Lecture # 24

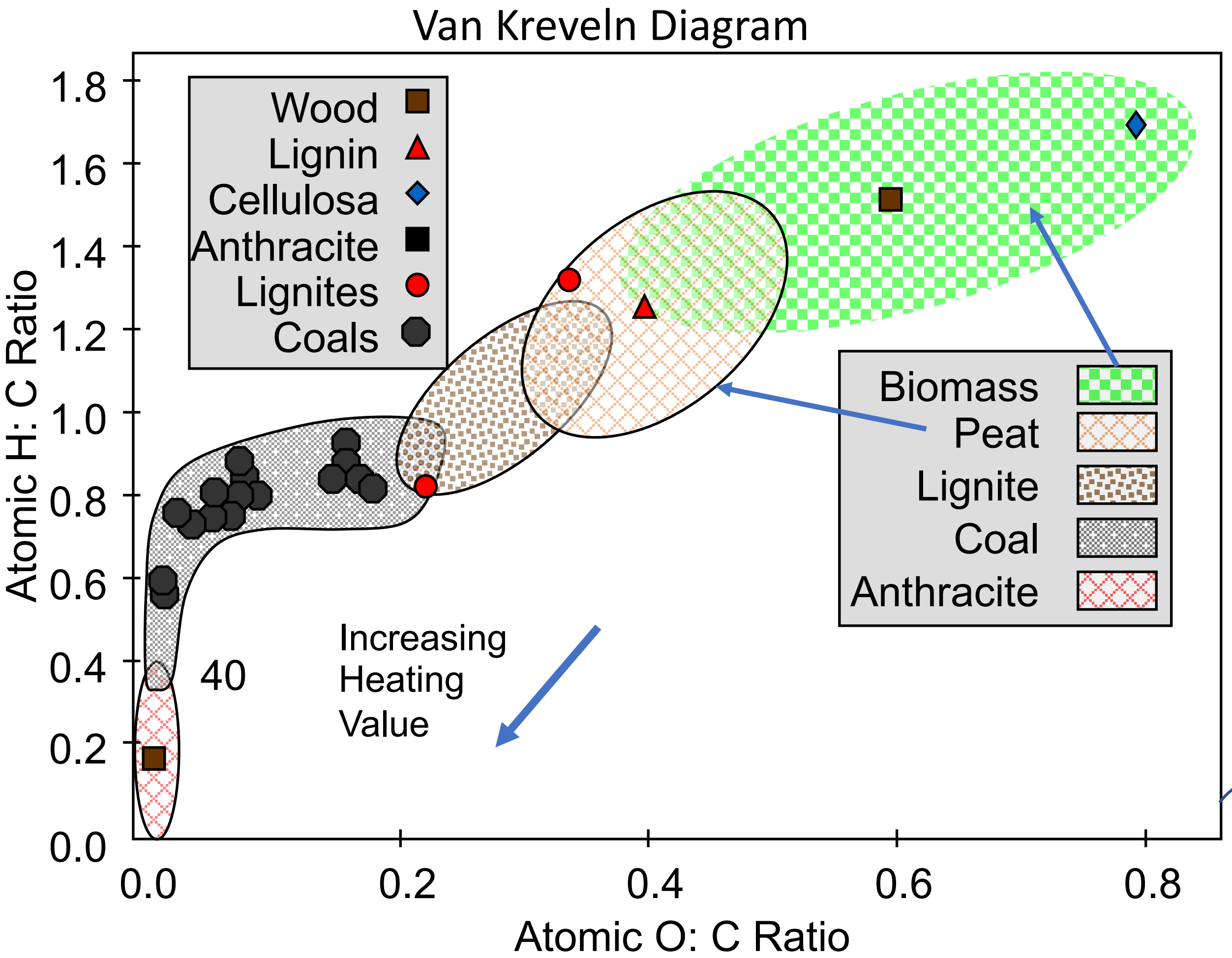
BIOMASS ENERGY

Ahmed Ghoniem

May 4, 2020

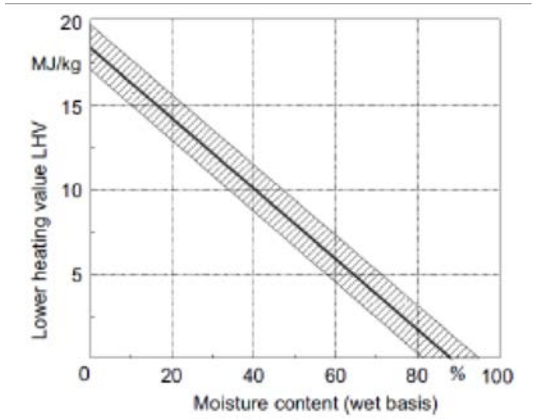
- Energy properties of biomass
- Some biomass fundamentals
- Fuel production from biomass
- Biomass conversion, biological and thermochemical
- Bioconversion, mass and energy balances
- Does bioconversion of corn to ethanol save energy?

Biomass composition and heating value



Biomass	C (%)	H (%)	O (%)	N (%)	S (%)	Ash (%)	HHV (MJ/kg)
Douglas fir					0	0.8	
Redwood		5.9	40.3	0.1	0	0.2	
Maple		6.0	41.7	0.3	0	1.4	
Sawdust		6.5	45.4	0	0	1.0	
Rice straw		5.1	35.8	0.6	0.1	19.2	
Rice husk		5.7	39.8	0.5	0	15.5	
Sewage sludge							

Ultimate analysis (on dry basis) of some plant biomass including woody and non woody, and sewage sludge, that can be used as fuel



Effect of moisture content on LHV of wood (MJ/kg). (UN Food and Agri. Org.)

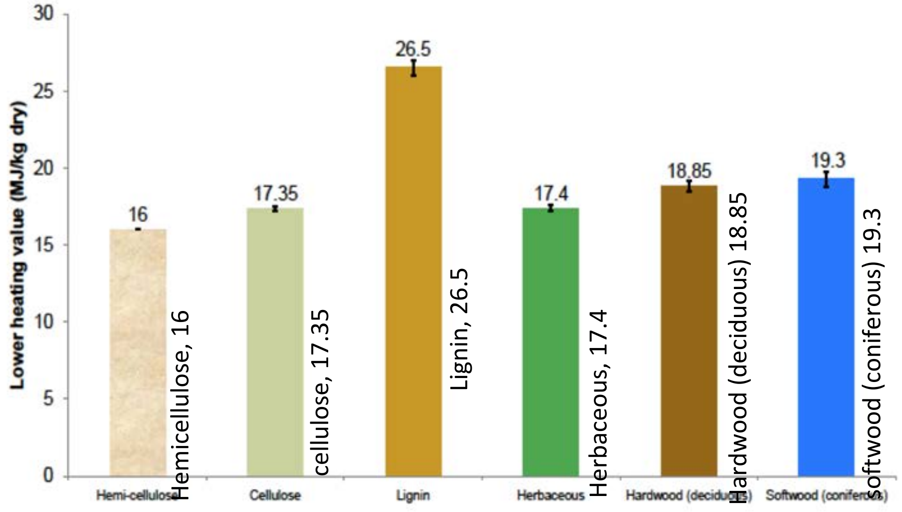


Figure 2-6 LHV of biomass and its cellulosic components (Francescato et al. 2008)

Some Biomass Fundamentals

Photosynthesis:

$$nCO_2 + mH_2O \xrightarrow[chlorophyll]{sunlight} C_n(H_2O)_m + nO_2$$

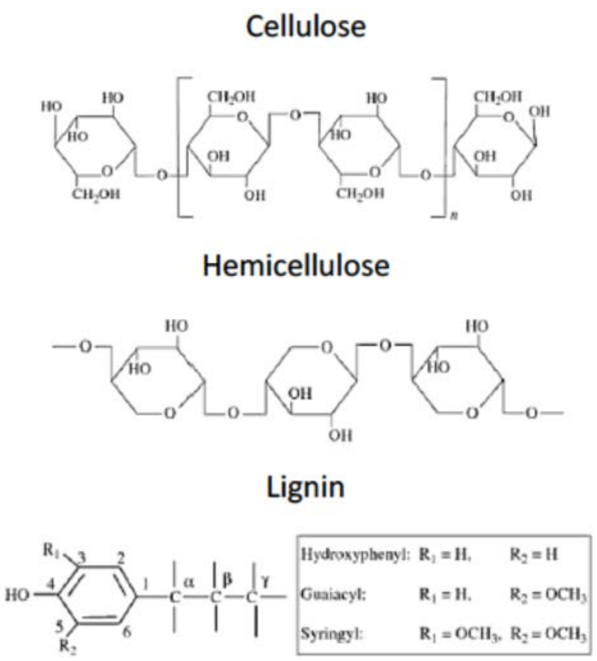
$$\Delta H_r = 470 kJ / mol$$

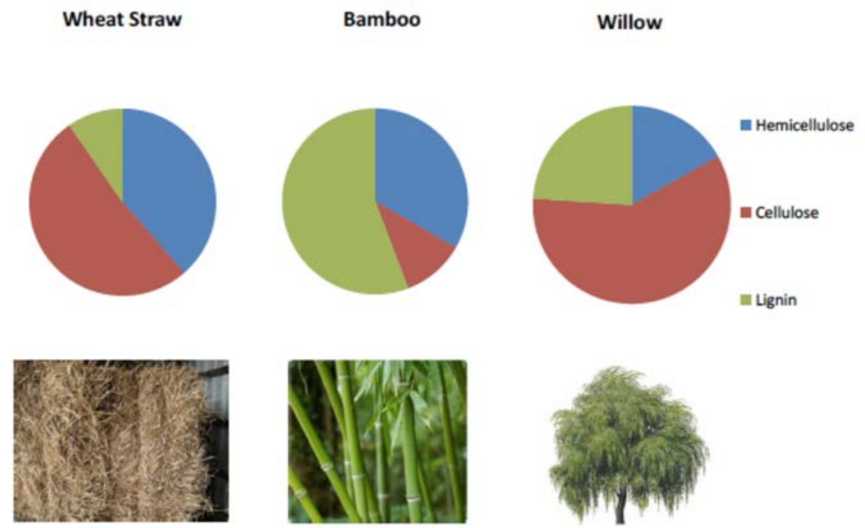
Photosynthesis produces "carbohydrates" such as sugar, starch and cellulose from water and carbon dioxide.

Efficiency of sunlight absorption/conversion during photosynthesis is 0.1-3%, but a fraction of it is lost in other products.

Carbohydrates are also called saccharides. They are sugars or polymers of sugar (defined next).

The three primary components of biomass:



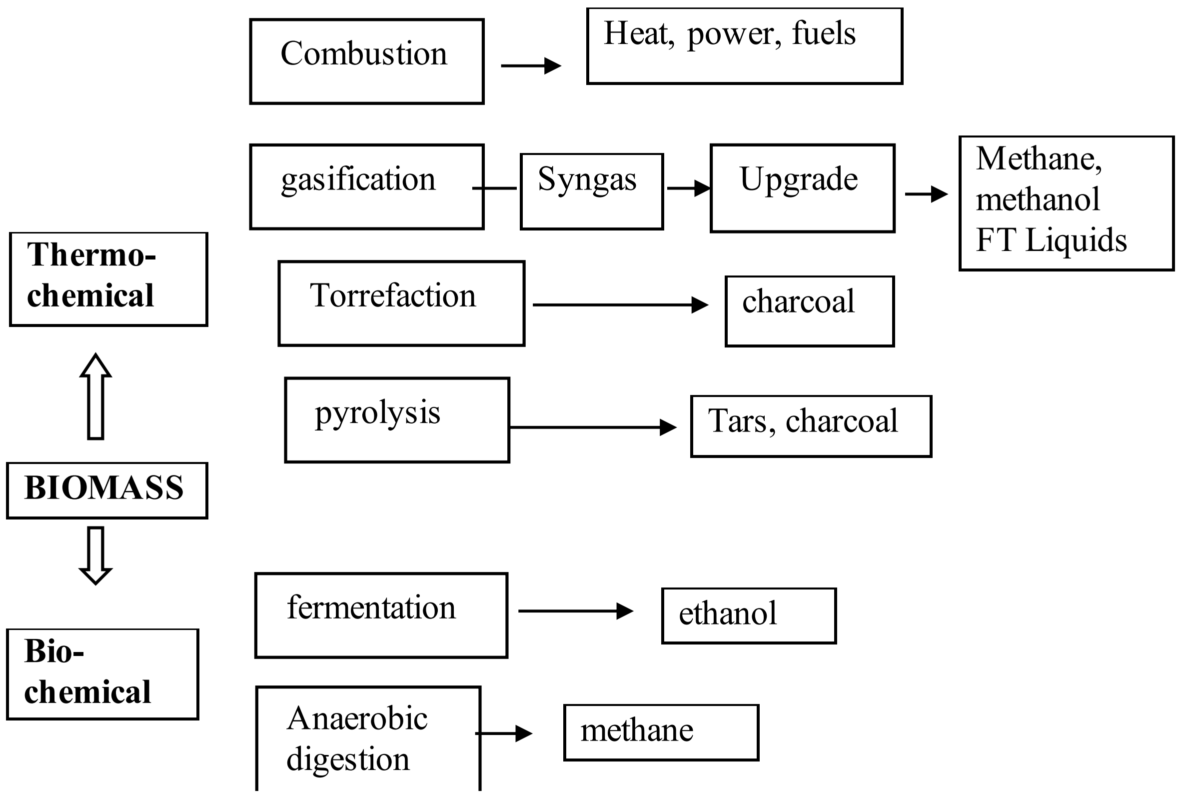


Biomass Utilization: production of heat and fuels

Three major conversion options:

1. Bioconversion to fuel (fermentation and anaerobic digestion),
2. Thermochemical conversion to fuel (pyrolysis and gasification).
3. Combustion to heat.

- Bio conversion is simpler and scalable, but limited to certain biomass components
- Gasification offers improved feedstock flexibility and production of drop-in fuels but is more compatible with larger scale production



Thermochemical processes work with (almost) any biomass:

Combustion is the simplest , but given the low heating value of wood, huge amounts are needed to power a typical power plant. Wood has open pore structure and high moisture content. On a dry basis, the heating value (~15-22 MJ/kg) is: $HHV=-1.3675+0.3137Y_C+0.7009Y_H-0.0318(1-Y_C-Y_H-Y_{ash})$

Other *thermochemica*l processes including pyrolysis (low temperature torrefaction to solids and intermediate temperature pyrolysis to liquids) and higher temperature gasification, may generally be preferable for recovering the energy of wood and lignin.

Bioconversion works well with sugar and grain crops:

Sugar crops include sugar cane, beet and sweet sorghum. Sugar cane produce nearly twice the energy of beet, measured as unit energy produce/land area, but its growth is restricted to warm climate, good soil and where plenty of water is available. Sugar crops can be more readily hydrolyzed (mixed with water and microbes) to fermentable sugars.

Grain crops include corn, wheat, rice, barley and other cereals. These plant products have high starch contents, which can be hydrolyzed (mixed with water, acids and enzymes) to fermentable sugars.

Property of plant material, as regards their potential for bio conversion:

Carbohydrates in plants are sugars and **polymers** of sugar: starch, hemicellulose and cellulose.

Sugars (oxygenated hydrocarbons) in fruit juices can be fermented (digested biologically) into alcohols.

Starch is granular polysaccharide found in seed, tubers, roots and stem pith; corn, potato, rice, tapioca. 10-20% of starch is soluble in water (alpha amylose) and the rest is insoluble (amylopectin). *It can be hydrolyzed to fermentable sugars using dilute acids and enzymes.*

Dry wood is 66% holocellulosic (combination of cellulosic and hemicellulsic) and 25% lignin, and the rest is resins, gums, tannins and waxes. About 25% of the holocellulose is hemicellulose, the rest is cellulose and some lignin.

Hemicellulose is made of polysaccharides, but they are more soluble than cellulose. *It is amorphous, is dissolved by dilute alkaline solutions, and can be hydrolyzed to fermentable sugars*

.

Cellulose is made of fibrous polysaccharides, the main constituent of cell walls, such as cotton, wood, hemp and straw. *They are insoluble and chemically inert, and resist acidic or enzymatic hydrolysis.*

Lignin is not a carbohydrate. It is a polymer of single benzene rings linked with aliphatic chains (mostly phenolic compounds).

Lignin is an important constituent of the walls of woody plants, providing the plant with glue and strength. It is amorphous and more soluble, *but completely resists hydrolysis and is resistant to microbial degradation*. It is removable by steaming or by solvent extraction. Removed lignin can be combusted.

Besides woods and plant crops (fruits, etc.) sources of plant biomass include crop residue, that is, material left after harvest. This material is low on sugar and starch, but high on lignocellulosic material. Thus it may be more suitable for thermal conversion and combustion.

Same is likely to be for switch grass.

Agricultural waste, left over after processing crops include sugar cane bagass, and cotton gin trash. Sold as animal feed, it can also be burned or used in thermal conversion processes.

Aquatic plants including ocean kelp, algae and buckweed. In general, it is more difficult to harvest than other types of biomass, although its growth can be encouraged to grow faster by supplying nutrients such as CO2.

Municipal solid waste include cellulosic material, may not work well with biochemical conversion processes, but lend themselves well to combustion and thermal conversion.

Animal waste is another source or organic biomass, which does not compete with food production, but supplies are limits.

Sugars and fermentation:

- Sucrose $C_{12}H_{22}O_{11}$ found in plant sap.
- Glucose $C_6H_{12}O_6$ in corn and grape.

Also found in the form of complex isomers in which the primary molecule is arranged in complex patterns, e.g., glucose can be found in D-glucose (destrose), D-mannose or D-fructose.

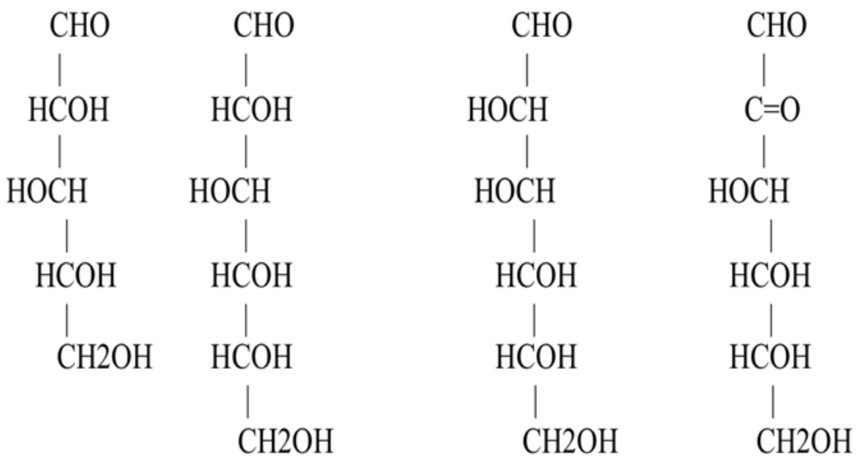
Sugar may be fermentable (that is, can be broken down biologically) or may not be fermentable.

Fermentation: $$2C_6H_{12}O_6 \underbrace{\rightarrow}_{\text{zymae}} 4\underbrace{C_2H_5OH}_{\text{ethanol}} + 4CO_2$$

Non fermentable sugars can be made fermentable by hydrolysis in the presence of an acid or an enzyme:

hydrolysis: $$\underbrace{C_{12}H_{22}O_{11}}_{\text{sucrose}} + H_2O \xrightarrow{invertase} \underbrace{C_6H_{12}O_6}_{\text{glucose}} + \underbrace{C_6H_{12}O_6}_{\text{fructose}}$$

Examples of fermentable (bio-processed) sugars



D-xylose D-glucose (dextrose) D-mannose D-fructose

Bio conversion: Ethanol from Sugar Cane

Fermentation: $2C_6H_{12}O_6 \underbrace{\rightarrow}_{\text{zymae}} 4\underbrace{C_2H_5OH}_{\text{ethanol}} + 4CO_2$

Glucose is converted to ethanol (after sucrose is broken down by getting dissolved in ater)
Two moles of ethanol are produced for each mole of glucose consumed.
The heat of reaction is glucose is 15.6 MJ/kg, or 2.81 GJ/kmol.
The amount of energy in the ethanol is 2 X 29.7 X 46 = 2.73 GJ.
Thus, the theoretical efficiency of conversion is 97.5%. The actual efficiency is lower.

- Fermentation plants receive "burned and cropped" (b&c), or 77% of the raw cane.
- Average b&c production is 58 ton/hectare/year (ton = 1000 kg).
  - Each ton yields ~ 740 kg juice, made up of 135 kg sucrose and water. Sucrose's HHV is 16.5 MJ/kg
- The residue is wet bagasse, which when dried yields 130 kg of dry bagasse.
- Dry bagasse has HHV of 19.7 MJ/kg that can be extracted by combustion.
- Thus the total HHV of a ton of b&c is (135x16.5+130x119.7)= 4.7 GJ.
- Per hectare per year, total biomass energy of cane is 270 G or 0.86 W/m^2.
- With average insolation of 225 W/m^2, the photosynthesis efficiency of sugar cane to energy (ethanol if conversion efficiency is 100%, see next) is 0.38%.

Ethanol from Corn

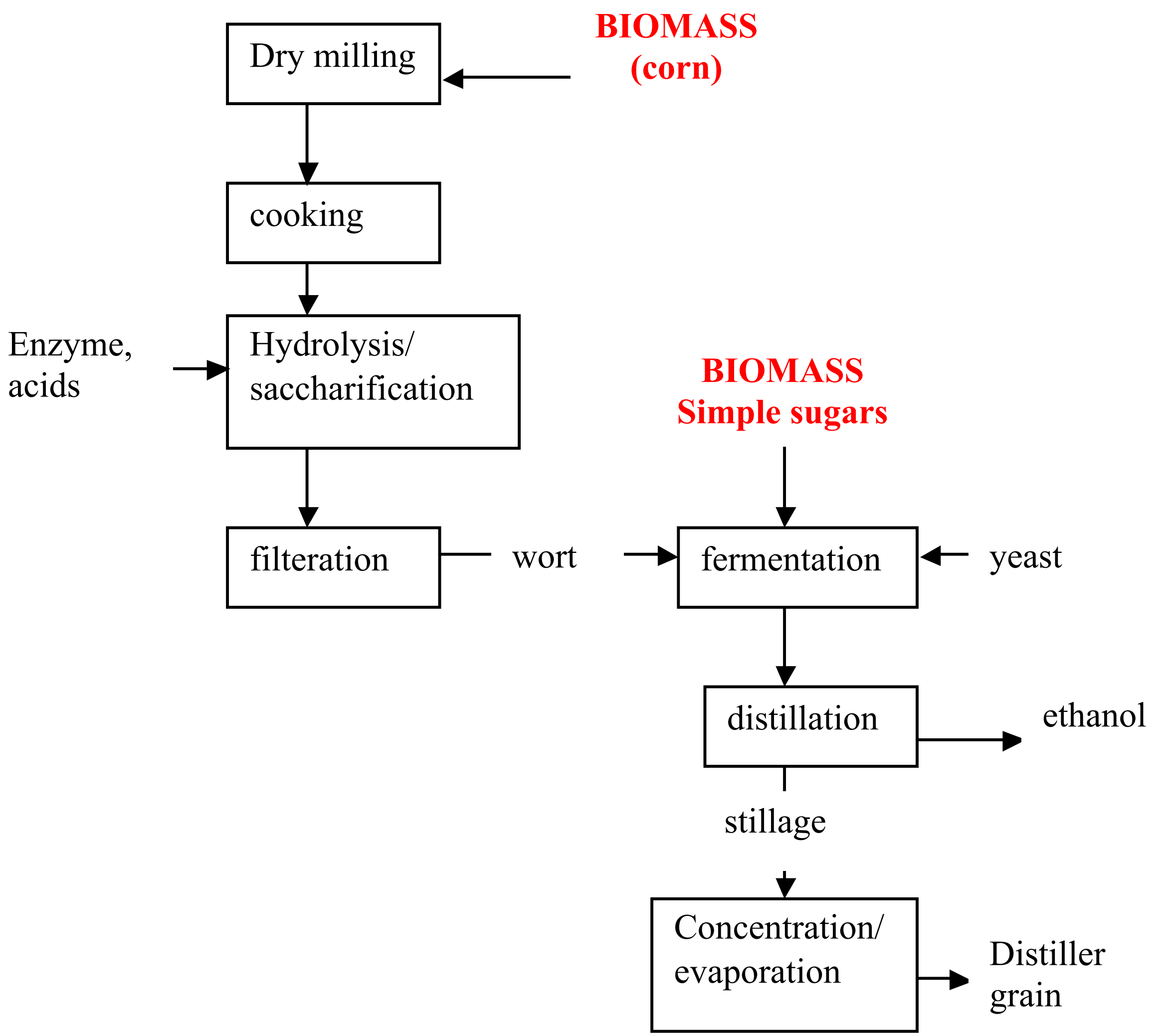
Conversion occurs in liquid medium using enzymes (proteins, such as glycolysis, produced by living cells) to produce liquid fuels. They have slow kinetics (1-2 orders of magnitude slower than thermal reactions).
Acids are used for hydrolysis at 140-190 C. Fermentation is exothermic and the environment must be cooled to 30 C.
The final products has ~ 14% alcohol, and must be distilled.
Distillation consumes ~ 7-11 MJ/L of the produced ethanol (nearly 30-45% of the HHV of the product).

saccharification: $\underbrace{2\left(\text{-}C_6H_{10}\text{-}O_5\text{-}\right)}_{\text{starch}} + H_2O \underbrace{\rightarrow}_{\text{diastase}} \underbrace{C_{12}H_{22}O_{11}}_{\text{maltose}}$

Fermentation: $C_{12}H_{22}O_{11} + H_2O \underbrace{\rightarrow}_{\text{maltase}} 2\underbrace{C_6H_{12}O_6}_{\text{glucose}}$

Fermentation: $2C_6H_{12}O_6 \underbrace{\rightarrow}_{\text{zymae}} 4\underbrace{C_2H_5OH}_{\text{ethanol}} + 4CO_2$

Thermal efficiency [ethanol/(corn + heat)] is 46%.



Ethanol from Corn
Is it energy positive of negative?

Using these equations, one can show that for 324 kg of starch used, 184 kg of ethanol is produced.
In practice, ~ 10% of the starch is converted into other byproducts, such as higher alcohols, glycerin and ethers.
Assuming corn is 61% starch and correcting for the 10 % to byproducts shows that 1 kg of ethanol requires 3.2 kg of corn, or a liter of ethanol requires 2.6 kg corn.

Given the higher heating value of corn, 14.1 MJ/kg, and ethanol, 29.7 MJ/kg, and subtracting the energy for milling, cooking, distillation and recovery of byproducts, an overall thermal efficiency defined as the ratio between the heating value of the produced ethanol divided by the sum of the corn heating value + other energy used, is 46%. The energy used is 65% of that of the enthalpy produced.

To cultivate and harvest the corn crop, these are estimated to be 42% of the energy of the ethanol produced, leading to a negative 7% energy overall.

For the production of ethanol from corn to be energy positive, crop residues and fermentation byproducts must be used to supply some of the heat required.

Thermodynamics of the Corn-Ethanol Biofuel Cycle

Tad W. Patzek (2004) "Thermodynamics of the Corn-Ethanol Biofuel Cycle", *Critical Reviews in Plant Sciences*, 23:6, 519-567, DOI: 10.1080/07352680490886905.

True Life Cycle Analysis of corn-to-ethanol, by T. Patzek

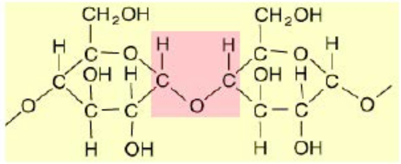


Figure 1: A typical starch molecule is constructed from α-glucosidic bonds (purple background), each of which links two dehydrated glucose molecules. Theses molecules form either unbranched or somewhat branched polymer chains with up to 360 or 1000 glucose units, respectively (Avers, 1976). In hydrolysis, the glucosidic bonds are broken, and each glucose unit gains one water molecule.

Fuel	Density kg/sm^3	HHV[a] MJ/kg	LHV[a] MJ/kg	HHV[a] MJ/kg	LHV[a] MJ/kg	Source[i]
Gasoline	720-800	46.7[b]	42.5[b]	46.8	43.6	Table 339
Diesel fuel	840	45.9	43.0	45.3	42.3	Table 350
Methane	0.66[d]	55.5[c]	50.1[c]	55.1(g)		Table 347
LPG[e]	0.58	50.0	46.0			
NG[f]	0.84	48.7	43.9			
Ethanol	787[h]	29.7[g]	26.7[g]	29.6	26.8	Table 353
Corn grain dry		18.8[j]				
Corn stover[k]		17.7	16.5			
Corn stalks[l]		15.8	14.8			
Corn meal[m]		16.0				
Corn oil[n]	909.5	39.5	38.8			

Corn Grain	→	Starch	→	Glucose	→	Ethanol
Steeping Grinding Germ Separation		Gluten Liquefaction Saccharification		Fermentation CO_2		Distillation Dehydration

Table 24: The First Law summary of the U.S. corn-ethanol production in 2004

29.6 million hectares	of corn harvested in the U.S.
299.67 million tonnes	of moist corn grain harvested
3.8 million hectares	of U.S. cropland growing corn for ethanol
12.7 %	of all U.S. corn is farmed for ethanol
0.399 liters	of ethanol from 1 kg of corn
12.28 GL/yr	of ethanol produced in the U.S.
3.25 billion gal/yr	of ethanol produced in the U.S.
9.21 GL GE/yr	as ethanol produced in the U.S.
10.16 GL GE/yr	burned to produce this ethanol
1.4 %	of U.S. automobile fuel from ethanol
25.9 million hectares	for 10% U.S. automobile fuel energy
$1.69 billion/yr	in federal subsidies for ethanol
$0.32 billion/yr	in average state subsidies for ethanol
$1.27 billion/yr	in corn-for-ethanol price subsidies
$3.28 billion/yr	in total ethanol subsidies

GL = Giga Liter = 10^9 L; GE = Gasoline Equivalent

Fuels for farming

Agricultural yield= energy of dry corn grain.
On average it is 125 GJ/ha*.
For perennial grasses 200-300 GJ/ha-crop
For sugarcane, 400 GJ/ha-crop

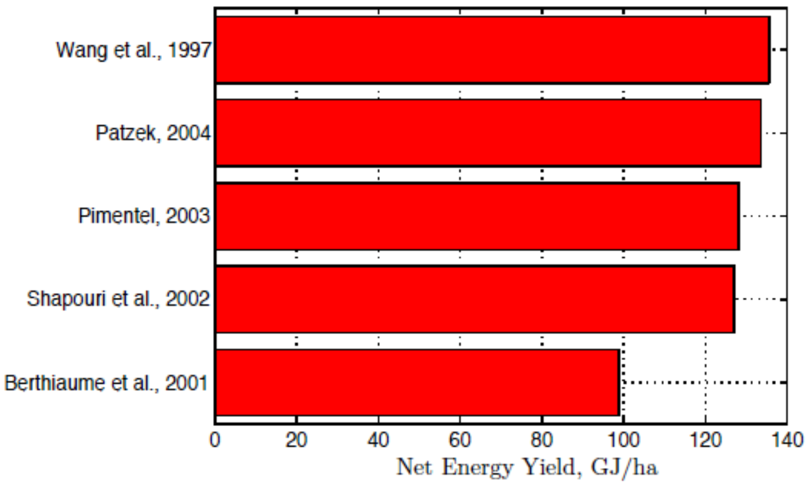


Figure 20: The net energy yield in industrial corn grain production is relatively small, 100 – 135 GJ/ha-crop. The HHV of dry corn grain is 18.8 MJ/kg, based on the mean of the values reported by SCHNEIDER & SPRAQUE (1955), p. 496, 2033 kcal/lb; and MILLER (1958), p. 639, 2059 kcal/lb. 1 thermochemical kcal = 4.184 kJ.

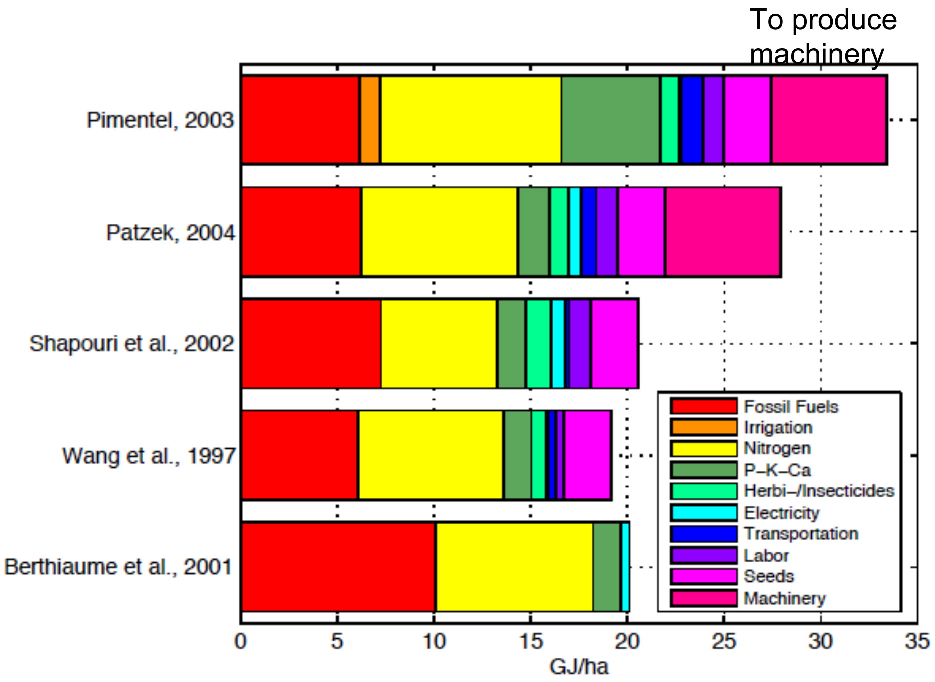


Figure 12: Major fossil energy inputs into corn farming.

* 1 ha produces about 8600 kg moist corn x 0.85 =7300 kg dry corn x 18.8 MJ/kg = 137 GJ/ha
(1 ha = 10000 m^2 = 2.47 acres.)
Or 130 bushels (wet) per acre (with 15% moisture).

Some estimates, like nitrogen and machinery, account for energy used to produce this commodity. P-K-Ca: more fertilizers

Fuels used for ethanol production from corn

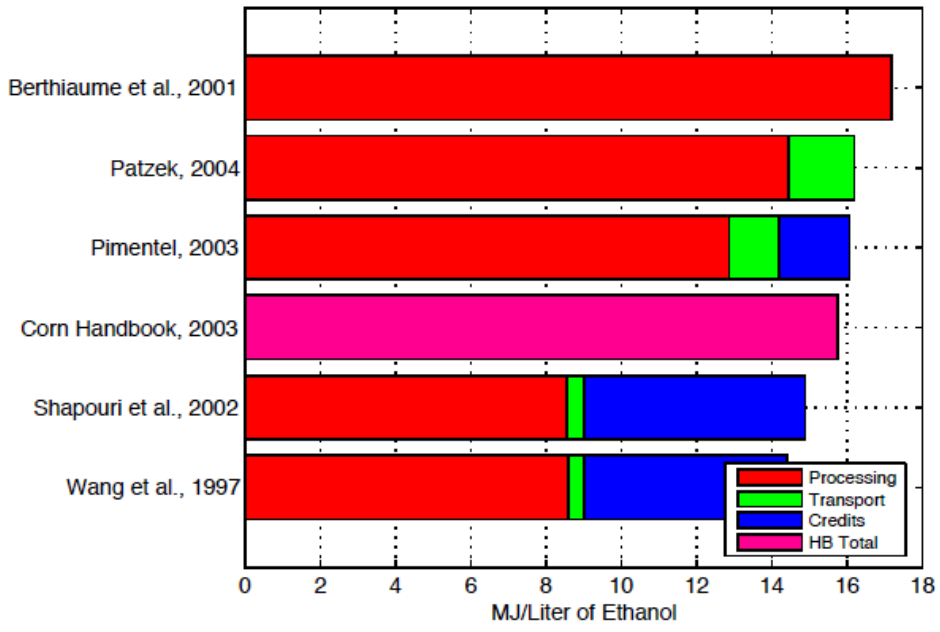


Figure 17: The average fossil energy inputs to ethanol production in a wet milling plant. The length of each bar is the total energy outlay to produce 1 liter of EtOH, and the blue parts denote the size of energy credits assumed by the different authors. The modern dry mill plants use 11.36 MJ/L as steam and 3.12 MJ/L as electricity, 14.5 MJ/L total, not counting transportation costs.

Production in terms of corn and ethanol

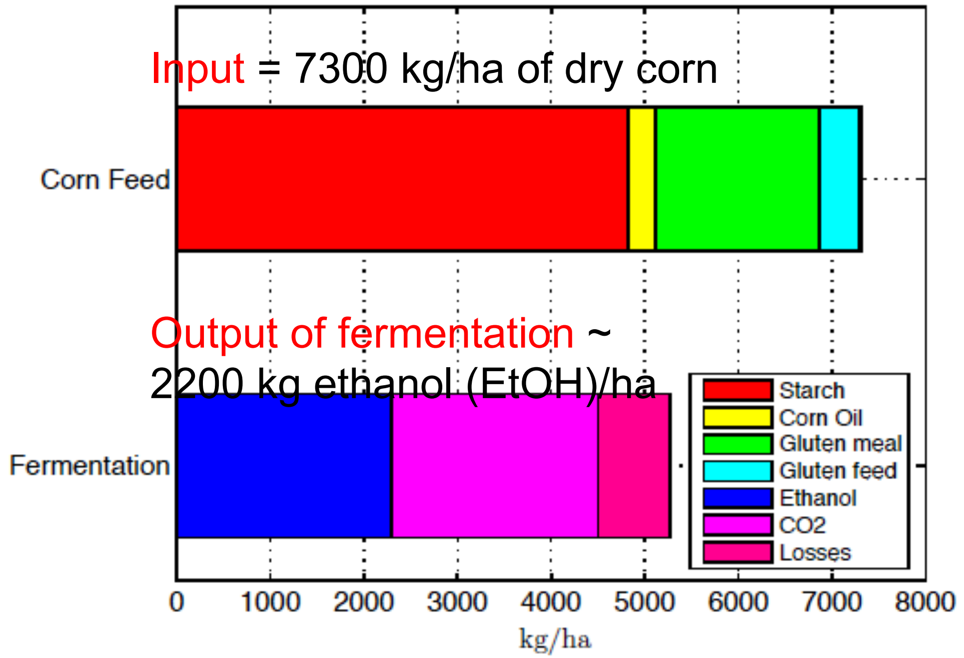


Figure 15: The result of practical corn conversion into ethanol with 16% losses is 0.399 L EtOH/kg dry corn grain = 2.682 gal EtOH/**dry** bushel = 2.28 gal EtOH/**wet** bushel with 15% moisture. Note that the dry starch is swollen by a factor of 180/162 caused by hydrolysis to glucose.

Taking 16 MJ/L, or 20.3 MJ/kg EtOH (x 2200 kg/ha) gives 44.7 GJ/ha of fossil fuel requirements to produce ethanol from corn.
Could be as low as 26 GJ/ha if credit is considered.

Energy input and output

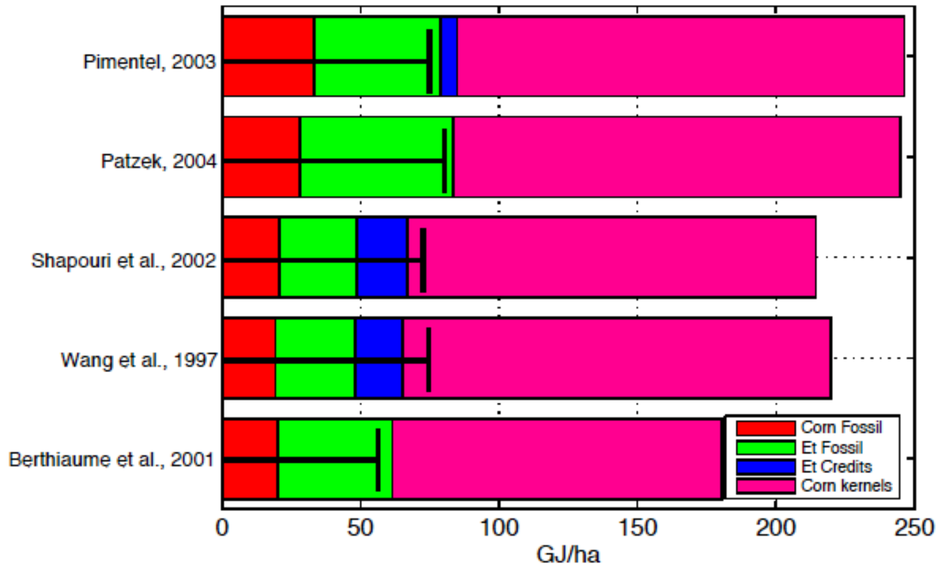


Figure 18: The overall energy balance of ethanol production. The two or three leftmost parts of each bar represent the specific fossil energy used in corn farming and ethanol production. The fossil energy inputs into ethanol production are the sum of the green part and the blue energy credit part for some authors. The rightmost part is the calorific value of corn grain harvested from 1 hectare. The total lengths of the horizontal bars represent all energy inputs into ethanol production. The horizontal lines with the vertical anchors represent the calorific value of ethanol obtained from one hectare of corn. Note that the total energy inputs into ethanol production are equivalent to ∼4–5 metric tonnes of gasoline per hectare. The ethanol's calorific value is equal to 1–1.3 metric tonnes of gasoline.

In terms of EtOH, we get 65 GJ/ha.

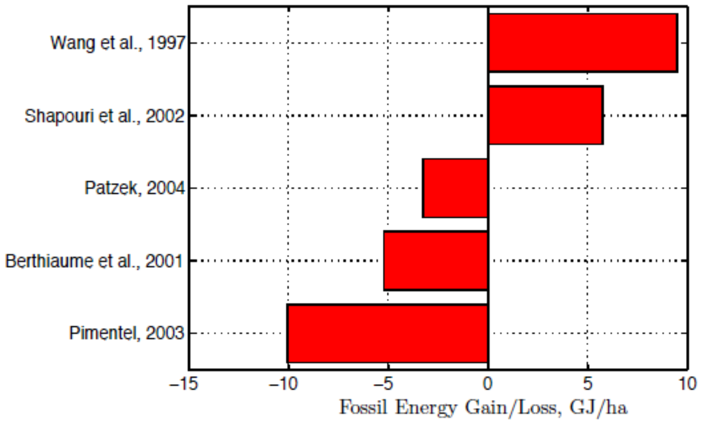


Figure 19: Fossil energy gain/loss in corn ethanol production. Note that the dubious energy credits described in Section 4.4 do not eliminate the use of fossil fuels in the first place, but present alternative useful outcomes of this use.

Farming: 20-33 GJ/ha,
EtOH production from corn, 26-44 GJ/ha,
Total fossil used: 46-77 GJ/ha.

Energy in EtOH (2200 kg/ha x 29 MJ/kg) 63 GJ/ha .

Ideal thermal efficiency of corn to ethanol: 46% .. …
That is, with 137 GJ/ha corn, should 63 yield GJ/ha in EtOH

Anaerobic Digestion

Anaerobic digestion:

Decomposition of complex organic molecules to methane and CO_2 through three stages: hydrolysis using bacteria, conversion to fatty acids using bacteria, and finally methanogesis using bacteria where biogas (CH_4+CO_2) is evolved.

$$(-C_6H_{10}O_5-) + H_2O \xrightarrow{\text{bacteria}} 2CO_2 + 3CH_4$$

162 kg 18 kg 132 kg 48 kg

These processes are mildly exothermic , and require temperatures in the range of 45-65 C. the overall thermal efficiency is 53%