La chimie durable : un paradigme pour de nouvelles (alternatives) voies scientifiques et technologiques

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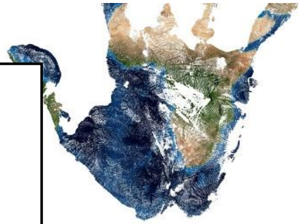
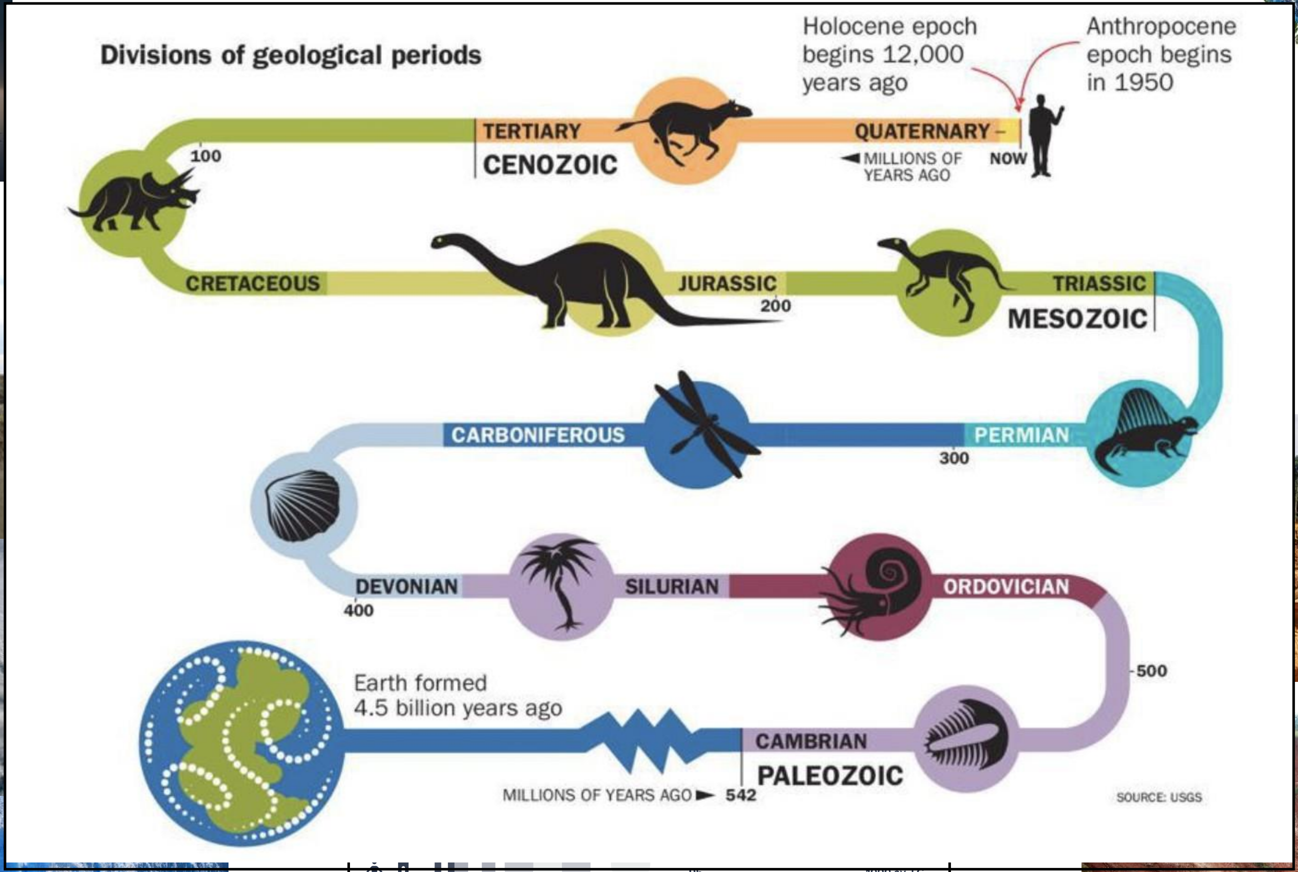
http://ic2mp.labo.univ-poitiers.fr

Yes, we do have an impact, no doubt!






THE END

Which options ?

Option 1 : extremist ideas
Get rid off chemistry !

Option 2 : re-think and re-invent chemistry
Go for a better society

Progress	**Profit**

Performances	**Society**	**Environment**

$$\% \text{ Atom economy} = \frac{M\ (\text{product})}{\Sigma\ M\ (\text{reactants})} \times 100$$

B. M. Trost, *Science*, **1991**, *254*, 1471

P. Anastas

J. Warner

The 12 principles on Green Chemistry

P. T. Anastas, J. C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, **1998**

$$\text{E Factor} = \frac{\Sigma\ m\ (\text{waste})}{m\ (\text{product})}$$

R. A. Sheldon, *C. R. Acad. Sci. IIc*, **2000**, 541

P. Anastas

J. Zimmerman

12 Principles of Green Chemistry

1. Prevent Waste
2. Atom Economy
3. Less Hazardous Chemical Syntheses
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-time Analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

Continuous Processing

12 Principles of Green Engineering

1. Inherent Rather Than Circumstantial
2. Prevention Instead of Treatment
3. Design for Separation
4. Maximize Efficiency
5. Output-Pulled Versus Input-Pushed
6. Conserve Complexity
7. Durability Rather Than Immortality
8. Meet Need, Minimize Excess
9. Minimize Material Diversity
10. Integrate Material and Energy Flows
11. Design for Commercial "Afterlife"
12. Renewable Rather Than Depleting

P. T. Anastas and J. B. Zimmerman, Environ. Sci. Technol., 2003, 37, 94A

P. Anastas

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White chemistry (biotechnology)

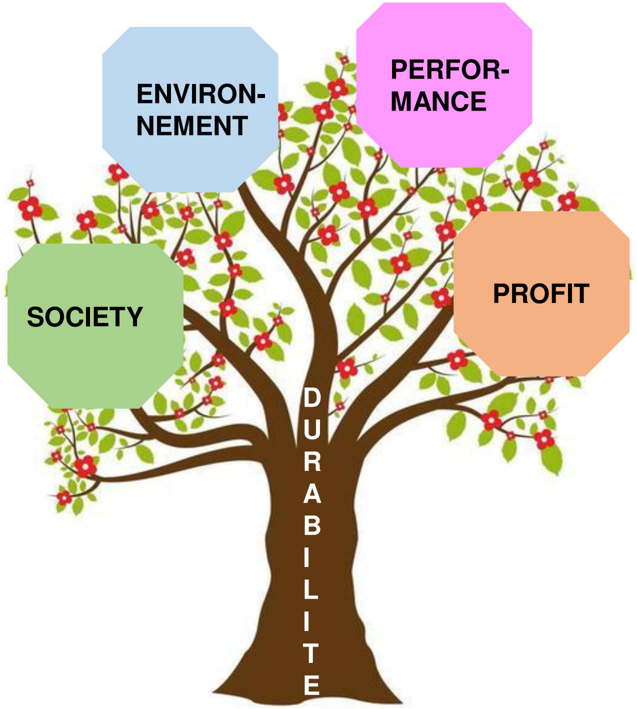
Blue chemistry (ocean)

Sustainable chemistry

Sustainable chemistry has the planet as system of interest

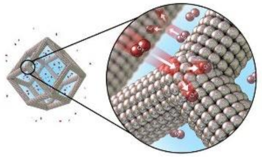
Sustainable chemistry considers the whole value chain of a chemical

- Supply of raw materials
- The manufacturing process (12 principle of green chemistry)
- The environmental and societal impact
- The end of life



On going strategies

CO_2 capture and/or conversion



Novel technologies

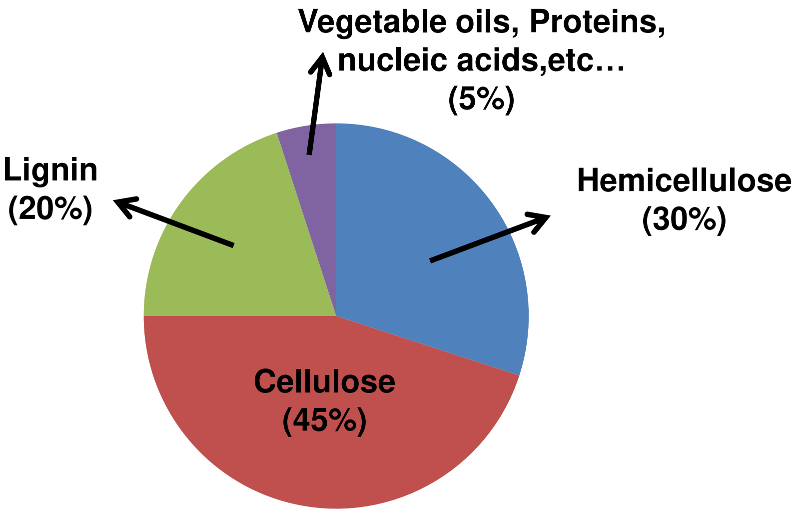
Chemical industry

Electrification

Reuse/recycle/reduce

Renewable carbon
(biomass, waste)

Lignocellulosic biomass waste

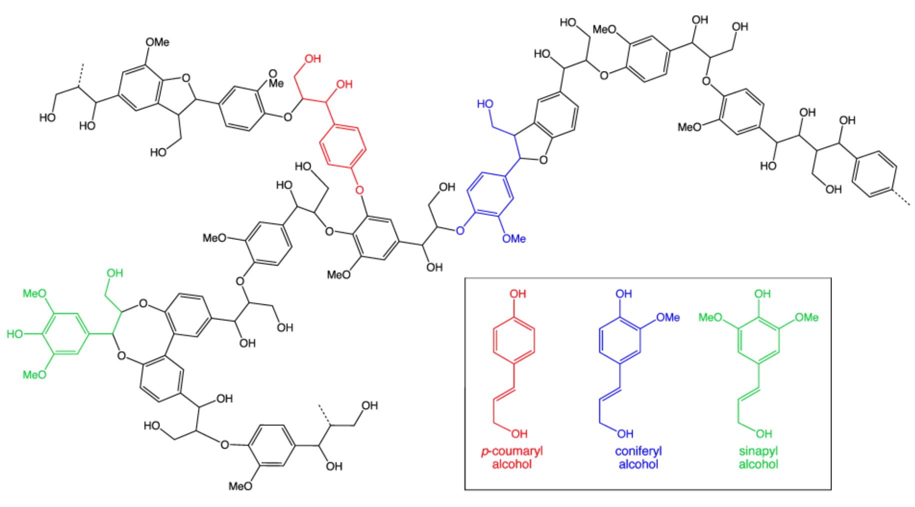


75 % of sugars

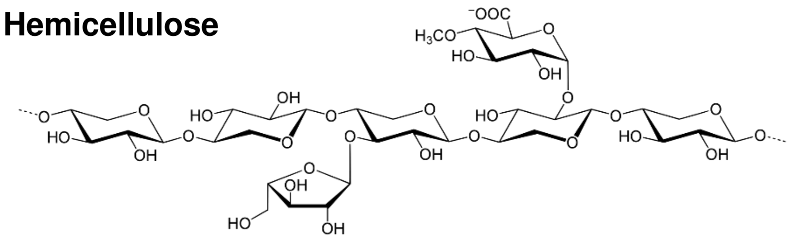
Potential stock of biomass (excluding food) = 6-18 Gt/year

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

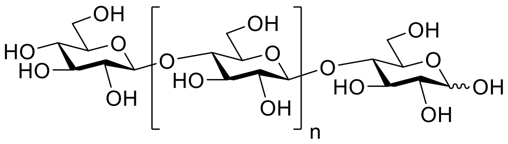
Lignin



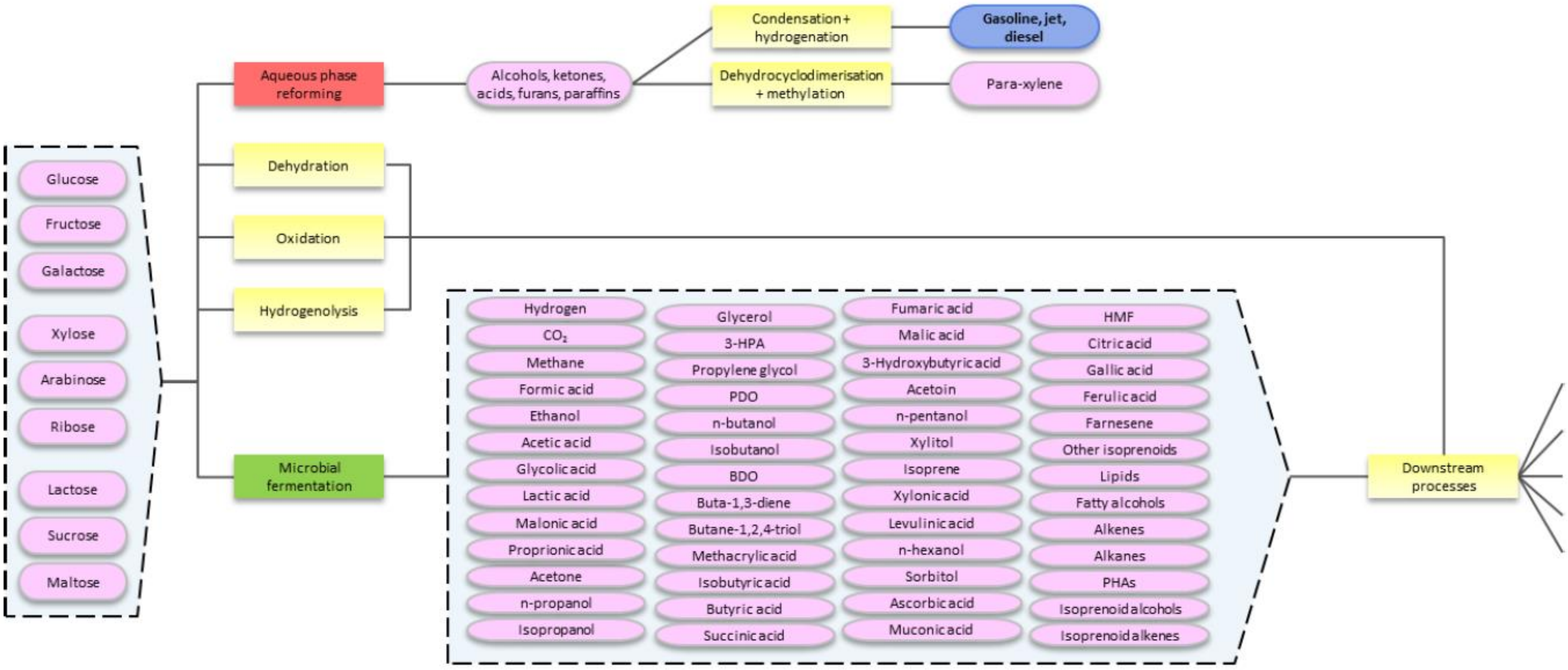
Hemicellulose



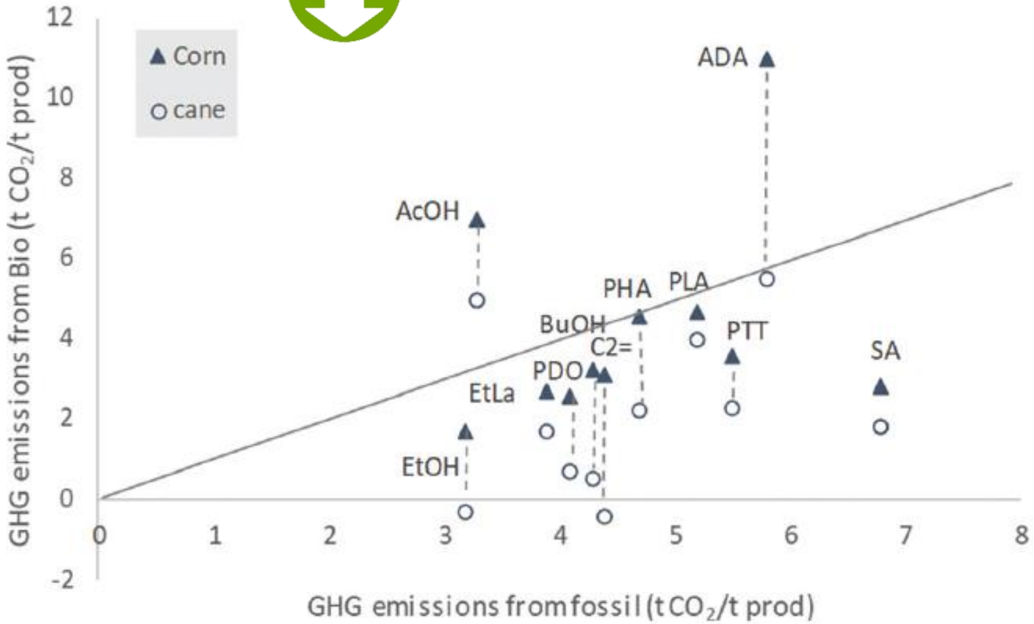
Cellulose



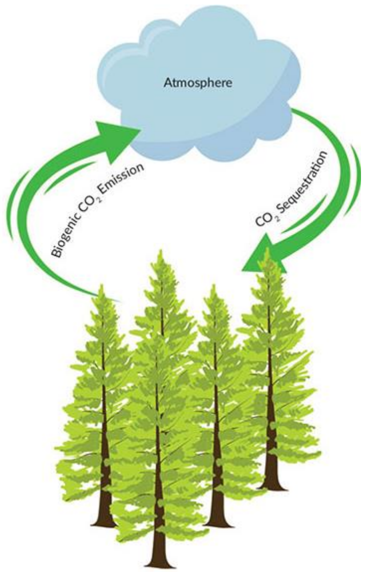
The sugar platform



CO_2 emissions



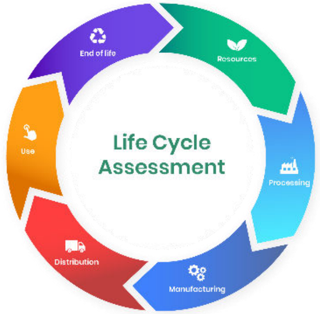
AcOH	acetic acid
ADA	adipic acid
BuOH	n-butanol
EtOH	ethanol
EtLa	ethyl lactate
PDO	1,3-propanediol
PHA	polyhydroxyalkanoate
PLA	polylactide
PTT	polytrimethyleneterephthalate
SA	succinic acid



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…**



Scale up

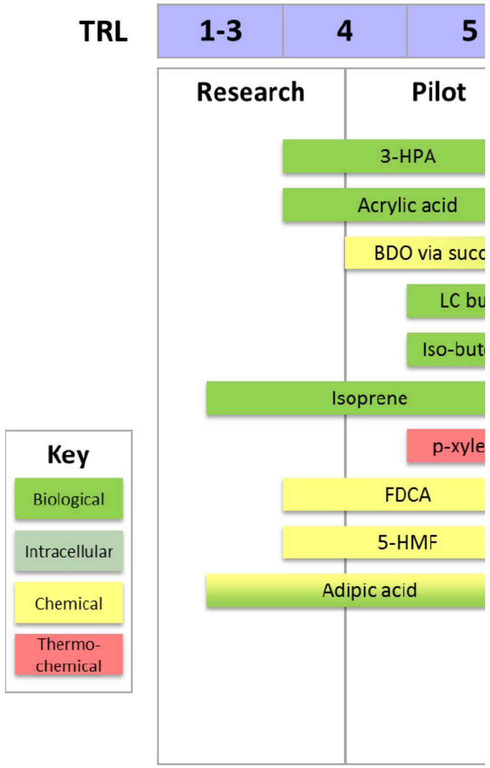


Table 1 | Suggested metrics for novel catalytic processes to manufacture fuels and commodity chemicals[4,20,23,24]

Criteria	Minimum requirement	Ideal value	Comments
Waste production[a] (t_{waste} per t_{prod})	<5	<1	Defined as by-products, fuel and inorganic chemicals
C footprint[a] (t_{CO_2} per t_{prod})	<6	<4	Defined from well-to-gate, including feed and utility
Selectivity	Stoichiometry > target	Experimental > target	Target selectivity defined in footnote[b]
Rea… (t_{pro}…			
Product concentration (wt%)	>5	>10	Determined by feed dilution and conversion per pass
Catalyst consumption (kg_{cat} per t_{prod})	<1	<0.1	Determined by catalyst lifetime and intrinsic activity
Distillation resistance (°C^{-1})	<15	<10	Defined in footnote[c]

[a]These targets have been defined for commodity chemicals; they should be tightened for fuel. [b]Target Selectivity (t_{prod} per t_{feed}) > (feed price + CC) (US$ per t_{feed}) /product price (US$ per t_{prod}). CC, conversion cost. [c]Distillation resistance Ω (°C^{-1}) = $100 \times \sum(f_i/\Delta T_i)$, where f_i is the weight fraction in the stream (wt/wt) and i represents the various components present in the stream; T_i is the temperature in °C. Prod, product; react, reactor; cat, catalyst.

How can we convert (selectively) concentrated feeds of bio-based chemicals ?

uirements

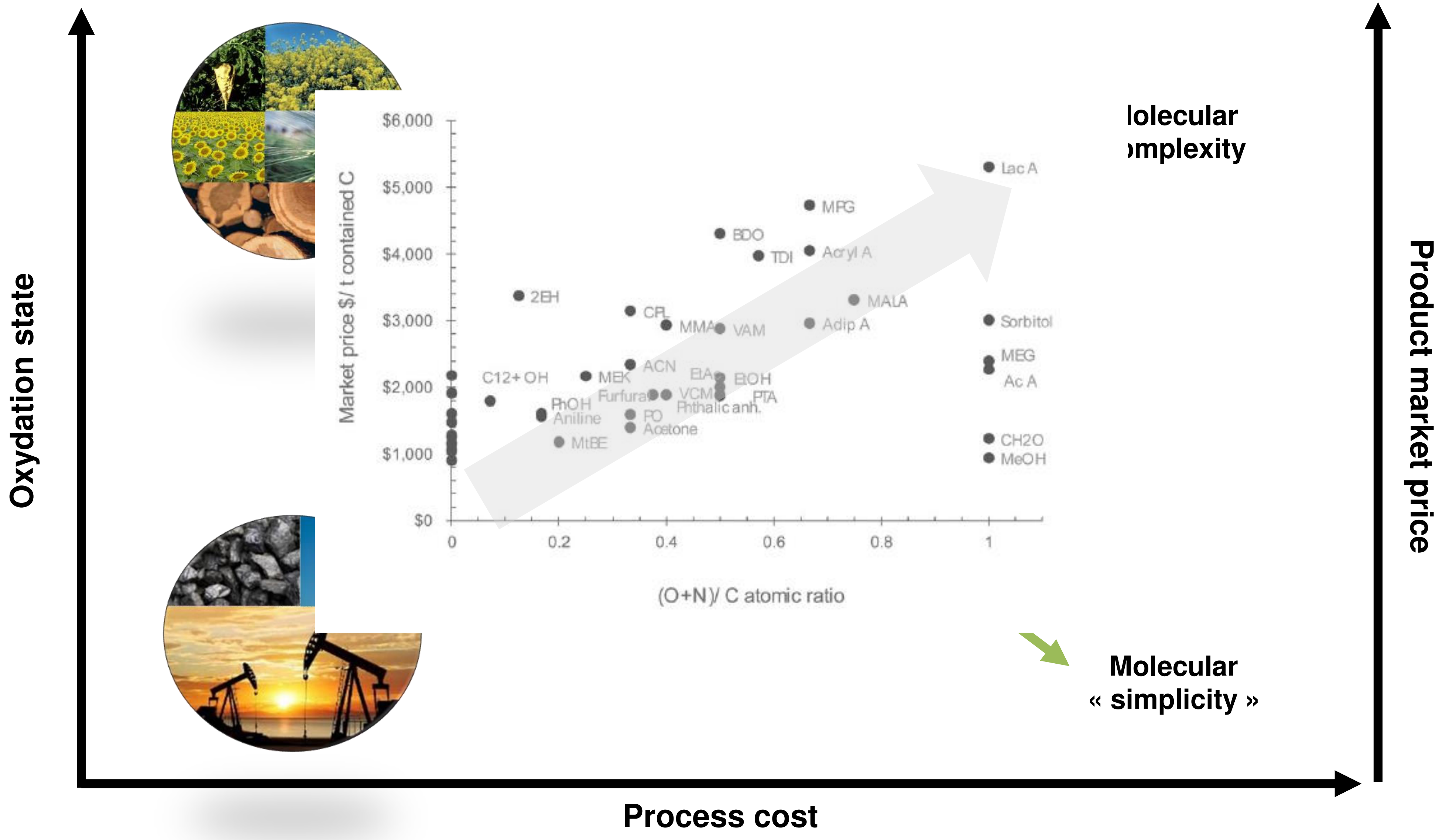
m³/h

100t_{prod}/kg_{cat}

15 wt% (*except for ns*)

Ed. **2015**, *54* ,13186-13197
'. **2016**, *6*, 4759-4767

Oxidation vs reduction



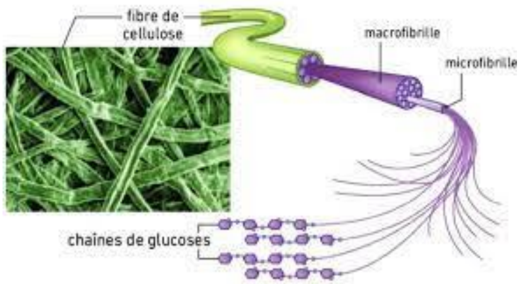
EU bio-based market (2019)

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
and biobased) equals the total EU market (fossil- and bio-based consumption).

Expectations in terms of innovation

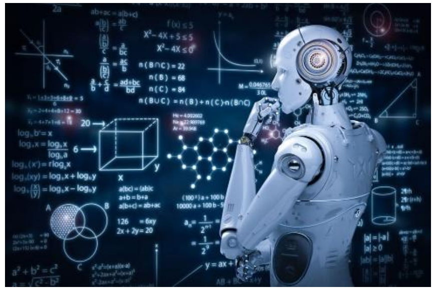
Better understanding of biomass



Better understanding of biological systems

New technologies

New tools (AI, machine learning, etc…)



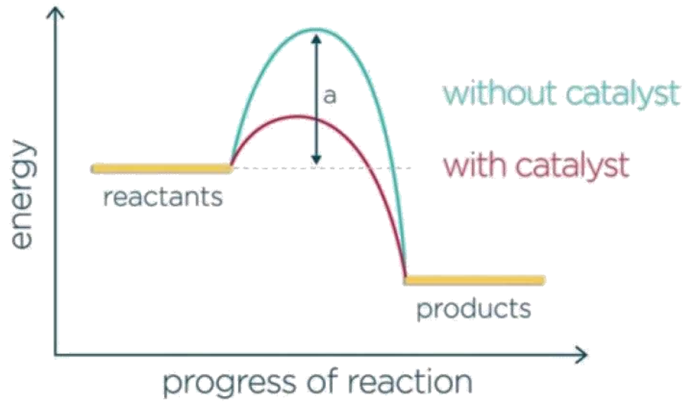
Humans versus Nature

HUMANS
Chemical activation

Catalyst

Energy →

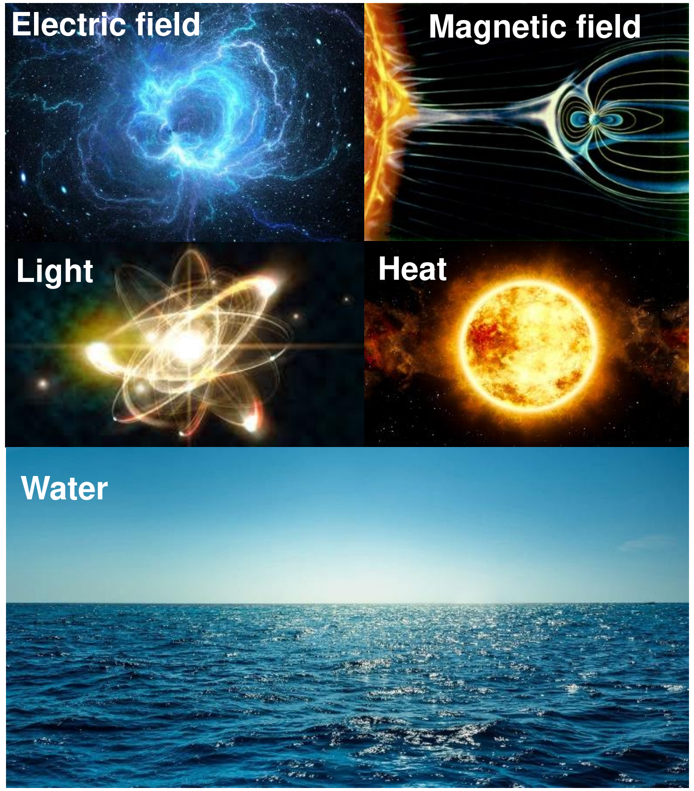
Fossil-based
(oil, coal, gas)



NATURE
Physical activation

Electrons, radicals, excited species

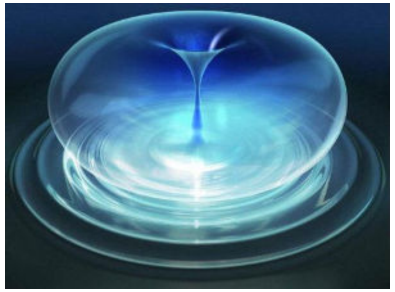
Energy → **Renewable**



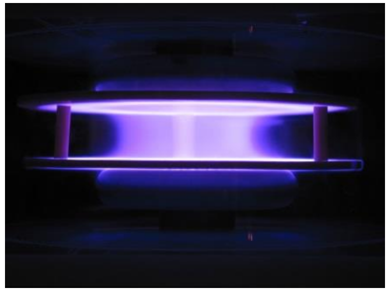
Molecular complexity

Nature : a source of inspiration

Microwaves

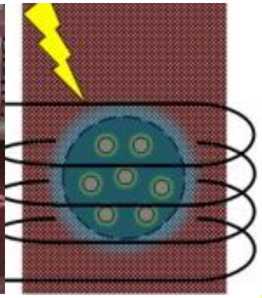


Ultrasound

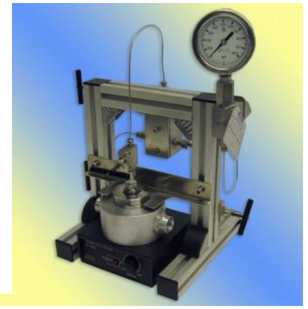


Plasma

Electro-
chemistry



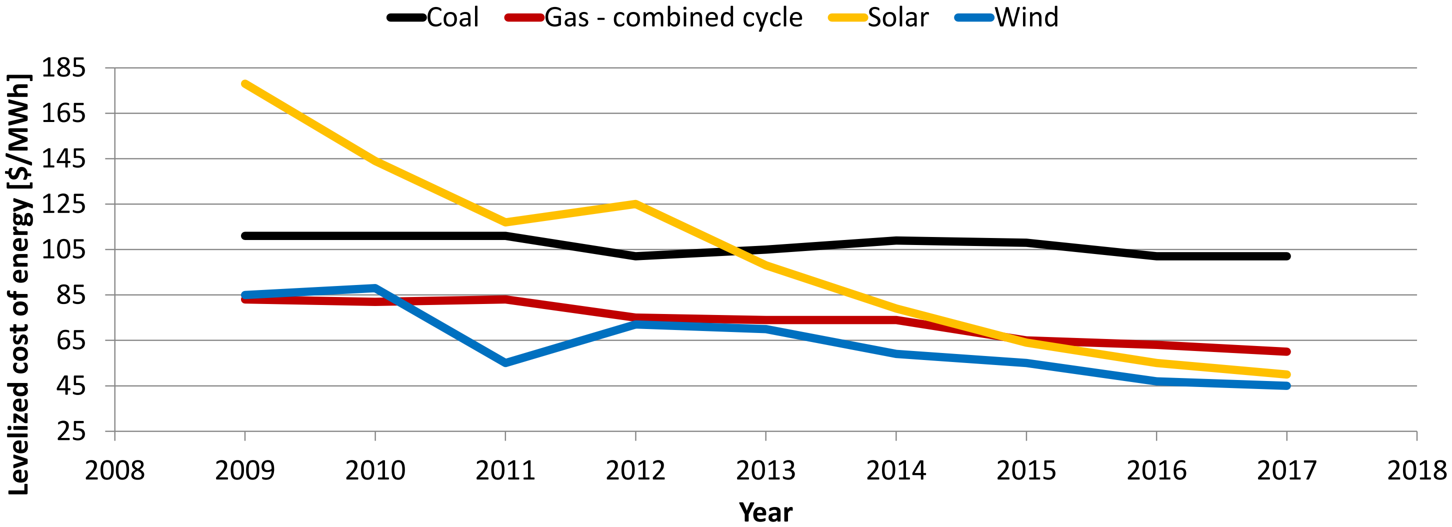
Magnetic
field



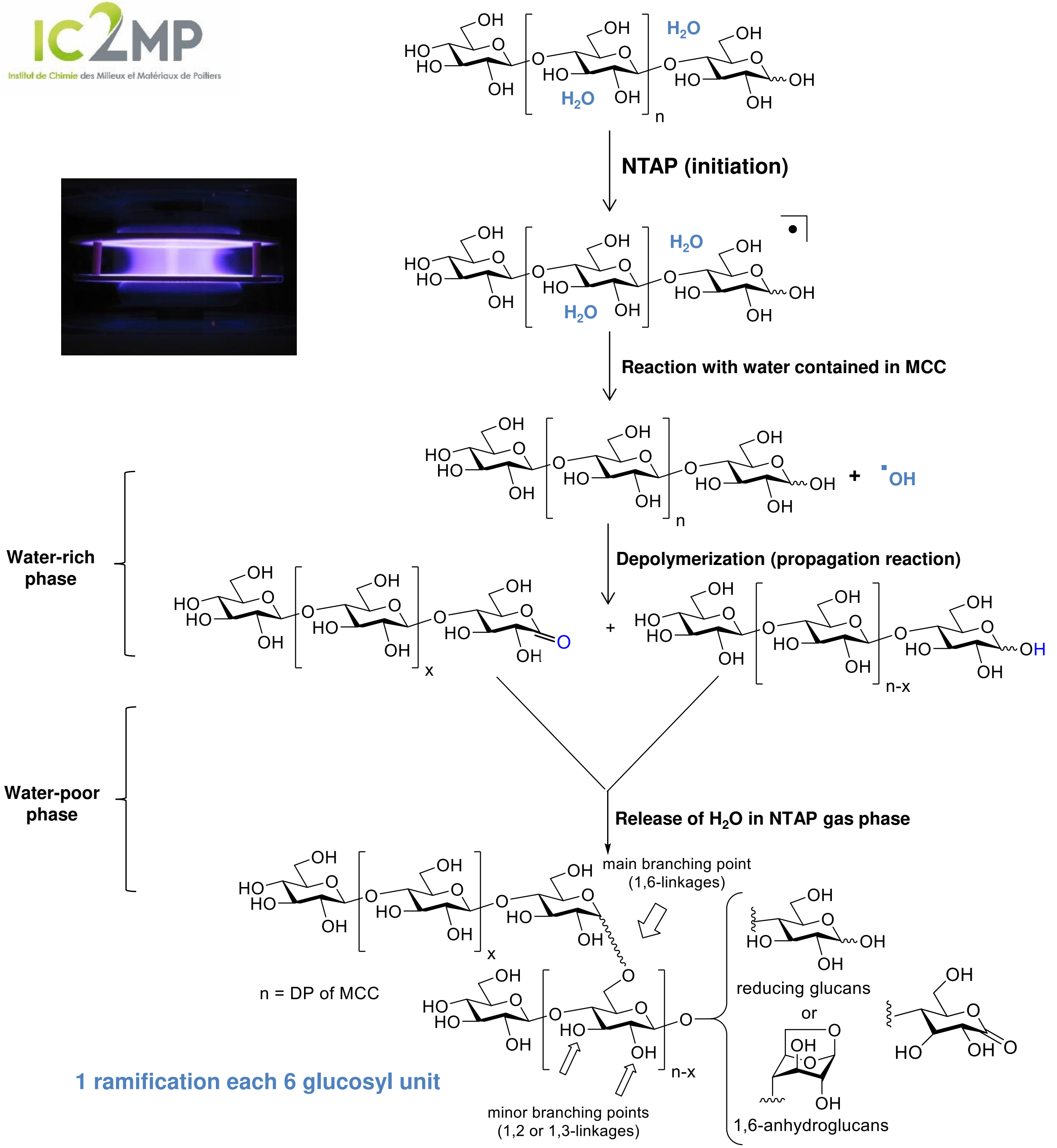
Pressure

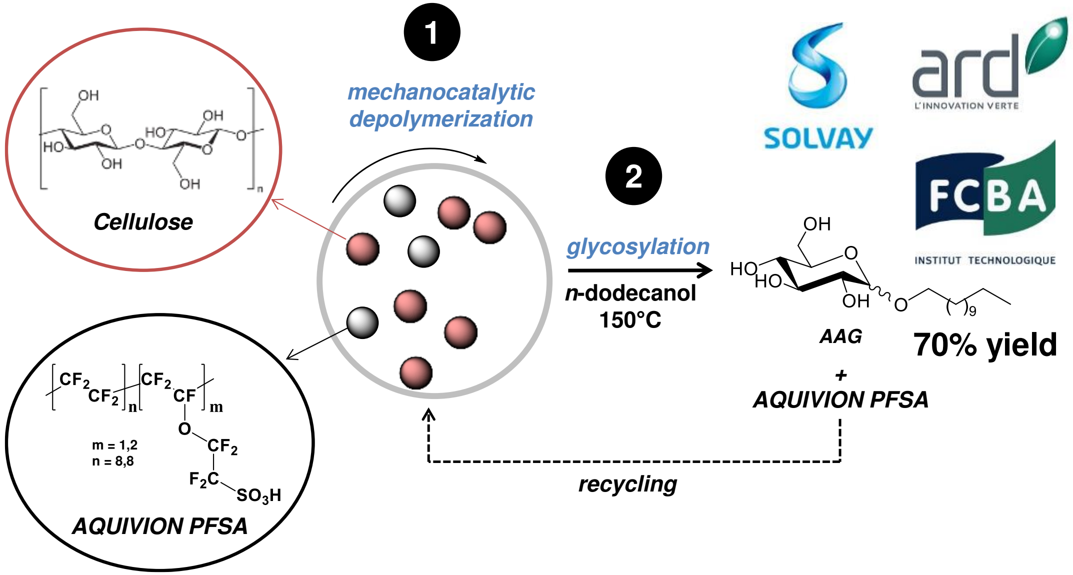
Photo-
chemistry

Mechano-
chemisry



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





▶ Reduction of CO_2 by a factor 7

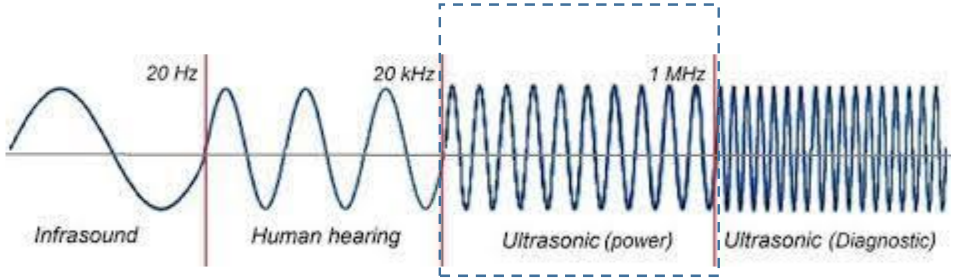
▶ 45 % reduction in waste water

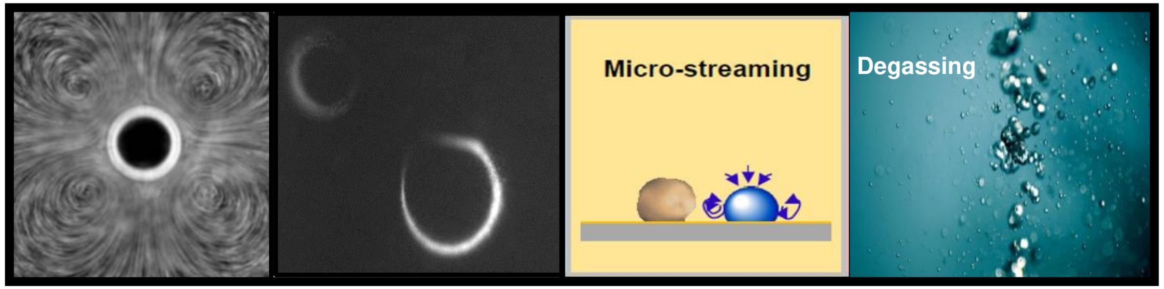
biosedev.com

M. Benoit et al., *Angew. Chem. Int. Ed.*, **2011**, 50(38), 8964

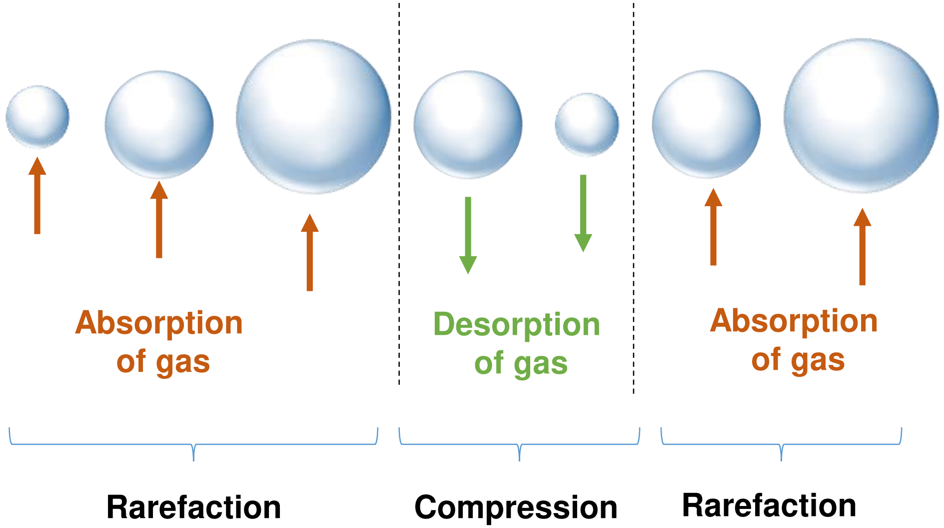
A. Karam et al., *ChemSusChem*, **2017**, 10, 3604-3610

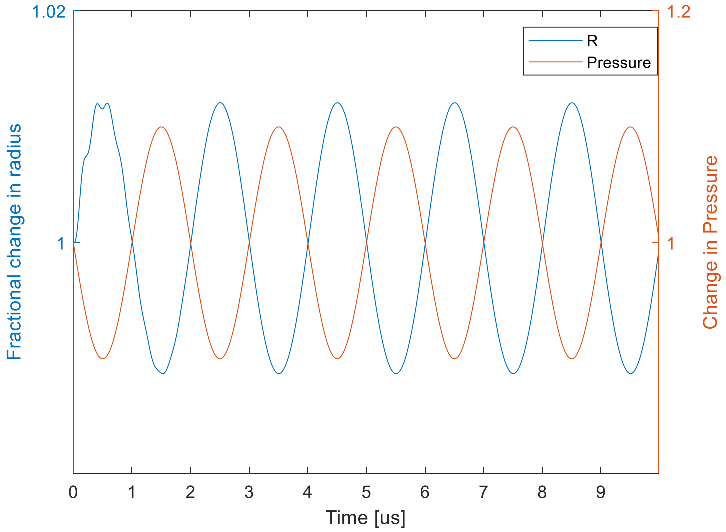
Ultrasound: when chemistry bubbles





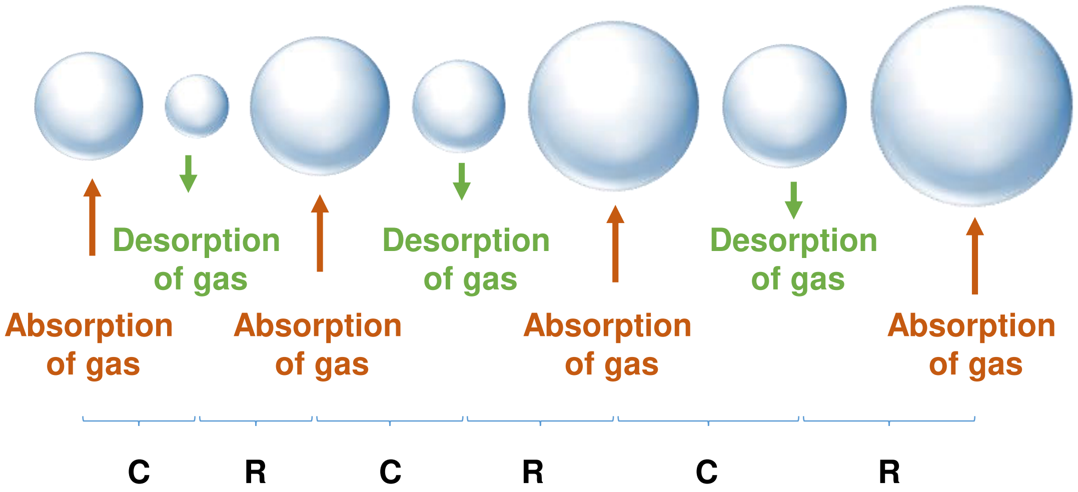
Stable cavitation bubbles



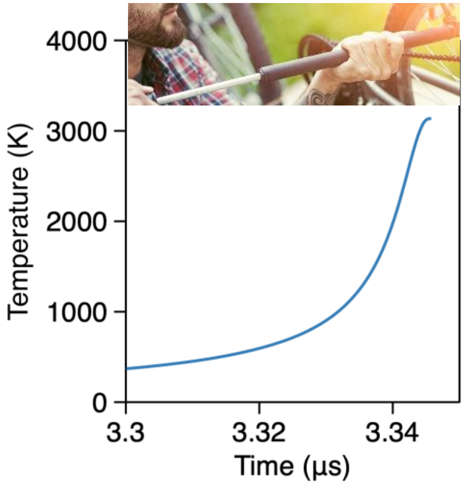


Ultrasound: when chemistry bubbles

Transcient cavitation bubbles



C = Compression; R = Rarefaction

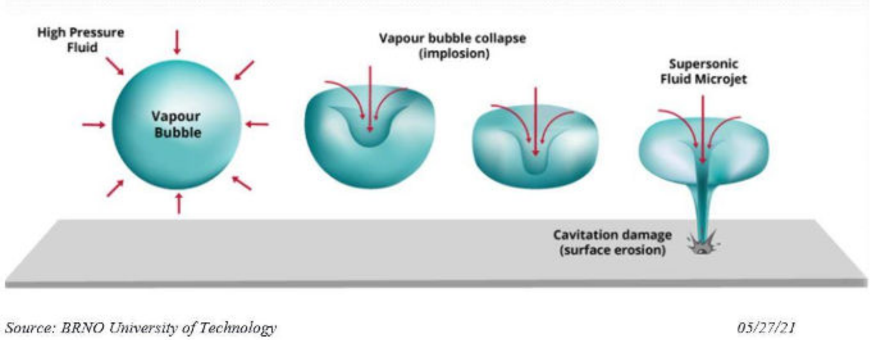


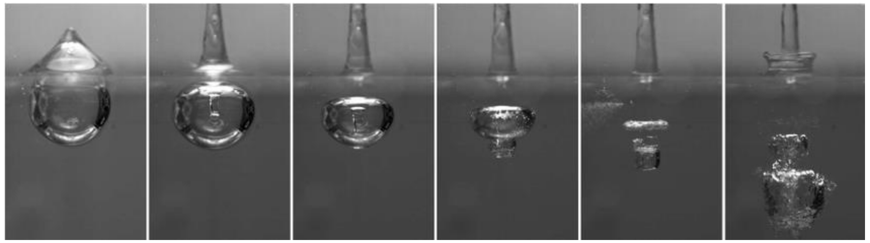
$$T_{max} = \frac{T_0 P_a(\gamma - 1)}{P_v}$$

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

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

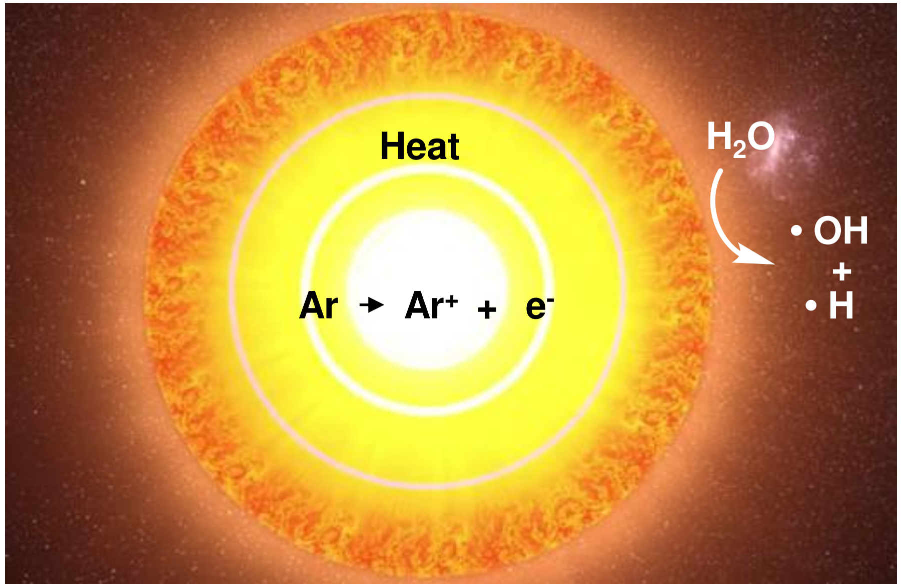
B. D. Storey, A, J. Szeri, *Proc. R. Soc. Lond. A*, **2001**, *457*, 1685–1700





O. Supponen et al. *Journal of Physics: Conference Series*, **2015**, 656, 012038

Cavitation bubbles as microreactors



Hydrothermal reaction

$R\text{-}X + H_2O \longrightarrow RH + X\text{-}OH$

Radical reaction

$R\text{-}H + \bullet OH \longrightarrow \bullet R + H\text{-}OH$

« Plasma-like » reaction

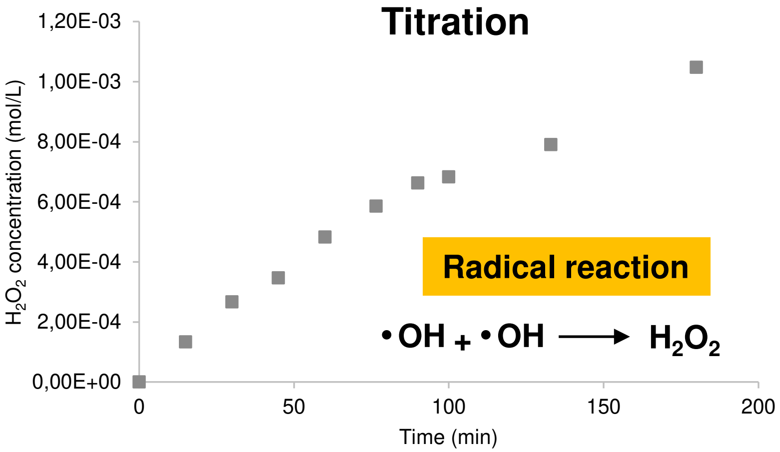
$R\text{-}H + e^- \longrightarrow R\text{-}H^{+\bullet} + 2e^-$

Sonoluminescence

Hydrothermal reaction

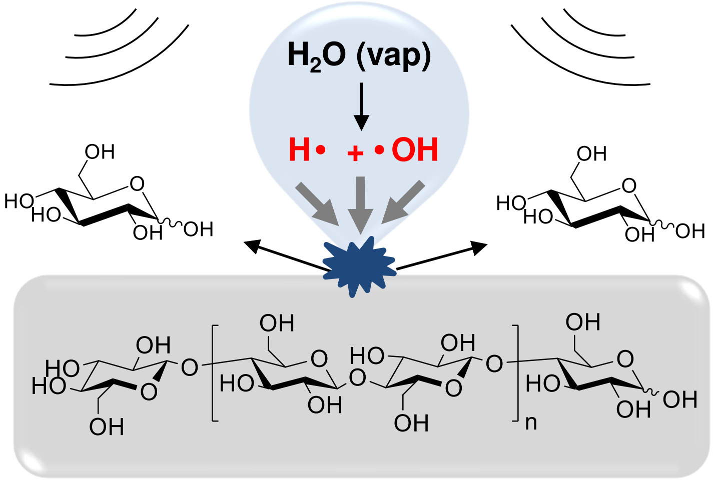
« Plasma-like » reaction

H, Xu, N, G. Glumac, K, S. Suslick, *Angew. Chem. Int. Ed.* **2010**, 49, 1079 –1082



Reactions induced by high frequency ultrasound

Depolymerization reactions

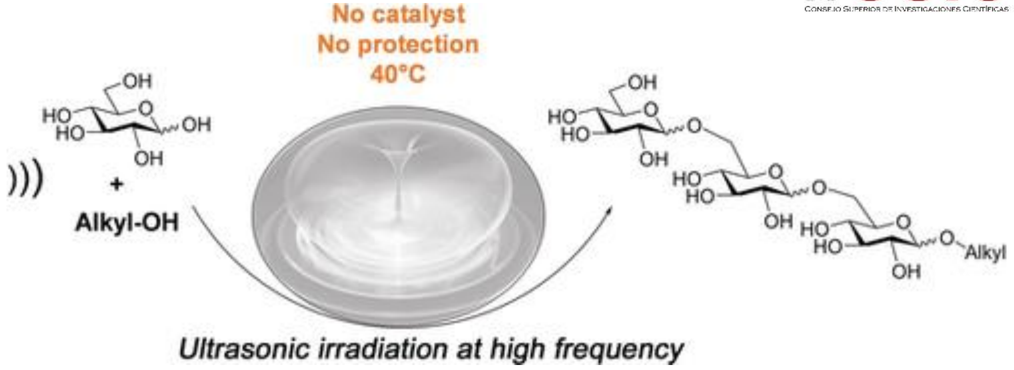


Chem. Sci., **2020**,11, 2664-2669

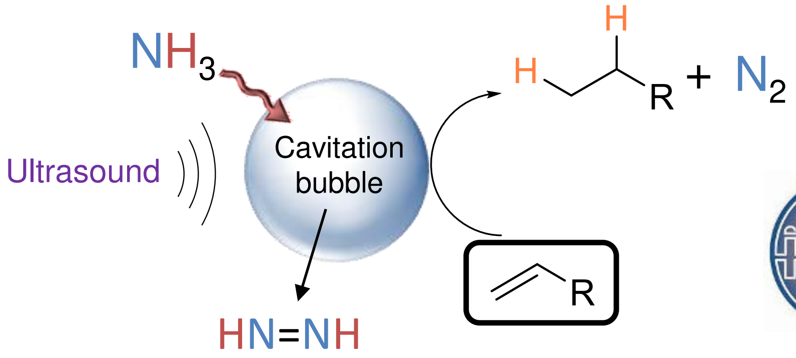
Oxidation reactions

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

Polymerization reactions



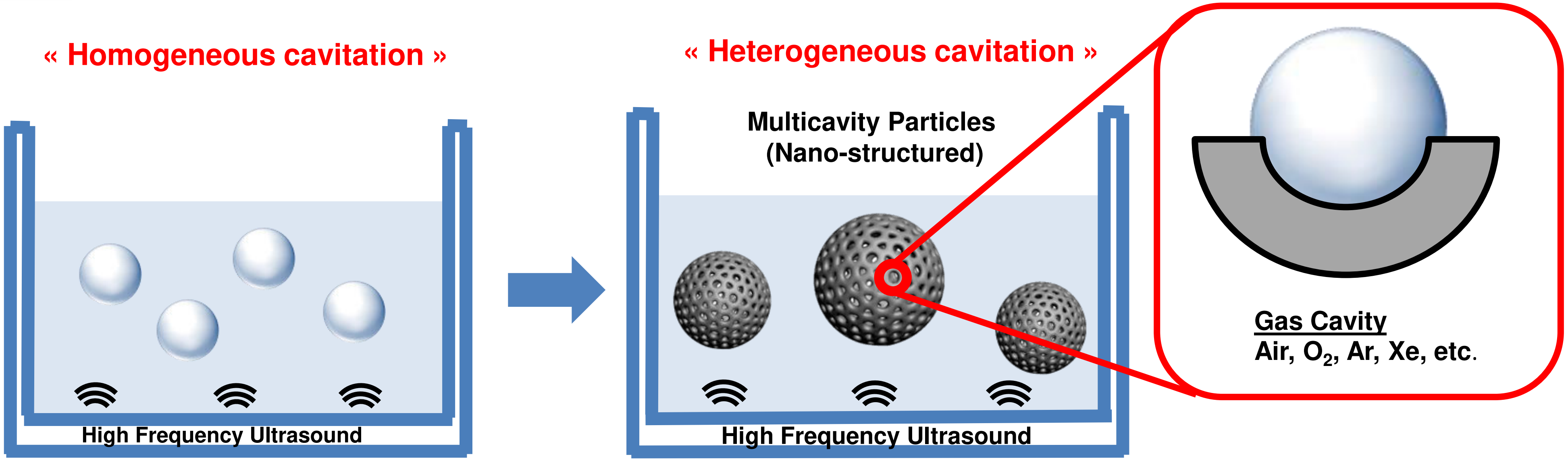
ChemSusChem., **2018**, 11 (16), 2673-2676

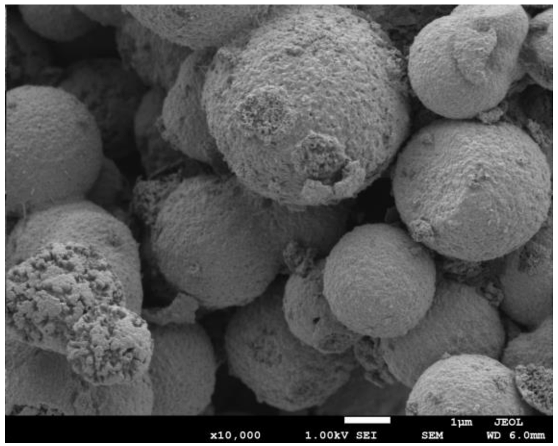


No catalyst, no hydrogen

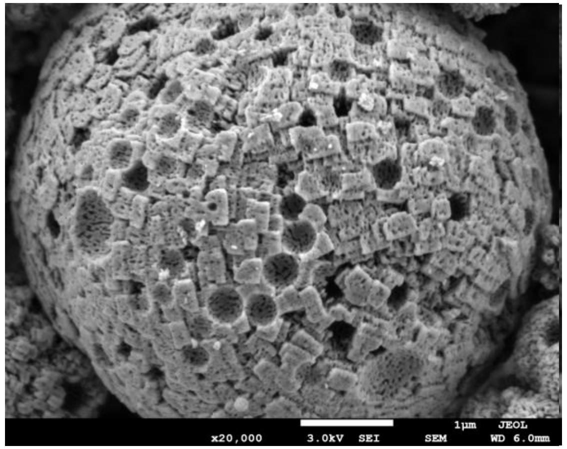
Angew Chem Int Ed. **2021**, 60, (48), 25230-25234
Angew Chem Int Ed. **2022**, accepted manuscript

Cavitation agent

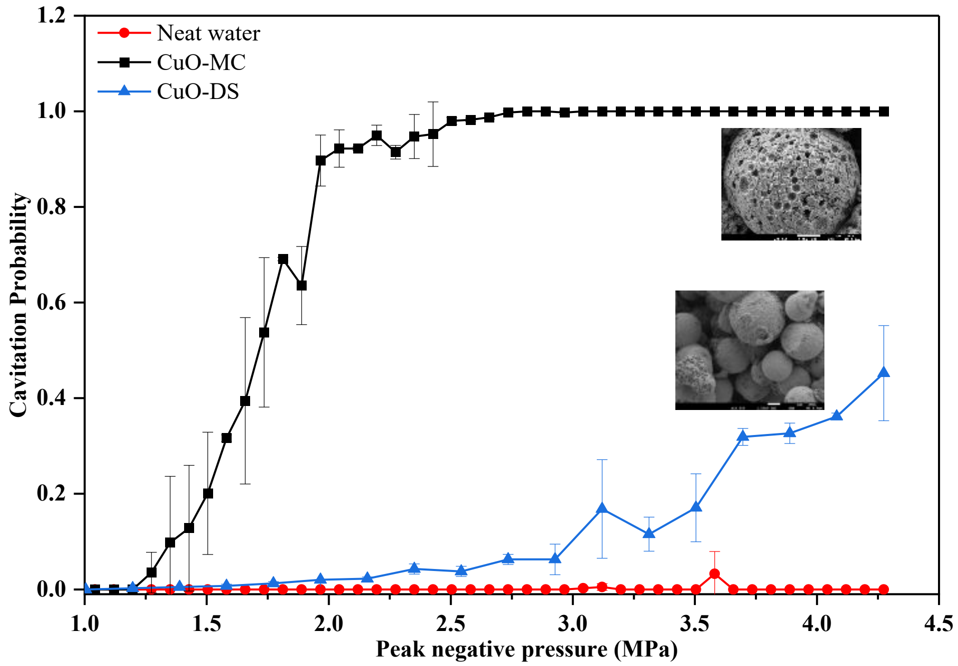




CuO Dense sphere



CuO Multicavities



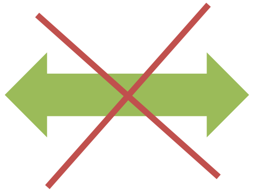
Taken home messages

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



recyclability

Product **not intended** to be dispersed in nature

biodegradability

Product **intended** to be dispersed in nature

ISGC

May 12nd-16th, 2025
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A high-level scientific congress

Topics

- Renewable carbon
- Smart use of fossil
- Polymers
- Environmental impact and Life cycle assessment
- Mechanism
- Networking and education
- Catalytic systems
- Alternative solvents
- Biotechnologies
- Non-thermal activation methods

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from academic and industry

1000 attendees expected

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- **1-to-1 meetings** between the 1000 expected participants