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Bio-sourced polymers

Etienne Grau

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Bio-sourced polymers

Dr Etienne Grau

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



1- Why ?

2- How ?

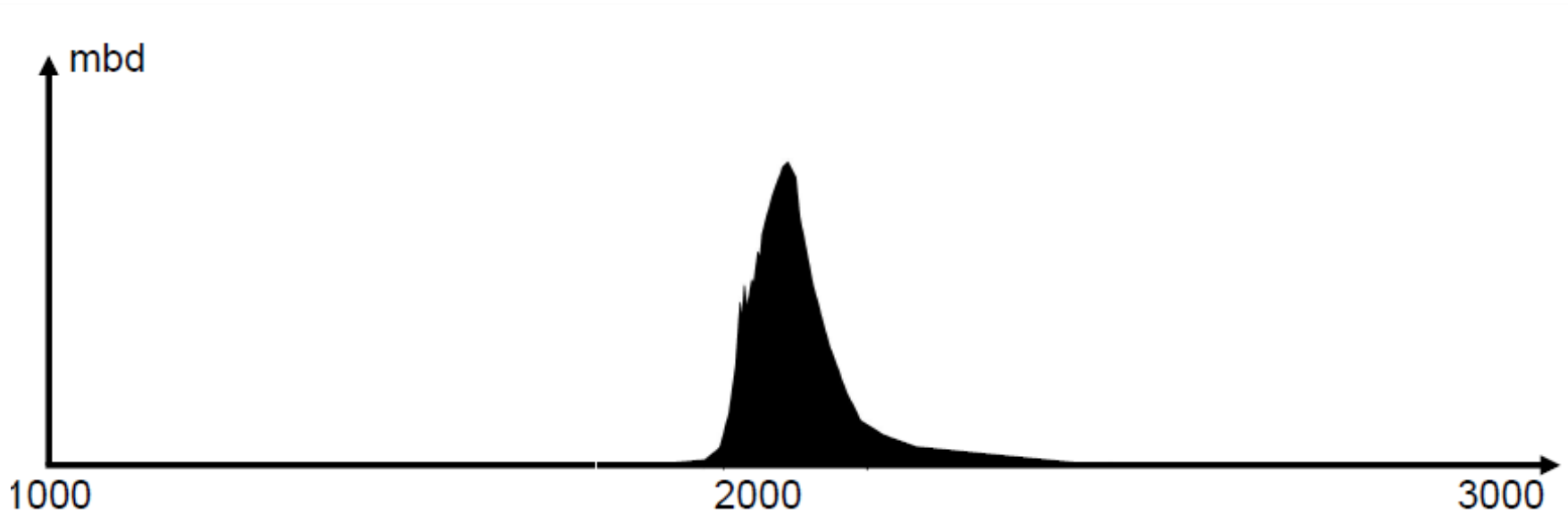
3- Bio-based plastics from natural polymers

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

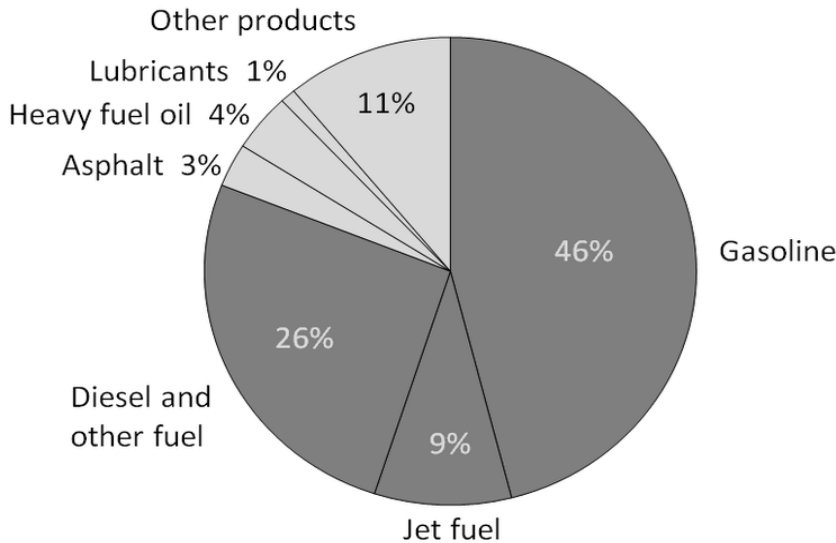


Petroleum is the starting materials of **99%** « commodity » chemicals

- 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, Cl₂, ...)
- 6% Fertilizers (NH₃)

Petroleum = C

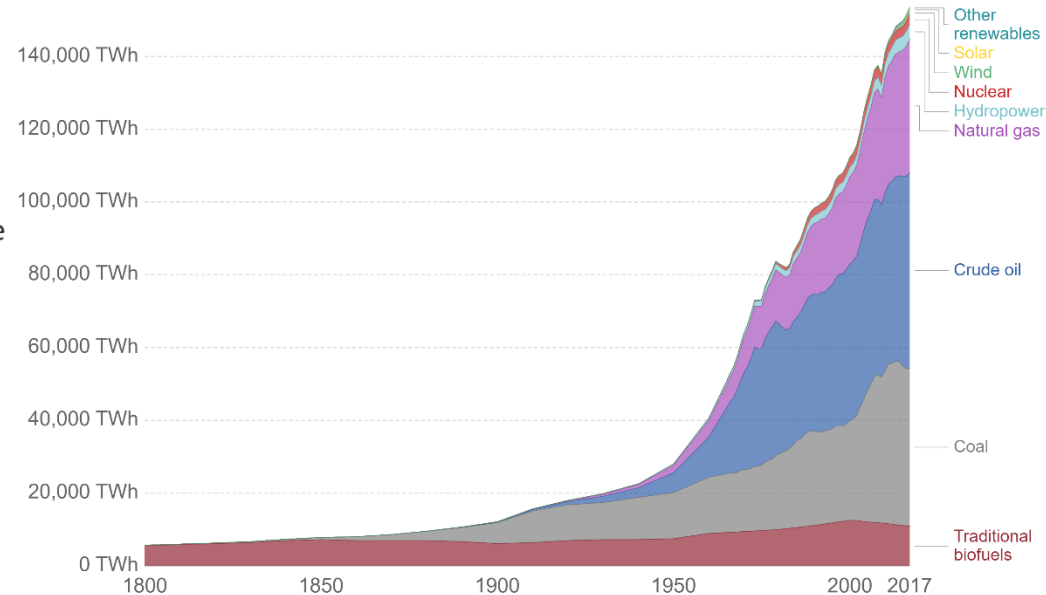
Petroleum = J



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

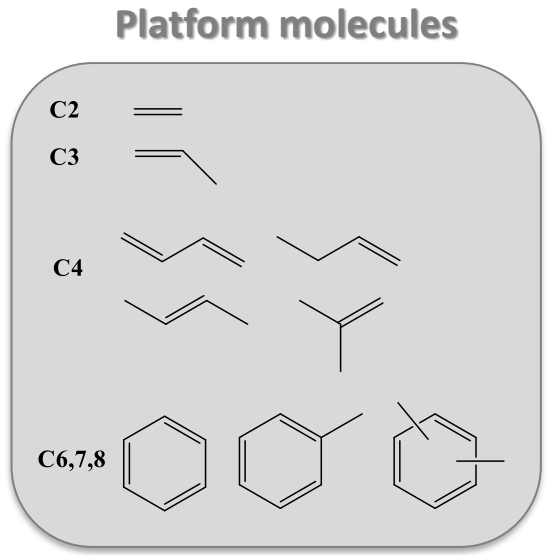


Source: Vaclav Smil (2017) and BP Statistical Review of World Energy

CC BY

Synthetic polymers are based on petroleum

**20th century:
A petroleum area**

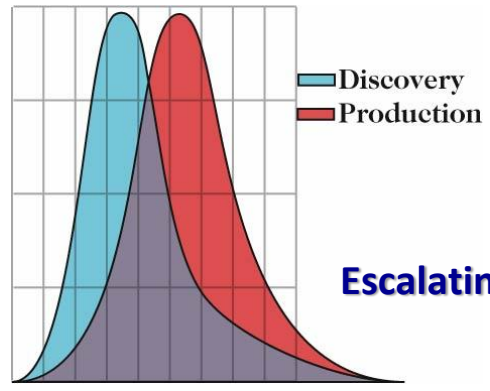
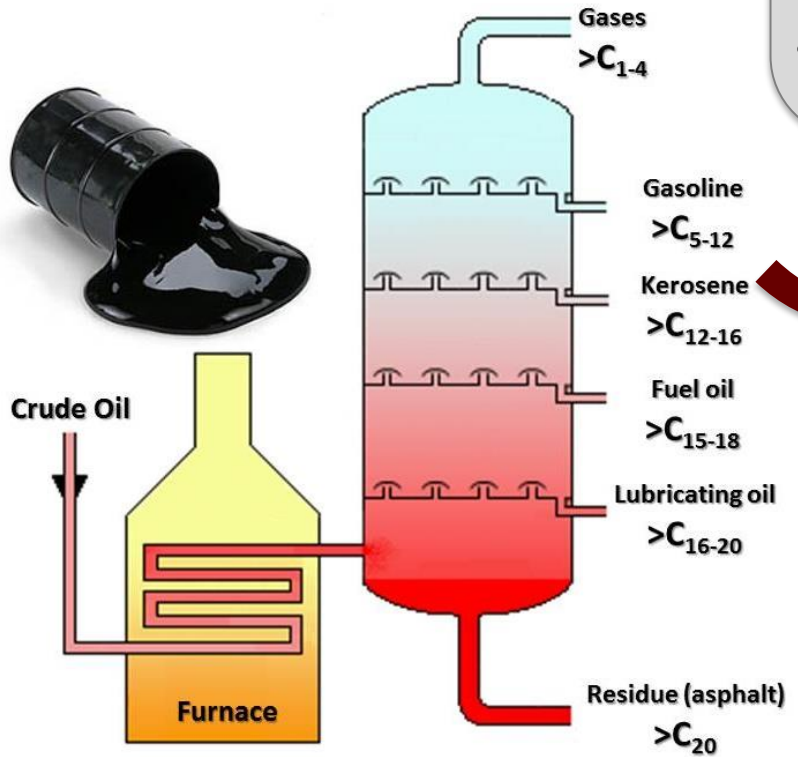


**~350 million tons
(annual global production)**

Steel 1800 Mt (230 Mm³)

PEAK OIL

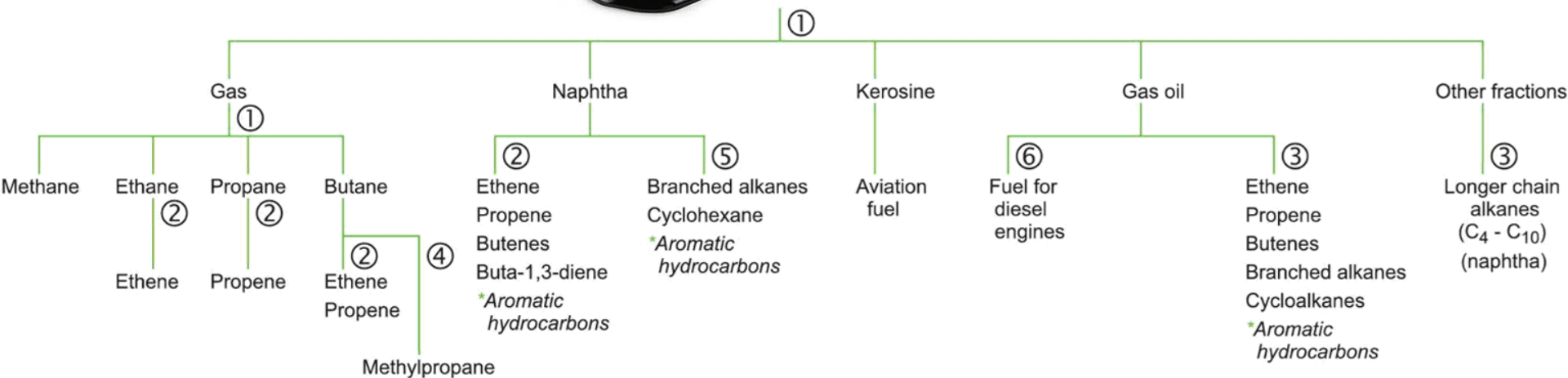
**Oil depletion
Escalating prices of oil resources**



From crude oil to platform molecules



Crude oil

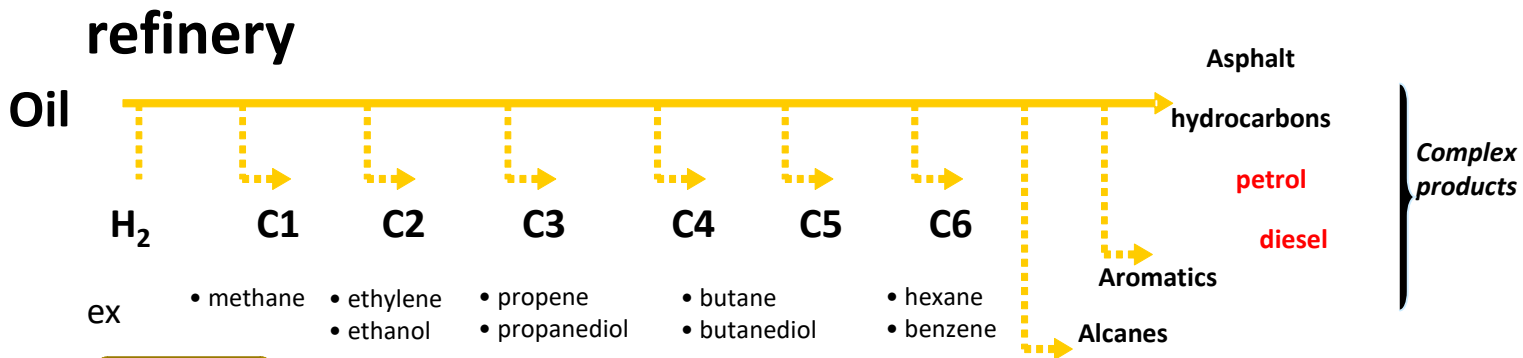


- ① Distillation
- ② Steam cracking
- ③ Catalytic cracking ('hydrocracking')
- ④ Isomerisation
- ⑤ Reforming ('platforming')
- ⑥ Sulfur is removed



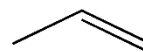
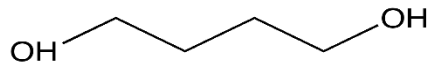
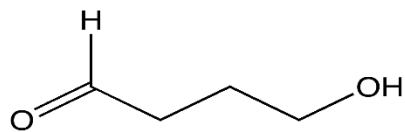
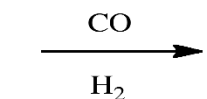
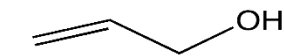
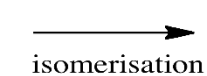
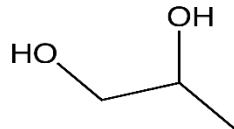
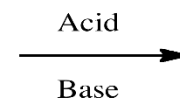
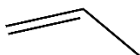
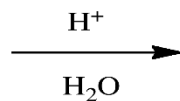
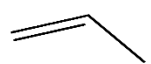
*Aromatic hydrocarbons:
benzene
methylbenzene
dimethylbenzenes
ethylbenzene

Oil refinery – example of the C3 platform



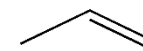
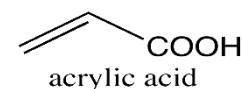
cuts

Naphta

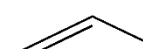
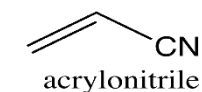


gas phase

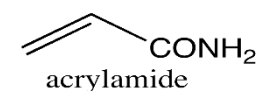
oxidation



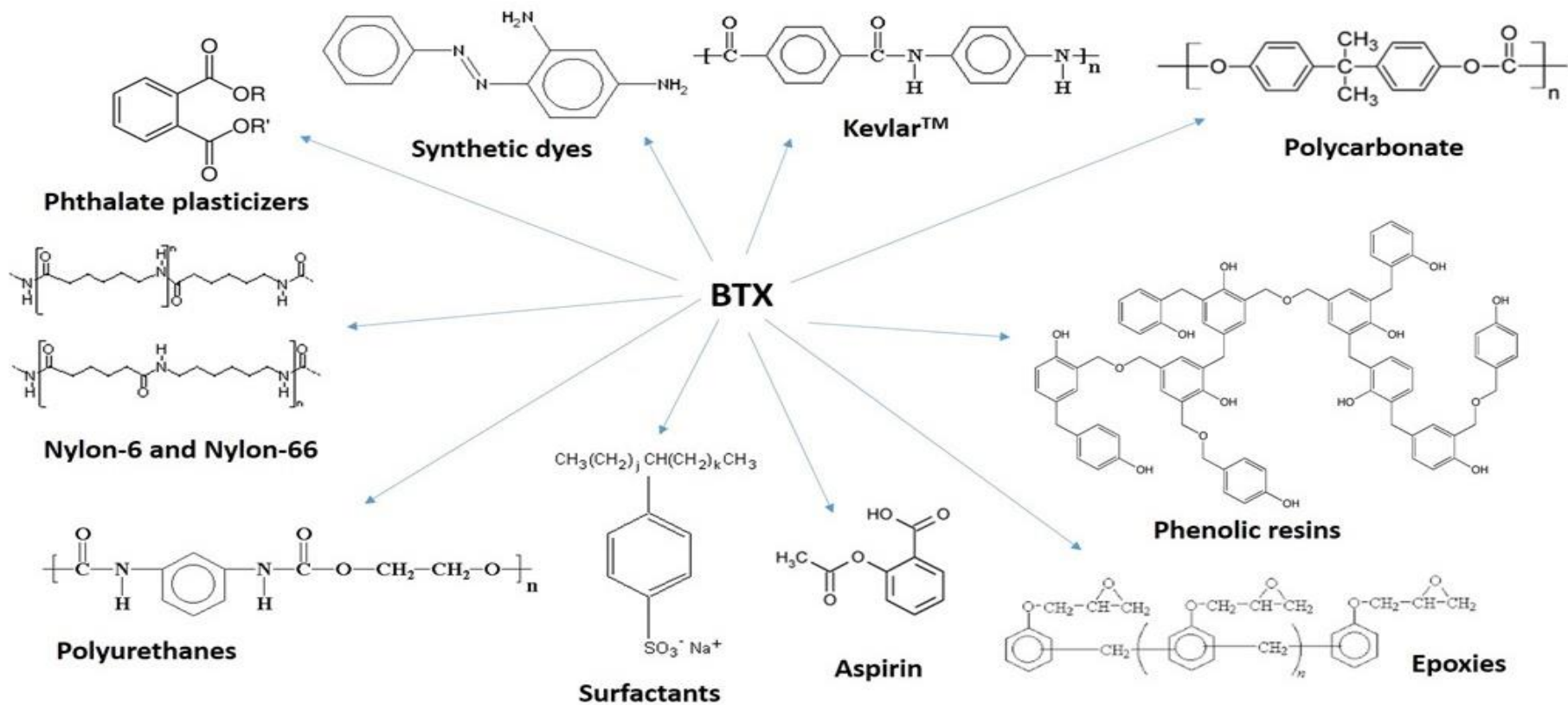
ammoxidation



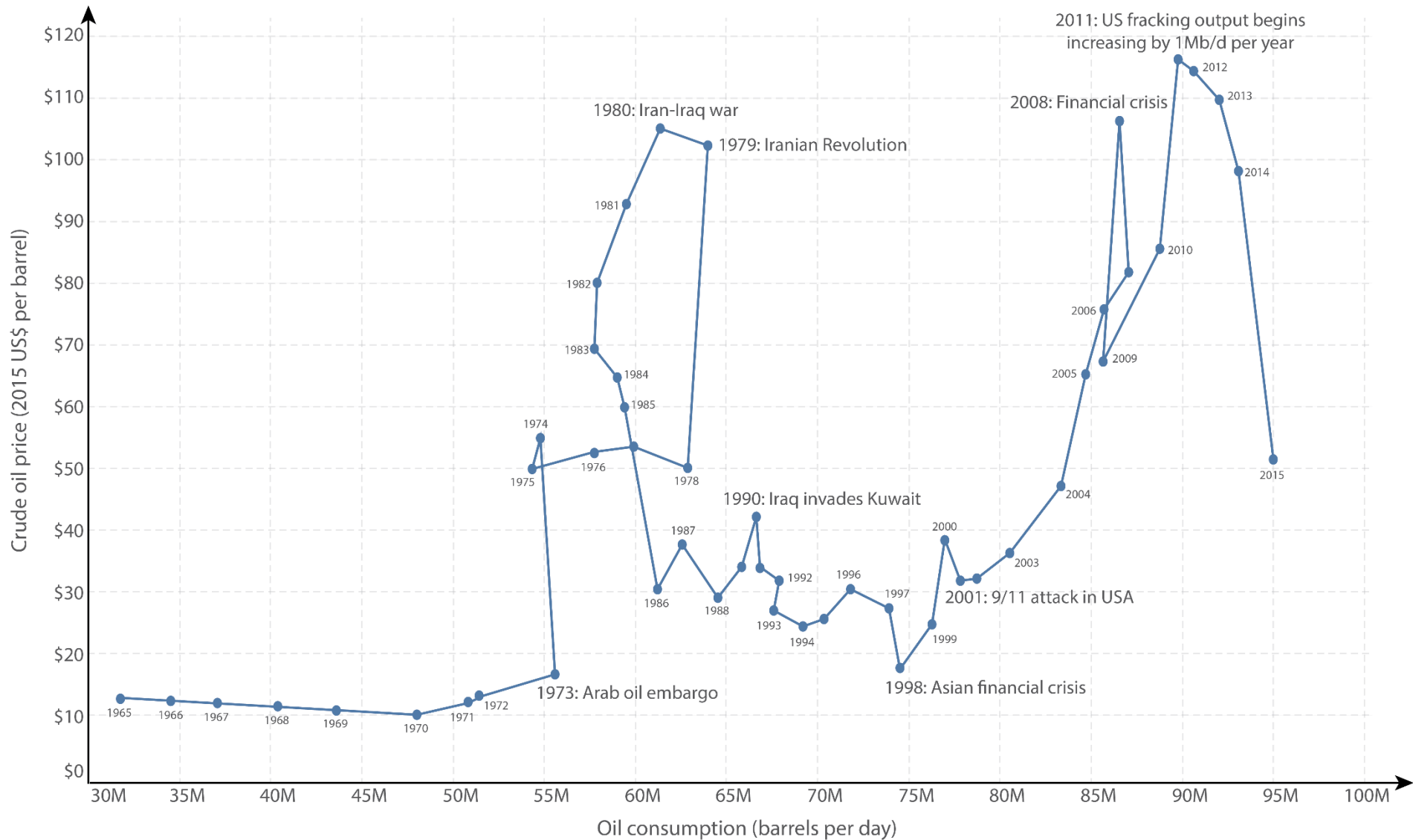
H₂O



Oil refinery – example of the BTX platform



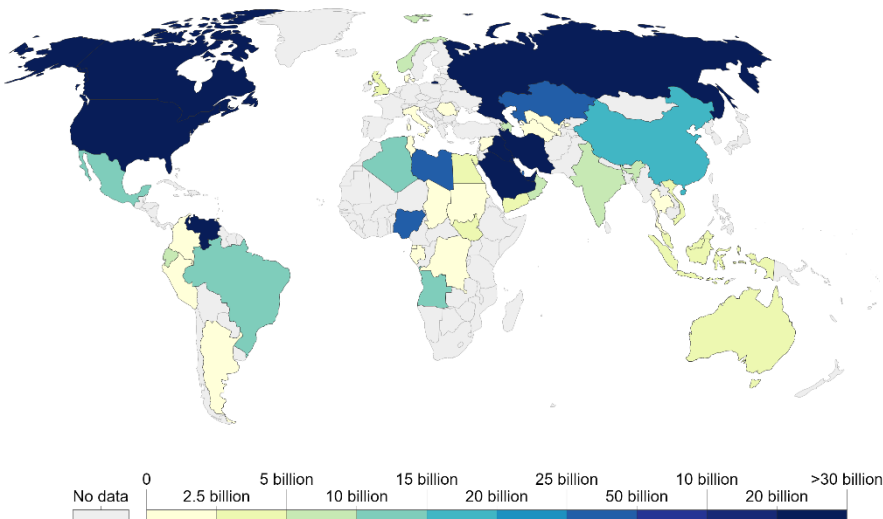
World crude oil price vs. oil consumption



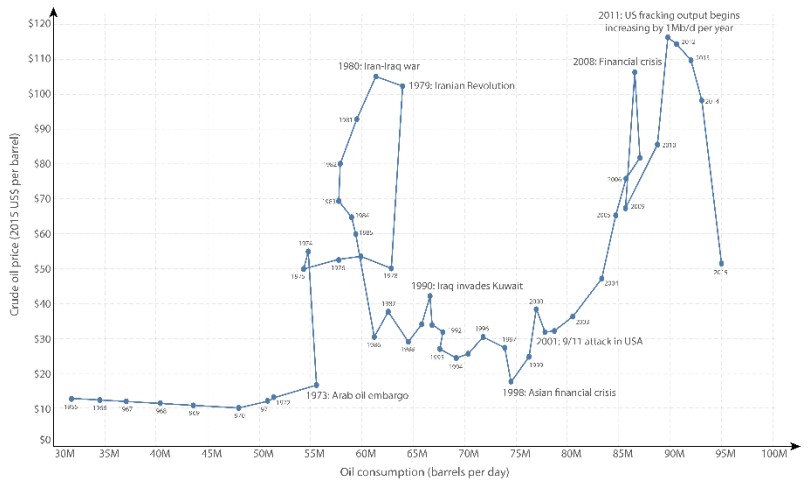
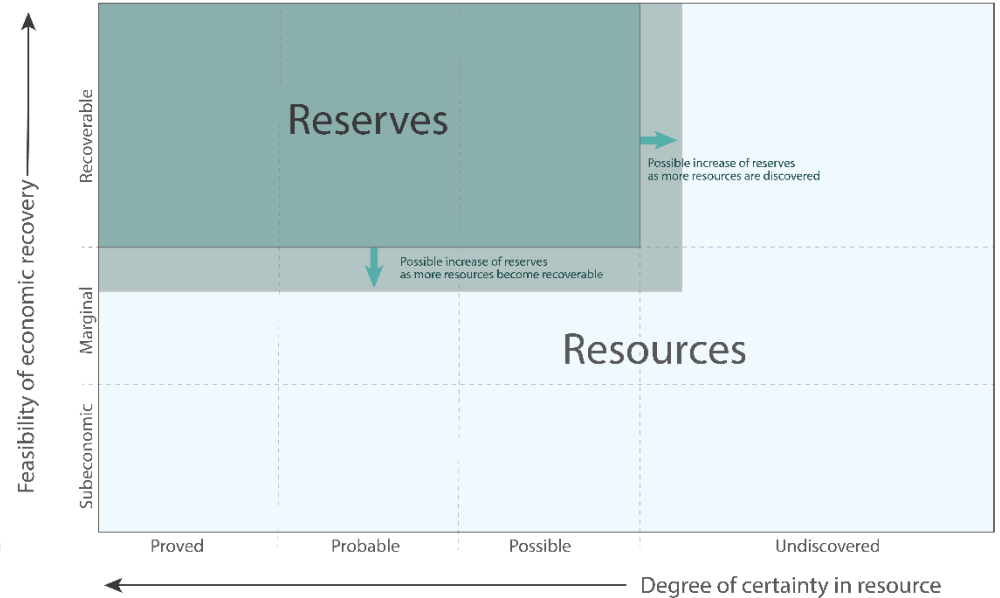
Data source: BP Statistical Review of World Energy 2016
 The data visualization is available at OurWorldinData.org. There you find research and more visualizations on this topic.

Licensed under CC-BY-SA by the authors Hannah Ritchie and Max Roser.

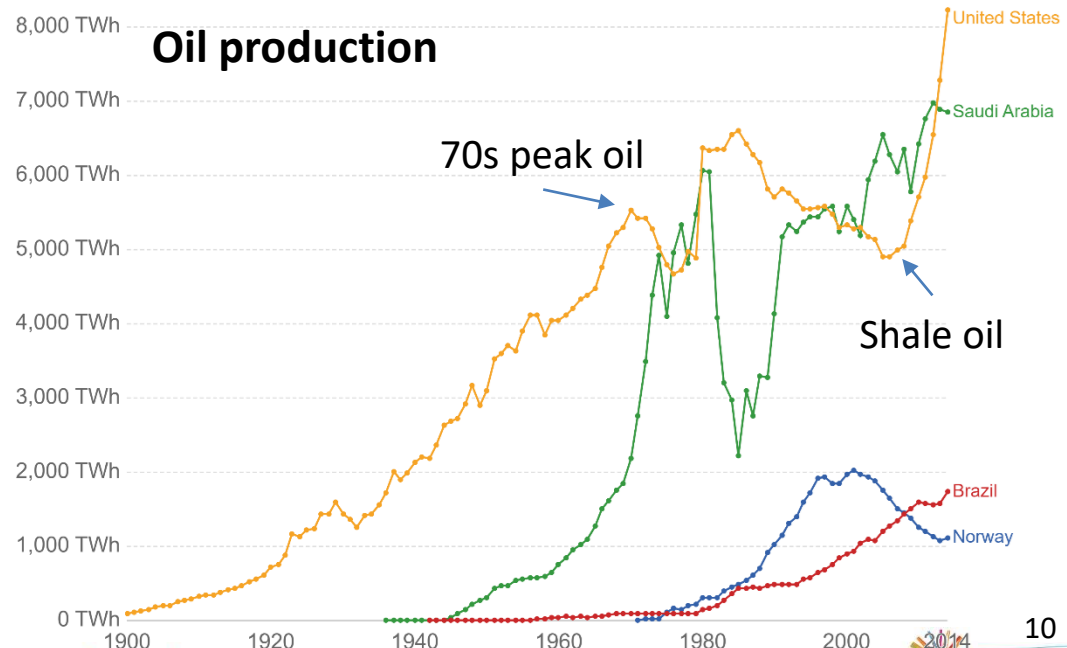
Worldwide oil reserves



Peak oil ?

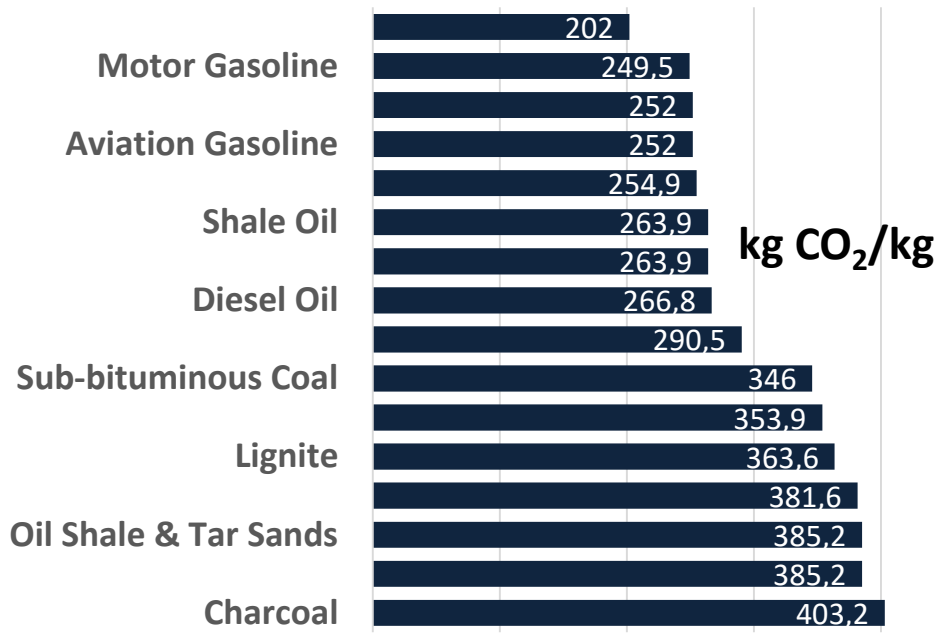
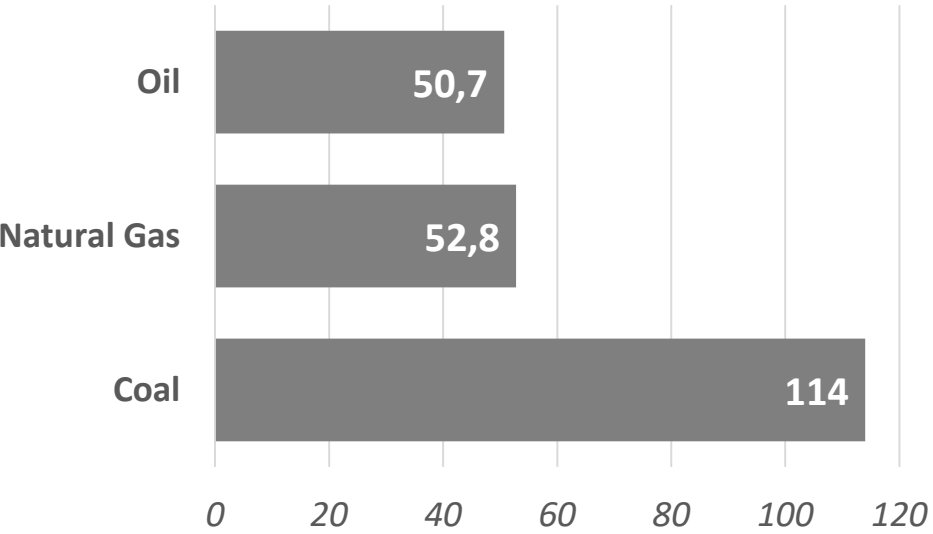


Data source: BP Statistical Review of World Energy 2016. The data visualization is available at OurWorldInData.org. There you find research and more visualizations on this topic. Licensed under CC BY SA by the authors Hannah Ritchie and Max Roser.

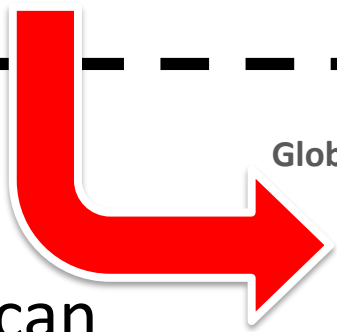


Fossil fuel reserves

Years of fossil fuel reserves left



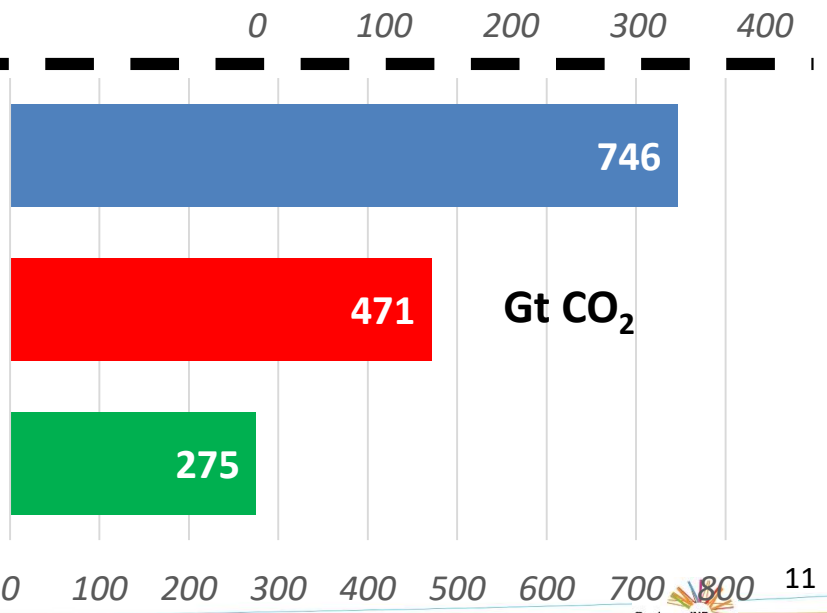
Only $\frac{1}{3}$ can be burned



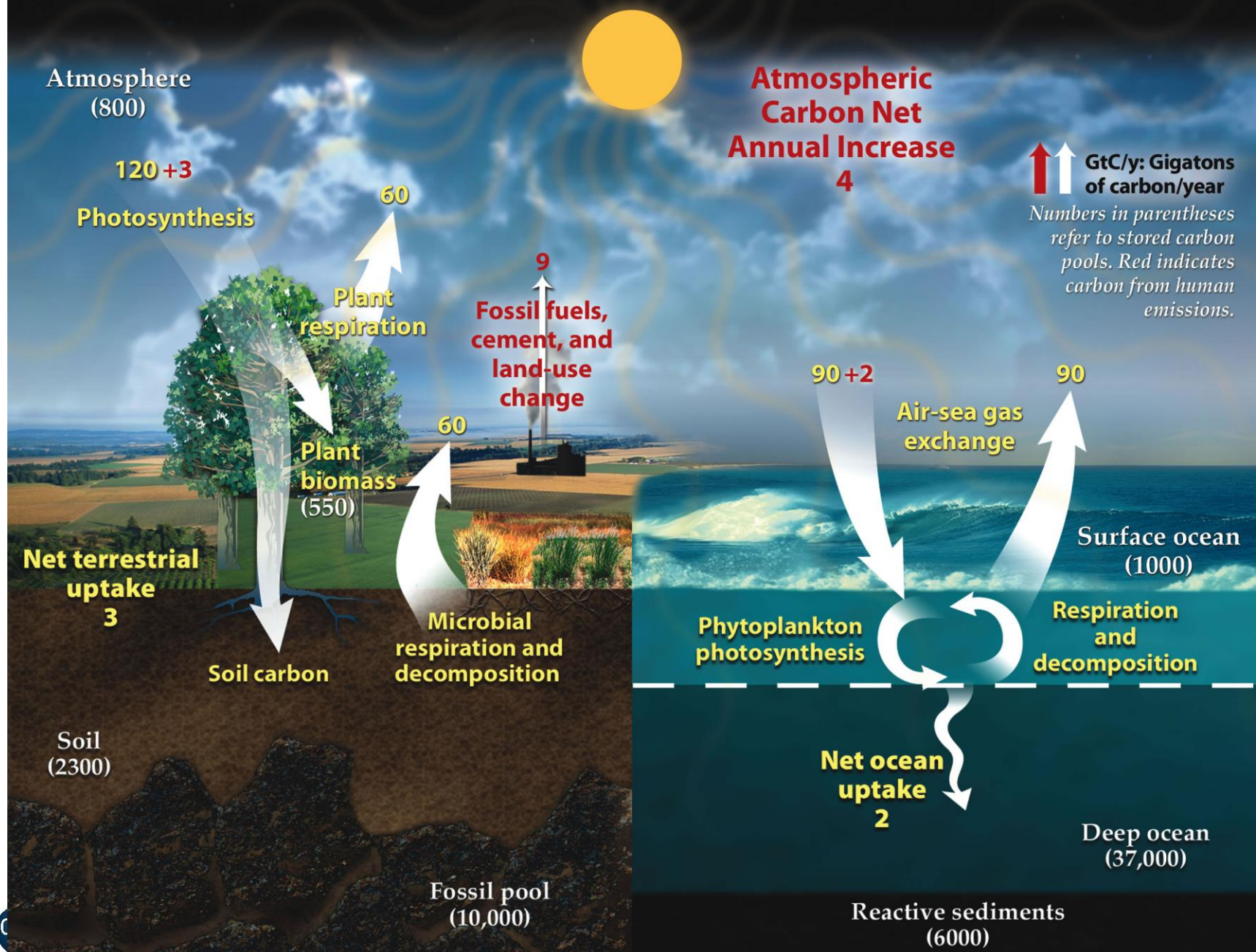
Global Fossil Fuel Reserves

Unburnable Reserves

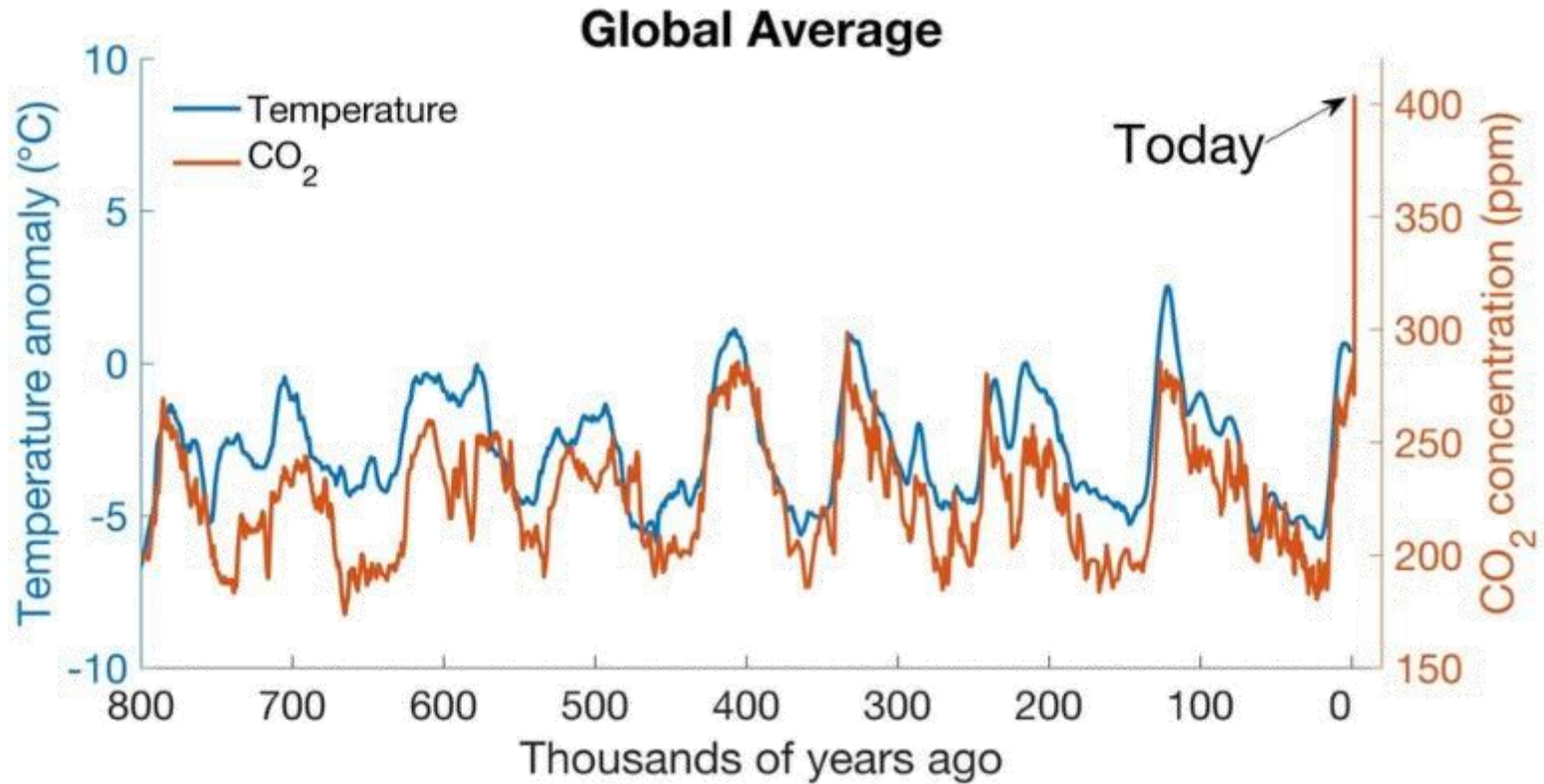
Carbon Budget for 2C



CO₂ cycle



CO₂ concentration keep increasing



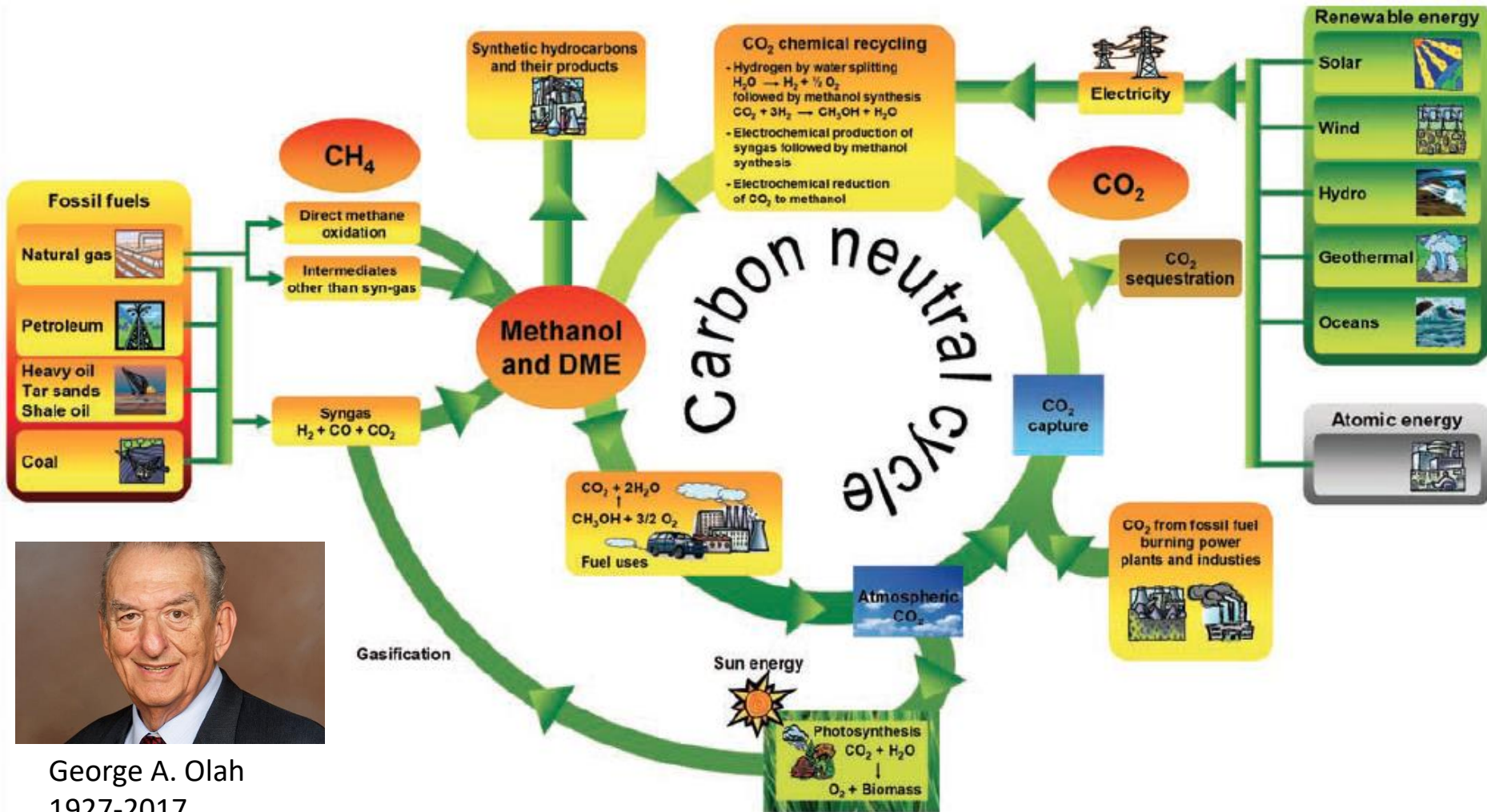
➔ Last time the CO₂ was that high the Human didn't exist
4 ppm/year more CO₂ in the atmosphere

May 2019: 415ppm
Since Sept 2016 > 400ppm

1987 : 350ppm

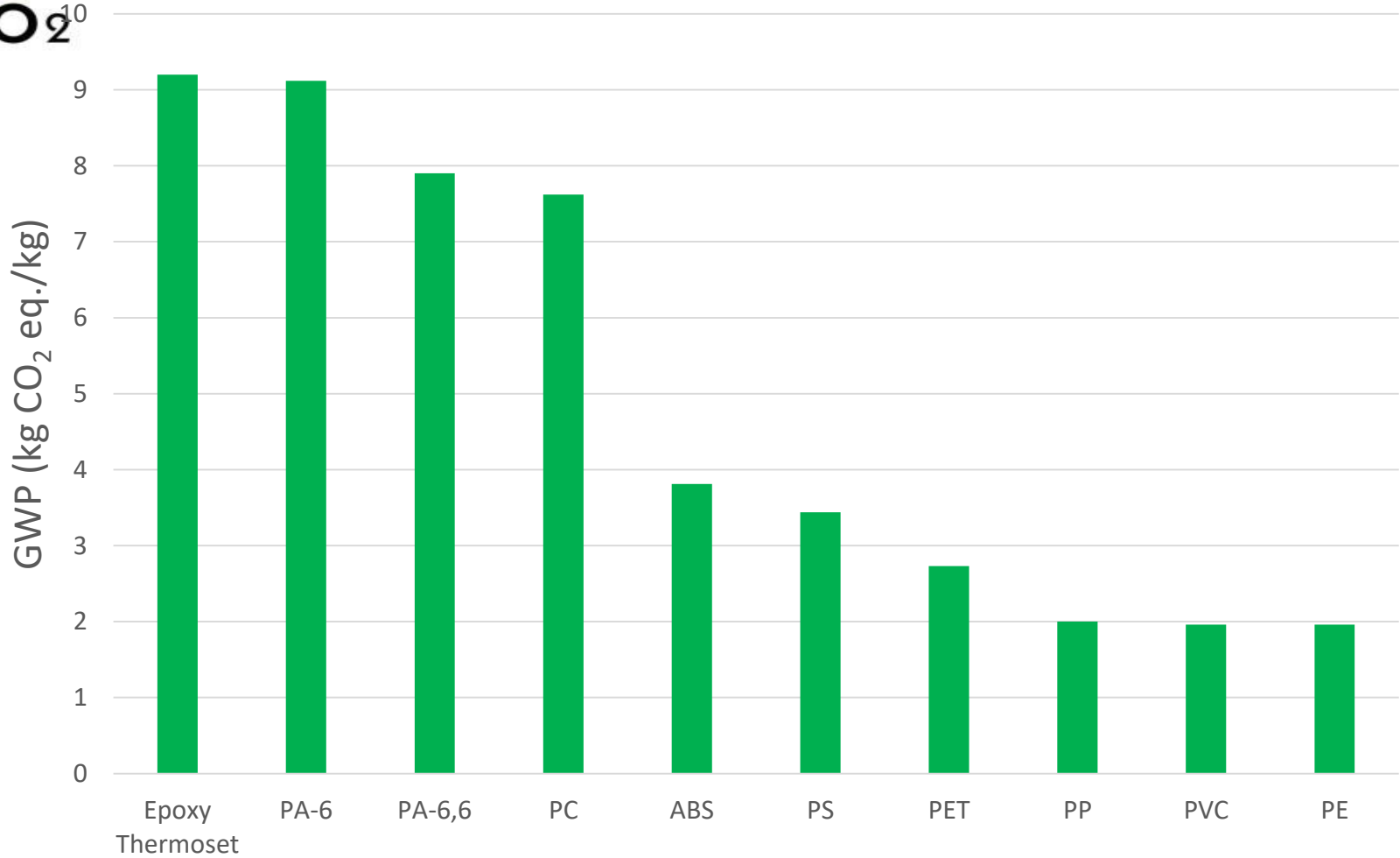
Reduce CO₂ emissions and trap it sustainably.

Carbon neutral society



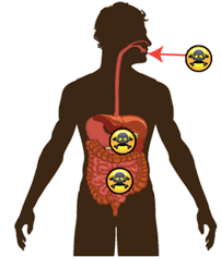
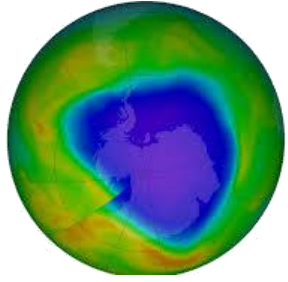
George A. Olah
1927-2017
Nobel Prize 1994

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



Woven PP



b)



polyester



biopolymer



paper



cotton

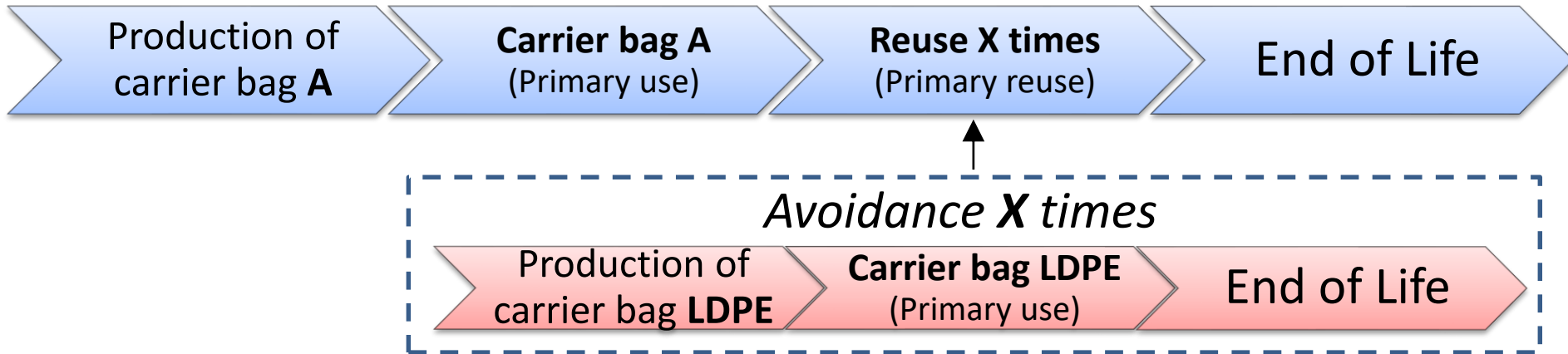


composite

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

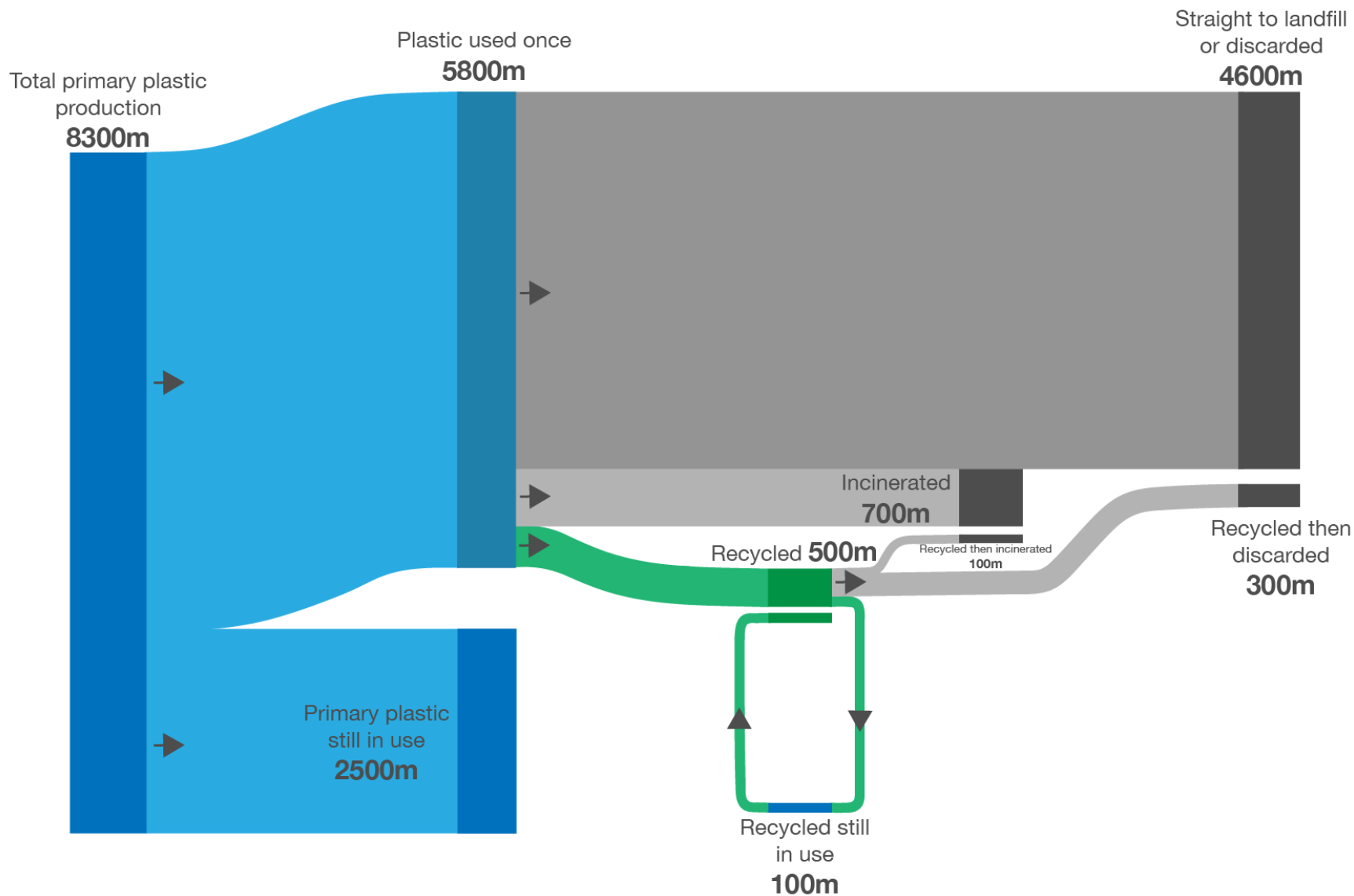


	Climate Change	All indicators
Non-woven PP, EOL = recycled	6	52
Woven PP, EOL = recycled	5	45
Recycled PET, EOL = recycled	8	84
Polyester, EOL = recycled	2	35
Biopolymer, EOL= waste bag or incinerated	0	42
Unbleached paper, , EOL= waste bag or incinerated	0	43
Bleached paper, EOL= waste bag or incinerated	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 year

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

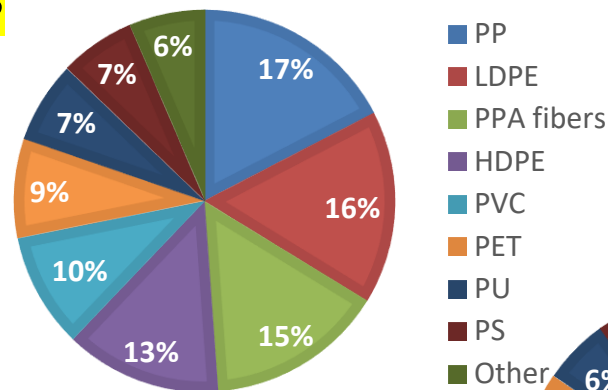
Mismanaged coastal plastic waste:
31.9 million tonnes per year

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).

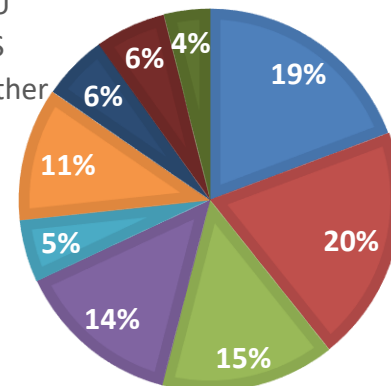
Plastic inputs to the oceans:
8 million tonnes per year

2 billion people living within 50km of coastline

PRODUCTION



WASTE



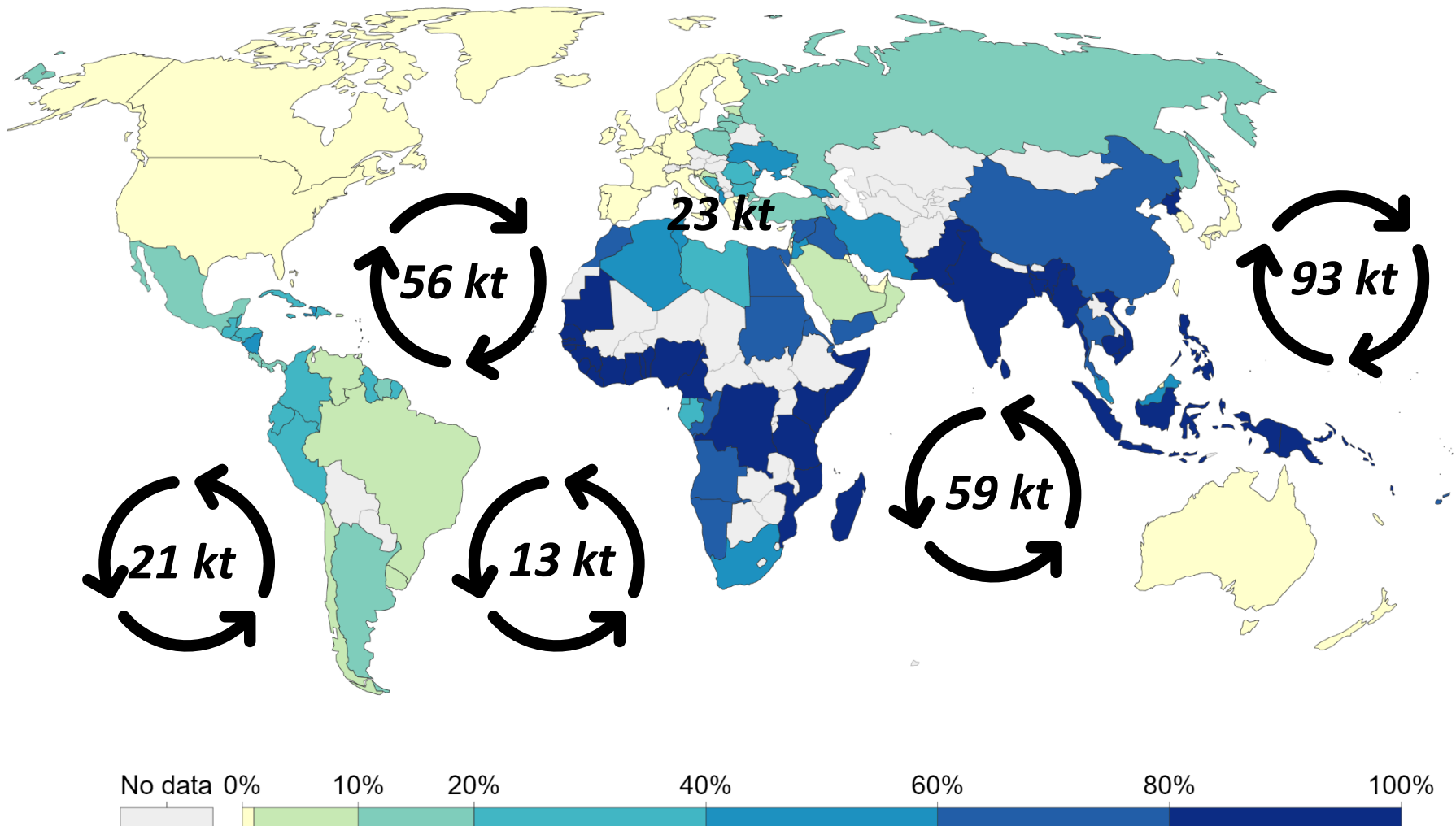
Plastic in surface waters:
10,000s to 100,000s tonnes

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.

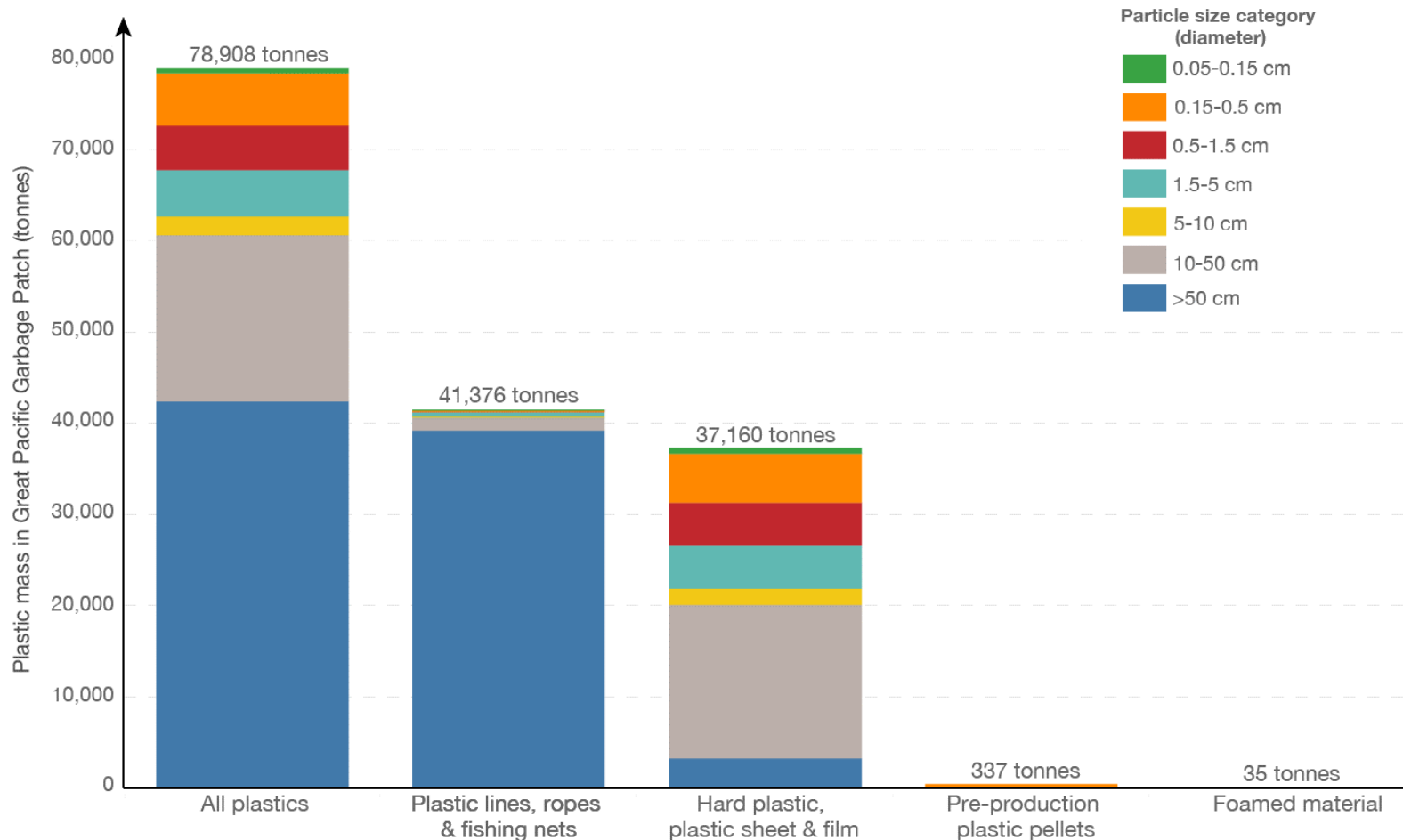


Share of plastic waste that is inadequately managed (2010)

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?

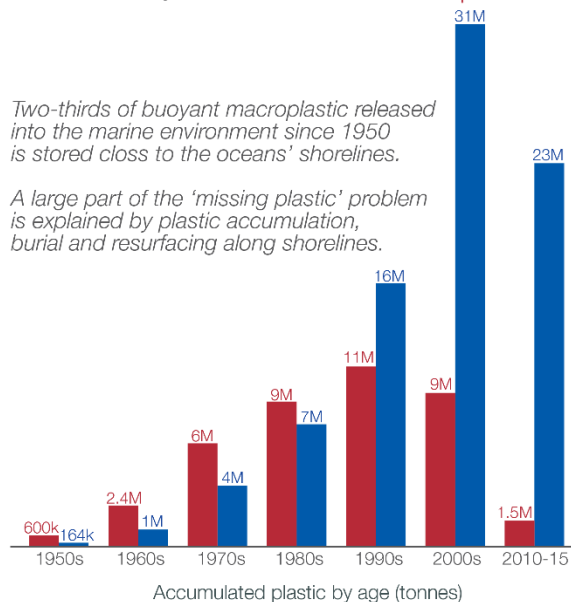
Macroplastics are greater than 0.5cm in diameter
Microplastics are smaller than 0.5cm

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.

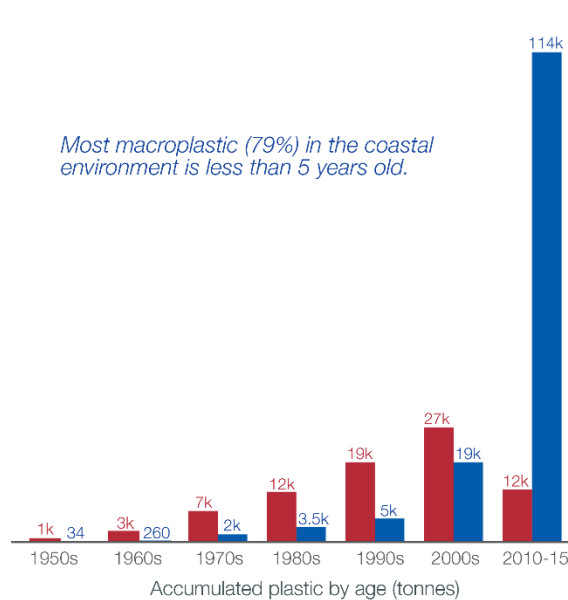
A large part of the 'missing plastic' problem is explained by plastic accumulation, burial and resurfacing along shorelines.



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.



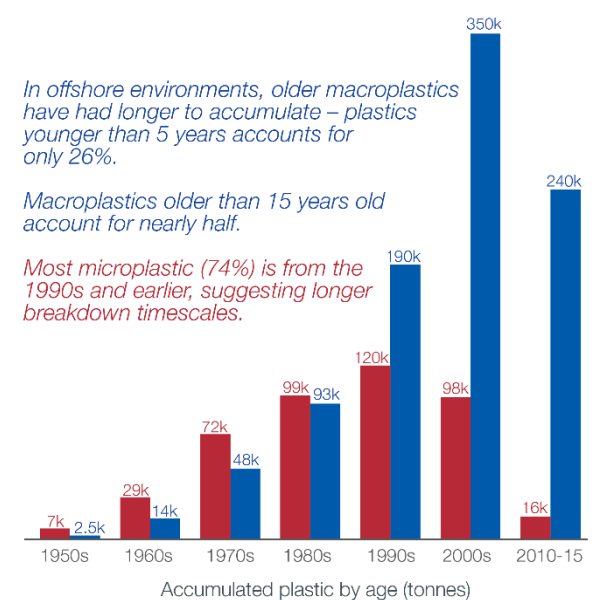
Offshore Deeper waters (>200m)

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.

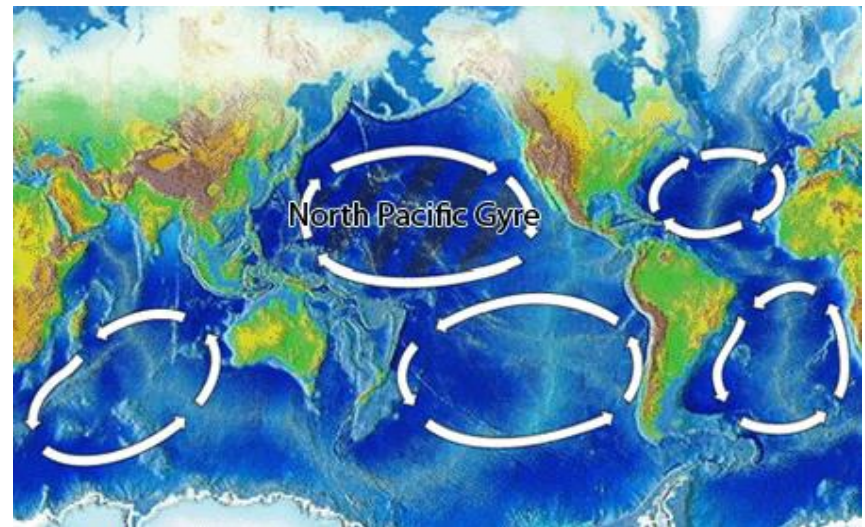
Most microplastic (74%) is from the 1990s and earlier, suggesting longer breakdown timescales.



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

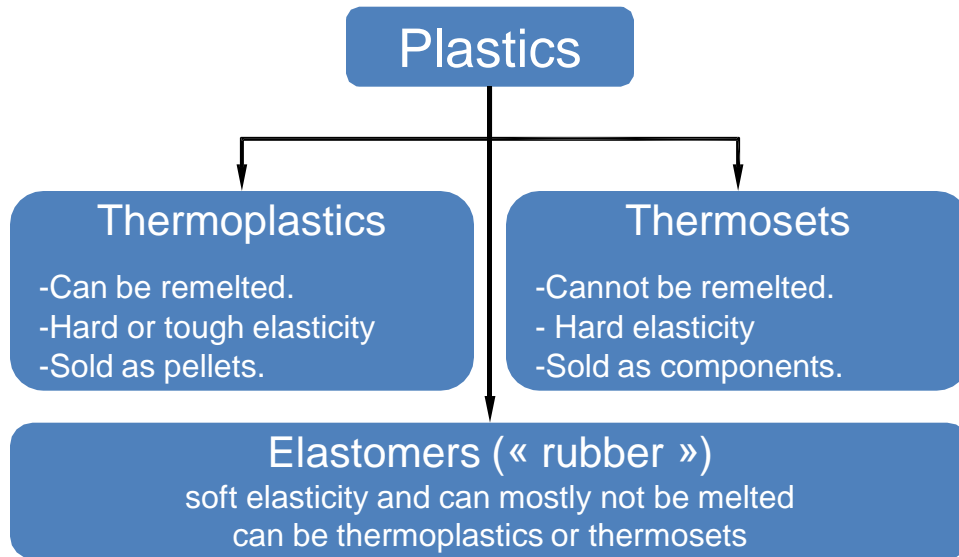
Plastic pollution

- 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

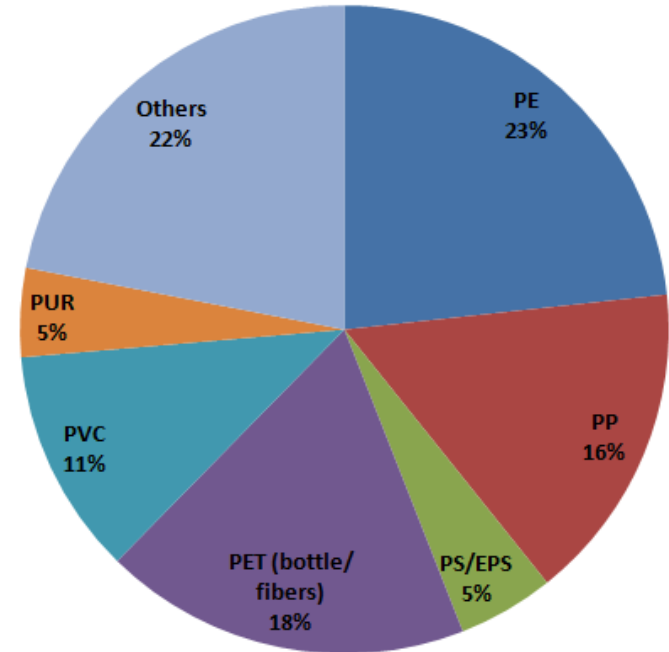


Plastic Pollution Coalition is a global alliance of individuals, organizations and businesses working towards a world free of plastic pollution and its toxic impacts.

PlasticPollutionCoalition



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, ...).

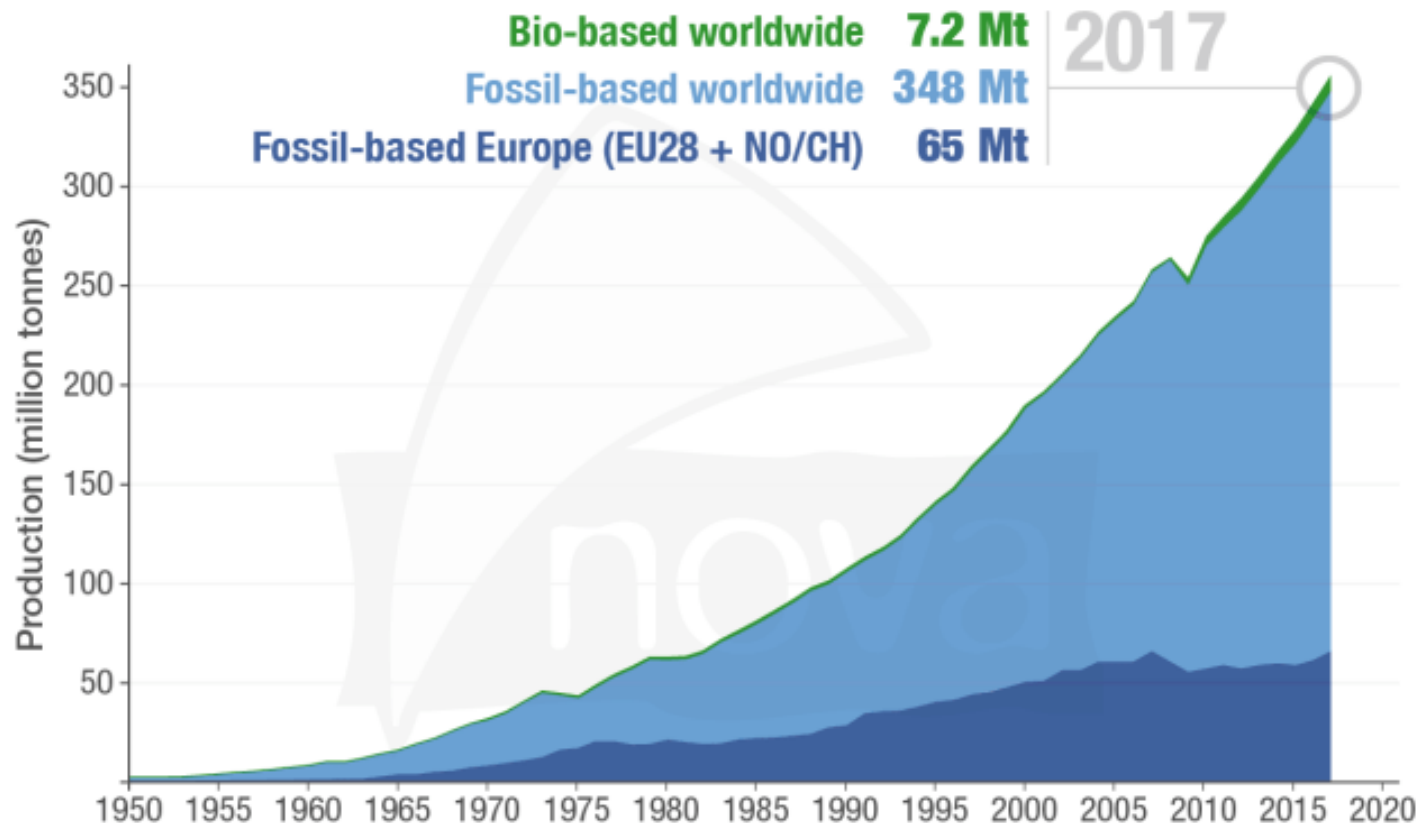
-Thermosets: PUR, UPR, Epoxy, Elastomers.

* 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.

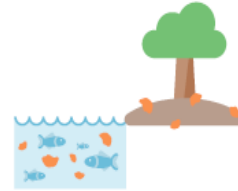
Data sources:
PlasticsEurope, Consultic and nova-Institute

© 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.

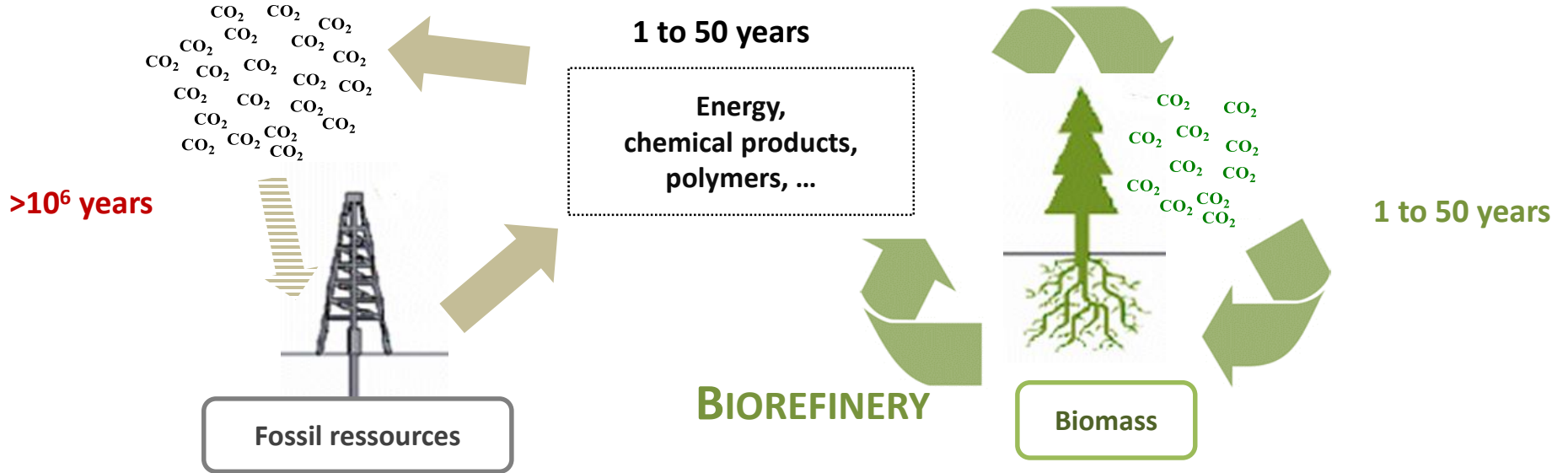
This plant photosynthetic process allows **the binding and storage of atmospheric carbon dioxide (CO₂) in the form of matter in plant tissues.**



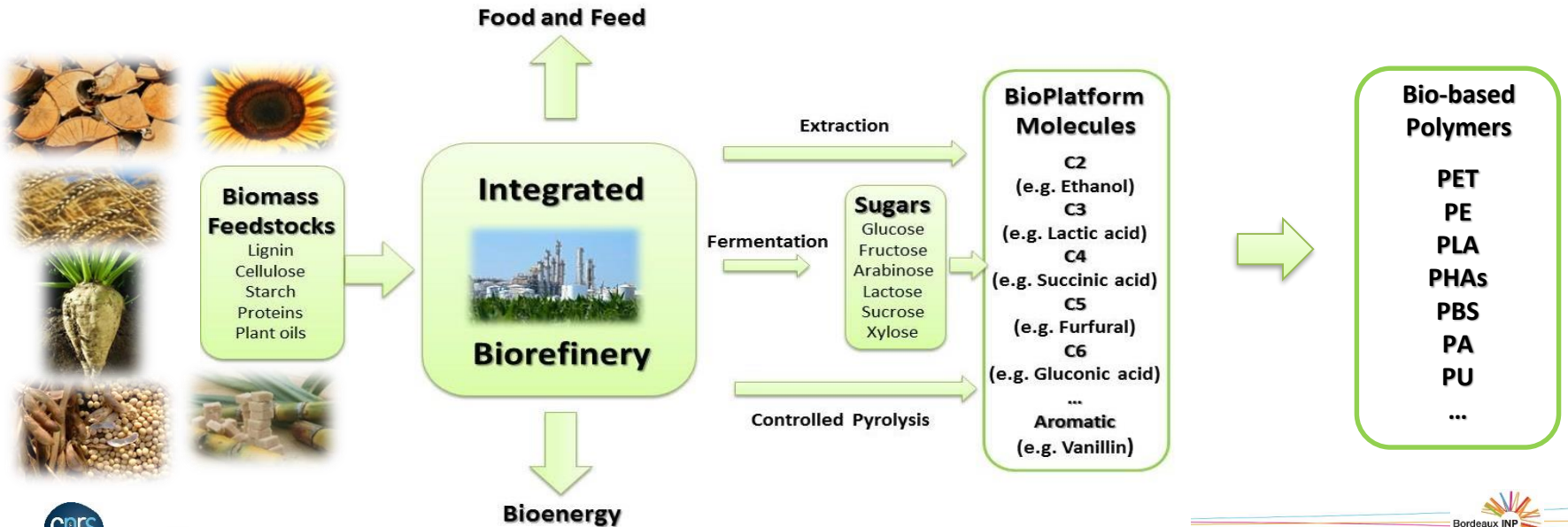
Plants, through this photosynthetic mechanism, thus produce **renewable natural carbon-based molecules.**

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

Ethanol

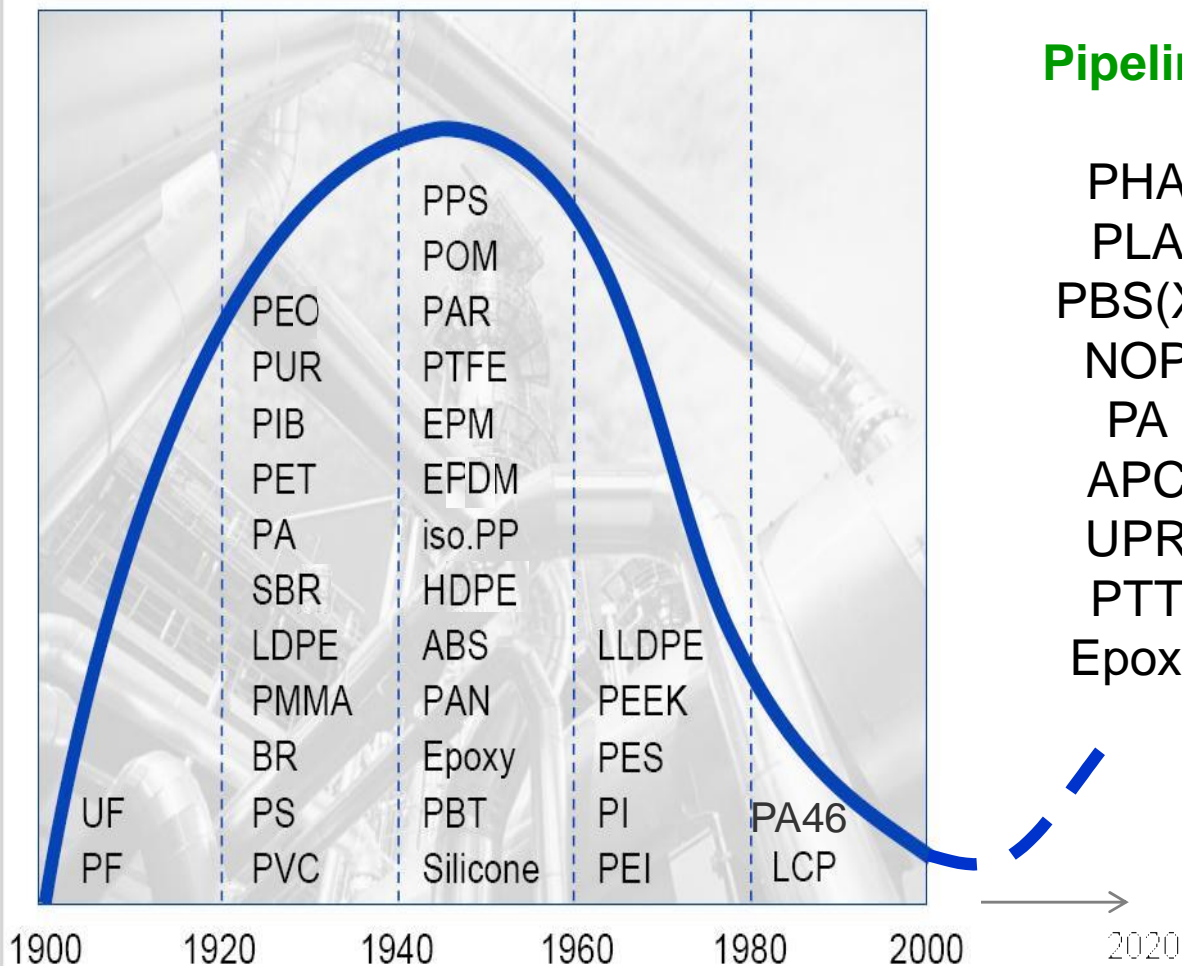
Sugar

Corn



What's new in the Plastic Industry ?

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



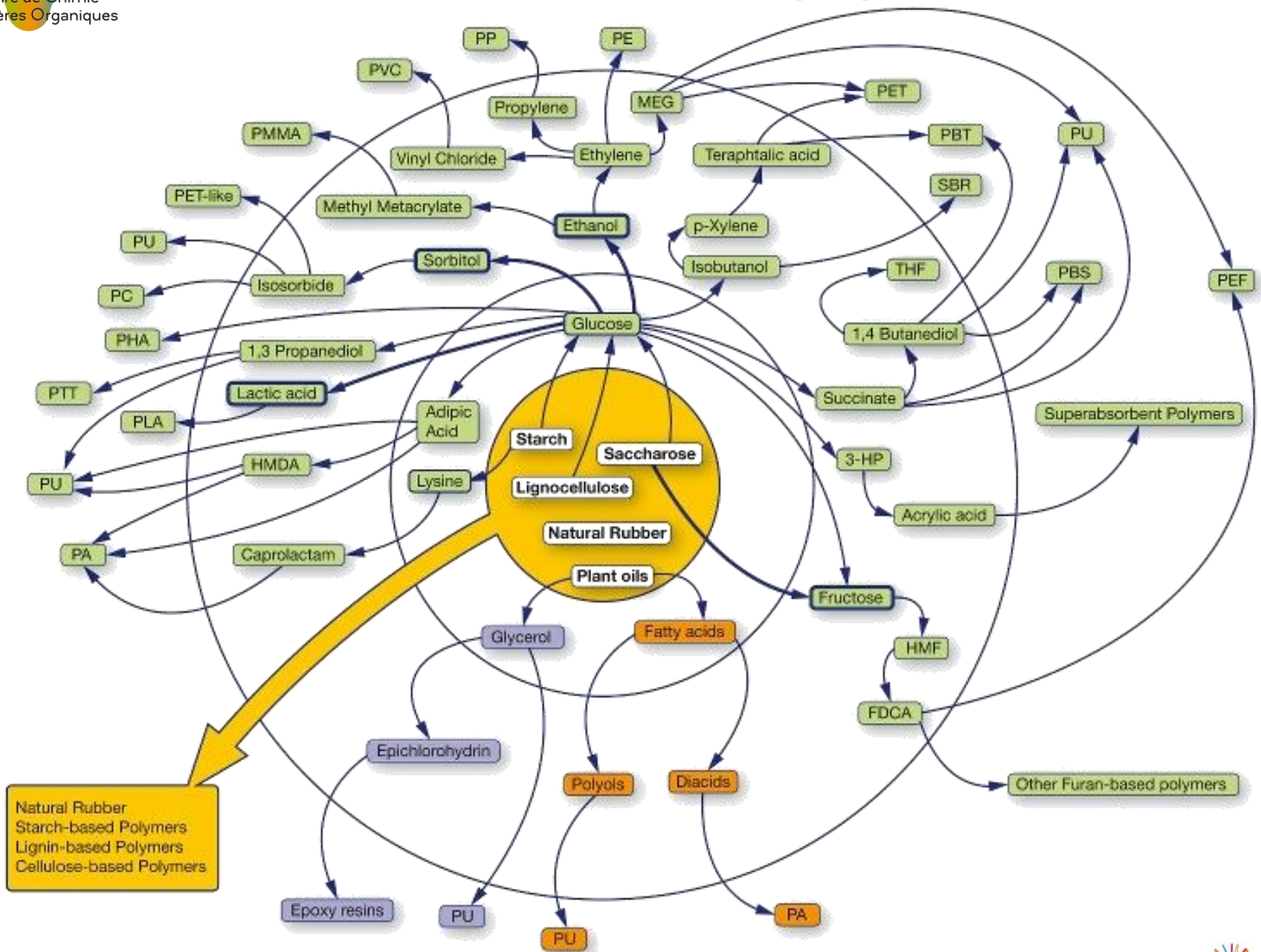
Pipeline

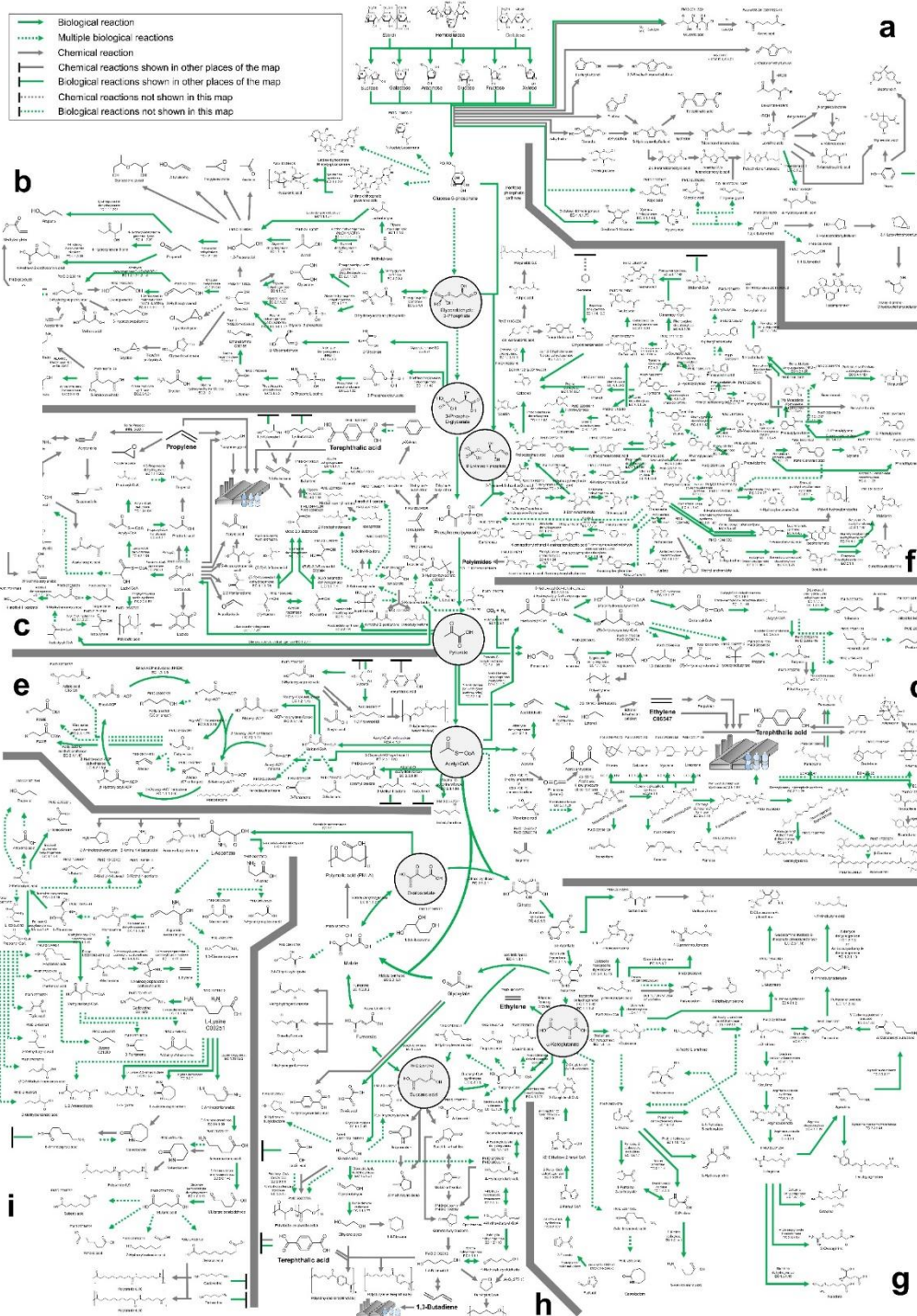
PHA
PLA
PBS(X)
NOP
PA
APC
UPR
PTT
Epoxy

- Propanediol
- Succinic Acid
- Lactic Acid
- Vegetable oils
- Hydroxy Alkanoates
- Isosorbide
- other

.....or Design novel polymers ?

From biomass to polymers





SUPPLEMENTARY INFORMATION

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

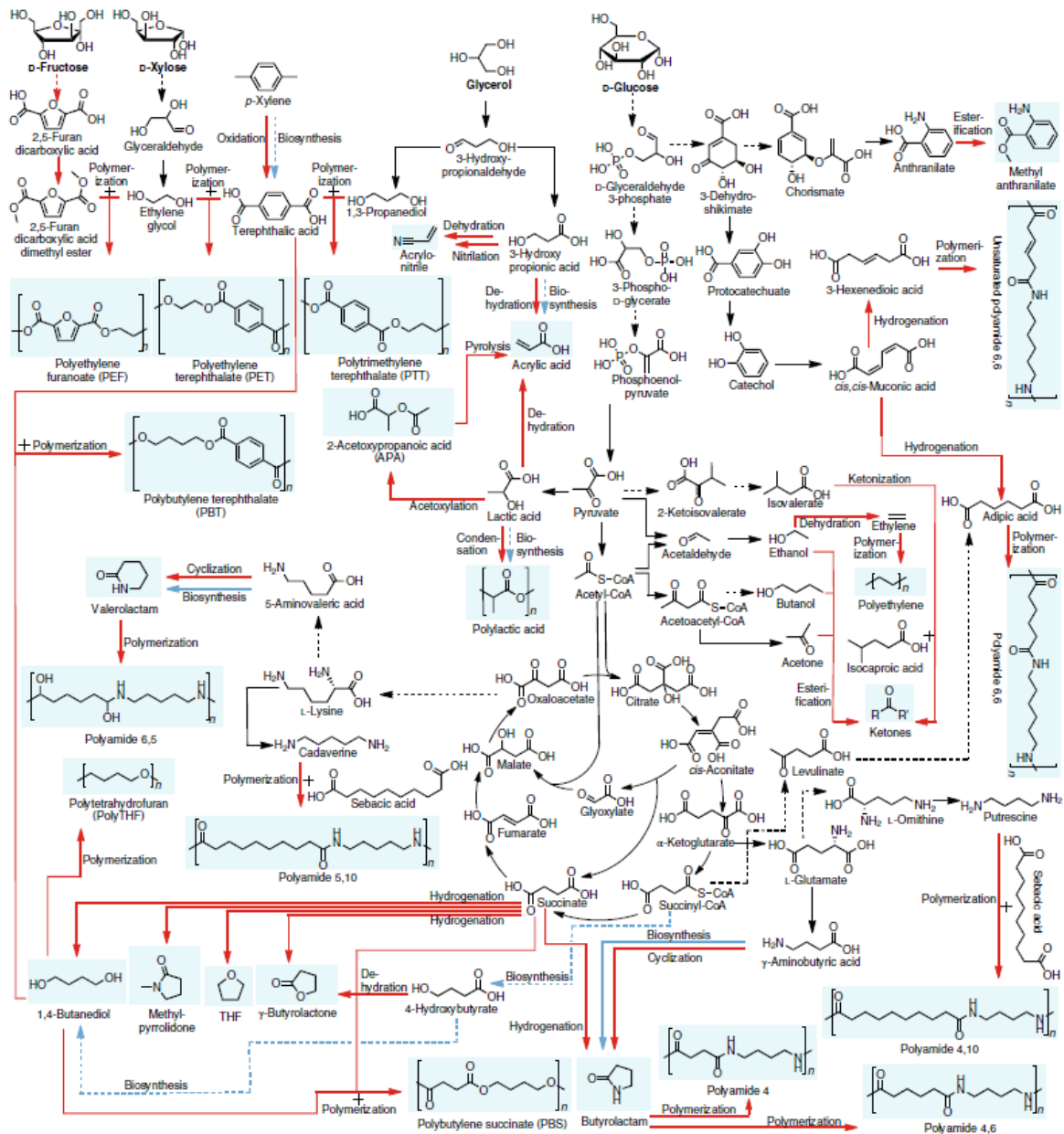
nature
catalysis

In the format provided by the authors and unedited.

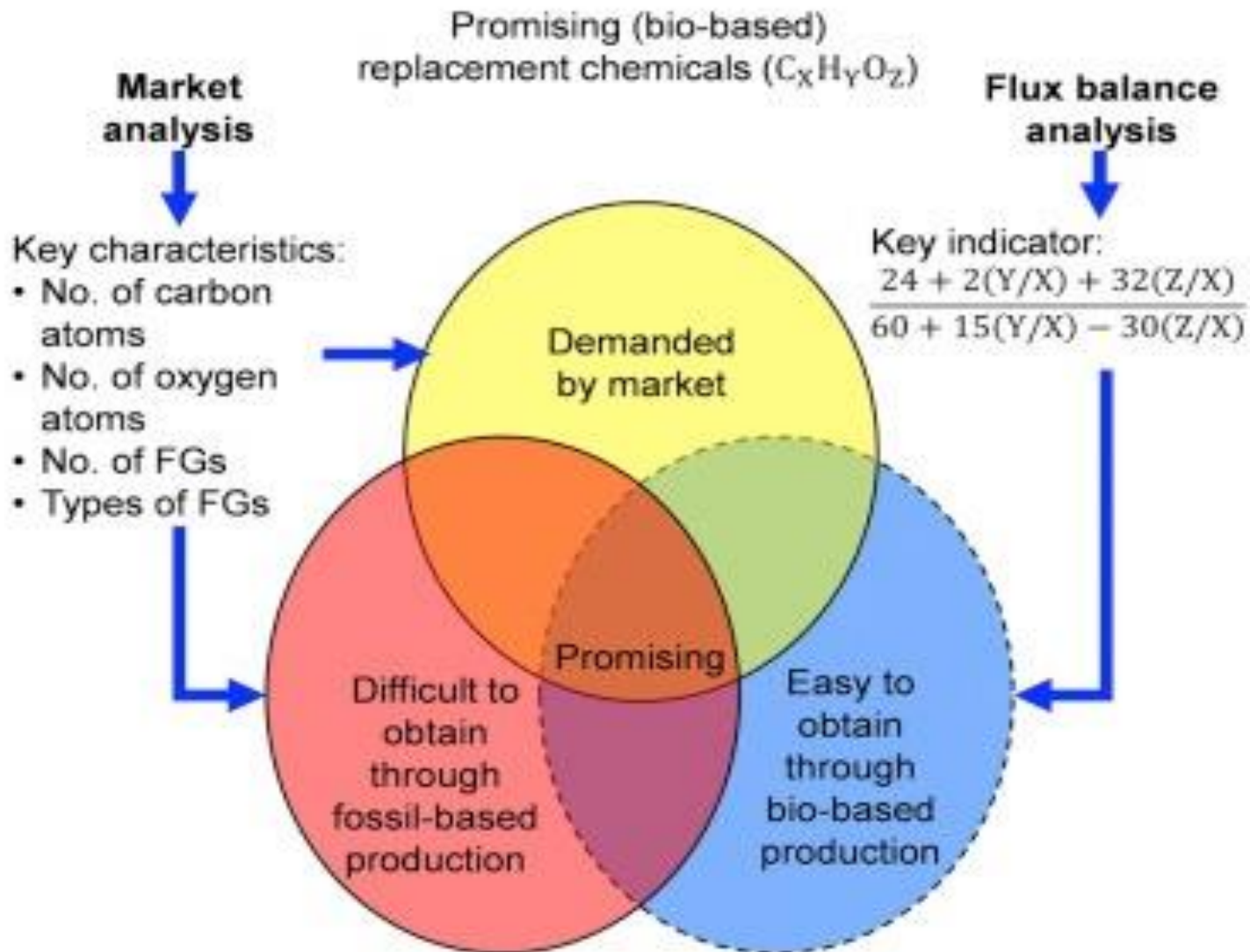
A comprehensive metabolic map for production of bio-based chemicals

Sang Yup 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}

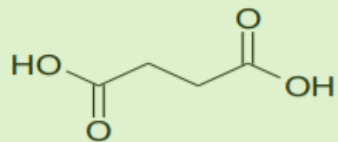
Example of the glucose platform



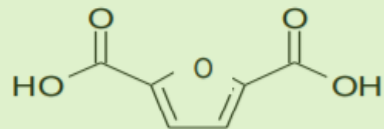
Promising bio-based chemicals



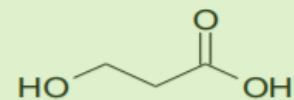
*FG: functional group



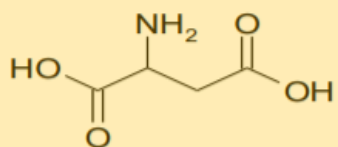
Succinic acid



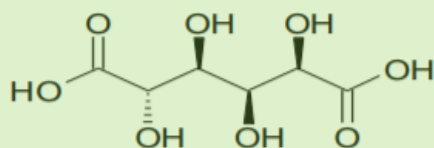
2,5-Furandicarboxylic acid



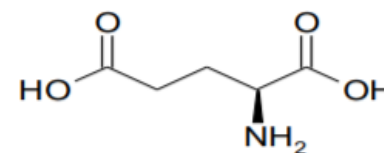
3-Hydroxypropionic acid



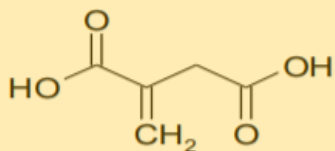
Aspartic acid



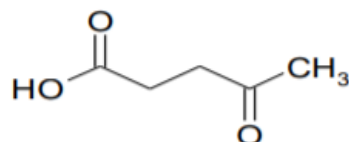
Glucaric acid



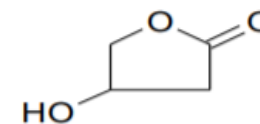
Glutamic acid



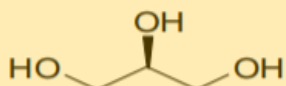
Itaconic acid



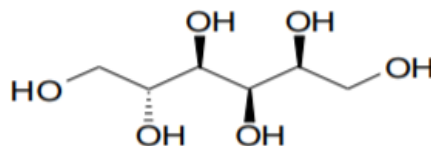
Levulinic acid



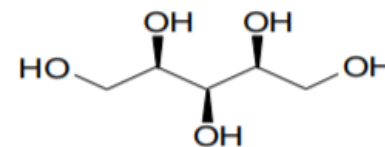
3-Hydroxybutyrolactone



Glycerol



Sorbitol

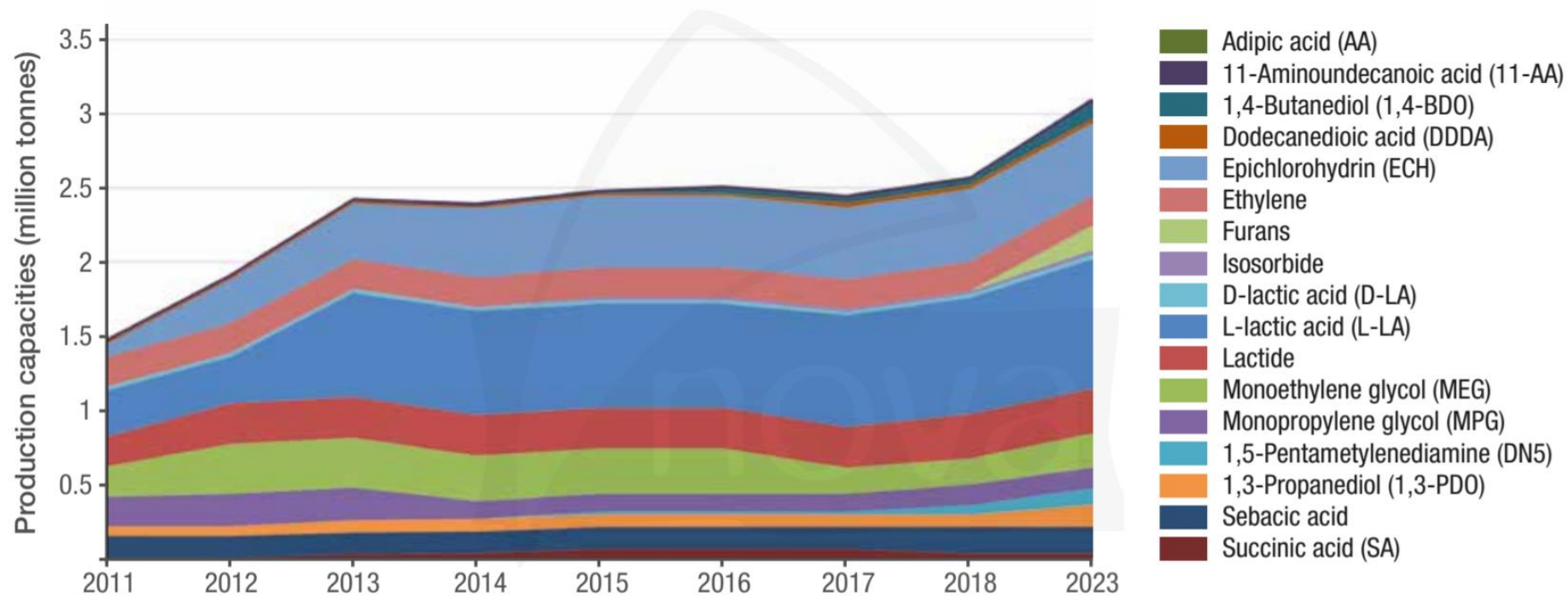


Xylitol

Most promising bio-based building blocks: DOE 2016

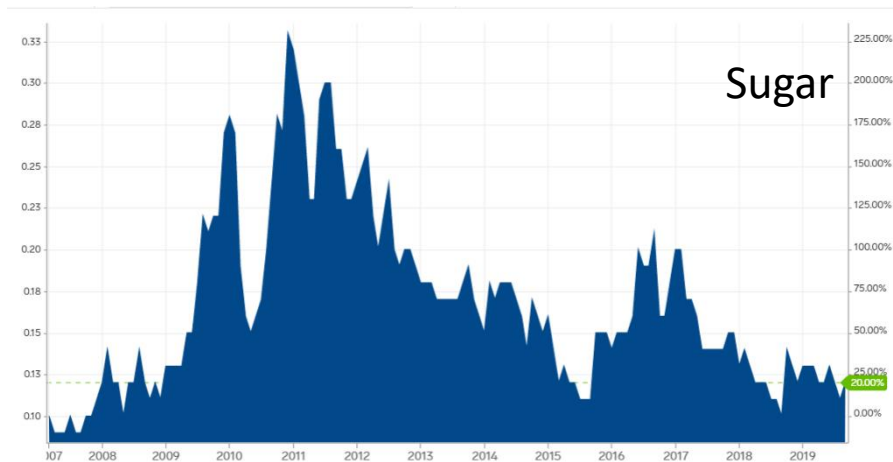
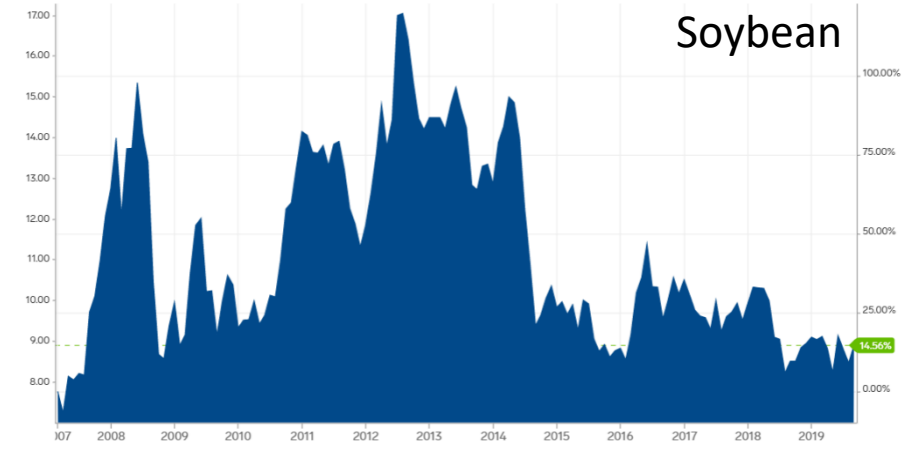
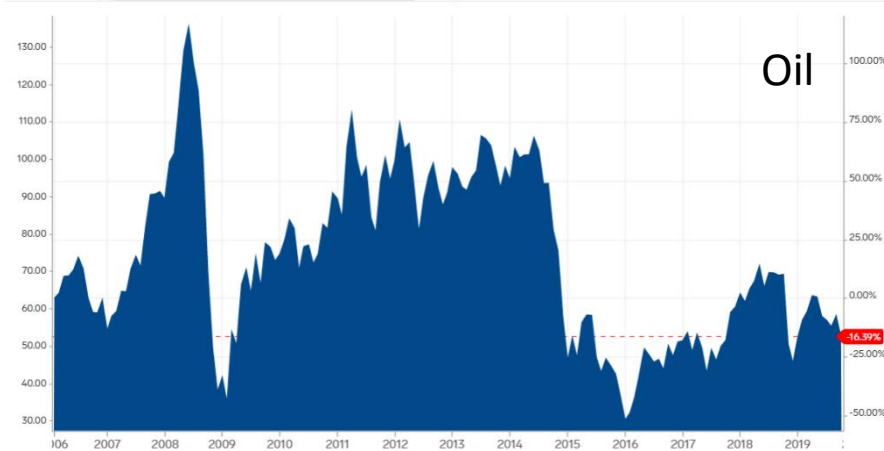
Chemical	Type	Conversion Pathway	TRL Level based on commodity feedstocks	R&D on-going for lignocellulosic feedstocks
Butadiene (1,3-)	Drop-in	BC – Biological TC/BC – Gasification/Fermentation	6	Y
Butanediol (1,4-)	Drop-in	BC – Biological	8	Y
Ethyl Lactate	Functional	BC– Biological	9	Y
Fatty Alcohols	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

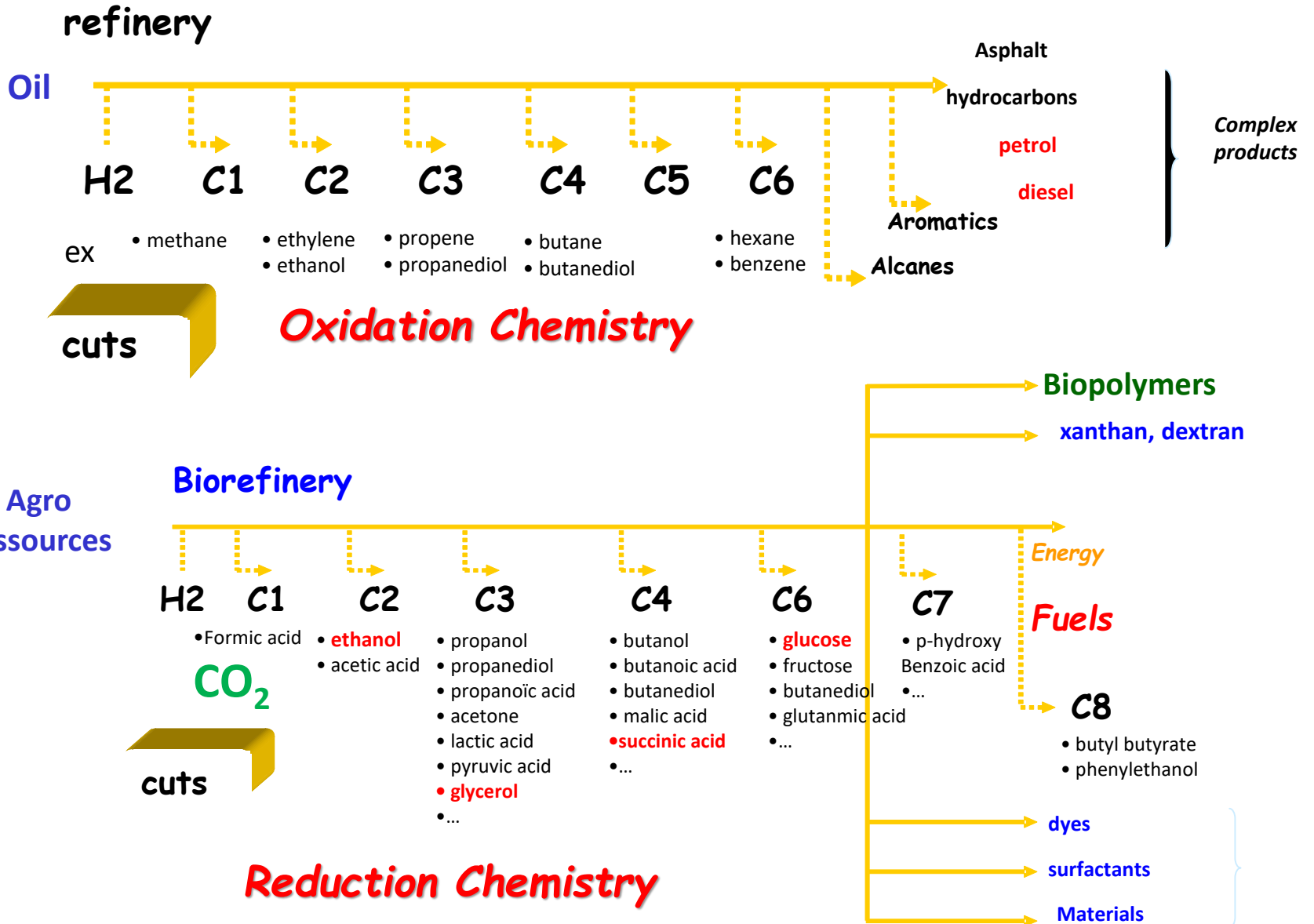


Ressources prize volatility

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



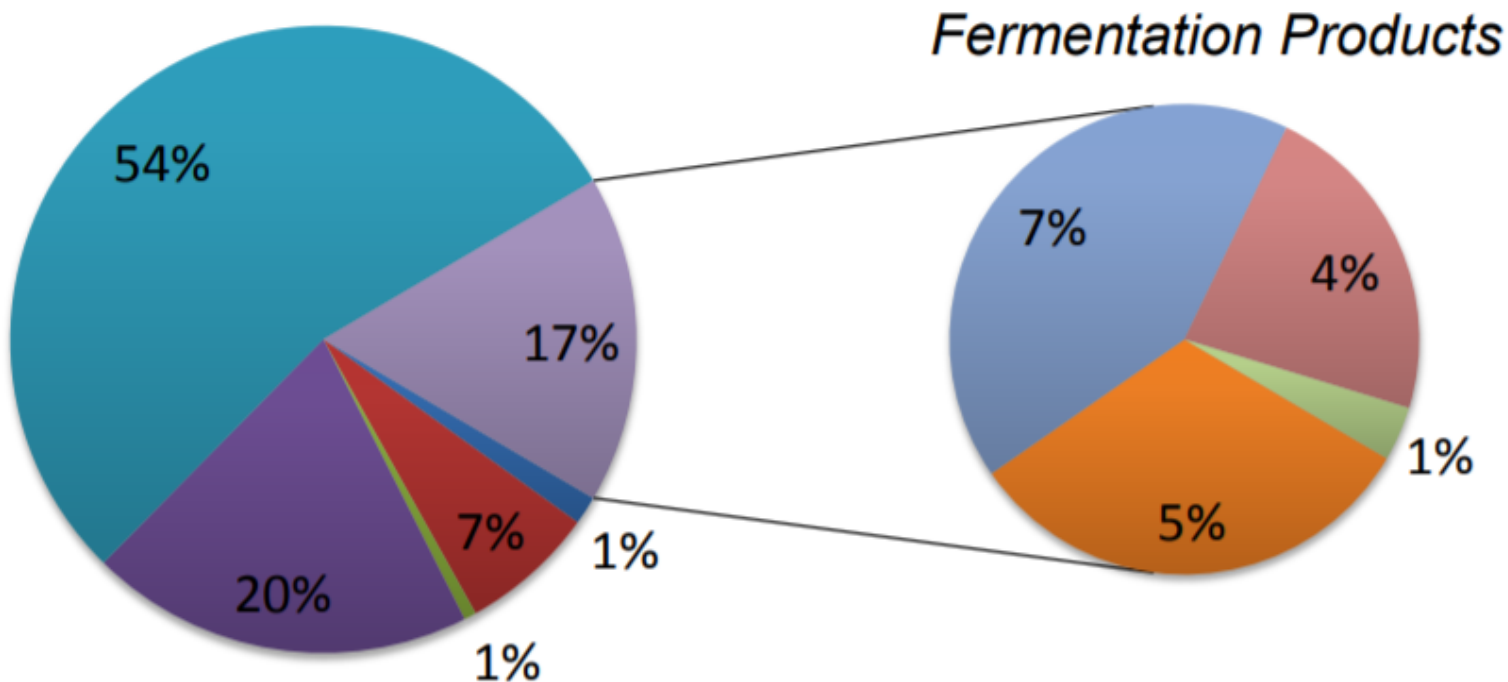
Refinery to Biorefinery



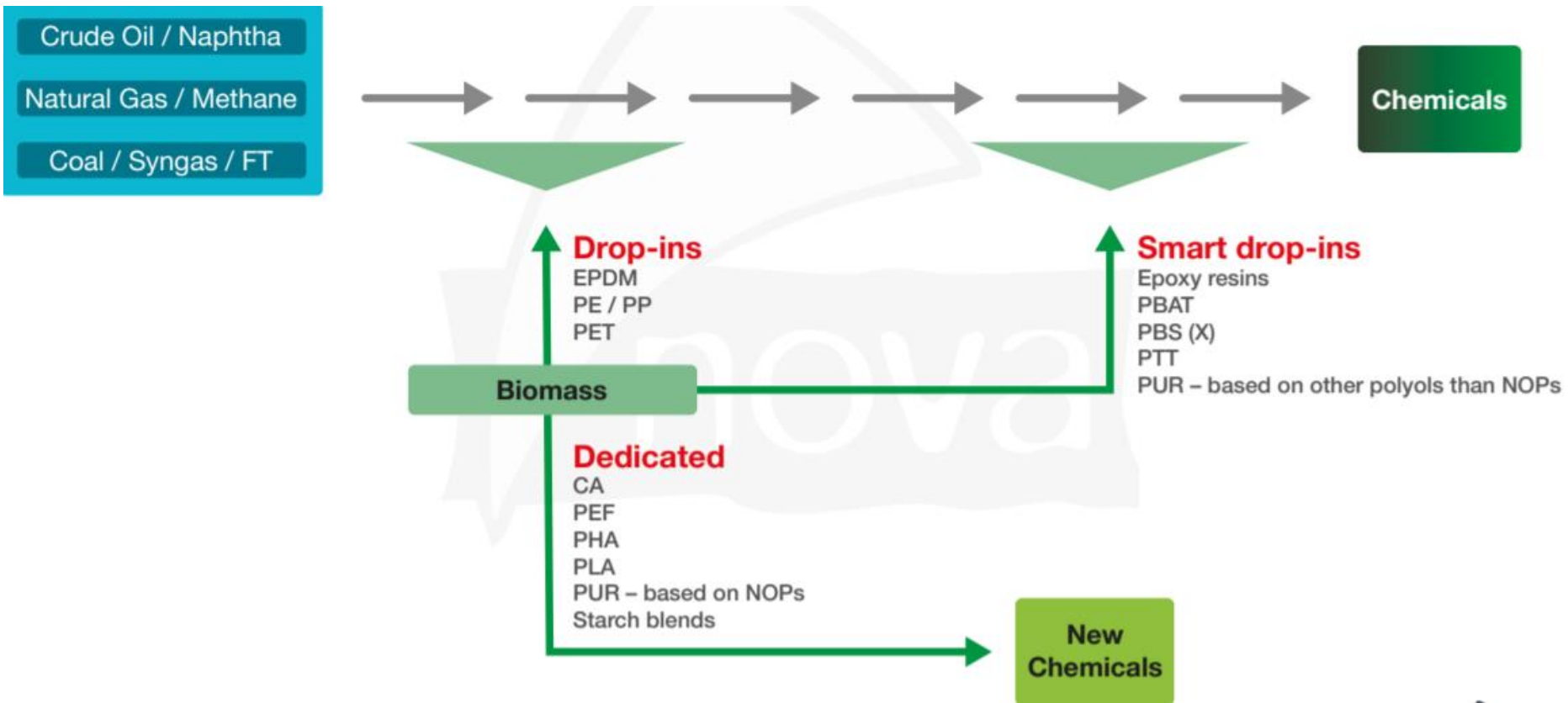
Bio-sourced chemicals and polymers

Market size ~ 50 million tones

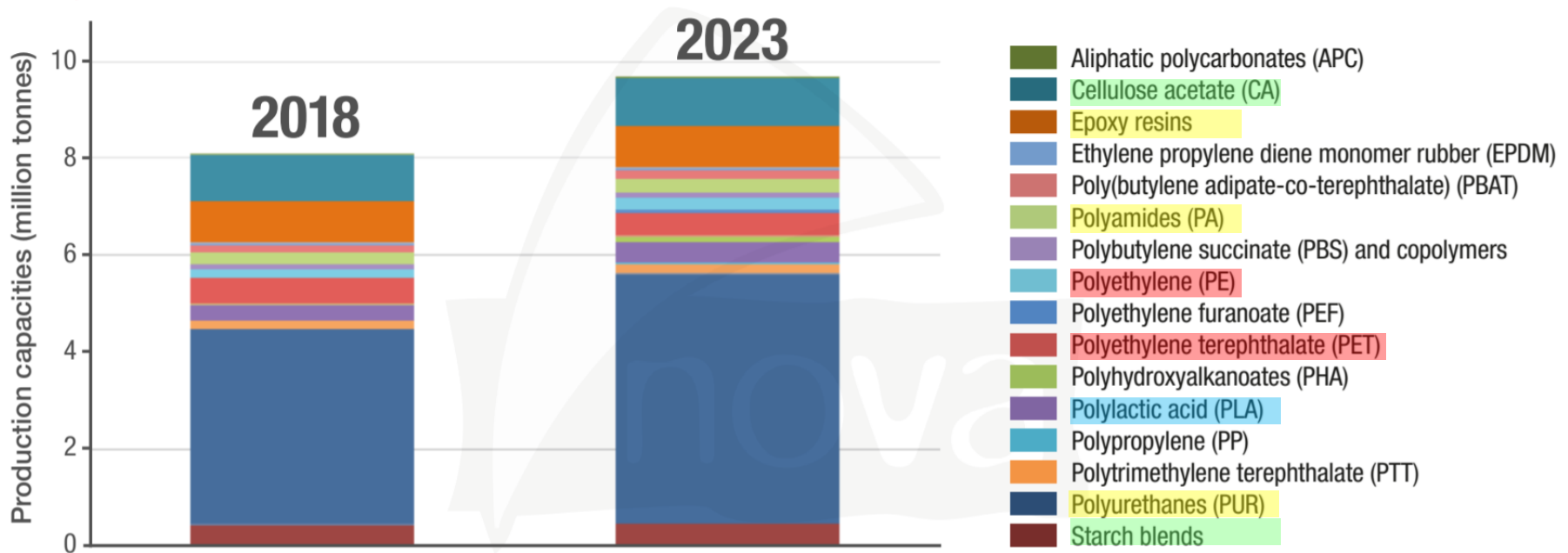
- Chemical Derivatives
- Naval Stores
- Natural Products
- Oleochemicals
- Biopolymers
- Amino Acids
- Alcohols
- Aliphatic acids
- Other



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



Worldwide production of bio-based polymers

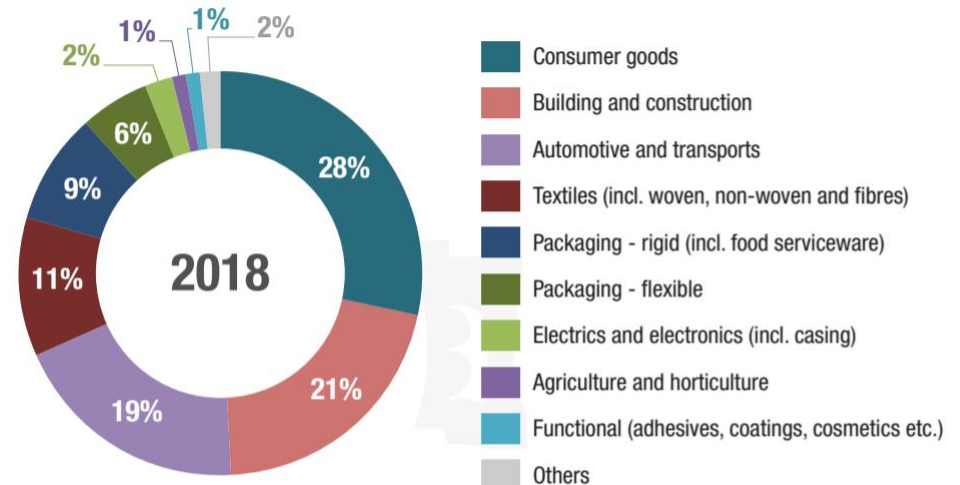
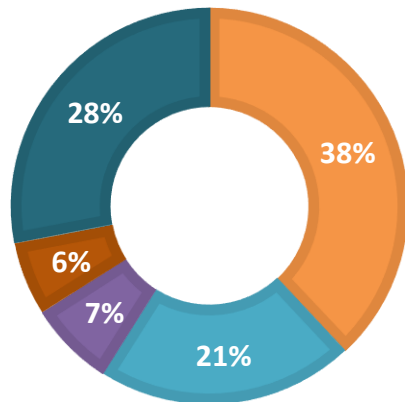


Polymer applications

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

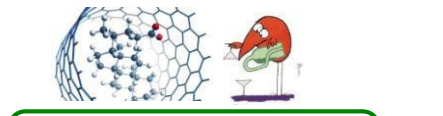
-(perceived) Raw material supply constraint drive development of bio-based ela



Cost-driven

- Biobased sil-

- 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,...

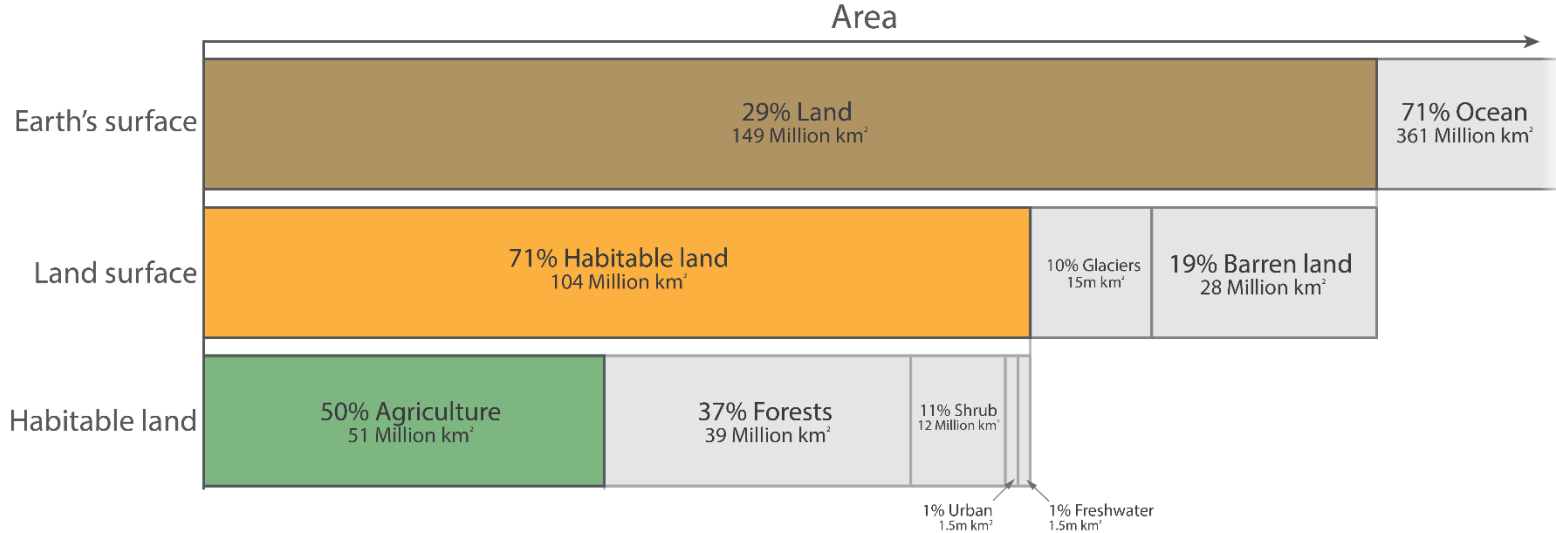


Legislation-driven

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?

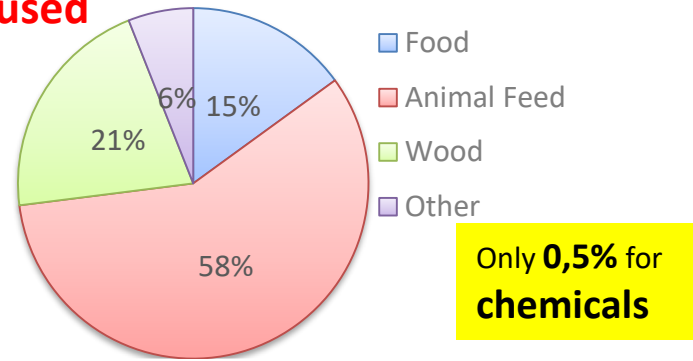
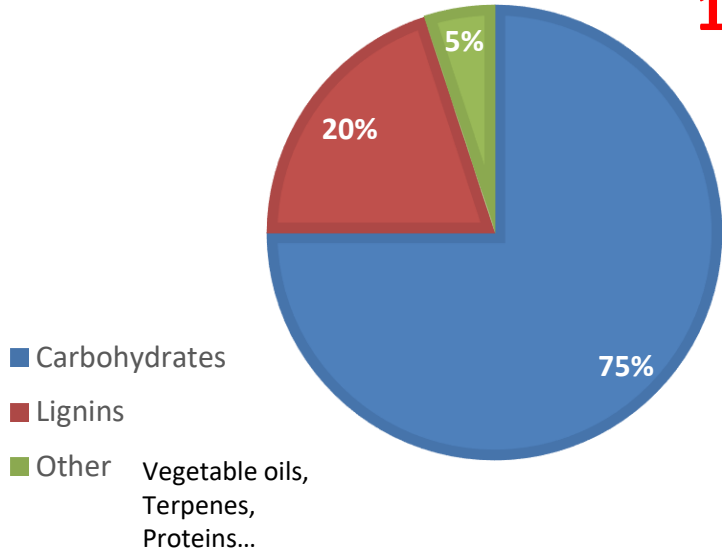
For a success story all 5 drivers are needed

Worldwide land use



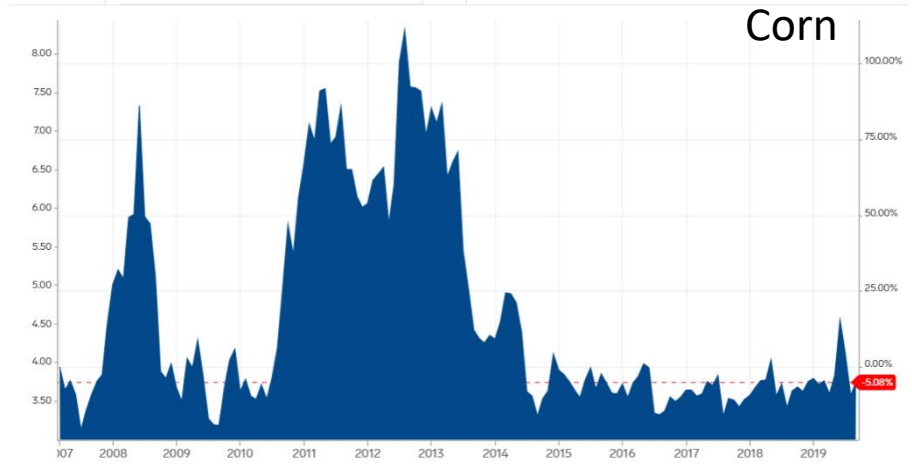
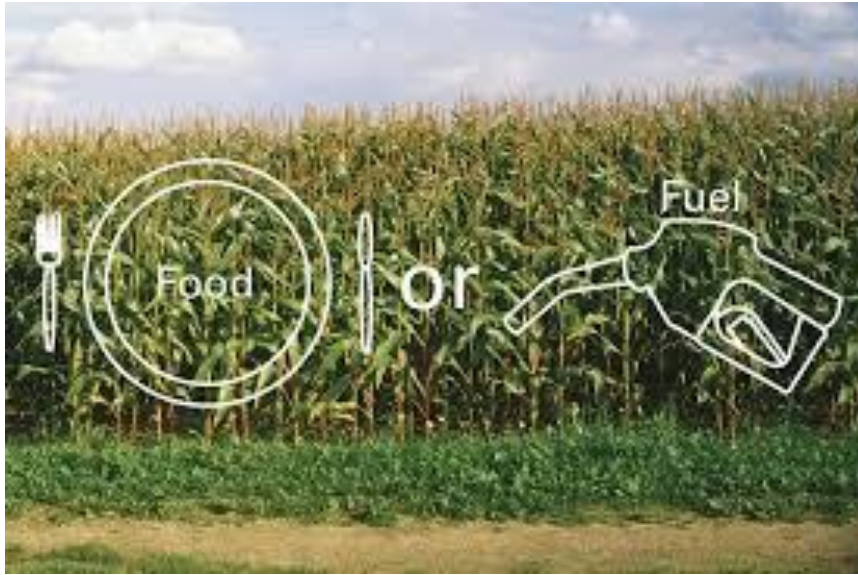
Biomass production ≈ 120 billions tons/year (210 with algae) vs. 350 millions tons/y of polymers

10% of the biomass is used



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

Food vs Fuel



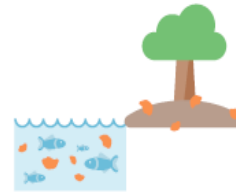
No impact on the price

- *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

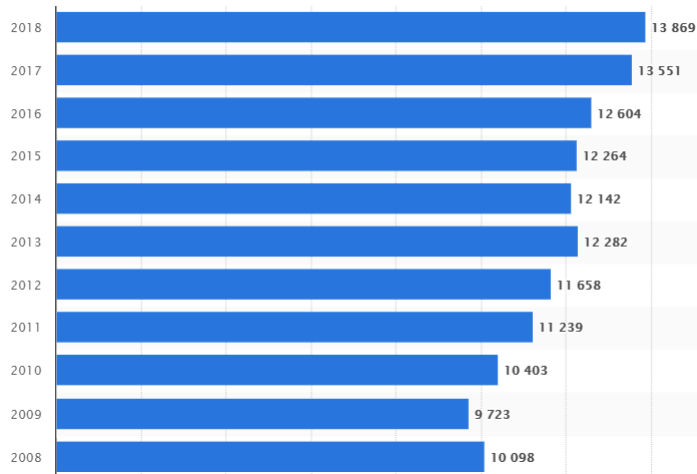
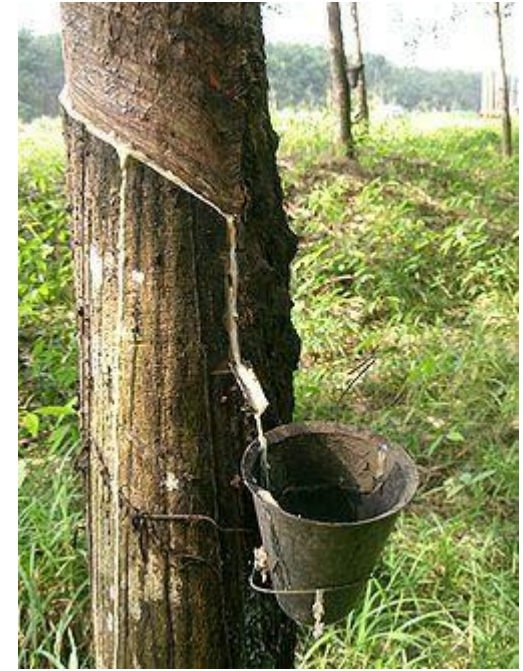
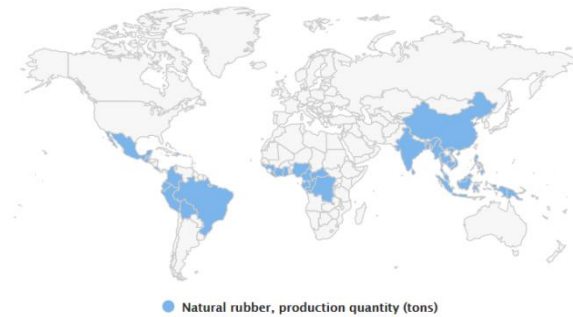
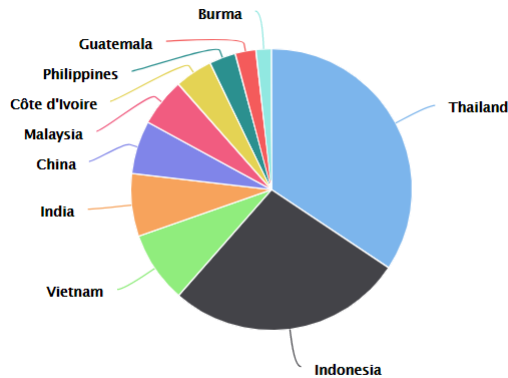
5- Smart drop-ins: Bio-based derivative of “fossil” polymers

6- New polymers from biomass

7- Conclusions and perspectives

Natural rubber from latex

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



Production increase is too slow for the worldwide demands

→ Other sources

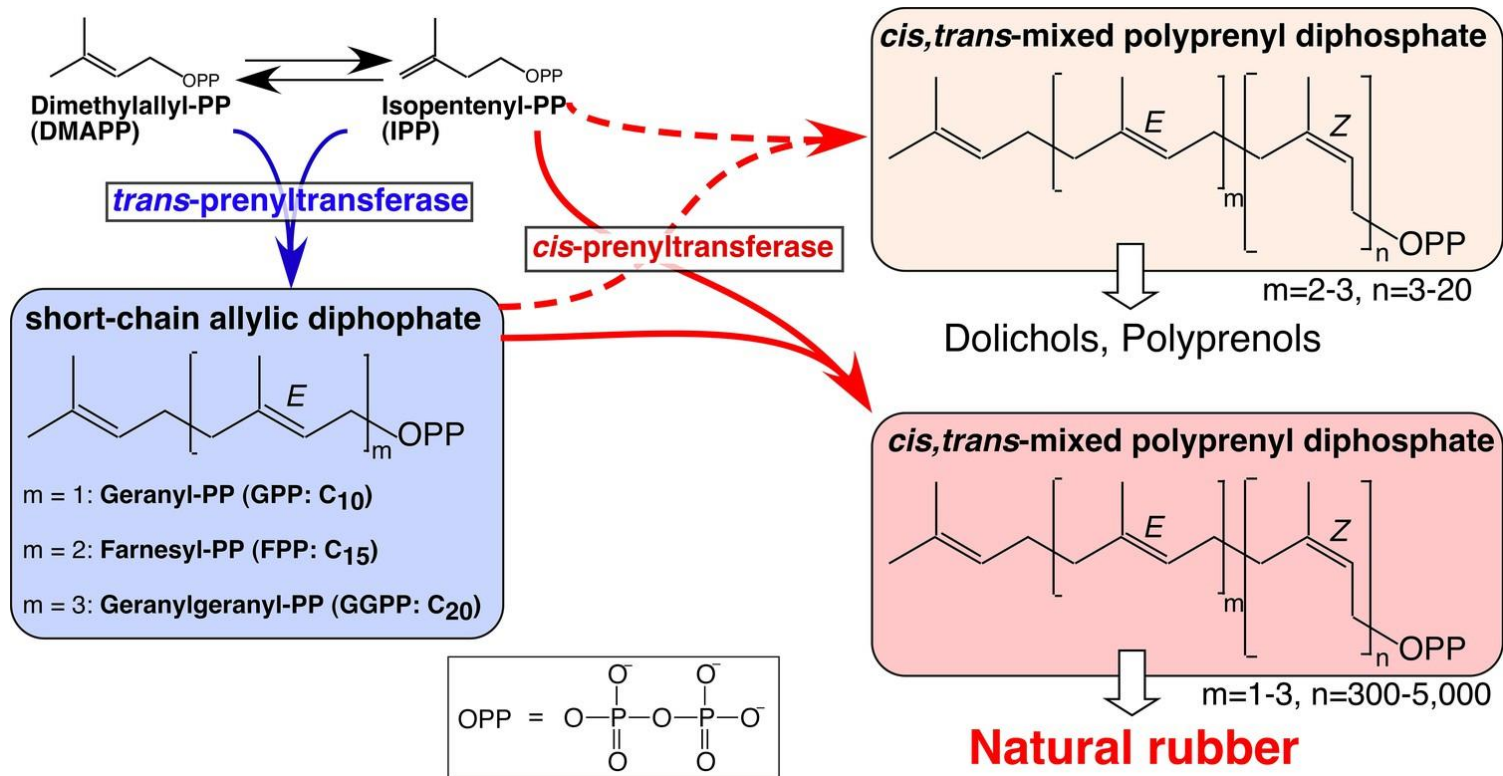
Synthetic polyisoprene: 15.6 Mt (2018)



shutterstock.com • 436160047

Natural rubber from latex

Biosynthesis pathway of natural rubber



Impossible to obtain by regular polymerization processes
 → Enzymatic pathway

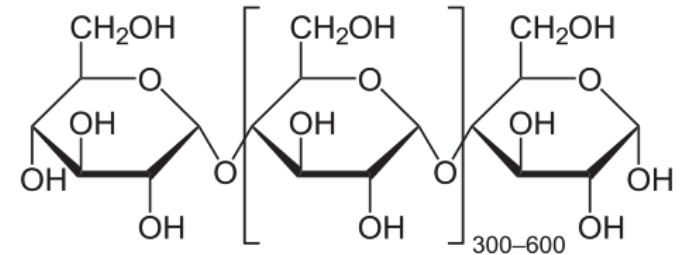
Starch based polymers

Starch blend with different polymers

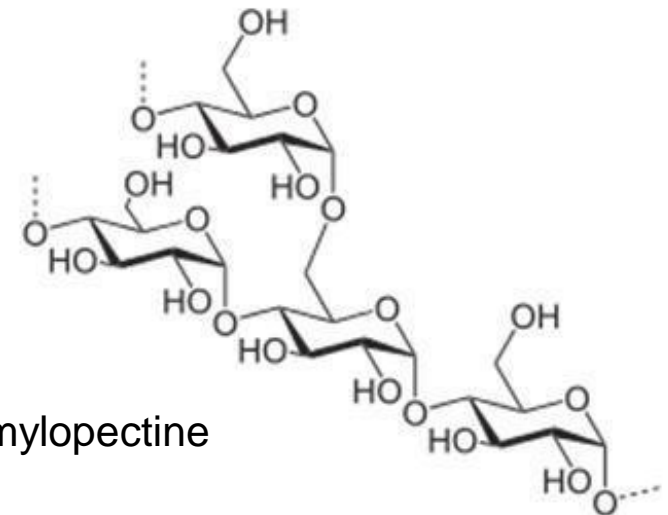
400 Kt (1Mt for the blend)

- 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

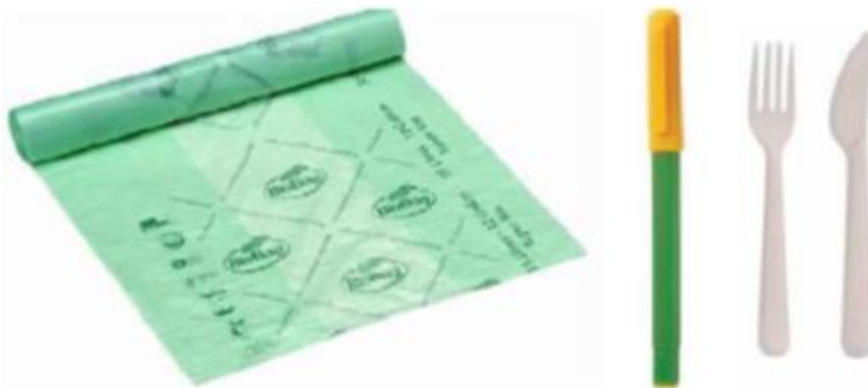
Bio-based Carbon content : 25 to 100 %



Amylose

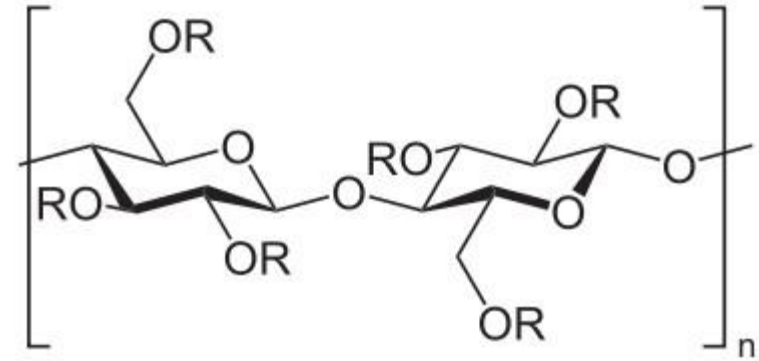
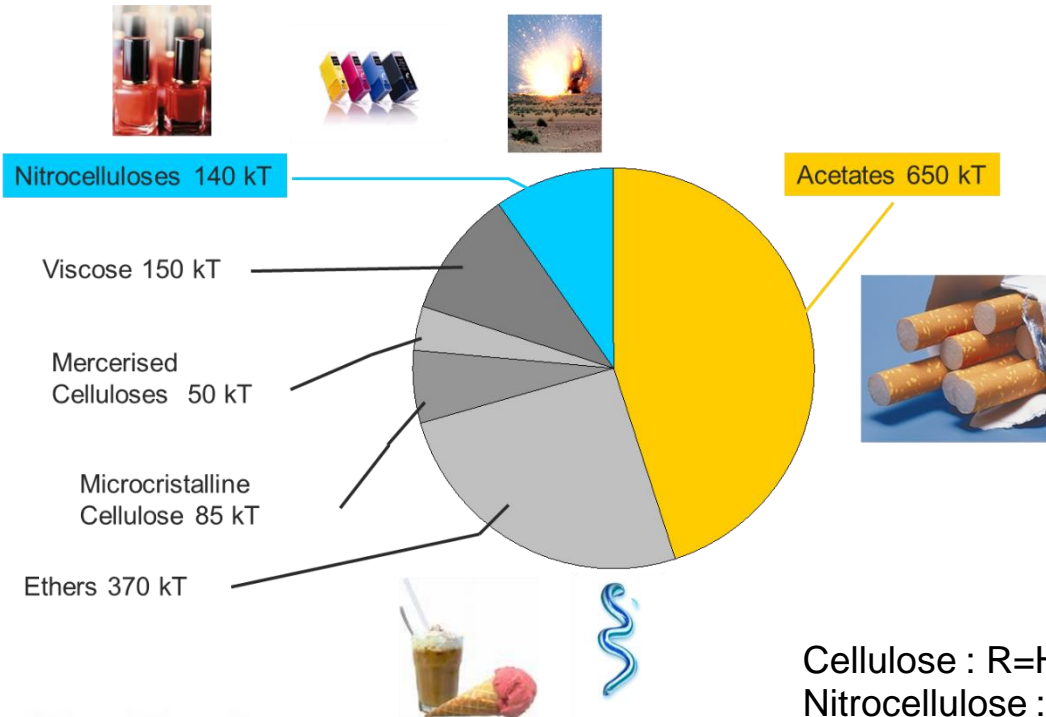


Amylopectine



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;

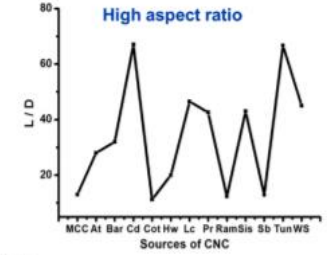
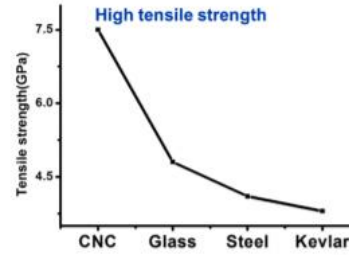
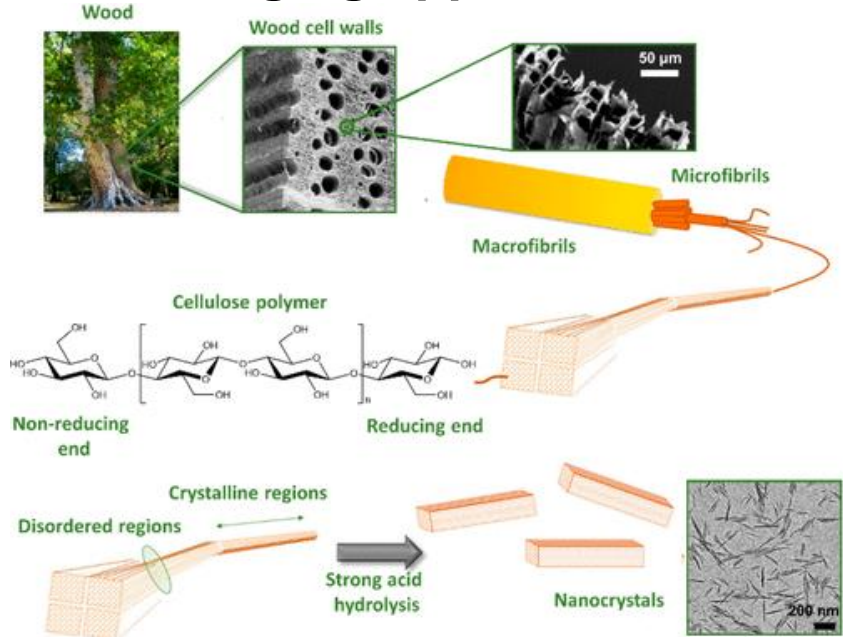
CH₂COOH



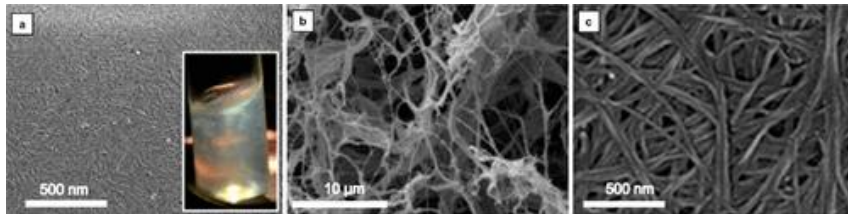
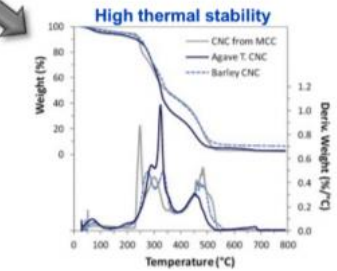
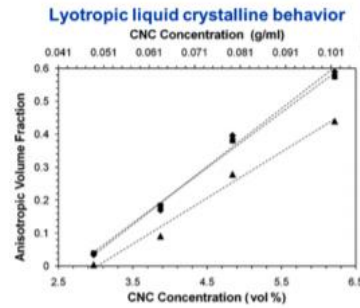
Not a thermoplastic

Cellulose-based polymers

Emerging application



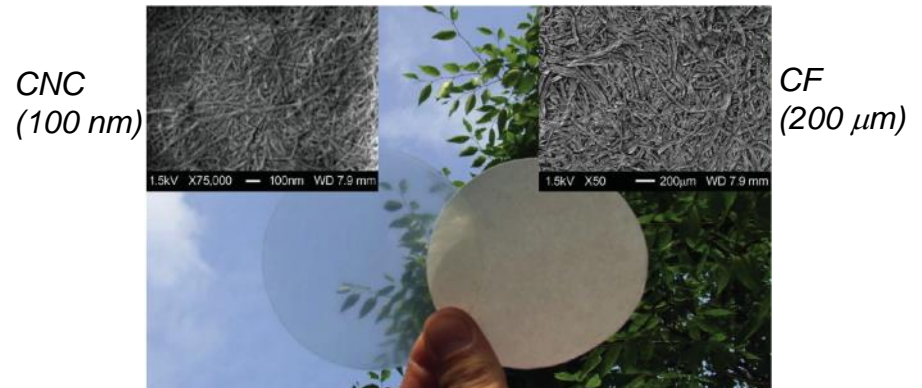
Cellulose nanocrystals



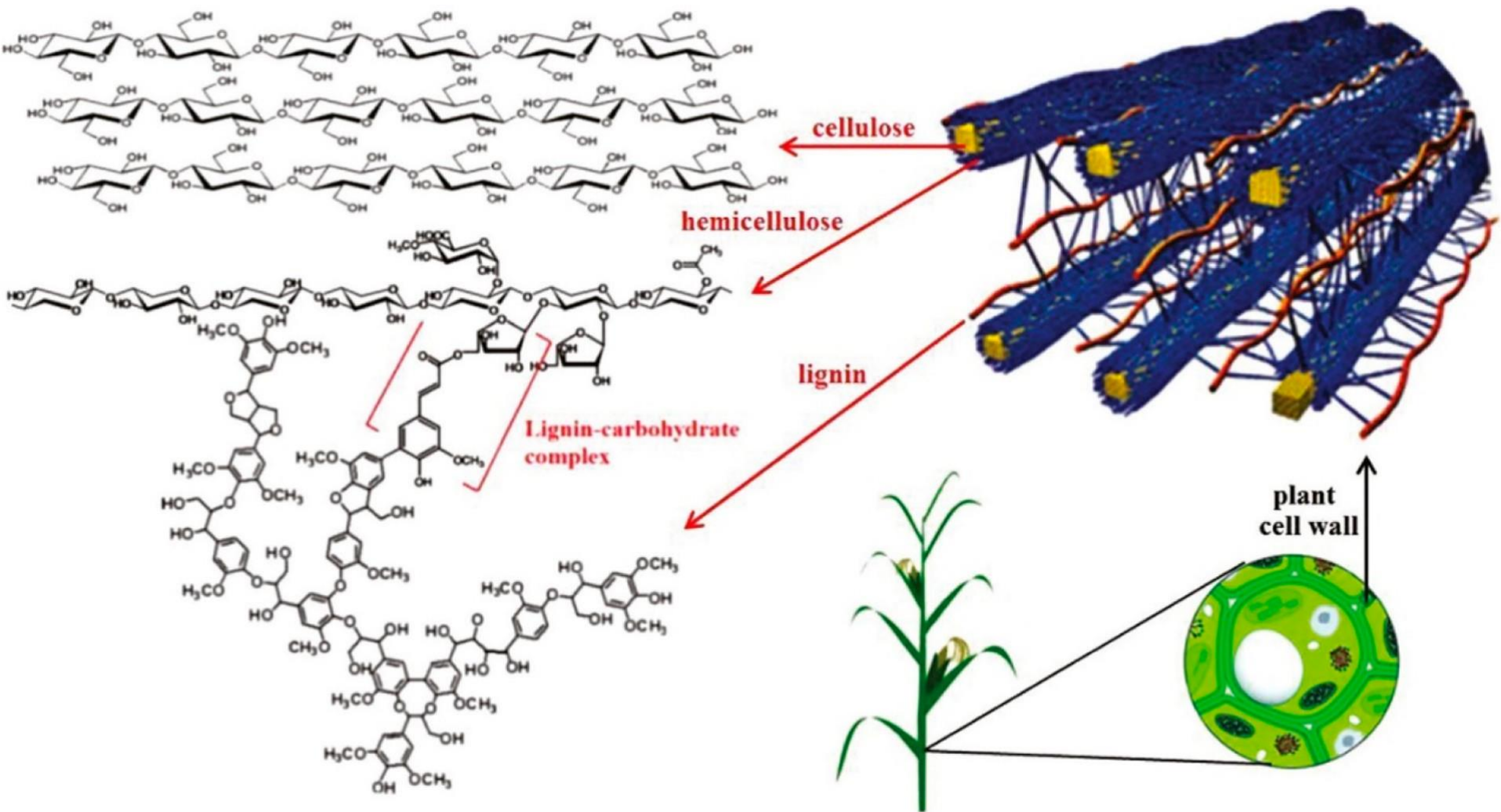
CNC

CNF

BC



Other polymers

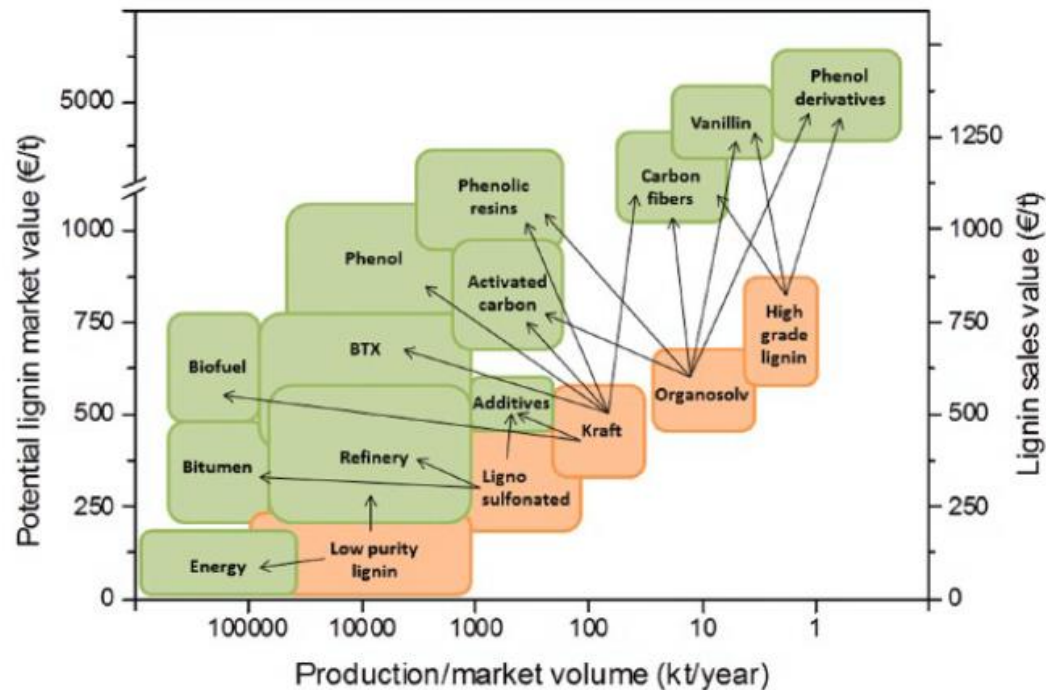
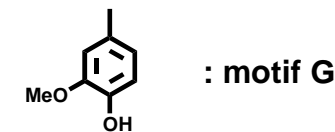
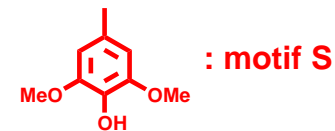
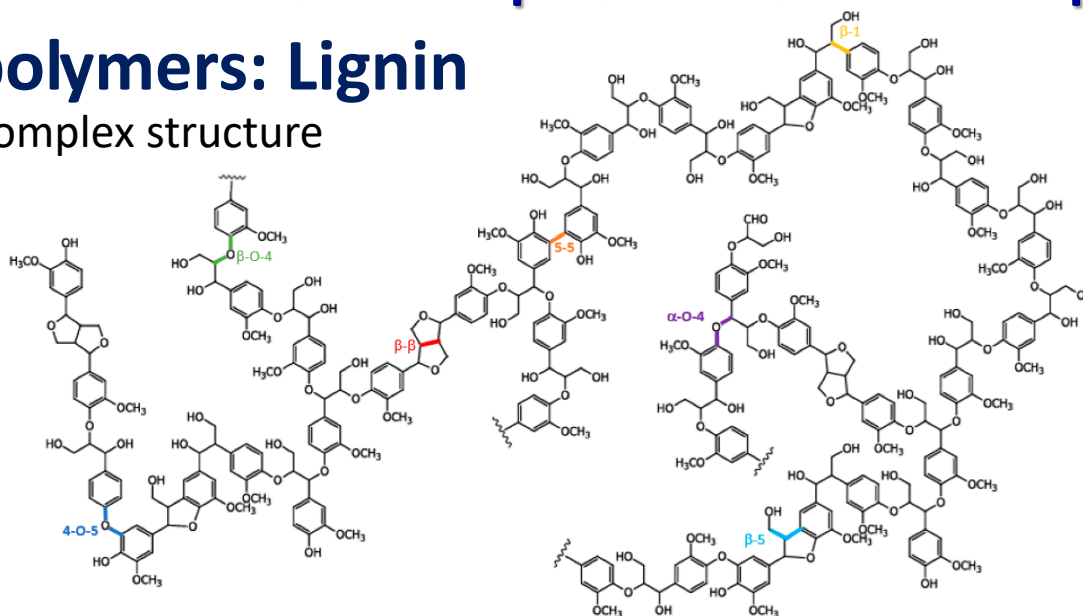


Bio-based plastics from natural polymers

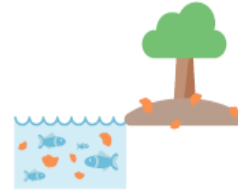
Other polymers: Lignin

Extremely complex structure

500 kt



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

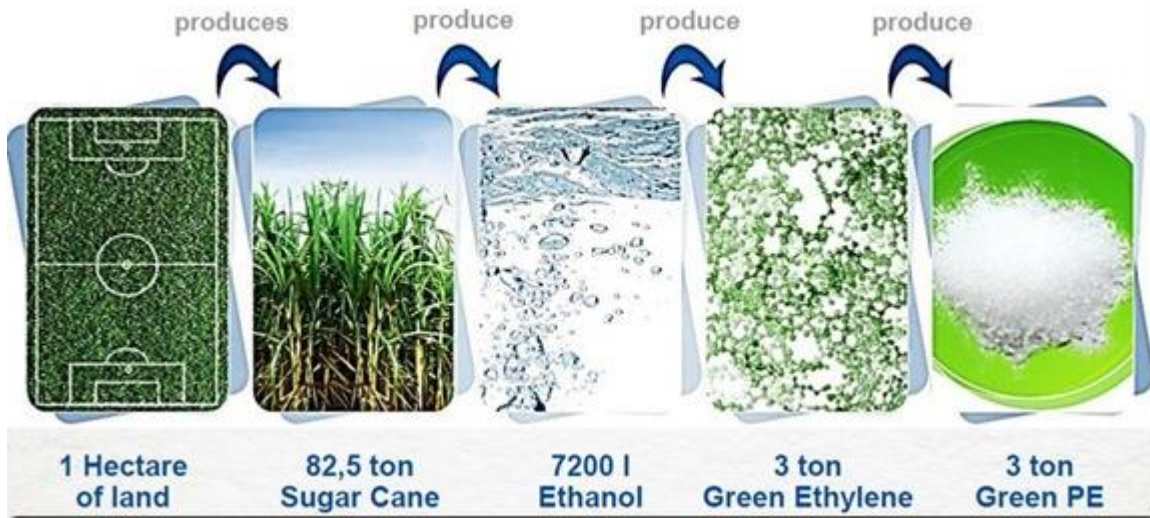
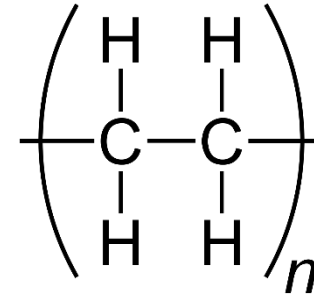
6- New polymers from biomass

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

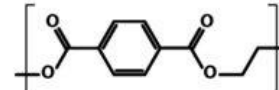
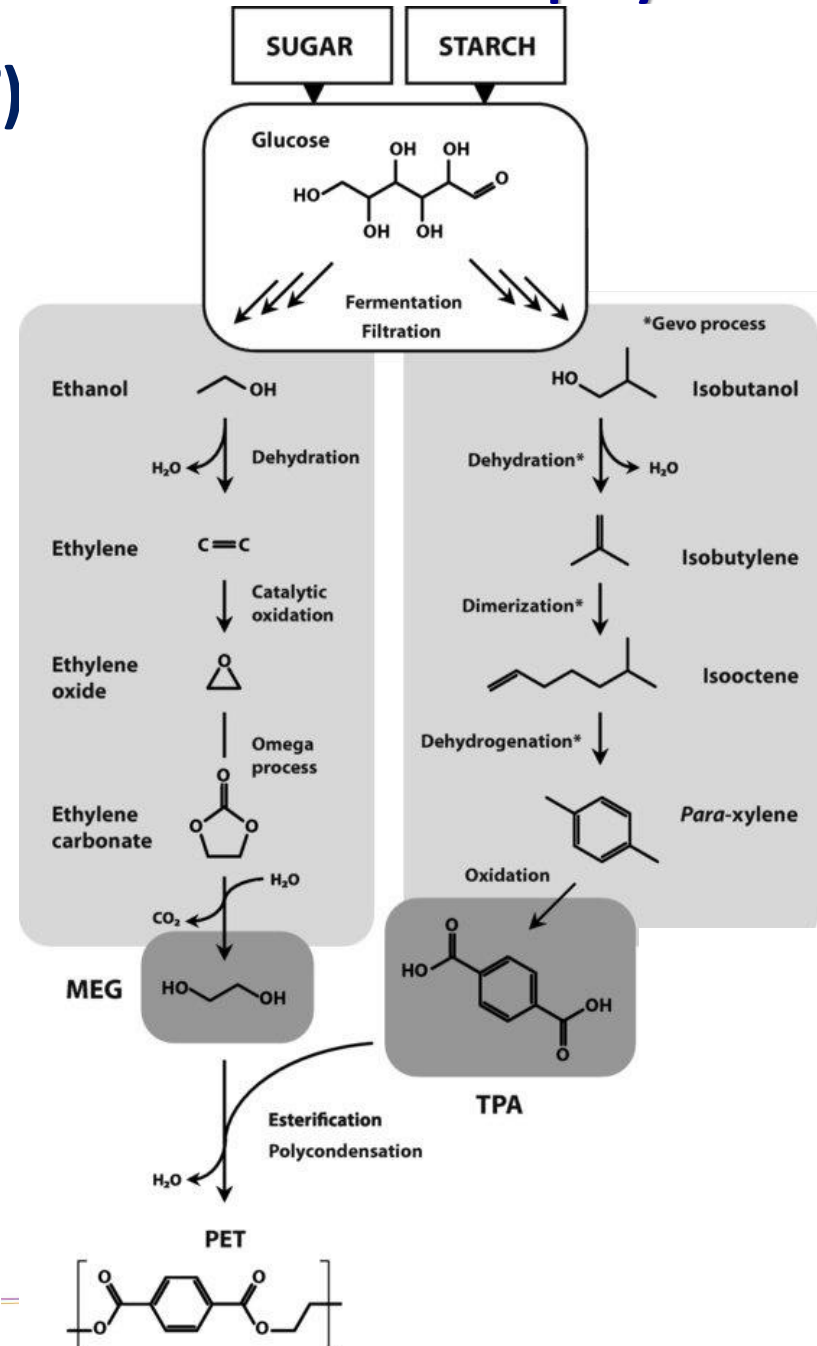
Most bio-based PET are only **30%** (20%) bio-based

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



4 kgCO₂e/kg

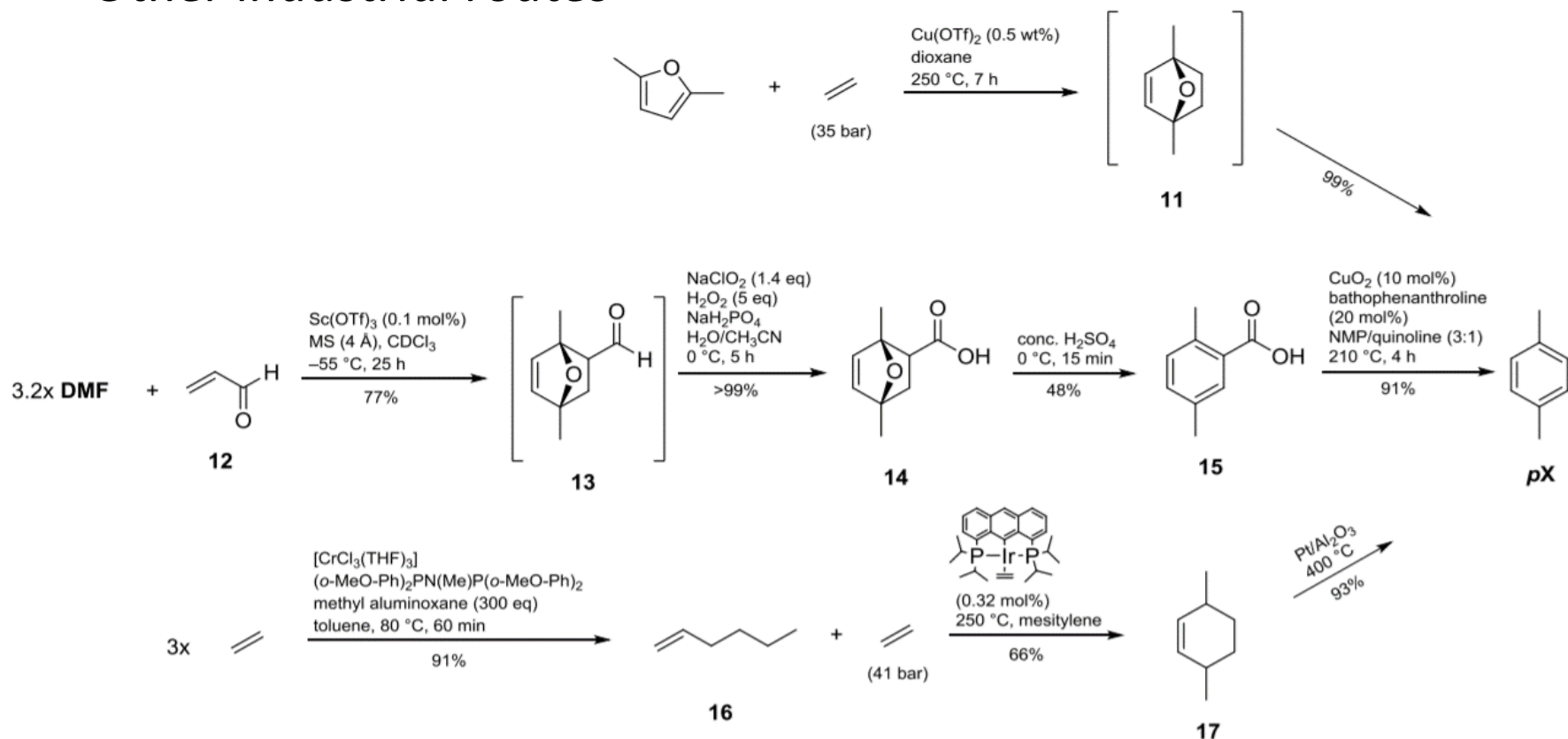
(vs 2.73 kgCO₂e/kg)



Polyethylene terephthalate (PET)

Other routes to terephthalic acid:

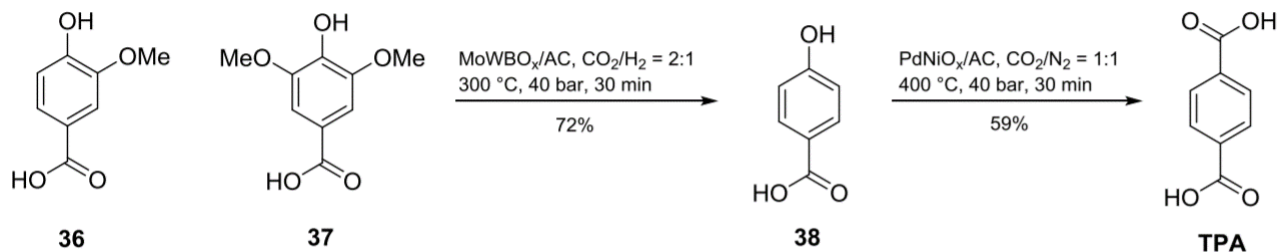
Other industrial routes



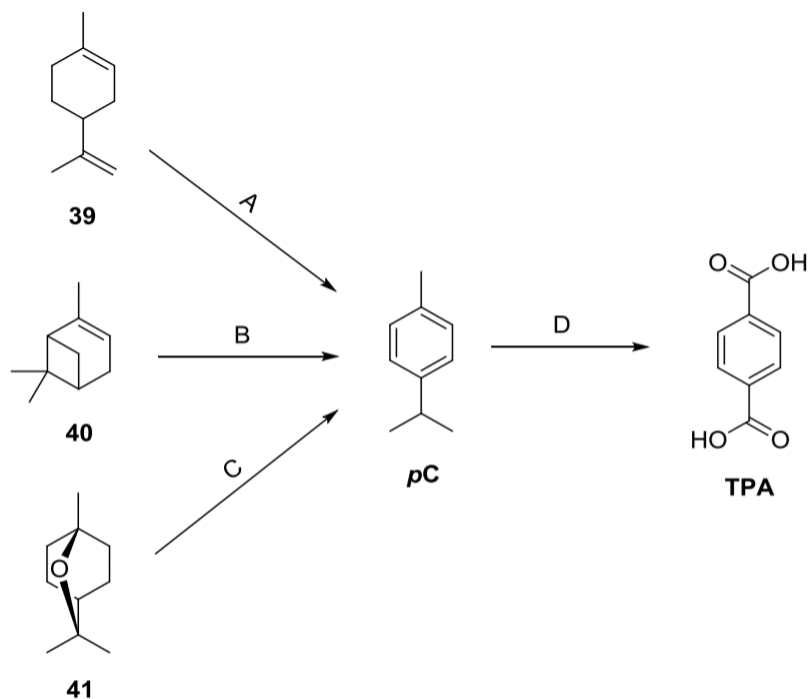
Polyethylene terephthalate (PET)

Other routes to terephthalic acid:

Lignin



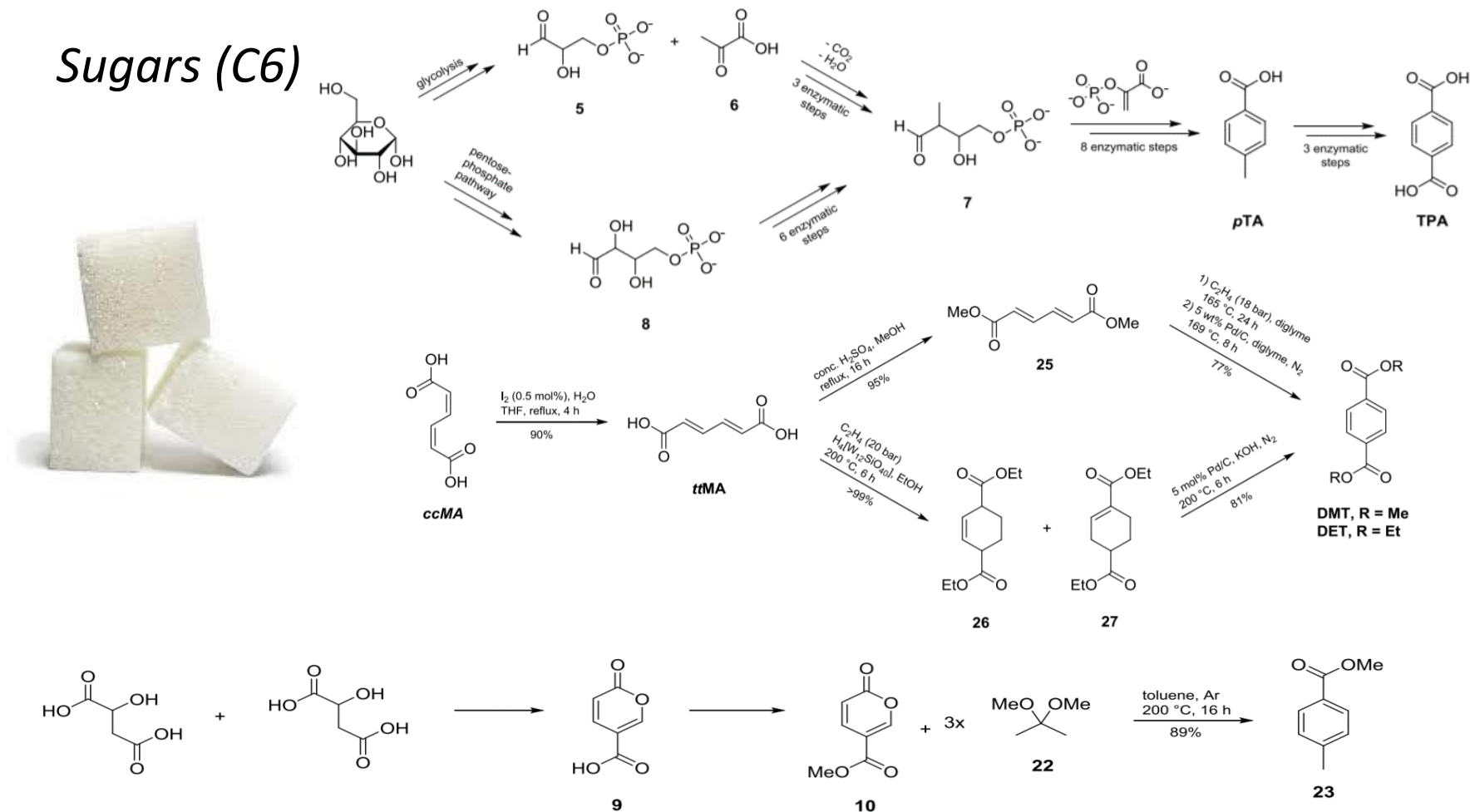
Terpens



Polyethylene terephthalate (PET)

Other routes to terephthalic acid:

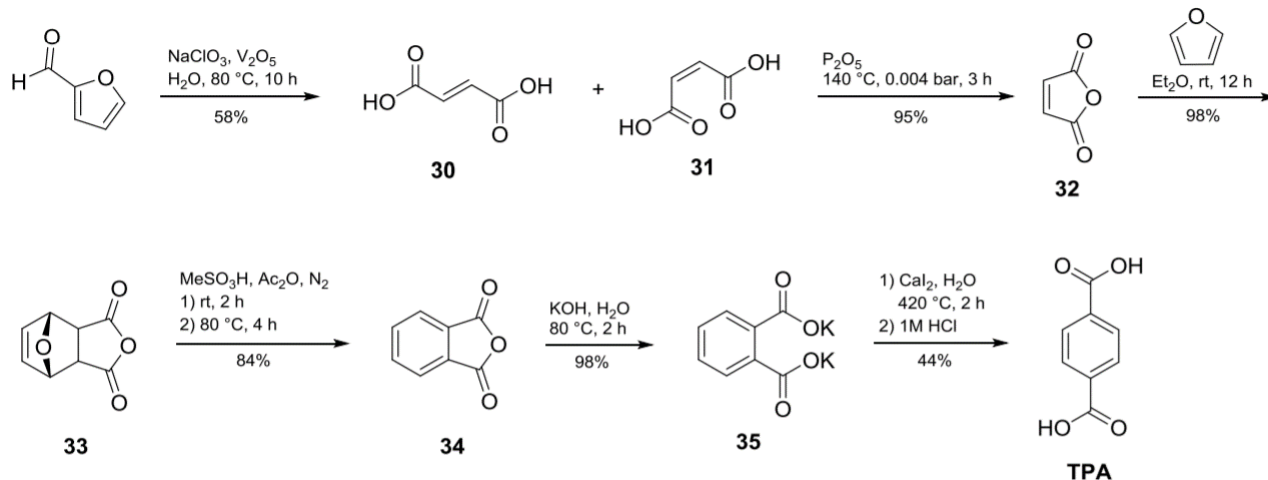
Sugars (C6)



Polyethylene terephthalate (PET)

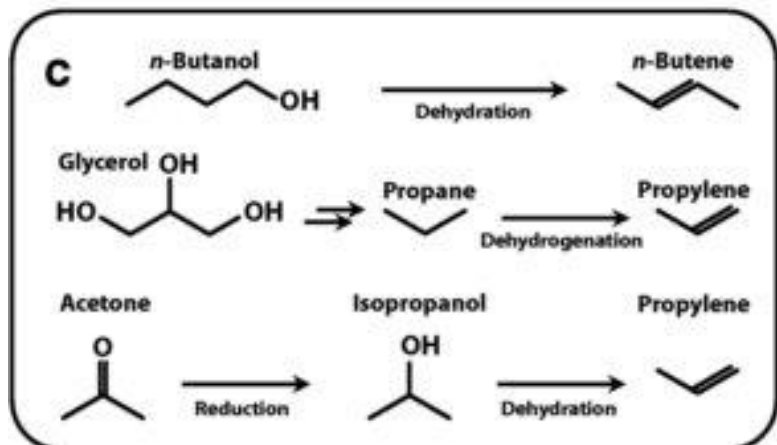
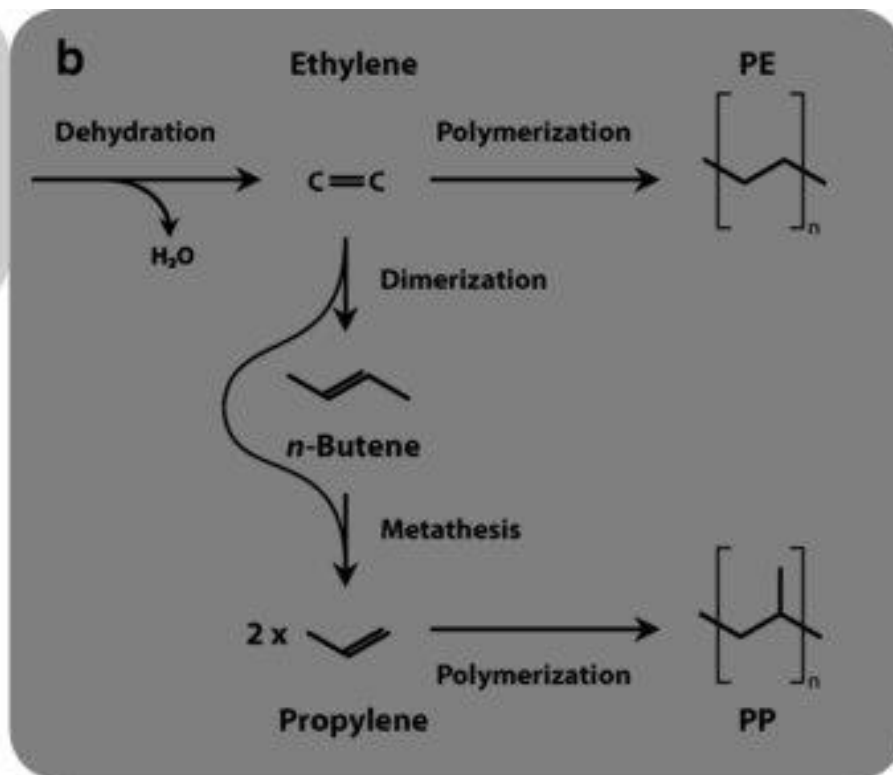
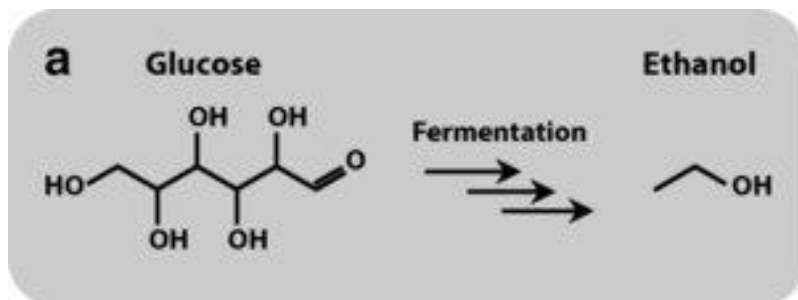
Other routes to terephthalic acid:

Sugars (C5)



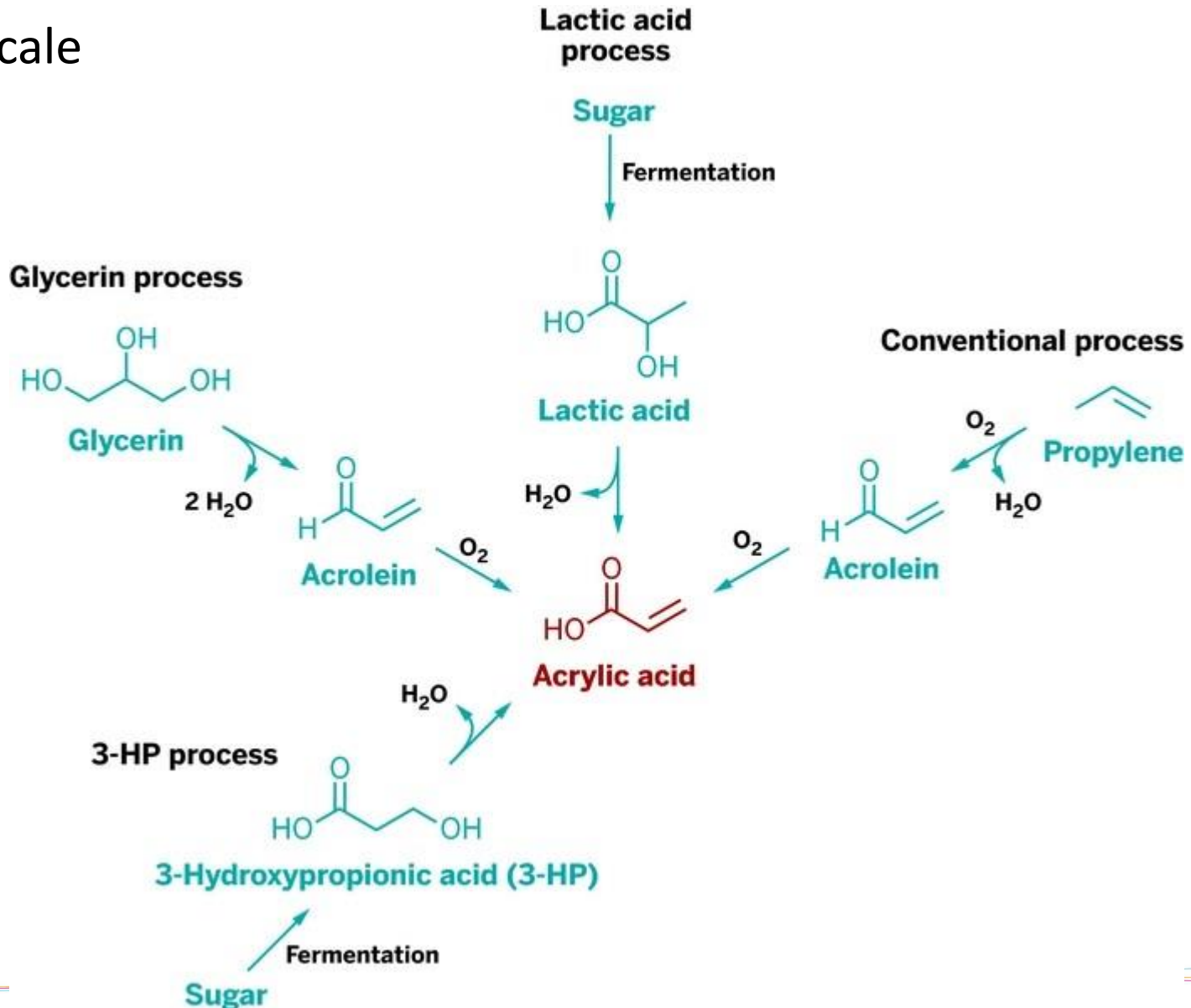
Polypropylene (PP)

20 kt



Super Absorbent polymers (SAP's)

Pilot scale

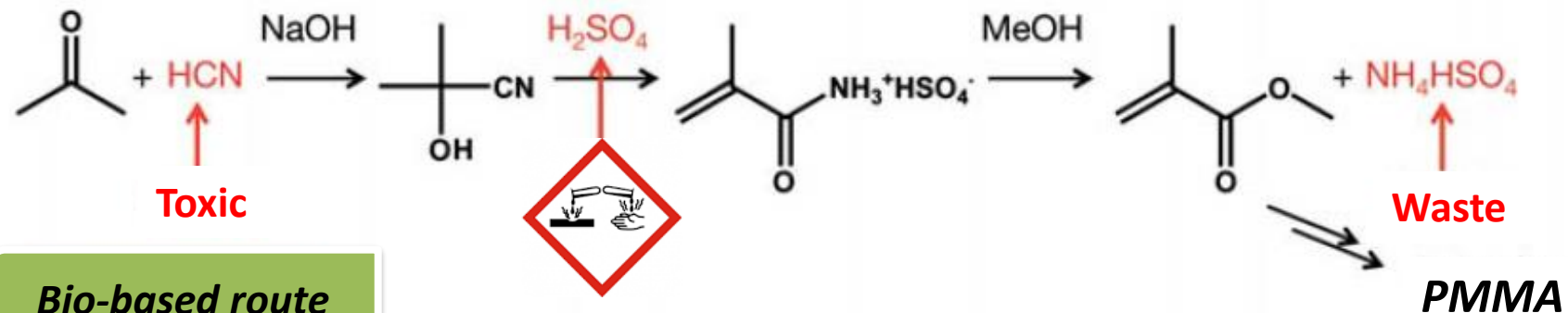


Drop-ins: Bio-based alternative to fossil-based polymers

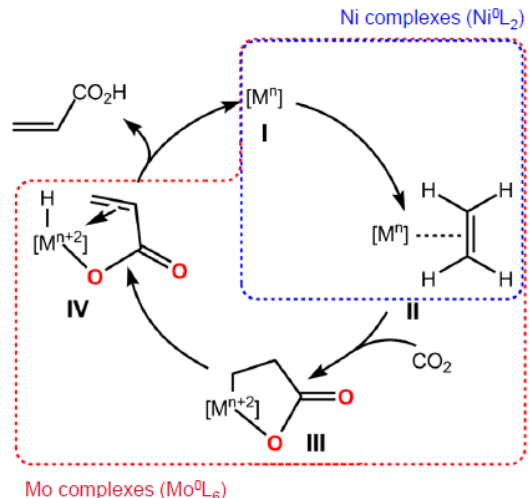
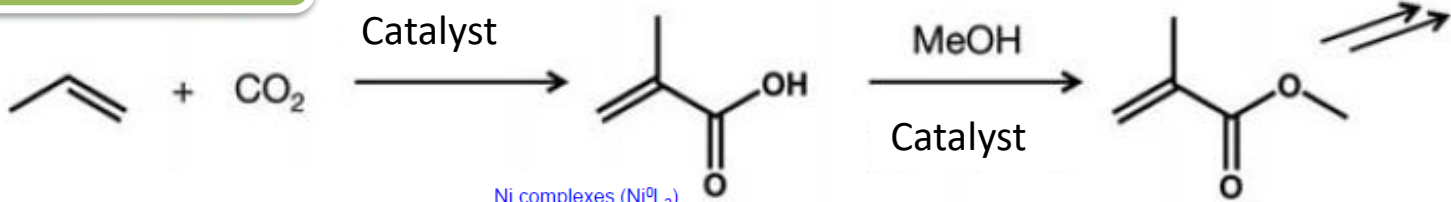
Poly(methyl methacrylate) (PMMA)

Pilot scale

Traditional route

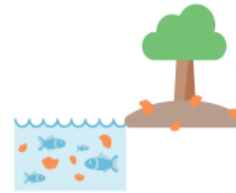


Bio-based route



- 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**

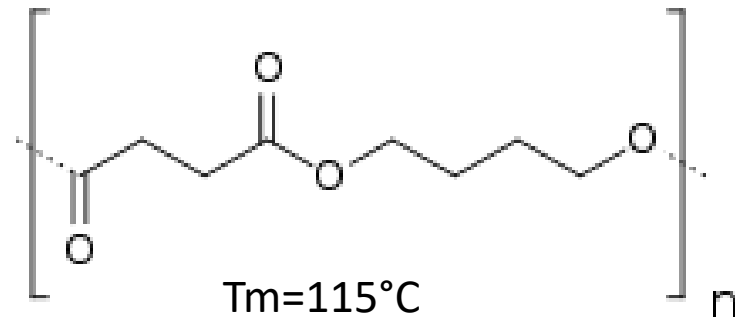
6- New polymers from biomass

7- Conclusions and perspectives

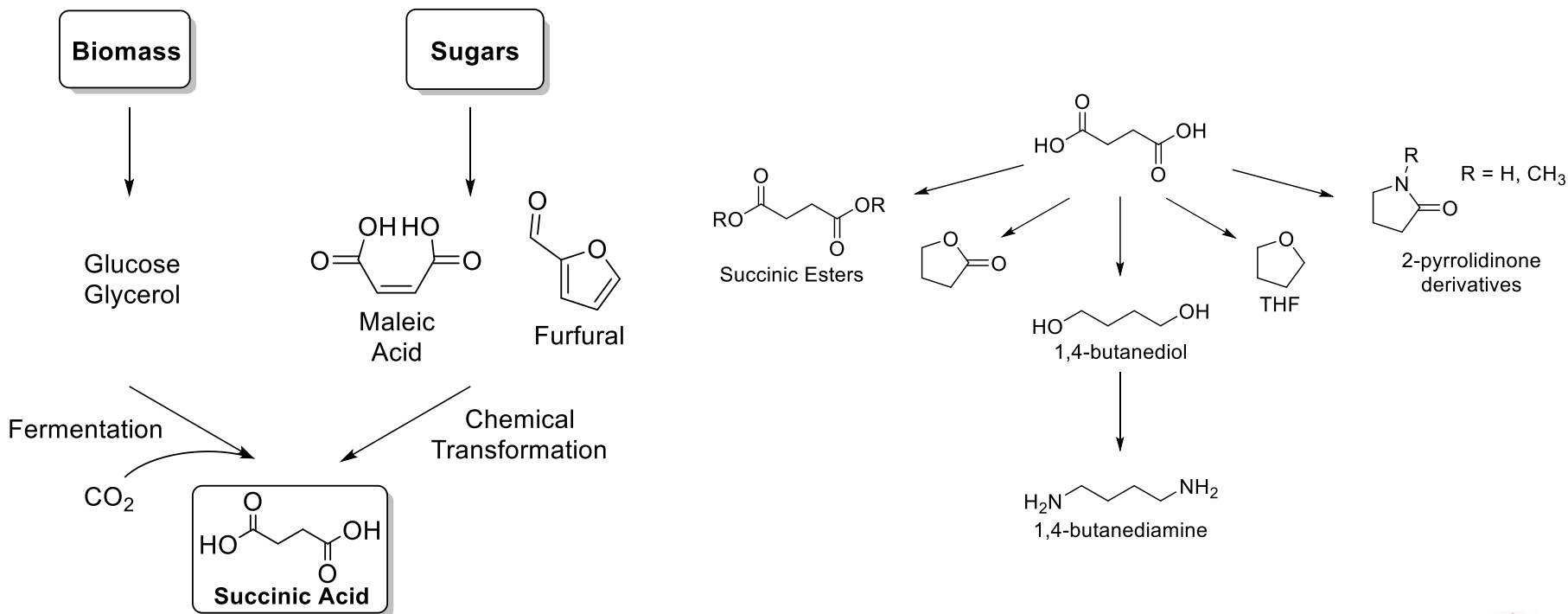
Polybutylene succinate (PBS)

100 kt

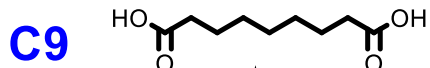
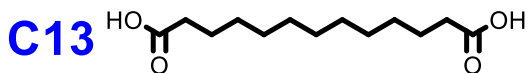
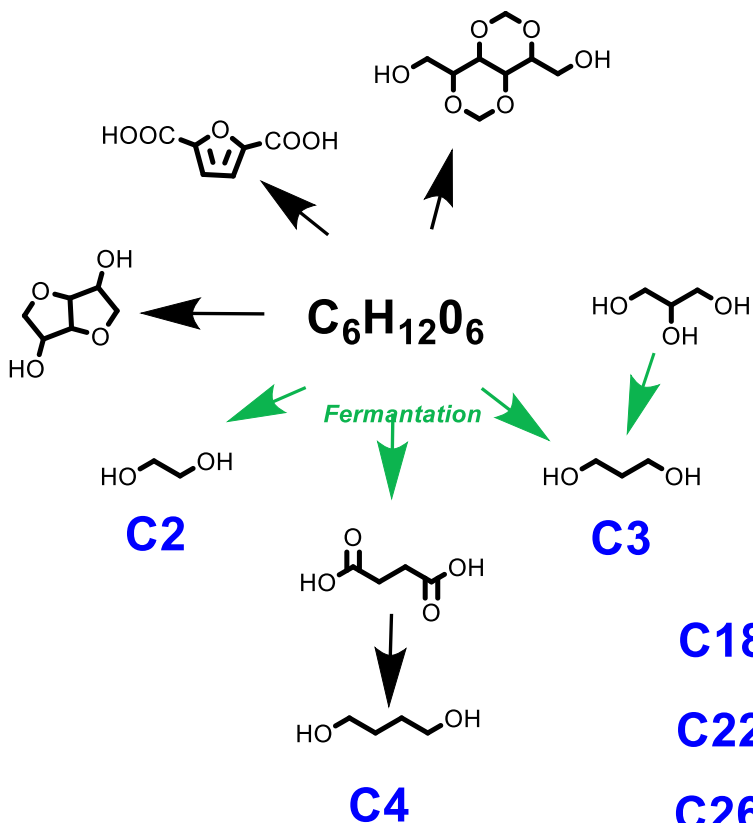
Bio-based succinic acid cost \approx fossil



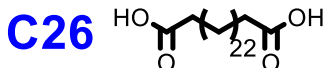
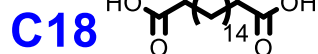
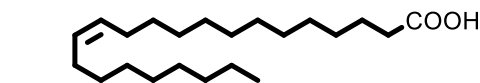
PBS polyethylene-like properties + biodegradable



Polyester

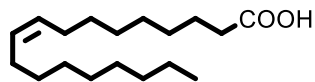
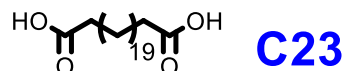
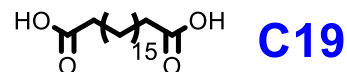


Triglycerides



Metathesis

Methoxycarbonylation

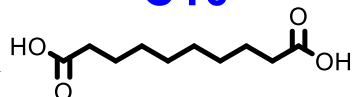


Ozonolysis

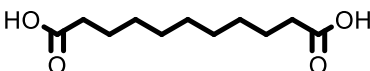
Alkali fusion

Pyrolysis

C10



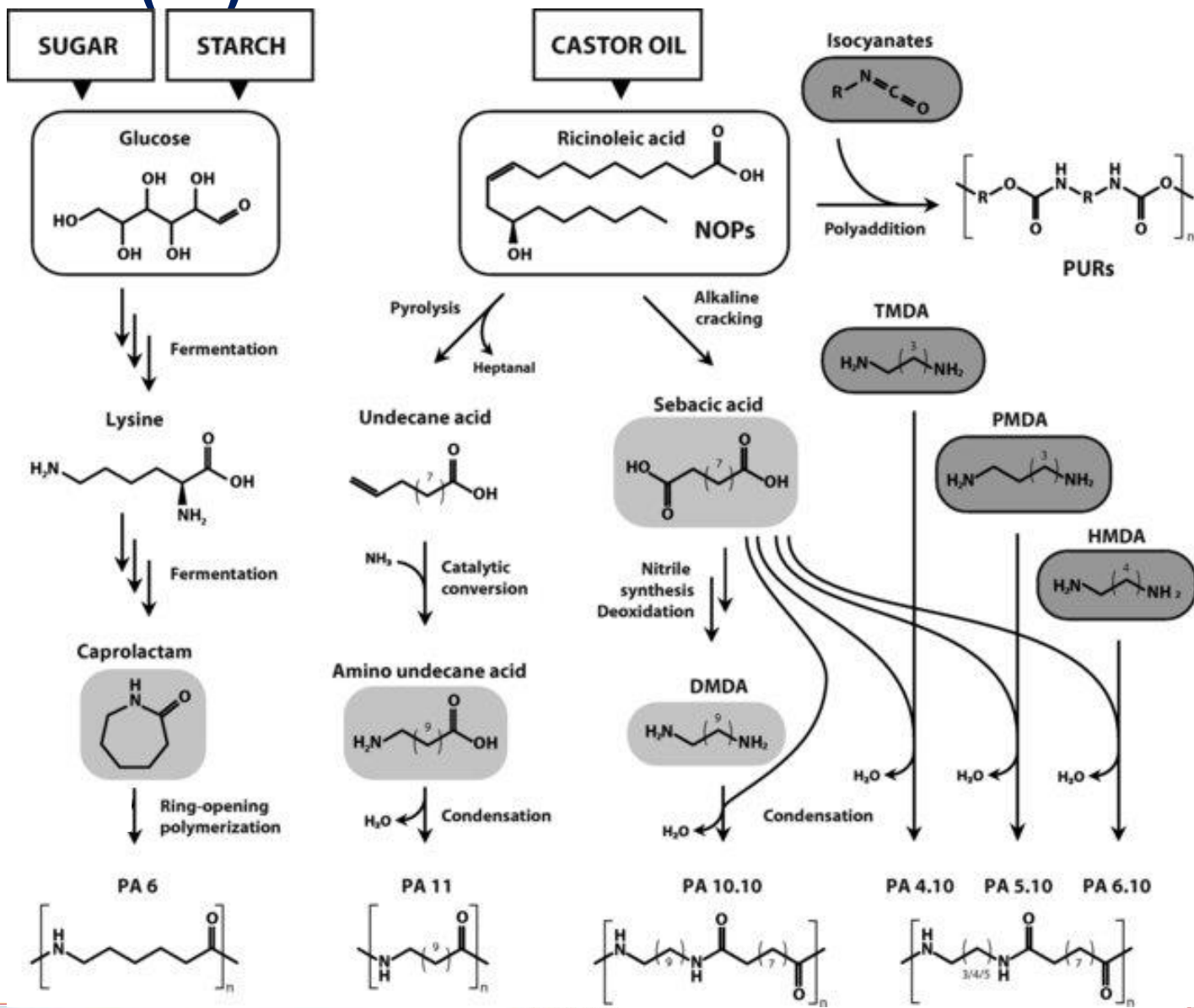
C11



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

Polyamides (PA)

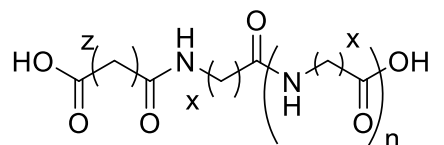
200 kt



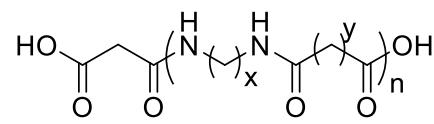
Polyamides (PA)

Stiffness ↑
↓ Hydrophobicity

- Polyamide**
- PA 6
 - PA 6-10
 - PA 11
 - PA 12



or

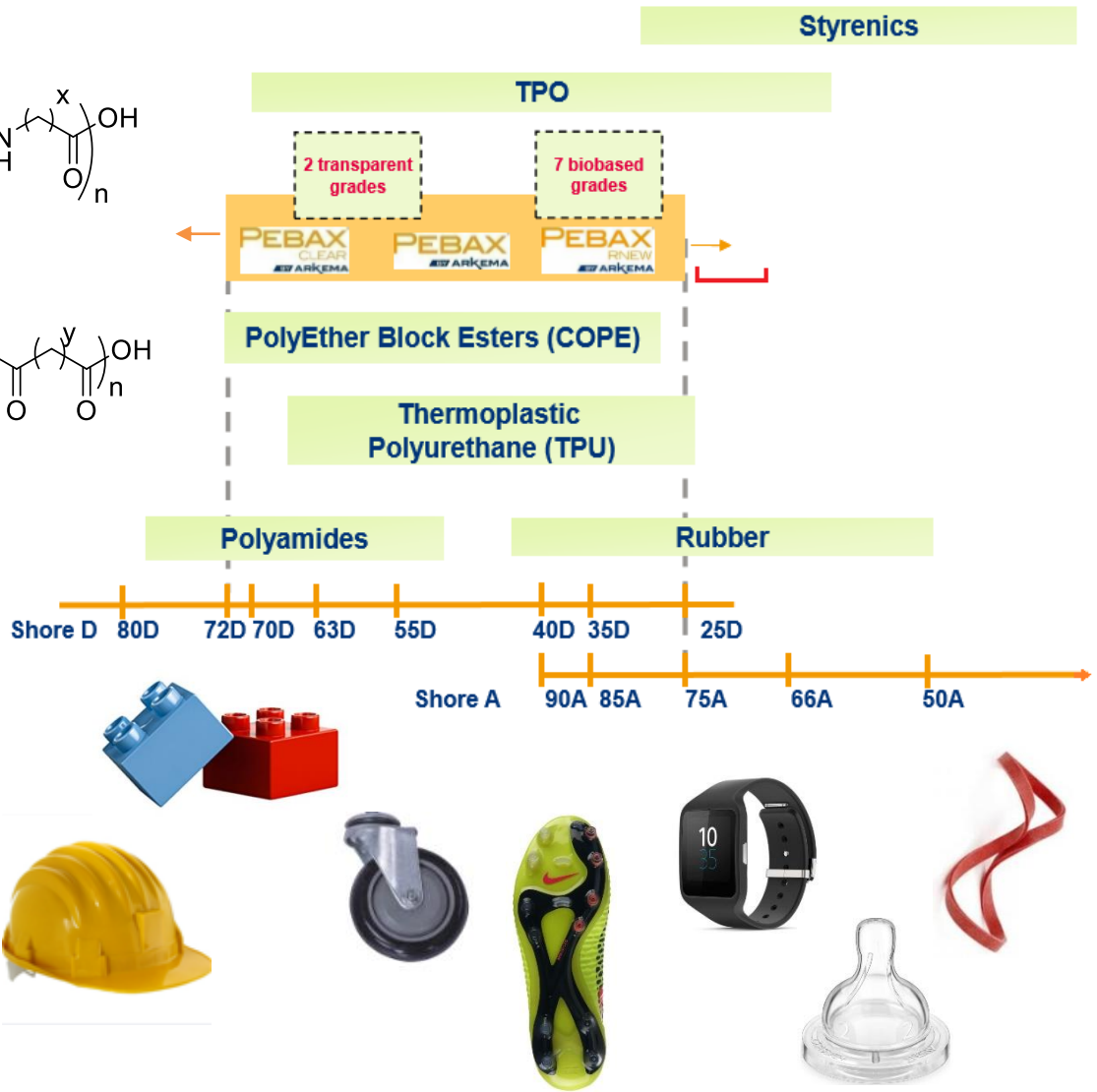


+ Polycondensation

Polyether

↓ Elasticity

- PEG
- PPG
- PTMO



Epoxy

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



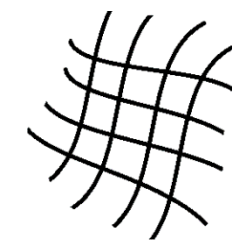
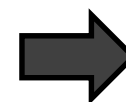
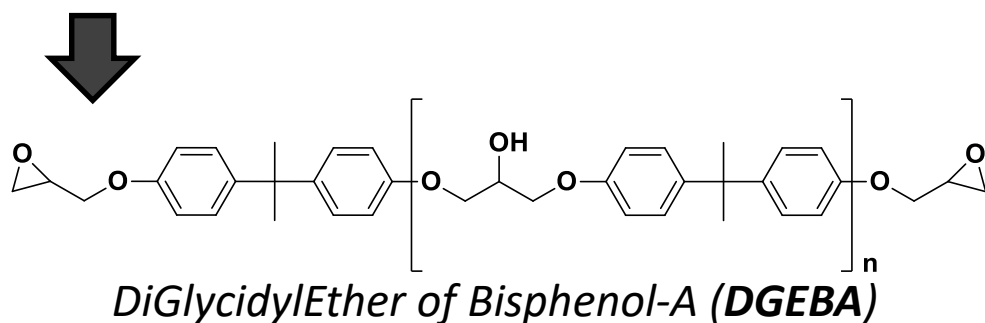
- ▶ Environnemental and economics concerns

- Petrochemicals → fossil carbon
- Price volatility

High risk of obsolescence of BPA



- ▶ Toxicity of BPA → *CMR^{1B}*

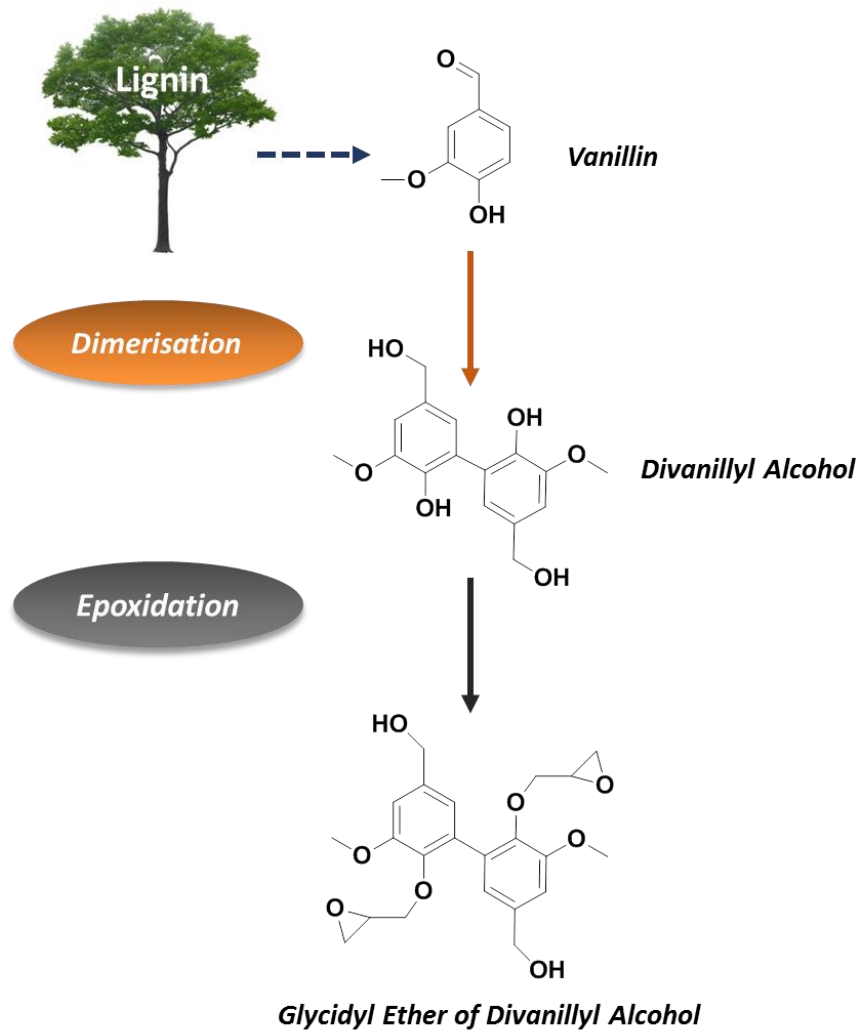
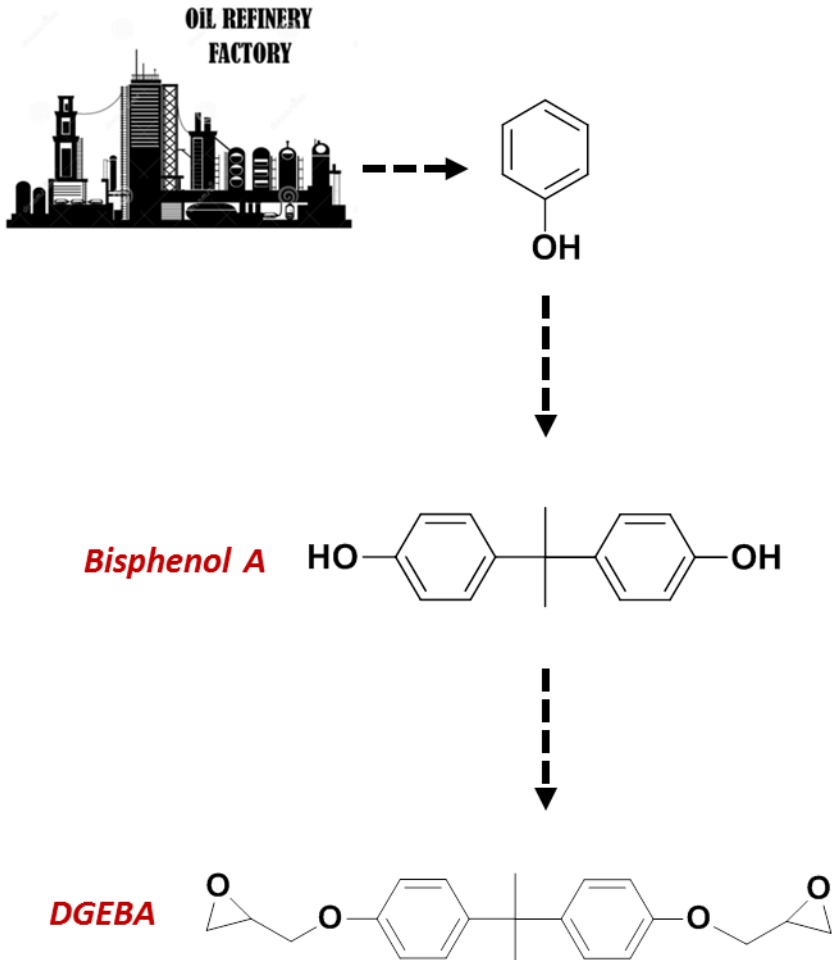


3D-network

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

Epoxy

From Lignin to epoxy resins...

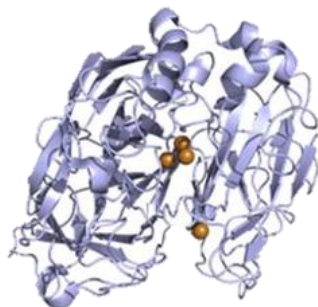


Epoxy

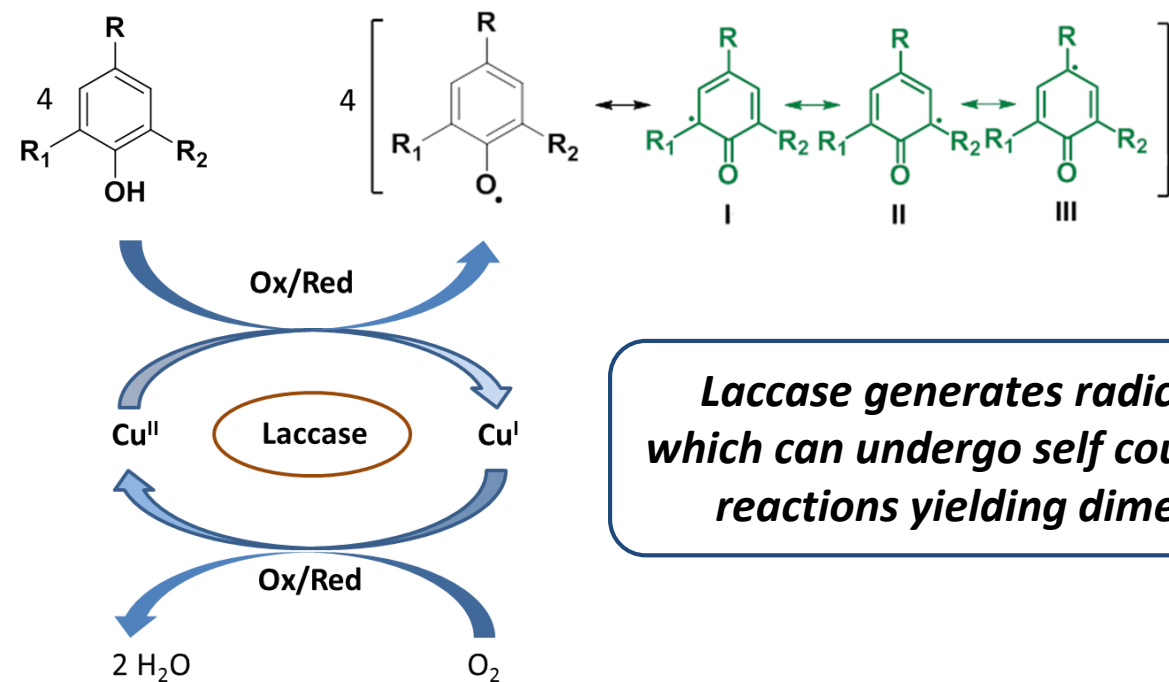


Trametes Versicolor

Enzymatic coupling

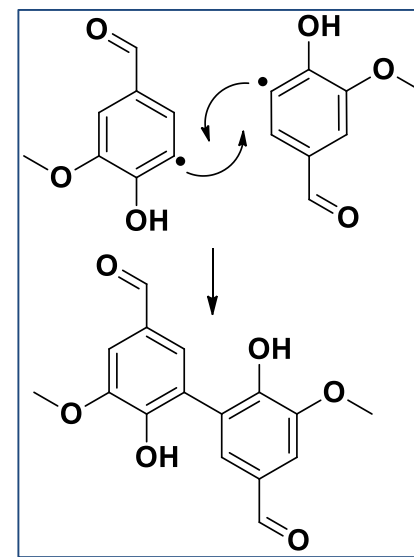


Laccase is an oxydative enzyme found in wood rotting fungi



Laccase generates radicals which can undergo self coupling reactions yielding dimers

Coupling of Vanillin



Divanillin

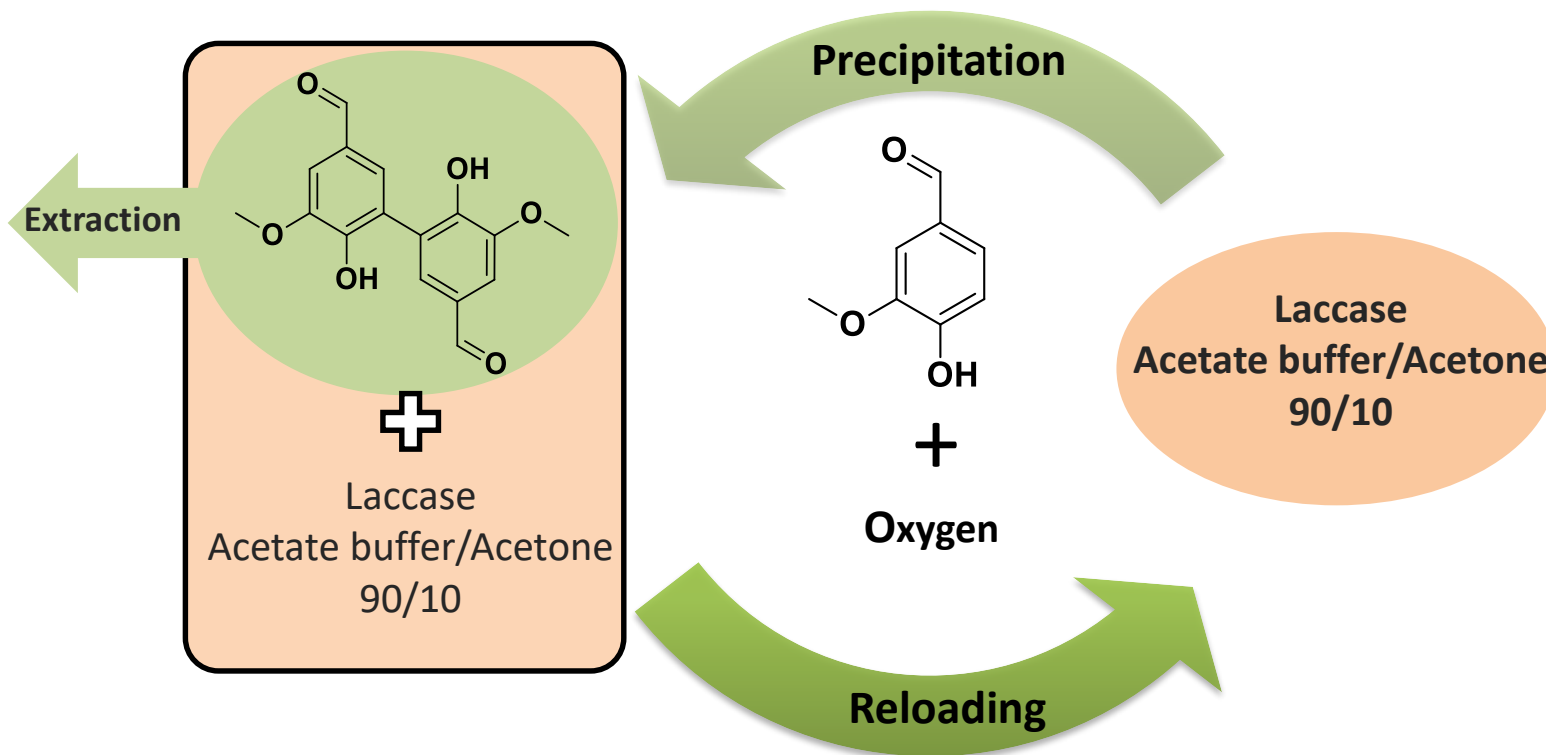
Kobayashi et al., *Chem. Rev.* 2009

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

Smart drop-ins: Bio-based derivative of "fossil" polymers

Synthesis of dimer from Vanillin

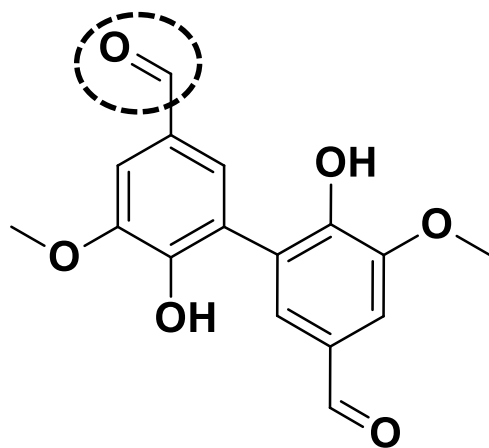
Epoxy



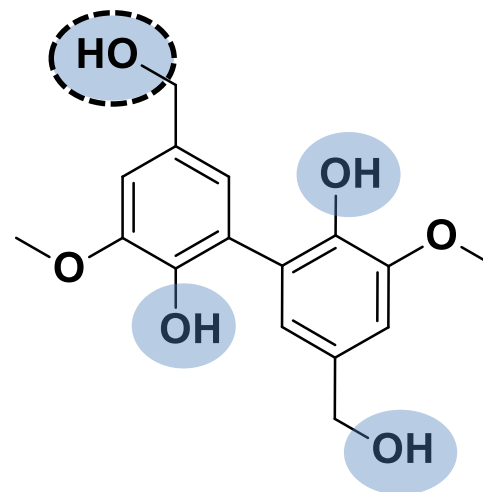
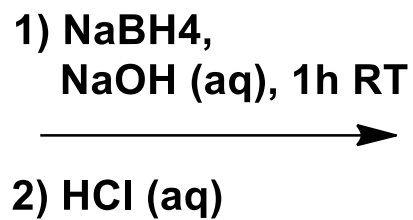
Self-sufficient process to synthesize dimers

Epoxy

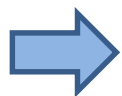
Aldehyde Reduction



Divanillin



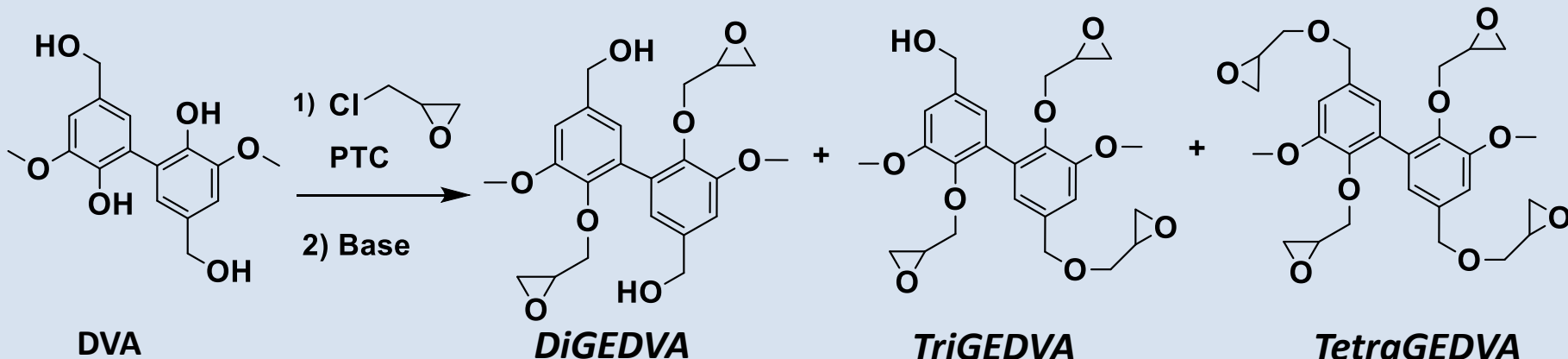
Divanillyl Alcohol (DVA)



4 functional groups available to achieve high mechanical properties

Epoxy

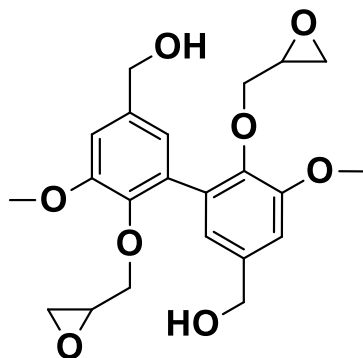
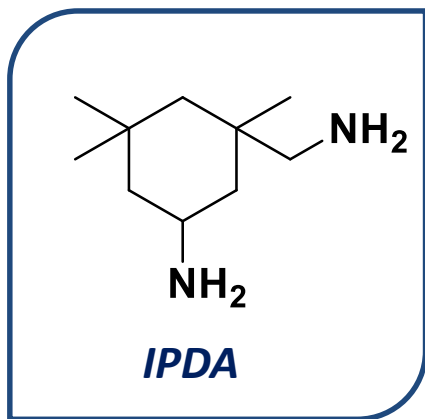
Synthesis of epoxy prepolymers from DVA



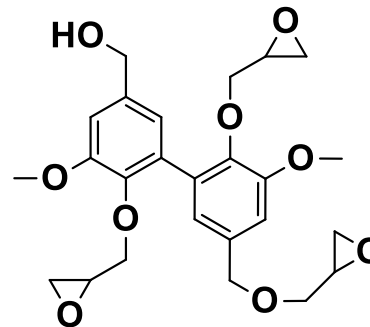
Properties	DGEBA	DiGEDVA	TriGEDVA	TetraGDVA
Melting point (°C)	45	-	-	-
Glass transition (°C)	-18	16	-6	-15
Viscosity at 25 °C (Pa.s)	5	<i>nd</i>	975	14
Viscosity at 40 °C (Pa.s)	1	1300	60	2
EEW th.	170	209	158	132
EEW exp.	171	232	164	129

Epoxy

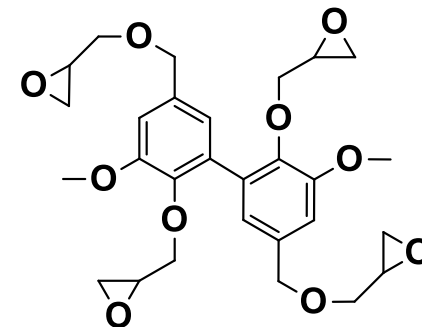
Synthesis of polyepoxyde network



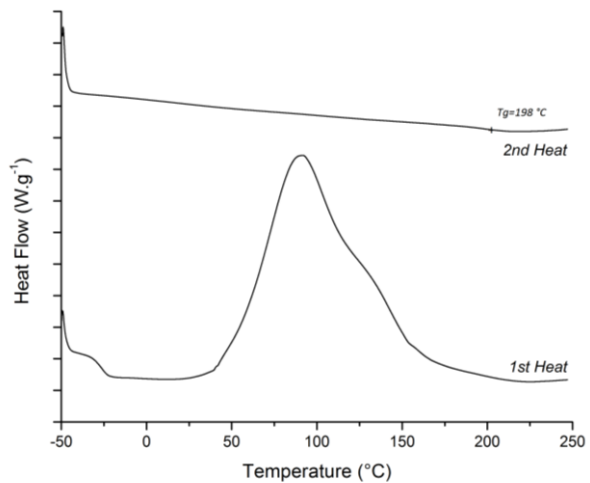
DiGEDVA



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

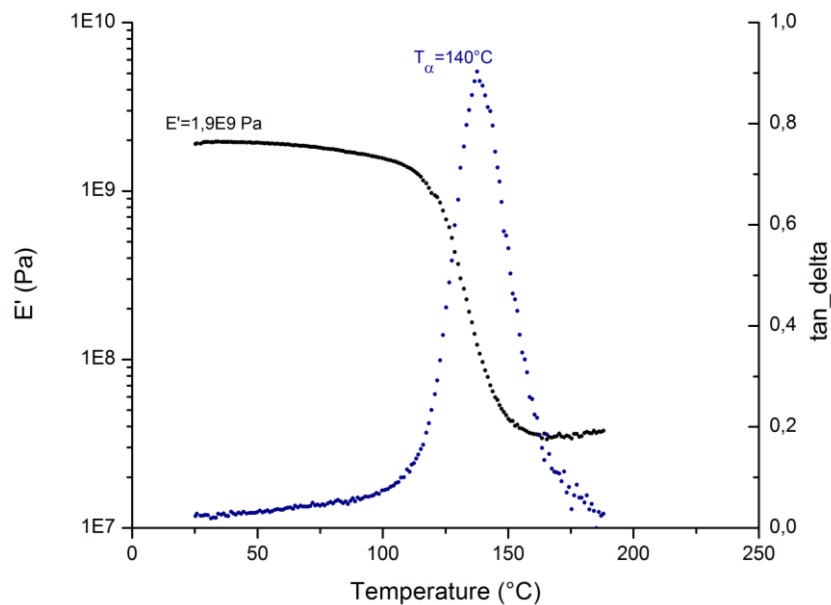
Epoxy

Dynamic Mechanical Analysis of epoxy resins cured with IPDA

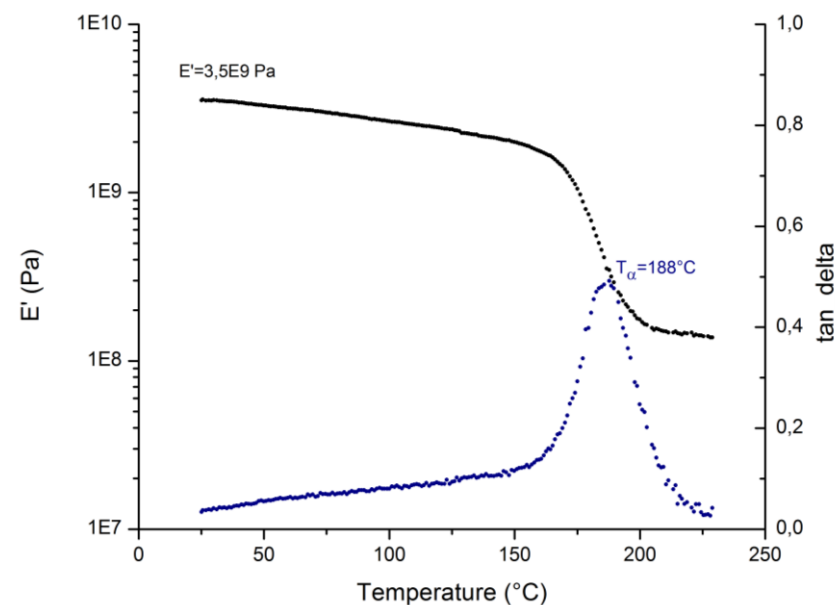
Epoxy prepolymer/IPDA	T_g^a (°C)	T_α^b (°C)	E'^b (Gpa)	$E'(T_{\alpha+30})^b$ (Gpa)	Network density (10^3mol.m^{-3})
DGEBA	152	155	1,7	0,035	9,2
DiGEDVA*	138	140	1,9	0,035	9,5
TriGEDVA	163	177	1,3	0,084	21
TetraGEDVA	198	188	3,5	0,15	36,7

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

DiGEDVA

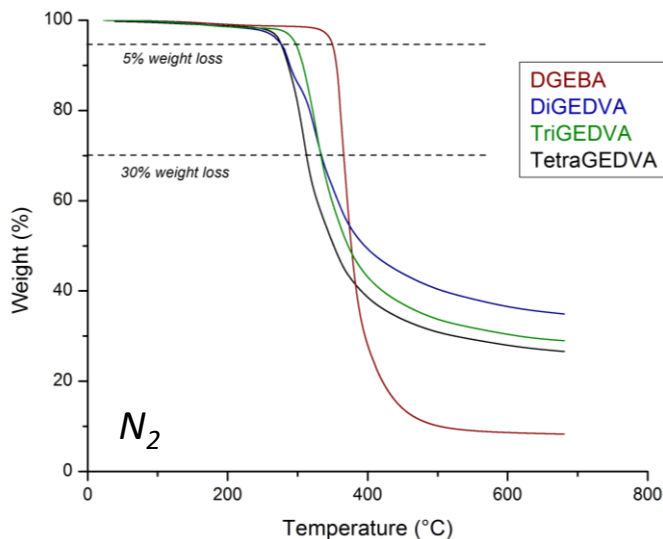
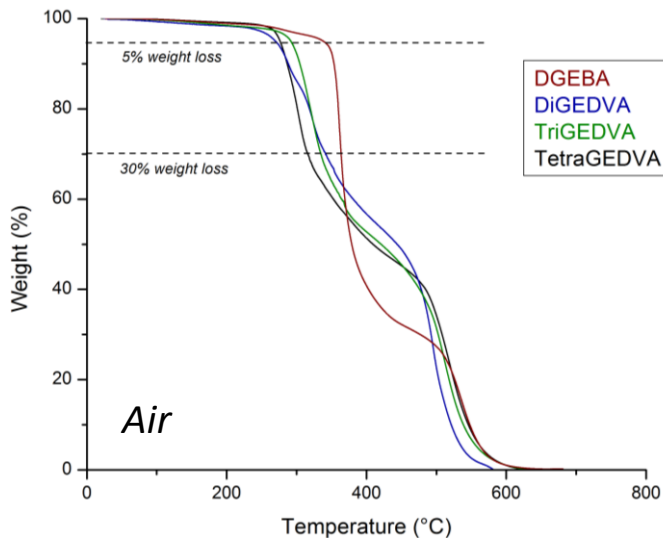


TetraGEDVA



Epoxy

Thermal degradation of epoxy resins cured with IPDA



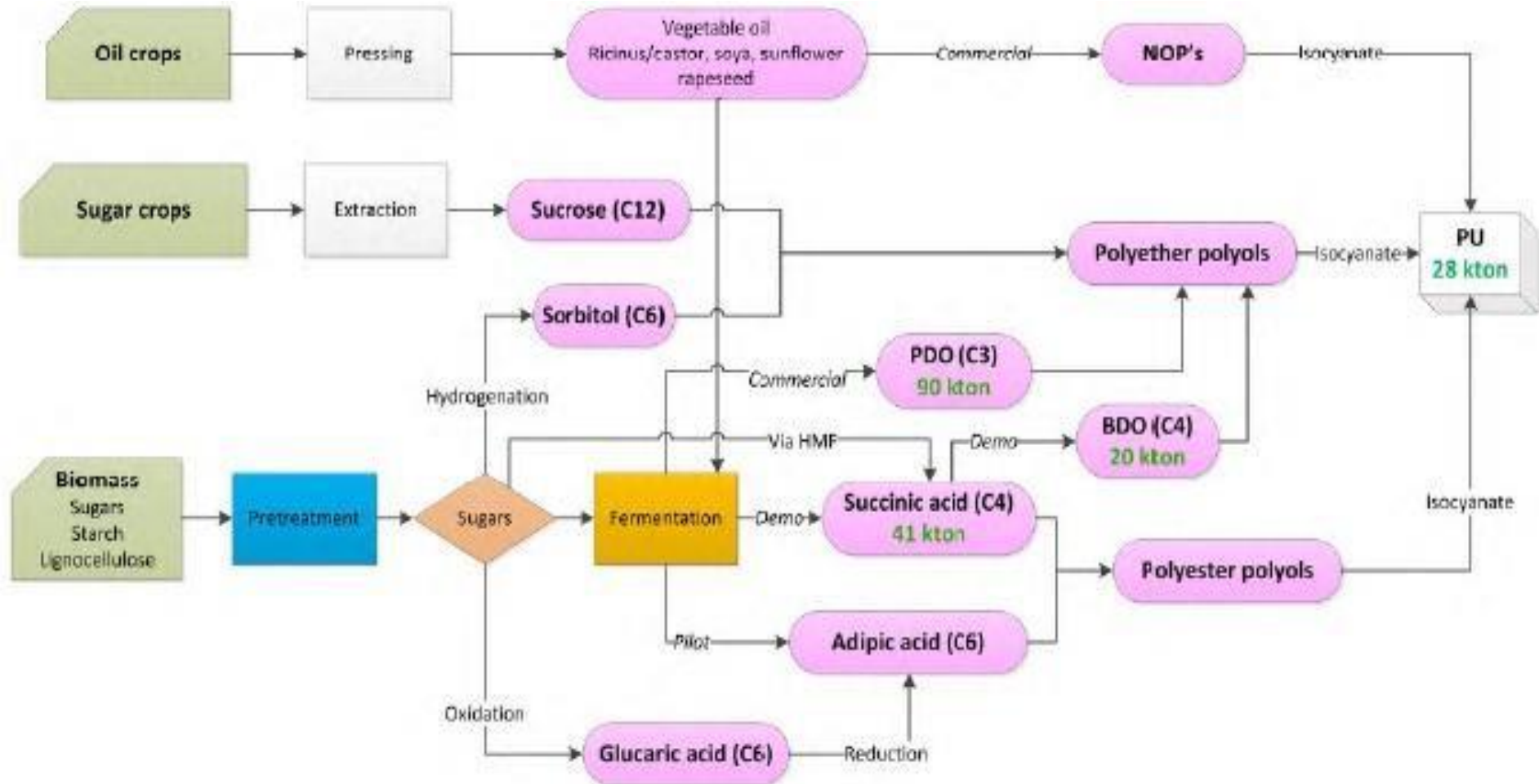
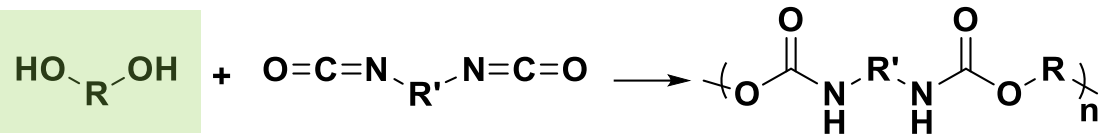
Epoxy prepolymer/IPDA	T_d 5% (°C)	T_d 30% (°C)	T_s
DGEBA	336	364	172
DiGEDVA	273	337	153
TriGEDVA	292	335	156
TetraGEDVA	275	316	147

- Slightly lower thermal heat resistance

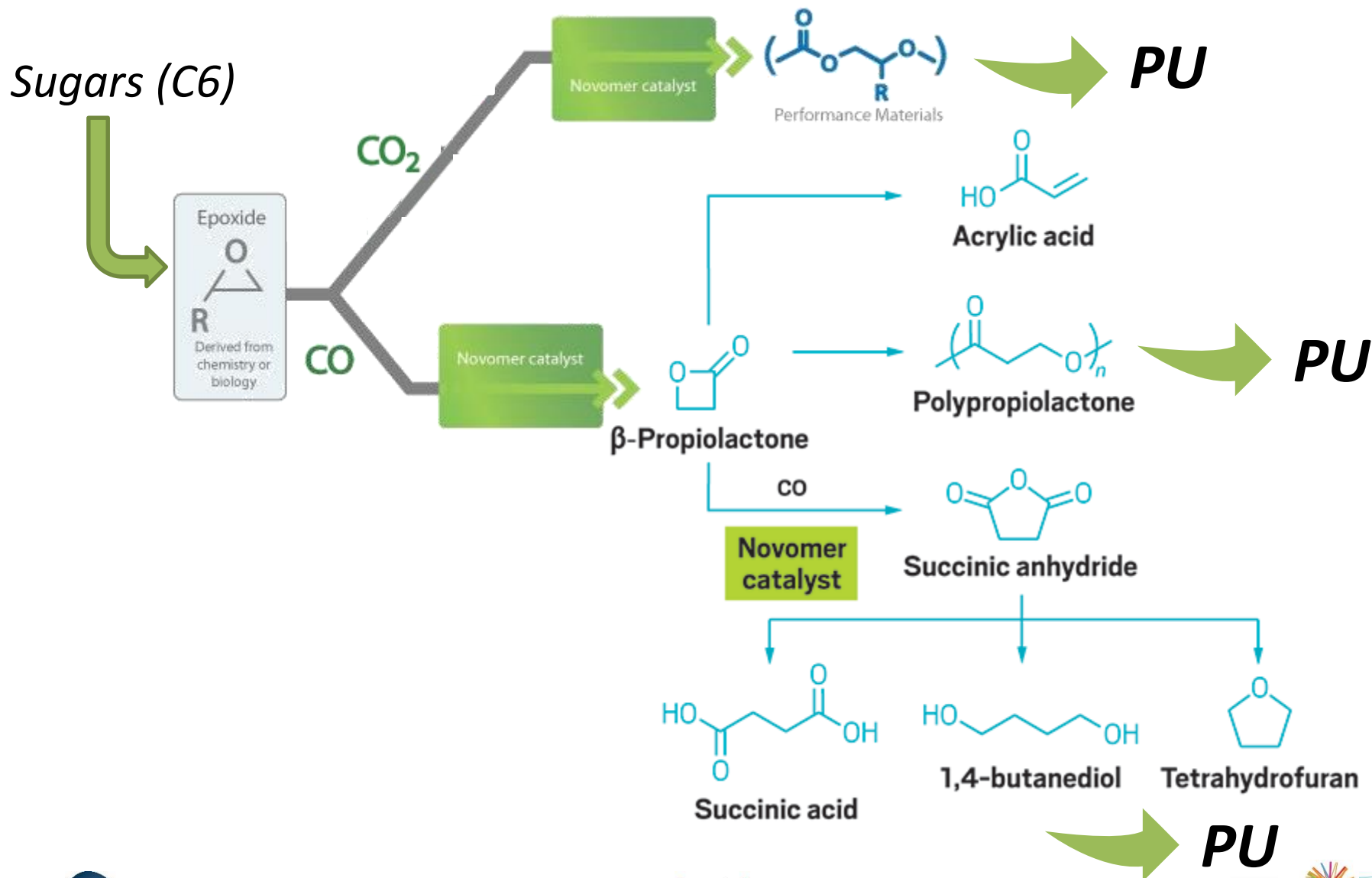
Epoxy prepolymer/IPDA	T_d 5% (°C)	T_d 30% (°C)	T_s	Char ₆₀₀ (%)
DGEBA	349	366	176	9
DiGEDVA	275	334	152	36
TriGEDVA	296	333	155	30
TetraGEDVA	276	313	146	28

- High char residue for biobased epoxy resins

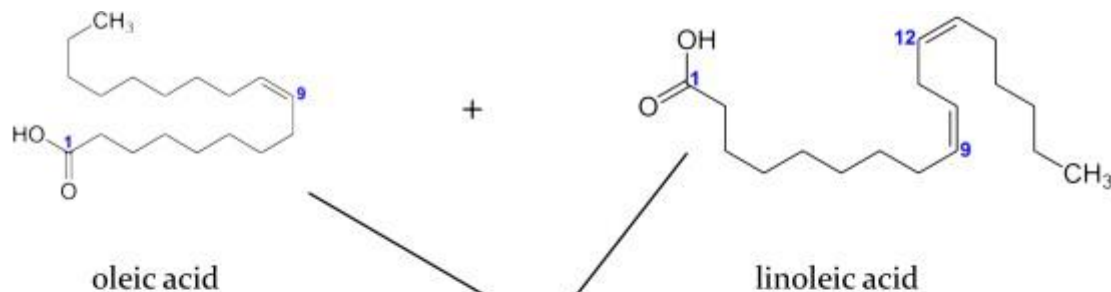
Polyurethanes



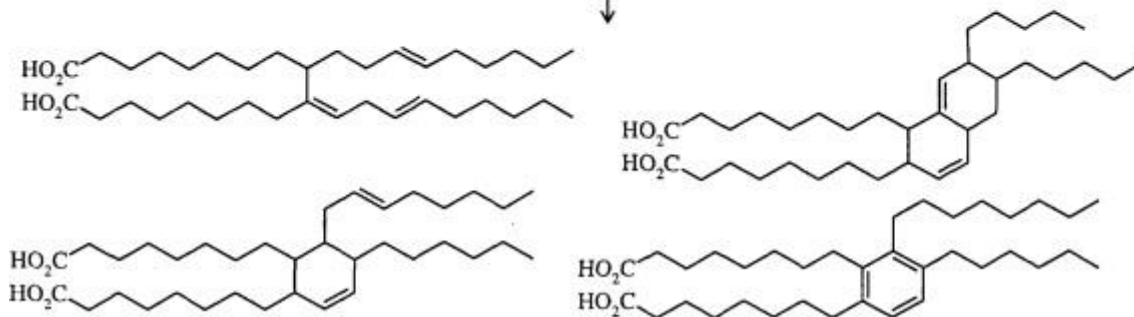
Polyurethanes: polyol



Polyurethanes: polyol



Acid catalyst

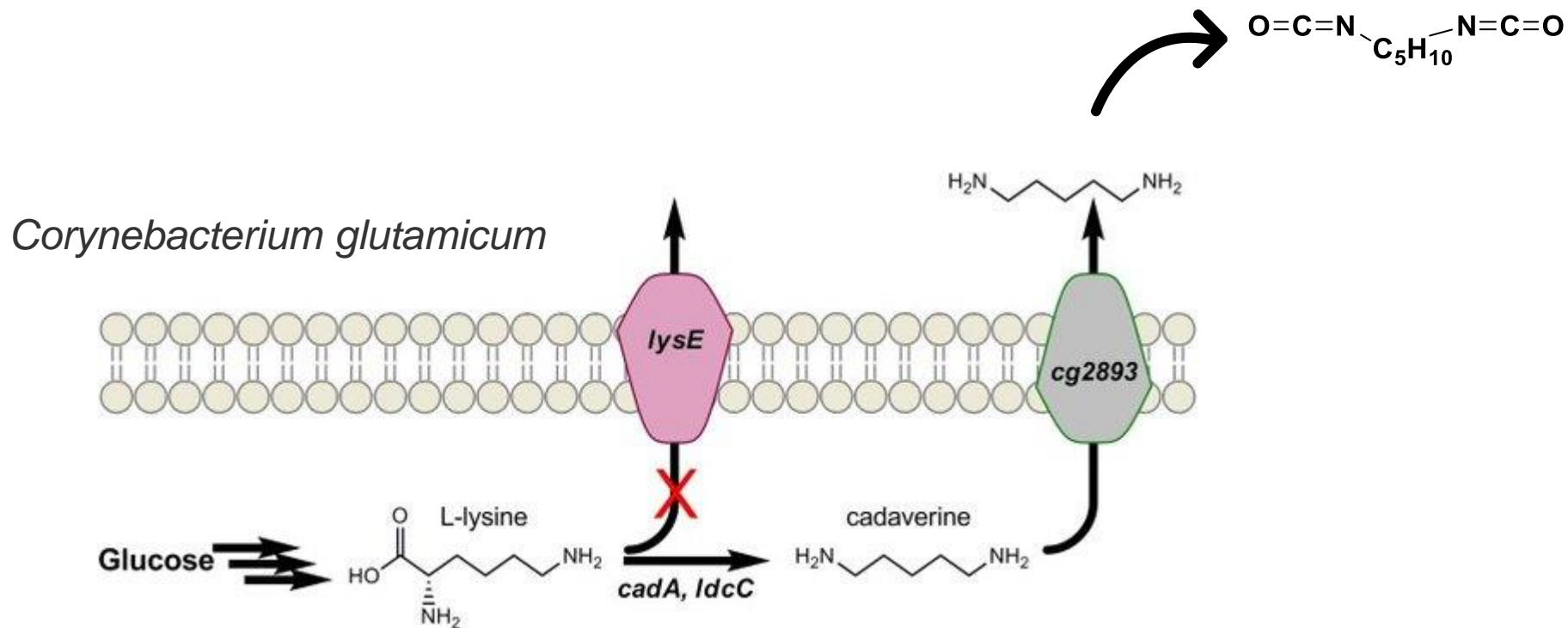


(Hydrogenation)/modification

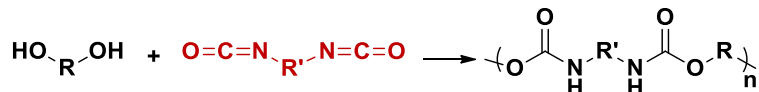


PU

Polyurethanes: isocyanate



Polyurethanes

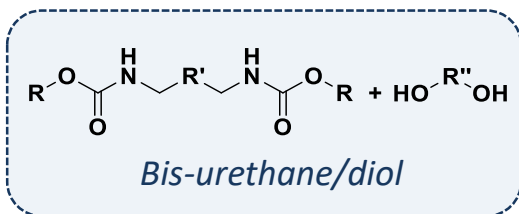


*Industrial process for the
production of Polyurethanes :*
The Isocyanate/alcohol route

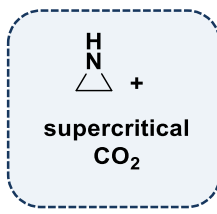


PU

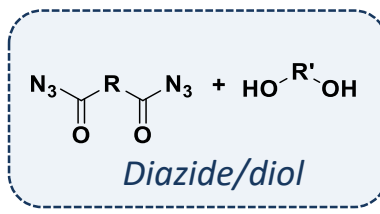
Non Isocyanate PolyUrethane



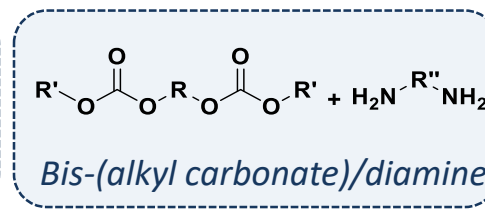
Transurethanization



Aziridine route



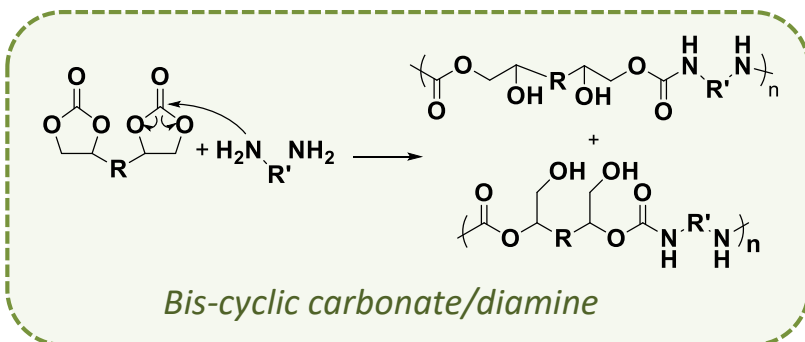
Rearrangements



Bis-(dialkyl carbonate) route

NIPU

Poly(HydroxyUrethane)



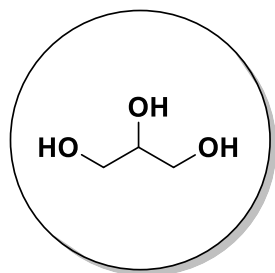
- ◆ | Phosgene- and isocyanate-free
- ◆ | Polyaddition : no by-product
- ◆ | Less moisture sensitive

↓
PHU

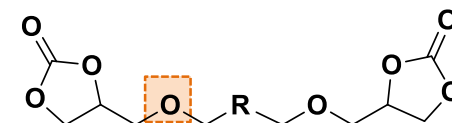
Polyurethanes: isocyanate

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

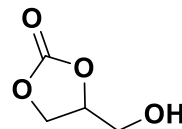
Glycerol platform



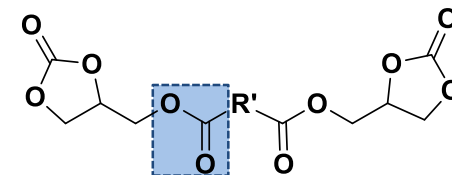
Alcohol



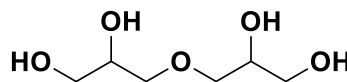
Glycerol Carbonate



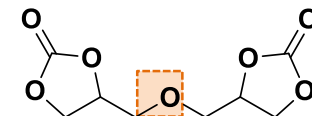
Acyl chloride



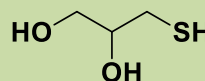
Diglycerol



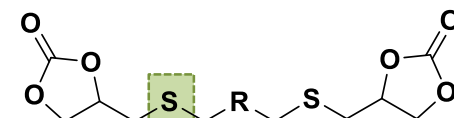
DMC



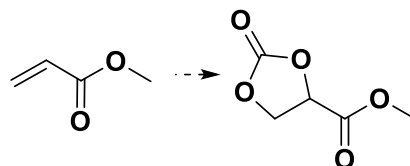
Thioglycerol



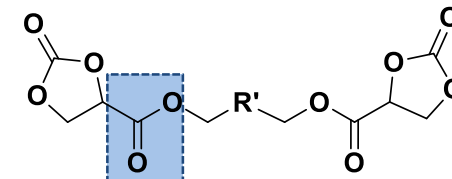
Diene



Methyl acrylate



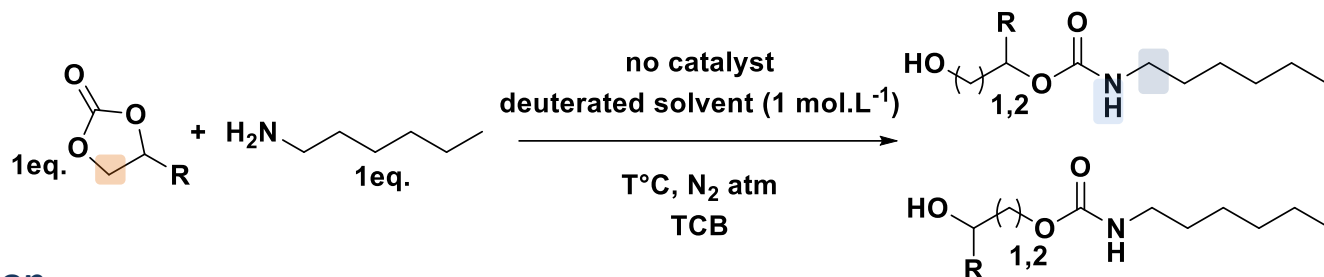
Alcohol



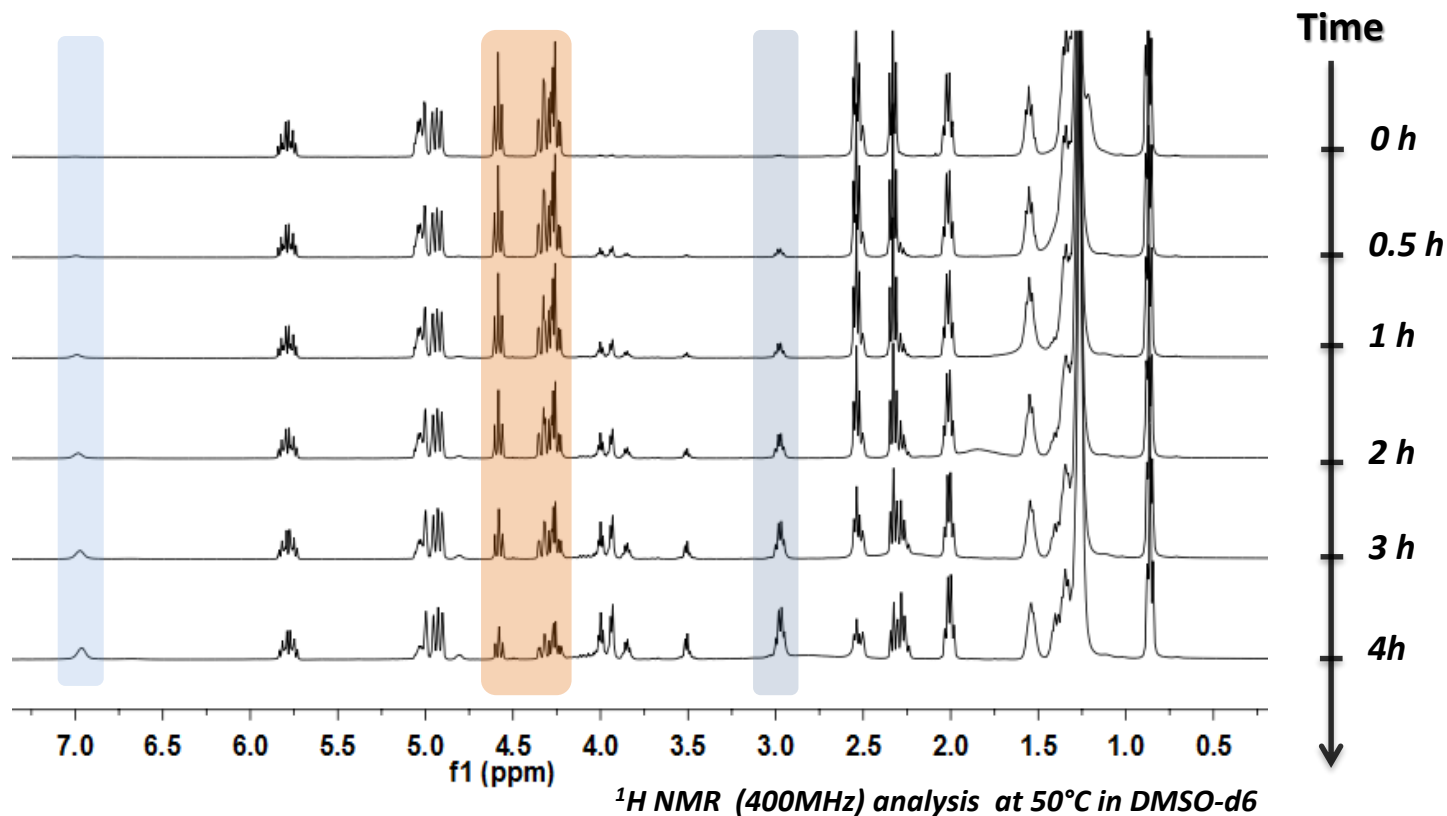
- Tunable **heteroatom nature and position** nearby the CC by varying the glycerol derivative
- **Ether, ester and thioether** functions inserted nearby the cyclic carbonate

Reactivity of various CC towards aminolysis

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

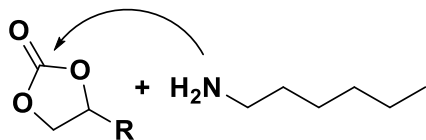


→ CC conversion calculation



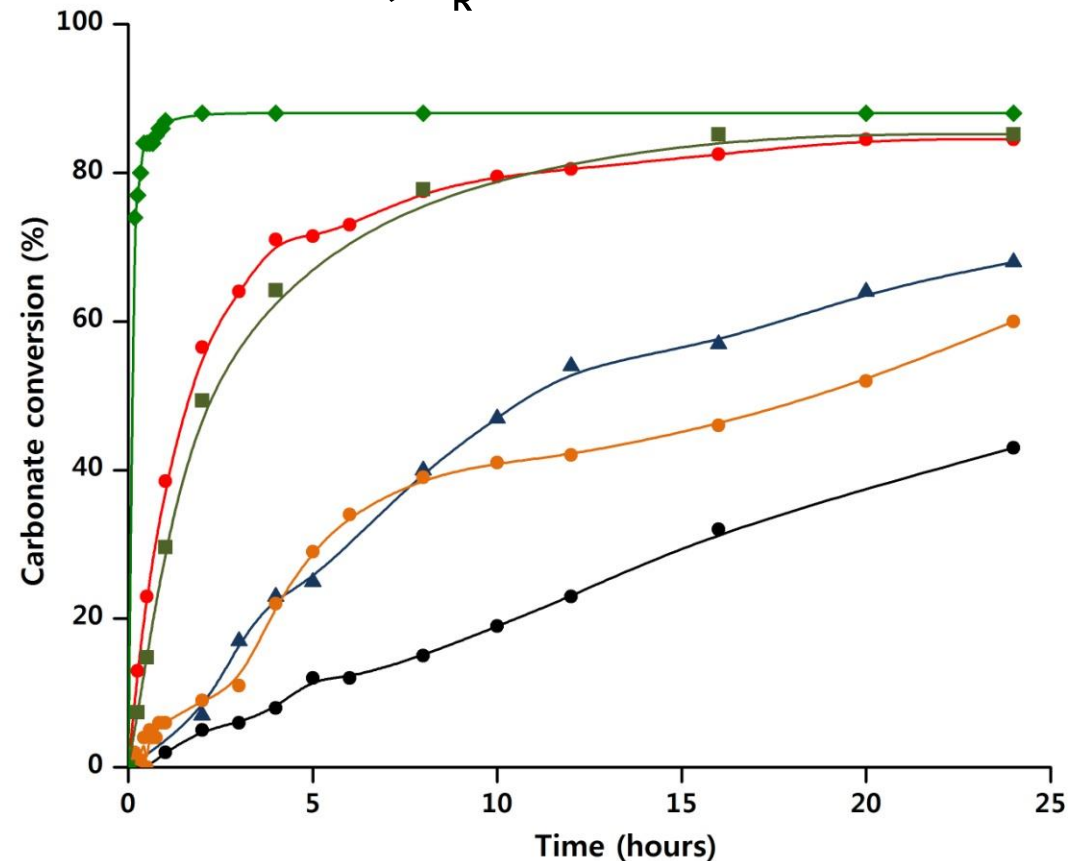
Scale of CC reactivity towards aminolysis

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

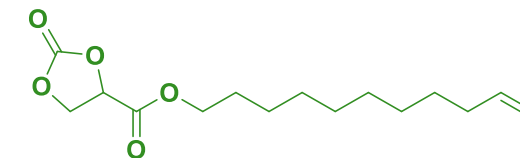


$$\frac{x}{1-x} = k_{app} C_0 \Delta t$$

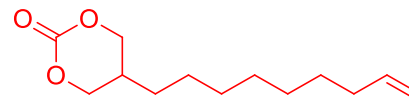
$+ k_{app}$
(L.mol⁻¹.h⁻¹)



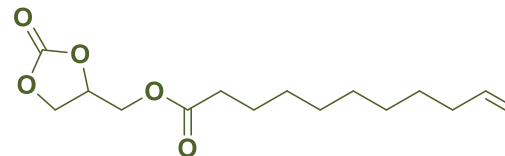
CC conversion in function of time (50°C, DMSO-d₆, 24h, ratio amine : CC = 1:1)



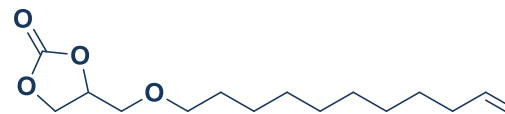
5CC-α ?



6CC 0.44



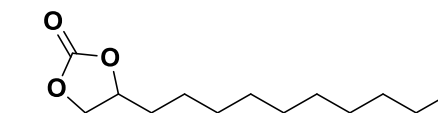
5CC-β 0.44



0.09



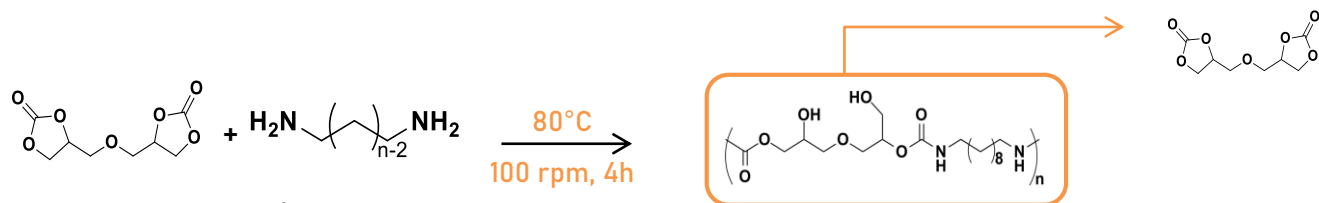
0.08



5CC 0.03



> From DGDC & various DAs



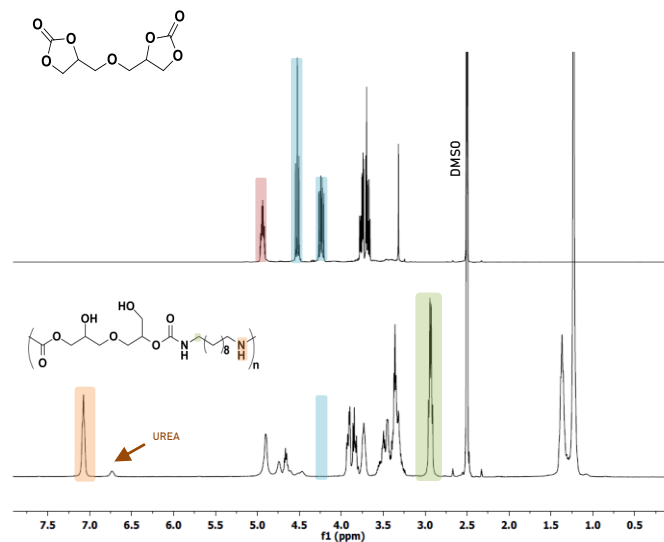
DGDC 6 / 10 DA
 $T_m = 76^\circ\text{C}$ $T_m = 45^\circ\text{C} / 60^\circ\text{C}$



Conversions (%) 99% / 99%
 Molar masses (g/mol)..... up to 46800 / 50 000
 T_g (°C) up to 18 / 17
 T_m (°C)..... -- / 108
 $T_{d5\%}$ (°C)..... up to 227 / 233

Colorless
 Rigid Fragile

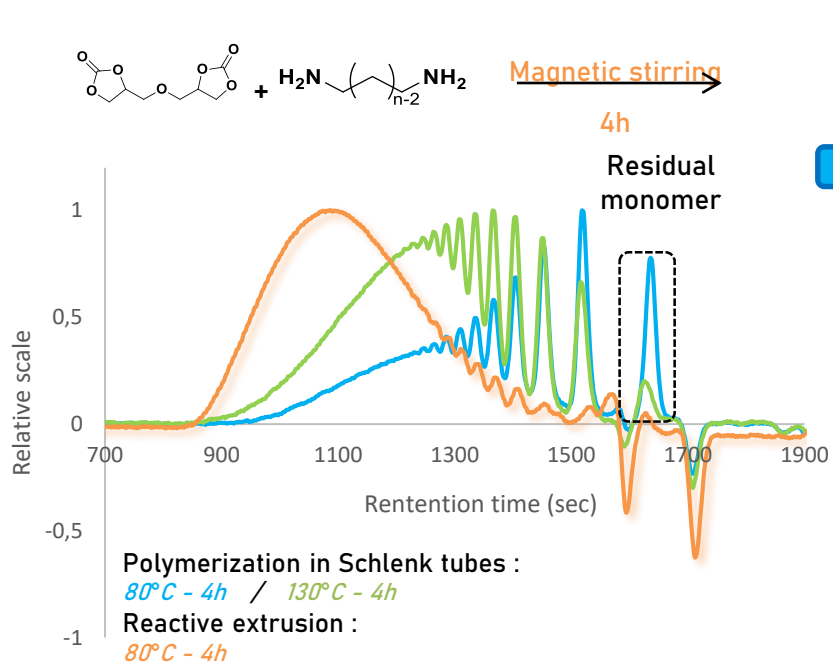
SEC analysis in DMF, with PS standards, at 50°C
 DSC second heating cycle at 10°/min
 TGA traces at 10°C/min



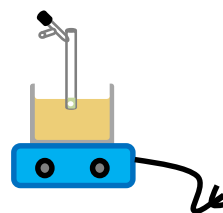
NMR spectra of DGDC monomer (up) and DGDC based PHU (down)



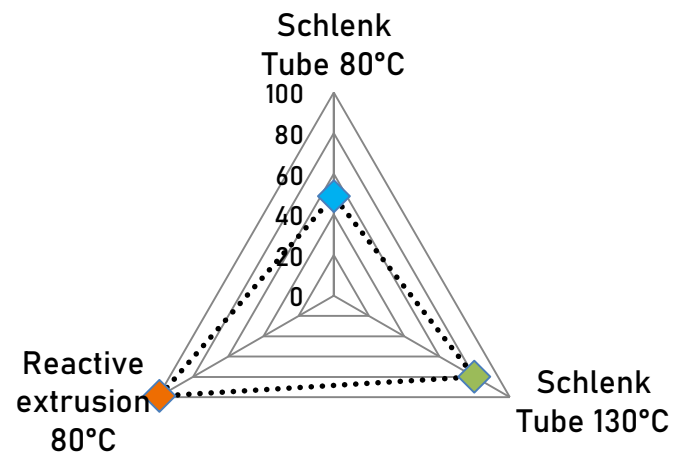
> Comparison with bulk polymerization in Schlenk tubes



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



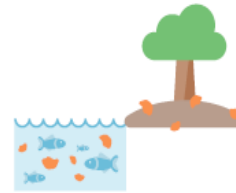
Conversion after 4h (%)



Conversions obtained by ¹HNMR analysis in DMSO-d₆ 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

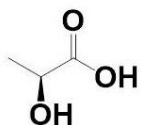
7- Conclusions and perspectives

New polymers from biomass: PLA

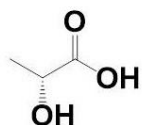
300 kt



Starchy Materials

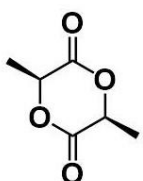


L-lactic acid

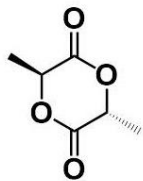


D-lactic acid

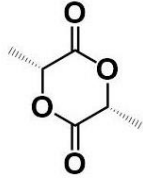
Condensation
and Depolymerization



L-lactide

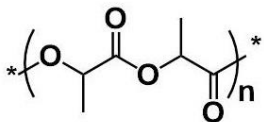


Meso-lactide



D-lactide

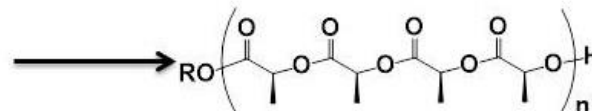
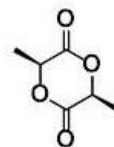
Catalytic Ring-Opening
Polymerization (ROP)



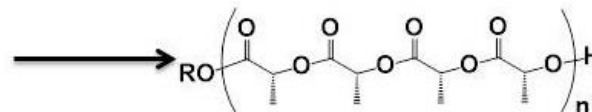
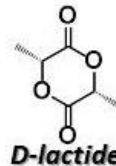
High Molecular Weight PolyLactide (PLA)

Microstructure control

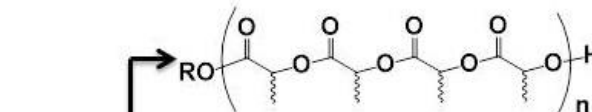
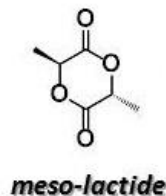
L-lactide



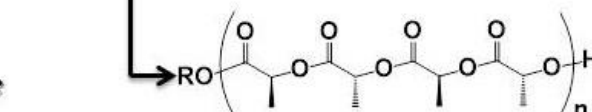
Isotactic PLLA



Isotactic PDLA



Atactic PDLLA



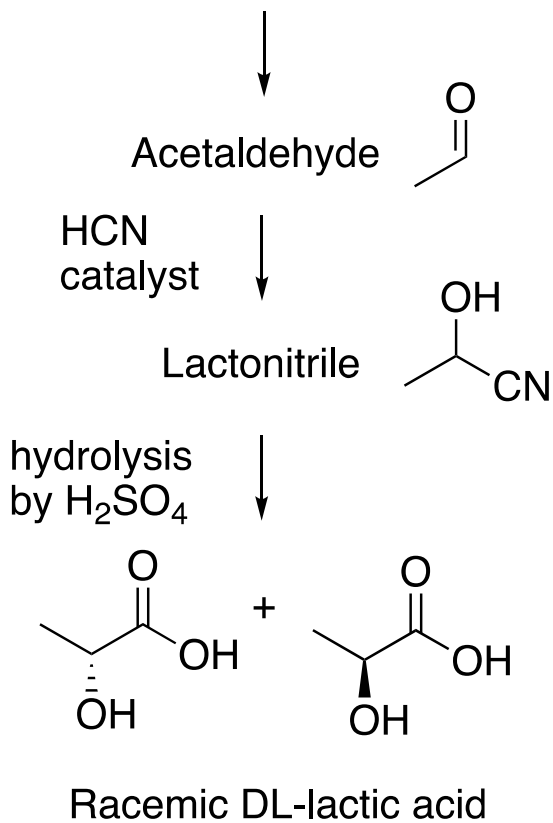
Syndiotactic PDLLA

Properties control

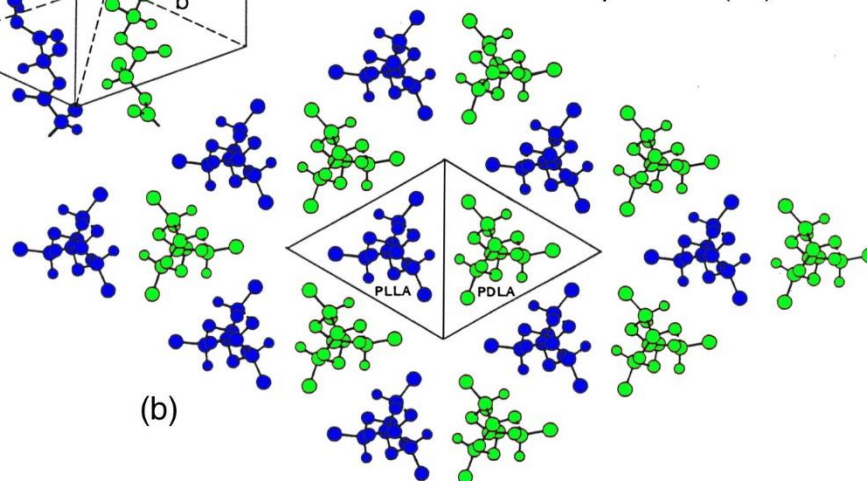
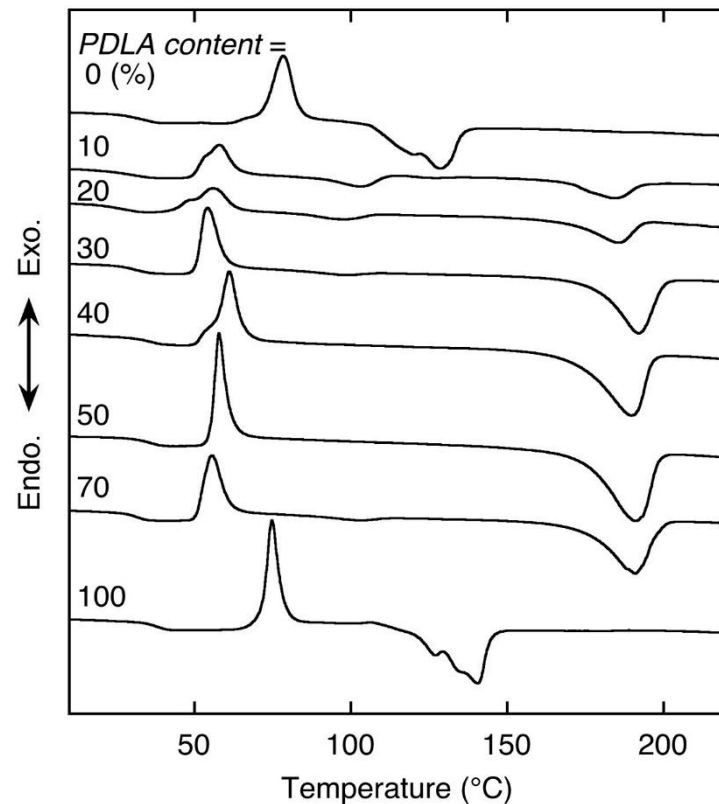
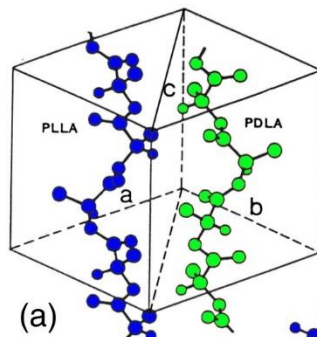
Physical properties	PLLA (PDLA)	Atactic PDLLA	Syndiotactic PDLLA
Tm (°C)	170-180	-	151
Tg (°C)	55-60	50-60	34
ΔHm (100%) (J.g ⁻¹)	93	-	-

Why PLA is not petro-sourced?

Petro-chemical resources



PLLA/PDLA stereocomplex

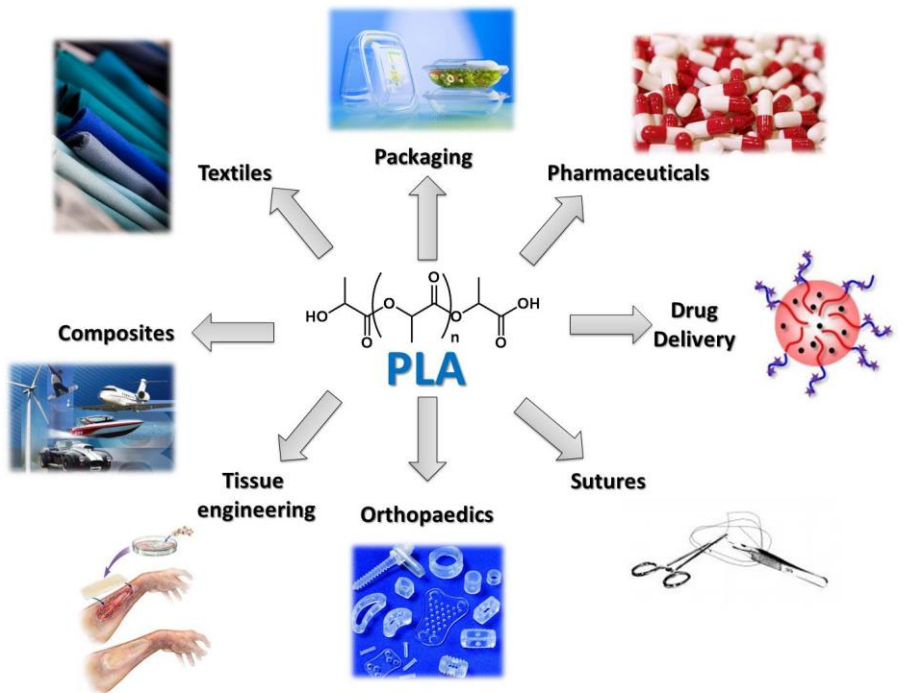


New polymers from biomass: PLA



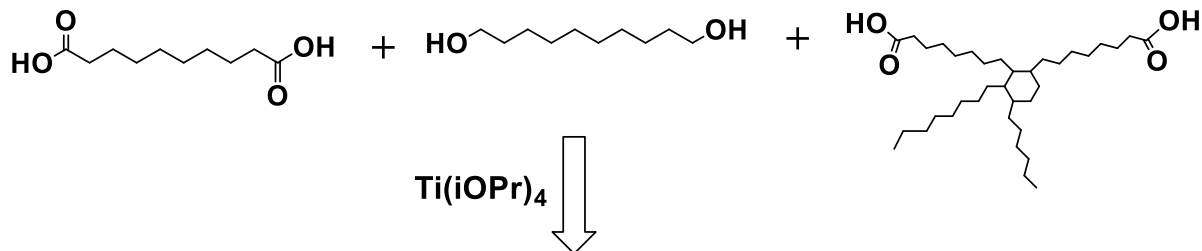
Biobased, Compostable, Stiff

	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

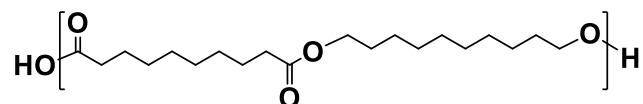


Heat stability, Low crystallization rate, Brittleness

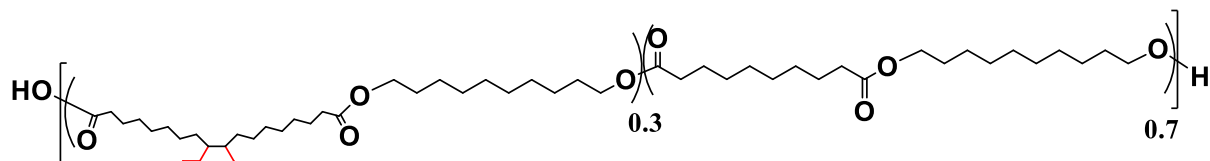
PLA additive: Synthesis



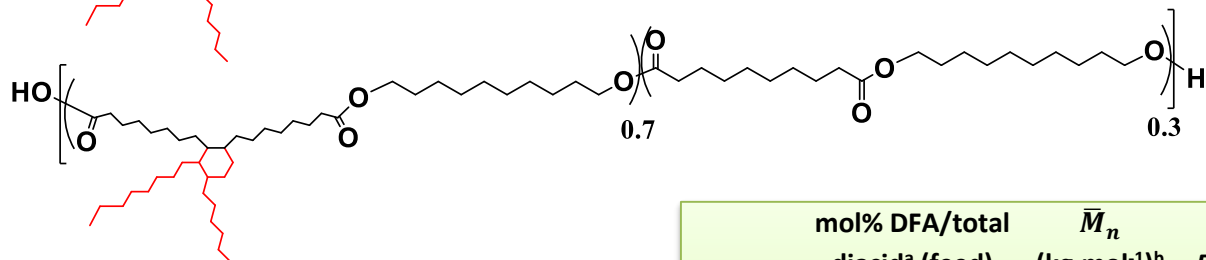
DFA0



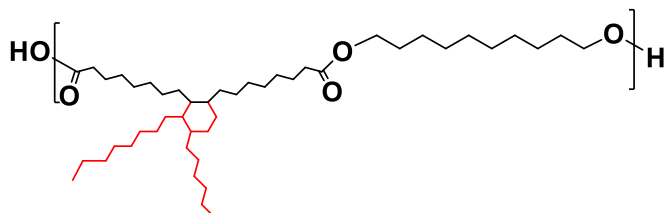
DFA0.3



DFA0.7



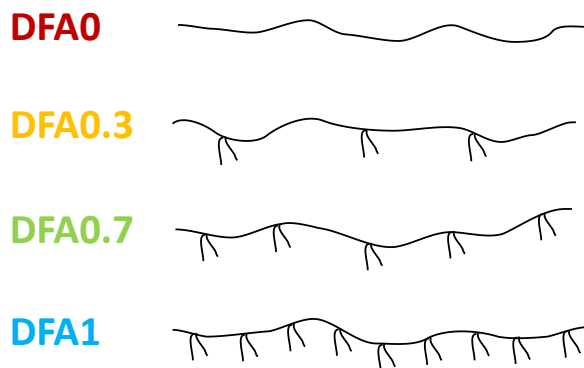
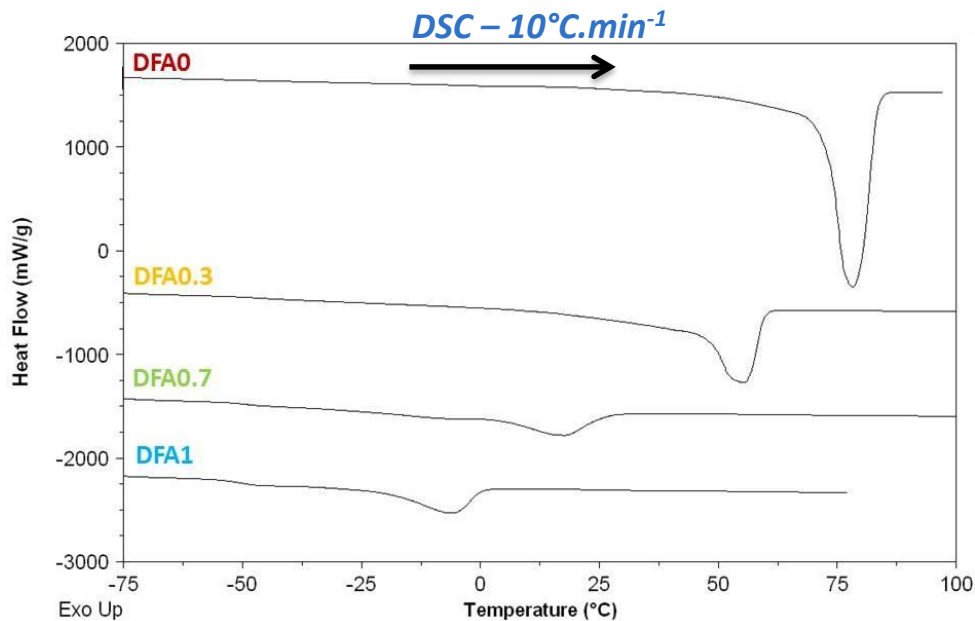
DFA1



	mol% DFA/total diacid ^a (feed)	\bar{M}_n (kg.mol ⁻¹) ^b	ρ^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

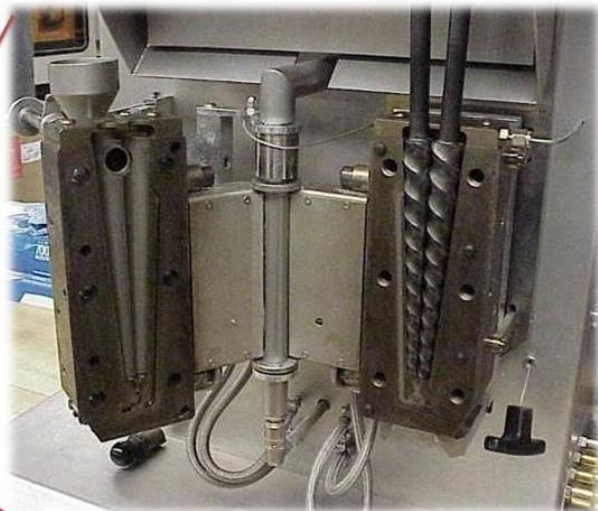
PLA additive: Properties



	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

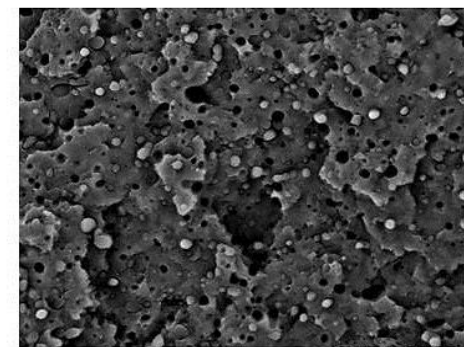
PLA additive: Processing



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



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



10%

30µm

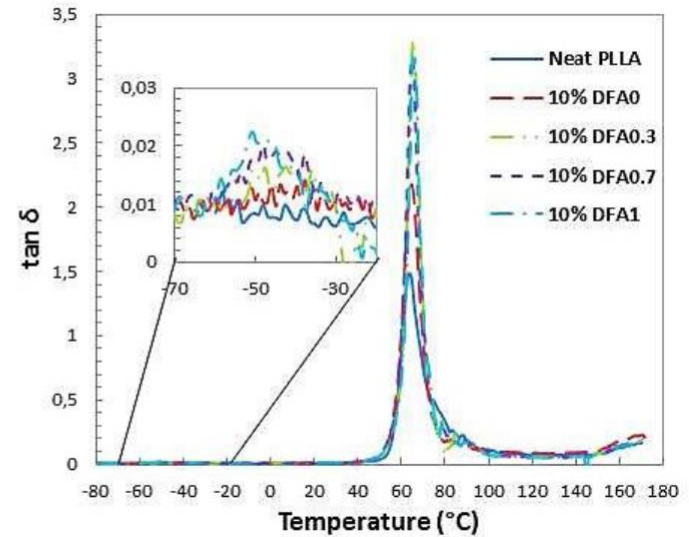
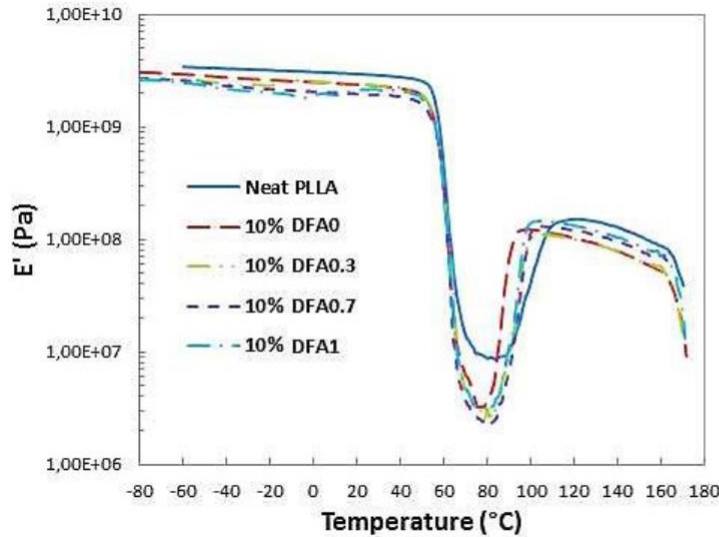
LCPO

Laboratoire de Chimie des
Polymères Organiques

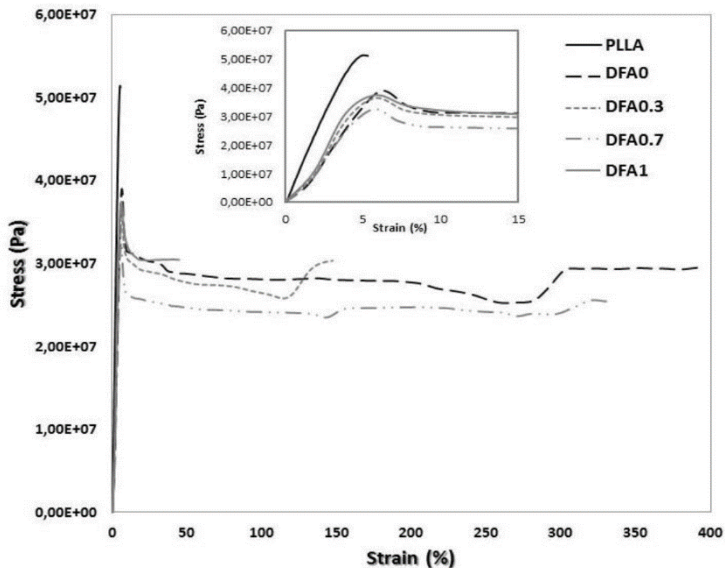
PLA additive: Mechanical Properties

DMA

Heat
stability



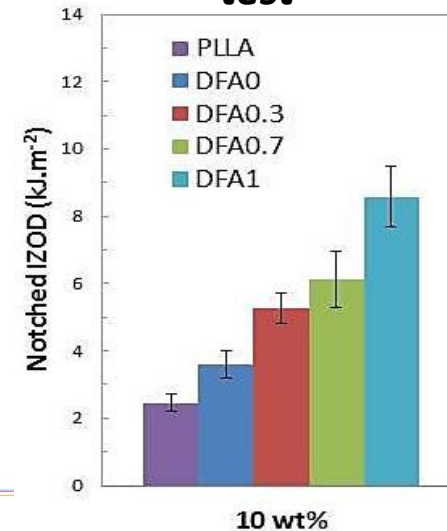
Tensile test



Brittleness

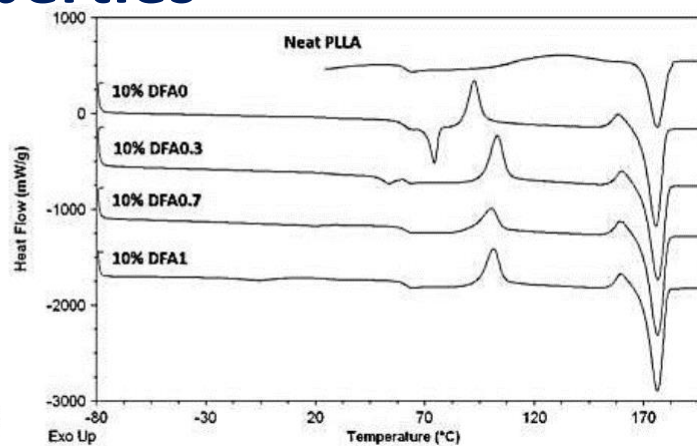
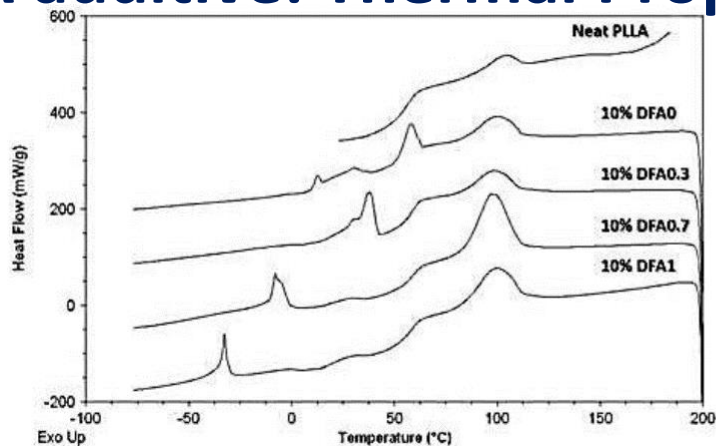


Impact strength
test



PLA additive: Thermal Properties

DSC



Isothermal crystallization

Avrami equation :

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

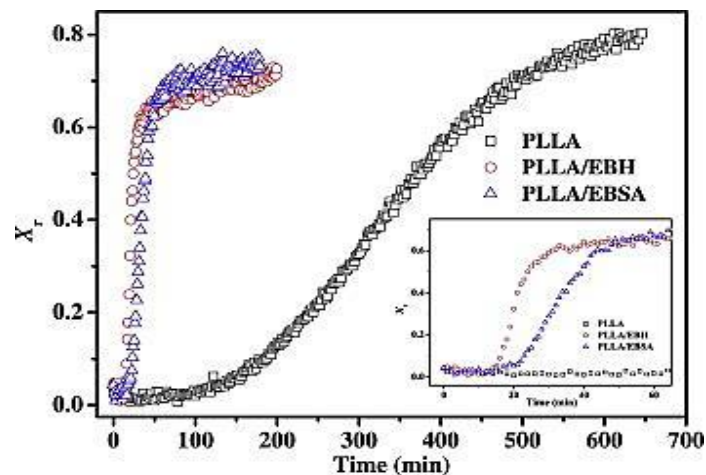
Half-time of crystallization :

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

α_c : the relative crystalline volume fraction

k : rate constant of crystallization

n : Avrami index



	n	k (min ⁻ⁿ)	t _{1/2} (min)
PLLA	1.80	0.027	6.12
10wt% DFA0	3.53	0.021	2.70
10wt% DFA0.3	3.73	0.014	2.85
10wt% DFA0.7	3.81	0.116	1.60
10wt% DFA1	4.20	0.015	2.48

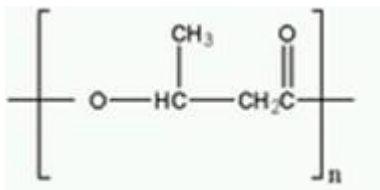
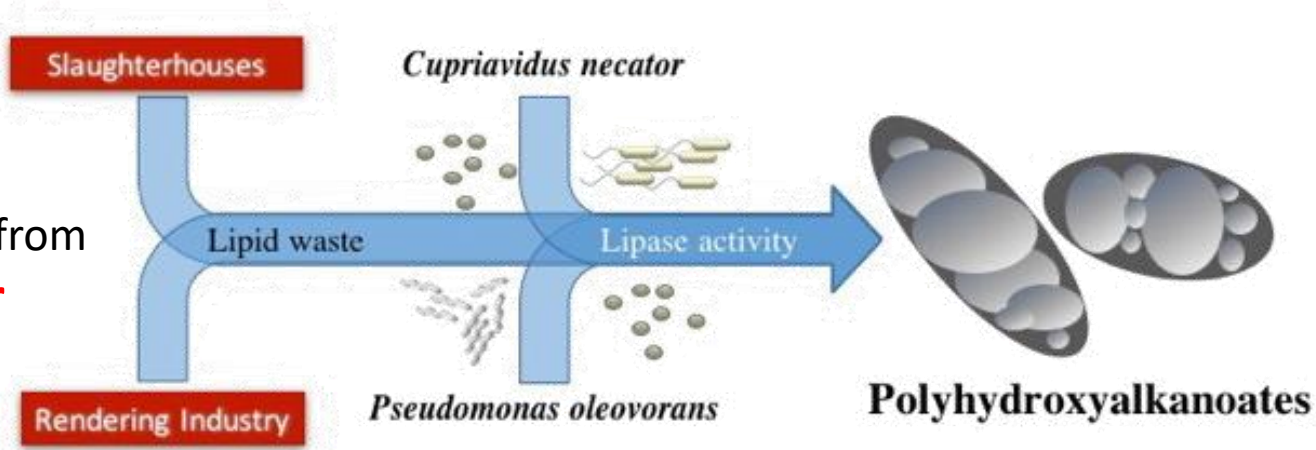


New polymers from biomass: PHA

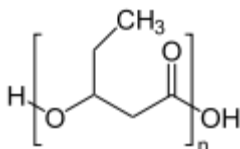
40 kt

One-pot biosynthesis from
biomass to polymer

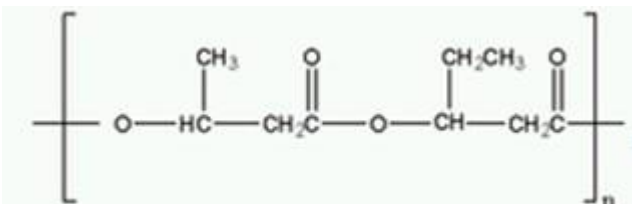
Max prod. 3 g.L⁻¹.h⁻¹



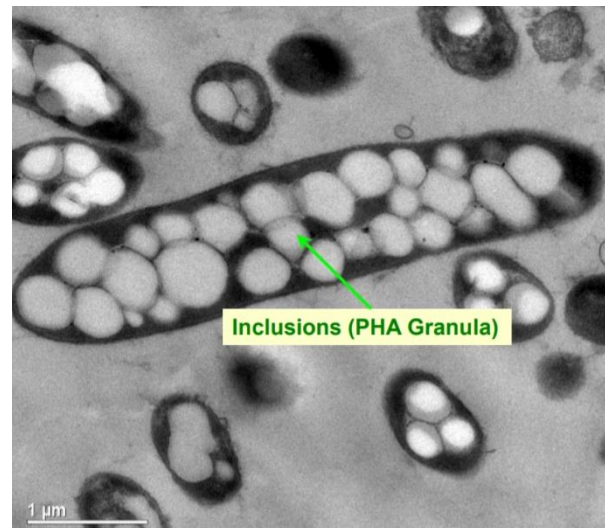
Polyhydroxybutyrate (PHB)



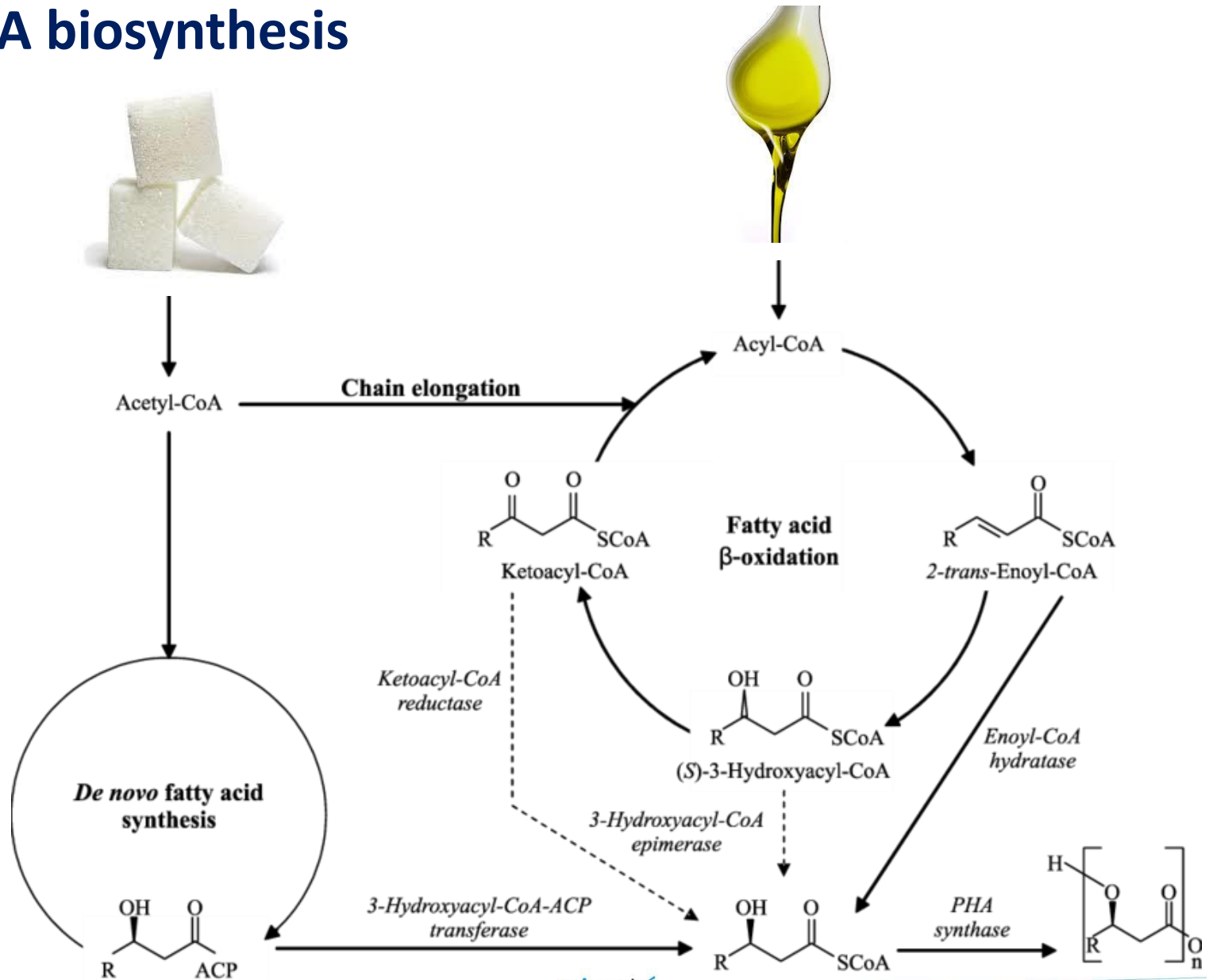
Poly-3-hydroxyvalerate (PHV)



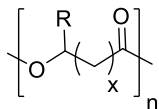
Poly(hydroxybutyrate-co-hydroxyalkanoates) (PHBV)



PHA biosynthesis



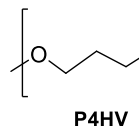
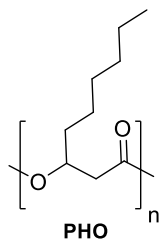
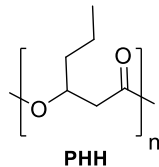
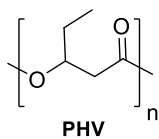
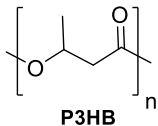
PHA properties



PHA general structure

x = 1-4

R = Saturated, unsaturated, branched or substituted alkyl chain

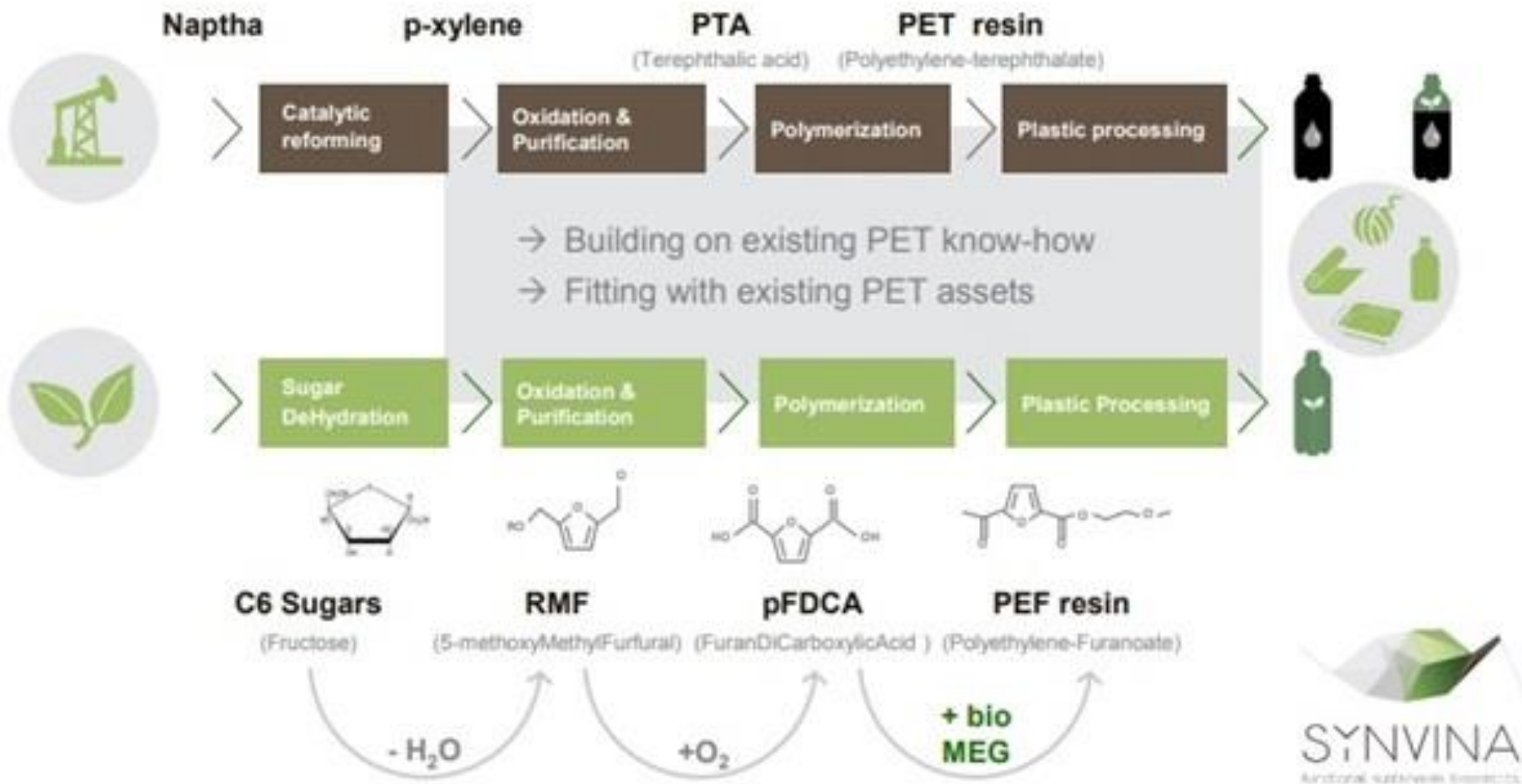


	PHB	PHBV	PHBHHx	MCL-PHA
Tm (°C)	170 to 180	130 to 170	95 to 150	40 to 60
Tg (°C)	-5 to 5	-10 to 0	-3 to -1	-60 to -30
Mw x 10 ³ (g mol ⁻¹)	Up to 1500	Up to 1200	/	50 to 300
Density (g cm ⁻³)	1.24	1.20	/	1.02
Crystallinity (%)	60 to 80	30 to 80	10 to 50	Up to 30
Tensile strength (MPa)	40	30 to 40	/	Up 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	<ul style="list-style-type: none"> Flexible Good moisture and oxygen barriers Ductile
	PLASTIC BAGS		LDPE		P(3HB-co-4HB) PBHH	<ul style="list-style-type: none"> Flexible Tough Ductile
	FOOD CONTAINERS		PP		PHBV	<ul style="list-style-type: none"> Stiff High operating temperature Tough
	DISPOSABLE CUTLERY		PS		PH3B PHBV	<ul style="list-style-type: none"> Strong Stiff High softening temperature
	MEDICAL SUTURES		PLA		P(3HB-co-4HB)	<ul style="list-style-type: none"> Biocompatible Resorbable Strong



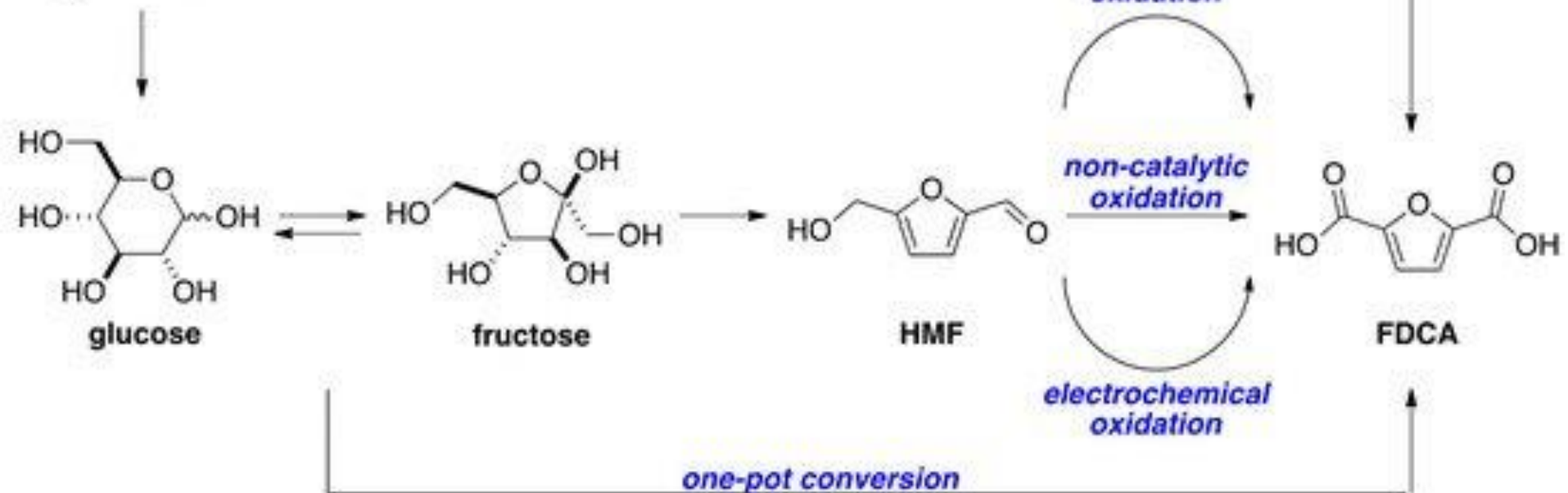
Pilot scale 40 t → 90 kt by 2025



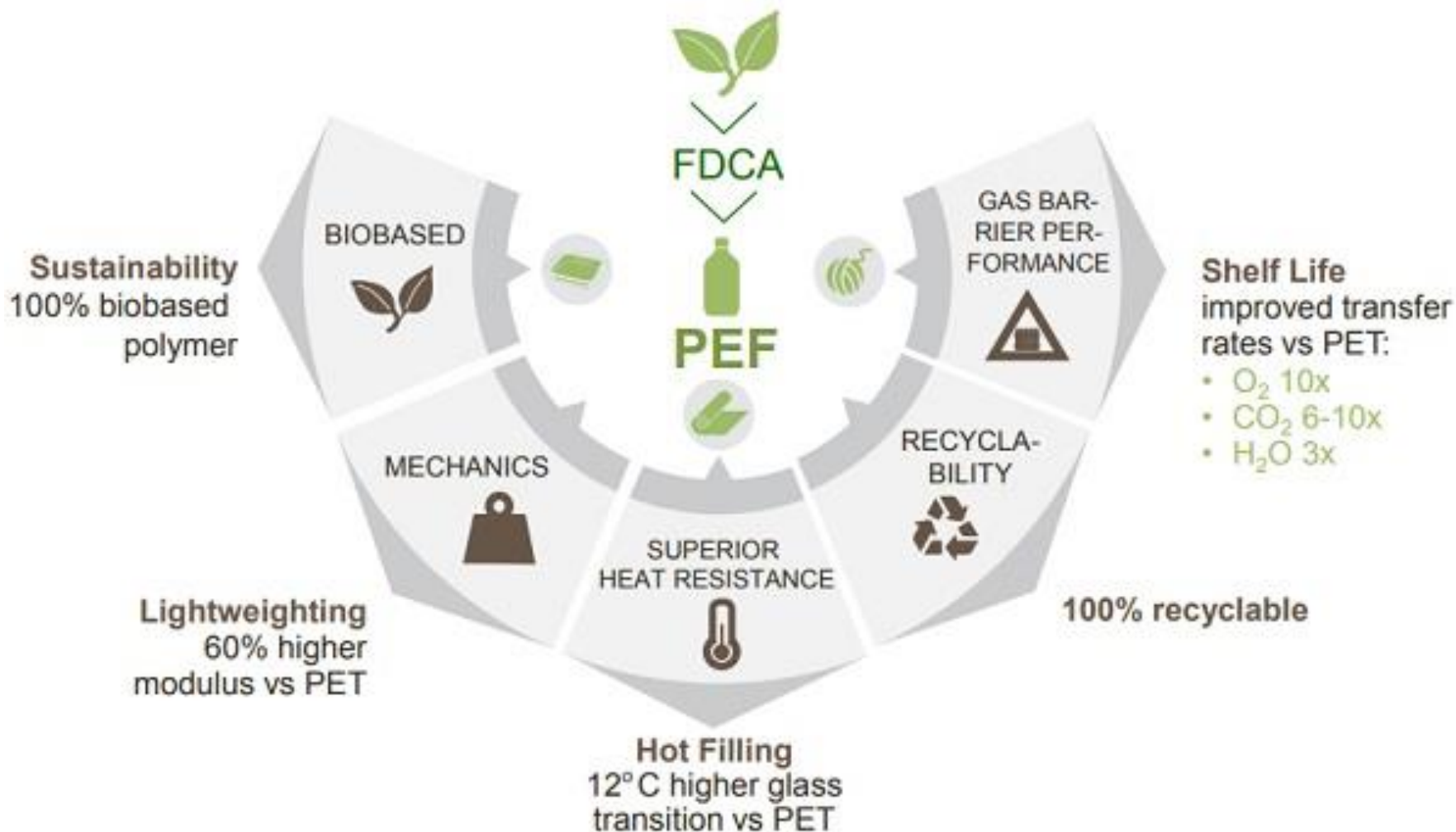
FDCA synthesis



lignocellulose

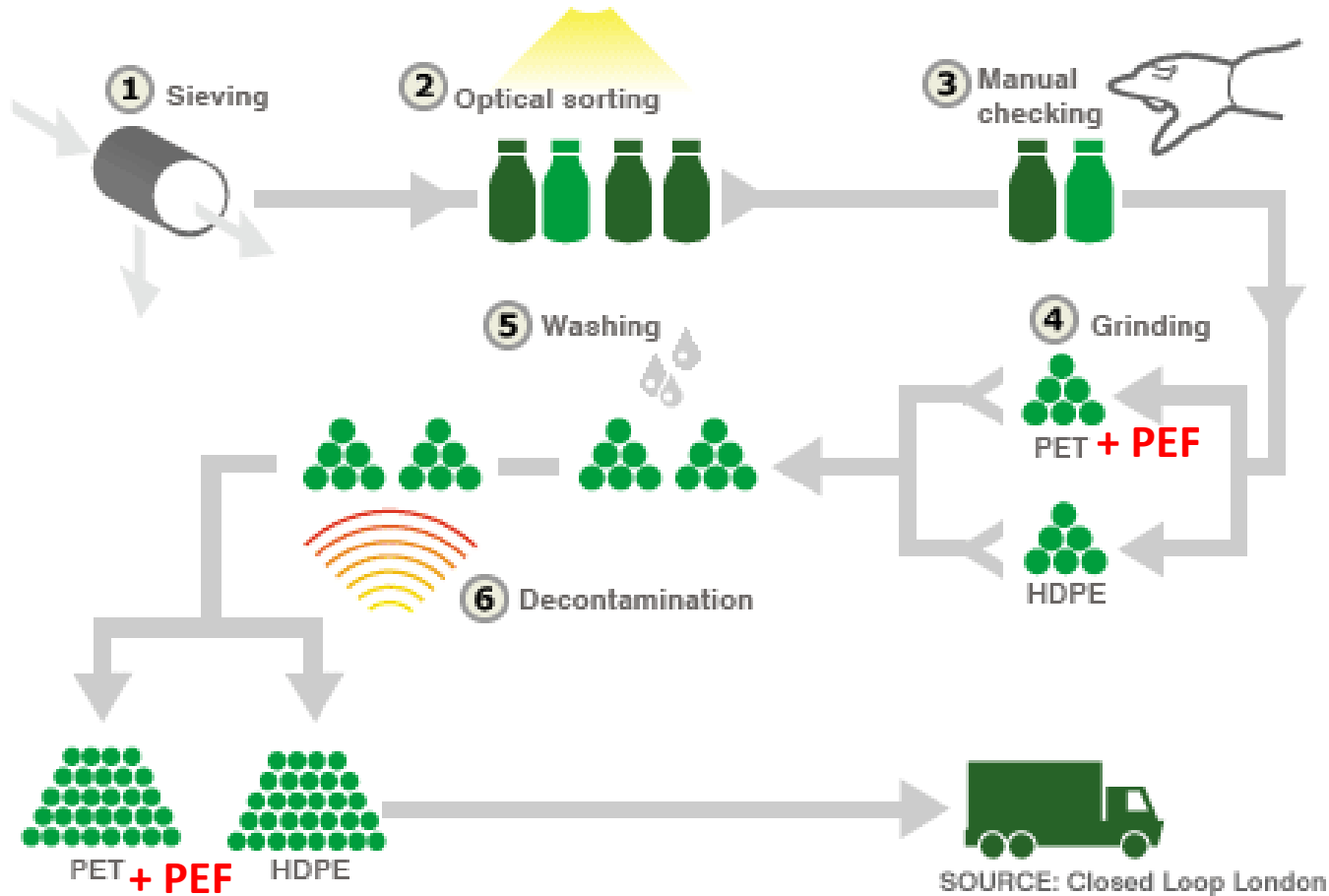


Properties



PEF as a drop-in from PET bottles ? No

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

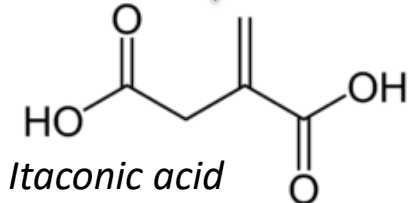


1) 100% bio-based PET is competitive in term of price

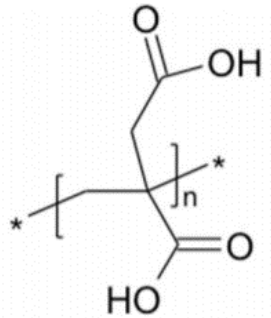
New polymers from biomass: SAP's



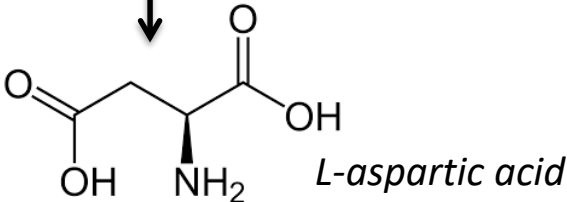
Fermentation



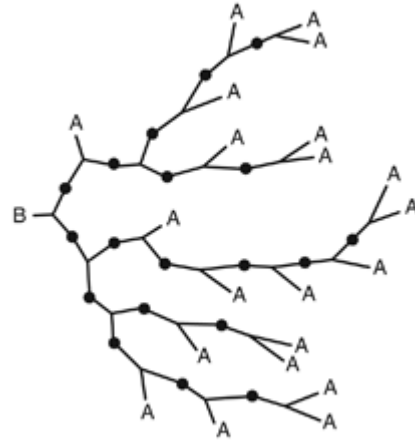
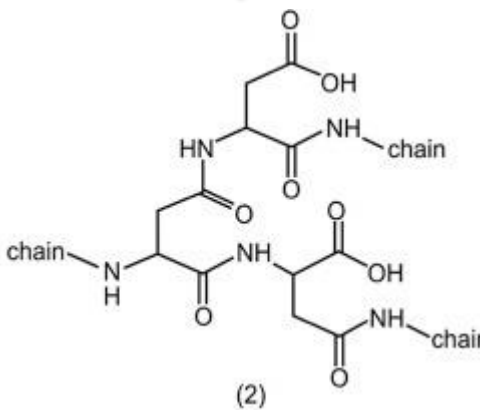
Polymerization



Fermentation



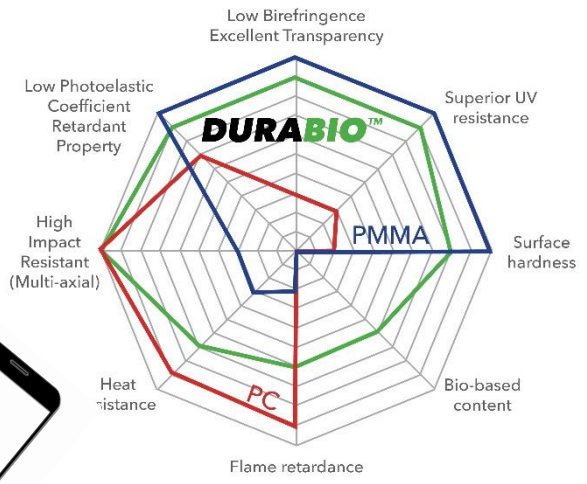
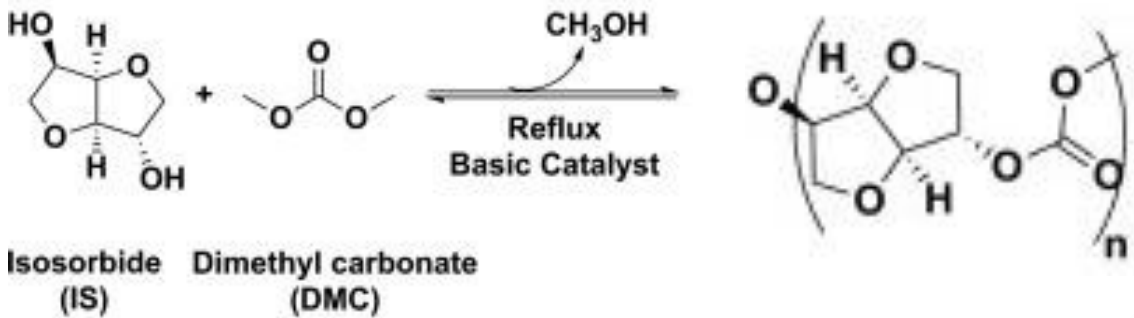
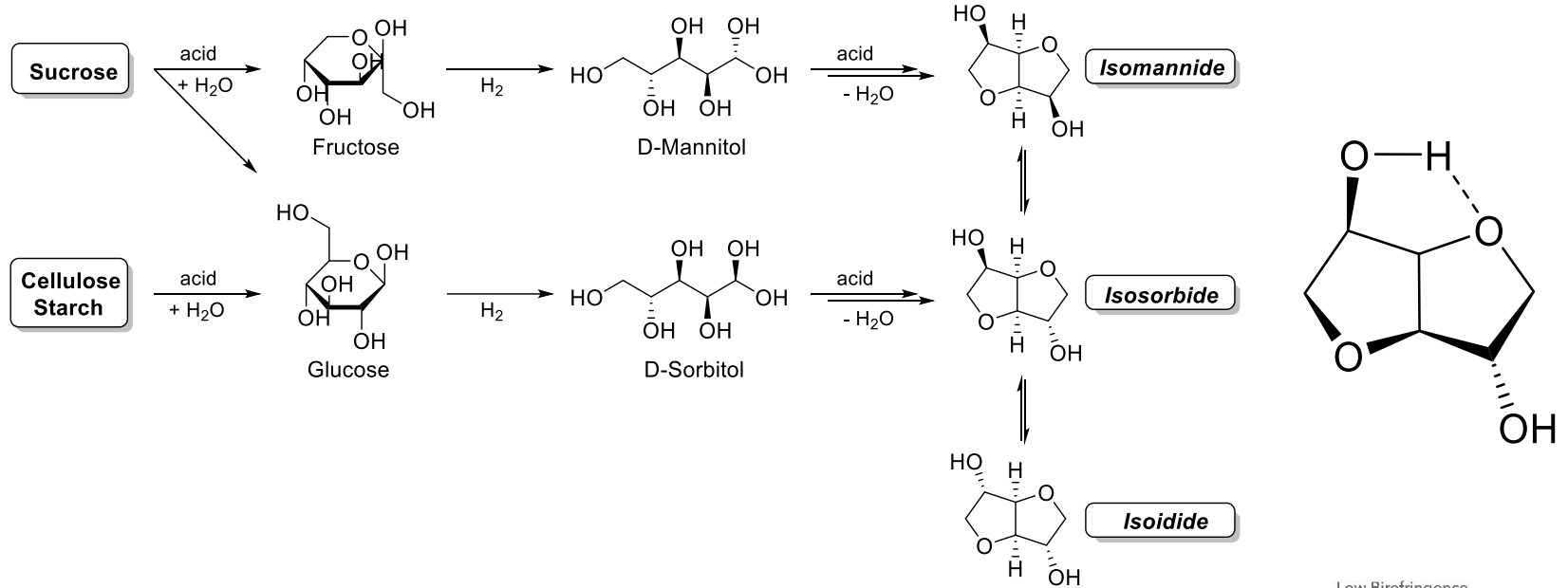
Polymerization



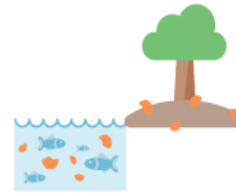
Hyperbranched Polymer

New polymers from biomass: PIC

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

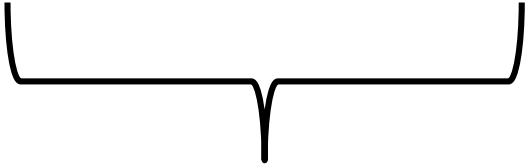
PLA, PHA, PEF

7- Conclusions and perspectives

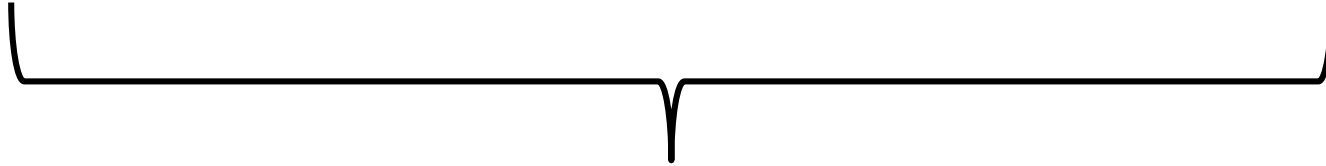
Conclusion and perspectives



Eucalyptus spruce pine coconut palm soybean rapeseed peanut castor bean



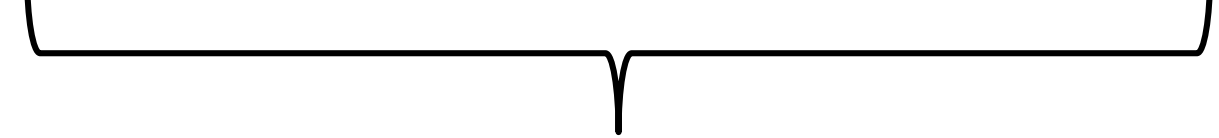
Lignocellulose



Vegetable Oil



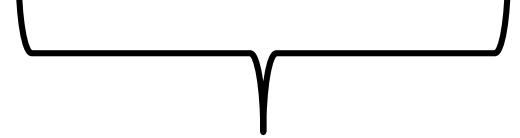
Sugarcane corn wheat rice guar



Carbohydrate

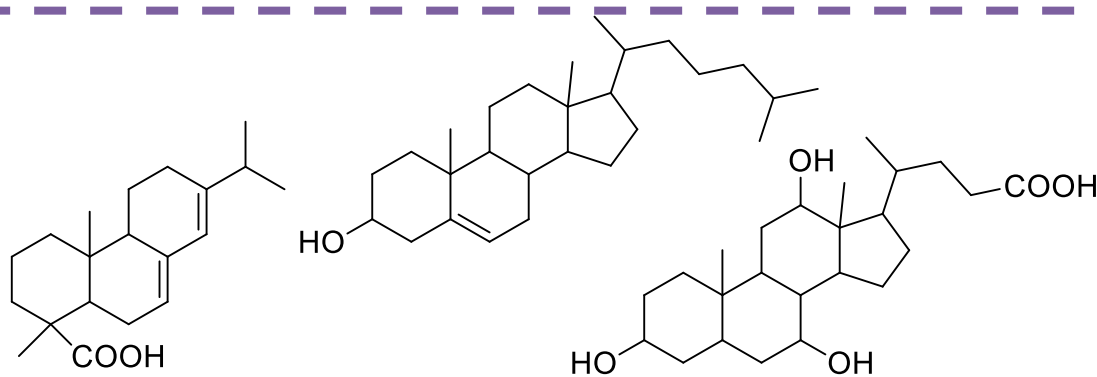
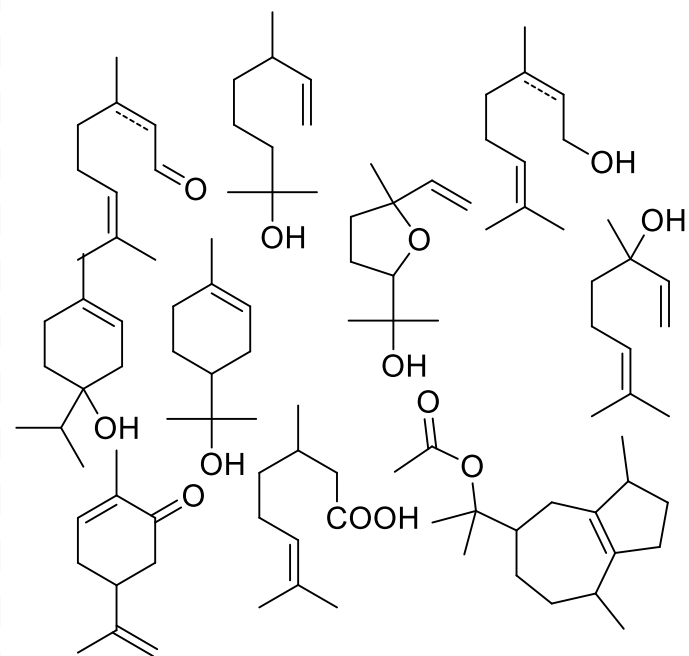
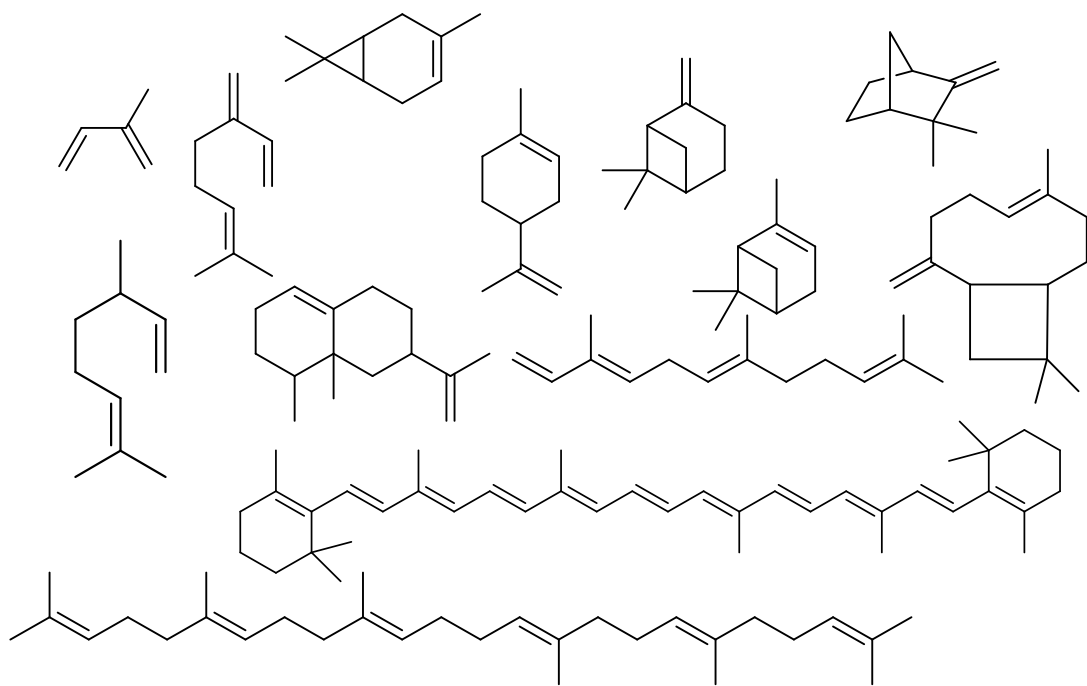


Clove citrus



Terpens?

Terpenes as a source of various backbones



> 1000 of skeletons

● ● ●

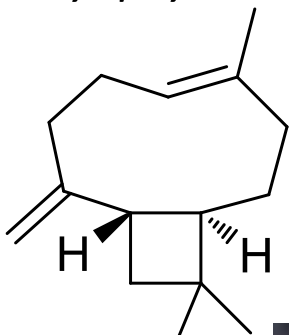


What can we do with a little of Hop?



1 €/kg

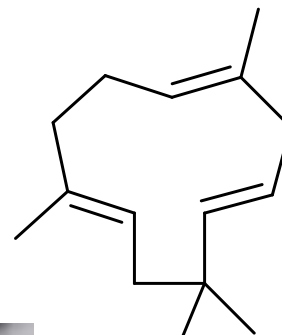
Caryophyllene



No! Polymers



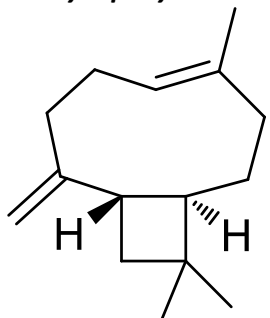
Humulene



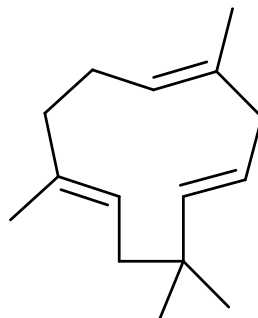
Beer !!!

First direct ROMP of natural compounds

Caryophyllene



Humulene



ROMP

ROMP

Can be performed

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

T_g = -32°C

T_g = -48°C

H₂ Pd/C

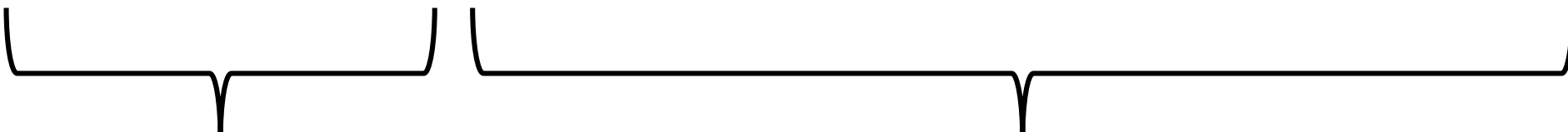
H₂ Pd/C

T_g = -16°C

T_g = -44°C

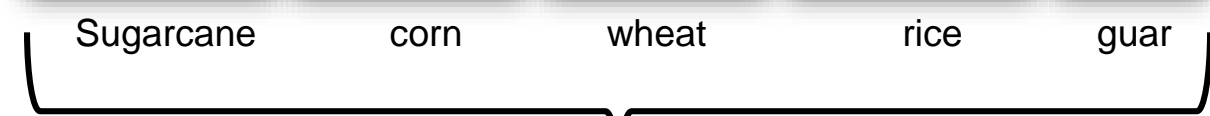


E. Grau, S. Mecking *Green Chem.*, 2013, **15**, 1112-111



Ligno

Crossing the biomass !!!



Carbohydrate

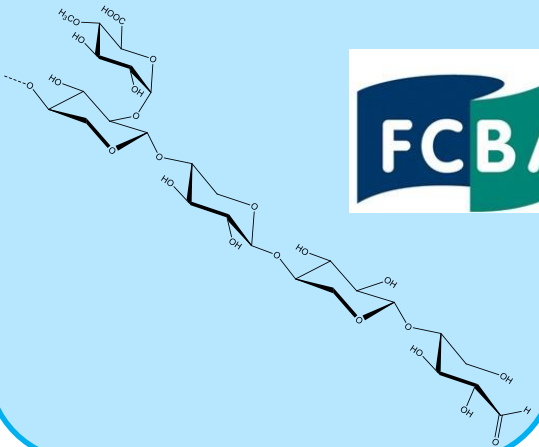


Terpens

Crossing the biomass

Wood

Xylo-oligosaccharides



FCBA

HYDROPHILIC



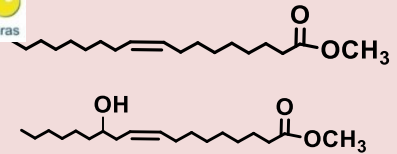
HYDROPHOBIC



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

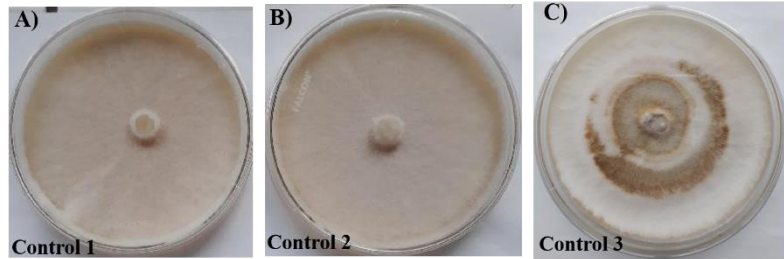
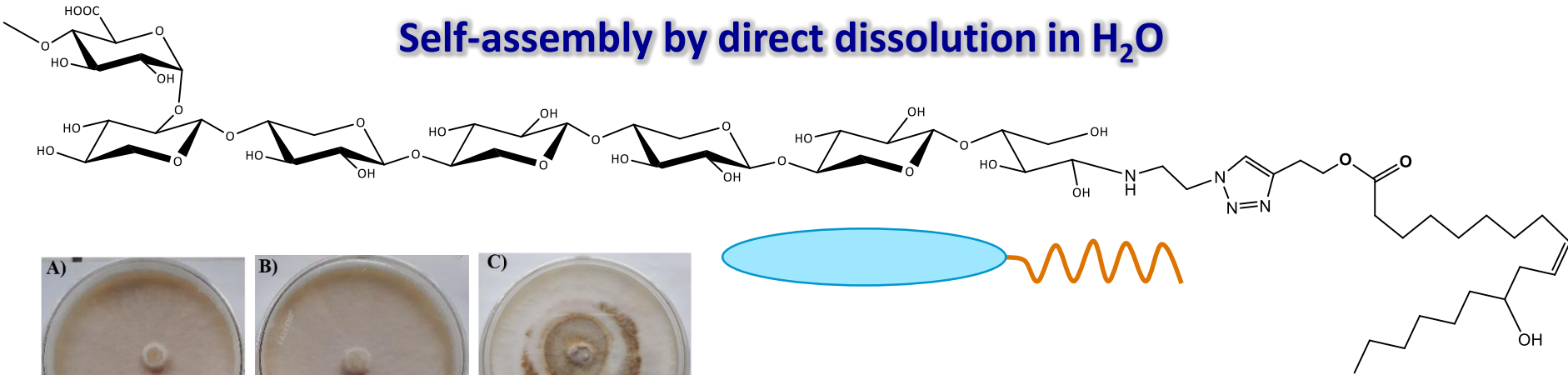
Use as emulsifier



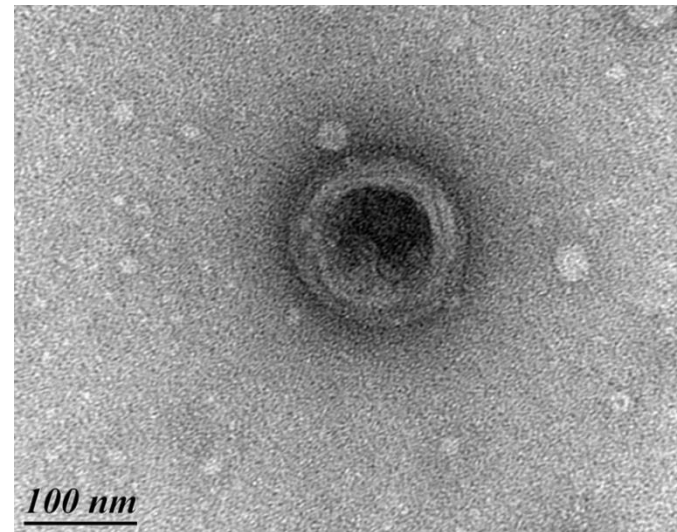
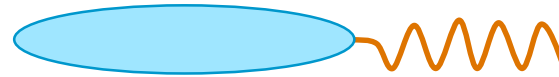
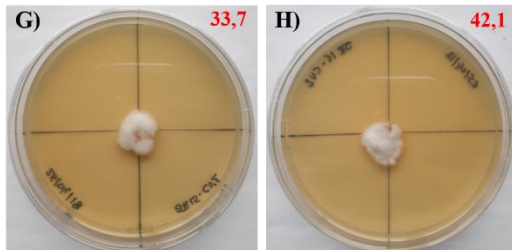
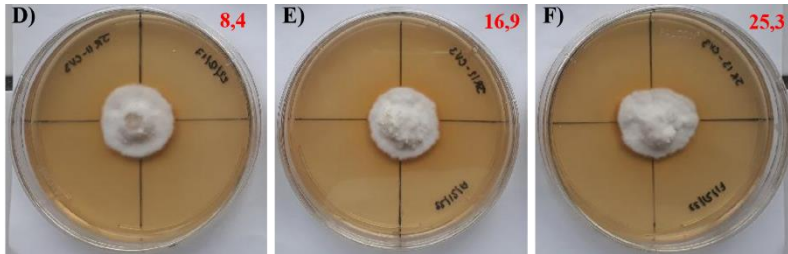
Detergents



Self-assembly by direct dissolution in H₂O

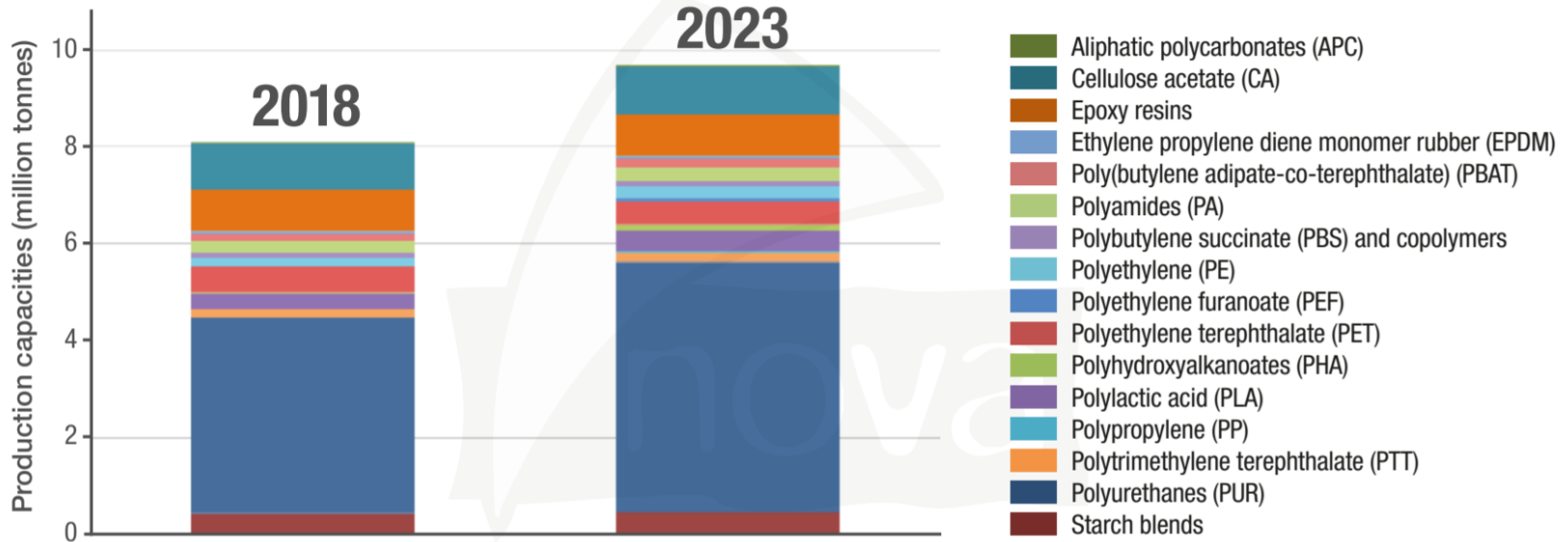


[Propiconazole] (nmol/mL)

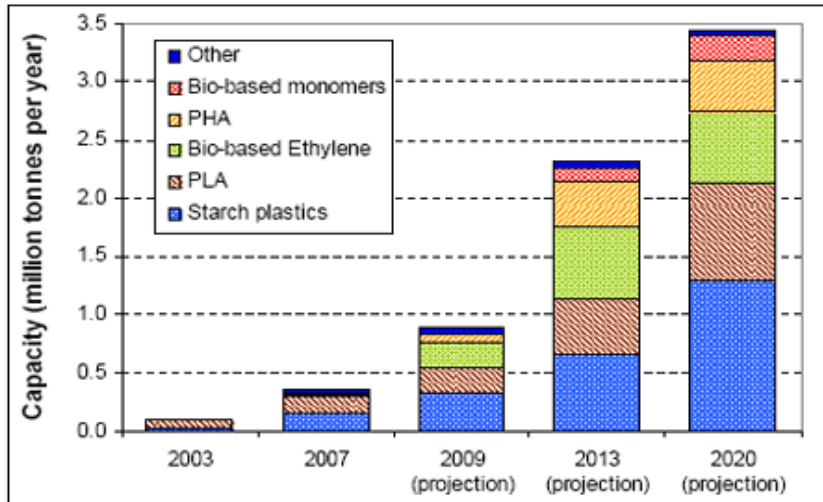


J. Rosselgong et al. Biomacromolecules, 20(1), 118-129 (2019)

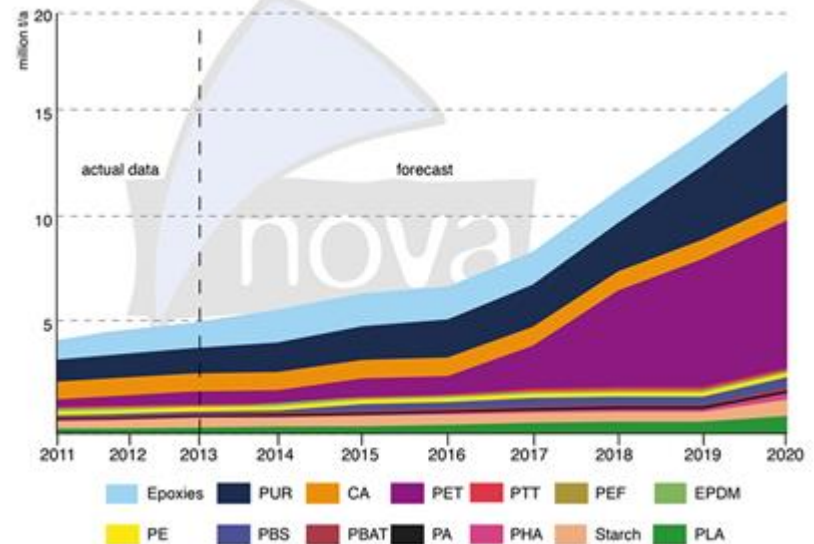
Bio-based polymers forecast



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 ???

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