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

Renewable and bio-sourced chemistry

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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

Anastas and Warner

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

Sustainable Chemistry

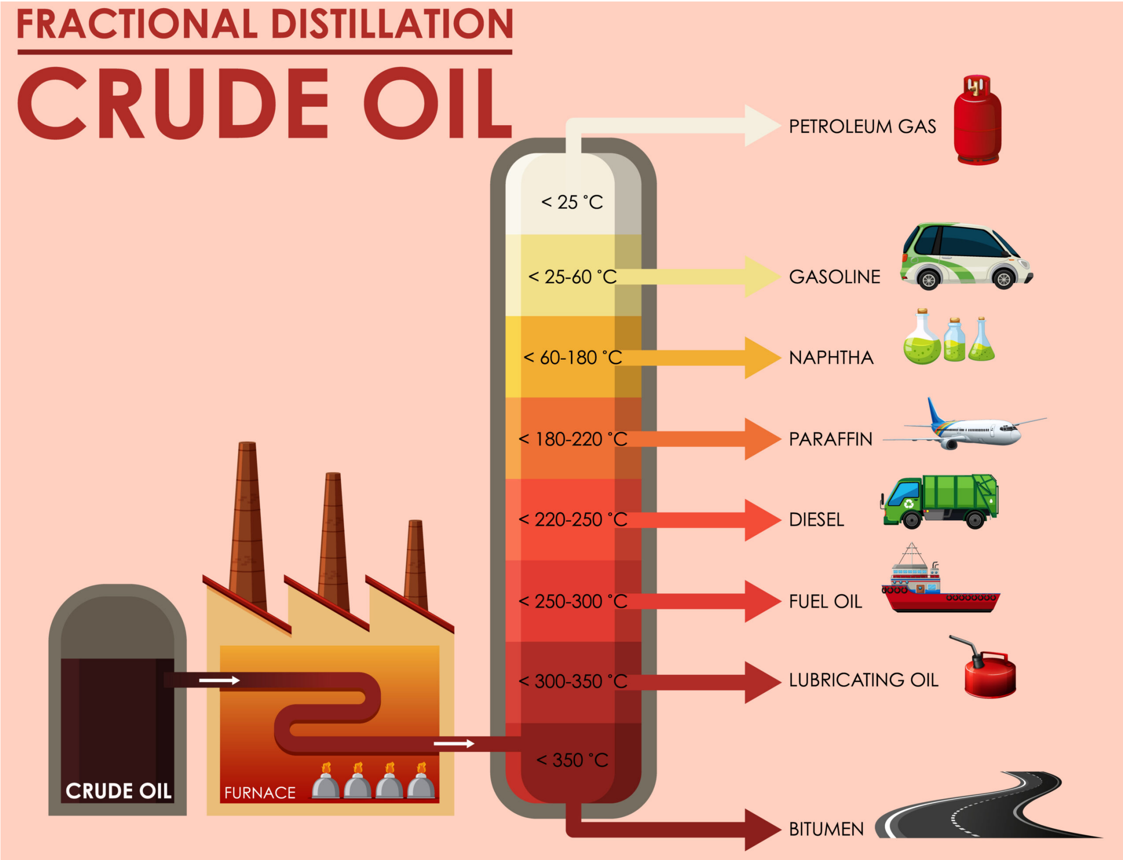
A scientific concept that seeks to improve the efficiency with which natural resources are used to meet human needs for chemical products and services.

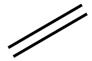
OECD

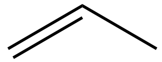
Organisation for Economic Cooperation and Development

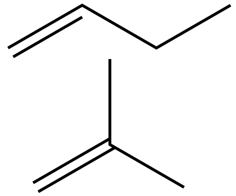
Fossil-derived Base Chemicals

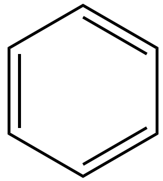
Feedstocks: Crude Oil, Natural Gas, Coal

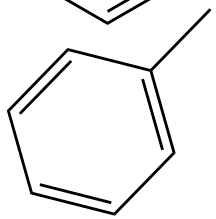


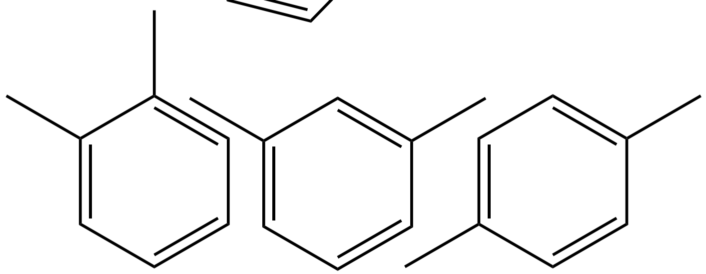

ethene


propene


butenes


benzene


toluene


xylene

Fossil-derived Base Chemicals – Bulk chemicals - Products

Naphta

catalytic/steam reforming

ethene
propene
butenes
benzene
toluene
xylene

ethene oxide
1,2-dichloroethane
vinyl chloride
propene oxide
propan-2-ol
ethylbenzene
styrene
phenol
cyclohexane
aniline
toluene diisocyanate
terephthalic acid
(iso)phthalic acid
acetic acid
methyl methacrylate
formaldehyde

polybutadiene rubber
polyethene
polyethene oxide
anti-freeze
polyvinyl chloride
polypropene
nylon
dyes
styrene-butadiene rubber
polyurethanes
polyetheneterephthalate
adhesives
polyesters
propandiols
solvents
bisphenol A
polycarbonates
latex
paints

Example: styrene-butadiene rubber

Naphta

catalytic/steam reforming

ethene
propene
butenes
benzene
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xylene

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Example: styrene-butadiene rubber

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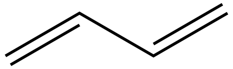
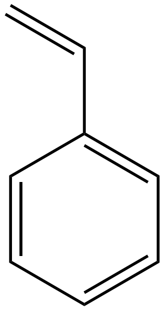
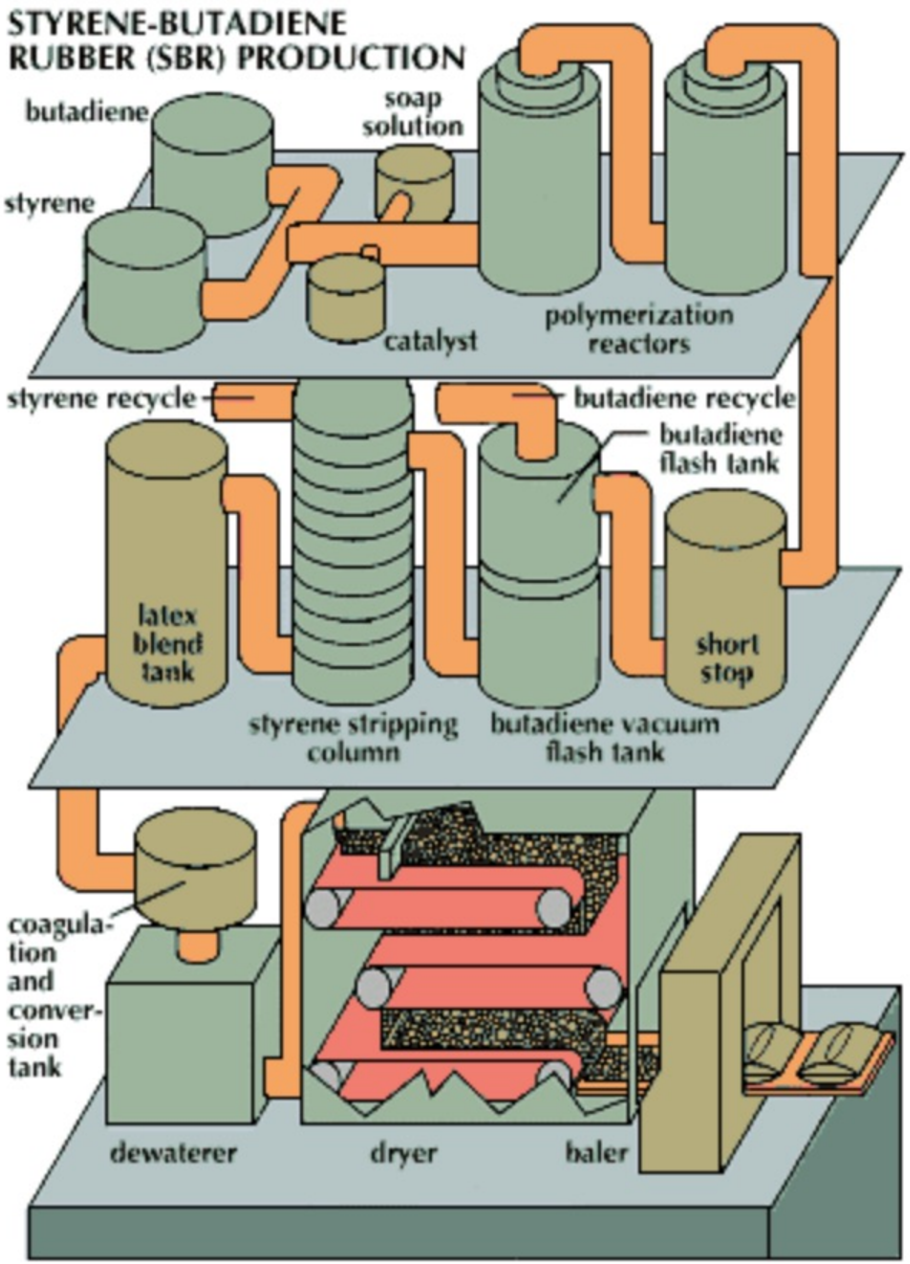
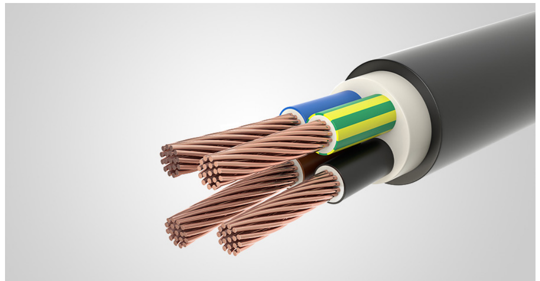
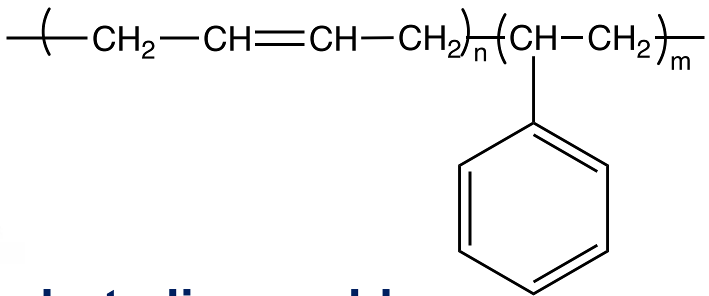




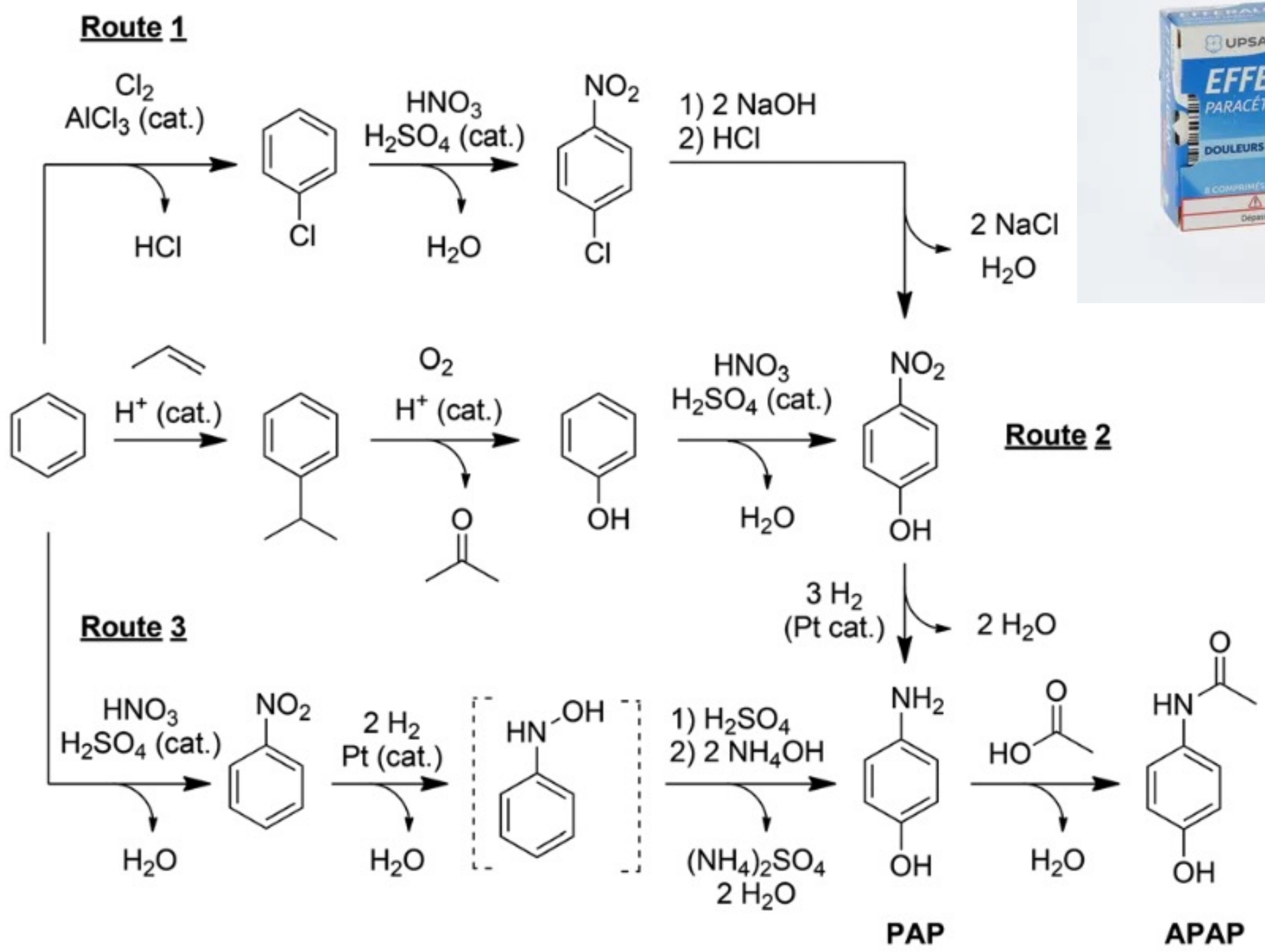






styrene-butadiene rubber

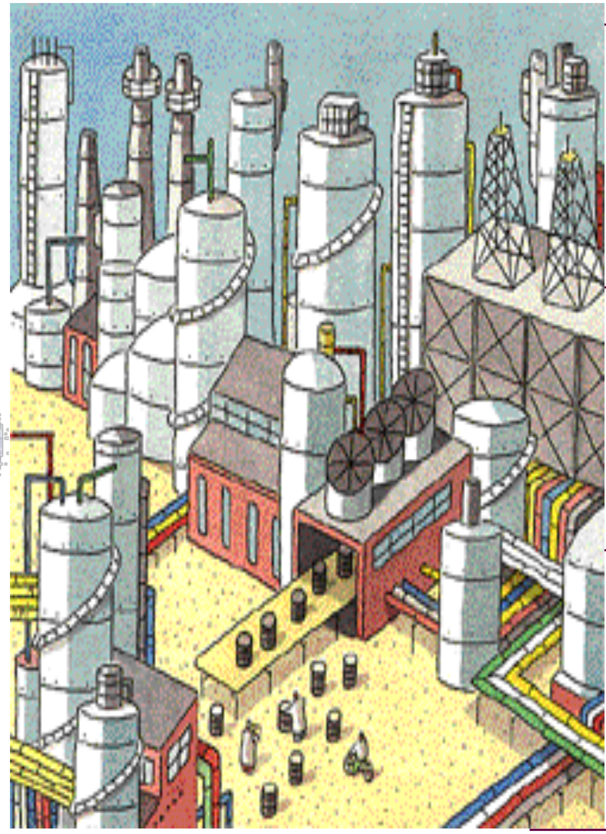
Paracetamol (acetaminophen)



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

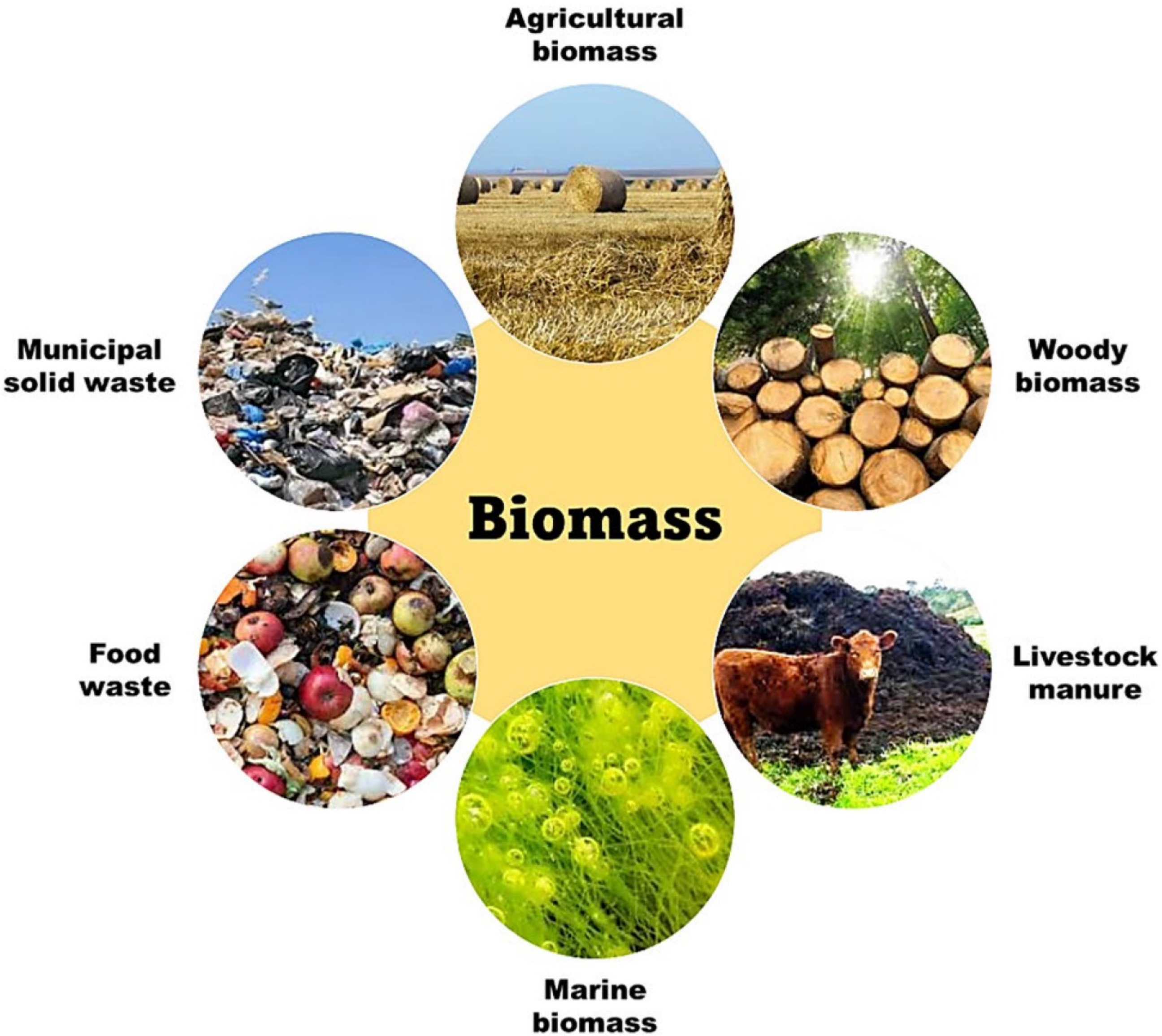
→ Base chemicals

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

→ Energy

plastics
pharmaceuticals
solvents
clothing
agro-chemicals
…

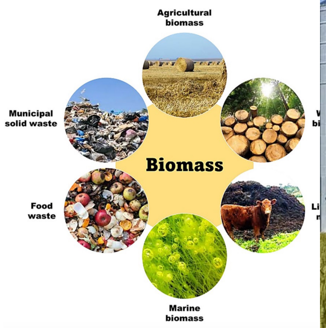
Renewable feedstocks: BIOMASS

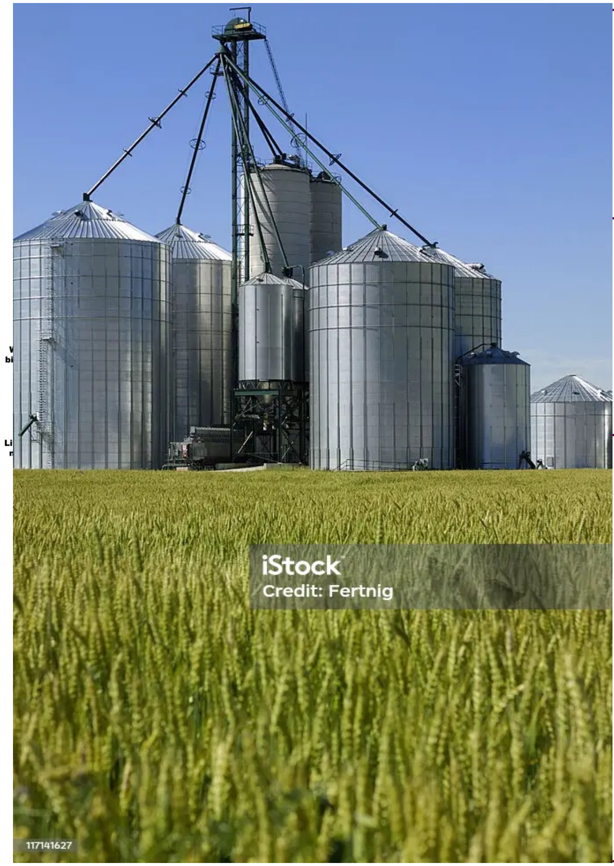


Sarker, T.R., Nanda, S., Meda, V. *et al.* Environmental Chemistry Letters (2023) 21:231–264

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

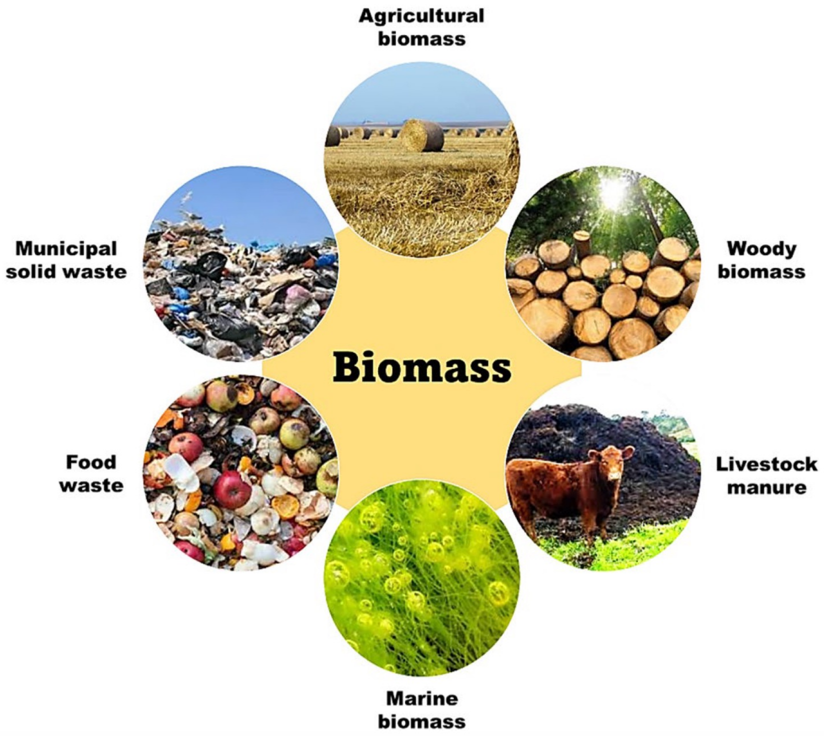
Polysaccharides (starch, cellulose, hemicellulose, chitin)

Mono/disaccharides (glucose, fructose, sucrose)

Lignin

Extracts

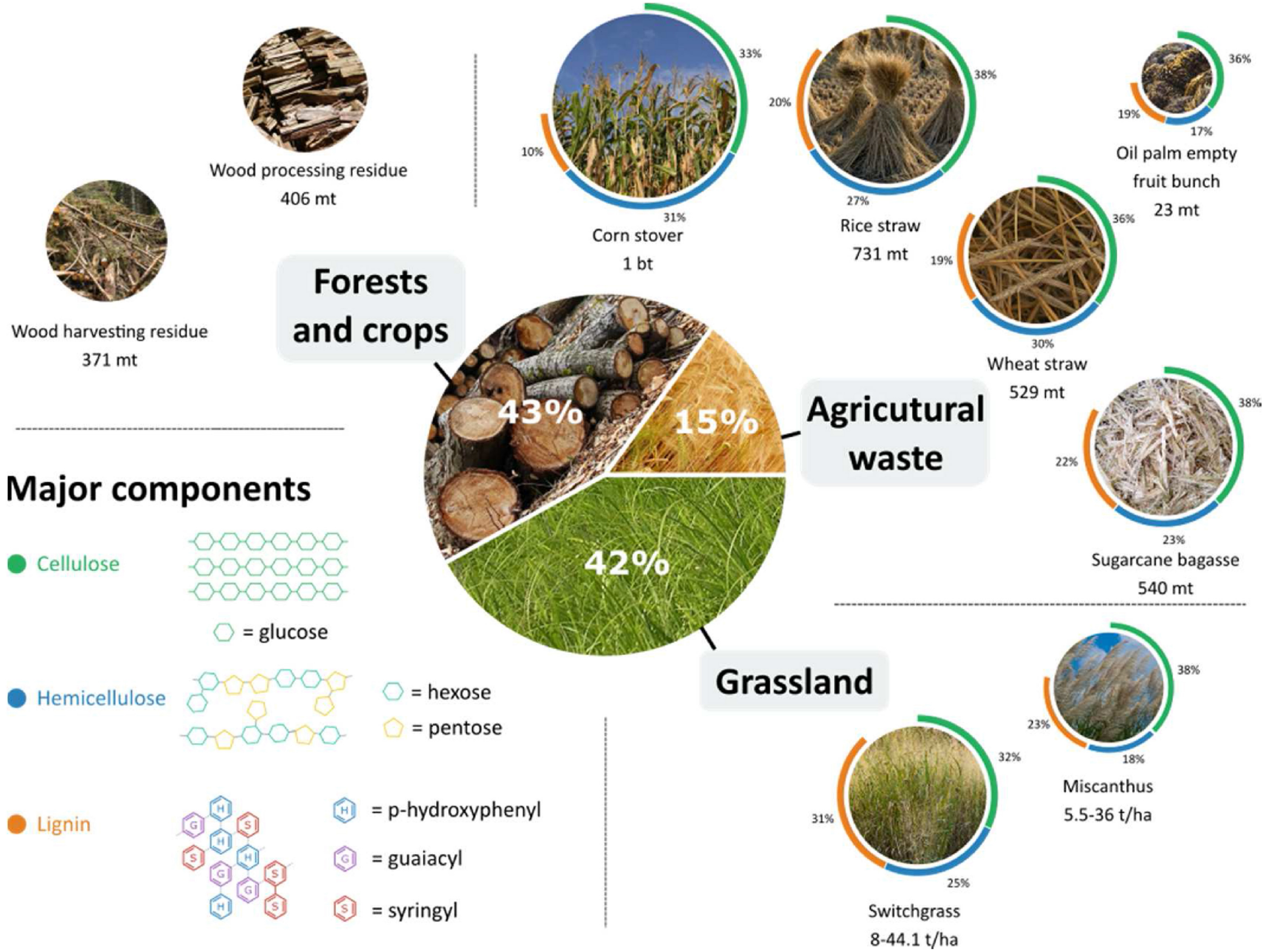
Protein



Processing technologies

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

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

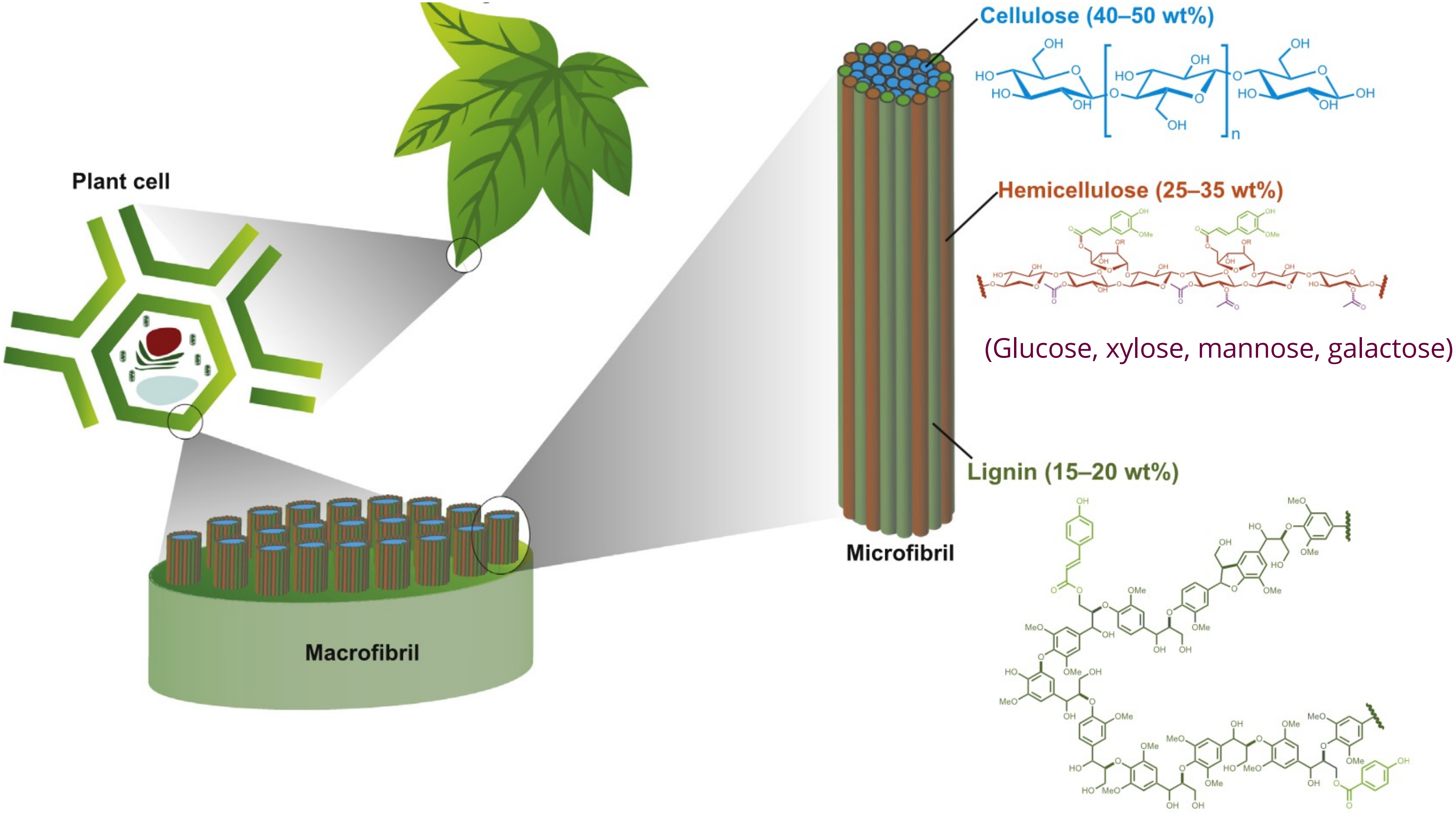


8.2 billion tons are utilized

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

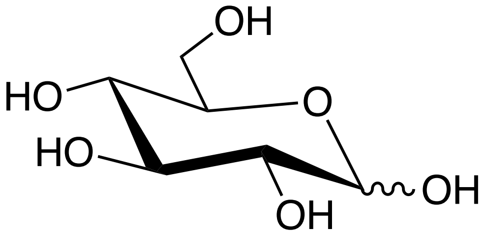
Catalytic conversion of lignocellulosic biomass into chemicals and fuels, W. Deng et al. *Green Energy Environ.*, **2023**, *8*, 10-114.

Lignocellulosic biomass

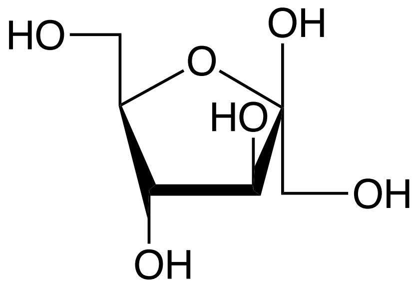


S.Bertella and J. S. Luterbacher Trends in Chemistry, May 2020, Vol. 2, No. 5

Saccharides

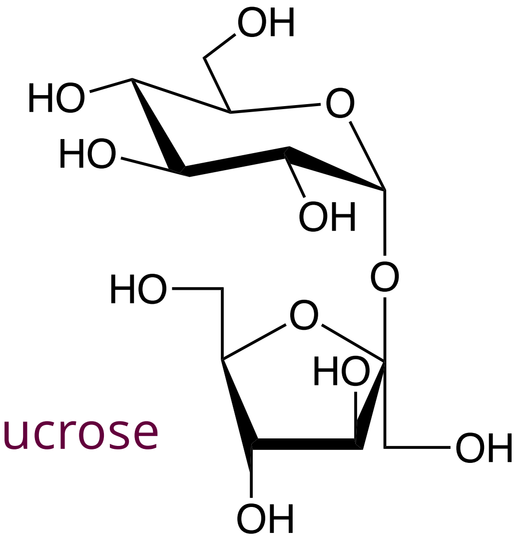


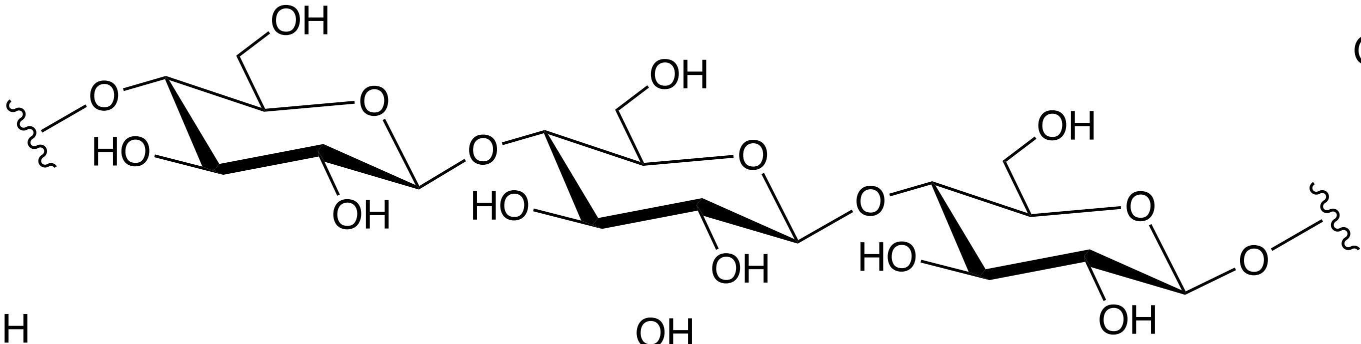
D- glucose (glucopyranose)



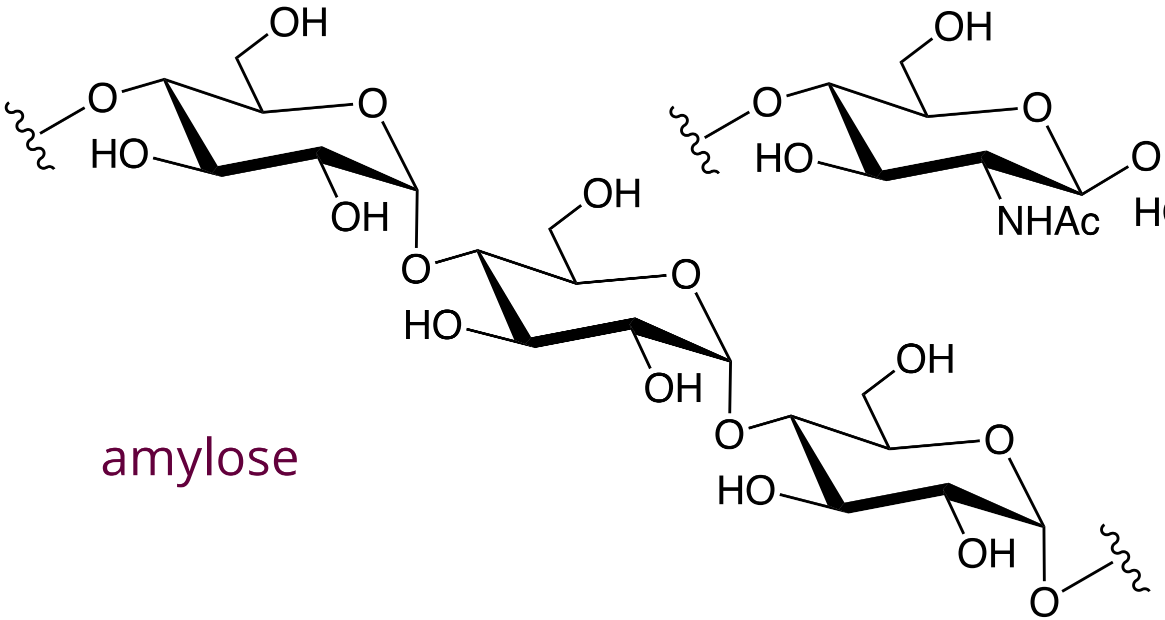
β-D- fructofuranose

sucrose

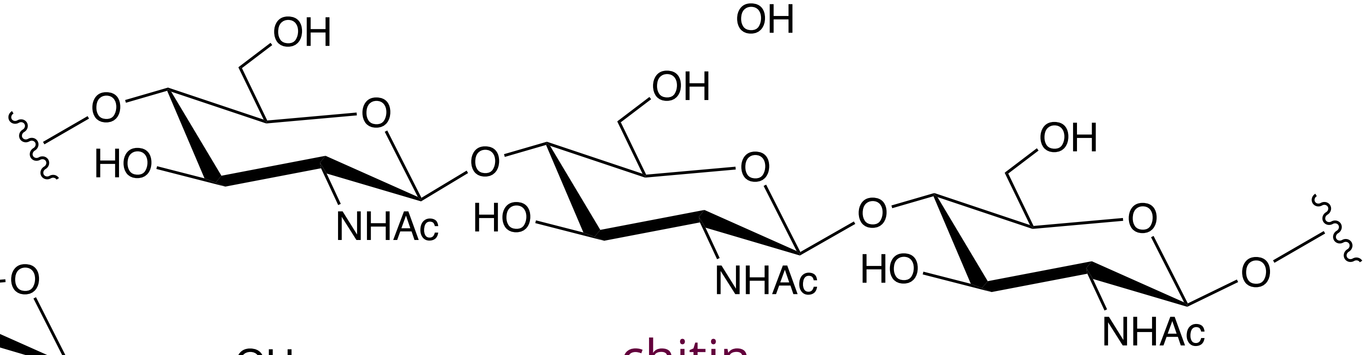




cellulose



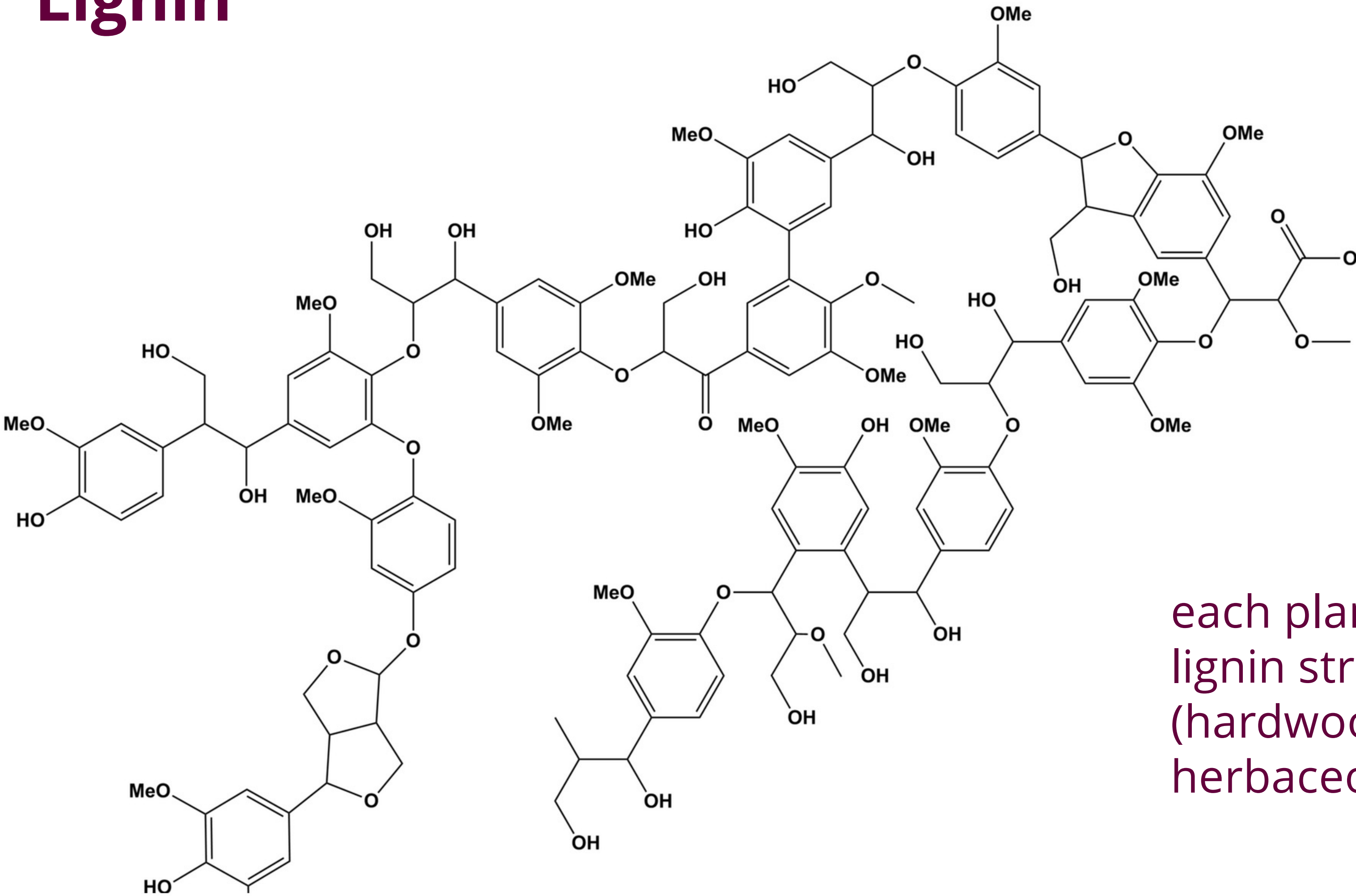
amylose



chitin

~ 75% of the biomass

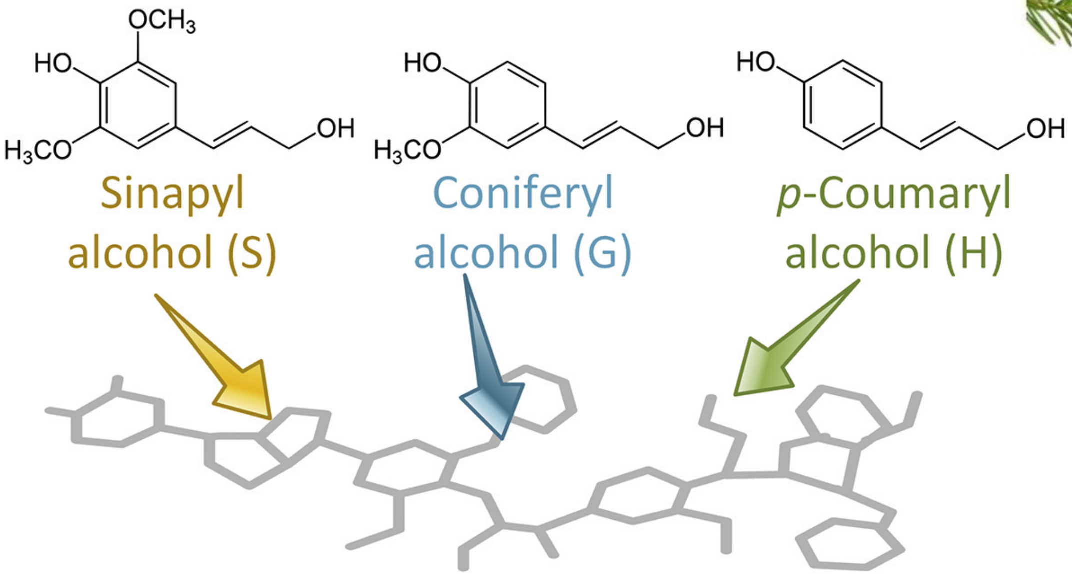
Lignin

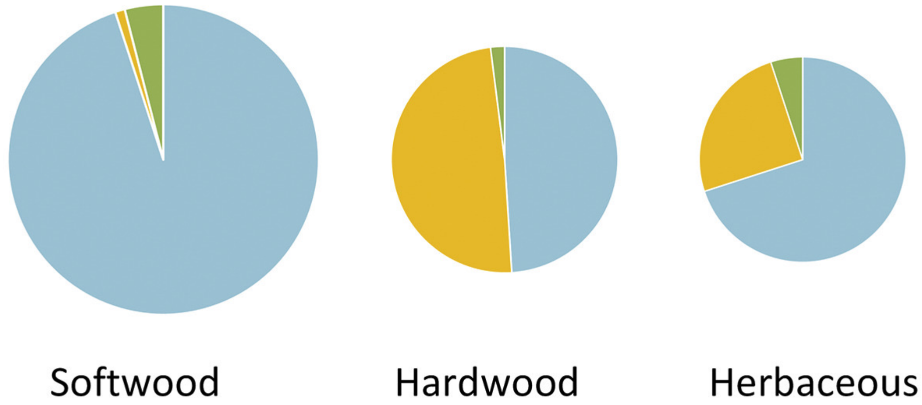


each plant has unalike lignin structures (hardwood softwood herbaceous plants)

~ 20% of the biomass

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

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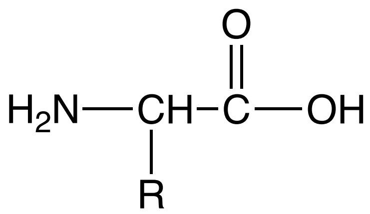
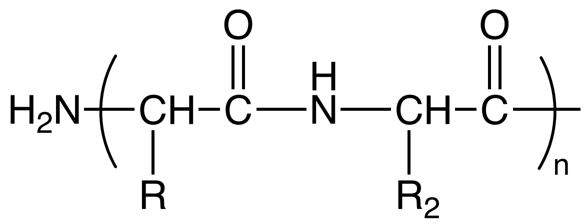
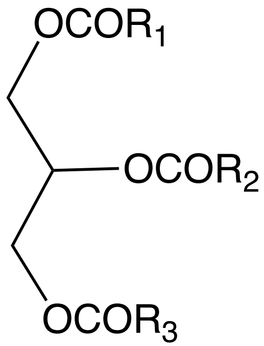
Proteins – fats – terpenoids – alkaloids- nucleic acids

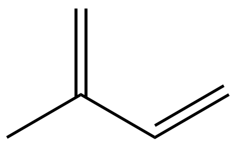




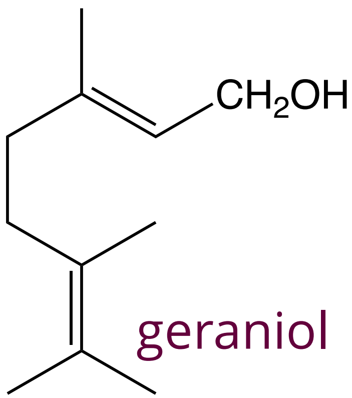
n ~ 10 : peptide
n -> 100+ : protein



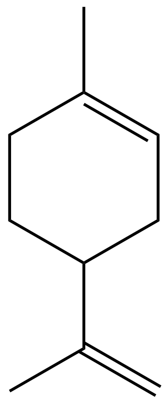
R_1, R_2, R_3 = fatty chains, saturated or unsaturated



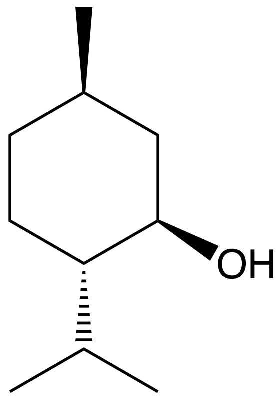
isoprene



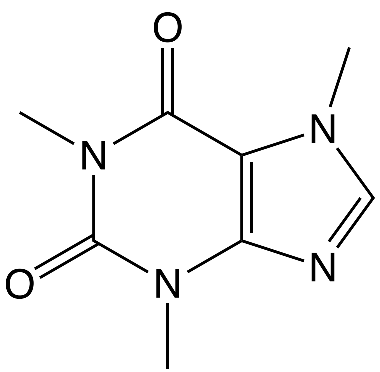
geraniol



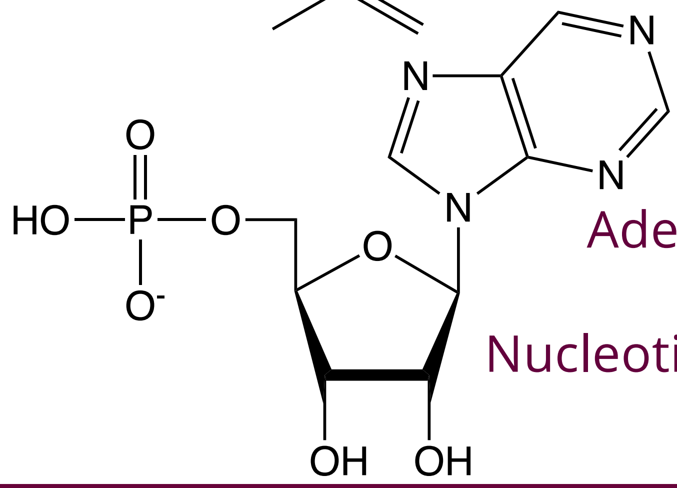
limonene



menthol



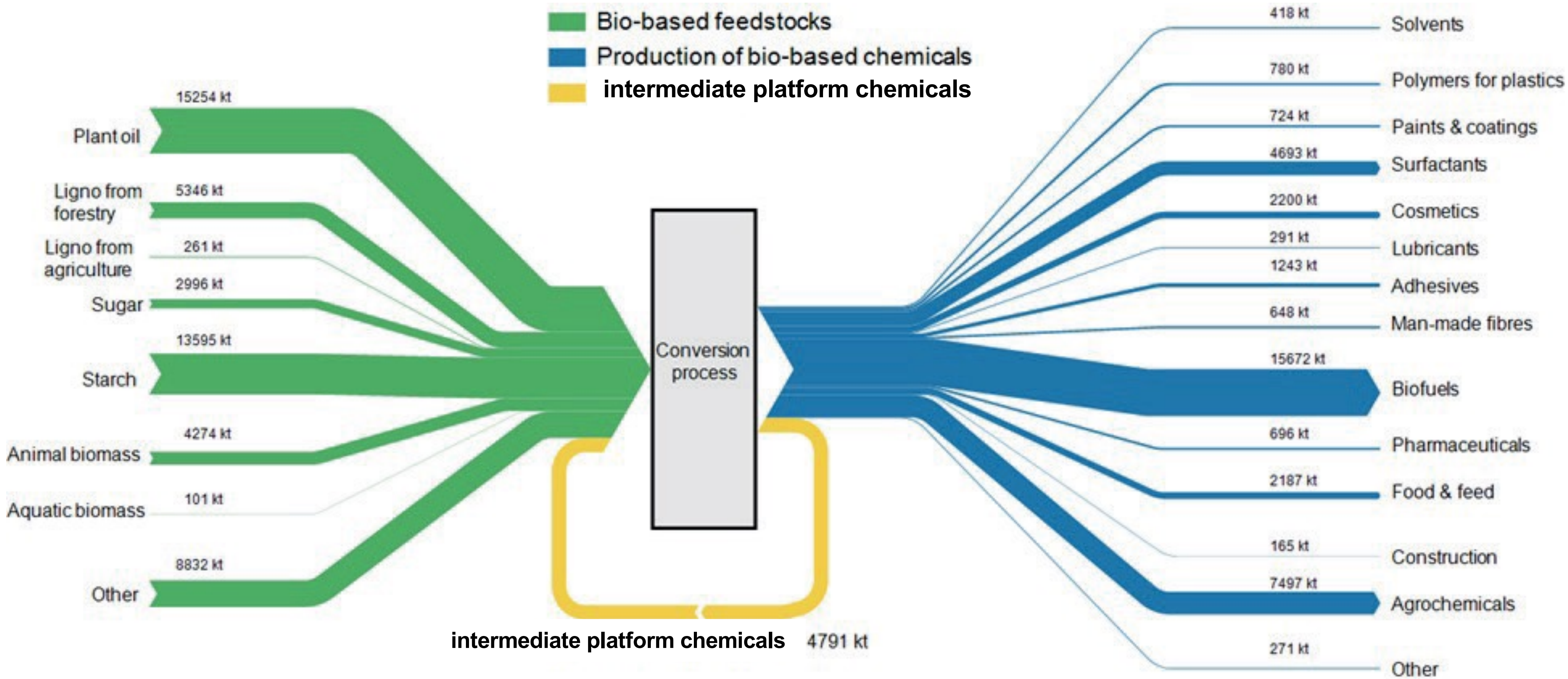
caffeine



Adenosine Monophosphate (AMP)

Nucleotide **~ 5% of the biomass**

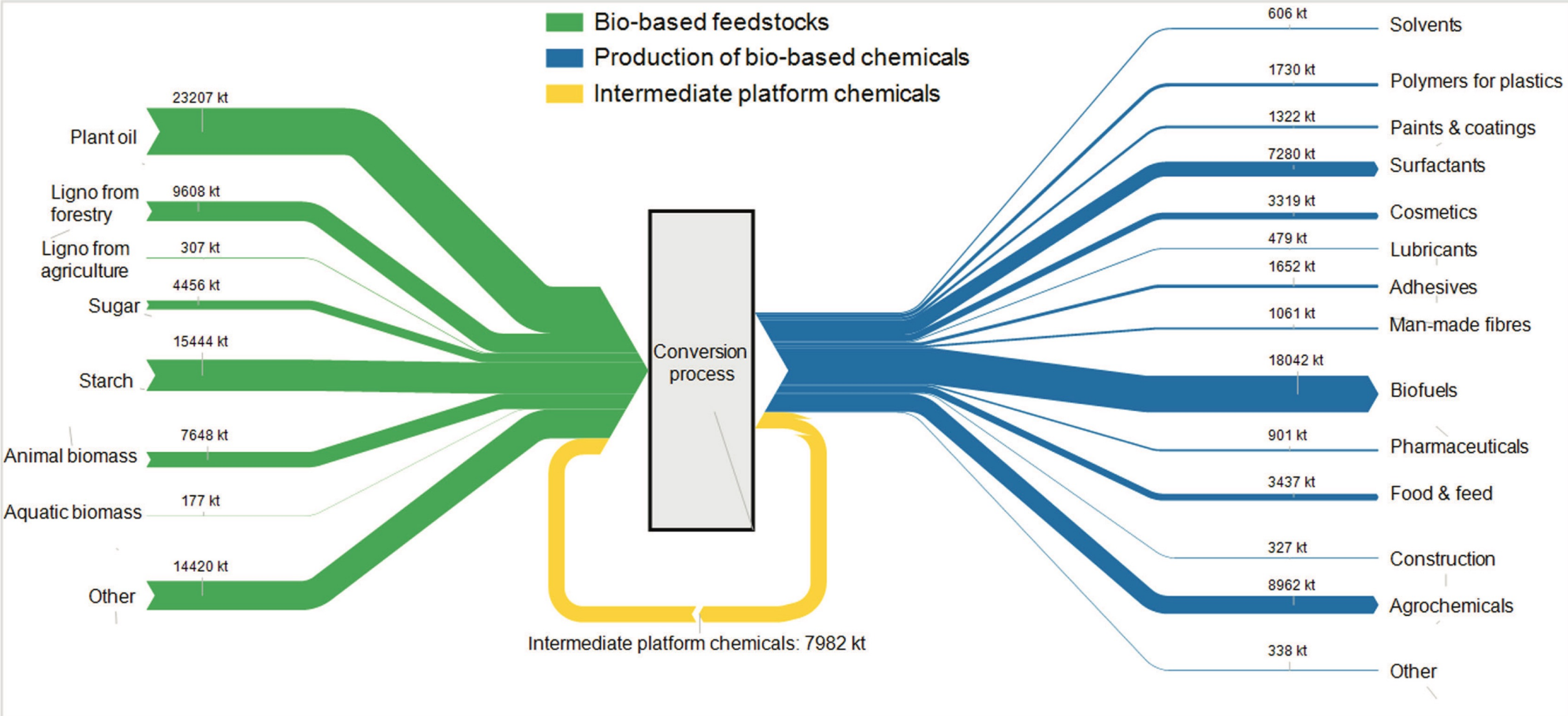
Biomass Supply and Uses in the EU (2018)



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

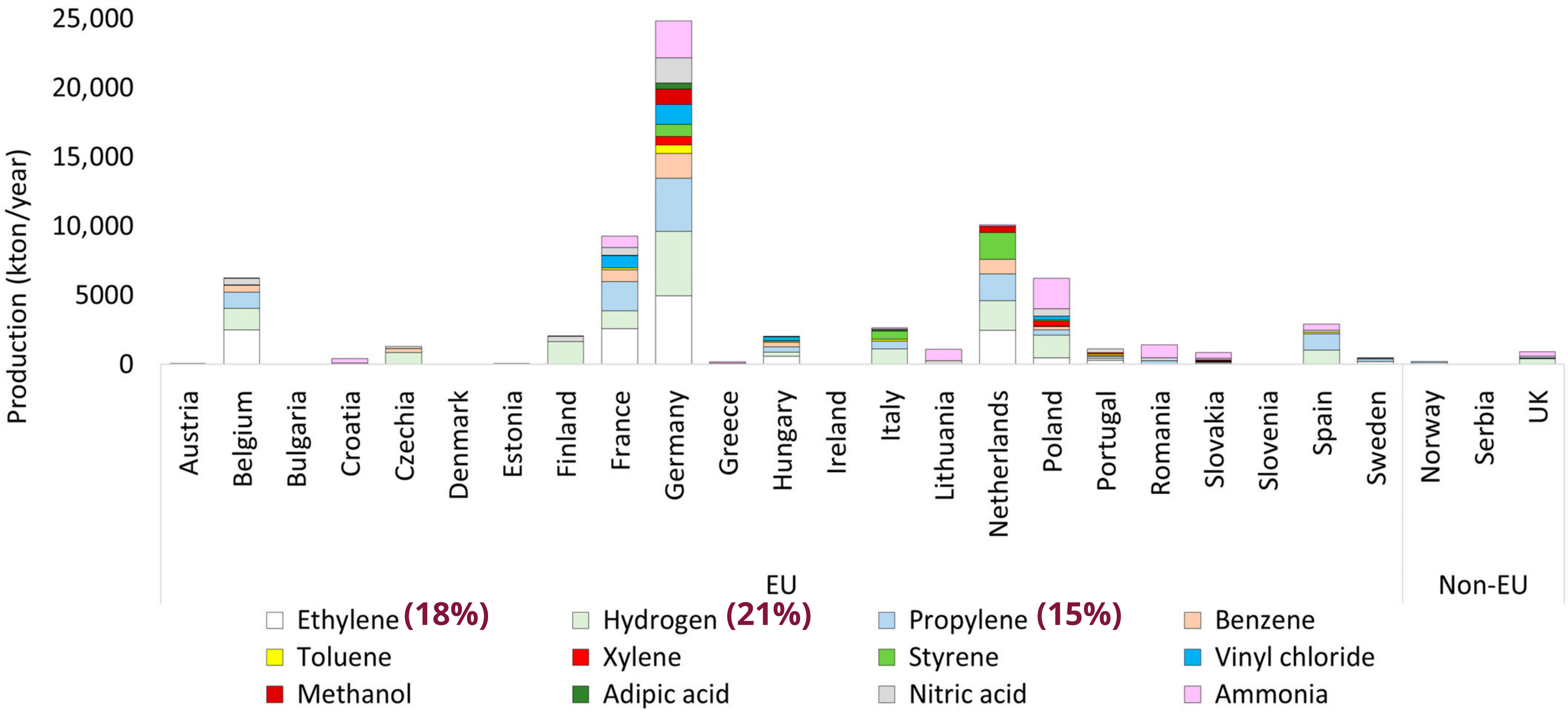
Sturm, V.; van Leeuwen, M.; Gonzalez-Martinez, A.; Verhoog, D.; Hark, N.; de Beus, N. Providing Insights into the Markets for Bio-Based Materials with BioMAT. Sustainability 2023, 15, 3064. https://doi.org/10.3390/su15043064.

Use of biological resources by bio-based chemical applications (kton) in EU, 2030



van Leeuwen, M., Gonzalez-Martinez, A., & Sturm, V. (2023). EU Outlook for Biomass Flows and Bio-based Products. *EuroChoices*, *22*(3), 13-20.

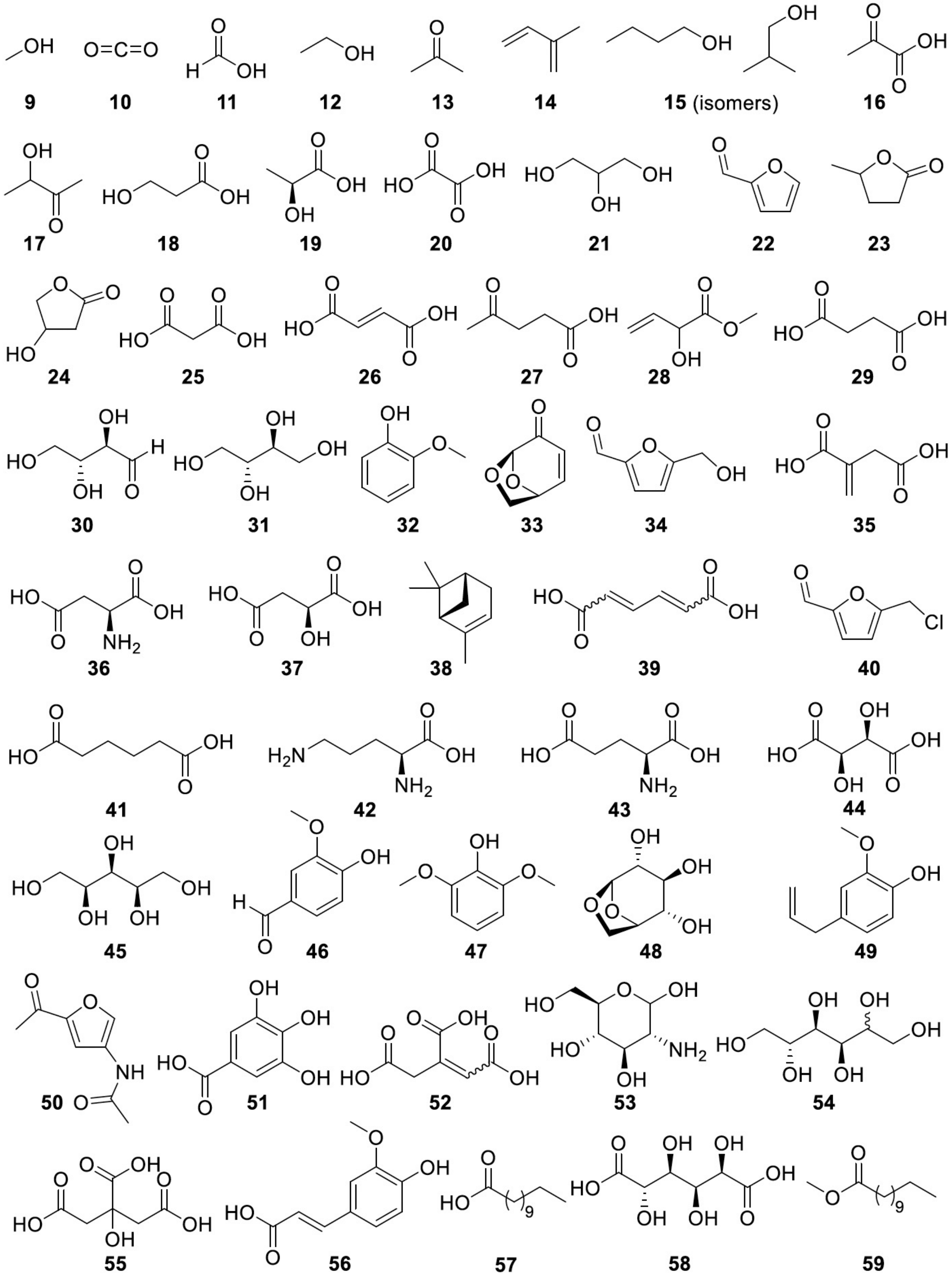
Production of chemicals in Europe, per country, average from 2011 to 2020.



80 Mt of production annually in the EU

WIREs Energy & Environment, Volume: 13, Issue: 4, First published: 01 August 2024, DOI: (10.1002/wene.534)

Platform chemicals



methanol **9**; carbon dioxide **10**; formic acid **11**; ethanol **12**; acetone **13**; isoprene **14**; butanol (n-, iso-) **15**; pyruvic acid **16**; acetoin **17**; 3-hydroxypropionic acid **18**; lactic acid **19**; oxalic acid **20**; glycerol **21**; furfural **22**; γ-valerolactone **23**; 3-hydroxybutyrolactone **24**; malonic acid **25**; fumaric acid **26**; levulinic acid **27**; methyl vinyl glycolate **28**; succinic acid **29**; erythrose **30**; erythritol **31**; guaiacol **32**; levoglucosenone **3**3; 5-(hydroxymethyl)furfural **34**; itaconic acid **35**; aspartic acid **36**; malic acid **3**7; D-limonene and pinenes **38**; muconic acid **39**; 5-(chloromethyl)furfural **40**; adipic acid **41**; L-lysine **42**; glutamic acid **43**; tartaric acid **44**; xylitol and arabitol **45**; vanillin **46**; syringol **47**; levoglucosan **48**; eugenol **49**; 3-acetamido-5-acetylfuran **50**; gallic acid **51**; aconitic acid **52**; glucosamine **53**; sorbitol and mannitol **54**; citric acid **55**; ferulic acid **56**; fatty acids (e.g. lauric acid) **57**; glucaric **58**; fatty acid alkyl esters (e.g. methyl laurate) **59**

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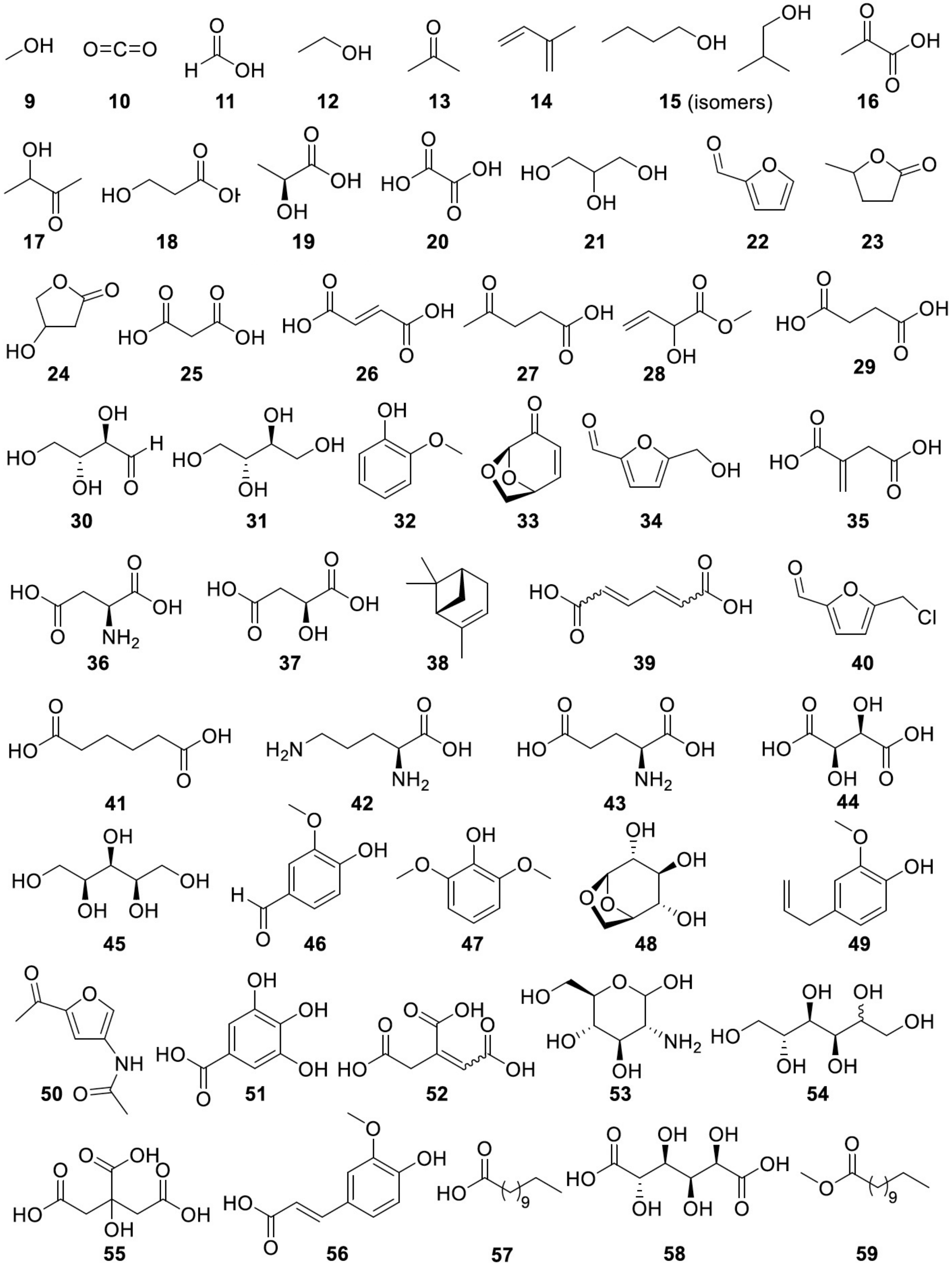
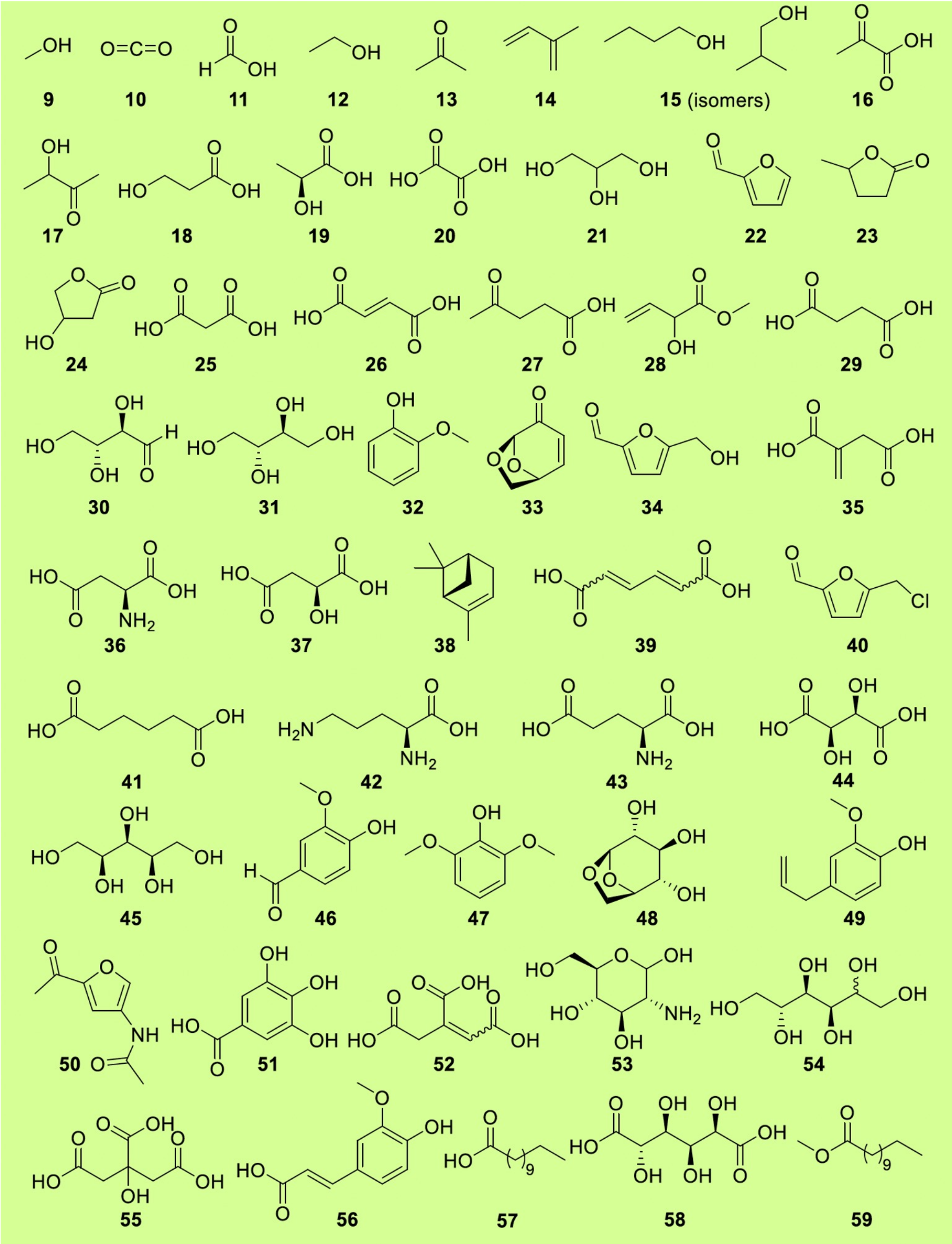
Platform chemicals



lactic acid **19** **54% of the world's production**

succinic acid **29** **46% of the world's production**

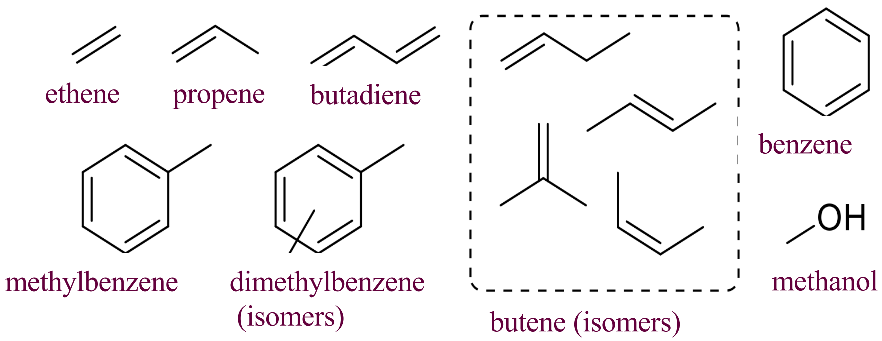
most produced bio-based chemicals in the EU



Platform chemicals

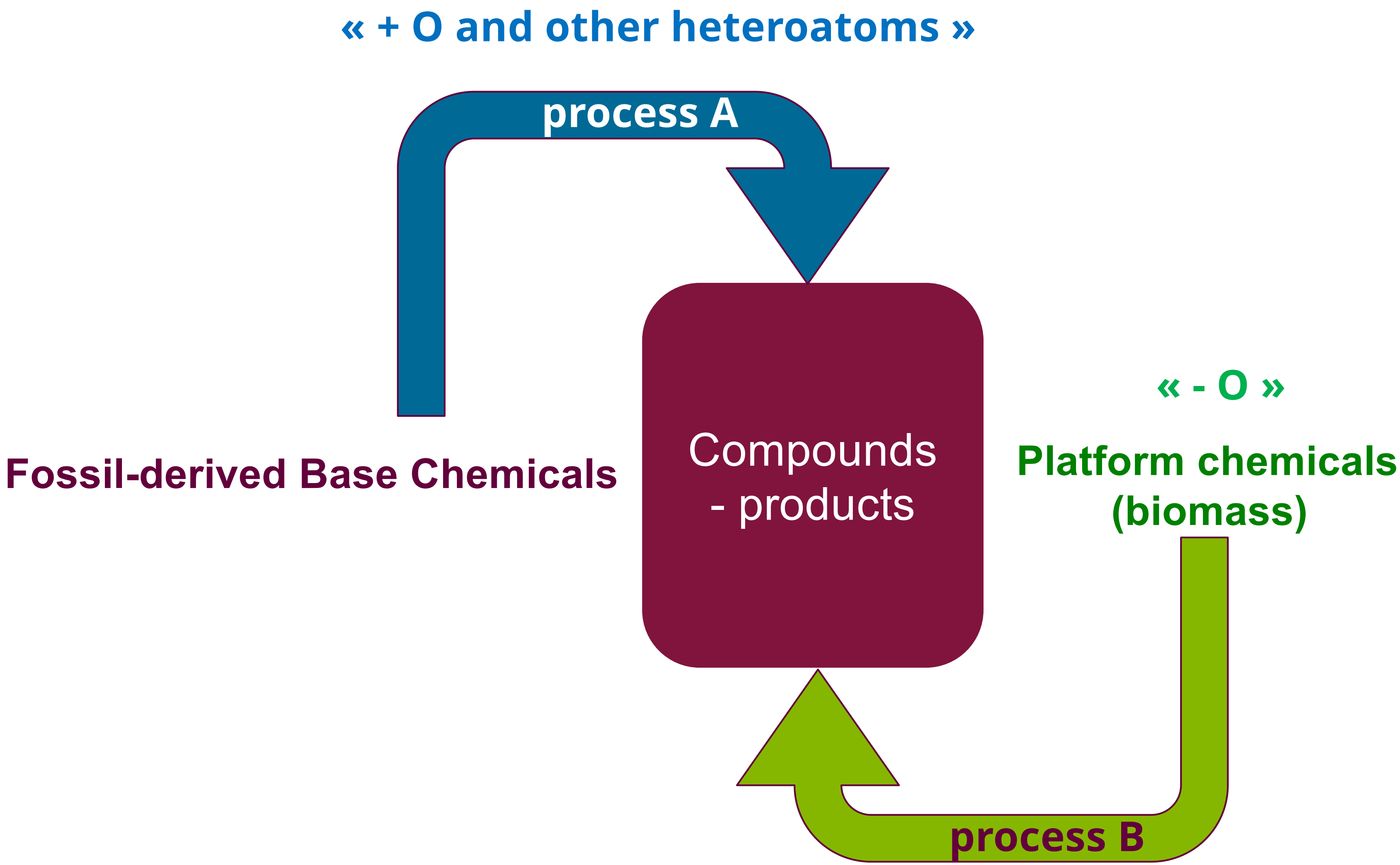
Platform chemicals (biomass-derived) are rich in heteroatoms, especially oxygen

Petroleum-derived base chemicals

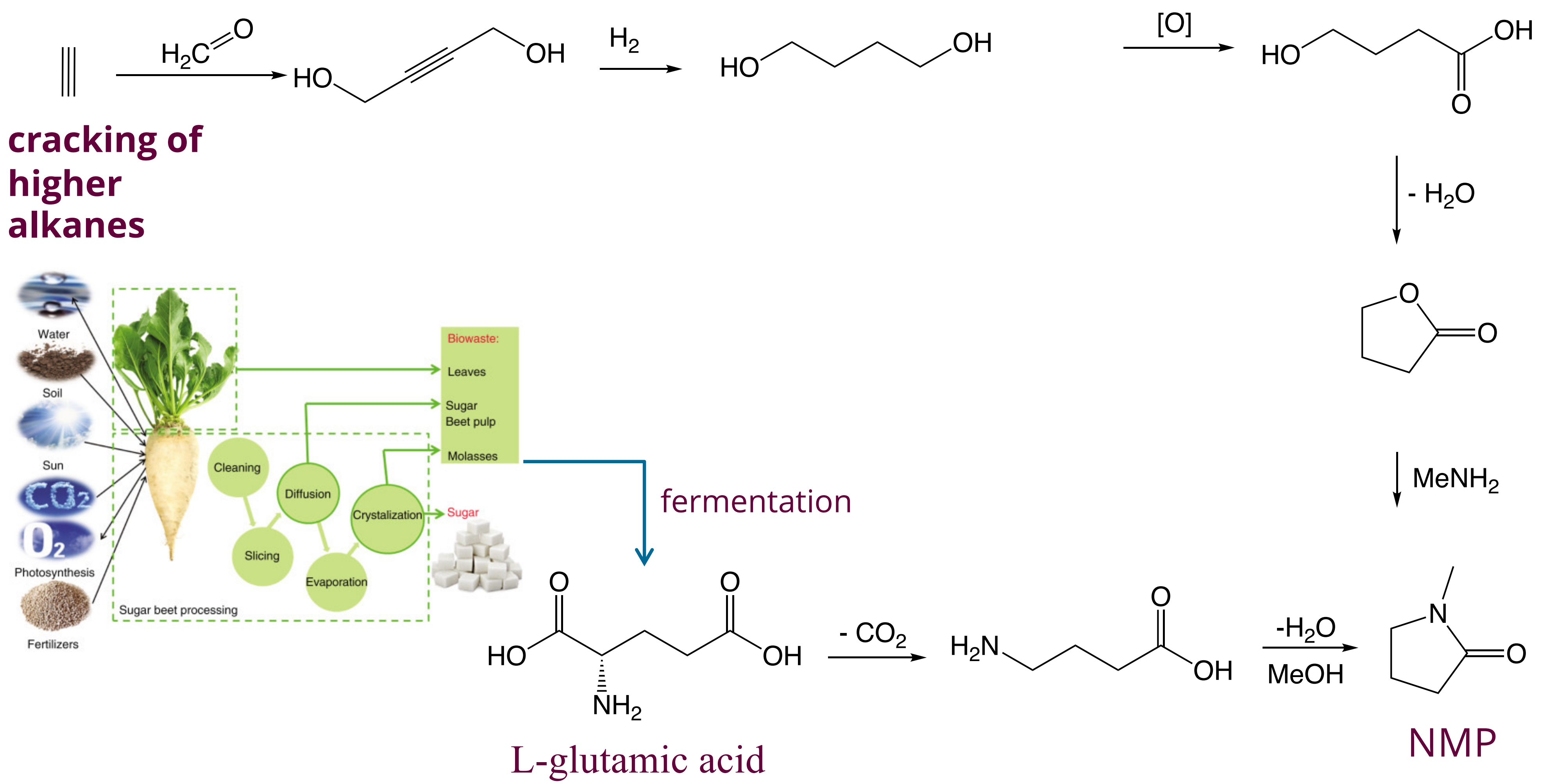


The petroleum-derived base chemicals of the current chemical industry are heavily depleted of heteroatoms

Structural approach

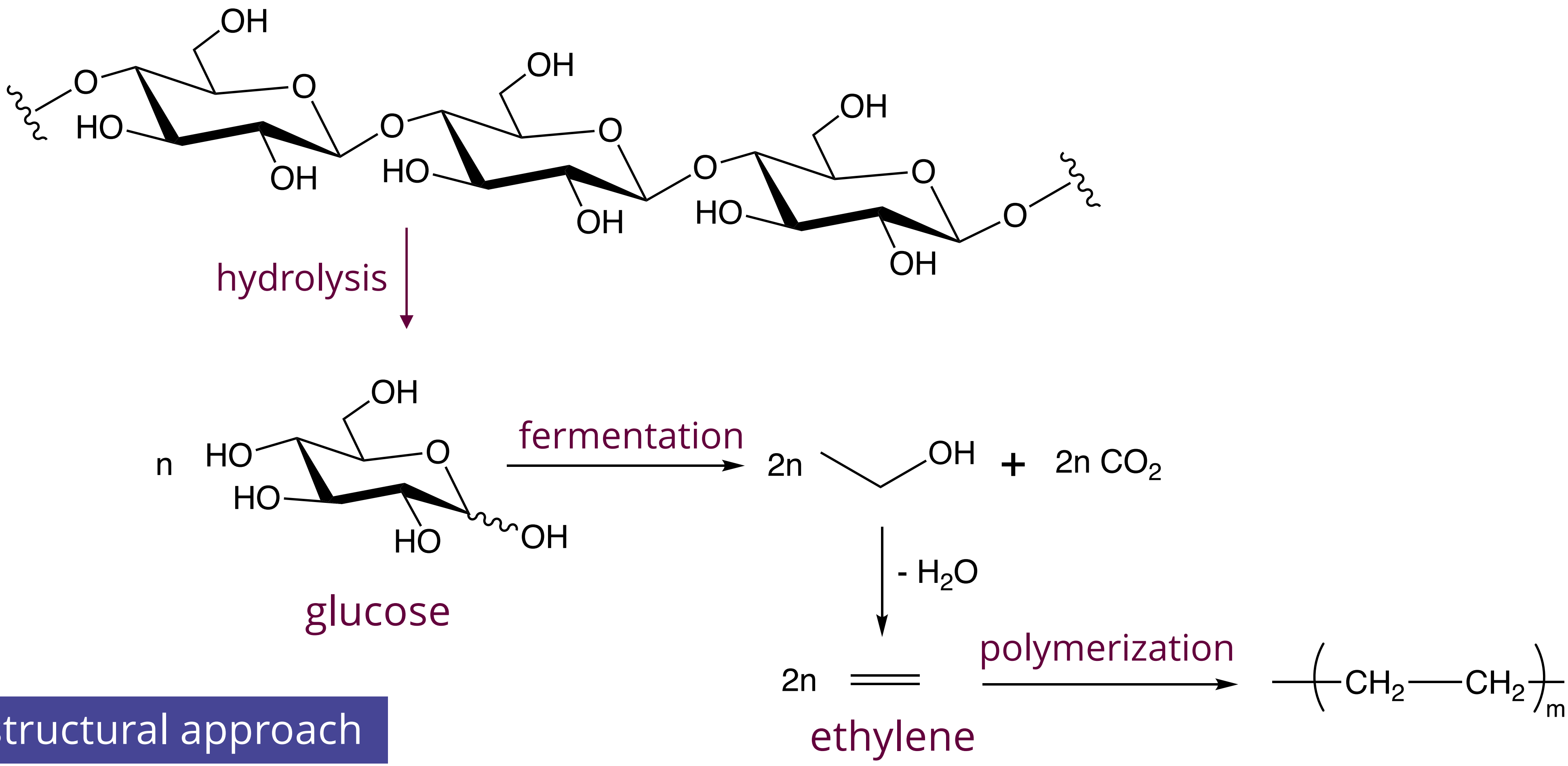


Example : (N-Methyl-2-pyrrolidone)



Applications in the petrochemicals, electronics, paints & coatings, agrochemicals and pharmaceuticals markets. The major drivers for this market are growing demand for lithium-ion batteries in electric vehicles and growing demand from pharmaceutical industry

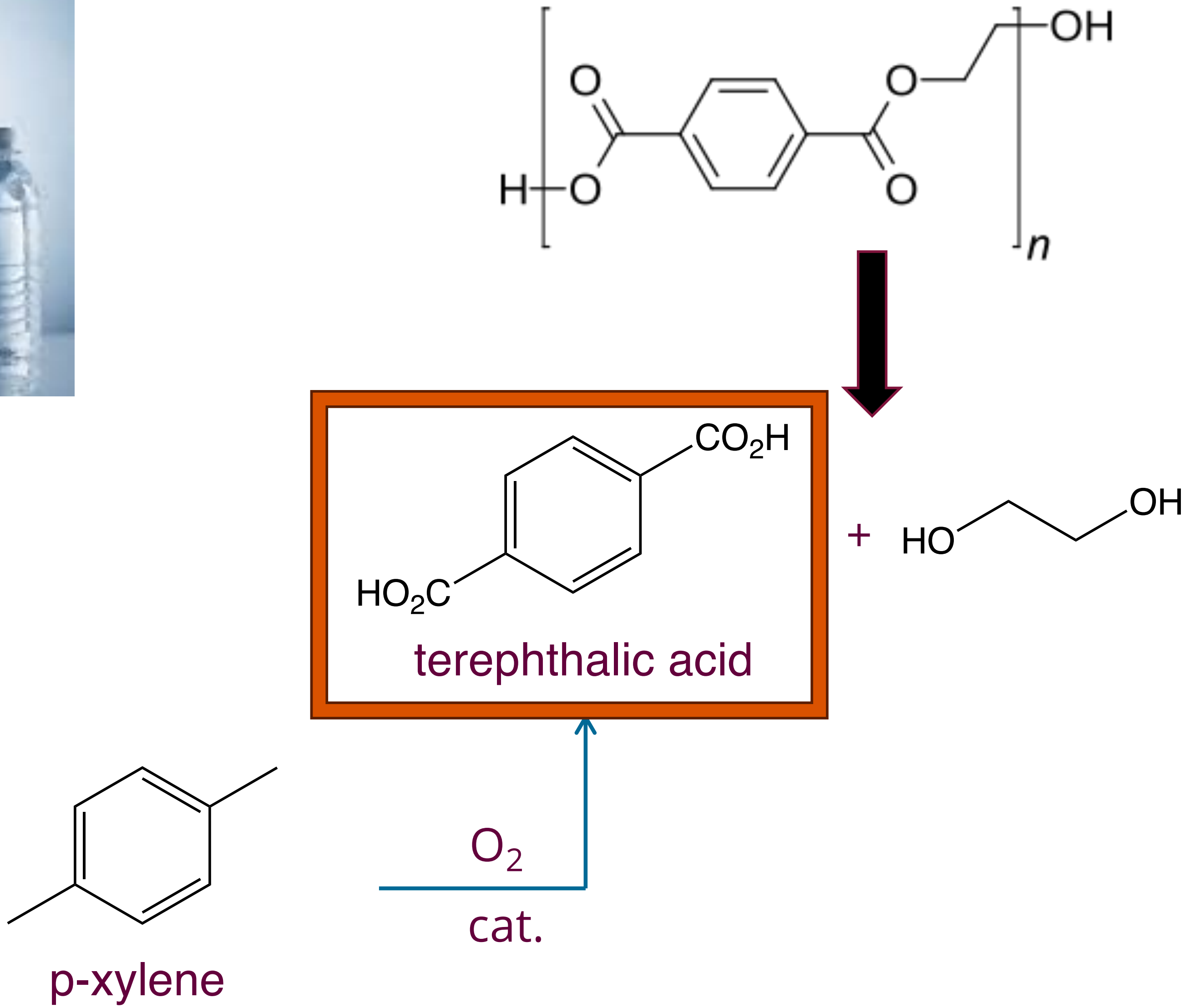
Examples: Bio-sourced polymers - Polyethylene (PE)

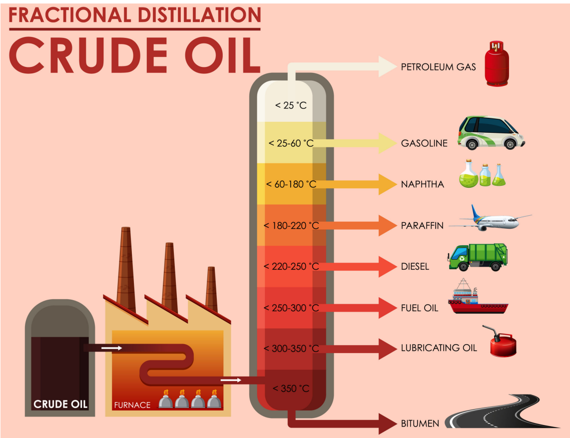


structural approach

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

Example : Polyethylene terephthalate, PET





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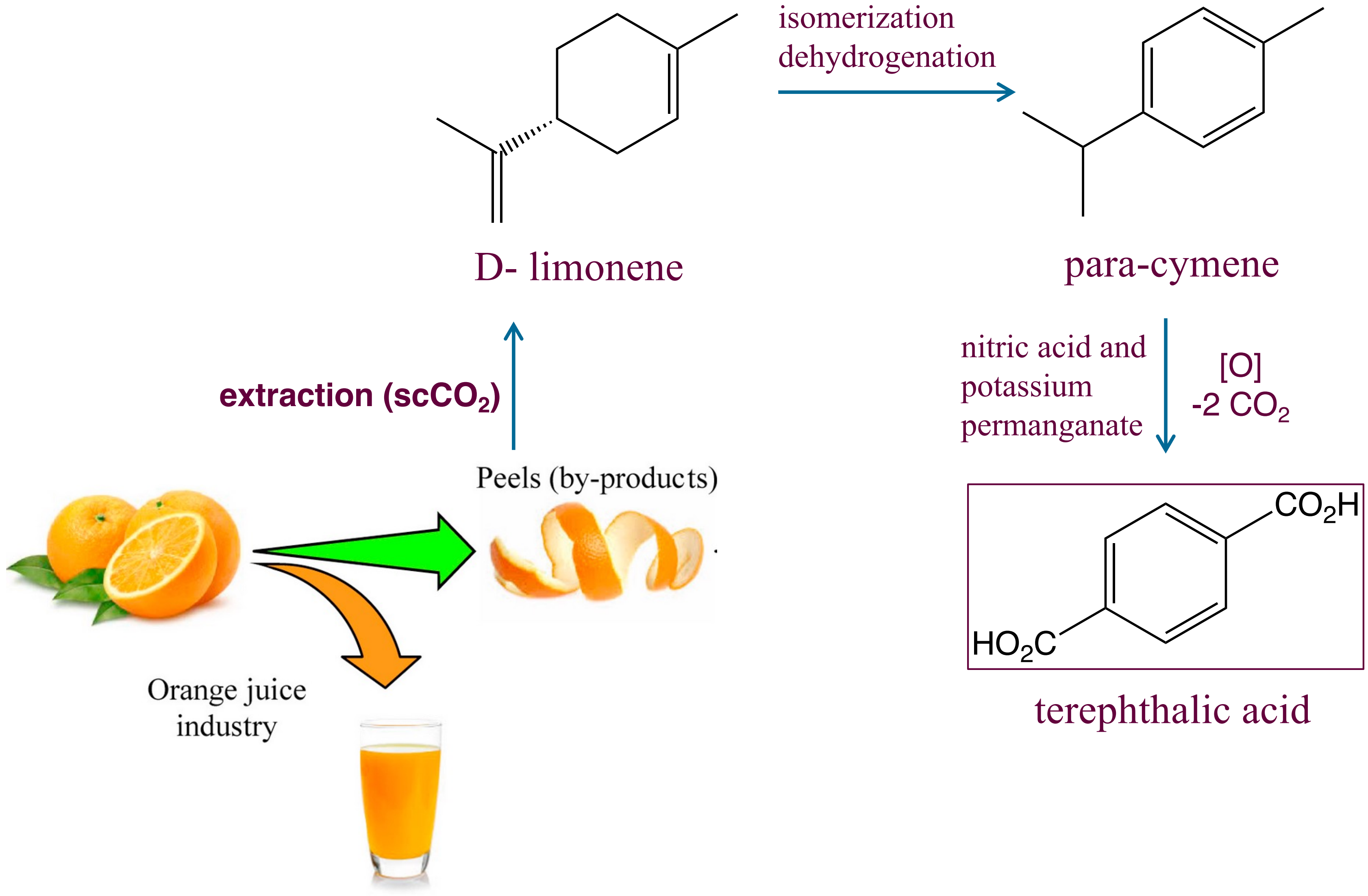
Example : Polyethylene terephthalate, PET

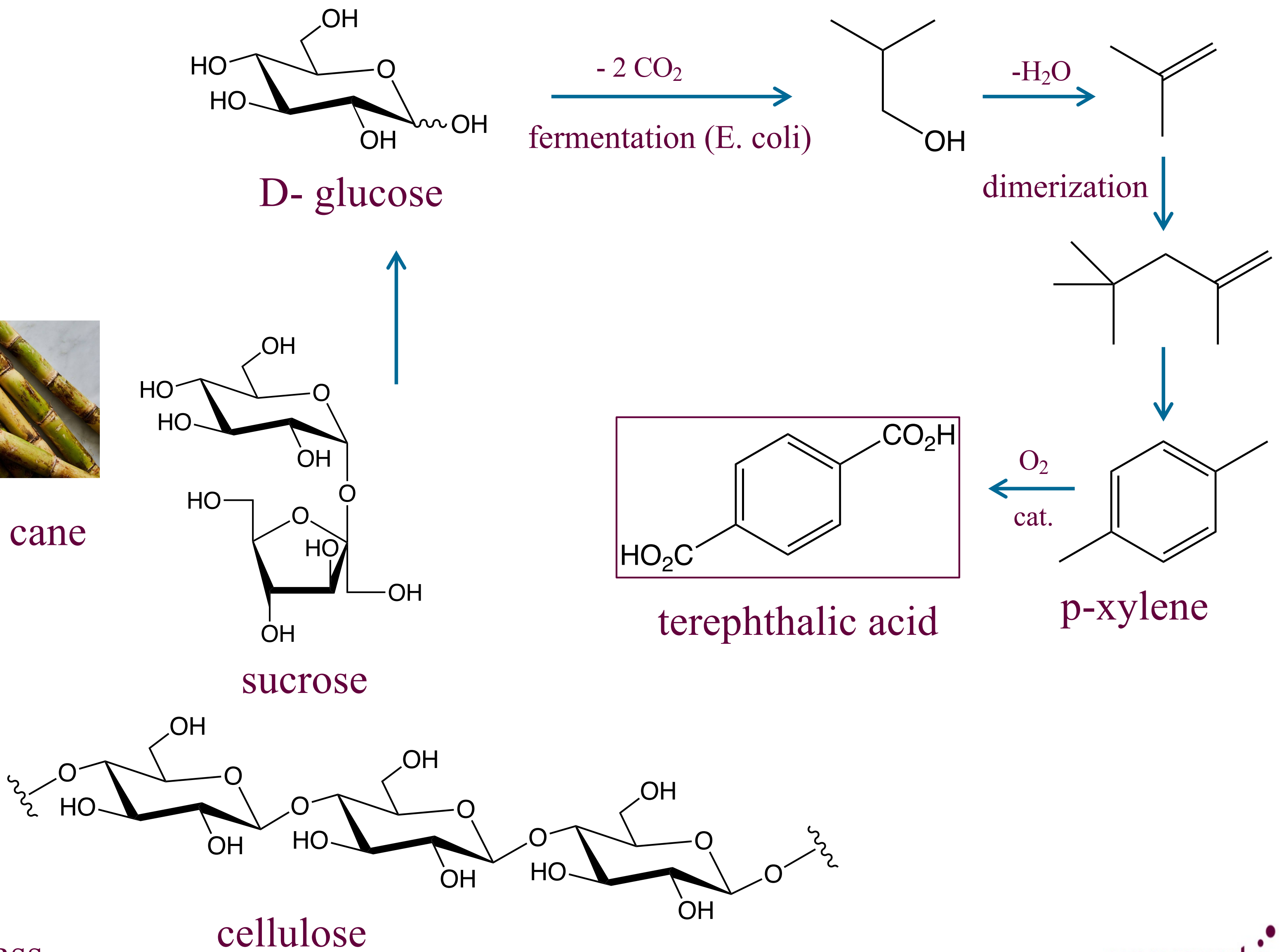


Example : Polyethylene terephthalate, PET

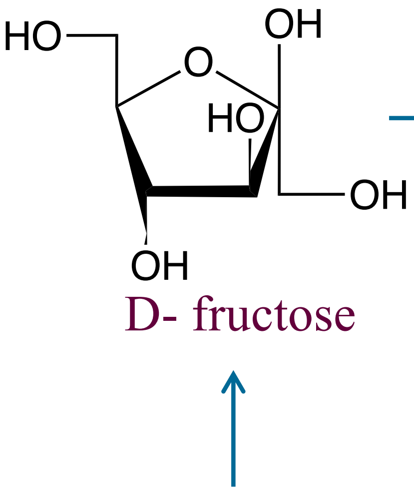
sugar beet

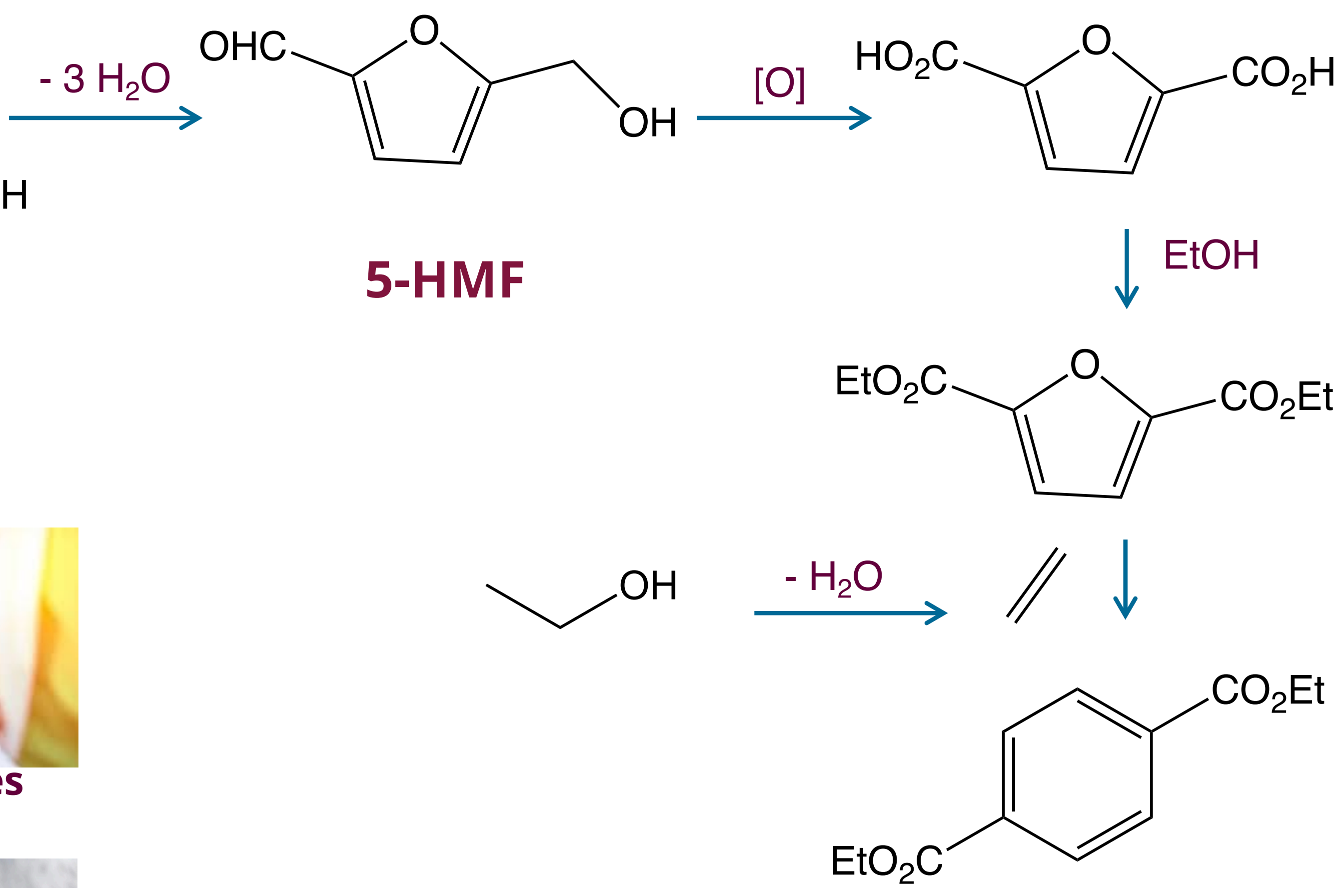
sugar cane

Lignocellulosic biomass



Example : Polyethylene terephthalate, PET



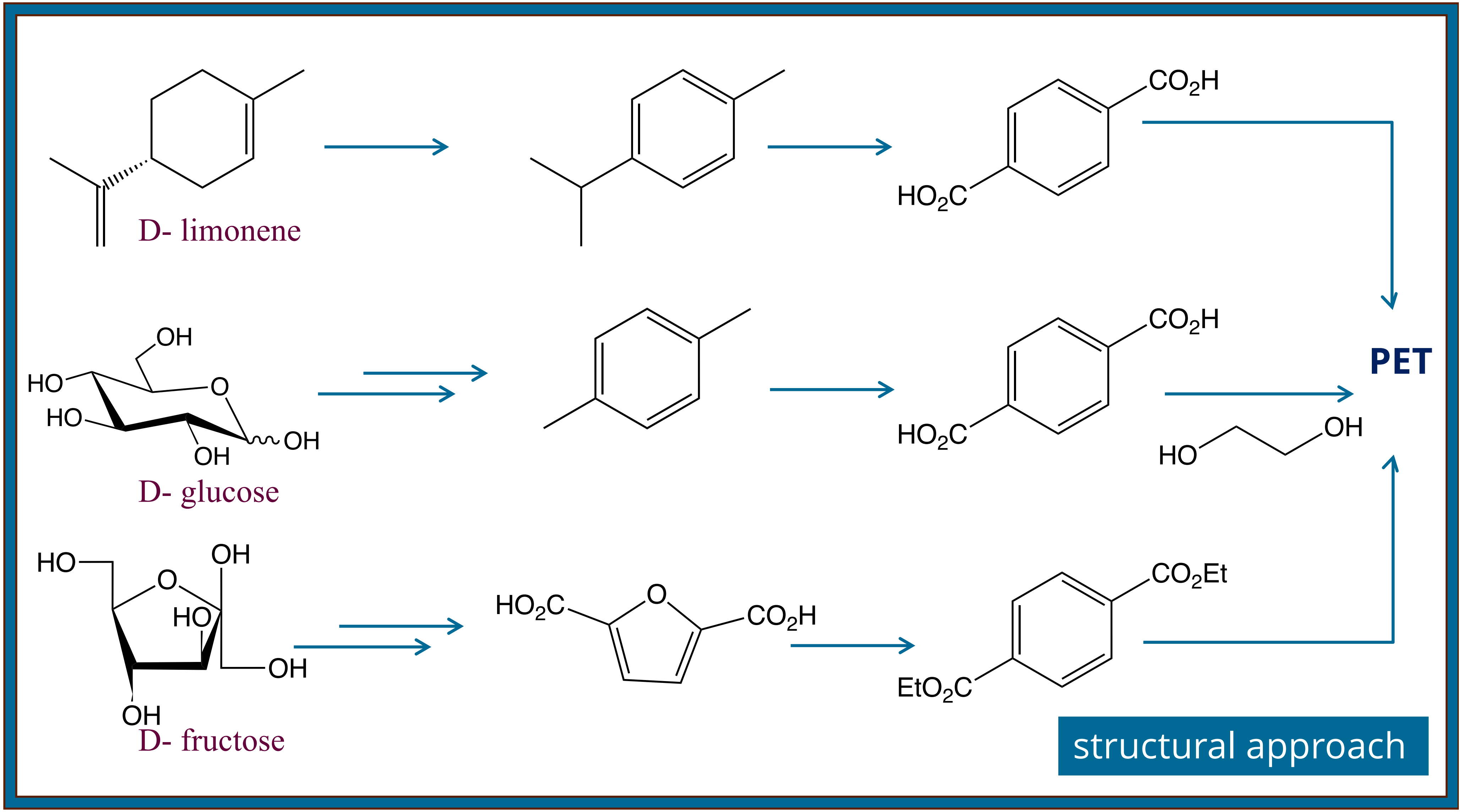


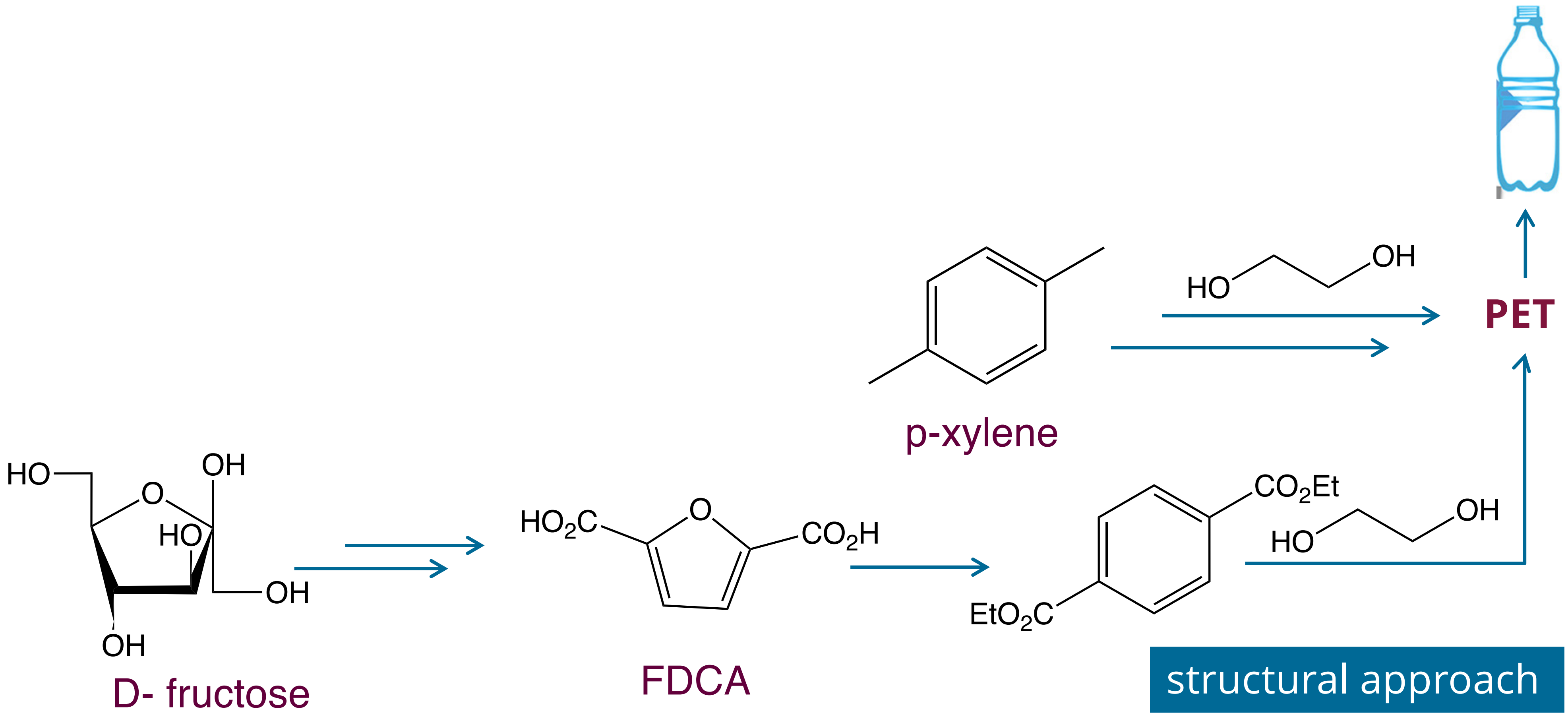

sugar molasses


sugar cane

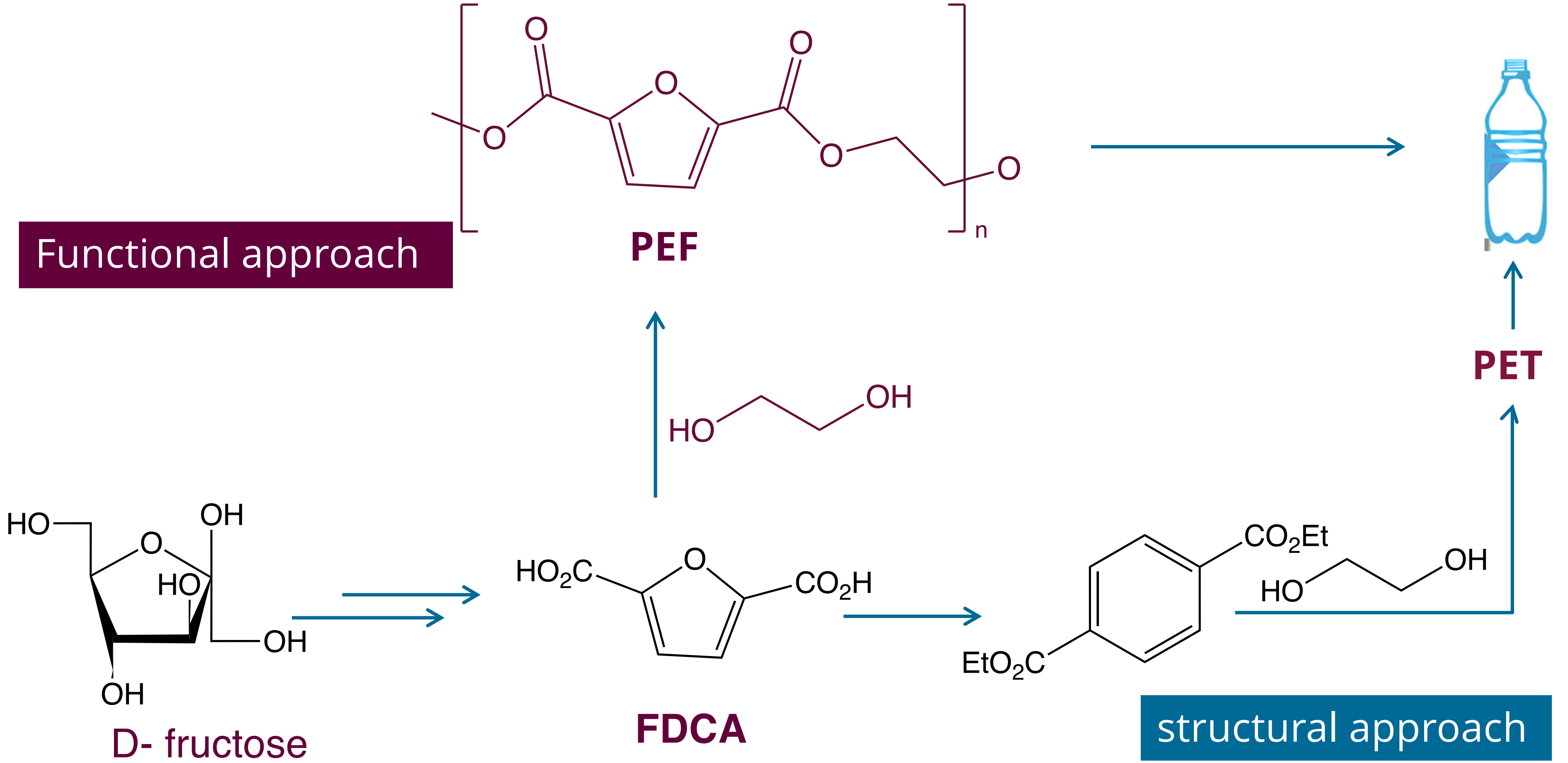

sucrose

Example : Polyethylene terephthalate, PET




PET
HO
OH
p-xylene
HO
OH
D- fructose
HO_2C
CO_2H
FDCA
CO_2Et
EtO_2C
HO
OH
structural approach

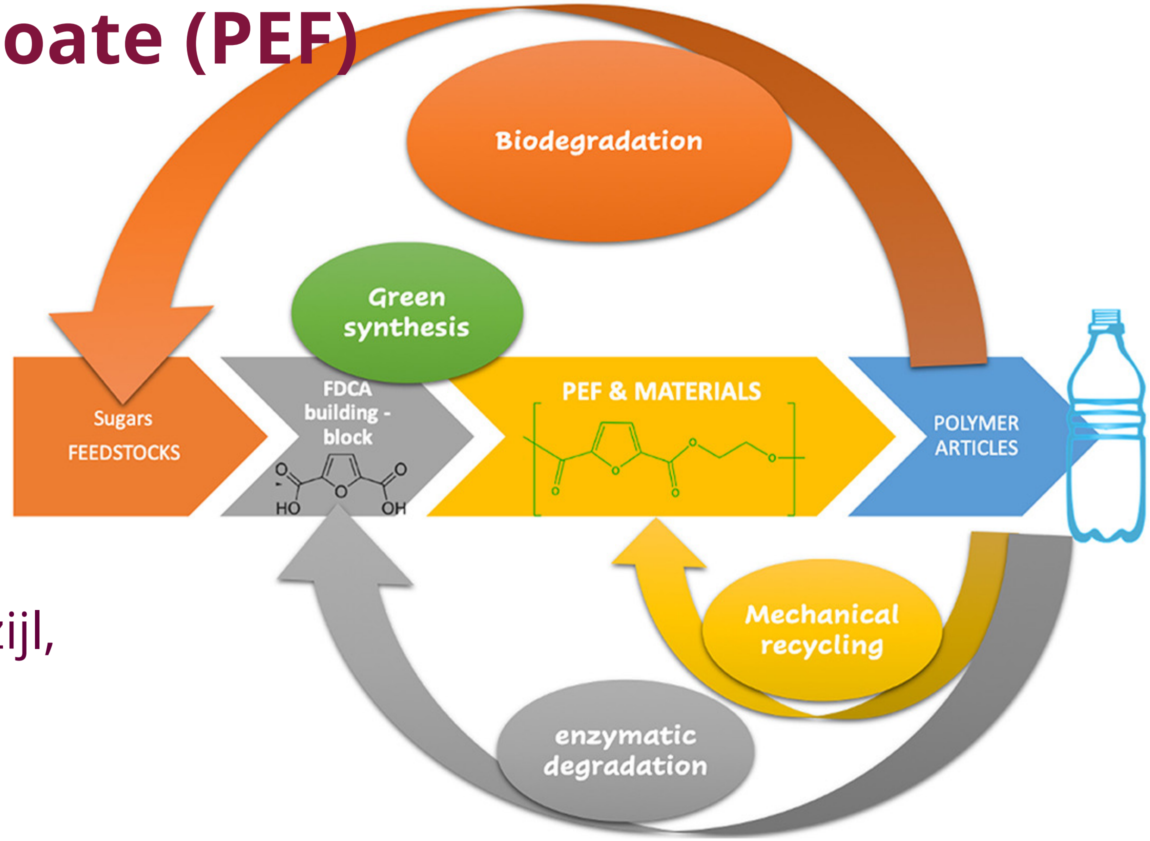
Other approach



polyethylene-furanoate (PEF)

avantium

R&D labs in Amsterdam, three pilot plants in Geleen and Delfzijl, and our FDCA Flagship Plant in Delfzijl, the Netherlands

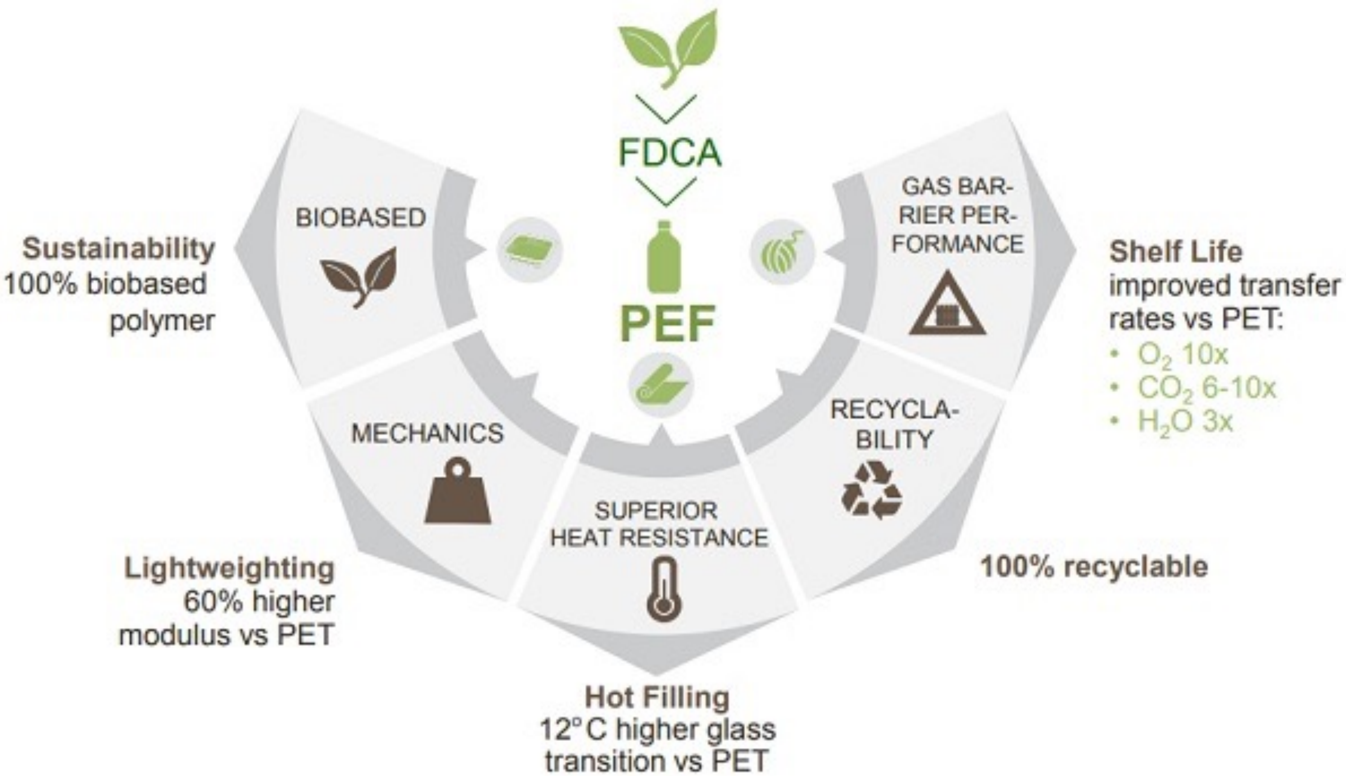


FDA Approves Avantium's PEF for Food Contact Applications in the United States

AMSTERDAM, 8 October 2024, 18:00 hrs CEST – Avantium N.V., a leading company in renewable and circular polymer materials, announces that the U.S. Food and Drug Administration (FDA) has granted Food Contact Notification (FCN) approval for the use of Avantium's PEF (polyethylene furanoate) in food contact articles, effective from 5 October 2024.

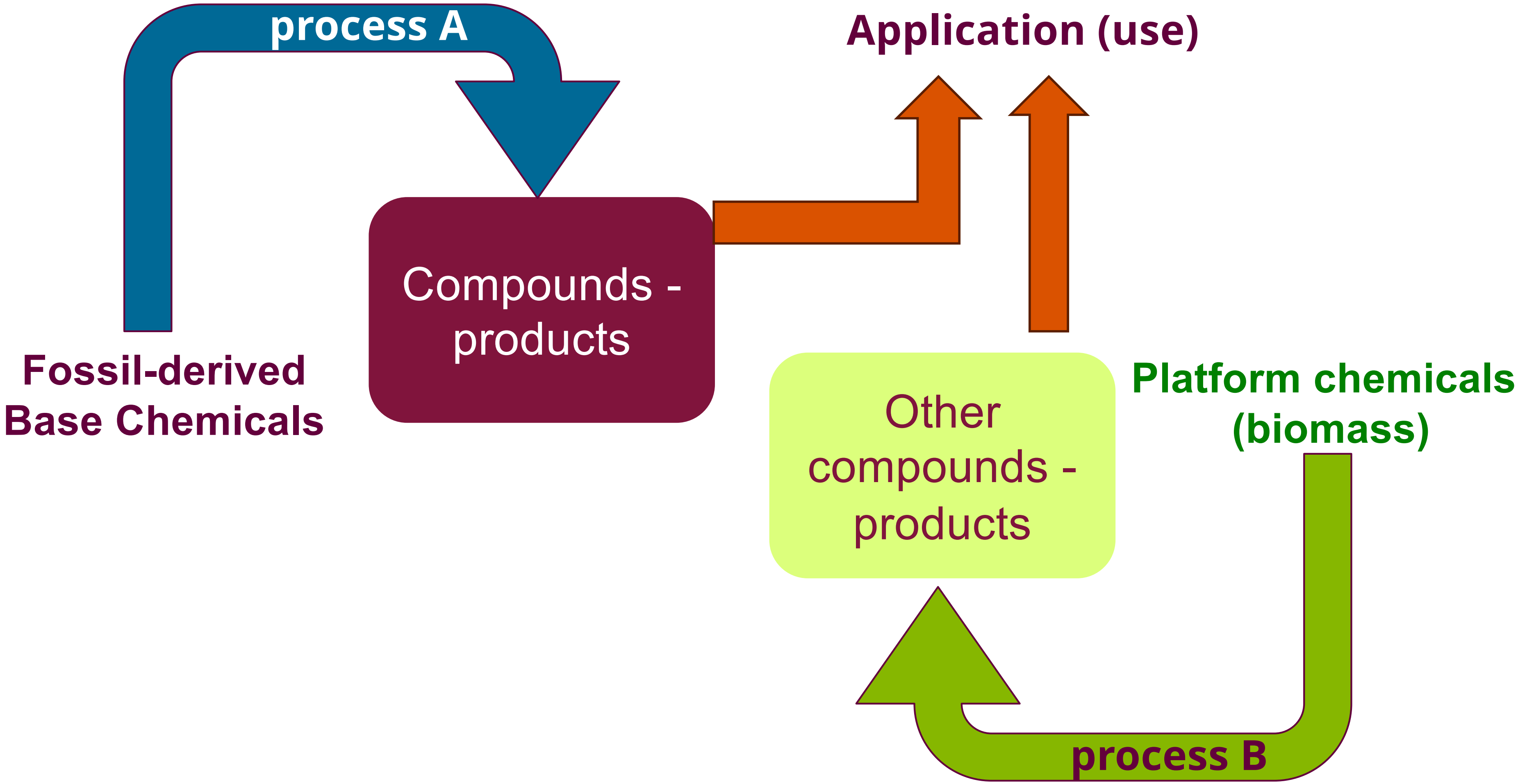
Loos K, Zhang R, Pereira I, Agostinho B, Hu H, Maniar D, Sbirrazzuoli N, Silvestre AJD, Guigo N and Sousa AF (2020) A Perspective on PEF Synthesis, Properties, and End-Life. Front. Chem. 8:585.

polyethylene-furanoate (PEF)



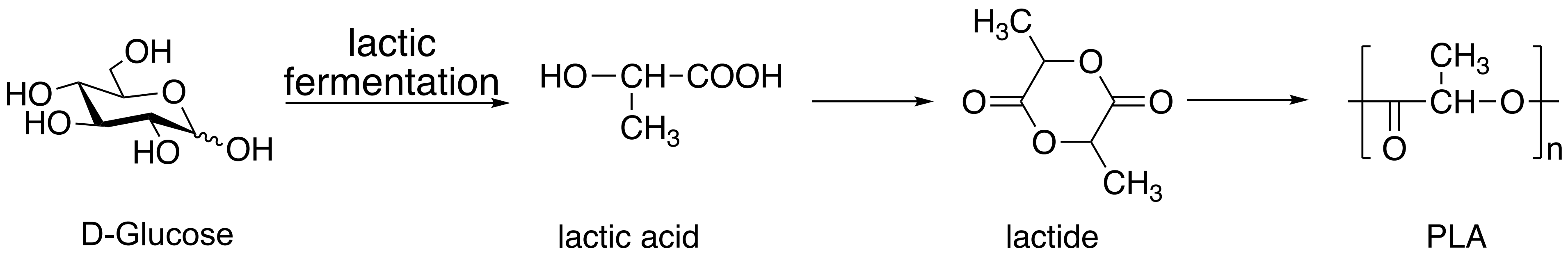
•Main applications Bottles: Water bottle, beverage bottle etc
•3D printing: filament for 3D printers
•Fibers: apparels, carpets, home furnishing, disposables commodities, fabrics, diapers, filters and industrial fibres
•Films: single use gloves, bags, agricultural films

Functional approach (application approach)



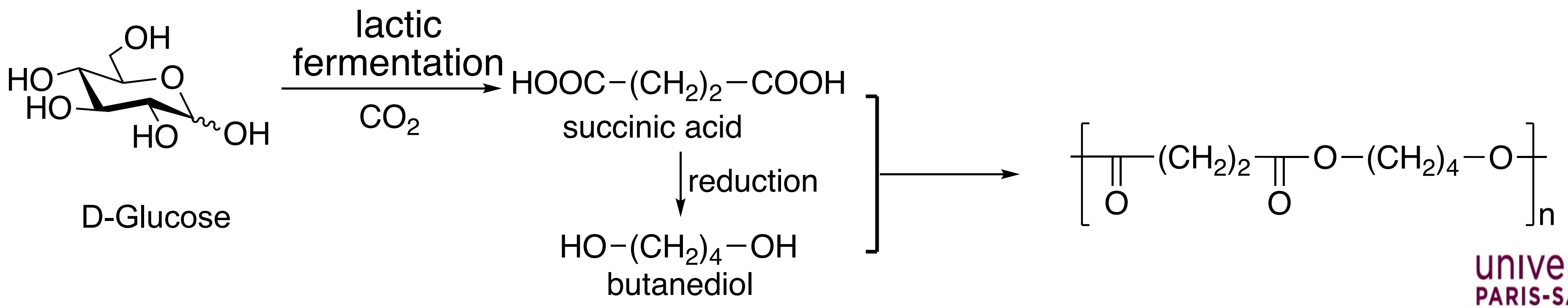
Bio-sourced polymers – other examples

polylactic acid (PLA)

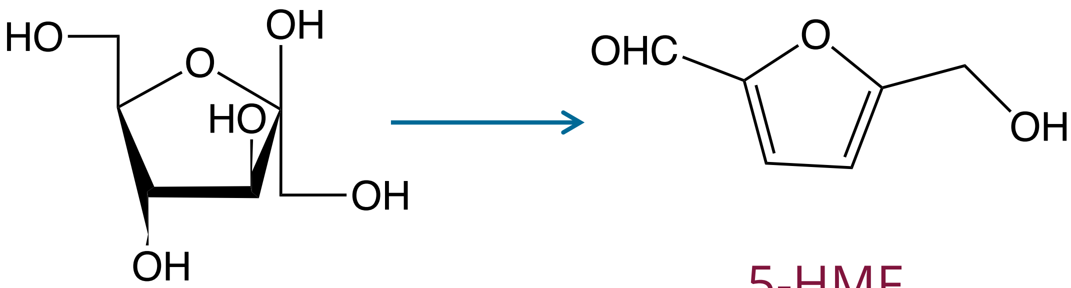


polyhydroxyalkanoates (PHA)

poly(butylene succinate) (PBS)



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

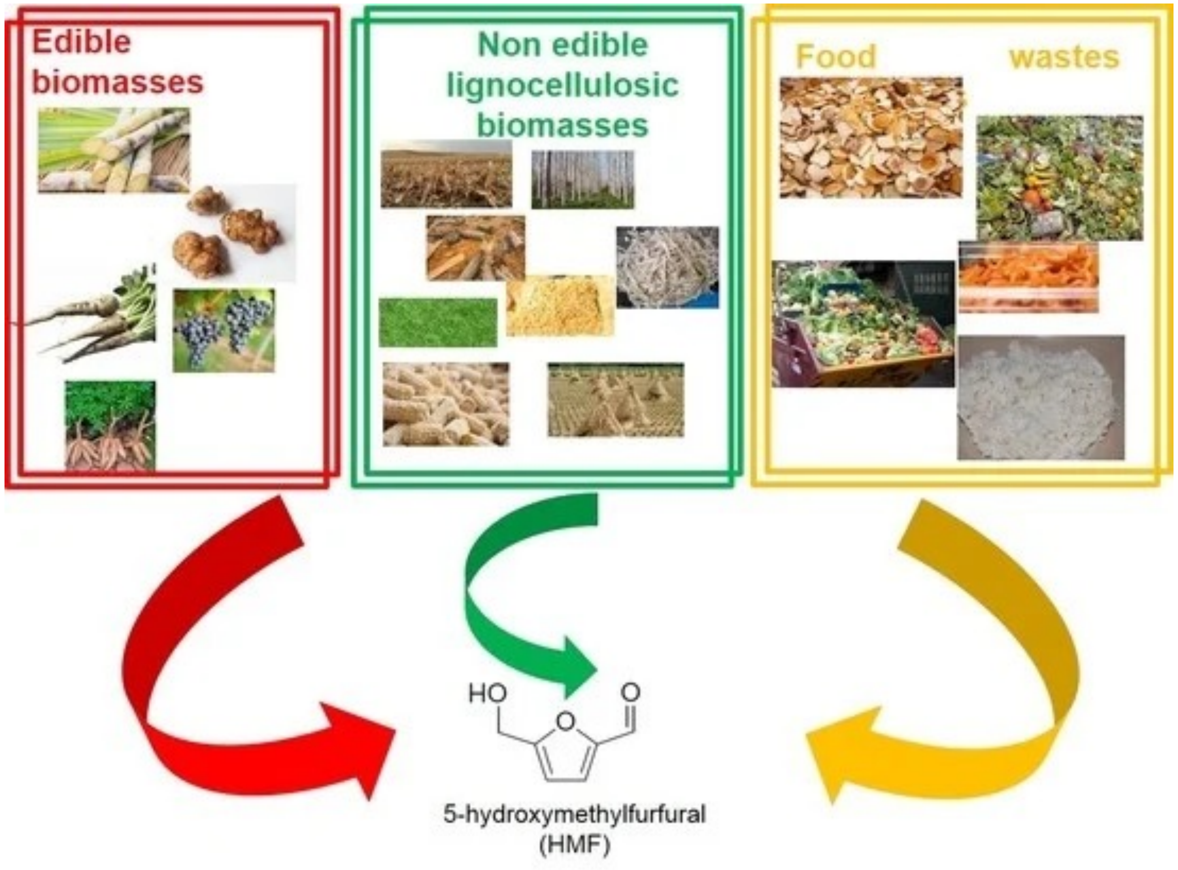


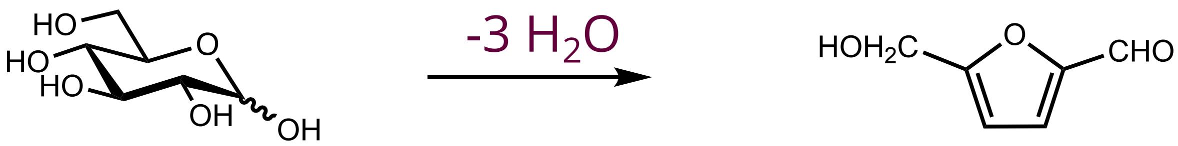
D- fructose

5-HMF

sugar molasses

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



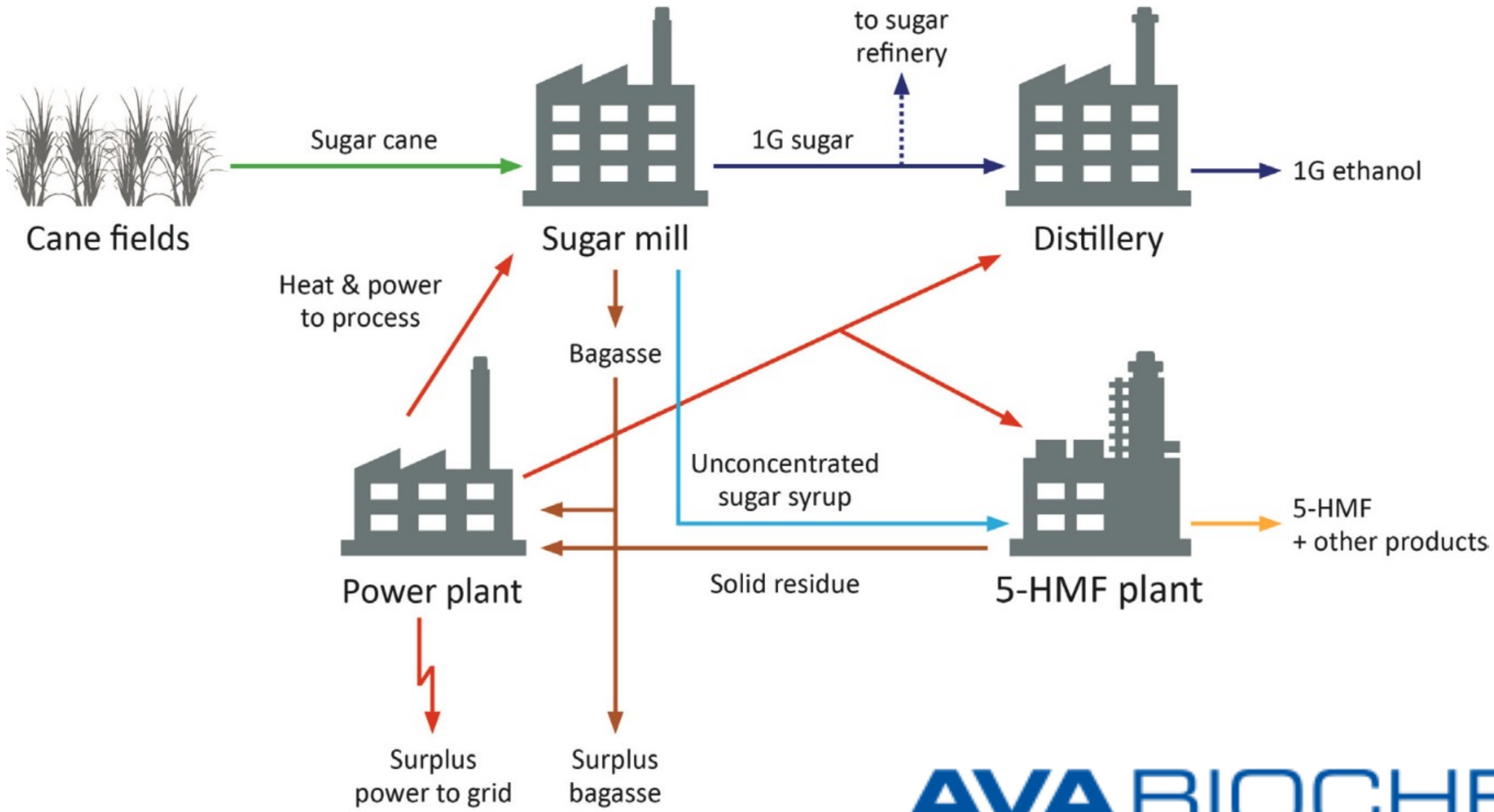


D-glucose
$C_6H_{12}O_6$

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

Industrial production of 5-HMF, an example



AVA BIOCHEM

T. Kläusli Green Process Synth 2014; 3: 235–23

5-HMF:

Press release
November 13, 2023, Rueil-Malmaison

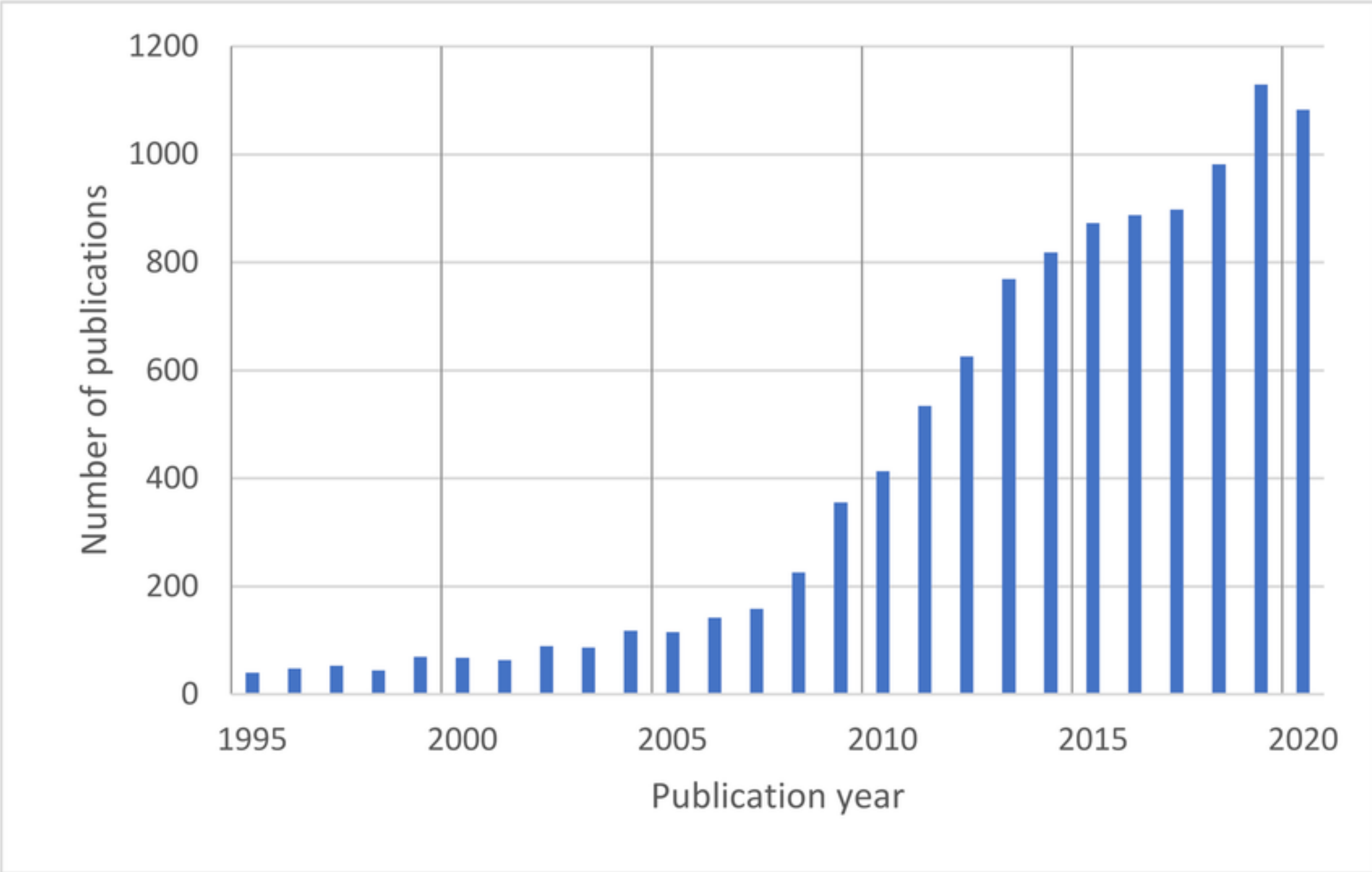
As part of a collaboration initiated at the end of 2021, IFP Energies nouvelles (IFPEN) and ResiCare, a Michelin Group entity, announce that they have co-developed a process for producing the molecule 5-hydroxymethylfurfural (5-HMF) from fructose, particularly used in the manufacture of bio-based resins. 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

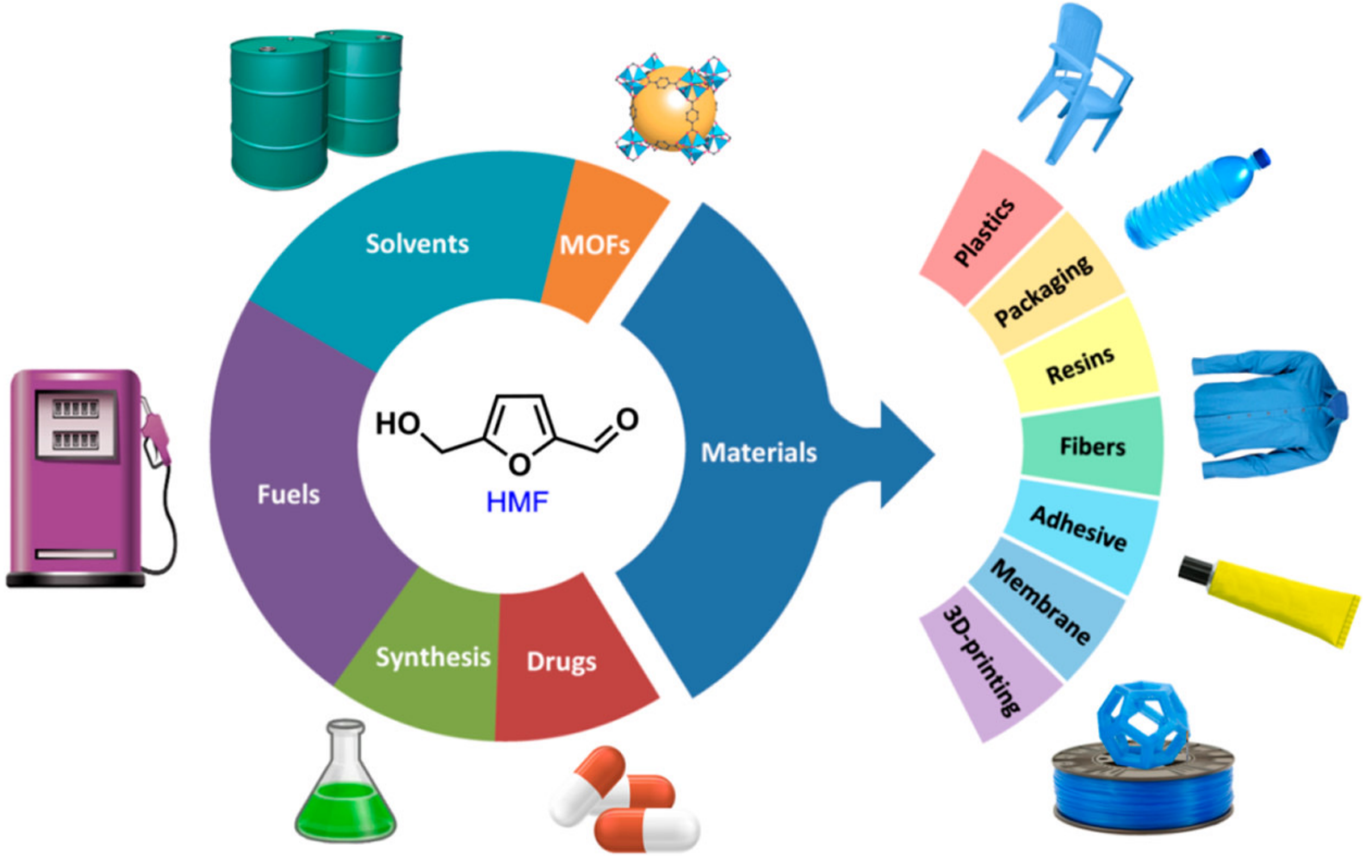
Following ten years of laboratory research on the conversion of fructose into a biosourced molecule, 5-HMF, IFPEN joined forces with ResiCare in 2021 to develop a process for producing 5-HMF on an industrial scale.

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

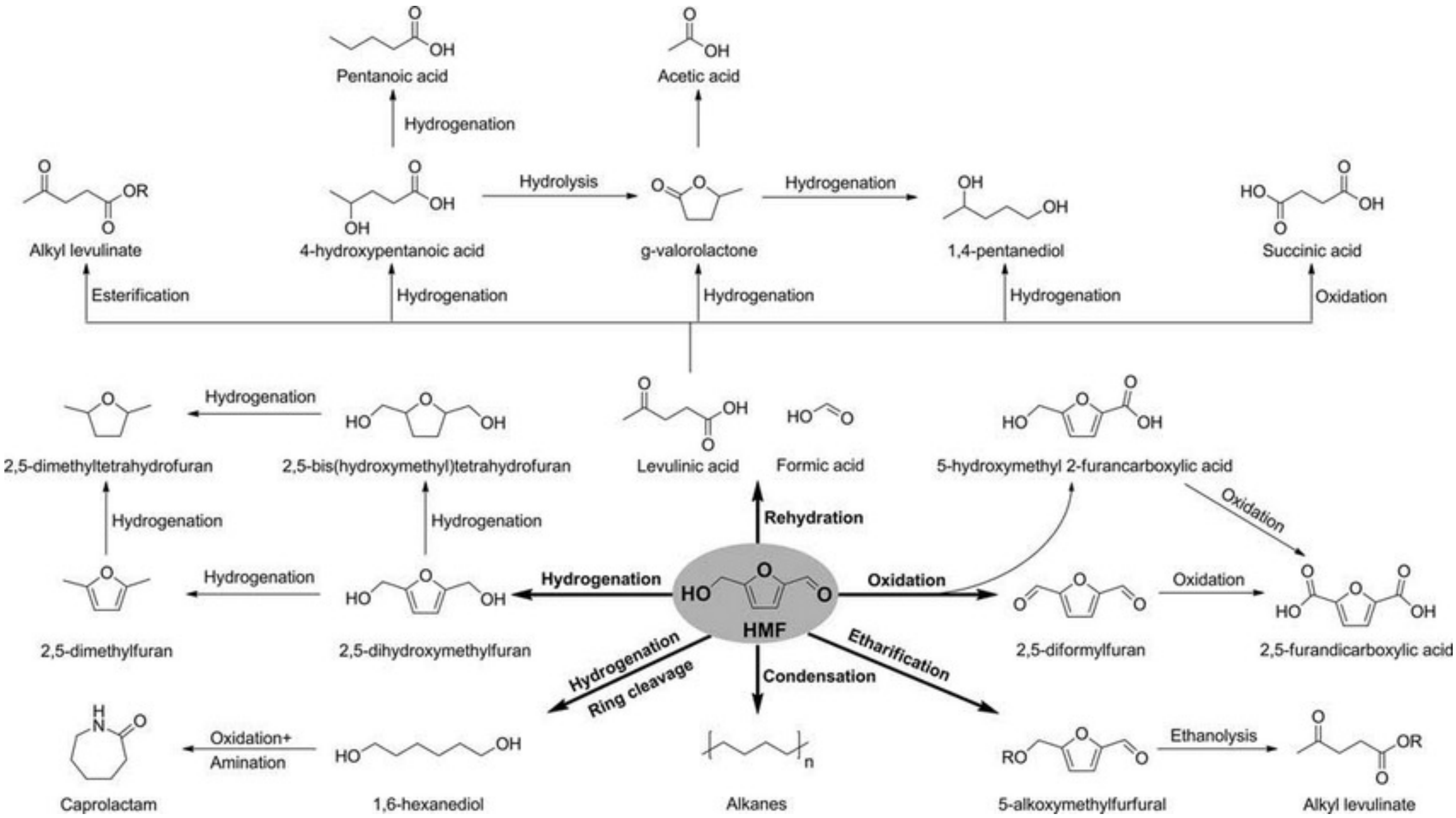
Publications-on-5-HMF-per-year-keyword-search-for-hydroxymethylfurfural-in-CAS



5-HMF: Potential applications



5-HMF: Furanic platform chemical



Prasenjit Bhaumik & Paresh Laxmikant Dhepe (2016) Solid acid catalyzed synthesis of furans from carbohydrates, Catalysis Reviews, 58:1, 36-112,

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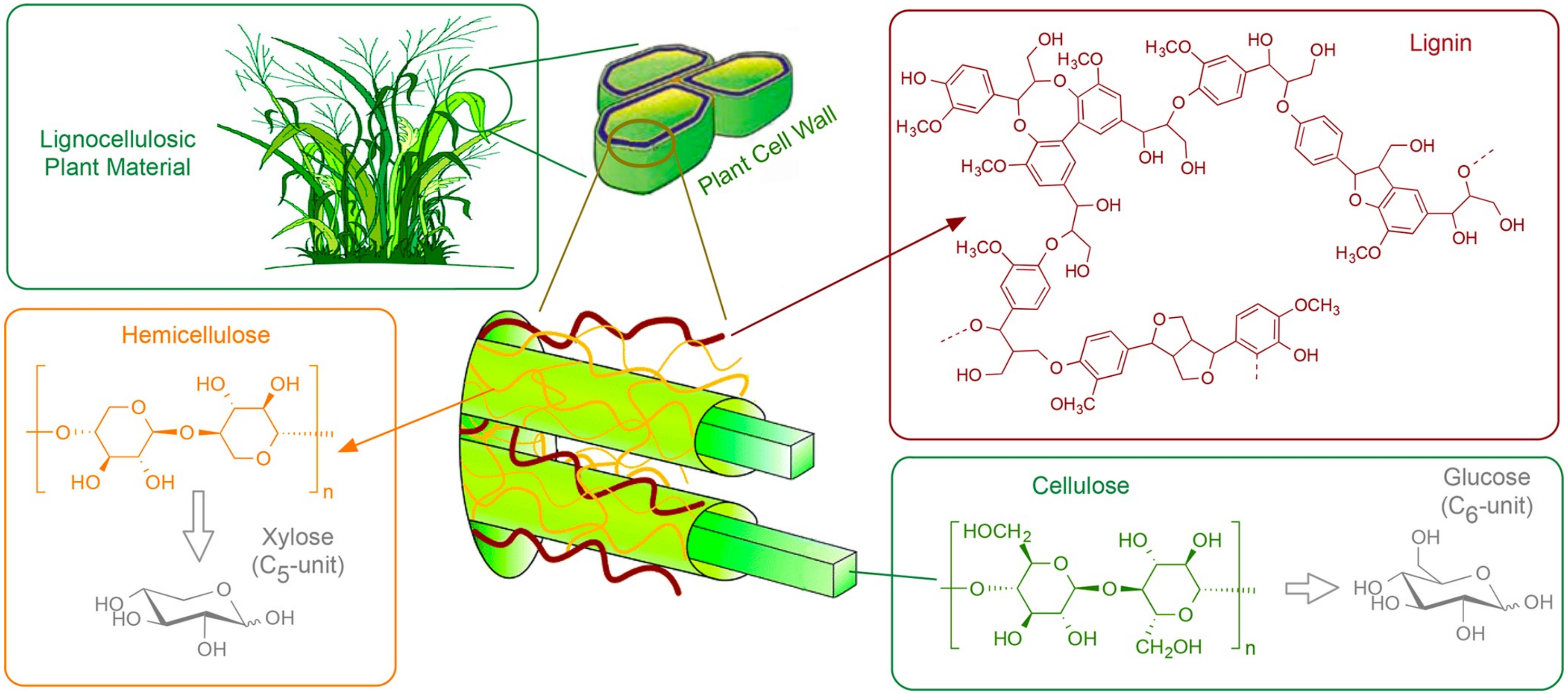
Lignocellulosic biomass

180-billion-ton annual production rate, 8.2 billion tons are utilized



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

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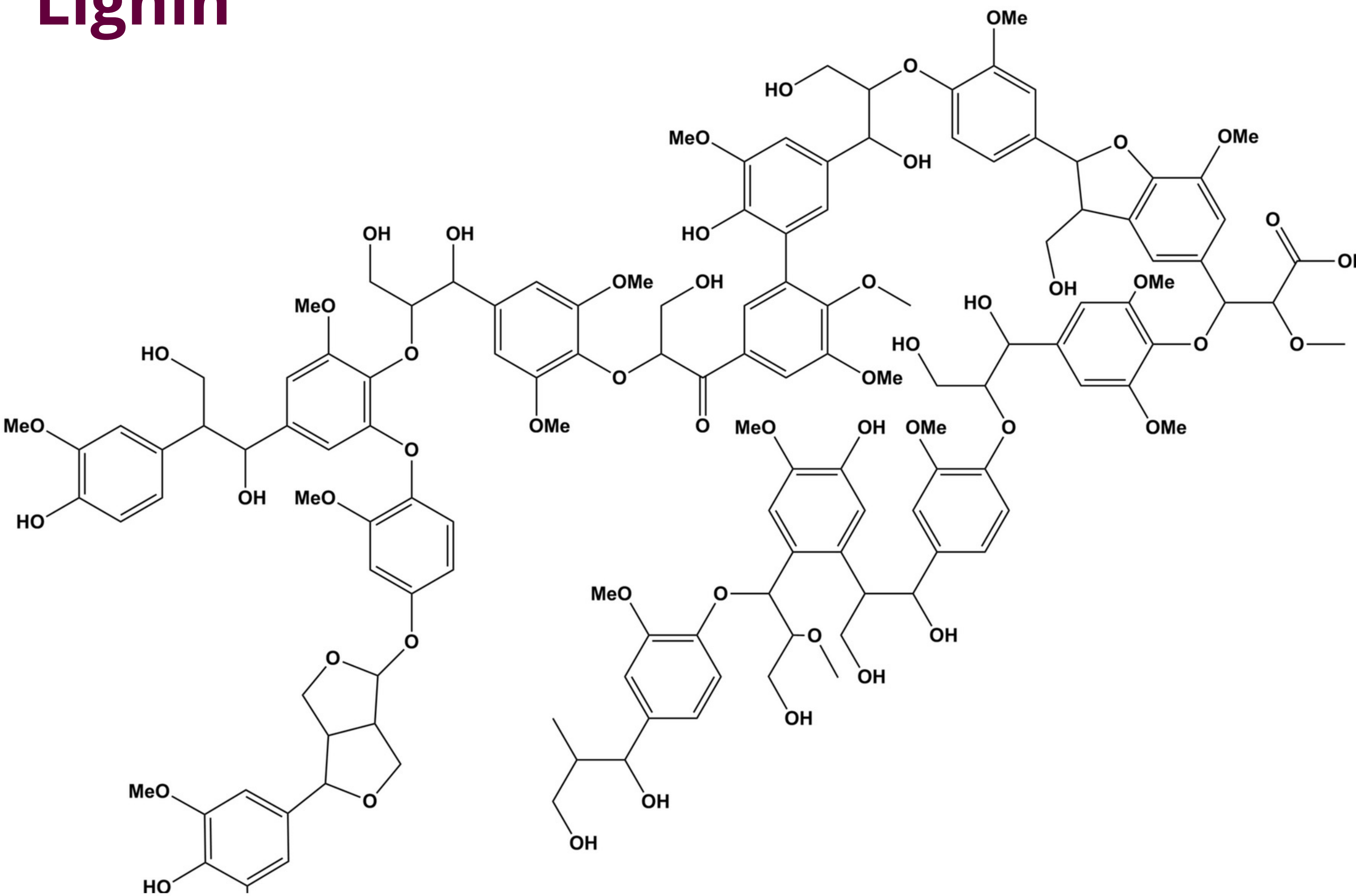
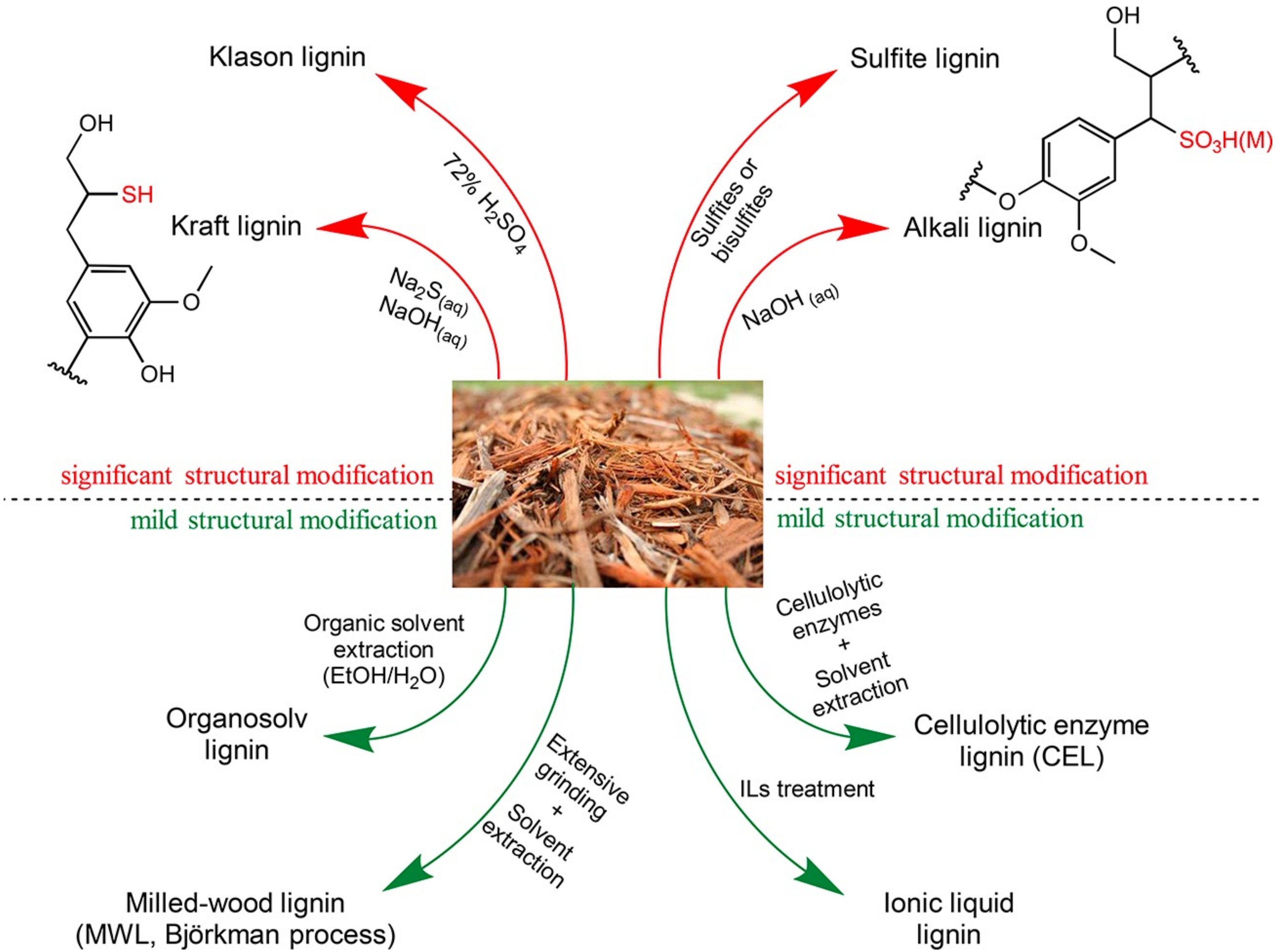
Lignin



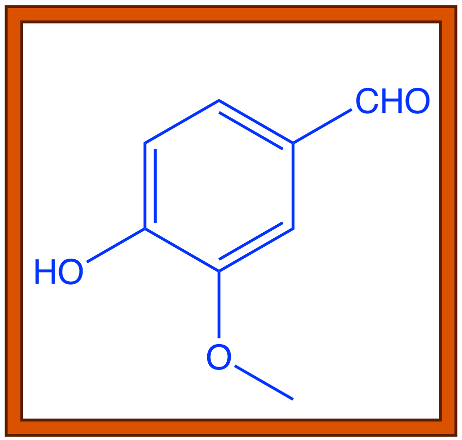
~ 20% of the biomass

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

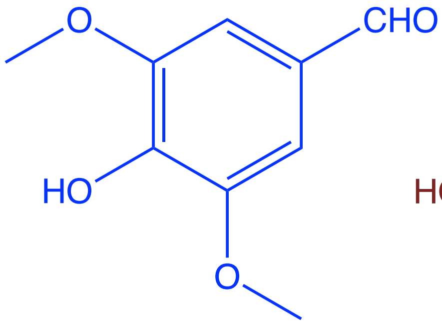


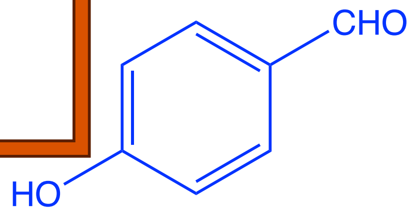
Sun et al. *Chem. Rev.* 2018, 118, 2, 614–678

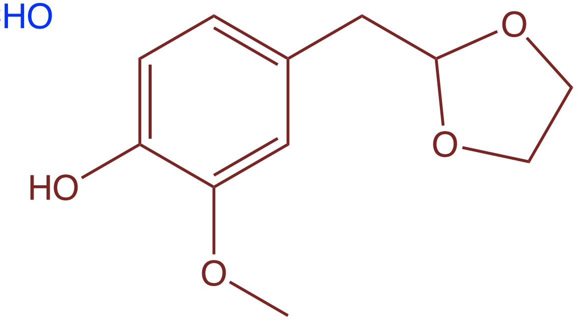
Lignin-derived monomers

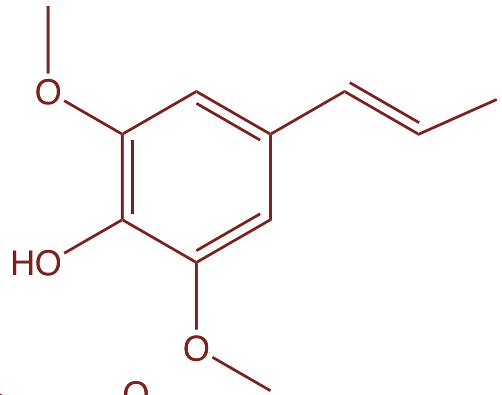


Vanillin

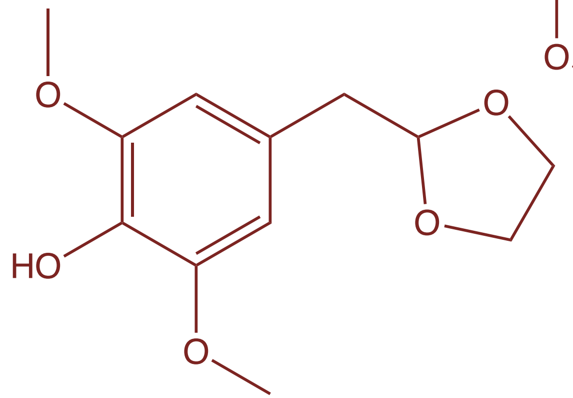


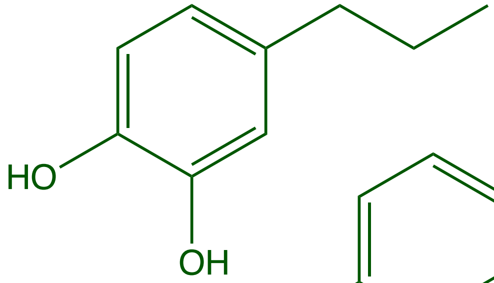


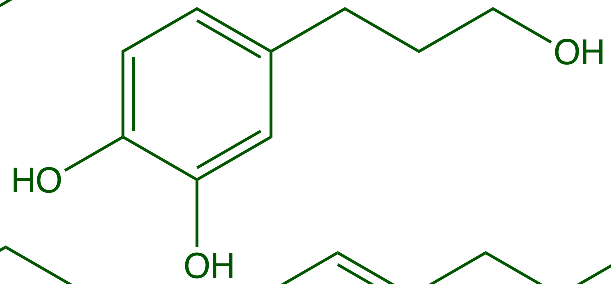


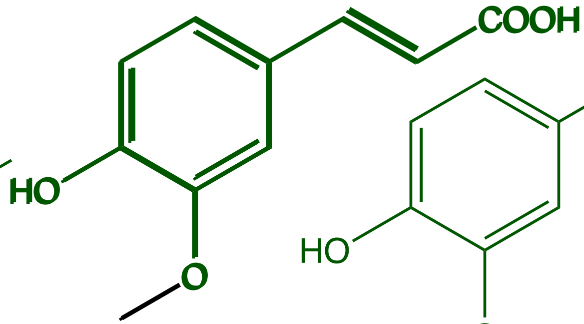


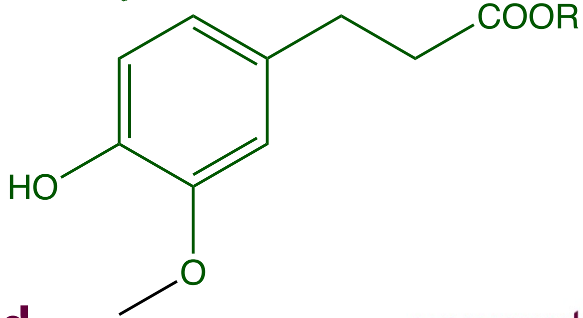
lignin

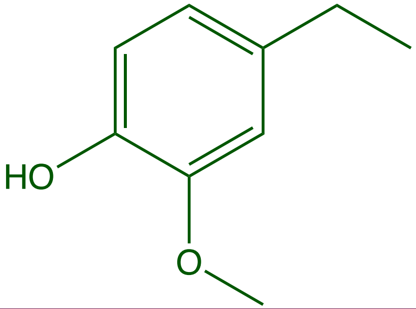


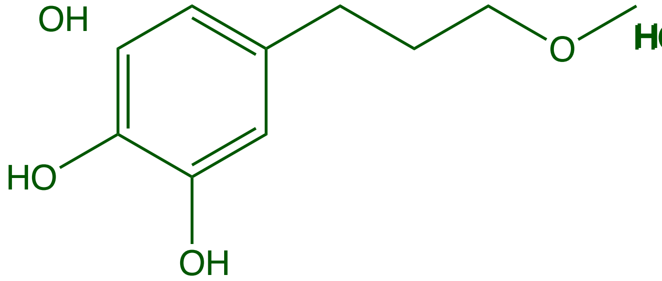






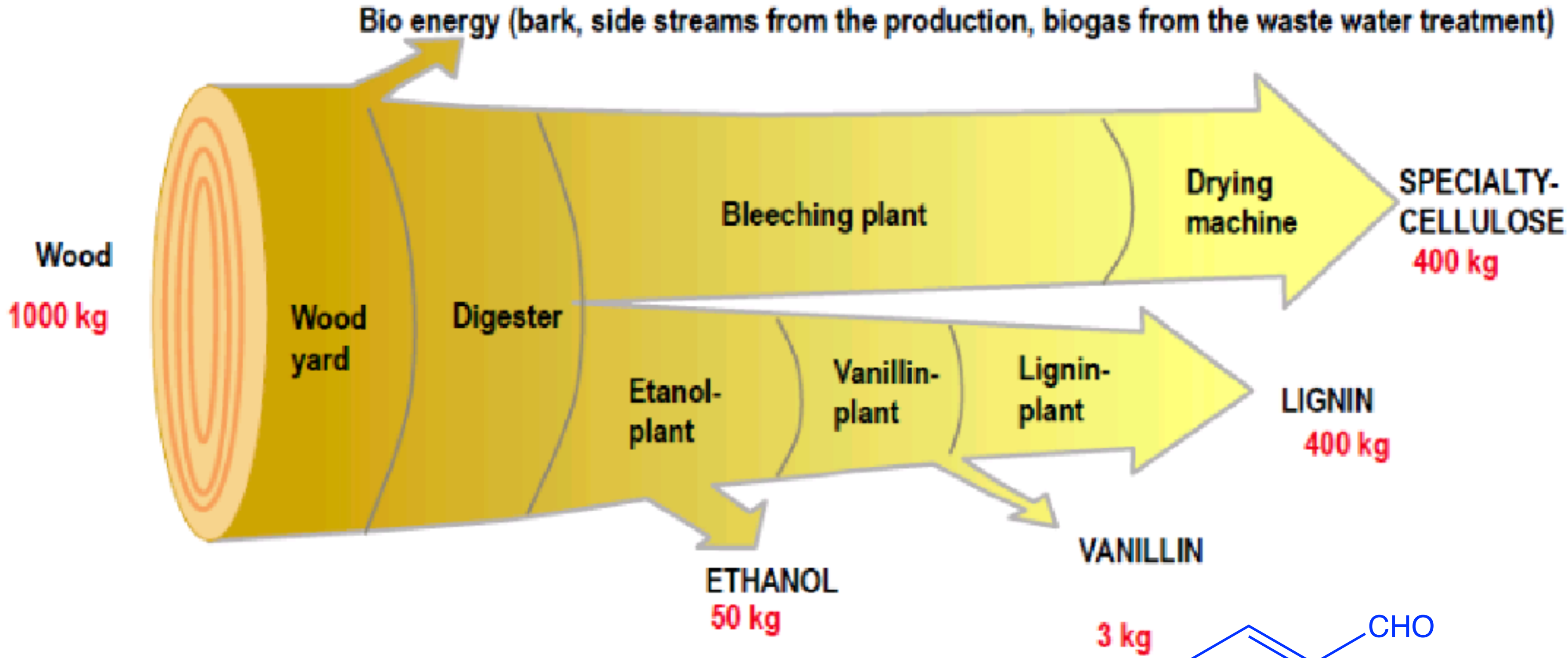


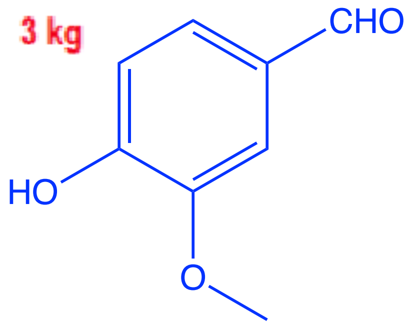




ferulic acid

Exemple : Borregaard biorefinerie (Norway)





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

Borregaard

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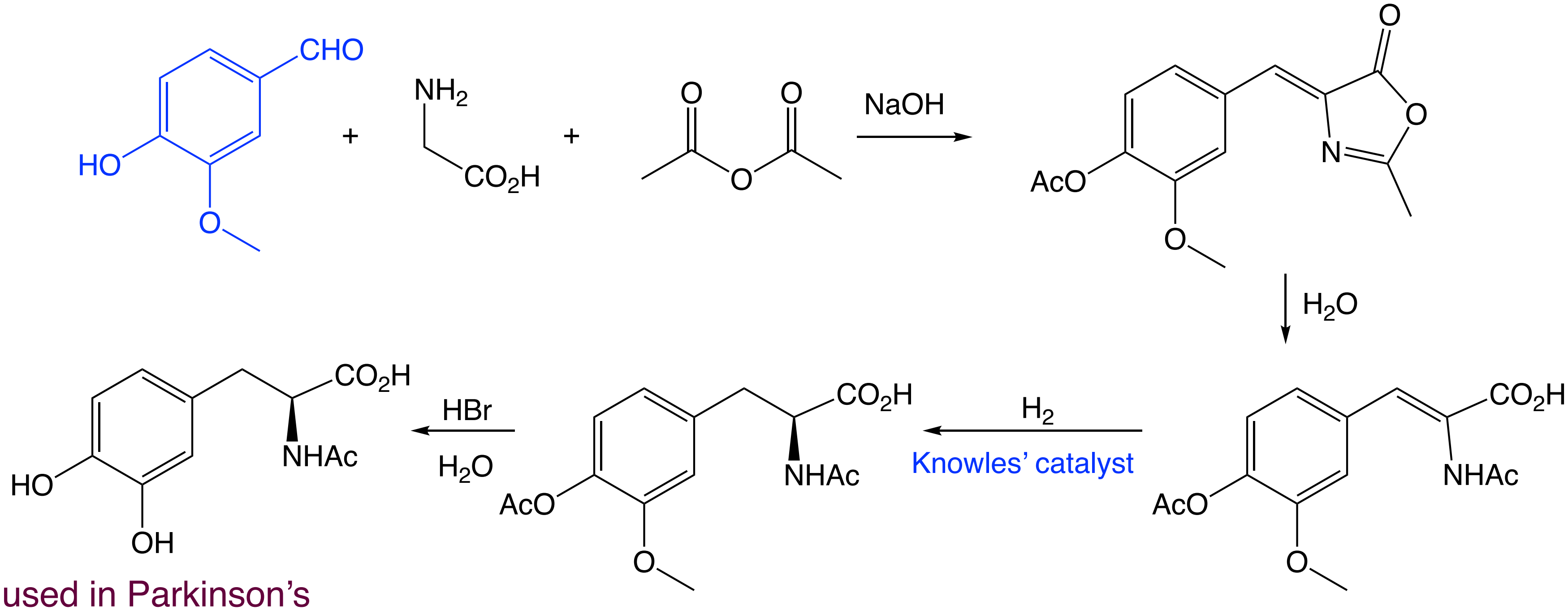
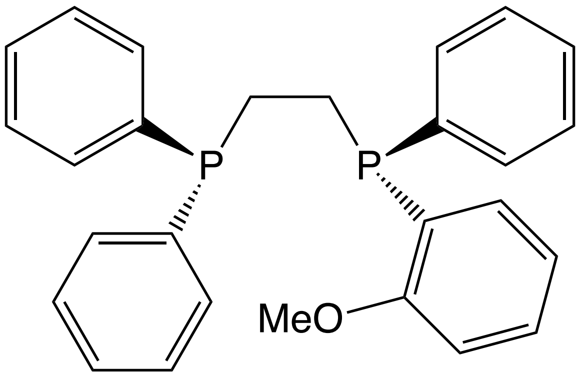
Synthesis of L-dopa from vanillin via the Monsanto Process



used in Parkinson's disease treatment

Knowles' catalyst

Rh(DiPAMP)

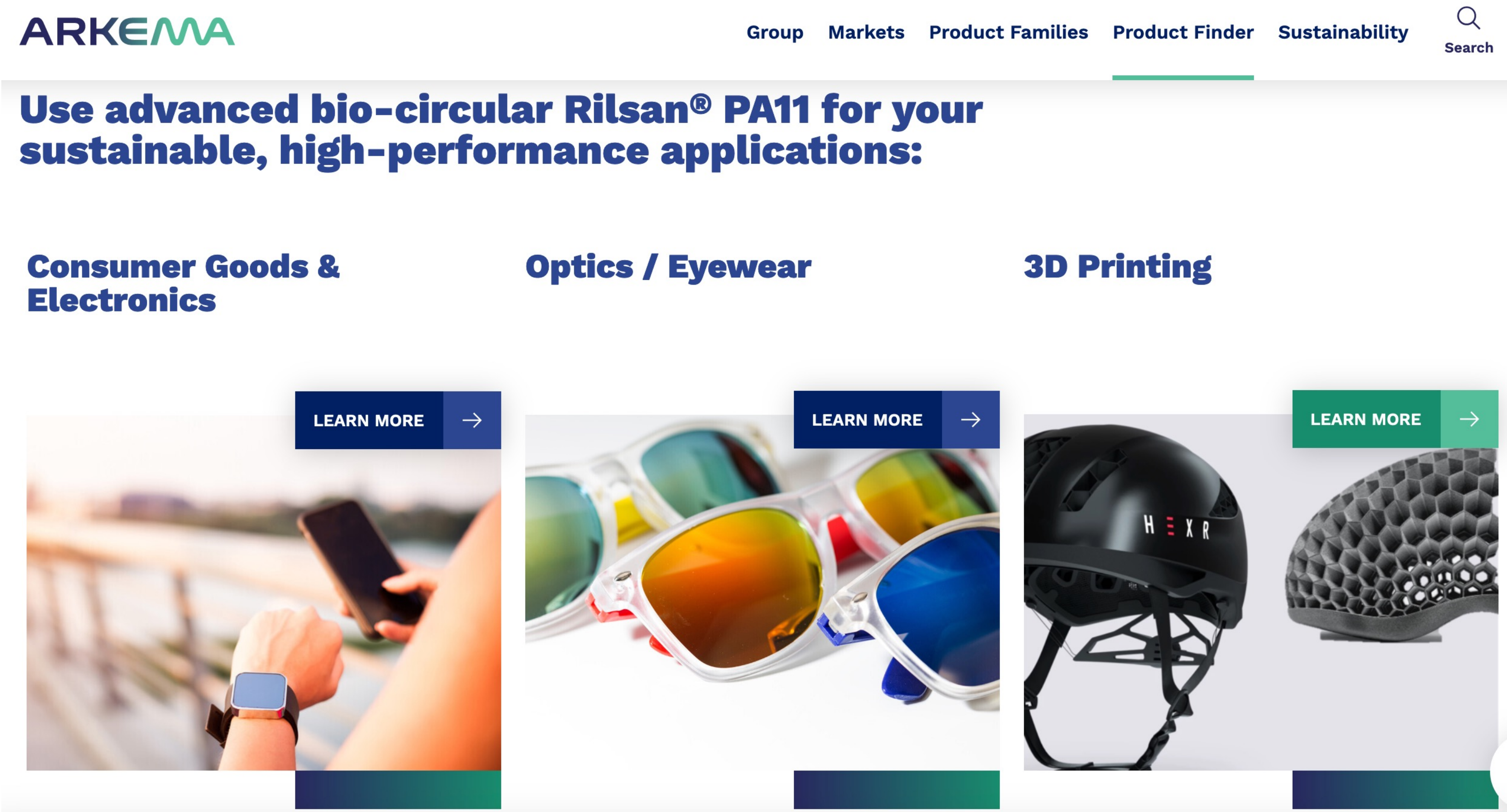


1,2-Ethanediylbis[(2-methoxyphenyl)(phenyl) phosphine]

MONSANTO

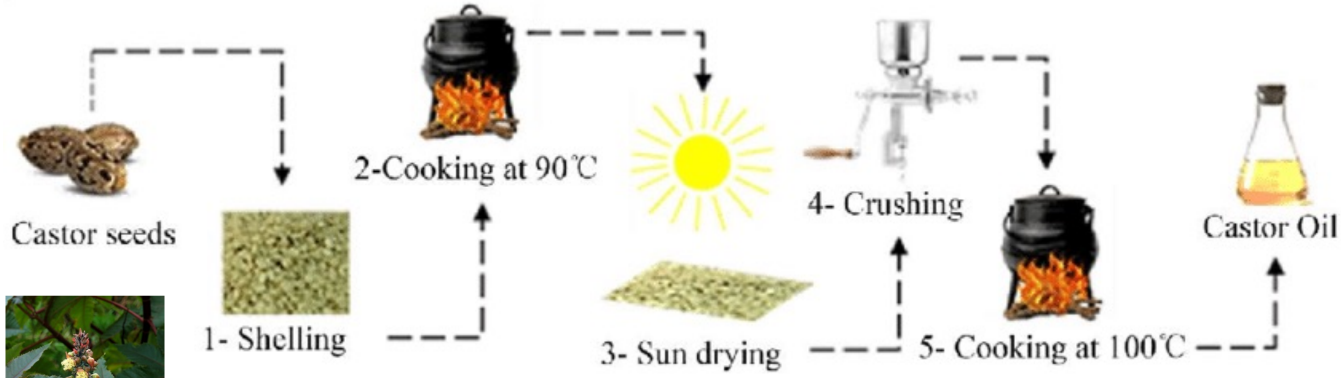
William S. Knowles
The Nobel Prize in Chemistry 2001

Examples: Bio-sourced polymers – Rilsan

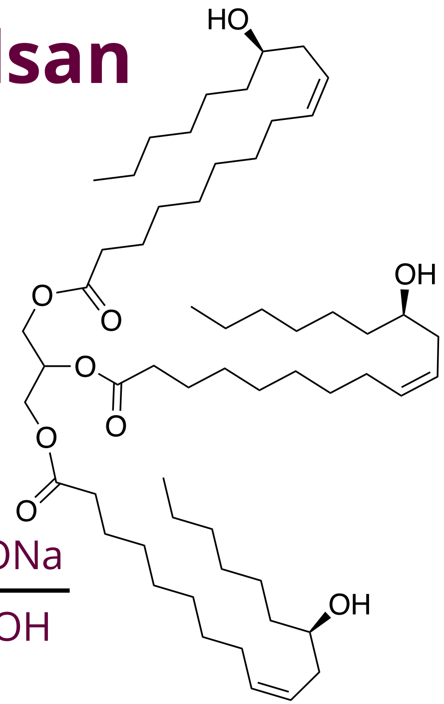


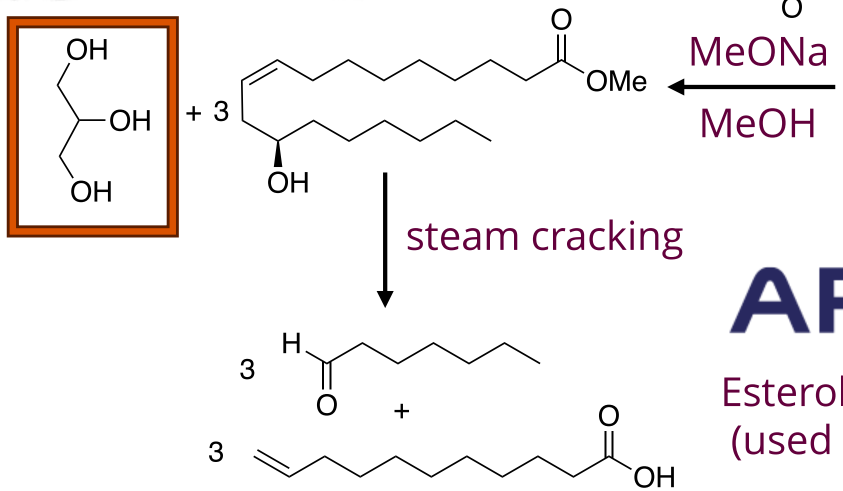
https://www.arkema.com/global/en/products/product-finder/product/technicalpolymers/rilsan-family-products/rilsan-pa11/

Examples: Bio-sourced polymers – Rilsan



ricinus

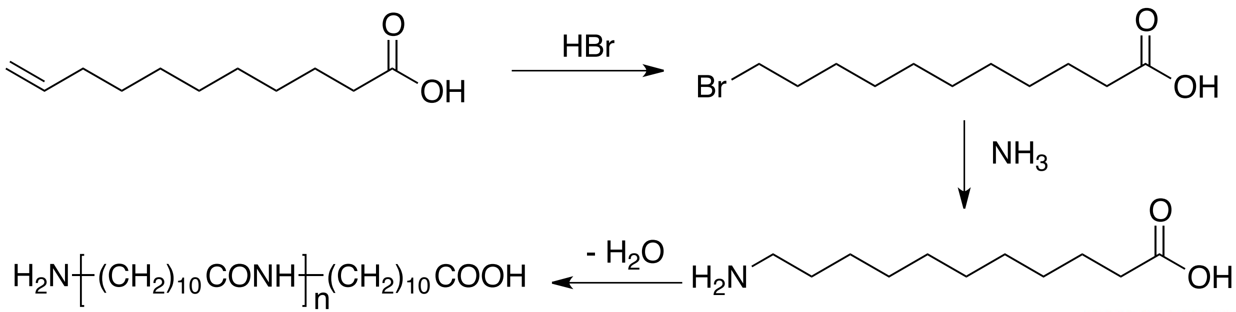




ARKEMA

Esterol
(used as a lubricant additive)

functional approach
(application approach)



Rilsan 11

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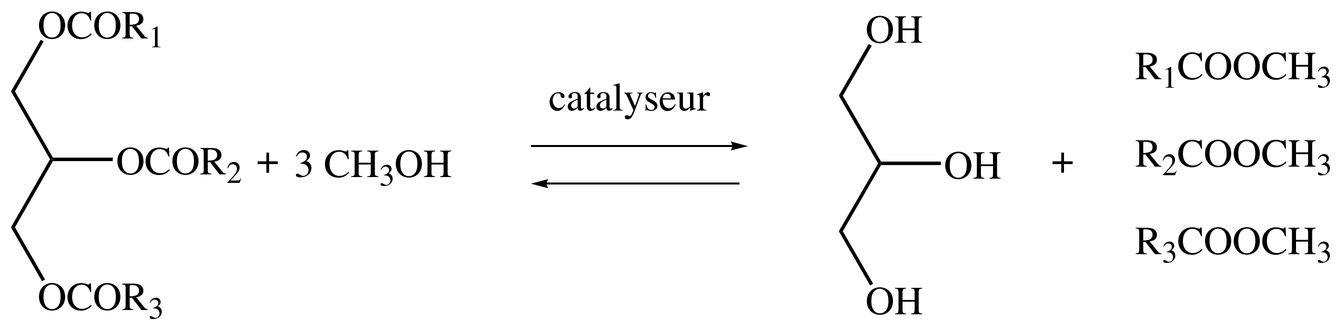
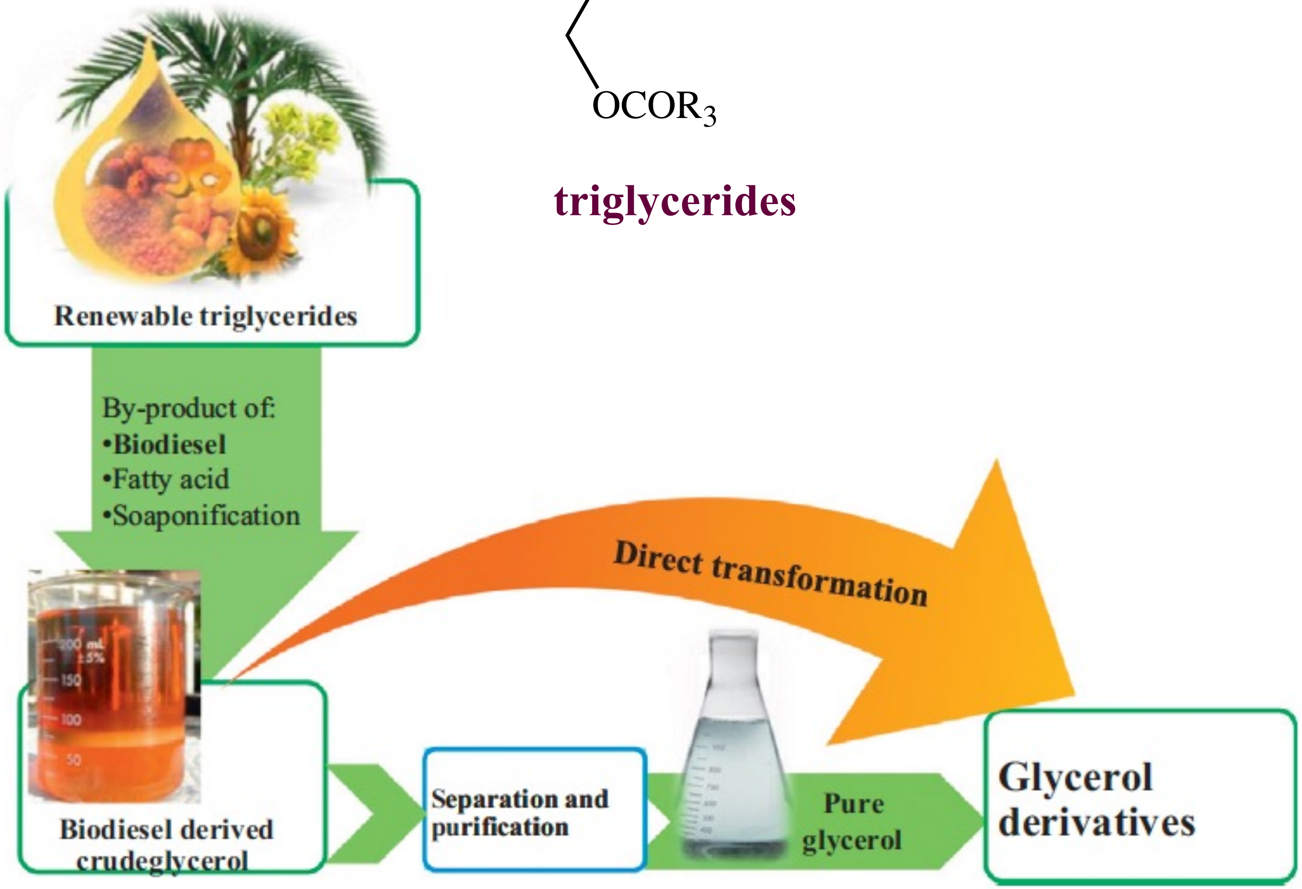
Glycerol

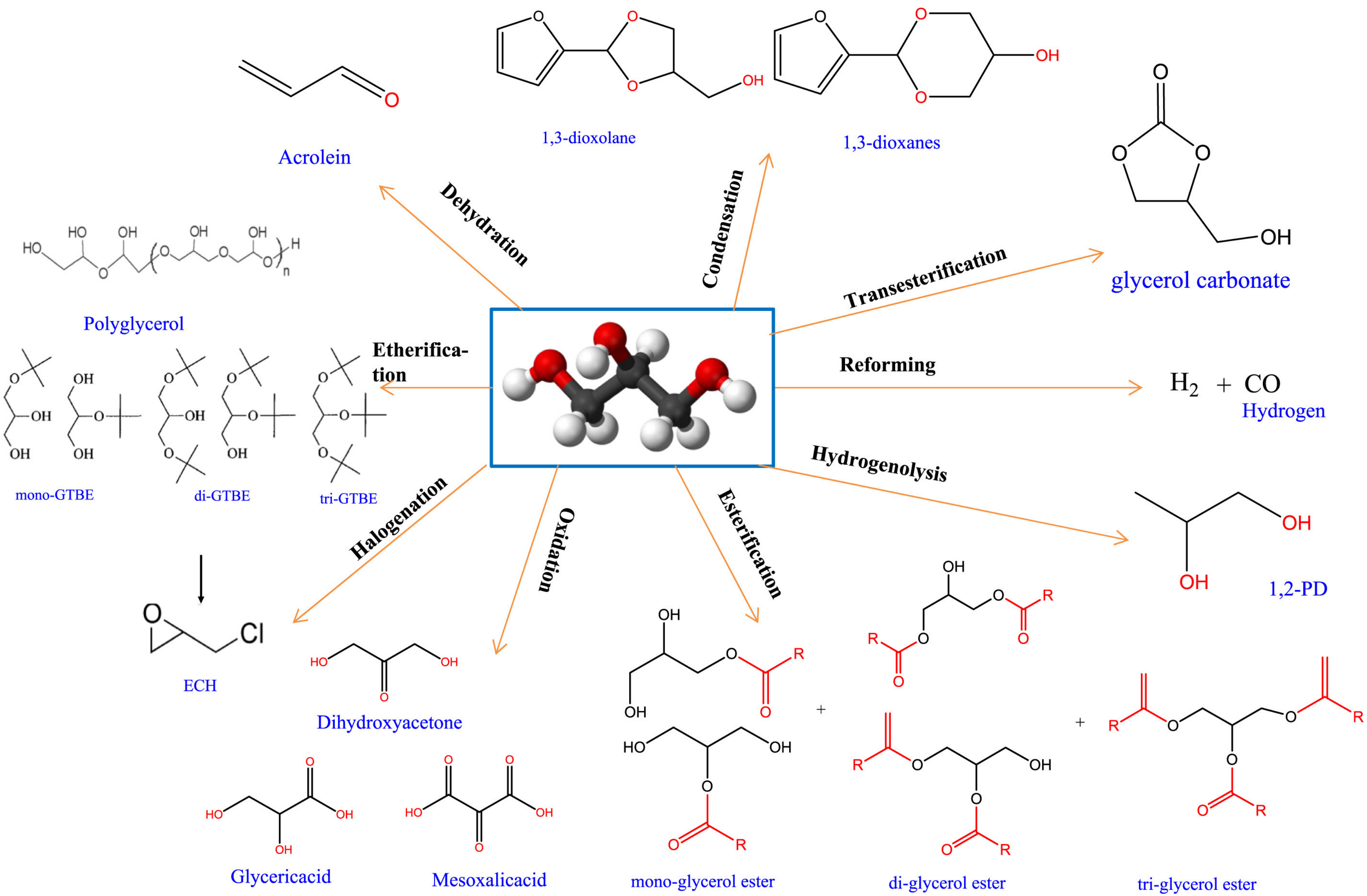


triglycerides **glycerol** **fatty esters**



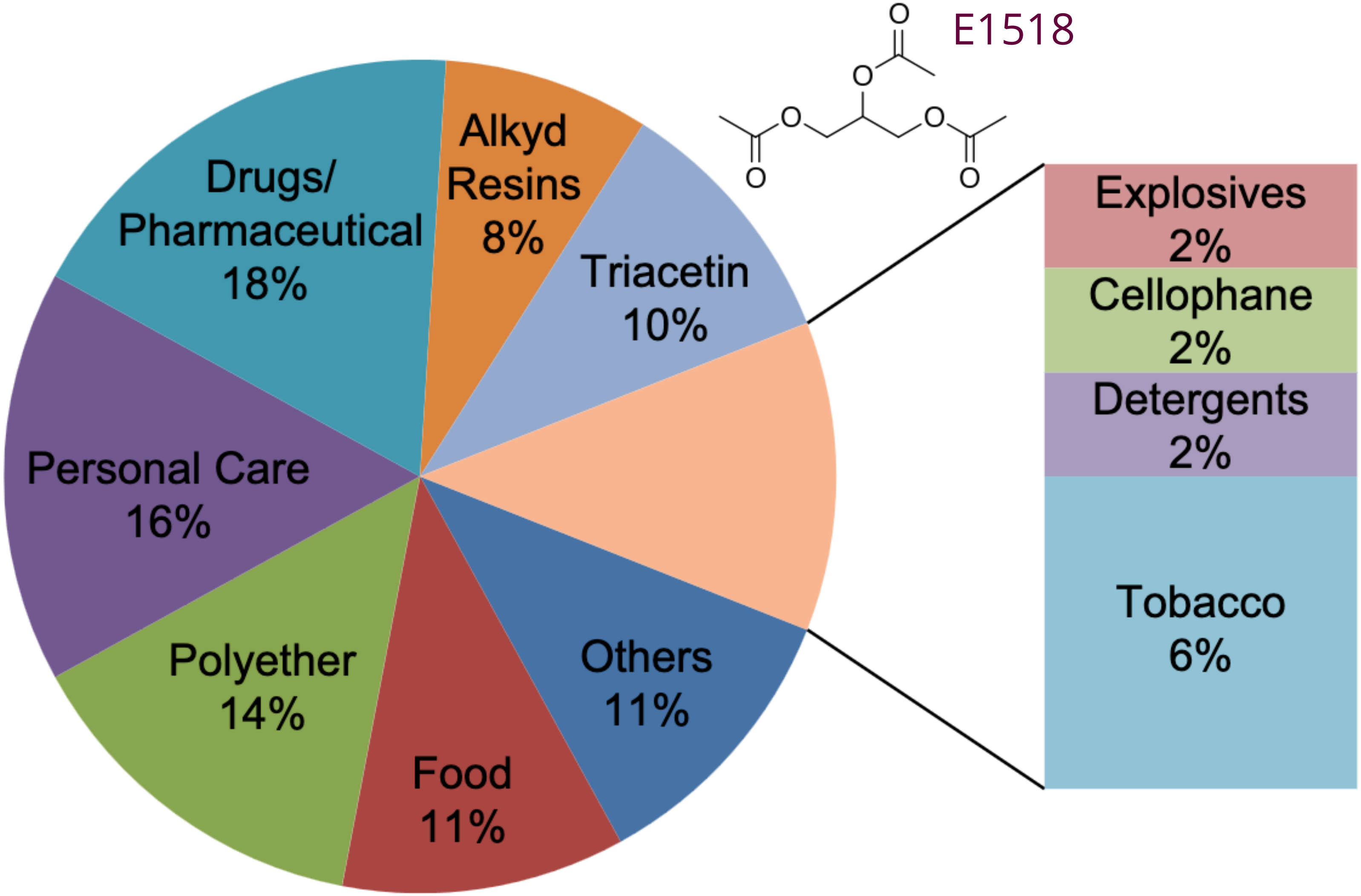
Recent Advances in Glycerol Catalytic Valorization: A Review. M. Checa, S. Nogales-Delgado, V. Montes, J. M. Encinar. Catalysts 2020, 10, 1279
Conversion of crude and pure glycerol into derivatives: A feasibility evaluation
P. S. Kong, M. K. Aroua , W. M. A.W. Daud. Renewable and Sustainable Energy Reviews 63 (2016) 533–555

Glycerol platform chemicals



Glycerol industrial applications

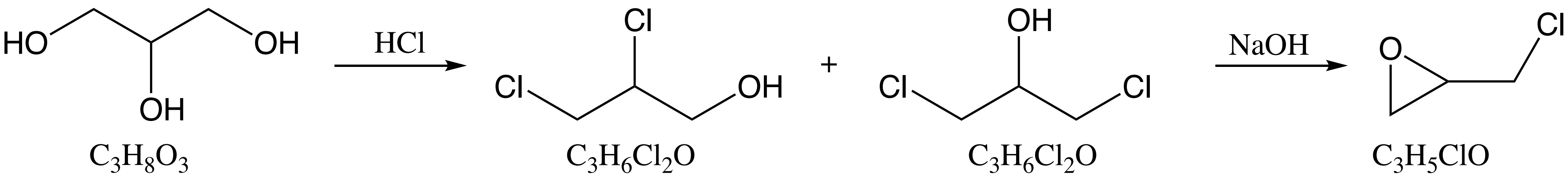
E1518



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.

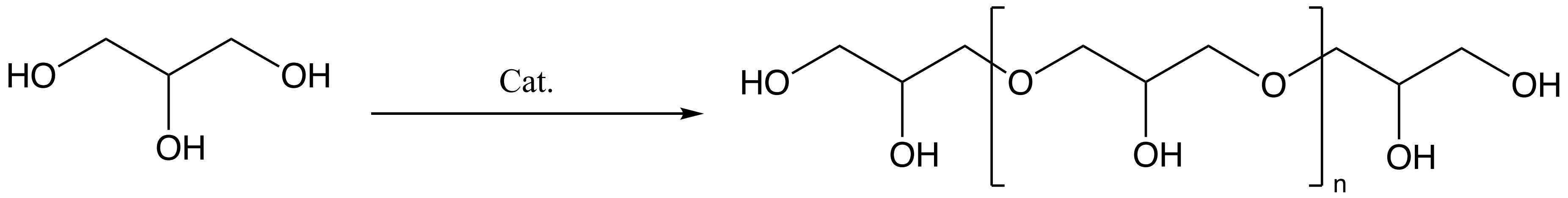
Glycerol platform chemicals: épichlorhydrine

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



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)

Glycerol platform chemicals: polyglycerols

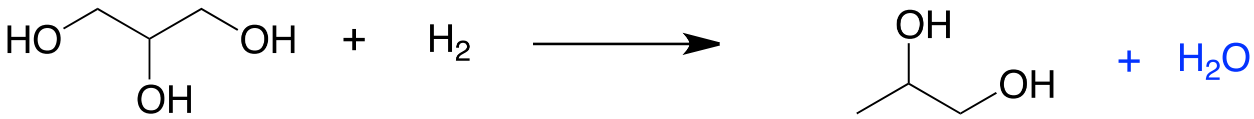


Nonionic surfactants widely used in cosmetics, additives, lubricants, biomedical and drug delivery systems.

Solvay (Belgium)
Sakamoto (Japan)

SOLVAY
asking more from chemistry®

Glycerol platform chemicals: 1,2-propanediol



Adkins catalyst: $Cu_2Cr_2O_5$
(copper chromite)

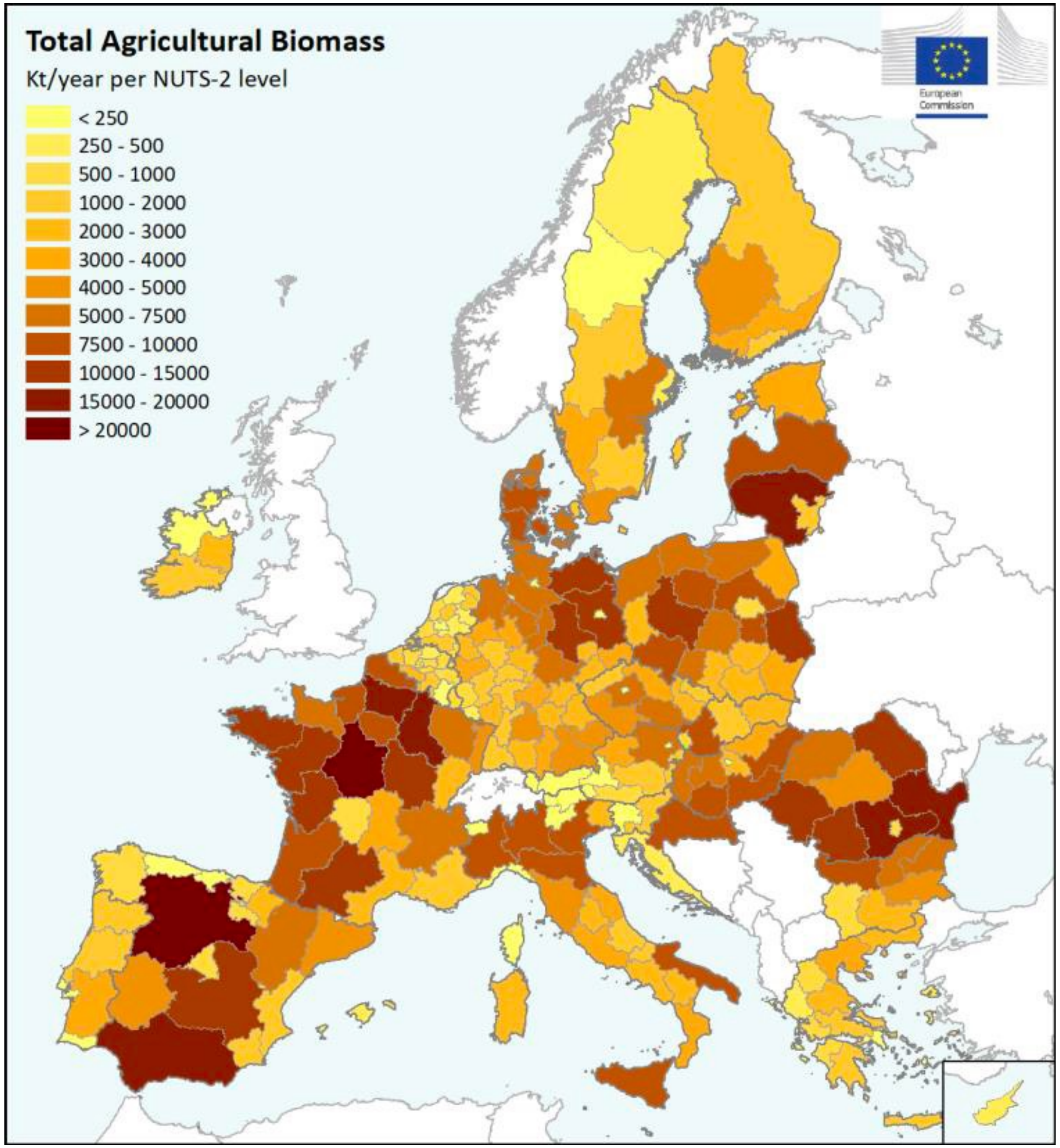
Antifreeze, additives in pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants and paints

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

Alternative feedstocks - renewable feedstocks

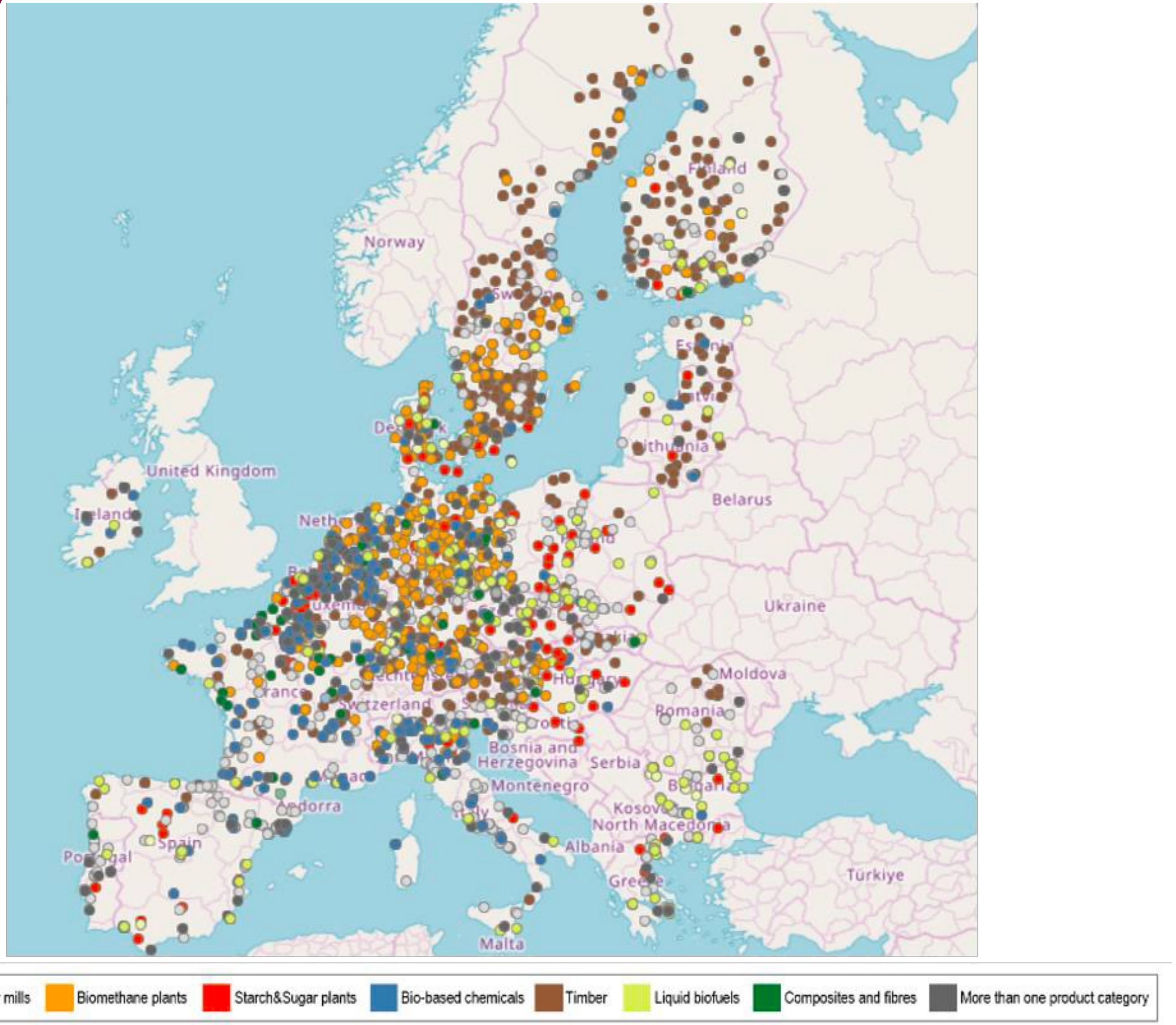


Distribution of agricultural biomass production (in Kt dry matter per year) across the EU for the reference period 2016-2020
Source: JRC 2022

Approximately 70% of the agricultural biomass is produced in

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

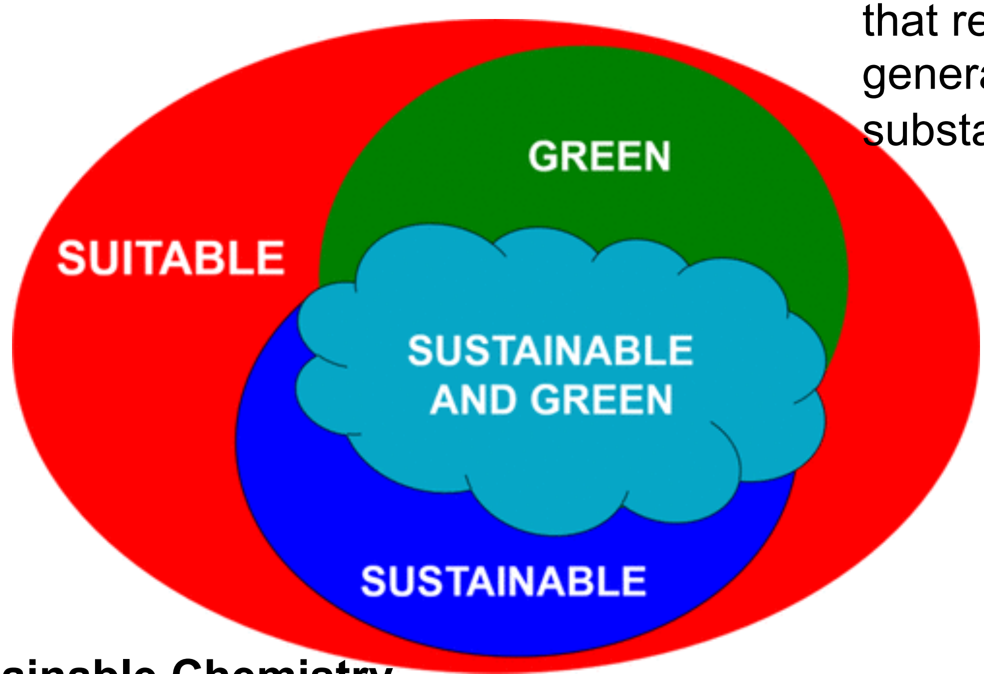
Territorial distribution of bio-based industries and biorefineries in the EU-27



Dots in lighter colour in each category indicate facilities that are currently inactive (but not necessarily as a permanent status)

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

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



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.

Sustainable development "*should meet the needs of the present without compromising the ability of future generations to meet their own needs*

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Couleurs de l'hydrogène et impact carbone

membranes-12-00173-v2

H2	PROCÉDÉ	MATIÈRE PREMIÈRE	ÉNERGIE	ÉMISSIONS DE CO_2
HYDROGÈNE NOIR	Gazéification	Charbon + eau	Combustibles fossiles	Très élevées
HYDROGÈNE BRUN		Charbon brun (lignite) + eau		
HYDROGÈNE GRIS	Vaporeformage	Méthane + eau		Élevées
HYDROGÈNE BLEU	Vaporeformage + captage du CO_2			Moyennement élevées
HYDROGÈNE JAUNE	Électrolyse	Eau	Électricité nucléaire	Faibles
HYDROGÈNE VERT			Électricité renouvelable	
HYDROGÈNE TURQUOISE	Pyrolyse	Méthane ou biométhane	Électricité (toutes origines)	Faibles ou nulles selon l'énergie utilisée

Illustration : Choisir.com

https://www.bioeconomie-grandest.fr/focus-sur-la-bioraffinerie-de-bazancourt-por

https://www.grandreims.fr/entreprendre-innover-etudier/recherche-innovation/bioe

Thénot, Maryline & Bouteiller, Christophe & Lescieux-Katir, Honorine. (2018). Des coopératives agricoles agents de symbiose industrielle : Étude de la bioraffinerie de Bazancourt-Pomacle (Marne, France). Revue internationale de l économie sociale Recma. N° 347. 10.3917/recma.347.0031.

- Implantation sur 260 hectares
- 1 200 emplois directs sur site
- 1 000 emplois indirects sur le bassin rémois
- 4 millions de tonnes de biomasse transformées chaque année

https://www.canal-u.tv/chaines/agreenium/seminaires-2021/presentation-de-la-bioraffinerie-de-bazancourt-pomacle-jean-marie

1 million de tonnes de blé et 2,5 millions de tonnes de betteraves pour servir de matière première à différents dérivés : carburant vert, cosmétiques végétaux, alcool ou encore, depuis peu, pellets (produit hautement calorifique qui peut remplacer le charbon de bois).

Le complexe Agro-industriel des Sohettes

Site de **Bazancourt - Pomacle**

POSITIONNEMENTS ET SYNERGIES

1 | synergie **EAU** : Récupération de Condensat
50 000 m3 de condensats excédentaires utilisés par Chamtor pendant la campagne.
Avantage : moins de prélèvements dans la nappe phréatique et récupération d'énergie.

2 | synergie **VAPEUR**
Un secours vapeur réciproque.
Avantage : fiabilisation des outils industriels.

3 | synergie **EFFLUENTS**
EPURATION – STOCKAGE – EPANDAGE
Avantage : Maîtrise et approche globale agronomique.

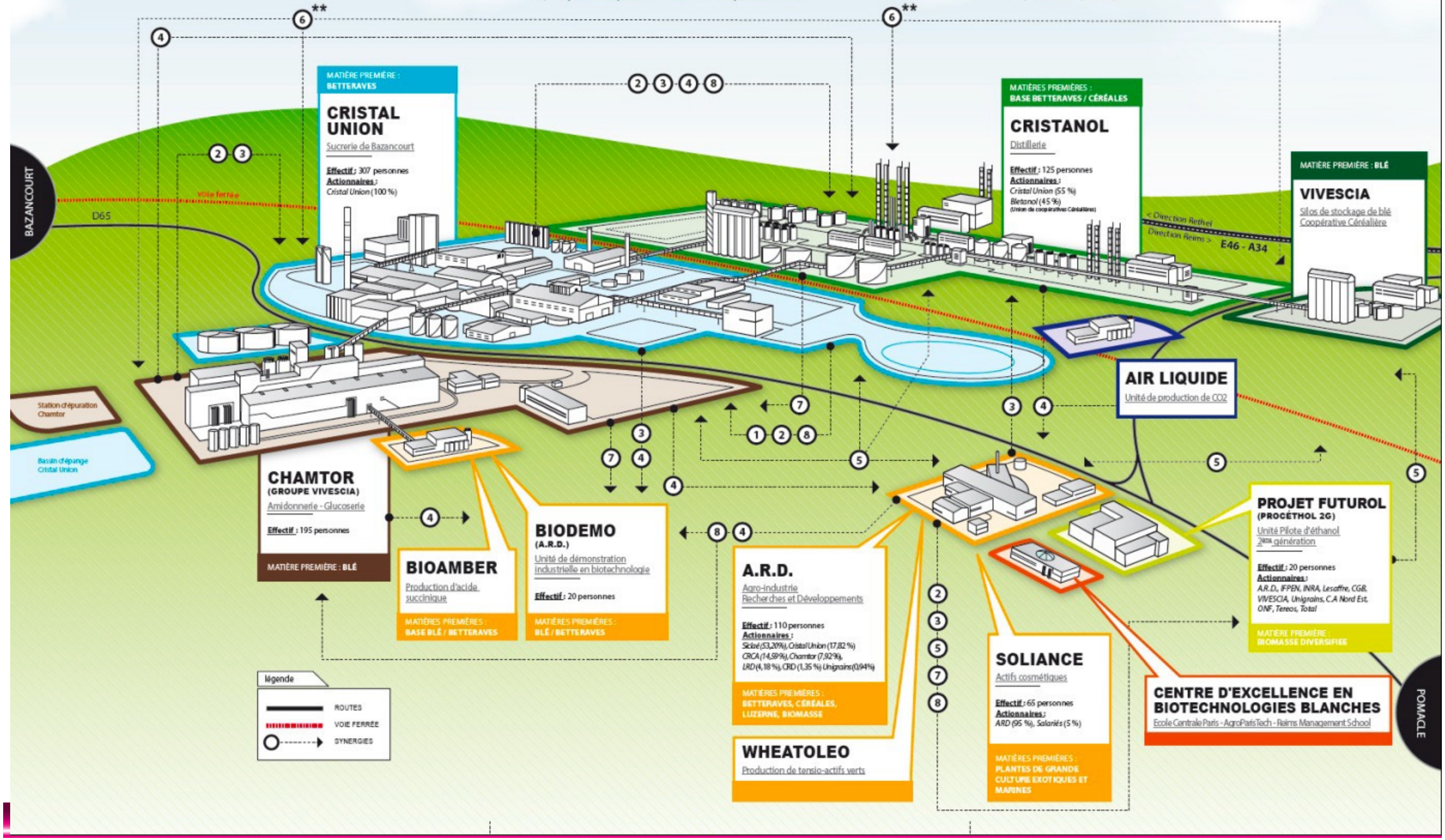
4 | synergie **PRODUITS**
Les produits ou coproduits de l'un sont les matières premières de l'autre.

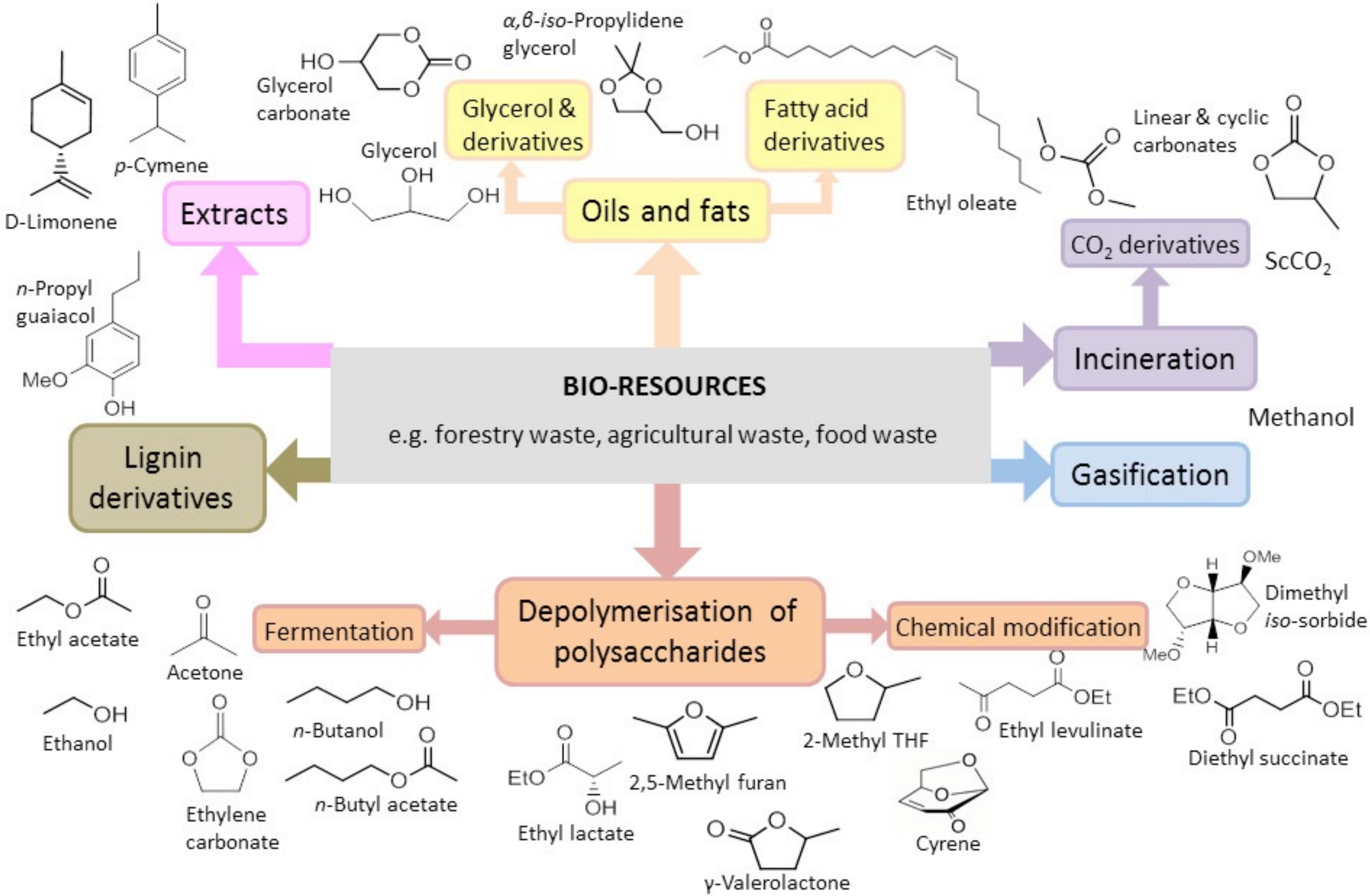
5 | synergie **R&D**
Des programmes de recherche décidés en coopération par les agro-industriels actionnaires de A.R.D.

6 | synergie **ENERGIE**
Production de **bioéthanol** à partir de coproduits betterave / blé.
* **Synergie Energie** : utilisation de la vapeur produite par cogénération
** **Synergie Energie** : production de bioéthanol

7 | synergie **ORGANISATIONNELLE**
Dans le cadre du **pôle de compétitivité I.A.R.** se sont mises en place des synergies organisationnelles : Assistance à la construction et à l'exploitation des installations et programmes de formation.

8 | synergie **FORAGE**
Production **d'eau brute**.





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