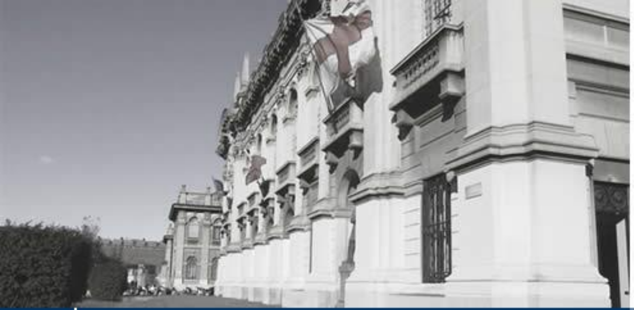


School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Building Blocks and Materials from Biomass.

Prof. Attilio Citterio

Dipartimento CMIC “Giulio Natta”

https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

Bio-Product Technologies & Pathways.

- Principles of (current) chemical processes, *pathways* and products
- Thermal, chemical and biological conversion of biomass (fermentation, AD, Enzymes, FT synthesis, hydrolysis, wet and dry milling, bio separation, distillation, catalytic conversion)
- Biotechnology tools including genetic modification and molecular engineering
- Integration with biofuel production
- Biorefineries and the importance of multi-product approaches: Biorefinery concepts & the chemical (rather than energy) outputs
- Overview of refinery platforms and feedstocks: classification of biorefineries and problems with classification
- A more detailed look at individual platforms (Syngas, biogas, C5 and C6 sugars, oil crops, algae and lignin) and products including DME, methanol, ethanol, butanol, sorbitol, furfural, HMF, levulinic acid, propylene glycol, acrylic acid, etc.
- Bio chemicals and products from algae – current technology, constraints / developments
- Bio fibers, biodegradable polymers and bio composites
- Bio lubricants, inks and paints
- Pharmaceuticals and nutraceuticals

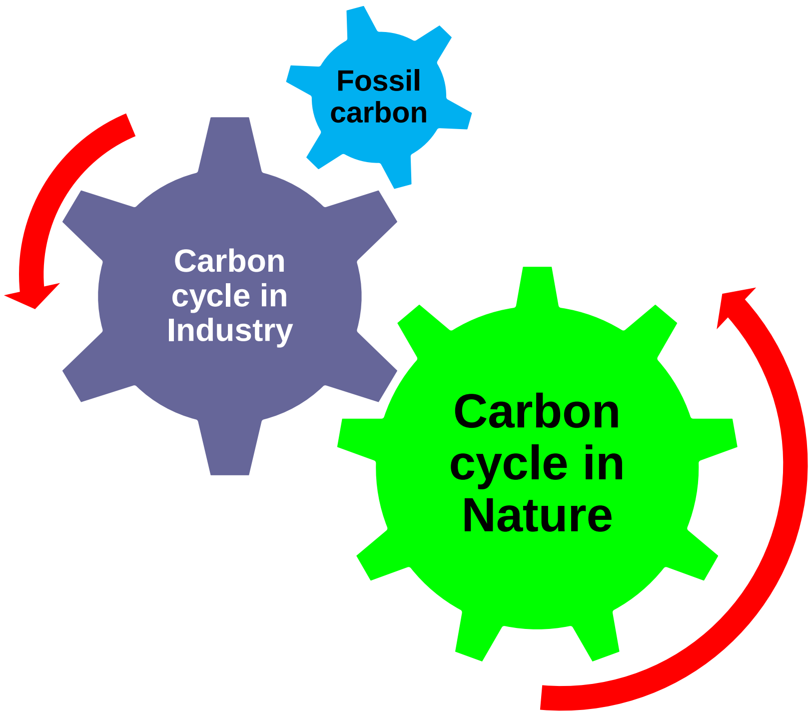
➢ The status of technologies – commercial / pilot or R&D

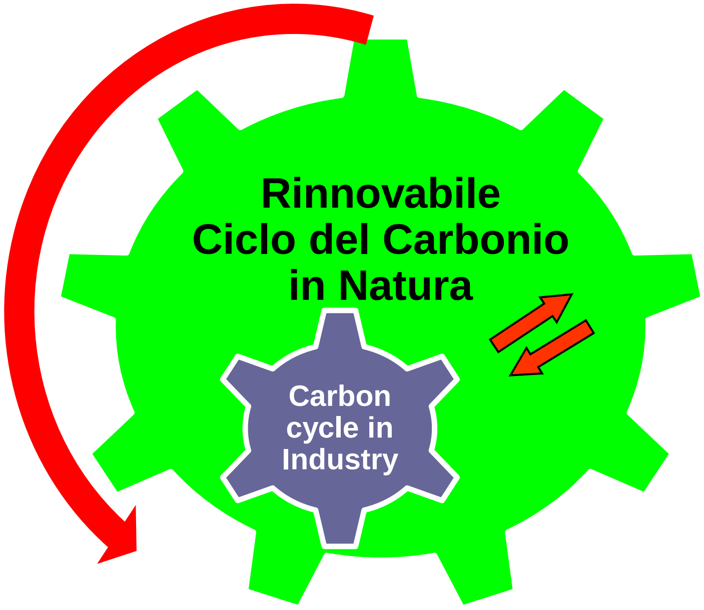
➢ Emerging technologies, products and platforms.

Advantages of Changing Feedstock.

Fossil Carbon Economy - carbon is used and discarded

Bioproducts Economy - carbon is recycled

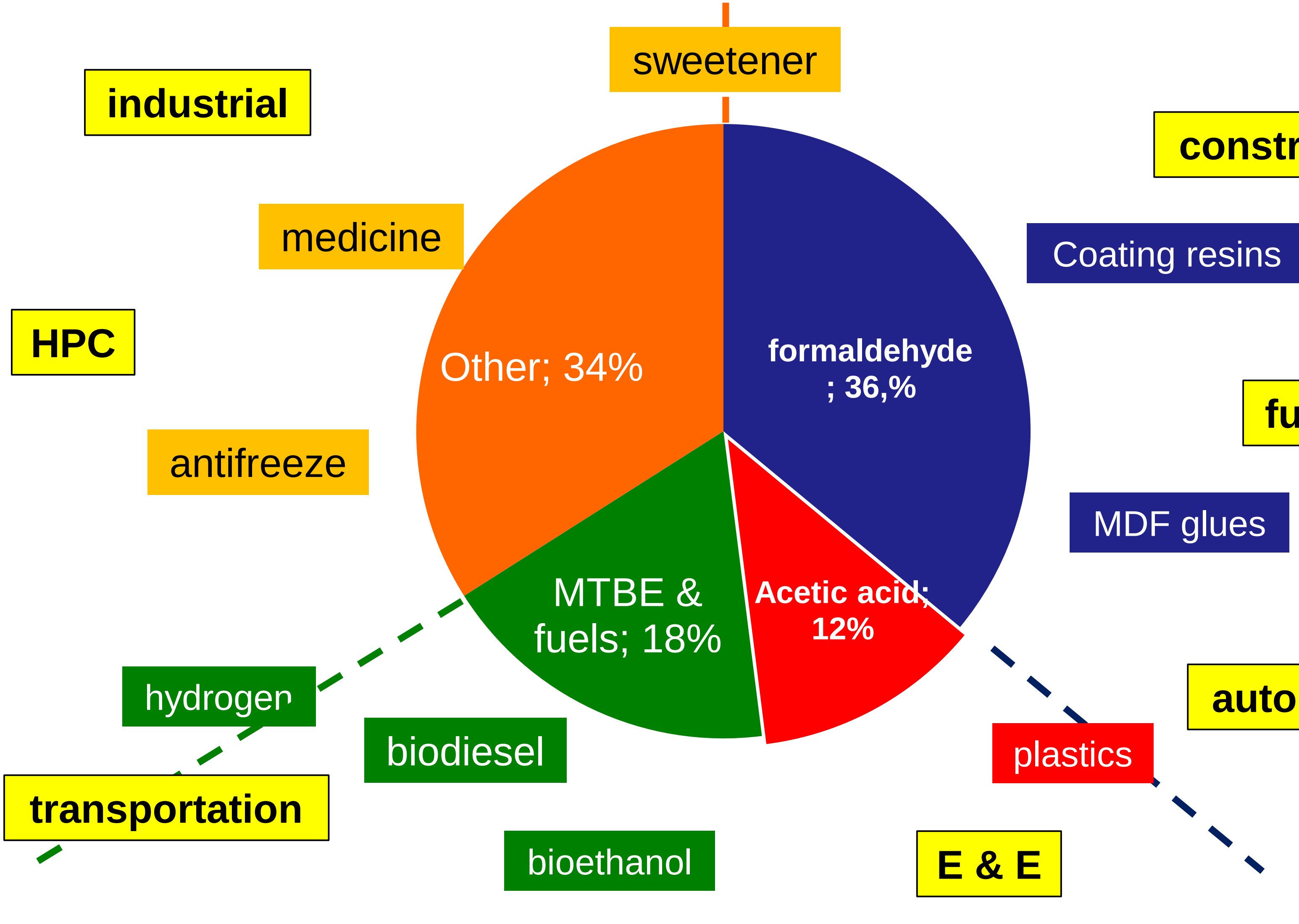




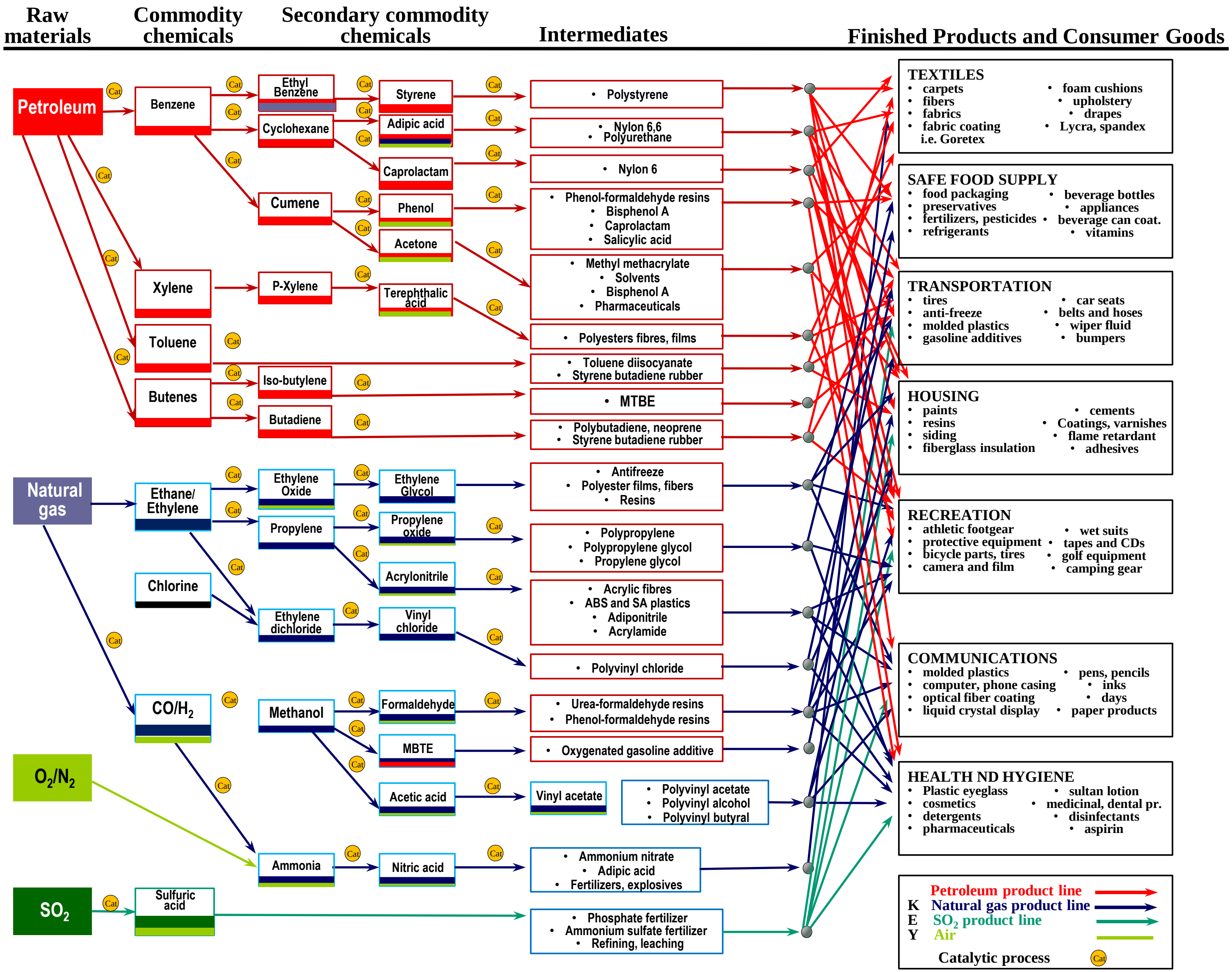
- Waste is a disposal problem
- Growth from increasing production volume

- Waste is a feedstock opportunity
- Growth from increasing value added

Market Opportunities to 'Go Green'.



Traditional Chemical Industry.



Biomass Resources and Key Issues.

Wood Residues:

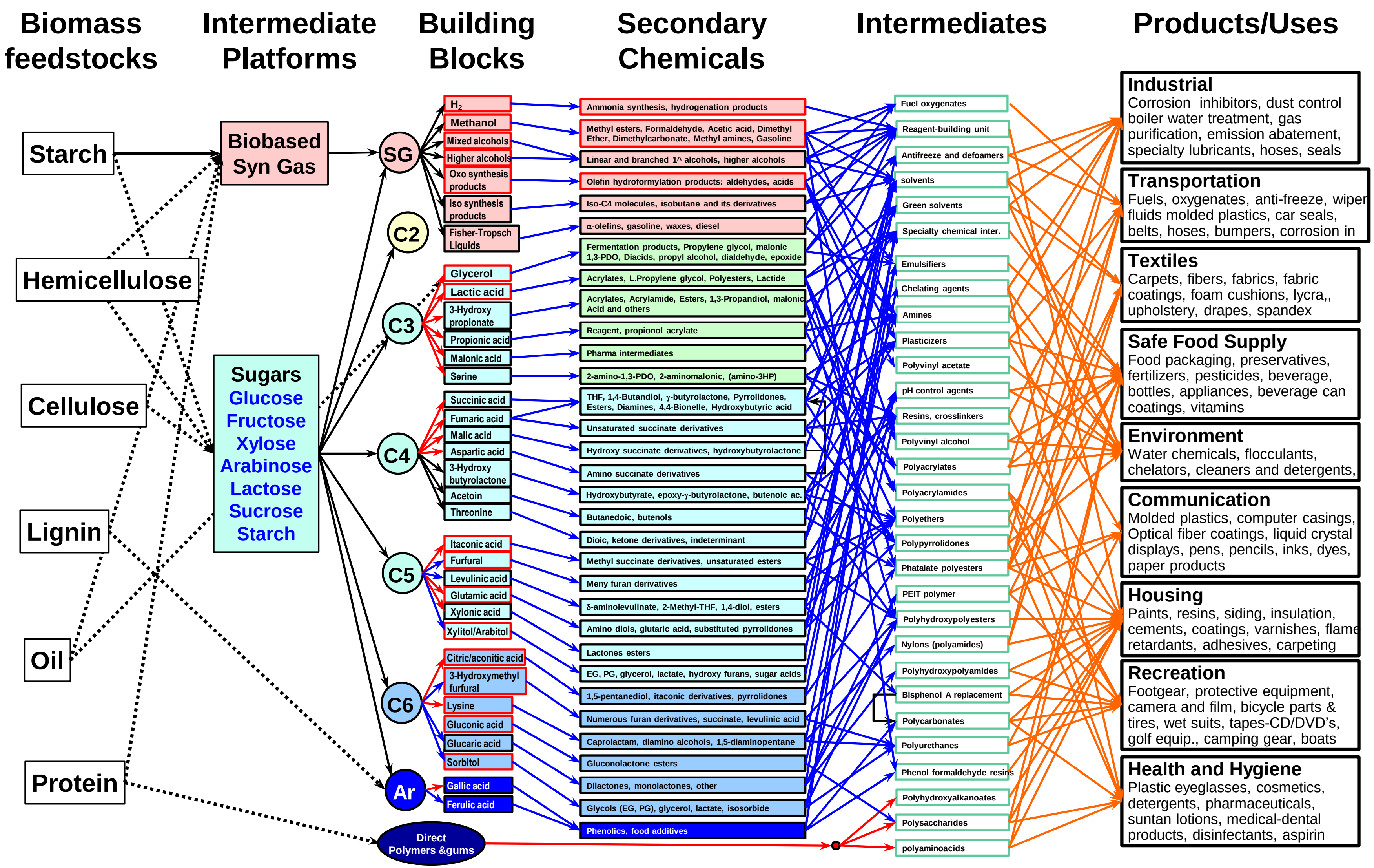
Sawdust
Wood waste
Pulp mill wastes

Agricultural Residues:

Corn Stover
Rice hulls
Sugarcane bagasse
Oil mill
Envelopes of food products and seeds
Waste material of seafood industries (skeletal material of crustaceans)
Animal waste

Energy Crops.

Biobased Product Flow Chart from Biomass Resources.



[Kamm, 2007]

What is a Biobased Product? (Definitions).

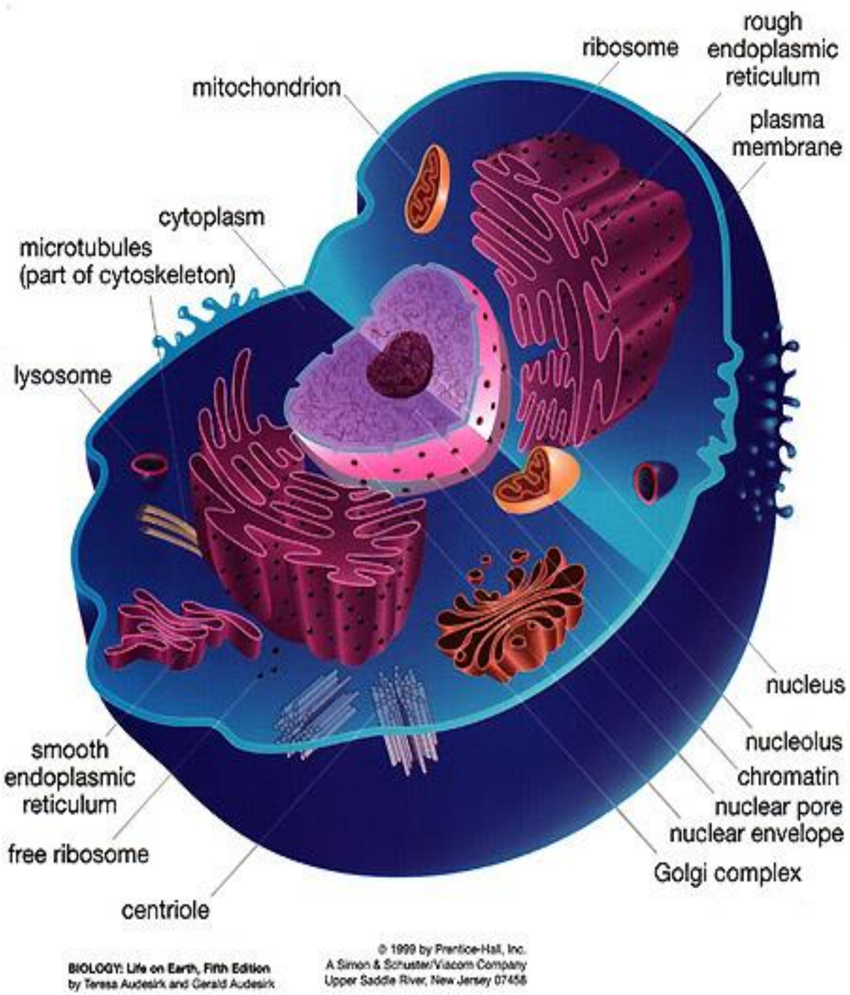
I. A product determined to be a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant, animal, and marine materials) or forestry materials."

II. Relies on plant or animal materials as the main ingredient. The plants or animals utilized are a renewable resource. With some exceptions, generally do not contain synthetics, toxins or environmentally damaging substances.

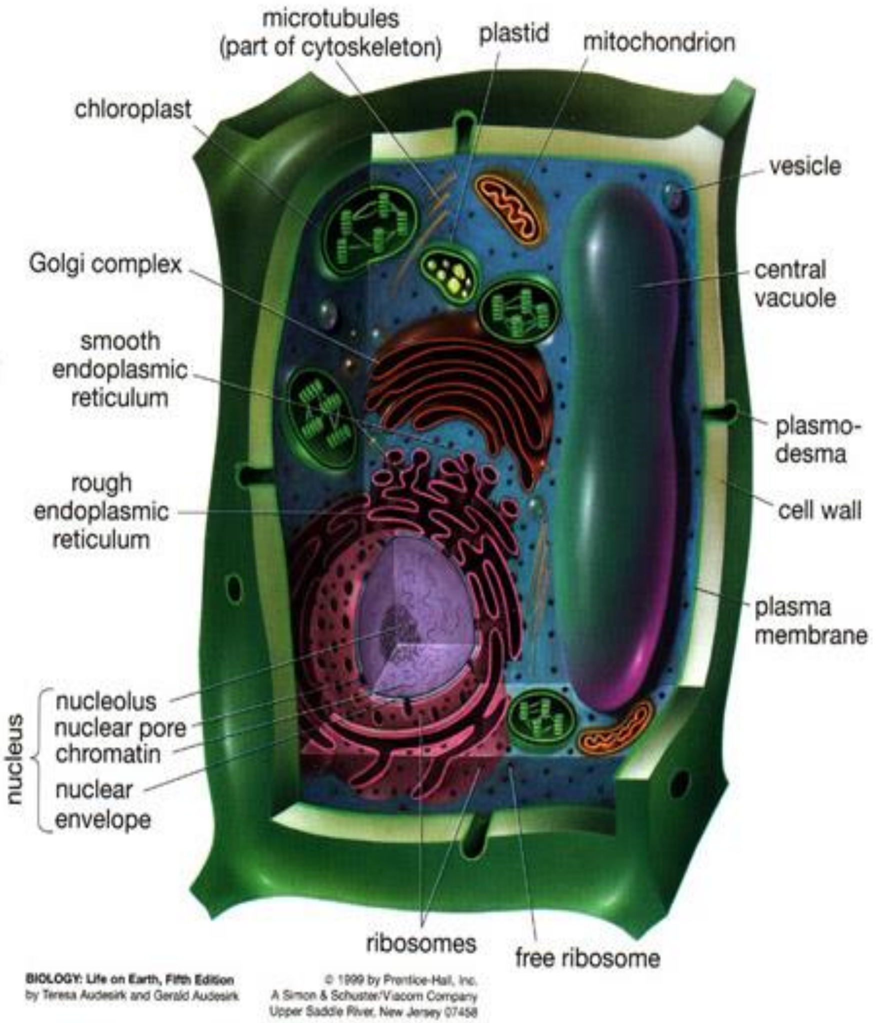
III. Benefits of Biobased Products

- Generally healthier and safer for the user
- Generally healthier for the environment
- Reduced dependence on imported materials
- Reduced dependence from oil
- Generally helpful to the economy
- Extremely helpful to the rural and forestry economy

Organized Structure of Animal and Vegetable Cell.



Animal Cell

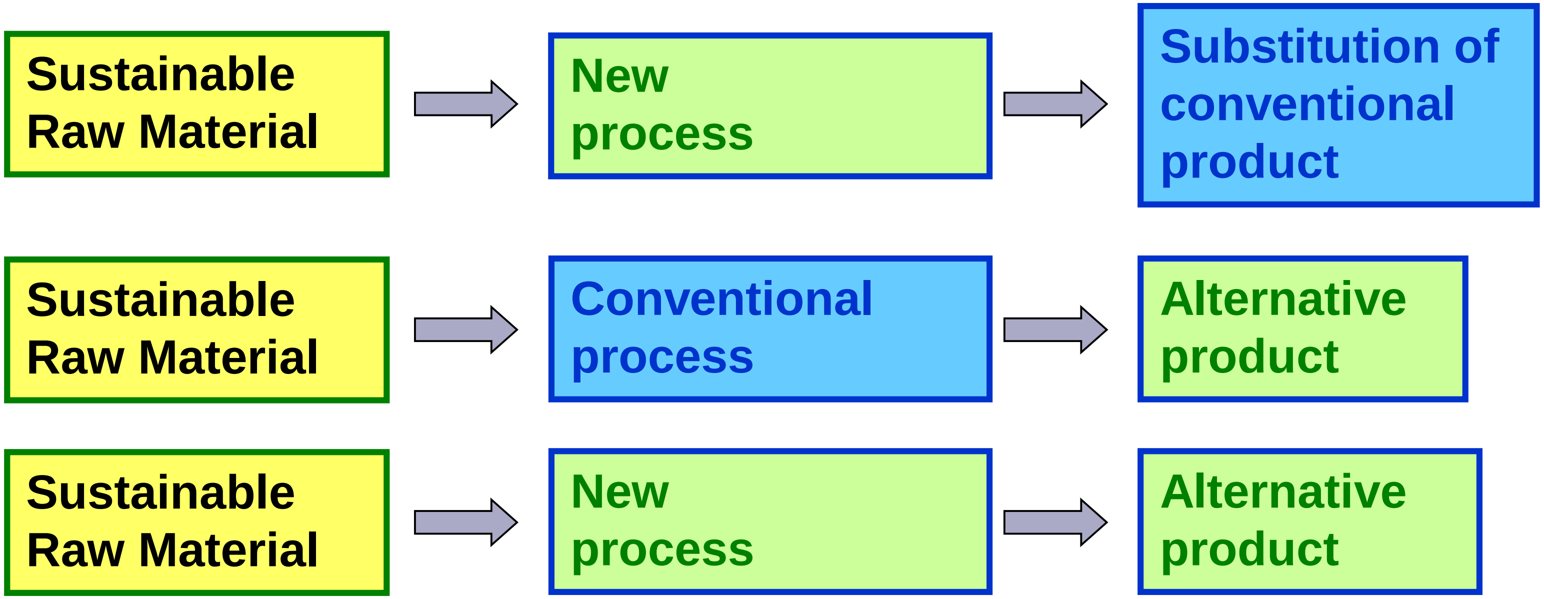


Plant Cell

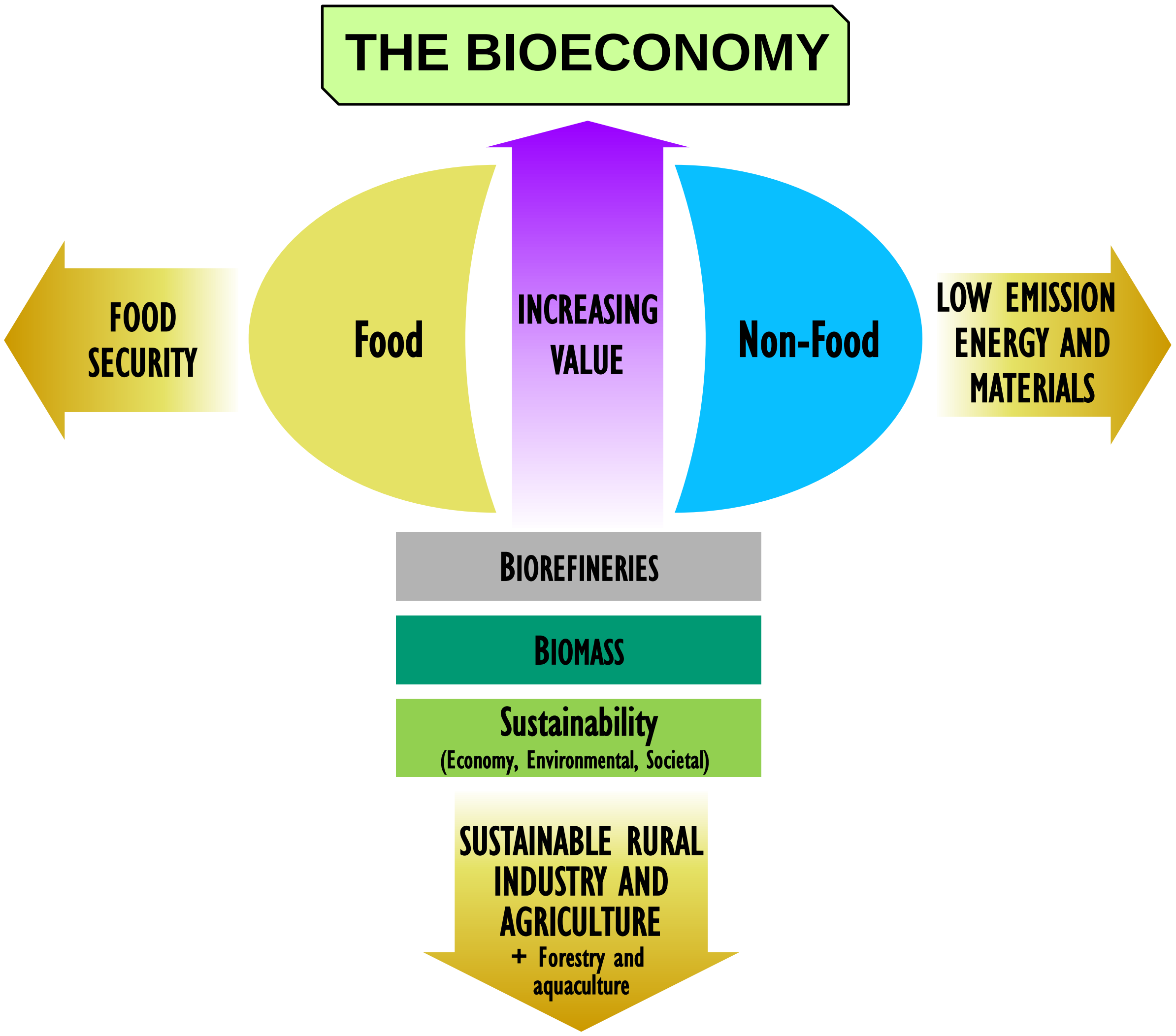
Raw Materials from Vegetables.

Approaches to the Use of Renewable Raw Materials.

- Duplication of products and structures: biomass used to prepare known petrochemical derivatives … with relative facility, but limited economic
- Duplication of properties: biomass is used to duplicate interesting service properties … with relative difficulty, but of wider economic opportunity
- Development of new eco-compatible products.



The Bioeconomy: Heart of the «New Bioeconomy».



Biobased Products Fall into Three Broad Categories.

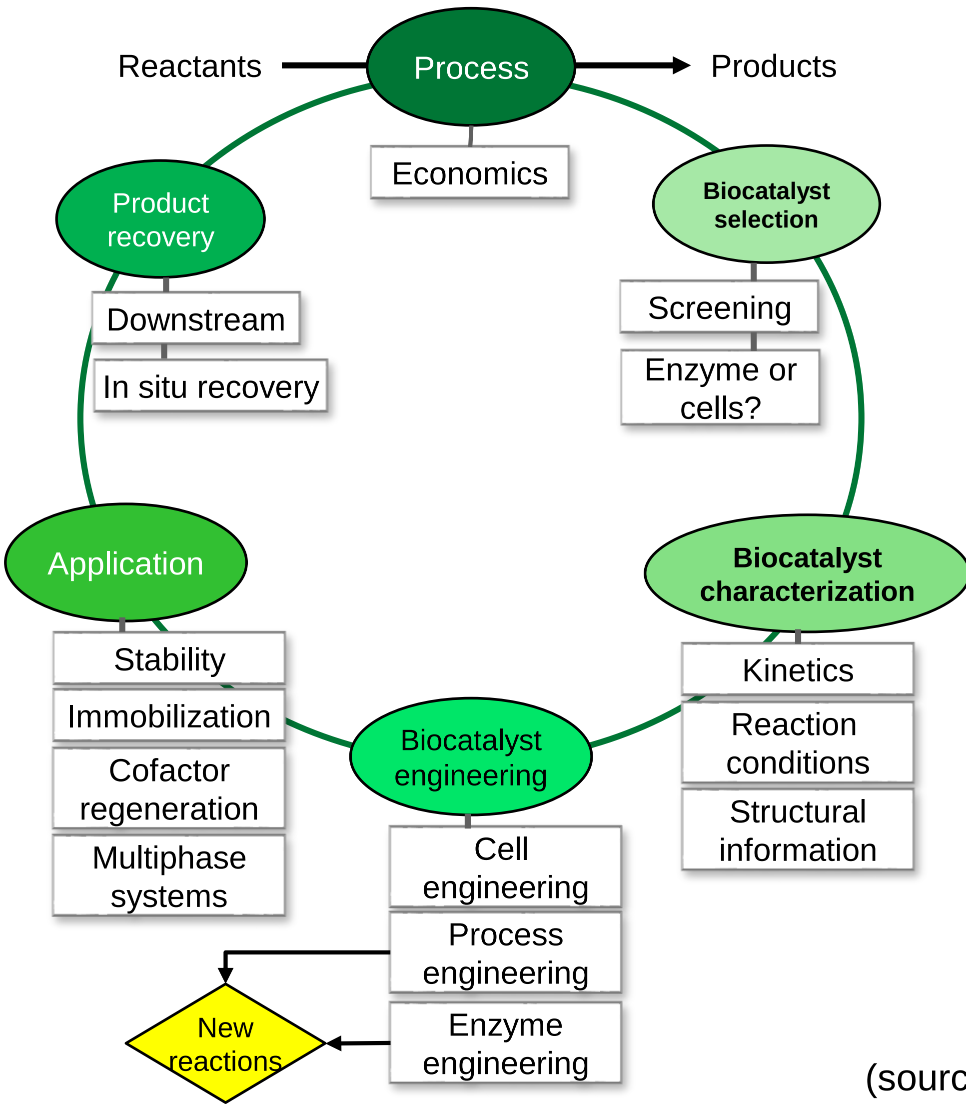
- **Biofuels** (oils, biodiesel, ethanol)
- **Biochemicals** (specialty chemicals such as paints, inks, surfactants, polymers, lubricants, solvents, and plant-made pharmaceuticals, etc.)
- **Biomaterials** (fiber products, lumber, leather, processed foods, laminates, roofing, plastics, insulation, etc.)

Two Main Alternatives.

a) **Separation of naturally produced polymers and compounds**
- Mechanical technologies
- Extraction technologies
- Other separation technologies

b) **Selection and production of a biocatalyst for the selective production of polymers and compounds (through GMO organisms)**
- Biocatalyst selection and characterization
- Biocatalyst engineering
- Application
- Product recovery.

The Cycle of Processes Involved in the Selection and Development of a Biocatalyst.



(source: Schmid et al, 2001).

Main Biomass Feeding Constituents.

Starch: 70-75% (wheat)

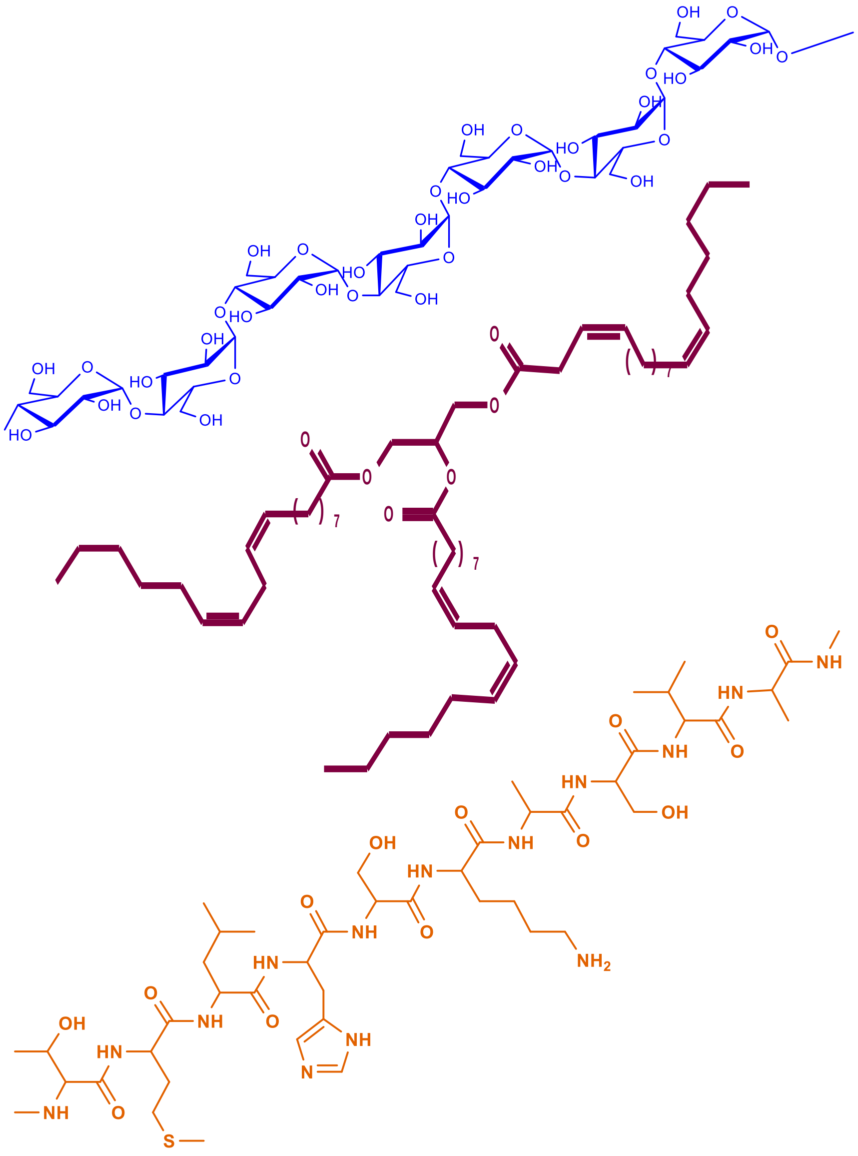
- Rapidly available and hydrolysable
- Basis for actual “biorefineries”

Oils: 4-7% (wheat), 18-20% (soy)

- Rapidly separable from plant
- Basis for oleochemistry and for biodiesel

Proteins: 20-25% (wheat), 80% (soy)

- Key components of foods
- Applications in chemical products



Main Biomass non Feeding Components.

Lignin : 15-25%

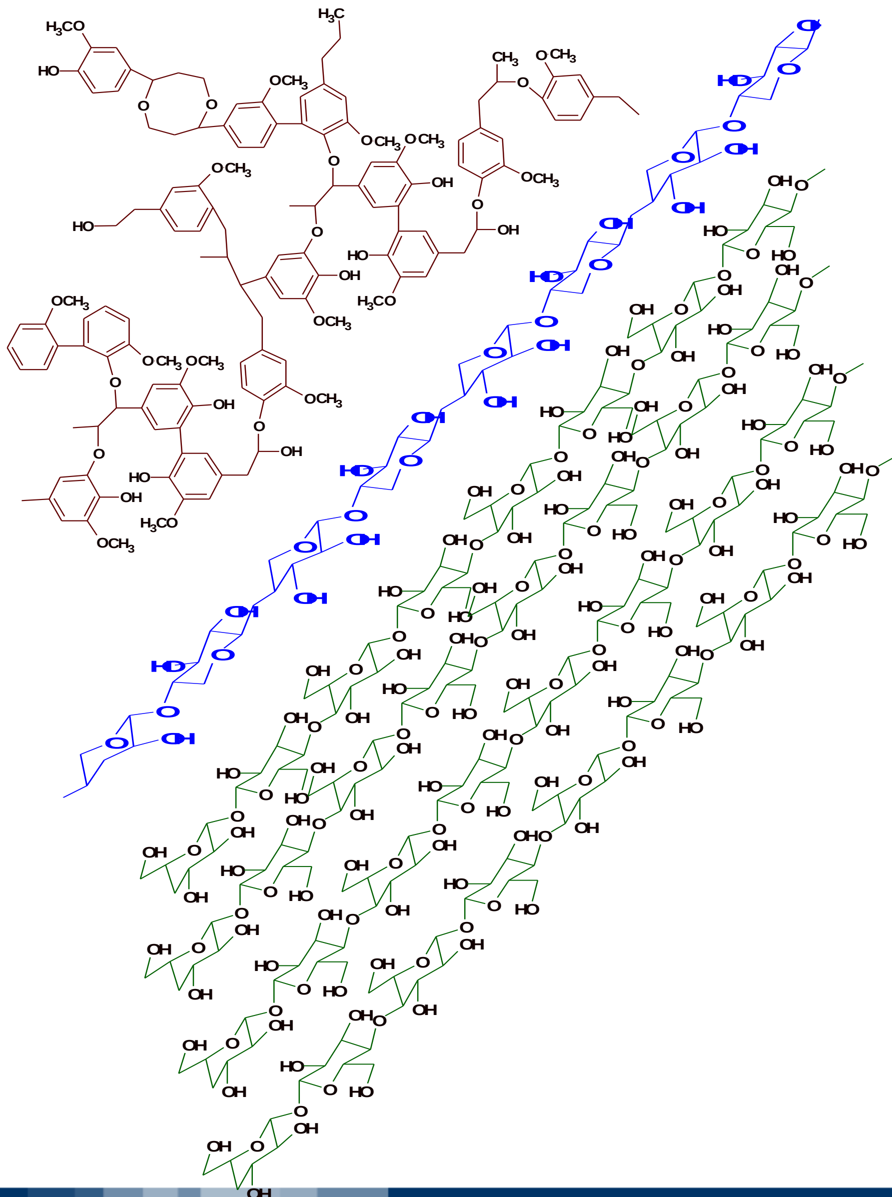
- Complex network of aromatics
- High energy content
- Resists biochemical conversion.

Hemicellulose : 23-32%

- Xylose is the 2nd most abundant sugar in biosphere
- A collection of 5- and 6-carbon sugars linked together in long, substituted chains- branched, marginal biochemical feed.

Cellulose : 38-50%

- Most abundant carbon form in biosphere
- Long polymer chains of beta-linked cellobiose, good biochemical feedstock.



Complementarity of Different Views on Biotechnology.

BIOTECHNOLOGIES

Red Biotechnologies

Medical applications

Therapeutic proteins, diagnostic, genetic therapy …

Green Biotechnologies

The vegetable

Agriculture, alimentation, OGM…

White biotechnologies

Industrial Biotechnologies

Fermentation, catalysis

Blue Biotechnologies

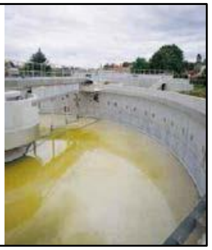
La see route

Organisms, algae…

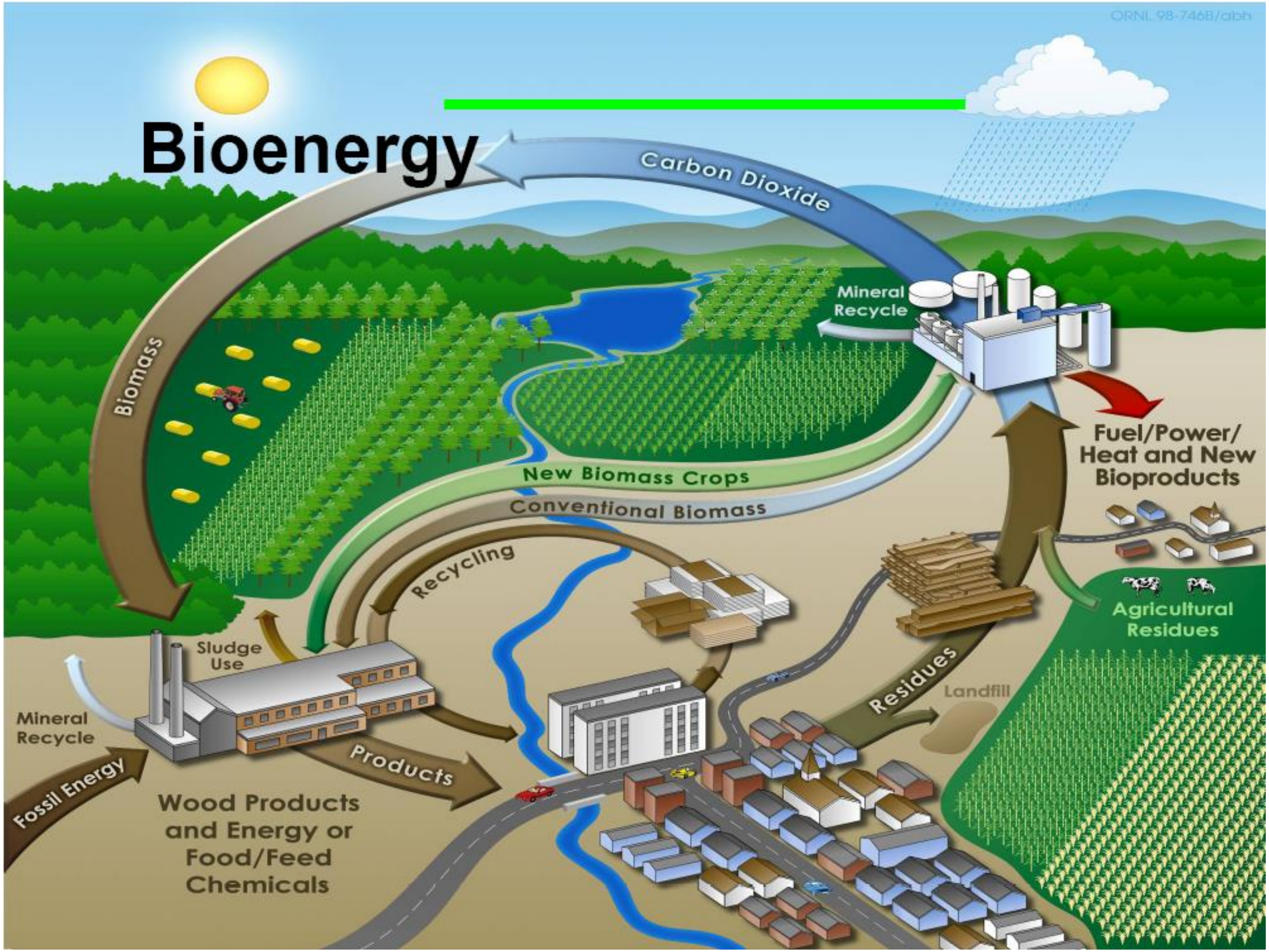
Yellow Biotechnologies

Environment

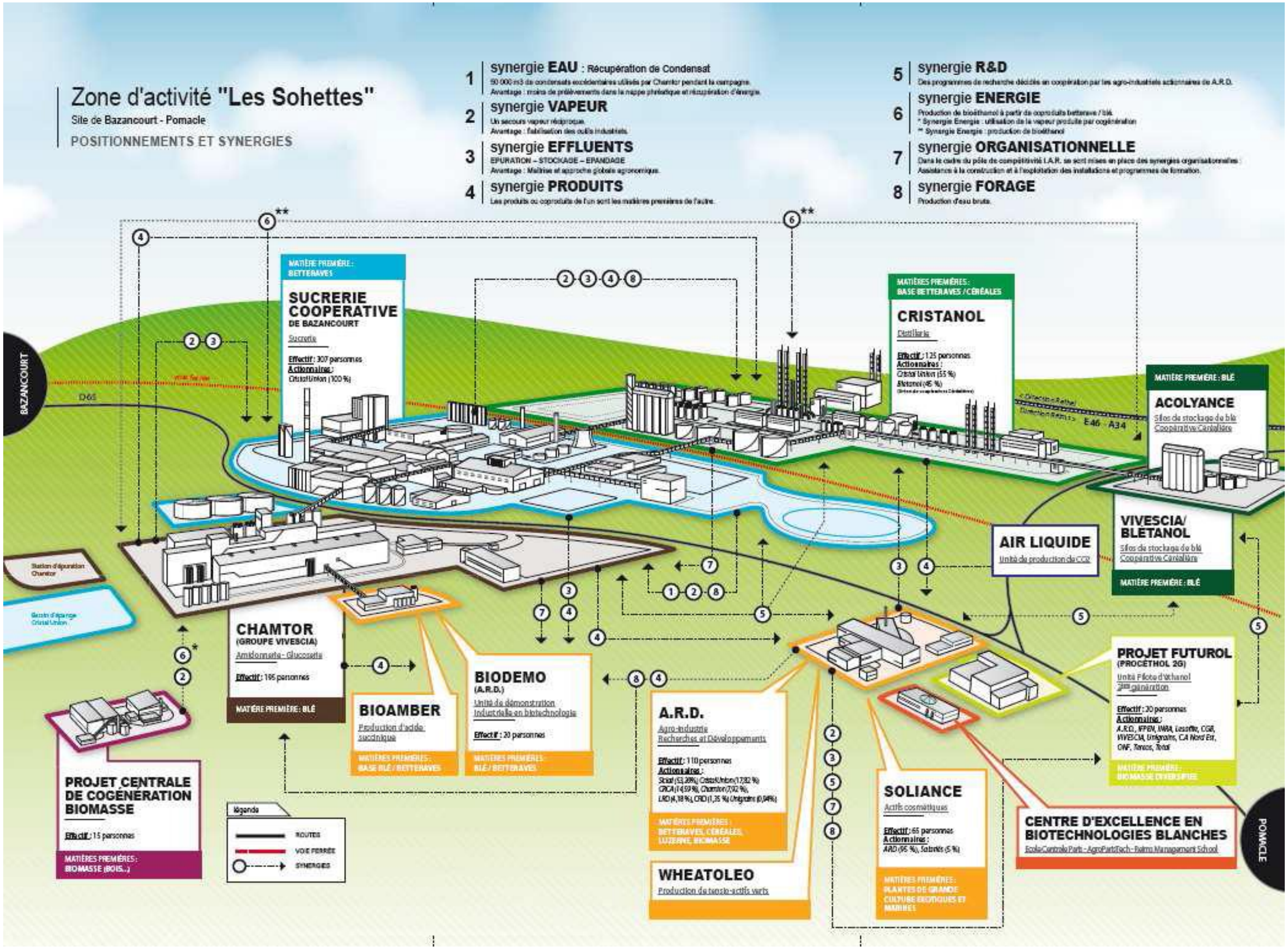
Bioremediation, water treatments…



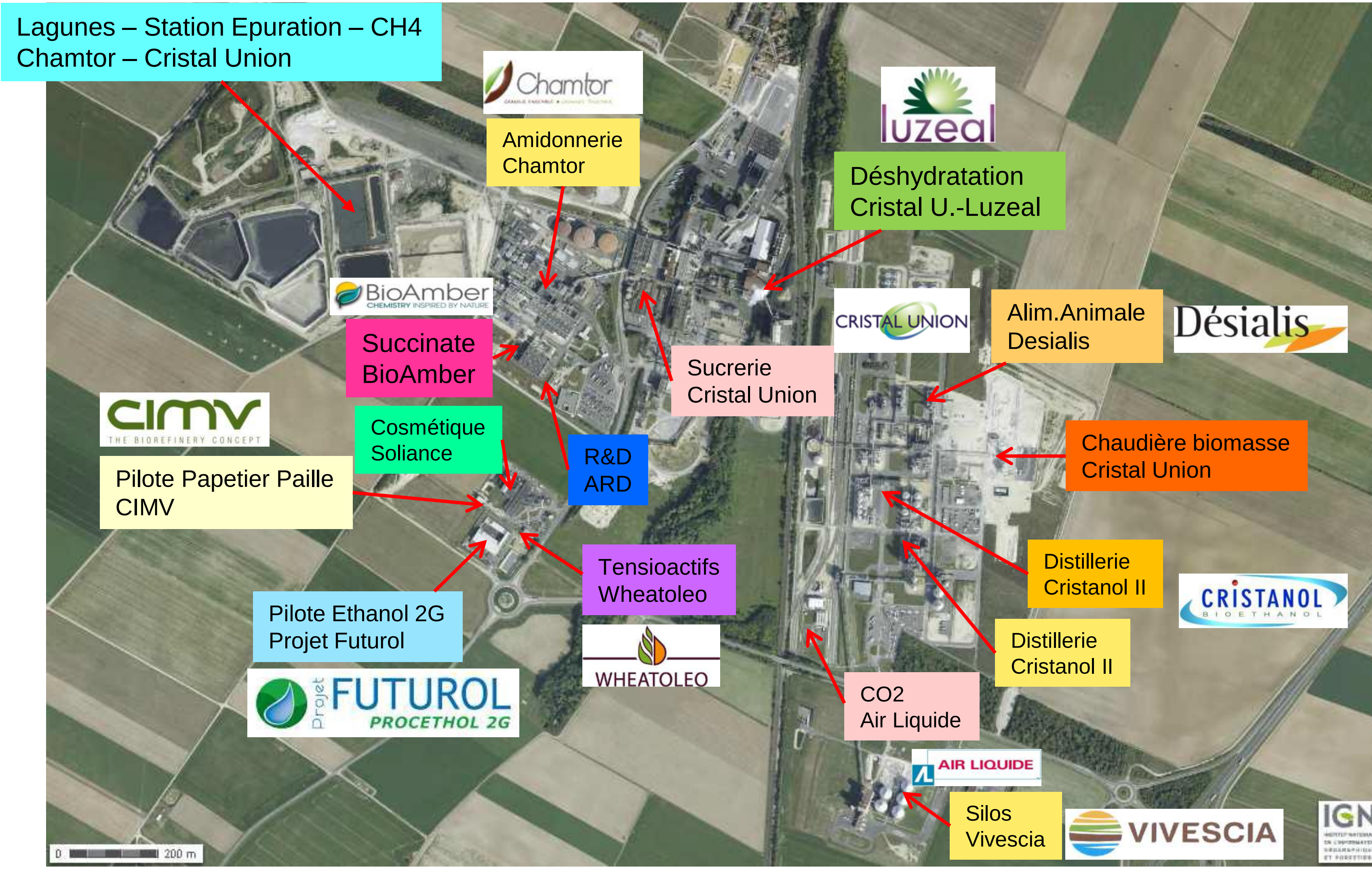
Holistic Vision of a Biorefinery.



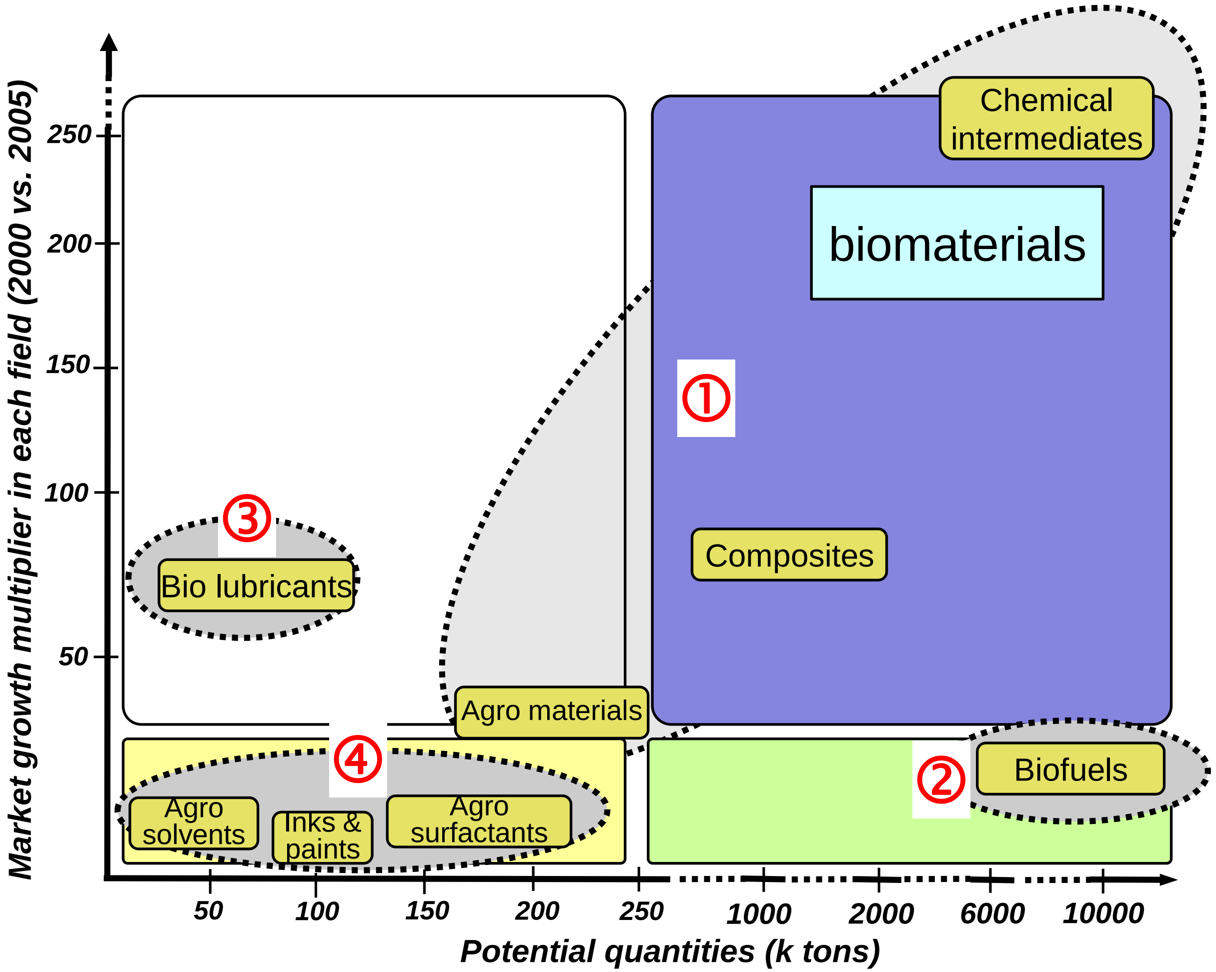
The Biorefinery of Pomacle-Bazancourt.



The Biorefinery of Pomacle-Bazancourt (2).



Market Evolution of Agro-Based Products in the Next Future.



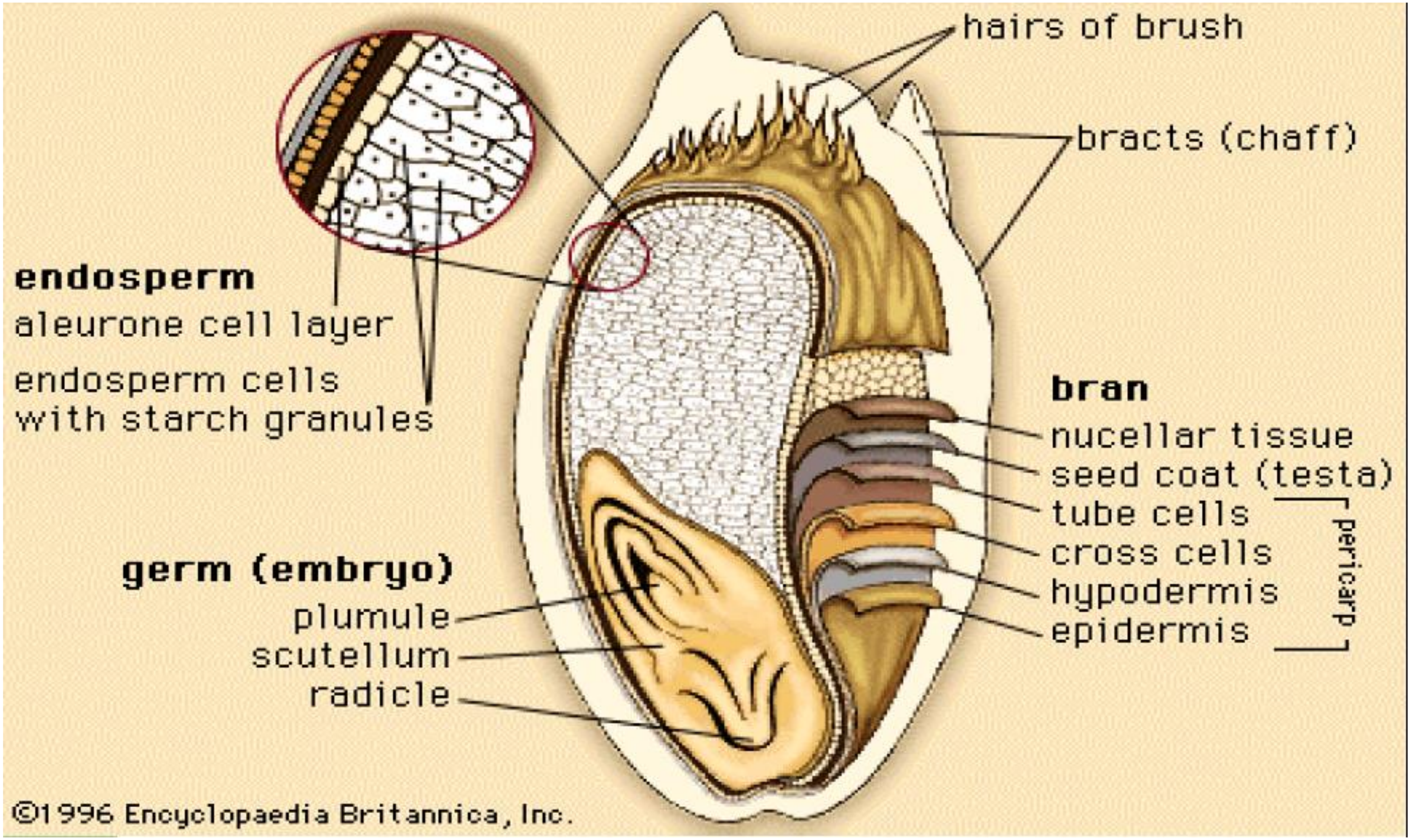
① High dynamic /high quantities

② Middle dynamic /high quantities

③ High dynamic / middle quantities

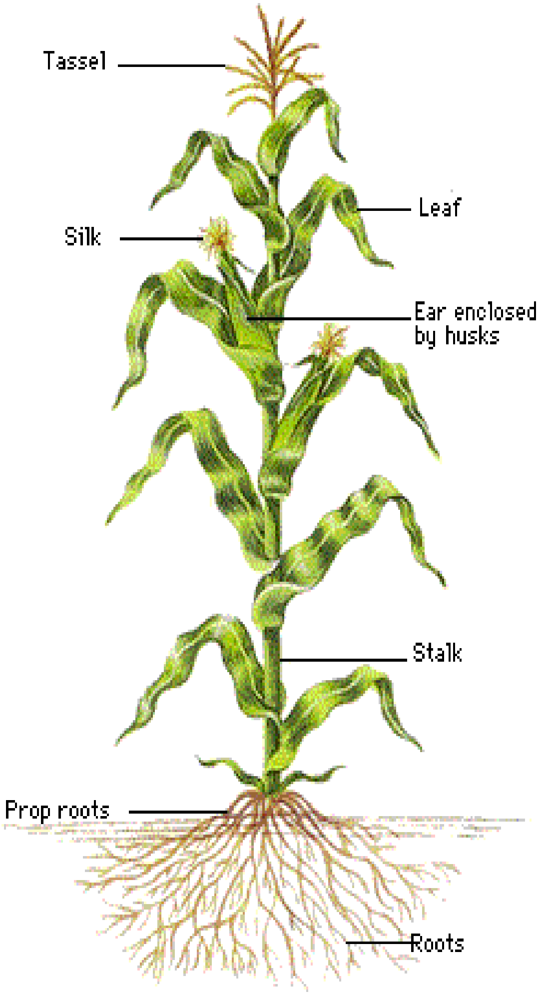
④ Middle dynamic /weak to middle quantities

Example of Raw Material: Corn Seed.

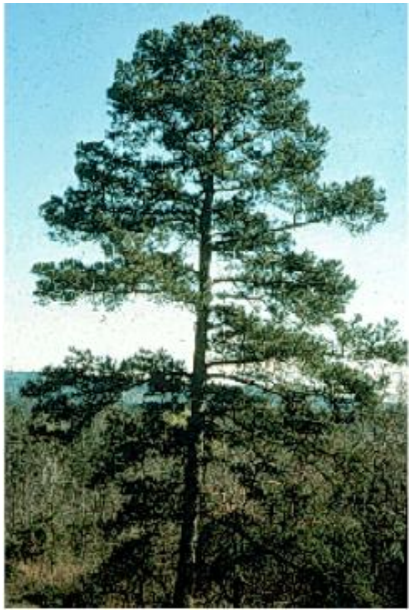


Composition of Corn Stover.

Chemical component	Composition %
Glucan	36.1 %
Xylan	21.4 %
Arabinan	3.5 %
Mannan	1.8 %
Galactan	2.5 %
Lignin	17.2 %
Protein	4.0 %
Acetyl	3.2 %
Ash	7.1 %
Uronic Acid	3.6 %
Non-structural Sugars	1.2 %

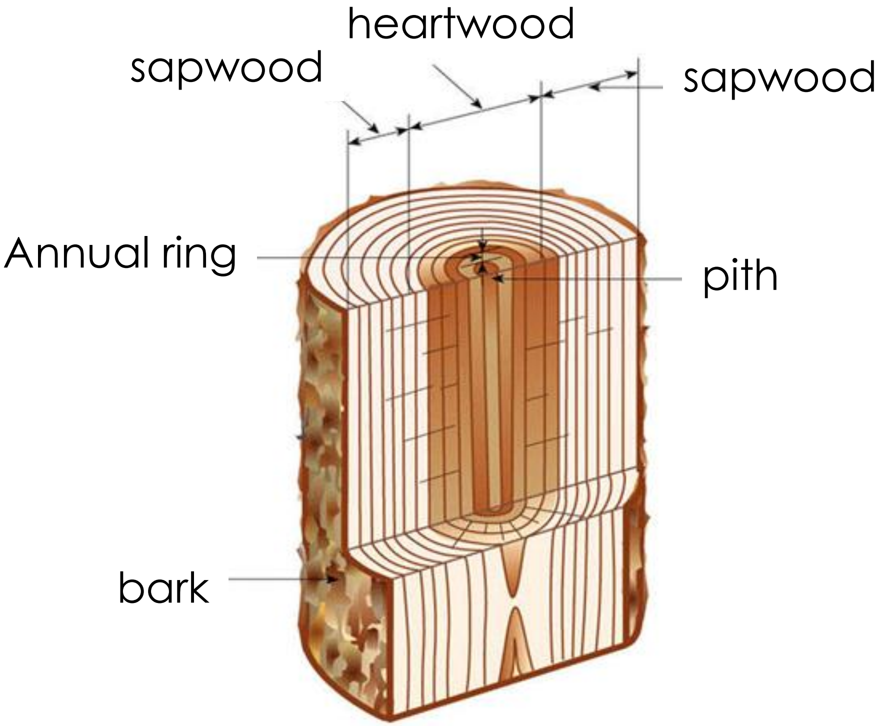


Chemistry of Wood.



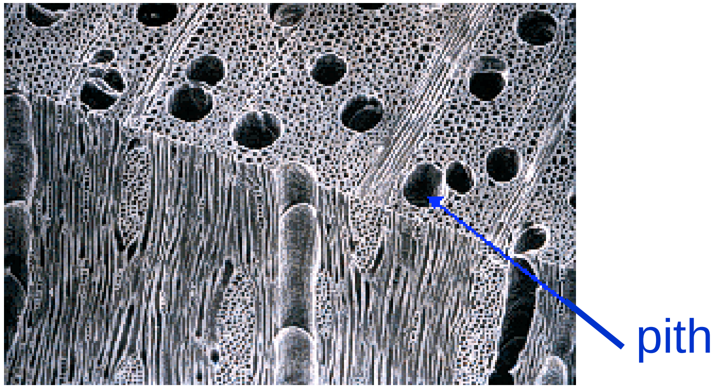
Wood belongs to the class of composite materials :

Matrix = lignin
Fiber to strengthen = cellulose
Interfacial agent = hemicellulose

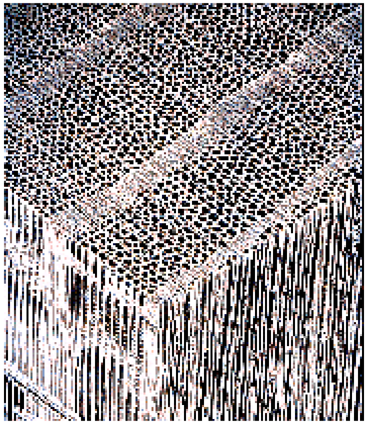


Macroscopic Structure of Wood.

Hardwood texture...



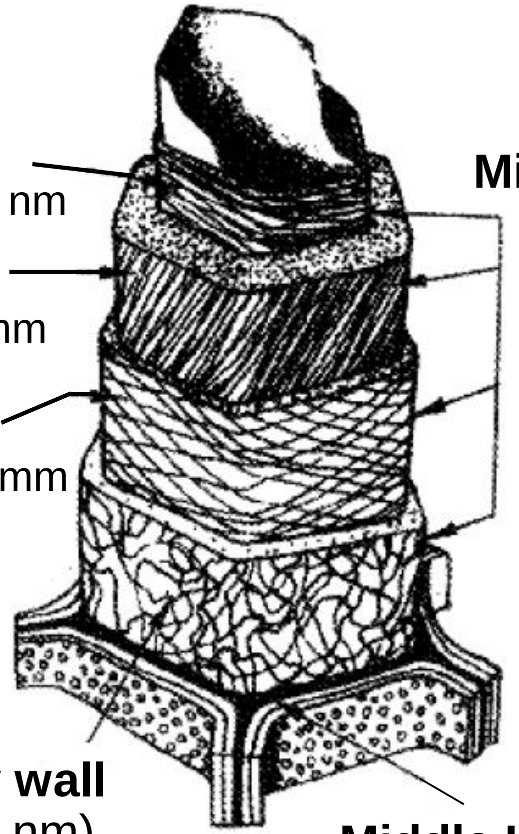
Softwood texture ...



Outer bark = dead cells

The wood (or xylem) grows each year
(annual ring structure)

Anatomic Structure of a Wood Fiber (tracheid).



Hardwood

ℓ = 1.5-5 mm

ϕ = 20-50 mm

Softwood

ℓ = 0.6-1.6 mm

ϕ = 10-30 mm

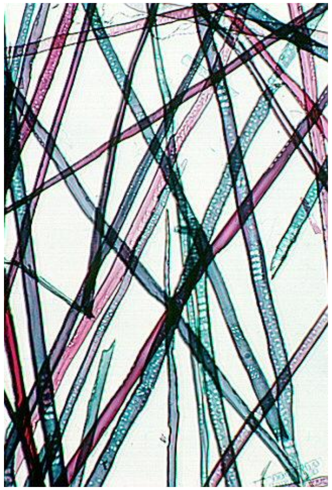
Lignin:
soft = 25%
hard = 21%

Hemi cellulose:
soft = 25%
hard = 35%

Extractives: 2-8%

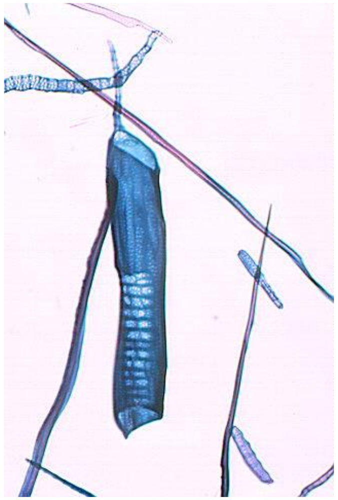
Two Types of Vegetal Species.

	Mass Composition (%)		Role
	Hardwood	***Softwood***	
Cellulose	40-45	38-50	Strengthen
Hemi-cellulose	7-15	19-26	Matrix
Lignin	26-34	23-30	Matrix
Extractives	4	4	Lubricant
Ash	< 1	<1	-

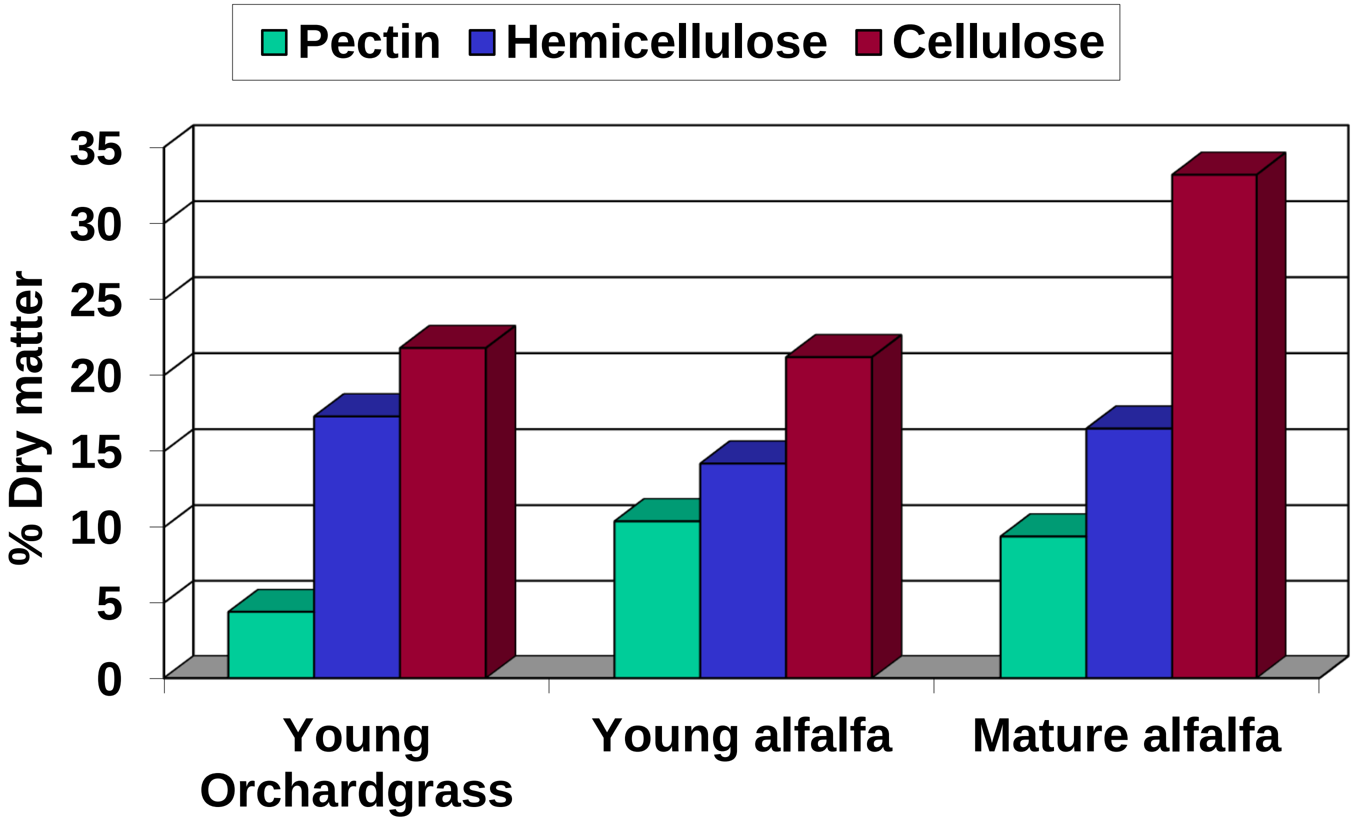


White Pine

Red Oak



Structural Carbohydrates in Plants.



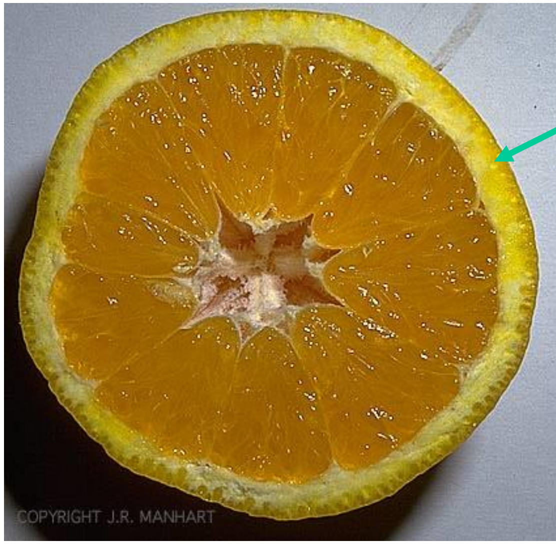
alfaalfa =
medicago sativa

- Pectins less in grass than legumes.
- Hemicellulose greater in grass than legumes.
- Hemicellulose and cellulose increase with maturity.

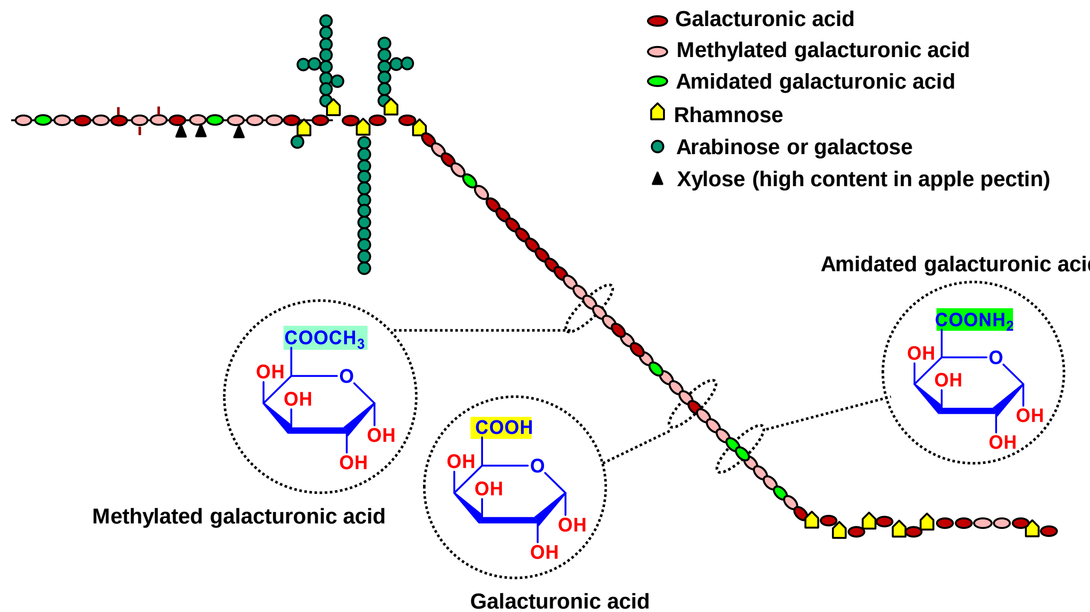
Mixed Polysaccharides – Pectins.

- **Pectins**
  - Pectins have a complex and not exact structure. Backbone is most often α-1,4 linked D-galacturonic acid
  - Rhamnose might be interspersed with galacturonic acid with branch-points resulting in side chains (1 - 20 residues) of mainly L-arabinose and D-galactose
  - Also contain ester linkages with methyl groups and side chains containing other residues such as D-xylose, L-fructose, D-glucuronic acid, D-apiose, 3-deoxy-D-*manno*-2-octulosonic acid and 3-deoxy-D-*lyxo*-2-heptulosonic acid attached to poly-α-(1,4)-D-galacturonic acid regions
  - Proteins called extensins are commonly found associated with pectin in the cell wall
  - Commonly form crosslinks and entrap other polymers
  - Composition varies among plants and parts of plants:
    - Citrus pulp, beet pulp, soybean hulls have high concentrations
    - Alfalfa intermediate concentrations of pectin
    - Grasses have low concentrations of pectin

Pectin: Structure and Sources.



Pectin-rich mesocarp



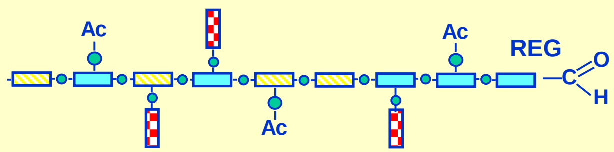
Sources of pectins:

- Apple pomace (residue after pressing for juice);
- Citrus peels.

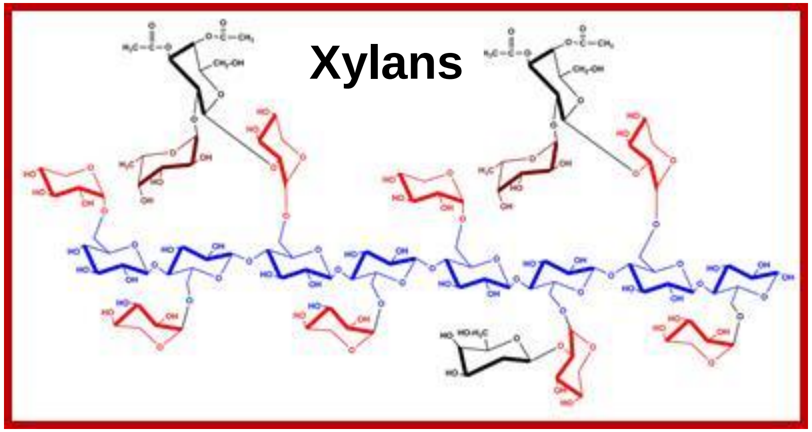
Mixed Polysaccharides – Hemicellulose.

- Branched polysaccharides that are structurally homologous to cellulose because they have a backbone composed of β-1,4 linked sugar residues – Most often xylans, no exact structure;
- Hemicellulose is abundant in primary walls but is also found in secondary walls;
- Various side chains: arabinose, glucuronic acid, mannose, glucose, 4-O-methylglucuronic acid – varies among species;
- In plant cell walls:
  - Close association with lignin – linkages to coumaric and ferulic acids - Not very resistant to chemical attack
  - Xylan polymers may be crosslinked to other hemicellulose backbones
  - Bound to cellulose in plant cell wall
  - Ratio of cellulose to hemicellulose ranges from 0.8:1 to 1.6:1.

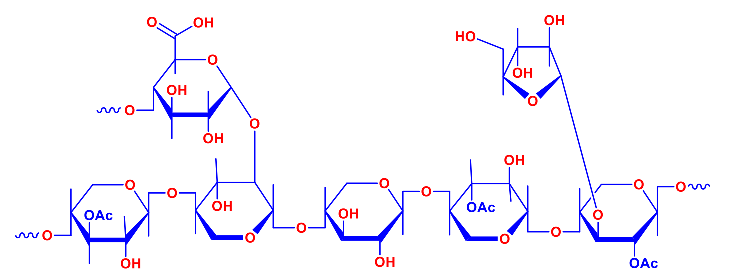
Molecular Structure of Hemicellulose.



Hemicellulose is a branched polymer DP ~ 50-300 (amorphous)

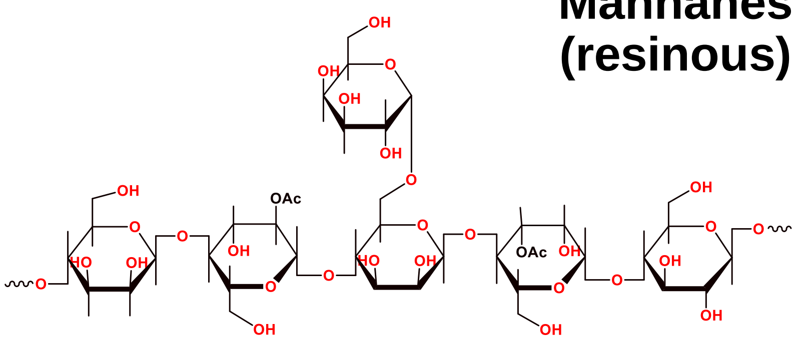


Hemicellulose is more abundant
in soft wood = Galactoglucomananes.

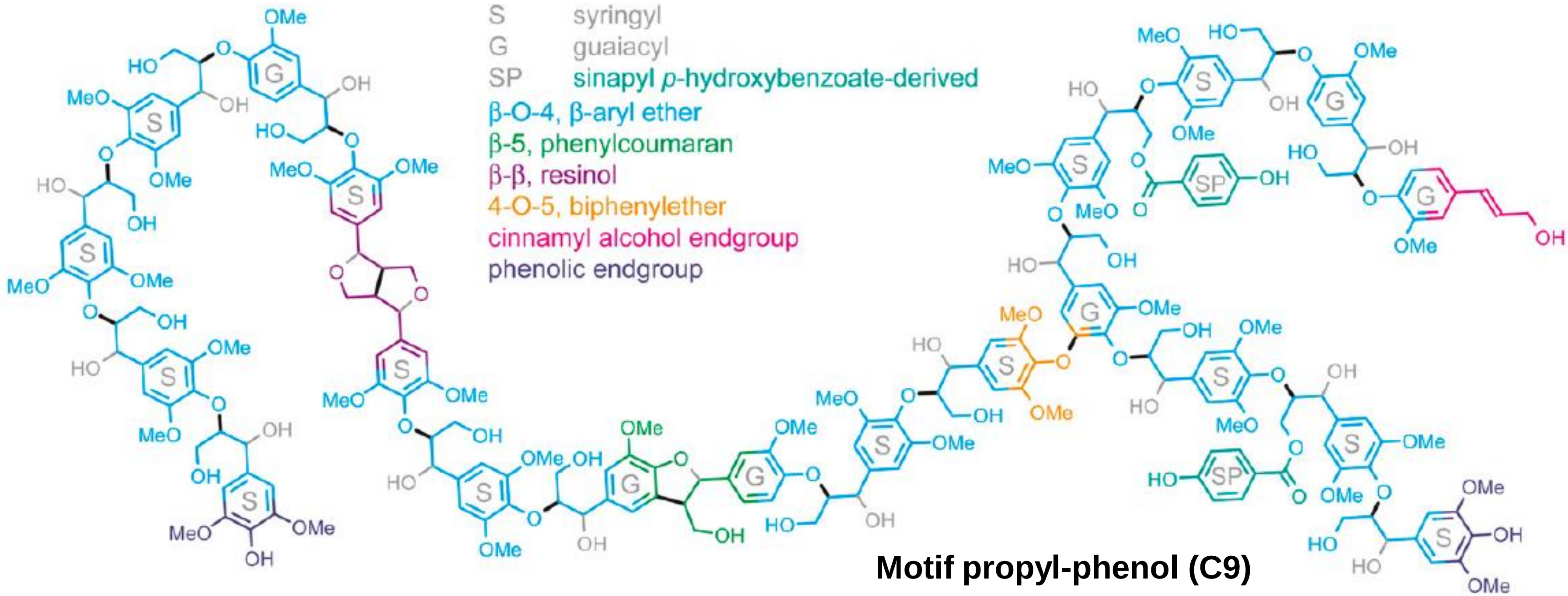


Food additives,
thickeners, emulsions
gel agents, adhesives.

Mannanes (resinous)

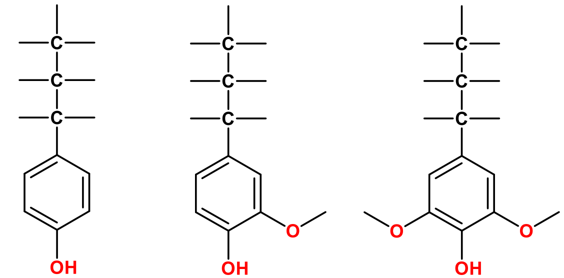


Lignin is a crosslinked amorphous high molecular weight polymer



Motif propyl-phenol (C9)

Lignin Monomers

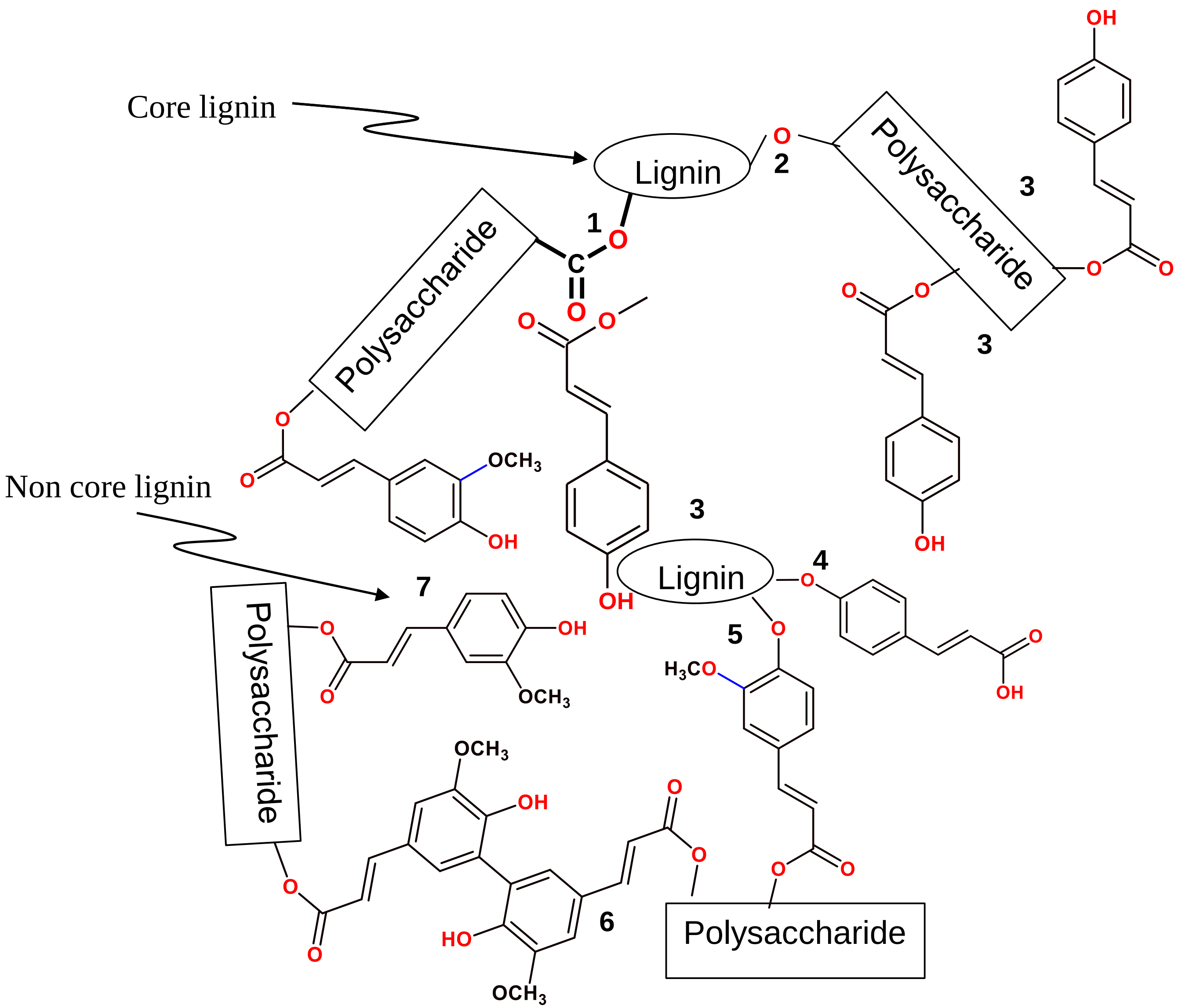


Annual plant

Resinous

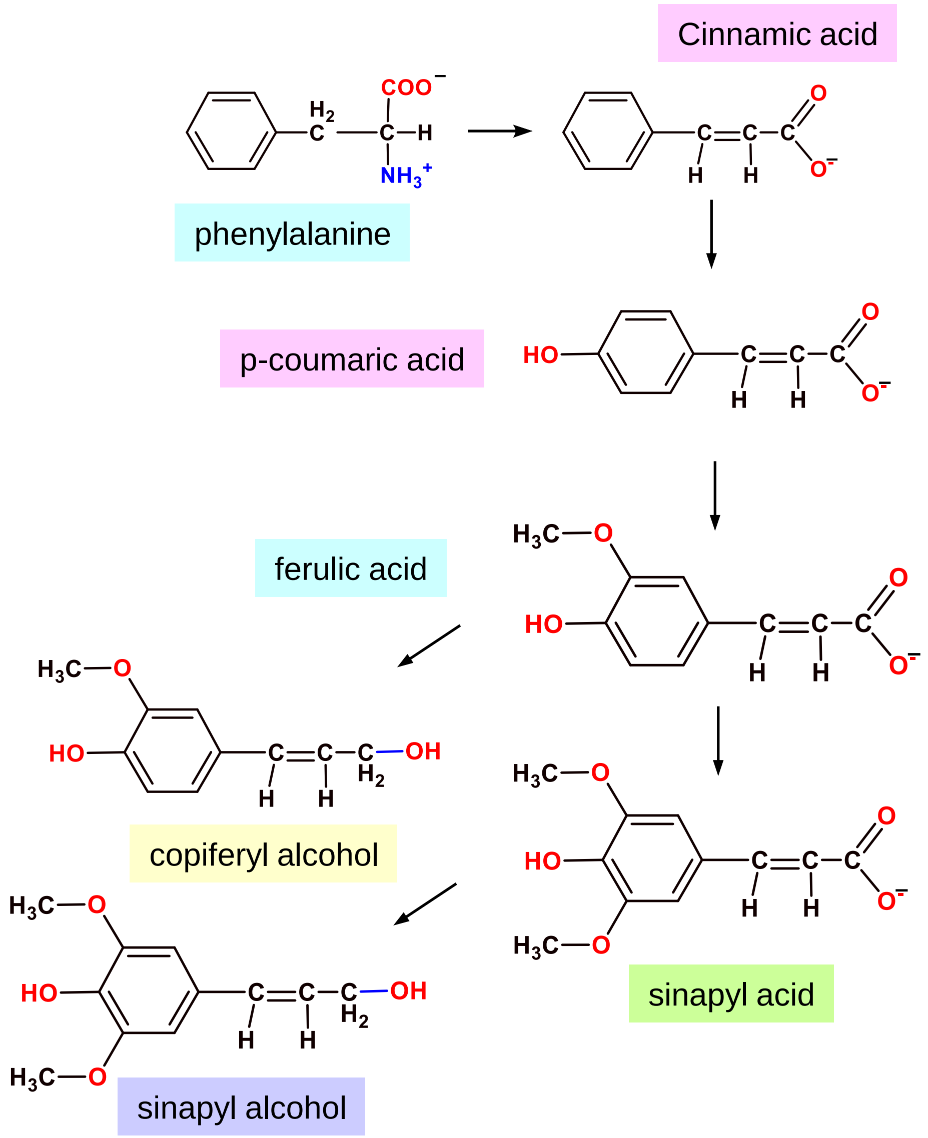
Foliage

Interaction of Lignin with Polysaccharides.



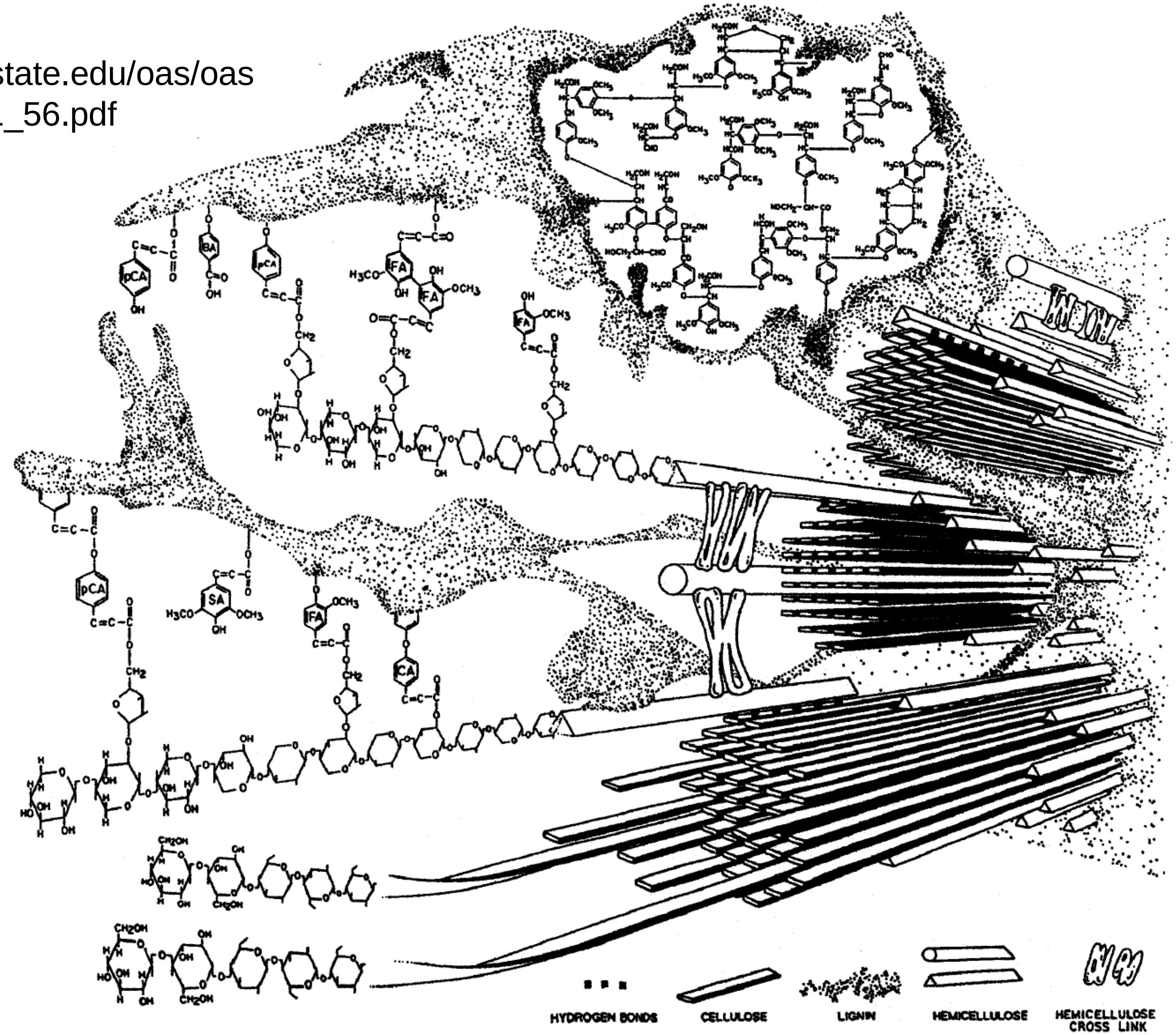
Lignin and its Monomers.

- Three dimensional polymer. Not a carbohydrate – does not contain sugars
- Large phenolic – very similar to phenolic resins used in plywood.
- The monomers are polymerized phenylpropane units, predominantly coumaryl alcohol [with an OH-group in position 4 of the phenyl ring], coniferyl alcohol (OH-group in position 4, $-OCH_3$ in position 3) and sinapyl alcohol (OH-group in position 4, $-OCH_3$ group in positions 3 and 5).
- The side groups of the monomers are reactive forming poorly defined structures that are heavily cross linked.
- Attach with hemicellulose and pectins
- Not digested in the rumen
- Dark in nature – especially after reacting with alkali – must be de-colored or removed to bleach pulp.

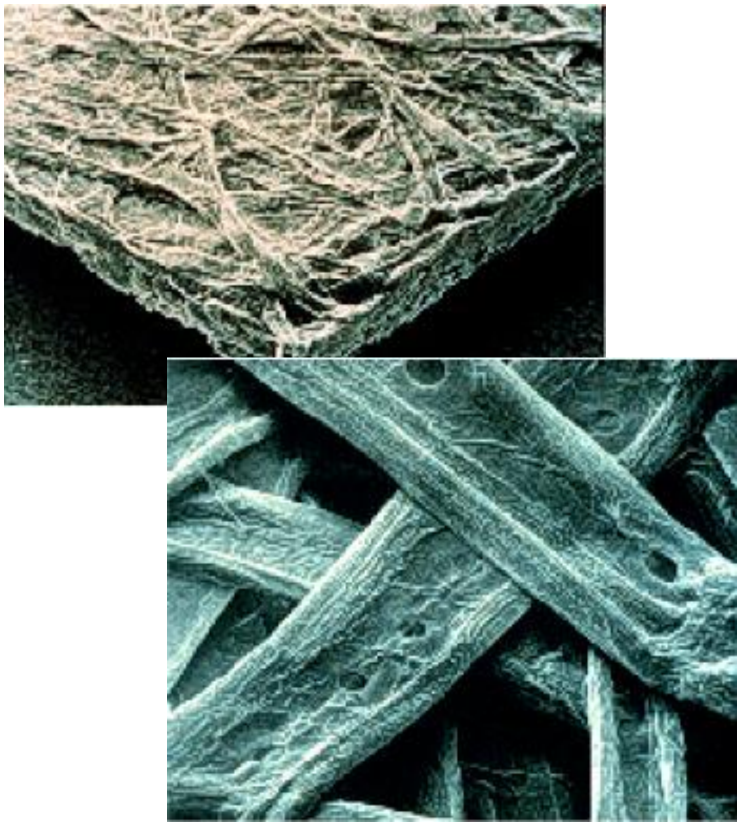


Wood: Secondary Wall Structure.

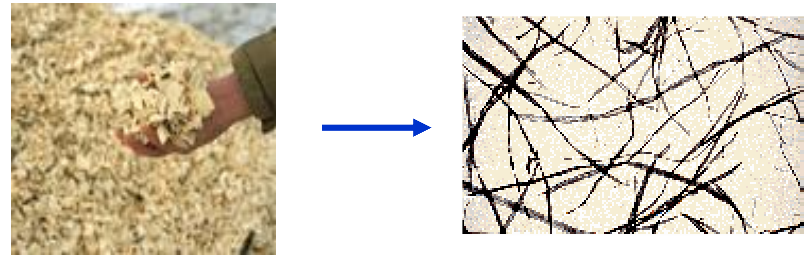
http://digital.library.okstate.edu/oas/oas_pdf/v72/p51_56.pdf



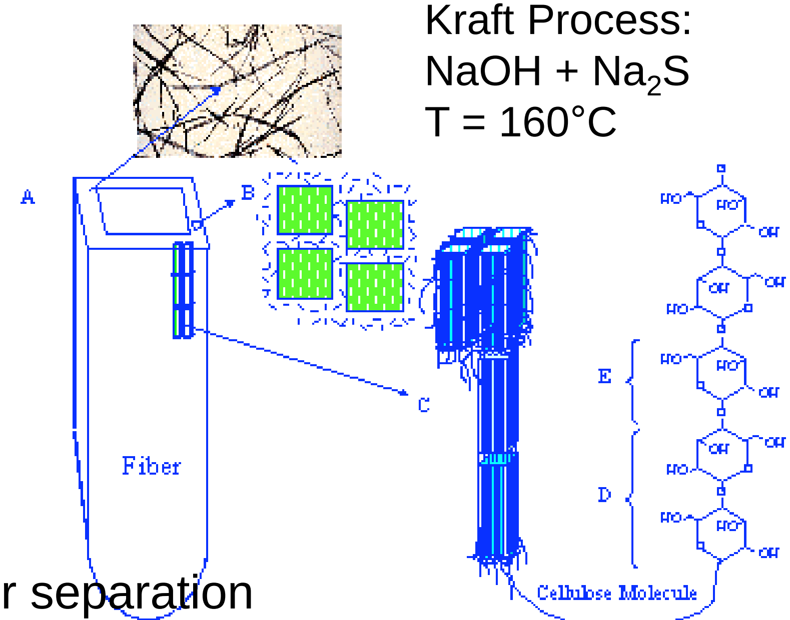
Paper Structure.



Lamella Separation

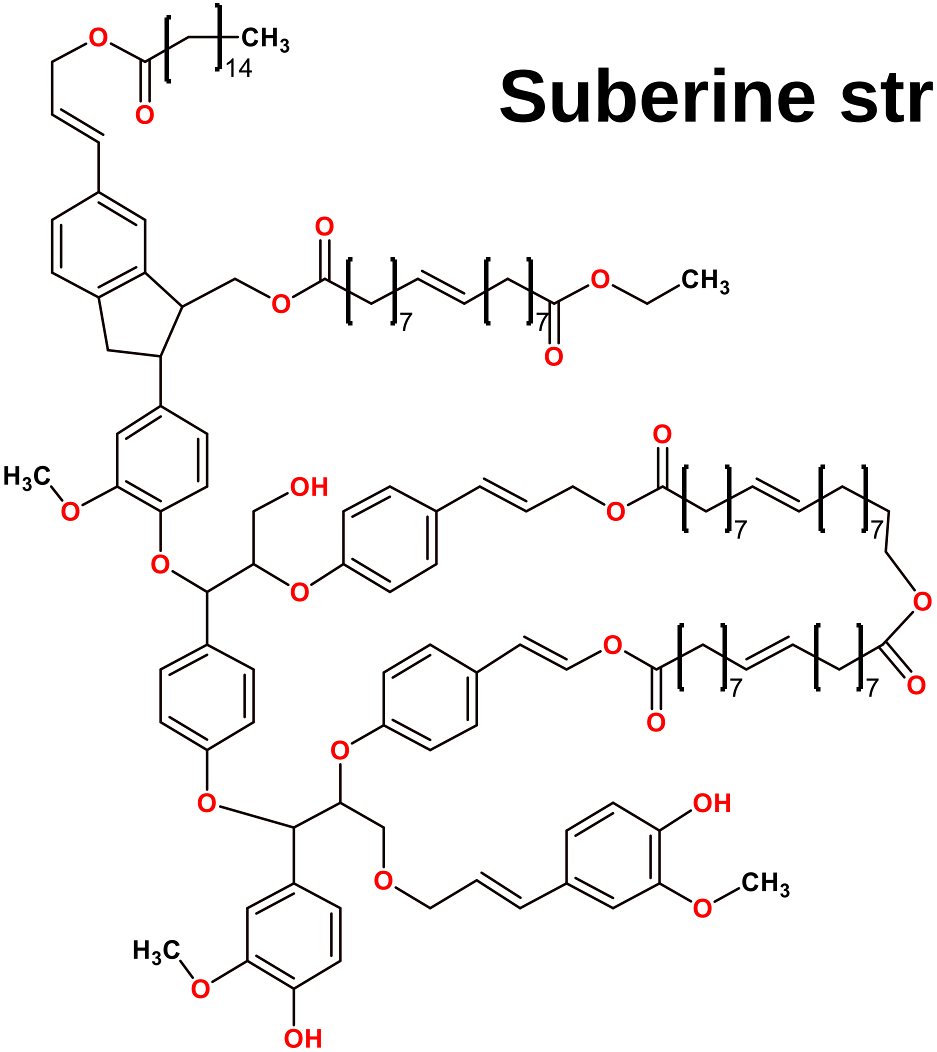


Kraft Process:
$NaOH + Na_2S$
T = 160°C



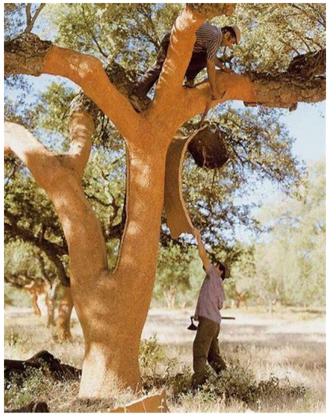
Fiber separation
= paper dough

The Cork Case (Suberine 40%).



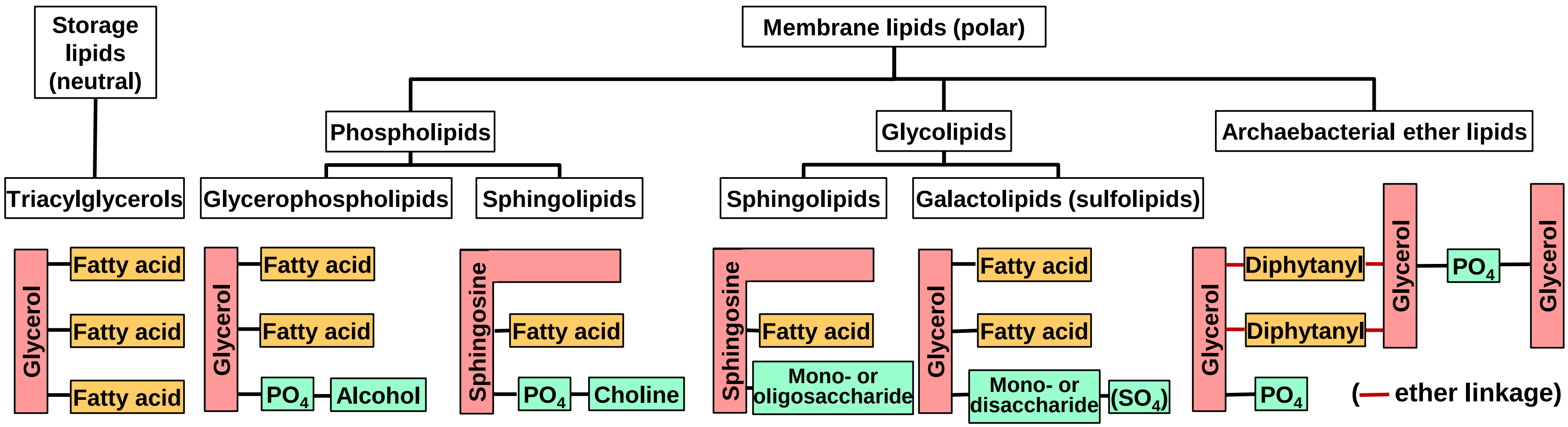
Suberine structure

Low density



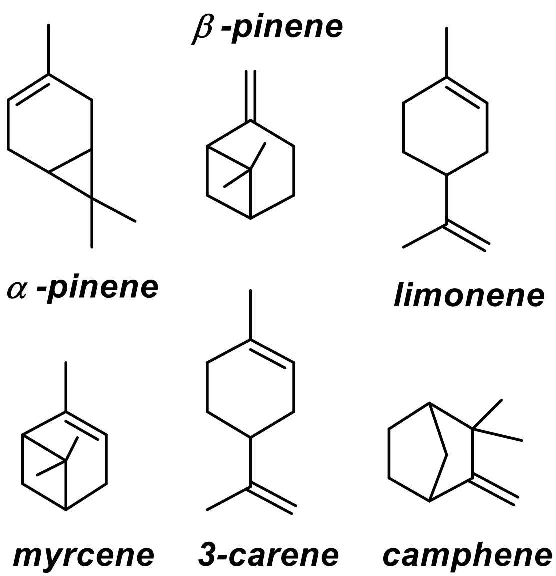
Hydrophobic and plastic

Some Common Storage and Membrane Lipids.



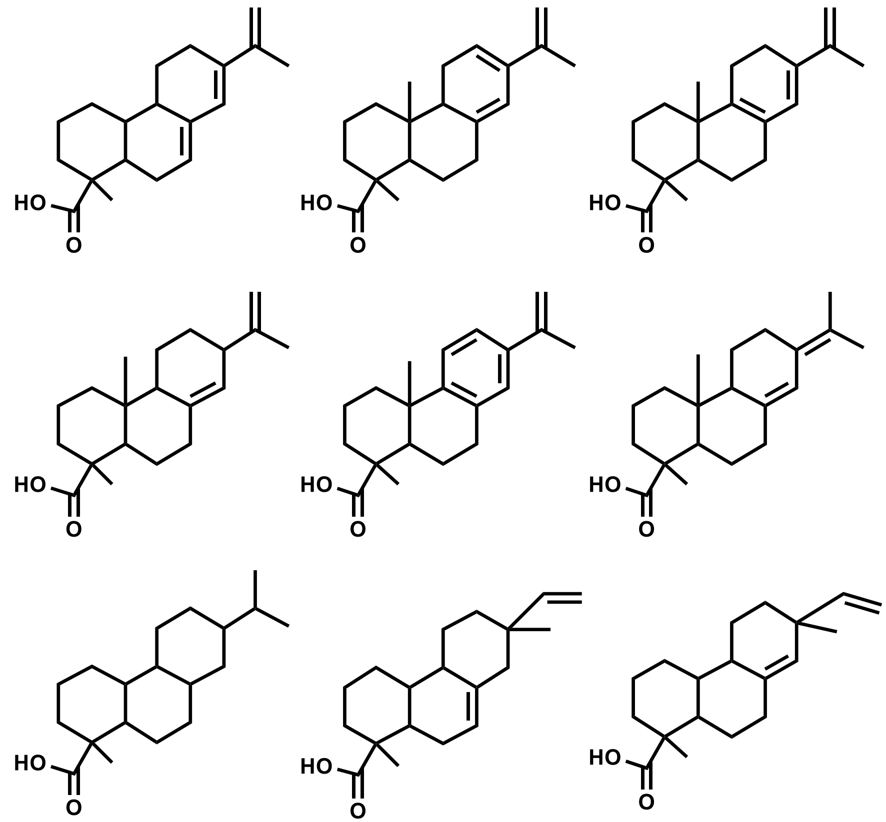
- In triacylglycerols, glycerophospholipids, galactolipids, and sulfolipids, the alkyl groups are fatty acids in **ester** linkage.
- Sphingolipids contain a single fatty acid, in amide linkage to the sphingosine backbone.
- In phospholipids the polar head group is joined through a phosphodiester, whereas glycolipids have a direct glycosidic linkage between the head-group sugar and the backbone glycerol.
- The membrane lipids of archaebacteria are variable; that shown here has two very long, branched alkyl chains, each end in **ether** linkage with a glycerol moiety.

Molecules from Wood: Terpenes.



Terpene's Family

"Turpentine oil"

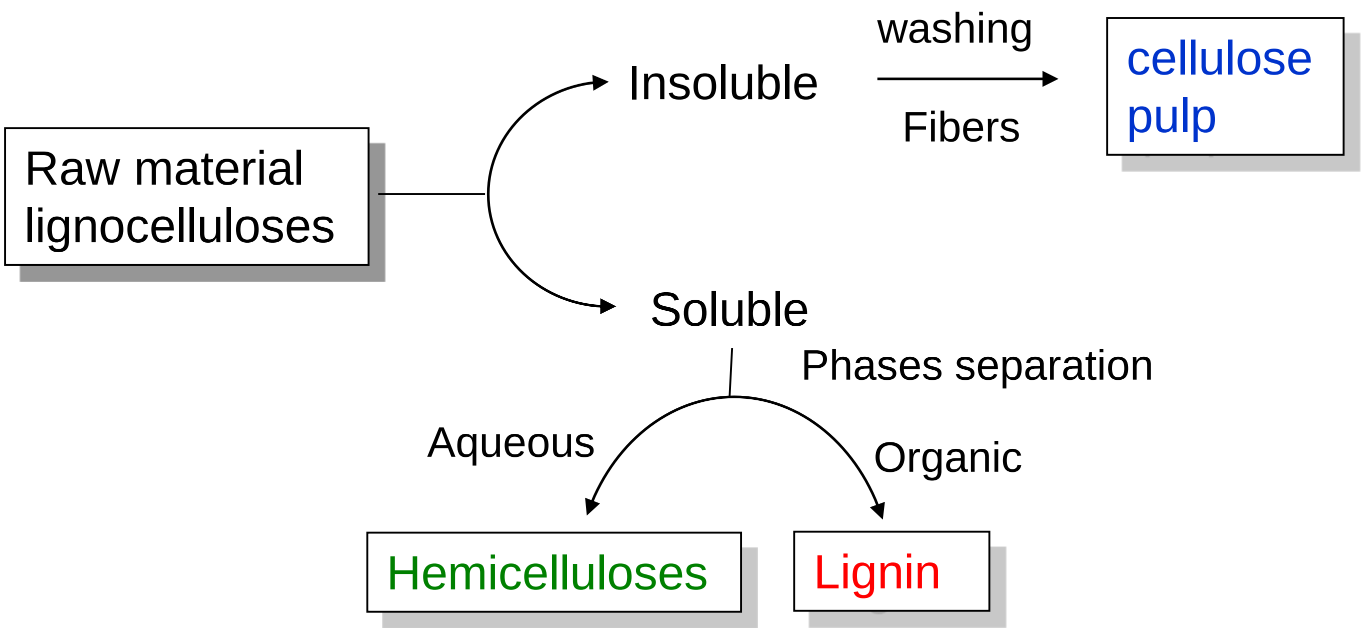


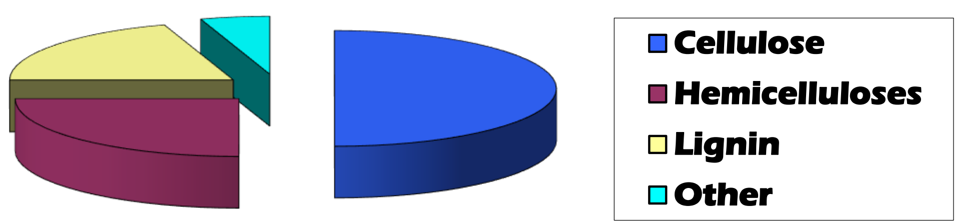
Abietic acid and homologs
"wood resins or colophony"
adhesives, paints, lubricants.

Distribution of Plant/Animal Resources as Raw Materials.

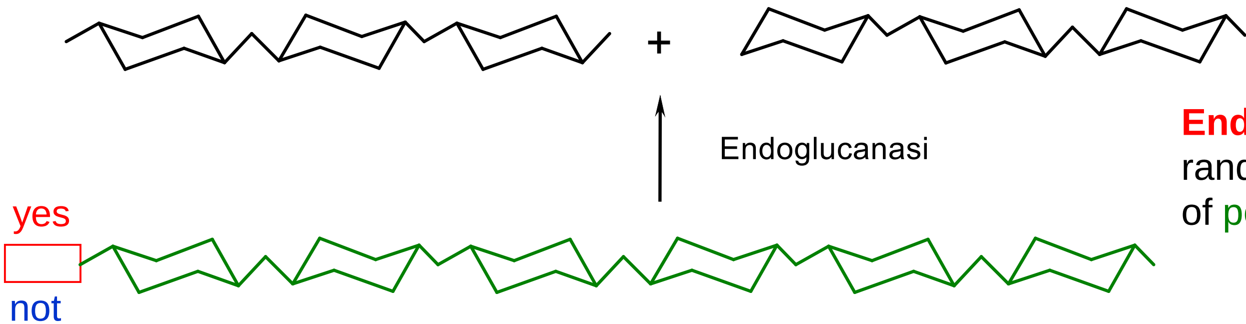
Resource	Millions of ton. used per year	Uses
Wood	80.9	Paper, carton, composites lignocelluloses
Industrial starch	3.0	Adhesives, polymers, resins
Vegetable Oils	1.0	Surfactants, inks, varnish
Natural rubber	1.0	Tires, toys
Wood extractives	0.9	Oils, rubbers
Cellulose	0.5	Textile fibers, polymers
Lignin	0.2	Adhesives, tanning, vanillin

Wood Fractioning Process.

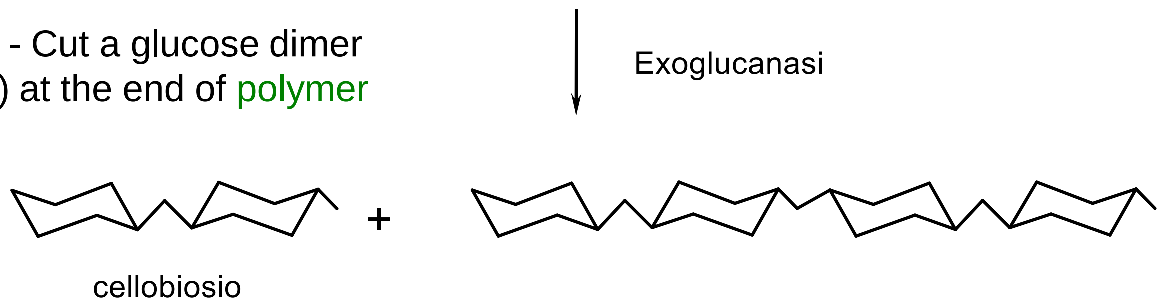




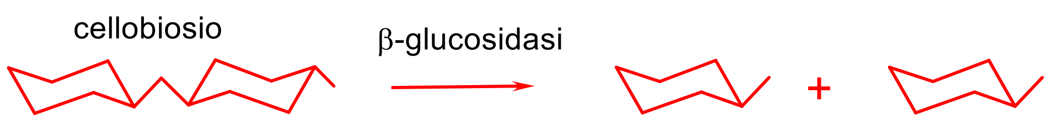
Enzymatic Degradation of Cellulose Involves Several Enzymes.



Endoglucanase – cut random in the middle of polymer chain.



Exoglucanase - Cut a glucose dimer unit (cellobiose) at the end of polymer chain.



Beta-Glucosidase - converts Cellobiose into glucose.

These enzymes are present in bacteria living in stomach of ruminants and termites, and in some fungi. The more active cellulase in lab are obtained from *Trichoderma reesei* fungus.

Concept of BioRefinery.

Generate multiple products from any given agricultural resource.

- *Need + Market + Economy based product -mix from multiple streams.*
- *Compact technologies in all stages to limit CAPEX.*

Technology Requirements:

- **Novel Processing Strategies**
  to yield process streams that facilitate flexibility in operation and obtaining variable product-mix.
- **Novel Separation Technologies**
  to yield products, especially low concentration-high price products, at low cost and high quality.

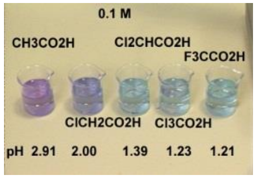
Bio-Refinery.

Corn

Fuels

Solvents

Bulk chemicals



Plastics

Fibers

Fine chemicals

Oils

Some “Co-products” of Cellulose Biorefinery.

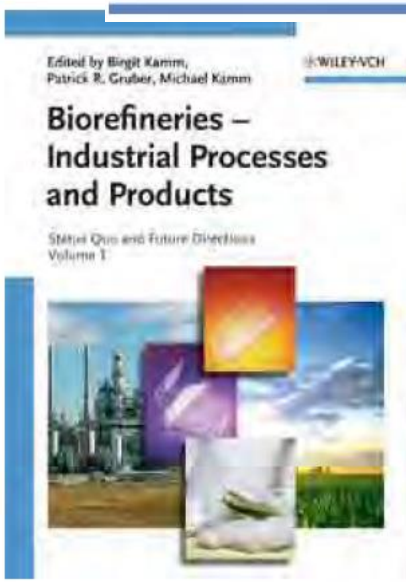
A *biorefinery* based on cellulose which produces **200 millions liters/year** of ethanol from stover & hay (at 200 liters/ton) will also produce:

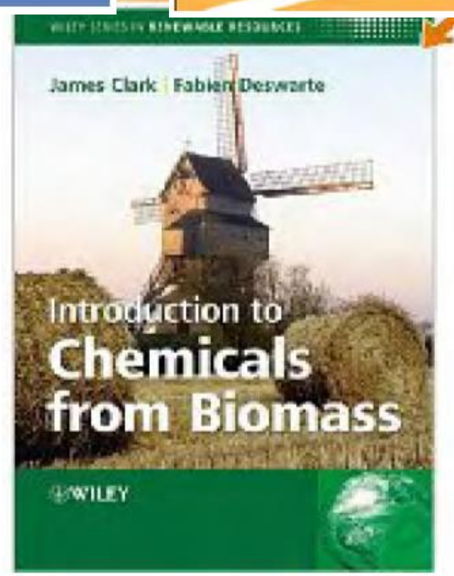
- 23,000 ton of Ca, K, Mg, P
- 22,000 ton of lipids, fats, waxes
- 57,000 ton of proteins (not included biomass cells)

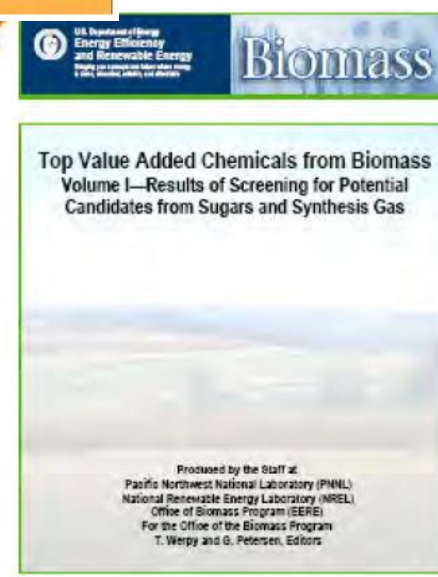
  (Proteins equivalent to 170,000 acres of soy)
- A lot of electricity (from lignin)
- (probably) residual sugars for animal feeding.

A biorefinery operates simultaneously in several ness fields (fuels, chemicals, power, food, etc.).

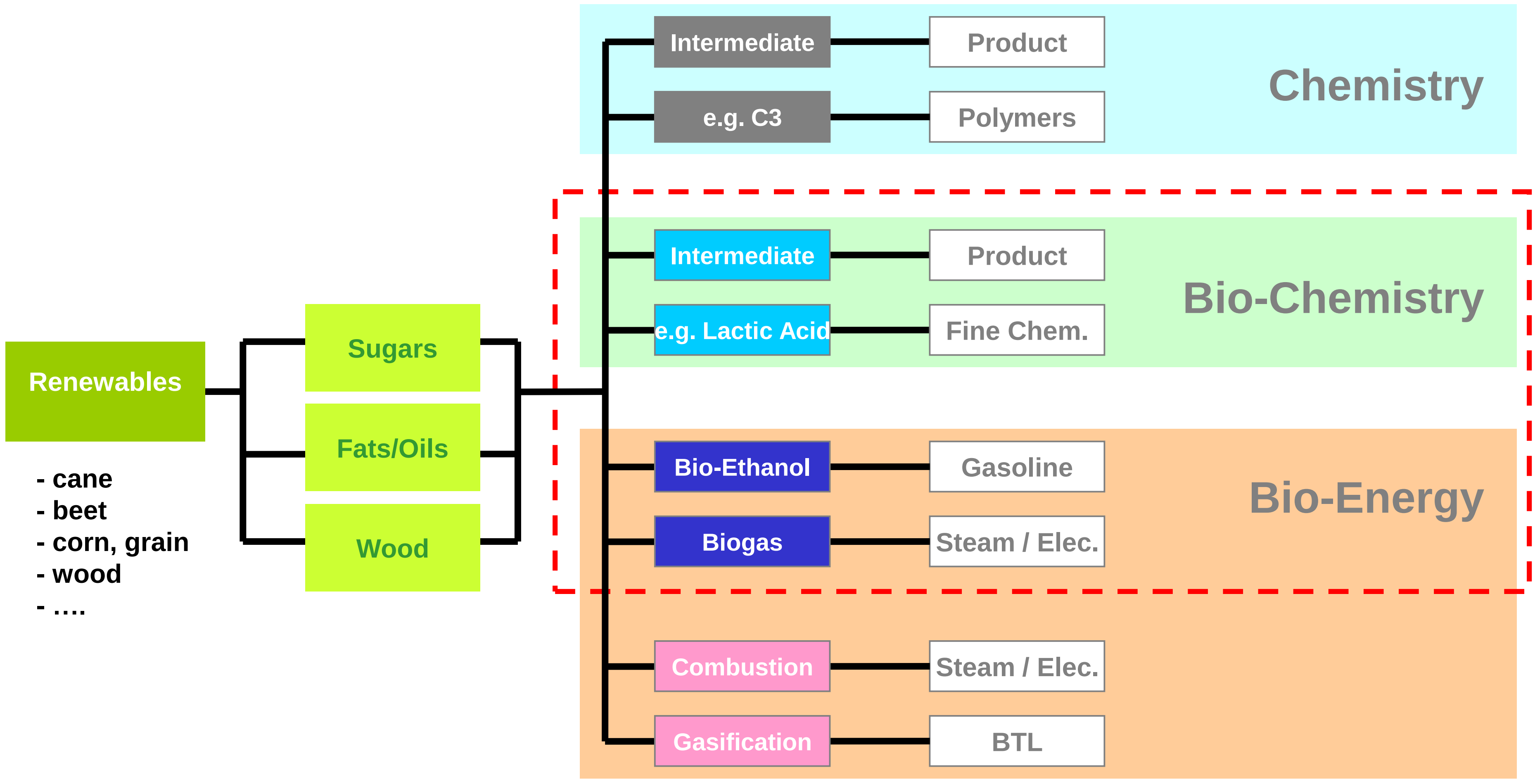
Some Reading on the Subject.







Chemical Products & Bio-Energy are Based on the Same Raw Material.



Basic C_n Platforms for Biorefineries.

Carbon Number	Potential Top 30 candidates
1	Carbon monoxide & hydrogen (syngas)
2	Ethanol
3	Glycerol, 3 hydroxypropionic acid, lactic acid, malonic acid, propionic acid, serine
4	Acetoin, aspartic acid, 1-butanol, fumaric acid, 3-hydroxybutyrolactone, malic acid, succinic acid, threonine
5	Arabinitol, furfural, glutamic acid, itaconic acid, levulinic acid, proline, xylitol, xylonic acid
6	Aconitic acid, citric acid, 2,5 furan dicarboxylic acid, glucaric acid, glucose, lysine, levoglucosan, sorbitol

C_n

Value-Added Building Blocks Derived From Sugars.

The DOE "Top 12" products from sugars:

Succinic, fumaric and malic acids,
2,5-Furandicarboxylic acid
3-hydroxypropionic acid
Aspartic acid
Glutaric acid
Glutamic acid
Itaconic acid
Levulinic acid
3-Hydroxybutyrolactone
Glycerol
Sorbitol
Xylitol/arabinitol

Biomass as a feedstock for products is an issue of current high interest to a wide range of industrial segments.

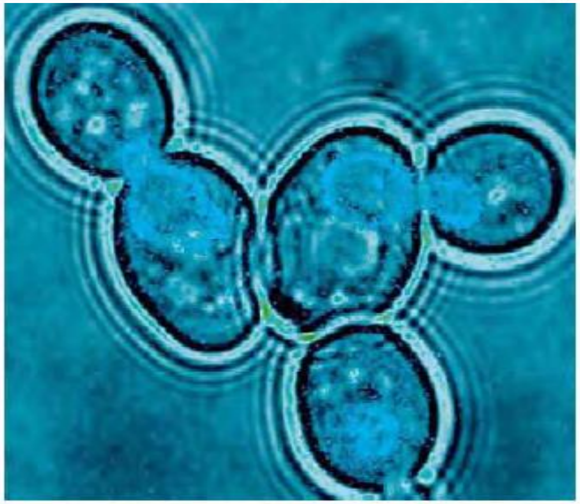
Technology to make inexpensive building blocks of defined carbon number has to be developed.

Lignin product development is important..

Technology development will have more impact than pre-identification of products with both fundamental and applied research needed!

World Production and World Market Prices for Important Microbial Fermentation Products.

	World Production (ton/year)	World market price (€/kg)
Bioethanol	38000000	0.40
L-Glutamic acid	1500000	1.50
Citric acid	1500000	0.80
L-Lysine	350000	2
Lactic acid	250000	2
Vitamin C	80000	8
Gluconic acid	50000	1.50
Antibiotics (bulk)	30000	150
Antibiotics (specialties)	5000	1500
Xanthan	20000	8
L-Hydroxyphenilalanine	10000	10
Vitamin B12	3	25000



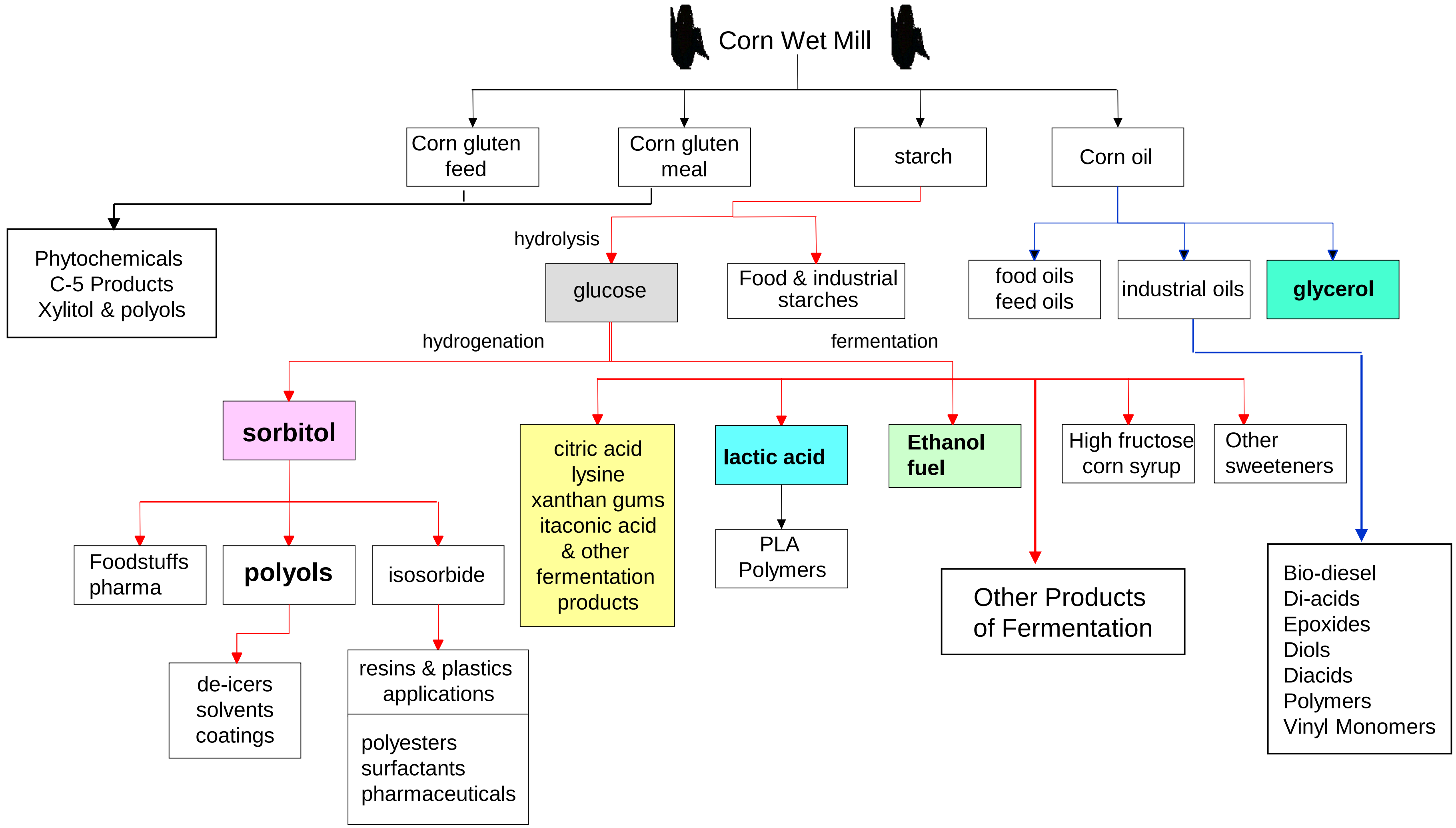
Source: W. Soetaert, E. Vandamme, Biotechnol. J. (2007)

White Biotechnology – Products Available in Ton-Scale.

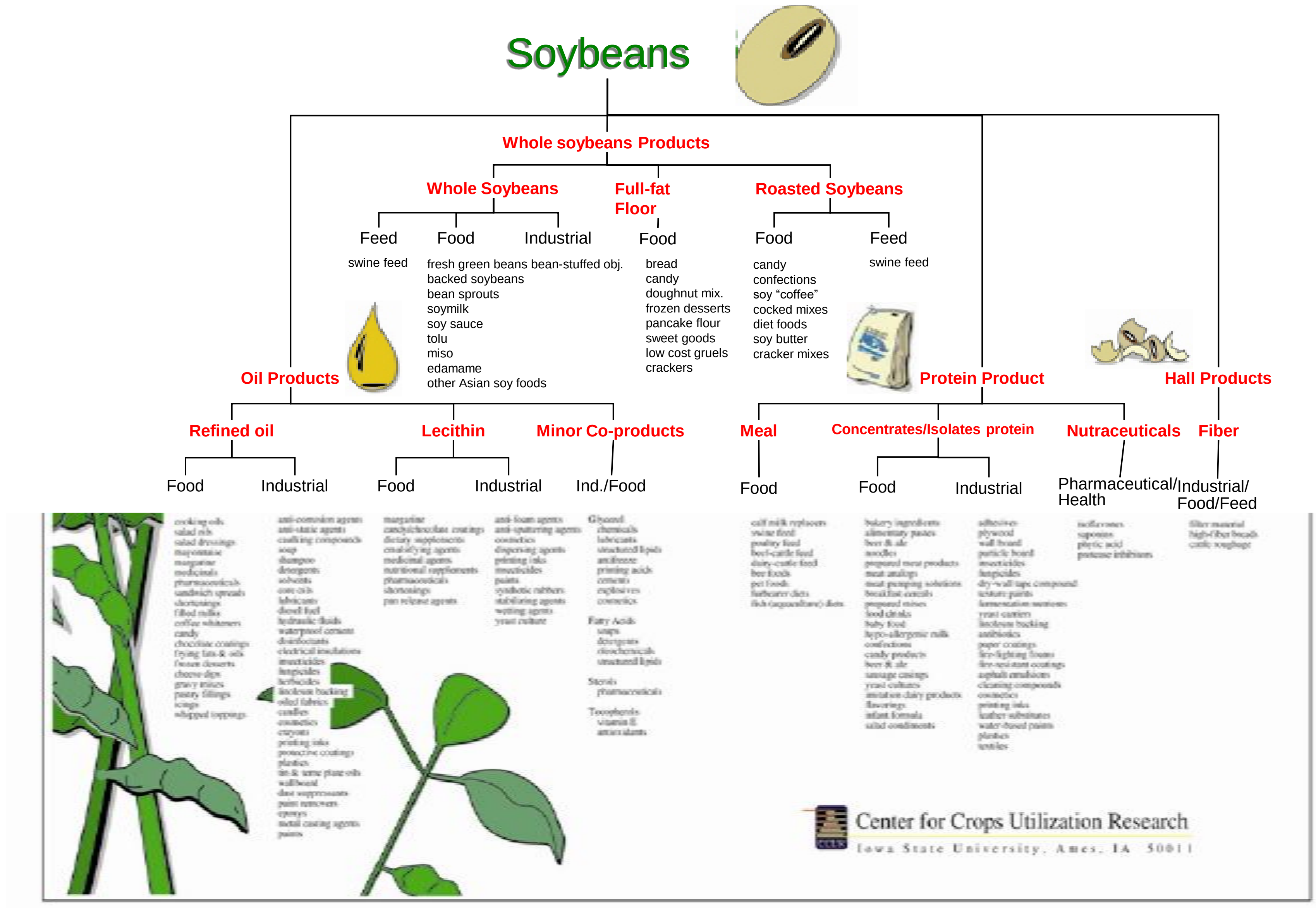
Product	Production (t/a)	Uses
Acids		
Citric	1.000.000	Food, cleaning
Acetic	190.000	Food
Gluconic	100.000	Food., Textiles, Metals
Itaconic	15.000	Plastic, paper, adhesives
L-lactic	100	Acidificant
Amino acids		
L-Glutamate	1.500.000	flavor enhancer
L-Lysine	700.000	feeding
L-Threonine	30.000	feeding
L-Aspartic Acid	13.000	Sweeteners Aspartame
L-Phenylalanine	10.000	Aspartame, pharma
L-Tryptophan	1.200	feeding
L-Arginine	1.000	Pharma, Cosmetics
L-Cysteine	500	Farma, food
L-Alanine	500	Infusion solution
L-Methionine	400	Infusion solution

Product	Production (t/a)	Uses
Antibiotics		
Penicillins	45.000	Pharma, Food
Cephalosporins	30.000	Pharma, Food
Tetracyclines	5.000	Pharma
Biopolymers		
Polylactic acid	140.000	Packaging
Xanthan	40.000	
Dextran (-deriv.)	2.600	
Vitamins		
Ascorbic acid	80.000	Pharma, additive
L-Sorbose	50.000	Pharma, additive
Vitamin A		Additive
Riboflavin (B_2)	30.000	Food
Carbohydrate		
Glucose	20.000.000	Substrate
Fructose syrup	8.000.000	Sweetener
cyclodextrins	5.000	Cosmetic, Pharma

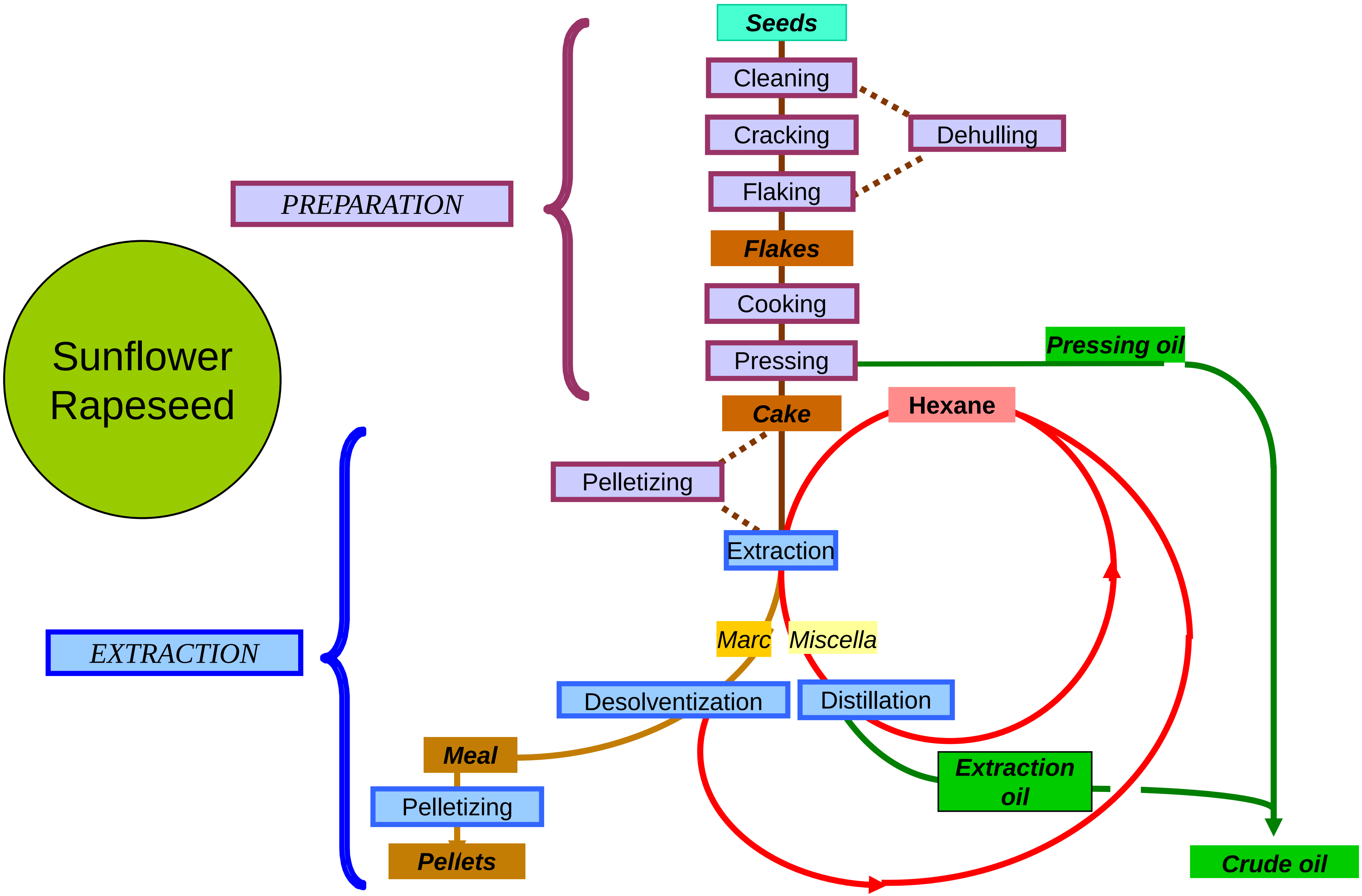
Example of Integrated Use of Corn.



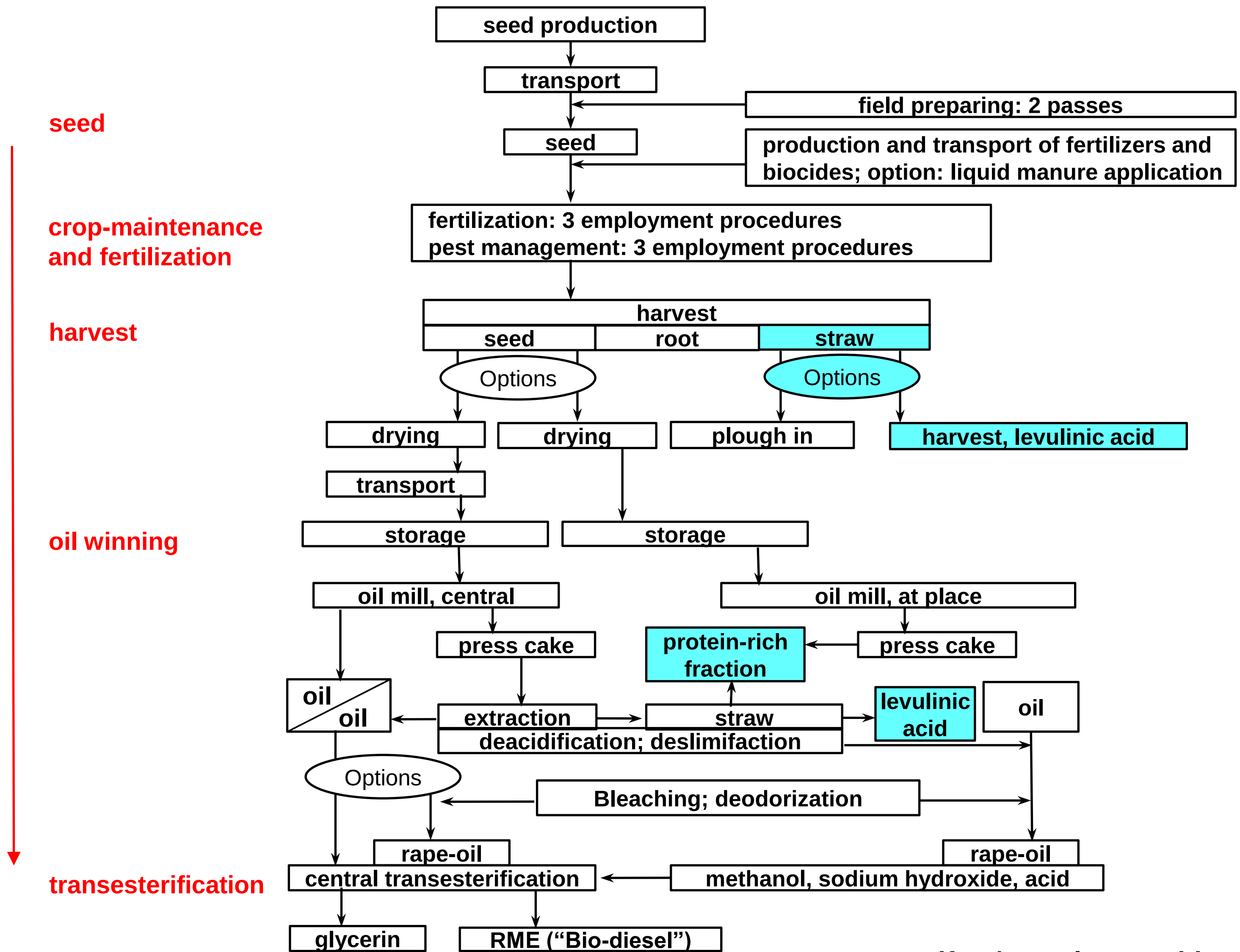
Example of Integrated Use of Soy.



Integrated Use of Sunflower, Rapeseed.



Fractionation of Whole Crop Oil Plant
Example: Rape Chain Flow Chart.



source: ifeu / supplement: biorefinery.de GmbH

Yields of Straw from Oil Crops.

Harvesting rape plant: 7 tons/ha

(2) Fractionation

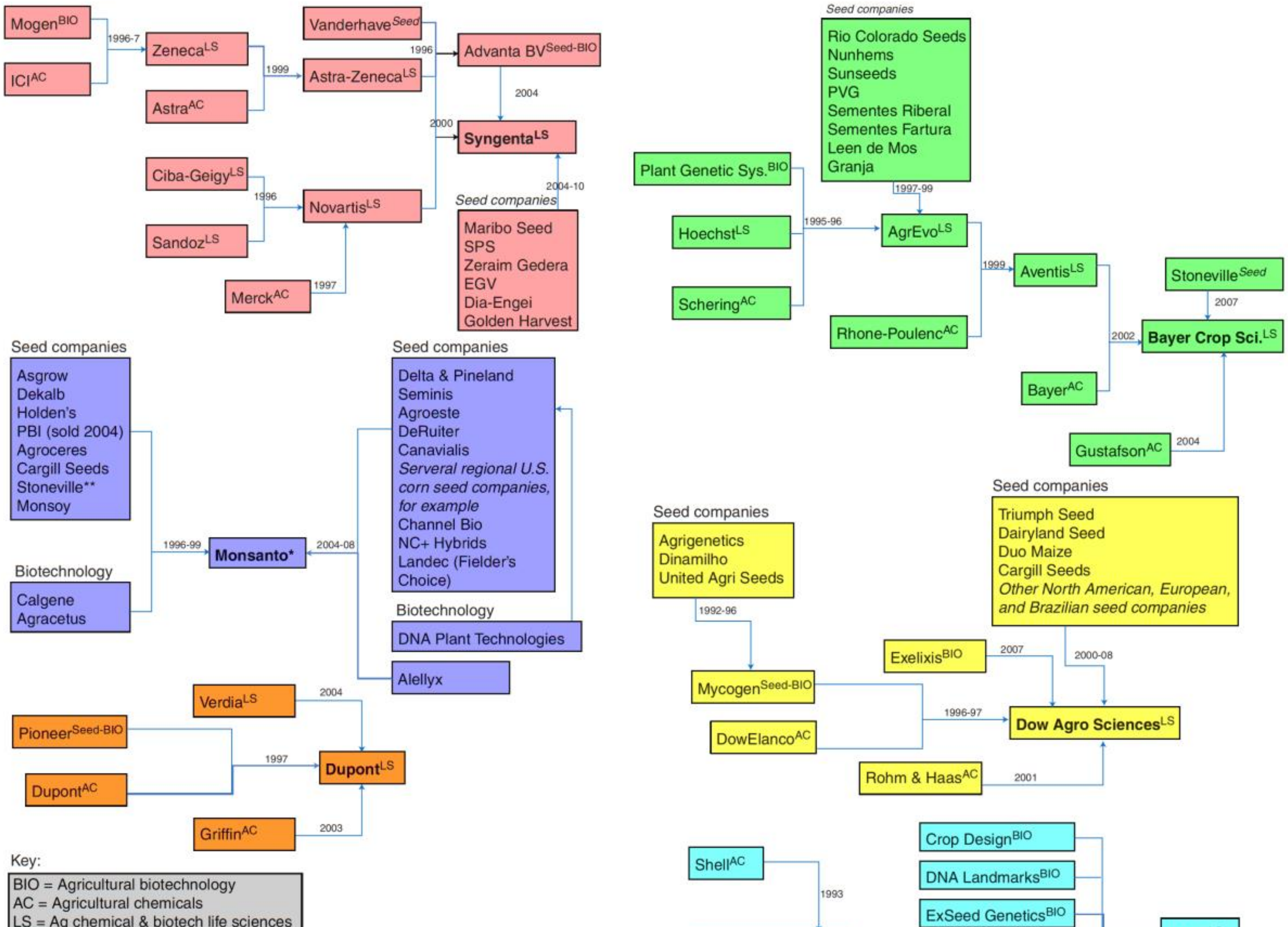
- **Seed: 3 tons/ha**
- **Straw: 4 tons/ha**

- **2 tons straw left in field**
- **2 tons straw go to processing**

(3) Press cake fractionation

- **Crude fibres from rapeseed:**
  - **10.3 % (on d.m.)**
- **Crude fibres from sunflower-seed:**
  - **17.3 % (on d.m.).**

Trend of 6 Main Industries in the Sector of Seeds Crops.



* The original Monsanto company was acquired by Pharmacia in 2000. In 2002, it was spun off as an independent "new" Monsanto.
Sources: USDA, Economic Research Service using Copping (2003), Fernandez-Cornejo (2004), Howard (2009), and company websites.

Interdisciplinary Aspects of BioEconomy.

Plant Science → **Production** → **Processing** →

Plant Science
- Genomics
- Proteomics
- Enzymes
- Metabolism
- Composition

Production
- Wood, trees
- Grasses
- Energy crops
- Agricultural Residues
- Animal wastes
- Municipal solid waste

Processing
- acid/enzymatic hydrolysis
- Fermentation
- Bioconversion
- Chemical conversion
- Gasification
- Combustion
- Co-firing
- Pulping

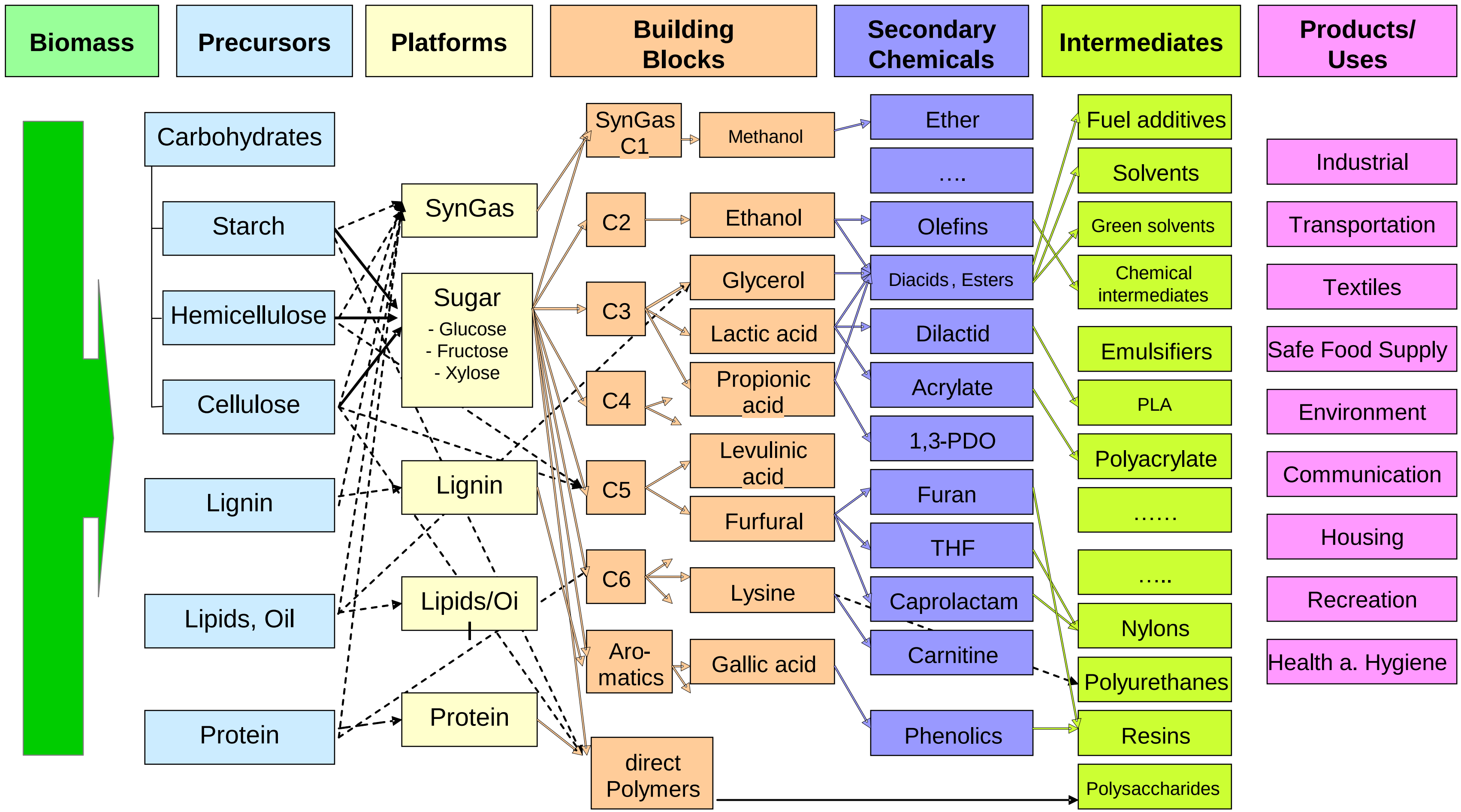
End-Uses

Products
- Plastics
- Functional Monomers
- Solvents
- Chemical Intermediates
- Phenolics
- Adhesives
- Hydraulic Fluids
- Fatty acids
- Carbon black
- Paints
- Dyes, Pigments, and Ink
- Detergents
- Pulp & paper products
- Horticultural products
- Fiber boards
- Solvents
- Adhesives
- Plastic filler
- Abrasives

Fuel

Power

Model for Production of Platform Chemicals.



Kamm, B.; Gruber, P.R.; Kamm, M.; Biorefineries, Industrial Processes and Products, Wiley-VCH, 2006

Acidolysis of Carbohydrates.

$$C_6H_{12}O_6 \xrightarrow{H^+} H_3C-C(=O)-CH_2-CH_2-COOH + HCOOH + H_2O$$

mp: 37°C, $Kp_{0.1}$: 95-96°C

sol. in H_2O, alcohol, ether

Yields of levulinic acid at T = 108°C in 20% HCl

Basic material	Carbohydrate/ acid ratio	t [h]	yield [%]
$C_6H_{12}O_6 \times H_2O$	1 : 2.5	5	46.7
glucose	1 : 10	5	62
potato starch (11.7% H_2O)	1 : 10	6-7	60.1
cellolignin (wood process.) cellulose-content 48.6%	1 : 10	8	60.3

Levulinic acid + ester
use: cosmetics industry, odoriferous substance, solvent, textile printing.

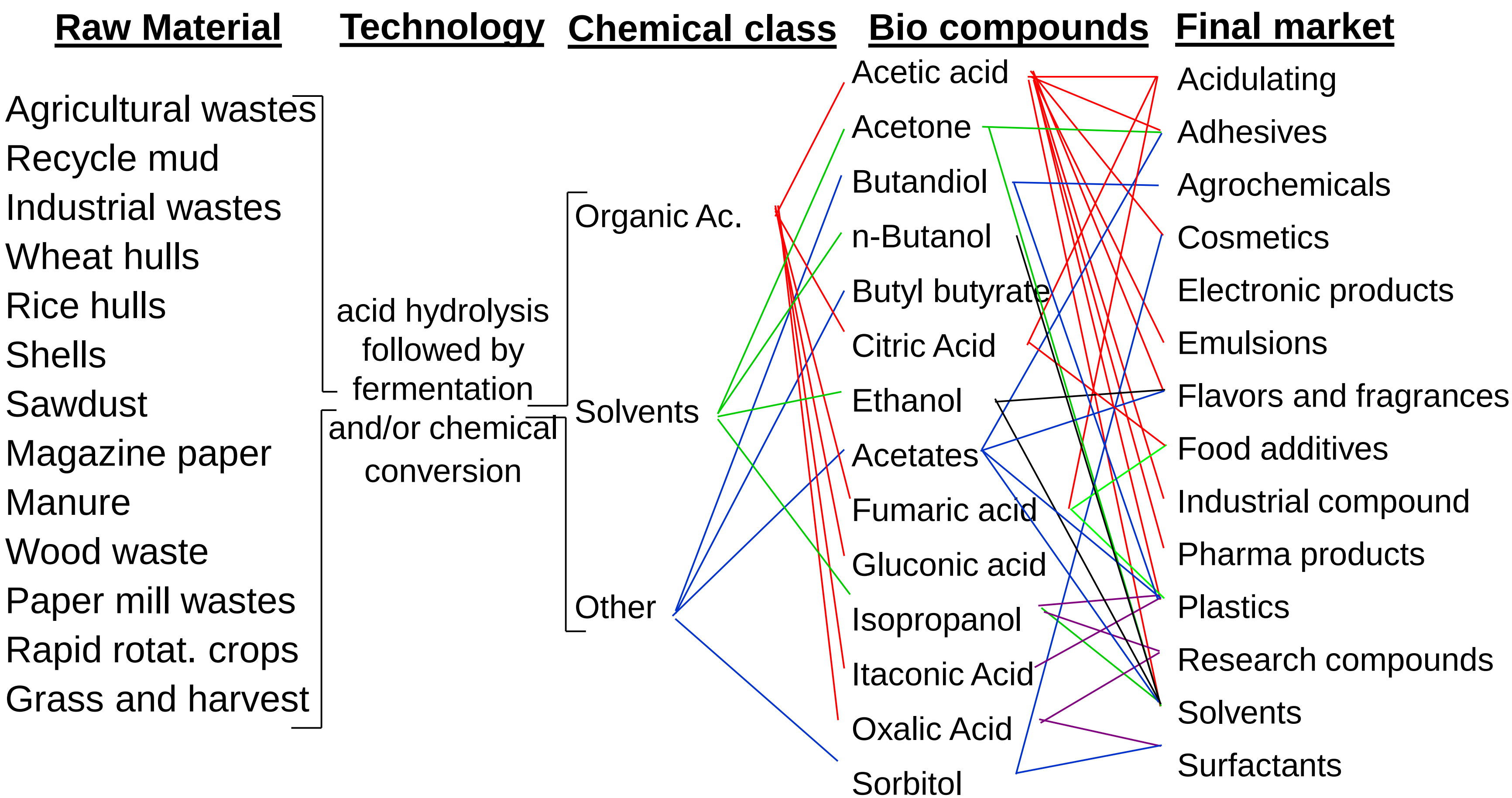
Chemical Conversion.

Hydrolysis (Chemical)

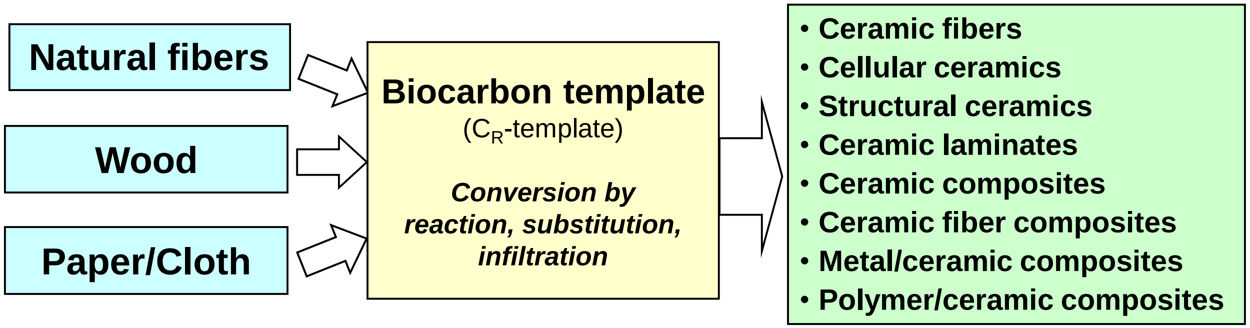
Fraction	Processes	Products
Hexoses	Fermentation	Alcohols (ethyl-, butyl, isopropyl-) Polyols (glycerol, ethylene glycol) Ketones (acetone) Acids (acetic, lactic, butyric) Yeast
	Dehydrogenation Hydrolysis Hydrogenation Crystallisation	Hydroxymethylfurfural Levulinic acid Polyols Glucose
Pentoses	Fermentation Dehydration Hydrogenation Crystallisation	Yeast Furfural Polyols (Xylitol) Xylose
Lignin	Hydrogenation Hydrolysis Oxidation	Phenol derivatives, hydrocarbons Phenol derivatives, catechols Vanillin

Molecular Specialties from Biomass.

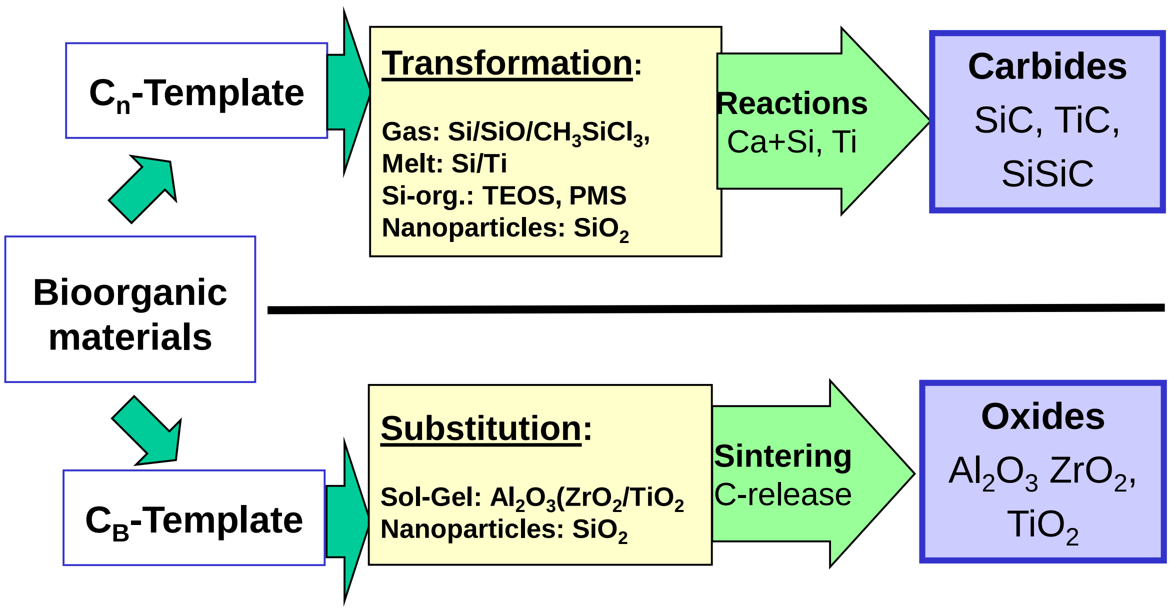
Relation between Biochemical Compounds and Market Interested Segment



Natural Polymers as Templates.

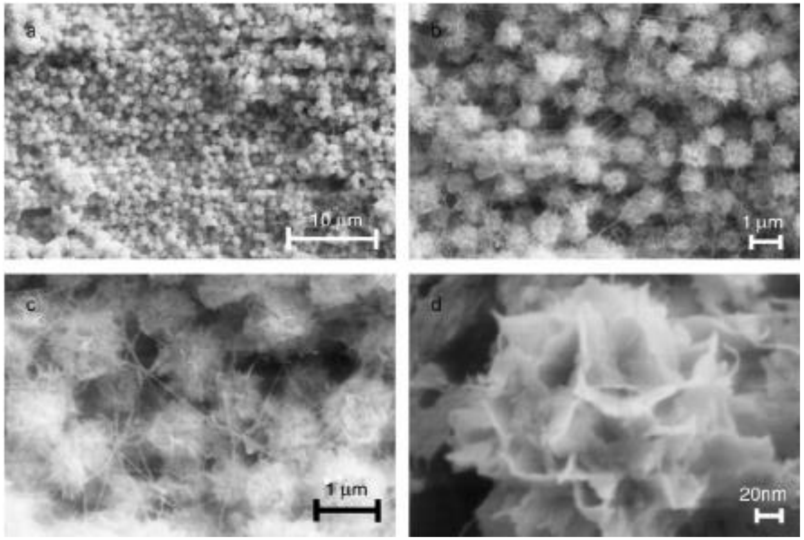


Conversion of bioorganic materials into structural ceramics and composites: materials

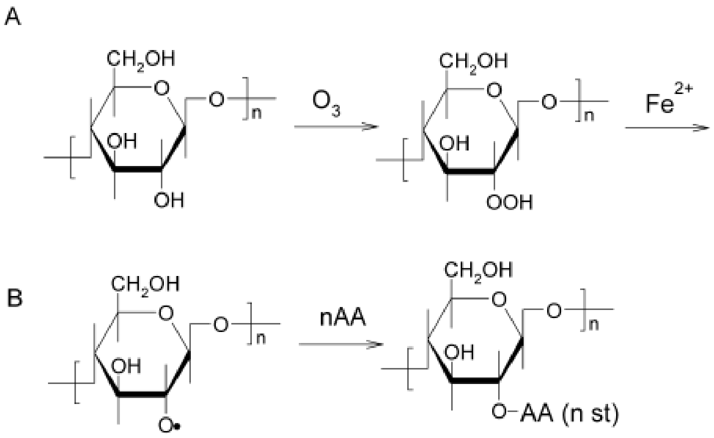


Conversion of bioorganic materials into structural ceramics and composites: processing

Cellulose/$CaCO_3$ Nanocomposites as Artificial Bone.



Biomaterials 06/27/4661

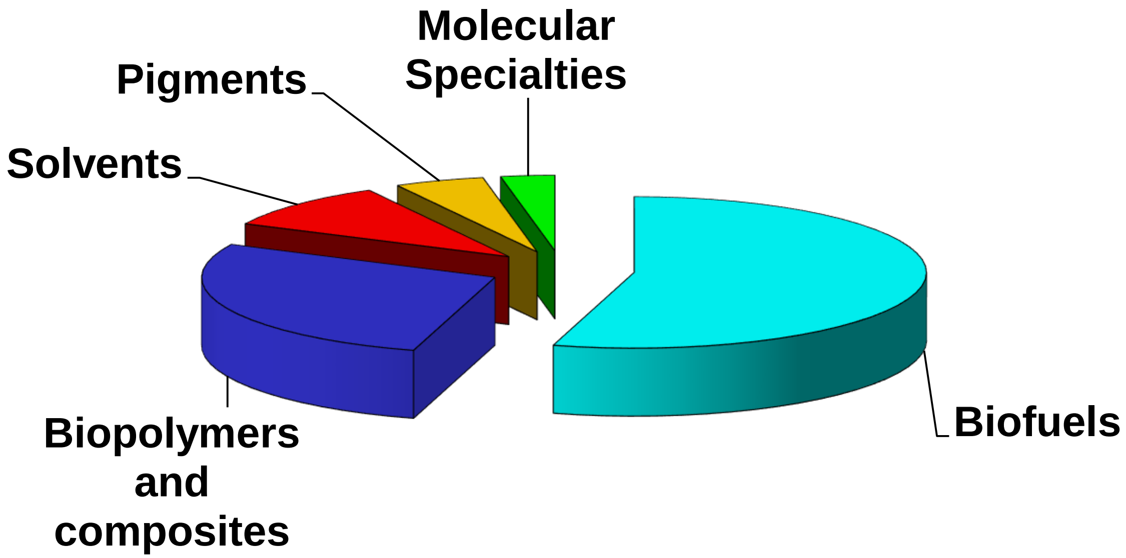


J. Biomater. Sci. Polym. Ed. 06/17/435

- Organized polymers can template $CaCO_3$
- Bacterial cellulose forms a fine, highly organized template
- Acid functionalization promotes biomineralization

Chemical Products from Biomass.

- oils and flavours
- antimicrobics
- specialty glicerides
- pharmaceutical products
- antioxidants
- crop protection
- solvents

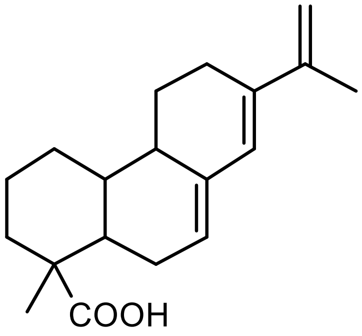


Essential Oils and Aromatic Molecules.

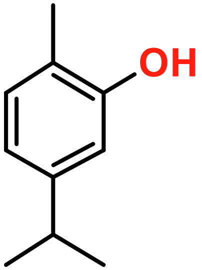
- Tenfold growth in Europe production since 1996
- Fully traceable production
- Wide range of products
- Industry is investing in agronomy, product extraction techniques and plant breeding
- Novel products available using CO_2 extraction.

Anti-microbial Plant Extracts and Molecules.

- Mostly terpenoids from aromatic plants.
- Currently being used in:
  - sugar beet and cane extraction - replaces formaldehyde and sulphites
  - brewing - replaces Nisin
  - food preservation - replaces hydroxybenzoates
  - oral care products - replaces Triclosan
  - animal feedstuffs - replaces antibiotics
  - Biofouling.



abietic acid
(*Pine* extracts)



carvacrol
(*Origanum* extracts)

Specialty Glycerides (Fats and Oils).

- LCO_2 or SCO_2 extraction maximizes yield without solvent residues
- Lower peroxide values and free fatty acid levels are achieved
  - Triglycerides with essential fatty acids, i.e. γ-linolenic and stearidonic acids
- Significantly lower color and aroma
- Opportunity of sequential trans-esterification using biocatalysts
  - Triglycerides with labile esters used as intermediates for novel molecules
  - Oils for personal care products
- Residues can be used for further processing.

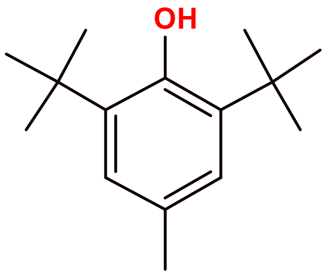
Anti-oxidants.

Synthetic materials such as BHT and BHA are still widely used.

Some natural antioxidants such as tocopherols and herb extracts already exist.

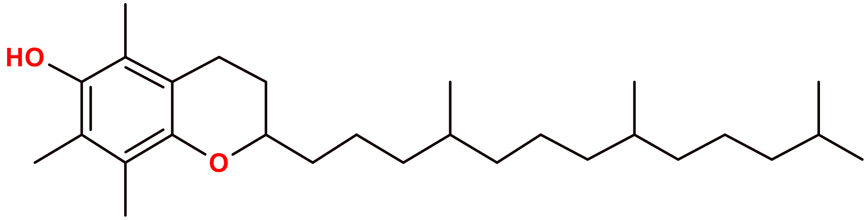
A combination of new crops and green extraction techniques can provide more effective natural extracts for lipid and aqueous systems:

- Purified hop extracts for lipid systems
  - essential oils (also prevents polymerisation of acyclic monoterpenes)
  - As effective as BHT and BHA
- Purified lemon balm extracts for aqueous systems (Effective at < 5 ppm)
  - Alcoholic and non-alcoholic beverages.



BHT

α-tocopherol



Crop Protection.

- Conventional plant pesticides rely on toxic mode of action; plant extracts work via non-toxic mechanisms.
- An integrated approach to pest control:
  - natural plant extracts
    - semiochemicals
    - anti-feedants
  - biological control
  - companion planting.

Crop Protection: Semiochemicals.

Peculiarity

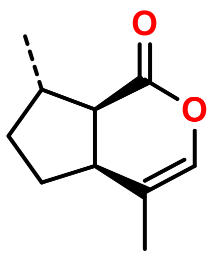
- "Signal" molecules (not pheromones)
- volatile, airborne molecules

Mode of action

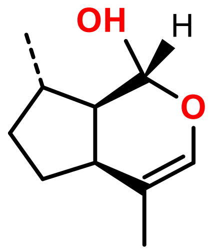
- Attract natural predators
- Mating disruption
- Attractants (lethal traps)

Very low concentrations needed

Released from designer polymers.



(4aS,7S,7aR)-nepetalacton (*cis,trans*)



(4aS,7S,7aR)-nepetalactol (*cis,trans*)

Crop Protection: Anti-feedants.

Activity

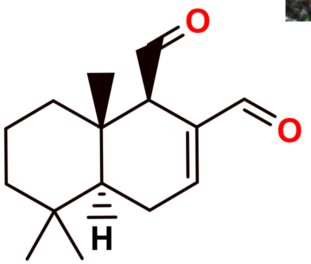
- Deter pests from settling on plants
- Reduce damage from arthropod crop pests
- Reduce transmission of viruses and pathogens

Insect species

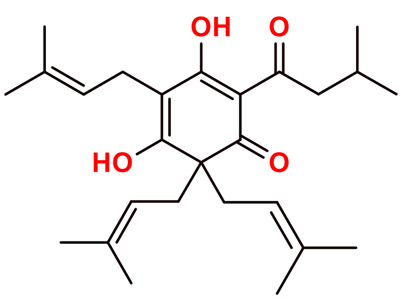
- Sucking pests (Aphids and whitefly)
- Leaf and root damaging pest (beetles and moth larvae)
- Virus / pathogen vectors (spider mites)

Plant extracts are sprayed onto crop.

Tasmania lanceolata

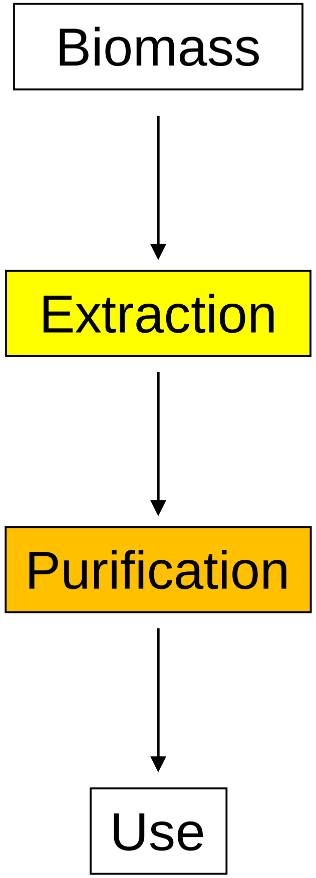


Humulus lupulus



Lupulone
Anti-microbial formulations

Simple Extraction of Materials.



Steam distillation:

- Reasonably cheap
- Simple apparatus
- Highly polar
- Simple separation

Solvent Extraction.

- Range of solvents
- Low temperature
- Isolation of highly volatile fragrances and oils
- Solvent recovery possible
- More expensive than steam distillation.

Supercritical Extraction.

- Clean technology
- Variable parameters
  - Temperature
  - Pressure
  - Polarity (mixed systems)
  - Particle size
- Current uses
  - Decaffeination of coffee
  - Dry cleaning
  - Extraction of hops
  - Essential oil extraction
  - Reaction solvent
  - Polymer processing
- Expensive.

Syngas Economy.

Syngas: mixture of carbon monoxide and hydrogen.

Current (fossil fuel) process:

$CH_4 + H_2O \rightleftarrows CO + 3\,H_2$

Nickel oxide catalyst, 300 °C, 30 atm

$CO + 2\,H_2 \rightleftarrows CH_3OH$

$CO_2 + 3\,H_2 \rightleftarrows CH_3OH + H_2O$

Cu and Zn catalyst,
300 °C, 100 atm.

Syngas from biomass:

- **Pyrolysis:**

  $C_6H_{10}O_5 \rightarrow 5\,CO + 5\,H_2 + C$

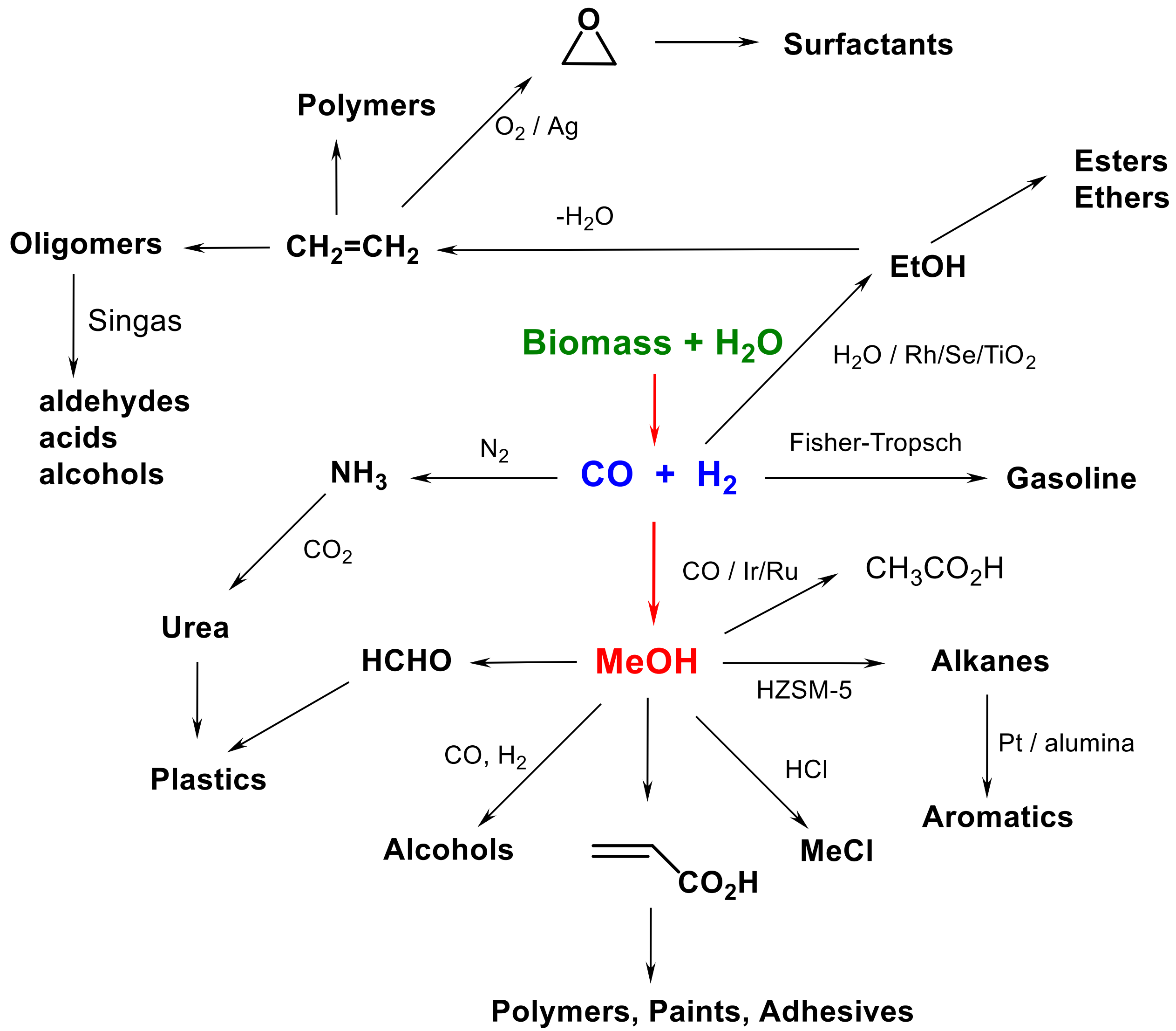
- **Partial oxidation:**

  $C_6H_{10}O_5 + O_2 \rightarrow 5\,CO + CO_2 + 5\,H_2$

- **Steam reforming:**

  $C_6H_{10}O_5 + H_2O \rightarrow 6\,CO + 6\,H_2$

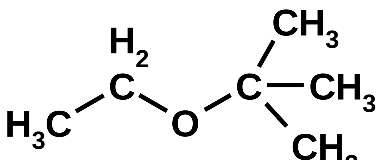
BioMethanol Economy (C-1).



Commodity Chemicals from Ethanol (C-2).

CH_3CH_2OH

→ $CH_3CH_2NH_2$ Ethylamine

→ 

ETBE

→ $CH_2{=}CH_2$ → CH_3CHO → CH_3CO_2H

$CH_2{=}CH_2$ →

- Ethyl benzene
- Ethyl bromide
- Ethyl chloride
- Ethylene chlorohydrin
- Ethylene diamine
- Ethylene dibromide
- Ethylene dichloride
- Ethylene glycol
- Ethyleneimine
- Ethylene oxide
- Diethyl ketone
- Diethylene glycol
- Glycol ethers, esters
- MEA, DEA, TEA
- Vinyl acetate
- Polymers, copolymers

CH_3CHO →

- Acetic acid
- Acetic anhydride
- Aldol products
- Butyl acetate
- Butyl alcohol
- Butyraldehyde
- Chloral
- Ethyleneimine
- Pyridines

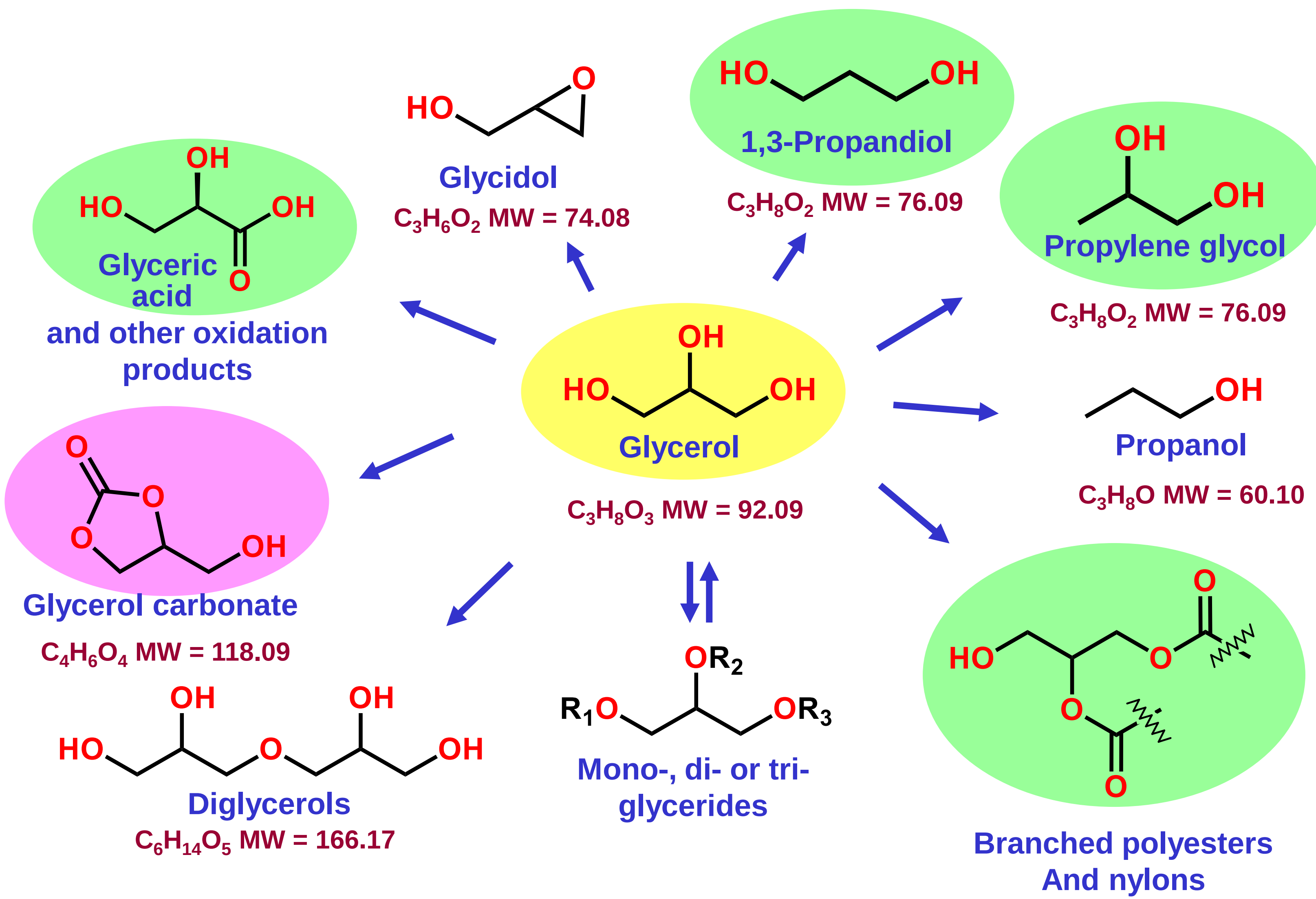
CH_3CO_2H →

- Acetamide
- Acetanilide
- Acetyl chloride
- Acetic anhydride
- Dimethyl acetamide
- Cellulose acetates
- Esters

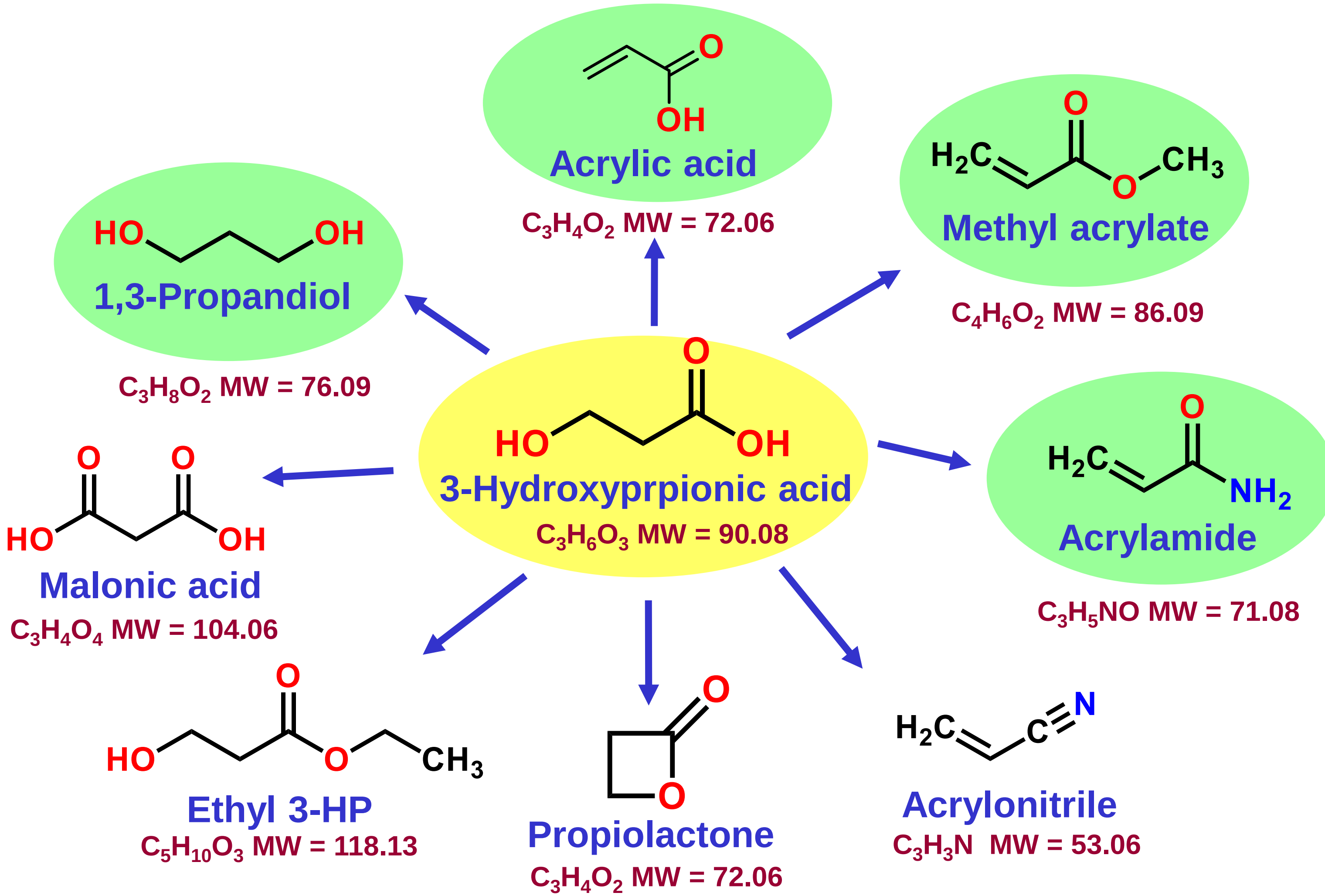
Commodity Chemicals from Ethanol.

Product	Production Capacity (10^9 kg/year)	Product	Production Capacity (10^9 kg/year)
Ethylene dichloride	1.011	Acrylonitrile	0.078
LD polyethylene	0.663	Ethyl acetate	0.060
Ethyl benzene	0.497	Ethylene glycol	0.030
Vinyl chloride	0.461	Acetic anhydride	0.026
HD polyethylene	0.397	Chloroacetic acid	0.024
Acetic acid	0.182	Diethanolamine	0.012
Ethylene oxide	0.163	Triethanolamine	0.012
Diethylene glycol	0.147	Chloromethane	0.007
Ethylene glycol	0.147	Pentaerithritol	0.007
Triethylene glycol	0.147	Chloral	0.004
Acetaldehyde	0.146	Acetylsalicyilic acid	0.003
Polyvinylacetate	0.143	Acetophenone	0.002
Ethylene	0.132	Ethyl ether	0.002
Monoethanolamine	0.122	Ethyl chloride	0.001
Vinyl acetate	0.080		

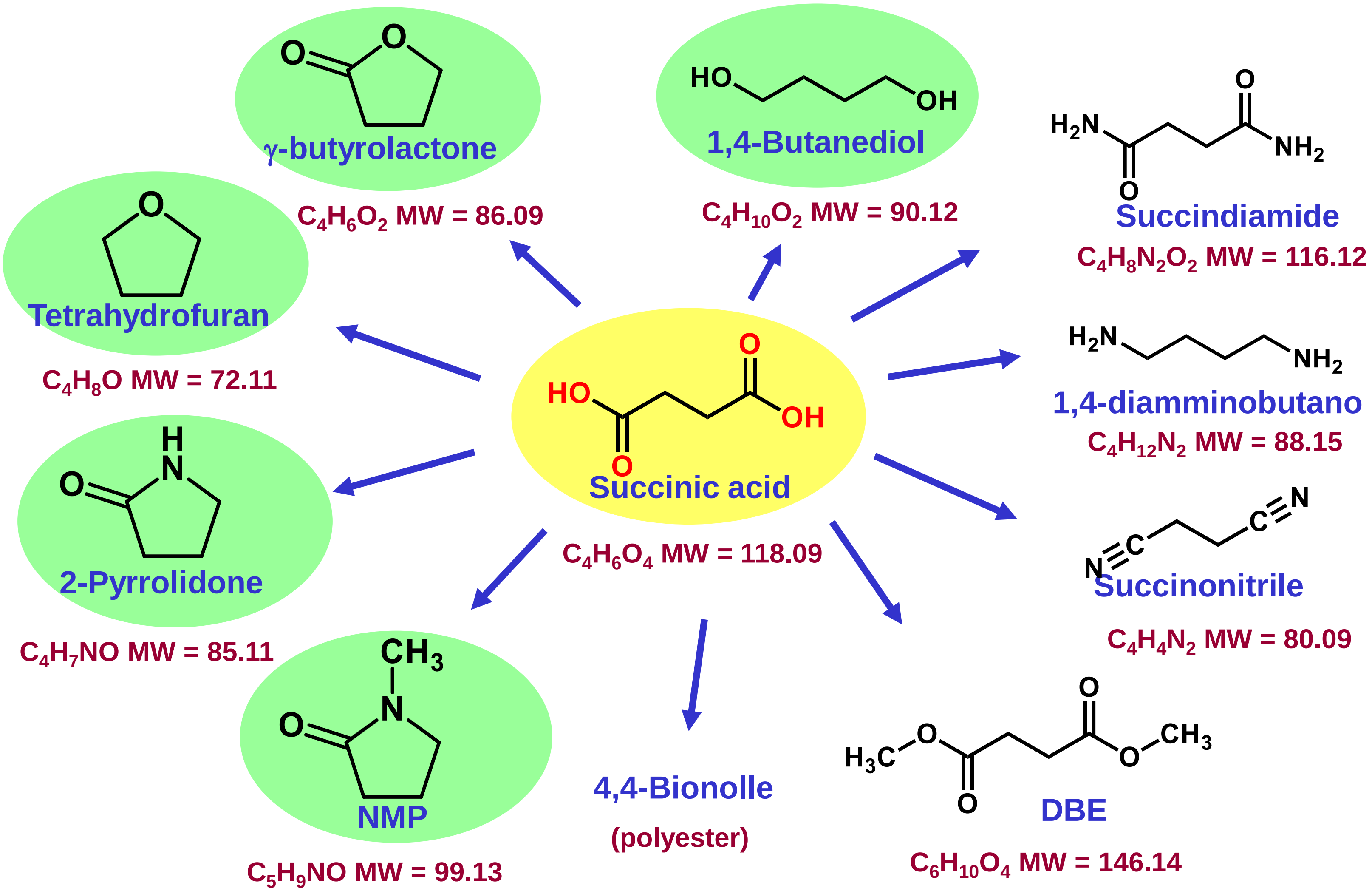
Glycerol (C-3) Derivatives.



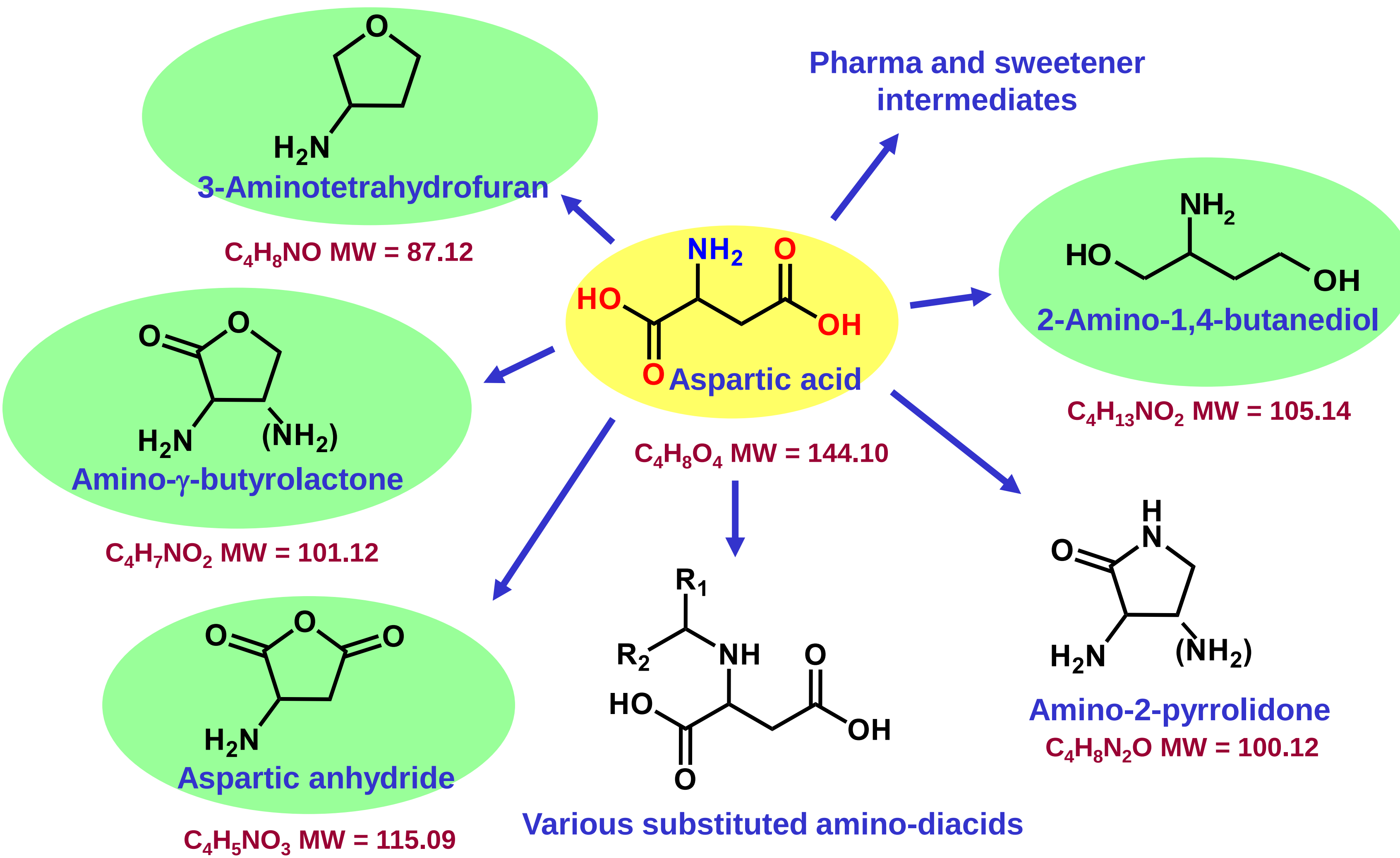
3-Hydroxypropionic Acid (C-3) Derivatives.



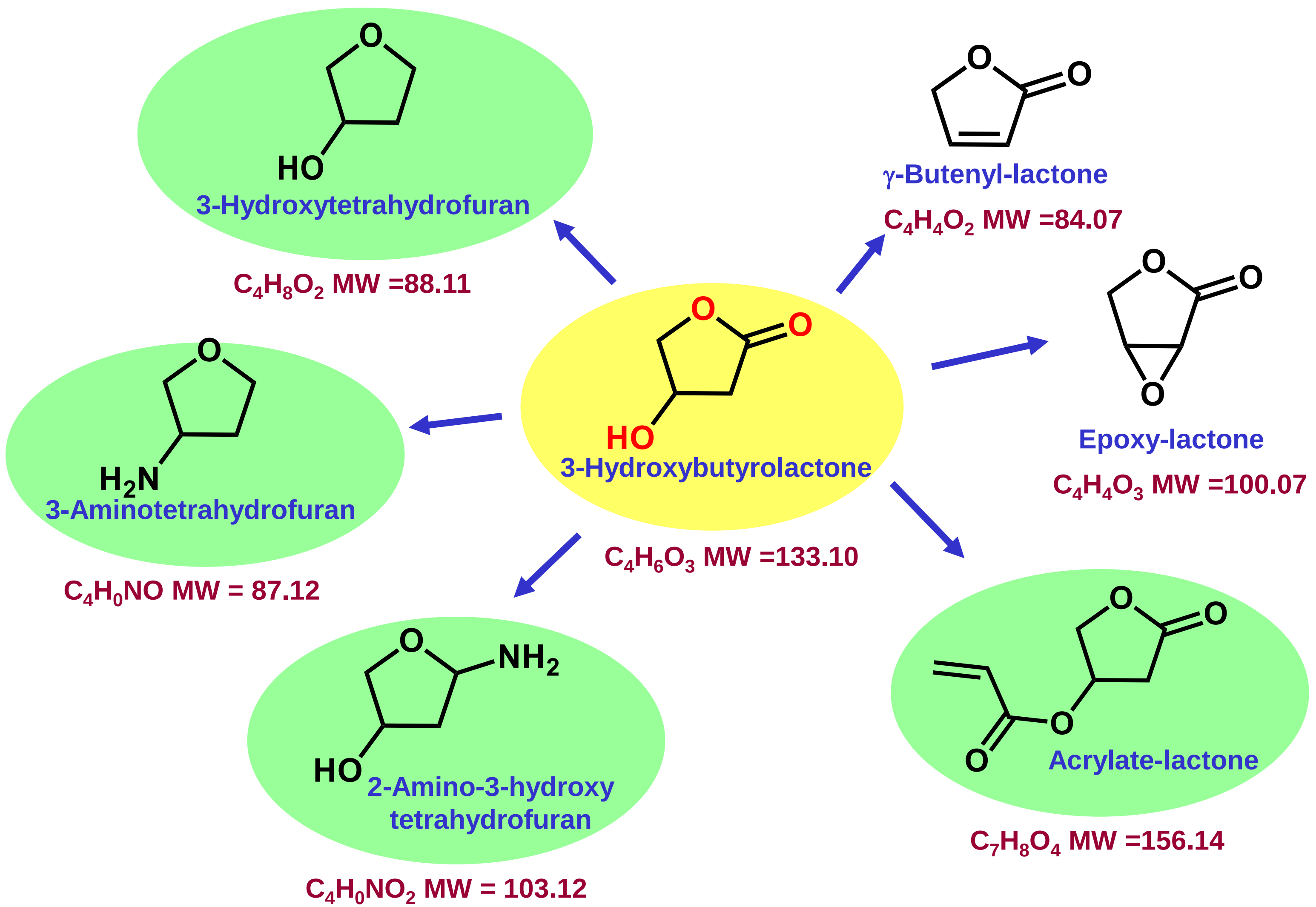
Succinic Acid (C-4) Derivatives.



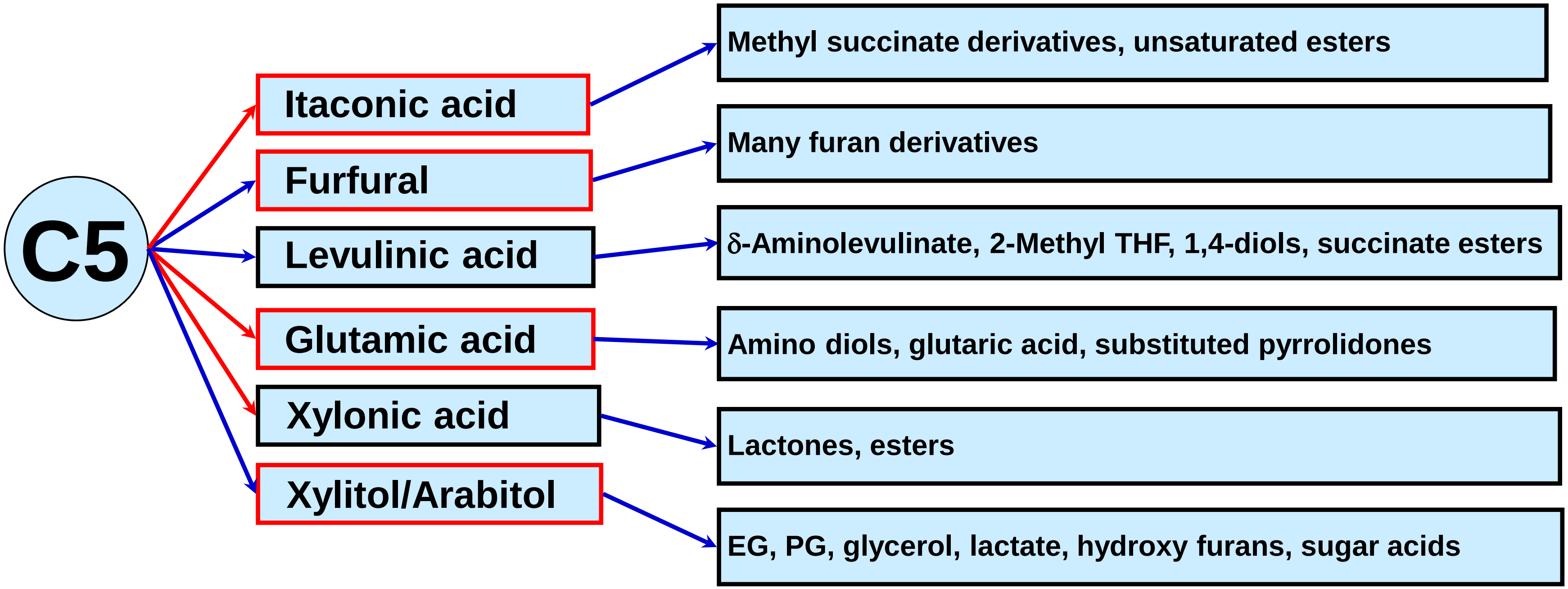
Aspartic Acid (C-4) Derivatives.



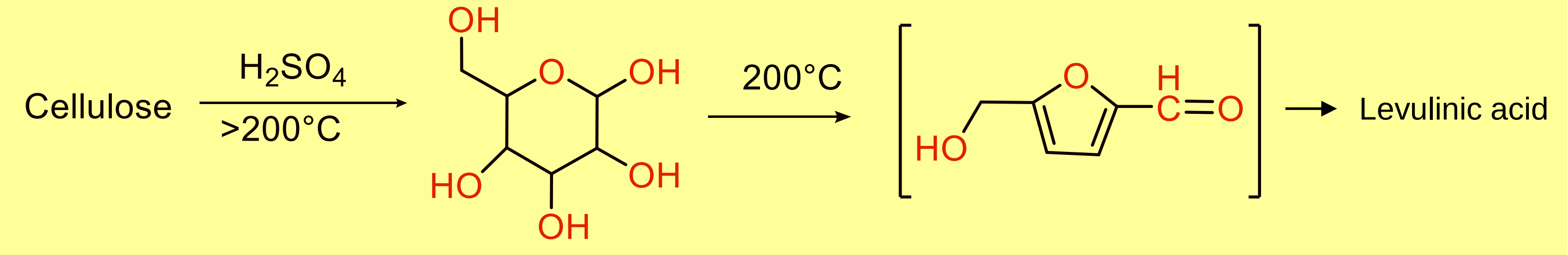
3-Hyroxybutirolactone (C-4) Derivatives.

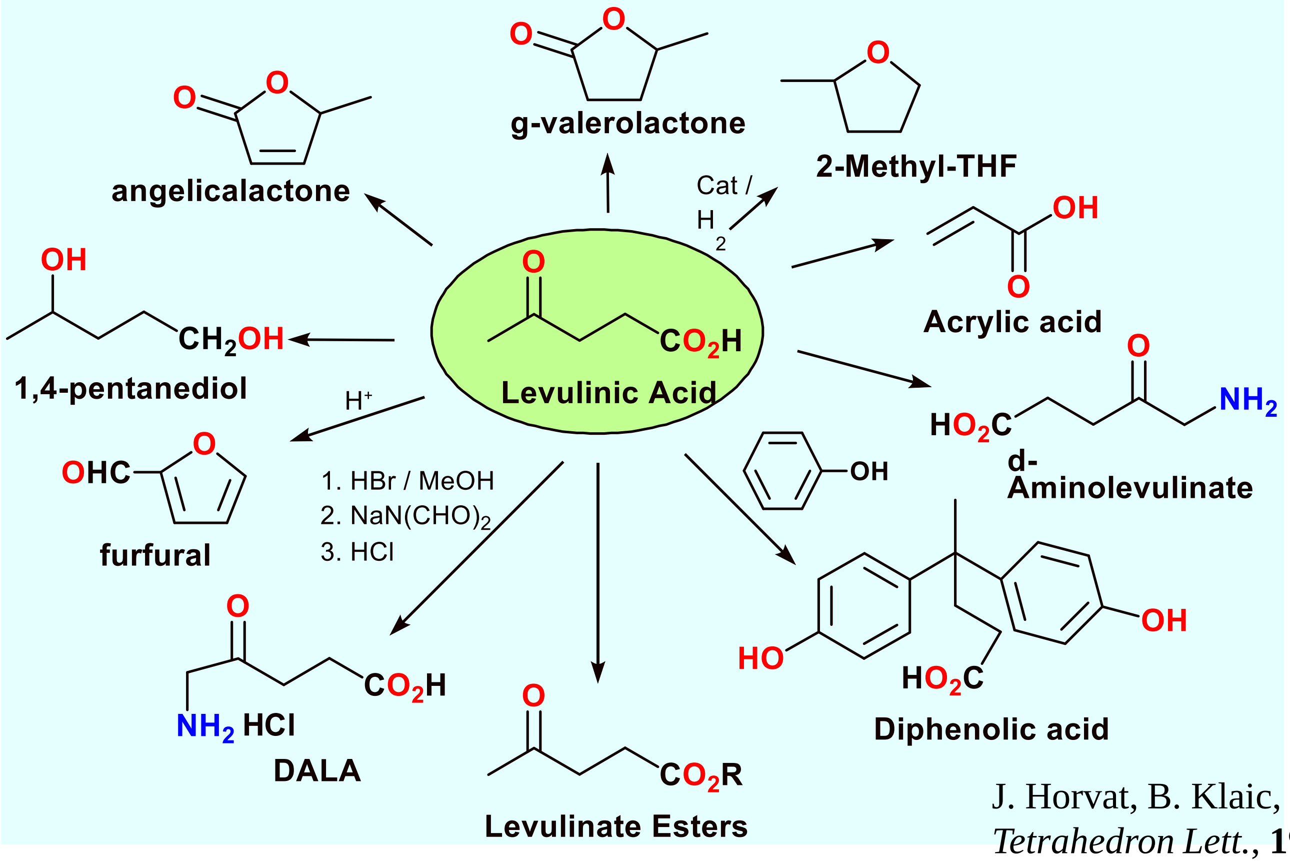


C5-Carbon Building Blocks.



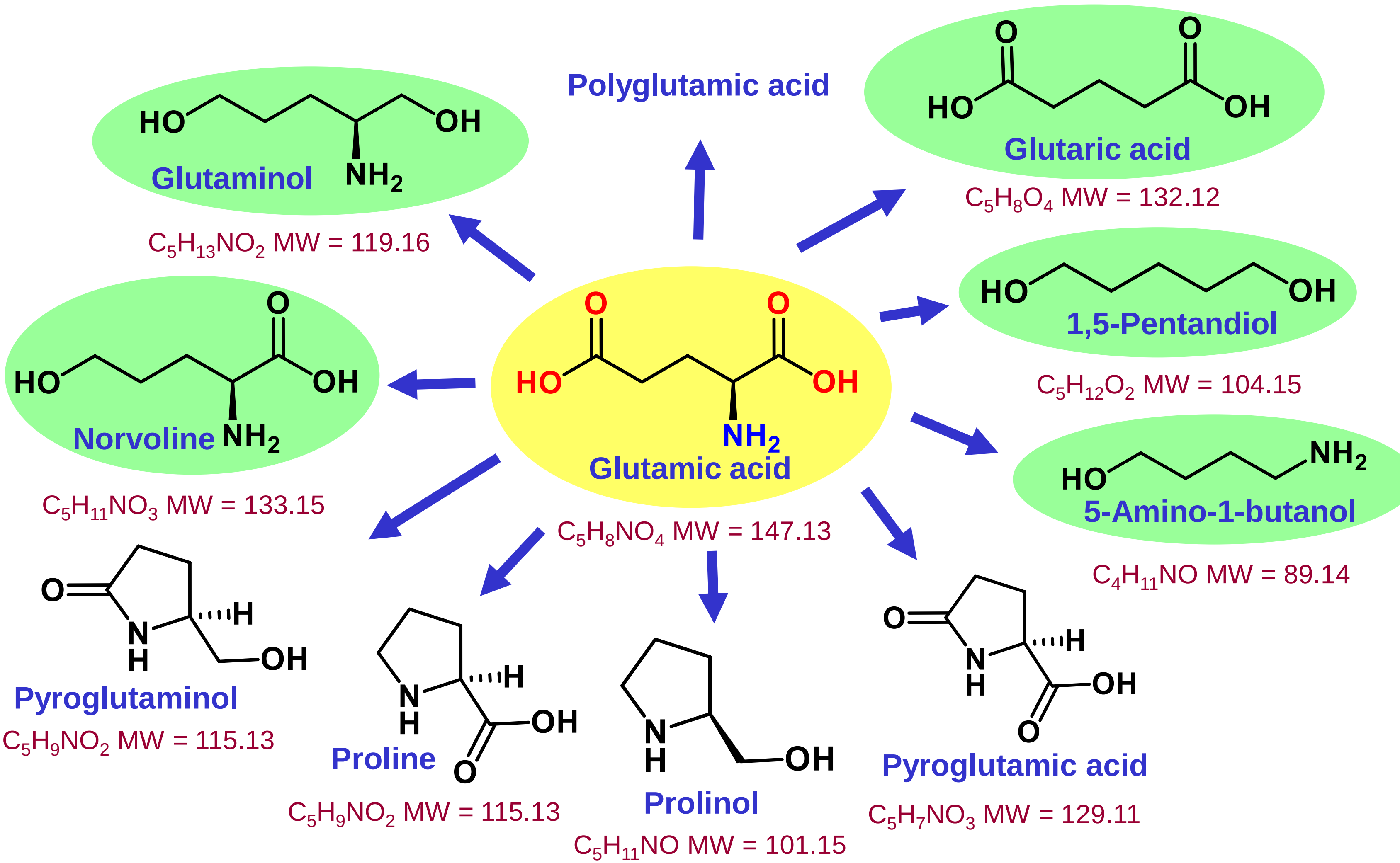
Levulinic Acid (C-5) Building Block.



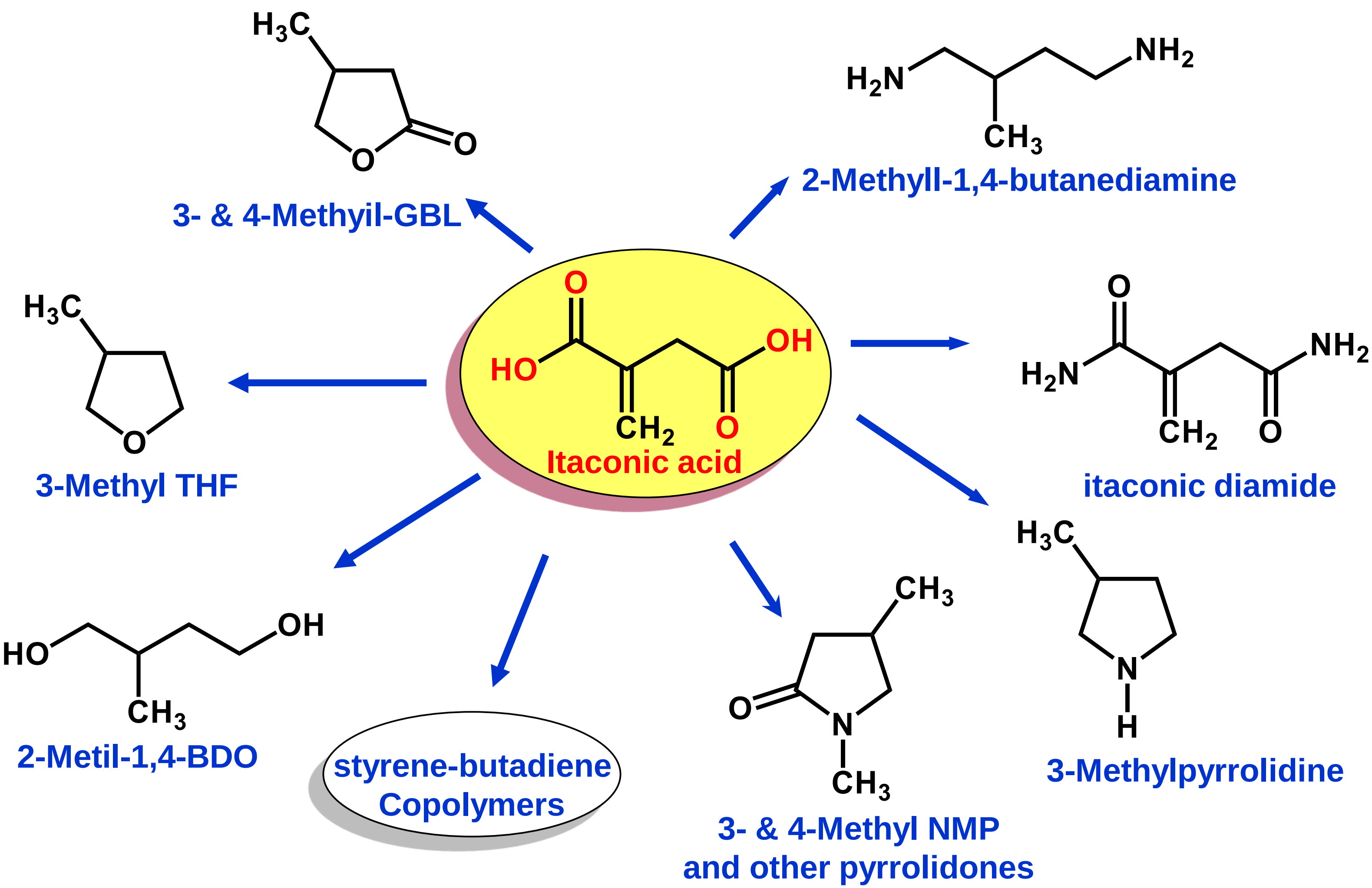


J. Horvat, B. Klaic, B. Metelko, V. Sunjic, *Tetrahedron Lett.*, **1985**, *26*, 2111

Glutamic Acid (C-5) Derivatives.

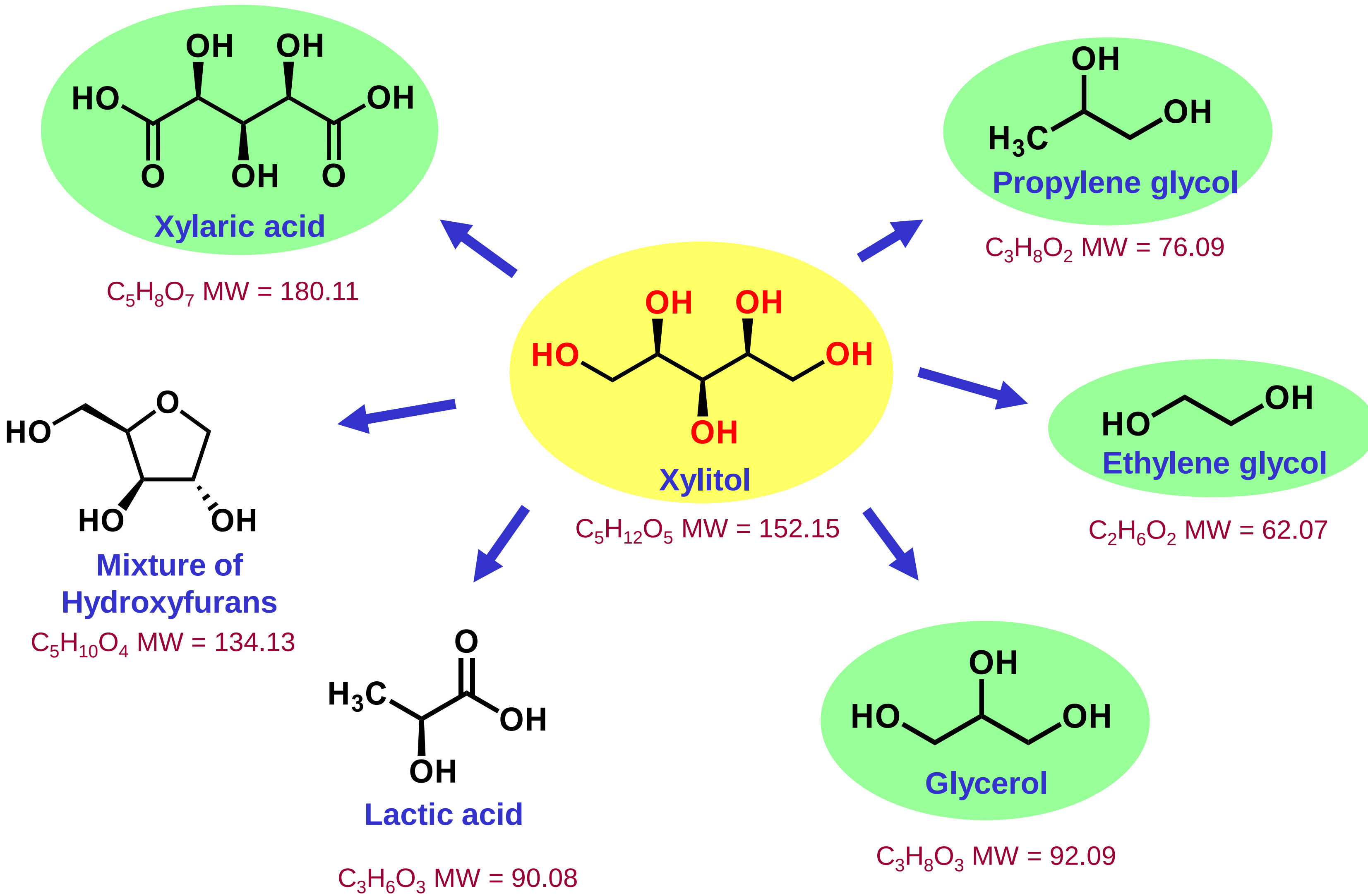


Itaconic Acid (C-5) Building Block.

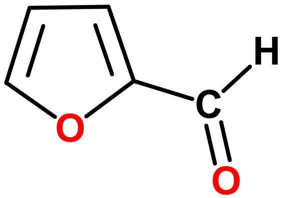


T. Werpy & G. Petersen, ed. 2004. Top Value Added Chemicals from Biomass. Vol. 1 Results of screening for Potential Candidates from sugars and synthesis gas.

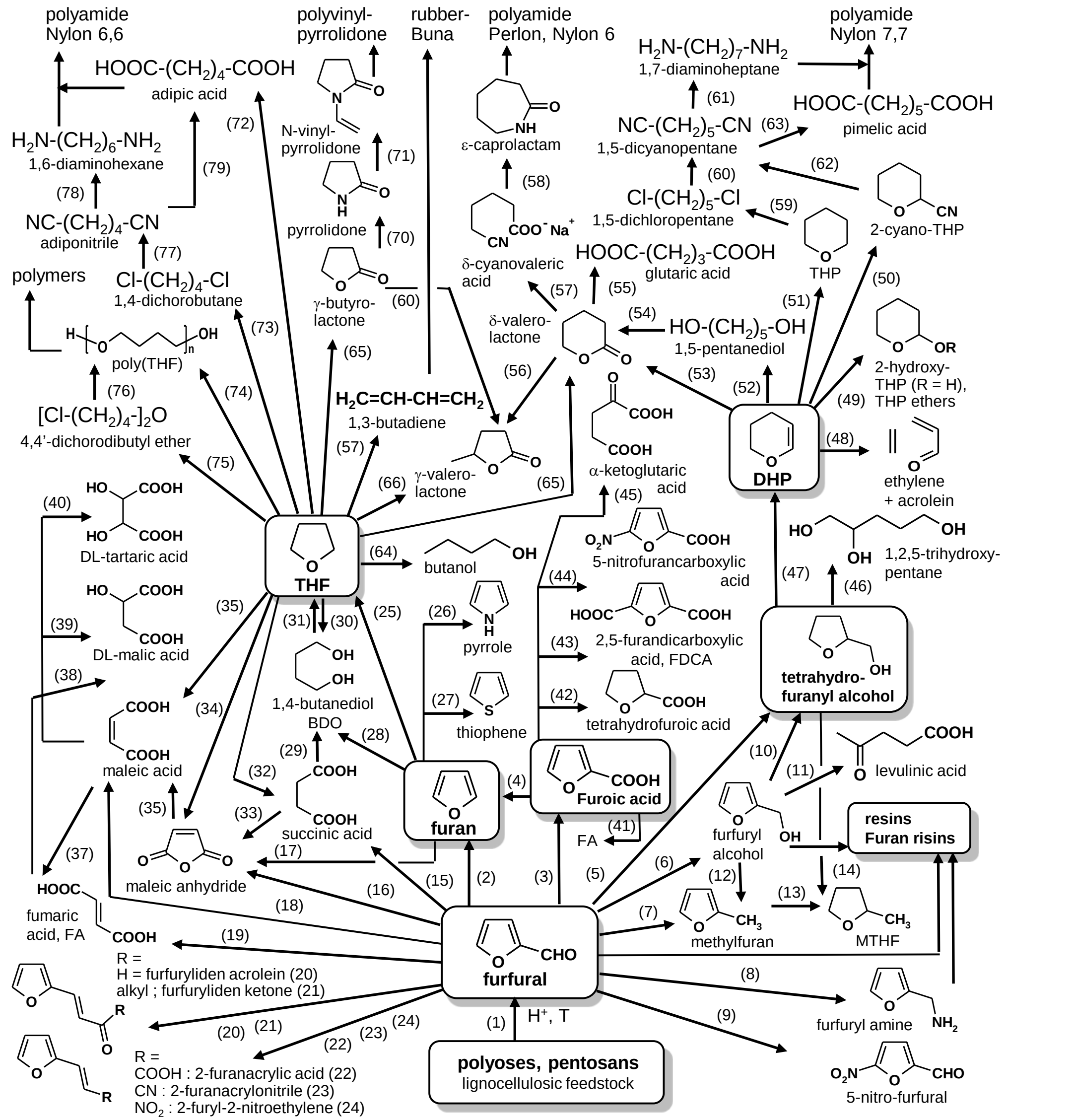
Chemistry to Derivatives of Xylitol (and Arabinitol) (C-5).



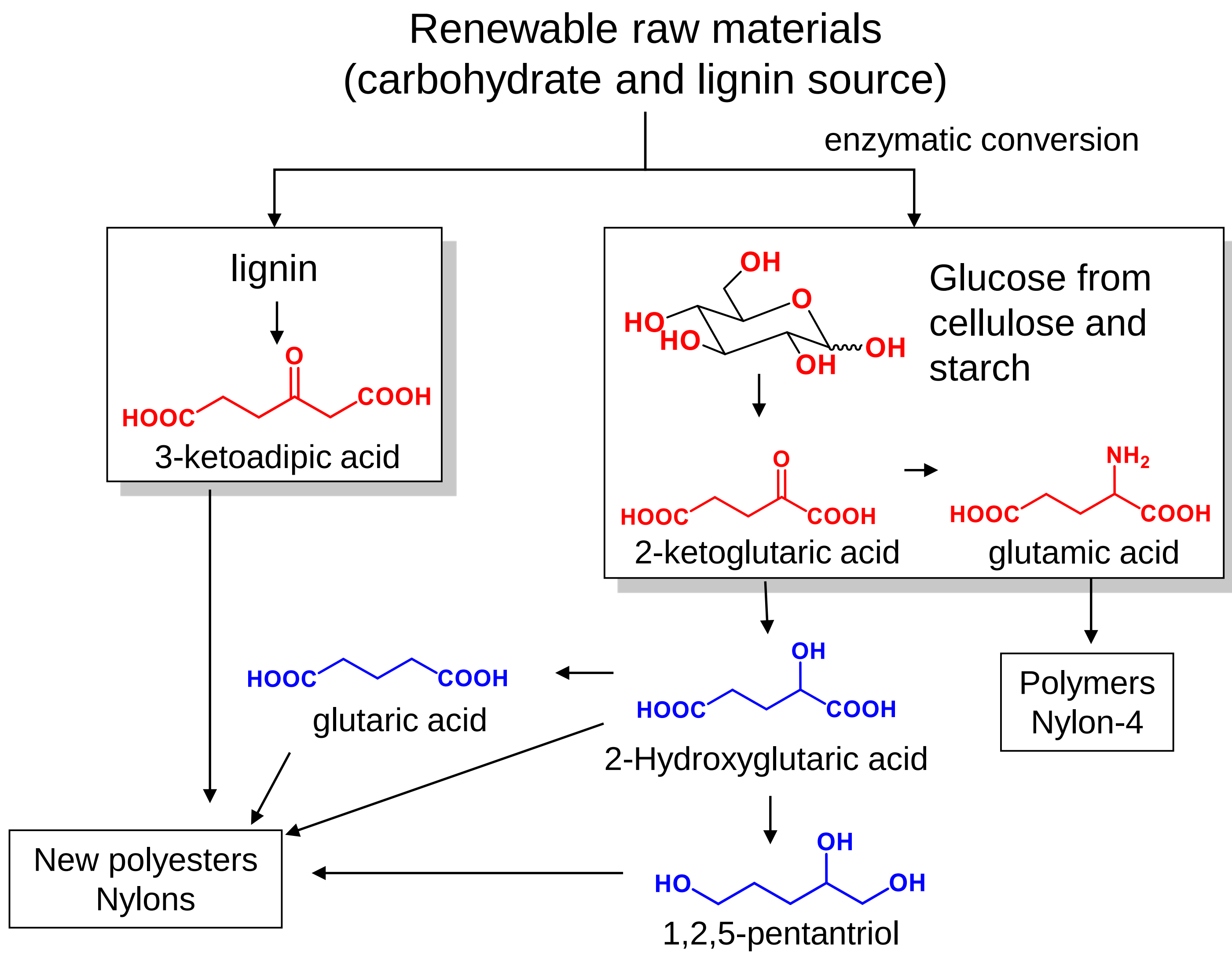
Potential Products from Furfural (C-5).



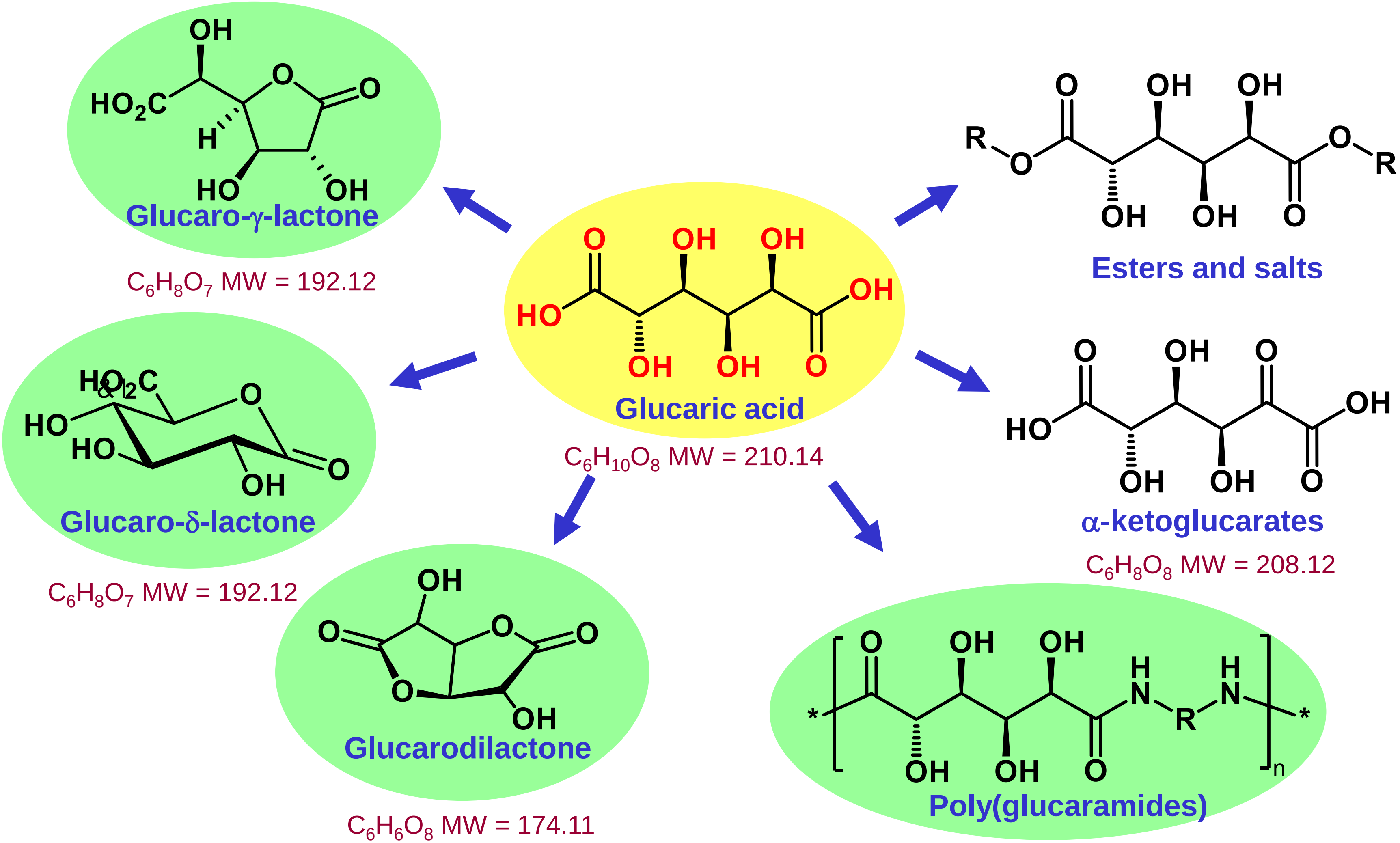
2-Furancarboxaldehyde



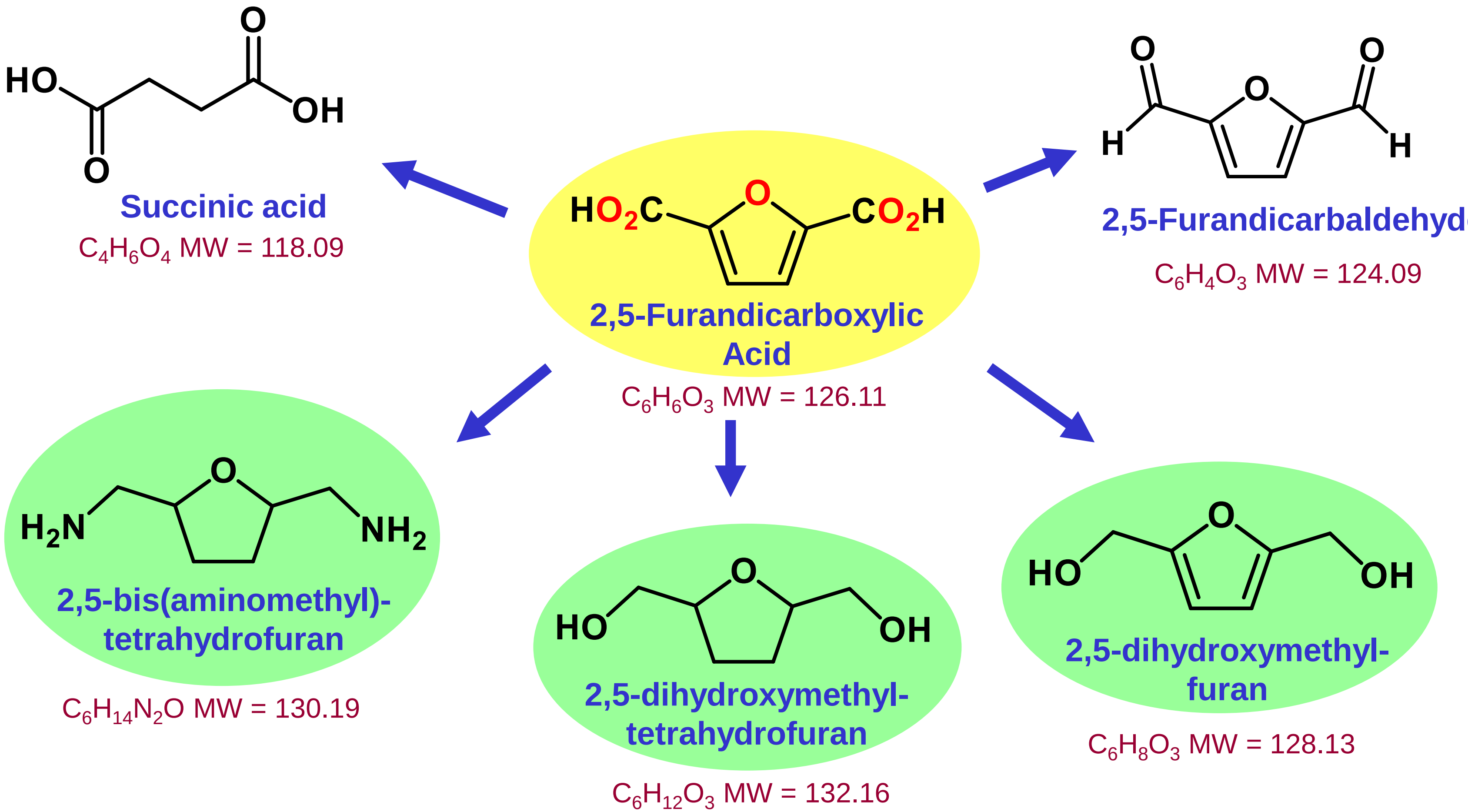
Other Uses of C-5/C-6 Units.



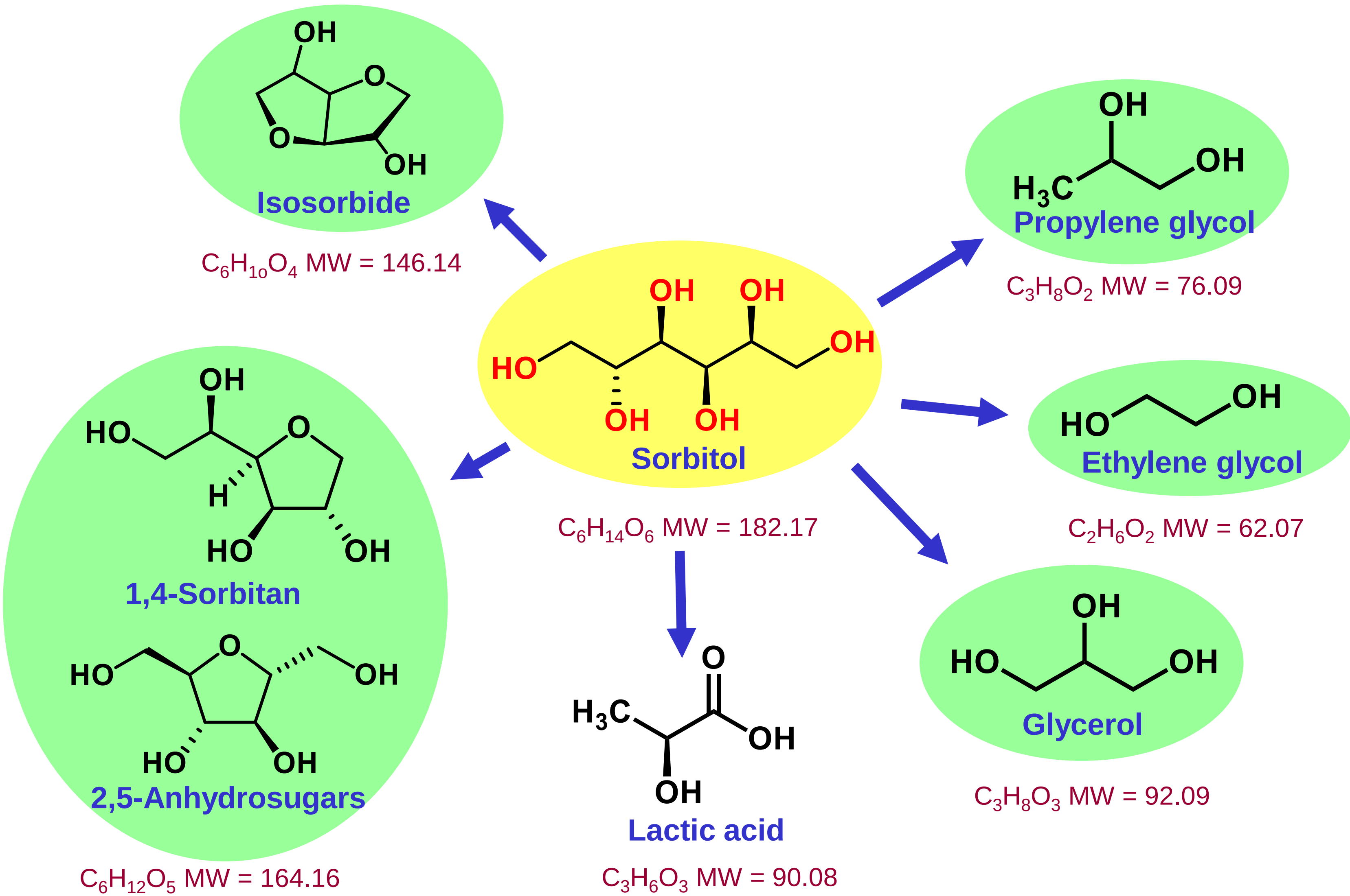
Glucaric Acid (C-6) Derivatives.



FCDA (C-6) Derivatives.

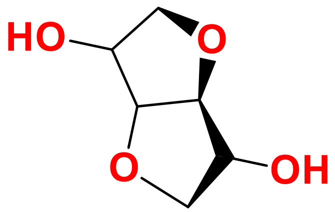


Sorbitol (C-6) Derivatives.



Isosorbide (C5).

Characteristics:



Isosorbide is a dianhydrosugar:

CAS No.:	652-67-5
Molecular formula: $C_6H_{10}O_4$ (Mw = 146.14 u)	
Appearance:	White crystalline powder, very hygroscopic
Melting point:	61-64°C
Boiling point:	160°C (10 *mm Hg*)
Solubility:	Soluble in water, alcohol, dioxane, ketones. Almost insoluble in hydrocarbons, esters, ethers
Other:	Very heat stable. Non-toxic, GRAS

current price: > $ 2.00.

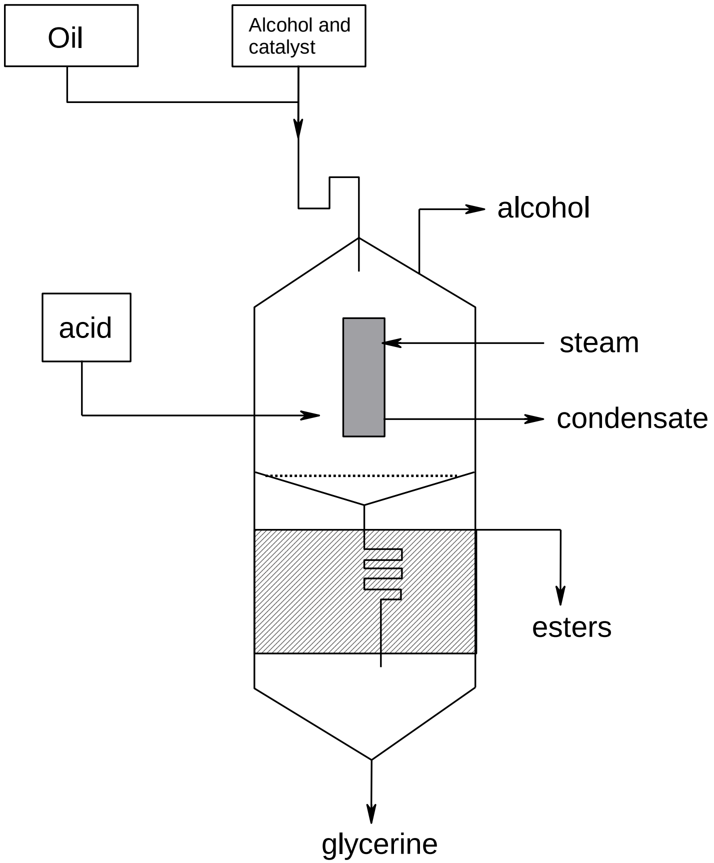
It is both non-toxic and biodegradable. It increases the use temp. of polymers.

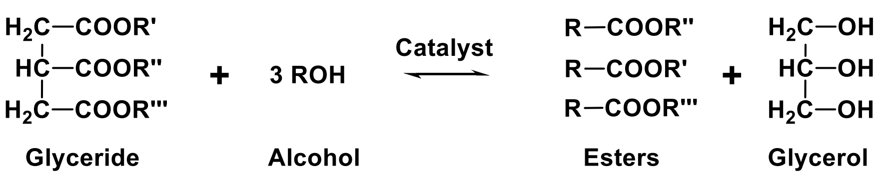
Largest current use is in the production of isosorbide di-nitrate, an angina medication.

Isosorbide Based Chemistries.

- Isosorbide is a potentially attractive building block for the polymer industry (at competitive pricing).
  - Bifunctional
  - Chiral, large, bulky and bent
  - Highly water soluble
  - Safe, renewable and green
- Isosorbide was developed as a polyester backbone modifier:
  - Raises T_g, lowers dX/dt in PET for next generation bottle resin (Hoechst, DuPont)
- Other potential applications include:
  - Thermosets (epoxies based on isosorbide diglycidyl ether)
  - Low molar mass additives (UV Stabilizers, Plasticizers, others)
  - New monomer for thermoplastics including:
    - Polyesters
    - Polycarbonates
    - Polyamides
    - Polyurethanes

- Short chain alcohol usually employed - methanol most common (NaOH soluble in MeOH)
- Catalyst used to improve yield (system loading 1 % w/w):
  - Basic catalyst most commonly used (e.g. sodium hydroxide) - lower ratio of glyceride to alcohol required (6:1). Supported guanidines have also been used successfully
  - Acidic catalyst can be used as well but higher ratio of glyceride to alcohol required (30:1) - however, system is water tolerant; wet substrate can be used
  - Enzyme catalysts have also been used - require lower reaction temperatures.



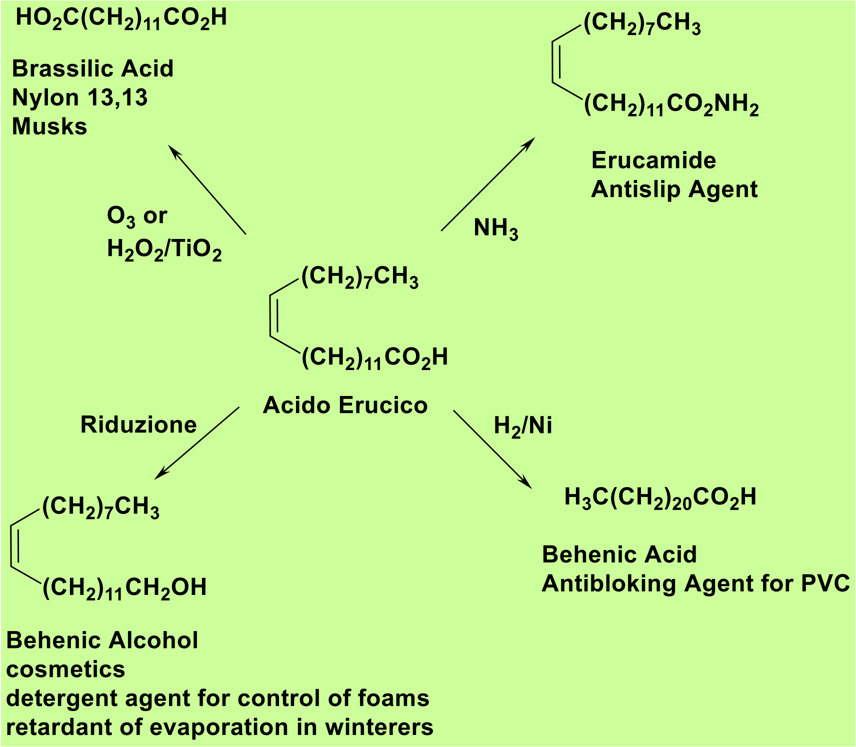


Fatty Acid Uses.

- The EU market for vegetable oils (2004) is split into four primary areas of usage:
  - Lubricants (2%)
  - Paints and surface coatings (8%)
  - Surfactants/soaps/various (31%)
  - Oleochemicals (59%).

- These figures are based on a non-fossil oil usage in the non-food sector of 2.5 – 3 million tonnes per year.

- Example shown is that Erucic acid isolated from rapeseed. It is also found in rocket lettuce.



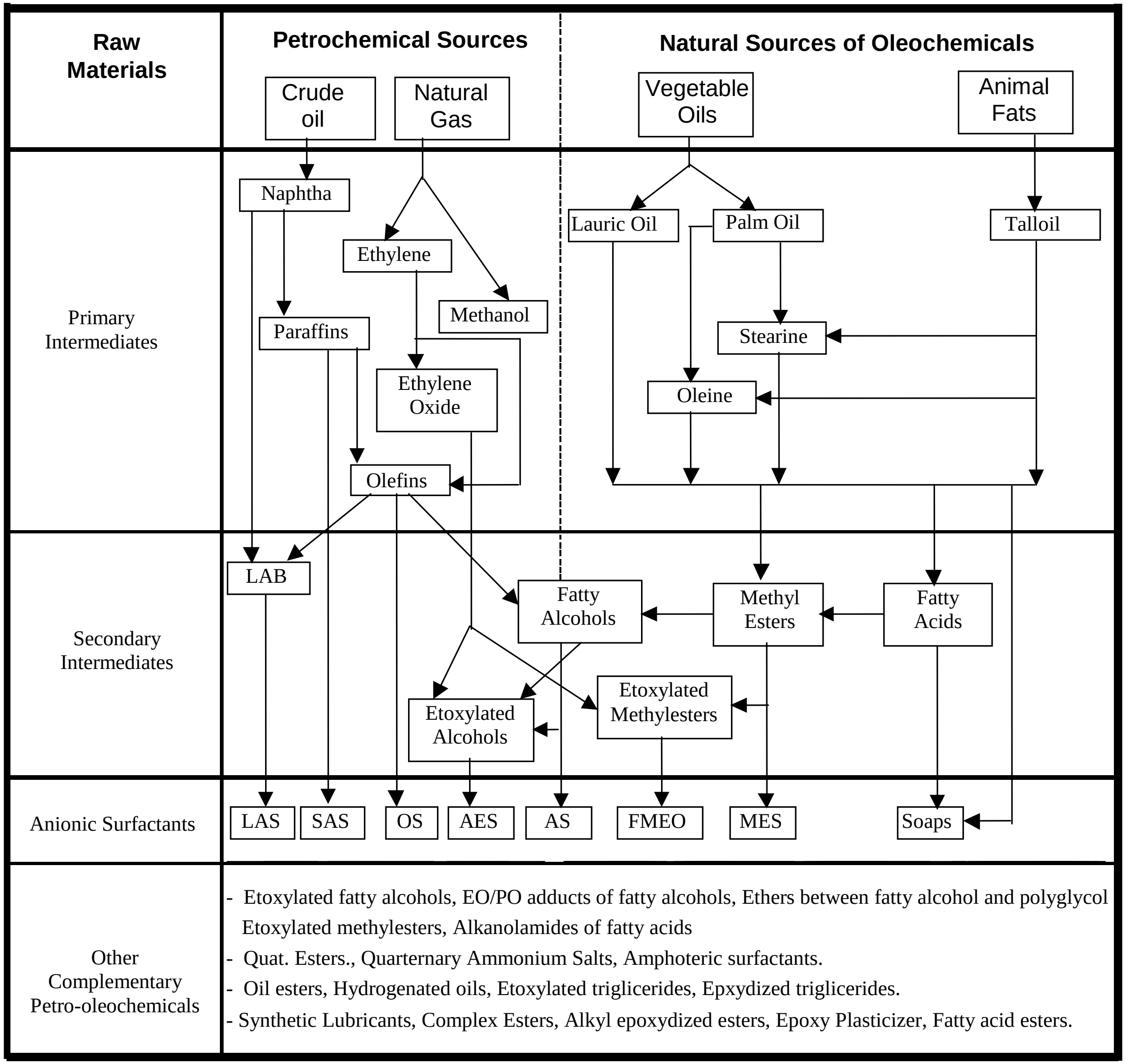
Sectors of Application for Technical Oleic Acid (> 65%).

Oleic Acid

- **Esters**
  - hydraulic systems
  - oils for cosmetics
  - lubricants
- **uns. Alcohols**
  - emulsifiers
  - defoamers
  - cosmetics
- **(Poly) Amides**
  - polymer additive
  - azelaic acid (monomer)
- **Soaps**
  - flotation
  - surfactant for cleaning agents
  - lubricants
  - polymer additive

Source: Cognis (adapted)

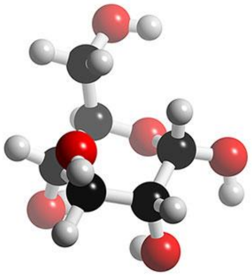
Fossil and Renewable Sources of Surfactants.

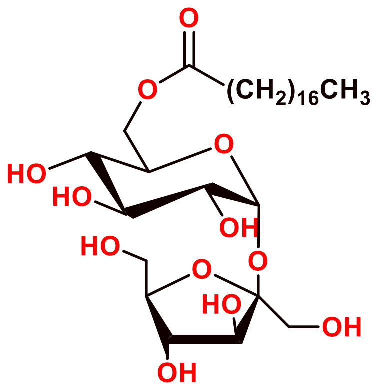


Alkyl Polyglucosides.

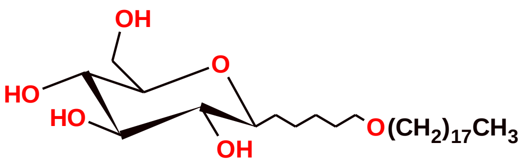
- Combining two natural resources these compounds are fully biodegradable and have excellent mild surfactant properties.
- Glucose unit is hydrophilic, fatty acid chain is hydrophobic.
- Uses are in cosmetics, textile finishing and industrial cleaning applications. The last two were developed due to the surfactant stability in alkaline solution.

Glucose

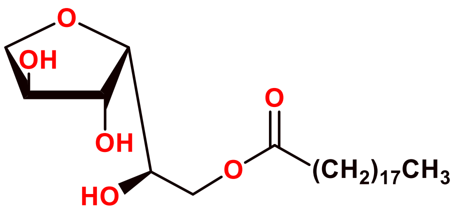




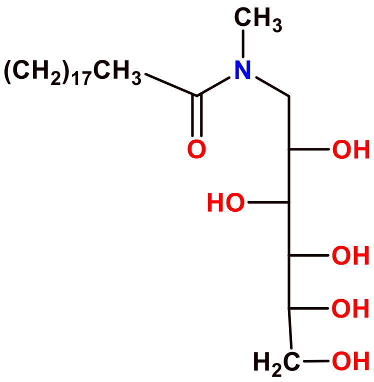
Saccharose esters



Alkyl glucoside



Sorbitol esters

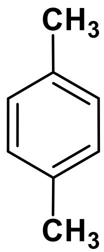


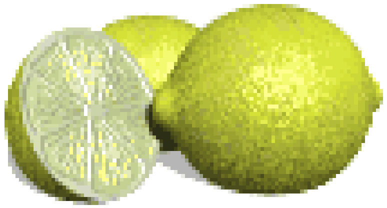
N-methyl glucamide

D-Limonene.

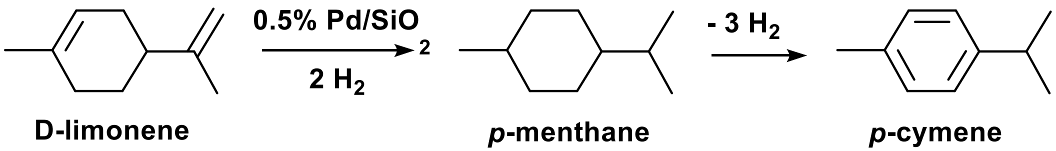
- Limonene is a by-product of the juice industry (5 Mt/y).
- It can be used as a stand-alone solvent, and is considered a potential, non-toxic, xylene replacement in some medical applications as it breaks down in the body benign metabolites.

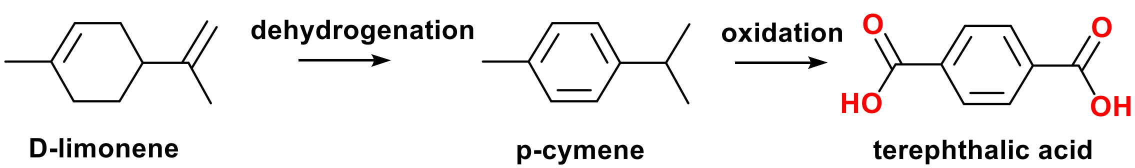
Alternative to *p*-xilene





- It can also be dehydrogenated to form *p*-cymene:
  - a solvent
  - an important intermediate in the fragrance industry
  - an intermediate
  - a *p*-cresol intermediate
  - a raw material for synthesis of non-nitrated musks.

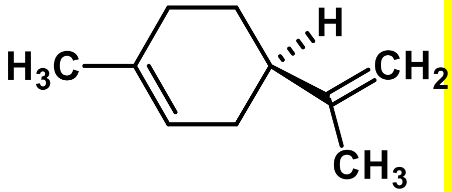




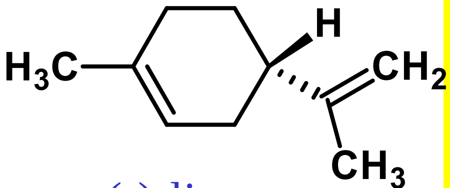
R. J. Grau, P. D. Zgolicz, C. Gutierrez, H. A. Taher, Journal of Molecular Catalysis A: Chemical, 148, (1999), 203-214

Limonene is a Chiral Molecule.

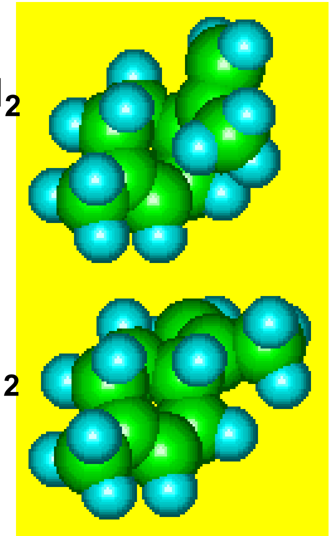
- D-limonene has a pleasant orange sent.
- L-limonene has a piney turpentine smell.



(+)-limonene



(-)-limonene



- Limonene occurs naturally in citrus fruits and vegetables, meats, spices.
- Limonene was first registered as an insecticide in 1958.
- Limonene was registered as an antimicrobial in 1971, and as a dog and cat repellant in 1983.
- Limonene is established as an inert, and in 1994 it was granted an exemption from specifying a max residual limit as solvent or as fragrance in pesticides.
- The FDA lists limonene as Generally Recognized as Safe, as a food additive or flavoring and fragrance additive.
- The orange juice industry produces over 5 million tons of peel waste annually.

Limonene Physical / Bio Properties.

Physical Properties

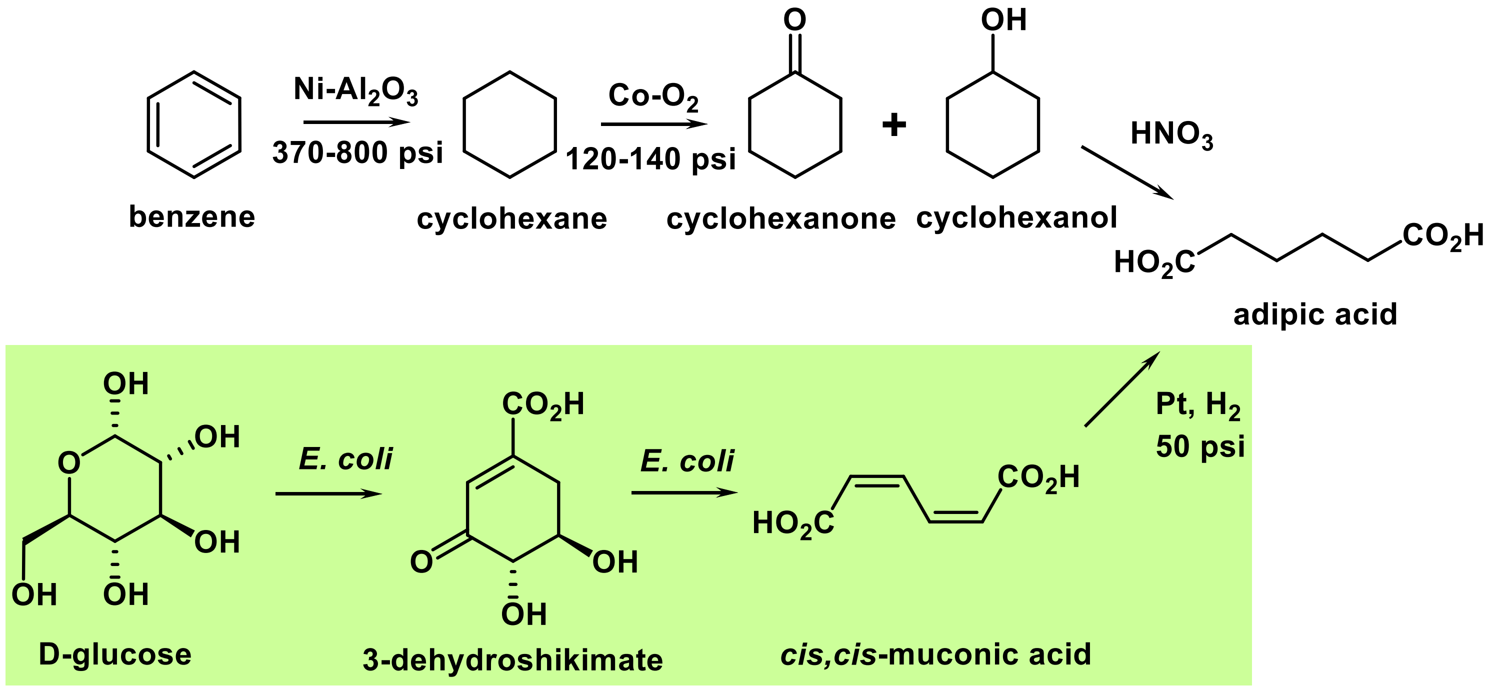
- Limonene is practically insoluble in water; miscible in alcohol.
- Liquid at room temperature
- Melting point -74.35 °C; Boiling point 175.5-176.0 °C
- Highly flammable with a flash point of 43°C
- Citrus odor
- Colorless to pale yellow

Biological Properties

- Limonene is corrosive and in concentrated quantities has been known to produce localized skin, mucus membrane, and lung irritation on contact.
- In the male rat, limonene causes tumors and damage to the kidneys, but a specific protein unique to the male rat is thought to play a crucial role in this damage. Kidney damage is not considered a relevant risk for humans or other mammals.
- As an insecticide limonene destroys the wax that coats the inside of the insect's respiratory system. Limonene used as an insecticide is effective as a contact spray only and has no residual effect.
- Dogs and cats are repelled by the scent of limonene, as long as the scent is applied frequently and remains fresh the repellant will continue to work.
- Bioaccumulation may occur in fish.

MRSEC. Center for the Science & Engineering of Materials. California Inst. of Technology. 2009 <http://www.csem.caltech.edu/_of_month/_lemons.html>.

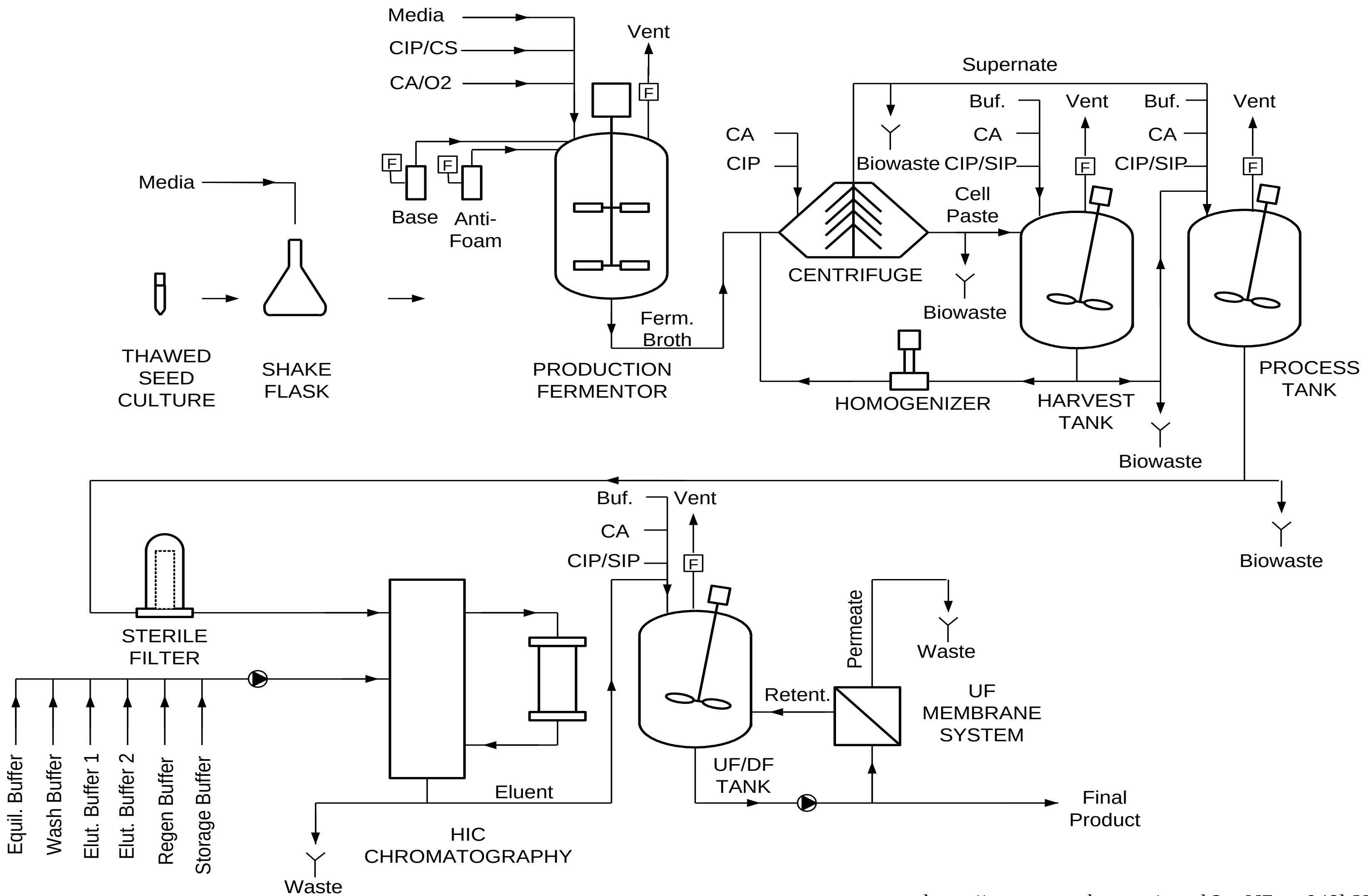
Draths-Frost Biotechnological Synthesis of Adipic Acid.



Typical feeder solution:

In 1 liter of water	6 g Na_2HPO_4	0.12 g $MgSO_4$	**Yield = 20.4 mmol**
10 g bacto triptone	3 g KH_2PO_4	1 mg thiamine	**% Yield = 33 %**
5 g bacto yeast	1 g NH_4Cl		
10.5 g NaCl	10 g glucose (62 mmol)		

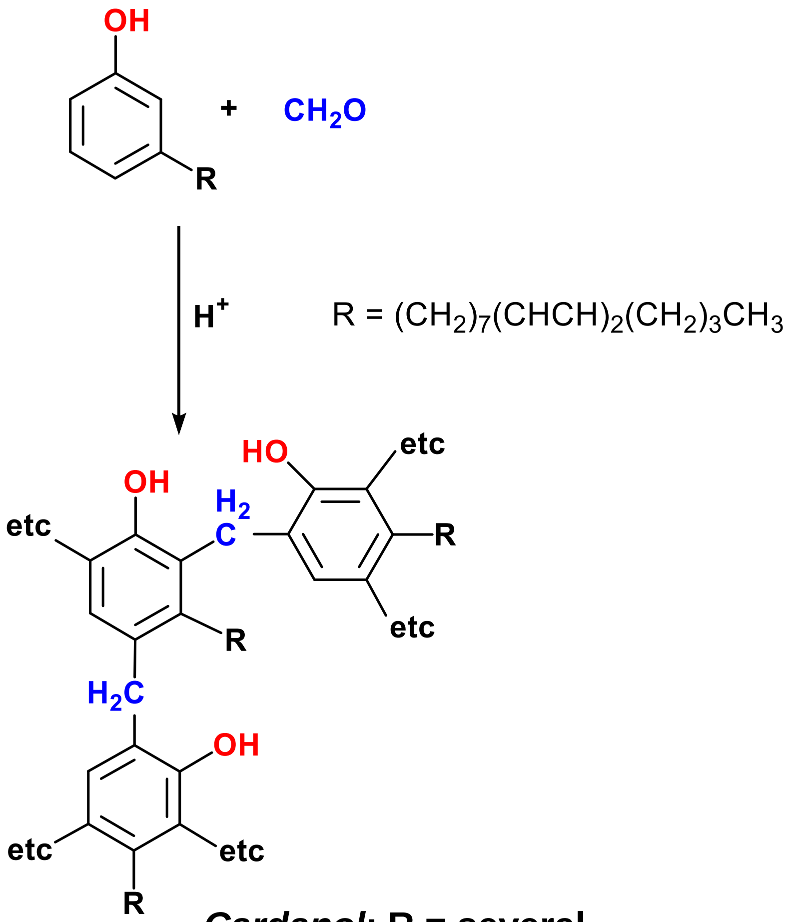
GFP Production Using Recombinant *E. Coli.*



https://www.youtube.com/watch?v=N7vxq948l-U

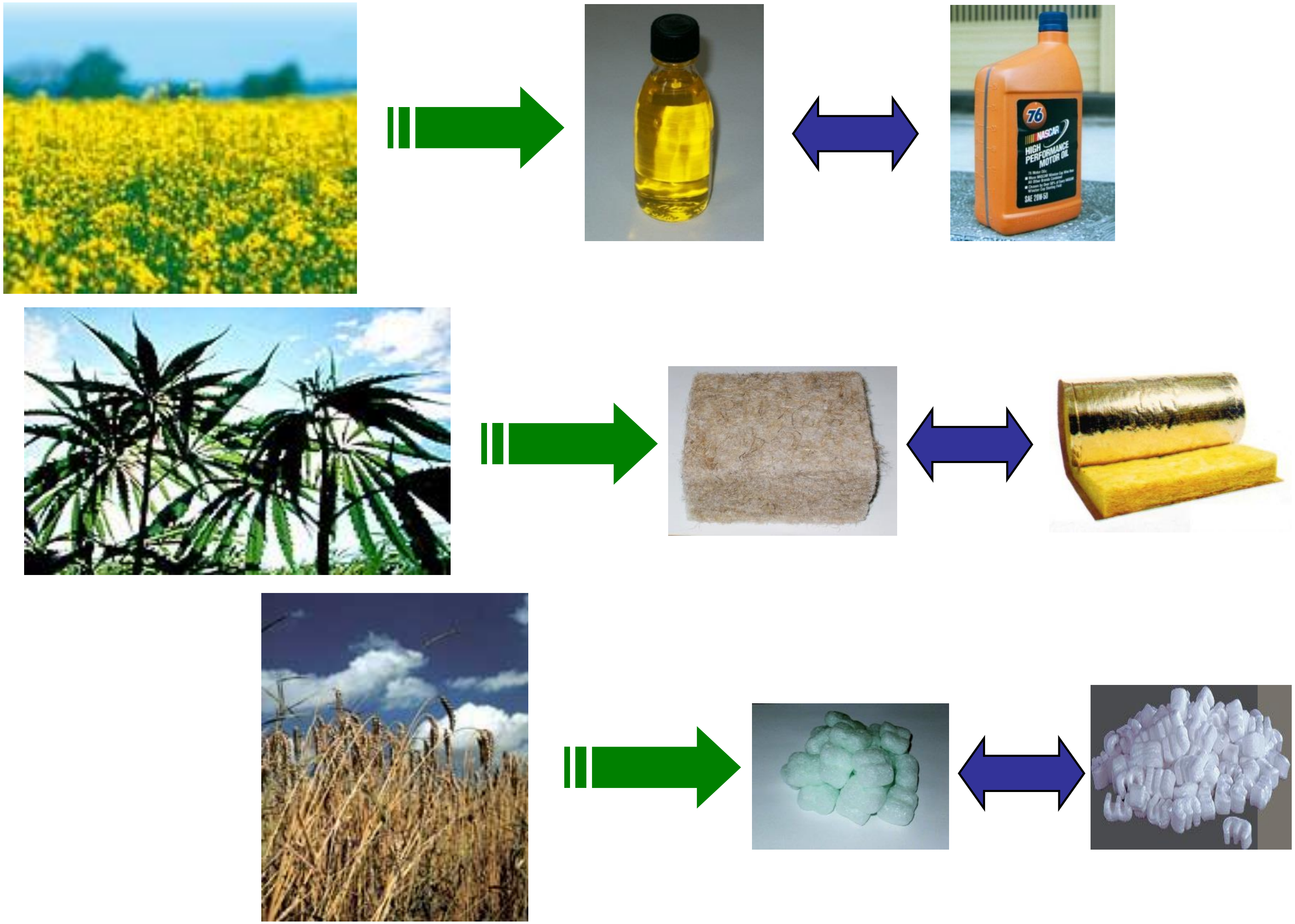
Cashew Nut Shell Liquid (CNSL).

- CNSL is obtained during the roasting process of cashew nuts. It is a rich source of the phenolic compound, cardanol.
- Cardanol consists of saturated and (mainly) unsaturated C-15 meta-alkyl phenols.
- CNSL-formaldehyde resins have long been used in car break linings due to:
  - very good friction properties
  - good thermal resistance (less noise)
- Also CNSL polymers are used in surface coatings for varnishes and waterproof roof coatings.



***Cardanol*: R = several saturated, mono, and tri-unsaturated C-15 alkyl groups.**

Products from Industrial Crops Compared to Conventional Ones.



Examples: Adhesives.

- Corrugated packaging
- Dust agglomeration
- Bricks and tiles
- Furnishings made from recycled material
- Laminated panels
- Carton sealants
- Insulation binders
- Straw tackifiers for erodible soils
- Wallpaper pastes
- Foamed plywood glue
- Furniture joint glues
- Remoistenable films
- Paper coatings
- Gypsum wallboard

Examples: Construction Materials & Composites.

- Interior paneling simulated wood finishes
- Spray foam insulation with no emissions
- Replacement for polyurethane foam carpet backing
- Dimension lumber formed from composite materials
- Molded millwork, trim, etc.
- Molded reinforced composites
- Drywall gypsum substitutes
- Particle board plywood substitutes
- Acoustical ceiling tiles

Fibers, Paper & Packaging.

- Biodegradable corrugated packaging
- Loose fill (peanut) packaging that dissolves in water or composting
- Paper coatings
- Biodegradable replacements for plastic bags of all kinds
- Facial tissues
- Carpets and carpet backing
- Sizing agents and pitch formation in papermaking
- Surface starches that improve opacity and enhance printability
- Paper & packaging strength retention agents
- Food service wraps
- Fiber fill for mattresses, pillows and pads
- Textiles & fabrics

Landscaping Materials, Compost & Fertilizer.

- Fertilizers
- Dust suppressants
- Embankment matting for erosion control
- Biodegradable gardening film for weed control
- Mulching products
- Composted materials for fertilizer
- Carrying agents for insecticides and fertilizers
- Composite landscape timbers and decking

Lubricants & Functional Fluids.

- 100% soy-based motor oil
- High pressure oil barrier lubricants
- Liquid wax ester oils
- 2-cycle engine oil
- Hi-performance motor oils
- Heavy-duty truck grease
- 5th wheel truck grease
- Industrial lubricants for salt spray or high humidity environments
- Multi-purpose machine shop grease
- Chain lubricant
- Wire cable corrosion inhibitors
- Slideway lubricants
- Rail curve lubricant with lithium thickeners
- Turbine lubricants
- Vacuum oils
- Penetrating oils

Lubricants & Functional Fluids (2).

- Rust inhibitors
- Transmission fluids
- Power steering fluids
- Pump oils
- Fire resistant dielectric fluid
- Degreasers
- Heavy duty gear box oils
- Hydraulic fluid
- Low temperature multipurpose lubricants
- Drip oils
- Metal cutting lubricants
- Tapping & drilling fluids
- Metal forming fluids
- Extreme pressure forming pastes
- Asphalt release agents
- Concrete release agents
- Concrete sealants
- Die-mold release agents

Examples: Plastics.

- Biodegradable foam food containers
- Biodegradable foam insulation products
- Films for bags and wraps
- Compostable shopping bags
- Biodegradable fast food plates, cups, straws & eating utensils
- Biodegradable disposable diaper out layers
- Compostable pen barrels
- Thermoplastic polymers for injection molded products
- Polymers used in cosmetics and personal care products
- Biodegradable trash bags

Paints & Coatings.

- Sealants for concrete, fiber cement and wood
- Tempura paints
- Glitter paints
- Washable paints
- Seed oil coatings
- Wall paints
- Deck sealer and waterproofer
- Concrete curing agents
- Glow-in-the-dark poster paints
- Poster paints
- Watercolor paints

Solvents & Cleaners.

- Asphalt equip. cleaner
- Waterless hand cleaners
- Graffiti cleaners for glass, brick, concrete and metal
- Cleaners for polyurethane equipment and lines
- All-purpose cleaners
- Adult shampoos & soaps
- Carpet shampoos
- Anti-allergen sprays
- Filter cleaners
- Fruit & vegetable washes
- Dishwasher and laundry detergents
- Mold, fungus, mildew cleaner
- Bath & shower gels
- Carpet spot removers
- Mastic removers
- Industrial parts washing fluids
- Textile and dyeing equipment cleaner

Solvents & Cleaners (2).

- Glue, adhesive, paint removers
- Biosolvents for cleaning beaches of oil spills
- Ink haze removers
- Reusable carburetor and parts cleaner
- Waterless electronic component cleaners
- Glass cleaners
- Fabric softeners
- Floor cleaning products
- Disinfectants
- Tub & tile cleaners
- Printing equipment cleaners
- Oil & grease emulsifiers

Solvents & Cleaners (3).

- HVAC cleaners
- Wood, leather, vinyl cleaners
- Ink removers
- Lip balms
- Trap and drain cleaners
- Fabric stain removers
- Oven cleaners
- Glass, fiberglass polishing agents
- Marine hull & cargo hold cleaners
- Hand creams & lotions
- Kitchen & bath cleaners
- Metal cleaners
- Concrete structure cleaners
- Char, grease and burnt residue cleaners

Sorbents and Inks.

- Multi-sorbent for oils, coolants, solvents and water
- Animal bedding & litter
- Carrier agent for herbicides, insecticides and pesticides
- Knitted material to absorb oil, coolants, solvents and water
- Superslurper to clean soil contaminants
- Soy-based black news inks
- Soy-based color news inks
- Soy-based UV coating, foil stamping and laser printing ink
- Heat set inks
- Soy-based varnish for tory or press tek plates
- Soy-based flexographic ink
- Corn based stamping ink

Products from Industrial Crops.

Environmental advantages and disadvantages:

+

- CO_2 neutral
- save energetic resources
- Biodegradable
- less transports
- etc.

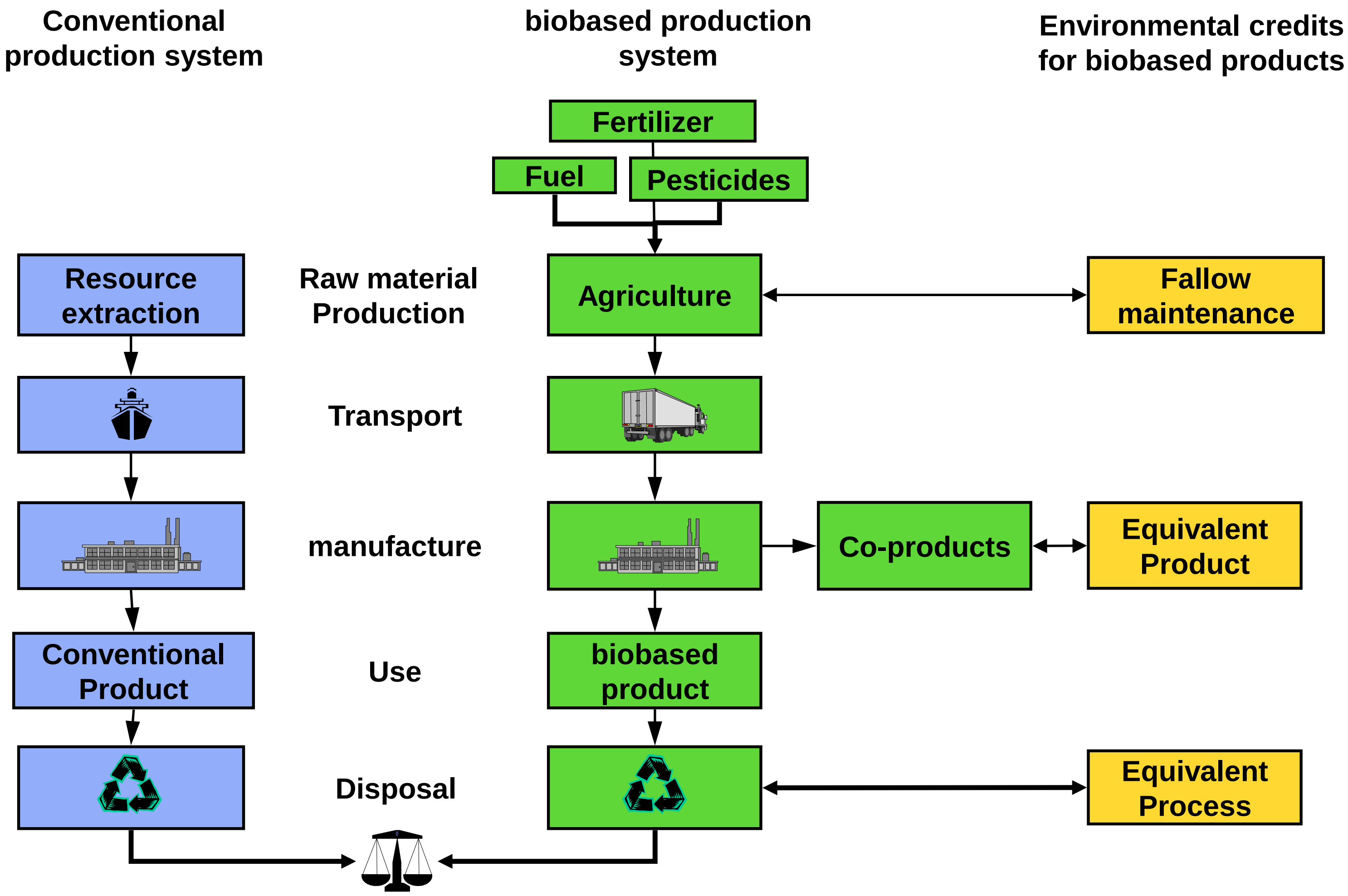
–

- Land use
- Eutrophication of surface waters
- Water pollution by pesticides
- Energy intensive production
- etc.

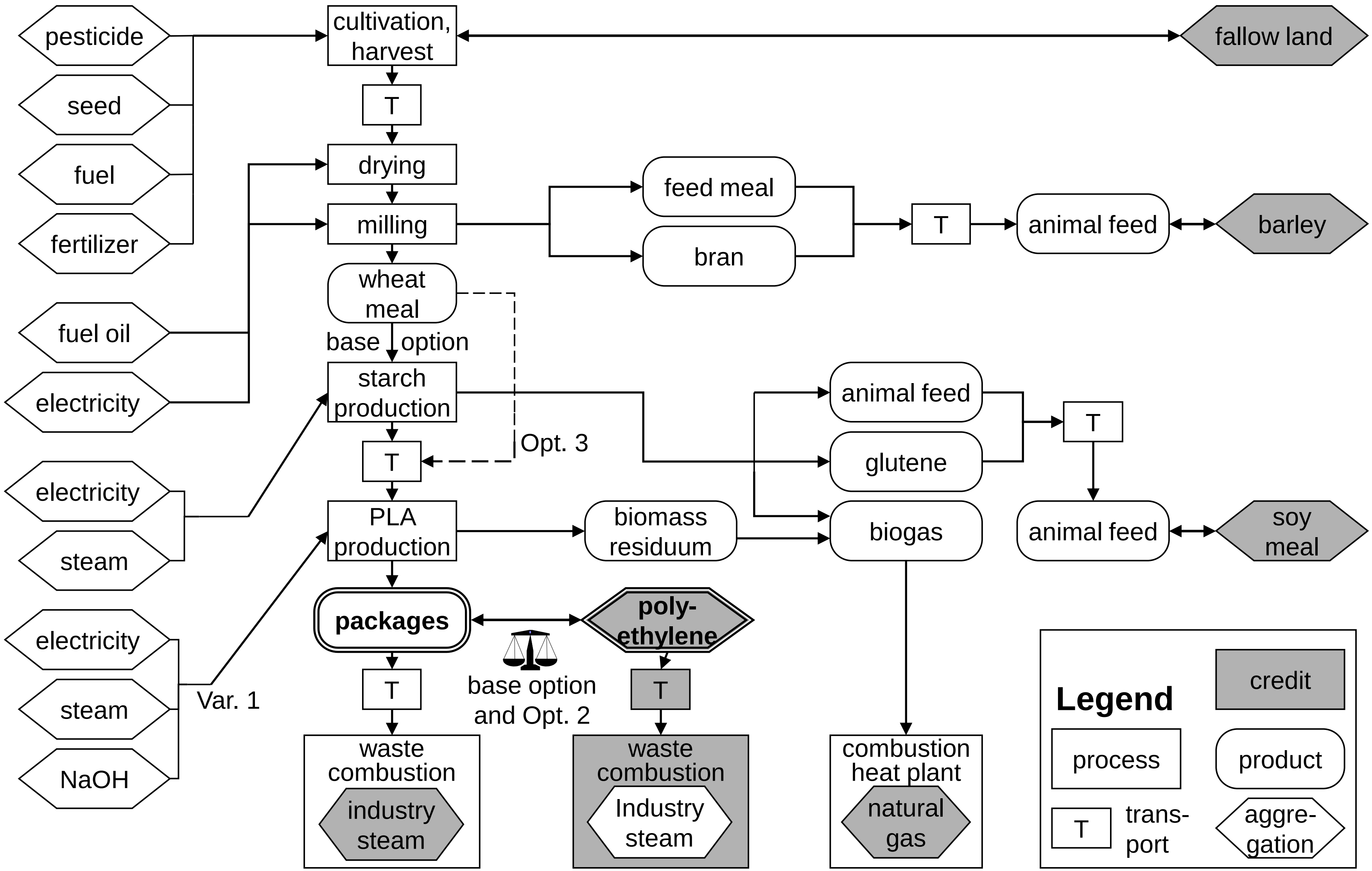
Total:
positive or negative

?

LCA Analysis of Bioproducts.

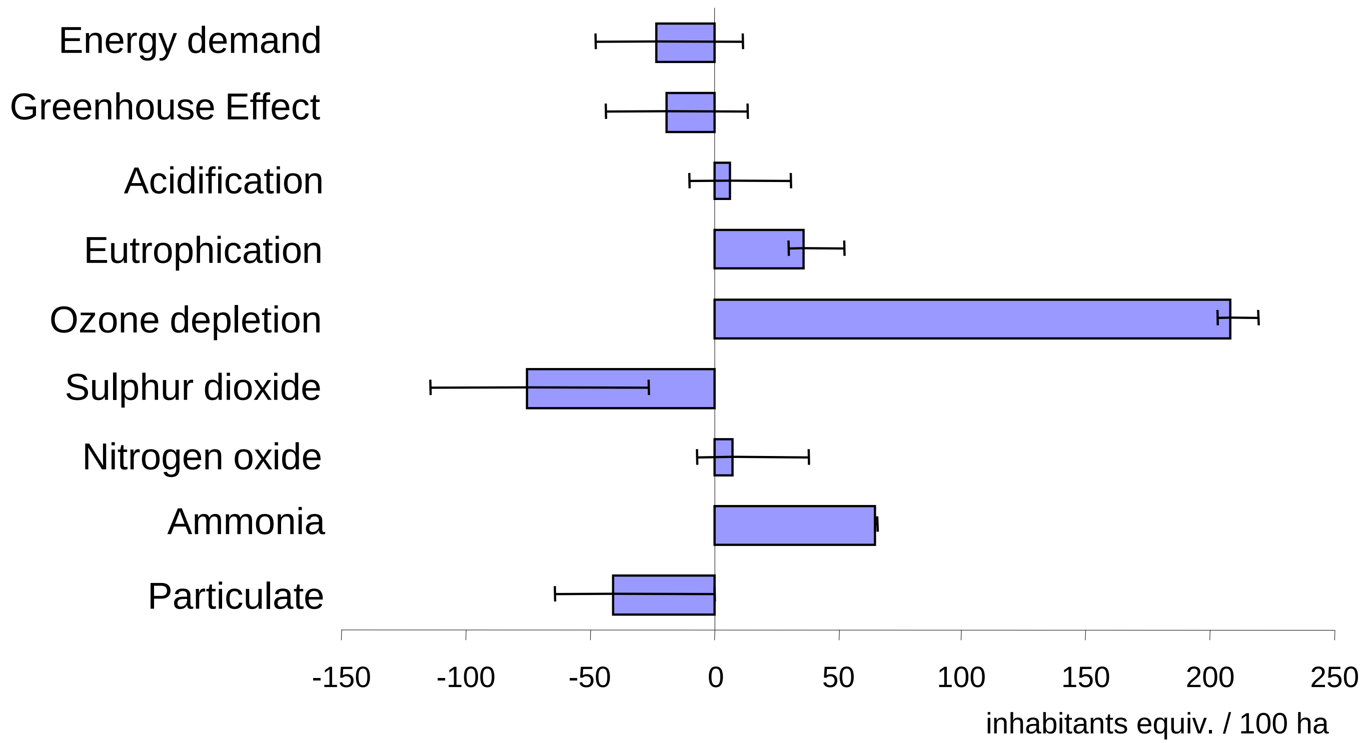


Packaging Material – Life Cycle.



Wheat PLA – Environmental Effects.

Advantages for wheat **Disadvantages for wheat**



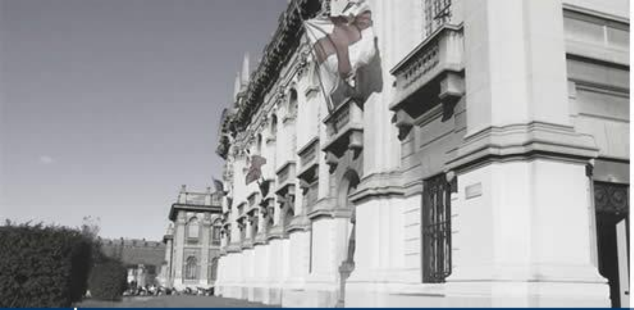
Scenarios

double / half the energy demand for PLA production

more / less weight of the reference product

direct utilization of whole meal wheat

conventional packaging from polypropylene instead of polyethylene



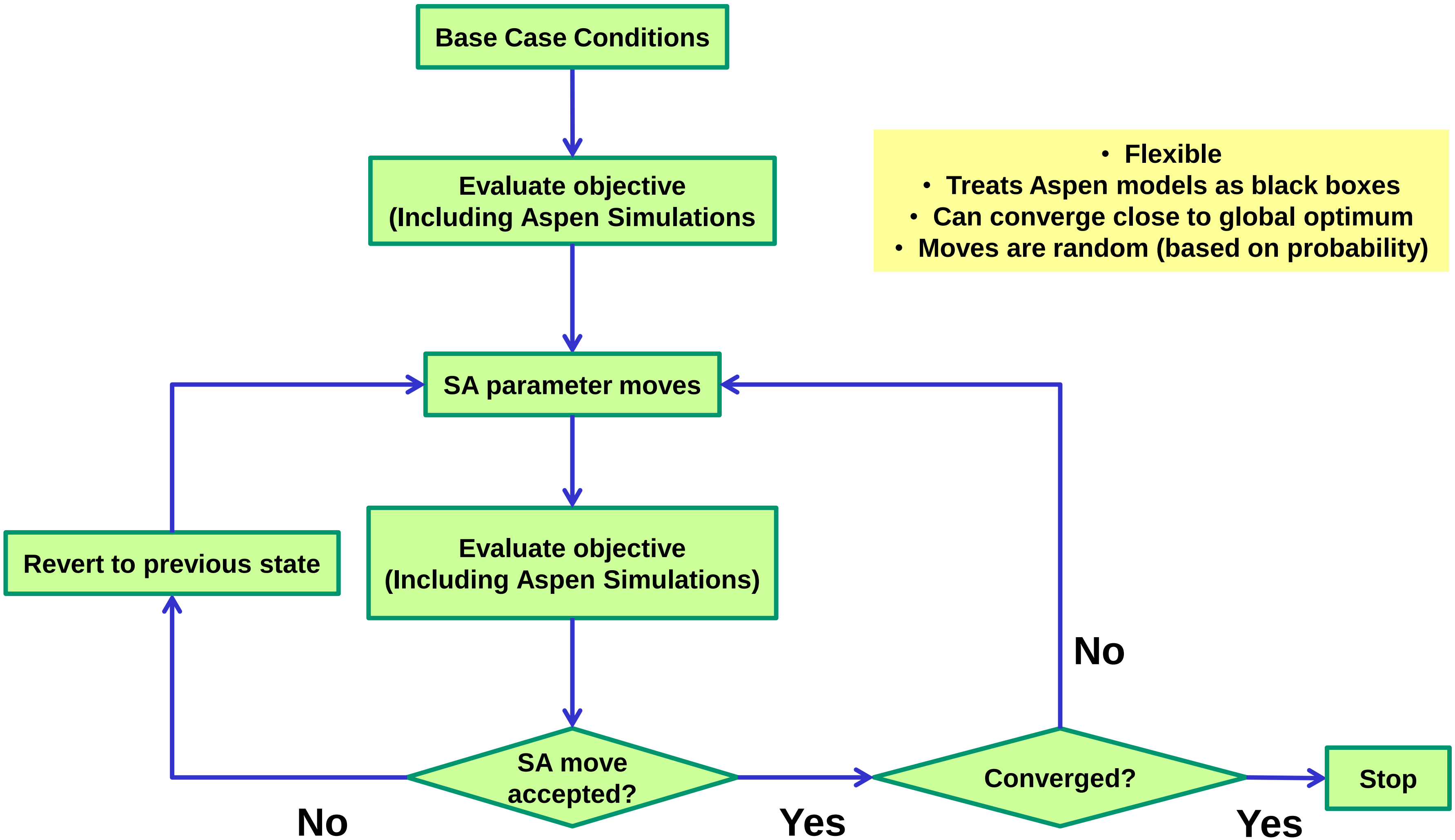
POLITECNICO DI MILANO





Cost Analysis (by simulation).

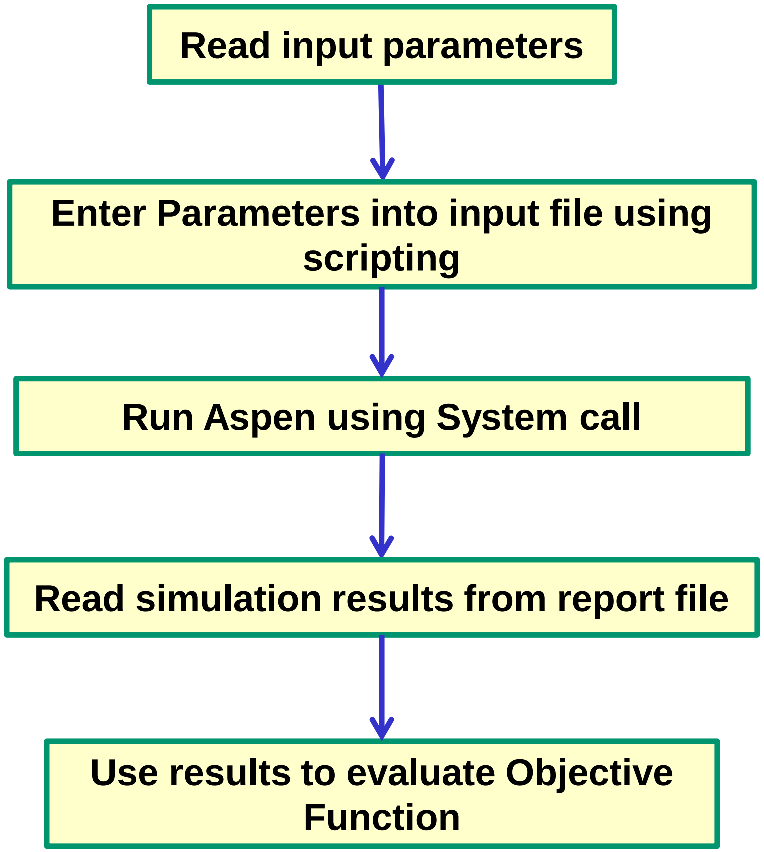
Simulated Annealing Based Process Optimization.



- Flexible
- Treats Aspen models as black boxes
- Can converge close to global optimum
- Moves are random (based on probability)

Objective Function.

This objective function works in the following way



Objective Function (minimisation)

Objective = -VP + CR + EC + CP + WC + EF

VP = Value of Products

CR = Cost of Raw Materials

EC = Energy Costs

CP = Capital costs (scaled to €/hr based on 10 y lifespan)

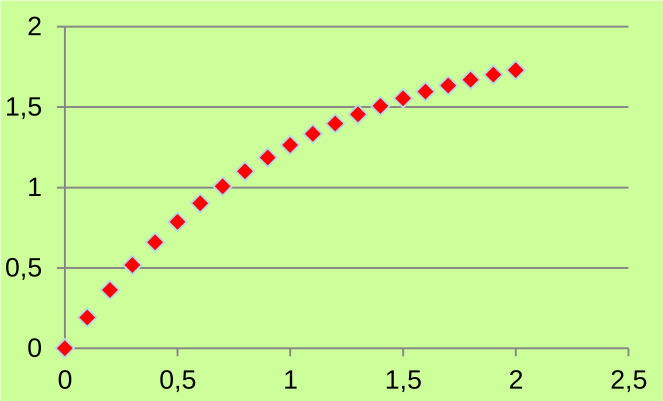
WC = Cost of liquid and solid waste treatment

EF = Error function (=1 $\times$ 10^9 if an error in the simulation otherwise = 0)

Life Cycle Analysis Data.

	Electricity data	Heating data	Waste
Cost (typical value)	0.0772 €·kWh^{-1} [a]	0.0772 €·kWh^{-1} [c]	0.0772 €·kg^{-1} [d]
Emission Factor ($kgCO_2$/kWh)	0.537[b]	0.201[c]	

Environmental Impact*

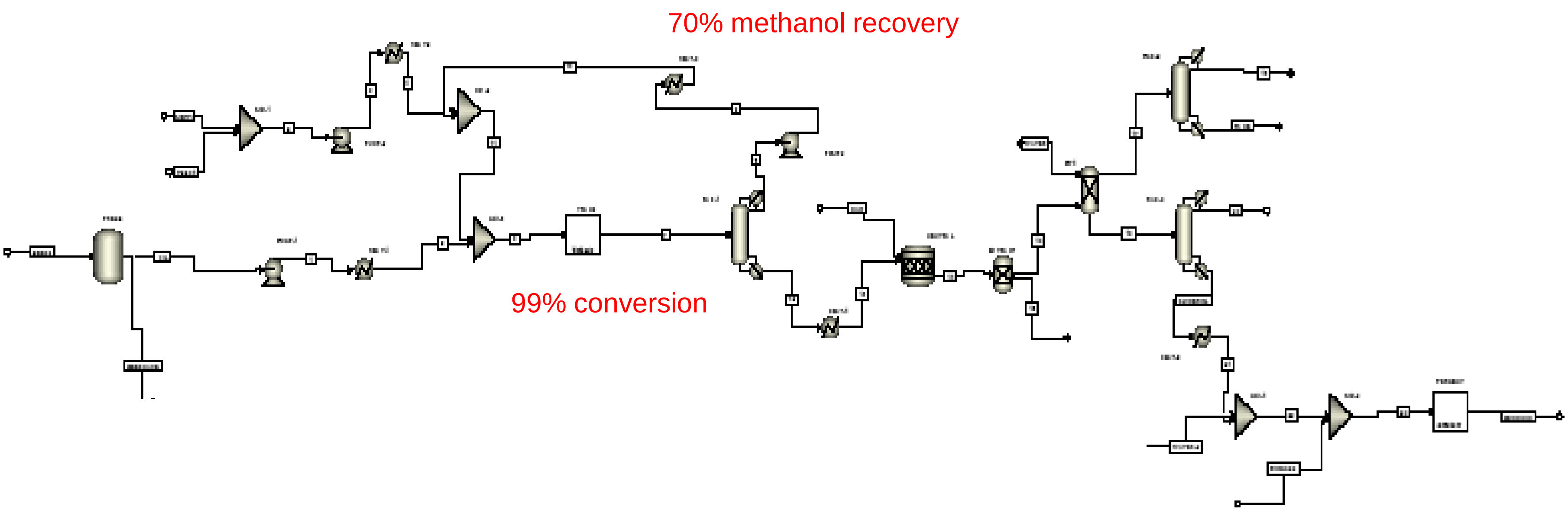


Profits

a. FERA, 2007
b. DEFRA, Market transformation programme, BNXS01
c. GEMIS database, http://www.oeko.de/service/gemis/en/
d. Turton et al. (2009), Analysis, synthesis and design of chemical processes, Pearson Education Inc.

* Azapagic A., Clift R., (1999), Computers and Chemical Engineering, 23, 1509-1526.

Biodiesel Production.



Inputs		Outputs	
Rapeseed	3,125 kg/hr	Biodiesel	1,237 kg/hr
Methanol	216.29 kg/hr	Rapeseed meal	1,875 kg/hr
Potassium Hydroxide	15 kg/hr	Crude Glycerol	93.56 kg/hr

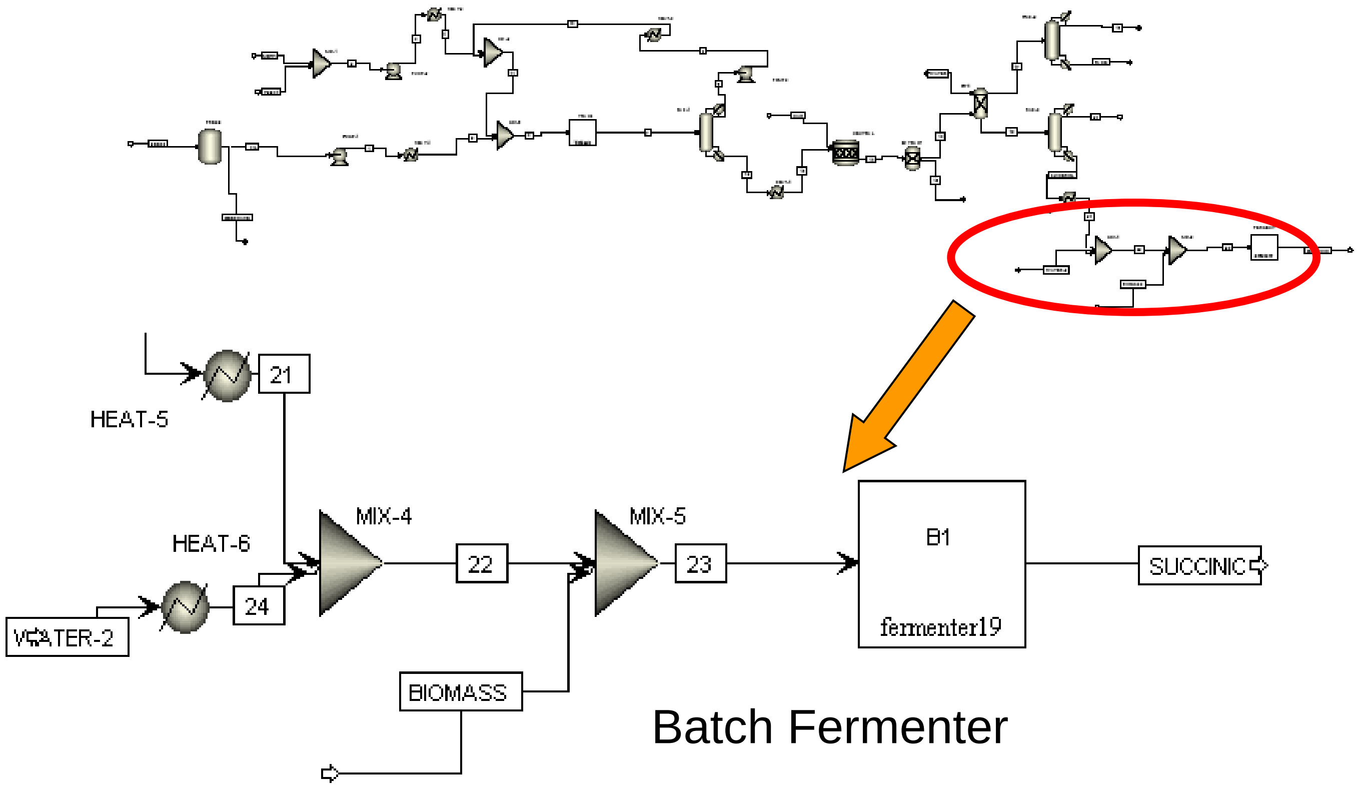
In this simulation the crude glycerol is 80% glycerol (mass fraction)

Comparison of Different Biodiesel Schemes.

Parameter	With co-production of succinic acid	With co-production of crude glycerol	With co-production of purified glycerol
Methanol Recovery (%)	84.07	84.07	86.94
Methanol Feed (ton/ton of feed)	0.0531	0.0531	0.0519
Profit (€/ton of feed)	138.33	85.77	91.73
Emissions (tons CO_2/ton of feed)	0.152	0.151	0.155
Waste (tons/ton of feed)	0.0421	0.0424	0.0452

Optimal Oil : Methanol ratio ~ 1 : 13

Bioconversion of Glycerol to Succinic Acid.



Batch Fermenter

Inputs

Crude Glycerol	93.56 kg/hr
Water	3,971 kg/hr
Biomass	0.492 kg/hr

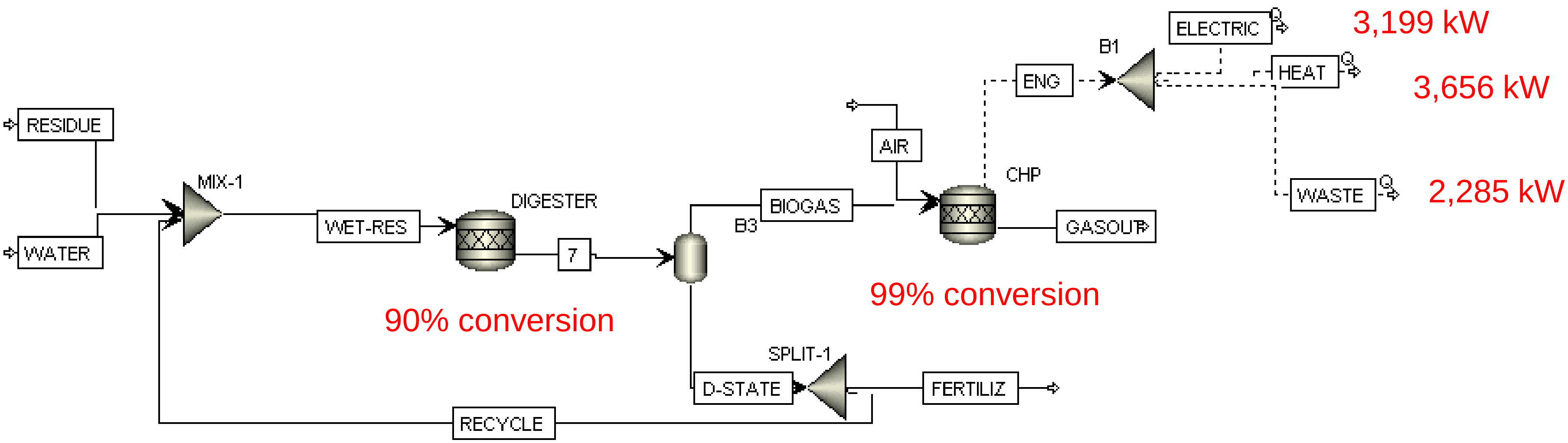
Outputs

Succinic Acid	41.1 kg/hr

Profits and emissions increases with H_2O use

Biogas Production.

Energy Outputs

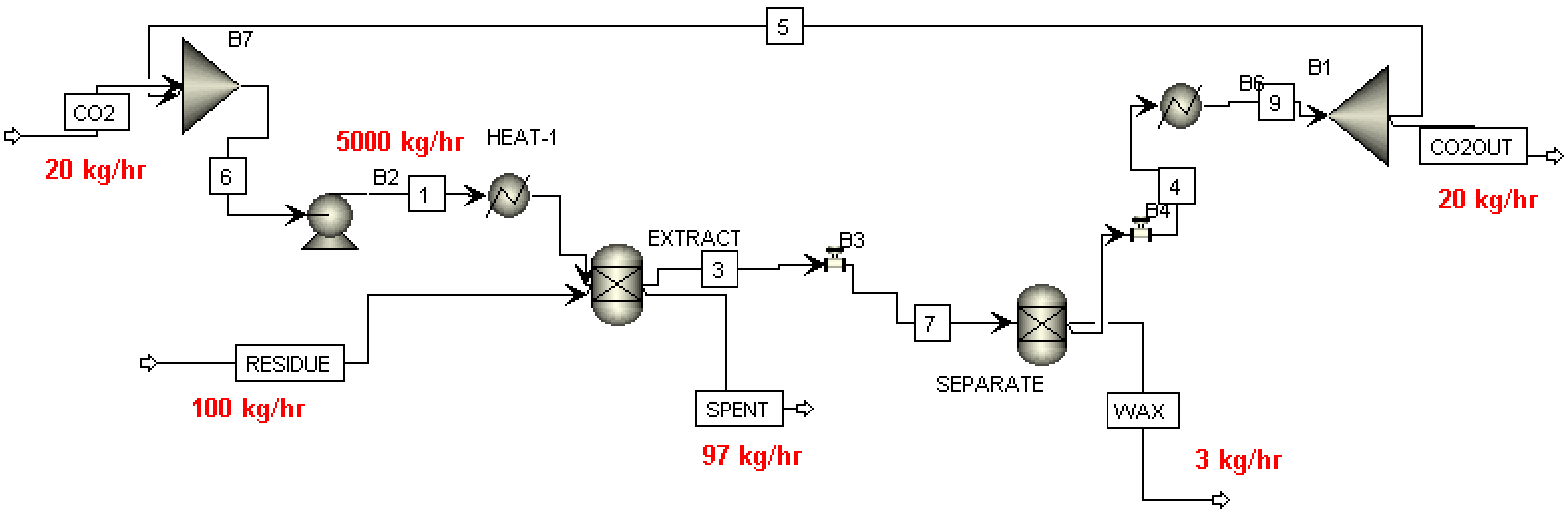


Inputs	
Residue	1,350 kg/hr
Water	1,450 kg/hr
Air	kg/hr

Outputs	
Digestate	1,424 kg/hr
Digestate(dry matter)	198 kg/hr
CO_2	2,324 kg/hr
CH_4	trace

This simulation includes a recycle rate of 50% for the digestate

Super Critical CO_2 Extraction.



Example: capacity 100 kg/hr (876 tons/year)

Inputs		Outputs	
Residue (Straw)	100 kg/hr	Spent straws	97 kg/hr
CO_2	20 kg/hr	Waxes	3 kg/hr
		CO_2	20 kg/hr

Process constructed based on information from UoY

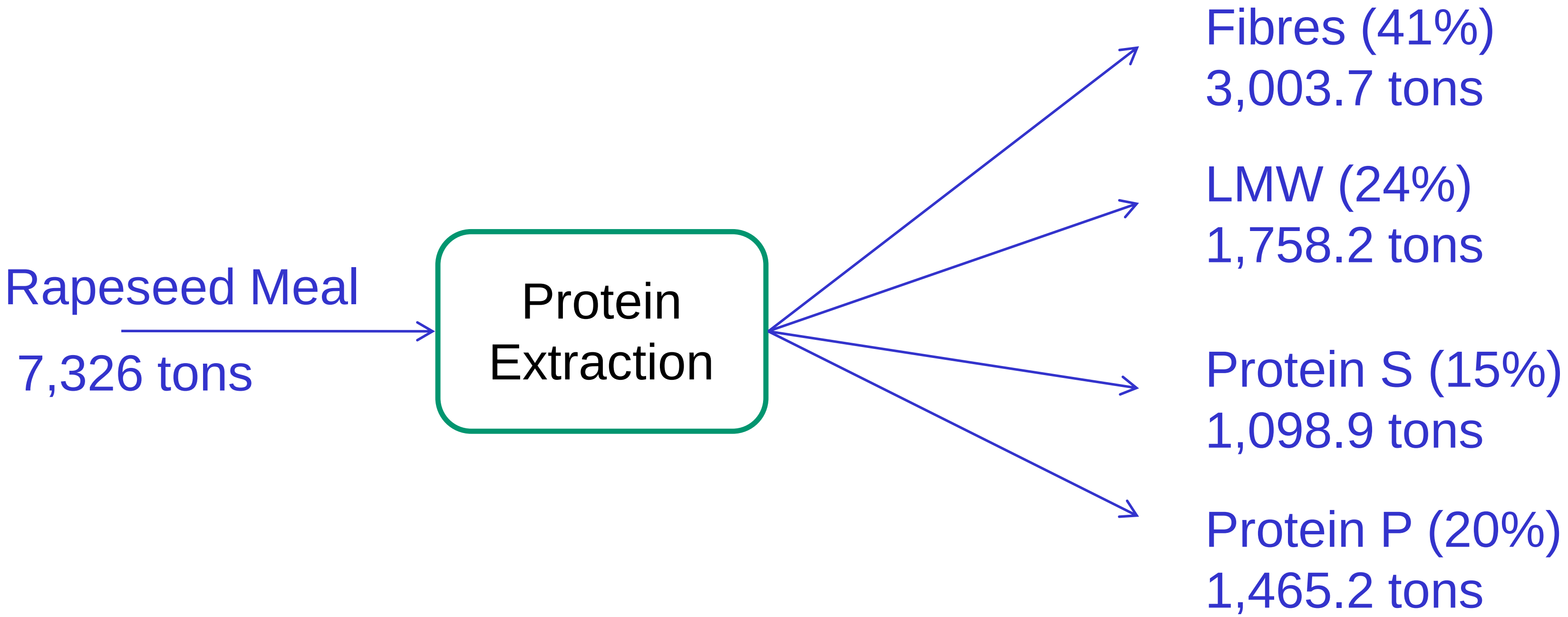
Comparison of Oil Extraction Methods (Rapeseed).

	Cold Pressing	Hexane-based Extraction
Costs	33.19 €/ton	28.32 €/ton
Energy	Electricity: 68 kWh/ton	Electricity: 63.2 kWh/ton; Natural gas: 240 kWh/ton
Emissions	36.5 kg/ton of seeds	68.8 kg/ton of seeds
Efficiency	83.3%	95.0%
Oil extracted **($3.125\ kg \cdot hr^{-1}$)**	$1{,}042\ kg \cdot hr^{-1}$	$1{,}042\ kg \cdot hr^{-1}$

So the larger Hexane based plant has cheaper costs per ton

However the hexane based method also emits more CO_2

Protein Extraction from Rapeseed Meal.



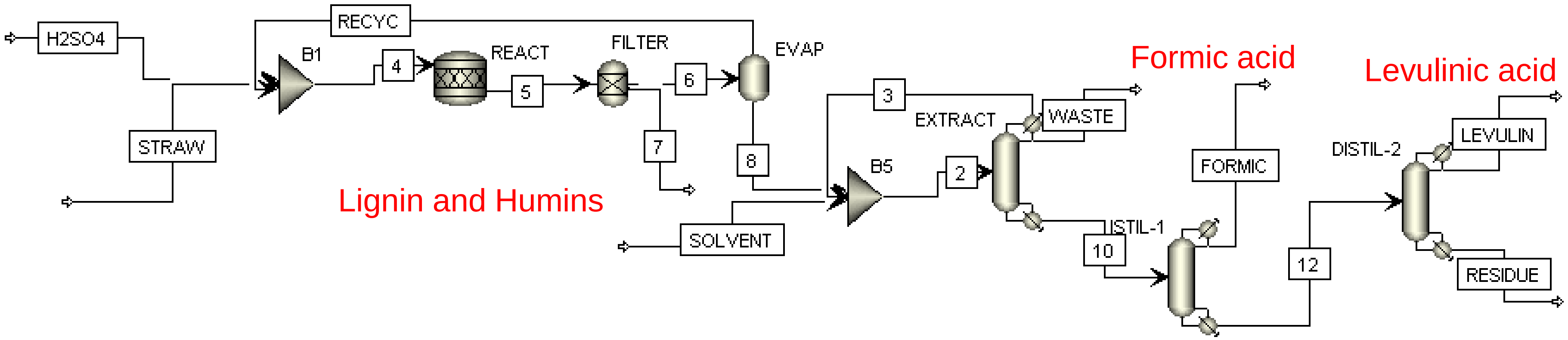
Electricity required: 475 kWh / ton

Heating required: 3,431 kWh / ton

Costs: 547.7 €/ton

Profits: 176.7 €/ton

Levulinic Acid.



Cellulose content of straws = 45%

0.45 kg cellulose → 0.23 kg Levulinic Acid

1 mol Glucose → 1 mol Levulinic Acid + 1 mol formic acid

Economic and Environmental Comparison.

Process	Optimal profits (€ per ton of feed)	Emissions (kg CO_2 per ton of feed)	Scale of plant (tons per year)
Cold pressing oil extraction	33.03	0.0365	11,000
Hexane based oil extraction	52.28	0.0688	1,000,000
Biodiesel with crude glycerol	85.77	0.151	25,000
Biodiesel with purified glycerol	91.73	0.155	25,000
Biodiesel with succinic acid	138.33	0.152	25,000
Protein extraction	201.45	0.945	7,326
Biogas production	281.32	1.821	10,854
Supercritical CO_2 extraction	488.40	0.983	36,227
Thermomoulding	1,413.20	4.762	69.700
Levulinic acid production	2,758.95*		

Conclusions.

- Biomass can be used as both a chemical feedstock and source of energy
- Extraction technologies have been developed to selectively isolate desired metabolites
- Transformation of biomass to chemical feedstocks possible through thermal, chemical or microbial methods
- A huge range of chemicals can be synthesized from RRMs
- A number of biodegradable polymers can be formed from RRMs
- The environmental impact of chemical products made from RRMs is not as favorable as anticipated but technological improvements can be expected by deeper studies.
- Use of renewable energy is key ...
- Reduction of greenhouse gas CO_2 is key…
- Reduction of water use is key ...