Quels synthons aliphatiques pour le développement de polymères bio-sourcés ?

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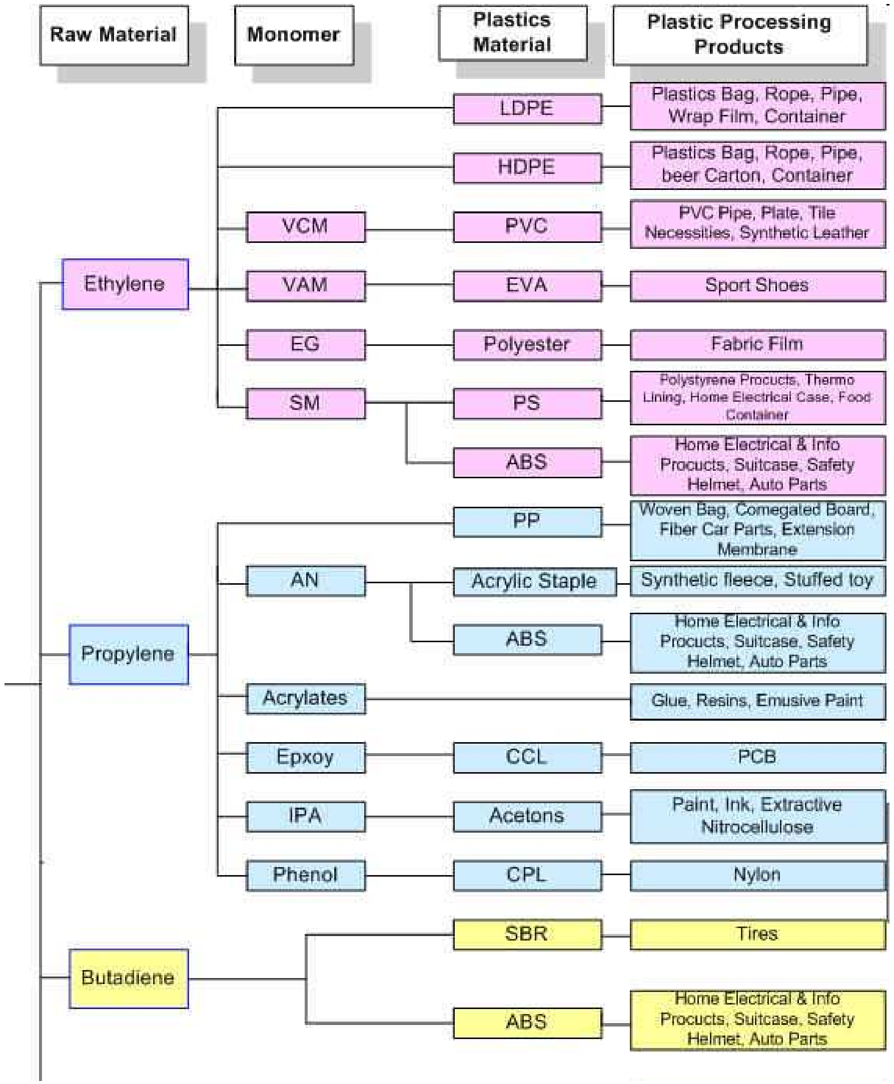
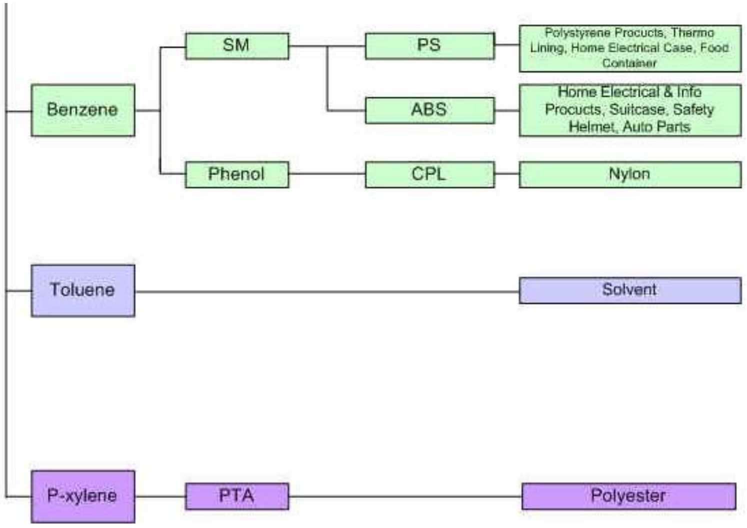
Atelier de Prospective du GFP :
Bio-raffineries : Les ressources pour les polymères de demain
Paris, 26 Janvier 2012

Intermédiaires & synthons actuels



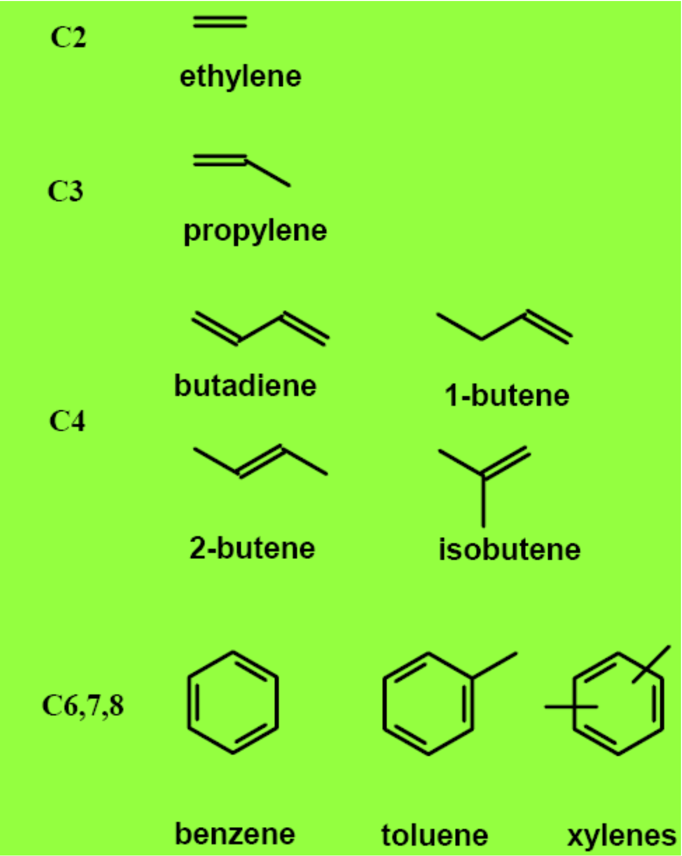
Intermédiaires issus du naphta



Intermédiaires & synthons actuels

Industrie chimique : intermédiaires majeurs issus du naphta

naphta



Synthons issus de la biomasse :

Approche 1 : convertir la biomasse en produits chimiques existants

- Avantages
  - Facilement intégrable aux infrastructures existantes
  - Continuation des polymères existant (haut niveau d'évolution technologique)
  - Focaliser sur monomères à fonctions O- et N- (amines, acides) difficiles à préparer à partir de la pétrochimie

- Inconvénients
  - Difficile : biomasse riche en oxygène, sur-fonctionnalisée et hydrophile avec faible stabilité thermique
  - L'élimination des groupes fonctionnels en excès doit se faire sans impact négatif sur l'exergie et l'économie d'atomes

Synthons issus de la biomasse :

Approche 2 : convertir la biomasse en nouveaux produits chimiques

- Avantages
  - Utilisation de la structure intrinsèque de la biomasse et suivi de la voie thermodynamiquement la plus efficace
  - Potentiellement produits biodégradables
  - Nouveaux produits & matériaux aux propriétés nouvelles

- Inconvénients
  - Besoin de nouveaux procédés et technologies
  - Nouveaux produits & matériaux aux propriétés inconnues
  - Facteurs de risques inconnus (environnementaux, toxicologiques)

Synthons issus de la biomasse :

Quelle approche suivre ?

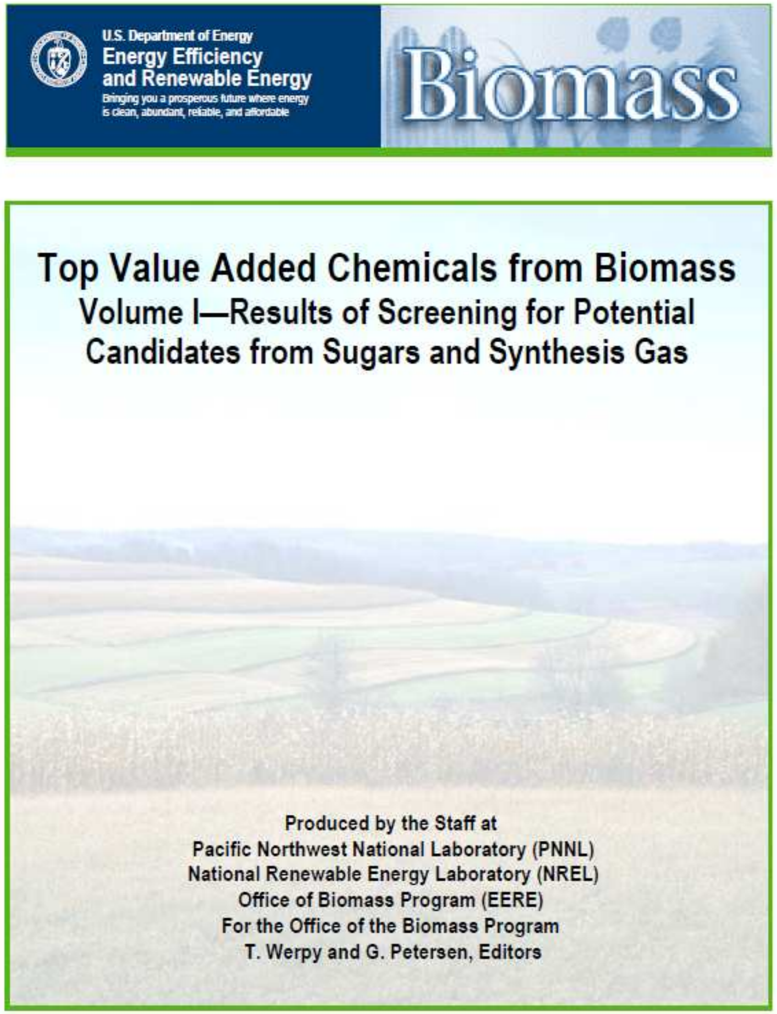
Les deux sont à explorer

- La plupart des matériaux synthétiques actuels ont un excellent rapport prix/performance (ne pas réinventer la roue)

- Importants gains d'exergie possible par substitution intelligente de synthons fonctionnalisés

- Possibilité de nouveaux matériaux aux propriétés nouvelles (améliorées)

Synthons issus de la biomasse :



U.S. Department of Energy
Energy Efficiency and Renewable Energy
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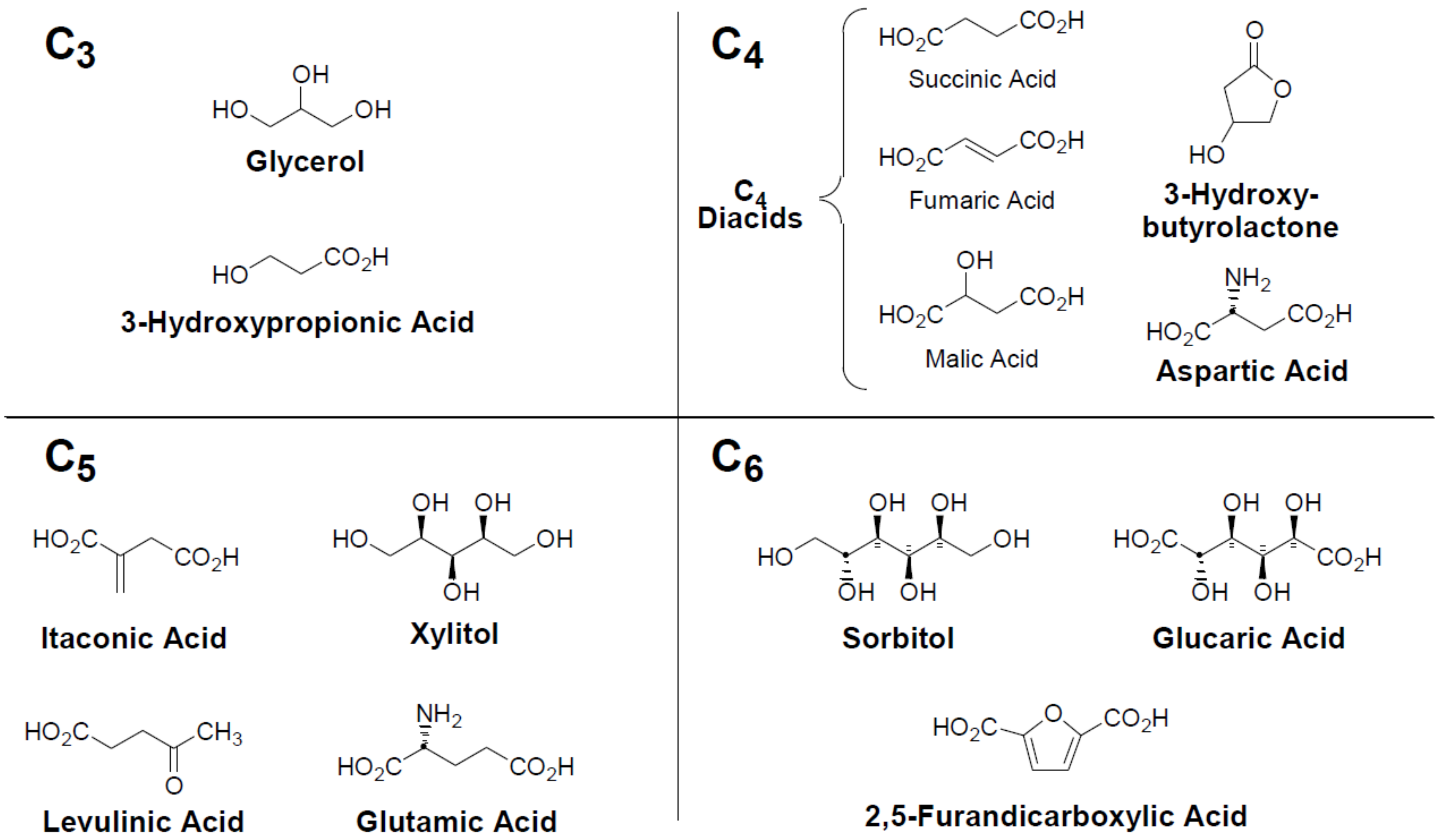
Biomass

Top Value Added Chemicals from Biomass

Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas

Produced by the Staff at
Pacific Northwest National Laboratory (PNNL)
National Renewable Energy Laboratory (NREL)
Office of Biomass Program (EERE)
For the Office of the Biomass Program
T. Werpy and G. Petersen, Editors

Synthons issus de la biomasse :



Synthons issus de la biomasse :

Technology development for the production of biobased products from biorefinery carbohydrates—the US DoE's "Top 10" revisited

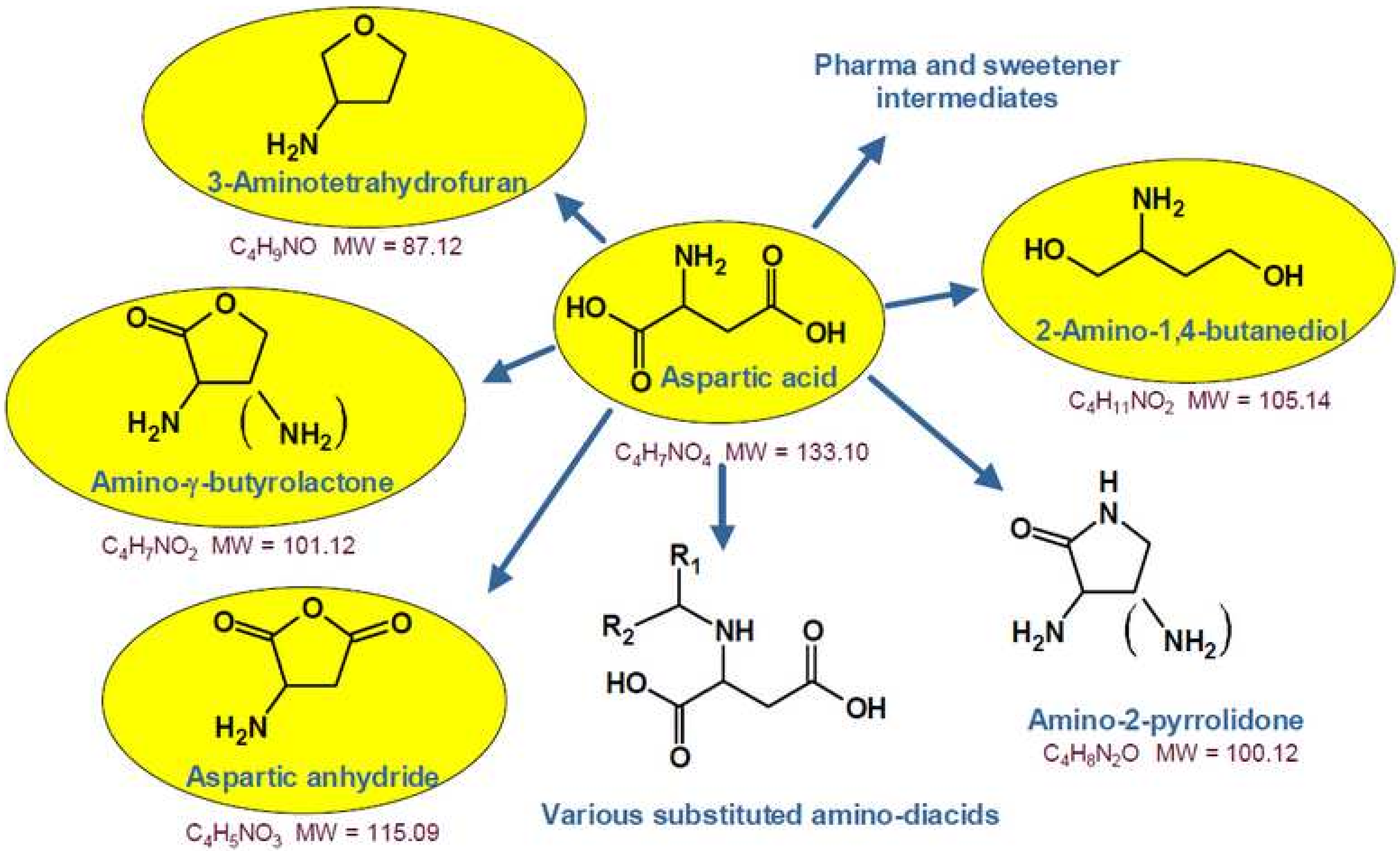
Ethanol
Glycerol
Lactic Acid
Hydroxypropionic Acid
Sorbitol

Furans
Biohydrocarbons
Succinic Acid
Levulinic Acid
Xylitol

Bozell and Peterson, *Green Chem.*, **12,** 539-554, 2010

(Biohydrocarbons: isoprene, …)

Aspartic acid

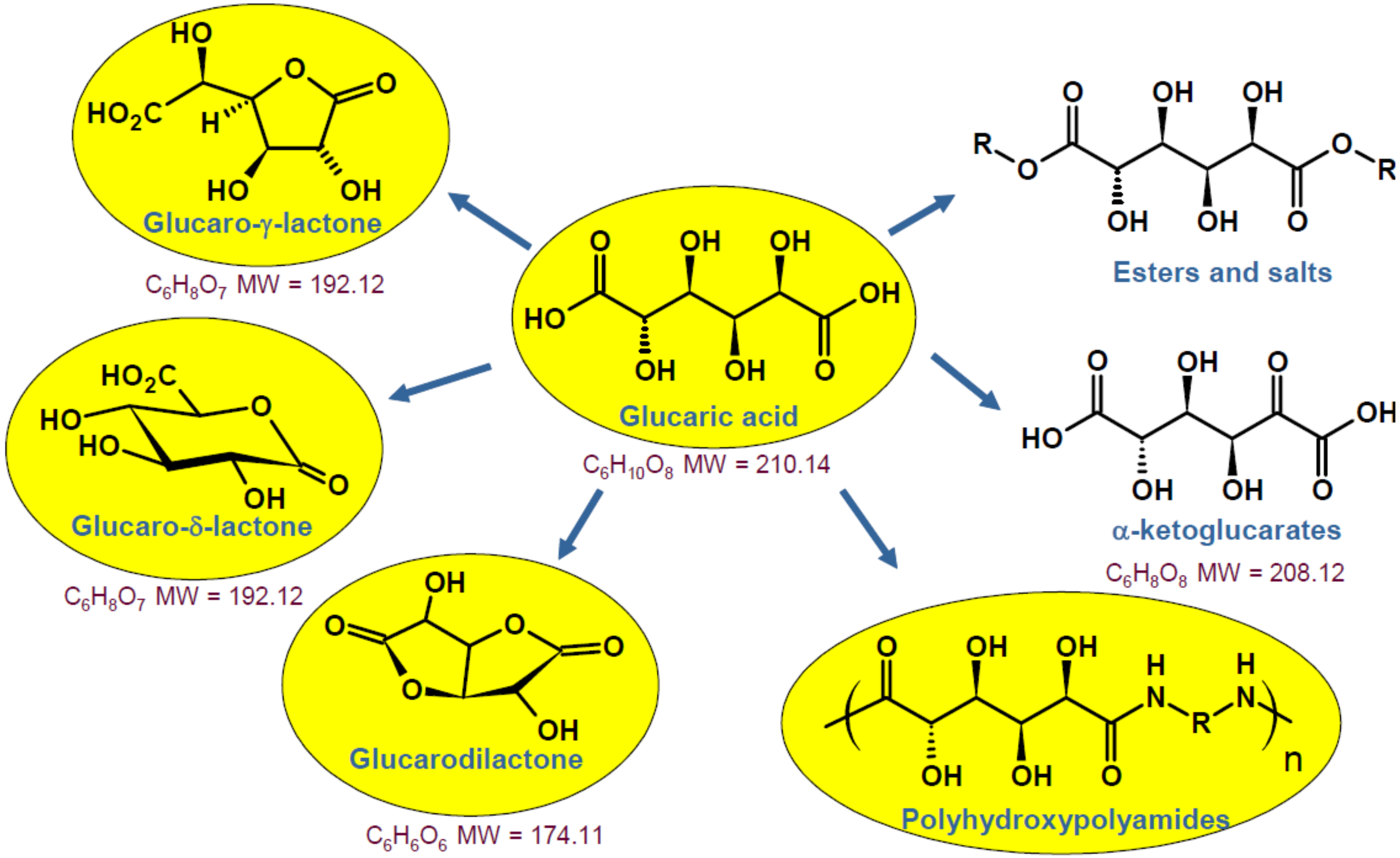


Aspartic acid

The major technical hurdles for the development of aspartic acid as a building block involve developing a direct fermentation route (using sugar substrate) that is cost-competitive with the existing enzymatic conversion process.

New biodegradable specialty polymers (polyaspartic acid and polyaspartates) could be potential substitutes for polyacrylic acid and polycarboxylates.

Glucaric acid



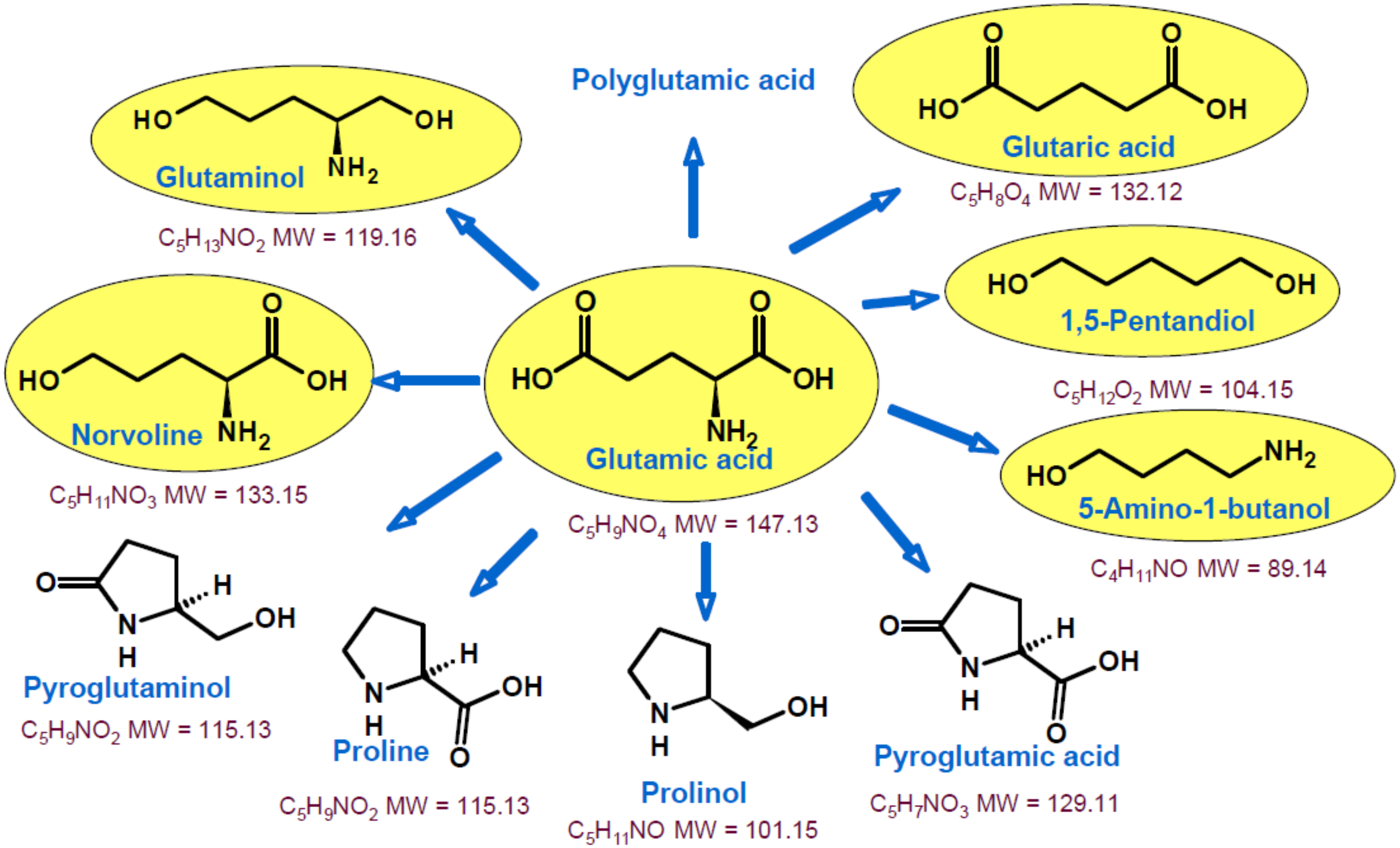
Glucaric acid

The technical barriers for this work include development of efficient and selective oxidation technology for glucose, and eliminating the need to use nitric acid as the oxidant.

Opportunity exists in the production of new nylons (polyhydroxypolyamides) and potential starting material for new types of hyperbranched polyesters

Rivertop: pilot plant of glucaric acid

Glutamic acid



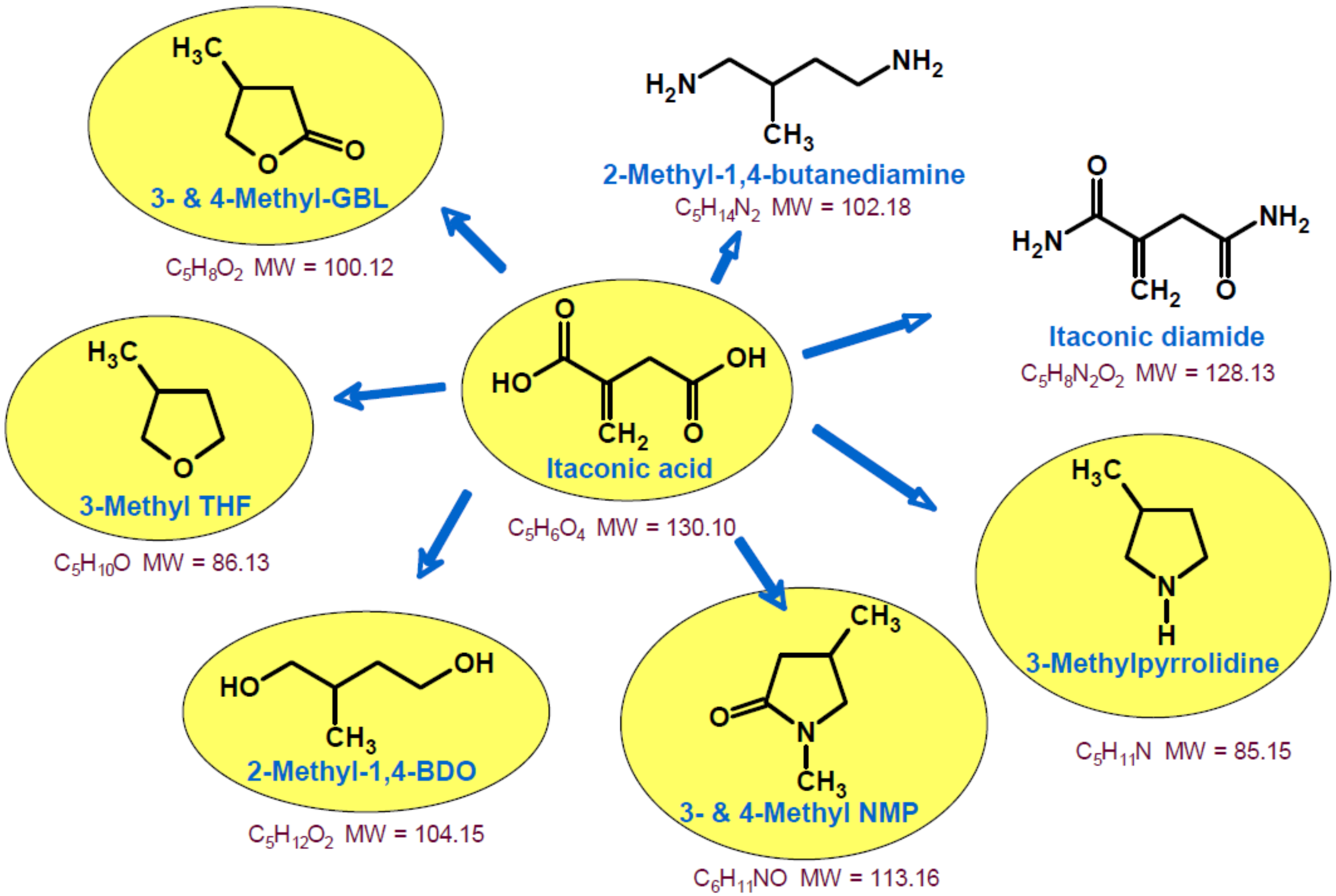
Glutamic acid

The major technical hurdles for the development of glutamic acid as a building block include the development of very low cost fermentation routes.

One of the major challenges for the development of a low cost fermentation is to develop an organism that can produce glutamic acid as the free acid (not sodium glutamate).

Potential monomers (diols, diacids…) for polyesters and polyamides.

Itaconic acid



Itaconic acid

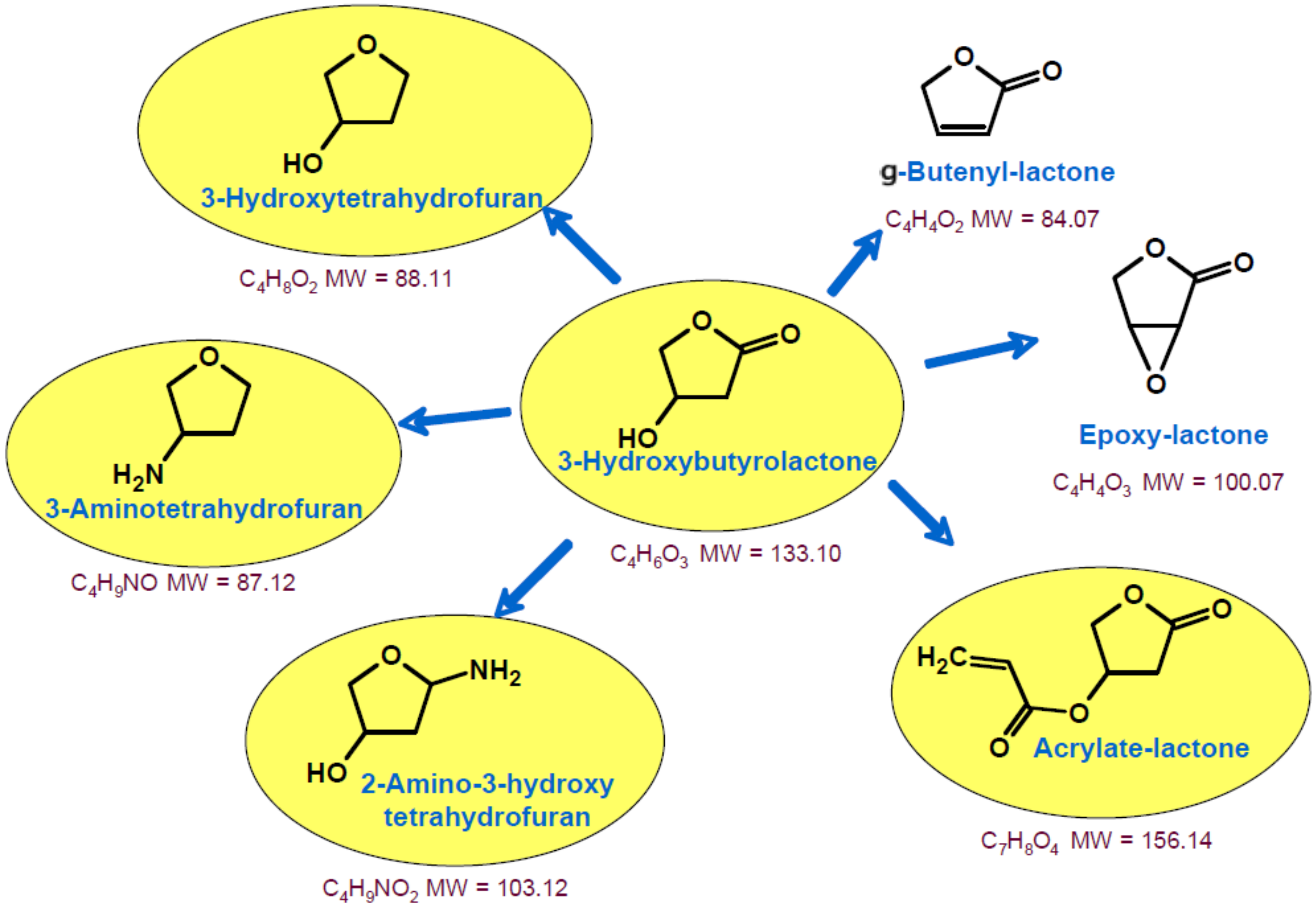
Itaconic acid is currently produced via fungal fermentation and is used primarily as a specialty monomer.

The major technical hurdles for the development of itaconic acid as a building block for commodity chemicals include the development of very low cost fermentation routes.

The major applications include the use as a copolymer with acrylic acid and in styrene-butadiene systems.

ITACONIX: working on bio-based itaconic acid and poly(itaconic acid)

3-Hydroxybutyrolactone (3-HBL)

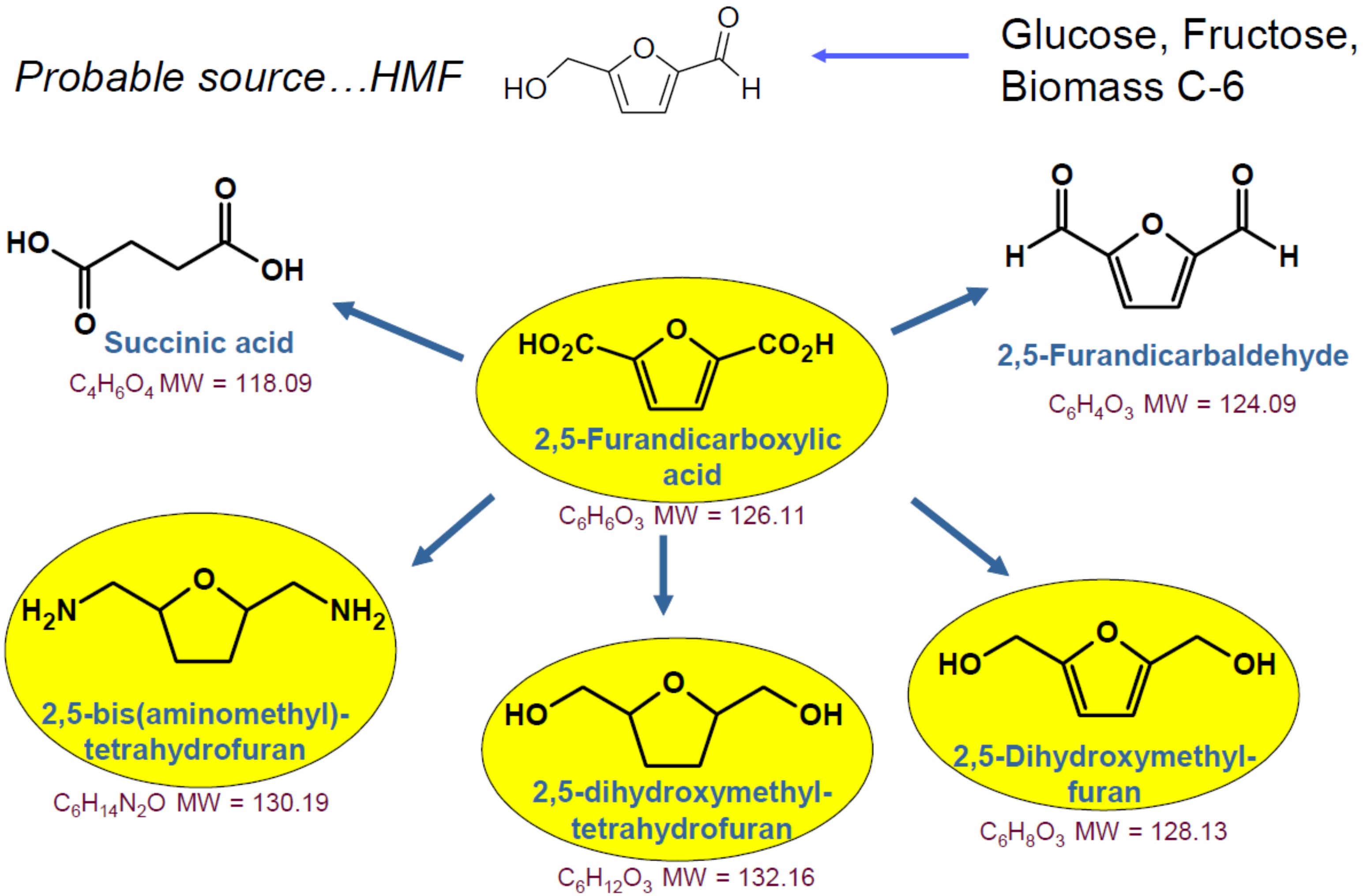


3-Hydroxybutyrolactone (3-HBL)

Conversion from fumaric to malic is done using fermentation. Thus, if biotechnology advances could lead to malic acid production from sugars, a more cost-effective pathway can be envisioned

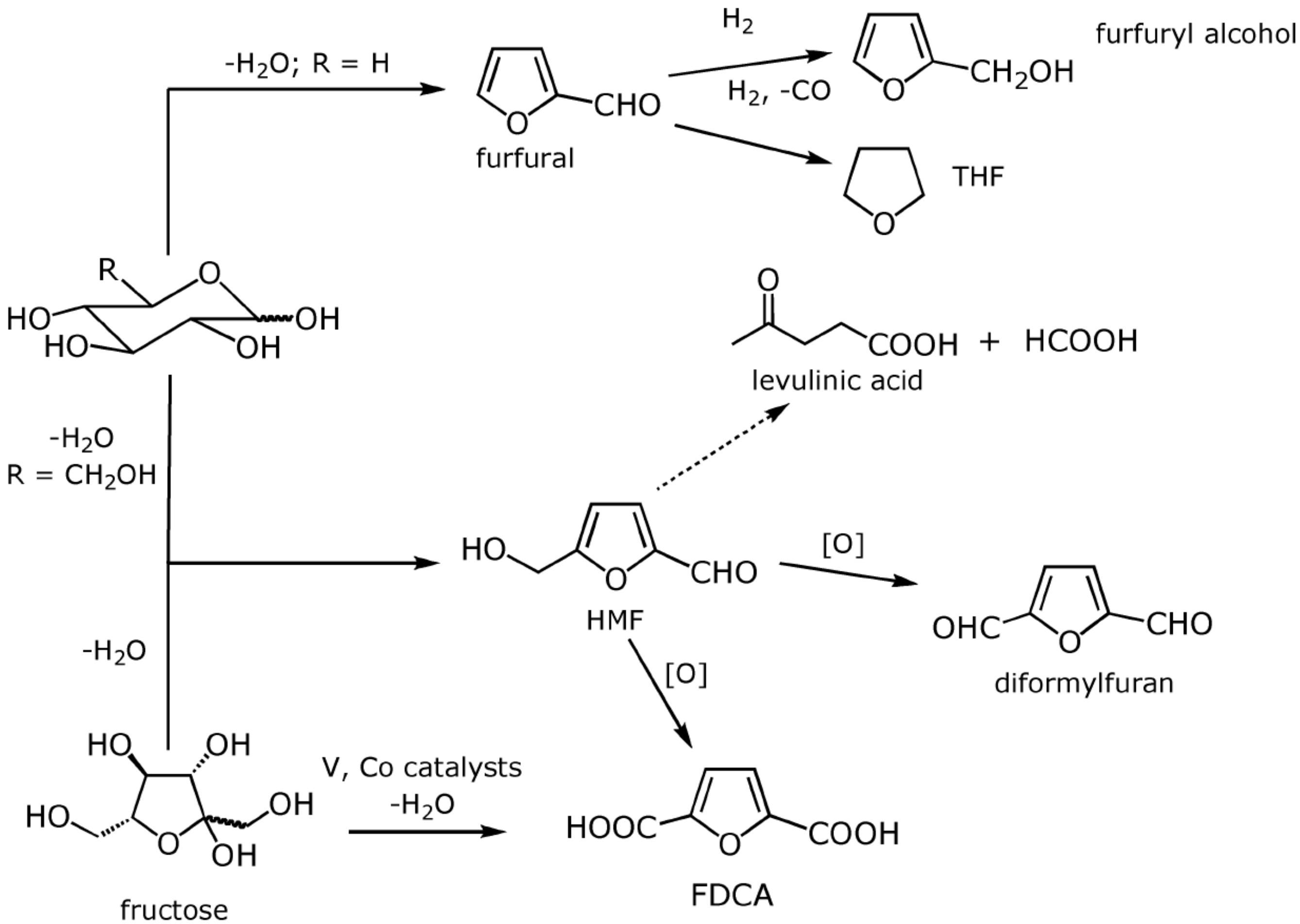
Malic acid can be cyclized to form hydroxysuccinic anhydride, which, via reduction, gives the hydroxybutyrolactone.

Furans (2,5-Furandicarboxylic acid)



Furanes

Technology development has improved the dehydration of sugars to furans, improving their potential as platform chemicals in the biorefinery



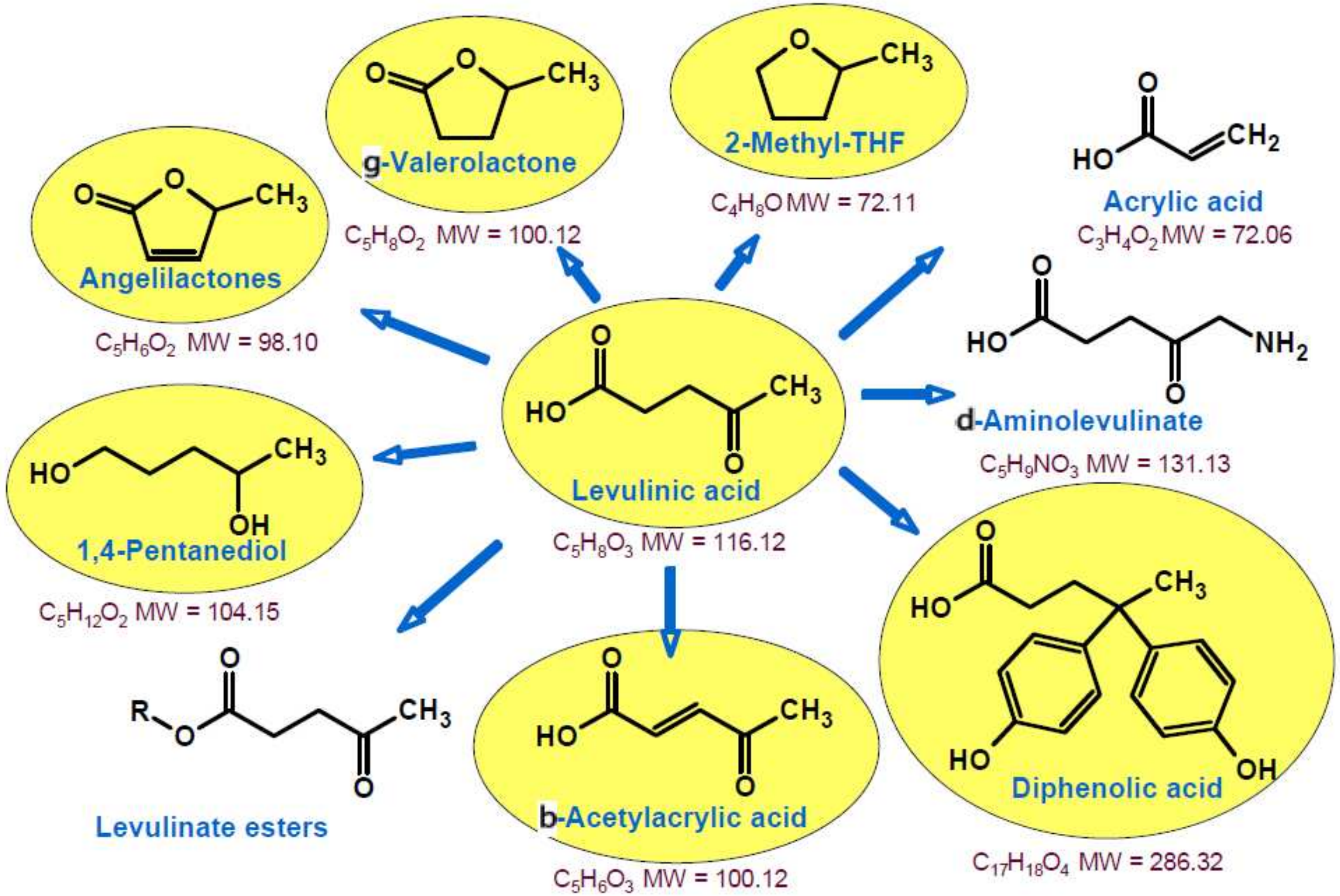
Furanes

Aromatics analogues

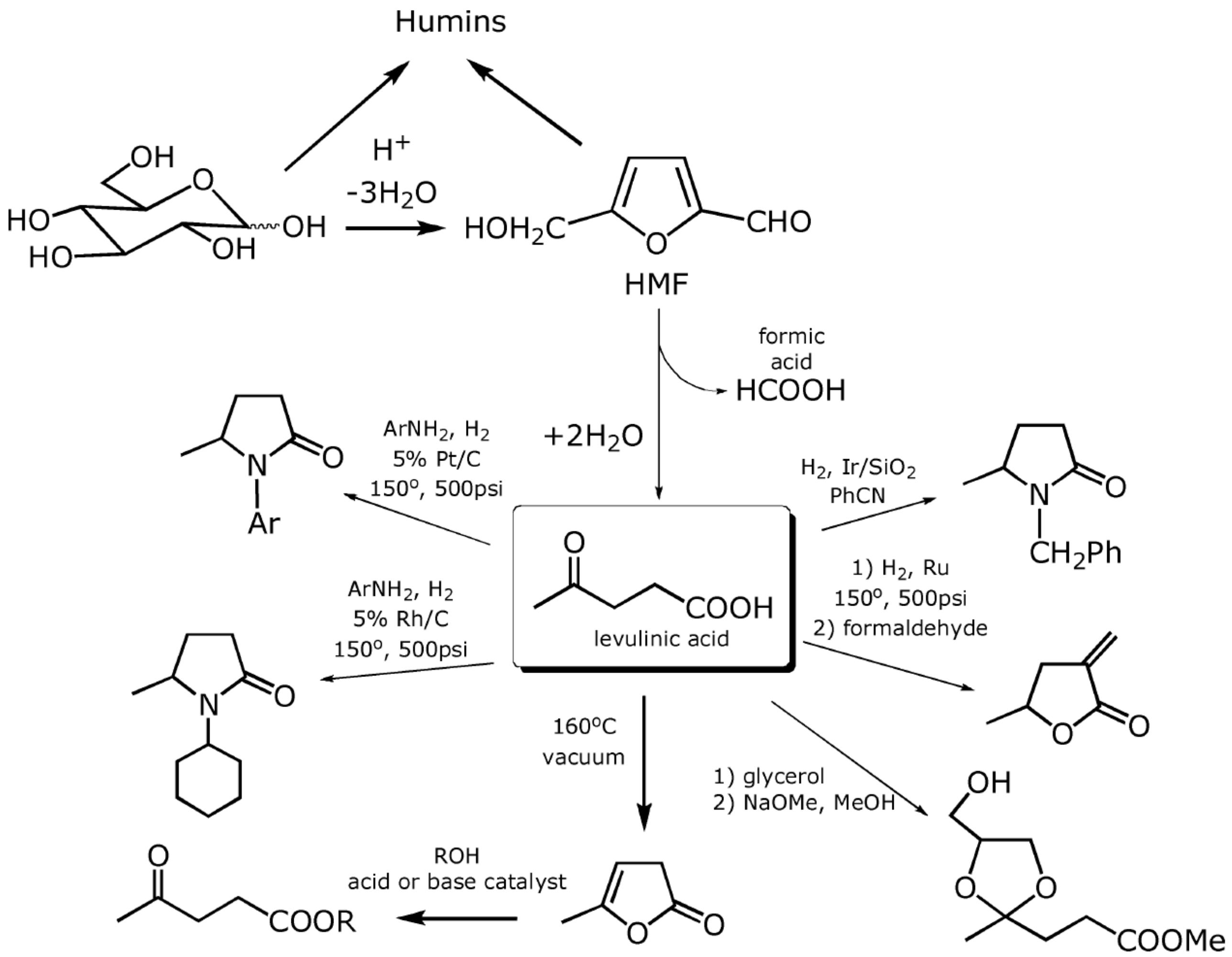
FDCA has a large potential as a replacement for terephthalic acid in polyethylene terephthalate (PET) and polybutyleneterephthalate (PBT).

Avantium (Furanix) : development of polyethylene furanoate (PEF)

Levulinic acid



Levulinic acid



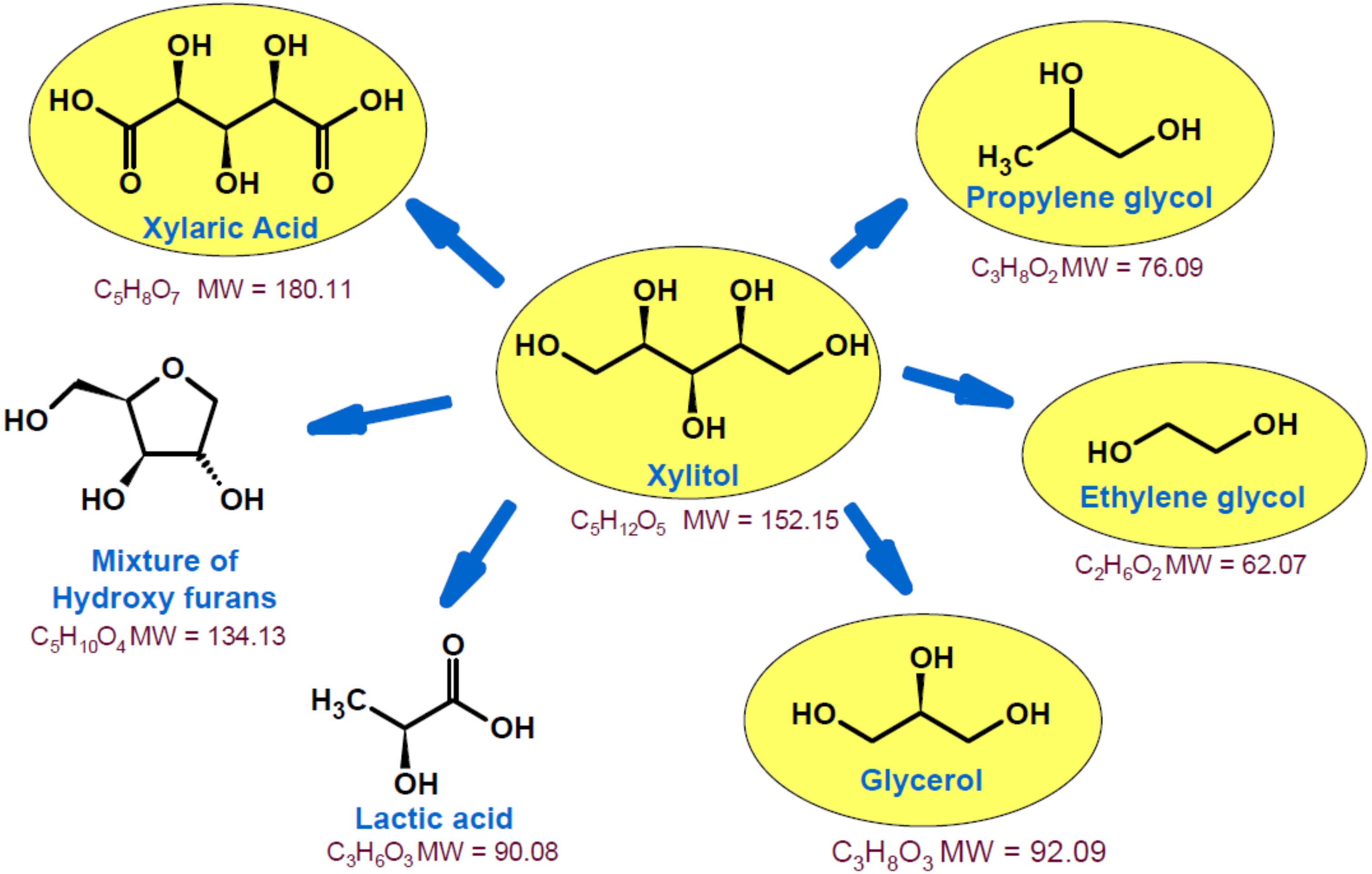
Levulinic acid

High potential as a building block and platform chemical because of its simple and relatively high yield production from acid treatment of C6 sugars.

Yield needs to be improved as well as its isolation/purification

Potential derivatives may include new acrylate polymers and levulinic acid conversion to diphenolic acid is of particular interest as a replacement for bisphenol A for polycarbonates

Xylitol



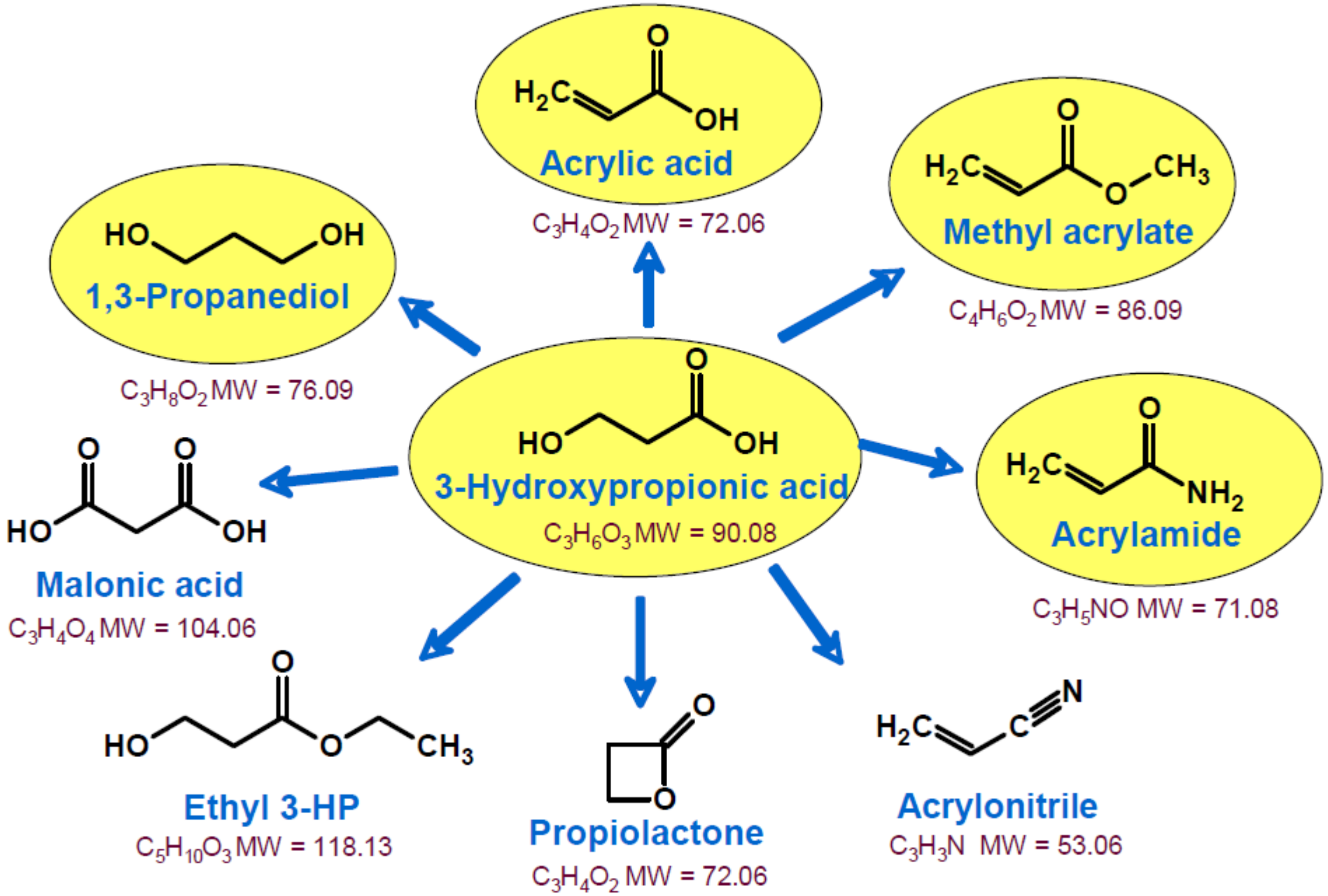
HO
OH
OH
OH
O
OH
O
Xylaric Acid
$C_5H_8O_7$ MW = 180.11
HO
H3C
OH
Propylene glycol
$C_3H_8O_2$ MW = 76.09
HO
O
HO
OH
HO
Mixture of
Hydroxy furans
$C_5H_{10}O_4$ MW = 134.13
OH
OH
HO
OH
OH
Xylitol
$C_5H_{12}O_5$ MW = 152.15
HO
OH
Ethylene glycol
$C_2H_6O_2$ MW = 62.07
O
H3C
OH
OH
Lactic acid
$C_3H_6O_3$ MW = 90.08
OH
HO
OH
Glycerol
$C_3H_8O_3$ MW = 92.09

Xylitol

There is no major technical barrier associated with the production of the five-carbon sugar alcohols xylitol and arabinitol

The conversion of these sugars to the sugar alcohol and subsequent conversion to glycols has been demonstrated and could be a first generation process for the production of propylene glycol and ethylene glycol.

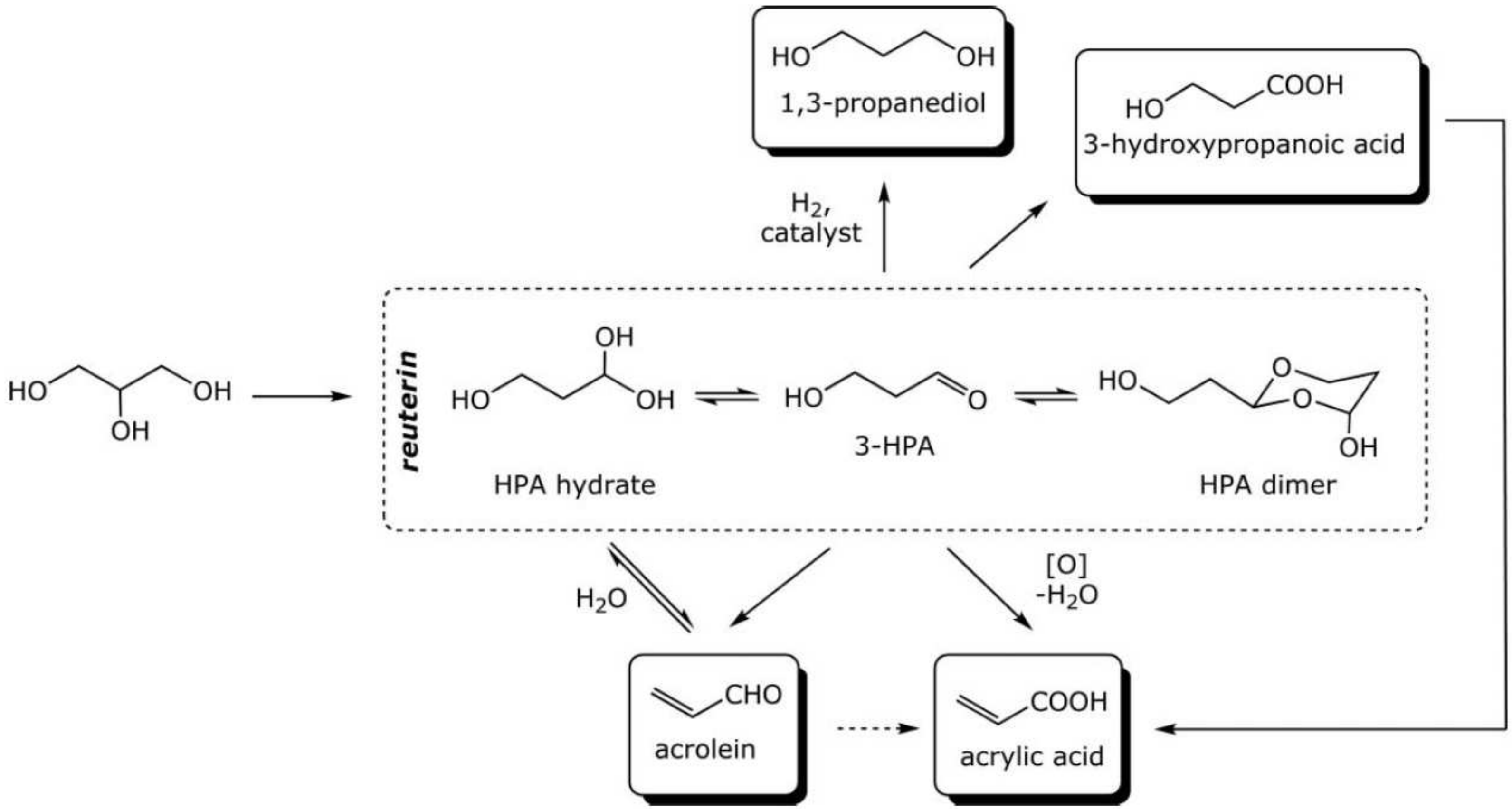
3-Hydroxypropionic acid (3-HPA)



3-Hydroxypropionic acid (3-HPA)

- C3 building block which has the potential to be a key building block for deriving both commodity and specialty chemicals.
- Bioproduction of HPA suffers from product inhibition because of its toxicity
- The major technical hurdles for the development of 3HPA as a building block include the development of efficient and very low cost fermentation routes.
- In order to be competitive with petrochemical routes to acrylates both the fermentation and catalysis must afford high yields.

3-Hydroxypropionic acid (3-HPA)



3-Hydroxypropionic acid (3-HPA)

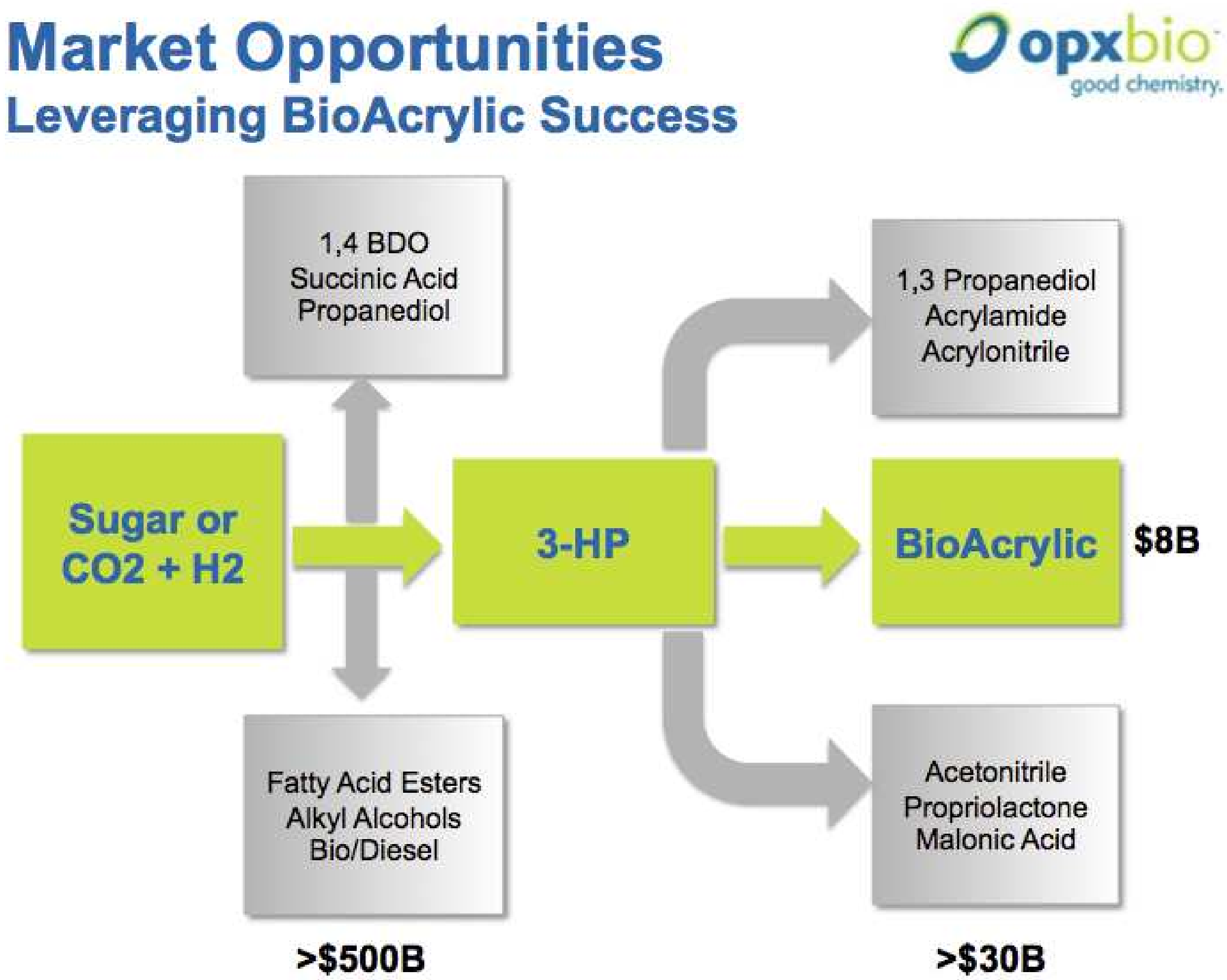
Cargill (with Novozymes) developed and patented a bioprocess to produce 3-HPA which converts glucose or other carbohydrate sources into 3-HPA using a multi-step enzymatic reaction within the cells of a microorganism.

Project stopped ?

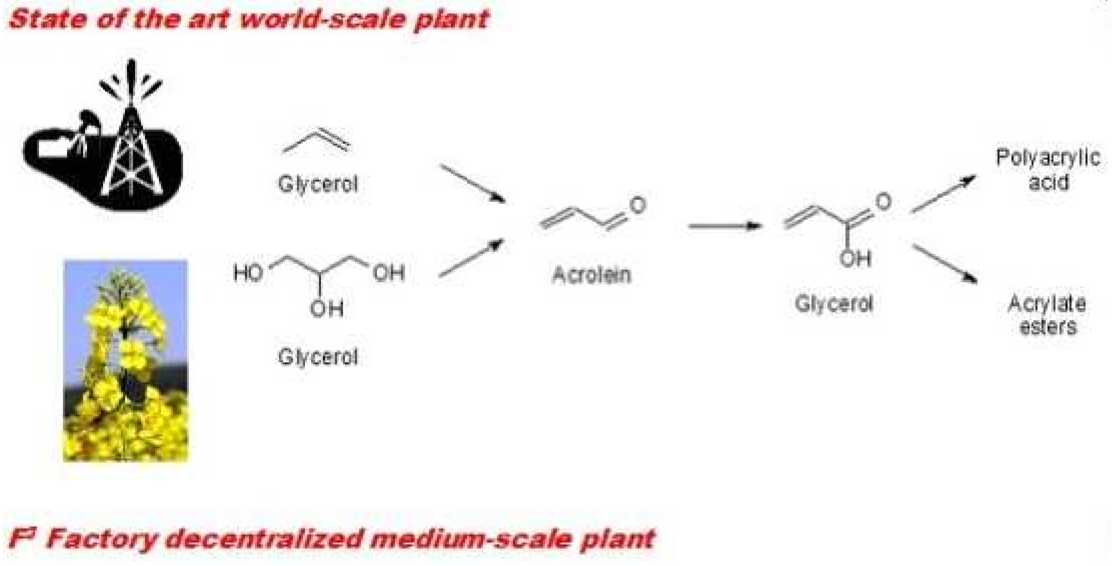
Perstorp also working on a similar project ?

OPXBio uses microorganism to biosynthesize 3-HPA by fermentation of sugar and subsequent dehydration of the 3-HPA to acrylic acid!

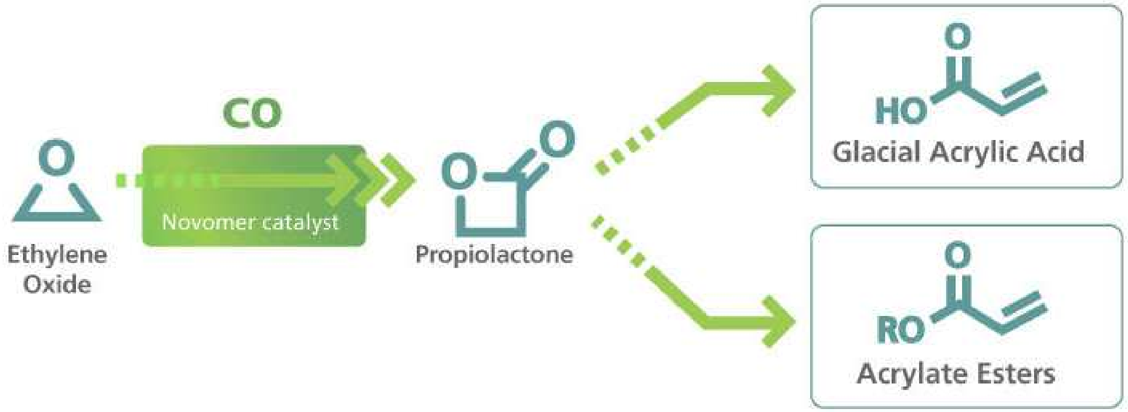
Acide acrylique



Acide acrylique



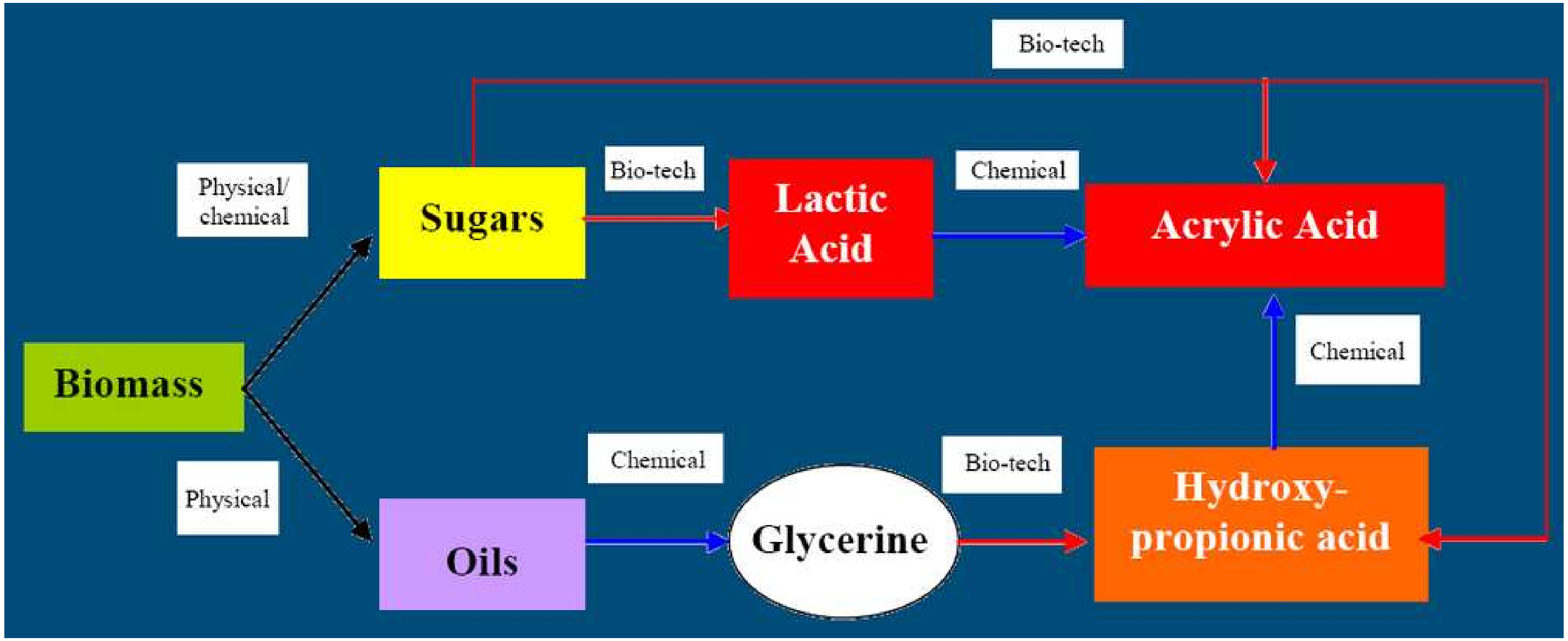
Arkema



Novomer

Acide acrylique

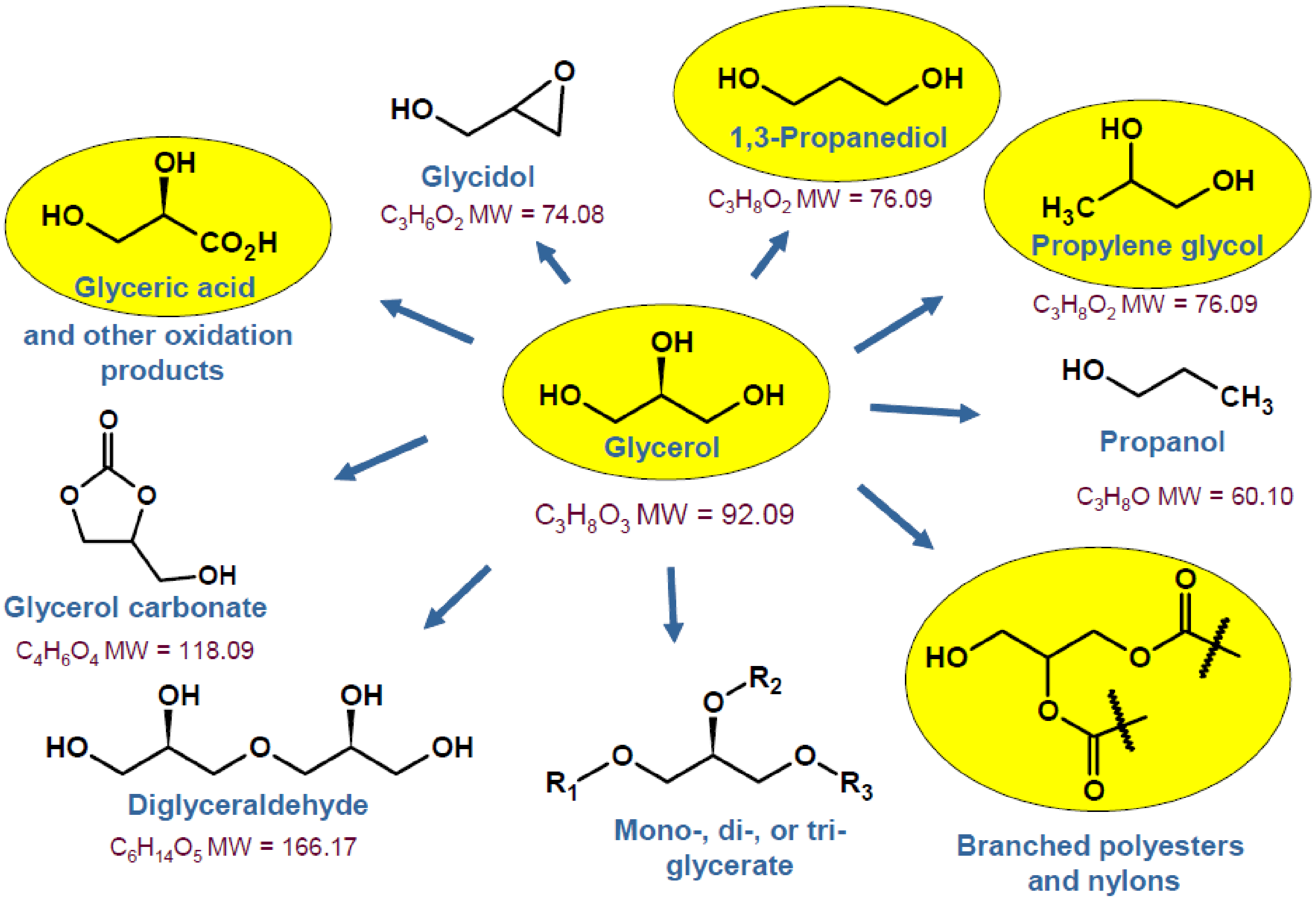
Alternative bio-sourcée pour l'acide acrylique



Dow / Arkema / BASF… : ongoing programs and demo plants for acrylic acid

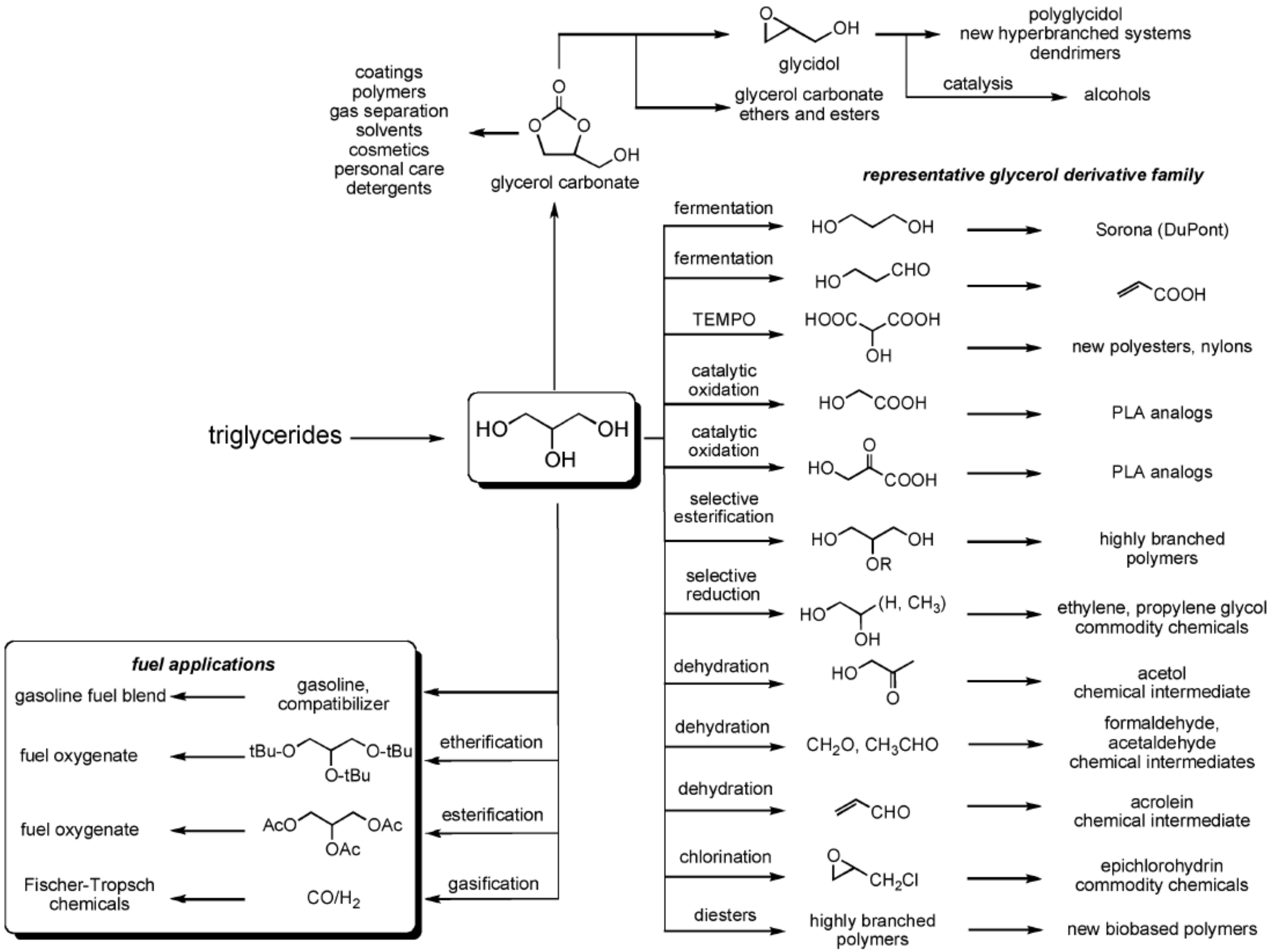
Bio-based MMA programs : Arkema / Evonik and Mitsubishi (target production 2016) ??

Glycérol



Others: Acrylic acid, Epichlorohydrin

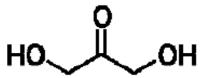
Glycérol



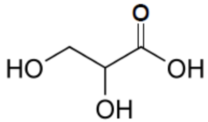
coatings
polymers
gas separation
solvents
cosmetics
personal care
detergents
glycerol carbonate
glycidol
polyglycidol
new hyperbranched systems
dendrimers
catalysis
alcohols
glycerol carbonate ethers and esters
representative glycerol derivative family
triglycerides
fermentation
Sorona (DuPont)
fermentation
TEMPO
new polyesters, nylons
catalytic oxidation
PLA analogs
catalytic oxidation
PLA analogs
selective esterification
highly branched polymers
selective reduction
ethylene, propylene glycol commodity chemicals
dehydration
acetol chemical intermediate
dehydration
CH_2O, CH_3CHO
formaldehyde, acetaldehyde chemical intermediates
dehydration
acrolein chemical intermediate
chlorination
epichlorohydrin commodity chemicals
diesters
highly branched polymers
new biobased polymers
fuel applications
gasoline fuel blend
gasoline, compatibilizer
fuel oxygenate
etherification
fuel oxygenate
esterification
Fischer-Tropsch chemicals
CO/H_2
gasification

Dérivés du glycérol

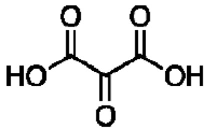
Oxidation to:



Dihydroxyacetone – artificial tanning agent, synthon for organic synthesis

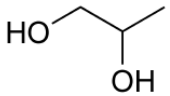


Glyceric acid – promising monomer and chelating agent, food additive, anti-cirrhosis agent

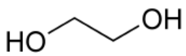


Mesoxalic acid – pharmaceutical precursor

Hydrogenolysis to:



Propylene glycol – commodity chemical used in resins, antifreeze, pharmaceuticals, foodstuffs, cosmetics, personal care products, paints, animal feedstuffs



Ethylene glycol – commodity chemical used in antifreeze, polymers, etc.

1,3 Propanediol – monomer used in PTT, also used in resins, engine coolants, dry-set mortars and water-based inks.

Pagliaro and Rossi, *The Future of Glycerol, New Uses of a Versatile Raw Material*, RSC Publishing, Cambridge, 2008.
Kraus, *Clean* **36** (2008) 648-651.

Need to find catalysts and supports that are stable in water under harsh conditions of oxidation and reduction catalysis

Temperatures up to 200 °C (473 K)

Elevated levels of base (molar levels of NaOH)

Glycérol

Huge potential to become a primary building block in biorefinery.

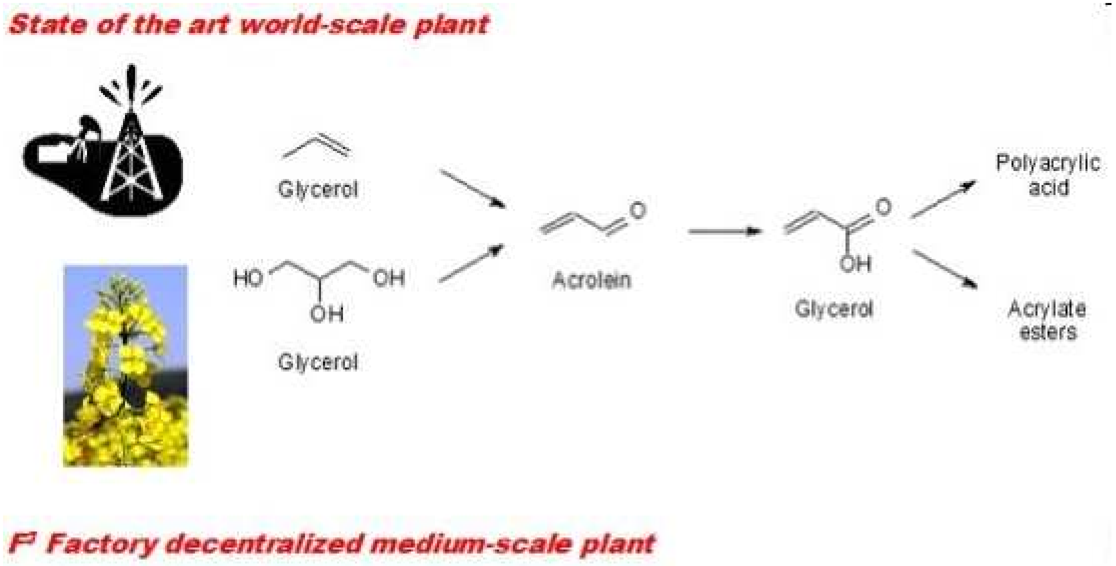
The expanding biodiesel market and demand for green biofuels suggest that large amounts of cheap glycerol will be available

Need to develop selective catalytic oxidation technology that can operate on a polyfunctional molecule such as glycerol.
The processes will also need to use simple oxidants, such as oxygen or air, to carry out the required transformations.

Glycerol conversion to acrolein has received recent attention as a precursor to acrylic acid

Glycerol is a feedstock in biochemical transformations, with the majority of current research focused on its conversion to 1,3-propanediol (1,3-PDO).

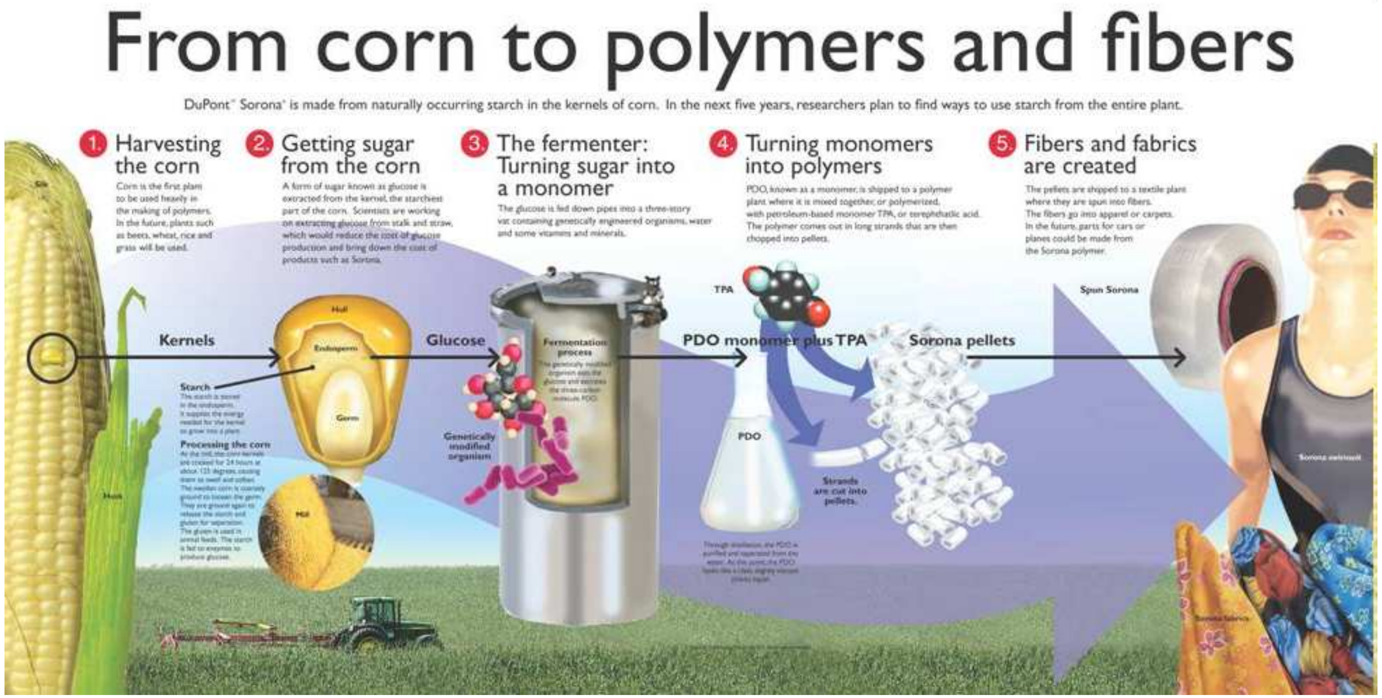
Acide acrylique à partir du glycérol



Arkema

1,3 PDO

DuPont Tate & Lyle BioProducts

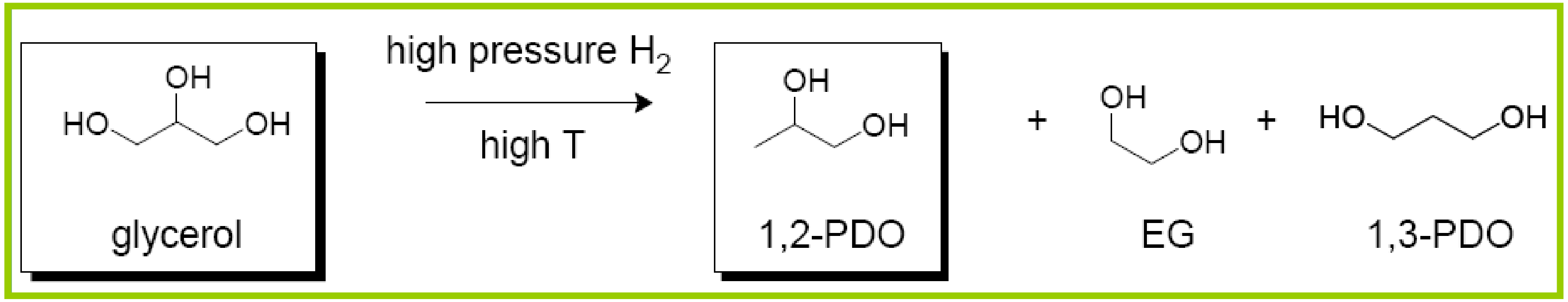


metabolic explorer

1,3-PDO from crude glycerol / Building plant in Malaysia

Propylene glycol

- Hydrogénolyse du glycérol
  - Augmenter rendements en propylene glycol (1,2-PDO)

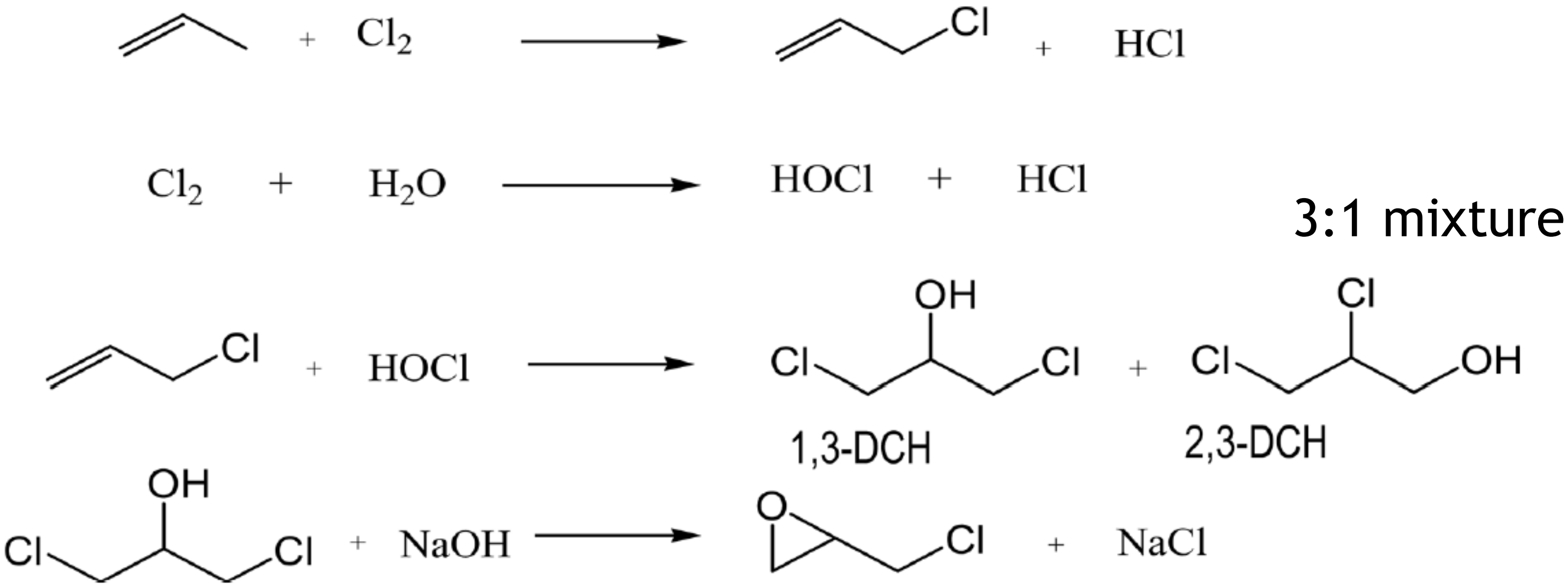


ADM producing propylene glycol from glycerol *via* catalytic hydrogenolysis.

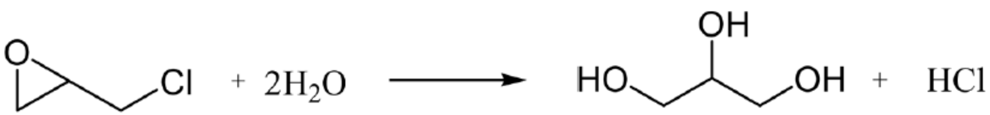
Other ongoing industrial projects announced by Cargill, Virent, Dow, …

Epichlorohydrine

Voie de synthèse traditionnelle (pétro-sourcée)

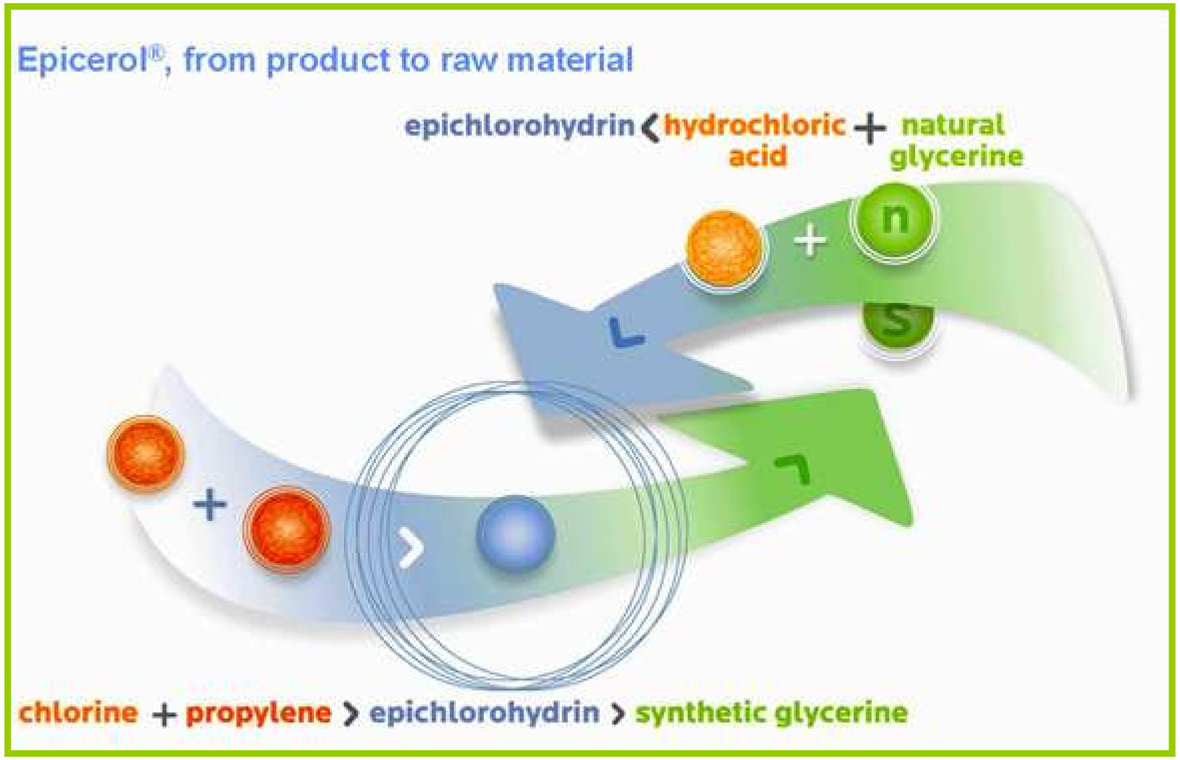


This process produces three equivalent of waste chloride.



Epichlorohydrine

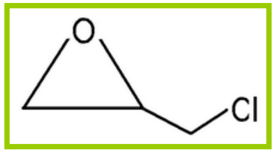
- A partir de glycérol (sous-produit du biodiesel) à la place du propylène (e.g. Solvay) : Epicerol (10kt/a capacité)



Source: Solvay

Epichlorohydrine

- Epichlorohydrin growing at 6-7% globally
- Propylene price continues to increase
  2x since 2003 / 4x since 1999
- 1T of biodiesel gives 0.1T glycerin
- Increasing amount of glycerin (price decrease)

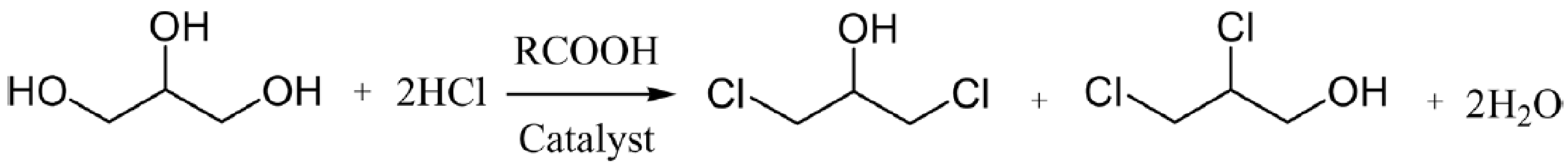


Marché
mondial
des époxy
en 2006
15 Md $

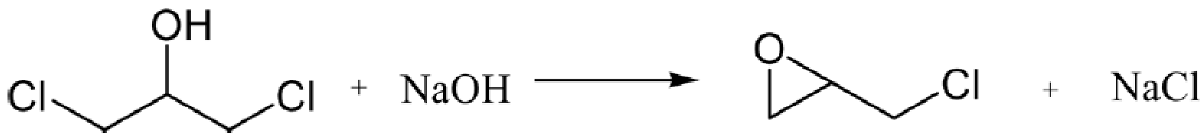
Acteurs principaux :

Solvay (Epicerol)
Yang Nong Jiang Su
Fujian Haobang Chemical
Tangshan Risun Chemical
Dow
Samsung…

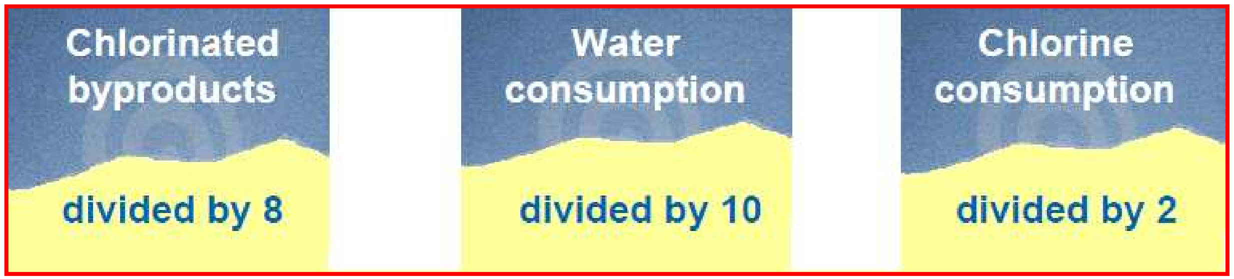
Epichlorohydrine



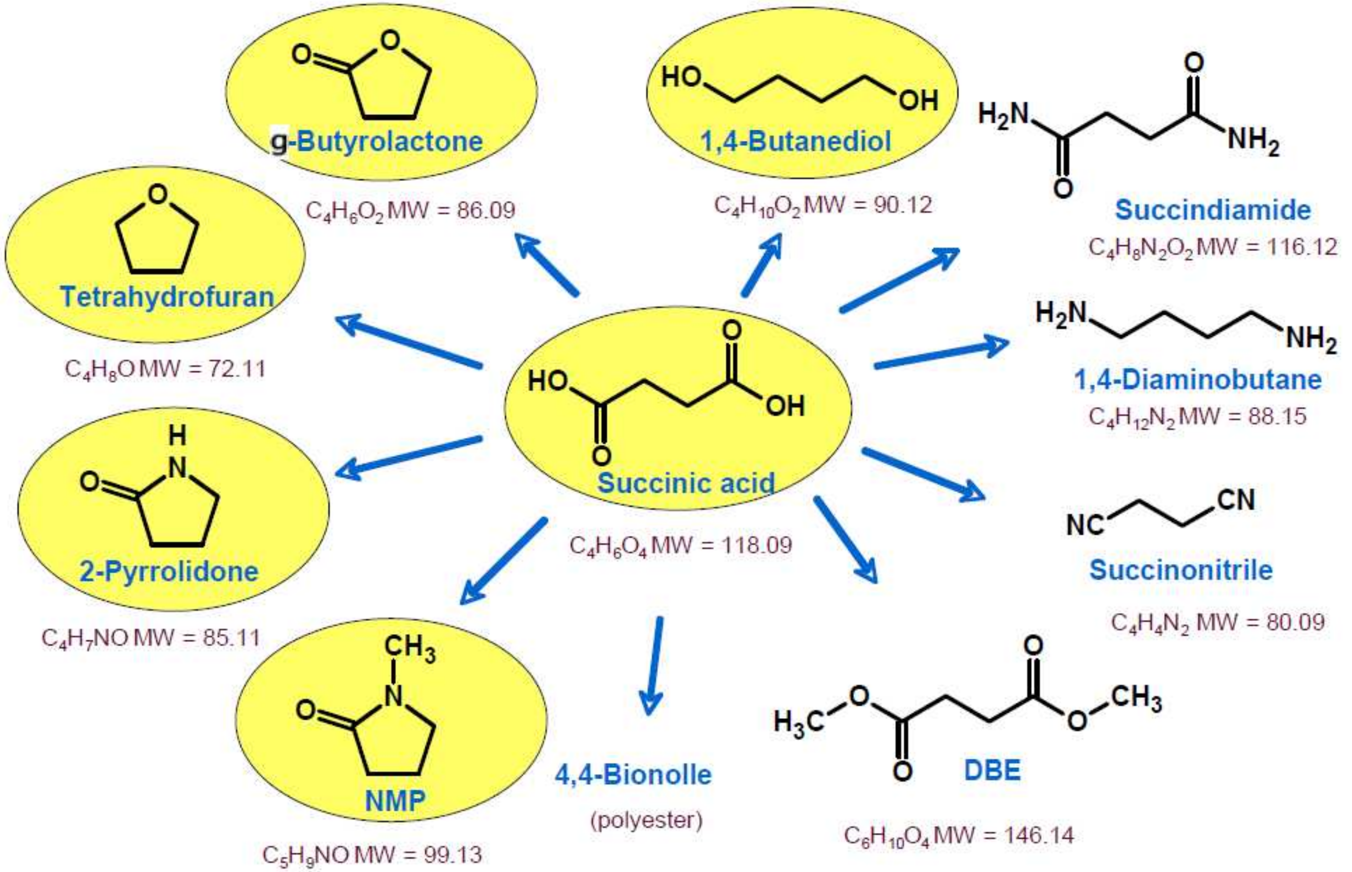
30-50:1 mixture



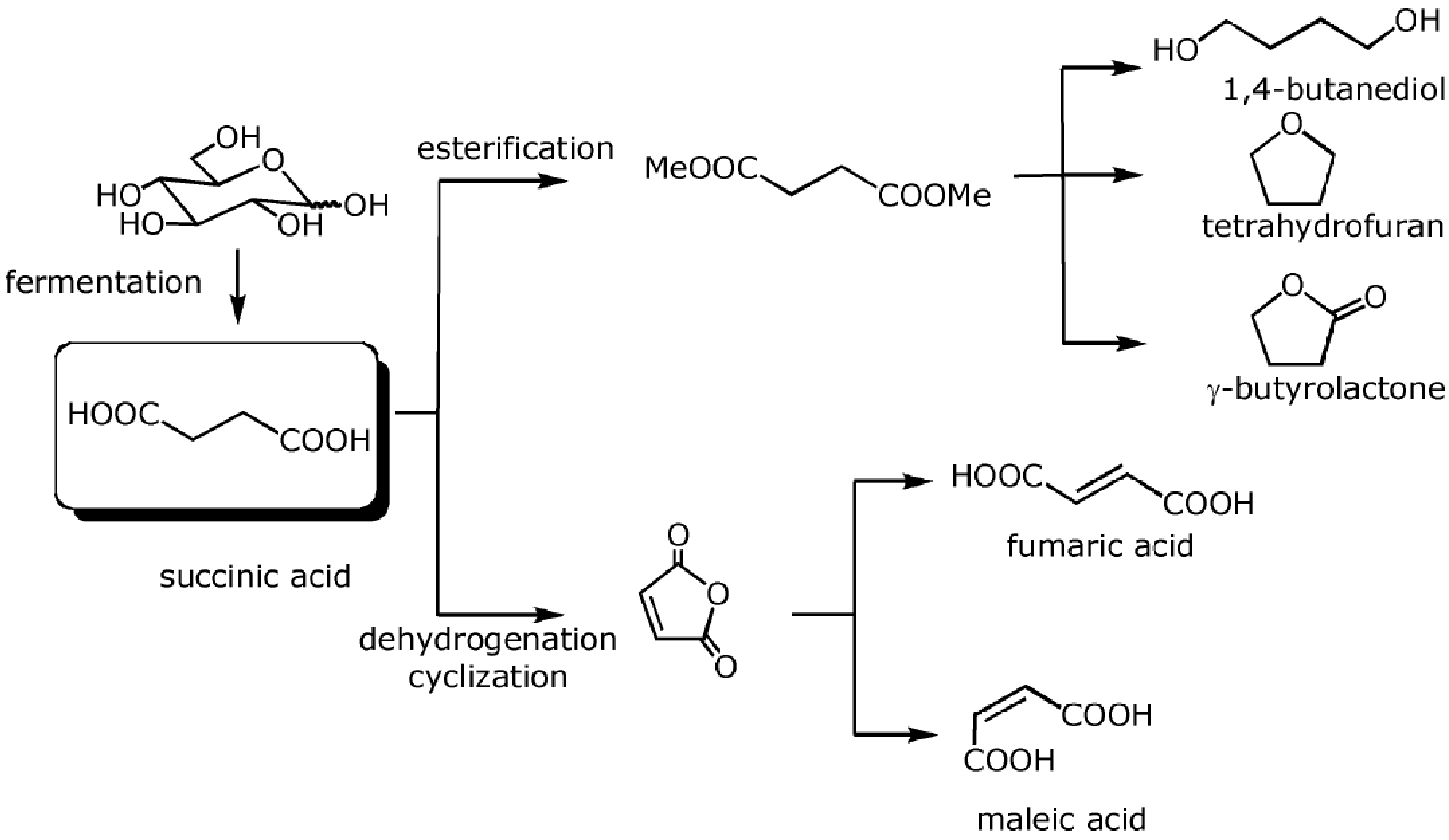
This process produces only one equivalent of waste chloride.



Succinic acid



Succinic acid



Succinic acid

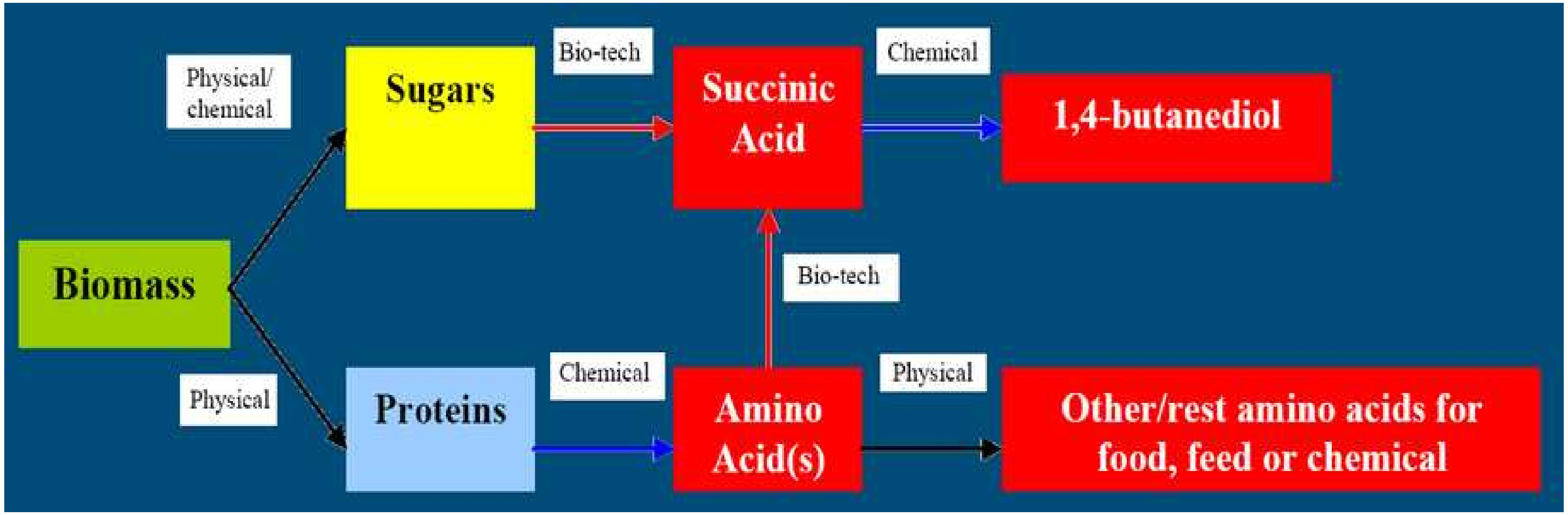
Succinic acid offers strong potential as a platform chemical. Succinate esters are precursors for known petrochemical products such as 1,4-butanediol, THF, g-butyrolactone…

Succinic acid is a component of biobased polymers, such as nylons or polyesters. Succinic acid could also be polymerized with isosorbide to form a new polyester for coating applications.

The market potential for succinic acid and its immediate derivatives has been projected to be as much as 245 x 10^3 tonnes per year, with an estimated market size for succinic acid-derived polymers being as high as 25 x 10^6 tonnes per year.

Bio-based succinic acid

Bio-based alternative for 1,4-butanediol and succinic acid



Développement en parallèle du 1,4-BDO
Exemple: Genomatica partenariats avec Mitsubish, Tate & Lyle…

Bio-based succinic acid

<u>Principaux acteurs industriels</u> :

DSM/Roquette (Reverdia JV) : 1 unité (Ita) / Production en 2012

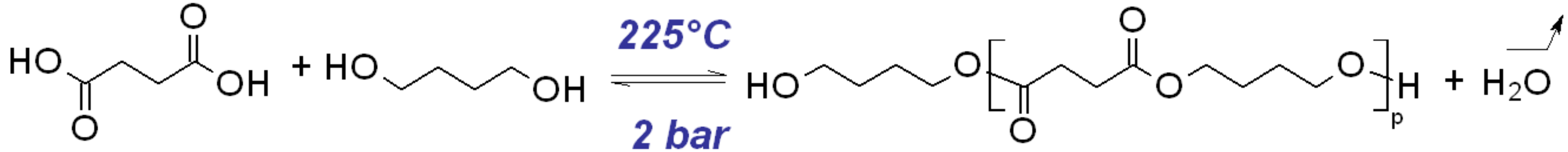
BioAmber : 3 unités de productions prévues pour 2013-2014 (également production BDO ?)
Partenariats avec Mitsui, PTT et Mitsubishi / 1 unité adossée à unité PBS

Myriant (avec PTT?) : 1 unité annoncée pour 2012

BASF/Purac : ? (2013 ??)

Poly(butylene succinate) (PBS) synthesis

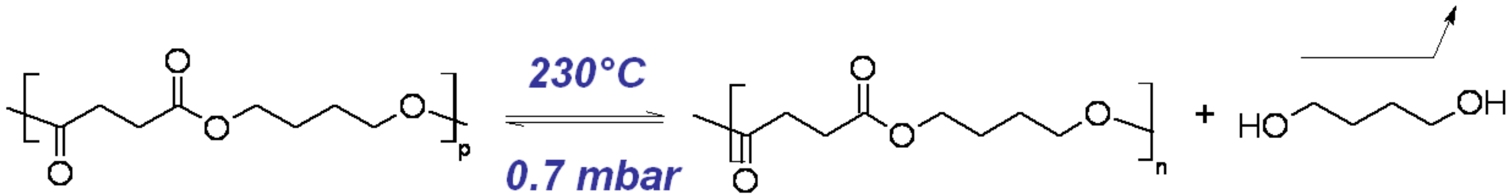
Esterification :



Succinic acid *Butanediol* *PBS oligomer*

Catalyst: GeO_2, Sb_2O_3, …

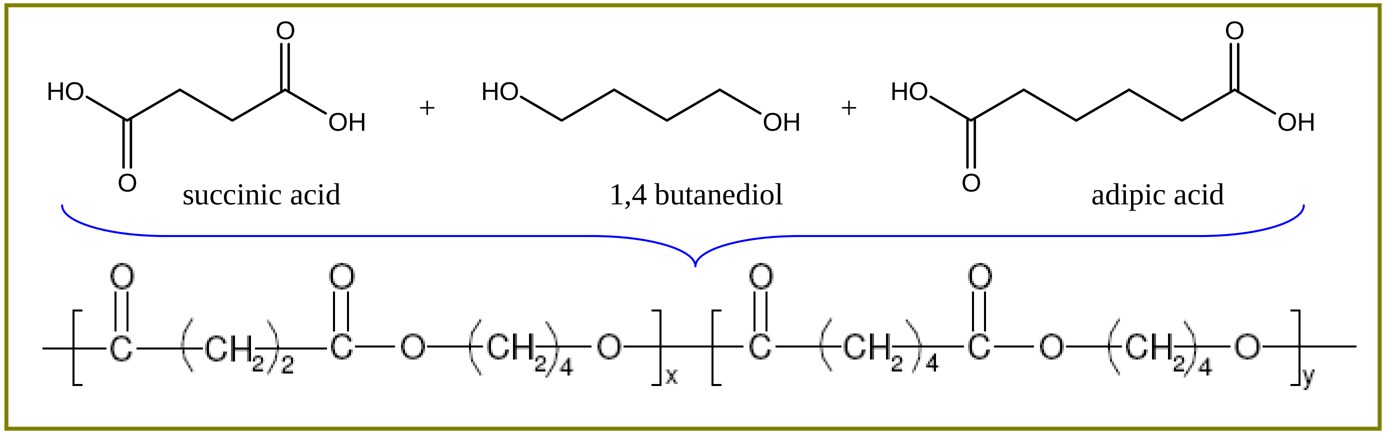
Trans-esterification:



PBS oligomer *PBS* *Butanediol*

Catalyst: $Ti(OBu)_4$, $Zr(OBu)_4$, $Sn(Oct)_2$, …

Poly(butylene succinate-*co*-adipate) (PBSA)



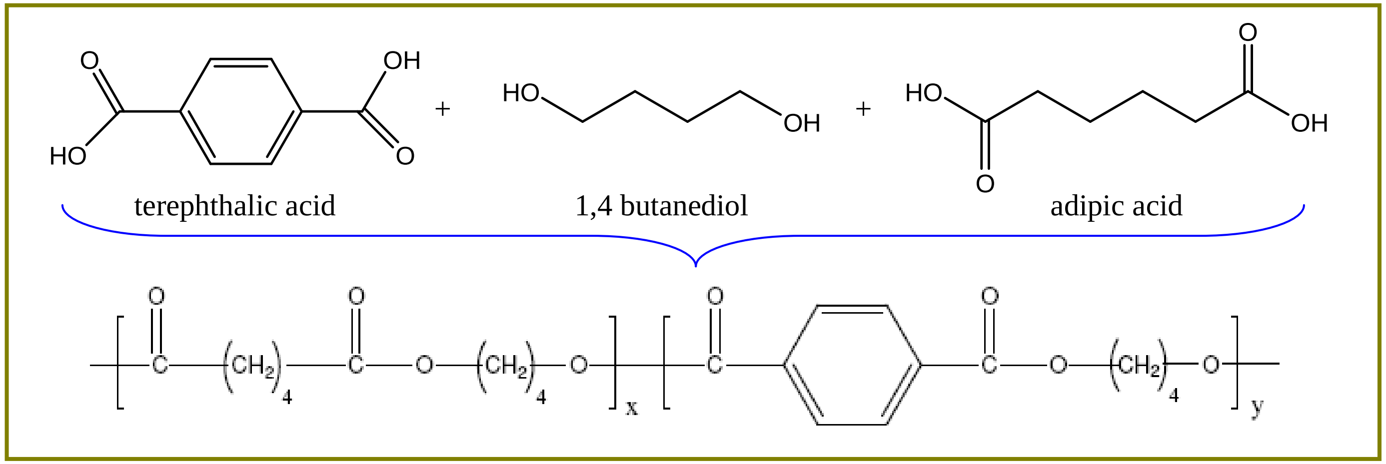
Characteristics:

Tg=-40°C, Tm=+100°C, E=250MPa, ε>500%

Showa HighPolymer
Ire Chemical
SK Chemicals
Nippon shokubai

Applications:

Poly(butylene adipate-*co*-terephthalate) (PBAT)



Eastman
BASF
Dupont
Novamont

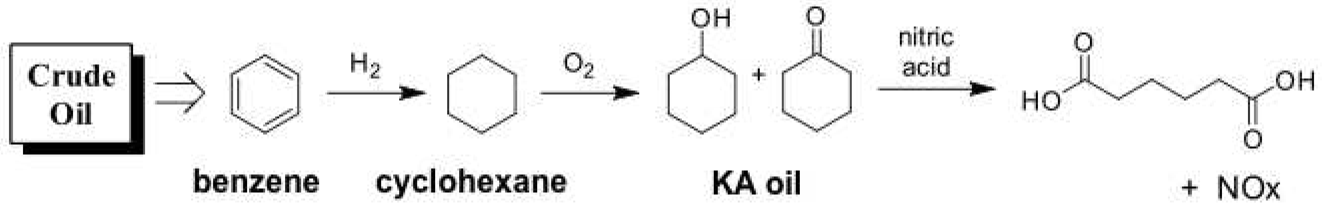
Characteristics :

Tg=-30°C, Tm=+110°C, E=50MPa, ε>500%

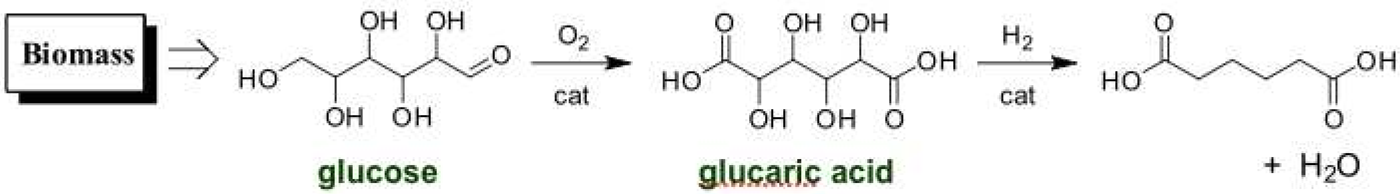
Applications:

Acide adipique

Current petrochemical process via cyclohexane:



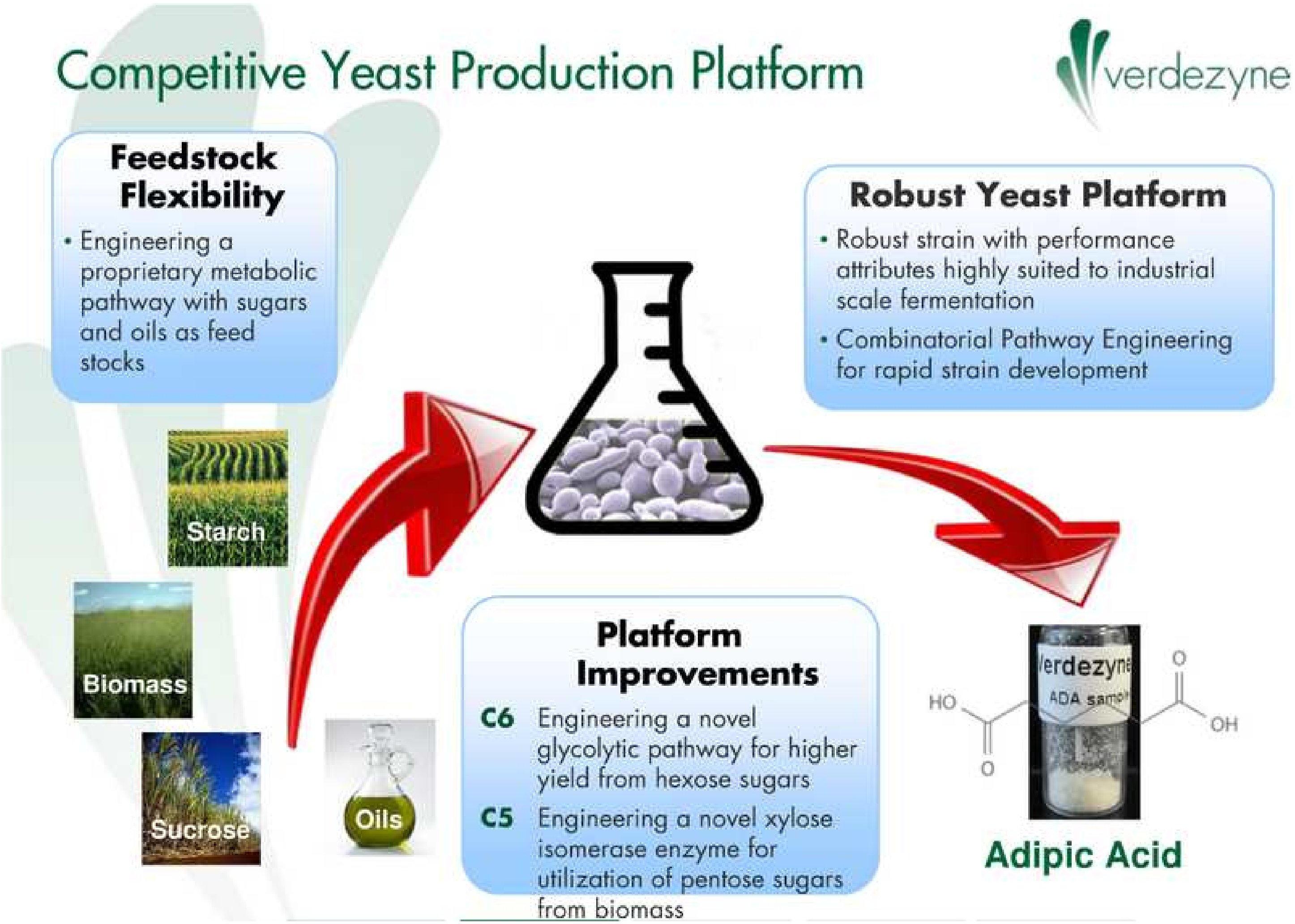
Rennovia renewable adipic acid process:



- Broad IP filed
- Preliminary cost estimates <u>below cash-cost</u> of cyclohexane process

Source : Rennovia

Acide adipique



Acide adipique

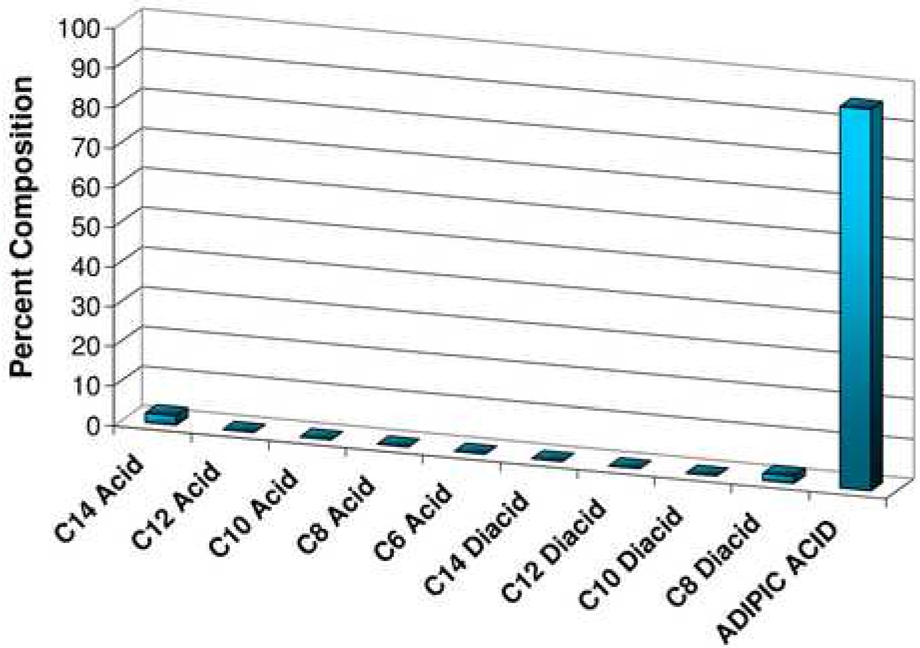
Demonstration of Adipic from Renewable Oils

verdezyne

- Engineered a yeast that selectively produces adipic acid from mixed plant-based oil feedstocks

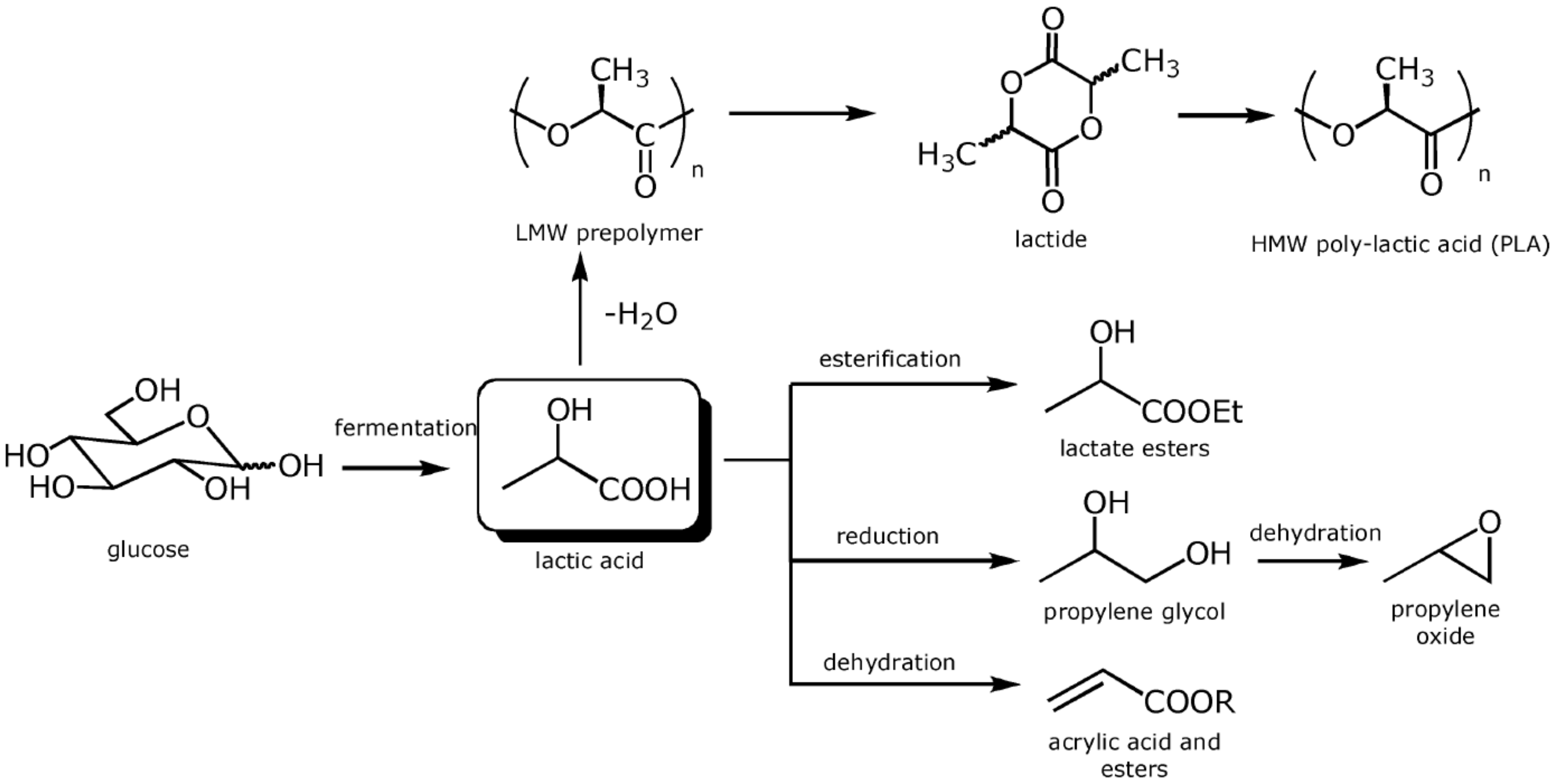
Fatty Acid Profile of Coconut Oil		
Formula	Name	Percent
C6:0	Caproic	0.5
C8:0	Caprylic	7.8
C10:0	Capric	6.7
C12:0	Lauric	47.5
C14:0	Myristic	18.1
C16:0	Palmitic	8.8
C18:0	Stearic	2.6
C20:0	Arachidic	0.1
C18:1	Oleic	6.2
C18:2	Linoleic	1.6

Acid/Diacid Profile Produced from Coconut Oil



Unités pilotes annoncées (Bioamber, Rennovia, Verdezyne)

Lactic acid



CH3
n
O
C
O
LMW prepolymer
O
CH3
O
O
H3C
O
O
lactide
CH3
n
O
O
HMW poly-lactic acid (PLA)
-H2O
OH
O
HO
HO
OH
OH
glucose
fermentation
OH
COOH
lactic acid
esterification
OH
COOEt
lactate esters
reduction
OH
OH
propylene glycol
dehydration
O
propylene
oxide
dehydration
COOR
acrylic acid and
esters

Lactic acid

Lactic acid is a well-recognized biobased chemical, commercially produced by glucose fermentation using organisms such as *Lactobacillus delbrueckii*.

Problem of neutralization and amount of waste $CaSO_4$

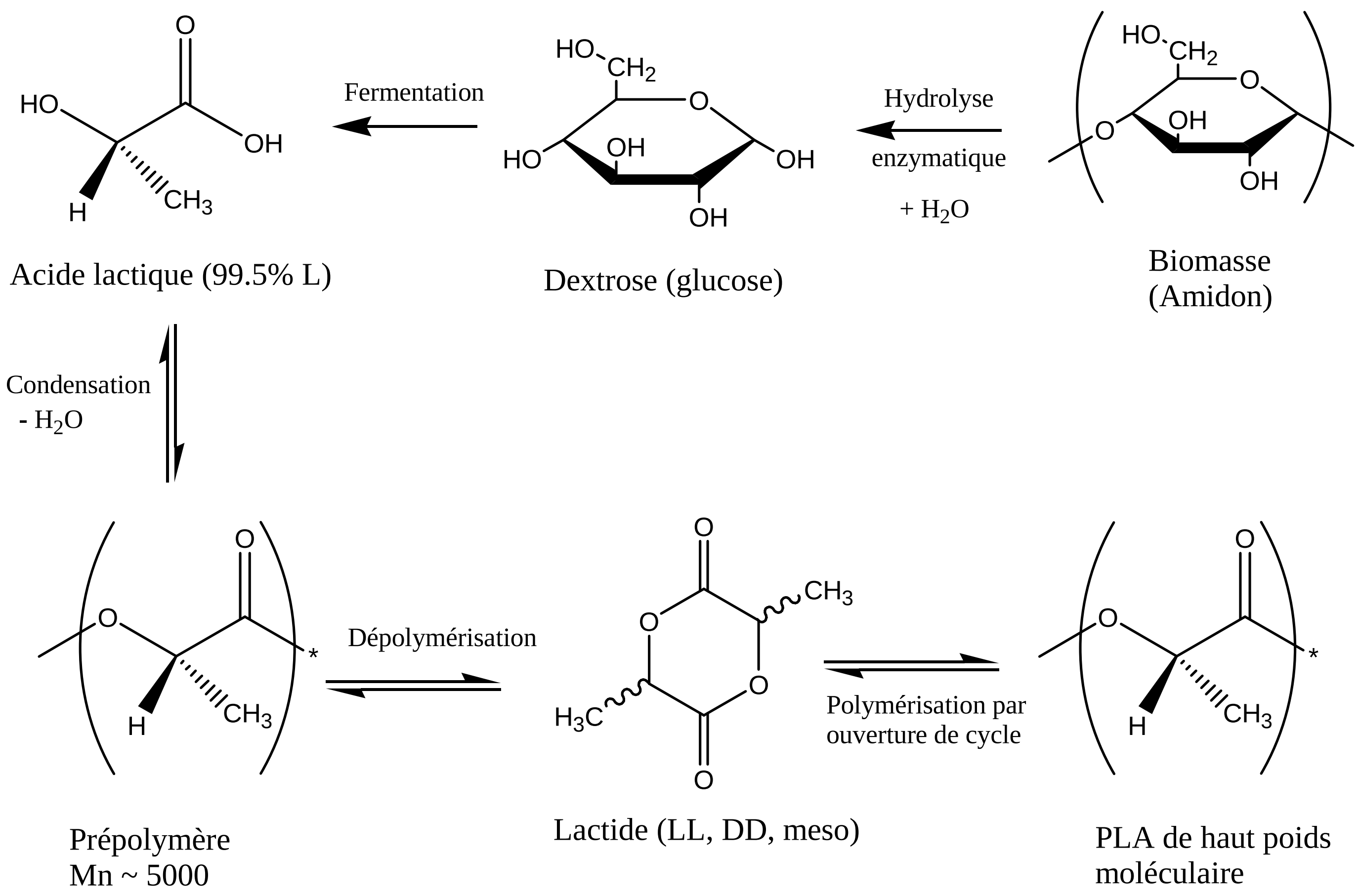
The primary use for lactic acid is the production of polylactic acid (PLA)

Catalytic reduction of lactic acid leads to propylene glycol, which can be further dehydrated to give propylene oxide.

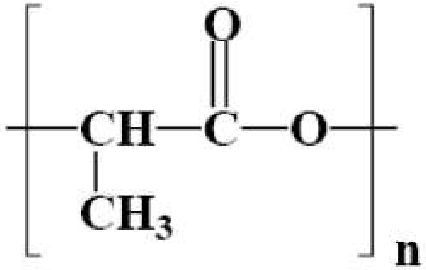
Alternatively, lactic acid can be dehydrated to give acrylic acid and esters, but in practice this conversion proceeds in low yield.

Bio-based synthetic polyester: PLA

PLA synthesis route:



Bio-based synthetic polyester: PLA



PLA

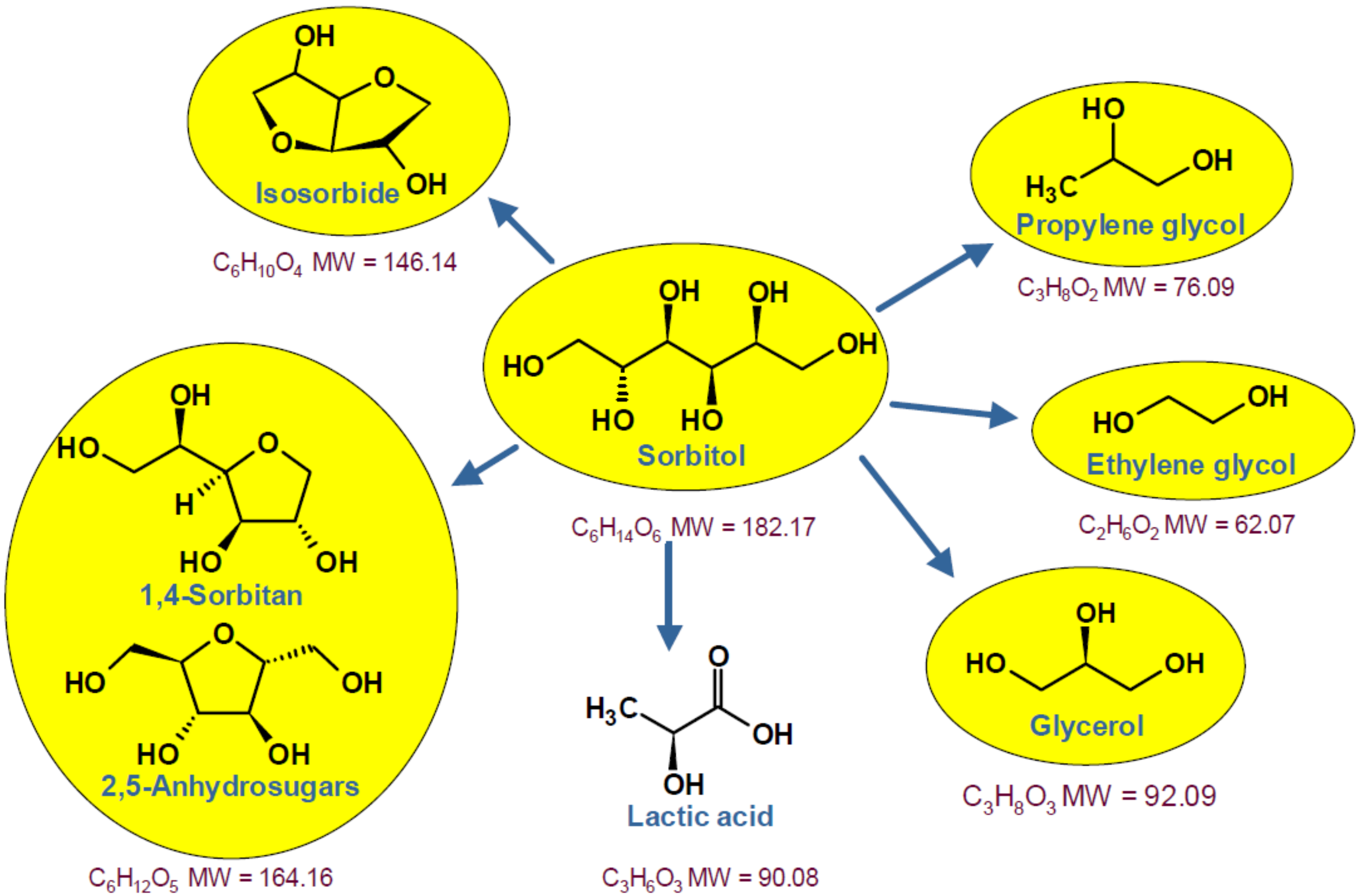
Characteristics: Tg=+60°C, Tm=+150°C, E=2000MPa, ε=10%

Main producer: Natureworks (Cargill-Dow) 50-150ktons/an

Other actors: Futerro (Galatic + Total), Purac, Hycail, Toyota,…

Average price: About 2 €/kg (data from 2009)

Sorbitol


OH
O
O
OH
Isosorbide
$C_6H_{10}O_4$ MW = 146.14
HO
OH
H_3C
Propylene glycol
$C_3H_8O_2$ MW = 76.09
OH OH
OH
HO
HO HO
Sorbitol
$C_6H_{14}O_6$ MW = 182.17
HO
OH
Ethylene glycol
$C_2H_6O_2$ MW = 62.07
OH
HO
O
H
HO
OH
1,4-Sorbitan
O
HO
OH
HO
OH
2,5-Anhydrosugars
$C_6H_{12}O_5$ MW = 164.16
O
H_3C
OH
OH
Lactic acid
$C_3H_6O_3$ MW = 90.08
OH
HO
OH
Glycerol
$C_3H_8O_3$ MW = 92.09

Sorbitol

The use of sorbitol as a building block for derivatives only needs to perform conversion of glucose to sorbitol in a continuous process instead of a batch process. This would make sorbitol a very inexpensive feedstock for producing derivatives.

Inexpensive sorbitol affords the potential for the production of isosorbide at low costs.
Isosorbide has been demonstrated to be a very promising monomer

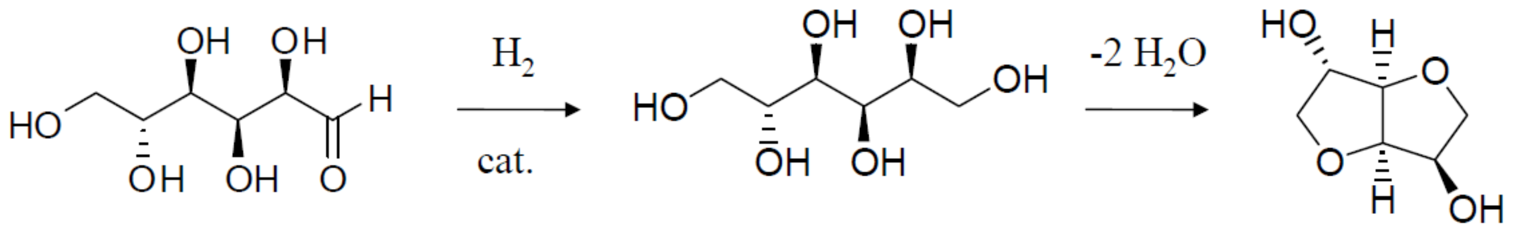
The conversion of sorbitol to glycols, namely propylene glycol is based on the hydrogenolysis of sorbitol. The major difficulty is producing propylene glycol in high yields.

New efficient biochemicals routes to obtain sorbitol from glucose have been identified

Sorbitol derivatives

Isosorbide

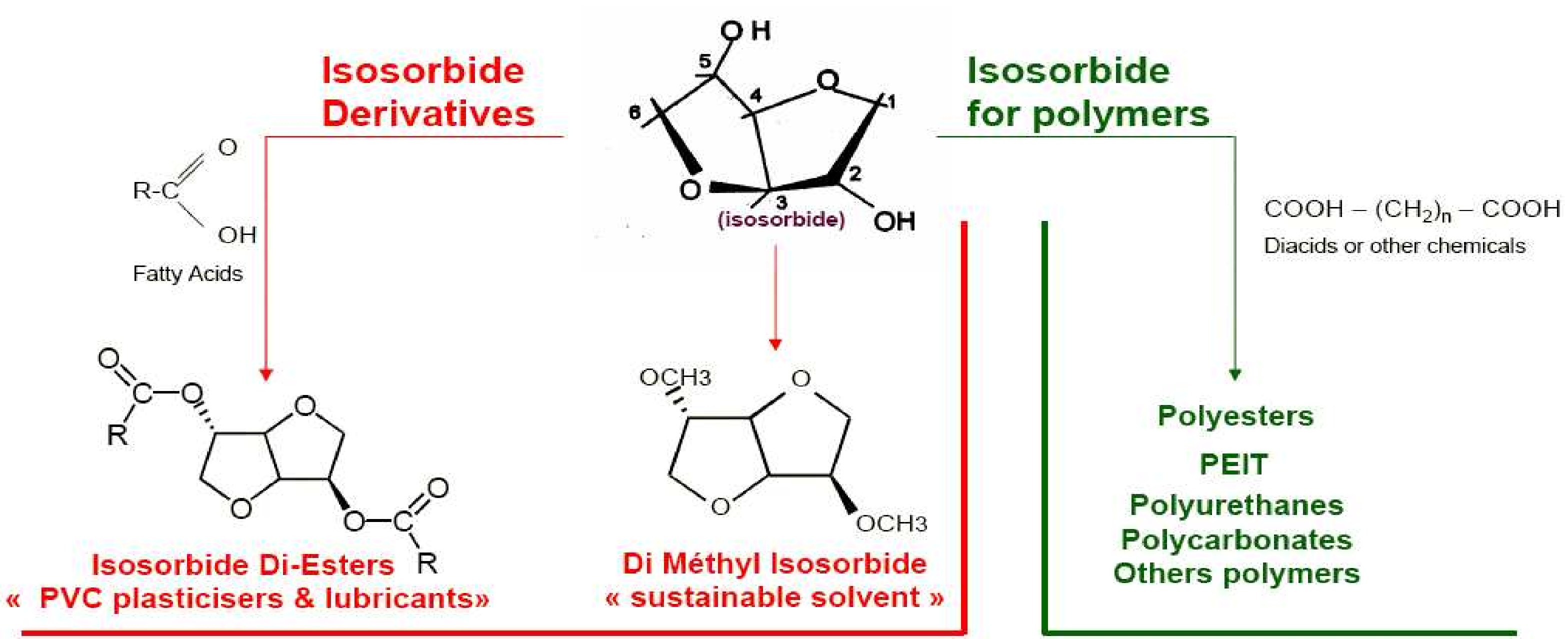
- Diol bicyclique rigide préparé à partir du sorbitol par cyclodéshydratation catalysée par un acide



Glucose (C6 sugars) — Sorbitol (C6 sugar polyols) — Isosorbide (dianhydrohexitols)

Isosorbide (issu du sorbitol)

- Utilisations de l'isosorbide



- Essentiel des développements par Roquette & Dupont (depuis 1995)

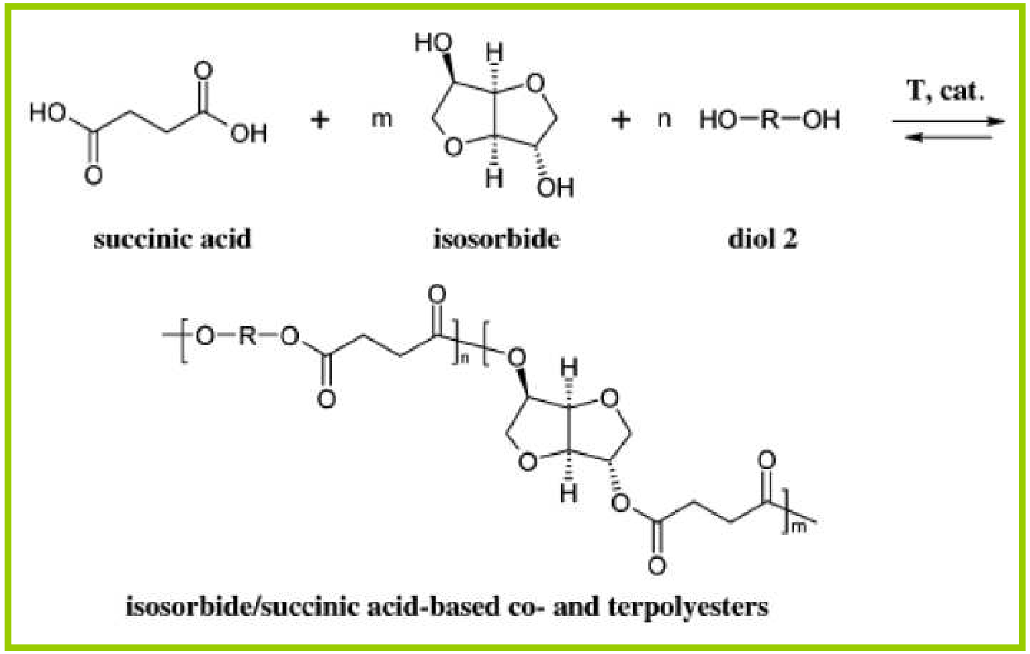
Isosorbide (issu du sorbitol)

- Monomère intéressant pour polymérisation par polycondensation

- Incorporation d'un diol rigide augmente Tg du polymère, permettant des applications à hautes températures

- Cristallinité réduite

- Incorporation >80% donne un polymère amorphe

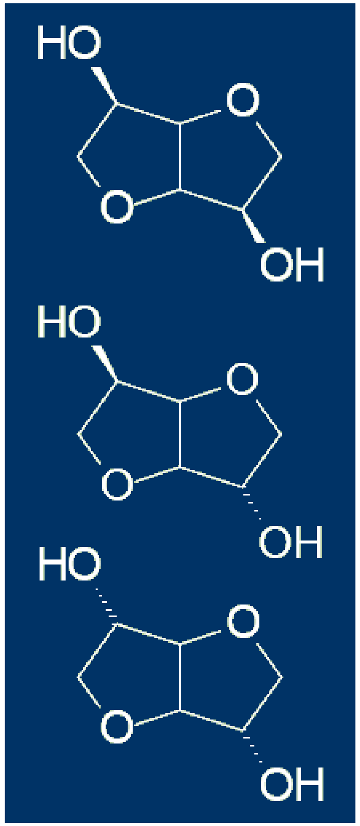


Source: Noordoveret al. Biomacromolecules 2006, 7, 3406-3416.

Isohexides (isosorbide, …)

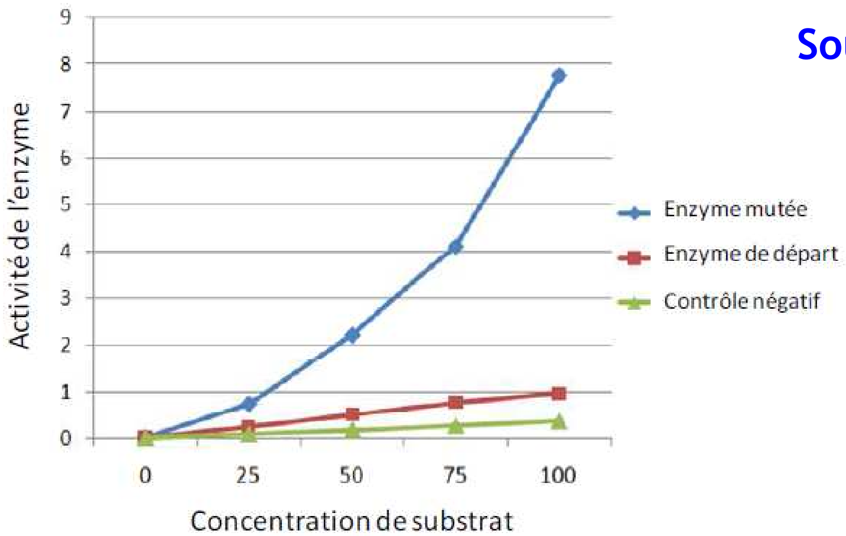
Trois isomères isohexide connus

- Isomannide (issu du mannitol) exo-exo
- Isosorbide (issu du sorbitol) exo-endo
- Isoidide endo-endo (iditol non disponible en quantité >g) peut être obtenu par isomérisation de l'isosorbide



Isobutene

Implémentation dans un microorganisme d'une voie métabolique artificielle (suite de réactions enzymatiques obtenues en détournant des enzymes de leur fonction naturelle.



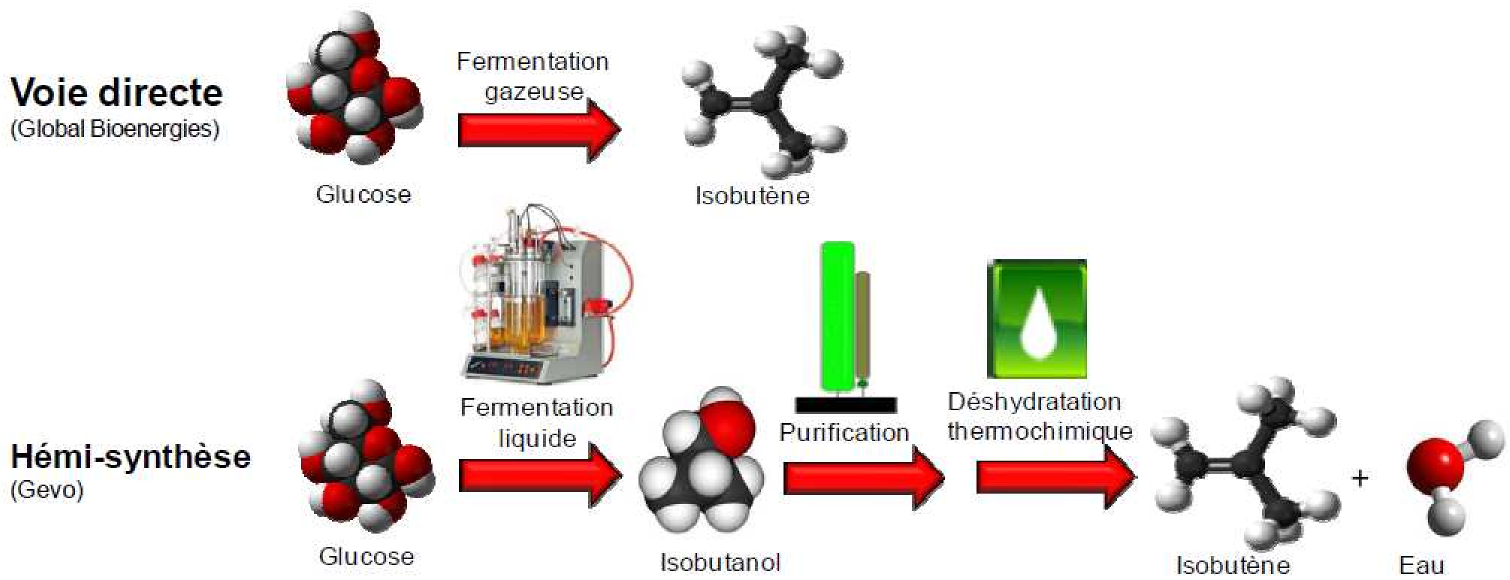
Amélioration d'une enzyme de la voie métabolique artificielle vers l'isobutène

Source: Global Bioenergies

Démarrage unité pilote

Coût : bio-isobutène ~ 0,6-1,1 $/kg *vs.* isobutène fossile ~ 2$/kg

Isobutene

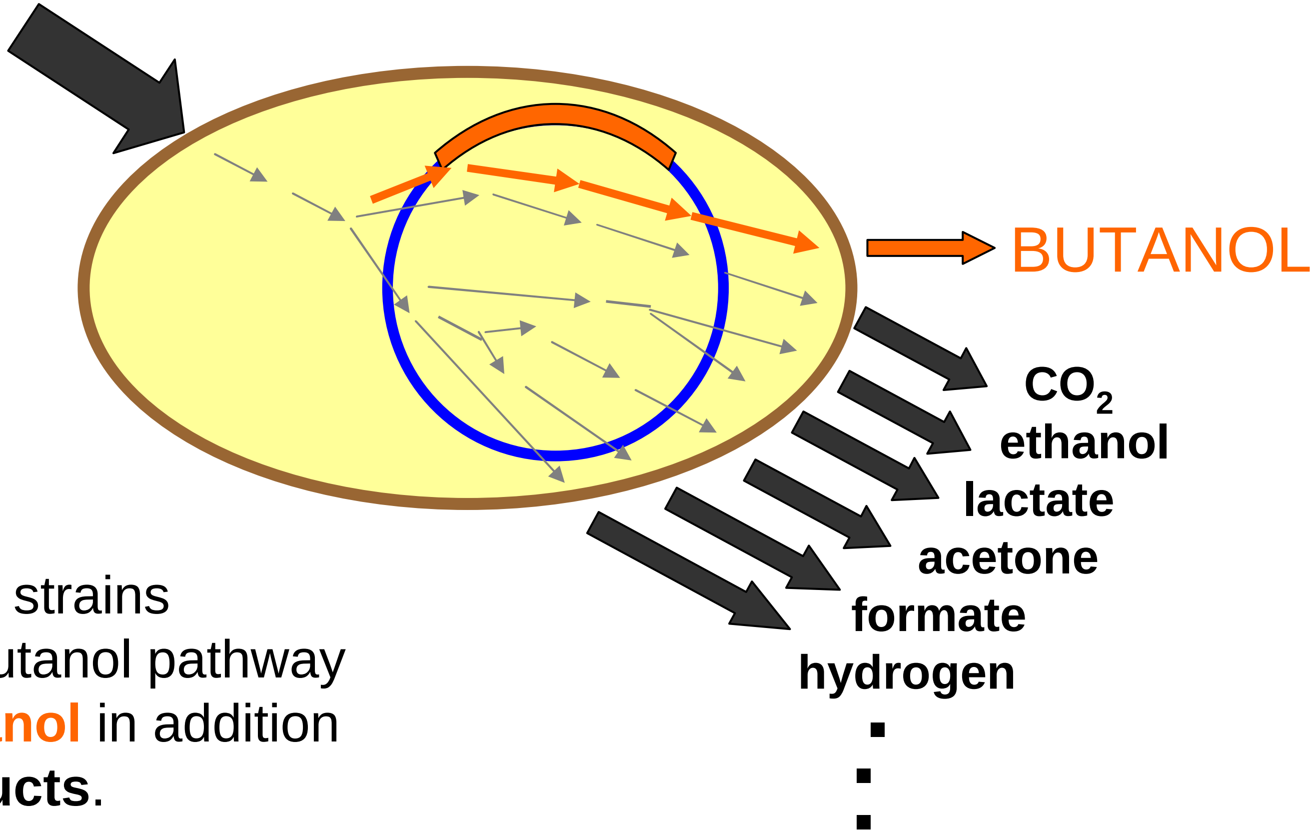


Gevo: unité de production pour 2012 ?

Partenariat avec Lanxess (et Cargill) pour rubber à partir de butène issu de butanol

Butanol

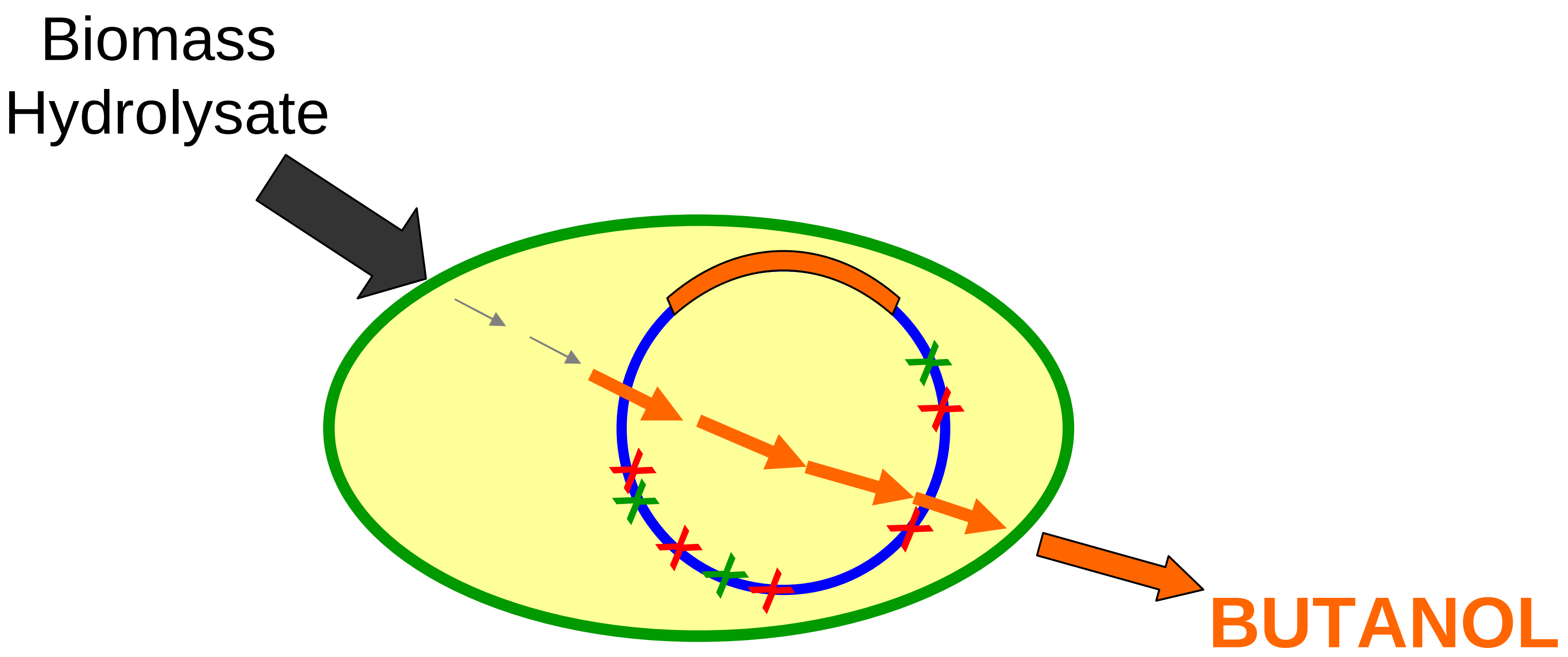
Biomass
Hydrolysate



A recombinant strains containing a butanol pathway produces **butanol** in addition to **other products**.

Source: Gevo

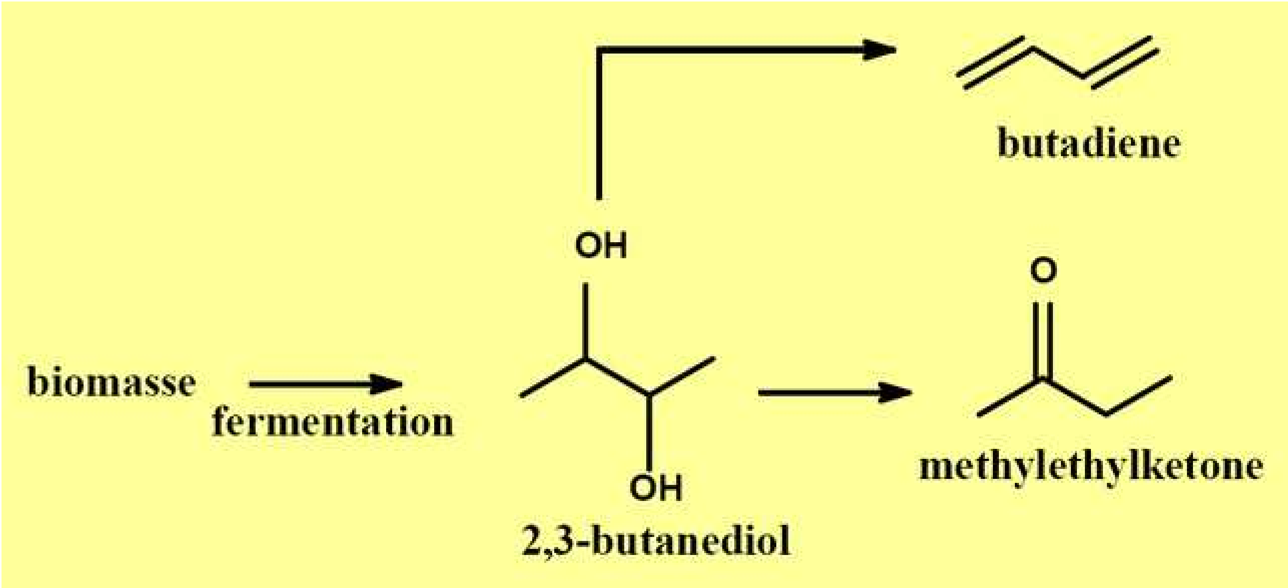
Butanol



Classical and genetic techniques are used to improve **butanol** tolerance.

Source: Gevo

2,3-Butanediol et Butadiene

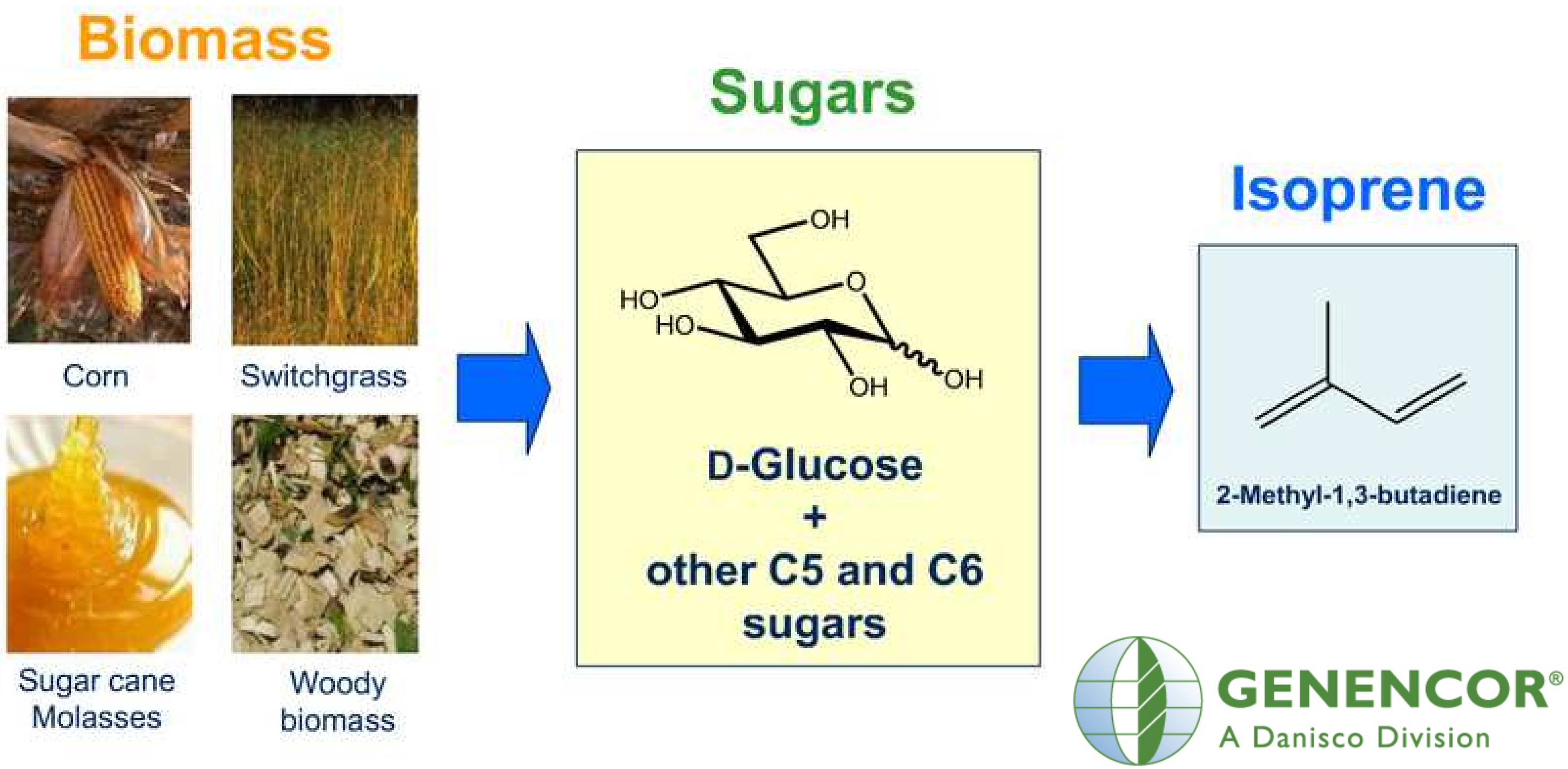


- Production fermentaire de 2,3-butanediol par *Klebsiella oxytoca* à partir du glucose

- La déshydratation chimique en **butadiène** est possible

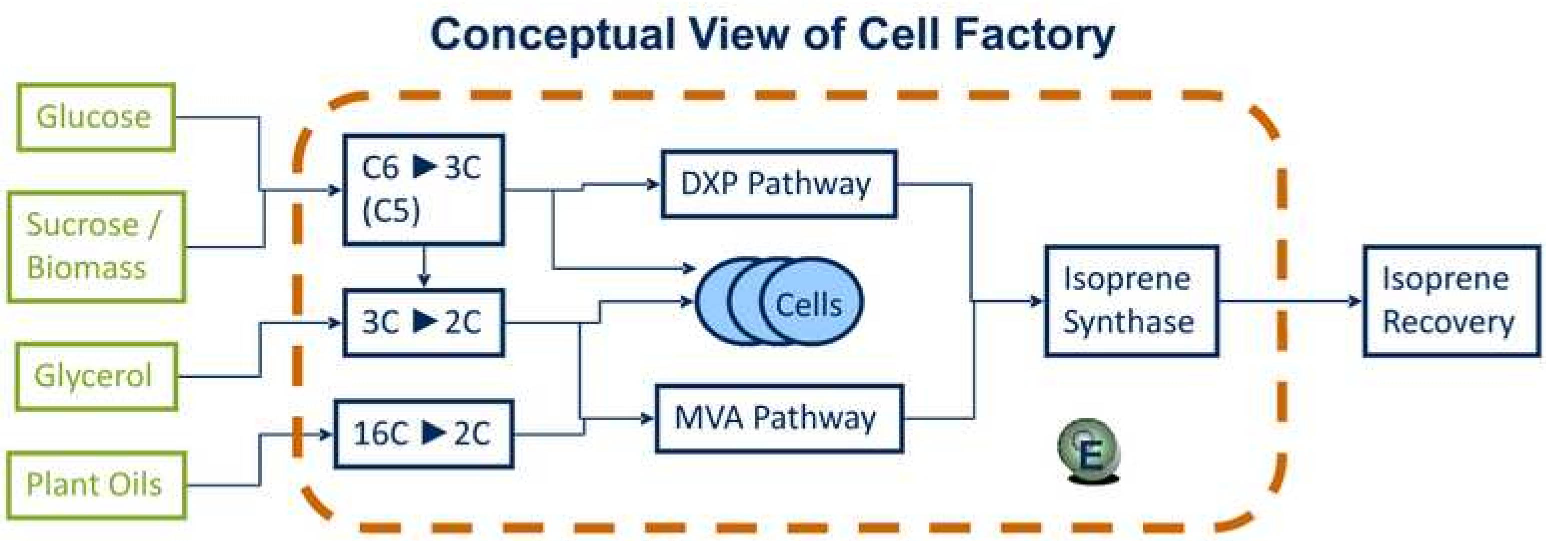
- Synthèse de 2-butanone (methylethylketone) à partir du 2,3-butanediol en utilisant un enzyme diol-déshydratase enzyme issue d'une souche de *Lactobacillus brevis*.

Isoprene



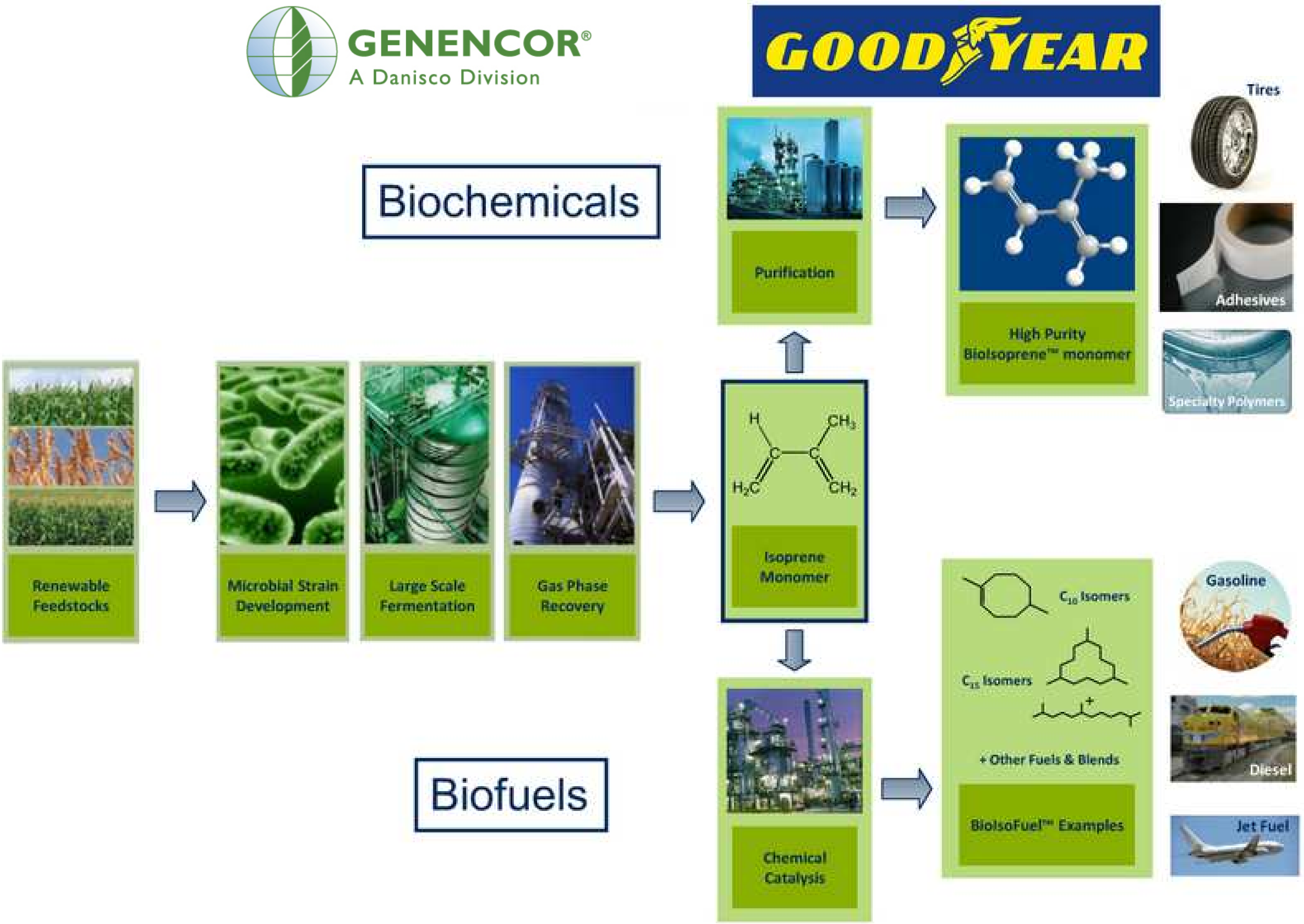
We aim to develop an efficient and sustainable fermentation route to isoprene from carbohydrate feedstocks

Isoprene

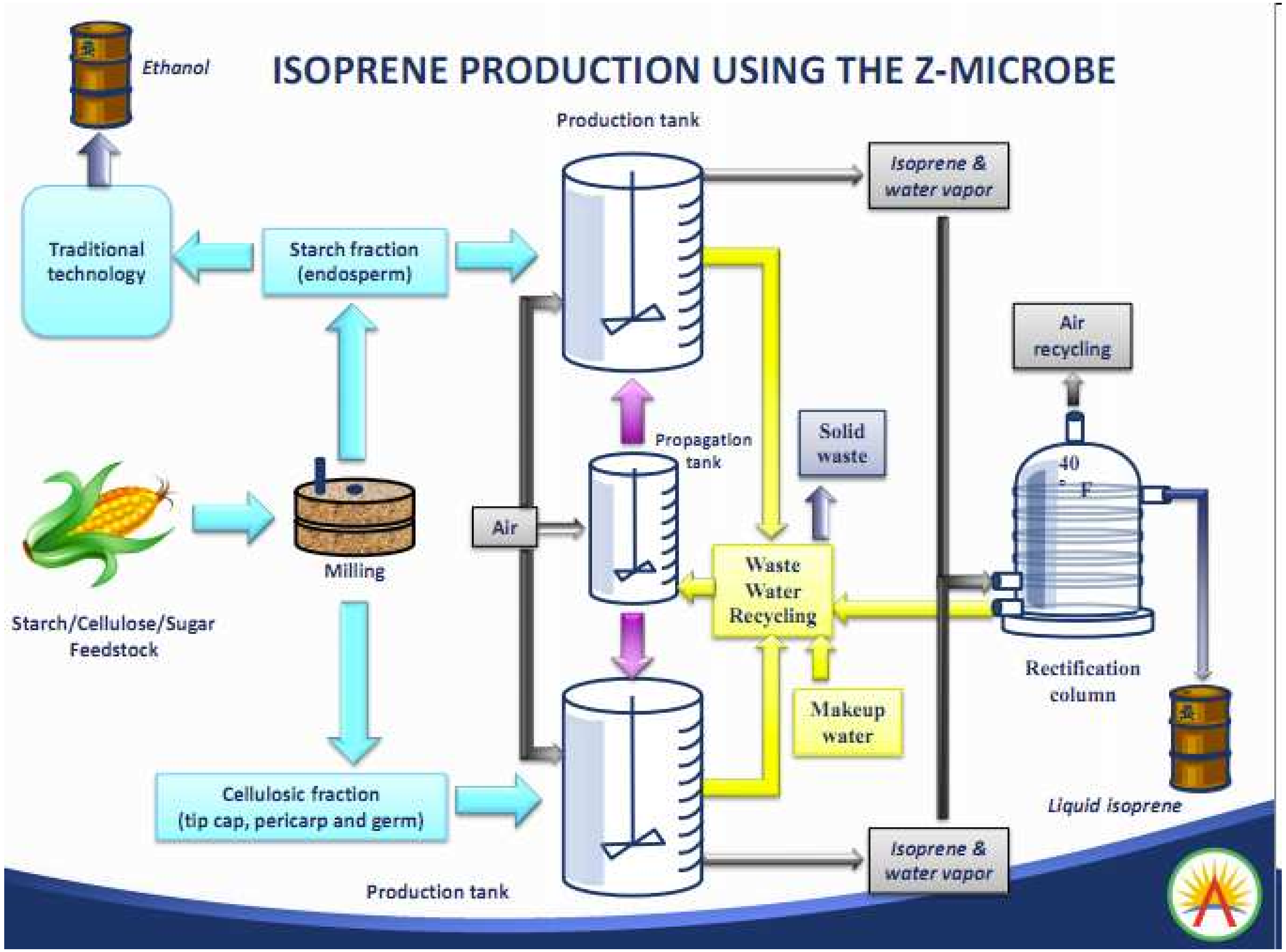


- Multiple feedstocks possible
- Two feeder pathways to isoprene precursor
- Isoprene synthase
- Gas Phase recovery

Isoprene

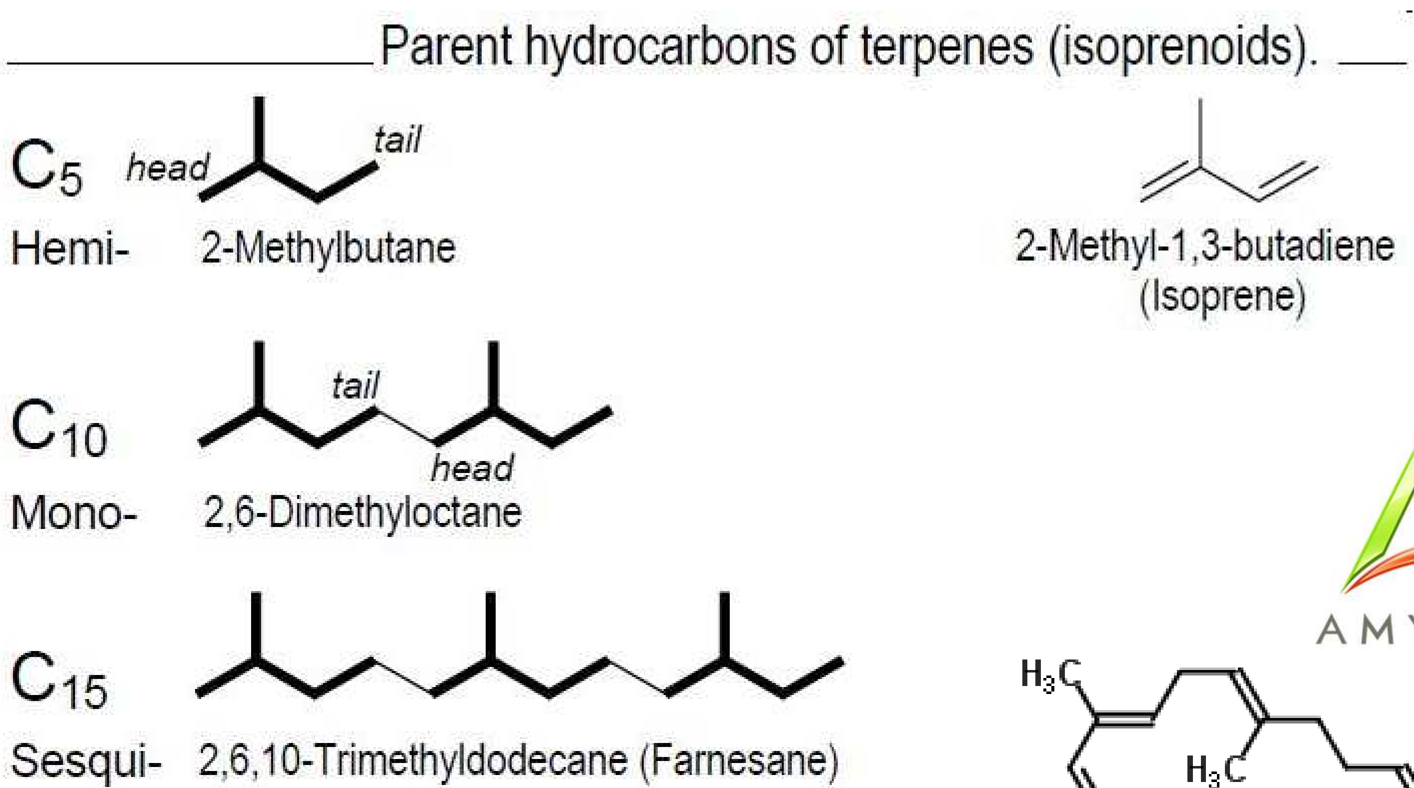

GENENCOR®
A Danisco Division
GOODYEAR
Biochemicals
Biofuels
Renewable Feedstocks
Microbial Strain Development
Large Scale Fermentation
Gas Phase Recovery
Isoprene Monomer
Purification
High Purity BioIsoprene™ monomer
Tires
Adhesives
Specialty Polymers
Chemical Catalysis
C10 Isomers
C15 Isomers
+ Other Fuels & Blends
BioIsoFuel™ Examples
Gasoline
Diesel
Jet Fuel

Isoprene

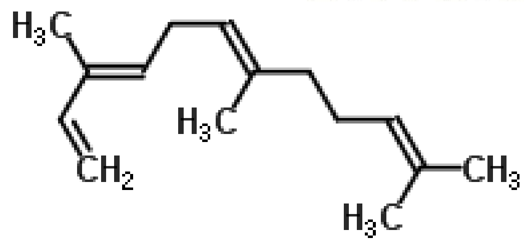


Aemetis (issu de la fusion AEBiofuels + Zemetis)

Isoprene



AMYRIS

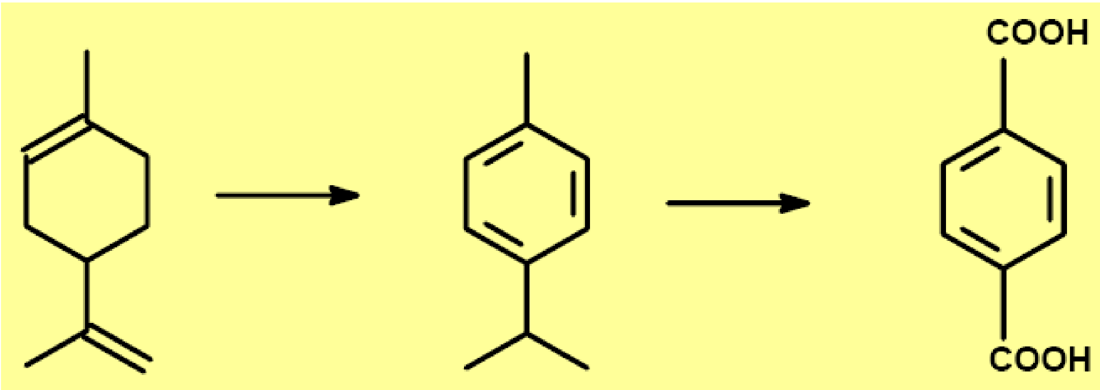


Amyris (+Total / + Michelin)

Farnesene

Dérivés terpéniques

Terpènes et dérivés

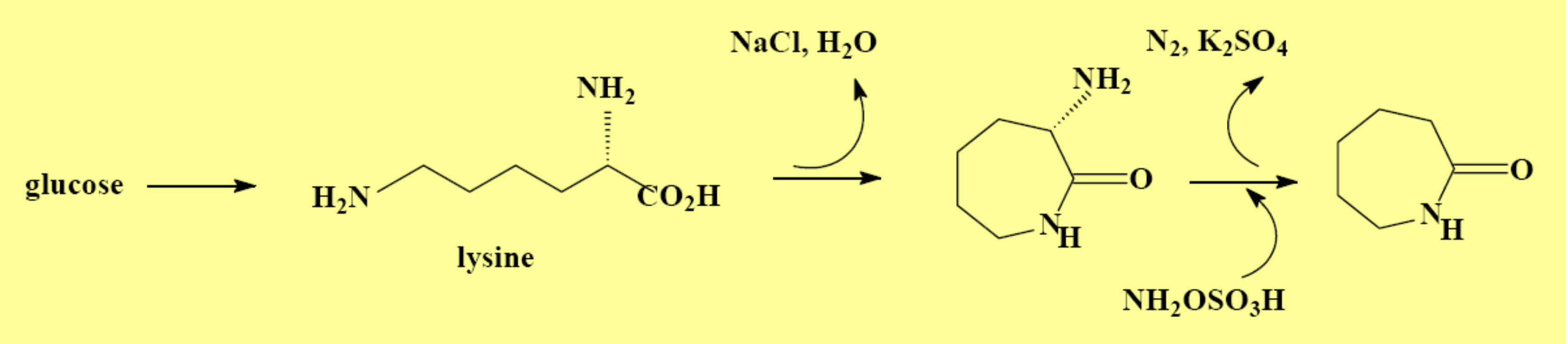


- Les terpènes tel que le limonène sont une solution pour la production de composés aromatiques bio-sourcés (e.g. acide téréphtalique)

- Problématique des faibles volumes de terpènes pour en faire des synthons bio-sourcés ?!

Synthons azotés

- Synthons azotés bio-sourcés très intéressants (polyamides)



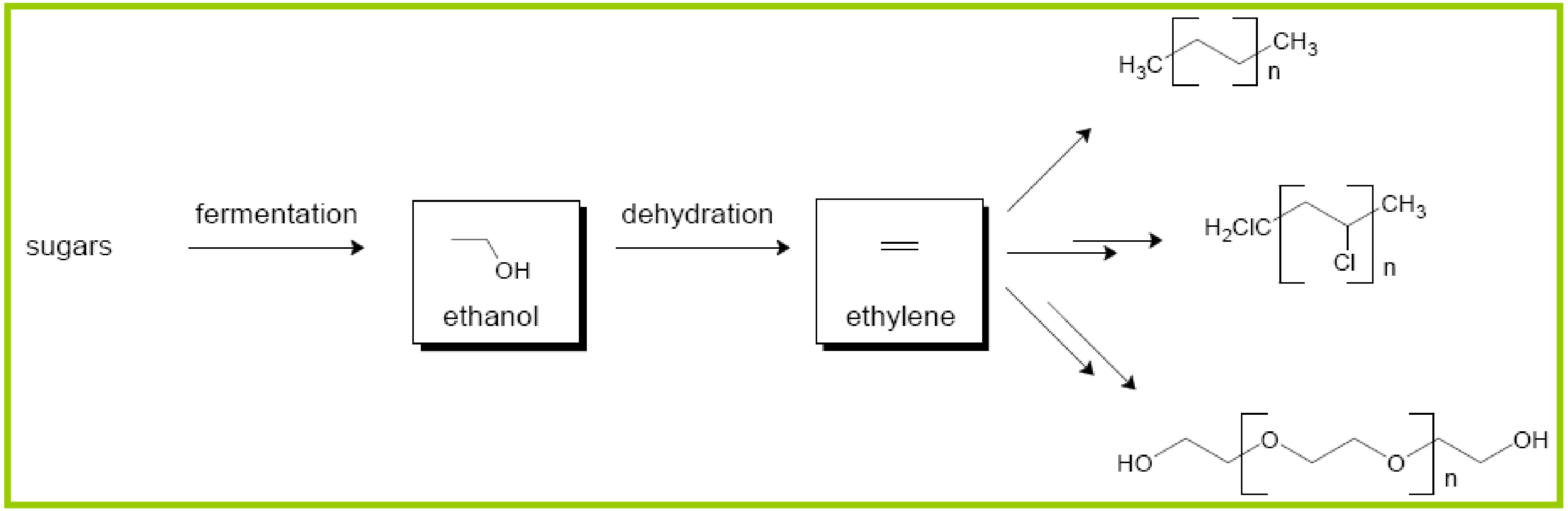
Conversion du glucose en caprolactame possible via la lysine

(JW Frost "Synthesis of caprolactam from lysine", WO2005123669)

Utilisation / valorisation des volumes croissants de résidus protéinés ?!

Bio-ethanol and PE

- Bioethylene (for polyethylene or vinyl chloride, …)
  - By dehydration of bioethanol (e.g. Braskem)



- Only viable in case of cheap bio-ethanol supply (today: Brazil)
  sugarcane bioethanol about 500€/ton vs ethylene 1200€/ton

- Is there enough bioethanol available for ethylene?
  (75 MioT worldwide in 2005, vs 40 MioT ethanol in 2006)

Bio-ethanol and PE

- **biomass to ethanol**
- **ethanol to ethylene**
- **ethylene to PE**

- Mid-2007: Braskem announces plans to produce polyethylene based on bioethanol

- Mid-2010: Braskem launch on market its "green" polyethylene based on bioethanol and announces production of "green" polypropylene for 2013

I'm green™

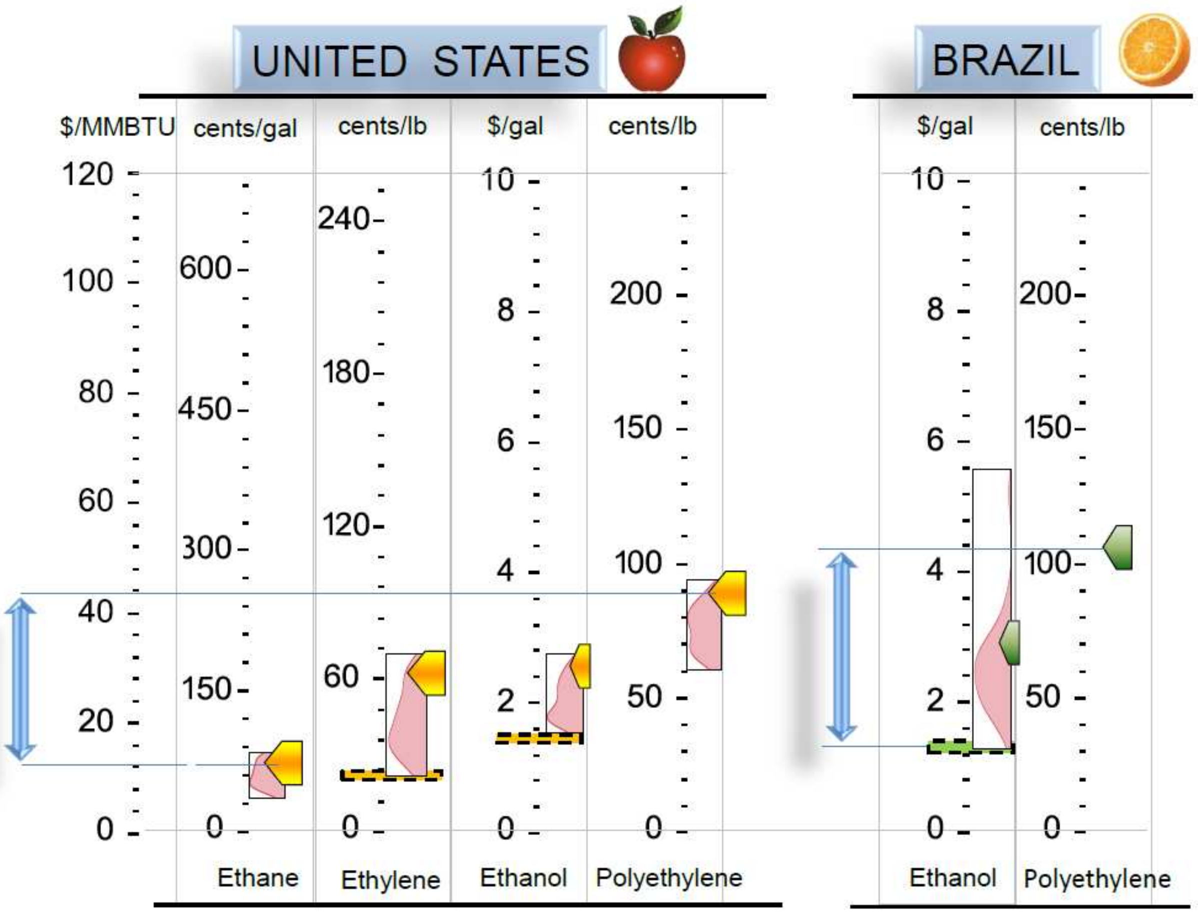
OK biobased VINÇOTTE S237

Bio-ethanol and PE

Market prices and selected costs on energy equivalent basis

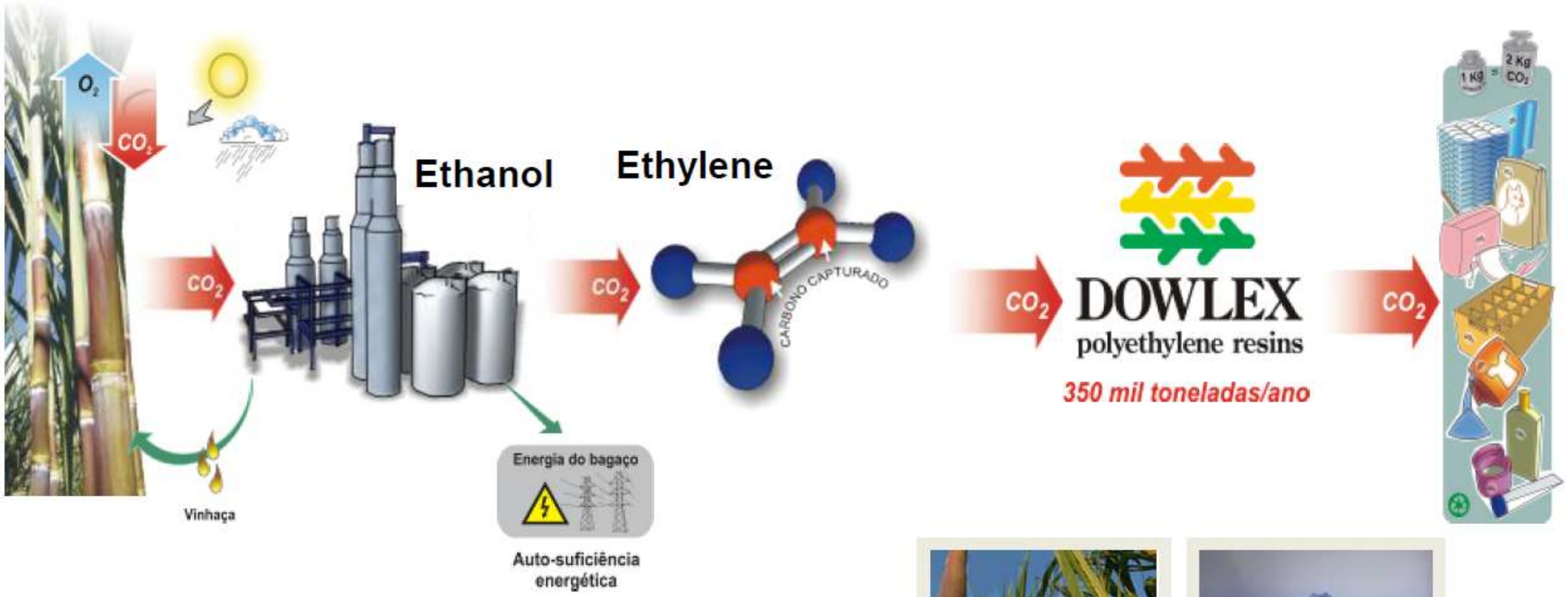
- Existing logistics for ethanol in Brazil
- High polyethylene price in Brazil
- Ethanol price fluctuation requires integration

Area required for produce ethanol to meet global PE production ~ 1x of Minnesota at Brazil cane productivity



Source: Dow

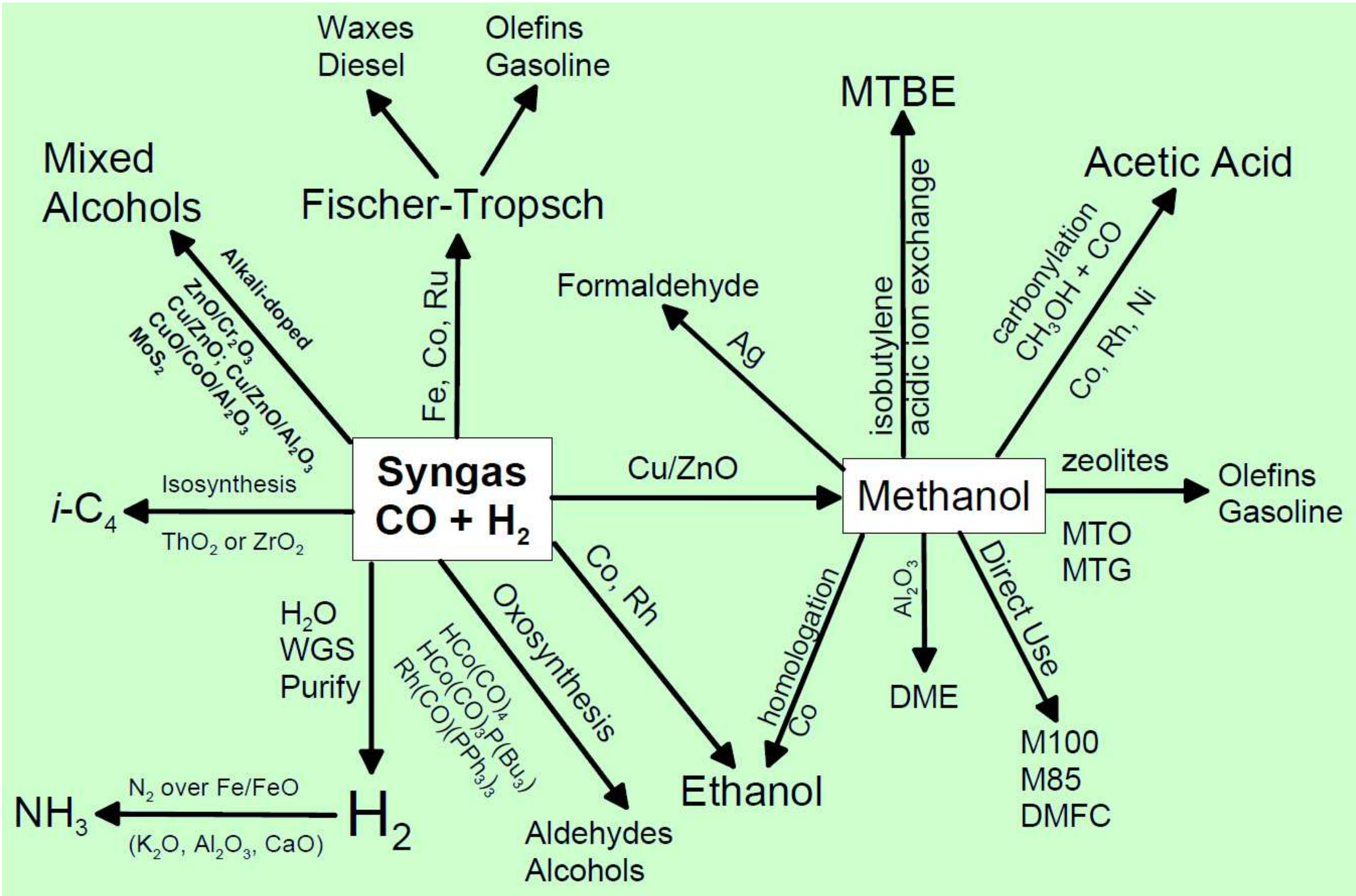
Bio-ethanol and PE



Fully-integrated facility in Brazil
Utilizes state-of-the-art Dow polymerization catalysis

Solvay to produce bio-ethylene for PVC production

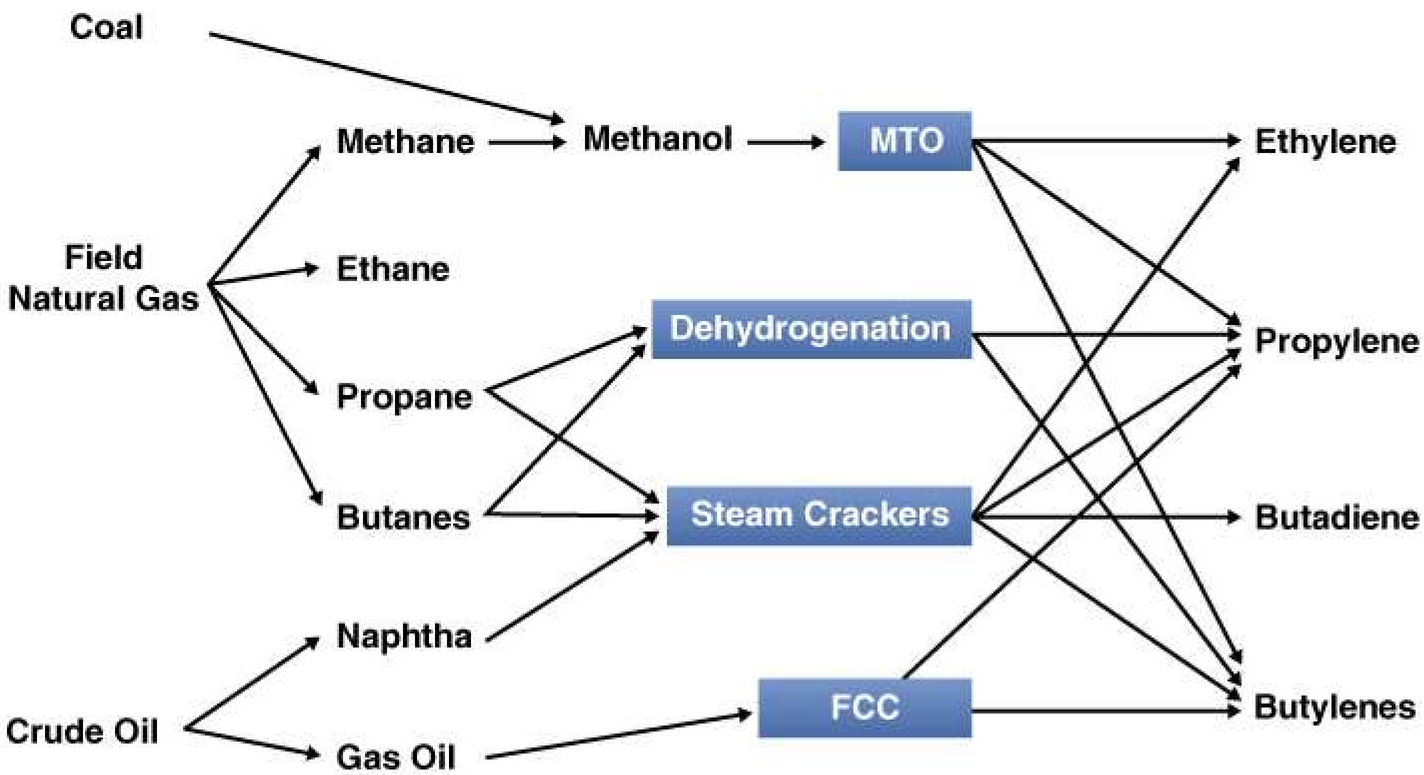
Syngas / Methanol



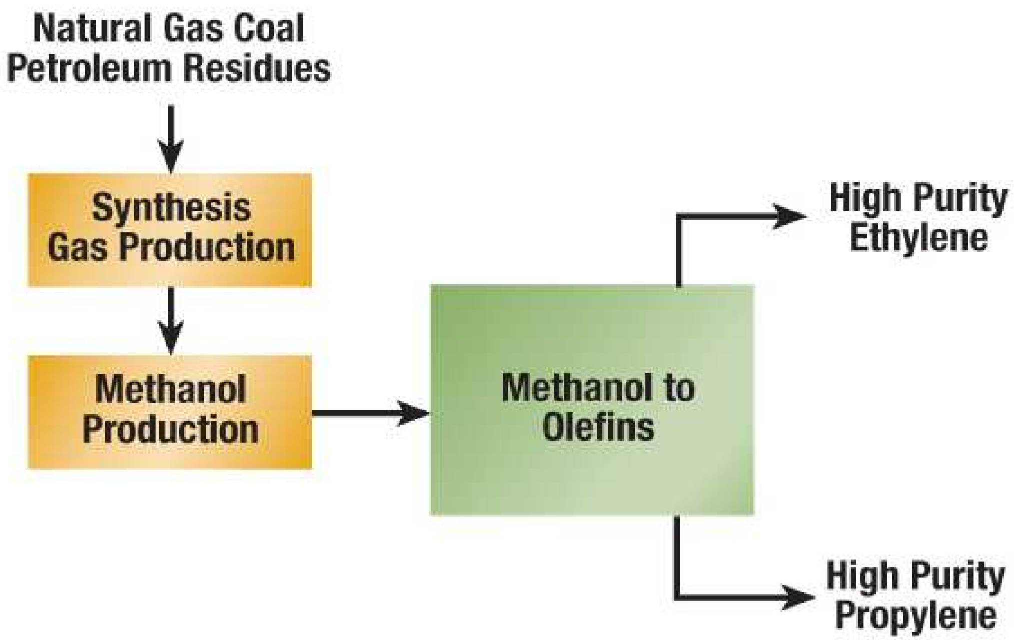
Methanol To Olefins (MTO) Process

Increasing demand for light olefins worldwide (mostly propylene)

Need for alternative solution to increase propylene production



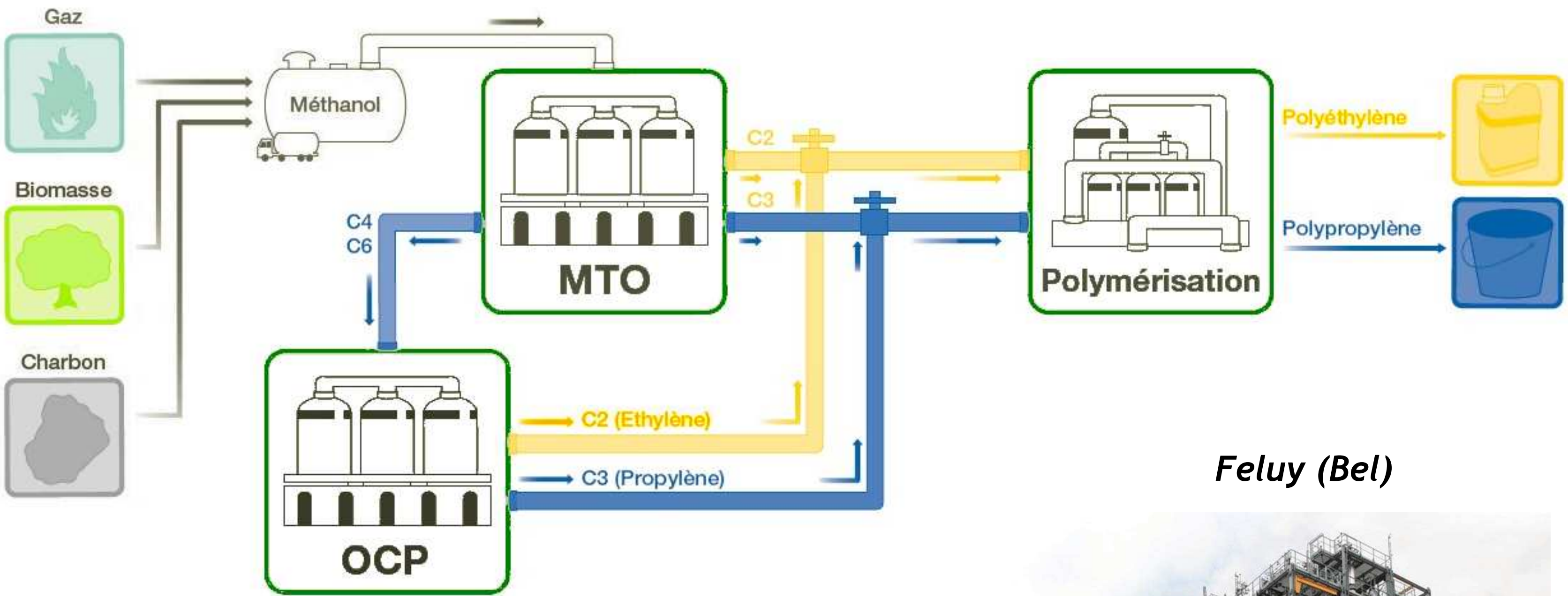
Methanol To Olefins (MTO) Process



$$2\,CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} \text{light olefins} \longrightarrow \begin{array}{l}\text{n/iso-paraffins}\\ \text{higher olefins}\\ \text{aromatics}\\ \text{naphthenes}\end{array}$$

Methanol to dimethyl ether (DME) to olefins

Methanol To Olefins (MTO) Process



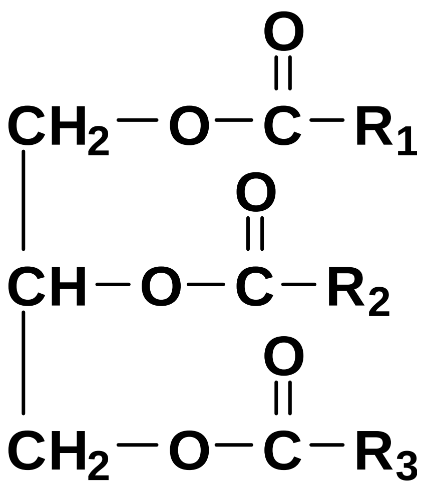
Feluy (Bel)

Olefin Cracking Process

maximize production and recovery of light olefins

Materials from vegetable oils

Oils are triglyceride esters of mixed fatty acids



where R_1, R_2, and R_3 are saturated or unsaturated fatty acids

Materials from vegetable oils

Unsaturated Fatty Acids in Vegetable Oils

$$HOOC—(CH_2)_7—CH{=}CH—(CH_2)_7—CH_3$$

9-Oleic Acid

$$HOOC—(CH_2)_7—CH{=}CH—CH_2—CH{=}CH—(CH_2)_4—CH_3$$

9,12-Linoleic Acid

$$HOOC—(CH_2)_7—CH{=}CH—CH_2—CH{=}CH—CH_2—CH{=}CH—CH_2—CH_3$$

9,12,15-Linolenic Acid

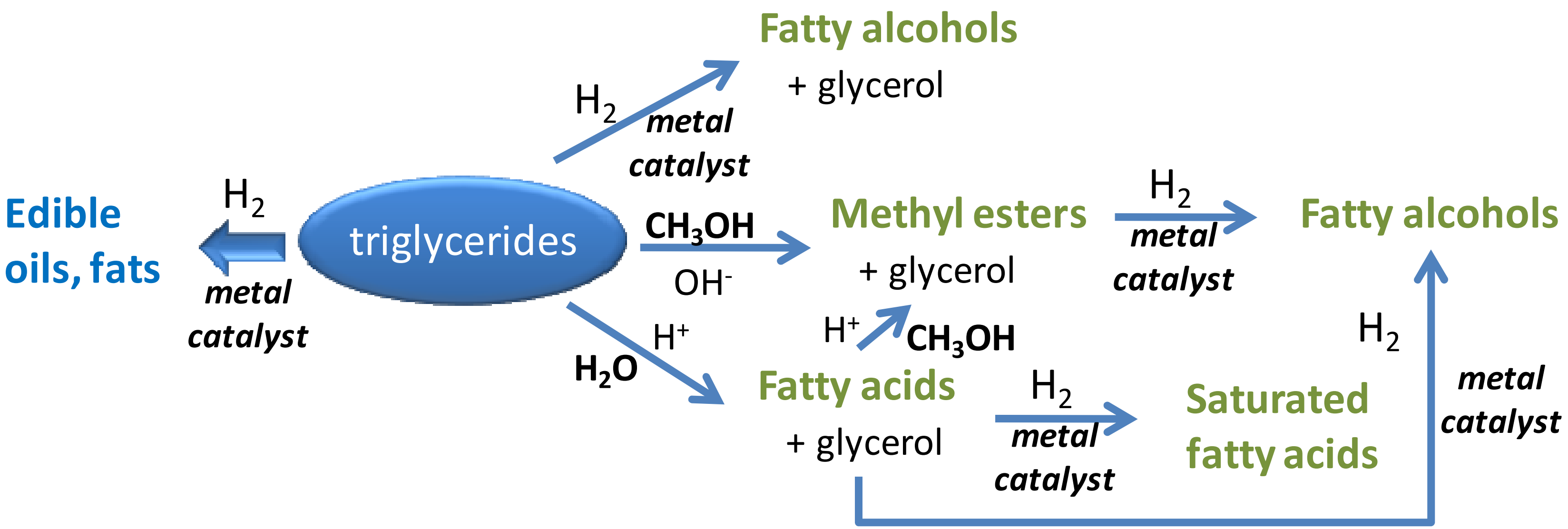
$$HOOC—(CH_2)_7—CH{=}CH—CH_2—\overset{OH}{\overset{|}{CH}}—(CH_2)_5—CH_3$$

Ricinoleic Acid

Materials from vegetable oils

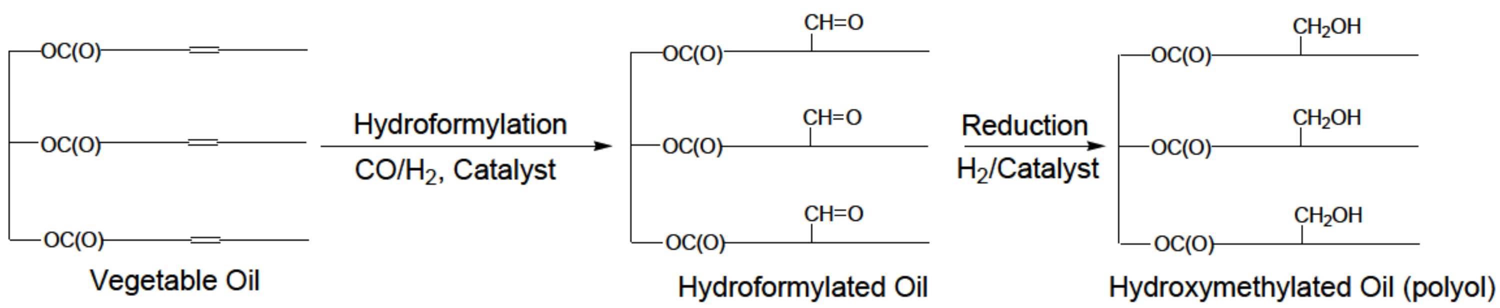
Fatty acid esters and fatty alcohols are useful platform molecules to prepare surfactants, emulsifier, lubricants and polymers.

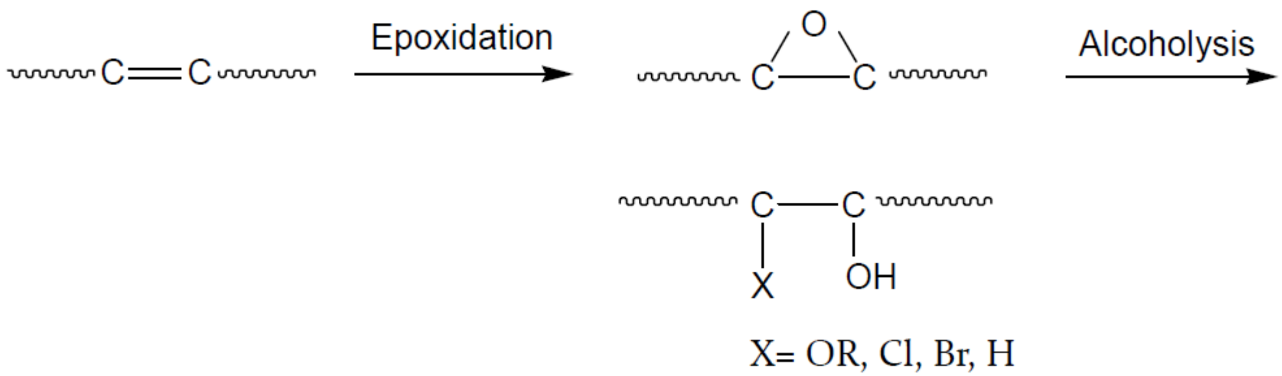
Need to improve catalysts



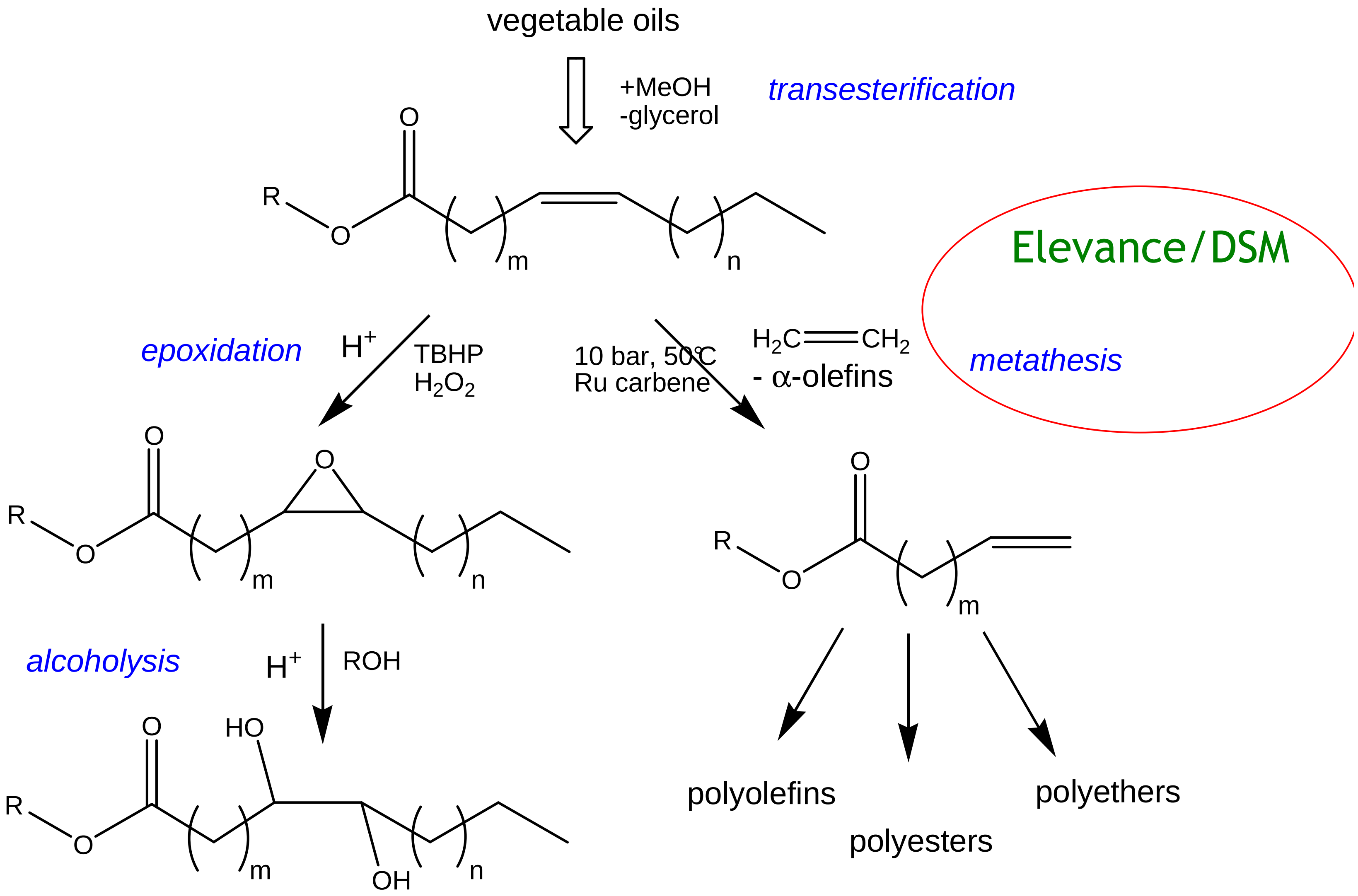
Materials from vegetable oils

Elaboration de polyols à partir de triglycérides



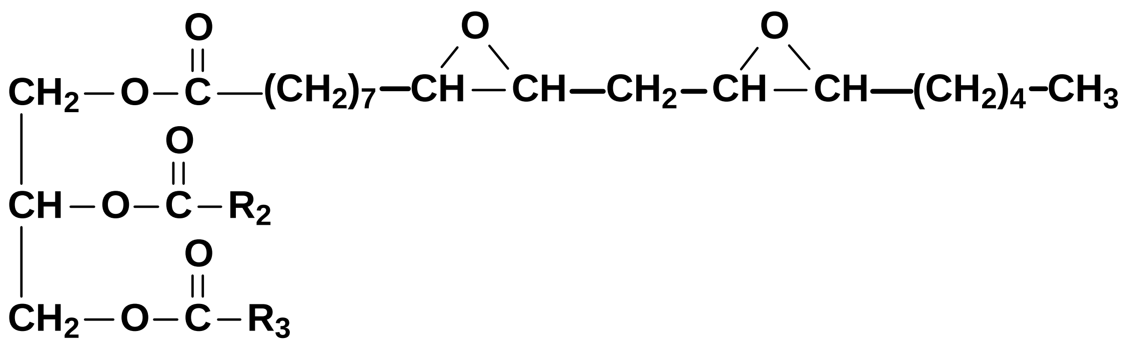


Materials from vegetable oils



Materials from vegetable oils

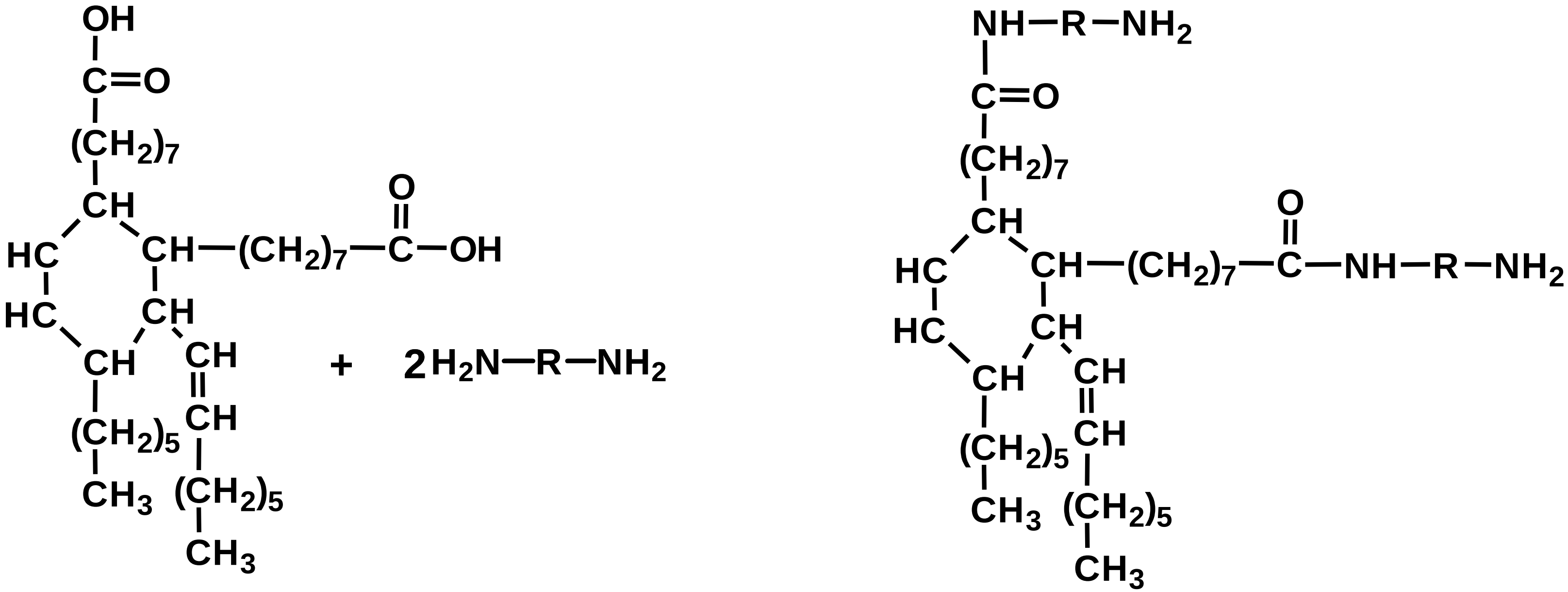
- *Epoxidized oils are synthesized by reacting vegetable oils (typically soybean and linseed oils) with peracids or hydrogen peroxide*



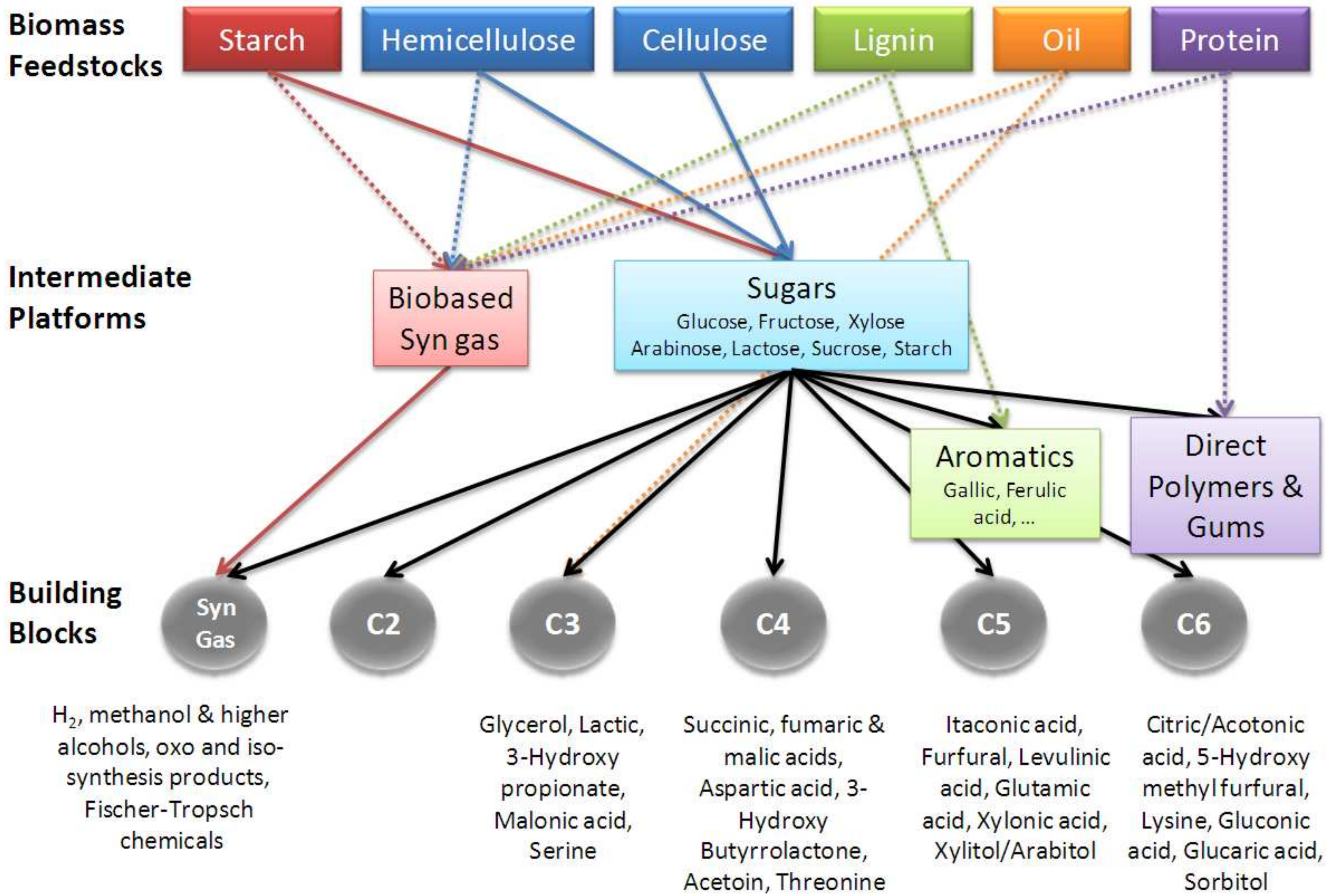
- *Epoxidized oils are employed as plasticizers for polyvinyl chloride or used to obtain polyols*

Materials from vegetable oils

Long chain fatty acid dimers derived from vegetable oils are reacted with slight excess of primary amines to synthesize polyamides



CONCLUSIONS


Biomass Feedstocks
Starch
Hemicellulose
Cellulose
Lignin
Oil
Protein
Intermediate Platforms
Biobased Syn gas
Sugars
Glucose, Fructose, Xylose
Arabinose, Lactose, Sucrose, Starch
Aromatics
Gallic, Ferulic acid, …
Direct Polymers & Gums
Building Blocks
Syn Gas
C2
C3
C4
C5
C6
H_2, methanol & higher alcohols, oxo and iso-synthesis products, Fischer-Tropsch chemicals
Glycerol, Lactic, 3-Hydroxy propionate, Malonic acid, Serine
Succinic, fumaric & malic acids, Aspartic acid, 3-Hydroxy Butyrrolactone, Acetoin, Threonine
Itaconic acid, Furfural, Levulinic acid, Glutamic acid, Xylonic acid, Xylitol/Arabitol
Citric/Acotonic acid, 5-Hydroxy methylfurfural, Lysine, Gluconic acid, Glucaric acid, Sorbitol

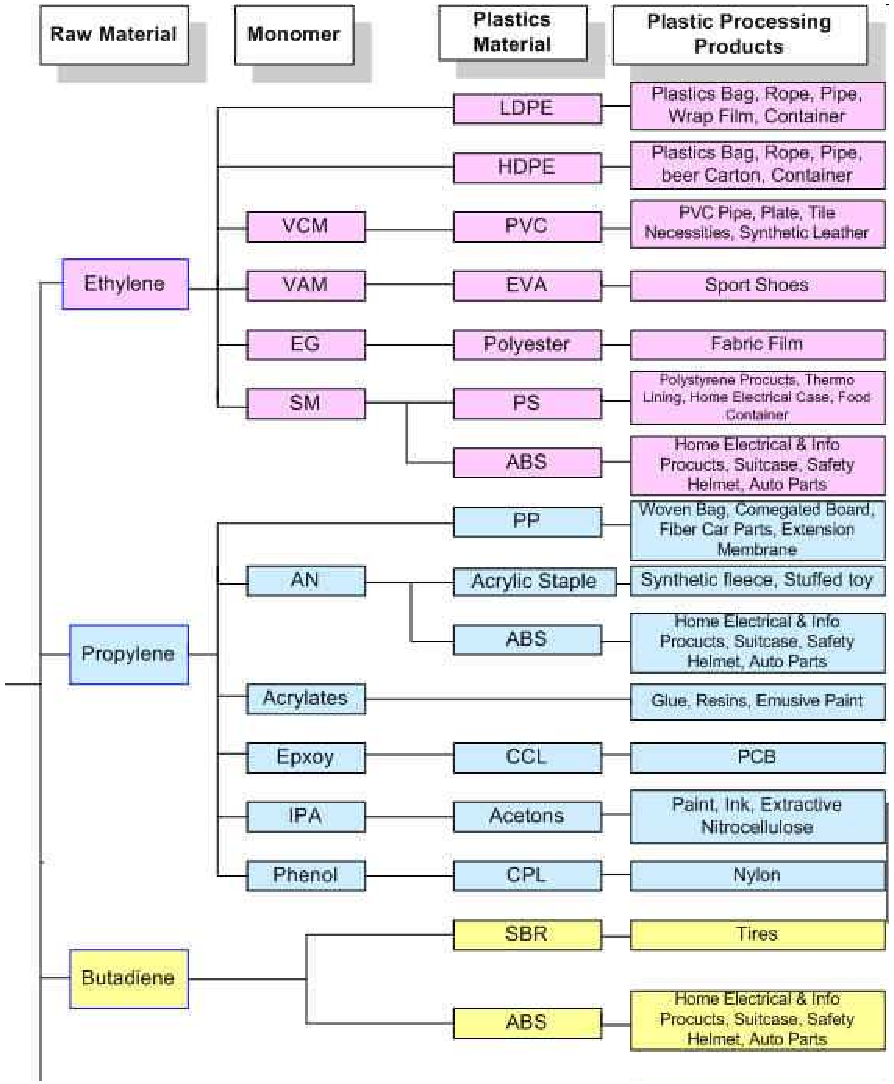
Développements actuels

- Le glycérol, sous-produit de la fabrication du biodiesel, est une solution très attrayante
- Polyols issus de biomasse végétale (polyesters, PU…)
- Production d'éthylène bio-sourcé / bio-PE
- Production de EG, PG, BDO, PDO (PET, …)
- Acide succinique (+ BDO) / PBS et autres
- Dérivés de sorbitol (isosorbide)
- Acide lactique / PLA
- PHA (sucres, glycerol, acides gras…)

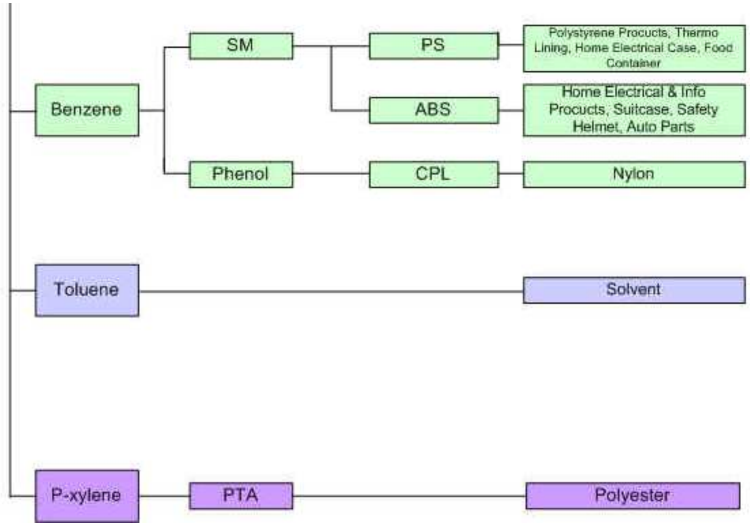
Développements à venir

- Production bio-sourcée de 3-HPA et d'acide acrylique (vers dérivés tels l'acrylonitrile, l'acrylamide...)
- ''Bio-PP'' et ''bio-PVC''
- butanol / butene…
- isoprene et diènes
- acide adipique
- furanes (PEF) ?
- itaconic acid ?
- …

Intermédiaires & synthons actuels



Intermédiaires issus du naphta



Les principaux défis à relever

- **Compétition avec l'alimentaire !**

  - Biochimie/Biotech (µ-organismes sélectionnés, modifiés…) pour améliorer les voies de synthèse (conversion, sélectivité)
  - Catalyseurs ''chimiques'' mieux adaptés (réactifs riches en O) et procédés plus verts
  - Caprolactam / synthons azotés ?
  - Ressources croissantes en protéines en font des matériaux de départ très intéressant pour l'obtention de synthons azotés.
  - La production d'éthylene bio-sourcé pourrait modifier la production actuelle d'éthylène et propylène issus du pétrole
  - L'obtention de synthons plus difficiles d'accès (aromatiques ou aliphatiques) pourrait s'envisager via la voie syngaz ??

Quels synthons aliphatiques pour le développement de polymères bio-sourcés ?

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