Technology & Engineering

Challenges of Ethanol Production from Lignocellulosic Biomass

Maha Dakar

Varieties of Carbohydrates

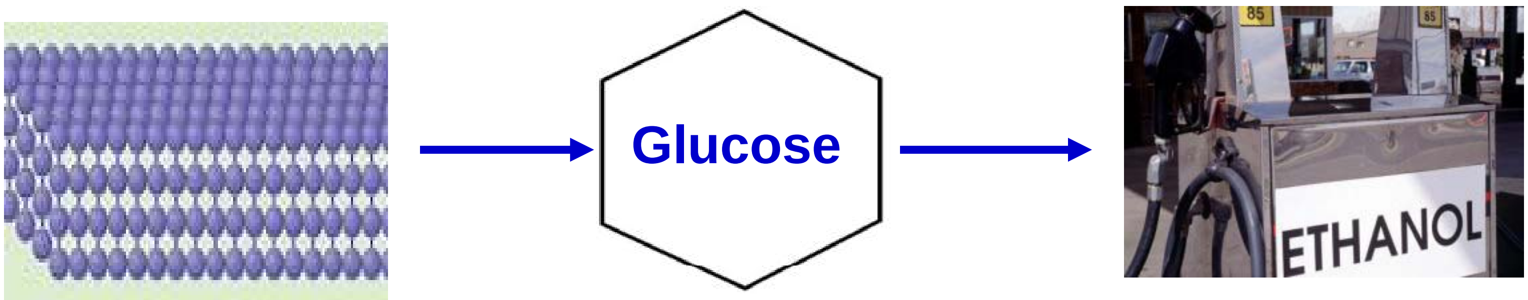
Sugar

Starch

Cellulose/Hemicellulose

What All Plants Have in Common

Cellulose



Why is it difficult to hydrolyze lignocellulosic biomass into sugar to make ethanol?

Lignocellulosic Biomass

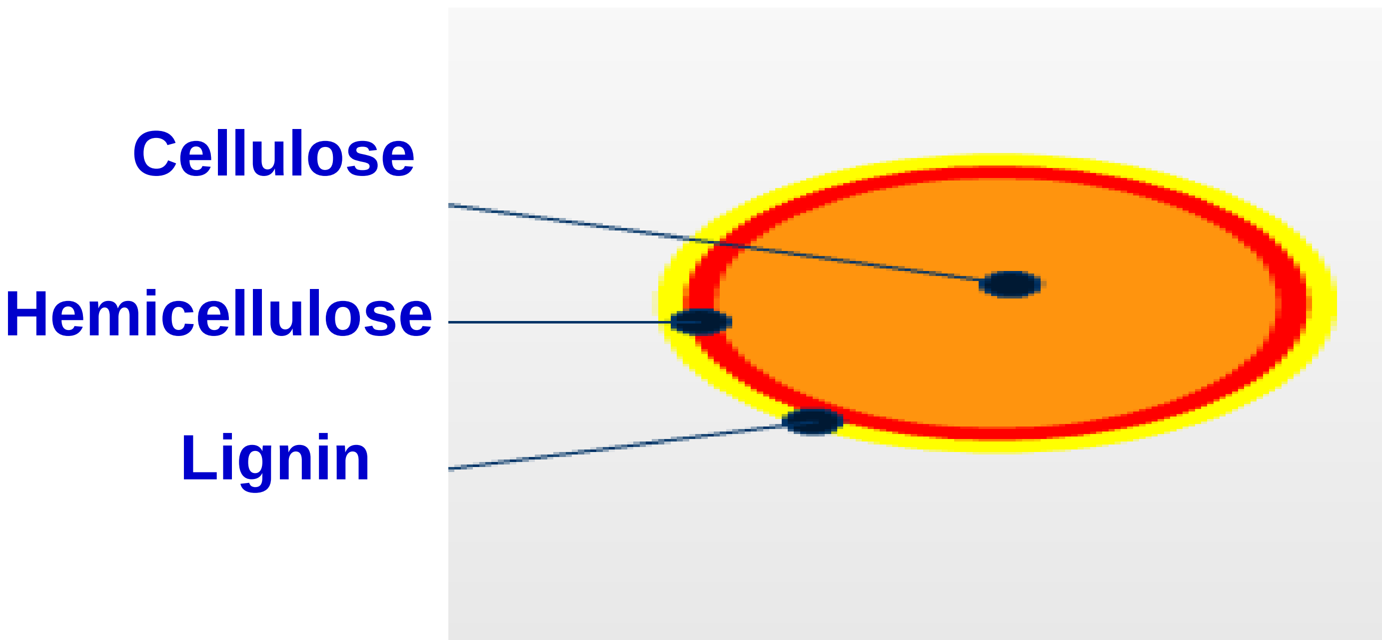
- Biomass: biological material derived from living organisms. Biomass for energy related to plant
- Lignocellulosic biomass: cellulose, hemicellulose (complex carbohydrates) & lignin
- Cellulose: structural material in plants & most abundant biomass in earth
- Lignocellulose: strength, resistance to degradation
- Cellulose & hemicellulose: polymers of sugars, potential source of fermentable sugars
- Lignocellulosic biomass do not directly go into food

Lignocellulosic Biomass Feedstock

- **Woody Biomass**
  - Forest residues
  - Wood waste
- **Non-Woody Biomass**
  - Agricultural Residues:
    - Straws (wheat, barley, rice)
    - Bagasse (sugarcane, sweet sorghum)
    - Stover (corn, milo)
- **Organic Waste**
  - Animal waste
  - Sewage sludge

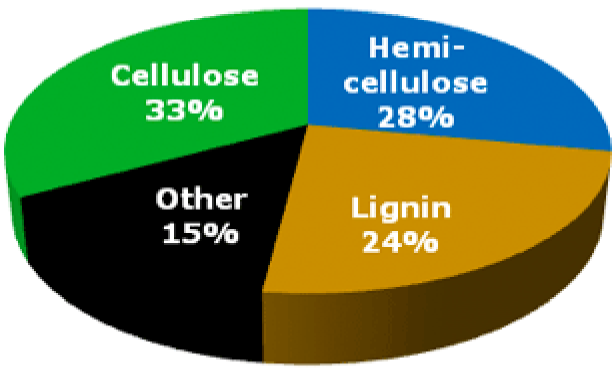
What is Lignocellulosic Material?

lignocellulose = lignin + cellulose + hemicellulose

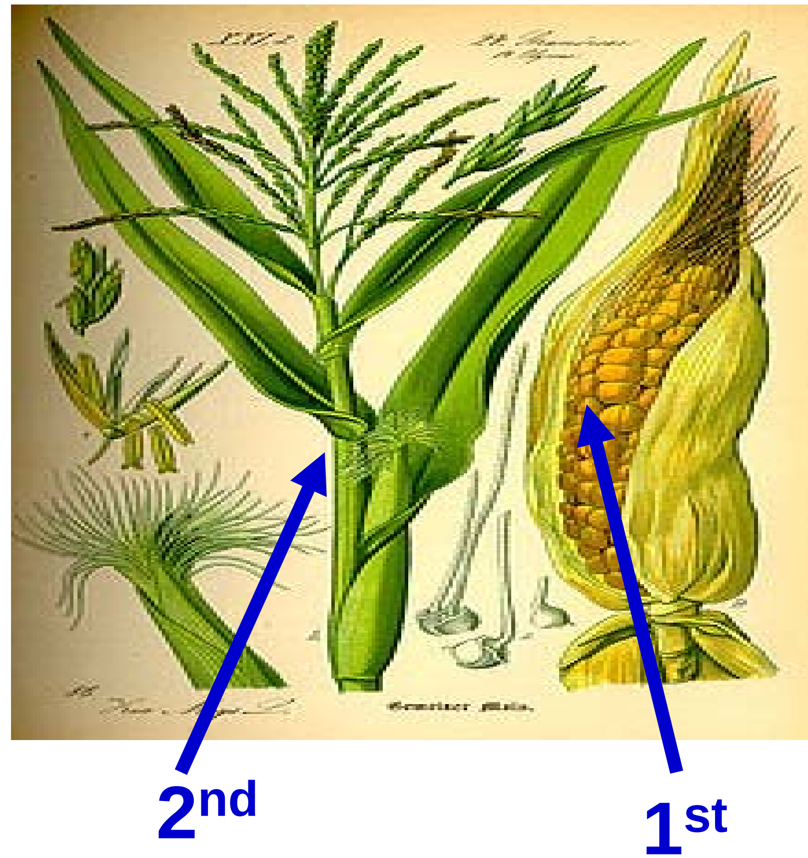


Composition of Lignocellulose

Lignocellulosic materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwoods stems	40–55	24–40	18–25
Softwood stems	45–50	25–35	25–35
Nut shells	25–30	25–30	30–40
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Paper	85–99	0	0–15
Wheat straw	30	50	15
Sorted refuse	60	20	20
Leaves	15–20	80–85	0
Cotton seed hairs	80–95	5–20	0
Newspaper	40–55	25–40	18–30
Waste papers from chemical pulps	60–70	10–20	5–10
Primary wastewater solids	8–15	NA	24–29
Swine waste	6.0	28	NA
Solid cattle manure	1.6–4.7	1.4–3.3	2.7–5.7
Coastal Bermuda grass	25	35.7	6.4
Switchgrass	45	31.4	12.0

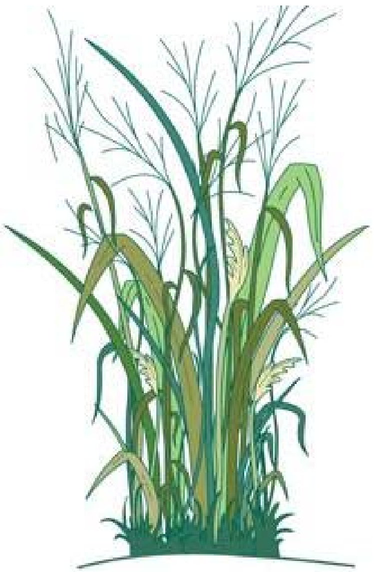


1^{st} Generation vs. 2^{nd} Generation



How Do We Go From

This To This?



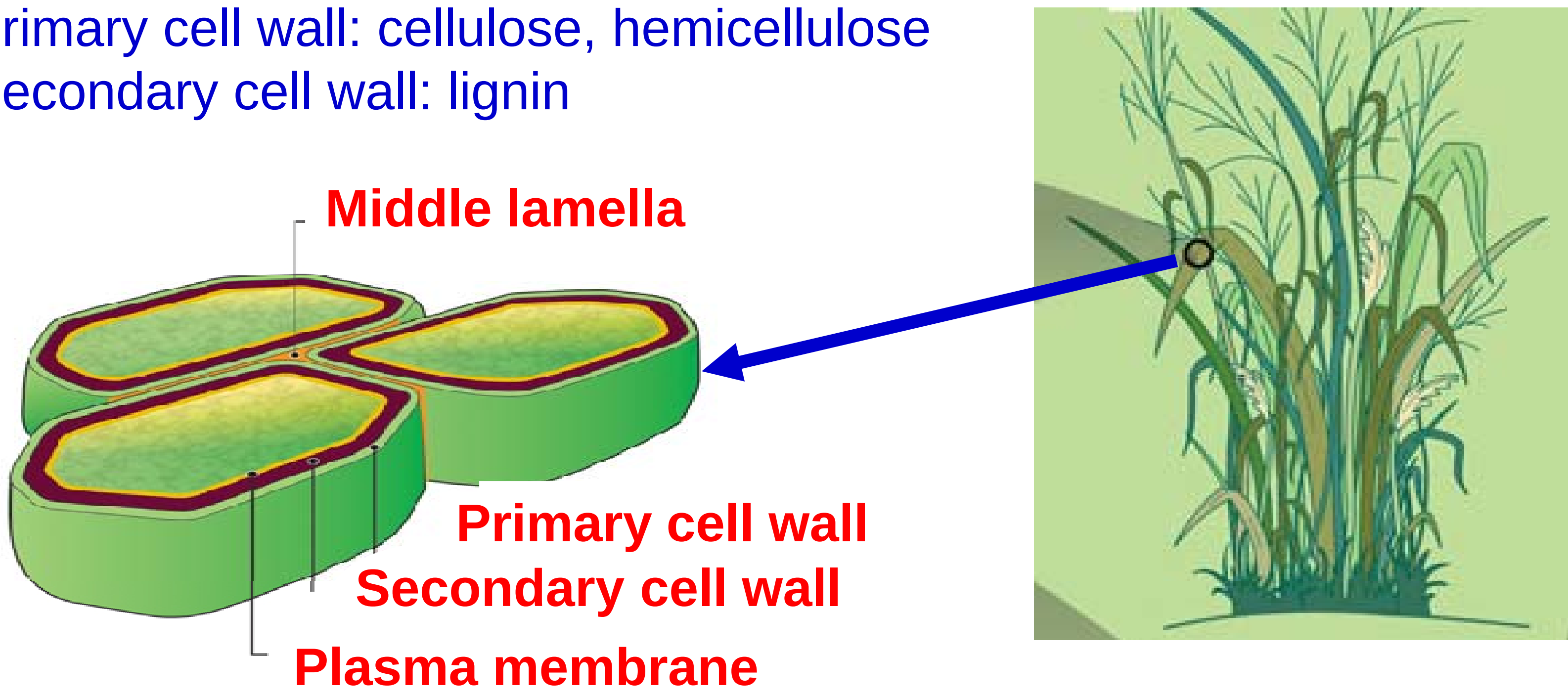
Switchgrass

Bagasse

Plants Cell Walls

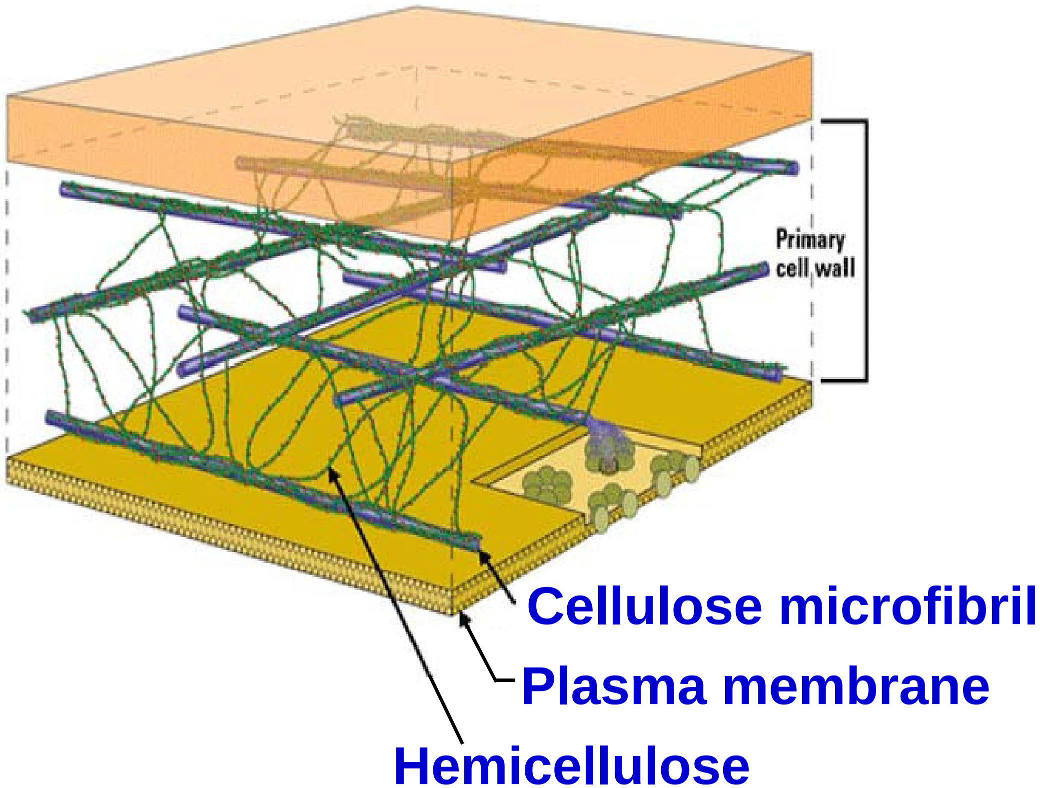
Plants Cell Walls:

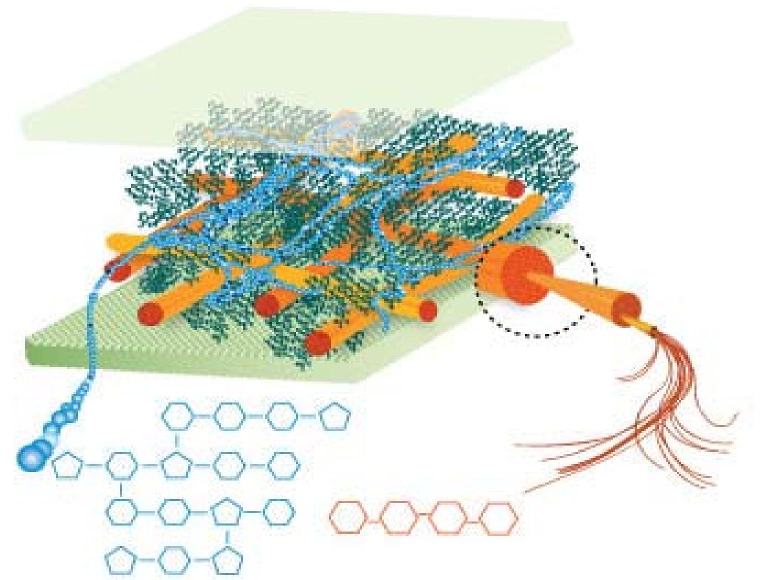
- Middle lamella: pectin
- Primary cell wall: cellulose, hemicellulose
- Secondary cell wall: lignin



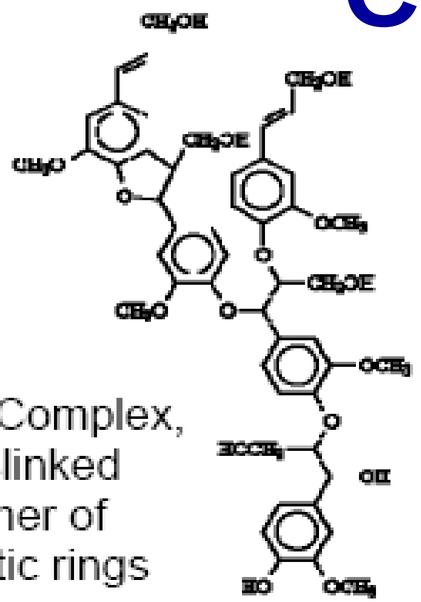
Optimizing plant biomass for efficient processing requires understanding of plant cell wall structure and function

Primary Cell Wall





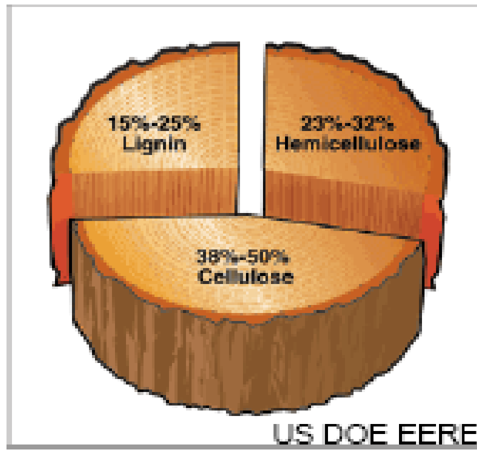
Cellulose, Hemicellulose, Lignin Composition

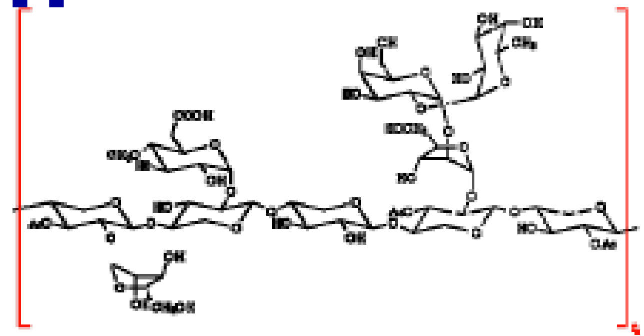


Lignin: Complex, crosslinked polymer of aromatic rings

(Phenolic monomers)

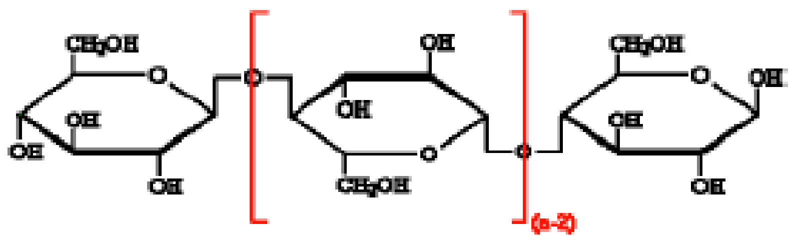
Very high energy content





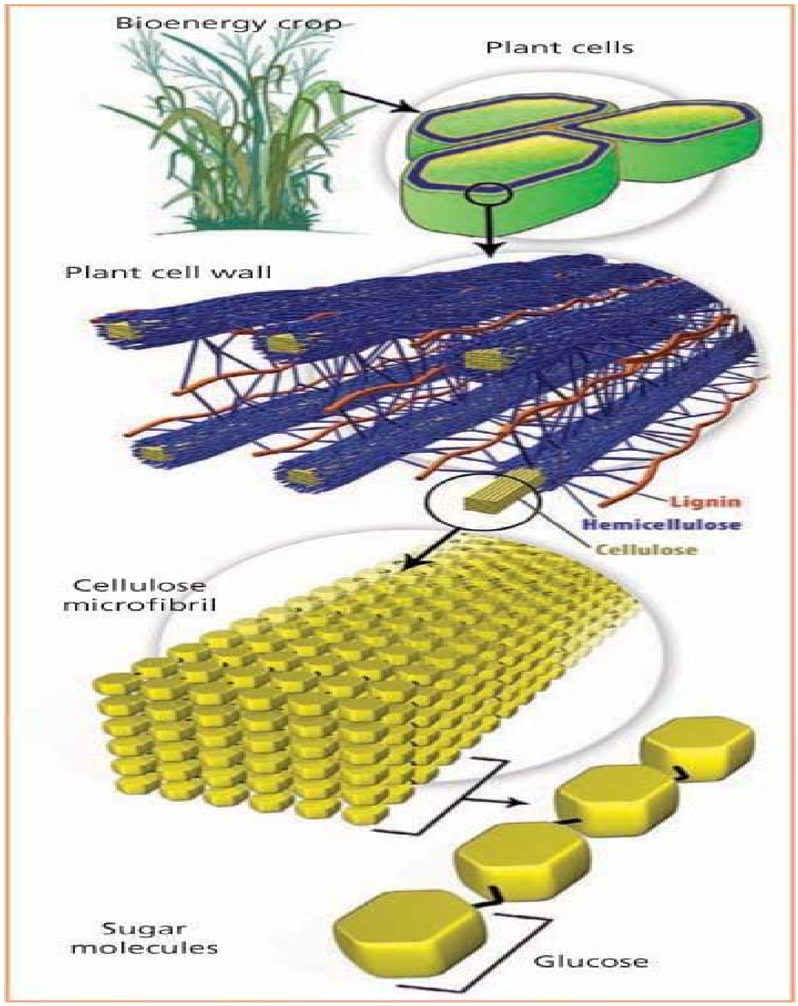
Hemicellulose: branching polymer of

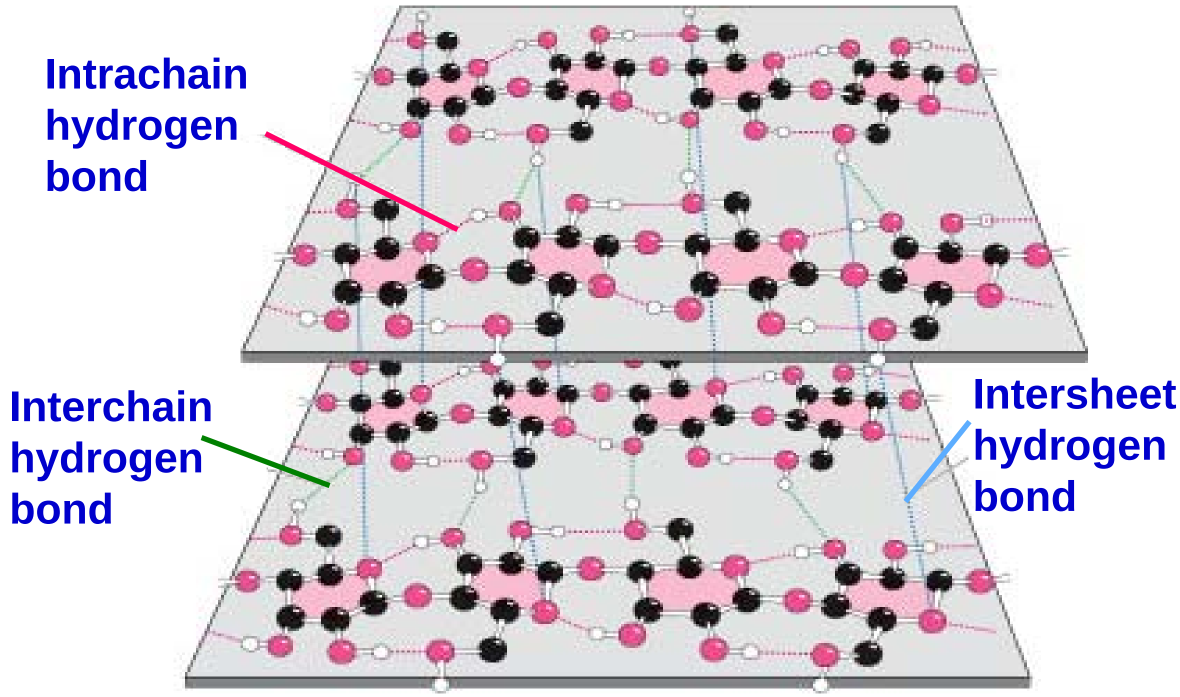
(C-5, C-6, uronic acid, acetyl derivatives)

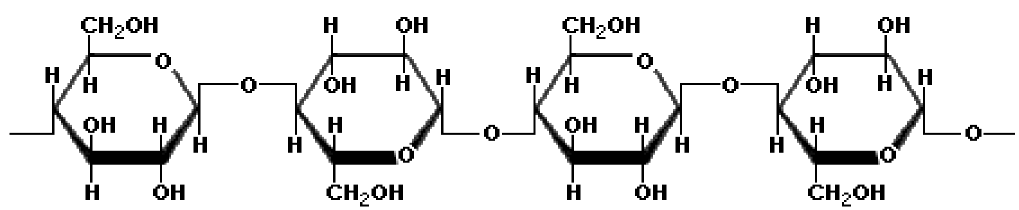


Cellulose: Rigid, linear polymer of glucose subunits

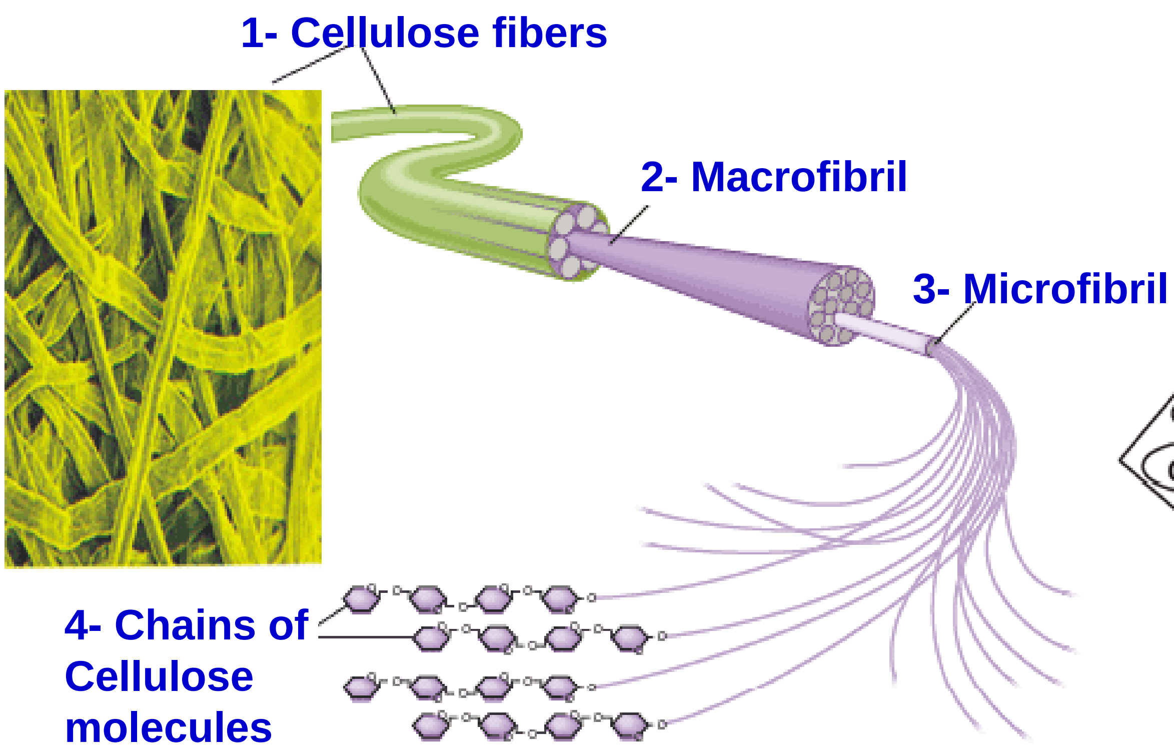
What We Know About Cellulose ?

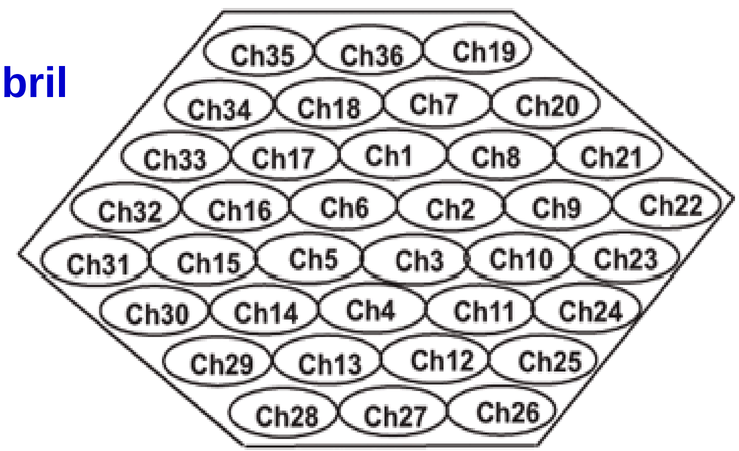






What We Know About Cellulose…





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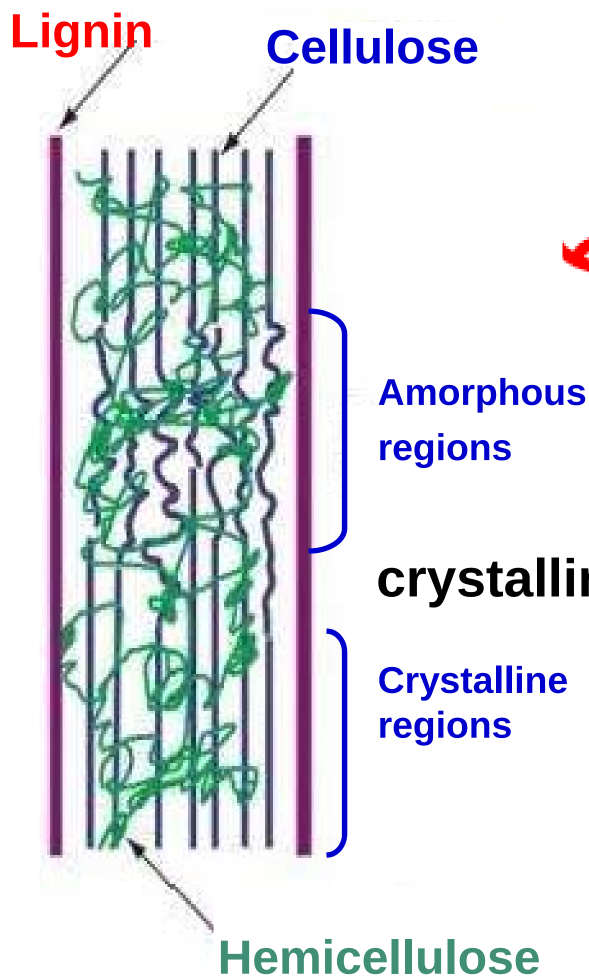
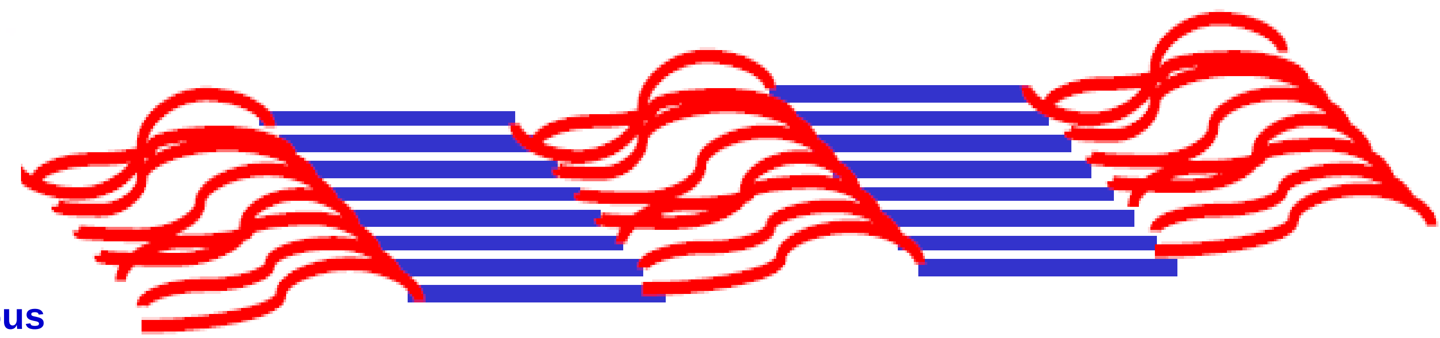




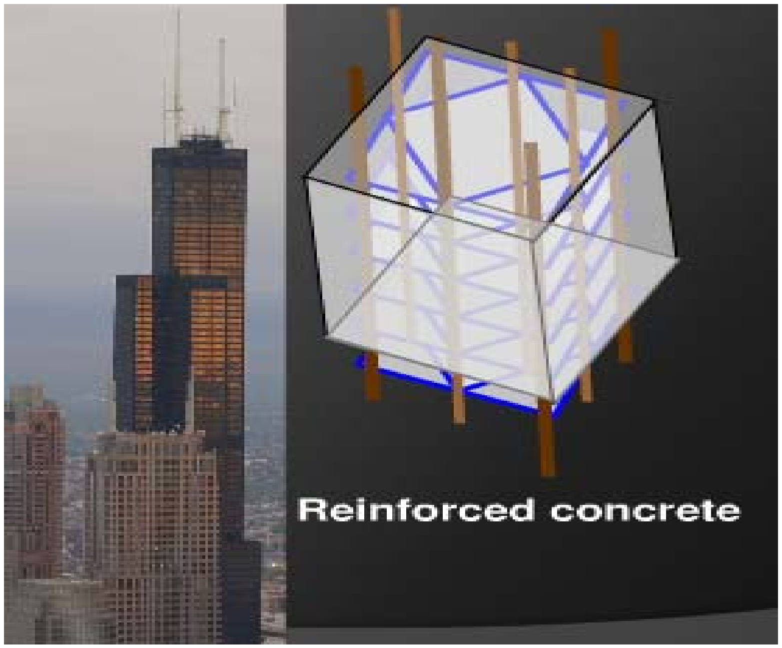
Cellulose consists of:

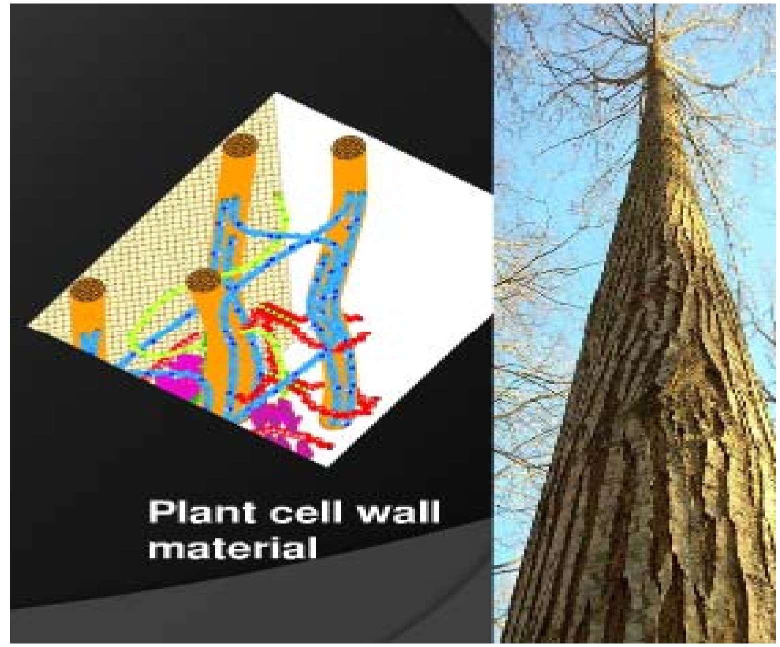
crystalline regions (blue) & amorphous/disordered regions (red)

Blue : Red

3 : 1

How An Engineer Can Visualize This?





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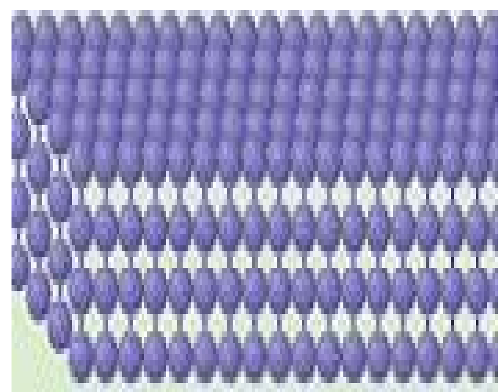
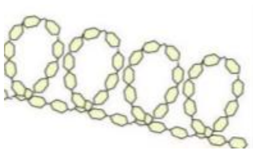
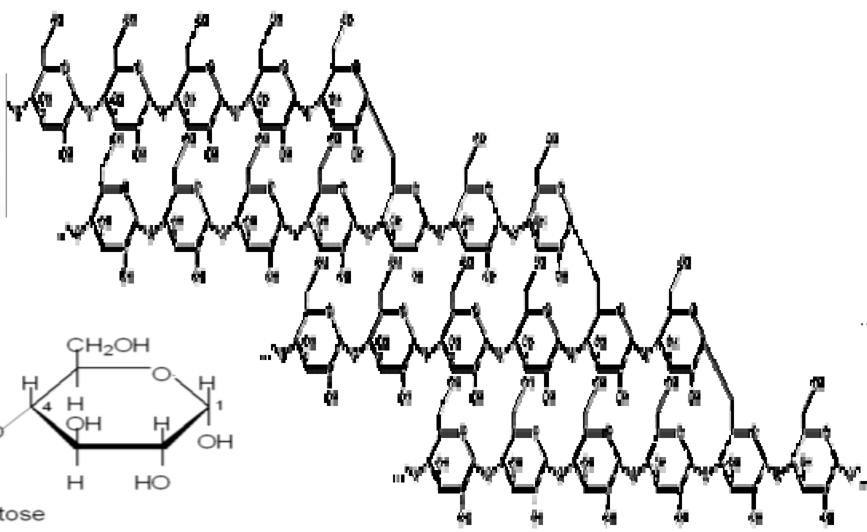
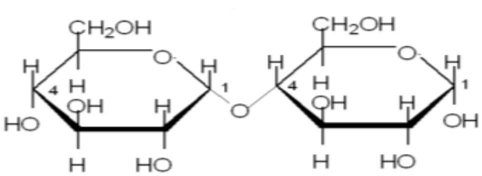


Starch vs. Cellulose

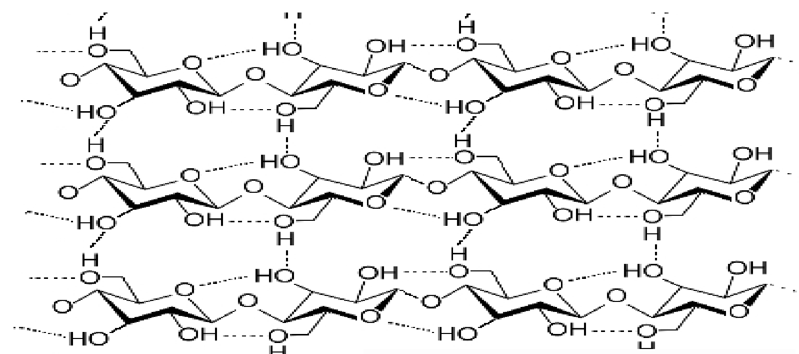
	Starch	Cellulose
Monomer:	glucose	glucose
Linkage:	α(1-4)(1-6)	β(1-4)
Dimer sugar:	maltose	cellobiose
Used for:	storage	structural (support)
Enzyme Hydrolysis:	fast	very slow
Branch:	branched	unbranched
Chains:	coiled/branched (bend)	extended (rigid)
Result:	granules	long fibers

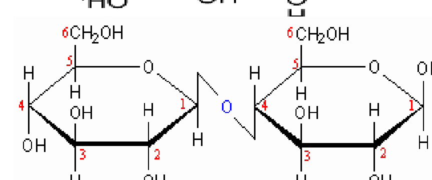






maltose





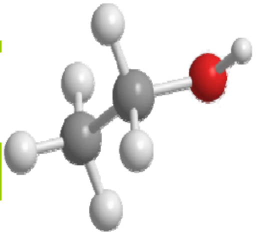
cellobiose

Ethanol Production Flowchart

Lignocellulose Process

Grain (starch) Process

Cane (Sugar) Process

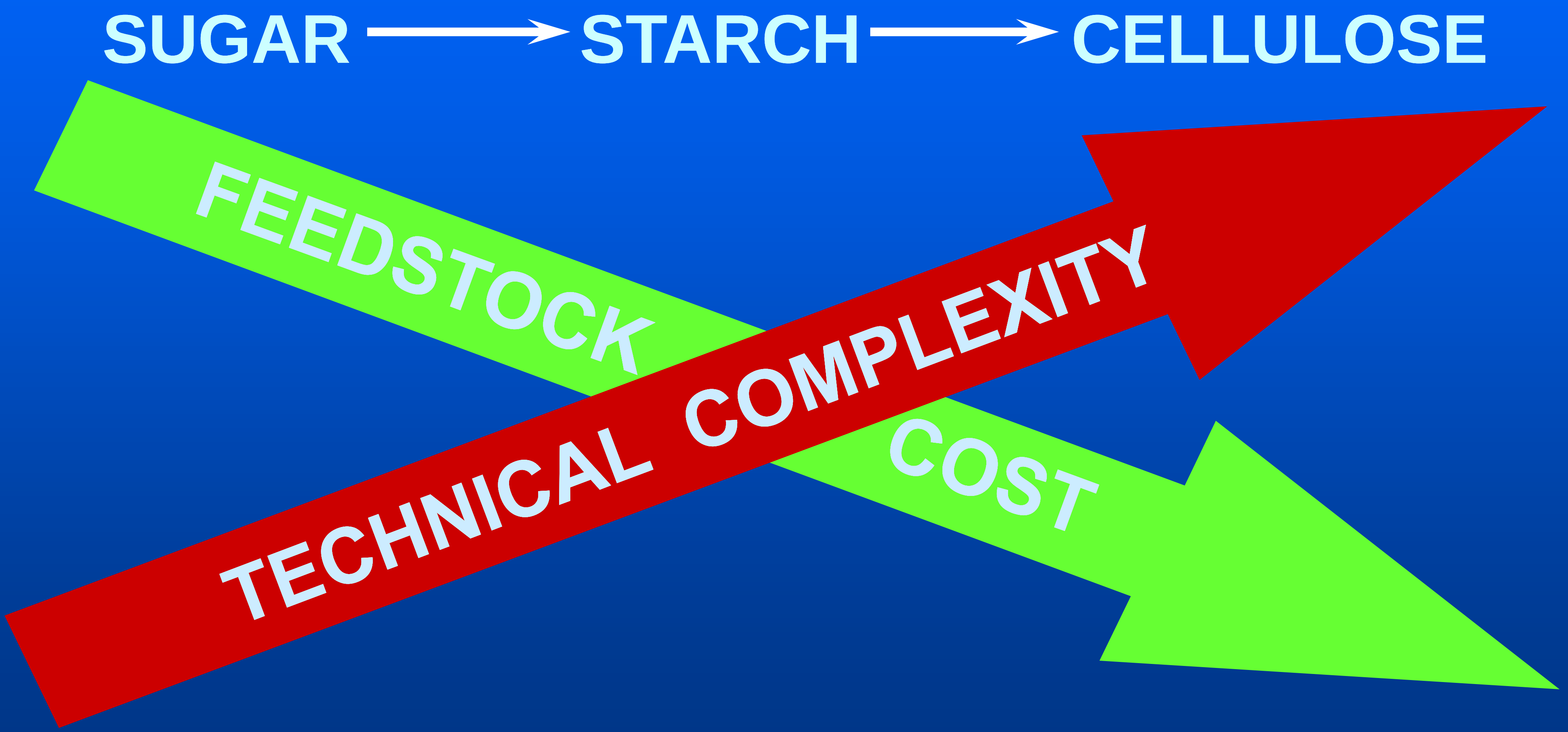


Sugar → Fermentation → Distillation

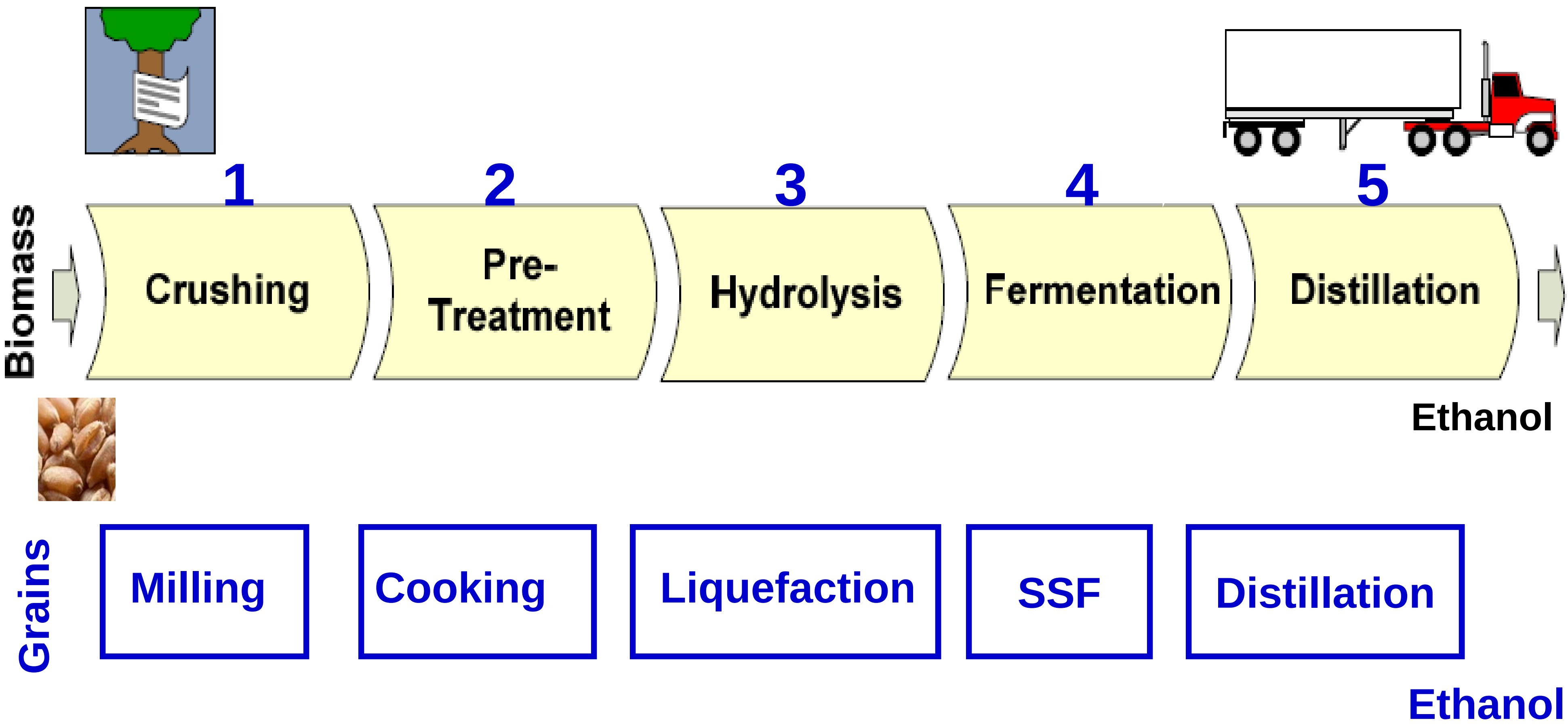
Starch Conversion (cook/hydrolysis) → Sugar

Lingocellulose Pretreatment → Cellulose Conversion (hydrolysis) → Sugar

BIOETHANOL


SUGAR → STARCH → CELLULOSE
FEEDSTOCK COST
TECHNICAL COMPLEXITY

Steps of Biomass Processing



1-Crushing

- **Size reduction: milling or chipping**
- **Accessibility for pre-treatment step**

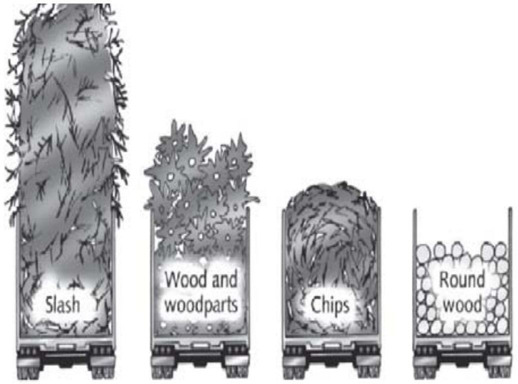
Obstacles

Collection:

- Type/sequence of collection operations & equipment efficiency
- Environmental restrictions (control erosion, soil productivity, carbon level)

Transportation:

- Distance from plant & biomass amount
- Bulky in nature
- Increase density by chipping, grinding or shredding



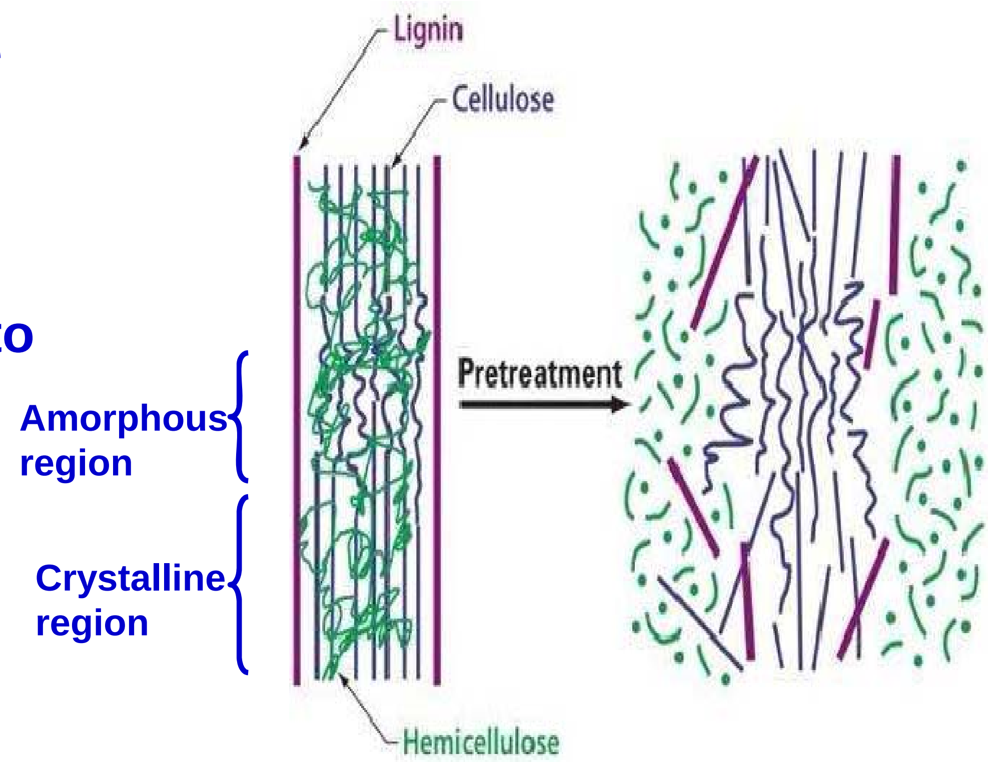
Storage:

- Hauled to plant
- Stored at production site

2- Pre-Treatment

The main purpose for pretreatment:

- Destroy lignin shell protecting cellulose and hemicellulose
- Decrease crystallinity of cellulose
- Increase porosity
- Must break this shell for enzyme to access substrate (sugar)



Pre-Treatment methods:

- Chemical
- Physical
- Biological

Chemical Pre-Treatmet

Pre-treatment Type	Example of the Chemical used	Conditions	Advantages and Disadvantages
Concentrated Acid	H_2SO_4, HCl	Concentrated acid Low temperature	Well known and already used High yields Hydrolysis is mainly included Corrosion problems Material loss due to degradation High demand for chemicals Environmental issues
Diluted Acid	H_2SO_4	w = 0,5-2% T > 160℃	Well known and already used Corrosion problems Low yields Material loss due to degradation
ARP Ammonia Recycled Percoration	Ammonia	w = 15% T = ~ 170℃	Research topic Media recoverable Environmental issues due to ammonia
Lye	NaOH, $Ca(OH)_2$	w = 0,5M T = ~ 80℃	Research topic Media not recoverable
Organosolv	Ethanol-Water, Butanol-Water, Ethylene-Glycol	T = 150-200℃	Costs of solvent Media recoverable
Ionic Liquids		T = ~ 110℃	Research topic Media recoverable Low energy consumption

Physical Pre-Treatment

Pre-treatment Type	Conditions	Advantages and Disadvantages
Steam-Explosion	p = 2,5-7 MPa T = 180-280℃	Well known and already used High yields No corrosion problems Undesired side-products possible High energy demand
LHW - Liquid Hot Water	T = 170-230℃	Research topic High yields Less side-products than in steam explosion No corrosion problems
CO_2 Explosion	p > 7,3 MPa T > 31,1℃ super critical CO_2	Research topic High costs expected Low environmental impact
AFEX Ammonia Fiber Explosion	Liq. Ammonia T = 90-100℃	Low inhibitor formation Media recoverable Environmental issues due to ammonia

Biological Pre-Treatment

Pre-treatment Type	Examples of organism	Advantages and Disadvantages
fungi nt with funghi	White-rot fungi Brown-rot fungi Soft-rot fungi	Research topic Slow conversion Low energy requirements No chemicals required Mild environment conditions
Pre-treatment with bacteria	Sphingomonas paucimobilis, Bacillus circulans	Research topic Slow conversion Low energy requirements No chemicals required Mild environment conditions

Obstacles

- **Most expensive stage in 2nd generation bioethanol**
- **<u>Inhibitors such as:</u>**
  - Phenolic from lignin degradation
  - Furfural from C-5 degradation
  - HMF from C-6 degradation
- **Corrosion problems**
- **Acid recovery is expensive**
- **Material loss**
- **Better understanding of plant cell wall structure & function**

3- Hydrolysis

Polysaccharides break down into monomers followed by fermentation and distillation

Cellulose can be hydrolyzed using:

- **Acid hydrolysis (Traditional method)**
- **Enzymatic hydrolysis (The current state-of-art method)**

Acid hydrolysis advantages:

- **Faster acting reaction**
- **Less residence time in reactor**

Enzymatic hydrolysis advantages:

- **Run at lower temperature**
- **Higher conversion**
- **Environmentally friendly**

3- Hydrolysis…

- **Cellulase enzyme depolymerize cellulose into fermentable sugars**

- **Cellulase synthesized by fungi and bacteria work together to degrade cellulose**

- **Cellulosic enzyme system:**

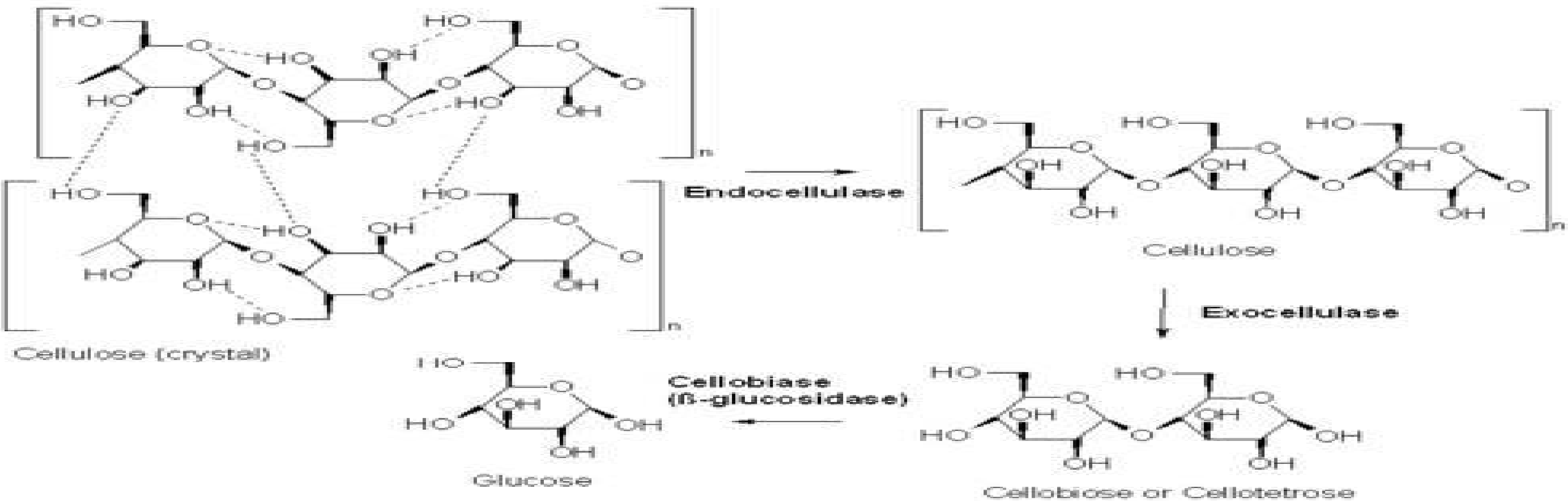
  1- Endo-ß-glucanase

  2- Exo-ß-glucanase

  3- ß-glucosidase

From Cellulose to Glucose

Reaction Pathway:



Optimum Parameters:

pH: **4-5**

Tempt: **40-50C**

Inhibitors: **glucose, cellobiose, some minerals**

Obstacles

- **Problems for industrial application:**
  1- High production cost (~40% of total)
  2- Low yield
- **Few microorganisms are capable of degrading cellulose**
- ***Trichoderma* produces endo-ß-glucanase, exo-ß-glucanase & low levels of ß-glucosidase**
- ***Aspergillus* produces endo-ß-glucanase, ß-glucosidase & low levels of exo-ß- glucanase**
- **Inhibitors formation**
- **Optimizing/understanding enzymes regulation and activity**
- **Understanding of plant cell wall structure & function**

4- Fermentation

- **Convert sugars (C-5 and or C-6) to ethanol using microbes**
- ***S.cerevisie* for ethanol from glucose (C-6)**
- ***S.cerevisie* not able to ferment (C-5)**
- **Some bacteria ferment C-5 & C-6 (*E.coli & Z.mobilis*)**

Obstacles

- <u>Inhibitors such as:</u>
    - Phenolic from lignin degradation
    - Furfural from C-5 degradation
    - HMF from C-6 degradation

- <u>R&D strategies:</u>
    - Robust organism to fermenting C-5 & C-6
    - Robust organism toward inhibitors/temperature

- Integrate hydrolysis and fermentation into a single microbe

- Low conversion rates for C-5 sugars

- Technology to remove inhibitors is expensive

After All These Challenges In Cellulose Hydrolysis, What About Hemicellulose?

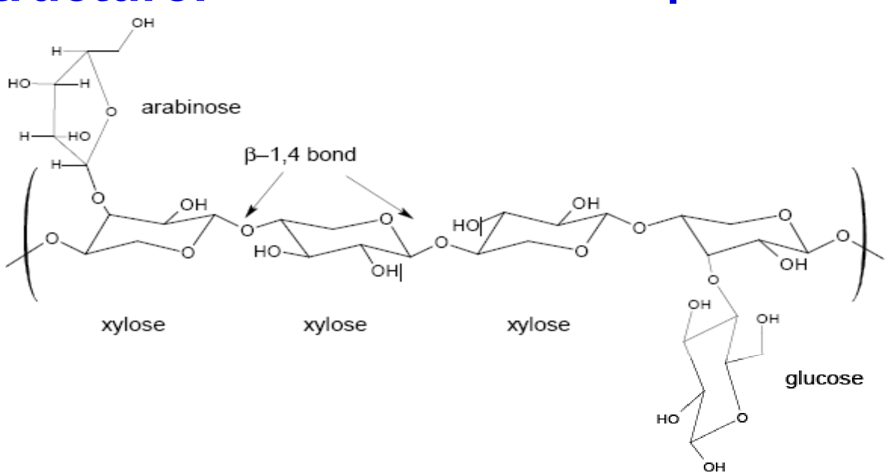
Hemicelullose

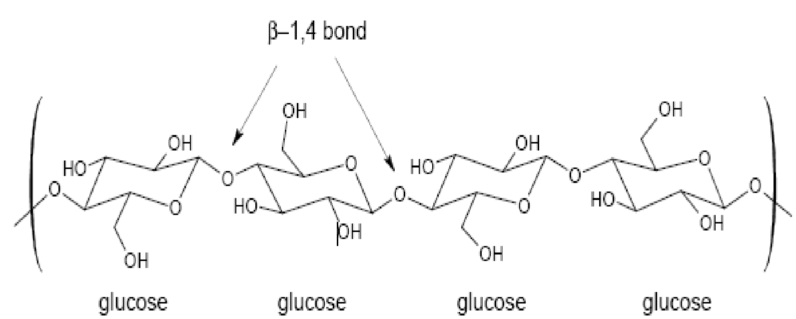
Polysaccharides that are more complex than sugar and less complex than cellulose

The second abundant renewable biomass in earth after cellulose

Hemicellulose vs Cellulose

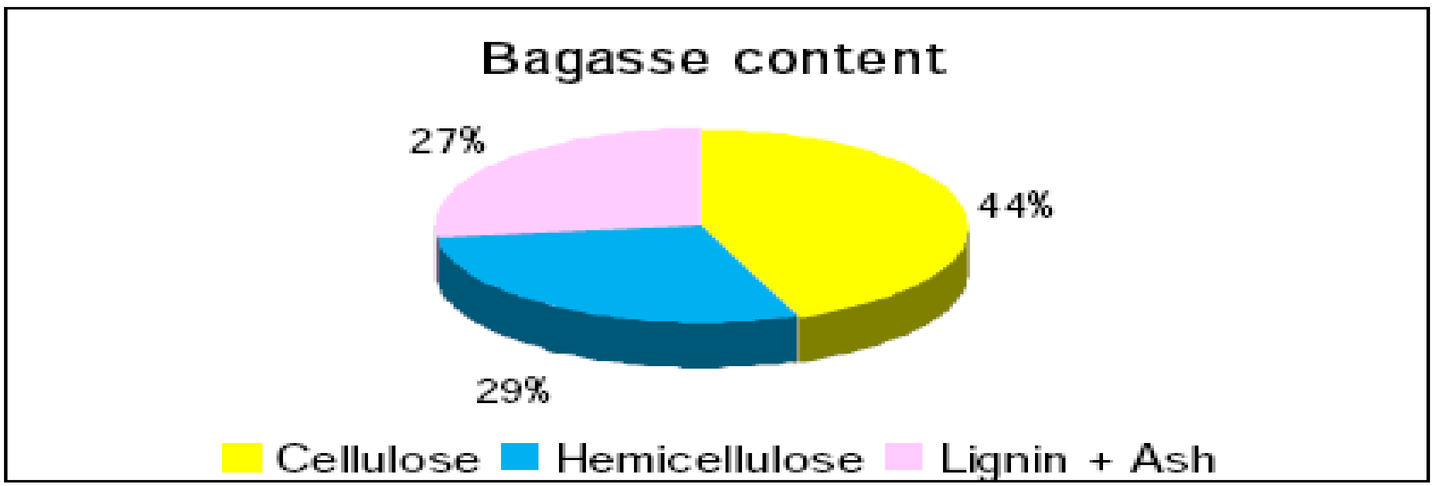
	Hemicellulose	Cellulose
Polysaccharides:	**hetro-polysaccharides**	**homo-polysaccharides**
Monomer:	**different sugar monomers** (xylose, glucose, mannose, galactose, uronic acid)	**same monomer** (glucose)
Acid Hydrolysis:	**fast**	**slow**
Branch:	**branched**	**unbranched**
DP:	**150-200**	**800-17000**
Structure:	**amorphous**	**crystalline**



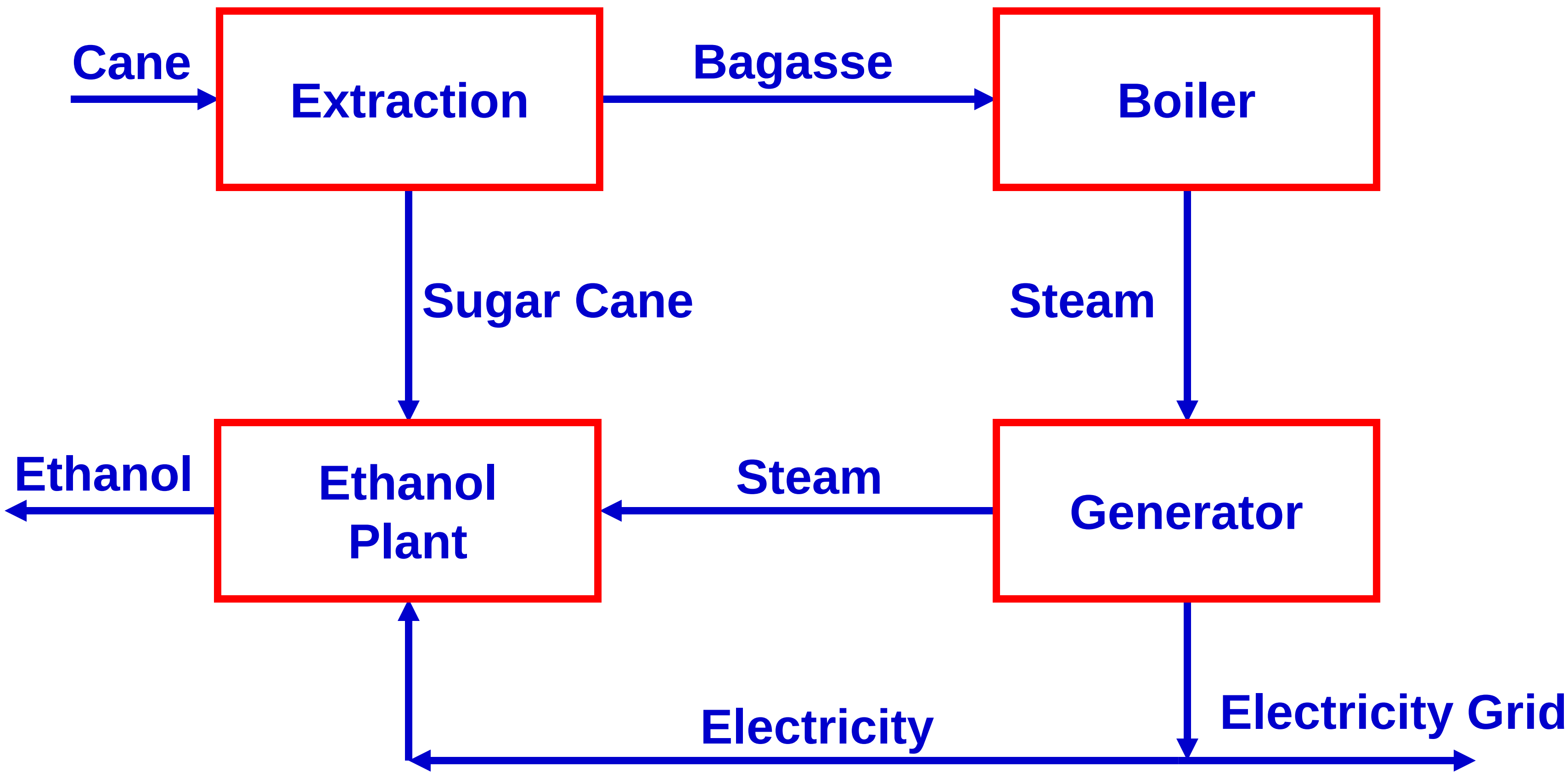


Bagasse Characteristics

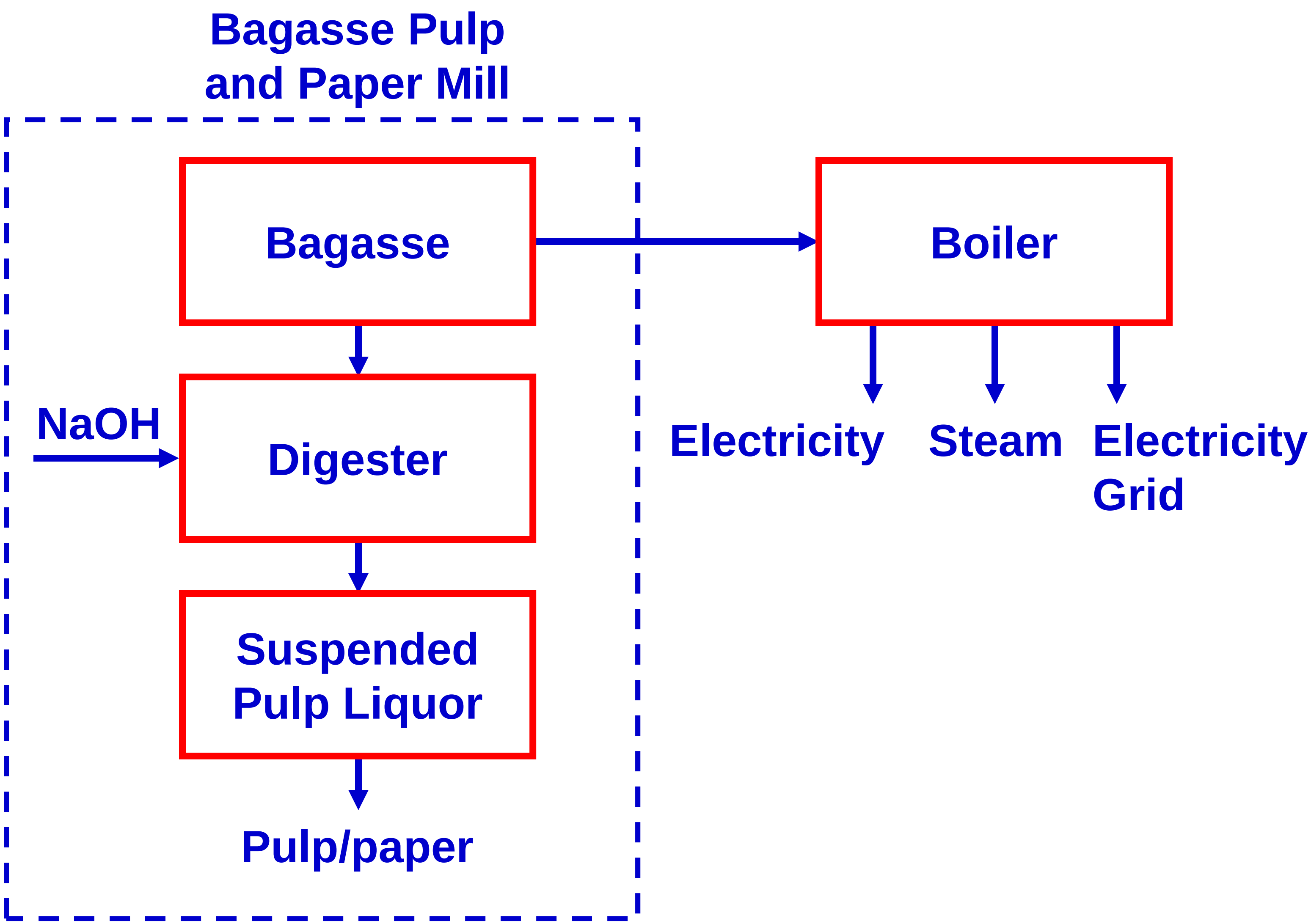
	Sugar Content as polymer basis [wt%-dry bagasse]						Acid Insoluble Lignin and Ash
	Glucose	Xylose	Arabinose	Galactose	Mannose	Total sugar	
Average	**44.2**	**26.6**	**2.1**	**0.0**	**0.3**	**73.1**	**26.9**
Maximum	47.1	29.1	2.6	0.0	1.1	77.1	29.8
Minimum	40.3	23.0	1.6	0.0	0.0	70.2	22.9



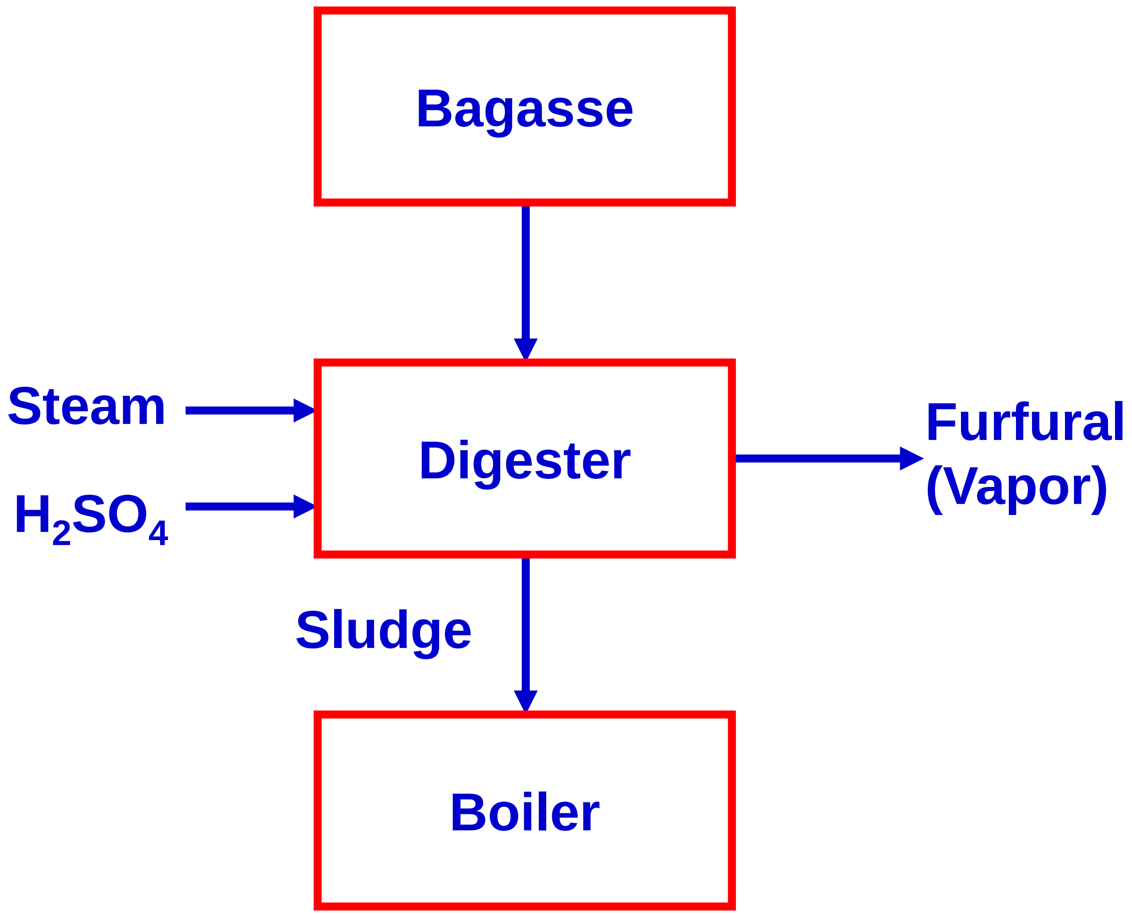
Brazil Strategy



Bagasse Usage



Bagasse Usage…



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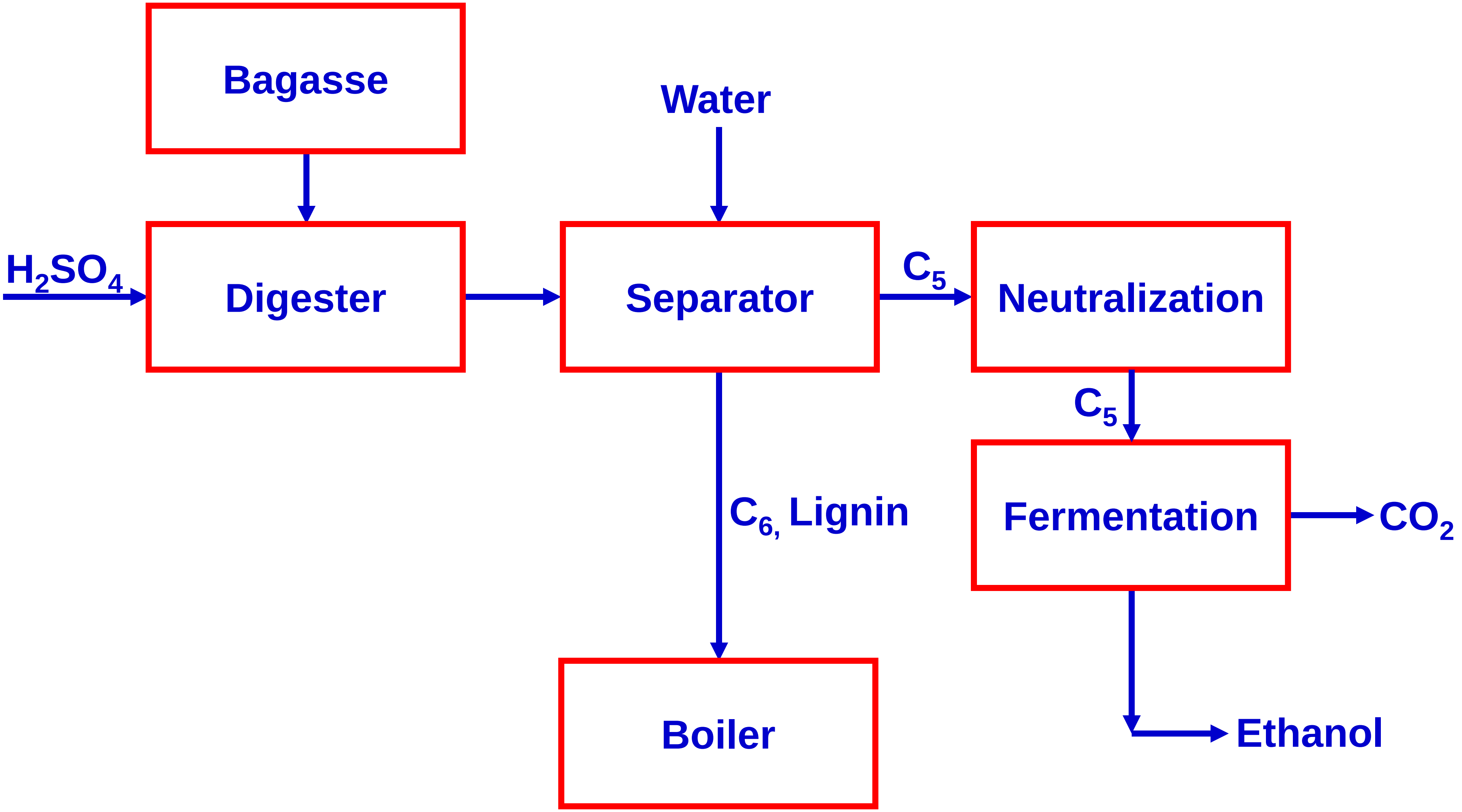

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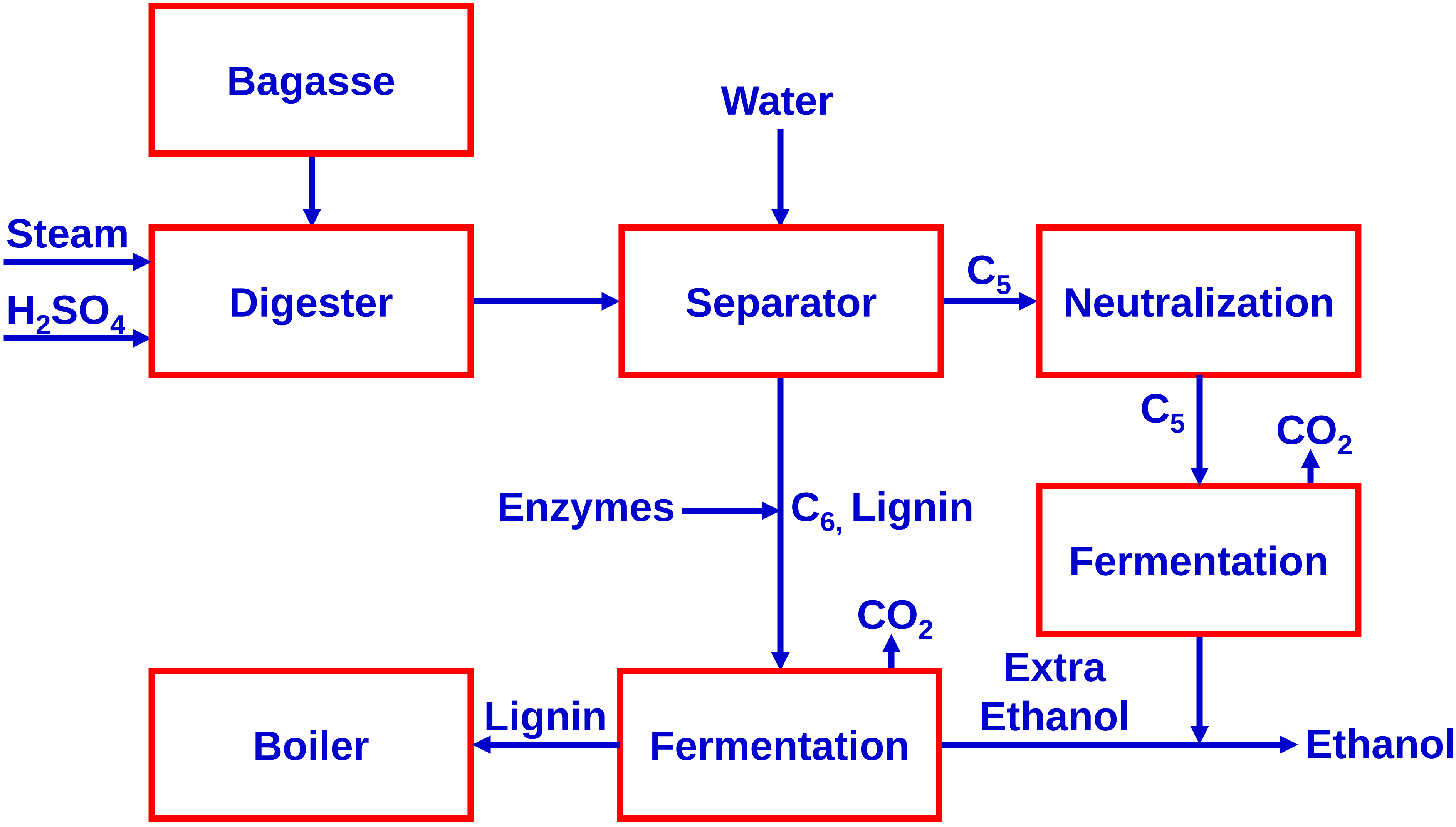

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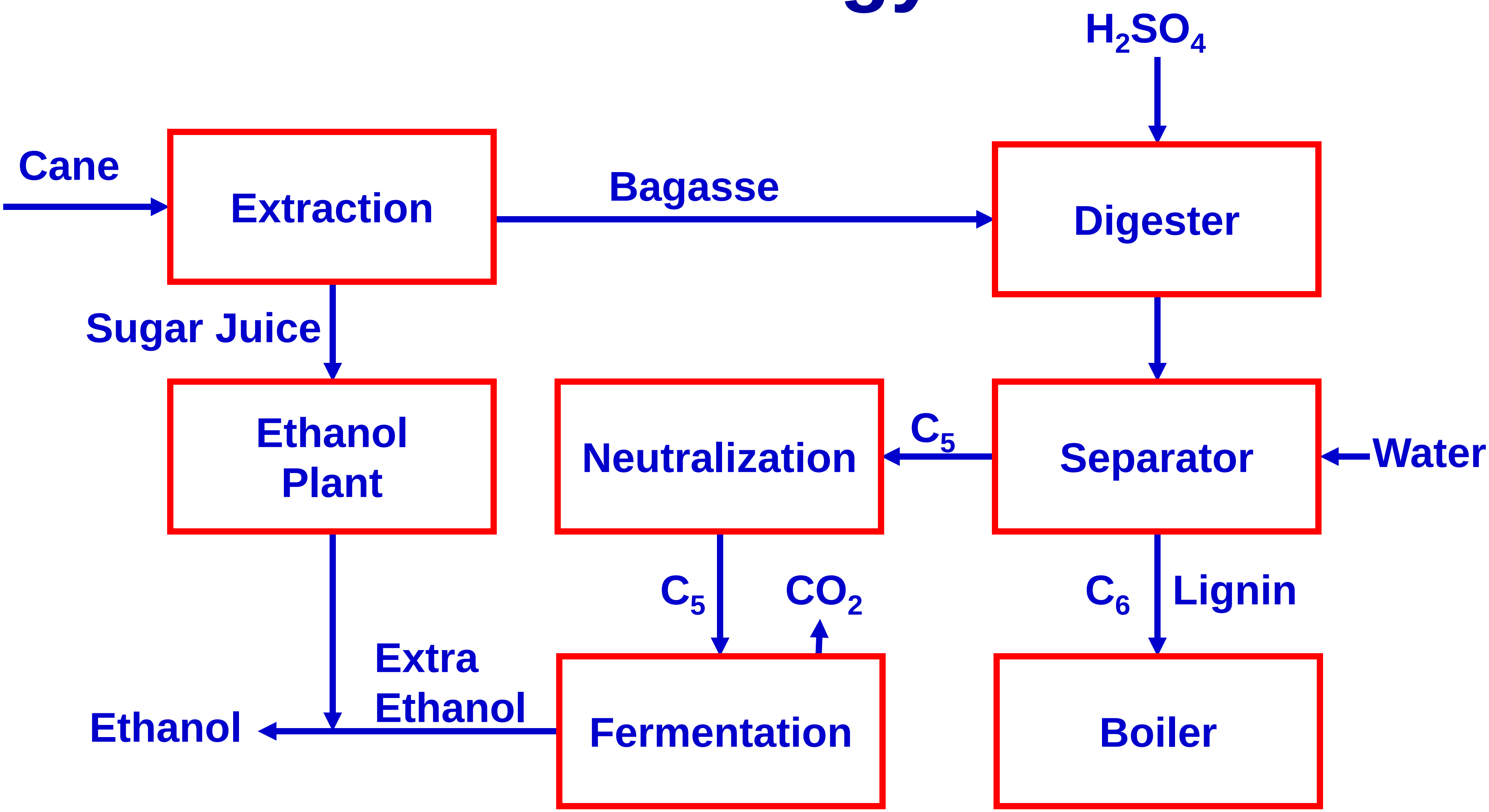

Where is KATZEN From This?

KATZEN has worked with cellulose feedstock for ethanol, pulp and paper & sulfite liquor over 50 years

After this long history, we say C_6 will have contribution as ethanol feedstock but limited to special circumstances

After this long history, we say YES for C_5

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