Introduction to Biomass Pretreatment and Lignocellulosic Biofuel Production

Lecture 5

Biofuels and Bioproducts

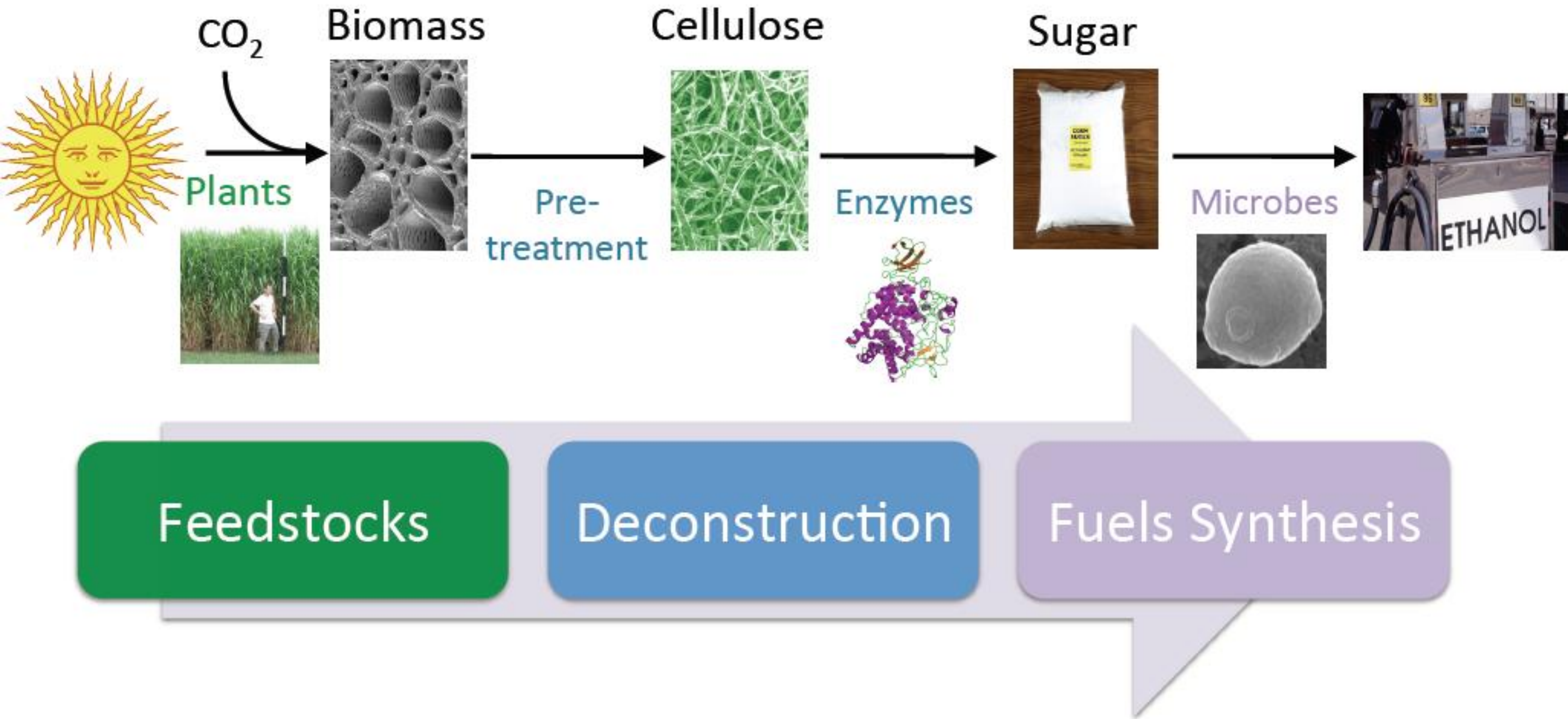
Bronx Community College - 2017

Chemistry and BioEnergy Technology for Sustainability NSF ATE 1601636

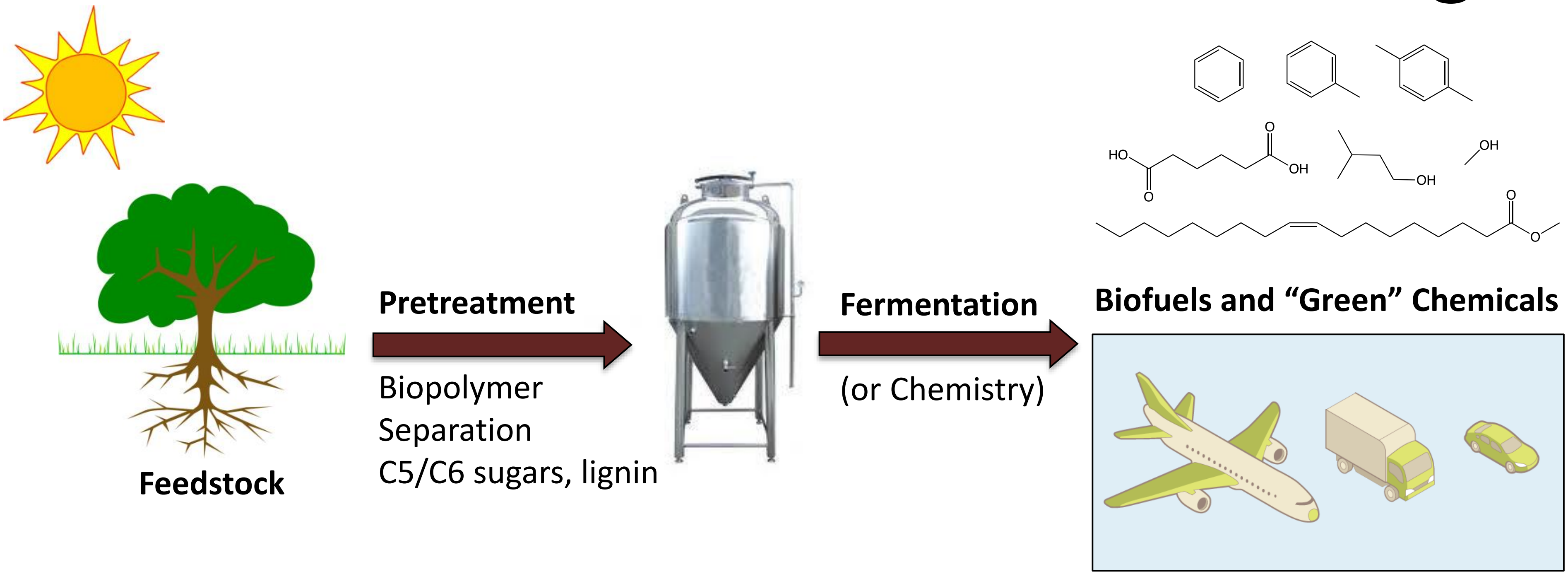
Biomass Pretreatment

- Can be chemical, physical and/or biological
- Enhances extent and rate of enzymatic saccharification
- Impacts feedstock selection, handling and processing
- Pretreatment vessel composition and size
- Fermentation efficiency
- Enzyme loading and composition
- Waste disposal/water Use
- Opportunities to generate co-products

From Biomass to Biofuels



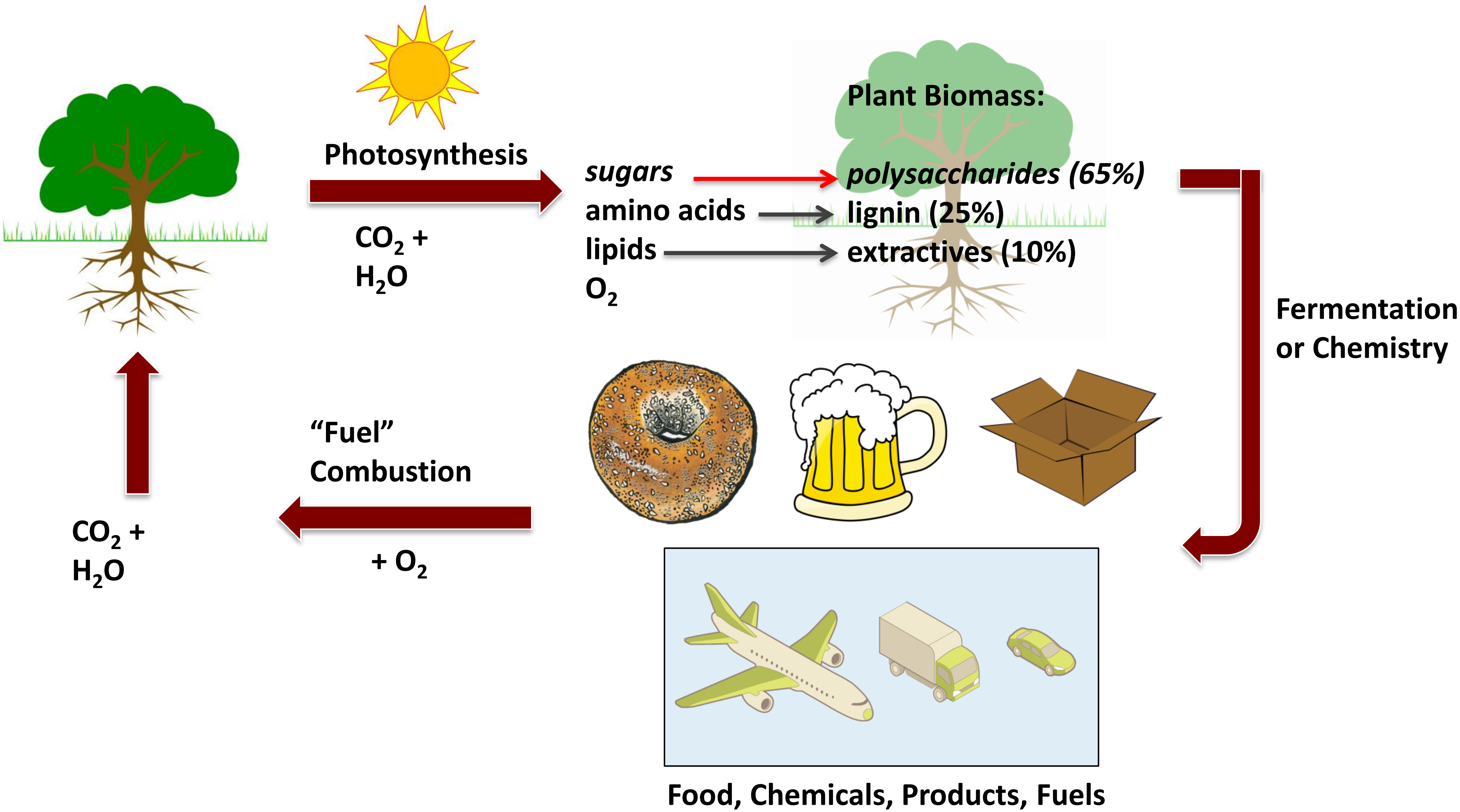
From Biomass to Biomanufacturing



- United States has 700M tons of non-food biomass/year[1]
- 50% conversion of this material could replace 50 billion gallons of oil/year[2]
- Global market for petroleum-replacement chemicals estimated at $500B[3]
- United States has committed to 36 billion gallons renewable fuel by 2020[4]

[1]Klein-Marcuschamer et al. *Biofuels Bioproducts and Biorefining*, 2011. **5** (5): p. 562-569.
[2]BIO, Current uses of synthetic biology for renewable chemicals and biofuels (2013)
[3]Frank and Solomon
[4]U.S. Energy Independence and Security Act of 2007

From Biomass to Bioproducts, and then Back to Biomass



Bio-Manufacturing via Synthetic Biology

- Genes coding enzymes for entire small molecule pathways cloned from plants to microbes

- Up to 12 genes have been cloned into individual yeast or bacterial hosts

- Additional enzymes, e.g. cellulase, hemicellulase, ion pumps have also been expressed in the host cell

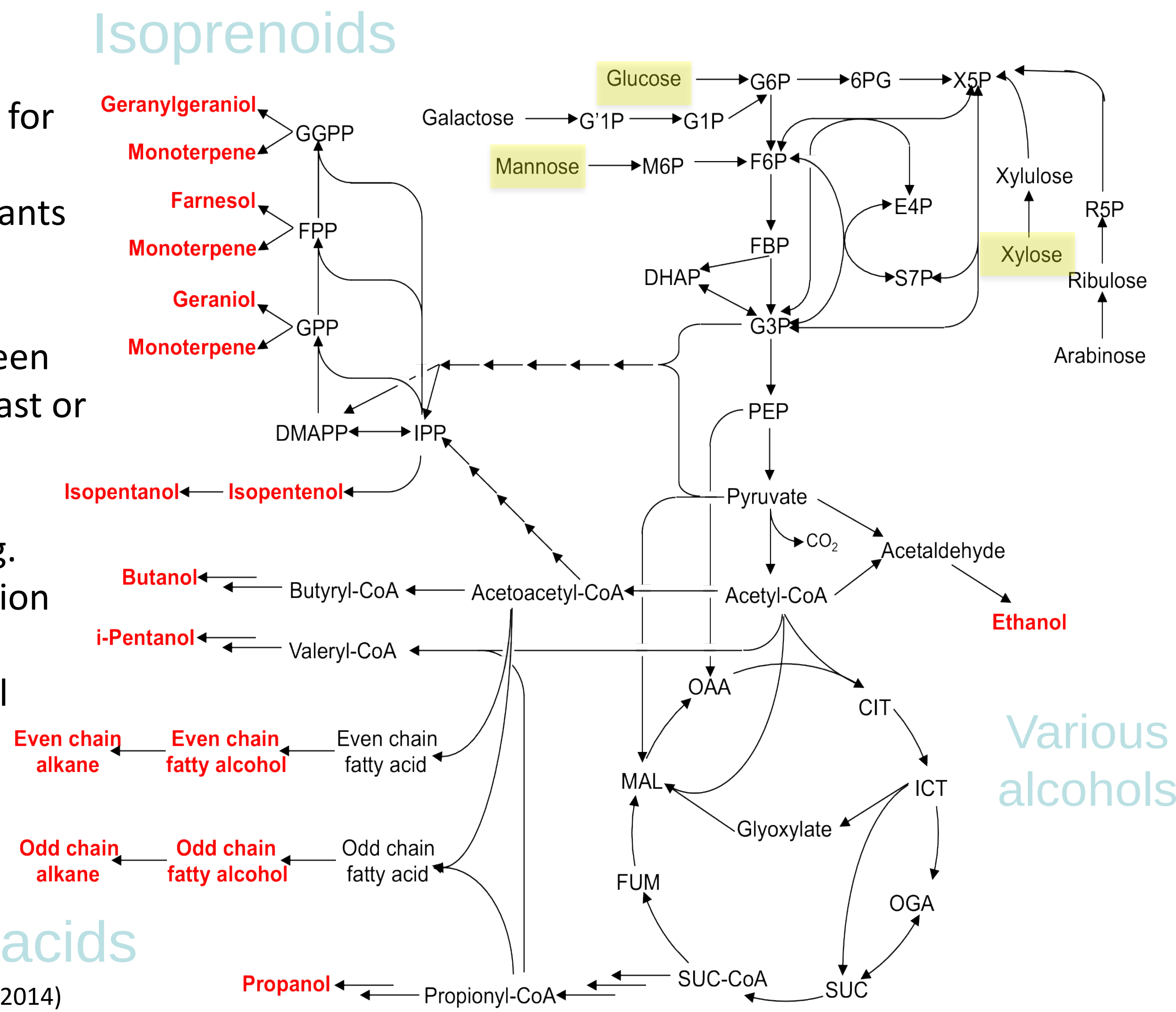
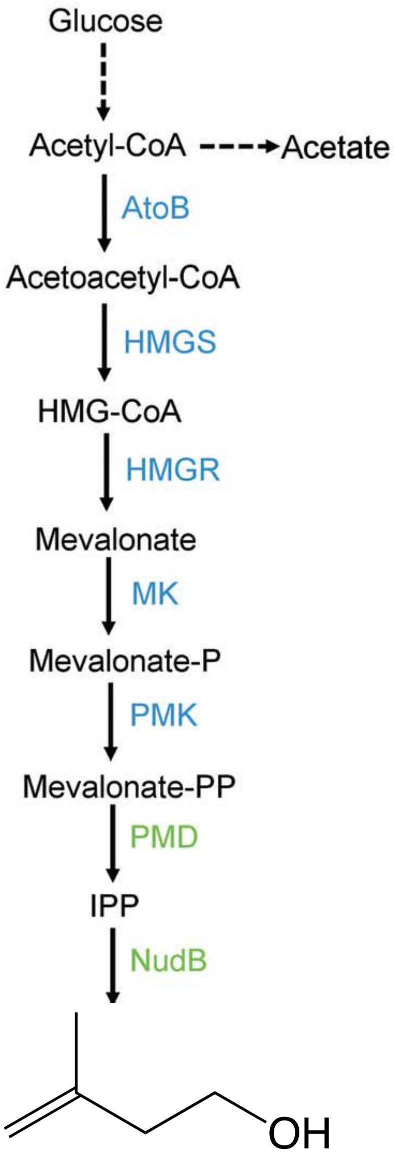


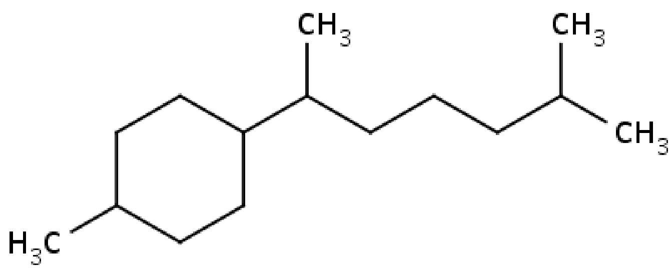
Figure courtesy of:
B. Simmons Joint BioEnergy Institute (2014)

Heterologous Expression of Terpene Biofuels (and Medicines)

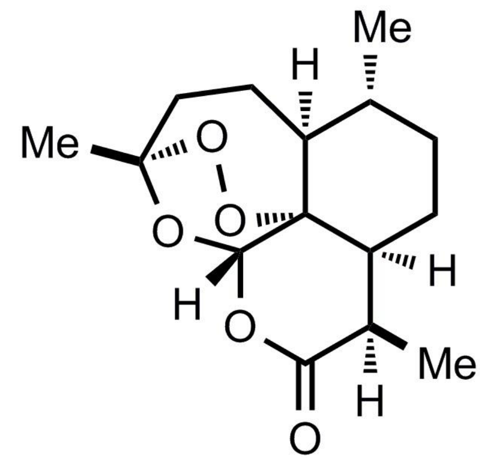


Isopentenol

a "drop-in" gasoline replacement



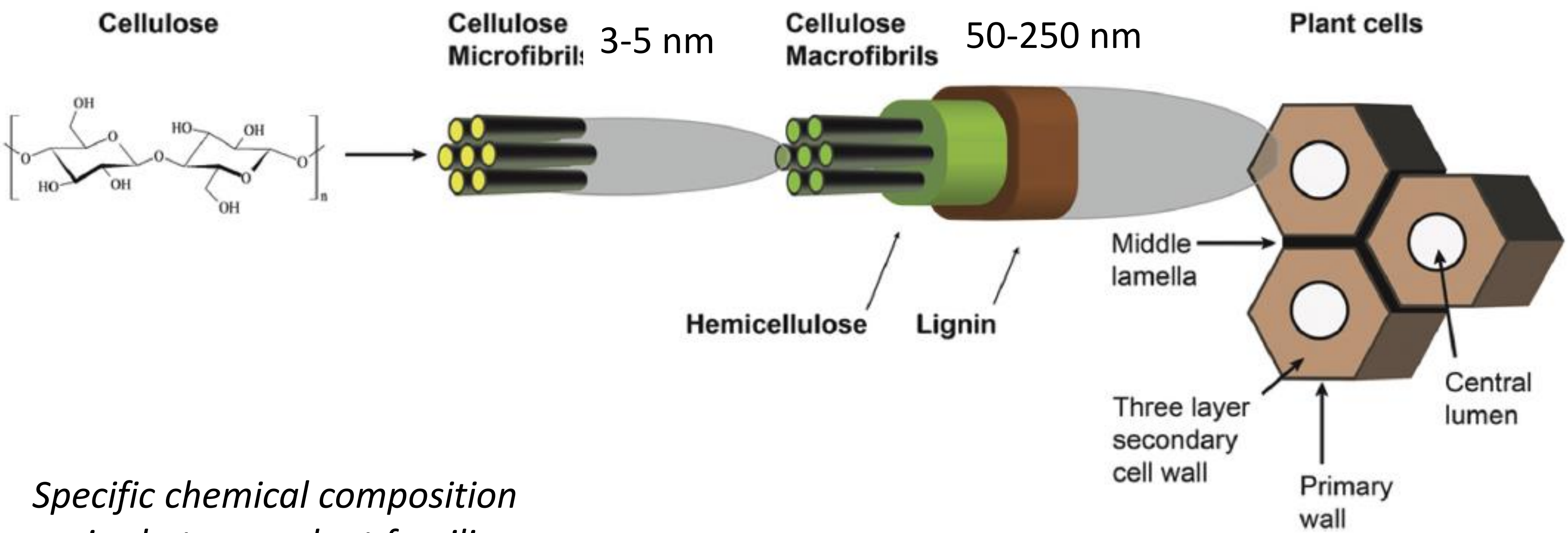
Bisabolane:
Produced heterologously in
S. cerevisiae and E. coli
- 125,000 BTU/Gal
- JP5 Fuel replacement
- model biofuel



Artemisinin:
- Antimalarial drug
- Modular production in Asia, Africa, South America (50+ tons 100 million treatments)

George et al Biotech Bioeng 2014 111
Ro et al *Nature* 440, 940, 2016
Keasling J. *Nature Communications* 2011, 483

The Lignocellulosic Substrate



Specific chemical composition varies between plant families (hardwood, softwood, grasses)

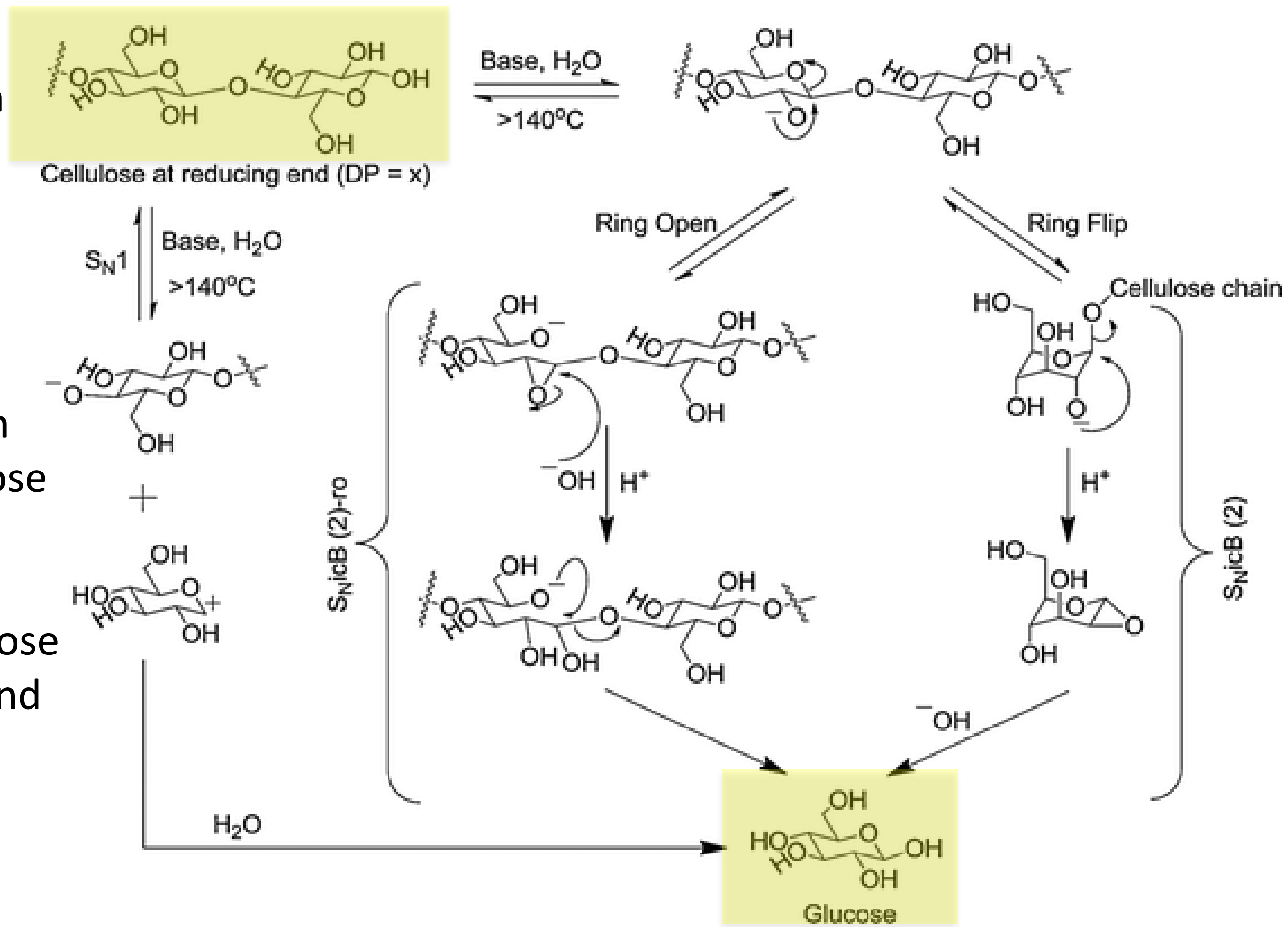
Generic Composition:
45% Cellulose
25% Hemicellulose
25% Lignin
5% Protein, Ash, Extractables

- Cellulose (hexose = glucose)
- Hemicellulose (pentose/hexose)
- Lignin (phenylpropanoid)

Image: Zhang. *Green Chem* **2016** (18) 360

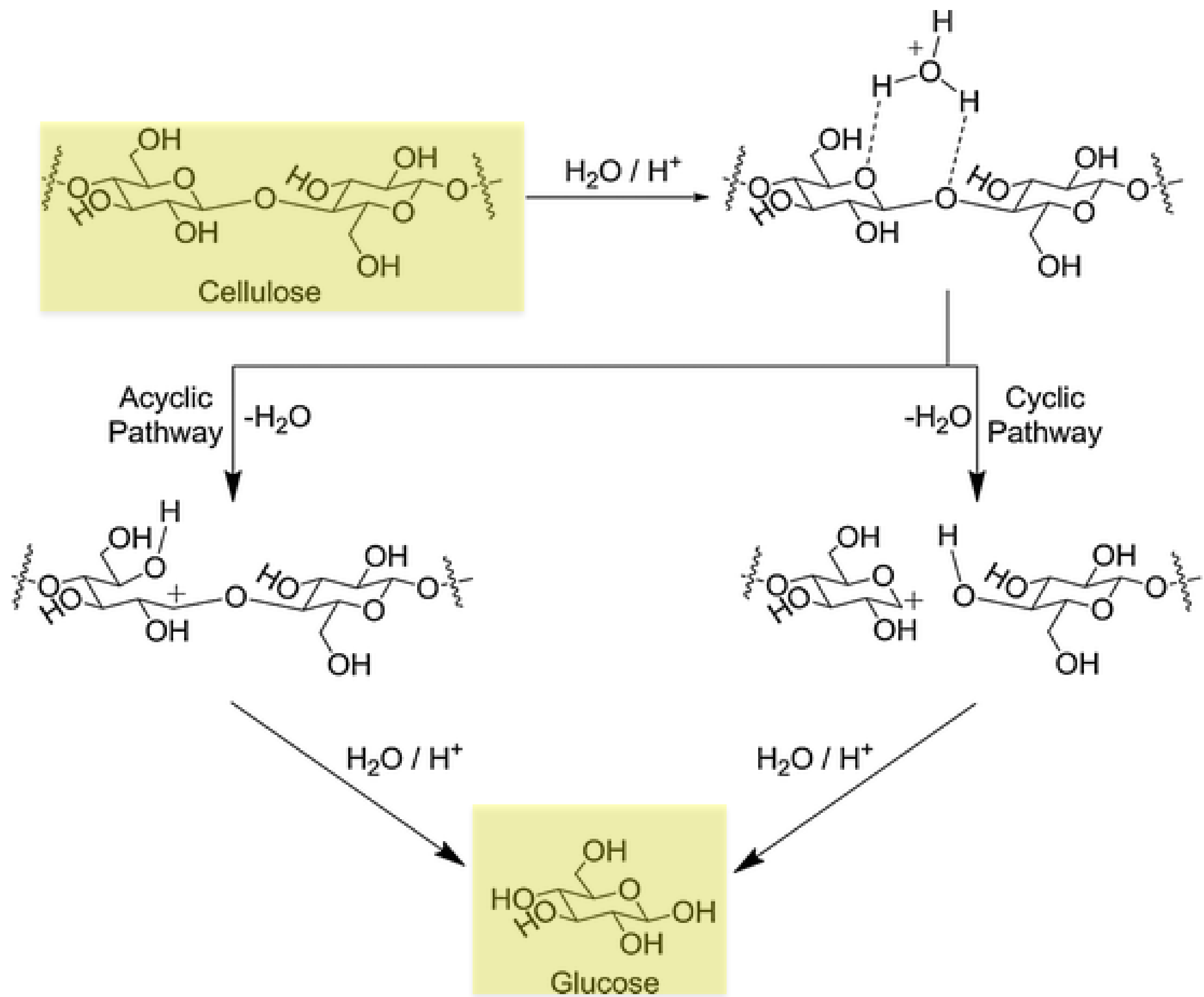
Chemical Conversion of Polysaccharides: Alkali-Catalyzed Hydrolysis of Cellulose to Glucose

- "Peeling" of individual glucose monomers from the reducing end of the polymer occurs slowly < 140°C
- At temps > 140°C, nucleophilic substitution reactions allow for glucose to form faster
- In alkali conditions, glucose isomerizes to fructose and mannose

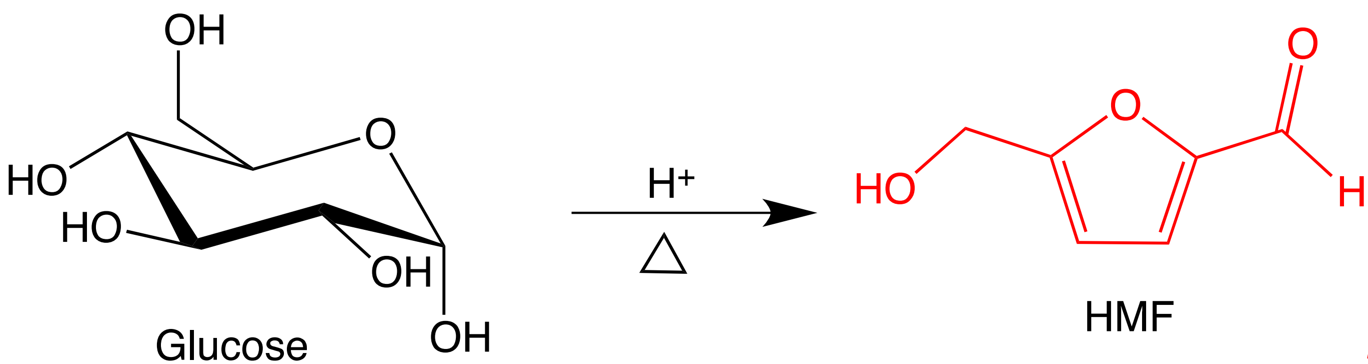


Chemical Conversion of Polysaccharides: Acid-Catalyzed Hydrolysis of Cellulose to Glucose

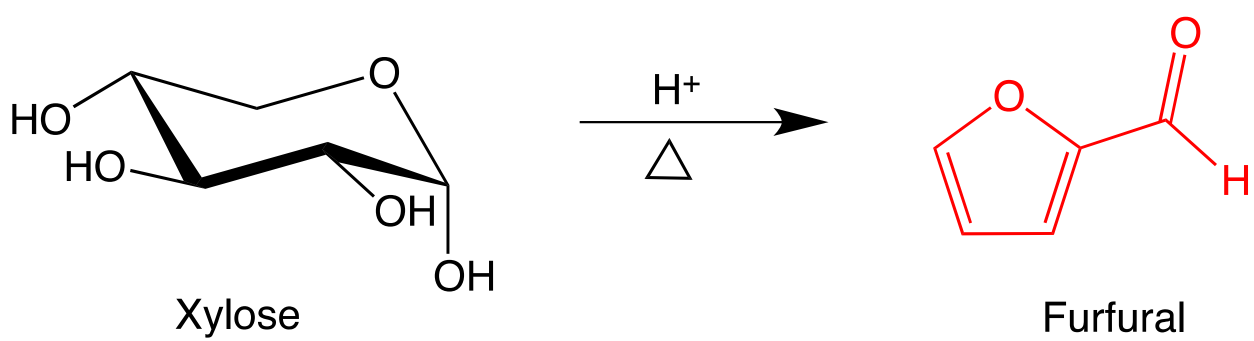
- Works with concentrated and dilute mineral acids and organic acids
- Activation energy cellulose ~ 175 kJ/mol with HCl or H_2SO_4
- First order kinetics with dependence on temperature, [acid] and cellulose crystallinity
- Glucose degradation to 5-hydroxymethylfurfural, formic and levulinic acids as well as condensed structures (humins) occur at ~140 kJ/mol
- Acids present corrosion issues, salt formation during workup, poor recyclability, toxicity, etc.



Formation of Furfurals from Acid Pretreatment



Furfurals =
Toxic to Microbes
(e.g. Yeast)



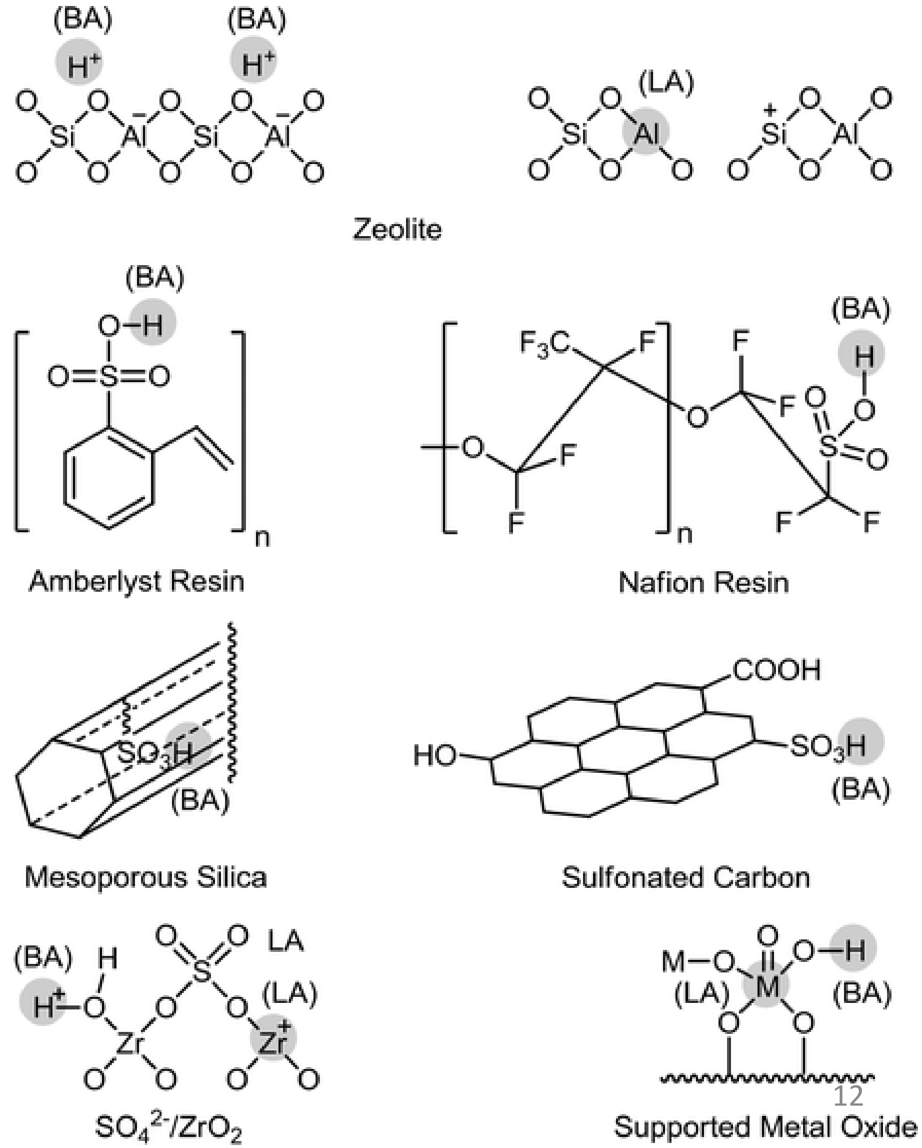
Additional Methods for Converting Cellulose to Glucose

- ***Enzyme Catalyzed***
  - Biofuel Companies = Iogen, POET, Abengoa, Shell/Cosan,
  - Enzyme Producers = Novozymes, Genecor

- ***Solid Acid Catalysts (shown)***
  - (80% of current industrial processes)

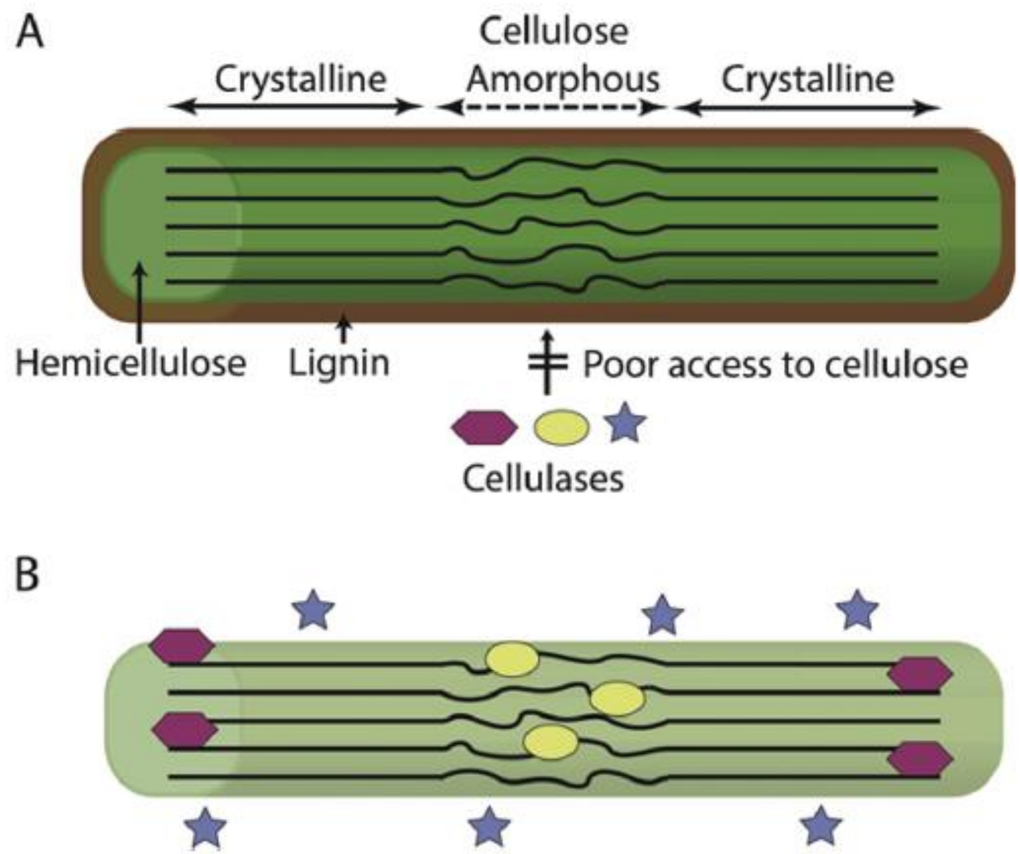
- BA = Brønsted Acid
- LA = Lewis Acid

- ***Ionic Liquids***
  - tunable
  - can also dissolve biomass (i.e. lignin and hemicellulose)



‘Organosolv’ Pretreatment

- Short-chain aliphatic alcohols, polyols, organic acids, acetone, dioxane, phenol, NMMO, 2Me-THF, Me-iBu-ketone, Ionic Liquids (ILs)
- Can produce “high quality lignin” e.g. low sulfur, less condensed
- Higher dielectric constant of solvent = higher ‘acid potential’ for catalyst
- Other considerations = cost, ease of recovery, toxicology, safety, environmental impact
- Solvent viscosity and ‘penetration’ into substrate
- H-Bonding and Polarizability



Reviewed: Zhang et al Green Chem 2016, 18, 360

Solvent Parameters

Substrate Solubilty:

- When δ is similar to the substrate, good dissolution is expected
- δ is not known for cellulose/lignocellulose
- δ is estimated at 22.5 for lignin
- Many of aforementioned organic solvents δ range is 17-27.

Solvent Reactivity (e.g. cellulose swelling):

- Measured empirically
- Calculated by multiple linear regression analysis
- Kamlet-Taft Parameters used for ILs

Hildebrand Solubility (δ)

$$\delta = \sqrt{c} = \left[\frac{\Delta H - Rt}{V_m}\right]^{1/2}$$

c = cohesive energy density ($MPa^{1/2}$)
ΔH = heat of vaporization ($J\ mol^{-1}$)
R = gas constant (8.324 $J\ K^{-1}\ mol^{-1}$)
t = temperature (^oC)
V_m = molar volume of solvent ($cm^3\ mol^{-1}$)

Kamlet-Taft Polarity (γ)

Well correlated with Cellulose Swelling

Measurement:

- ILs and IL water mixtures are tested
- Reichardt's Dye and TMS references
- H-bond acceptor and donor solvents (below)

$$\gamma = \gamma_0 + s\pi^* + A\alpha + B\beta$$

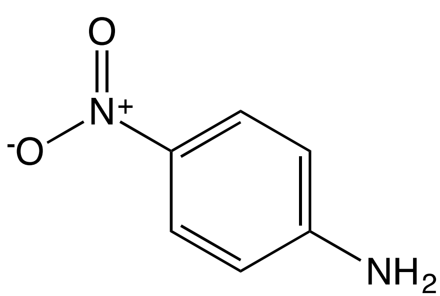
γ_o = regression value based on a reference solvent

π^* = index of solvent dipolarity/polarizability

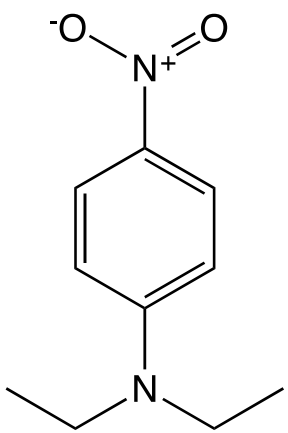
α = solvent hydrogen bond donor acidity

β = solvent hydrogen bond acceptor basicity

s, A, B = regression coefficients



4-nitroaniline



N,N-diethyl-4-nitroaniline

Physical Properties and Biomass Dissolution

Kamlet Taft Parameters

- α = H bond donor
- β = H bond acceptor
- π^* = polarizability

Lignocellulose Dissolution[1]
= β correlation

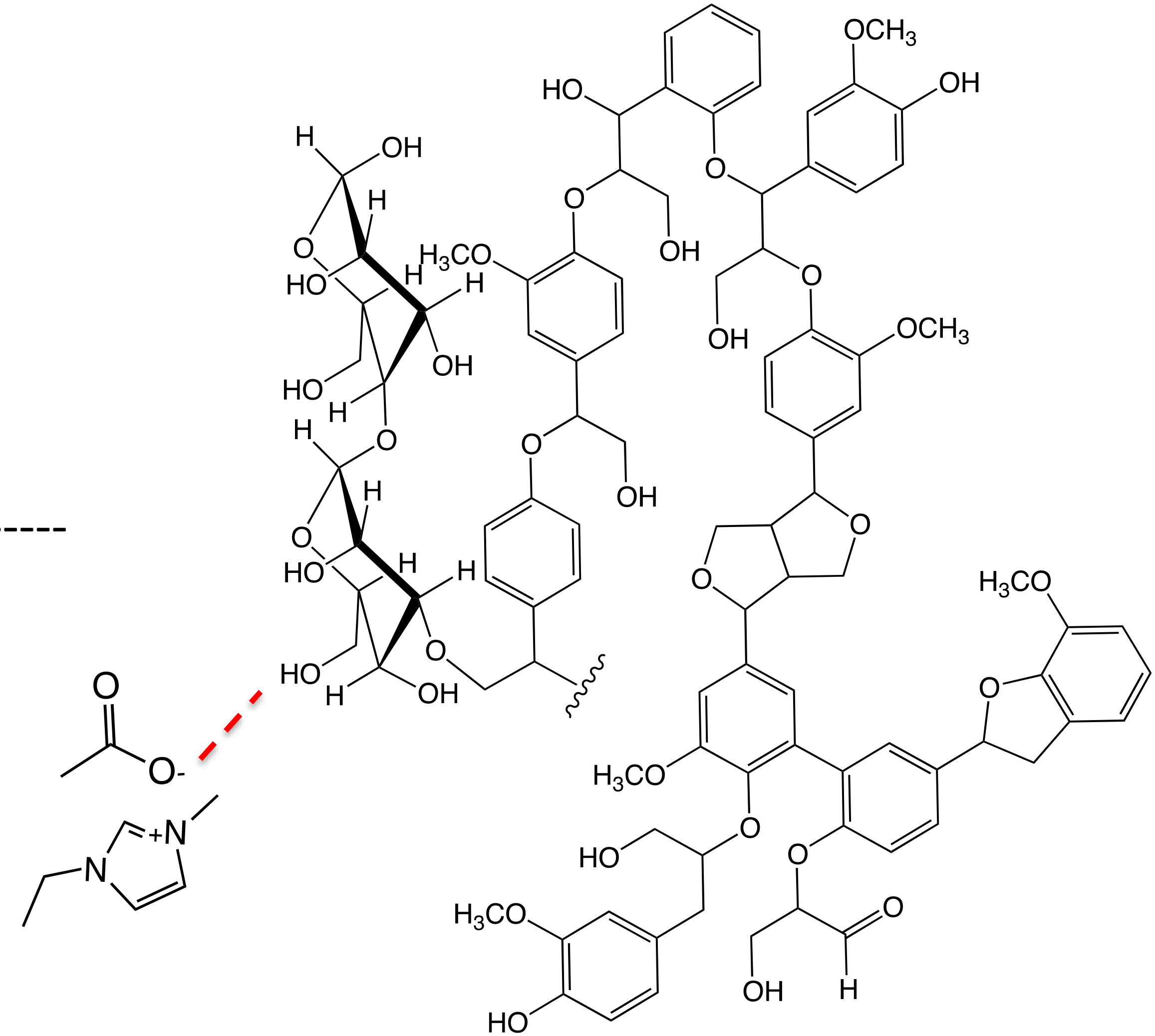
Net Basicity

$B^{IL} = n^2 / x$

n = chemical hardness

x = electronegativity

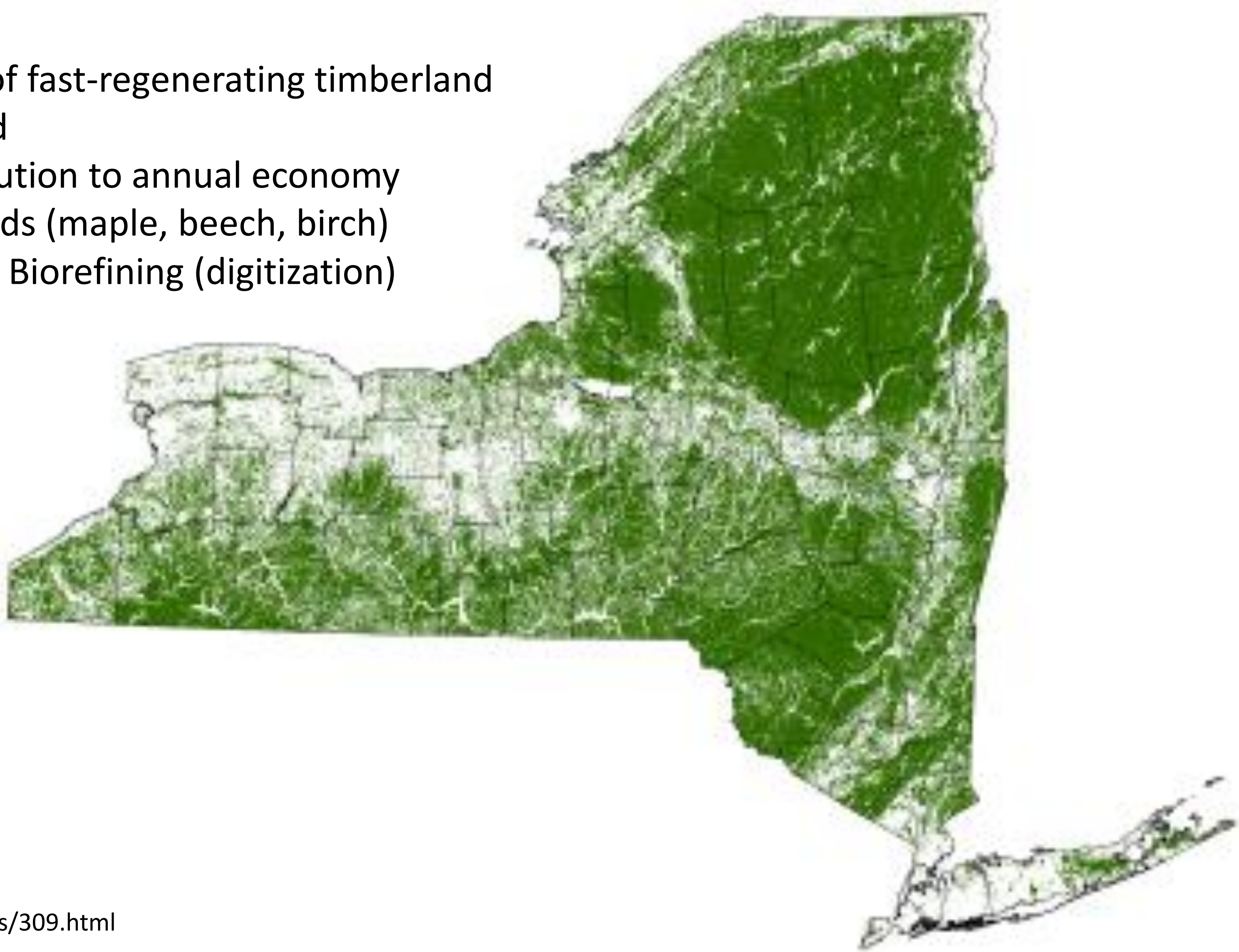
Cellulose dissolution[2,3]
= B^{IL}



[1] Brandt et al. Green Chem 12(4):672–679
[2] Hauru et al. Biomacromolecules 13(9): 2896–2905.
[3] Parviainen A, et al. ChemSusChem 6(11):2161–2169.

NY State as a Sustainable Source of Biomass

- 18.5M acres of fast-regenerating timberland
- 60K employed
- $4.6B contribution to annual economy
- 53% hardwoods (maple, beech, birch)
- Pulp/Paper -> Biorefining (digitization)

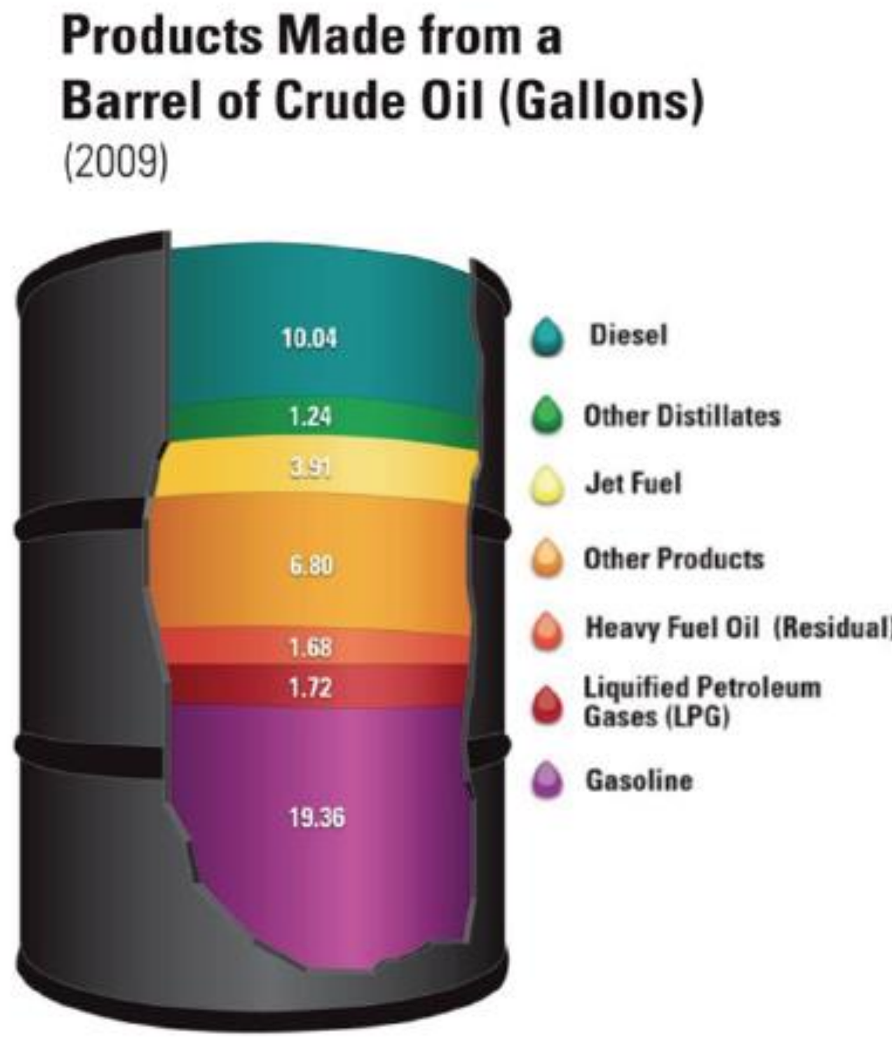


http://www.dec.ny.gov/lands/309.html

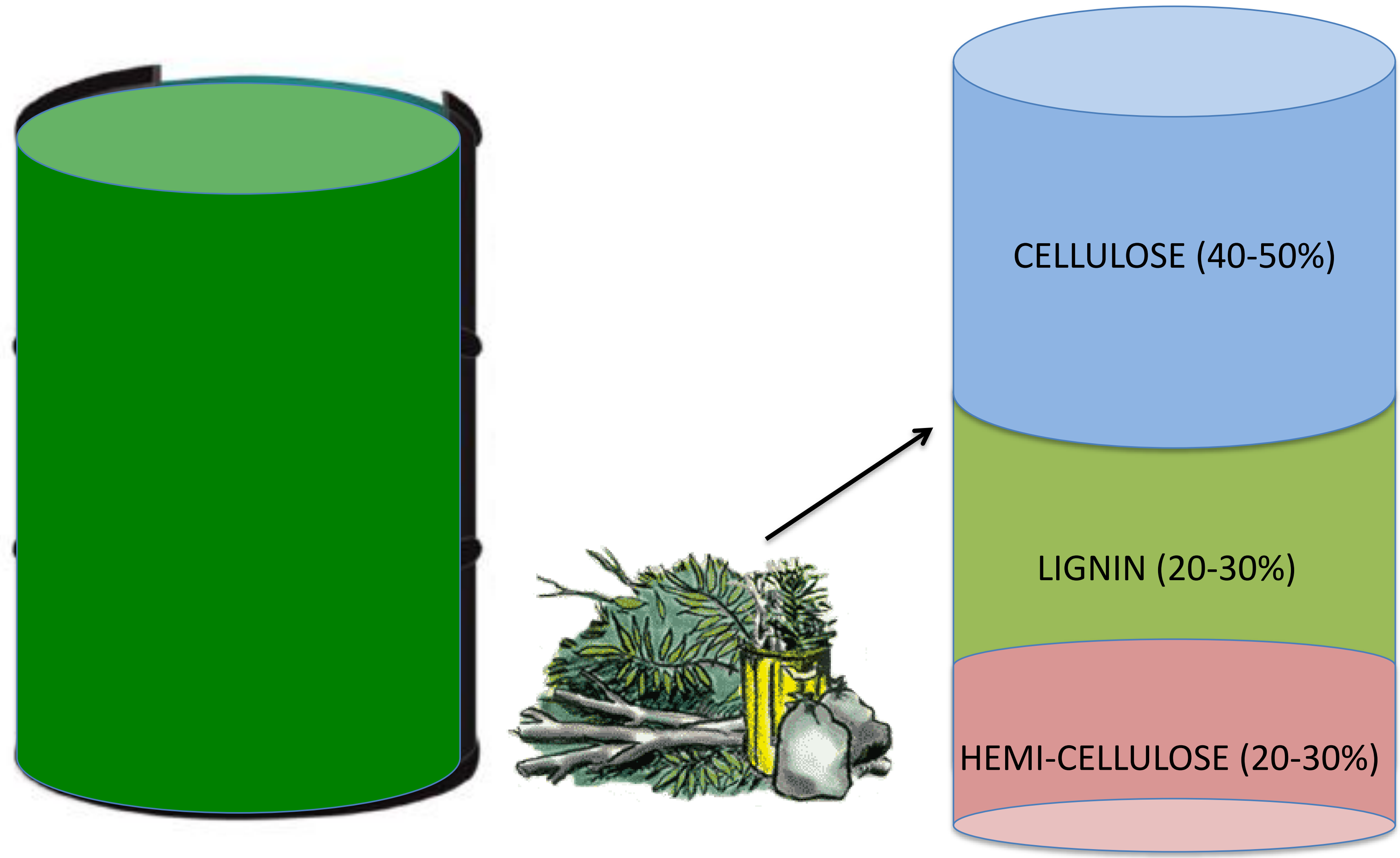
Ethanol, etc…

- "Bio-based" economy requires replacement of all products currently derived from oil.

- "System of systems" approach to feedstock valorization

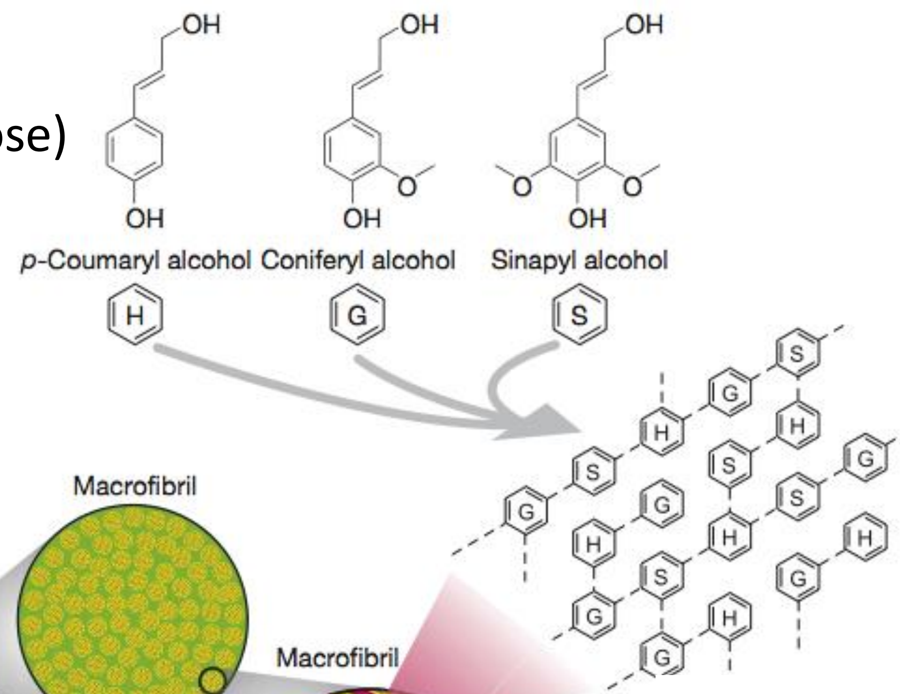


Replacement of Petroleum with Plant Biomass



The Plant Cell Wall

- Cellulose (C6, glucose)
- Hemicellulose (C5, e.g. xylose and glucose)
- Lignin (phenylpropanol)



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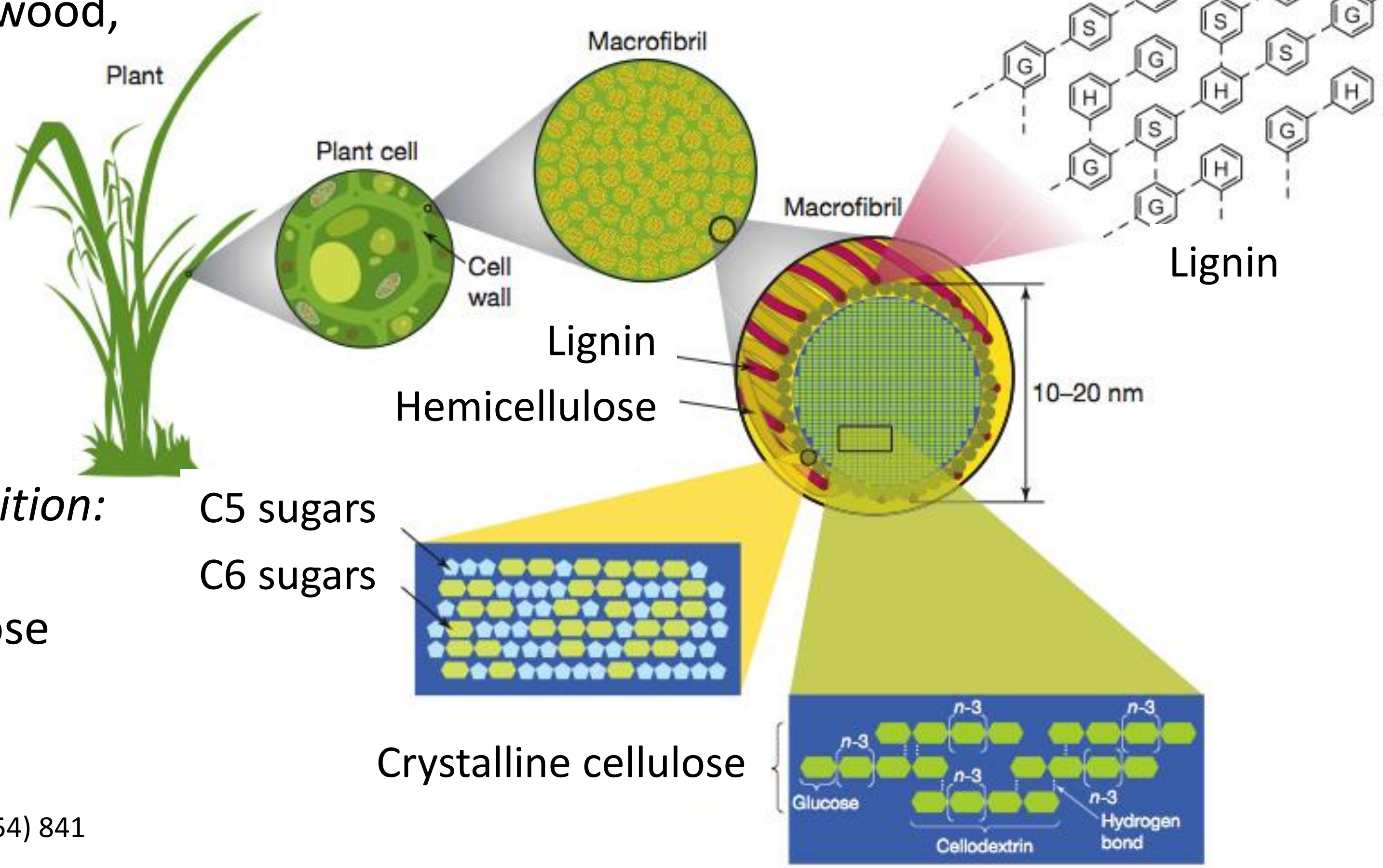
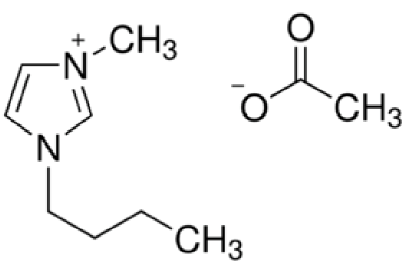


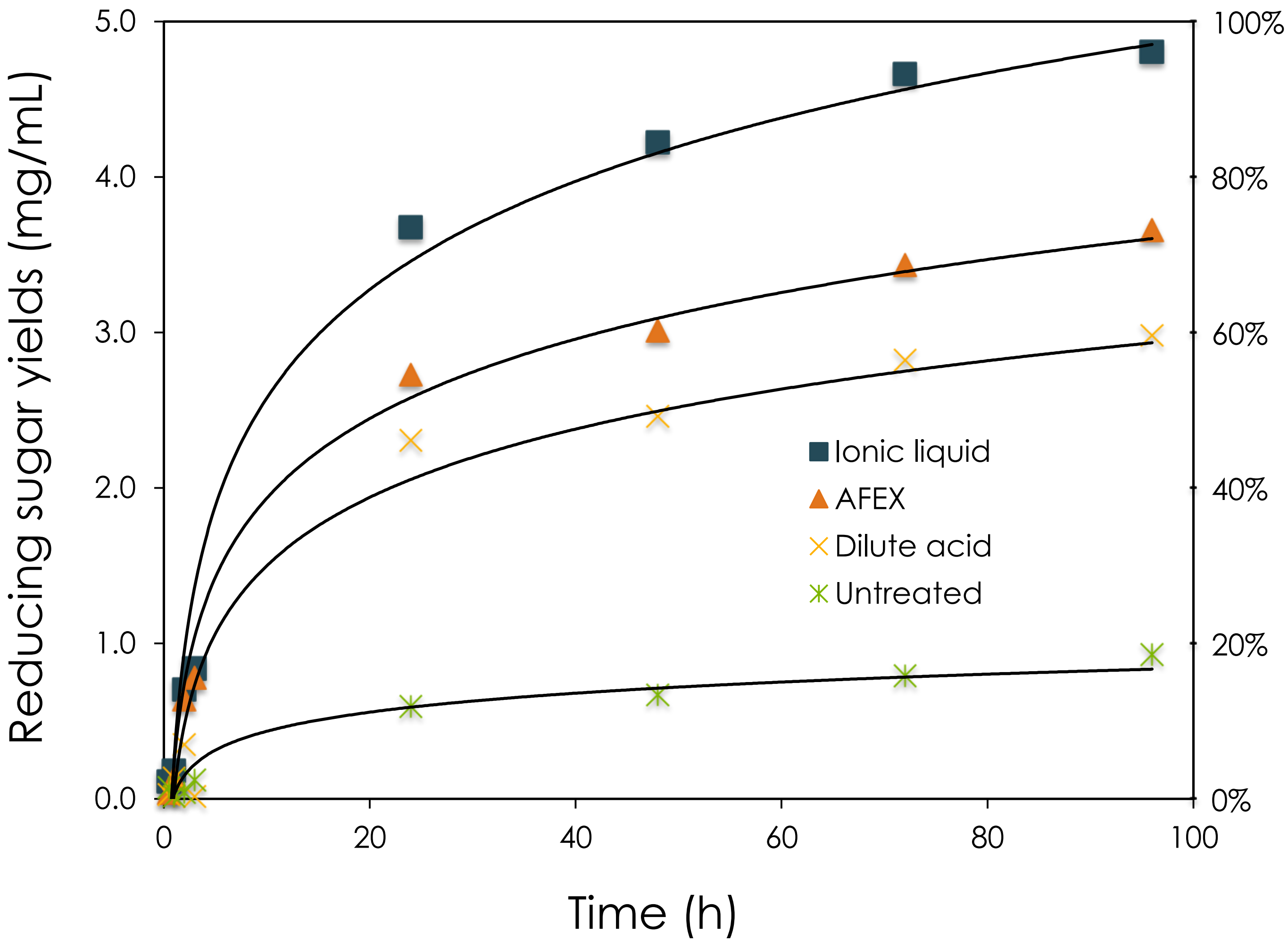
General Composition:
45% Cellulose
25% Hemicellulose
25% Lignin
5% Protein

Rubin EM. *Nature* **2008** (454) 841

Biomass Pretreatment

IL increases
- Sugar yields
- Rate
- Energetics
- Water use
- Cost





Li et al., *Biores. Tech.* (2011), 102(13), 6928-6936; Li et al., *Biores. Tech.* (2010), 101 (13), 4900-4906