Energy as feedstock in chemical industries: from petrol to green chemistry

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Overview

- Part 1: Materials from Atoms

How we currently make fuels and synthetic materials from oil and natural gas: sorting and transforming molecules. Green chemistry to minimize waste.

- Part 2: Energy

Energy utilization in the current system.

Economic & Environmental motivations for improving energy efficiency.

Options for reducing CO_2 emissions in the fuels/transportation sector.

Take Raw Materials Out of the Ground…and Make them into the Fuels & Materials Society Needs

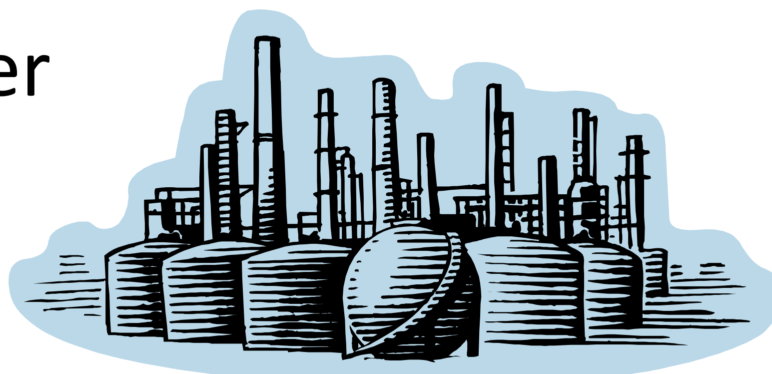
Inputs:

Crude Oil

Natural Gas

Liquid Water

Air



Refinery/
Petrochemical
Complex

Outputs:

Liquid Fuels:

Petrol, Diesel, Jet

Polymers, Fibers

Chemicals

Lubricants

Electricity

Asphalt, Coke

$H_2O(g)$, $CO_2(g)$

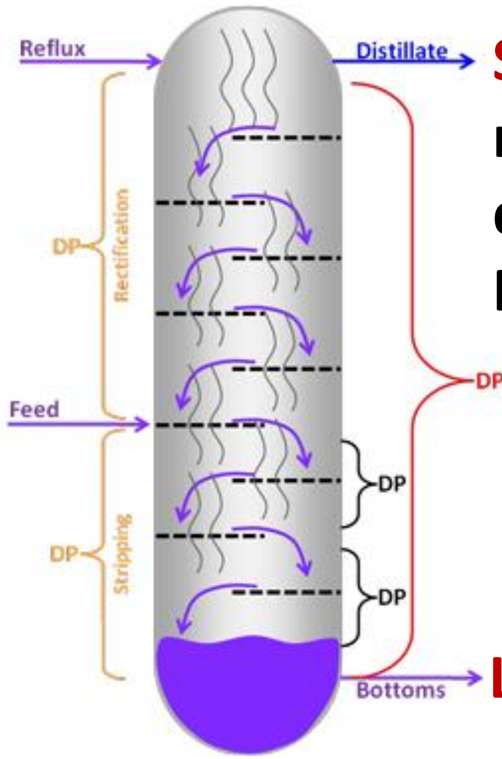
Overview: Atoms are Conserved…But We Change how they are Bonded together

- Inputting many C and H atoms, bonded together in huge variety of different molecular arrangements
  - Some molecules include S atoms.
- In the refinery we separate these molecules according to size (vapor pressure), then break up and rearrange some of the molecules using heat and catalysts, separating away the sulfur atoms.
- Same number of C,H,S atoms coming out, but many now in valuable small or medium size molecules.
- **Most of the output molecules we blend into fuels**
  - a few molecules we react to make materials.

Step 1: Distill (Boil) the Crude Oil

Small molecules evaporate, come out the top;
Larger molecules stay in liquid phase, fall to bottom

Input:
Crude Oil
(mixture of thousands of different molecules, all sizes)



Smaller molecules:
most can be used directly in Fuels & Chemicals

Larger Molecules ($>C_{20}$):
most need to be cracked (more demand for small molecules than big ones)

Why more demand for small molecules than larger molecules?

- Fuels: Petrol (gasoline) engines rely on the fuel evaporating and mixing well with air before combustion.
  - Diesel and Jet engines make less soot if the fuel evaporates before burning.
  - Large fuel molecules are hard to evaporate.
- Chemicals: Easier to separate smaller molecules, so you can start with pure reagents (and so make purer products).
  - Most synthetic materials are made from molecules with 8 or fewer carbon atoms.

Step 2: Crack the Big Molecules

Input:

Heavy Fraction
from
Distilling Crude Oil

Fluidized-Bed Catalytic Cracking Unit

Outputs:

Petrol (Gasoline)
Small Alkenes
Small Aromatics
Heavy Fuel Oil

Some of the carbon is burned inside the Cat Cracker to provide heat to drive the endothermic cracking reactions

How does Catalytic Cracking work?

1) Heavy oil is squirted onto a hot solid acid catalyst powder flowing in the reactor.
   +Large molecules stick to the catalyst surface.
2) Catalyst pulls hydride anions (H-) from hydrocarbon molecules on surface, leaving an unstable cation.
3) Large hydrocarbon cation cleaves to alkene + small cation. Alkene evaporates.
4) Small cation grabs back the H- to be come a small neutral hydrocarbon that evaporates.
5) Gaseous product is separated from the solid catalyst.
6) Carbon that sticks to the catalyst through this process is burned, heating up the catalyst for next pass.

Sulfur is a Big Problem

- Crude Oil contains ~1% sulfur
  - some S from its biological source, and some S from reactions with S-containing minerals underground.
- When burned, sulfur forms toxic SO_2
  - SO_2 reacts in atmosphere to form acid rain
- Sulfur “poisons” many catalysts, including
  - catalysts used in automobile emission control systems
  - catalysts used to make polymers and chemicals.
- Modern cars and trucks require very low sulfur fuels (~20 ppm = 0.002%).

Step 3: Remove Sulfur

$$2H_2(g) + C_xH_yS = H_2S(g) + C_xH_{y+2}$$

This reaction is carried out at T~600 K and P~100 atm on a solid catalyst containing Molybdenum, with excess H_2.

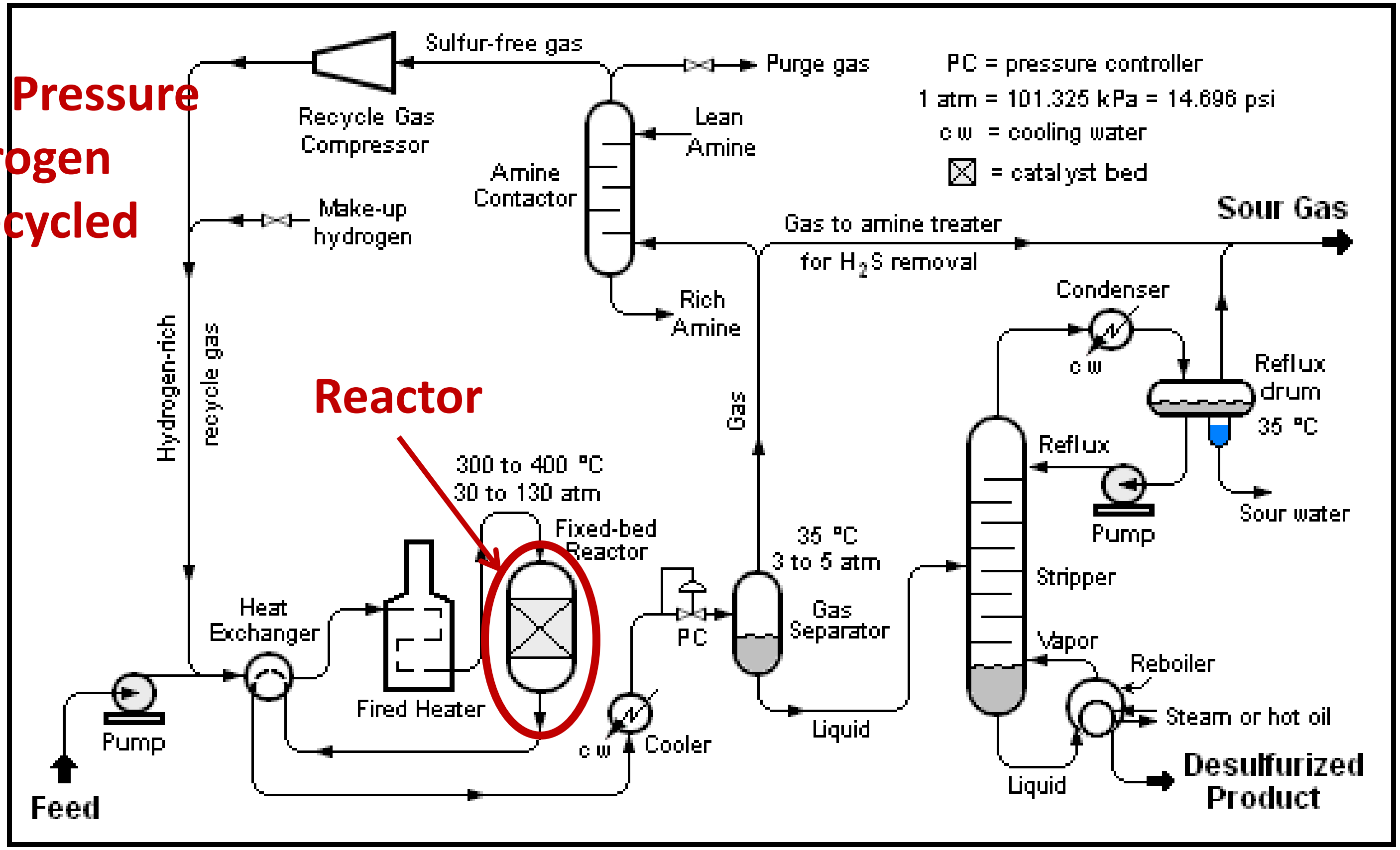
The H_2S is then captured by bubbling the gas through an amine solution (H_2S dissolves). It is later released from the amine into a different reactor.

The pure H_2S is reacted with O_2 in another complicated process to make sulfuric acid (e.g. for use in lead-acid batteries):

$$H_2S + 2\ O_2 = H_2SO_4$$

Complicated Hydrodesulfurization Process is big part of modern refinery

High Pressure Hydrogen Is Recycled



"Sour Gas": $H_2 + H_2S$ to separator, ultimately to Sulfuric Acid.

In: Organic Liquid with Sulfur

Out: Organic Liquid, almost no Sulfur

Step 3a: Convert H_2S to H_2SO_4

We moved S atoms from organics into “Sour Gas” H_2 + H_2S. What to do with that?

1) Separate H_2S from H_2 by bubbling the gas through an amine solution (H_2S dissolves).
   + H_2 is recycled to hydrodesulfurization unit
2) Flow amine solution into a different reactor and release the dissolved H_2S by heating.
3) The pure H_2S is reacted with O_2 in a complicated process to make sulfuric acid (ultimately used to make fertilizer):

$$H_2S + 2\ O_2 = H_2SO_4$$

We need H_2 reagent to remove the S. Where does the H_2 come from?

- Some H_2 is made as a byproduct in refinery (e.g. in steam cracker).
- H_2 is made from fossil fuels by catalytic "steam methane reforming" process, e.g.

$$CH_4 + 2\ H_2O + \text{heat} \rightarrow CO_2 + 4\ H_2$$

The heat required for this endothermic process is made by burning some of the fossil fuel. The reaction runs to the right at high T because $\Delta S>0$ due to increase in number of moles of gas.

Need Monomers to Make Polymers

- Most petroleum makes fuel, but materials made from petrochemicals are much more valuable than fuels.
- Humans use synthetic materials for cloth, packaging, coatings, most manufactured goods.
- Most synthetic materials are polymers of small organic molecules: polyethylene, polypropylene, polyester (PETE), nylon, rubber, etc.
- Simple refining doesn't make enough ethene C_2H_4 and propene C_3H_6 to meet the huge demand for those monomers: the rest is made by thermal pyrolysis of light alkanes (from oil or from natural gas), a process called "steam cracking".

Some important polymers & their uses

- Polyethylene $-CH_2CH_2CH_2CH_2-$

  Bottles, toys, wrap, bags, electrical insulation
- Polypropylene $-CH_2CH(CH_3)CH_2CH(CH_3)-$

  Carpet, upholstery
- Polyethylene terephthalate (PETE)

  $-CH_2CH_2-O-C(O)-C_6H_4-C(O)-O-$

  Clothing, bottles, Mylar, tape, packaging

Step 4: Separate, make monomers.

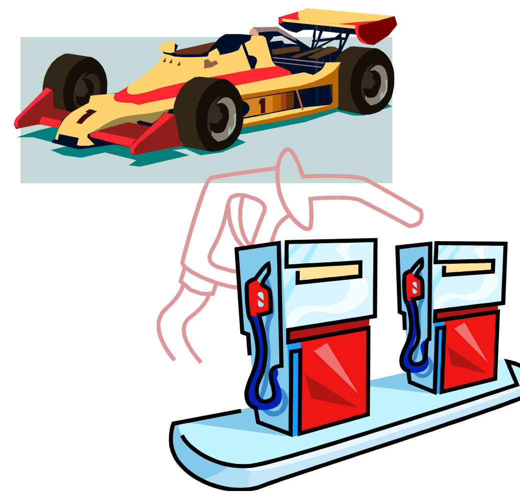
- In USA & Persian Gulf natural gas is cheap. Natural gas includes some C_2H_6 and C_3H_8; these molecules are captured using cryogenic separations.
- In places were natural gas is not so cheap, some of the light alkanes in crude oil (called “naphtha”) are separated out by distillation.
- Either way, the light alkanes are sent to steam crackers where they form alkene monomers + H_2.

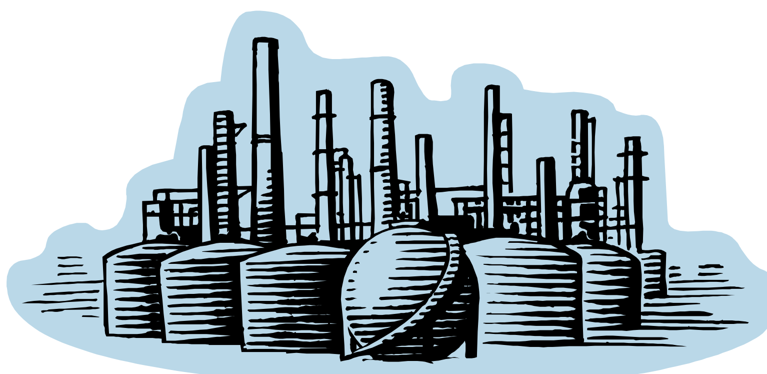
Step 5: From simple monomers to consumer products

- A few products are made directly in a single step from the simple monomers, e.g. polyethylene plastic and ethylene glycol antifreeze from C_2H_4.
- Most products derived from petrochemicals are more complicated, involving multiple chemical steps followed by many manufacturing steps.
  - For example a car may contain more than 500 kg of material derived from crude oil, in many different forms: upholstery, doors, steering wheel, dashboard, windows, paint, tires, antifreeze, hoses, bumpers, etc.
  - All those carbon atoms came from crude oil or natural gas!

Humans have figured out how to convert messy stuff in the ground into wonderful & convenient goods… Amazing. Are all the problems solved?

Oil Well





Refinery/Petrochemical Complex

In addition to the desirable main products, Refineries make byproducts: lots of CO_2
+ some wastewater, air pollutants, and solid waste.

Because of huge scale, must <u>minimize</u> waste!

Humans consume almost 10^7 barrels of oil/day. So if we convert 99% of the oil into the desired products and only 1% into waste…

…we would be making 100,000 barrels of waste every day!

- + Critical to reduce waste to very low level!!
- + Very challenging: very few chemical reactions have >99% selectivity.

Green Chemistry

Green Chemistry =

devising processes that increase the ratio

(desired products)/(waste)

+ Usually yield of desired products is already pretty high, so focus is on reducing the (small) waste stream.

+ Requires careful analysis of even minor sources of wastes and impurities.

Green Chemistry Strategies

+ Both “avoid making waste” and “efficiently destroy waste” strategies can be effective; combination is often best.

+ Better: sometimes a new use can be found for a waste material, turning it from “waste” to “valuable product”.

Green Chemistry is a major line of research in the energy / chemical industries: processes cannot be used if there is no good way to handle the associated waste, no matter how valuable the product.

A Green Chemistry example

- When Coal is burnt (e.g. to make electricity), makes some ash.
- Historically, coal ash was a waste product, needed to be landfilled: costly, and potential environmental and safety hazard.
- Green Discovery: If properly formed, fly ash from coal is great for strengthening concrete
  - reduces the air bubbles in the concrete making it more solid
  - now ash is a money making product, not a waste, and coal power plants are carefully operated to make this valuable type of ash!

“Dilution is the Solution”

- Materials that would be harmful at high concentrations are often harmless or even helpful when very dilute.
  - You would never drink concentrated phosphoric acid, but diluted phosphoric acid adds flavor to Coca-Cola and other sodas
- Some ‘waste’ organics can be diluted into very large fuel streams adding energy value without decreasing fuel performance.

Looking for Optimal Way to Operate Refinery/Petrochemical Complex

- Many different internal units which can be operated with different adjustable flows.
- Making many different products (and some wastes), each with its own selling price (or cost of disposal).
- The input crude oil composition changes frequently, and prices also fluctuate.
- Refinery operators do a complicated “constrained optimization” calculation on the computer to decide best way to set the flows each day.

Materials from Renewable Sources

- Most synthetic materials now made from fossil fuels; eventually the materials degrade to CO_2 (climate impact).
  - If slow to degrade, they fill up landfills
- Can we start from a renewable raw material instead, to reduce environmental impact?
- In old days we used plants (wood, sisal) to make many material goods – can we make modern products from plants?

The feed for Porto Torres biorefinery

Native plant, doesn't need farmland or fertilizers.
Naturally Renewable!

Green Chemistry from Greenery!

- Matrica (a joint venture of ENI and Novamont) is building a ***biorefinery*** in Porto Torres, Sardinia (Italy)
- Input: **Thistle plants** instead of petroleum!
  - Seed oil makes monomer for materials
  - Proteins make animal feed
  - Rest of plant is burned to make electricity & heat.
- Output: lubricants, polymers, animal feed
- Much more sustainable than conventional approach!

Part 2: Energy

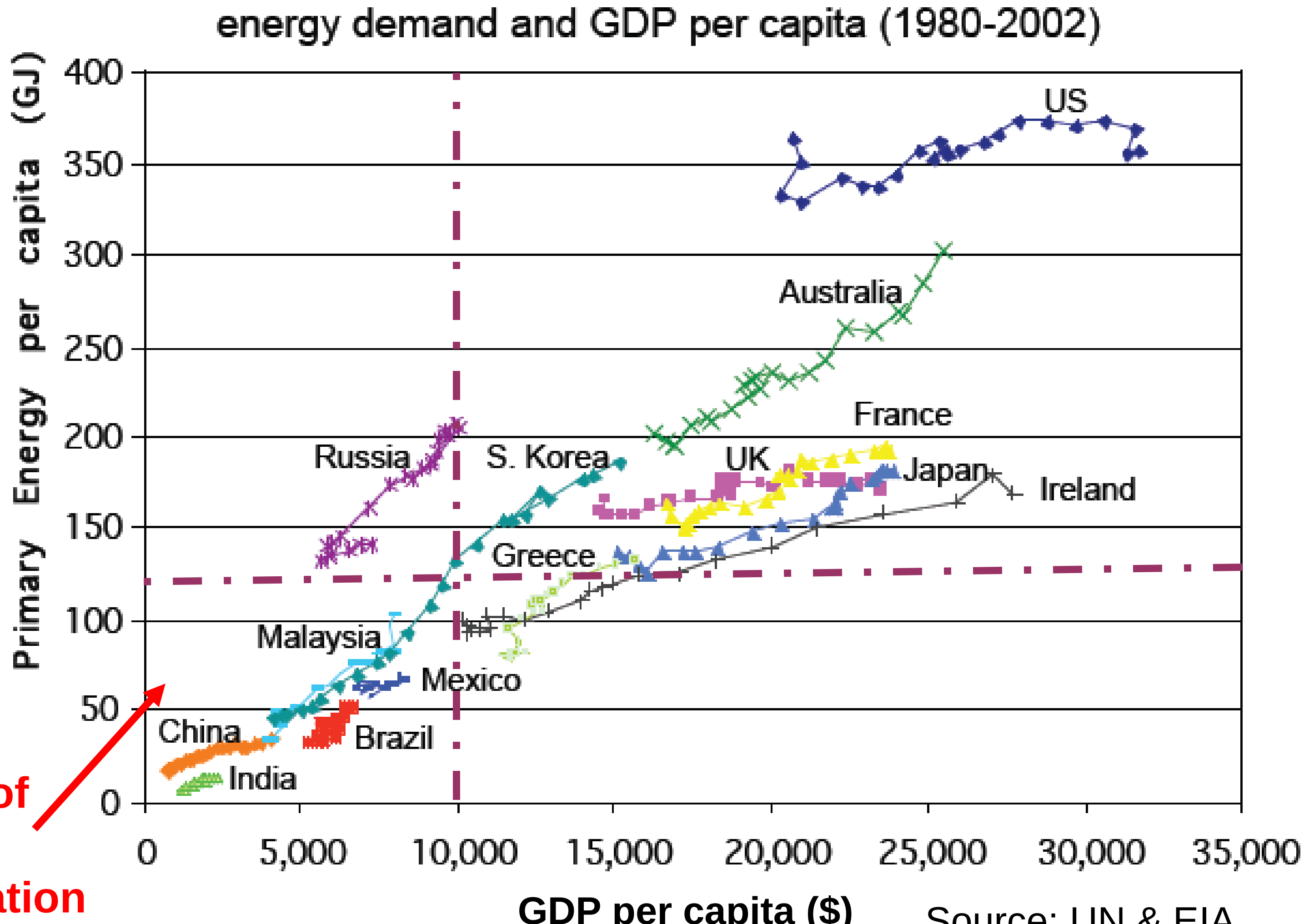
So far, we focused on the atoms,
making the desired molecules & materials.
This is correct, atoms are conserved, and
most customers want to buy stuff:
    fuels or synthetic materials.

But energy is also conserved, it gives a
different way of looking at things…

Transformations Consume Energy

- Converting crude oil & natural gas into desirable fuels and materials takes energy.
  - Distillation & endothermic reactions require heat
  - Purifications need energy input (reduce entropy)
  - Exothermic reactions convert chemical energy to heat, only some of that energy can be recovered.
- To make the needed energy, some of the oil or gas is burned to make CO_2.

High energy use correlates to high standard of living



>80% of world population in this quadrant

Source: UN & EIA

World demands more energy!

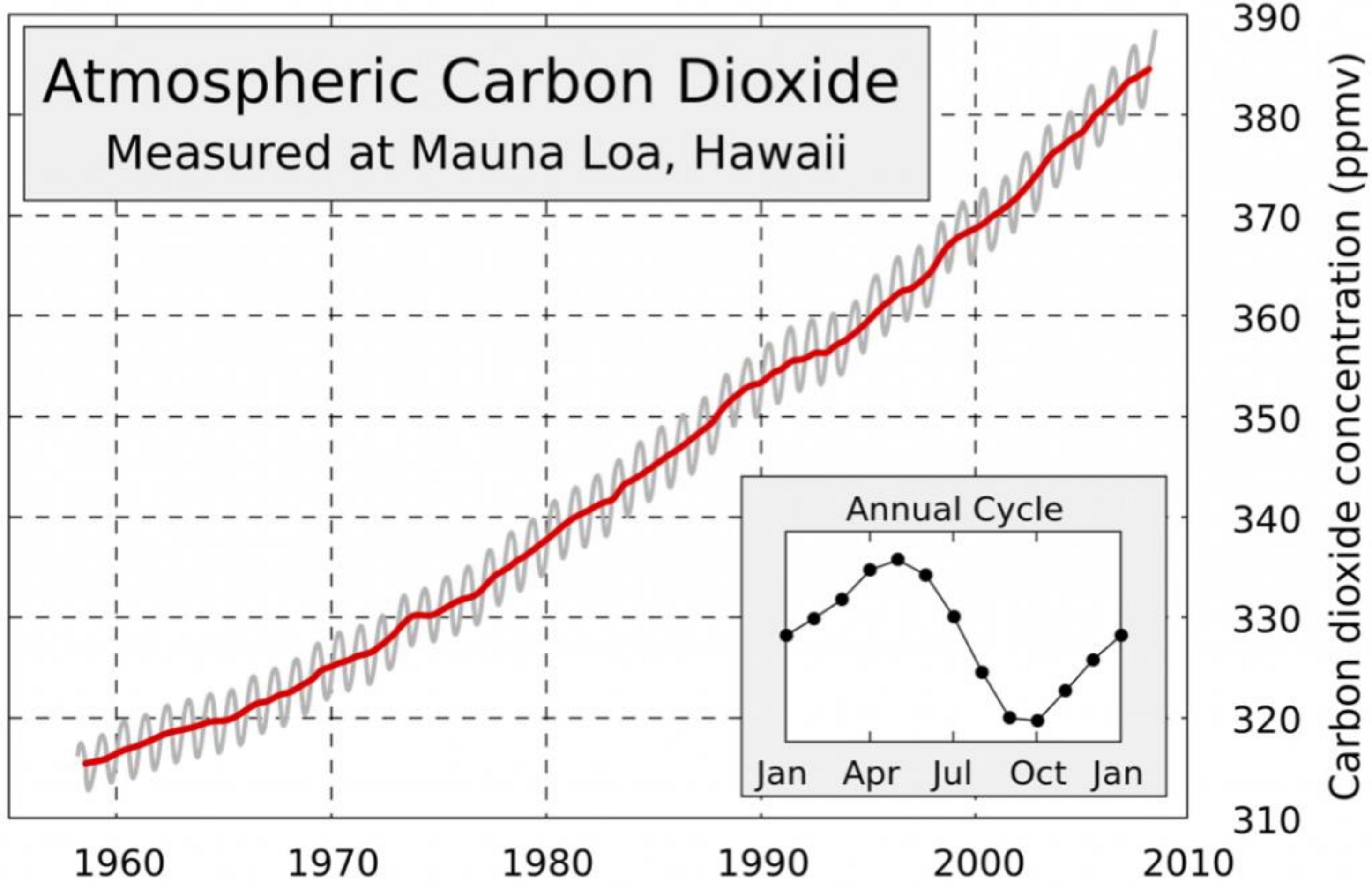
Motivations for Energy Efficiency

- Improving energy efficiency means more of the oil and gas can be converted to valuable products: economic motivation.
  - High motivation for oil, since oil is now expensive.
- Improving energy efficiency also reduces CO_2 emissions: climate motivation.
  - At present CO_2 emissions are not tightly regulated, but this is beginning to change as climate-change threat becomes clearer.

Energy Efficiency Realities

- Currently, >90% of transportation energy coming from petroleum (via liquid fuels).
- Fuels much bigger volume than materials, so much bigger impact on energy efficiency and CO_2
- Most fuel energy is consumed when the fuel is burned. For current transportation system this is in the car, not the refinery.
- Increasing energy efficiency usually requires investment in new equipment (or new automobiles); payback period may be long.
  – So Economic Motivation is not always very strong

Climate Motivation: CO_2 is rapidly accumulating in atmosphere, will change climate significantly this century



What do we need to do to stabilize global climate?

- Need to cut CO_2 emissions in approximately in half by 2050.
- However, projections are that increasing (and increasingly wealthy) population of world will demand about twice as much energy by 2050.
- So we need to improve energy efficiency (useful work per CO_2 emitted) by about a factor of 4 -- this is a big challenge for engineers and scientists

How could we improve energy efficiency so much?

- The big CO_2 emitters are electricity production, heating, and transportation.
- Many relatively easy opportunities for reducing CO_2 emissions related to electricity. Technically feasible (but expensive) to achieve factor of 4.
- Reducing CO_2 emissions from heating is tougher, very hard to reach factor of 4 by 2050.
- What can we do to reduce CO_2 emissions from transportation?

Options for Improving CO_2 efficiency of Transportation System

Option 0: Use Less Transportation

1) **Smart Urban Planning** can drastically reduce Travel Distance
   + But what to do with our existing poorly planned cities?

2) **Breakthroughs in videoconferencing** etc.
   + reduce need for business travel
   + make telecommuting more viable?

Option #1: Improve Engine Efficiency!

- Use less fuel and so make less CO_2!
- Possible to gain factor of 2, maybe more
  - Lots of interesting engine R&D underway, really great!
  - But in this lecture we focus on fuels, so you'll need to go a mechanical engineering lecture to hear details about engine innovations…

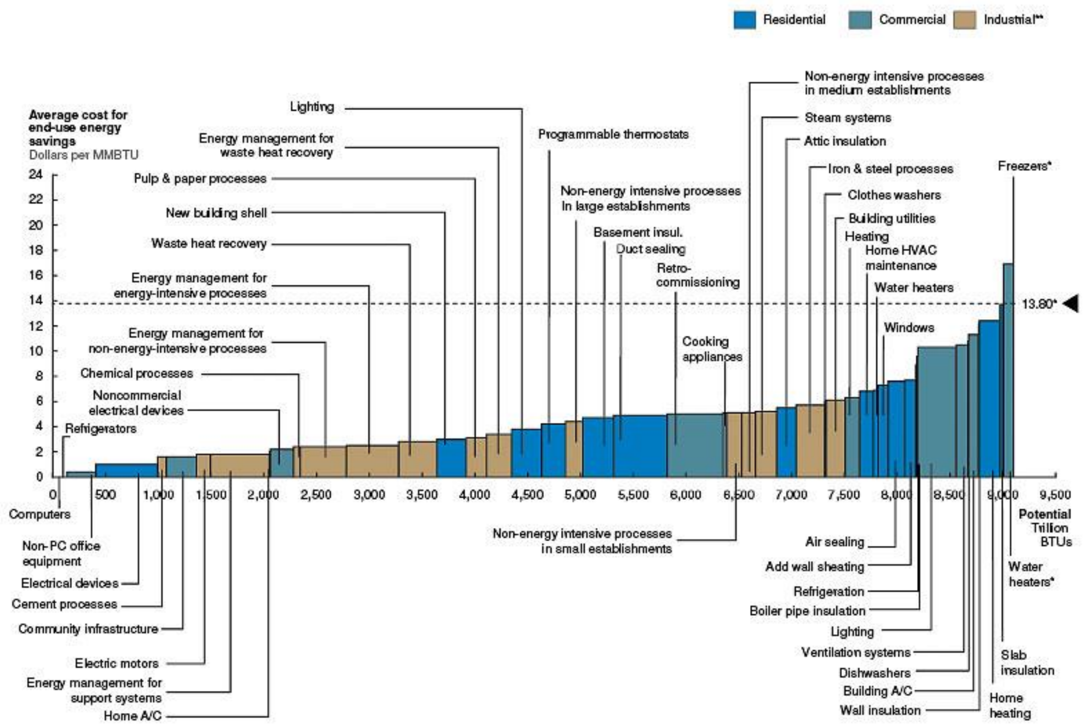
Tradeoffs:

  - Size, Power, Speed vs. Energy Efficiency
  - Better engines usually cost more
    - **Vehicle cost often more than fuel cost, so economic incentives not perfectly aligned with environmental needs**

"McKinsey Curve" for Energy Efficiency: shows cost and potential scale of different efficiency technology options

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

Breakeven Oil Price



* 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

Displays Amount of Energy that could be Saved by Investing in Each Efficiency Technology.

Option #2: Battery-Powered Cars

- Commercial: Nissan Leaf, Chevy Volt, Tesla
- Great for Energy Security
- Reduces Performance
  - Reduced Range (low energy density)
  - Slow Recharge
- Batteries are expensive!
  - Needs subsidy at present (e.g. in USA ~$8000/car)
  - Need recharging infrastructure
- Where would the electricity come from to recharge the batteries?
  - If Coal: CO_2 emissions are worse than regular cars
  - If Gas, others: CO_2 emissions less than regular cars
  - 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

- CNG engines are already commercial
  - e.g. some buses at airports and in USA cities
  - USA may convert some long-haul trucking to CNG
  - Widely used in automobiles in some countries
- Reduced Range (lower energy density)
  - Not high enough for airplanes, but adequate for cars, trucks.
- Would require significant investment in fuel distribution system, and either new vehicles or conversions of existing vehicles
  - But maybe cheaper overall than current system?
  - In some countries, CNG more popular than petrol.
- Natural Gas emits somewhat less CO_2 than oil, but not a factor of 2 different. Perhaps modest improvement in climate and modest cost savings in regions with cheap natural gas.
- Maybe better to use natural gas to replace coal, where there is a much bigger environmental benefit?

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

- Huge 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
- Economics favors use of tar, but conventional oil is better for the environment.

Canadian Tar Sands:
World's largest earthmoving operation

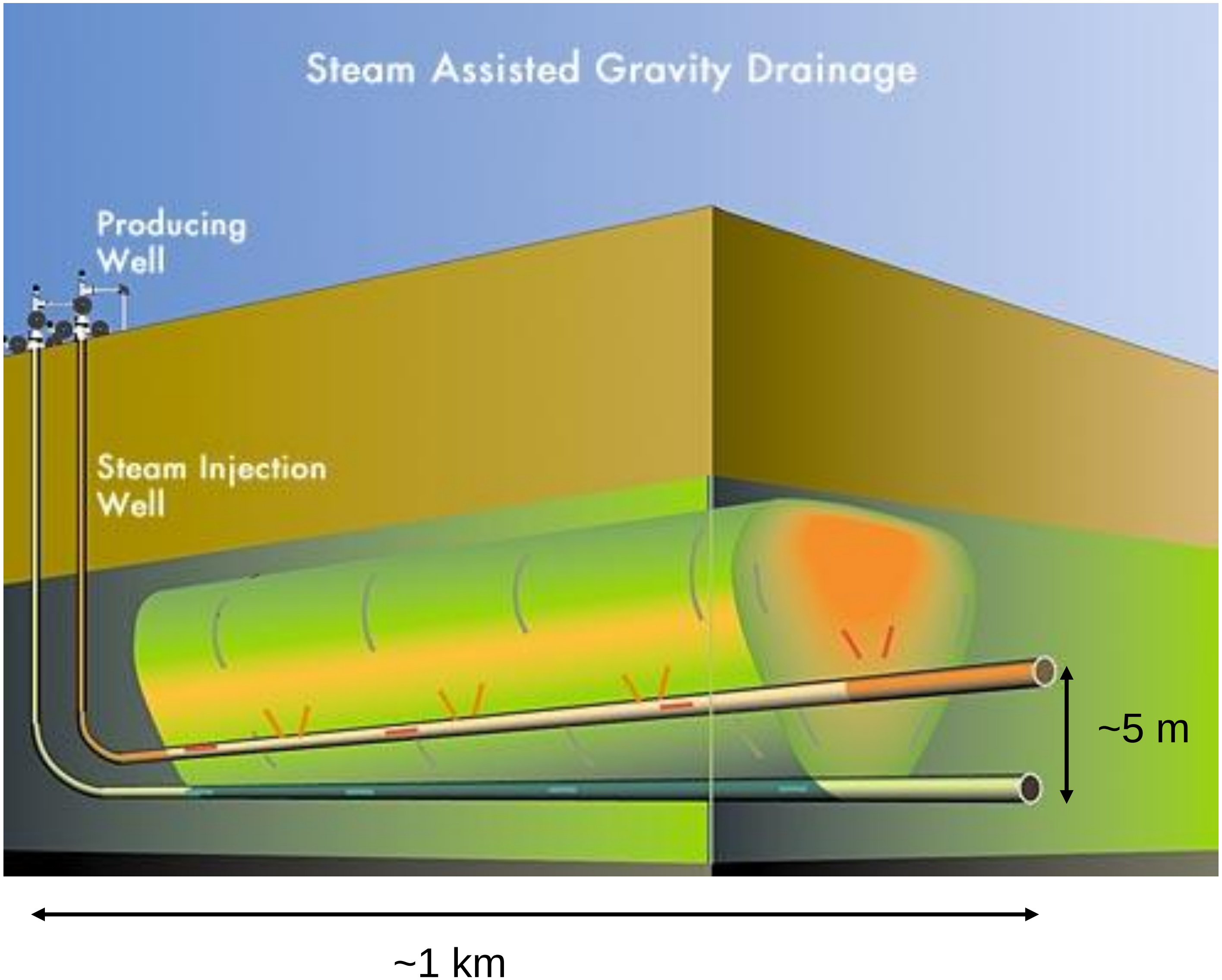
Truck is bigger than a house, costs $5M.

~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 burning 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.**
- Too small to achieve even factor of 2. Minor effect on climate and fuel supply.

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 converted to heat and wasted.
  - Economics depend strongly on gas price, abundance.
  - Can work economically, **but not helpful for climate problem**.
- More efficient CH_4 reaction paths to make liquids??
  - Conversion to methanol is easy, used to make chemicals.
  - Many proposed other paths, but none successful so far
  - General problem: CH_4 is less reactive than products
  - Need a **Green Chemistry** breakthrough!

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 sells for ~$100/day or $36,500/year: ~3 year pay back if gas is free & oil prices stay high…

But very large CO_2 emissions

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:

$$CO + H_2O = CO_2 + H_2$$

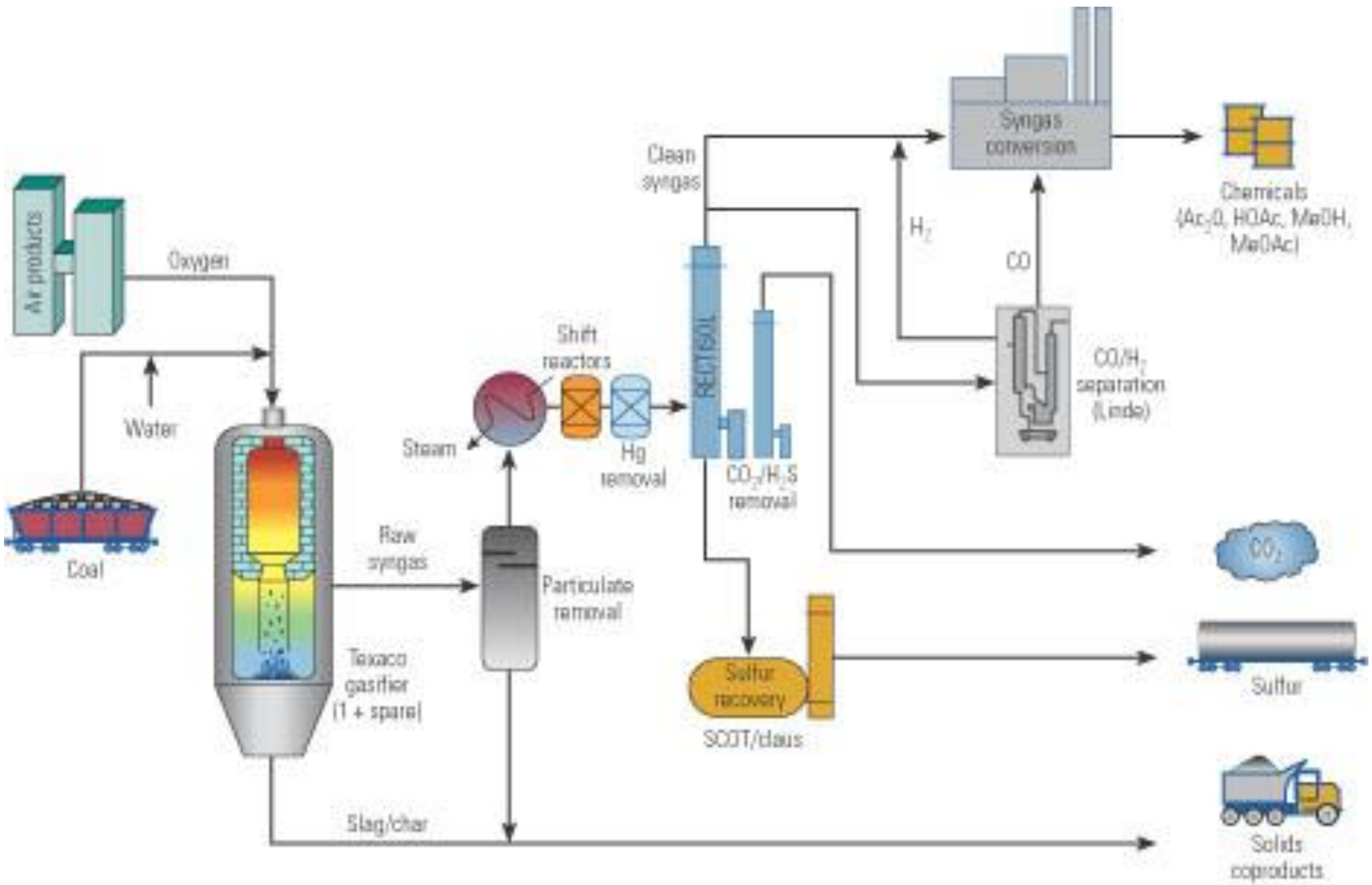
Then either Fischer-Tropsch to make hydrocarbons:

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

or methanol synthesis:

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

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



Larger (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

Option #8: Fuels from Biomass

- Much more Biomass than Food
- Waste Biomass now equivalent to ~20% of liquid fuel consumption 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 H_2.

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.
  - 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.

Possible **Green Chemistry** solution: **reduces CO2 emissions and maybe not too expensive.** Needs more R&D: costs, benefits, best process still unclear.

Option #9: Liquid Fuels from CO_2 as carbon source

- Plants convert CO_2 into fuel:

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

- Biological photosynthesis has disadvantages
  - ~1% efficiency from photons to fuel energy
  - Huge Arable Land Use, Lots of Fresh Water
  - Main product is solid (wood), not liquid fuel
- $CO_2 \rightarrow$ fuel + O_2 is *very* endothermic, requires lots of input energy (e.g. sunlight, or heat)

Liquid Fuels from CO_2 as carbon source: How?

– How to collect the CO_2? CO_2 in atmosphere is too dilute, would take a lot of energy to concentrate it.
  - High-concentration CO_2 electric power plants could provide the CO_2 in future, but only a few exist today.

– Input Heat and run an endothermic reaction?
  - We need a lot of heat to make huge amount of fuel required.
  - Heat from the sun: solar tower?
  - Heat from nuclear power plant?

– Direct Solar Photochemistry (e.g. Ru water splitting)
  - So far this does not work well, but lots of ongoing research

– Solar to Electricity to Electrochemical synthesis?
  - Good progress in solar water splitting to H_2 + O_2
  - Observation of CO_2 reduction to hydrocarbons (low yield)

Looks Difficult: a major **Green Chemistry** R&D challenge….

Solar Tower /Mirrors concentrate sunlight

Today: used to boil water to generate electricity.

Future: convert CO_2 to liquid fuels?

Summary

- Current Refinery/Petrochemical system efficiently converts crude oil to useful fuels and materials.
  - Rearranges C,H atoms in crude into more useful molecules.
  - Enables modern goods and transportation.
  - Green Chemistry could reduce environmental impact.
- Most difficult environmental challenge is CO_2 emissions from burning fossil fuels
  - Burning fossil fuels provide most of the world's energy
  - High levels of CO_2 cause climate change
  - How to reduce CO_2 emissions from transportation?
- Some methods known to increase useful energy / CO_2 emitted, but need additional Green Chemistry breakthroughs to meet increasing affordable energy demand without causing major climate change.