



Bio-sourced polymers

Etienne Grau

► To cite this version:

| Etienne Grau. Bio-sourced polymers. Master. France. 2019. hal-02373076

HAL Id: hal-02373076

<https://hal.science/hal-02373076>

Submitted on 20 Nov 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Bio-sourced polymers

Dr Etienne Grau

egrau@enscbp.fr



There is no such thing as a stupid question,
so please, do not hesitate to interrupt me



1- Why ?

2- How ?

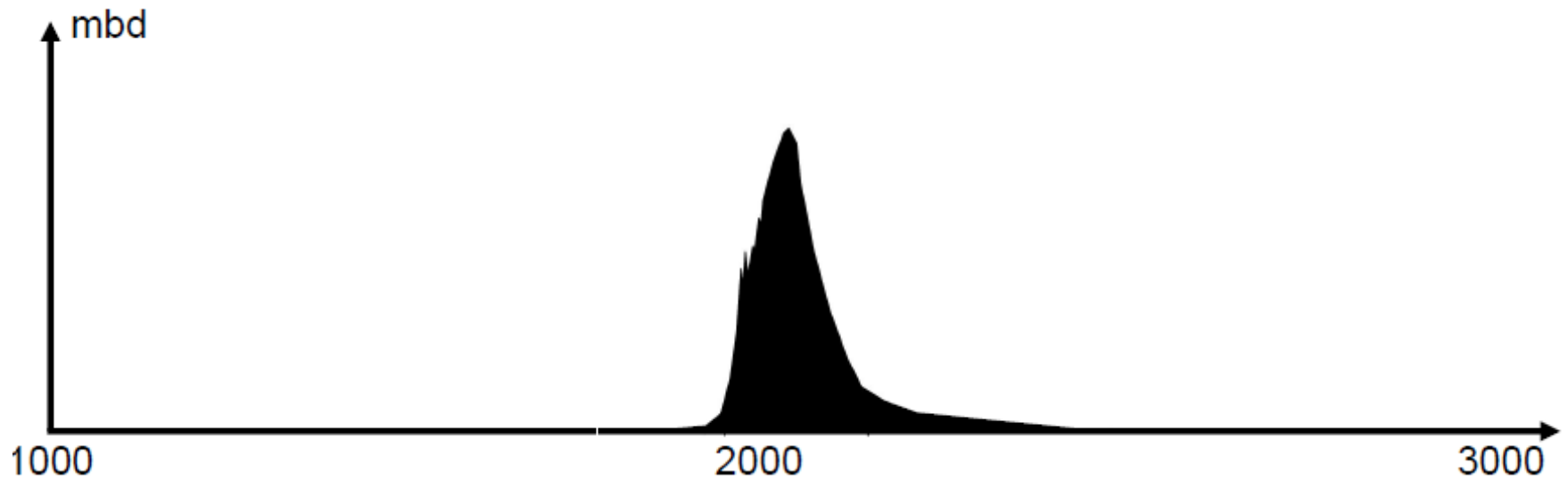
3- Bio-based plastics from natural polymers

4- Drop-ins: Bio-based alternative to fossil-based polymers

5- Smart drop-ins: Bio-based derivative of “fossil” polymers

6- New polymers from biomass

7- Conclusions and perspectives



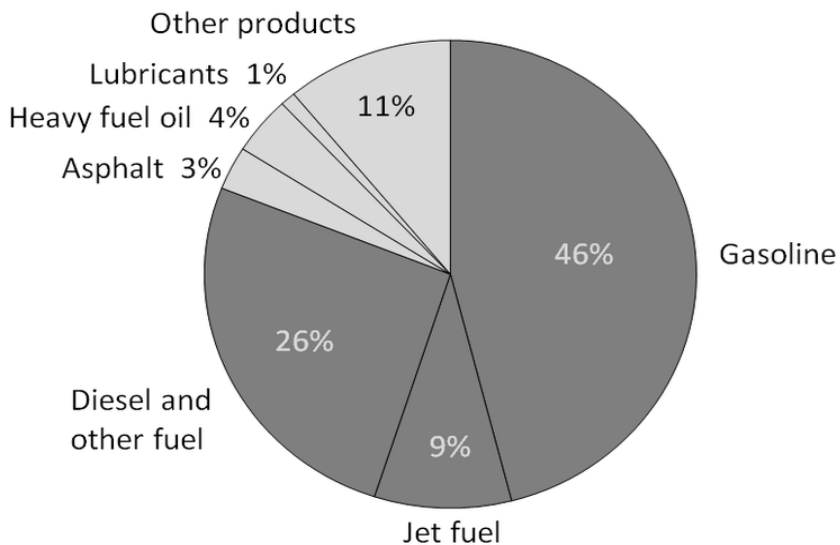
Petroleum: The Source of Chemicals

Petroleum is the starting materials of **99%** « commodity » chemicals

- 33% polymers (PE, PVC, PET, PMMA, PS, nylon ...)
- 30% organic molecules (acetone, toluene, petroleum ether...)
- 20% others (surfactants, pigment, carbon black, ...)
- 12% Inorganic component (soda, acids, Cl_2 , ...)
- 6% Fertilizers (NH_3)

Petroleum = C

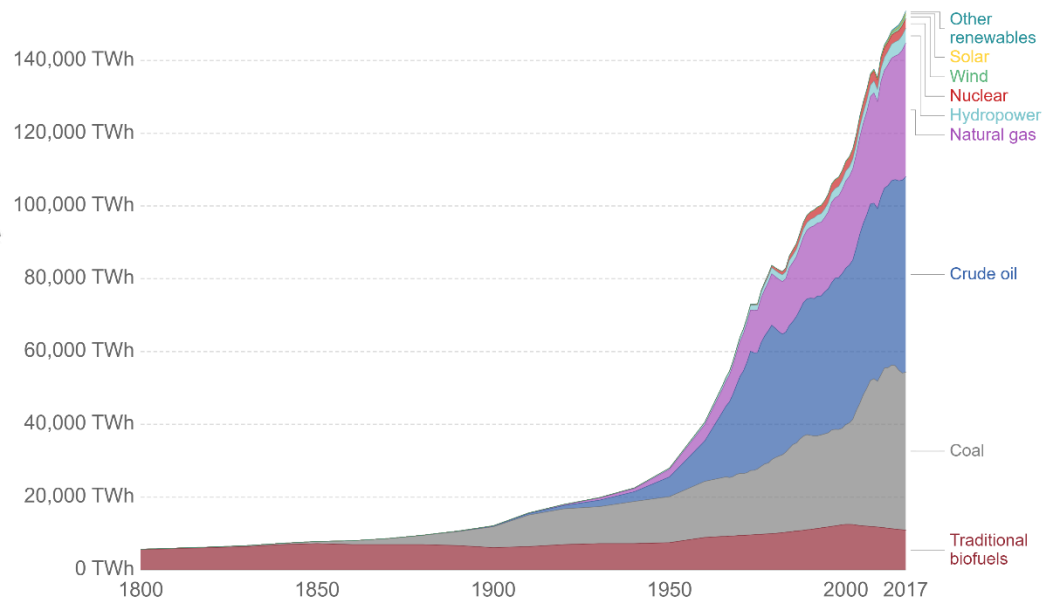
Petroleum = J



Global primary energy consumption

Global primary energy consumption, measured in terawatt-hours (TWh) per year. Here 'other renewables' are renewable technologies not including solar, wind, hydropower and traditional biofuels.

Our World
in Data

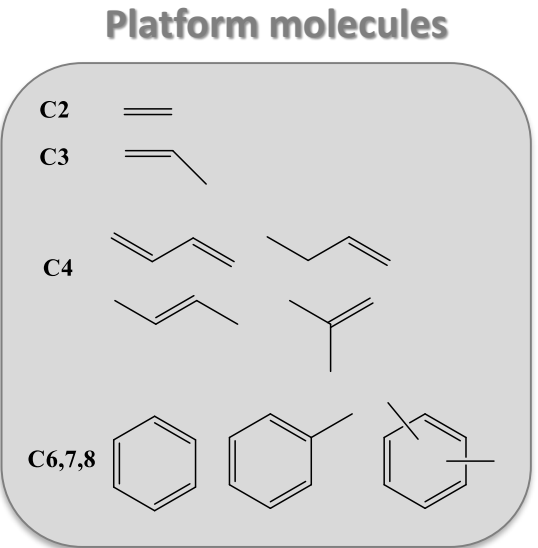
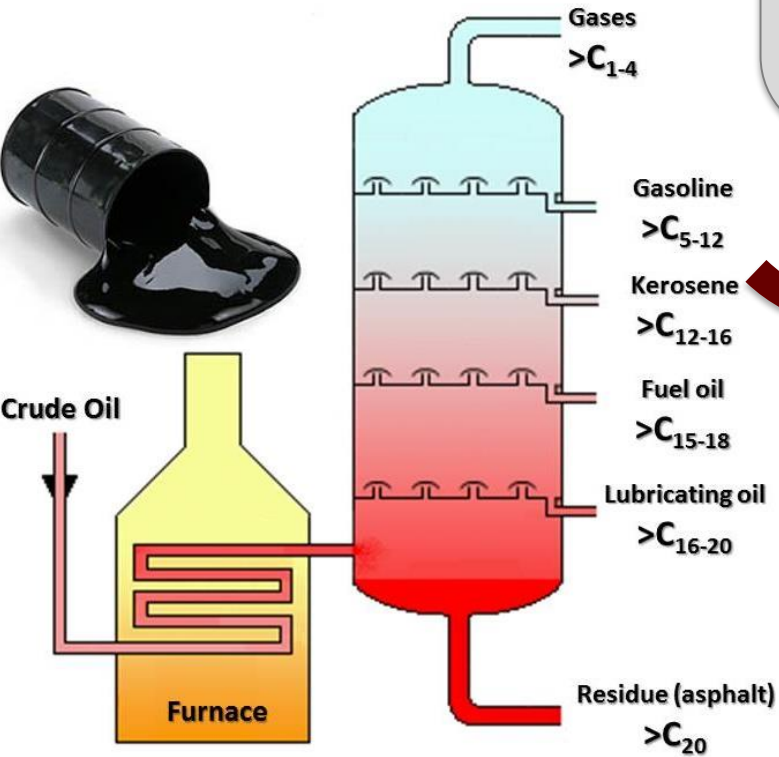


Source: Vaclav Smil (2017) and BP Statistical Review of World Energy

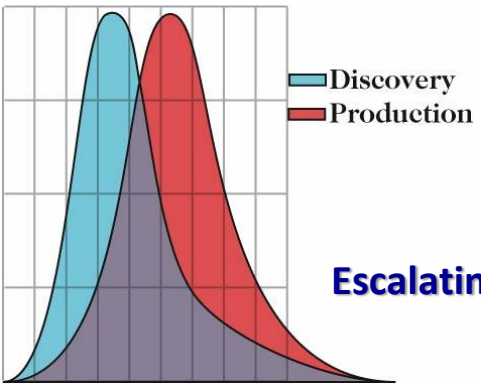
CC BY

Synthetic polymers are based on petroleum

20th century:
A petroleum area



Steel 1800 Mt (230 Mm³)



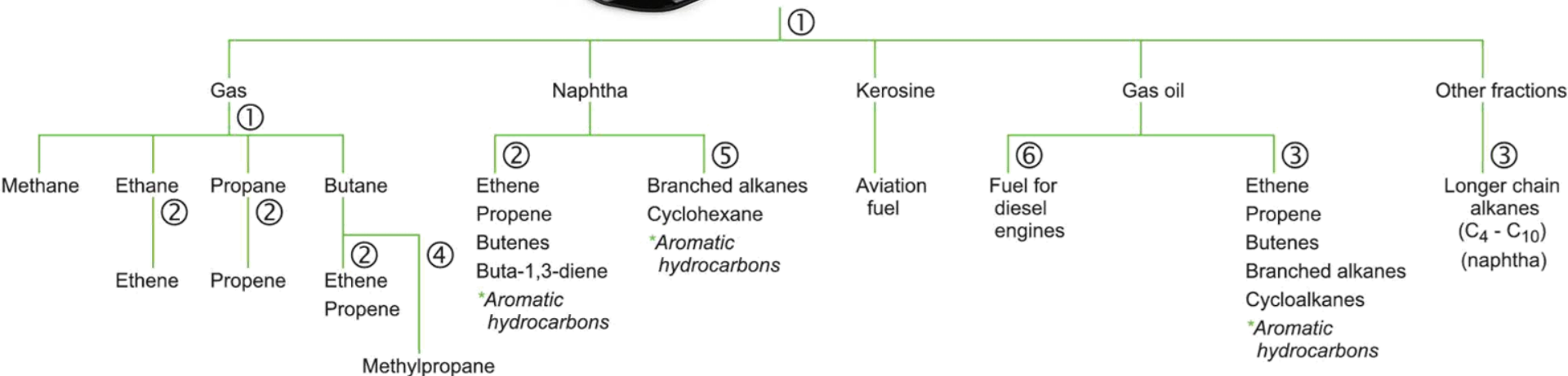
PEAK OIL

Oil depletion
Escalating prices of oil resources

From crude oil to platform molecules



Crude oil

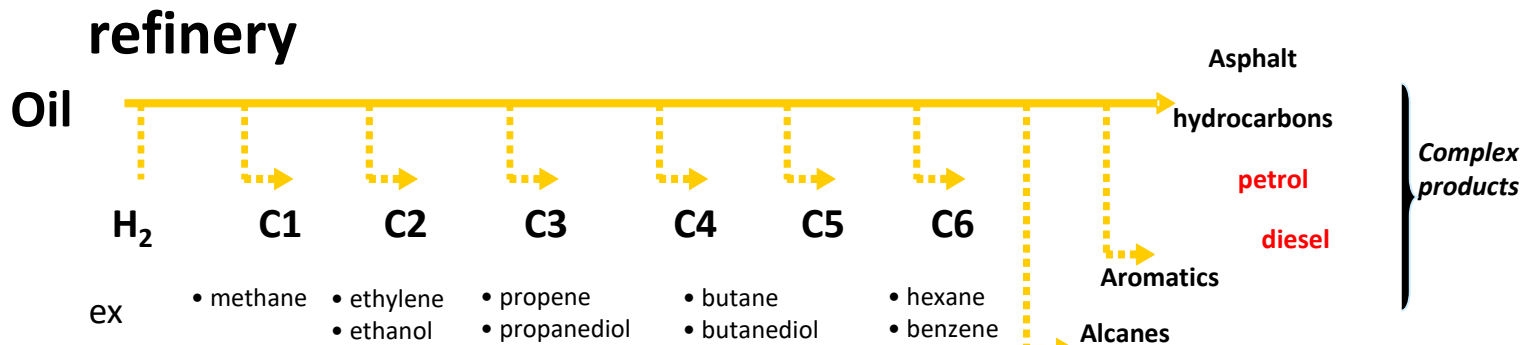


- ① Distillation
- ② Steam cracking
- ③ Catalytic cracking ('hydrocracking')
- ④ Isomerisation
- ⑤ Reforming ('platforming')
- ⑥ Sulfur is removed



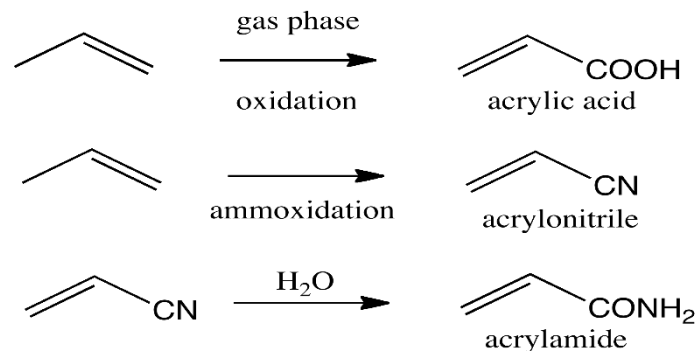
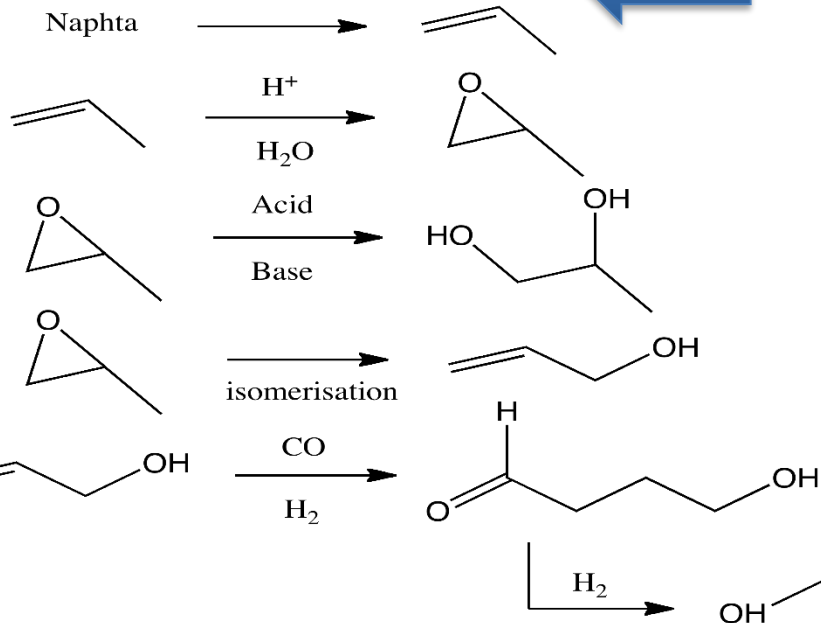
**Aromatic hydrocarbons:*
benzene
methylbenzene
dimethylbenzenes
ethylbenzene

Oil refinery – example of the C3 platform

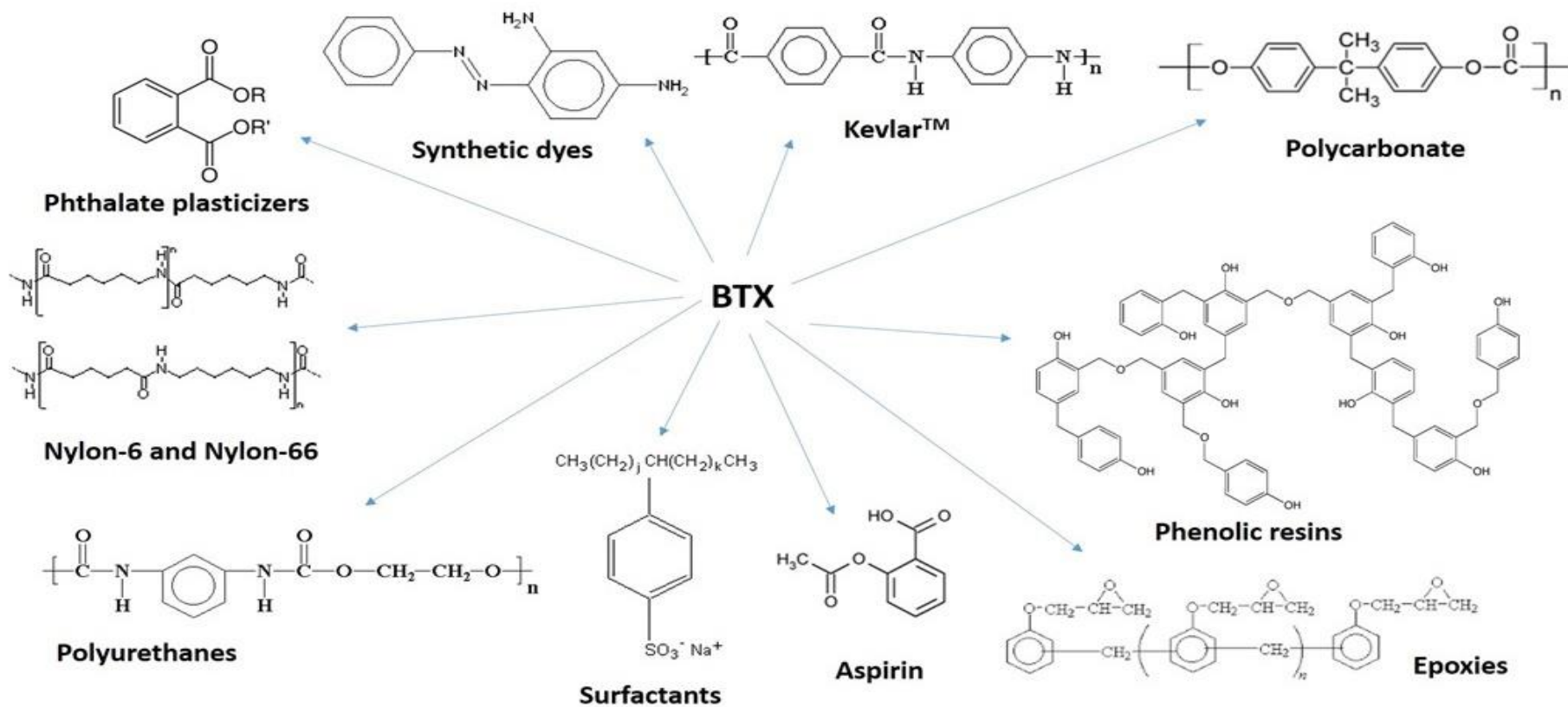


cuts

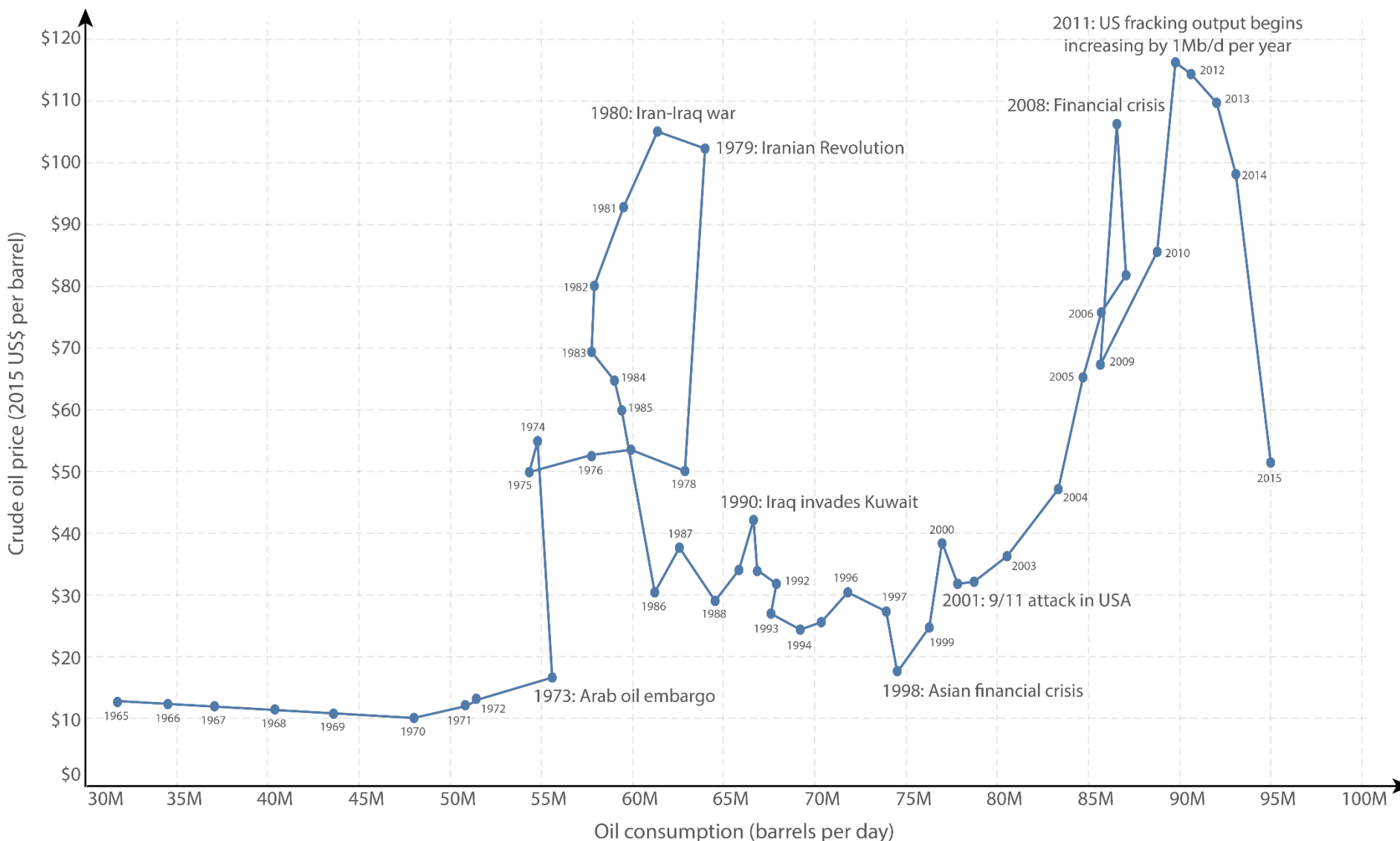
Naphta



Oil refinery – example of the BTX platform

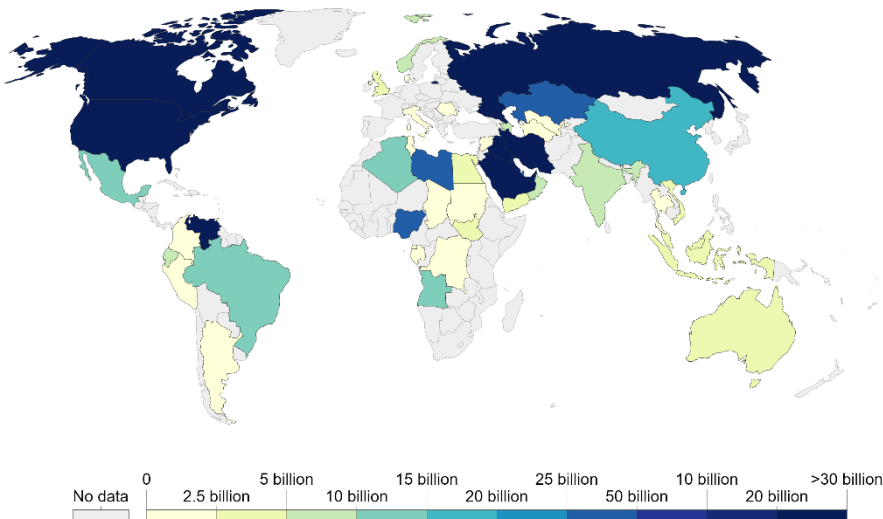


World crude oil price vs. oil consumption

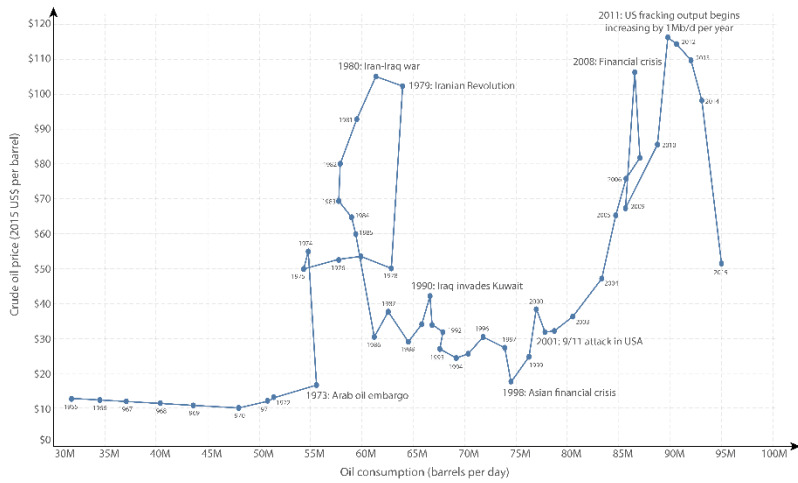
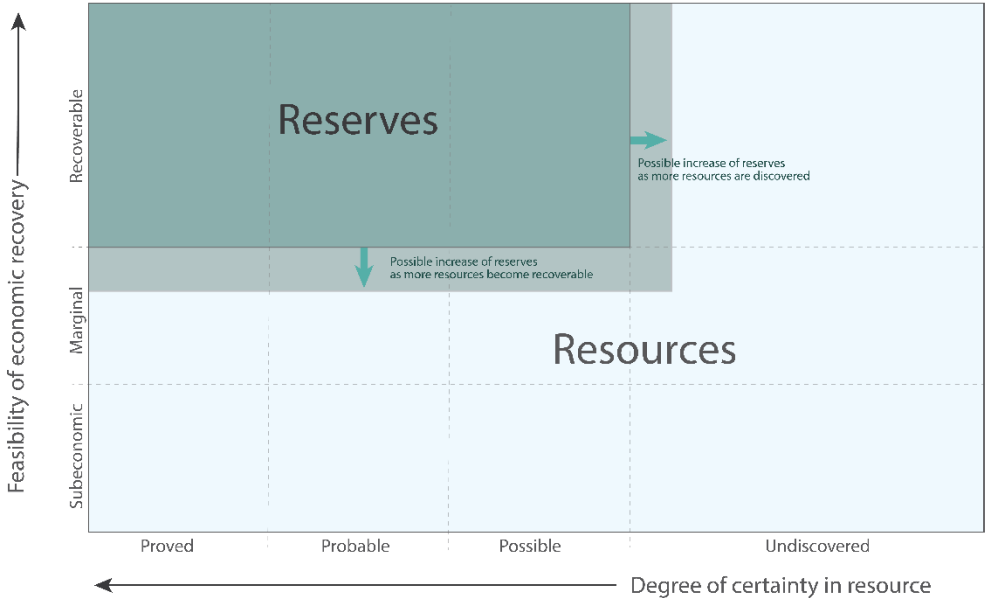


Data source: BP Statistical Review of World Energy 2016
The data visualization is available at OurWorldinData.org. There you find research and more visualizations on this topic.
Licensed under CC-BY-SA by the authors Hannah Ritchie and Max Roser.

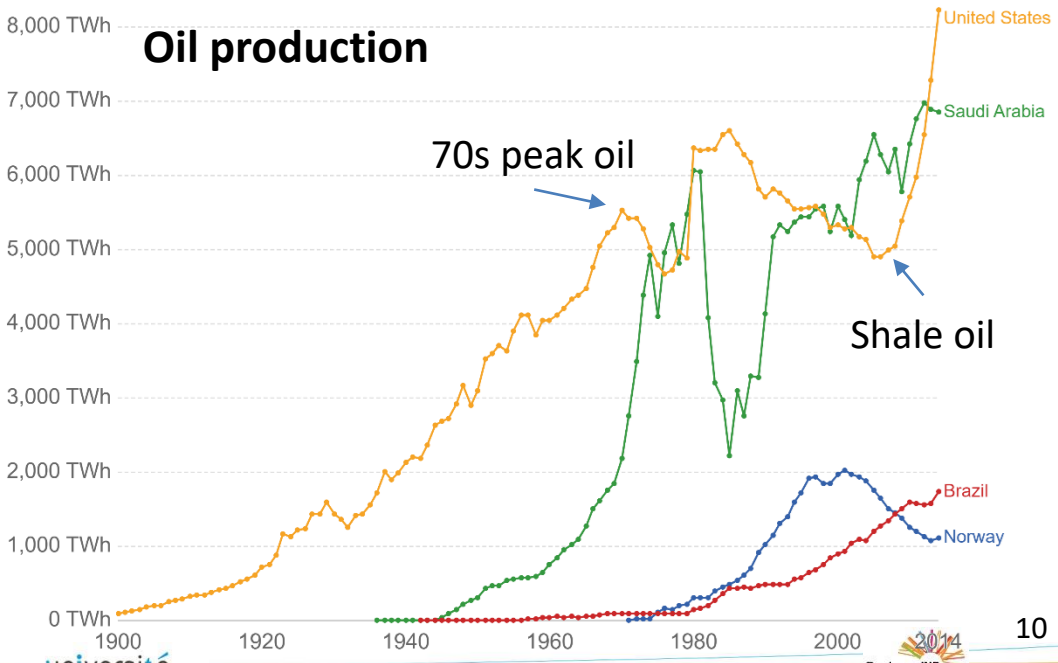
Worldwide oil reserves



Peak oil ?



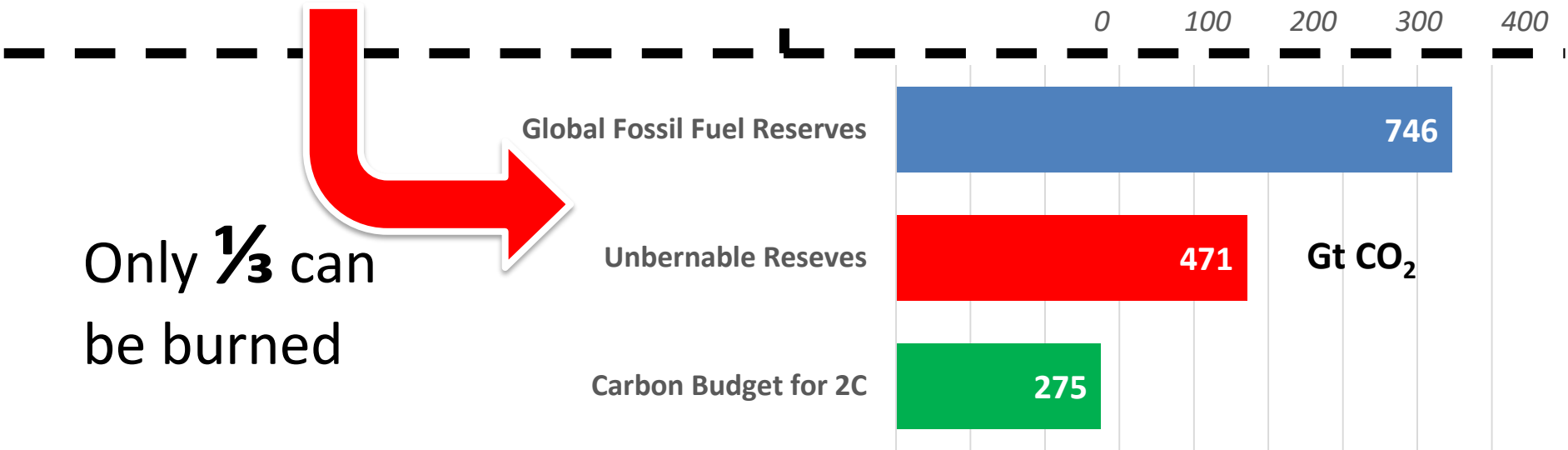
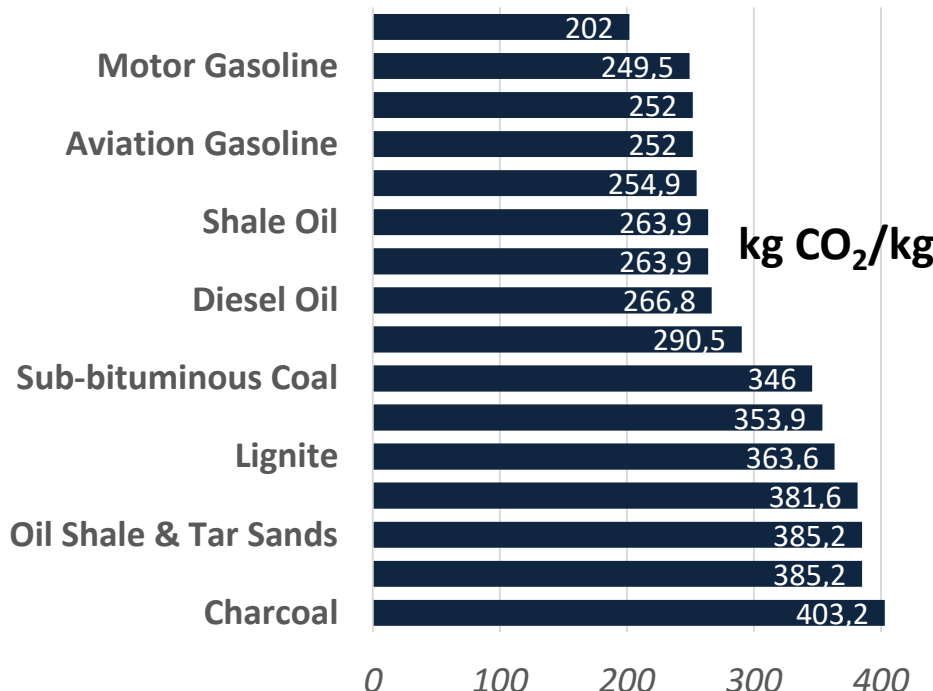
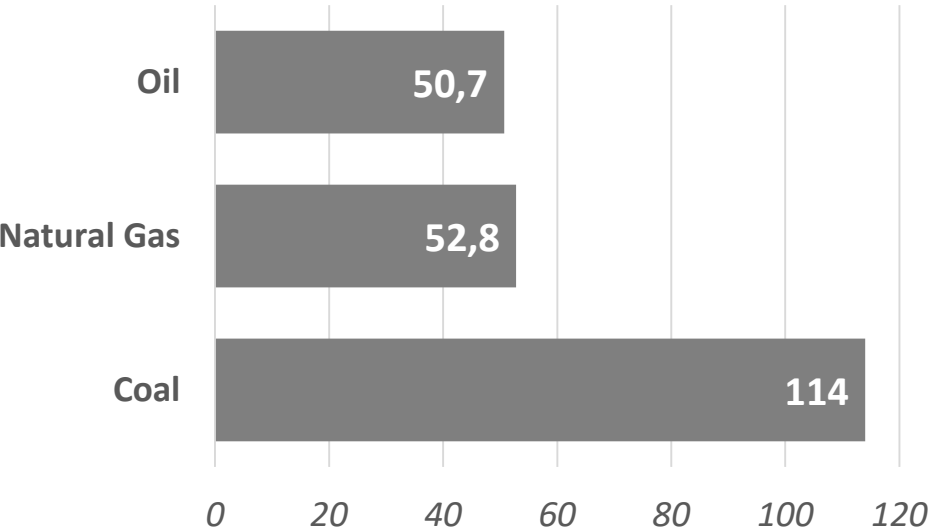
Oil production



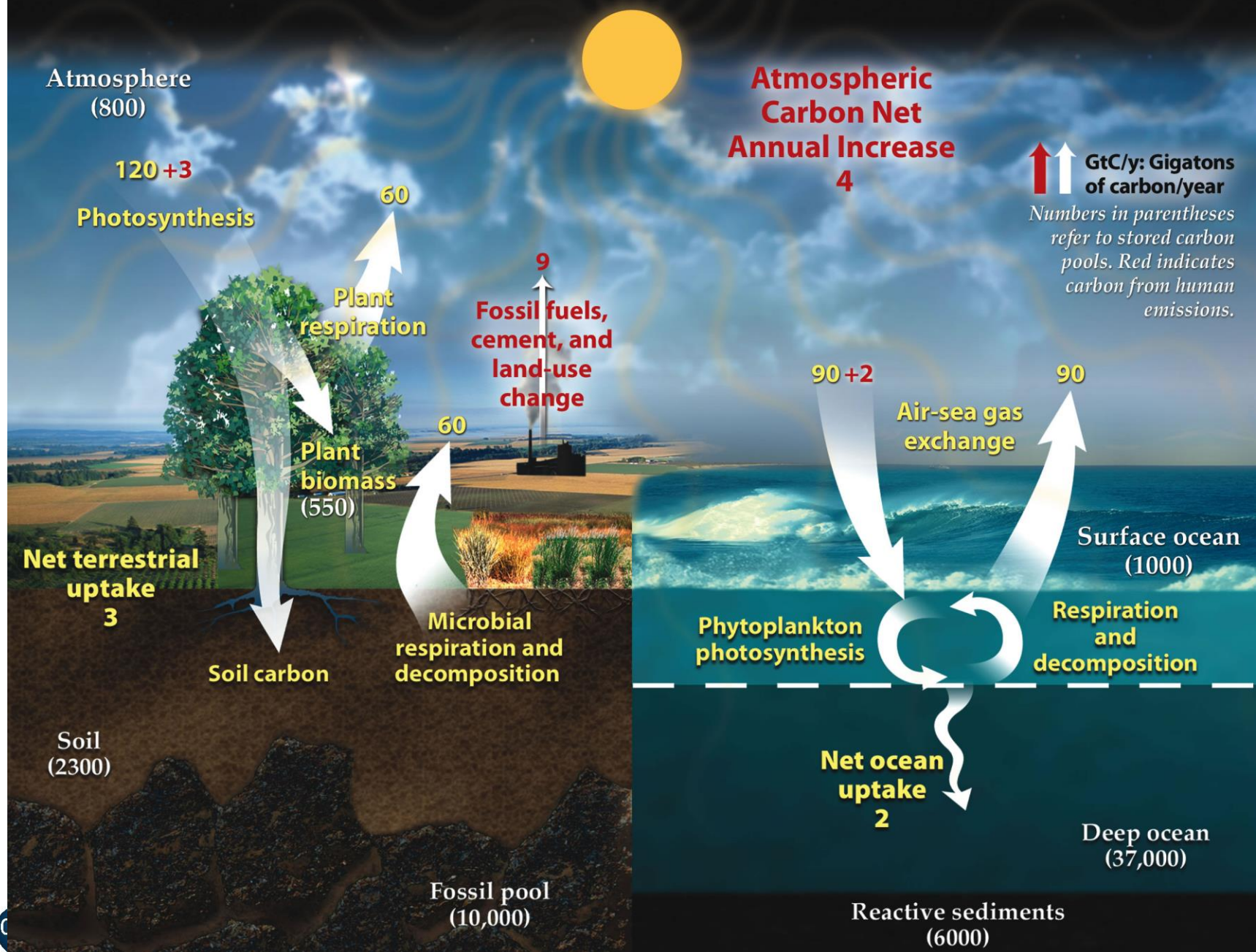
Data source: BP Statistical Review of World Energy 2016.
The data visualization is available at OurWorldInData.org. There you find research and more visualizations on this topic.
Licensed under CC BY SA by the authors Hannah Ritchie and Max Roser.

Fossil fuel reserves

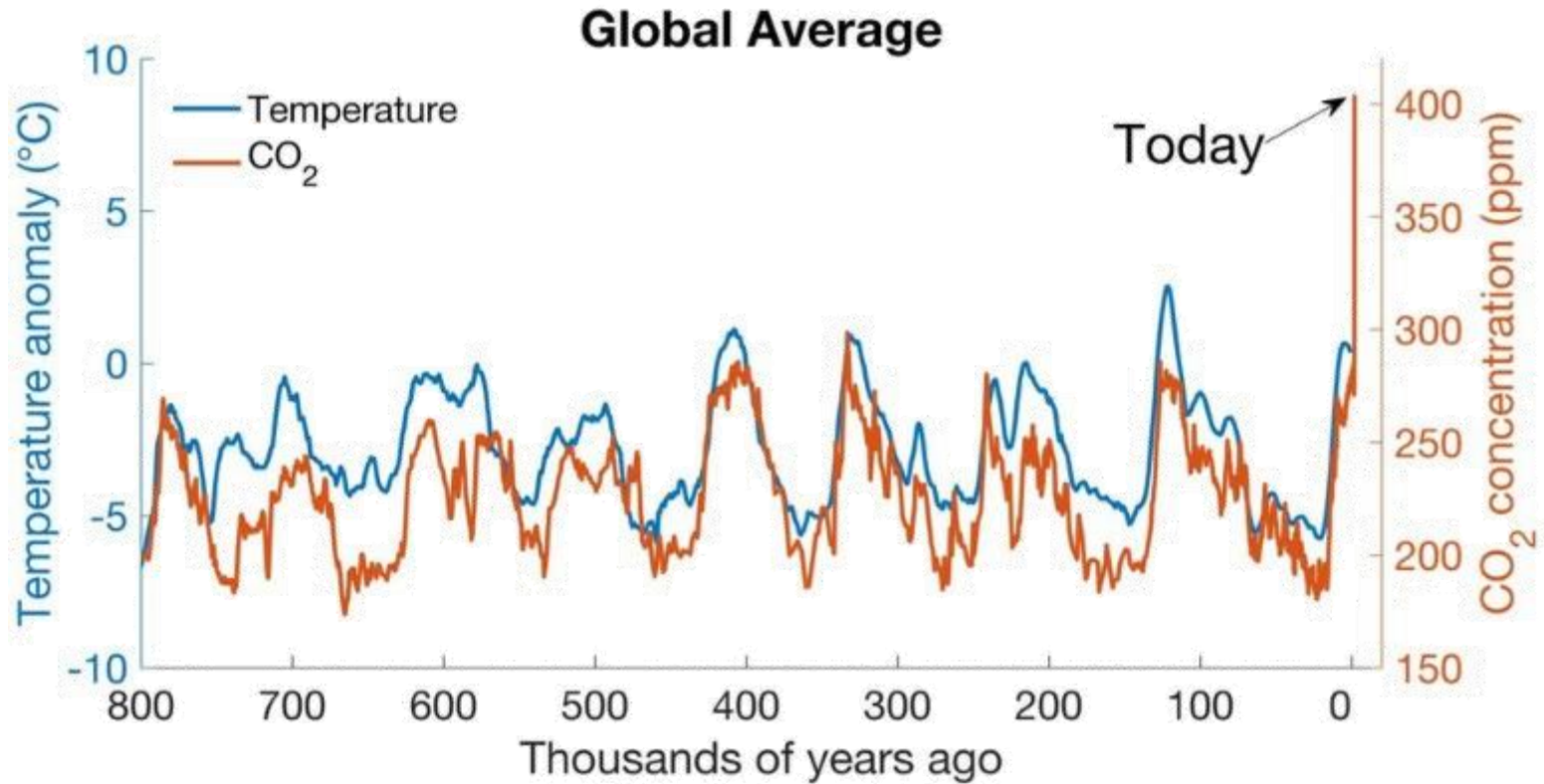
Years of fossil fuel reserves left



CO₂ cycle



CO₂ concentration keep increasing



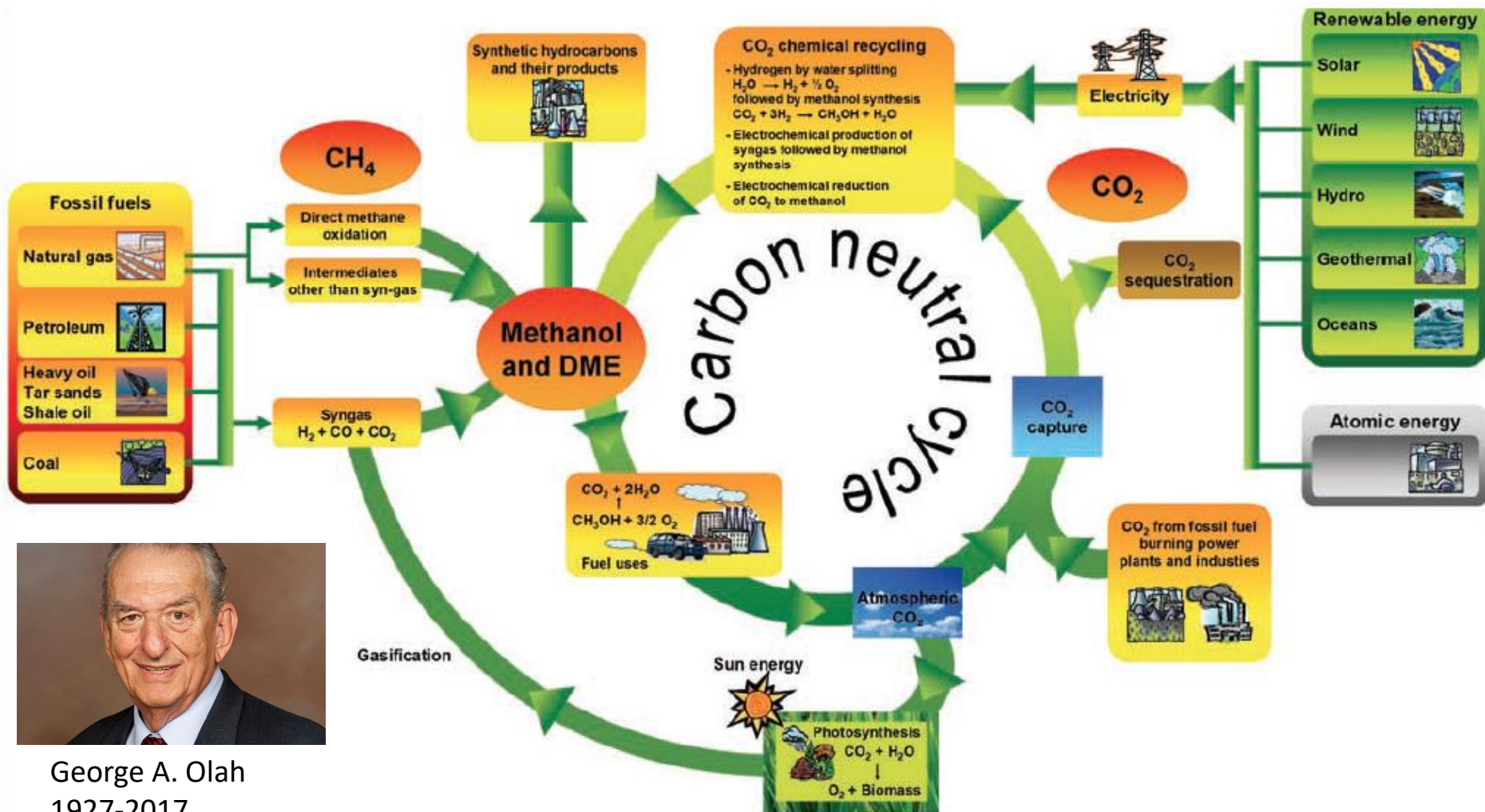
➔ Last time the CO₂ was that high the Human didn't exist
4 ppm/year more CO₂ in the atmosphere

May 2019: 415ppm
Since Sept 2016 > 400ppm

1987 : 350ppm

Reduce CO₂ emissions and trap it sustainably.

Carbon neutral society



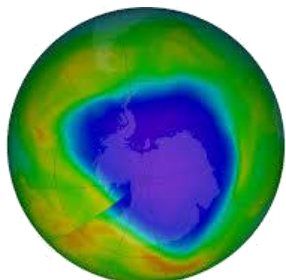
George A. Olah
1927-2017
Nobel Prize 1994

CO₂ emissions from cradle to factory gate



Life cycle analysis

| Impact category | Units |
|------------------------------------|------------------------|
| Climate change | kg CO ₂ eq. |
| Ozone depletion | kg CFC-11 eq. |
| Human toxicity, cancer effects | CTUh |
| Human toxicity, non-cancer effects | CTUh |
| Respiratory inorganics | kg PM2.5 eq. |
| Respiratory organics | kg NMVOC eq |
| Ionizing radiation | kBq U235 eq. |
| Terrestrial acidification | mol H ⁺ eq |
| Eutrophication terrestrial | mol N eq |
| Eutrophication freshwater | mol P eq |
| Eutrophication marine | mol N eq |
| Ecotoxicity freshwater | CTUe |
| Non-renewable energy | MJ |
| Depletion of abiotic ressources | kg Sb eq. |
| Water | L |



LCA: Example of the grocery bags



Simple LDPE



Non-woven PP

b)



Recycled PET



Rigid handle LDPE

a)



Woven PP

b)



polyester



biopolymer



paper



cotton

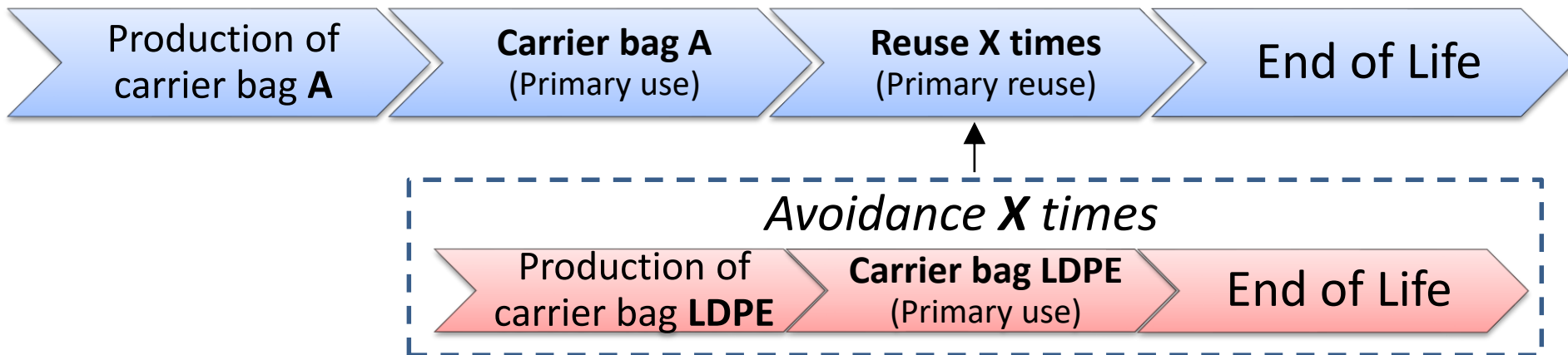


composite

LCA: Example of the grocery bags

| Impact category / bag | LDPE | PET | Bioplastique | Cotton | Units |
|--------------------------------|----------------------|----------------------|---------------------|---------------------|------------------------|
| Climate change | $1.1 \cdot 10^{-1}$ | $7.7 \cdot 10^{-1}$ | $9.0 \cdot 10^{-2}$ | 3.9 | kg CO ₂ eq. |
| Ozone depletion | $1.2 \cdot 10^{-9}$ | $6.4 \cdot 10^{-8}$ | $1.5 \cdot 10^{-8}$ | $1.0 \cdot 10^{-5}$ | kg CFC-11 eq. |
| Human tox., cancer effects | $1.3 \cdot 10^{-9}$ | $7.0 \cdot 10^{-9}$ | $2.3 \cdot 10^{-9}$ | $1.7 \cdot 10^{-7}$ | CTUh |
| Human tox., non-cancer effects | $-1.1 \cdot 10^{-8}$ | $-1.6 \cdot 10^{-8}$ | $3.1 \cdot 10^{-8}$ | $5.6 \cdot 10^{-7}$ | CTUh |
| Respiratory inorganics | $1.6 \cdot 10^{-5}$ | $2.7 \cdot 10^{-5}$ | $1.2 \cdot 10^{-4}$ | $3.8 \cdot 10^{-3}$ | kg PM2.5 eq. |
| Respiratory organics | $2.0 \cdot 10^{-4}$ | $9.6 \cdot 10^{-4}$ | $3.4 \cdot 10^{-4}$ | $8.7 \cdot 10^{-3}$ | kg NMVOC eq |
| Ionizing radiation | $6.0 \cdot 10^{-4}$ | $1.4 \cdot 10^{-2}$ | $3.8 \cdot 10^{-3}$ | $1.3 \cdot 10^{-1}$ | kBq U235 eq. |
| Terrestrial acidification | $1.1 \cdot 10^{-4}$ | $1.1 \cdot 10^{-3}$ | $7.4 \cdot 10^{-4}$ | $2.0 \cdot 10^{-2}$ | mol H ⁺ eq |
| Eutrophication terrestrial | $8.7 \cdot 10^{-5}$ | $1.9 \cdot 10^{-4}$ | $1.4 \cdot 10^{-3}$ | $4.9 \cdot 10^{-2}$ | mol N eq |
| Eutrophication freshwater | $-5.6 \cdot 10^{-7}$ | $3.8 \cdot 10^{-5}$ | $1.6 \cdot 10^{-5}$ | $4.8 \cdot 10^{-4}$ | mol P eq |
| Eutrophication marine | $2.3 \cdot 10^{-5}$ | $2.2 \cdot 10^{-4}$ | $2.4 \cdot 10^{-4}$ | $3.4 \cdot 10^{-3}$ | mol N eq |
| Ecotoxicity freshwater | $7.2 \cdot 10^{-2}$ | $5.1 \cdot 10^{-1}$ | $1.3 \cdot 10^{-1}$ | 12 | CTUe |
| Non-renewable energy | 1.7 | 12 | 2.9 | 72 | MJ |
| Depletion of ressources | $1.9 \cdot 10^{-6}$ | $2.1 \cdot 10^{-5}$ | $5.1 \cdot 10^{-6}$ | $1.6 \cdot 10^{-4}$ | kg Sb eq. |
| Water | $4.4 \cdot 10^{-2}$ | 1.4 | $2.4 \cdot 10^{-1}$ | 27 | L |

LCA: Example of the grocery bags

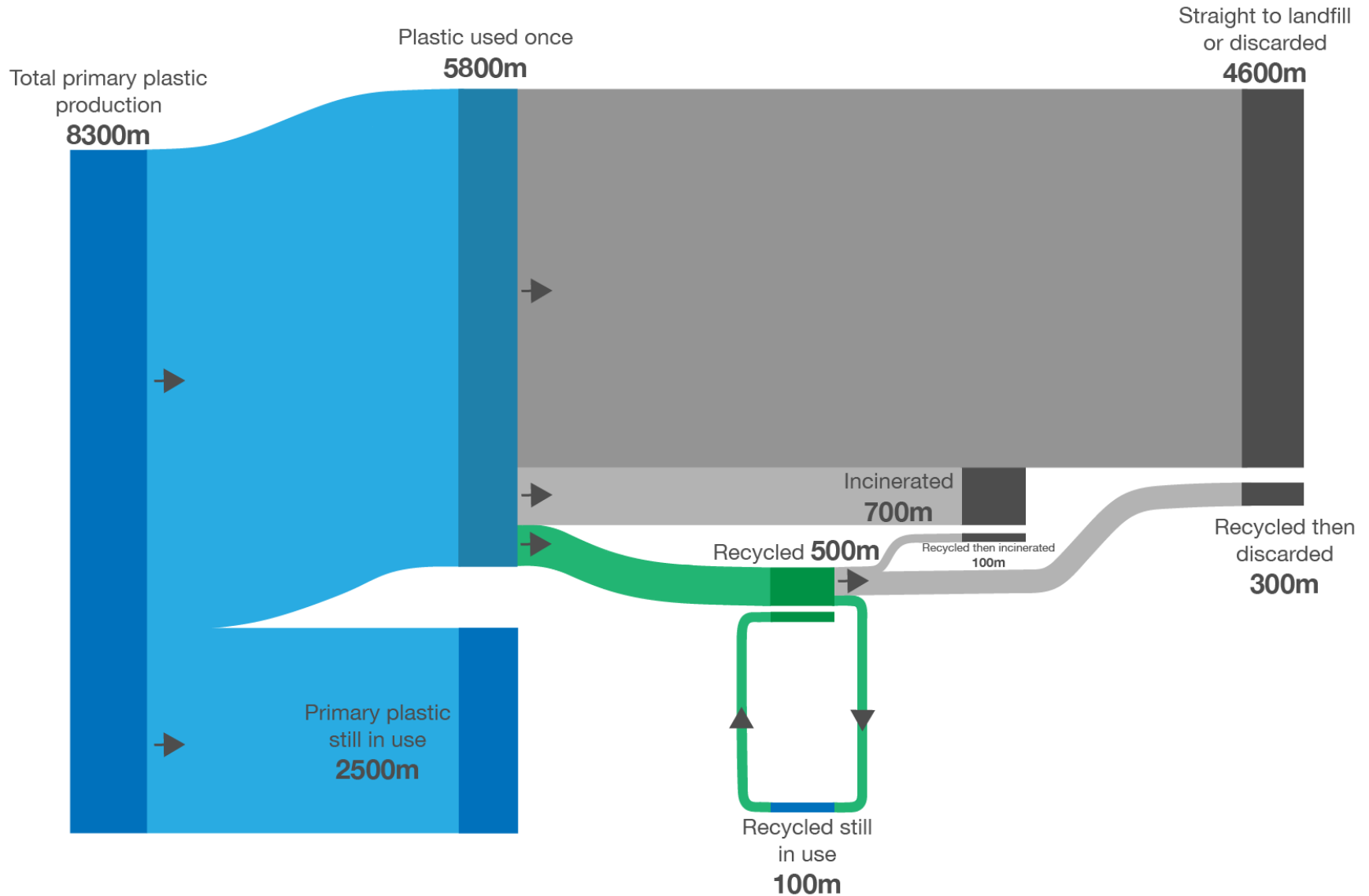


| | Climate Change | All indicators |
|---|----------------|----------------|
| Non-woven PP, EOL = recycled | 6 | 52 |
| Woven PP, EOL = recycled | 5 | 45 |
| Recycled PET, EOL = recycled | 8 | 84 |
| Polyester, EOL = recycled | 2 | 35 |
| Biopolymer, EOL= waste bag or incinerated | 0 | 42 |
| Unbleached paper, , EOL= waste bag or incinerated | 0 | 43 |
| Bleached paper, EOL= waste bag or incinerated | 1 | 43 |
| Organic cotton, EOL= incinerated | 149 | 20000 |
| Conventional cotton, EOL= incinerated | 52 | 7100 |
| Composite, EOL= waste bag or incinerated | 23 | 870 |

Global plastic production and its fate (1950-2015)

Balance of plastic production and fate (m = million tonnes)

8300m produced → 4900m discarded + 800m incinerated + 2600m still in use (100m of recycled plastic)



The route by which plastic enters the oceans

2% of the plastics enter the oceans
→ **160 Mt**

Global primary plastic production:
270 million tonnes per year

Global plastic waste:
275 million tonnes per year

It can exceed primary production in a given year since it can incorporate production from previous years.

Coastal plastic waste:
99.5 million tonnes per

This is the total of plastic waste generated by all populations within 50 kilometres of a coastline (therefore at risk of entering the ocean).

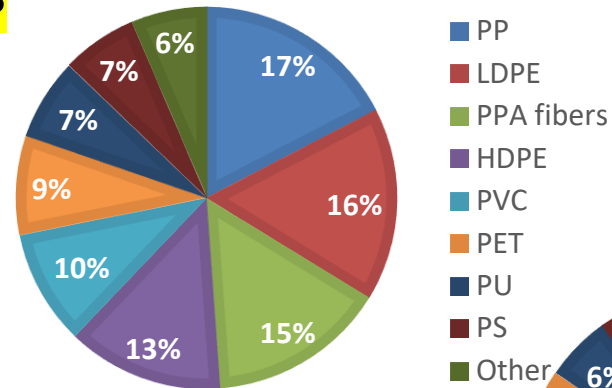
Mismanaged coastal plastic waste:
31.9 million tonnes per year

This is the annual sum of inadequately managed and littered plastic waste from coastal populations. Inadequately managed waste is that which is stored in open or insecure landfills (and therefore at risk of leakage or loss).

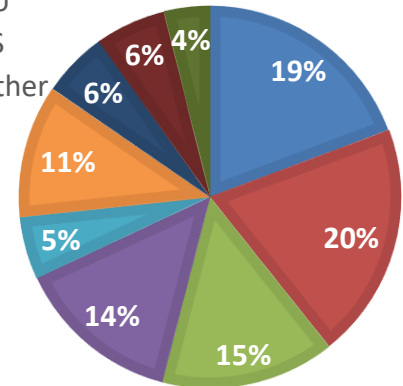
Plastic inputs to the oceans:
8 million tonnes per year

2 billion people living
within 50km of coastline

PRODUCTION

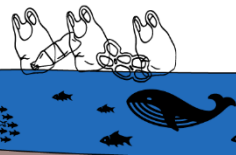


WASTE



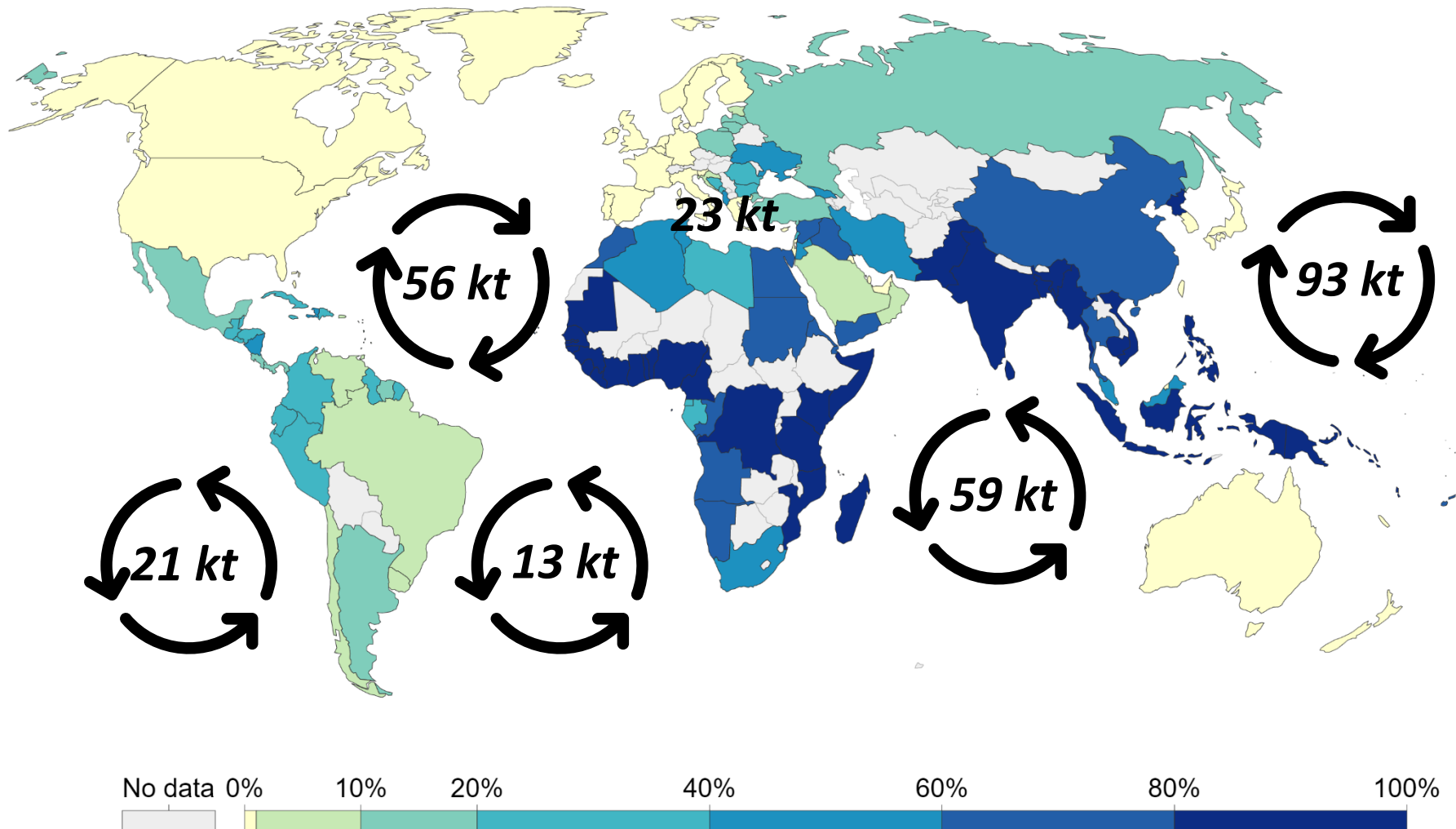
Plastic in surface waters:
10,000s to 100,000s tonnes

There is a wide range of estimates of the quantity of plastics in surface waters. It remains unclear where the majority of plastic inputs end up — a large quantity might accumulate at greater depths or on the seafloor.

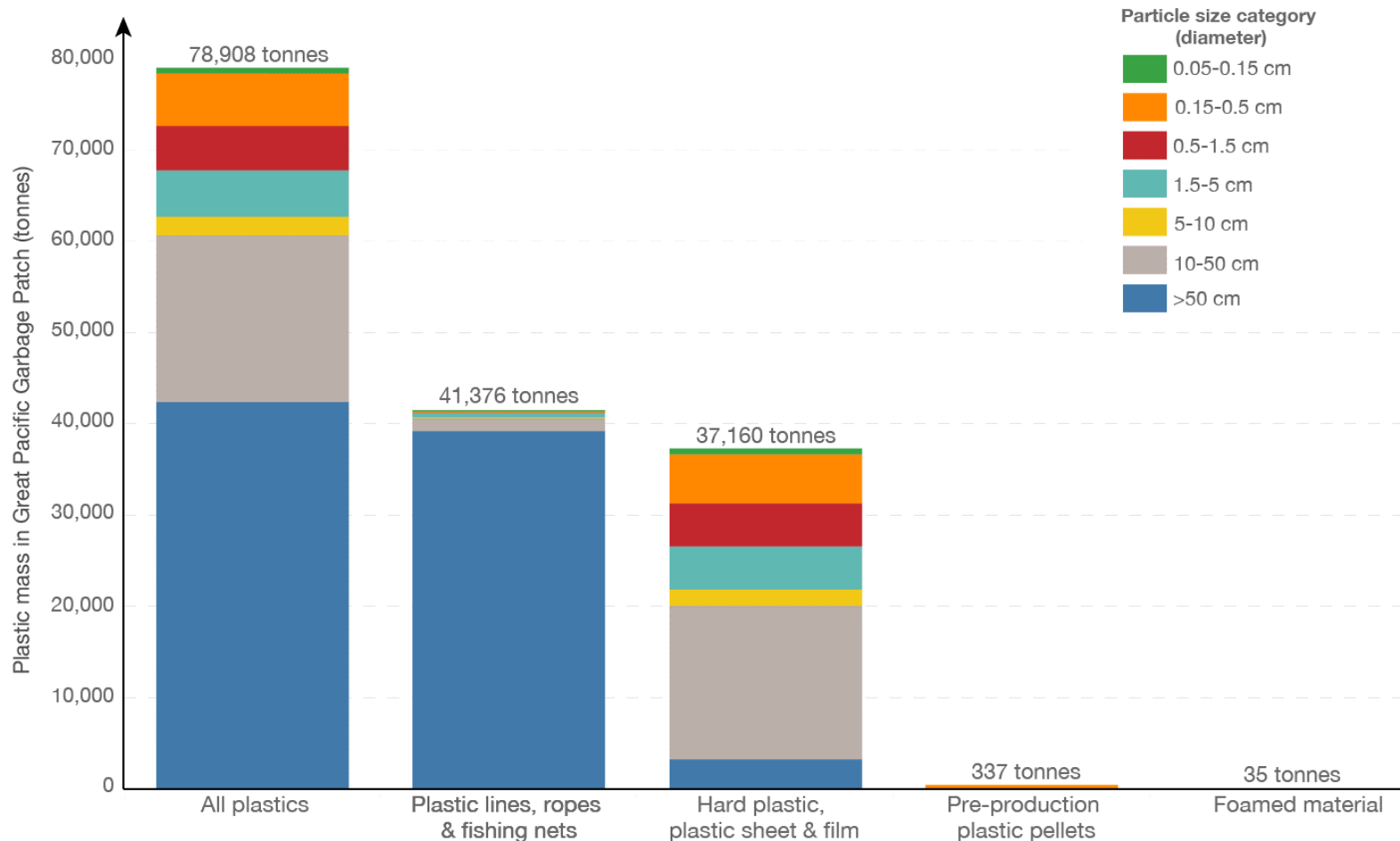


Share of plastic waste that is inadequately managed (2010)

260 kt in the ocean's gyres but **8 Mt/y** of plastic enters the oceans



Great Pacific Garbage Patch (GPGP) plastic sources



Ultraviolet light (UV) and mechanical wave forces break large pieces of plastic into smaller ones called **microplastics**

Microplastic was up to **four orders of magnitude** more abundant (per unit volume) in deep-sea sediments than in surface waters.

Where does plastic accumulate in the ocean?

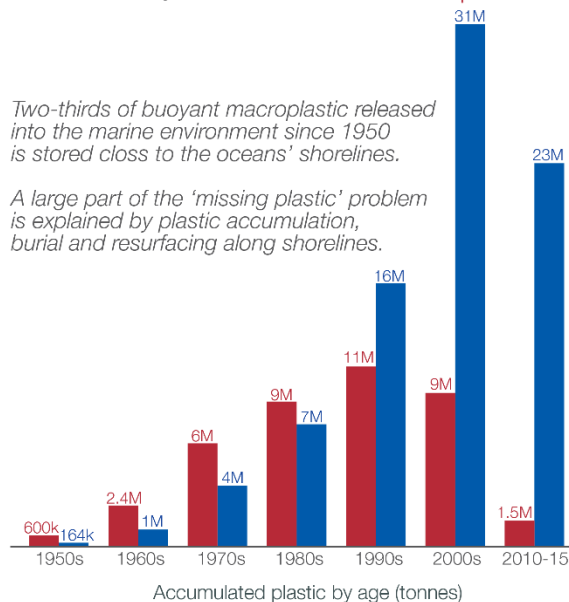
Macroplastics are greater than 0.5cm in diameter
Microplastics are smaller than 0.5cm

Shoreline Dry lands

Total from 1950 to 2015:
82M tonnes macroplastic
40M tonnes microplastic

Two-thirds of buoyant macroplastic released into the marine environment since 1950 is stored close to the oceans' shorelines.

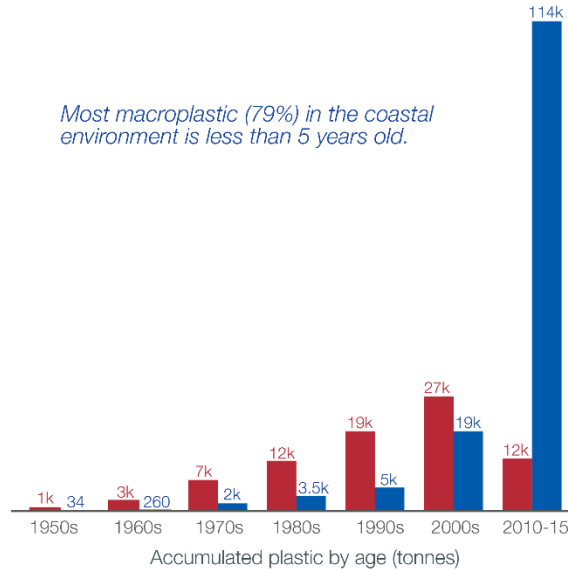
A large part of the 'missing plastic' problem is explained by plastic accumulation, burial and resurfacing along shorelines.



Coastal Shallow waters (<200m)

Total from 1950 to 2015:
150,000 tonnes macroplastic
80,000 tonnes microplastic

Most macroplastic (79%) in the coastal environment is less than 5 years old.



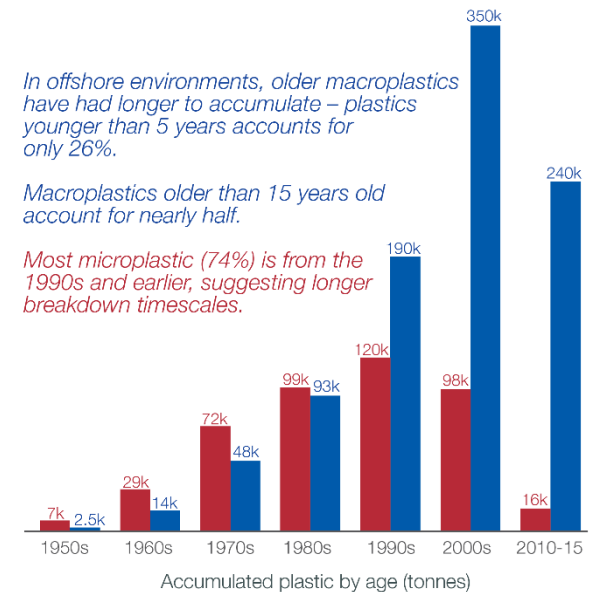
Offshore Deeper waters (>200m)

Total from 1950 to 2015:
1M tonnes macroplastic
0.5M tonnes microplastic

In offshore environments, older macroplastics have had longer to accumulate – plastics younger than 5 years accounts for only 26%.

Macroplastics older than 15 years old account for nearly half.

Most microplastic (74%) is from the 1990s and earlier, suggesting longer breakdown timescales.



125 Mt in the ocean's gyres but **8 Mt/y** of plastic enters the oceans

Plastic pollution

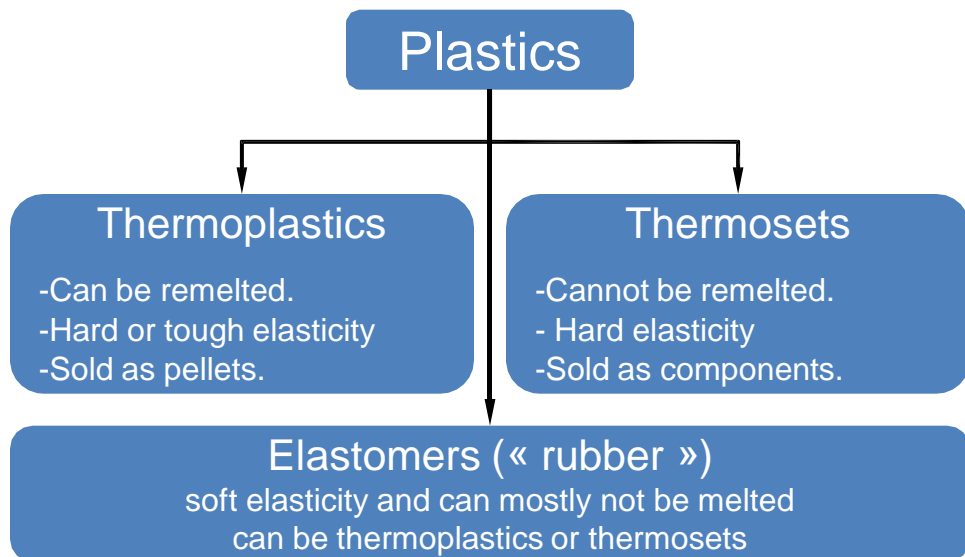
- Each year, we use and throw away :
 - 3,7 billions of plastic cups,
 - 365 billions of plastics bottles,
 - 3650 billions of plastic bags,
 - by 2050 more plastics than fish
 - 10% of the plastics go to the sea
- Pacific ocean accumulations:
 - o Plastic particles in suspension
 - o Concentration : 5.1 kg/km²
 - o More than 5 millions tons (?)
- Alliances of individuals, organizations and businesses working together to stop plastic pollution and its toxic impacts



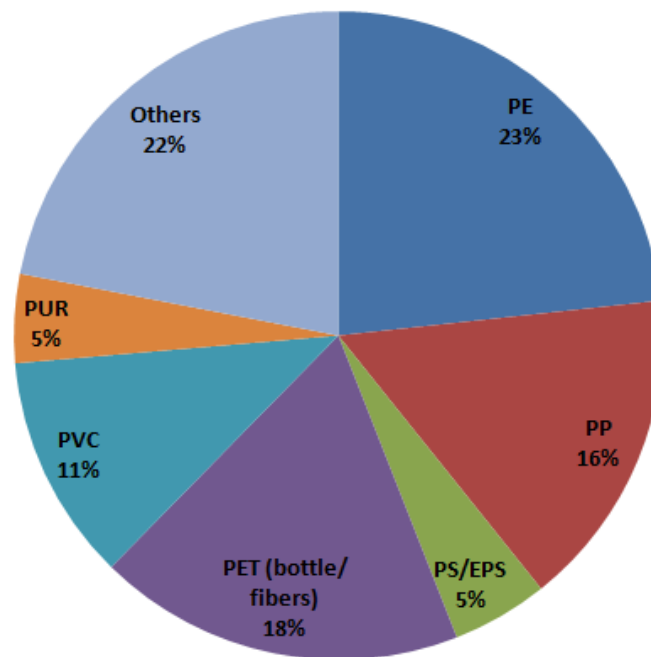
Plastic Pollution Coalition is a global alliance of individuals, organizations and businesses working towards a world free of plastic pollution and its toxic impacts.

PlasticPollutionCoalition

World plastic market



Global plastics demand 2017 ~350MT



Source: Total info, Plastics Europe
ICIS, IHS, Tecnon Orbichem, Nexant

350 Mt* plastics demand can be split into

-Thermoplastics: PE, PP, PS, PVC, PET, Engineering plastics (PA, PC, PEEK, TPE, ...).

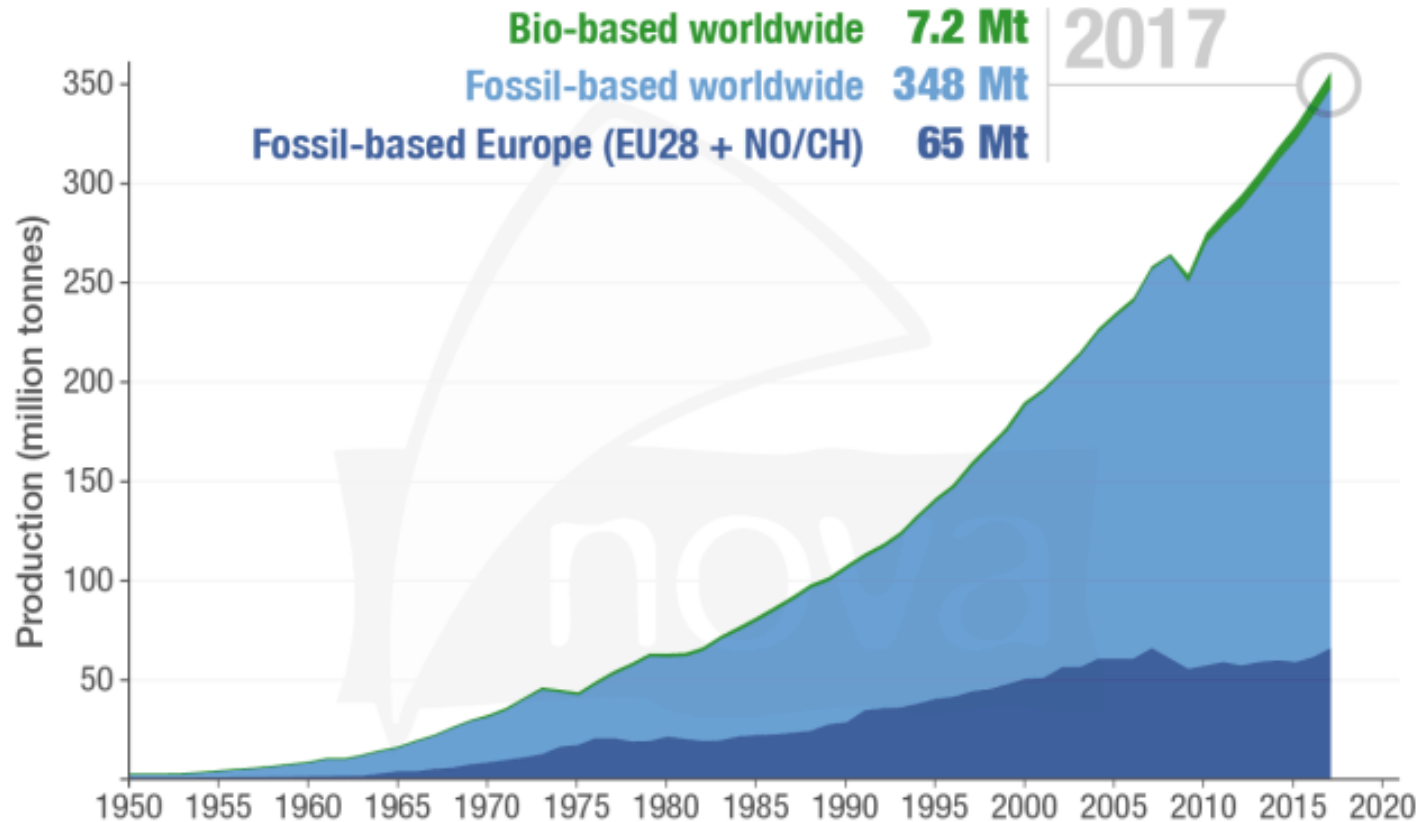
-Thermosets: PUR, UPR, Epoxy, Elastomers.

* Plastics Europe reports 299MT demand, but we included polyester, PA and acrylic fibers.

- Others include: engineering plastics, other thermosets and fibers, elastomers and blends & compounds

* TOP 5 polymers (PE, PP, PS/EPS, PVC & PET bottles/fibers) represent almost 75% of the market.

Plastics production from 1950 to 2017



includes thermoplastics, polyurethanes, thermosets, elastomers, adhesives, coatings and sealants and PP-fibres. Not included PET-, PA-, and polyacryl-fibres.

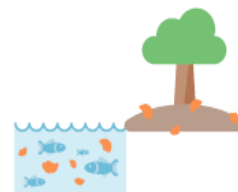
Data sources:
PlasticsEurope, Consultic and nova-institute

© nova-institute.eu



Huge market with continuous growth for more than 50 years (4% per year)
But still based on fossil raw materials (for more than 99%)

1- Why ?



2- How ?

3- Bio-based plastics from natural polymers

4- Drop-ins: Bio-based alternative to fossil-based polymers

5- Smart drop-ins: Bio-based derivative of “fossil” polymers

6- New polymers from biomass

7- Conclusions and perspectives

So what is the solution?



Plant photosynthesis uses sunlight energy to produce sugars (glucose (C₆H₁₂O₆)). This glucose is then condensed by the plant into natural polymers such as starch or cellulose.

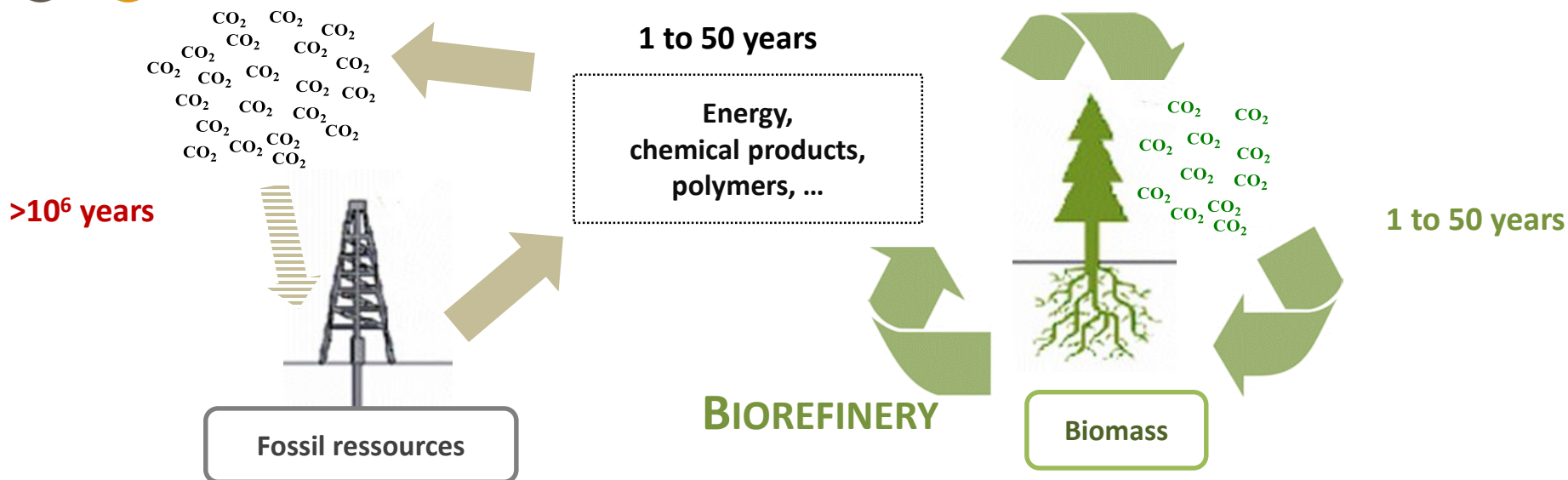
This plant photosynthetic process allows the binding and storage of atmospheric carbon dioxide (CO₂) in the form of matter in plant tissues.



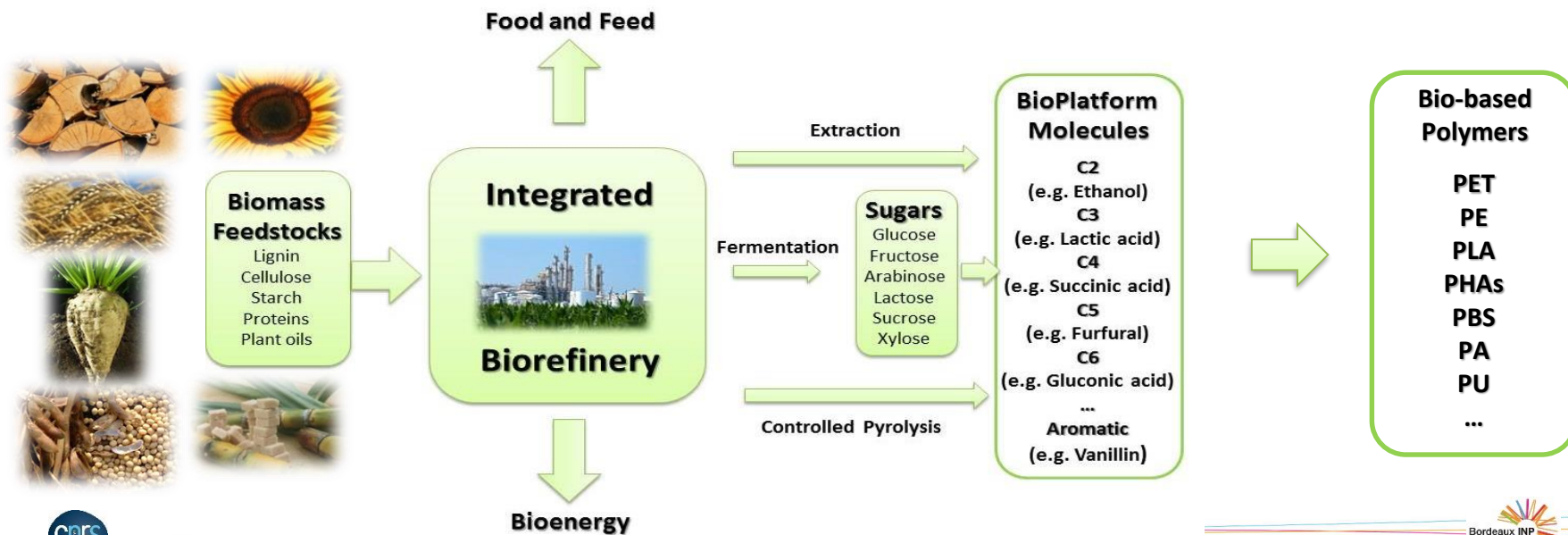
Plants, through this photosynthetic mechanism, thus produce renewable natural carbon-based molecules.

Annual plants such as wheat in the grains or potatoes in the tubers, synthesize starch that is renewed each year.

Biorefinery Concept



Emergence of biorefineries: use of biomass as raw materials instead of fossil resources

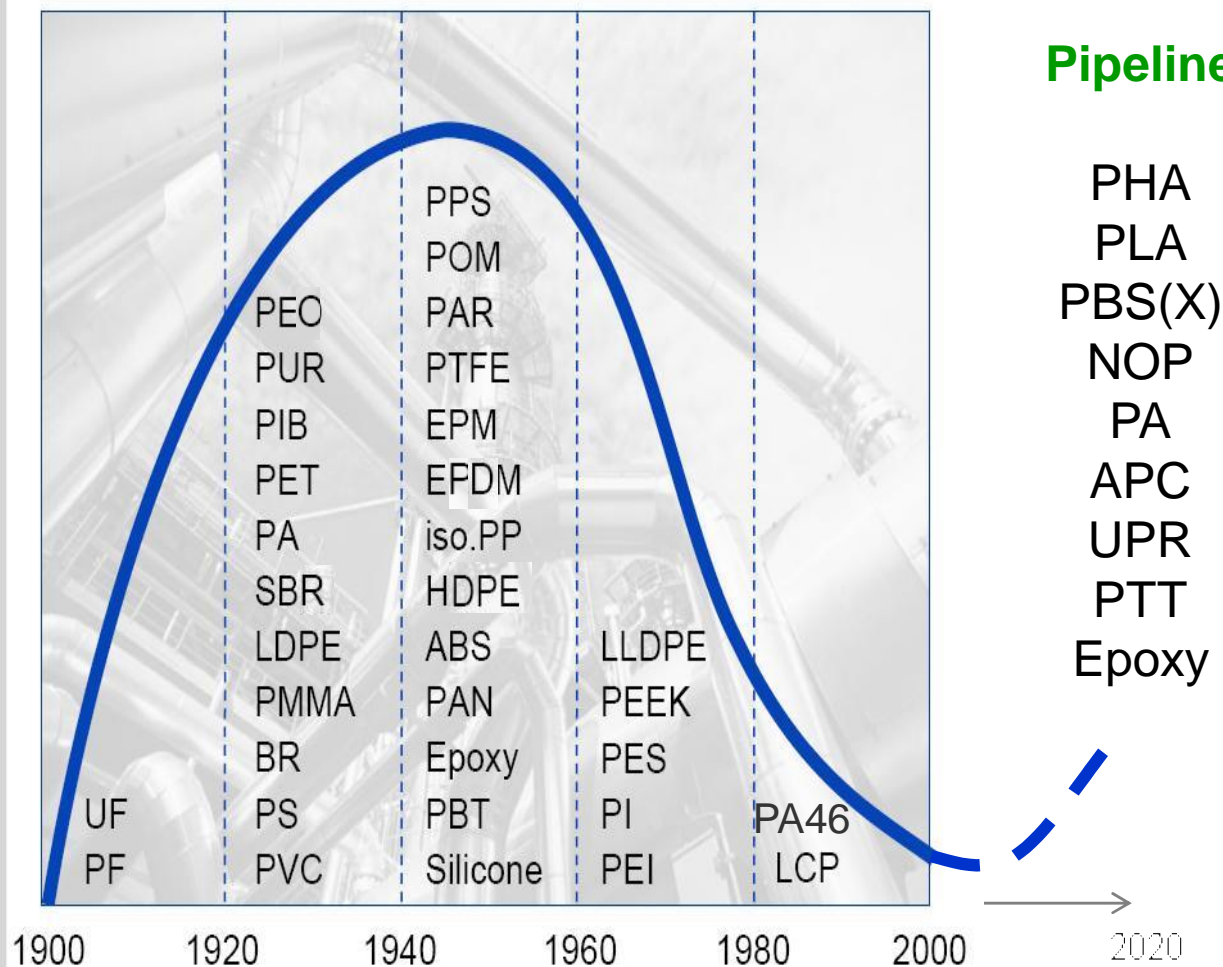


Example of a Biorefinery



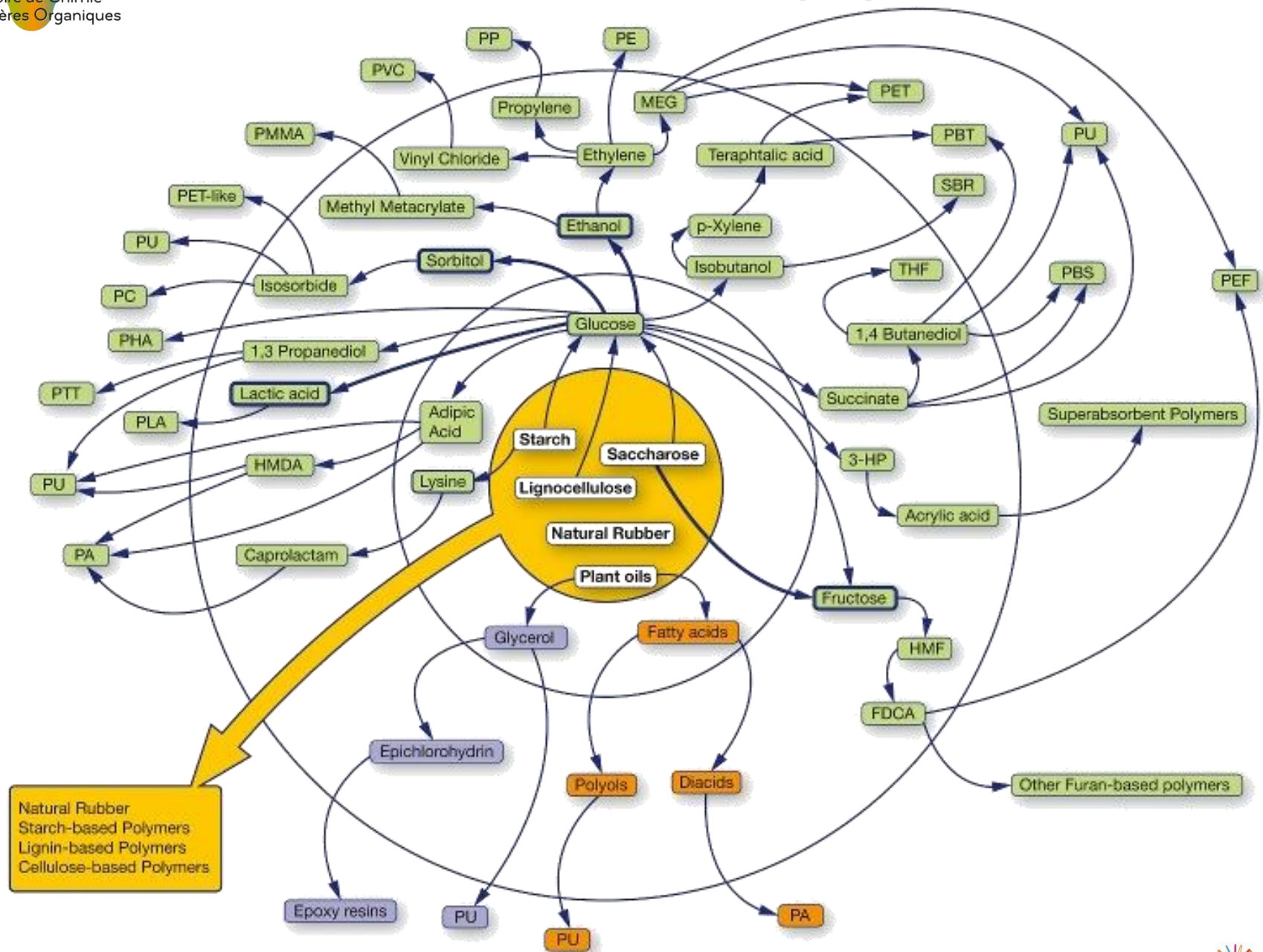
What's new in the Plastic Industry ?

Find new pathways to 'old' polymers....?



.....or Design novel polymers ?

From biomass to polymers



SUPPLEMENTARY INFORMATION

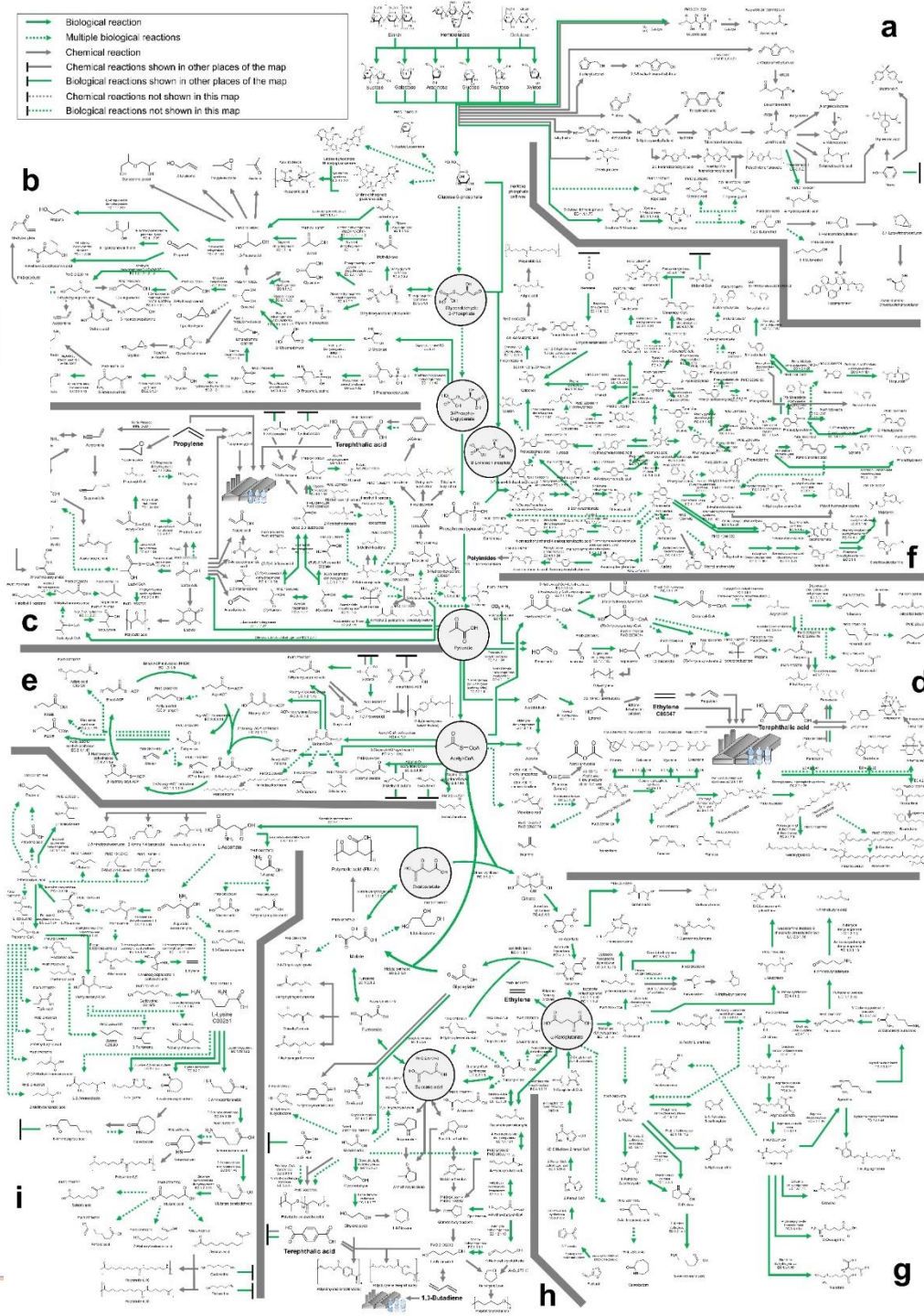
<https://doi.org/10.1038/s41929-018-0212-4>

nature
catalysis

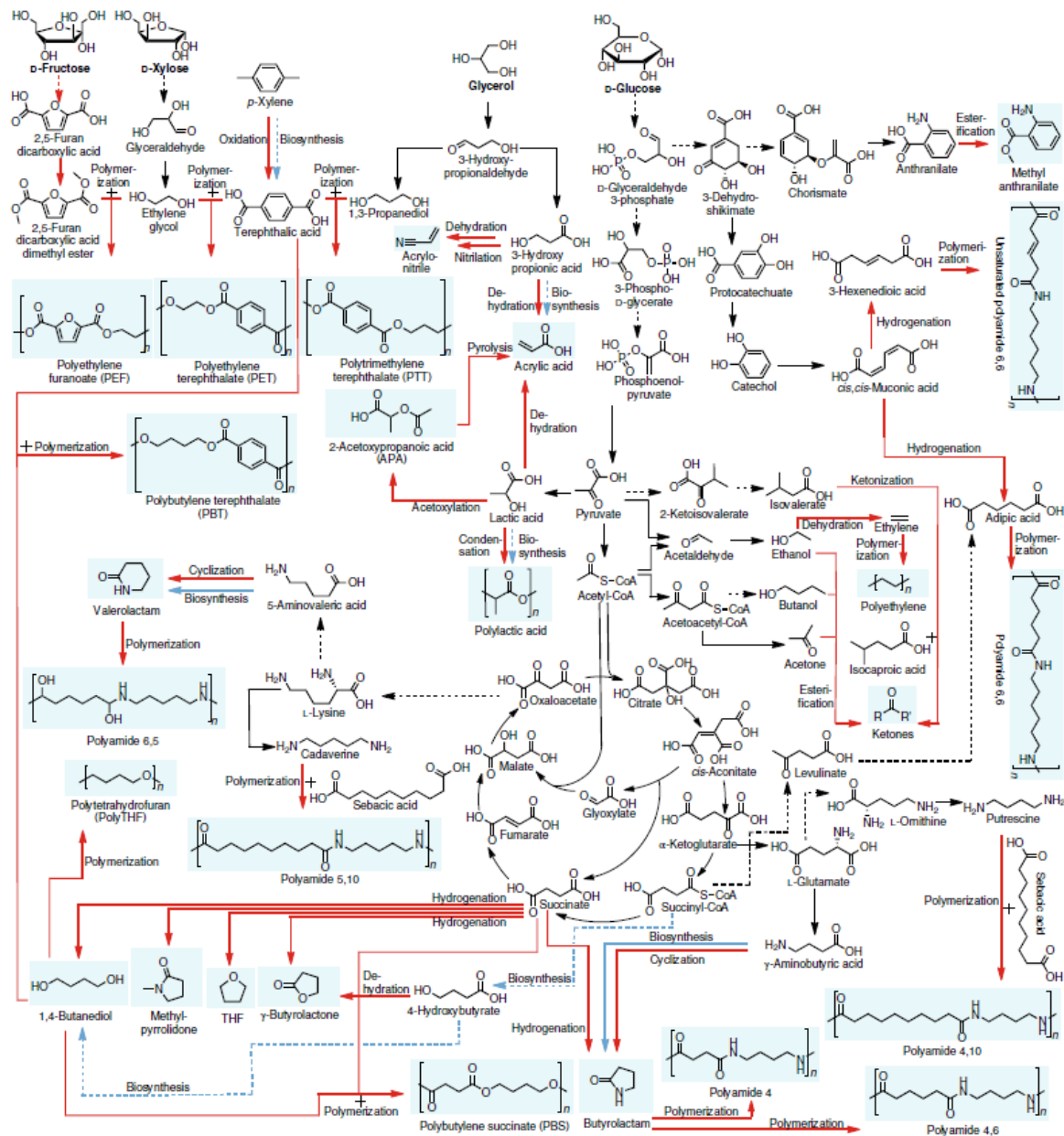
In the format provided by the authors and unedited.

A comprehensive metabolic map for production of bio-based chemicals

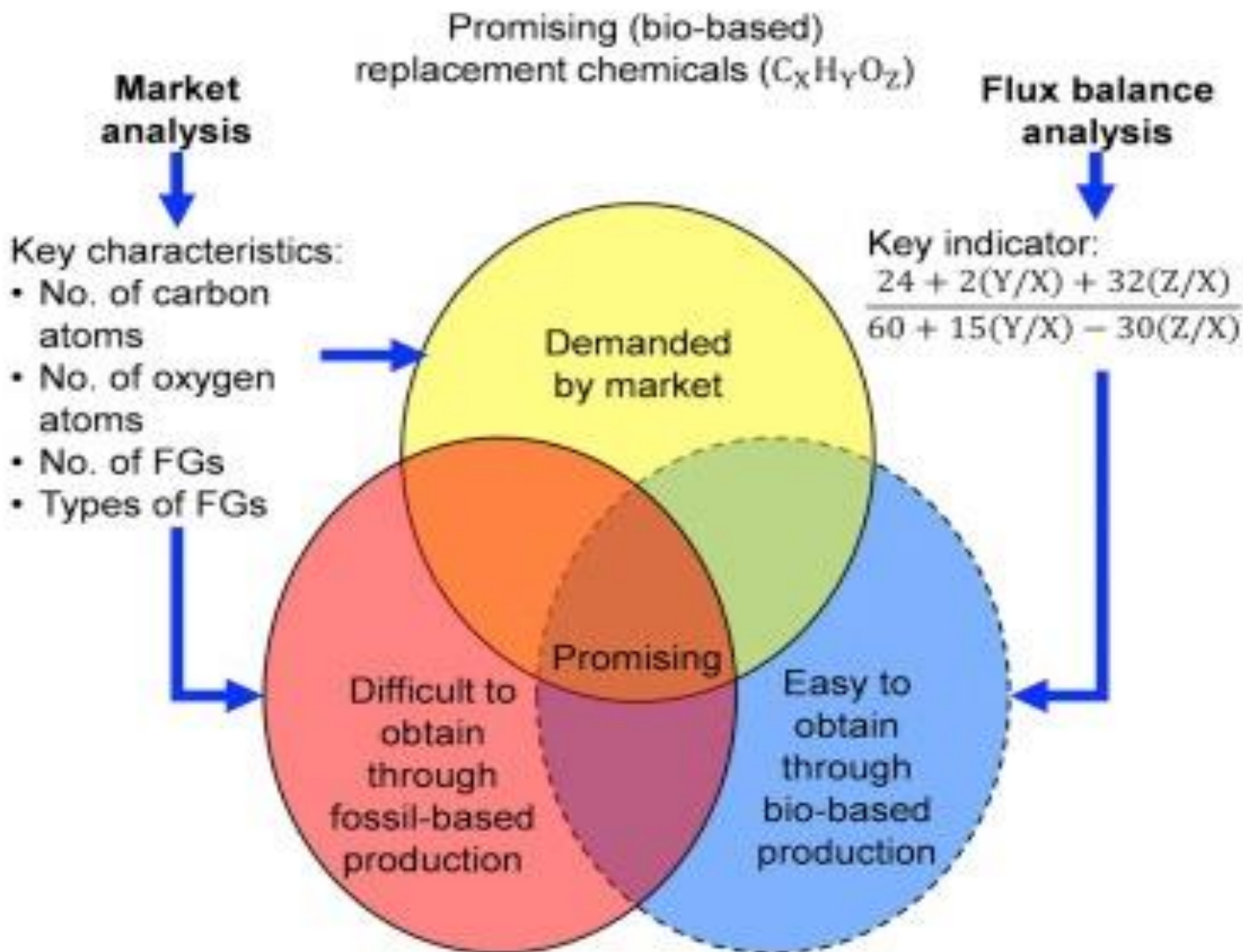
SangYup Lee^{1,2,3,4*}, Hyun Uk Kim^{2,3,5}, Tong Un Chae^{1,2}, Jae Sung Cho^{1,2}, Je Woong Kim^{1,2},
Jae Ho Shin^{1,2}, Dong In Kim^{1,3}, Yoo-Sung Ko^{1,2}, Woo Dae Jang^{1,3} and Yu-Sin Jang^{1,6}



Example of the glucose platform

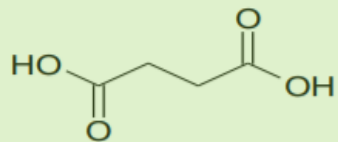


Promising bio-based chemicals

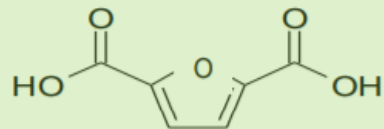


*FG: functional group

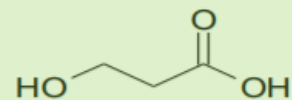
Most promising bio-based building blocks: DOE 2004



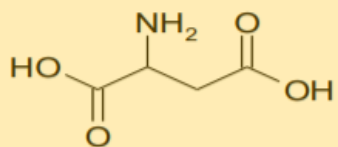
Succinic acid



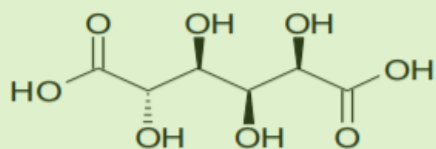
2,5-Furandicarboxylic acid



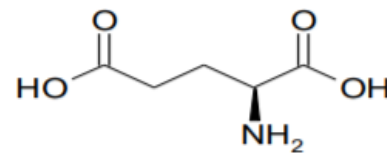
3-Hydroxypropionic acid



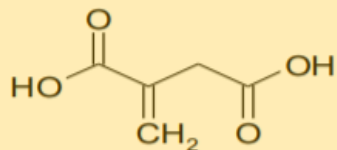
Aspartic acid



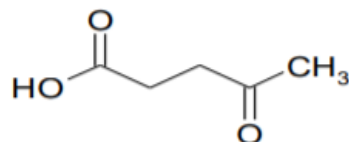
Glucaric acid



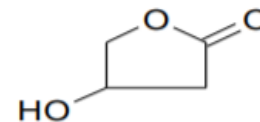
Glutamic acid



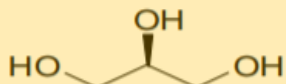
Itaconic acid



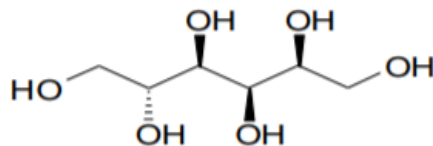
Levulinic acid



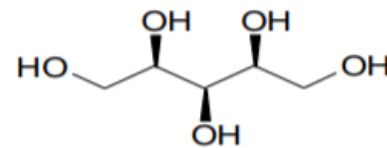
3-Hydroxybutyrolactone



Glycerol



Sorbitol

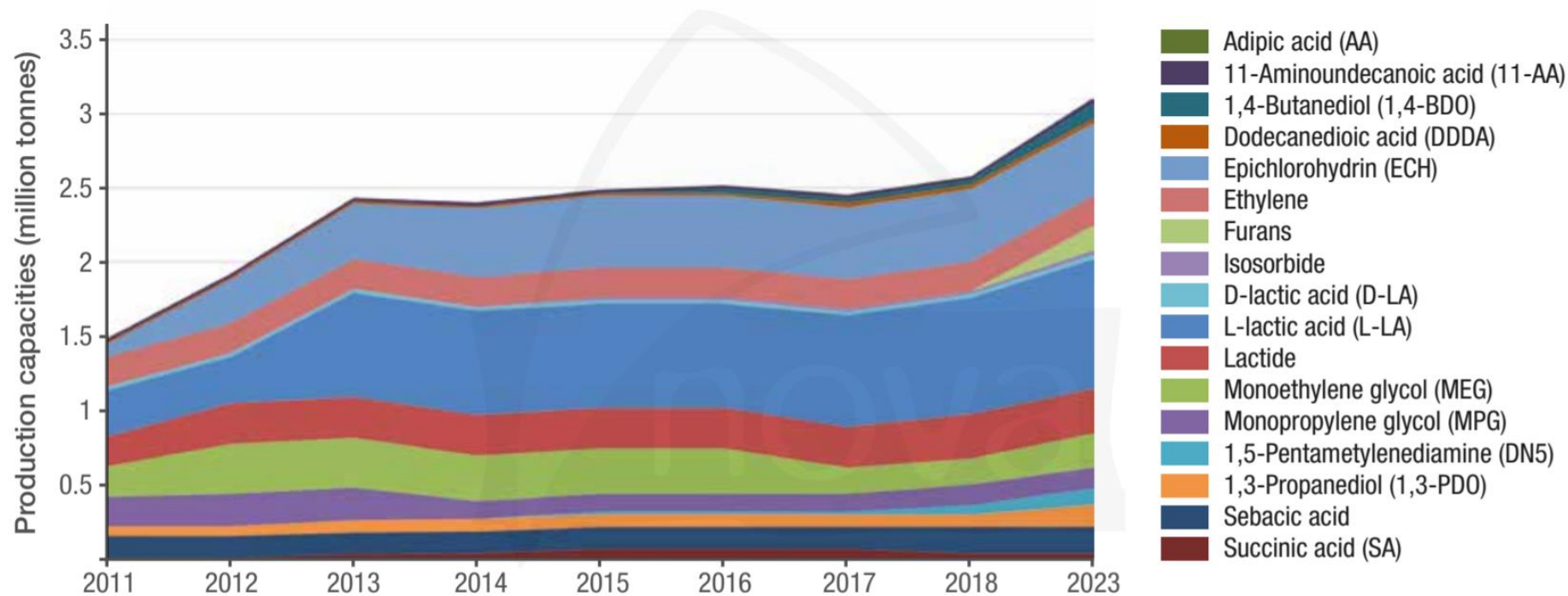


Xylitol

Most promising bio-based building blocks: DOE 2016

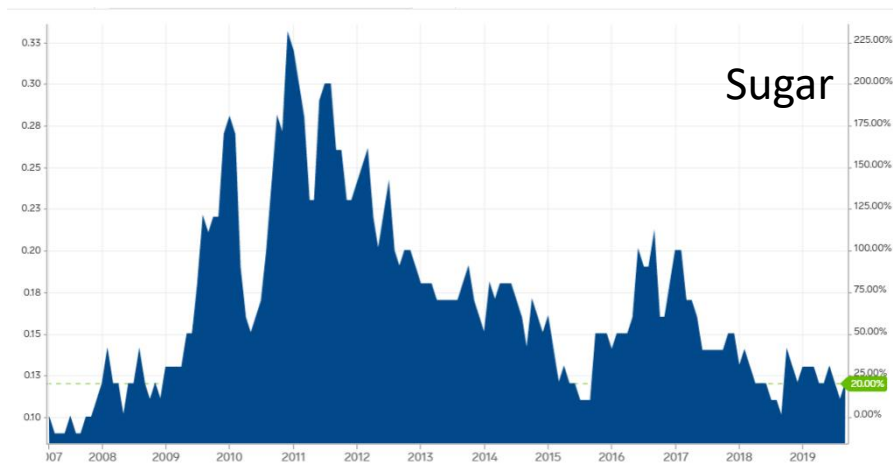
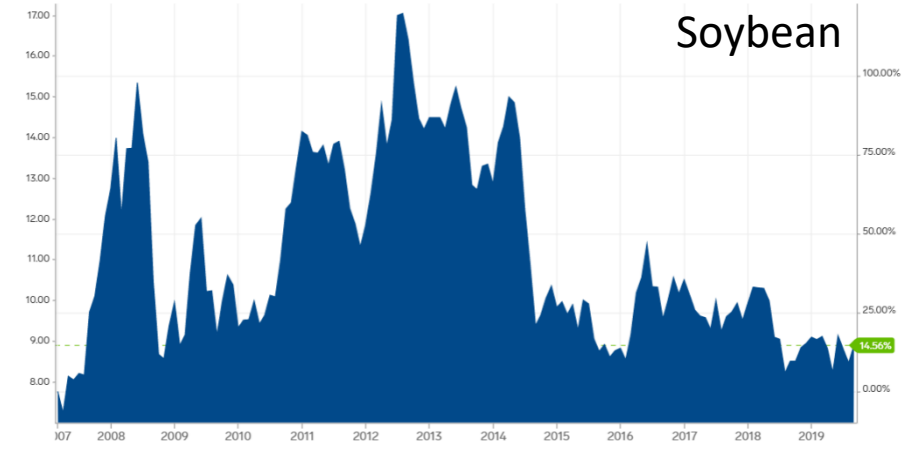
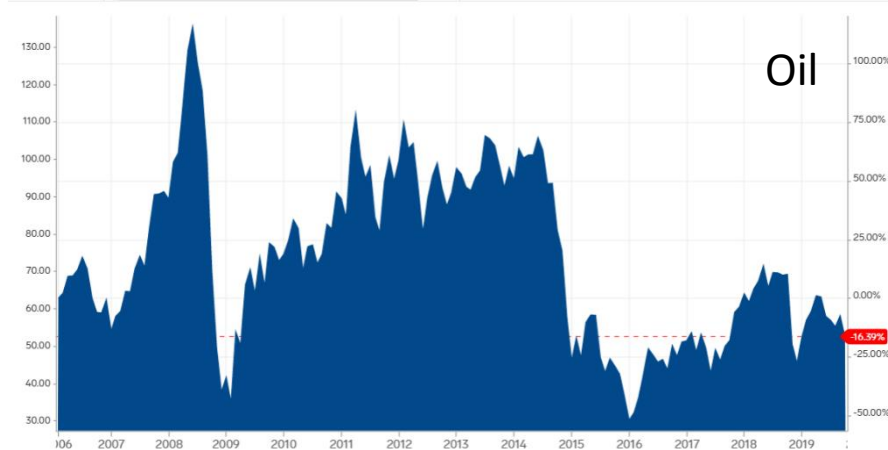
| Chemical | Type | Conversion Pathway | TRL Level based on commodity feedstocks | R&D on-going for lignocellulosic feedstocks |
|---------------------------|------------|---|---|---|
| Butadiene (1,3-) | Drop-in | BC – Biological TC/BC – Gasification/Fermentation | 6 | Y |
| Butanediol (1,4-) | Drop-in | BC – Biological | 8 | Y |
| Ethyl Lactate | Functional | BC– Biological | 9 | Y |
| Fatty Alcohols | Drop-in | TC – Gasification, BC – Biological, Algae | 9 | Y |
| Furfural | Functional | TC– Pyrolysis, BC – Catalytic | 9 | Y |
| Glycerol | Functional | Algae | 9 | Y |
| Isoprene | Drop-in | BC – Biological | 6 | |
| Lactic Acid | Functional | BC – Biological | 9 | Y |
| Propanediol (1,3-) | Functional | BC – Biological | 9 | |
| Propylene Glycol | Functional | BC – Biological | 9 | |
| Succinic Acid | Functional | BC – Biological | 9 | Y |
| Xylene (para) | Drop-in | BC – Catalytic TC – Pyrolysis | 6 | Y |

Worldwide production of bio-based chemicals

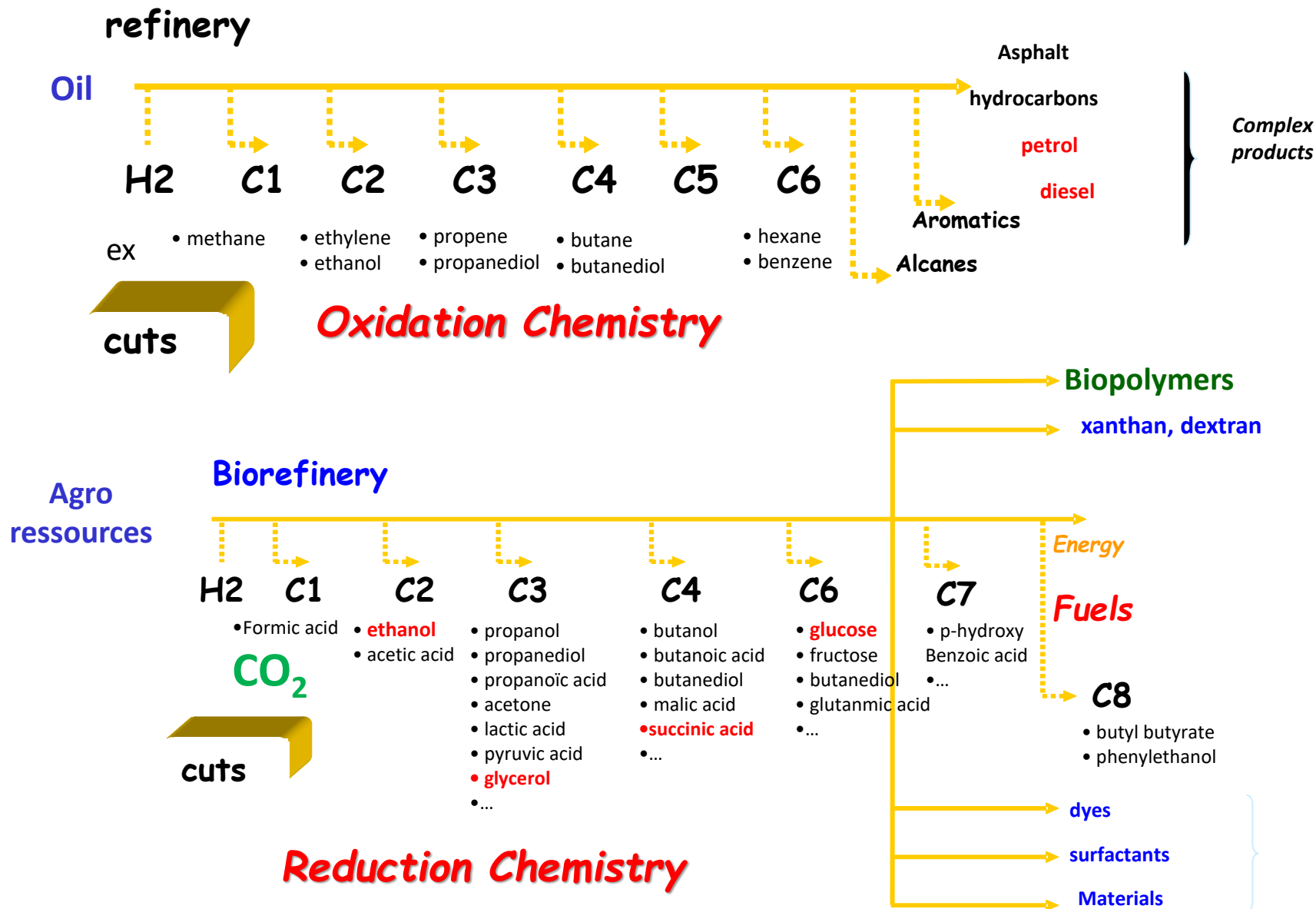


Ressources prize volatility

Extracted 9/10/2019 from <https://markets.businessinsider.com>

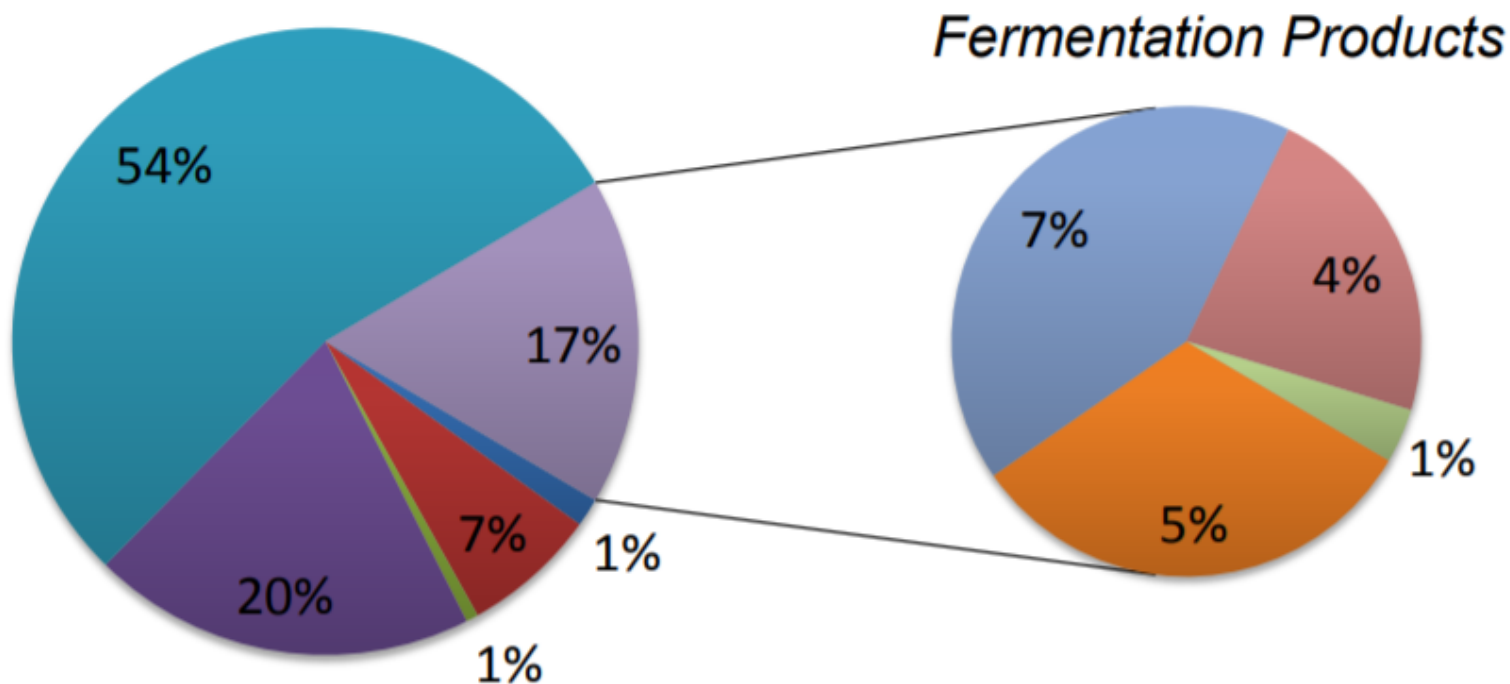
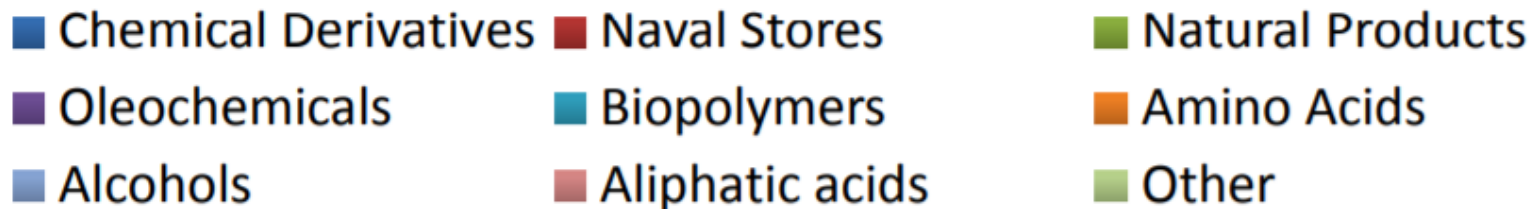


Refinery to Biorefinery

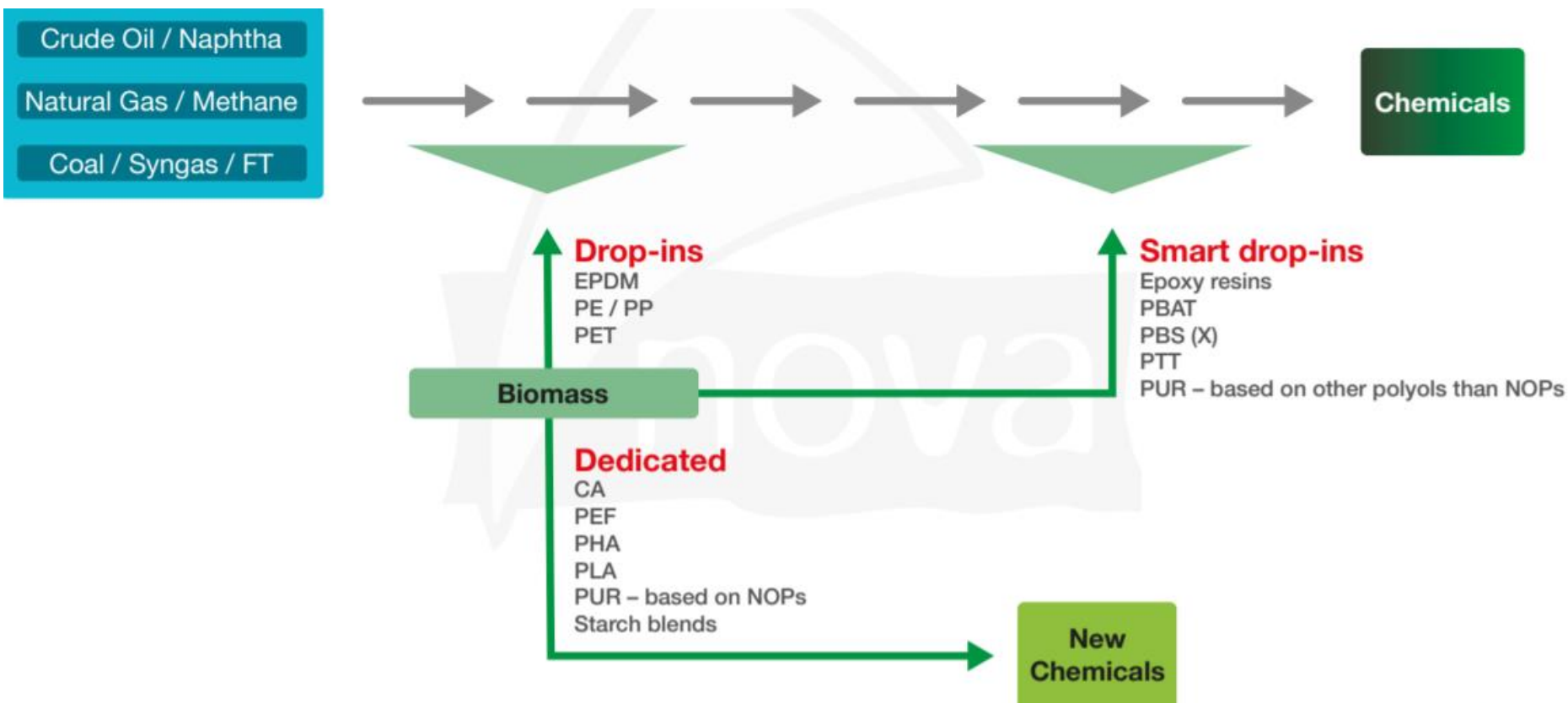


Bio-sourced chemicals and polymers

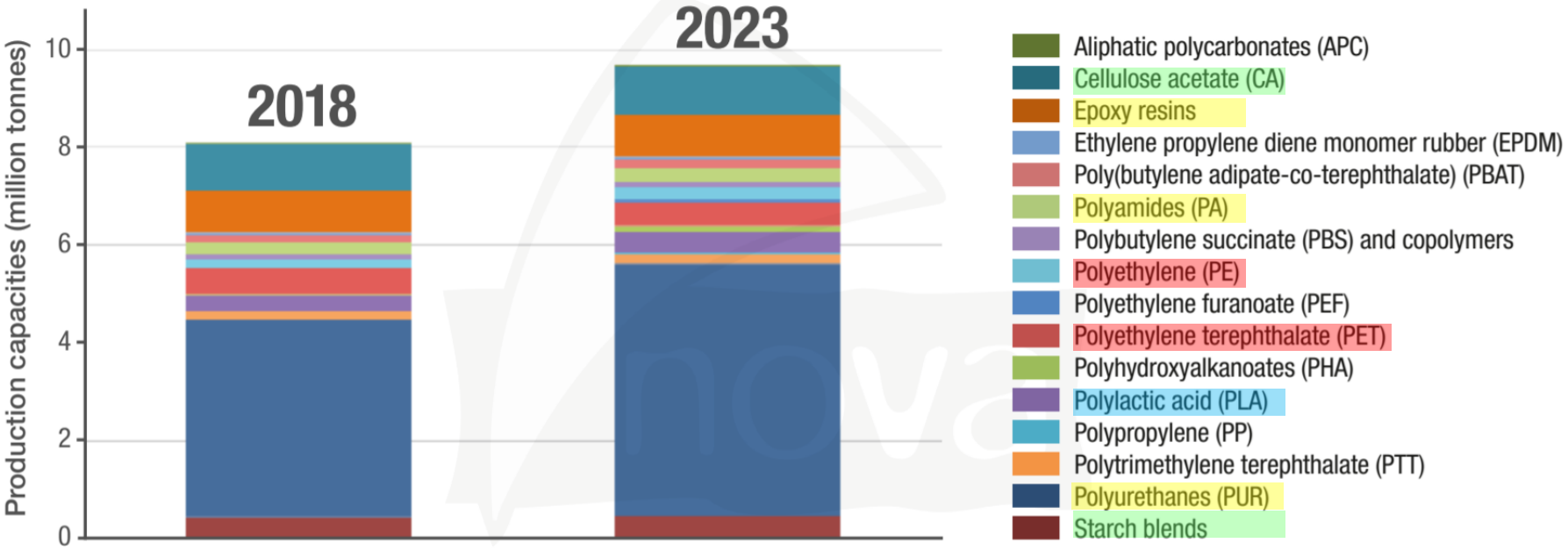
Market size ~ 50 million tones



Schematic differentiation of pathways of drop-in, smart drop-in and dedicated bio-based chemicals



Worldwide production of bio-based polymers

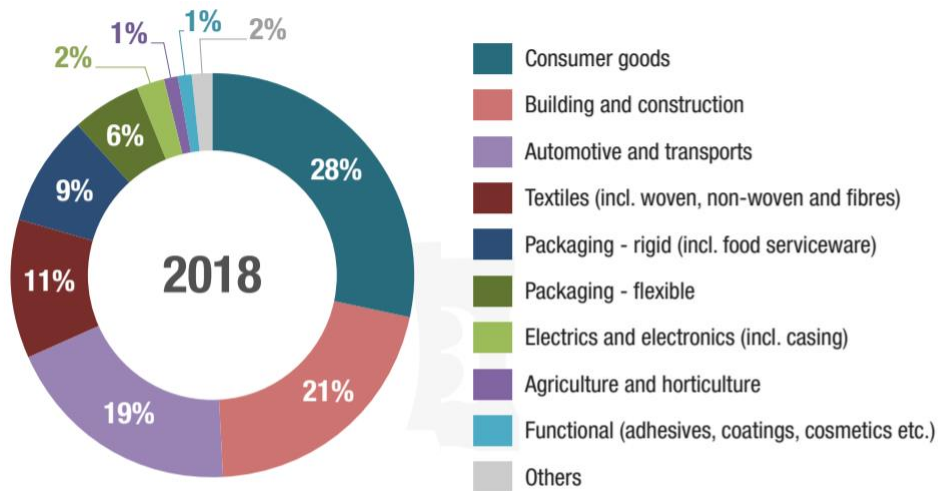
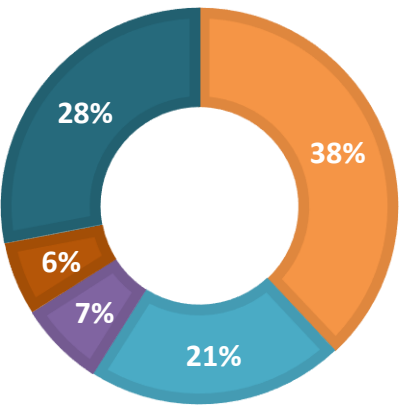


Polymer applications

vs

bio-based polymer applications

- Packaging
- Building & Construction
- Automotive
- E & E
- Others



Bio-based polymers : five drivers for development

Bio-based polymers development is driven by five main trends, combined or not:



Demand-driven

- Societal demand for bio-based, lower environmental impact plastics drive development of drop-in bioplastics: PE, PP, ...

- **Specific premium required on bio-plastics to compensate higher cost**



Supply-driven

-(perceived) Raw material supply constraint drive development of bio-based elastomers

- C
the

**For a success story all
5 drivers are needed**



Cost-driven

- Bio
bas

- Fermentation of (flared) natural gas to PHA, for use pure or in blend with PP



Functionality-driven

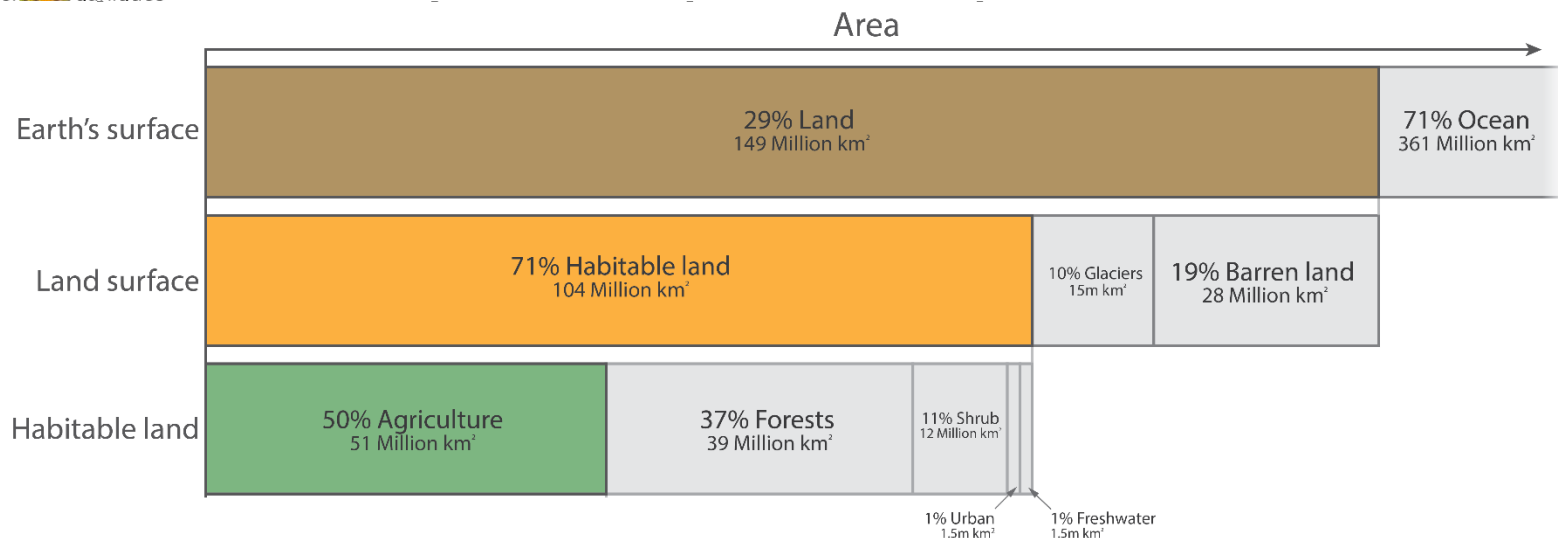
Bio-based plastic has no fossil-based equivalent. Its development is driven by new functionality: PLA, PHA, PEF,...



Legislation-driven

For some applications and in some countries (eg. FR, IT), the government imposes legislations obliging biodegradable packaging and maybe tomorrow tax incentives or obligations on bio-based plastics?

Worldwide land use

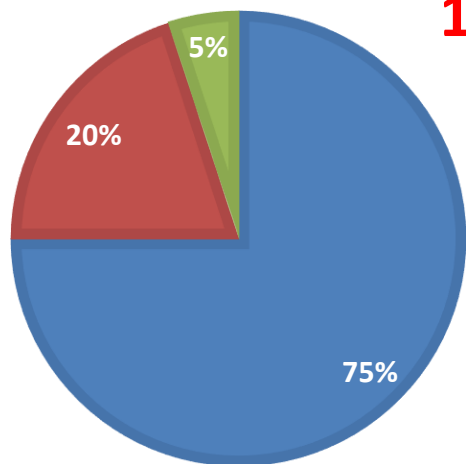


Biomass production \approx 120 billions tons/year
(210 with algae)

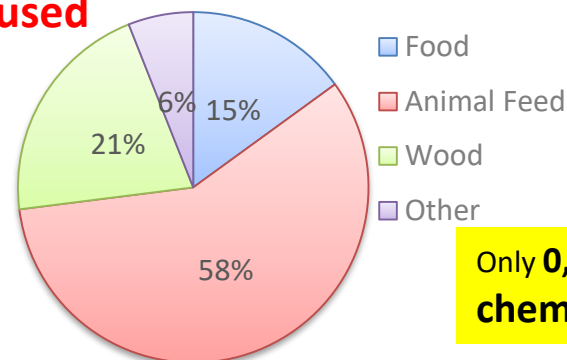
vs.

350 millions tons/y of polymers

10% of the biomass is used



■ Carbohydrates
■ Lignins
■ Other Vegetable oils, Terpenes, Proteins...



Only 0,5% for chemicals

Cellulose production \approx 400 millions tons/year
Less 1% of the worldwide cellulose production
 \approx 25% of the harvest wood

Food vs Fuel



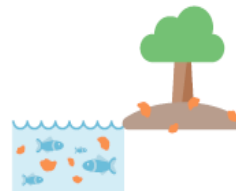
No impact on the price

- *Can use crop wastes* (traditionnaly use as soil fertilizer)
- *Develop specific crops with high yield*

| Crop | Oil content (%) | Oil yield (L/ha/year) |
|----------------|--------------------|-----------------------|
| Corn | 3.1–5.7 | 172 |
| Soybean | 18–22 | 446 |
| Canola/Mustard | 40–45 | 1190 |
| Jatropha | 20–40 | 1892 |
| Coconut | 17 | 2689 |
| Oil palm | 23 | 5950 |
| Microalgae | 30 (min. scenario) | 58,700 |
| Microalgae | 70 (max. scenario) | 136,900 |

Petroleum consumption in France **10 GL/y**
100 kha of microalgae needed
2 ‰ of France surface

1- Why ?



2- How ? → Biomass transformation to platform chemicals

3- Bio-based plastics from natural polymers

4- Drop-ins: Bio-based alternative to fossil-based polymers

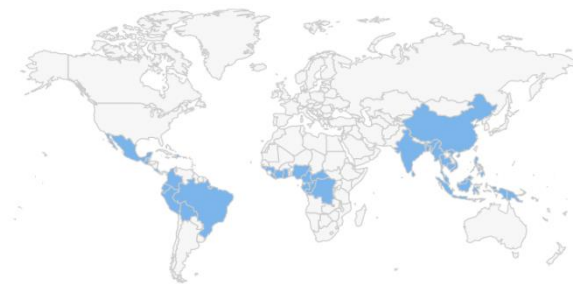
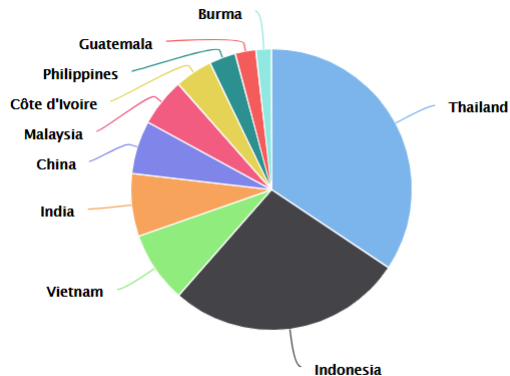
5- Smart drop-ins: Bio-based derivative of “fossil” polymers

6- New polymers from biomass

7- Conclusions and perspectives

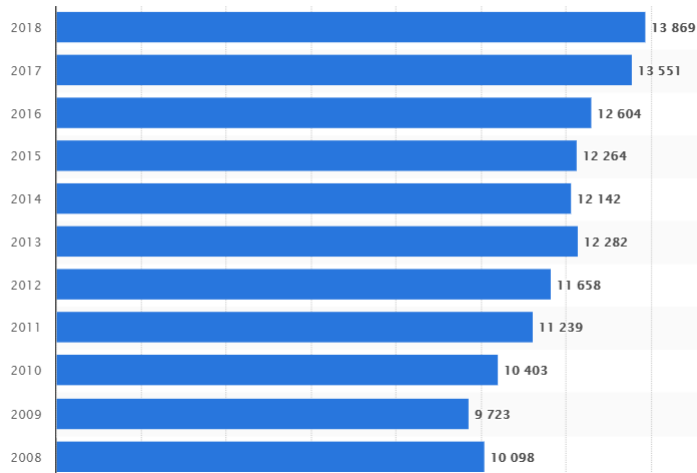
Natural rubber from latex

- Rubber products : polyisoprene 1,4-cis
13.9 Mt (2018)



● Natural rubber, production quantity (tons)

Source: FAOSTAT © Natural Earth



Production increase is too slow for the worldwide demands

→ Other sources

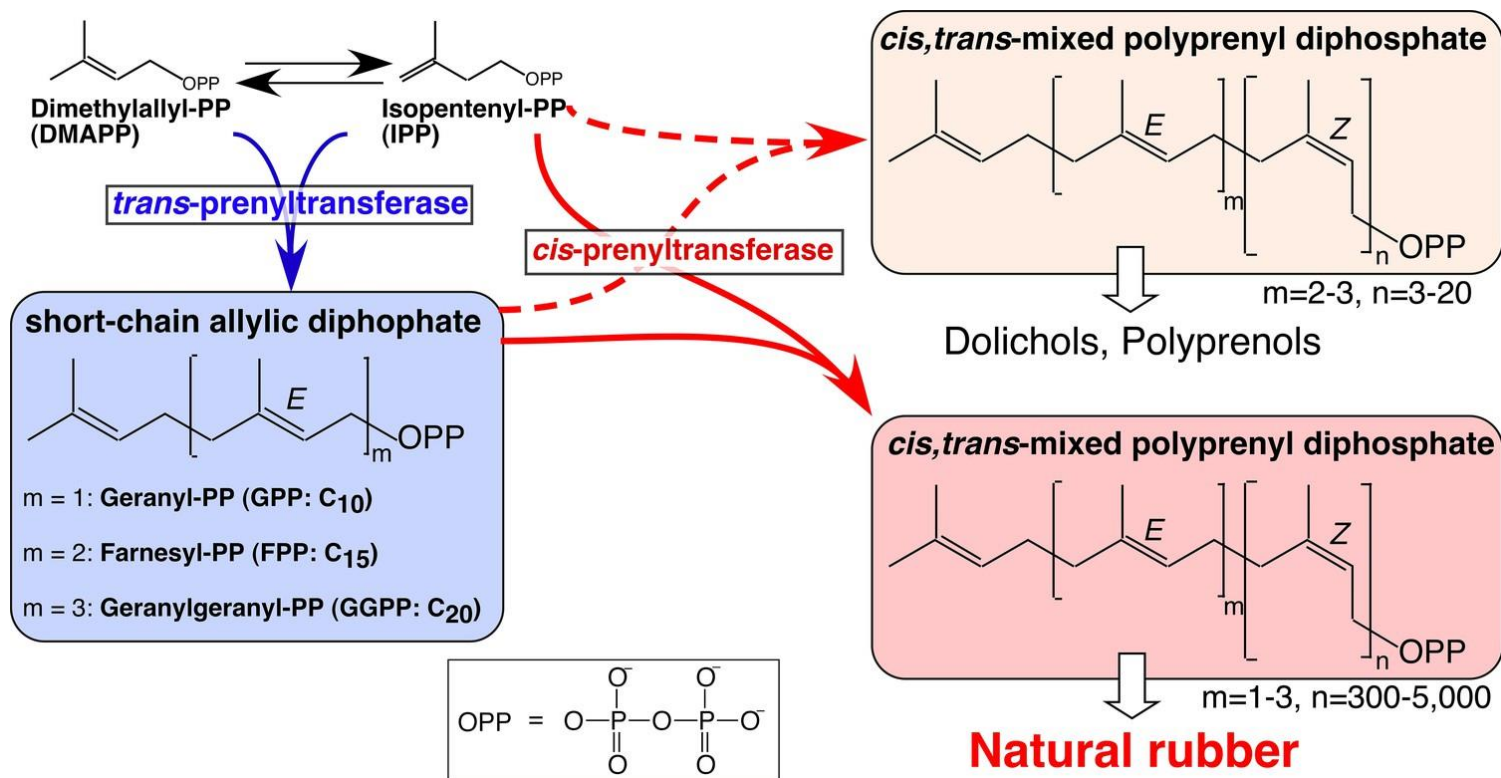
Synthetic polyisoprene: 15.6 Mt (2018)



shutterstock.com • 436160047

Natural rubber from latex

Biosynthesis pathway of natural rubber



Impossible to obtain by regular polymerization processes
→ Enzymatic pathway

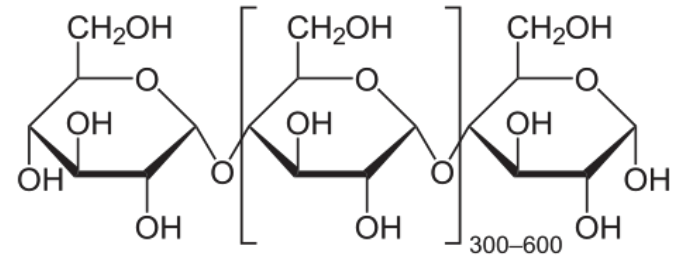
Starch based polymers

Starch blend with different polymers

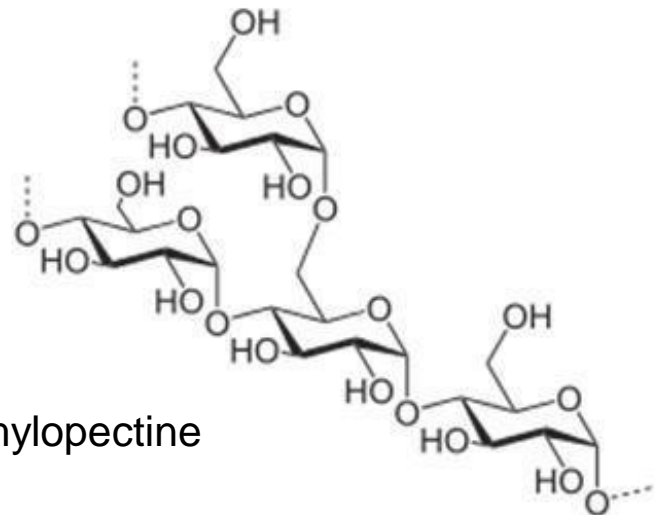
400 Kt (1Mt for the blend)

- Starch in blends with polyesters
 - Polycaprolactone
 - Poly(butylene adipate-co-terephthalate) (PBAT)
 - Poly(butylene azelate) (PBAZ)
 - PLA, PHA, PBS, ...
- Starch acetate in alloys with Polyolefins

Bio-based Carbon content : 25 to 100 %



Amylose

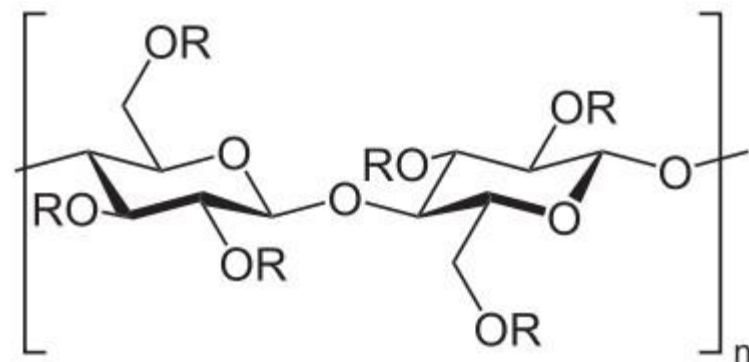
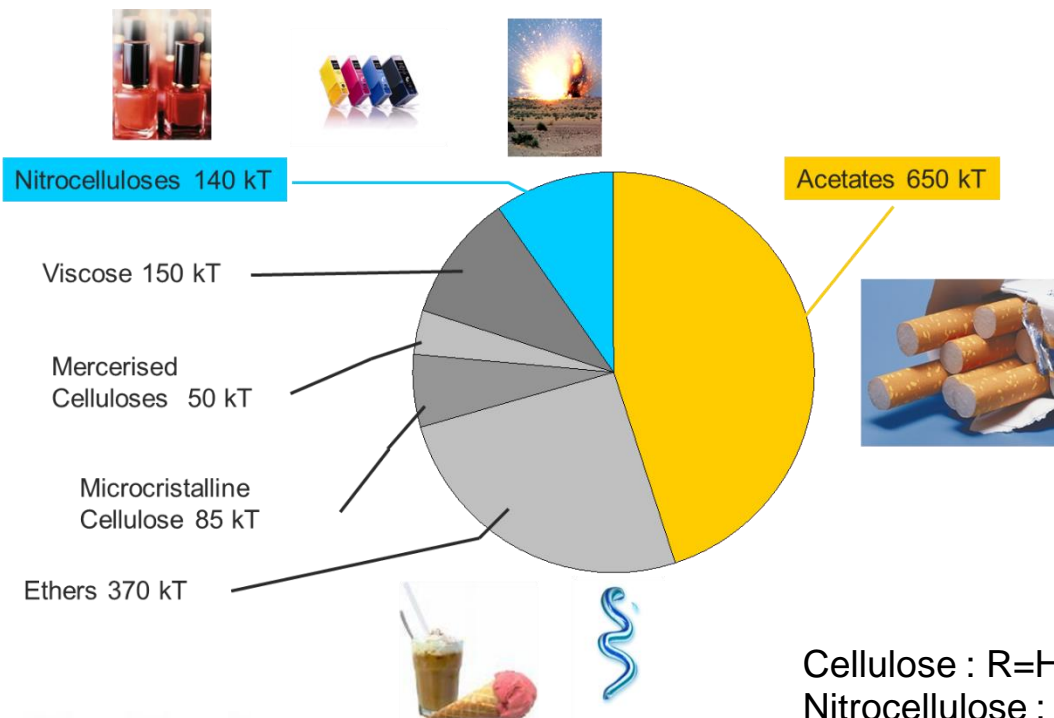


Amylopectine



Cellulose-based polymers

Mature market with small growth (1.5Mt)



Cellulose : R=H

Nitrocellulose : R=H & NO₂

Cellulose acetate : R=CH₃CO

Cellulose acetate/butyrate : R=CH₃CH₂CH₂CO

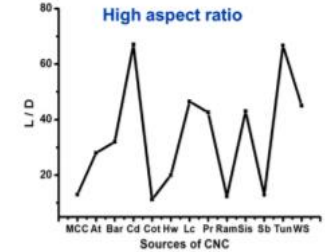
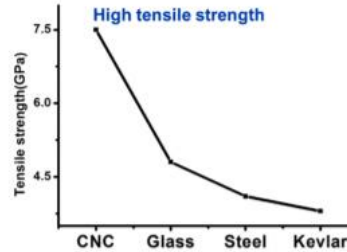
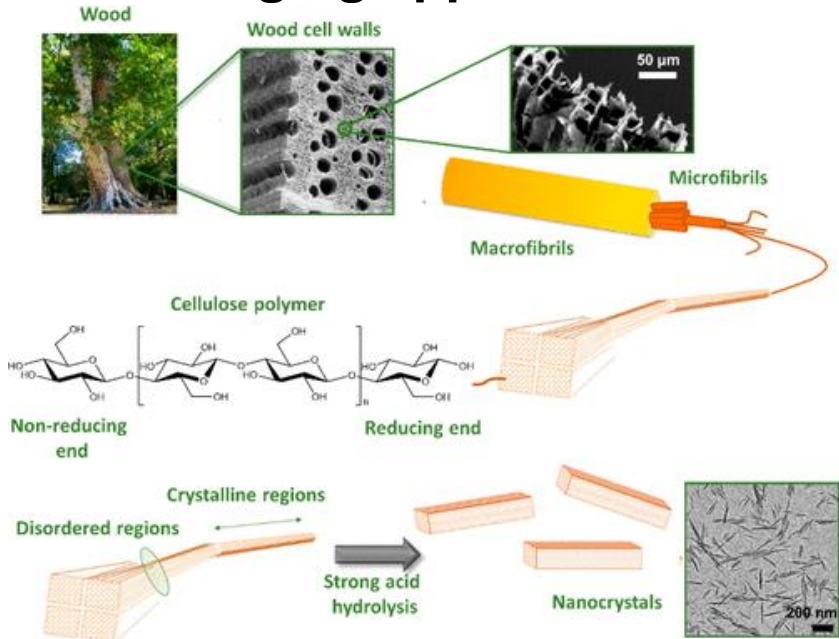
Hydrophilic cellulose ethers: R=CH₂CH₂OH; CH₂CH(CH₃)OH; CH₂COOH



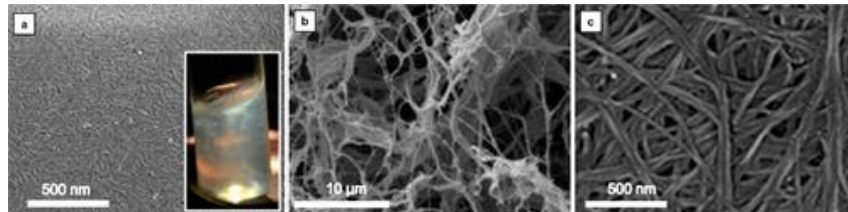
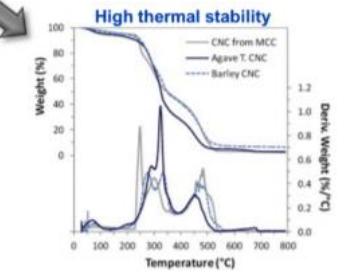
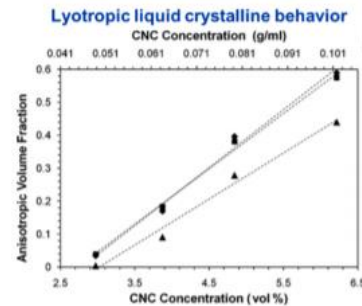
Not a thermoplastic

Cellulose-based polymers

Emerging application



Cellulose nanocrystals

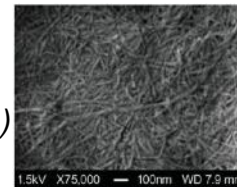


CNC

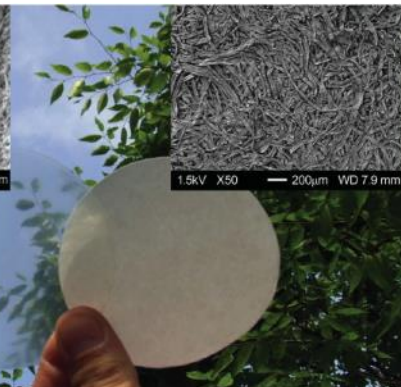
CNF

BC

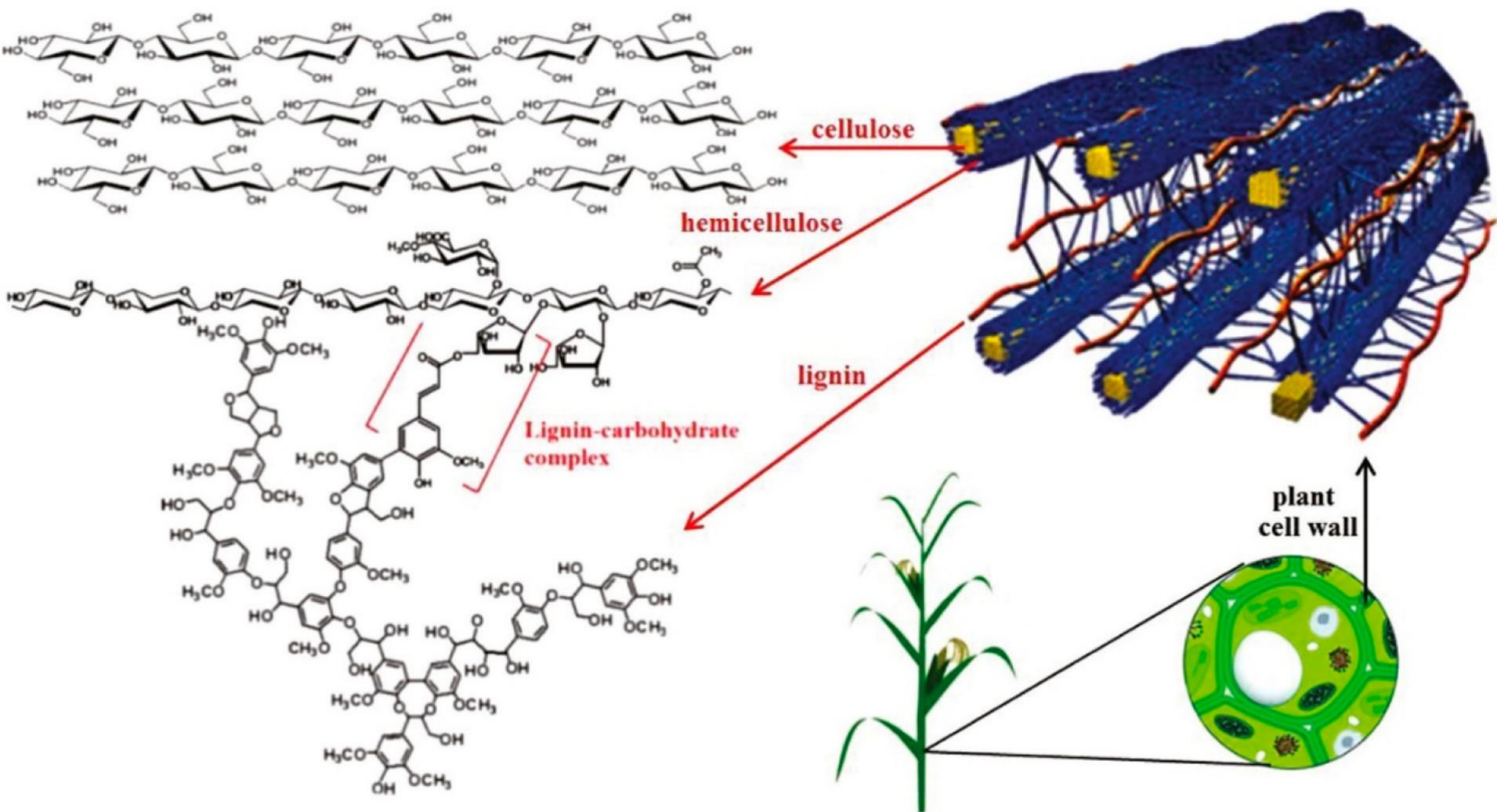
CNC
(100 nm)



CF
(200 μm)



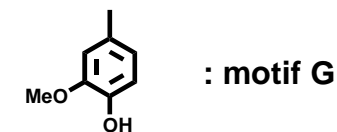
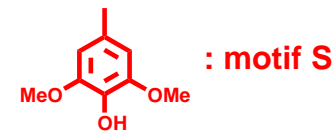
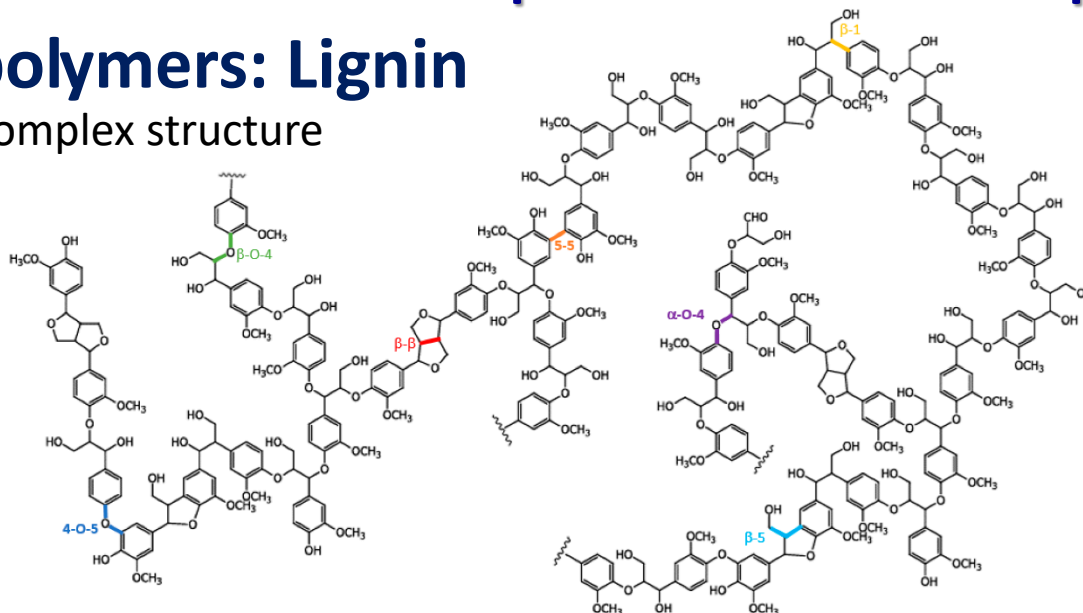
Other polymers



Other polymers: Lignin

Extremely complex structure

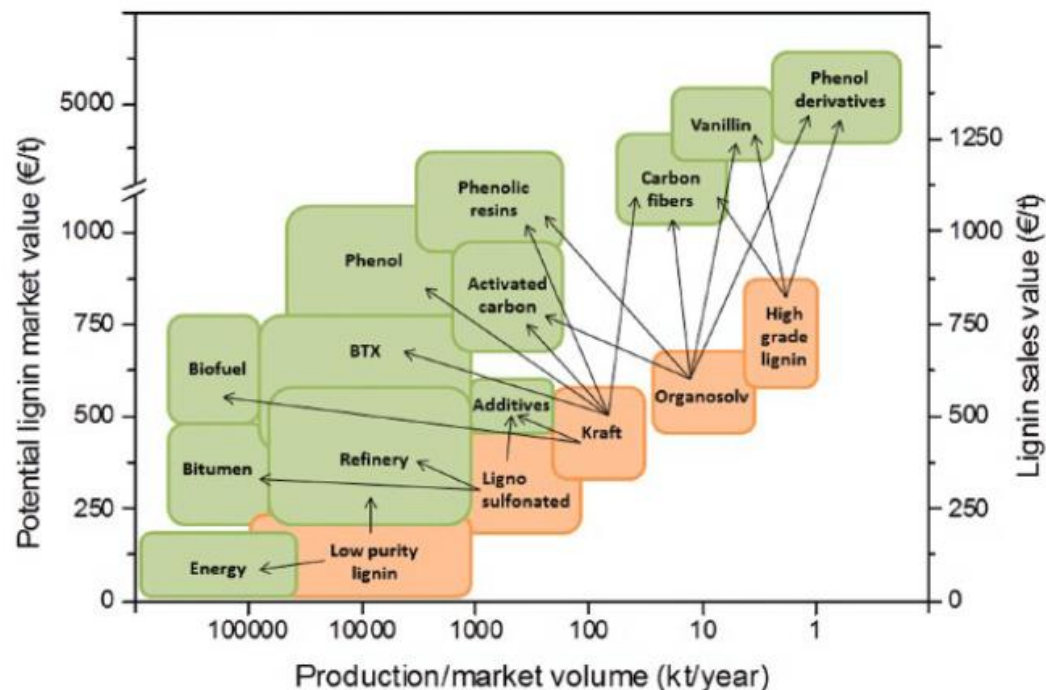
500 kt



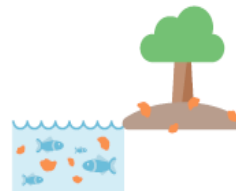
No plasticizer



Lignosulfonate, 0.4%



1- Why ?



2- How ?

→ Biomass transformation to platform chemicals

3- Bio-based plastics from natural polymers

Cellulose, lignin, Natural rubber

4- Drop-ins: Bio-based alternative to fossil-based polymers

5- Smart drop-ins: Bio-based derivative of “fossil” polymers

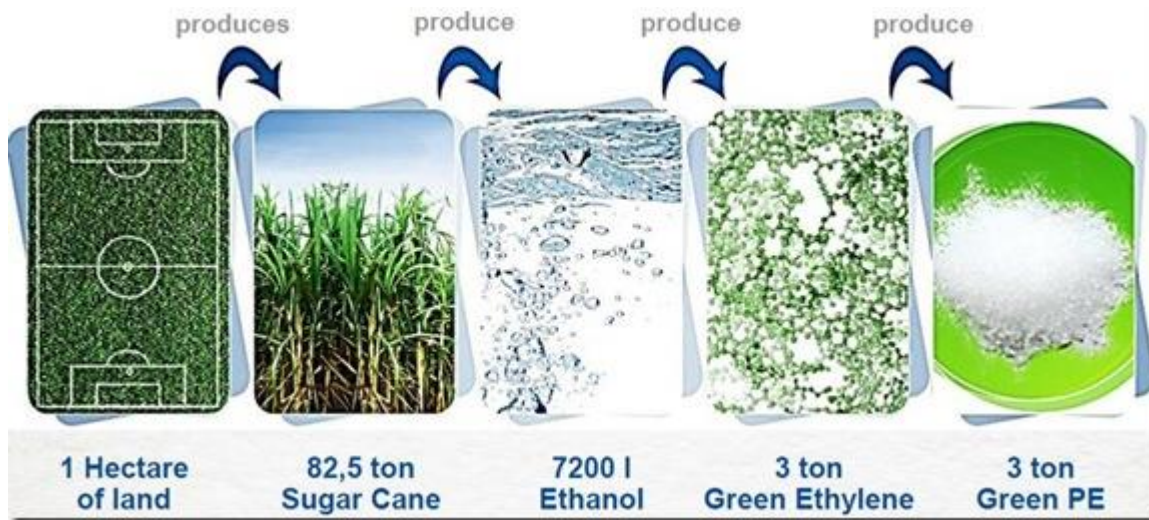
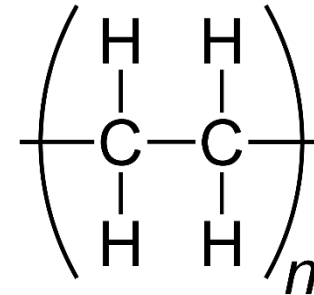
6- New polymers from biomass

7- Conclusions and perspectives

Polyethylene (PE)

200 Kt

- Industrial plant in Brazil (Braskem)
- Premium value on the market due to bio-origin
- Too expensive outside Brazil



-3.09 kgCO₂e/kg

(vs 1.96 kgCO₂e/kg)

27 Mha



vs. **80 Mt** of PE

¼ of the habitable land !!!

Polyethylene terephthalate (PET)

600 Kt

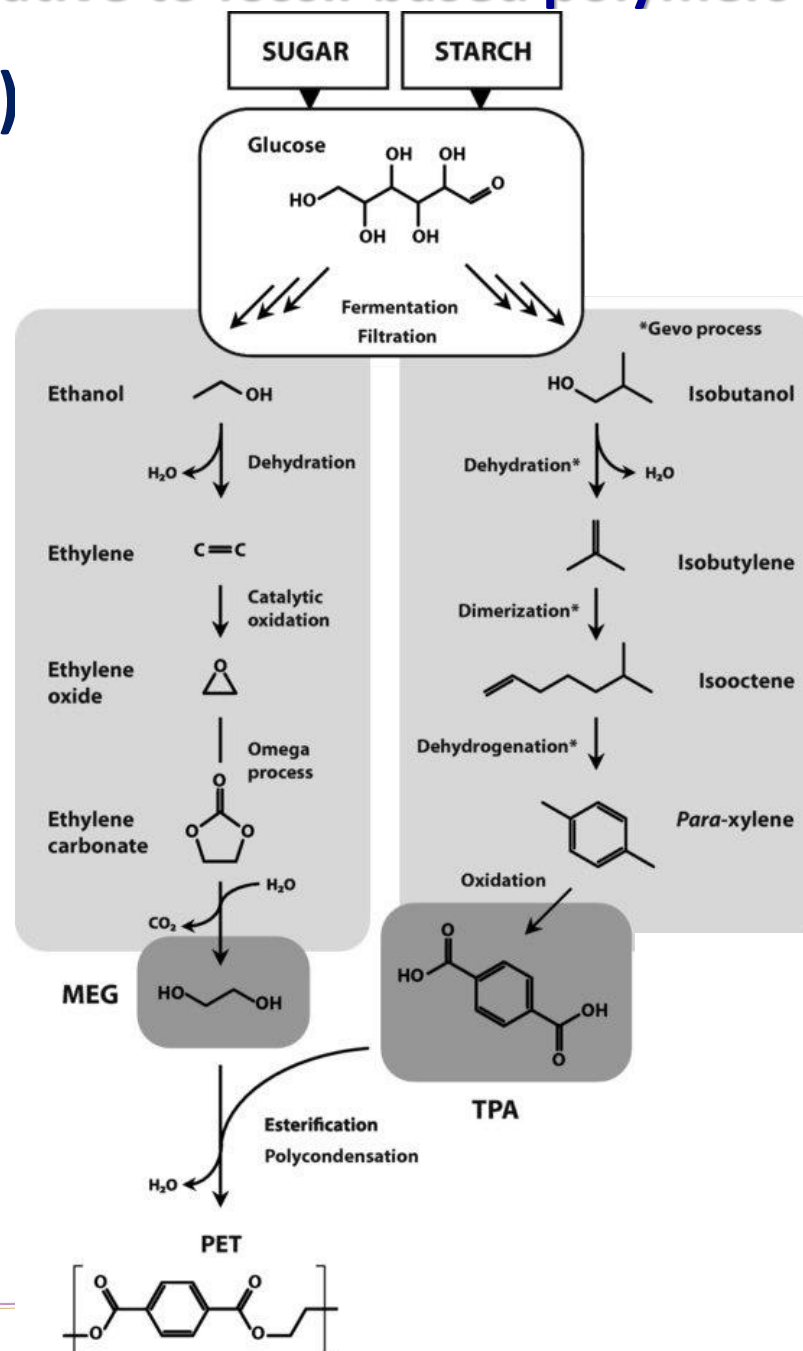
Most bio-based PET are only **30%** (20%) bio-based

Since 2015, Coca-Cola company produce **100%** bio-based
by 2020 all their PET bottles will be 100% bio-based



4 kgCO₂e/kg

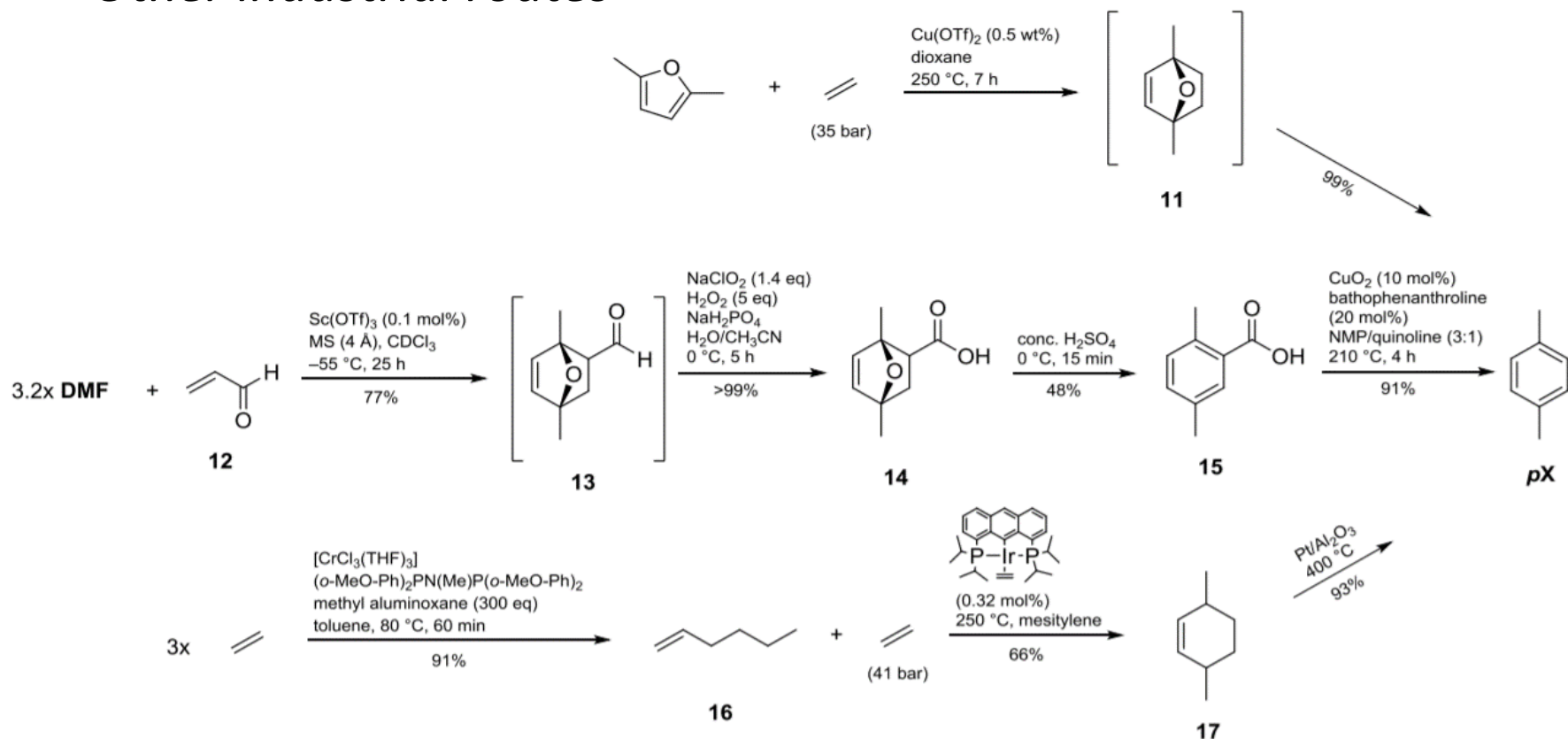
(vs 2.73 kgCO₂e/kg)



Polyethylene terephthalate (PET)

Other routes to terephthalic acid:

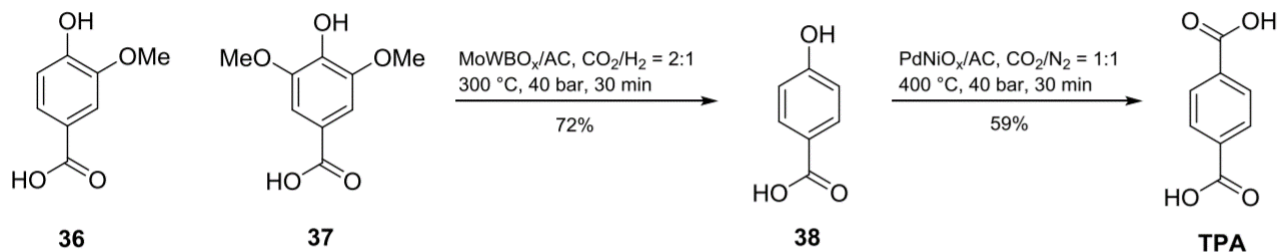
Other industrial routes



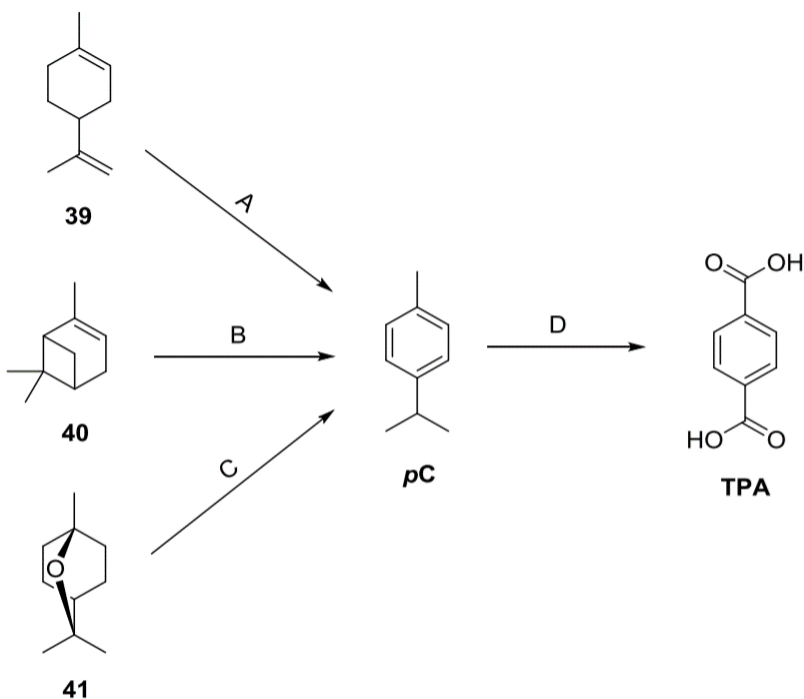
Polyethylene terephthalate (PET)

Other routes to terephthalic acid:

Lignin



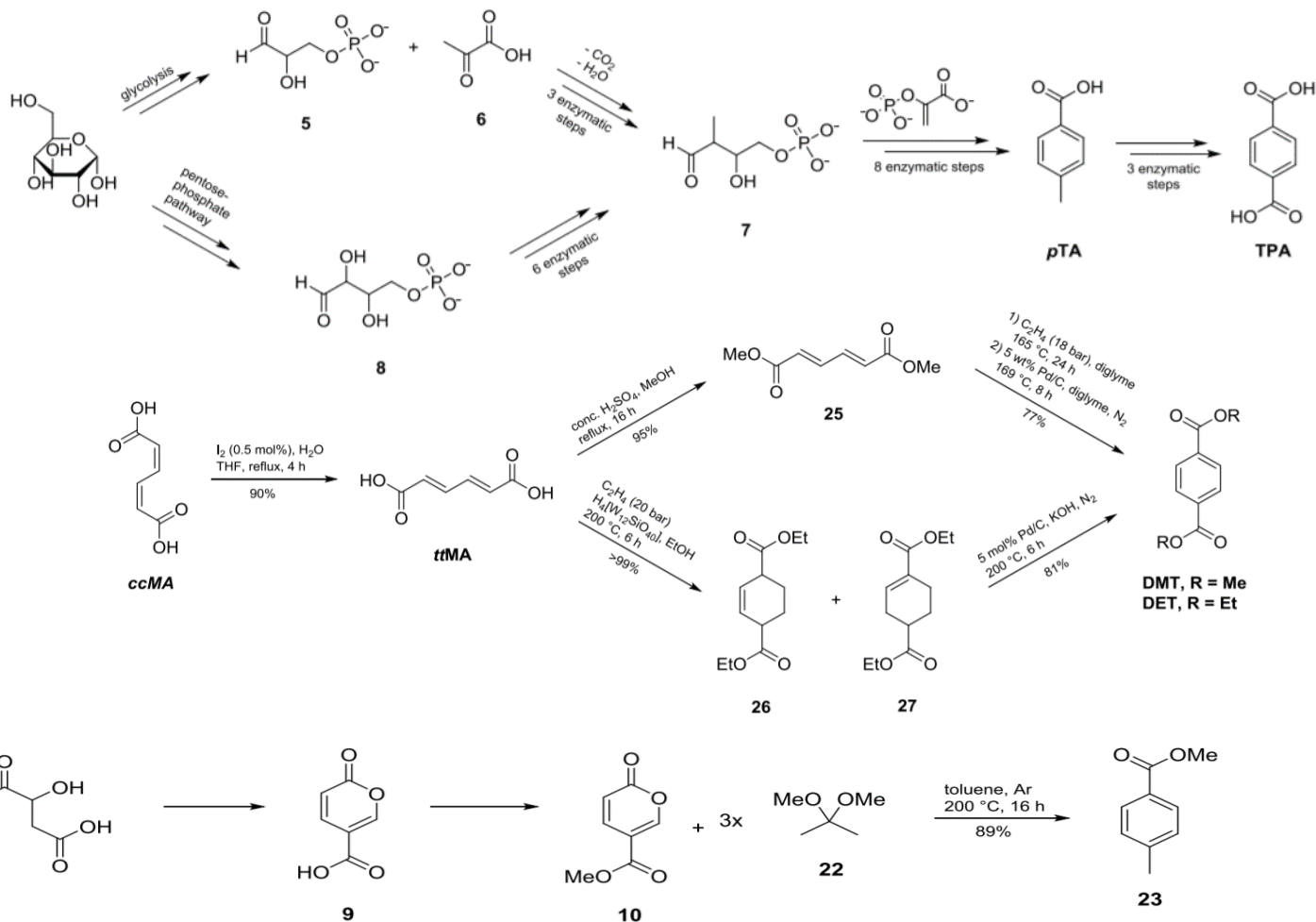
Terpens



Polyethylene terephthalate (PET)

Other routes to terephthalic acid:

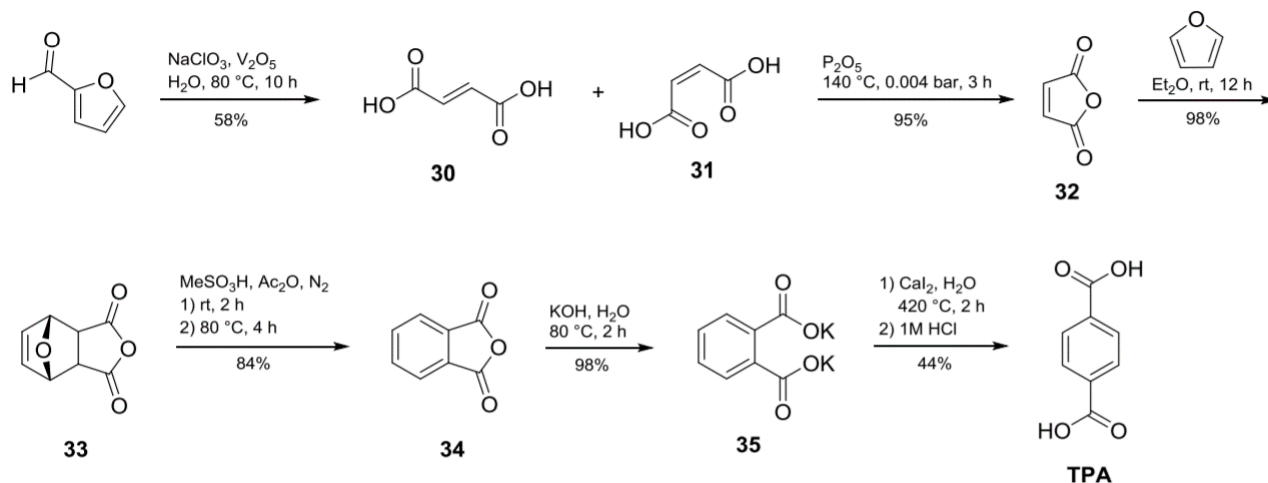
Sugars (C6)



Polyethylene terephthalate (PET)

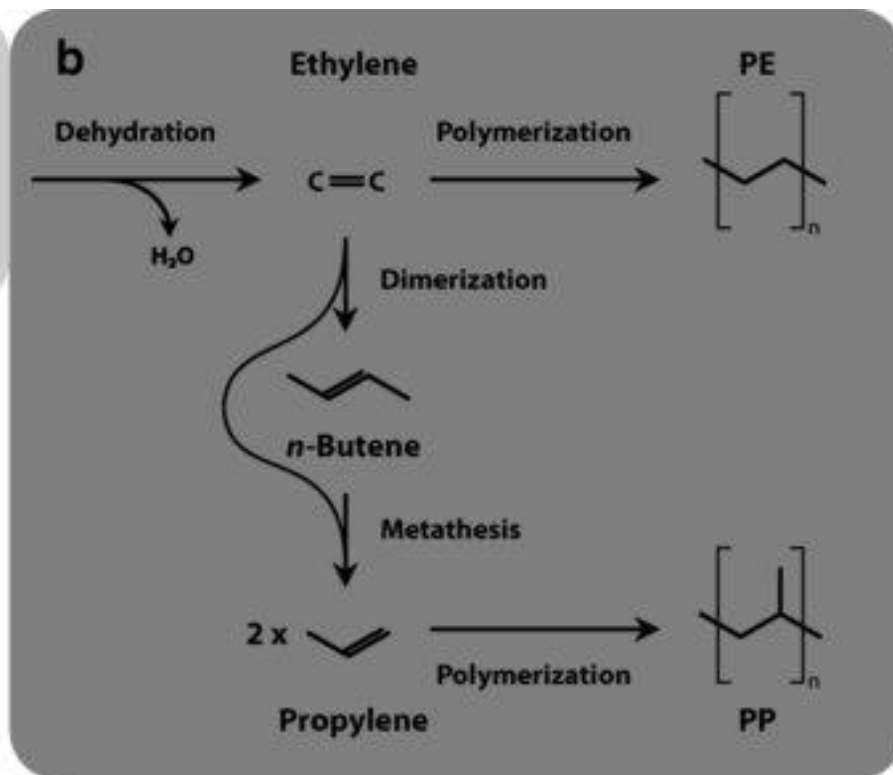
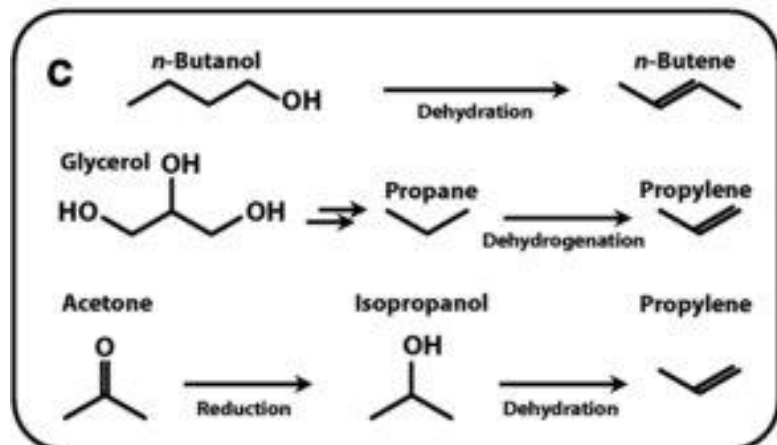
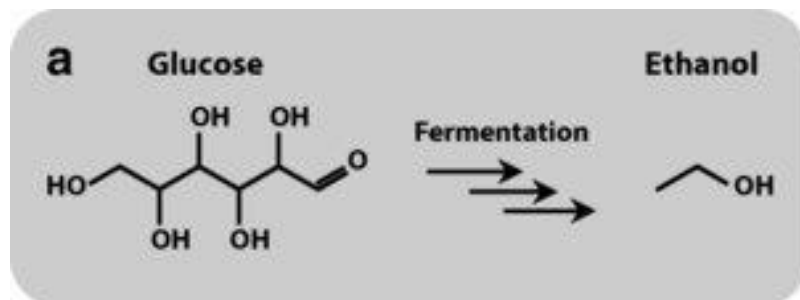
Other routes to terephthalic acid:

Sugars (C5)



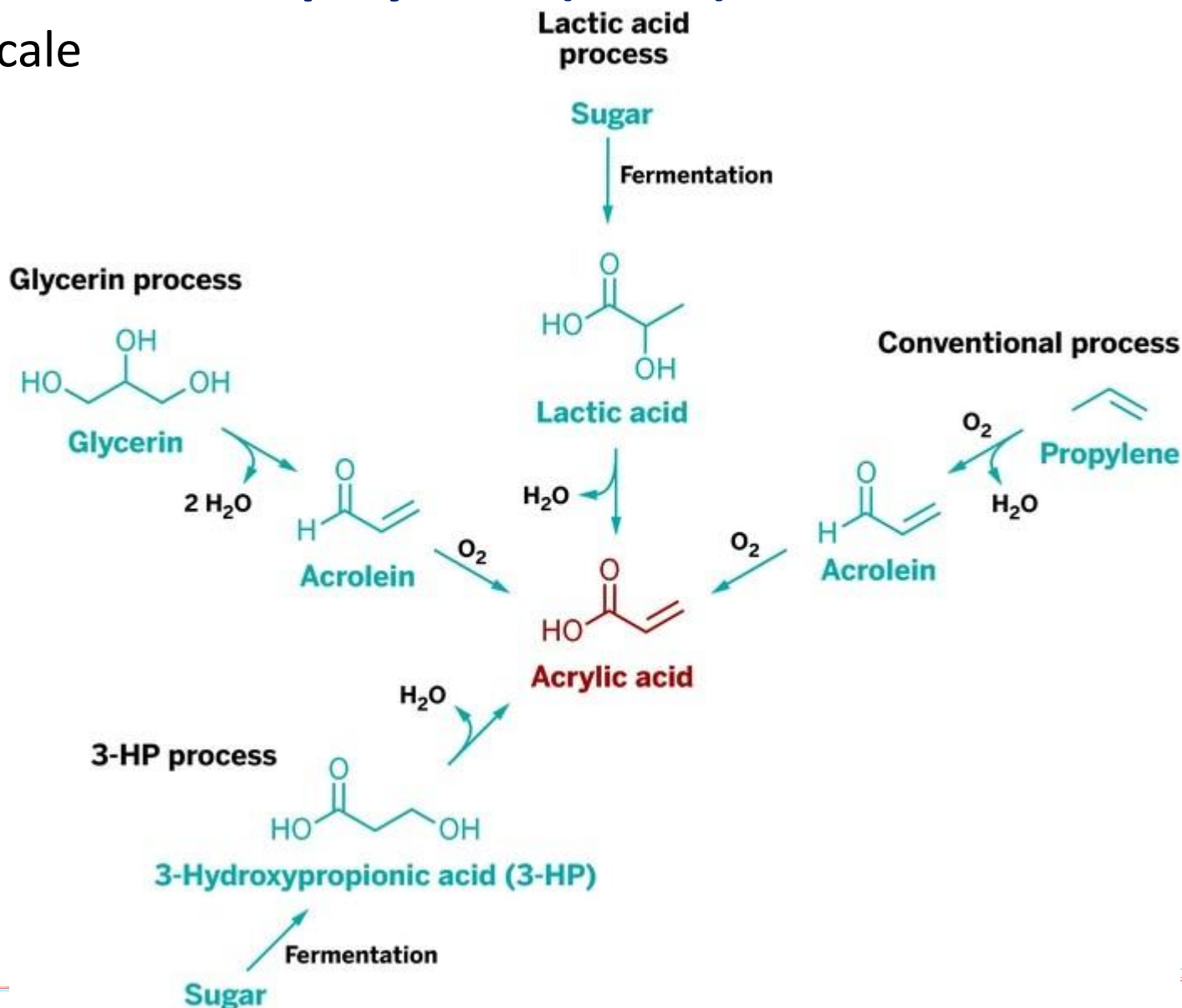
Polypropylene (PP)

20 kt



Super Absorbent polymers (SAP's)

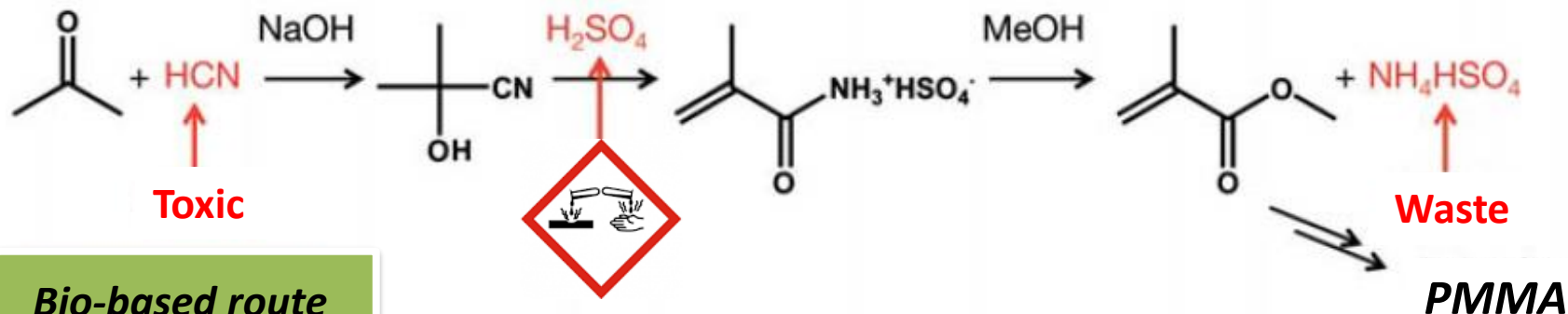
Pilot scale



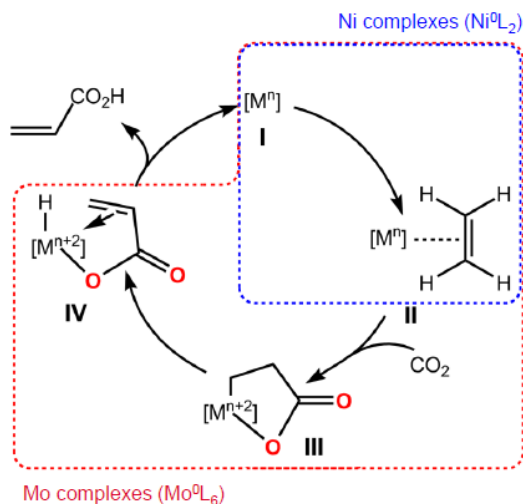
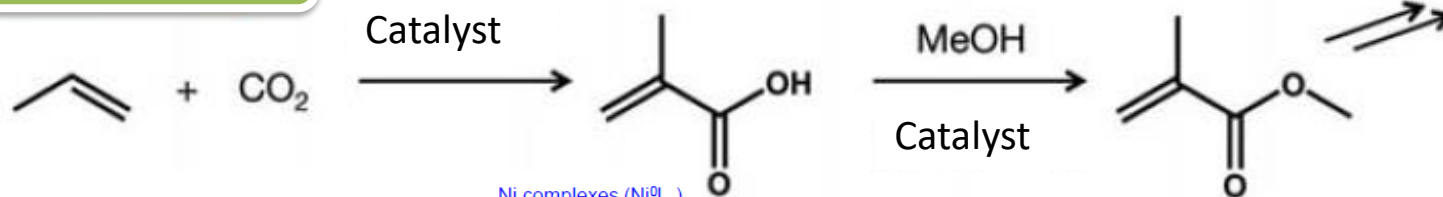
Poly(methyl methacrylate) (PMMA)

Pilot scale

Traditional route



Bio-based route

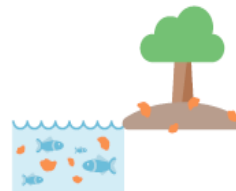


Greener ✓

Safer ✓

Bio-based ✓

1- Why ?



2- How ?

→ Biomass transformation to platform chemicals

3- Bio-based plastics from natural polymers

Cellulose, Natural rubber

4- Drop-ins: Bio-based alternative to fossil-based polymers

PE, PET

5- **Smart drop-ins: Bio-based derivative of “fossil” polymers**

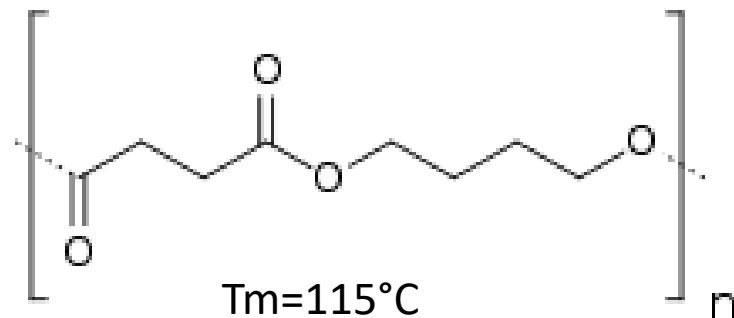
6- New polymers from biomass

7- Conclusions and perspectives

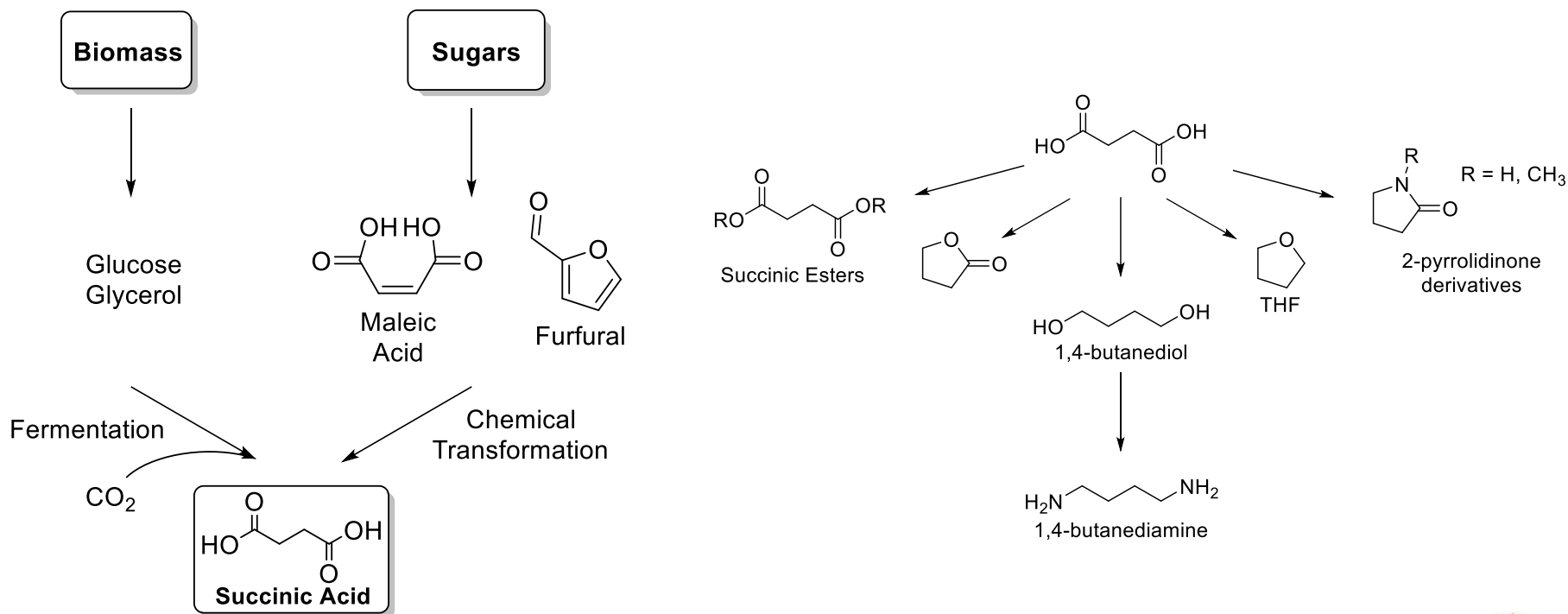
Polybutylene succinate (PBS)

100 kt

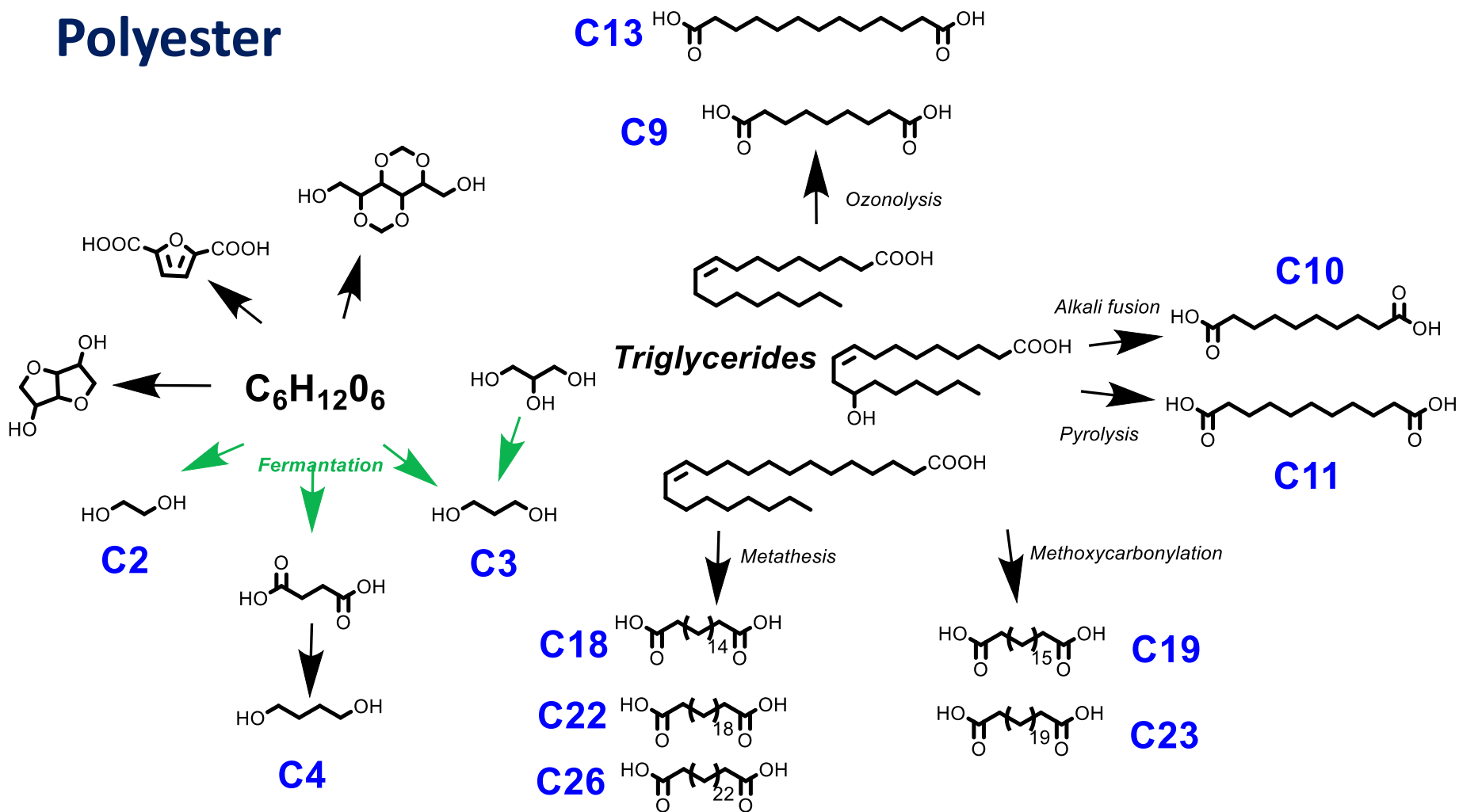
Bio-based succinic acid cost \approx fossil



PBS polyethylene-like properties + biodegradable



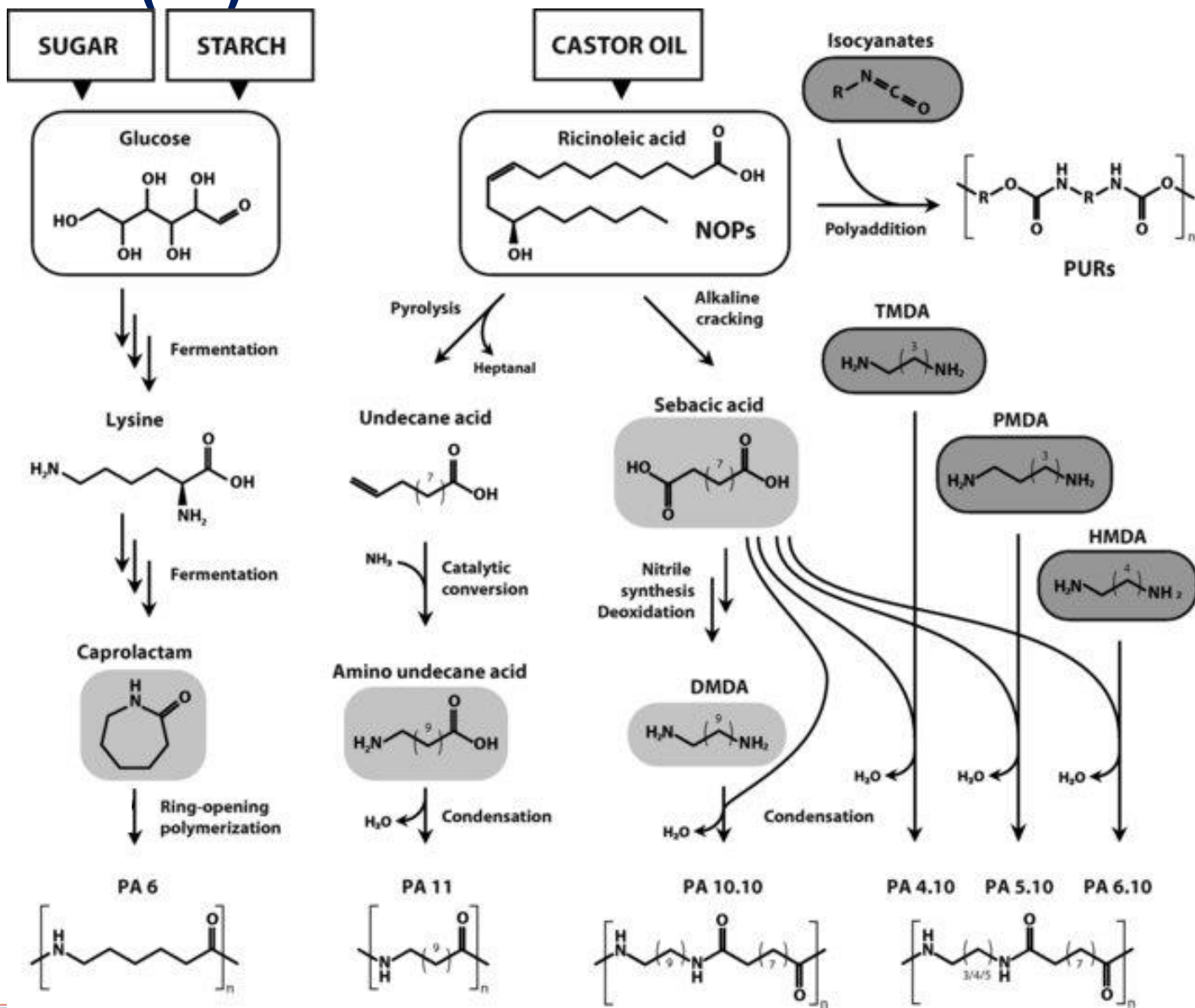
Polyester



PET, PPT, PBT, PBS, PBAz ... polyethylene mimick

Polyamides (PA)

200 kt



Polyamides (PA)

Stiffness
↑
Hydrophobicity
↓
Elasticity

Polyamide

PA 6

PA 6-10

PA 11

PA 12

+

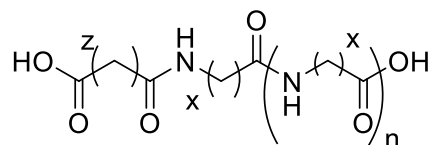
Polycondensation

Polyether

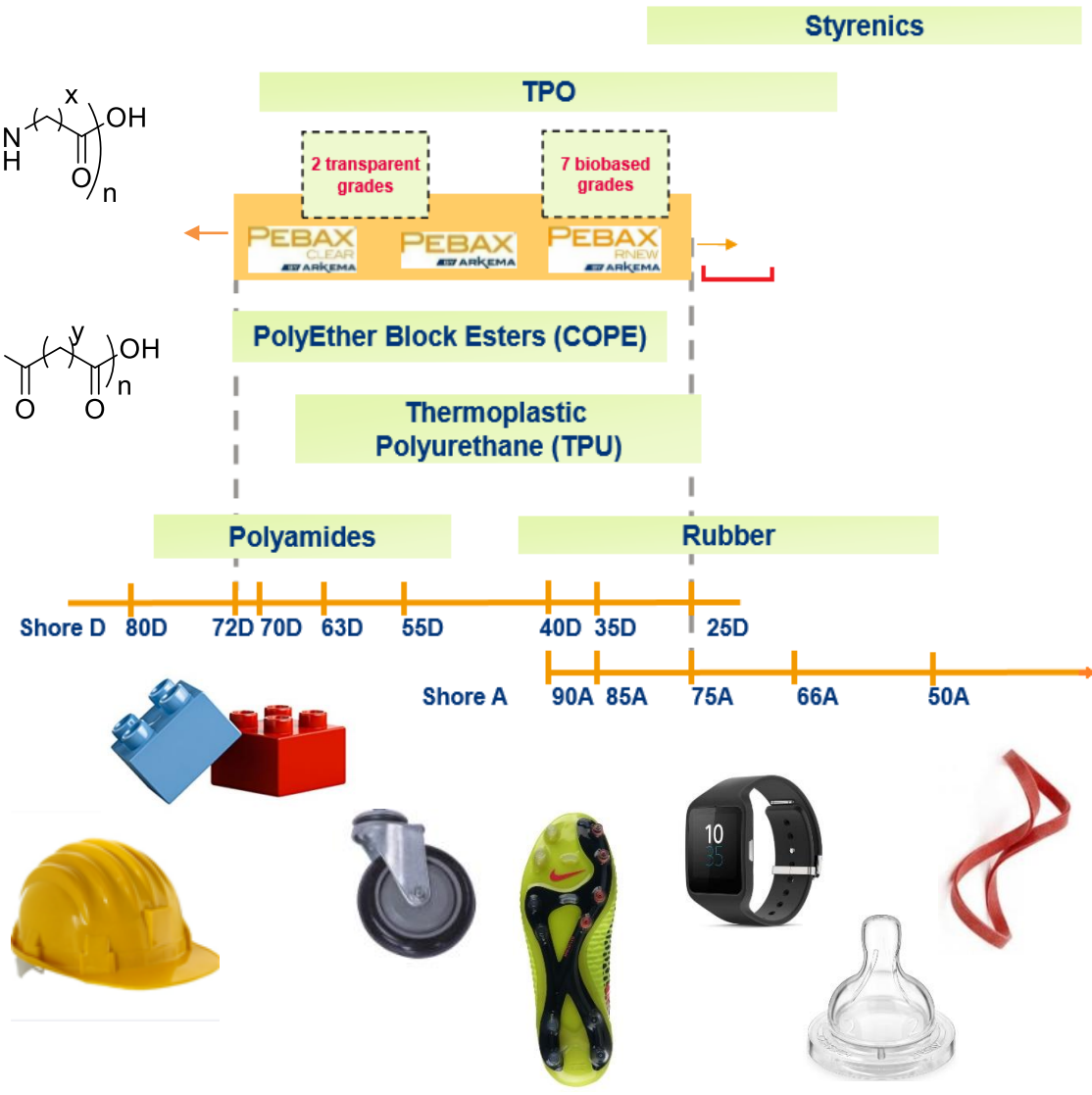
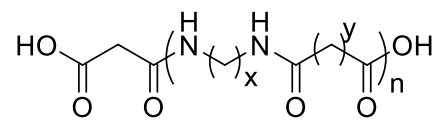
PEG

PPG

PTMO

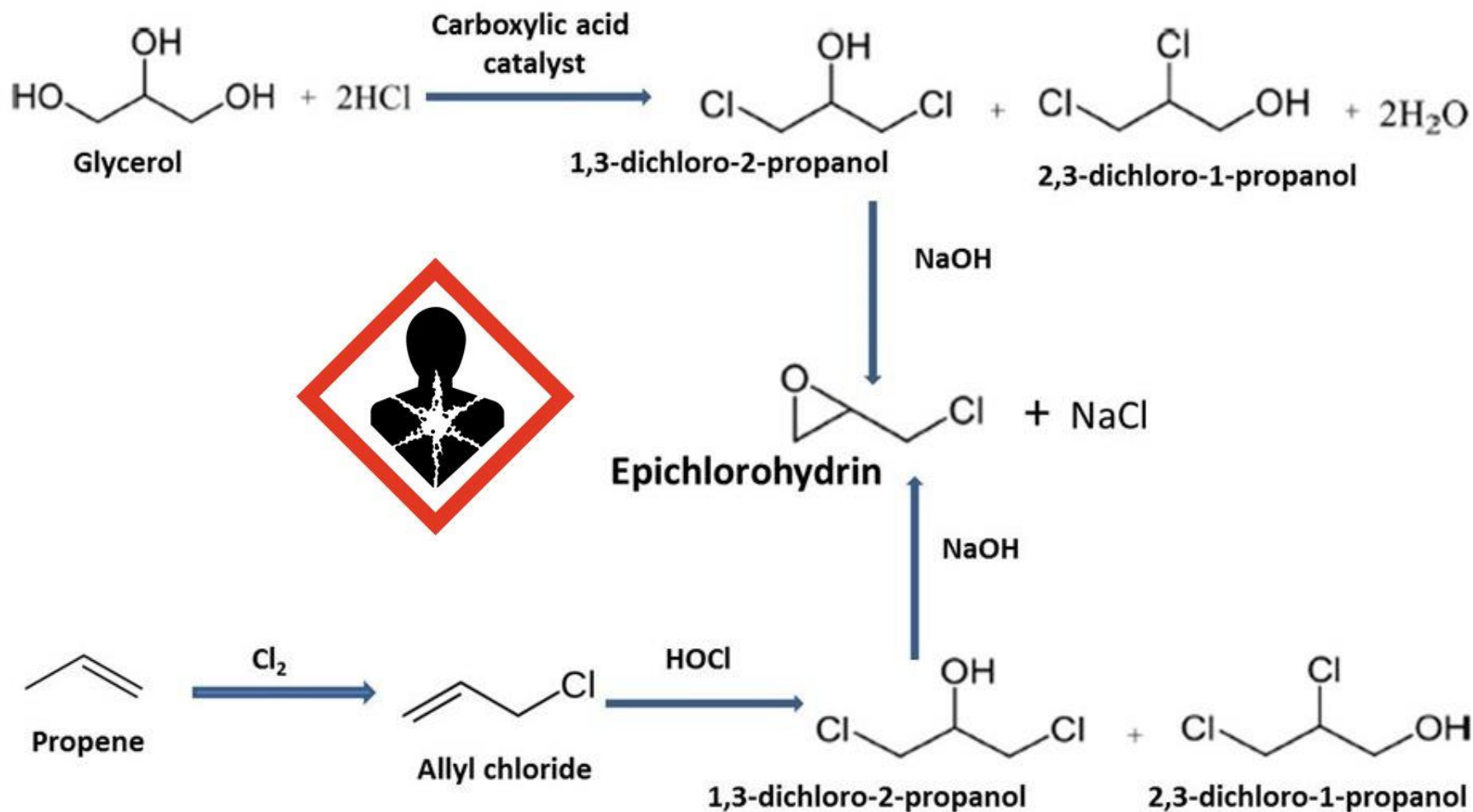


or



Epichlorohydrin

1.5 Mt



Epoxy

- ▶ 75% of epoxy are derived from Bisphenol-A (BPA)



OIL REFINERY
FACTORY

- ▶ Environnemental and economics concerns

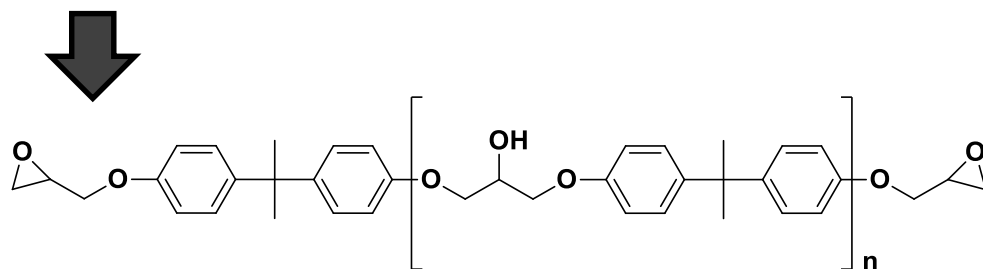
- Petrochemicals → fossil carbon
- Price volatility

High risk of obsolescence of BPA

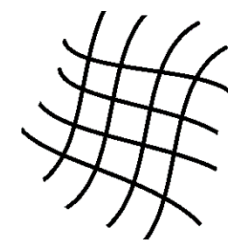
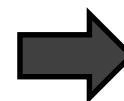


Bisphenol-A

- ▶ Toxicity of BPA → *CMR*^{1B}



DiGlycidyl Ether of Bisphenol-A (**DGEBA**)

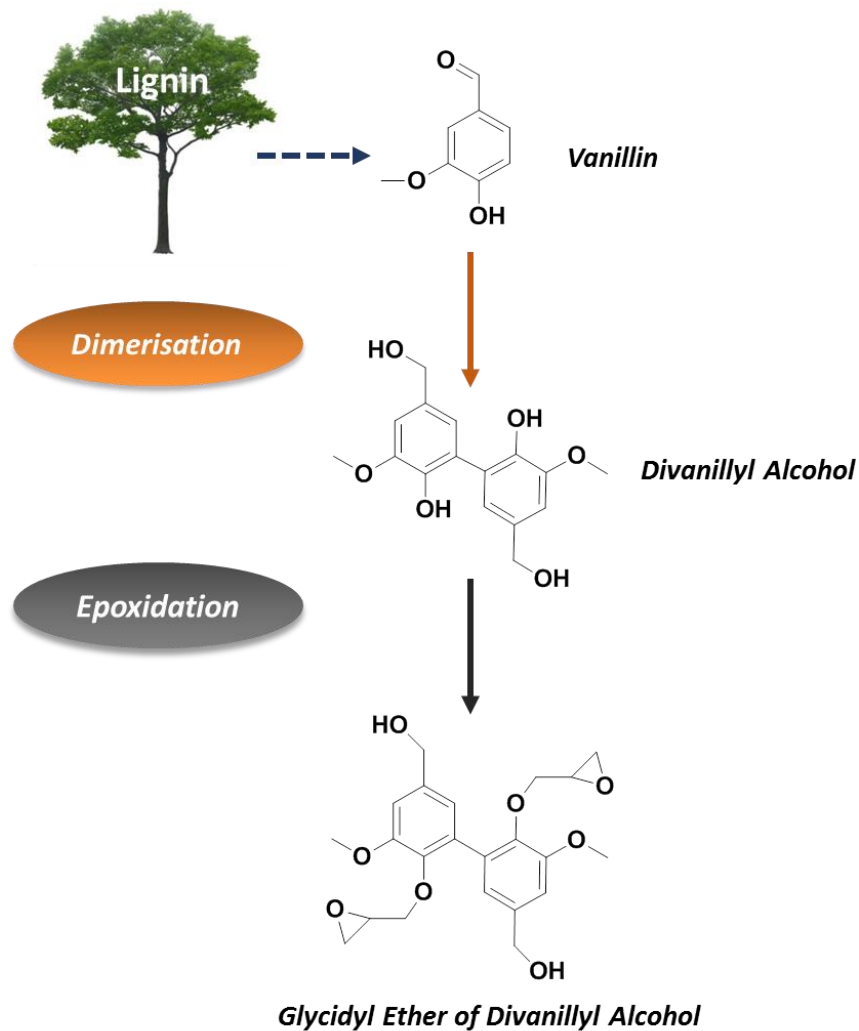
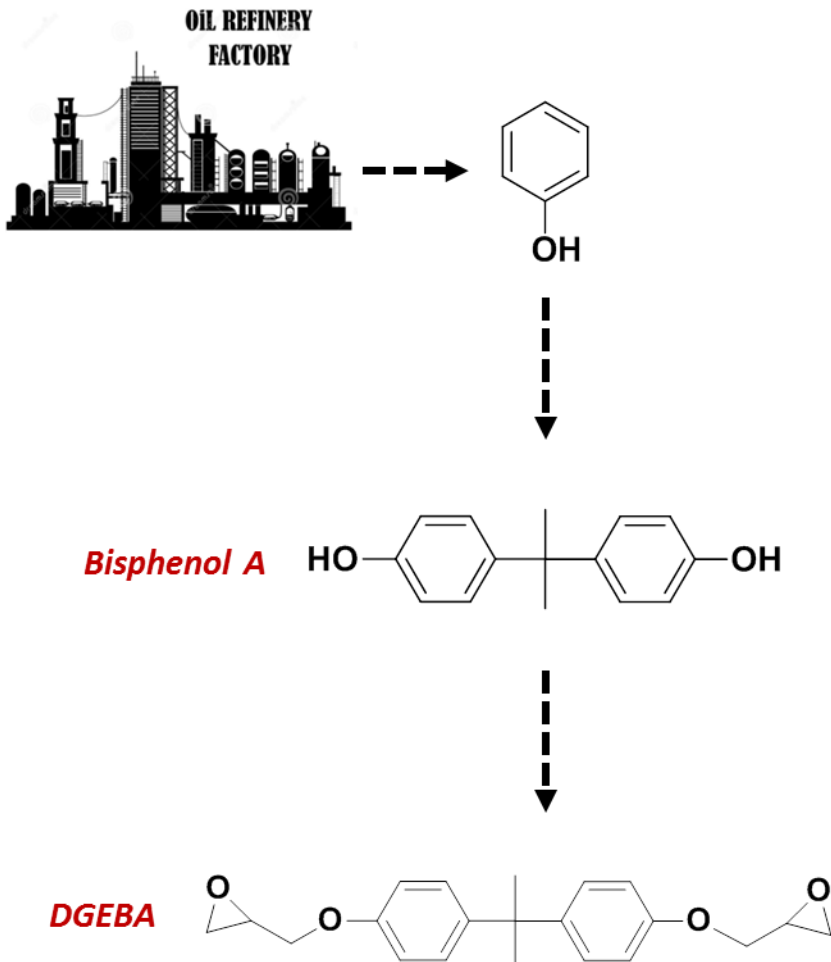


3D-network

40-25% bio-based if epichlorohydrine bio-sourced

Epoxy

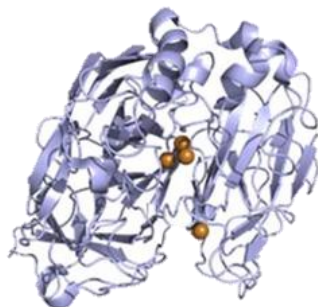
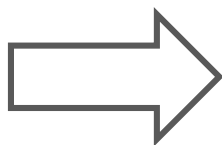
From Lignin to epoxy resins...



Epoxy

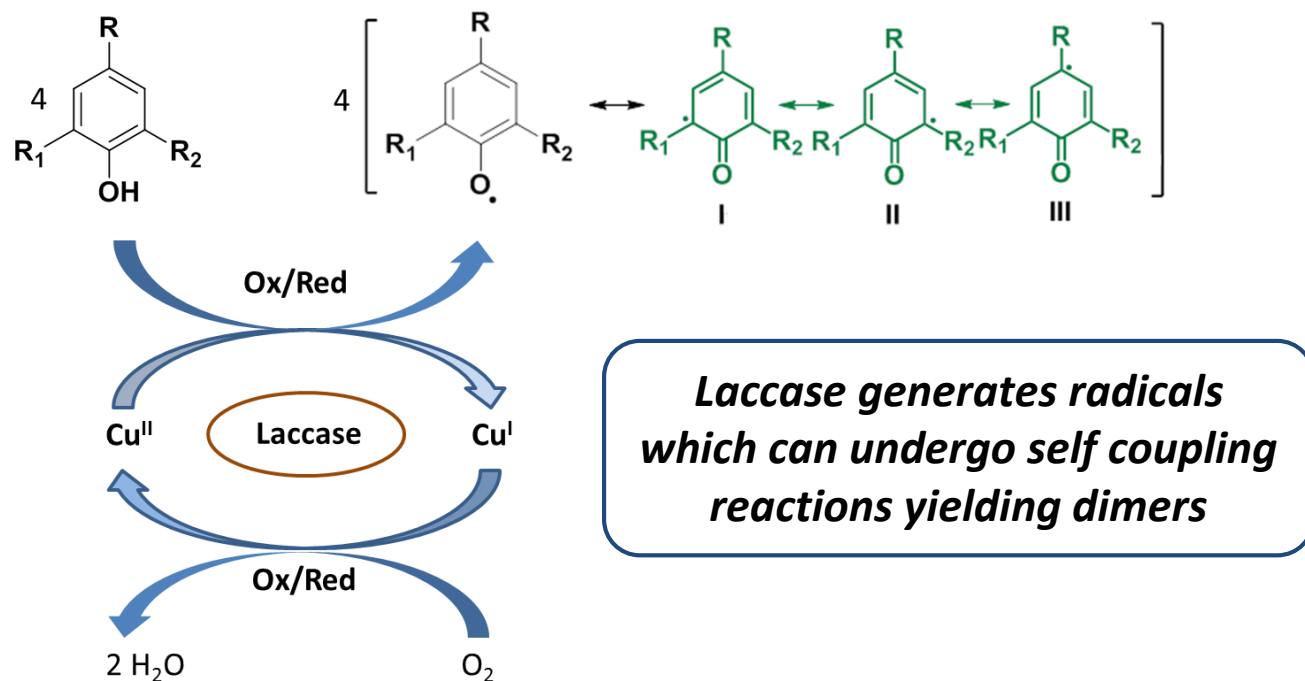


Trametes Versicolor



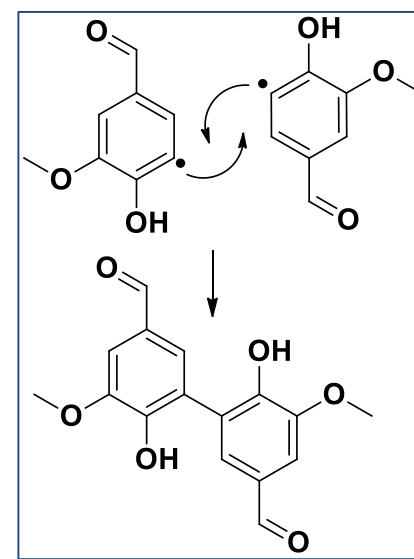
Laccase is an oxydative enzyme found in wood rotting fungi

Enzymatic coupling



Kobayashi et al., Chem. Rev. 2009

Coupling of Vanillin



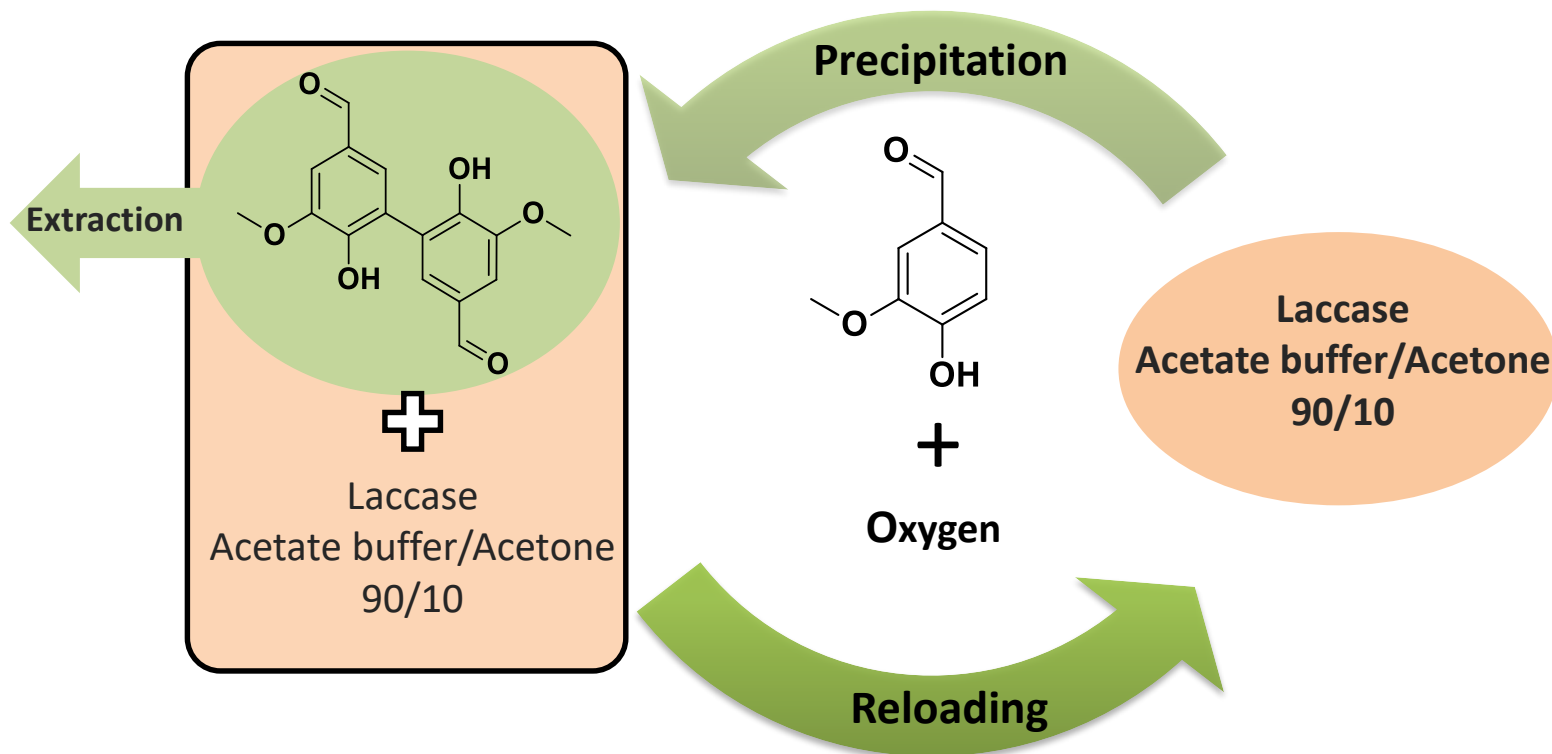
Divanillin

Llevot et al., Polym. Chem. 2015, 6 (33)

Smart drop-ins: Bio-based derivative of “fossil” polymers

Synthesis of dimer from Vanillin

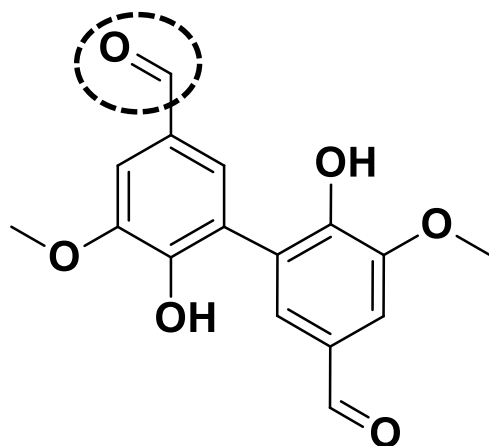
Epoxy



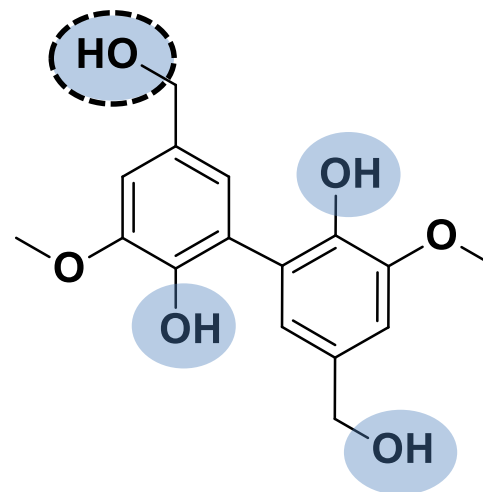
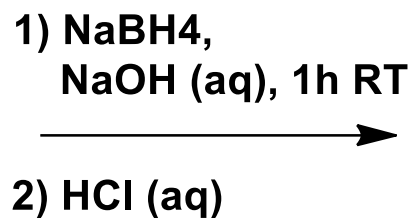
Self-sufficient process to synthesize dimers

Epoxy

Aldehyde Reduction



Divanillin

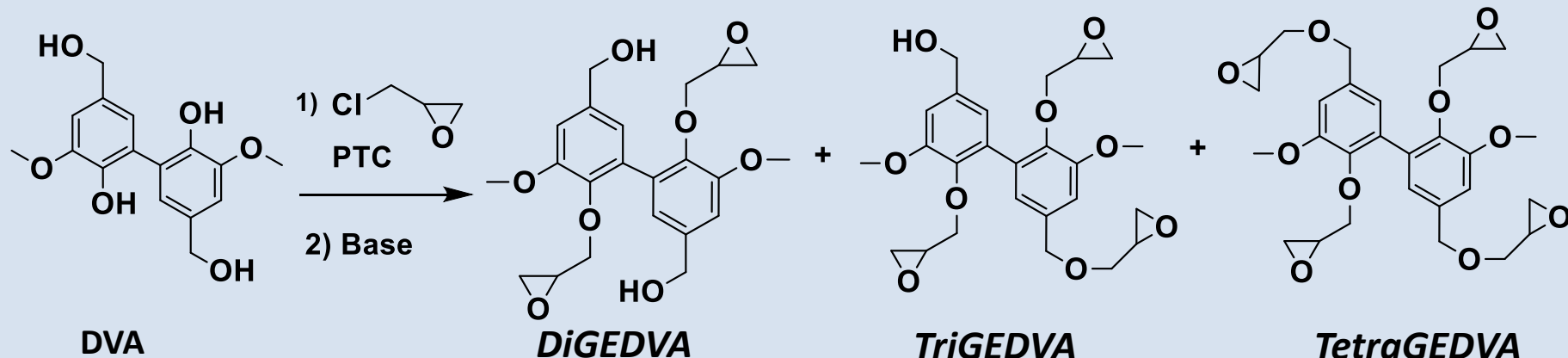


Divanillyl Alcohol (DVA)

➡ 4 functional groups available to achieve high mechanical properties

Epoxy

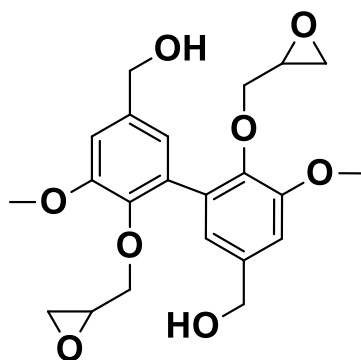
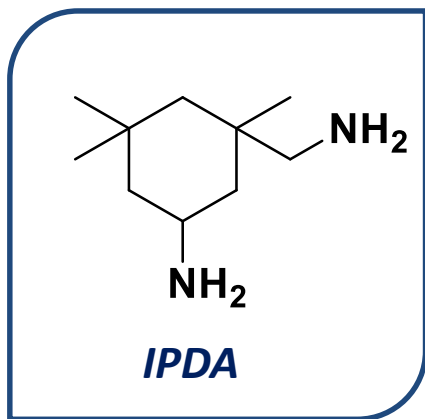
Synthesis of epoxy prepolymers from DVA



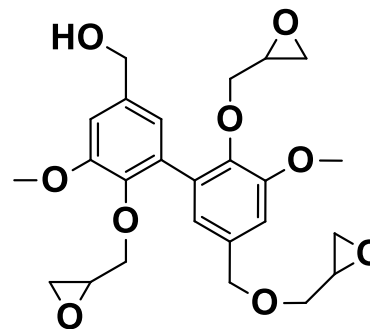
| Properties | DGEBA | DiGEDVA | TriGEDVA | TetraGDVA |
|---------------------------|-------|-----------|----------|-----------|
| Melting point (°C) | 45 | - | - | - |
| Glass transition (°C) | -18 | 16 | -6 | -15 |
| Viscosity at 25 °C (Pa.s) | 5 | <i>nd</i> | 975 | 14 |
| Viscosity at 40 °C (Pa.s) | 1 | 1300 | 60 | 2 |
| EEW th. | 170 | 209 | 158 | 132 |
| EEW exp. | 171 | 232 | 164 | 129 |

Epoxy

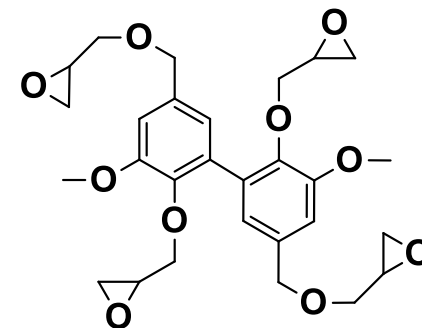
Synthesis of polyepoxyde network



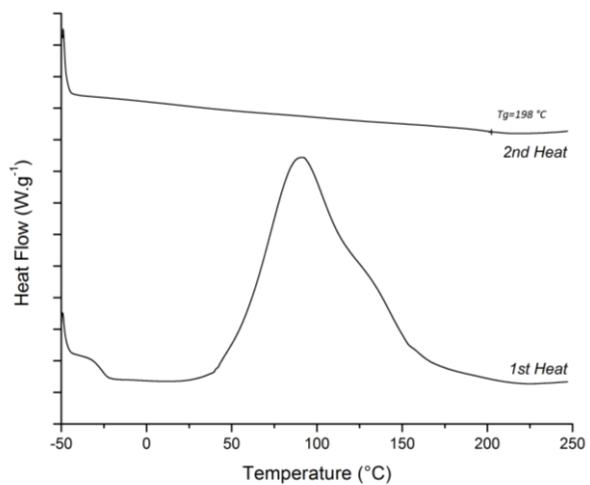
DiGEDVA



TriGEDVA



TetraGEDVA



| Epoxy prepolymers/IPDA | T _{onset} (°C) | T _{exotherm} (°C) | ΔH (J.g ⁻¹) |
|---------------------------|----------------------------|-------------------------------|----------------------------|
| DGEBA | 73 | 111 | 430 |
| DiGEDVA | 47 | 107 | (180) |
| TriGEDVA | 48 | 113 | (198) |
| TetraGEDVA | 50 | 92 | 426 |

- Reactivity at lower temperature for biobased epoxy prepolymers

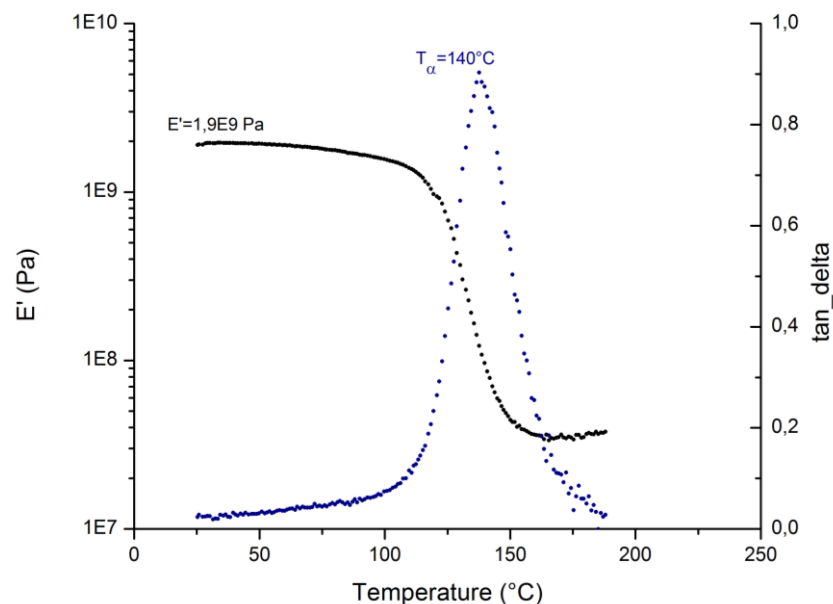
Epoxy

Dynamic Mechanical Analysis of epoxy resins cured with IPDA

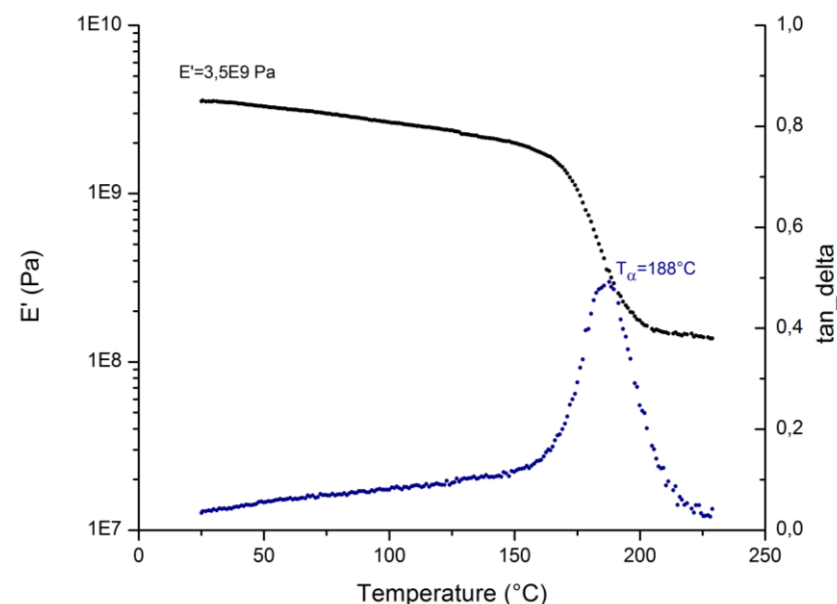
| Epoxy prepolymer/IPDA | T_g^a (°C) | T_α^b (°C) | E'^b (Gpa) | $E'(T_{\alpha+30})^b$ (Gpa) | Network density (10^3mol.m^{-3}) |
|--------------------------|-----------------|----------------------|-----------------|--------------------------------|---|
| DGEBA | 152 | 155 | 1,7 | 0,035 | 9,2 |
| DiGEDVA* | 138 | 140 | 1,9 | 0,035 | 9,5 |
| TriGEDVA | 163 | 177 | 1,3 | 0,084 | 21 |
| TetraGEDVA | 198 | 188 | 3,5 | 0,15 | 36,7 |

^adetermined by DSC, ^b by DMA, *80%DiGEDVA-20%TriGEDVA

DiGEDVA

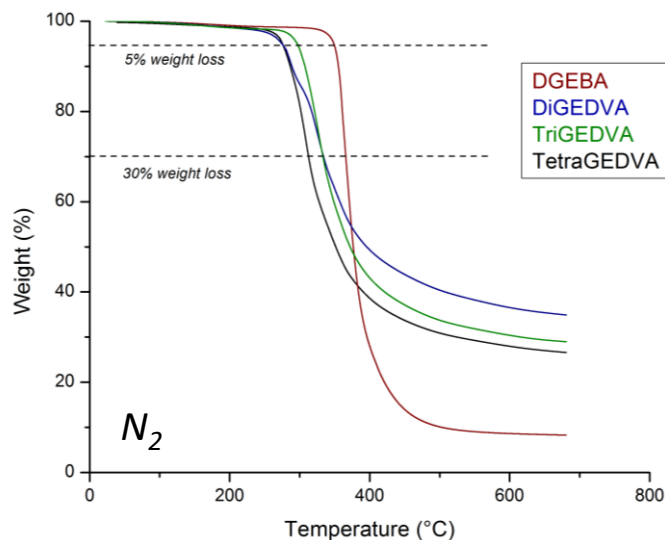
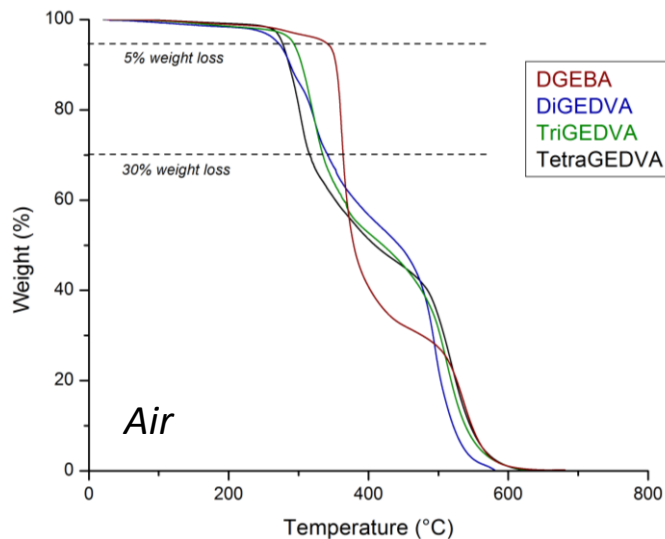


TetraGEDVA



Epoxy

Thermal degradation of epoxy resins cured with IPDA



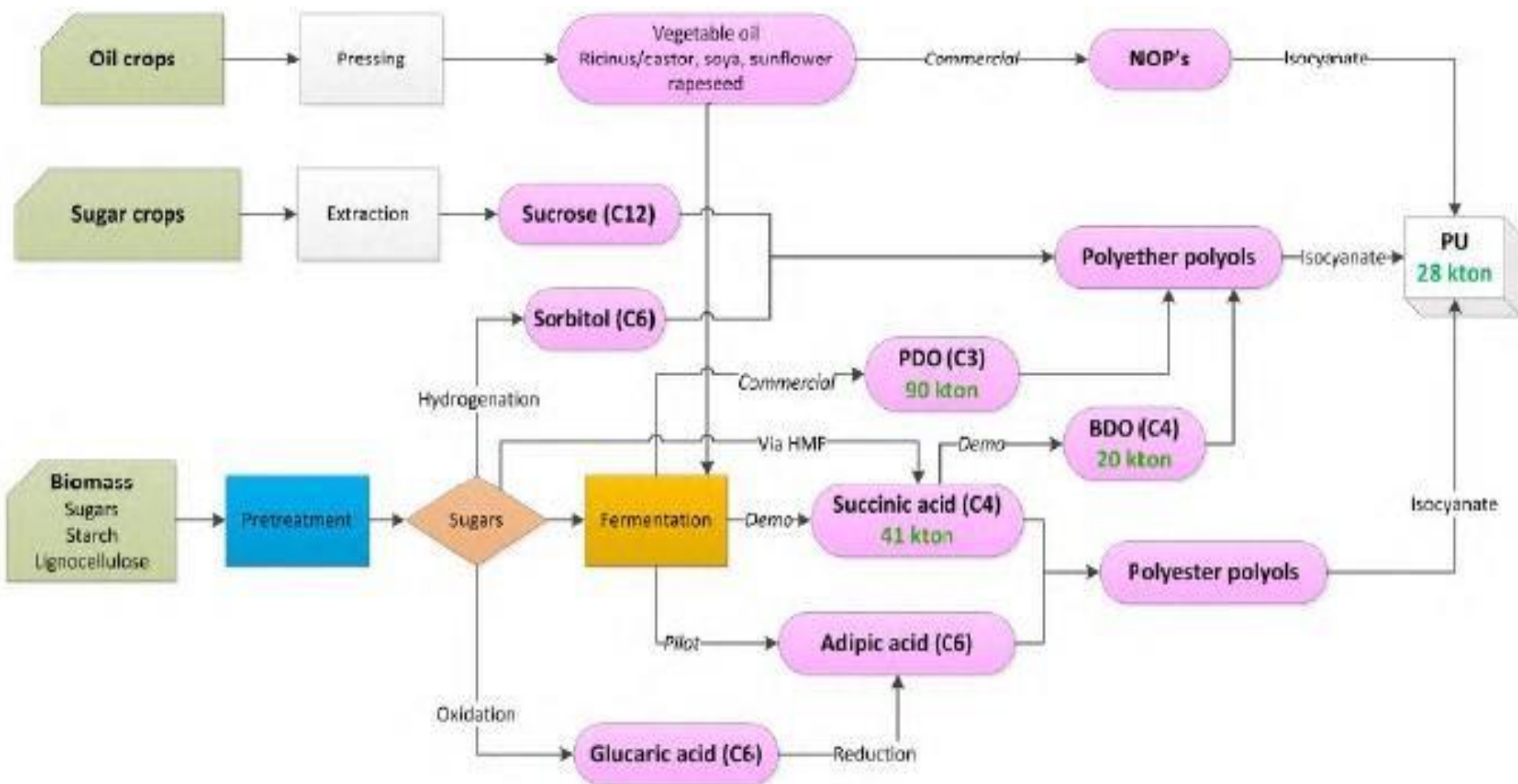
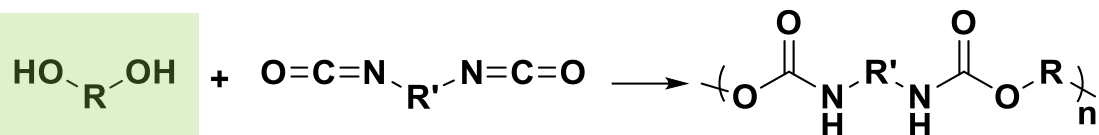
| Epoxy prepolymer/IPDA | T _d 5% (°C) | T _d 30% (°C) | T _s |
|--------------------------|---------------------------|----------------------------|----------------|
| DGEBA | 336 | 364 | 172 |
| DiGEDVA | 273 | 337 | 153 |
| TriGEDVA | 292 | 335 | 156 |
| TetraGEDVA | 275 | 316 | 147 |

- Slightly lower thermal heat resistance

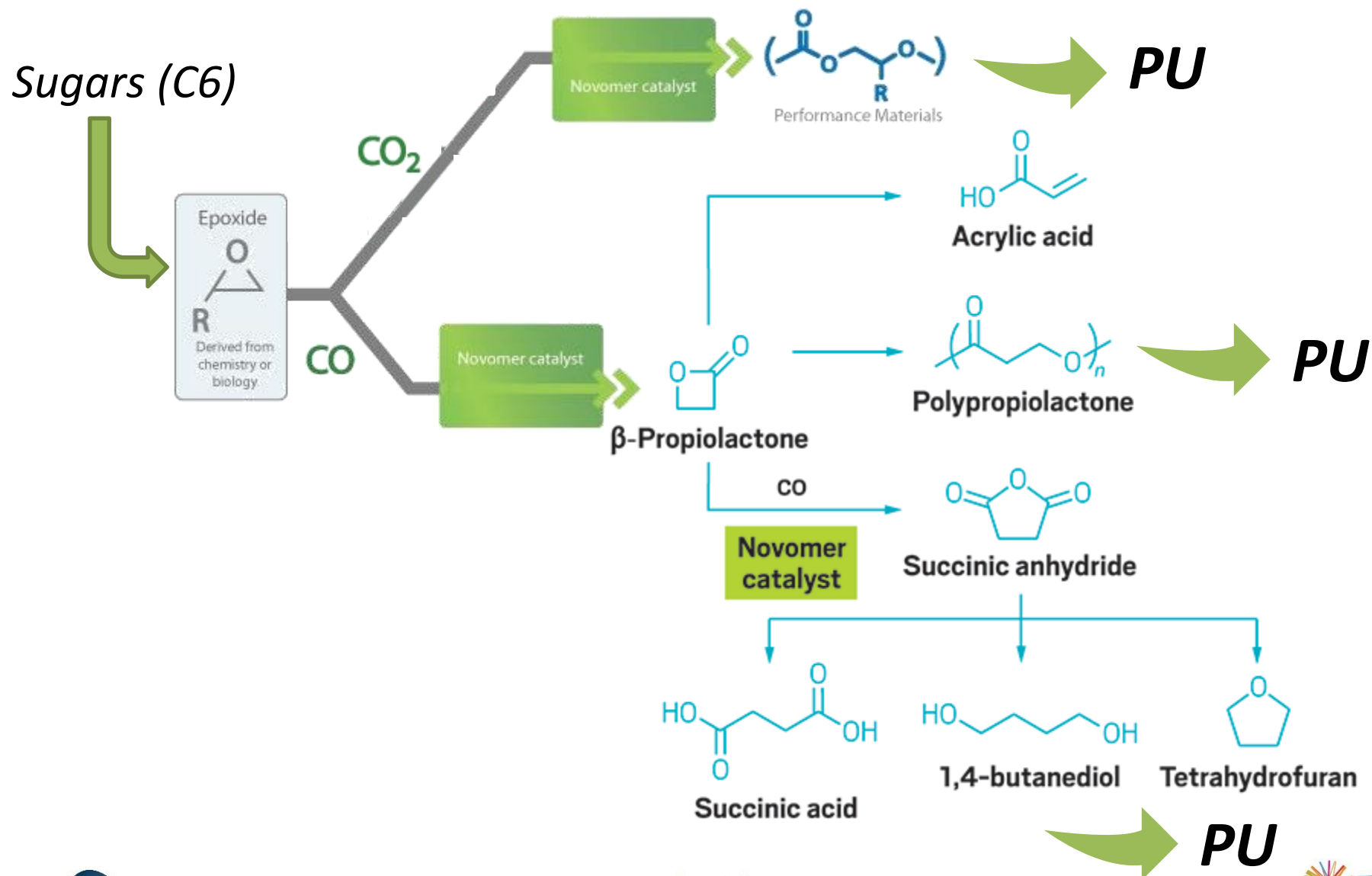
| Epoxy prepolymer/IPDA | T _d 5% (°C) | T _d 30% (°C) | T _s | Char ₆₀₀ (%) |
|--------------------------|---------------------------|----------------------------|----------------|----------------------------|
| DGEBA | 349 | 366 | 176 | 9 |
| DiGEDVA | 275 | 334 | 152 | 36 |
| TriGEDVA | 296 | 333 | 155 | 30 |
| TetraGEDVA | 276 | 313 | 146 | 28 |

- High char residue for biobased epoxy resins

Polyurethanes



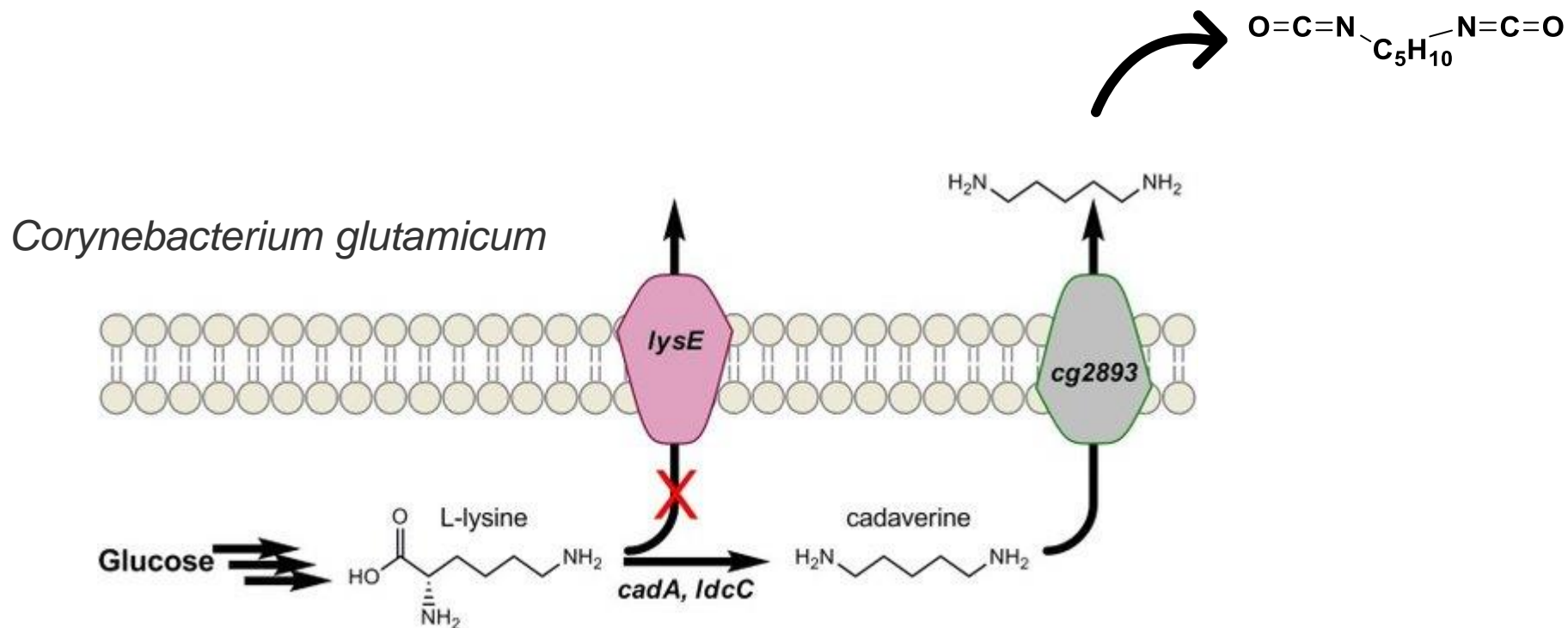
Polyurethanes: polyol



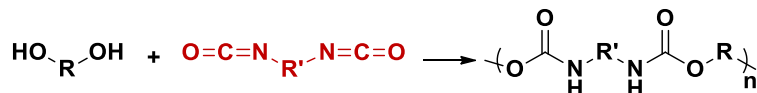
Polyurethanes: polyol



Polyurethanes: isocyanate



Polyurethanes



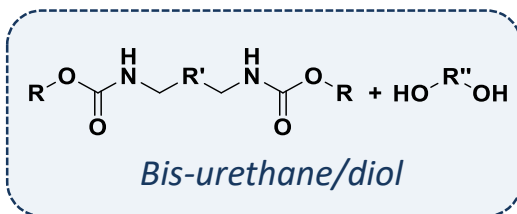
Industrial process for the
production of Polyurethanes :

The Isocyanate/alcohol route

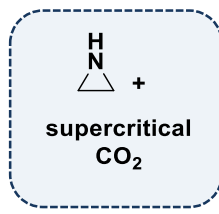


PU

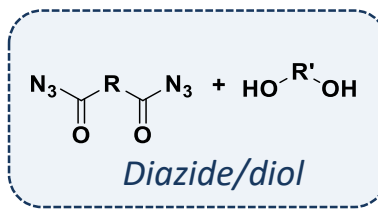
Non Isocyanate PolyUrethane



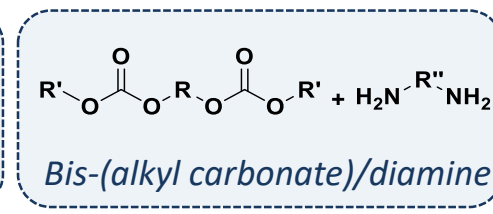
Transurethanization



Aziridine route



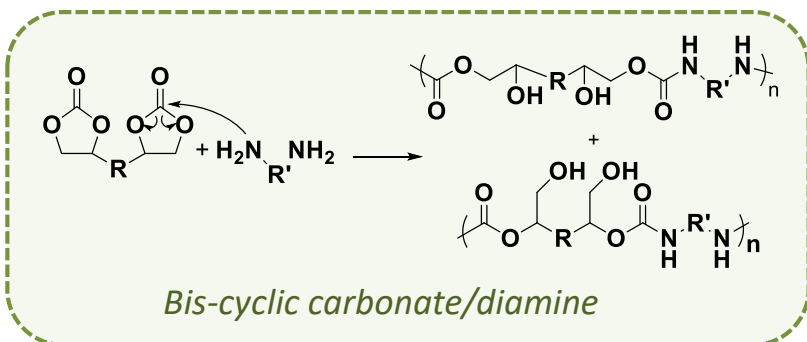
Rearrangements



Bis-(dialkyl carbonate) route

NIPU

Poly(HydroxyUrethane)

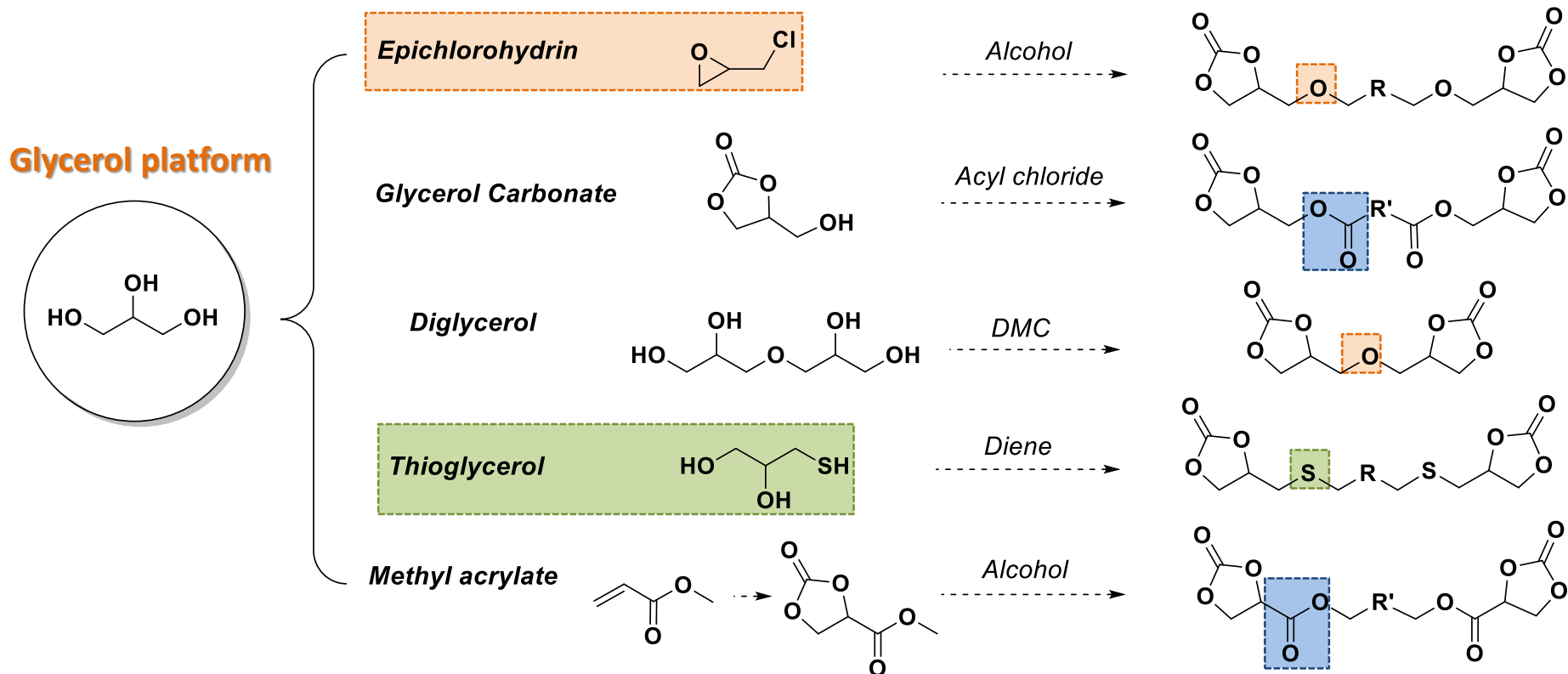


- ◆ | Phosgene- **and** isocyanate-free
- ◆ | Polyaddition : no by-product
- ◆ | Less moisture sensitive

↓
PHU

Polyurethanes: isocyanate

Objective : Design substituted fatty acid- and glycerol-based cyclic carbonates

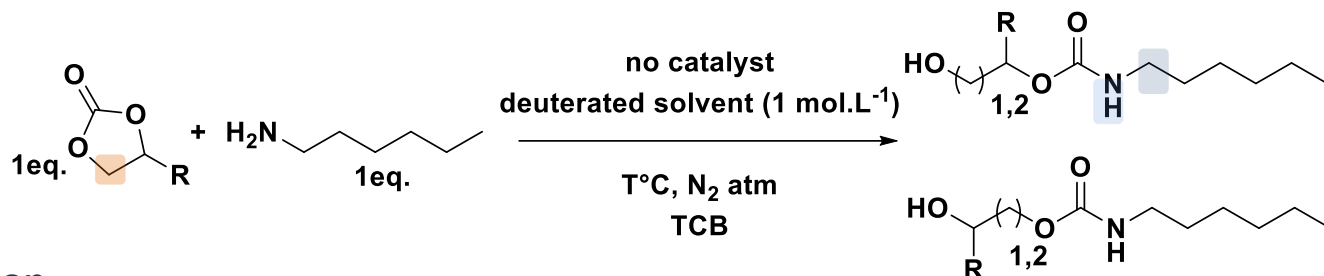


→ Tunable **heteroatom nature and position** nearby the CC by varying the glycerol derivative

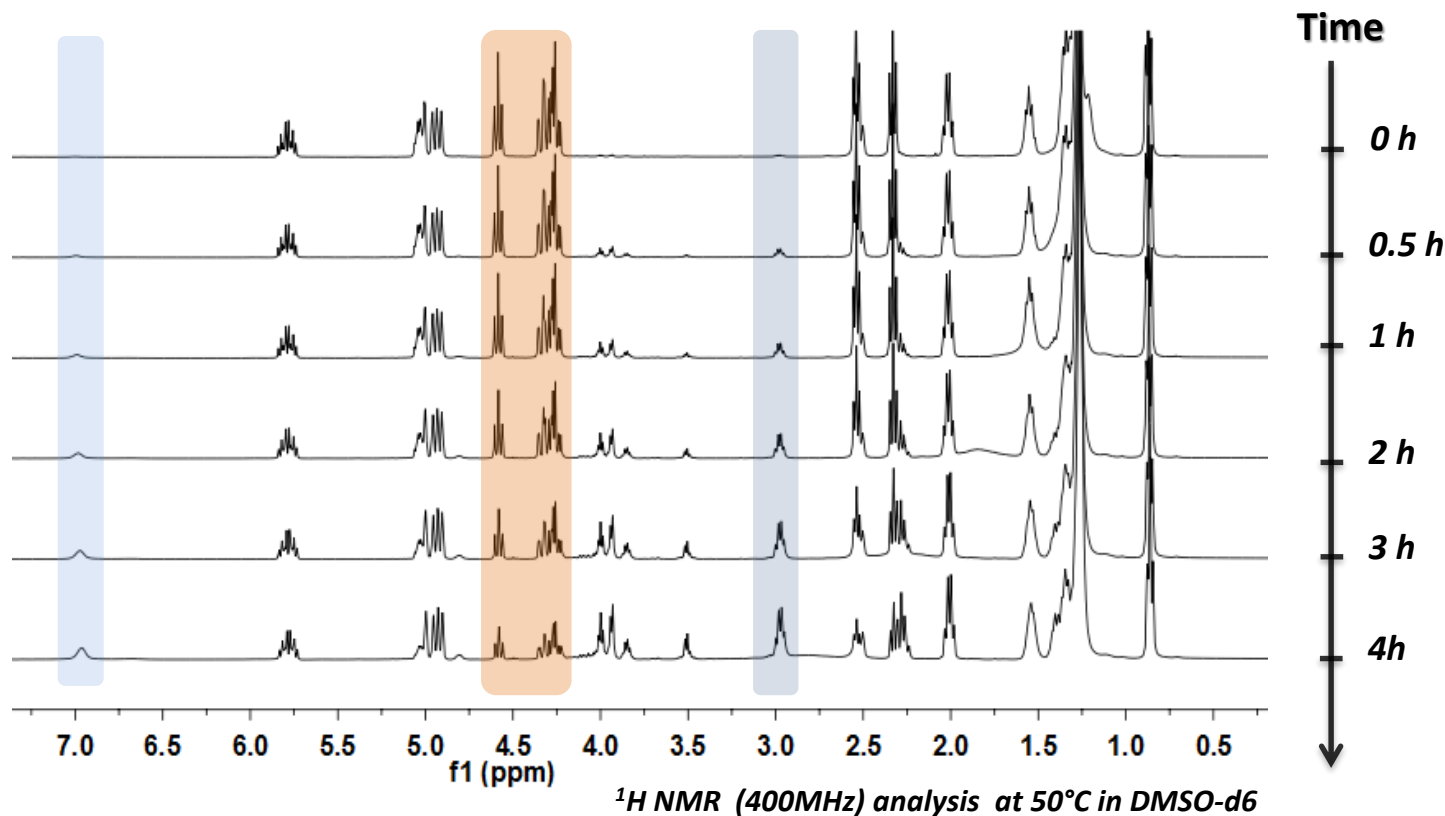
→ **Ether, ester and thioether** functions inserted nearby the cyclic carbonate

Reactivity of various CC towards aminolysis

In situ measurements
NMR Tube
24h, 50°C
DMSO-d6



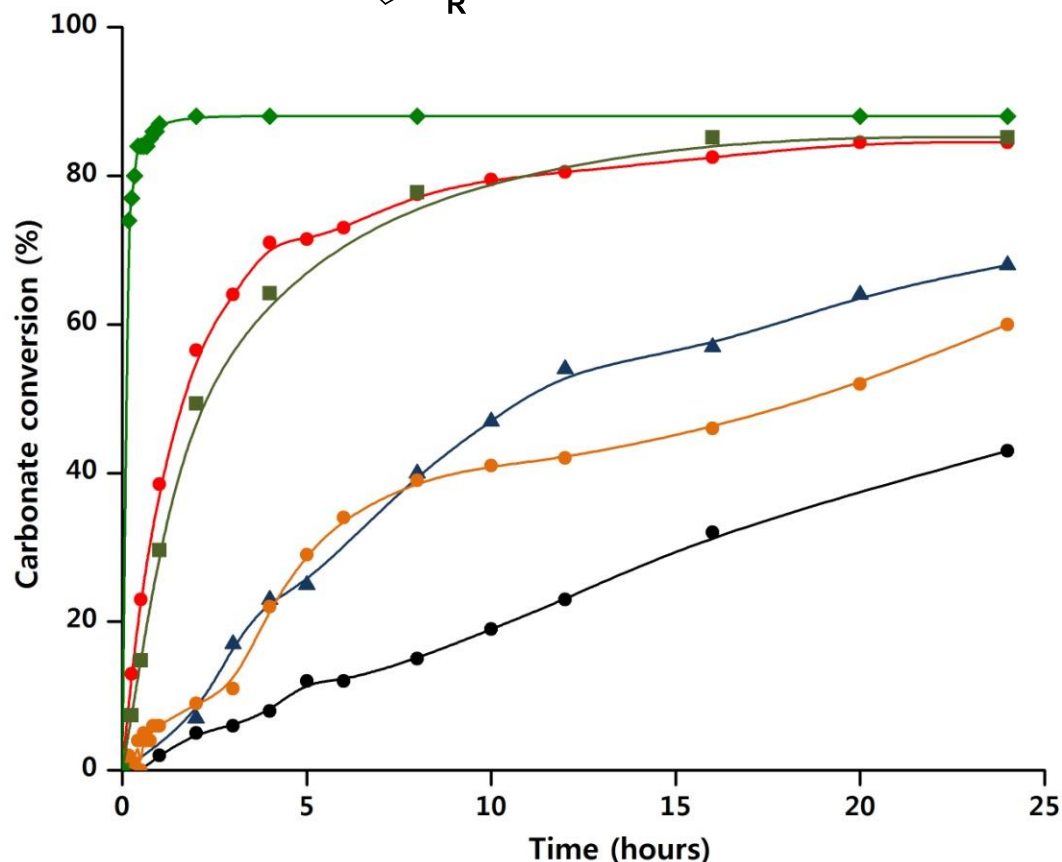
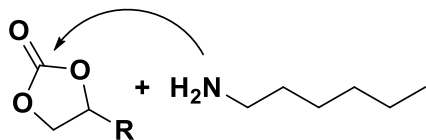
→ CC conversion calculation



Smart drop-ins: Bio-based derivative of “fossil” polymers

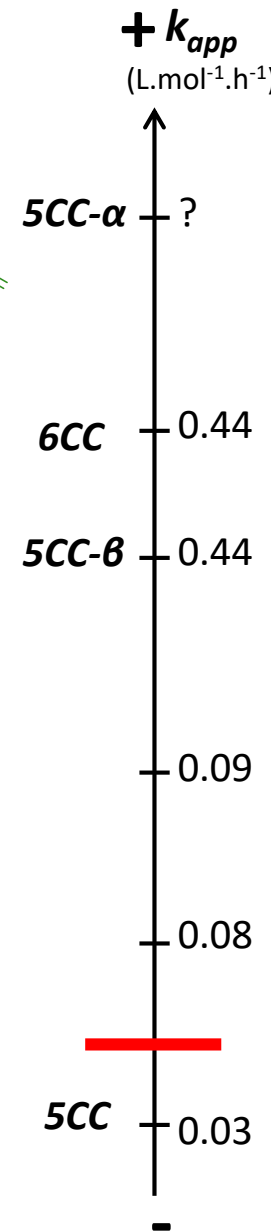
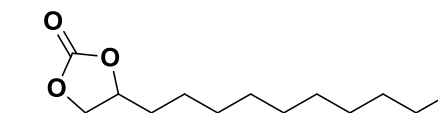
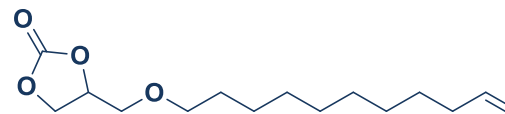
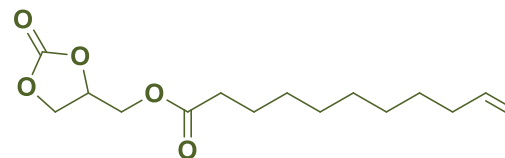
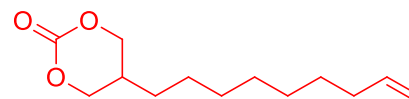
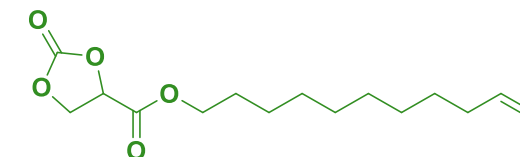
Scale of CC reactivity towards aminolysis

→ 2nd kinetic order law during the first hours - k_{app}



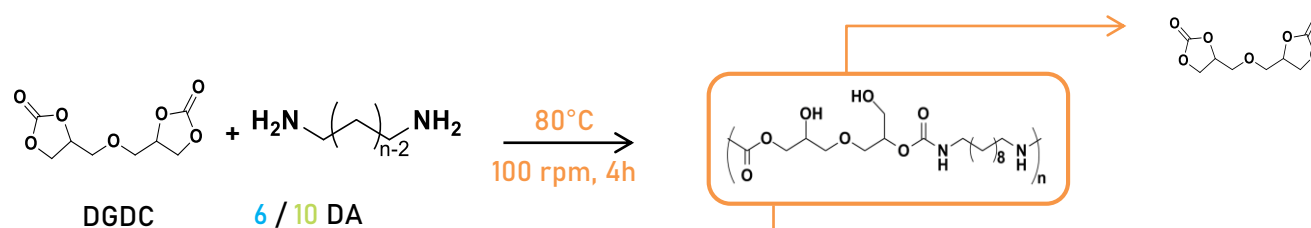
CC conversion in function of time (50°C, DMSO-d₆, 24h, ratio amine : CC = 1:1)

$$\frac{x}{1-x} = k_{app} C_0 \Delta t$$





➤ From DGDC & various DAs



$T_m = 76^\circ\text{C}$ $T_m = 45^\circ\text{C} / 60^\circ\text{C}$



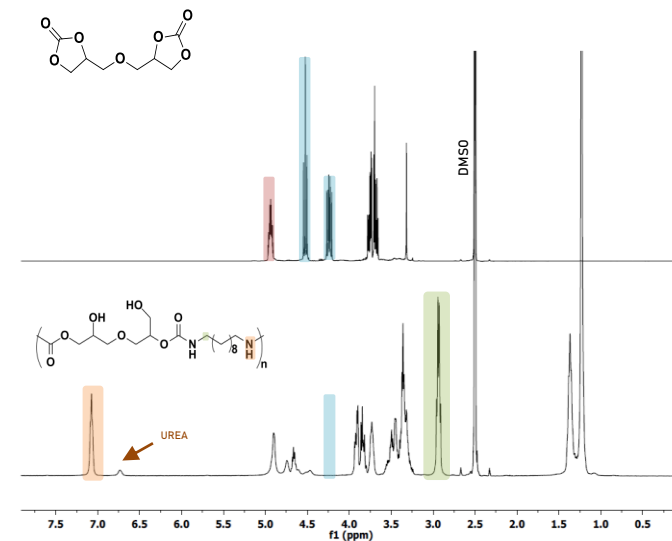
Conversions (%) 99% / 99%
Molar masses (g/mol)..... up to 46800 / 50 000
T_gs (°C) up to 18 / 17
T_m (°C)..... -- / 109
T_{d5%} (°C)..... up to 227 / 233

Colorless

Rigid

Fragile

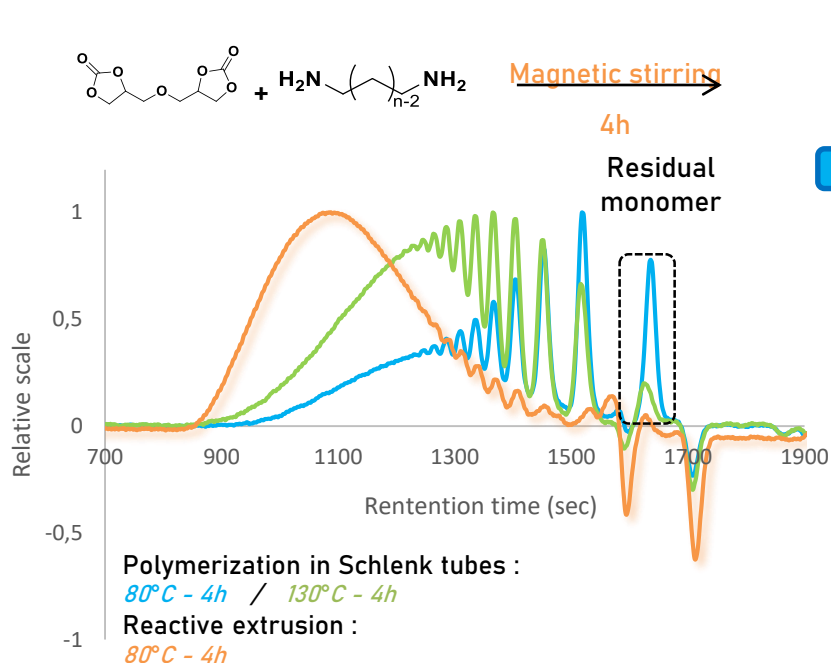
SEC analysis in DMF, with PS standards, at 50°C
DSC second heating cycle at 10°/min
TGA traces at 10°C/min



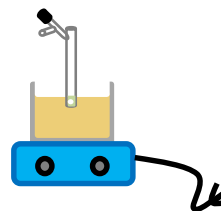
NMR spectra of DGDC monomer (up) and
DGDC based PHU (down)



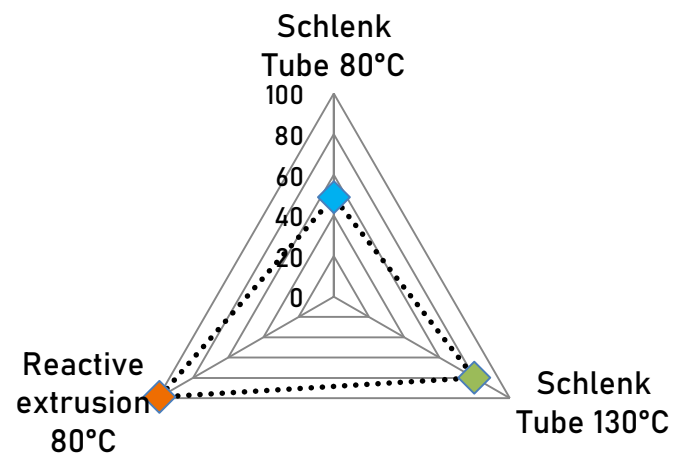
> Comparison with bulk polymerization in Schlenk tubes



SEC analysis in DMF, 50°C, 1g/L of Libr,
conventional calibration column with PS standards

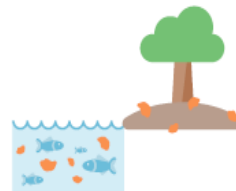


Conversion after 4h (%)



Conversions obtained by ^1H NMR analysis in $\text{DMSO}-d_6$ at RT

1- Why ?



2- How ? → Biomass transformation to platform chemicals

3- Bio-based plastics from natural polymers

Cellulose, Natural rubber

4- Drop-ins: Bio-based alternative to fossil-based polymers

PE, PET

5- Smart drop-ins: Bio-based derivative of “fossil” polymers

PBS, Epoxy, PU

6- New polymers from biomass

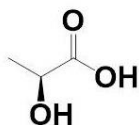
7- Conclusions and perspectives

New polymers from biomass: PLA

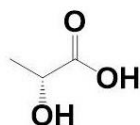
300 kt



Starchy Materials

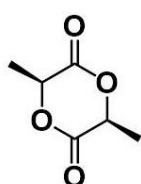


L-lactic acid

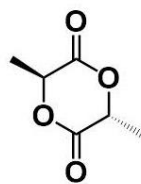


D-lactic acid

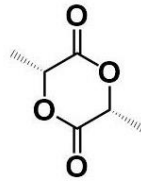
Condensation
and Depolymerization



L-lactide

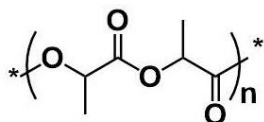


Meso-lactide



D-lactide

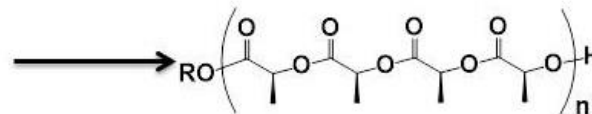
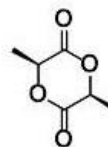
Catalytic Ring-Opening
Polymerization (ROP)



High Molecular Weight PolyLactide (PLA)

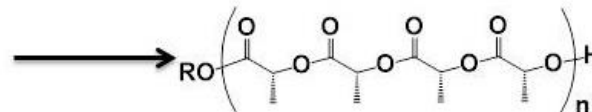
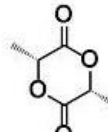
Microstructure control

L-lactide



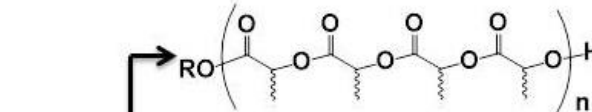
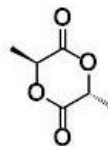
Isotactic PLLA

D-lactide

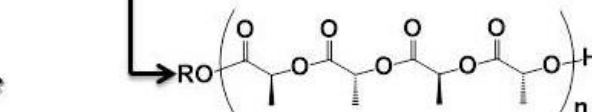


Isotactic PDLA

meso-lactide



Atactic PDLLA



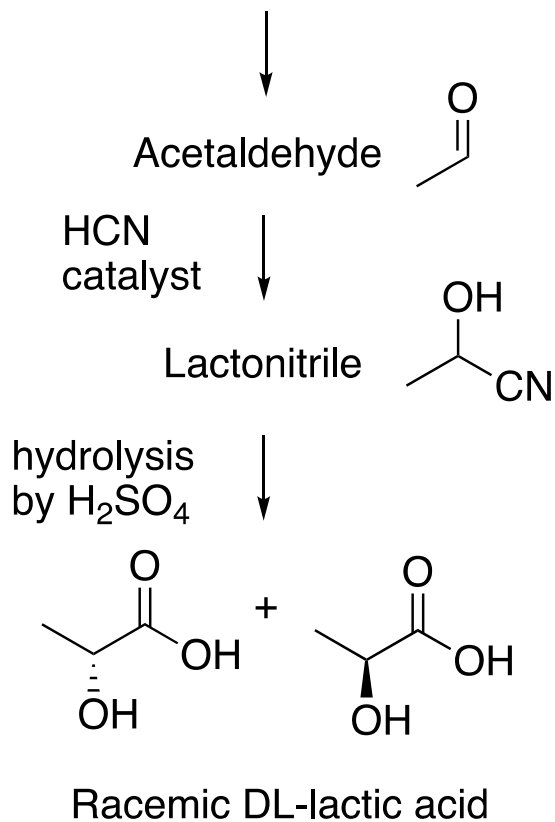
Syndiotactic PDLLA

Properties control

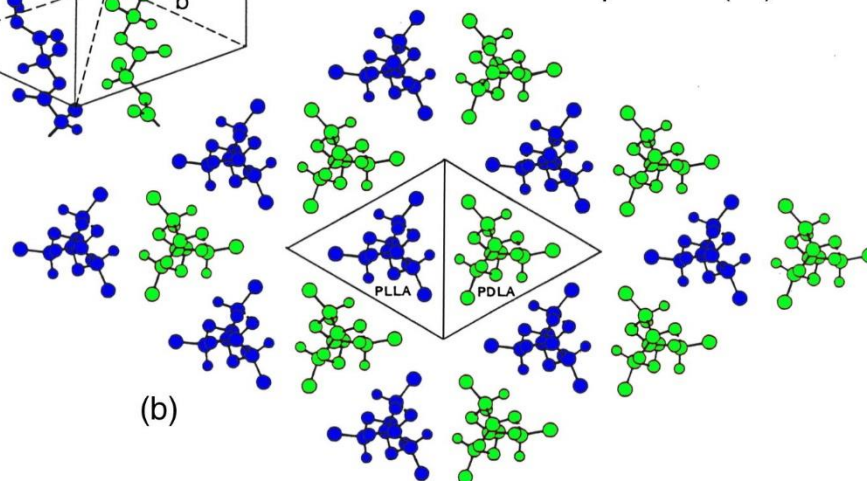
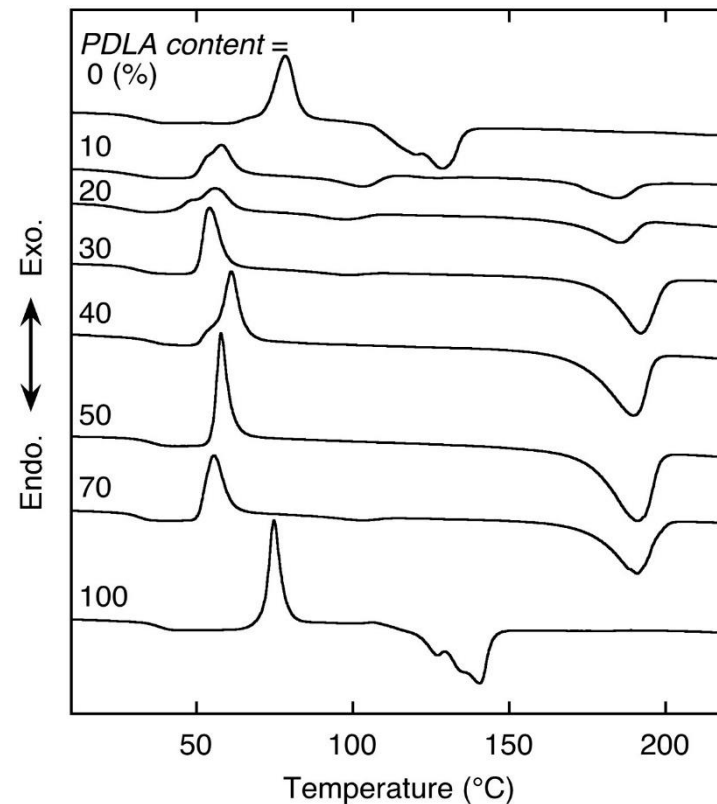
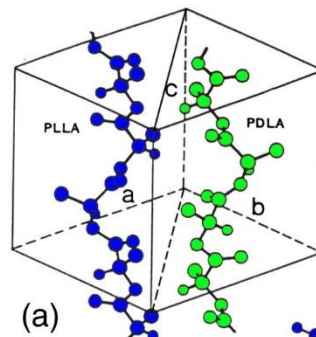
| Physical properties | PLLA (PDLA) | Atactic PDLLA | Syndiotactic PDLLA |
|---|-------------|---------------|--------------------|
| T _m (°C) | 170-180 | - | 151 |
| T _g (°C) | 55-60 | 50-60 | 34 |
| ΔH _m (100%) (J.g ⁻¹) | 93 | - | - |

Why PLA is not petro-sourced?

Petro-chemical resources



PLLA/PDLA stereocomplex

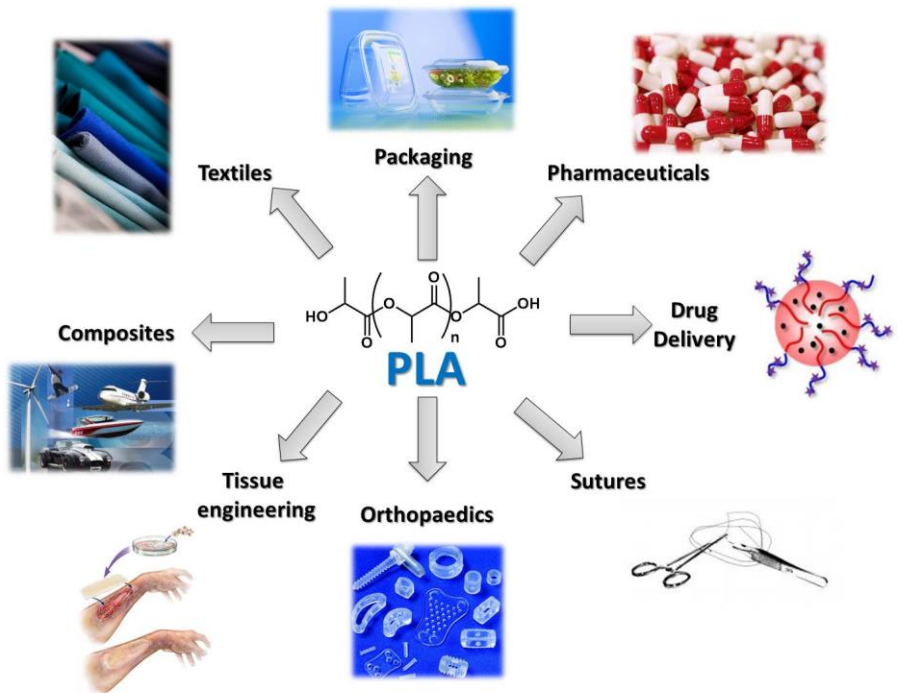


New polymers from biomass: PLA

 **CO₂ 0 kgCO₂e/kg**

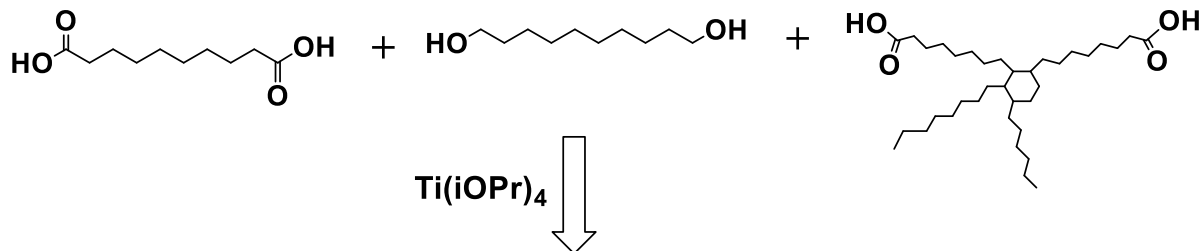
 **Biobased, Compostable, Stiff**

| | PLLA | PS | PET |
|--------------------------------------|------|------|---------|
| Density (kg.m ⁻³) | 1.26 | 1.05 | 1.40 |
| Tensile strength (MPa) | 59 | 45 | 57 |
| Elastic modulus (GPa) | 3.8 | 3.2 | 2.8-4.1 |
| Elongation at break (%) | 4-7 | 3 | 300 |
| Notched IZOD IS (J.m ⁻¹) | 26 | 21 | 59 |
| Heat deflection (°C) | 55 | 75 | 67 |

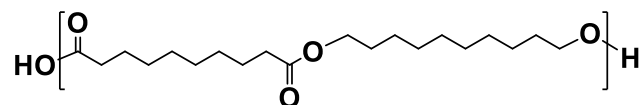


 **Heat stability, Low crystallization rate, Brittleness**

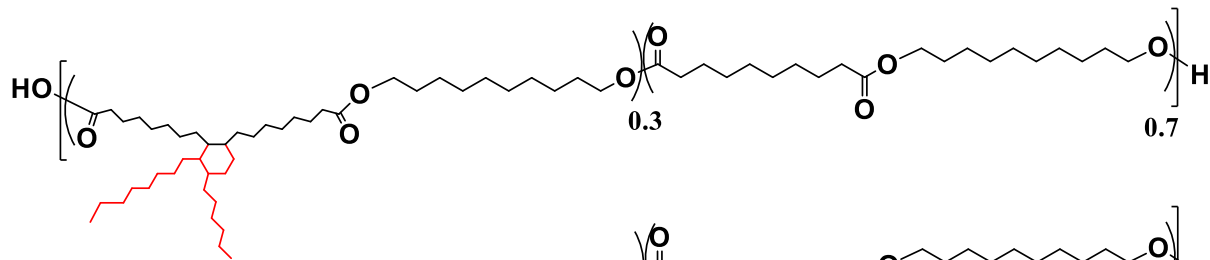
PLA additive: Synthesis



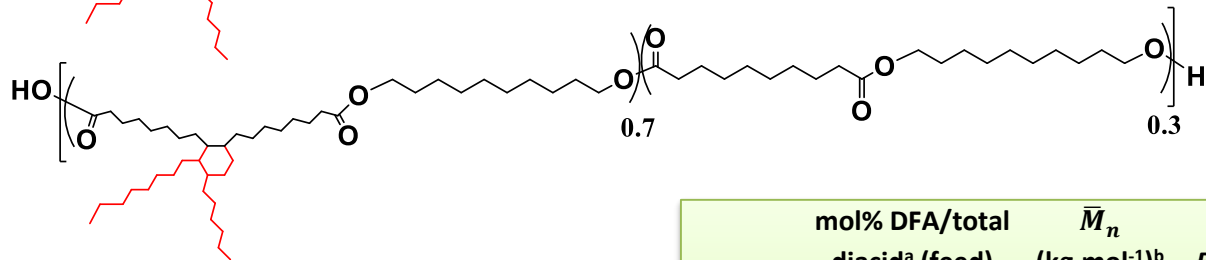
DFA0



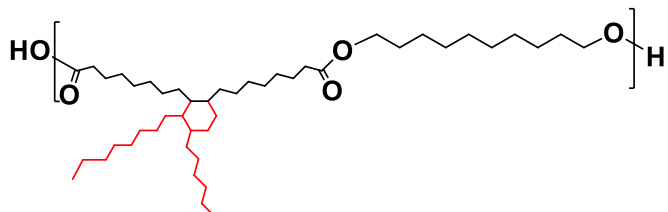
DFA0.3



DFA0.7



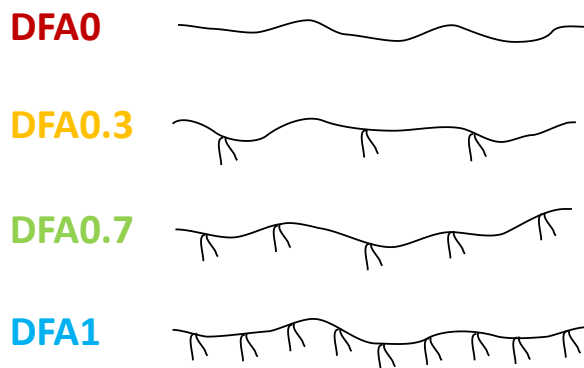
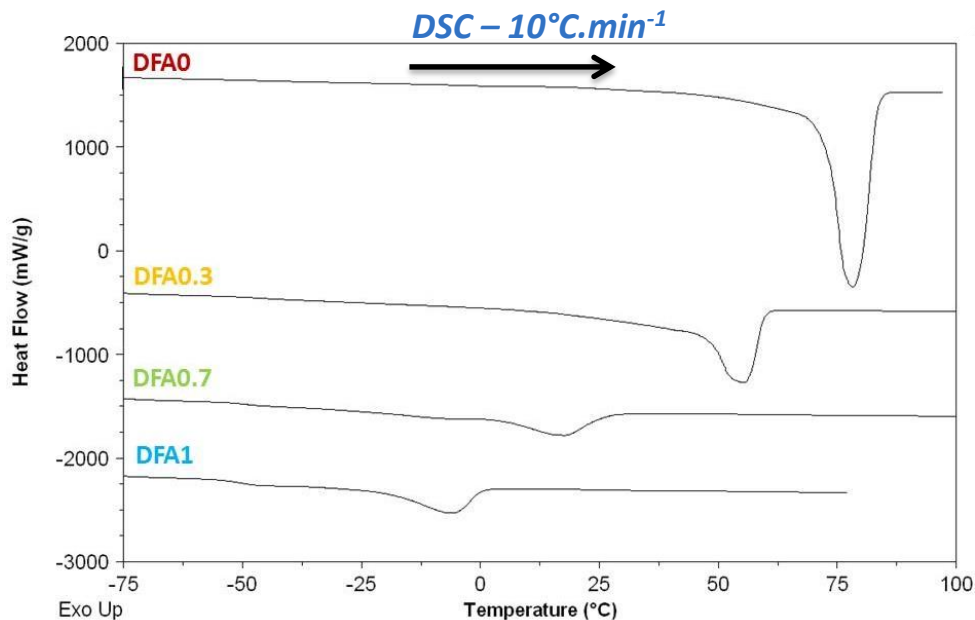
DFA1



| | mol% DFA/total diacid ^a (feed) | \bar{M}_n (kg.mol ⁻¹) ^b | \mathcal{D}^b |
|--------|--|---|-----------------|
| DFA0 | 0 (0) | 59 | 2.1 |
| DFA0.3 | 0.40 (0.3) | 44 | 1.8 |
| DFA0.7 | 0.78 (0.7) | 64 | 2.0 |
| DFA1 | 1 (1) | 36 | 2.0 |

(a) 1H-NMR (b) SEC in THF, PS calibration

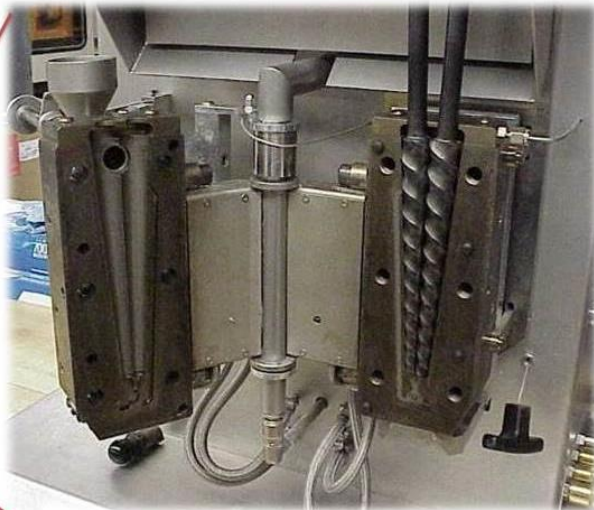
PLA additive: Properties



| | T _m (°C) ^a | ΔH _m (J.g ⁻¹) ^a | T _g (°C) ^a | T _{5%} (°C) ^b |
|---------------|----------------------------------|---|----------------------------------|-----------------------------------|
| DFA0 | 78.2 | 100.9 | - 48.6 | 338 |
| DFA0.3 | 55.2 | 57.7 | - 45.9 | 389 |
| DFA0.7 | 17.7 | 22.4 | - 49.0 | 399 |
| DFA1 | - 5.8 | 16.2 | - 50.0 | 394 |

(a) DSC- 10°C.min⁻¹

PLA additive: Processing

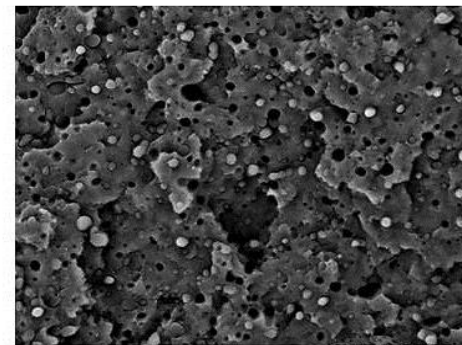


Melt-blending :
Twin-screw mini-extrusion
190°C for 5 min



Sample preparation:
Injection molding
200°C → 50°C

10%



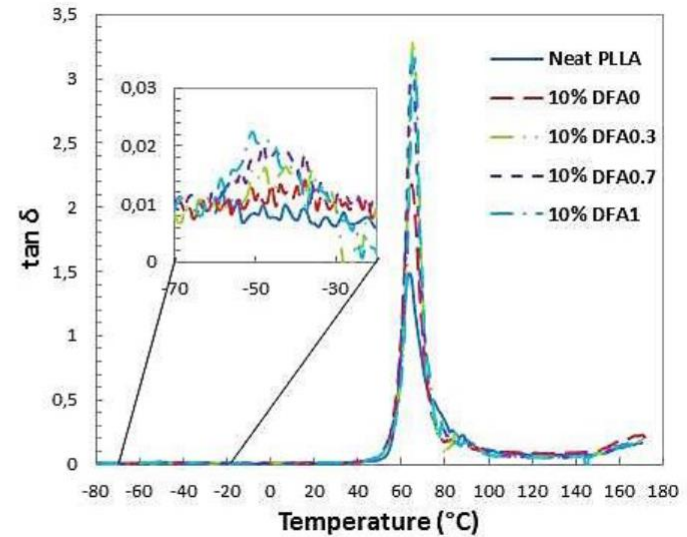
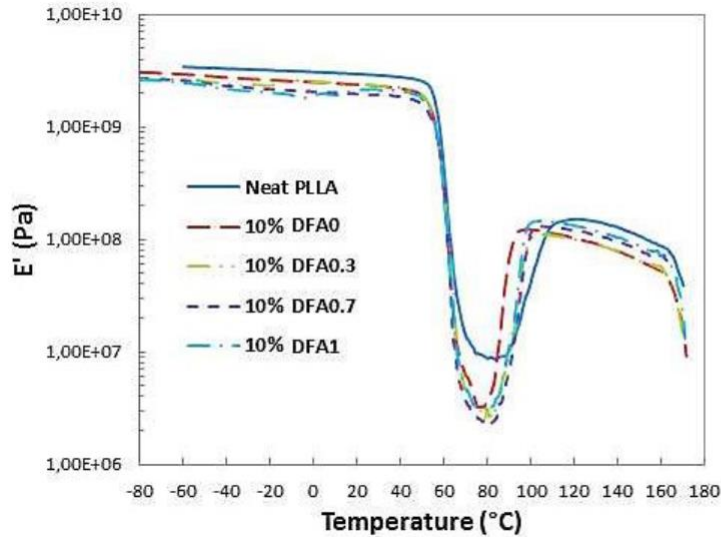
30µm

LCPO
Laboratoire de Chimie des
Polymères Organiques

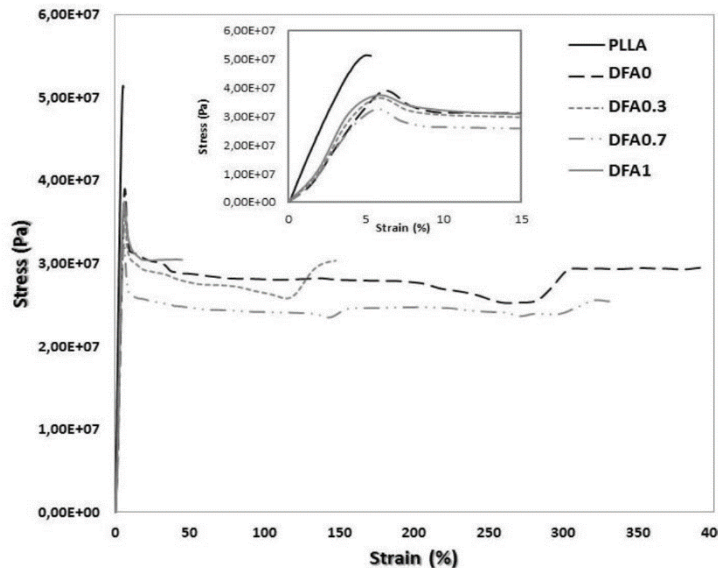
PLA additive: Mechanical Properties

DMA

**Heat
stability**



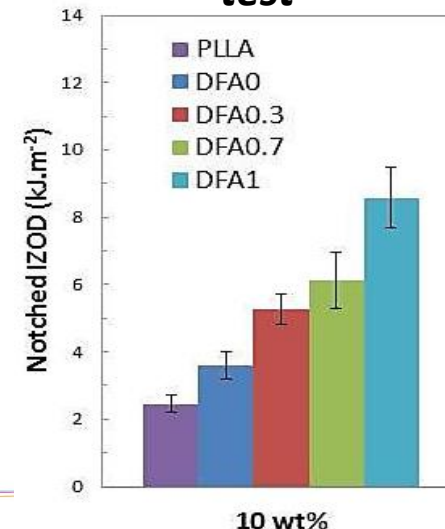
Tensile test



Brittleness

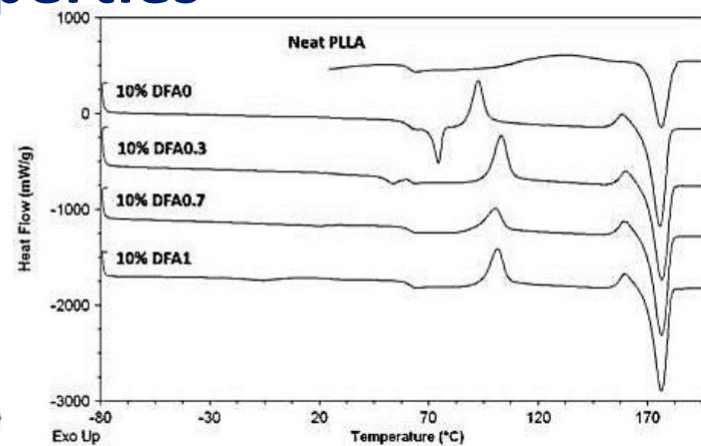
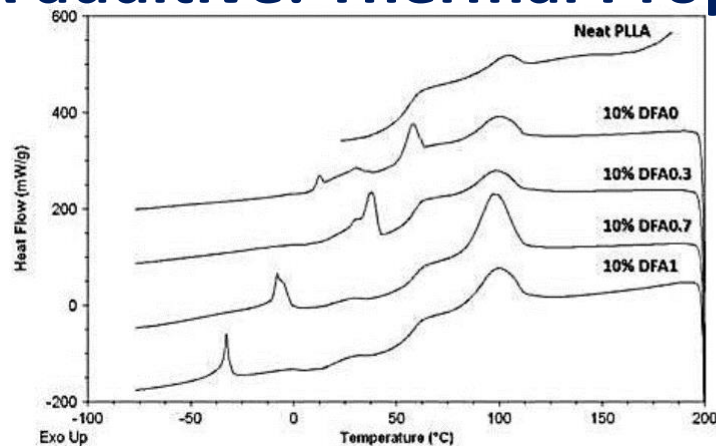


**Impact strength
test**



PLA additive: Thermal Properties

DSC



Isothermal crystallization

Avrami equation :

$$\alpha_c = 1 - \exp(-k \cdot t^n)$$

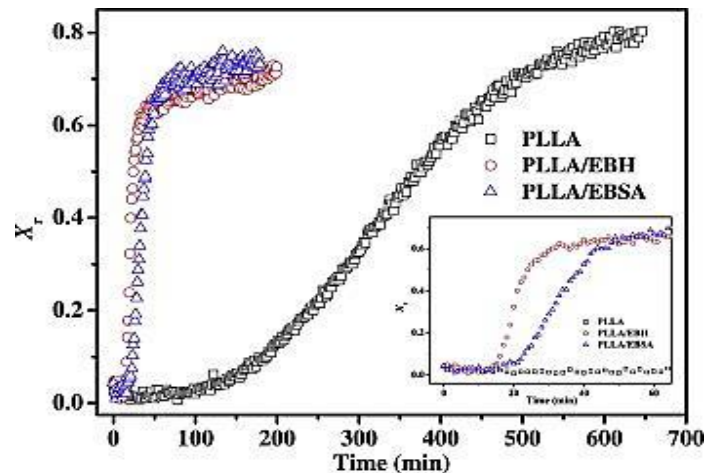
α_c : the relative crystalline volume fraction

k : rate constant of crystallization

n : Avrami index

Half-time of crystallization :

$$t_{1/2} = \left(\frac{\ln 2}{k} \right)^{1/n}$$



| | n | k (min ⁻ⁿ) | t _{1/2} (min) |
|--------|------|------------------------|------------------------|
| PLLA | 1.80 | 0.027 | 6.12 |
| DFA0 | 3.53 | 0.021 | 2.70 |
| DFA0.3 | 3.73 | 0.014 | 2.85 |
| DFA0.7 | 3.81 | 0.116 | 1.60 |
| DFA1 | 4.20 | 0.015 | 2.48 |

10wt%

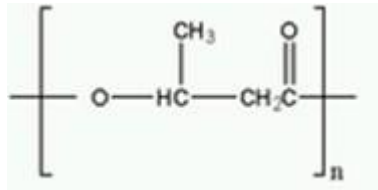
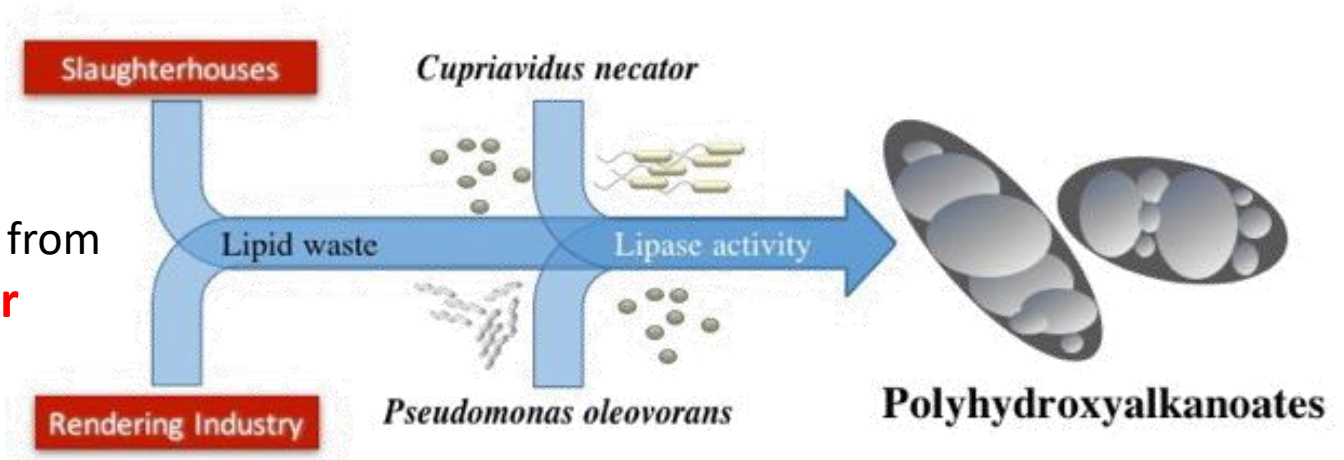


New polymers from biomass: PHA

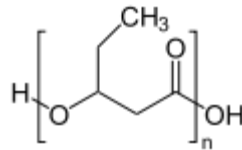
40 kt

One-pot biosynthesis from biomass to polymer

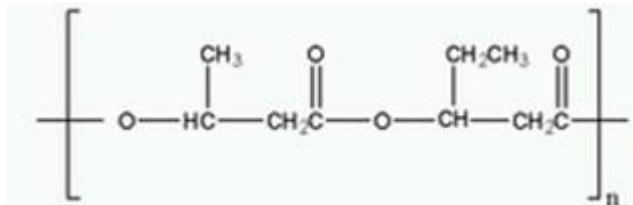
Max prod. **3 g.L⁻¹.h⁻¹**



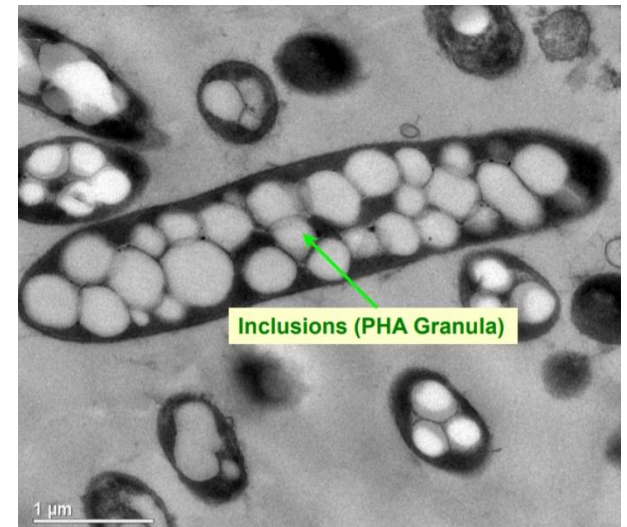
Polyhydroxybutyrate (PHB)



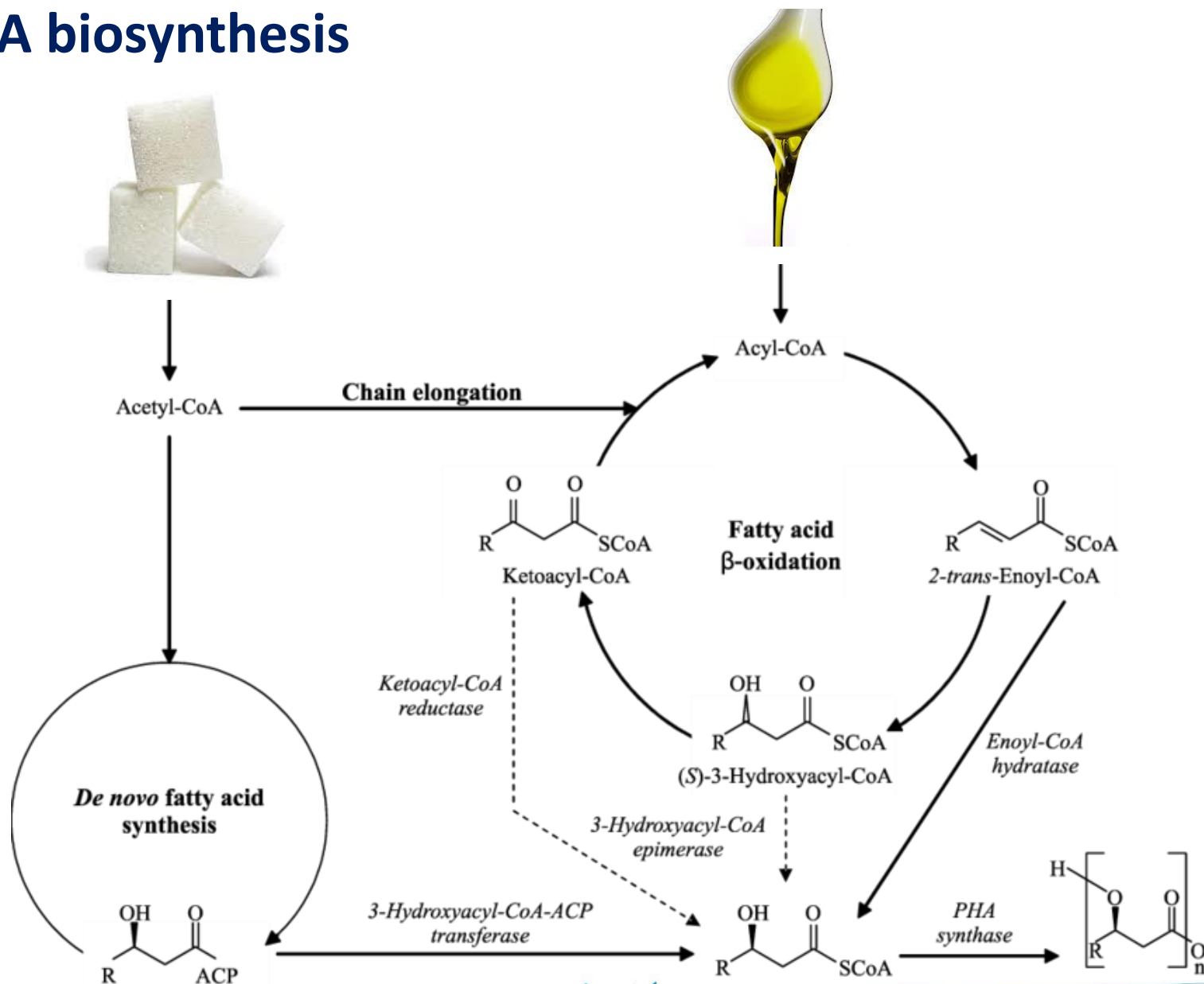
Poly-3-hydroxyvalerate (PHV)



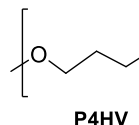
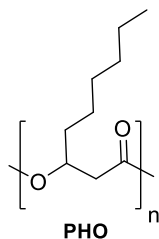
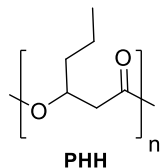
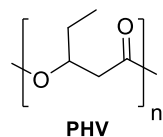
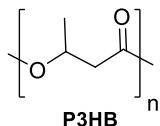
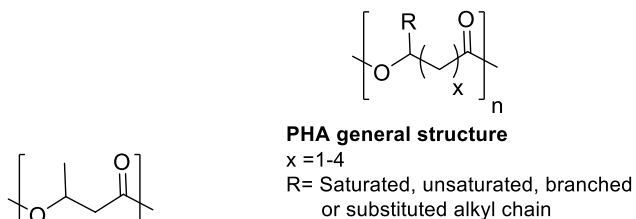
Poly(hydroxybutyrate-co-hydroxyalkanoates (PHBV))



PHA biosynthesis



PHA properties



| | PHB | PHBV | PHBHHx | MCL-PHA |
|---|----------------------------|----------------------------|--------------|------------|
| Tm (°C) | 170 to 180 | 130 to 170 | 95 to 150 | 40 to 60 |
| Tg (°C) | -5 to 5 | -10 to 0 | -3 to -1 | -60 to -30 |
| Mw x 10 ³ (g mol ⁻¹) | Up to 1500 | Up to 1200 | / | 50 to 300 |
| Density (g cm ⁻³) | 1.24 | 1.20 | / | 1.02 |
| Crystallinity (%) | 60 to 80 | 30 to 80 | 10 to 50 | Up to 30 |
| Tensile strength (MPa) | 40 | 30 to 40 | / | Up to 10 |
| Young's modulus (MPa) | 3.5 to 4 x 10 ³ | 0.7 to 3 x 10 ³ | 500 (10%HHx) | Up to 15 |
| Elongation to break (%) | 3 to 8 | Up to 100 | Up to 400 | Up to 450 |



PACKAGING
FILM



PVC



P4HB
PBHH

- Flexible
- Good moisture and oxygen barriers
- Ductile



PLASTIC
BAGS



LDPE



P(3HB-co-4HB)
PBHH

- Flexible
- Tough
- Ductile



FOOD
CONTAINERS



PP



PHBV

- Stiff
- High operating temperature
- Tough



DISPOSABLE
CUTLERY



PS



PH3B
PHBV

- Strong
- Stiff
- High softening temperature



MEDICAL
SUTURES



PLA



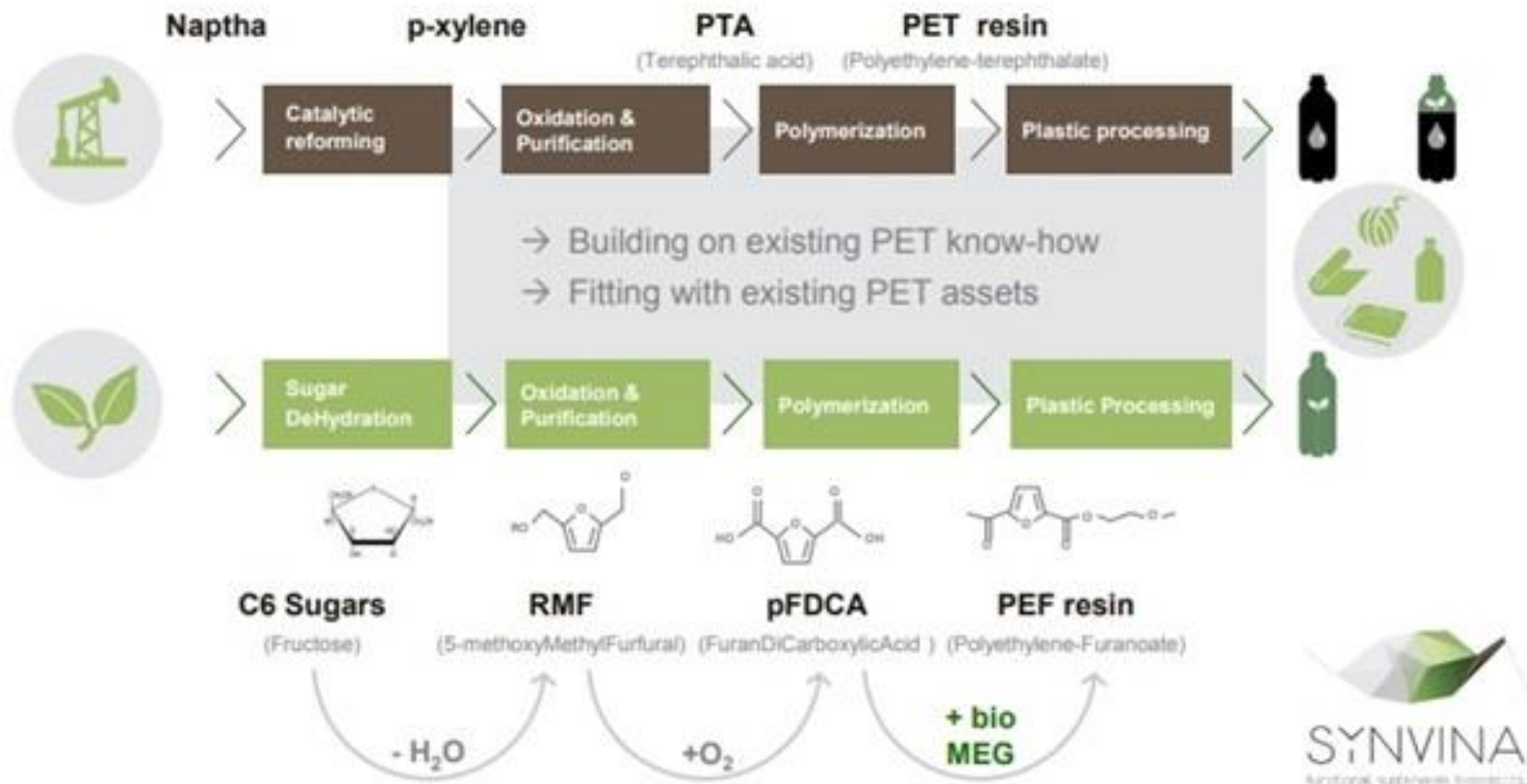
P(3HB-co-4HB)

- Biocompatible
- Resorbable
- Strong

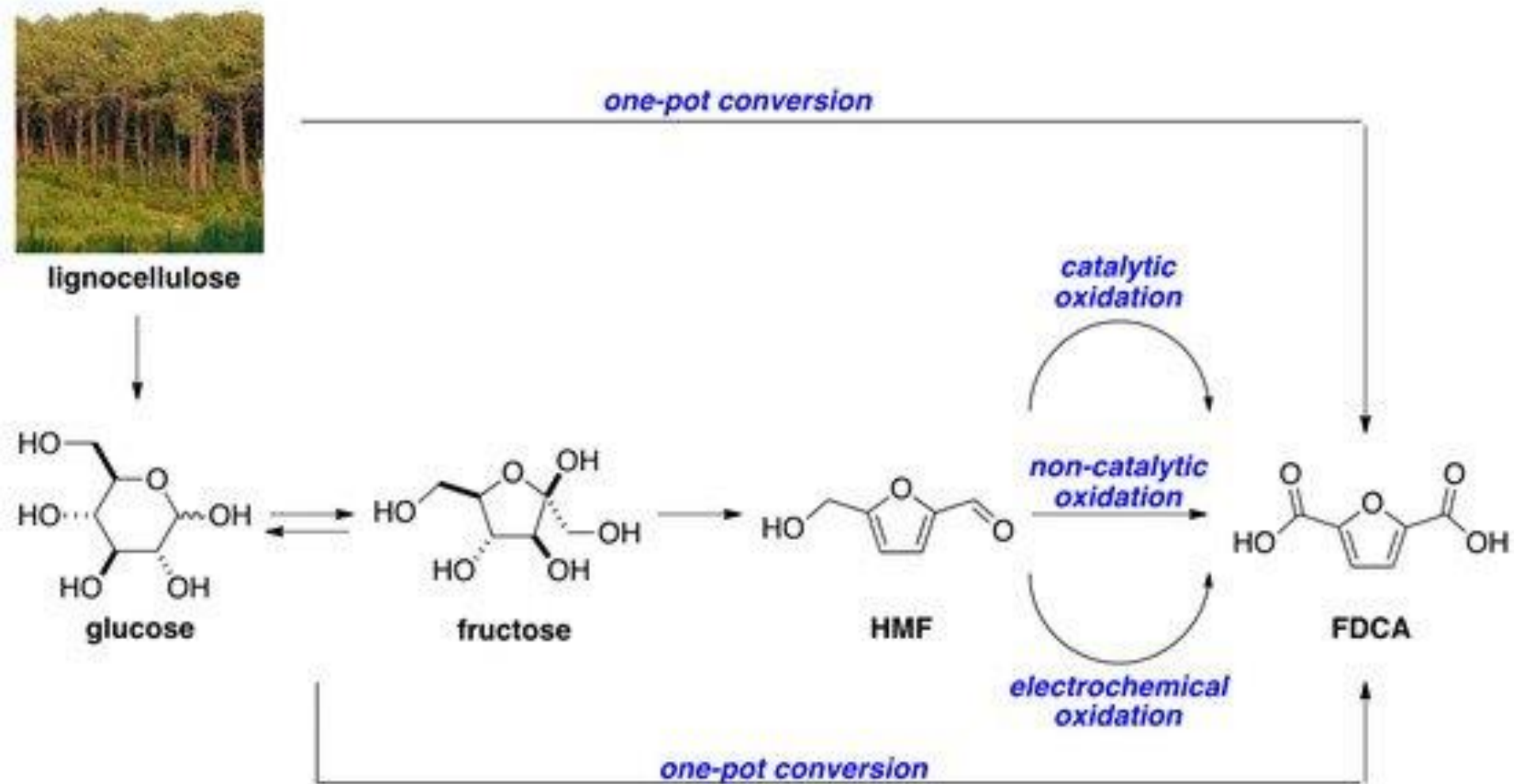


New polymers from biomass: PEF

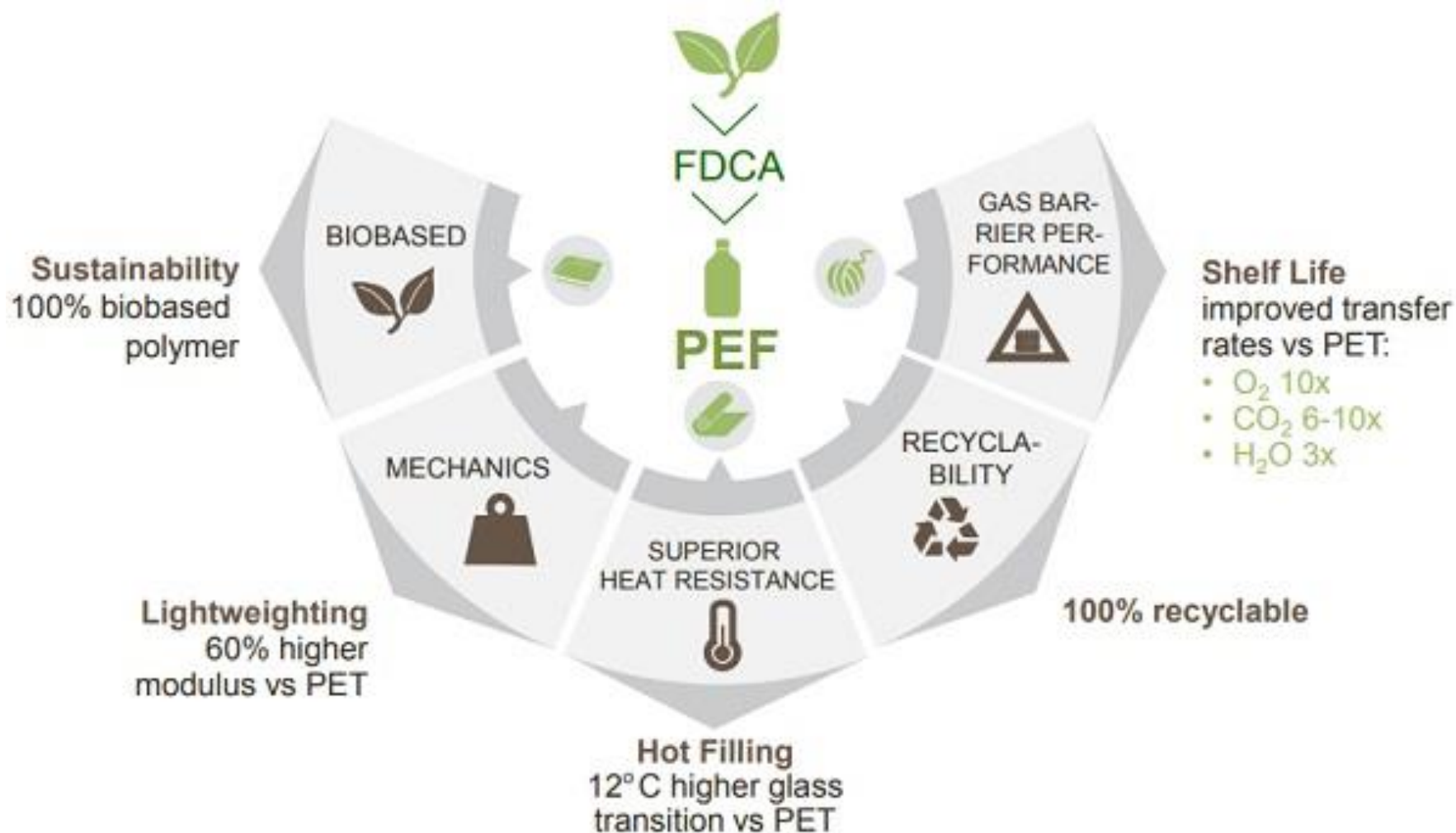
Pilot scale 40 t → 90 kt by 2025



FDCA synthesis

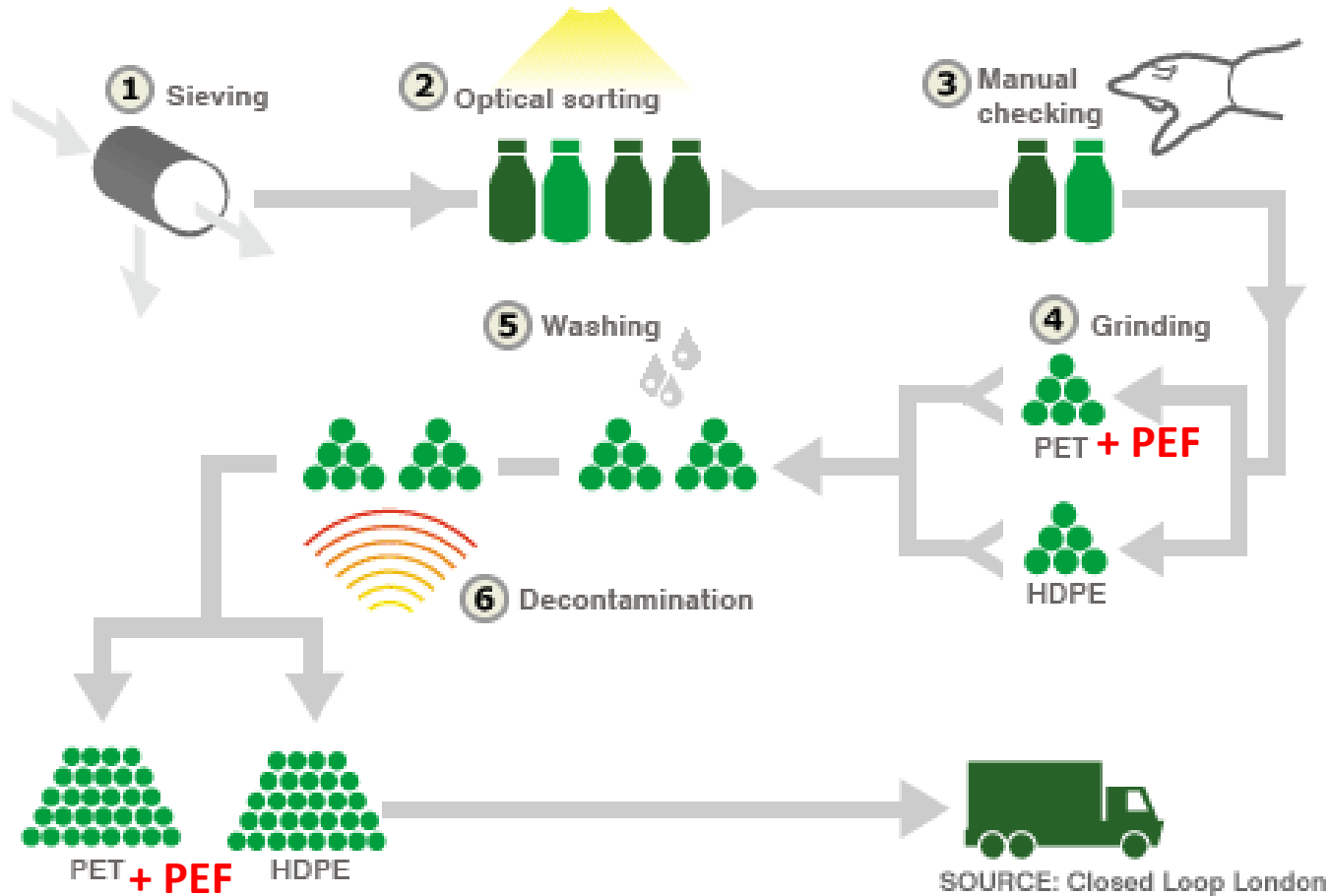


Properties



PEF as a drop-in from PET bottles ? No

1) PET is one of the best recycled plastic (30% worldwide)

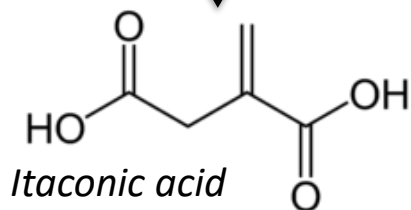


1) 100% bio-based PET is competitive in term of price

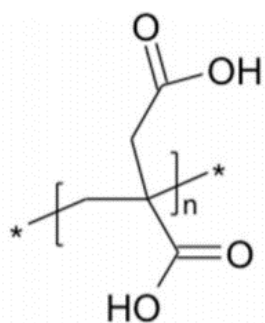
New polymers from biomass: SAP's



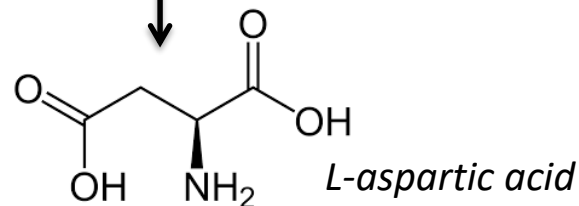
Fermentation



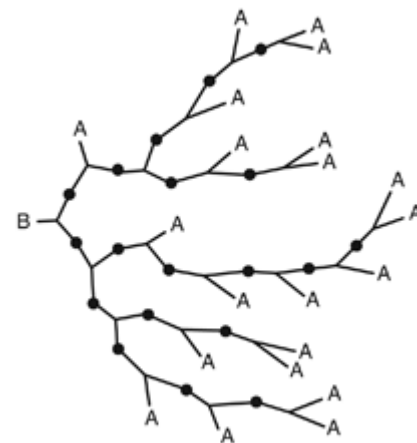
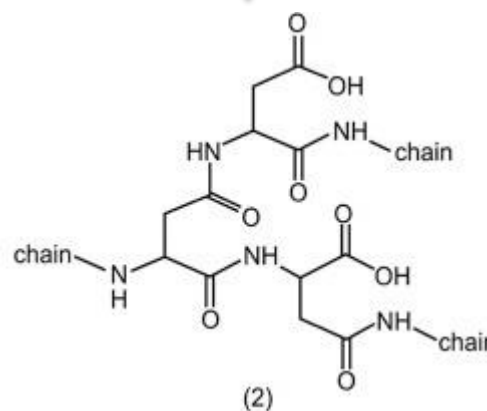
Polymerization



Fermentation

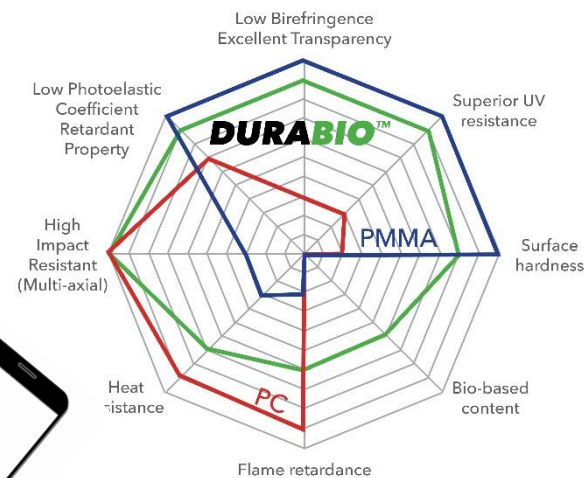
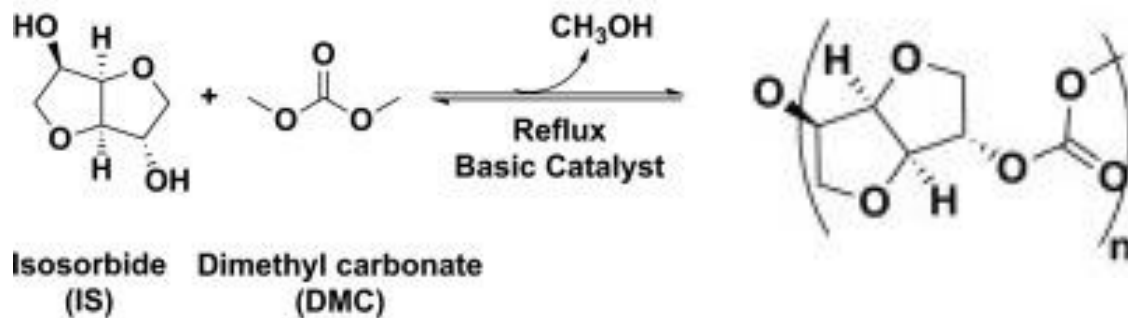
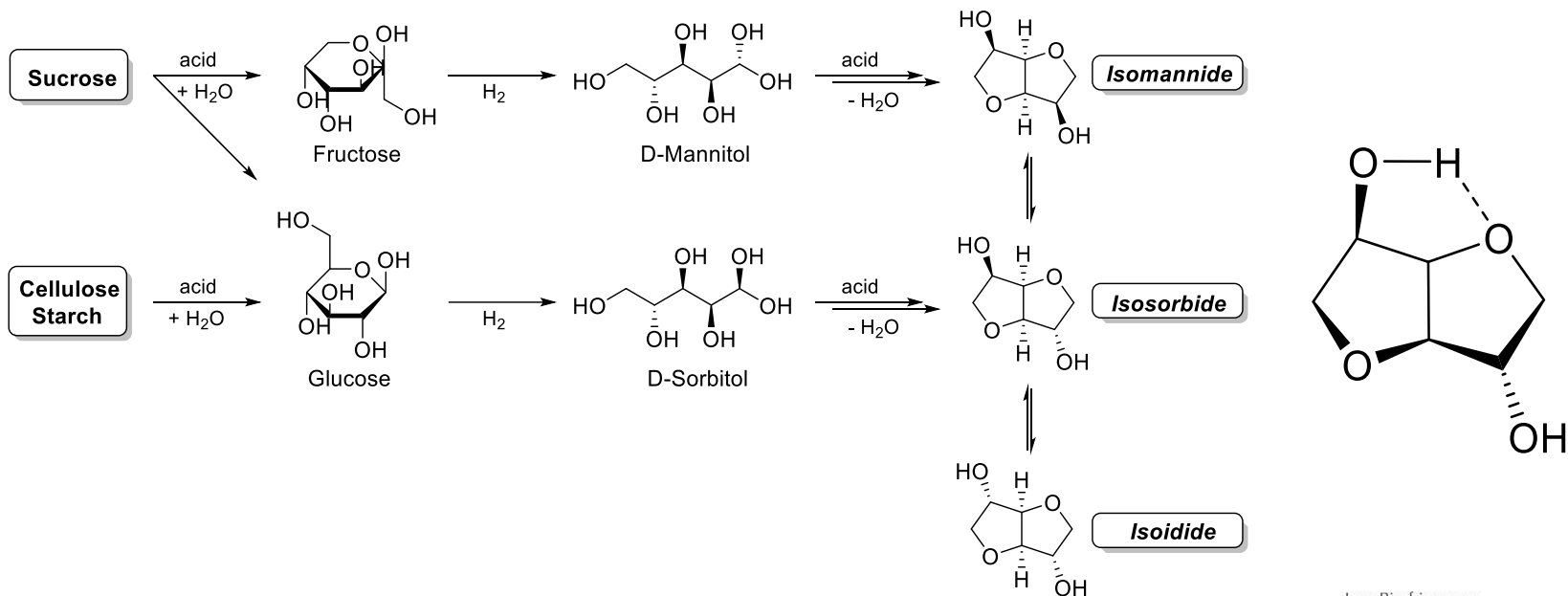


Polymerization

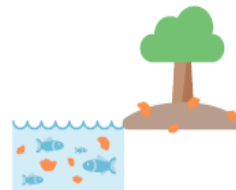


Hyperbranched Polymer

Isorbide: « regular » chemistry to transform sugar



1- Why ?



2- How ?

→ Biomass transformation to platform chemicals

3- Bio-based plastics from natural polymers

Cellulose, Natural rubber

4- Drop-ins: Bio-based alternative to fossil-based polymers

PE, PET

5- Smart drop-ins: Bio-based derivative of “fossil” polymers

PBS, Epoxy, PU

6- New polymers from biomass

PLA, PHA, PEF

7- Conclusions and perspectives

Conclusion and perspectives



Lignocellulose

Vegetable Oil

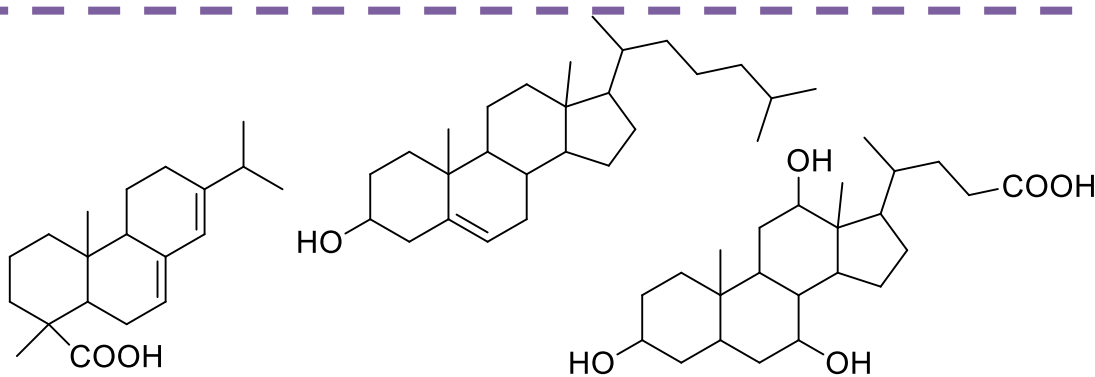
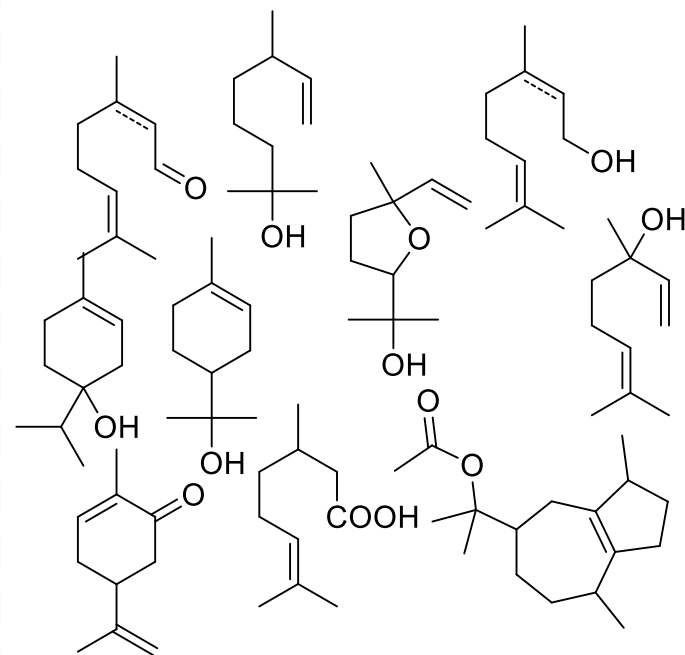
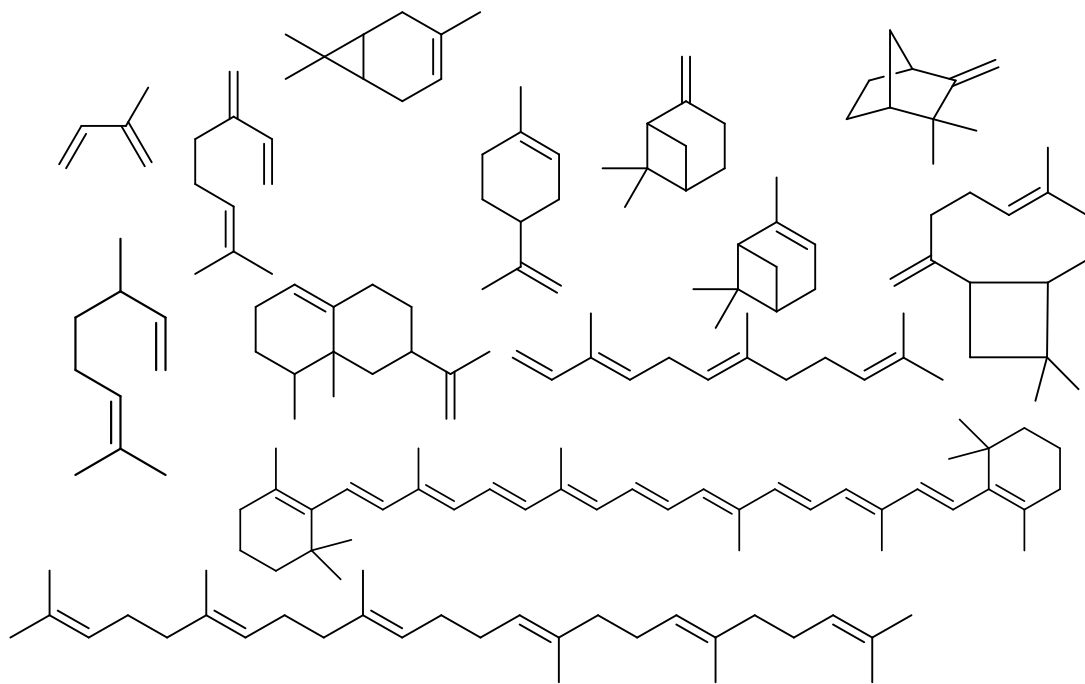


Carbohydrate



Terpens?

Terpenes as a source of various backbones



> 1000 of skeletons

...

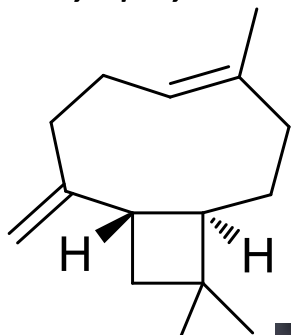


What can we do with a little of Hop?



1 €/kg

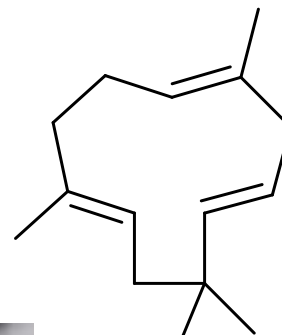
Caryophyllene



No! Polymers



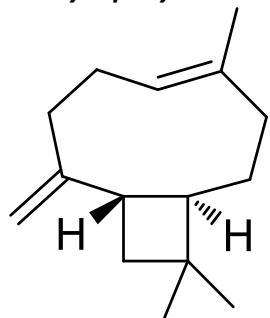
Humulene



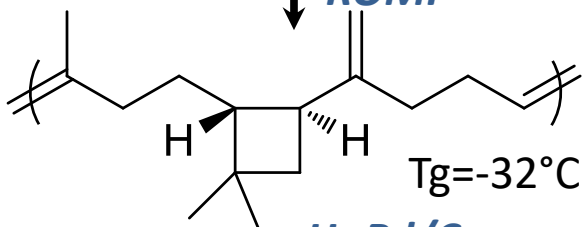
Beer !!!

First direct ROMP of natural compounds

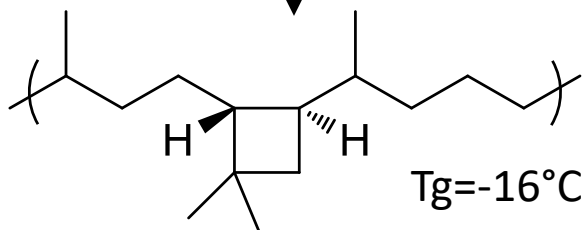
Caryophyllene



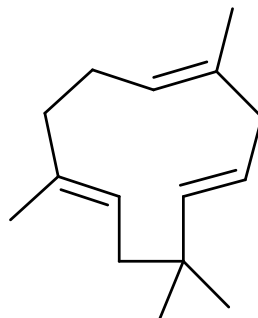
ROMP



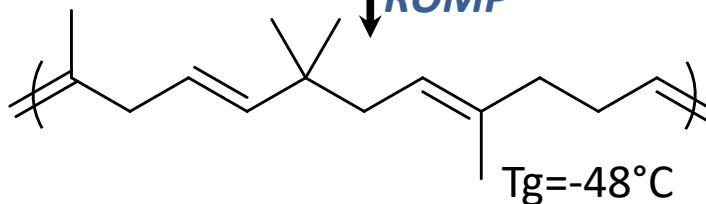
H₂ Pd/C



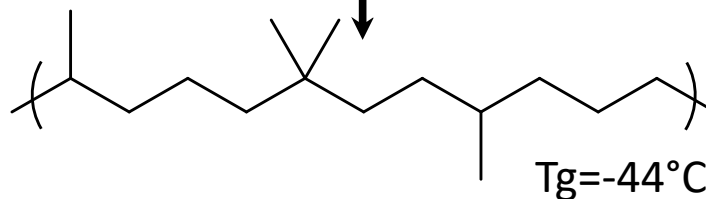
Humulene



ROMP



H₂ Pd/C



Can be performed

- In bulk at RT
- In water dispersion
- In hop/clove oil



E. Grau, S. Mecking *Green Chem.*, 2013, **15**, 1112-111

Conclusion and perspectives



Ligno

Crossing the biomass !!!



Carbohydrate

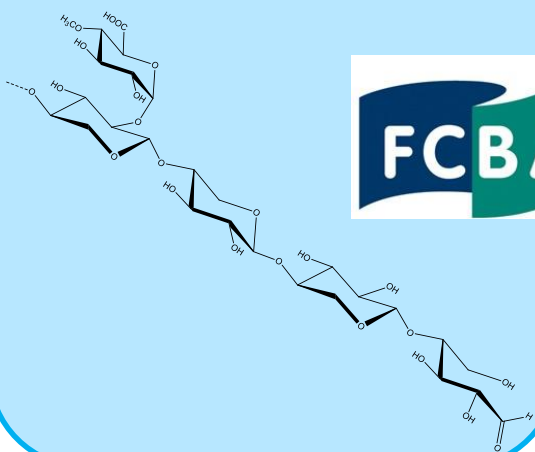


Terpens

Crossing the biomass

Wood

Xylo-oligosaccharides



FCBA

HYDROPHILIC



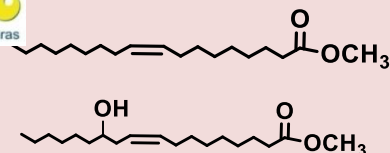
HYDROPHOBIC



ITERG
Expertise Corps Gras

Oil

Fatty esters



- 💧 Renewable feedstock
- 💧 Abundant
- 💧 High purity (up to 99%)
- 💧 Polymerizable



Cosmetics

Emulsifiers -Foaming agents -
Solubilizers -Wetting agents



Pharmaceutical

Biocompatible, drug delivery



Food

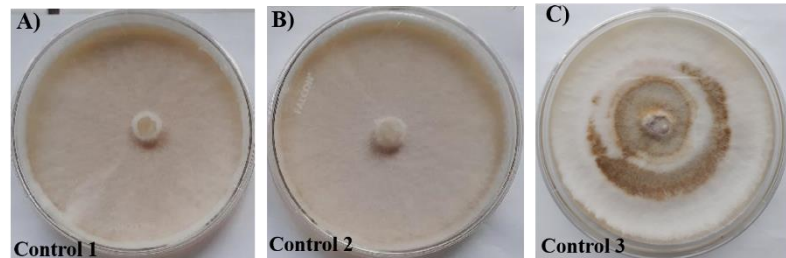
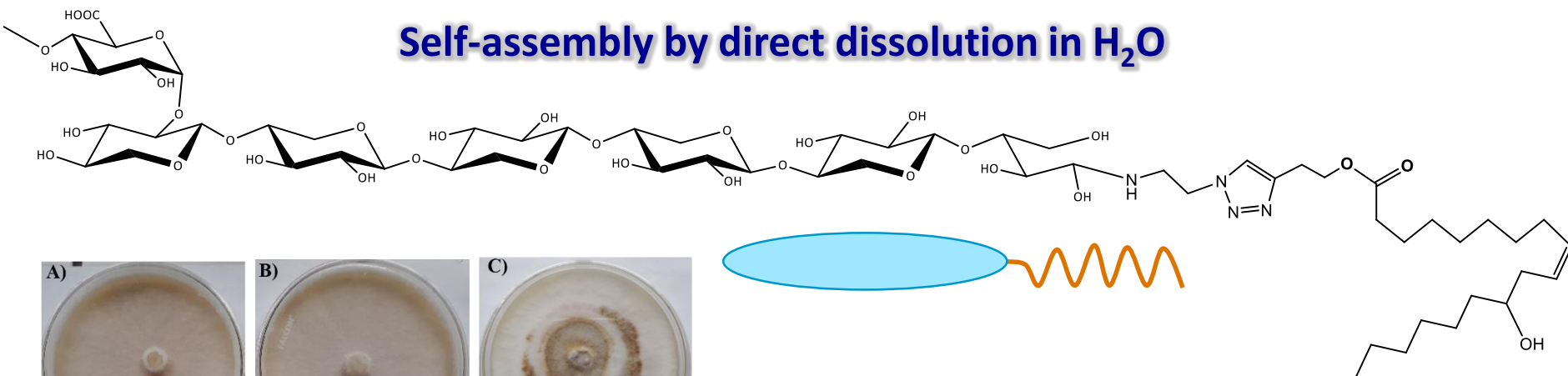
Use as emulsifier



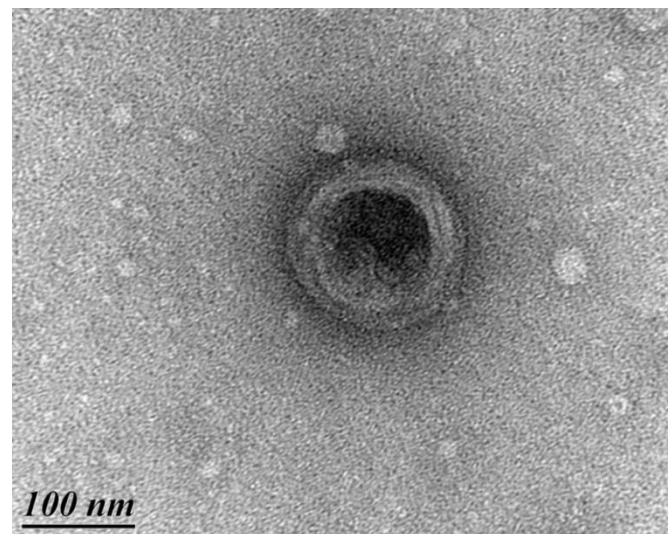
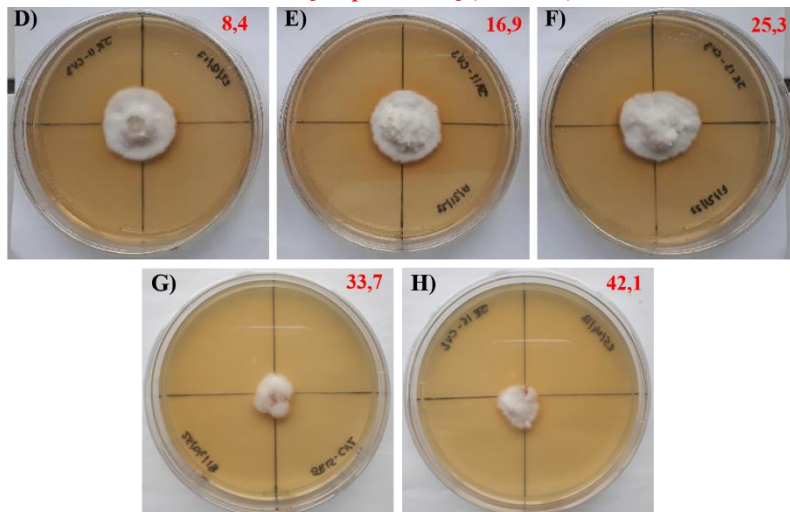
Detergents



Self-assembly by direct dissolution in H₂O

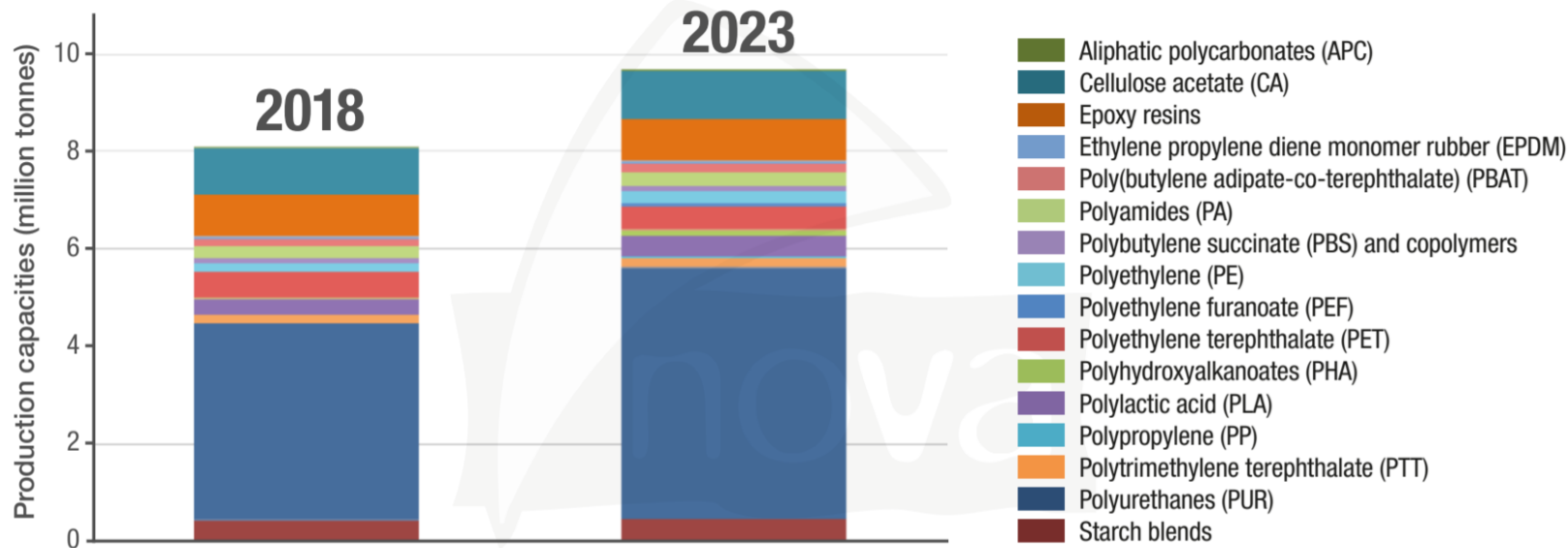


[Propiconazole] (nmol/mL)

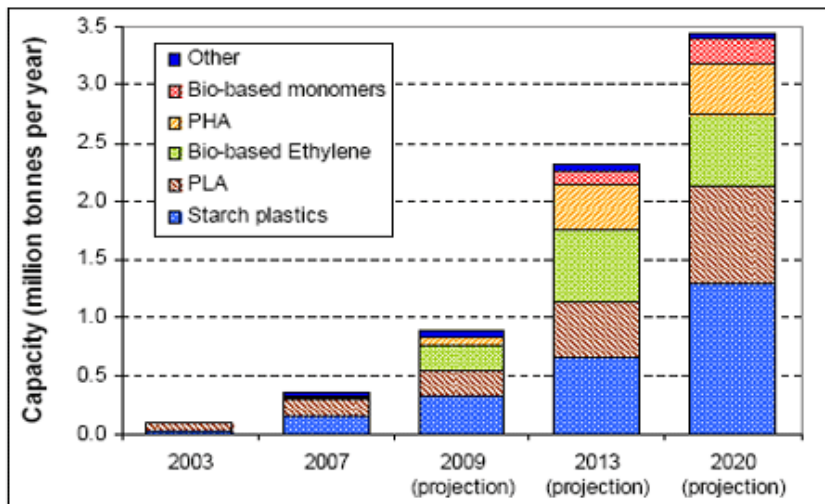


J. Rosselgong et al. Biomacromolecules, 20(1), 118-129 (2019)

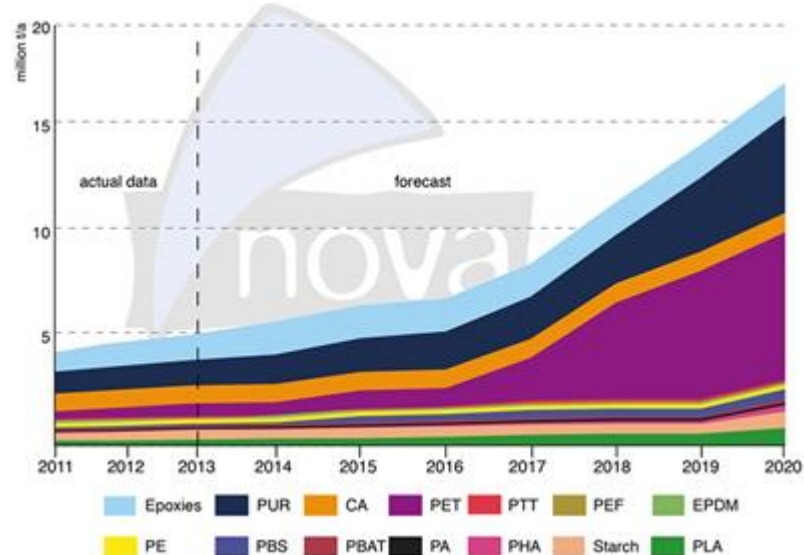
Bio-based polymers forecast



vs. 350 Mt of polymer



Note: Category "other" includes cellulose films, PTT from bio-based 1,3-PDO, bio-based polyamide and PUR from bio-based polyols; category "Bio-based monomers" includes primarily bio-based epichlorohydrin.





Thank you all !

Questions ???

egrau@enscbp.fr



université
de **BORDEAUX**

