Biomass Part II: Producing Biofuels

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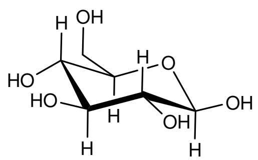
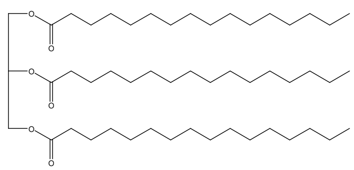
Biomass needs to be converted to useful fuels.

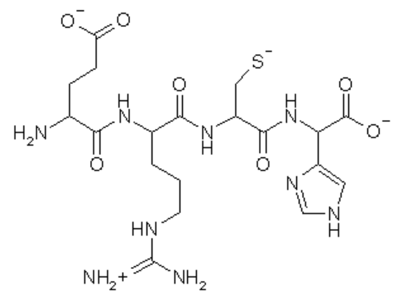
	Biomass	Conventional Fuels
State	• Generally solids	• Liquids or gases
Energy Density	• Low [Lignocellulose: ~10-20 MJ/kg]	• High [Gasoline: 43.4 MJ/kg]
Moisture Content	• High [Corn: 15% moisture delivered]	• No moisture content
Oxygen Content	• High [Often 10-40% oxygen]	• No oxygen content [<1% oxygen]
Compatibility	• Generally not compatible with existing engines, boilers, and turbines	• Combust efficiently in existing engines, boilers, and turbines

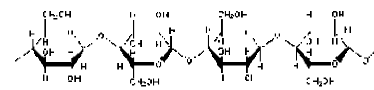
Biomass contains more oxygen and is structurally different from fuels.

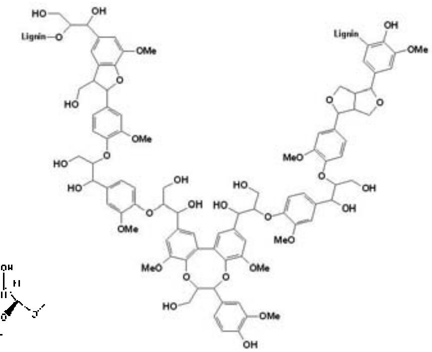


D-glucose



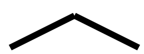


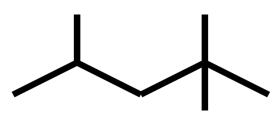




Carbohydrates **Fats** **Proteins** **Cellulose** **Lignin**

H_2 CH_4





Hydrogen

Natural Gas
Methane

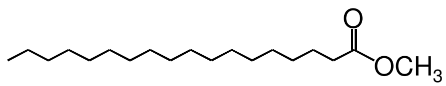
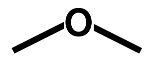
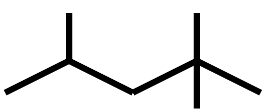
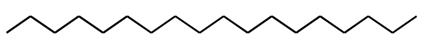
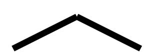
Propane
LPG / NGL
Autogas

Gasoline
Petrol
Naptha

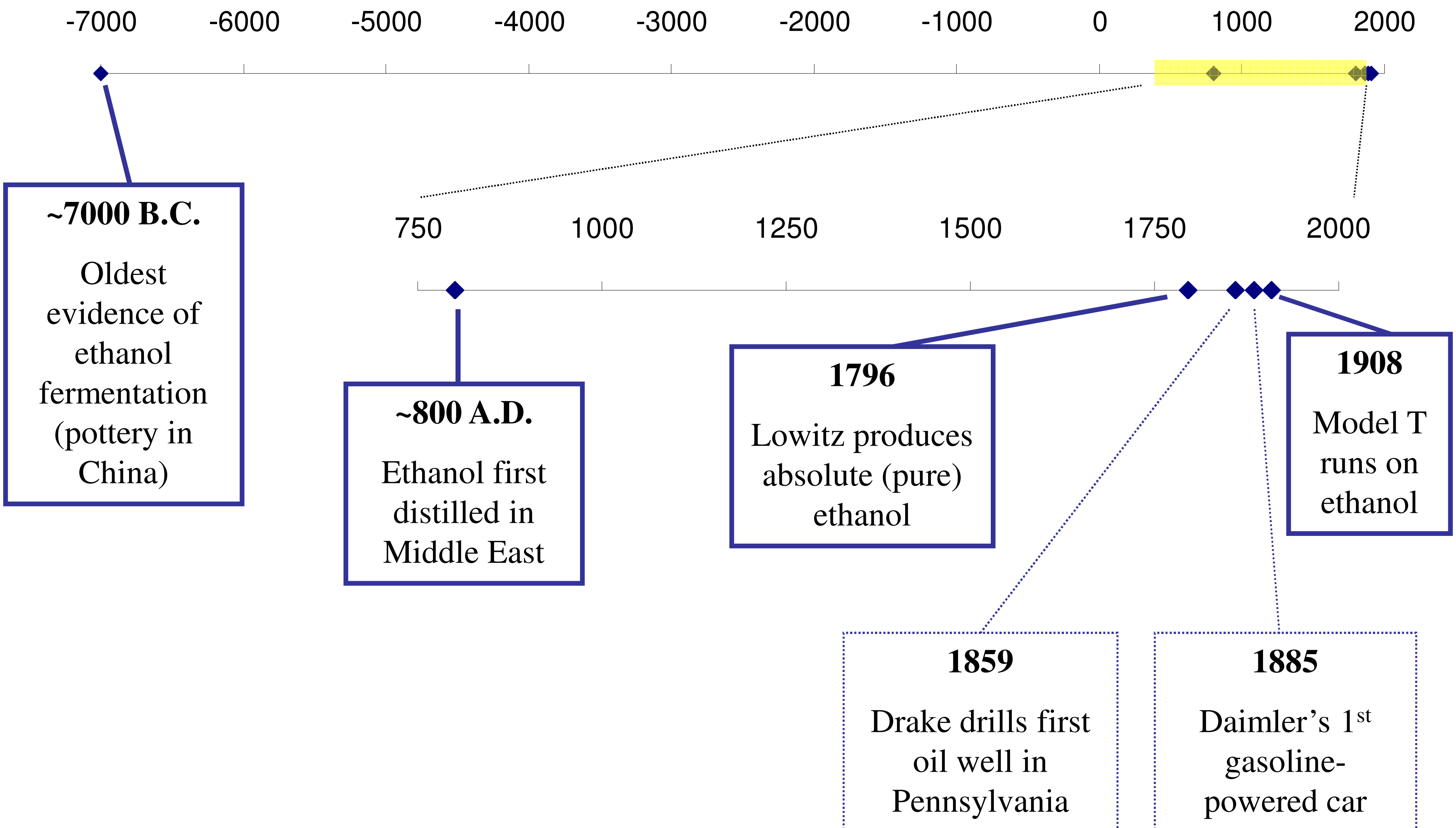
Diesel

Lignin image from wikimedia foundation, peptide image from http://www.steve.gb.com.

Most first-generation biofuels are imperfect fuel replacements.

Ethanol	Biodiesel	DME	"Synthetic" natural gas
			CH_4
26.9 MJ/kg	37.5 MJ/kg	28.9 MJ/kg	49.5 MJ/kg
Gasoline	**Diesel**	**Propane**	**Natural gas**
			CH_4
43.4 MJ/kg	42.8 MJ/kg	46.3 MJ/kg	49.5 MJ/kg

Ethanol: the original biofuel.



Ethanol is made by yeast when no oxygen is present.

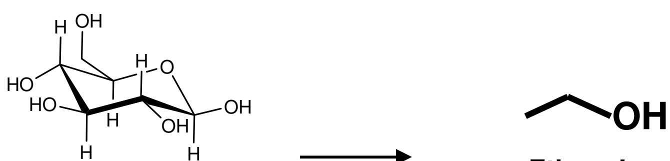
If oxygen is available, cells use it-

$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + (36\text{ or }38)\ ATP$$

Without oxygen, cells salvage a little energy with fermentation-

$$C_6H_{12}O_6 \rightarrow 2\ \boxed{C_2H_5OH} + 2\ CO_2 + 2\ ATP$$

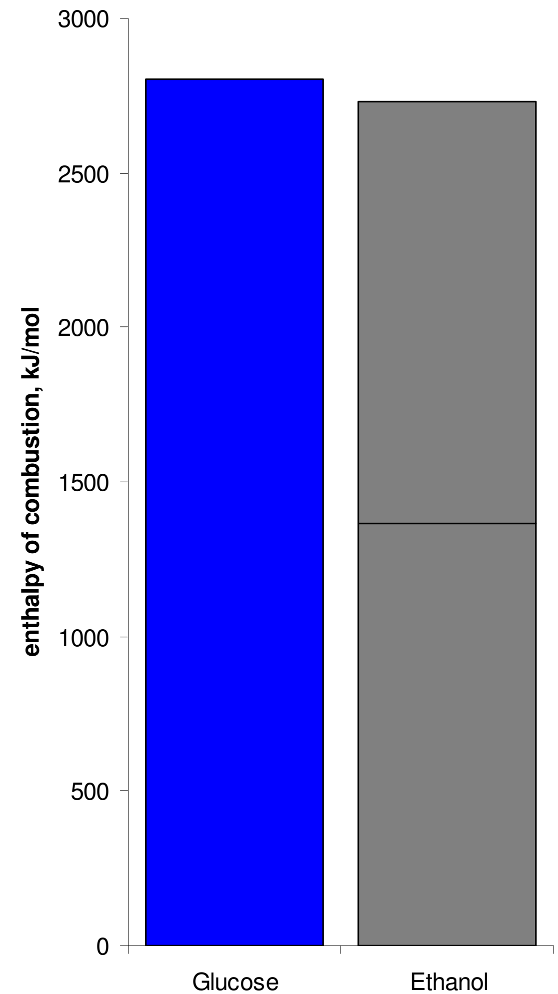
Fuel upgrading



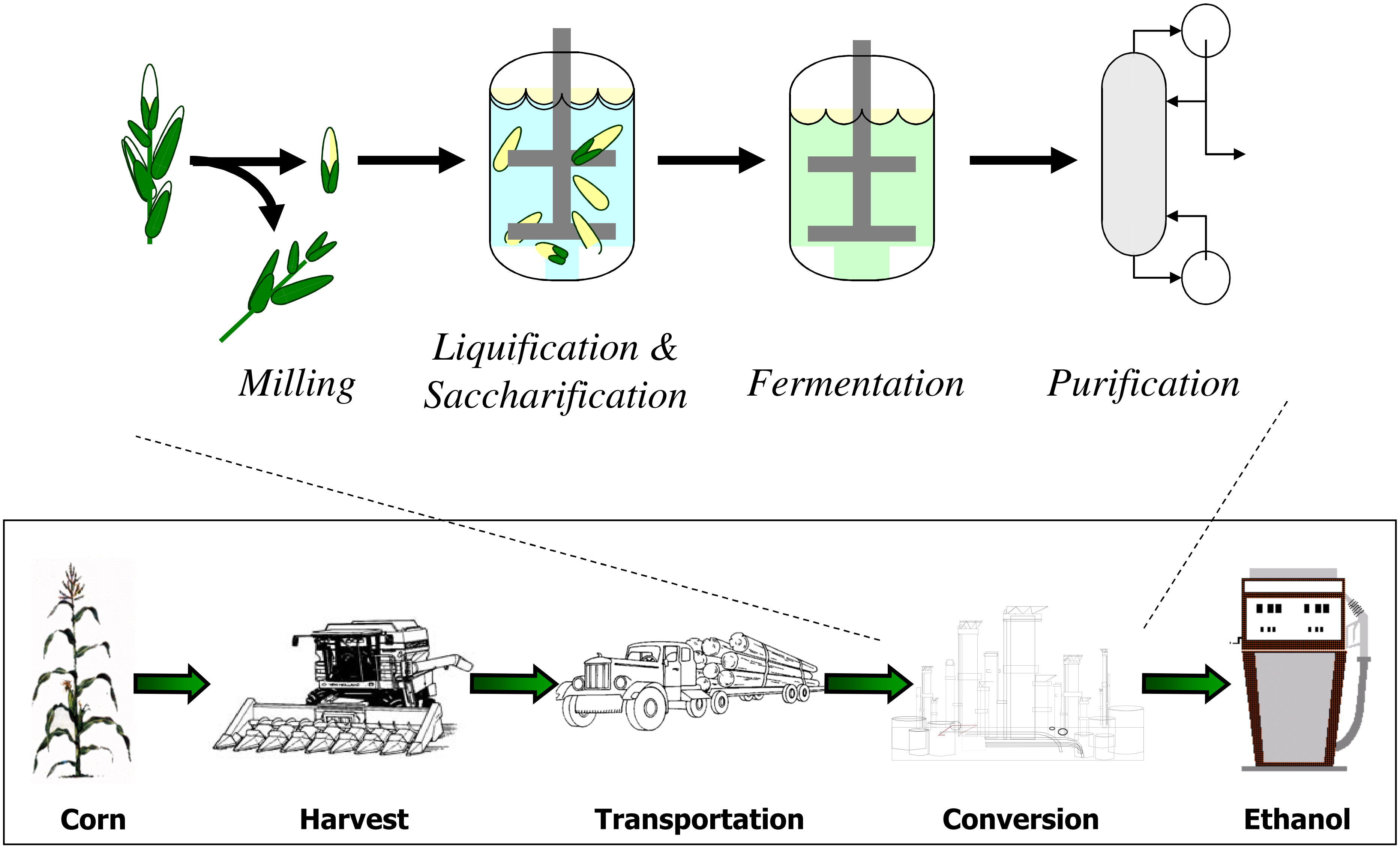
D-glucose → **Ethanol**

16 MJ/kg, solid

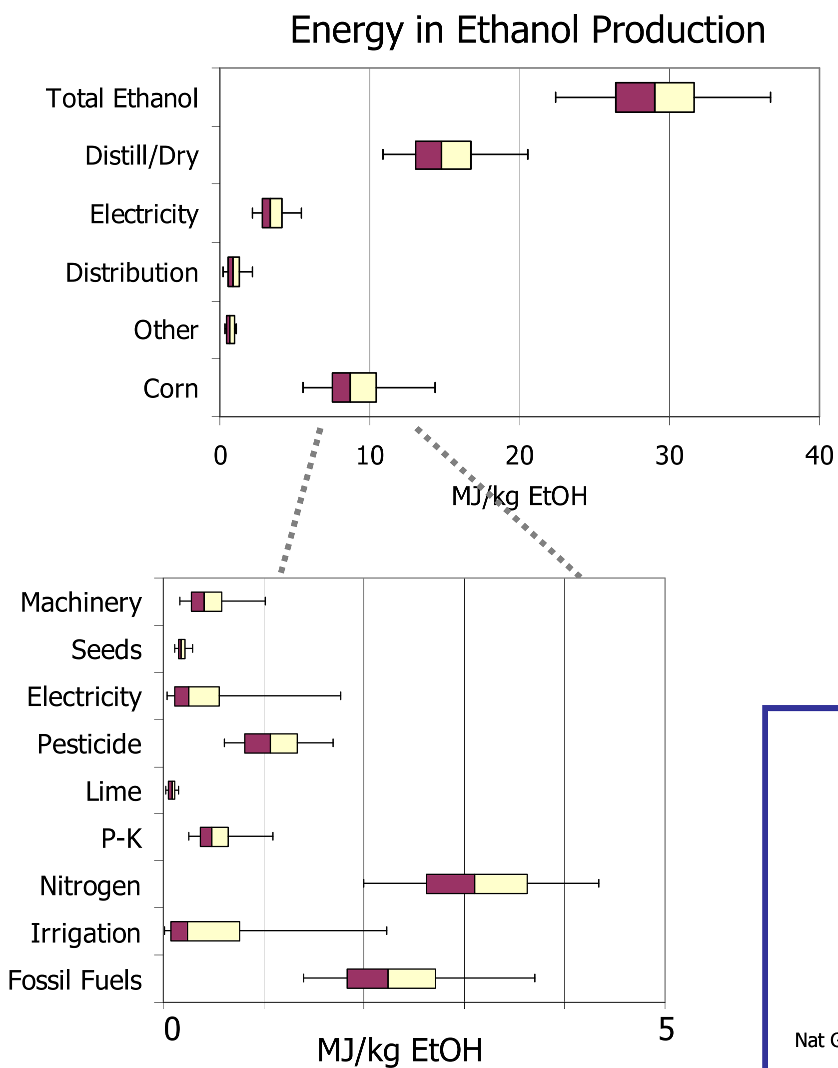
27 MJ/kg, liquid

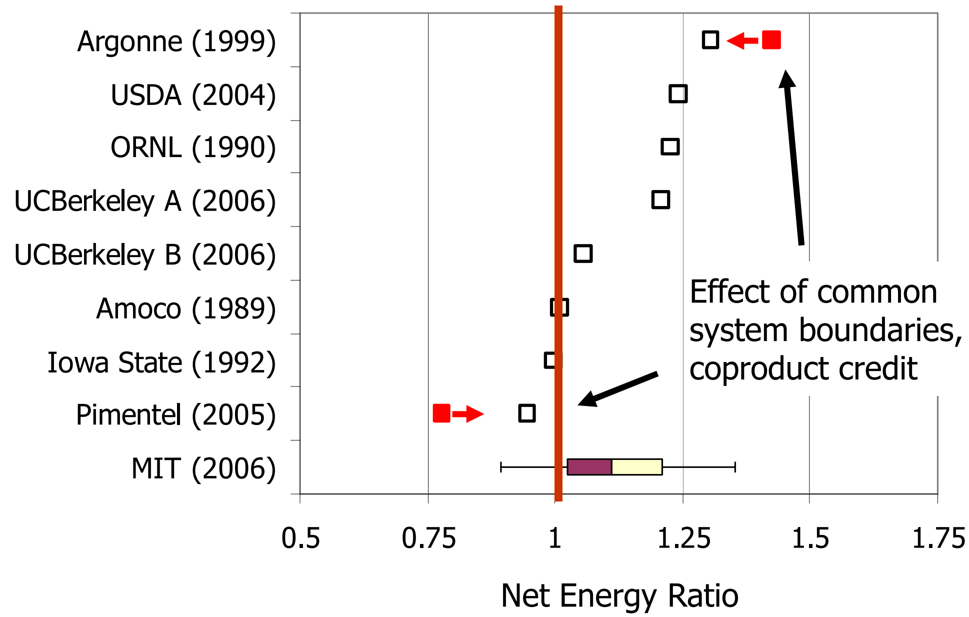


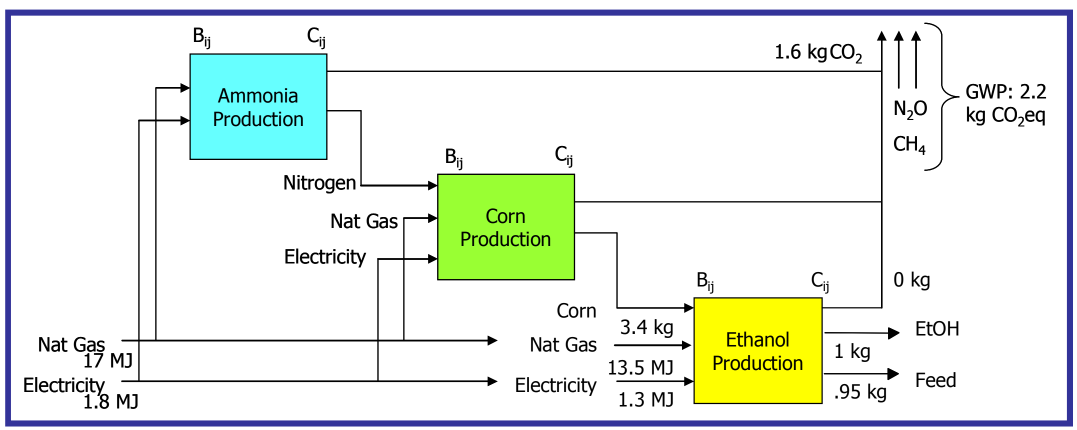
Ethanol processing is much more complex than fermentation.



Careful accounting must be made of the energy used to make ethanol.







A Berkeley Lifecycle Analysis found strong hope for ethanol made from lignocellulose.

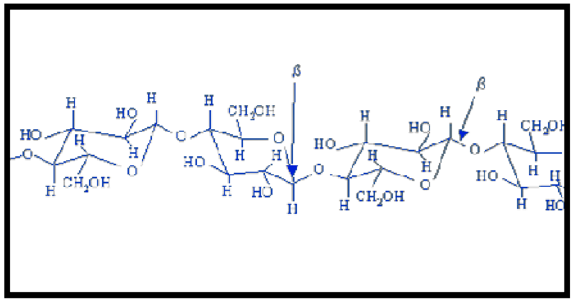
Image removed due to copyright restrictions. Please see Fig. 1 in Farrell, Alexander E., et al. "Ethanol Can Contribute to Energy and Environmental Goals." *Science* 311 (2006): 506-508.

Farrell *et al.* also consolidated corn-ethanol studies, but found cellulosic ethanol to be highly preferable on all counts.

Science 311(5760) 506-508 2006. doi: 10.1126/science.1121416

‘Lignocellulose’ is actually three distinct components.

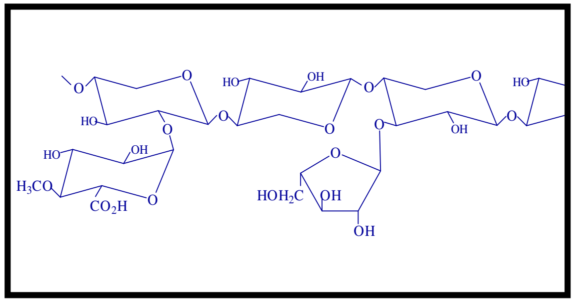
Cellulose



- Glucose units
  [fermentable]
- Structure:
  - β-(1-4)-glycosidic linkages
  - much hydrogen bonding
  - linear; crystalline

  [difficult to break down]
- ~17 MJ/kg

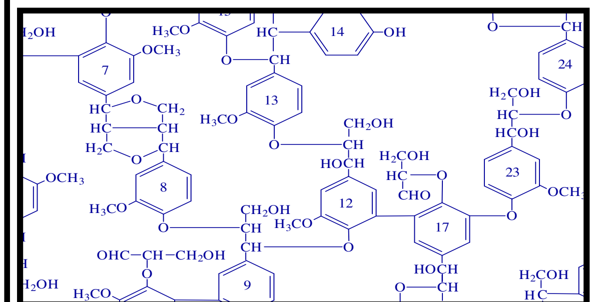
Hemicellulose



- Xylose, glucose, galactose, mannose, etc., units
  [not as easily fermentable]
- Structure:
  - branched; amorphous

  [easy to break down]
- ~17 MJ/kg

Lignin

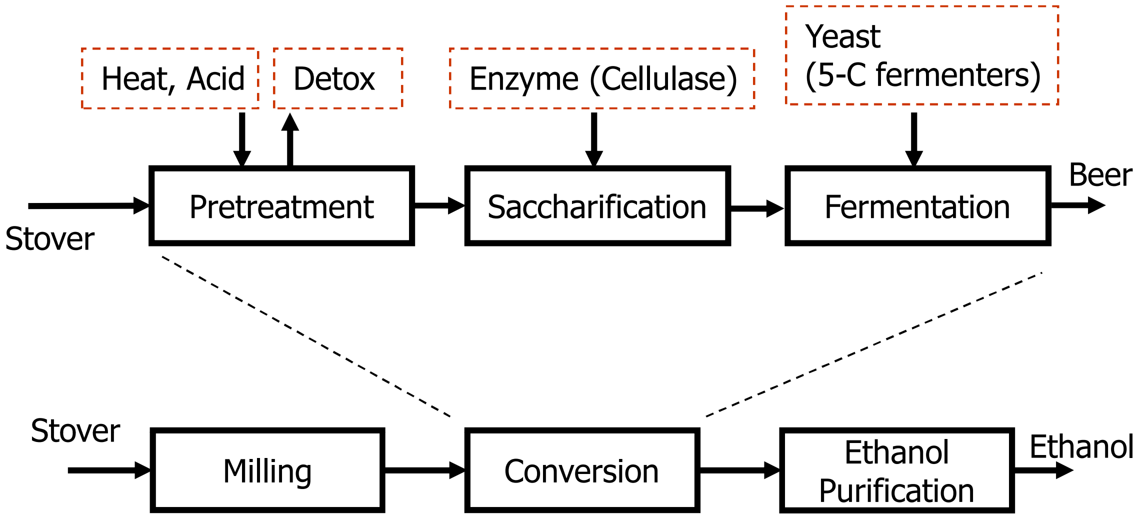


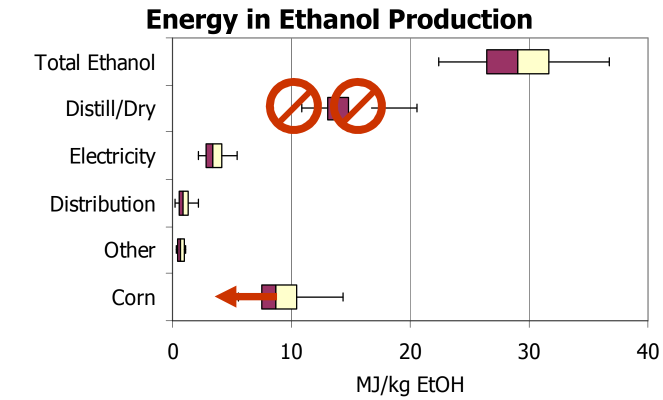
- Phenylpropane units
  [not fermentable]
- Structure:
  - highly polymerized
  - cement-like role in cells

  [difficult to break down]
- ~21 MJ/kg

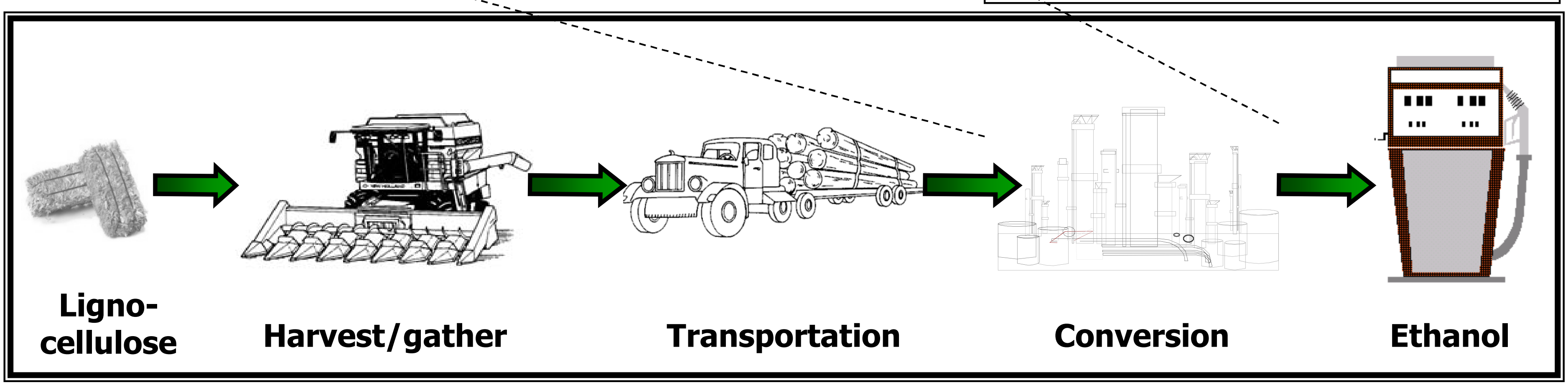
Cellulosic ethanol processing requires pretreatment and burns lignin.

(Fermentation route.)





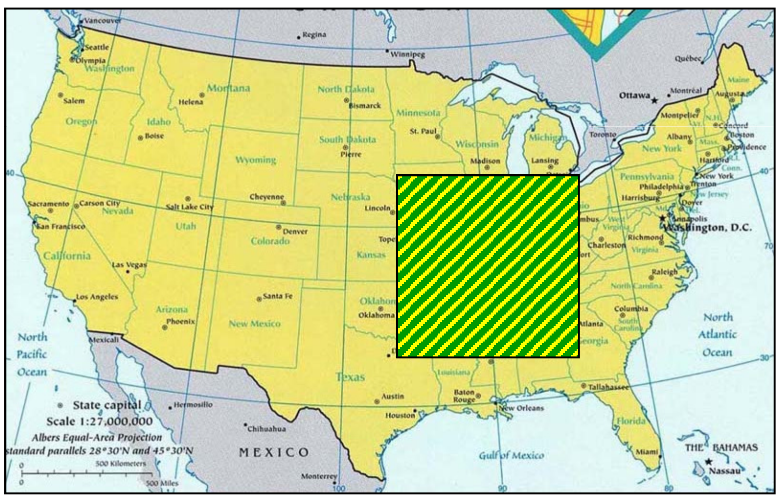
- No DDGS: no drying animal feed.
- Lignin has no value: burned to power distillation column.
- Lower ag inputs than corn production.



Corn ethanol limited by land requirements; cellulose more available than corn sugars

Corn ethanol

- To replace 1/3 transportation petroleum with corn ethanol: ~320 million acres corn
- Total ag land: ~450 million acres



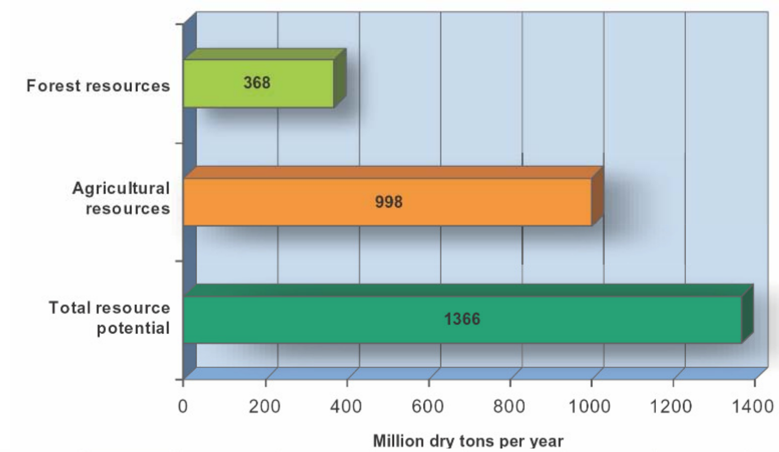
Map from CIA World Factbook.

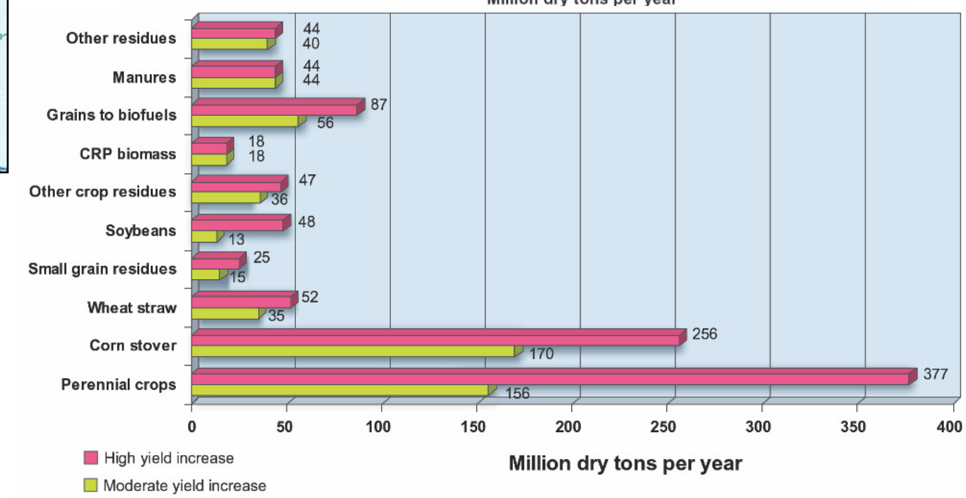
Assumptions:
2.8 gal EtOH/bu
140 bu/acre
1/3 of 5 x 10^9 bbl transport. petrol.

Billion-ton Study: DOE/GO-102995-2135 2005.

DOE/USDA Billion-ton study

- 1.4 billion (dry) tons can be sustainably harvested annually: energy content equal to ~1/3 of US petroleum consumption
- Residuals, forestry, energy crops: largely lignocellulosic

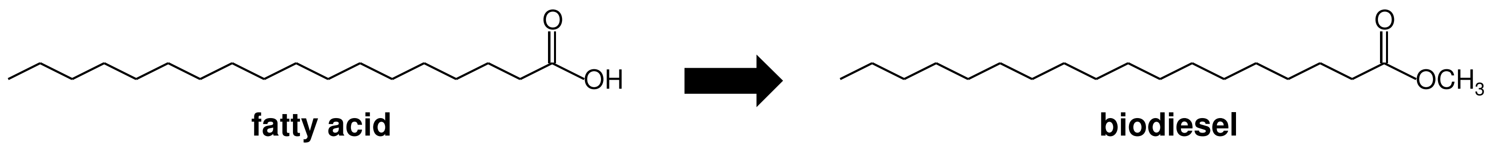




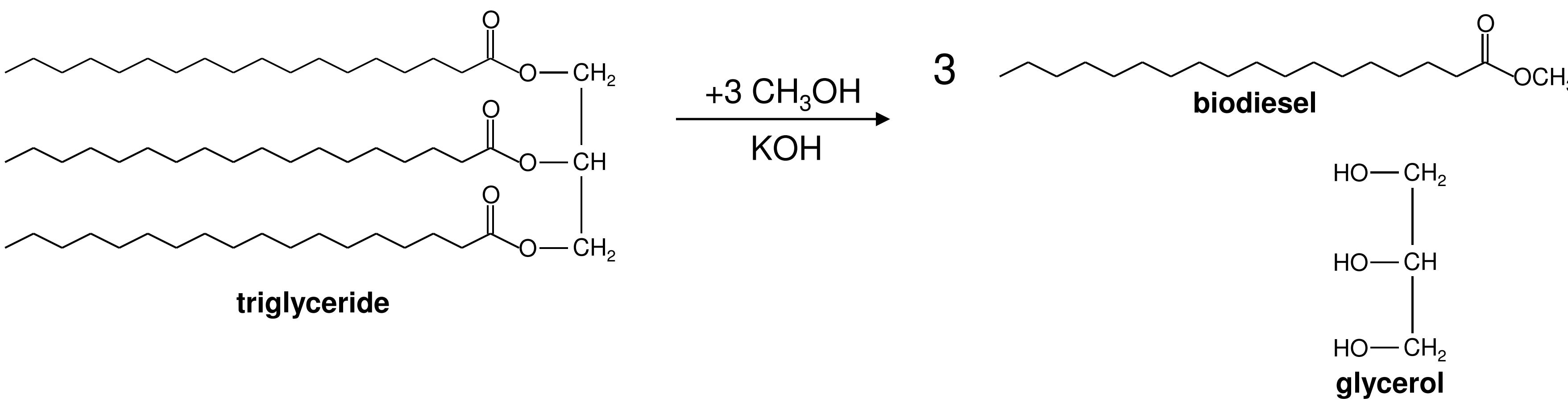
Images from Perlack, Robert D., et al. "Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply." April 2005. DOE/GO-102995-2135 / ORNL/TM-2005/66.

Biodiesel is a fatty acid converted to behave more like diesel.

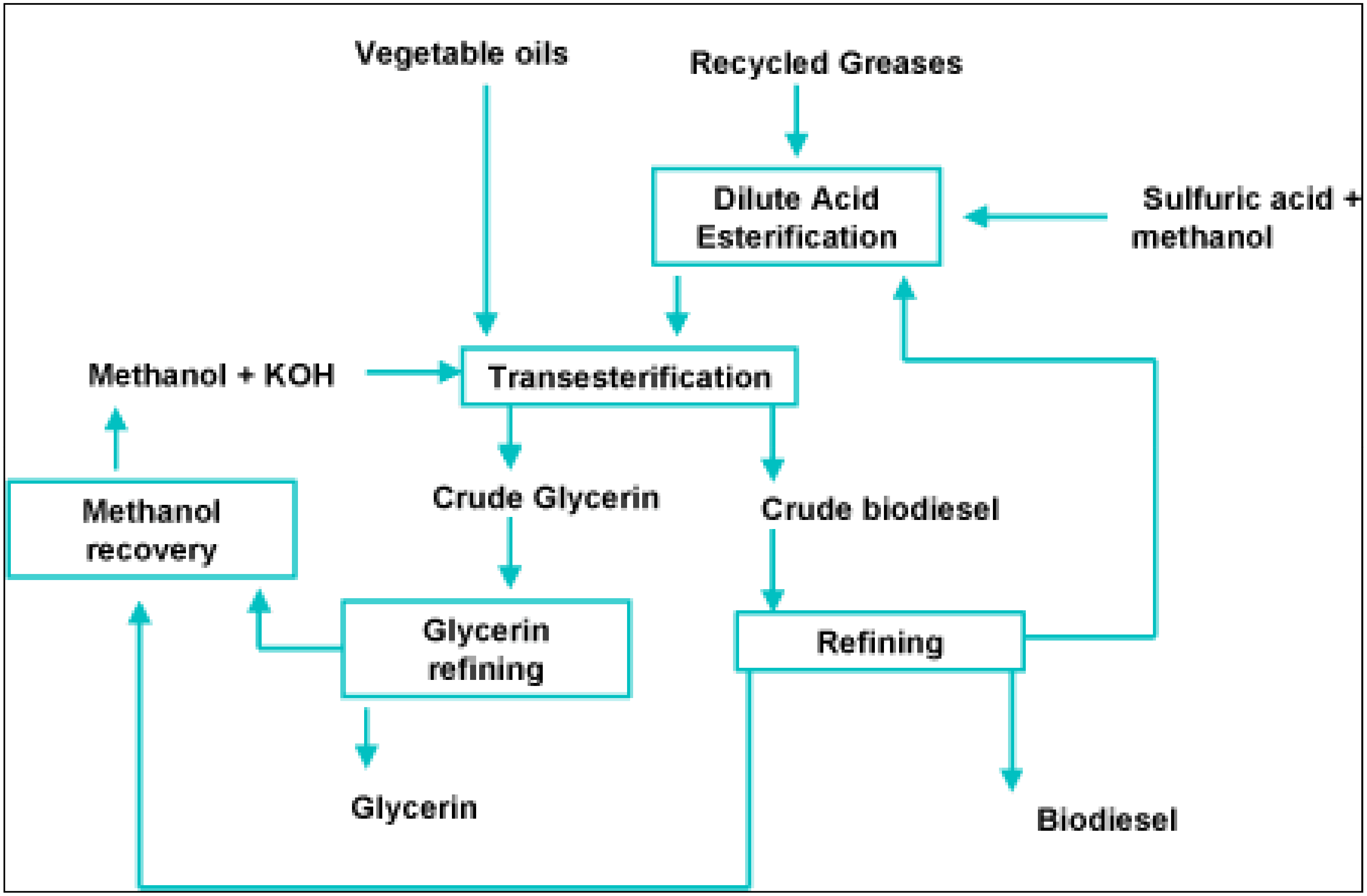
Goal:



Detailed:



Biodiesel processing is fairly mild.



PFD from DOE EERE.

Mild temperatures: 50-80℃
Atmospheric pressure

Biodiesel is a pretty good fuel. Where does it come from? Why don't we use more of it?

- Feedstock: oil crops, used cooking oil, etc.
- Problem is SCALE, use of farmland or rainforest:
  - Oil Palm: 600 gallons/acre/yr
    - Replacing Asian rainforest with oil palm plantations to meet EU biodiesel demand.
  - Rapeseed (Canola): 127 gallons/acre/yr
  - Soybeans: 48 gallons/acre/yr
    - If you sell it for $2/gallon, that is only $96/year for use of an acre of farm land.
- Future directions:
  - Bacteria, yeast can convert sugars to lipids: make biodiesel from cellulose?
  - Industry, airlines would like to take O out of biodiesel:

  Thermal decarboxylation; thermal hydrodeoxygenation

Bioenergy as Goal or Bioenergy as Byproduct

- Historically, biomass products (food, lumber) have been considered more valuable than biomass energy.
- Existing policies and practices focus on agriculture, lumber, land use, etc.; only waste or surplus biomass used as energy.
- Focus needs to shift for biomass to become important on global energy scale.
- Last year's food price shocks and food riots have raised awareness of the issues…

Most biomass conversion techniques are put in two main camps.

Biological

- Using microbes to convert biomass to fuels
- Pros
  - Can make chemicals with high specificity
  - Works well in aqueous media at reasonable temperatures and pressures
- Cons
  - Requires specific chemical inputs (sugar)
  - Low throughput
- Examples:
  - Ethanol, CH_4, butanol

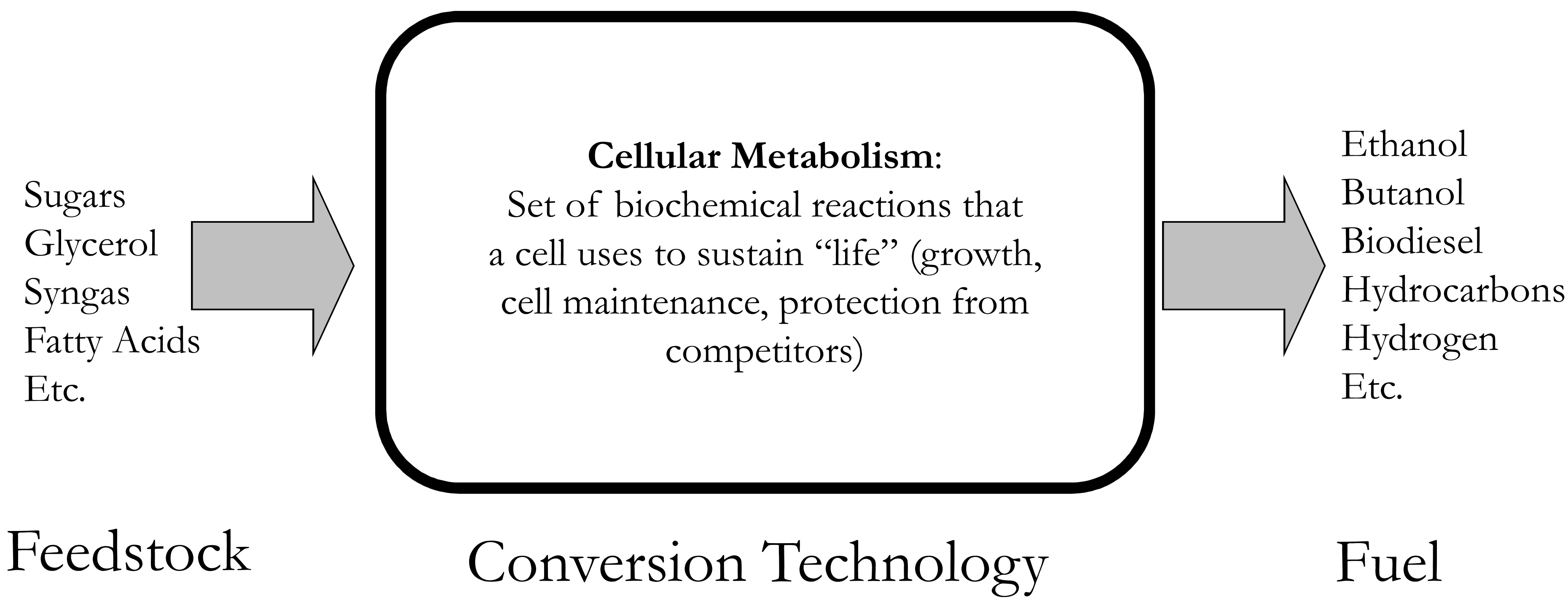
Thermochemical

- Using traditional chemical processing methods
- Pros
  - Often doesn't require chemical specificity of feedstocks
  - Higher throughput
- Cons
  - Extreme T, P may be needed
  - Subject to catalyst fouling, inorganic precipitation
- Examples
  - Biodiesel, syngas, CH_4, H_2, diesel, gasoline

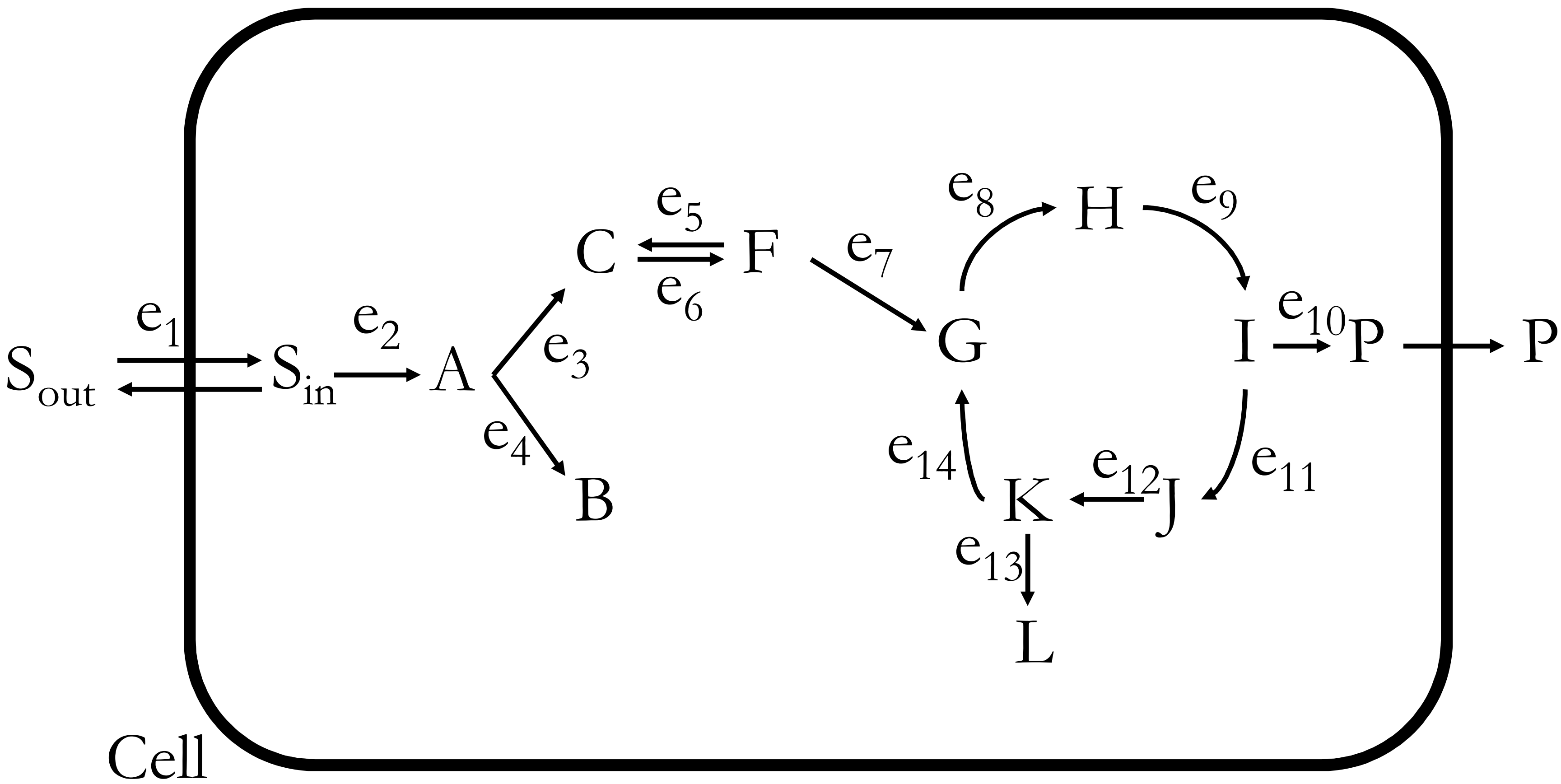
Advanced fermentation techniques may produce better fuels from cheaper feedstocks.

- Better fuels
  - butanol, propanol, etc.
  - high lipids
  - hydrocarbon excretion
- Better feedstock utilization
  - Cheaper enzymes
  - Lynd's single-pot technique
  - Syngas: H_2, CO

Biomass to Biofuels using Microorganisms



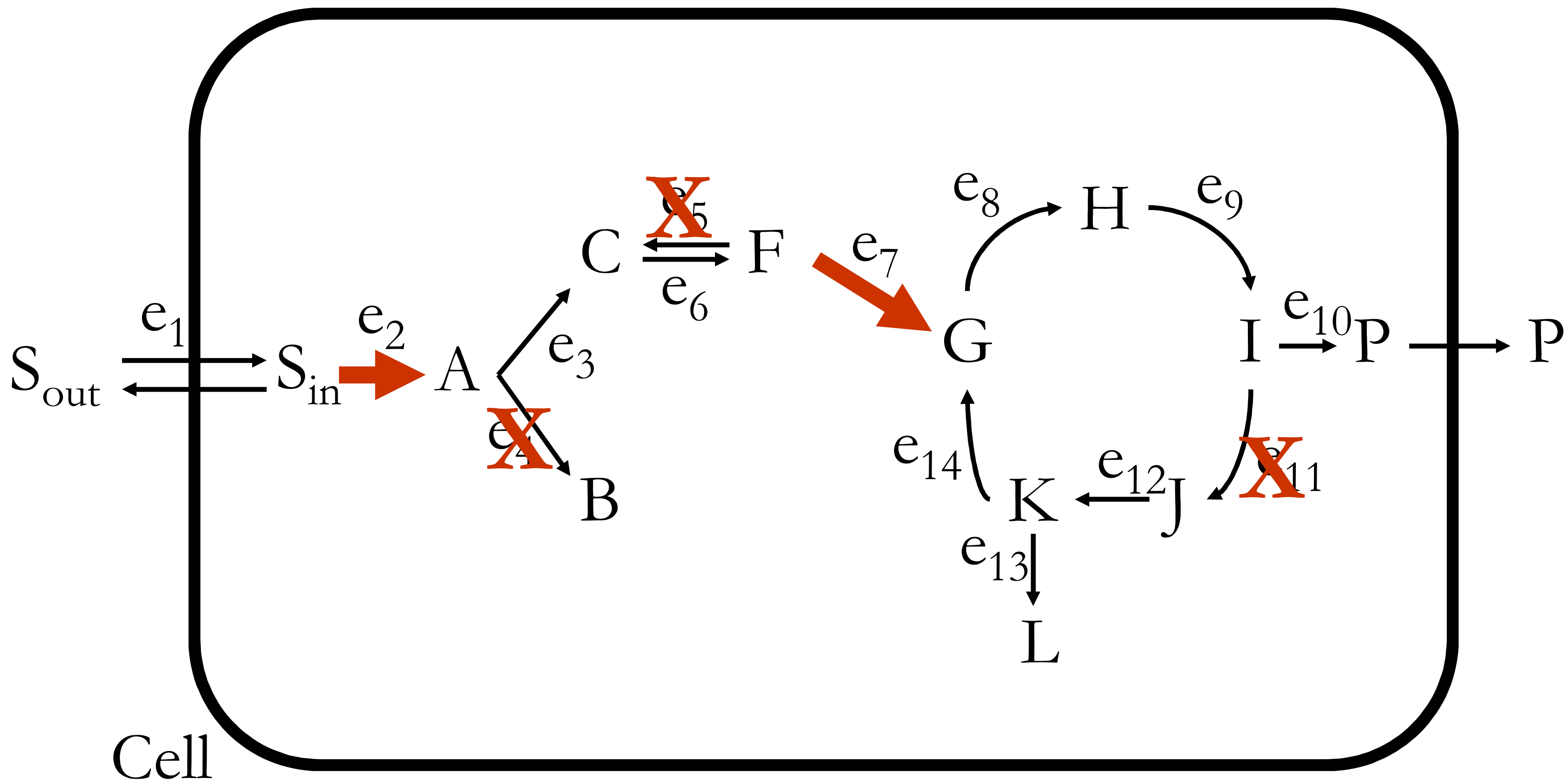
What is Metabolic Engineering?



e_i = Enzyme i

Slide courtesy of Daniel Klein-Marcushamer.

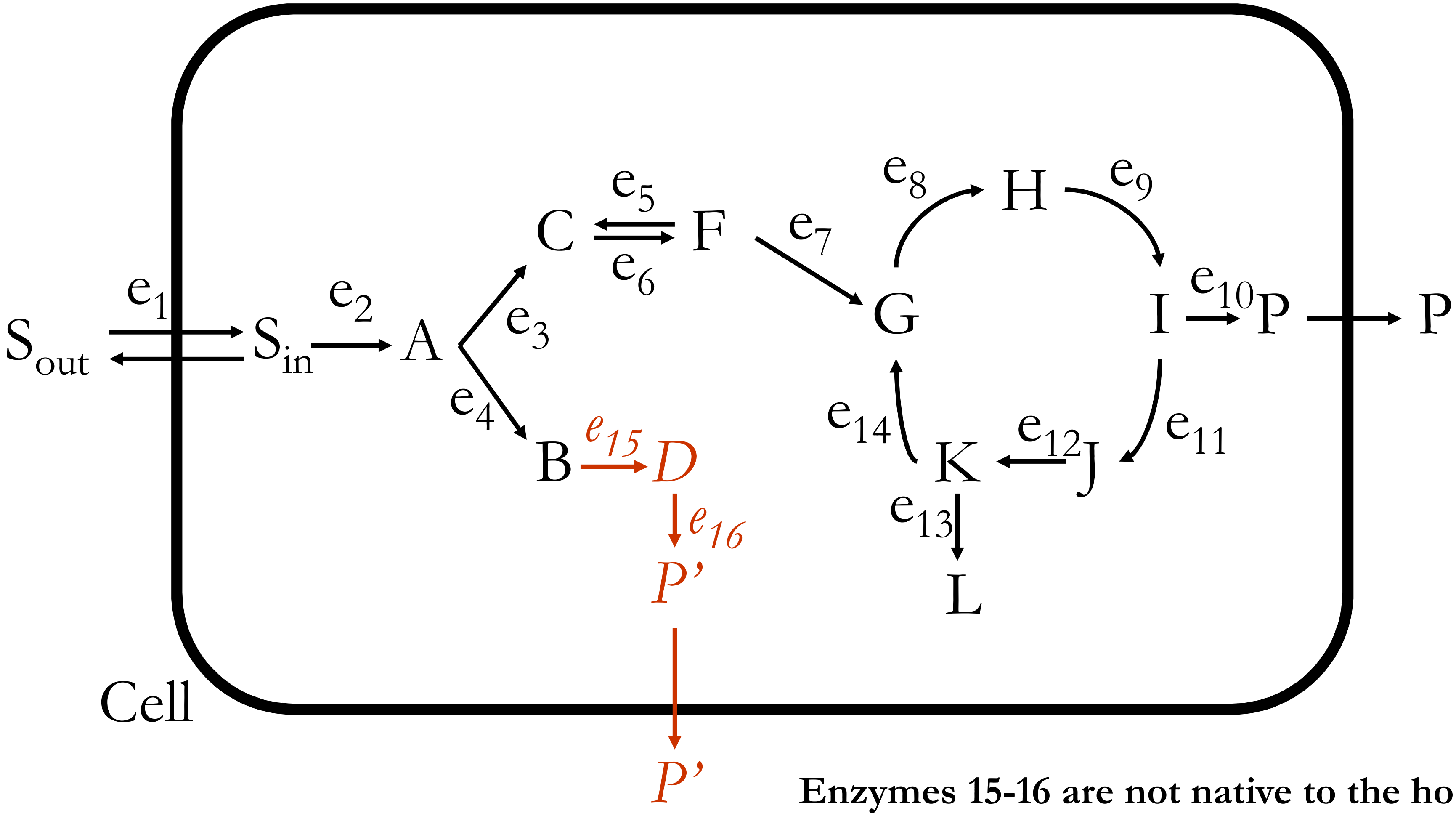
What is Metabolic Engineering?: Gene overexpression and deletion



e_i = Enzyme *i*

Slide courtesy of Daniel Klein-Marcushamer.

What is Metabolic Engineering?: Introduction of heterologous genes



Enzymes 15-16 are not native to the host

Slide courtesy of Daniel Klein-Marcushamer.

Xylose-fermenting *Saccharomyces cerevisiae*

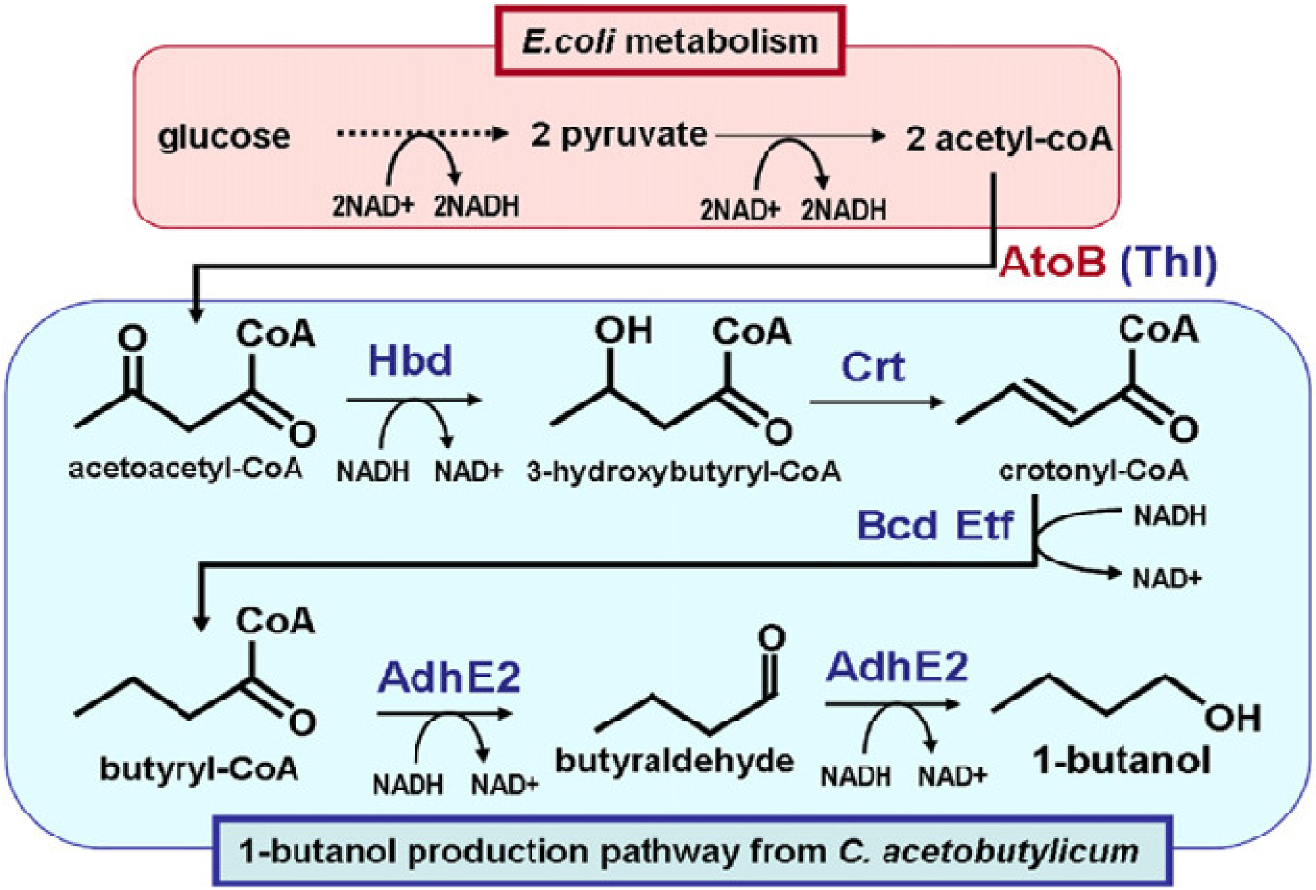
Slide courtesy of Daniel Klein-Marcushamer.

Glycerol-fermenting *Escherichia coli*

Image removed due to copyright restrictions.
Please see Fig. 1 in Murarka, Abhishek, et al. "Fementative Utilization of Glycerol by Escherichia coli and Its Implications for the Production of Fuels and Chemicals." *Applied and Environmental Microbiology* 74 (February 2008): 1124-1135.

Slide courtesy of Daniel Klein-Marcushamer.

Butanol-producing *Escherichia coli*



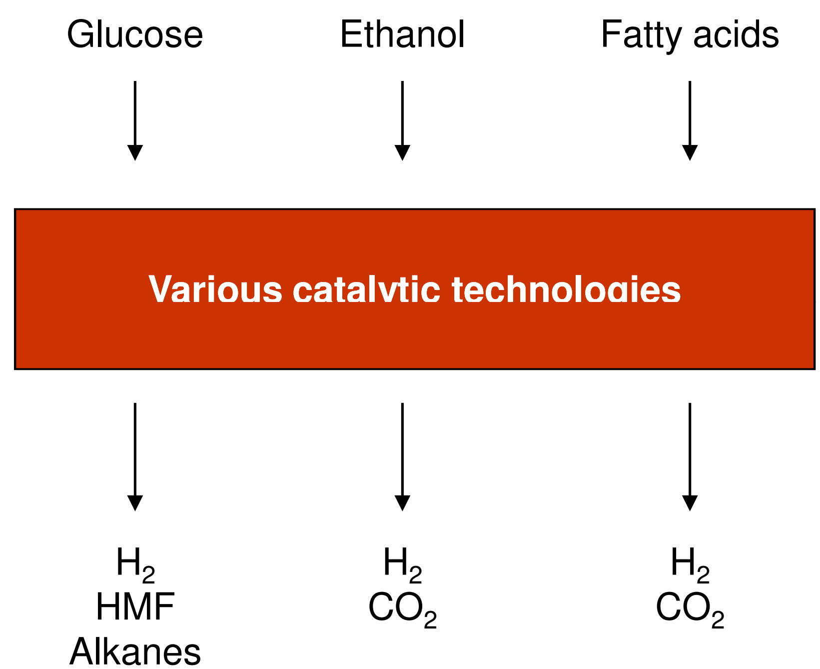
Source: *Metab. Eng.* 2008. doi:10.1016/j.ymben.2007.08.003

Slide courtesy of Daniel Klein-Marcushamer.

Chemical conversion of biomass.

- Specific catalysts developed to convert biomass to hydrogen, ethanol, alkanes

- Early stage technology
  - Many catalysts subject to fouling with whole biomass streams
  - Usually combine catalysis with pyrolysis or pre-treatment/separation.



Examples: Dumesic (Wisconsin), Schmidt (Minn.), Huber (U.Mass.), Brown (Ames), Roman (MIT)

Pyrolysis oils are crude condensation products of 'cooked' biomass.

- Pyrolysis: decomposition or transformation of a compound caused by heat (AHD)
- Rapid heating of biomass in the absence of oxygen
- Various complex oils and organics formed: needs further refining
- Options for oils produced:
  - Combustion in stationary generators
  - Upgrading (hydrodeoxygenation)
  - Gasification (concentration method)

Fast Pyrolysis

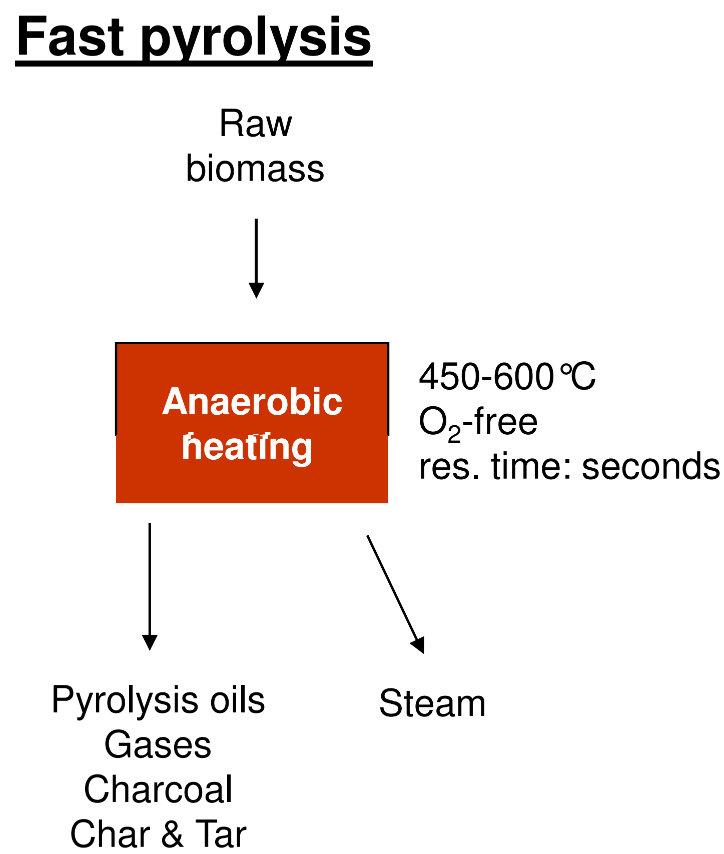
- Short residence times (seconds)
- Atmospheric pressure
- Harder to refine oil
- Energetic losses to evaporation

Hydrothermal Liquefaction

- High-pressure (>40 atm)
- Longer residence times (minutes)
- Higher efficiency possible
- Easier to refine oil

Fast pyrolysis makes bio-oils at atmospheric pressure in a few seconds.

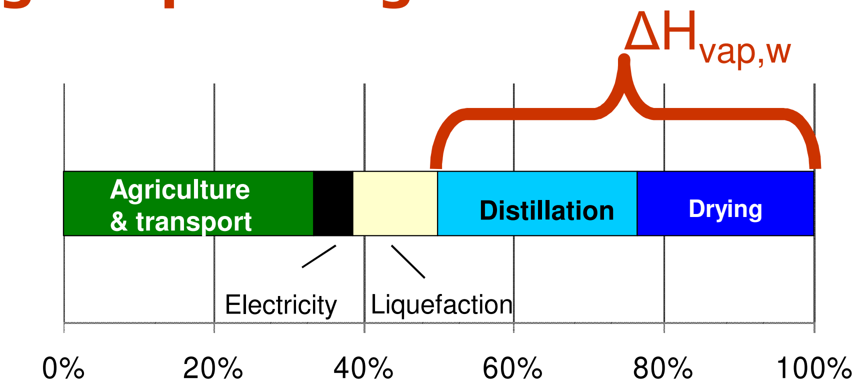
- Often uses fluidized beds of sand or catalyst as heat transfer medium.
- Produces oil (containing up to 15-20% moisture), char, and gases.
- Feedstocks need to be pre-dryed to around 10% moisture



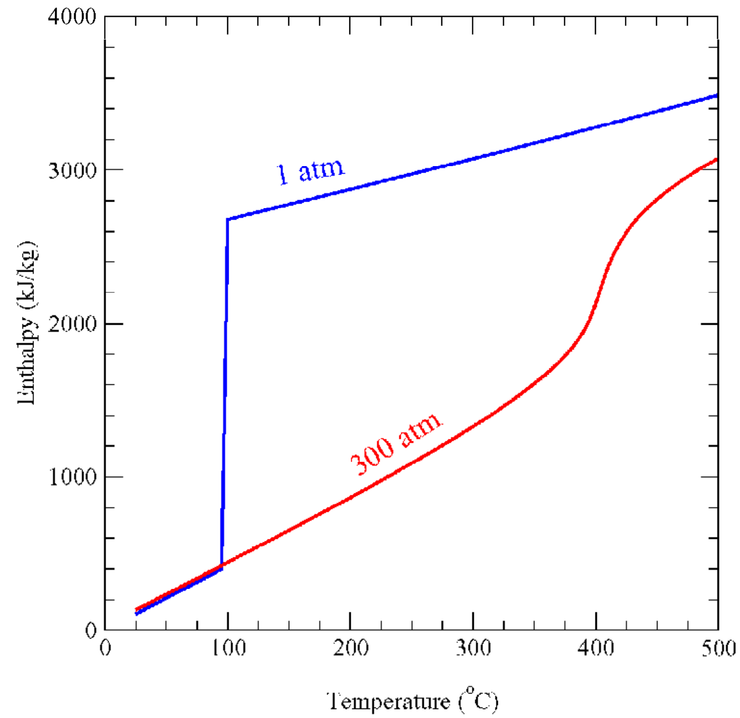
Another approach: Hydrothermal technologies can have higher efficiencies by avoiding evaporating water.

- Most energy inefficiencies in biofuels production result from water evaporation
  - Ethanol: distillation, drying
  - Gasification: pre-drying

- Heating under intense pressure avoids phase change; makes heat recoverable.
  - Produce water *in*soluble fuels for easy separation.

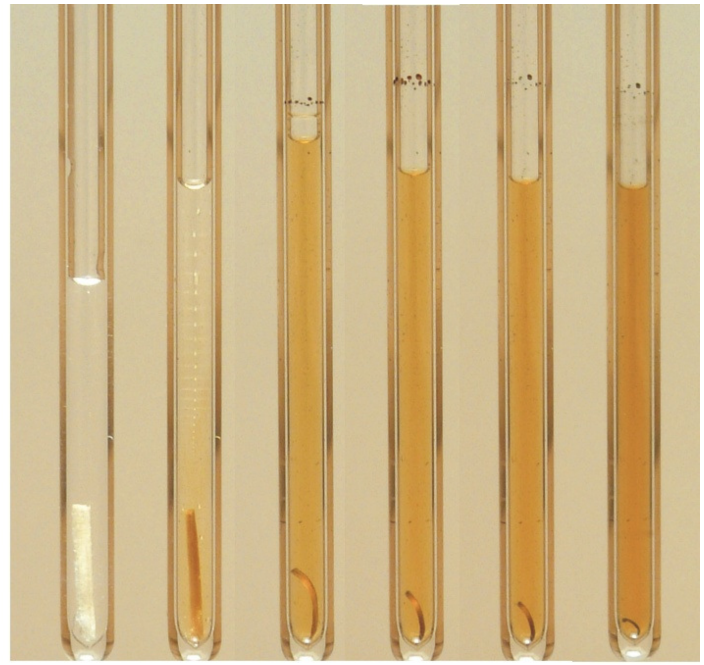


Energy inputs in corn-grain ethanol production



Hydrothermal liquefaction involves heating under pressure in the water phase.

- Example process: HTU (hydrothermal upgrading)
  - Dutch collaboration including Shell
- “Biocrude” formation – raw material for further conventional refining
  - Diesel & kerosene
- Process conditions: ~330℃, ~100 bar
- Demonstration on onion peels
  - (high lignocellulosic, high sulfur)



Time, min 0 1 2 3 4 5

Wood conversion to “biocrude” at 340℃.

Courtesy of Dragan Knezevic, Sascha Kersten, and Wim van Swaaij. Used with permission.

Image source: Naber & Goudriaan, ACS Meeting, Fuel Chem Division, 31 Aug 2005.

Comparison of fast pyrolysis and hydrothermal liquefaction oils.

Source: Peterson *et al.* Energy Env Sci 1(1): 32 2008.

Hydrodeoxygenation (HDO) removes oxygen, using techniques from refining.

- 'Bio-crudes' typically more viscous and higher in oxygen than conventional petroleum
- Hydrogen is used to break up and remove oxygen from the biomolecules
- Adapted from other techniques in refining:
  - hydrodesulfurization (HDS)
  - hydrodenitrogenation (HDN)
  - hydrocracking (HCK)

Oxygen can be removed as water.

$$C_6H_9O_4 + 2.5\ H_2 \rightarrow C_6H_{12} + 2\ H_2O$$

	HDO of biocrude	**HDS, HDN, HCK or petroleum**
Equipment, plant	(same)	(same)
Pressures	3-10 MPa	3-10MPa
Catalysts	Co, Ni, Mo (sulfided)	Co, Ni, Mo (sulfided)
Size	10,000 tonnes/a	5,000 – 1,000,000 tonnes/a
H_2 consumption	340-730 Nm^3/tonne	200-800 Nm^3/tonne

Energ Fuel 21:1792, 2007. *Appl Cat A* 199:147 (2000). *Cat Today* 29:297 (1996).

Hydrodeoxygenation (HDO) may also drastically increase yields.

- "Hydrogen-enriched" biofuel
- Dietenberger & Anderson propose expanding biomass resource by coupling to renewable H_2 source.
- May vastly increase the amount of recoverable resource (venting H_2O instead of CO_2)
- Additionally, can couple with waste heat from H_2 source.

Oxygen can be removed as water.

$$C_6H_9O_4 + 2.5\ H_2 \rightarrow C_6H_{12} + 2\ H_2O$$

Image removed due to copyright restrictions. Please see Fig. 5 in Dietenberger, Mark A., and Mark Anderson. "Vision of the U.S. Biofuel Future: A Case for Hydrogen-Enriched Biomass Gasification." *Industrial and Engineering Chemistry Research* 46 (December 19, 2007): 8863-8874.

IECR 46(26) 8863 2007.

Thermochemical diesel techniques may overcome disadvantages of biodiesel.

Various techniques can recover lipids for use as fuels without the limitations of biodiesel:

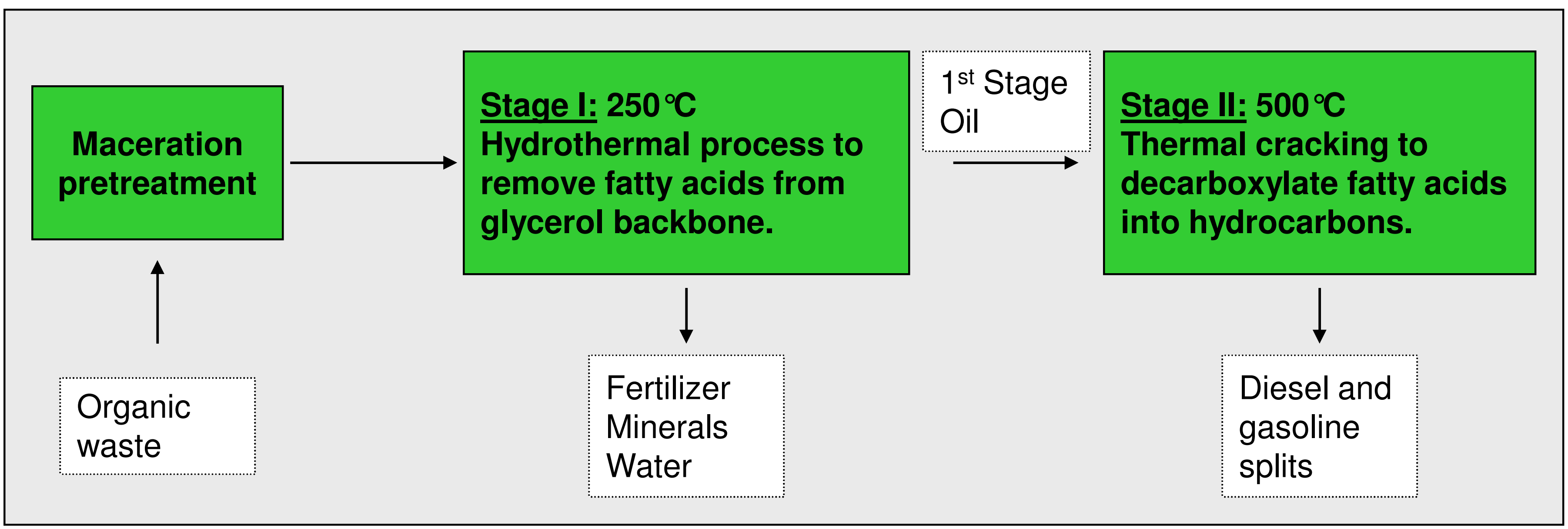
1. CWT hydrothermal liquefaction process.

2. Hydrodeoxygenated diesel process.

3. Supercritical methanol/ethanol biodiesel.

Changing World Technologies converted lipid-rich turkey offal into diesel plus fertilizers and carbon… …before they went bankrupt in 2009

Photos of poultry remnants and petroleum end products removed due to copyright restrictions.

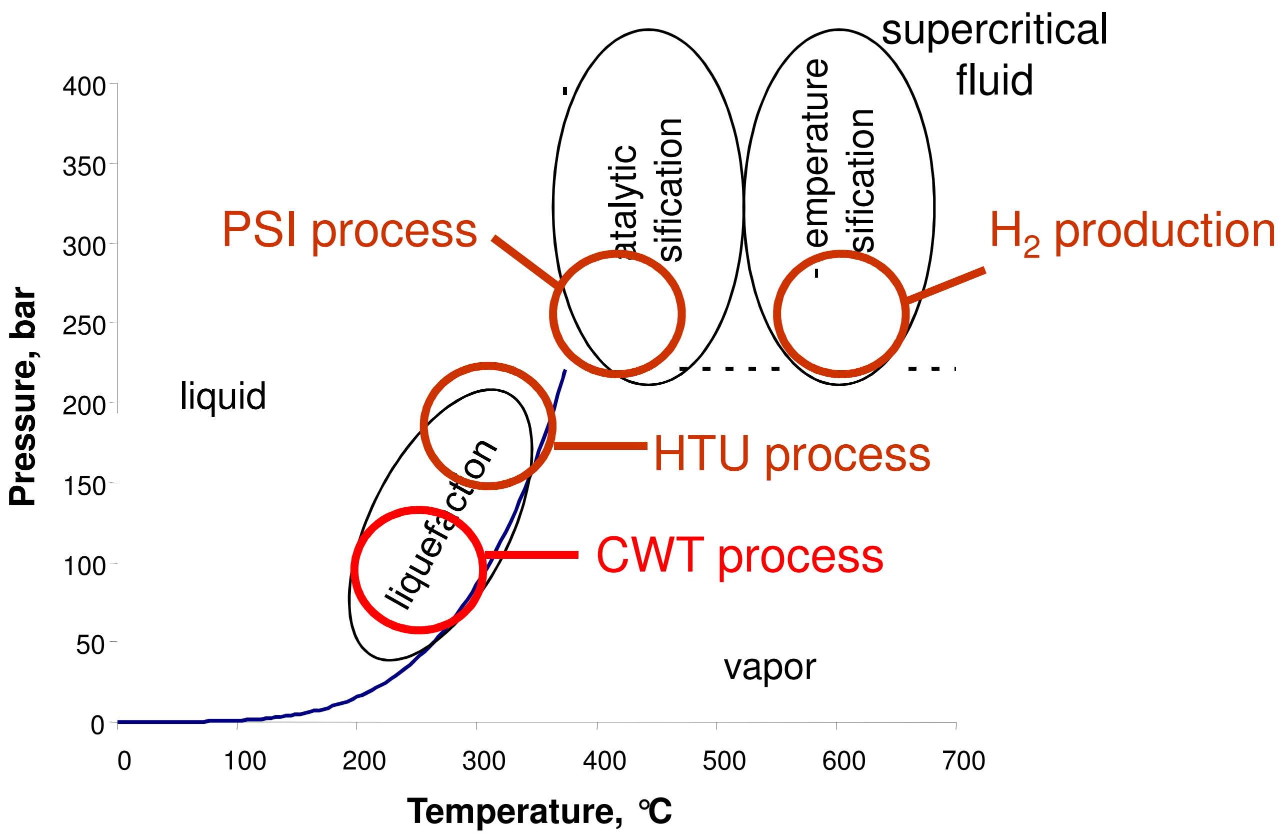


Courtesy of Changing World Technologies. Used with permission.

Conventional refinery techniques can be used to make 'green' diesel.

Neste Oil and UOP use refinery techniques:
- catalytic saturation
- hydrodeoxygenation
- decarboxylation
- hydroisomerization

Hydrothermal technologies can be used to gasify directly.



Hydrothermal gasification can produce methane in a single step from a range of biomass.

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Please see, for example, "Scientific Challenges Towards an Efficient Hydrothermal Biomass Gasification Process," "Fuels From Biomass: Use of Neutron Radiography to Improve the Design of a Salt Separator in Supercritical-Water Biomass Gasification," and other research findings from Prof. Frédéric Vogel's Catalytic Process Engineering Group, Paul Scherrer Institute.

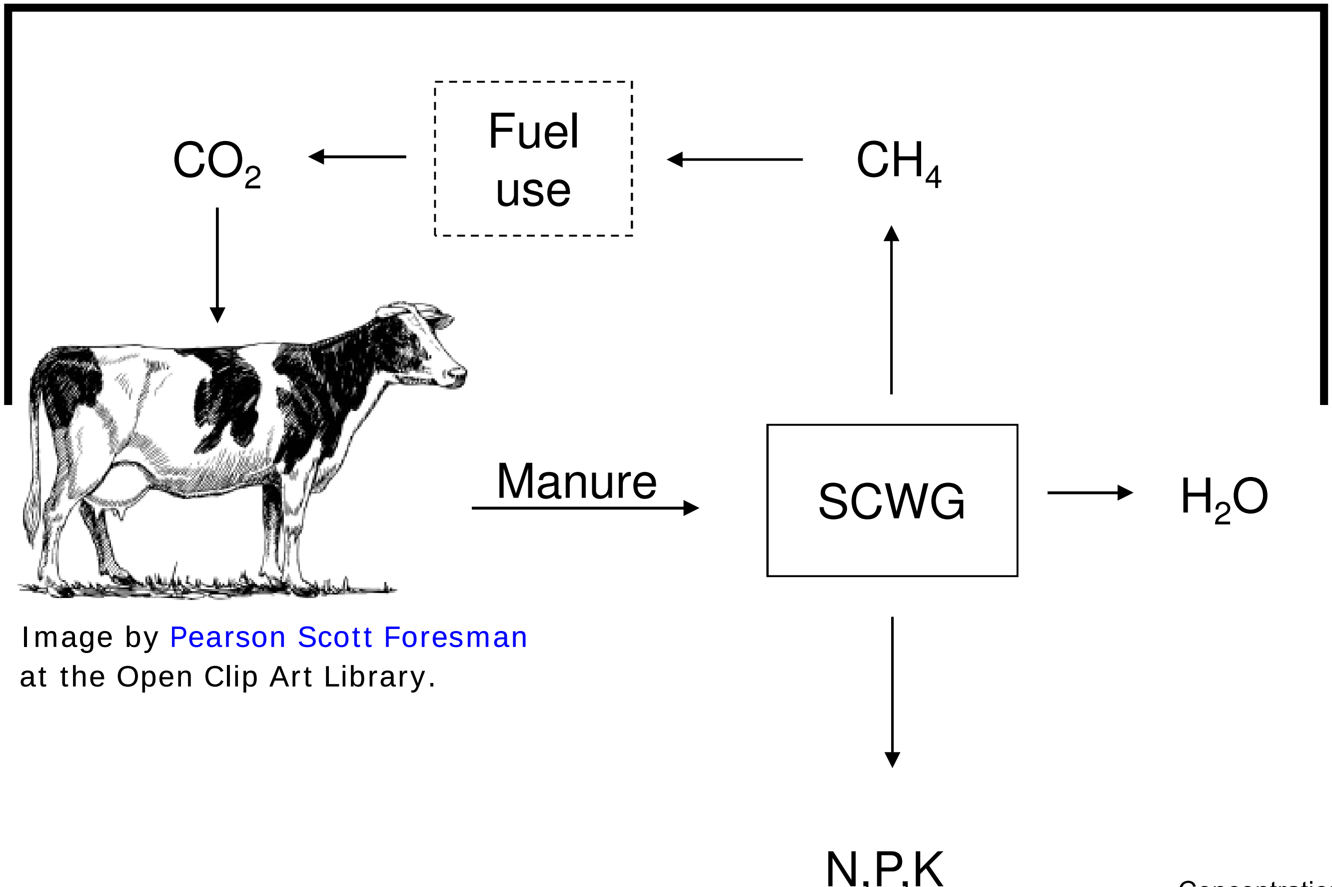
Supercritical gasification provides single-step methanation, which reduces heat requirements.

Catalyst lifetime and salts have hindered supercritical water gasification to methane.

- Elliott (PNNL) found early deactiviation of catalyst while running with DDG&S
- Primarily sulfates:
  - SEM w/ energy-dispersive x-ray
  - XPS

Elliott et al. *Ind. Eng. Chem. Res.* 43(9) 1999-2004 (2001).

Integrated biofuels & fertilizer vision



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Ionic constituents of Swiss swine manure solids as measured with ion chromatography after soxhlet extraxction

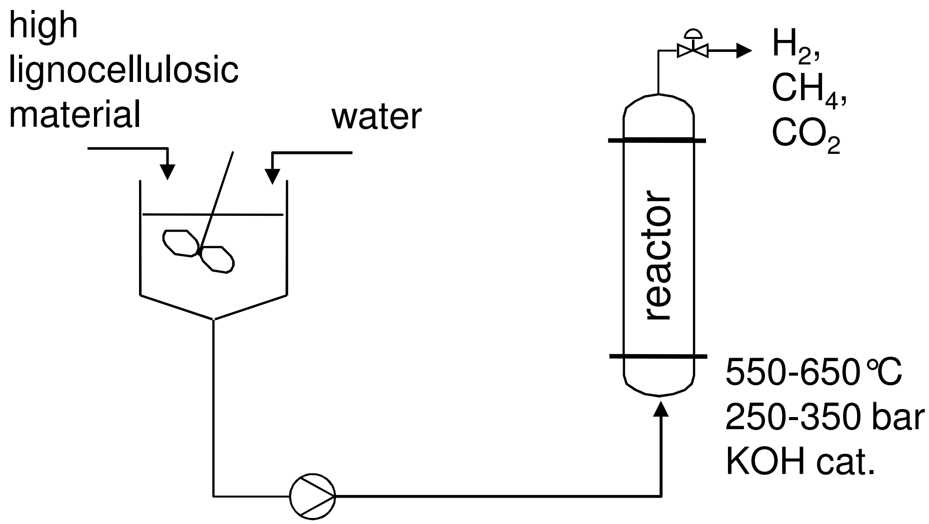
Cation	mg/kg
NH_4^+	47,000
K^+	9,100
Na^+	6,700
Mg^{2+}	3,800
Ca^{2+}	2,700

Anion	mg/kg
PO_4^{3-}	67,000
NO_3^-	21,000
SO_4^{2-}	11,000
Cl^-	5500
$S_2O_3^{2-}$	1600
$(COO)_2^{2-}$	1200
F^-	38
$C_2H_5COO^-$	30
CH_3COO^-	ND

Concentrations are given in mg/kg on a dry basis. ND: not detected.

Hydrogen can be made from biomass via supercritical water gasification at higher temperatures.

- H_2-rich gas produced
- 600℃, 300 bar, alkaline catalyst
- Lab-scale tests in Germany and China
  - Feeds such as sawdust, wheat straw, peanut shells, …



See Peterson *et al.* Energy Env Sci 1(1): 32 2008 for more details on all hydrothermal processing.

Biofuel conversions: some take-away points.

1. Don't invent new fuels, find ways to make existing fuels from biomass. If you want to make a new fuel, need to demonstrate it has big performance advantages over existing fuels.

2. Chemically, the goal is oxygen removal.

3. For efficiency, the most important thing you can do is handle water intelligently. Biosynthesis of water-insoluble fuels greatly reduces separation costs.

4. There exists enough waste biomass to supply about 25% of the demand for liquid fuels. However, it is widely distributed over the globe. Big unresolved questions about economics, land use, policy, as well as which conversion technologies are best.