	2.0	400 wt%	90	4.3
$In(OTf)_3$	2.5	1 mol %	92	26
$H_3PW_{12}O_{40}$	3	16 wt%	50	< 1
$H_4SiW_{12}O_{40}$	3	16 wt%	60	< 1
$[MIMBS]_3PW_{12}O_{40}$	2.2	5 mol%	90	5
H_2SO_4	1	1.6 mol%	97	2
$AlCl_3$	3	4 mol %	75	11
Hierarchical zeolites	25	10 wt%	40	16

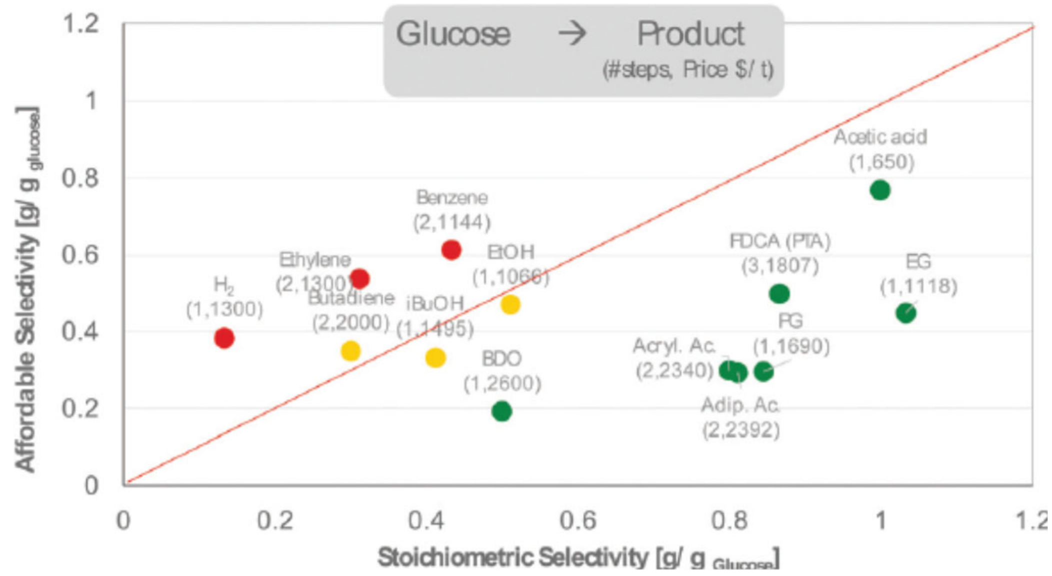
A. Chappaz, *et al.* ACS Chem. Sust Eng. , 2018, 6, 3, 4405-4411

Oxidation vs reduction



Which chemicals?





$$\text{Affordable selectivity} = \frac{\text{(feed price + 200 x N steps)}}{\text{Product price}}$$

Calcd for glucose = 300 $/ton

Higher you make use of oxygen in biomass, higher the valuability of chemicals

EU bio-based market (2019)

Product category	EU Biobased production (kt/a)	Total EU production (kt/a)	EU bio-based production share (%)
Platform chemicals	181	60,791	0.3
Solvents	75	5,000	1.5
Polymers for plastics	268	60,000	0.4
Paints, coatings, inks and dyes [a]	1,002	10,340	12.5
Surfactants	1,500	3,000	50.0
Cosmetics and personal care products [a]	558	1,263	44.0
Adhesives [a]	237	2,680	9.0
Lubricants [a]	237	6,764	3.5
Plasticisers [a]	67	1,300	9.0
Man-made fibers	600	4,500	13.0
Total	**4,725**	**155,639**	**3.0**

[a] No total EU production data were found; it has been assumed that total EU p
and biobased) equals the total EU market (fossil- and bio-based consumption).

Main market of biobased chemistry

Construction

Automobile

Packaging

Detergence

Cosmetic

- Turn over of 10 billion euros/year
- 11% of bio-based raw materials
- Good public perception
- annual growth rate of 5% (predicted to 15% in 2035)

Biobased is not always the solution

Fossil

Ethylene

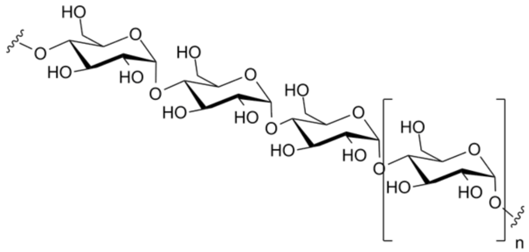
Polyethylene

Renewable

Bioethanol

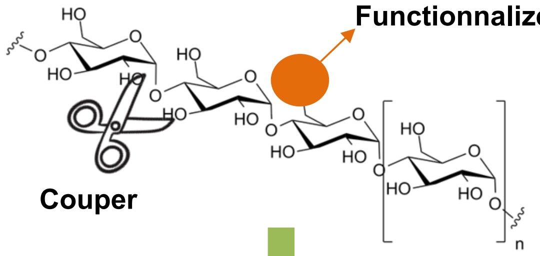
Bioethylene

Biopolyethylene



Polysaccharides

Functionnalize



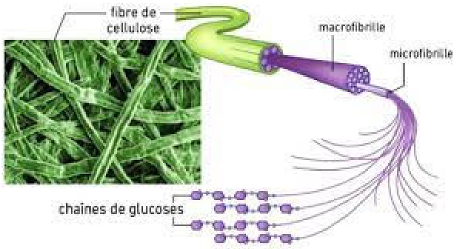
Couper

Physicochemical properties that cannot be obtained with fossil-based polymers

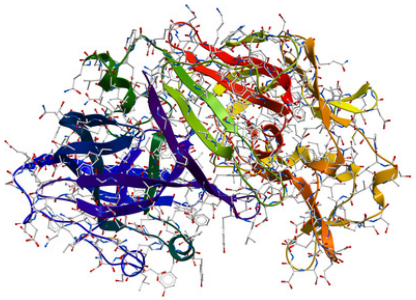
Potentially biodegradable

Expectations in terms of innovation

Better understanding of biomass

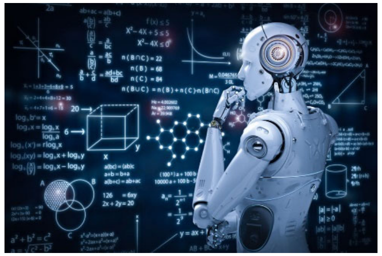


Better understanding of biological systems



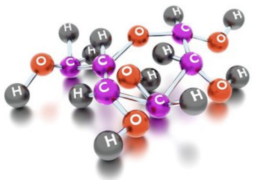
New technologies

New tools (AI, machine learning, etc…)



New products from biomass waste: which technologies?

shutterstock.com · 1489280417

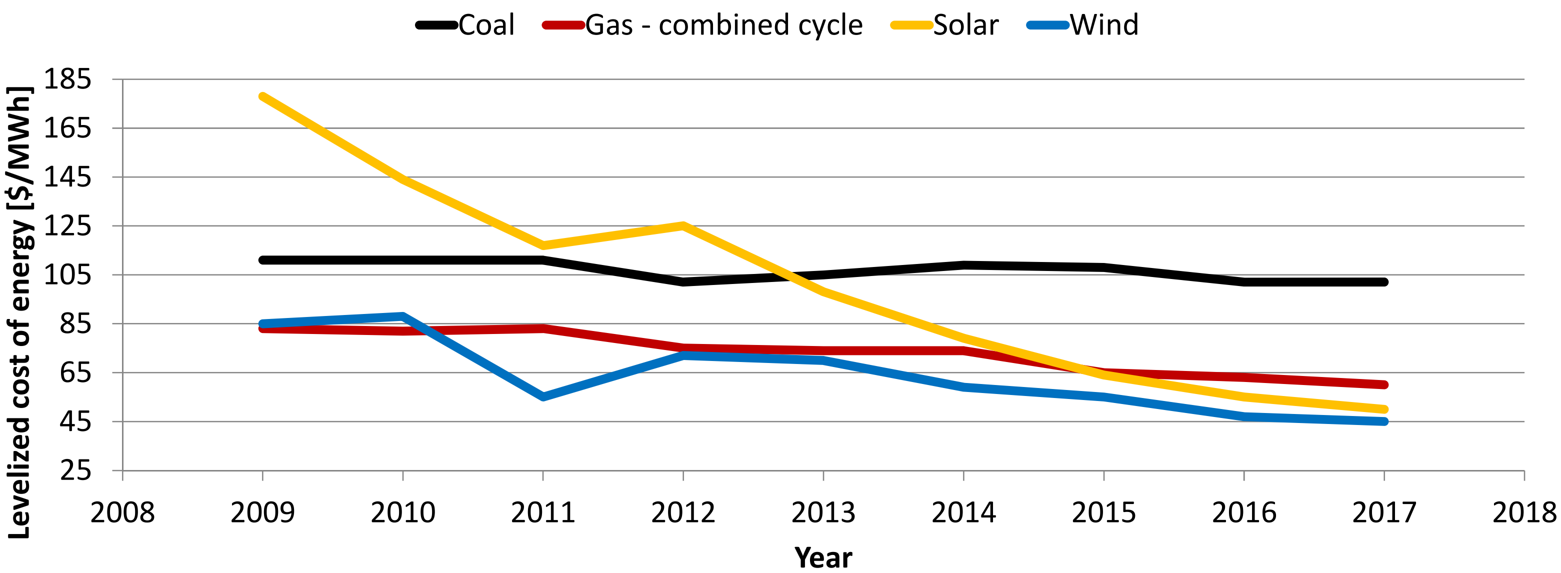


shutterstock.com · 476195278

Electrification of our society: renewable energy becomes accessible

Wind

Solar

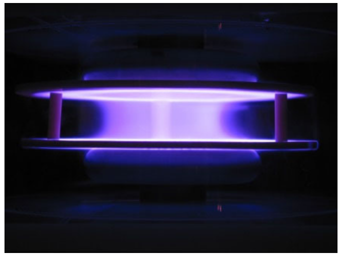


https://www.lazard.com/perspective/levelized-cost-of-energy-2017/

Alternative technologies

Microwaves

Ultrasound

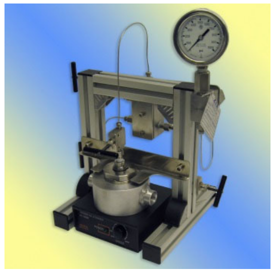


Plasma

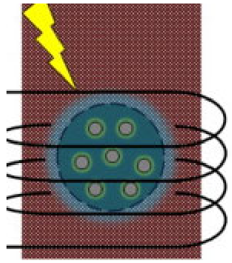
Electrochemistry

Milling

Photochemistry

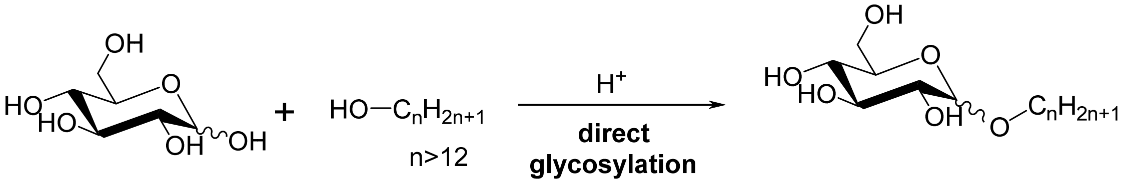


Pressure



Magnetic field

Fischer glycosylation of glucose with fatty alcohols



Refined glucose: 0,45 €/kg

Predicted US$ 1.3 billion in 2022

Biosurfactants

- Stable
- Biodegradable
- Non-toxic

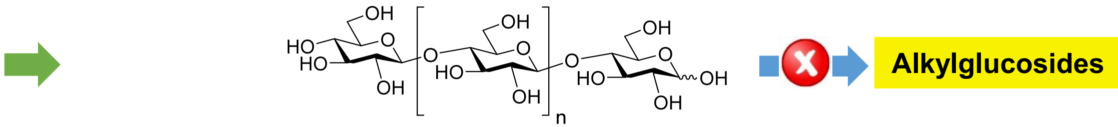
Price of AlkGlycoside: 1,5 €/kg
(vs ~ 1 €/kg for fossil derived analogs)

→ **Optimization of the catalytic process**

→ **Start from a cheaper source of glucose**

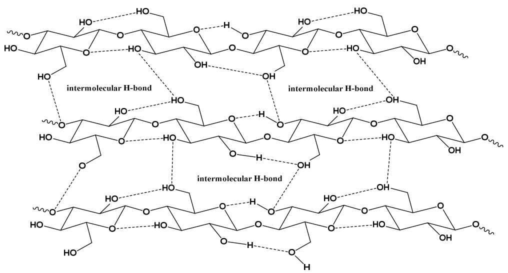
Understand cellulose

Wheat straw < 0,1 €/kg

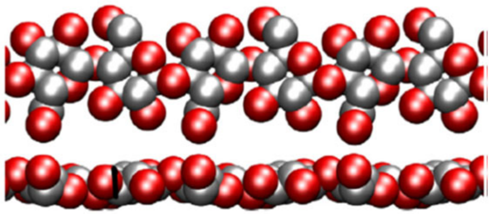


cellulose

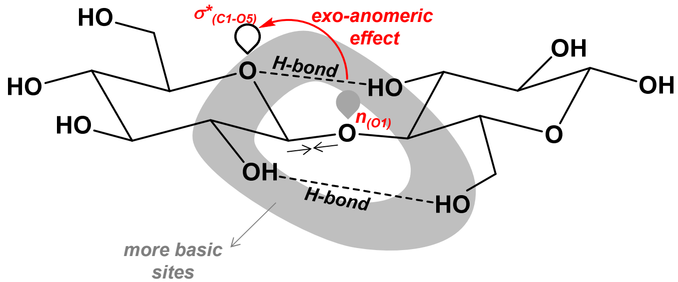
Hydrogen bond network



Hydrophobic interaction

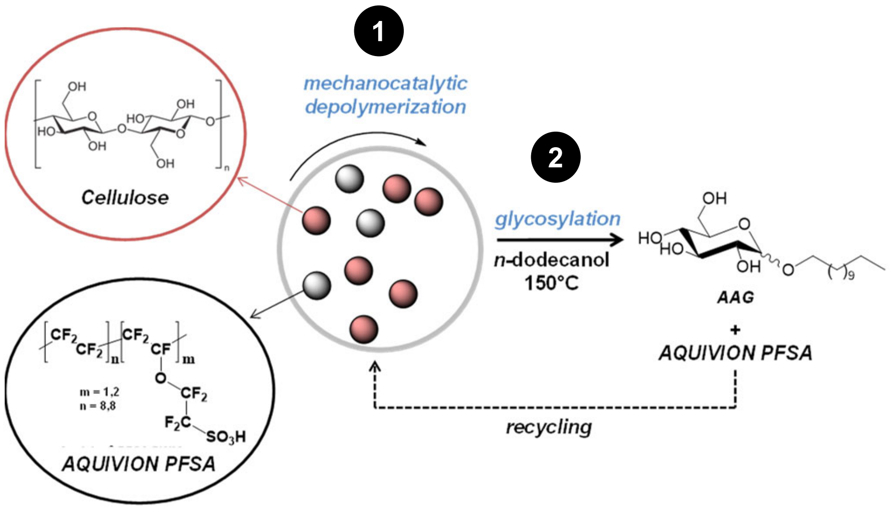


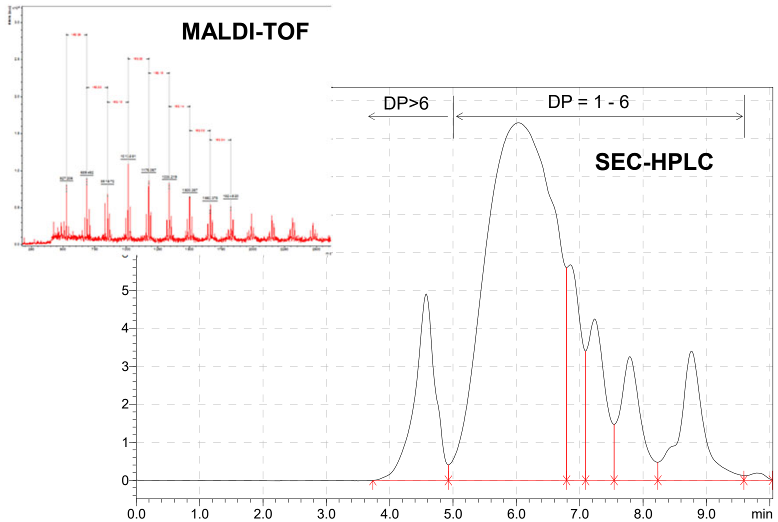
Electronic effects



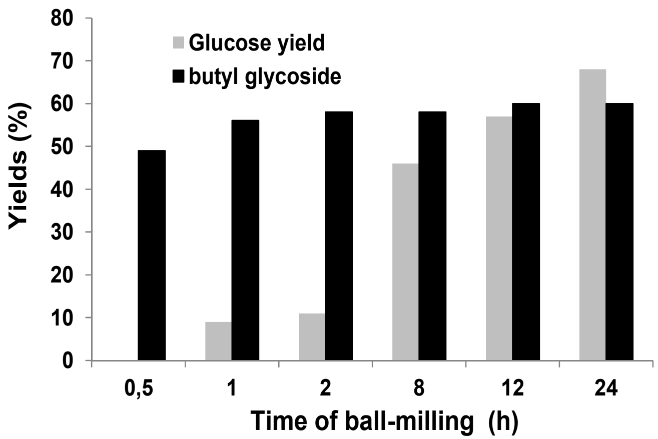
C. Loerbroks et al. *Chem. Eur. J.* **2013**, *19*, 16282-16294

Glycosylation of cellulose with n-dodecanol





Hydrolysis vs glycosylation



Catalyst	AAG yield (%)	r_{AAG} (h^{-1})	Space time yield ($kg/m^3/h$)
H_2SO_4	0	0	0
Aquivion PFSA PW98	70	40	250
Amberlyst-15	0	0	0
Kaolinite	0	0	0
Montmorillonite	0	0	0

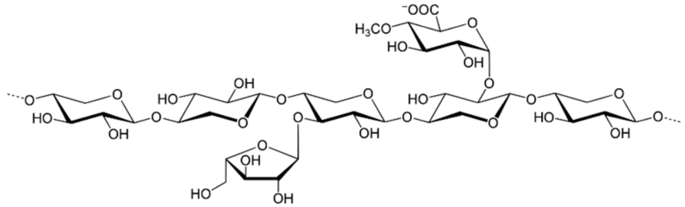
3h of ball-mlling and then glycosylation at 150°C, 10 eq. fatty alcohol

A. Karam *et al.*, *ChemSusChem*, **2017**, 10, 3604-3610

And from cellulosic biomass?

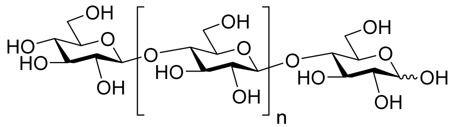
Wheat straw < 0,1 €/kg

lignin



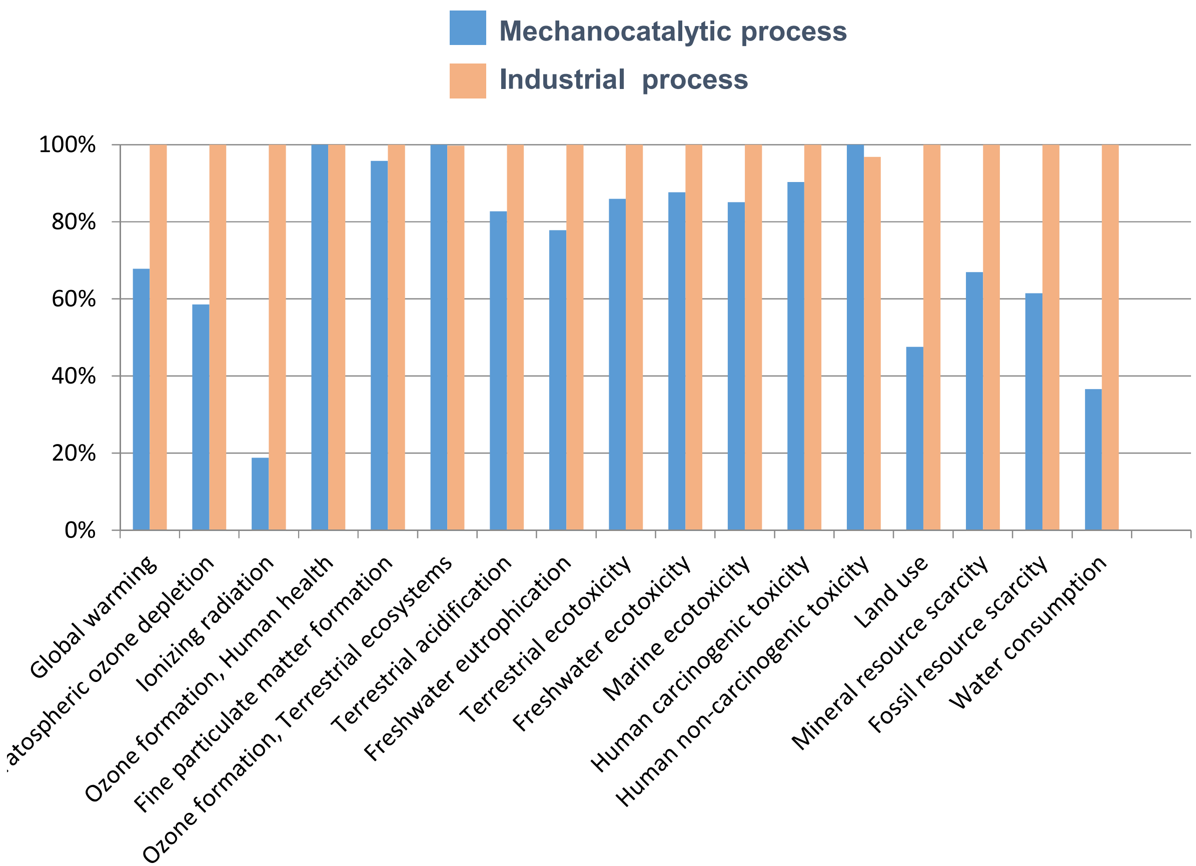
hemicellulose

Alkylpentosides



Alkylglucosides

Life cycle assessment



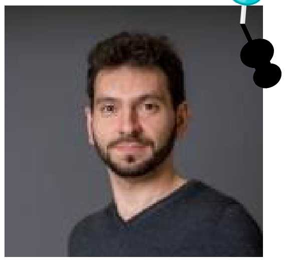
- ► Reduction of CO_2 by a factor 7
- ► 30% reduction in global warming
- ► 40 % reduction in atmospheric ozone depletion
- ► 30 % reduction in mineral resource
- ► 45 % reduction in waste water

In both processes, the main impacts on the environnement (80%!) come from the production of fatty alcohol

Incineration of co-generated lignin provides 98% of the energy demand for the glycosylation reaction and the generation of steam

G. Sonneman *et* al., *Green Chem.*, **2018**, 20, 2135-2141

Start-up BIOSEDEV



Florent

biosedev.com

Julien

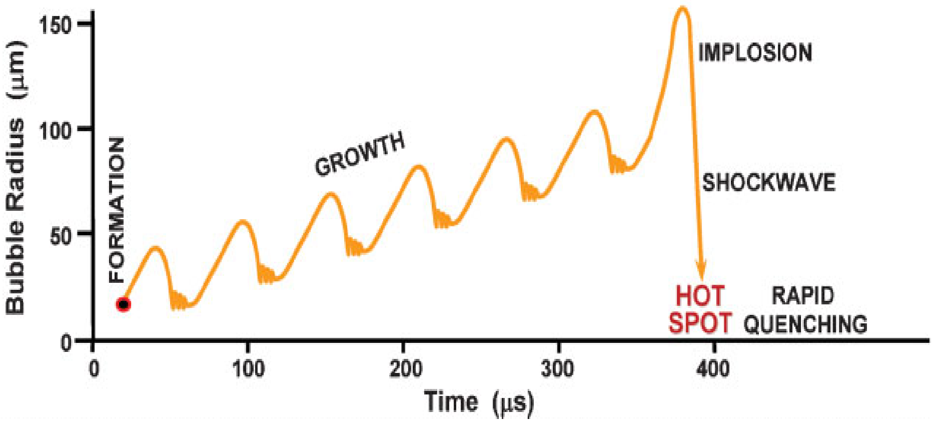
CRÉDIT D'IMPÔT RECHERCHE — AGRÉMENT CIR

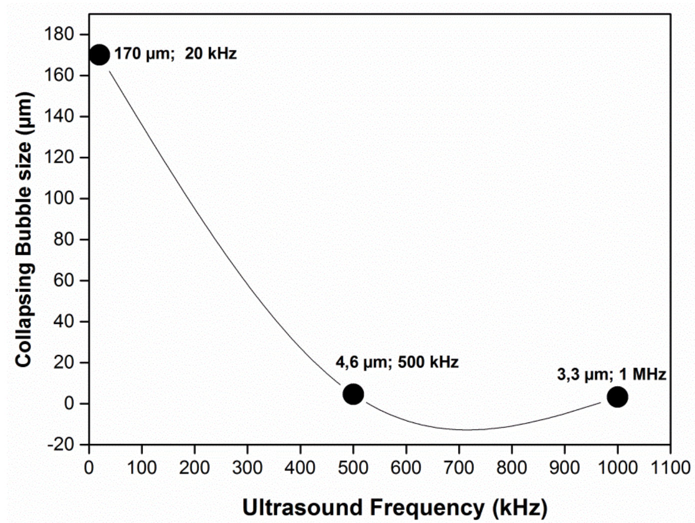
BIOSEDEV

IC2MP · Université de Poitiers · ENSIP · CNRS · La Technopole Grand Poitiers · AGIR Agro Alimentaire Innovation Recherche · Xylofutur Membre du Pôle de Compétitivité Xylofutur · French Tech bpifrance · Région Nouvelle-Aquitaine

BioseDev - 1 rue Marcel Doré 86000 Poitiers

High frequency ultrasound





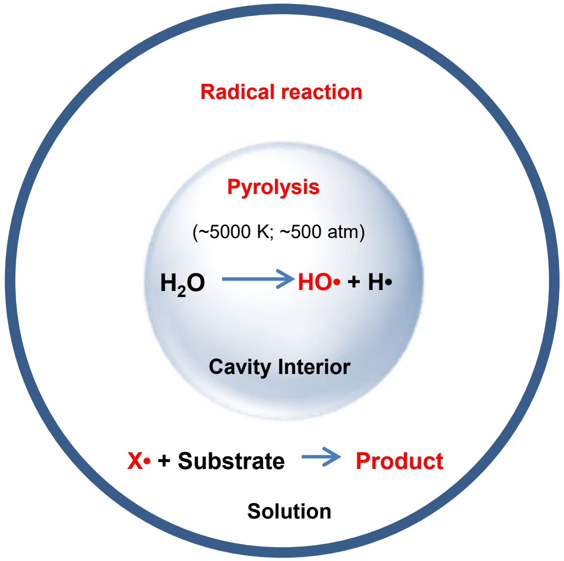
CAVITATION PHENOMENON

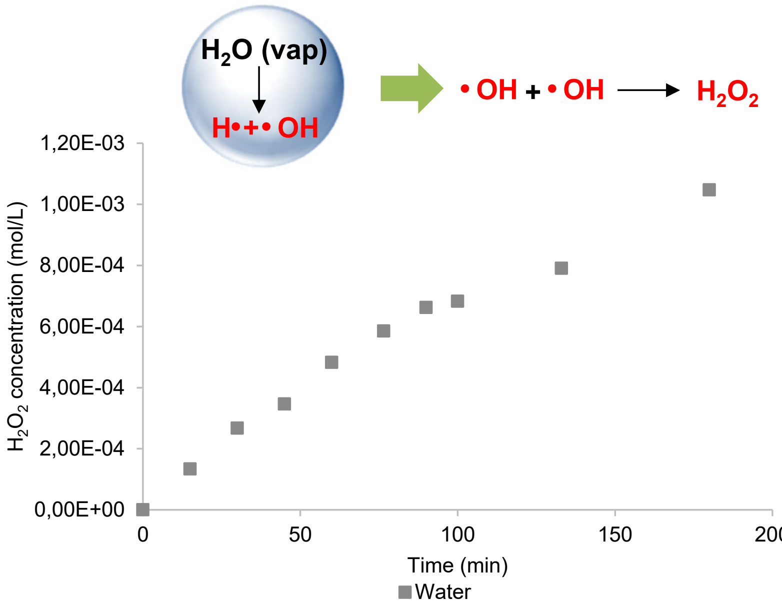
Low frequencies (20 to 80 kHz) →	**physical effects** (shockwaves, microjets, micro-convection,…)
High frequencies (150 to 2000 kHz) →	**chemical effects** (production of HO· radicals)

$$R_{max} = \frac{4}{3\omega_a}(P_A - P_h)\left(\frac{2}{\rho P_A}\right)^{1/2}\left[1 + \frac{2}{3P_h}(P_A - P_h)\right]^{1/3}$$

Frequency (ω_a), Density (ρ), Amplitude (P_A), Pressure (P_h)

High frequency ultrasound





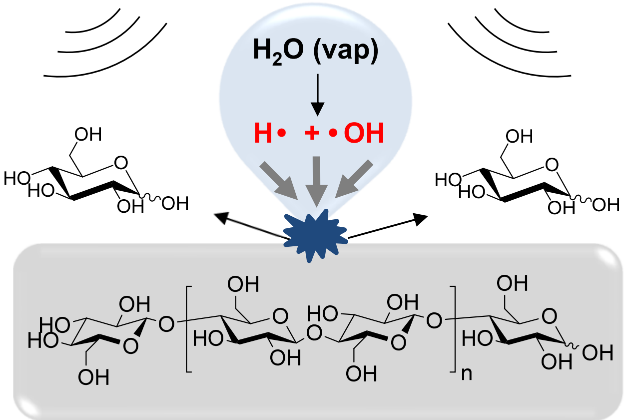
$$T_{max} = \frac{T_0 P_a (\gamma - 1)}{P_v}$$

$$P_{max} = P_v \left\{ \frac{P_a (\gamma - 1)}{P_v} \right\}^{[\gamma / \gamma - 1]}$$

T_0: temperature of the liquid
P_a: Acoustic power
γ: Specific heat
P_v: Vapor pressure

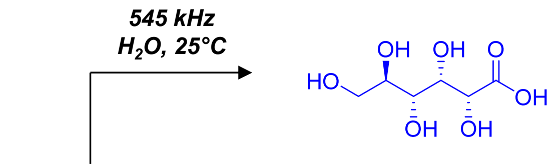
Reactions induced by high frequency ultrasound

Depolymerization reactions



Chem. Sci., **2020**,11, 2664-2669

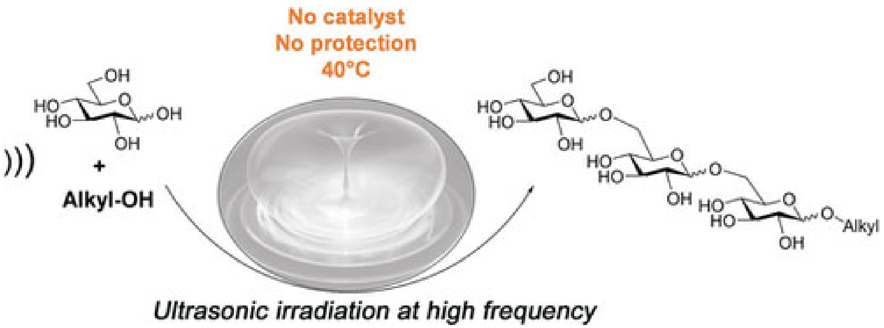
Oxidation reactions



Scientific Report., **2017**, 7, 40650

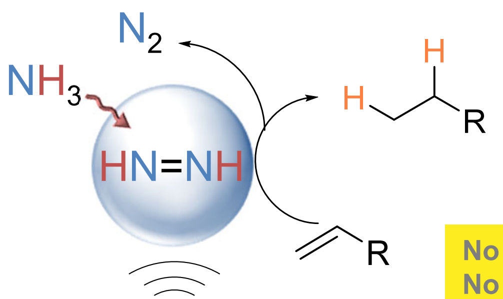
J. Am. Chem. Soc.., **2019**, 141 (37), 14772-14779

Polymerization reactions



ChemSusChem., **2018**, 11 (16), 2673-2676

Activation of NH_3

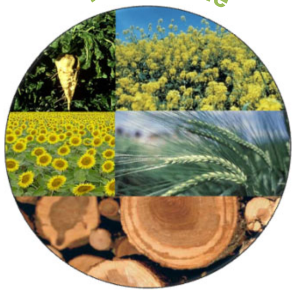


No metal/catalyst
No hydrogen

Unpublished results

Conclusion

Renewable



ALCOOLS
ACIDES

Fossil

CHEMICALS

Open innovation to revisit the activation/conversion of biobased feedstocks

TAKEN HOME MESSAGES

A biobased product does not mean a sustainable product

Don’t compete with fossil-based feedstocks : improve performances