Bio-sourced polymers

Etienne Grau

Bio-sourced polymers

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

Outlines

1- Why ?

2- How ?

3- Bio-based plastics from natural polymers

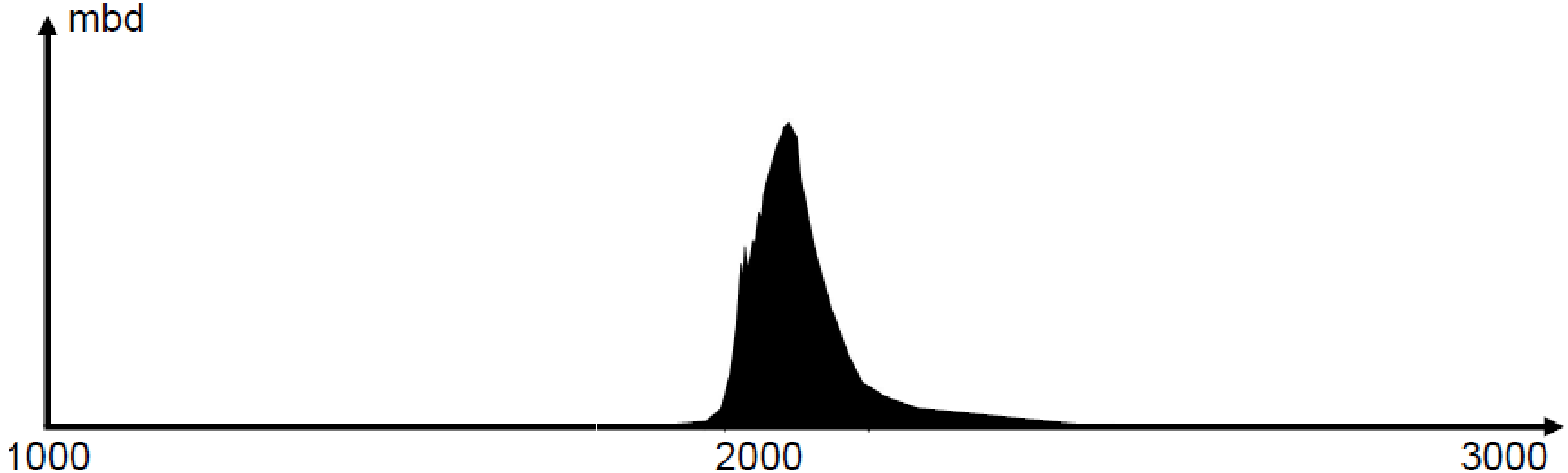
4- Drop-ins: Bio-based alternative to fossil-based polymers

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

6- New polymers from biomass

7- Conclusions and perspectives

Age of Oil



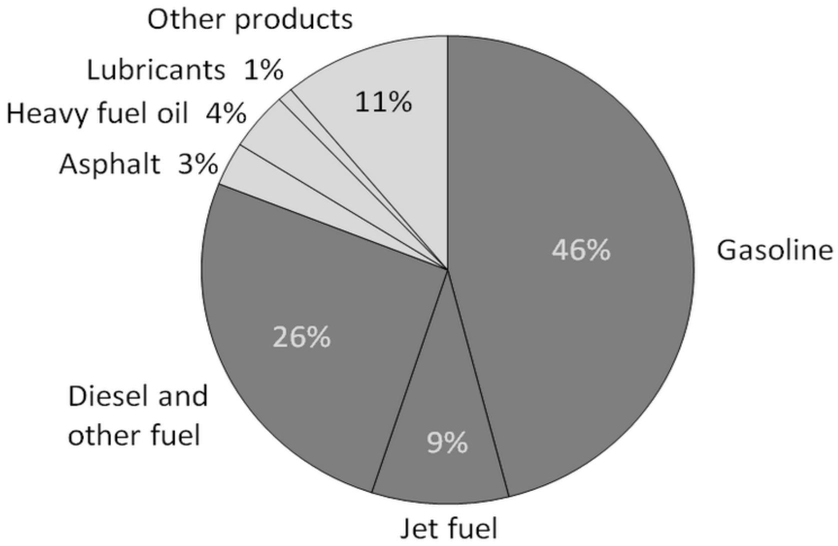
Petroleum: The Source of Chemicals

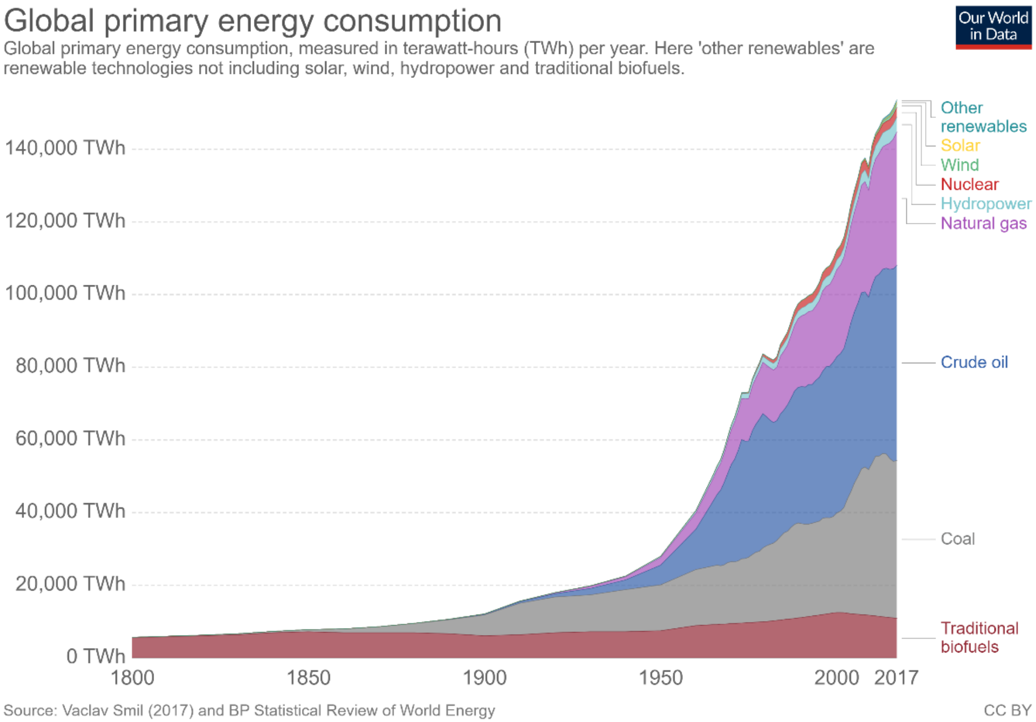
Petroleum is the starting materials of 99% « commodity » chemicals

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

Petroleum = C

Petroleum = J

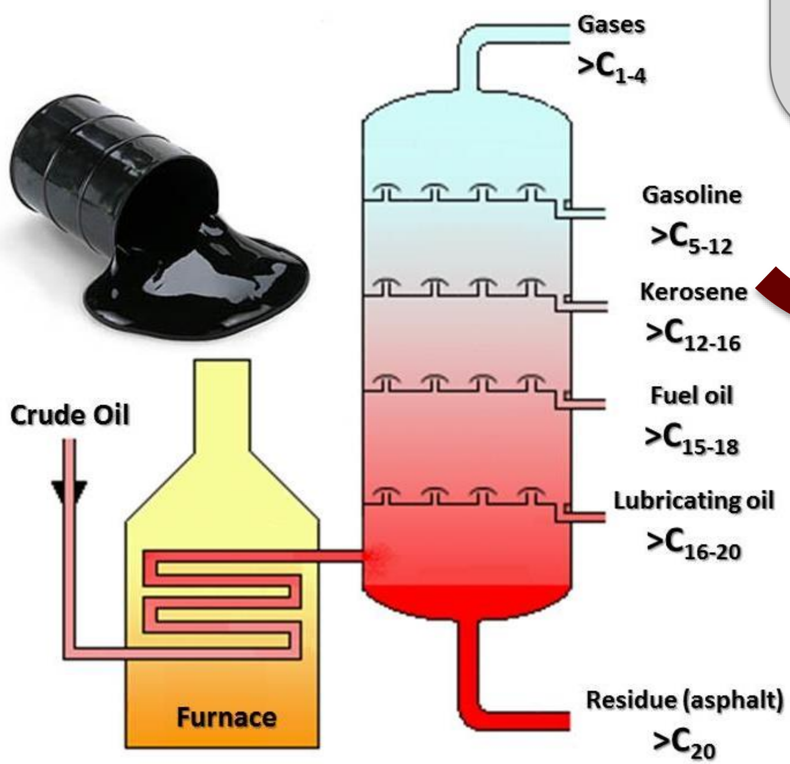




Synthetic polymers are based on petroleum

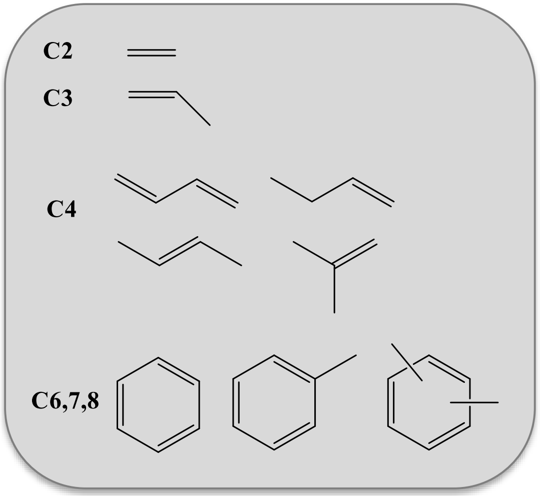
20th century:

A petroleum area



Cracking

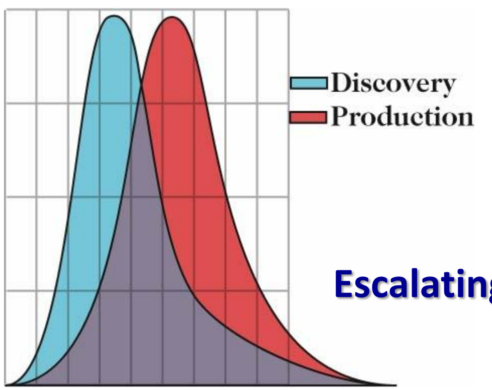
Platform molecules



Synthetic polymers

~350 million tons
(annual global production)

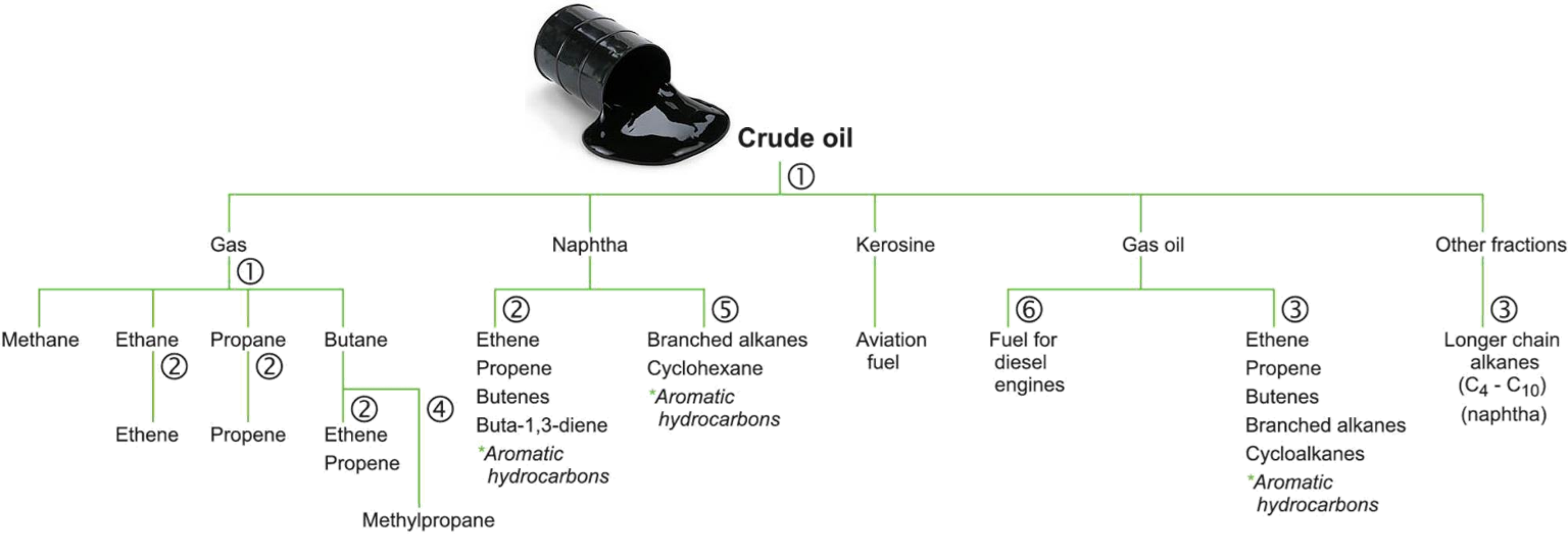
Steel 1800 Mt (230 Mm^3)



PEAK OIL

Oil depletion
Escalating prices of oil resources

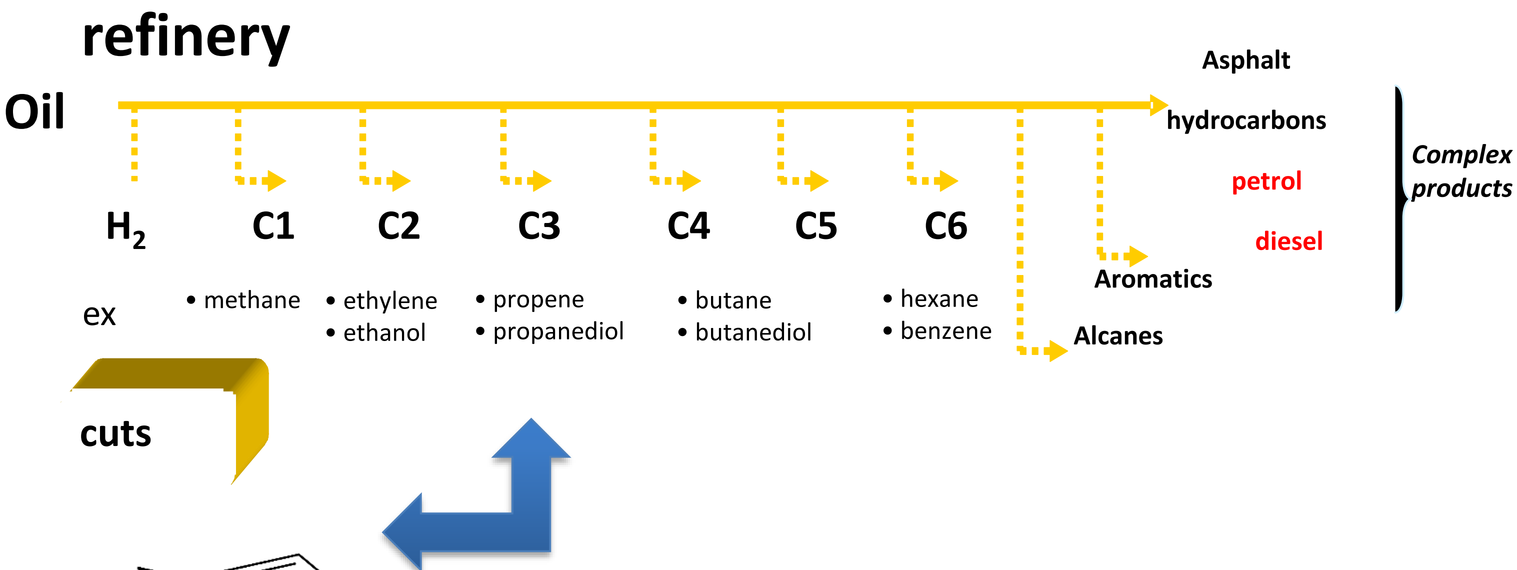
From crude oil to platform molecules

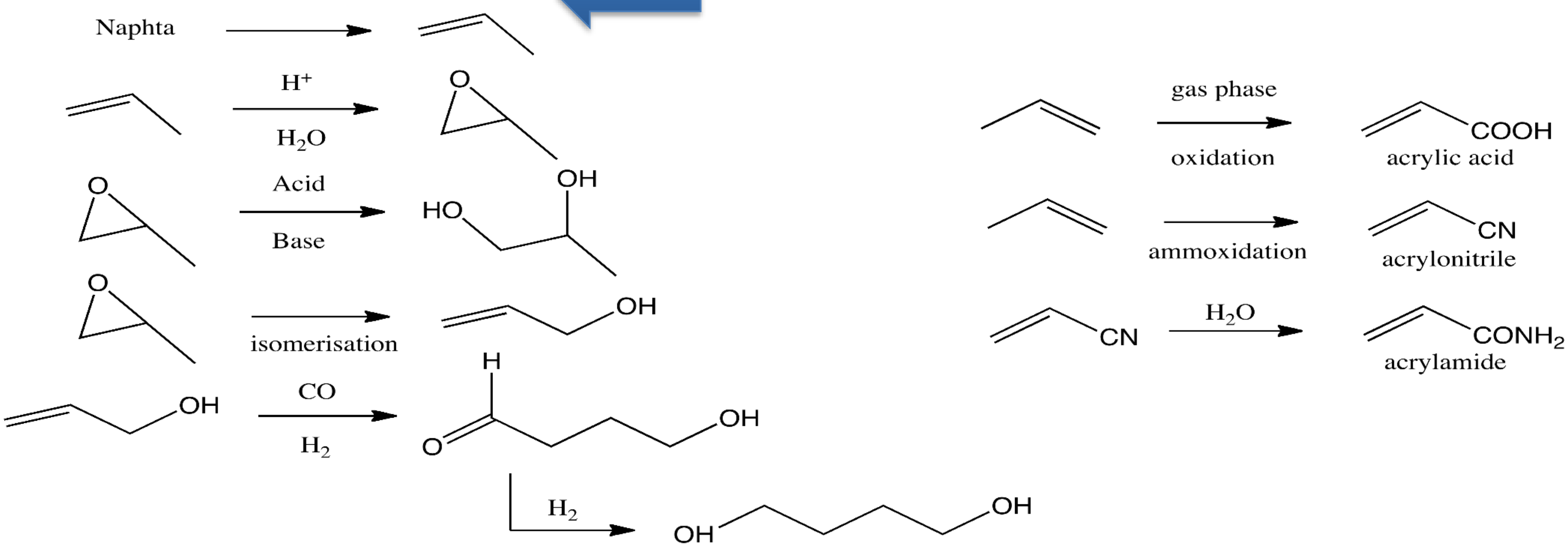


① Distillation
② Steam cracking
③ Catalytic cracking ('hydrocracking')
④ Isomerisation
⑤ Reforming ('platforming')
⑥ Sulfur is removed

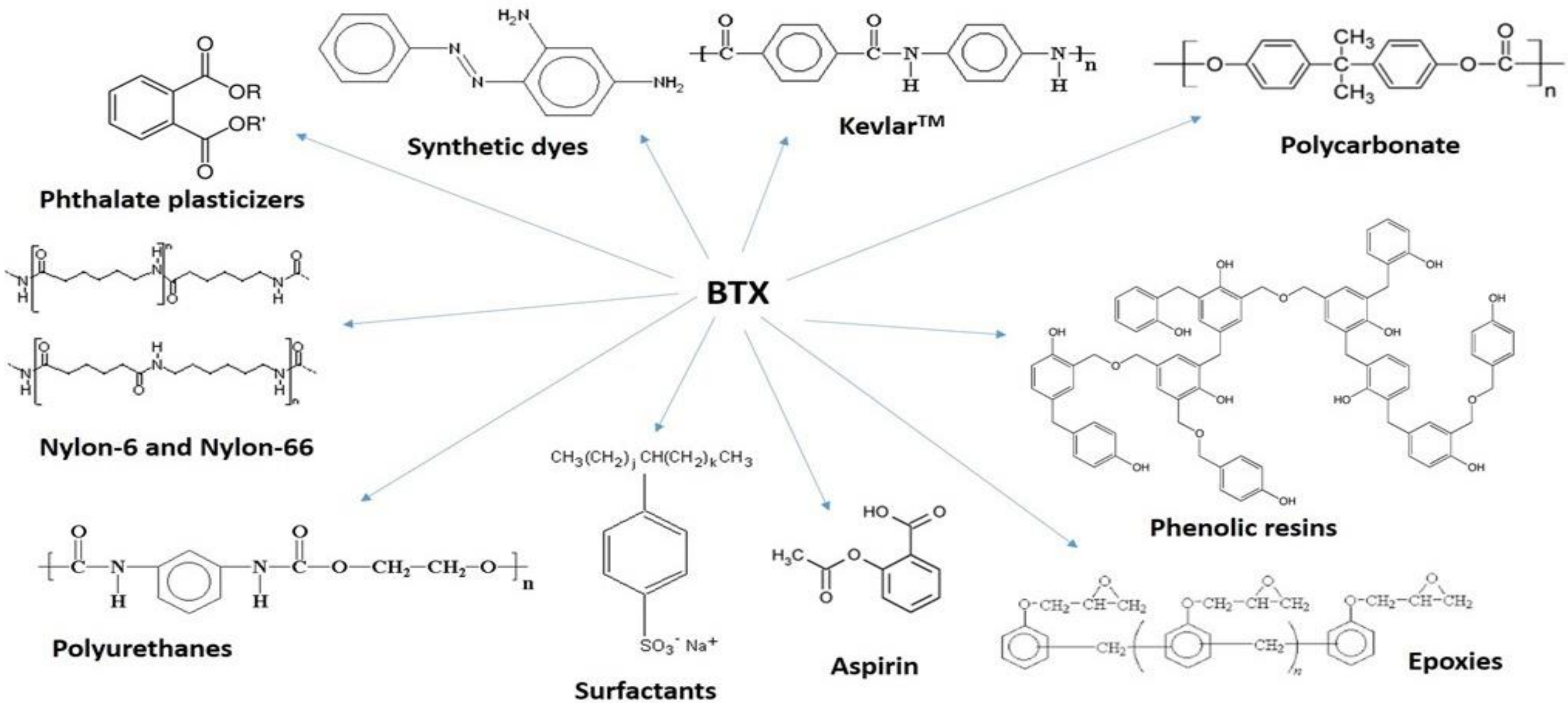
Aromatic hydrocarbons:
- benzene
- methylbenzene
- dimethylbenzenes
- ethylbenzene

Oil refinery – example of the C3 platform

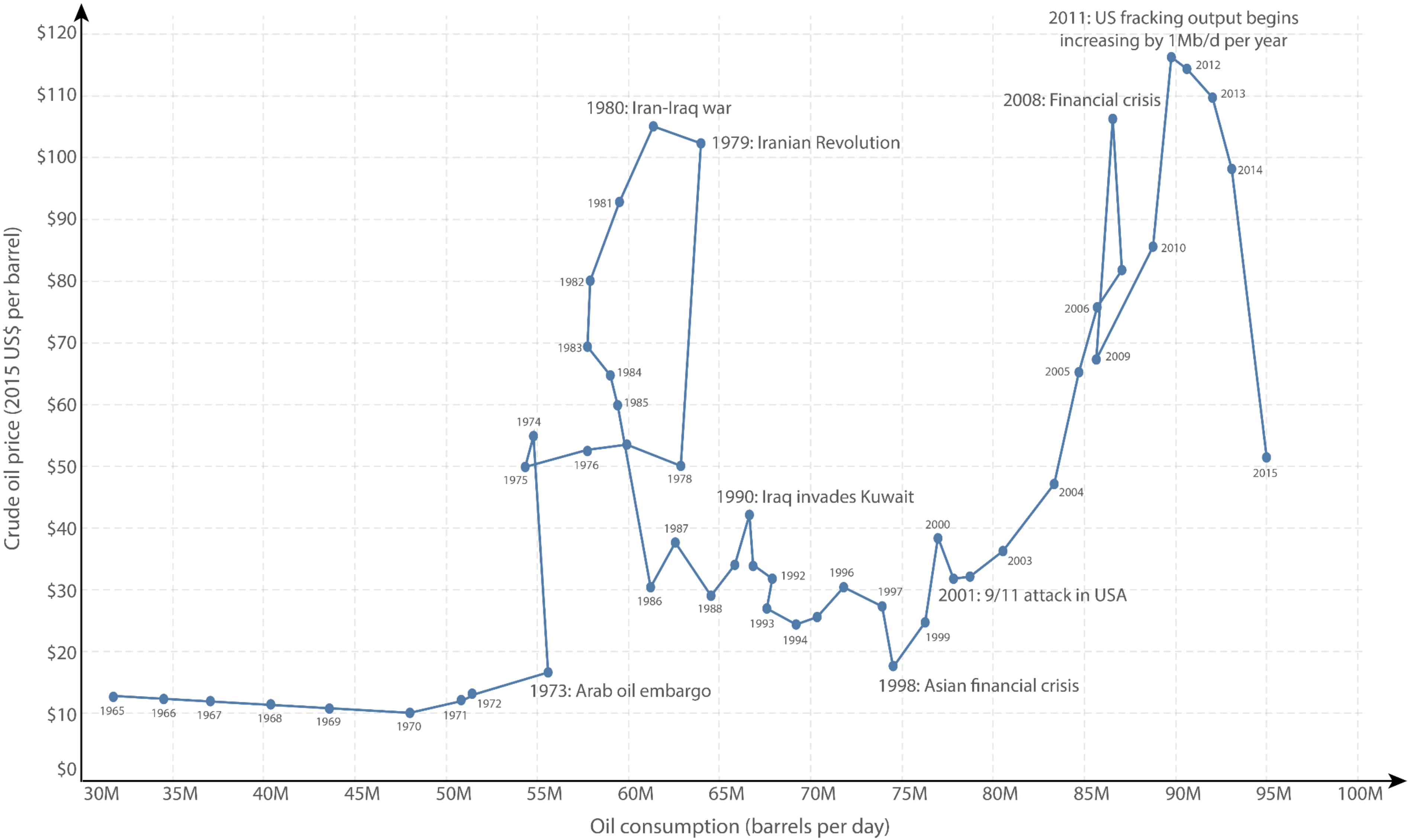




Oil refinery – example of the BTX platform



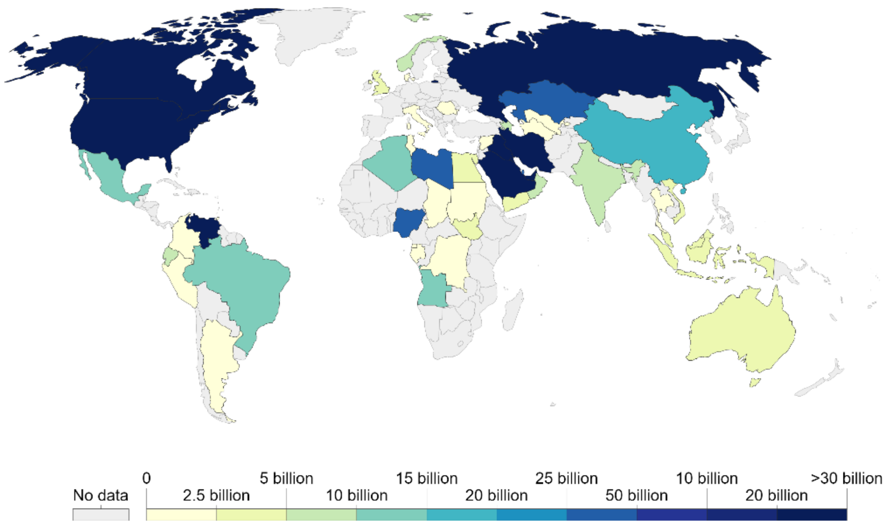
World crude oil price vs. oil consumption

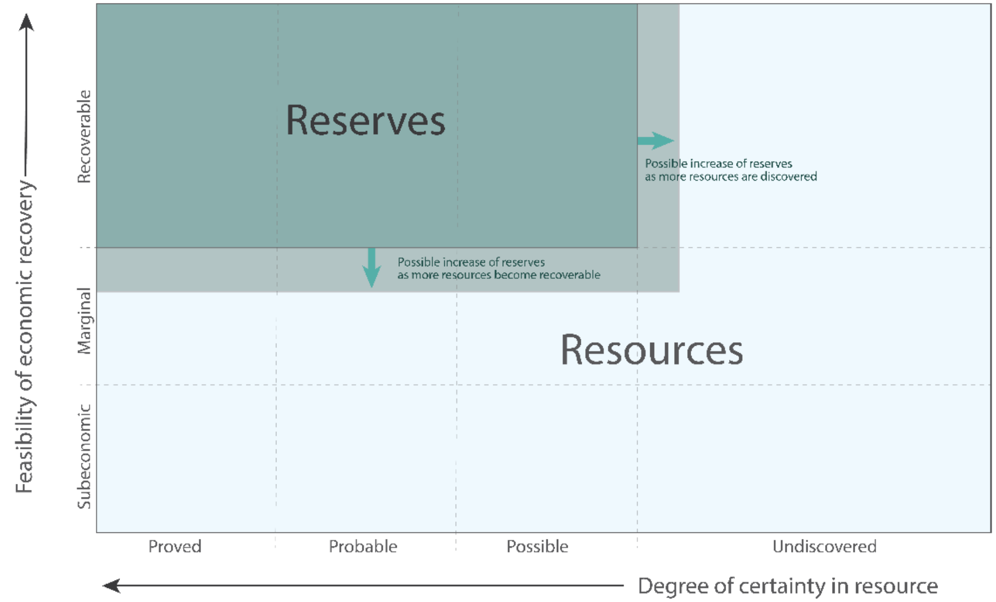


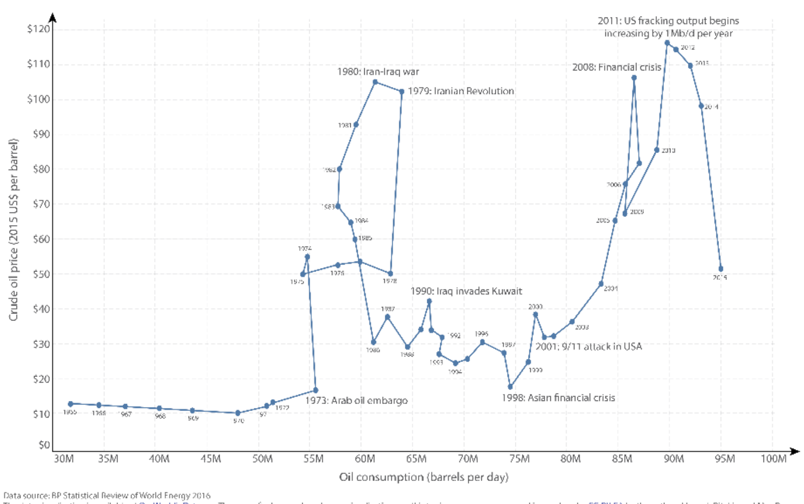
Data source: BP Statistical Review of World Energy 2016
The data visualization is available at OurWorldinData.org. There you find research and more visualizations on this topic.

Peak oil ?

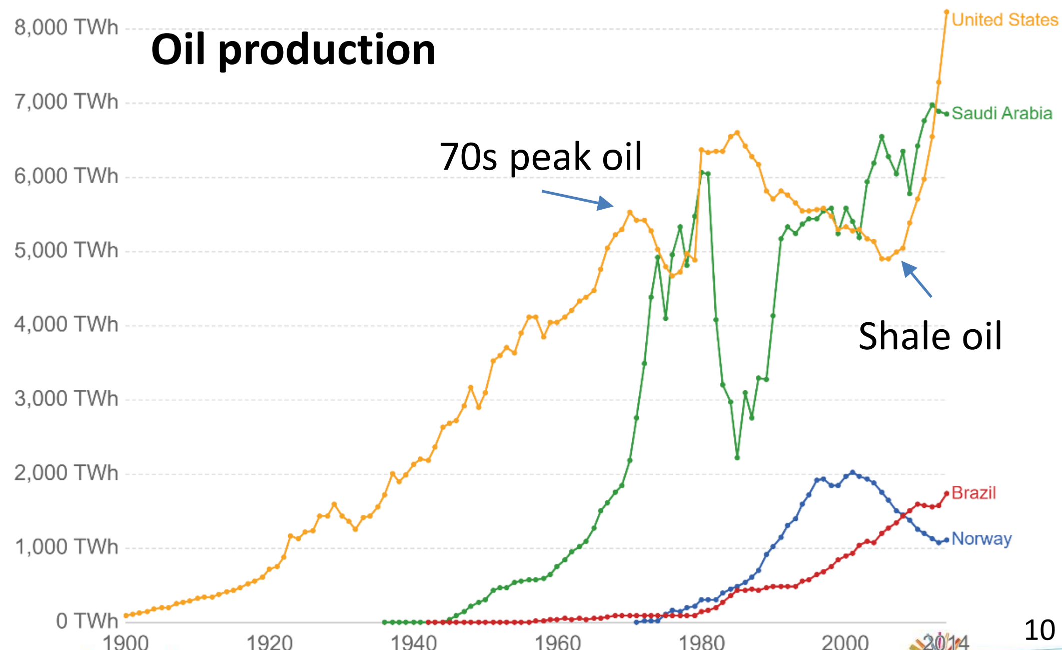
Worldwide oil reserves



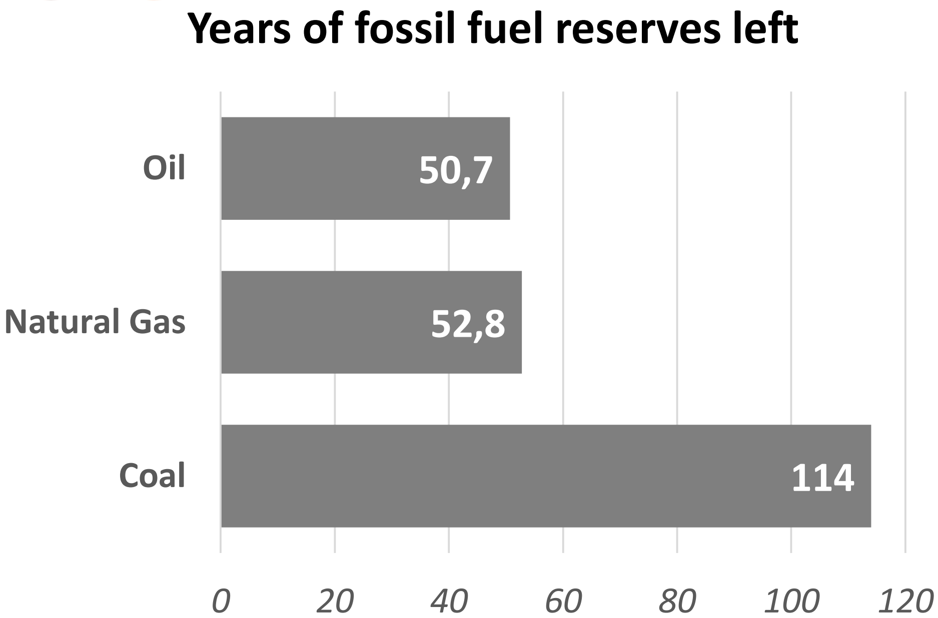


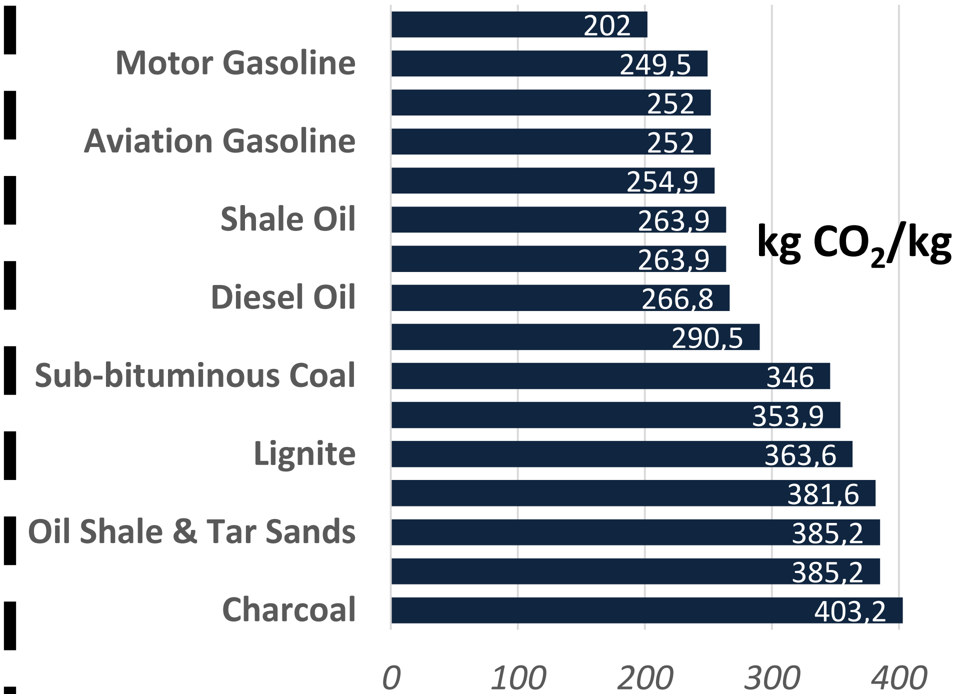


Oil production

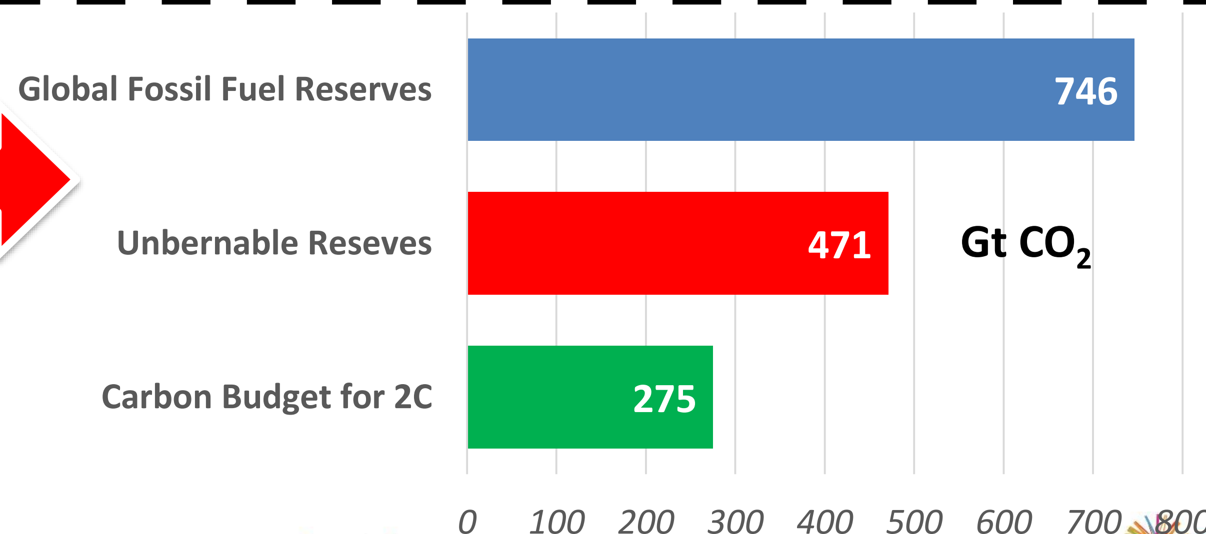


Fossil fuel reserves

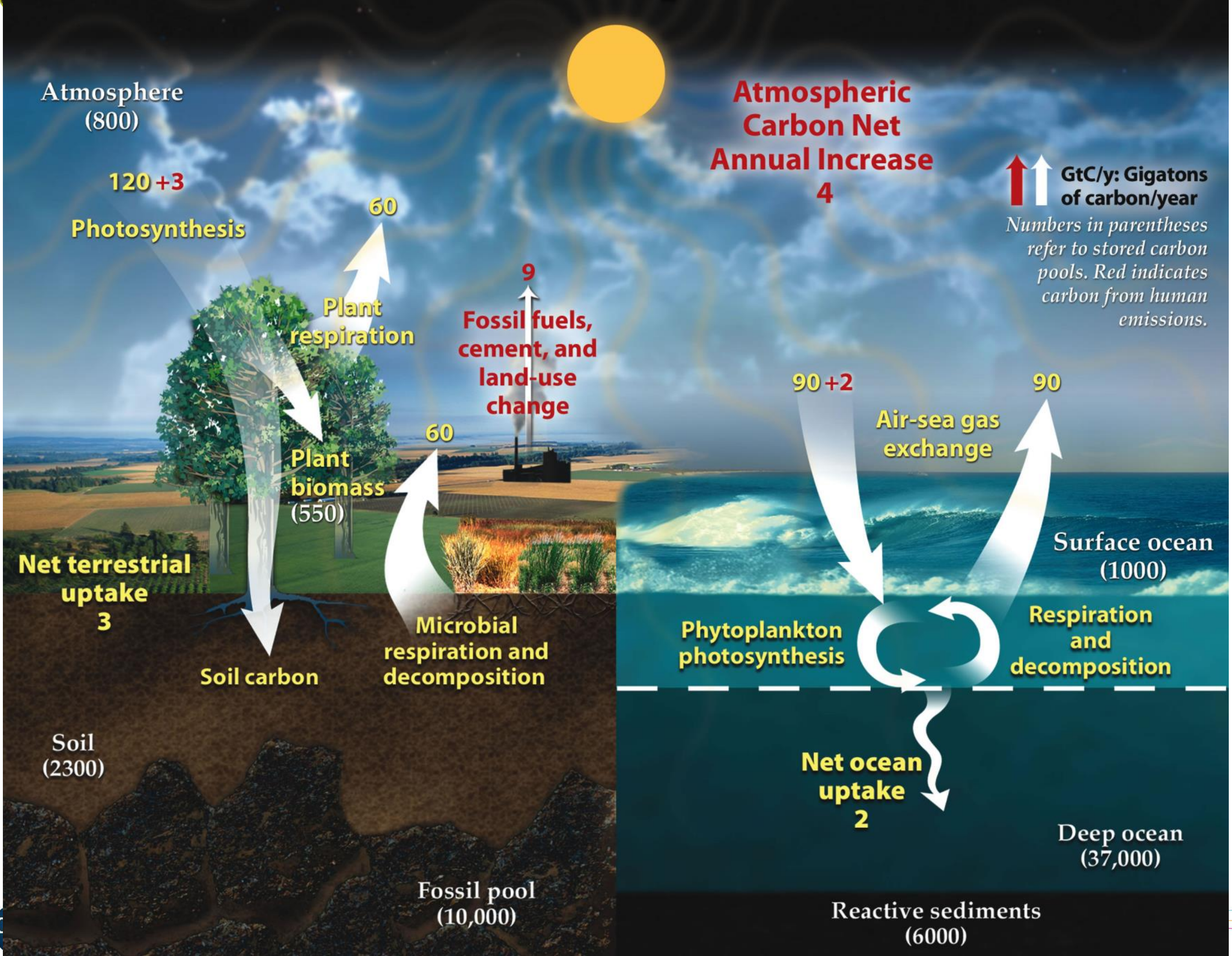




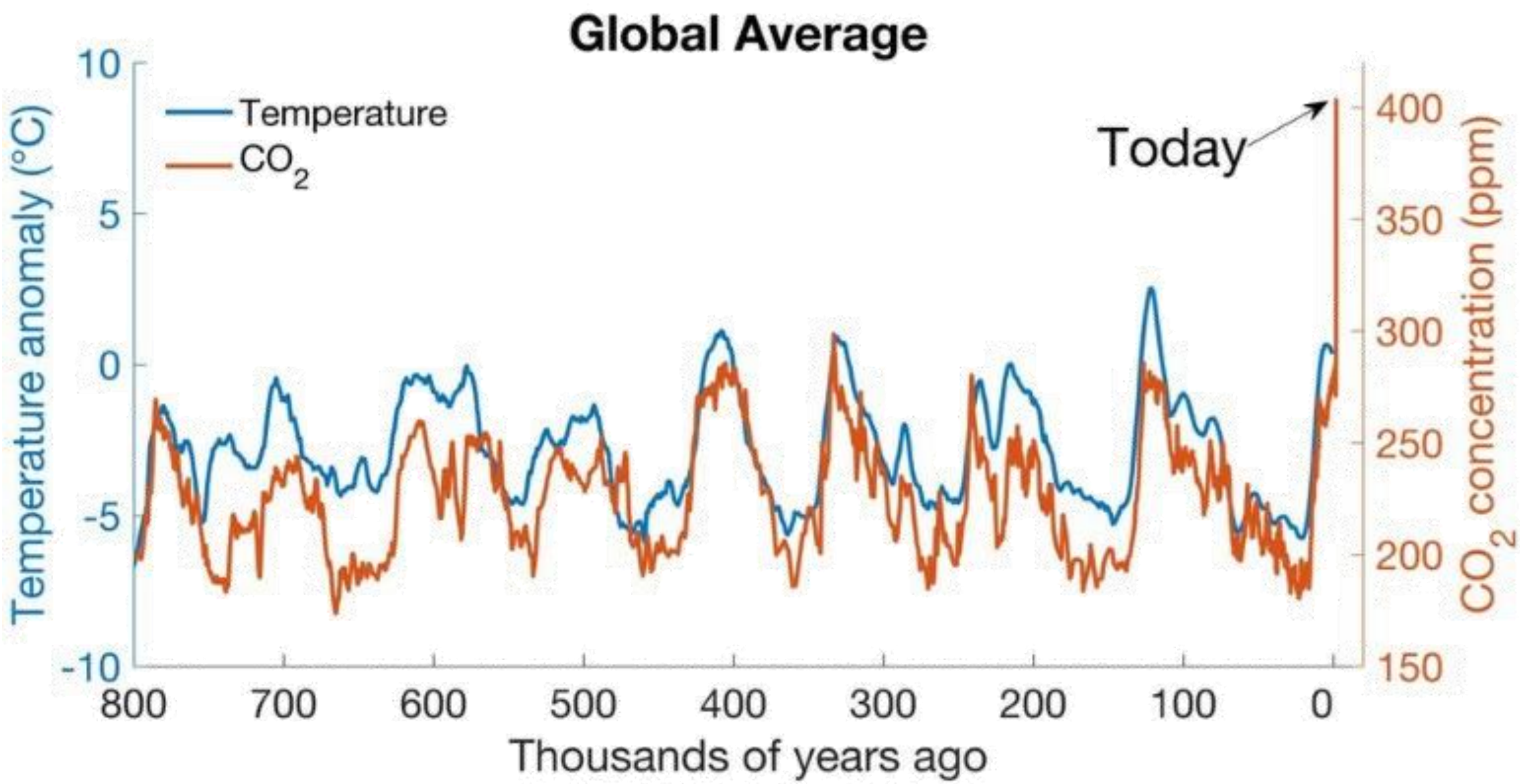
Only ⅓ can be burned



CO_2 cycle


Atmosphere
(800)
120 +3
Photosynthesis
60
Plant
respiration
9
Fossil fuels,
cement, and
land-use
change
Atmospheric
Carbon Net
Annual Increase
4
GtC/y: Gigatons
of carbon/year
Numbers in parentheses
refer to stored carbon
pools. Red indicates
carbon from human
emissions.
60
Plant
biomass
(550)
Net terrestrial
uptake
3
Soil carbon
Microbial
respiration and
decomposition
Soil
(2300)
Fossil pool
(10,000)
90 +2
90
Air-sea gas
exchange
Surface ocean
(1000)
Phytoplankton
photosynthesis
Respiration
and
decomposition
Net ocean
uptake
2
Deep ocean
(37,000)
Reactive sediments
(6000)

CO_2 concentration keep increasing



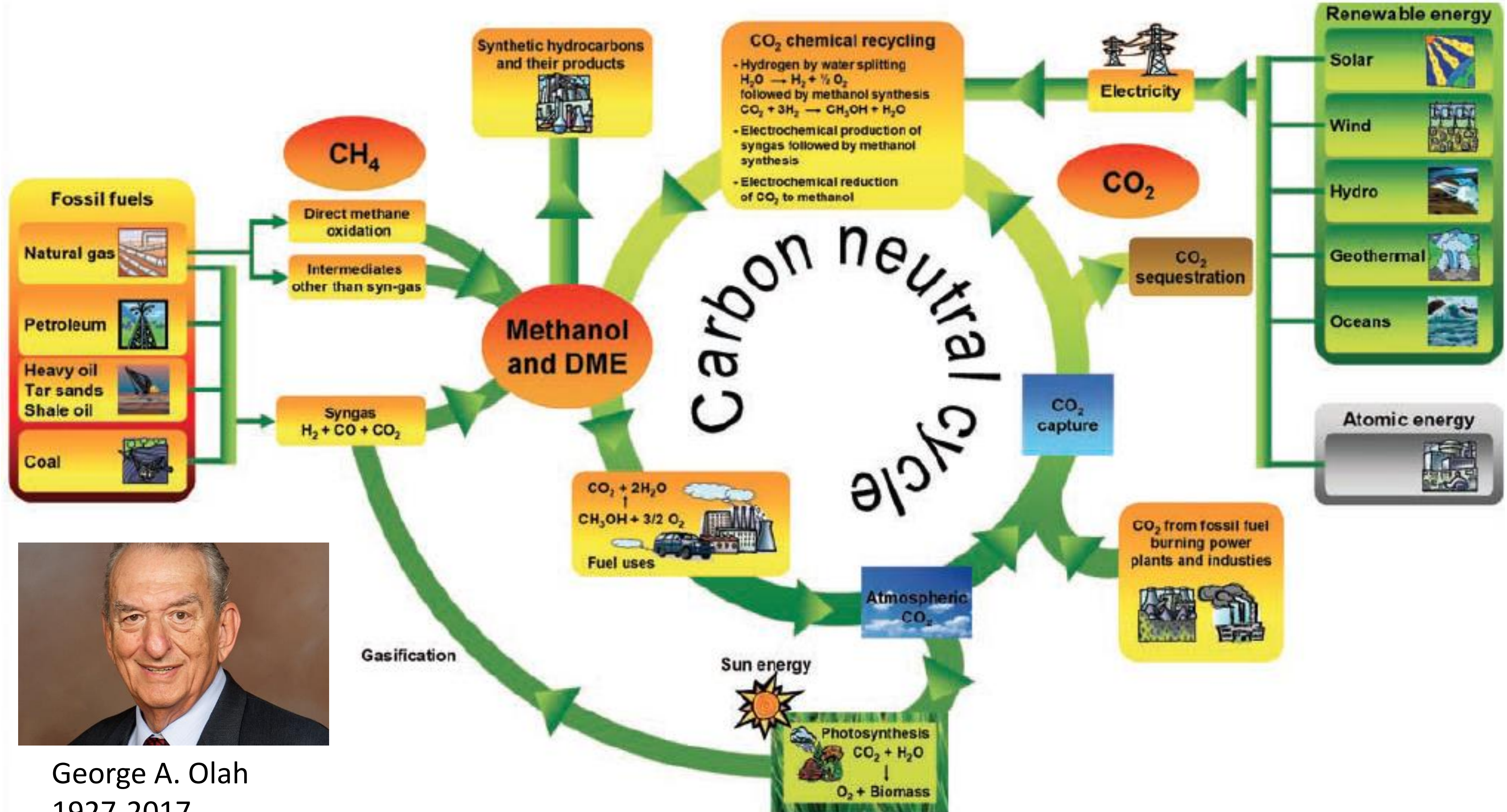
May 2019: 415ppm
Since Sept 2016 > 400ppm

1987 : 350ppm

➡ **Last time the CO_2 was that high the Human didn't exist**
4 ppm/year more CO_2 in the atmosphere

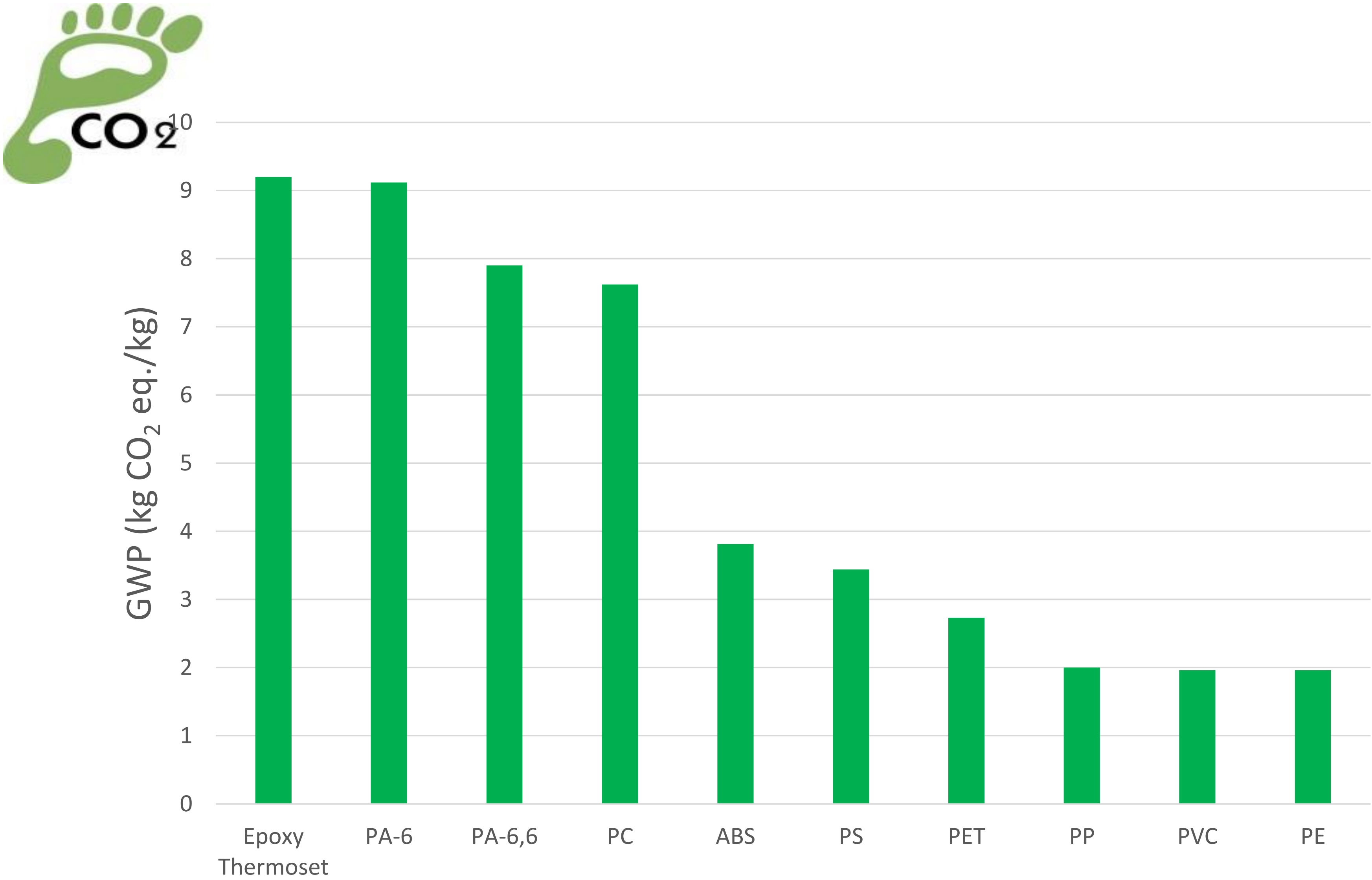
Reduce CO_2 emissions and trap it sustainably.

Carbon neutral society

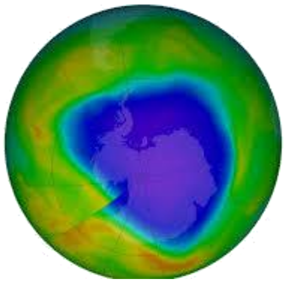


George A. Olah
1927-2017
Nobel Prize 1994

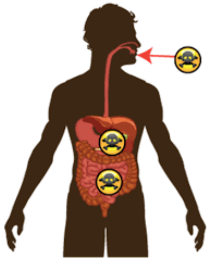
CO_2 emissions from cradle to factory gate



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-rewenable energy	MJ
Depletion of abiotic ressources	kg Sb eq.
Water	L



LCA: Example of the grocery bags

Simple LDPE

a)

b)

Non-woven PP

Recycled PET

Rigid handle LDPE

a)

b)

Woven PP

polyester

biopolymer

paper

cotton

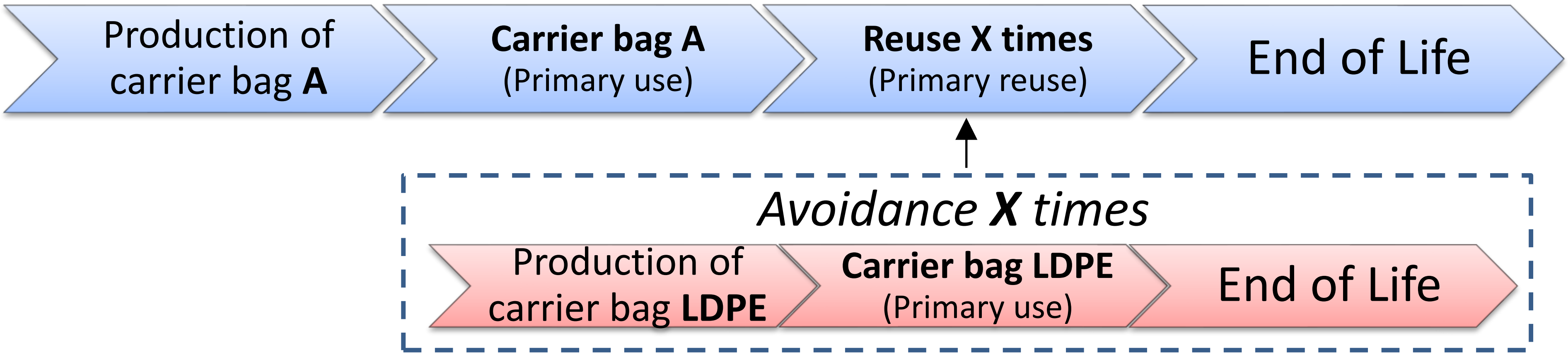
composite

LCPO Laboratoire de Chimie des Polymères Organiques

LCA: Example of the grocery bags

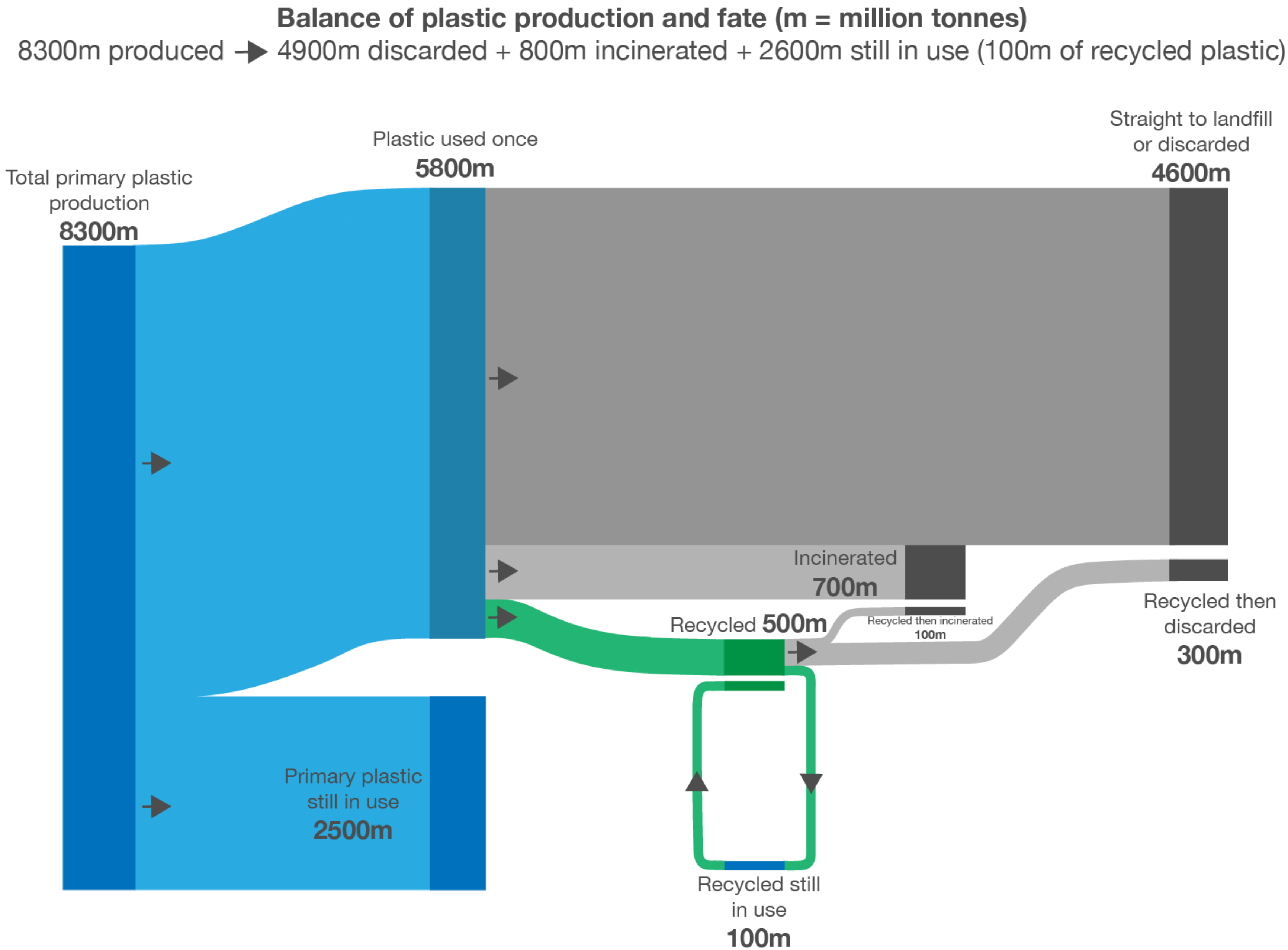
Impact category / bag	LDPE	PET	Bioplastique	Cotton	Units
Climate change	$1.1\ 10^{-1}$	$7.7\ 10^{-1}$	$9.0\ 10^{-2}$	3.9	kg CO_2 eq.
Ozone depletion	$1.2\ 10^{-9}$	$6.4\ 10^{-8}$	$1.5\ 10^{-8}$	$1.0\ 10^{-5}$	kg CFC-11 eq.
Human tox., cancer effects	$1.3\ 10^{-9}$	$7.0\ 10^{-9}$	$2.3\ 10^{-9}$	$1.7\ 10^{-7}$	CTUh
Human tox., non-cancer effects	$-1.1\ 10^{-8}$	$-1.6\ 10^{-8}$	$3.1\ 10^{-8}$	$5.6\ 10^{-7}$	CTUh
Respiratory inorganics	$1.6\ 10^{-5}$	$2.7\ 10^{-5}$	$1.2\ 10^{-4}$	$3.8\ 10^{-3}$	kg PM2.5 eq.
Respiratory organics	$2.0\ 10^{-4}$	$9.6\ 10^{-4}$	$3.4\ 10^{-4}$	$8.7\ 10^{-3}$	kg NMVOC eq
Ionizing radiation	$6.0\ 10^{-4}$	$1.4\ 10^{-2}$	$3.8\ 10^{-3}$	$1.3\ 10^{-1}$	kBq U235 eq.
Terrestrial acidification	$1.1\ 10^{-4}$	$1.1\ 10^{-3}$	$7.4\ 10^{-4}$	$2.0\ 10^{-2}$	mol H^+ eq
Eutrophication terrestrial	$8.7\ 10^{-5}$	$1.9\ 10^{-4}$	$1.4\ 10^{-3}$	$4.9\ 10^{-2}$	mol N eq
Eutrophication freshwater	$-5.6\ 10^{-7}$	$3.8\ 10^{-5}$	$1.6\ 10^{-5}$	$4.8\ 10^{-4}$	mol P eq
Eutrophication marine	$2.3\ 10^{-5}$	$2.2\ 10^{-4}$	$2.4\ 10^{-4}$	$3.4\ 10^{-3}$	mol N eq
Ecotoxicity freshwater	$7.2\ 10^{-2}$	$5.1\ 10^{-1}$	$1.3\ 10^{-1}$	12	CTUe
Non-rewenable energy	1.7	12	2.9	72	MJ
Depletion of ressources	$1.9\ 10^{-6}$	$2.1\ 10^{-5}$	$5.1\ 10^{-6}$	$1.6\ 10^{-4}$	kg Sb eq.
Water	$4.4\ 10^{-2}$	1.4	$2.4\ 10^{-1}$	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

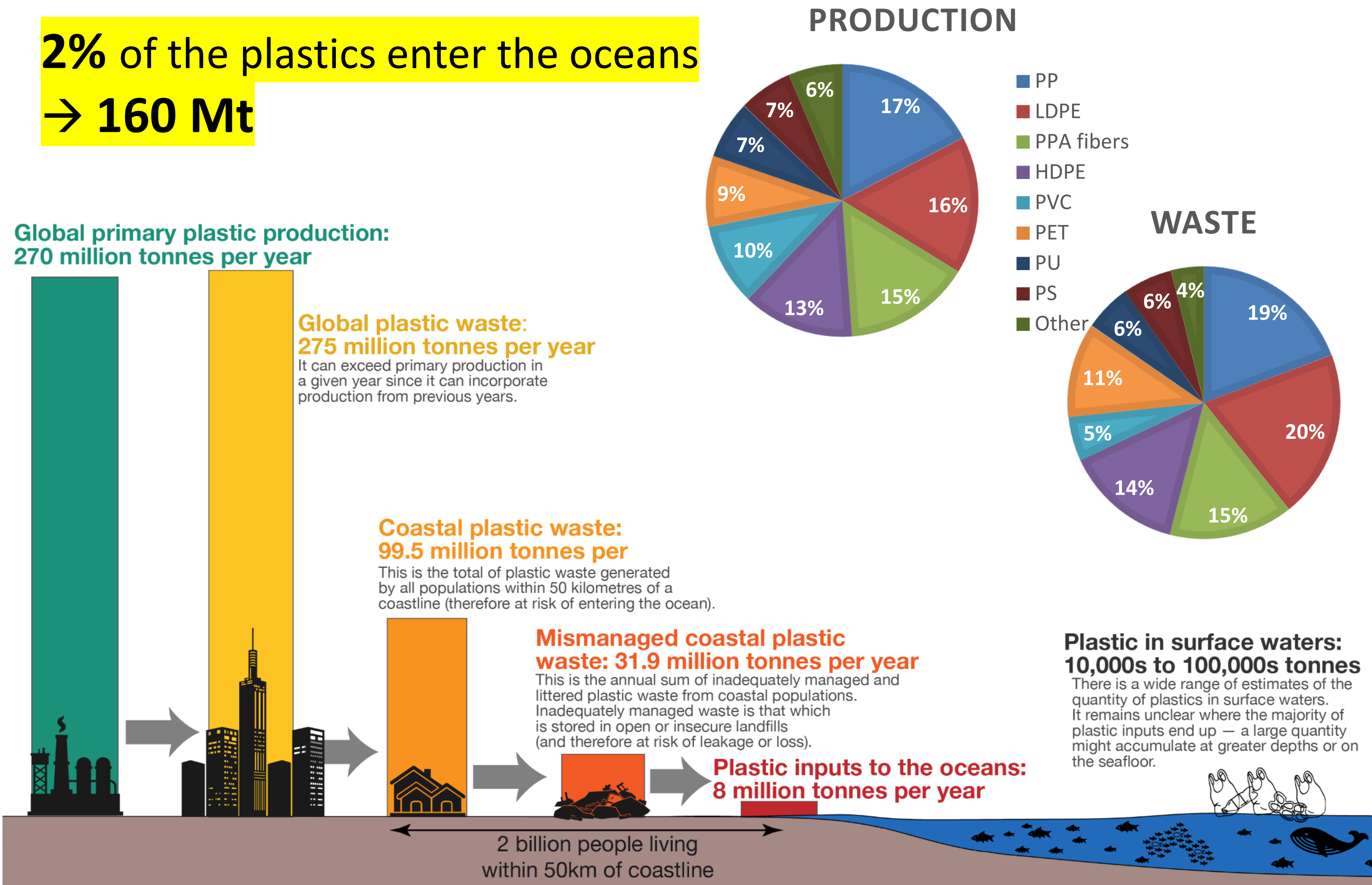
Global plastic production and its fate (1950-2015)



The route by which plastic enters the oceans

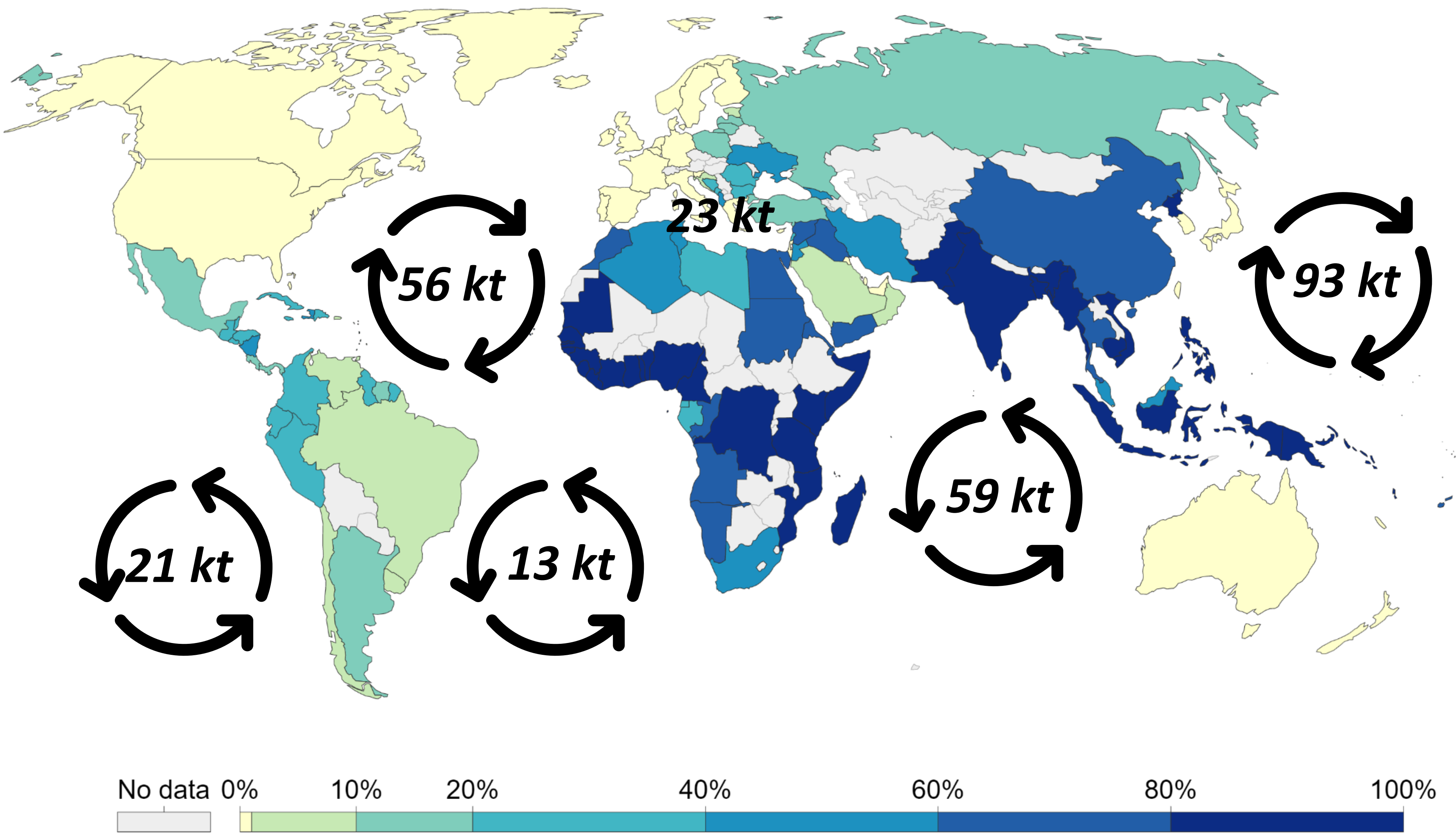
2% of the plastics enter the oceans

→ **160 Mt**



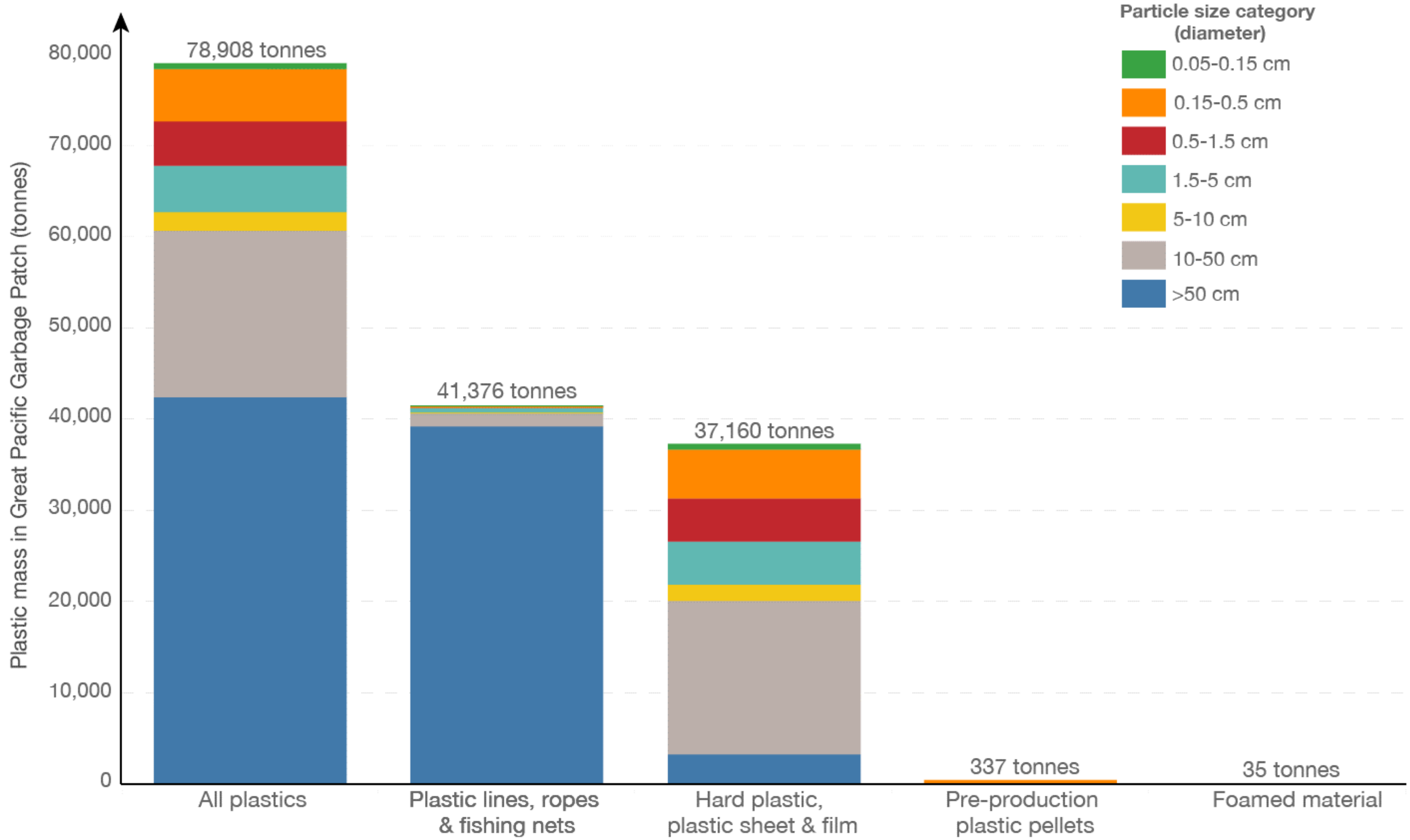
Share of plastic waste that is inadequately managed (2010)

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



Source: Jambeck et al. (2015)

Great Pacific Garbage Patch (GPGP) plastic sources

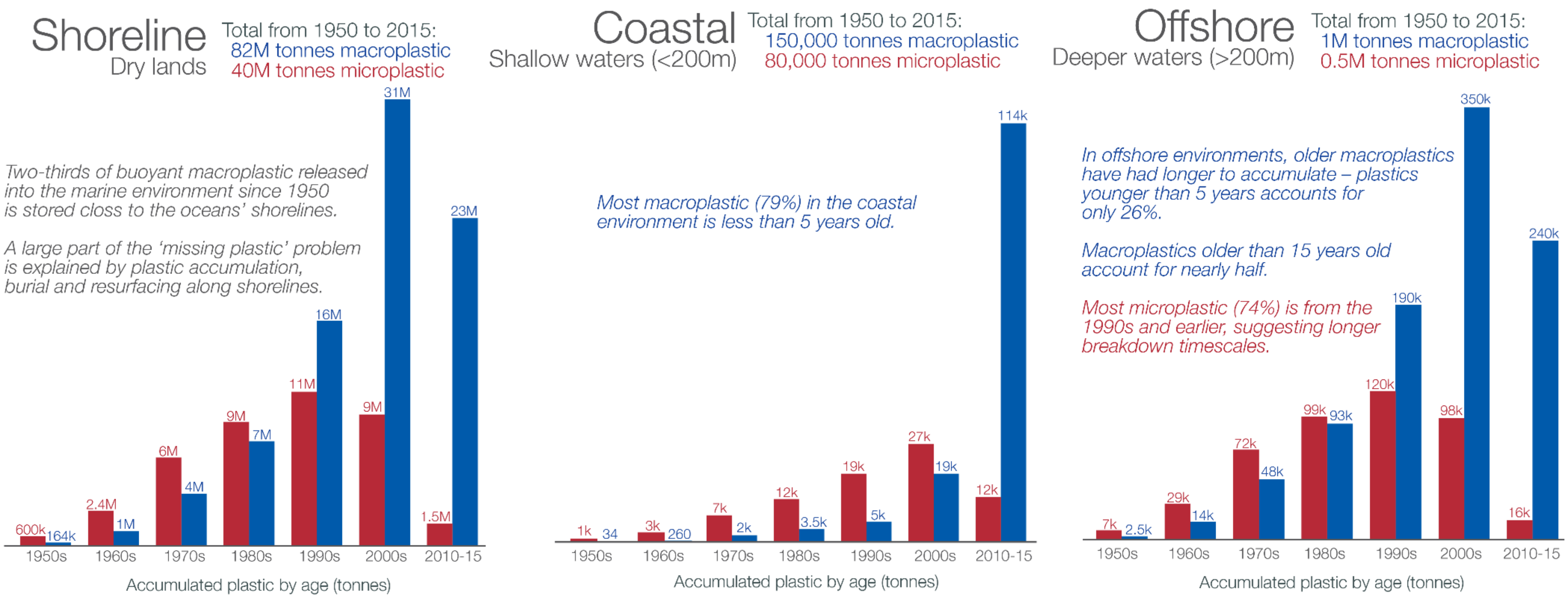


Ultraviolet light (UV) and mechanical wave forces break large pieces of plastic into smaller ones called **microplastics**

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



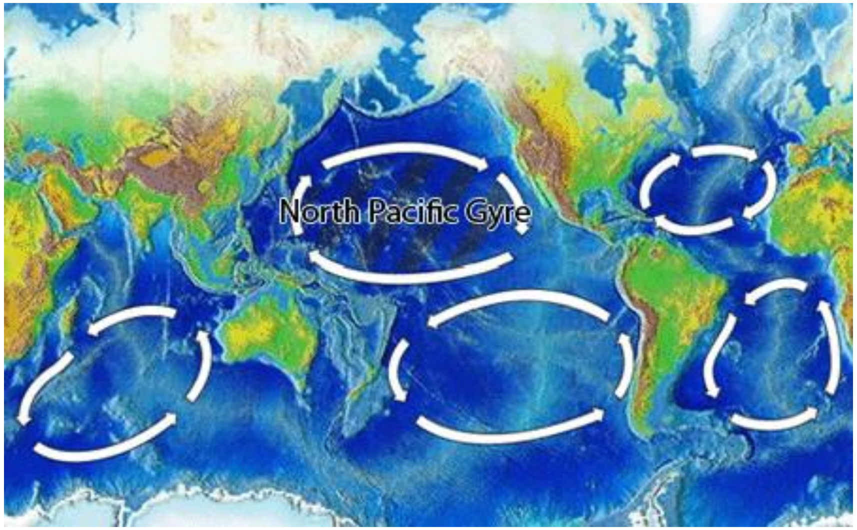
125 Mt in the ocean's gires but **8 Mt/y** of plastic enters the oceans

Plastic pollution

- Each year, we use and throw away :
  - 3,7 billions of plastic cups,
  - 365 billions of plastics bottles,
  - 3650 billions of plastic bags,
  - by 2050 more plastics than fish
  - 10% of the plastics go to the sea

- Pacific ocean accumulations:
  - o Plastic particles in suspension
  - o Concentration : 5.1 kg/km²
  - o More than 5 millions tons (?)

- Alliances of individuals, organizations and businesses working together to stop plastic pollution and its toxic impacts



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

PlasticPollutionCoalition

World plastic market

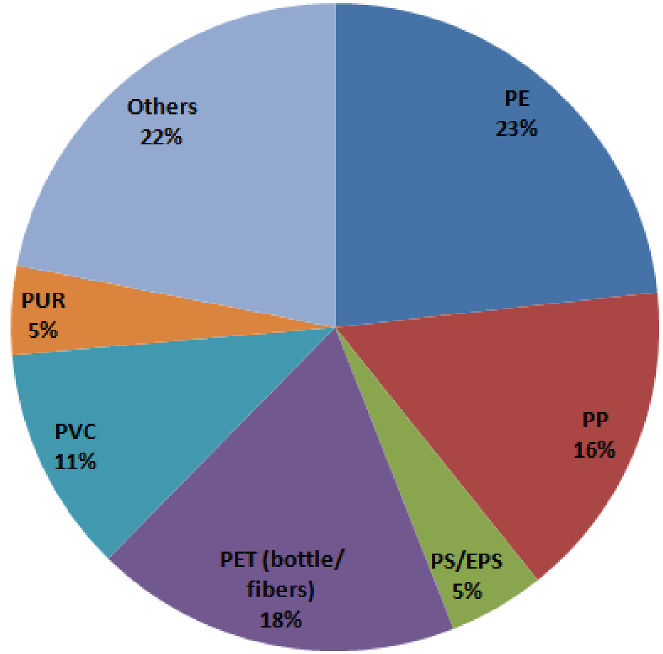
Plastics

Thermoplastics
- -Can be remelted.
- -Hard or tough elasticity
- -Sold as pellets.

Thermosets
- -Cannot be remelted.
- - Hard elasticity
- -Sold as components.

Elastomers (« rubber »)
soft elasticity and can mostly not be melted
can be thermoplastics or thermosets

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, …).

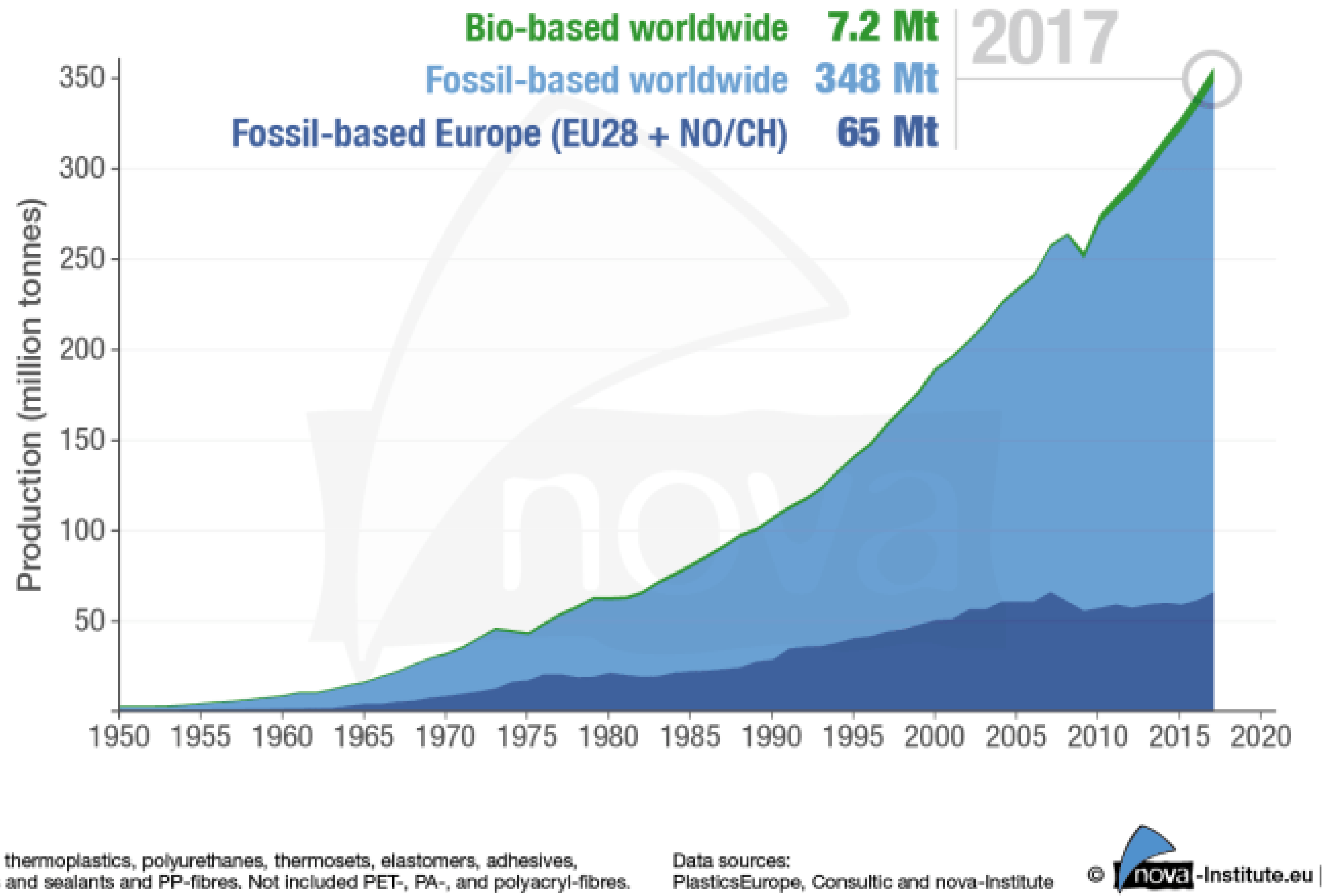
-Thermosets: PUR, UPR, Epoxy, Elastomers.

* 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

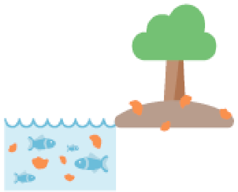


Huge market with continuous growth for more than 50 years (4% per year)

But still based on fossil raw materials (for more than 99%)

Outlines

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 ($C_6H_{12}O_6$)).
This glucose is then condensed by the plant into natural polymers such as starch or cellulose.

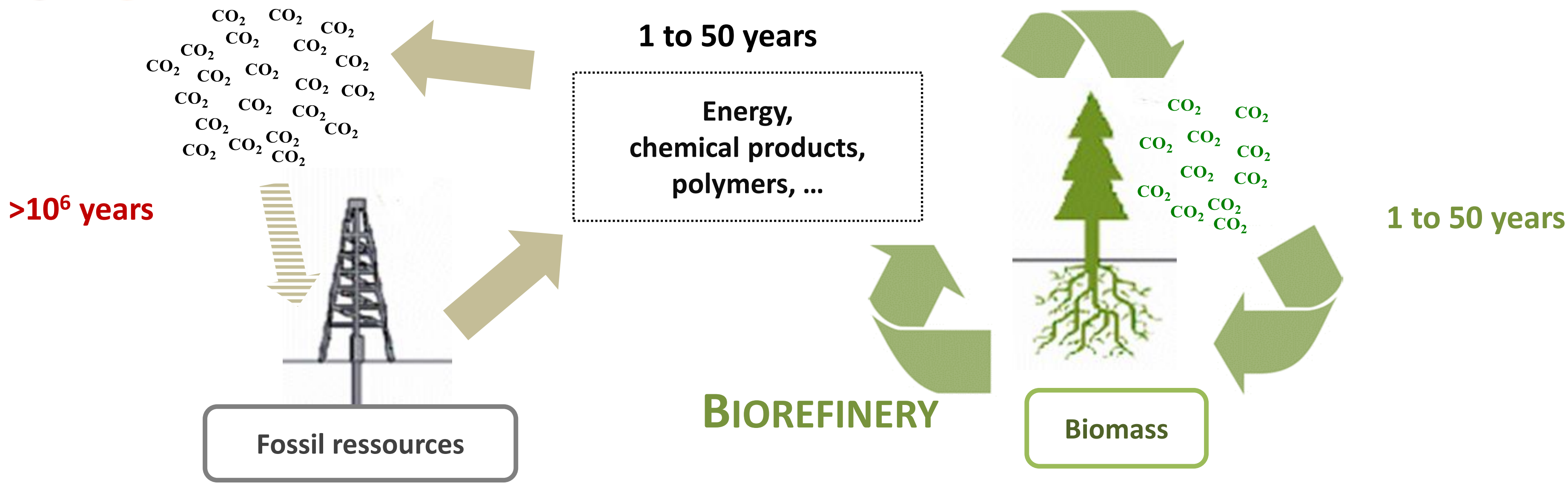
This plant photosynthetic process allows the binding and storage of atmospheric carbon dioxide (CO_2) in the form of matter in plant tissues.

$$6\ CO_2 + 12\ H_2O + \text{light} \rightarrow C_6H_{12}O_6 + 6\ O_2 + 6\ H_2O$$

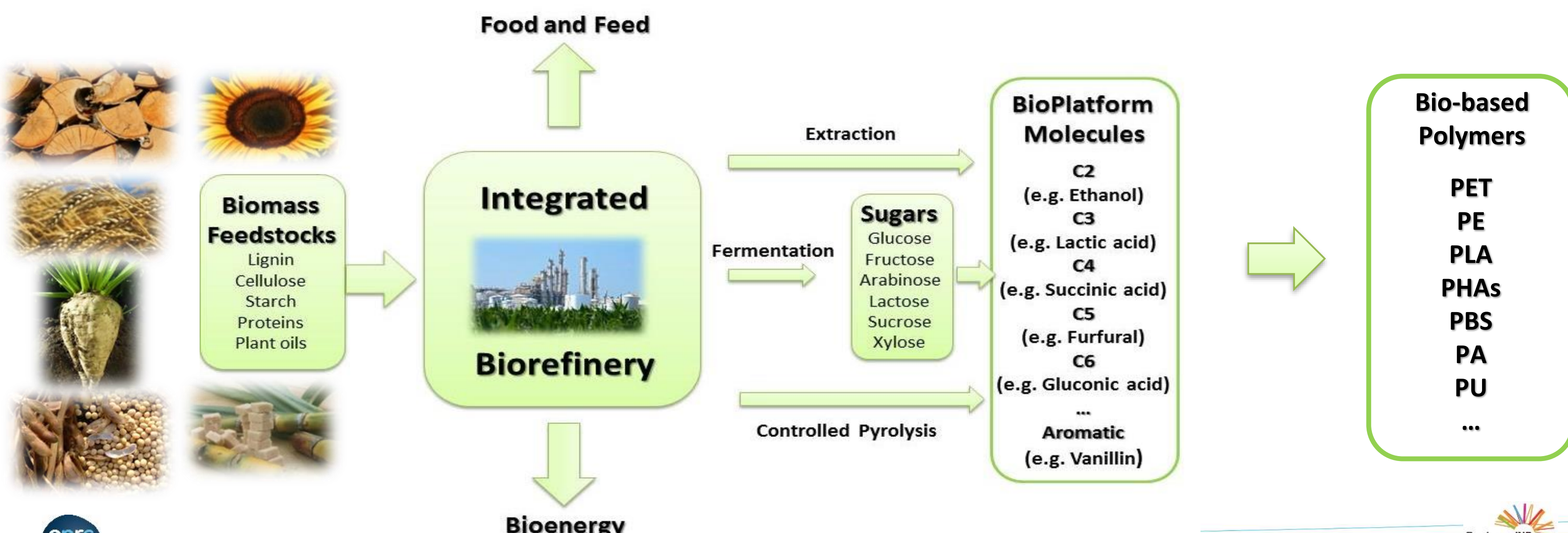
Plants, through this photosynthetic mechanism, thus produce renewable natural carbon-based molecules.

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

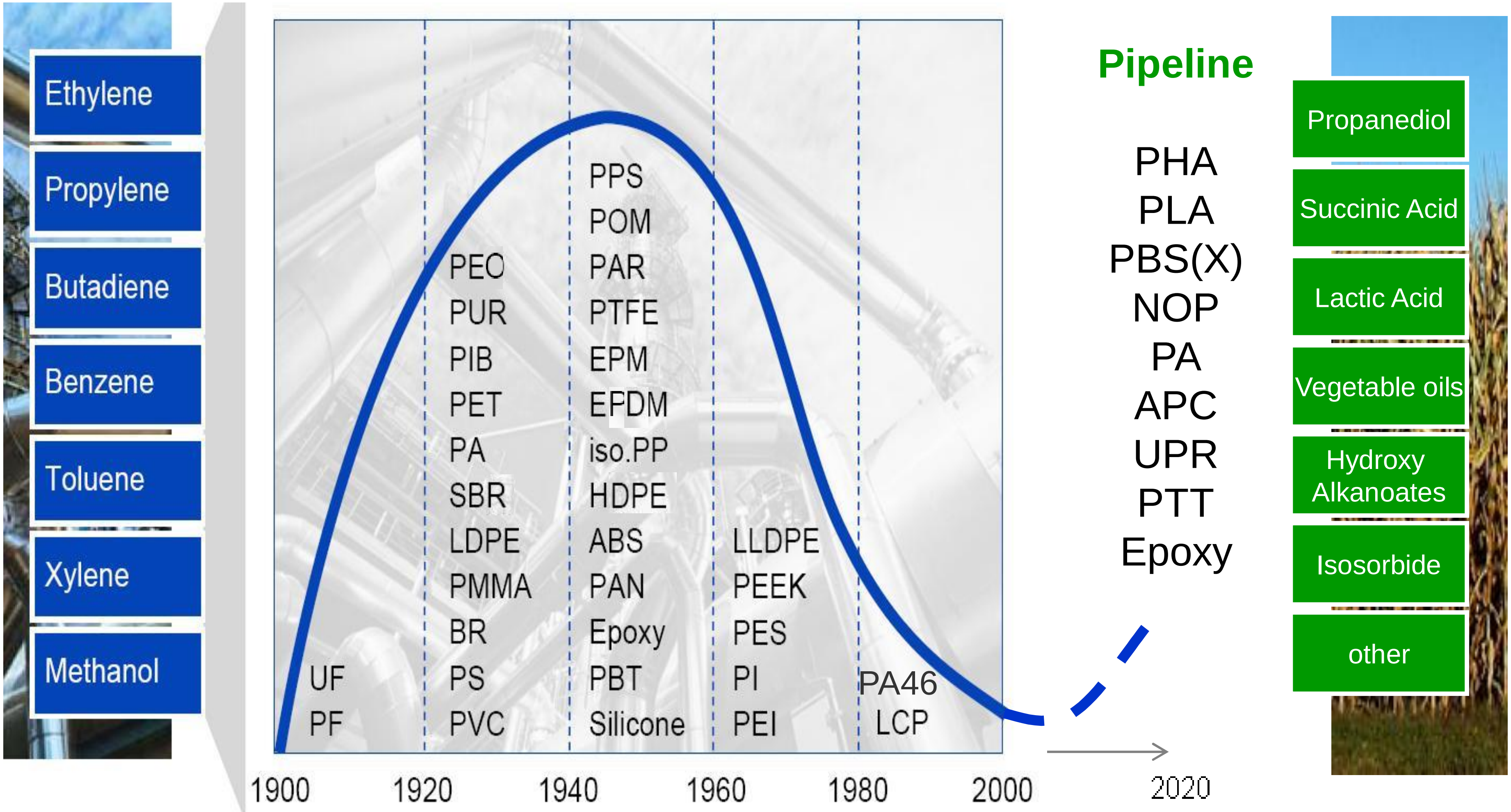
Ethanol

Sugar

Corn

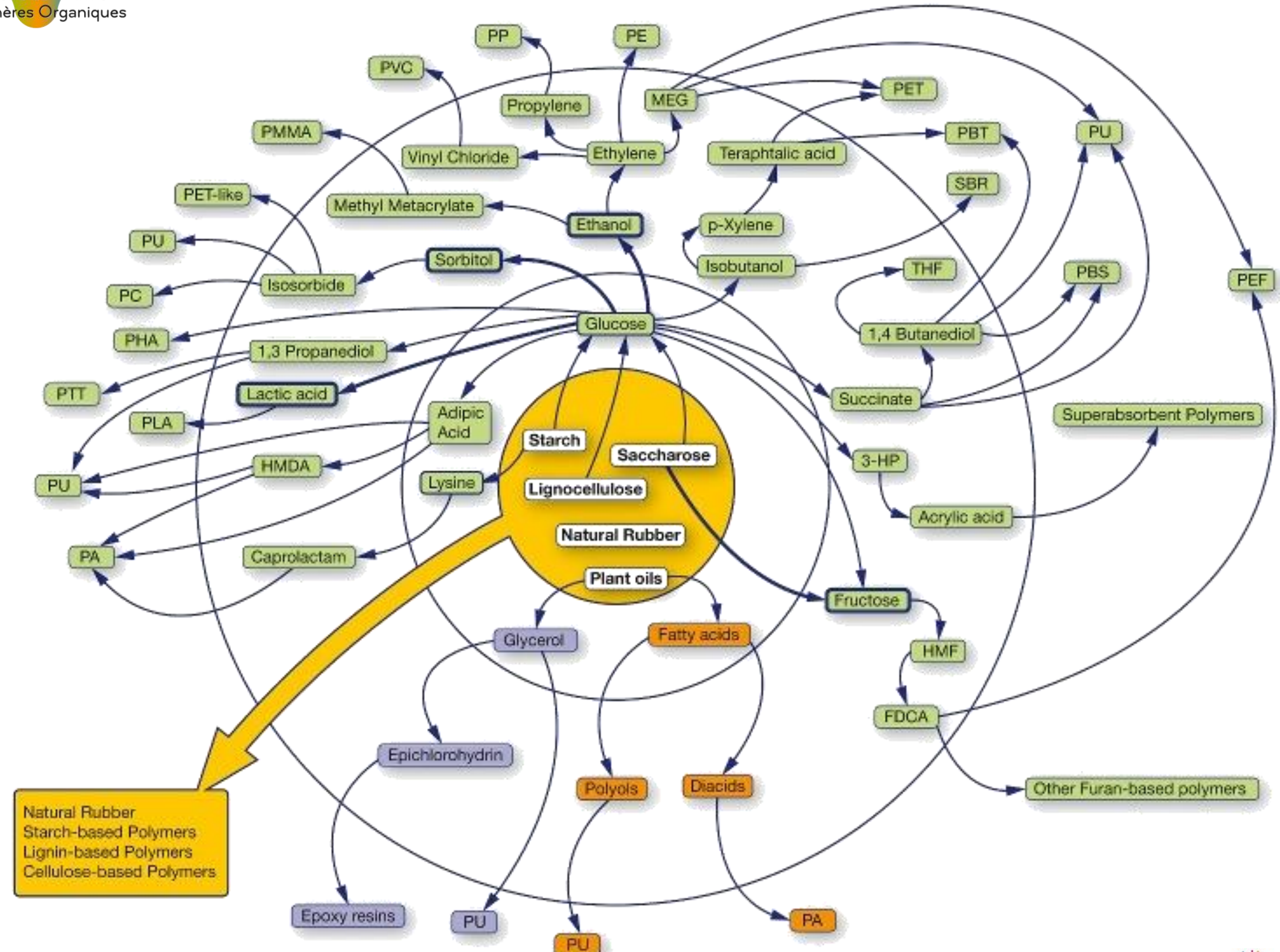
What's new in the Plastic Industry ?

Find new pathways to 'old' polymers….?



…..or Design novel polymers ?

From biomass to polymers

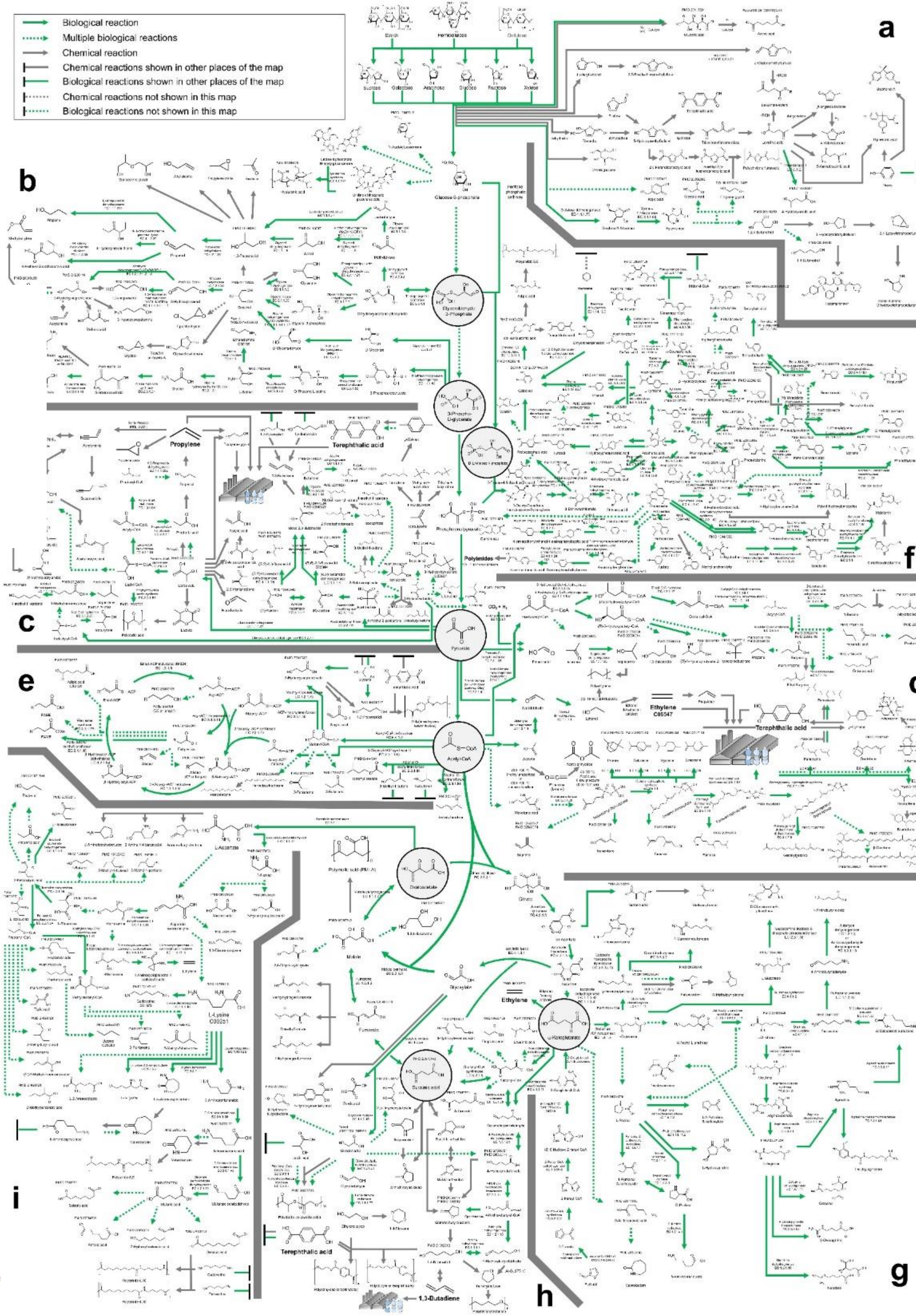


Laboratoire de Chimie des Polymères Organiques

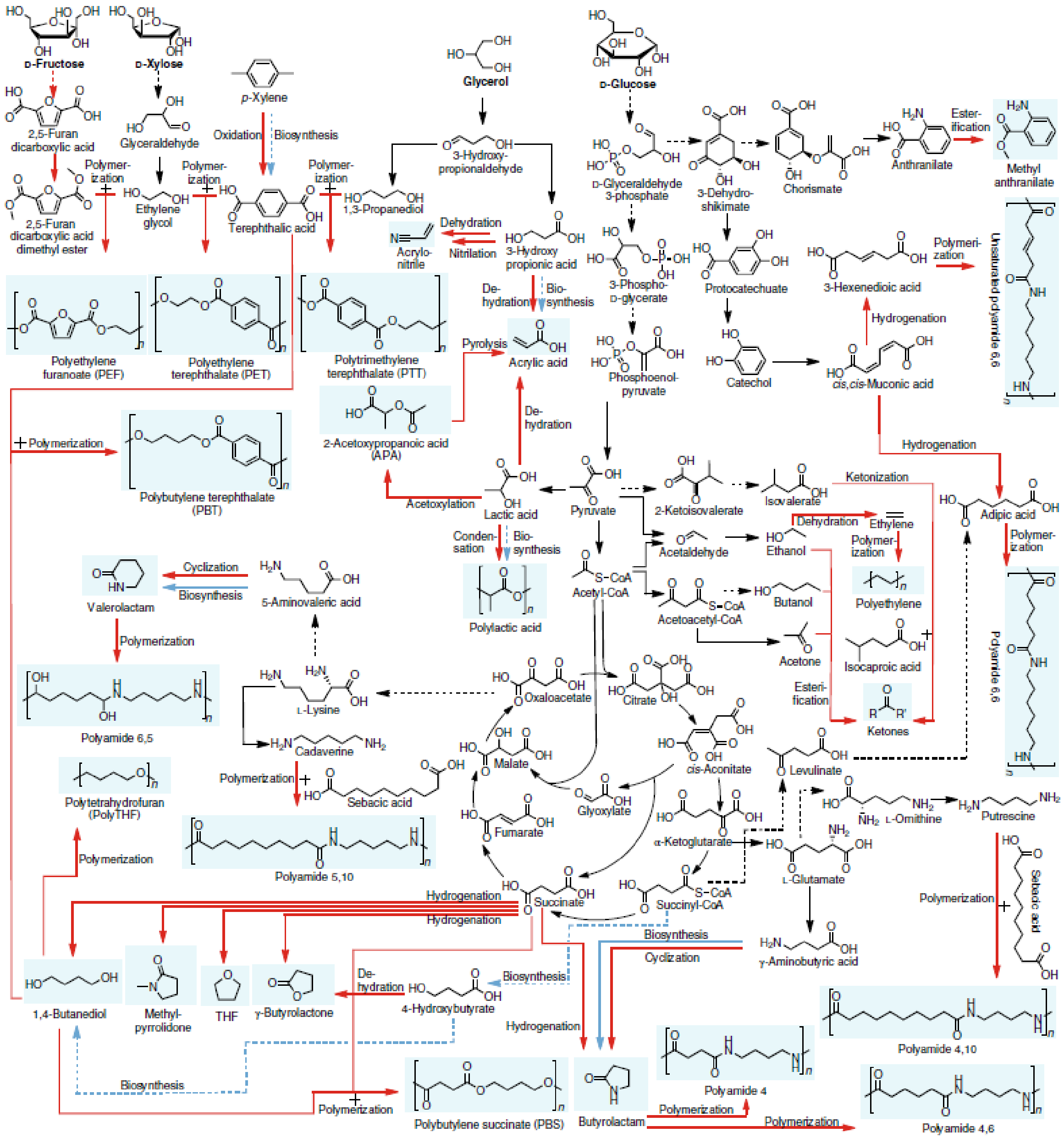
SUPPLEMENTARY INFORMATION
https://doi.org/10.1038/s41929-018-0212-4
nature catalysis
In the format provided by the authors and unedited.

A comprehensive metabolic map for production of bio-based chemicals

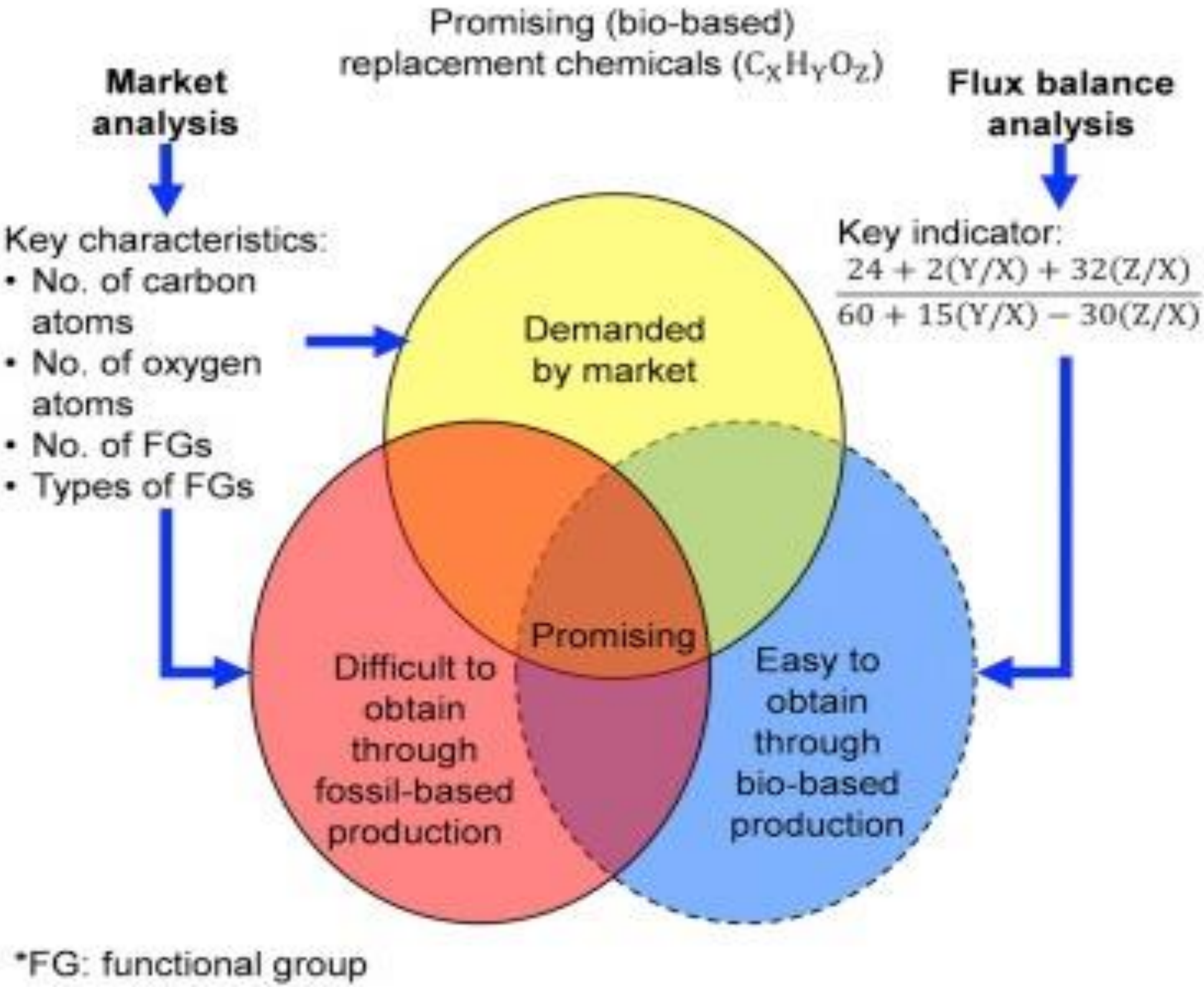
Sang Yup Lee[1,2,3,4*], Hyun Uk Kim[2,3,5], Tong Un Chae[1,2], Jae Sung Cho[1,2], Je Woong Kim[1,2], Jae Ho Shin[1,2], Dong In Kim[1,3], Yoo-Sung Ko[1,2], Woo Dae Jang[1,3] and Yu-Sin Jang[1,6]



Example of the glucose platform

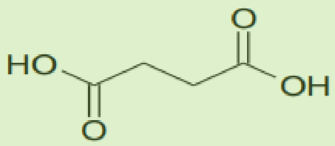


Promising bio-based chemicals

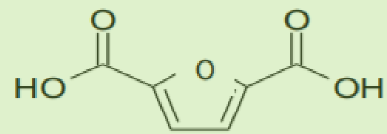


Maravelias *et coll*. *iScience*, **2019**, 15, 136

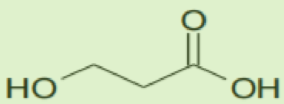
Most promising bio-based building blocks: DOE 2004



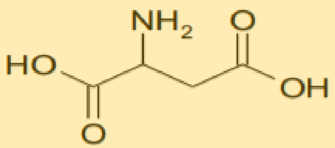
Succinic acid



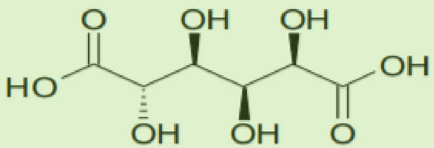
2,5-Furandicarboxylic acid



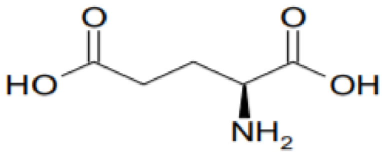
3-Hydroxypropionic acid



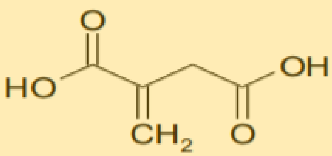
Aspartic acid



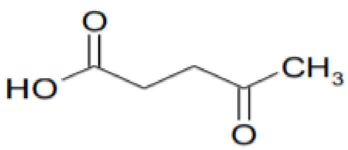
Glucaric acid



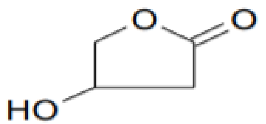
Glutamic acid



Itaconic acid

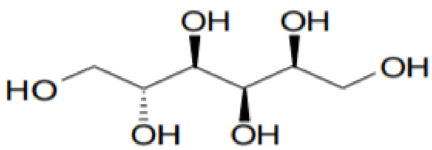


Levulinic acid

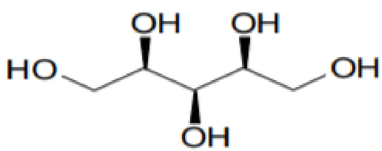


3-Hydroxybutyrolactone

Glycerol



Sorbitol

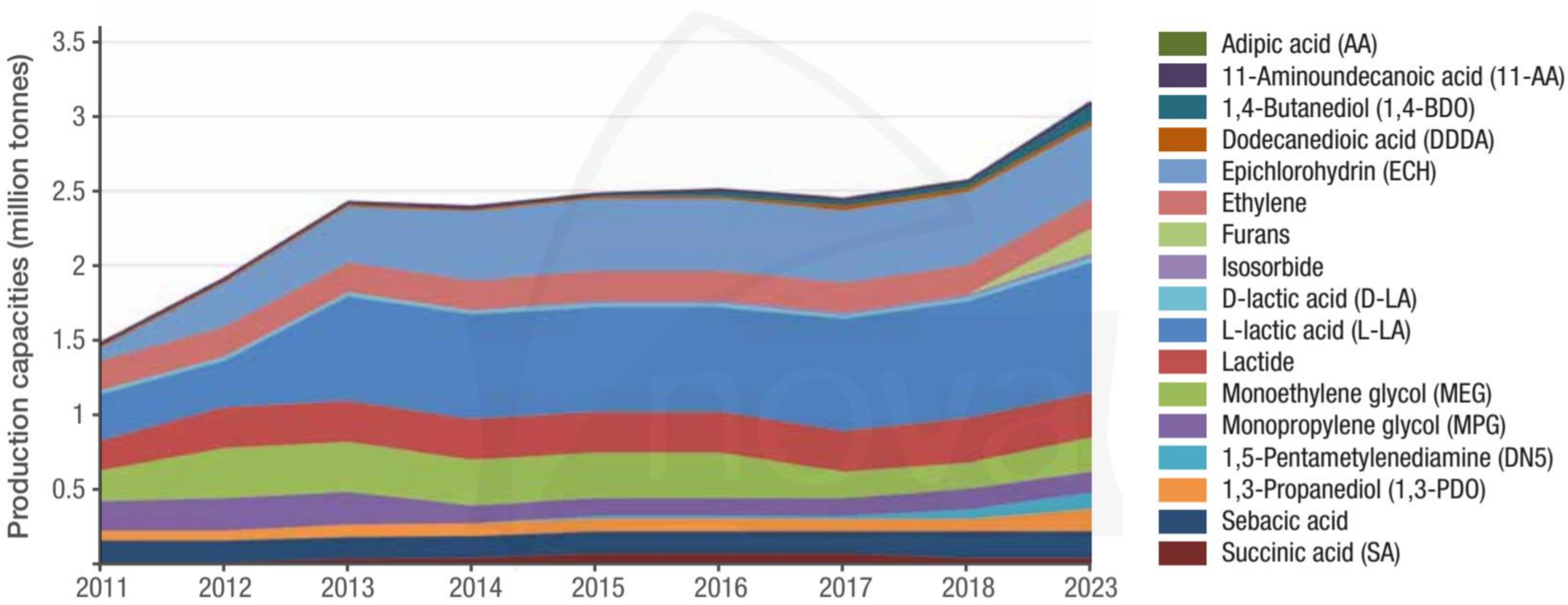


Xylitol

Most promising bio-based building blocks: DOE 2016

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

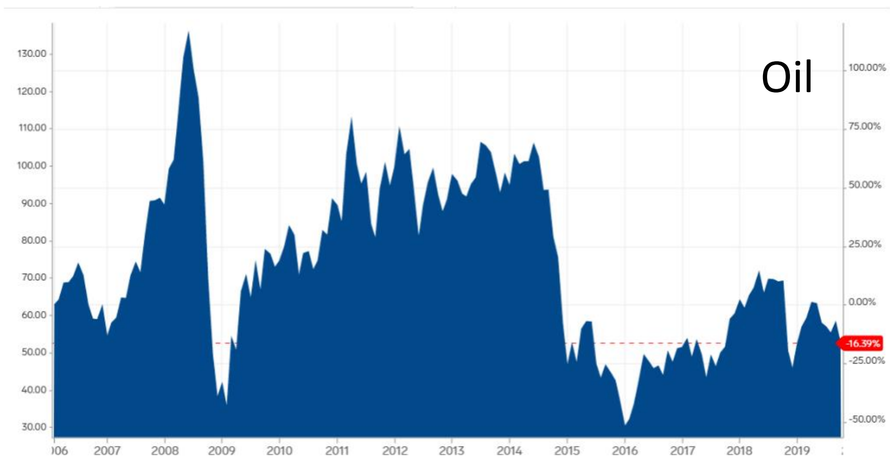
Worldwide production of bio-based chemicals

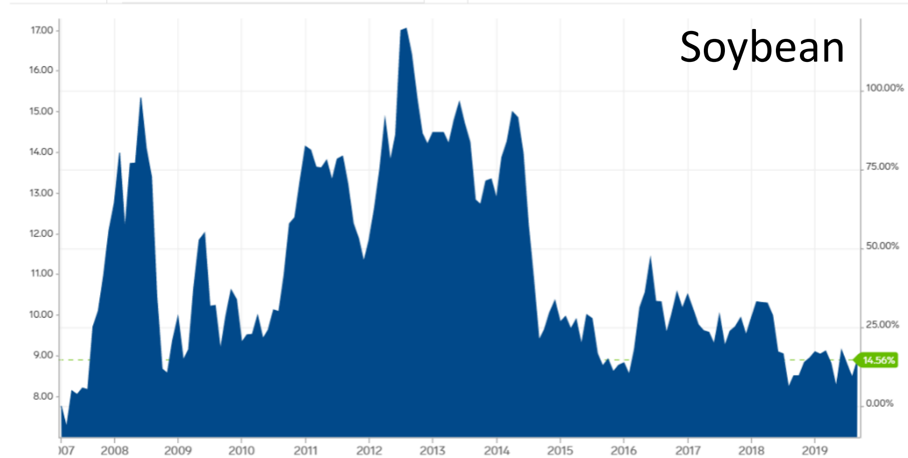


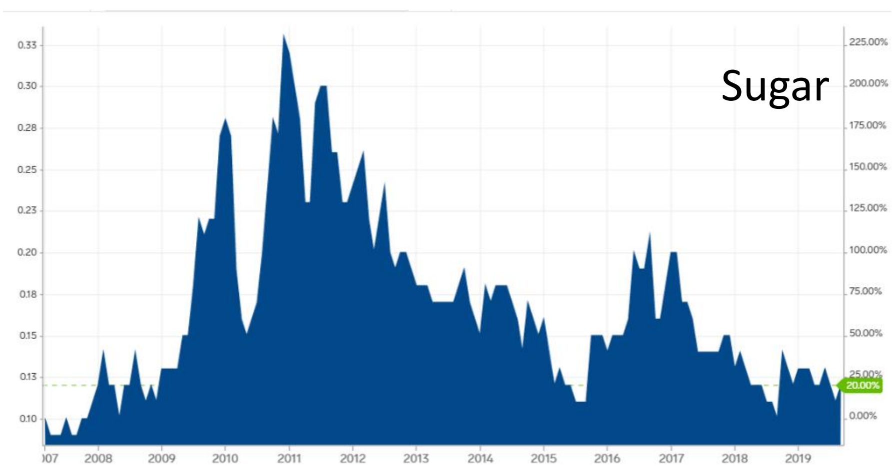
LCPO
Laboratoire de Chimie des Polymères Organiques

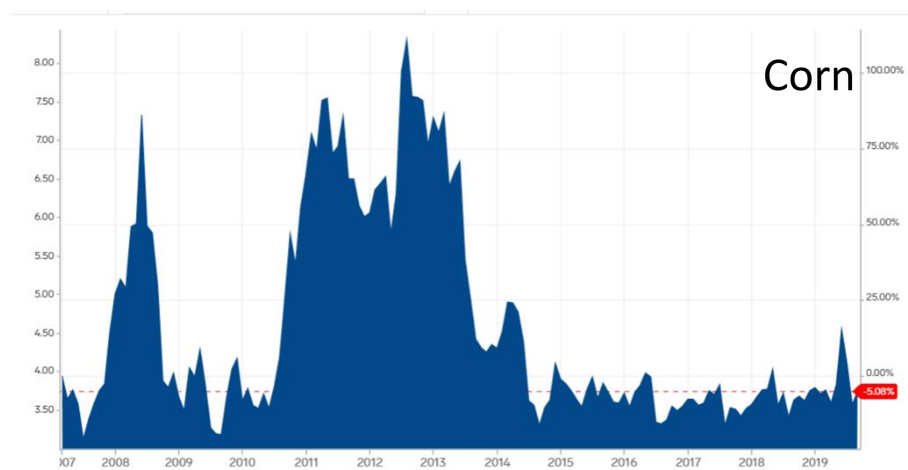
Ressources prize volatility

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









Refinery to Biorefinery

refinery

Oil

H2	C1	C2	C3	C4	C5	C6
ex	• methane	• ethylene • ethanol	• propene • propanediol	• butane • butanediol		• hexane • benzene

- Alcanes
- Aromatics
- Asphalt
- hydrocarbons
- petrol
- diesel

Complex products

cuts

Oxidation Chemistry

Biorefinery

Agro ressources

H2	C1	C2	C3	C4	C6	C7
	•Formic acid	• ethanol • acetic acid	• propanol • propanediol • propanoïc acid • acetone • lactic acid • pyruvic acid • glycerol •…	• butanol • butanoic acid • butanediol • malic acid •succinic acid •…	• glucose • fructose • butanediol • glutanmic acid •…	• p-hydroxy Benzoic acid •…

CO_2

cuts

Energy

Fuels

C8

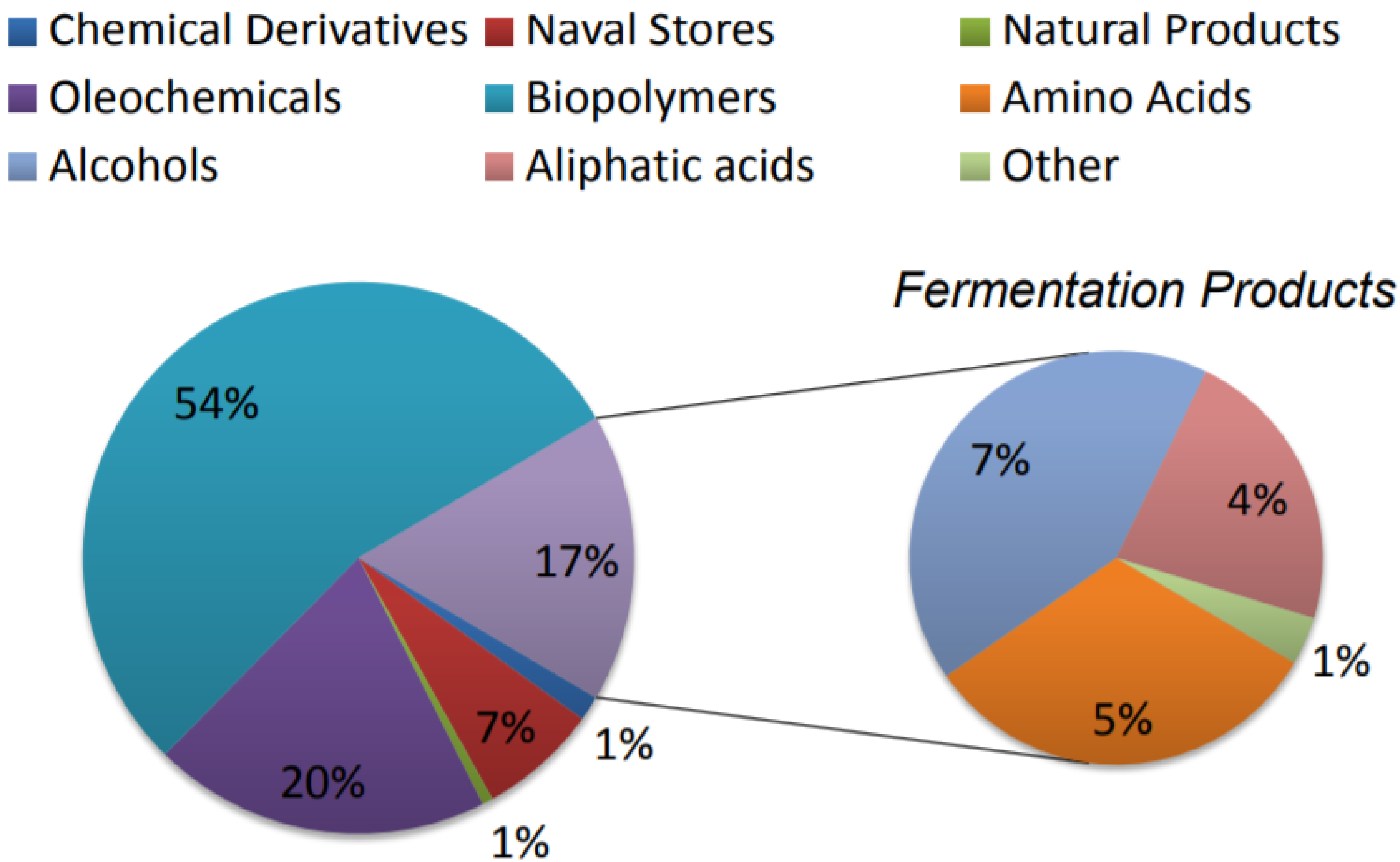
- butyl butyrate
- phenylethanol

- Biopolymers
- xanthan, dextran
- dyes
- surfactants
- Materials

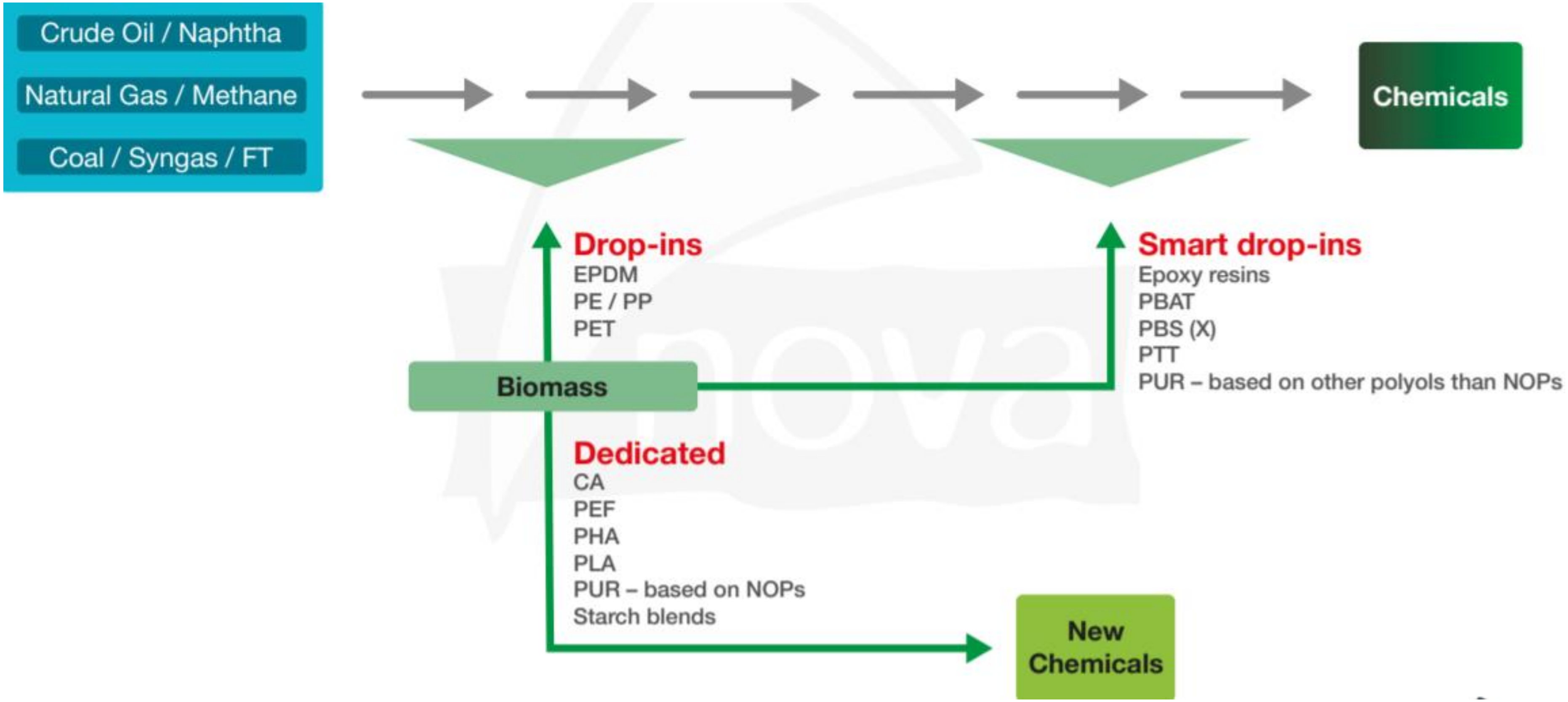
Reduction Chemistry

Bio-sourced chemicals and polymers

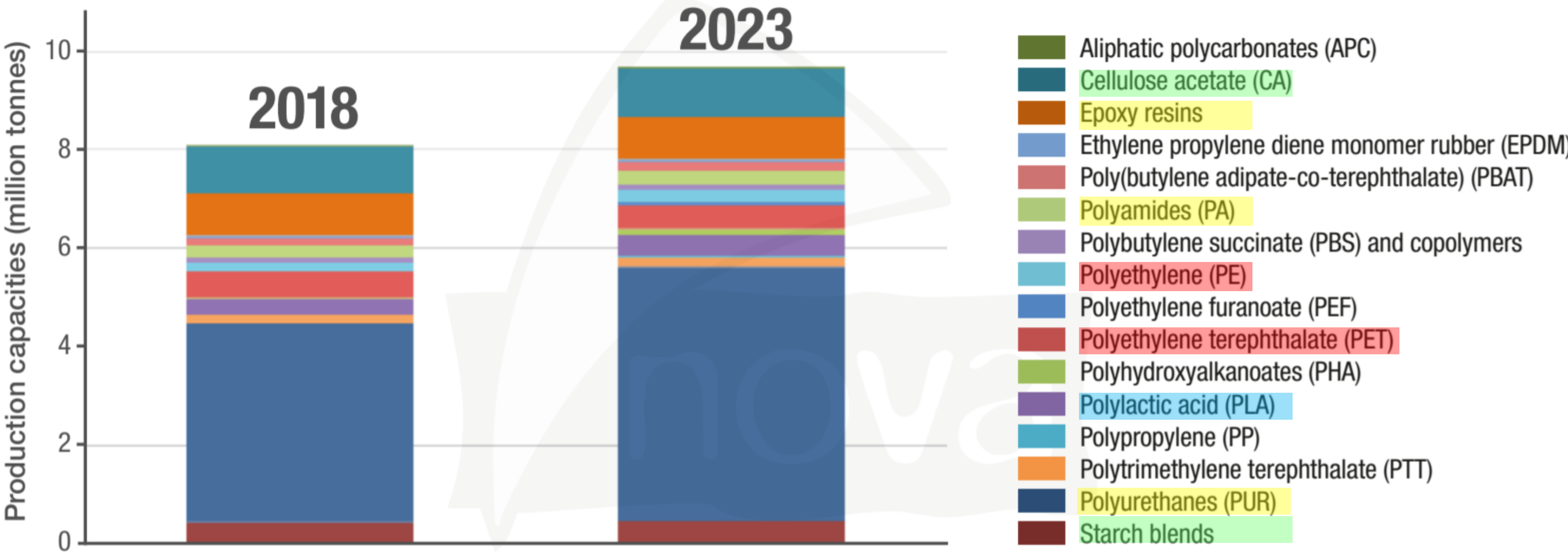
Market size ~ 50 million tones



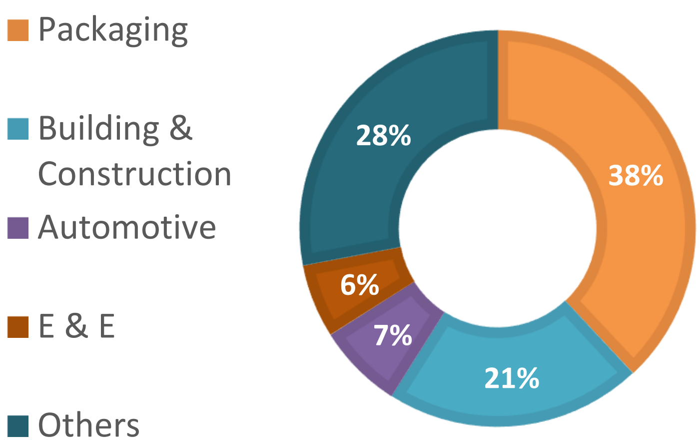
Schematic differentiation of pathways of drop-in, smart drop-in and dedicated bio-based chemicals

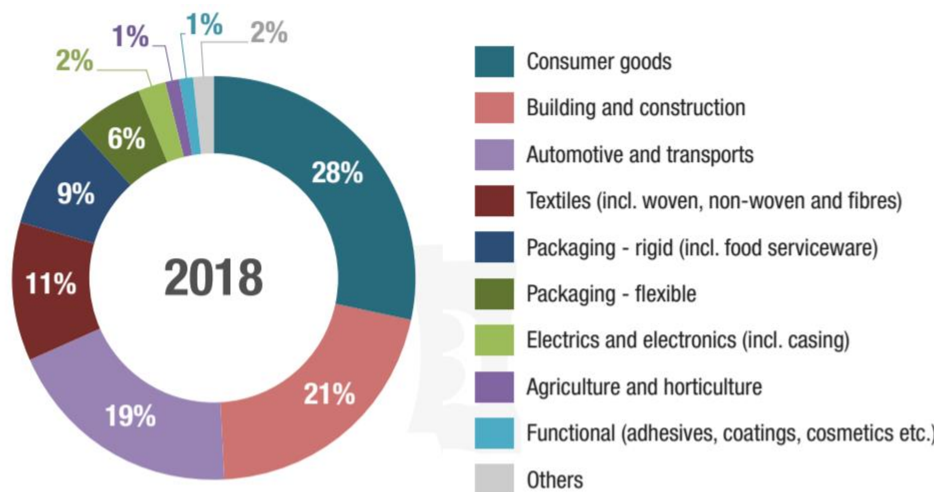


Worldwide production of bio-based polymers



Polymer applications *vs* bio-based polymer applications





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

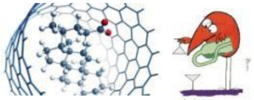
- Cl
the

For a success story all 5 drivers are needed

Cost-driven

-Bi sil-
bas

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



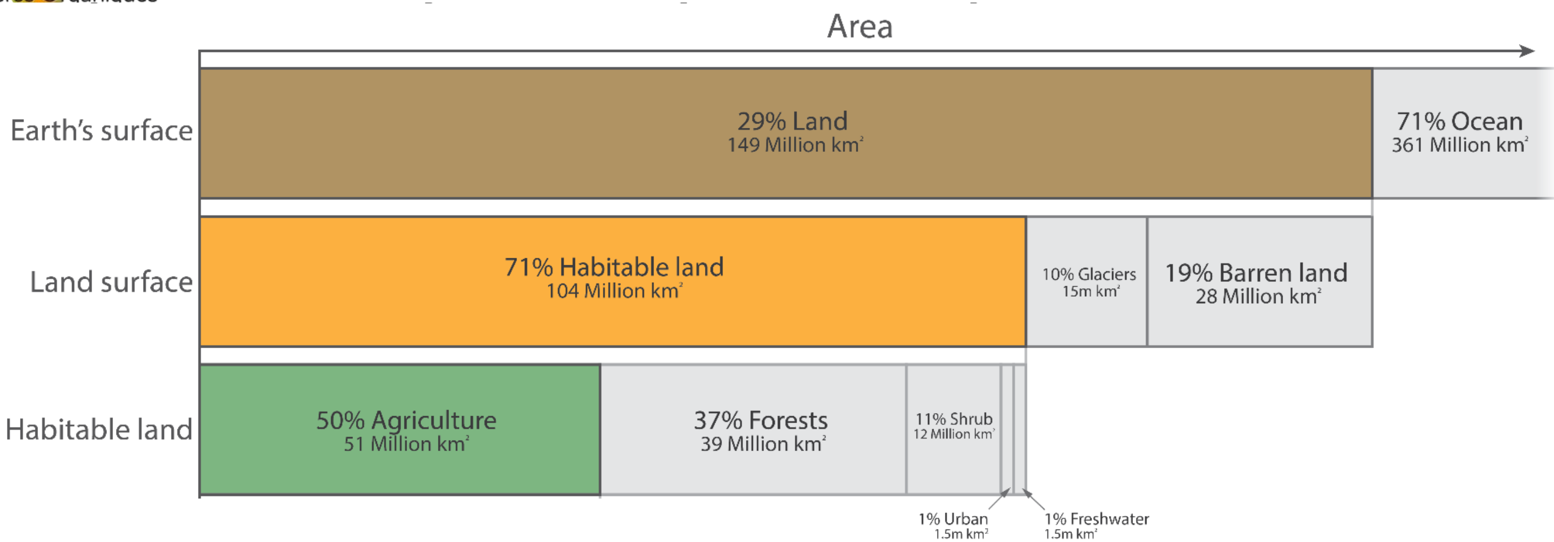
Functionality-driven

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

Legislation-driven

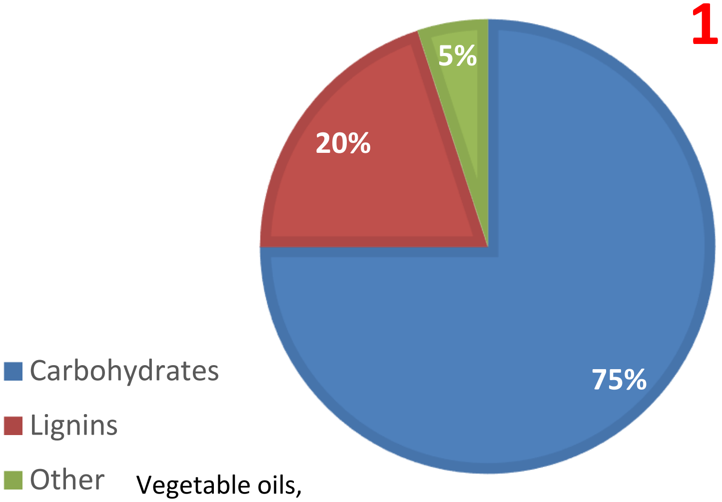
For some applications and in some countries (eg. FR, IT), the government imposes legislations obliging biodegradable packaging and maybe tomorrow tax incentives or obligations on bio-based plastics?

Worldwide land use



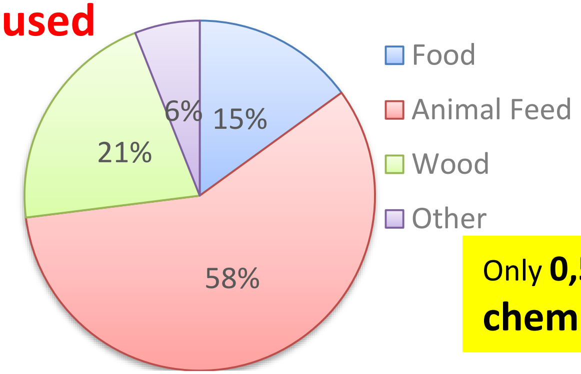
Biomass production ≈ 120 billions tons/year **vs.** **350 millions tons/y of polymers**

(210 with algea)



Vegetable oils,
Terpenes,
Proteins…

10% of the biomass is used



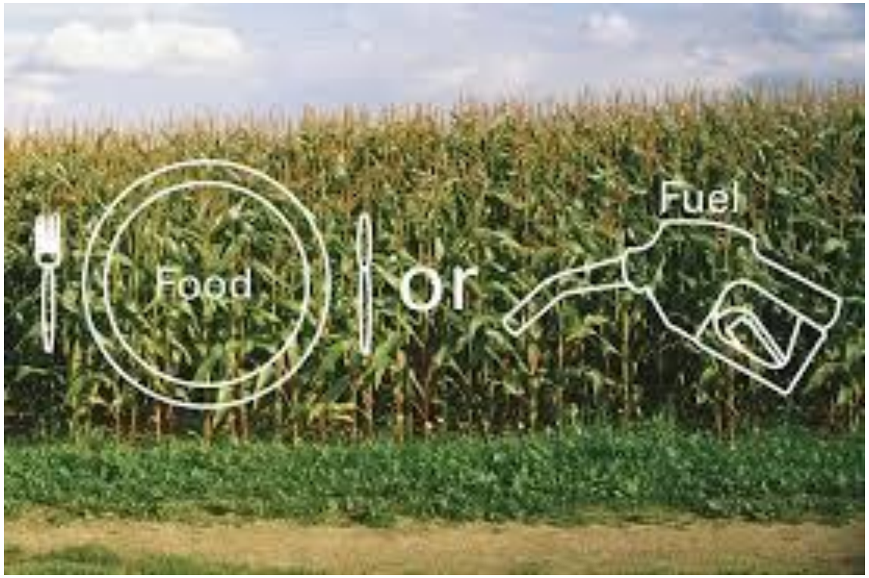
Only **0,5%** for **chemicals**

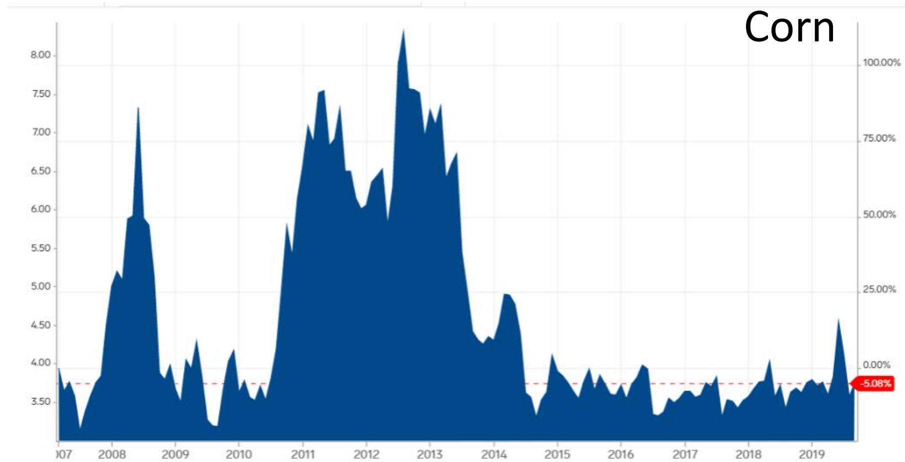
Cellulose production ≈ 400 millions tons/year

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 microalgea needed

2 ‰ of France surface

Outlines

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

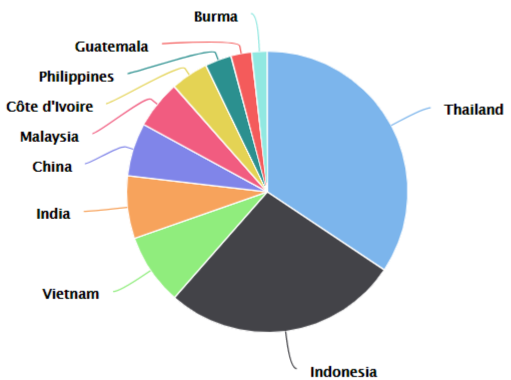
6- New polymers from biomass

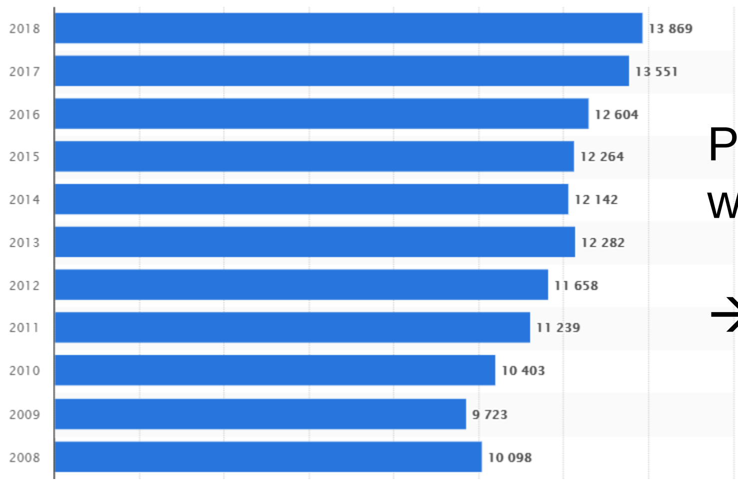
7- Conclusions and perspectives

Natural rubber from latex

- **Rubber products : polyisoprene 1,4-cis**

  13.9 Mt (2018)





Production increase is too slow for the worldwide demands

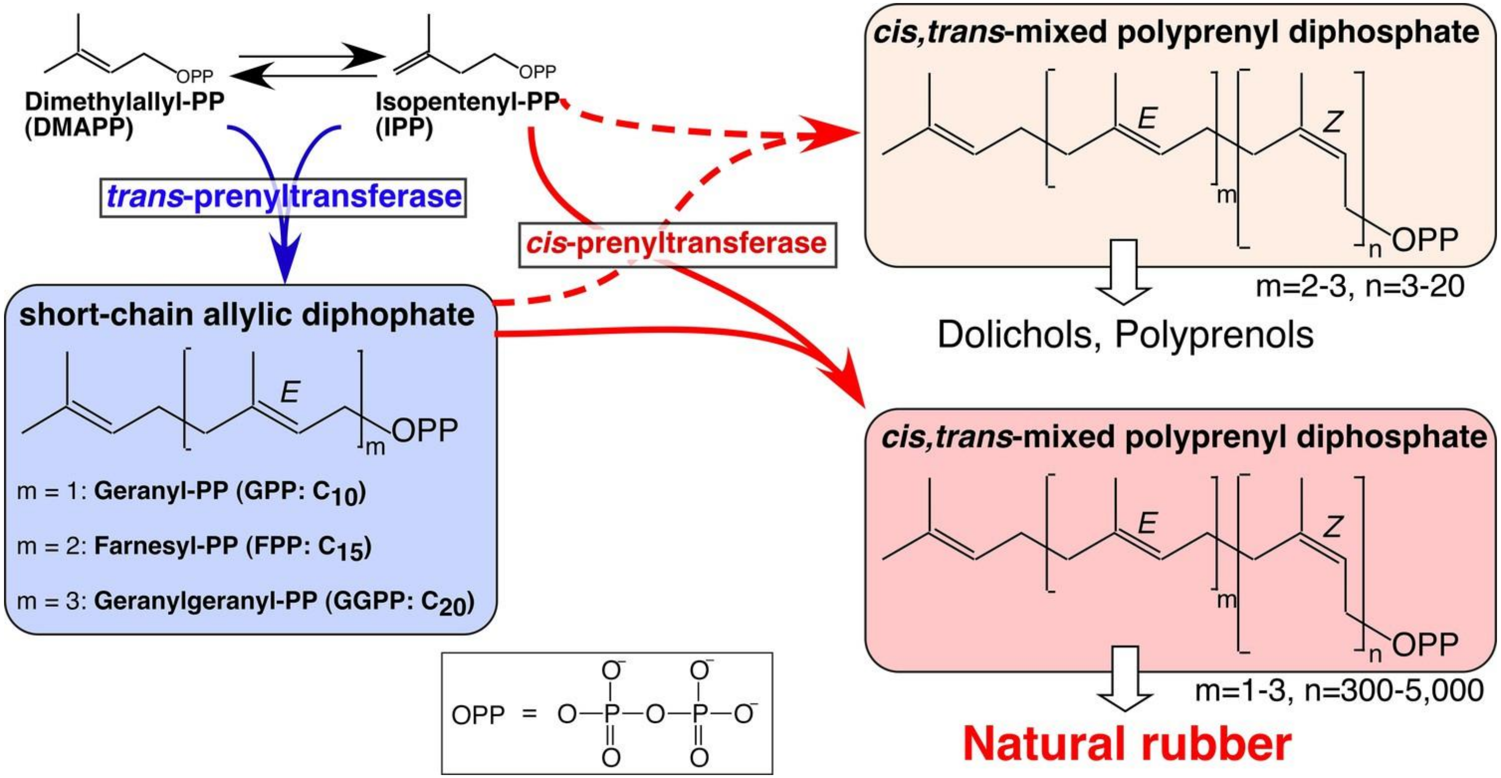
→ Other sources

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

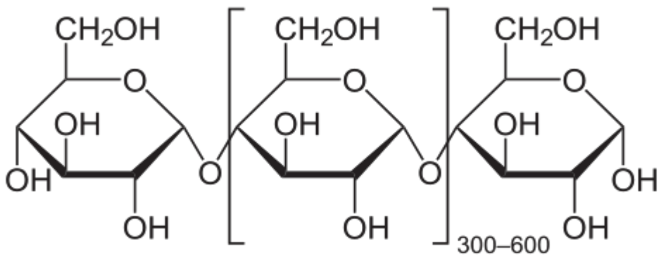
Bio-based plastics from natural polymers

Starch based polymers

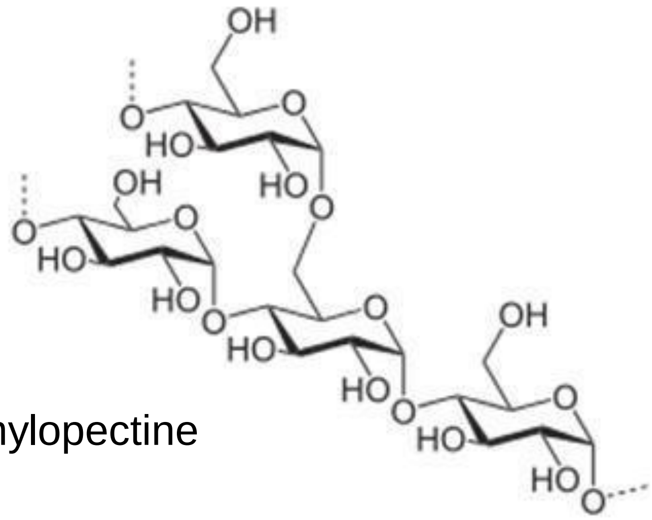
Starch blend with different polymers
400 Kt (1Mt for the blend)

- 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 %



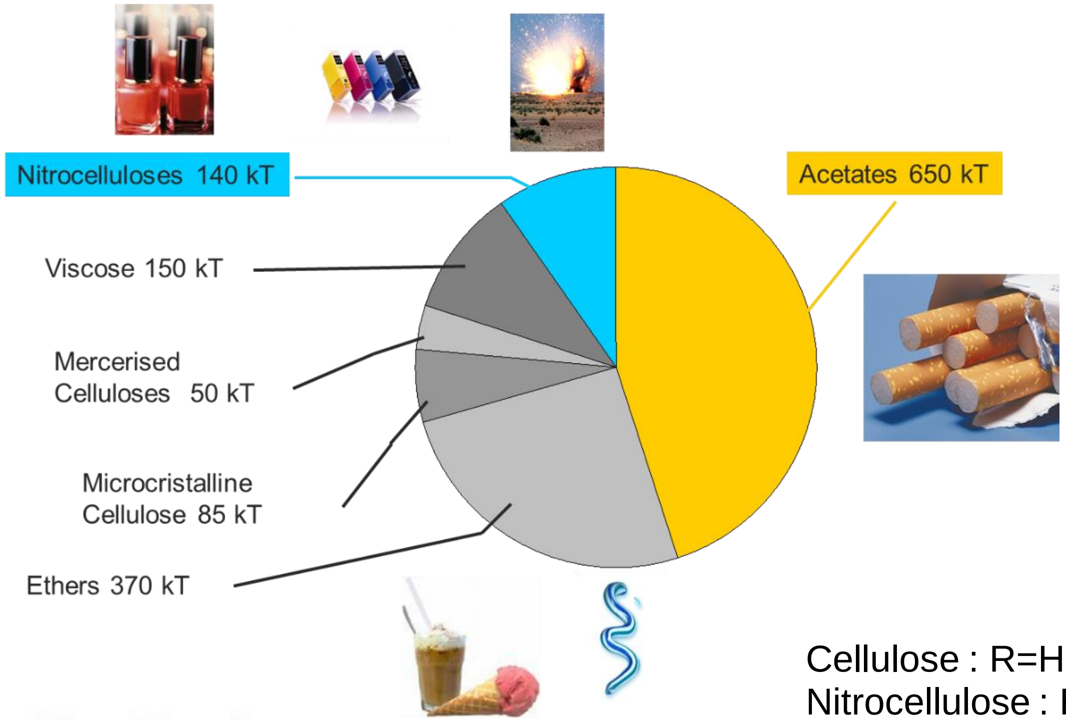
Amylose

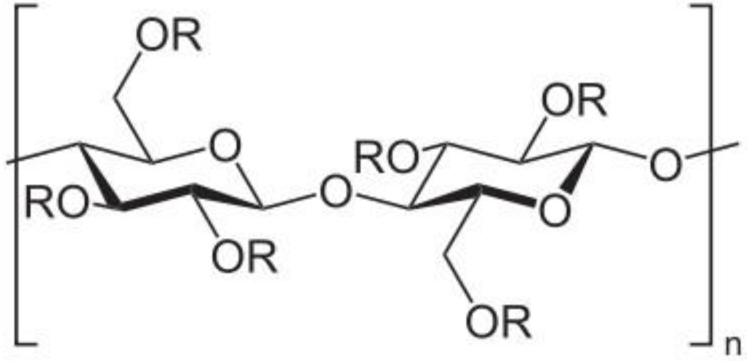


Amylopectine

Cellulose-based polymers

Mature market with small growth (1.5Mt)





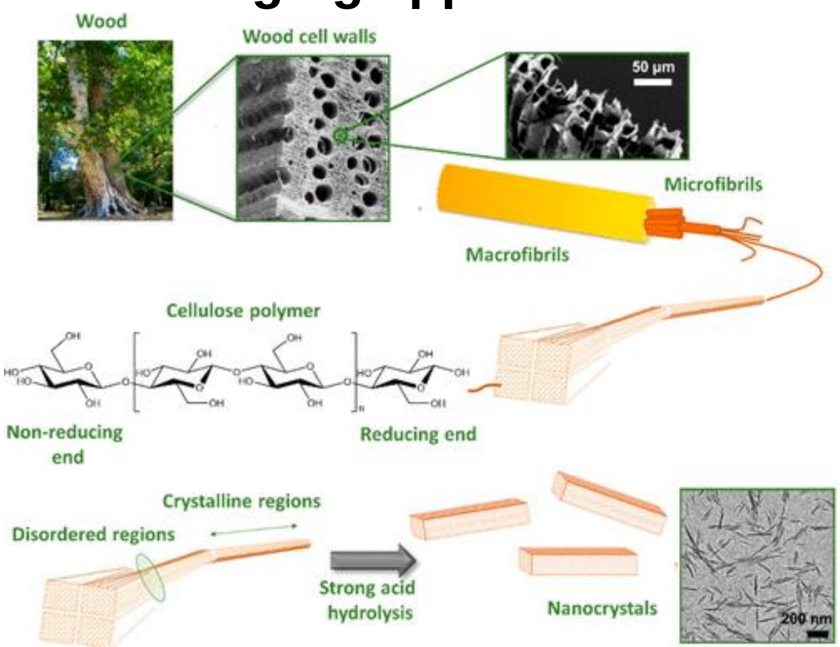
Cellulose : R=H
Nitrocellulose : R=H & NO_2
Cellulose acetate : R=CH_3CO
Cellulose acetate/butyrate : R=$CH_3CH_2CH_2CO$
Hydrophilic cellulose ethers: R=CH_2CH_2OH; $CH_2CH(CH_3)OH$; CH_2COOH

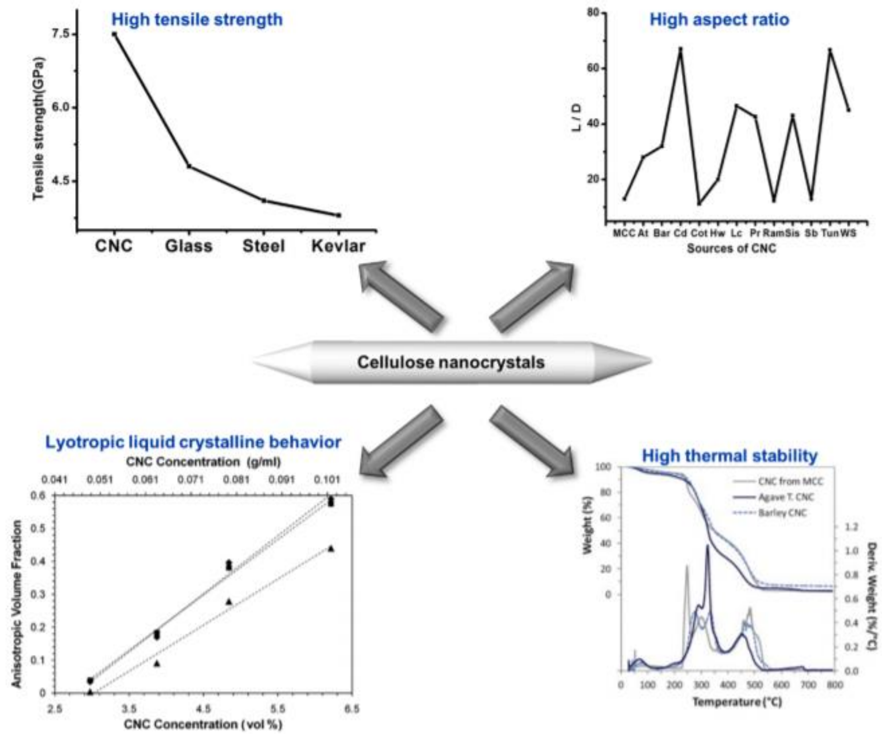
Not a thermoplastic

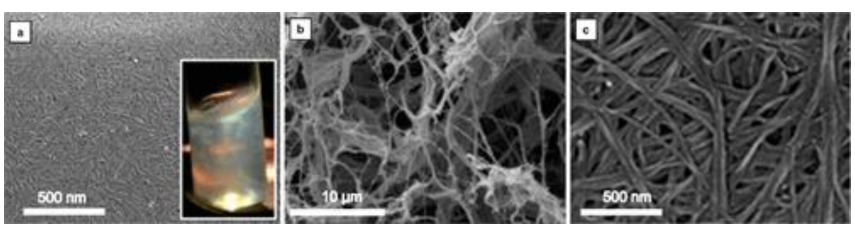
Bio-based plastics from natural polymers

Cellulose-based polymers

Emerging application

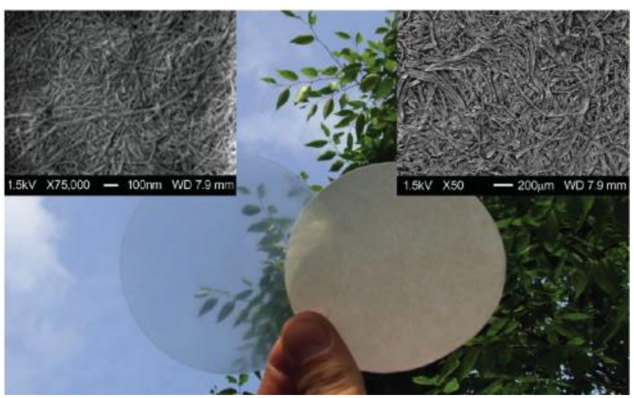






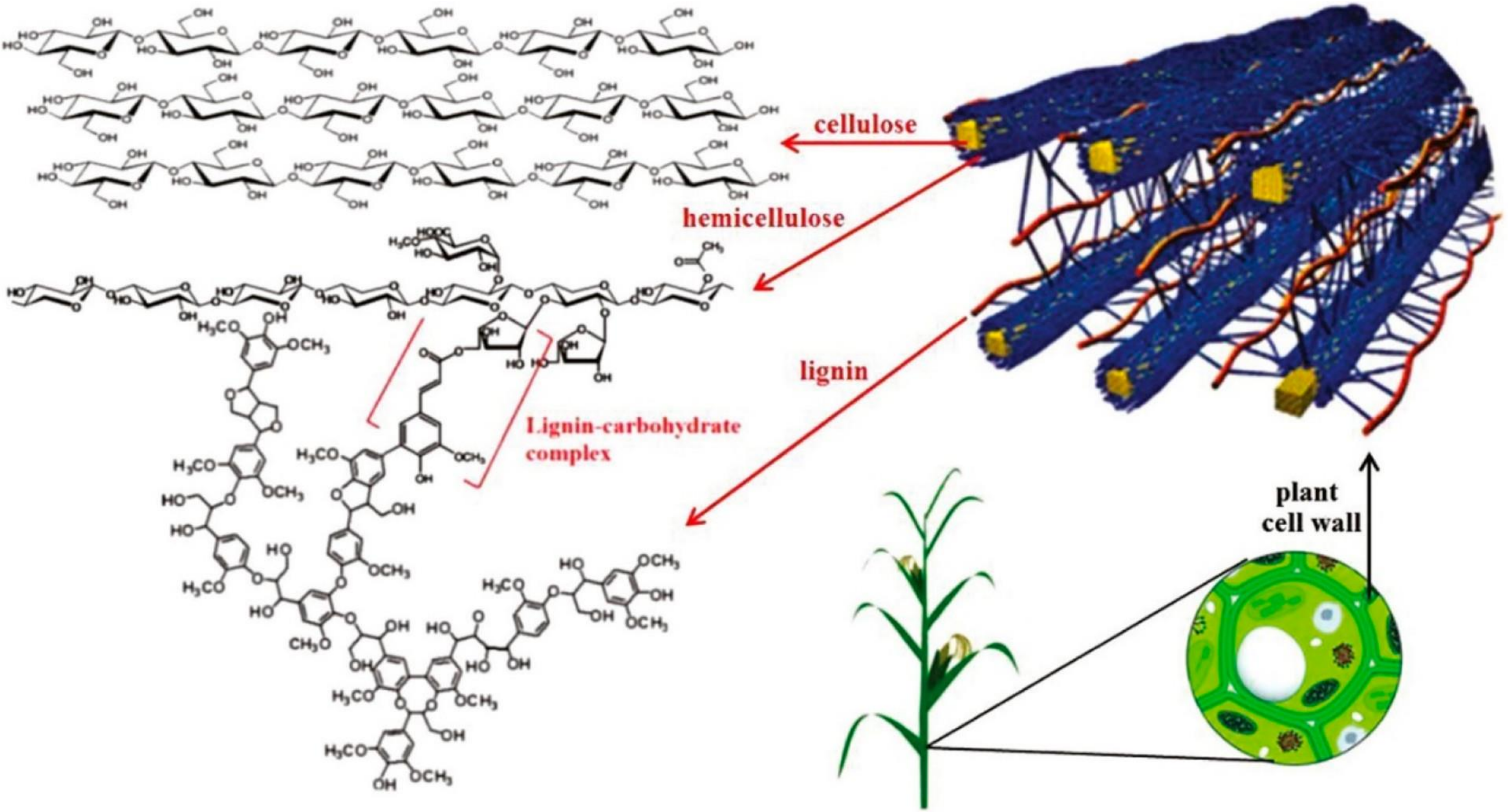
CNC CNF BC

CNC (100 nm)



CF (200 µm)

Other polymers

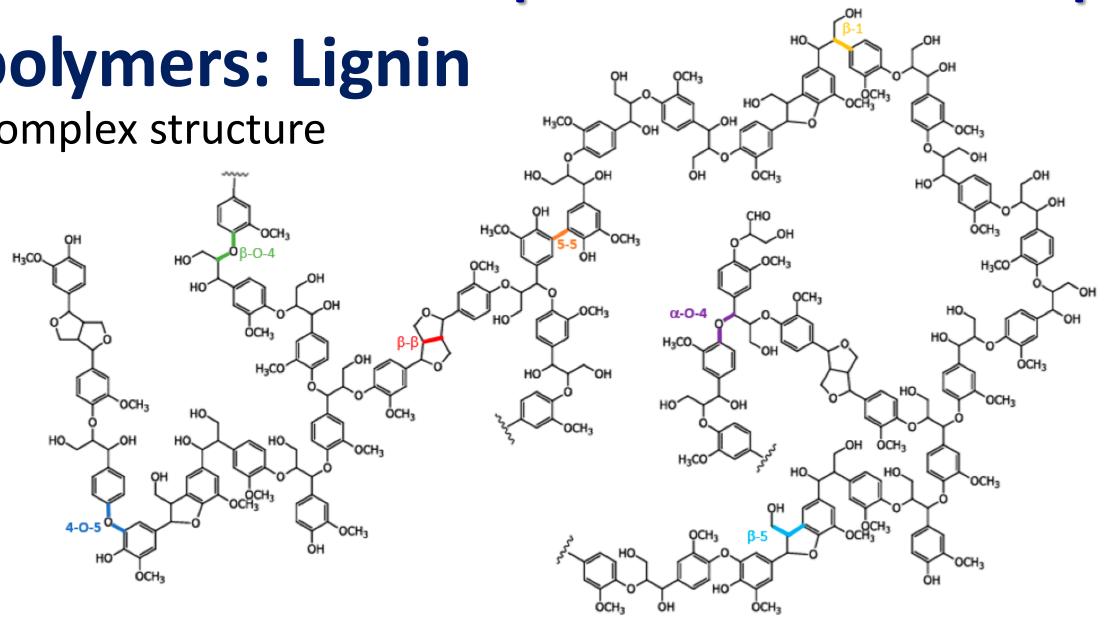


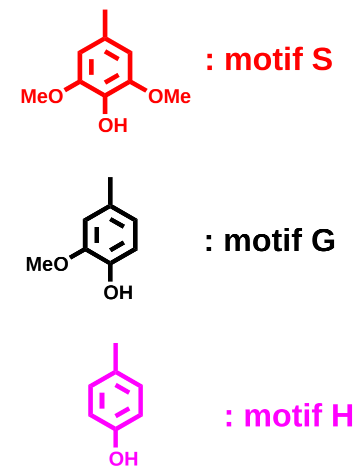
Bio-based plastics from natural polymers

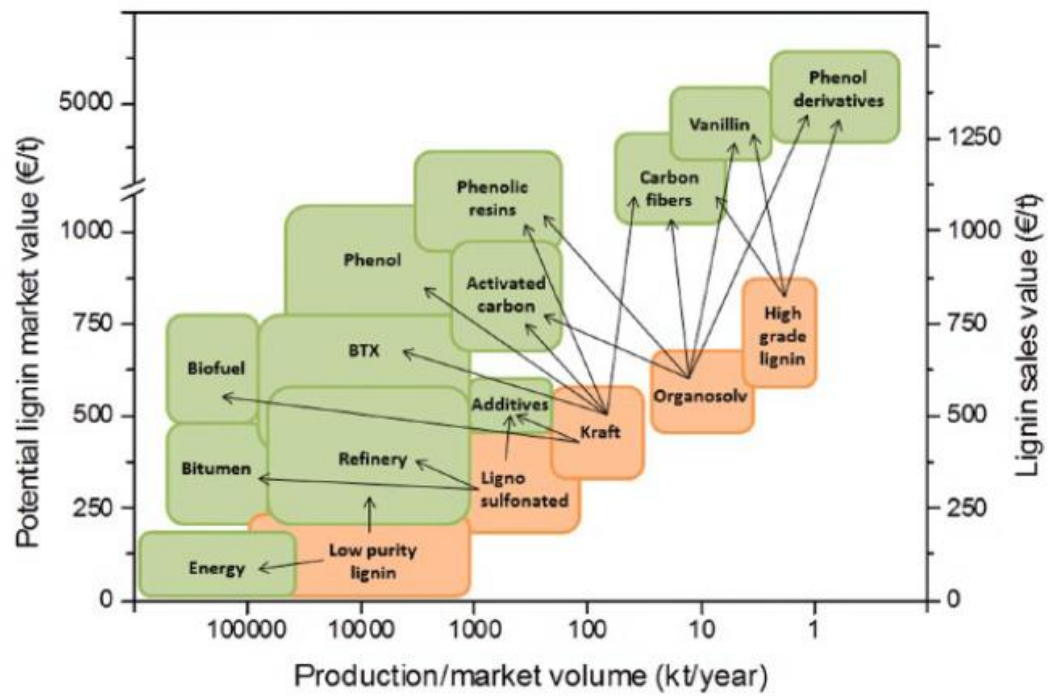
Other polymers: Lignin

Extremely complex structure

500 kt

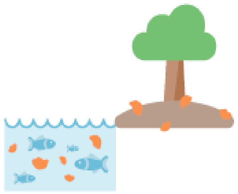






Outlines

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

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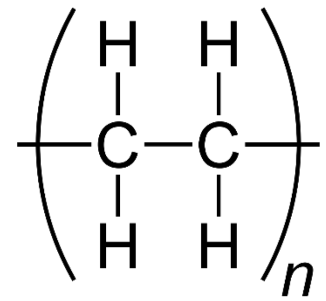
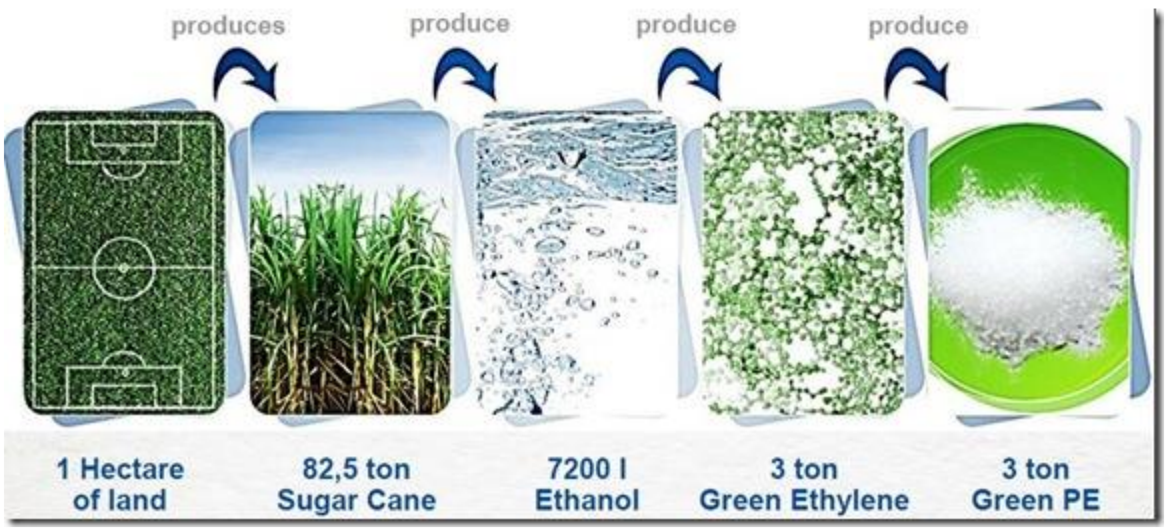
Drop-ins: Bio-based alternative to fossil-based polymers

Polyethylene (PE)



200 Kt

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



-3.09 kgCO_2e/kg

(vs 1.96 kgCO_2e/kg)

27 Mha *vs.* **80 Mt** of PE

¼ of the habitable land !!!

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

Polyethylene terephtalate (PET)

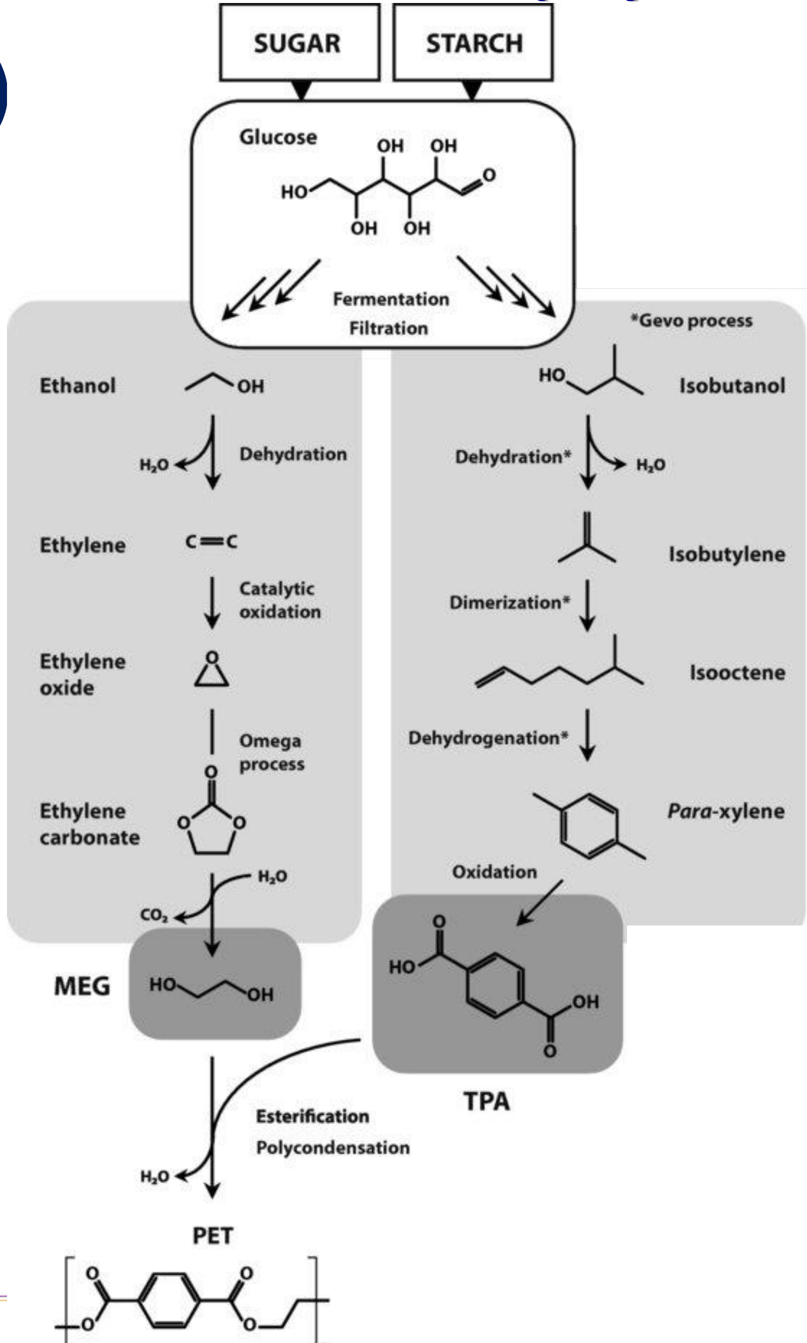
600 Kt

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

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

4 $kgCO_2e/kg$

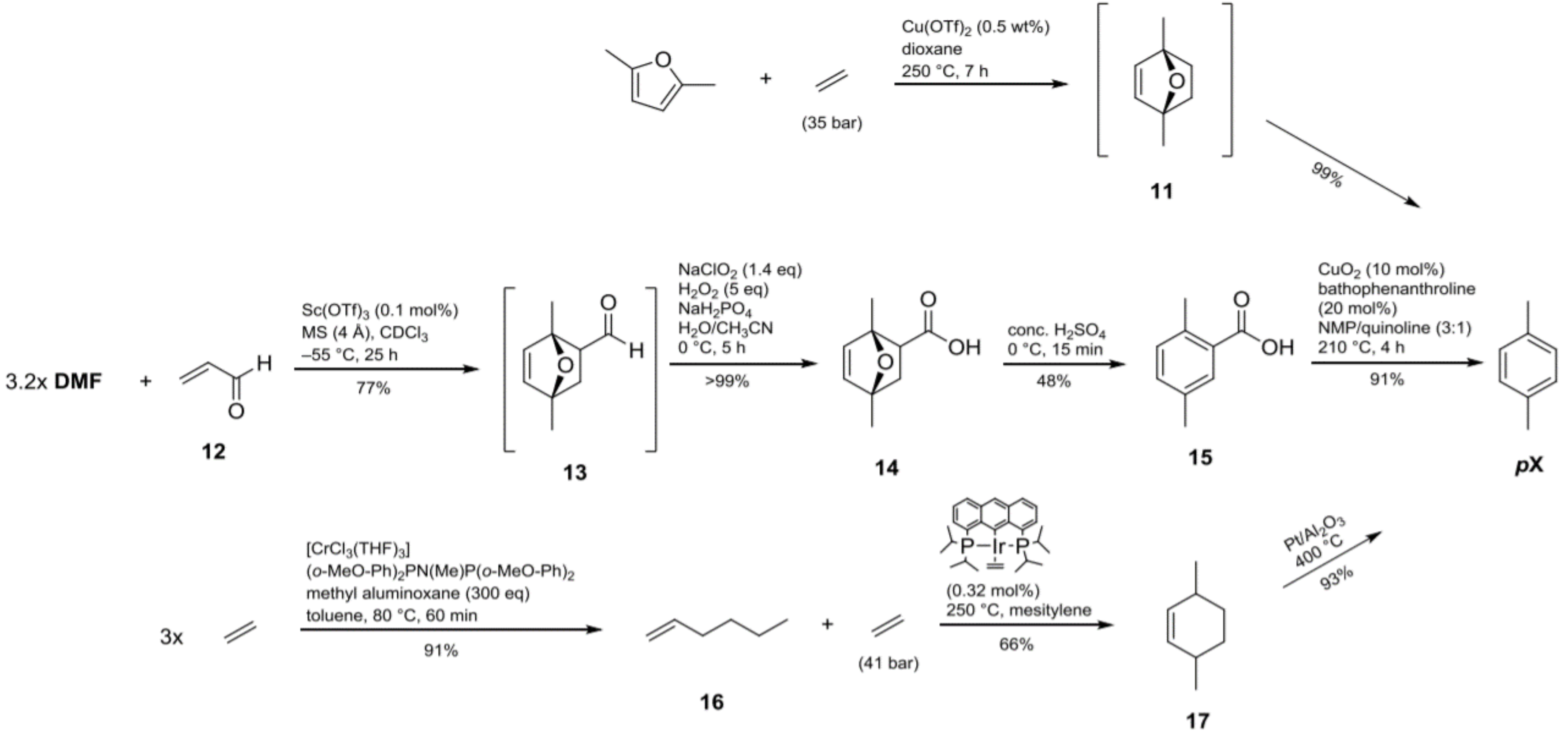
(vs 2.73 $kgCO_2e/kg$)



Polyethylene terephtalate (PET)

Other routes to terephatalic acid:

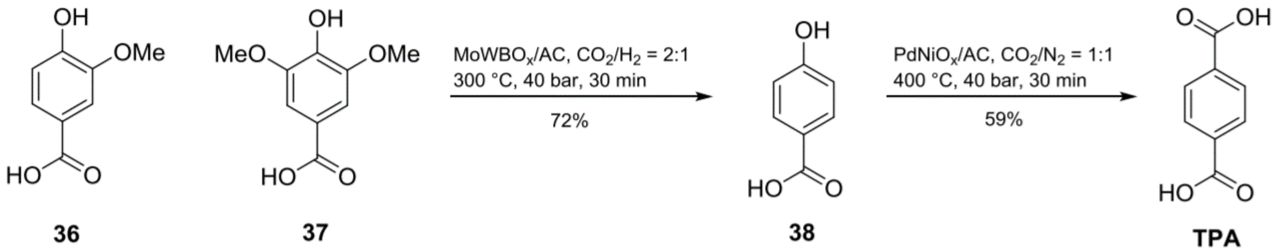
Other industrial routes



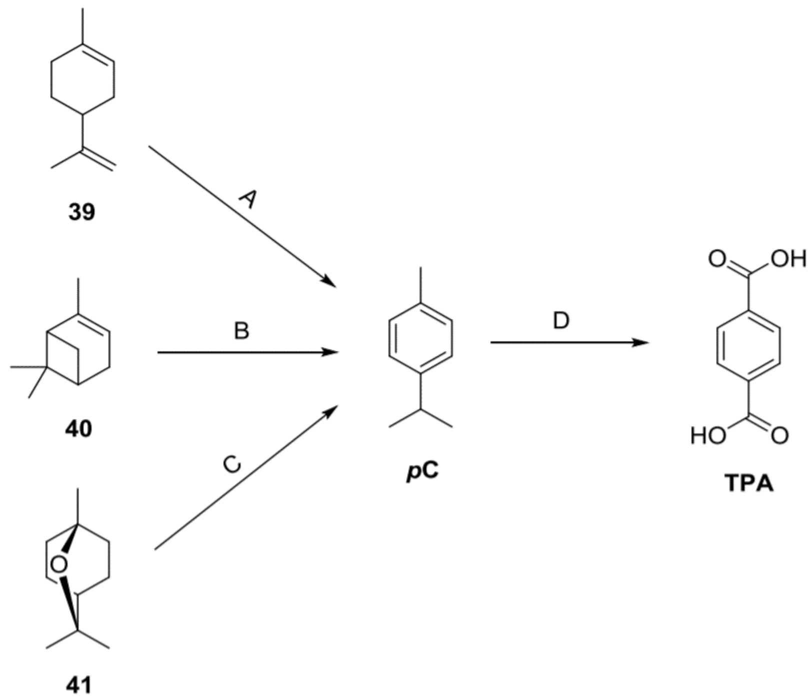
Polyethylene terephtalate (PET)

Other routes to terephatalic acid:

Lignin



Terpens

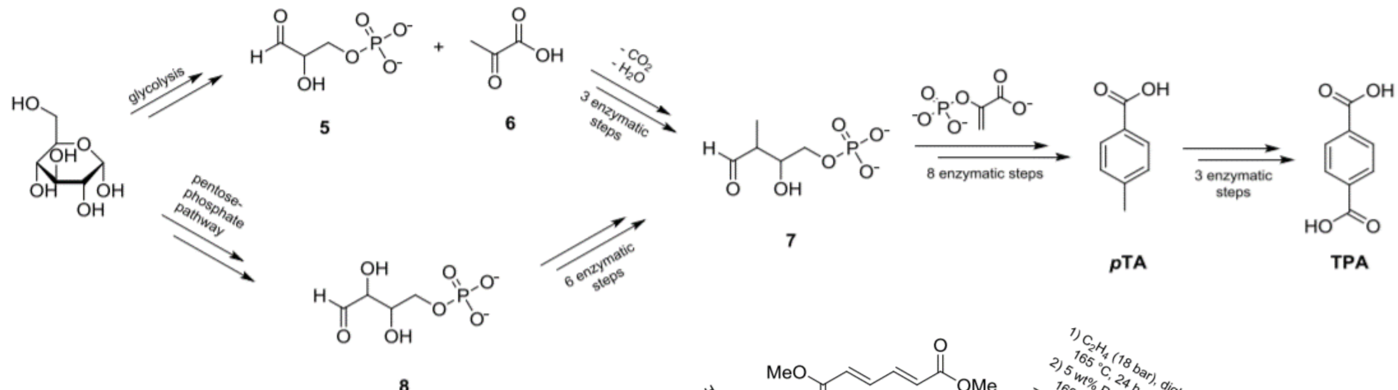


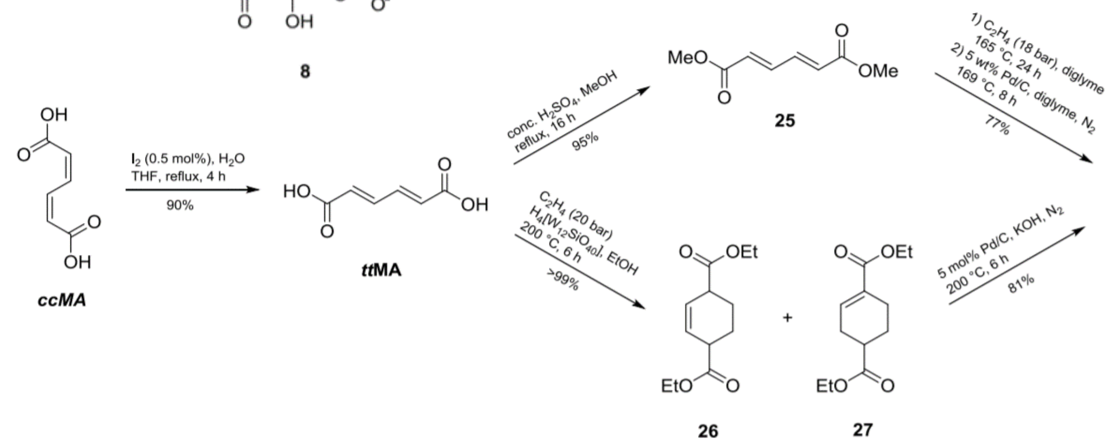
Drop-ins: Bio-based alternative to fossil-based polymers

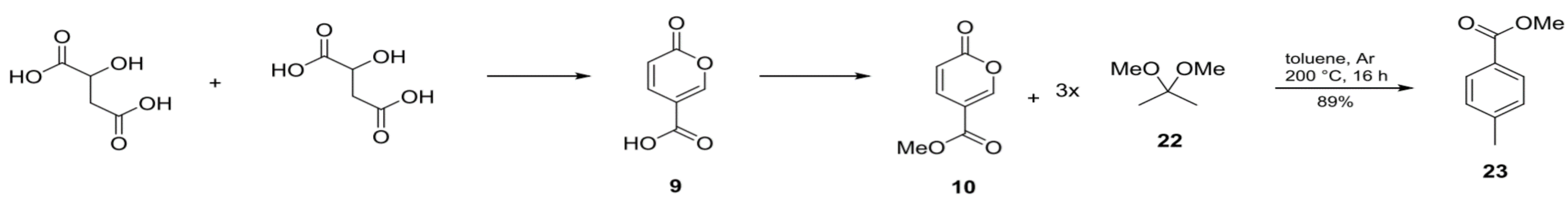
Polyethylene terephtalate (PET)

Other routes to terephatalic acid:

Sugars (C6)





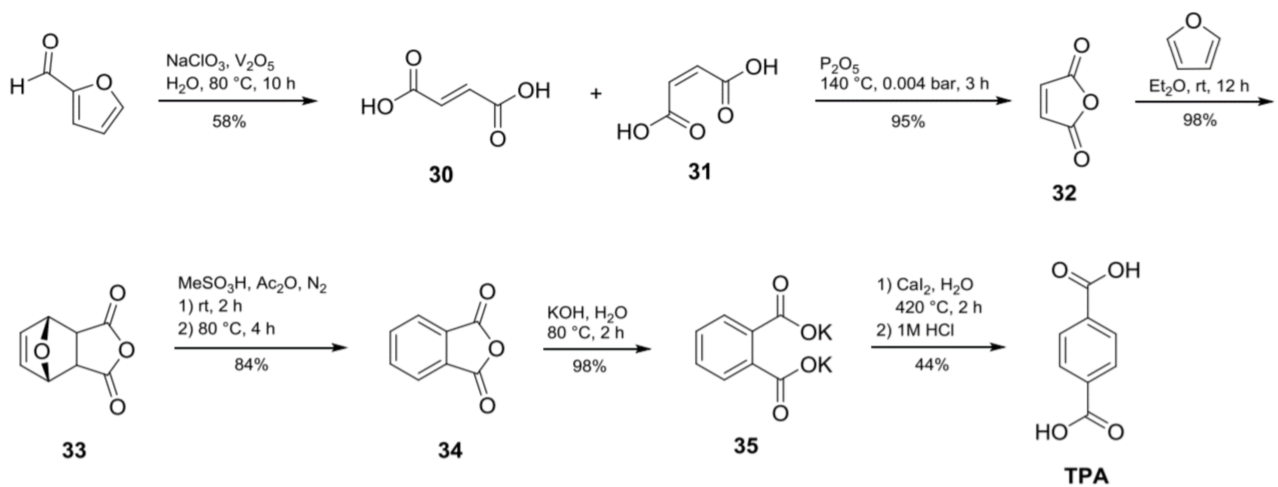


Drop-ins: Bio-based alternative to fossil-based polymers

Polyethylene terephtalate (PET)

Other routes to terephatalic acid:

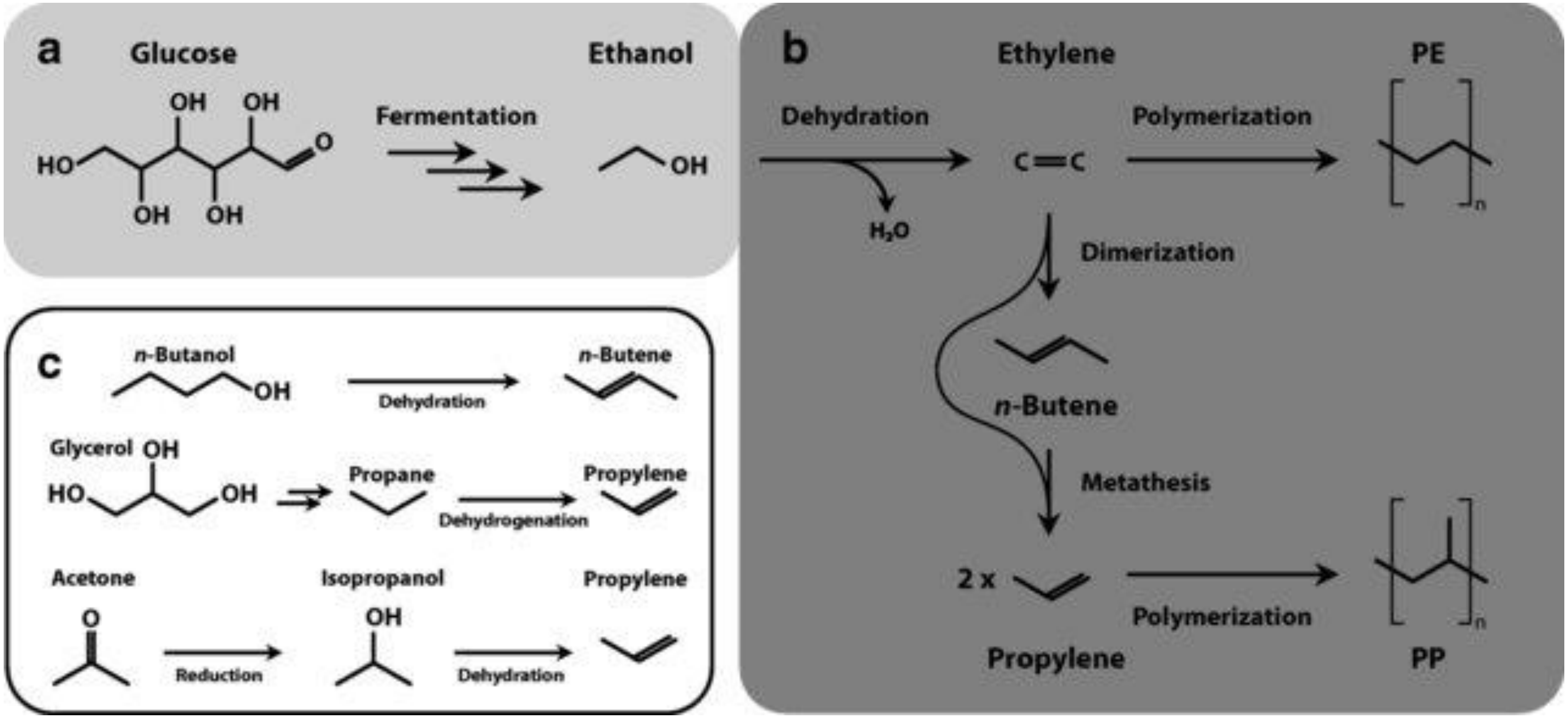
Sugars (C5)



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

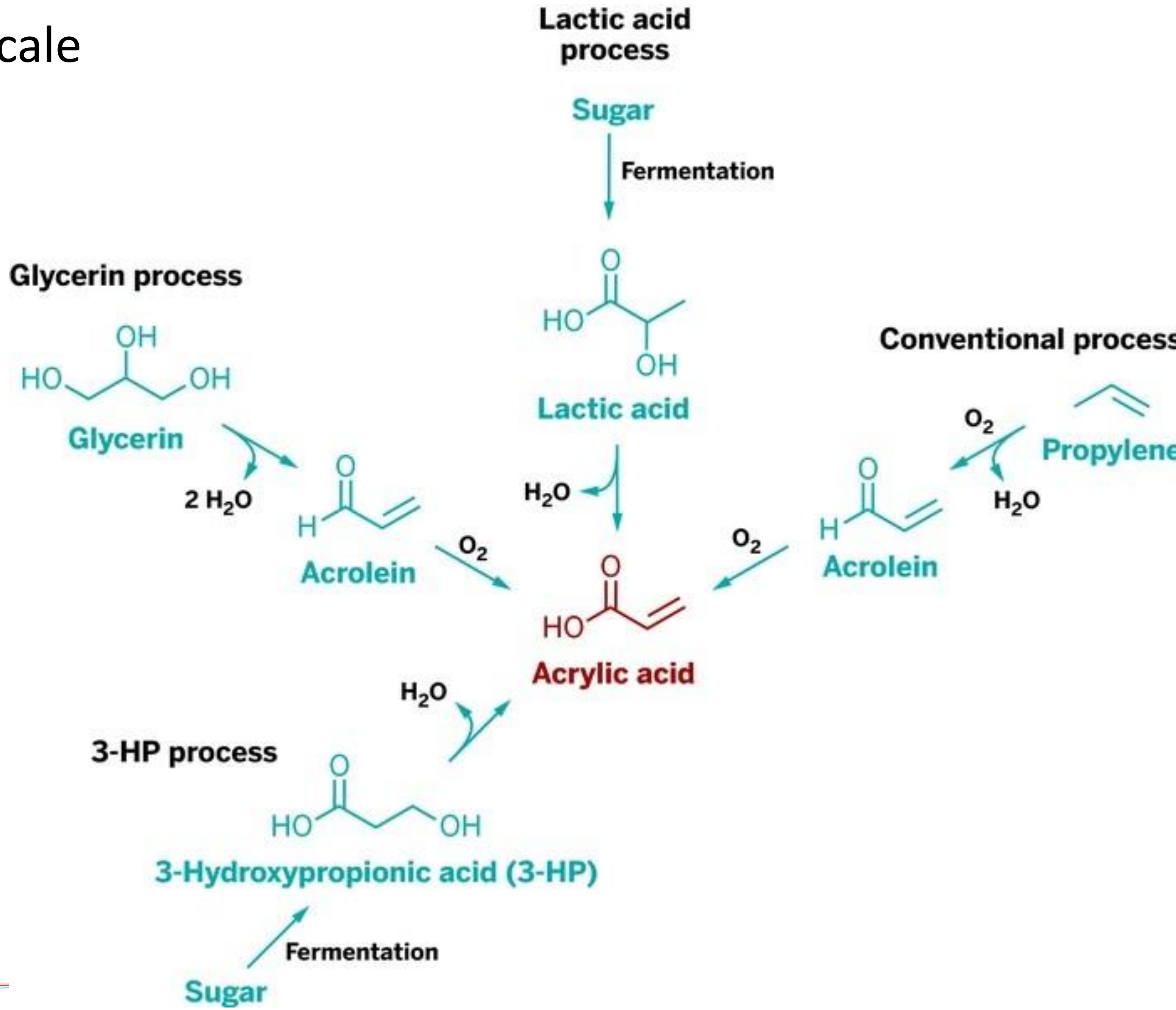
Polypropylene (PP)

20 kt



Super Absorbent polymers (SAP's)

Pilot scale

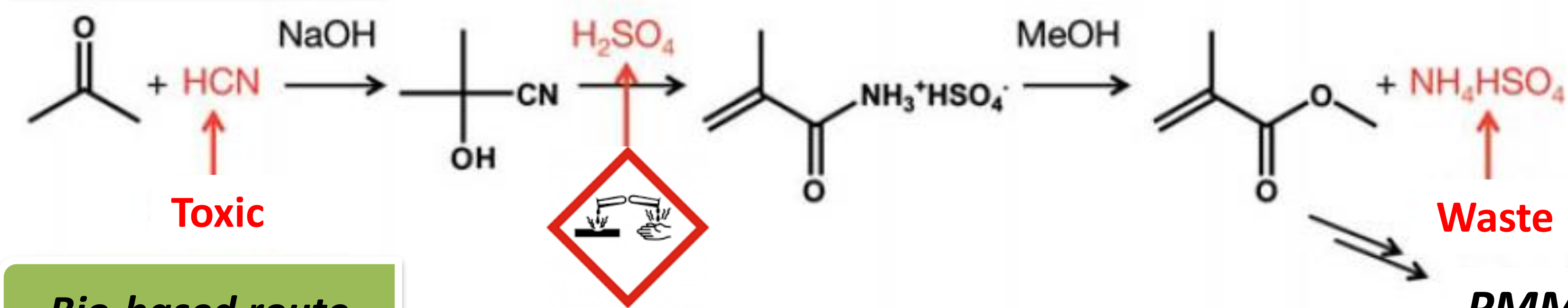


Drop-ins: Bio-based alternative to fossil-based polymers

Poly(methyl methacrylate) (PMMA)

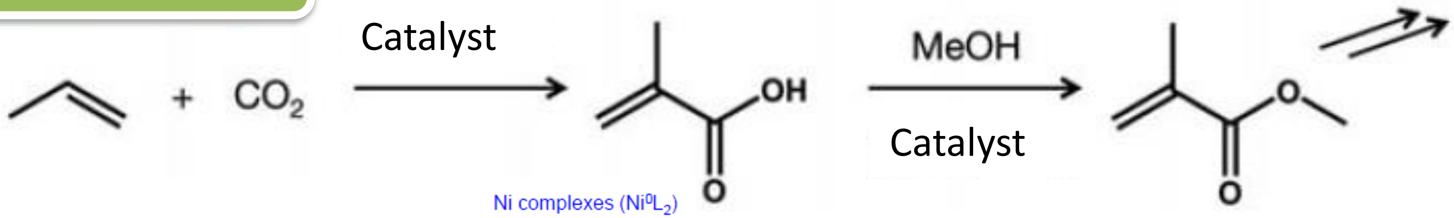
Pilot scale

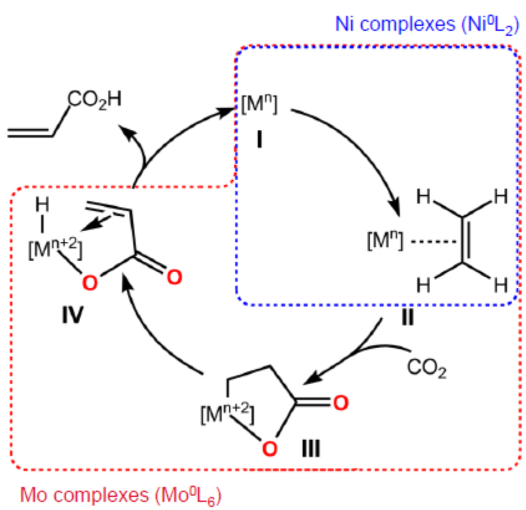
Traditional route



PMMA

Bio-based route





Greener ✓

Safer ✓

Bio-based ✓

Outlines

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

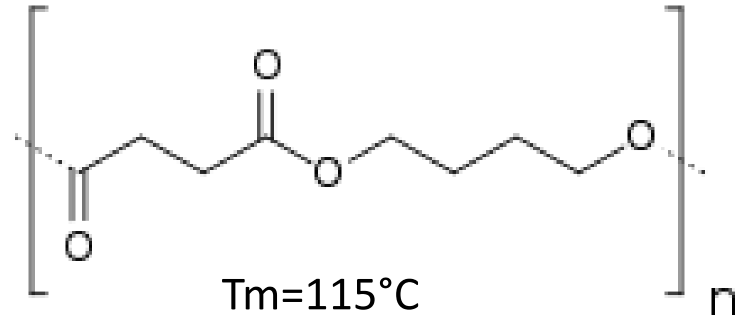
7- Conclusions and perspectives

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

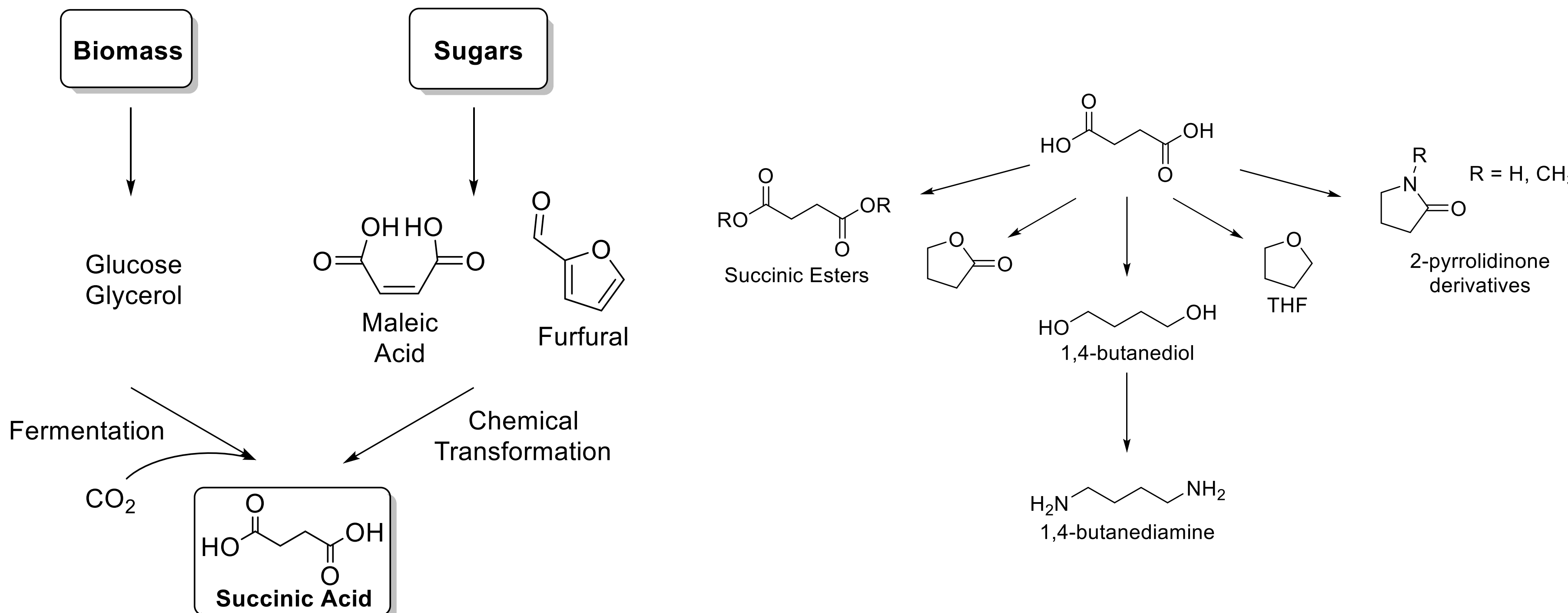
Polybutylene succinate (PBS)

100 kt

Bio-based succinic acid cost ≈ fossil

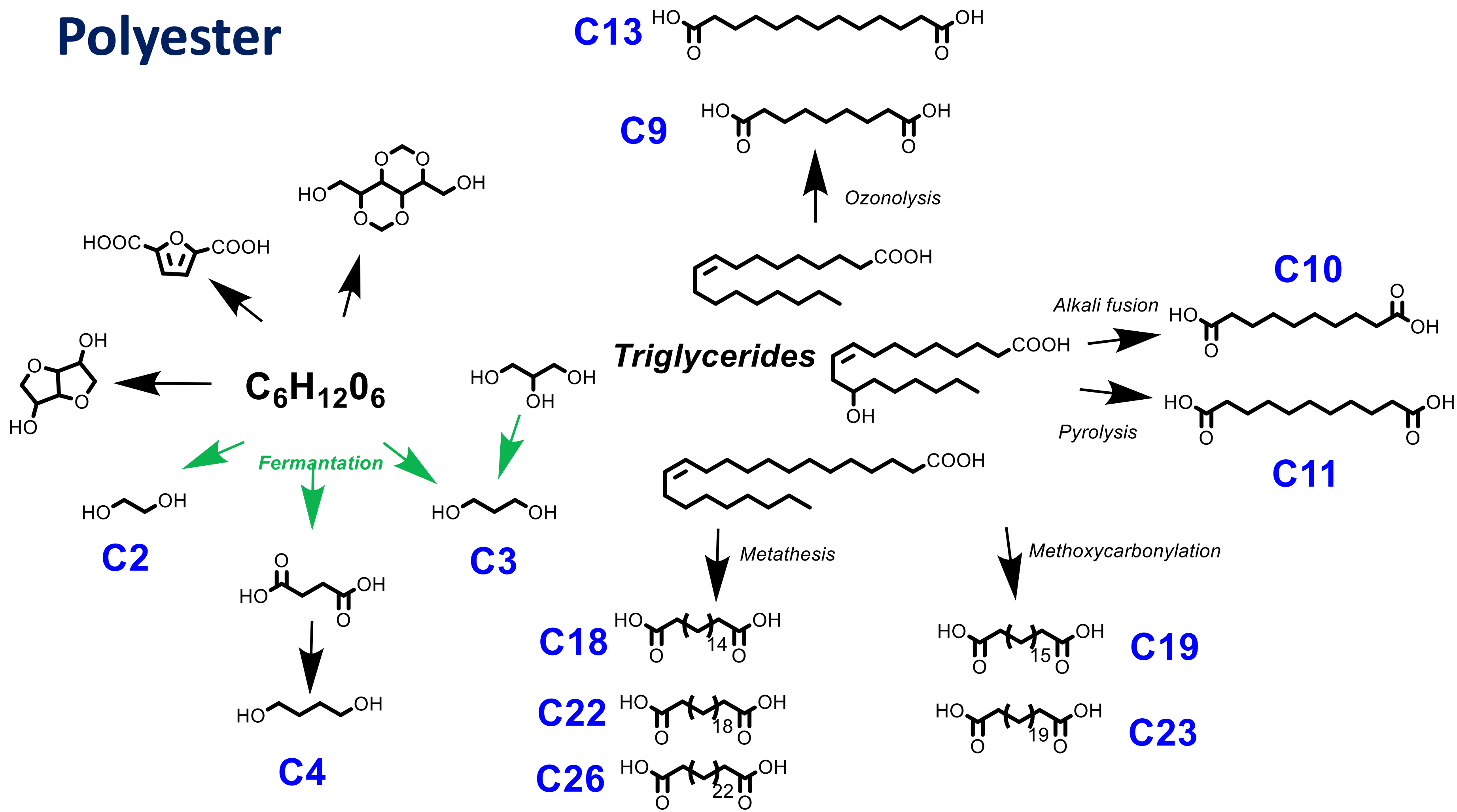


PBS polyethylene-like properties + biodegradable



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

Polyester

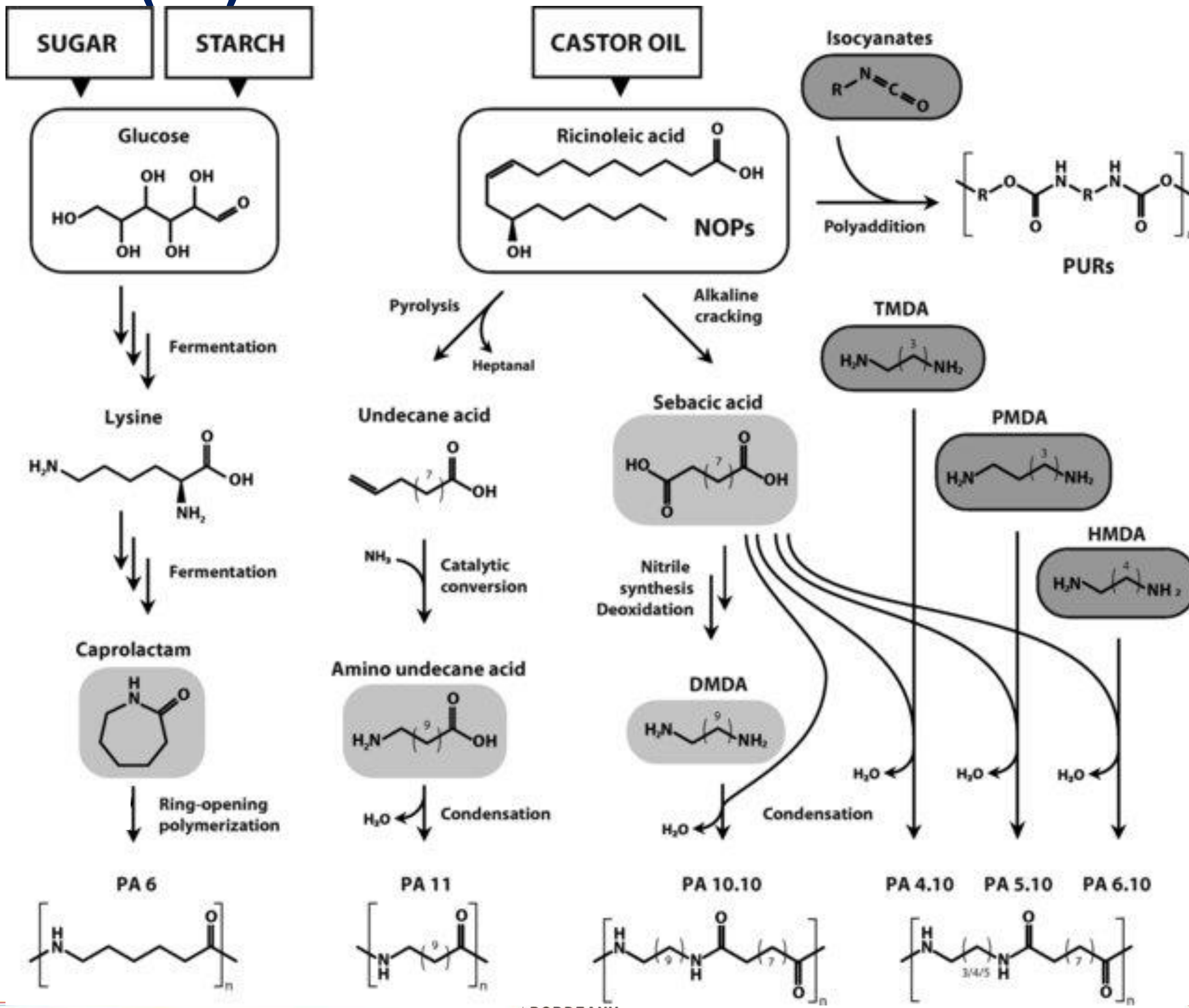


PET, PPT, PBT, PBS, PBAz … polyethylene mimick

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

Polyamides (PA)

200 kt



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

Polyamides (PA)

Stiffness

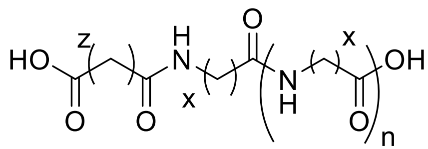
Polyamide

PA 6

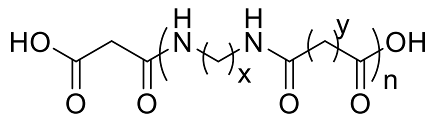
PA 6-10

PA 11

PA 12



or



Hydro-
phobicity

+ Polycondensation

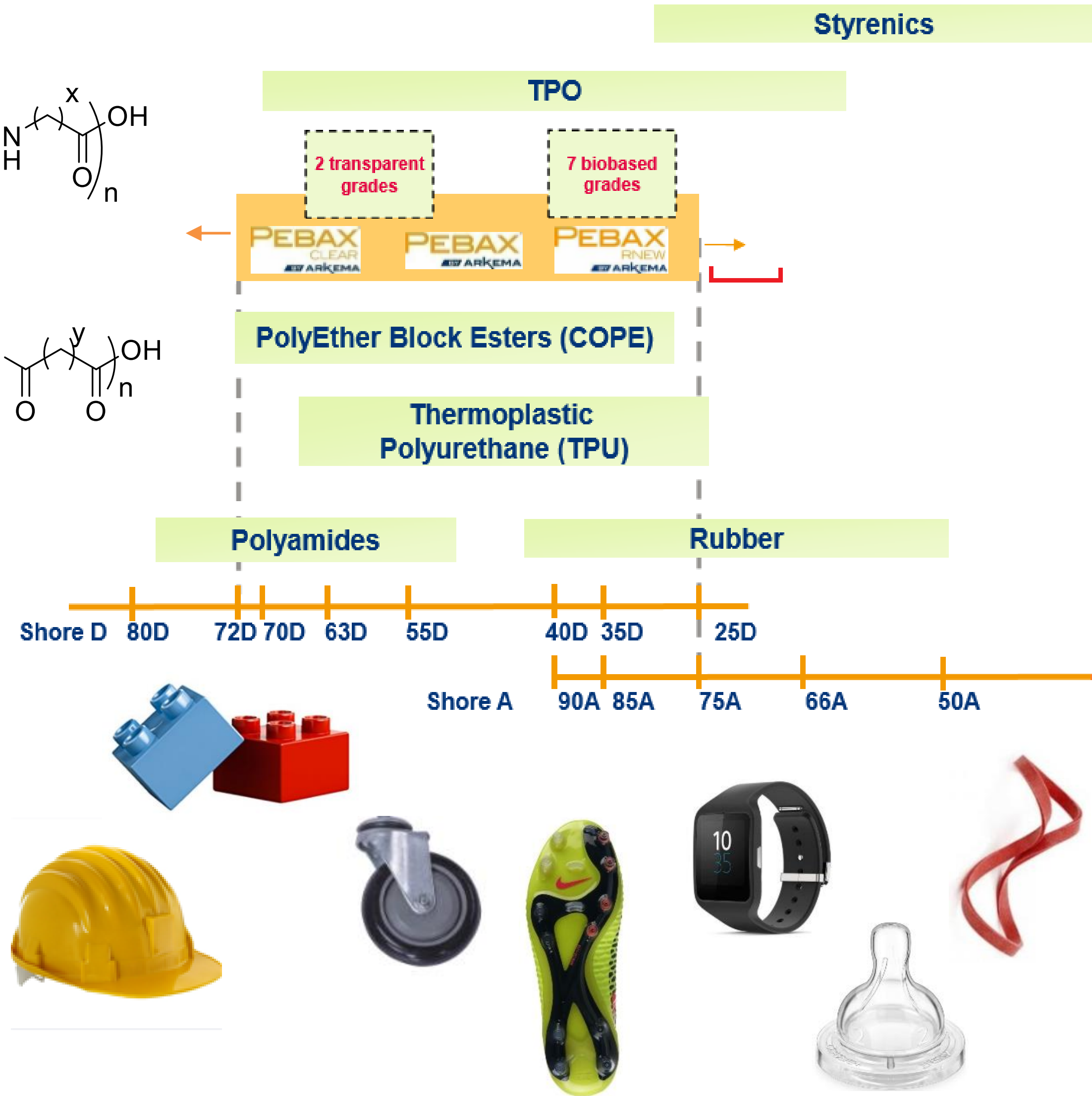
Polyether

PEG

PPG

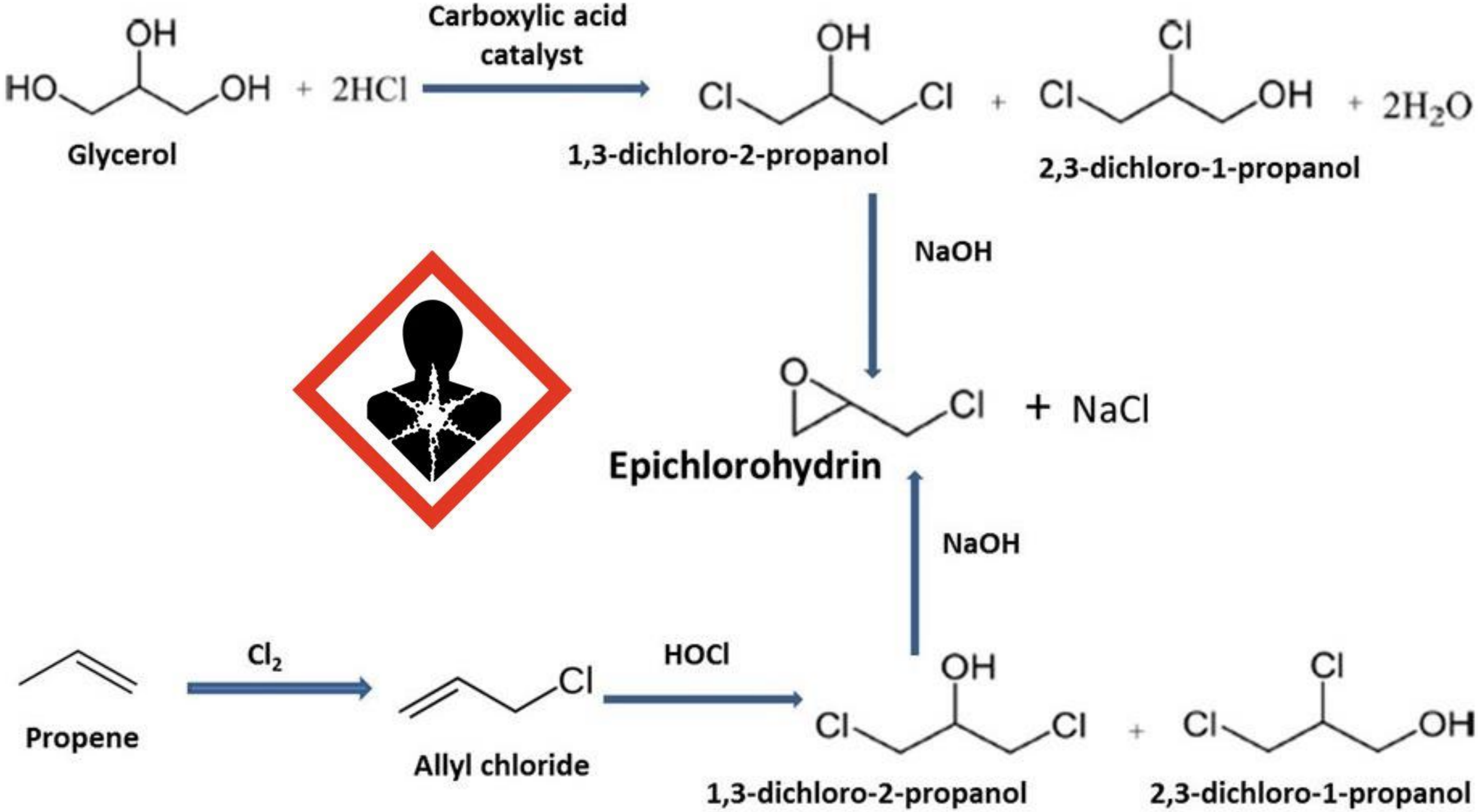
PTMO

Elasticity



Epichlorohydrin

1.5 Mt



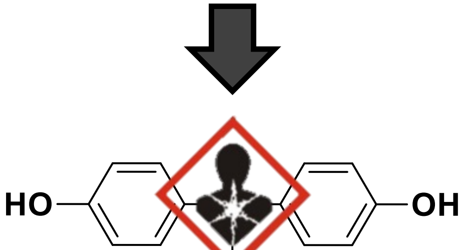
Smart drop-ins: Bio-based derivative of "fossil" polymers

Epoxy

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

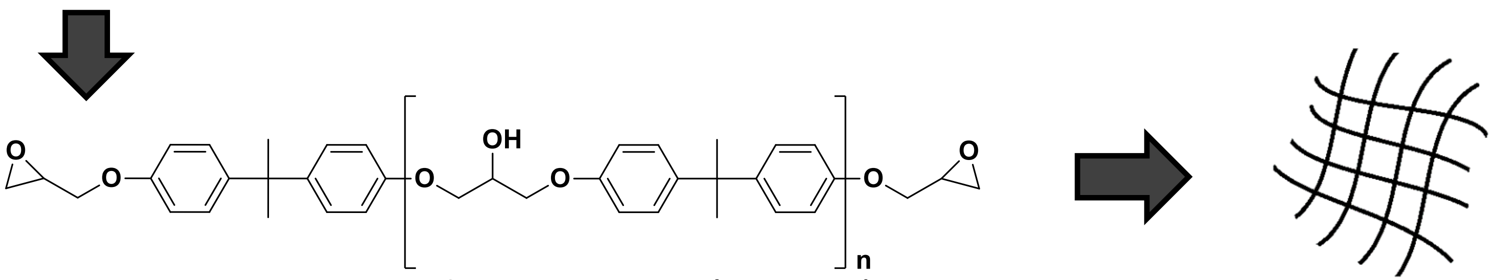
- Environnemental and economics concerns
  - Petrochemicals → fossil carbon
  - Price volatility

High risk of obsolescence of BPA



Bisphenol-A

- Toxicity of BPA → *CMR* [1]*B*



*DiGlycidylEther of Bisphenol-A (**DGEBA**)*

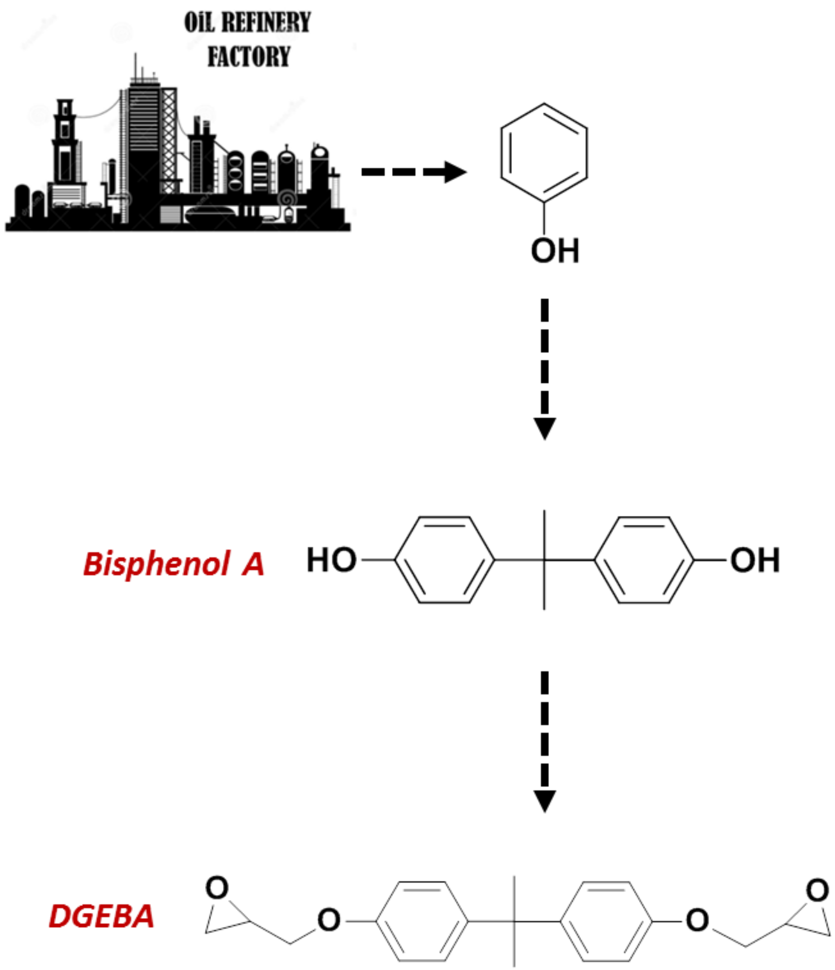
3D-network

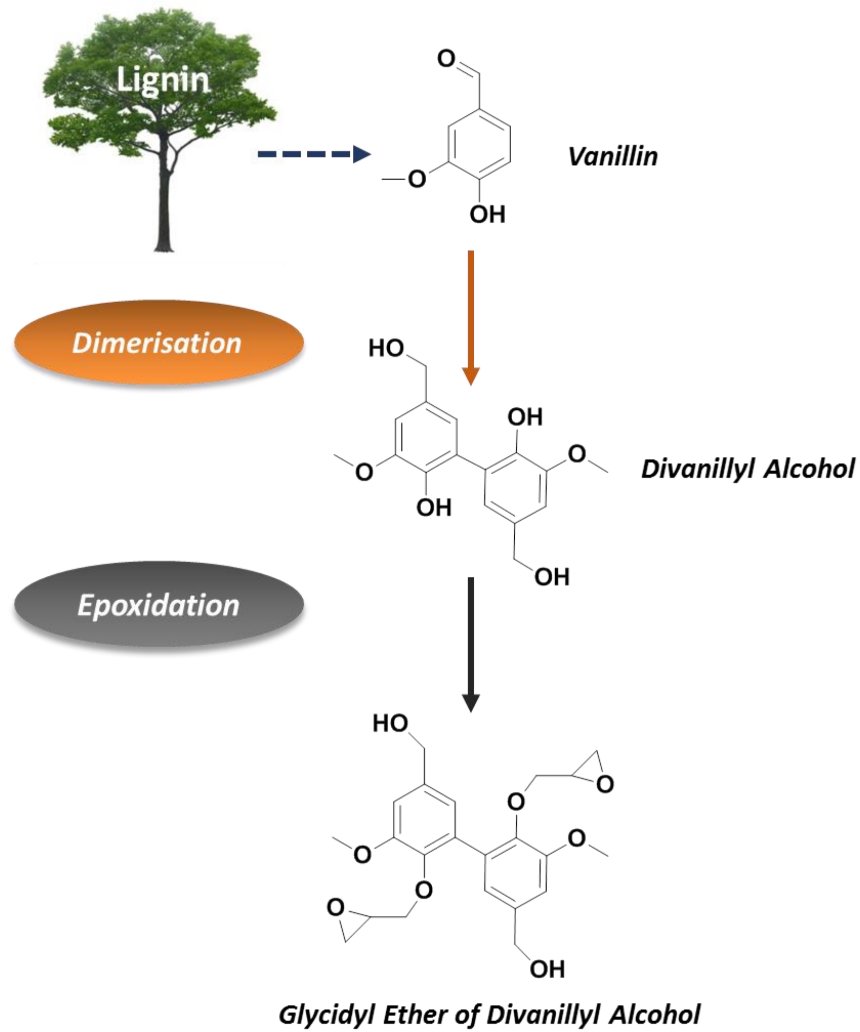
40-25% bio-based if epichlorohydrine bio-sourced

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

Epoxy

From Lignin to epoxy resins…



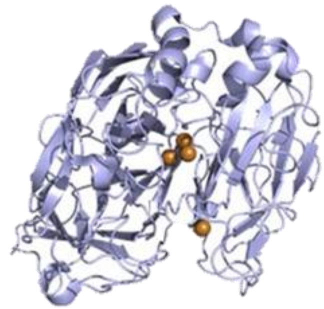


Smart drop-ins: Bio-based derivative of “fossil” polymers

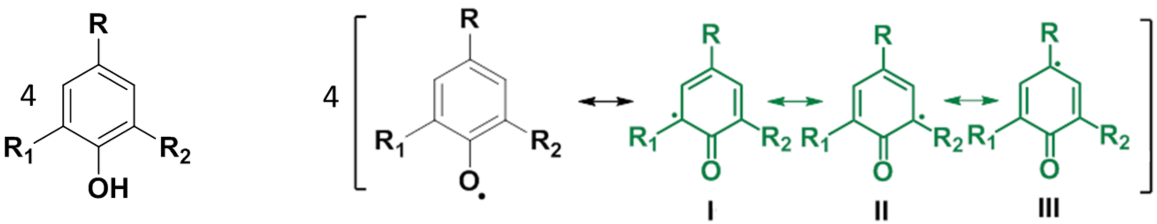
Epoxy

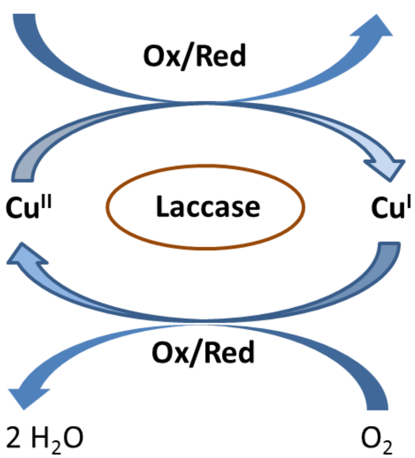
Enzymatic coupling

Trametes Versicolor



Laccase is an oxydative enzyme found in wood rotting fungi

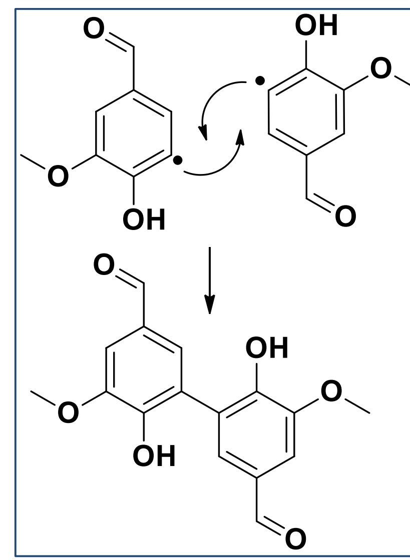




Kobayashi et al., *Chem. Rev.* **2009**

Laccase generates radicals which can undergo self coupling reactions yielding dimers

Coupling of Vanillin



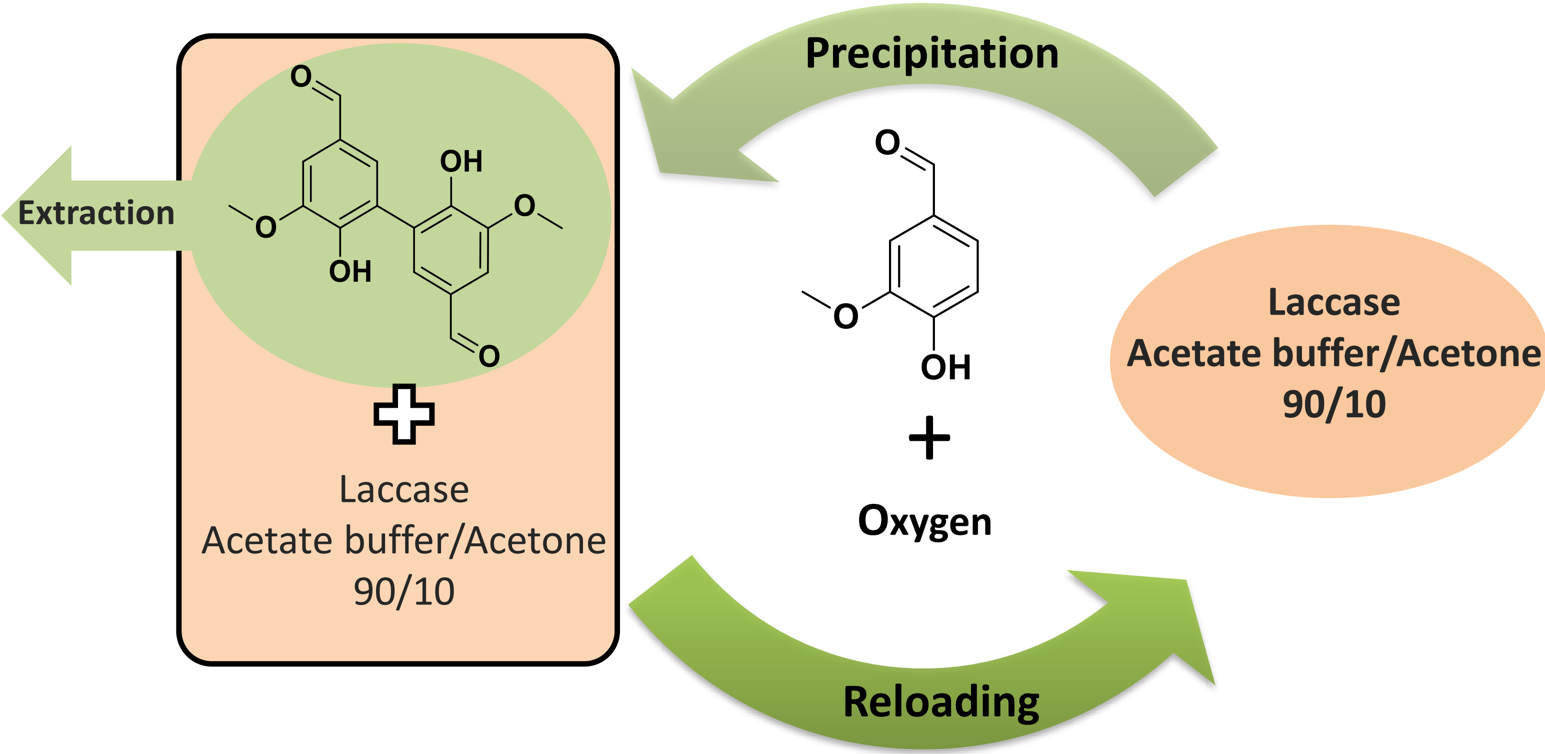
Divanillin

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

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

Epoxy

Synthesis of dimer from Vanillin



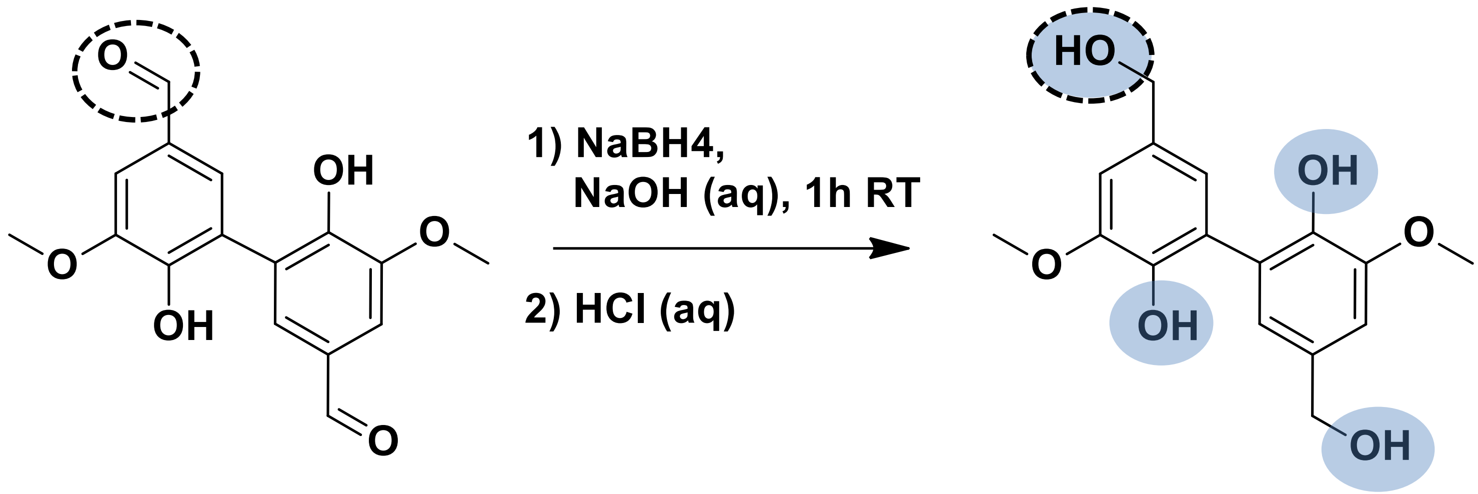
Self-sufficient process to synthesize dimers

Llevot et al., Polym. Chem. ***2015****, 6 (33) 6058-6066*

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

Epoxy

Aldehyde Reduction



Divanillin

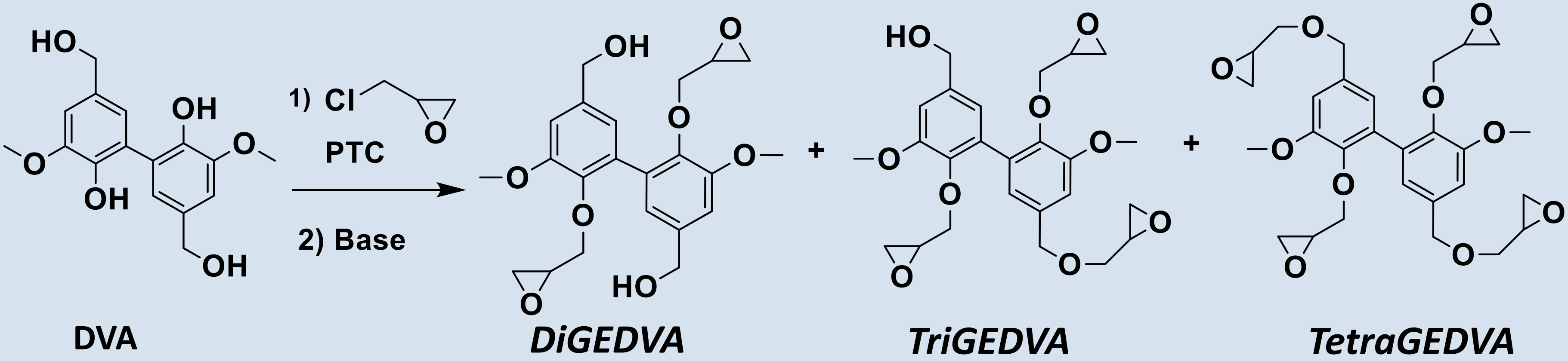
Divanillyl Alcohol (DVA)

⇨ 4 functional groups available to achieve high mechanical properties

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

Epoxy

Synthesis of epoxy prepolymers from DVA

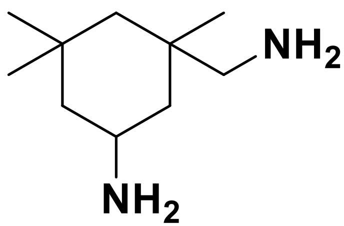


Properties	DGEBA	DiGEDVA	TriGEDVA	TetraGDVA
Melting point (°C)	45	-	-	-
Glass transition (°C)	-18	16	-6	-15
Viscosity at 25 °C (Pa.s)	5	*nd*	975	14
Viscosity at 40 °C (Pa.s)	1	1300	60	2
EEW th.	170	209	158	132
EEW exp.	171	232	164	129

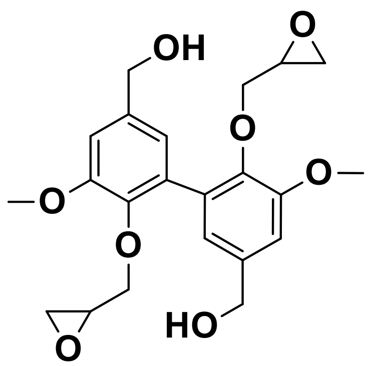
Smart drop-ins: Bio-based derivative of "fossil" polymers

Epoxy

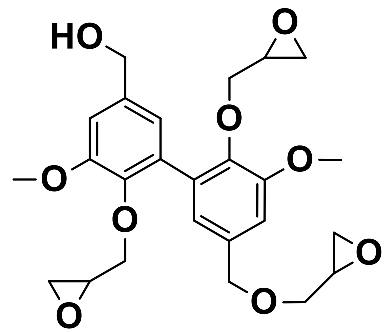
Synthesis of polyepoxyde network



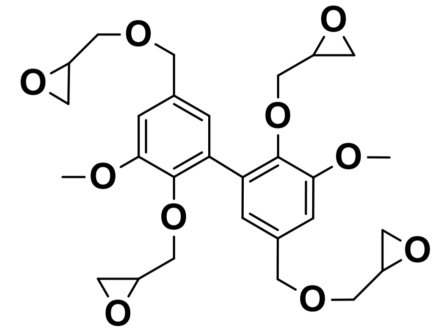
IPDA



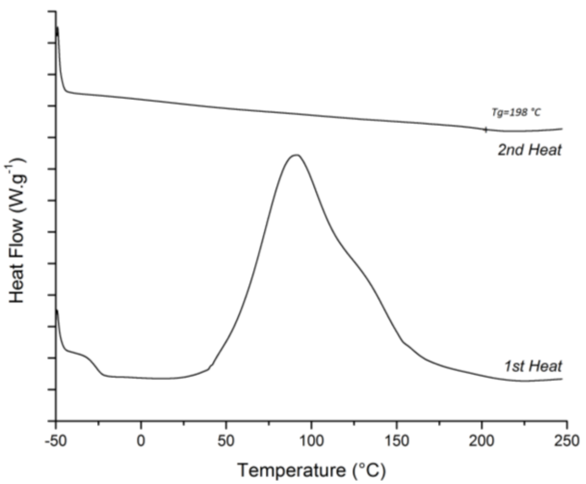
DiGEDVA



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**

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

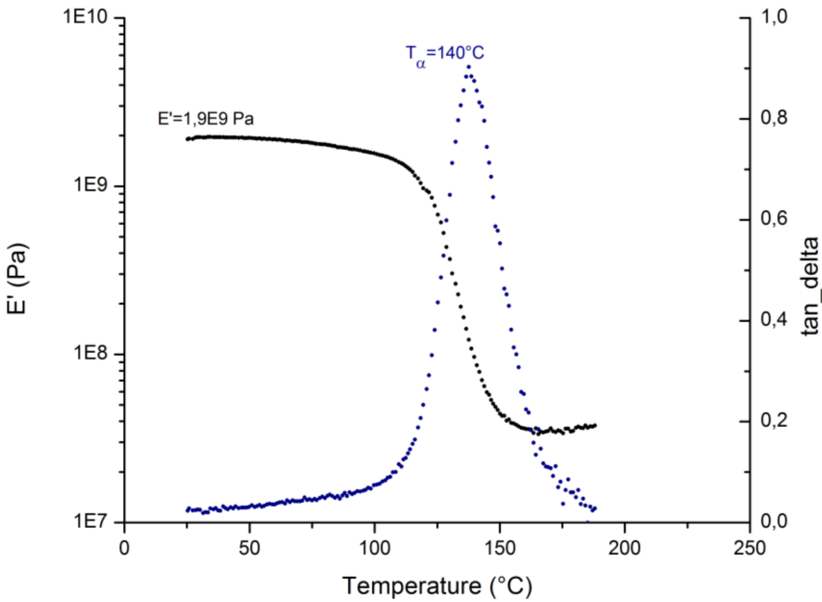
Epoxy

Dynamic Mechanical Analysis of epoxy resins cured with IPDA

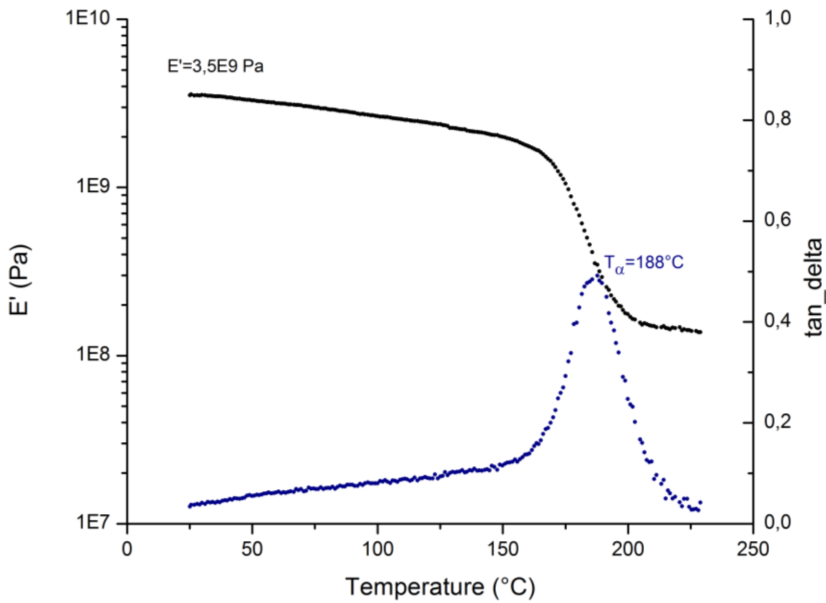
Epoxy prepolymer/IPDA	T_g[a] (°C)	T_α[b] (°C)	E'[b] (Gpa)	$E'(T_{\alpha+30})$[b] (Gpa)	Network density ($10^3 mol.m^{-3}$)
DGEBA	152	155	1,7	0,035	9,2
DiGEDVA*	138	140	1,9	0,035	9,5
TriGEDVA	163	177	1,3	0,084	21
TetraGEDVA	198	188	3,5	0,15	36,7

*[a]determined by DSC,[b] by DMA, *80%DiGEDVA-20%TriGEDVA*

DiGEDVA



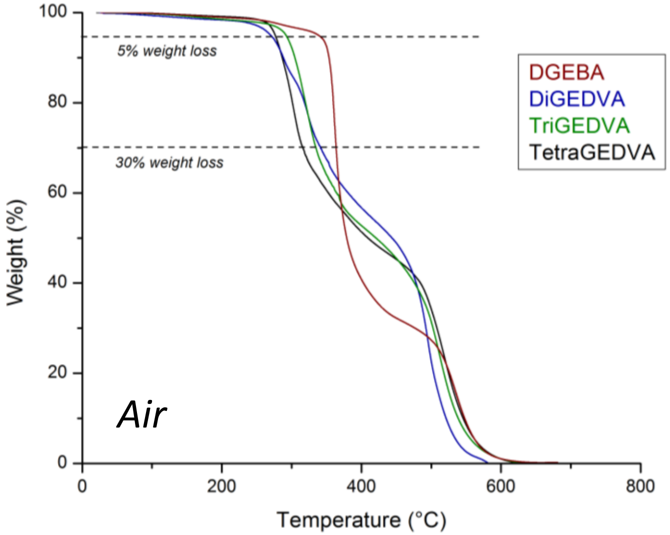
TetraGEDVA



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

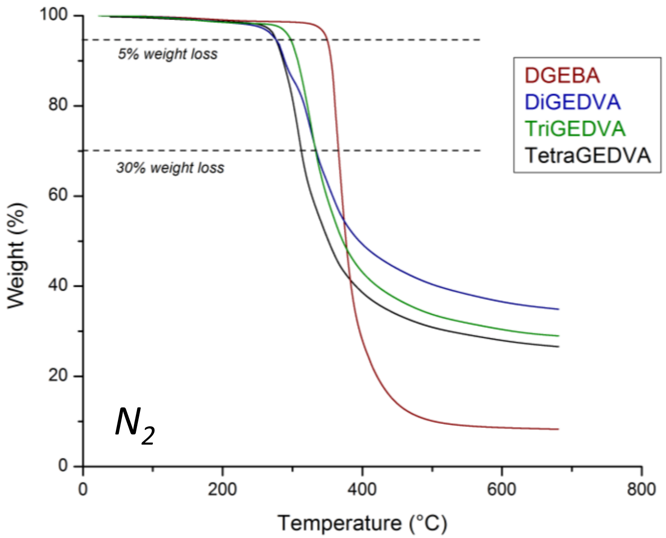
Epoxy

Thermal degradation of epoxy resins cured with IPDA



Epoxy prepolymer/IPDA	$T_{d\,5\%}$ (°C)	$T_{d30\%}$ (°C)	T_S
DGEBA	336	364	172
DiGEDVA	273	337	153
TriGEDVA	292	335	156
TetraGEDVA	275	316	147

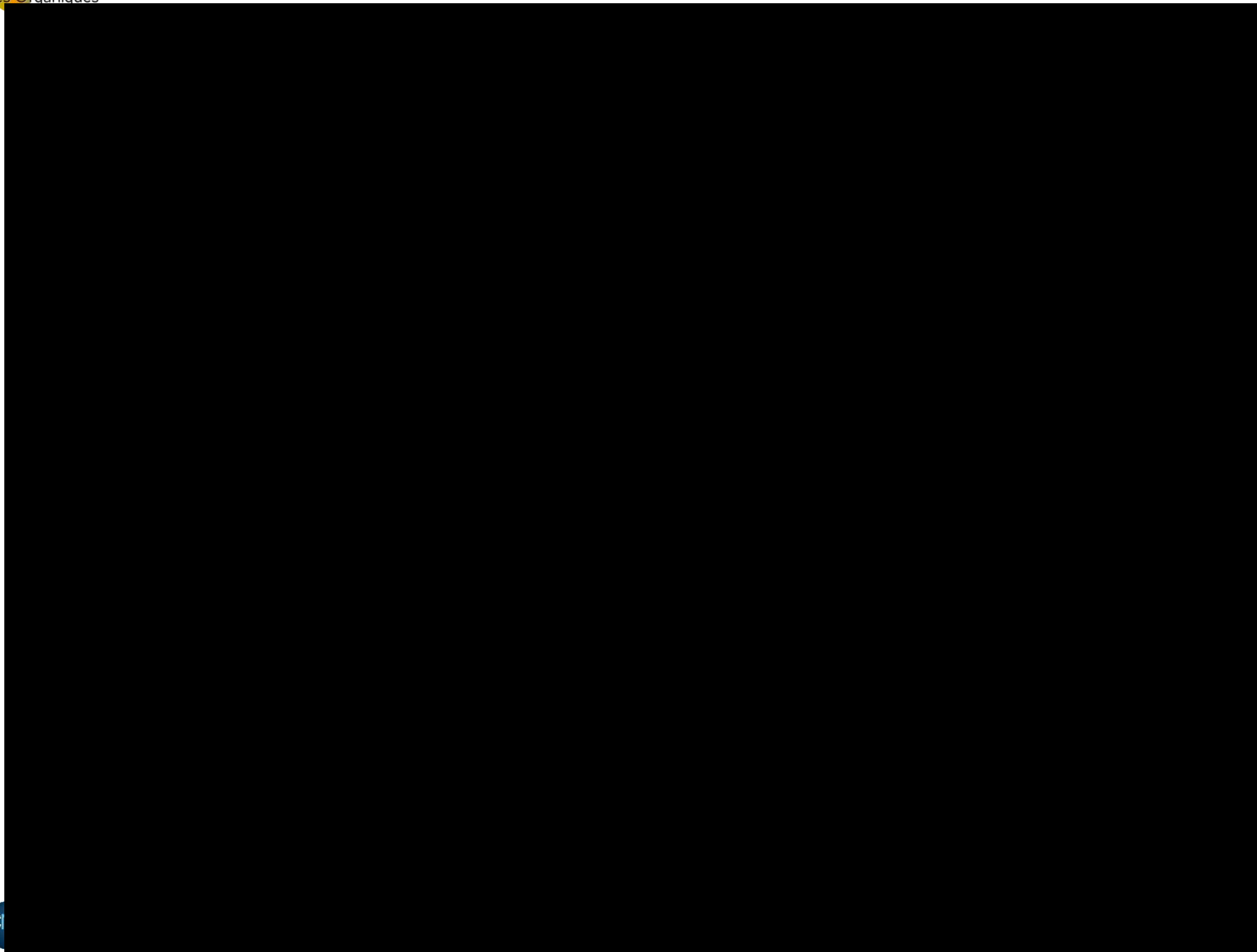
- **Slightly lower thermal heat resistance**



Epoxy prepolymer/IPDA	$T_{d\,5\%}$ (°C)	$T_{d30\%}$ (°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

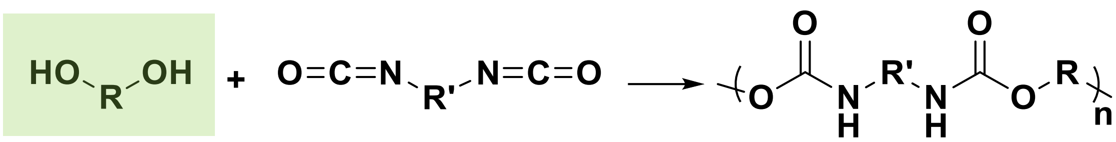
- **High char residue for biobased epoxy resins**

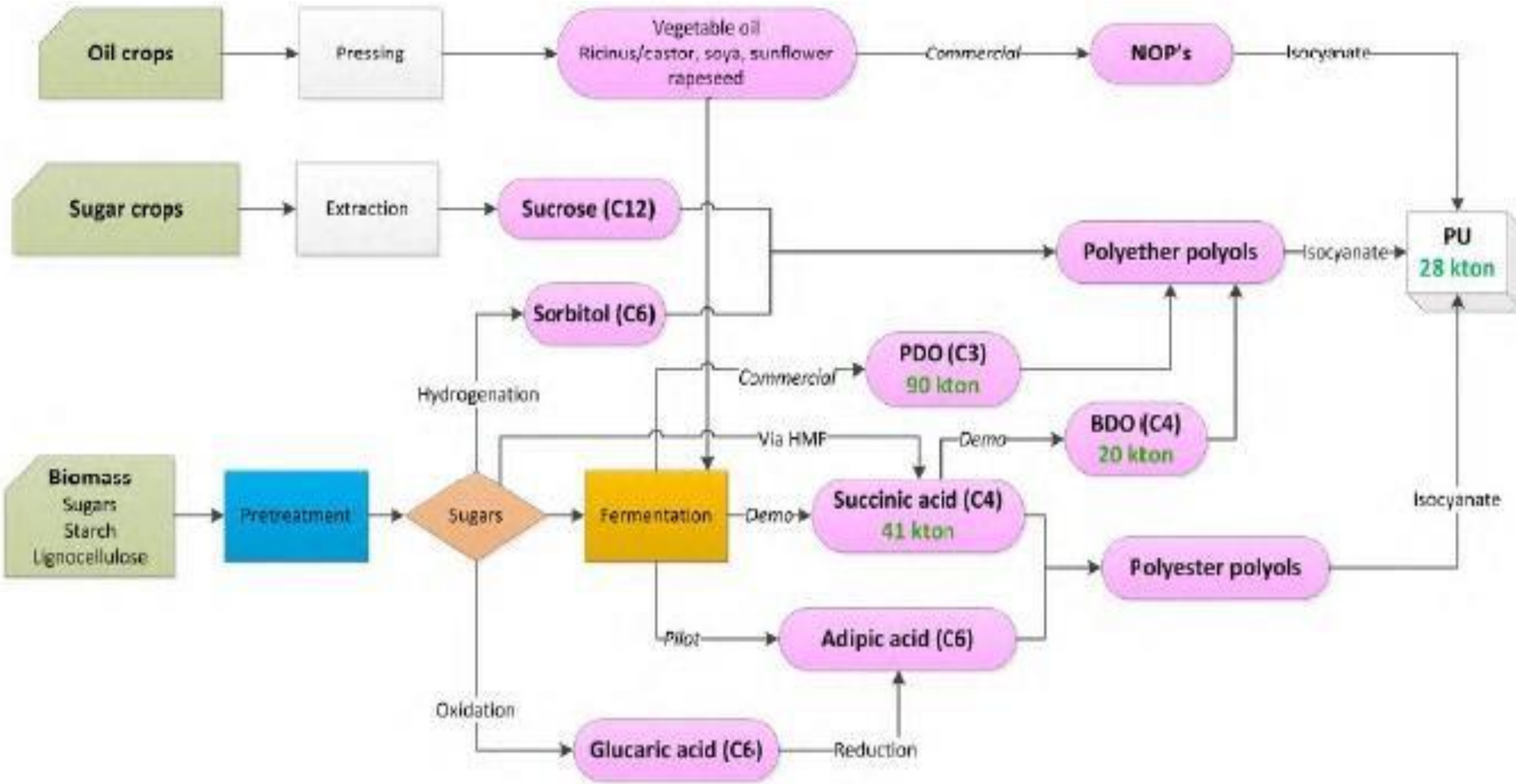
Flaming test of epoxy resins cured with IPDA



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

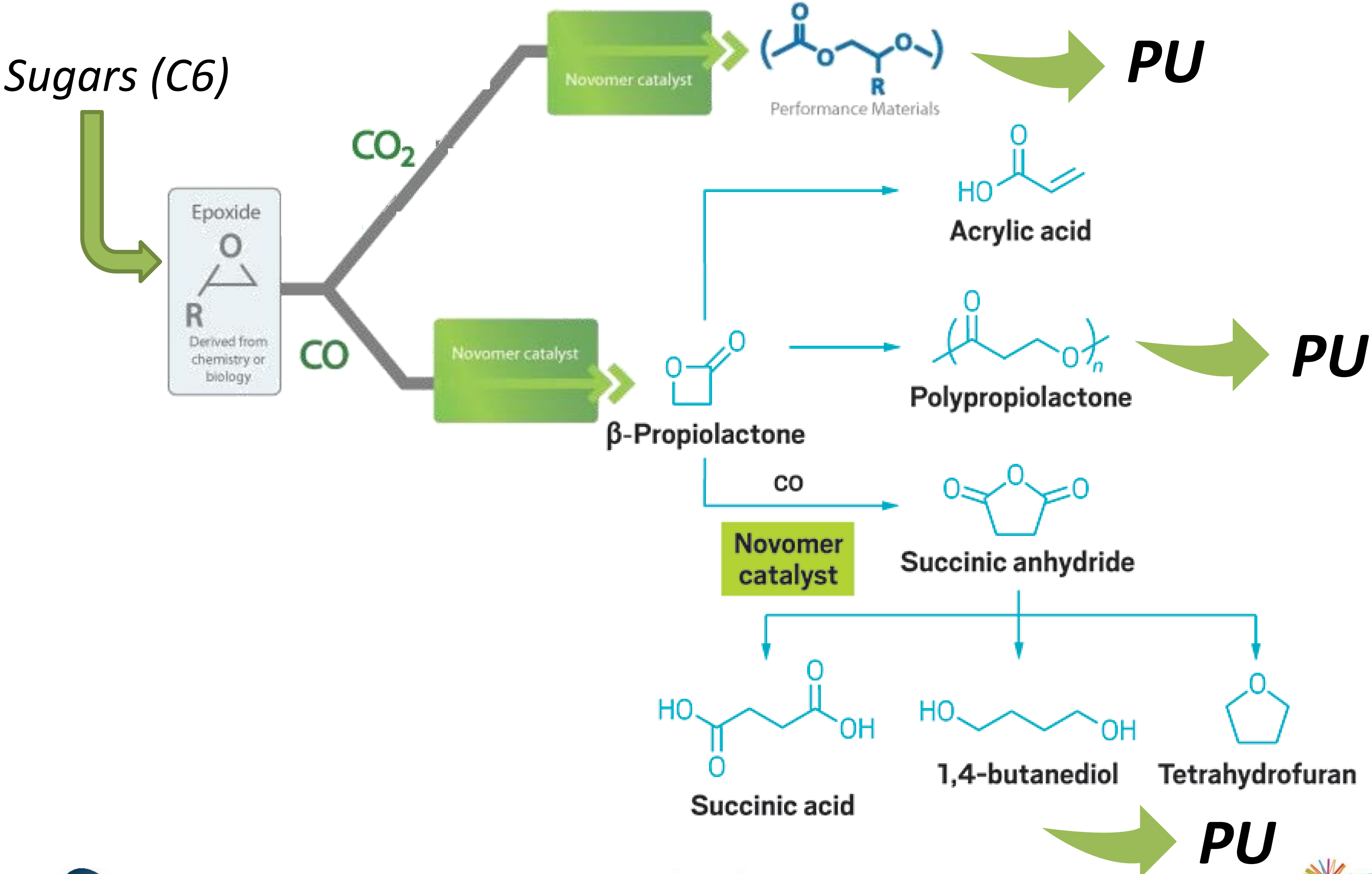
Polyurethanes





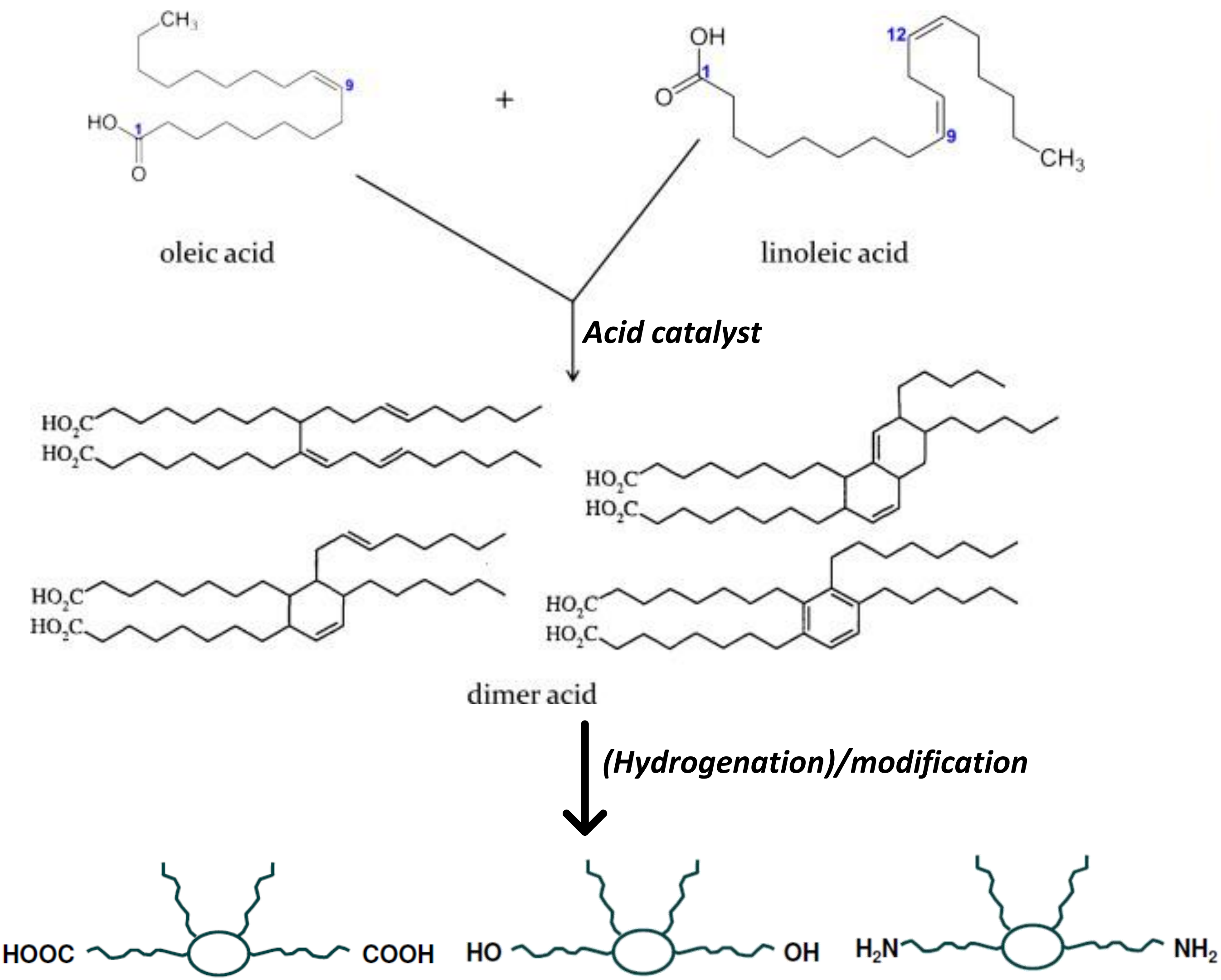
Smart drop-ins: Bio-based derivative of “fossil” polymers

Polyurethanes: polyol



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

Polyurethanes: polyol

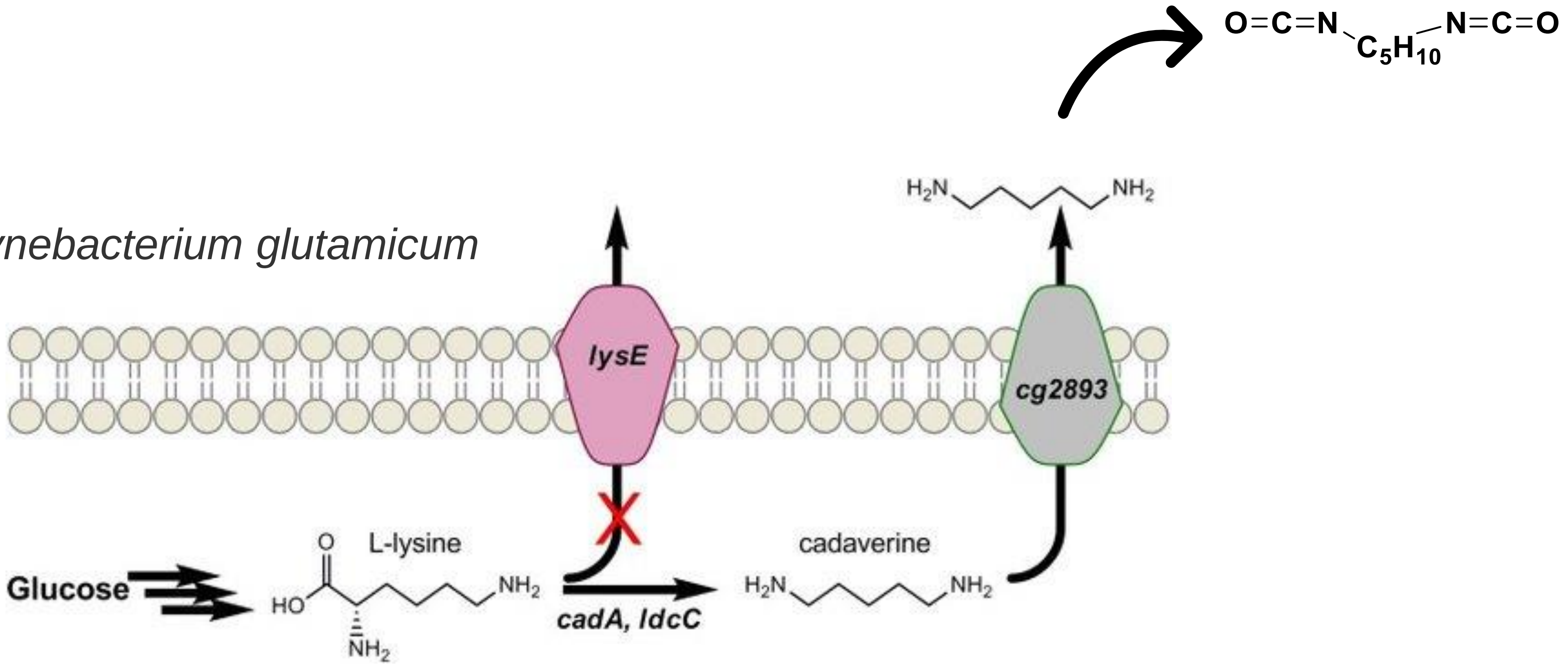


PU

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

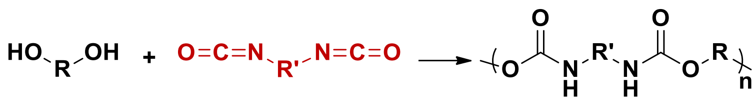
Polyurethanes: isocyanate

Corynebacterium glutamicum



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

Polyurethanes

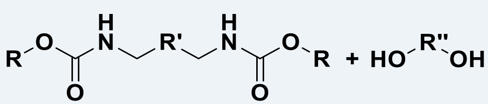


Industrial process for the production of Polyurethanes :

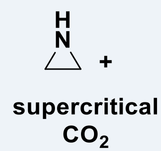
The Isocyanate/alcohol route

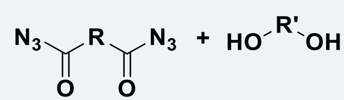
PU

Non Isocyanate PolyUrethane

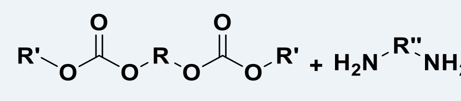


Bis-urethane/diol





Diazide/diol

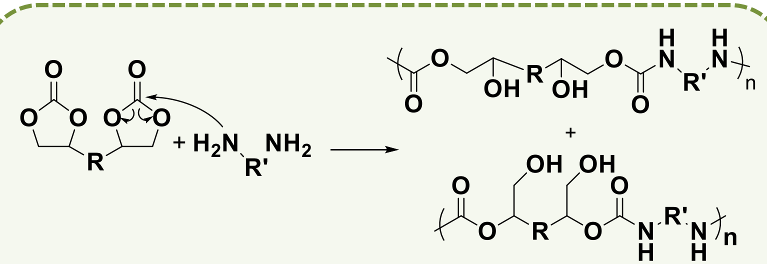


Bis-(alkyl carbonate)/diamine

Transurethanization **Aziridine route** **Rearrangements** **Bis-(dialkyl carbonate) route**

NIPU

Poly(HydroxyUrethane)



Bis-cyclic carbonate/diamine

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

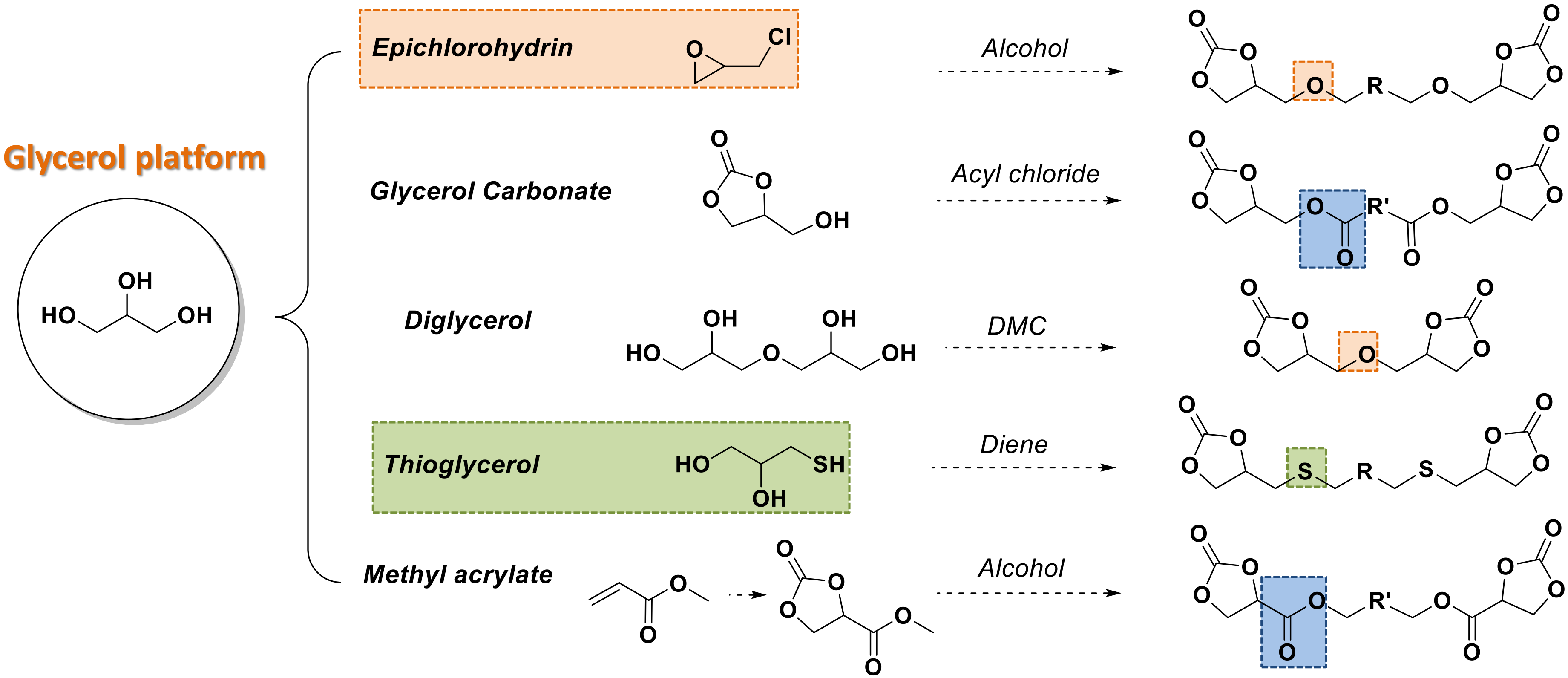
PHU

L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau, H. Cramail, *Chemical Reviews*, **2015**, 115 (22),12407–12439

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

Polyurethanes: isocyanate

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



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

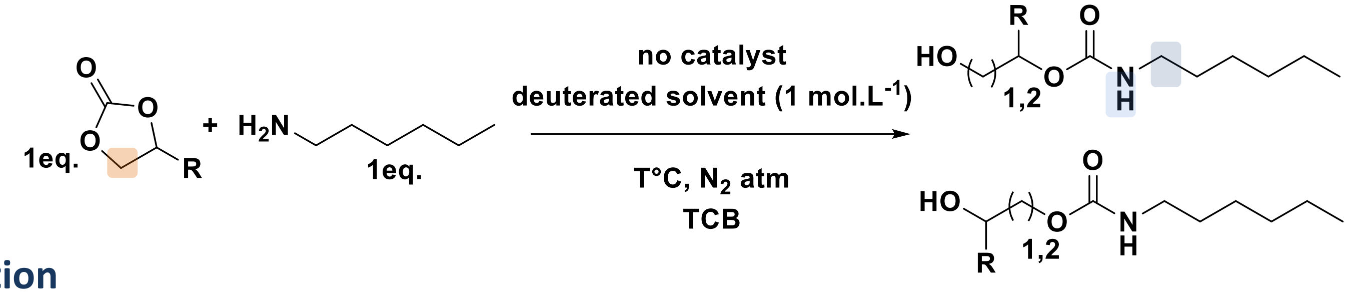
→**Ether**, **ester** and **thioether** functions inserted nearby the cyclic carbonate

LCPO Laboratoire de Chimie des Polymères Organiques

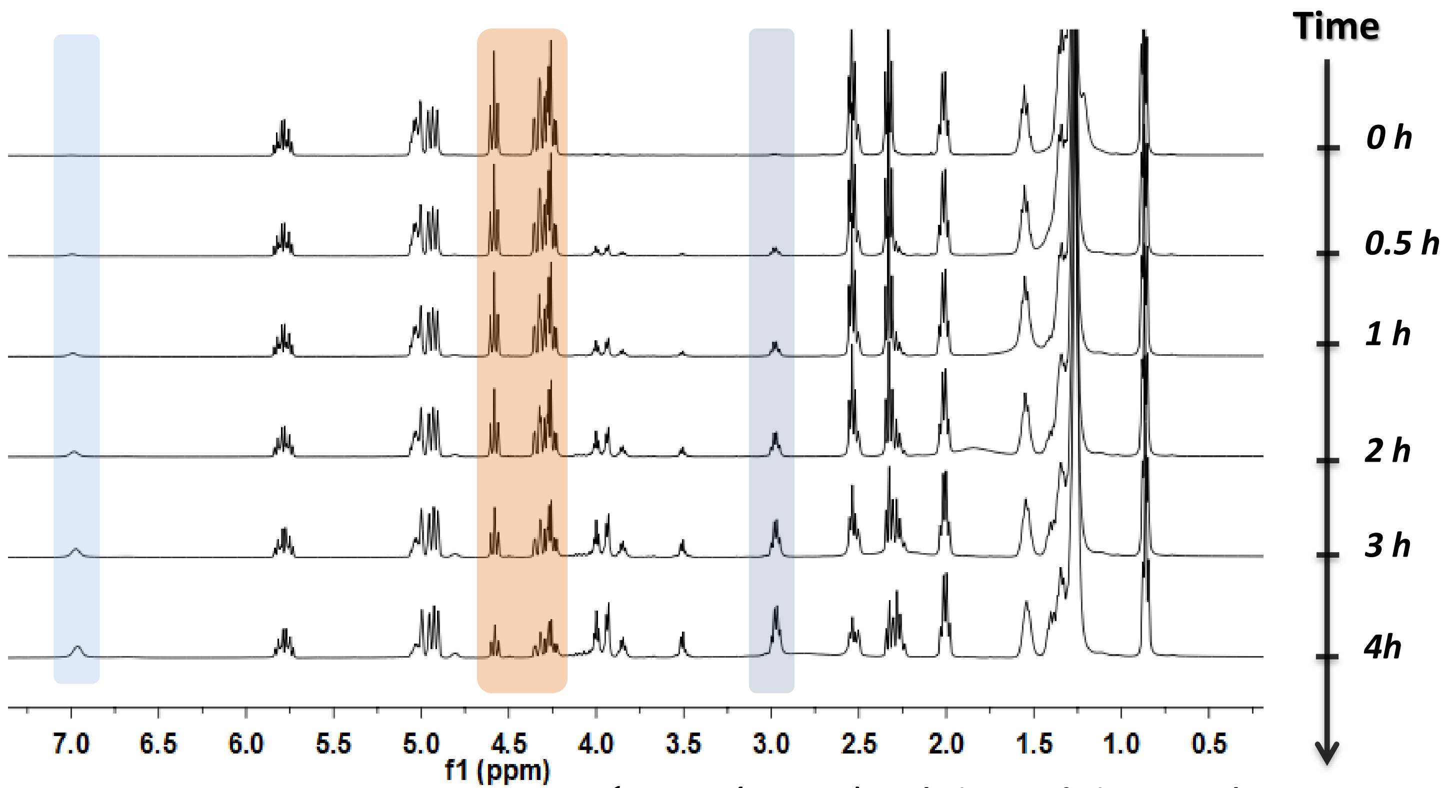
Smart drop-ins: Bio-based derivative of "fossil" polymers

Reactivity of various CC towards aminolysis

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



→CC conversion calculation



¹H NMR (400MHz) analysis at 50°C in DMSO-d6

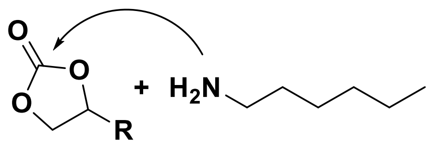
Lamarzelle, O.; Durand, P.-L.; Wirotius, A.-L.; Chollet, G.; Grau, E.; Cramail, H. *Polym. Chem.* **2016**, *7*, 1439–1451.

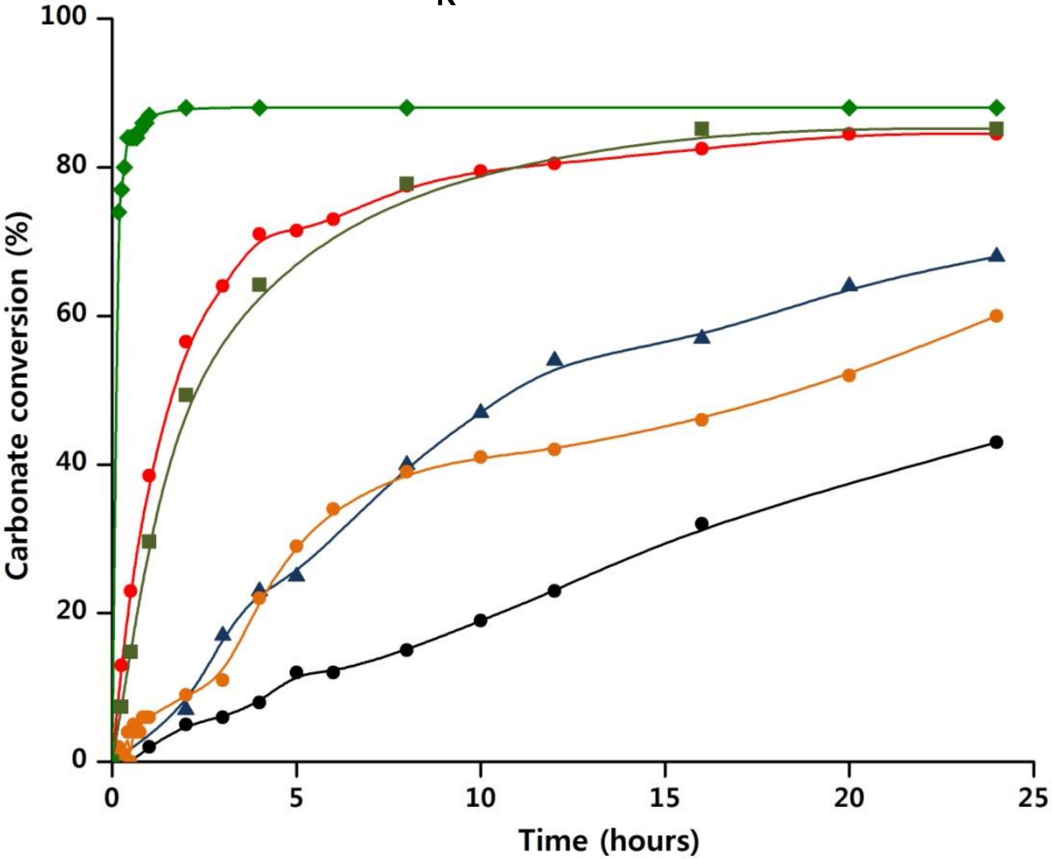
Smart drop-ins: Bio-based derivative of "fossil" polymers

Scale of CC reactivity towards aminolysis

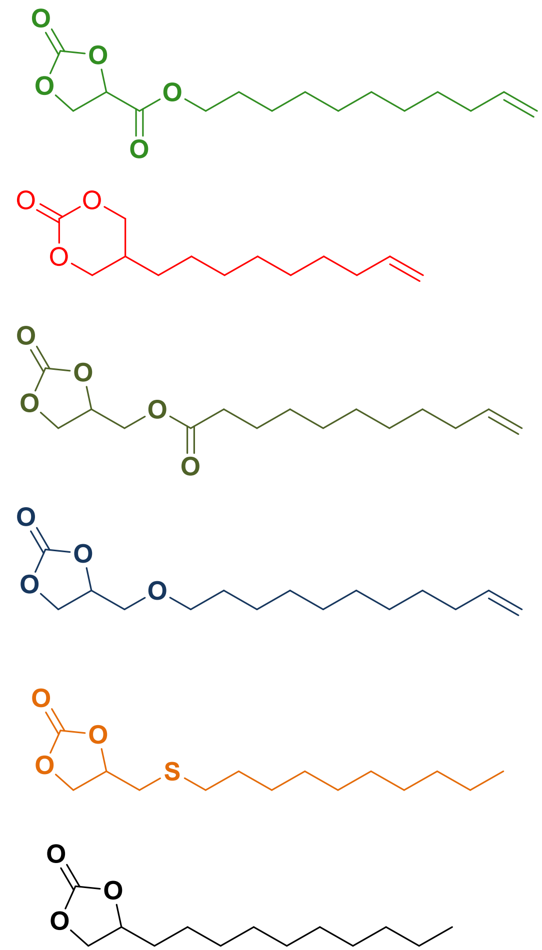
→ 2nd kinetic order law during the first hours - $\mathbf{k_{app}}$

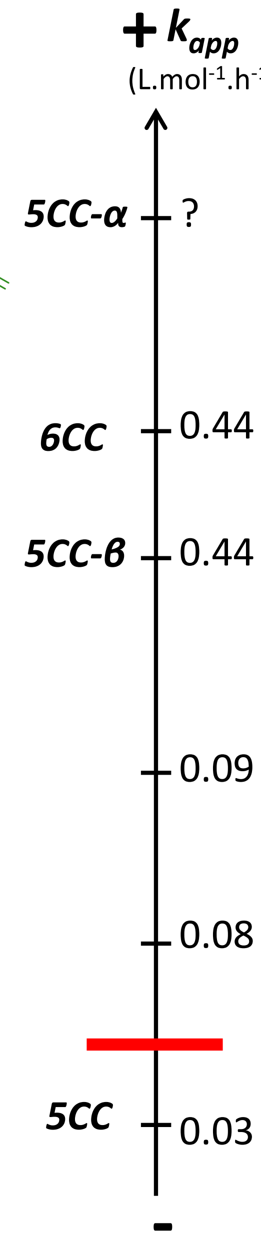
$$\frac{x}{1-x} = k_{app} C_0 \Delta t$$





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

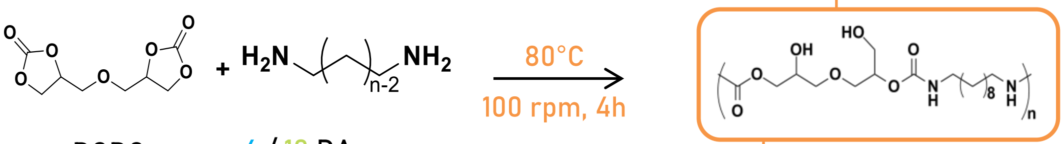




Lamarzelle, O.; Durand, P.-L.; Wirotius, A.-L.; Chollet, G.; Grau, E.; Cramail, H. *Polym. Chem.* **2016**, *7*, 1439–1451.

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

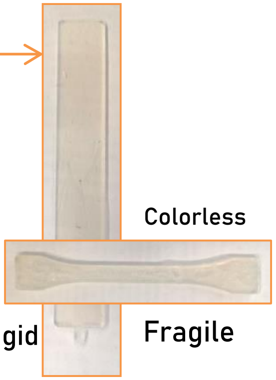
> From DGDC & various DAs

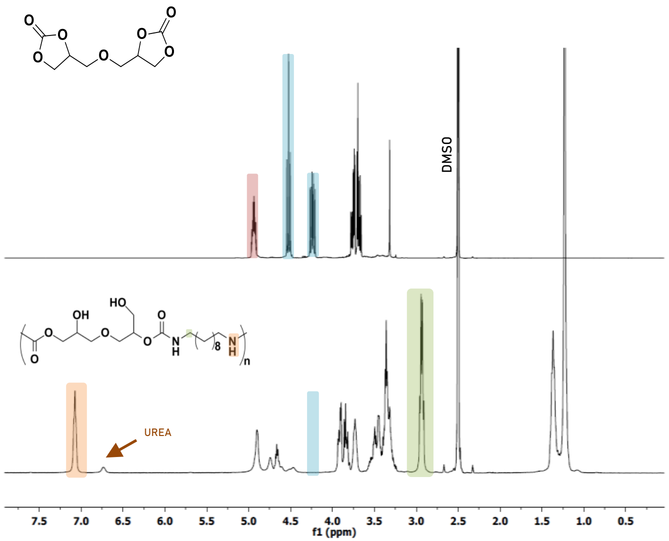


DGDC   6 / 10 DA

T_m = 76°C T_m = 45°C / 60°C

Conversions (%) .... 99% / 99%
Molar masses (g/mol)........ up to 46800 / 50 000
T_gs (°C) .... up to 18 / 17
T_m(°C)....................................... -- / 100
$T_{d5\%}$ (°C)................................up to 227 / 233



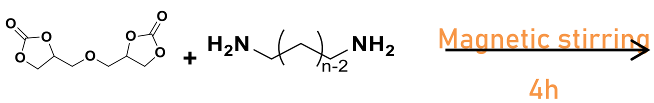


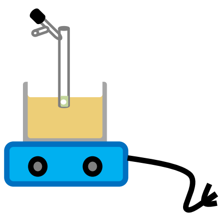
NMR spectra of DGDC monomer (up) and DGDC based PHU (down)

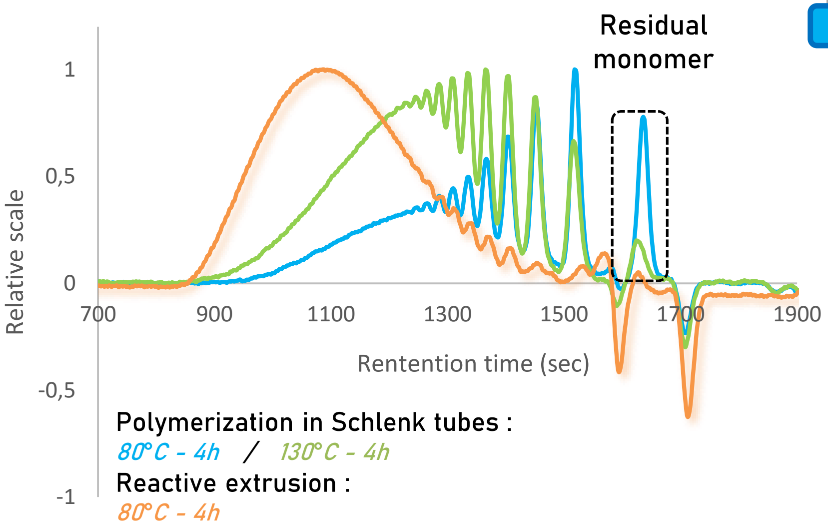
SEC analysis in DMF, with PS standards, at 50°C
DSC second heating cycle at 10°/min
TGA traces at 10°C/min

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

> Comparison with bulk polymerization in Schlenk tubes

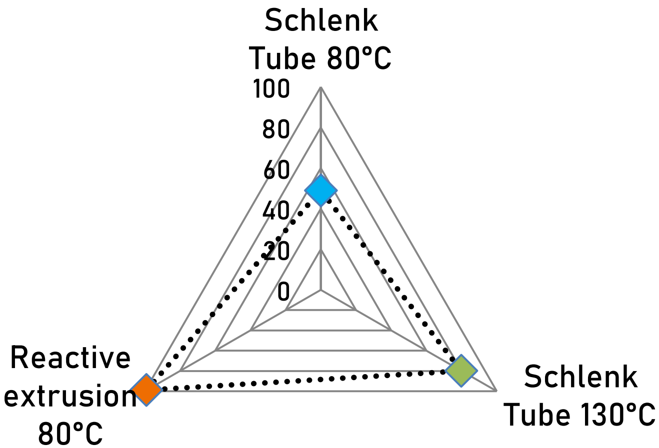






SEC analysis in DMF, 50°C, 1g/L of Libr,
conventional calibration column with PS standards

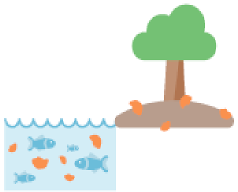
Conversion after 4h (%)



Conversions obtained by [1]HNMR analysis in DMSO-d6 at RT

Outlines

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

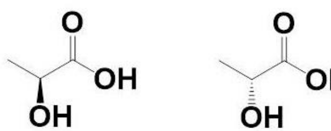
6- New polymers from biomass

7- Conclusions and perspectives

New polymers from biomass: PLA

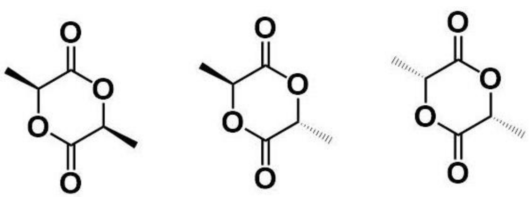
300 kt

Starchy Materials



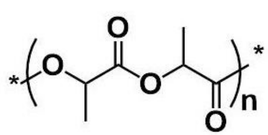
L-lactic acid D-lactic acid

Condensation and Depolymerization



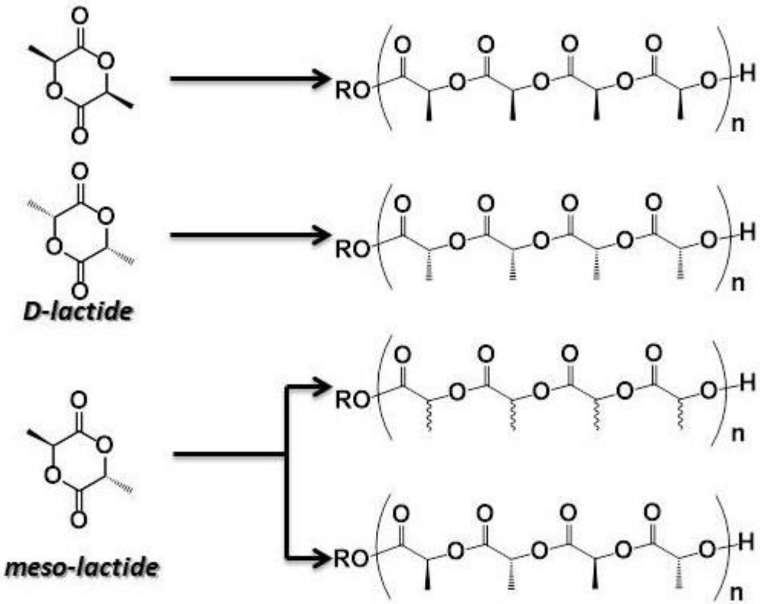
L-lactide Meso-lactide D-lactide

Catalytic Ring-Opening Polymerization (ROP)



High Molecular Weight PolyLactide (PLA)

Microstructure control



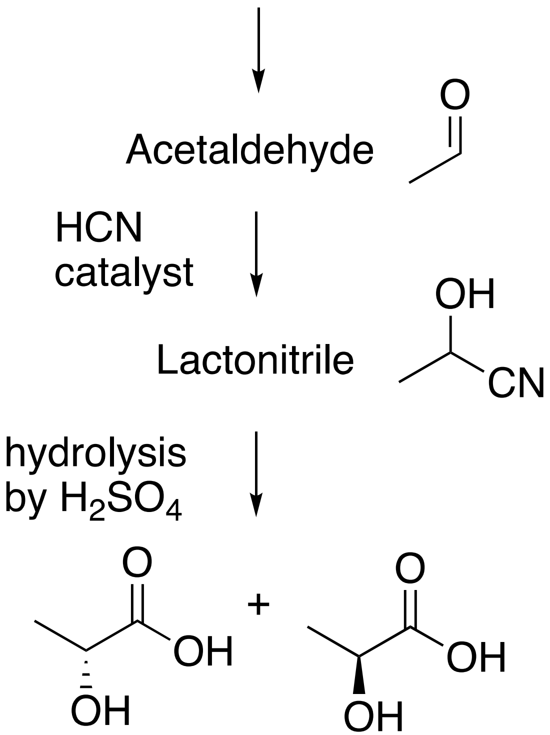
Properties control

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	-	-

New polymers from biomass: PLA

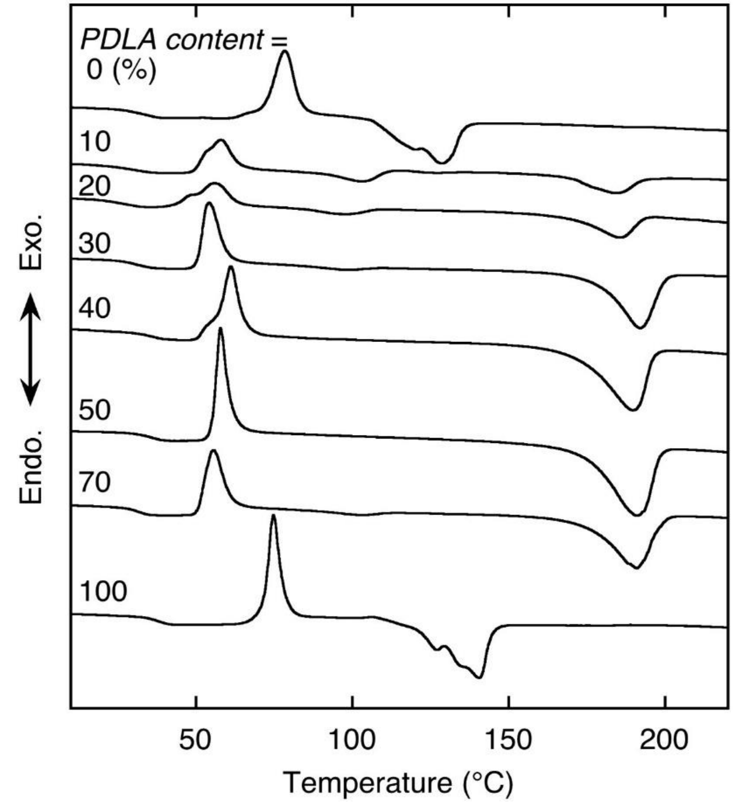
Why PLA is not petro-sourced ?

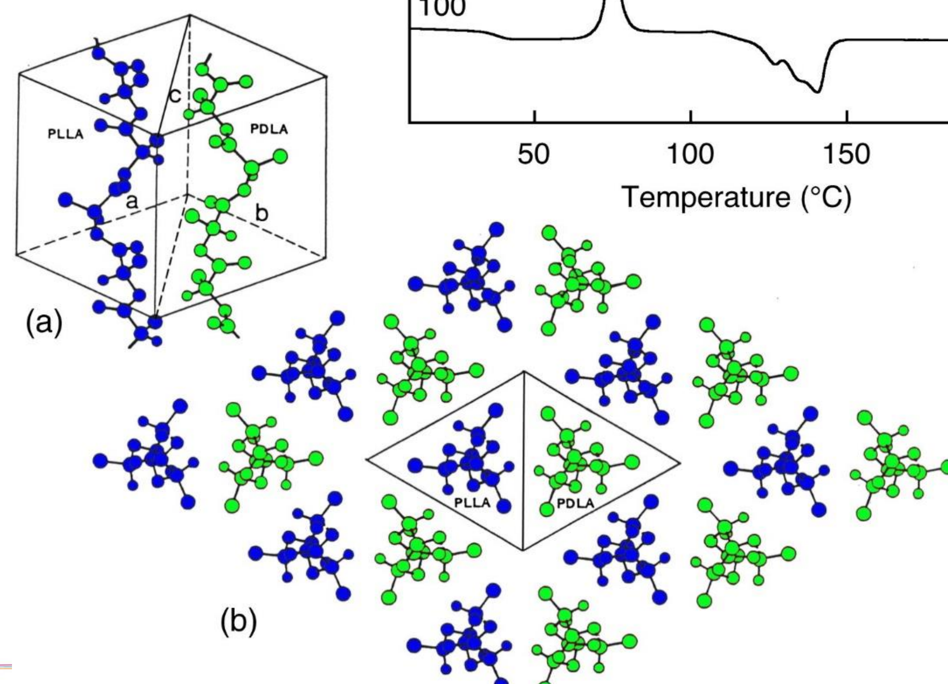
Petro-chemical resources



Racemic DL-lactic acid

PLLA/PDLA stereocomplex





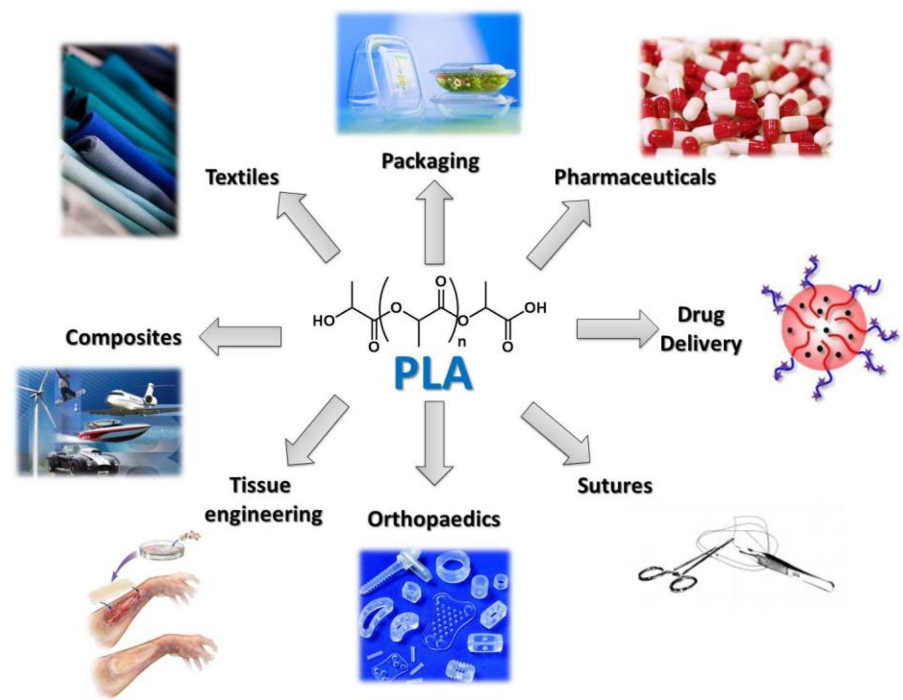
New polymers from biomass: PLA

0 kgCO_2e/kg

Biobased, Compostable, Stiff

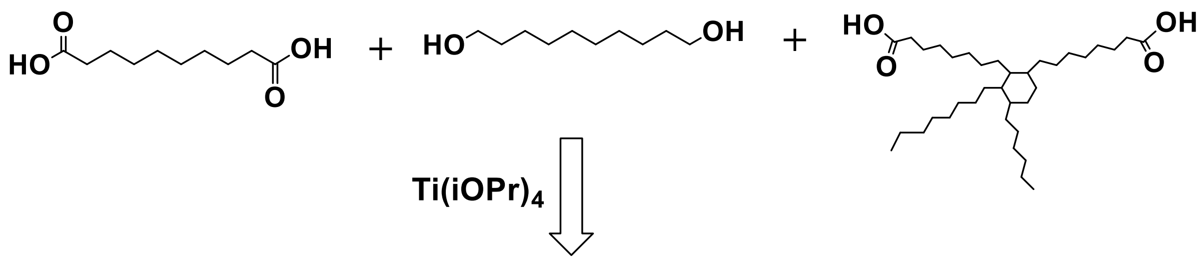
	PLLA	PS	PET
Density (kg.m^{-3})	1.26	1.05	1.40
Tensile strength (MPa)	59	45	57
Elastic modulus (GPa)	3.8	3.2	2.8-4.1
Elongation at break (%)	4-7	3	300
Notched IZOD IS (J.m^{-1})	26	21	59
Heat deflection (°C)	55	75	67

Purac website

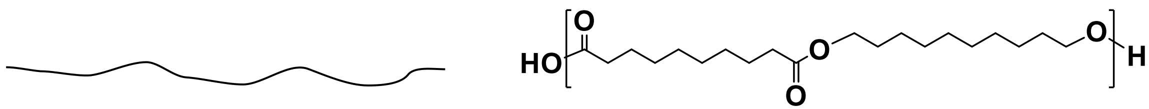


Heat stability, Low crystallization rate, Brittleness

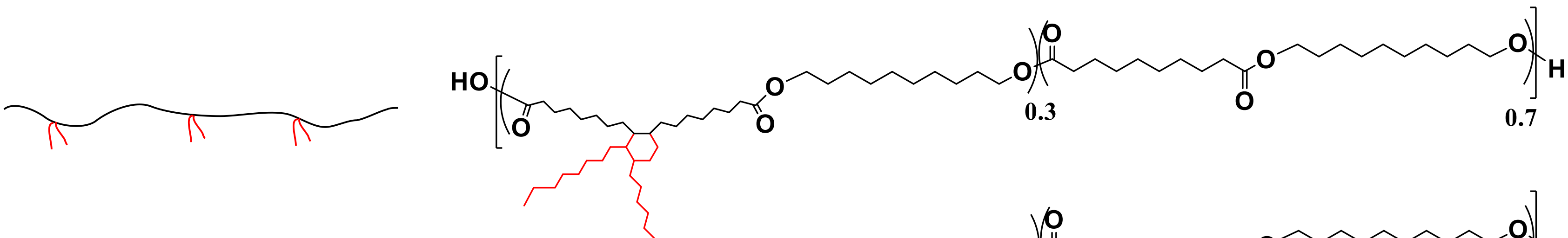
PLA additive: Synthesis



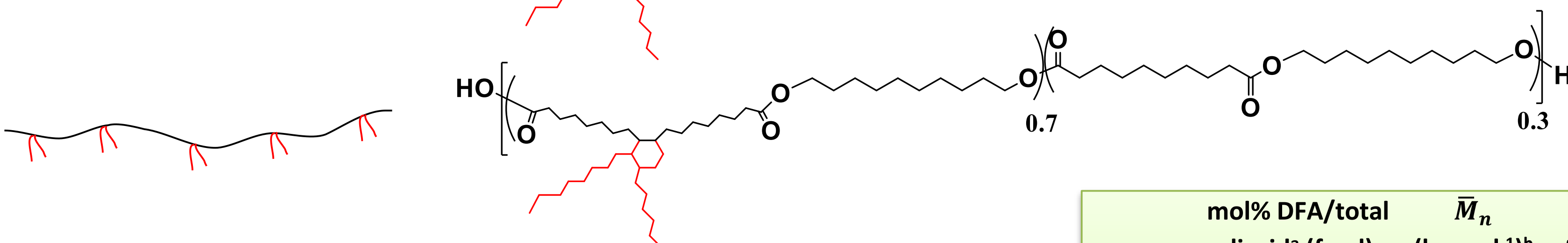
DFA0



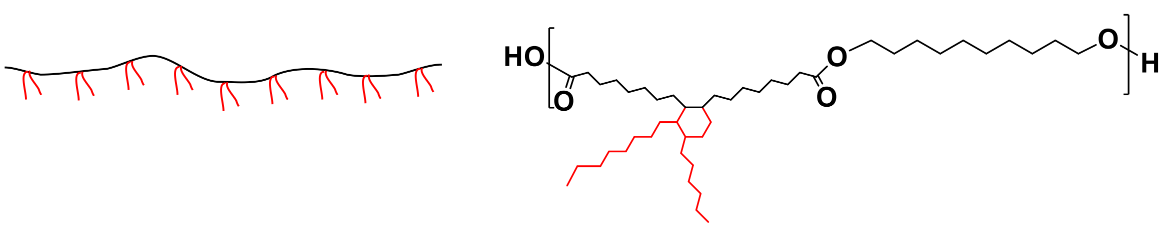
DFA0.3



DFA0.7



DFA1

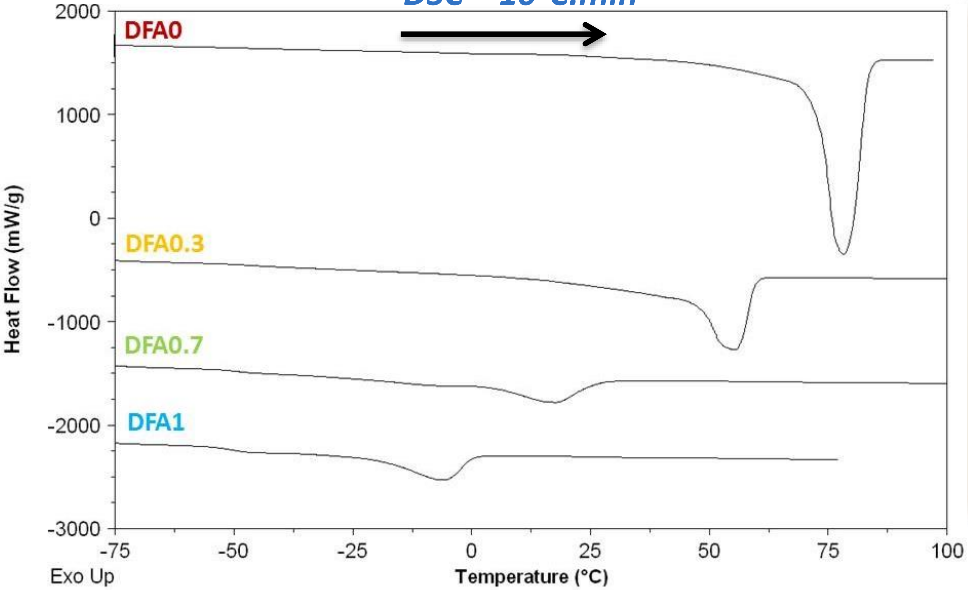


	mol% DFA/total diacid[a] (feed)	$\overline{M}_n$ (kg.mol^{-1})[b]	$Đ$[b]
DFA0	0 (0)	59	2.1
DFA0.3	0.40 (0.3)	44	1.8
DFA0.7	0.78 (0.7)	64	2.0
DFA1	1 (1)	36	2.0

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

PLA additive: Properties

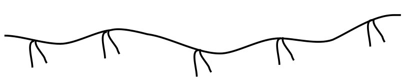
DSC – 10°C.min^{-1}



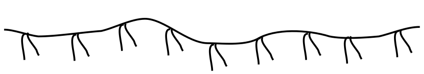
DFA0

DFA0.3

DFA0.7



DFA1



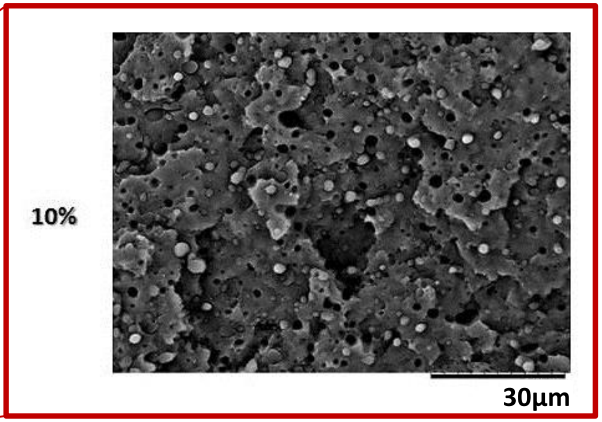
	Tm (°C)[a]	ΔHm (J.g^{-1})[a]	Tg (°C)[a]	$T_{5\%}$(°C)[b]
DFA0	78.2	100.9	- 48.6	338
DFA0.3	55.2	57.7	- 45.9	389
DFA0.7	17.7	22.4	- 49.0	399
DFA1	- 5.8	16.2	- 50.0	394

(a) DSC- 10°C.min^{-1}

PLA additive: Processing

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

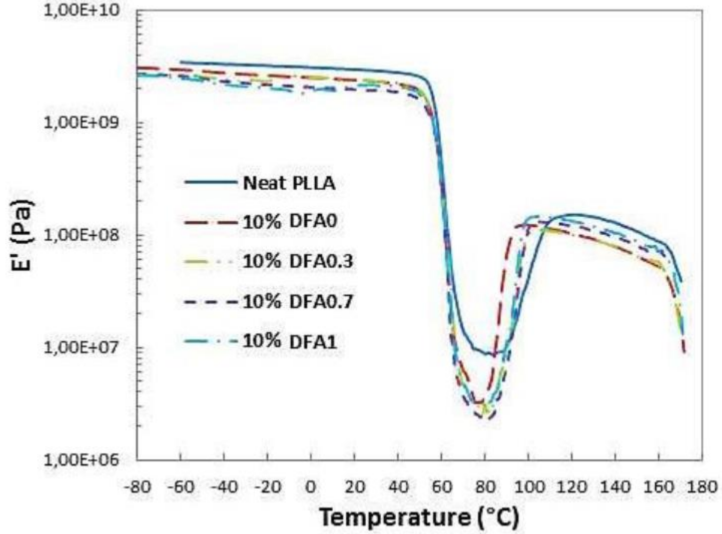
Sample preparation:
Injection molding
200°C → 50°C

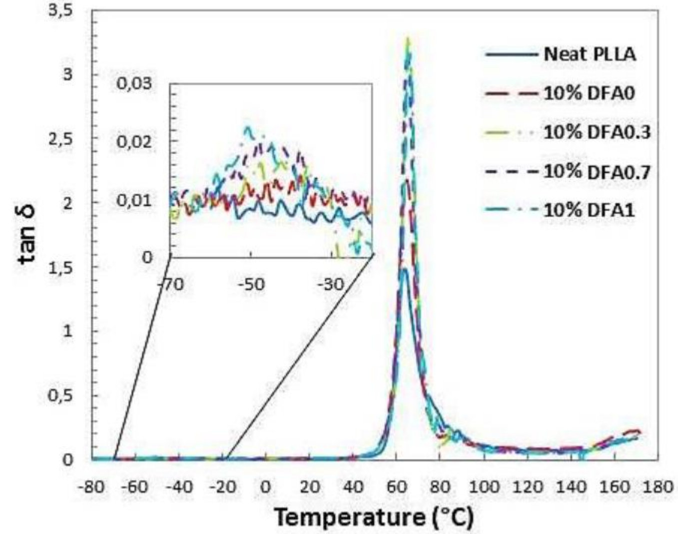


PLA additive: Mechanical Properties

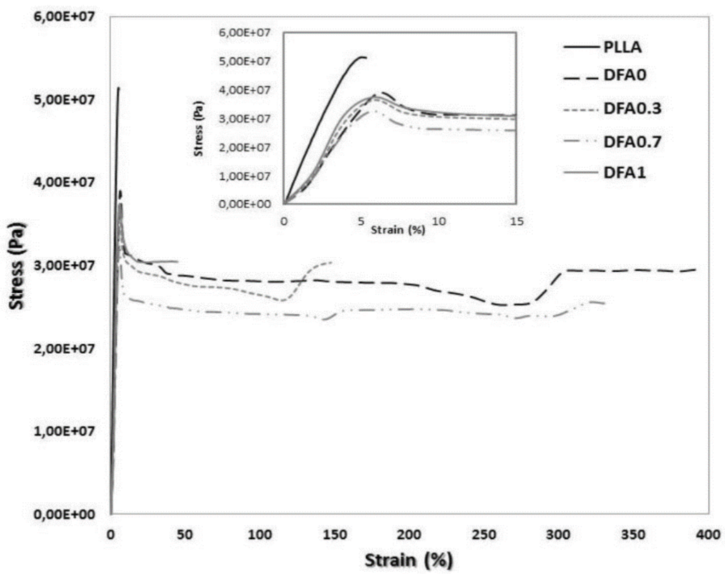
DMA

Heat stability



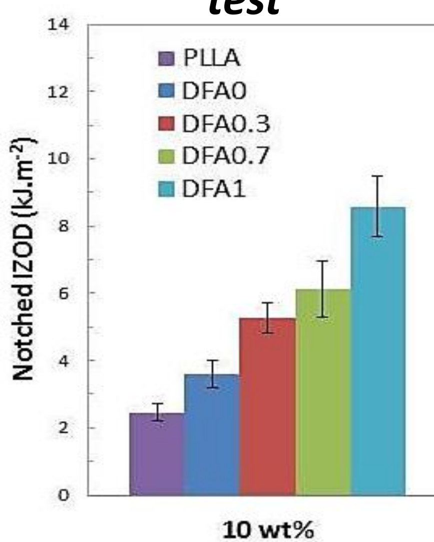


Tensile test



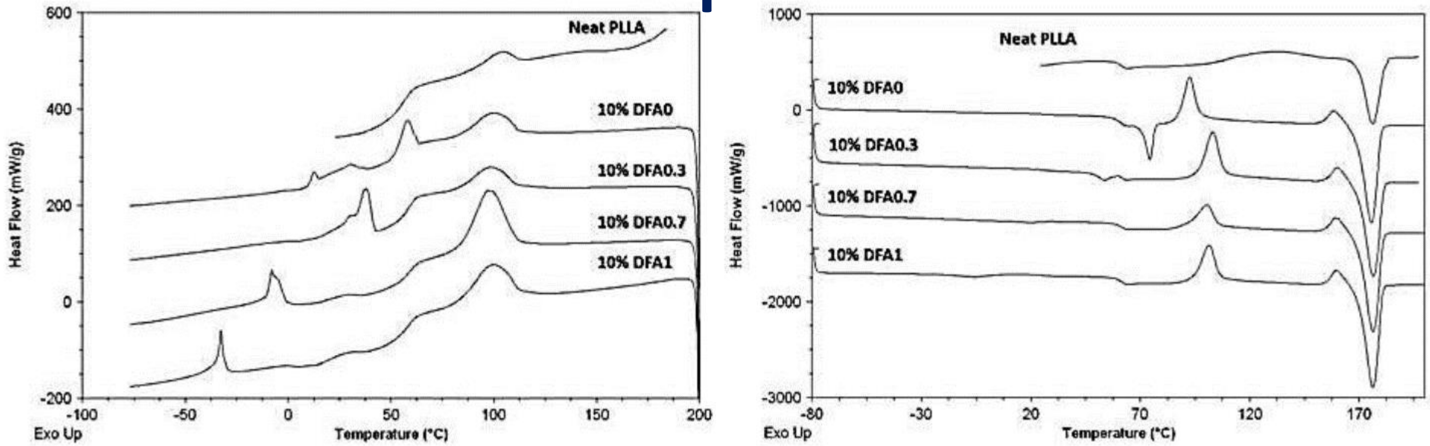
Brittleness

Impact strength test

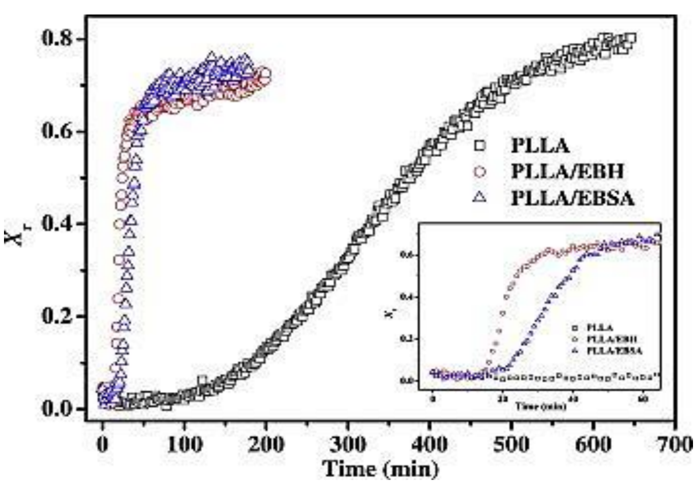


PLA additive: Thermal Properties

DSC



Isothermal crystalization



Avrami equation :

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

α_c: *the relative crystalline volume fraction*

k: *rate constant of crystallization*

n: *Avrami index*

Half-time of crystallization :

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

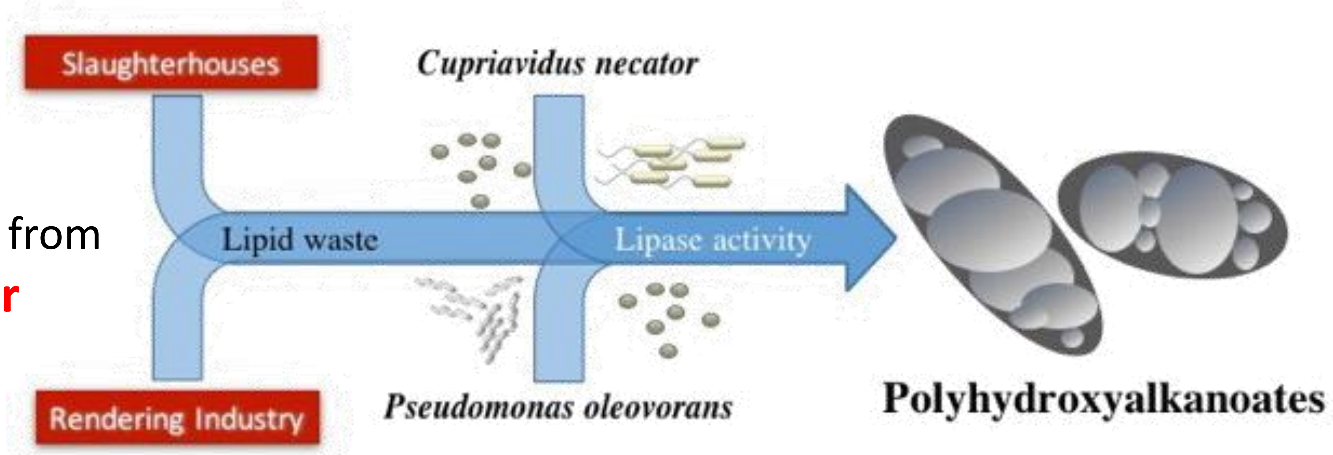
		n	k (min^{-n})	$t_{1/2}$ (min)
	PLLA	1.80	0.027	6.12
10wt%	DFA0	3.53	0.021	2.70
	DFA0.3	3.73	0.014	2.85
	DFA0.7	3.81	0.116	1.60
	DFA1	4.20	0.015	2.48

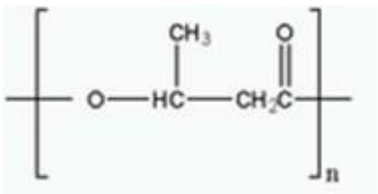
New polymers from biomass: PHA

40 kt

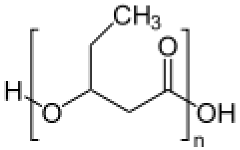
One-pot biosynthesis from
biomass to polymer

Max prod. **3 $g.L^{-1}.h^{-1}$**

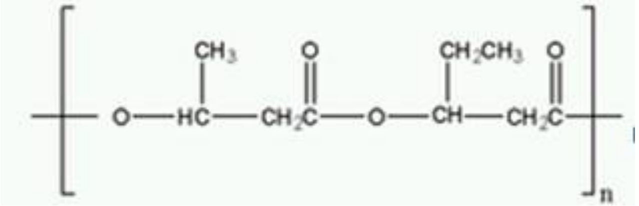




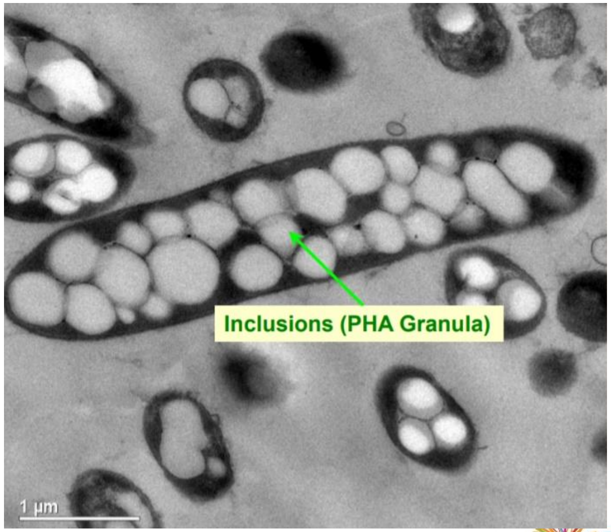
Polyhydroxybutyrate (PHB)



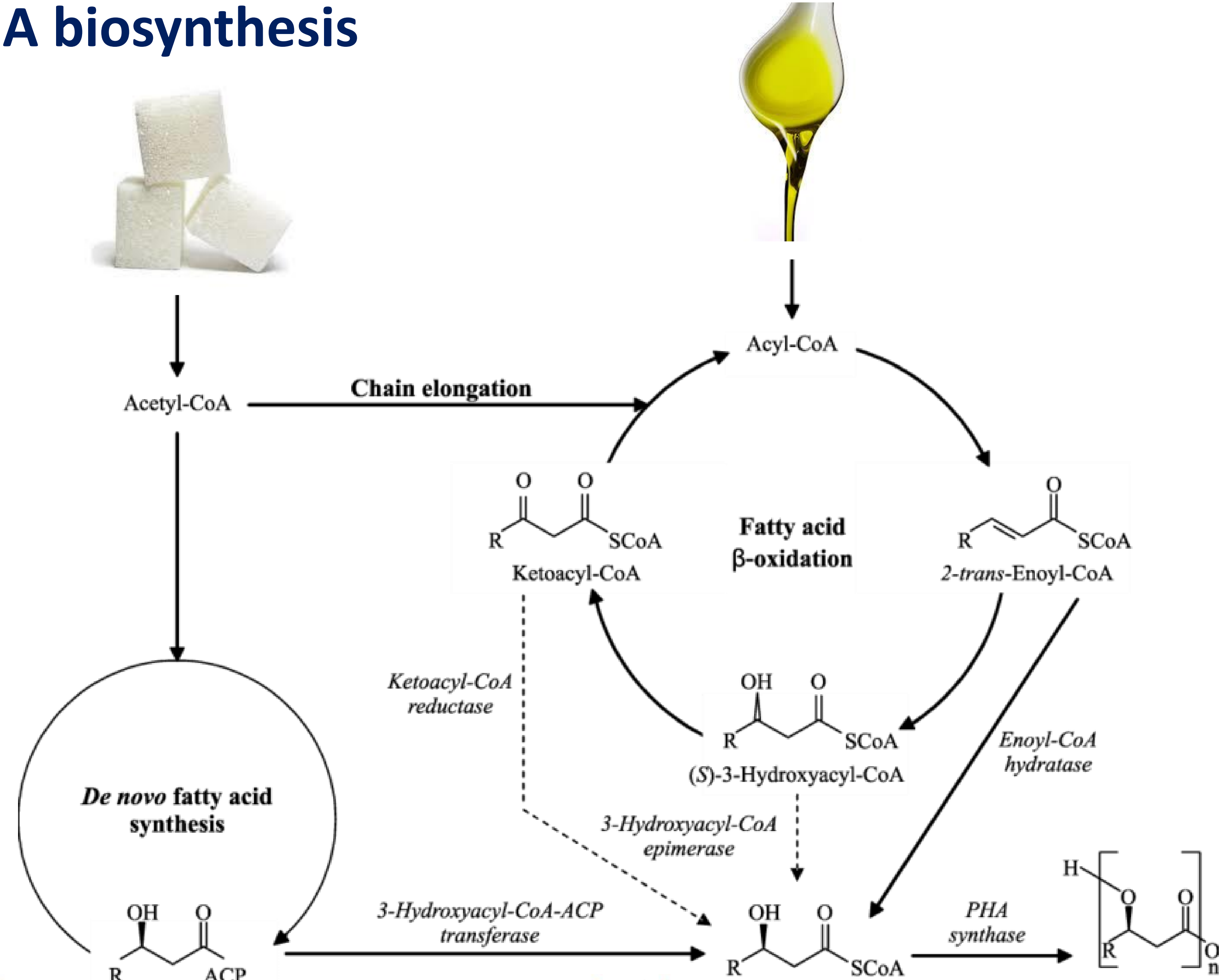
Poly-3-hydroxyvalerate (PHV)



Poly(hydroxybutyrate-co-hydroxyalkanoates (PHBV)

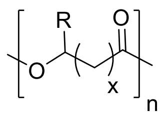


PHA biosynthesis

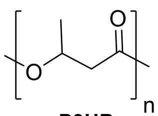


New polymers from biomass: PHA

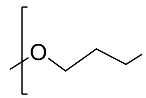
PHA properties



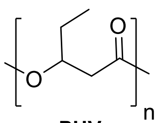
PHA general structure
x =1-4
R= Saturated, unsaturated, branched or substituted alkyl chain



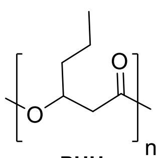
P3HB



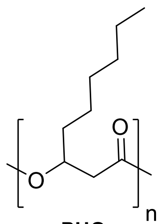
P4HV



PHV

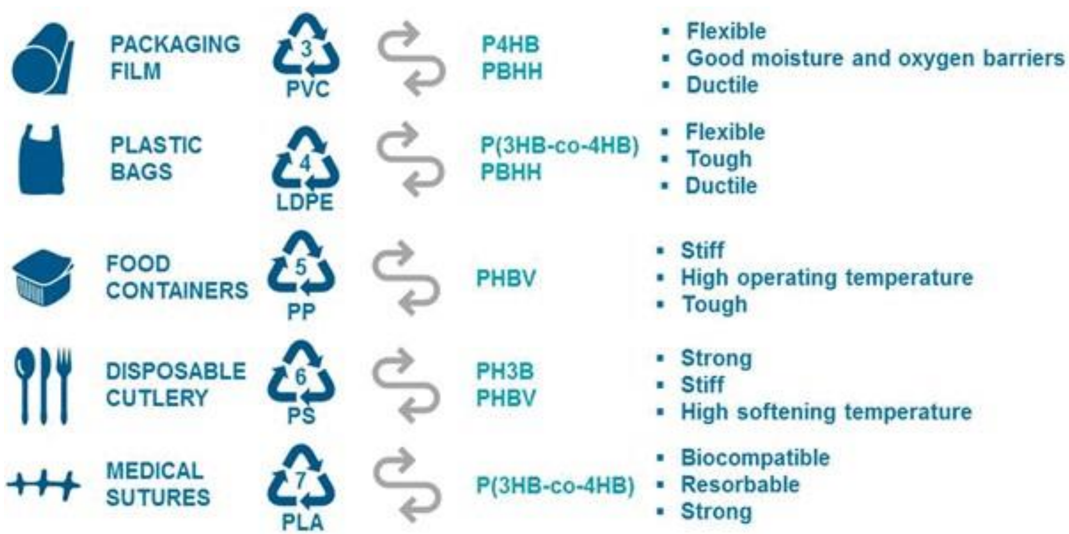


PHH



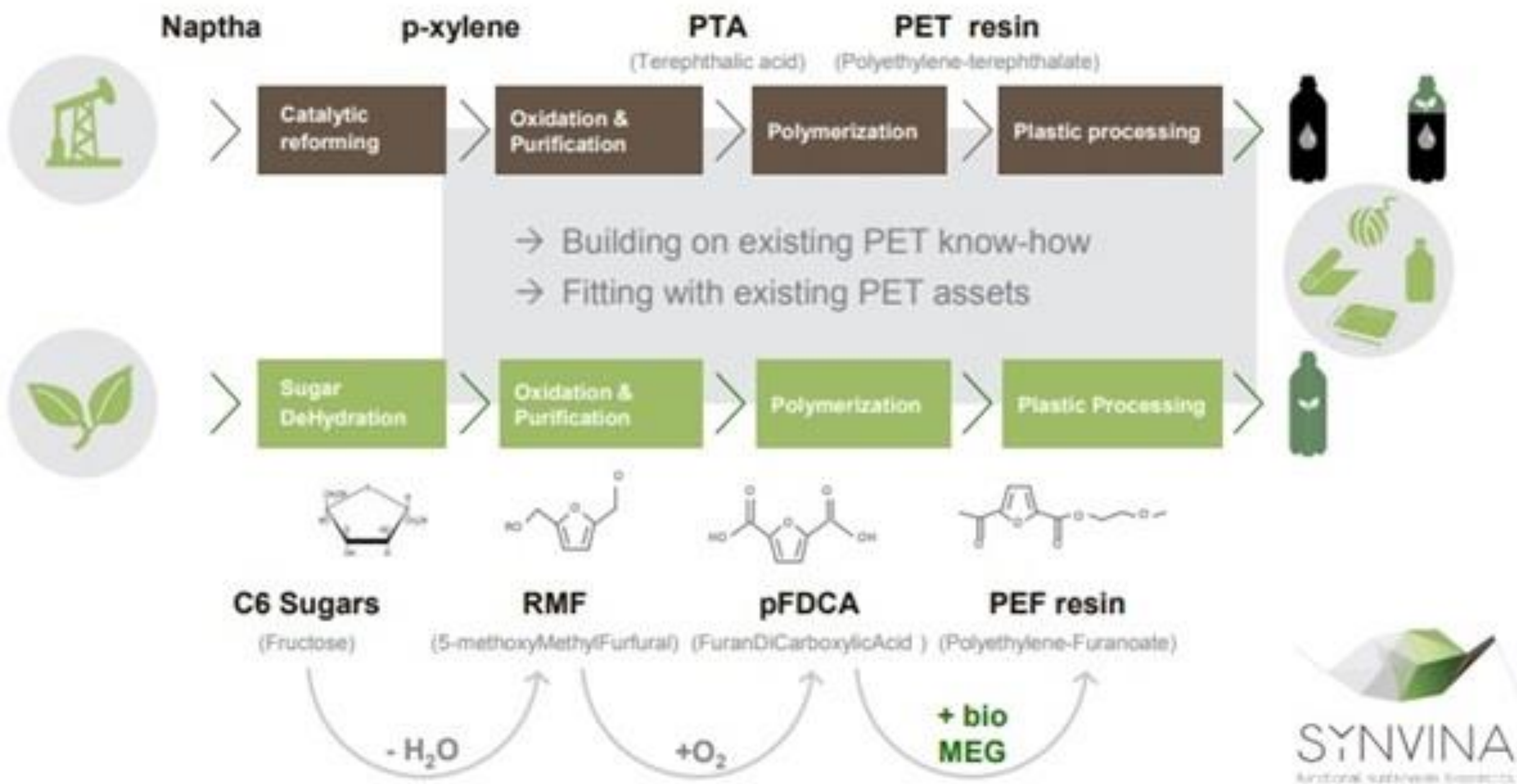
PHO

	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



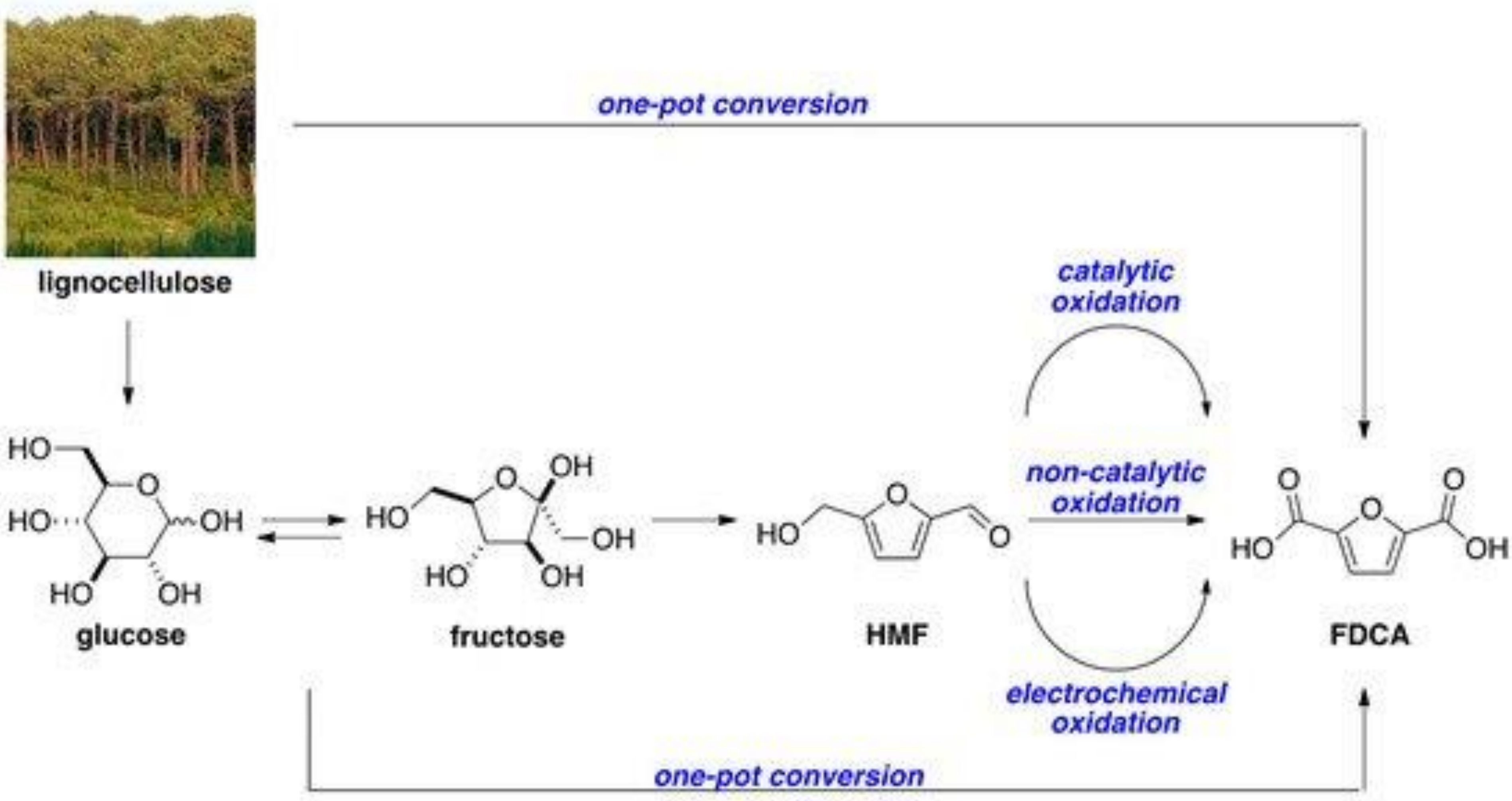
New polymers from biomass: PEF

Pilot scale 40 t → 90 kt by 2025



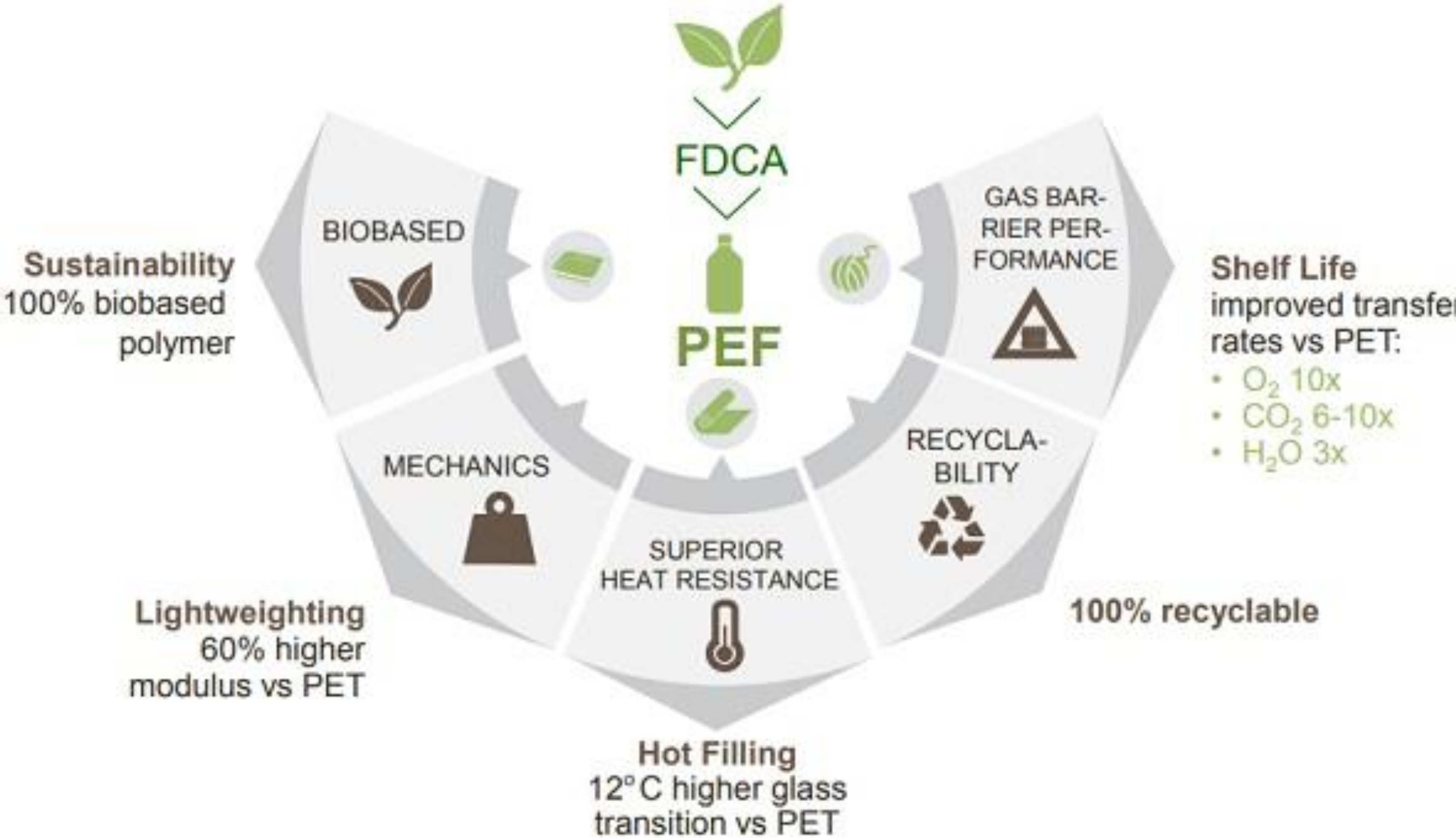
New polymers from biomass: PEF

FDCA synthesis



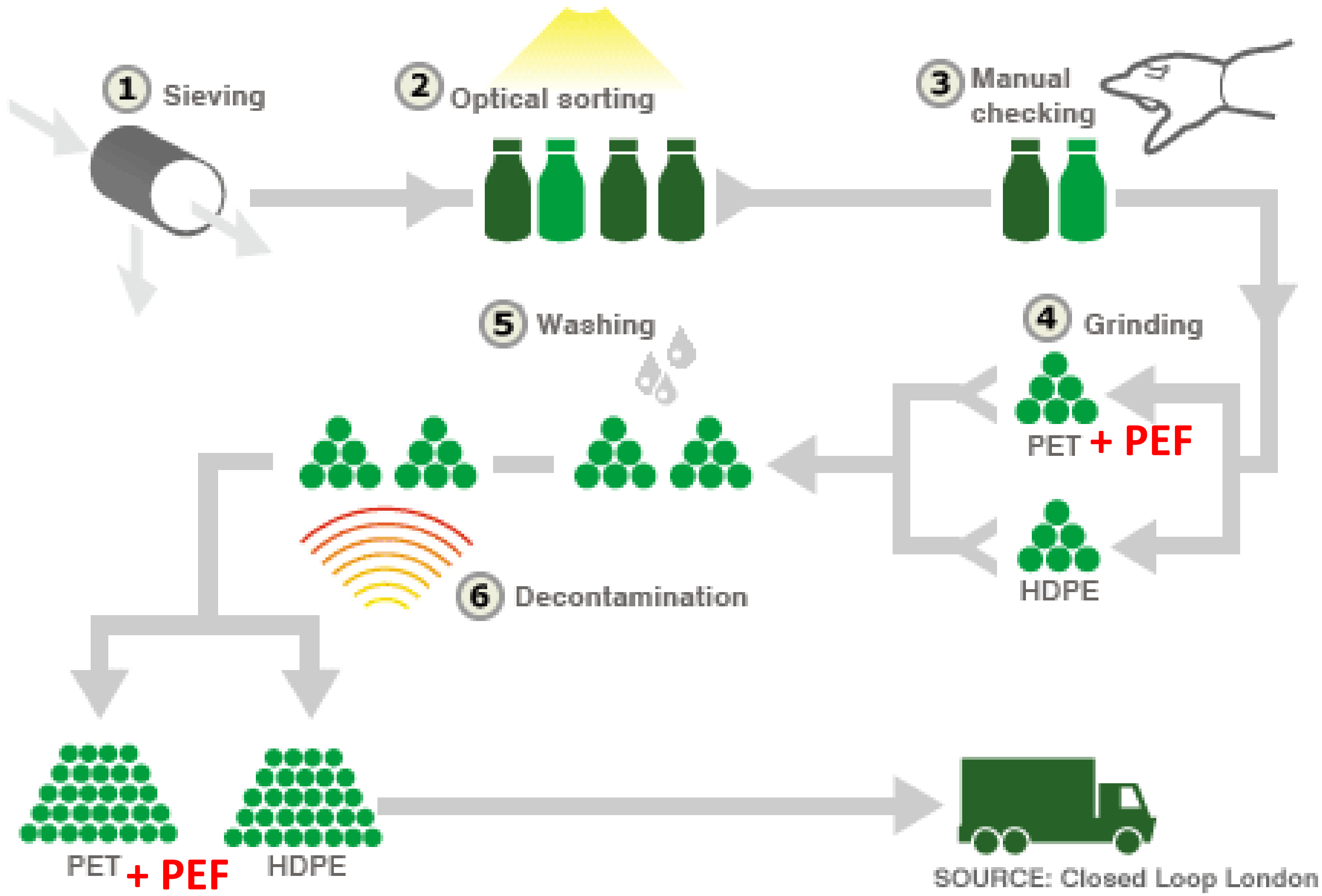
New polymers from biomass: PEF

Properties



PEF as a drop-in from PET bottles ? No

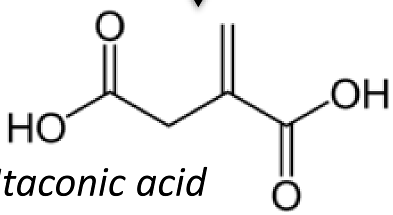
1) PET is one of the best recycled plastic (30% worldwide)



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

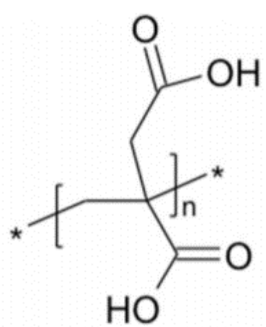
New polymers from biomass: SAP's

Fermentation

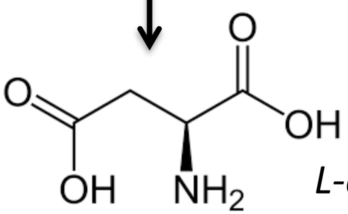


Itaconic acid

Polymerization

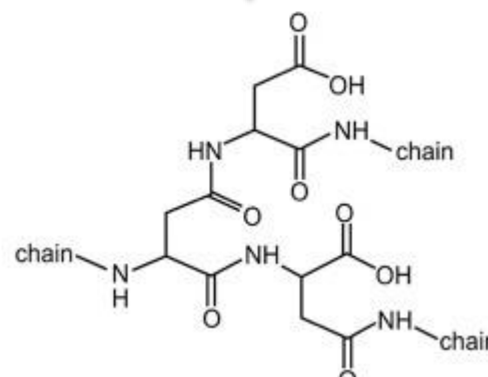


Fermentation

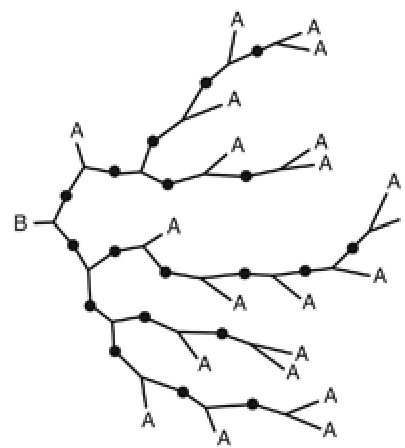


L-aspartic acid

Polymerization

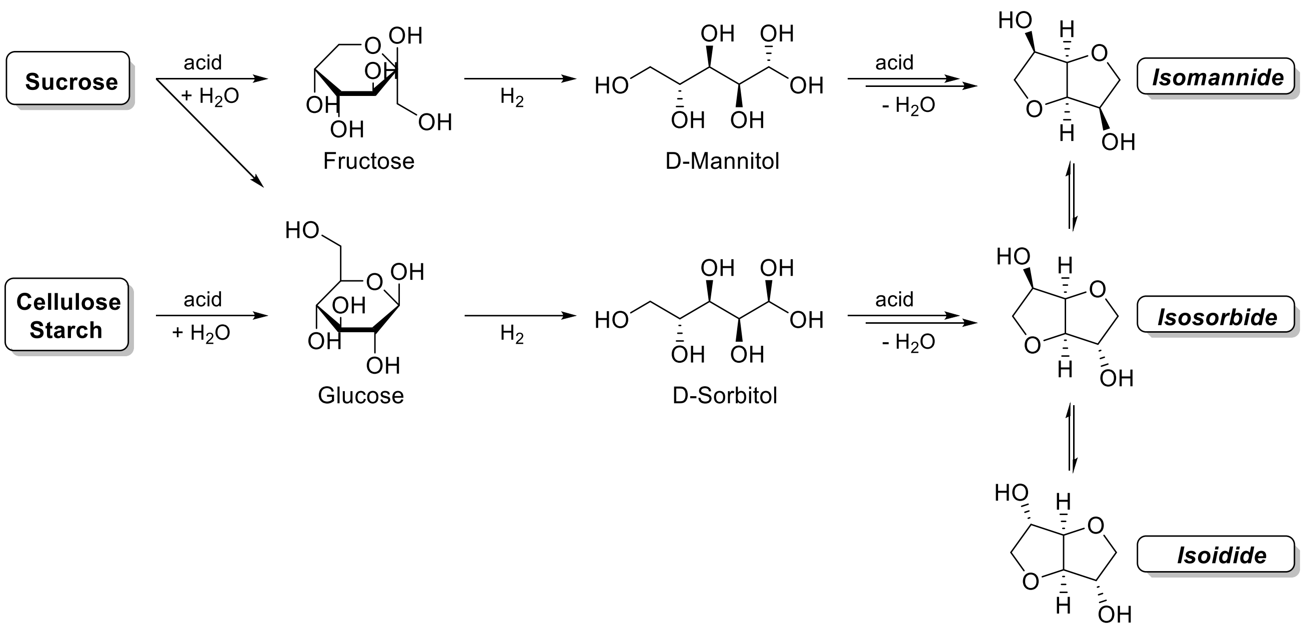


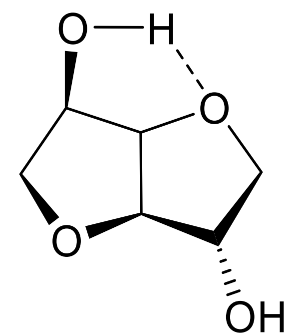
(2)

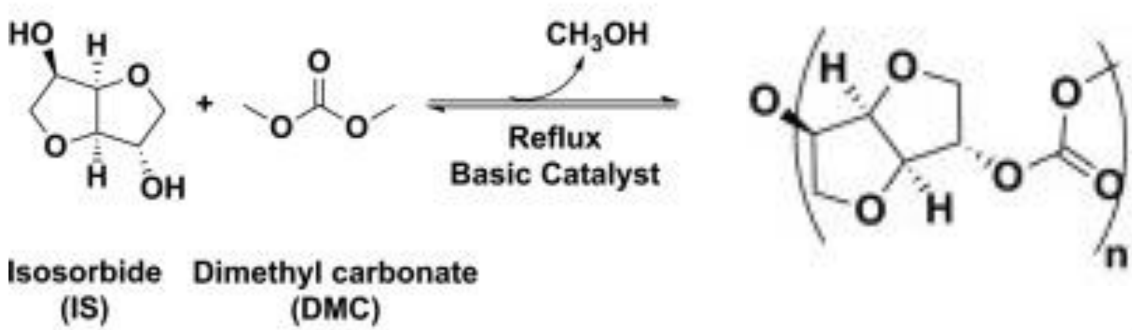


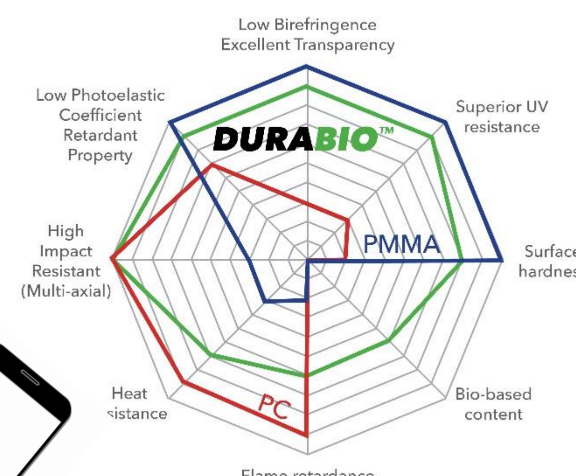
Hyperbranched Polymer

Isorbide: « regular » chemistry to transform sugar



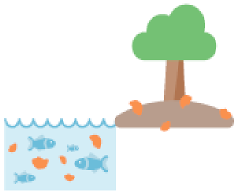






Outlines

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

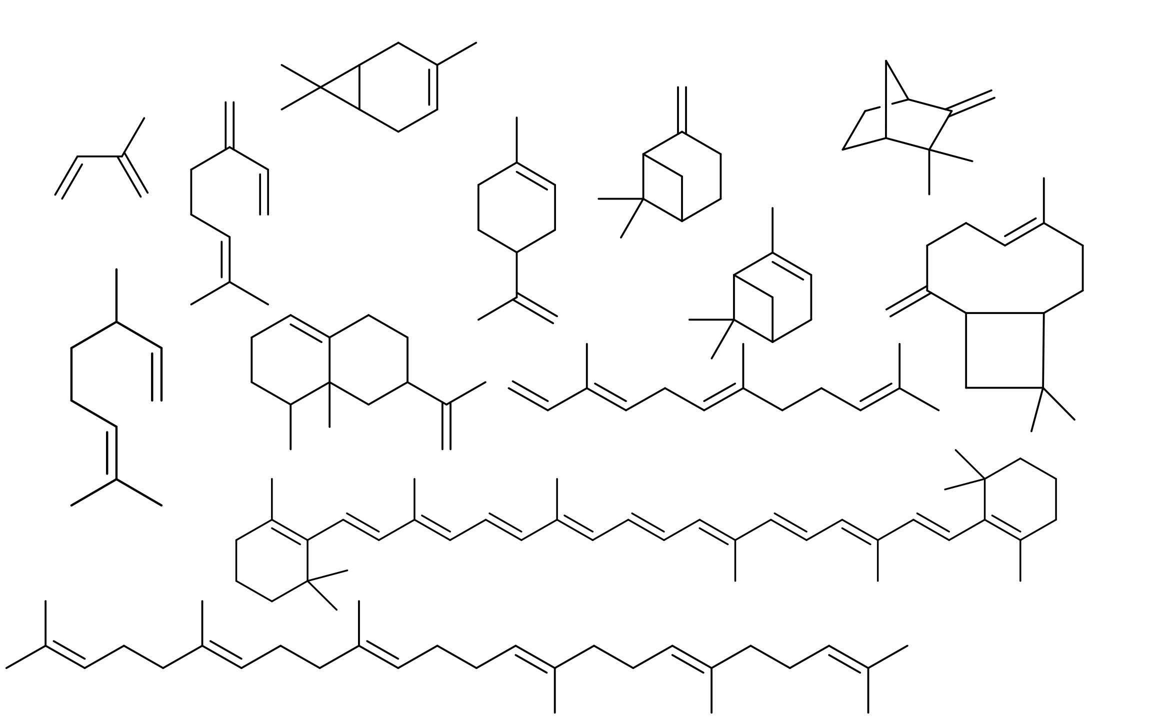
Sugarcane corn wheat rice guar

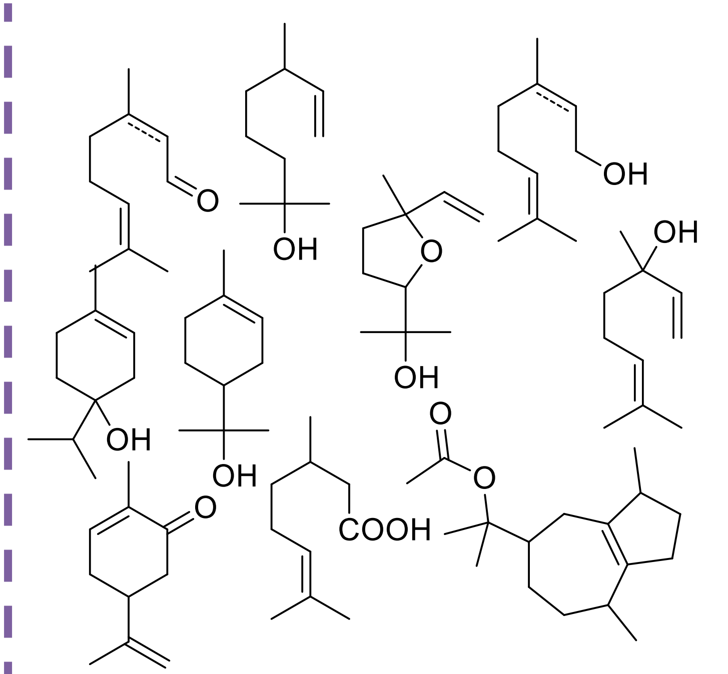
Clove citrus

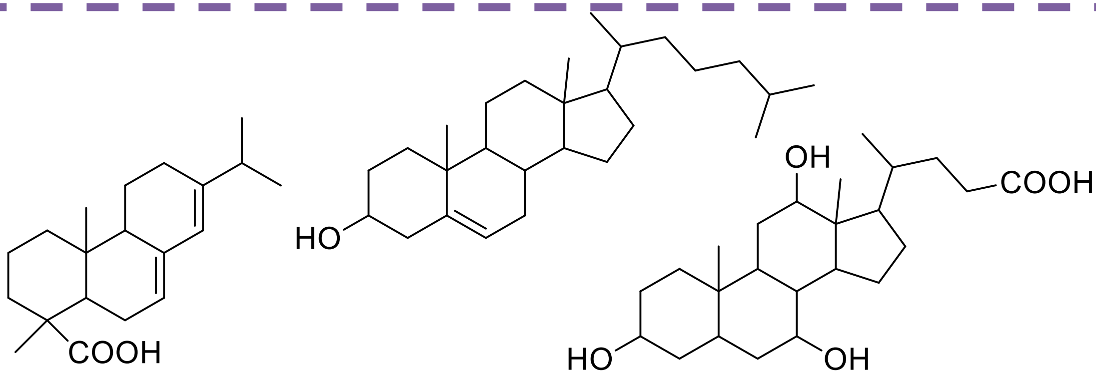
Carbohydrate

Terpens?

Terpenes as a source of various backbones







> 1000 of skeletons

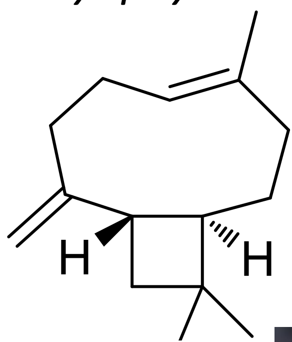
...

What can we do with a little of Hop?

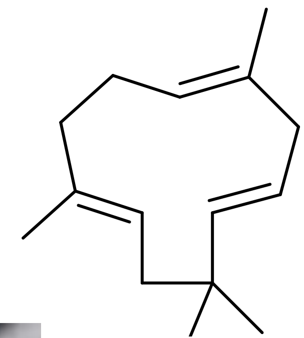
1 €/kg

No! Polymers

Caryophyllene

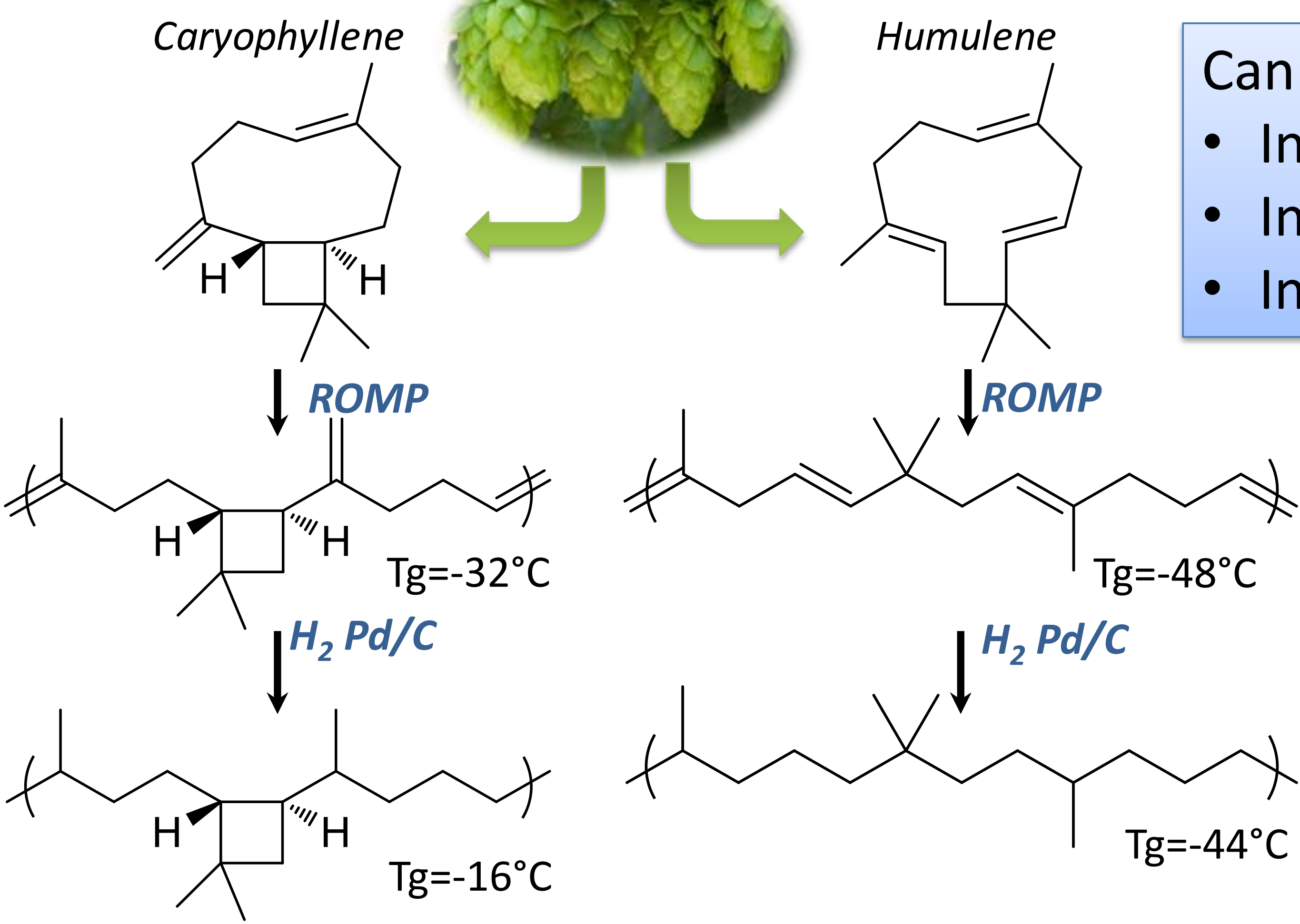


Humulene



Beer !!!

First direct ROMP of natural compounds



Can be performed

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

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

Conclusion and perspectives

Eucalyptus spruce pine coconut palm soybean rapeseed peanut castor bean

Ligno

Crossing the biomass !!!

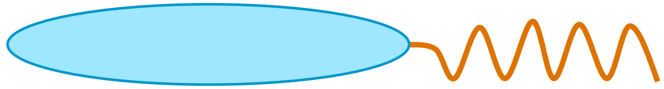
Sugarcane corn wheat rice guar

Carbohydrate

Clove citrus

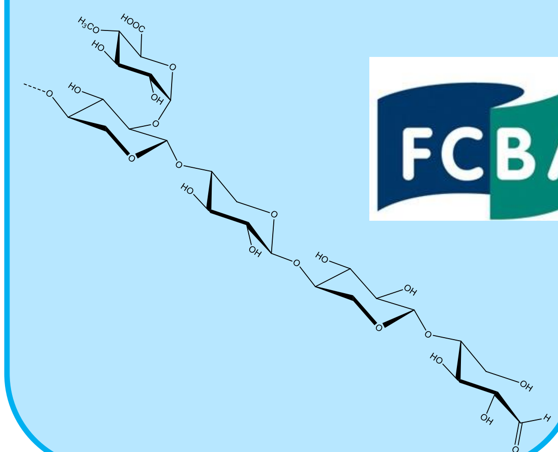
Terpens

Crossing the biomass



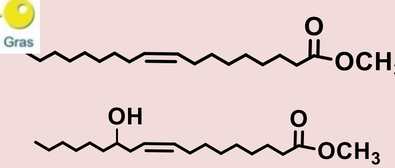
Wood

Xylo-oligosaccharides



Oil

Fatty esters



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

Detergents

Cosmetics

Emulsifiers -Foaming agents -
Solubilizers -Wetting agents

Pharmaceutical

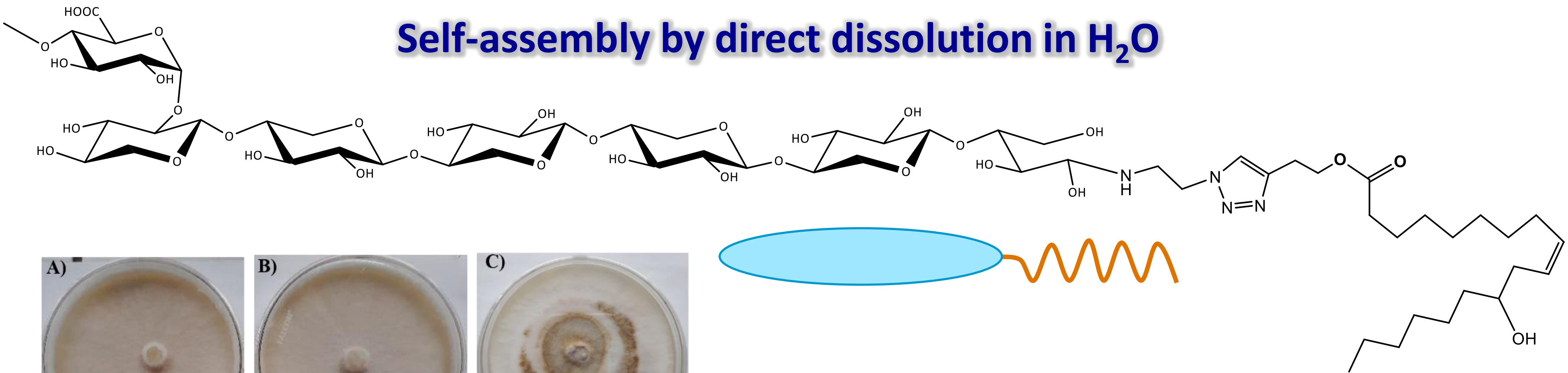
Biocompatible, drug delivery

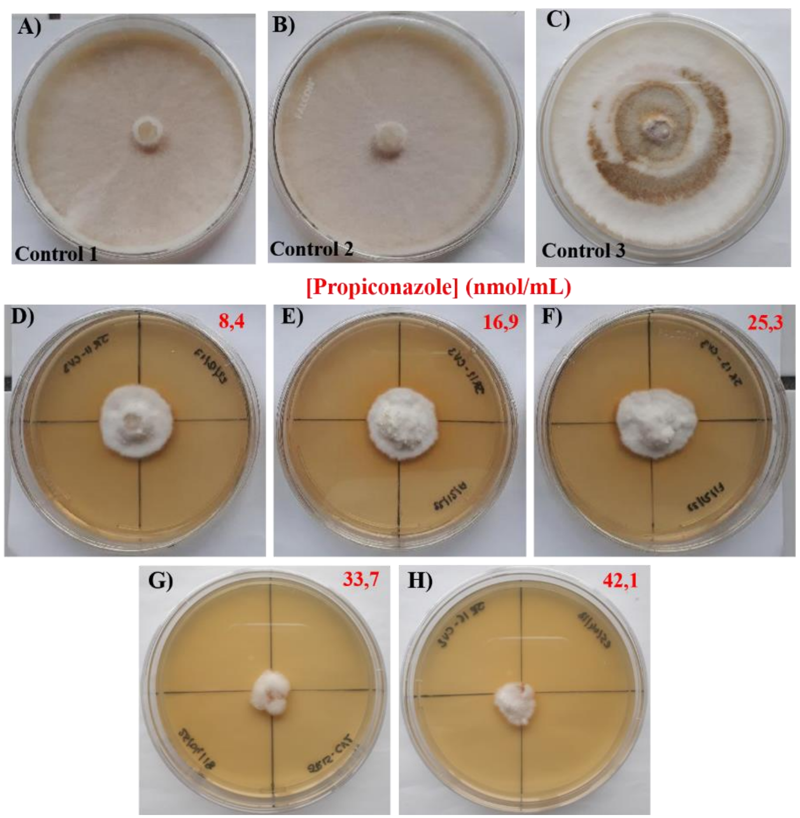
Food

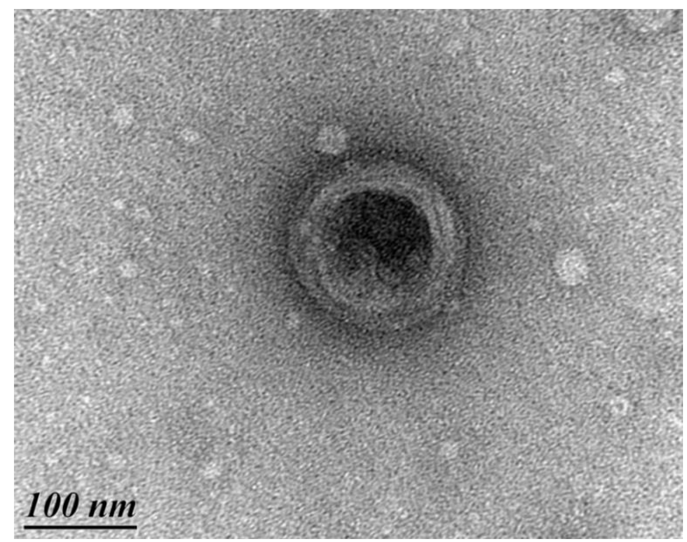
Use as emulsifier

Crossing the biomass

Self-assembly by direct dissolution in H_2O

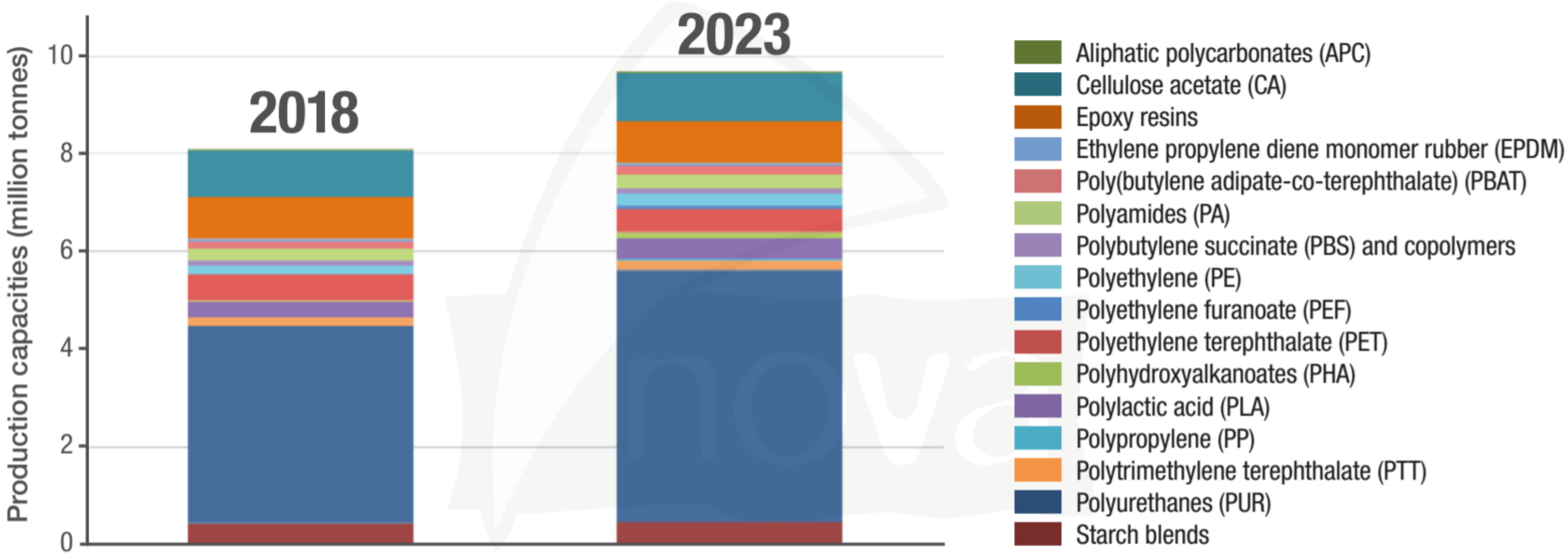




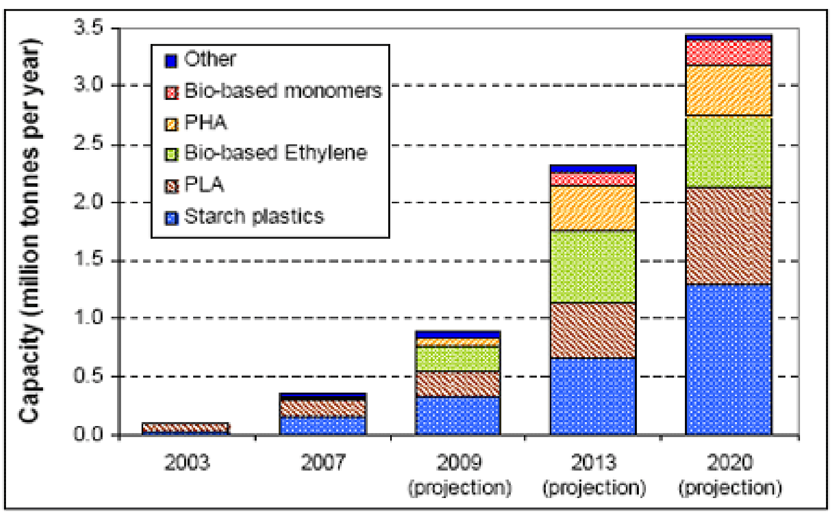


J. Rosselgong et al. Biomacromolecules, 20(1), 118-129 (2019)

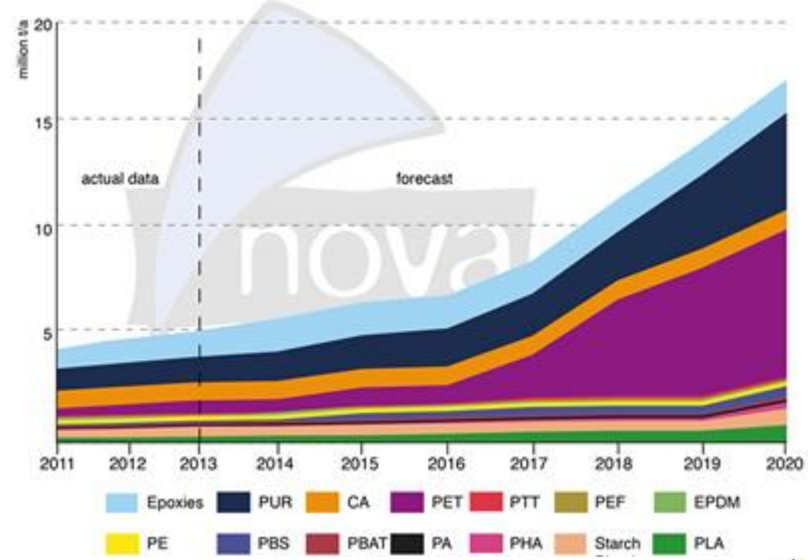
Bio-based polymers forecast

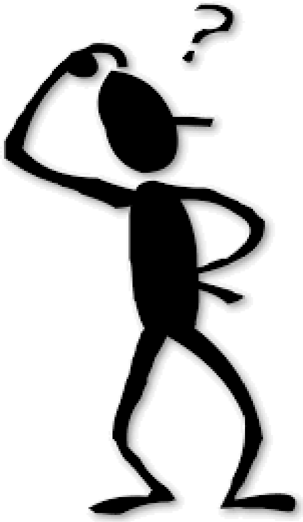


vs. 350 Mt of polymer



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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