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Mapping twenty years of Green Chem: Four Productive Heritages moving towards "Doubly Green Chemistry"

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The turning point in Green Chem

- 1990s: GC deals primarily with problems of pollution, ecotoxicity and (late 90s) global warming and remediation
- From 2000 on: GC deals primarily with using Renewable Carbon
 - Green Chem..57 of the 63 articles (forthcoming in 2012), while it would be hard to find one in the first issue of the journal.
 - ChemSusChem, (first issues in 2008): no articles indexed with the keyword "biomass" in its first two issues and no with the term "renewable resources" before the 8th number. 103 on the first tag, on the second and 88, against 41 indexed with the keyword "green chemistry"

• (consultation Scopus 16 December 2011) the seventh principle

- Presidential Green Chemistry Challenge Awards: Of the first 16 awarded in 1996, 1997, 1998, only two referred to the seventh principle. Over the past three years, 11 out of 15 awards can be directly referred to bio-based products as reactants or as substrates.
 - But is chemistry of renewable carbon always green and sustainable?
 - Quid of a "Doubly Green Chemistry" = DGC

The need of systemic points of view

• Even when we approach some of the big sustainability challenges... we approach these challenges in a fragmented manner. ... We often wind up doing the "right things, wrong". We purify water with acutely lethal substances. We make energy-efficient bulbs with neurotoxins, and solar energy with scarce, depleting and toxic metals. » foreword of P. Anastas to R. Höfer (Editor) (2009) Sustainable Solutions for Modern Economies (RCS Ed) »

Four Dimensions to observe systematic points of view

Science: GC is more than just synthetic chemistry! Physico-Chemistry, Biochemistry, Biology Materials science and "omics"

Technology:

How can novelty integrate existing technologies with new ones to achieve coherence? Economy: Not only technical change, but also actors' interests? How they seek to preserve their supply chain

<u>Social</u>: preserving the territories or activities of social groups and meet the challenges of preserving the biosphere Beyond Fashions in green chem as Ionic liquids, or various catalysts

Two philosophies of chemistry Four productive heritages

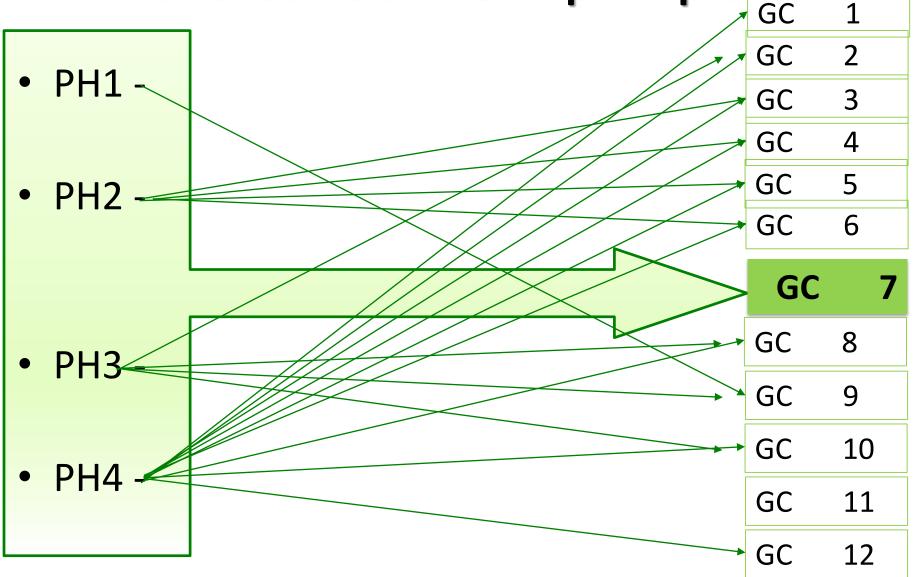
"Intensive deconstruction" pathways (typical of oil industry, although conceptually well-mastered by petrochemists)

PH1 – Extensive thermal deconstruction to $C_1 - C_6$ syngas FDC, HMF Thermo chemical transformation of biomass into syngas and reforming. PH2 - Biotechnological Extensive deconstruction to $C_2 - C_{10}$ EtOH, PLA, PHA Enzymatic transformation of biomass into small molecules, synthons, building blocks (for chemiosynthetic polymers e.g. PLA PHA)

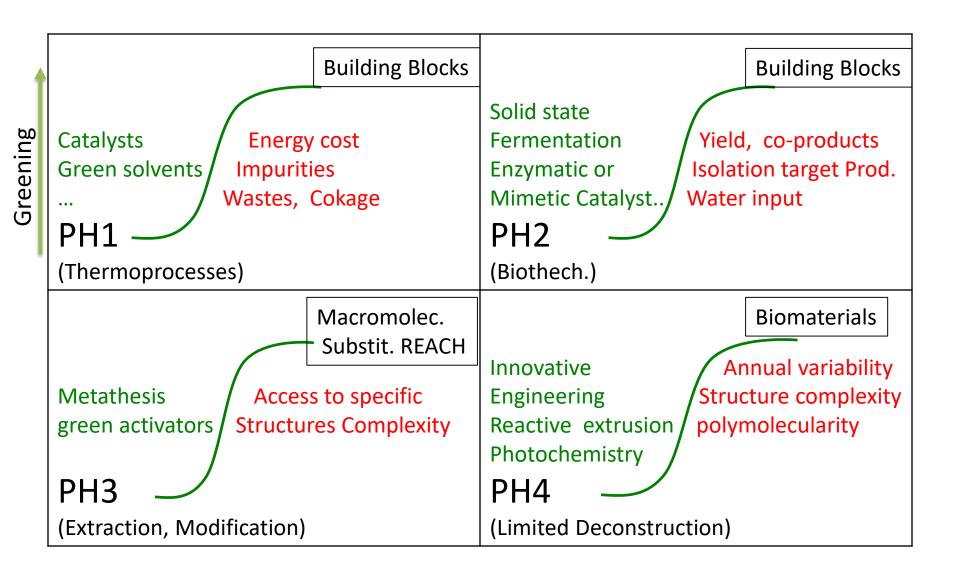
Moderate "destructuring" pathways (i.e. : which preserve the functional properties contained in complexity of living organisms).

PH3 - Limited chemical modification of extracted $C_5 - C_{30}$ Use of naturally occurring synthons (e.g. modified fatty acids for polymers) PH4 - Limited deconstruction and transformations $C_x - C_n$ Use of plant components complexity using innovative technologies (e.g. reactive extrusion, modif. Starch, whole plant process)

Each productive heritage claims its own use of some of the 12 principles

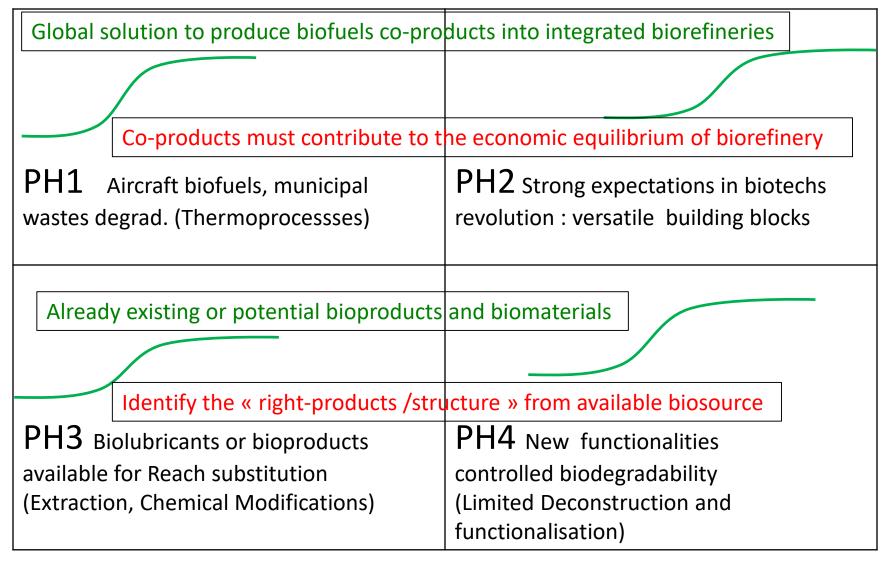


Each PH seeks to enforce its own green identity



Economic dimension contributes to enforce this lasting variety

Scientific competition, but satisfaction of specific needs, and complementarities of market niches



Fashions and expectations of a "Microsoft" of biomass conversion

- miraculous plant (myscantus?),
- miraculous process
- biotechs? catalyst ? biomass recalcitrance breaking enzyme ?)
- miraculous intermediate and building block (one of the top 10?)

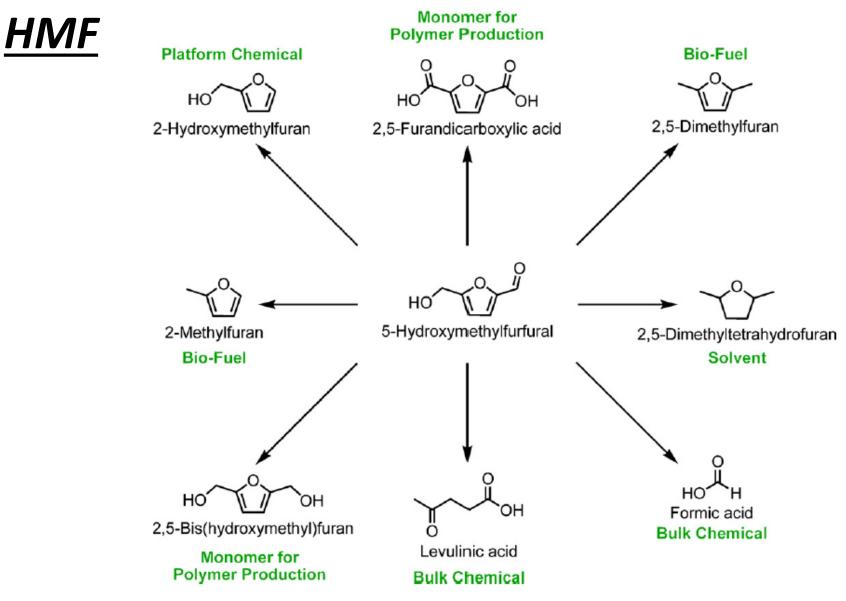


Fig. 1 – HMF as a precursor for a range of commercial chemicals.

A. Boisen et al. Chem. Eng. Res. Des., 2009, 87, 1318.

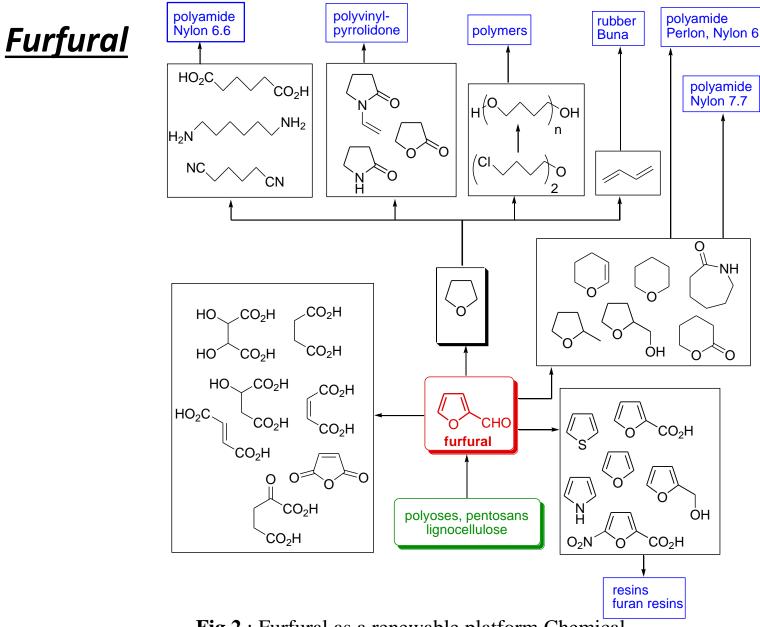


Fig 2 : Furfural as a renewable platform Chemical.

F. Martel et al. Top. Curr. Chem., 2010, 294, 79.

Glycerol

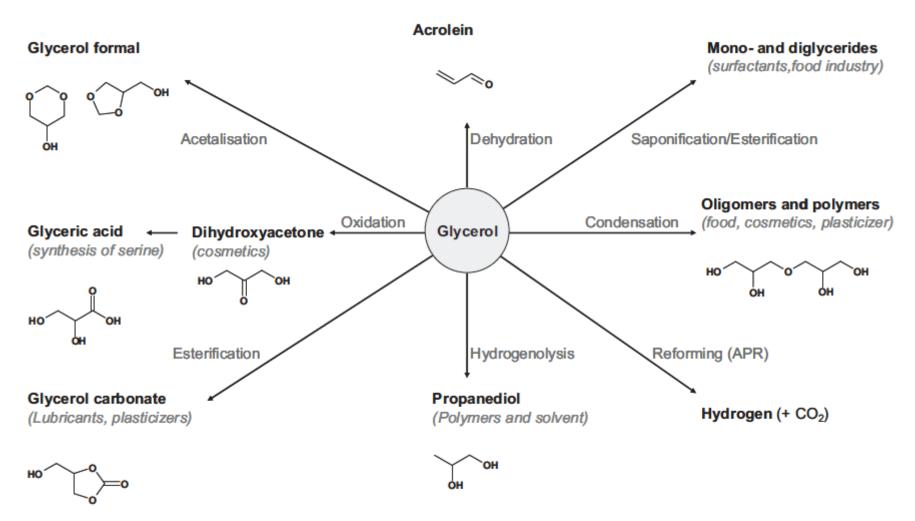


Figure 3. Glycerol valorization routes toward intermediates and final products via different types of chemical transformations.

A. Martin et al. Eur. J. Lipid. Technol., 2012, 114, 10.

Succinic <u>Acid</u> ,OH HO 1,4-butanediol ΟН esterification MeOOC COOMe HO **~**OH HO OH tetrahydrofuran fermentation γ-butyrolactone HOOC COOH HOOD соон fumaric acid succinic acid dehydrogenation cyclization соон ĊООН maleic acid

Fig. 6 Succinic acid as a platform chemical.

J.J Bozell, G.R Petersen, *GreenChem.*, 2 012, 12, 539.

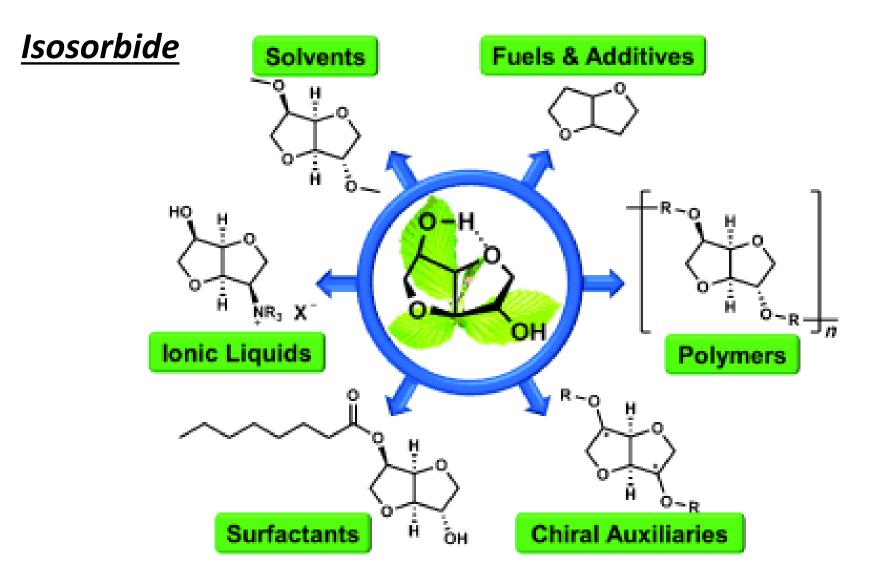
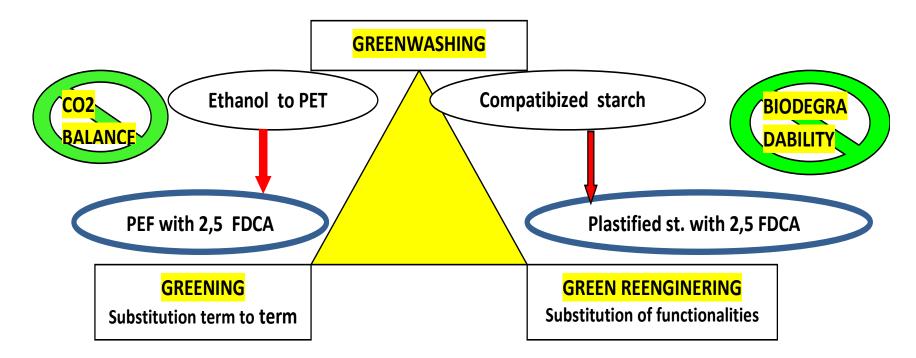


Fig : Isosorbide as a renewable platform Chemical.

No miraculous solutions, but two systemic learning pathways



And work and work + recombination of technologies ...

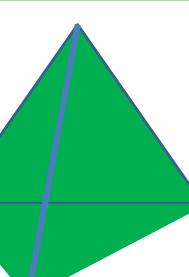
Conclusion

Green economy needs new green products and not only a greening of the existing products

1. Economic dimension

Easy transformation into small molecules to obtain versatile building-block **or** fighting with the complexity and variability of renewable material?

4. Scientific Dimension



Portfolio of solutions and pertinent recombination is more important than one leading technology

2. Technological dimension:

3 Social dimension:

Biofuel-based biorefineries with unsustainable scale-up ? Are non—biofuels-biorefineries possible ? adaptation to specificities of local resources and small scale production?