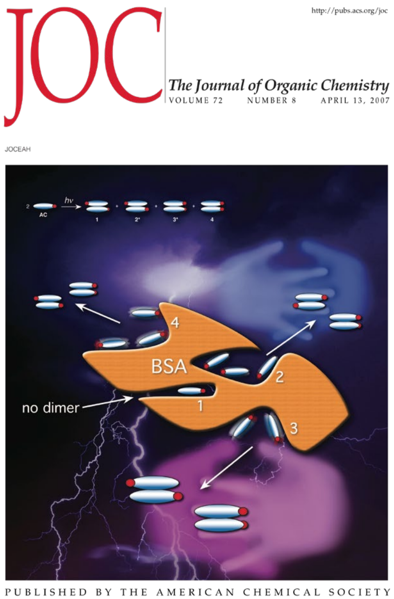
Chem 300A: Chemistry in Modern Society

The World of Chemistry

Chemical and Engineering News (C&EN) (2009) 87 (24), 7.

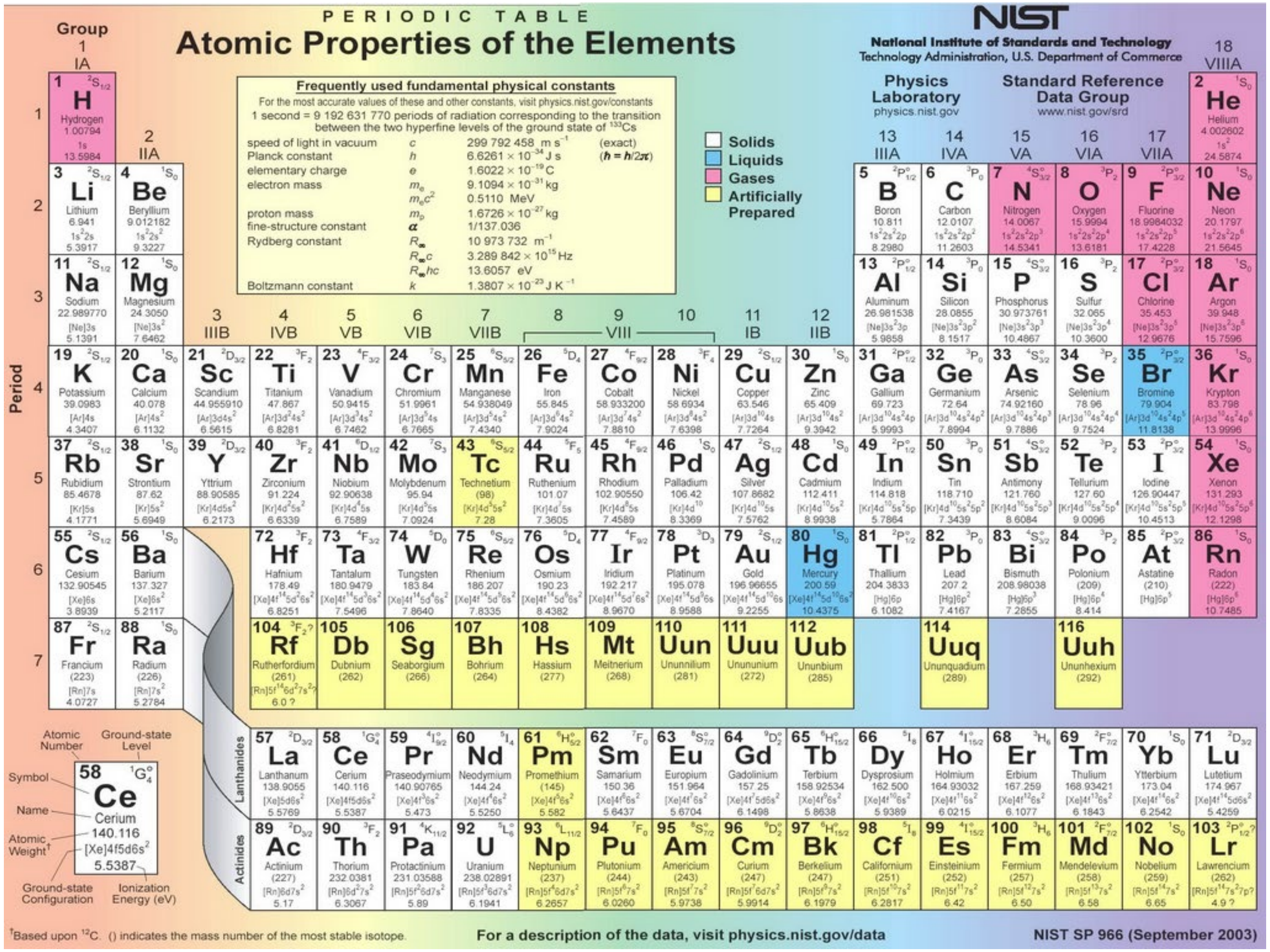
C&EN (2009) 87 (14), 10.

C&EN (2009) Latest news March 10



Nishijima et al. (2007)
J. Org. Chem. *72,* 2707.

The World of Chemistry



Energy – Costs and Requirements

Dragonfly accelerating to 50 km/h	2×10^{-7} kJ
Good MLB fastball (95 mph)	1.3×10^{-1} kJ
Car accelerating from 0-90 km/h	~ 10^{2} kJ
Burning 1kg wood	**1.4×10^{4} kJ**
Burning 1kg coal	**3×10^{4} kJ**
Burning 1kg gasoline	**5×10^{4} kJ**
Burning 1kg natural gas	**5.5×10^{4} kJ**
Flying a 747 jet at 640 mph	13×10^{7} kJ
Nuclear fission 1kg ^{235}U	**8×10^{10} kJ**
Nuclear fusion 1kg ^{2}H	**34×10^{11} kJ**
US daily energy consumption	3×10^{14} kJ
World daily energy consumption	1×10^{15} kJ
Daily solar output	**3×10^{28} kJ**

Energy

Uphill energetically

endothermic $$2800\text{ kJ} + 6\,CO_2(g) + 6\,H_2O(l) \xrightarrow{\text{chlorophyll}} \underset{\text{glucose}}{C_6H_{12}O_6(s)} + 6\,O_2(g)$$

exothermic $$C_6H_{12}O_6(s) + 6\,O_2(g) \longrightarrow 6\,CO_2(g) + 6\,H_2O(l) + 2800\text{ kJ}$$

Downhill energetically

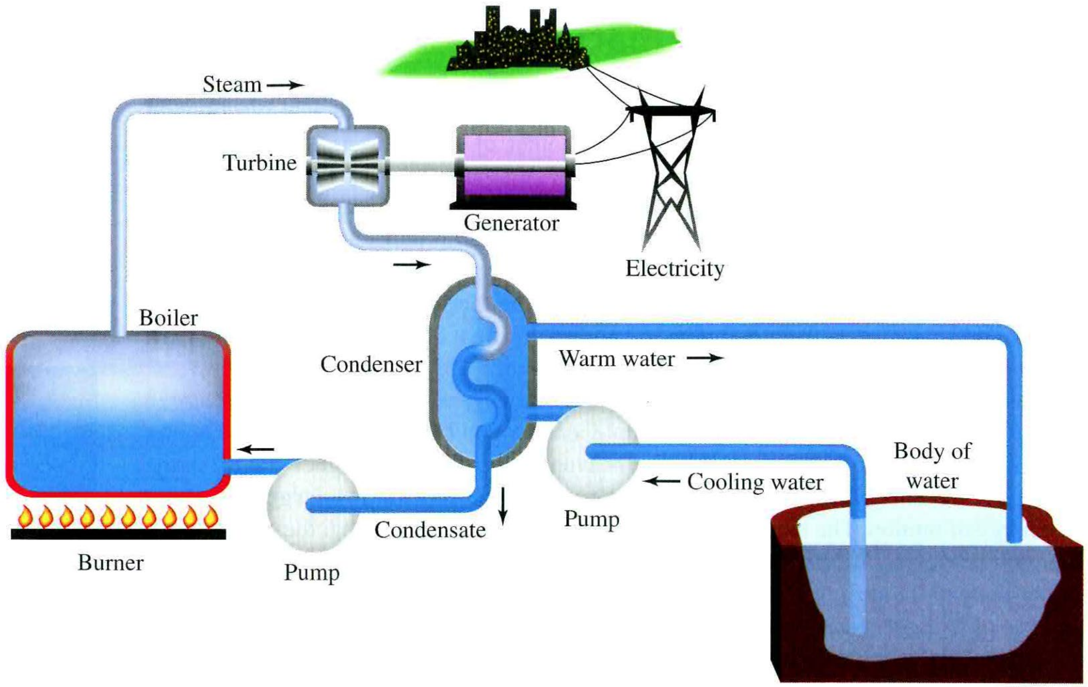
Glucose is the energy currency here

NOTE: one 'food' calorie = 1 kcal = 4.18 kJ

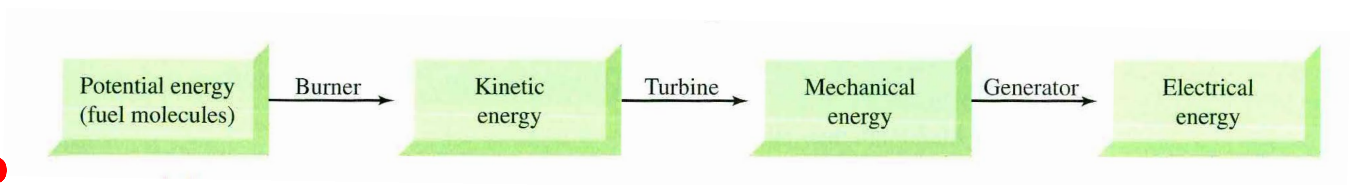
Energy - Petroleum

Energy = Potential energy + kinetic energy

Energy is conserved



Losses occur at each step



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Potential energy Is stored in the bonds of molecules

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.

A + B → C

Energy balance = Energy of C – (Energy of A + Energy of B)

Energy balance < 0 corresponds to a favorable reaction – exothermic

Energy balance > 0 corresponds to an unfavorable reaction - endothermic

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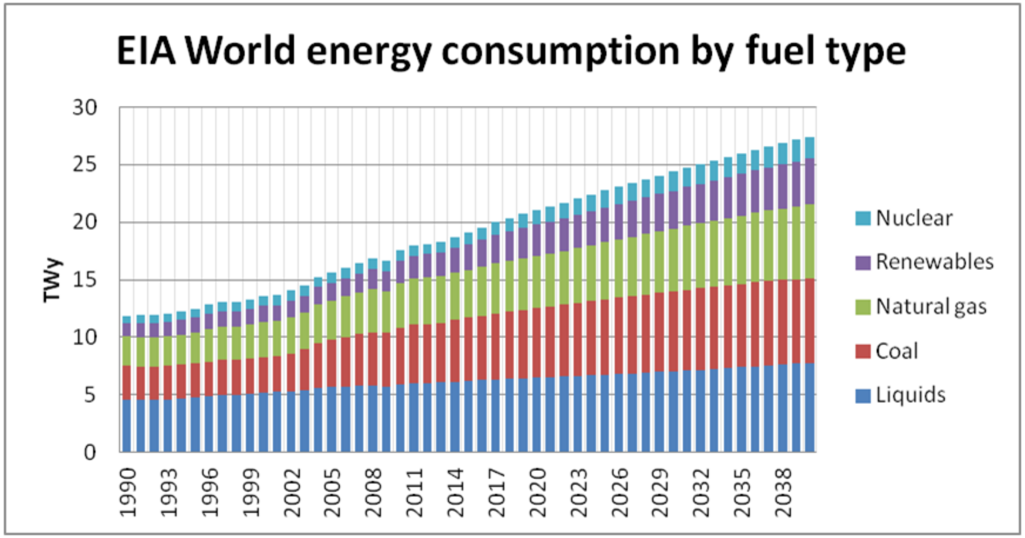
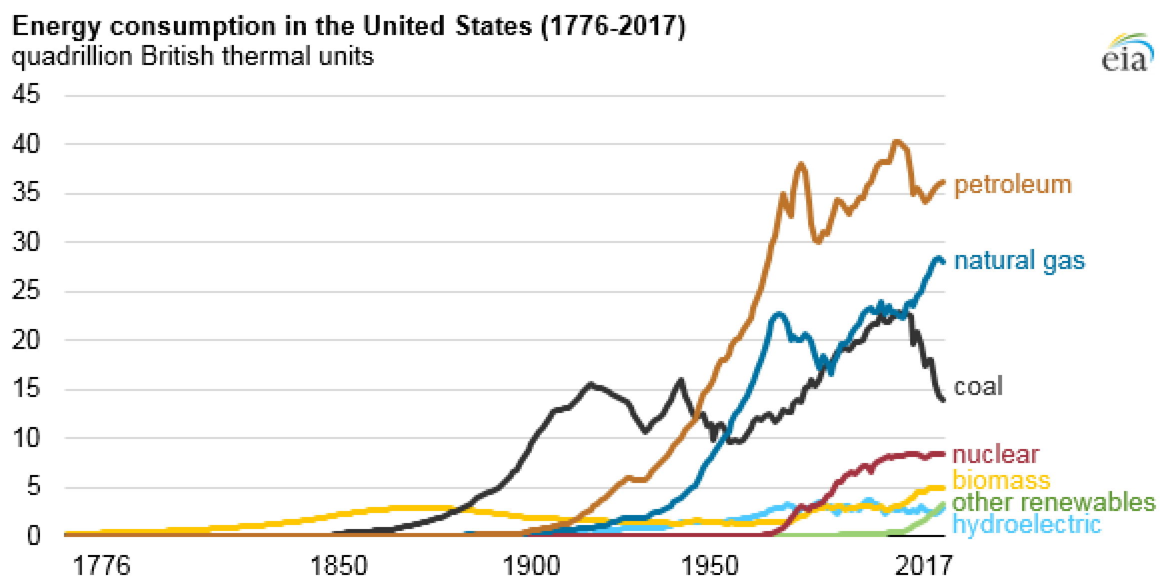


Projected world energy needs

US is about 1/3 of world total

Euanmearns.com

US EIA



US energy consumption:

Canada is the highest consumer of energy per capita on the planet

Energy content of fuels

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

Coal = 2 x heat of wood

- approximate formula $C_{135}H_{96}O_9NS$
- also contains small amounts of Si, Na, Ca, Al, Ni, Cu, Zn, As, Pb, Hg

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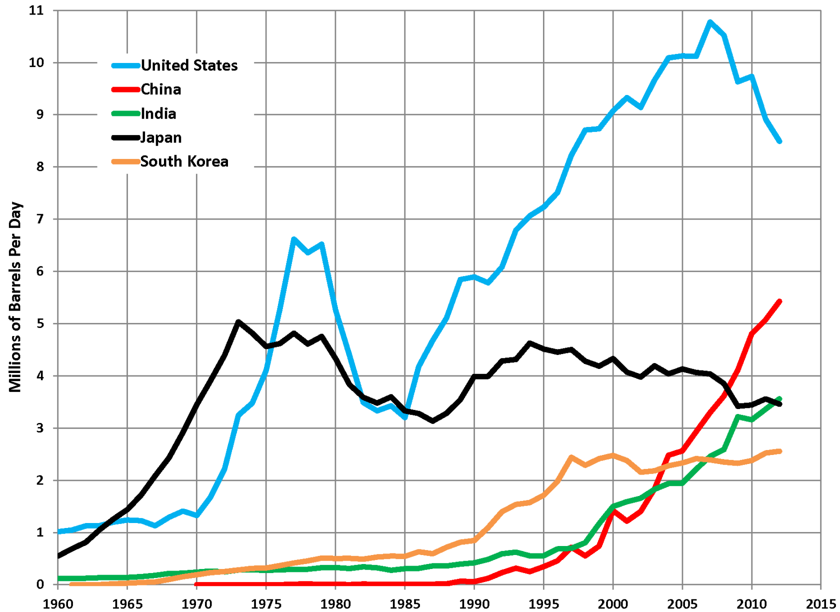
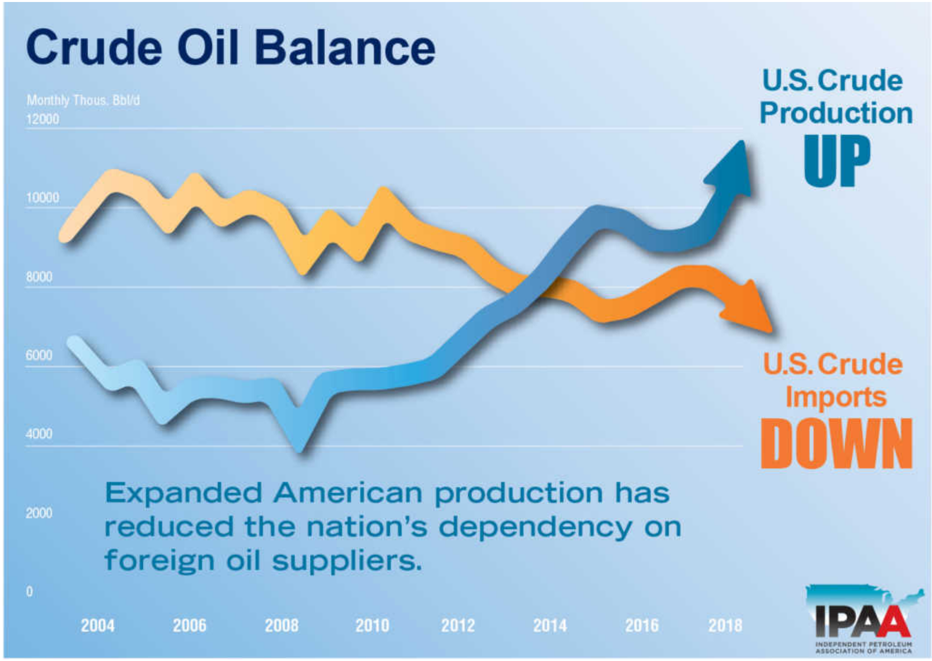
Petroleum

More concentrated source of energy – 40-60% more energy per gram than coal

Canada is a net exporter

US production – was a net importer



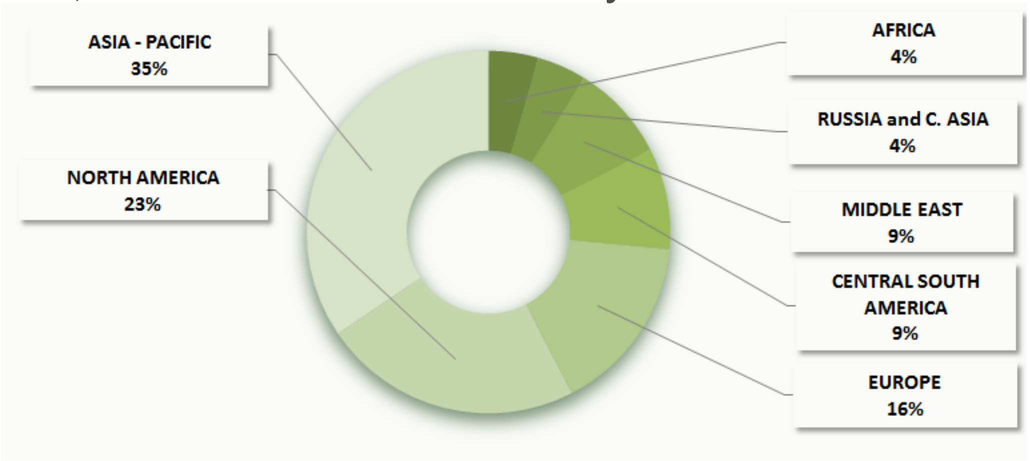


Recent reversal of this trend due to rapidly increasing shale oil production

Petroleum

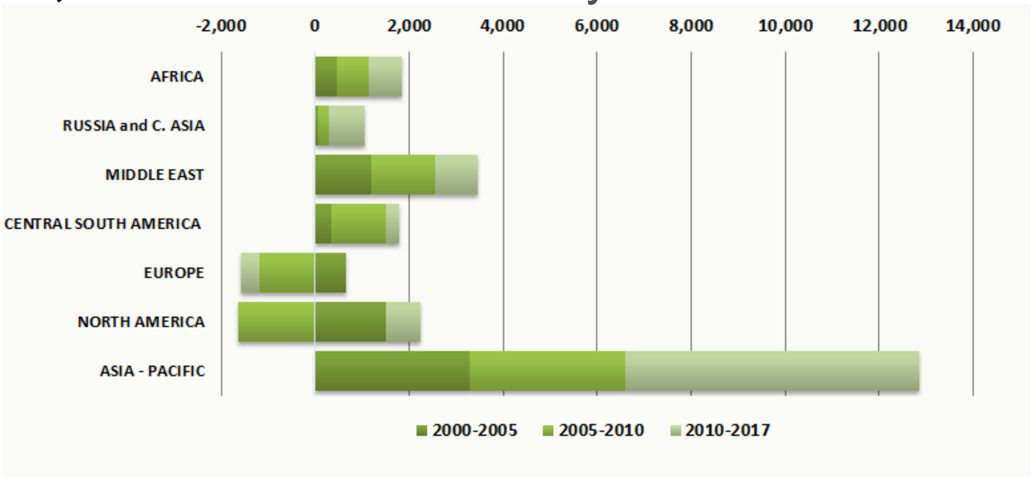
World Oil Consumption (2017)

97,815 thousand barrels/day



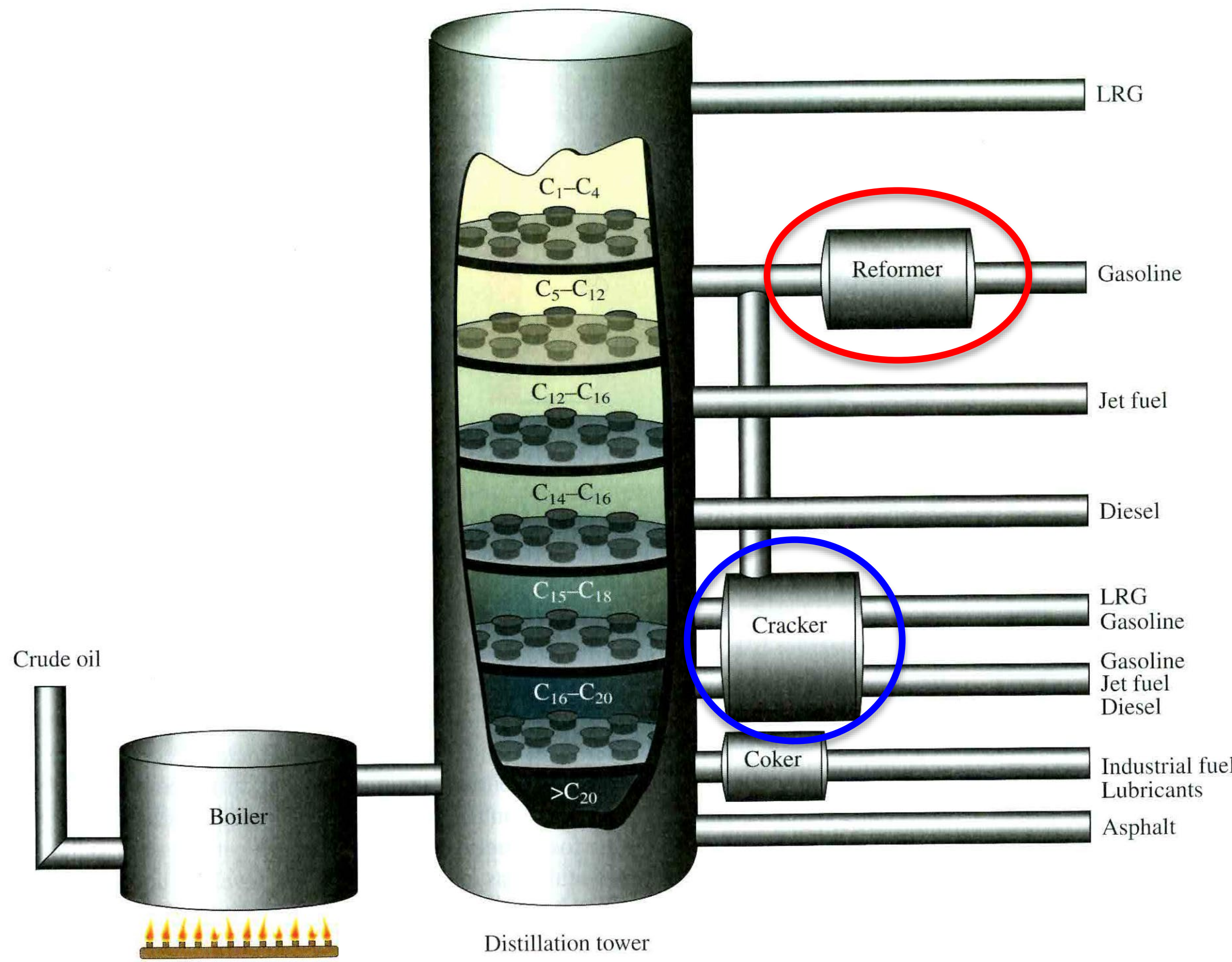
World Oil Consumption Growth (2000-2017)

20,676 thousand barrels/day



From: World Oil and Gas Review 2018, Vol. 1

Petroleum Refining: fractional distillation



LRG = liquefied refinery gas

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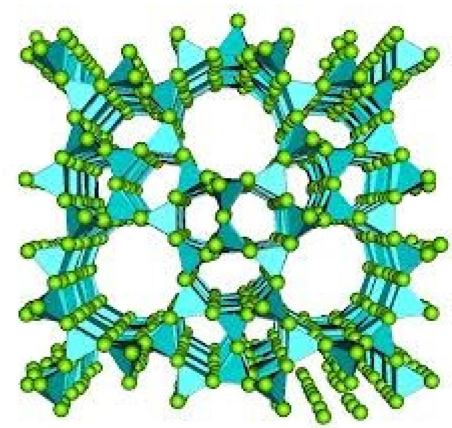
Petroleum fractions and cracking

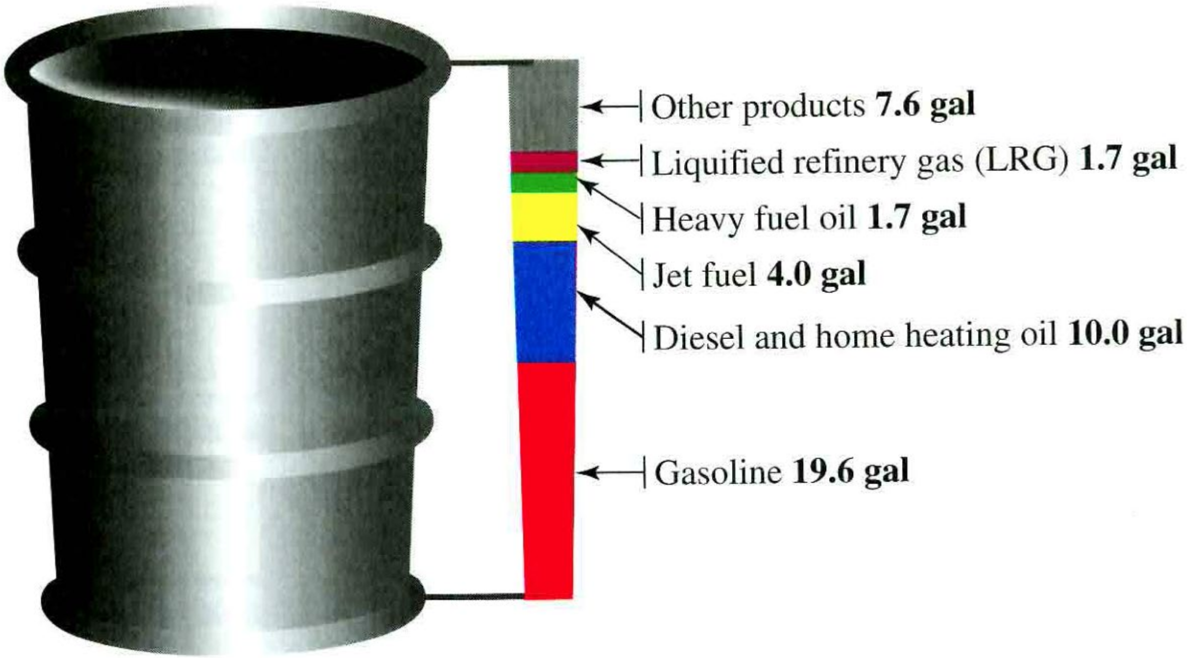
Gases	< 20 C	C1-C4 alkanes	synthesis	
Petroleum ether	20-70 C	C5-C6 alkanes	gas additives	
Gasoline	**70-180 C**	**C6-C10 alkanes**	**gasoline**	**cracking**
Kerosene	180-230 C	C11-C12 alkanes	jet fuel	
Light gas oil	**230-305 C**	**C13-C17 alkanes**	**diesel and furnace fuel**	
Heavy gas oil	**305-405 C**	**C18-C25 alkanes**	**lube oil**	
Lubricants	405-515 C	> C25 alkanes	grease, pet jelly	
Solids	> 515 C	PAH, high MW alkanes	roofing and road asphalt	

Catalytic cracking at high T and P over a catalyst (usually a ***Zeolite***) breaks long chains down to shorter ones via **radicals** and/or **alkyl cations**:

$$C_{14}H_{30} \longrightarrow C_7H_{16} + C_7H_{14} \text{ (alkene)}$$



Fractions of petroleum



Natural gas = 87-96% methane + 2-6% ethane + other

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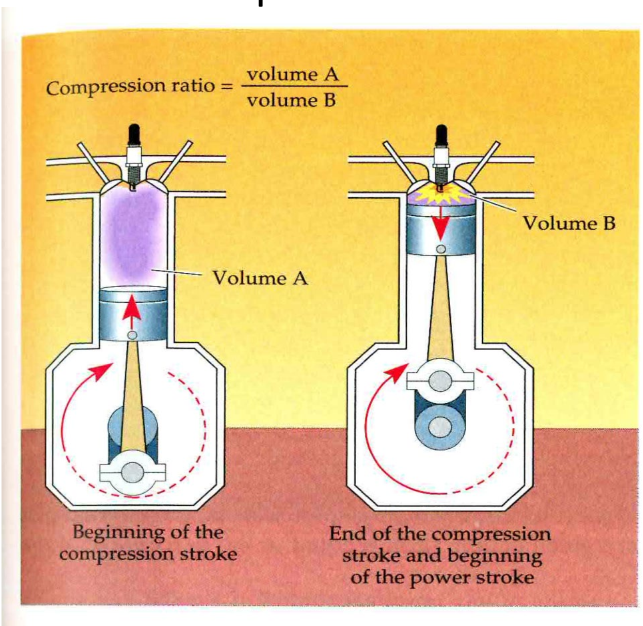
Not all 'gasoline' fractions are created equal: the need for 'reforming'

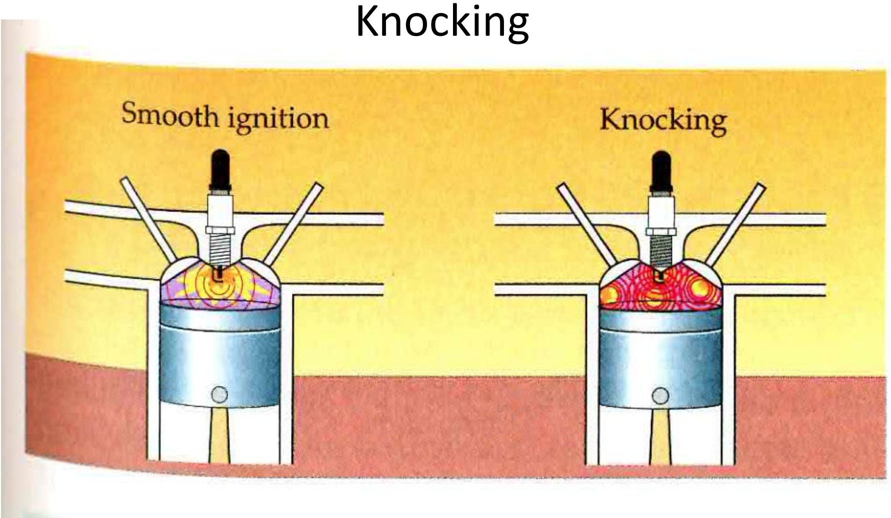
Compression



For optimal power output, we need **smooth combustion** at the very top of the piston stroke: **when spark plug fires**

Knocking is caused by **multiple ignition points or pre-ignition** and it depends on the ***structure*** of the hydrocarbon fuel

Knocking

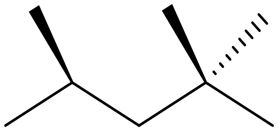


The Extraordinary Chemistry of Ordinary Things, 4th Ed.

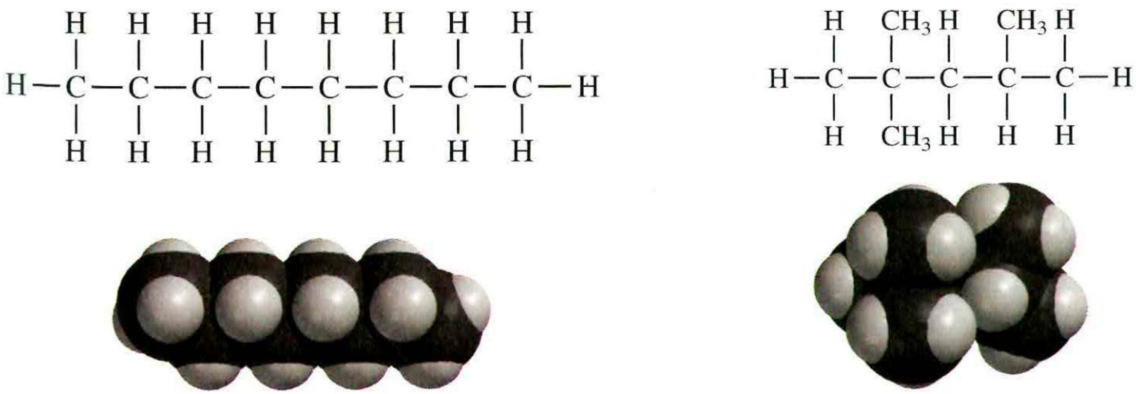
Octane number and structure

n-butane	C_4H_{10}	94 Octane number
n-pentane	C_5H_{12}	62
2-methylbutane		94
n-hexane	C_6H_{14}	25
2-methylpentane		73
2,2-dimethylbutane		92
n-heptane	$\mathbf{C_7H_{16}}$	**0**
2-methylhexane		42
2,3-dimethylpentane		90
n-octane	C_8H_{18}	-20
2-methylheptane		22
2,3-dimethylhexane		71
2,2,4-trimethylpentane		**100 (isooctane = the standard)**
Benzene		106
Toluene		118
o-xylene		107
Ethanol		**108**
MTBE (methyl t-butyl ether)		**116**

Arbitrarily set **isooctane at 100** and **n-heptane at 0**; all others rated against a ***blend of the two***



Reforming = rearranges the carbon backbone into more branched hydrocarbons



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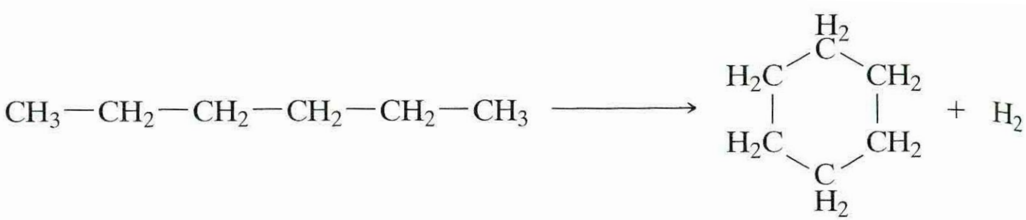
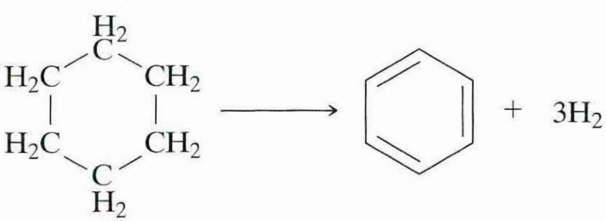


Typical catalysts are **Pt** or **Re** on SiO_2 or SiO_2/Al_2O_3



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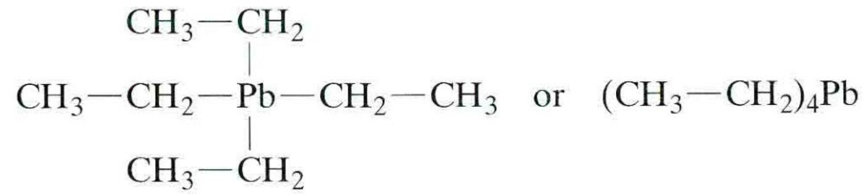
Octane boosters: *gasoline anti-knock agents*

Tetraethyllead – raises octane ratings

(TEL) 1920's until late 70's



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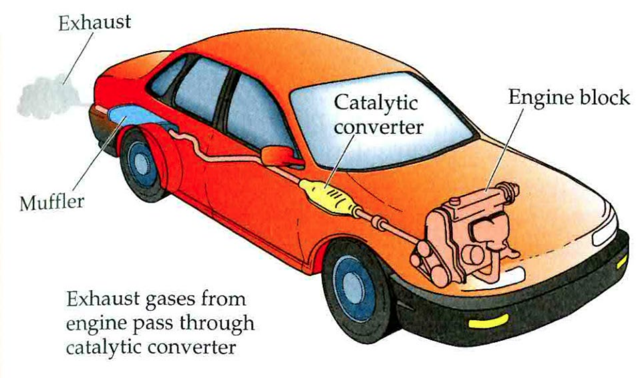
Why it works: Pb-C bond is weak and breaks readily providing many ethyl radicals that enhance combustion

Issues: Pb is highly toxic and organoleads are readily absorbed and fat soluble

By mid-70's roadside levels were often found to be as high as **3 mg/g of soil** (about 200x background)

Phased out NOT because of acute toxicity effects of Pb but because **TEL** killed the catalytic converters introduced to remove NOx and SOx byproducts (that eventually oxidized to HNO_3 and H_2SO_4, forming acid rain)



Catalytic converter: Pd and Pt

$2\ NO_x \longrightarrow x\ O_2 + N_2$

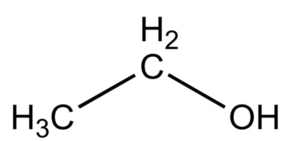
$CO + \frac{1}{2} O_2 \longrightarrow CO_2$

Alkanes + $O_2 \longrightarrow CO_2 + H_2O$

Other octane enhancers – **methyl–*tert*-butyl *ether - MTBE***

Higher octane rating
Oxygenates CO to CO_2

Ethanol



E10 = gasoline with 10% ethanol

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Ethanol: renewable gasoline alternative or more trouble than its worth?

US government mandated use of ethanol blends E10, E15 and now up to E85

Many questions exist however:

lower fuel efficiency (up to 30% less)
massive subsidy to producers in US (51 cents per gallon in 2011)
severe corrosion problems in fuel lines and pumps
net zero or negative impact on CO_2 emissions

Substantial impact on world food sources:

'The diversion of US maize into the production of biofuels, amid high energy prices, have pushed maize prices 84% higher year on year fueling rising global food prices, a report released by the World Bank Tuesday said.' from Platts News Agency, 2011

See also: https://www.factcheck.org/2015/11/ethanol-higher-emissions-or-lower/

Sources:

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Sherman, A. and Sherman S.J. “Chemistry in Our Changing World”, 3rd Ed. (1992), Prentice Hall