Lecture Twenty Eight

Course Review

Biofuel Feedstocks and Production

BEE 499/599
Winter, 2015
3 Credit Hours

Bioethanol is one of the important alternatives to fossil fuels. This course will provide an overview of the biofuel feedstocks for production of fuels, feed and industrially valuable chemicals. Issues in feedstock utilization such as suitability, availability, sustainability and economic viability will be addressed. This course will cover the preprocessing, post processing and fermentation technologies in ethanol production in detail. Influence of feedstock composition and process technologies on ethanol and coproducts will be discussed.

Topics Covered

1. **Overview of a biobased economy**
2. **Feedstocks: classification, properties and selection**
3. **Biochemical technologies for ethanol production**
4. **Other bioprocessing technologies for fuels and chemicals**
5. **Systems analysis**

Course Schedule and Location

MWF 9.00-9.50 am; 100 HOV

Course Format

Three lectures per week, class tests, exams and a review of Journal articles (Graduate).

Instructors

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Course Objectives

By the end of this course, you must be able to:

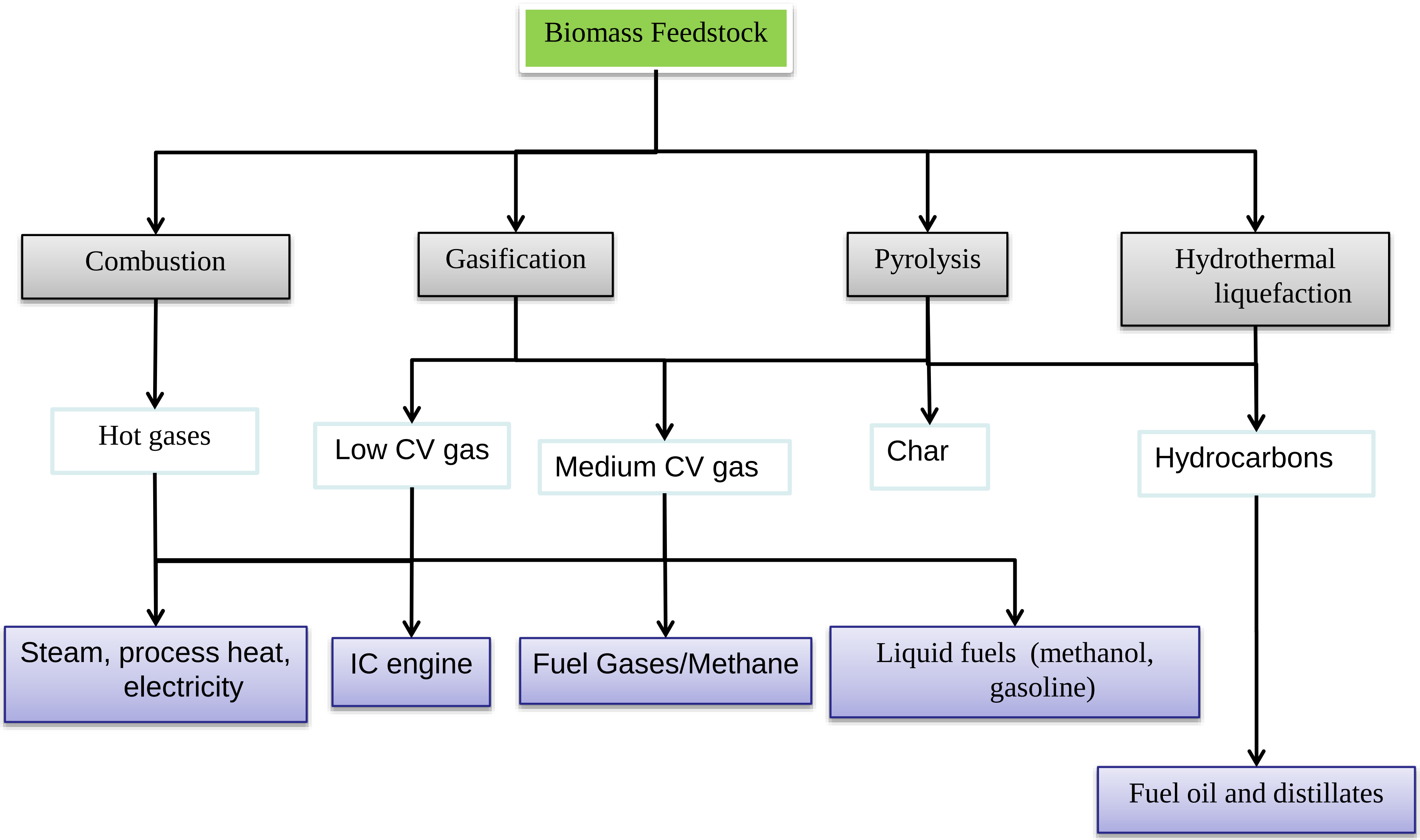
1. Identify potential feedstocks for biofuels and bioproducts.
2. Propose suitability of feedstocks based on chemical composition, agroclimatic conditions and process technologies.
3. Describe key processes in ethanol production from biobased feedstocks.
4. Differentiate starch and cellulose based ethanol production technologies.
5. Assess effects of process conditions and analytical techniques used in ethanol production.
6. Evaluate sustainability of feedstock production and assess its impact on socio economic parameters.

Need for Sustainable Biobased Economy

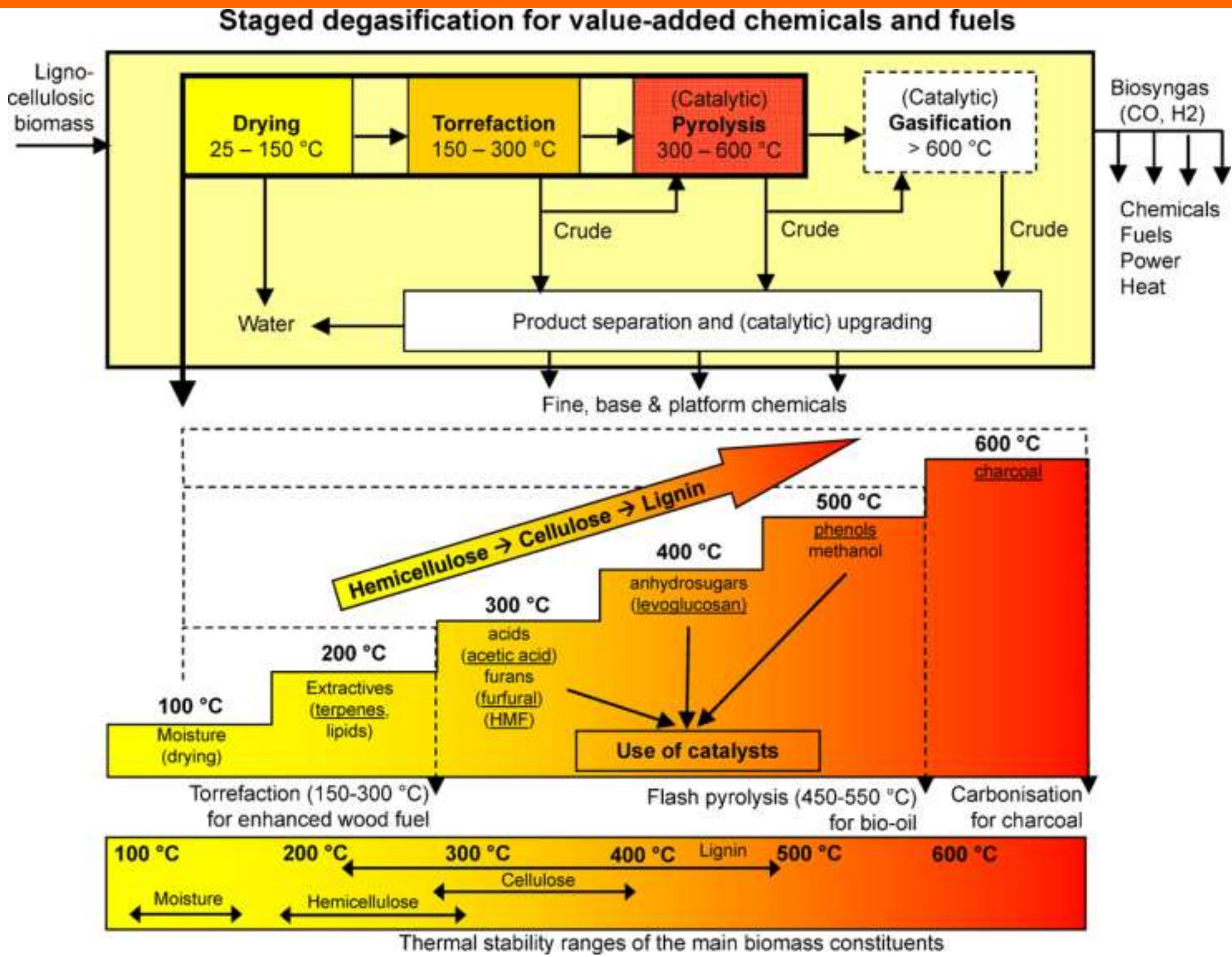
Three important considerations

- Energy resources and their contribution
- Population growth and economy
- Global climate change

Thermochemical Platform

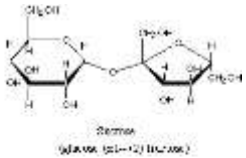


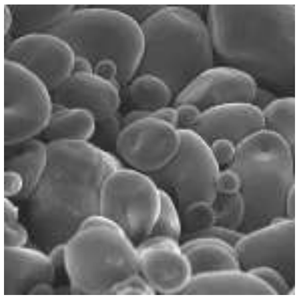
Thermochemical Platform



Starch Synthesis and Properties

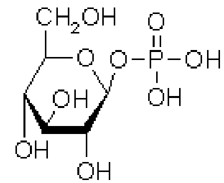
How is starch synthesized?

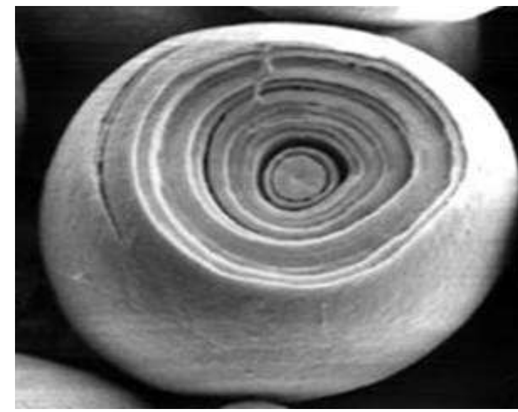




Sucrose

Glucose-1-phosphate



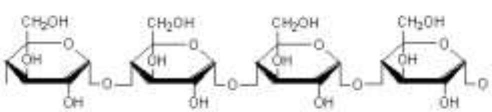


ADP-Glucose

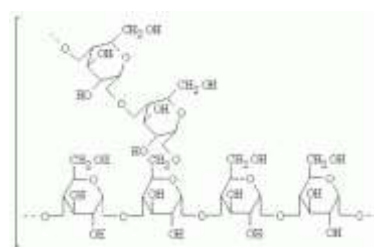
Amyloplast membrane

ADP-Glucose

Granule bound starch syntha Soluble starch synthase



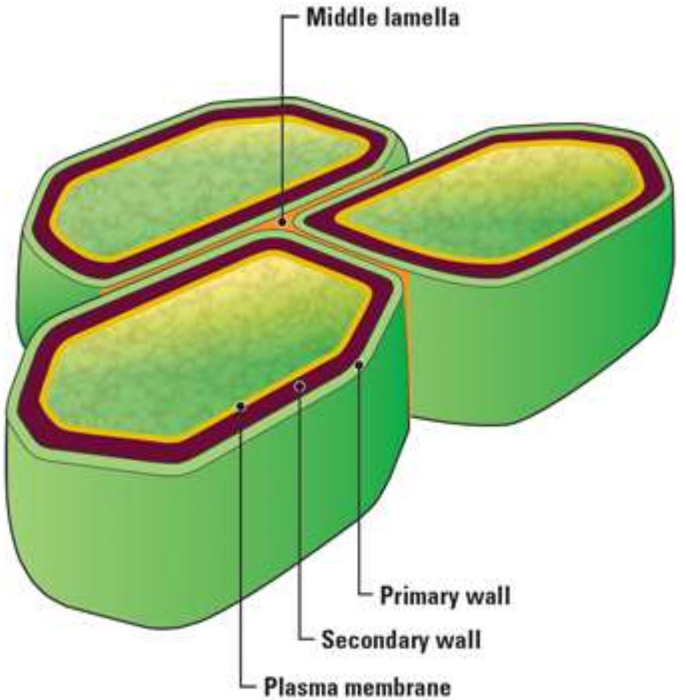
Amylose/ Amylopectin

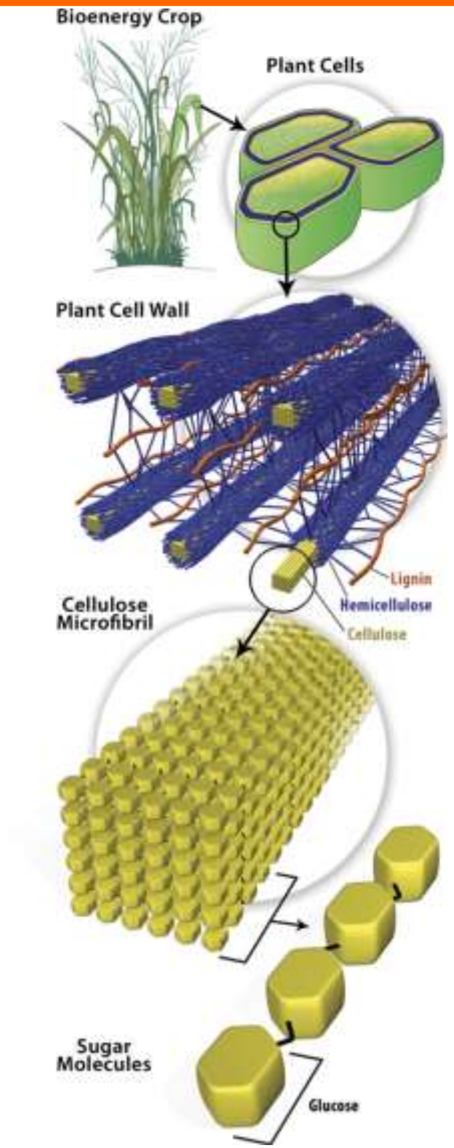


Starch Granule

Plant Cells

Plant cell wall structure



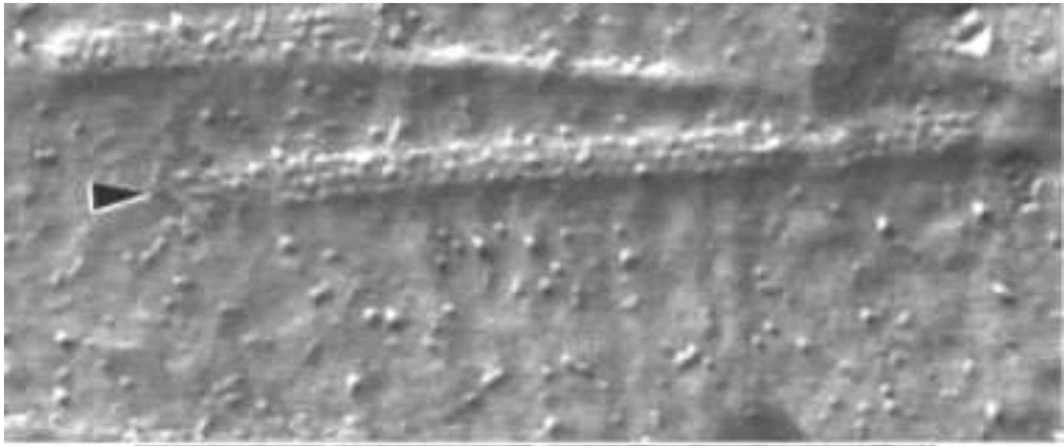


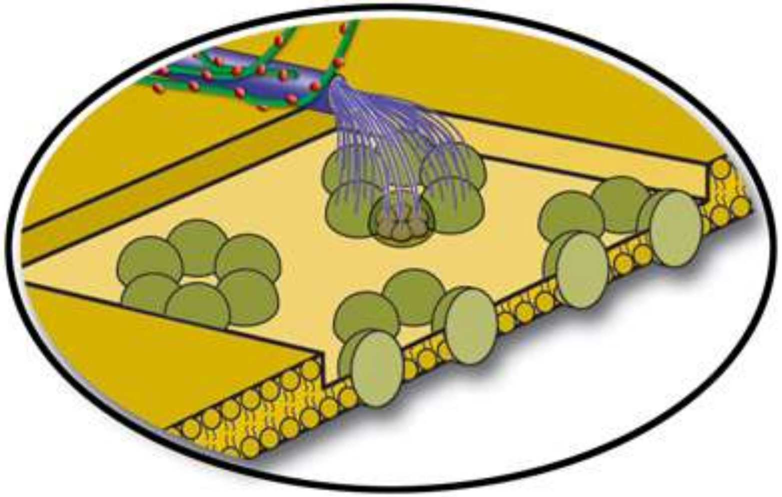
Ref: http://genomicsgtl.energy.gov/biofuels/.

Cellulose Synthesis

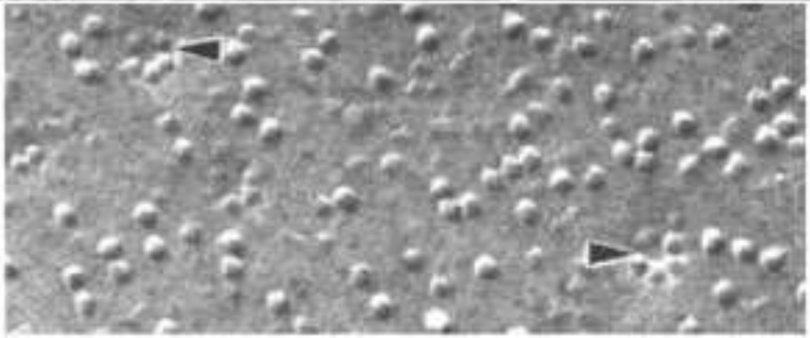
Cellulose synthase complexes are involved in cellulose microfibril synthesis. These complexes called terminal complexes (TC) are arranged in different patterns in the cell membrane.

Linear TC in *Oocystis apiculata*





Cellulose synthase complexes

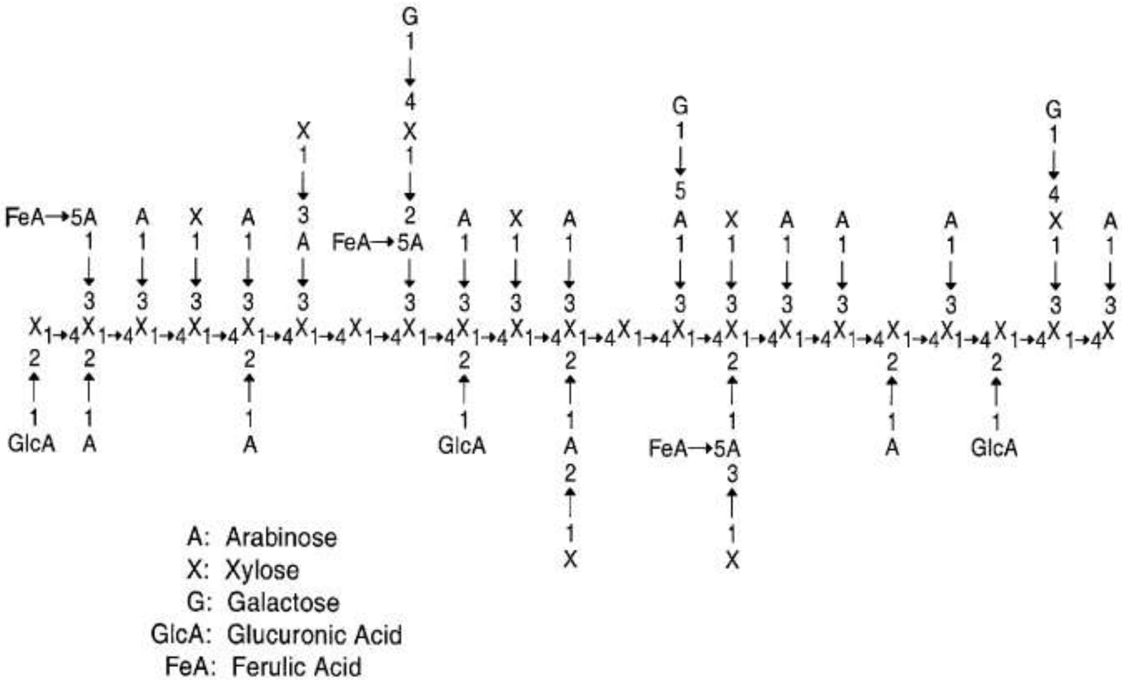


Rosette TC in *Zea mays*

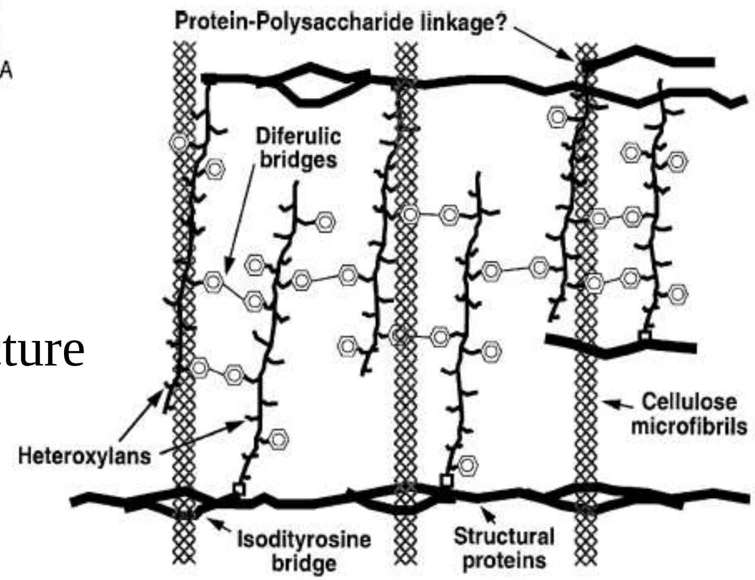
Ref: http://genomicsgtl.energy.gov/biofuels/.

Hemcellulose

Heteroxylan structure



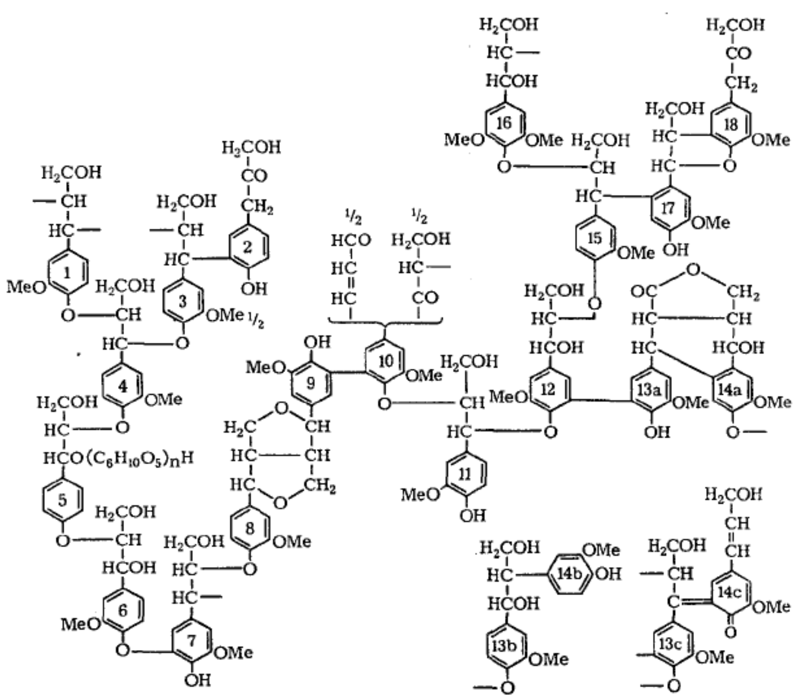
Corn fiber cell structure



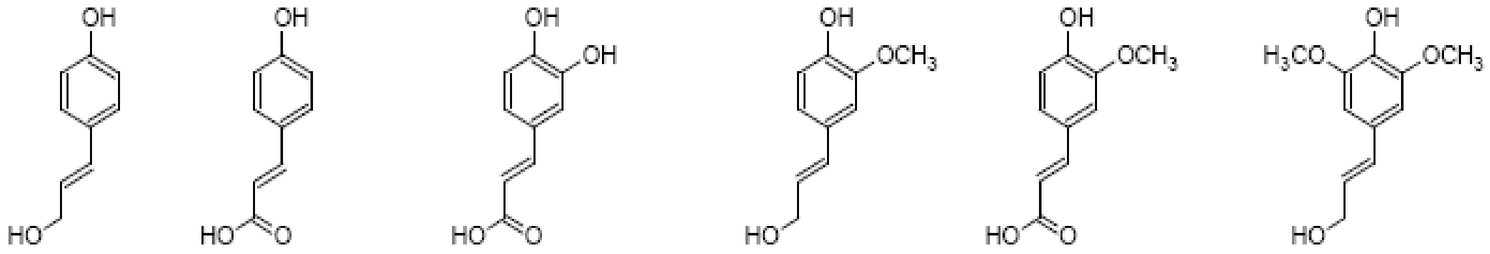
Ref: Saha (2003)

Lignin Composition and Synthesis

Lignin: A racemic, heteropolymer consisting of three hydroxycinnamyl alcohol monomers (C9) differing in their degree of methoxylation: p-coumaryl, coniferyl and sinapyl alcohols



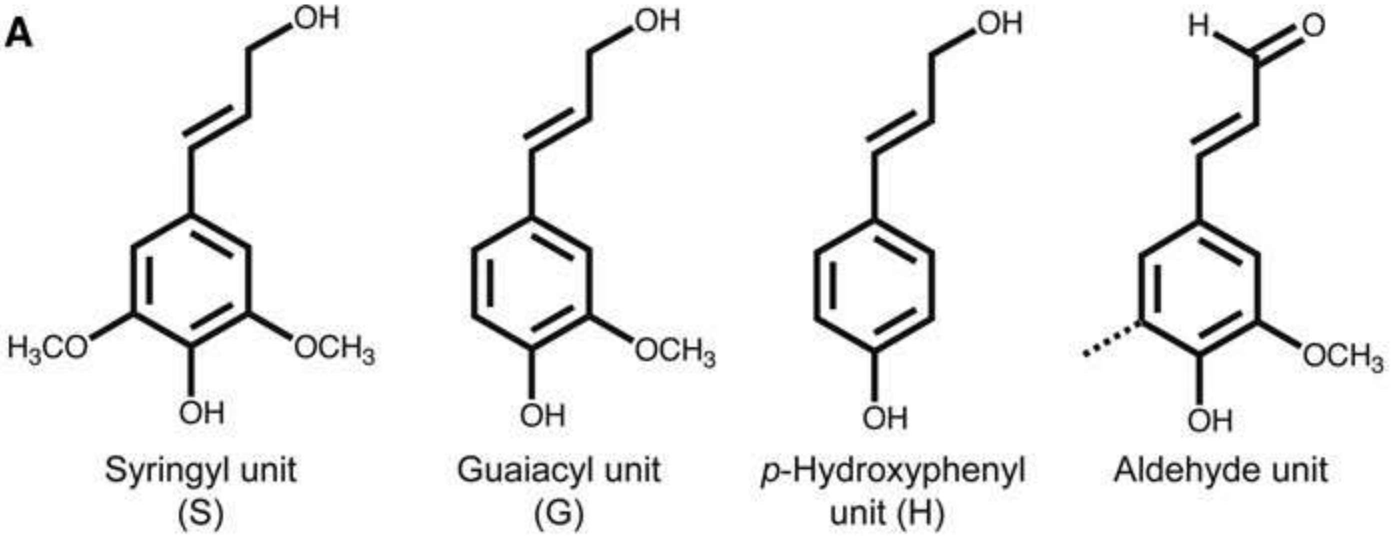
phenol units | Guaiacol units | Syringol units



Coumaryl alcohol | Coumaric acid | Hydroxycinnamic acid | Coniferyl alcohol | Ferulic acid | Sinapyl alcohol

Ref: Boerjan at al. (2003) and Holladay et al (2007)

Lignin Composition and Synthesis

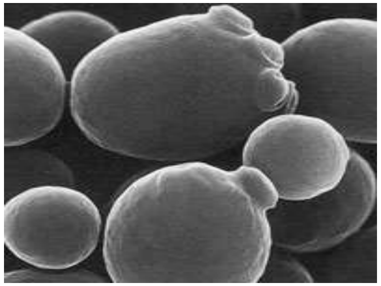


Ref: Talbot et al. (2011)

Summary of Analytical Techniques

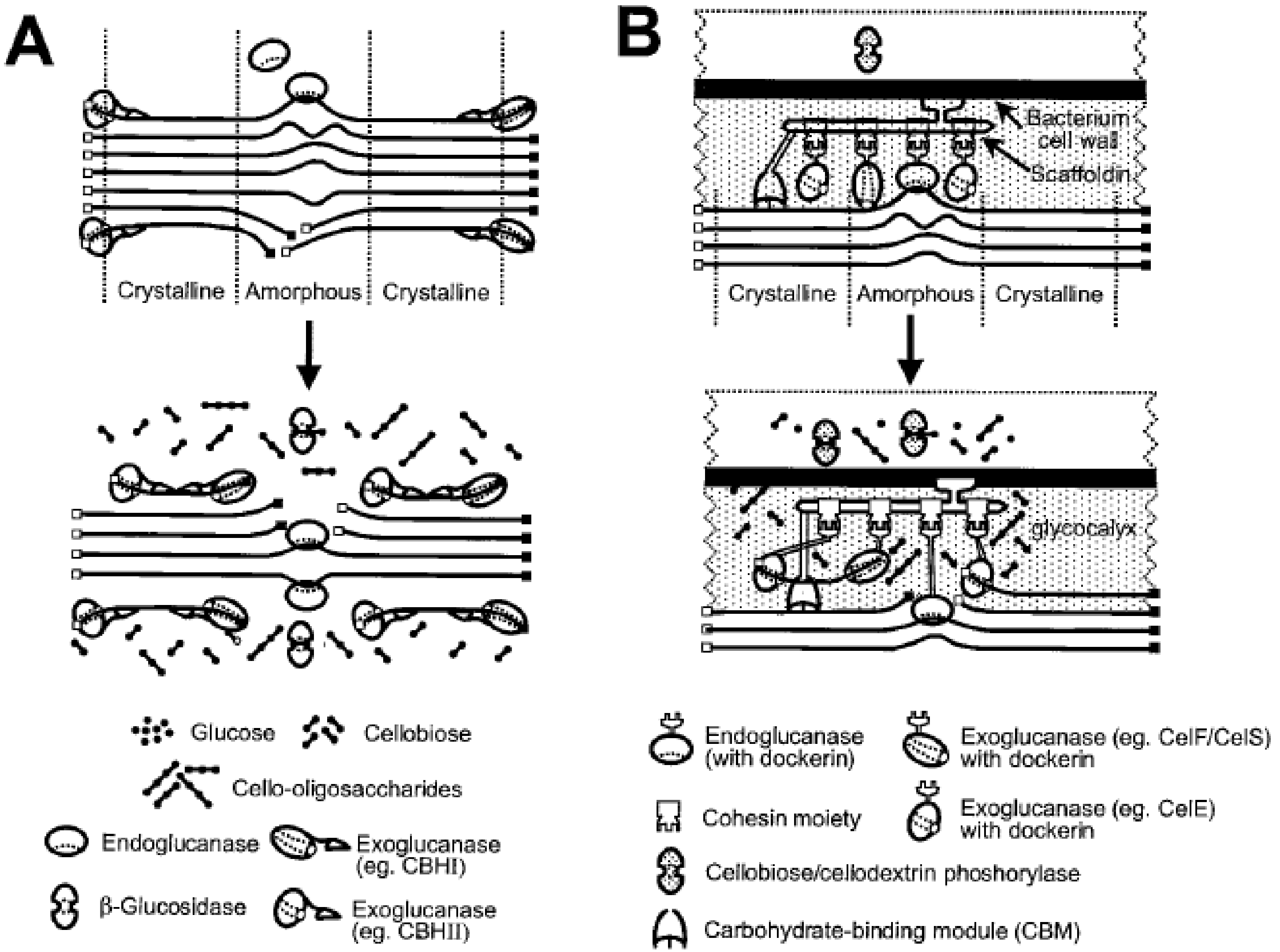
What are some of the important parameters in fermentations process?

- Particle size distribution of feedstock.
- Moisture content of feedstock.
- Presence of toxin producing fungi (ex. *Aspergillus niger*)
- Temperature and pH



- Sugar composition of feedstock (Starch, cellulose and hemicellulose).
- Enzyme activity and stability.
- Yeast cell numbers, viability, vitality.
- Sugars, alcohols (primarily ethanol and glycerol), organic acids
- Protein and lipid content of feedstock and coproducts.
- Dextrose Equivalent

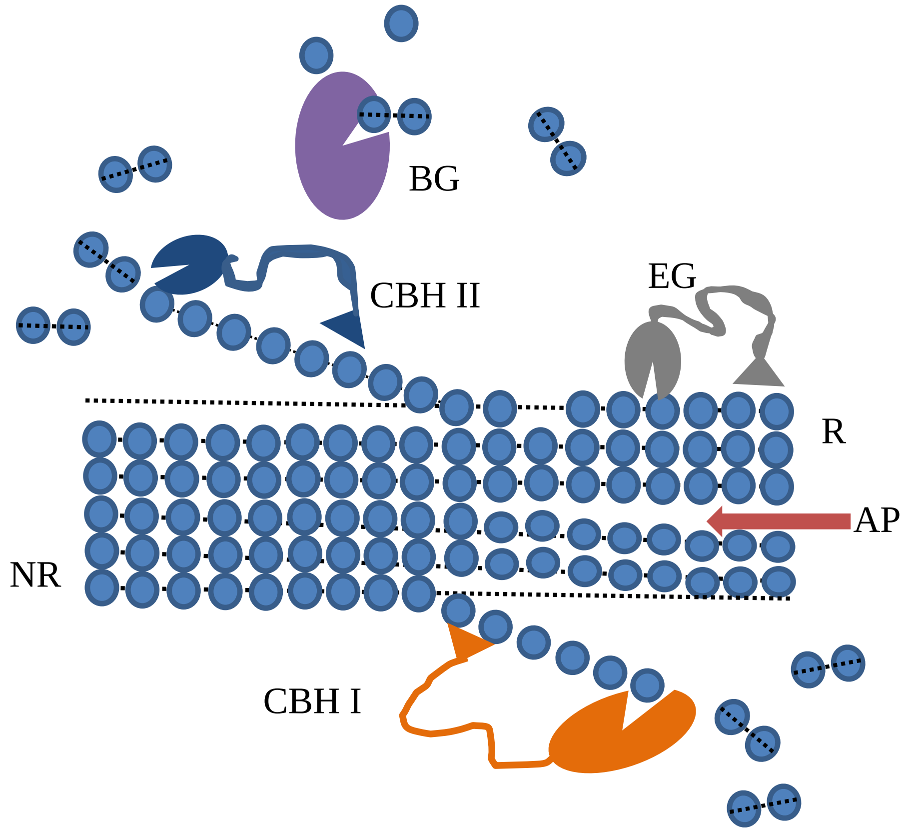
Enzymes



Ref: Lynd et al. 2002

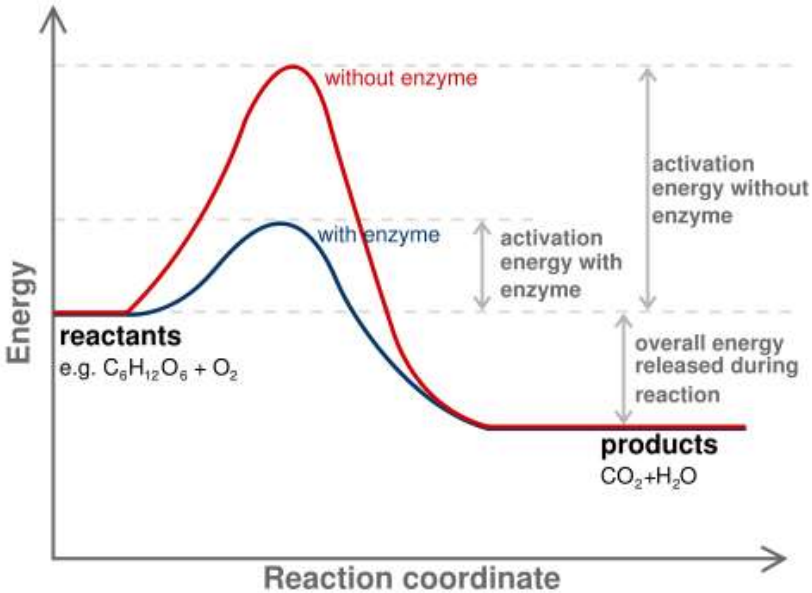
Cellulase Enzymes

Endoglucanases (EG) act on internal chains to create additional chains. Cellobiohydrolases (CBHI and CBHII) cleave the -1,4 bonds creating cellobiose units. CBH I act from the reducing ends (R) while CBH II act from the non-reducing ends (NR). Betaglucosidase (BG) acts of the cellobiose/cellodextrins to produce glucose. Accessory proteins (AP) facilitate the hydrolysis through a currently unknown mechanism.



Enzymes

Enzyme Kinetics: Enzyme reactions are most commonly described using Michaelis-Menton Equation (Important: assumes quasi steady state).



$$E + S \underset{K_{-1}}{\overset{K_1}{\longleftrightarrow}} ES \xrightarrow{K_2} E + P$$

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} \qquad k_m = \frac{k_{-1} + k_2}{k_1}$$

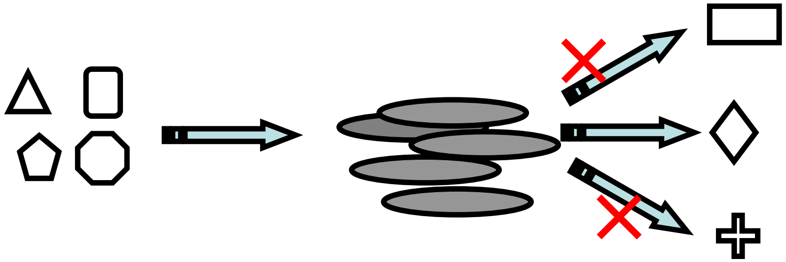
$$\frac{dP}{dt} = k_2[ES] = V_{\max} \frac{[S]}{k_m + [S]}$$

Under what conditions is Michaelis-Menton equation inadequate to explain enzyme action? Limited/ restricted mobility of enzymes, two phase reactions, enzyme is not limiting, allosteric regulation

Yeast

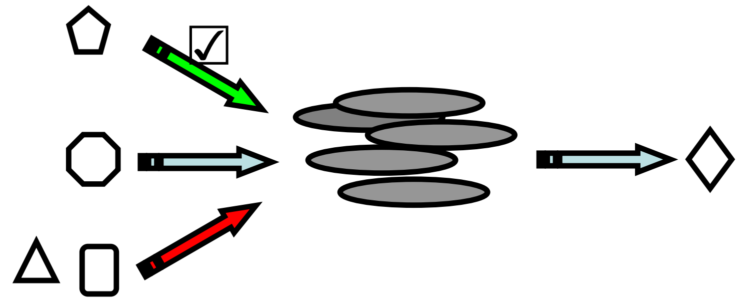
- Yeast is a eukaryotic microorganism. *Saccharomyces cerevisae* is the most common yeast used in ethanol fermentations.
- Yeast can switch to complete anaerobic or aerobic respiration depending on the environmental conditions.
- Size of yeast cell varies between 5-10μm.
- Yeast reproduces asexually by budding although sexual reproduction also occurs in nature.
- Exhibits diauxic growth pattern.

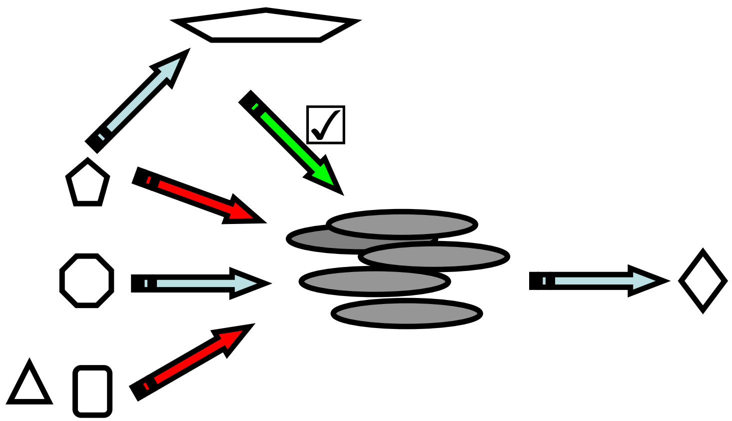
Three Major Strategies for Pentose Utilization



Efficient utilization of diverse sugars → Genetically engineer to produce only ethanol

Efficient ethanol producer → Genetically engineer to metabolize pentoses

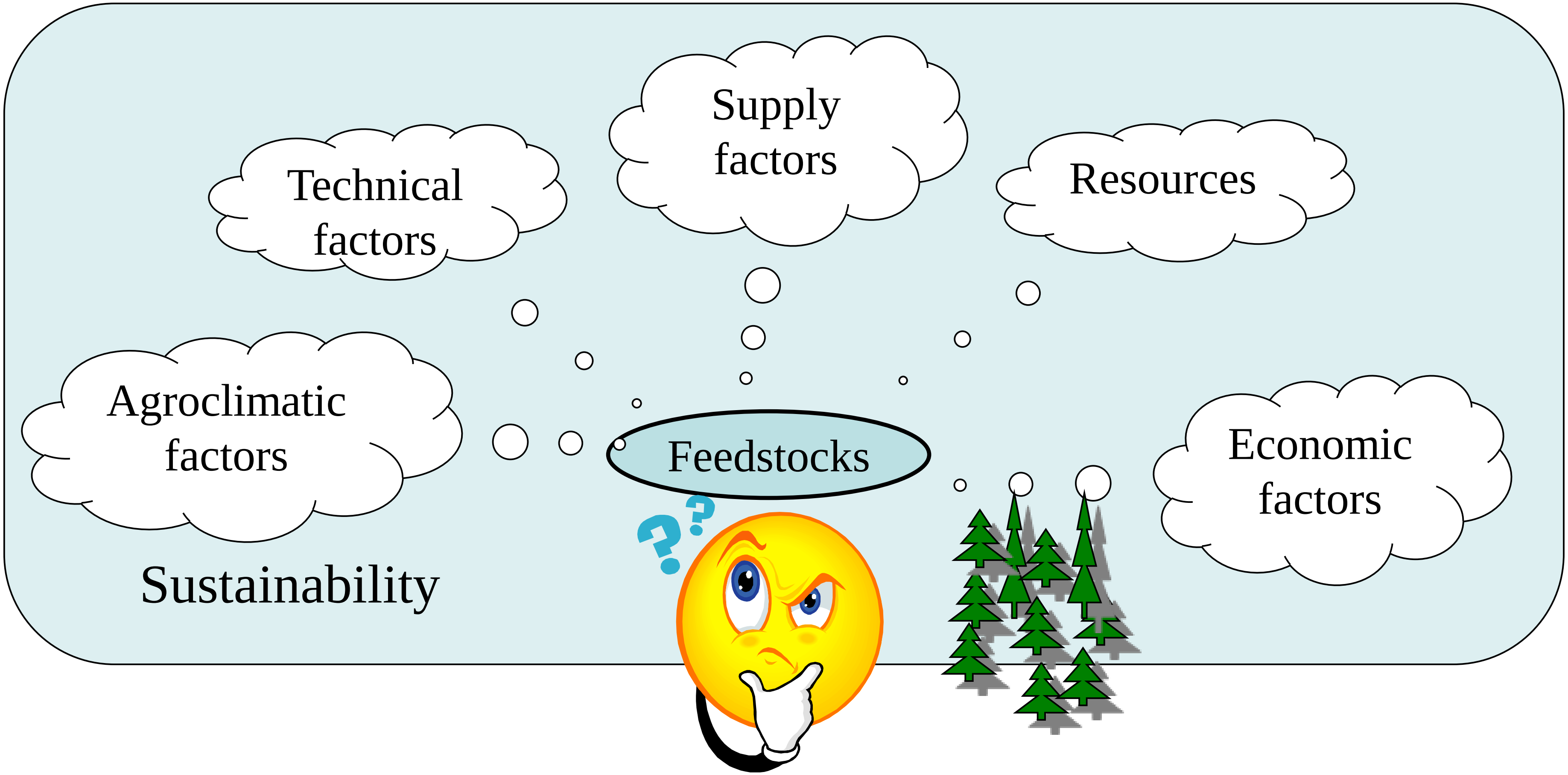




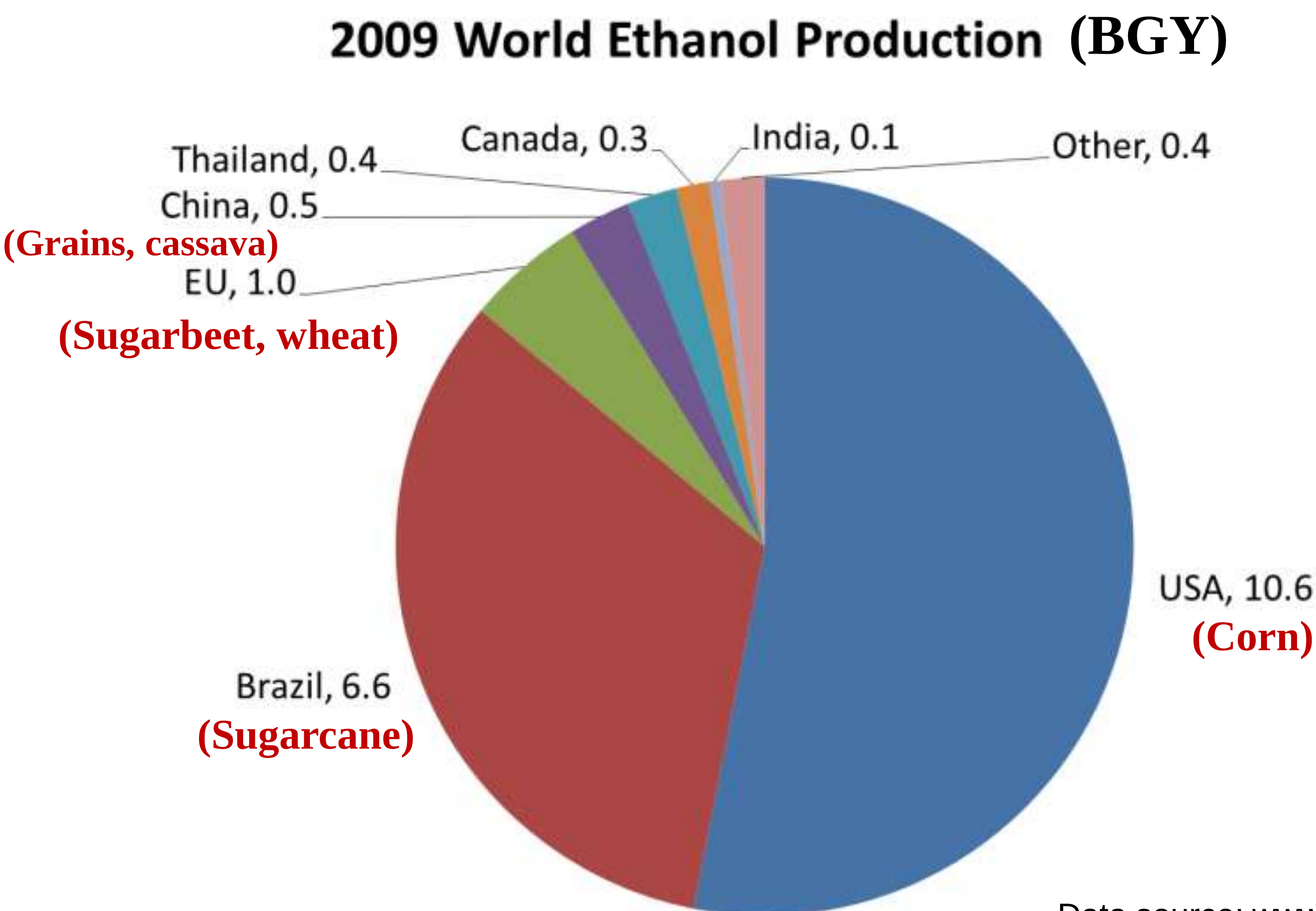
Convert the sugars into a metabolizable form → Xylulose production by xylose isomerization.

Feedstock Potential Evaluation

What are the critical factors that must be considered in evaluating/comparing feedstocks?

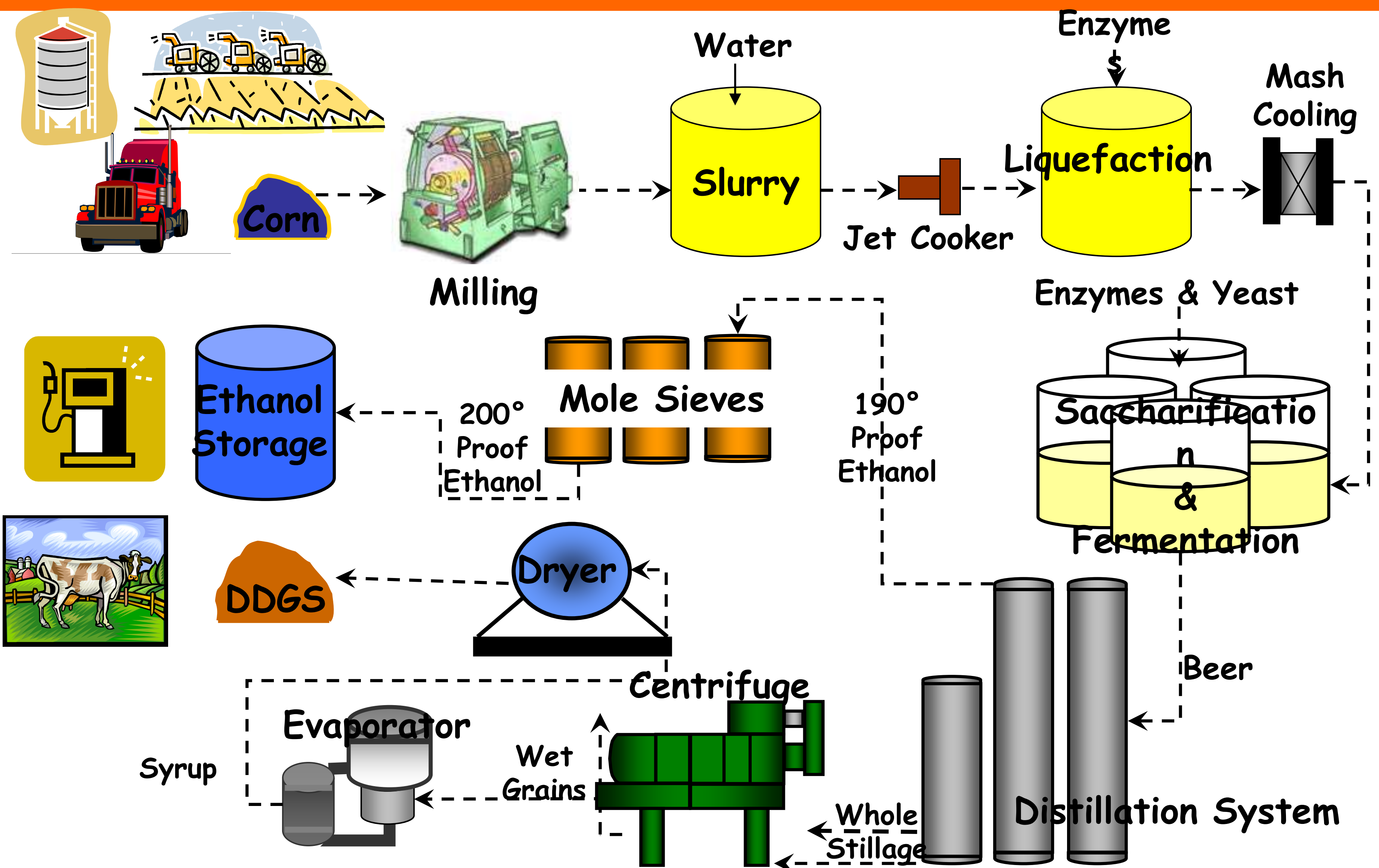


World Ethanol Production



Data source: www.ethanolrfa.org

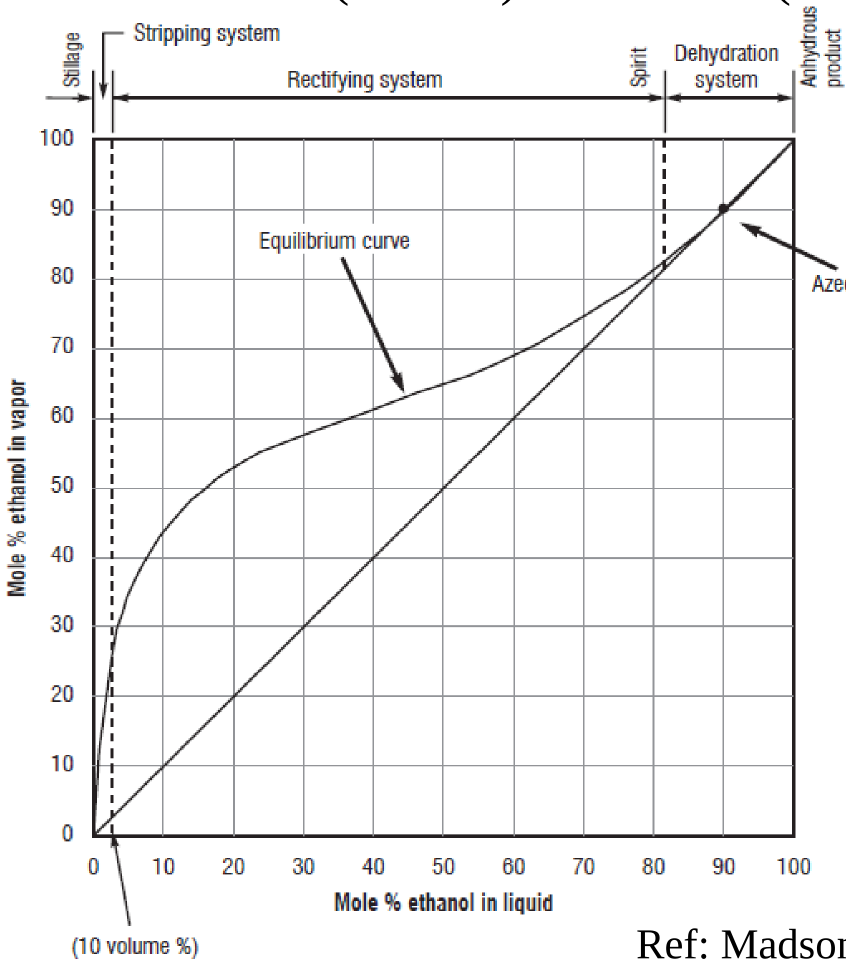
Dry Grind Corn Process

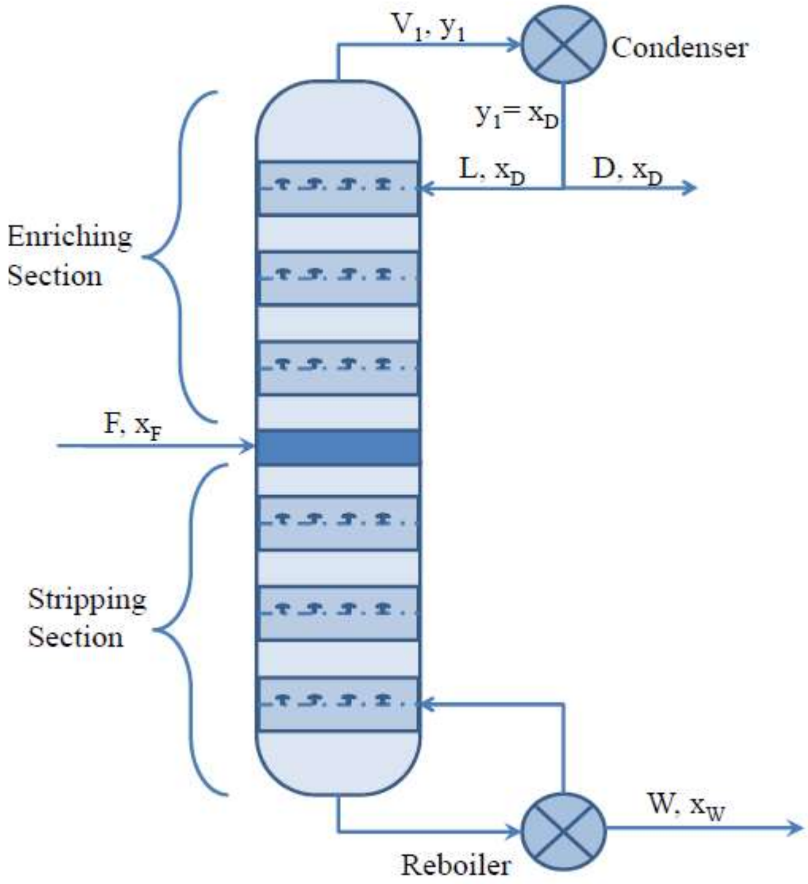


Dry Grind Corn Process

Water and ethanol form a ‘positive azeotrope’ or minimal boiling mixture.

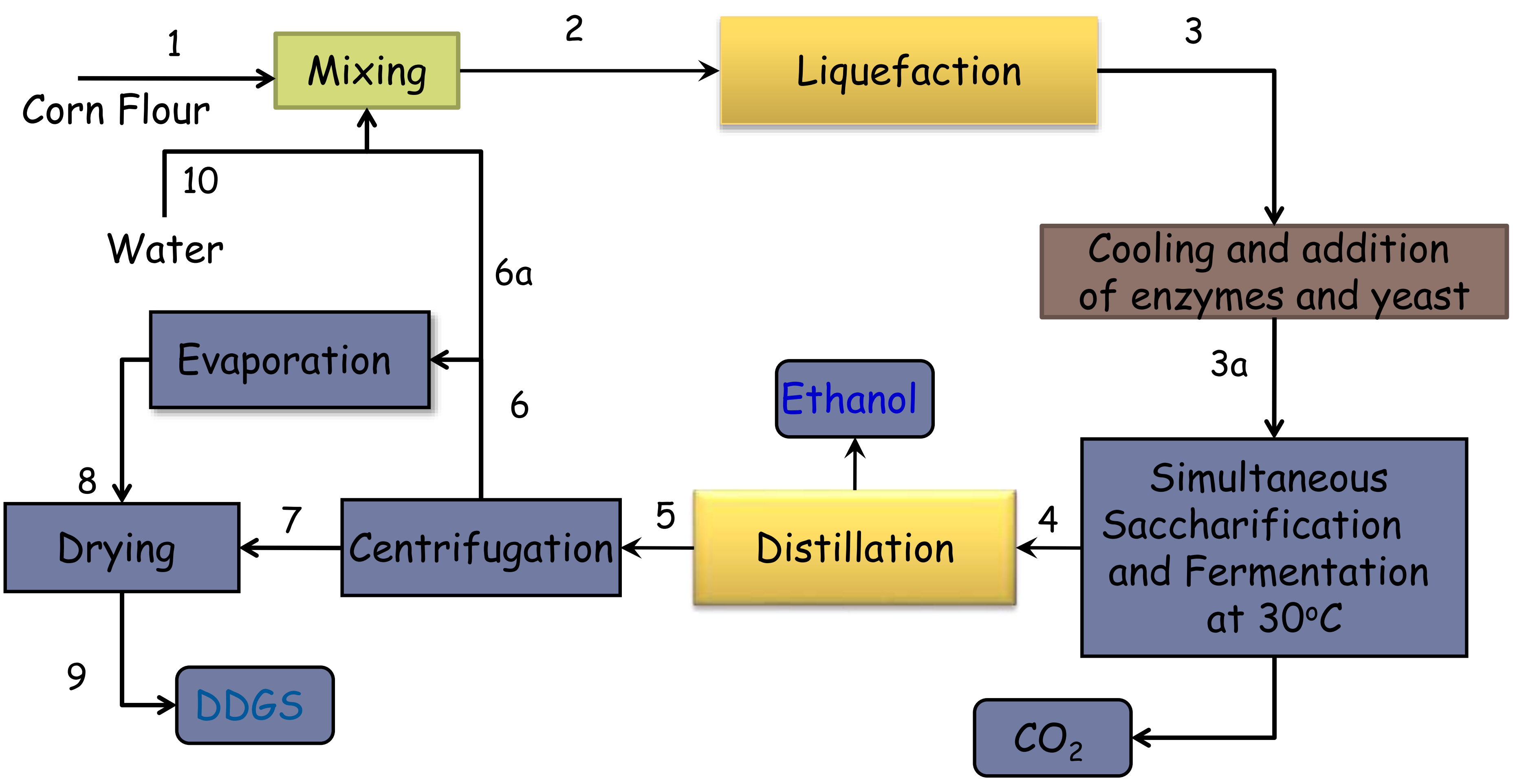
Pure ethanol (78.4°C) Pure water (100°C) Water-ethanol azeotrope (78.1°C)



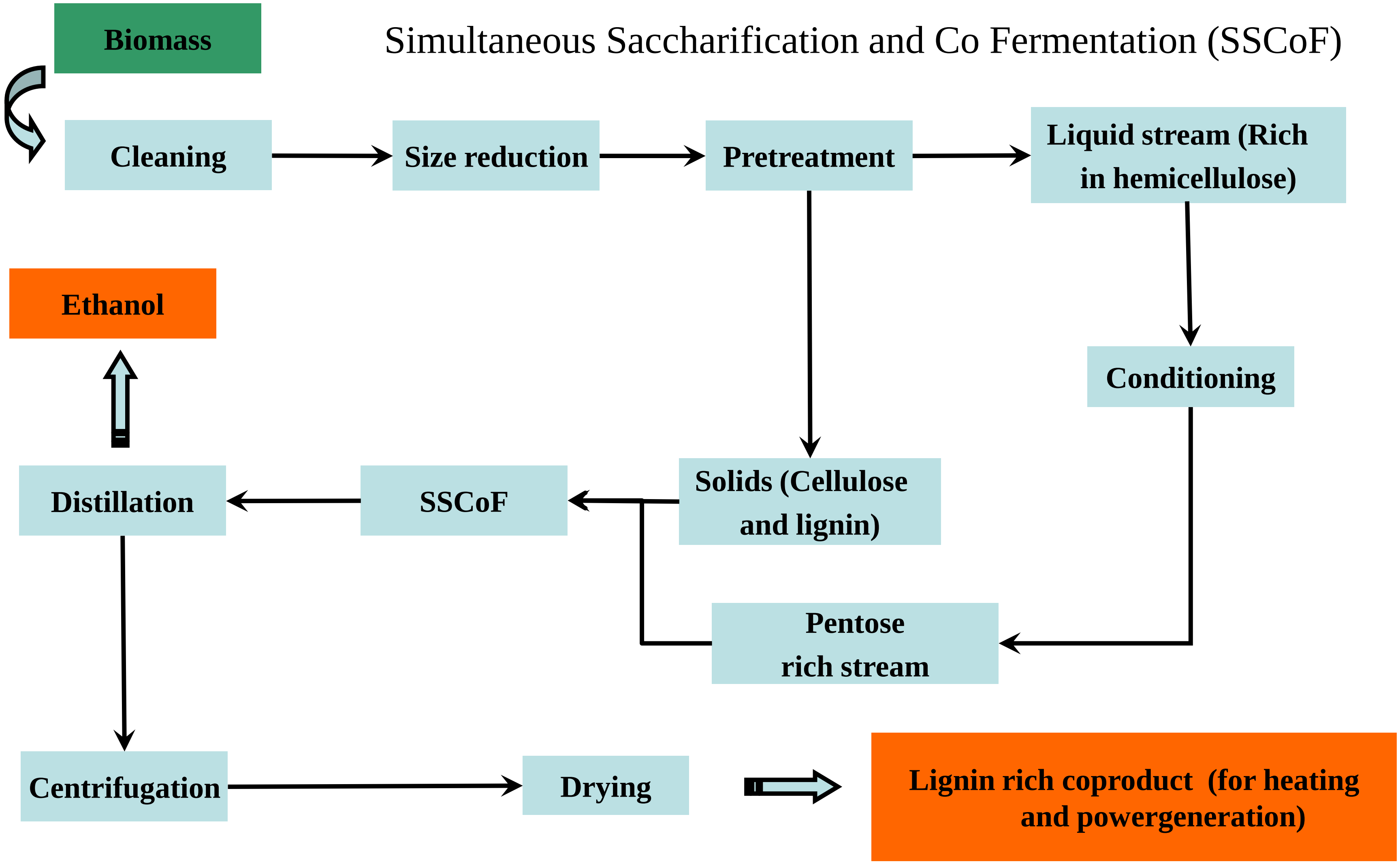


Ref: Madson, P.W. Ethanol distillation fundamentals in Alcohol textbook

Ethanol Production: Process Flow Calculations



Cellulosic Ethanol



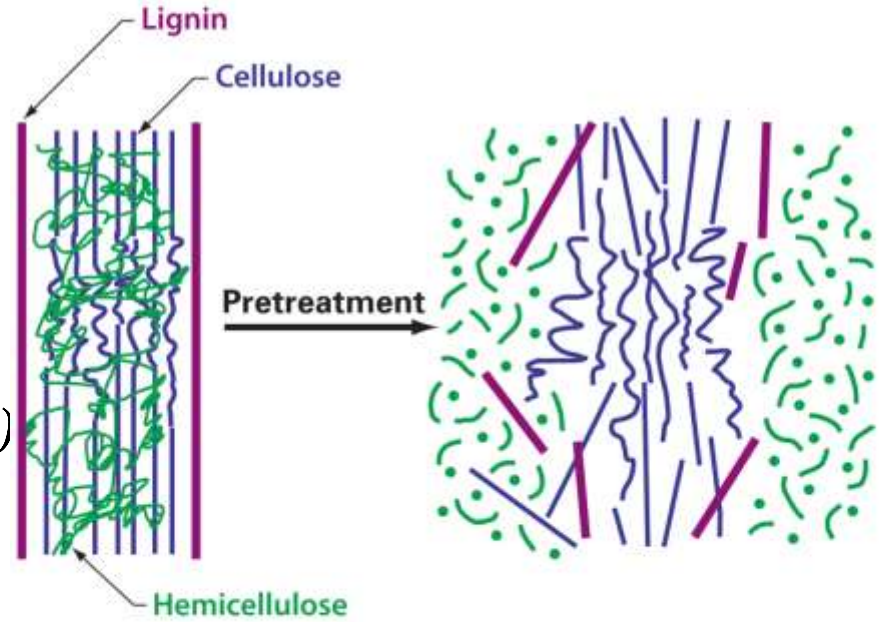
Pretreatment of Biomass

Physio-Chemical Methods

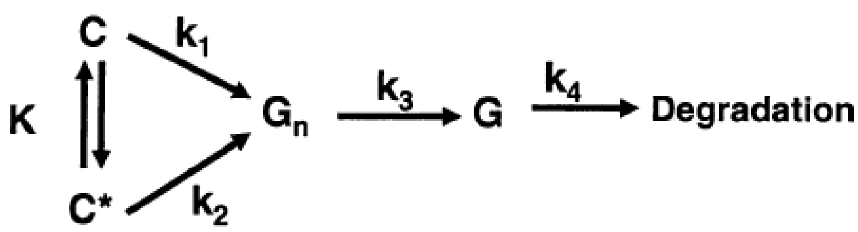
- *Steam Explosion*
- *Liquid Hot Water*
- CO_2 Explosion
- *Ammonia Fiber Explosion (AFEX)*

Chemical Methods

- *Acid Hydrolysis*
- *Alkali Hydrolysis*
- Ozonolysis
- *Organosolv Process*
- Oxidative Delignification



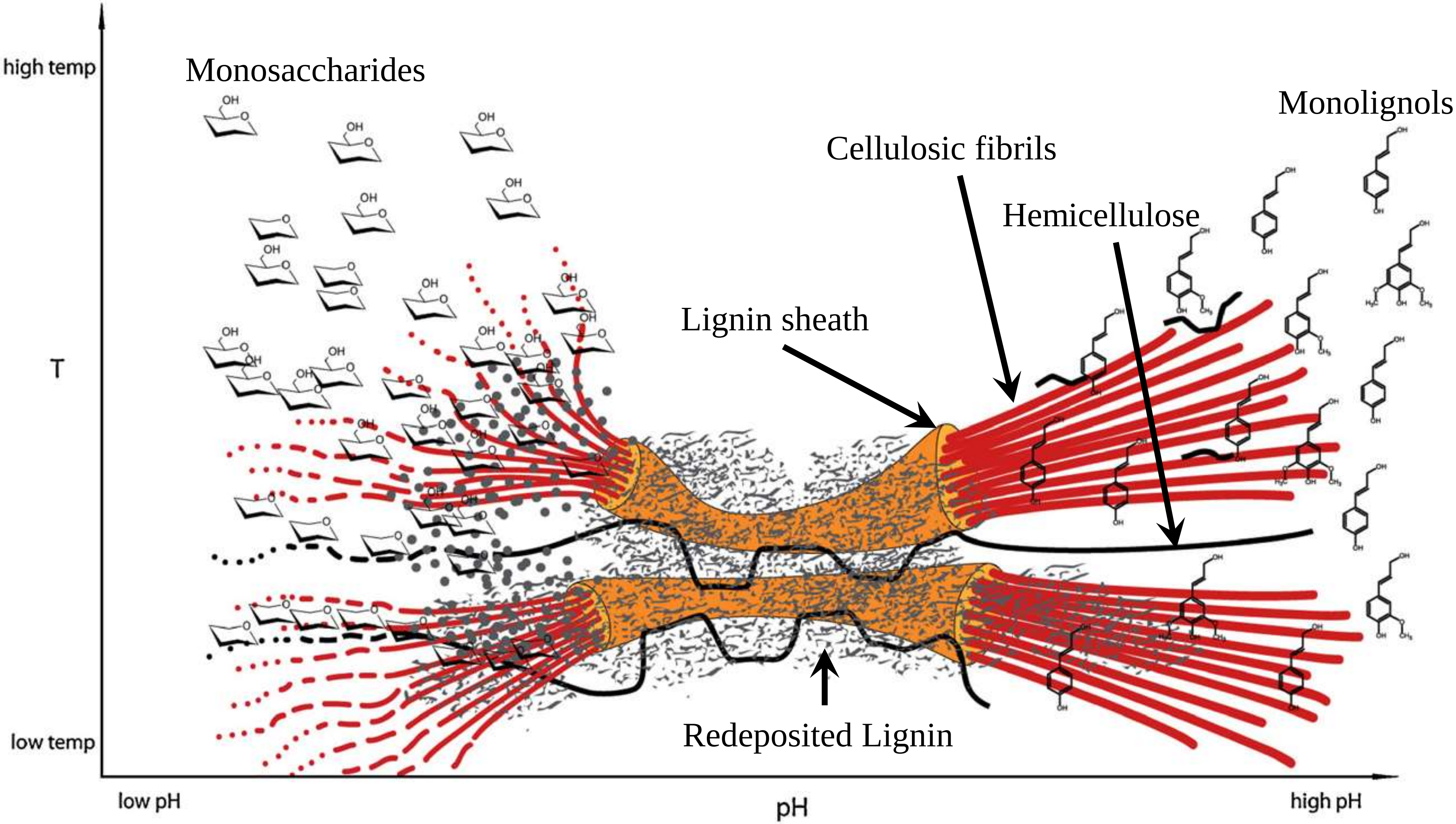
Pretreatment Model



$k_2, k_3, >> k_1$

Ref: Sun and Cheng (2002)

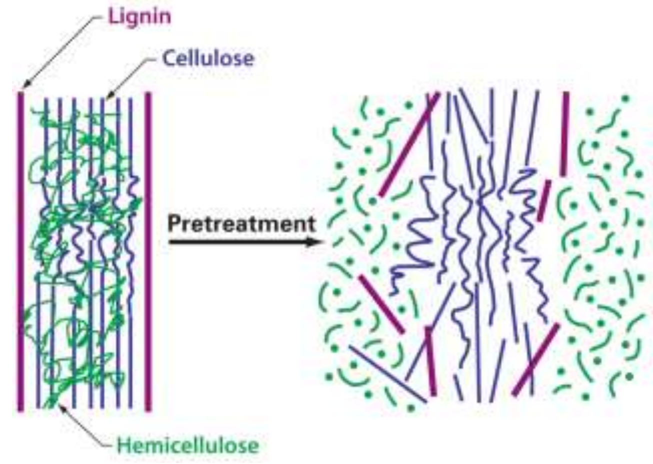
Effect of Temperature and pH on Pretreatments on Biomass



Ref: Pendersen Meyer (2010)

Severity Index of Pretreatment Process

Severity factor is an indicator of the combined effect of temperature (T, °C), reaction time (t, min). This is specific for a particular feedstock and specific pretreatment method.



$$R_o = \int_a^b \exp\left(\frac{T(t) - 100}{14.75}\right) dt = t \cdot \exp\left(\frac{T(t) - 100}{14.75}\right)$$

$$M_o = t \cdot C^n \cdot \exp\left(\frac{T(t) - 100}{14.75}\right)$$

C is the concentration of the chemical catalyst

n=0.849 for H_2SO_4 and 3.90 for NaOH

$$R'_o = R_o \cdot [\mathrm{H}^+]$$

$$\log(R'_o) = \log(R_o \cdot [\mathrm{H}^+]) = \log(R_o) - \mathrm{pH}$$

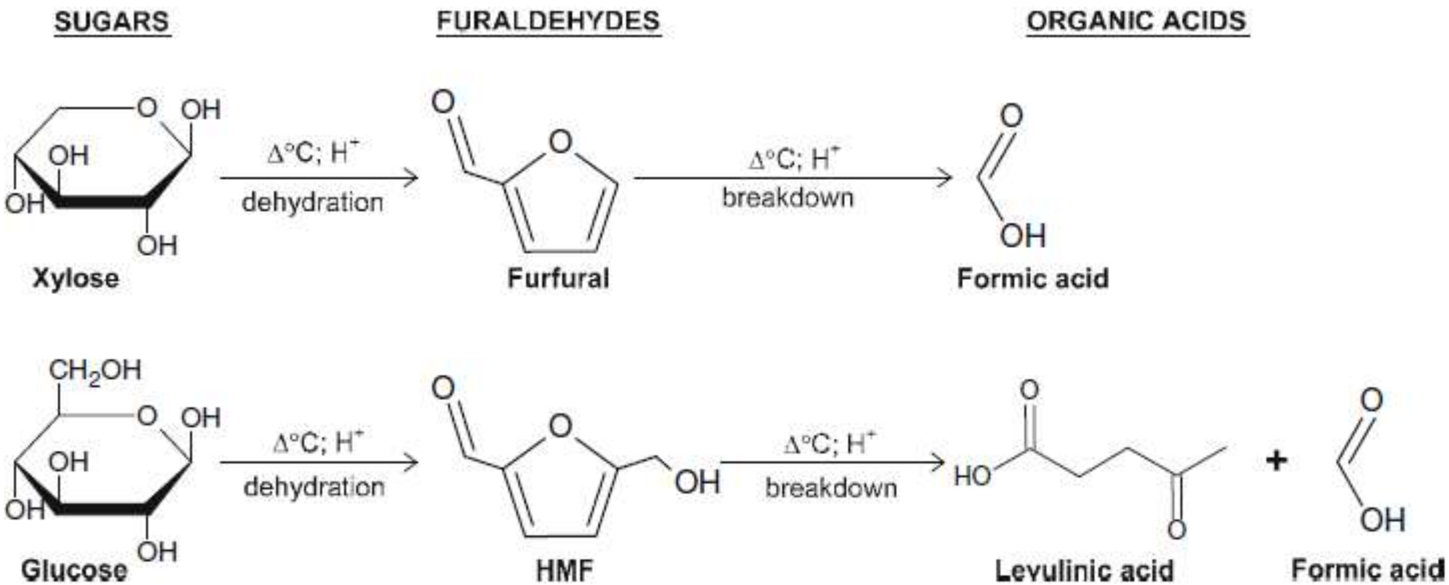
$$\boxed{\log(R''_o) = \log(R_o) + |\mathrm{pH} - 7|}$$

Ref: Palmqvist et al. (2000)

Inhibitors Formation During Pretreatment

Inhibitors produced during pretreatment:

- Sugars: Hydroxy Methyl Furfural (HMF) , Furfural
- Lignin: Cinnamaldehyde, p-hydroxybenzaldehyde and syringaldehyde
- Hemicellulose degradation products: acetate, formic, glucuronic and galacturonic acids)



Ref: Sanchez and Cardona (2008) Almeida et al. (2009)

Inhibitor Action Mechanism

Inhibitors action can be classified into three broad categories:

- Chemical interference with cell maintenance functions
- Inhibition on ethanol production pathways.
- Osmotic effect on cells.

Types of inhibitors

- Furfural and HMF: Glycolysis especially dehydrogenases.
- Phenolics: loss of membrane integrity, interfere with sugar transport and cell growth.
- Weak acids: Proton gradients and increased cell maintenance.
- Aldehydes: Hydrophobicity, NADH and NADPH requirement and other unknown effects. Do not disrupt membrane integrity or effect proton gradients.
- Alcohols: membrane structure. Less toxic than weak acids and aldehydes.

Ref: Pienkos and Zhang (2009)

Pretreated Biomass Conditioning/Detoxification

Removal of inhibitors and toxic compounds is an important downstream step in cellulosic biomass processing. Some of the methods are:

- Evaporation:
- Extraction with organic solvents
- Ionic exchange resins
- Adsorption on activated charcoal, molecular sieves
- *Alkaline Detoxification (Over liming)*
- Combined alkaline and sulfite detoxification
- Enzymatic detoxification
- Microbial detoxification

Ref: Sanchez and Cardona (2008), Palmqvist et al. (2000)

Cellulase Enzymes

• Endo Cellulases: Facilitate hydrolysis by exposing cellulose chains and disrupting the crystalline structure

• Exo cellulases (Cellobiohydrolases or CBH I and II): They further hydrolyze cellulose and yield cellobiose (a disaccharide)

• Cellobiase: These enzymes hydrolyze cellobiose to glucose.

• Oxidative cellulases: "Depolymerize cellulose by radical reactions"

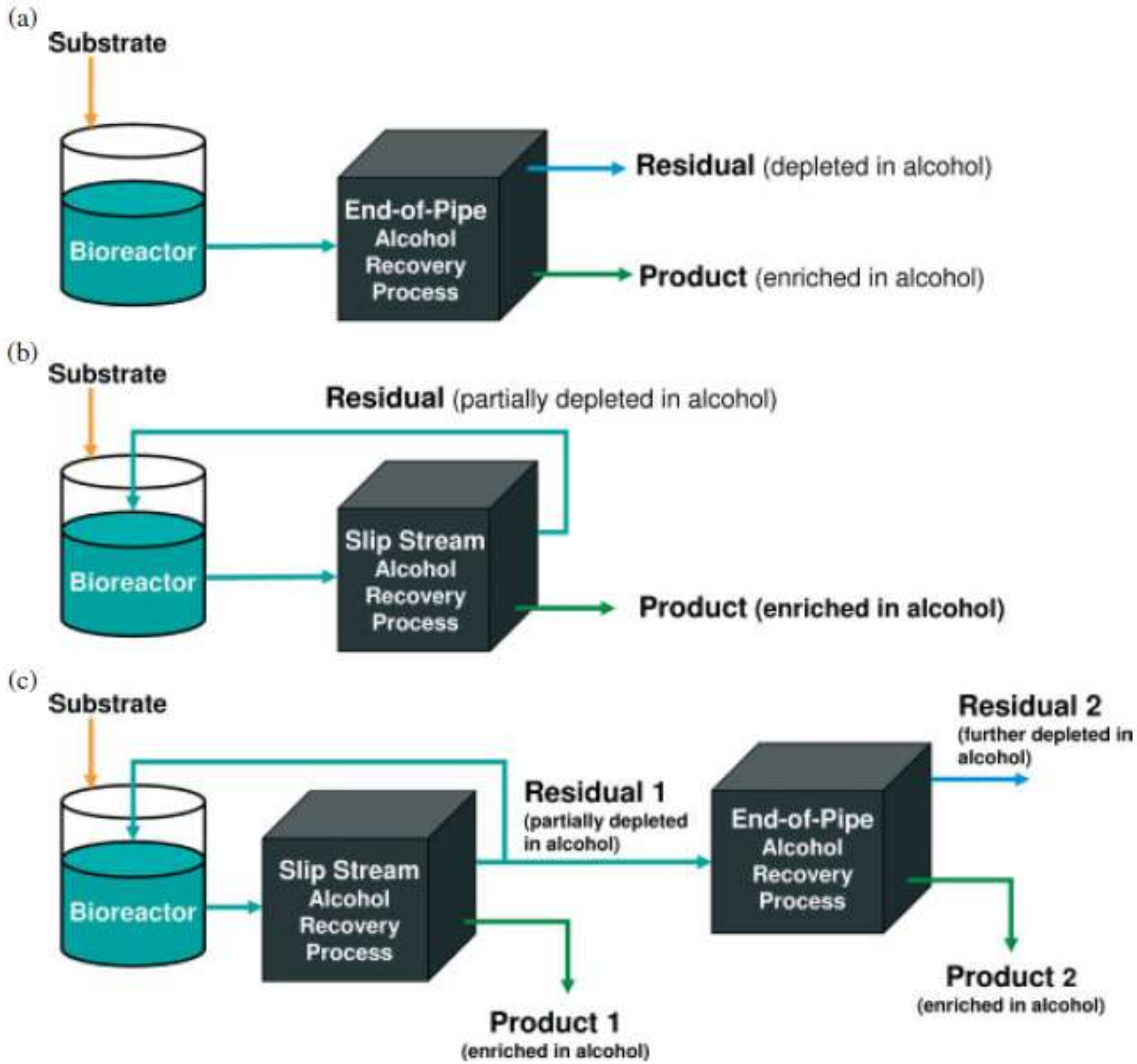
• Cellulose phosphorylases: "Depolymerize cellulose using phosphates instead of water"

• Processive and non-processive cellulases

Ref: Wilson, D.B. (2009, 2011); Gowen and Fong (2010)

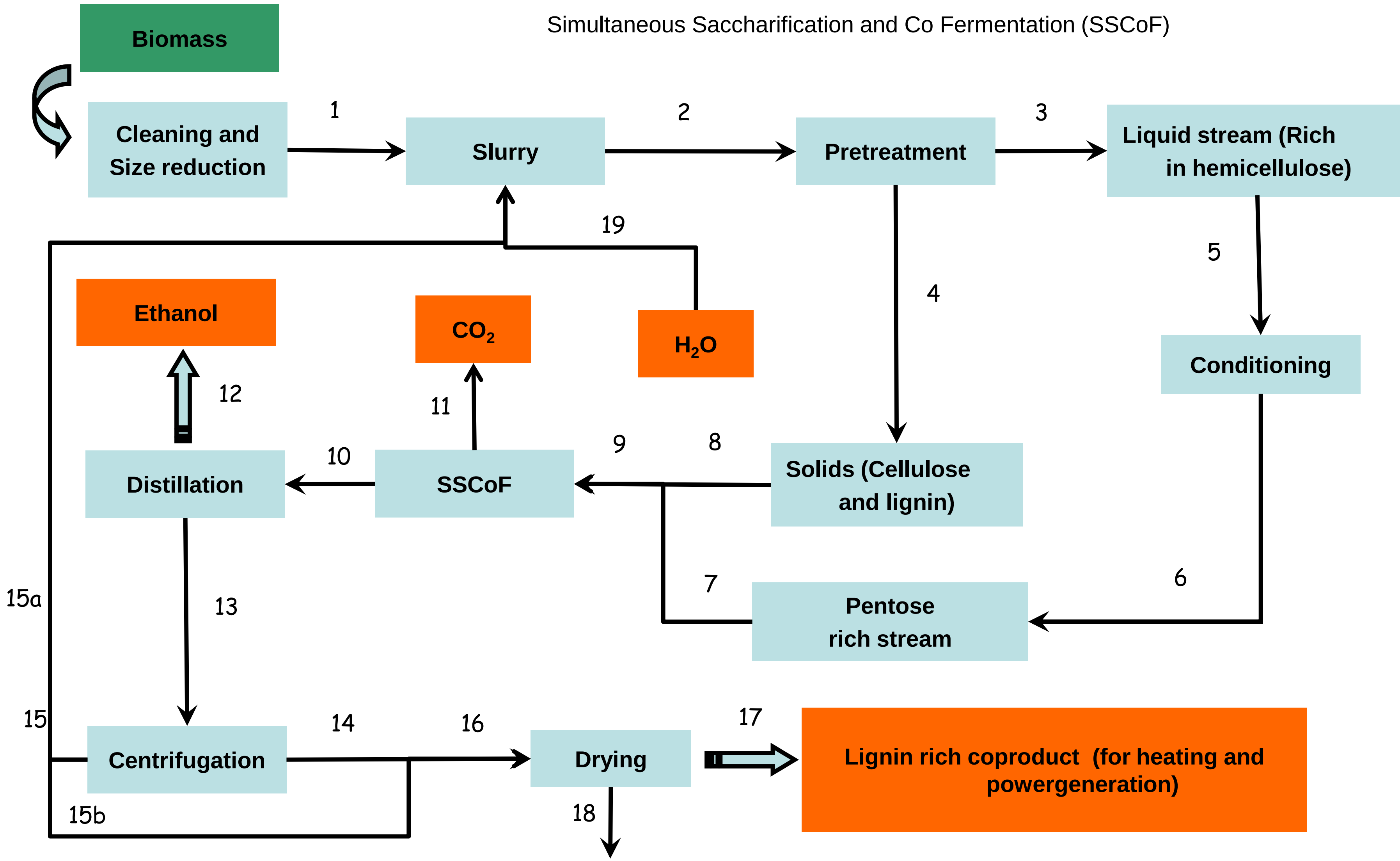
Ethanol Recovery Technologies

- Distillation
- Gas/steam stripping
- Liquid Liquid extraction
- Adsorption
- Pervaporation

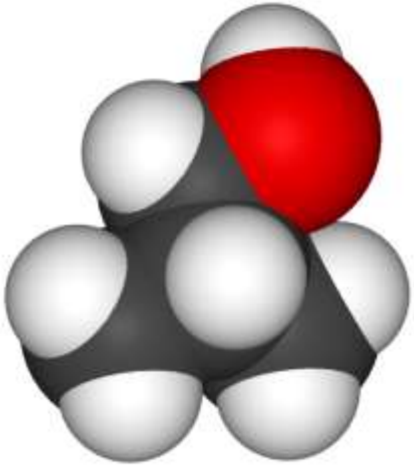


Ref: Vane (2008)

Ethanol Production: Process Calculations Using MS Excel



What is Butanol?

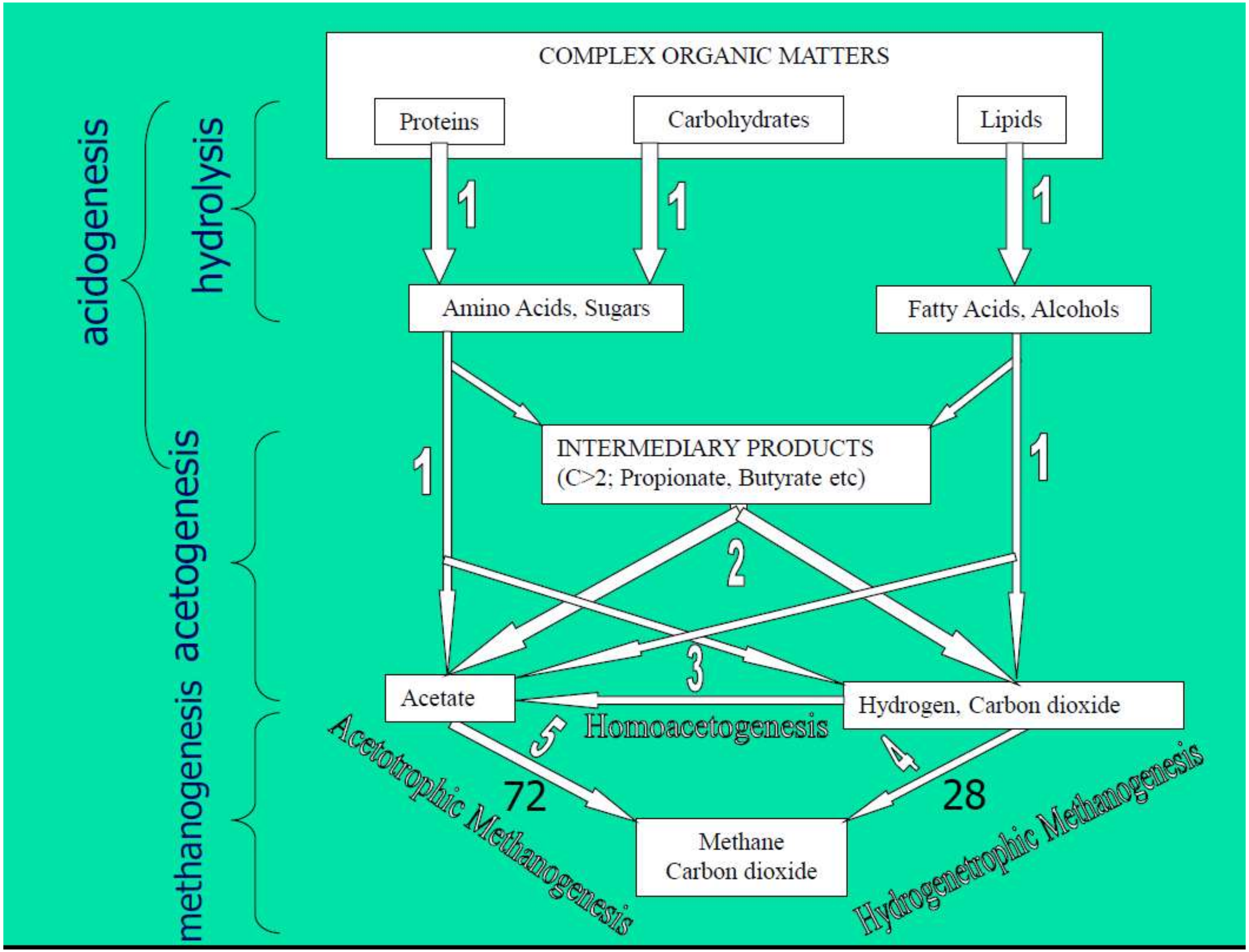


- Butanol is a 4-Carbon Alcohol (Most common forms are normal butanol (n-buOH) and iso-butanol (i-buOH)

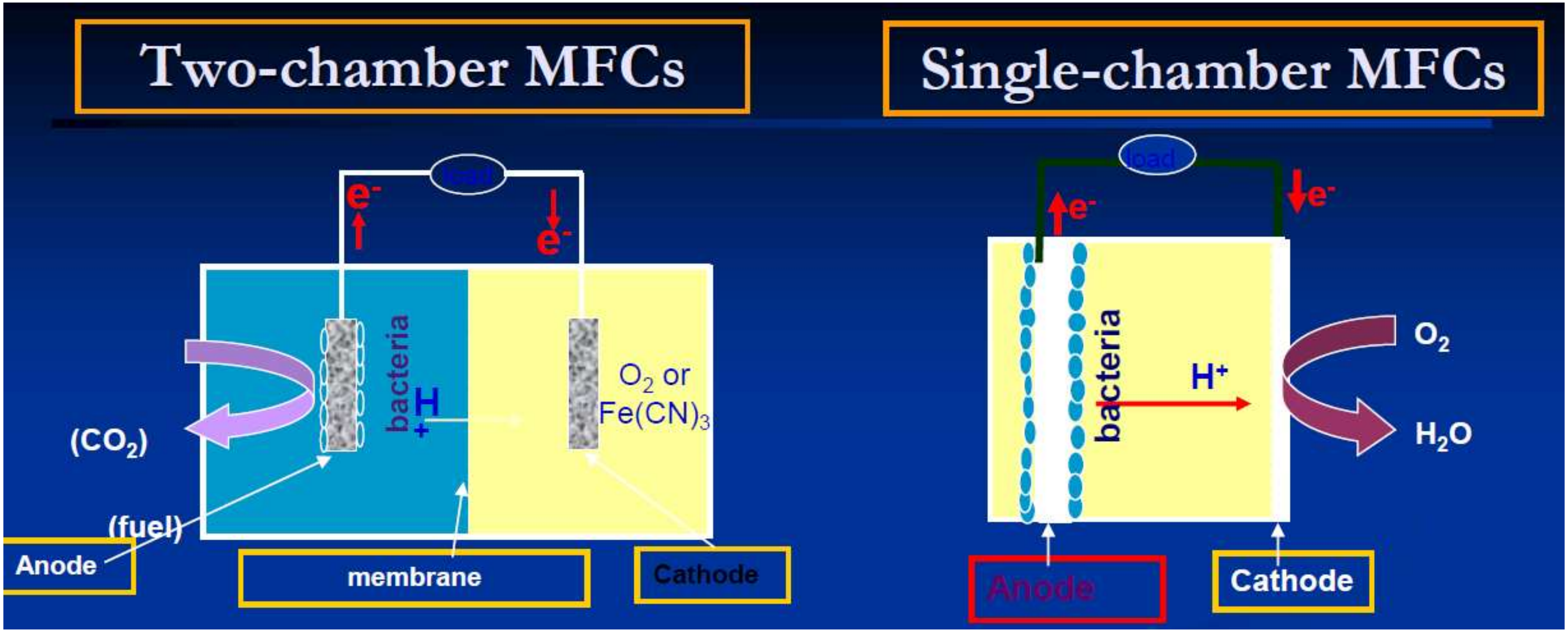
Advantages: Next generation biofuels?

- Higher energy content than ethanol
- Less hydrophilic than ethanol
- More compatible with oil infrastructure
- Lower vapor pressure and higher flash point than ethanol
- Less corrosive
- n-butanol works well with diesel
- Both n-buOH and iso-buOH have good fuel properties

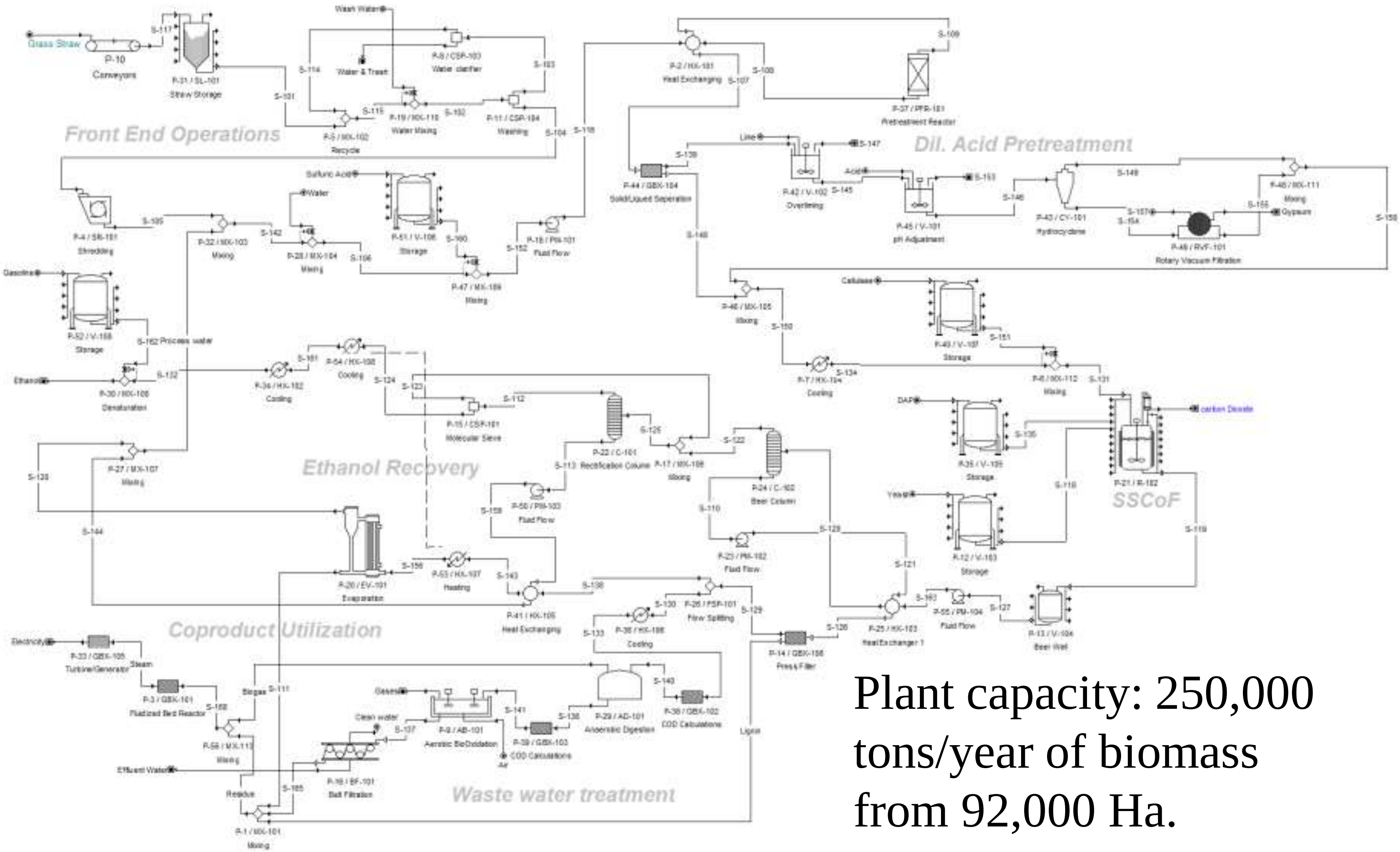
Anaerobic Digestion



Microbial Fuel Cells

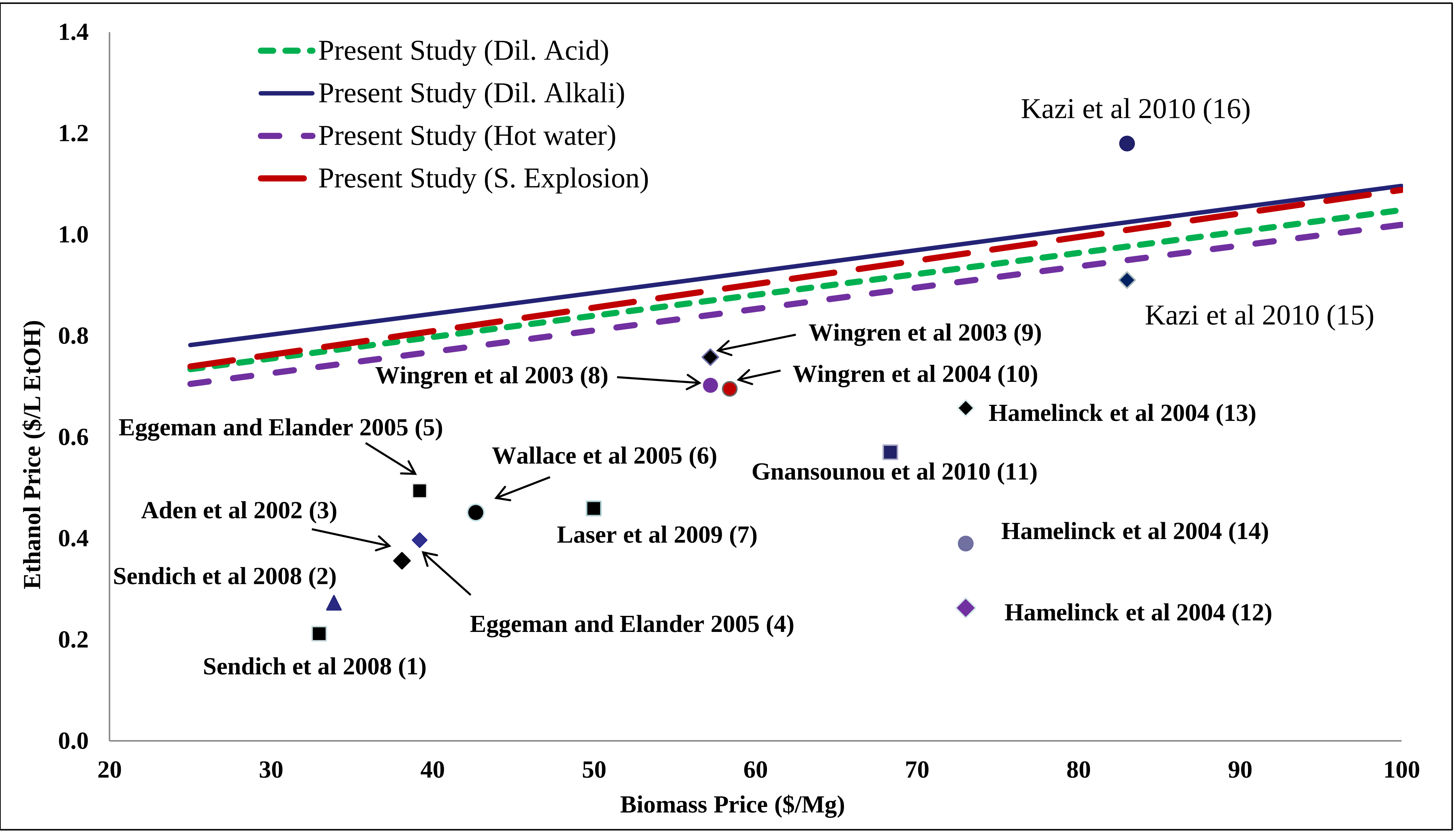


Process Model Development: Dilute Acid Pretreatment



Plant capacity: 250,000 tons/year of biomass from 92,000 Ha.

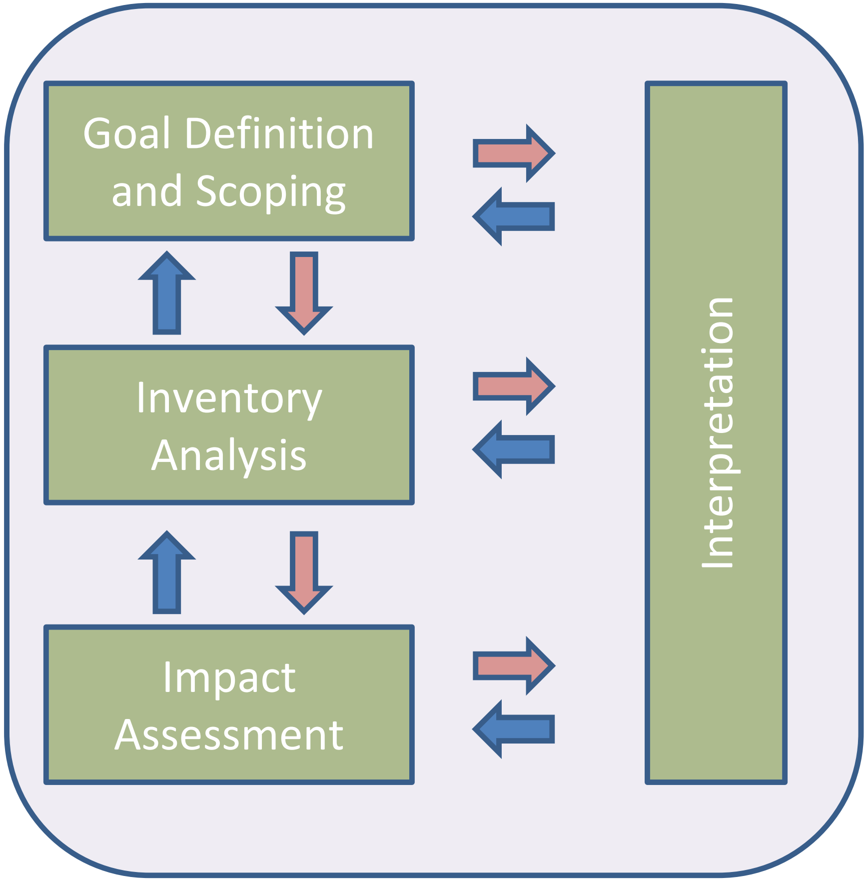
Comparison of Present Study to Extant Literature



Life Cycle Analysis: Summary of Process Steps

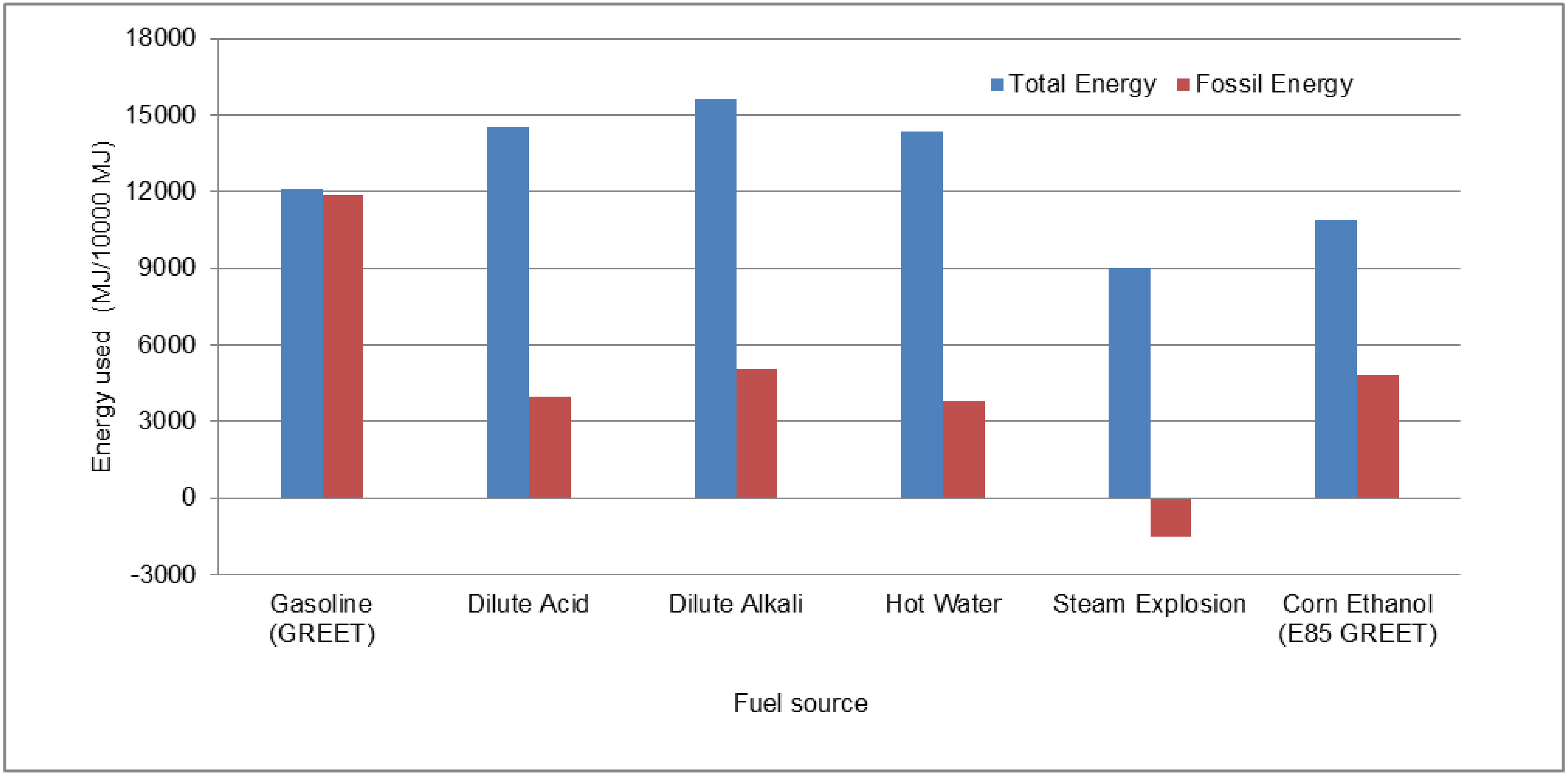
LCA is divided into four distinct stages:

1. Goal Definition and Scoping
2. Life Cycle Inventory
3. Life Cycle Impact Assessment
4. Life Cycle Interpretation



Ref: Life Cycle Analysis: Principles and Practice. EPA/600/R-06/060 (2006)

Cellulosic Ethanol: Life Cycle Assessment Results



Ref: Kumar and Murthy, 2012. IJLCA. doi:10.1007/s11367-011-0376-5

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