Alternative Fuels including BioFuels

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June 2012

Outline of This Talk

Part 1: Big picture, big issues

Part 2: What are the alternatives to petroleum for powering transportation?

Part 3: What do you want in a new fuel?

Part 4: A third fuel at gas station?

Part 5: BioFuels

There will be a Quiz, have a paper & pen ready.

Part 1: The Big Picture on Fuels

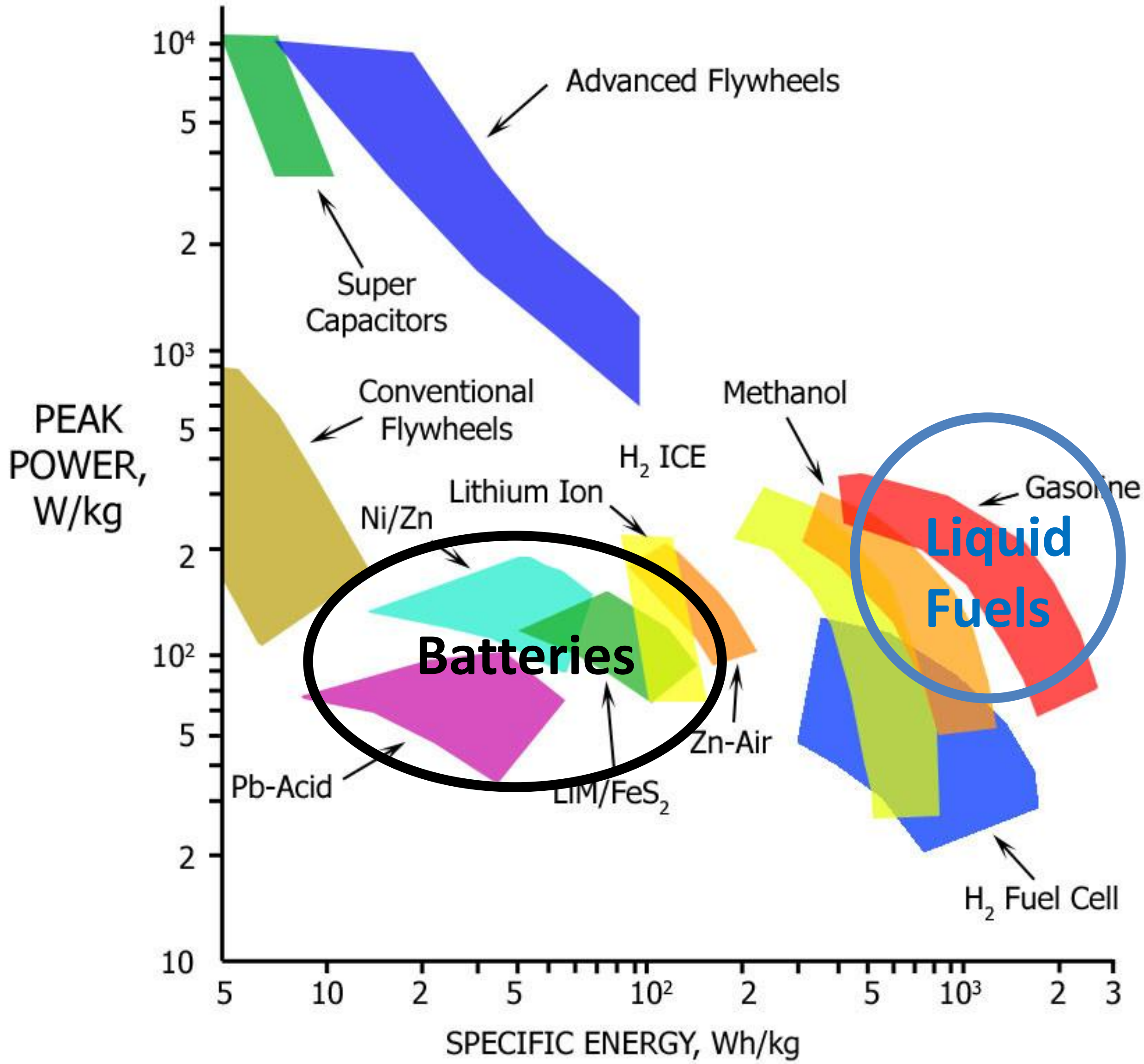
Transportation Fuel: Big Issues

- People want, economy depends on transportation
  - Cars (growing rapidly in Asia)
  - Trucks (critical for economy everywhere)
  - Airplanes (growing rapidly everywhere)
  - Demand for Fuel is "Inelastic": once they have invested in a vehicle, people will pay to fuel it even if price is high
- Liquid Fuels are Best
  - Liquids Flow (solids are hard to handle!)
  - High volumetric and mass energy density
  - Easy to store, distribute.

Huge volume of liquid fuel is being used now: ~80 Mbpd

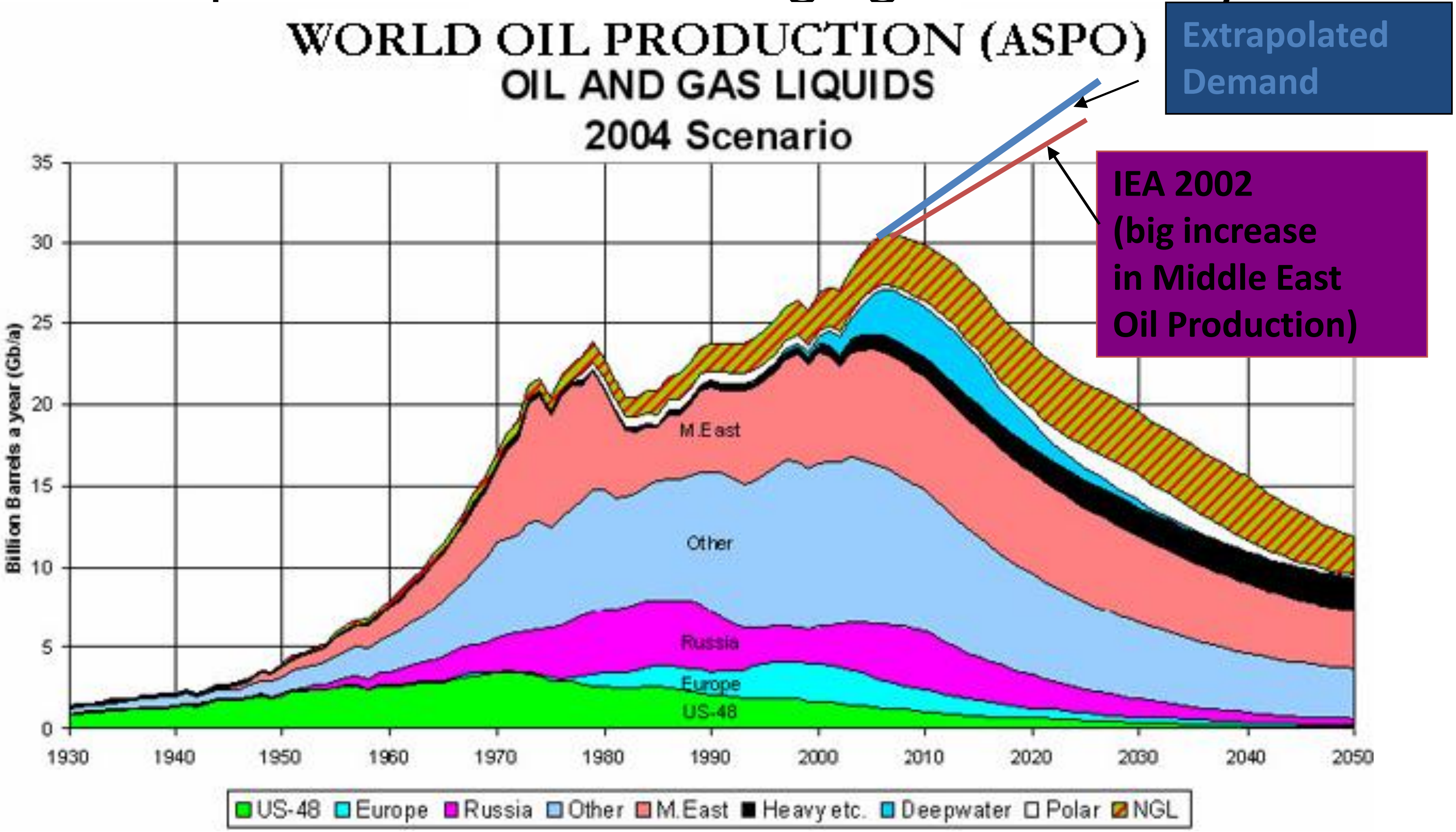
Downsides of Liquid Fuels

- Liquid Fuels are Expensive
  - 3-10x more $/Joule than coal and natural gas
  - The Big Money in Energy is in liquid fuels & vehicles
  - Trillion $/yr balance-of-payments flows
    - ~ $2000/yr/person in USA (~5% of total income)
    - Prices are very high compared to incomes in poor countries
- Energy Security: oil located far from populations
  - Several Blockades, Embargoes in last 100 years
- Big part of greenhouse gas problem (~30%)
  - Also major contributor to Urban air pollution
- Important…so Government is heavily involved
  - Must consider political and behavioral as well as technological and economic issues



Energy Density Matters!

Liquid Fuel Market Changing Dramatically



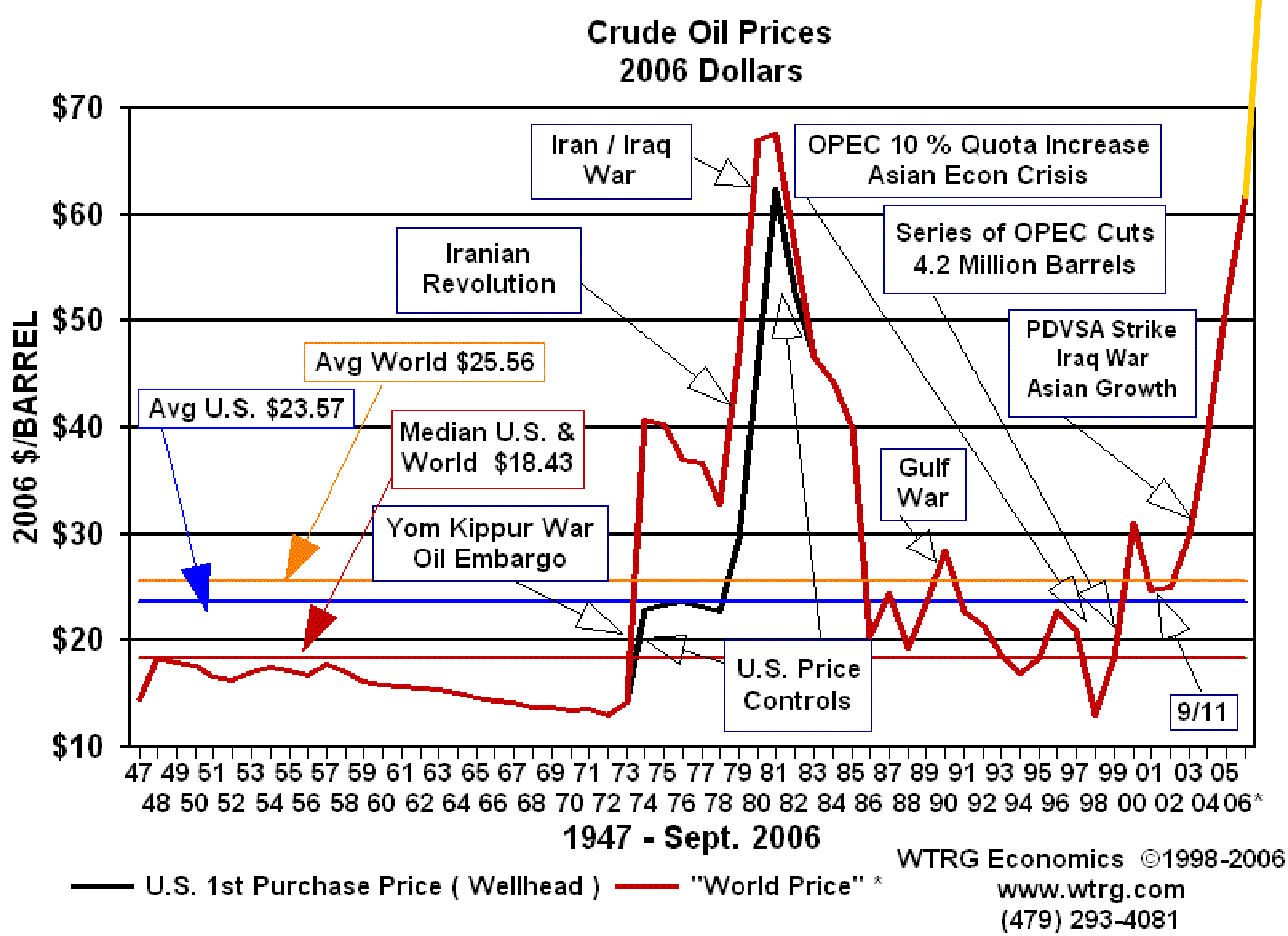
"…these are considered pessimistic projections. Others predict far higher production for the future… The optimists premise their estimates for the future entirely on production from the Middle East and Central Asia."

\- U.S. Army Corps of Engineers

Experience with Oil Projections

- Historically, Nothing is ***Smooth***!
  - i.e. the smooth projections are Nonsense
  - Wars, economic cycles, natural disasters
  - Political changes (positive & negative)
  - Technology changes
- Fuel demand is not very elastic
  - prices can climb and fall very quickly
- High prices will inspire production
  - Big increase in Middle East production
  - Increases in all sorts of alternatives as well
  - Lag times of ~5 years in production increases
  - High price can drive world economy into recession.

Price is almost *impossible* to predict.
Fuel taxes, subsidies & regulations even worse.



Fuel Price Fluctuations are a Big Problem

- Very high fuel prices help drive the world economy into recession (1974, 1980, 2008, 2011?)
- Adds Large Risk to Alternative Fuel projects
  - Many dramatic business failures in late 1980's
  - Price fluctuation often larger than technological uncertainties, biggest risk
  - Possibility that OPEC will intentionally drop price to drive competitors into bankruptcy.
  - Investors demand high rate of return because of risk; less lucrative processes are never built.

Why & Why Not use Fossil Fuels?

- **Finite but Very Large Amount of Fossil Fuel**
  - **We are definitely going to run out of fossil fuel energy… in a century or two: *Long Term issue***
  - **Fossil fuels are available now in huge scale**

    (unlike most other energy sources)

  - Although price is high at the moment, cost of production is low
- **Greenhouse Effect on Climate Change is the *Medium-Term issue***
  - **We'll "run out of atmosphere" to hold the CO_2 before we run out of fossil fuel.**
  - **Might even run out of capacity to store CO_2 underground or in ocean…**

Conventional Oil is

- Expensive (at the moment)
- (Maybe) Running Out
- Not Secure
- A Greenhouse Gas Problem

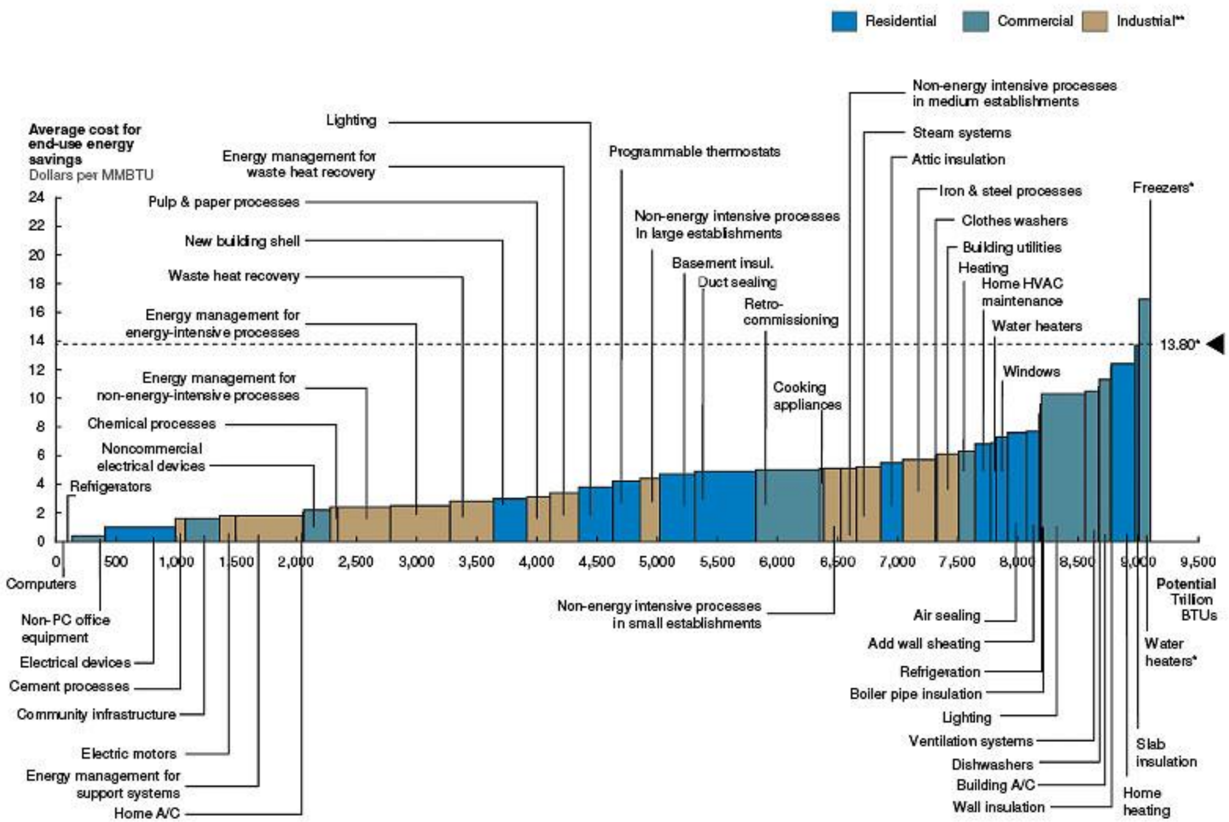
Part 2: What are the Alternatives for Powering Transportation?

Option #1: Improve Efficiency!

- Use less fuel: helps with all the problems!
- Possible to gain factor of 2, maybe more
  - Lots of interesting R&D underway, really great!
  - But in this talk our main focus is on alternatives to petroleum, so we will only talk about vehicle efficiency tangentially
- Tradeoffs
  - Size, Power, Speed vs. Energy Efficiency
  - Better engines usually cost more
    - **Vehicle cost usually more than fuel cost.**

McKinsey Supply Curve for Energy Efficiency: shows cost and potential scale of dozens of efficiency technologies.

Exhibit 7: U.S. energy efficiency supply curve – 2020



* Average price of avoided energy consumption at the industrial price; $35.60/MMBTU represents the highest regional electricity price used; new build cost based on AEO 2008 future construction costs

** Our 49th source of savings, refining processes, offers no NPV-positive savings

Source: EIA AEO 2008, McKinsey analysis

Quiz Question #1

- Diesel engines are significantly more efficient than Otto cycle (SI) engines, but also more expensive to manufacture. Why does it make sense for Europeans to use diesel cars, but not Americans?

Option #2: Batteries

- Commercial: Nissan Leaf, Chevy Volt, Tesla
- Works for cars, but not airplanes.
  - Reduced Range (low energy density)
  - Slow Recharge
- Batteries are expensive!
  - Needs subsidy at present (e.g. in USA ~$8000/car)
  - Need recharging infrastructure
- Great for Energy Security
- Where would the electricity come from?
  - If Coal: CO_2 emissions are worse than regular cars
  - If Gas, Nuclear, Renewables: CO_2 emissions better than oil
  - If Wind/Solar: less economically attractive, and if deployed at huge scale would need to solve energy storage issue (for intermittent electricity sources)

Option #3: Compressed Natural Gas

- Already commercial
  - e.g. some buses at Logan airport
  - Serious interest in converting long-haul trucking to CNG
- Reduced Range (lower energy density)
  - Not high enough for airplanes, but adequate for cars, trucks.
- Would require significant investment in distribution system, and either new vehicles or conversions of existing vehicles
  - But maybe cheaper overall than relying on oil?
  - In some countries, conversions are very popular
- If implemented at scale would probably require large scale LNG imports from Persian Gulf or Russia
  - No more secure than oil?
- Current track: USA is using domestic gas to make electricity. If we redirect the gas to transportation, will we use coal for electricity? Nuclear? Something else?

Gaseous Fuels: CNG is simple and abundant

Probably beneficial to environment, but this is disputed (due to fugitive emissions).

Cost-effective for buses, trucks which consume a lot of fuel.

Would require significant investment in fueling stations.

Natural Gas supplies limited in EU, China, Japan. Maybe better to use natural gas for heating, chemicals, electricity?

CNG COULD WORK, BUT LIQUID FUEL HAS MANY ADVANTAGES!

Option #4: Oil from Tar

- Large Resource, e.g. in Alberta and Venezuela
- Cost effective if oil price >$50/barrel
- Production & Conversion requires a lot of energy: Significant CO_2 emissions
  - Mostly natural gas, also some of the tar is burned
  - Sound bite: "'Game over' for the climate"
- Alberta tar sand production large and growing, already several million barrels/day.
  - Current controversies over proposed pipelines
  - Big local environmental impacts

Canadian Tar Sands:
World's largest earthmoving operation

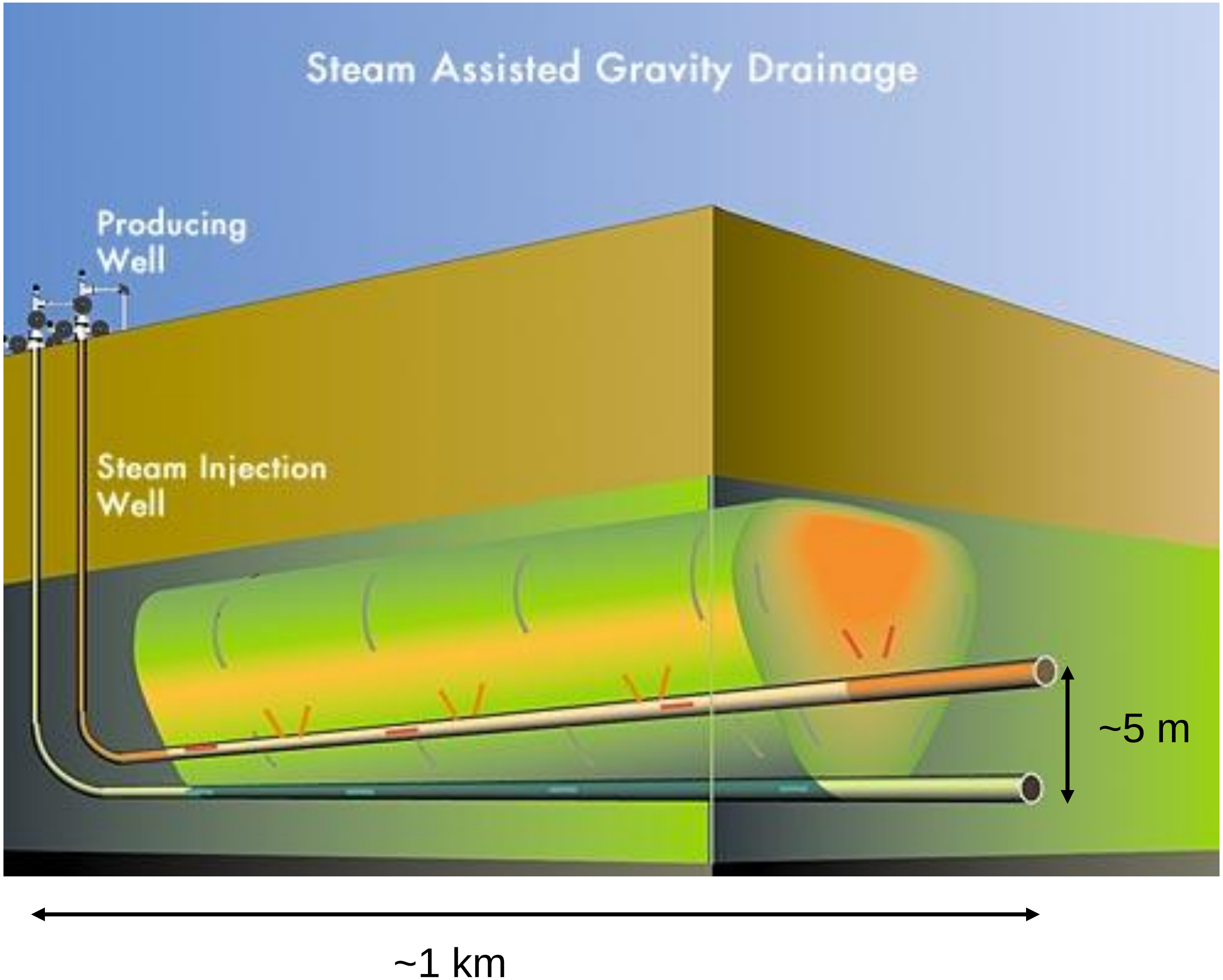
Truck is bigger than a house, costs $5M.

~5 tons of sand and peat moved and **~1 barrel of wastewater produced per barrel of oil**.

At 2 mbd, that is a lot of polluted water!

Aerial view of one of the Tar Sand upgrading facilities

In-situ production from tar sands



Cleaner and safer than surface mining, but still requires a lot of fresh water, and requires vast quantities of natural gas to make the steam.

Option #5: Biofuels from Food

- Current practice in USA: ethanol from corn
  - Natural gas + farmland + subsidy = liquid fuel
  - Reducing oil imports by ~5%
  - Primarily a farm subsidy program?
- Current practice in EU: biodiesel from canola
  - Lots of farmland + subsidy = small amount of fuel
  - Definitely a farm subsidy program
- **Not enough farmland to make enough food to replace significant fraction of fuel demand.**
- If you try, you will definitely push up food prices…

Option #6: Chemically Convert Natural Gas to Liquid Fuel

- Gasification then Fischer-Tropsch to diesel:
  - $CH_4 + ½\ O_2 = CO + 2\ H_2$
  - $n\ CO + (2n+1)\ H_2 = C_nH_{2n+2} + n\ H_2O$
  - A lot of chemical energy being converted to heat and wasted. Marginal economics at present.
  - Not good for security, greenhouse, cost. But good for supply.
- Other CH_4 reaction paths to make liquids??
  - Conversion to methanol is easy, used to make chemicals
  - Variety of other concepts / patents, none successful so far
  - General problem: CH_4 is less reactive than products
  - Some biological routes may be competitive with chemistry

World's largest Gas-to-Liquids Conversion Facility: Shell's Pearl GTL plant in Qatar

240 kbd for $24B capital investment: ~$100,000/barrel/day

1 barrel/day ~ $100/day or $36,500/year:

3 year pay back if the gas is free & oil prices stay high

Quiz Question #2

- Shell has invested in Gas-to-Liquids to make liquid diesel fuel in Qatar. US truck companies are investing to develop trucks that burn Compressed Natural Gas. Can they both be right?

Option #7: Coal to Liquids

- Similar to Gas-To-Liquids

  Coal + H_2O + O_2 = CO + CO_2 + H_2

  to make enough H_2, need to "shift" some of the CO to H_2:

  $$CO + H_2O = CO_2 + H_2$$

  Then either Fischer-Tropsch to make hydrocarbons:

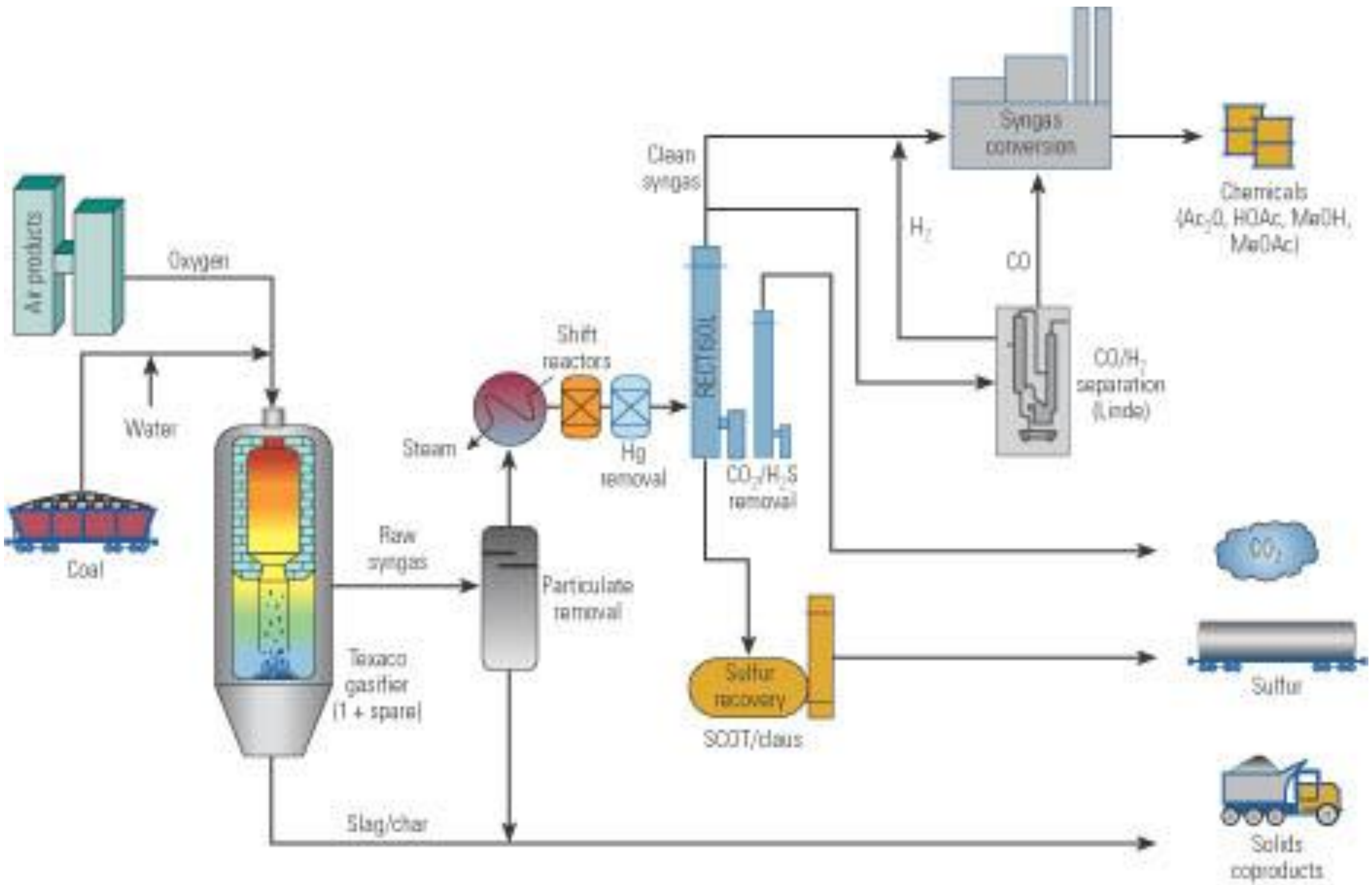
  $$n\,CO + (2n+1)\,H_2 = C_nH_{2n+2} + n\,H_2O$$

  or methanol synthesis:

  $$CO + 2\,H_2 = \text{methanol}$$

  - Was practiced for a long time in South Africa
  - Now practiced in China
- Good for Energy Security
- Marginal Economics
- Much worse CO_2 emissions than oil
  - Possible to capture & sequester CO_2
  - CO_2 capture is expensive, uncommon

Eastman Chemical Coal to Liquids Plant (Kingsport, Tennessee, 1250 tons/day)



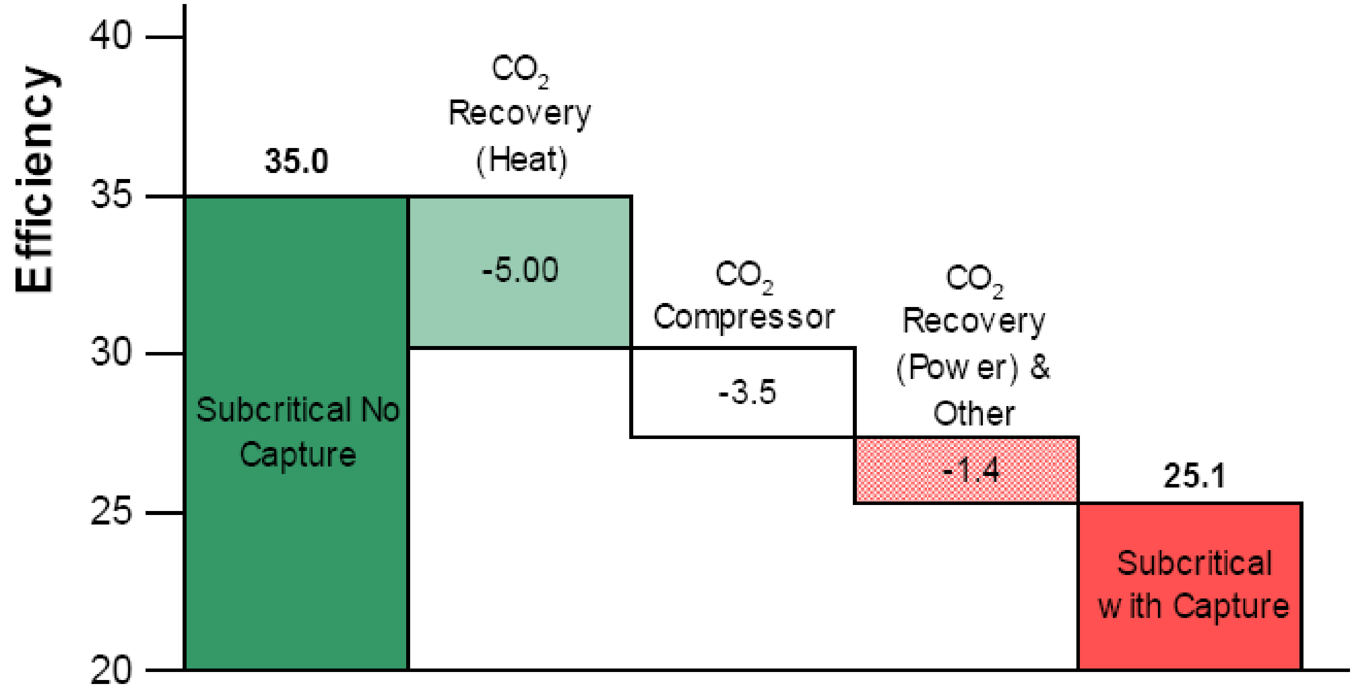
Large (24kbd) direct Coal Liquefaction Plant recently built in Inner Mongolia

Coal to Liquids Overview

- Well-established technology for CTL via syngas
  - Coal liquefaction, Coal + H_2 = liquids, appears to be competitive but not as well-developed.
- Good for Energy Security
- More coal available than oil, will last longer
- Marginal Economics despite cheap coal cost.
- Much worse CO_2 emissions than oil
  - Possible to capture & sequester CO_2
  - CO_2 capture is expensive, uncommon

CO_2 capture and underground sequestration significantly increases both capital & operating costs

Parasitic Losses for Subcritical PC with Capture



Efficiency Loss with Capture 35.5 % → 25.1%

So need to mine 40% more coal than w/o CCS!

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Public acceptance and unresolved policy issues even more problematic

Option #8: Fuels from Biomass

- Much more Biomass than Food
- Waste Biomass now equivalent to ~20% of liquid fuel consumption in US and worldwide
- Good for Energy Security and Climate
- Could farm algae, energy crops on waste land
  - So maybe significantly more than 20% of fuel?
- Many routes to convert Biomass to different fuels
  - none are commercial at present, many in R&D
  - probably will not be cheap. How to market?

Many Biomass Conversion Routes Now Being Studied / Commercialized

- Biological routes, e.g.:
  - Acid and/or enzyme treatment of biomass partially decompose biomass to sugars
  - Fermentation of the sugars
    - To alcohols or esters with bacteria or yeast
  - Burn rest of biomass to provide process heat
- Thermochemical routes, e.g.:
  - Fast pyrolysis with catalysts to bio-oil + acids
  - Need to react the mixture quickly to stabilize, then do more chemistry (add H_2) to reduce amount of O in fuel.

Best routes convert about 40% of C in biomass into useful liquid fuel.

Can convert more of the C's with an external source of H2.

Collection, Transport of Biomass

- Need to collect biomass, bring it to converter
  - Biomass has very low energy density: not cost-effective to ship it very far.
  - May be possible to increase energy density (e.g. by torrefaction) at the source.
  - Biomass is usually not free; cost is significant.
  - Need locations with a lot of biomass which is not currently being used for a high-value purpose, or excess arable land.
  - Cannot harvest so much biomass that one damages the soil.
- Locations, biomass not uniform. Many niche opportunities. Hard to achieve huge scale desired.
- Biomass availability varies seasonally, so capital equipment may not be effectively employed year round.

Quiz Question #3

Which of the 8 alternatives to petroleum presented do you think are worth pursuing? What are the weak points of your favorite option?

Part 3: What do you want in a new fuel?

And what constraints does any new fuel need to satisfy?

What do you want in a new fuel?

- **Liquid with reasonably high energy density**
- **Only contains C,H,O, maybe N.**
  - **So will burn to non-polluting products.**
- **Not Corrosive**
- **Suitable Volatility.**
- **Ignition delay correct for engine cycle.**
- **Flame speed fast enough for engine.**
- **Cheap! Plentiful! Will be competing with fossil fuels.**

Usually less important but still significant:

- **Solubility/Phase behavior**
- **Consistency from batch-to-batch of fuel.**
- **Environmental impacts**
- **Safety issues in handling/storing**
- **Stable in Storage**
- **Right Viscosity**

What properties do we desire in a fuel?

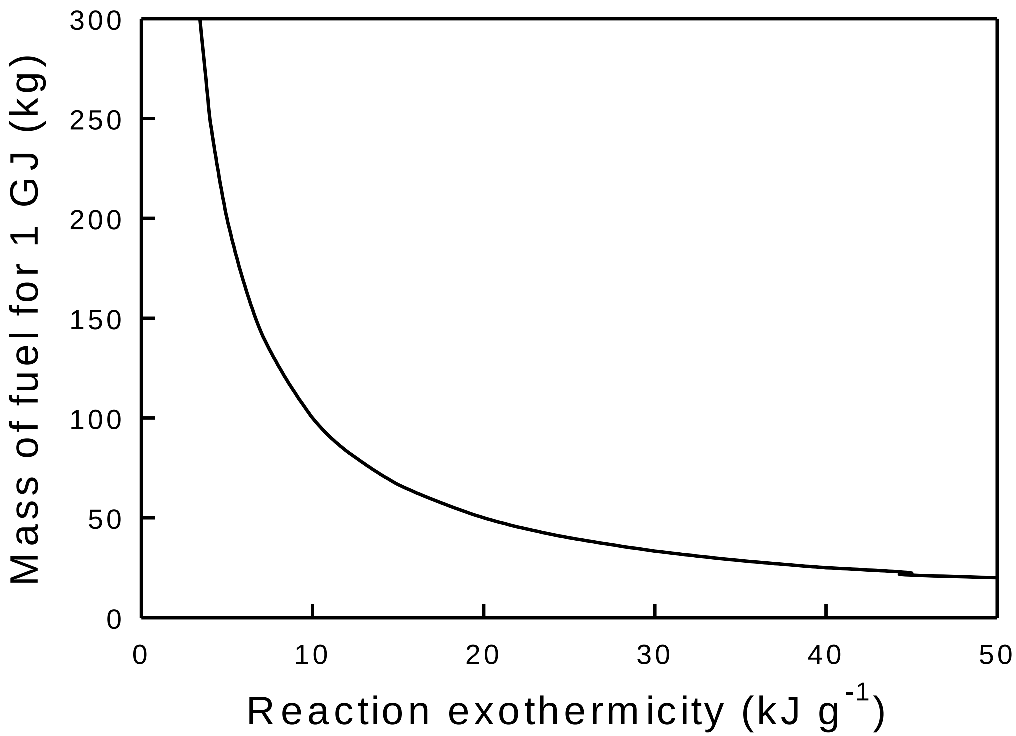
- **Prefer not to carry more than one reactant on vehicle; take second reactant from the atmosphere.**
  - Air is 78% N_2, 21% O_2, 1% Ar. N_2 is poor reactant (N≡N bond too strong), Ar is unreactive, leaves O_2.
- **Fuel should have highly exothermic reaction with O_2**
- **Fuel should be abundant in nature or easy to make. And cheap.**
  - We need need millions of tons every day.
- **Fuel itself should be environmentally benign and renewable**
- **Prefer to dump exhaust so we don't have to carry its weight. Exhaust should be environmentally benign (even if we carry it: we are making Mtons/day!)**
- **Both fuel & exhaust must be liquids or gases: no solids handling!**

Thanks to Tim Wallington.

Periodic Table

Period \ Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

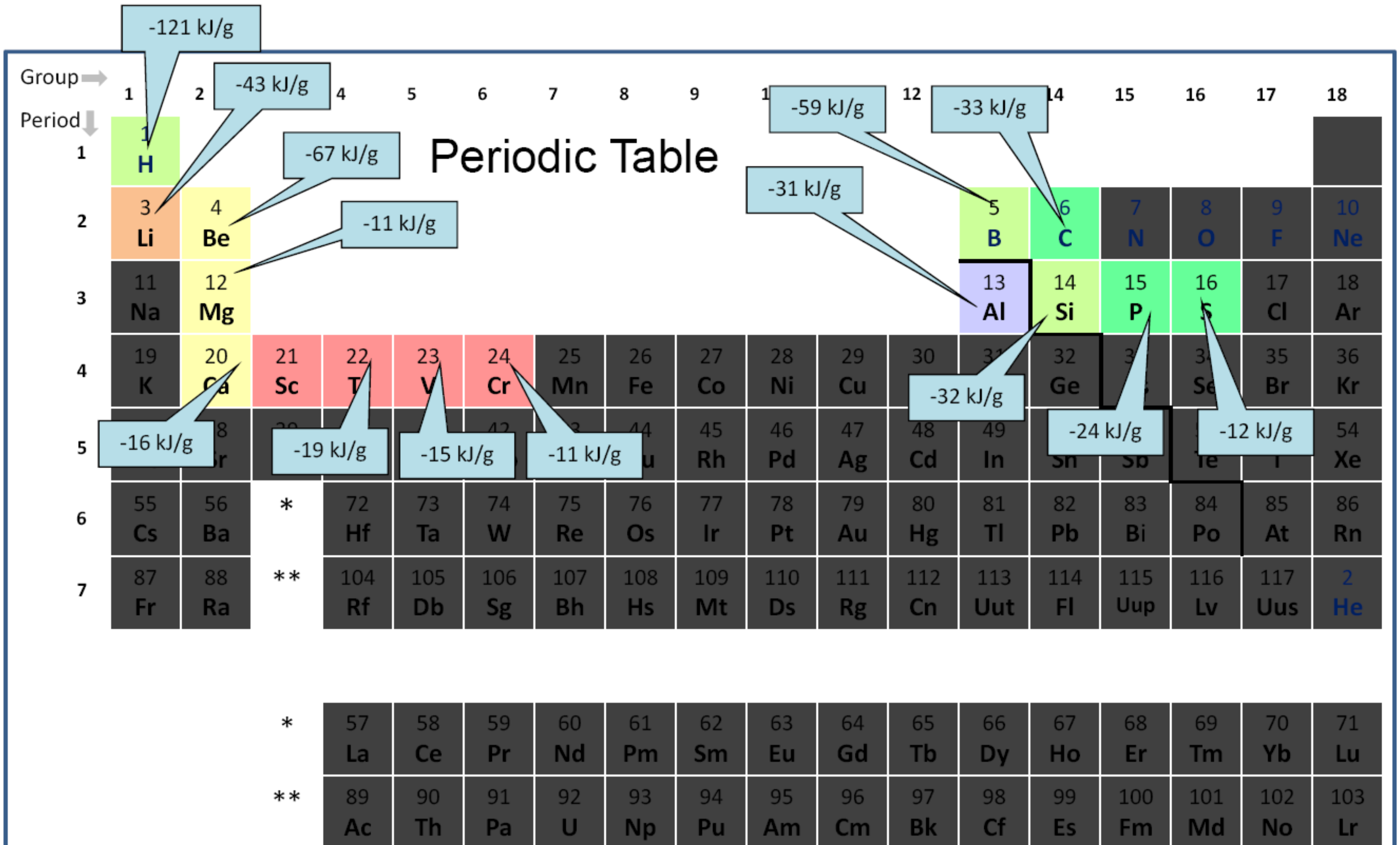
Gravimetric Energy Density



* 10-20 gallons of gasoline weighs approximately 30-60 kg, and releases approximately 45 kJ/g.

Need to carry about 1-2 GJ (equivalent to approx.10-20 gallons of gasoline*) to match functionality of current vehicles. Impractical to carry > 100 kg fuel. Hence, fuel needs to release > 10 kJ/g (preferably >> 10 kJ/g)

Highly endothermic compounds tend to be unstable. Equate maximum exothermicity of oxidation of compounds with exothermicity of oxidation of their constituent elements



Elements with enthalpy of oxidation > 10 kJ g^{-1}

Periodic Table

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1	1 H																	2 He
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3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Elements with non-solid oxides

Hydrogen and Carbon

Periodic Table

Group → / Period ↓	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
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3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu

Elements with enthalpy of oxidation > 10 kJ g^{-1} and non- solid (or non-toxic) oxides.

Oxygen and Nitrogen

Not desirable from a gravimetric and volumetric energy density standpoint, but…

Oxygenated fuels tend to have lower emissions of carbon monoxide, soot, and unburned hydrocarbons.

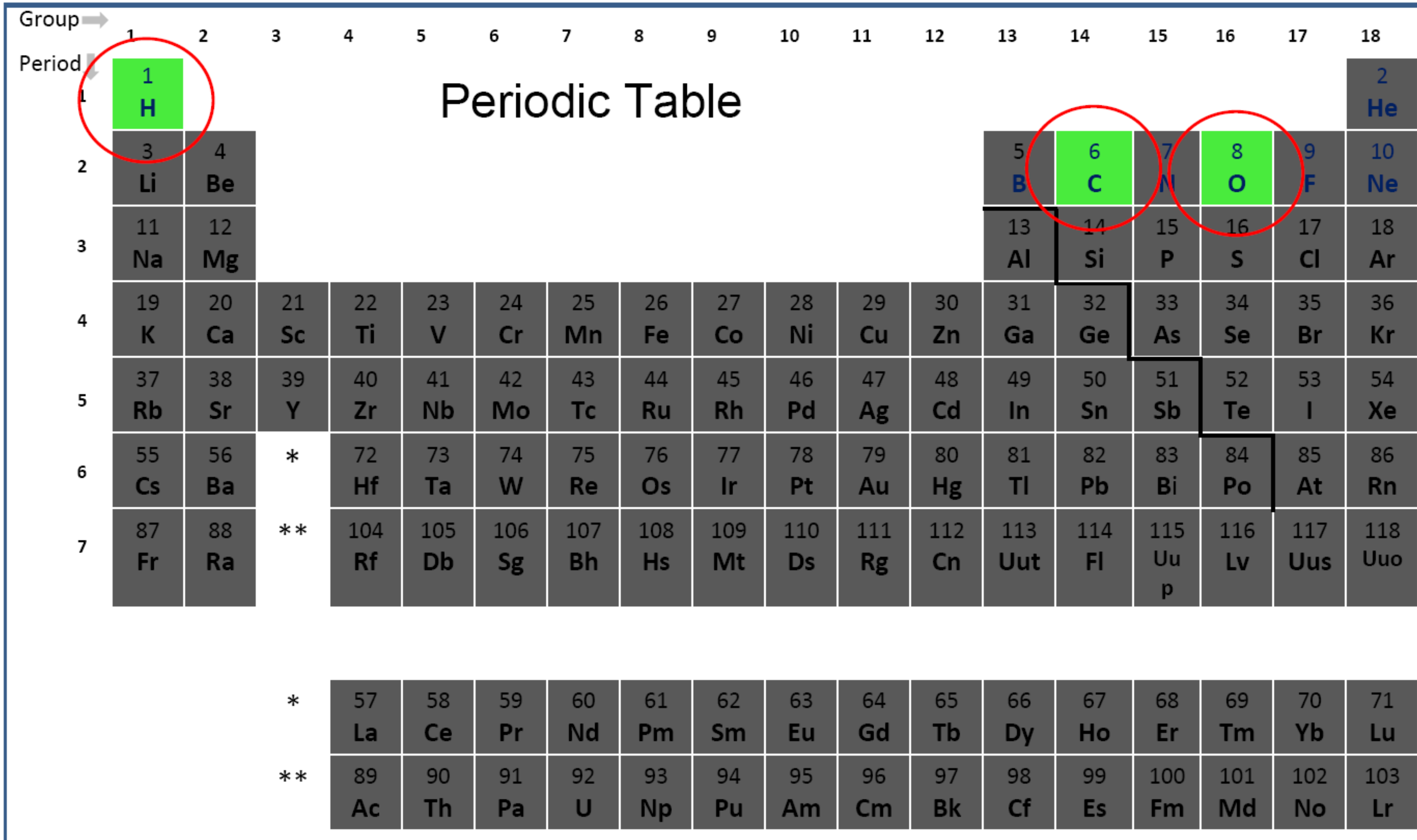
N containing fuels have higher NOx emissions, but can reduce to N_2 with catalyst and urea. A little bit of N is good for cleaning fuel injectors.

Hydrogen bonding in liquid fuels containing O and N results in enhanced evaporative cooling

+ decreases the likelihood of autoignition; increases fuel octane
+ increases amount of air in cylinder, and so power density

Biomass feedstocks (and some fossil fuels) contain a lot of O (glucose = $C_6H_{12}O_6$, cellulose = glucose polymer = $(C_6H_{10}O_5)_n$). Also some N. Perhaps it is not necessary to remove all the O and N from biofuels?

Hydrogen, Carbon, and Oxygen



Successful alternative fuels will be compounds containing H, C, and possibly O. (Maybe also some N.)

Elaborating on requirements

- Liquid with reasonably high energy density
  - Must remain liquid to -20 C, maybe lower
    - Serious safety issue in aircraft, cold countries
  - Want energy density > 8 MJ/liter
    - Comparable to or better than CNG
- Only contains C,H,O, maybe N
  - So it burns to CO_2 + H_2O. Other elements burn to harmful products.
  - N will burn to NO_x, but maybe catalyst can convert to N_2.

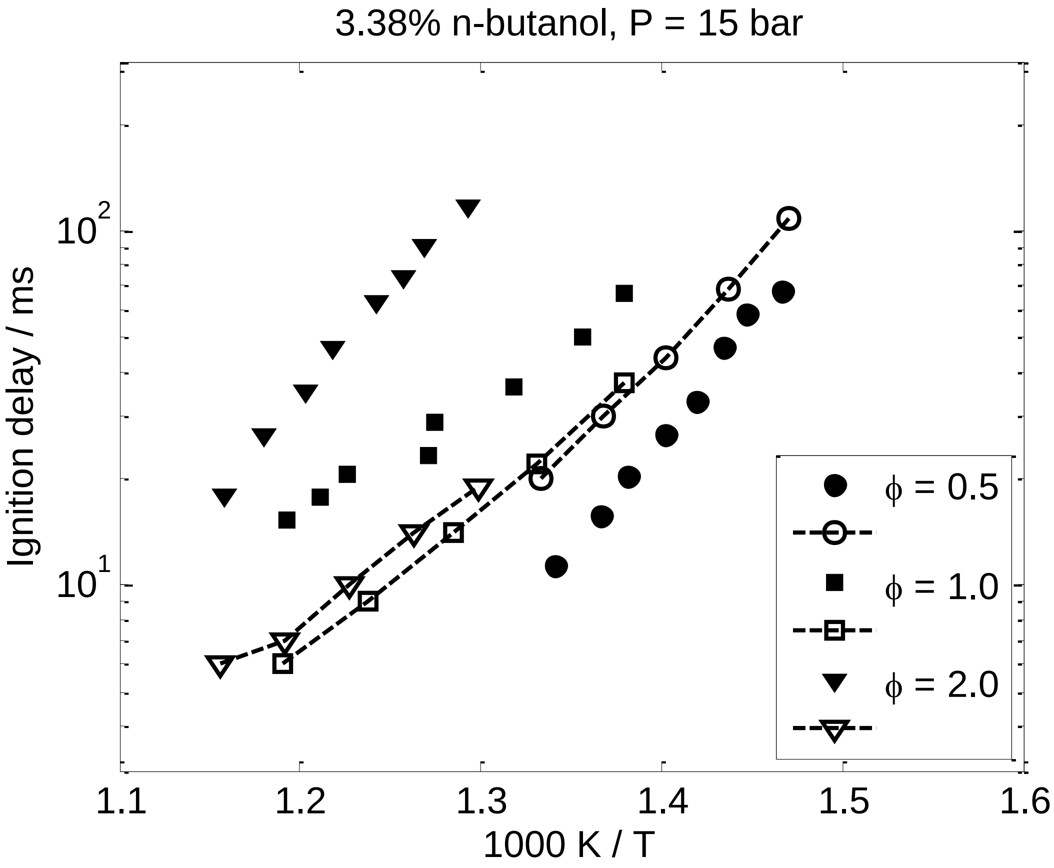
Requirements, Continued

- Not Corrosive
  - "Corrosive" depends on materials used in engine
  - "Backwards Compatible": want new fuel to work in old vehicles
  - Known issues with acids (in biofuels), high concentrations of alcohols
- Suitable Volatility
  - Must match fuel injection system
  - Want liquid to quickly evaporate to flammable gas.
  - Some molecules (e.g. sugars) pyrolyze to solids before they evaporate – <u>not</u> good transportation fuels.

Ignition Delay Suitable for Engine Cycle

- Ignition Delay Fundamentals:
  - Hot fuel+air mixtures spontaneously ignite after a delay.
  - Ignition Delay is *very sensitive* to fuel structure
  - Ignition delay also sensitive to T, P, stoichiometry
  - Measured as “octane” or “cetane”
- Different Engines require different delays
  - Diesels require spontaneous ignition (short delay)
    - Short delay also beneficial for turbines.
  - Spark Ignited engines do not want spontaneous ignition called “knock”: (want long ignition delays)
  - Not yet clear what is best for HCCI / Low-T combustion engines
    - Rely on spontaneous ignition, but don’t want all fuel to ignite simultaneously.
    - Rolf Reitz’s engine wants 2 fuels with very different ignition delays.

In Engine-Relevant Range, Ignition Delay Sensitive to T, P, [O_2], Molecular structure



10% change in T:
Order of magnitude in τ

Factor of 3 change in [O2]:
Order of magnitude in τ

n-butanol to iso-butanol:
86 to 98 octane

Sufficient Flame Speed

- Sensitive to T, P, stoichiometry, dilution
- Many fuels have very similar flame speeds
  - H_2, acetylene have unusually high flame speeds
- Flame speed very important in turbines running near lean limit, or in high speed flows
  - Flame can "blow out"
- Helpful in Spark-Ignited Engines

New Fuel Must be Cheap, Plentiful!

- New Fuel will be competing with petroleum.
  - Subsidies or regulations favoring new fuel will not last forever!
- It takes work to verify new fuel will not cause problems.
- It takes capital to build fuel production facilities.
- This work will not be done, and investors will not provide the capital, unless fuel looks economically viable and likely to be available in large volumes (millions of barrels).

Other Important Fuel Properties

- **Solubility/Phase behavior**
- **Consistency from batch-to-batch of fuel**
- **Environmental impacts**
- **Safety issues in handling/storing**
- **Storage Stability**
- **Viscosity**

Solubility / Phase behavior

- Most new fuels will be diluted into petroleum
  - If too much new fuel, may exceed solubility limit
    - Phase separation can form emulsion, may clog fuel filter or fuel injection system
  - Fuel is often exposed to water. Some fuel components may bind to water….
    - In pipeline (why ethanol shipped by truck)
    - In leaky gas station tank (migrate into groundwater)
      - Polar fuel components should be nontoxic/biodegradable!
    - In car fuel tank (can induce phase separation).
- Similar solubility limits and phase separation problems for fuels not mixed into petroleum

Batch-to-Batch Consistency

- Fuels composed of materials in nature are variable
  - Fossil Fuels differ from place to place
  - Biomass differs depending on plant, soil, weather
- Engine and fuel processing/distribution system work well for limited range of fuels
  - Industry has many fuel specifications
- An off-spec batch of fuel can be a very big economic loss (10 kbd = $1M/day)

Fuel Specs to Reduce Environmental Impacts

- High volatility leads to high evaporative emissions: air pollution
  - Reid Vapor Pressure spec, vapor recovery systems
- In some situations, some fuels lead to a lot of particulates (soot, aerosols) : health, climate
  - Public Health studies: big effect on mortality
  - Aromatics spec, some soot specs
- Emissions control is often most important constraint on engine design/operation
  - Sulfur spec, metals specs
- Some fuel will be spilled in environment. Some fuels much more harmful than others in spills.
  - Biodegradable?

Fuel Safety Issues

- Most fuels are dangerous!
  - Fire: 35 MJ/liter !
  - Toxic, Carcinogenic, fumes affect brain, etc.
- Fuel design can reduce the fire risk
  - Low volatility fuels hard to ignite (lean limit)
  - High volatility fuels: vapor flushes air out of tank
  - But all fuels can burn, and fuel storage/handling has to scrupulously follow fire safety procedures
  - Some fuels are particularly dangerous
    - Form explosive peroxides on storage
    - Invisible flame
    - Detonatable mixture can form
    - Penetrate skin on contact

Fuel Storage Stability

- Most fuels slowly react with air
  - Make peroxides and other oxygenates
  - Can phase-separate as “gum” or explosive crystals
- Some fuels polymerize
  - Particularly if high concentration of dienes
  - Untreated bio-oil rapidly polymerizes (acid-catalyzed condensation of oxygenates)
- Origin of “olefin” spec on gasoline
- Many fuels are treated with additives (antioxidants, radical traps) to increase storage stability. Still a problem if fuel is stored for months.

Viscosity

- Big advantage of liquid fuels over solids is that they flow.
- Viscous fluids don't flow easily, not good fuels
  - Glycerol (from production of biodiesel)
  - Sugars (from biomass)
- Fuel injection systems are designed for certain viscosity range: more specs fuel has to meet

We want alternatives to reduce environmental impact, increase supply and security, reduce/cap price (Part 1).

We reviewed many alternatives (Part 2), and the properties alternative fuels must satisfy (Part 3).

Most alternative fuels are diluted into gasoline or diesel, and so priced like oil. But production cost of new fuel is more than production cost for petroleum.
Is there another way forward?

Part 4: A third fuel at gas stations?

Alternative Liquid Fuels: The $64,000 Question

- Currently most new liquid fuels are diluted into petroleum-derived gasoline or diesel
  - Minimizes engine perturbation
  - No need for new distribution infrastructure
  - New fuel valued about same as oil. (**Risk: oil price can fall below cost to produce the new fuel**).
- In the future, will gas stations stock some new 3rd fuel in addition gasoline and diesel?
  - Would open up many new engine possibilities.
  - Could insulate new fuel from oil price shocks.
  - New fuel might command higher price than oil.
    - **But only if it provides a big advantage!**

Some possible 3rd fuels

(which would be kept separate from gasoline & diesel)

- Oil insoluble biodegradable fuels?
  – Polyols, certain other polyoxygenates
  – Most likely from biomass
  – Relatively little is know about this option.
- Oil-soluble molecules with **special advantages**
  – Methanol, ethanol (GTL, CTL, or bio)
    - Unusual vaporization & energy density
    - Octane boost when directly injected into cylinder
  – Heavier oil-soluble oxygenates (from biomass)??
    - Similar to oil, any advantage to keep separate??

What is needed for a 3rd Fuel to become established?

- All stakeholders must consent
  - Vehicle makers
  - Fuel makers/distributors
  - Political leaders
  - Consumers
- Mutual consent must persist for many years
- What could prompt such remarkably broad and long-lived consensus?

What could prompt long-lived consensus on a new fuel?

- All the stakeholders should derive some benefit from the new fuel's introduction.
  - There must be a significant advantage to the 3rd fuel.
  - How to share the benefit amongst all shareholders?
- Most challenging for fuels which mix into oil.
  - ***Must be a clear advantage in keeping the new fuel separate, otherwise it will be diluted in petroleum.***

Dual-Fuel Engines Might Provide a Niche for a New Distinct Fuel

- John Heywood et al. (MIT) invented a dual-fuel gasoline+alcohol engine, more efficient than conventional SI
- Rolf Reitz et al. (Wisconsin) invented a dual fuel gasoline+diesel engine, more efficient and lower emissions than conventional diesel
  - "…can improve diesel engine fuel efficiency by an average of 20%...the best tests achieved 53% thermal efficiency" *Mech. Eng.* (Nov. 2009)

Approaching a fork in the road…

- Huge change in liquid fuel mix is coming:
  - There is not enough oil! It is expensive!
  - Current system is not environmentally responsible.
  - No one has energy security.
- Difficult to predict which fuels will fill gap
  - depends on policy decisions (climate, security, economics)
- Window of opportunity to add a 3rd fuel at the pump
  - Electricity (e.g. plug-in hybrid)?. Gases?? Polar liquids??
  - A third oil-soluble fuel could become widely available, if…
    - new vehicle technology can deliver big advantages by keeping the third fuel distinct.
    - The benefits of the new fuel are perceived and shared amongst the many stakeholders.

Quiz Question #4

- The military has explored the possible use of NH_3 (ammonia) as an alternative fuel. List some concerns you have that would need to be explored before this fuel is widely deployed.

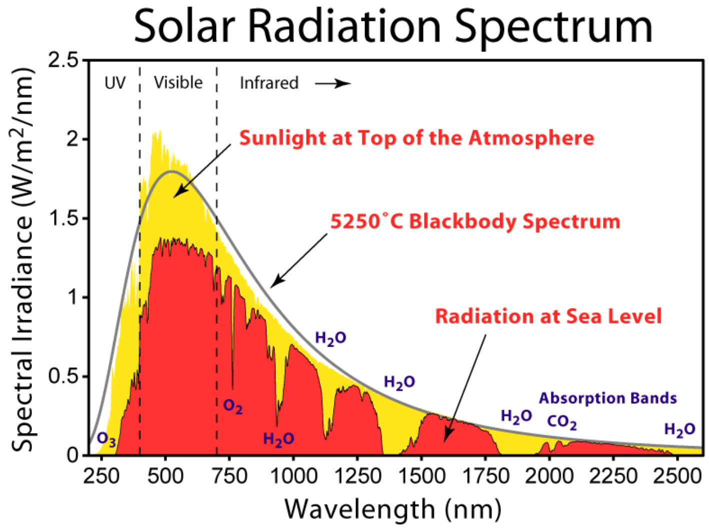
Part 5: BioFuels

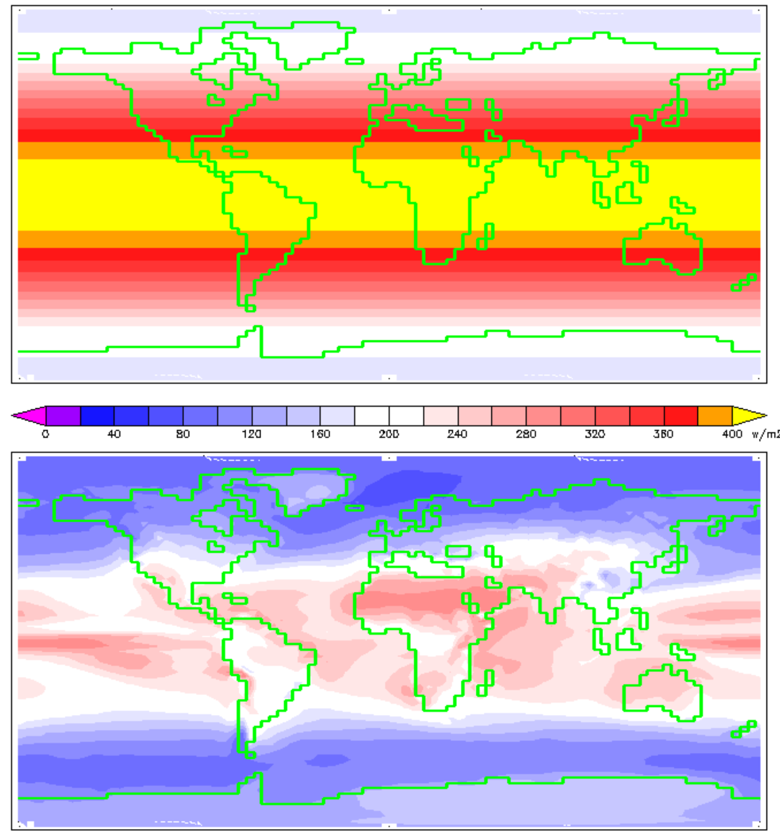
a) The Source: Biomass. Competing Uses.
b) Current BioFuels: Ethanol & Biodiesel
c) Biological Processing
d)Thermochemical Processing

Biomass Overview

- Historically, biomass was main energy source for mankind
  - Well-established low-capital solar-energy technology
- Currently, the most-used renewable energy source
- Many historical examples of biomass resource depletion
  - England, Easter Island deforestation
  - Sahel desertification
  - Whale oil
- Scale and Land Use resources are a challenge
- Possible better ways:
  - Waste from agriculture, forestry
  - Energy crops / algae on waste land

Photosynthesis captures some Solar Energy





- Solar “constant”: 1366 W/m^2
  - Measured outside the earth’s atmosphere
  - Varies with seasons

$$6\ CO_2 + 6\ H_2O + \text{photons} = C_6H_{12}O_6 + 6\ O_2$$

Photosynthesis ~ 1% efficient

Energy stored <3 MW / $(km)^2$ arable land

Biomass Source Fundamentals

- Photosynthesis stores **~300 EJ/yr** as biomass energy
  - Human energy use **~400 EJ/yr**
  - Carbon cycle: plants die, decay to CO_2
  - In fertile areas ~ 10^{-5} $EJ/(km)^2/yr$
    - Requires ~250 kg H_2O to grow 1 kg biomass
    - Often requires fertilizers, esp. N fixed using fossil fuel process
  - Earth's total land surface ~$10^8 (km)^2$
- For large scale biomass energy NEED LOTS OF LAND (even much more than solar) and WATER
- If you have spare land and fresh water, relatively inexpensive to grow and harvest (e.g. much less capital than photovoltaic solar!)
  - But conversion process to good liquid fuel is not free
- Less of an energy security issue than other fuels: population is highest in fertile areas full of biomass

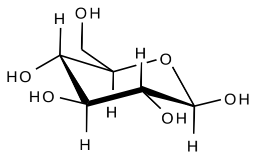
What is biomass? Properties

- Solid carbon-based fuel (like coal)
  - H:C ~1.5 , O:C ~1
  - Significant metals, S, N
- Wet: about 50% water before drying
  - Low energy density ~9 MJ/kg wet
  - Can preprocess (“torrefaction”) to ‘charcoal’
- Diffuse production, relatively low energy density: **expensive to harvest, ship**.
- Annual cycle: biomass available only at harvest time, may need to be stored.

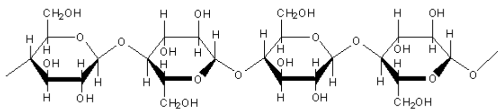
The main components of biomass are

carbohydrates & lignin (+proteins, lipids, salts)

Carbohydrates



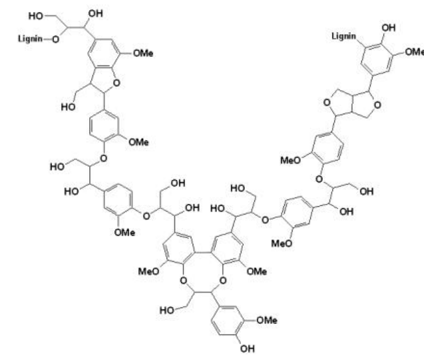
D-glucose



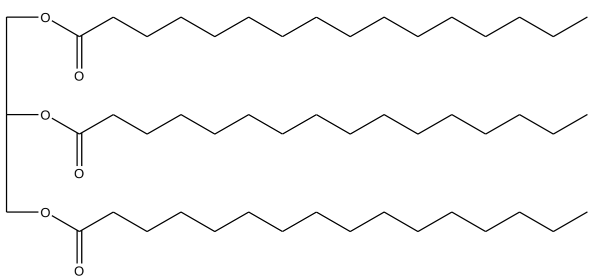
Cellulose

Mostly cellulose & hemicellulose

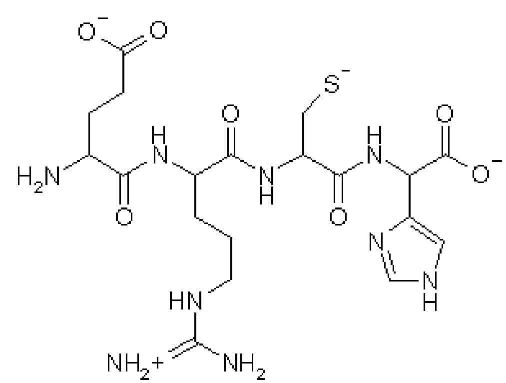
Lignin



Fats



Proteins



Lignin image from wikimedia foundation, peptide image from http://www.steve.gb.com/images/molecules/amino_acids/glu_arg_cys_his_(pH_10).png.

Biomass has many uses, not just energy!

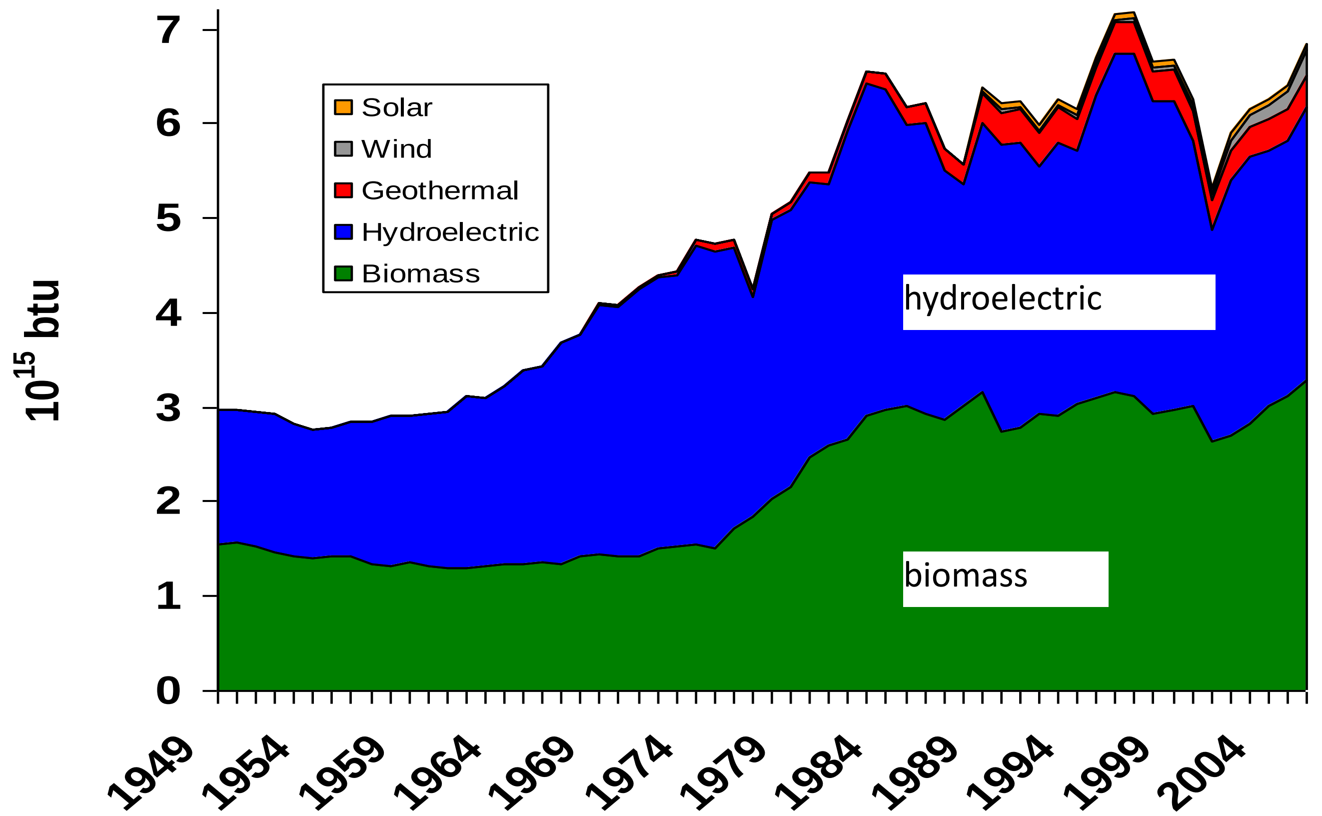
- Energy uses
  - Heat
  - Electricity (including co-firing)
  - Liquid Fuels for Transportation

- Many important non-energy uses
  - Food for humans
  - Animal feed (a major and growing use)
  - Lumber & other construction materials
  - Clothing (cotton, wool, linen, leather)
  - Paper, packaging, etc.

Bioenergy as Goal or Bioenergy as Byproduct?

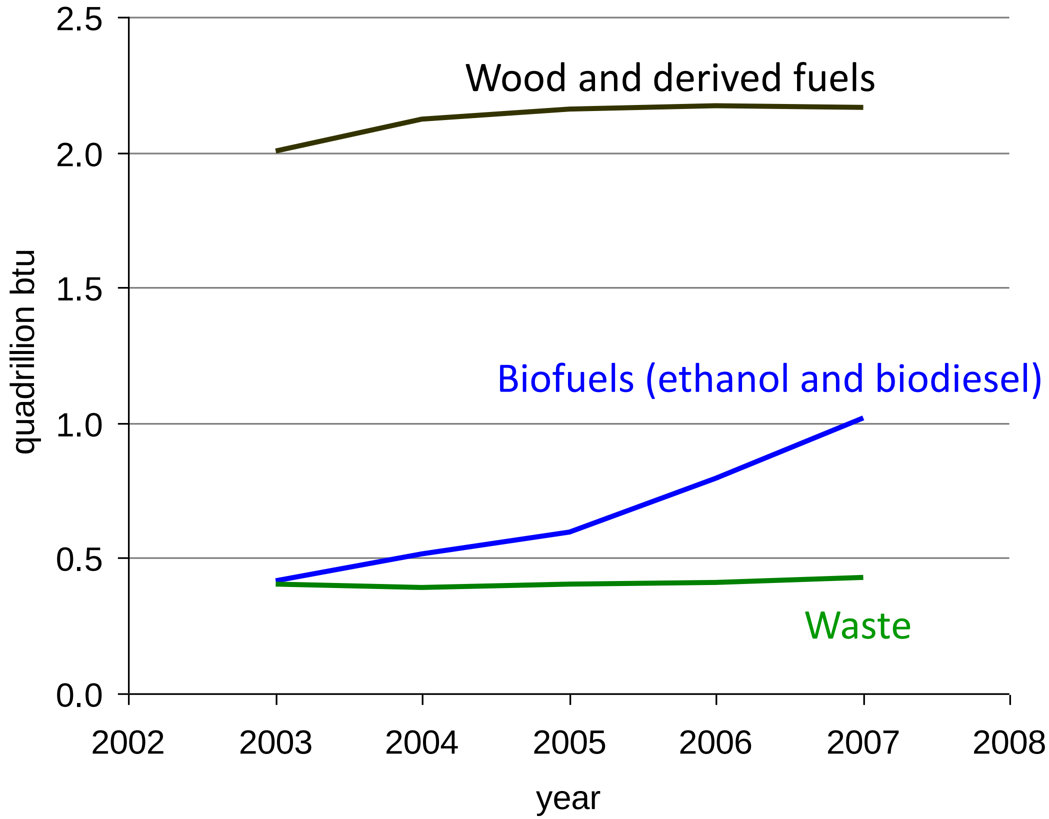
- Historically, biomass products (food, lumber) have been considered more valuable than biomass energy.
- Existing policies and practices focus on agriculture, lumber, land use, etc.; only waste or surplus biomass used as energy.
- Focus needs to shift for biomass to become important on global energy scale.
- Food price shocks and food riots a few years ago have raised awareness of the important competing uses of biomass, arable land, water, etc. Unclear how much land etc. society should devote to energy (vs. food and other important land uses.)

Biomass is largest source of renewable fuels



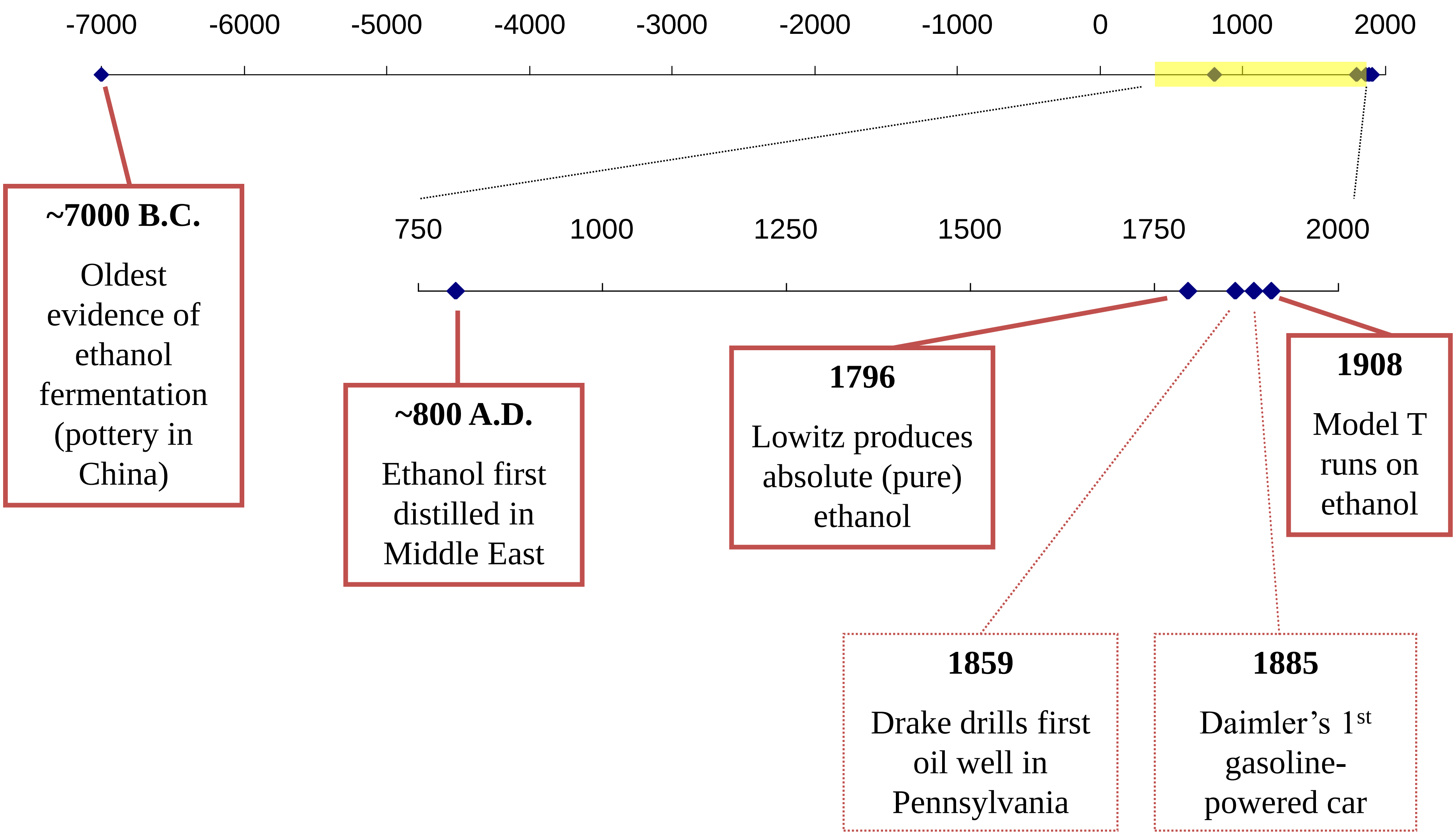
Biomass is currently the largest source of renewable energy. Relatively simple to convert many biomass components into liquid fuels

Biomass energy use is currently dominated by wood, but government regulations driving rapid expansion of ethanol and biodiesel production



CURRENT BIOFUELS: ETHANOL & BIODIESEL

Ethanol: the original biofuel.



Ethanol is made by yeast when no oxygen is present.

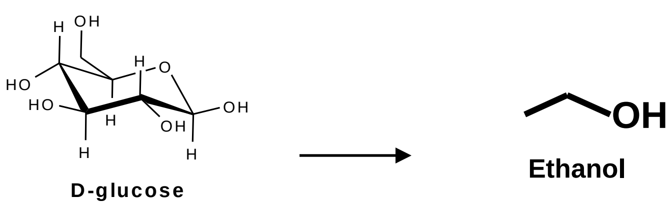
If oxygen is available, cells use it-

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

Without oxygen, cells salvage a little energy with fermentation-

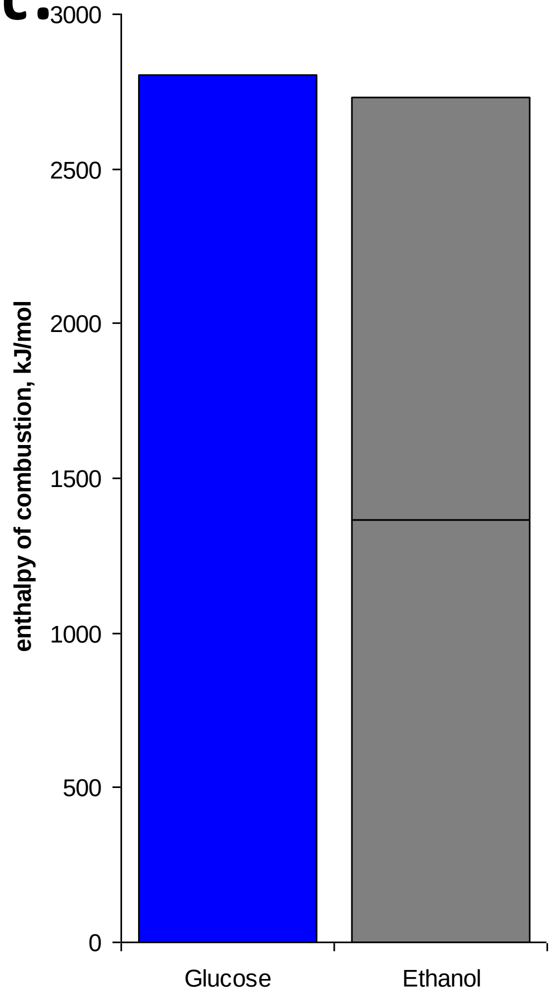
$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 + 2\ ATP$$

Fuel upgrading

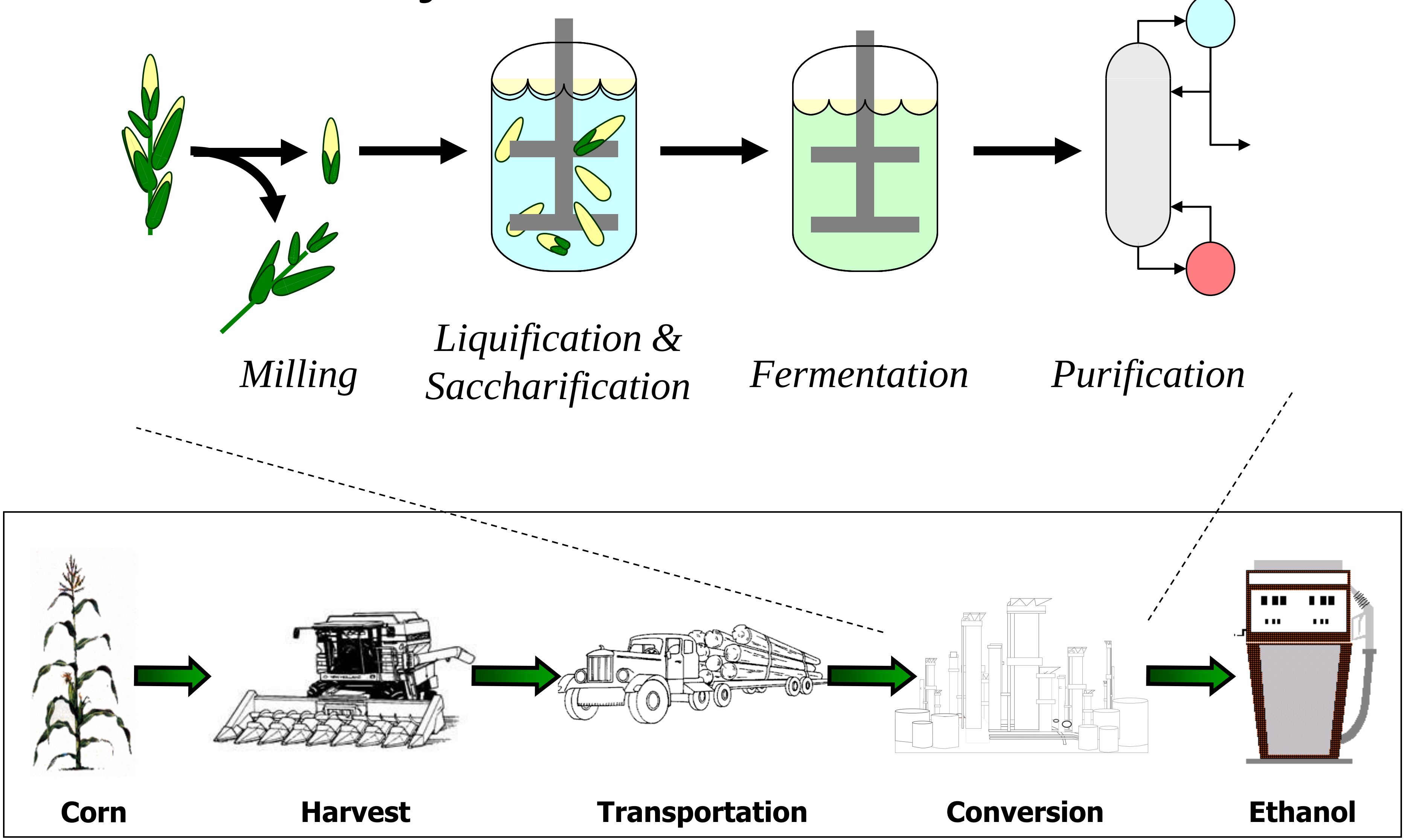


16 MJ/kg, solid

27 MJ/kg, liquid



Ethanol production involves more than just fermentation.



Slide adapted from Jeremy Johnson, MIT PhD 2006.

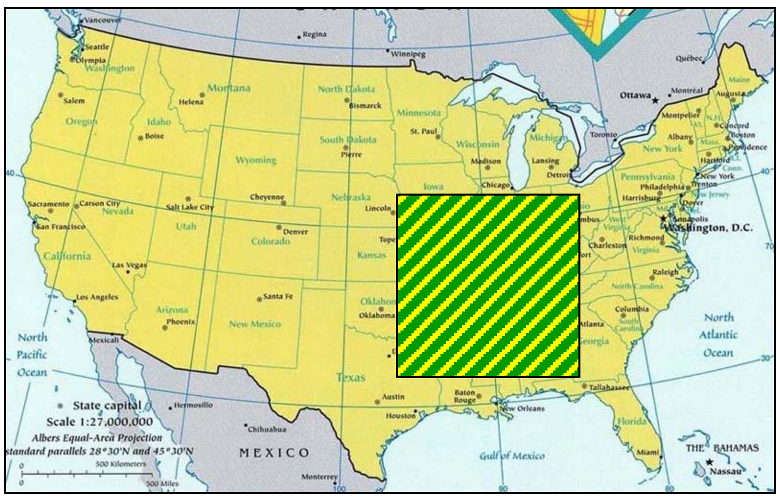
Cornstarch takes too much land.
Waste Biomass could replace up to 1/3 of fuel

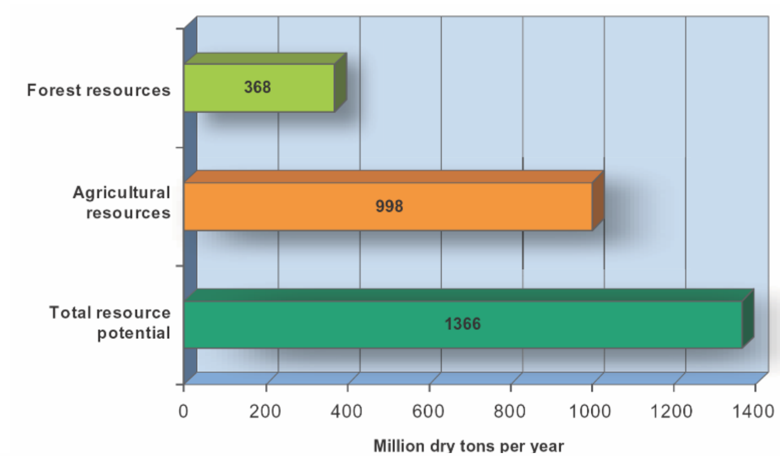
<u>Corn ethanol</u>

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

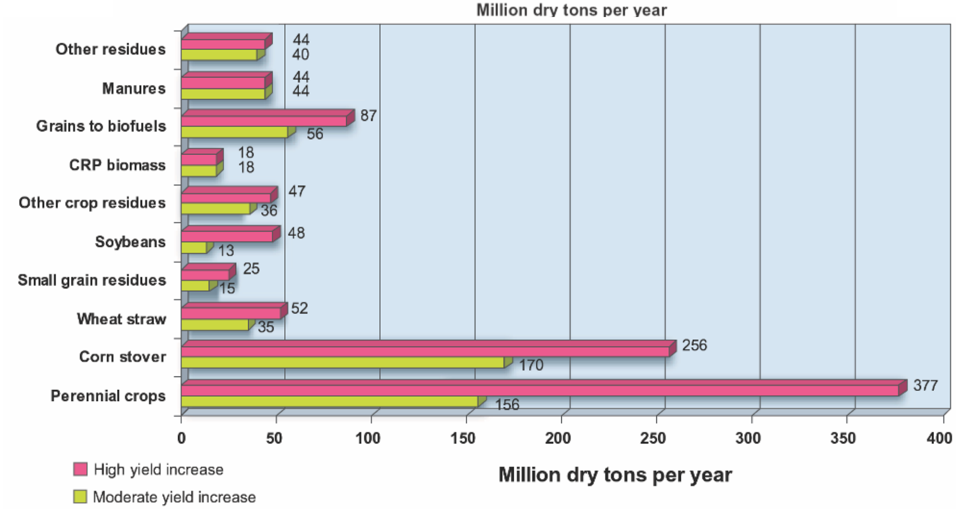
<u>DOE/USDA Billion-ton study</u>

- 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



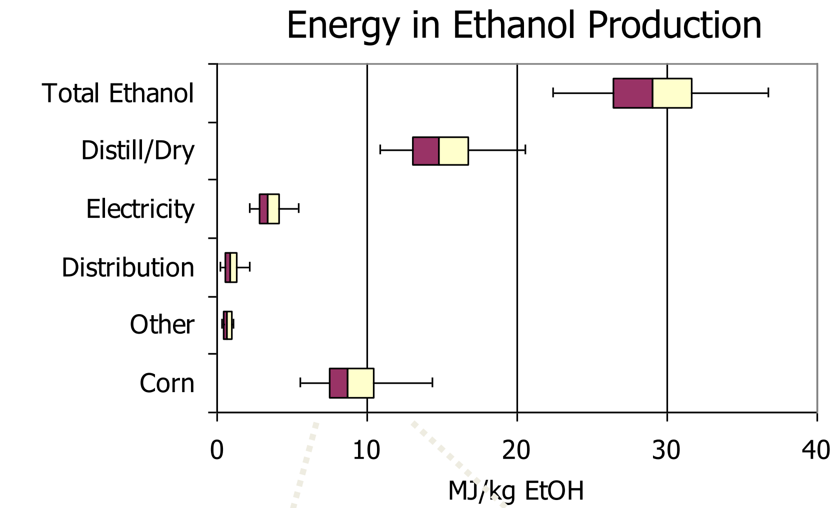


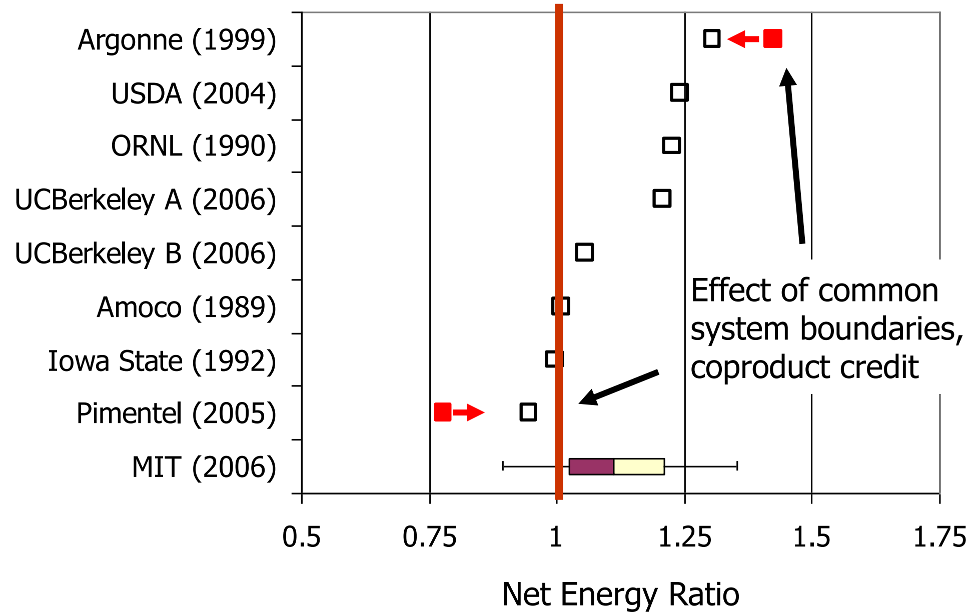
Currently, Corn Ethanol replaces about 5% of gasoline energy in USA. Industry believes it could expand: E10 vs. E15 debate now underway

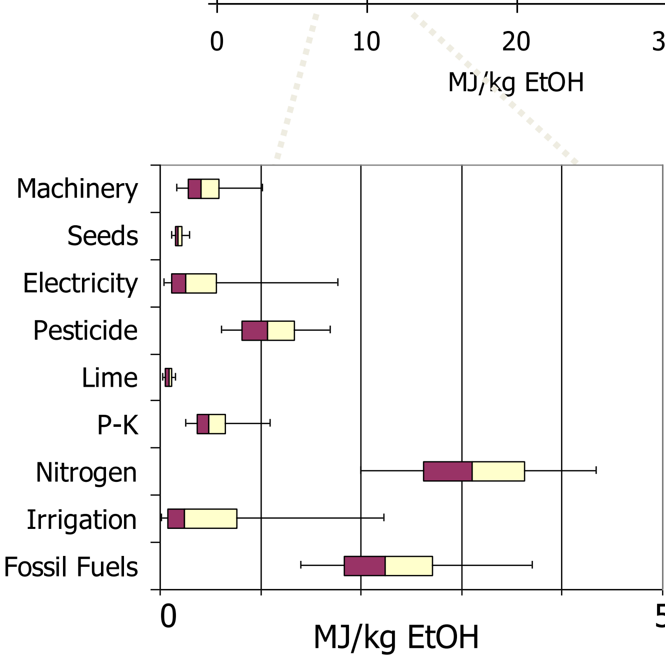


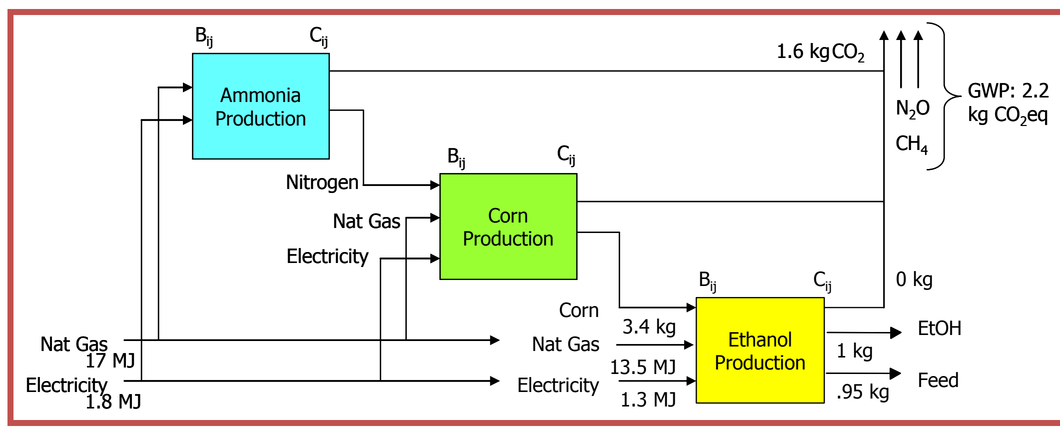
Billion-ton Study: DOE/GO-102995-2135 2005.

Corn Ethanol Energy Content = Energy of Fossil Fuels used to make it!



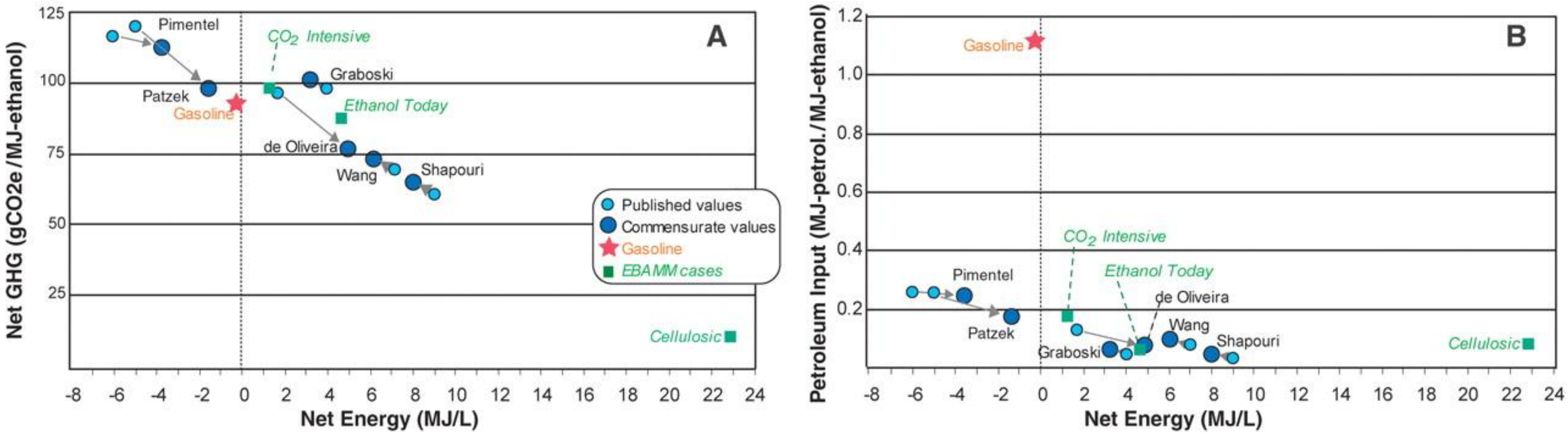






Slide adapted from Jeremy Johnson, MIT PhD 2006.

Lifecycle Analysis shows Ethanol made from biomass (whole plant, not just cornstarch) would have GHG benefits



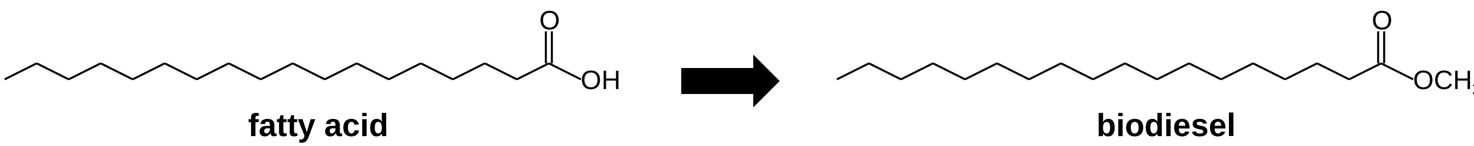
Science 311(5760) 506-508 2006. doi: 10.1126/science.1121416

Unfortunately, despite active R&D, subsidies, a government mandate, and many companies working on it, ethanol from whole biomass not yet commercial. Price of production ~$120/barrel.

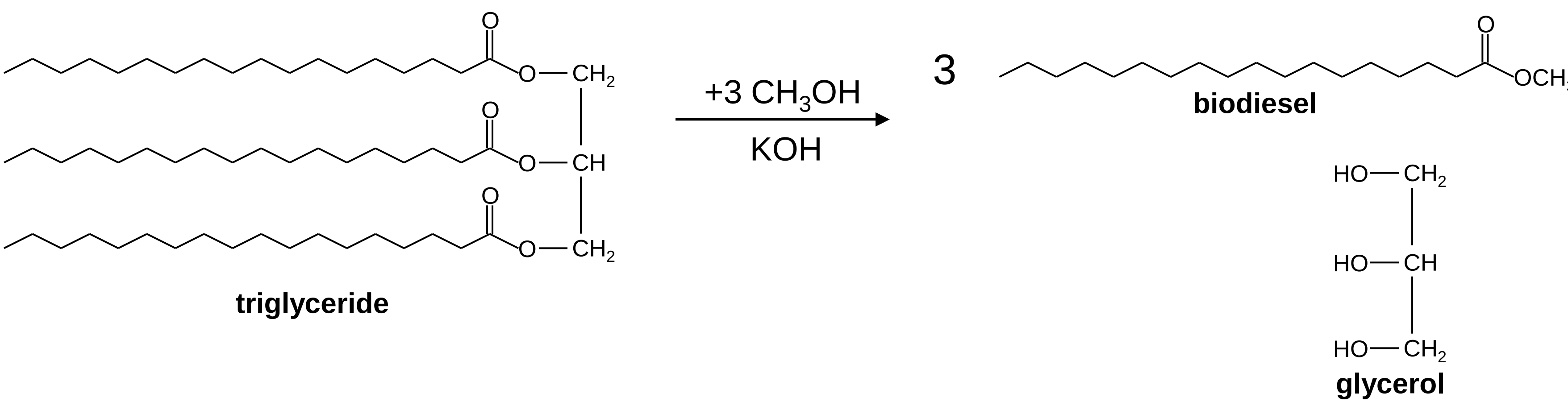
Biggest plant (under construction in Italy) is < 1 kbd.

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

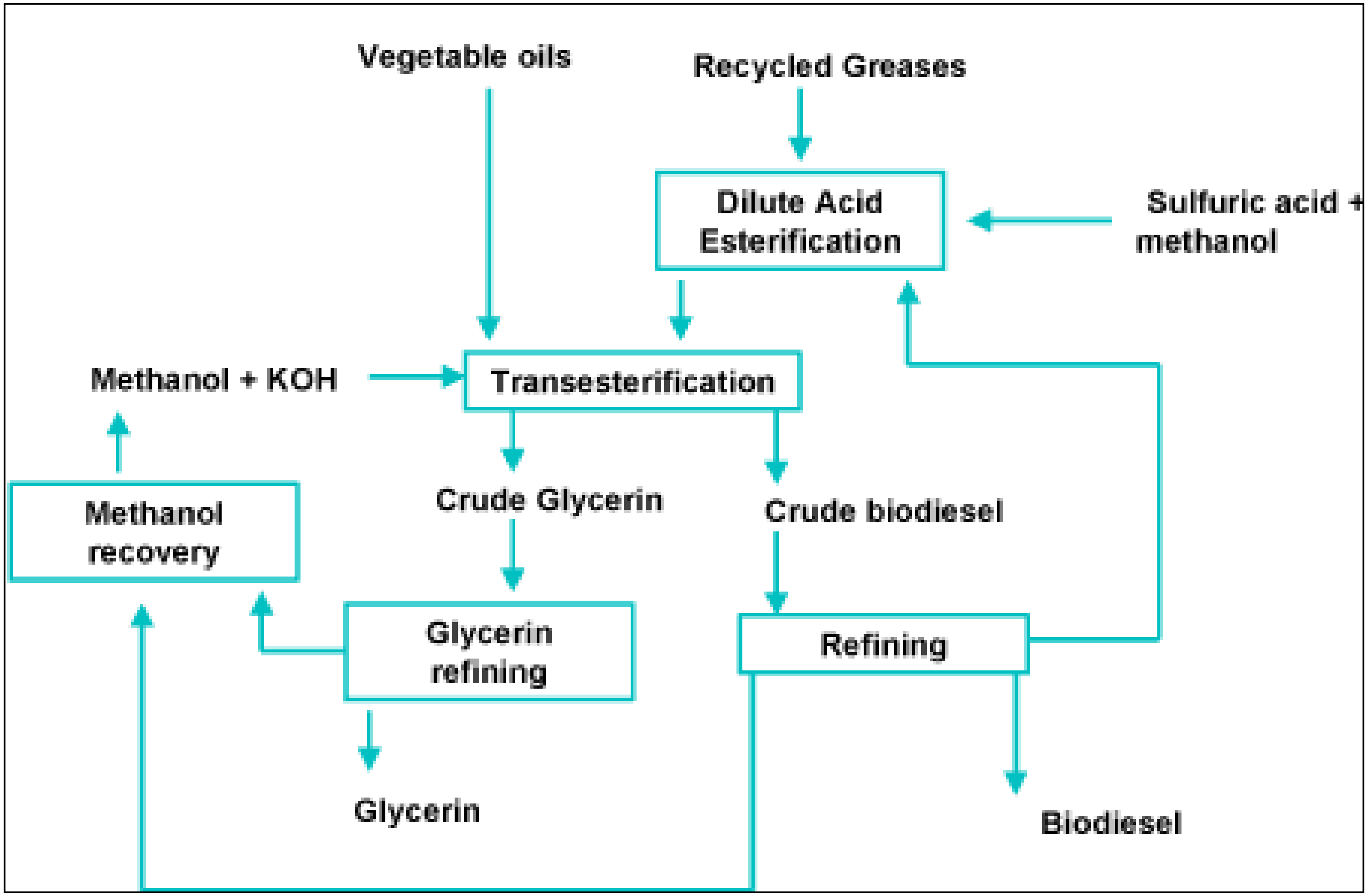
Goal:



Detailed:



Biodiesel processing is fairly mild.



Mild temperatures: 50-80°C
Atmospheric pressure

PFD from DOE EERE.

Biodiesel is a good fuel. Why don't we use more of it?

- Problem is SCALE, use of farmland or rainforest:
  - Oil Palm: 600 gallons/acre/yr
    - Replaced some 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 good 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: R&D underway on decarboxylation & hydrodeoxygenation

Quiz Questions #5 & #6

- Write down some likely consequences if someone were to invent a very inexpensive method for converting wood into high quality liquid transportation fuel.
- Would this invention solve the Energy problem? Briefly explain your answer.

Biomass to BioFuel Conversion Options:

BIOLOGICAL CONVERSION OF BIOMASS

Using biomass for energy: options

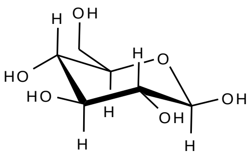
- Burn it for electricity or heat
  - US Paper/Wood industry: 6 GWe
  - Coal is usually cheaper for large-scale
  - Good option with carbon cap: mix biomass with coal.
- Convert to Gas (CH_4 or CO/H_2)
  - Widely practiced on small-scale using waste
  - Coal-to-syngas and natural gas are cheaper
  - Only economical with very tight carbon cap
- Convert to Liquid Fuels
  - Looks to be most profitable on large scale:

    not many good competing alternatives to oil!

Biomass is a low-BTU solid: needs to be chemically converted to be good fuel.

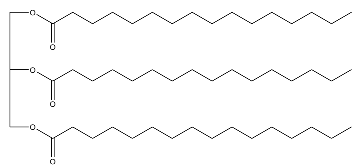
	Biomass	Conventional Fuels
State	• Solid	• Liquids or gases
Energy Density	• Low [Lignocellulose: ~10-20 MJ/kg]	• High [Gasoline: 43.4 MJ/kg]
Moisture Content	• High [Corn: 15% moisture delivered]	• No moisture content
Oxygen Content	• High [Often 10-40% oxygen]	• No oxygen content [<1% oxygen]
Compatibility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

Biomass contains more oxygen and is structurally different from fuels.

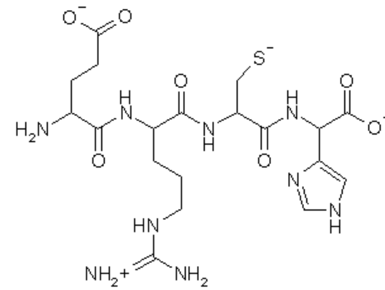


D-glucose

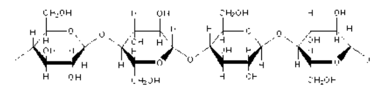
Carbohydrates



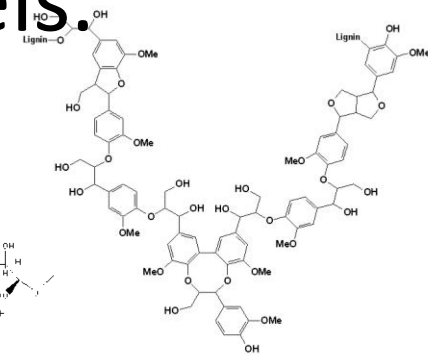
Fats



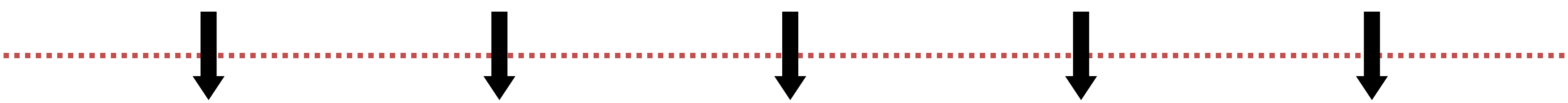
Proteins



Cellulose



Lignin

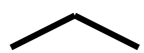


H_2

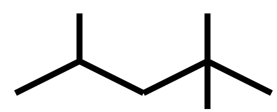
Hydrogen

CH_4

Natural Gas
Methane



Propane
LPG / NGL
Autogas



Gasoline
Petrol
Naptha

Diesel

Lignin image from wikimedia foundation, peptide image from http://www.steve.gb.com/images/molecules/amino_acids/glu_arg_cys_his_(pH_10).png.

Biomass conversion techniques

Biological

- Using microbes to convert biomass to fuels
- Growing plants or algae which produce fuels directly.

- Pros
  - Can engineer organisms to make chemicals with high specificity
- Cons
  - Requires specific chemical inputs (e.g. certain sugars)
  - Low throughput
  - Separations issues for both feed and product fermentation broth.
- Examples:
  - Ethanol, CH_4, butanol

Thermochemical

- Using traditional chemical processing methods

- Pros
  - Can handle less pure feedstocks
  - Higher throughput
- Cons
  - Extreme T, P may be needed: capital cost.
  - Subject to catalyst fouling, inorganic precipitation
  - Product is a mixture.
- Examples
  - Biodiesel, syngas, pyrolysis bio-oil

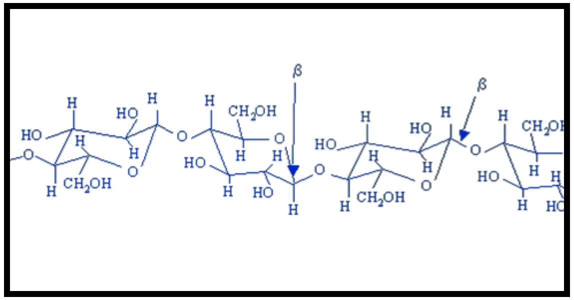
Photosynthesis directly to fuels?

- Commercial example: palm oil
  - Pretty good, but still requires too much arable land.
  - Maybe possible to engineer even more efficient fuel-producing plants
- Lots of interest in algae which make oils
  - Could grow in brine ponds in desert
  - Very dilute in water: separation issues!
  - Prone to contamination killing desired algae strain
- Possible to engineer plants in many ways to ease conversion to BioFuels
  - Release cellulose from lignin when harvested?

But most researchers have decided to leave agriculture alone, instead try to process existing plant biomass into BioFuels using microbes.

Biomass is mostly ‘Lignocellulose’: three polymeric components.

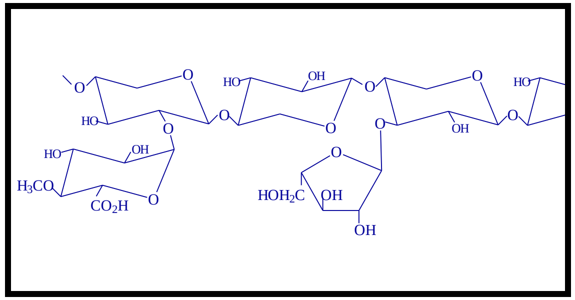
Cellulose



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

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

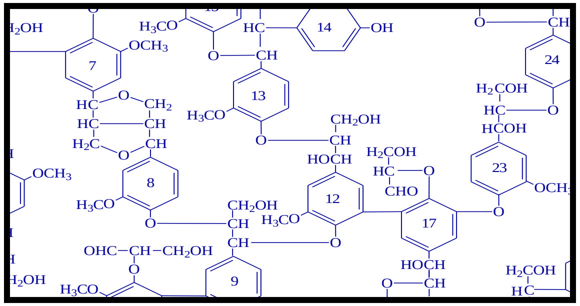
Hemicellulose



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

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

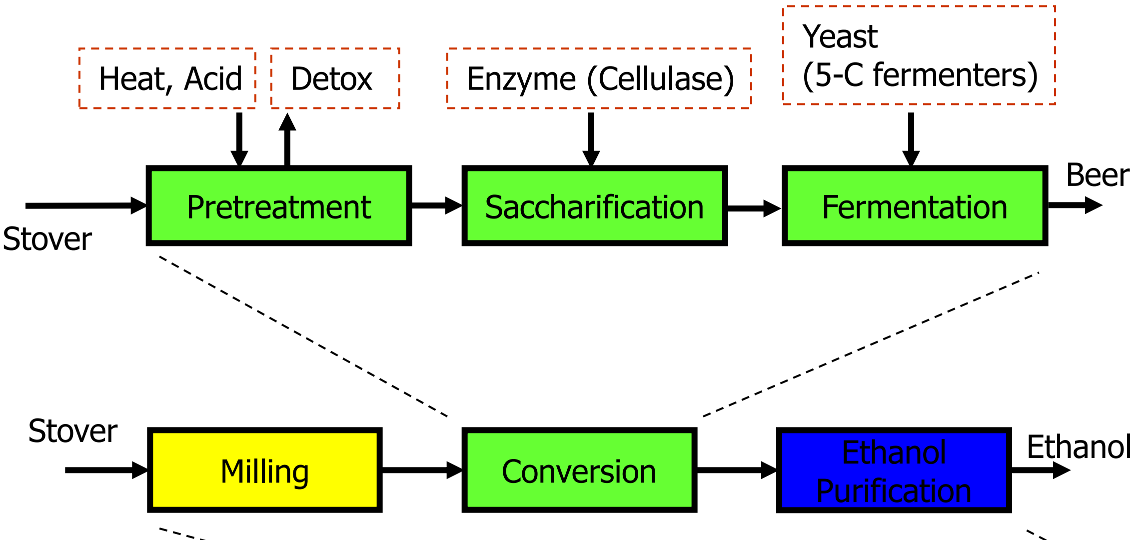
Lignin

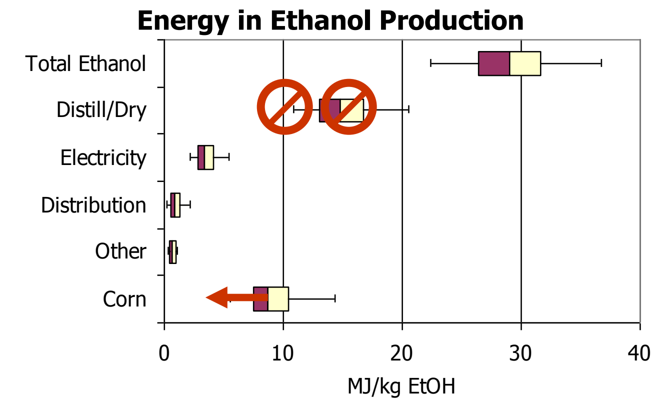


- Phenyl ether units [not fermentable]
- Structure:
  - highly polymerized
  - epoxy-like role in cells

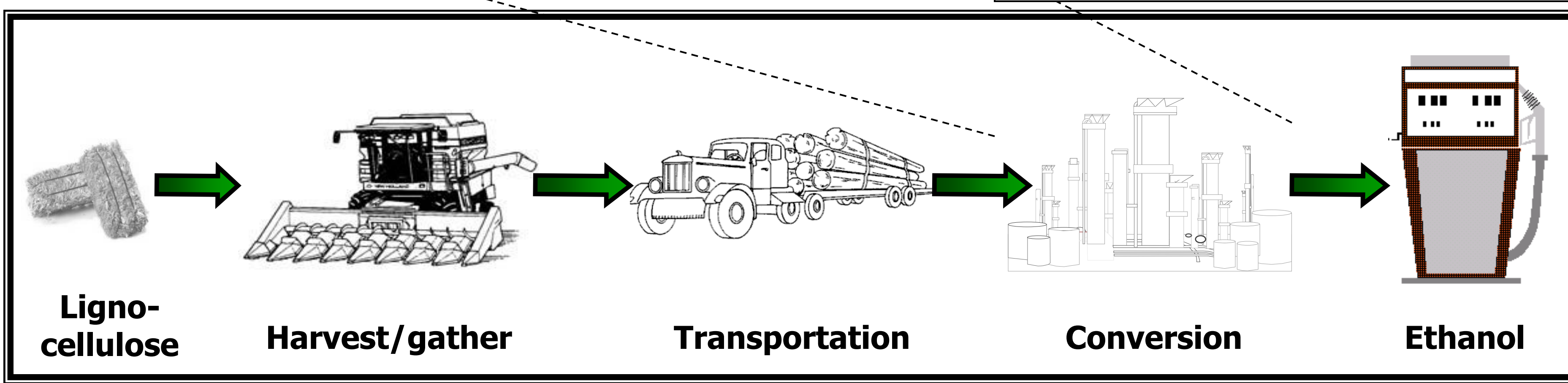
  [difficult to break down!!]
- ~21 MJ/kg

Cellulosic ethanol via sugar fermentation requires pretreatment, burns lignin.



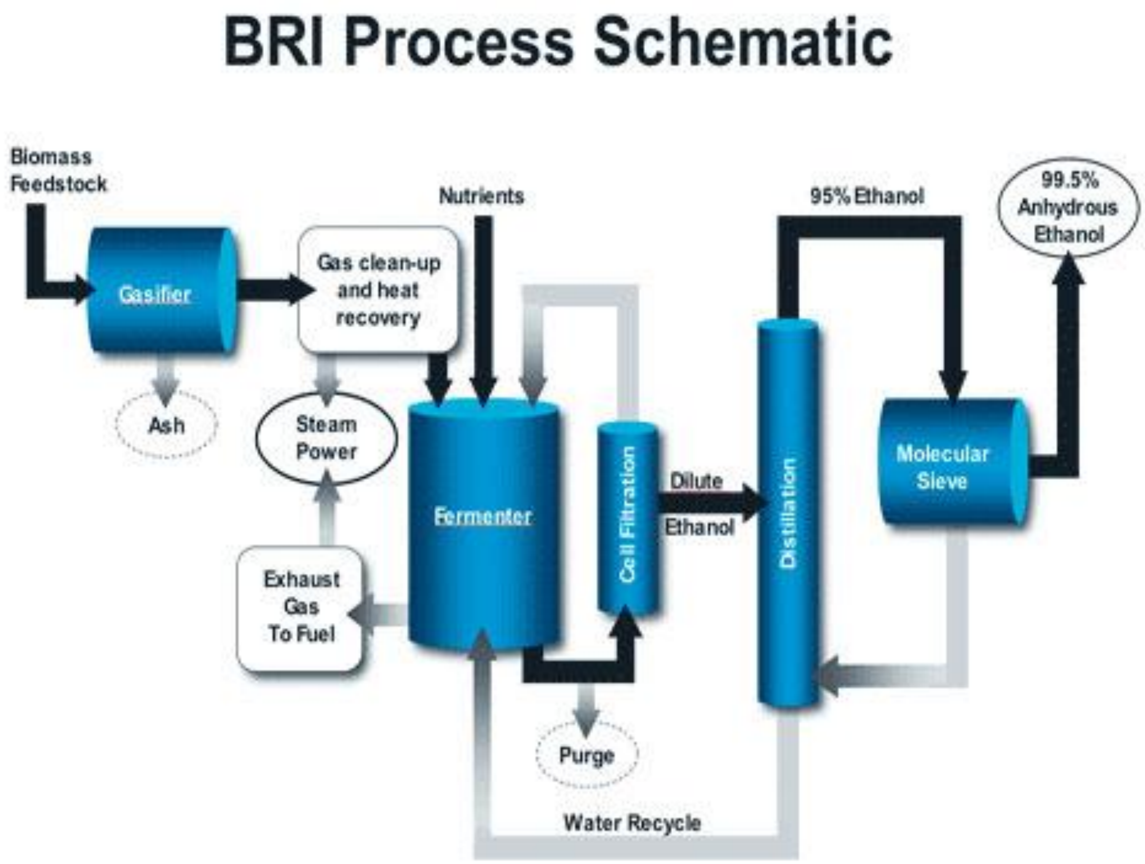


- No DDGS: no drying animal feed.
- Lignin has no value: burned to power distillation column.
- Lower ag inputs than corn production.



Slide adapted from Jeremy Johnson, MIT PhD 2006.

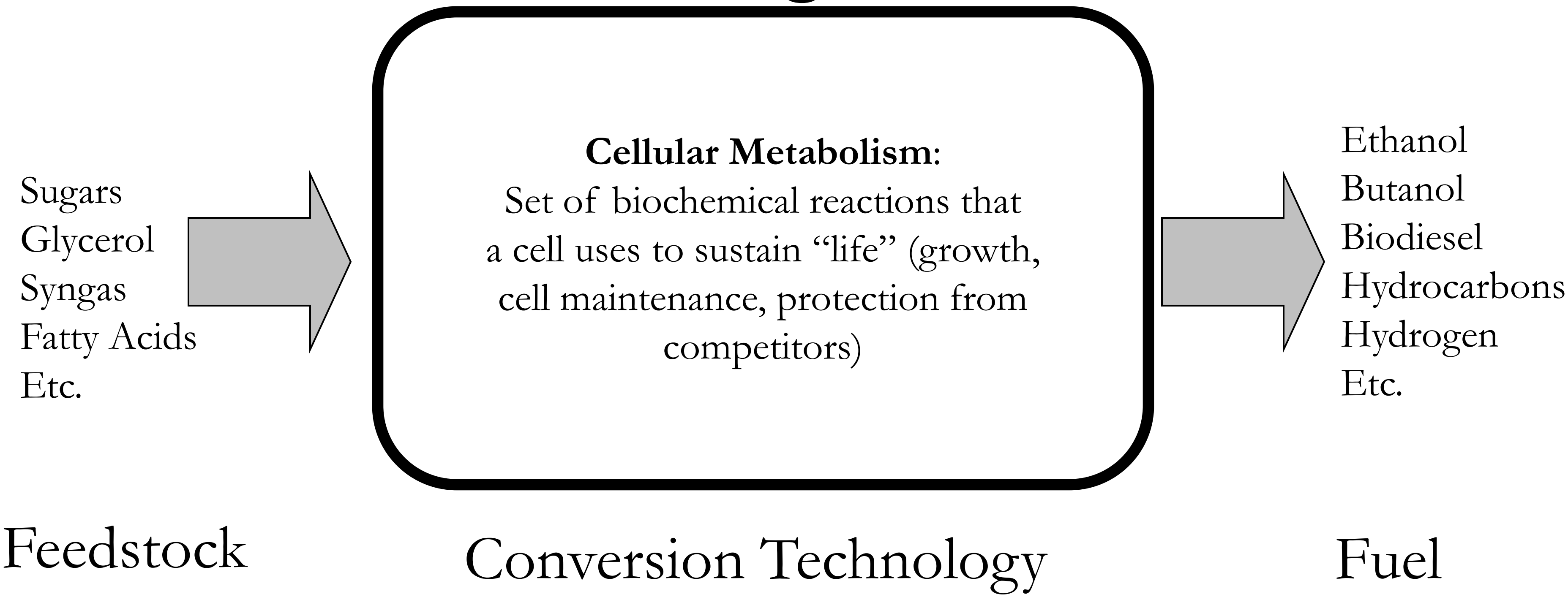
Alternative to converting biomass to sugars: can gasify biomass to syngas, and feed syngas to certain bugs.



- Hybrid thermochemical / biological process
- Syngas produced from biomass
- Syngas fermented into ethanol
- Ethanol from the whole plant, rather than only sugars
  - Both cellulose & lignin gasified; most other cellulosic ethanol doesn't use lignin

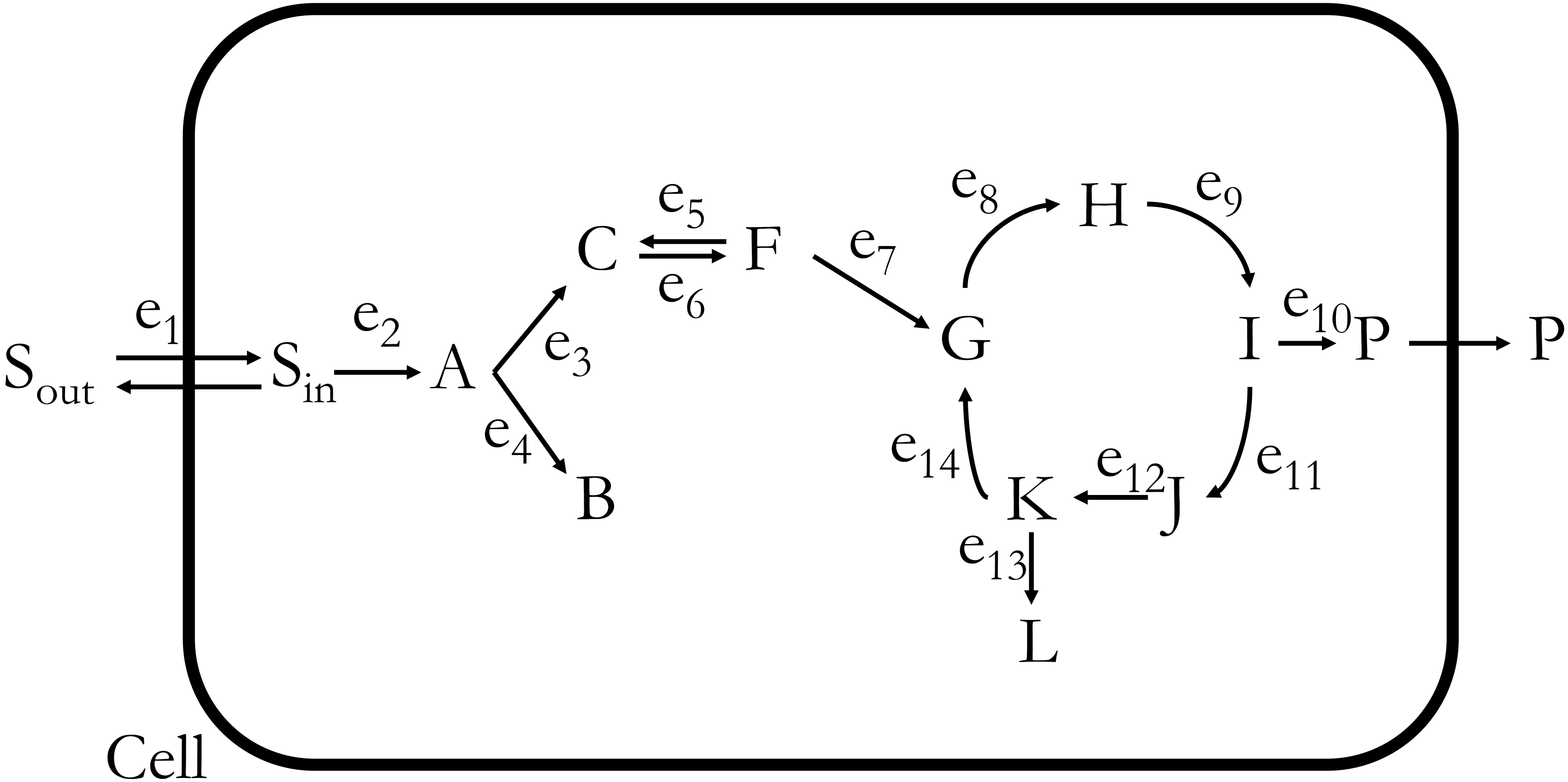
Source: BRI company website, http://www.brienergy.com/pages/process01.html

Biomass to Biofuels using Microorganisms



Slide courtesy of Daniel Klein-Marcushamer.

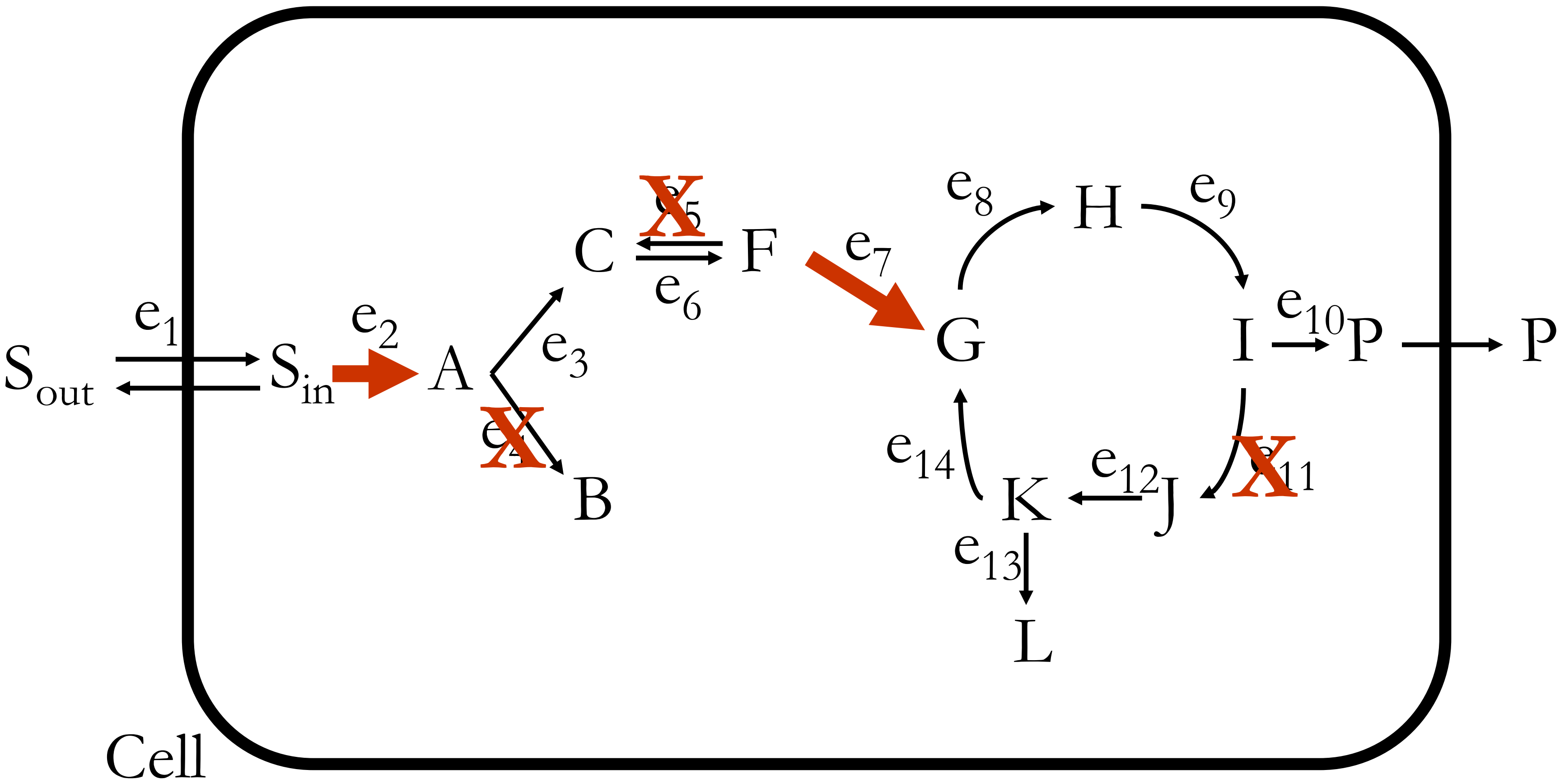
What is Metabolic Engineering?



e_i = Enzyme *i*

Slide courtesy of Daniel Klein-Marcushamer.

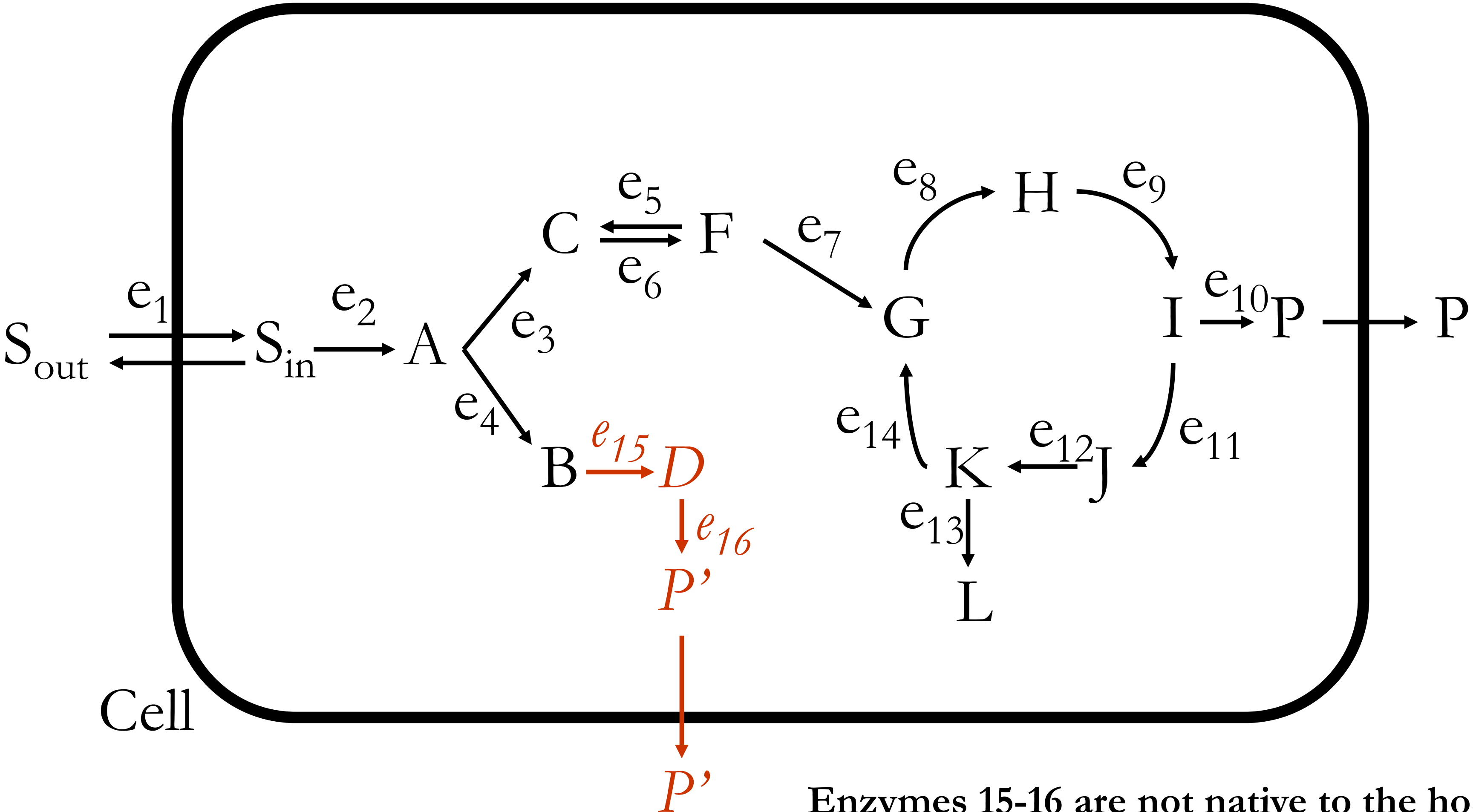
What is Metabolic Engineering?: Gene overexpression and deletion



e_i = Enzyme *i*

Slide courtesy of Daniel Klein-Marcushamer.

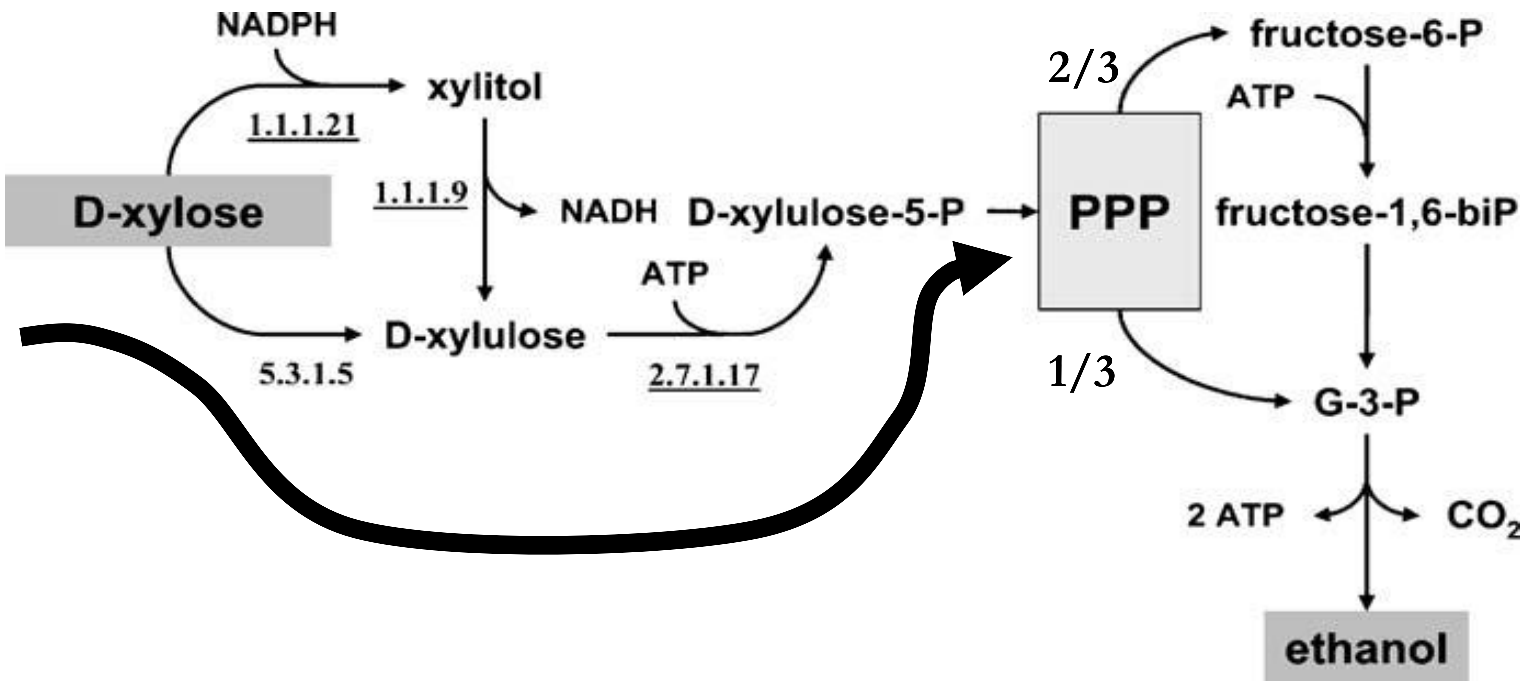
What is Metabolic Engineering?: Introduction of heterologous genes



Enzymes 15-16 are not native to the host

Slide courtesy of Daniel Klein-Marcushamer.

Metabolic Engineering example: Xylose-fermenting *Saccharomyces cerevisiae*



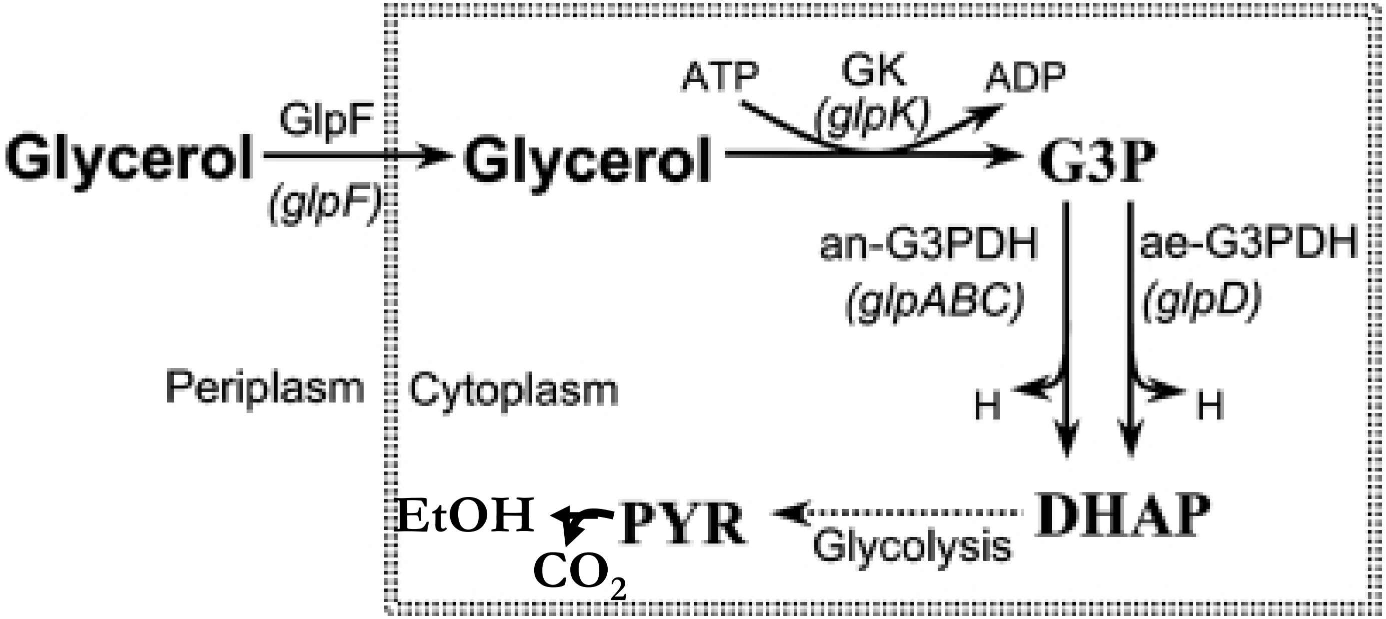
Heterologous route is preferred:

6 Xylose = 10 Ethanol + 10 CO_2 + 10 ATP

Source: *Adv Biochem Engin/Biotechnol.* 2007. doi 10.1007/10_2007_057

Slide courtesy of Daniel Klein-Marcushamer.

Another Example:
Glycerol-fermenting *Escherichia coli*

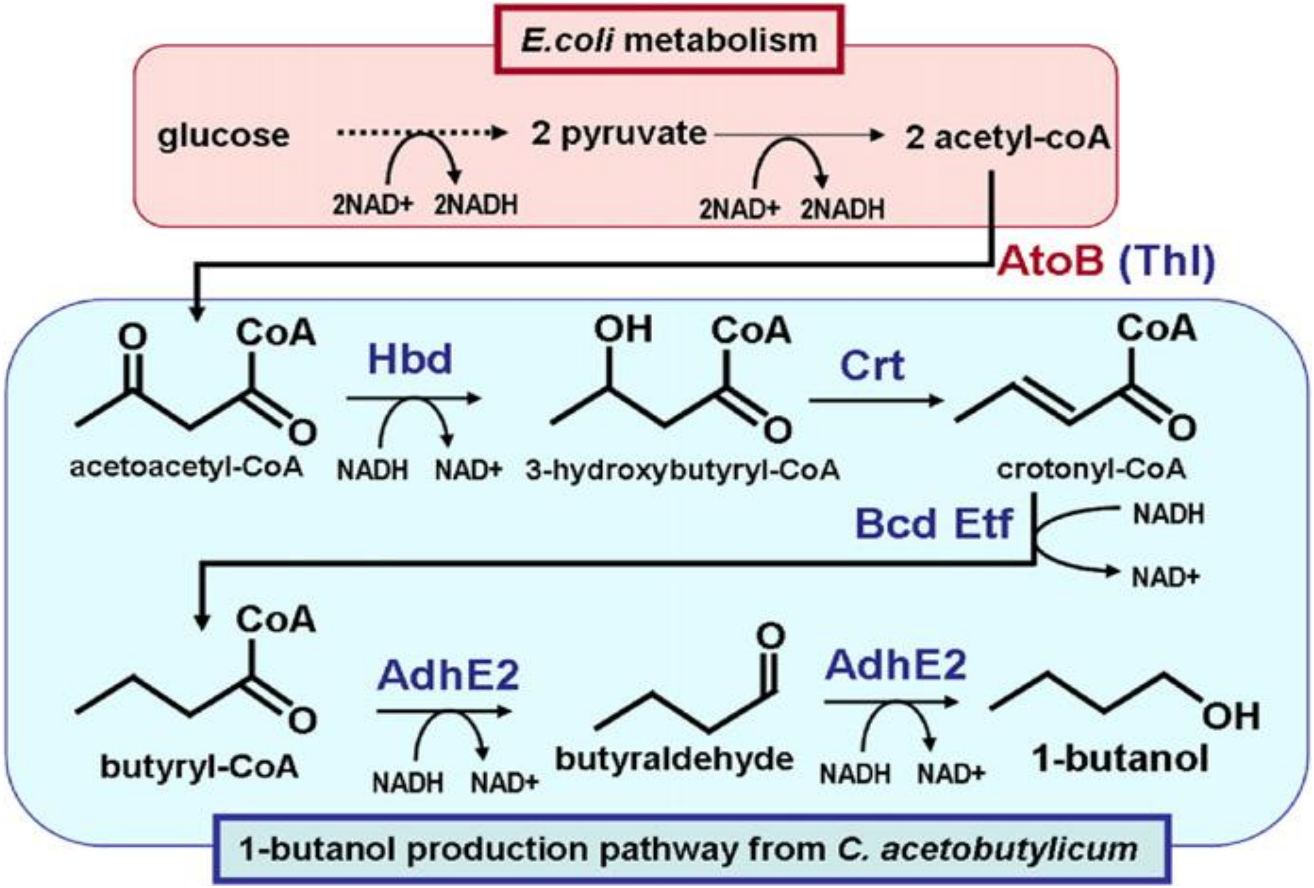


Source: *Appl Environ Microbiol.* 2008 doi: 10.1128/AEM.02192-07

Slide courtesy of Daniel Klein-Marcushamer.

Inserting whole pathways:

Butanol-producing *Escherichia coli*



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

Slide courtesy of Daniel Klein-Marcushamer.

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

LS9 plans to make petroleum from sugar

Mascoma has microbes that make cellulase and ethanol

BP and DuPont aim to commercialize butanol

Coskata plans ethanol from syngas for $1/gal

And dozens of other companies, this is just a sampling
Not an endorsement of these particular companies!

Biological Conversion Summary

- Many biological routes. Could engineer plant or algae, but most researchers converting products from existing plants.
- Bio-processes are slow, but equipment (fermentation tanks, stills) is not expensive.
- Most bugs require pure sugars
  - Harvesting/transporting biomass is expensive
  - Converting biomass to pure sugars is expensive
- Can engineer bugs to make specific fuel molecules you want in high purity: What do you want?
  - Easy to separate from fermentation broth?
    - Products usually present in grams/liter water (~0.1%)
    - Ethanol titer is unusually high: ~12%
    - Separation (distillation) is significant energy cost
  - Choose a molecule with Special Fuel Advantages??
    - Might help protect new fuel from oil price fluctuations

Biomass to BioFuel Conversion Options:

CHEMICAL CONVERSION OF BIOMASS

Many biomass conversion options

- Direct processes on whole biomass
  - Fast pyrolysis (maybe with catalysts)
  - Gasification to syngas (H_2 + CO) & thence synfuels
  - Hydrothermal conversions
- Preprocess biomass to sugars (as in bio routes)
  - Reduces fouling of catalysts
  - With pure feeds, can optimize catalysts

Cooking Biomass Unzips Polymers, Makes Some Liquids: "Bio-Oil"

- Rapid heating of biomass in the absence of oxygen
- Various complex oils and organics formed: needs further chemical conversion steps
- Process produces some (fairly useless) solids and some gases as well as desired liquids.

Fast Pyrolysis

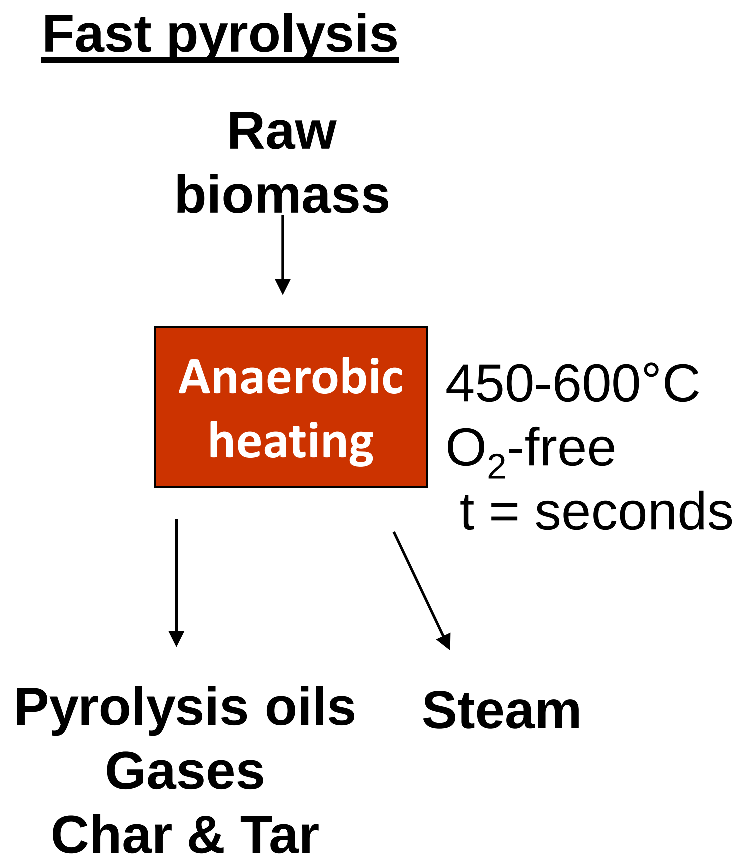
- Short residence times (seconds)
- Atmospheric pressure
- Raw bio-oil is acidic, reactive
- Energetic losses to evaporation

Hydrothermal Liquefaction

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

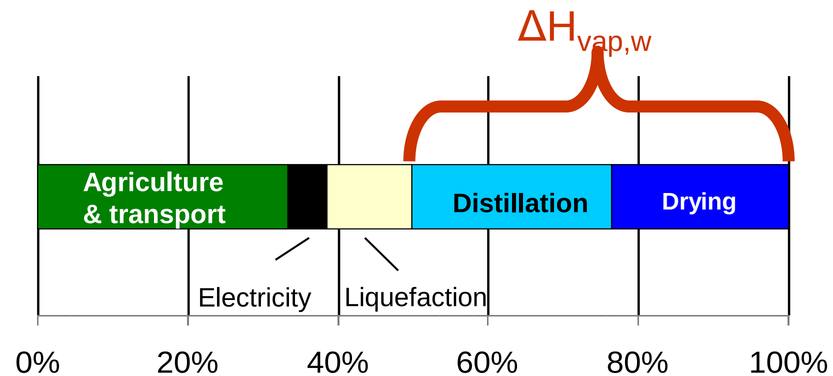
Fast pyrolysis makes bio-oils at atmospheric pressure in a few seconds.

- Often uses fluidized beds of sand or catalyst as heat transfer medium.
- Produces oil (containing up to 15-20% moisture), char, and gases.
- Bio-oil contains a lot of oxygen in form of acids and phenols.
- Acid catalyzes polymerization!
- Corrosive
- Product needs to be stabilized, e.g. by hydrogenation (using H_2 from natural gas)



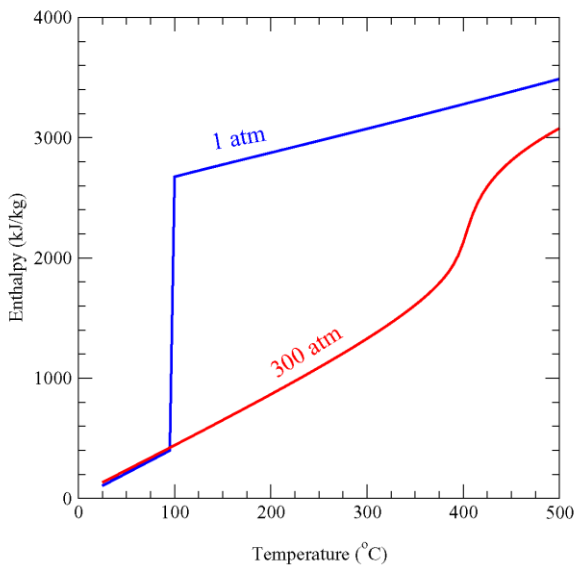
Competing approach: Hydrothermal technologies can have higher efficiencies by avoiding evaporating water.

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



Energy inputs in corn-grain ethanol production

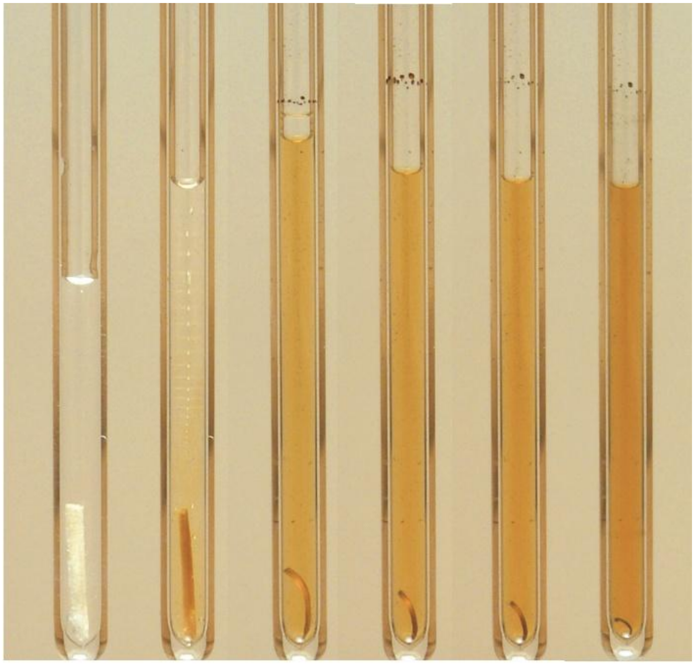
- Heating under intense pressure avoids phase change; makes heat recoverable.
  - Produce water *in*soluble fuels for easy separation.



Ethanol energy balance: Jeremy Johnson, MIT PhD Thesis, 2006.

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°C, ~100 bar



Time, min 0 1 2 3 4 5

Wood conversion to "biocrude" at 340°C.

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

Comparison of fast pyrolysis and hydrothermal liquefaction oils.

Table 3 Comparison of sample bio-oils produced from hydrothermal liquefaction and from fast-pyrolysis. Adapted from Elliott and Schiefelbein.[148] The heating content provided is the higher heating value (HHV)

	Hydrothermal liquefaction	Fast pyrolysis
Moisture (wt%)	5	25
Elemental analysis (dry basis, wt%)		
C	77	58
H	8	6
O	12	36
Heating content ($MJ\ kg^{-1}$)	35.7	22.6
Viscosity (cps)	15 000 @ 61 °C	59 @ 40 °C

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 remove oxygen from the bio-crude
- Adapted from other techniques in refining:
  - hydrodesulfurization (HDS)
  - hydrodenitrogenation (HDN)
  - hydrocracking (HCK)

Oxygen can be removed as water.

$$C_6H_{12}O_6 + 7\ H_2 \rightarrow C_6H_{14} + 6\ H_2O$$

	HDO of biocrude	**HDS, HDN, HCK of 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 m^3/tonne	200-800 m^3/tonne

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

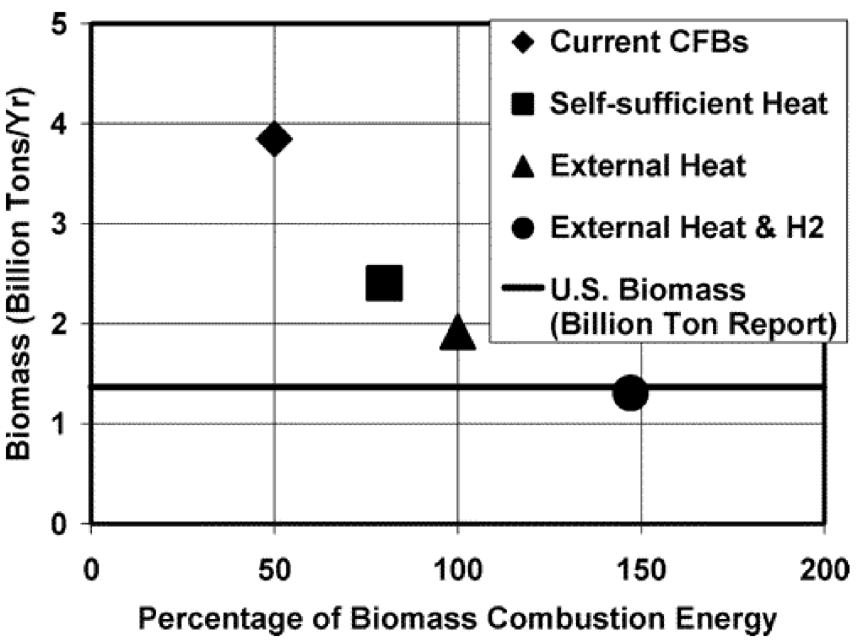
Adding H_2 from external source could significantly increase yields of liquid fuel.

- "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)
- However, at present there is no renewable H_2 source: H_2 is made from natural gas, releasing CO_2! Need a lot of energy to make so much H_2
- However, natural gas is a lot cheaper than liquid fuel, so this might be economical.

Oxygen can be removed as water.

$$C_6H_{12}O_6 + 7\ H_2 \rightarrow C_6H_{14} + 6\ H_2O$$

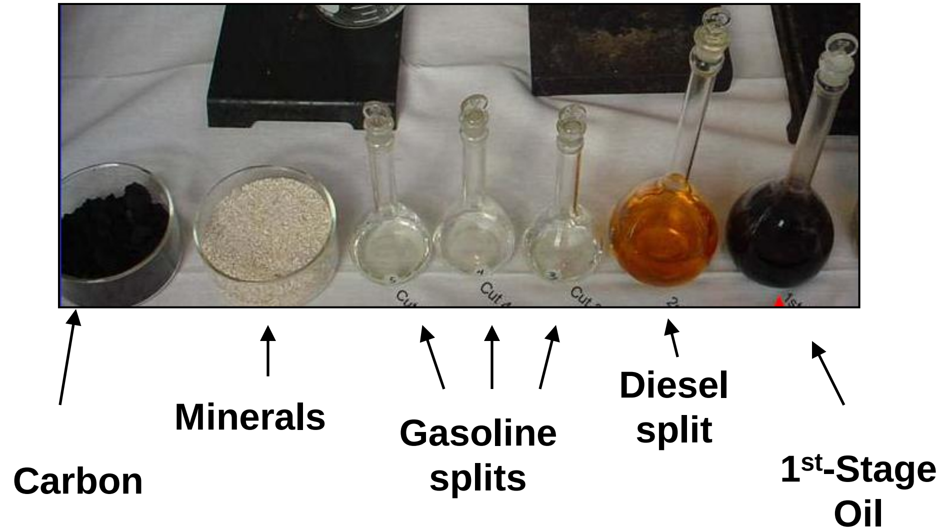
Biomass required to displace all US transportation petroleum



IECR 46(26) 8863 2007.

Changing World Technologies used hydrothermal process on turkey offal to make diesel plus fertilizers and carbon… …before they went bankrupt in 2009

Feedstock is waste from adjacent ConAgra Butterball turkey processing plant



Maceration pretreatment ← Organic waste

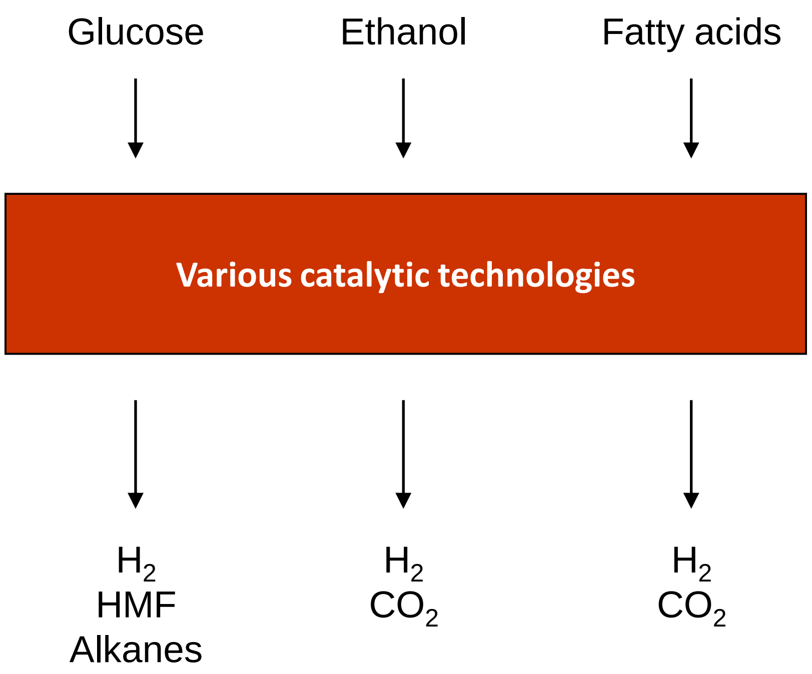
→ **<u>Stage I:</u> 250°C Hydrothermal process to remove fatty acids from glycerol backbone.** → Fertilizer, Minerals, Water

→ 1st Stage Oil →

<u>Stage II:</u> 500°C Thermal cracking to decarboxylate fatty acids into hydrocarbons. → Diesel and gasoline splits

Chemical conversion of biomass components

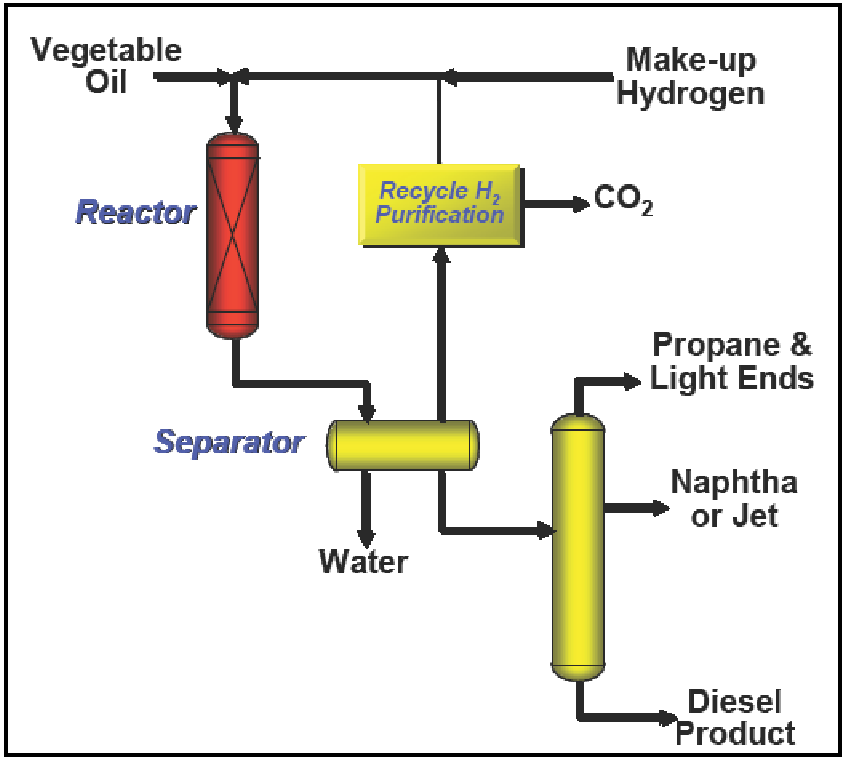
- Specific catalysts developed to convert biomass components to hydrogen, ethanol, alkanes
- Early stage technology
  - Many catalysts subject to fouling with whole biomass streams
  - Usually combine catalysis with pyrolysis or pre-treatment/separation.



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

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

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



Reported product yields and hydrogen consumption.

Feeds, wt-%	
Vegetable Oil	100
Hydrogen	1.5 – 3.8
Products, vol-%	
Propane	8-9
Naphtha/Kerosene	1-10
Green Diesel	88-99

Reported specifications more closely match conventional diesel.

	Petroleum ULSD	Biodiesel (FAME)	Green diesel
% Oxygen	0	11	0
Specific Gravity	0.84	0.88	0.78
Sulfur, ppm	<10	<1	<1
Heating Value, MJ/kg	43	38	44
Cloud Point, °C	-5	-5 to +15	-10 to +20
Distillation, °C	200-350	340-355	265-320
Cetane	40	50-65	70-90
Stability	Good	Marginal	Good

Data and figures from UOP.

Chemical conversion summary

- Chemical conversion vs. Bio conversion:
  - Chemical conversion runs at higher T,P: smaller reactors, higher throughput
  - High P reactors are expensive, particularly an issue for hydrogenation and gasification
  - Many chemical routes greatly reduce need for biomass pretreatment/separations, and also simpler separations of product.
  - Much less specificity in the chemistry, will make a mixture (that might be hard to analyze)
- Several chemical conversion routes appear to be technologically practical in short term, but not yet economical (despite subsidies and mandates).

BioFuel: some take-away points.

1. Practical to make material that can be diluted into existing (petroleum-based) fuel. However, need to be aware of oil price!
2. If you want to make a new "3rd" fuel, need to demonstrate it has big performance advantages over existing fuels. If you could do this, might be able to get price premium over oil.
3. Chemically (and biologically), the goal is oxygen removal. Can remove it as CO_2 or H_2O; latter is better if you have H_2 available.
4. For efficiency, the most important thing you can do is handle water (and other separations) intelligently. Biosynthesis of water-insoluble fuels could greatly reduce separation costs.
5. There exists enough waste biomass to supply about 25% of the demand for liquid fuels. However, it is widely distributed over the globe, expensive to collect and transport.
6. Big unresolved questions about economics, land use, policy, as well as which conversion technologies are best.