Universität für Bodenkultur Wien
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Bio-based platform chemicals

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April 22nd 2020, UniTS, Online Lecture

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The 12 Principles of Green Chemistry

01 Waste Prevention

02 Atom Economy

03 Less Hazardous Chemical Synth.

04 Designing Safer Chemicals

05 Safer Solvents & Auxiliaries

06 Design for Energy Efficiency

07 Use of Renewable Feedstocks

08 Reduce Derivatives

09 Catalysis

10 Design for Degradation

11 Real-Time Pollution Prevention

12 Safer Chemistry for Accident Prevention

Anastas & Warner, *Green Chemistry: Theory and Practice*, Oxford University Press: New York, **1998**

The Challenge

Principle No.7: A raw material or feedstock should be renewable rather than depleting wherever technically and economically practical

- Fossil resources are depleting
  - Used for fuel, energy and….
- Majority of products from the chemical industry are currently derived from these non-renewable fossil resources (petrochemicals)
  - The petrochemical industry is well established (and highly optimised)

The Solution(s)

- Convert biomass to chemicals/materials
  - Already done but significant advances needed

- Compare drop-in replacements (*e.g.* bio-based terephthalic acid) with new chemicals (*e.g.* 2,5-furandicarboxylic acid)
  - How best to compare? Economics (new chemistry = new chemical plants)? LCA? Safety?

- Don’t just green the bulk chemicals but green the products too
  - We need the future chemical industry to think about **end-of-life** too

The Current Chemical Industry

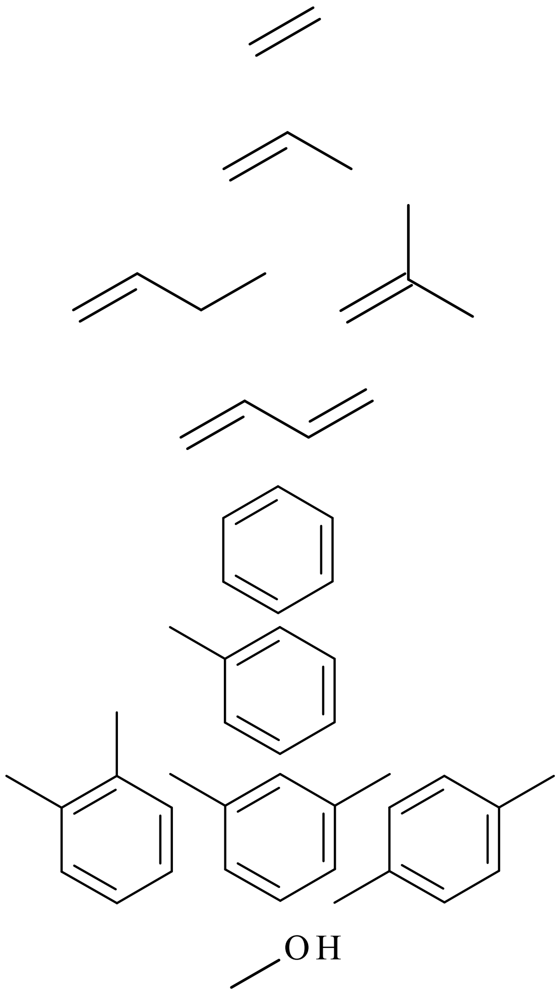
Crude oil
<u>feedstock</u>
3.6 billion tonnes
in 2010

DISTILLATION

- methane, ethane, naphtha (10%)
- Fuel (~90%)

Base Chemicals

- Ethene
- Propene
- Butenes
  - ↓ Butadiene
- Benzene
- Toluene
- Xylene
- syn gas → Methanol



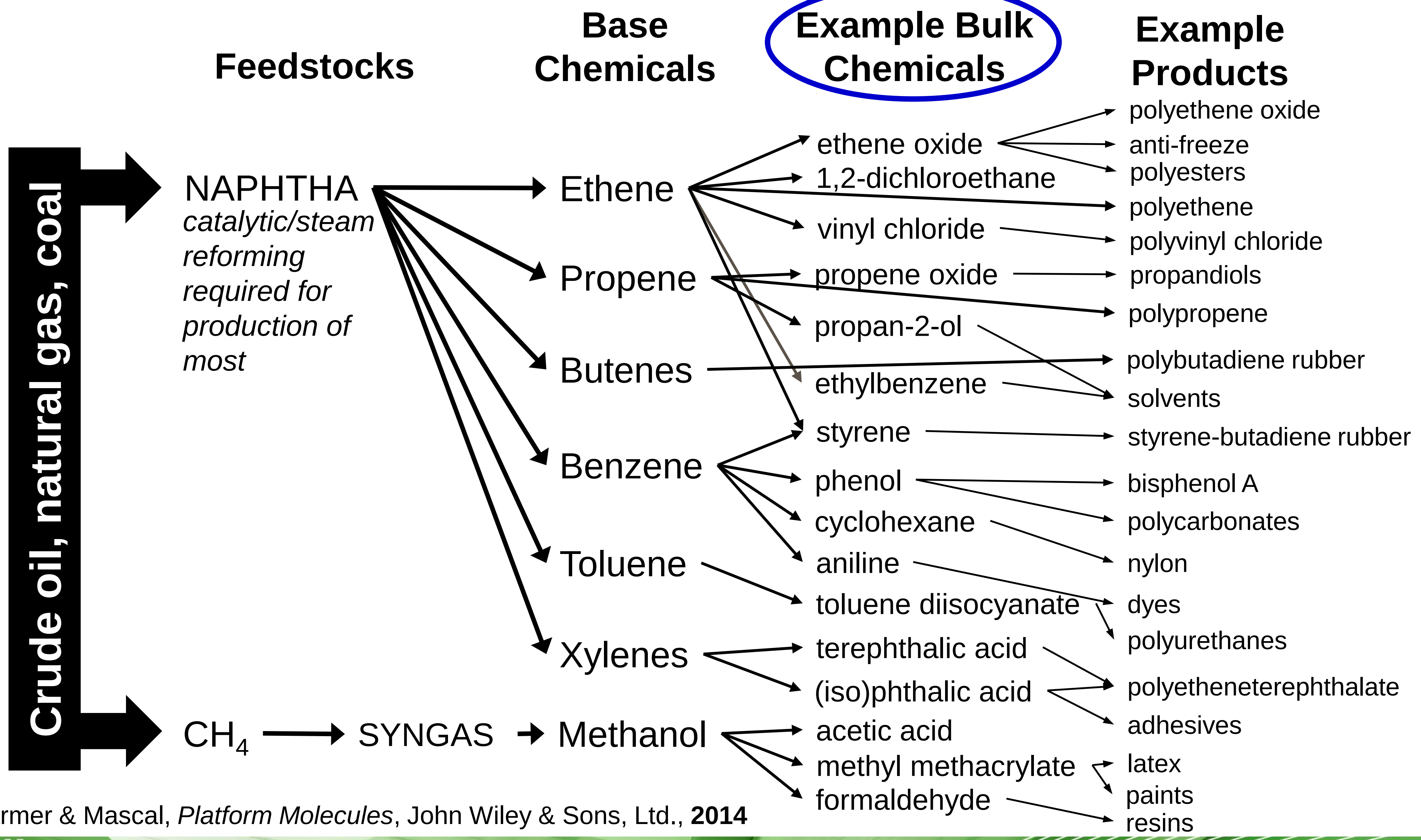
Term Alert!

Base Chemical

A simple, cheap, building-block chemical produced from fossil resources via simple processing (steam cracking, catalytic cracking, isomerisation, reforming). They are produced on a very large scale (>10 million tonnes $annum^{-1}$)

A small number of base chemicals are used to synthesise nearly all (~85%) of the organic chemicals/materials produced by the chemical industry.

Fossil-derived base chemicals



Farmer & Mascal, *Platform Molecules*, John Wiley & Sons, Ltd., **2014**

Term Alert!

Bulk Chemical

Bulk chemicals are produced in large quantities (greater than 1000 tonnes annum^{-1}), usually with highly optimized continuous processes and to a relatively low price

Bulk chemicals include the base chemicals and also the initial (~300) high-volume / low-value chemicals made from simple large-scale conversion of the base chemicals

Examples include ethylene oxide, styrene and acetic acid

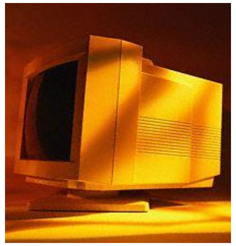
The Scale of Production

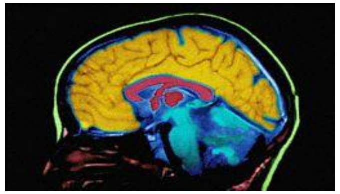
Base chemical	Predominant feedstock	Annual production from fossil sources (tonnes/annum)
Ethene	Oil, gas	123,300,000
Propene	Oil, gas	74,900,000
Butadiene	Oil, gas	10,200,000
Benzene	Oil	40,200,000
Toluene	Oil	19,800,000
Xylenes (o-, m-, p-)	Oil	42,500,000
Methanol	Syngas	49,100,000
TOTAL		**360,030,000**

~3,589,600,000 tonnes of crude oil produced in the same year

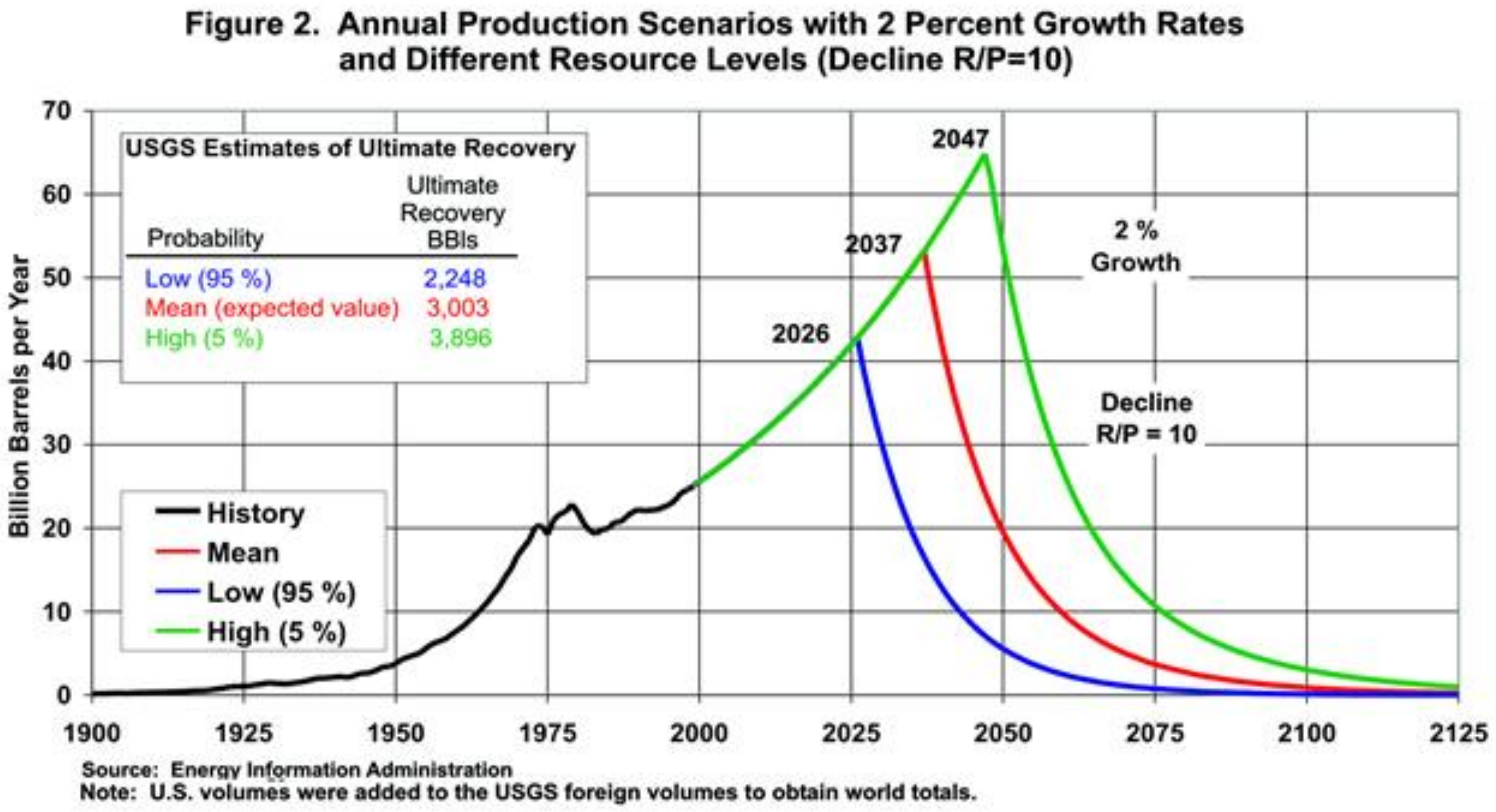
Davis, S., *Chemical Economics Handbook Product Review: Petrochemical Industry Overview*, SRI Consulting, **2011**

We Need Chemicals!





Problem: Peak Oil!



Even conservative estimates show Peak Oil to occur in our lifetime!

Platform Molecules from Biomass

Going from:

Oil Refining

Crude Oil

OIL REFINERY

- Fuel
- Asphalt
- Base Chemicals
- Energy

Base Chemicals:

- Plastics
- Agro-chemicals
- Pharmaceuticals
- Nutraceuticals
- Solvents
- Clothing
- Many more……

“>90% of organic chemicals are derived from non-renewable fossil resources.”

Kümmerer & Hempel, *Green and Sustainable Pharmacy*, Springer, **2010**

To the:

Biorefinery

Waste Biomass

BIOREFINERY

- Fuel
- Materials
- Chemicals
- Energy

Platform Molecules

- Plastics
- Agro-chemicals
- Pharmaceuticals
- Nutraceuticals
- Solvents
- Clothing
- Many more……

Term Alert!

Platform Molecule

"…a bio-based (or bio-derived) chemical compound whose constituent elements originate wholly from biomass (material of biological origin, excluding fossil carbon sources), and that can be utilised as a building block for the production of other chemicals."

They are typically small, relatively simple molecules of low value and ideally high production volumes (or at least the potential to be produced on scale), and are seen as the bio-based equivalent to fossil base chemicals.

Examples: ethene, butadiene, succinic acid, acetic acid

To the:

Biorefinery

Waste Biomass

BIOREFINERY

- **Fuel**
- **Materials**
- **Chemicals**
- **Energy**

Chemicals → **Platform Molecules**

- **Plastics**
- **Agro-chemicals**
- **Pharmaceuticals**
- **Nutraceuticals**
- **Solvents**
- **Clothing**
- **Many more……**

Which polymers do we currently use from biomass?

Term Alert!

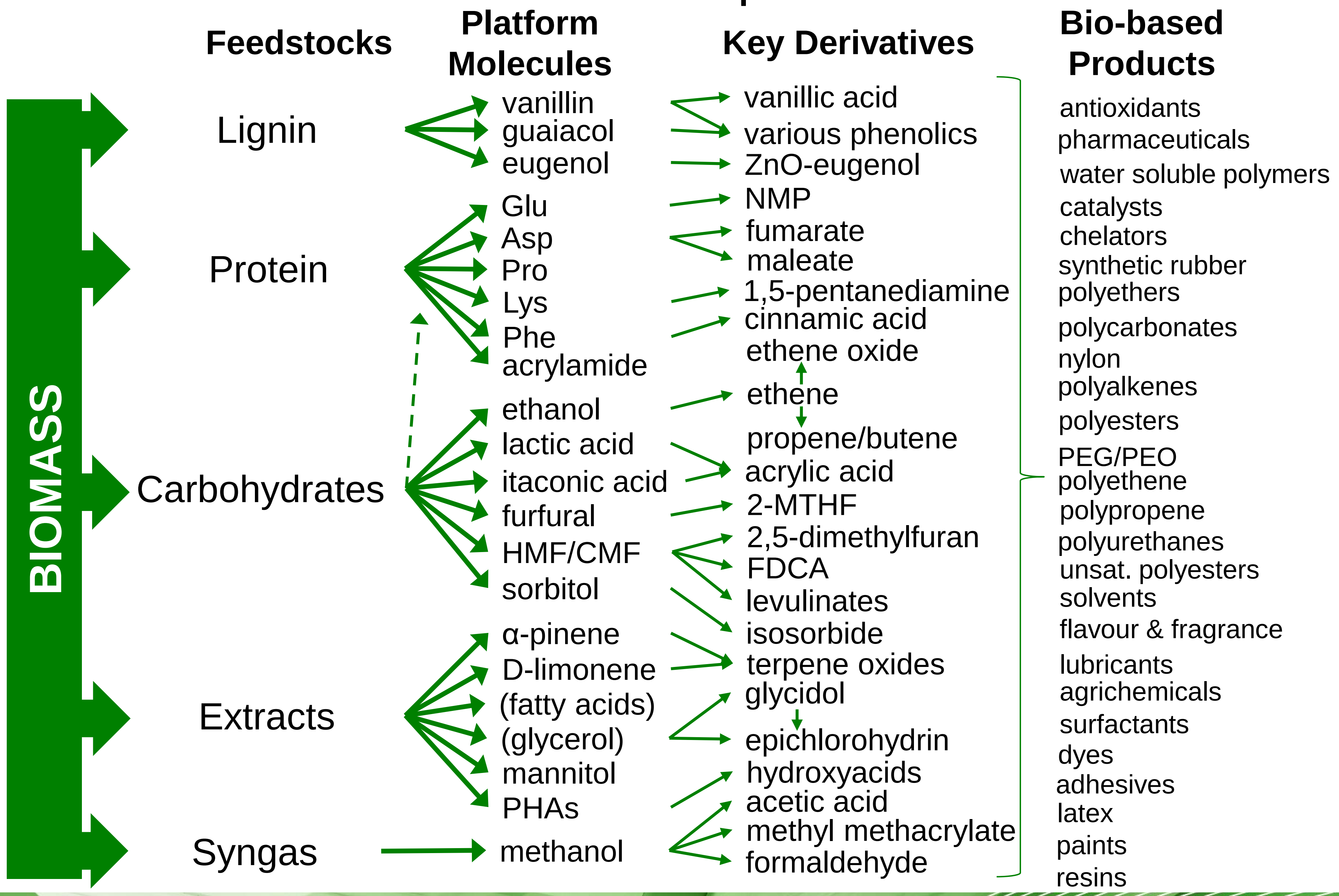
Drop-in Replacement

In the context of the bio-economy it is a bio-based chemical that is of the exact same chemical structure as a fossil-derived equivalent, therefore meaning the same down-stream processing and use of that molecule can be applied

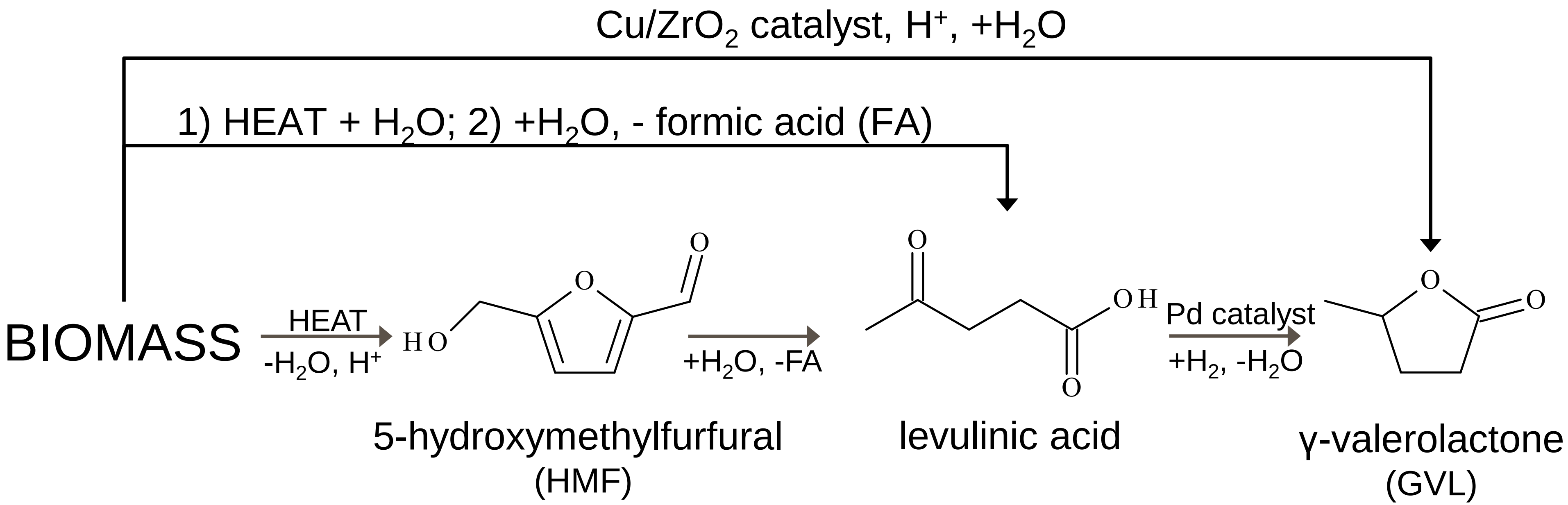
Advantage: no new processing plant needed or consideration of new safety or environmental issues

Disadvantage: harsh chemical processes to reach the drop-in from biomass and miss opportunities for new chemistry

Platform molecules replace base chemicals

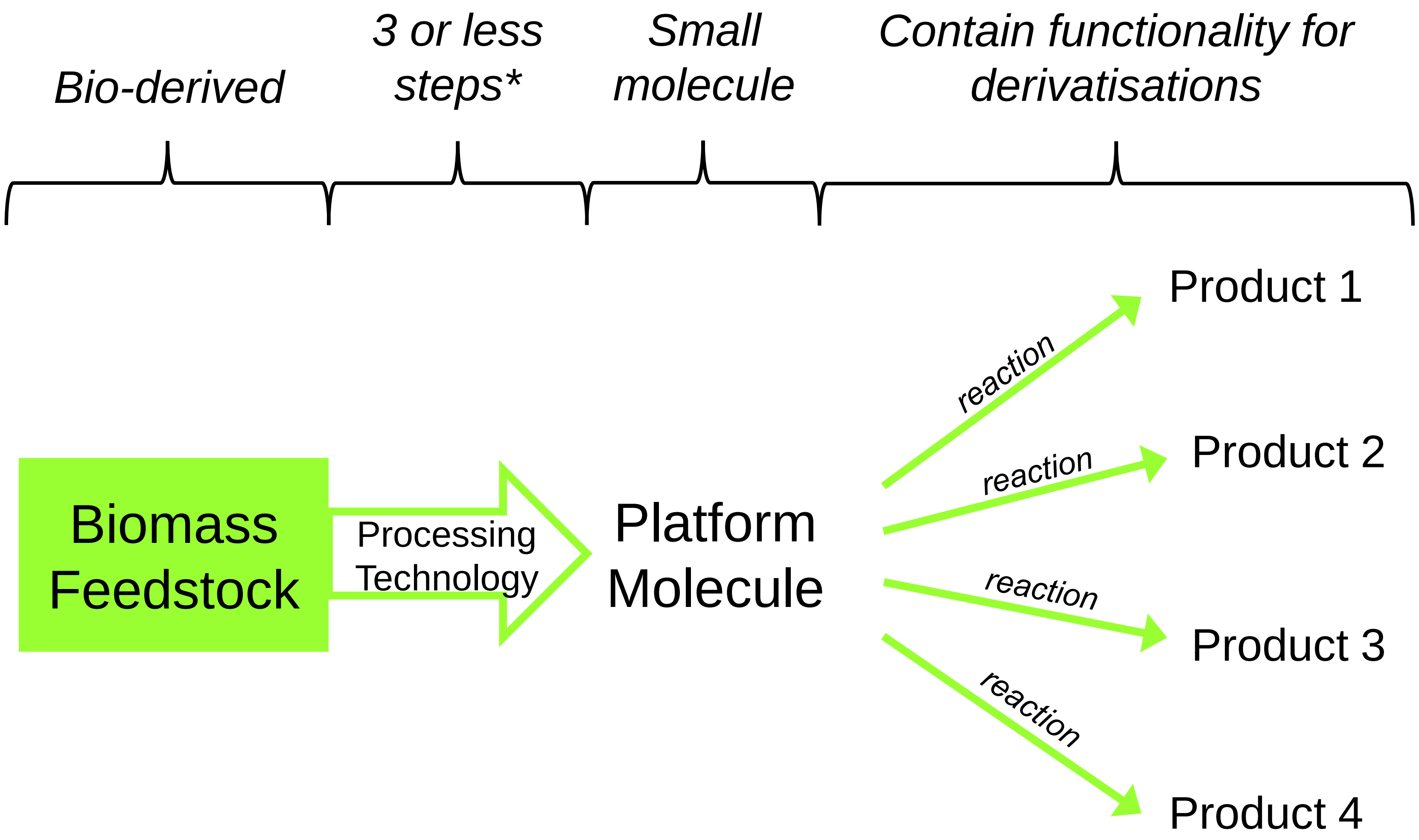


How to define a platform molecule?



All three are platform molecules, but only if they are produced directly from **feedstocks**

A Simpler View



*Steps could include fractionation and purification as well

Term Alert!

Feedstock

Any unprocessed materials used to supply a manufacturing process. In this context refers to unprocessed biomass (including waste) that is used to produce chemicals or materials

Biomass

Material of biological origin excluding material embedded in geological formations and/or fossilised.

Feedstocks

Feedstocks (1)

Main constituents of **biomass**:

- Polysaccharides (*e.g.* starch, cellulose, hemicellulose, chitin) - *competition with food?*
- Mono-/di-saccharides (*e.g.* glucose, fructose, sucrose) - *competition with food?*
- Lignin
- Proteins (polyamides)
- Extracts (e.g. terpenes, triglycerides, D-mannitol, waxes, sterols) - *quantity?*
- Lignocellulose, crude **biomass**, mixed waste

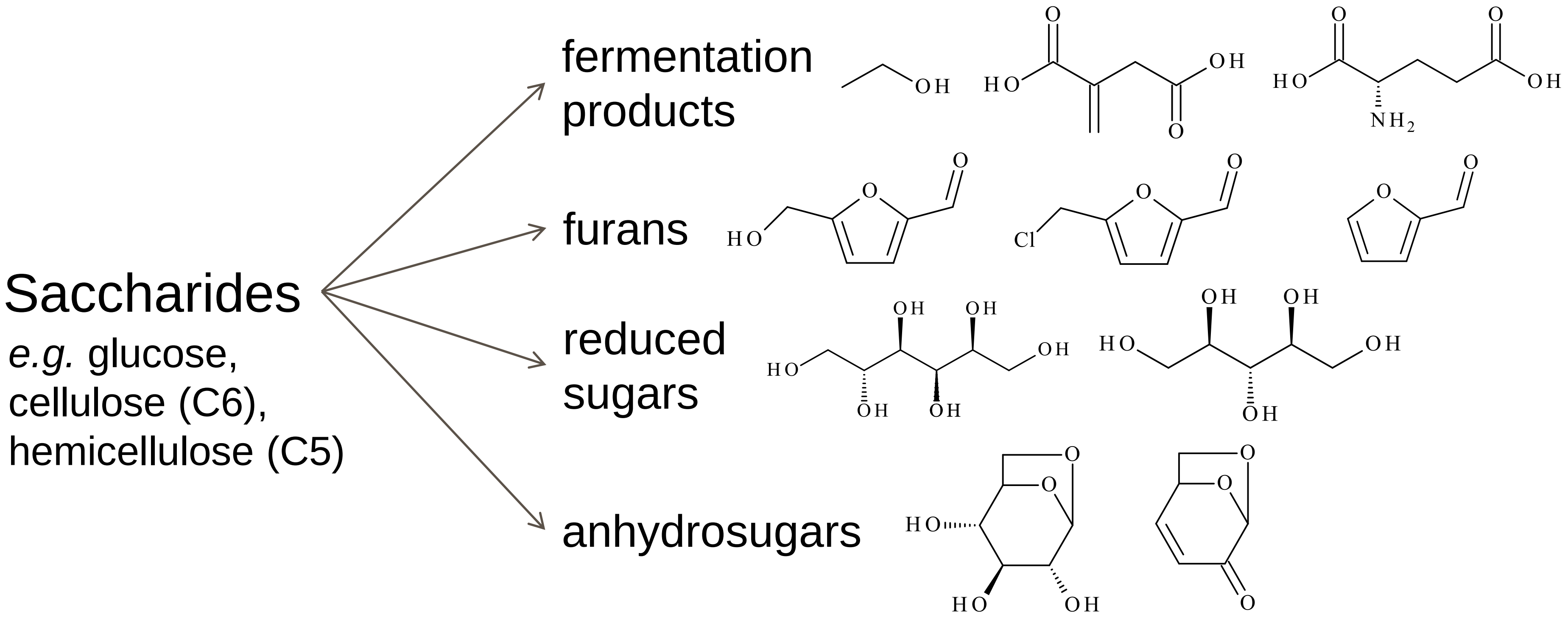
Feedstocks (2)

Categorisation by **feedstock**

- Different constituents of biomass lead to differ platform molecules
- Biorefineries will likely separate biomass to its constituent parts prior to platform molecule production
  - Lignin, cellulose and hemicellulose may be combined (known as lignocellulose)
- It is the composition of the biomass that will determine the most suitable platform molecules to produce
  - Seasonality and specie variation could prove important in the future

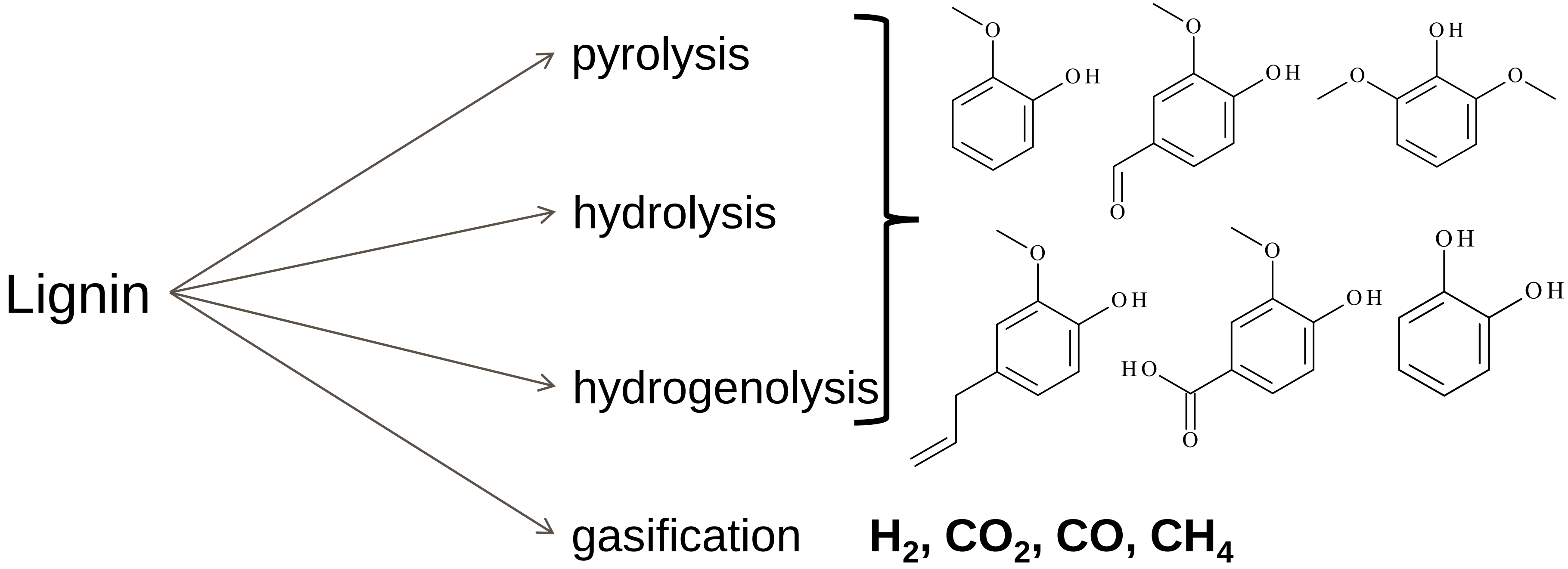
Saccharides

- Saccharides (mono-, di-, poly-)
  - Most abundant constituent of biomass (>60% wt) with many processing options:



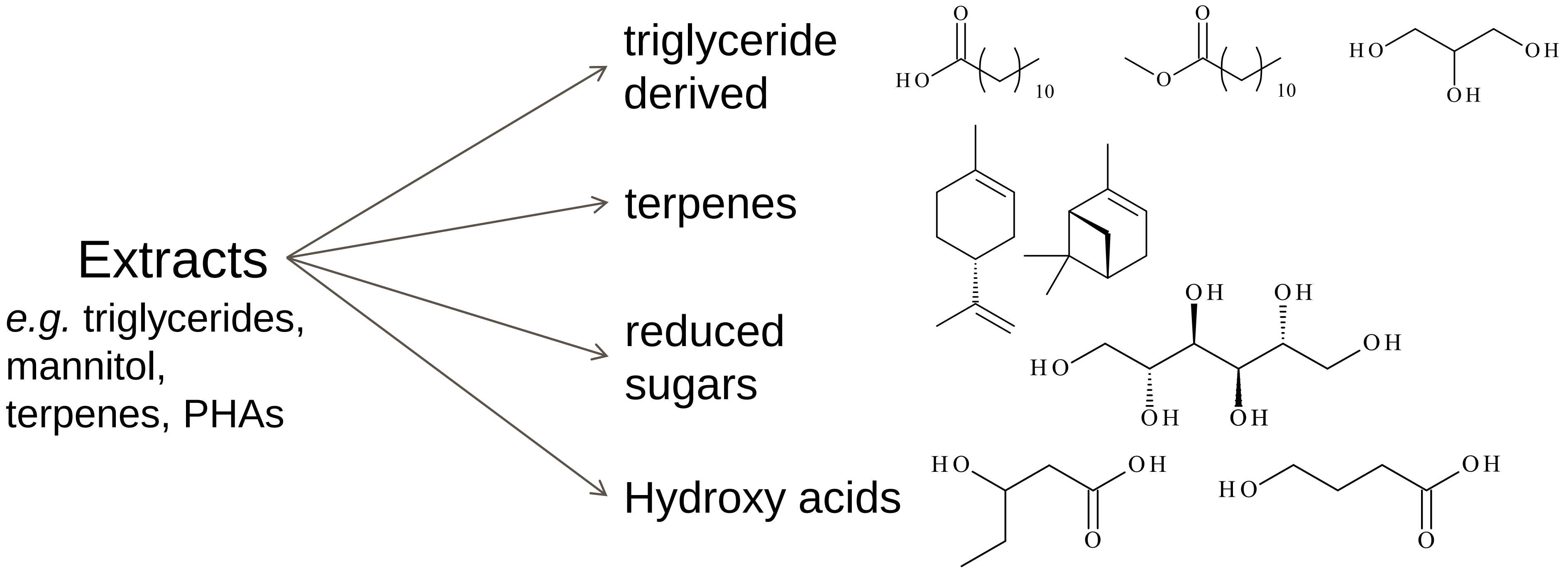
Lignin

- Lignin
  - Generally viewed as the ideal source for aromatics, though it is very recalcitrant (resistant to processing)



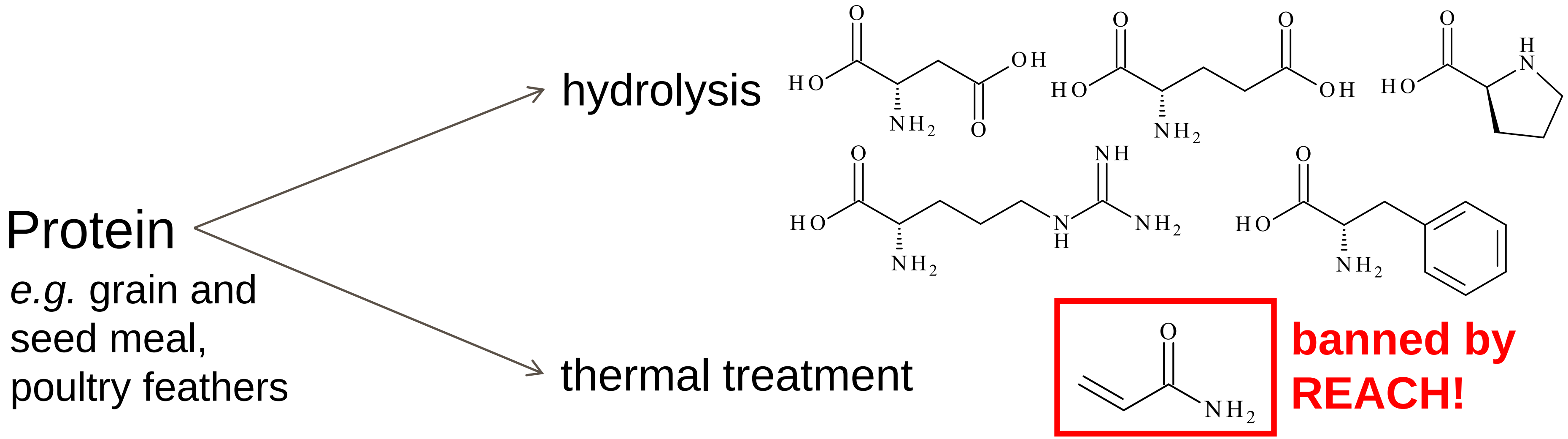
Extracts

- Extracts
  - More varied than other feedstocks
  - Only present in small quantities, very species specific
  - Is within the biomass already, not made from it



Proteins (1)

- Proteins
  - Polymer of amino acids (>20 different residues present)
  - Often used as feed
  - Wide variation of %wt in biomass
  - Hydrolysis and separation a challenge



What is REACH? (1)

REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals

- REACH is a regulation of the European Union
  - improve the protection of human health and the environment from the risks that can be posed by chemicals
  - enhancing the competitiveness of the EU chemicals industry
  - promotes alternative methods for the hazard assessment of substances
  - reduce the number of tests on animals

What is REACH? (2)

REACH: Registration, Evaluation, Authorisation and Restriction of Chemicals

- REACH applies to **all chemical substances**
  - industrial processes
  - day-to-day lives (cleaning products, paints) reduce the number of tests on animals
  - and articles (clothes, furniture and electrical appliances)
  - This regulation has an impact on most companies across the EU
  - It entered into force on 1 June 2007

How does REACH Work?

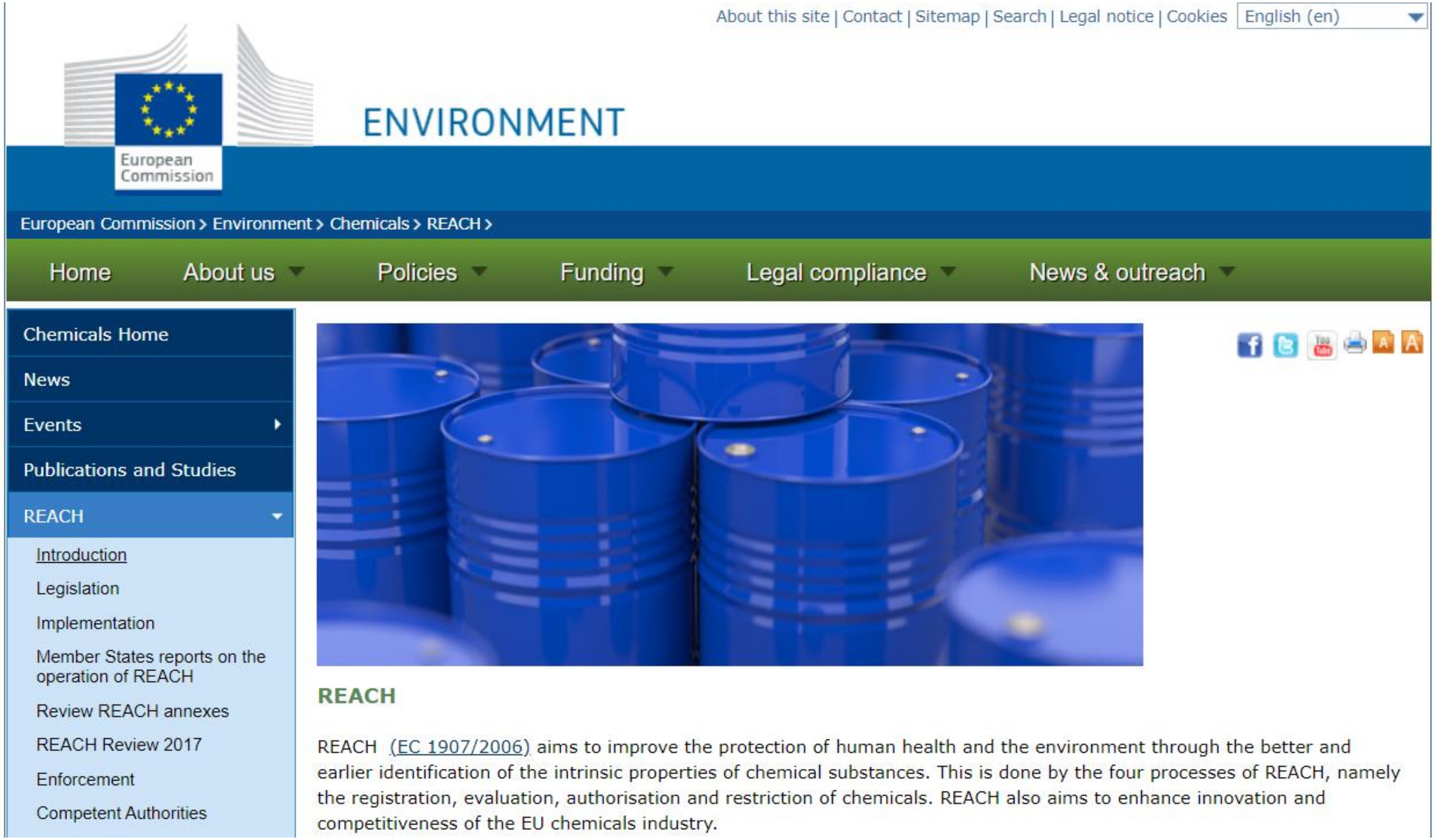
- REACH establishes procedures for collecting and assessing information on the properties and hazards of substances

- **Companies need to** register their substances and to do this they need to **work together** with other companies who are registering the same substance

- ECHA receives and evaluates individual registrations for their compliance, and the EU Member States evaluate selected substances to clarify initial concerns for human health or for the environment. Authorities and ECHA's scientific committees assess whether the **risks of substances** can be managed

- Authorities can **ban hazardous substances** if their risks are unmanageable. They can also decide to restrict/authorize the use

For Further Info about REACH



https://ec.europa.eu/environment/chemicals/reach/reach_en.htm

Proteins (1)

- Proteins
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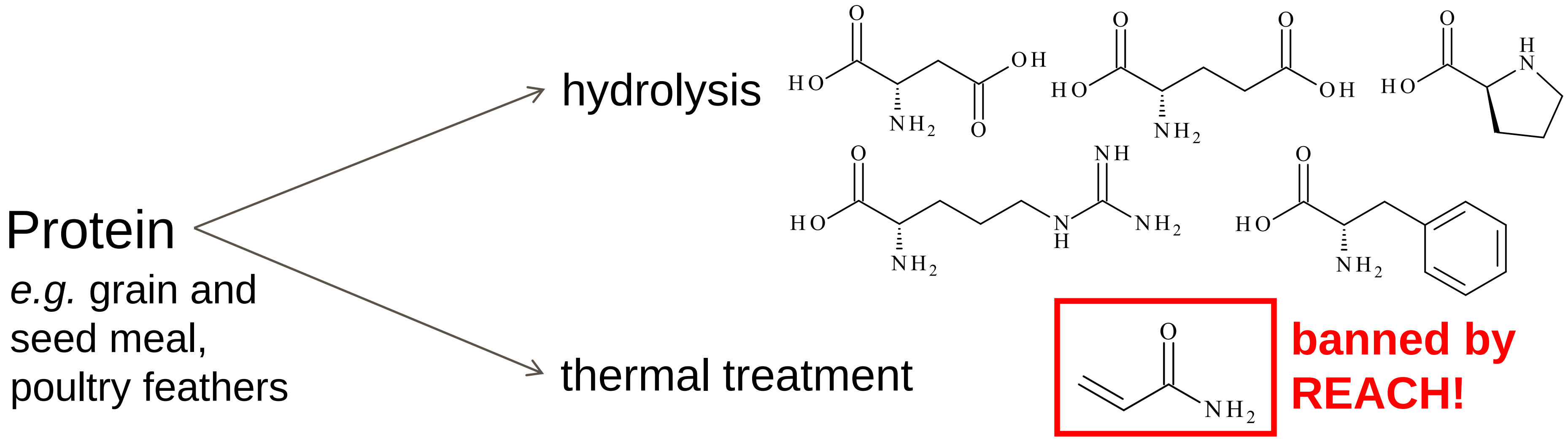
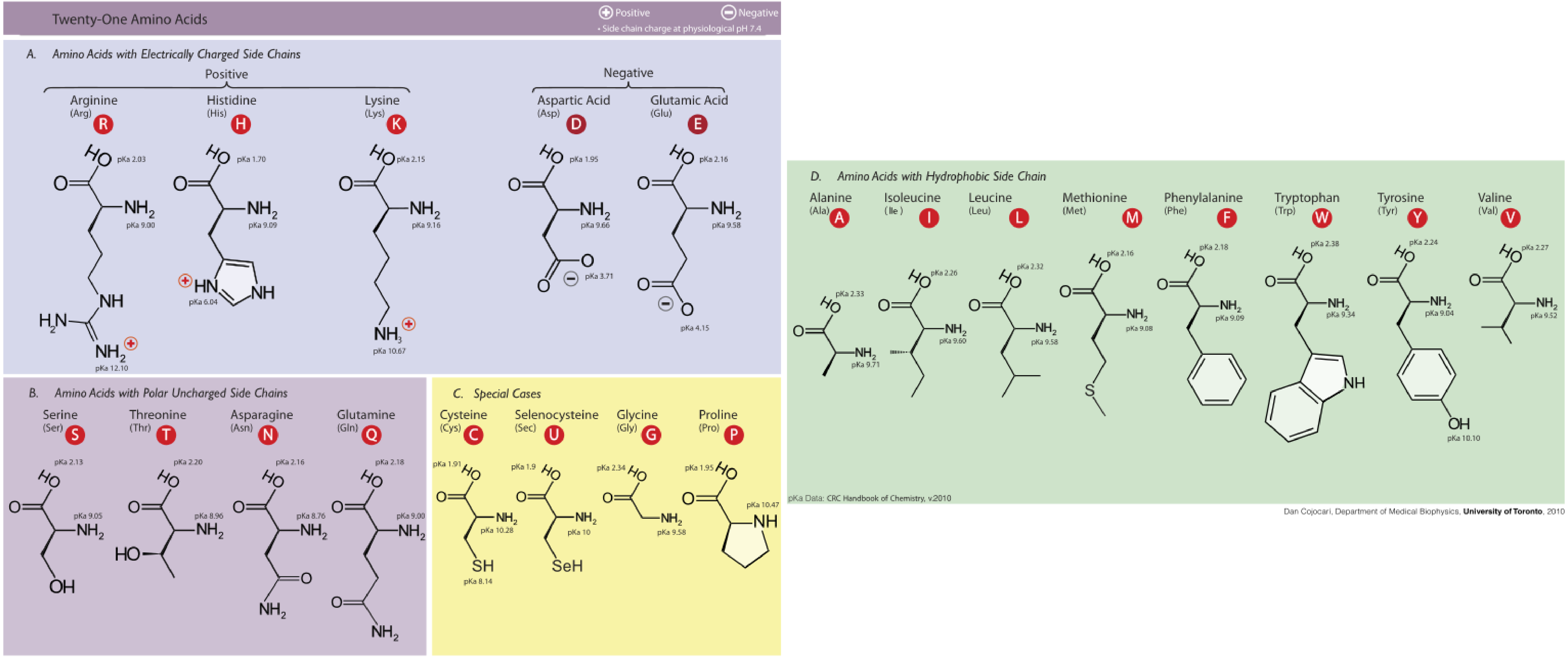


Proteins (2)


Twenty-One Amino Acids
Positive
Negative
• Side chain charge at physiological pH 7.4
A. Amino Acids with Electrically Charged Side Chains
Positive
Negative
Arginine (Arg) R
Histidine (His) H
Lysine (Lys) K
Aspartic Acid (Asp) D
Glutamic Acid (Glu) E
B. Amino Acids with Polar Uncharged Side Chains
Serine (Ser) S
Threonine (Thr) T
Asparagine (Asn) N
Glutamine (Gln) Q
C. Special Cases
Cysteine (Cys) C
Selenocysteine (Sec) U
Glycine (Gly) G
Proline (Pro) P
D. Amino Acids with Hydrophobic Side Chain
Alanine (Ala) A
Isoleucine (Ile) I
Leucine (Leu) L
Methionine (Met) M
Phenylalanine (Phe) F
Tryptophan (Trp) W
Tyrosine (Tyr) Y
Valine (Val) V
pKa Data: CRC Handbook of Chemistry, v.2010
Dan Cojocari, Department of Medical Biophysics, University of Toronto, 2010

Crude Biomass & Lignocellulose

- Crude Biomass & Lignocellulose
  - Most likely scenario is using crude biomass with a mixture of all the above components
  - Probably remove high-value, low-volume extracts first (terpenes, triglycerides, waxes, sterols, pigments, aromas etc.)
  - Then target easily accessed or processed components
  - Sugars, starches and hemicellulose
  - Recover protein (for feed?)
  - Finally process the recalcitrant lignocellulose

From Feedstocks to Platform Molecules

Processing Technologies (1)

There are four main process technologies that we can use to produce platform molecules from biomass, these are:

- Thermal
- Chemical (and thermochemical)
- Biological
- Extraction

Within each there are many different ways in which to perform the process (e.g. thermal treatment could be fast pyrolysis or heating with microwaves)

Processing Technologies (2)

- Thermal
  - Heating biomass to produce chemicals
    - Often poor selectivity
    - Examples include fast pyrolysis and microwave pyrolysis

- Chemical (and thermochemical)
  - Use of chemicals (acid, base, solvents, water, others) to assist platform molecule formation from biomass
    - Can use heat (thermo-chemical), but not always needed
    - Better selectivity than thermal alone, but sometimes uses hazardous chemicals
    - Examples include acid treatment of cellulose and transesterification of triglycerides

Processing Technologies (3)

- Biological
  - Use of enzymes, bacterium and yeast to breakdown biomass and to form new molecules
    - Can be used to convert polysaccharides to sugars
    - Can be used to convert sugars to platform molecules
    - Pre-treatment and chemical isolation are expensive
    - Includes itaconic acid and ethanol from sugars

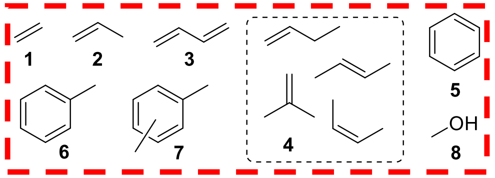
- Extraction
  - Use of solvents or mechanical processes to recover chemicals present in biomass
    - Examples include limonene from citrus peel or D-mannitol from seaweed

Which extraction could you easily perform at home?

A Simple Homemade Extraction: Limoncello

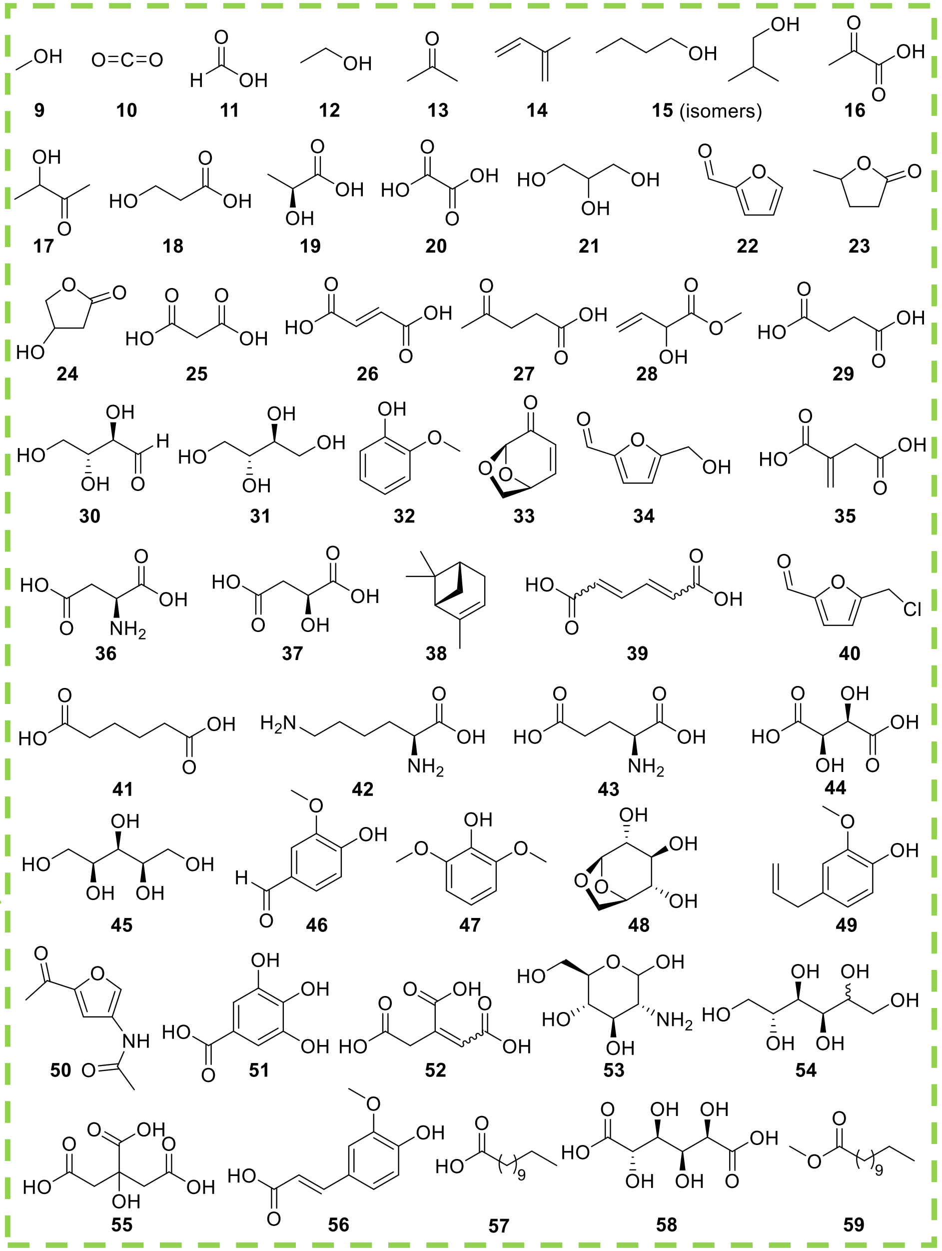
Conversion of Platform Molecules to Products

BioLogicTool: Plotting Heteroatom Content



Base chemicals

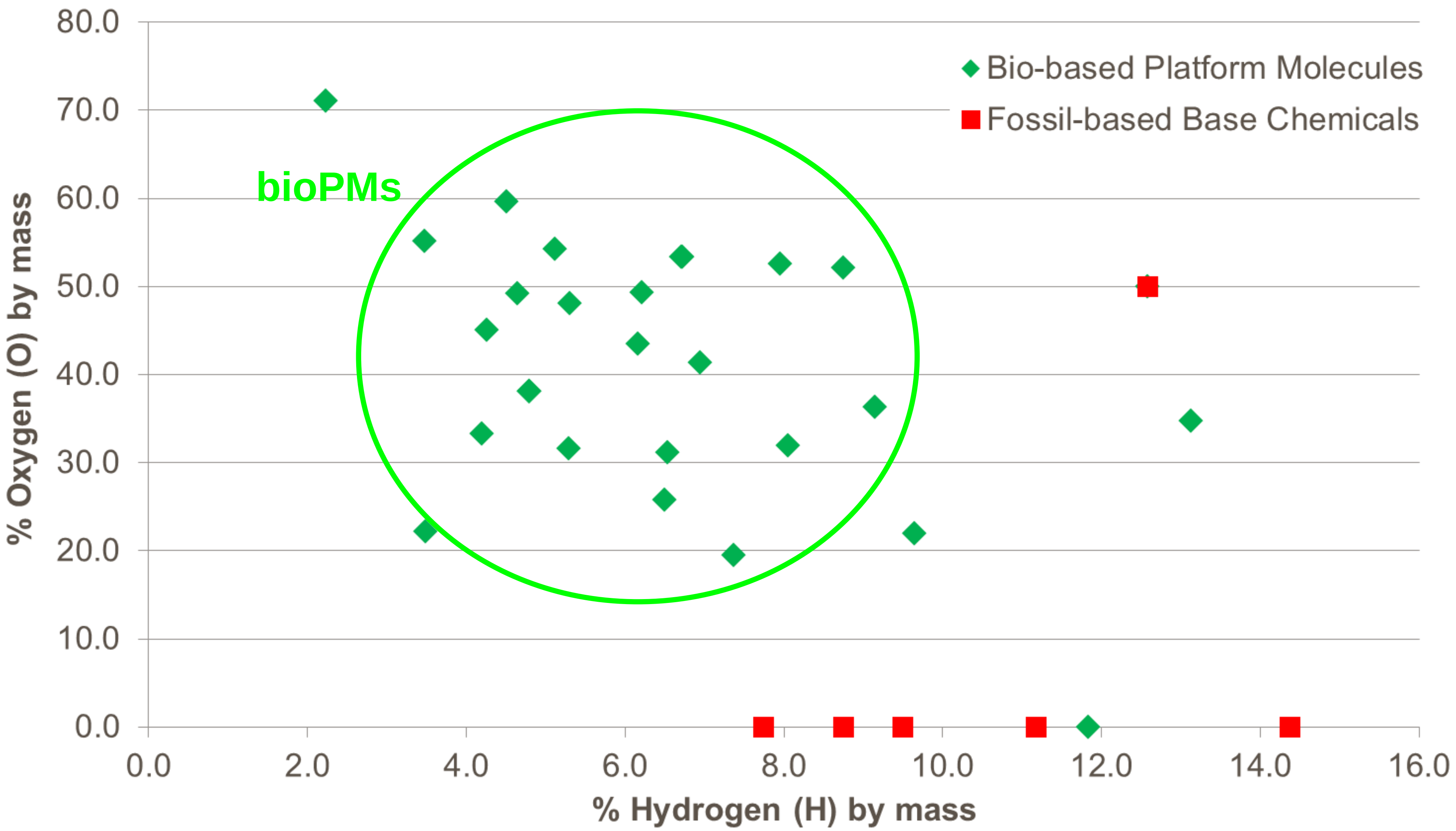
Bio-based platform molecules



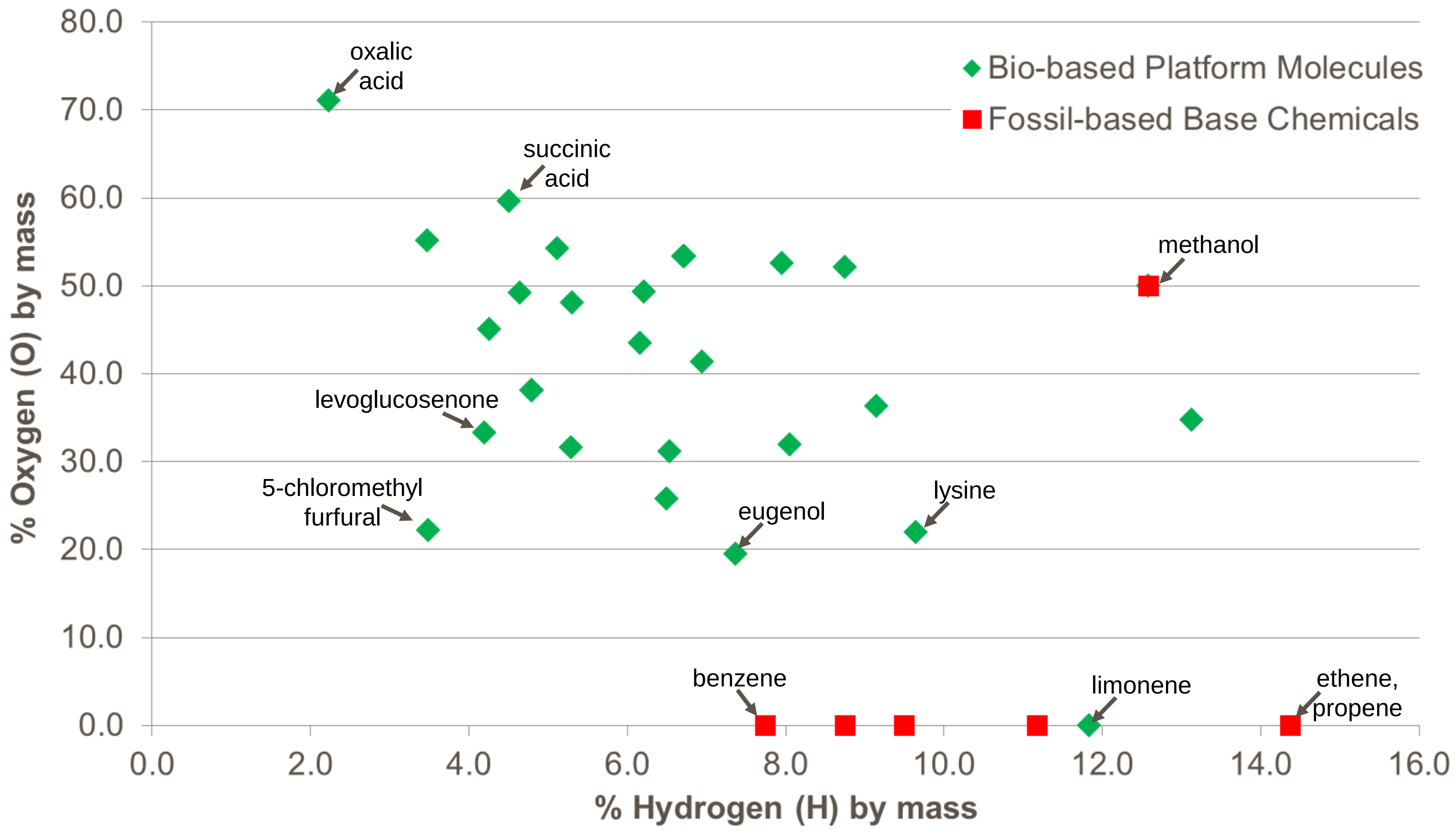
Differences?

Lie, Y. et al., **2019**, *Ind. Eng. Chem. Res.*, 58, 15945-15957

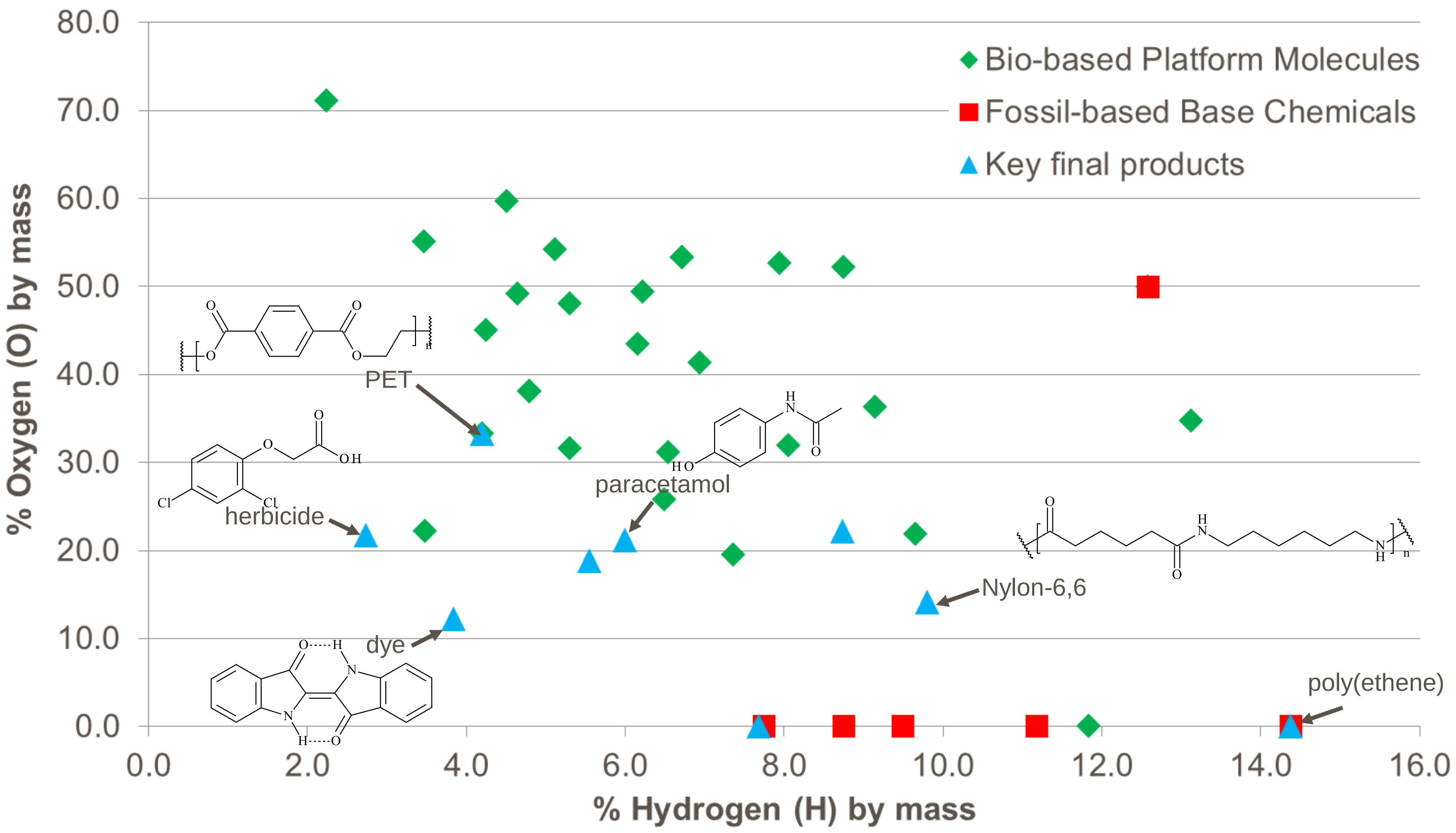
Oxidation vs Reduction (1)



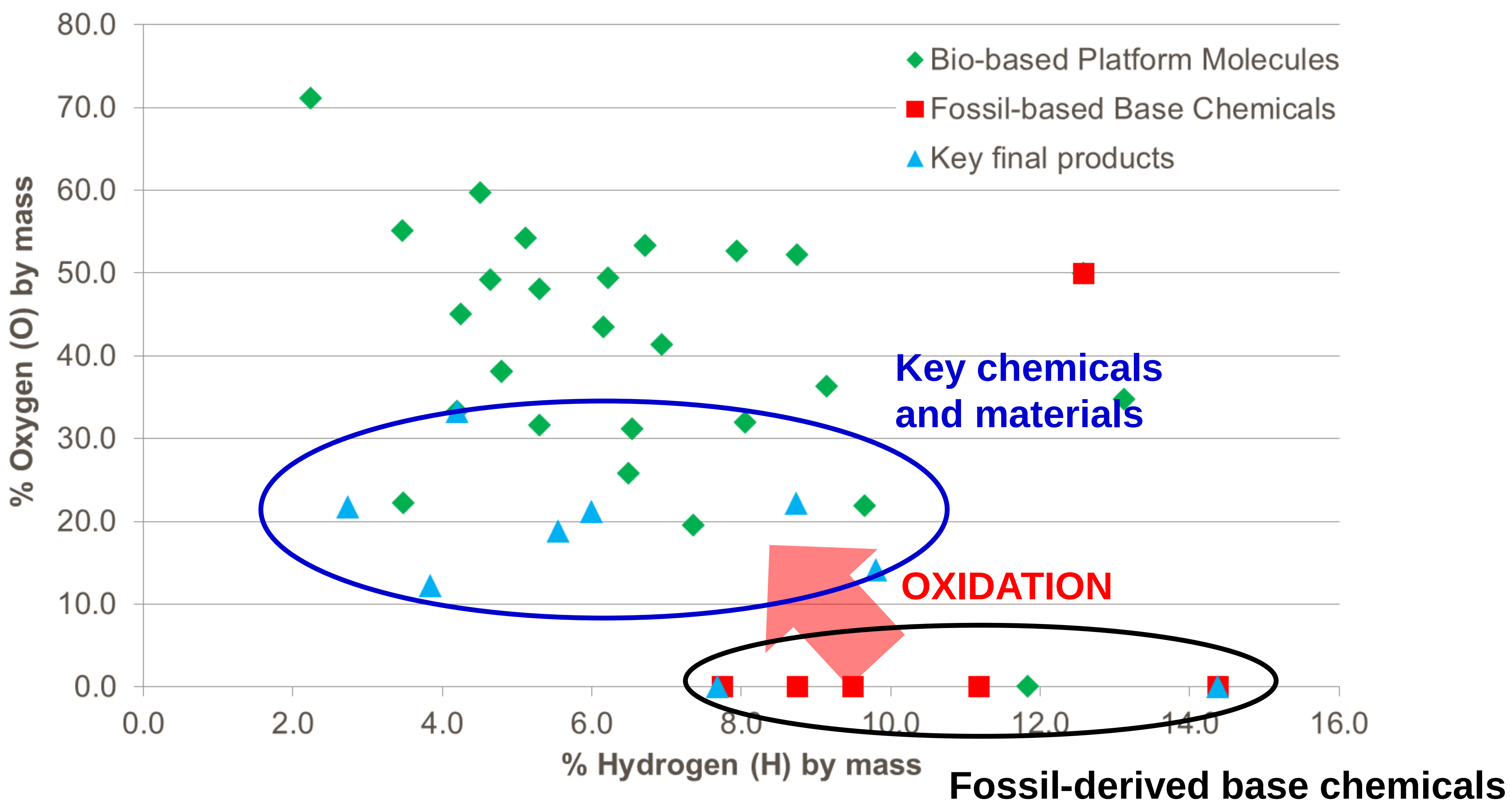
Oxidation vs Reduction (1)



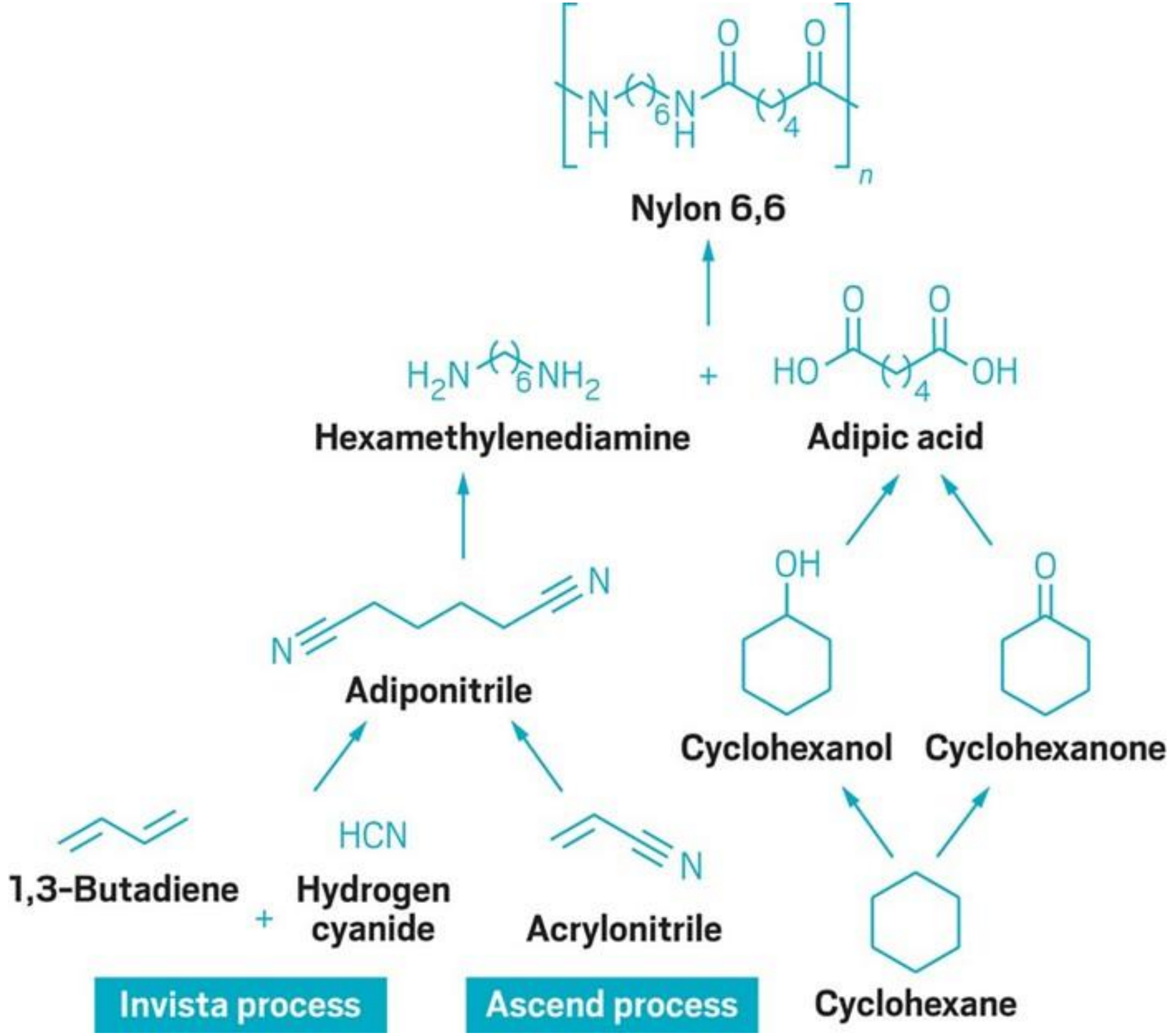
Oxidation vs Reduction (2)



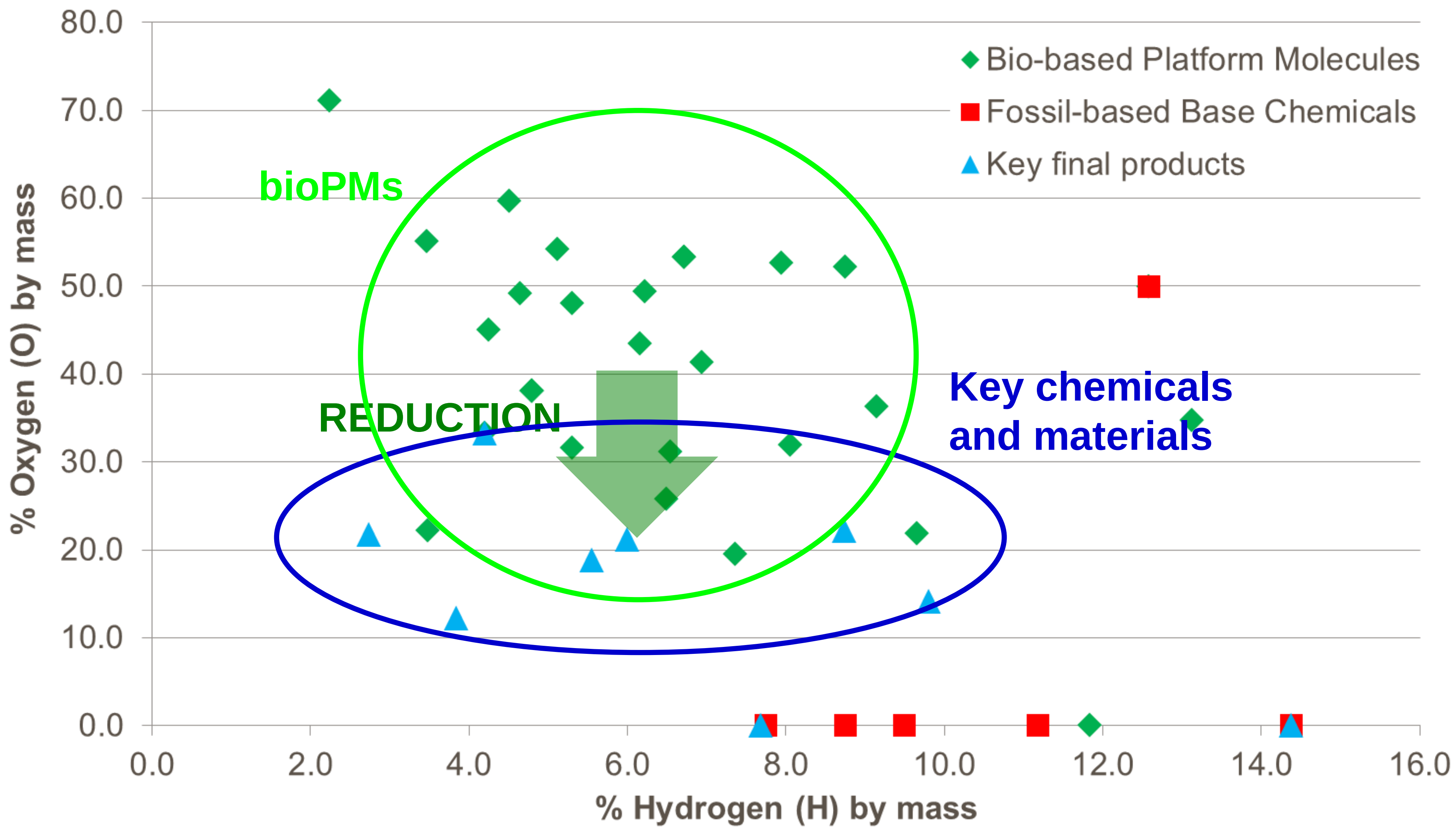
Oxidation vs Reduction (3)



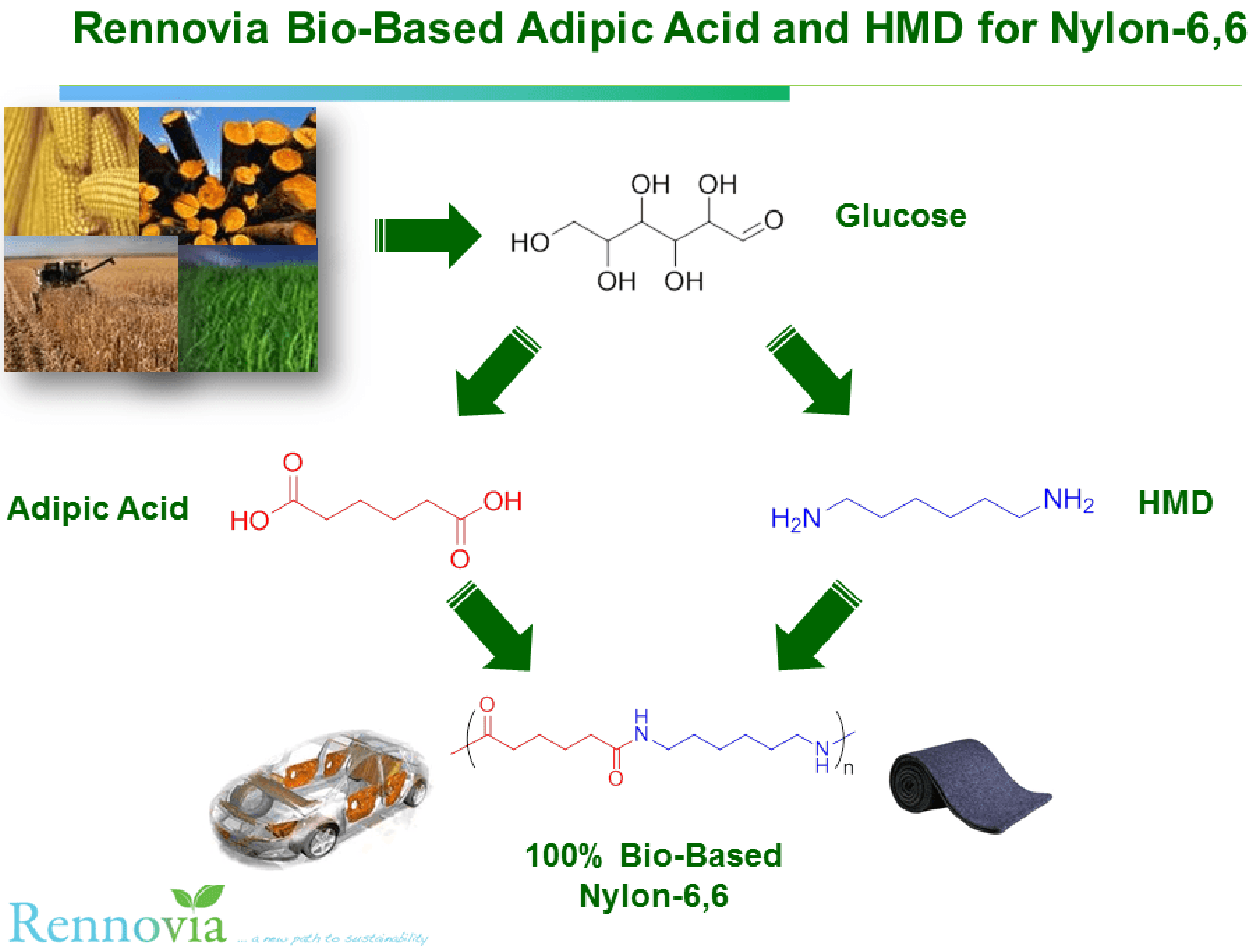
Oxidation Example - Nylon 6,6



Oxidation vs Reduction (4)



Reduction Example - Nylon 6,6



Strategy for using Biomass as a Feedstock

Use high O-content constituents for large volume applications and low O-content parts for low volume / high value products.

Waste Biomass
(inc. food waste)

- **glucose, fructose**
- **cellulose, hemicellulose**
- mannitol
- **chitin**
- **protein**
- **lignin**
- anacardic acid
- triglycerides
- terpenes

High O-content

Low O-content

bold: high volume

Some Examples

Most promising platform molecules (1) - U.S. DoE

2004 (Top 12)

Four carbon 1,4-diacids (succinic, fumaric and malic)

2,5-furandicarboxylic acid (FDCA)

3-Hydroxy propionic acid (3-HPA)

Aspartic acid

Glucaric acid

Glutamic acid

Itaconic acid

Levulinic acid

3-Hydroxybutyrolactone

Glycerol

Sorbitol

Xylitol/arabinitol

2010 (Top 10)

Ethanol

Furans

Glycerol (and derivatives)

Biohydrocarbons (isoprene)

Lactic acid

Succinic acid

Hydroxypropionic acid/aldehyde

Levulinic acid

Sorbitol

Xylitol

Werpy & Petersen, *Top Value Added Chemicals From Biomass,* U.S. Department of Energy, **2004**

Bozell & Petersen, **2010**, *Green Chem.*, 12, 539-552

Most promising platform molecules (2) - U.S. DoE

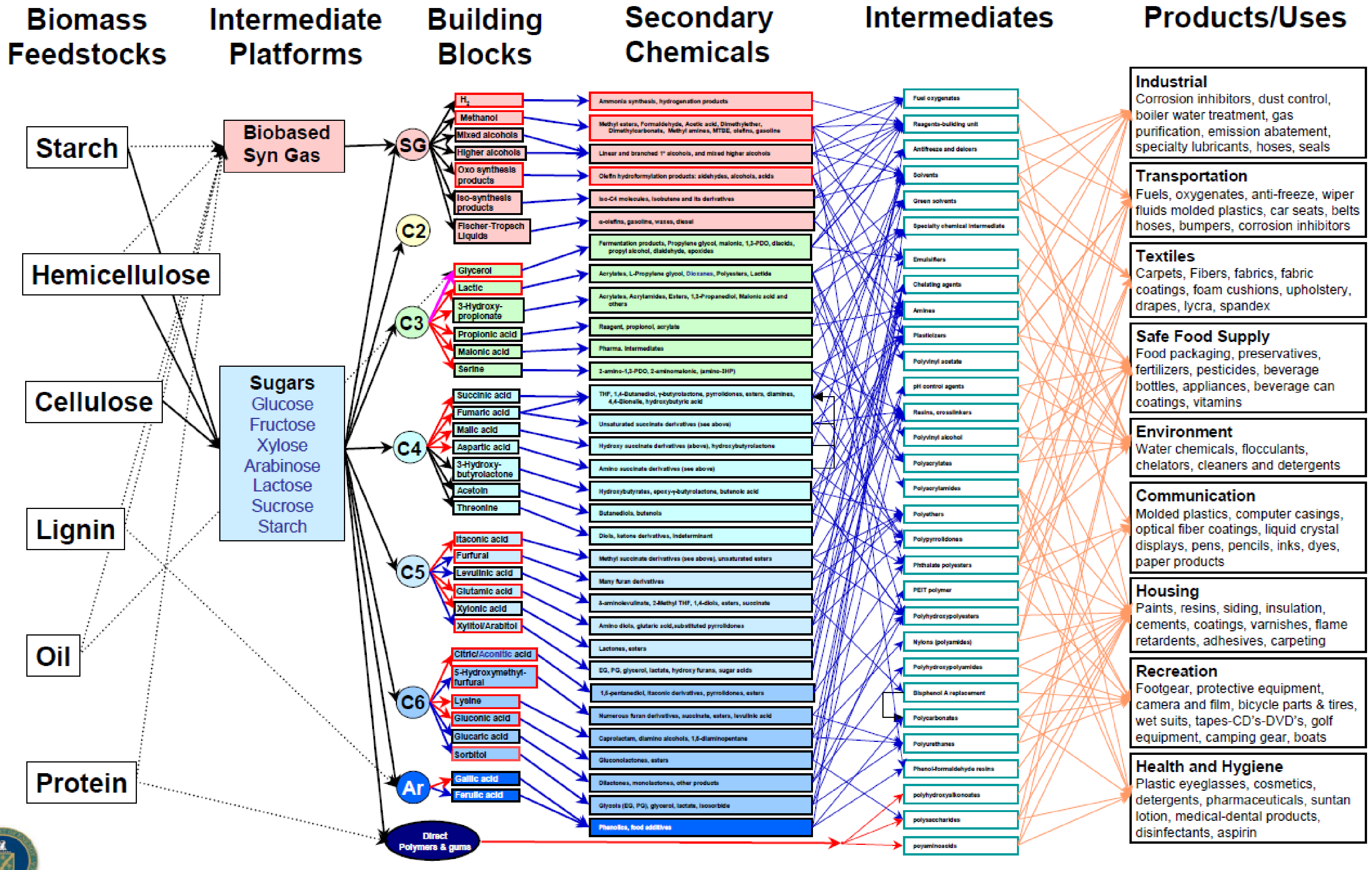
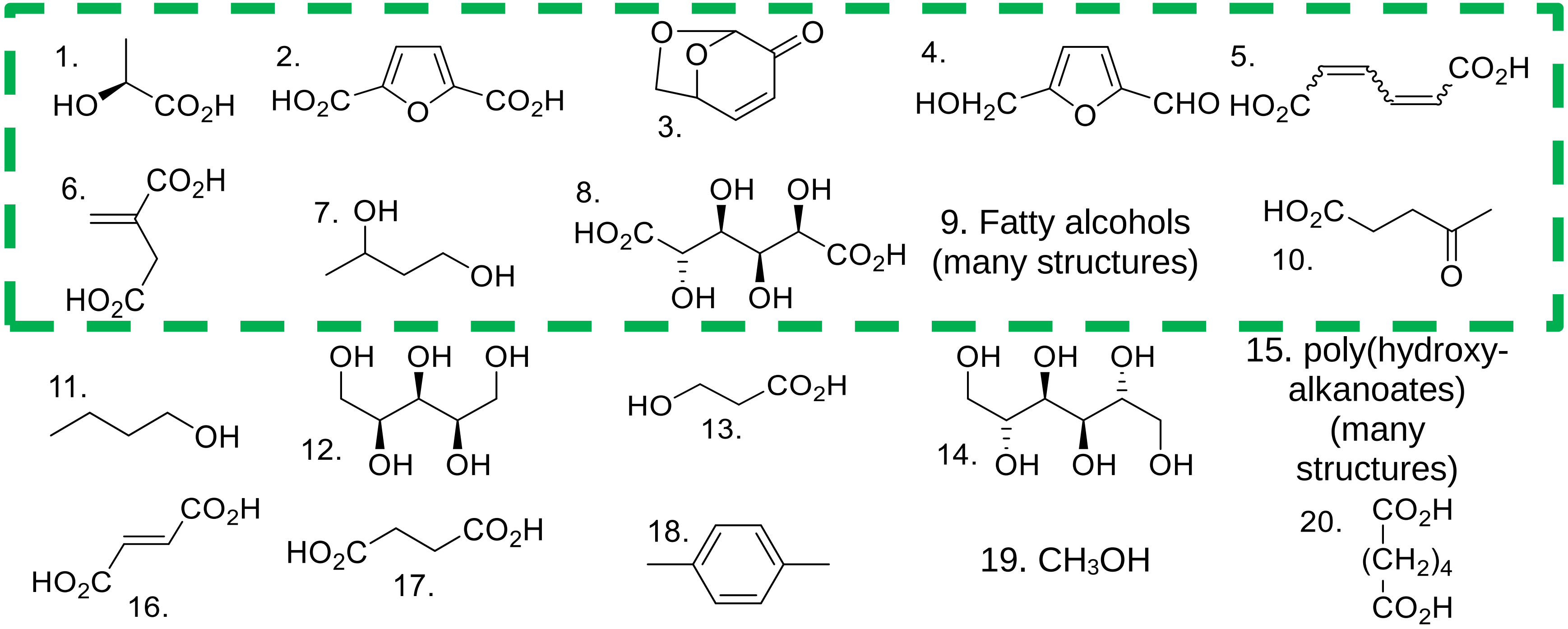


Figure 1 – Analogous Model of a Biobased Product Flow-chart for Biomass Feedstocks

Most promising platform molecules (3) - UK

UKBioChem10 is a list of the UK's **most promising** bio-derived building-block chemicals (platform molecules). The list contains both:

1) molecules the UK **already has a strong foothold** in
2) molecules which are **envisaged to become** very significant to industry in the future and therefore require further support in their development.



http://ukbiochem10.co.uk/

Most promising platform molecules (3) - UK

UKBioChem10

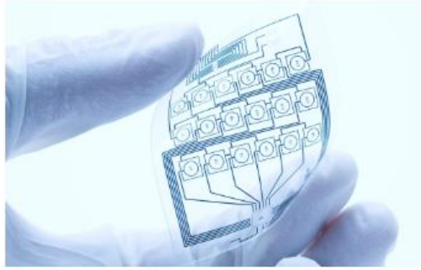
BACKGROUND TOP TEN OUR GOALS WHO WE ARE NEWS

LACTIC ACID

Used to make PolyLactic Acid (PLA), which can form biodegradable plastics.

2,5-FURANDICARBOXYLIC ACID (FDCA)

Can be used to make polymers such as PEF, a stronger alternative to PET, which is a fibre used to make plastic bottles, food packaging and carpets.



LEVOGLUCOSENONE

A safer alternative to harmful solvents used in pharmaceutical manufacturing, and also used in flavours and fragrances.

5 HYDROXYMETHYL FURFURAL (HMF)

A versatile chemical with potential to replace chemicals used in plastics and polyesters, and for producing high energy biofuel.

MUCONIC ACID

Derivatives could replace non-sustainable chemicals used in the

GLUCARIC ACID

Prevents deposits of limescale and

ITACONIC ACID

A replacement for petroleum-based acrylic acid, used to make absorbent

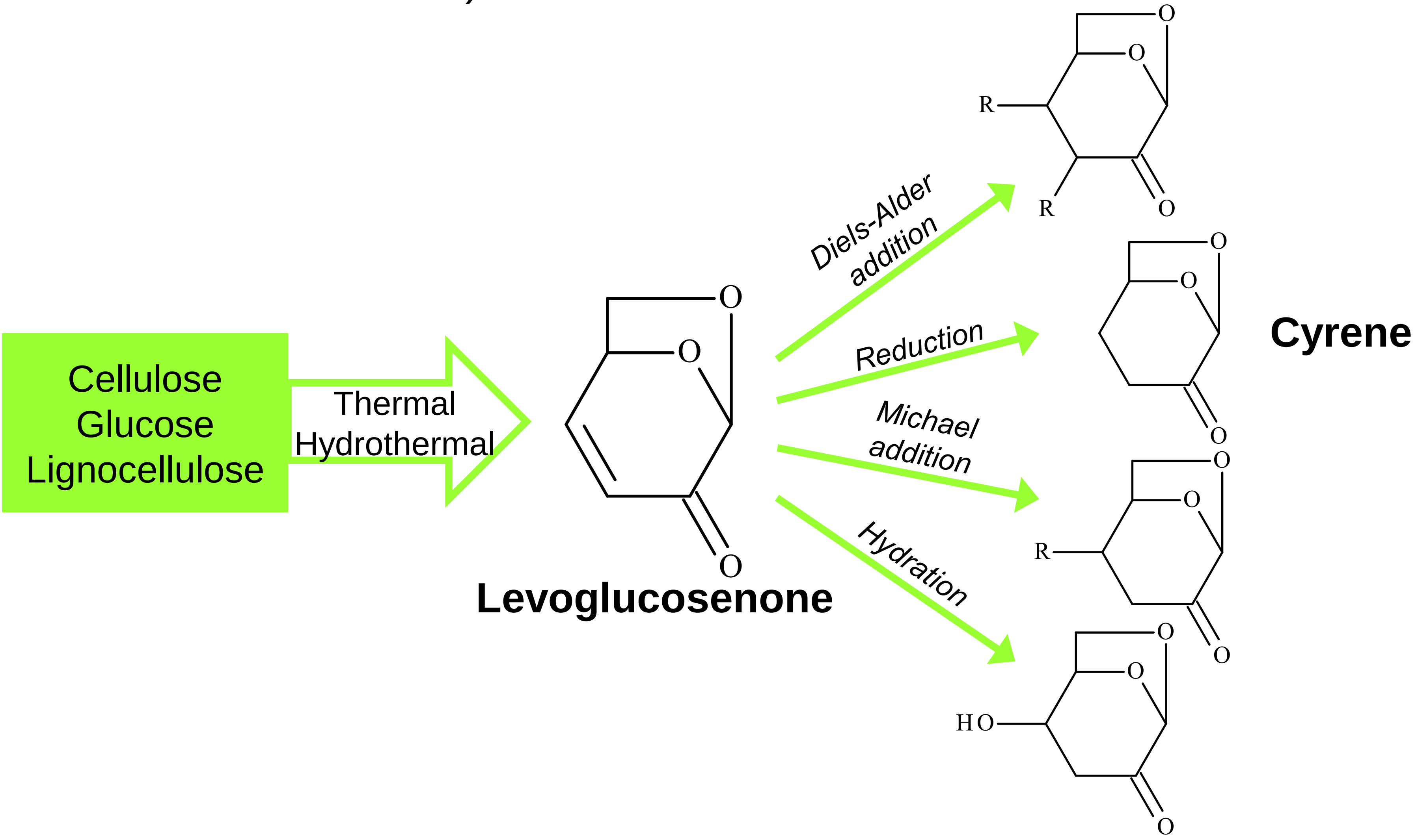
1,3-BUTANEDIOL (1,3-BDO)

A building block for many high value products including pheromones,

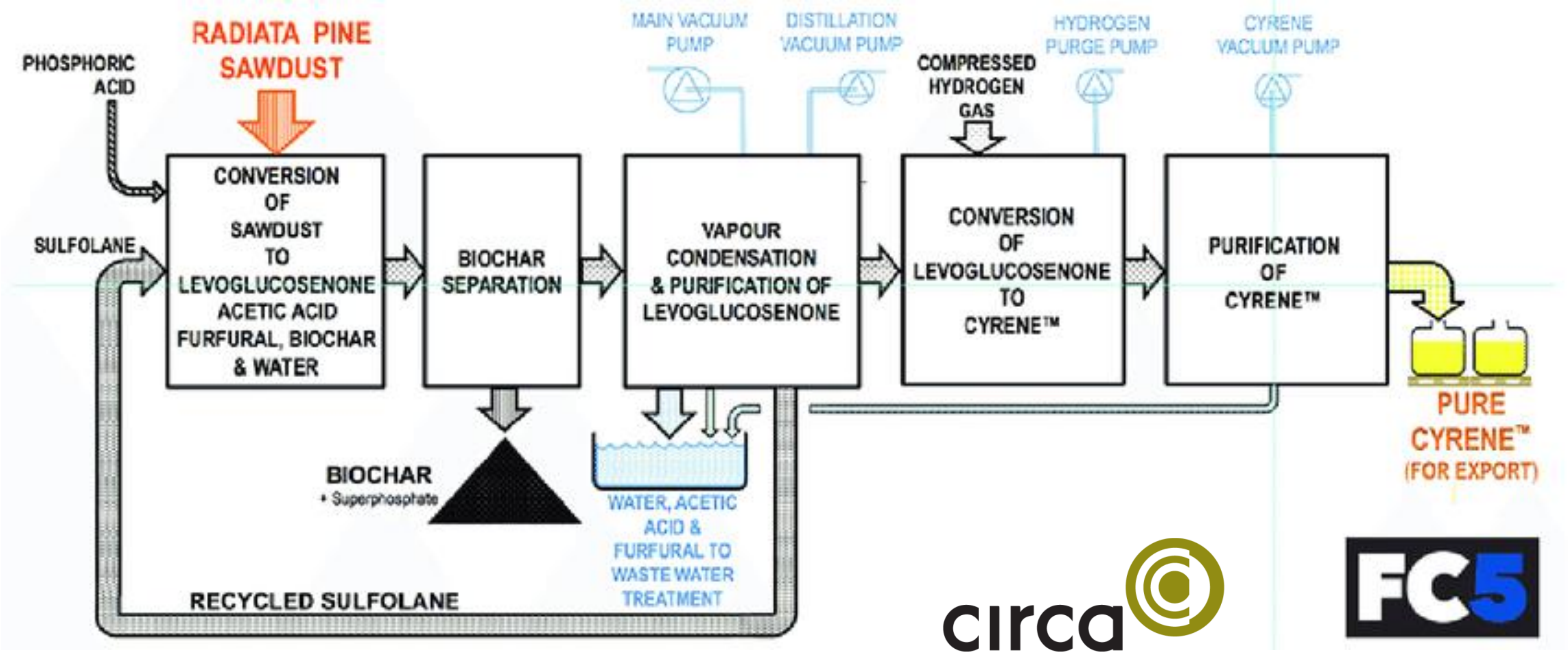
http://ukbiochem10.co.uk/

Levoglucosenone

Example of a **thermal process** (sometimes assisted by an acid catalyst, then would be **thermo-chemical**)



Levoglucosenone - The Process



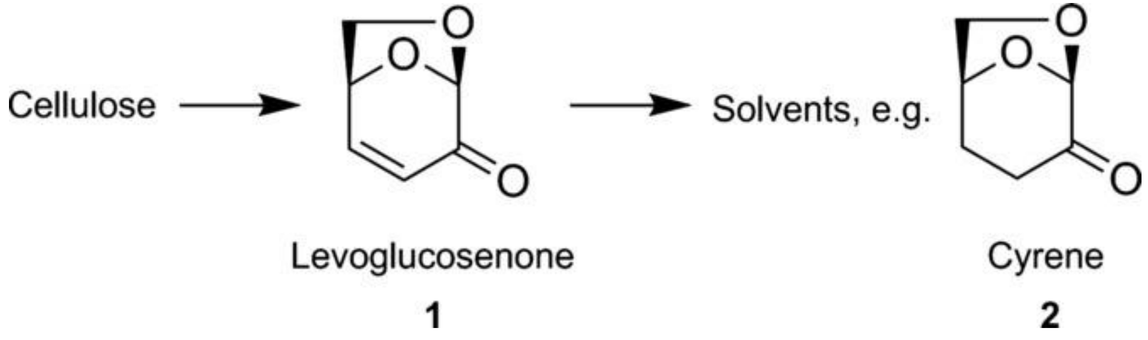
The **Furacell™** process is currently the only technology that allows production of LGE and **Cyrene™** on a scalable basis

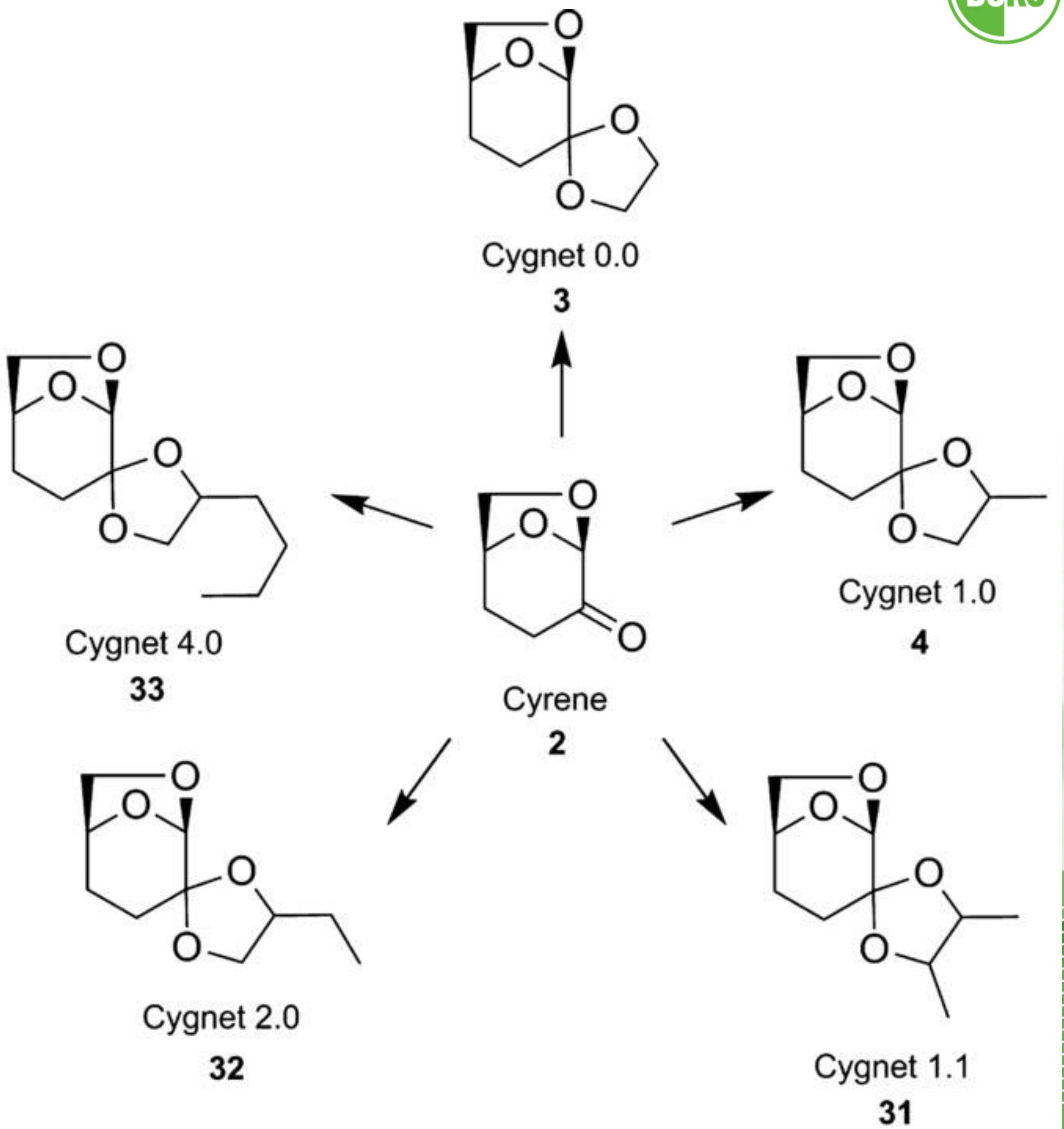
Levoglucosenone - Biocatalysis

- Enzymatic process involving alkene reductases: wild-type Old Yellow Enzyme 2.6 (OYE 2.6 wt.) from *Pichia stipitis* and its mutant (OYE 2.6 Tyr78Trp)
- No formation of side-products, total conversion (99%)
- Cyrene® successfully isolated by continuous extraction, quantitative yield (99%)

Mouterde et al. **2018**, *Green Chem.*, 20, 5528-5532

Levoglucosenone - What‘s next?

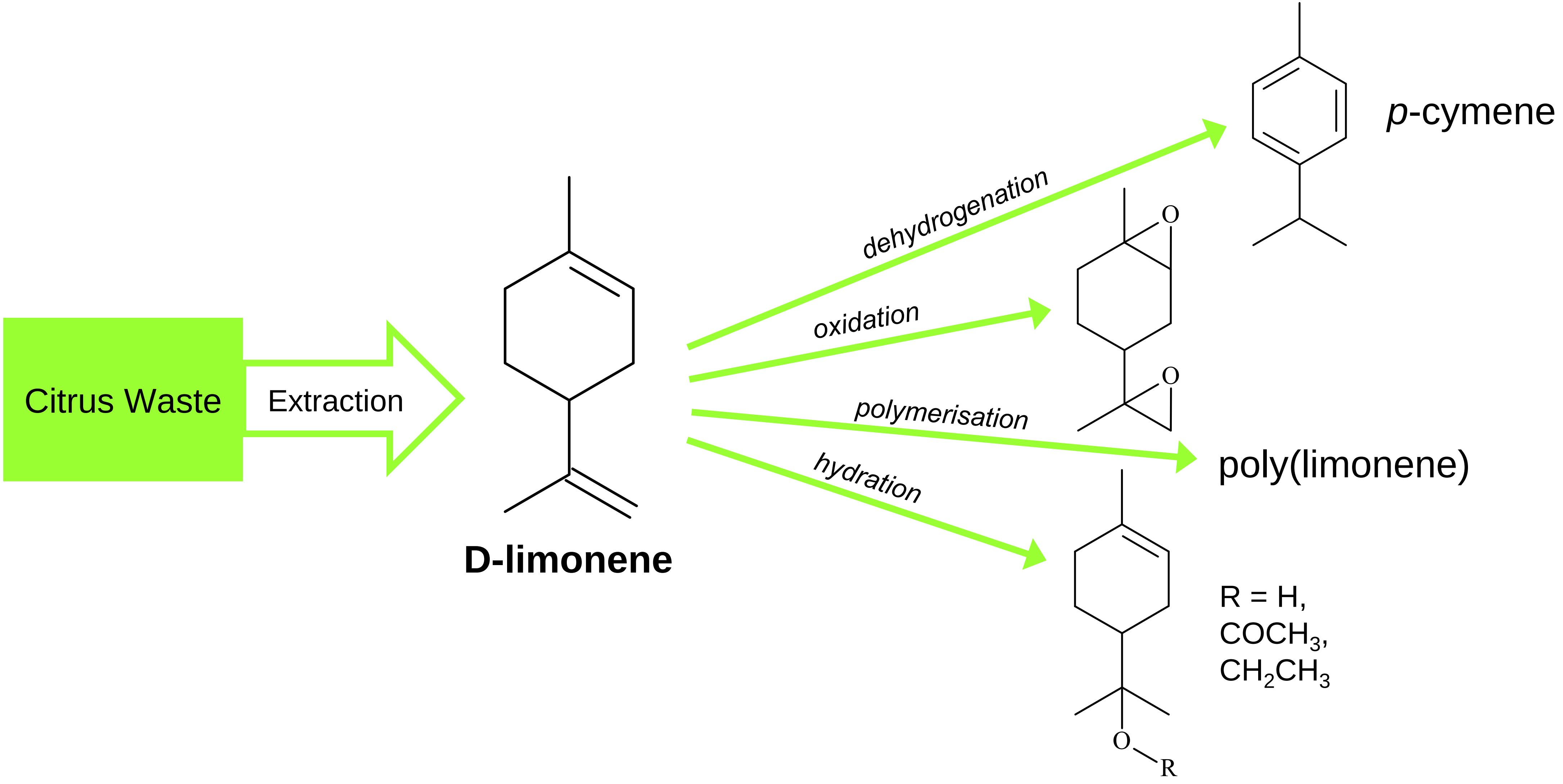




Costa Pacheco et al. **2016**, *ChemSusChem*, 9 (24), 3503-3512

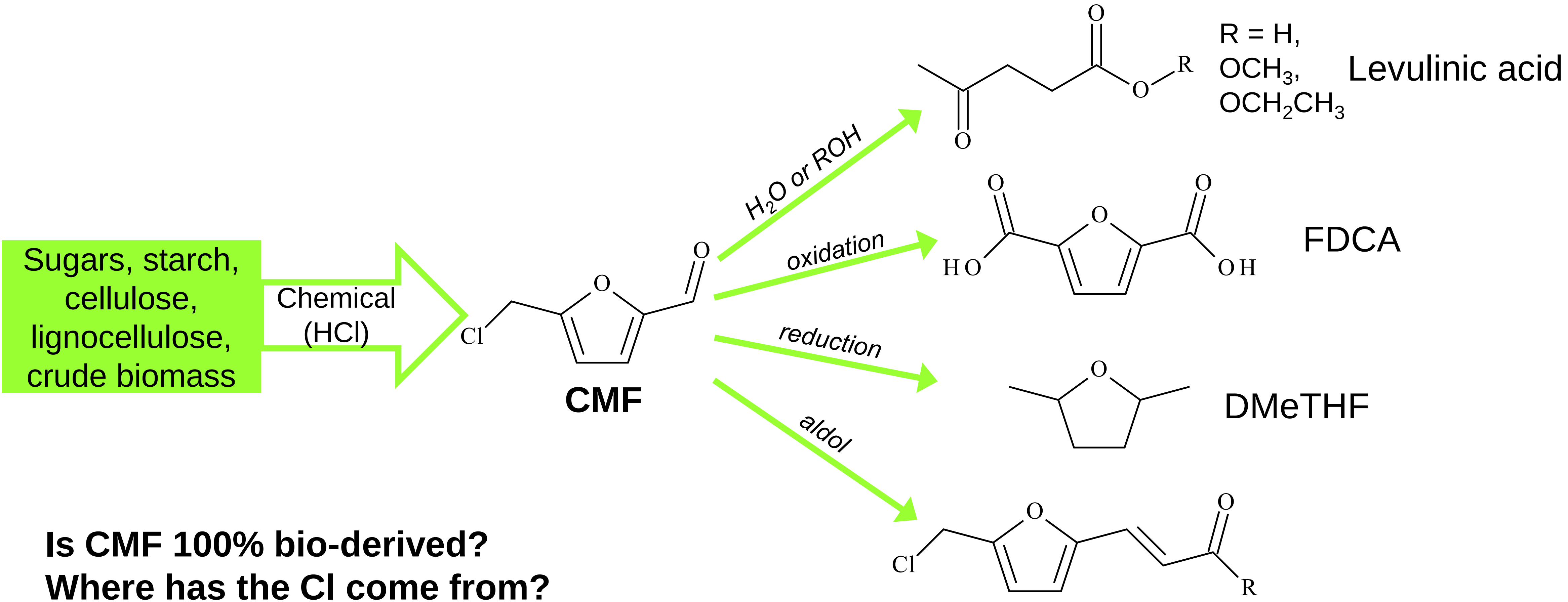
D-Limonene

Example of an **extraction process**. Limonene is already present in biomass and so needs to be removed (extracted) *via* pressing, steam distillation, $scCO_2$ extraction etc.



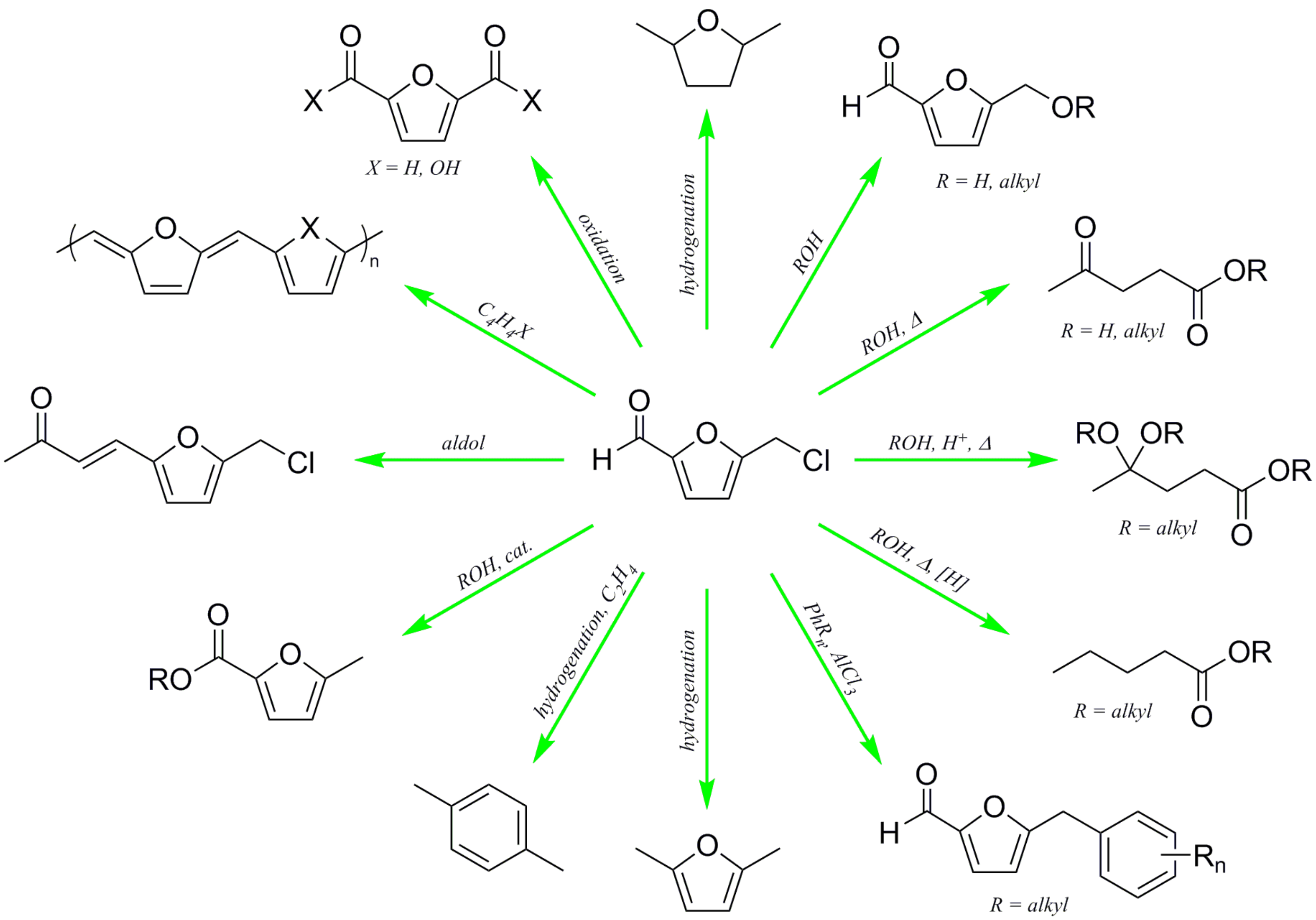
5-(chloromethyl)furfural

Example of a **chemical process**. CMF is formed from several dehydration of sugars and also includes the addition of a Cl atom *via* nucleophilic substitution



Is CMF 100% bio-derived?
Where has the Cl come from?

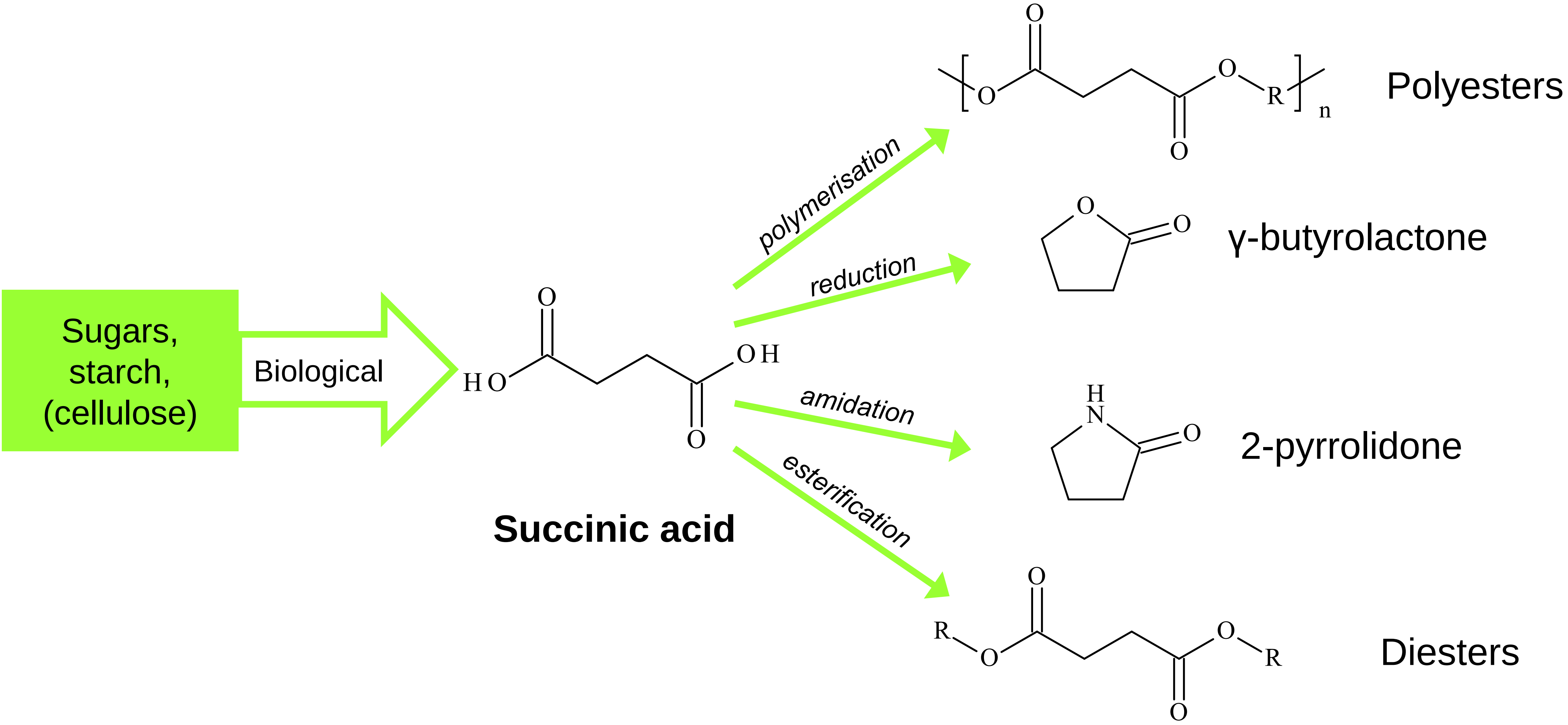
5-(chloromethyl)furfural - derivatives



Farmer & Mascal, *Platform Molecules*, John Wiley & Sons, Ltd., **2014**

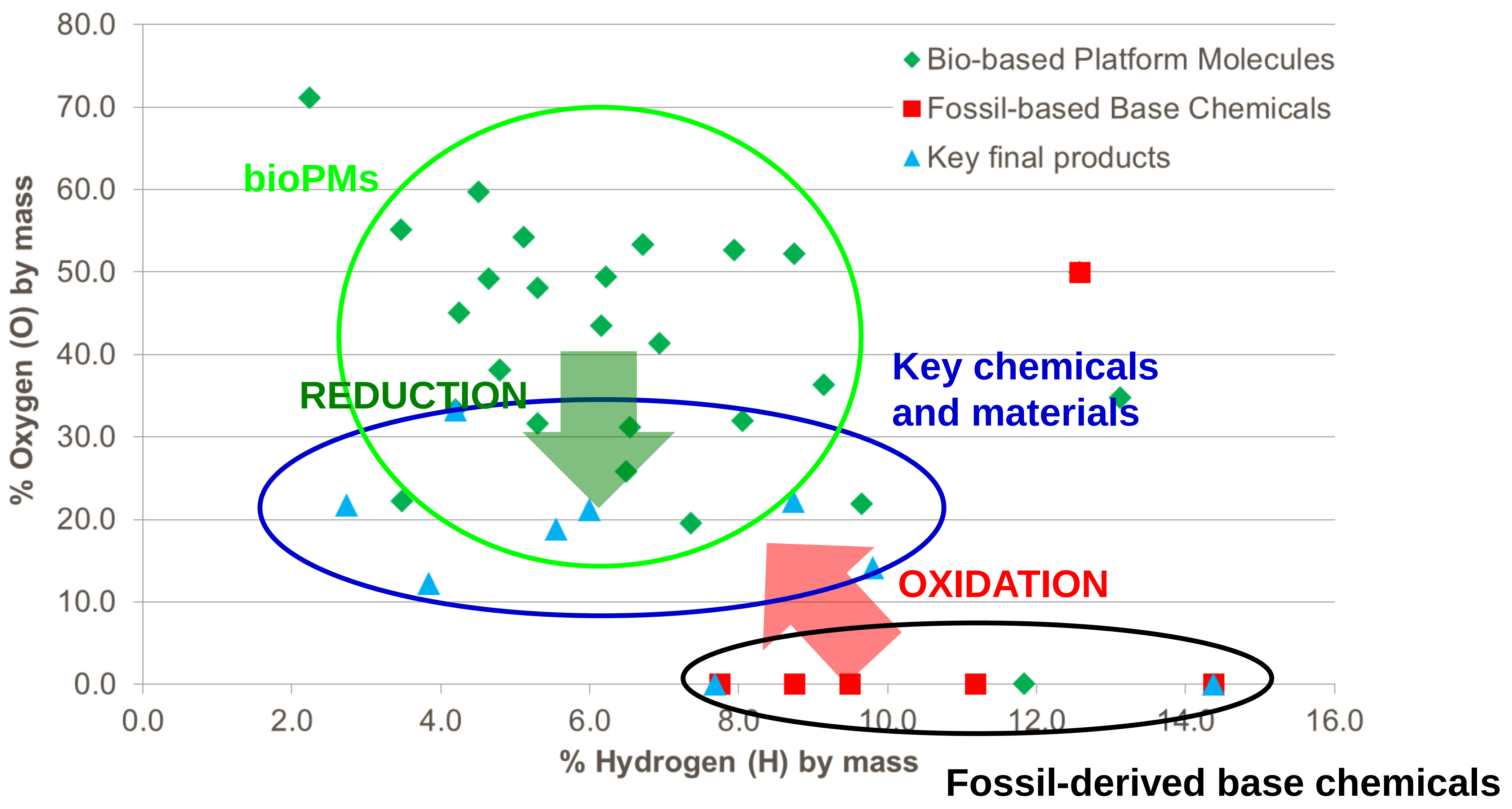
Succinic Acid

Example of a **biological process**. Carbohydrates (i.e. sugars) are fermented *via* bacteria or yeasts (single cell funghi) to produce succinic acid

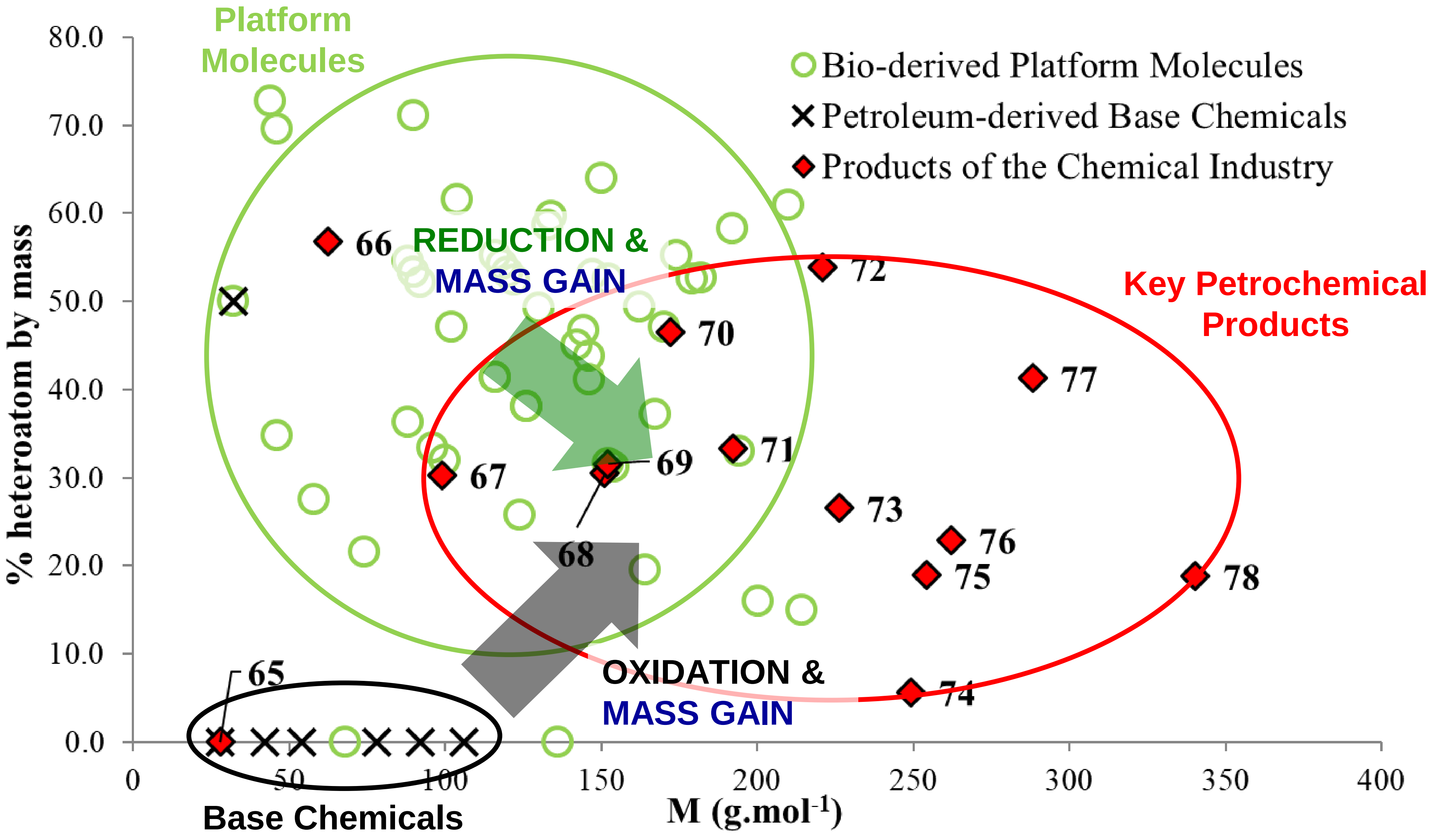


Polymers from Biomass

Oxidation vs Reduction - Summary

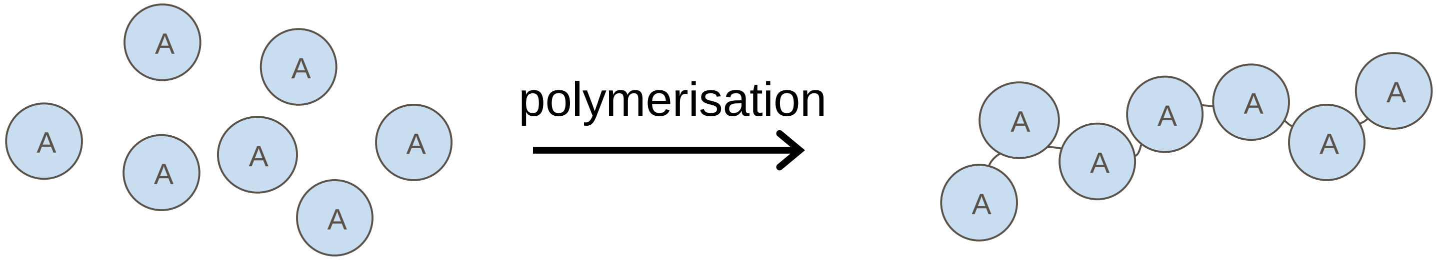


BioLogicTool: Plotting Heteroatom Content



Lie, Y. et al., **2019**, *Ind. Eng. Chem. Res.*, 58, 15945-15957

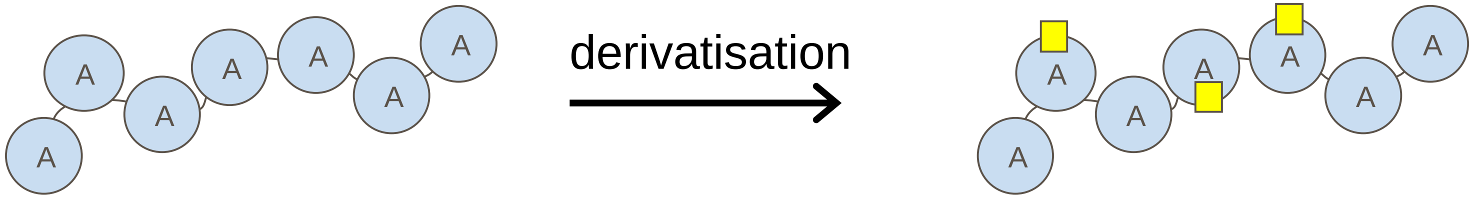
■ Polymerization



Monomers

Polymer
Step-growth or chain-growth

■ Modification/Functionalization



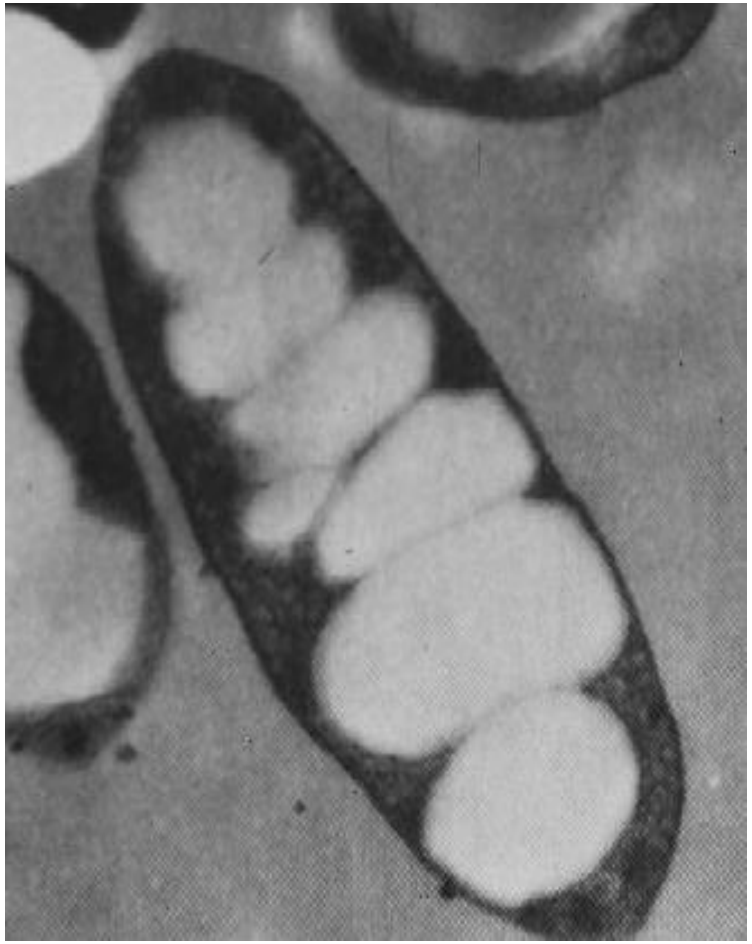
Polymer

Derivatised polymer

Poly(hydroxyalkanoates) (PHA)

Poly(hydroxyalkanoates) PHA's are linear polyesters produced by bacteria as a means to store carbon and energy (equivalent of fat that human produce for winter energy storage/hibernation.

- No economically viable PHA process has yet emerged.
- The challenge facing fermentative PHA production led to a series of attempts to engineer crop plants for the production of PHAs.
- An improved method comes from the use of PHA producing bacteria (E. coli) in a fermenter, using a glucose feedstock. The E. coli internally concentrate the PHA, which can be removed by simple extraction.



Bacterial cell (*Ralstonia eutropha*) producing a PHA polymer. The round objects are polymer granules.

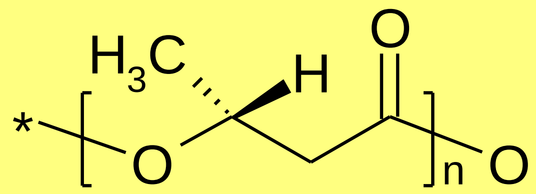
Poly(hydroxyalkanoates) (PHA) - Structure

- **Polyhydroxybutyrate (PHB)** simplest and most studied polymer. This is the easiest polymer to synthesised and the most common polymer found in bacteria

- Changes in the E. coli, or simply in the feedstock can result in the **formation of copolymers**

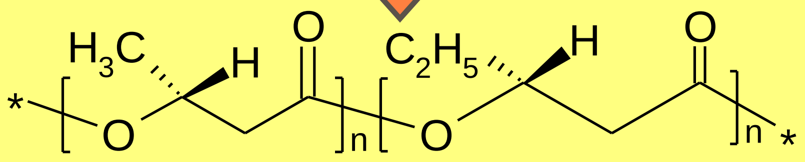
- By varying the nature of the copolymer the properties of the materials can be altered

- Monsanto began to focus on producing PHB from GM plants instead of bacteria



poly[R-3-hydroxybutyrate] homopolymer

polyhydroxy valerate (PHV)
the most common copolymer, forming P(3HB-co-3HV).



(*R*)-3HB **(*R*)-3HV**

P(3HB-co-3HV)

Poly(hydroxyalkanoates) (PHA) - Properties & Potential Uses

Wide range of properties highly dependent on the constituting monomer units (to date >120 distinct monomers have been characterized) and molecular weight.

PHB ⇨ stiff, highly crystalline materials

PHO ⇨ rubbery elastomers

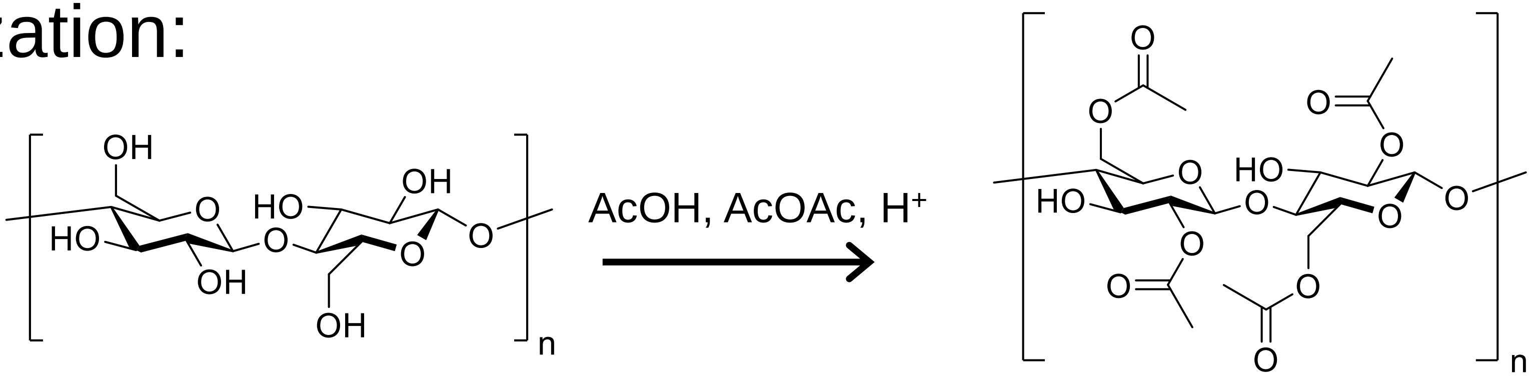
The uses of such polymers depend on their properties.

- PHB has properties that mean it could replace polypropylene (Greenpeace biodegradable credit card).
- PHO could be used to replace natural rubber.

PHBV (commercially named Biopol^{TM})

Cellulose Acetate

- Derivatization:

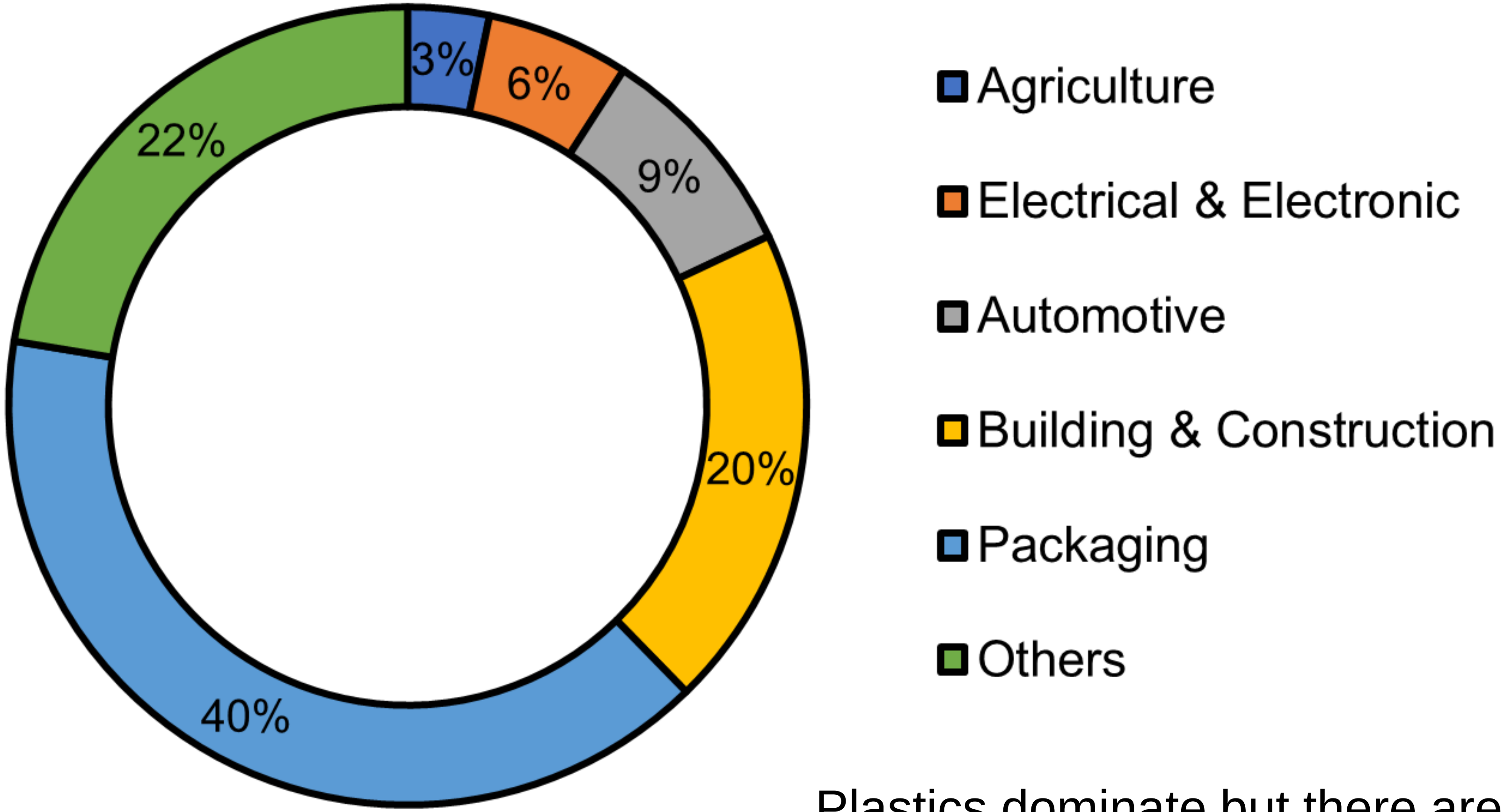


Cellulose (i.e. from purified wood pulp)

Cellulose Acetate (>92% acetylation)

- After derivatisation:
  - Is a thermoplastic
  - Can be dissolved in many organic solvents
  - Can be dyed
  - Can be composted

Uses of Polymers



Plastics dominate but there are other uses:

- Water-soluble polymers
- Adhesives
- Coatings
- Fabrics
- "glass" (Perspex)
- Dentistry
- Synthetic rubber

Data from: Plastics Europe (2016). Plastics - the Facts **2016**

Term Alert!

Biopolymer

IUPAC definition: “Biobased polymer derived from biomass or issued from monomers derived from the biomass and which, at some stage in its processing into finished products, can be shaped by flow.”

Bioplastic is generally used as the opposite of polymer derived from fossil resources

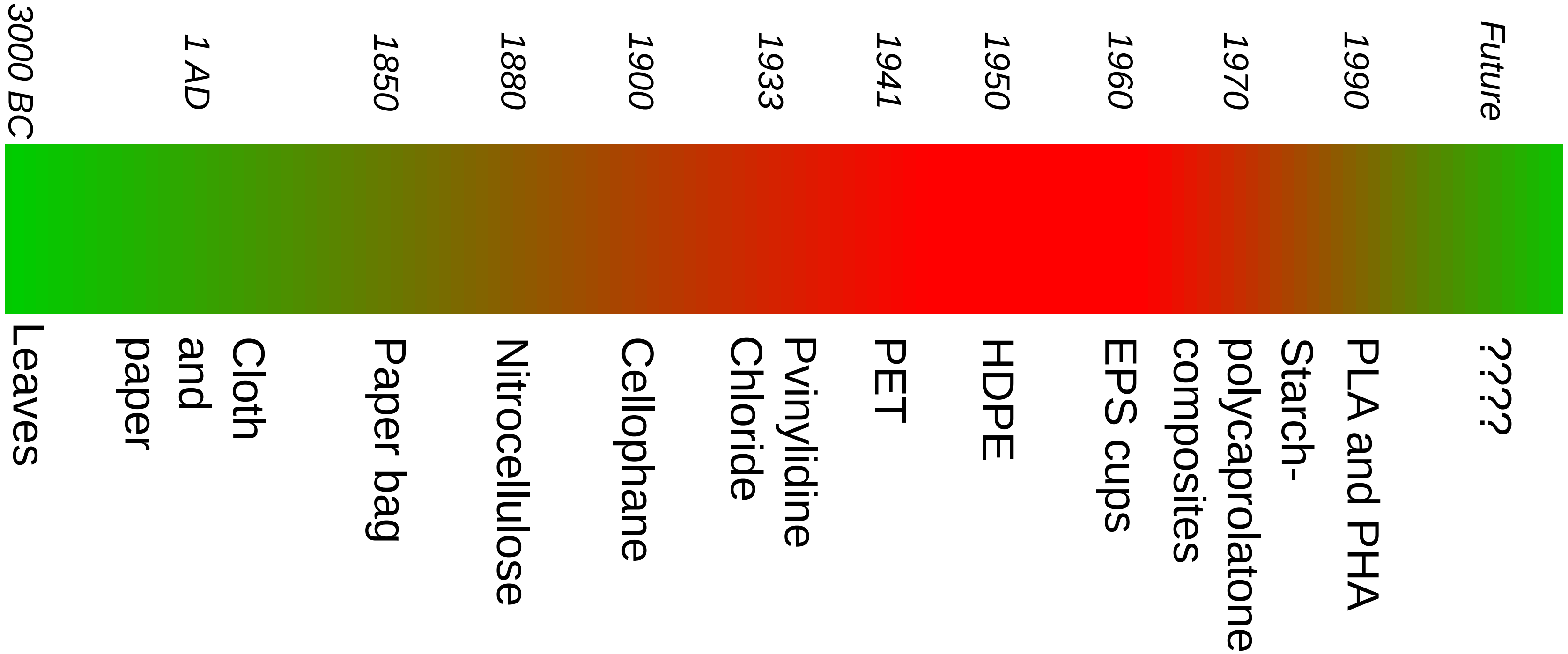
Bioplastic is misleading because it suggests that any polymer derived from the biomass is environmentally friendly

The use of the term "bioplastic" is discouraged. Use the expression "**biobased polymer**".

A bio-based polymer similar to a petrol-based one does not imply any superiority with respect to the environment unless the comparison of respective **life cycle assessments** is favourable.

Vert et al. **2012**, *Pure and Applied Chemistry*, 84, 377-410

The Future of Food Packaging: The Past?



Bio-based
Bio-degradable
Re-circulatable

Fossil-based
Non-Biodegradable
Issues with re-circulation

Bio-based
Bio-degradable
Re-circulatable

Back to the past but we need to be smarter (and we need more choice)

An Example Product - An Old Chair

- 150 years ago (and before)
  - Wood:



Biodegrade

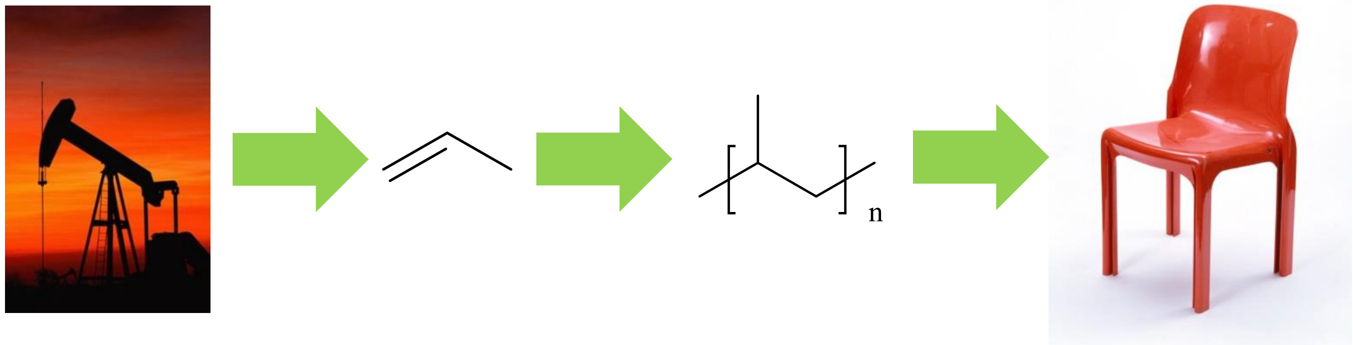
- 100 years ago
  - Steel:



Recycle

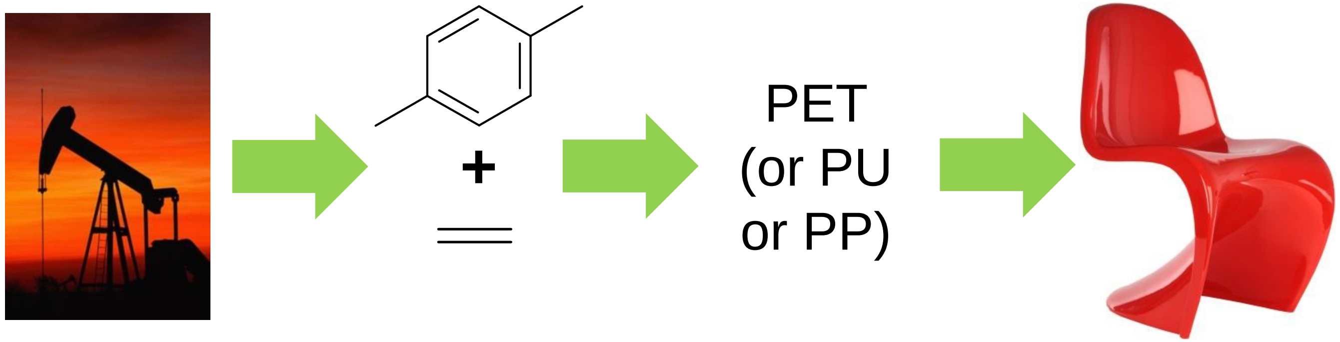
An Example Product - A 1960‘s Chair

- 1960’s
  - Moulded Plastic Chair (Selene) – polypropylene:



Landfill (no obvious economical recycling of PP)

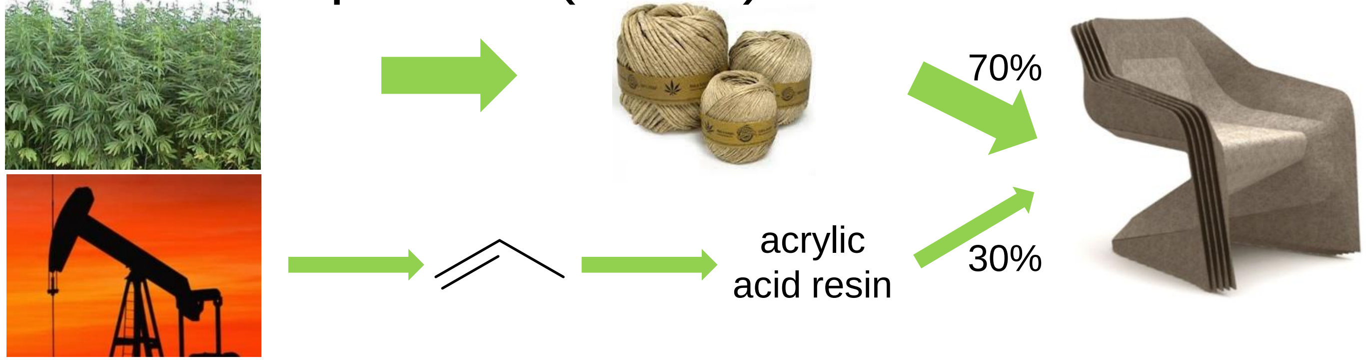
  - Moulded Plastic Chair (Panton) – fibreglass supported PET:



Challenges of composite recycling, or PUs or PP

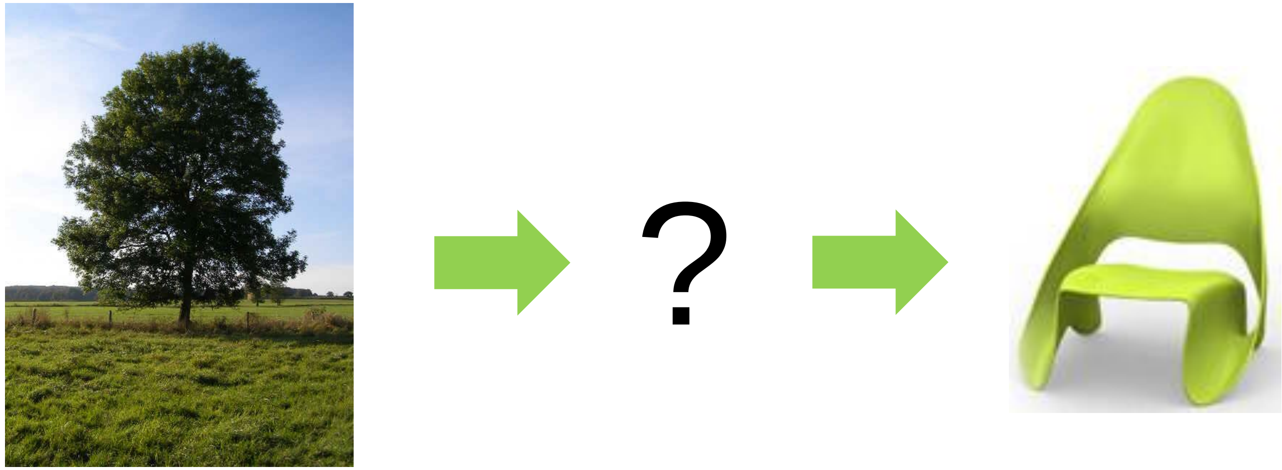
An Example Product - A Modern Chair

- Now (if you are environmentally conscientious)
  - Hemp Chair (BASF):



Biodegradable but what about the resin?

  - Pandanus Chair (cellulose?):



Lack of information. Marketing states that it is bio-based so it is biodegradable!

Universität für Bodenkultur Wien
University of Natural Resources and Applied Life Sciences, Vienna

Bio-based platform chemicals

The end

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