ER 100:
Energy Toolkit I: Combustion

September 2, 2015

Overview

- What do we do with fossil fuels: *burn 'em*
  - Combustion: impacts
- Fuels
- Balancing combustion chemical equations
- Combustion products
- Equivalence ratios
- Energy content and temperature

Importance of fossil fuels

- The major contributors to Energy Use in the US and in the world

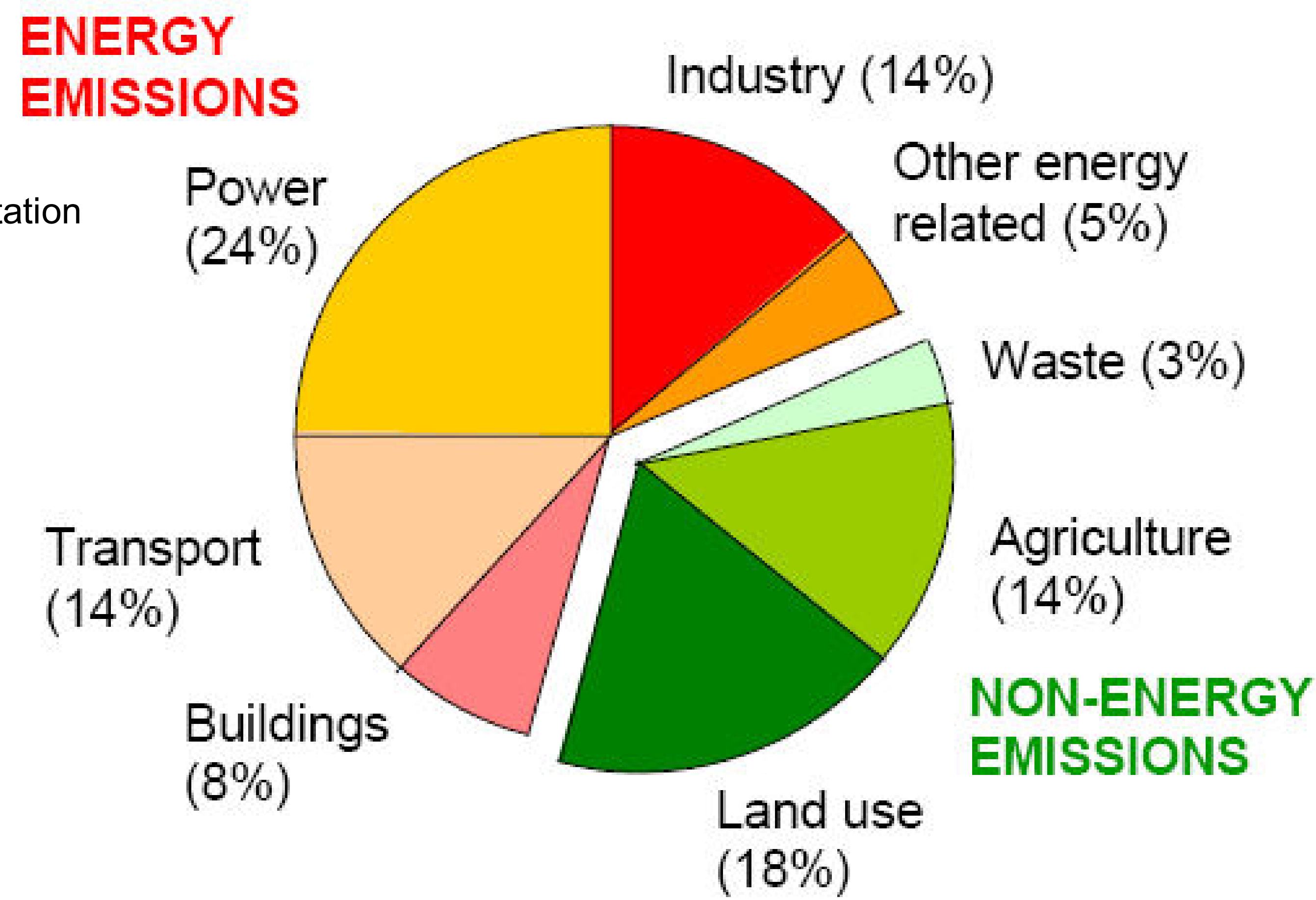
Energy Supply 2010	**World**	**U.S.**
Total Energy use (Quads)	428	97
Coal (%)	33	38
Natural Gas (%)	22	26
Biomass fuels (%)	13	4
Hydropower (%)	6	4
Nuclear (%)	6	8
Solar, wind, geothermal (%)	<0.5	0.4

Electricity Supply 2010	**World**	**U.S.**
Net generation (TWh)	12,500	3,400
Fossil fuel (%)	62	68
Hydropower (%)	19	9
Nuclear (%)	17	20
Biomass and other (%)	5	3

Emissions By Source (2010)

Note: land use means deforestation and the like.

- Land use and agriculture are major contributors.



Energy emissions are mostly CO_2 (some non-CO_2 in industry and other energy related).
Non-energy emissions are CO_2 (land use) and non-CO_2 (agriculture and waste).

Source: Stern Review, from data drawn from World Resources Institute Climate Analysis Indicators Tool (CAIT) on-line database version 3.0

Emissions: Terms of Discussion

- Mole fraction (%, ppm, ppb)
- mass/energy in (pollutant/MMBtu, Kg/KJ)
- mass/distance (g/mile) [vehicle standards]
- mass/volume = $\mu g/m^3$
- reference emissions to corrected oxygen content in exhaust to prevent apparent emission reductions by dilution
  - Remember, the solution to pollution is … dilution.

What happens in combustion?

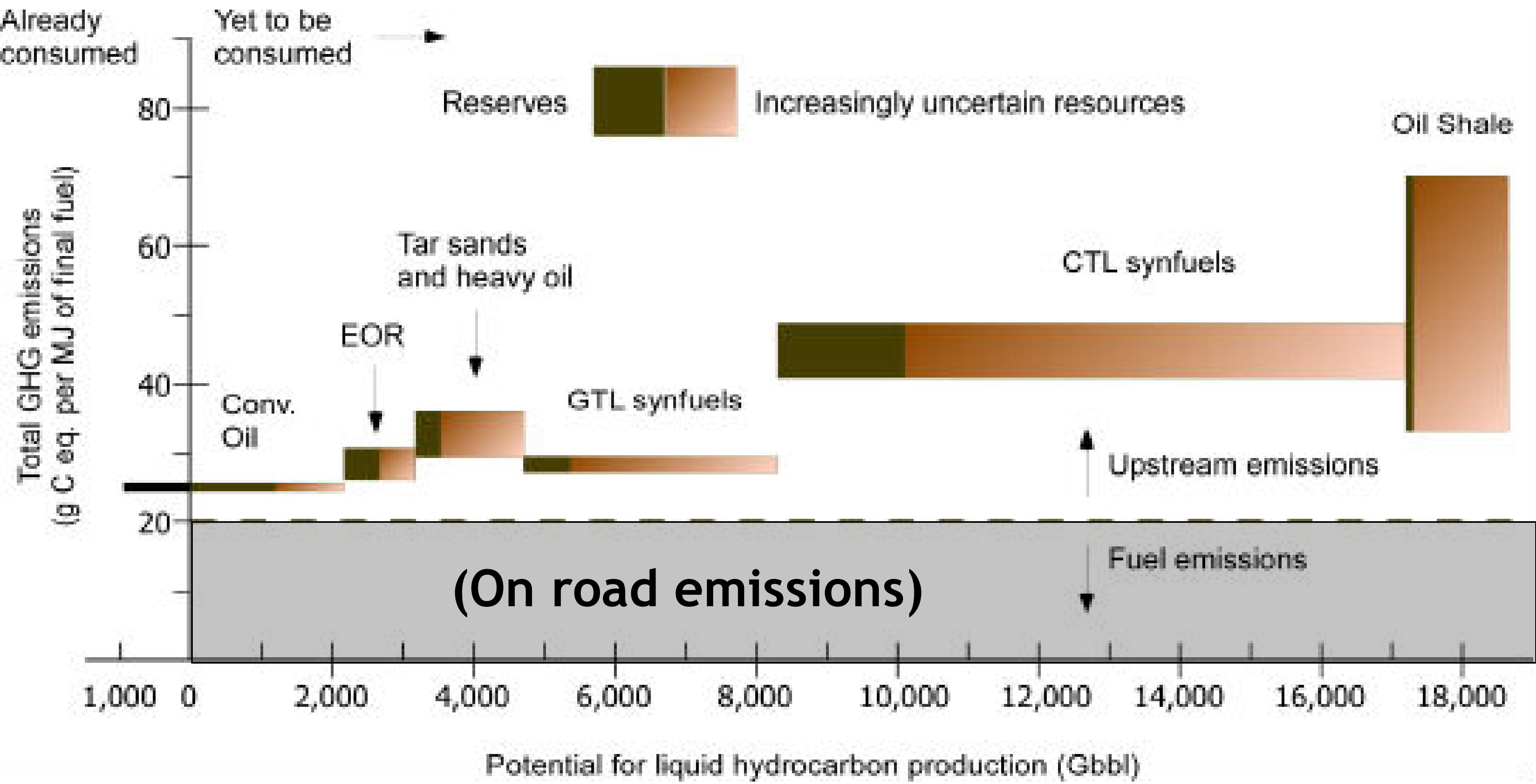
- Fuel + oxidizer -> Products + light + heat
- Combustion, in its simplest form, e.g: methane

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_20$$

A clean reaction, except for the issue of carbon dioxide and the global climate

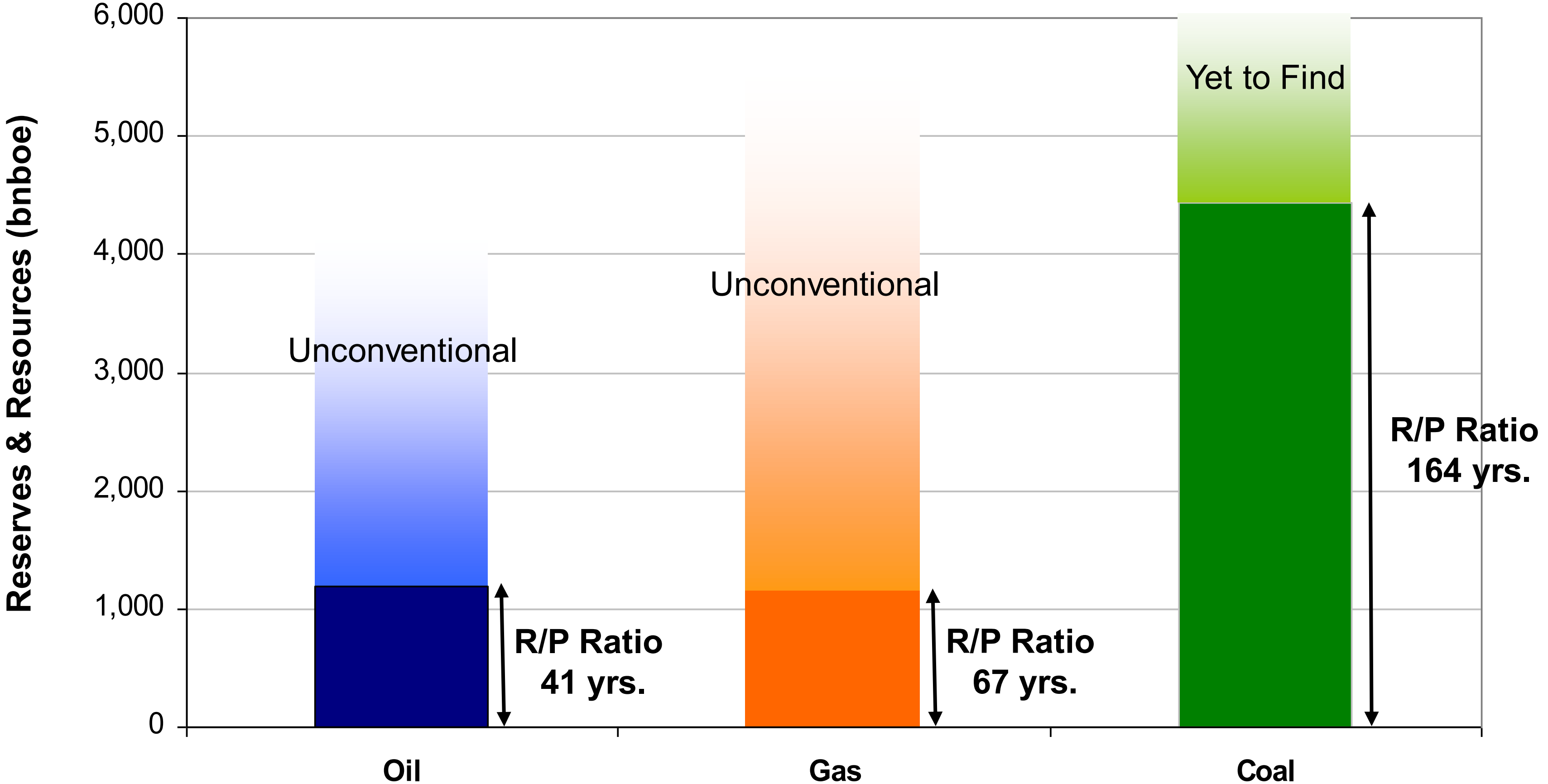
This idealized reaction takes place in an 'atmosphere' (oxygen) free of impurities

Context: combustion is *part* of the story



Source: Brandt and Farrell (2006) ***Environmental Research Letters (erl.iop.org)***

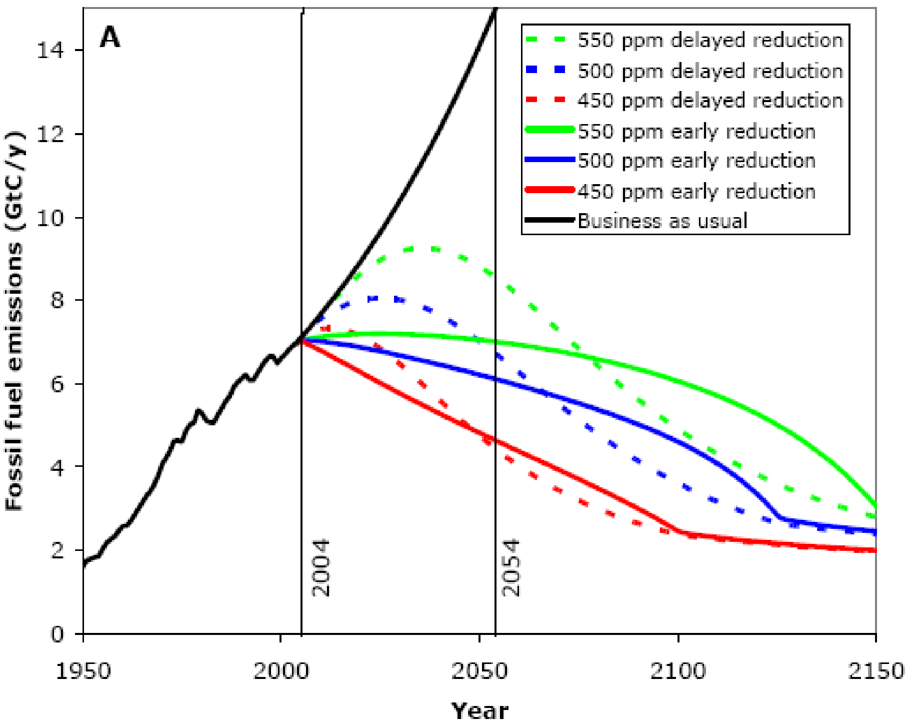
Fossil Fuel Supply



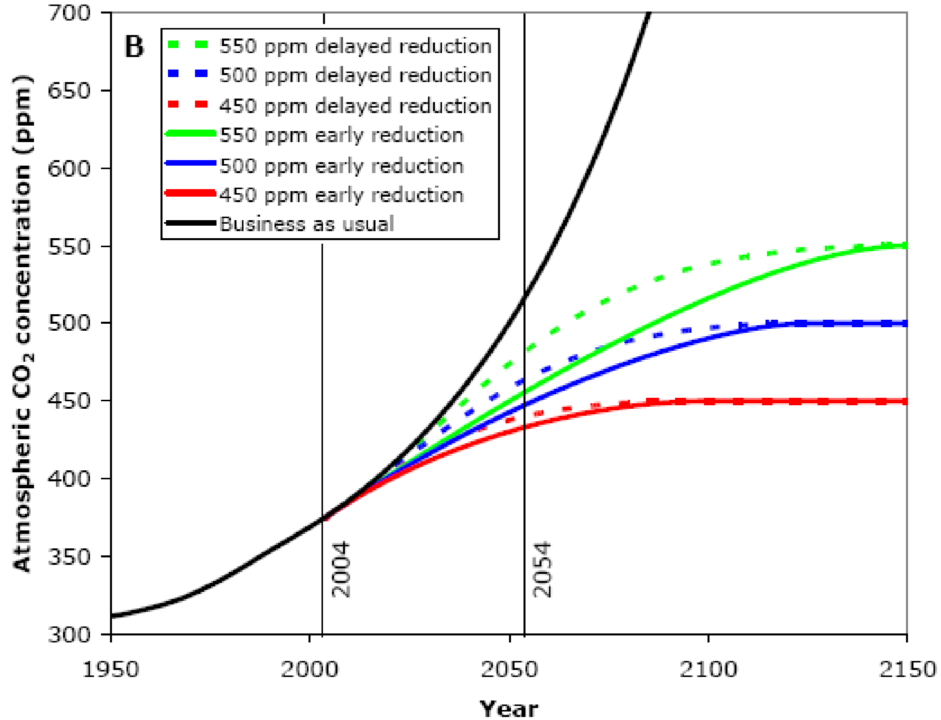
Source: World Energy Assessment 2001, HIS, WoodMackenzie, BP Stat Review 2005, BP estimates

Things to Know About CO_2 In the Atmosphere in Order to Solve

Emissions



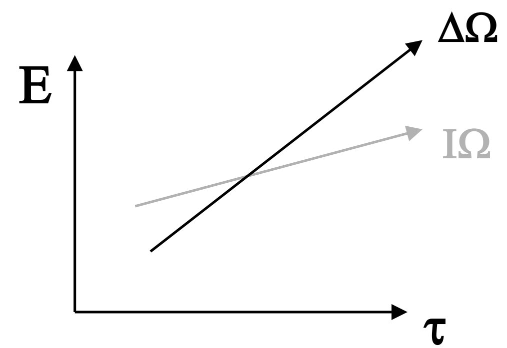
Concentration



- The lifetime of CO2 in the atmosphere is about 100 years
- About half of what we put up there stays up there
- A bend in the emissions graph will just delay the time that we cross the dangerous CO2 level threshold
- Rule of thumb: every 10 percent reduction in emissions buys you about 7 years before reaching the max
- We need to reduce emissions by a factor of two from current levels to remain stable at the 550 ppm level, and this in the face of doubling the demand of energy by the middle of the century, so we need to cut the common intensity of our energy system by a factor of four

Emissions Facts

- **21st Century emissions from the Developing World (DW) will be more important than those from the Industrialized World (IW)**
  - DW emissions growing at 2.8% vs. IW growing at 1.2%
  - DW will surpass IW during 2015 - 2020



- **Sobering facts**
  - When DW ~ IW, each 10% reduction in IW emissions is compensated by < *4 years* of DW growth
  - If China's (or India's) per capita emissions were those of Japan, global emissions would be 40% higher
- **Reducing emissions is an enormous, complex challenge; technology development will play a central role**

Fuel: Data Summary

❑ Properties of Selected Fuels

	CH_4	C_2H_6	C_3H_8	Other HC_s	H_2S	Heating Value
			(wt%)			(10^6 J/m^3)
Natural gas (No.1)	87.7	5.6	2.4	1.8	2.7	43.2
Natural gas (No.2)	88.8	6.4	2.7	2.0	0.0004	41.9

(Ultimate analysis)	C	H	N	O	S	Heating value
				(wt%)		(10^6 J kg^{-1})
Gasoline (No.2)	86.4	12.7	0.1	0.1	0.4-0.7	

(Approximate analysis)	Carbon	Volatile matter	Moisture	Ash	Heating value
	(%)	(%)	(%)	(%)	(10^6 J kg^{-1})
Anthracite (PA)	77.1	3.8	5.4	13.7	27.8
Bituminous (PA)	70.0	20.5	3.3	6.2	33.3
Subbituminous (CO)	45.9	30.5	19.6	4.0	23.6
Lignite (ND)	30.8	28.2	34.8	6.2	16.8

Data from Flagan and Seinfeld, Fundamentals of Air Pollution Engineering, 1988, Prentice-Hall.

How much CO_2 is produced when 1 ton of cellulose ($C_6H_{12}O_6$) is burned?

Balance the equation:

$$C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$$

First the carbon:

$$C_6H_{12}O_6 + O_2 \rightarrow 6CO_2 + H_2O$$

Then the hydrogen:

$$C_6H_{12}O_6 + O_2 \rightarrow 6CO_2 + 6H_2O$$

Last, the oxygen (because you can change the oxygen without altering other elements):

$$C_6H_{12}O_6 + O_2 \rightarrow 6CO_2 + 6H_2O,$$

Oxygen: 6 + x

Oxygen: 12 + 6 =18

So, $6 + x = 18 \rightarrow x = 12$, or 6 O_2 The balanced equation is:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

What about the grams per mole of wood (molecular weight):

$C_6H_{12}O_6$ = (6 x 12) + (12 x 1) + (6 x16) = 180 grams/mole

How much CO_2 is produced when 1 metric ton of wood is burned, continued ...

From the equation we can find out how much CO_2 we get per metric ton of wood.

So, from $C_6H_{12}O_6 \rightarrow 6CO_2 + 6H_2O$, we see that:

$$\frac{180\text{g } C_6H_{12}O_6}{\underbrace{264\text{g } CO_2}} = \frac{10^6\text{g } C_6H_{12}O_6}{X \text{ g}CO_2}$$

(12+(2x16)) = 44 grams per mole of CO_2

$$x = \frac{264\text{g x } 10^6\text{g}}{180\text{g}} = 1.47 \text{x } 10^6\text{g} = 1.47 \text{ tons of } CO_2$$

Practice:

http://education.jlab.org/elementbalancing/

Combustion Stoichiometry: More elegant solution

- **Combustion in Oxygen**

$$C_nH_m + O_2 \rightarrow CO_2 + H_2O$$

1. **Balance the above equation.**
2. **Write the reactions for combustion of methane and benzene in oxygen, respectively.**

Answer

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$

Combustion Stoichiometry

- **Combustion in Air (O_2 = 21%, N_2 = 79%)**

$$C_nH_m + (O_2 + 3.78N_2) \rightarrow CO_2 + H_2O + N_2$$

1. **Can you balance the above equation?**
2. **Write the reactions for combustion of methane and benzene in air, respectively.**

Answer

$$C_nH_m + \left(n + \frac{m}{4}\right)(O_2 + 3.78N_2) \rightarrow nCO_2 + \frac{m}{2}H_2O + 3.78\left(n + \frac{m}{4}\right)N_2$$

$$CH_4 + 2(O_2 + 3.78N_2) \rightarrow CO_2 + 2H_2O + 7.56N_2$$

$$C_6H_6 + 7.5(O_2 + 3.78N_2) \rightarrow 6CO_2 + 3H_2O + 28.35N_2$$

Real Combustion

- If combustion occurs without complete oxidation instead, we get:

$$CH_4 + O_2 + N_2 \rightarrow \text{mostly } (CO_2 + 2H_20 + N_2) + \text{traces } (CO + HC + NO\ldots)$$

- This can occur when:
  - temperature too low,
  - insufficient O,
  - combustion too rapid,
  - poor mixing of fuel and air, etc. ...

Real, Real (fully nasty), Combustion

- At higher temperatures, N reacts with O:

  air(N_2 +O_2) + heat → NO_x (thermal)

- So much for pure fuels, now add impurities:

  enter N, S, metals and ash (non-combustibles)

What we really get:

- Fuel (C, H, N, S, ash) + air (N_2 +O_2) →
  (CO_2, H_2O, CO, NO_x, SO_x, VOCS, particulates) + ash
  - Volatile Organic Compounds: VOCs

Air-Fuel Ratio

- **Air-Fuel (AF) ratio**

$$AF = m_{Air} / m_{Fuel}$$

Where: m_{air} = *mass of air in the feed mixture*

m_{fuel} = *mass of fuel in the feed mixture*

Fuel-Air ratio: $FA = m_{Fuel} / m_{Air} = 1/AF$

- **Air-Fuel molar ratio**

$$AF_{mole} = n_{Air} / n_{Fuel}$$

Where: n_{air} = *moles of air in the feed mixture*

n_{fuel} = *moles of fuel in the feed mixture*

Air-Fuel Ratio

- **Rich mixture**

  - more fuel than necessary

    $(AF)_{mixture} < (AF)_{stoich}$

- **Lean mixture**

  - more air than necessary

    $(AF)_{mixture} > (AF)_{stoich}$

Most combustion systems operate under lean conditions.
Why is this advantageous?

Consider the combustion of methanol in an engine.

If the Air-Fuel ratio of the actual mixture is 20, is the engine operating under rich or lean conditions?

Equivalence Ratio

Equivalence ratio: shows the deviation of an actual mixture from stoichiometric conditions.

$$\phi = \frac{(FA)_{actual}}{(FA)_{stoich}} = \frac{(AF)_{stoich}}{(AF)_{actual}}$$

The combustion of methane has an equivalence ratio Φ=0.8 in a certain condition. What is the percent of excess air (EA) used in the combustion?

How does temperature change as Φ increases?

Formation of NOx and CO in Combustion

❑ Thermal NOx

- Oxidation of atmospheric N_2 at high temperatures

$$N_2 + O_2 \leftrightarrow 2NO$$

$$NO + \tfrac{1}{2}O_2 \leftrightarrow NO_2$$

- Formation of thermal NOx is **favorable** at higher temperature

❑ Fuel NOx

- Oxidation of nitrogen compounds contained in the fuel

❑ Formation of CO

- Incomplete Combustion
- Dissociation of CO_2 at high temperature

$$CO_2 \leftrightarrow CO + \tfrac{1}{2}O_2$$

Air Pollutants from Combustion

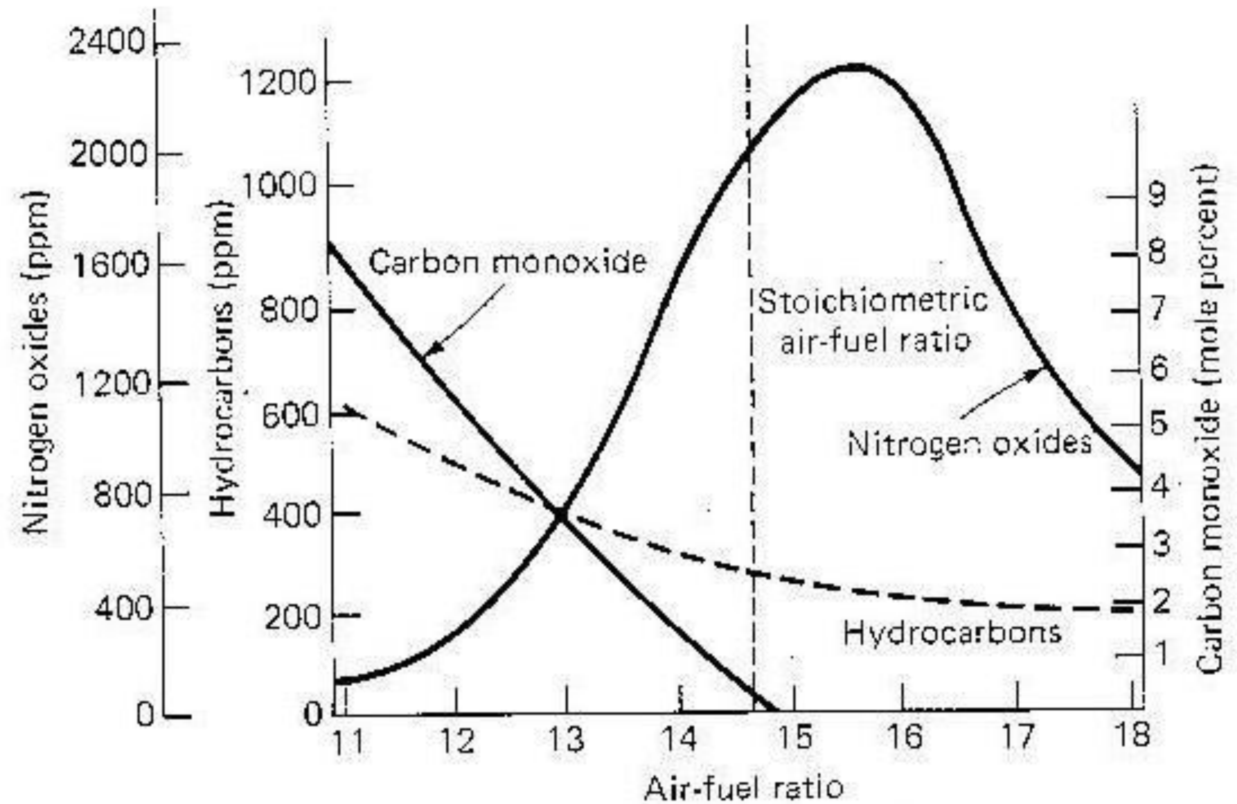


Figure 3.6. Exhaust hydrocarbons, carbon monoxide, and nitric oxide as a function of air–fuel ratio.

How do you explain the trends of the exhaust HCs, CO, and NOx as a function of air-fuel ratio?
How do you minimize NOx and CO emission?

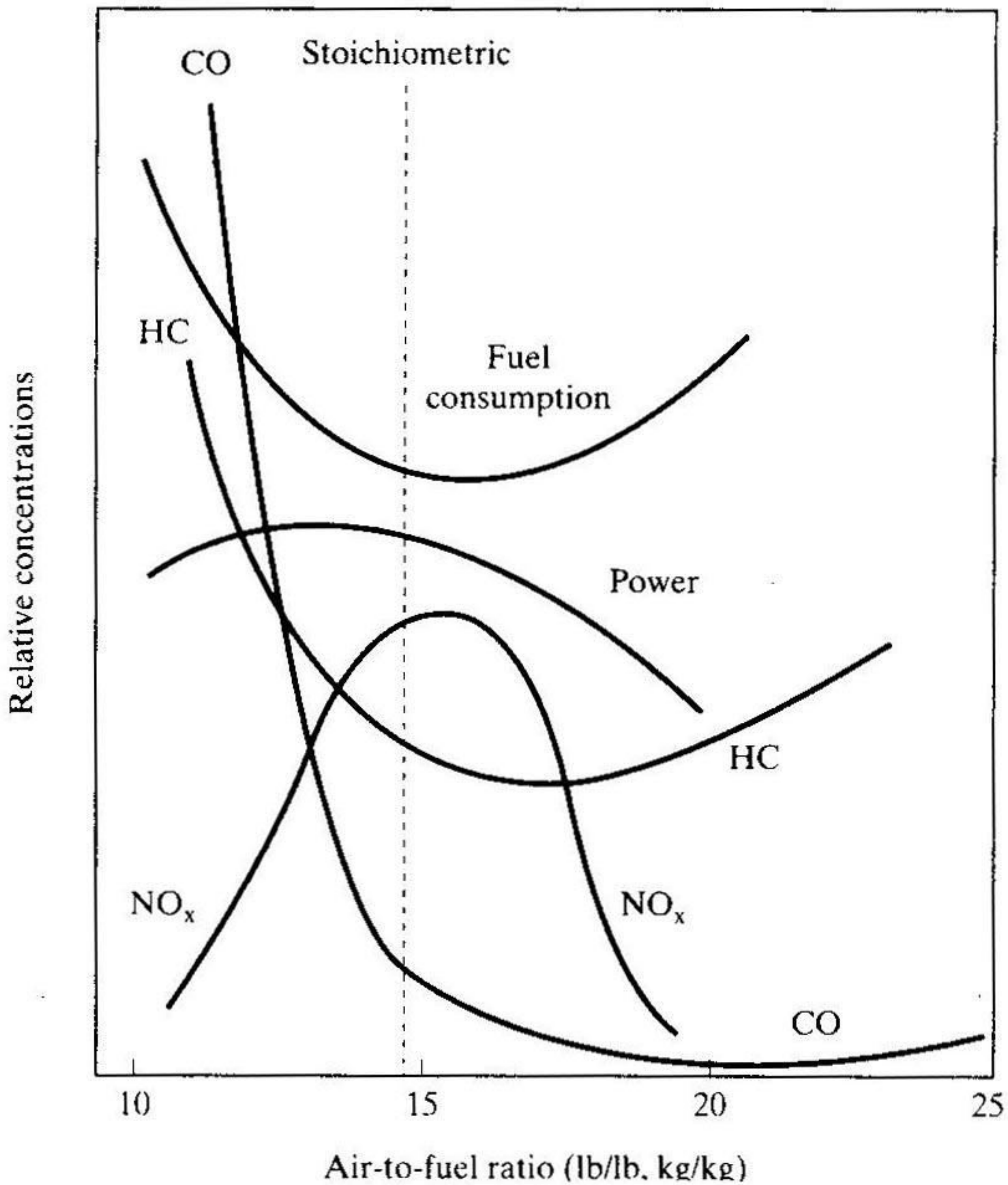
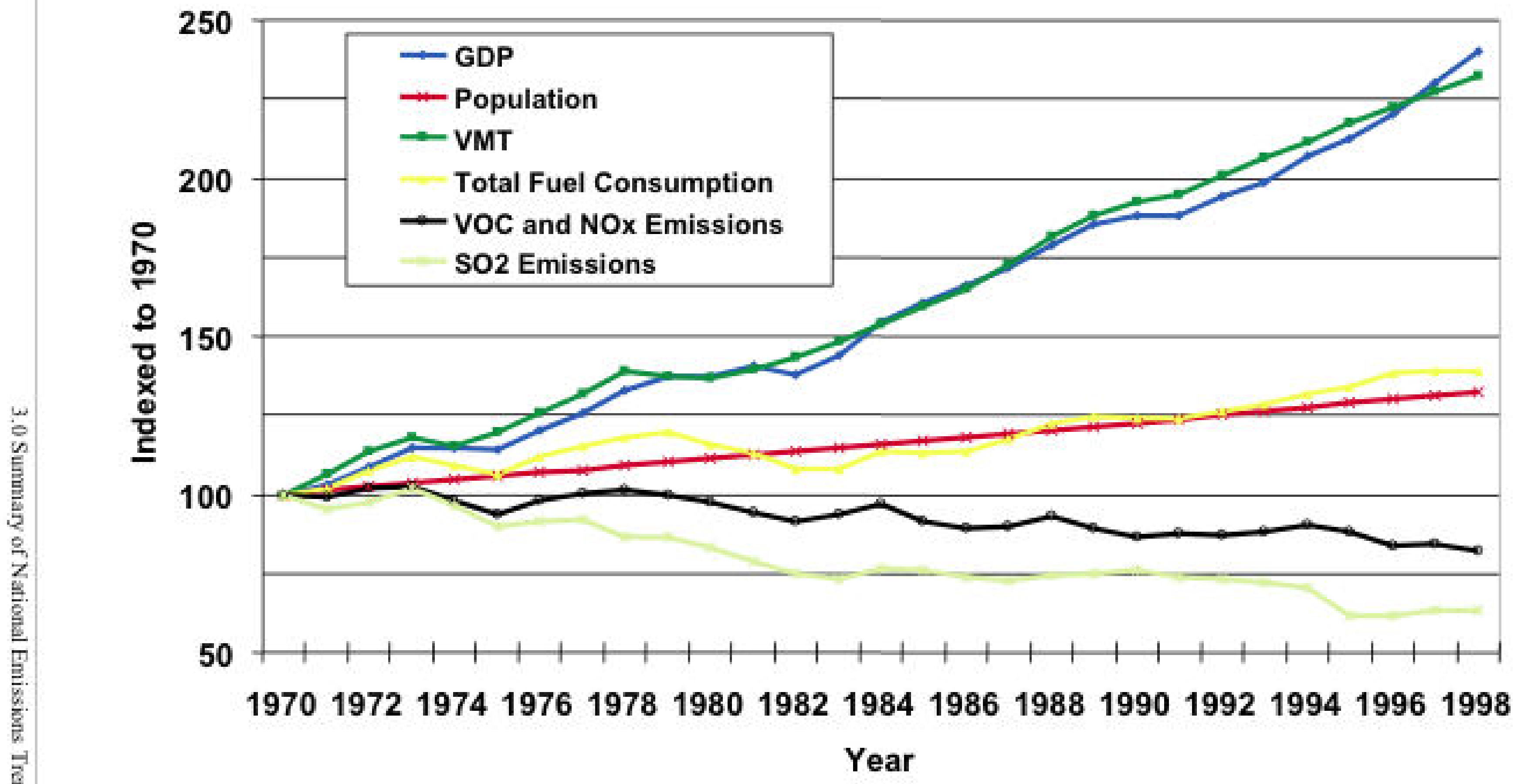


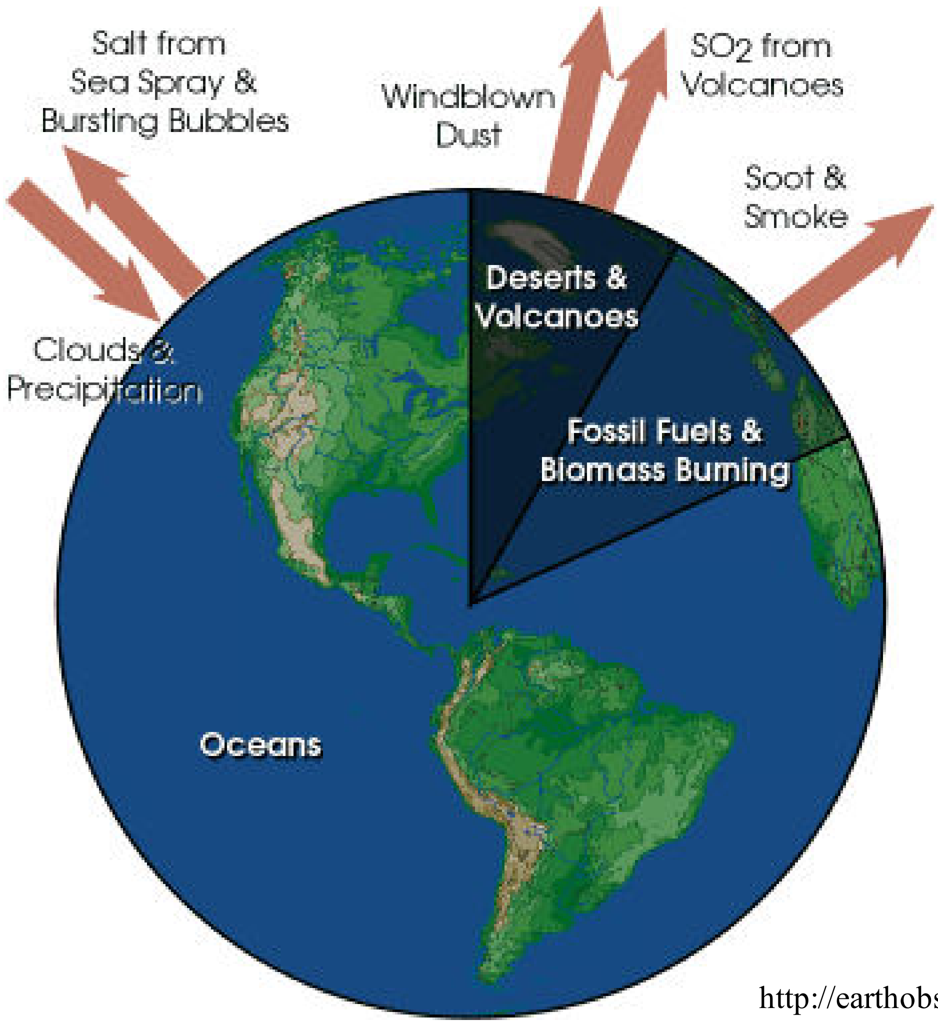
FIGURE 7.22 Effect of air-to-fuel ratio on emissions, power, and fuel economy.

Another IPAT

Figure 3-1. Trend in Gross Domestic Product, Population, Vehicle Miles Traveled, Total Fuel Consumption, combined VOLATILE ORGANIC COMPOUND and NITROGEN OXIDES Emissions, and SULFUR DIOXIDE Emissions, 1970 to 1998

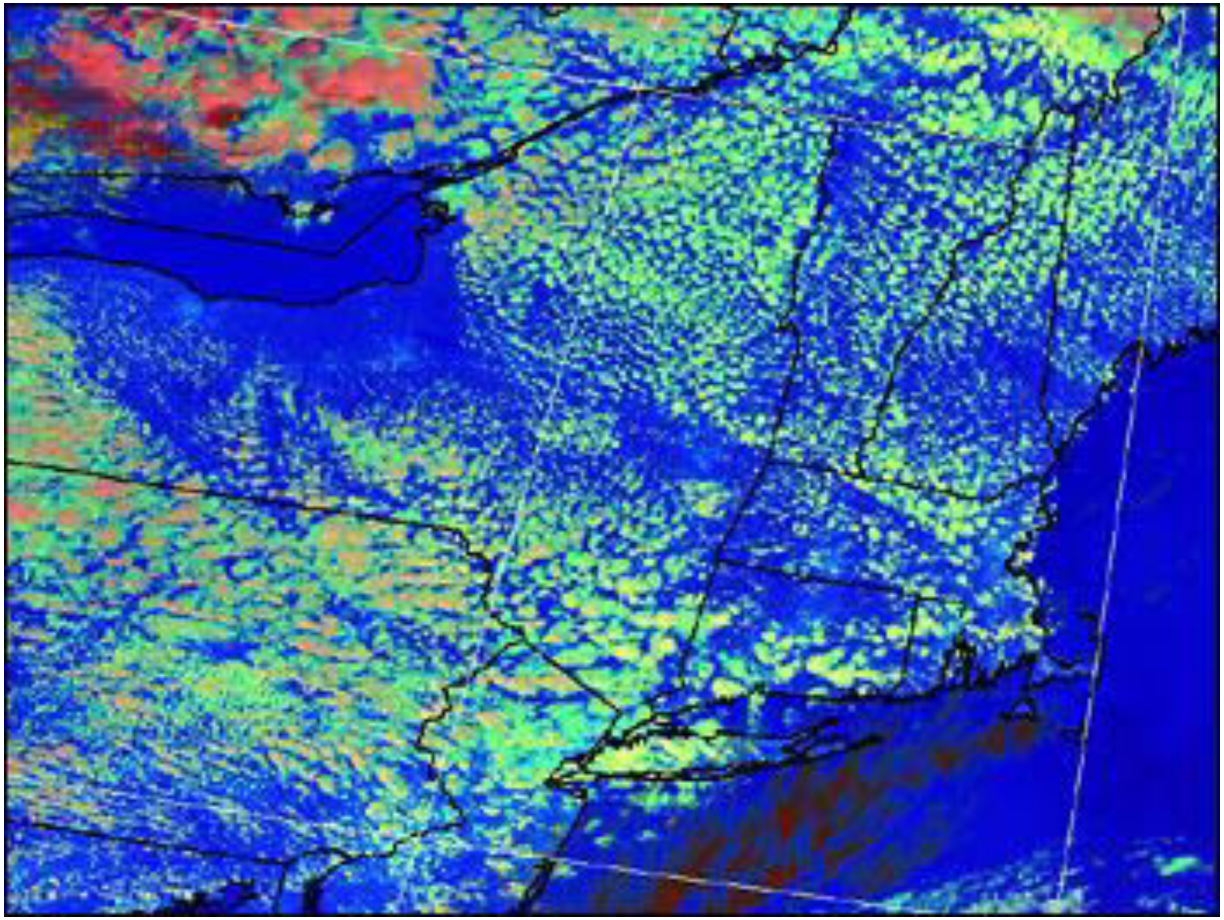


Aerosols



http://earthobservatory.nasa.gov/Library/Aerosols/

Aerosols: from power plants & cars



http://earthobservatory.nasa.gov/Library/Aerosols/

Summary: Combustion Products

- Air, N_2, O_2, Ar
- Products of complete combustion: CO_2, H_2O
- Products of incomplete combustion: trace hydrocarbons, unburned hydrocarbons, CO, H_2, aldehydes, soot
- Fuel impurities: SO_2, SO, metals, metal oxides, ash (silica, sand)
- Nitrogen compounds: N source is the air or the fuel, e.g.

  NO, NO_2, N_2O, HONO, NH_2

Fossil fuel combustion (chemistry)

- Coal = Carbon (C) + impurities (e.g., sulfur)
- Oil = Mixture of hydrocarbons (C_xH_y) + imp.
- Natural Gas = methane (CH_4) + carbon dioxide (CO_2) + imp.
- Combustion = oxidation, exothermic

$$C_xH_y + O_2 \Rightarrow CO_2 + H_2O + \text{ENERGY} + (CO+C)$$

$$N_2 + O_2 \Rightarrow NO_x$$

$$S + O_2 \Rightarrow SO_x$$

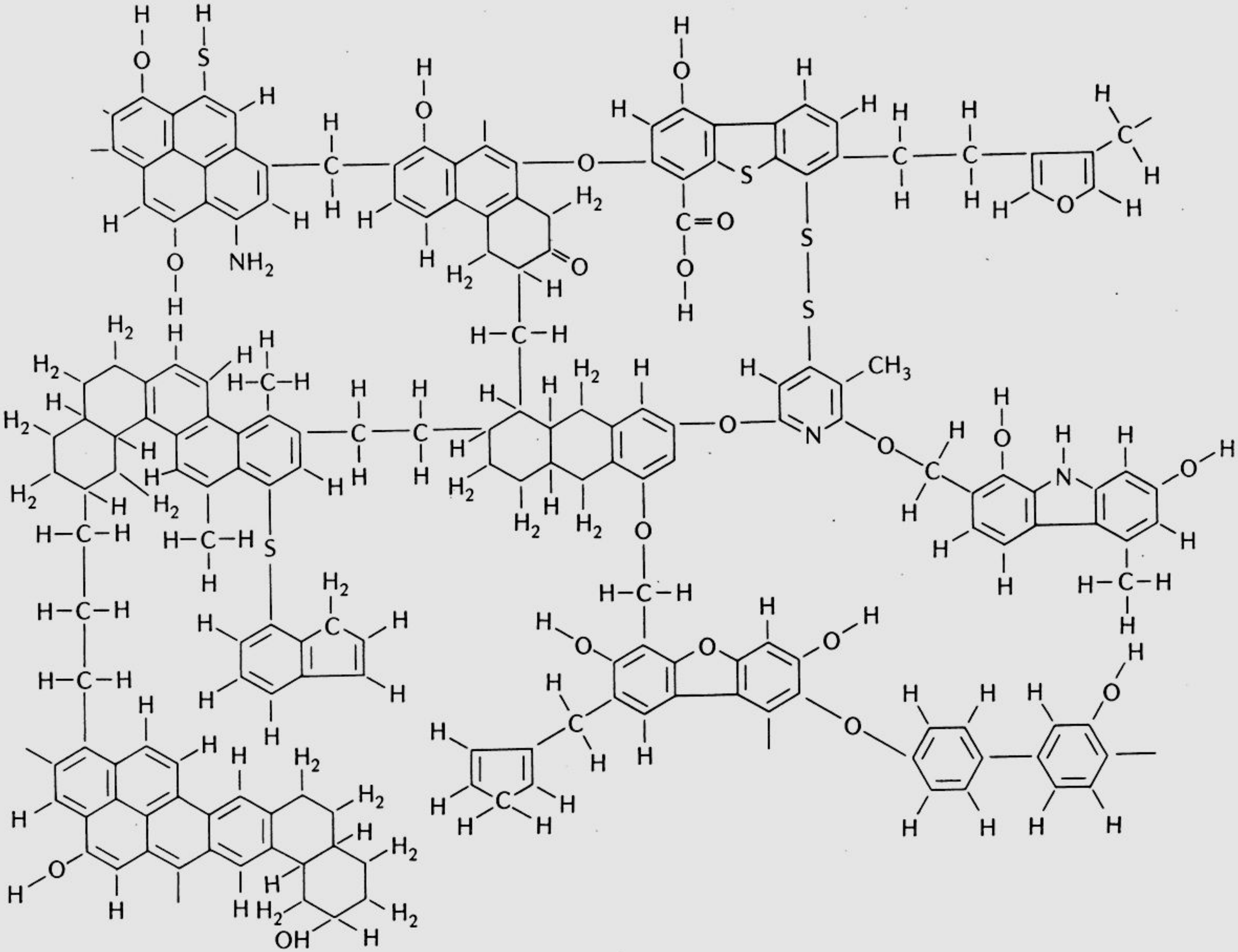
- Ratio of x:y determines ratio of CO_2:H_2O
- CH_4 has lowest x:y and thus lowest CO_2 per energy
- Carbon has the highest ratio

Solid fuels

- Peat
- Coal (moisture, volatiles, fixed carbon, ash) ($CH_{0.8}$)
- Wood (moisture, volatiles, fixed carbon, ash)
- Charcoal (devolatilized wood)
- Coke (devolatilized coal or petroleum)

- Key difference among fuels: the quantity of CO_2 formed per unit of energy released. Natural gas releases ~ 42% less CO_2 than coal

Chemical Structure of Coal



Gas and Liquid Fuels

- Natural gas: CH_4, C_2H_6, N_2, CO_2
- Propane(C_3), Butane (C_4), LPG (mixture)
- Synthetic gases (from biomass, coal products)
- Petroleum derived fuels (~CH_2);
  - Gasoline (C_4 to C_{10}, avg: C_8)
  - Diesel (C_{12})
  - Turbine fuels, kerosene (C_{10})
  - Heavy fuel oils
- Shale oil derived liquids
- Alcohols, ethers (have oxygen in the fuel)
- Hydrogen

Extra (But Interesting)

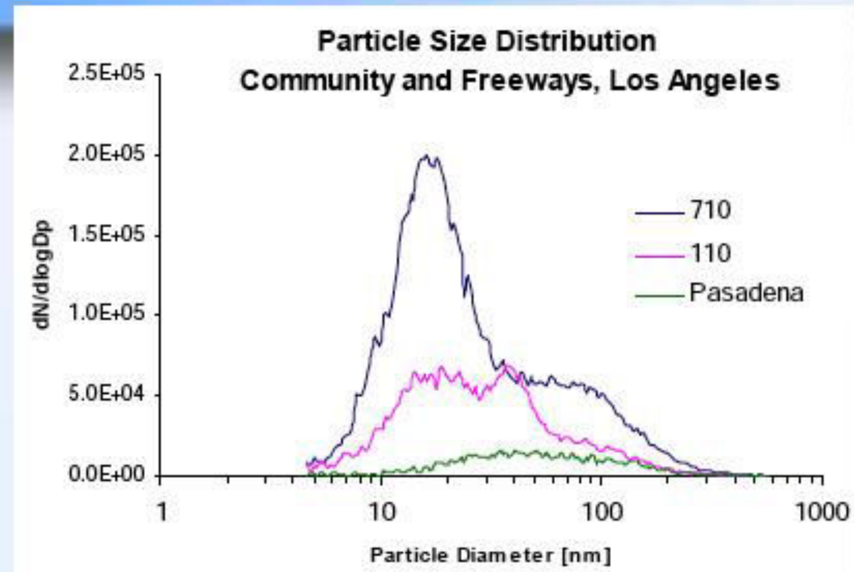
Exposure and diurnal variations

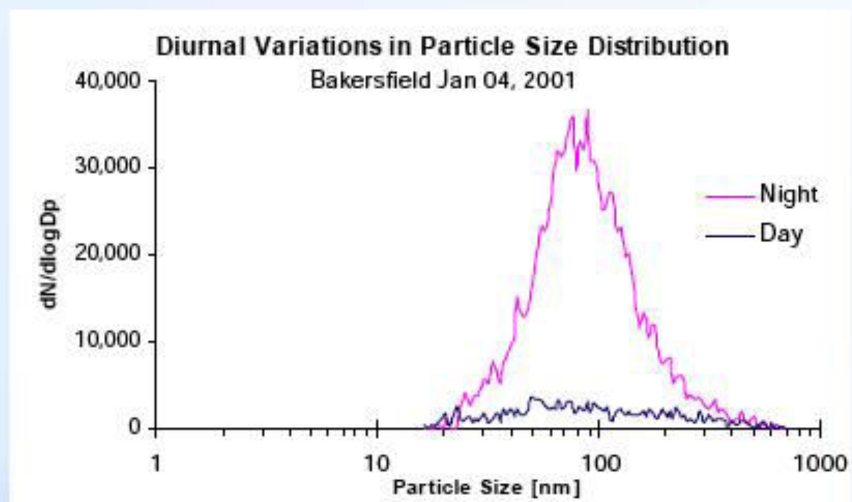
Exposure to ultrafine particles is very different on a freeway dominated by diesel trucks (710), or by light-duty vehicles (110), and in the community.

Westerdahl and Fruin, AE (2005)

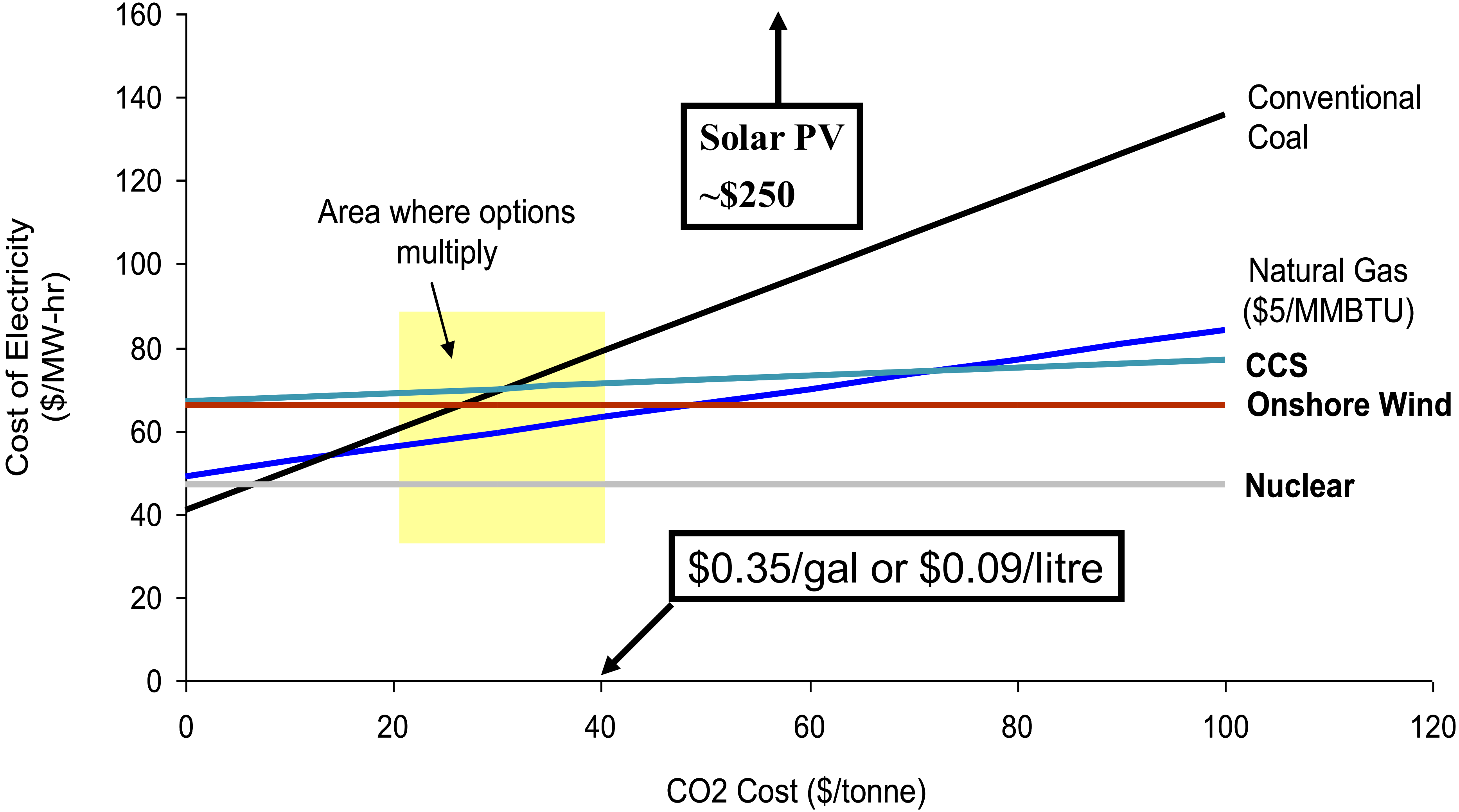
Diurnal variations of ultrafine particle concentrations in the community can be significant. In the San Joaquin Valley, emissions from evening wood burning can greatly increase concentrations.

Herner and Kleeman, unpublished





Preview of what is to come: Electricity Cost vs. CO_2 Cost



Source: IEA Technology Perspectives 2006, IEA WEO 2006 and BAH analysis

Notes: 1) Add solar 2) $40/tonne CO2 cost or tax is $0.35/gallon of gasoline or $0.09 (or 5p)/litre