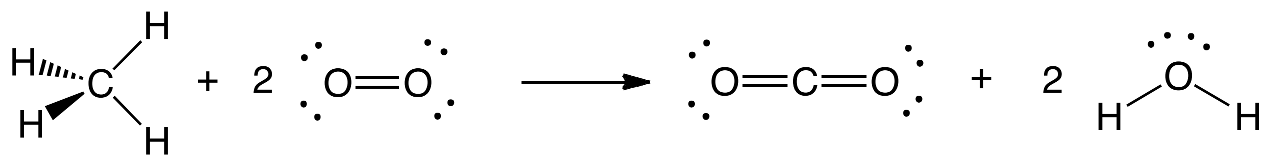
Overview of Fossil Fuels

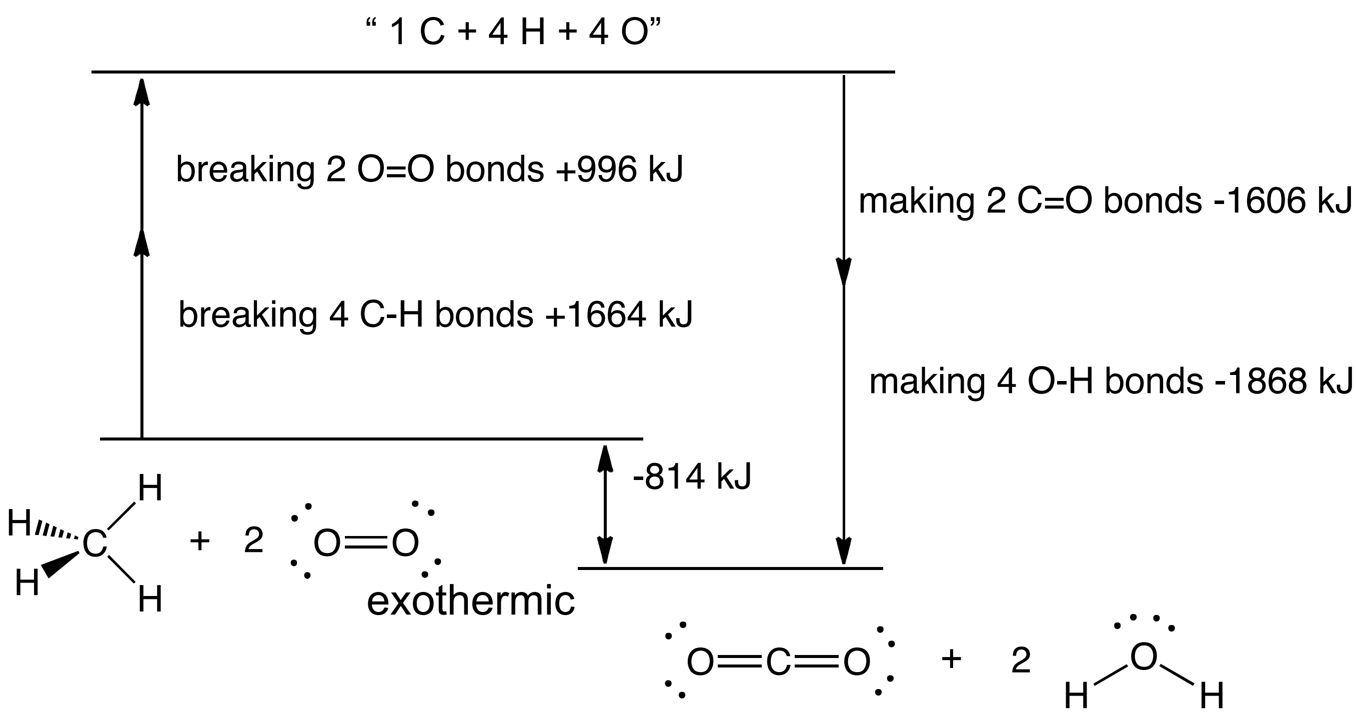
Thermochemical Cycle for Combustion of Methane

Burning methane (from an energy standpoint) to generate power:



A mole of C-H bonds is 416 kJ (we have 4)
A mole of O=O bonds is 498 kJ (we have 2)

A mole of O-H bonds is 467 kJ (we have 4)
A mole of C=O bonds is 803 kJ (we have 2)



Exothermic Reactions Require Bond Breaking to Cost Less Energy than Bond Making…

Hydrocarbons make good fuels because: O-H & C=O bonds are stronger than O=O, C-H, and C-C bonds

Table 4.2 Bond Energies (in kJ/mol)

	H	C	N	O	S	F	Cl	Br	I
Single Bonds									
H	436								
C	416	356							
N	391	285	160						
O	467	336	201	146					
S	347	272	—	—	226				
F	566	485	272	190	326	158			
Cl	431	327	193	205	255	255	242		
Br	366	285	—	234	213	—	217	193	
I	299	213	—	201	—	—	209	180	151

Multiple Bonds

C=C	598	C=N	616	C=O	803 in CO_2
C≡C	813	C≡N	866	C≡O	1073
N=N	418	O=O	498		
N≡N	946				

Source: Data from Darrell D. Ebbing, *General Chemistry,* Fourth Edition, 1993 Houghton Mifflin Co. Data originally from *Inorganic Chemistry: Principles of Structure and Reactivity,* Third Edition, by James E. Huheey, 1983, Addison Wesley Longman.

Energy Content of (Fossil) Fuels

Note: these are energies per unit mass; energies per mol change the order a bit…

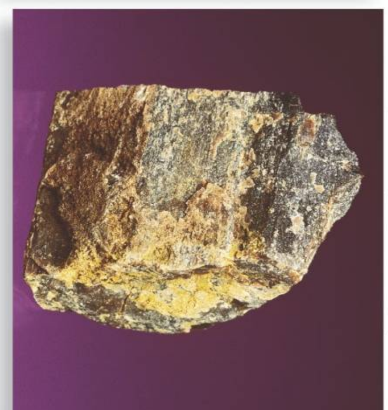
Table 4.3 Energy Content of Fuels

Source	kJ/g
Hydrogen	140
Methane	56
Propane	51
Gasoline	48
Coal (hard)	31
Ethanol	30
Wood (oak)	14

Table 4.4 Energy Content of Various U.S. Coals

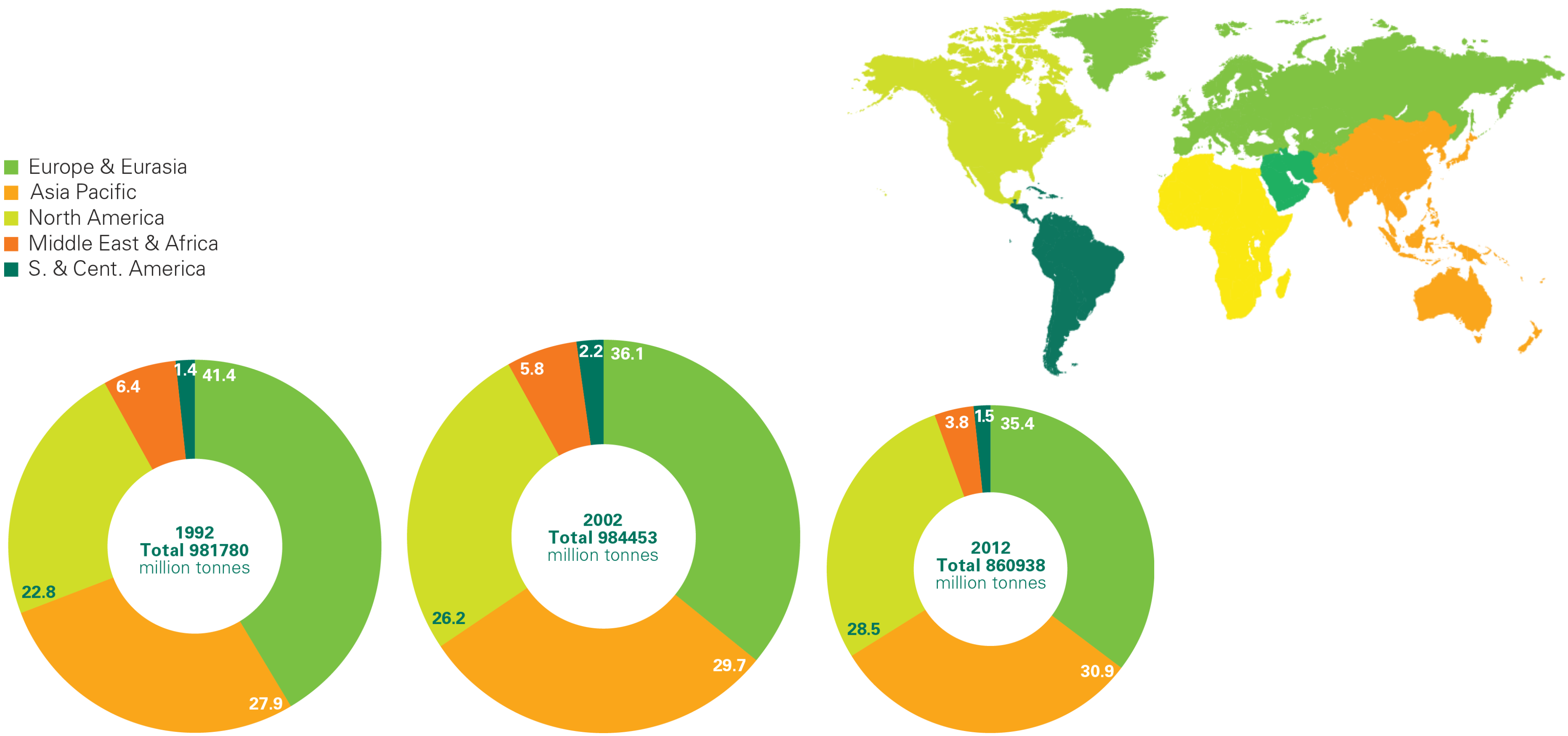
Type of Coal	State of Origin	Energy Content (kJ/g)
Anthracite	Pennsylvania	30.5
Bituminous	Maryland	30.7
Subbituminous	Washington	24.0
Lignite (brown coal)	North Dakota	16.2
Peat	Mississippi	13.0
Wood	Various	10.4–14.1

anthracite coal



lignite coal

Distribution of proved coal reserves in 1992, 2002 and 2012



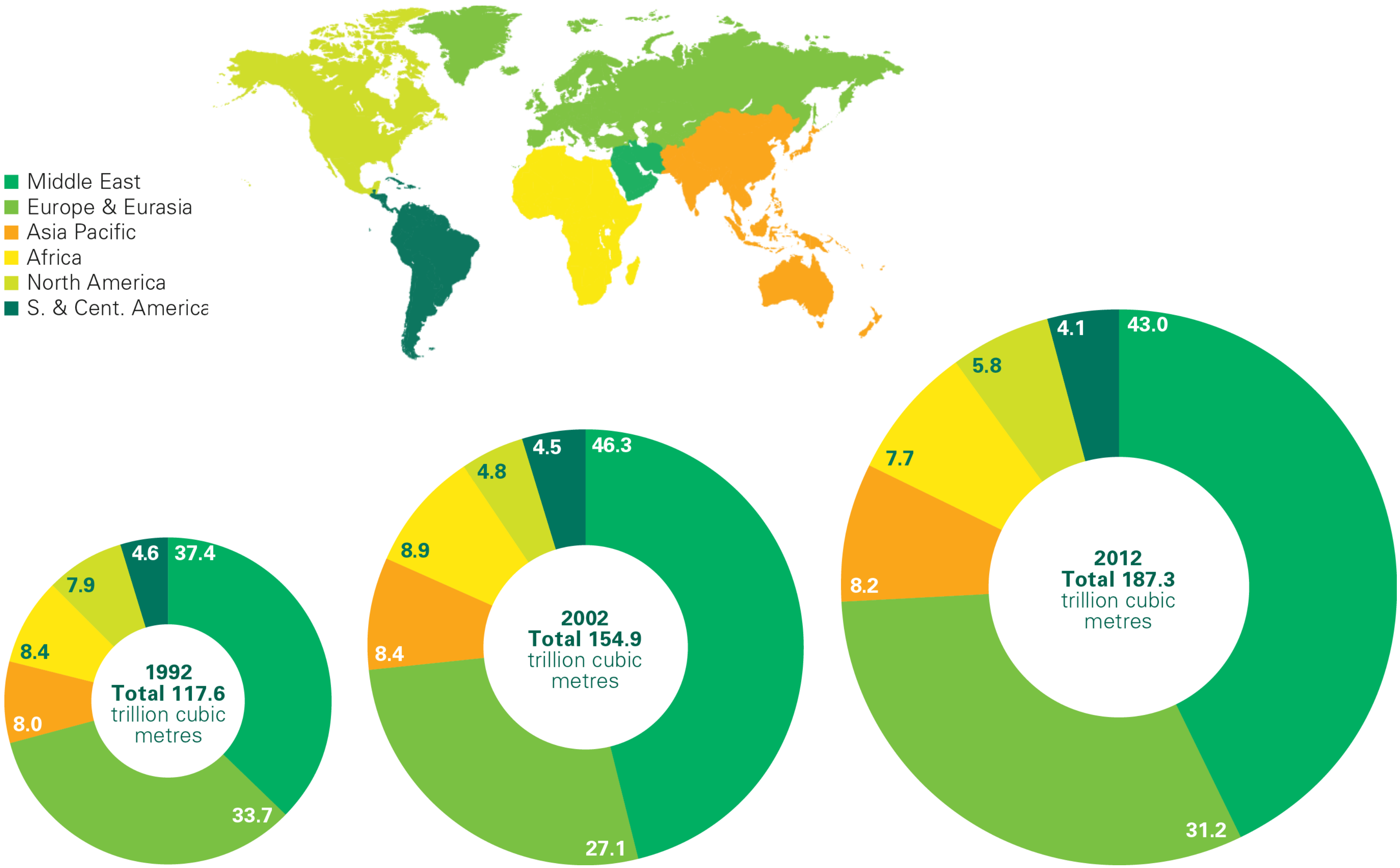
$$8.61\times10^{11}\ \text{Metric ton}\times\frac{1\times10^{3}\ \text{kg}}{1\ \text{Metric ton}}\times\frac{1\ \text{short ton}}{907.2\ \text{kg}}\times\frac{2.13\times10^{10}\ \text{J}}{1\ \text{short ton}}=20.2\times10^{21}\ \text{J}$$

$=20{,}200\ \text{EJ}$ $\left(1\ \text{EJ}=10^{18}\ \text{J}\right)$ World used 540 EJ in 2011

Source: Survey of Energy Resources 2010, World Energy Council.

BP Statistical Review of World Energy 2013

Distribution of proved gas reserves in 1992, 2002 and 2012

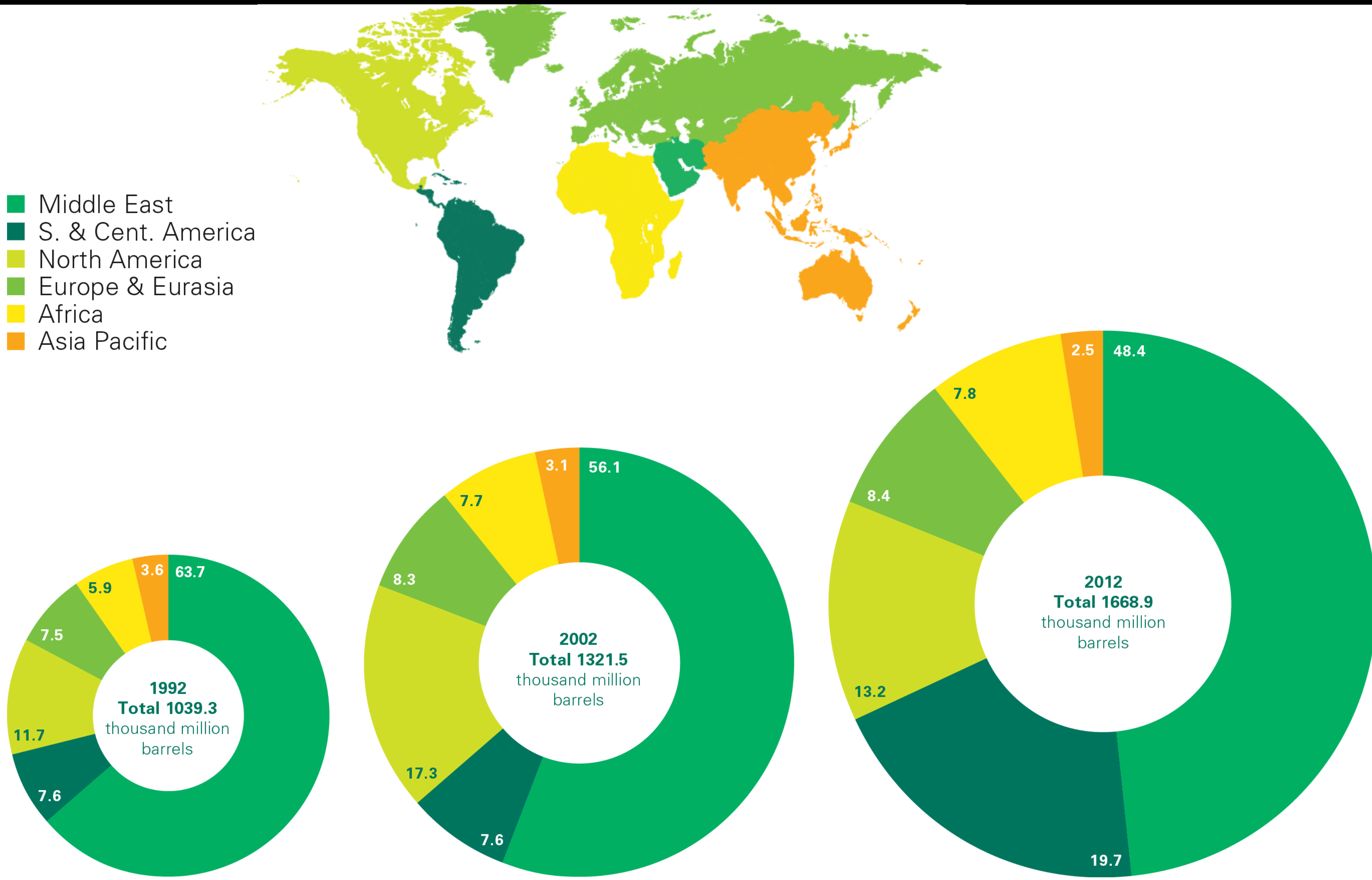


$$1.873\times10^{14}\ \text{m}^3 \times \frac{3.83\times10^{7}\ \text{J}}{1\ \text{m}^3} = 7.17\times10^{21}\ \text{J} = \boxed{7{,}170\ \text{EJ}}$$

World used 540 EJ in 2011

BP Statistical Review of World Energy 2013

Distribution of proved oil reserves in 1992, 2002 and 2012

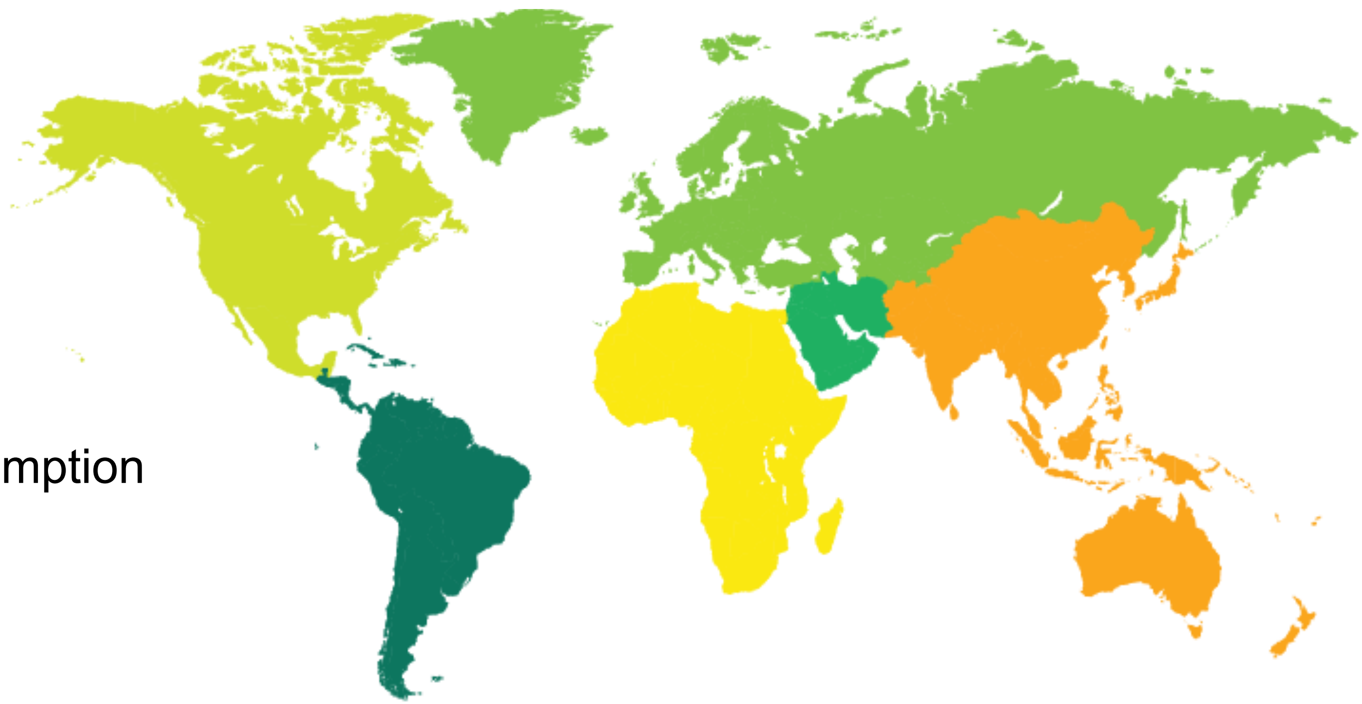


$$1.6689 \times 10^{12} \text{ barrels} \times \frac{6.12 \times 10^{9} \text{ J}}{1 \text{ barrel}} = 10.2 \times 10^{21} \text{ J} = 10{,}200 \text{ EJ}$$

BP Statistical Review of World Energy 2013

Fossil Fuel Distribution Worldwide (2012 Proved Reserves)

Coal	20,200 EJ
Natural Gas	7,170 EJ
Oil	10,200 EJ

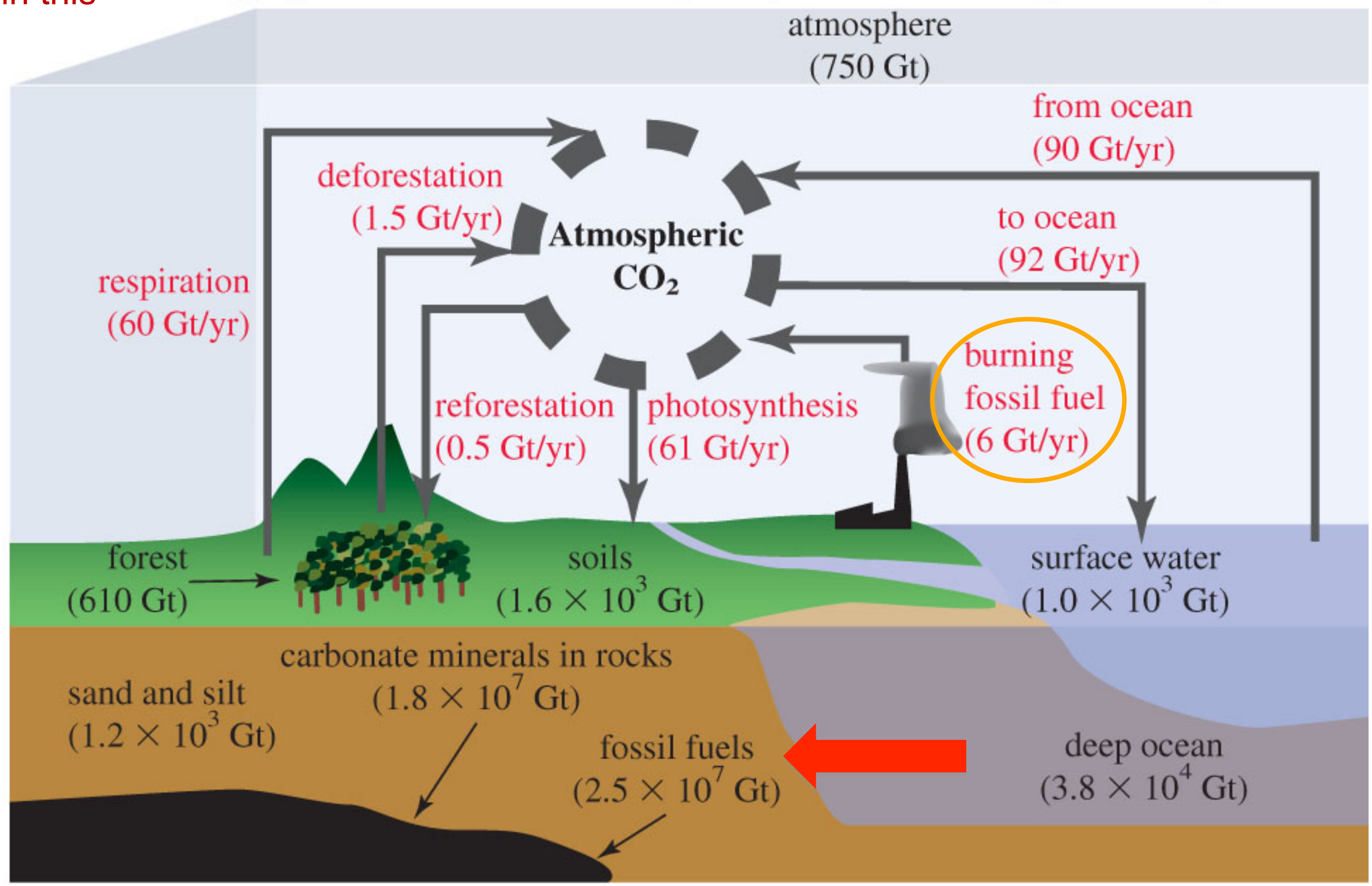


Worldwide consumption
in 2011 540 EJ

Carbon (C) Cycle

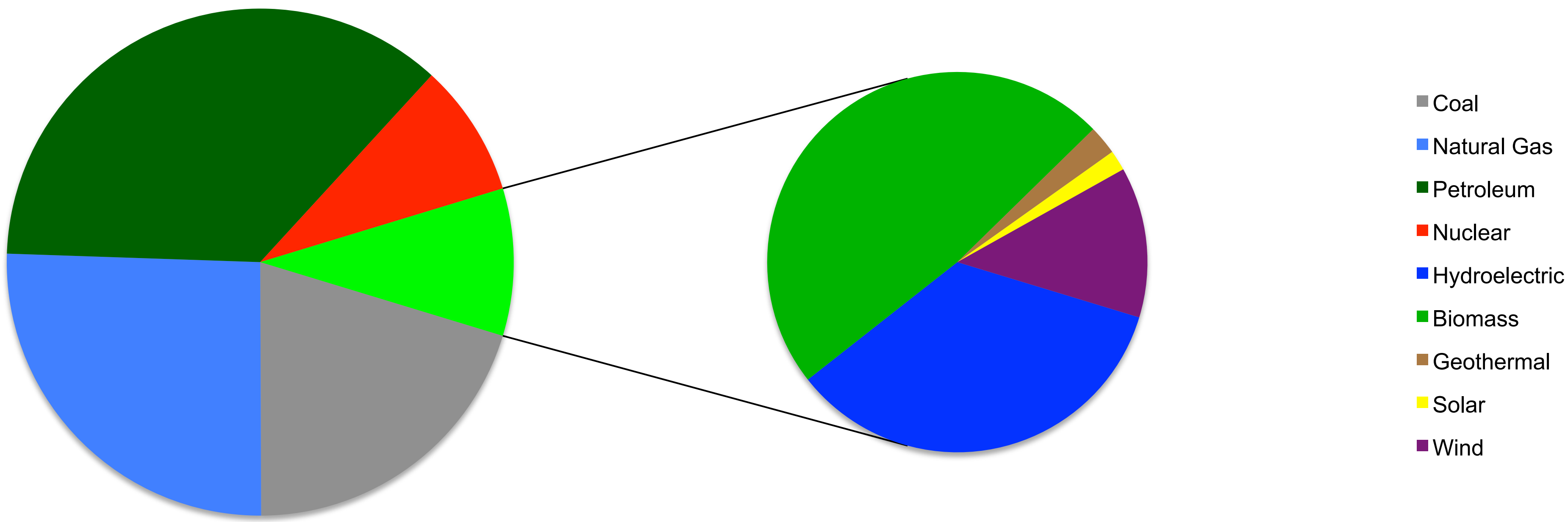
Plenty of fossil fuels left in this earth…

current combustion practices contribute to net ~3-4 Gt C/year addition to atmosphere



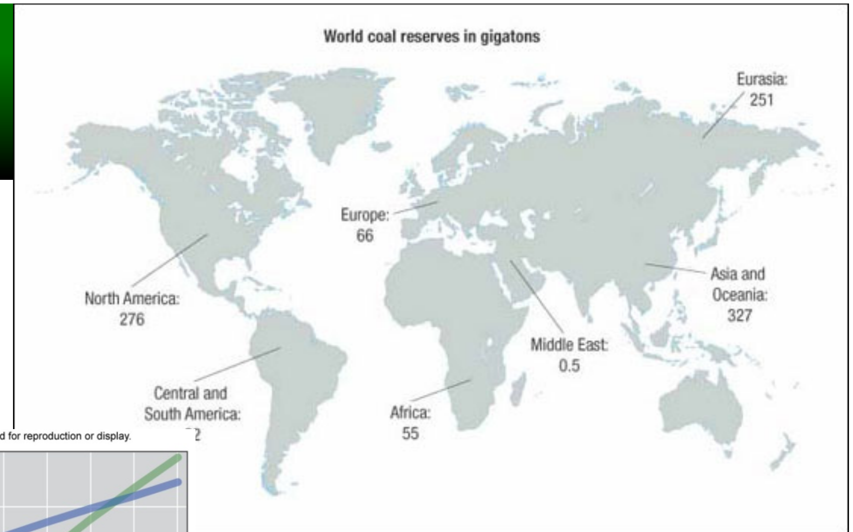
Gt=gigatonne (a billion metric tons (10^9), 2200 billion pounds ($2.2x10^{12}$)

85% of Our Energy Comes From Fossil Fuels

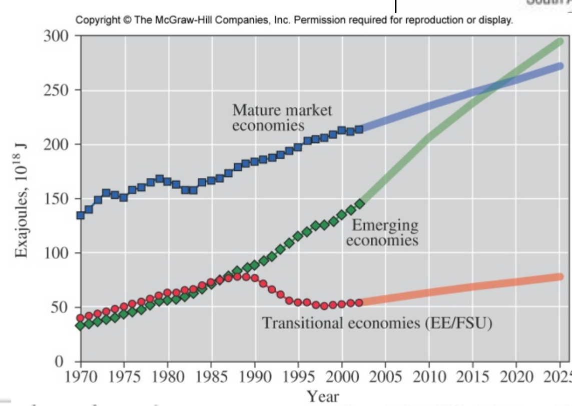


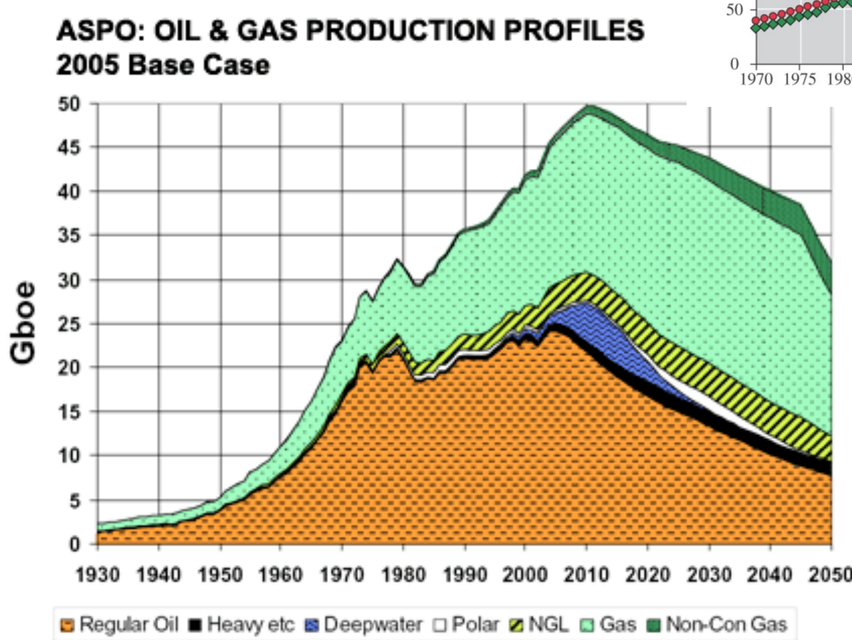
Energy Issues / Challenges

1. Global Climate Change (CO_2)
2. Peak Oil
3. Energy Security
4. Growing Demand
5. Impact on Economy
6. Air & Water Pollution

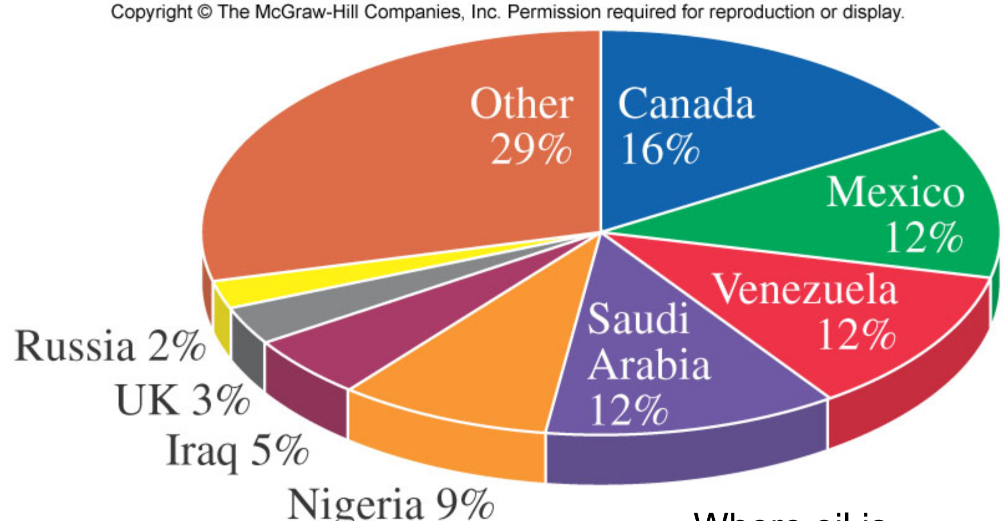


2005 EIA report





Source: Association for the Study of Peak Oil



Where oil is

Useful Energy Conversion Factors

Note: these would be provided for an exam

1 barrel (42 gallons) of crude oil = 6.12×10^9 J

1 gallon gasoline = 1.31×10^8 J

1 cubic ft natural gas = 1.08×10^6 J

1 short ton coal = 2.13×10^{10} J *(note:1 short ton = 907.2 kg)*

1 kilowatt-hour of electricity = 3.60×10^6 J

Coal

+ Abundant
+ Distributed throughout the globe
– A solid
– Lower energy content than petroleum, more CO_2 emission per unit energy
– Difficult & dangerous to obtain
– Environmentally disruptive to obtain & utilize (remember SO_2 & NO_2 are side products)

Photo by Platte River Power Authority

Figure 6.1 – Coal pile at a coal-fired power plant

Coal in the USA

19.7 Quads of Energy from Coal in the US in 2011

World Reserves:	
Coal	20,200 EJ
Natural Gas	7,170 EJ
Oil	10,200 EJ
US use:	
Coal	20.8 EJ

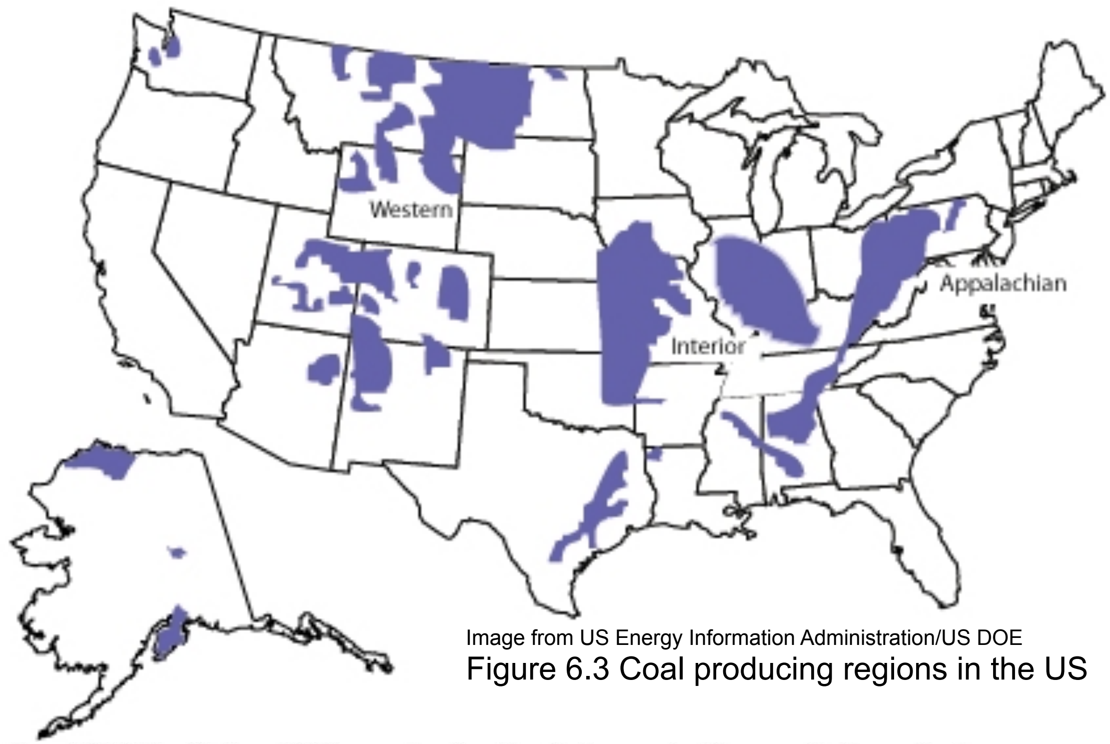


Image from US Energy Information Administration/US DOE

Figure 6.3 Coal producing regions in the US

Remember, different types of coal have different energy contents:

Table 4.4 Energy Content of Various U.S. Coals

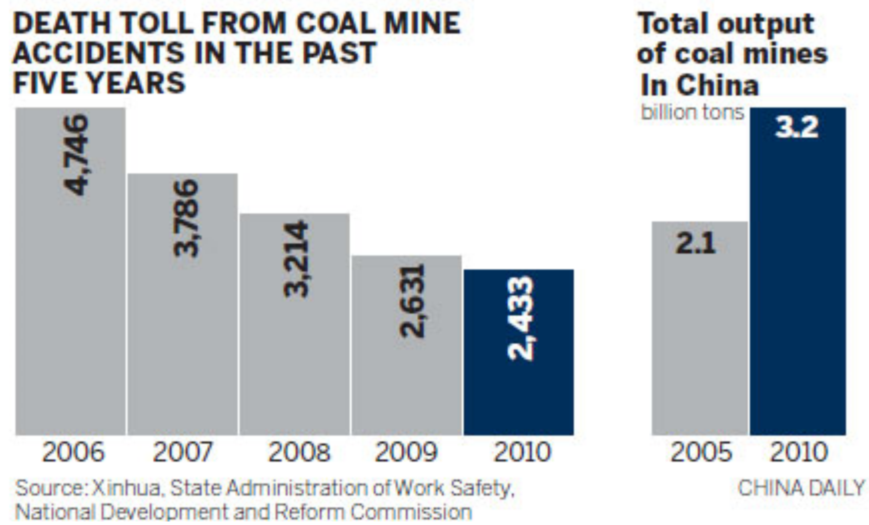
Type of Coal	State of Origin	Energy Content (kJ/g)
Anthracite	Pennsylvania	30.5
Bituminous	Maryland	30.7
Subbituminous	Washington	24.0
Lignite (brown coal)	North Dakota	16.2
Peat	Mississippi	13.0
Wood	Various	10.4–14.1

Coal Costs

- Deaths from mining accidents
  - 48 in 2010 in US: http://www.huffingtonpost.com/2010/12/30/us-coal-mine-deaths-in-20_n_802790.html
  - 3242 in 1907 in US: http://www.msha.gov/mshainfo/factsheets/mshafct2.htm

- Hundreds die each year from black lung disease: http://www.npr.org/templates/story/story.php?storyId=126021059

- Air pollution linked to 2 million premature deaths per year according to the WHO: http://www.who.int/mediacentre/factsheets/fs313/en/index.html



http://sweetandsoursocialism.wordpress.com/2011/03/02/chinas-coal-mine-deaths-fall-but-still-remain-high-peoples-daily/

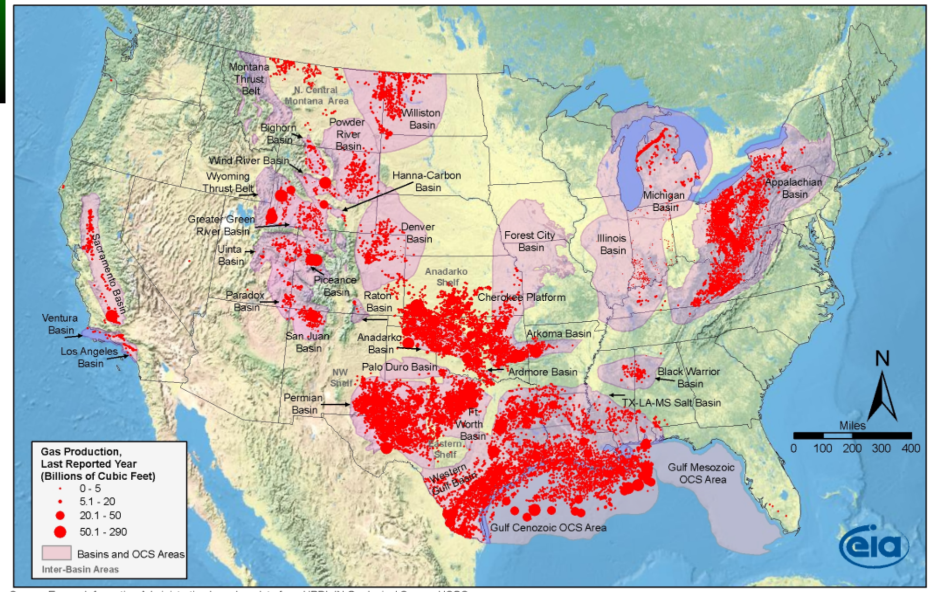
Natural Gas in the USA

Composition: mostly methane (CH_4)
Smell: mercaptans added to the gas

24.9 Quads of natural gas used in US in 2011:

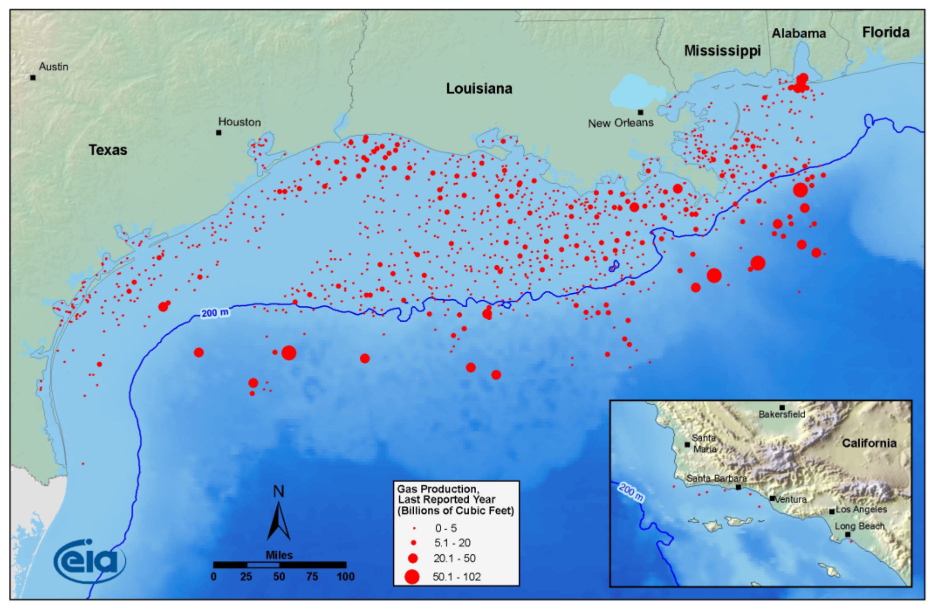
World Reserves:	
Coal	20,200 EJ
Natural Gas	7,170 EJ
Oil	10,200 EJ
US use:	
Coal	20.8 EJ
Natural Gas	26.3 EJ

Gas Production in Conventional Fields, Lower 48 States



Source: Energy Information Administration based on data from HPDI, IN Geological Survey, USGS
Updated: April 8, 2009

Gas Production in Offshore Fields, Lower 48 States



Source: Energy Information Administration based on data from MMS, HPDI, CA Dept of Oil , Gas & Geothermal
Updated: April 8, 2009

Getting to Natural Gas Deposits: Hydraulic Fracturing

- aka “fracking”
- Rocks not always porous enough to allow access to the natural gas
- Solution: pump in some fluid (steam + other stuff) at high pressure, break up the rocks
  - prop up the holes with something porous, like bits of sand
- Issues:
  - possible ground water contamination
  - fracking fluids & products can be carcinogenic
  - opens many new sites for gas extraction
  - Waste/produced water may overwhelm water treatment facilities

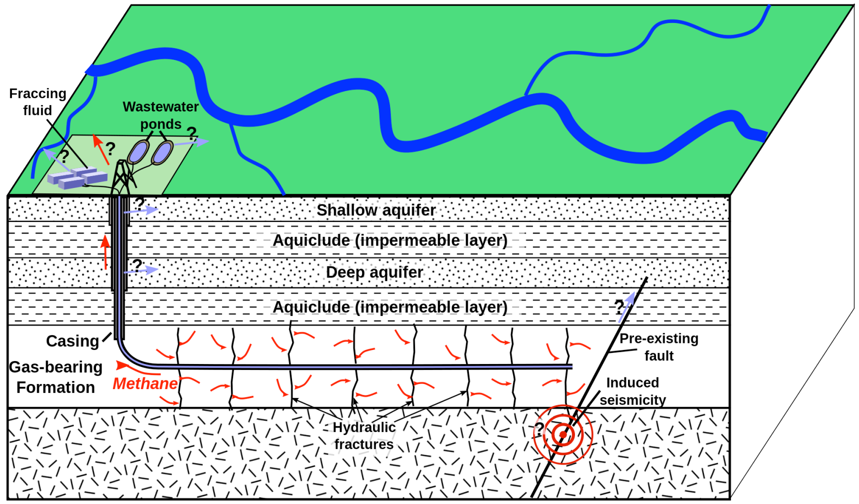
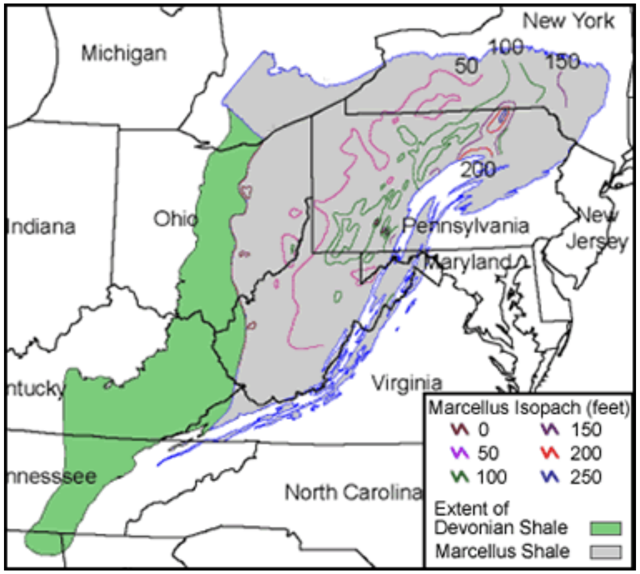


Image by Mike Norton/CC BY-SA 3.0

Figure 6.9 – Hydraulic fracturing (fracking)

http://geology.com/articles/hydraulic-fracturing/



Hydraulic fracturing, cont.

Hydraulic Fracturing Fluid Product Component Information Disclosure

Fracture Date	6/11/2012
State:	CO
County:	Weld
API Number:	05-123-35265
Operator Name:	Great Western Oil & Gas Company
Well Name and Number:	JBL 34-44
Longitude:	-104.87574
Latitude:	40.52732
Long/Lat Projection:	NAD83
Production Type:	Gas
True Vertical Depth (TVD):	7,293
Total Water Volume (gal)*:	416,123

Hydraulic Fracturing Fluid Composition:

Trade Name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by mass)**	Maximum Ingredient Concentration in HF Fluid (% by mass)**	Comments
Sand (Proppant)	CWS	Propping Agent					
DAP-925	CWS	Acid Corrosion Inhibitor					
DWP-621	CWS	Friction Reducer					
DWP-913	CWS	Clay Control					
DWP-937	CWS	Surfactant					
DWP-944	CWS	Biocide					
Hydrochloric Acid	CWS	Clean Perforations					
			2,2-Dibromo-3-Nitrilopropionamide	10222-01-2	40.00%	0.01086%	
			Aluminum oxide	1344-28-1	1.50%	0.01029%	
			Apatite	64476-38-6	0.10%	0.00083%	
			Biotite	1302-27-8	0.10%	0.00083%	
			Calcite	471-34-1	1.00%	0.01746%	
			Choline chloride	67-48-1	100.00%	0.03969%	
			Citrus terpenes	94266-47-4	60.00%	0.07956%	
			Crystalline silica (Quartz)	14808-60-7	100.00%	8.39521%	
			Fatty acids	Trade Secret	30.00%	0.00023%	
			Formaldehyde	50-00-0	0.10%	0.00000%	
			Goethite	1310-14-1	0.10%	0.00249%	
			Hydrochloric acid	7647-01-0	37.00%	0.08703%	
			Isopropanol	67-63-0	50.00%	0.06630%	
			Methanol	67-56-1	60.00%	0.00046%	
			Triethylene glycol	112-27-6	20.00%	0.02652%	
Water	Customer & CWS	Base Fluid & Mix Water	Water	7732-18-5	100.00%	91.30765%	

* Total Water Volume sources may include fresh water, produced water, and/or recycled water

** Information is based on the maximum potential for concentration and thus the total may be over 100%

Ingredient information for chemicals subject to 29 CFR 1910.1200(i) and Appendix D are obtained from suppliers Material Safety Data Sheets (MSDS)

Oil

Photo by Walter Siegmund/CC BY-SA 3.0

Figure 6.10 – The oil refinery in Anacortes, Washington

World Reserves:	
Coal	20,200 EJ
Natural Gas	7,170 EJ
Oil	10,200 EJ
US use:	
Coal	20.8 EJ
Natural Gas	26.3 EJ
Oil	37.2 EJ

US consumption in 2011 35.3 Quads

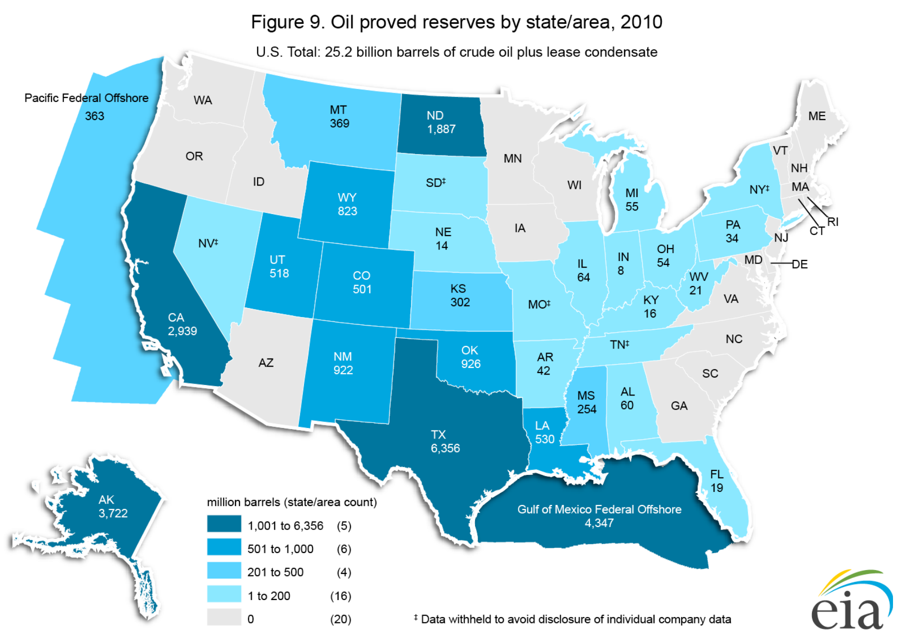


Image from US Energy Information Administration/US DOE

Figure 6.14 – US proved reserves of crude oil

US Peak Oil

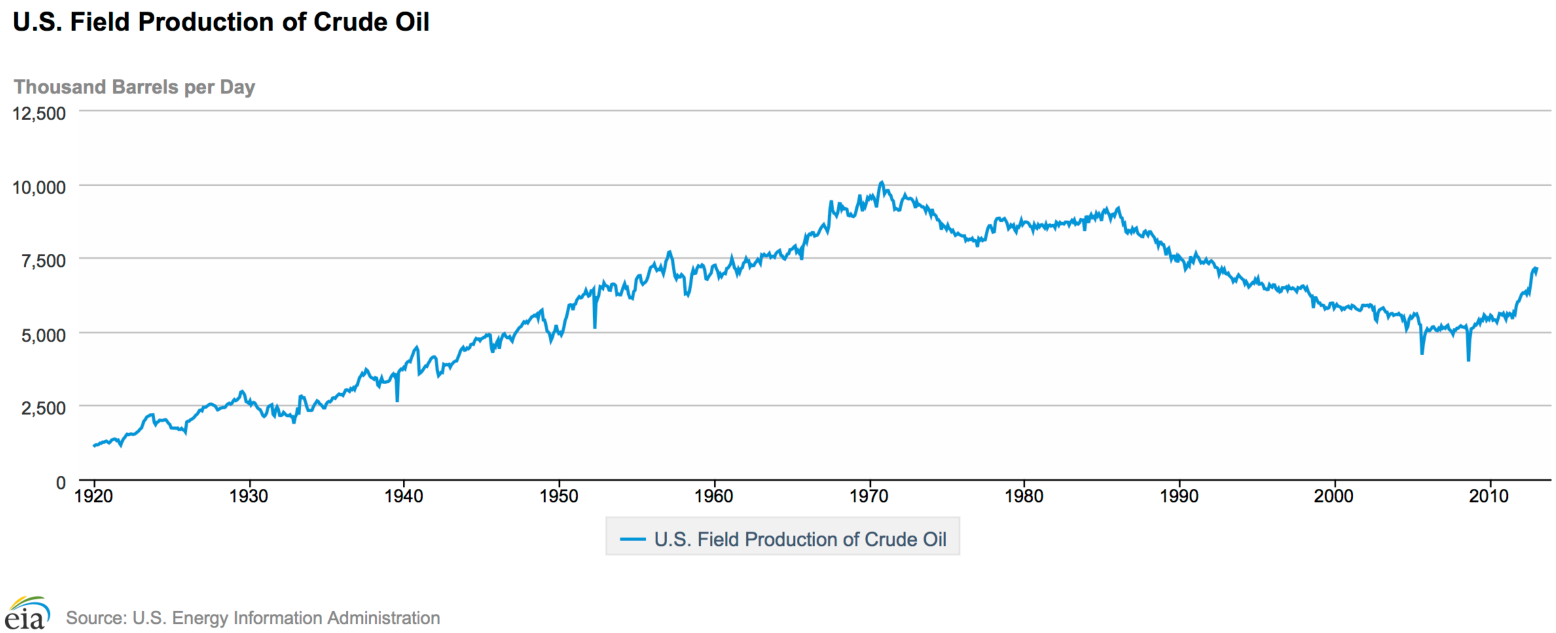


Image from US Energy Information Administration/US DOE

Figure 6.16 – Peak oil production in the US was 10,044 thousand barrels per day in November 1970

Oil impacts

Photo by US NOAA
Amoco Cadiz off the coast of France in 1978 spilled 1.6 million barrels of crude oil.

Photo by US NOAA
The *Exxon Valdez* in the Prince William Sound off the south coast of Alaska in 1989 spilled up to 750,000 barrels of crude oil.

Photo by US Coast Guard
The *Deepwater Horizon* or BP oil spill in 2010 resulted 4.9 million barrels of crude oil spilling into the Gulf of Mexico.

Oil Refining

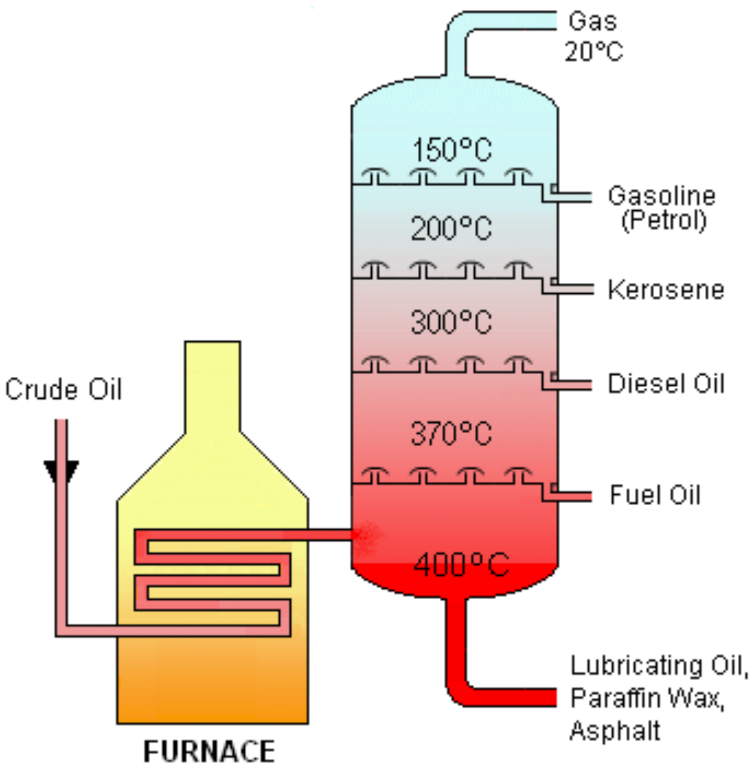


Image by Theresa Knott/CC BY-SA 3.0

Figure 6.11 – Fractional distillation

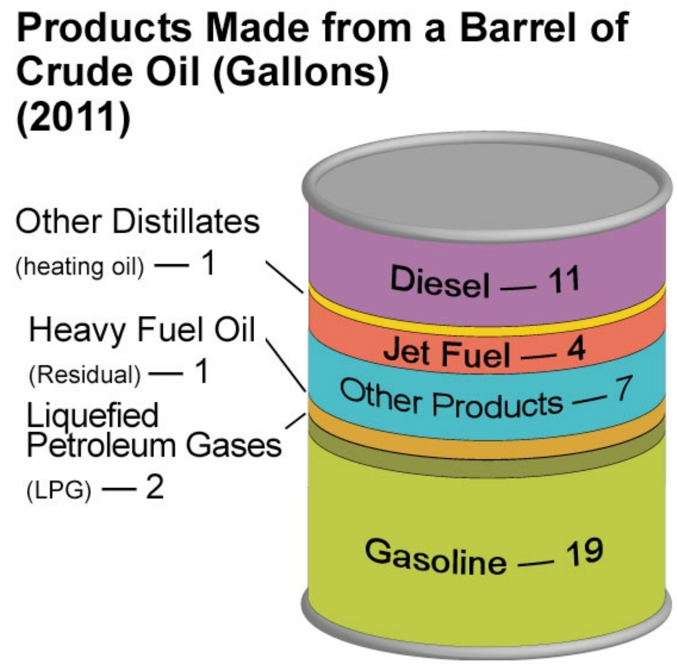


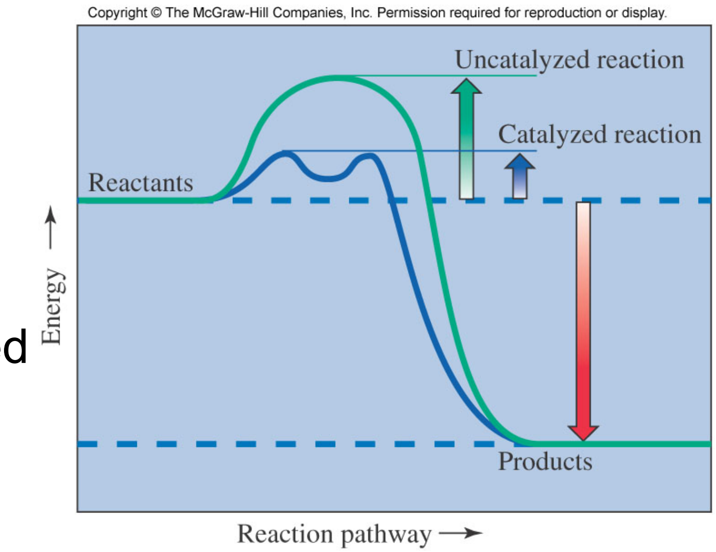
Image from US EIA/US DOE

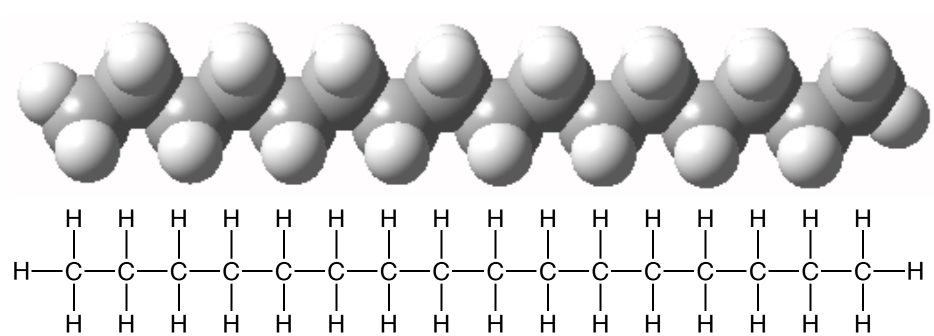
Figure 6.12 – End products for a barrel of crude oil

10% of a barrel of crude will **distill** to gasoline,
Where does the other ~37% come from?

Cracking (section 4.8)

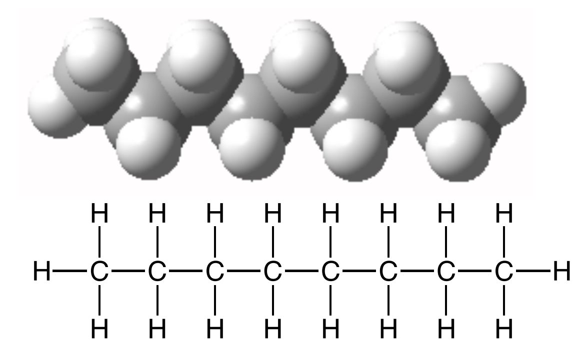
Cracking: process of breaking down long chain hydrocarbons into smaller molecules
(a) **Thermal cracking**: high temperatures required
(b) **Catalytic cracking**: a catalyst reduces the **activation energy** required to start the cracking process





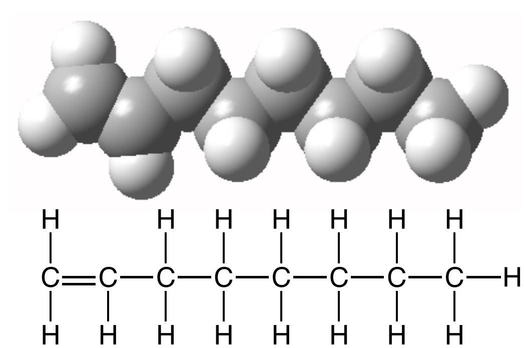
$C_{16}H_{34}$

catalyst



C_8H_{18}

+

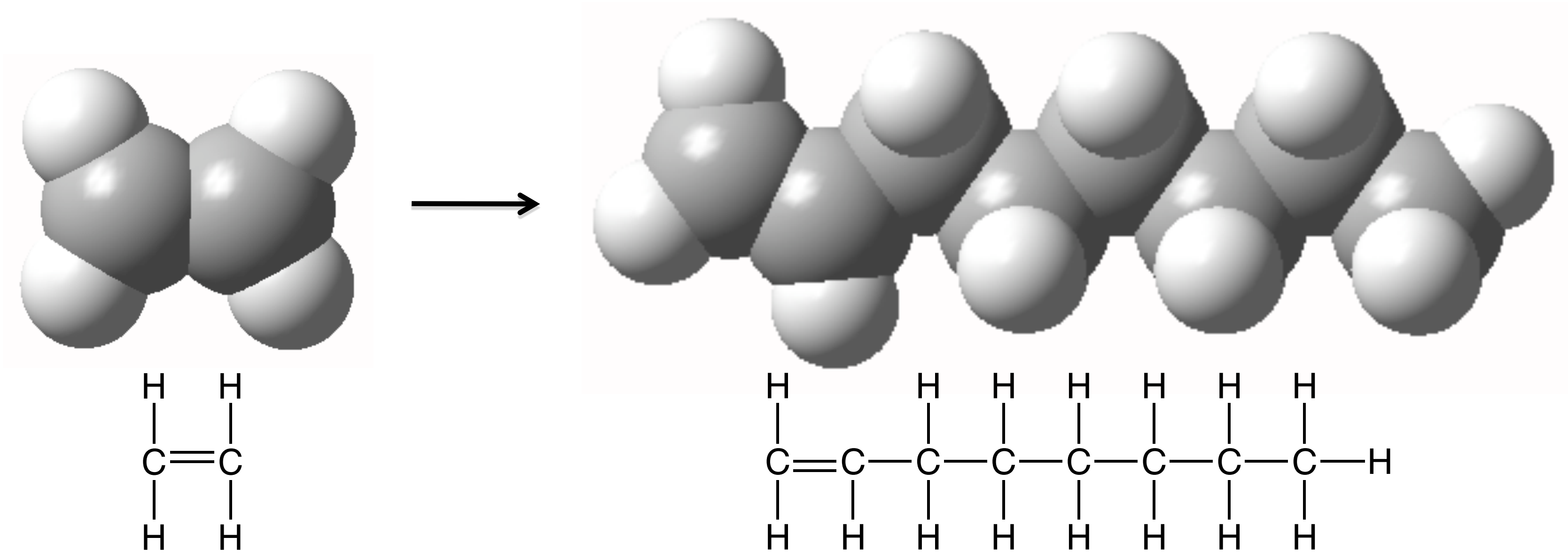


C_8H_{16}

Other ways to crack this compound depend on temperature and the catalyst used…

Building Larger Molecules Through Oligomerization

Example:

4 

(Catalysts are an integral part of the oligomerization process)

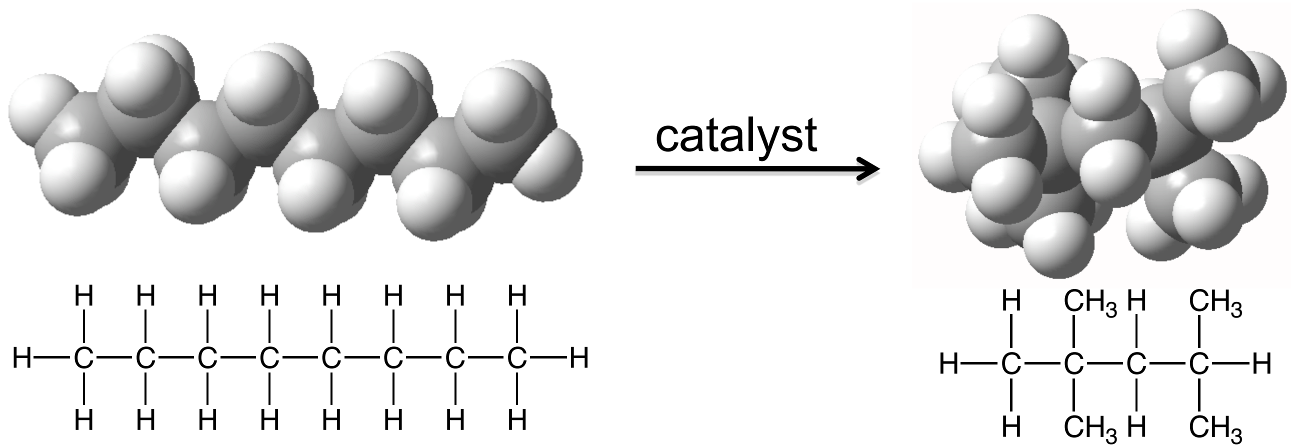
Polymerization (Chapter 9)

example: 10,000 C_2H_4 -> $C_{20,000}H_{40,000}$

Isomers and Reforming to Improve Octane Ratings

Isomers have the same chemical formula but different structure
Example: there are 18 different structures possible for octane (C_8H_{18})

The **reforming** process converts one isomer to another:



n-octane isooctane

Octane rating: higher numbers indicate less propensity for engine knocking; gasoline with rating = 87 has the same knocking *characteristics* as 87% isooctane + 13% *n*-heptane

Table 4.6 Octane Ratings of Several Compounds

Compound	Octane Rating	
n-Octane	−20	
n-Heptane	0	← **defined**
Isooctane	100	← **defined**
Methanol	107	
Ethanol	108	
MTBE	116	

Oxygenated Fuels (section 4.9)

- oxygen-containing molecules with octane ratings > 100
  - ethanol (C_2H_6O, also written as C_2H_5OH)
  - MTBE: methyl *tert*-butyl ether ($C_5H_{12}O$, also written as $CH_3OC(CH_3)_3$)
- **oxygenated gasolines**
  - burn more cleanly—less CO formed
- **reformulated gasolines**
  - a subset of oxygenated gasolines
  - lower percentage of more volatile hydrocarbons (e.g. benzene)
  - purpose: reduce volatile organic compounds (the ones that contribute to ground level ozone production)
- risk-benefit analysis of oxygenated gasolines:
  - positive: substantially less pollutants coming out of the tailpipe
  - negative: additives like MTBE are soluble in water—potential health consequences…

Question: do oxygenated fuels provide more energy than non-oxygenated fuels?