Ways to improve biomass conversion to chemicals (ecology and economy)

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Recent reviews:

-P. Gallezot,
Conversion of biomass to selected chemical products,
ChemSocRev, **2012**, *41*, 1538-1558

M. Besson, P. Gallezot, C. Pinel,
Conversion of biomass into chemicals over metal catalysts,
ChemRev, **2014**, doi.org/10.1021/cr4002269

How to improve biomass conversion processes?

How to obtain cost competitive products?

Do not forget basic economy principles from the start:

feedstock availability and price, investments, energy, waste, market needs

New strategies of conversion

→ Improve green character

→ Minimize energy

→ Decrease the number of conversion steps

New products with innovative properties

→ avoid unnecessary competition with existing chemicals

- Only 5% of oil production used to synthesize chemicals

How green are current conversion processes?

J. H. Clark*: “The use of sustainable feedstocks is not enough to ensure a prosperous future for later generations; protection of the environment using greener methodologies is a must”

Evaluation tools:

- Simple metrics: Atom Economy (Trost) or E-factor (Sheldon) cannot be applied because uncertainty in boundary conditions
- Life cycle analysis: cumbersome, too many options
- Semi quantitative methods developed by industry (BASF, Shell)

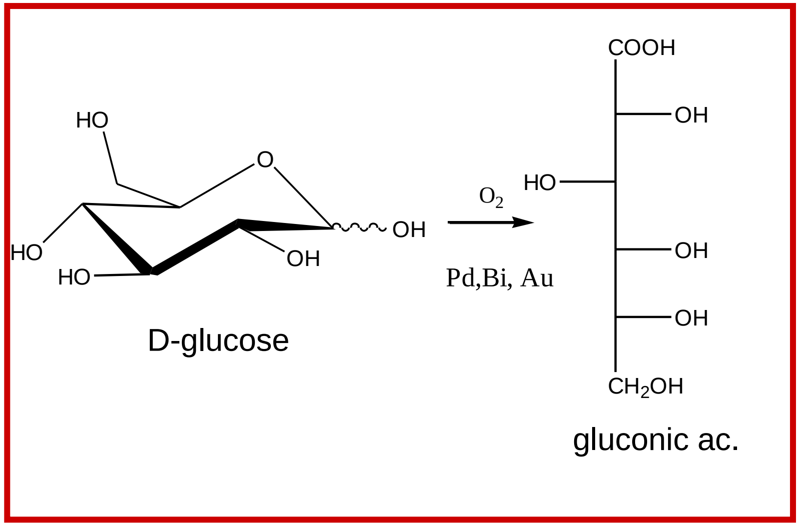
→ quantitative evaluation is difficult

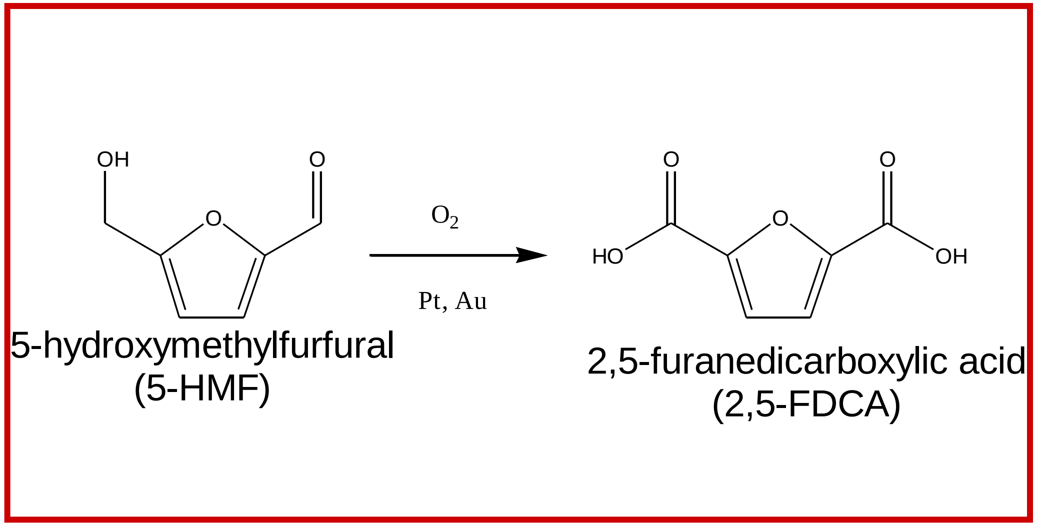
*J.H. Clark, The integration of green chemistry into future biorefineries Biofuels, Bioproducts&Biorefining (2009), 3, (1), 72-90.

Several processes are clearly efficient and green:

Oxidation reactions of carbohydrates and furanic compounds

- Water, air, atmospheric pressure, near ambient temperature
- <u>Recyclable</u> supported metal catalysts (metal and support do not leach)
- Close to 100% yield → <u>Atom Economy 100% ‘</u>
- High productivity (concentrated solutions and high reaction rate)





→ Hydrogenation reactions of carbohydrates and derivatives

Examples: glucose → sorbitol levulinic acid → γ-valerolactone

Some processes are clearly not efficient and green:

- Low efficiency (reaction by-products)
- Catalytic system and reaction medium containing toxic compounds
- Are ionic liquids green? (toxicity, energy intensive recovery)
- Leaching of metals or metal complexes
- Leaching of supporting materials

Example: glucose → 5-HMF

Yield 80%
Reaction medium: HCl, $CrCl_2$, LiBr, N,N-dimethylacetamide (DMA)

Cellulose → 5-HMF

Yield : 48%
Reaction medium: HCl, LiCl, $CrCl_2$,DMA, ethyl, methyl-imidazolium

sensitive subject: a complete documented assessment would be needed !

Availability and price of starting feedstocks

Applications must be commensurate with availability and price

Glycerol:	2	MTon/y,	€ 0.6/kg
Sucrose:	180	MTon/y	€ 0.3/kg
Cereal (starch):	2 000	MTon/y	€ 015-0.2/kg
Cellulose:	2 000 000	MTon/y (potential)	

But, thousand studies on glycerol → chemicals, fuels, H_2

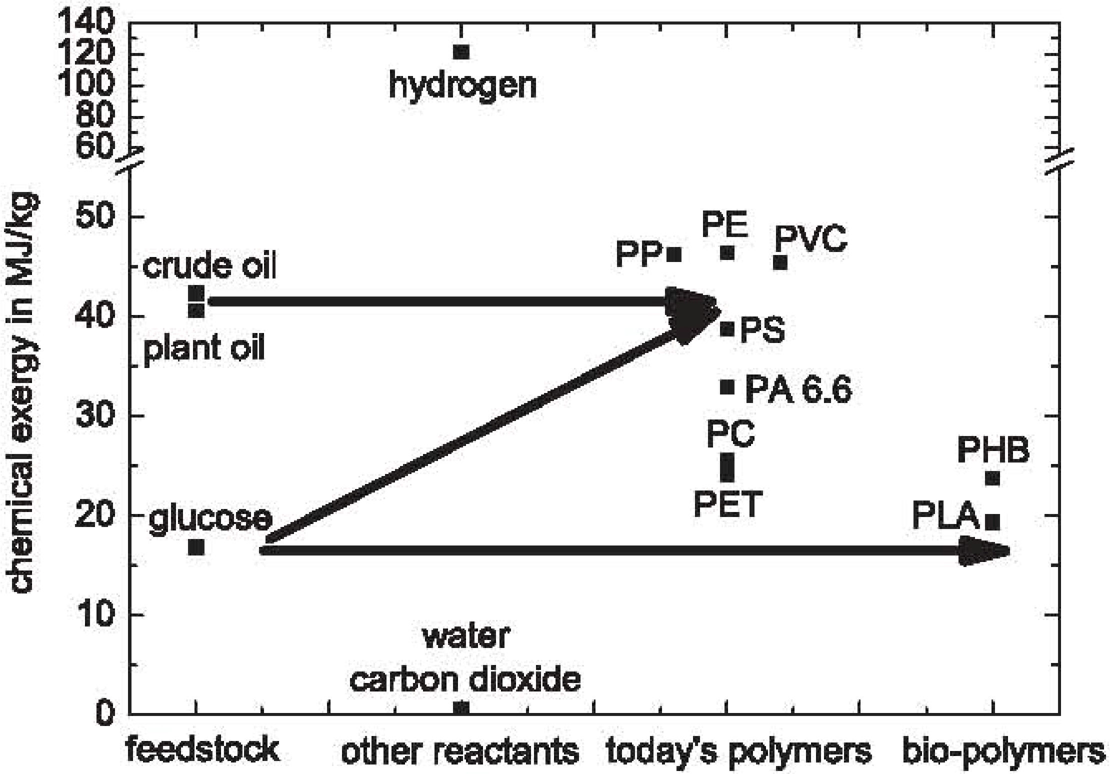
* Glycerol has already hundreds of applications
* Industrial developments to high tonnage intermediates:

→ epichlorohydrin, PDO, acrolein

Ultimately, risk of cheap glycerol shortage

Preferably, use glycerol for high value added chemicals

Minimize energy

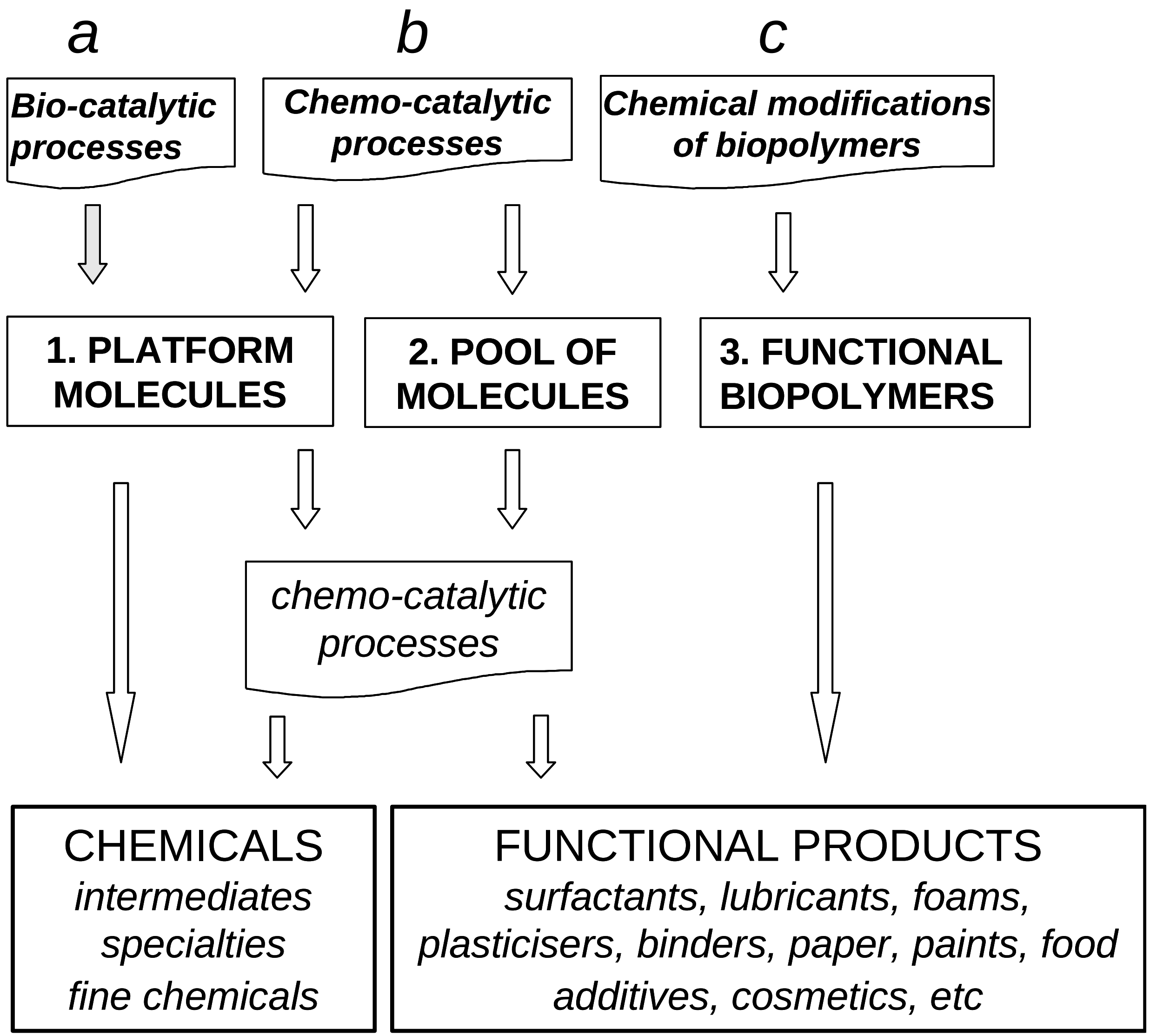


Frenzel et al,
Chem. Eng. Res. Dev. 2014

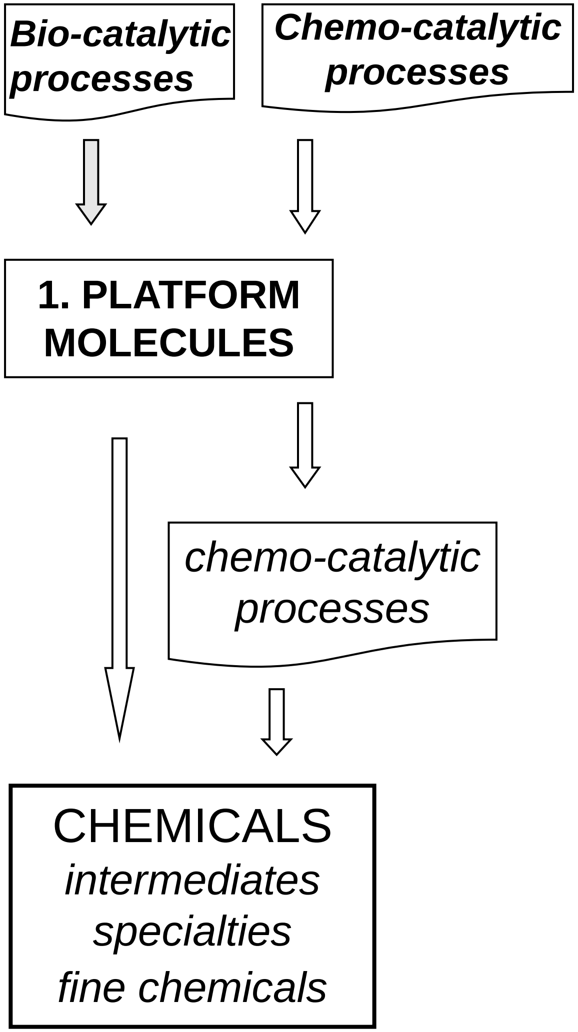
Glucose → Ethylene → PE 30 MJ/kg
Glucose → PLA 3 MJ/kg

Avoid extensive deoxygenation
Target oxygenated products

Strategies toward cost competitive processes



Strategy (*a*): conversion via platform molecules to produce pure, isolated chemicals



Widely practiced approach ("Top 10 chemicals")

Often target chemicals from fossil fuels

Problem: cost and quality competitiveness

- biosuccinic acid: success story

- bioadipic acid: not competitive, market price 2010; $ 2500/ton 2013: $ 1500/ton

Better chance of success for the production of chemicals that have no synthetic counterparts:

Isosorbide and derivatives
PLA polymer
alkylpolyglucosides surfactants
……

Strategy (*b*): conversion in one or few steps into a mixture of molecules with similar functionalities for the manufacture of functional end-products

Chemo-catalytic processes

⇩

2. POOL OF MOLECULES

⇩

chemo-catalytic processes

⇩

FUNCTIONAL PRODUCTS
surfactants, lubricants, foams, plasticisers, binders, paper, paints, food additives, cosmetics, etc

•Isolated , pure chemicals are not necessary (Similarity with food industry)

•Drastic reduction of processing steps (reactions, isolation, purification)
→ cost competitive high tonnage products

From mixture of carbohydrate-derived polyols:
→ polyesters, surfactants, complexing agents

From mixture of plant oils
→ surfactants lubricants, platicizers, polymers

From lignin depolymerization:
→ phenol-formaldehyde resins

At Ircelyon:

Polyols for water soluble polyesters
Plasticizers to substitute phthaltes

Strategy (*c*): chemical modifications of biopolymers

cellulose, hemicellulose, starch, inulin, chitin, lignin, proteins

used 150 years ago for cellulose derivatives

- Avoid degradation into small molecules
  graft new functionalities on polymer chians

- produce functional materials

→ One-step reaction at moderate temperatures, in water, without further separation

→ Low energy, low waste processes to new functional materials

Many new applications from cellulose

Y. Habibi, ChemSocRev. DOI: 10.1039/c3cs60204d

Chemical modifications of biopolymers

↓

FUNCTIONAL BIOPOLYMERS

↓

FUNCTIONAL PRODUCTS
surfactants, lubricants, foams, plasticisers, binders, paper, paints, food additives, cosmetics, etc

At IRCELYON
→ hydrophilic or hydrophobic starch
→ cationization of hemicellulose

Concluding remarks

• Strategies (*b*) and (*c*) are not intended to substitute chemicals already marketed but to manufacture high tonnage end- products.

• Reduce drastically the cost of biomass processing due to one step conversion and no need of separation.

• One-pot modification of biopolymers is preferable to the deconstruction to small molecules that are used as monomers

• Approach could greatly accelerate the industrial development of products based on renewable carbon.