Second and Third Generation Biofuels: A Review of the Chemistry, Feedstocks, Processes and Projects

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Ligno-cellulosic Feedstocks Conversion
State of the Technology

- Introduction
  - Transportation Fuels
  - First Generation Biofuels
  - Biofuels Technology Matrix
- Feedstock
  - Basic Chemistry
  - Feedstock Composition
- Second Gen. Biofuels
  - Sugar Platform
  - Thermo-chemical Platform
- Third Gen Biofuels

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Petroleum & First Generation Biofuels

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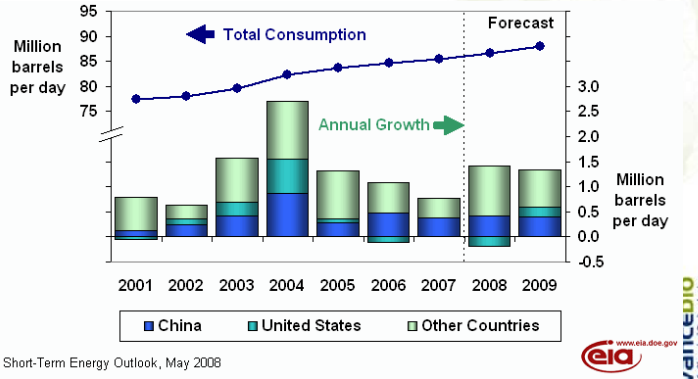
World Oil Consumption



Short-Term Energy Outlook, May 2008

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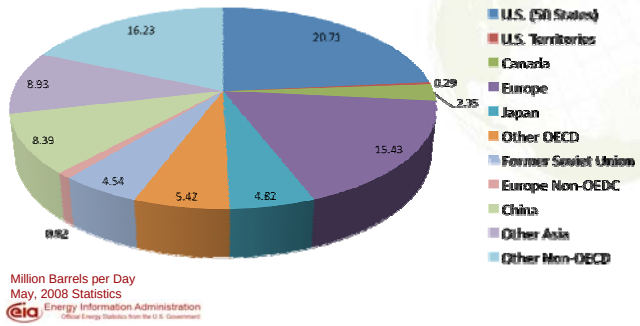
World Oil Consumption



Million Barrels per Day
May, 2008 Statistics
Energy Information Administration

OECD: Organization for Economic Cooperation and Development: Australia, Austria, Belgium, Canada, the Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Japan, Luxembourg, Mexico, the Netherlands, New Zealand, Norway, Poland, Portugal, Slovakia, South Korea, Spain, Sweden, Switzerland, Turkey, the United Kingdom, and the United States.

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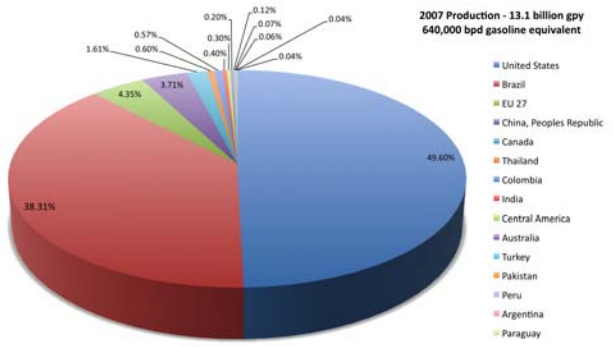
First Generation Biofuels - Production



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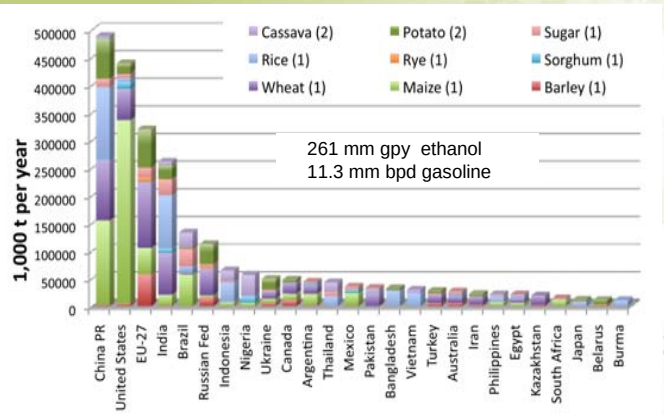
First Generation Biofuels - Feedstocks



(1) United States Department of Agriculture, 2006-2007 Crop Year,
(2) Food and Agricultural Organization of the United Nations, 2005 Crop Year

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General Comment

- Oil prices increase 700% in ten years.
- Exxon records $40 billion in profits - 2007.
- US spends $500 billion + and countless lives protecting Middle Eastern oil fields.

GOOD

- Corn prices increase 200% in 100 years.
- America can stop paying farmers not to farm.
- American migration from farms to cities will be reversed.

BAD

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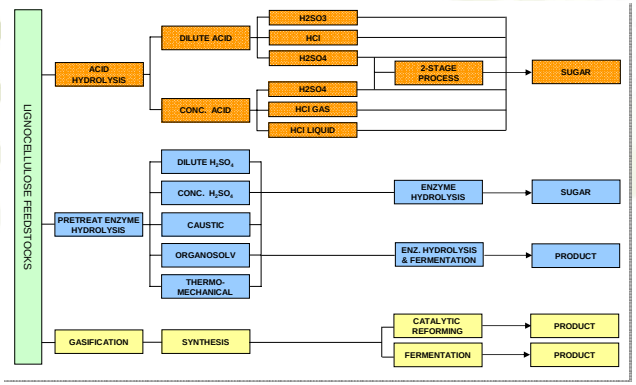
Second Generation Biofuels Technologies

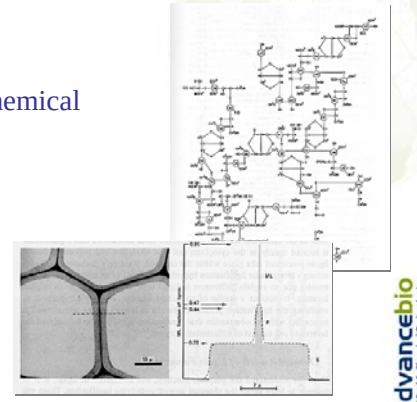
Biomass Process Matrix



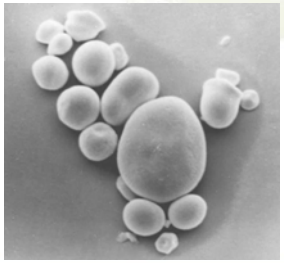
Second Generation Biofuel Technologies

Research & Development Areas

- Sugar Platform
  - Chemical
  - Chemical / Biochemical
- Thermochemical
  - Metallic Catalyst
  - Biocatalyst



Second Generation - Sugar Platform Chemistry and Process Basics



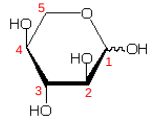
Carbohydrate Chemistry

- Simple Sugars
  - Monosaccharides (reducing sugars)
    - Xylose, Glucose / Dextrose
    - Fructose
  - Disaccharides
    - Sucrose, Maltose
- Complex Sugars
  - Polysaccharides
    - Starch, Cellulose, Hemi-cellulose, Beta-glucan, Arabinoxylan

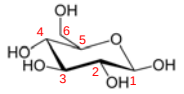
General Carbohydrate Classes

- Simple sugars
  - Building blocks
  - Quick access energy
- Starches
  - Energy storage
- Cellulose, Hemicellulose
  - Structural

Simple Sugars

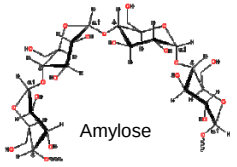


Xylose
C-5

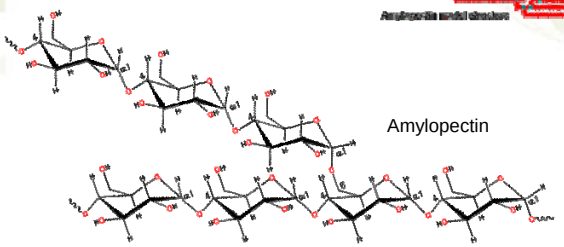


Glucose
C-6

Starch Structure

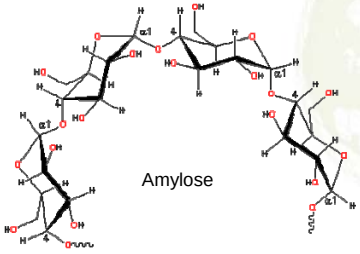


Amylose

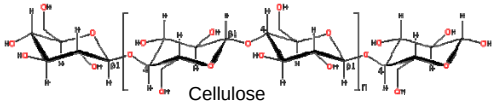


Amylopectin

Starch - Cellulose Comparison

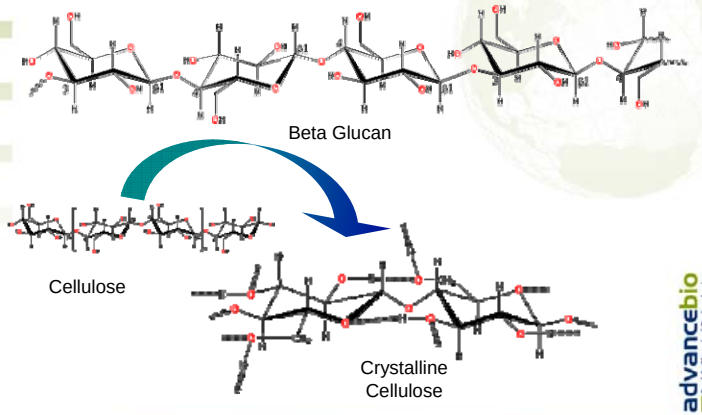


Amylose

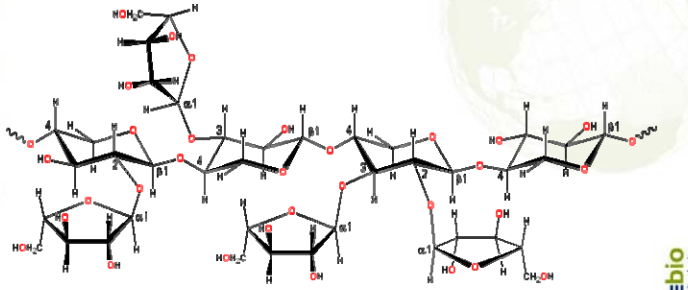


Cellulose

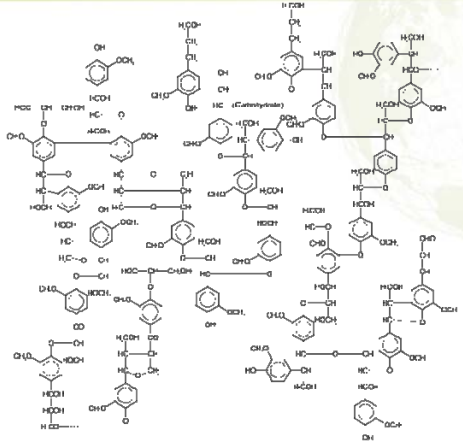
Glucan Structure



Arabinoxylan Structure

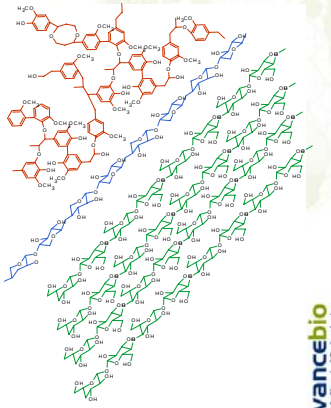


Lignin Structure

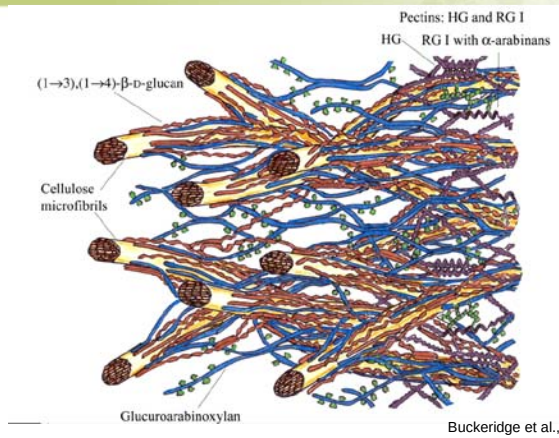


Constituents of Biomass

- Lignin: 15%–25%
  - Complex aromatic structure
  - Very high energy content
  - Resists biochemical conversion
- Hemicellulose: 23%–32%
  - Xylose is the second most abundant sugar in the biosphere
  - Polymer of 5- and 6-carbon sugars, marginal biochemical feed
- Cellulose: 38%–50%
  - Most abundant form of carbon in biosphere
  - Polymer of glucose, good biochemical feedstock

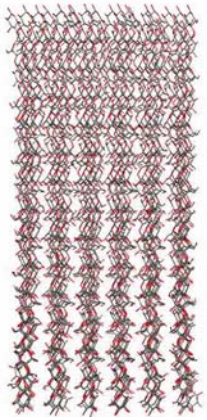


Plant Cell Wall Model



Buckeridge et al., 2004

Cellulose Crystalline Structure



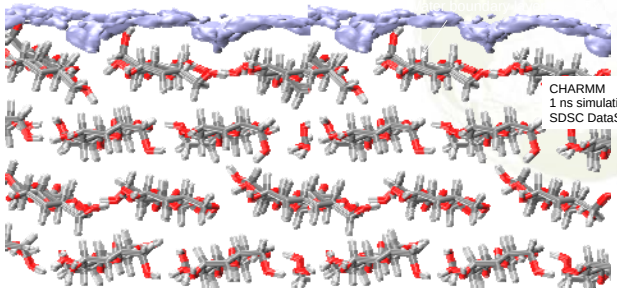
Cellulose is a crystalline structure that resists water penetration

This makes disassembly very difficult since the enzymes and acid catalysts are in solution.

CHARMM
1 ns simulation
SDSC DataStar

John Brady, Cornell
NREL subcontractor

Detail of Water Boundary Layer

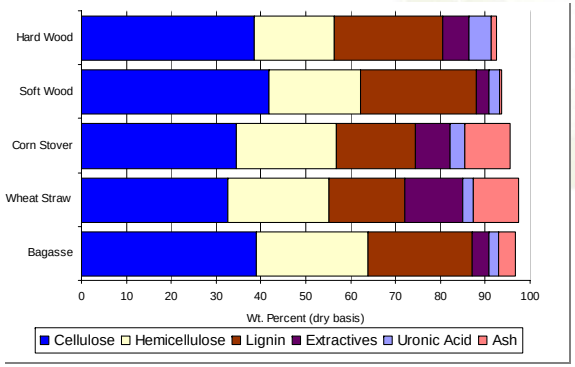


CHARMM
1 ns simulation
SDSC DataStar

John Brady, Cornell

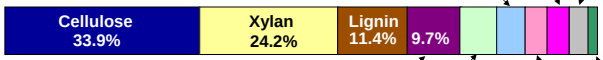
"Computer Simulations of Water Structuring Adjacent to Microcrystalline Cellulose 1beta Surfaces," J.F. Matthews, C.E. Skopec, P.E. Mason, P. Zuccato, R.W. Torget, J. Sugiyama, M.E. Himmel, and J.W. Brady, Carb. Res. 341, 138-152, 2006.

Biomass Feedstocks
General Composition



Corn Stover Composition

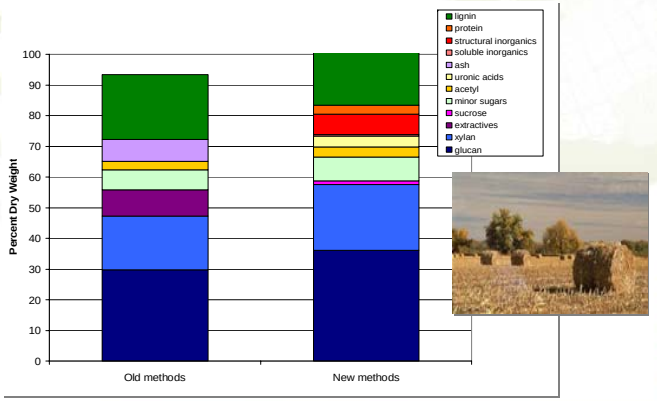
Corn Stover



(dry weight basis)

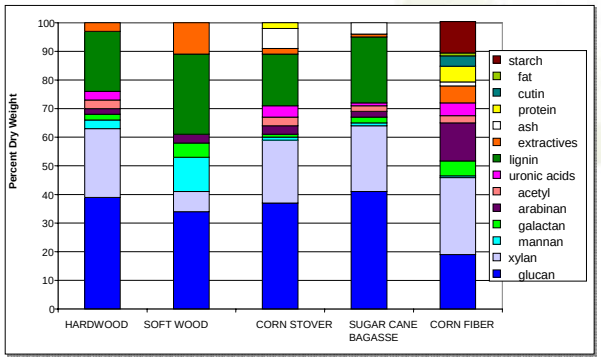
Biomass Feedstocks

Improvements in Analysis

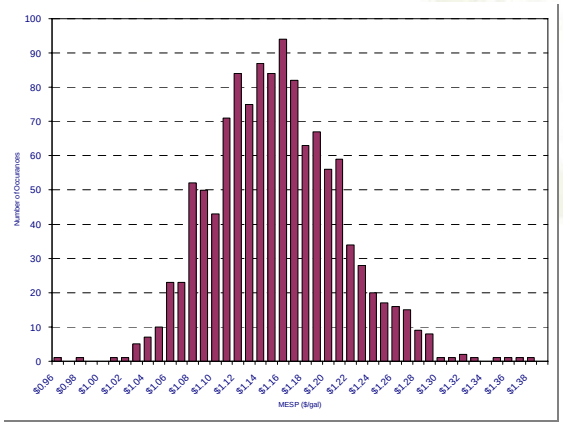


Biomass Feedstocks

Specific Composition



Effect of Stover Compositional Variability



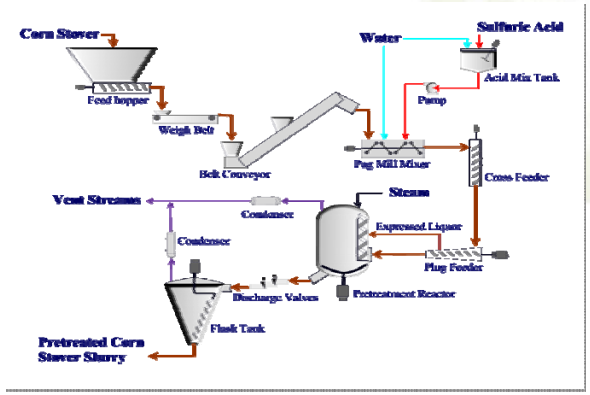
Starch Hydrolysis Reaction Mechanisms

Substrate + H_2O (Starch)	Energy + Enzyme → (Alpha Amylase)	Product (Dextrins)
Substrate + H_2O (Dextrins)	Enzyme → (Gluco Amylase)	Product (Glucose)
Substrate (Glucose)	Yeast + Nutrients →	Product (Ethanol, CO_2, Biomass)

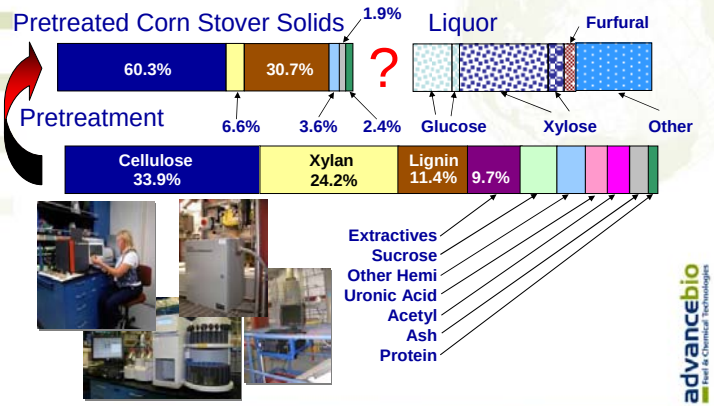
Biomass Hydrolysis Reaction Mechanisms

Substrate + H_2O (Biomass = Cellulose, Hemicellulose, Lignin)	Energy + Catalyst → (Acid)	Product (Xylose, Xylans, Cellulose, Lignin)
Substrate + H_2O (Cellulose)	Enzyme → (Cellulase "Package")	Product (Glucose)
Substrate (Glucose)	Yeast + Nutrients → (Cellulase "Package")	Product (Ethanol, CO_2, Biomass)
Substrate (Glucose, Glucans, Xylose, Xylans)	GMO + Nutrients →	Product (Ethanol, CO_2, Biomass)

Pilot-Scale Acid Pretreatment System



Tracking Composition and Mass



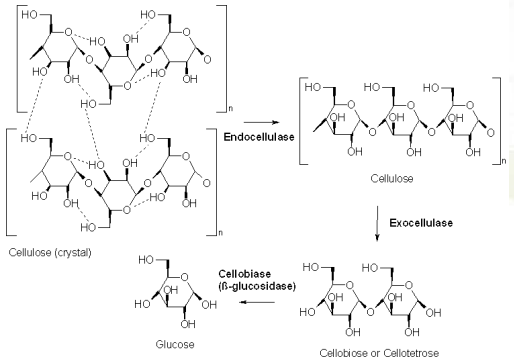
Cellulose Hydrolysis

BAGASSE

CORN STOVER

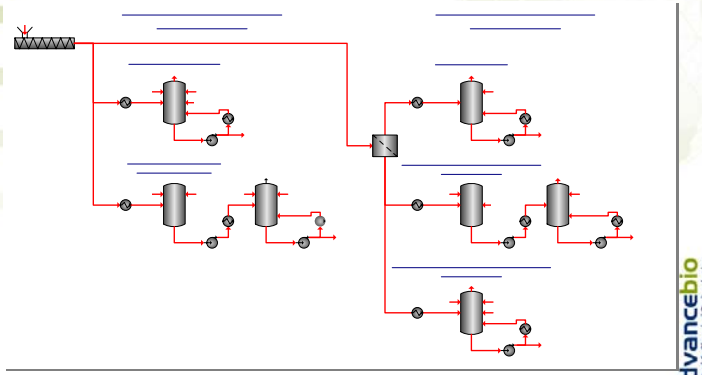
- Higher C6 cake solids are critical to reducing production costs.

Cellulose Enzymatic Hydrolysis Reaction



Sugar Platform Fermentations

Choices and Challenges



Second Generation

Thermochemical Platform

Chemistry and Process Basics

Thermochemical Pretreatment
Gasification

- Process
  - Partial combustion in controlled O_2 atmosphere
- Types
  - Air
  - Oxygen
  - Steam

Thermochemical Pretreatment
Gasification Stoichiometry

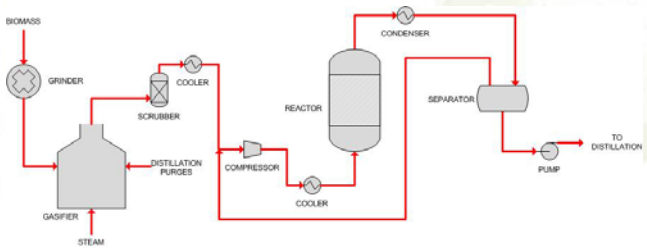
Air / Oxygen Blown Gasifier Stoichiometry

$$8\ \underset{\text{Biomass}}{CH_2O} + O_2 + (4\ N_2) \longrightarrow 6\ CO + 2\ CO_2 + 8\ H_2 + (4\ N_2)$$

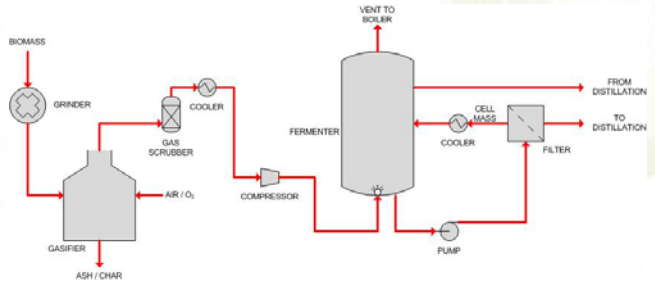
Steam Blown Gasifier Stoichiometry

$$5\ \underset{\text{Biomass}}{CH_2O} + 2\ H_2O \longrightarrow 3\ CO + 7\ H_2 + 2\ CO_2$$

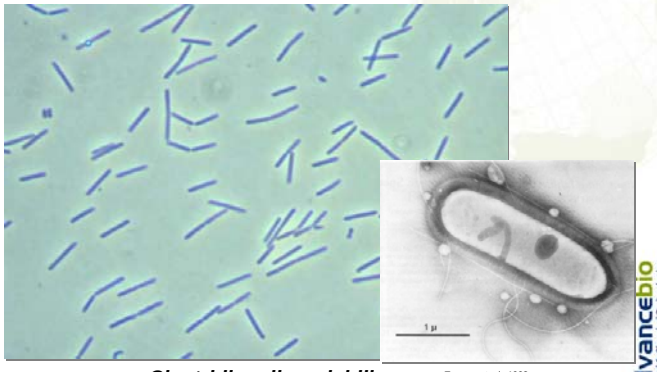
Ethanol from Synthesis Gas
Catalytic Route



Ethanol from Synthesis Gas
Biological Route



Ethanol from Synthesis Gas
Biological Route



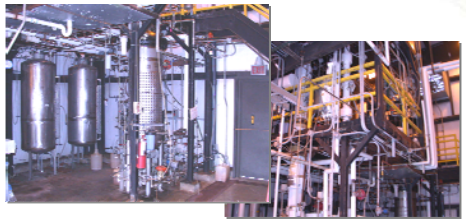
Clostridium ljungdahlii

Tanner, *et. al.*, 1993

Ethanol from Synthesis Gas
Biological Route – Basic Reactions

$$6\ CO + 3\ H_2O \rightarrow CH_3CH_2OH + 4\ CO_2$$

$$6\ H_2 + 2\ CO_2 \rightarrow CH_3CH_2OH + 3\ H_2O$$



Ethanol from Synthesis Gas
Biological Route - Stoichiometry

Air / Oxygen Blown Gasifier

$$\underset{\text{Biomass}}{8\ CH_2O} + O_2 + (4\ N_2) \xrightarrow{\Delta} 2.33\ CH_3CH_2OH + 3.33\ CO_2 + H_2O + (4\ N_2)$$

Theoretical Yield : 136 Gal / Dry Ton Biomass

Steam Blown Gasifier

$$\underset{\text{Biomass}}{8\ CH_2O} \xrightarrow{\Delta} 1.67\ CH_3CH_2OH + 1.67\ CO_2$$

Theoretical Yield : 136 Gal / Dry Ton Biomass - Air Blown
155 Gal / Dry Ton Biomass - Steam Blown

Third Generation Biofuel Technologies

Third Generation Technologies

- LS9
  - Sugar
  - GMO Fermentation
  - Hydrocarbon properties
- Virent
  - Sugar
  - Catalytic / Chemical
  - Hydrocarbon properties

Third Generation Technologies

- DuPont / British Petroleum
  - Sugar
  - GMO Fermentation
  - Hydrocarbon properties
- Greenfuel Technology
  - CO_2
  - Algae
  - Lipids and carbohydrates

Third Generation Technologies

- Amyris
  - Sugar
  - GMO Fermentation
  - Hydrocarbons
- Synthetic Genomics
  - CO_2 , Carbohydrates
  - GMO Fermentation
  - Lipid and carbohydrates

Always remember….
….a bad day fishing is still better than a good day at work….