Premio ambiente & futuro 2014

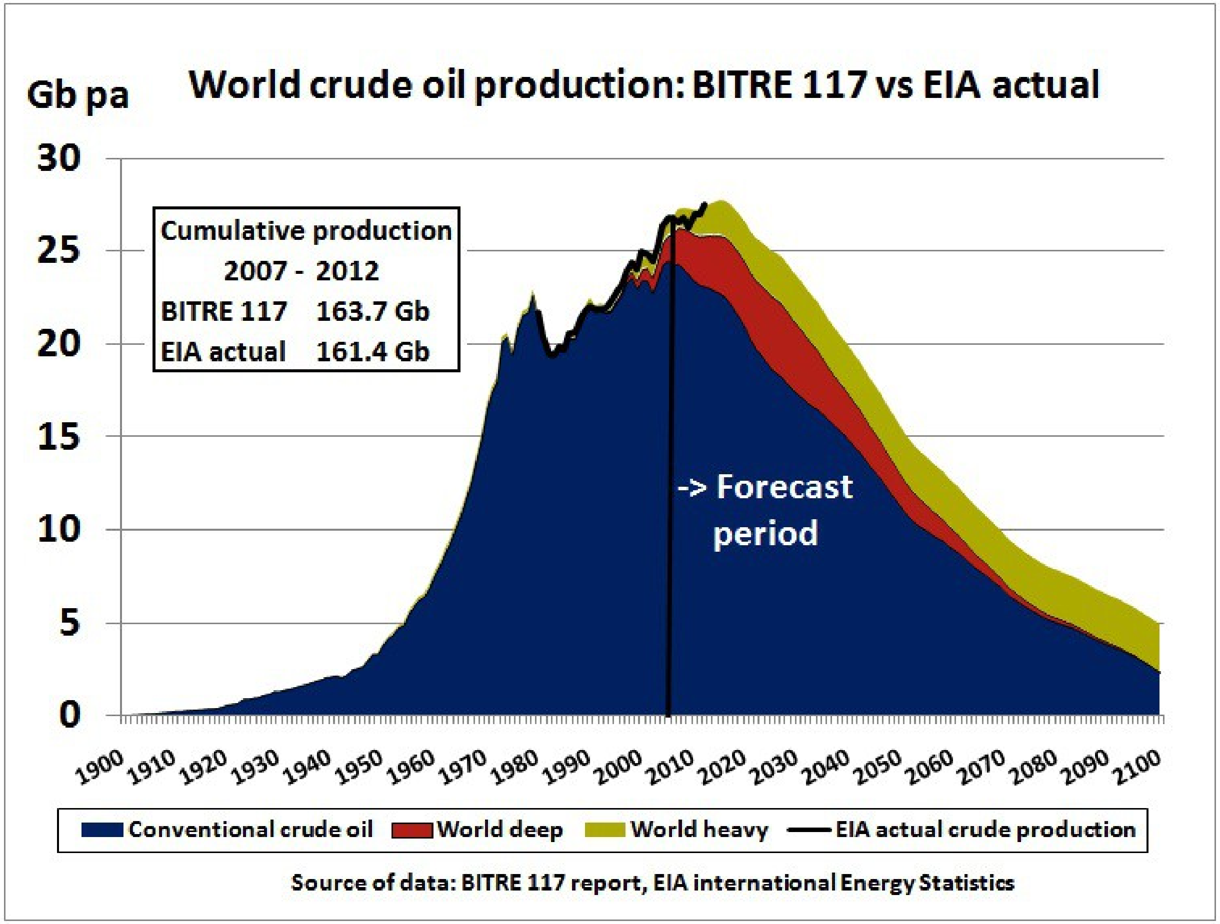
Emilio Tagliavini

Fonti rinnovabili per la chimica e per l'energia: un'opportunità sostenibile che non possiamo rifiutare

Ravenna – Sala Cavalcoli, 1 Dicembre 2014

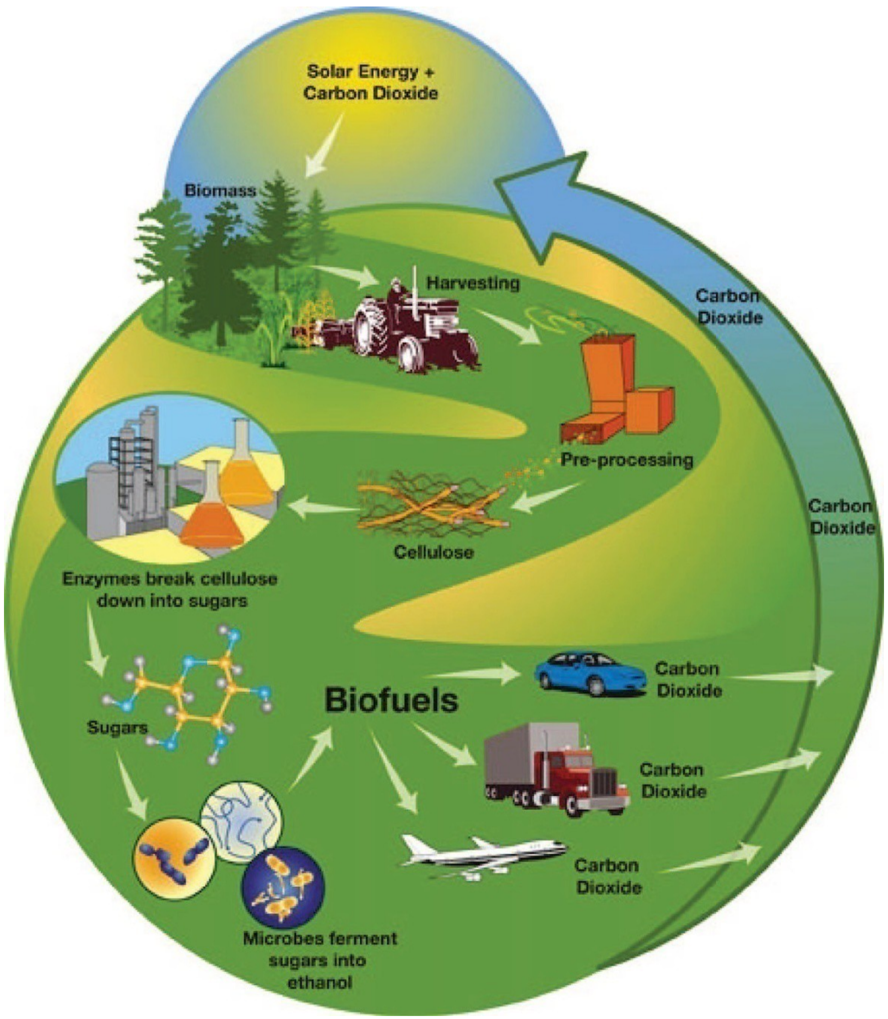
Perché accettare la sfida delle fonti rinnovabili per la Chimica e per l'Energia?

Fonti Rinnovabili - Sostenibilità



Entro poco tempo la quantità di materia organica da fonti fossili disponibile per la Chimica e per l'Energia è destinata a diminuire

Fonti Rinnovabili
Riduzione dell'Effetto Serra

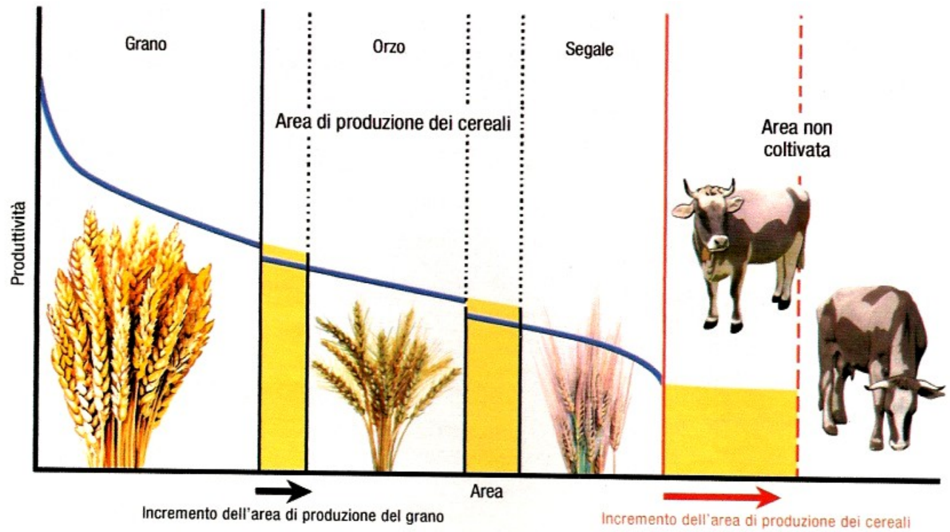


Angew. Chem. Int. Ed. 2008, 47, 9200 – 9211

Uso del Suolo: l'Effetto ILUC

L'uso indiretto del suolo (Indirect Land Use Change - ILUC) consiste nella destinazione di aree sempre meno produttive all'agricoltura che richiede superfici sempre più vaste

ATTENZIONE! Occorre anche considerare l'uso indiretto del suolo



La Crisi dei Prezzi 2007-2008

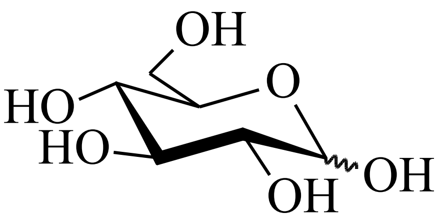
Evoluzione dei prezzi di alcuni prodotti agricoli (commodity) nel mercato internazionale

Prodotto	Gennaio 2006 (US $)	Febbraio 2008 (US $)	% di incremento
Mais (FOB) (Chicago)	120	250	
Frumento (FOB) (Chicago)	170	439	158 %
Olio di soia (FOB) (Amsterdam)	532	1.400	163 %
Pellets di soia (CIF) (Rotterdam)	207	453	118 %
Latte in polvere (FOB) (Oceania)	2.175	4.550	109 %
Carne congelata (FOB) (Argentina)	1.965	2.773	41 %

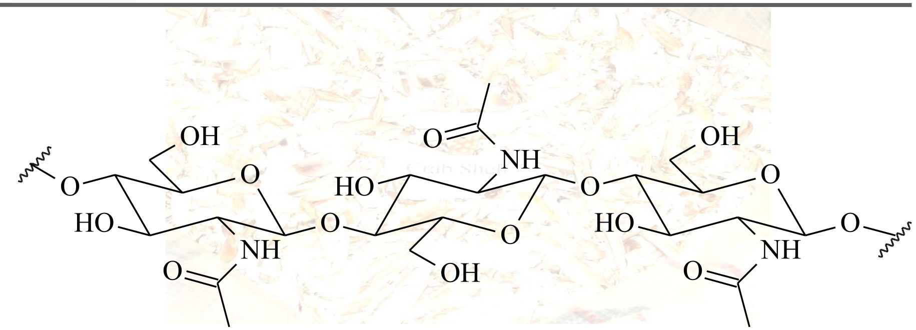
Fonte: FAO – ICO

Cosa sono?
BIOMASSA

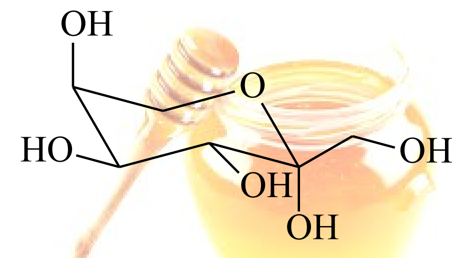
Carboidrati



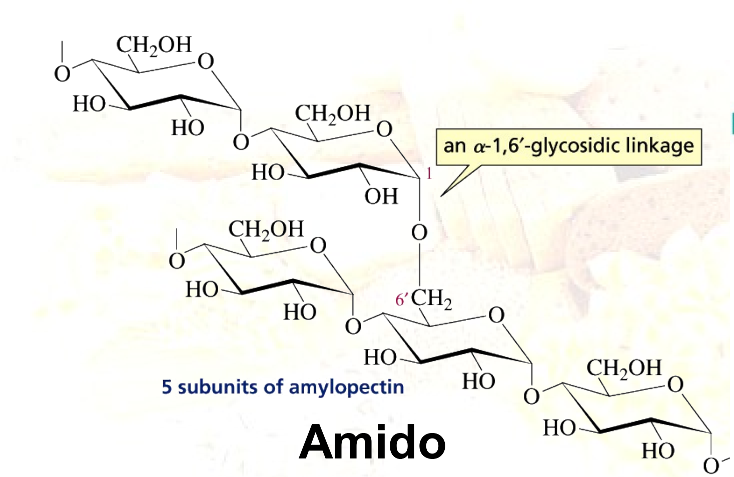
Glucosio



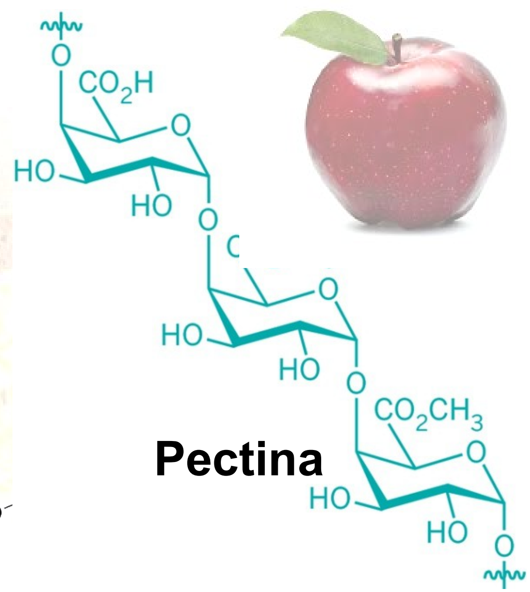
Chitina



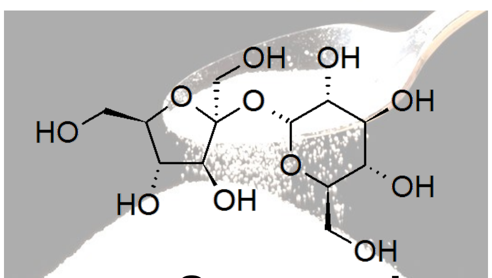
Fruttosio



Amido

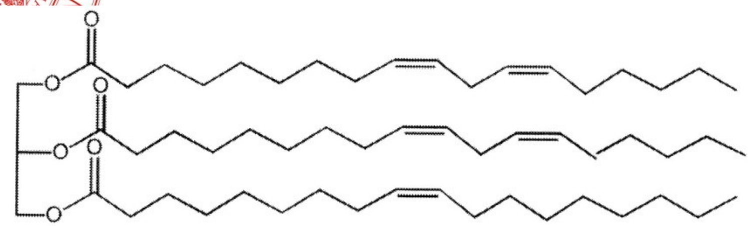


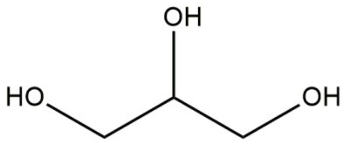
Pectina



Saccarosio

Trigliceridi e Polioli





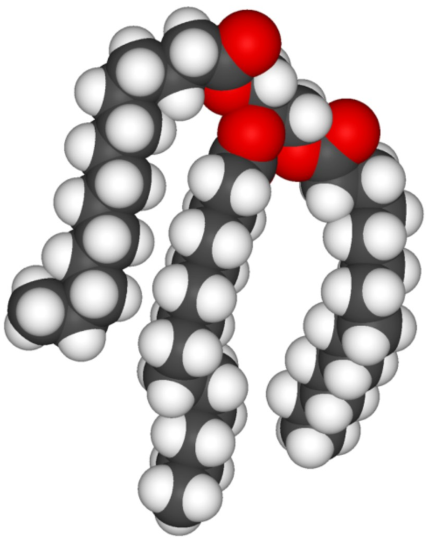


Table 3.1 Common naturally occurring fatty acids

Saturated

butyric	$CH_3(CH_2)_2CO_2H$	4:0	stearic	$CH_3(CH_2)_{16}CO_2H$	18:0
caproic*	$CH_3(CH_2)_4CO_2H$	6:0	arachidic	$CH_3(CH_2)_{18}CO_2H$	20:0
caprylic*	$CH_3(CH_2)_6CO_2H$	8:0	behenic	$CH_3(CH_2)_{20}CO_2H$	22:0
capric*	$CH_3(CH_2)_8CO_2H$	10:0	lignoceric	$CH_3(CH_2)_{22}CO_2H$	24:0
lauric	$CH_3(CH_2)_{10}CO_2H$	12:0	cerotic	$CH_3(CH_2)_{24}CO_2H$	26:0
myristic	$CH_3(CH_2)_{12}CO_2H$	14:0	montanic	$CH_3(CH_2)_{26}CO_2H$	28:0
palmitic	$CH_3(CH_2)_{14}CO_2H$	16:0	melissic	$CH_3(CH_2)_{28}CO_2H$	30:0

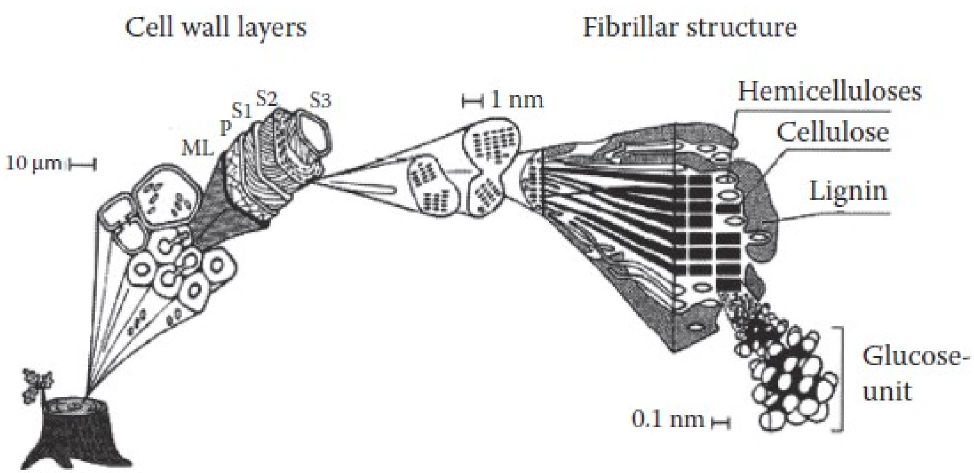
*To avoid confusion, systematic nomenclature (hexanoic, octanoic, decanoic) is recommended

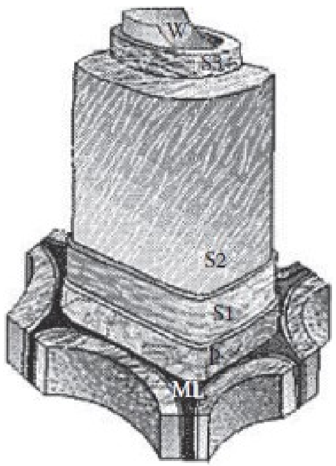
Unsaturated

palmitoleic	$CH_3(CH_2)_5CH{=}CH(CH_2)_7CO_2H$	16:1 (9c)
oleic	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	18:1 (9c)
cis-vaccenic	$CH_3(CH_2)_5CH{=}CH(CH_2)_9CO_2H$	18:1 (11c)
linoleic	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	18:2 (9c,12c)
α-linolenic	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7CO_2H$	18:3 (9c,12c,15c)
γ-linolenic	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_4CO_2H$	18:3 (6c,9c,12c)
gadoleic	$CH_3(CH_2)_9CH{=}CH(CH_2)_7CO_2H$	20:1 (9c)
arachidonic	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3CO_2H$	20:4 (5c,8c,11c,14c)
eicosapentaenoic (EPA)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_3CO_2H$	20:5 (5c,8c,11c,14c,17c)
erucic	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}CO_2H$	22:1 (13c)
docosapentaenoic (DPA)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_5CO_2H$	22:5 (7c,10c,13c,16c,19c)
docosahexaenoic (DHA)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_2CO_2H$	22:6 (4c,7c,10c,13c,16c,19c)
nervonic	$CH_3(CH_2)_7CH{=}CH(CH_2)_{13}CO_2H$	24:1 (15c)

all double bonds are *Z* (*cis*)

Lignocellulosa





La Biomassa Lignocellulosica è il materiale organico più abbondante sulla terra. E' prodotto il quantità pari a 170 × 109 ton/anno (Bozell and Patel, 2006), dei quali solo il 3% circa è raccolto ed utilizzato come cibo o per altri scopi.

Emilio Tagliavini 2014

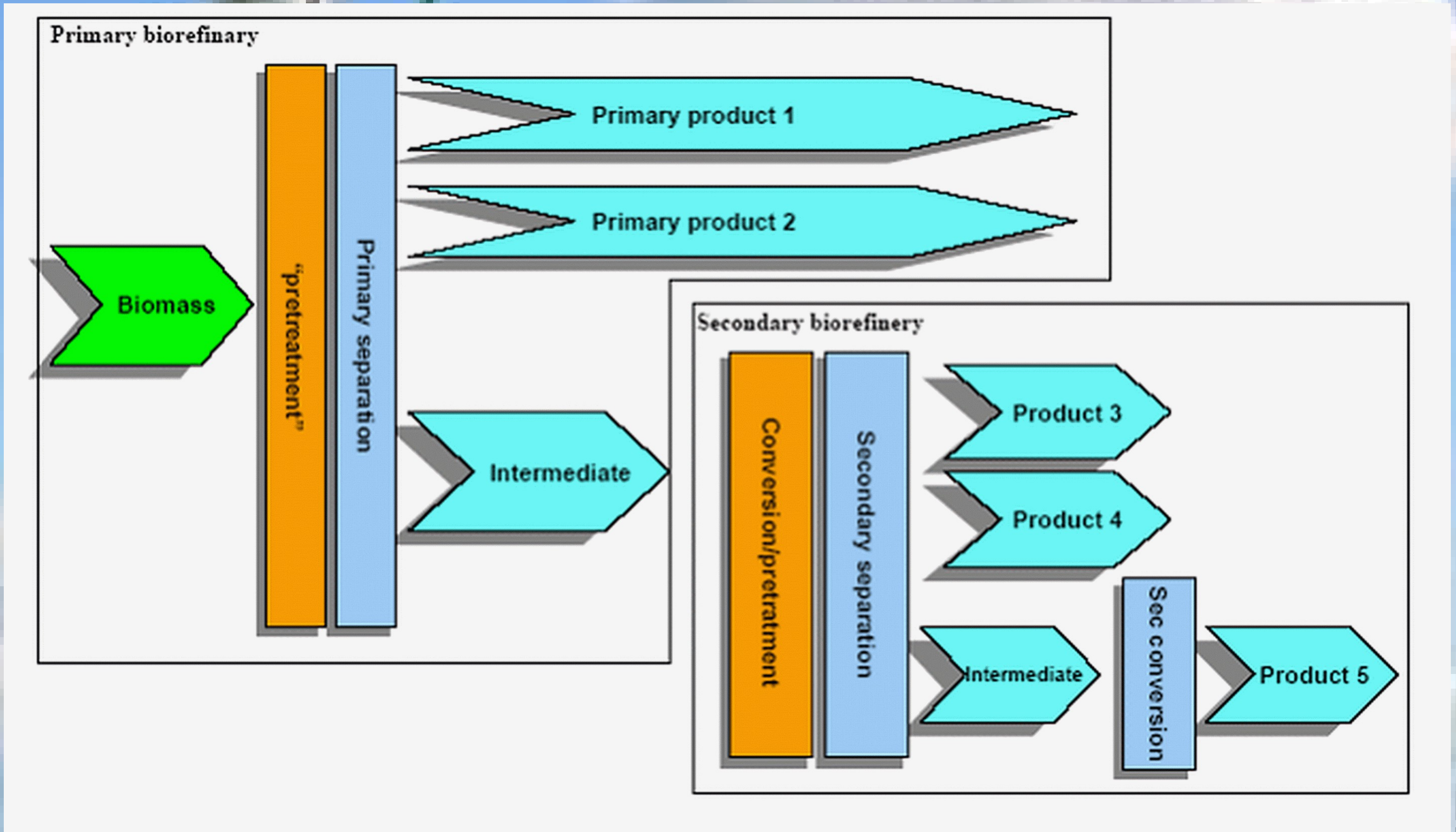
Fonti Rinnovabili

Come usarle?

BIORAFFINERIA

Bioraffinerie

Biorefineries



Generazioni di Bioraffinerie

Generazioni di Bioraffinerie

Biorefineries

Generazione	Materia prima	Prodotti
Bioraffinerie di prima generazione	Zucchero, amido, oli vegetali, grassi animali	Bio-alcoli, biodiesel, bio-gas, biosyngas. Bio-platform chemicals, biopolimeri
Bioraffinerie di seconda generazione	Coltivazioni non alimentari, paglia, residui agicoli, colture energetiche	Bio-alcoli, biodiesel, biohydrogen, bio-Fischer–Tropsch diesel, Bio-platform chemicals,
Bioraffinerie di terza generazione	Algae	Oli Vegetali, bio-diesel
Bioraffinerie di quarta generazione	Oli vegetali, Rifiuti urbani	Bio-gasolio

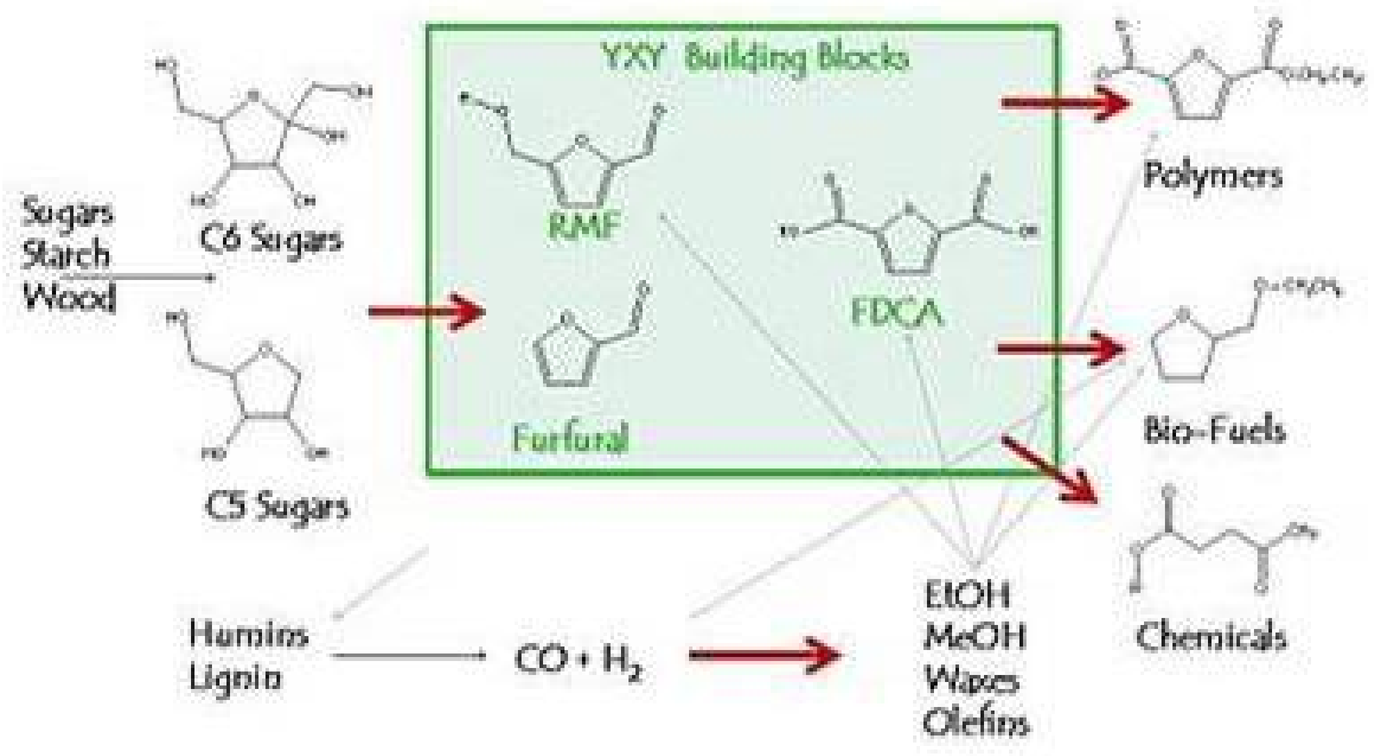
Fonti Rinnovabili

Per la Chimica

Platform Chemicals

Biopolimeri

Biorffinaria basata su Idrossimetilfuraldeide HMF



Avantium Co. in Olanda ha prodotto **HMF** dalla Biomassa a costi competitivi. I derivati di HMF sono commercializzati col marchio **YXY Technology**

Bio-Plastiche Biodegradabili

Modified Starch Polymers
Si basno su **Amido modificato** o miscele di Amido e altri polimeri biodegradabili

Mater-Bi® (Νοϖαμοντσ) **Σολανψλ**® (Ροδενβυργσ) **Βιοπλαστ**® (Βιοτεχ)
Υσι: Ιμβαλλαγγι, Πνευματιχι, Ριεμπιτιϖο, Ποσατε υσα ε γεττα.

Polylactic Acid (PLA)
Polimerizzazion dell'Acido Lattico (via Lattide)

Ottime proprietà meccaniche e/o plasticità. A seconda della composizione stereoisomerica.
Usi: Imballabbi, Fibre tessili, Riempitivo, Ausili medici e Impianti.

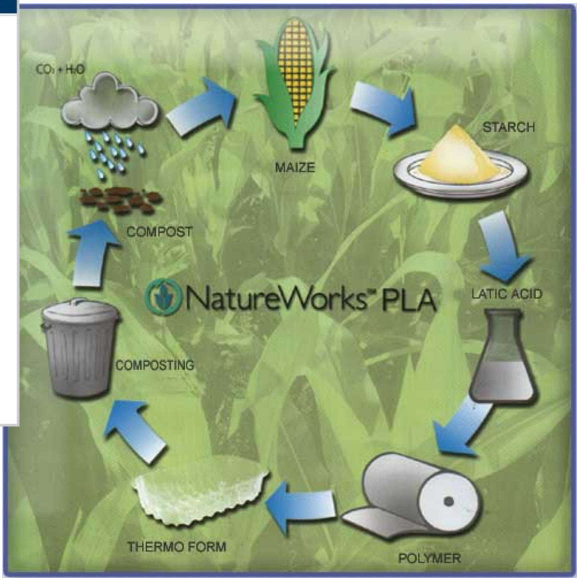
Polyhydroxyalcanoates (PHA)

Materiale di riserva di energia e massa di alcuni Batteri

Ottime proprietà meccaniche.
Candidato a sostituire PET e HDPE.
Usi: Oggetti, Imballaggi, Ausili medici.

Bioplastiche

Amido modificato



Acido Polilattico PLA

Poliidrossialcanoati PHA

Fonti Rinnovabili

Per l'Energia

BioEtanolo

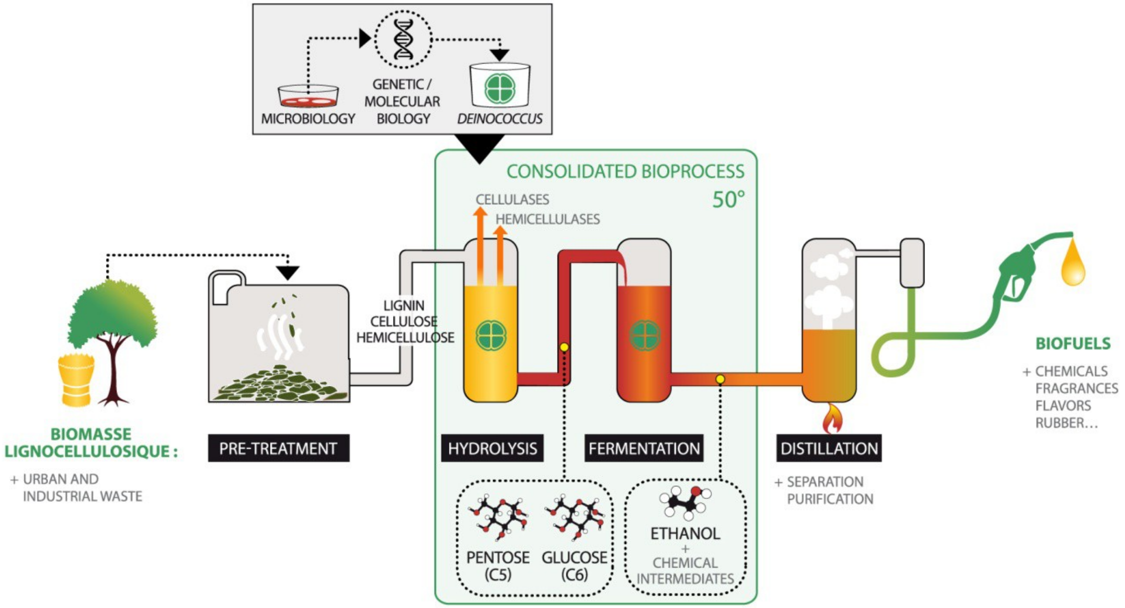
BioDiesel

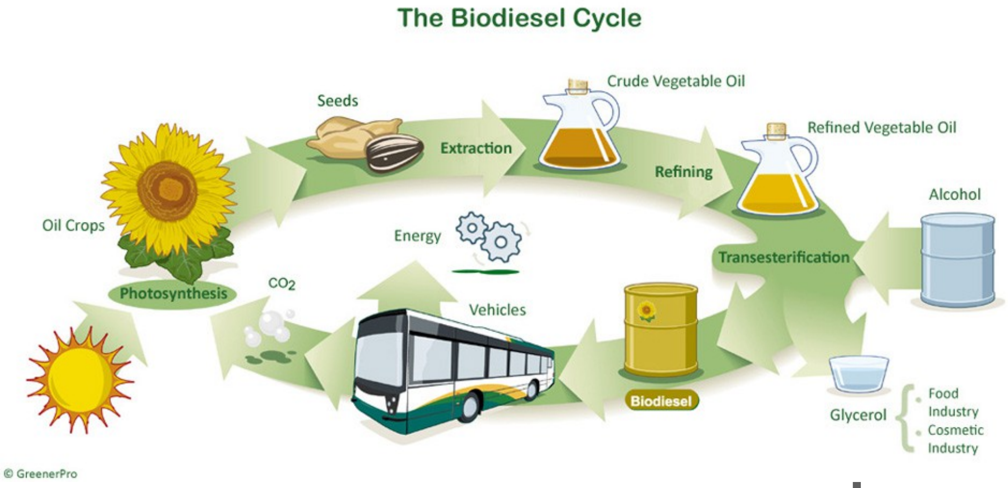
BioGas SynGas

Come ottenere Biocarburanti dalla Biomassa

- Processi Chimico-fisici
  - Estrazione, separazione (Lipidi da Alghe)
- Processi Chimici
  - Transesterificazione, conversione del Syngas
- Processi Biochimici
  - Fermentazione (Bioetanolo, BioIdrogeno)
  - Biogas
- Processi Termochimici
  - Pirolisi
  - Gassificazione

I BioCarburanti



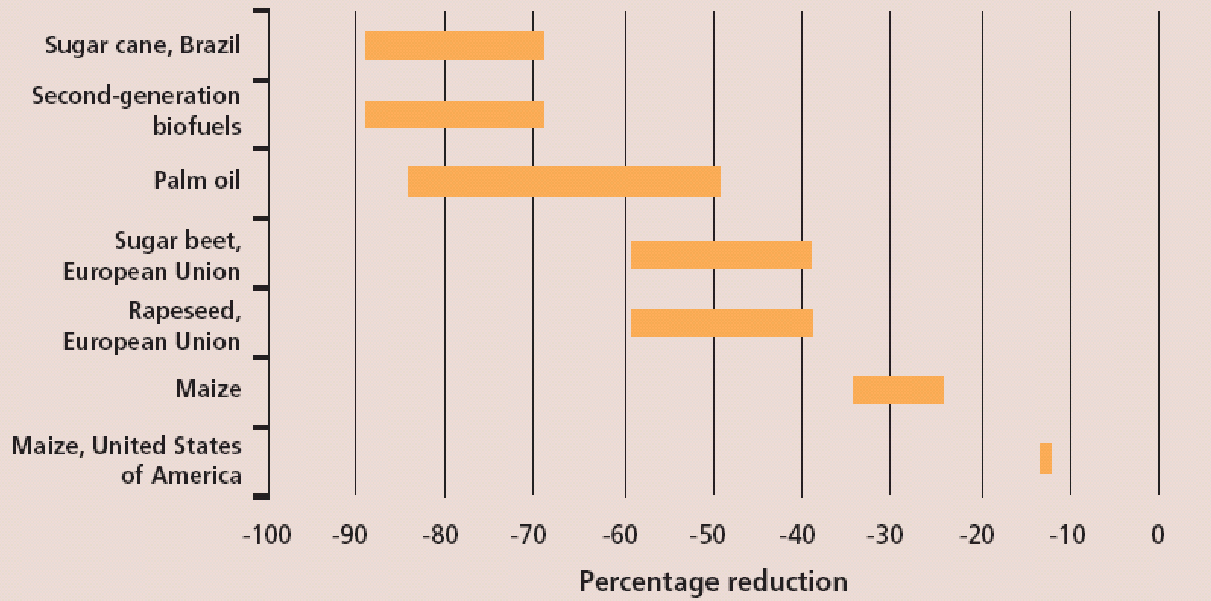


Perché i BioCarburanti?

- *Rinnovabilità*
  - La riserva di Biomassa si rinnova rapidamente (tipicamente ogni anno)
- *Sostenibilità ambientale*
  - Potenzialmente non c'è produzione netta di gas-serra o, perfino, una riduzione del contenuto di CO_2 in atmosfera
- *Economia*
  - L'instabilità dei prezzi dei combustibili fossili danneggia l'economia
- *Aspetti Geopolitici*
  - La produzione di combustibili fossili è concentrata in aree politicamente instabili
  - Prezzi e disponibilità di combustibili fossili sono stati usati come deterrente politico

Quanto è vero?

FIGURE 23
Reductions in greenhouse gas emissions of selected biofuels relative to fossil fuels



Note: Excludes the effects of land-use change.

Sources: IEA, 2006, and FAO, 2008d.

ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

GRAZIE PER L'ATTENZIONE

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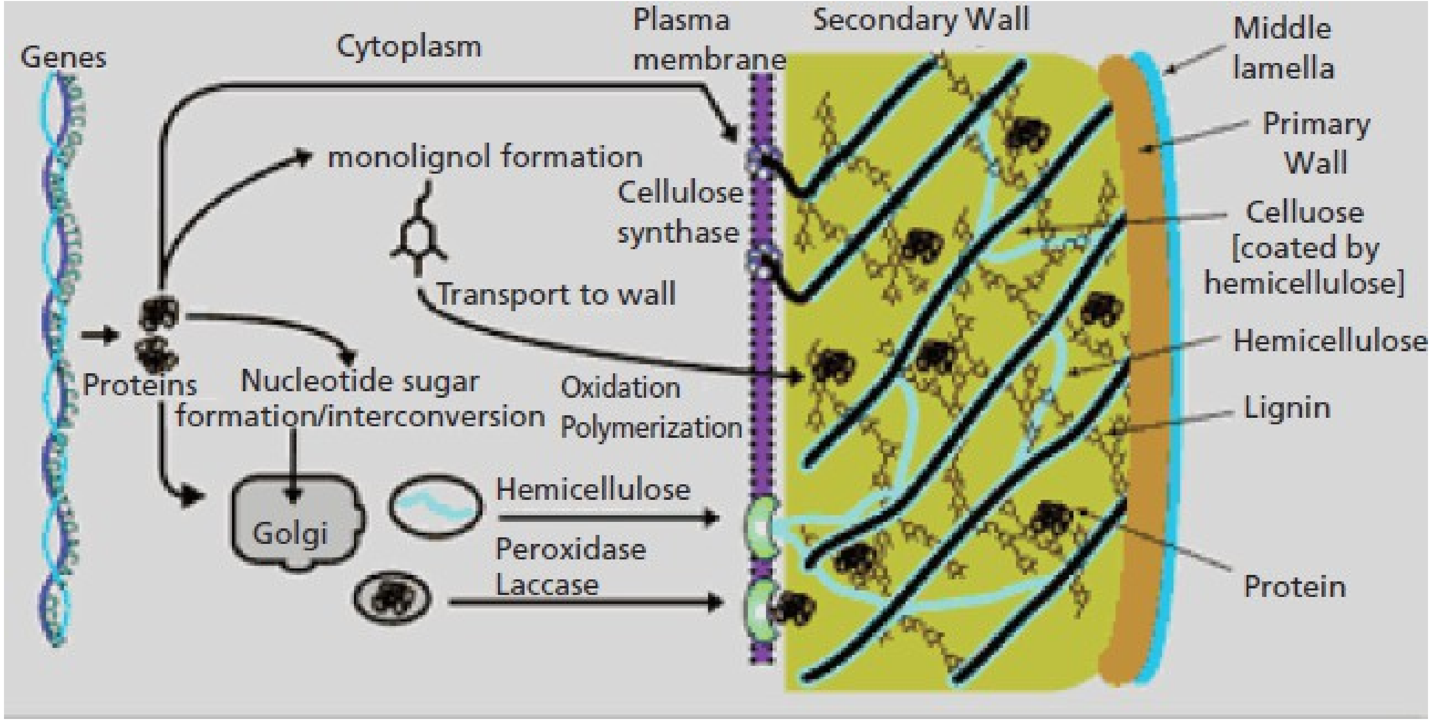
Biogenesis of Lignocellulose



La Via Termochimica

Gasification → Gas CO, H2 (Syngas)

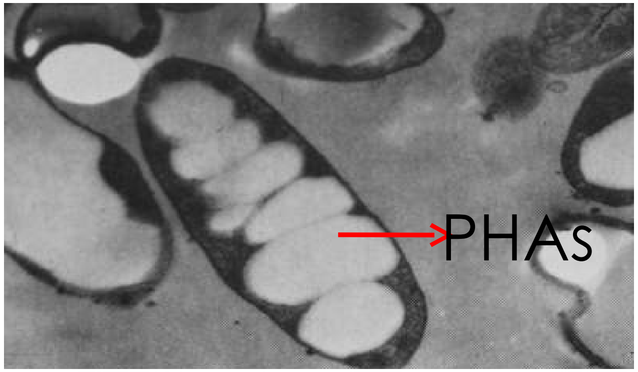
Pyrolysis *Fast/flash* → Liquid Bio-oil

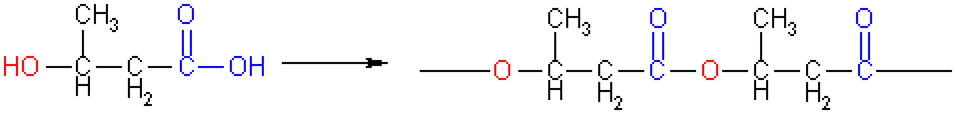
www.dynamotive.com

Carbonization → Solid (*char*)

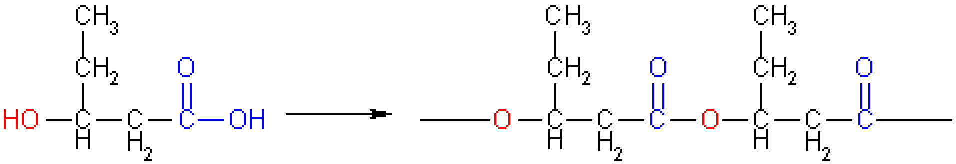
Polyhydroxyalkanoates PHA

- Produced by Micoorganisms
- Pure Cultures, Mixed cultures, Plants
- Eubacteria and Archaea; 75 different genera of Gram+ and Gram- bacteria (≈ 300 bacteria)
- Insoluble inclusions in the cytoplasm
- Synthesized and stored inside the cells as energy and carbon storage material
- 90% of PHA by cell dry weight, usually under conditions of nutrient limitation (N, P, Mg) with excess of carbon





PHB



PHV

Starch-based Bioplastics

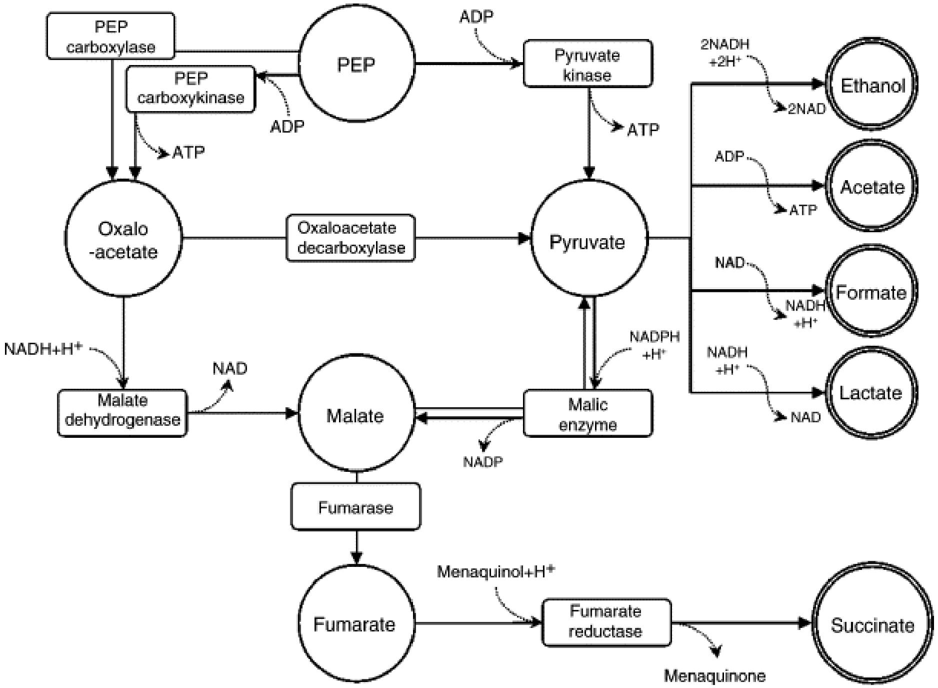
- So-called **Plastified Starch** consists of starch composites with *starch content being more than 50% by mass*. Exhibits mechanical properties similar to conventional plastics but at a lower price.
- Bioplastics with amount of *starch higher than 50%* are usually referred to as **Thermoplastic Starch**.
- Usually, the components to blend with starch are aliphatic polyesters, **polyvinyl alcohol (PVA)** and biopolymers. The

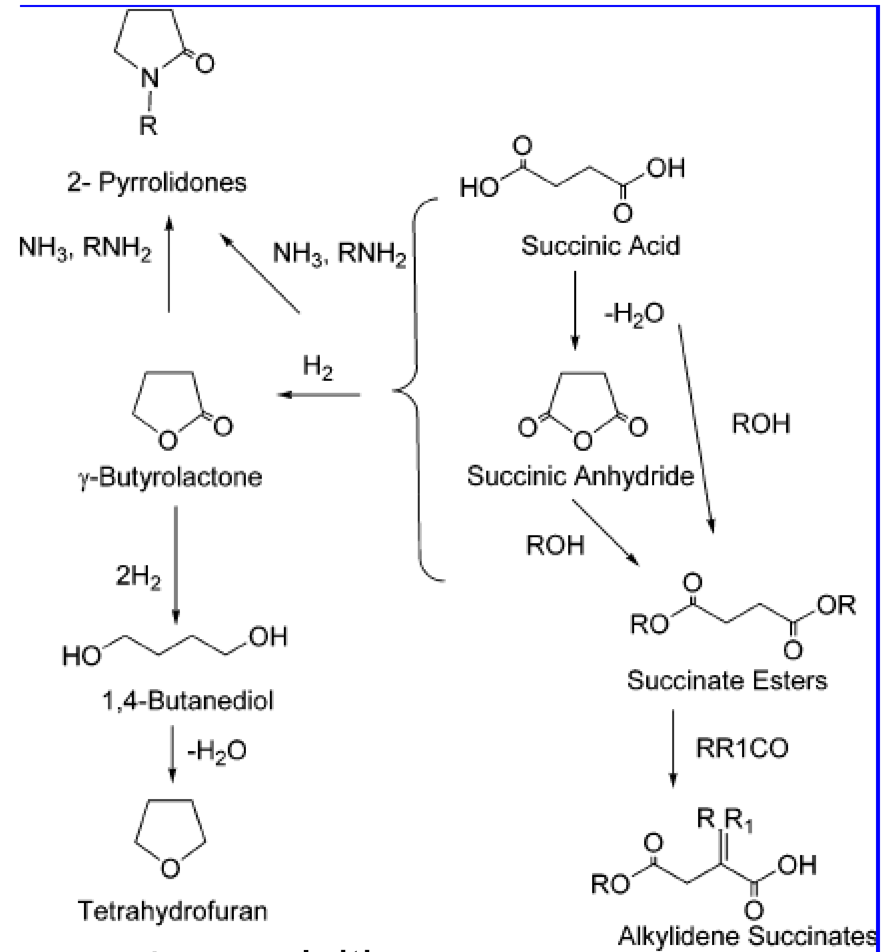
Polyhydroxyalkanoates PHA

- The most common representative of these biopolymers is poly-3-hydroxybutyrate (PHB). PHB constitutes a rather stiff and brittle material with a low extension to break. These mechanical properties can be enormously enhanced by incorporation of different co-monomers into the PHB matrix. This results in co- and terpolyesters possessing mechanical properties similar to high-tech materials.
- Due to a high degree of polymerization

Succinic Acid Platform

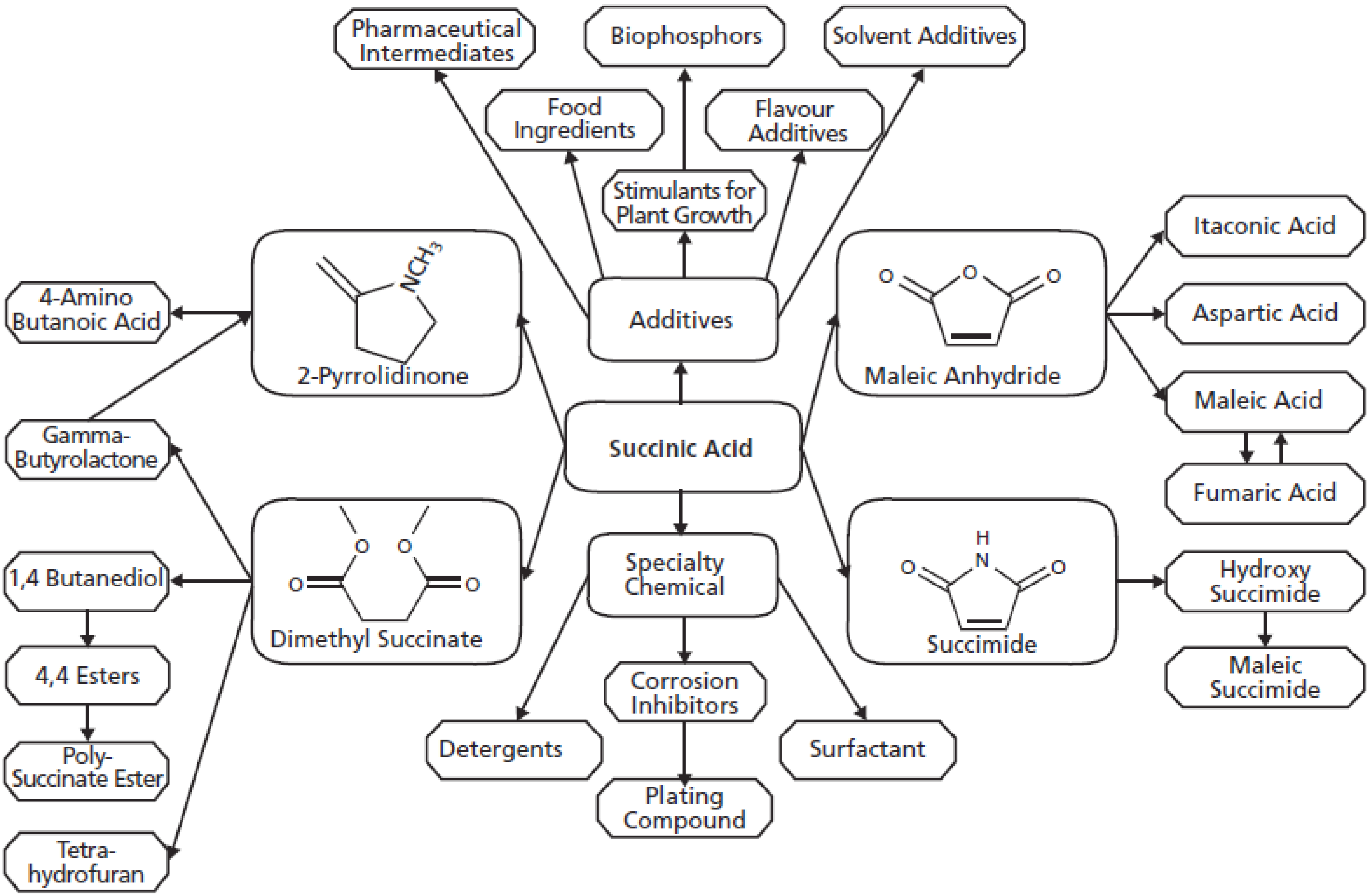
From Sugars *via* Phosphoenolpyruvate (PEP) carboxylation to give Oxalacetic Acid, followed by the reaction of Krebs Cycle affording Fumaric Acid that is finally reduced to Sucinic Acid



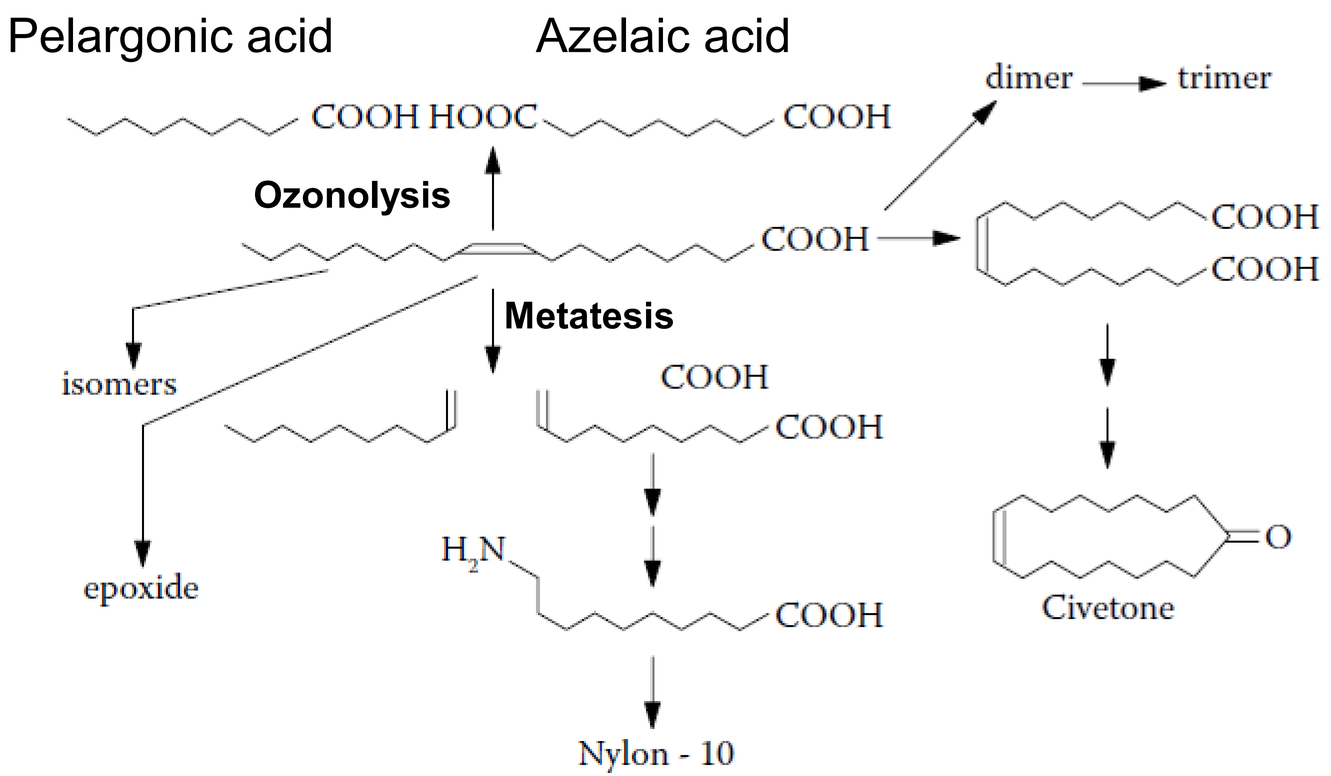


BioAmber Inc. has realized the industrial implementation exploiting genetically engeneered *E. coli* strain

Chemicals from Succinic Acid



Oleic Acid Platform



EVONIC in Germany ha developed a biobased production of Nylon 10-10

Third generation: Biofuels from Algae

- Fast growth
- Very efficient photosynthesis: better utilization of sunlight energy
- High lipid content: some strain contain up to 30% weight lipids (on dry mass)
- Little competition with food-chain use
- Use of marginal or desertic lands
- Marine and freshwater species available
- Main drawback: need of dewatering. It is highly energy costing.