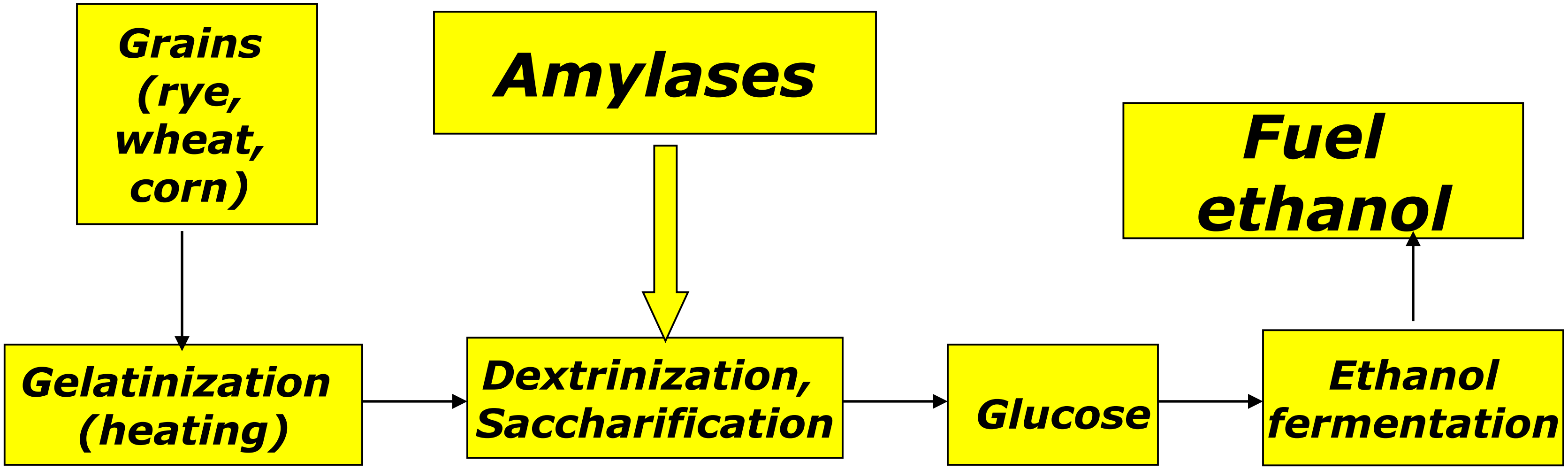
Second generation biofules: beyond the competition for soil and food

First generation biofuels:
ethanol from starch & grains



Grains (rye, wheat, corn)

Amylases

Fuel ethanol

Gelatinization (heating)

Dextrinization, Saccharification

Glucose

Ethanol fermentation

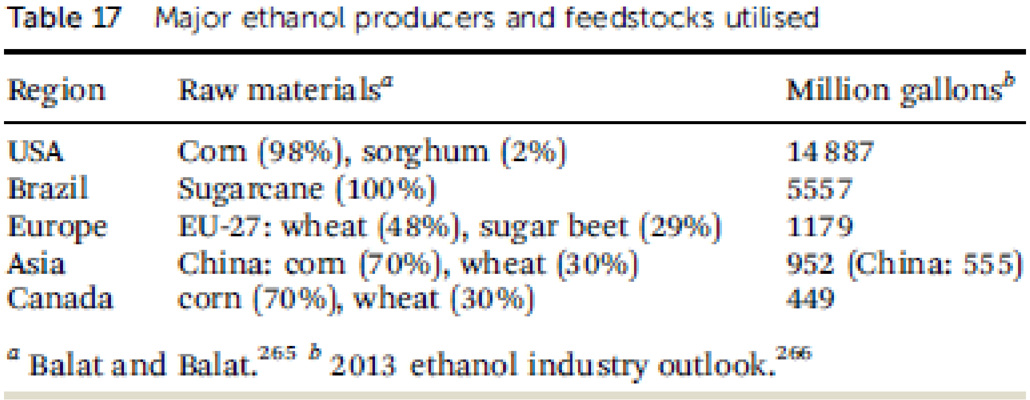


Table 17 Major ethanol producers and feedstocks utilised

Region	Raw materials[a]	Million gallons[b]
USA	Corn (98%), sorghum (2%)	14 887
Brazil	Sugarcane (100%)	5557
Europe	EU-27: wheat (48%), sugar beet (29%)	1179
Asia	China: corn (70%), wheat (30%)	952 (China: 555)
Canada	corn (70%), wheat (30%)	449

[a] Balat and Balat.[265] [b] 2013 ethanol industry outlook.[266]

Biomass platforms for lignocellulosic feedstocks for second generation biofuels

Options

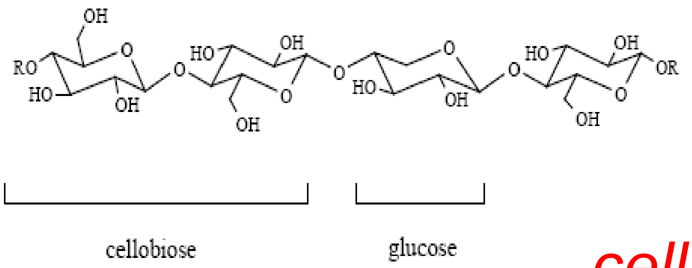
- Agricultural crop residues
- Dedicated biomass crops
- Residues from forestry and the forest products industry
- Municipal solid wastes
- Food processing wastes

Feedstocks composition

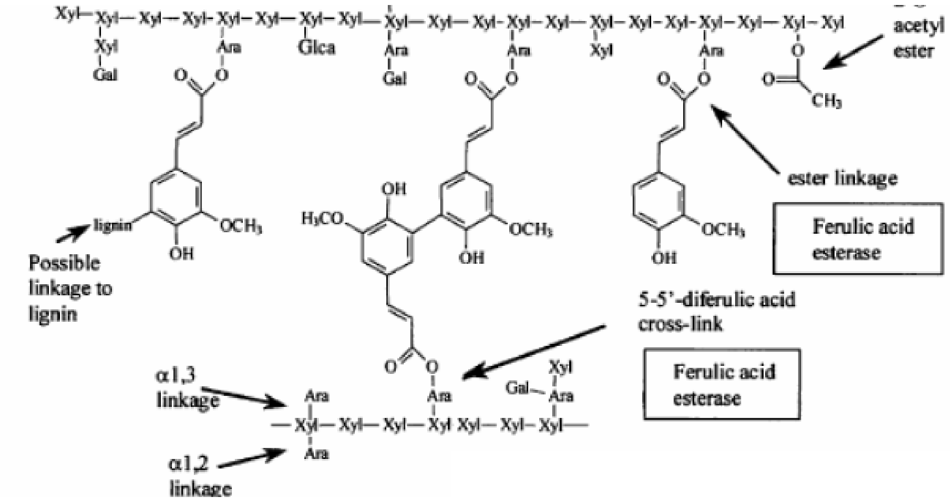
In general lignocellulosic feedstocks contain about 40% of the carbon bound as cellulose, 30% as lignin and 26% as hemicelluloses and other polysaccharides.

While cellulose is a uniform component of most types of cellulosic biomass, the proportions and composition of hemicelluloses and lignin differ between species.

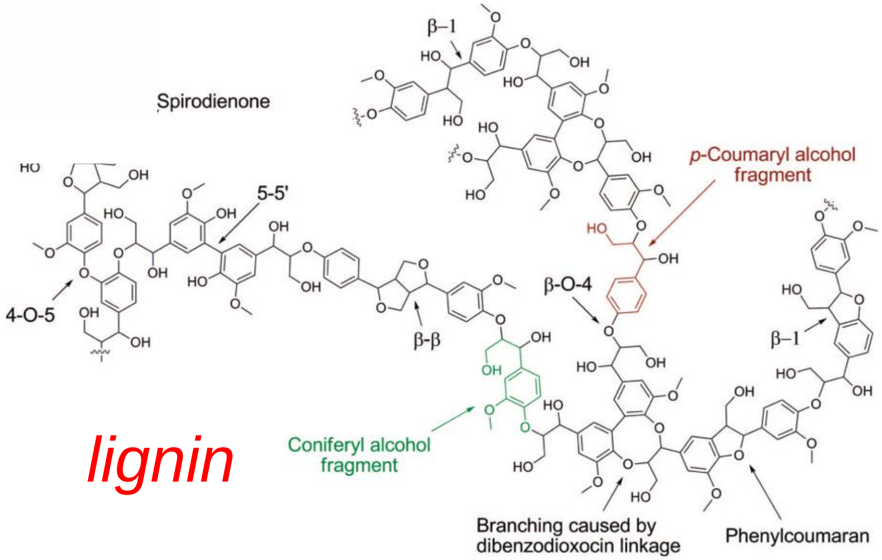
The chemistry of plant cell wall



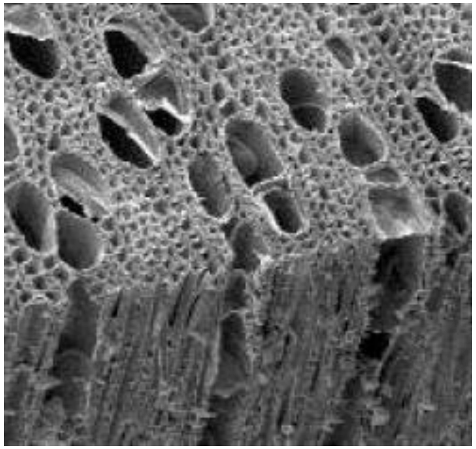
cellulose



hemicellulose

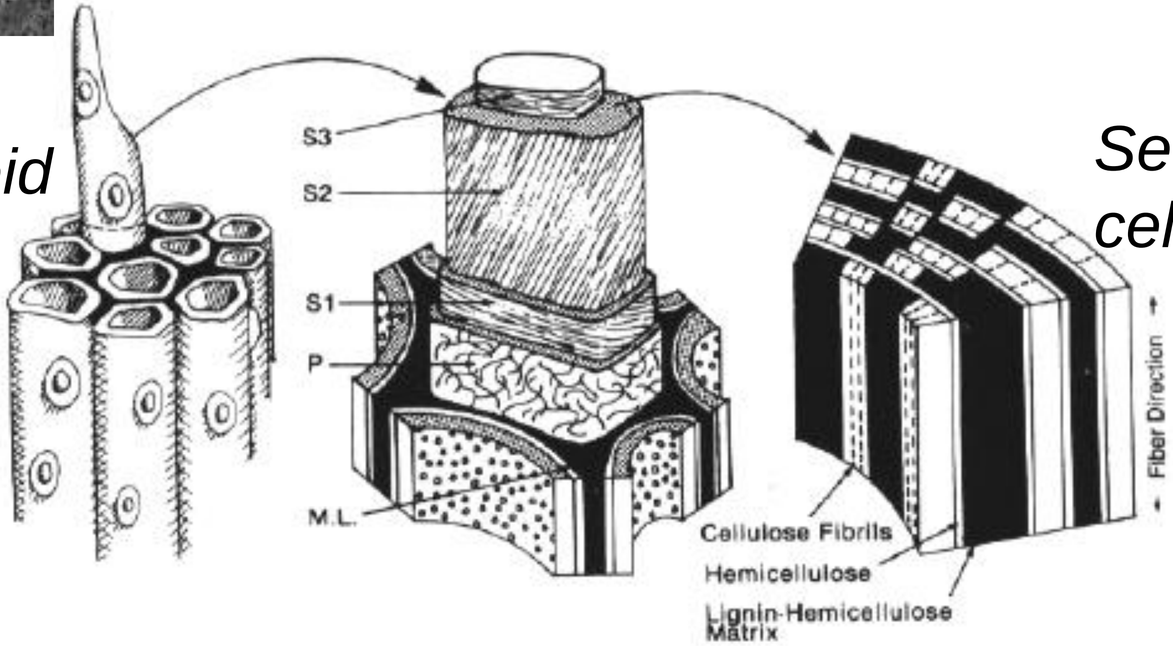


lignin



Pre-treatment of ligno-cellulosic biomass: Cell wall

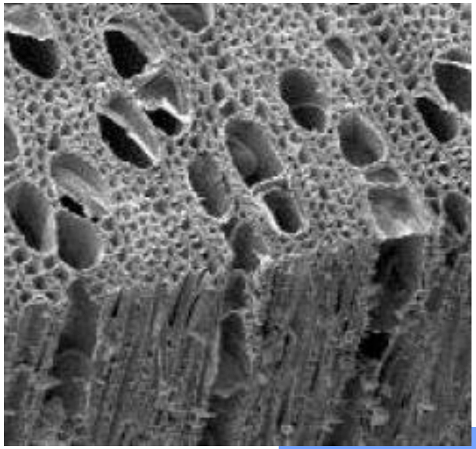
***Tracheids** are elongated cells of vascular plants that serve in the transport of water and mineral salts.*



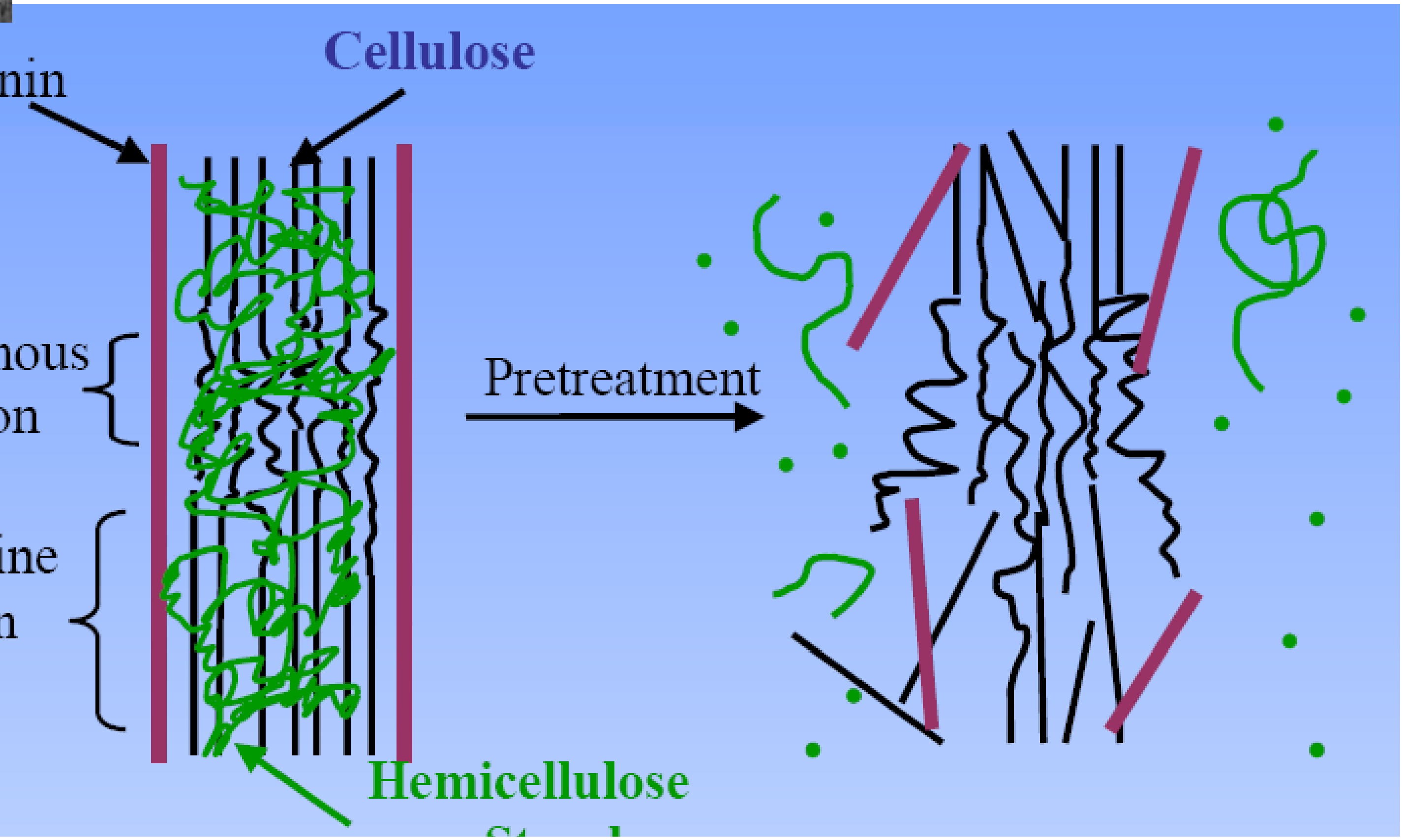
Tracheid
25 µm

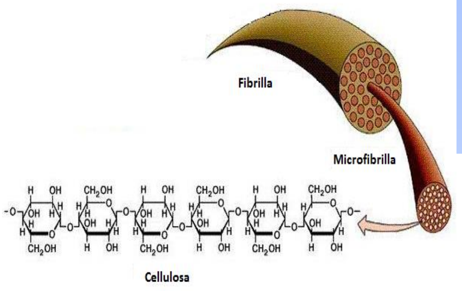
Secondary
cell wall

S1-S3: Secondary cell wall layers
P: primary wall
M.L.: middle lamella



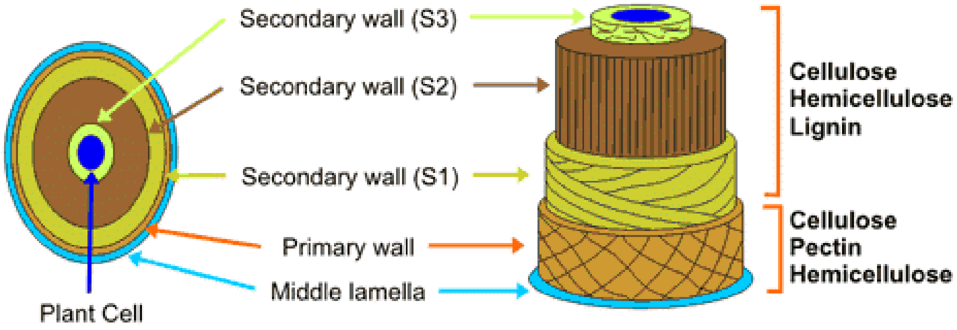
Lignocellulosic biomass: cell wall must be “cracked” open to allow complete enzymatic hydrolysis





Plant cell wall

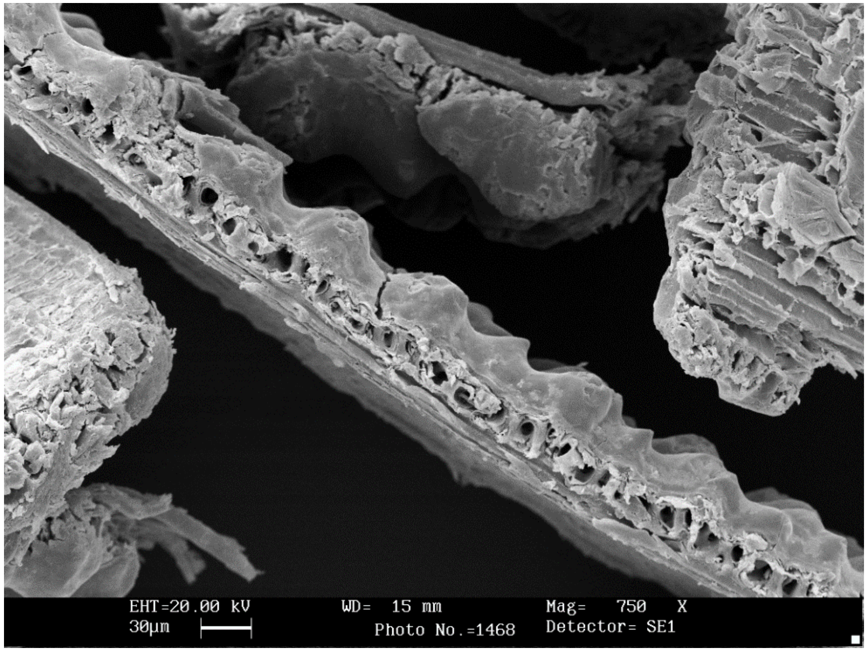
The cell walls contains layers of cellulose fibers interspersed within a hemicellulose packing. Adjacent cell walls are cemented together by <u>pectins</u> in a layer called the ***middle lamella****.*
The cell wall forms outside the plasma membrane initially as a thin ***primary cell wall****. Thereafter, the primary cell wall may thicken or a more durable* ***secondary cell wall*** *can form between the primary cell wall and plasma membrane.*

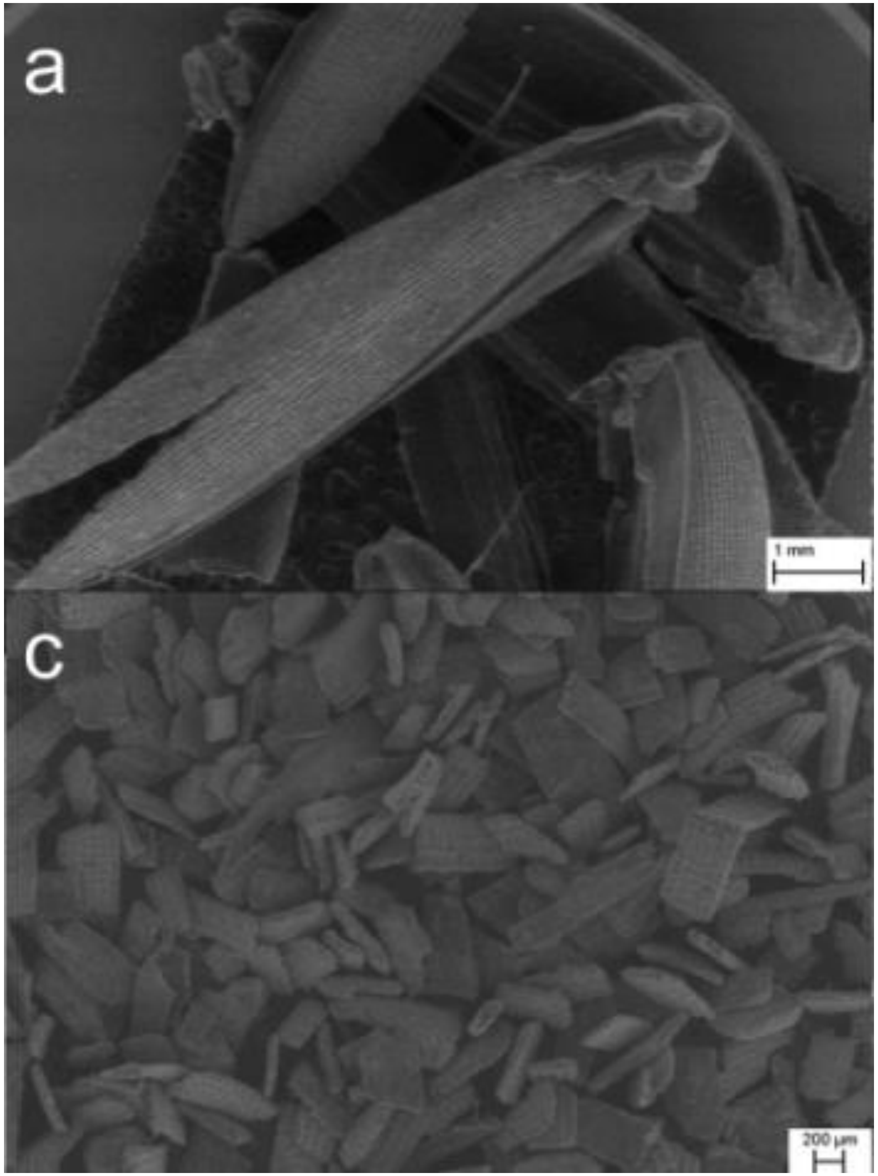


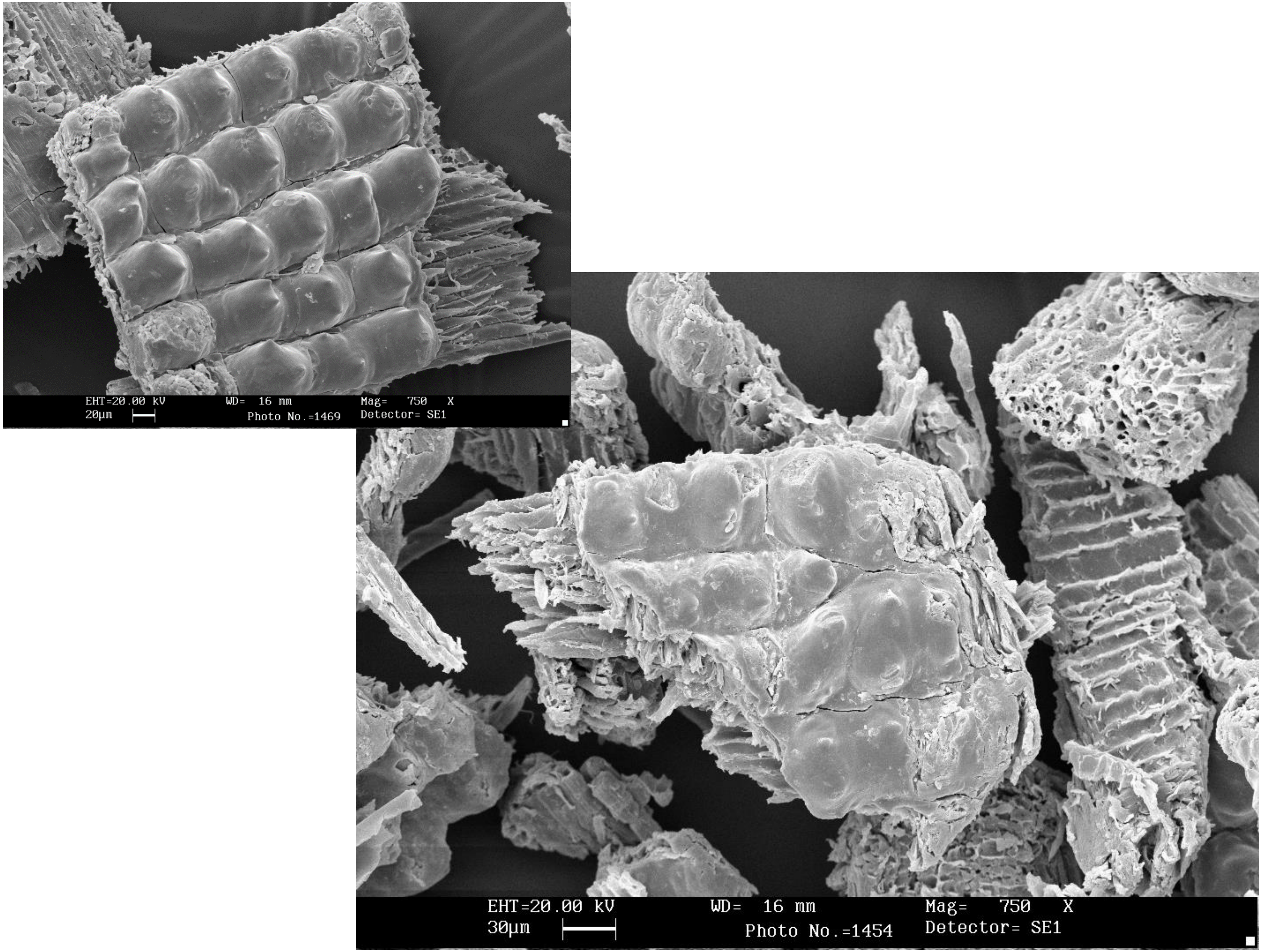
In plants, a ***secondary cell wall*** *is a thicker additional layer of cellulose which increases wall rigidity. Additional layers may be formed by lignin in xylem cell walls, or suberin in cork cell walls. These compounds are rigid and waterproof, making the secondary wall stiff. Wood and bark cells of trees have secondary walls. Other parts of plants such as the leaf stalk may acquire similar reinforcement to resist the strain of physical forces.*

Rice Husk

cellulose, hemicellulose, lignin, SiO_2



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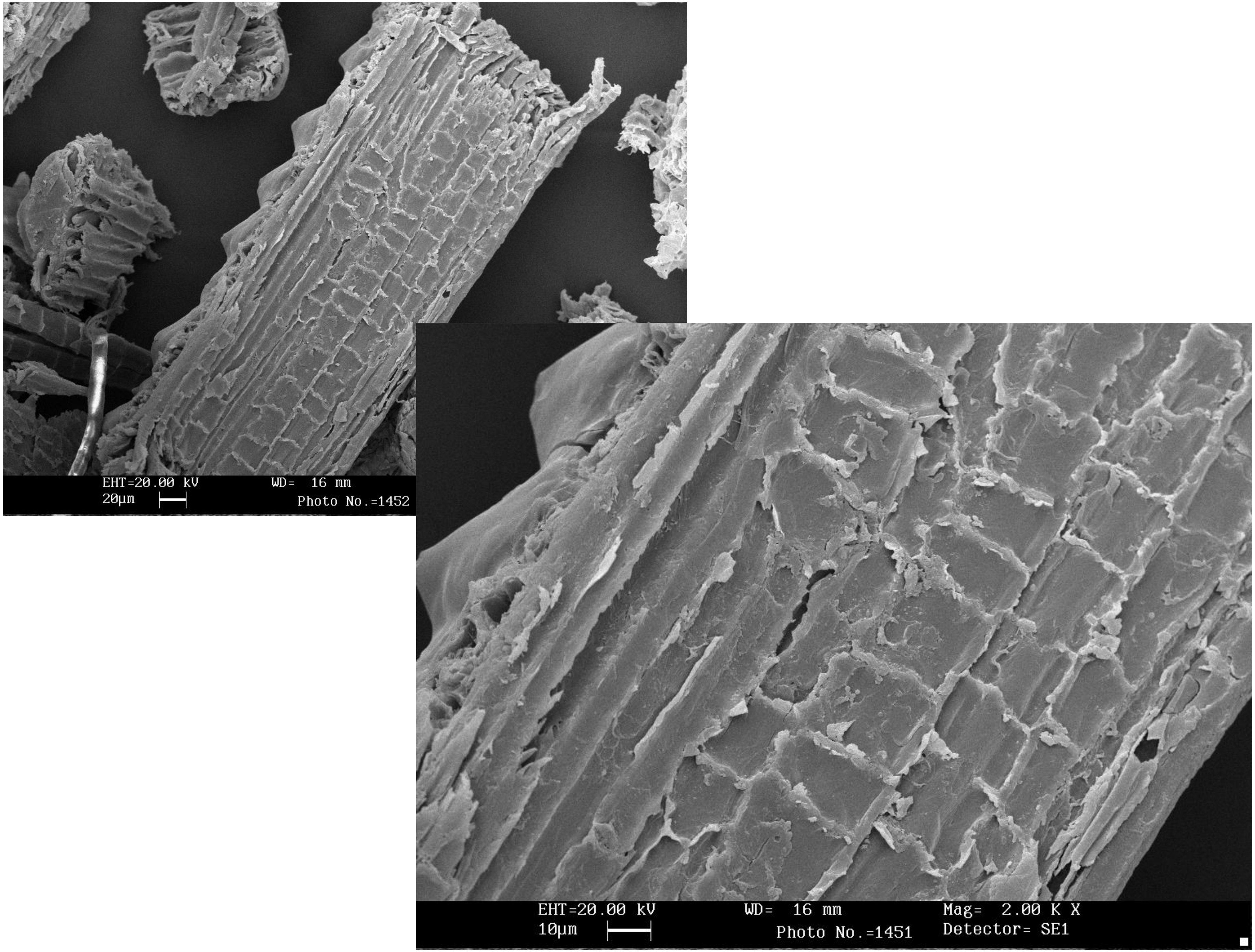
Il materiale dopo la macinatura conserva in parte la morfologia della superfice superiore ed inferiore. Dalle figure si osserva l'organizzazione della regione interna della lolla di riso. Nel tessuto interno sono presenti in parte strutture fibrose tubolari, che costituiscono il tessuto meccanico del materiale, ma anche i singoli elementi di conduzione dell'acqua e di nutrienti (denominati trachee o tracheidi). In ogni caso la struttura vascolare che si osserva è composta da cellule vegetali morte a maturità di cui sono rimaste solo le pareti lignocellulosiche, contenenti un'alta percentuale di matrice polisaccaridica. Gli ingrandimenti delle sezioni della lolla di riso mostrano come le fibre lignocellulosiche risultino essere più esposte a seguito della macinatura.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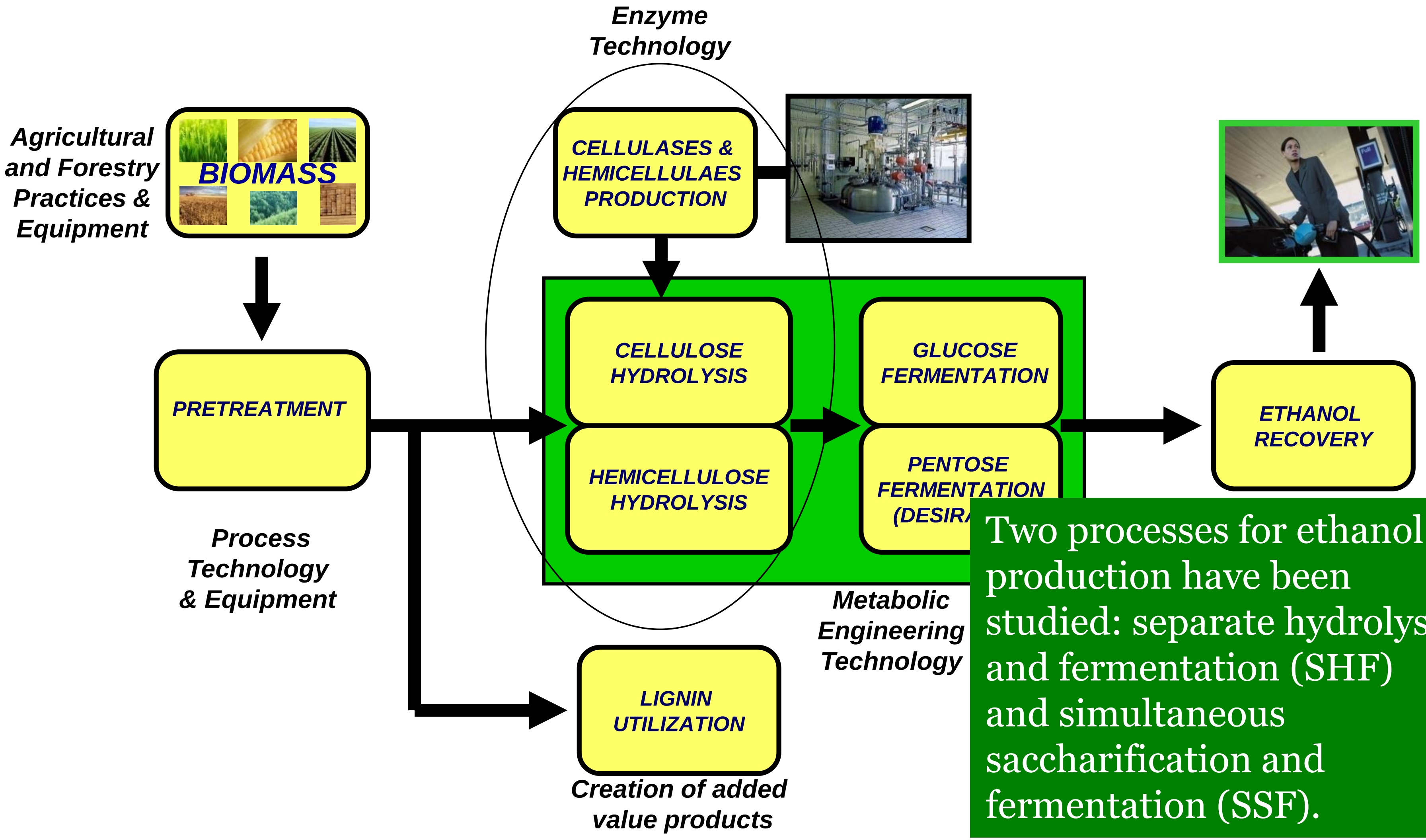
Fuel ethanol from lignocellulosic feedstocks: second generation bioethanol.

Beyond completion for food and land use



Agricultural and Forestry Practices & Equipment

BIOMASS

PRETREATMENT

Process Technology & Equipment

Enzyme Technology

CELLULASES & HEMICELLULAES PRODUCTION

CELLULOSE HYDROLYSIS

HEMICELLULOSE HYDROLYSIS

GLUCOSE FERMENTATION

PENTOSE FERMENTATION (DESIRA

Metabolic Engineering Technology

ETHANOL RECOVERY

LIGNIN UTILIZATION

Creation of added value products

Two processes for ethanol production have been studied: separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF).

Pretreatment before enzymatic hydrolysis of cellulose

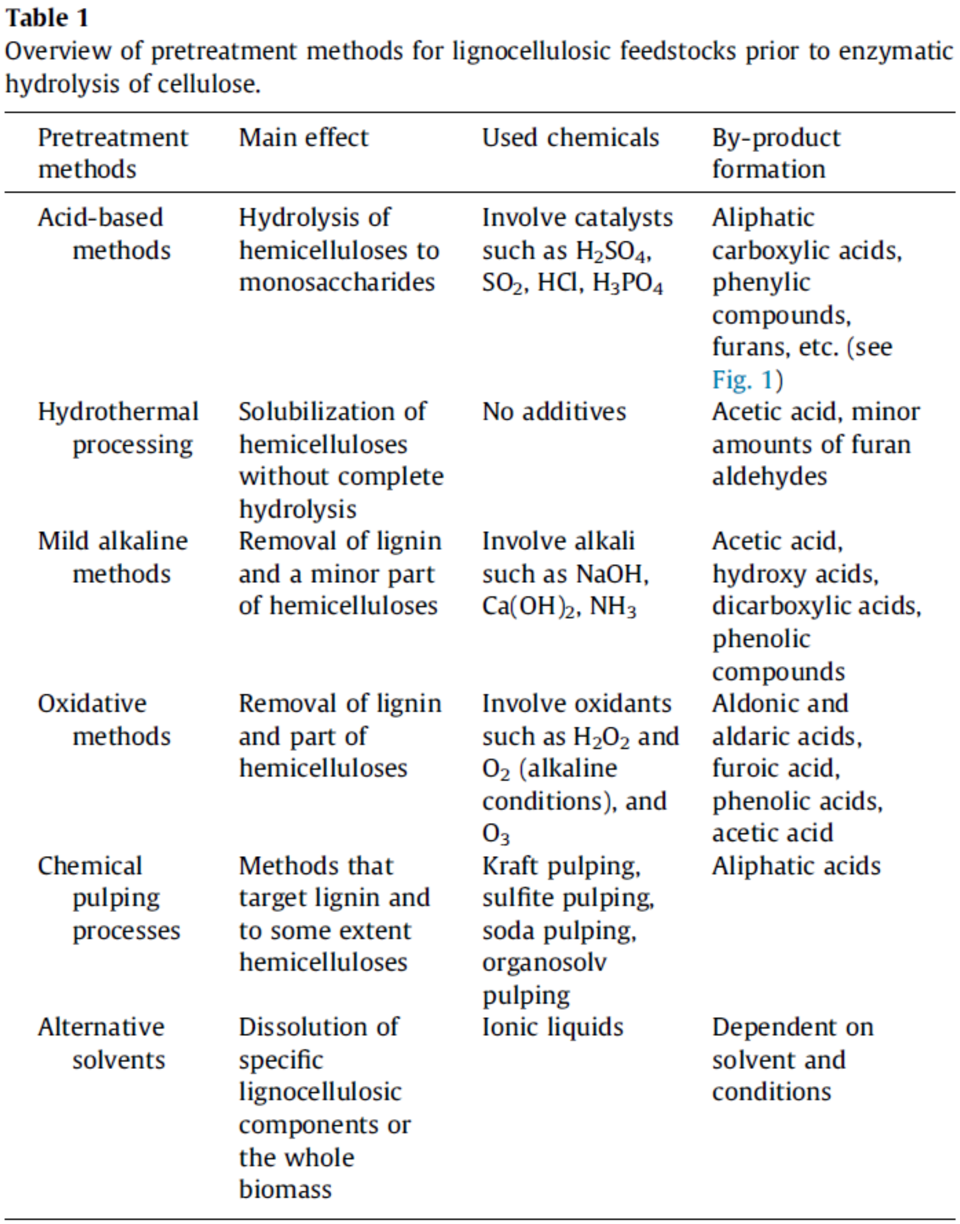
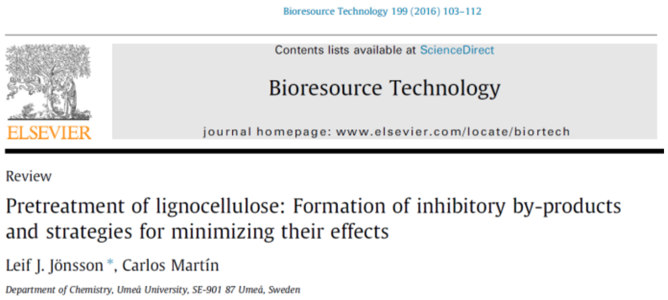


Table 1
Overview of pretreatment methods for lignocellulosic feedstocks prior to enzymatic hydrolysis of cellulose.

Pretreatment methods	Main effect	Used chemicals	By-product formation
Acid-based methods	Hydrolysis of hemicelluloses to monosaccharides	Involve catalysts such as H_2SO_4, SO_2, HCl, H_3PO_4	Aliphatic carboxylic acids, phenylic compounds, furans, etc. (see Fig. 1)
Hydrothermal processing	Solubilization of hemicelluloses without complete hydrolysis	No additives	Acetic acid, minor amounts of furan aldehydes
Mild alkaline methods	Removal of lignin and a minor part of hemicelluloses	Involve alkali such as NaOH, $Ca(OH)_2$, NH_3	Acetic acid, hydroxy acids, dicarboxylic acids, phenolic compounds
Oxidative methods	Removal of lignin and part of hemicelluloses	Involve oxidants such as H_2O_2 and O_2 (alkaline conditions), and O_3	Aldonic and aldaric acids, furoic acid, phenolic acids, acetic acid
Chemical pulping processes	Methods that target lignin and to some extent hemicelluloses	Kraft pulping, sulfite pulping, soda pulping, organosolv pulping	Aliphatic acids
Alternative solvents	Dissolution of specific lignocellulosic components or the whole biomass	Ionic liquids	Dependent on solvent and conditions



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Review

Pretreatment of lignocellulose: Formation of inhibitory by-products and strategies for minimizing their effects

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Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden

Acid hydrolysis is one of the most promising pretreatment methods with respect to industrial implementation. It is usually performed with mineral acids, but organic acids and sulfur dioxide
are other options.

Dilute sulfuric acid pretreatment has been studied for a wide range of lignocellulosic biomass .

It results in high recovery of the hemicellulosic sugars in the pretreatment liquid, and in a solid cellulose fraction with enhanced enzymatic convertibility. Acid pretreatment has also some drawbacks, such as high cost of the materials used for construction of the reactors, gypsum formation during neutralization after treatment with sulfuric acid, and formation of inhibitory by-products.

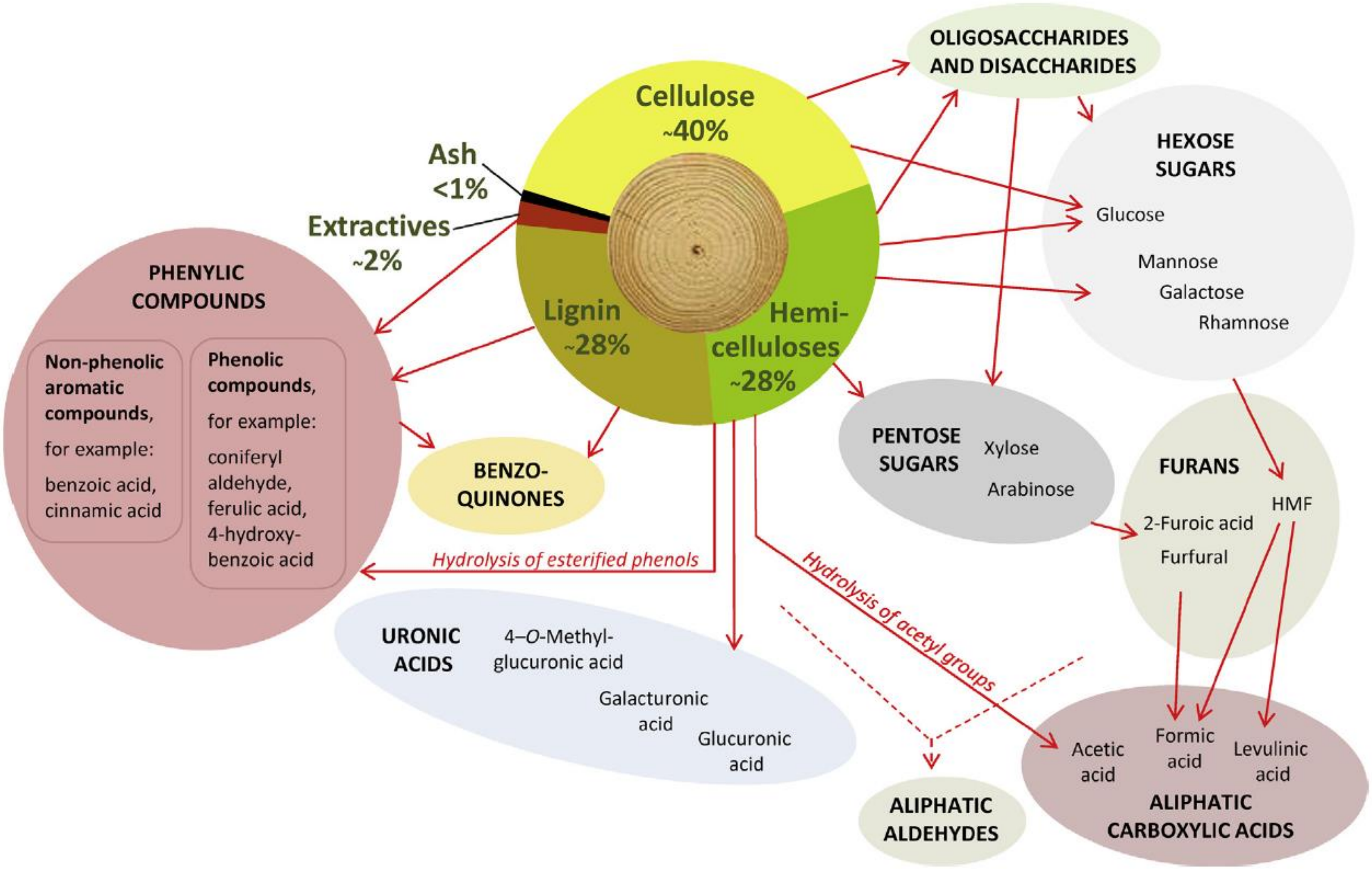


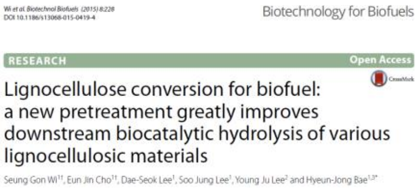
Fig. 1. Degradation products from lignocellulose as a result of pretreatment under acidic conditions. Numbers indicate fractions of constituents of wood of Norway spruce. Red arrows indicate tentative formation pathways. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Steam explosion is a successful pretreatment option that involves heating lignocellulose with superheated steam followed by a sudden decompression.

The high-pressure steam modifies the cell wall structure, yielding a slurry, which upon filtration renders a filtrate with hemicellulosic sugars and a cellulose-rich filter cake containing also lignin and residual hemicellulose.

Steam explosion can be assisted by impregnation with an acid catalyst, for instance sulfuric acid or sulfur dioxide. If no impregnating agent is used, the process is catalyzed through autohydrolysis.

Acetic acid and uronic acids released from hemicellulose, and formic and levulinic acids resulting from sugar degradation contribute to acidification, and can inhibit downstream biochemical processes.


Wi et al. Biotechnol Biofuels (2015) 8:228
DOI 10.1186/s13068-015-0419-4

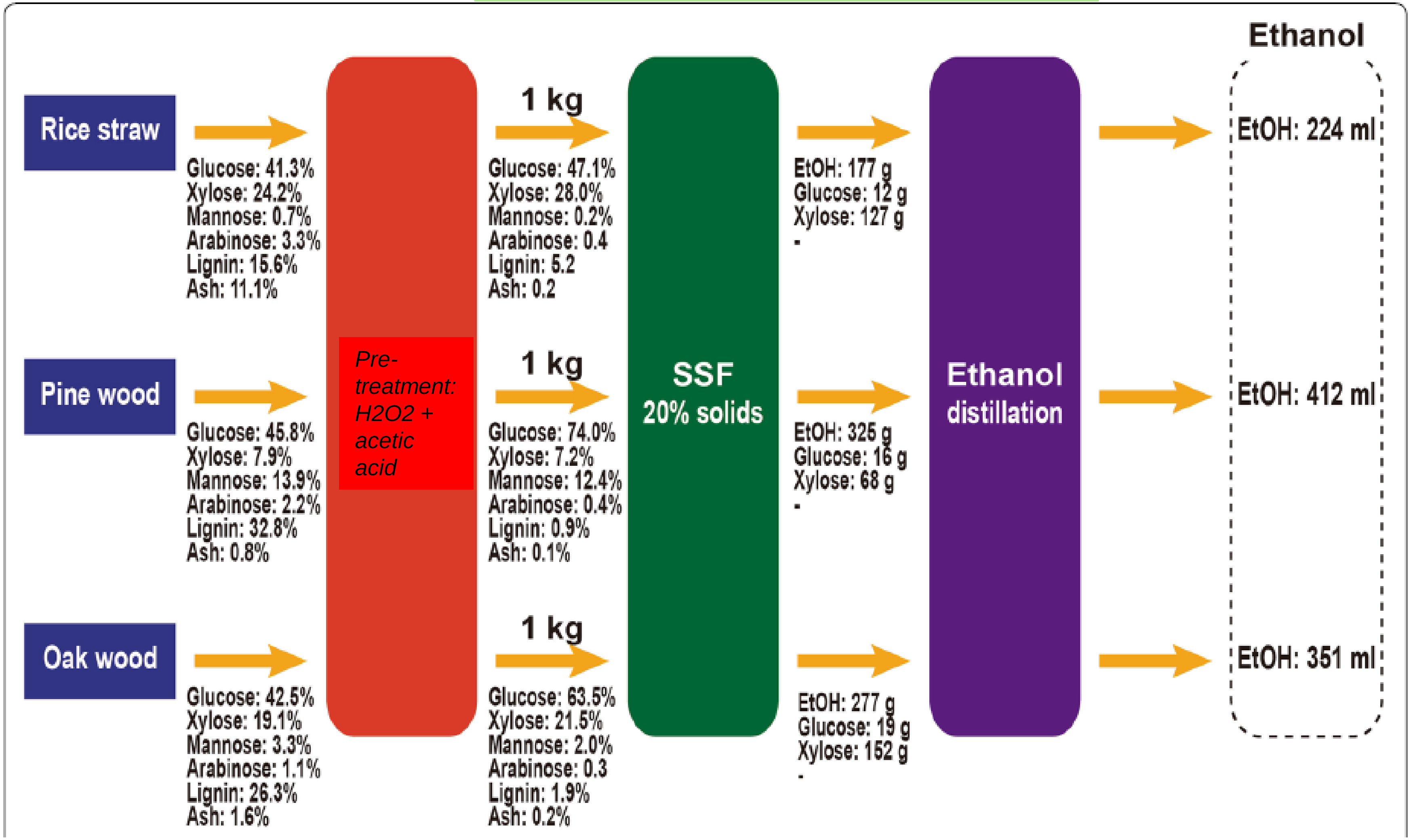
Biotechnology for Biofuels

RESEARCH Open Access

Lignocellulose conversion for biofuel: a new pretreatment greatly improves downstream biocatalytic hydrolysis of various lignocellulosic materials

Seung Gon Wi[1†], Eun Jin Cho[1†], Dae-Seok Lee[1], Soo Jung Lee[1], Young Ju Lee[2] and Hyeun-Jong Bae[1,3*]

Pre-treatment:
H_2O_2 + acetic acid



Rice straw

Glucose: 41.3%
Xylose: 24.2%
Mannose: 0.7%
Arabinose: 3.3%
Lignin: 15.6%
Ash: 11.1%

Pine wood

Glucose: 45.8%
Xylose: 7.9%
Mannose: 13.9%
Arabinose: 2.2%
Lignin: 32.8%
Ash: 0.8%

Oak wood

Glucose: 42.5%
Xylose: 19.1%
Mannose: 3.3%
Arabinose: 1.1%
Lignin: 26.3%
Ash: 1.6%

Pre-treatment: H2O2 + acetic acid

1 kg

Glucose: 47.1%
Xylose: 28.0%
Mannose: 0.2%
Arabinose: 0.4
Lignin: 5.2
Ash: 0.2

1 kg

Glucose: 74.0%
Xylose: 7.2%
Mannose: 12.4%
Arabinose: 0.4%
Lignin: 0.9%
Ash: 0.1%

1 kg

Glucose: 63.5%
Xylose: 21.5%
Mannose: 2.0%
Arabinose: 0.3
Lignin: 1.9%
Ash: 0.2%

SSF
20% solids

EtOH: 177 g
Glucose: 12 g
Xylose: 127 g
-

EtOH: 325 g
Glucose: 16 g
Xylose: 68 g
-

EtOH: 277 g
Glucose: 19 g
Xylose: 152 g
-

Ethanol
distillation

Ethanol

EtOH: 224 ml

EtOH: 412 ml

EtOH: 351 ml

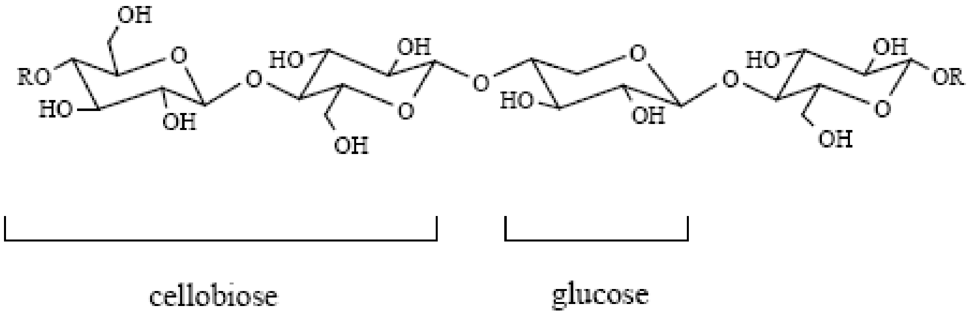
simultaneous saccharification and fermentation (SSF)

Cellulases: Cellulose enzymatic degradation

The polysaccharide consists of D-glucose residues linked by ß-1,4-glycosidic bonds to form linear polymeric chains of over 10 000 glucose residues.

The individual chains adhere to each other along their lengths by hydrogen bonding and van der Waals forces, and crystallise shortly after biosynthesis.

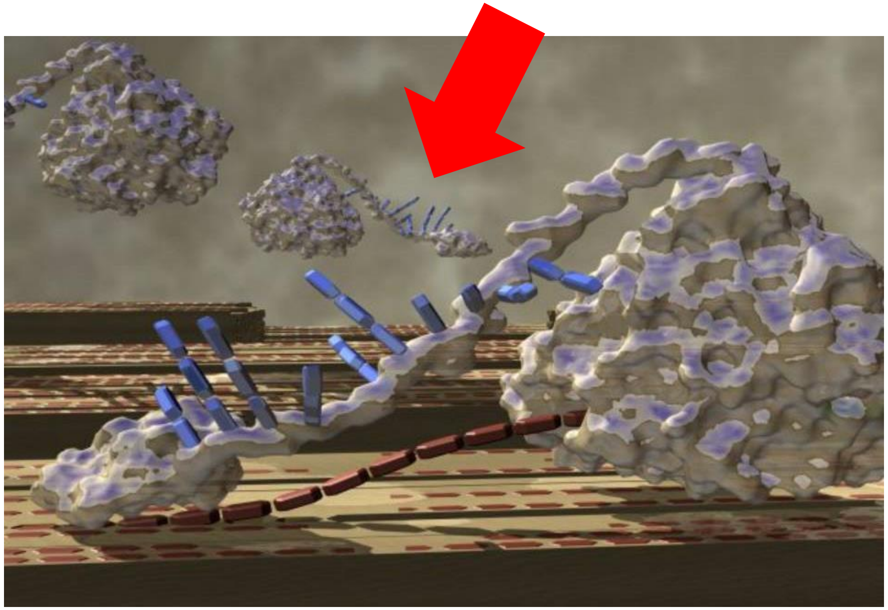
Multiple enzyme systems are required to efficiently degrade cellulose.

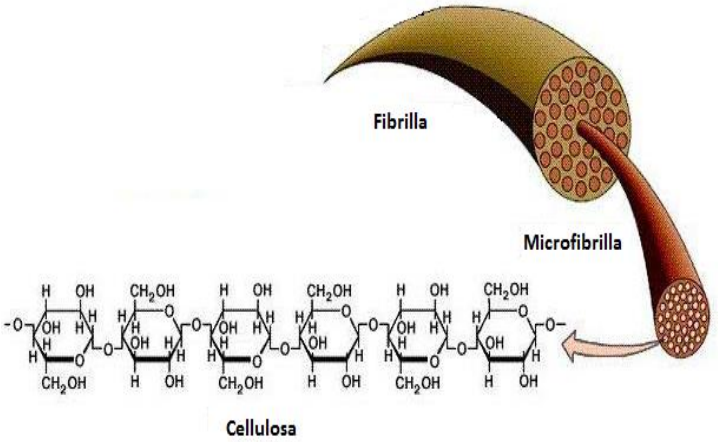


cellulose

Mechanism of cellulose hydrolysis

All cellulolytic enzymes share the same chemical specificity for ß-1,4-glycosidic bonds, which they cleave by a general acid-catalysed hydrolysis. A common feature of most cellulases in different fungal genera is a domain structure with a catalytic domain linked with an extended linker region to a cellulose-binding domain

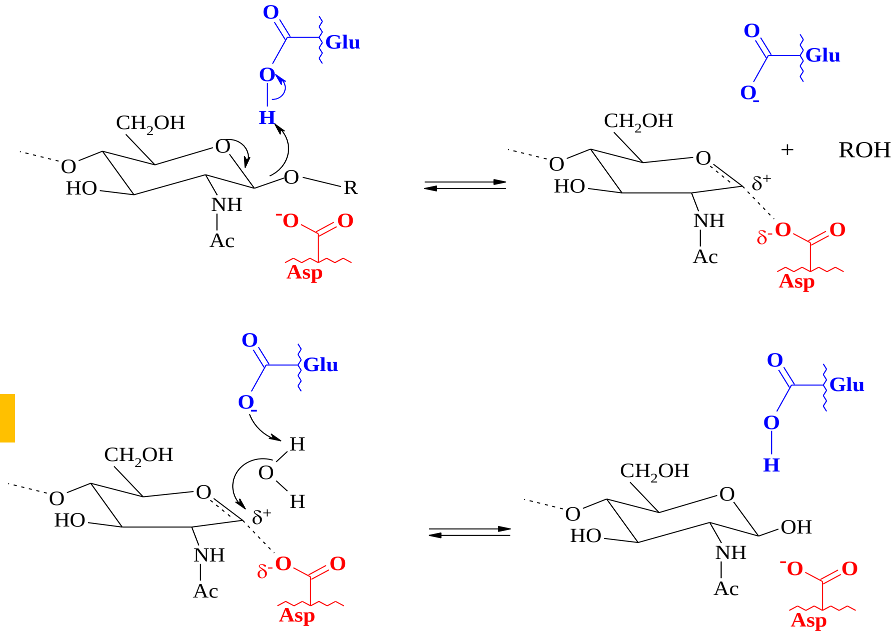




Ref: Himmel, M. et al, NREL (2000)

Mechanism of Glycosidases (hydrolases)

Mechanism: the glycosidic oxygen is protonated by the acid catalyst (i.e. the carboxylic function of a glutamic residue occurring on the glycosidase) and nucleophilic assistance to the departing aglycone is provided by a base (i.e. the charged carboxylate function of an aspartic residue); the resulting glycoside-enzyme is finally hydrolysed by water generating a stereocenter with the same configuration.

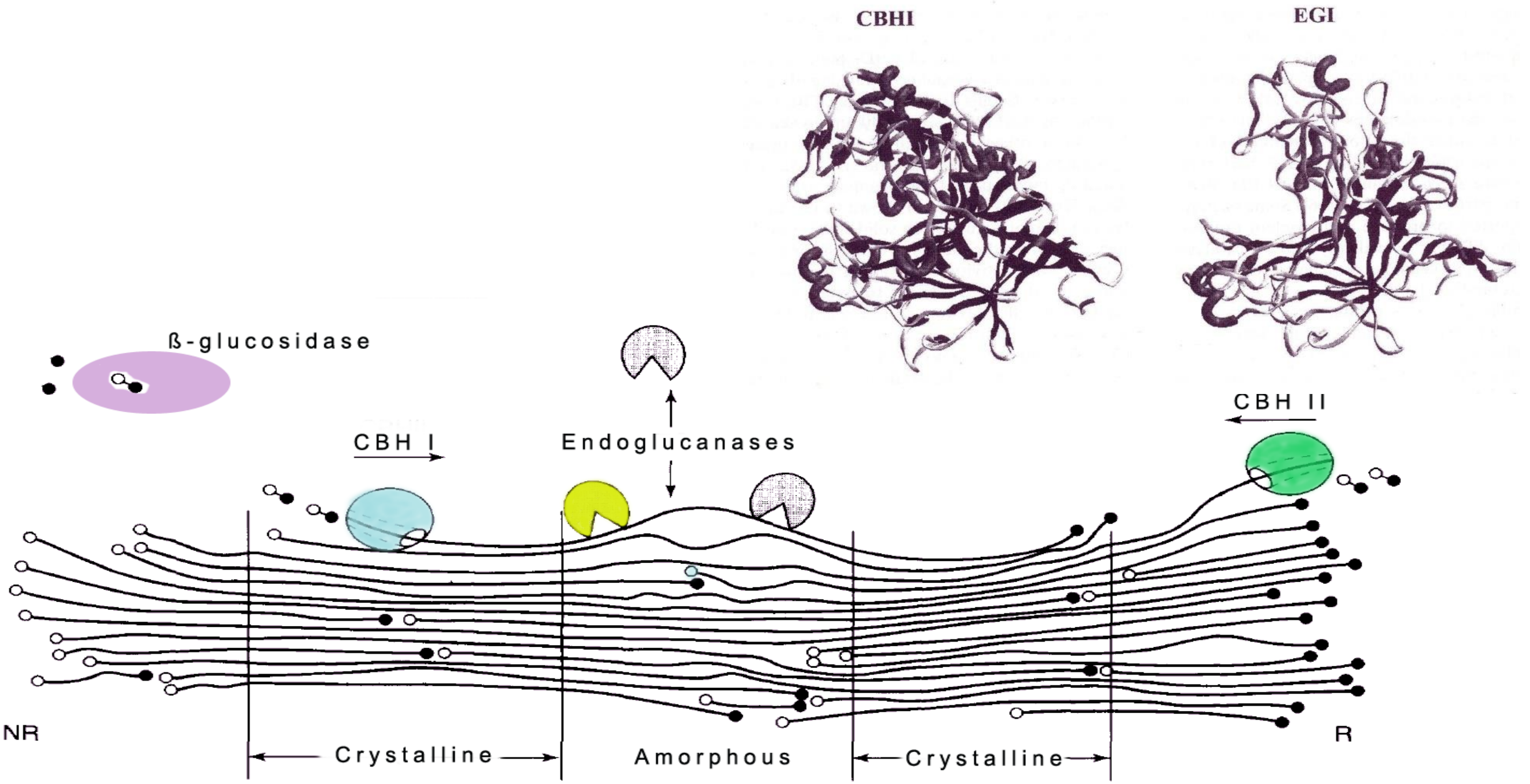


protonation

Glycoside-enzyme

Nucleophilic attack

Hydrolysis product



The complementary activities of endo- and exotype enzymes lead to synergy.

Endoglucanases (EGs, E.C. 3.2.1.4) attack cellulose microfibrils preferentially in the amorphic parts of the fibril. The catalytic region of the enzyme is groove-shaped that enables the attachment of the enzyme and the hydrolysis in the middle part of the cellulose fibre.

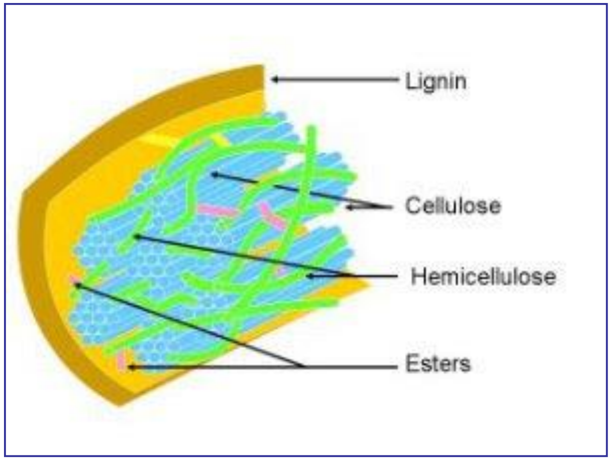
Cellobiohydrolases (CBHs, E.C. 3.2.1.91) are exo-type enzymes that attack cellulose fibres from both reducing and non-reducing ends. The product of CBH action, cellobiose is hydrolysed by ß-glucosidases (E.C. 3.2.1.21) to two glucose units.

Hemicellulose

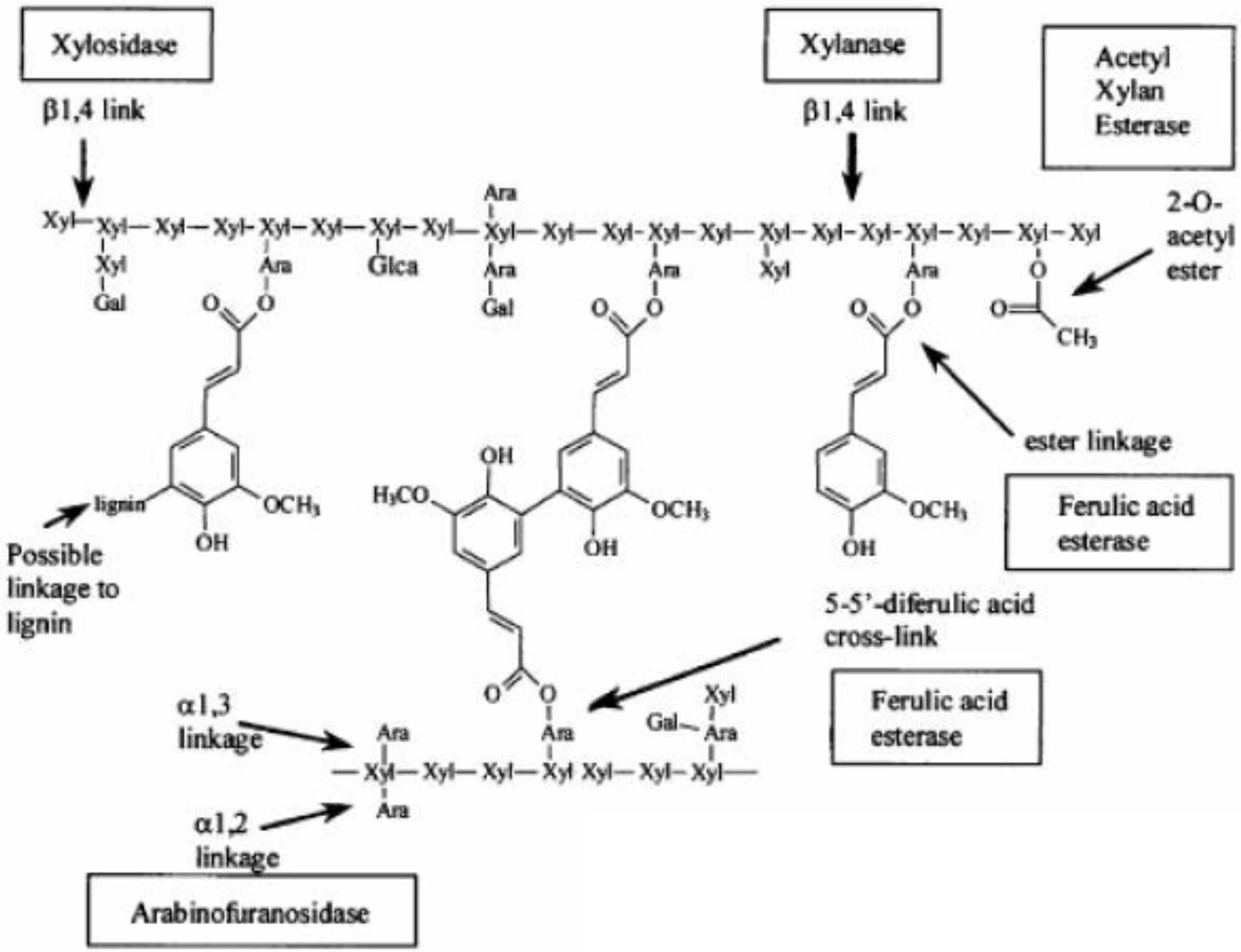
Hemicellulose consists of several different sugar units and substituted side chains in the form of a low molecular weight linear or branched polymer.

This polymer is more soluble than cellulose with a DP (degree of polimerzation) of less than 200.

Hemicellulose can be hydrolyzed by weak acid: it is not crystallin but rather a gel.



Branched polymers contain neutral and/or acidic side groups. These groups render hemicelluloses noncrystalline or poorly crystalline, so that they exist more like a gel than as oriented fibres.



Hemicelluloses form a matrix together with pectins and proteins in primary plant cell walls and with lignin in secondary cell walls.

Covalent hemicellulose-lignin bonds involving ester or ether linkages form lignin-carbohydrate-complexes (LCCs)

Cellulose *vs.* Hemicellulose

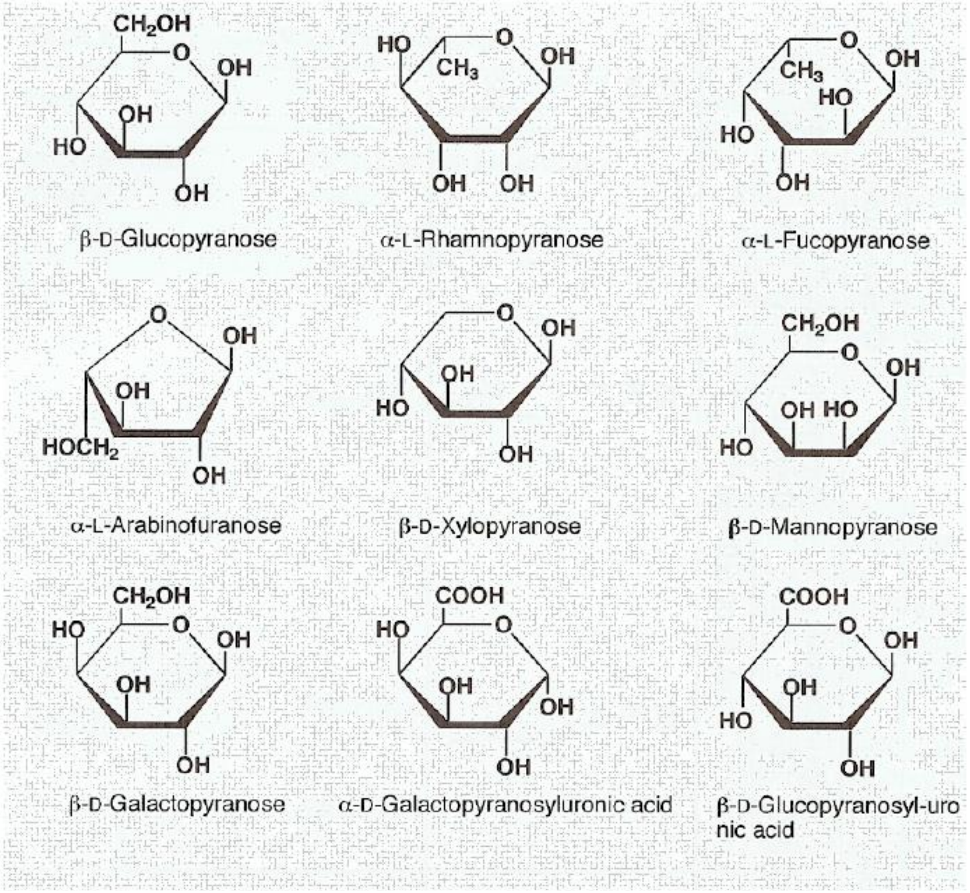
	Cellulose	Hemicellulose
Monomer	Pure glucose	Mixed sugars
Polymer chain length	Long (5μm)	Short
M.W.	High (10000 units)	Low (hundred units)
Polymer topology	Linear	Branched
Side groups substitution	No substitution	On C_2, C_3, and C_6
Polymer morphology	Crystalline + amorphous	Amorphous
Solubility	Low	High
Reactivity	Less reactive	More reactive
Hydrolysis	Partial	Readily (susceptible)

Principal Structural Difference between Cellulose and Hemicellulose

- Hemicellulose are mixed polymer, whereas cellulose is a pure polymer of glucose.
- Apart from arabinogalactan, which is heavily branched, the hemicellulose have short side-chains. Cellulose is a long unbranched polymer.
- Hemicellulose are low molecular weight polymers, however, cellulose has a very high degree of polymerization.
- Hemicellulose may have large side groups substituting for the hydroxyls on the C_2, C_3 and C_6 positions.
- The solubility and susceptibility to hydrolysis of hemicellulose are greater than cellulose. (low molecular weight and amorphous structures).

Hemicellulose

Hemicelluloses include xylan, glucuronoxylan, arabinoxylan, glucomannan, xyloglucan



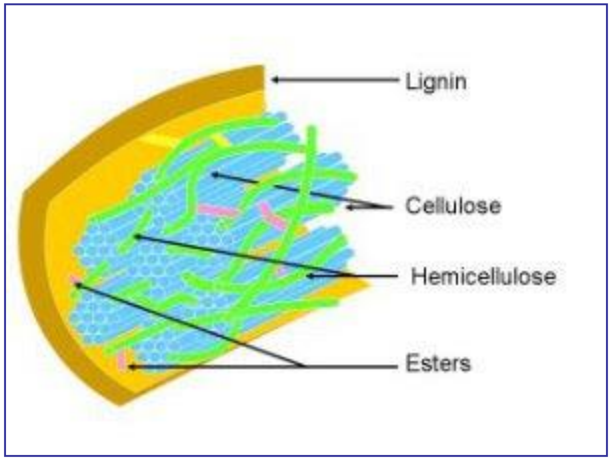


TABLE 3-5. The Major Hemicellulose Components

Hemicellulose type	Occurrence	Amount (% of wood)	Composition: Units	Composition: Molar ratios	Composition: Linkage	Solubility[a]	$\overline{\mathrm{DP}}_n$
Galactoglucomannan	Softwood	5–8	β-D-Man*p*	3	1 → 4	Alkali, water*	100
			β-D-Glc*p*	1	1 → 4		
			α-D-Gal*p*	1	1 → 6		
			Acetyl	1			
(Galacto)glucomannan	Softwood	10–15	β-D-Man*p*	4	1 → 4	Alkaline borate	100
			β-D-Glc*p*	1	1 → 4		
			α-D-Gal*p*	0.1	1 → 6		
			Acetyl	1			
Arabinoglucuronoxylan	Softwood	7–10	β-D-Xyl*p*	10	1 → 4	Alkali, dimethylsulfoxide*, water*	100
			4-*O*-Me-α-D-Glc*p*A	2	1 → 2		
			α-L-Ara*f*	1.3	1 → 3		
Arabinogalactan	Larch wood	5–35	β-D-Gal*p*	6	1 → 3, 1 → 6	Water	200
			α-L-Ara*f*	2/3	1 → 6		
			β-L-Ara*p*	1/3	1 → 3		
			β-D-Glc*p*A	Little	1 → 6		
Glucuronoxylan	Hardwood	15–30	β-D-Xyl*p*	10	1 → 4	Alkali, dimethylsulfoxide*	200
			4-*O*-Me-α-D-Glc*p*A	1	1 → 2		
			Acetyl	7			
Glucomannan	Hardwood	2–5	β-D-Man*p*	1–2	1 → 4	Alkaline borate	200
			β-D-Glc*p*	1	1 → 4		

[a] The asterisk represents a partial solubility.

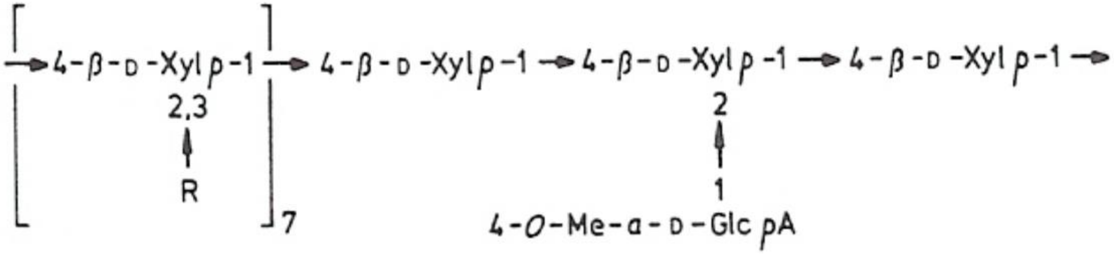
Hemicellulose – Softwood vs. Hardwood

- Softwood
  - Contains significantly more mannan, galactan and lignin
  - More mannan and less xylan in latewood than in earlywood
- Hardwood
  - Contains appreciable more xylan and acetyl.
- Softwoods have a high proportion of mannose units and more galactose units than hardwoods, and hardwoods have a high proportion of xylose units and more acetyl groups than softwood.

Hemicellulose in Hardwood - Glucuronoxylan

- **Xylose** is the most important hemicellulosic monomer followed by **mannose, glucose, galactose**, with small amount of arabinose and rhamnose.
- The xylose occurs predominantly as ***O*-acetyl-4-*O*-methylglucurono-xlan** (DP of 100-400).
- The basic skeleton of all xylans is a linear backbone of **β-D-1,4' xylopyraose** units.
  - Approximately 40 to 70% of the xylose units are **acetylated** on the **C_2 or C_3** position.
  - **D-glucuronic acid** or **4-*O*-methyl-D-glucuronic acid** groups usually attach themselves to about one in ten of the xylose residues in the main chain, by an α-link to the C_2, or occasionally to the C_3 position.

Abbreviated Formula of Glucuronoxylan



R: acetyl group

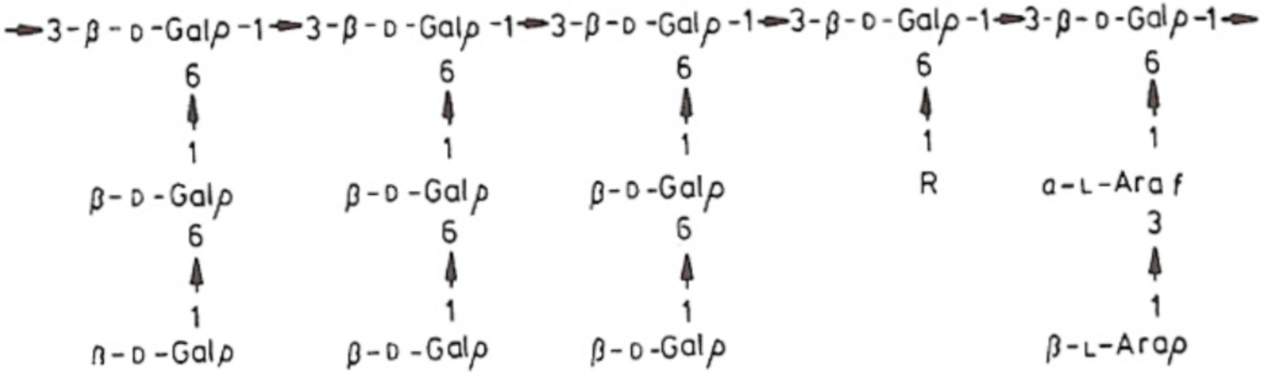
Hemicellulose in Hardwood - Glucomanna

- **Glucomannan** is present in hardwood but is of minor significance compared to the more abundant xylans.
- It is a linear **1,4’- copolymer** with no substitution on the C_2 and C_3 positions (DP of 60-70).
- The Glucose to mannose ratio varies from 1:1 to 1:2.

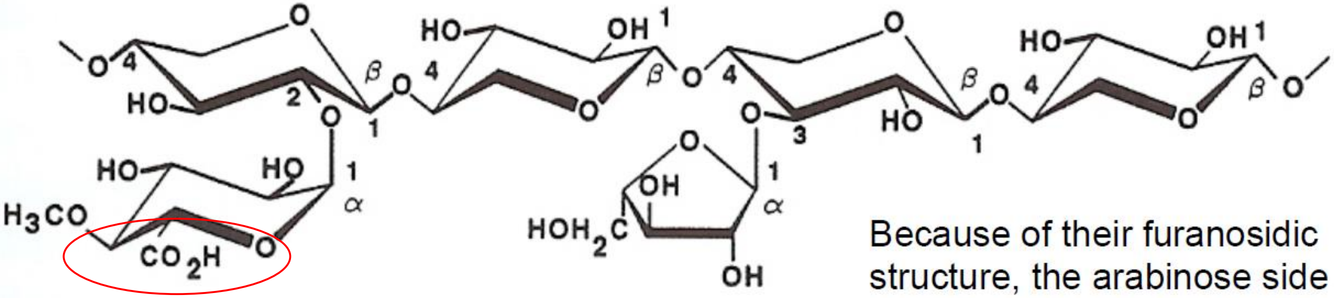
→4-β-D-Glcp-1→4-β-D-Manp-1→4-β-D-Glcp-1→4-β-D-Manp-1→4-β-D-Manp-1→

Hemicellulose in Softwood - arabinogalactan

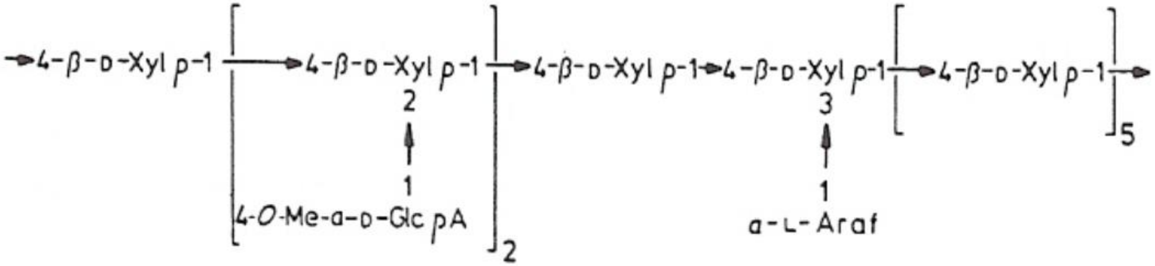
- Arabinogalactan’s backbone is build up by (1→3)-linked β-D-galactopyranose units.
- Almost every unit carries a branch attached to position 6, largely (1→6)-linked β-D-galactopyranose residues but also L- arabinose.



Principal Structure of Arabinoglucuronoxylan



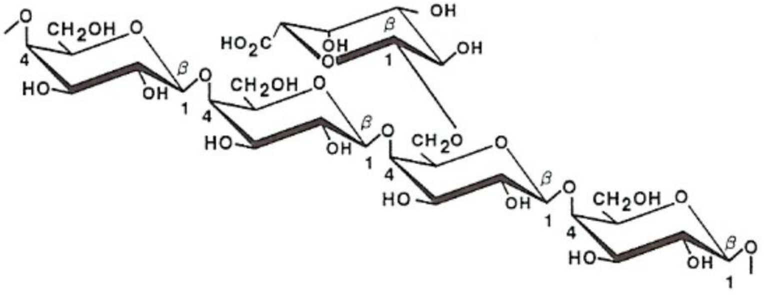
Because of their furanosidic structure, the arabinose side chains are easily hydrolyzed by acids.

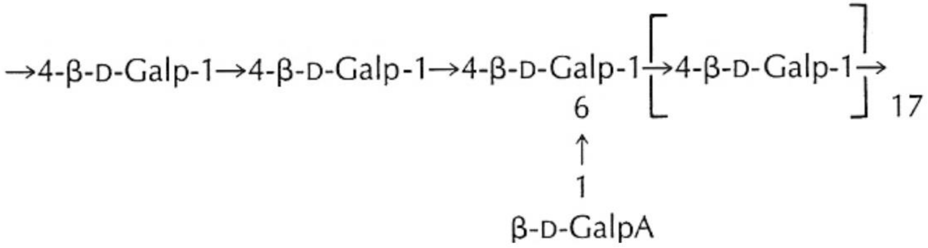


Both the arabinose and uronic acid substituents stabilize the xylan chain against alkali-catalyzed degradation.

- The backbone is composed of about 200 β-D-1,4' xylopyranose units which are partially substituted at C_2 position by 4-*O*-methyl-α-D-glucuronic acid groups (approximately one group for every 5-6 xylose units).
- Also an α-L-arabino-furanose units is linked by a 1,3' bond on approximately every 6 to 10 xylose units.

Principal Structure of Galactan in Compression Wood



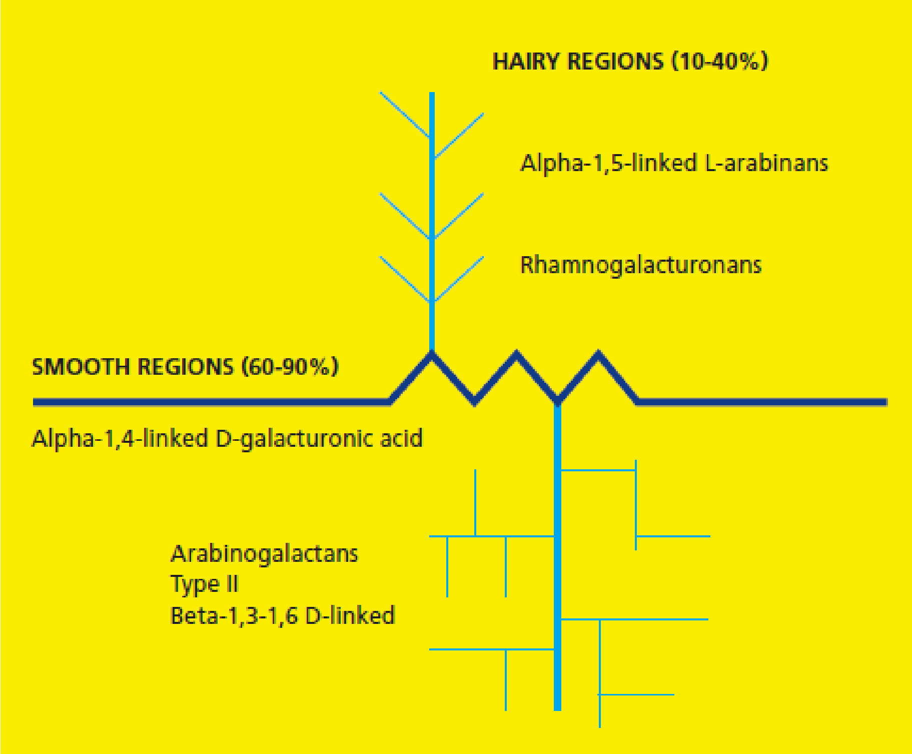


$$\rightarrow 4\text{-}\beta\text{-D-Gal}p\text{-}1\rightarrow 4\text{-}\beta\text{-D-Gal}p\text{-}1\rightarrow 4\text{-}\beta\text{-D-}\underset{\substack{6\\ \uparrow\\ 1\\ \beta\text{-D-Gal}p\text{A}}}{\text{Gal}p}\text{-}1\left[\rightarrow 4\text{-}\beta\text{-D-Gal}p\text{-}1\rightarrow\right]_{17}$$

- Galactans occur in minor quantities both in normal wood and tension wood, but high amounts are present in compression wood (about 10% of the wood weight).
- The backbone of galactans, which is slightly branched, is build up of (1→4)-linked β-D-galactopyranose units substituted at C-6 with α-D-galacturonic acid residues.

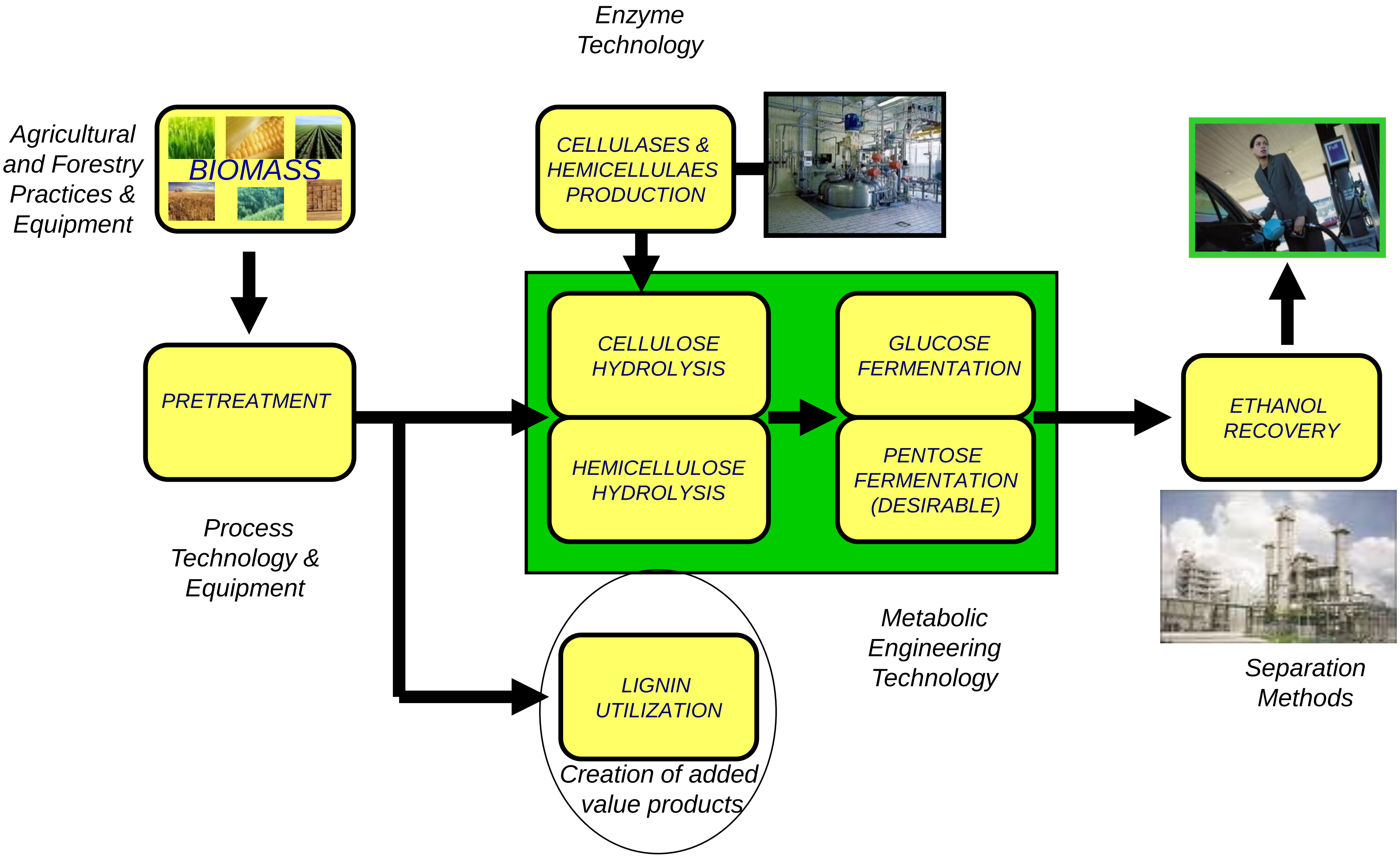
Pectin

- Group of amorphous polymers.
- rich in **galacturonic acid**
- They exist in nature both in a **methylesterified** and in a free **acidic** form.
- Polymers also contain neutral sugars, notably D-galactose, L-arabinose, L-rhamnose, D-xylose,



The hairy regions (shown as branches), are more difficult to break down

Lignin from biorefineries



Agricultural and Forestry Practices & Equipment

BIOMASS

PRETREATMENT

Process Technology & Equipment

Enzyme Technology

CELLULASES & HEMICELLULAES PRODUCTION

CELLULOSE HYDROLYSIS

HEMICELLULOSE HYDROLYSIS

GLUCOSE FERMENTATION

PENTOSE FERMENTATION (DESIRABLE)

Metabolic Engineering Technology

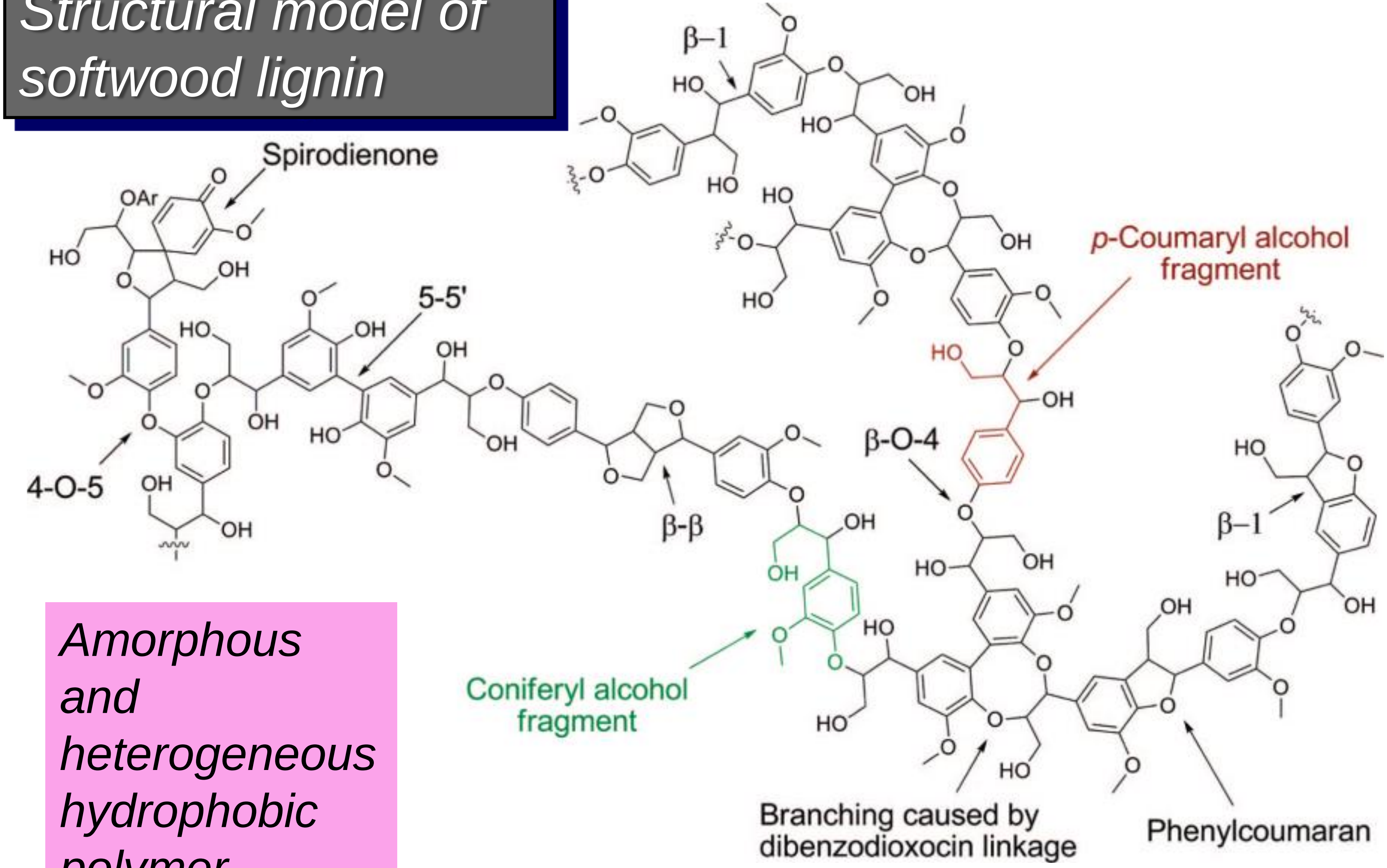
ETHANOL RECOVERY

Separation Methods

LIGNIN UTILIZATION

Creation of added value products

Structural model of softwood lignin



Amorphous and heterogeneous hydrophobic polymer

G. Brunow, “Oxidative coupling of phenols and the biosynthesis of lignin”, In: Lewis N.G. and Sarkanen S. Ed, “Lignin and lignan biosynthesis”, 1998 American Chemical Society, Washington, DC, p.131.

Use of lignin

The processing of 140 million tons cellulose and pulp in paper production lead to 50 million tons lignin

About 95% is burned
Only 5% reutilized

Opportunities that arise from utilizing lignin fit into three categories:

- *power, fuel and syngas (near-term)*
- *macromolecules (medium-term; <10y)*
- *aromatics and miscellaneous monomers (long-term; >10y)*

Potential applications of lignin

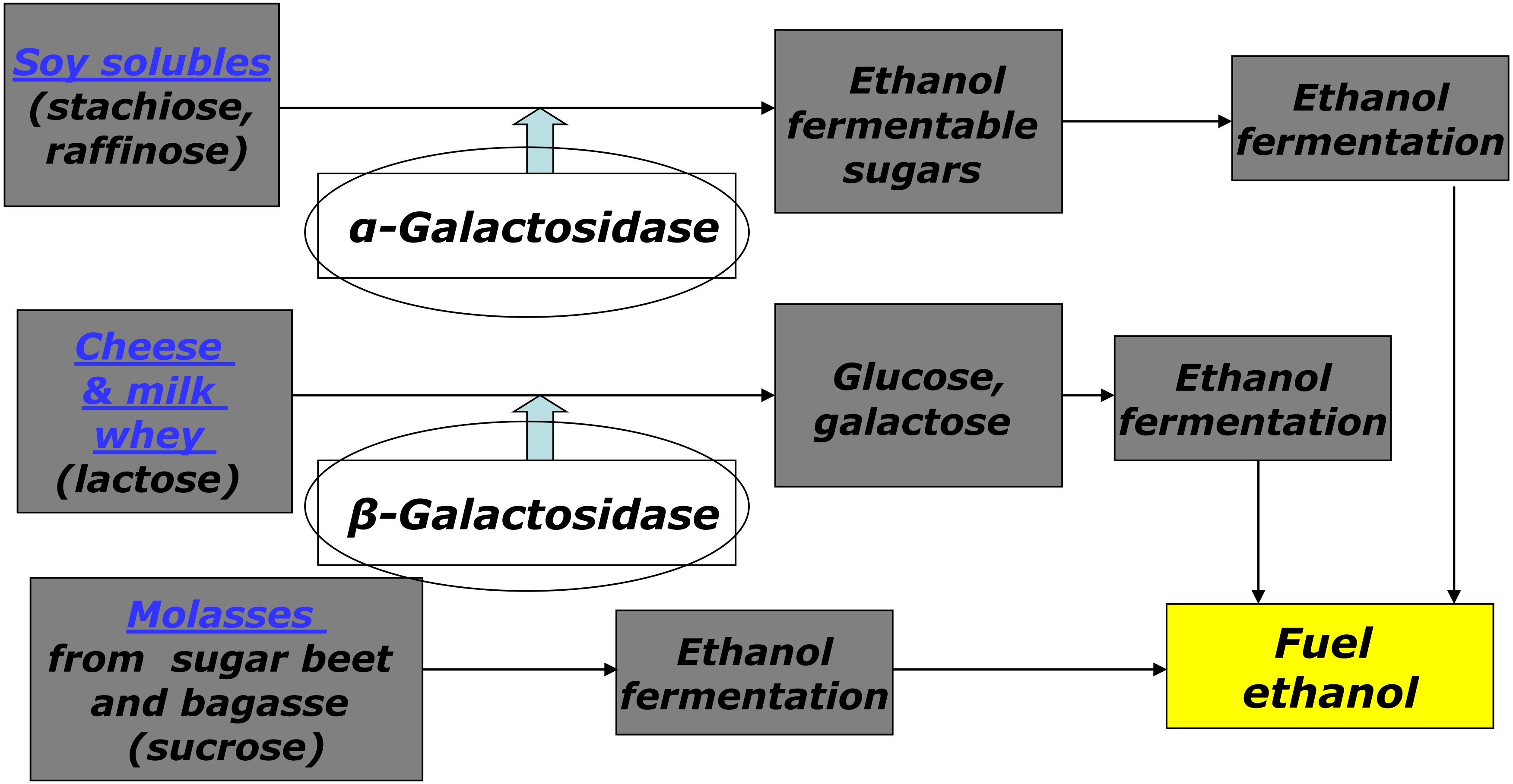
- ***Production of vanillin***
- ***Dimethyl sulfide***
- ***Methyl mercaptan***
- ***Dye dispersants***
- ***Pesticide dispersant***
- ***Carbon black dispersants***
- ***Water treatment / industrial cleaning***
- ***Complexing agents for micronutrients (Fe, Cu, Zn, Mn, B) for soils***
- ***Oil-weel cement retarders***
- ***Leather tanning***

Enzymes for lignin degradation: laccases (oxidative enzymes)

*Since **white-rot fungi** are the only organisms capable of efficient lignin degradation, their ligninolytic enzyme system has been studied extensively.*

Lignin polymer structure is irregular, which means that the degradative enzymes must show lower substrate specificity compared to the hydrolytic enzymes in cellulose or hemicellulose degradation.

Different Options for Second generation fuel ethanol



Soy solubles (stachiose, raffinose)

α-Galactosidase

Ethanol fermentable sugars

Ethanol fermentation

Cheese & milk whey (lactose)

β-Galactosidase

Glucose, galactose

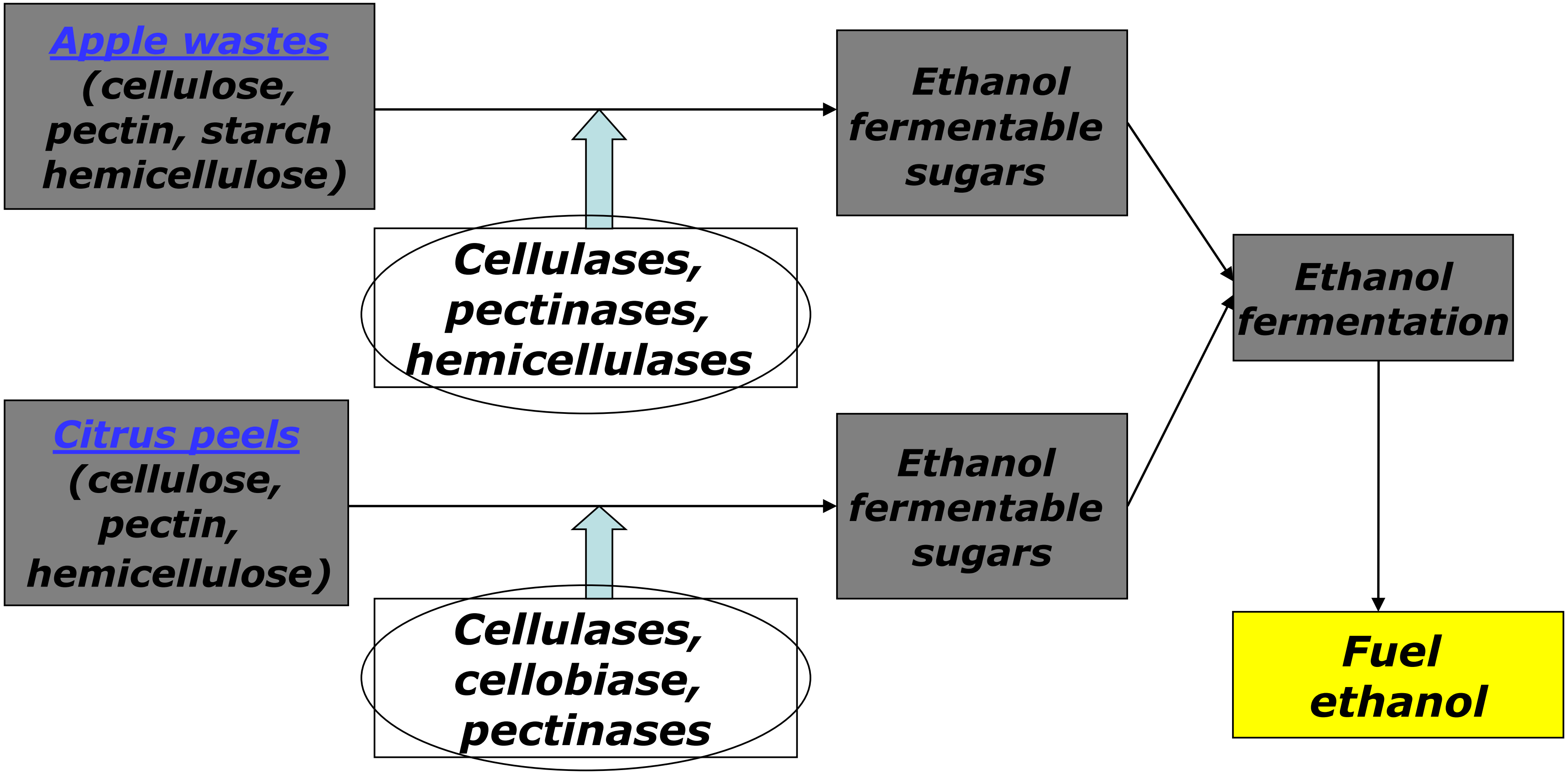
Ethanol fermentation

Molasses from sugar beet and bagasse (sucrose)

Ethanol fermentation

Fuel ethanol

Fuel ethanol from food & feed wastes



Apple wastes (cellulose, pectin, starch hemicellulose)

Cellulases, pectinases, hemicellulases

Ethanol fermentable sugars

Citrus peels (cellulose, pectin, hemicellulose)

Cellulases, cellobiase, pectinases

Ethanol fermentable sugars

Ethanol fermentation

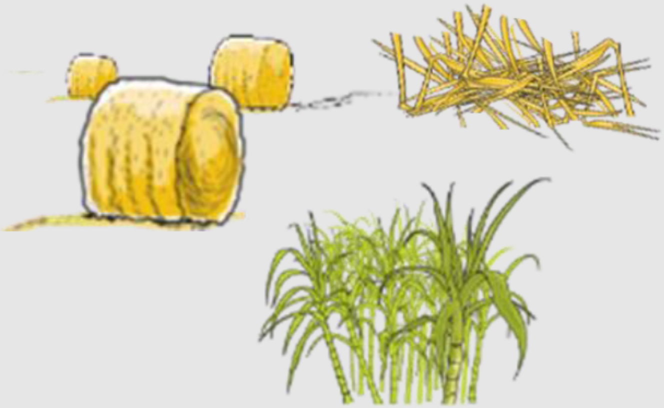
Fuel ethanol

Any biofuel capable to address all the policy obligations and long term expectations?

biochemtex

According to the current policy framework and expectations, post-2020 allowed biofuels shall feature at least:

- ✓ No competition vs food
- ✓ High GHG saving vs fossil
- ✓ Minimal use of land
- ✓ Price competition
- ✓ Technology innovation
- ✓ Benefits for rural areas



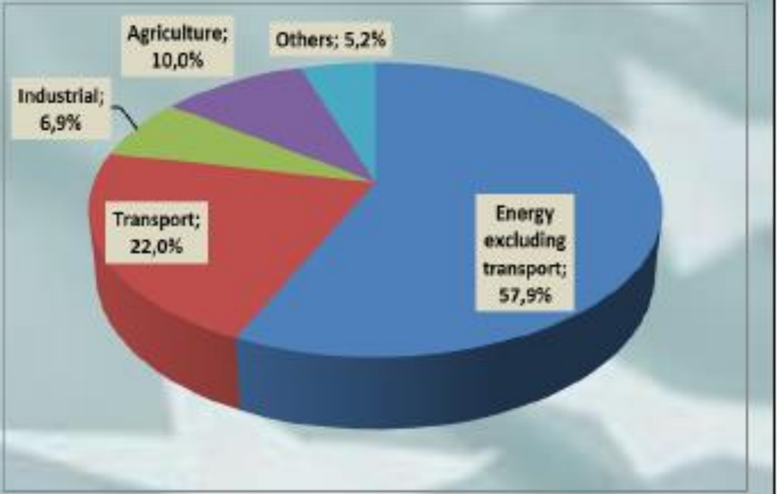
THIS IS WHAT WE CALL **ADVANCED BIOFUELS** !

SANDRO COBROR
Head of Public Affairs
Biochemtex spa

EU vision is a sustainable, low carbon and climate friendly economy

- In feb 2015 EC launched the Energy Union Package: low carbon technology, efficiency and job creation are the pillars and EU target -40% GHG emissions by 2030.
- BUT….
  - "Latest data shows that the EU imported 53% of its energy at a cost of around EUR 400 billion"
  - "94% of transport relies on oil products, of which 90% is imported"
  - 22% of GHG emissions relate to transport

In last 20 yrs transport emissions increased by 20% while all other sectors'emissions decreased by around 15-20%



SANDRO COBROR
Head of Public Affairs
Biochemtex spa

What is EU doing to address the trasport issue

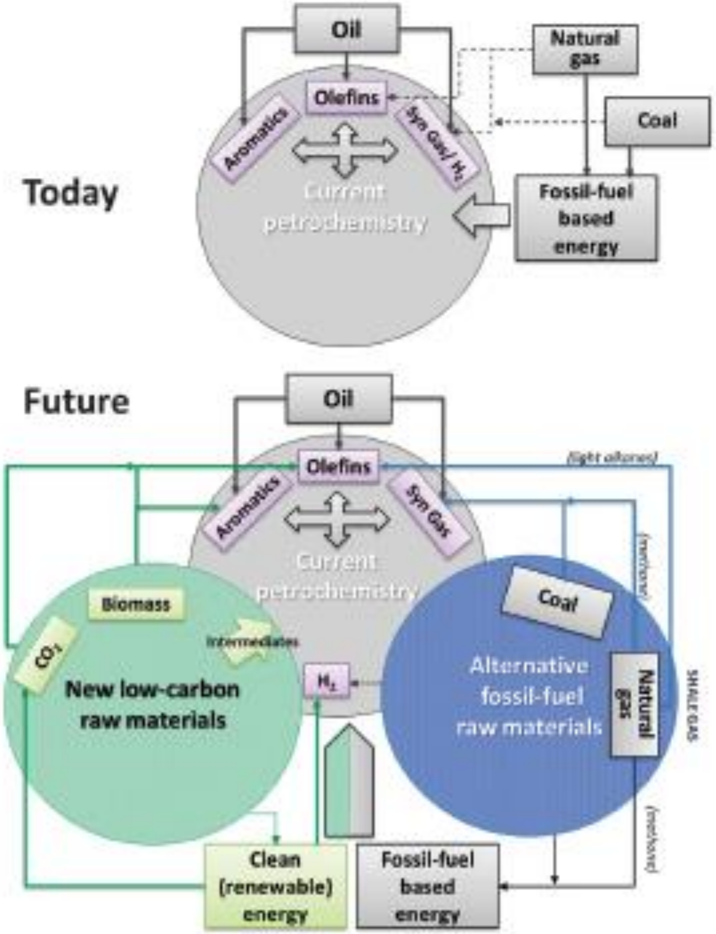
- 2009: Renewable Energy Directive sets 10% renewable energy in the transport sector by 2020. Only sustainable biofuels can be used to meet the target.
- 2012: ILUC Proposal. The Commission published a proposal to limit global land conversion for biofuel production, and raise the climate benefits of biofuels used in the EU. The use of food-based biofuels to meet the 10% renewable energy target of the RED should be limited.

Scenario in 2030 ?
Deglobalization and regional-based economic system

Chemical production will progressively move from an oil-centric common vision to different regional-based systems.

US: use of shale-gas,
China: coal
Middle East: oil
Europe: to remain competitive must foster the use of its own resources, biomass, waste and CO2

Considering 30% as the target for biomass substitution of fossil fuels in year 2030, and 50% as the average yield in converting biomass, the available biowaste is in excess.

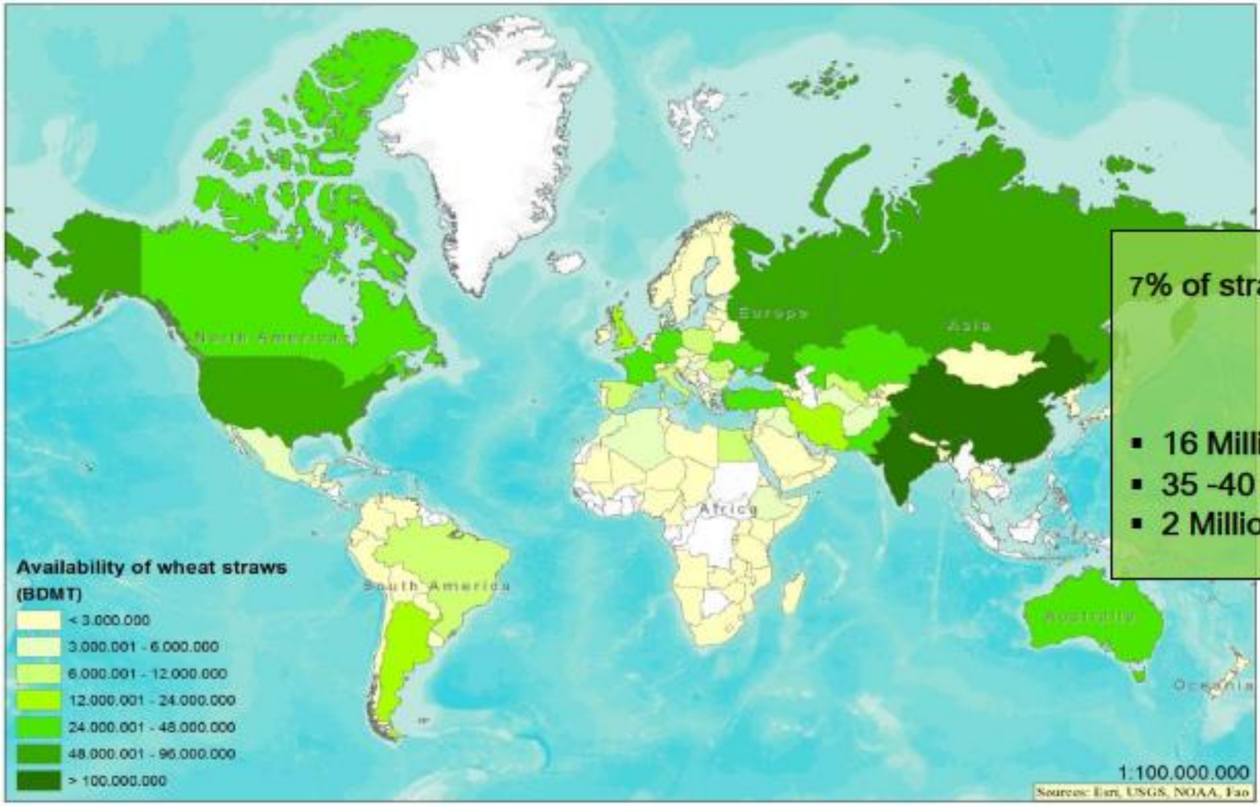



Cite this: *Chem. Soc. Rev.*, 2014, 43, 7562

Catalysis for biomass and CO_2 use through solar energy: opening new scenarios for a sustainable and low-carbon chemical production†

Paola Lanzafame, Gabriele Centi and Siglinda Perathoner*

Biomasses widely available worldwide: the wheat straw scenario



Sources: Esri, USGS, NOAA, Fao

7% of straw produced in EU :

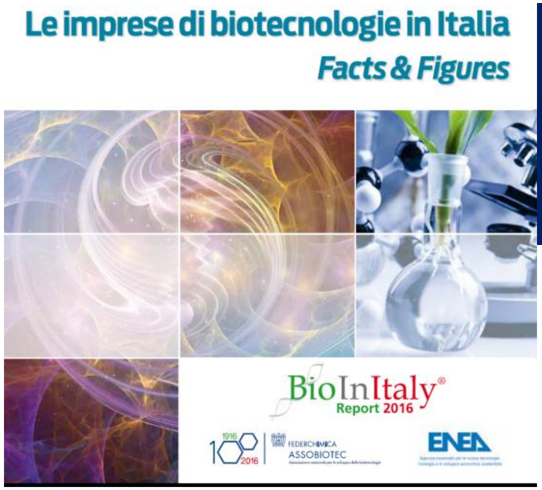
- 16 Million tons of biomass
- 35 -40 2G plants
- 2 Million toe Etoh

Recent studies calculate around 18000 PJ the potential of waste+residues available in the EU

Around 150% total fuel consumption in the EU

SANDRO COBROR
Head of Public Affairs
Biochemtex spa

The Italian Scenario

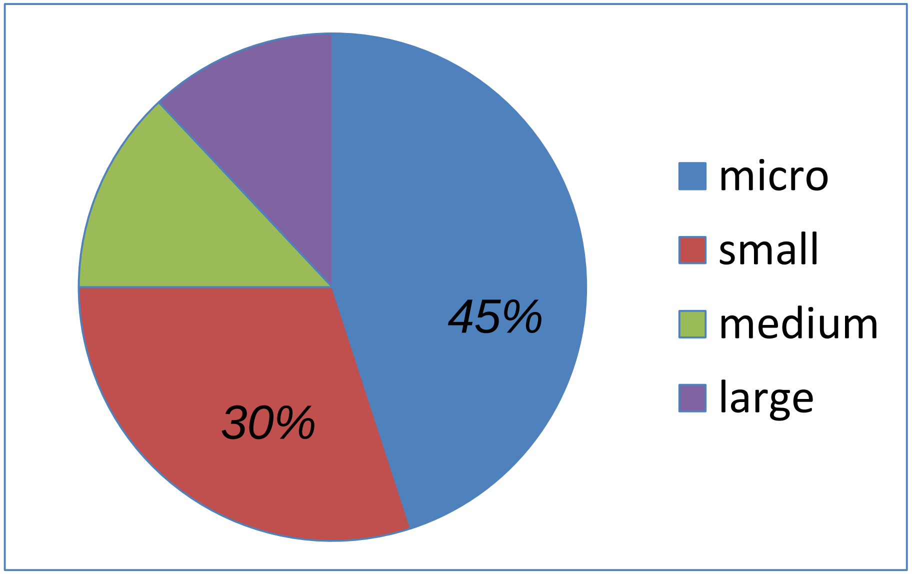

Le imprese di biotecnologie in Italia
Facts & Figures
BioInItaly Report 2016

FEDERCHIMICA
ASSOBIOTEC
Associazione nazionale per lo sviluppo delle biotecnologie

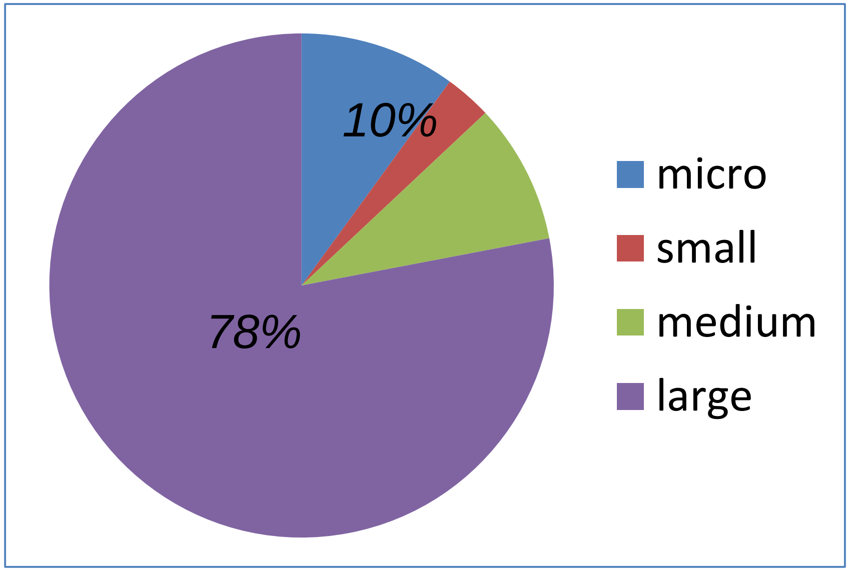
75% of biotechnology firms are micro or small enterprises
88% of pure biotec firms are micro or small

Strong focus on R&I activities

Number of Italian Biotec firms by size (%)



Turnover generated by firms by size (%)



Mossi Ghisolfi background

SANDRO COBROR
Head of Public Affairs
Biochemtex spa

1953 - 1979	1979 - 2000	2000 - TODAY	
Packaging Manufacturing Phase	Chemical Specialty Manufacturing Phase	PET expansion phase	*Renewables*
HDPE and PVC packaging production	Development and production of PET resins for food packaging	Acquisition of PET Shell activities and Rhodia from Rhone Poulenc Acquisition of Chemtex from Mitsubishi Corporation Construction of the world's largest plants for PET production in Altamira (Mexico) and Suape (Brasil) Plans announced for a new plant in Corpus Christi (Texas, USA)	2006 -2008 - Lab scale technology development for 2nd gen ethanol 2009 - Pilot plant for cellulosic ethanol 2011 - Beta Renewables is founded, dedicated to sustainable chemistry. 2012 - Beta Renewables and Novozymes partnership. Oct 2013 - World's 1st commercial-scale biofuel plant from non-food biomass (40.000 ton/year)

Guido Ghisolfi

Italy's approach to advanced biofuels

January 2013: IT Governement signed an agreement (Protocollo d'Intesa) with Gruppo Mossi Ghisolfi to foster the deployment of second and third generation biorefineries in Italy

May 2014: IT Government signed an agreement with MG to build up 3 cellulosic ethanol plants in the South of Italy

October 2014: DM set minimum quota of adv biofuels from 2018 on (from 0,6% in 2018 to 1% in 2022). This translates into around 180ktoe/y in 2018 and 300ktoe/y in 2022.

MOSSI GHISOLFI
GROUP

Beta Renewables has invested over $200 million in the development of the PROESA™ process. The company has built the world's first commercial-scale cellulosic ethanol facility in Crescentino

PROESA is a 'second-generation' technology for using non-food energy crops or agricultural waste and turning them into different types of sugary liquids, and is designed to produce them at a lower cost than competing approaches.

…using a variety of sustainable (non-food) biomasses…

Non-food cellulosic crops

- ✓ Arundo donax (Giant reed)
- ✓ Miscanthus giganteus
- ✓ Panicum virgatum (Switchgrass)

Agricultural residues

- ✓ Wheat straw
- ✓ Rice straw
- ✓ Corn stover
- ✓ Sugarcane bagasse

Lignocellulosic crops

- ✓ Eucalyptus
- ✓ Poplar

Might grow on marginal/abandoned land, creating additional income for farmers

The cellulosic biorefinery today ….

Ethanol
(up to -85% GHG saving)

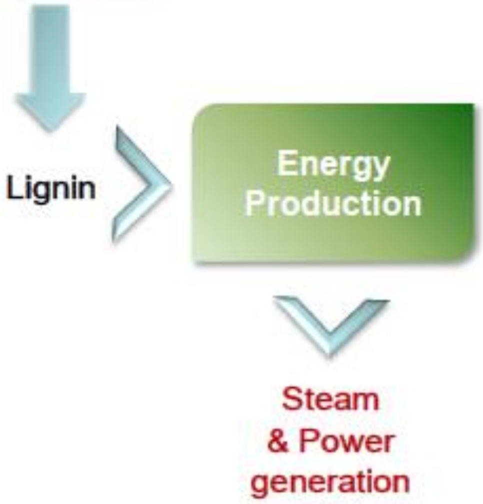
Non food Biomass

PROESA® Technology

Fermentable Sugars

Fermentation

Separation



Lignin

Energy Production

Steam
& Power
generation

2nd Gen Ethanol Plant (Crescentino – Italy) – Awarded FP7 support

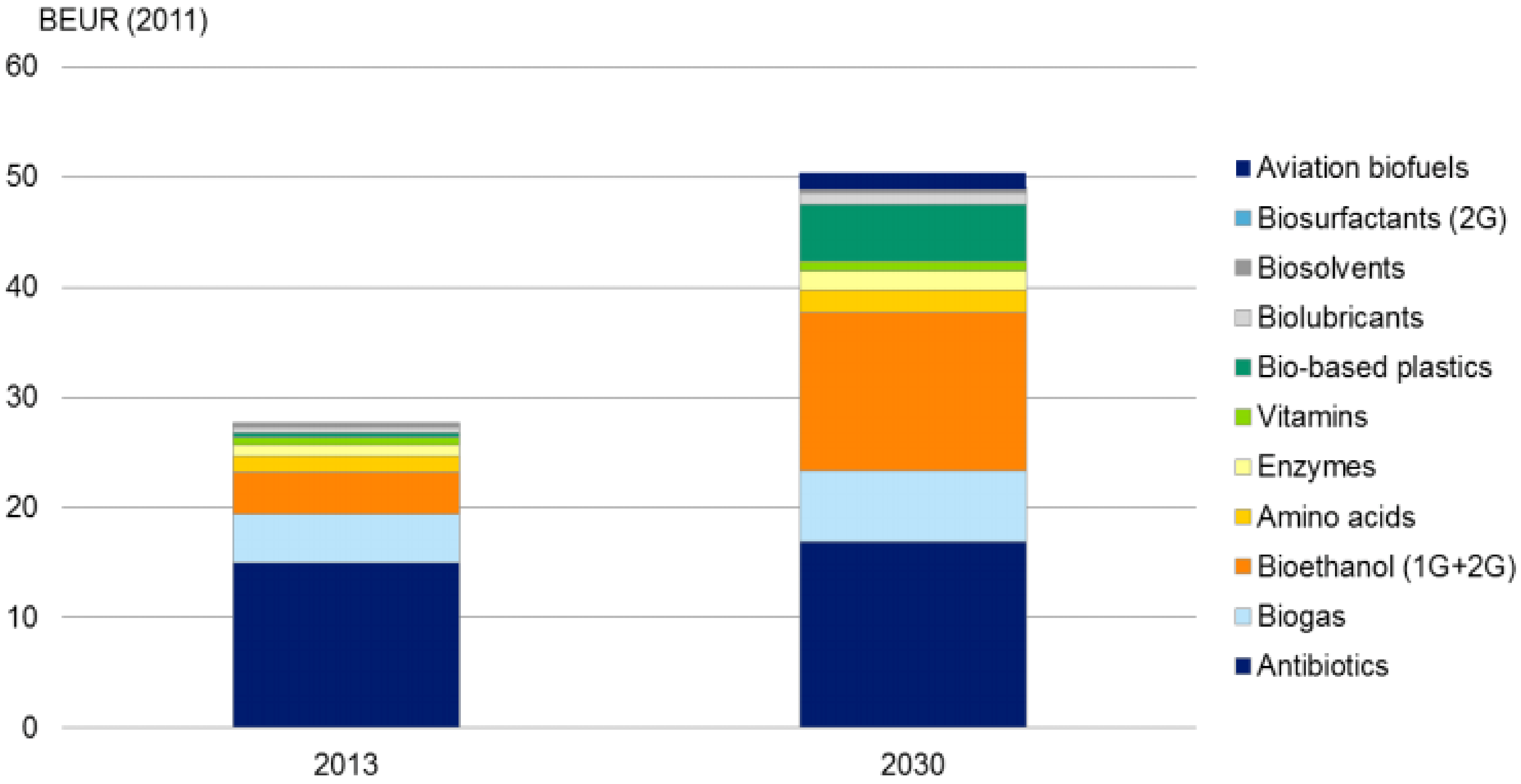
Efficient exploitation of biomass

- *it has been evaluated that production of chemicals and polymer resins from sugars and biomass result in two to four times more added value, create six to eight times more employment and require less percentage of feedstock compared to biofuel production.*
- ***Therefore, renewable carbon should be utilized for integrated production of fuels and chemicals.***

*Estimated bio-based products <u>market demand</u> in the EU up to 2030**


The bioeconomy enabled

A roadmap to a thriving industrial biotechnology sector in Europe



** BIO-TIC project*

http://www.industrialbiotech-europe.eu/new/wp-content/uploads/2015/06/BIO-TIC-roadmap.pdf

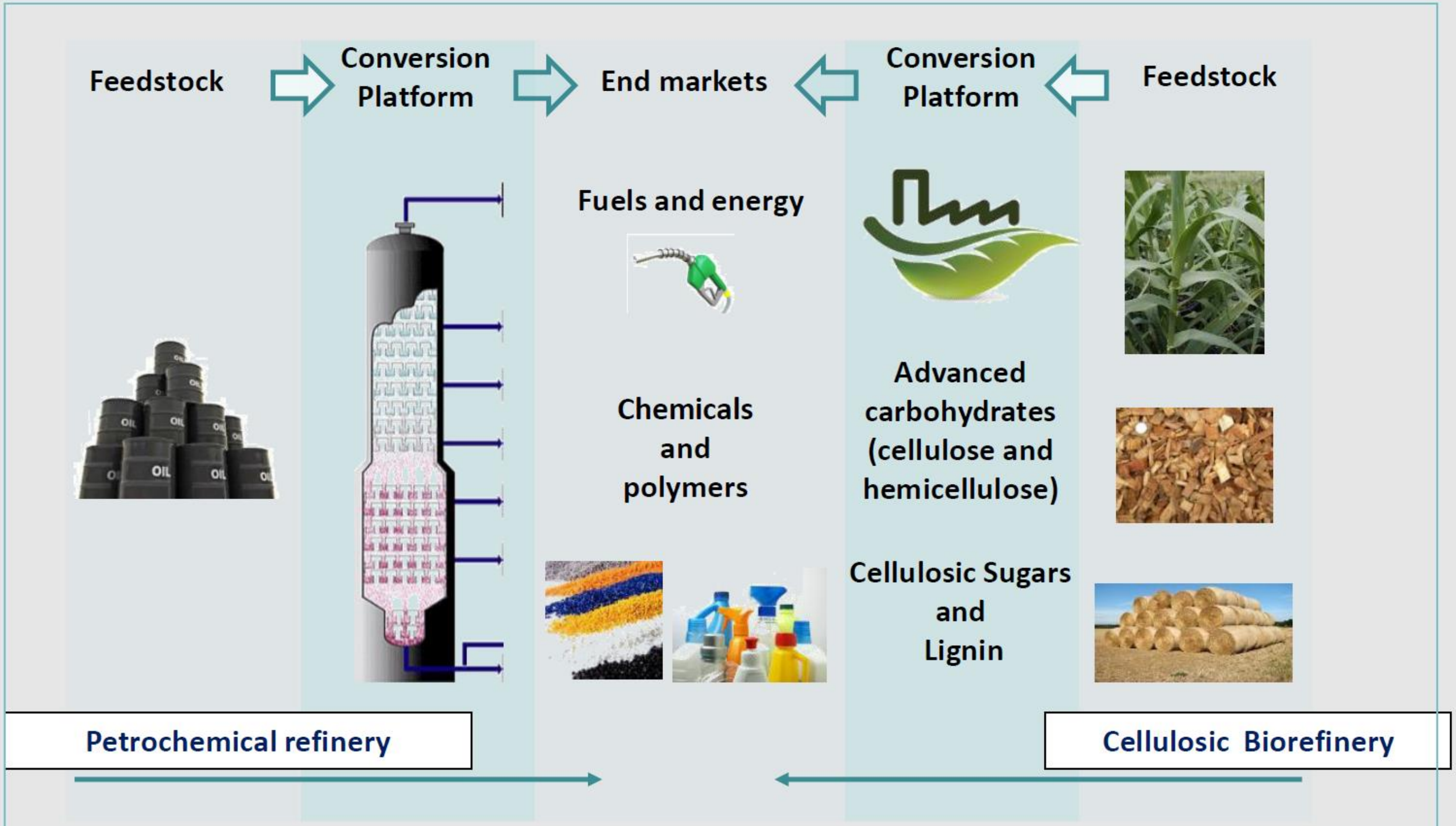
Not only Ethanol: Bio-Based Chemical, building blocks and polymers from biorefineries

What chemistry needs

The chemical industry relies on six basic chemicals or chemical groups including ethylene, propylene, the C4 olefins (butadiene and butenes), the aromatics (benzene and toluene), the xylenes (ortho, meta and para) and methane.

We want to develop the Cellulosic Biorefinery Concept

The biorefinery concept is similar to today's oil refinery, which produces multiple fuels and chemicals from crude oil.



Feedstock → Conversion Platform → End markets ← Conversion Platform ← Feedstock

Fuels and energy

Chemicals and polymers

Advanced carbohydrates (cellulose and hemicellulose)

Cellulosic Sugars and Lignin

Petrochemical refinery →

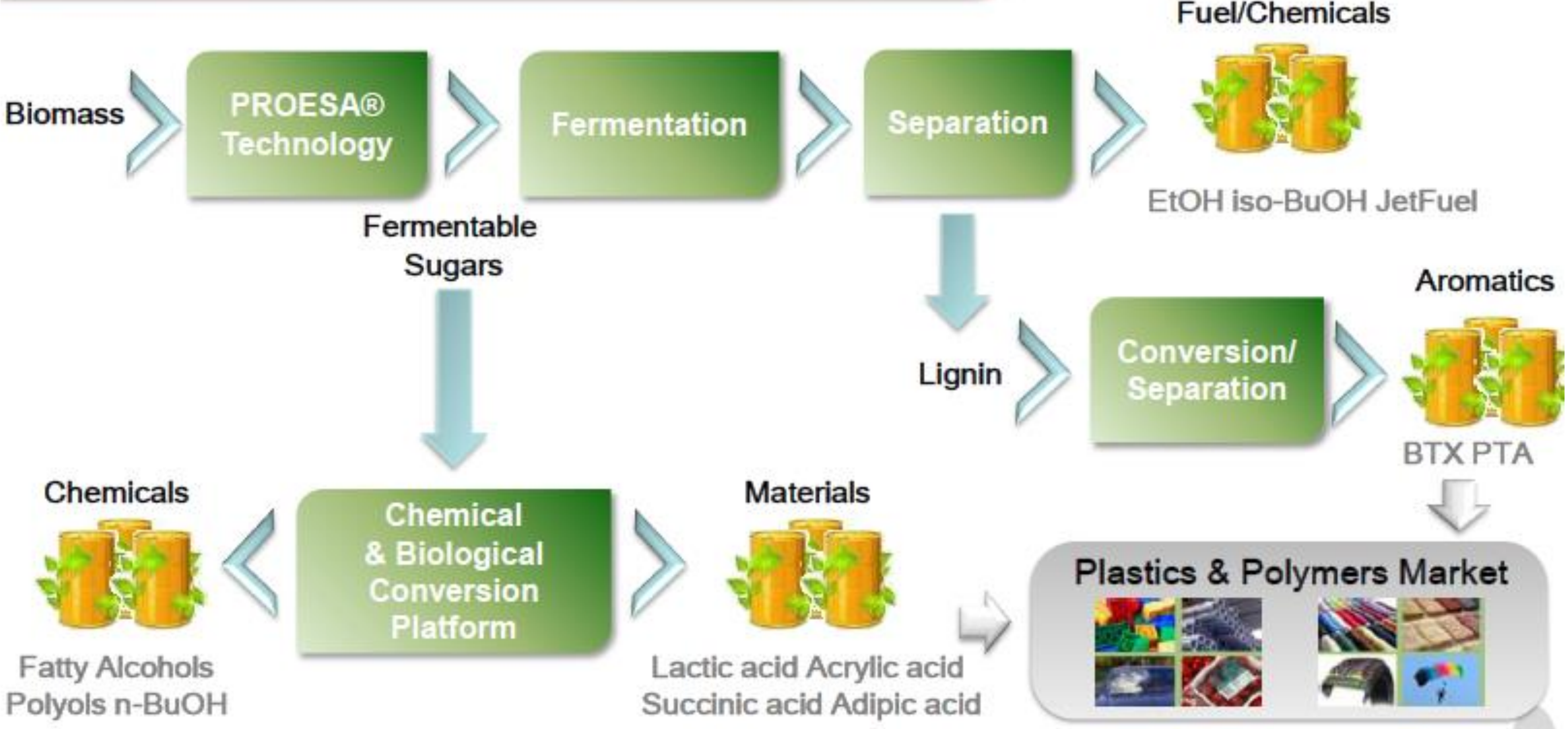
← Cellulosic Biorefinery

SANDRO COBROR
Head of Public Affairs
Biochemtex spa

The Biorefinery opportunity -

SANDRO COBROR
Head of Public Affairs
Biochemtex spa

The cellulosic biorefinery tomorrow



Biomass

PROESA® Technology

Fermentation

Separation

Fuel/Chemicals

EtOH iso-BuOH JetFuel

Fermentable Sugars

Lignin

Conversion/ Separation

Aromatics

BTX PTA

Chemicals

Chemical & Biological Conversion Platform

Materials

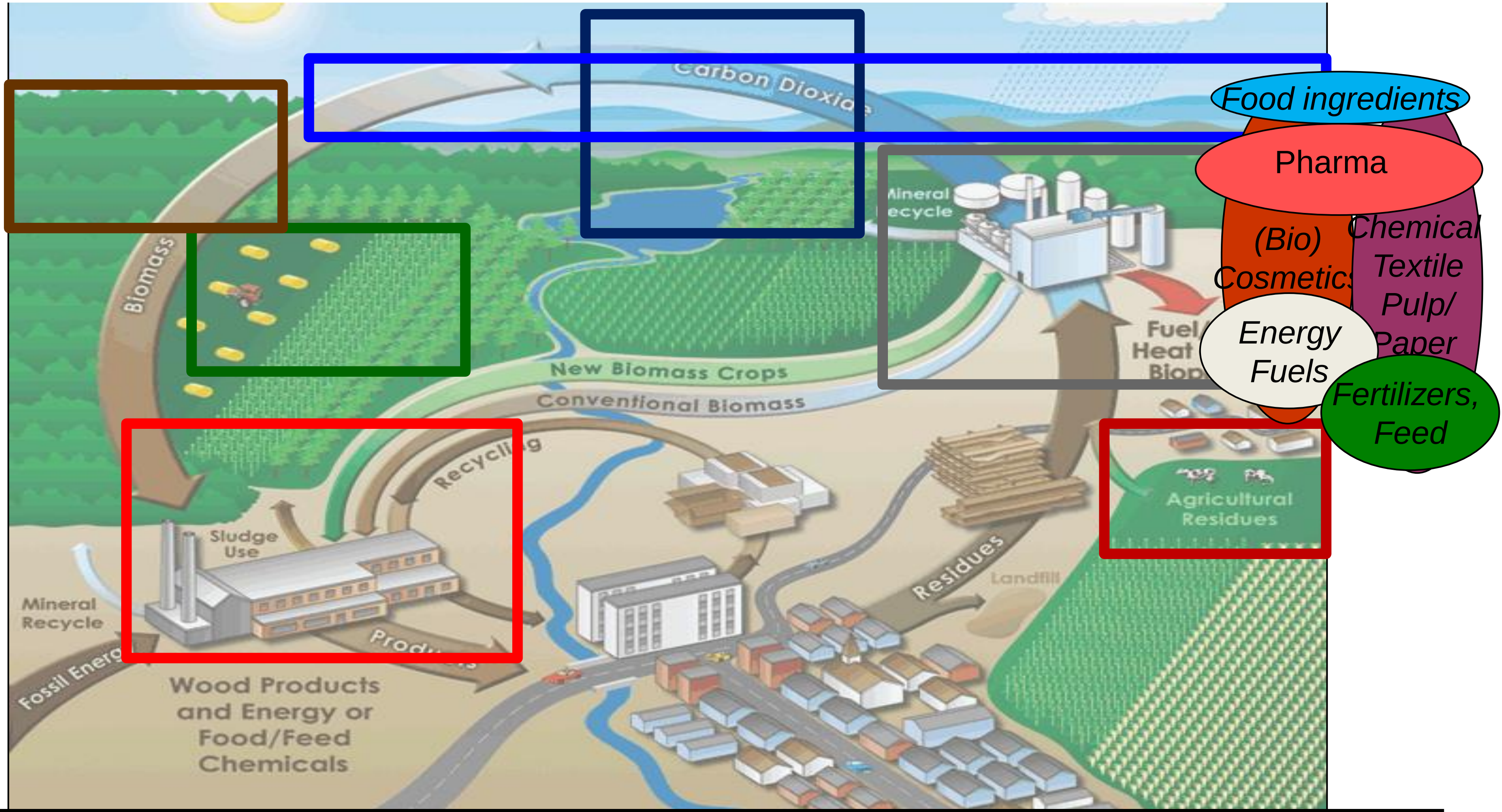
Fatty Alcohols Polyols n-BuOH

Lactic acid Acrylic acid Succinic acid Adipic acid

Plastics & Polymers Market

Integrated Biorefineries

*The term **“biorefinery”** describes the process that entails refining of biomass in a commercial context for the production of fuels, chemicals, polymers, materials, food, feed and value-added ingredients.*



Biorefinery: chemistry meets biotechnology

Greg Project – Green Glycols

Raw Biomass → Pre-Treatment → C_6 → PROESA → Ethanol

Pre-Treatment → C_5 → GREG → EG, PG

GREG process products

- Ethylene Glycol (EG) to PET production
- 1,2-Propylene Glycol (PG) to cosmetic, pharmaceutical and resin industries

Green chemistry with PROESA, not just fuel: MOGHI - lignin based technology

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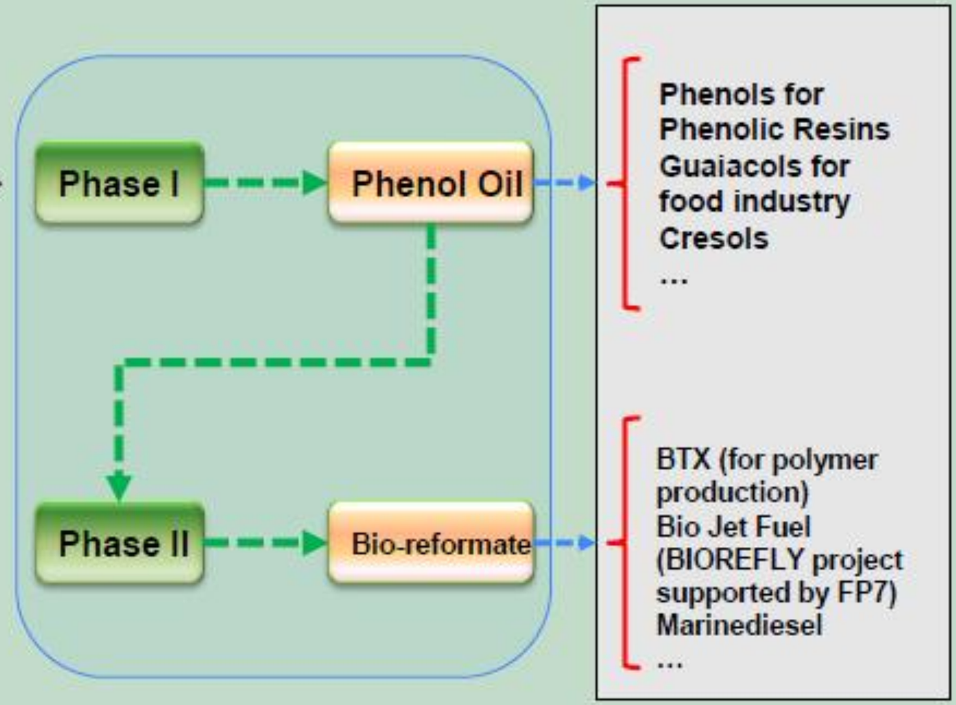
Lignin sourced from PROESA process



Phase I → **Phenol Oil**

- **Phenols for Phenolic Resins**
- **Guaiacols for food industry**
- **Cresols**
- **...**

Phenol Oil → **Phase II** → **Bio-reformate**

- BTX (for polymer production)
- Bio Jet Fuel (BIOREFLY project supported by FP7)
- Marinediesel
- ...

Italian Biorefineries

SPRING
Sustainable Processes and Resources for Innovation and National Growth
Italian Cluster of Green Chemistry

R&I Activities

④ Biorefyning and related activities in the country

- ● PILOT PLANTS
- ● DEMO PLANTS
- ● INDUSTRIAL SITES
- ● FLAGSHIPS

Piemonte

PILOT PLANT Fatty Alcohol (Rivalta Scrivia – AL)

PILOT PLANT Biomonomers (Novara)

INDUSTRIAL PLANT Lignocellulosic Bioethanol (Crescentino – VC)

FLAGSHIP Succinic Acid (Cassano Spinola – AL)

Lombardia

PILOT PLANT for Biobased Butadiene (Mantova)

Veneto

FLAGSHIP 1,4 BDO from RRM (Adria – RO)

Umbria

PILOT PLANT and **DEMO PLANT** Oleaginous crops and Biolubricants from local crops (Terni)

INDUSTRIAL PLANT Bioplastics based on Starch and Polyesters from vegetable oils (Terni)

Lazio

INDUSTRIAL PLANT Biodegradable Polyesters (Patrica – FR)

Campania

INDUSTRIAL PLANT Levulinic Acid (Caserta)

Puglia

PILOT PLANT and **DEMO PLANT** Aromatic Biochemicals from lignin (Modugno – BA)

FLAGSHIP Aviation Fuel (Modugno – BA)

Sardegna

1 FLAGSHIP basis for Bioplubricants and Bioadditives for Rubber (Porto Torres – SS)

1 FLAGSHIP Azelaic Acid and Pelargonic Acid (Porto Torres – SS)

Location TBD

FLAGSHIP for the extraction of Natural Rubber and other valuable products (resins, etc.)

⑤ Biobased R&D centers and experimental fields

- ● EXPERIMENTAL FIELDS
- ● R&D CENTERS

Piemonte

R&D CENTER Biochemicals and Biofuel from renewables (Rivalta Scrivia – AL)

R&D CENTER Bioplastics and Biochemicals from RRM

R&D CENTER Chemistry from renewables (Novara)

EXPERIMENTAL FIELD

EXPERIMENTAL FIELD

Lombardia

R&D CENTER Biolubricants (San Donato Milanese – MI)

R&D CENTER Green Chemistry, process engineering and biolubricants (Mantova)

EXPERIMENTAL FIELD

Emilia Romagna

R&D CENTER and **EXPERIMENTAL FIELD** Bioelastomers (Ravenna)

Umbria

R&D CENTER Oleaginous crops and biolubricants from local crops (Terni)

EXPERIMENTAL FIELD

Lazio

EXPERIMENTAL FIELD Biodegradable Polyesters (Patrica – FR)

Campania

R&D CENTER Biotechnological (Piana di Monte Verna – CE)

EXPERIMENTAL FIELD

Puglia

R&D CENTER Aromatic Biochemicals from lignin (Modugno – BA)

Basilicata

EXPERIMENTAL FIELD

Sardegna

R&D CENTER (Porto Torres – SS)

EXPERIMENTAL FIELD

Sicilia

EXPERIMENTAL FIELD