

The World Today



The World of Chemistry



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



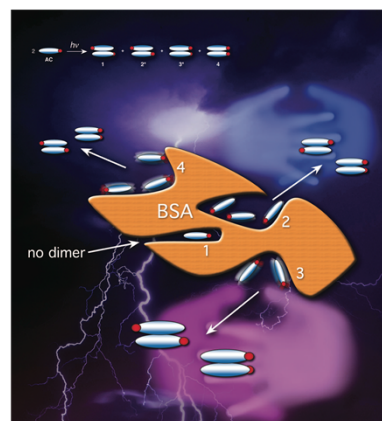
C&EN (2009) 87 (14), 10.



C&EN (2009) Latest news March 10

JOC http://pubs.acs.org/joc
The Journal of Organic Chemistry
VOLUME 72 NUMBER 8 APRIL 13, 2007

JOC&AH



PUBLISHED BY THE AMERICAN CHEMICAL SOCIETY

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

The World of Chemistry

PERIODIC TABLE
Atomic Properties of the Elements

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Frequently used fundamental physical constants

For the most accurate values of these and other constants, visit physics.nist.gov/constants
1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ¹³³Cs

speed of light in vacuum	c	299 792 458 m s ⁻¹ (exact)
Planck constant	h	6.6261 × 10 ⁻³⁴ J s ($h = h/2\pi$)
elementary charge	e	1.6022 × 10 ⁻¹⁹ C
electron mass	m_e	9.1094 × 10 ⁻³¹ kg
	$m_e c^2$	0.5110 MeV
proton mass	m_p	1.6726 × 10 ⁻²⁷ kg
fine-structure constant	α	1/137.036
Rydberg constant	R_∞	10 973 732 m ⁻¹
	$R_\infty c$	3.289 842 × 10 ¹⁵ Hz
	$R_\infty hc$	13.6057 eV
Boltzmann constant	k	1.3807 × 10 ⁻²³ J K ⁻¹

Physic Laboratory
physics.nist.gov

Standard Reference Data Group
www.nist.gov/stdref

13 IIIA

14 IVA

15 VA

16 VIA

17 VIIA

18 VIIIA

5 B

6 C

7 N

8 O

9 F

10 Ne

11 Na

12 Mg

3 IIIB

4 IVB

5 VB

6 VIB

7 VIIB

8 VIII

9 VIII

10 VIII

11 IB

12 IIB

13 Al

14 Si

15 P

16 S

17 Cl

18 Ar

19 K

20 Ca

21 Sc

22 Ti

23 V

24 Cr

25 Mn

26 Fe

27 Co

28 Ni

29 Cu

30 Zn

31 Ga

32 Ge

33 As

34 Se

35 Br

36 Kr

37 Rb

38 Sr

39 Y

40 Zr

41 Nb

42 Mo

43 Tc

44 Ru

45 Rh

46 Pd

47 Ag

48 Cd

49 In

50 Sn

51 Sb

52 Te

53 I

54 Xe

55 Cs

56 Ba

57 La

58 Ce

59 Pr

60 Nd

61 Pm

62 Sm

63 Eu

64 Gd

65 Tb

66 Dy

67 Ho

68 Er

69 Tm

70 Yb

71 Lu

72 Hf

73 Ta

74 W

75 Re

76 Os

77 Ir

78 Pt

79 Au

80 Hg

81 Tl

82 Pb

83 Bi

84 Po

85 At

86 Rn

87 Fr

88 Ra

89 Ac

90 Th

91 Pa

92 U

93 Np

94 Pu

95 Am

96 Cm

97 Bk

98 Cf

99 Es

100 Fm

101 Md

102 No

103 Lr

104 Rf

105 Db

106 Sg

107 Bh

108 Hs

109 Mt

110 Uun

111 Uuu

112 Uub

113 Uuq

114 Uuq

115 Uuh

116 Uuh

Period

1

2

3

4

5

6

7

Group

1 IA

2 IIA

3

4

5

6

7

8

9

10

11

12

13

14

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17

18

Atomically Prepared

Artificially Prepared

58 Ce

Atomic Number: 58

Ground-state Level: ¹G₄

Symbol: Ce

Name: Cerium

Atomic Weight: 140.116

Ground-state Configuration: [Xe]4f5d6s²

Ionization Energy (eV): 5.5387

†Based upon ¹²C. () indicates the mass number of the most stable isotope.

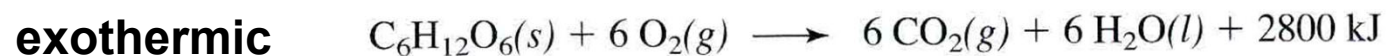
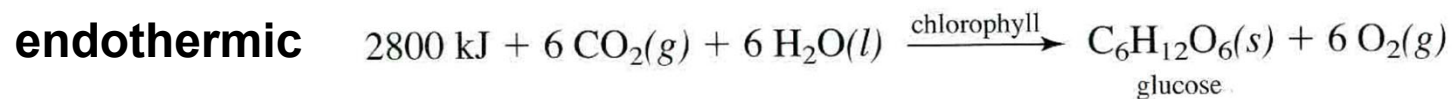
For a description of the data, visit physics.nist.gov/data

NIST SP 966 (September 2003)

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	$\sim 10^2$ 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 ^2H	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



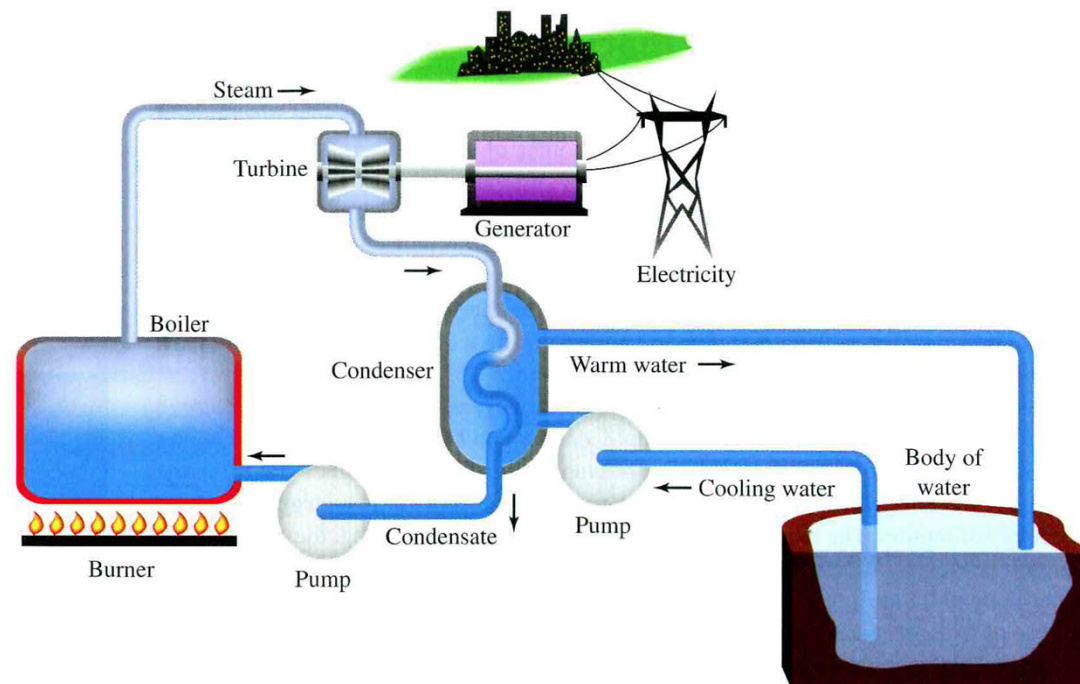
Glucose is the energy currency here

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

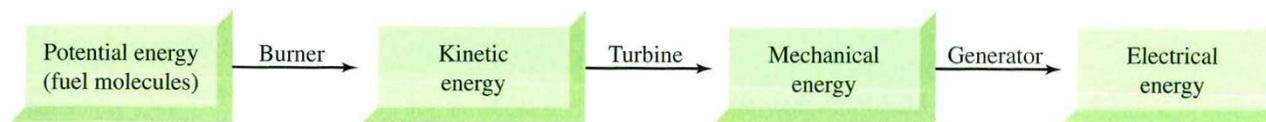
Energy - Petroleum

Energy = Potential energy + kinetic energy

Energy is conserved



**Losses
occur at
each step**



Chemistry in Context 6th Edition, ACS, McGraw-Hill

Table 4.2 Bond Energies (in kJ/mol)

	H	C	N	O	S	F	Cl	Br	I
<i>Single Bonds</i>									
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
<i>Multiple Bonds</i>									
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.

Potential energy is stored in the bonds of molecules

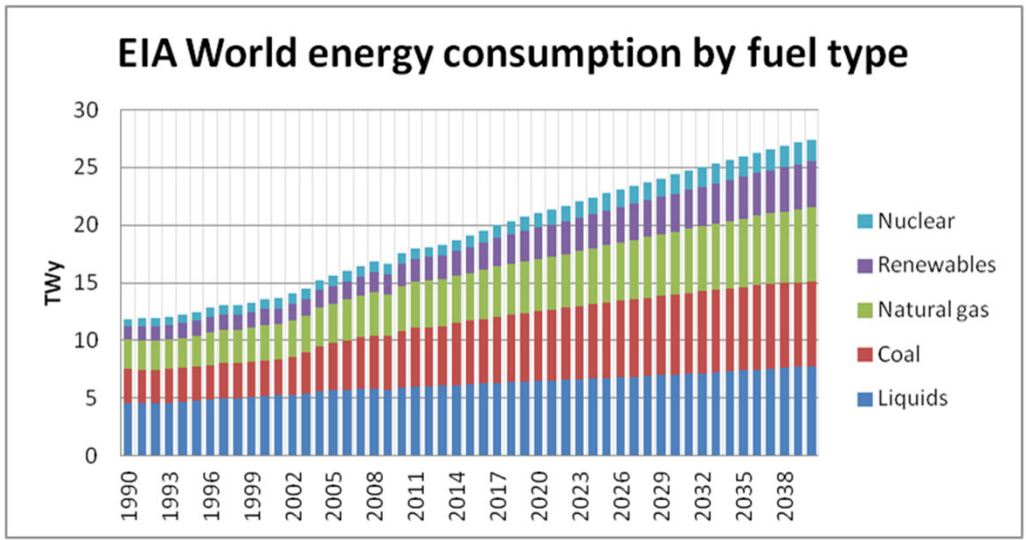


Energy balance = Energy of C – (Energy of A + Energy of B)

Energy balance < 0 corresponds to a favorable reaction – **exothermic**

Energy balance > 0 corresponds to an unfavorable reaction - **endothermic**

EIA World energy consumption by fuel type



Projected world energy needs

US is about 1/3 of world total

Euanmearns.com

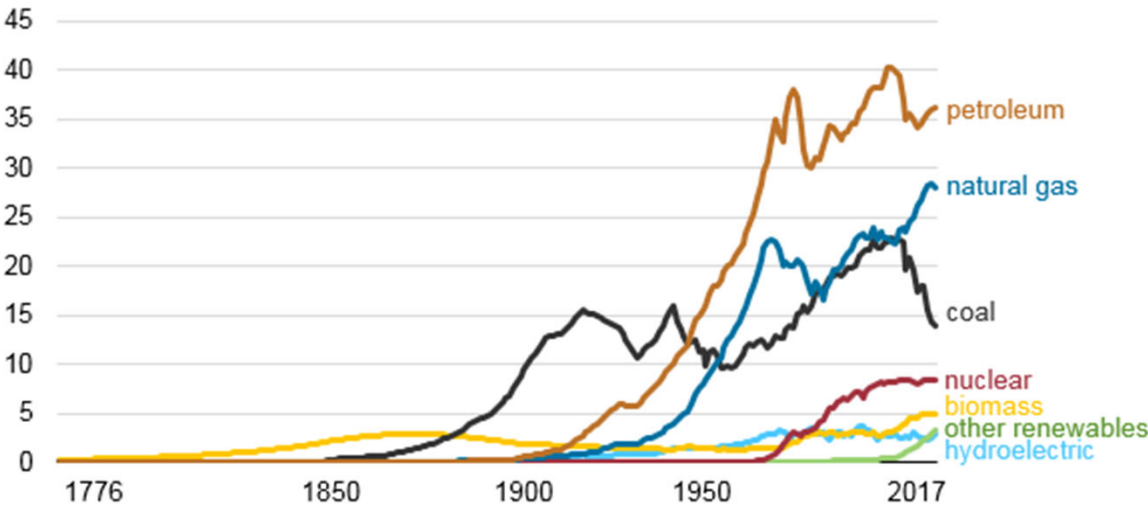
US EIA



US energy consumption:

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

Energy consumption in the United States (1776-2017)
quadrillion British thermal units



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 $C_{135}H_{96}O_9NS$

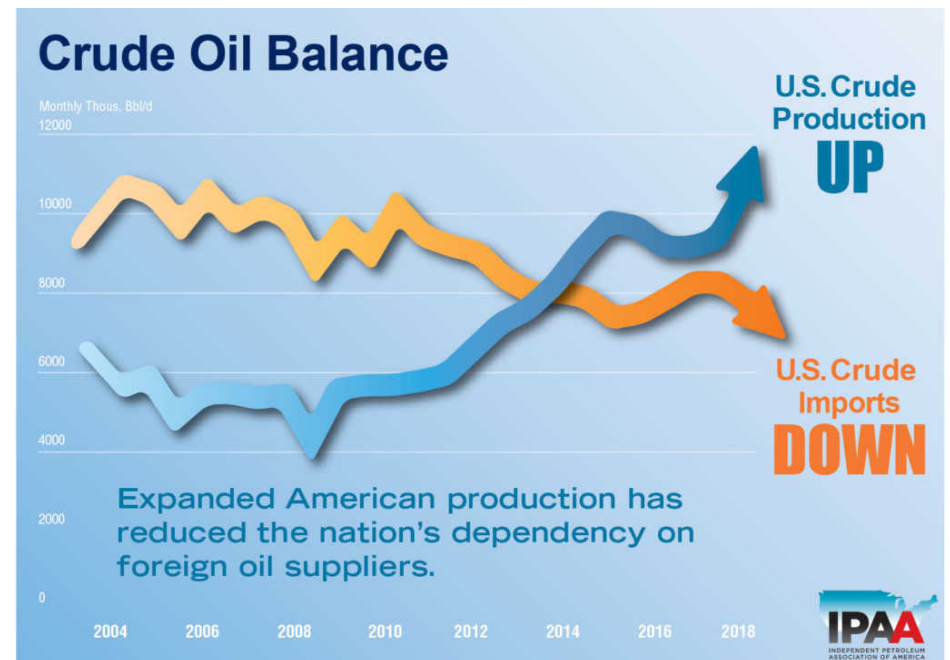
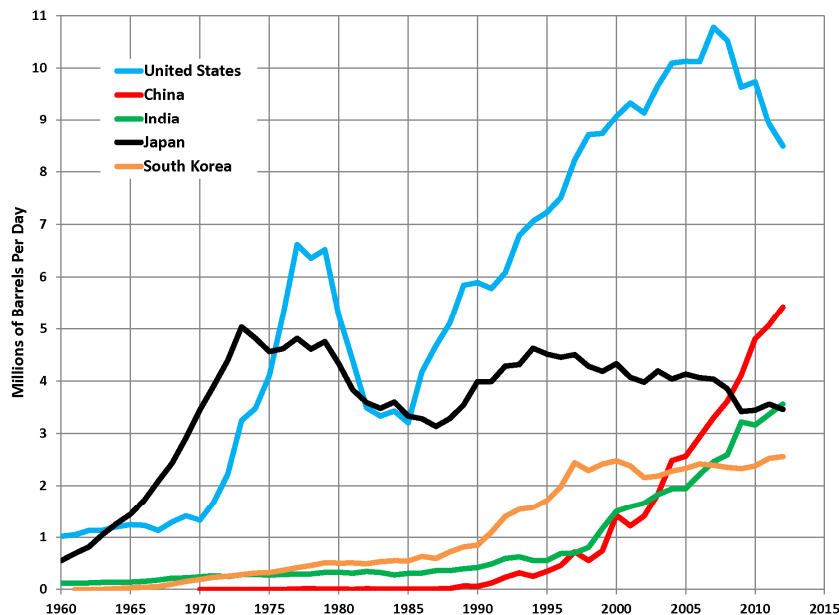
- also contains small amounts of Si, Na, Ca, Al, Ni, Cu, Zn, As, Pb, Hg

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

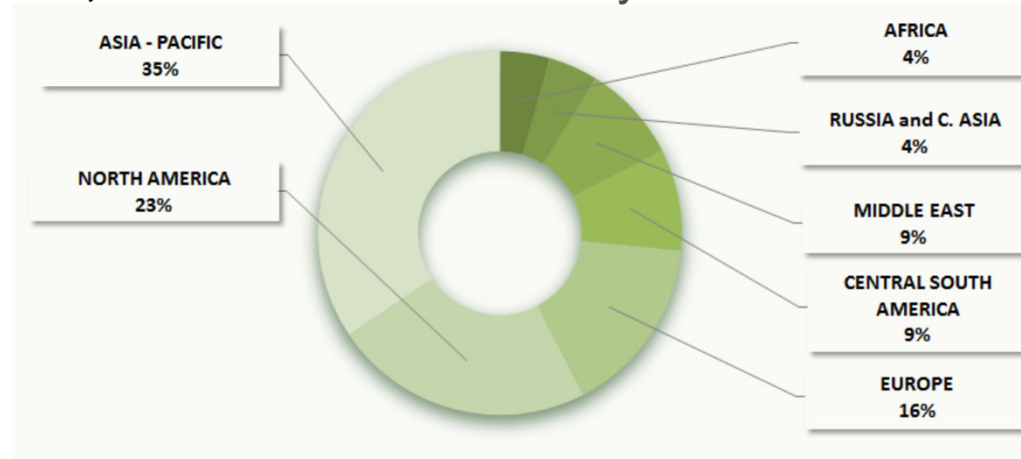


Recent reversal of this trend due to rapidly increasing shale oil production

Petroleum

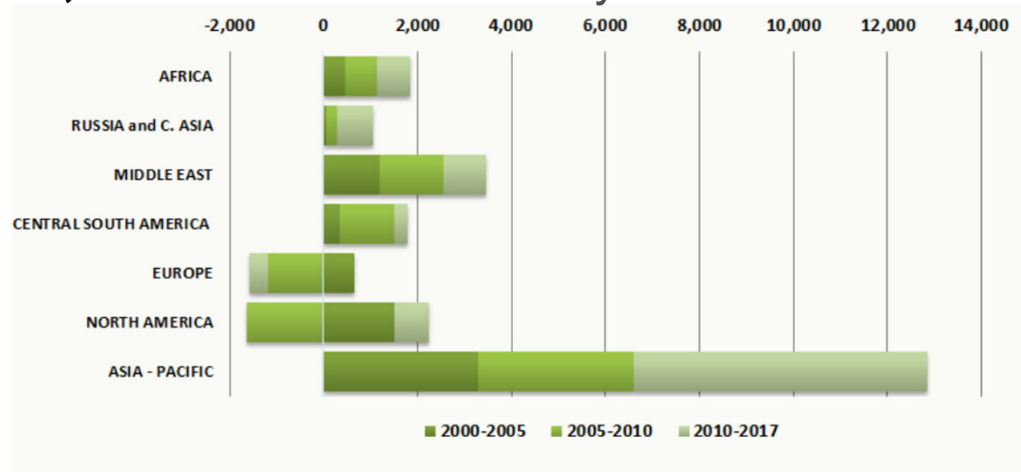
World Oil Consumption (2017)

97,815 thousand barrels/day



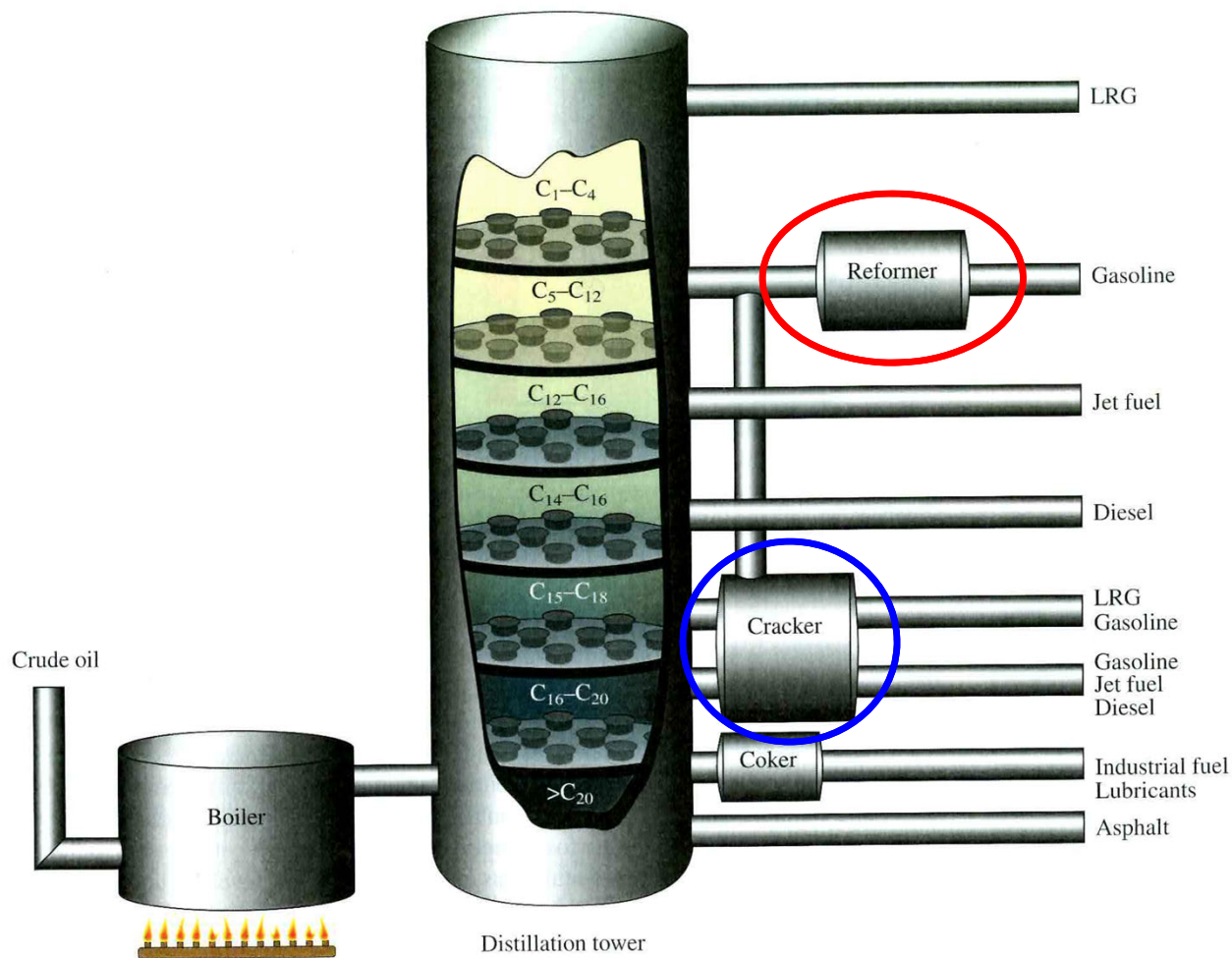
World Oil Consumption Growth (2000-2017)

20,676 thousand barrels/day



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

Petroleum Refining: fractional distillation



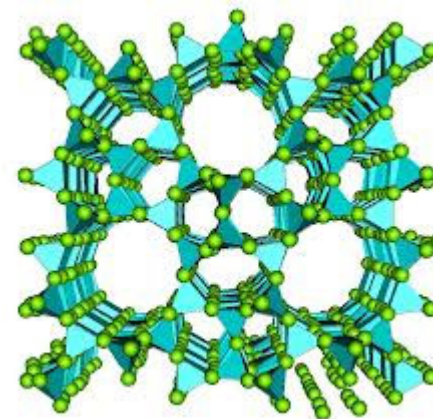
LRG = liquefied refinery gas

Chemistry in Context 6th Edition, ACS, McGraw-Hill

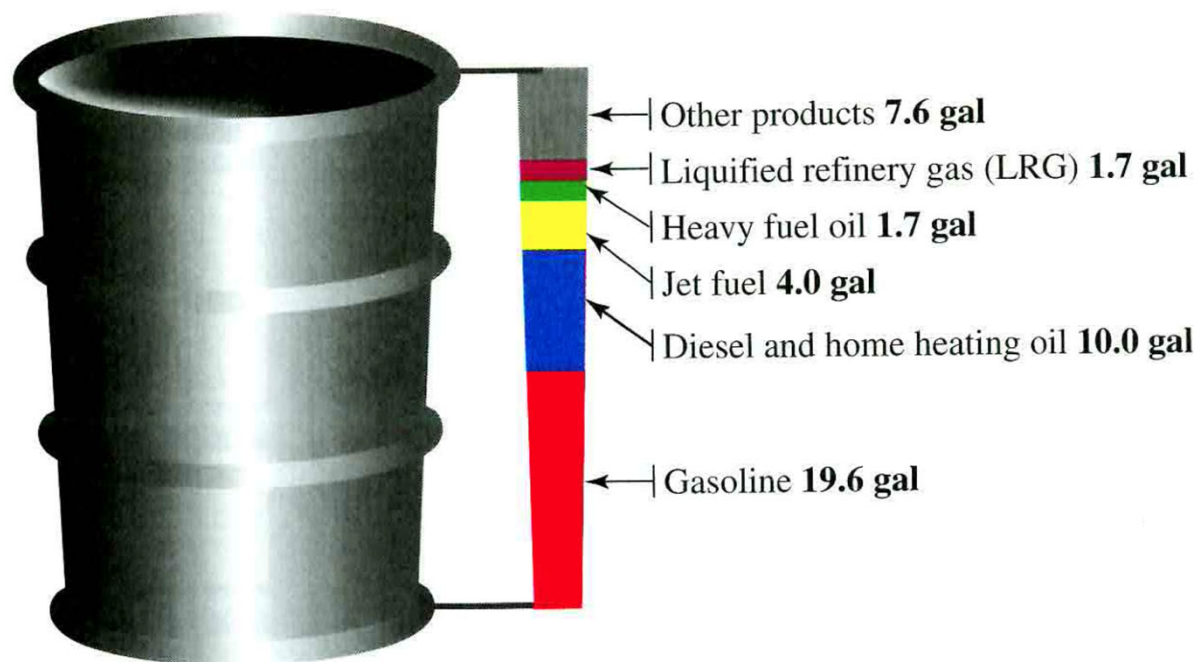
Petroleum fractions and cracking

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

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**:



Fractions of petroleum

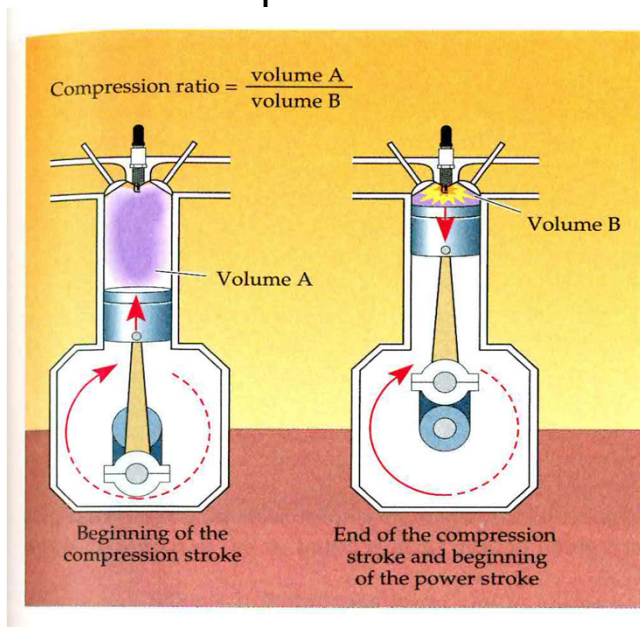


Natural gas = 87-96% methane + 2-6% ethane + other

Chemistry in Context 6th Edition, ACS, McGraw-Hill

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

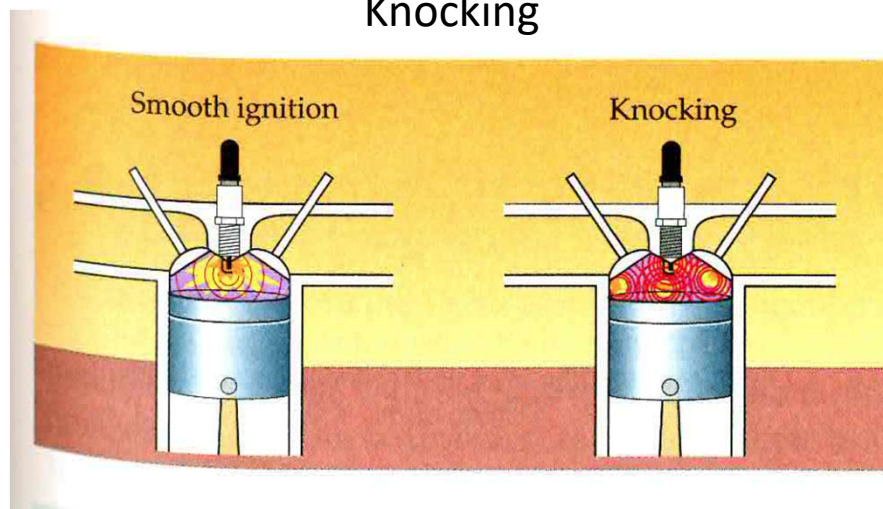
Compression



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

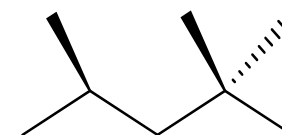
n-heptane C_7H_{16} **0**
2-methylhexane 42
2,3-dimethylpentane 90

n-octane C_8H_{18} -20
2-methylheptane 22
2,3-dimethylhexane 71

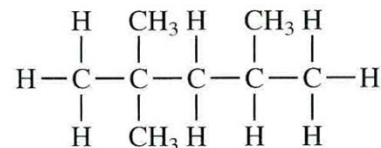
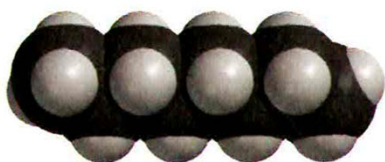
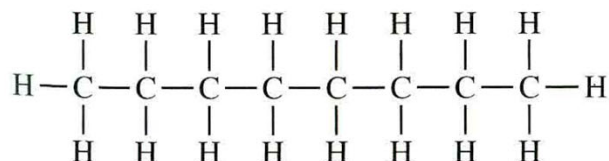
2,2,4-trimethylpentane **100 (isooctane = the standard)**

Benzene 106
Toluene 118
o-xylene 107
Ethanol 108
MTBE (methyl t-butyl ether) 116

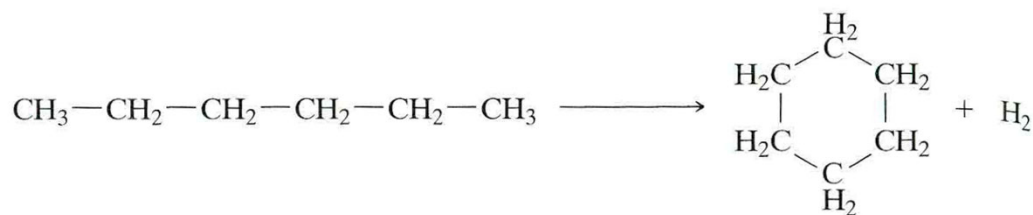
Arbitrarily set **isooctane at 100**
and **n-heptane at 0**; all others
rated against a *blend of the two*



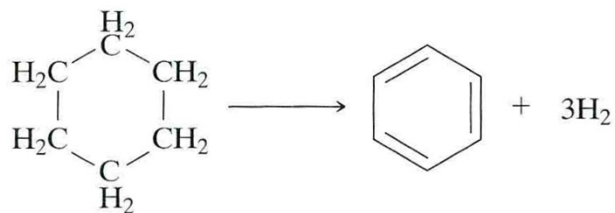
Reforming = rearranges the carbon backbone into more branched hydrocarbons



Chemistry in Context 6th Edition, ACS, McGraw-Hill



Typical catalysts are **Pt** or **Re** on SiO_2 or $\text{SiO}_2/\text{Al}_2\text{O}_3$

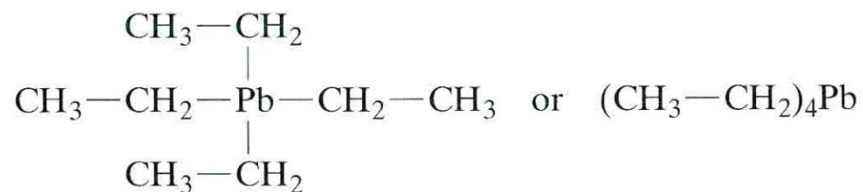


The Extraordinary Chemistry of Ordinary Things, 4th Ed.

Octane boosters: *gasoline anti-knock agents*

Tetraethyllead – raises octane ratings

(TEL) 1920's until late 70's



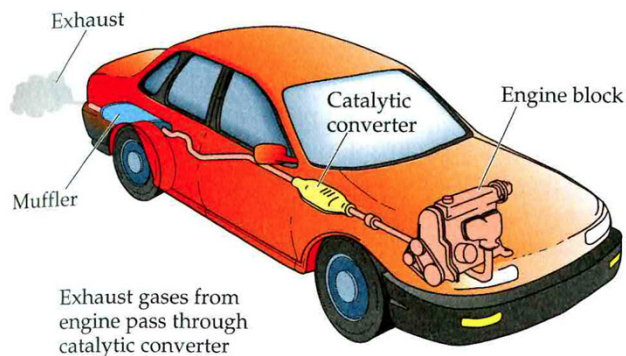
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Why it works: **Pb-C bond is weak** and breaks readily providing many ethyl radicals that enhance combustion

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 NO_x and SO_x byproducts** (that eventually oxidized to HNO₃ and H₂SO₄, forming acid rain)



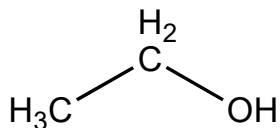
Catalytic converter: Pd and Pt



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

Higher octane rating
Oxygenates CO to CO₂

Ethanol



E10 = gasoline with 10% ethanol

The Extraordinary Chemistry of Ordinary Things, 4th Ed.

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 CO₂ 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:

Eubanks, L.P., Middlecamp, C.H. Hetzel, C.E. and Keller, S.W. "Chemistry in Context: Applying Chemistry to Society" 6th edition (2009), A Project of the American Chemical Society, McGraw Hill Higher Education

Snyder, C.H. "The Extraordinary Chemistry of Ordinary Things" (2003), Wiley.

Platts News Agency, Singapore, Aug. 16, 2011

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