université PARIS-SACLAY | GRADUATE SCHOOL Chimie

Digital Micro-Certification
"**The Challenges of Sustainable Chemistry**"

January – February 2024

Project Managers

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Renewable and bio-sourced chemistry

Marie-Christine SCHERRMANN
ICMMO – Université Paris-Saclay

Green Chemistry and Sustainable Chemistry

12 principles of green chemistry

1. Prevent waste
2. Maximize atom economy
3. Design less hazardous chemical syntheses
4. Design safer chemicals and products
5. Use safer solvents and reaction conditions
6. Increase energy efficiency
7. Use renewable feedstocks
8. Avoid chemical derivatives
9. Use catalysts, not stoichiometric reagents
10. Design chemicals and products to degrade after use
11. Analyze in real time to prevent pollution
12. Minimize the potential for accidents

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

Anastas and Warner

Sustainable Chemistry

A scientific concept that seeks to improve the efficiency with which natural resources are used to meet human needs for chemical products and services.

OECD

Organisation for Economic Cooperation and Development

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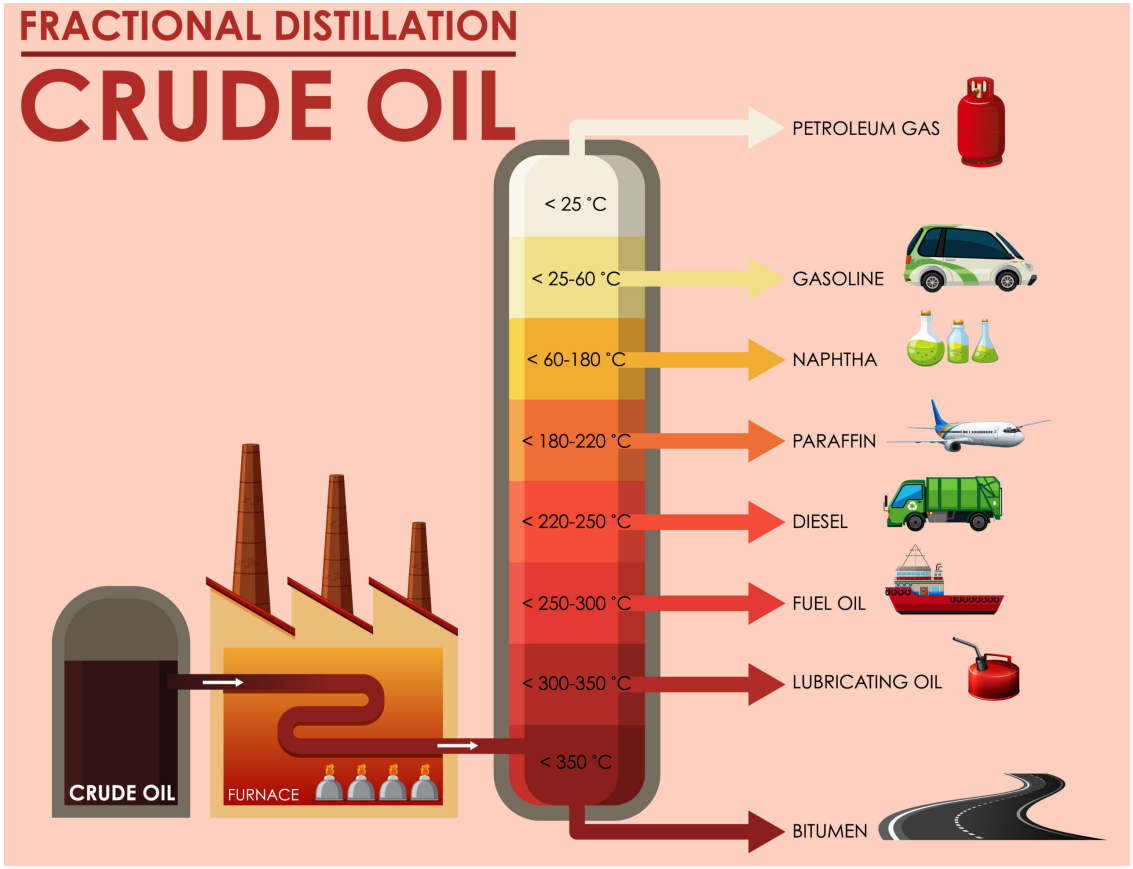
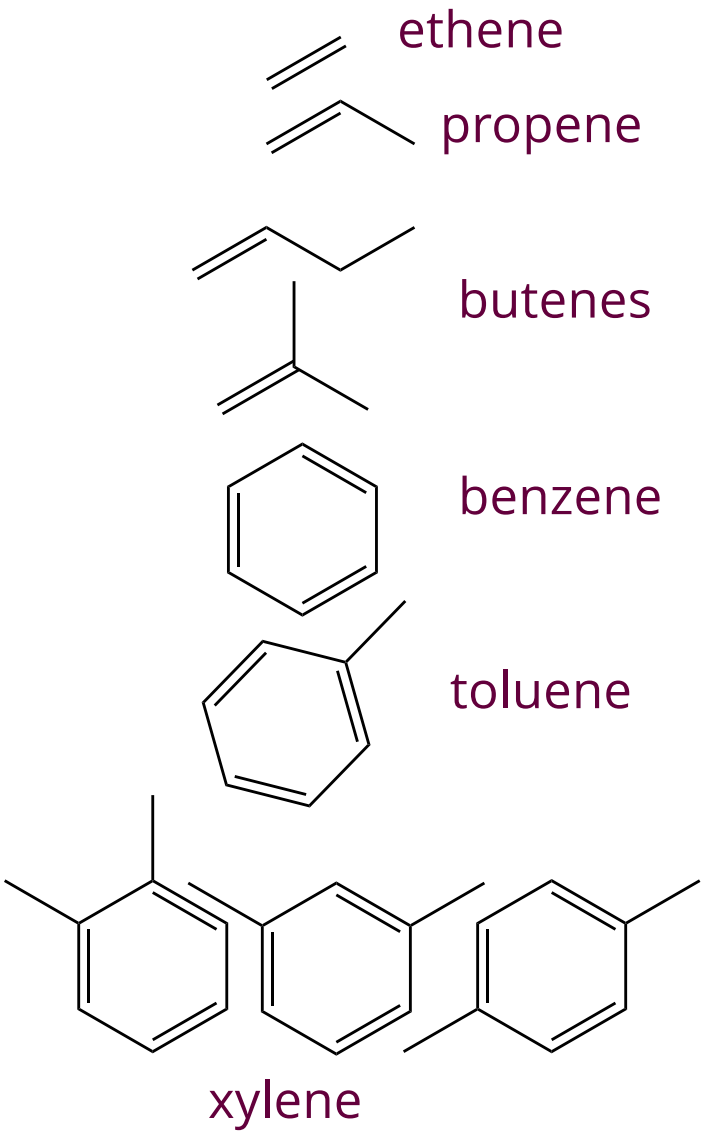
Fossil-derived Base Chemicals

Feedstocks: Crude Oil, Natural Gas, Coal





Fossil-derived Base Chemicals – Bulk chemicals - Products

Naphta *catalytic/steam reforming*	ethene		polybutadiene rubber polyethene
	propene	ethene oxide 1,2-dichloroethane vinyl chloride propene oxide	polyethene oxide anti-freeze polyvinyl chloride polypropene
	butenes	propan-2-ol ethylbenzene styrene	nylon dyes styrene-butadiene rubber
	benzene	phenol cyclohexane aniline	polyurethanes polyetheneterephthalate adhesives
	toluene	toluene diisocyanate terephthalic acid (iso)phthalic acid acetic acid	polyesters propandiols solvents
	xylene	methyl methacrylate formaldehyde	bisphenol A polycarbonates latex paints

Example: styrene-butadiene rubber

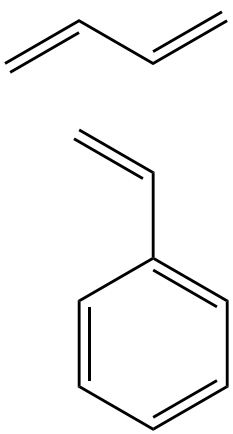
Naphta	ethene		polybutadiene rubber
			polyethene
catalytic/steam reforming	propene	ethene oxide	polyethene oxide
		1,2-dichloroethane	anti-freeze
		vinyl chloride	polyvinyl chloride
		propene oxide	polypropene
	butenes	propan-2-ol	nylon
		ethylbenzene	dyes
		styrene	**styrene-butadiene rubber**
	benzene	phenol	polyurethanes
		cyclohexane	polyetheneterephthalate
		aniline	adhesives
		toluene diisocyanate	polyesters
	toluene	terephthalic acid	propandiols
		(iso)phthalic acid	solvents
		acetic acid	bisphenol A
		methyl methacrylate	polycarbonates
	xylene	formaldehyde	latex
			paints

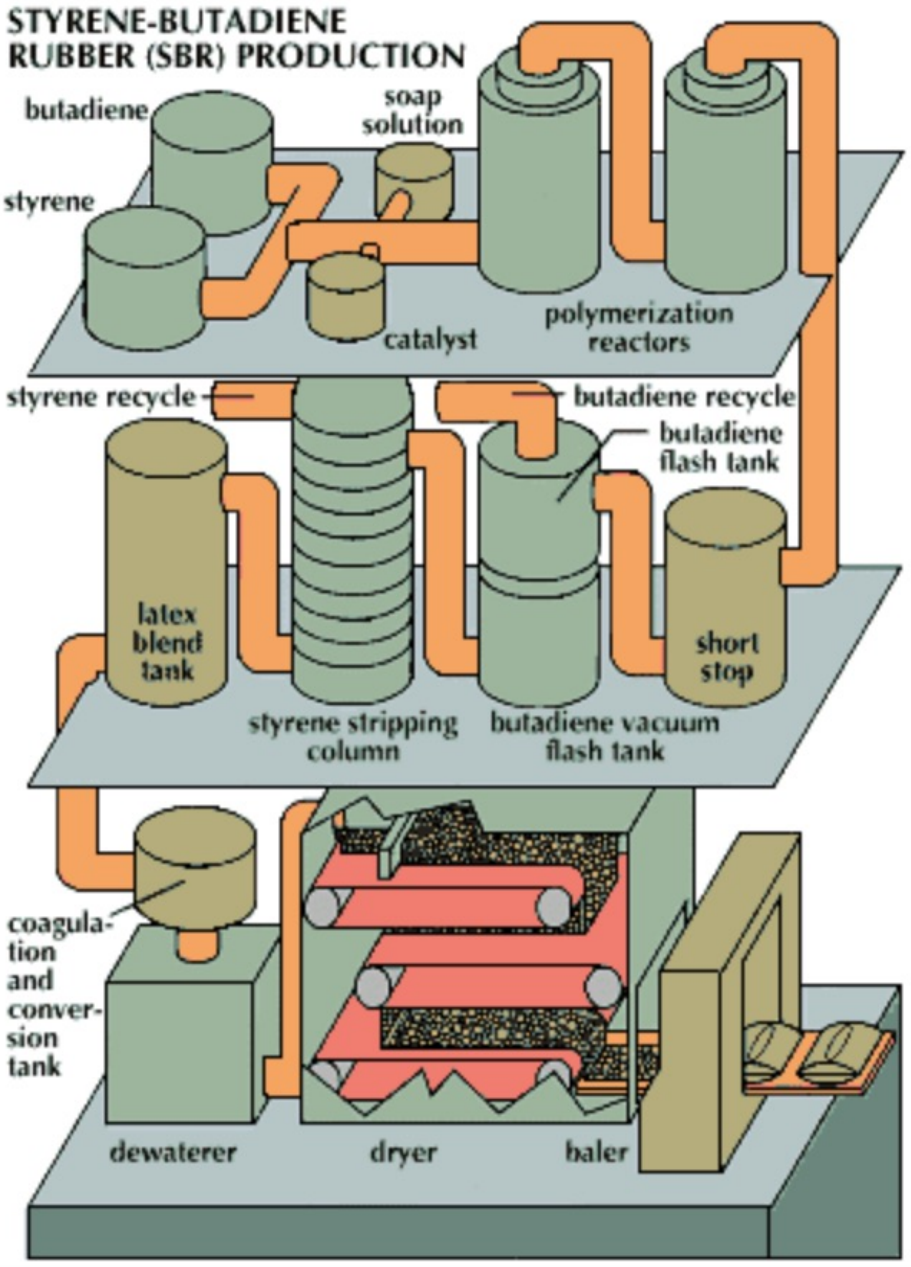
Example: styrene-butadiene rubber

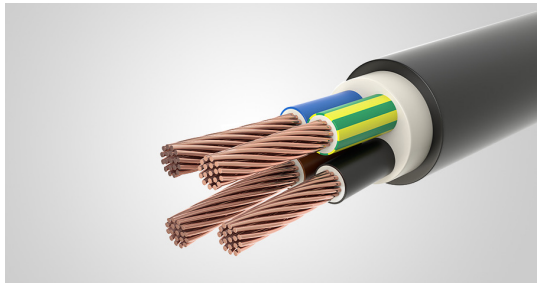
Naphta

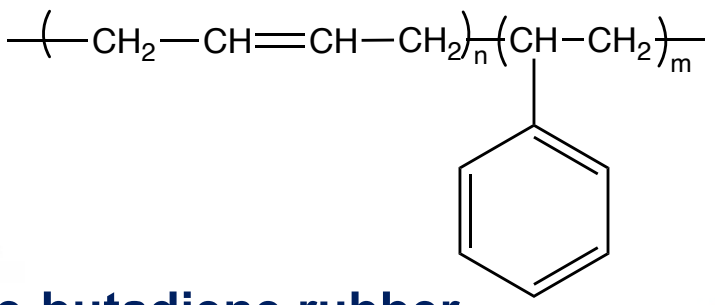
catalytic/steam reforming

ethene		polybutadiene rubber polyethene
propene	ethene oxide 1,2-dichloroethane vinyl chloride propene oxide	polyethene oxide anti-freeze polyvinyl chloride polypropene
butenes	propan-2-ol ethylbenzene **styrene**	nylon dyes **styrene-butadiene rubber**
benzene	phenol cyclohexane aniline toluene diisocyanate	polyurethanes polyetheneterephthalate adhesives
toluene	terephthalic acid (iso)phthalic acid acetic acid	polyesters propandiols solvents
xylene	methyl methacrylate formaldehyde	bisphenol A polycarbonates latex paints



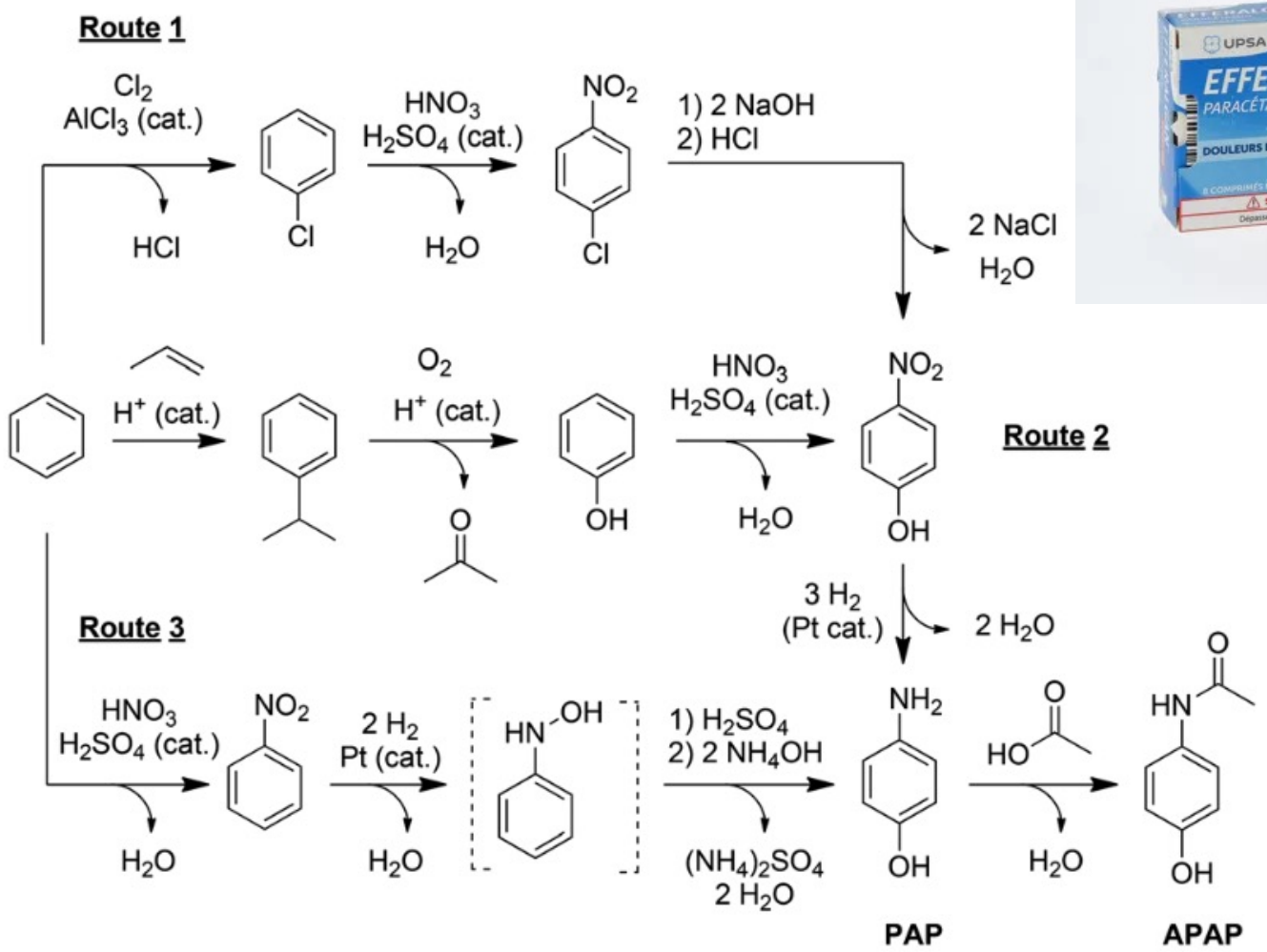






styrene-butadiene rubber

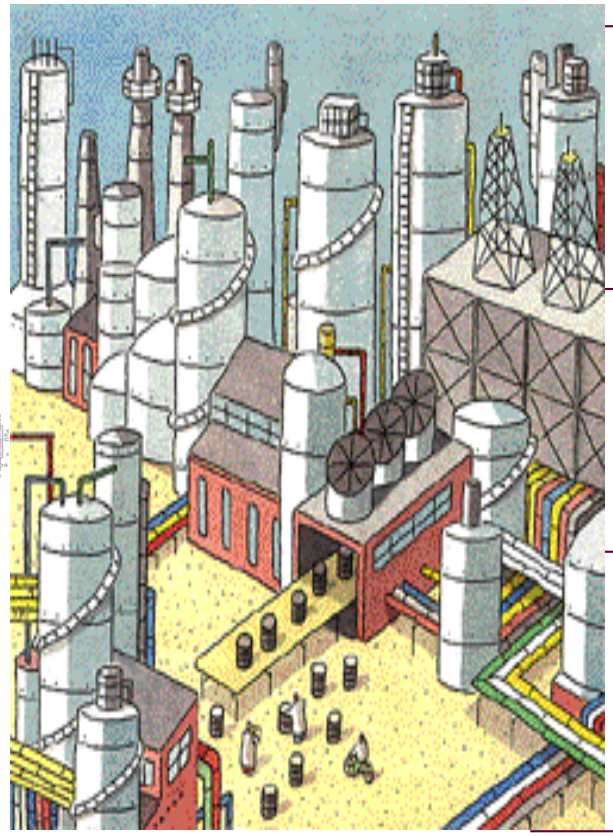
Paracetamol (acetaminophen)



Scheme 2 Commercial routes for paracetamol production.

R. Joncour, N. Duguet, E. Métay, A. Ferreira and M. Lemaire. Green Chem., 2014, 16, 2997

Oil refinery



→ Fuel

→ Asphalt

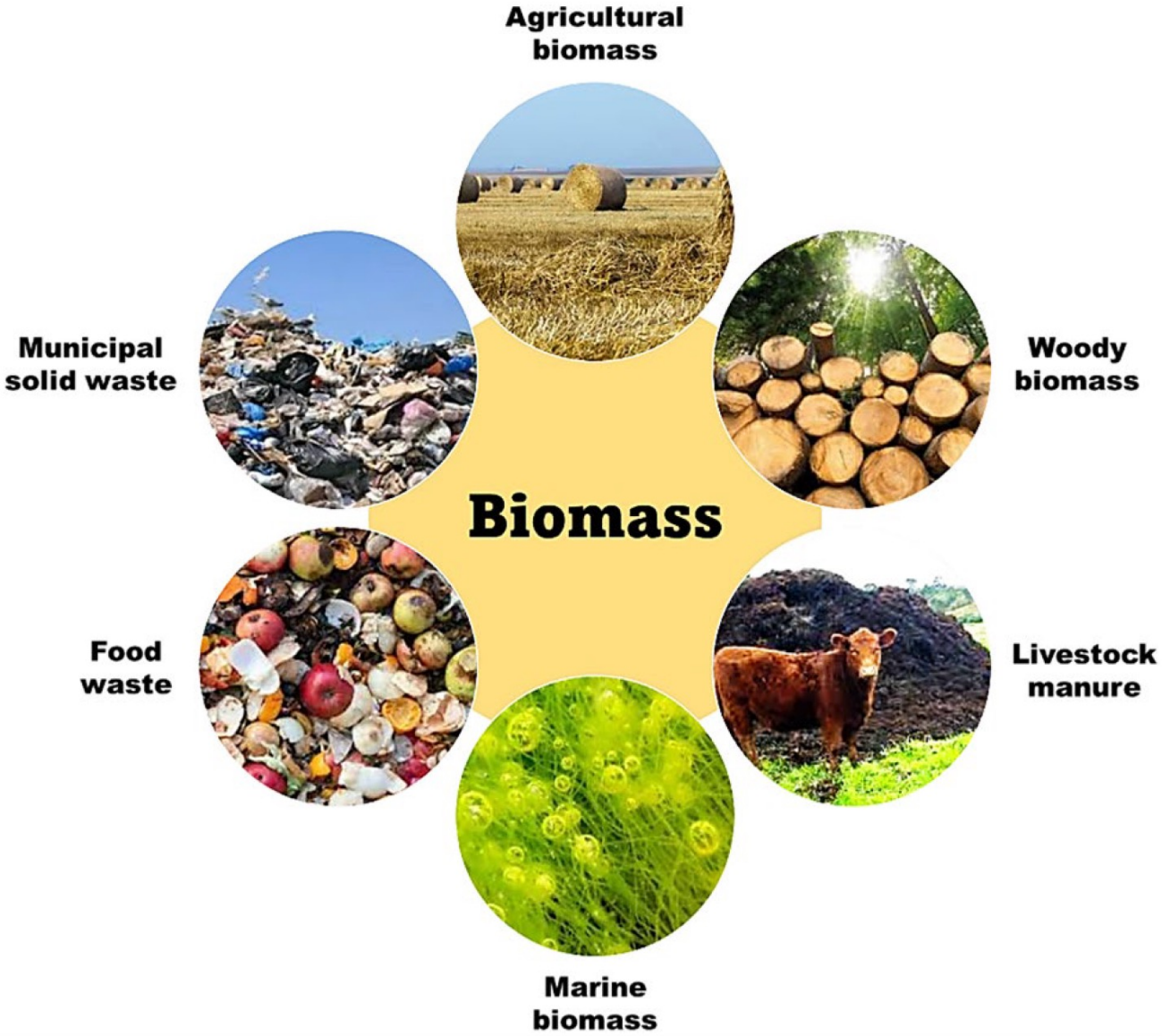
→ Base chemicals

plastics
pharmaceuticals
solvents
clothing
agro-chemicals
…

Simple building-block chemical produced via simple processing (steam cracking, reforming…)

→ Energy

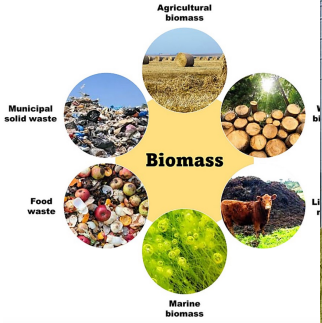
Renewable feedstocks: BIOMASS



Sarker, T.R., Nanda, S., Meda, V. *et al.* Environmental Chemistry Letters (2023) 21:231–264

Biorefinery

The International Energy Agency defined biorefining as "the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, materials) and bioenergy (biofuels, power and/or heat)



→ Fuel

→ Materials

→ Chemicals

plastics
pharmaceuticals
solvents
clothing
agro-chemicals
…

Platform molecules: bio-based chemical compound whose constituent elements originate wholly from biomass (excluding fossil carbon sources)

→ Energy

B. Annevelink, L. Garcia Chavez, R. van Ree & I. Vural Gursel, Global biorefinery status report 2022 – IEA Bioenergy: Task 42 Biorefining in a circular economy

Feedstocks

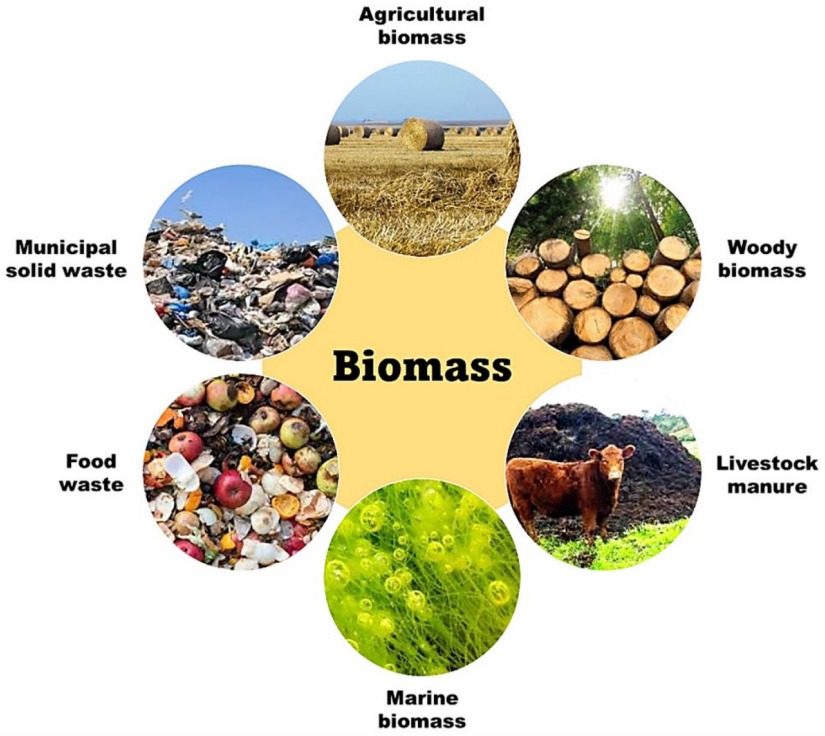
Polysaccharides (starch, cellulose, hemicellulose, chitin)

Mono/disaccharides (glucose, fructose, sucrose)

Lignin

Extracts

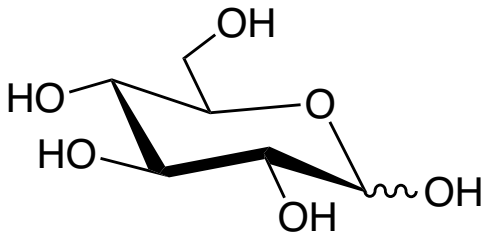
Protein



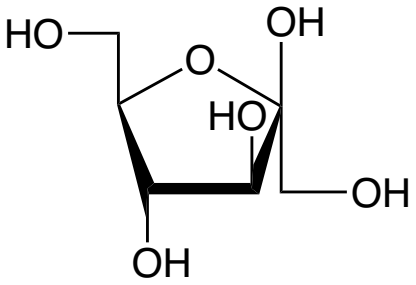
Processing technologies

- Physical (grinding, ultrasound, extrusion...)
- Chemical (hydrolysis, dehydration, extraction, precipitation…)
- Biochemical (enzymatic reaction, fermentation, etc.)
- …

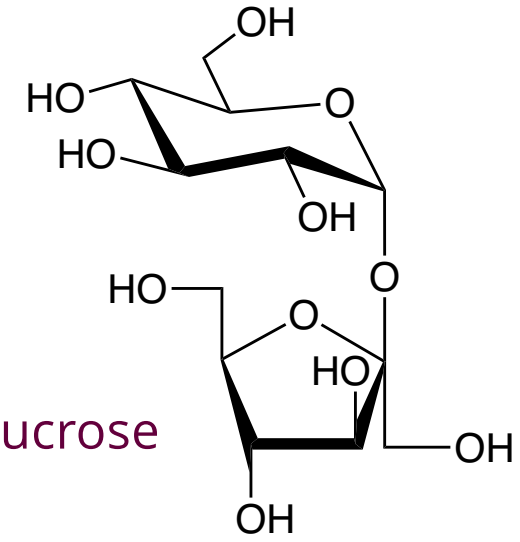
Saccharides



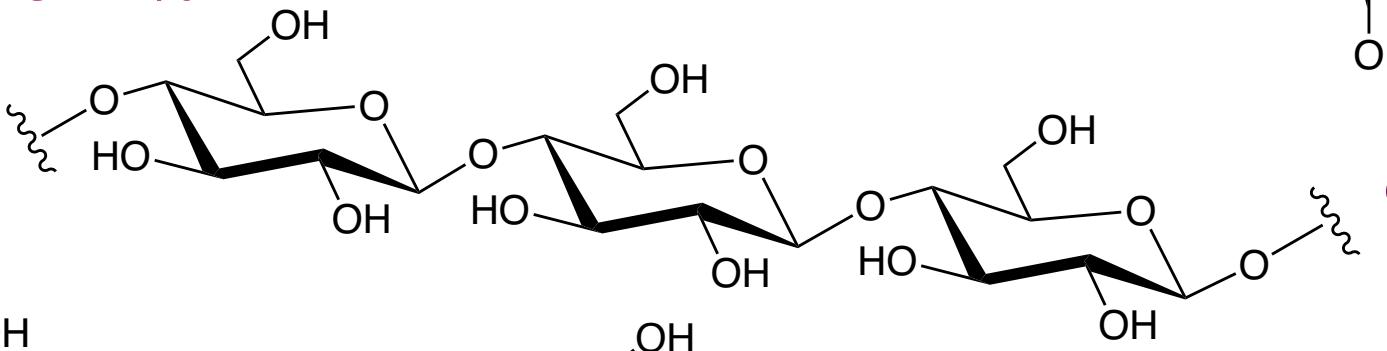
D- glucose (glucopyranose)



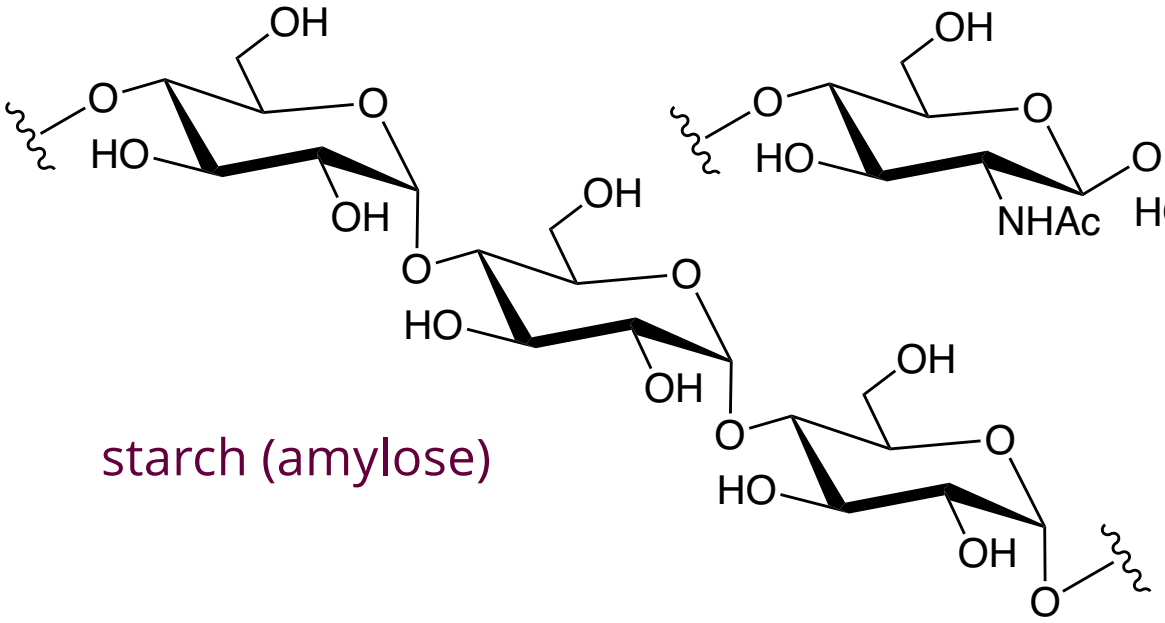
β-D- fructofuranose



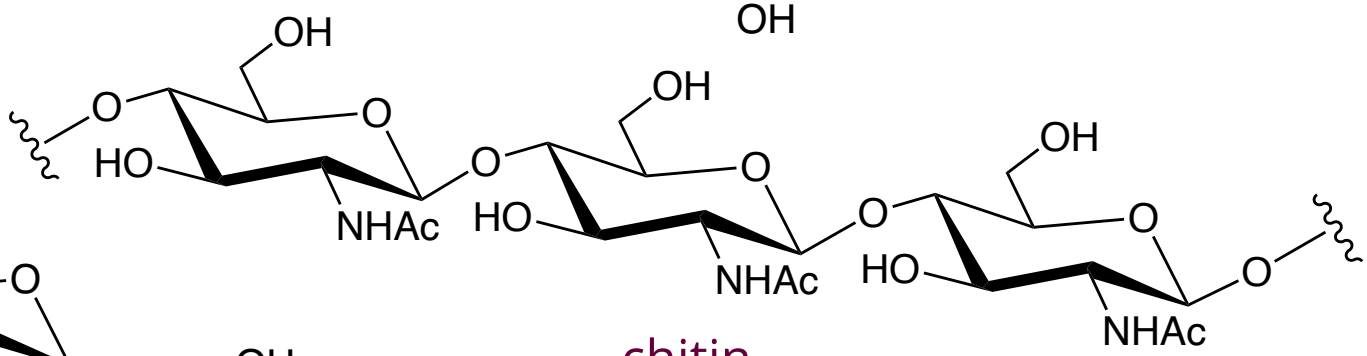
sucrose



cellulose



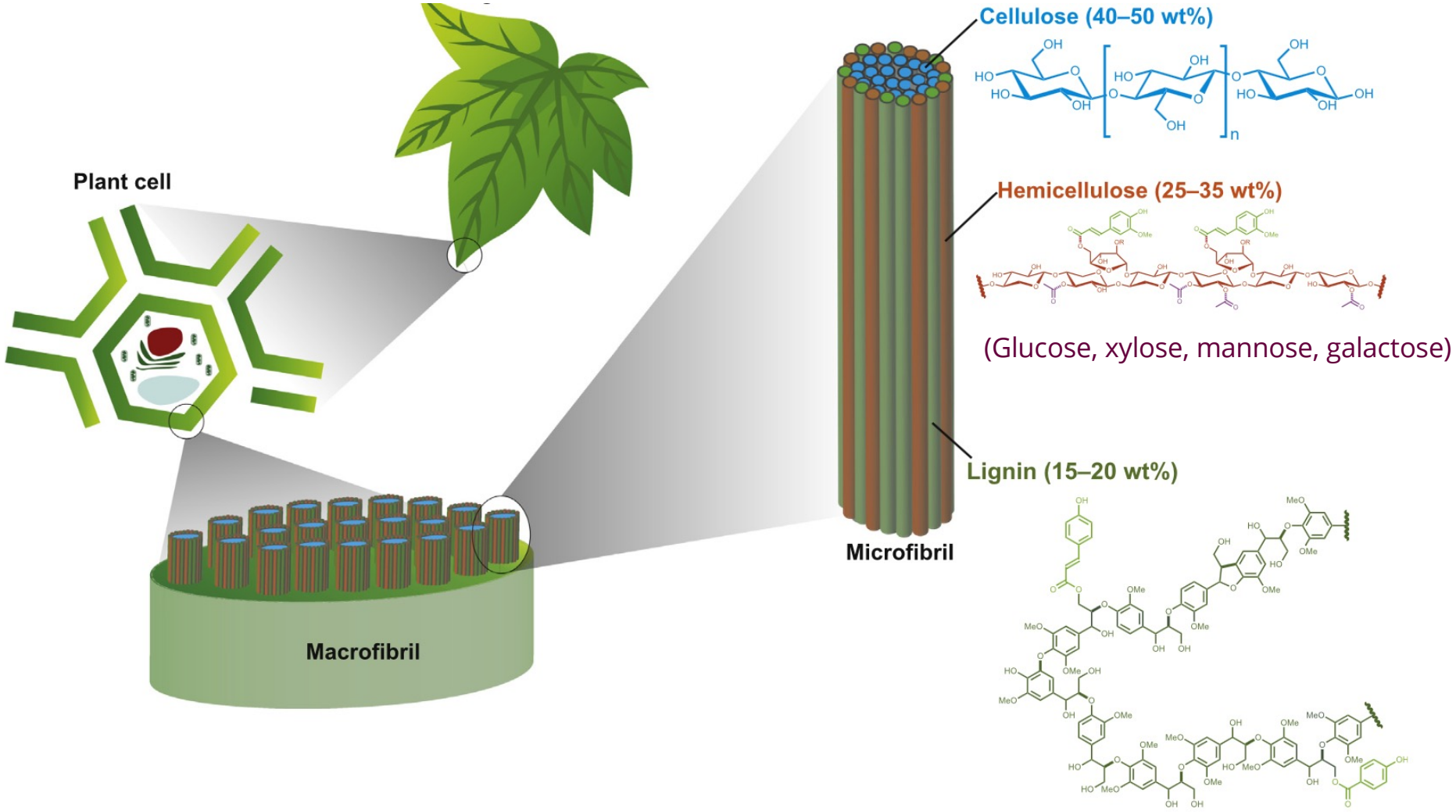
starch (amylose)



chitin

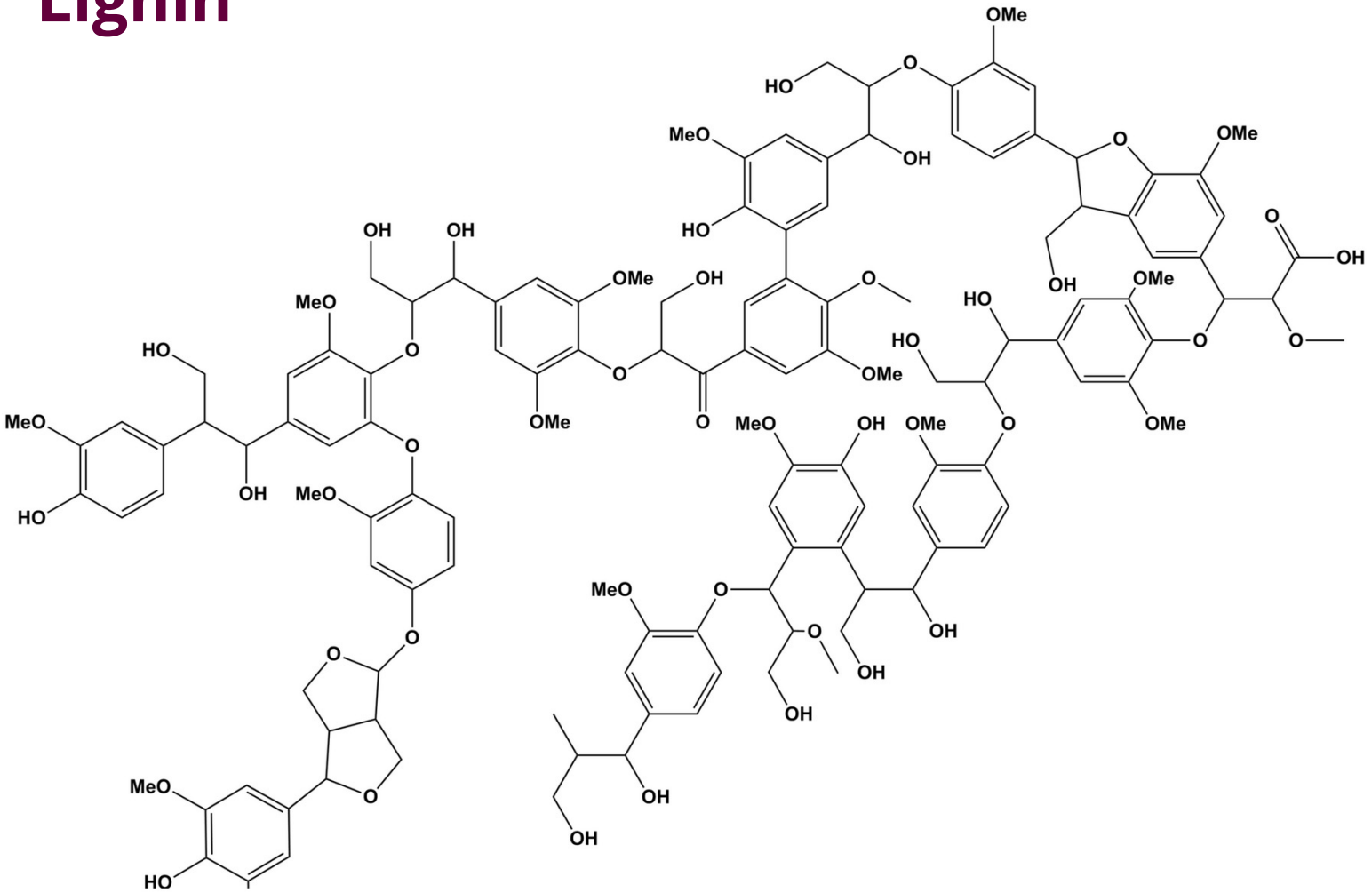
~ 75% of the biomass

Lignocellulosic biomass



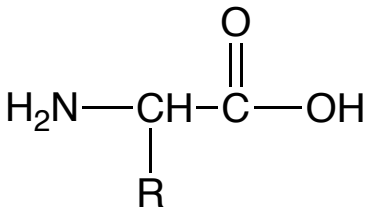
S.Bertella and J. S. Luterbacher Trends in Chemistry, May 2020, Vol. 2, No. 5

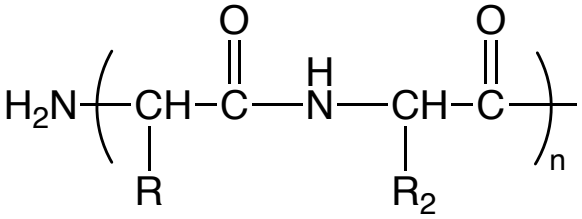
Lignin



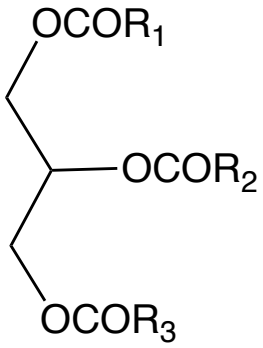
~ 20% of the biomass

Proteins – fats – terpenoids – alkaloids- nucleic acids

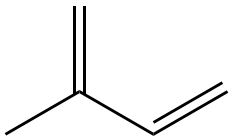




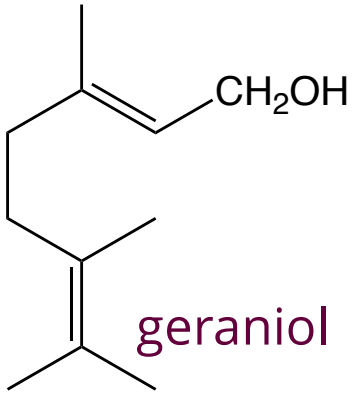
n ~ 10 : peptide
n -> 100+ : protein



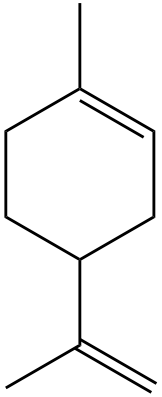
R_1, R_2, R_3 = fatty chains, saturated or unsaturated



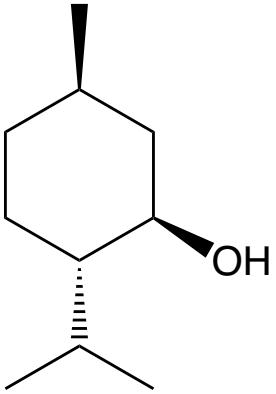
isoprene



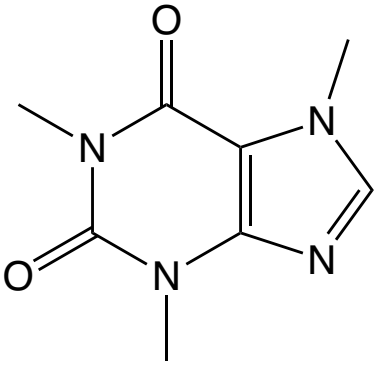
geraniol



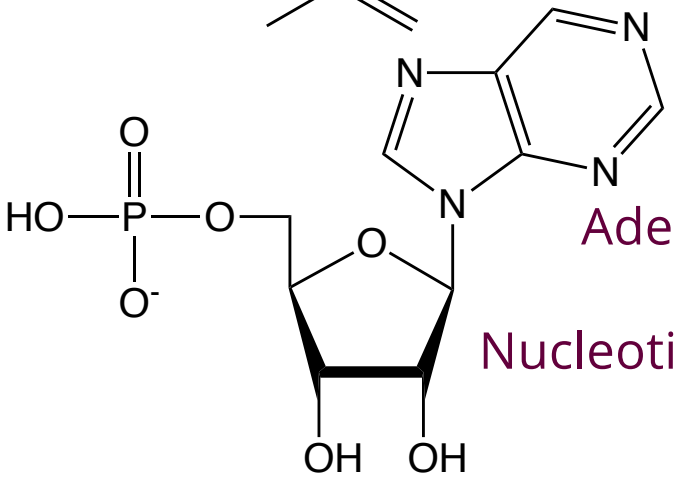
limonene



menthol



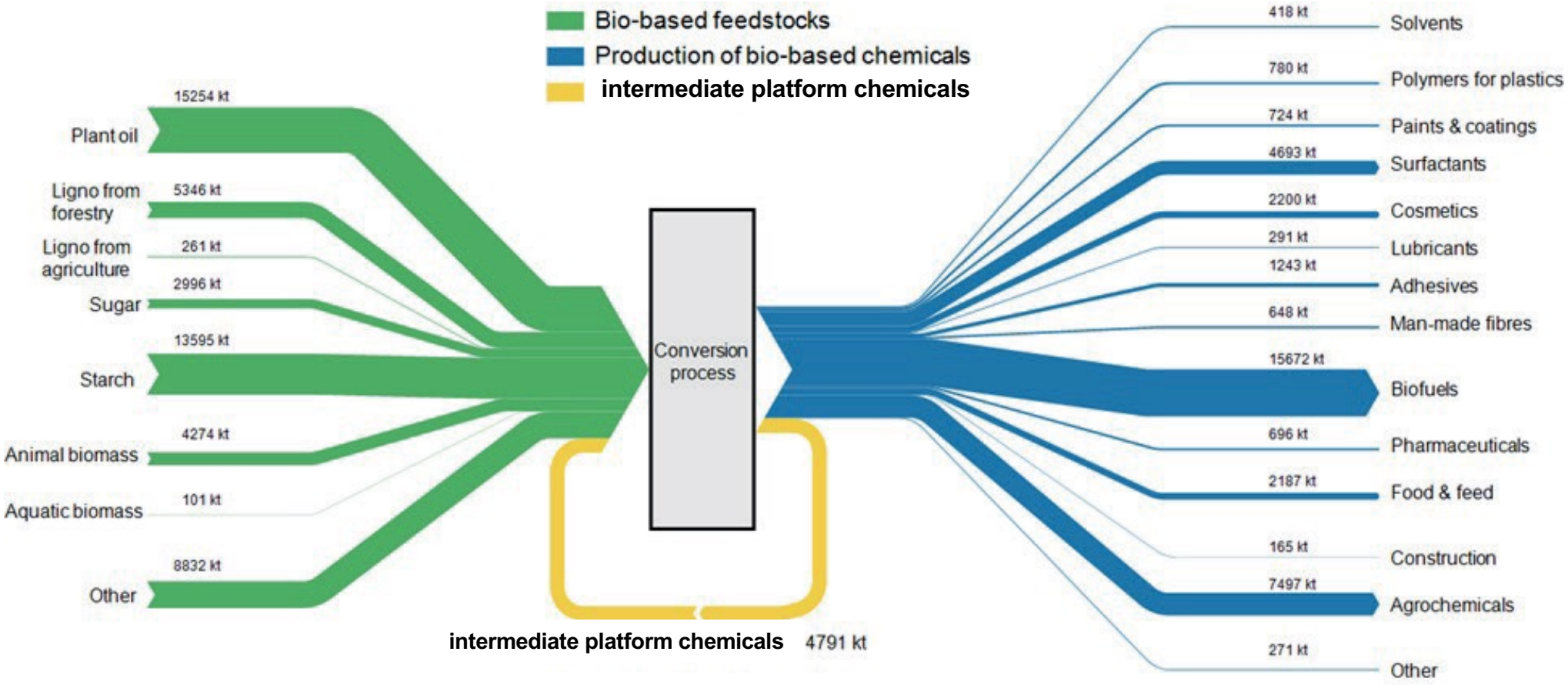
caffeine



Adenosine Monophosphate (AMP)

Nucleotide **~ 5% of the biomass**

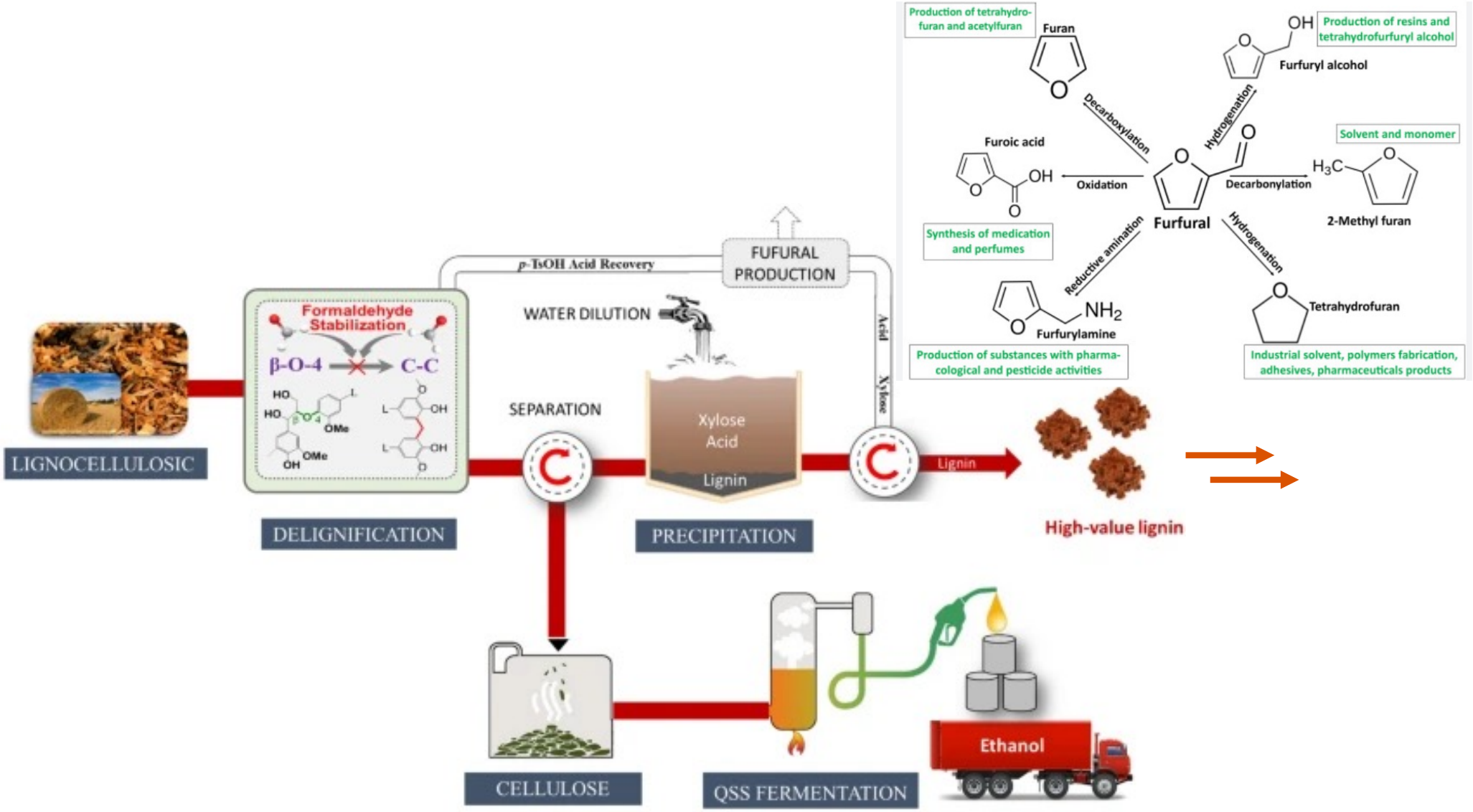
Biomass Supply and Uses in the EU



Flow chart for the feedstocks for the selected bio-based industrial products , (EU-27+UK, 2018)

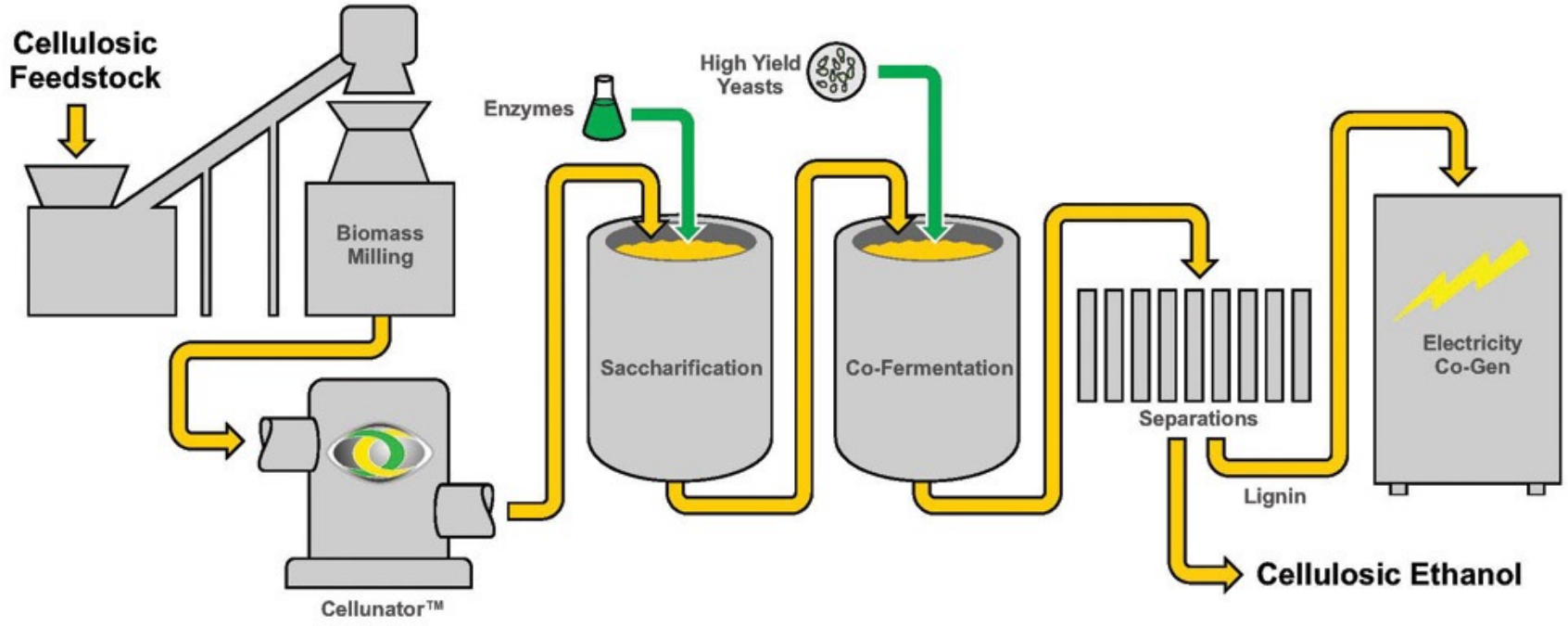
Sturm, V.; van Leeuwen, M.; Gonzalez-Martinez, A.; Verhoog, D.; Hark, N.; de Beus, N. Providing Insights into the Markets for Bio-Based Materials with BioMAT. Sustainability 2023, 15, 3064. https://doi.org/10.3390/su15043064.

Example: From lignocellulosic residues to products



A hydrotrope pretreatment for stabilized lignin extraction and high titer ethanol production. Ji et al. *Bioresour. Bioprocess.*, **2022**, 9:40

Bio-ethanol



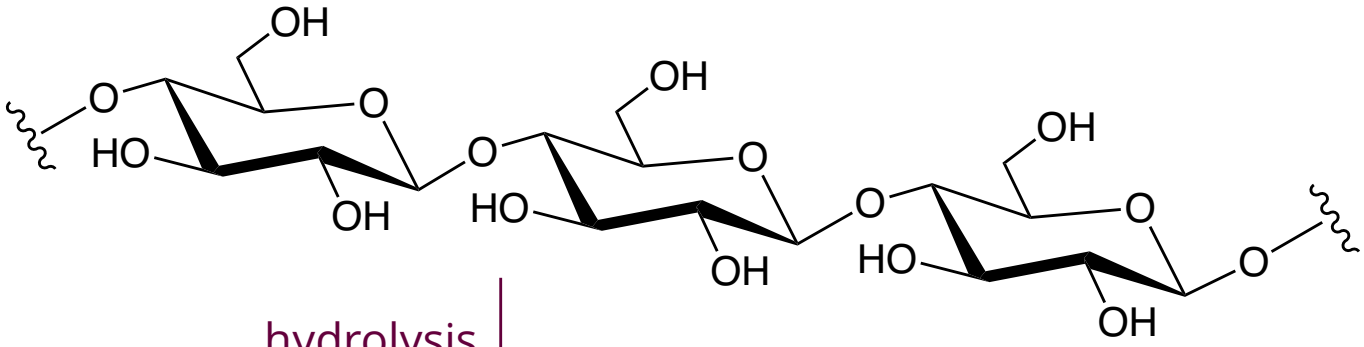
Europe Bioethanol Company List

- Abengoa
- ALCOGROUP SA
- Lantmnnen Agroetanol AB
- ADM
- AGRANA Beteiligungs-AG
- Cargill
- ALMAGEST AD
- Anora Group Plc
- BIOAGRA S.A.
- RYAM

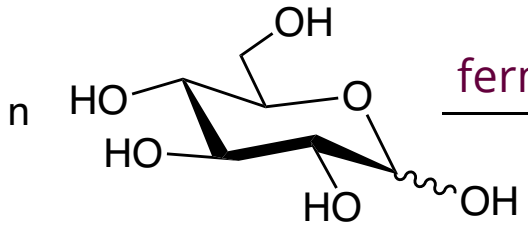
ILLUSTRATION: EDENIQ INC

Source: https://www.mordorintelligence.com/industry-reports/europe-bioethanol-market/companies

Examples: Bio-sourced polymers - Polyethylene (PE)

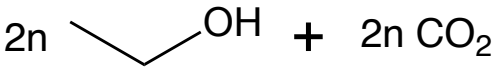


hydrolysis

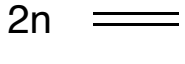


glucose

fermentation

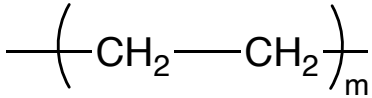


- H_2O



ethylene

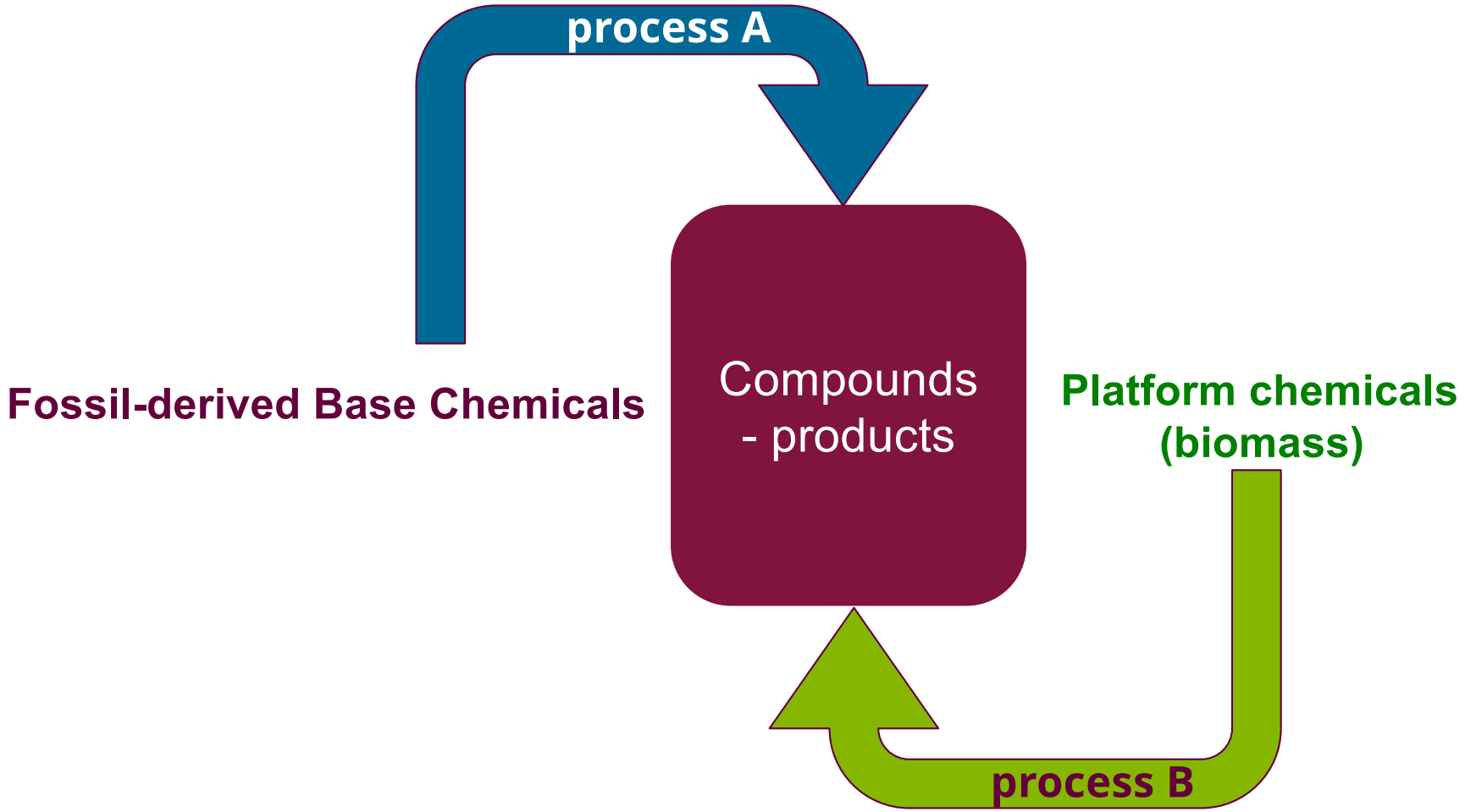
polymerization



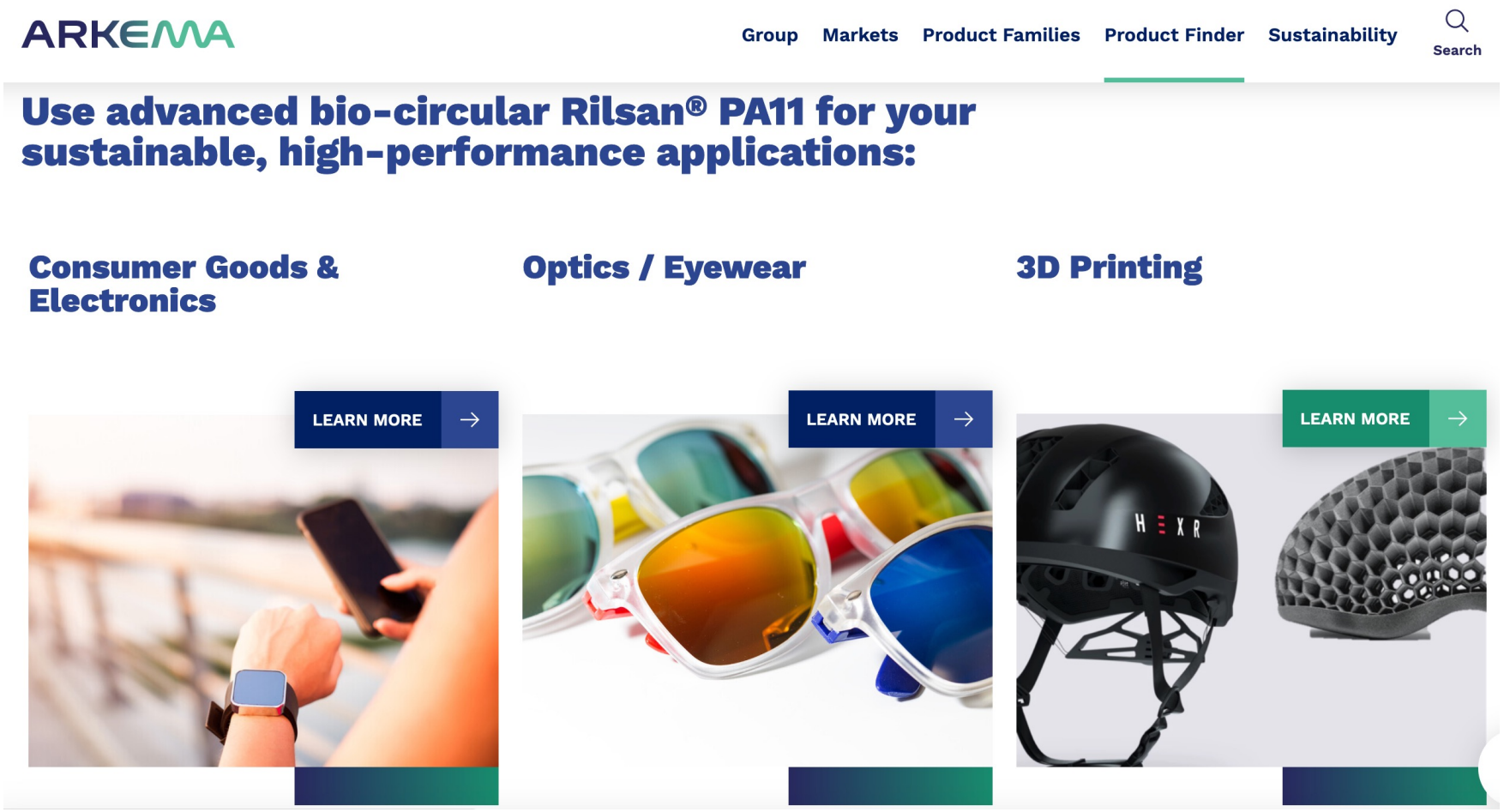
structural approach

- ethane-rich natural gas (USA)
- naphtha from the fractional distillation of petroleum (Europe) by steam cracking.

Structural approach

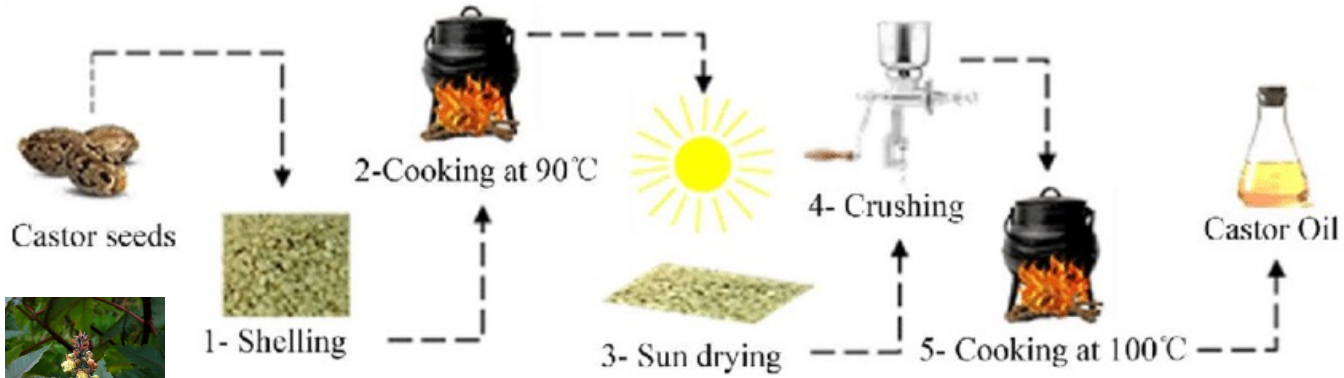


Examples: Bio-sourced polymers – Rilsan

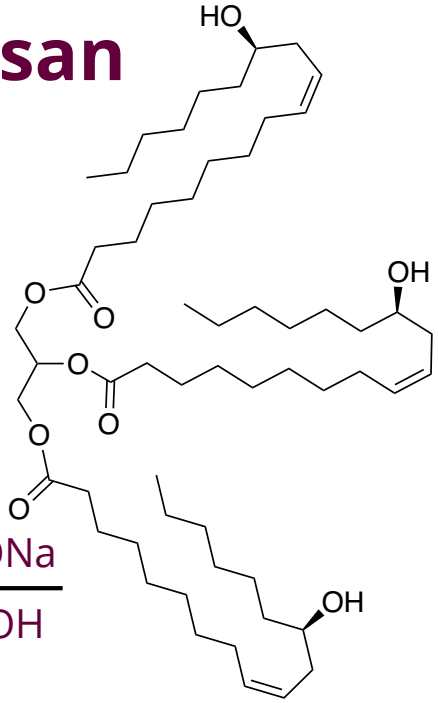


https://www.arkema.com/global/en/products/product-finder/product/technicalpolymers/rilsan-family-products/rilsan-pa11/

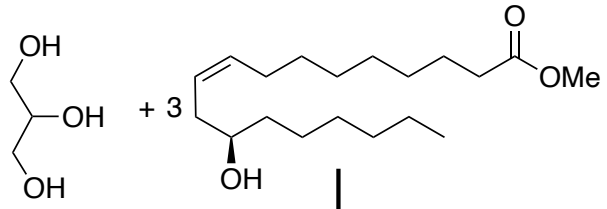
Examples: Bio-sourced polymers – Rilsan



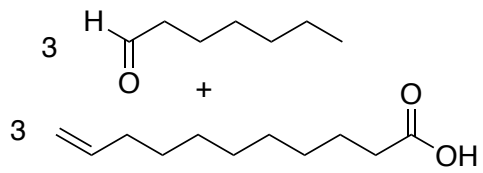
ricinus



MeONa
MeOH

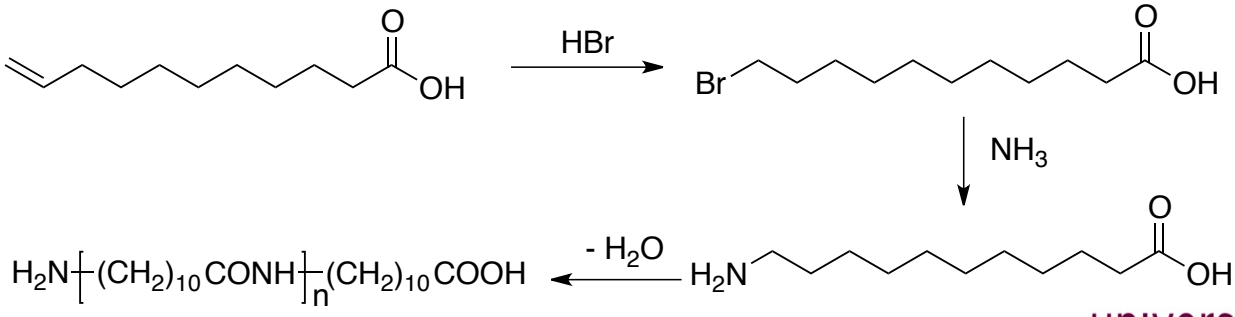


steam cracking



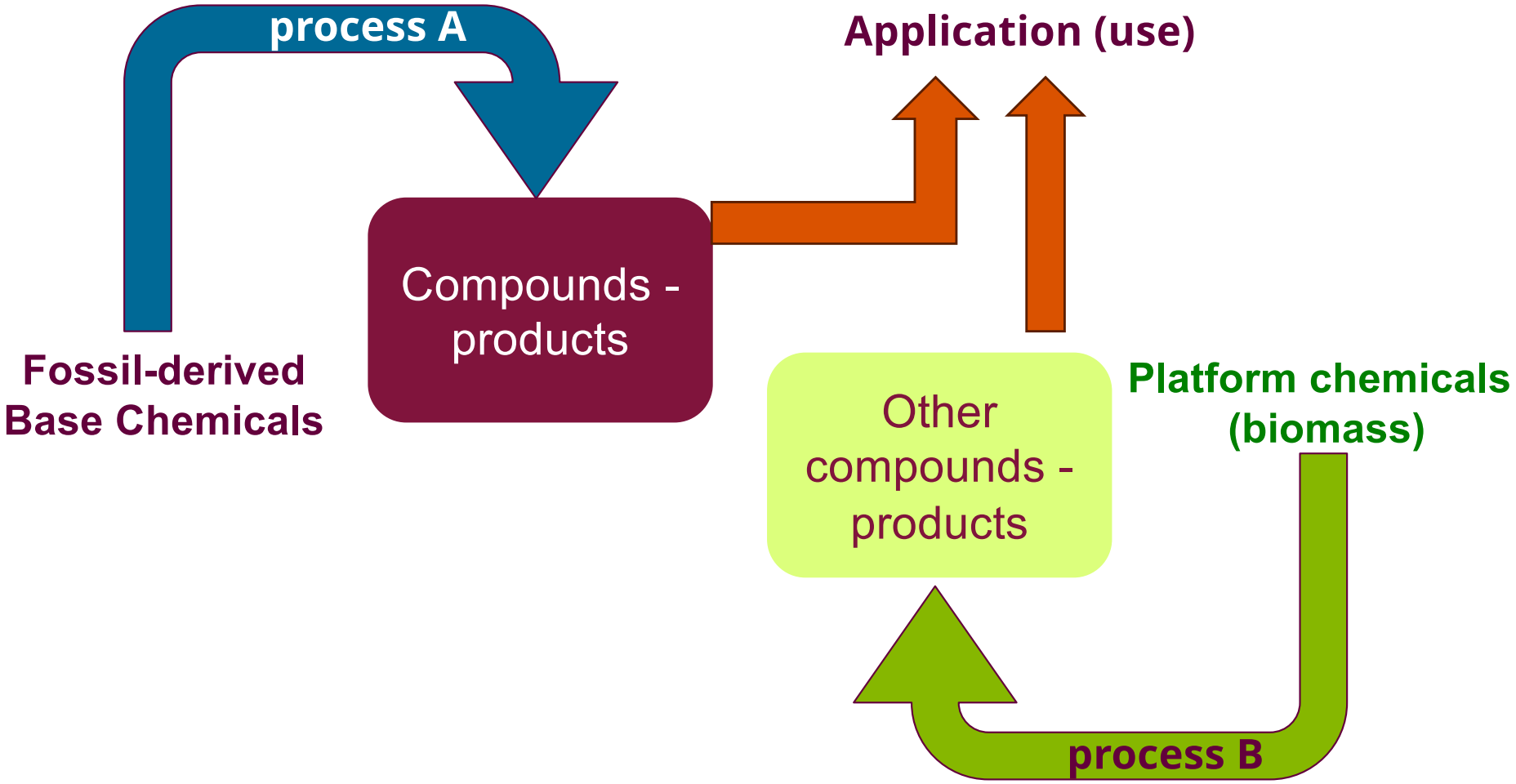
Esterol
(used as a lubricant additive)

functional approach
(application approach)



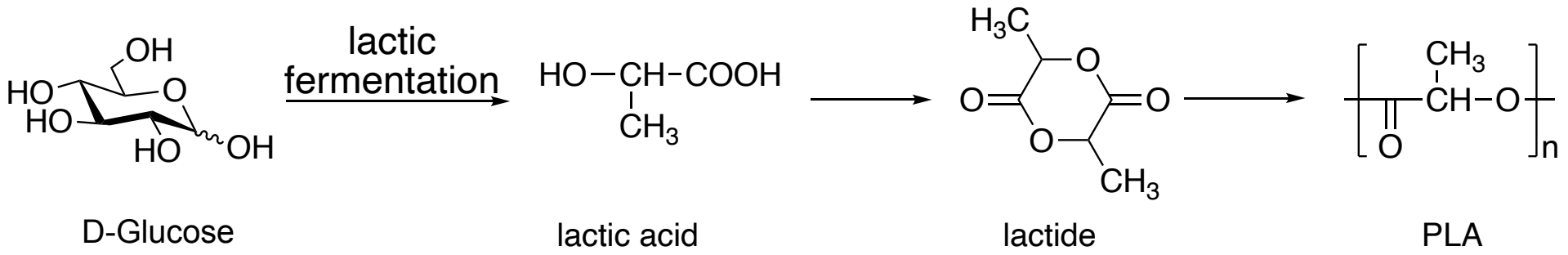
Rilsan 11

Functional approach (application approach)



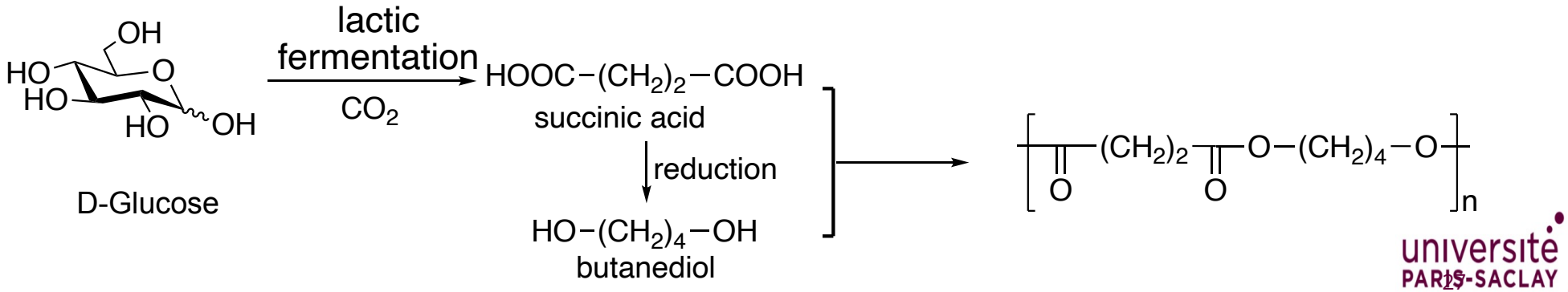
Bio-sourced polymers – other examples

polylactic acid (PLA)

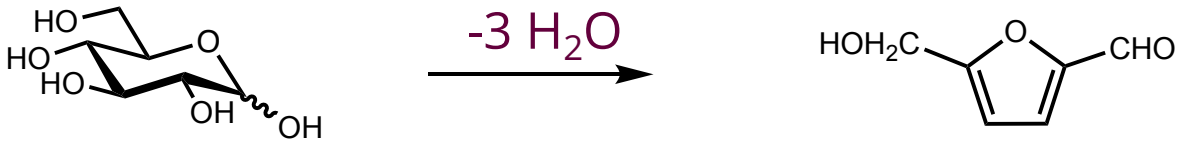


polyhydroxyalkanoates (PHA)

poly(butylene succinate) (PBS)



5-HMF: One of the most intensively studied biomass-derived molecules of the past decade

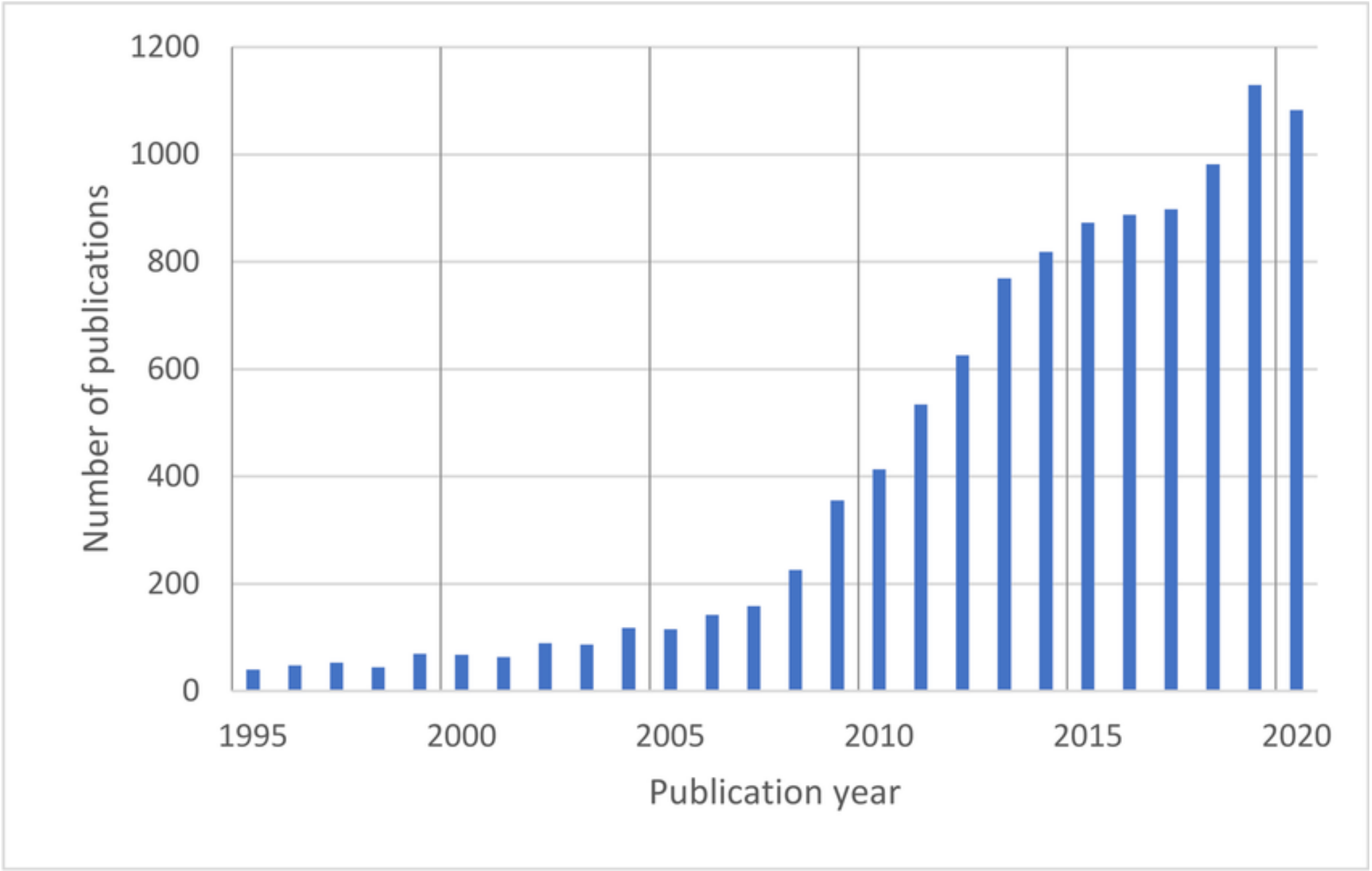


D-glucose
$C_6H_{12}O_6$

5-Hydroxymethylfurfural (HMF)
$C_6H_6O_3$

F. A. Kucherov, L. V. Romashov, K. I. Galkin, and V. P. Ananikov, *ACS Sustainable Chem. Eng.* 2018, 6, 7, 8064–8092

Publications-on-5-HMF-per-year-keyword-search-for-hydroxymethylfurfural-in-CAS



5-HMF:

Press release
November 13, 2023, Rueil-Malmaison

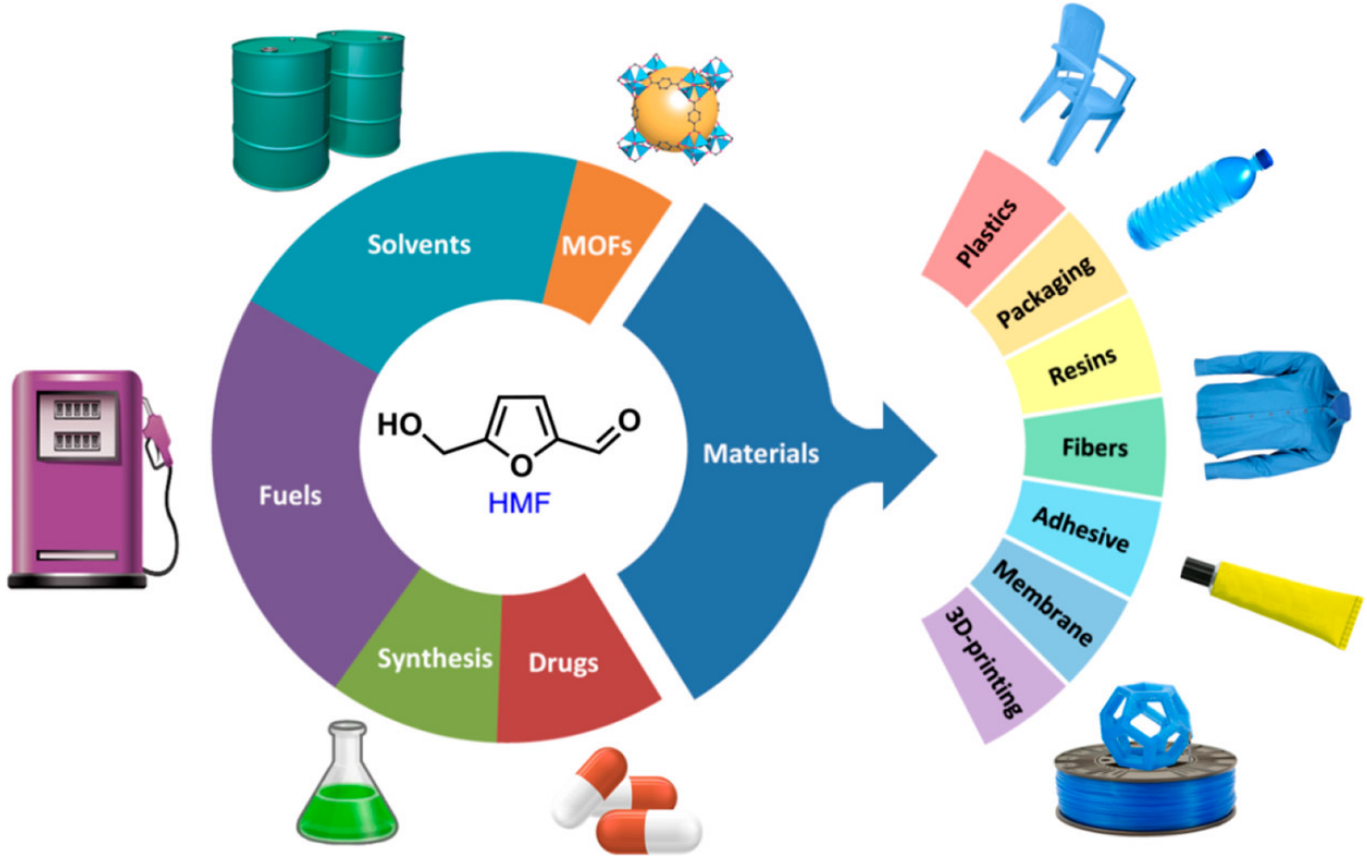
As part of a collaboration initiated at the end of 2021, IFP Energies nouvelles (IFPEN) and ResiCare, a Michelin Group entity, announce that they have co-developed a process for producing the molecule 5-hydroxymethylfurfural (5-HMF) from fructose, particularly used in the manufacture of bio-based resins. All the stages of industrial development have been completed, from tests on various scales to pre-FEED and FEED engineering studies for an industrial unit.

5-HMF, a biobased molecule with multiple applications

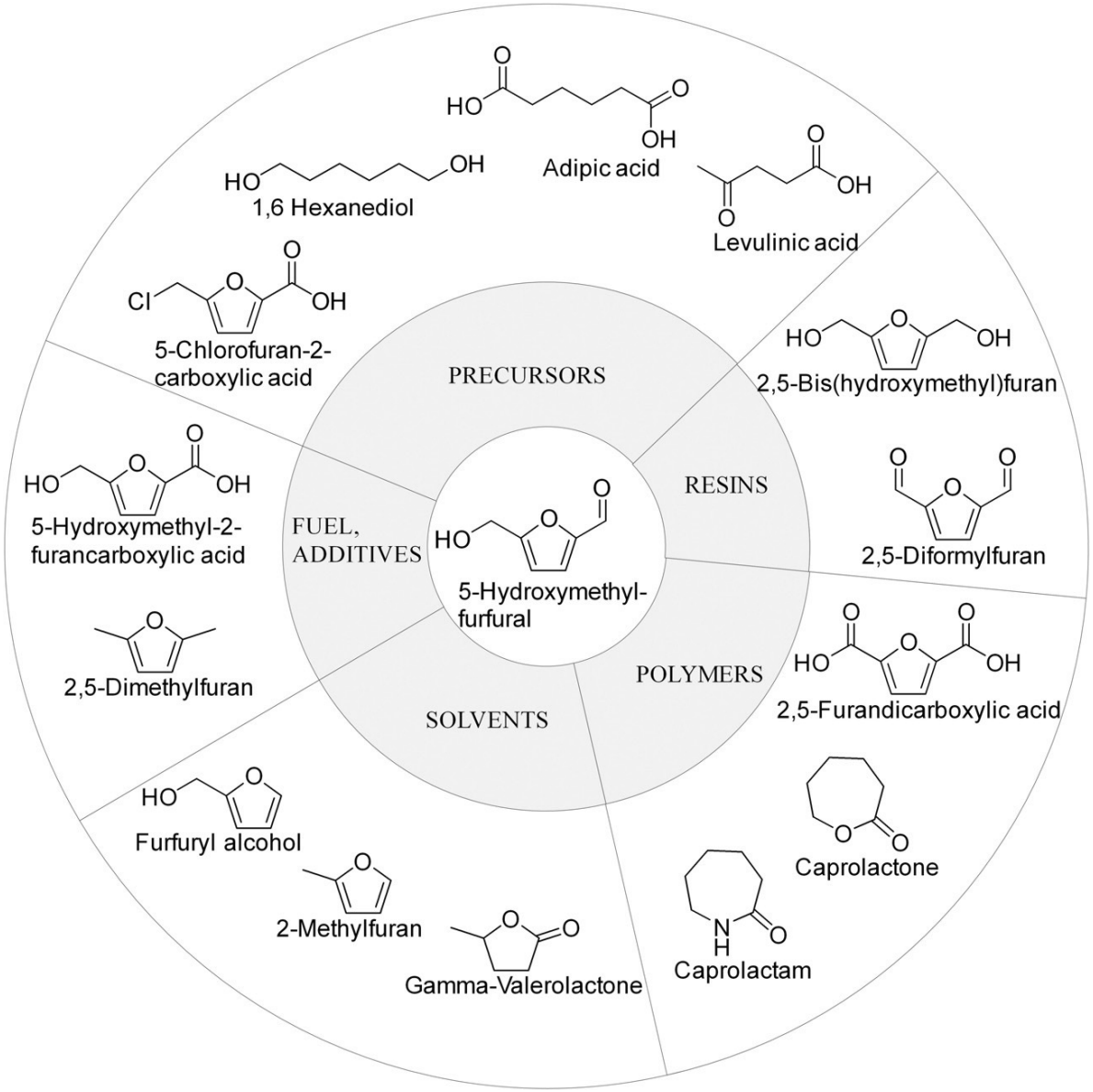
Following ten years of laboratory research on the conversion of fructose into a biosourced molecule, 5-HMF, IFPEN joined forces with ResiCare in 2021 to develop a process for producing 5-HMF on an industrial scale.

https://www.ifpenergiesnouvelles.com/article/ifp-energies-nouvelles-and-resicare-leaders-development-production-process-non-toxic-biobased-molecule-5-hmf

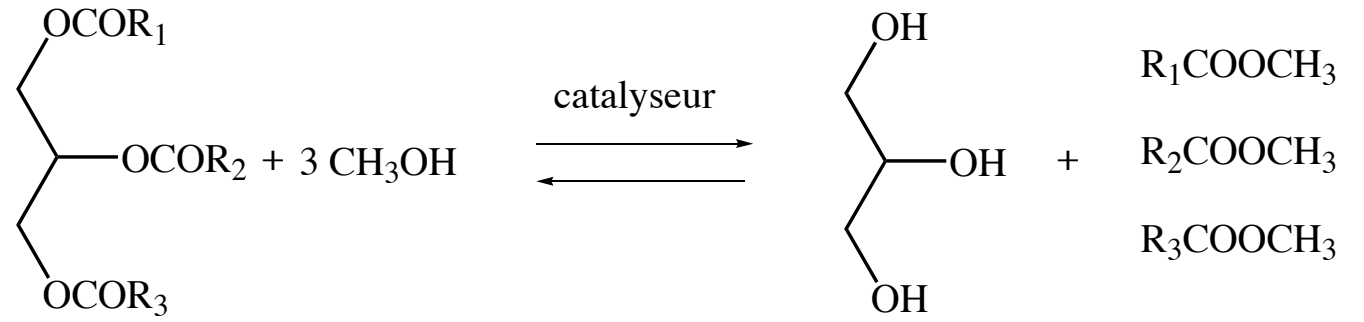
5-HMF: Potential applications



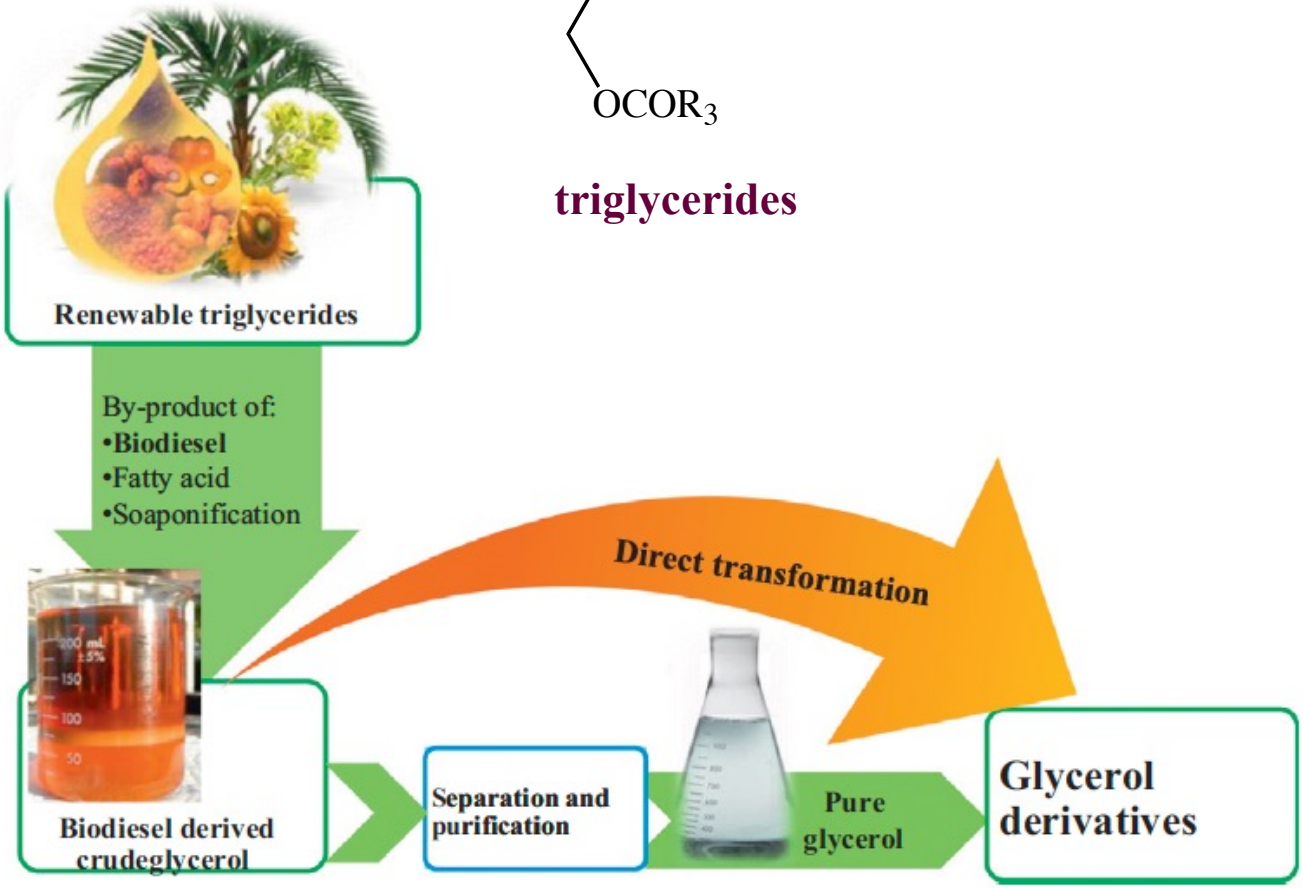
5-HMF: Furanic platform chemical



Glycerol



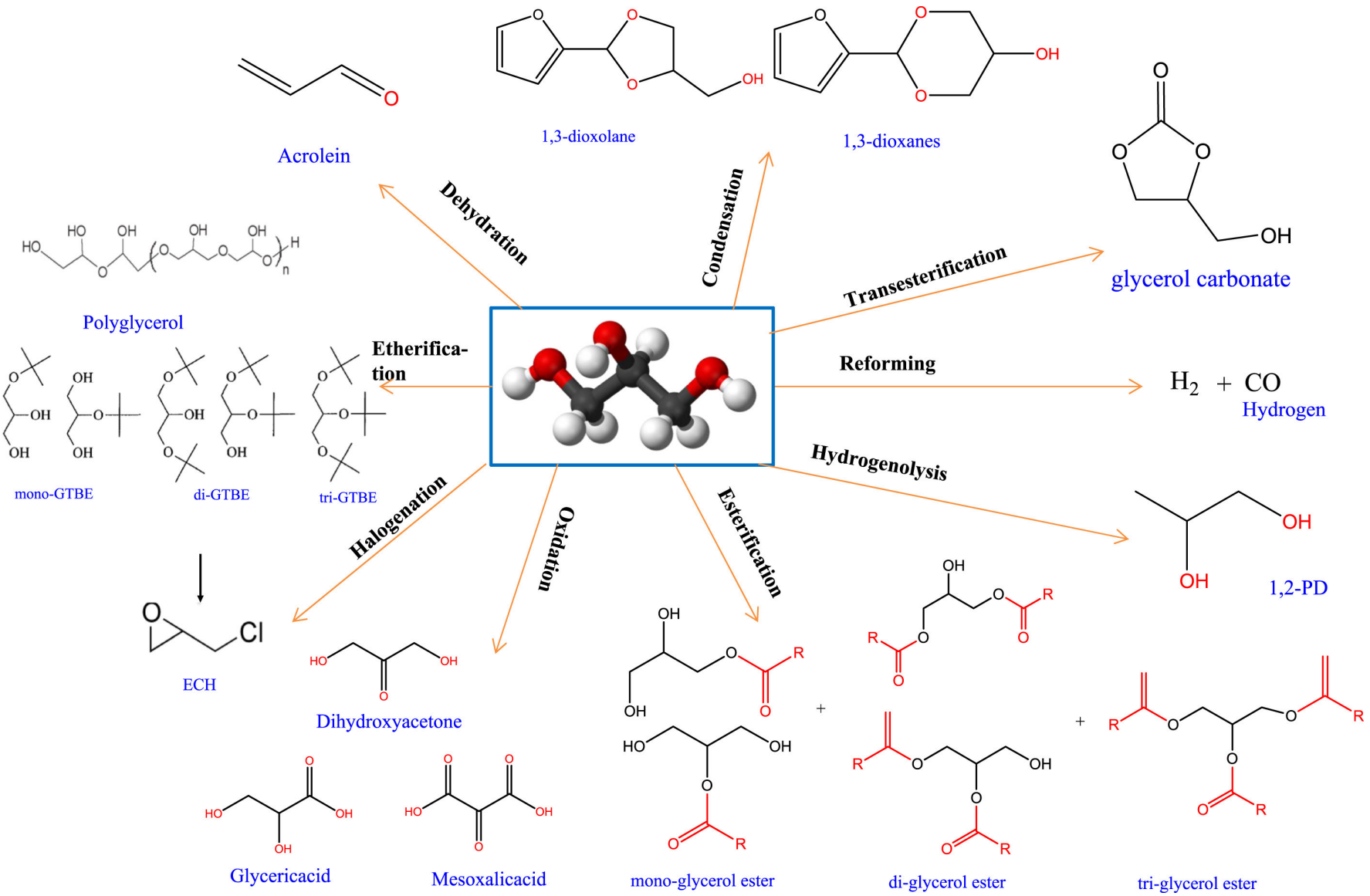
triglycerides **glycerol** **fatty esters**



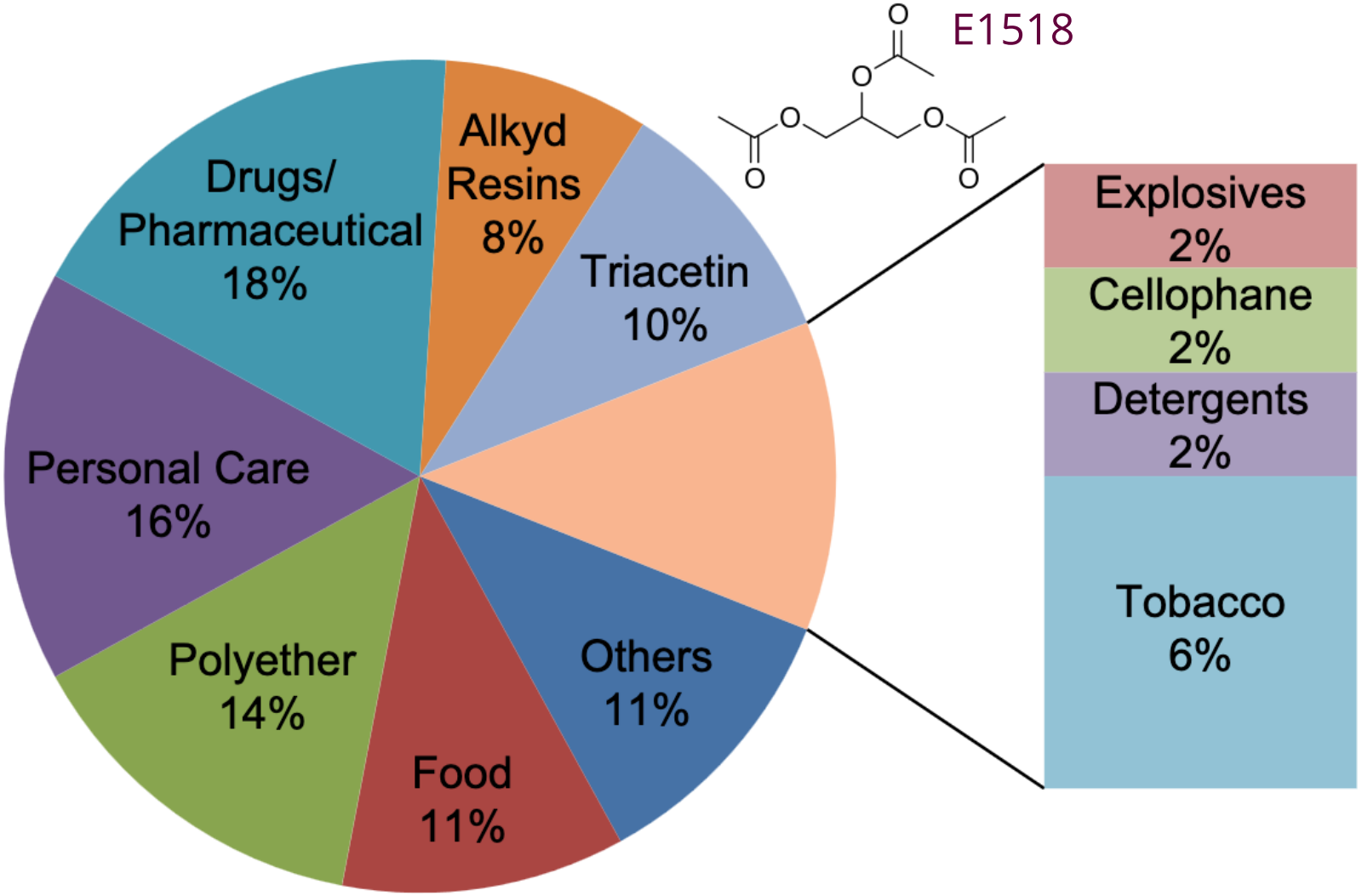
Recent Advances in Glycerol Catalytic Valorization: A Review. M. Checa, S. Nogales-Delgado, V. Montes, J. M. Encinar. Catalysts 2020, 10, 1279

Conversion of crude and pure glycerol into derivatives: A feasibility evaluation
P. S. Kong, M. K. Aroua , W. M. A.W. Daud. Renewable and Sustainable Energy Reviews 63 (2016) 533–555

Glycerol platform chemicals

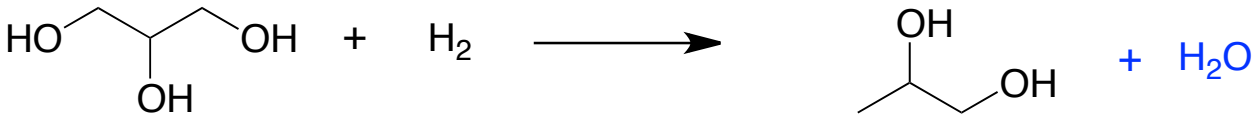


Glycerol industrial applications



Tan, H., Abdul Aziz, A., & Aroua, M. (2013). Glycerol production and its applications as a raw material: A review. *Renewable and Sustainable Energy Reviews*, *27*, 118-127.

Glycerol platform chemicals: 1,2-propanediol



Adkins catalyst: $Cu_2Cr_2O_5$
(copper chromite)

Antifreeze, additives in pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants and paints

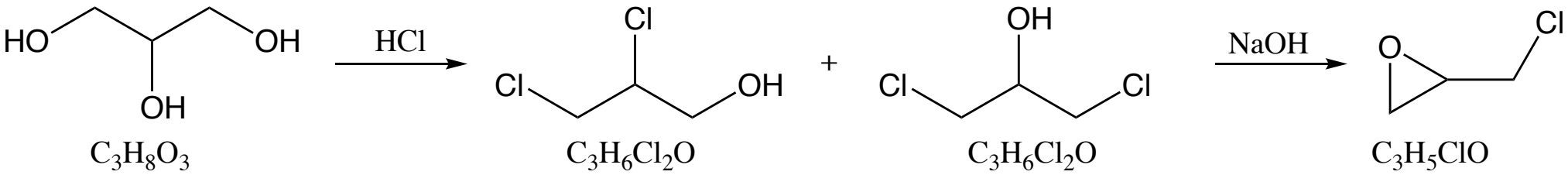
Oleon, (oleochemical company), collaborated with BASF to establish a manufacturing plant to produce bio-1,2-PD from glycerol in Ertvelde, Belgium, in 2012. Oleon is the first company to produce bio- 1,2-PD commercial worldwide.

oleon
a natural chemistry

BASF
We create chemistry

Glycerol platform chemicals: épichlorhydrine

A chemical intermediate mainly used to manufacture epoxy resins, elastomers, polyamide-epichlorohydrin resins, polyols and various glycidyl derivatives.



MOMENTIVE performance materials

SOLVAY asking more from chemistry®

海麗集團 HAILI GROUP

Formosa Plastics™

NAMA CHEMICALS

The Dow Chemical (USA)
Momentive Performance Materials Holdings LLC (USA)
Solvay Chemicals SA (Belgium)
Shandong Haili Chemical Industry Co. Ltd (China)
NAMA Chemicals (Saudi Arabia)
Spolchemie A.S. (Czech Republic)
Formosa Plastics Group (Taiwan)

SPOLCHEMIE

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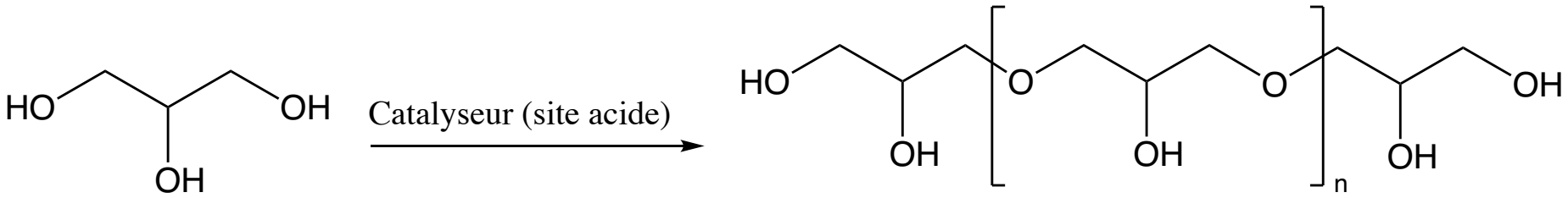
Glycerol platform chemicals: polyglycérols

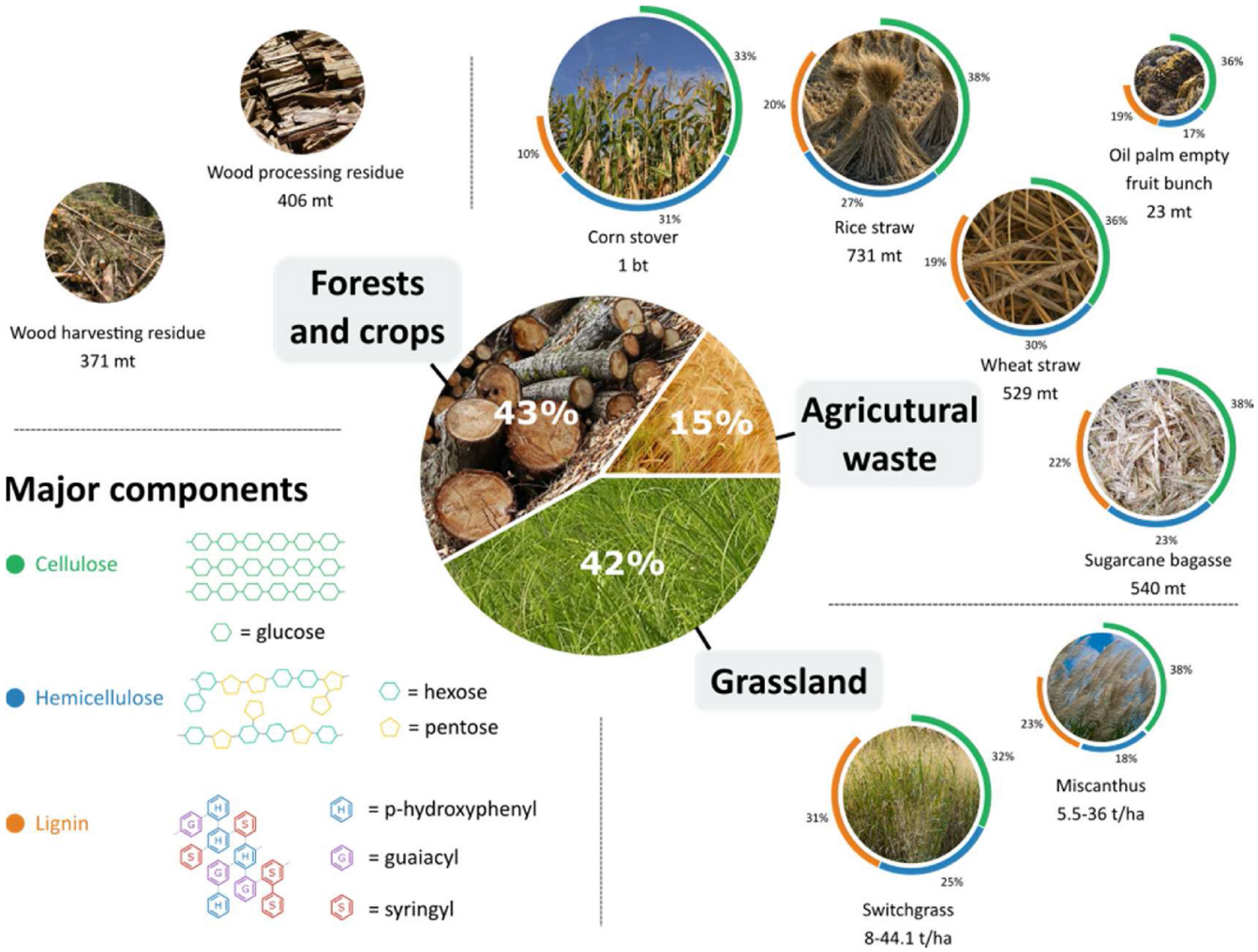


Nonionic surfactants widely used in cosmetics, additives, lubricants, biomedical and drug delivery systems.

Solvay (Belgium)
Sakamoto (Japan)

SOLVAY
asking more from chemistry®

Lignocellulosic biomass (180-billion-ton annual production rate) a promising feedstock for commodity chemicals and transportation fuels for a low carbon future

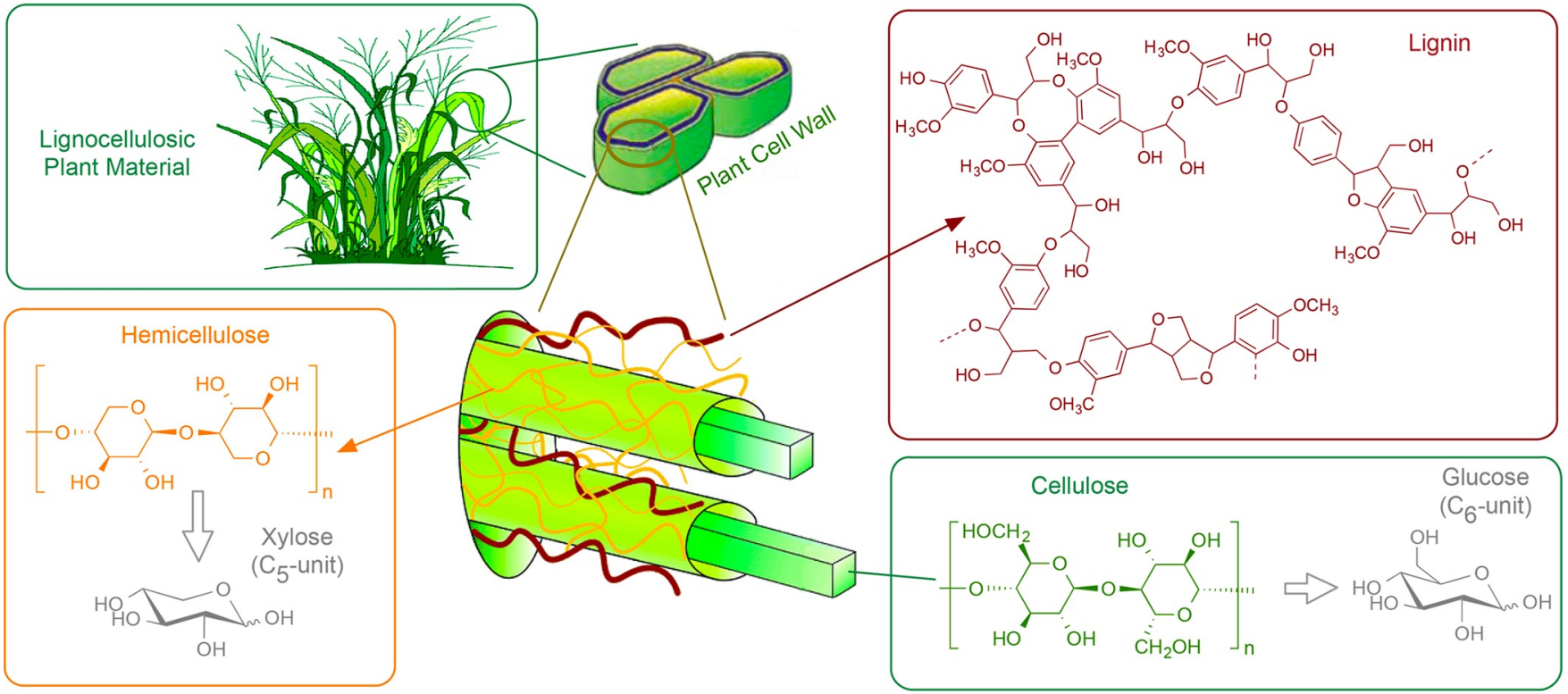


8.2 billion tons are utilized

Average concentration of cellulose, hemicellulose, lignin, and annual yield of some lignocellulosic biomass

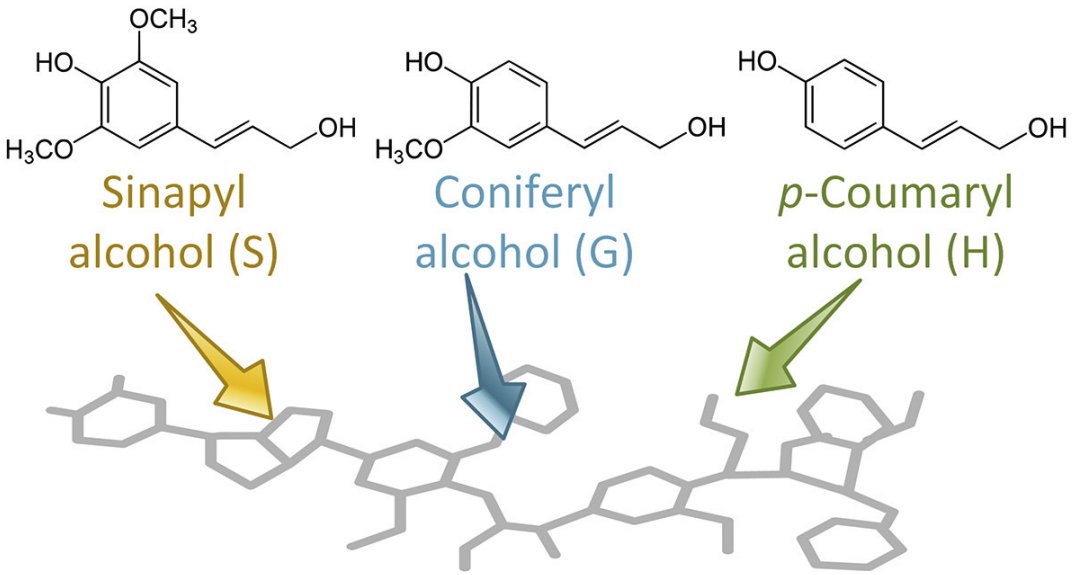
Catalytic conversion of lignocellulosic biomass into chemicals and fuels, W. Deng et al. *Green Energy Environ.*, **2023**, *8*, 10-114.

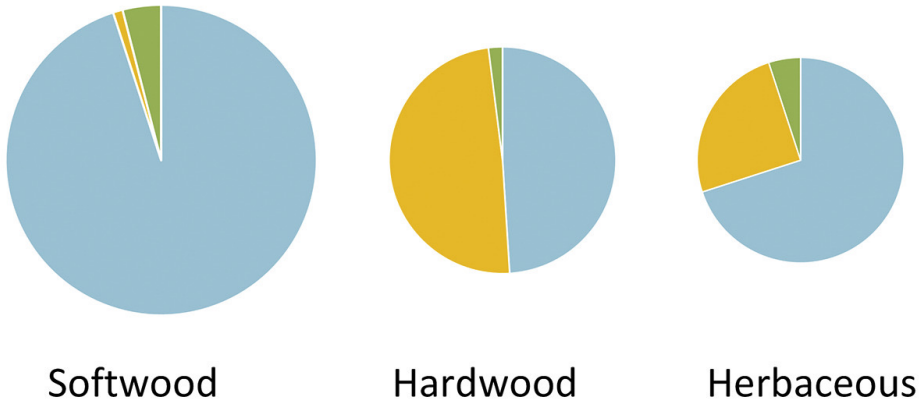
Schematic illustration of lignocellulose



L.T. Mika et al. *Chem. Rev.* 2018, 118, 2, 505–613

Lignin composition

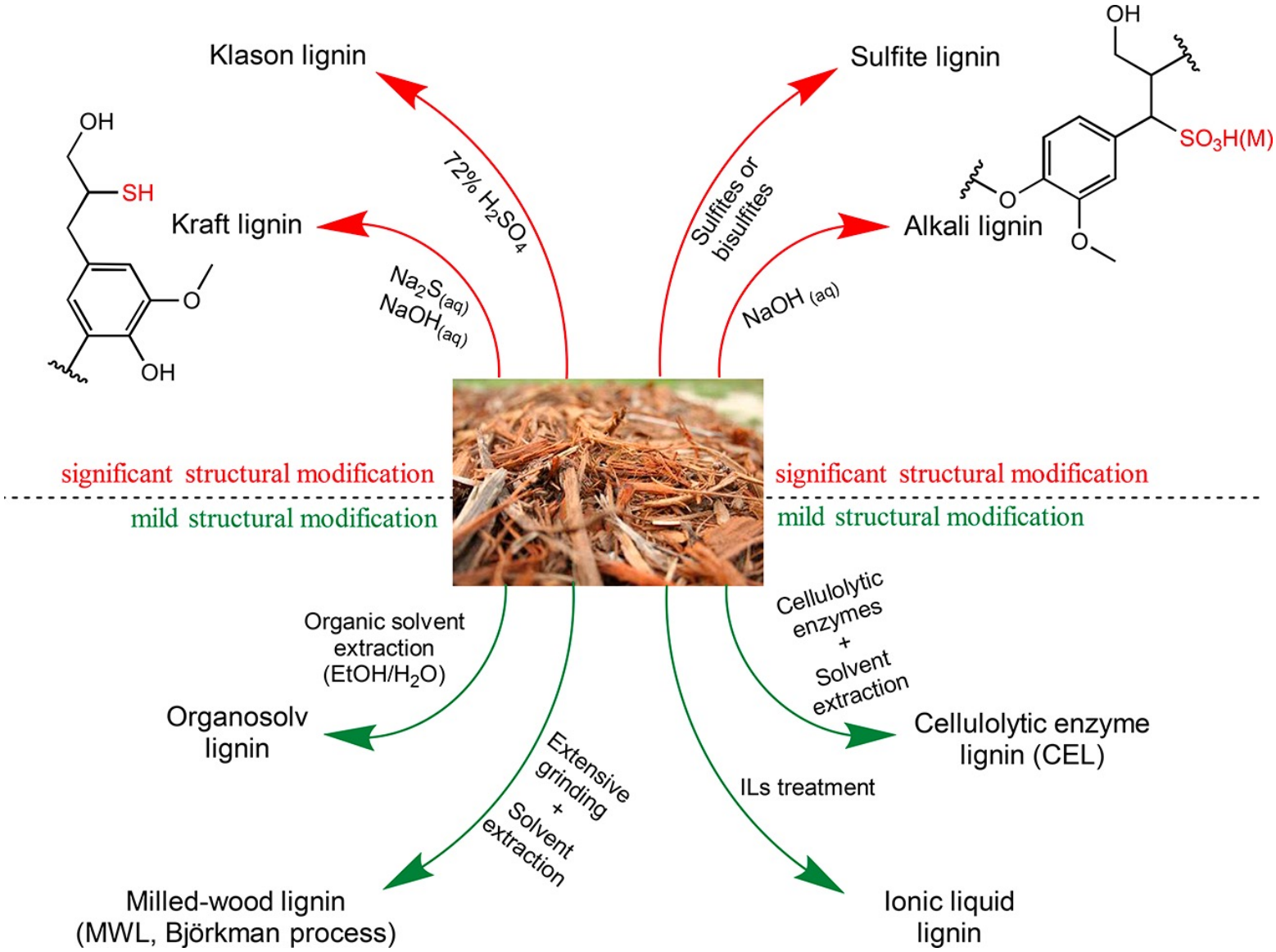




Plant Type	*p*-Coumaryl Alcohol (%)	Coniferyl Alcohol (%)	Sinapyl Alcohol (%)
Coniferous; softwoods	<5 [a]	>95	0 [b]
Eudicotyledonous; hardwoods	0–8	25–50	45–75
Monocotyledonous; grasses	5–35	35–80	20–55

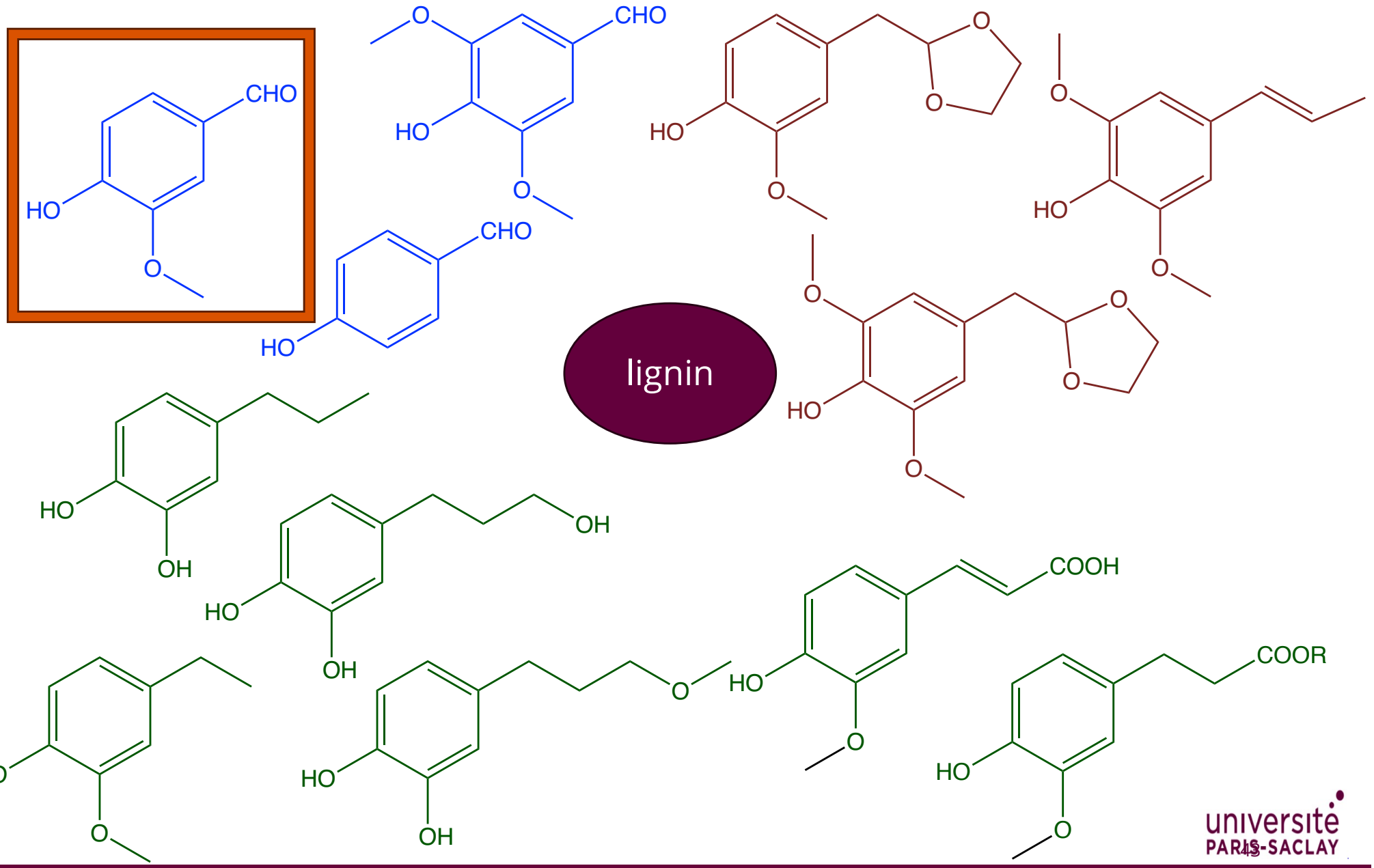
J. Becker, C. Wittmann Biotechnology Advances 37 (2019) 107360

Different structures depending on the procedures for isolation of lignin from lignocellulose

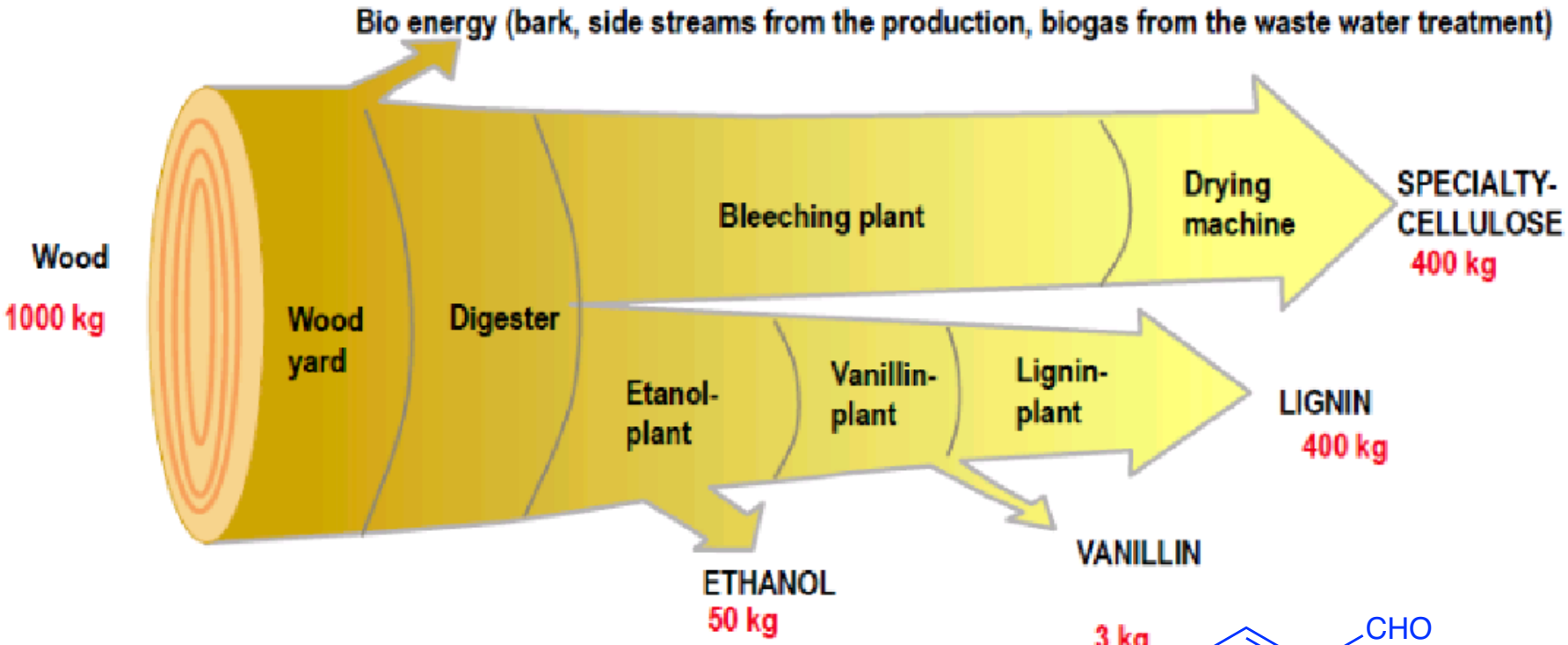


Sun et al. *Chem. Rev.* 2018, 118, 2, 614–678

Lignin-derived monomers



Exemple : Borregaard biorefinerie (Norway)

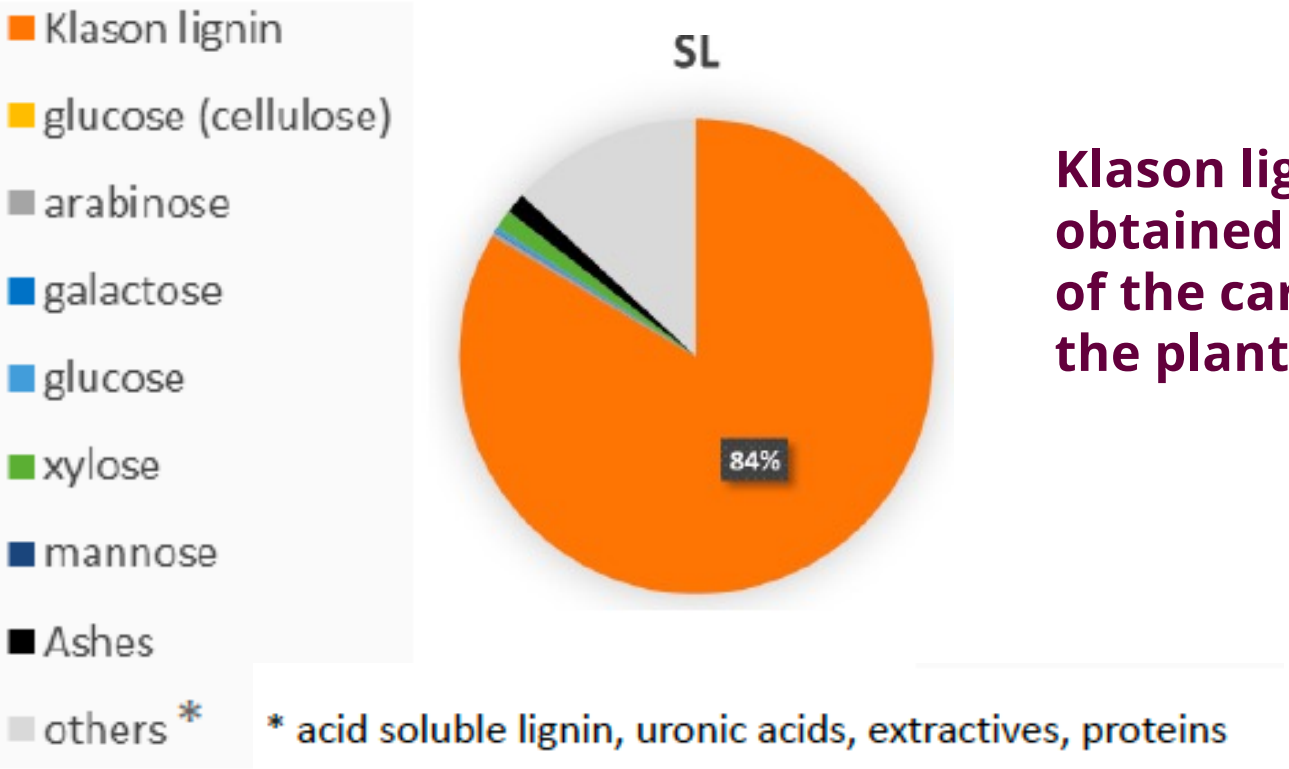


15% of the world's production of vanillin is produced from lignosulfonates

Borregaard

In our research team

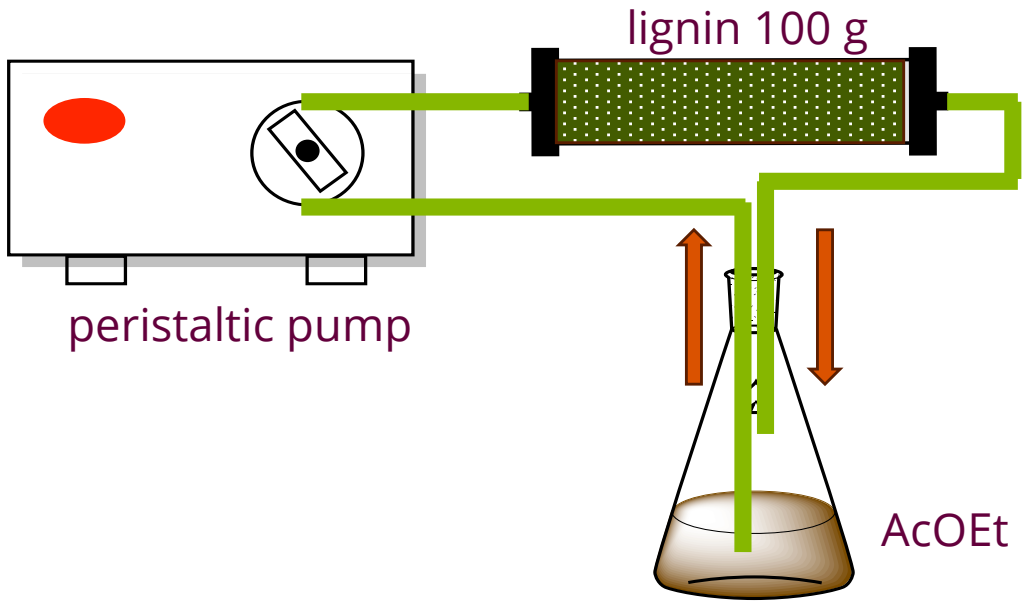
SL=grass soda lignin (Protobind 1000, Green value LLC)



Klason lignin is the residue obtained after acid hydrolysis of the carbohydrate portion of the plant

Collaboration : S. Baumberger, AgroParisTech

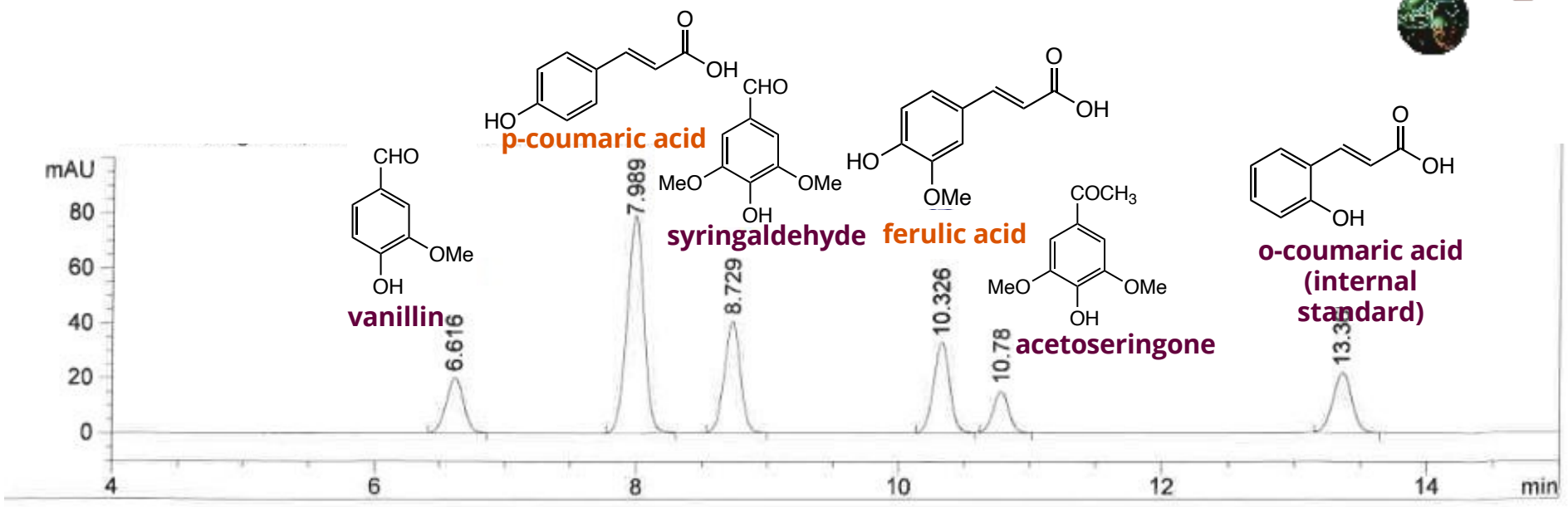
In our research team



Continuous extraction of phenolic compounds

Collaboration : S. Baumberger, AgroParisTech

HPLC analysis

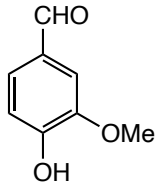


C18 (50x2.1 mm, 2,7 µm); ACN/H_2O, HCO_2H 1 ‰ (5:95➡20:80 16 min); 250 µL/min; 32 °C; 230 nm

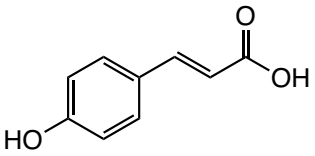
vanillin	6.5 g
p-coumaric acid	2.8 g
syringaldehyde	7.7 g
ferulic acid	1.8 g
acetoseringone	11.5 g

Collaboration : S. Baumberger, AgroParisTech

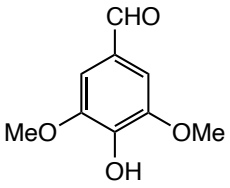
Functionalization of the hydroxycinnamic acids



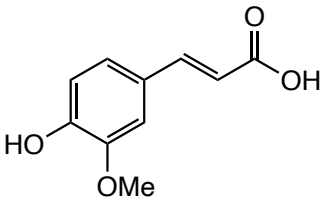
vanillin



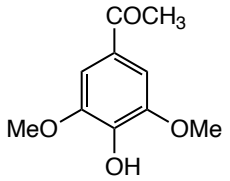
p-coumaric acid



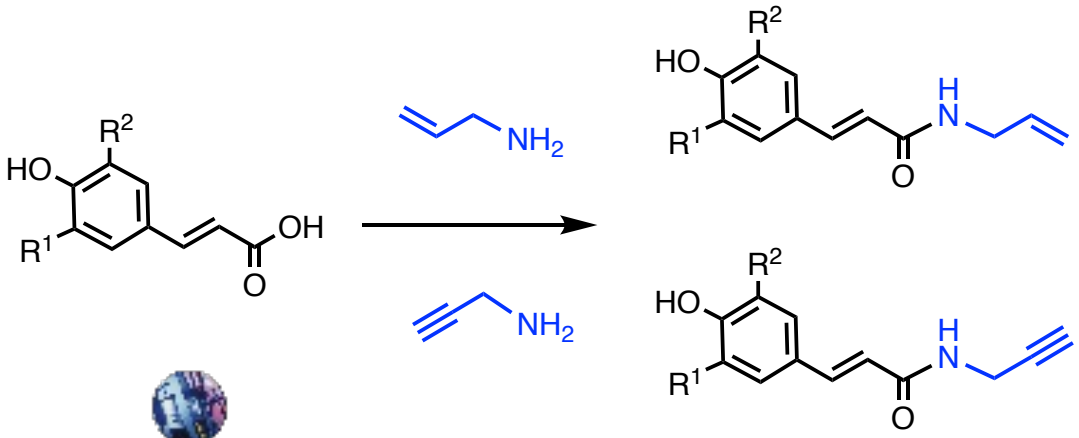
syringaldehyde

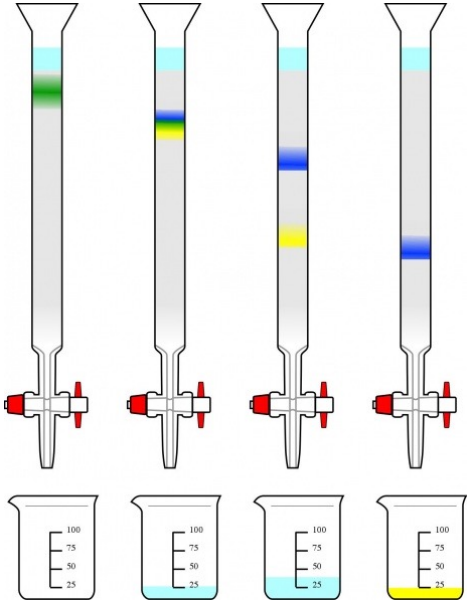


ferulic acid

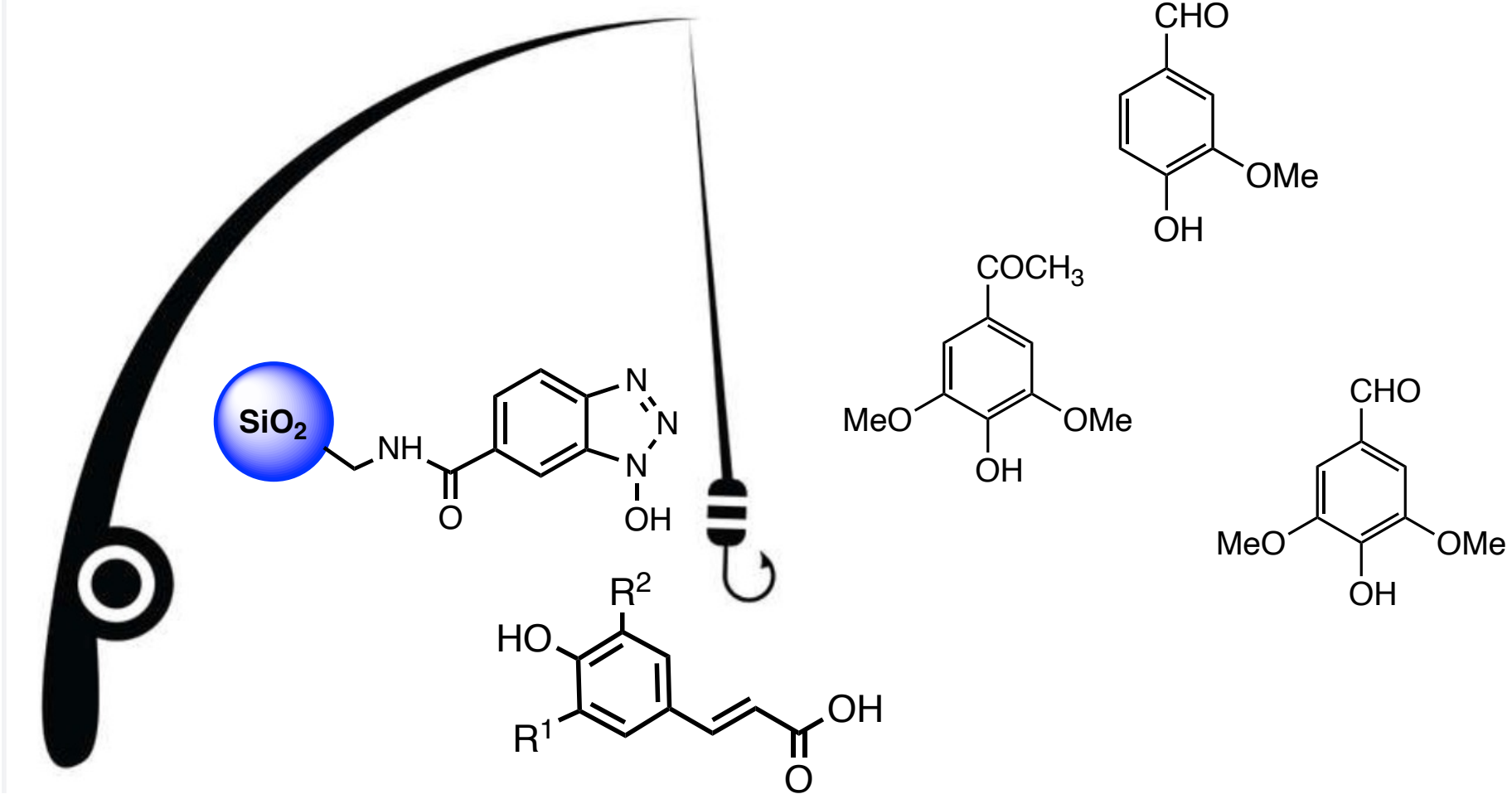


acetoseringone

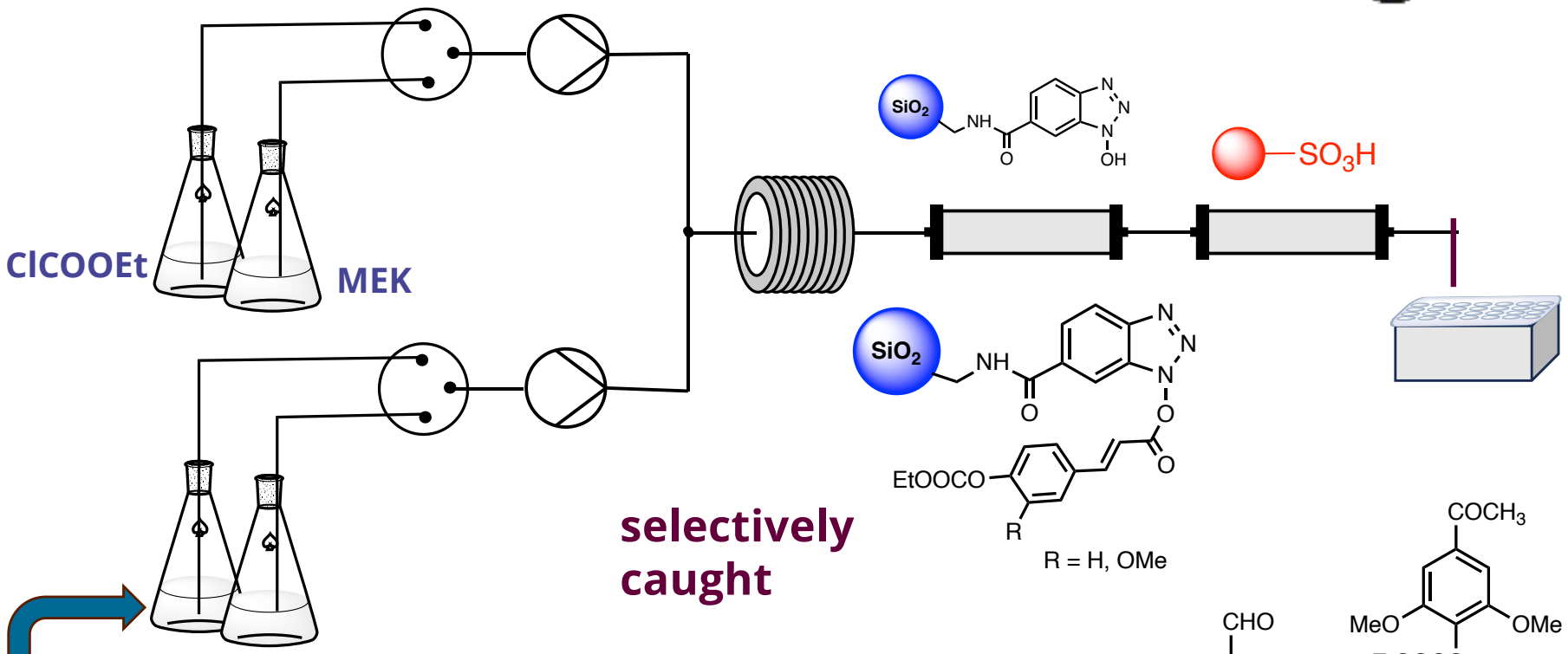




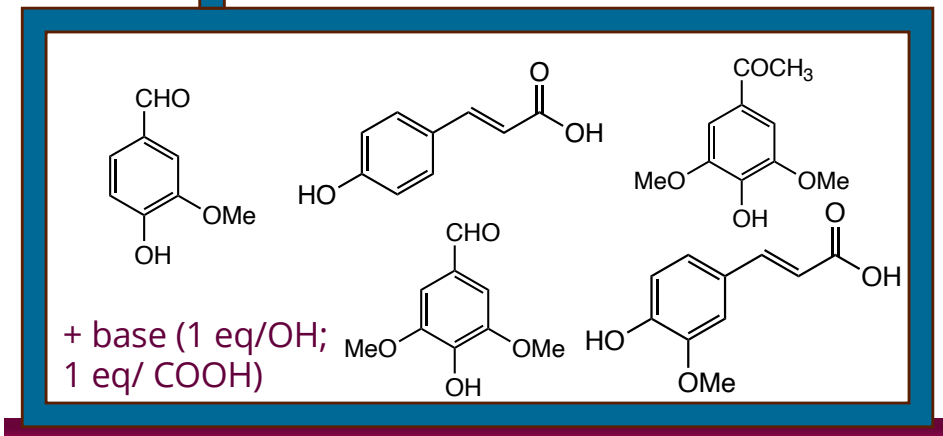
Collaboration : A. Marra, IBMM, Université Montpellier

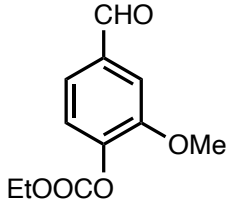

SiO2
NH
O
N
N
N
OH
R2
HO
R1
OH
O
CHO
OMe
OH
COCH3
MeO
OMe
OH
CHO
MeO
OMe
OH

Continuous flow synthesis

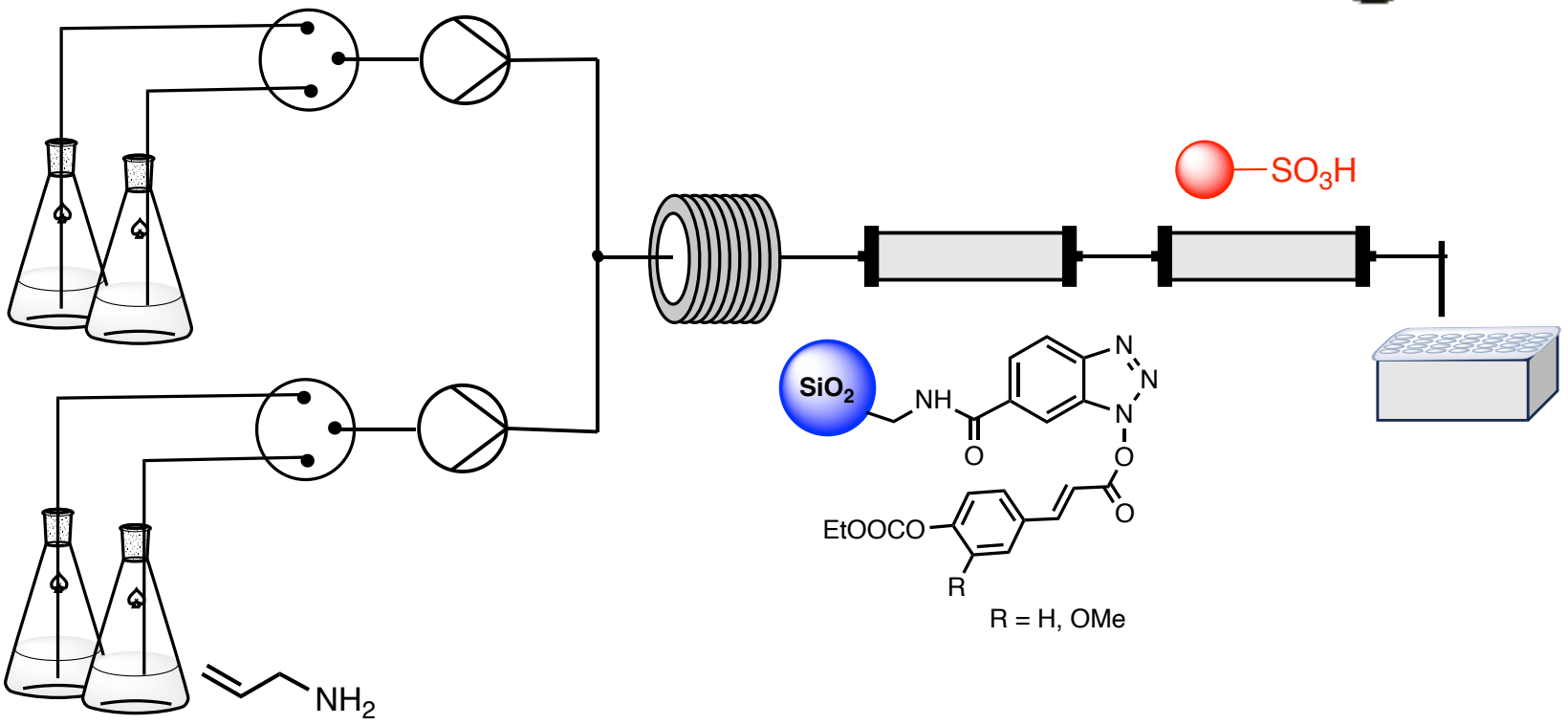


selectively caught

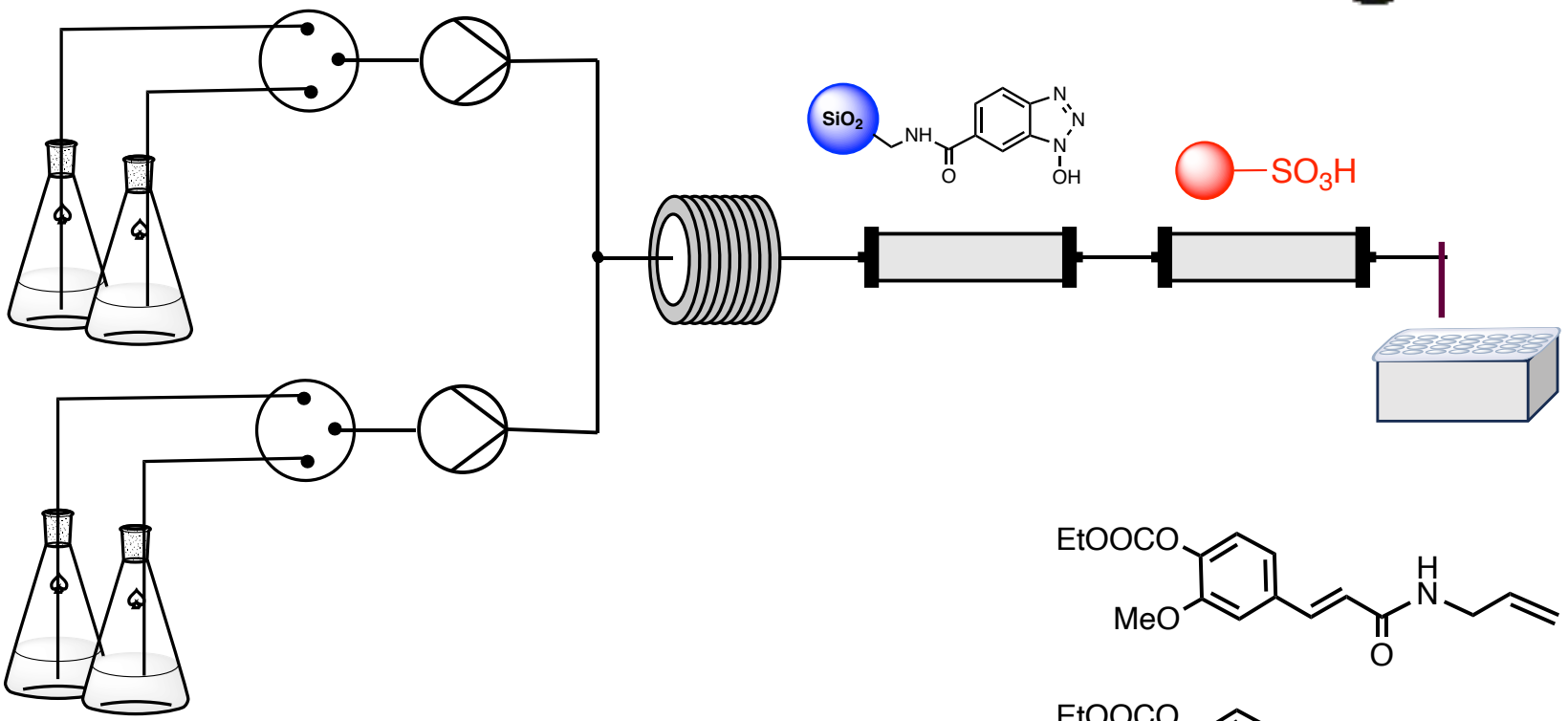


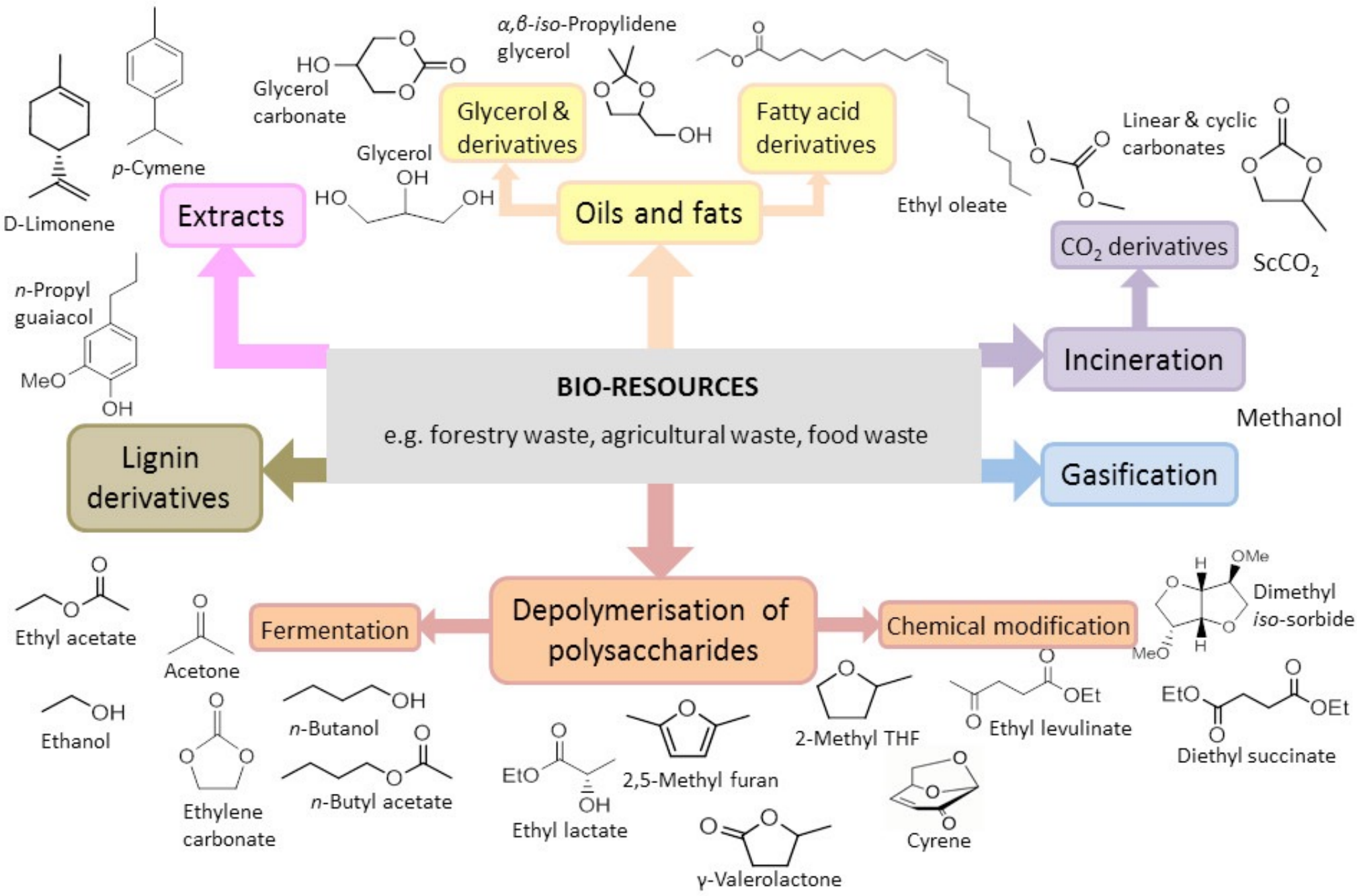


Continuous flow synthesis

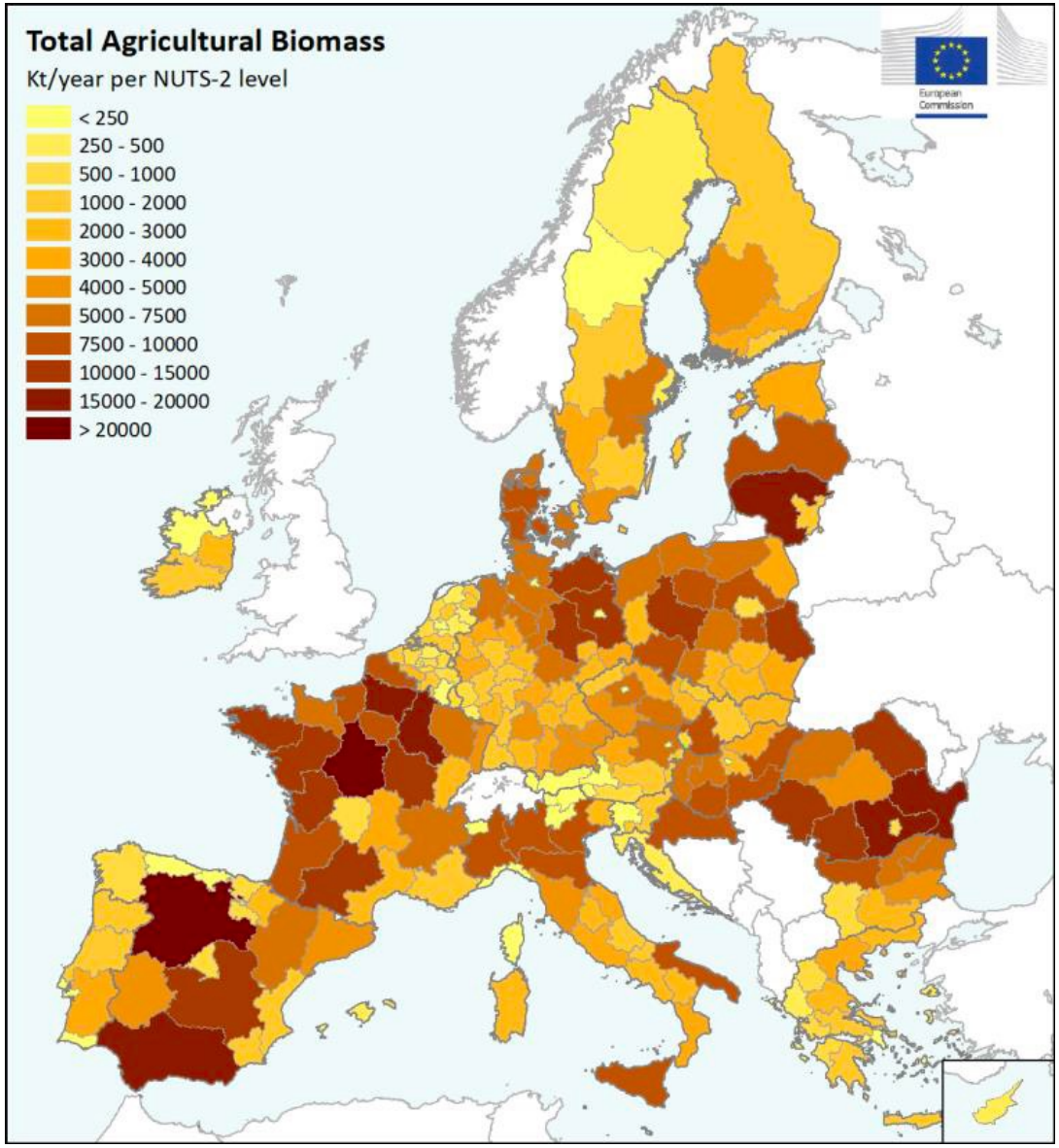


Continuous flow synthesis




BIO-RESOURCES
e.g. forestry waste, agricultural waste, food waste
Extracts
Oils and fats
Glycerol & derivatives
Fatty acid derivatives
Lignin derivatives
Incineration
CO2 derivatives
Gasification
Depolymerisation of polysaccharides
Fermentation
Chemical modification
D-Limonene
p-Cymene
Glycerol carbonate
α,β-iso-Propylidene glycerol
Glycerol
Ethyl oleate
Linear & cyclic carbonates
ScCO2
n-Propyl guaiacol
Methanol
Ethyl acetate
Acetone
Ethanol
n-Butanol
Ethylene carbonate
n-Butyl acetate
Ethyl lactate
2,5-Methyl furan
γ-Valerolactone
2-Methyl THF
Cyrene
Ethyl levulinate
Dimethyl iso-sorbide
Diethyl succinate

Alternative feedstocks - renewable feedstocks



Distribution of agricultural biomass production (in Kt dry matter per year) across the EU (NUTS-2 regions) for the reference period 2016-2020
Source: JRC 2022

Approximately 70% of the agricultural biomass is produced in

- France,
- Germany,
- Italy,
- Poland,
- Spain,
- Romania.

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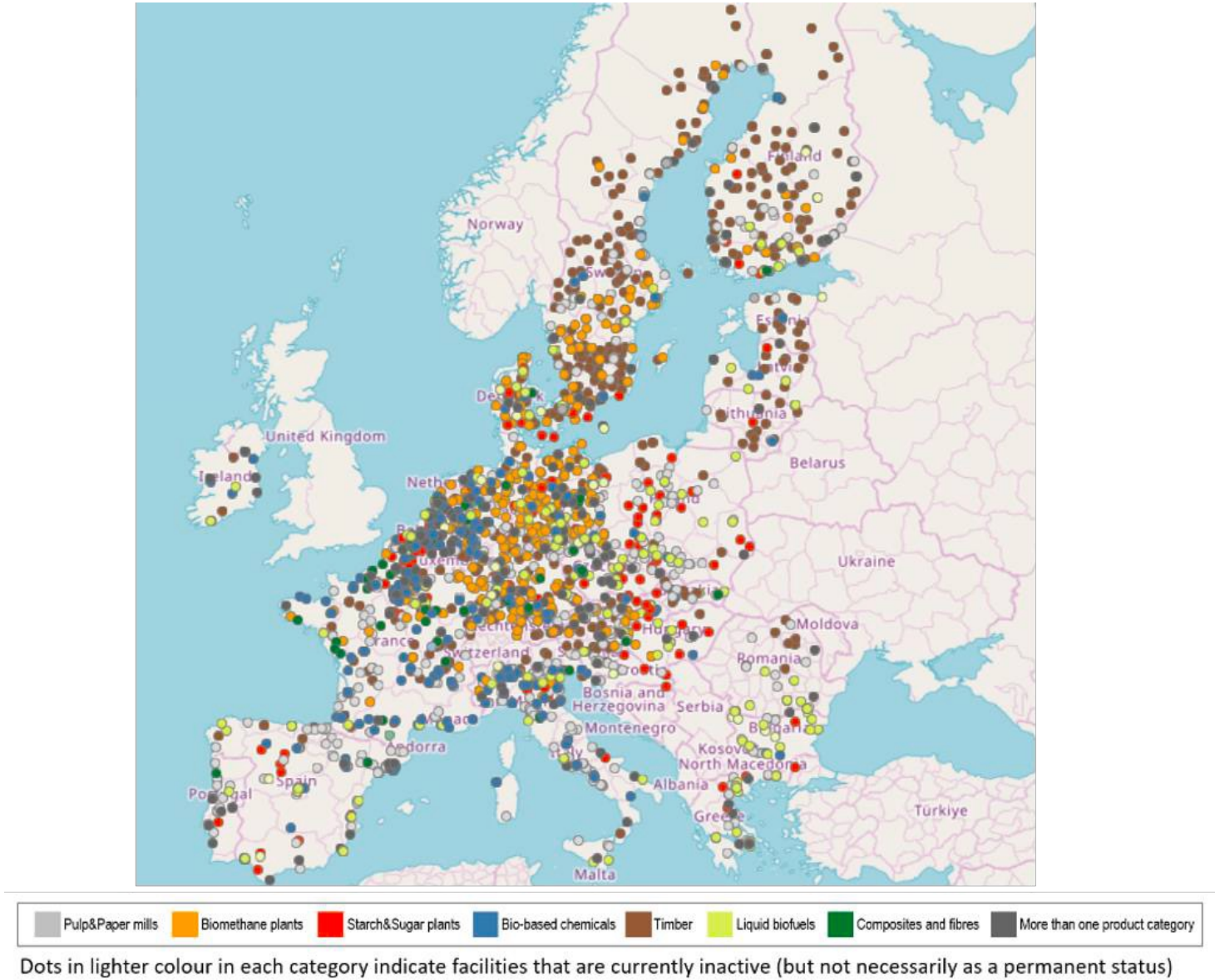
Territorial distribution of bio-based industries and biorefineries in the EU-27.



Parisi, Claudia; Baldoni, Edoardo; M'barek, Robert (2020): Bio-based industry and biorefineries. European Commission, Joint Research Centre (JRC) [Dataset] PID: http://data.europa.eu/89h/ee438b10-7723-4435-9f5e-806ab63faf37

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