Platform Molecules I: Strategies from Biomass to Platform Molecules

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Literature

- Biorefineries – Industrial Processes and Products
  Birgit Kamm, Patrick R. Gruber, Michael Kamm (Eds.), Wiley-VCH, 2010.

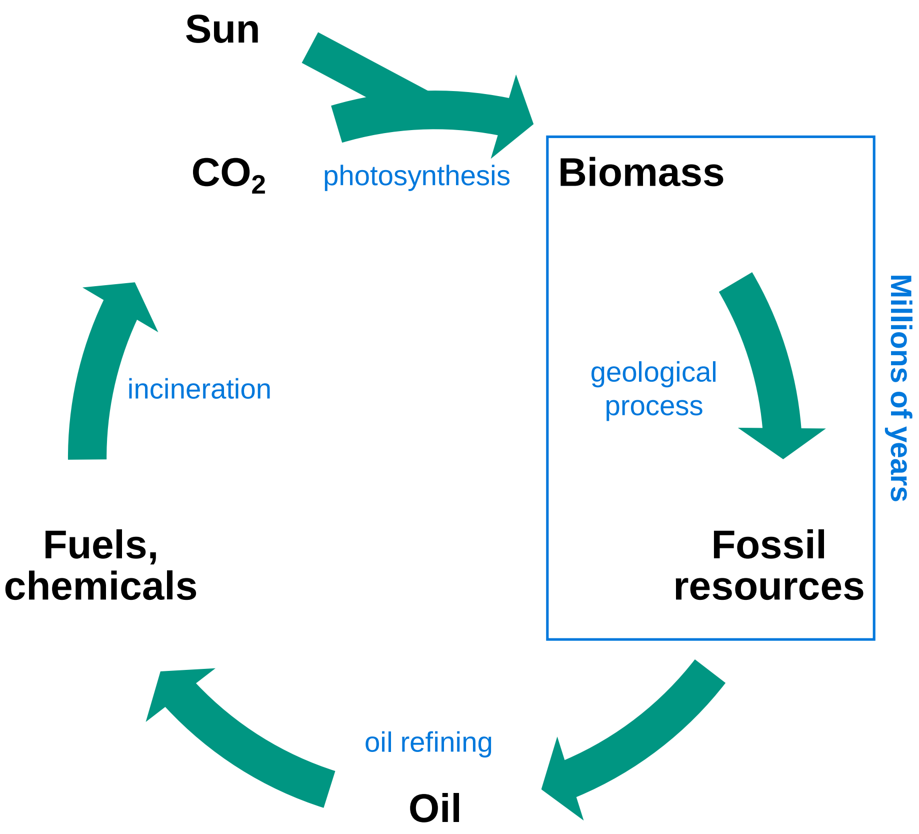
- “Introduction to Chemicals from Biomass“
  James Clark, Fabien Deswarte, Wiley Series in Renewable Resources, John Wiley & Sons, Ltd., 2008.

- Christensen et al., ChemSusChem, 1, 283 (2008)
- Vennstrøm et al., Angew. Chem. Int. Ed. 50, 10502 (2011)

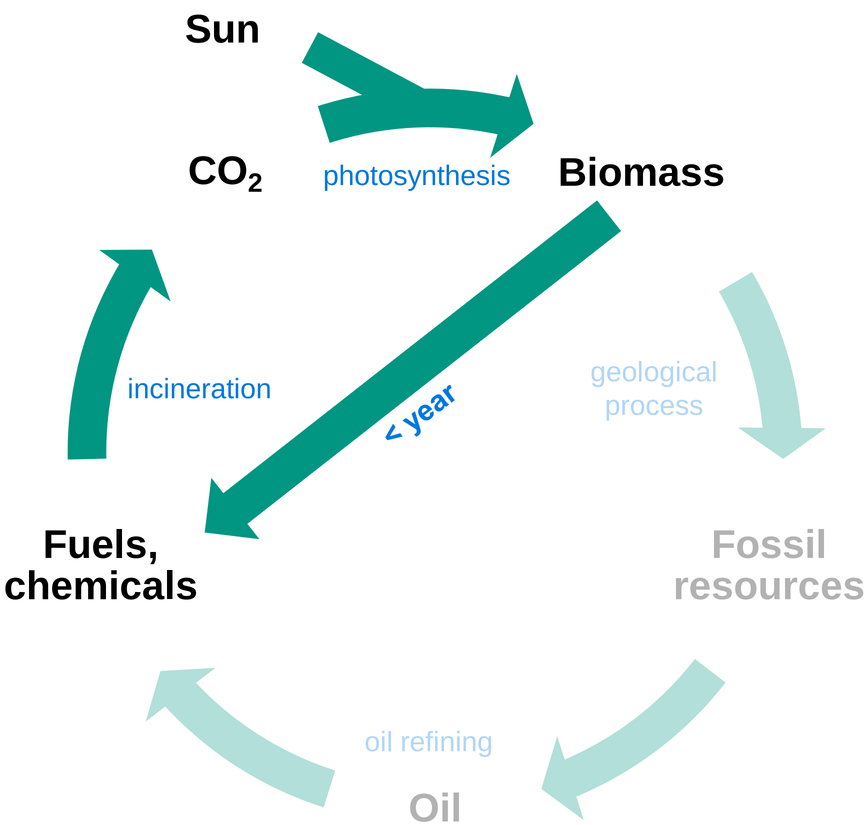
- Serrano-Ruiz et. al., Chem. Soc. Rev., 40, 5266 (2011)
- Luterbacher et. al., Green Chem., 16, 4816 (2014)
- Sheldon, Catal. Today, 167, 3, (2011)

(Pictures taken from these sources unless otherwise indicated)

Fossil vs. biomass resources



Fossil vs. biomass resources



It's not just about energy

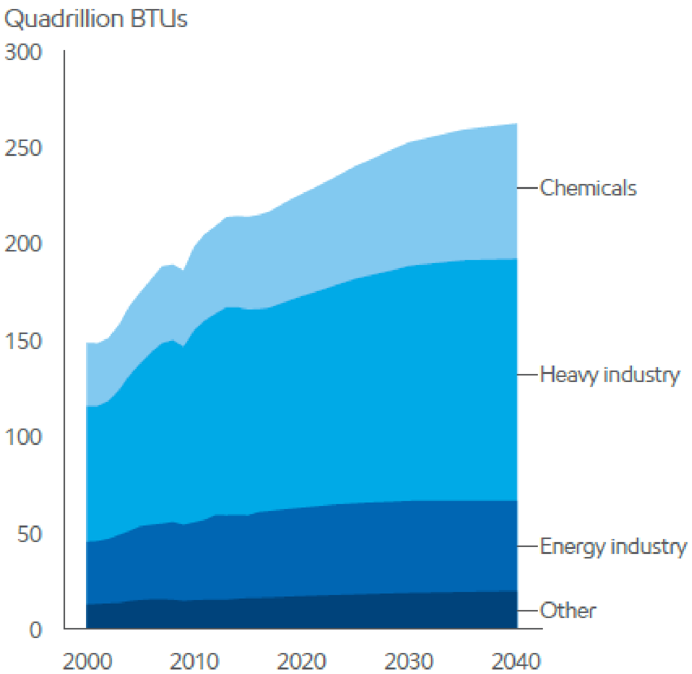
 = **Energy**

 = **Energy**, plastics, chemicals, cosmetics and medicines

Non-food biomass feedstock will play an increasingly important role in our economy

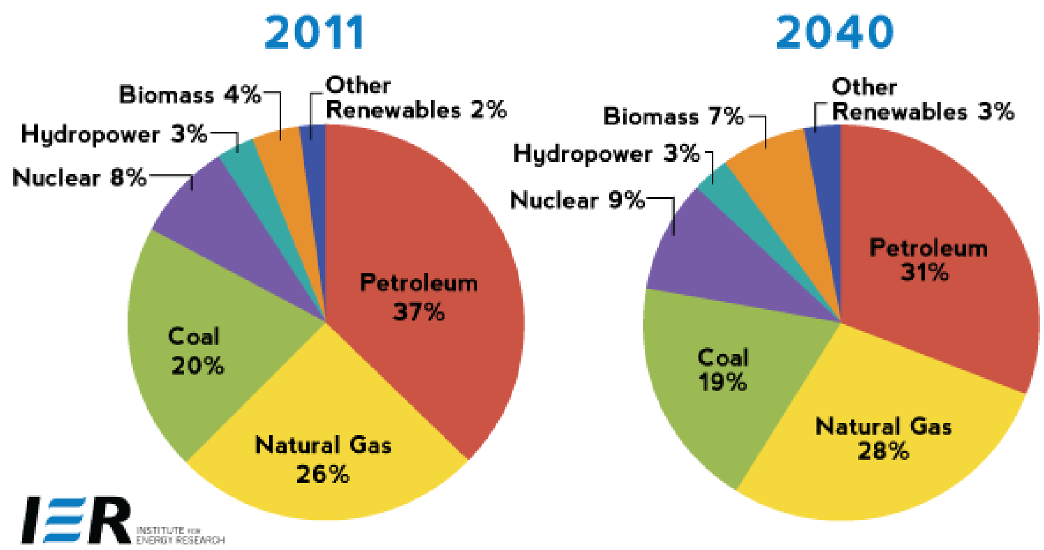
Demand for Fuels and Chemicals

Industrial demand economic activity



http://cdn.exxonmobil.com/~/media/global/files/outlook-for-energy/2017/2017-outlook-for-energy.pdf

Projection of status on energy sources



http://www.essentialchemicalindustry.org/processes/cracking-isomerisation-and-reforming.html

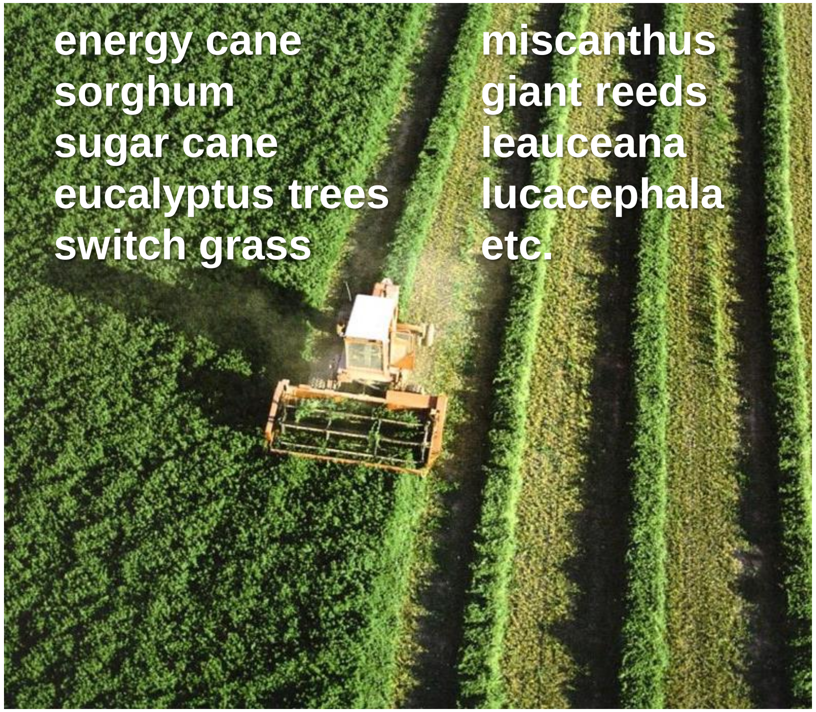
- Alternative resources to meet demand for fuels and chemicals

Biomass Resources

Biomass Resources: all forms of organic materials

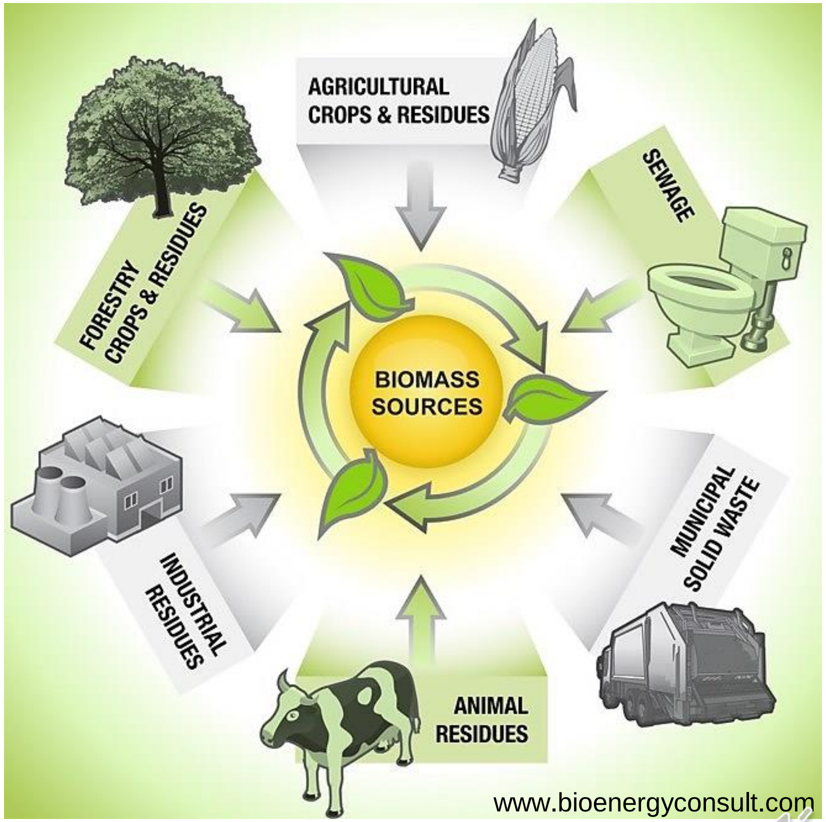
- plant matter both living and in waste form
- animal matter and their waste product

1. dedicated energy crops

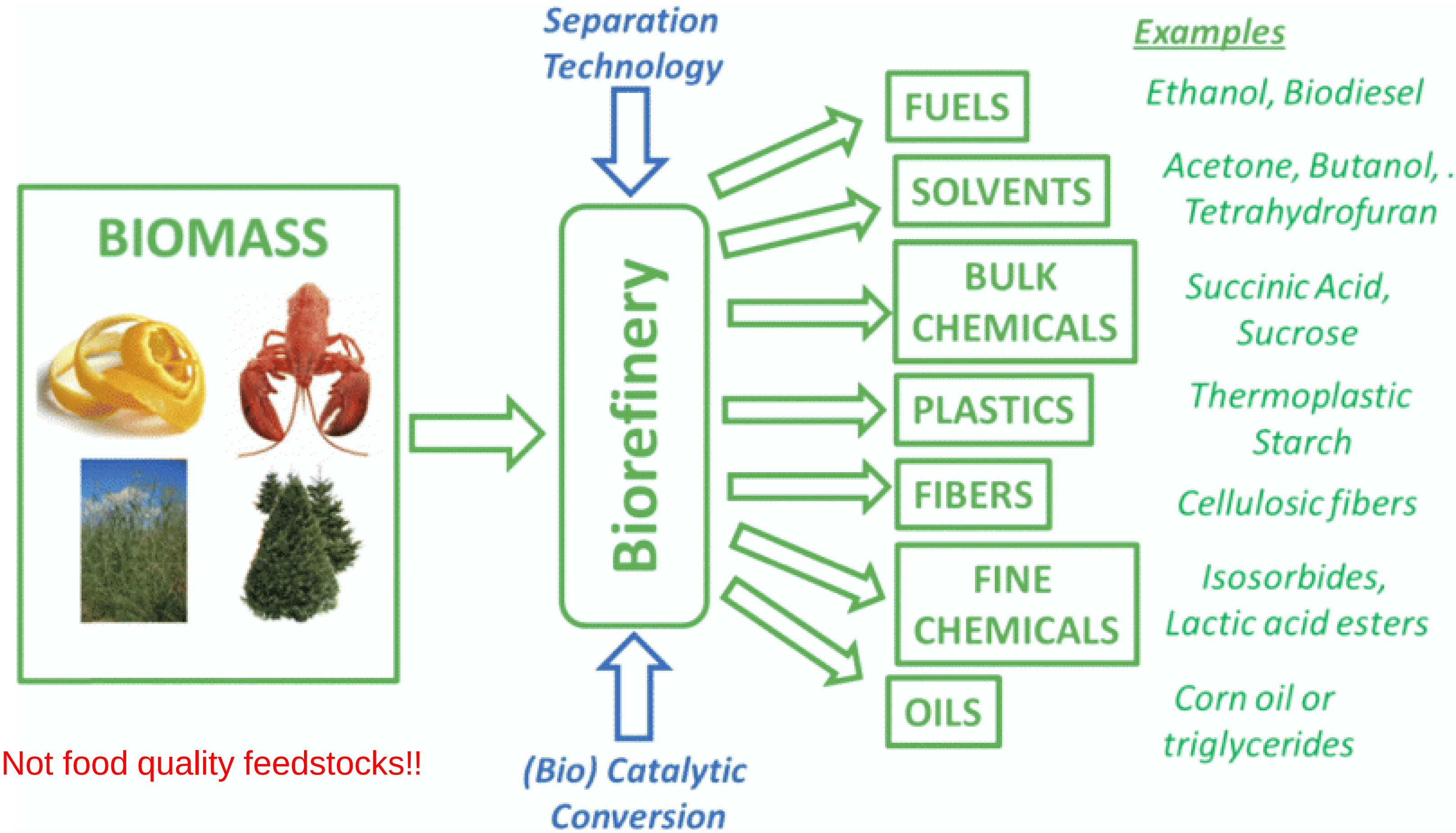


www.bioenergycrops.com

2. waste materials



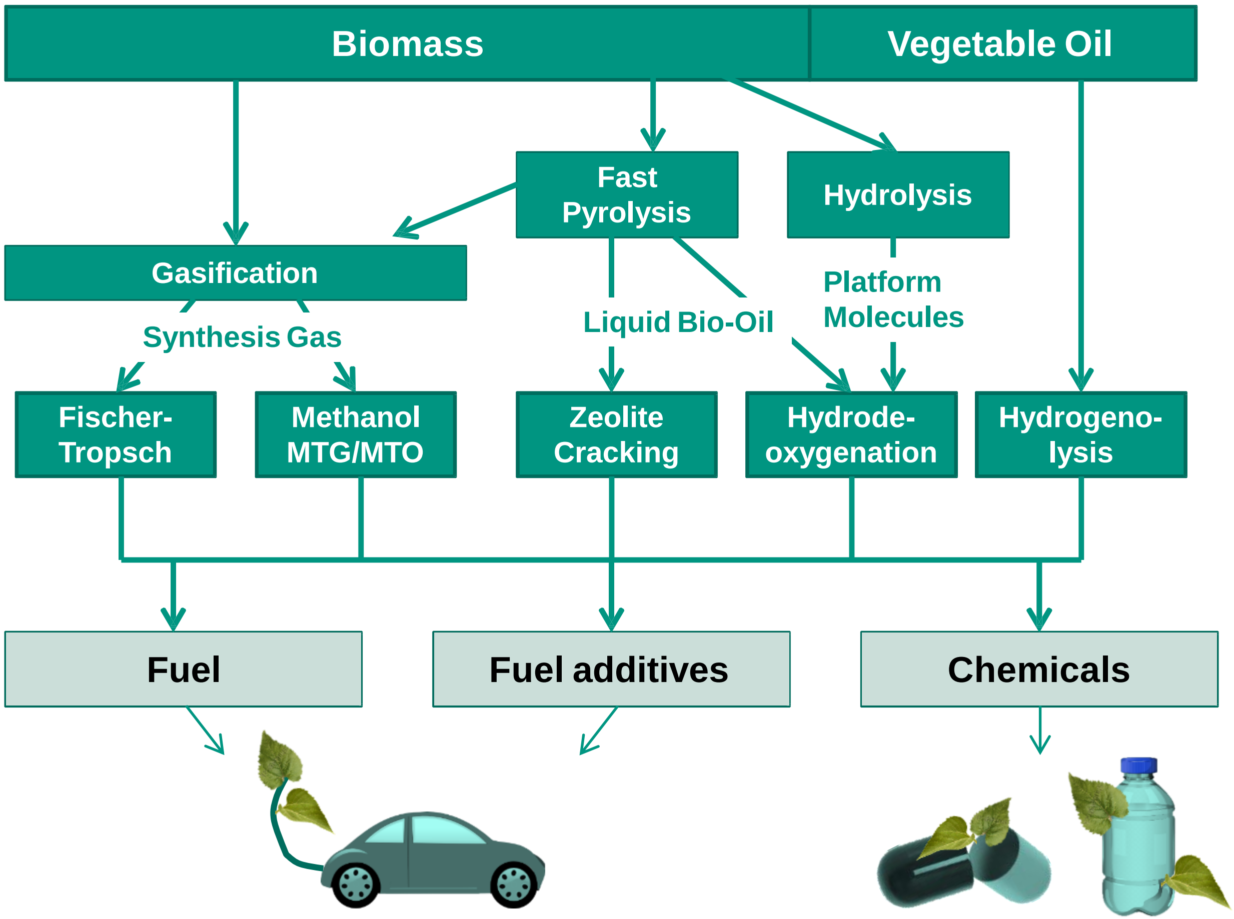
Biorefinery



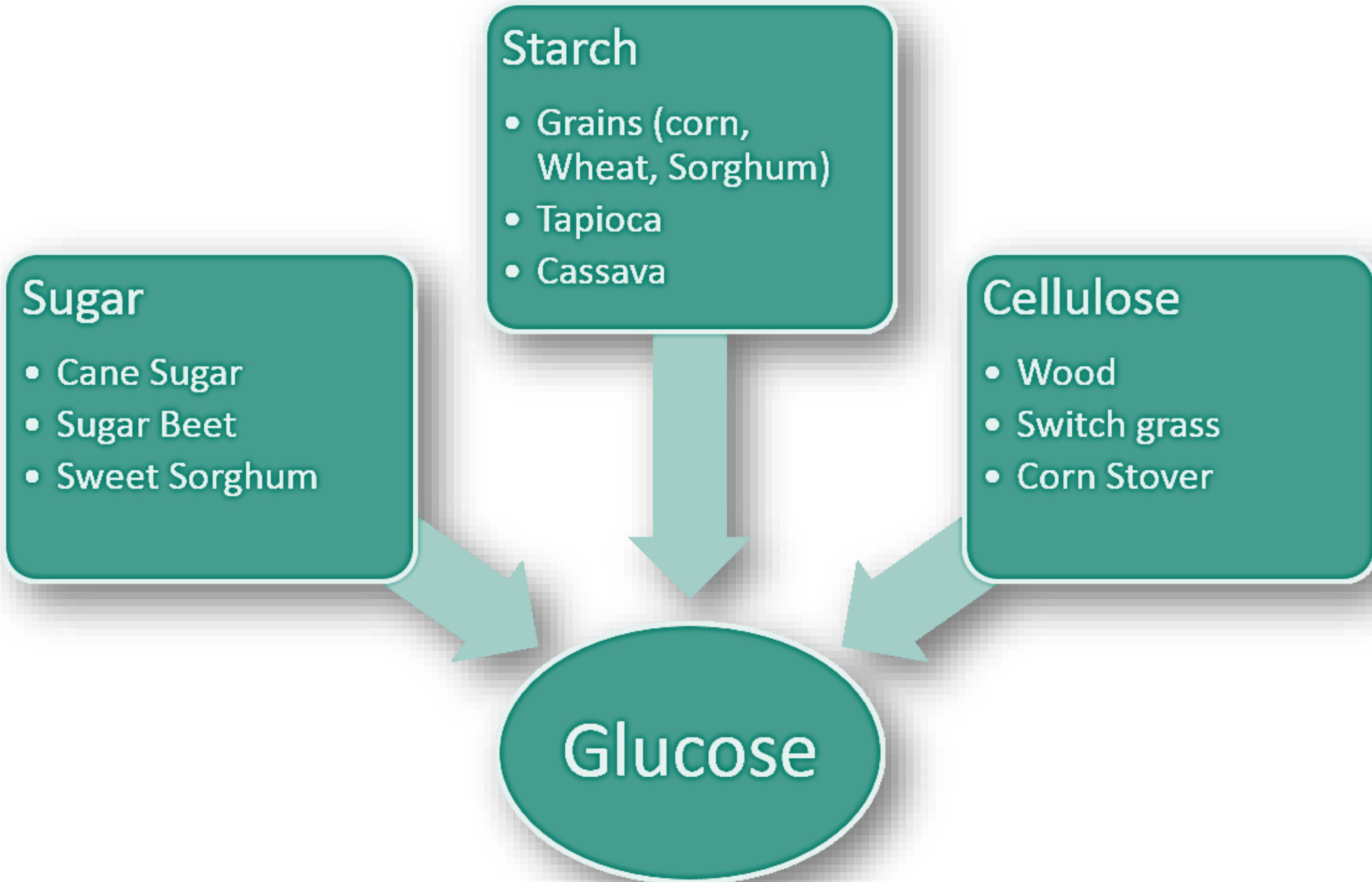
Not food quality feedstocks!!

https://labiotech.eu/biorefinery-review-europe-biobased/

Routes to Sustainable Biofuels and Chemicals



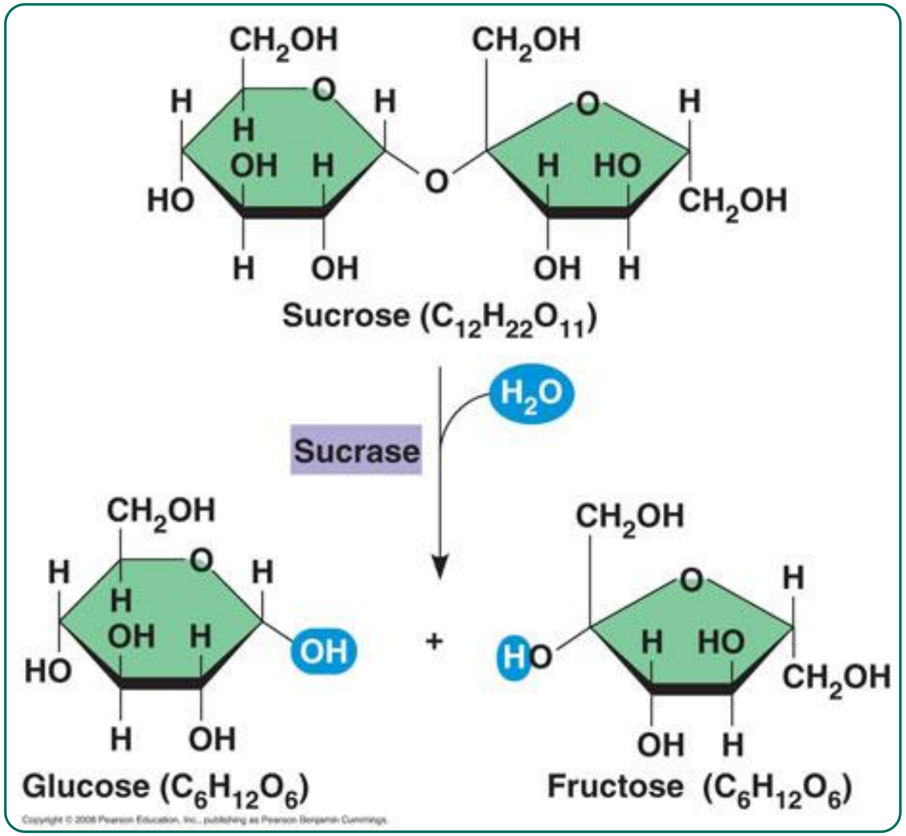
Biomass Sugar Sources



Hydrolysis of Biomass

Source: Sugar cane

- Biomass **hydrolysis**: the process converting the biomass biopolymers to fermentable sugars
- Most common source: Crystalline sugar from **sugar cane** and from sugar beet (saccharose)
- Sugar cane usage from 8000 B.C.
- 1900 11 Mio t/a sugar
- Nearly thermo-neutral (ΔH = -20 kJ/mol)

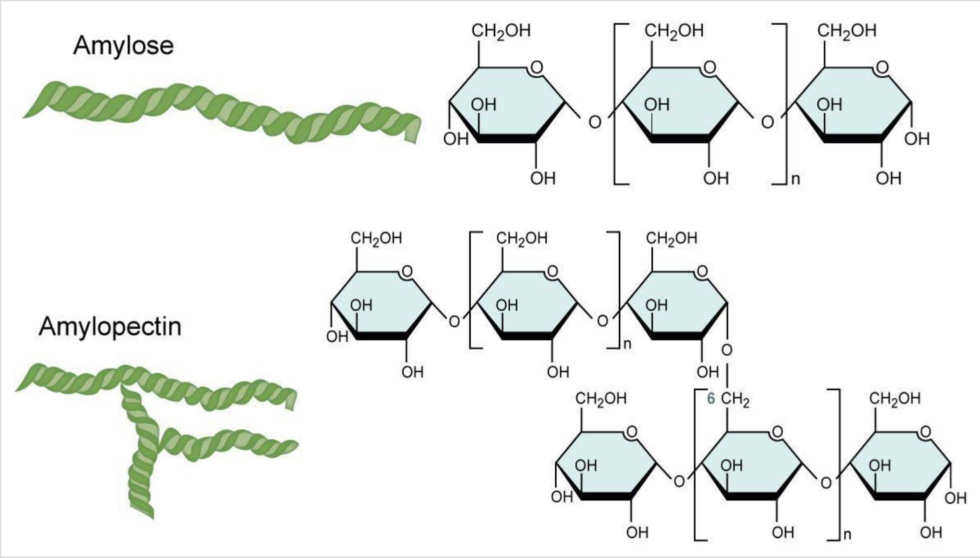


Hydrolysis of Biomass

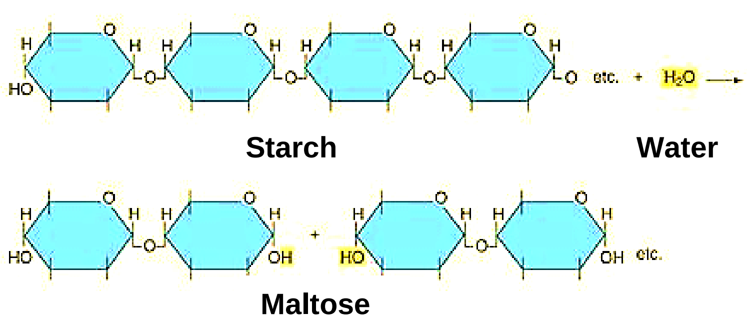
Karlsruhe Institute of Technology

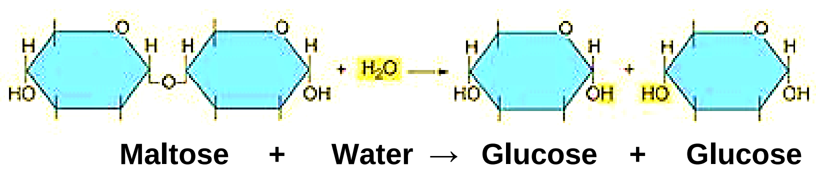
Source: Starch

- **Starch: 20 – 30 % Amylose**
  70 – 80 % Amylopektin
- A starch molecule contains hundreds of glucose molecules, branched (Amylopektin) or unbranched (Amylose)
- 1811: Kirchhoff found that potato starch was converted to „grape sugar“
- Berzelius in 1835 introduced the term „catalysis“ with the hydrolysis of starch to sugar
- Hydrolysis of α-1,4-glycosidic linkage



R. F.Tester, J. Karkalas, X. Qi. J. Cereal Sci. 39 (2004) 151



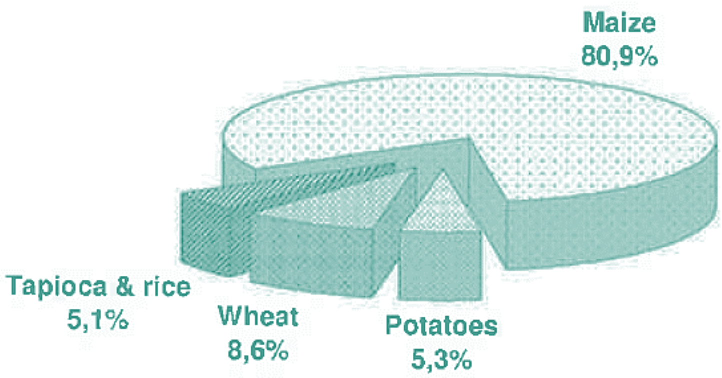


Hydrolysis of Biomass

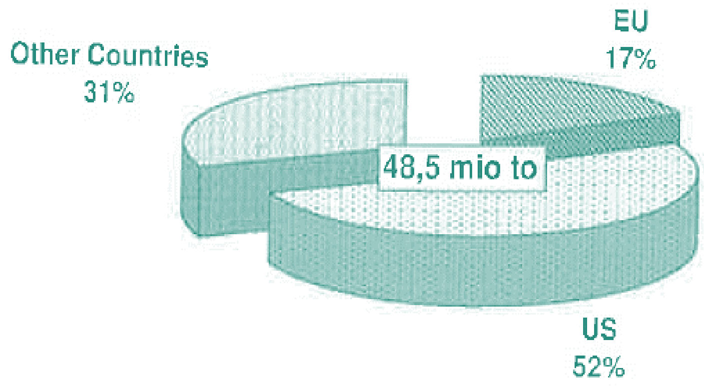
Source: Starch

Nowadays: Raw Material for Starch Production

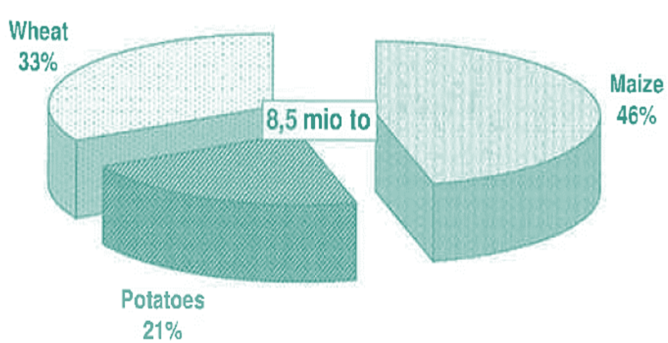
Starch production by raw material



Starch production world-wide



Starch production in EU

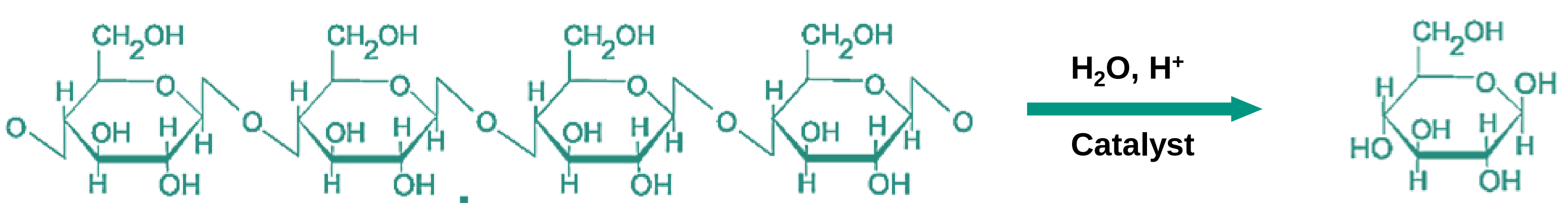


https://www.starch.eu/

Hydrolysis of Biomass

Source: Cellulose

- **1819**: Braconnot observed that wood and sulfuric acid give glucose
- **1855**: Mesens reported that also in dilute acid (higher temperature)
- **Cellulose**: glucose units connected through β-1,4-glycosidic bonds
  - Breakage of the **β-1,4-glycosidic bonds** by acids leads to the hydrolysis of cellulose polymers
  - produce the **glucose** molecule (or oligosaccharides)



Hydrolysis of Biomass

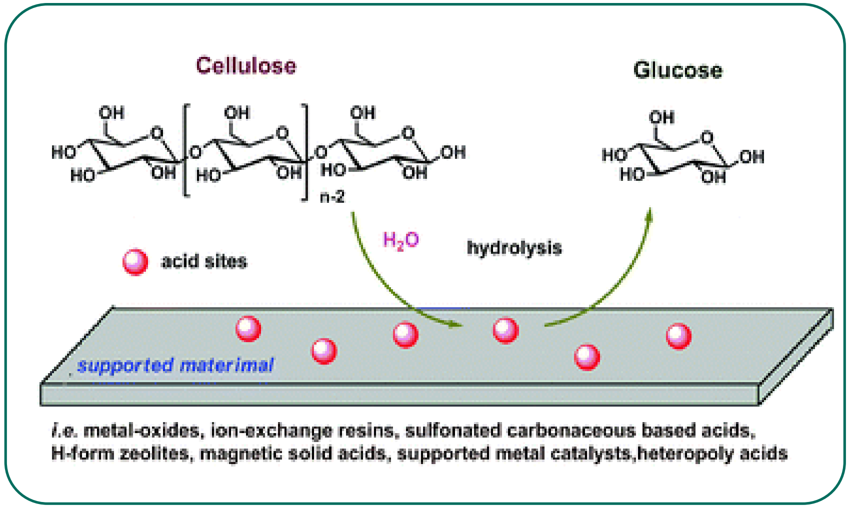
Source: Cellulose

General points about cellulose hydrolysis

- Cellulose very difficult to cleave – high crystallinity
- Cleavage of glycosidic bonds like in starch
- Acid or base catalysis between 100 and 300 °C
- Acid catalysis: more common
  - Ca. 70 % conversion
  - Side reaction: formation of 5-hydroxymethylfurfural by dehydration

$$\text{cellulose} + \text{water} \xrightarrow[k_1]{} \text{glucose} \xrightarrow[k_2]{} \text{degradation products}$$

- Base catalysis more side reactions, rarely used
- Enzyme catalysis
  - 50 °C, 100 % conversion

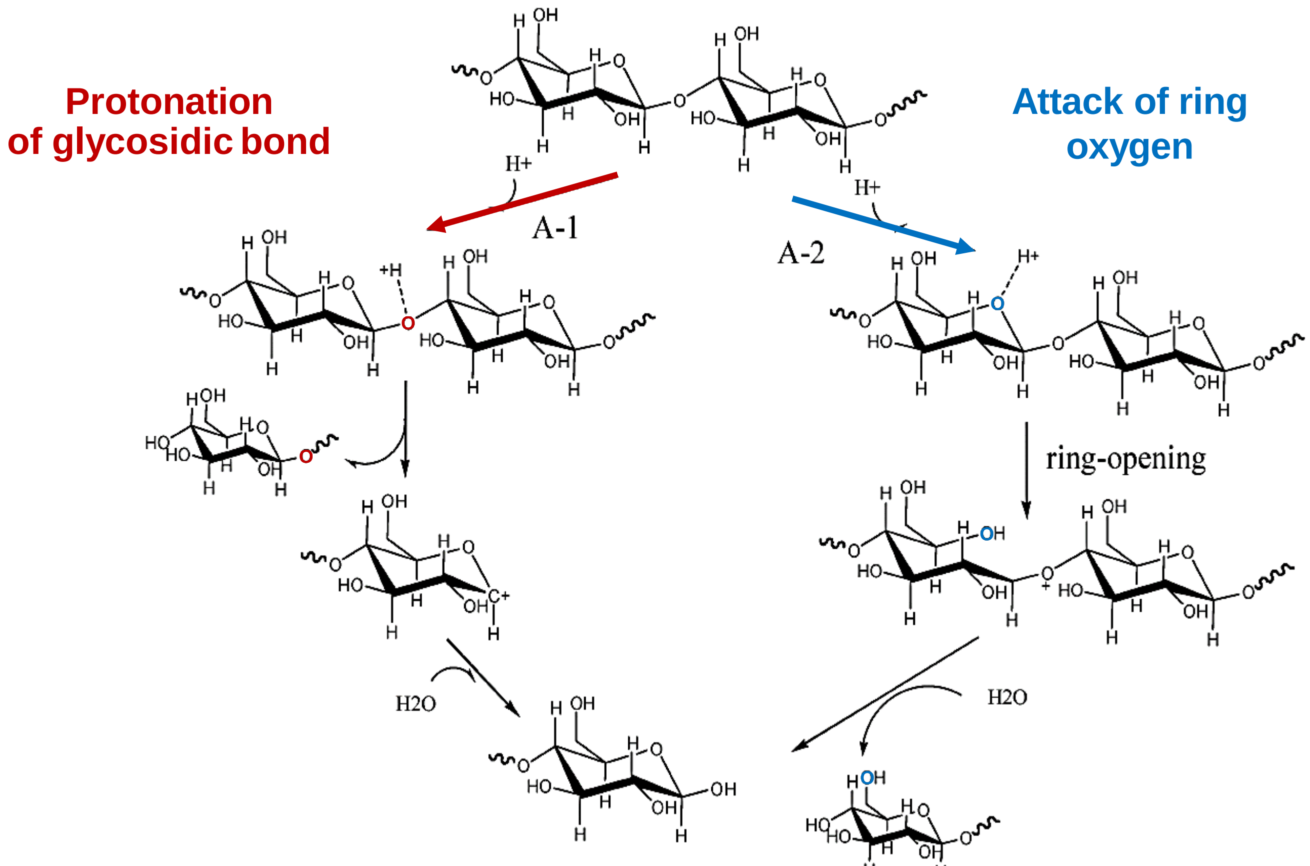


Y.-B. Huanga, Y. Fu. Green Chem. 15 (2013) 1095

Hydrolysis of Biomass

Source: Cellulose

Mechanism of cellulose hydrolysis

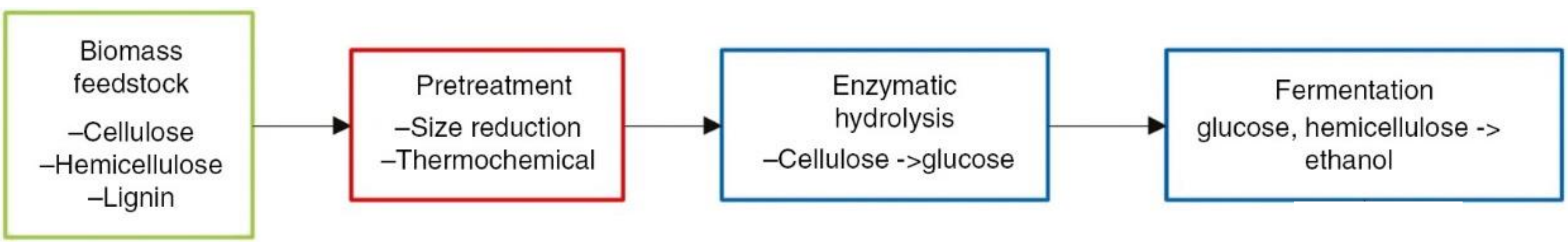


da Silva A.S., Sposina R., Oliveira R., Santana V., da Rocha R., Ferrara M.A. and Pinto E. (2013) Sugarcane and woody biomass pretreatments for ethanol production In Sustainable Degradation of Lignocellulosic Biomass- Techniques, Applications and Commercialization. Chandel A., editor. (ed). ISBN: 978-953-51-1119-1, InTech. doi: 10.5772/53378

Hydrolysis of Biomass

Enzymatic hydrolysis

- Prior to enzymatic hydrolysis: Structure is opened by pre-treatment
- Reaction with enzyme cellulase
  - Endoglucanase (internal amorphous cellulose sites)
  - Exoglucanase (end of cellulose)
  - β-glucosidases (cellodextrins: cellobiose, cellotriose, cellotetraose)
- Glucose inhibts process → fermentation to ethanol

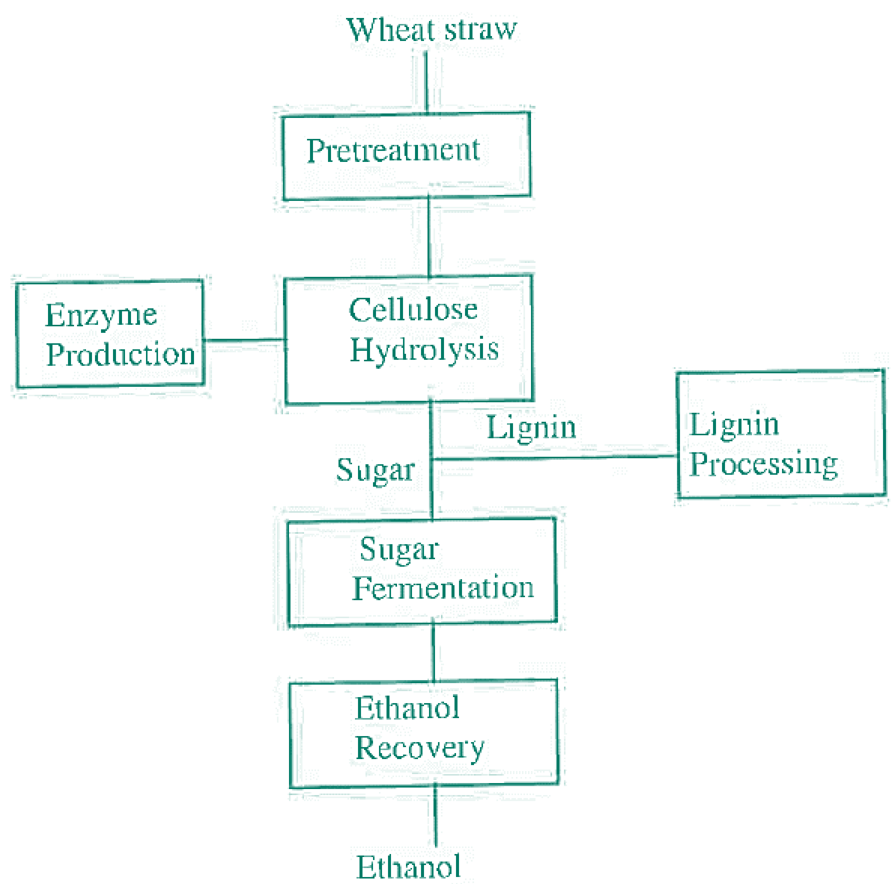


L.P. Walker, D.B. Wilson. Bioresource Technology 36 (1991) 3

Hydrolysis of Biomass

Wheat to bio-ethanol with sugar fermentation

- Hydrolysis with cellulases
- Lignin thermo-processing → energy for the whole process
- Sugar fermentation (Saccharomyces yeast) – not only glucose but also xylose



F. Talebnia, D. Karakashev, I. Angelidaki. Bioresource Technology 101 (2010) 4744

Hydrolysis of Biomass

Bio-ethanol producing species

Species	Ethanol yield (g/g substrate)	Productivity (g/l h)	References
Saccharomyces cerevisiae (wild type)	0.35	1.20	Alper et al. 2006
S. cerevisiae spt 15–300	0.40	2.03	
S. cerevisiae S3–10	0.42	2.43	Hou 2010
S. cerevisiae	Np	3.30	Grange et al. 2010
Kluyveromyces marxianus	0.43	1.81	
Escherichia coli	0.57	2.50	
Klebsiella oxytoca	0.52	2.10	
Zymomonas mobilis	0.69	2.29	Santos et al. 2010

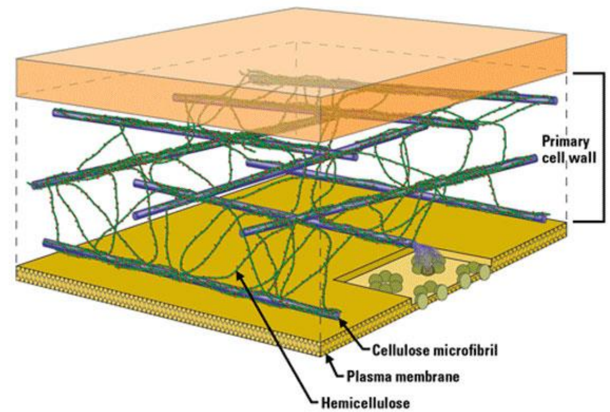
F. Talebnia, D. Karakashev, I. Angelidaki. Bioresource Technology 101 (2010) 4744

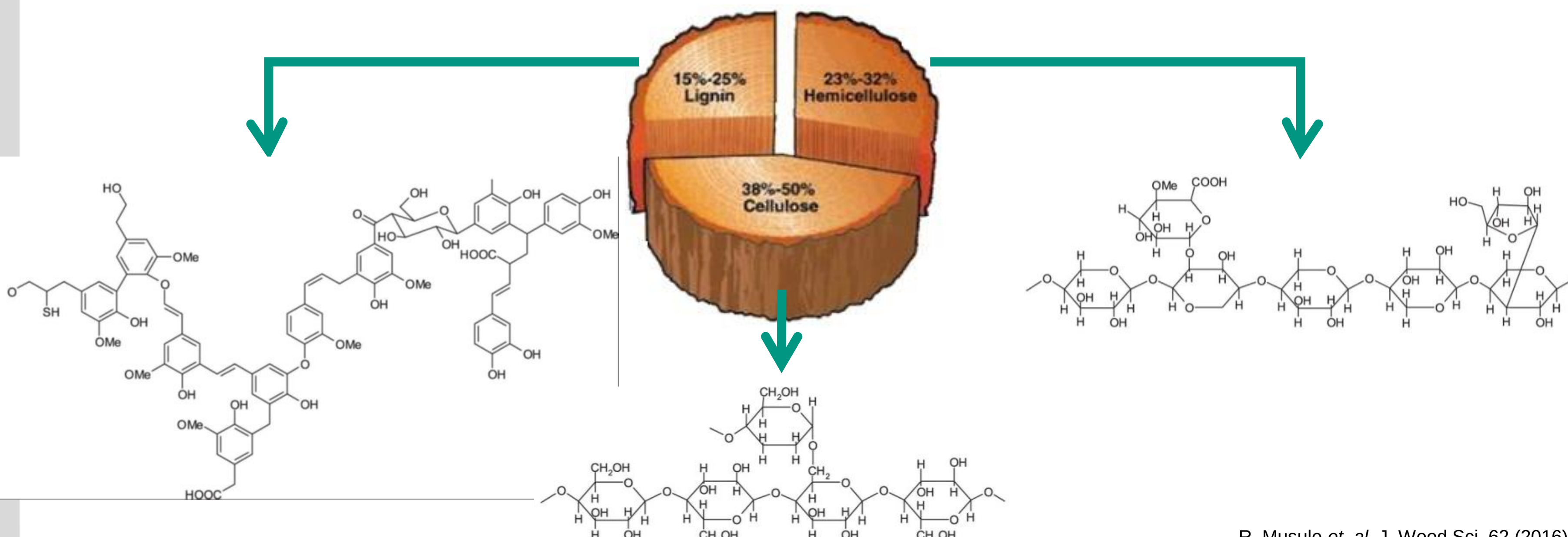
Hydrolysis of Biomass

Source: Wood

Composition of lignocellulosic biomass

- Cellulose
  - like a frame to keep the structure of plants
- Hemicellulose
  - like a string to bind the cellulose fibers
- Lignin
  - like cement to harden the structure





R. Musule *et. al*. J. Wood Sci. 62 (2016) 537

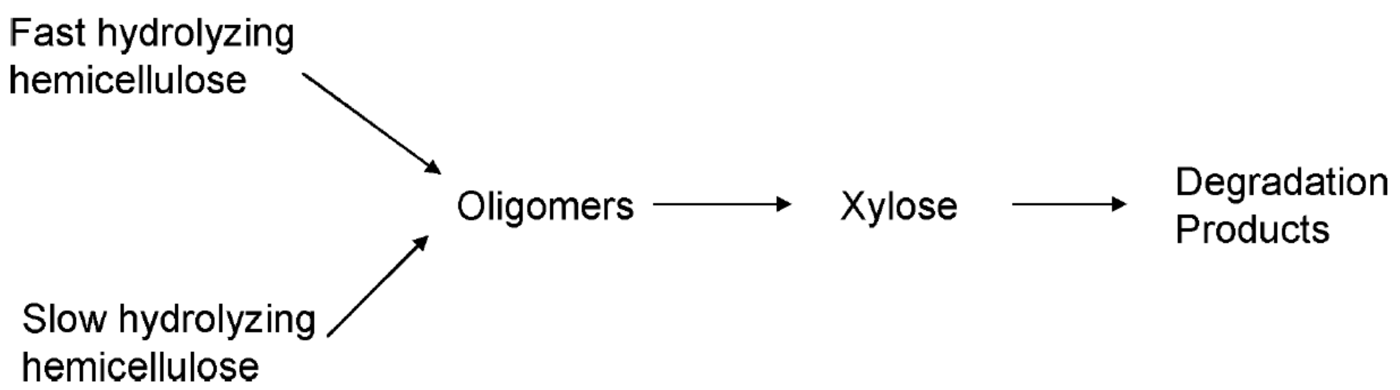
Hydrolysis of Biomass

Source: Wood - hemicellulose

Acid hydrolysis of hemicellulose

- Faster than cellulose because it is an amorphous polymer
- Even in hot water (210 °C) leads to acetic acid which catalyzes the reaction
- 160°C, 0.7wt% acid, up to 90 % hemicellulose sugars
- Also in this case further degradation

Kinetic model of hemicellulose degragation (Wyman et al.)

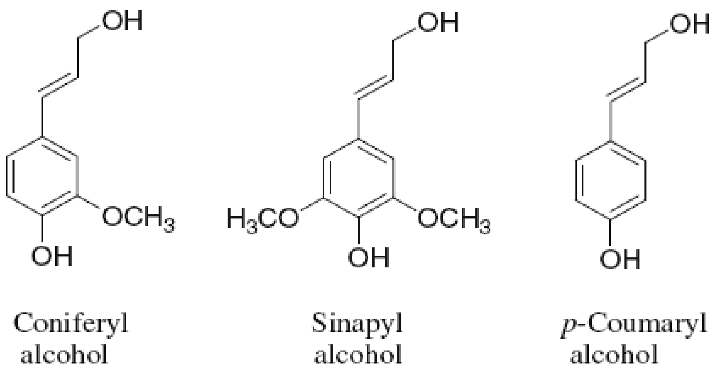


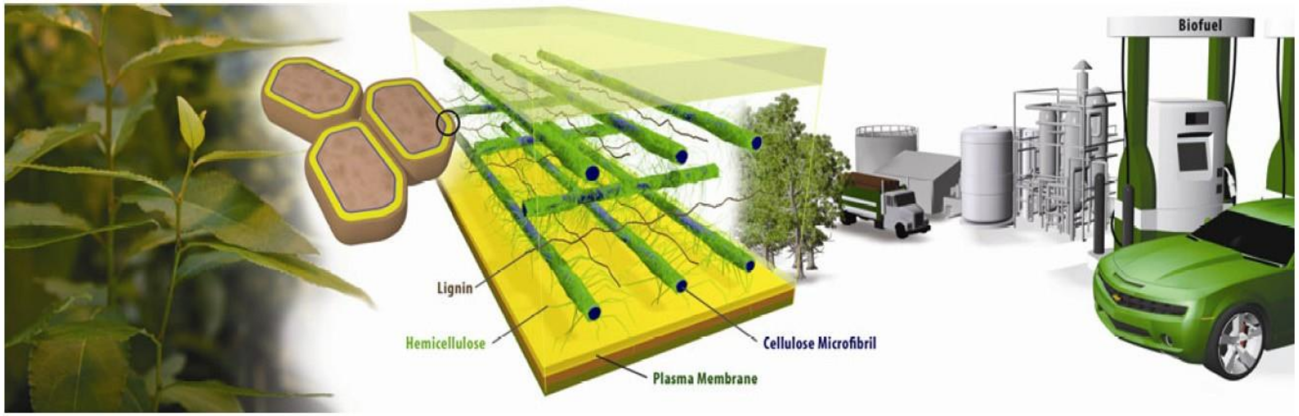
Wang Y., Yuan B., Ji Y., Li H.Carbohydr. Polym. 97 (2013) 518

Hydrolysis of Biomass

Source: Wood - Lignin

- After cellulose most common organic substance
- Used for polymer based on phenol subunits



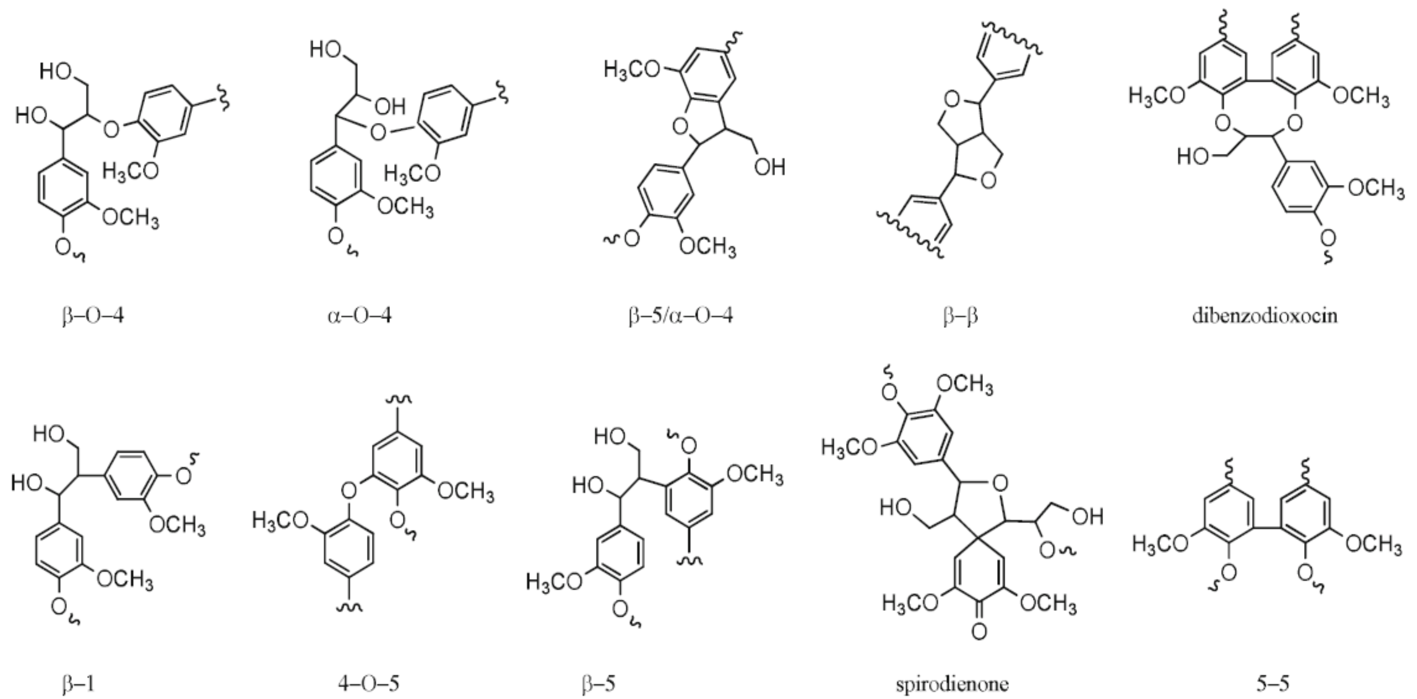


Hydrolysis of Biomass

Source: Wood – Lignin

- After cellulose most common organic substance
- Used for polymer based on phenol subunits

Different type of linkages in the lignin molecule



R. Datta *et. al*. Sustainability 2017, 9(7), 1163

Hydrolysis of Biomass

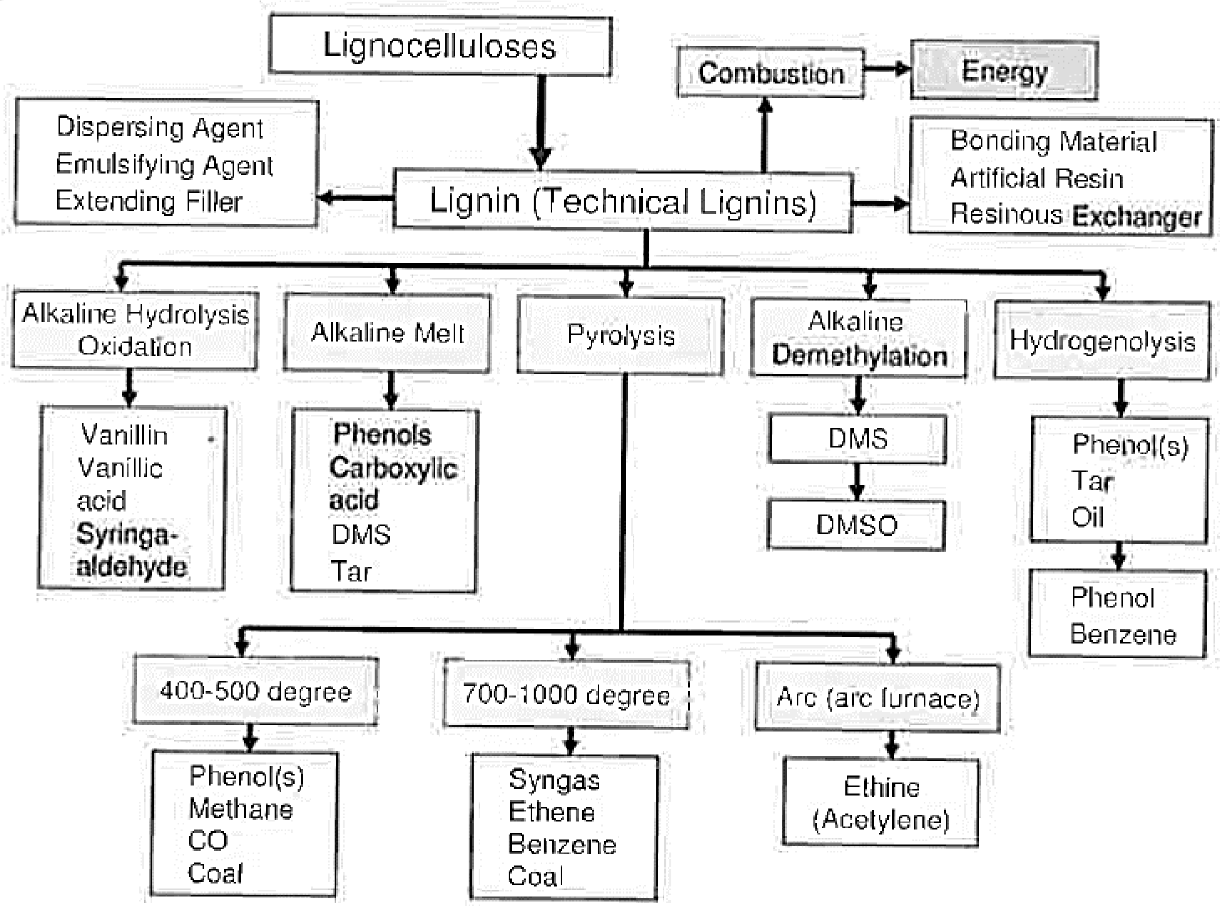
Source: Wood – Lignin

- First steps are the removal of cellulose and hemicellulose
- Lignin remains as polymer
  - Natural binder and adhesives
  - Sub-bitimuous coal
  - Sulfur-free solid fuel; often directly used in biorefineries
- Enzymatic Methods: Difficult, little degradation, often below 20 %
- Only way: harsher chemical treatment

Hydrolysis of Biomass

Source: Wood – Lignin

Lignin-based product family tree



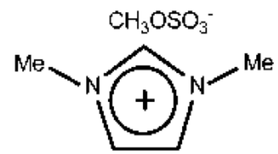
C. Løhre et. al. Int. J. Mol. Sci. 18 (2017) 225

Karlsruhe Institute of Technology

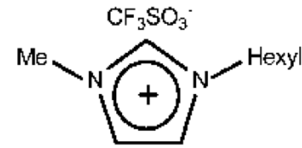
Source: Wood – Lignin

Lignin solubility is low

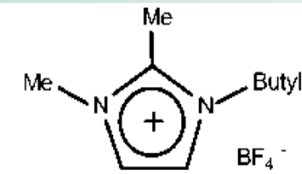
Dissolvable in ionic liquids



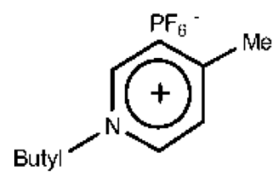
[mmim][MeSO4]



[hmim][CF3SO3]



[bm2im][BF4]



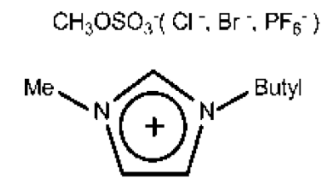


Table 2. Solubility of residual softwood kraft pulp lignin in ionic liquids

Ionic liquid	Temp./°C	Solubility (g L^{-1})
[mmim][$MeSO_4$]	50	344
	25	74.2
[hmim][CF_3SO_3]	70	275
	50	<10
[bmim][$MeSO_4$]	50	312
	25	61.8
[bmim]Cl	75	13.9
[bmim]Br	75	17.5
[bmim][PF_6]	70–120	Insoluble
[bm_2im][BF_4]	70–100	14.5
[bmpy][PF_6]	70–120	Insoluble

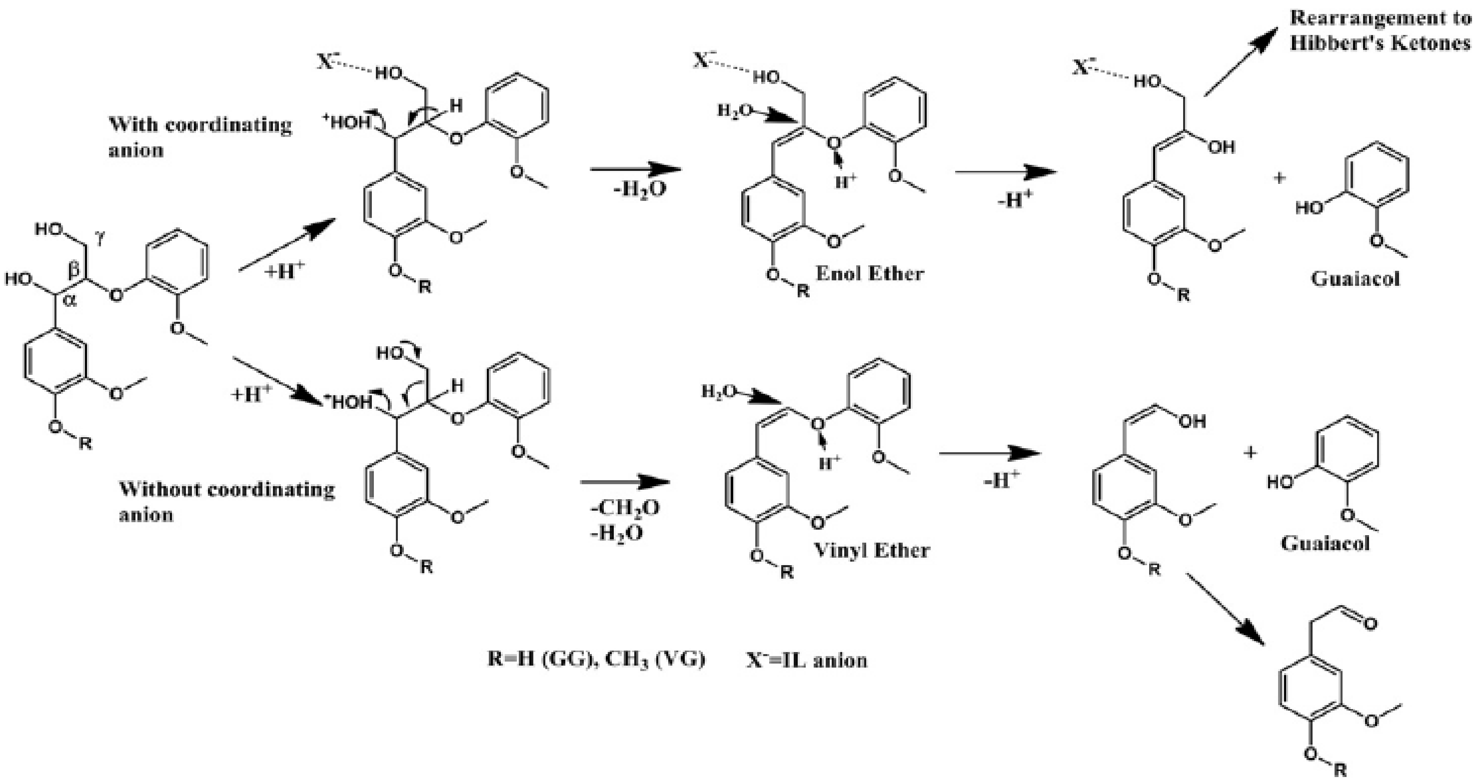
Ionic Liquid as a Green Solvent for Lignin

Yunqiao Pu [a] , Nan Jiang [b] & Arthur J. Ragauskas [b]

Biomass Processing

Source: Wood – Lignin

Degradation of Lignin



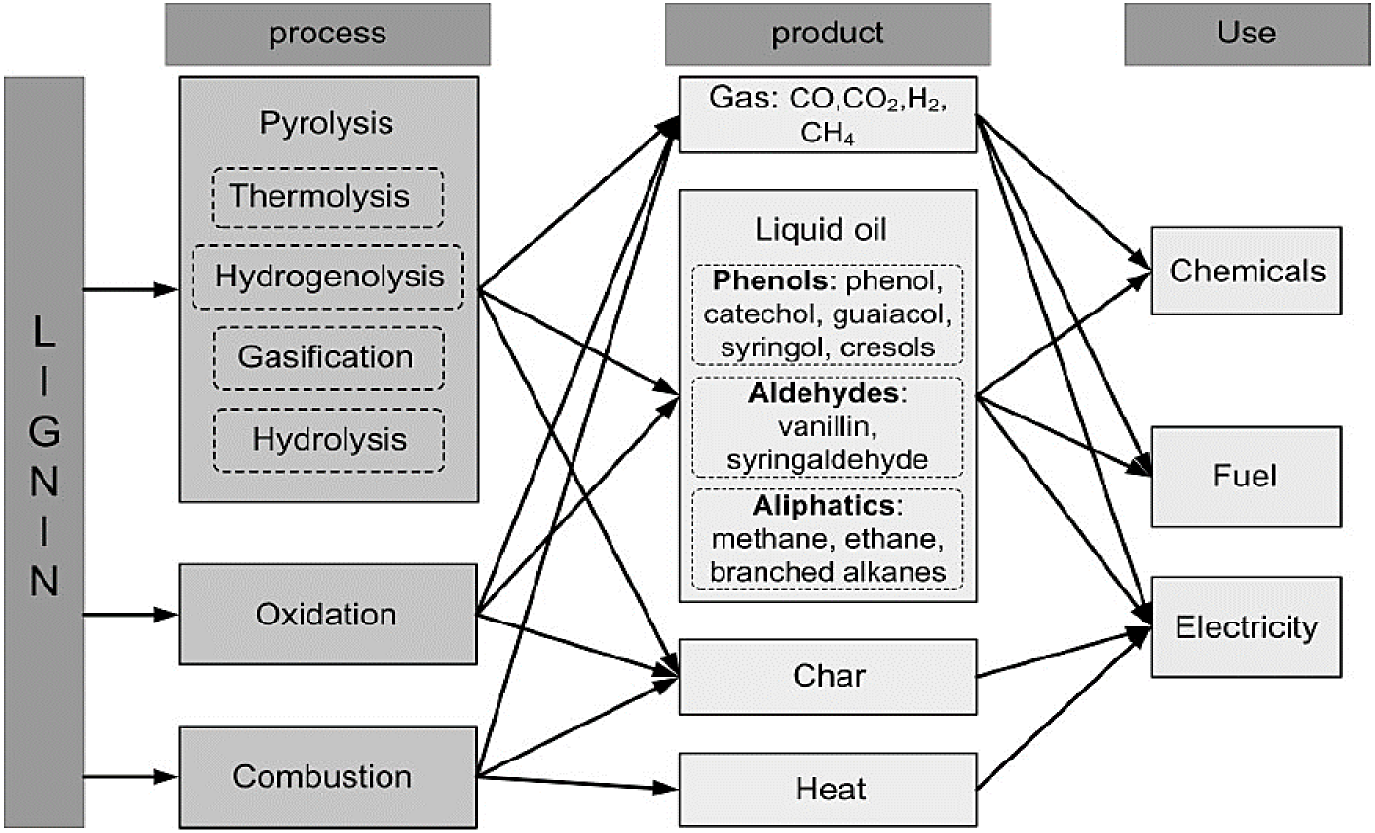
Scheme 1. Pathways of GG and VG degradation in acidic ILs. Analogous chemistry occurs with GG and VG dimers.

Catalytic degradation of lignin model compounds in acidic imidazolium based ionic liquids: Hammett acidity and anion effects

Blair J. Cox [a], Songyan Jia [a,b], Z. Conrad Zhang [c], John G. Ekerdt [a,*]

Source: Wood – Lignin

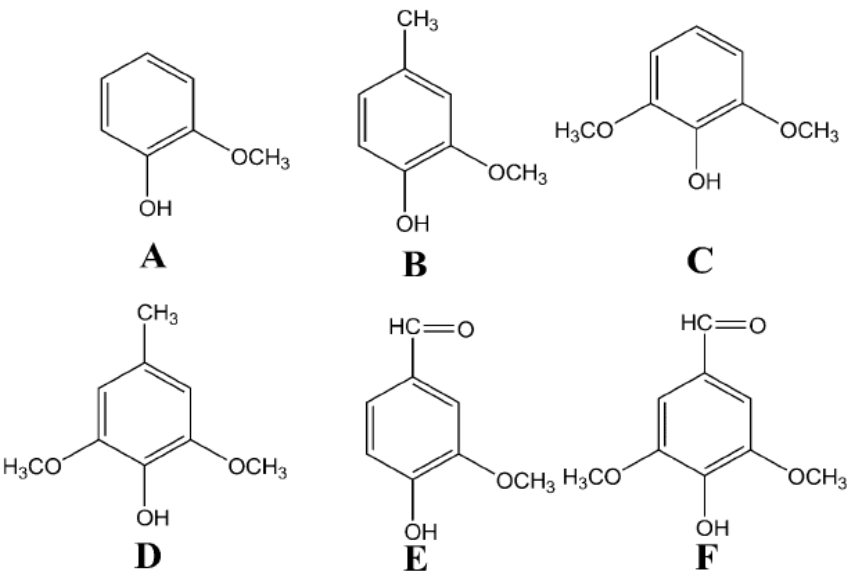
Major Thermochemical Conversion Processes



(Panday & Kim, 2011)

Source: Wood – Lignin

Major products during pyrolysis of lignin



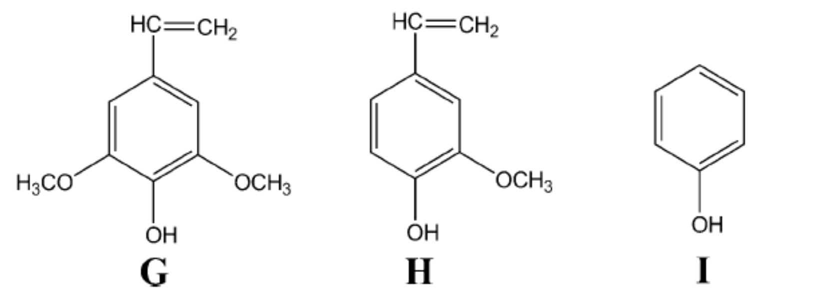
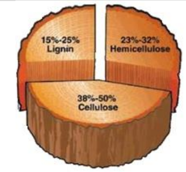


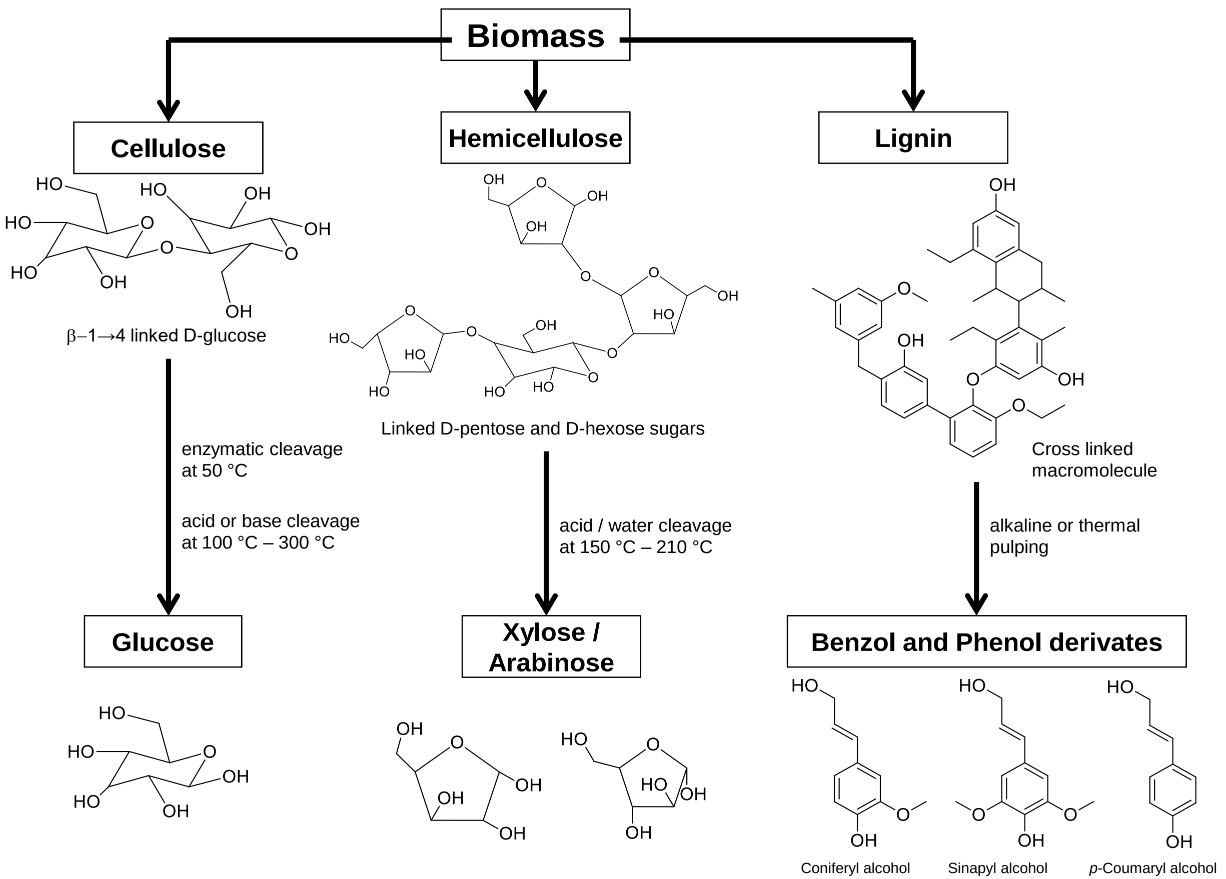
Figure 3. Major products obtained during lignin pyrolysis: (A) guaiacol, (B) methyl guaiacol, (C) syringol, (D) methyl syringol, (E) vanillin, (F) syringaldehyde, (G) vinyl syringol, (H) vinyl guaiacol, (I) phenol.

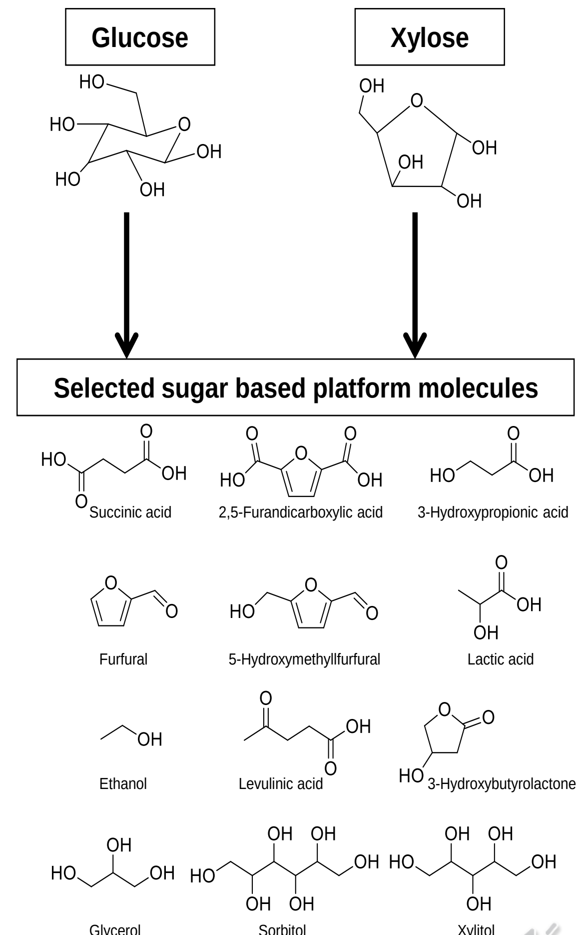
C.Saiz-Jimenez *et. al*. Organic Geochemistry 10 (1986) 869

Products from lignocellulosic biomass



- **Cellulose 38 – 50 %**
  - Long chains of beta-linked glucose
  - Semicrystalline structure
- **Hemicellulose 23 – 32 %**
  - A collection of 5- and 6-carbon sugars linked together in long, substituted chains- branched
  - Xylose, arabinose, glucose, mannose and galactose
- **Lignin 15 – 25 %**
  - Complex network of aromatic compounds
  - High energy content
  - Treasure trove of novel chemistry





K. Hengst, M. Schubert, W. Kleist, J.-D. Grunwaldt, in Catalytic Hydrogenation for Biomass Conversion (R. Rinaldi, Editor), RSC Energy and Environment Series No.13, The Royal Society of Chemistry, 2015, p. 125-150.

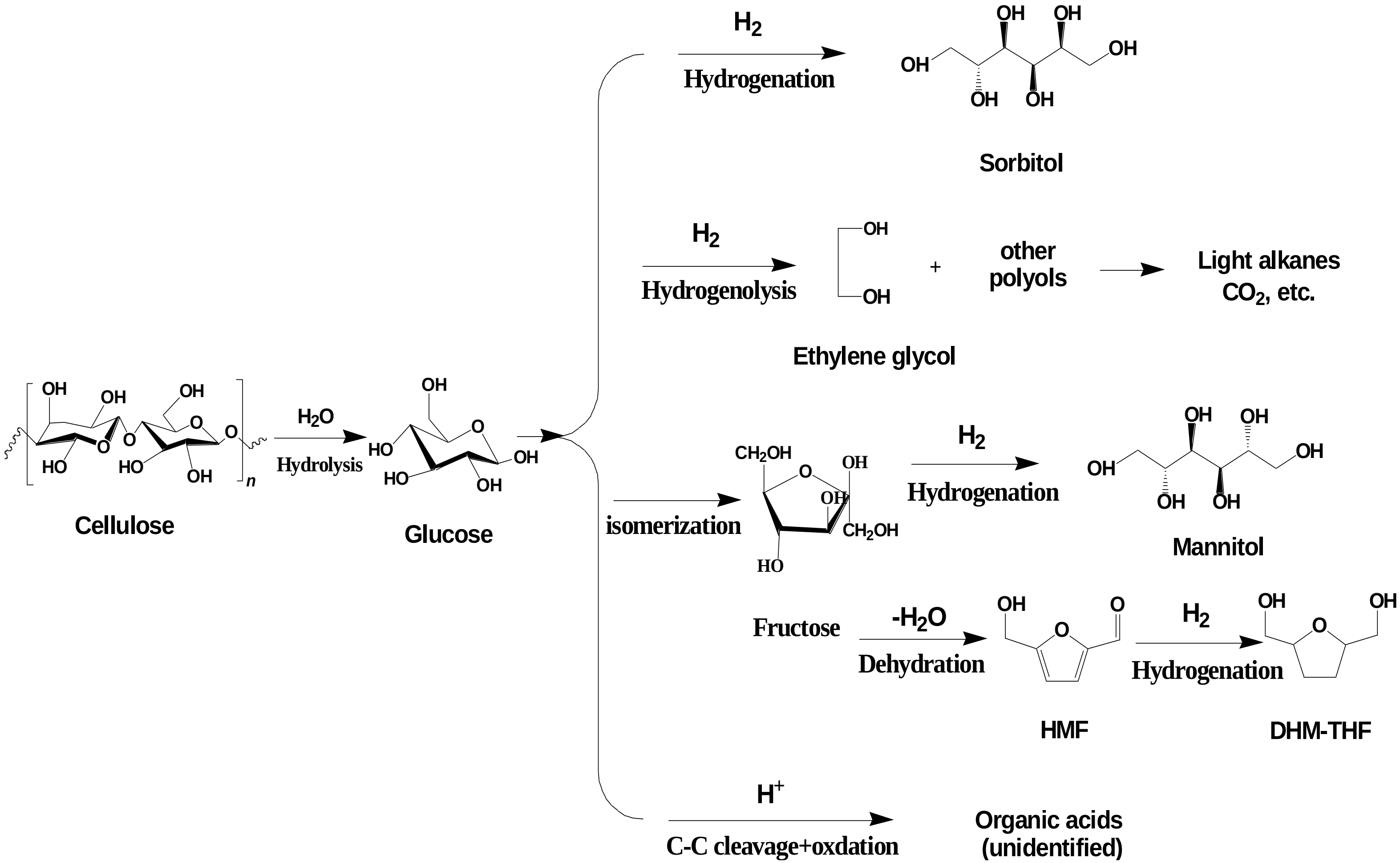
Sugar-Based Building Blocks–Biomass Platform Molecules

- 12 building block chemicals that can be produced from sugars via biological or chemical conversions.
- The twelve building blocks can be subsequently converted to a number of high-value bio-based chemicals or materials.
- Building block chemicals are molecules with multiple functional groups that possess the potential to be transformed into new families of useful molecules.

Building Blocks	
1,4-diacids (succinic, fumaric and malic)	*Bernsteinsäure, Fumarsäure, Äpfelsäure*
2,5-furandicarboxylic acid	*2,5-Furandicarbonsäure*
3-hydroxy propionic acid	*3-Hydroxypropionsäure*
aspartic acid	*Asparaginsäure*
glucaric acid	*Glucarsäure*
glutamic acid	*Glutaminsäure*
itaconic acid	*Itaconsäure*
levulinic acid	*Lävulinsäure*
3-hydroxybutyrolactone	*3-Hydroxybutyrolacton*
glycerol	*Glycerin*
sorbitol	*Sorbitol*
xylitol, arabinitol	*Xylitol, Arabinitol*

https://www.nrel.gov/docs/fy04osti/35523.pdf

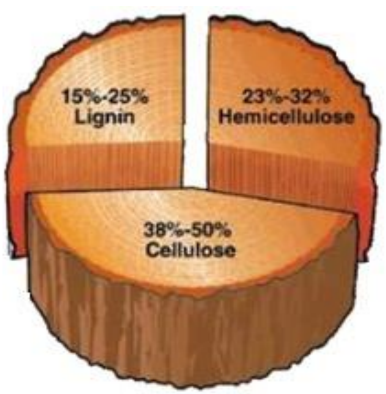
Biomass Platform Molecules
Catalytic Conversion of Cellulose to Chemicals

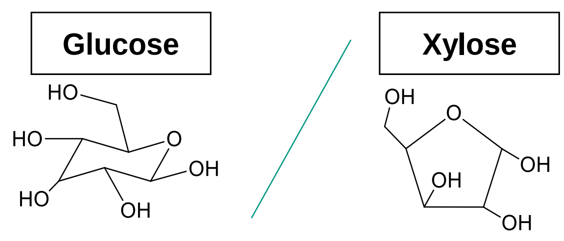


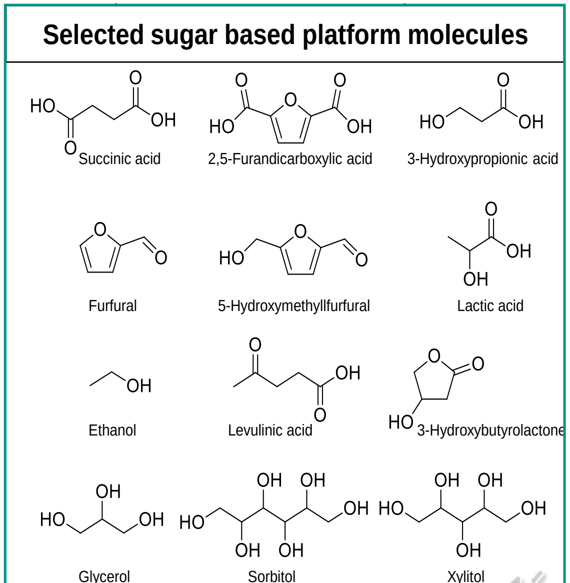
Angew. Chem. Int. Ed. 47 (2008) 8510
Chinese J. Catal. 35 (2014) 602

Summary

- Biomass is a C-rich renewable resource
- Biomass to sugars is known since centuries
- Platform molecules from biomass via sugars – major potential for the chemical industry
- Biomass treatment: hydrolysis (bio-/chemical)
  - Starch / sugars / cellulose, hemicellulose **hydrolysis** to **glucose**
  - Lignin is a challenge
    - With suitable treatment, promising products can be extracted
- 12 main biomass-derived building blocks







Platform Molecules I:
Strategies from Biomass to Platform Molecules

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