

# On the 12 principles and the innovation pathways in doubly green chemistry

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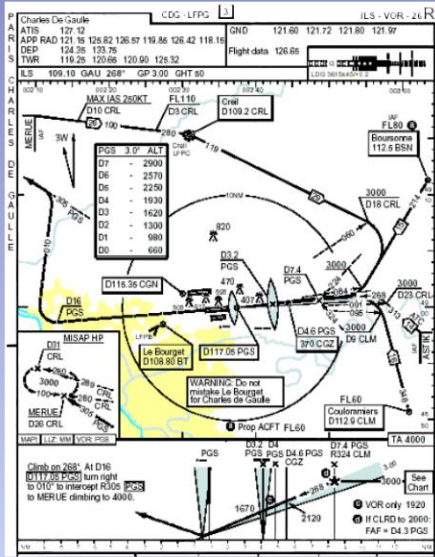
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# On the 12 principles and the innovation pathways in doubly green chemistry

- Articles; Patents; Awards
- Interviews (i.e. Gembloux)
- Focus groups
- Economists ; Chemists





OR



# The turning point in Green Chem

- **1990's**: GC deals primarily with problems of **pollution, ecotoxicity** and (late 90's) **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 -1999).
  - *Presidential Green Chemistry Challenge Awards – USA*): 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?

**New playing ground for a “Doubly Green Chemistry” ?**

## **Green Chemistry : 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)*

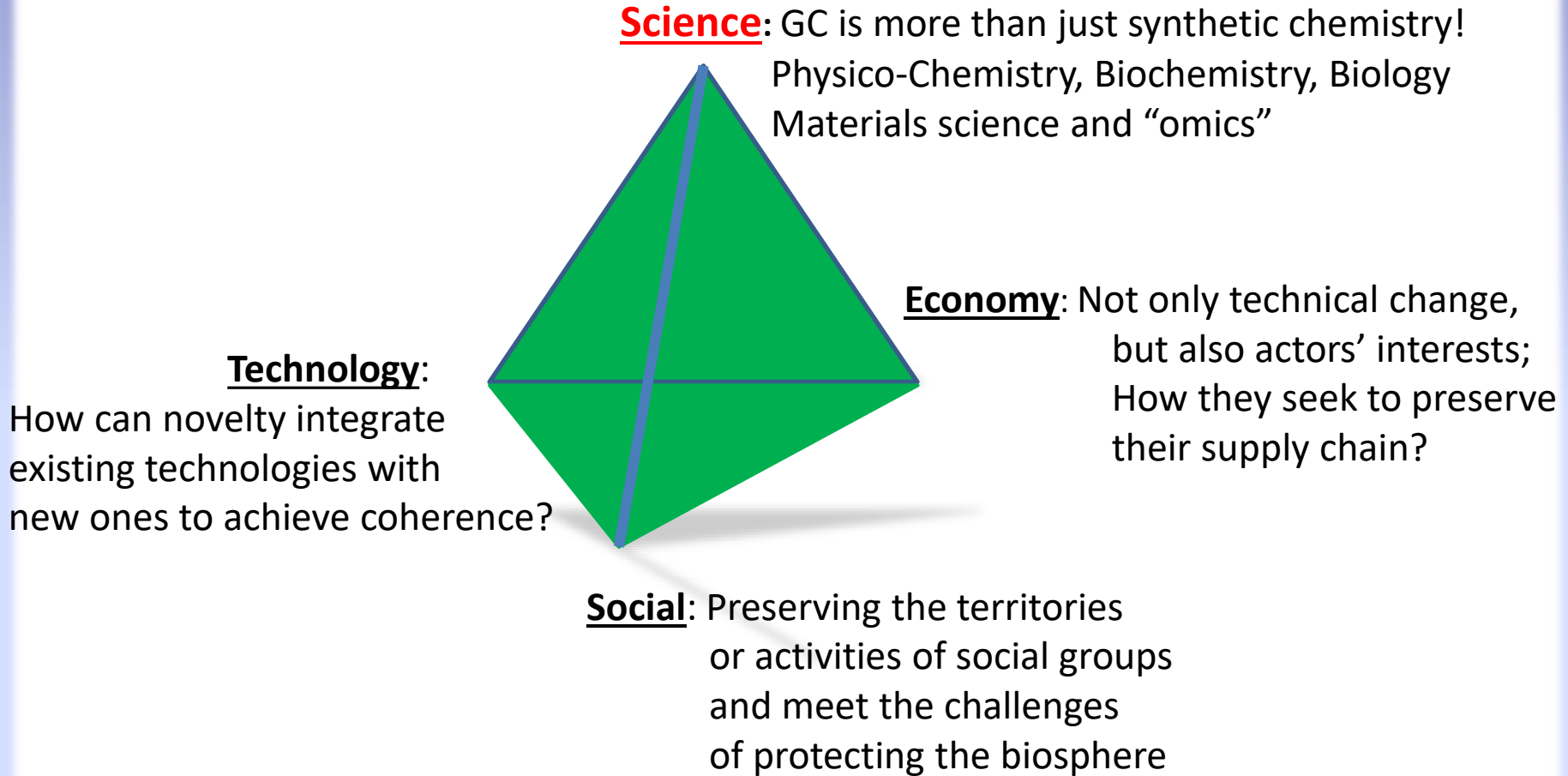
**Sustainable Solutions for Modern Economies (RCS Ed)**

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1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

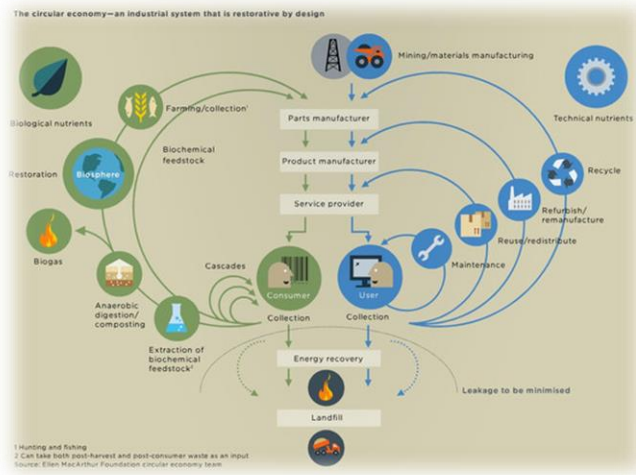
**FIGURE 1.** The 12 Principles of Green Chemistry.

## Four Dimensions to observe systematic points of view





# Has biomass a problem with green chemistry?



Or the opposite?

How does this inhibit / trigger innovation?

How does this regulate strong but hasty expectations?

# 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/Microbial 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).***

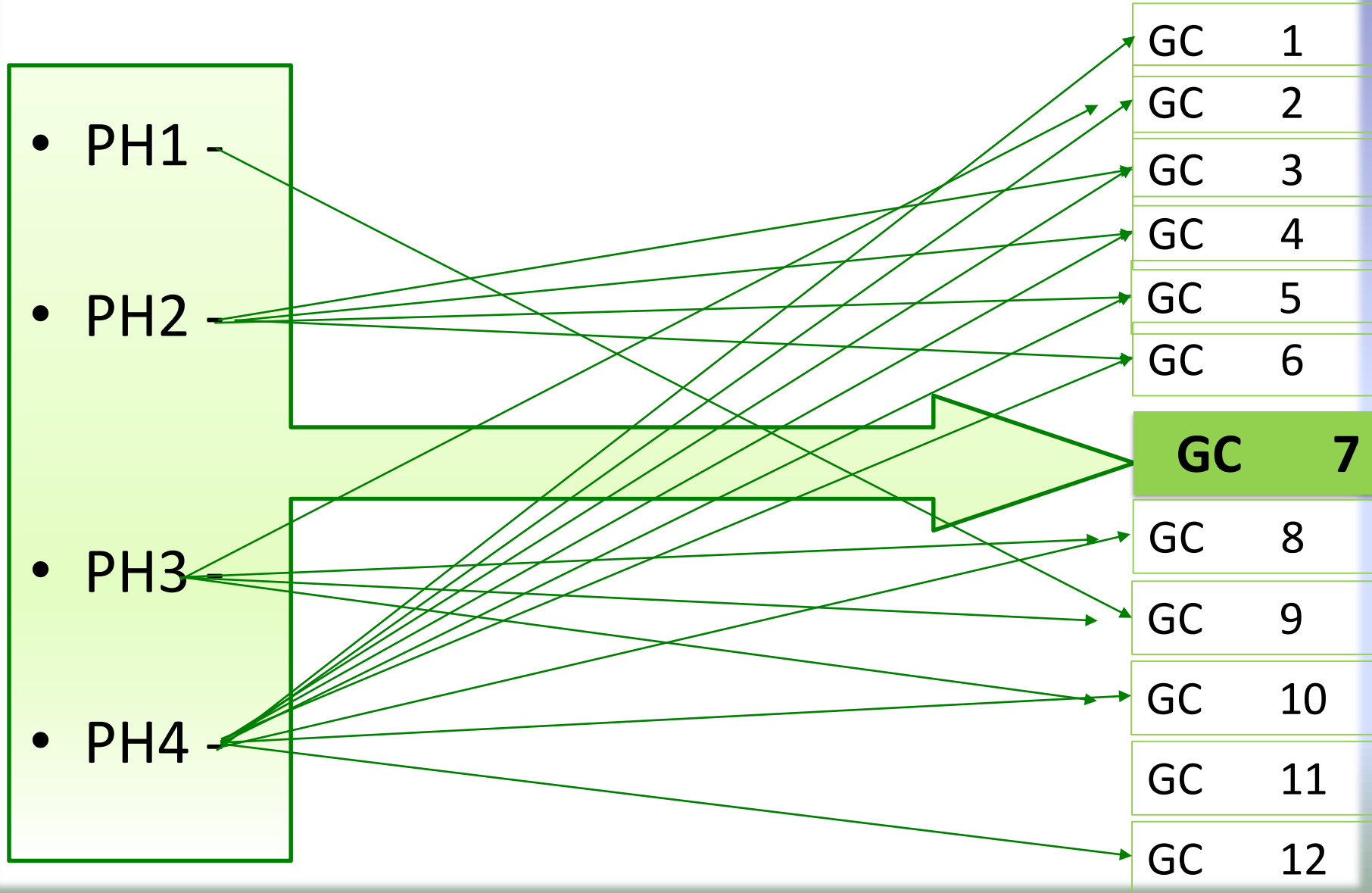
**PH3 - Limited chemical modification of extracted  $C_5 - C_{30}$**

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

Origins, S

• PH1

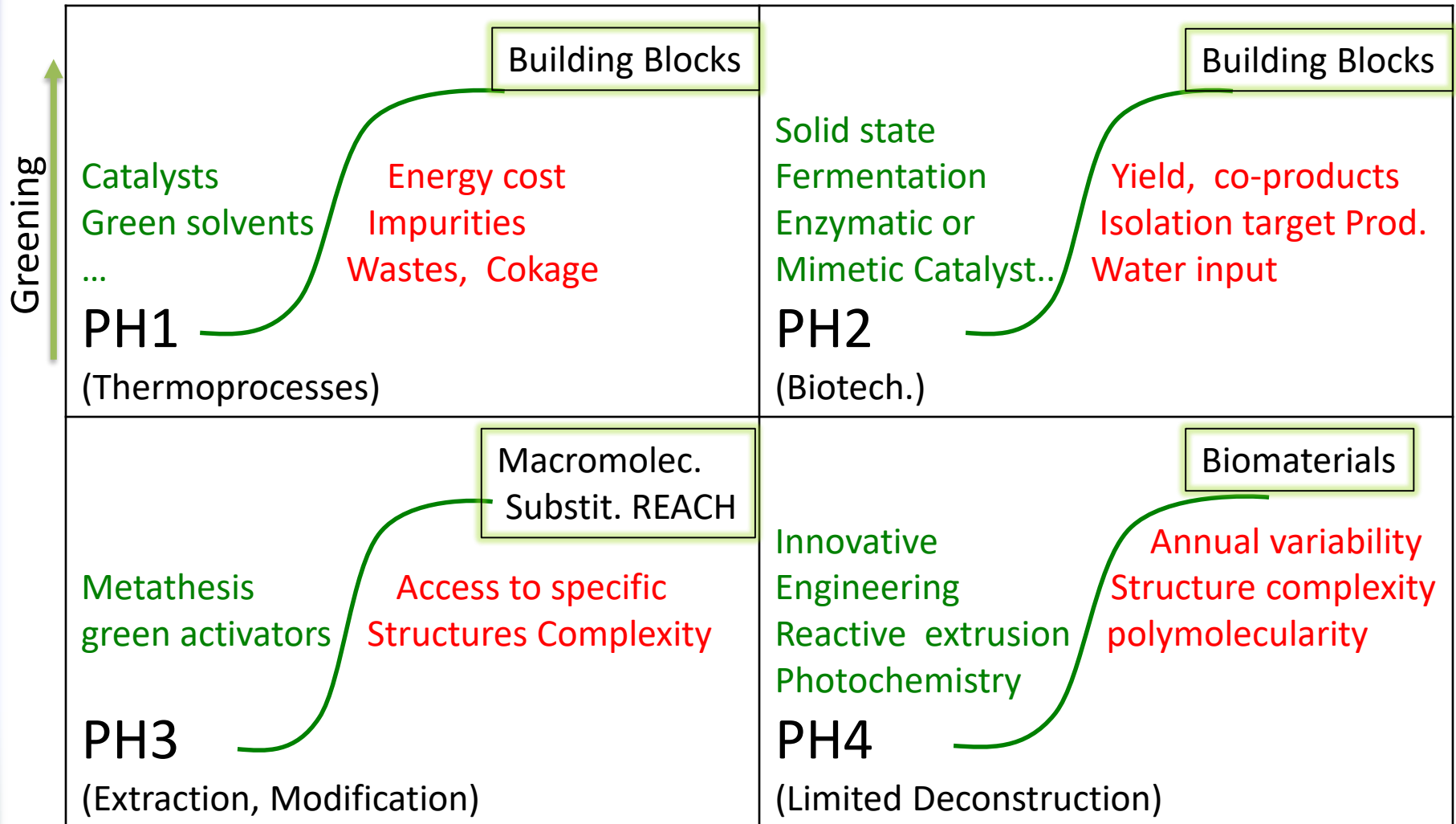
• PH2

• PH3

• PH4

1. It is better to prevent waste than to clean up after it.
2. Synthetic methods should be designed to minimize the use of auxiliary substances (inert, extraneous, and non-volatile) and to avoid auxiliaries that become part of the final product.
3. Wherever practicable, synthetic methods should be designed to use substances that possess little or no toxicity to humans and the environment.
4. Chemical products should be designed to be effective at the lowest possible concentrations.
5. The use of auxiliary substances (e.g., solvents, reagents, and catalysts) should be avoided wherever possible and innocuous auxiliaries should be used.
6. Energy requirements should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material of feedstock should be used as efficiently as possible and waste should be minimized.
8. Unnecessary derivatization (blocking groups, protecting groups, temporary modifications, etc.) should be avoided. Temporary modifications should be chosen that are easy to remove.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. Chemical products should be designed to be effective at the lowest possible concentrations.
11. Analytical methodologies need to be developed and used to control prior to the formation of products.
12. Substances and the form of a substance should be chosen to minimize the potential for chemical accidents (including releases, exposures, or incidents).

# Each PH seeks to enforce its own green identity



# Good news: Economy requires this lasting variety

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

**Global solution to produce biofuels co-products into integrated biorefineries**

**Co-products must contribute to the economic equilibrium of biorefinery**

**PH1** Aircraft biofuels, municipal wastes degrad. (Thermoprocesses)

**PH2** Strong expectations in biotech revolution : versatile building blocks

**Already existing or potential bioproducts and biomaterials**

**Identify the « right-products /structure » from available biosource**

**PH3** Biolubricants or bioproducts available for Reach substitution (Extraction, Chemical Modifications)

**PH4** New functionalities controlled biodegradability (Limited Deconstruction and functionalisation)

# Fashions and expectations of a for biomass conversion



- “Universal” plant (miscanthus?)
  - “Miraculous” process (one pot)
  - “Super enzyme cluster” for breaking down biomass recalcitrance
  - “The big bang” building block (one of the top 10?)
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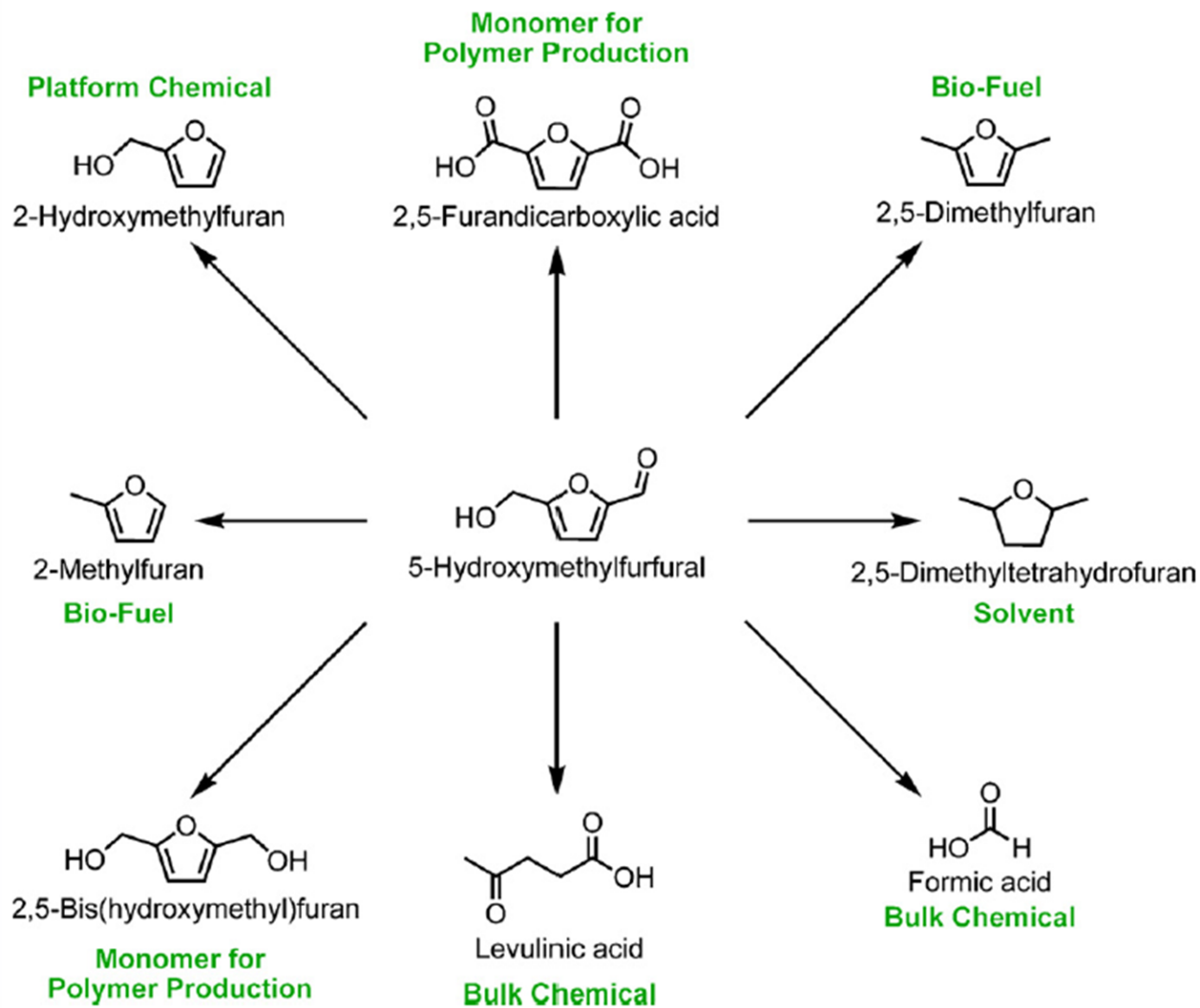
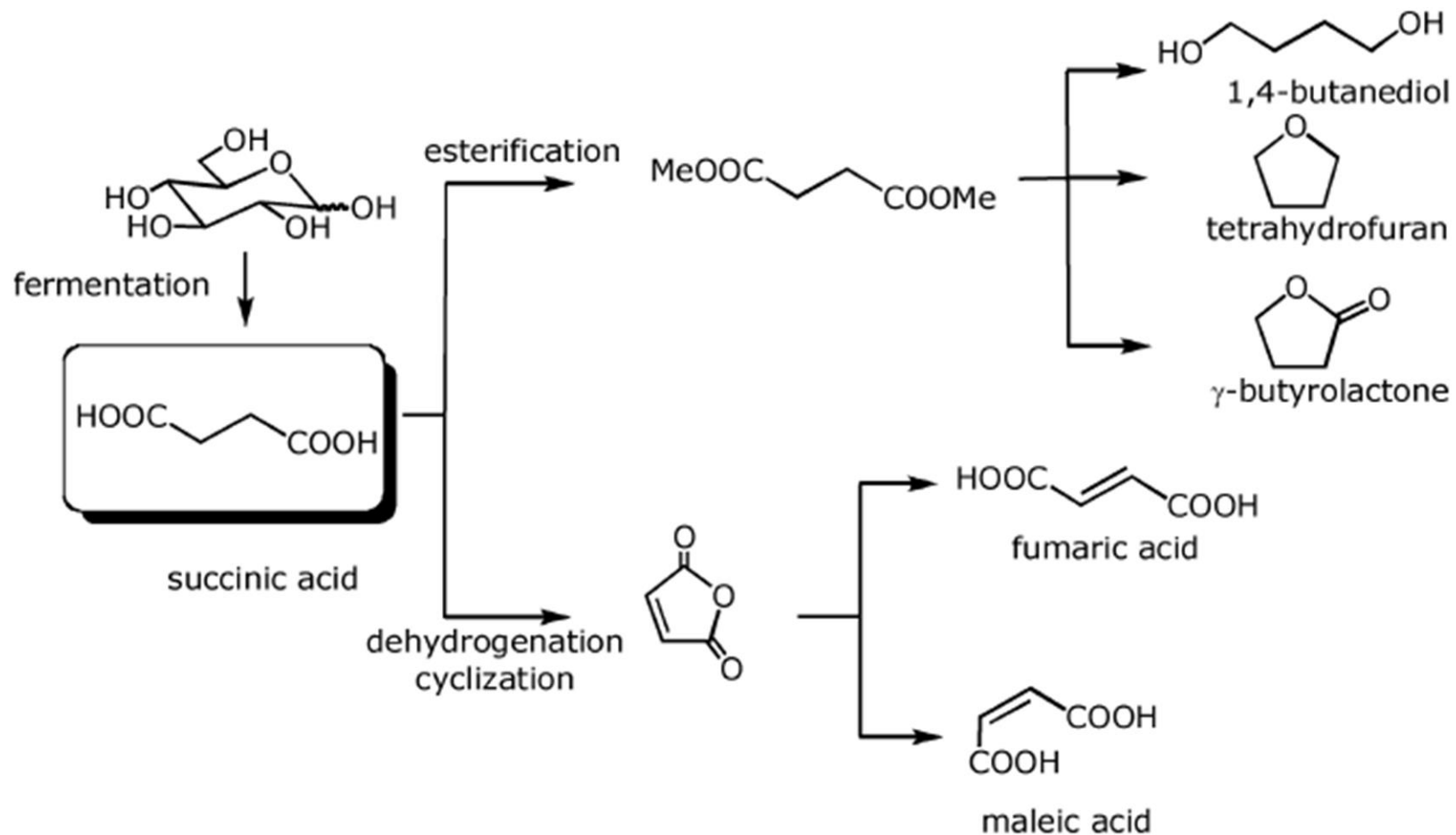


Fig. 1 – HMF as a precursor for a range of commercial chemicals.



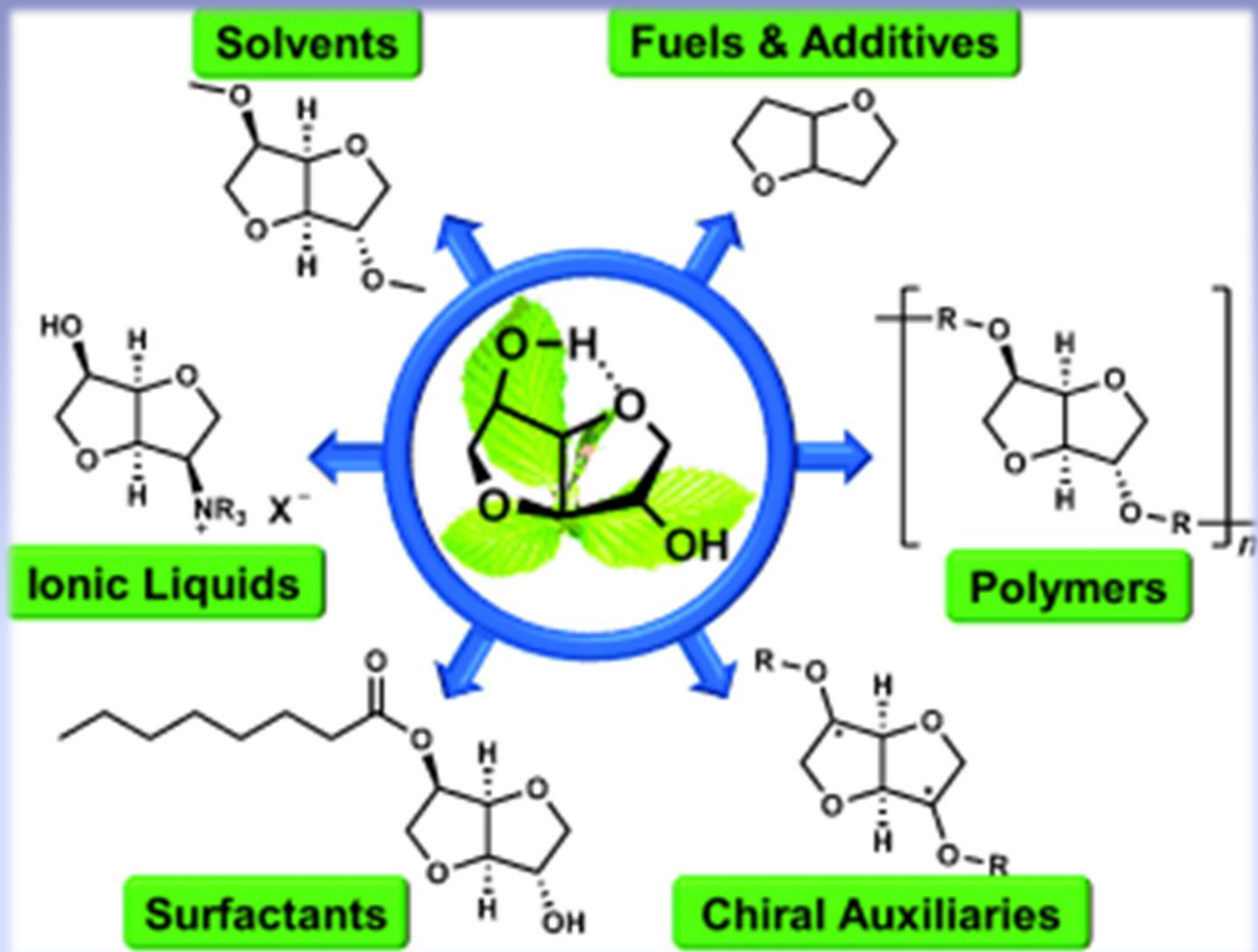


# Succinic Acid



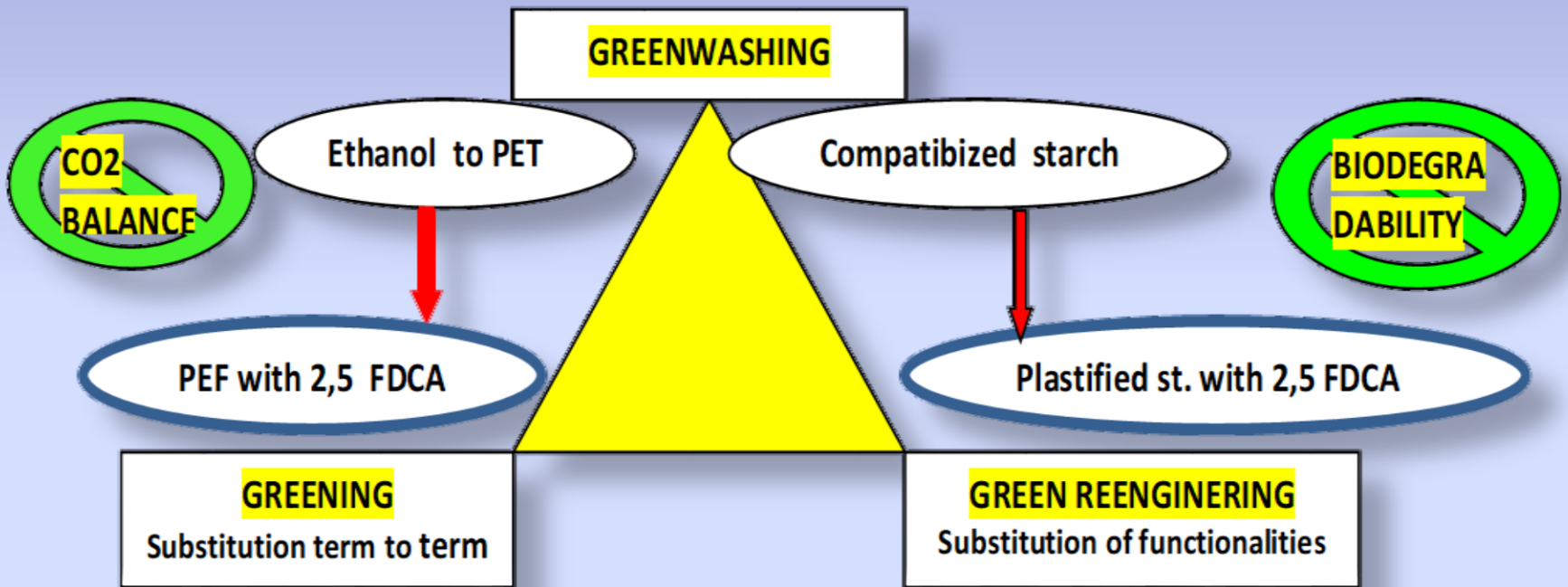
**Fig. 6** Succinic acid as a platform chemical.

# Isosorbide



**Fig :** Isosorbide as a renewable platform Chemical.

# No universal solutions, but two systemic learning pathways



**Fundamentals + Combination of technologies  
and Work, Work, Work.....**

# Innovations

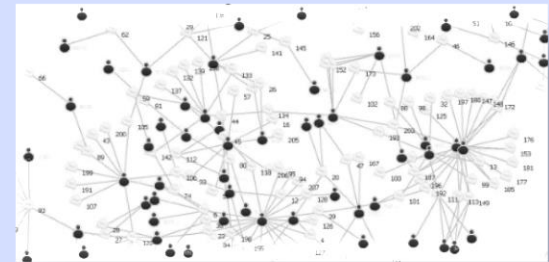
Green washing:

= social education; recognition of the problems; short term + transition solutions

Greening and re-engineering:

= economic innovation as the driver; revision of all pathways

Green revolution: from « old resources » to the « new end-users »



# Conclusions

Green economy needs new green products and not only a greening of the existing products (Energy seems apart)

## 1. Economic dimension

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

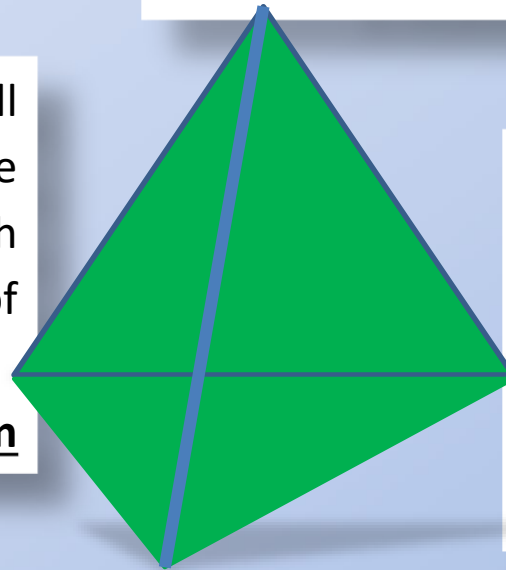
## 4. Scientific Dimension

Portfolio of solutions and pertinent recombination are more important than one leading technology (Chemistry vs Energy)

## 2. Technological dimension

## 3. Social dimension

New “producers”: biomass from agriculture; sea; wastes; ...  
New “end-user”; Jobs and territories: small local vs huge harbor biorefineries





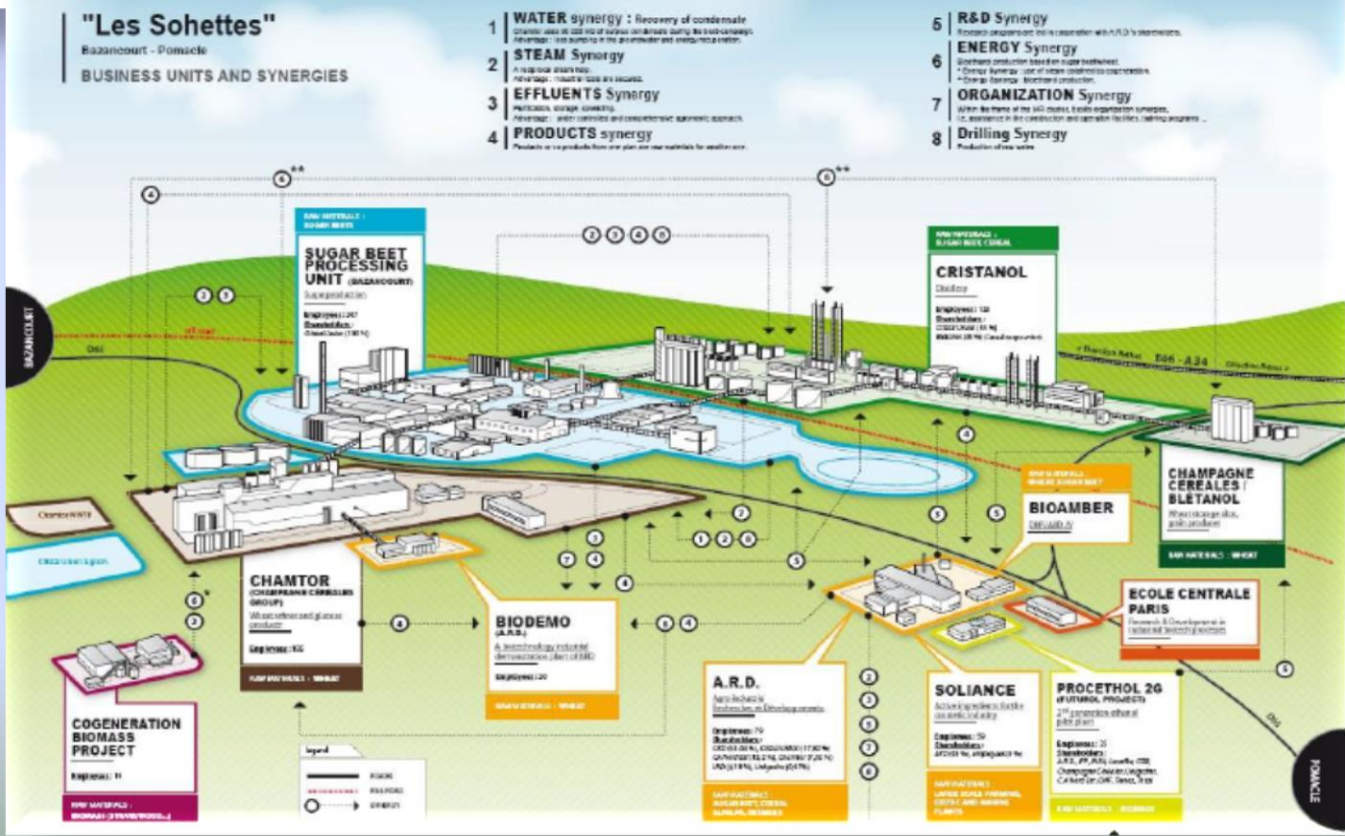
# Biomass and Biorefinery : what can be really expected?

Pr. Daniel THOMAS  
University of Technology of Compiègne

Pdt French Competitiveness cluster « Industries a

# Bazancourt-Pomacle – Near REIMS (Fr)

## Biorefinery: toward an industrial metabolism



[www.college-de-france.fr](http://www.college-de-france.fr)

# Thank you for your attention!!!!

