Green Chem: Part II

Alternative Energy

Presentation

- Thursday is the deadline for getting a topic and having it approved by me.
- Extend to next Tuesday?
- Next Thursday we will sign up for presentation slots.
- The selection order will be based on the order in which approval occurred.

Grading/Homework

- Reading Assignments
  - Papers posted for each class. Three papers on energy balance of biofuels posted for Thursday.
- Class participation
- Assigned problems

Energy Consumption Breakdown

Fuel type	**Power (TW)**	**Energy (10^{18} J/yr)**	**%**
Oil	5.6	180	38
Gas	3.5	110	24
Coal	3.8	120	26
Hydroelectric	0.9	30	6
Nuclear	0.9	30	6
Geo, wind, solar, wood	0.13	4	0.9
Total	**14.83**	**474**	**100**

Why do we need Alternative Energy Sources?

- Running out of fossil fuels?
  - Total energy consumption:15 TW (10^{12}) in 2004 (86.5 % from fossil fuels)
  - This corresponds to $5 \cdot 10^{20}$ J/yr
  - Worldwide reserves of fossil fuels -$4000 \cdot 10^{20}$ J (800 yrs)
  - $2.5 \cdot 10^{24}$ J of uranium reserves
- We are not running out!!
- But future sources are more difficult to extract, costing more money and presenting difficult safety challenges.

Why do we need Alternative Energy Sources?

- National Security
  - No nation wants to be dependent on others for energy sources
  - The fact that many parts of the world that are blessed by abundant fossil fuel are also those parts of the world in chaos and turmoil, is probable not coincidental.
  - Economic turmoil

Why do we need Alternative Energy Sources?

- Environmental Impacts
  - Global warming
    - Dransfield showed you some compelling (and scary) evidence
  - Off-shore drilling
    - Gulf Coast BP disaster
  - Nuclear Disasters
    - Japanese earthquake

Solar Flux

- Renewable energy flux from the sun (radiation, wind, waves) 120 PW (10^{15}) or $3.8 \cdot 10^{24}$ J/yr
- About 10^4 times what the world consumes.
- What are the challenges of harvesting this potential in ways that are environmentally conscience?

Energy Efficiency and Renewable Energy, DOE $3.2 B/yr

- Biomass ($340 M)
- Vehicle Technologies/batteries ($588 M)
- Fuel Cells ($100 M)
- Hydrogen (cut from budget in 2010, considered too long term)
- Solar cells ($457 M)

Continued…

- Wind ($127 M)
- Water/Geothermal ($38 M / $101 M)
- Green Buildings ($470 M)
- Financing for states, industry and consumers to encourage adoption ($53 M)
- Nuclear Reactor Concepts ($223 M))
- Fusion ($400 M)

Goal

- Look at the state-of-the-art developments in these areas
- Discuss the positives and negatives of each in terms of the goals of energy independence and the shift away from fossil fuel use.
- Tonight we will do a brief overview
- Then, we will dive in a little deeper.

Biofuels

Biofuels (Pros and cons)

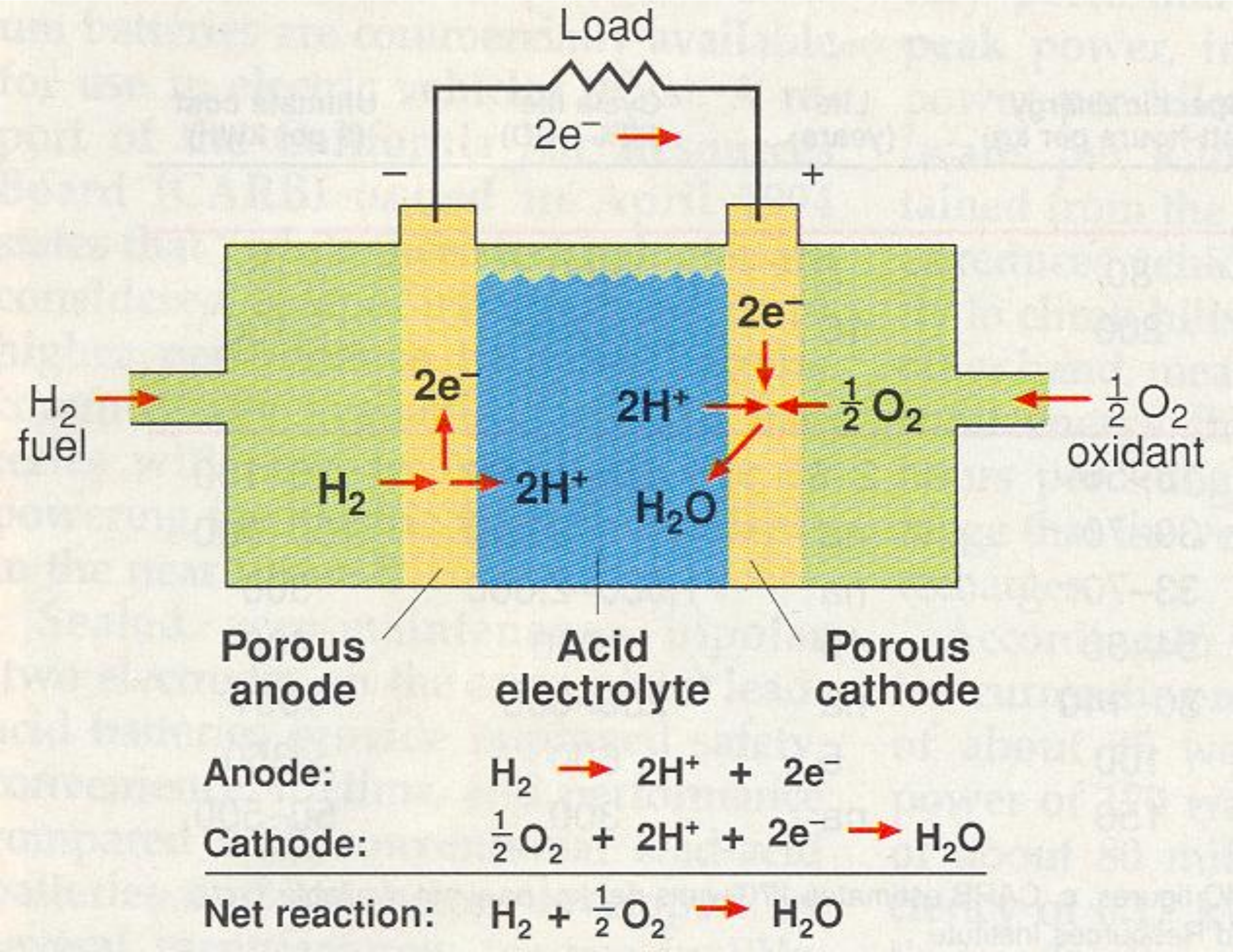
- Potential Pros
  - In theory, No net release of CO_2; CO_2 released from burning the biofuel was sequestered during the growth of crop.
  - Can use lots of different crops, so many nations could potentially contribute.
- Potential Cons
  - Combustion engine requires a mix of gasoline and ethanol
  - Energy intensive process
  - Using land for fuel instead of food
  - Increase food prices
  - Resource depletion
  - Political football

Chevy Volt

Batteries/Electric Car

- Pro
  - Capable of replacing combustion engine entirely
  - Eliminate smog issue in many cities
- Con
  - Research required to produce more powerful batteries to enhance performance
  - Only green if there is a way to recharge the battery using a renewable energy source (change in infrastructure required)

Electrochemistry of Hydrogen Fuel Cell



Fuel Cells

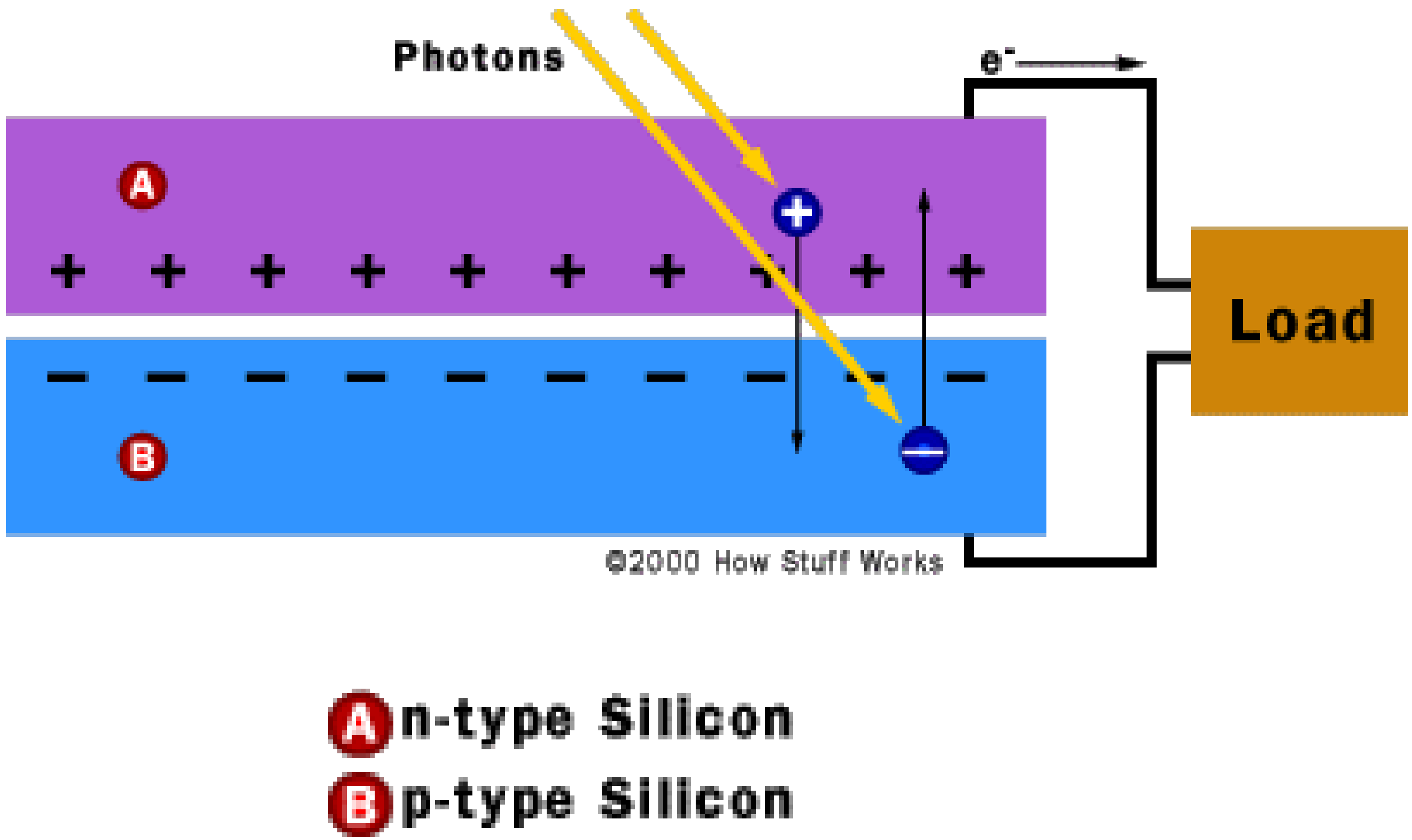
- Batteries powered by green fuel; hydrogen or biofuel
- Pro
  - High performance, zero emission
- Con
  - Relies on biofuels or hydrogen and the production of biofuels and hydrogen might not be green

Hydrogen Economy

Hydrogen

- Pro
  - Burning hydrogen is clean. The only product is water
  - It may be possible to produce hydrogen from solar or nuclear power
- Con
  - Transportation of the H_2 fuel is energy intensive and potentially dangerous
  - Storage is difficult and costly
  - Infrastructure change is required at the filling stations

Solar Cell


Photons
e⁻
A
B
Load
©2000 How Stuff Works
A n-type Silicon
B p-type Silicon

Potential for Solar

- Pro
  - Truly renewable, with a net positive energy life cycle
  - Can use at the site of use
  - Can be converted to electricity
- Con
  - Requires storage of energy to ensure reliable energy availability.
  - Requires massive infrastructure change to link solar into the electrical grid.
  - Would require a land mass of about 100x100 miles in the Southwest U.S to provide as much electricity as presently consumed in the United States.

Wind

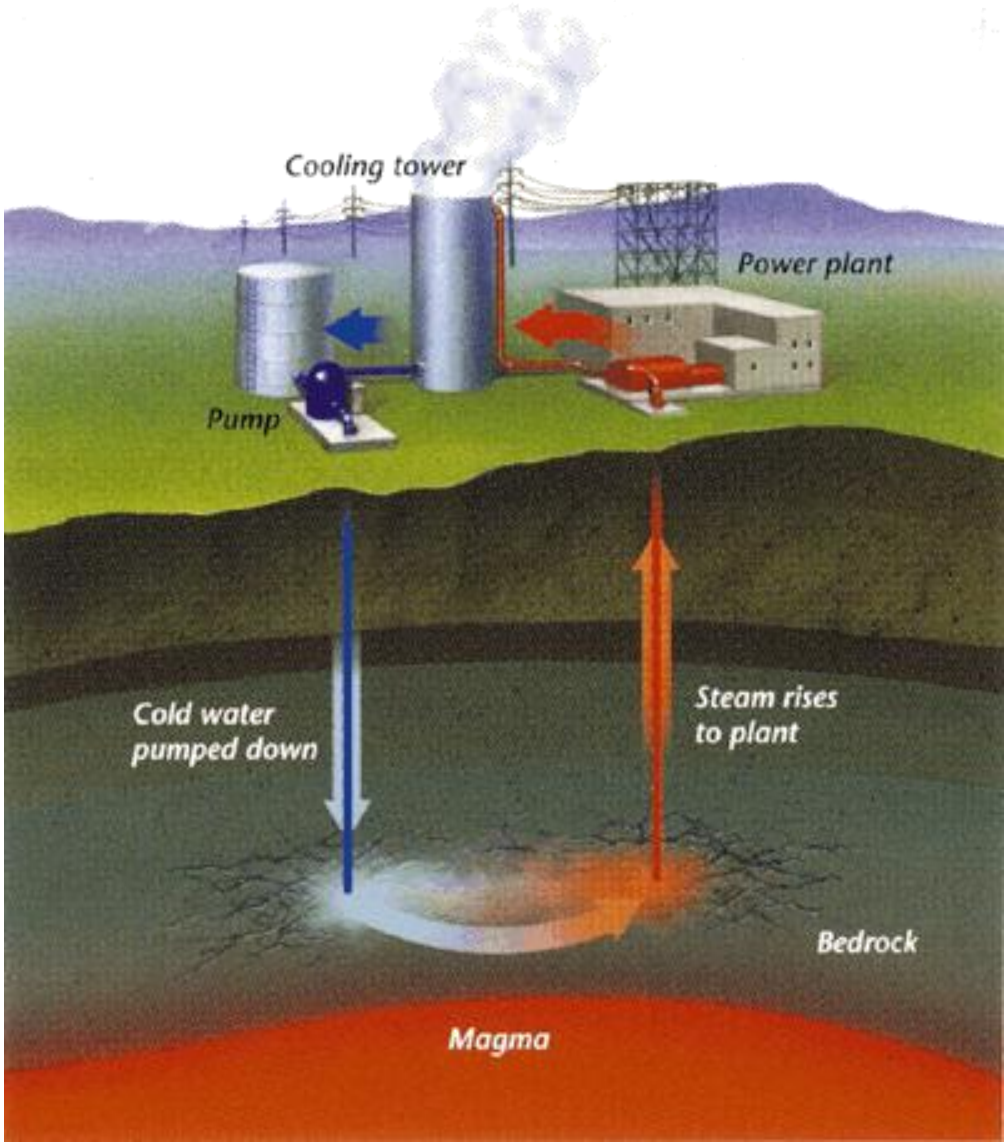
- Pro
  - Truly renewable source
  - Technology is advanced and readily available
- Con
  - Requires storage of energy to ensure reliable energy availability.
  - “not in my backyard” mentality
  - Not feasible in all areas
  - Deep water wind mills required to make a significant contribution
  - Environmental Issues/ bird migration

Hydrodynamic Power

Water

- Hydrodynamic Power – Dams
- Pro
  - Renewable and Clean
- Con
  - Limited locations available
  - Environmental damage to ecosystem of the river
- Newer, less developed wave technologies

Geothermal Energy Plant



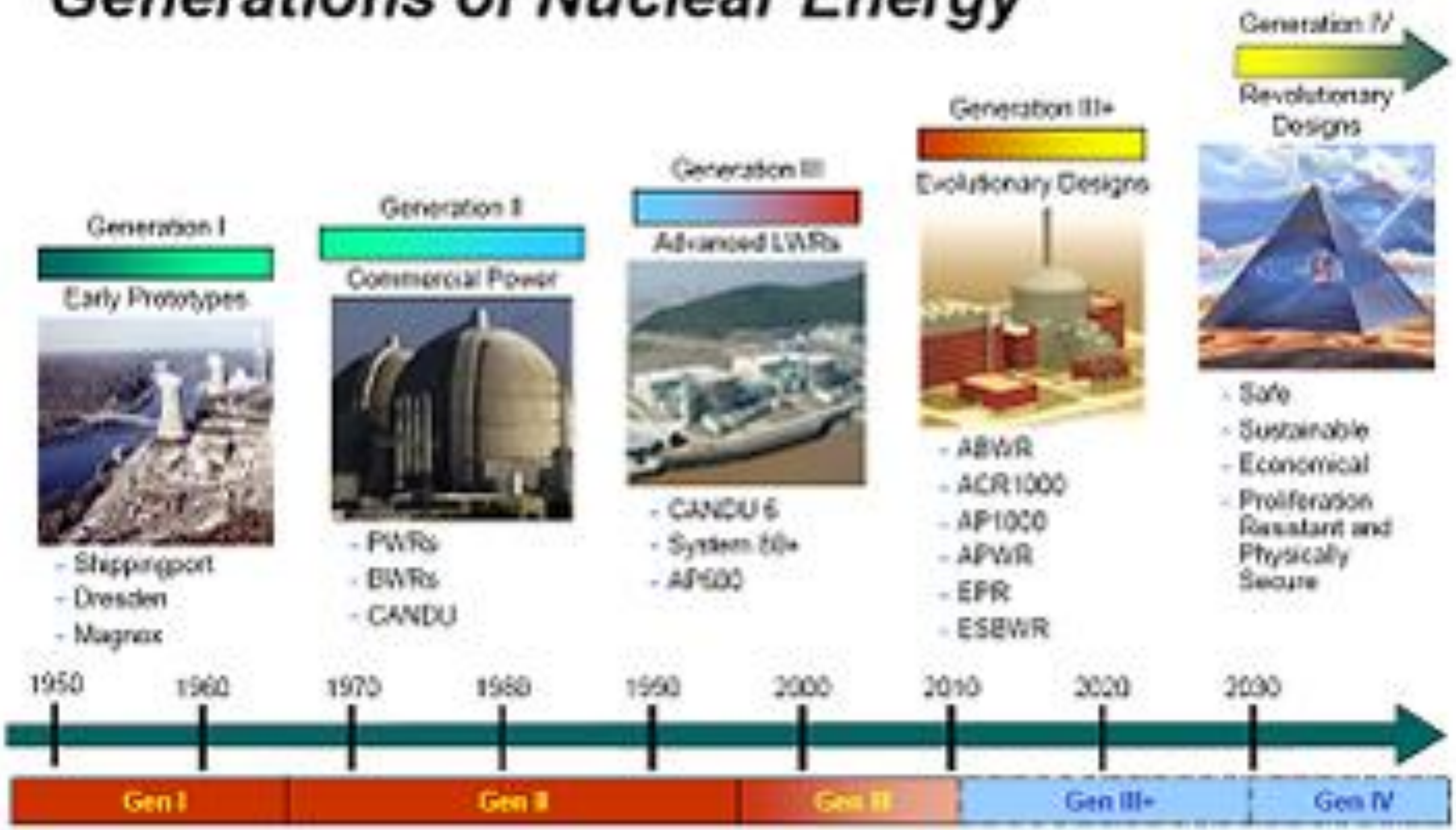
Geothermal

- Using steam from Geothermal activity to produce electricity (or hydrogen)
- Pro
  - green
- Con
  - Limited scope; Iceland has the largest, most successful operation

Nuclear Fission

- Advanced technology; used for over 60 years
- Pro
  - No CO_2 produced
  - Ample supply of uranium
  - Could be a good bridge between fossil-fuel based energy system and a future renewable Energy system
  - Future technology will essentially eliminate risks of meltdown
- Con
  - Not really renewable
  - Disposal of spent fuel is a large environmental problem
  - When accidents occur, they are catastrophic (Chernobyl, Japan)

Generations of Nuclear Energy



Nuclear Fusion

$$^{2}_{1}\mathrm{H} + ^{3}_{1}\mathrm{H} \rightarrow ^{4}_{2}\mathrm{He} + ^{1}_{0}\mathrm{n} + 17.6\ \mathrm{MeV}$$

- Reaction that occurs in the sun
  - Nuclei confined by magnetic field
  - Capture neutrons
    - Extract heat
    - Drive reaction (self-sustained)
  - Steam-turbine-electricity
- Pro
  - Releases an enormous amount of energy
  - Potentially 2 GW
  - Green; no CO_2 emissions, no nuclear waste
  - Inexhaustible supply
- Con
  - Very young technology (will it work?)
  - Lots of unknowns; materials, physics of plasma, stability at 1 M C

Biomass – the basics

- Grow a suitable crop (hopefully in a sustainable manner)
- Harvest crop
- Ferment
- Distill ethanol
- Use ethanol as liquid fuel source

The New Agriculture

- Brazil – sugar cane to ethanol
- US – corn to ethanol
- Europe – wheat to ethanol
- Can ethanol replace fossil fuels as an energy source?
- Is it a feasible solution to our dependence on foreign oil?
- Is it a feasible solution to global warming?
- Is it green?

Continue

- Are ethanol subsidies an good example of science directing politics or is it bad politics getting in the way of science?
- Are there better solutions; algae, municipal waste, H_2 fuel cells, solar energy, nuclear energy?

Corn to Ethanol (the process)

- Growing corn (fertilizer, herbicide, pesticide, man power, seeds, irrigation)
- Harvesting corn (farm machinery, man power)
- Transport to ethanol plant
- Processing/distillation
- Co-products (dried grains, corn gluten feed and meal) as animal feed.

What makes it green (ideally)?

- CO_2 emissions/per energy produced is similar to petroleum.
- However, CO_2 released is recaptured by next years crops. So, there is no net CO_2 added
- But is there? What if we *take into account the energy required for harvesting and transporting the corn and converting it to ethanol*?

The Case Against Ethanol (Patzek)

- A detailed energy balance shows that more energy from fossil fuels is required to produce the ethanol from corn than the energy produced from burning the ethanol product.
- Ethanol from corn is unsustainable (we are spending our precious entropy).
- Environmental impact (depletion of resources)

Thermodynamics

- The First Law
  - The energy of the universe is constant
  - You can not win
- The Second Law
  - The Entropy of the universe is constantly increasing.
  - The energy put into transforming the seeds into ethanol has to be greater than the energy content of the ethanol.
  - You lose heat in the process as entropy.
  - You can not break even
  - What are the energy inputs? Energy outputs? Let’s do a mass and energy balance.

Energy Balance

- Inputs
  - Resources that goes into the production of ethanol from corn require the energy obtained from the burning of fossil fuels.
  - This energy input can be estimated and summed.
- Compare this to the energy available from the ethanol product.
- Different investigators obtain different results and therefore draw different conclusions about the future of “growing ethanol”.

Energy Inputs

- Corn Production
- Ethanol Production

Corn Production

- Solar energy
- minerals
- Seeds, Fertilizer, pesticides, herbicides
- Irrigation
- fuel
- farm machinery
- manual labor
- Electricity
- Transport
- 2500 kcal/L ethanol produced (Patzek)

Ethanol Production

- Transportation of corn harvest to plant
- Distillation
- infrastructure
- Transporting ethanol product and co-products and waste
- purifying waste water
- Electricity
- Steam
- 4100 kcal/L ethanol produce

Energy output from ethanol

- Ethanol, 5130 kcal/L
- Co-products, ?
- Net: 5100-2500-4100 = -1500 kcal /L
- Or about 30 % more energy from fossil fuels goes into the production of ethanol from corn than the energy in the ethanol that can replace fossil fuel use.

Co-products

- Gluten meal and gluten feed
- Replacement for soy bean meal – 1450 kcal/L
- Impact on cattle
- Impact on sustainability

Under estimate

- This does not take into account the costs of long term environmental remediation
- Another estimate states that it costs 1.8 gallons of gasoline to produce an amount of ethanol that has the energy equivalent of 1 gallon of gasoline.
- Ethanol has 63 % of the caloric value of gasoline

CO_2 emissions

- Yes, CO_2 is recycled by next years crop, but not fossil fuel inputs, which produce 6700 kg of CO_2 per 1 ha of corn/ethanol farming.
- Burning an amount of gasoline equivalent to the amount of ethanol produced per ha would produce only 5100 kg CO_2
- 1600 kg/ha extra CO_2 is produced

Entropy and Sustainability

- To be sustainable a process must be
  - Reversible
  - Must only produce heat and no chemical waste.
  - The heat produced must not exceed the capacity of the earth to dissipate the heat to the universe
- The burning of fossil fuels is not sustainable.
- Large scale agriculture is not sustainable (nutrient depletion, soil erosion)

Subsidizing the Corn/ethanol Industry

- Corn subsidies to farmers, mostly large conglomerates
- National ethanol subsidies
- State ethanol subsidies
- Our natural resources
- $3.5 billion /yr

And even if all this was not true

- 12% of US corn fields are devoted to ethanol providing less than 2% of our energy needs
- Very little capacity is left to make a meaningful dent in the energy crisis.
- So, can it ever be worth the tax payers money to grow corn for ethanol?

Farrell Article

- Net energy balance (NEV) vs Net Energy Ratio (NER)
- Separate Input Energies
  - Corn Ethanol requires far less petroleum than the production of the equivalent (in terms of energy) amount of gasoline
- Cellulosic case; based on futuristic probability model by by M.Q. Wang at the Center for Transportation Research, Energy Systems Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439

The case for ethanol

- What is wrong with the analyses of Patzek and Pimentel?
  - Treatment of co-products
  - Disagreements about input data
    - Ethanol yield per dry corn
    - Citations are lacking or do not match up or are based on old data not relevant to current practices
    - Assumes no improvement in yield and energy efficiency going forward.

New metric

- Compare the petroleum used to create 1 MJ of gasoline to the petroleum used to create 1 MJ equivalent of ethanol
- Ratio is approximately 0.05 (or about 2 according to Patzek's adjusted data).
- Patzek: 5-12 times more fossil fuel energy to produce corn ethanol than it does to produce gasoline of equivalent energy.
- How can these analyses be so different?

Switchgrass

- The potential of switchgrass 1450 Gal/acre, about 15 % more than corn
- Requires about 1/3 of the energy input required to grow corn
- Cellulose to ethanol
- Farrell predicts it has the potential to be a factor of 5-10 times more energetically efficient.
- Easier to farm than corn, requiring less energy input, provides excellent yield, potentially much more environmentally sustainable.
- 1 kcal input/11 kcal output of switchgrass
- However: Cost of producing ethanol from cellulose is very energy intensive (steam and electricity)

Switchgrass

- Cellulose is difficult to break down
- Lignin problem
  - Protective sheath
  - Redeposition
  - waste
- Enzymatically, Harsh chemicals, Long reaction times/ need for sterile environment
- Bugs need to work under these conditions

Switchgrass

- Genetic engineering
- Gasification:A thermochemical approach; Switchgrass to syngas to ethanol
  - Could process lignin
- National Renewable Energy Labs

Sugarcane

- Brazil and India
- Double the yield of corn (130 vs. 71 GJ/acr·year)
- Year round growing season
- Low nutrient requirement
- Waste used to produce energy to distill the ethanol
- 40 years of technology; fairly smooth and efficient
- 4.5 billion Ga/yr

Sugarcane

- Loss of nutrients
- Wastewater cleanup
- Sustainable?
  - Patzek claims only if one uses a 60 % efficient fuel cell (which does not exist).
- Limited Capacity for expansion

Biodeisel

- TAGs + $NaOCH_3$ → FAMEs + glycerol
- Soybeans and rapseeds
- Need methanol or ethanol
- B20 vs. B100
- Glycerol glut; the GB glycerol challenge
- 90 % of all biodeisel comes from Europe
- 5-6 million tonnes in 2006 and rapidly growing
- 490 million tonnes of demand for petrodeisel
- Limited room for expansion

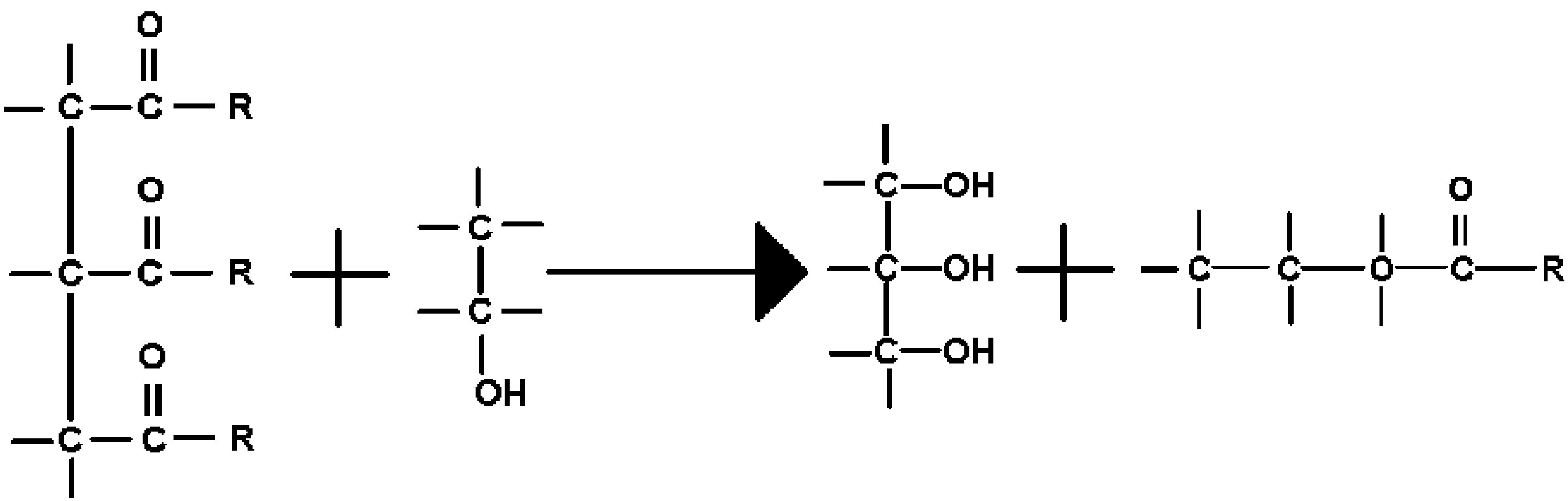
Some typical yields

Crop	Yield	
	L/ha	US gal/acre
Algae[n 1]	~3,000	~300
Chinese tallow[n 2][n 3]	907	97
Palm oil[n 4]	4752	508
Coconut	2151	230
Rapeseed[n 4]	954	102
Soy (Indiana)[54]	554-922	59.2-98.6
Peanut[n 4]	842	90
Sunflower[n 4]	767	82
Hemp[*citation needed*]	242	26

1.^ est.- see soy figures and DOE quote below
2.^ Klass, Donald, "Biomass for Renewable Energy, Fuels, and Chemicals", page 341. Academic Press, 1998.
3.^ Kitani, Osamu, "Volume V: Energy and Biomass Engineering, CIGR Handbook of Agricultural Engineering", Amer Society of Agricultural, 1999.
4.^ [a] [b] [c] [d] Biofuels: some numbers

Fatty acids esters from algae

Ethanol + Na → CH_3CH_2ONa, used as catalyst



Algae

- 30 times the energy per acre than soybean
- Farming algae on land the size of Maryland could replace petroleum diesel
- 10000 Gallons biodiesel/acre·y
- Can use CO_2 from power plants
- Can use dirty water
- Need for bioreactor ($$$?)?

Issues

- The big problem has been figuring out how to collect and press the algae, and in the case of open ponds, to prevent contamination by invasive species.
- Open air vs bioreactor
- High costs
- GreenFuel Technologies

Solena

- Zero CO_2 Emissions
  Solena's NASA-based technology was designed specifically to produce renewable energy without fossil fuels. Using a plasma gasifier, Solena's technology converts all forms of biomass into a synthetic gas (syngas). The syngas is then conditioned and fed into a gas turbine to produce electricity. Solena's revolutionary sequestration program recycles CO_2 and in the process produces biomass for a continual renewable source of fuel.

Aurora Biofuels

- Operating large scale plant for over 18 months
- 25 times more productive than sugarcane; 70-100 times more productive than soybean
- Uses arid land and salt water
- The company is actively scaling its technology for industrial production and expects to complete a 20-acre demonstration plant in 2010 and achieve full commercial production in 2012.

Isolation of biodiesel

- Ether and salt to remove glycerol, sodium, water
- centrifuge