Fossil fuels

Petroleum (= "rock oil"), natural gas and coal have fueled the Industrial Revolution

Exemplified by US energy use — more than 50% from burning wood at time of Civil War — now 90% from fossil fuels

Oil and natural gas:

Source is buried organic carbon, mostly the remains of microscopic oceanic phytoplankton (algae)

↳ "phyto" = Greek for plant

Photosynthesis of these microscopic plant fixes 70 GtC/yr (pre-industrial). This oceanic NPP ≈ terrestrial NPP.

$$CO_2 + H_2O \xrightarrow{\text{sun}} \underset{\text{organic matter}}{CH_2O} + O_2$$

The phytoplankton are grazed & metabolized by a host of respiring organisms:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O + \text{energy}$$

All oceanic photosynthesis occurs in uppermost 100 m — photic zone.

Only 7-10% sinks to below 100 m.

Only 0.2 GtC/yr escapes consumption and is buried.

This 0.2 GtC/yr of buried organic carbon is the source of all oil and gas.

The amount buried depends on the flux into the sediment top and the efficiency of burial.

The flux is high in regions of high productivity — ~~[illegible]~~ coastal regions where rivers supply needed nutrients (nitrate and phosphate)

The burial efficiency is ~~[illegible]~~ highest in regions of high sedimentation rate (deltas)

The efficiency peaks at 20% — 30% for sedimentation rates exceeding 1 m/1000 yrs = 1 km/Myr

Rivers transport $2 \cdot 10^{13}$ kg ~~[illegible]~~ = 20 Gt of sediments to the ocean each year.

The average organic C content of oceanic shales should therefore be

$$\frac{0.2 \text{ GtC/yr}}{20 \text{ Gt seds/yr}} = 1\%$$

← recall this is organic C, not C in $CaCO_3$

The measured range is

deep ocean → 0.05% — 5% ← near shore

measured mean 1%

The small fraction with organic C exceeding 5%
are petroleum source rocks.

Once the organic compounds are buried
they can no longer be oxidized (no O_2)

<u>Anerobic</u> bacteria can, however, consume
them via the reaction

$$2CH_2O \xrightarrow[\text{bacteria}]{} CH_4 + CO_2$$

↑ biogenic methane
in uppermost 1-2 km

Most of this biogenic methane is expelled
by <u>compaction</u> during further burial

At greater depths and temperatures between
100°C – 200°C a complex series of
reactions breaks the organic molecules
down into petroleum.

Typically 5–40 C atoms per molecule of
petroleum.

The late stages of this process yield
natural gas, mostly methane CH_4.
The ultimate product is graphite

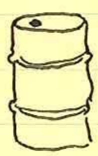
The "oil window" 60°–200°C occurs at depths
2–7 km, depending upon the geothermal
gradient

Oil can remain in the source rocks ("oil shales") or it can be mobilized into more permeable (sandier) formations.

Once there it can migrate — much escapes in oil seeps such as the La Brea tar pits in LA. Also collects in a wide variety of "traps" where it can be drilled and pumped.

The first well — Drake's folly — was drilled in 1861 in Titusville, PA.

Traditional unit of oil measurement:



1 barrel = 42 gallons
= 159 liters
= 0.137 metric tons

1 bbo = 1 billion barrels of oil

Most oil is found in relatively young rocks — ~~a few million years old~~ tens of Myr old. The longer it has been around, the more chance it has had to escape.

King Coal:

Coal is formed from large leafy plants growing in swamps, often in slowly sinking coastal areas.

The swampy conditions can lead to burial of almost pristine organic matter with very little oxidation

Some methane is found in freshwater swamps due to

$$2CH_2O \xrightarrow[\text{anerobic bacteria}]{} \underset{\text{"swamp gas"}}{CH_4} + CO_2$$

Increasing burial leads to devolatilization. Main reaction is <u>dewatering</u>:

$$CH_2O \rightarrow \underset{\text{graphite}}{C} + H_2O$$

The %C goes up and the %O and %H go down. The ~~best~~ highest-grade coal (anthracite) is ~90% C.

Organic matter in brackish swamps is high in H_2S due to reaction

$$2CH_2O + \underset{\text{sulfate ion in seawater}}{SO_4^{2-}} \xrightarrow[\text{anerobic bacteria}]{} 2HCO_3^- + \underset{\text{hydrogen sulfide}}{H_2S}$$

The H_2S then reacts with Fe to form pyrite FeS_2.

Such coal is "high sulfur" — produces SO_2 sulfur dioxide — acid rain — upon combustion.

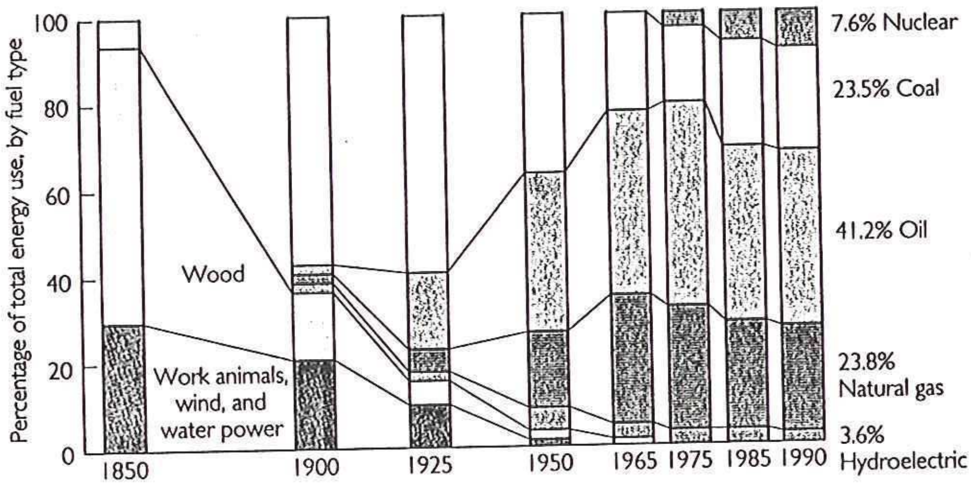
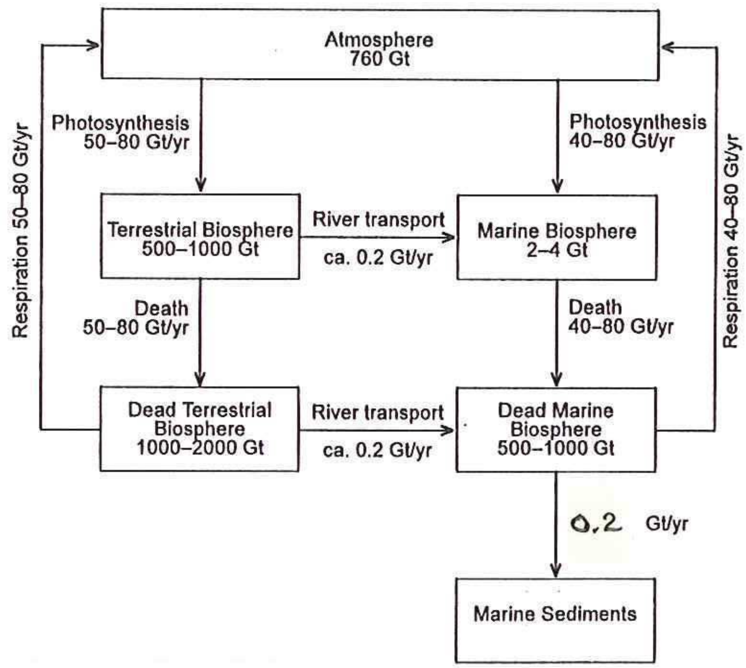


FIGURE 22.3 Percentages of various types of energy used in the United States from 1850 to 1990. (Data from U.S. Energy Information Agency, 1991.)

Figure 5.4. The biological parts of the carbon cycle. The carbon content of the several reservoirs is in Gt carbon (1 Gt = 10^{15} gm C). (Data from the compilation of Sundquist 1985)



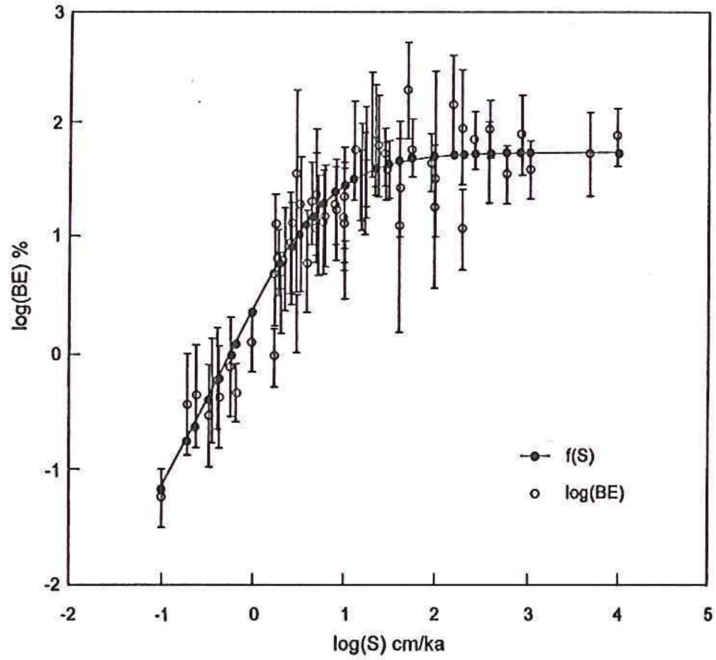


Figure 7.8.
Plot of the burial efficiency, BE, of organic carbon with marine sediments vs. the sedimentation rate (S), in centimeters per 1,000 years. (Betts and Holland 1991)

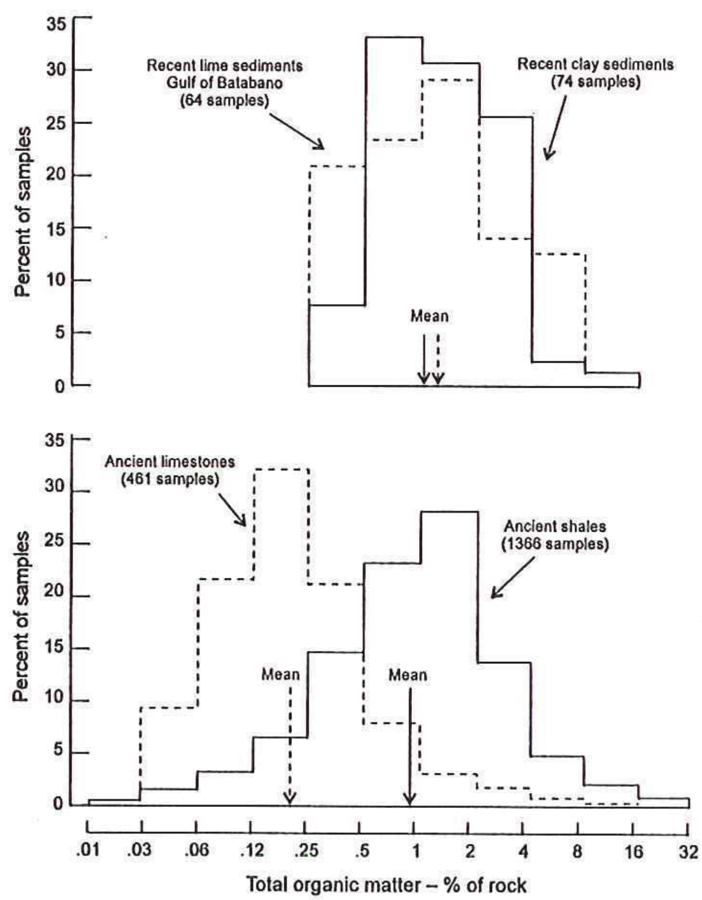


Figure 7.9.
The total organic carbon content of recent and ancient limestones and shales. (Gehman 1962)

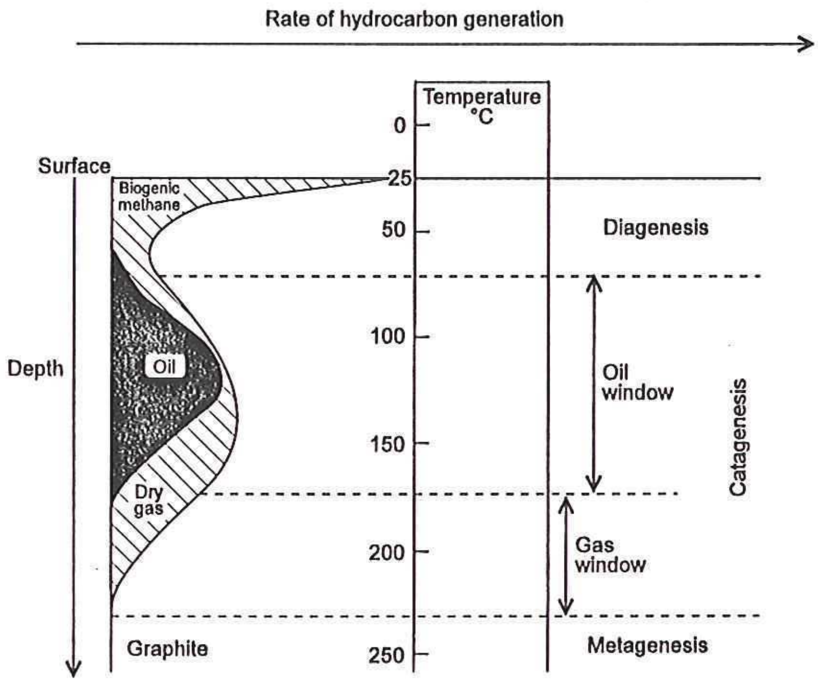


Figure 8.17. Correlation between temperature and the rate of hydrocarbon generation during the burial of organic matter in marine sediments. (Selley 1985)

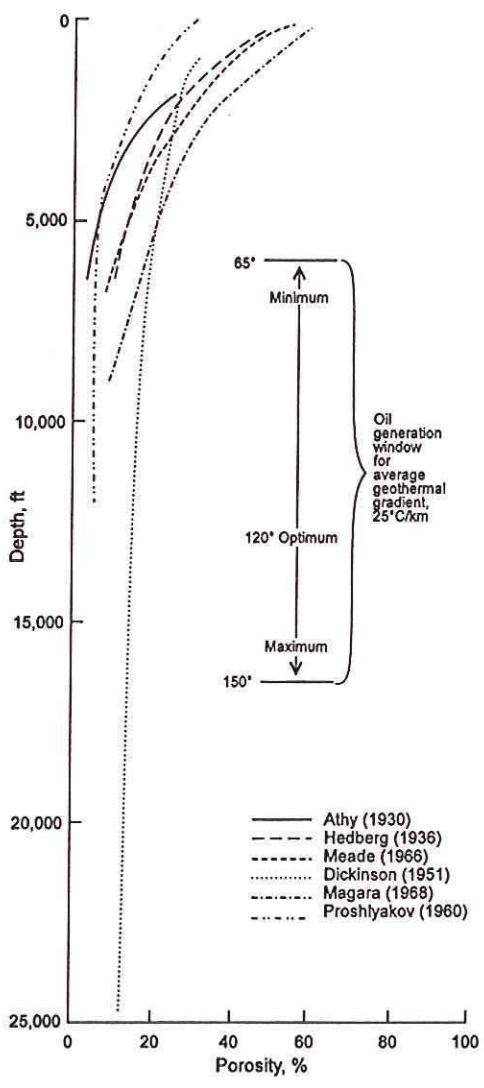


Figure 8.18. Shale compaction curves from various sources. Note that there is only a small amount of water loss due to compaction over the depth range of the oil window.

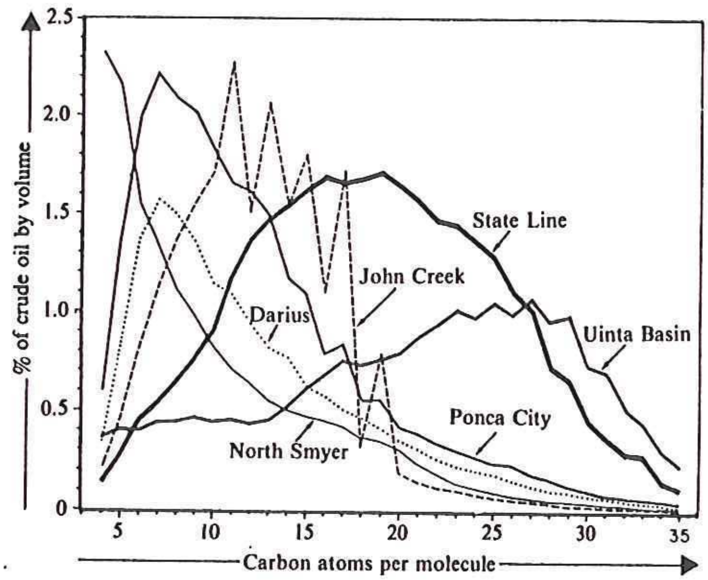
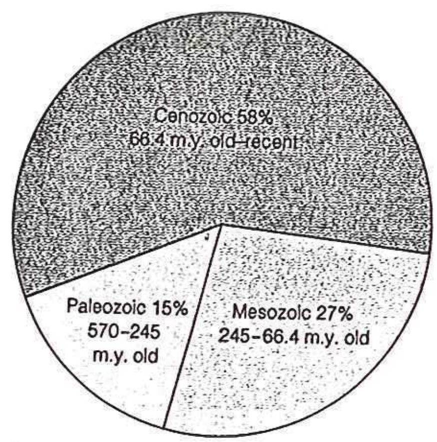


Figure 3.3. Distribution of *n*-alkanes in different types of crude oils. (From Martin et al., 1963; republished with permission of Nature)



▲ FIGURE 11.2
Percentages of total world oil production from rocks of different ages. (m.y. stands for million years.)

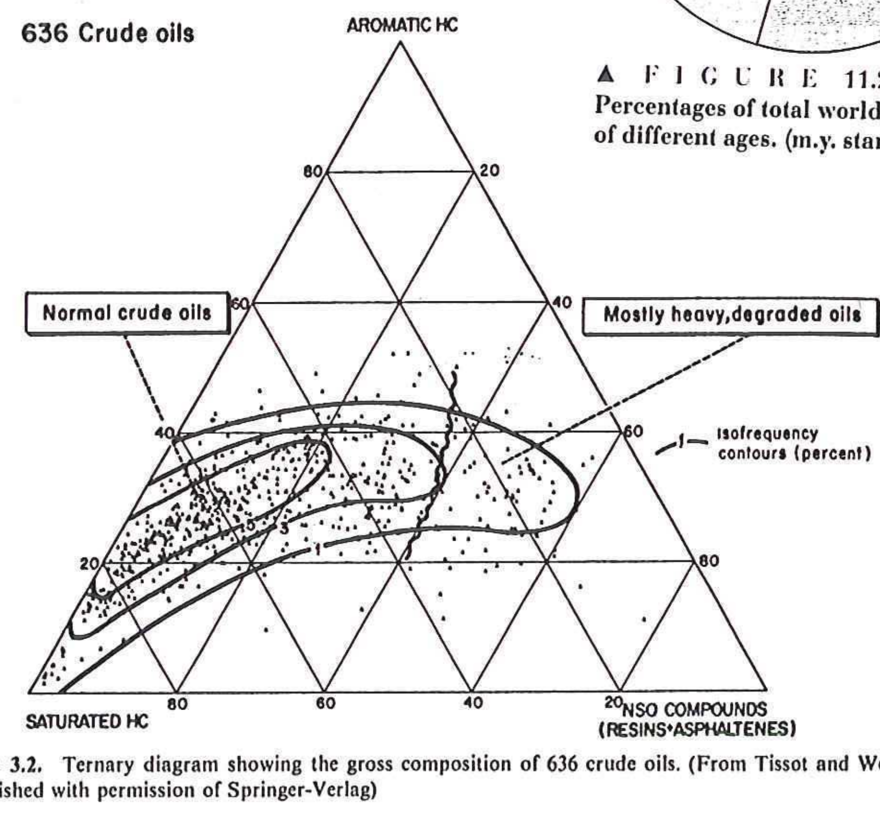


Figure 3.2. Ternary diagram showing the gross composition of 636 crude oils. (From Tissot and Welte, 1978: republished with permission of Springer-Verlag)

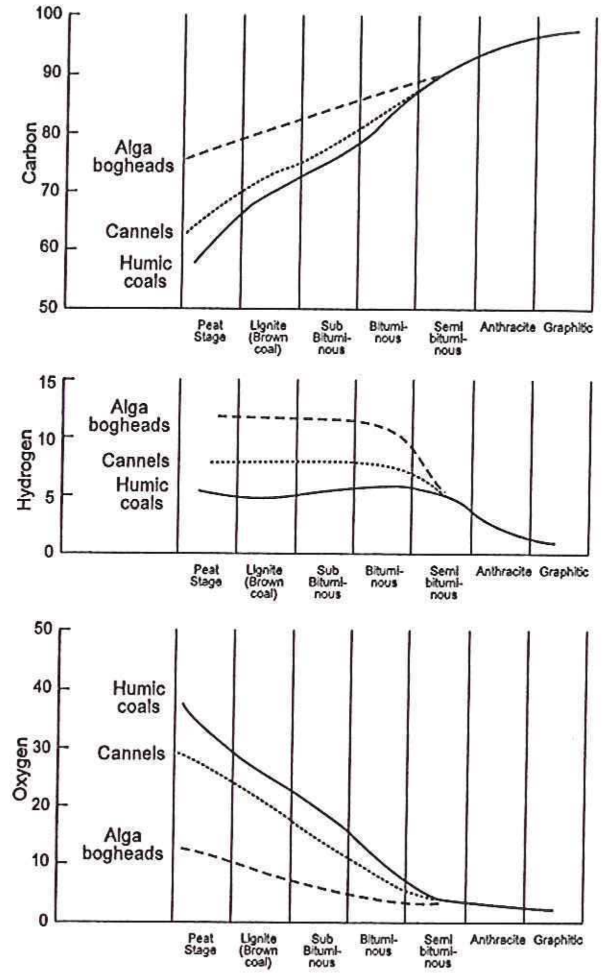


Figure 7.12. Changes in carbon, hydrogen, and oxygen content during the evolution of normal (humic) coals and algal (sapropelic) coals. (White 1925)

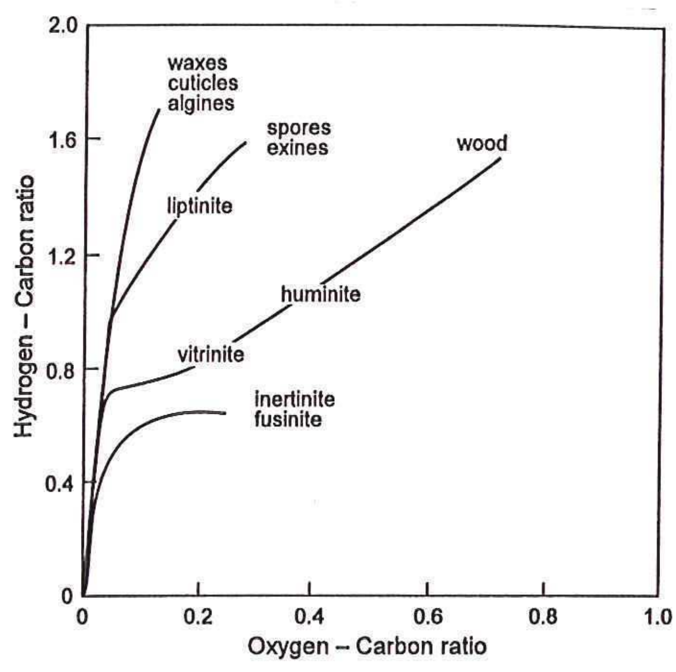


Figure 7.13. Van Krevelen diagram (H/C versus O/C atomic ratios) for the main components of coal and their predecessors with lines of dehydration, decarboxylation, demethanation, dehydrogenation, oxidation, and hydrogenation. (Modified after van Krevelen 1961; Tissot and Welte 1984; from Damberger 1991)

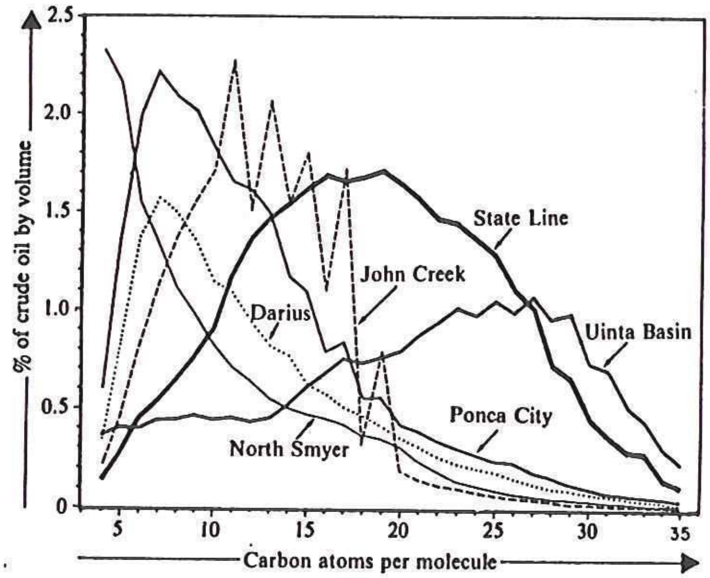
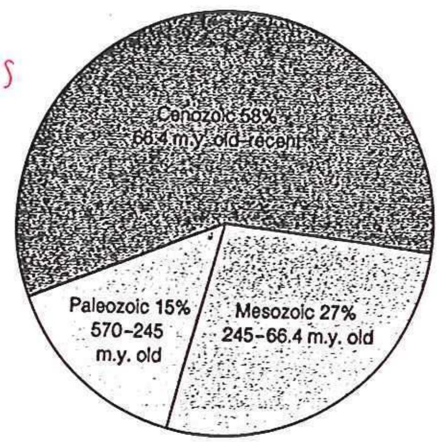


Figure 3.3. Distribution of *n*-alkanes in different types of crude oils. (From Martin et al., 1963; republished with permission of Nature)

Cenozoic rocks ≈60%



▲ FIGURE 11.2
Percentages of total world oil production from rocks of different ages. (m.y. stands for million years.)

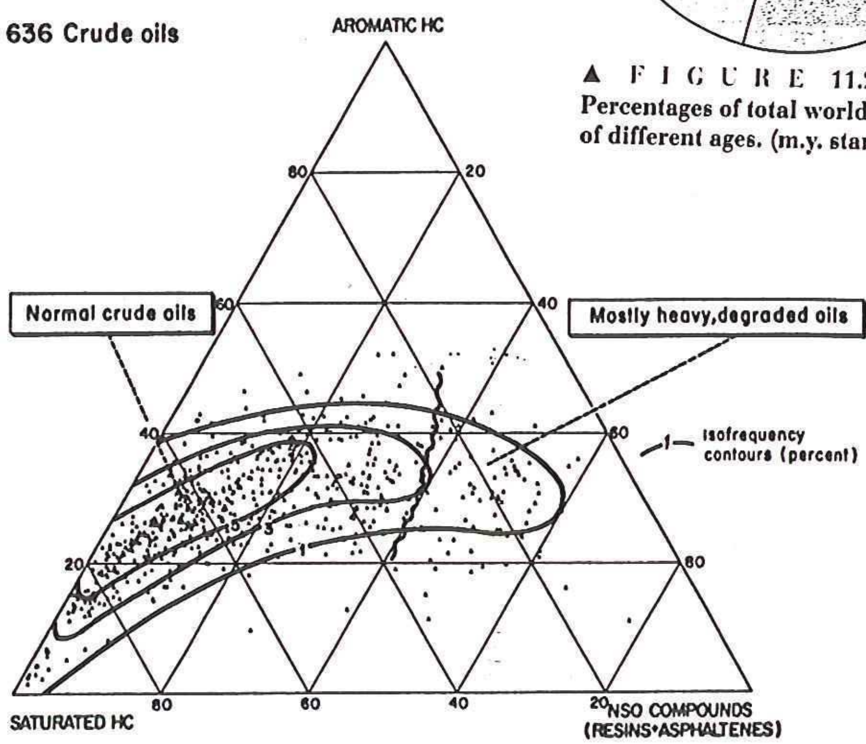


Figure 3.2. Ternary diagram showing the gross composition of 636 crude oils. (From Tissot and Welte, 1978: republished with permission of Springer-Verlag)

Fossil fuel consumption: best viewed in context of energy use as a whole.

Simplest to convert everything to energy units.

Some conversion factors are handy:

1 BTU (British Thermal Unit) = energy required to raise 1 lb of water 1°F.

$1 \text{ BTU} = 1055 \text{ J}$

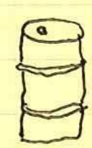
$$1 \text{ quad} = 1 \text{ quadrillion BTU}$$
$$= 10^{15} \text{ BTU} = 1.055 \cdot 10^{18} \text{ J}$$
$$\approx 1 \text{ EJ (exajoule)}$$

↑ unit commonly used for global accounting

Oils differ but it is conventional to adopt a nominal average:

1 barrel of oil (upon burning)

$$= 5.8 \text{ MBTU} = 6.1 \text{ GJ}$$



so... 1 bbo (billion barrels of oil) ≈ 6 quads

To make matters more confusing:

Natural gas resources are commonly measured in tcf = trillions of cubic feet

1000 cu ft = 1 MBTU ≈ 1 GJ, so

$$1 \text{ tcf} \approx 1 \text{ quad} \approx 1 \text{ EJ}$$

Finally, coal consumption is measured in tons.

$$1 \text{ Gt coal} = 27.8 \text{ quads} = 27.8 \text{ EJ}$$

↑ nominal average

Current world-wide energy consumption (1996):

350 quads / yr ← 87% fossil fuel

World-wide is increasing at 2.7% per year — almost twice as fast as population

More confusion — electrical utility companies charge by the kilowatt-hour (kWh)

$$1 \text{ kWh} = 3.6 \text{ MJ} = 3412 \text{ BTU}$$

A typical electrical power plant has a full capacity of ~ 1 GW. Typically operates at ~ 60% capacity, producing 0.6 GW.

Burning 1 barrel of oil produces 1700 kWh

A typical coal-burning plant requires ~ 10,000 BTU ~ 0.3 tons of coal to produce 1 kWh. Efficiency of electrical conversion ~ 33%

How does fossil fuel consumption compare to food consumption?

$$\left(350 \cdot 10^{18}\ \text{J/yr}\right)\ (.85)$$

energy use × ↑ 85% fossil fuel

$$= 3 \cdot 10^{20}\ \text{J/yr}$$

$$= 10^{13}\ \text{W} \approx \tfrac{1}{4} \times \text{heat flow from the } \oplus$$

Food consumption, as we have seen, amounts to $2.4 \cdot 10^{19}$ J/yr $= 8 \cdot 10^{11}$ W

Humans consume 12 times as much fossil fuel (a nonrenewable resource) as food (a renewable resource)

Terrestrial NPP by photosynthetic plants is ~ $8 \cdot 10^{13}$ W, so

fossil fuel consumption is ~ 12% of terrestrial NPP

[illegible]

Energy units

Table 1. Conversion of units.[a,b]

General

1 short ton (ton) = 2000 lb = 0.907185 tonne
1 metric ton (tonne) = 1000 kg
1 barrel = 42 U.S. gallons = 159.0 litres

1 Btu (British thermal unit) = 1055 J (Joules)
1 kWh (kilowatt hour) = 3.6 MJ = 3412 Btu
1 kWh of electricity requires on average 10,253 Btu to produce, corresponding to a mean thermal efficiency of 33% (1988 U.S. fossil-fuel average)

Large units

1 quadrillion Btu = 10^9 MBtu = 10^{15} Btu
1 exajoule (EJ) = 10^3 PJ = 10^{12} MJ = 10^{18} J
1 terawatt-yr (TWyr) = 10^9 kWyr = 8.76×10^{12} kWh

	Quad	EJ
1 Quad	1.000	1.055
1 EJ	0.948	1.000
1 TWyr (100% conversion)	29.89	31.54
1 TWyr (33% efficiency)	90.6	95.6
10^9 tonne coal equiv (Gtce)	27.76	29.29
10^9 barrel oil equiv (bboe)	5.80	6.12
10^9 tonne oil equiv (Gtoe)	42.43	44.76
10^9 tonne oil equiv (Gtoe)[c]	39.69	41.87

Fuel values

1 barrel of crude oil = 0.137 metric ton
1 million barrels per day of crude oil = 2.12 quad/yr = 2.23 EJ/yr

	MBtu	GJ
Nominal or standard equivalents:		
1 barrel of crude oil (boe)	5.8	6.12
1000 cu. ft. of natural gas	1.000	1.055
1 short ton of coal	25.18	26.57
Average heat content (U.S. 1988):		
1 barrel of petroleum products	5.408	5.705
1000 cu. ft. of natural gas	1.029	1.086
1 short ton of coal	21.53	22.72
1 cord of dry wood (1.25 ton)	21.5	22.7
1 barrel of natural gas liquids	3.812	4.022
1 barrel of aviation gasoline	5.048	5.326
1 barrel of motor gasoline	5.253	5.542
1 barrel of distillate fuel oil	5.825	6.145
1 barrel of residual fuel oil	6.287	6.633

a. Adopted from Ref. 1.
b. Based on *Annual Energy Review* 1988 (Ref. 2), *Monthly Energy Review* (Ref. 3), and IIASA report (Ref. 4).
c. Alternate equivalent, used by OECD (Ref. 5).

Figure 8.31. The major sources of world energy in 1992. (*Annual Energy Review 1993*)

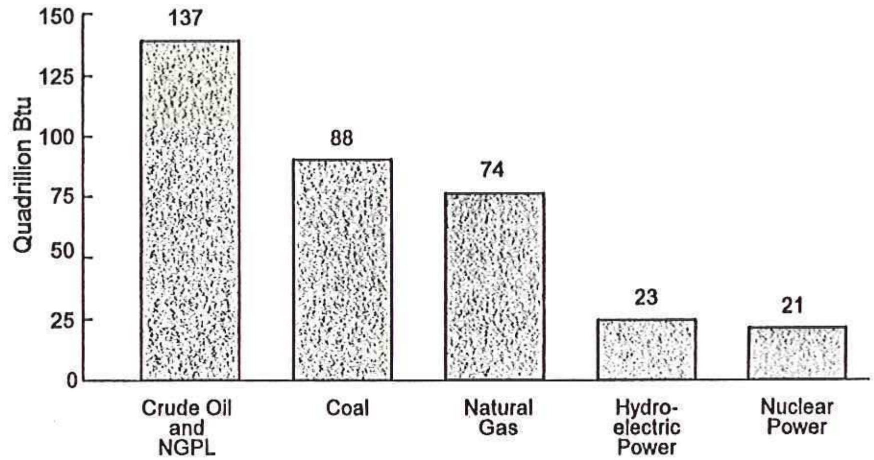


Figure 8.30. World primary energy production between 1973 and 1992. (*Annual Energy Review 1993*)

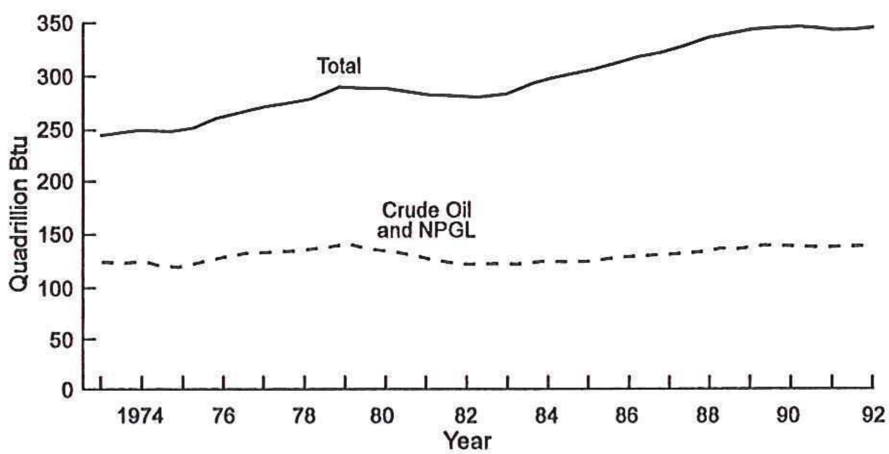


Figure 8.32. World primary energy production by source between 1973 and 1992. (*Annual Energy Review 1993*)

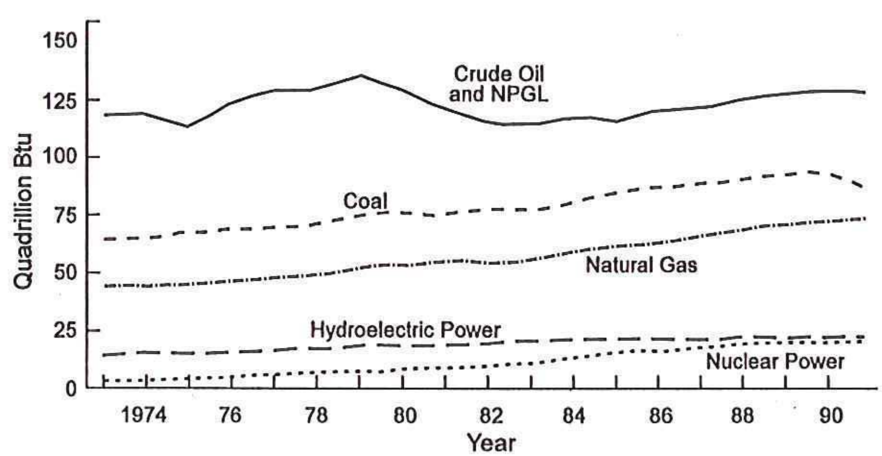


Figure 8.33a. The eleven major primary energy-producing countries in 1992. (*Annual Energy Review 1993*)

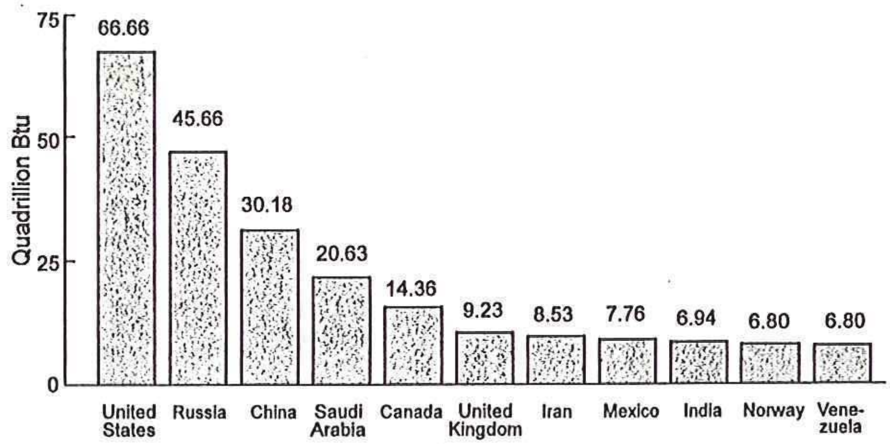


Figure 8.40. 1993 oil production by the twelve most important oil-producing countries. (*Annual Energy Review 1993*)

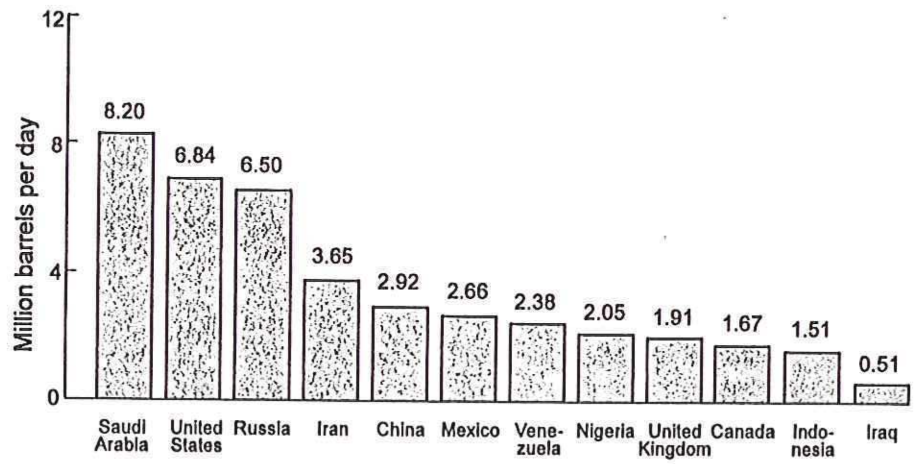


Figure 8.42. The major producers of natural gas in 1991. (*Annual Energy Review 1993*)

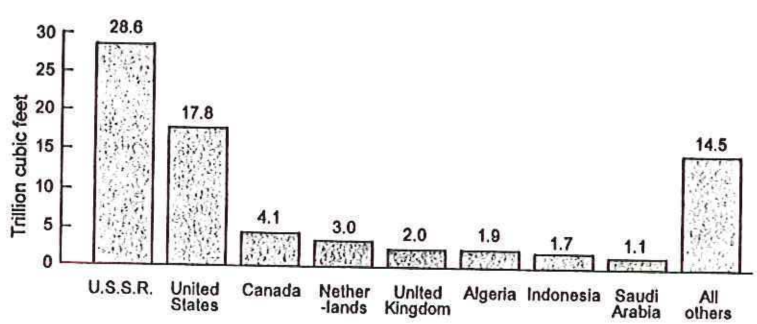
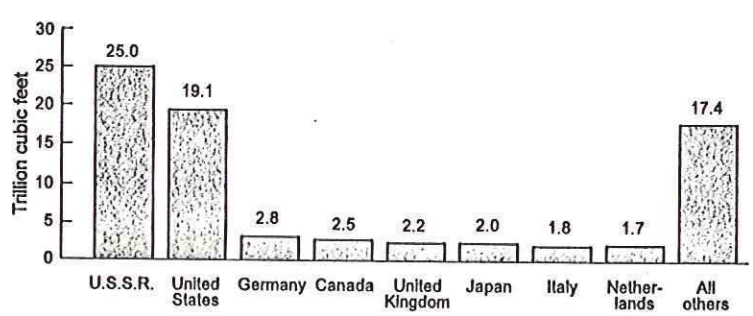


Figure 8.43. The major consumers of natural gas in 1991. (*Annual Energy Review 1993*).



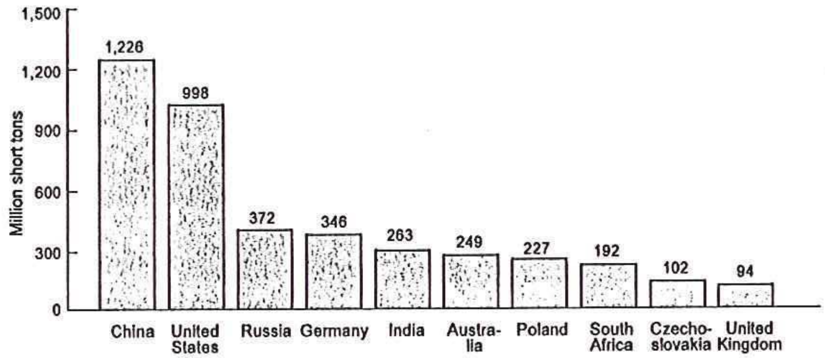


Figure 8.34. 1992 production of coal in the ten leading countries. (*Annual Energy Review 1993*)

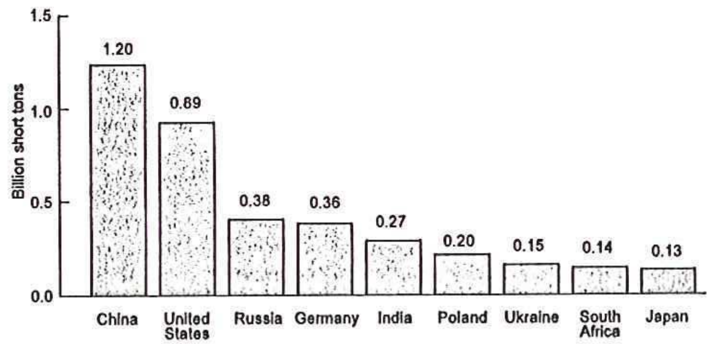


Figure 8.35. 1992 consumption of coal in the nine most coal-consuming countries. (*Annual Energy Review 1993*)

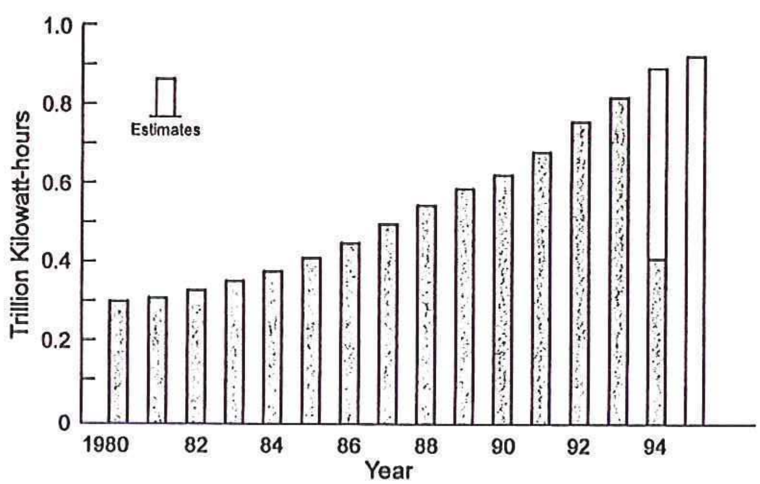
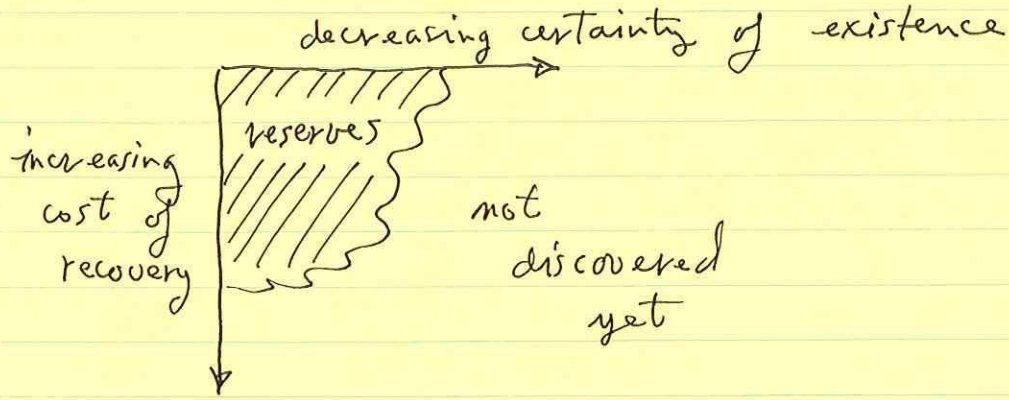


Figure 8.33b. Electricity generation in China since 1980. (*New York Times*, November 7, 1994)

So... how much is left?

Not easy to estimate — economic as well as scientific questions are relevant

The reserves of any nonrenewable resource are a floating target:



US — intense oil exploration — reserves are relatively well known

About 300 bbo pumpable oil in ground. We have already consumed ~ 50% of all pumpable oil in US since time of Drake's folly — 135 years ago.

World reserves are more uncertain. Total reserves, including undiscovered oil, could be as high as 2000 bbo = 12,000 quads

Current consumption rate 20 bbo/yr ⇒ 100 years' supply left.

Remember, however, that world-wide consumption is increasing at 3% per year

World reserves of natural gas estimated to be 8000 tcf = 8000 quads (about 100 years' supply at current consumption rates)

Coal is even more plentiful. Some estimates as high as 3000 Gt = 80,000 quads!

US very rich in coal: 1/4 – 1/5 of world reserves.

Subeconomic sources (tar sands, oil shales) — oil that has not been cooked enough to be pumped.

New extraction techniques are required.

Current production rates are minuscule because of expense — but potential reserves are huge — may be as high as 20,000 bbo equivalent = 120,000 quads (10 times as much as pumpable oil reserves)

Total remaining — all sources:

oil — 12,000 quads
gas — 8,000 quads
coal — 80,000 quads
other — 120,000 quads

total — 220,000 quads

$$\frac{220{,}000 \text{ quads}}{350 \text{ quads/yr}} \approx 600 \text{ years}$$

But both numerator & denominator are uncertain

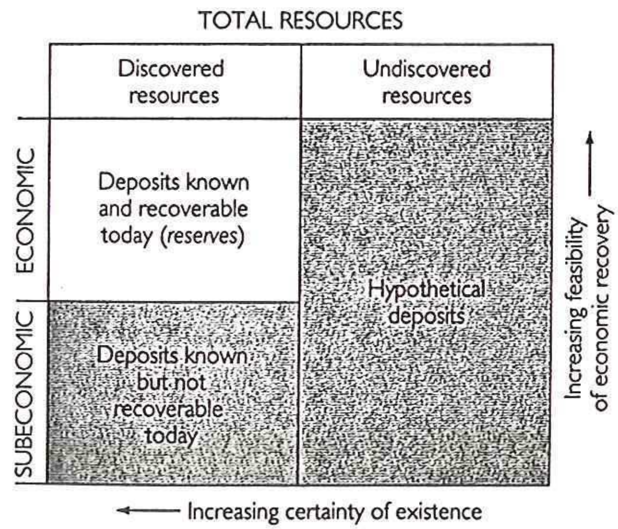


Table 1. United States oil resources (in billions of barrels).

Orignal proven conventional recoverable resources	226
Already produced	142
Remaining	84
Estimated undiscovered resources	46
Domestic production (per year)	3
Domestic consumption, including imports (per year)	5.5
Years left, under current production conditions, and no increase in imports	28–43

Note 1: If imports decrease or use increases, the number of years left will be smaller.
Note 2: As supplies shrink, increasing costs will decrease use, so reserves will increase number of years left.

Table 2. United States natural gas resources (in trillions of cubic feet).

Proven conventional recoverable resources (including Alaska, and at less than $5 per thousand cubic feet)	384
Production rate (per year)	17
Recent yearly addition to proven recoverable resources	14–15
Estimated total remaining conventionally recoverable resources (lower 48)	400–900
Estimated unconventional recoverable resources (price of recovery not determined, but probably high)	140–700
Total estimated resources	540–1600
Years left at current rate	35–95
Years left at double current rate	17–47

Note: Current cost of natural gas is about $1.70 per thousand cubic feet.

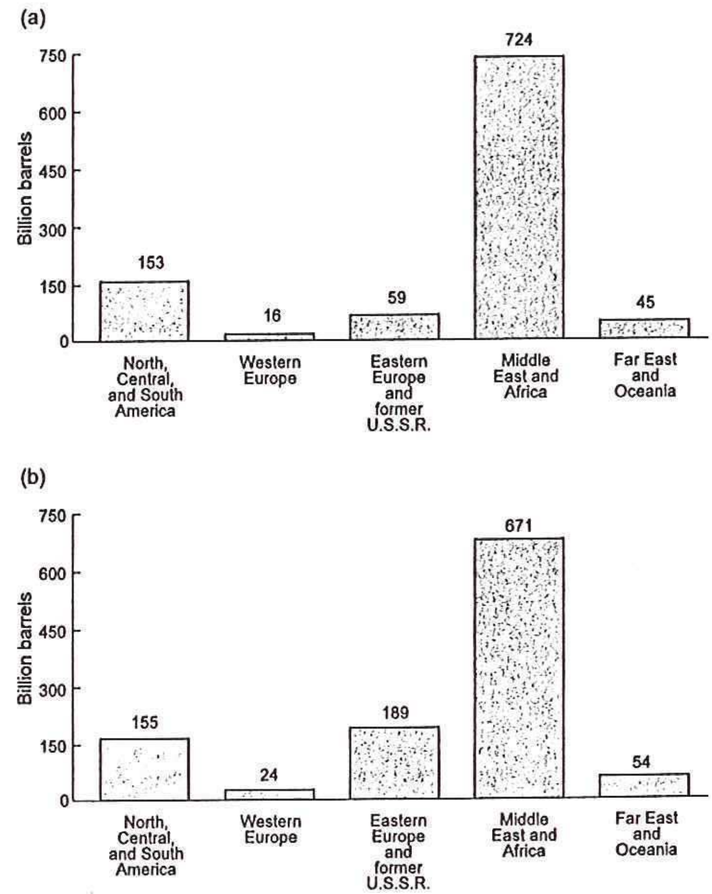


Figure 8.41. The distribution of world oil reserves in 1993. Sources (a) *Oil and Gas Journal*; (b) *World Oil*. (*Annual Energy Review 1993*)

Table 3. Global resources.

Oil (in billions of barrels)	
Original resources	1900
Produced	673
Remaining	1227
Production (per year)	21
Years left at current rate	60
Note: Undiscovered and unconventional resources could approximately double the total supplies, but at undetermined cost.	
Natural gas (in trillion of cubic feet)	
Estimated remaining resources	8100
Production rate (per year)	
Years left at current rate	120

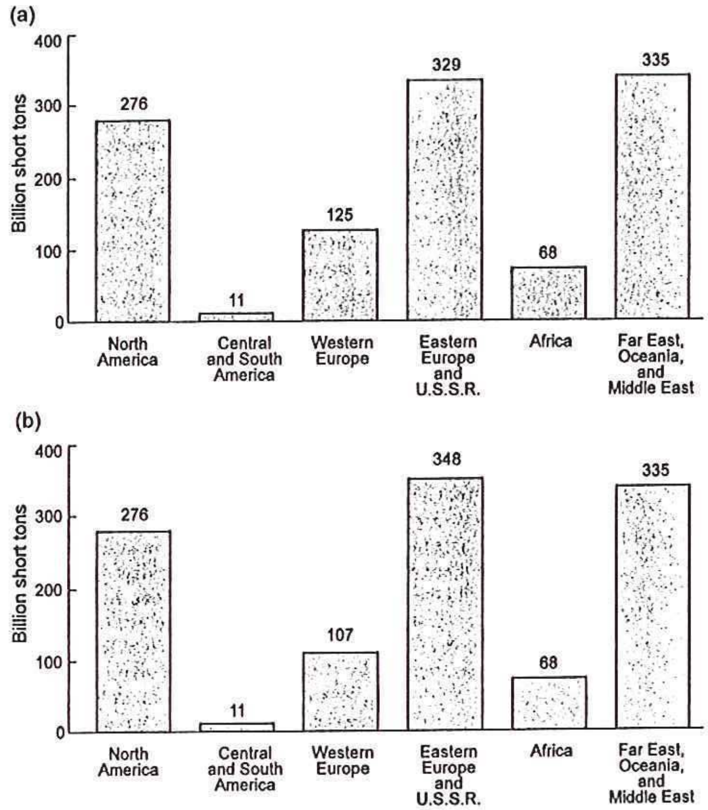


Figure 8.37. World reserves of coal estimated by (a) the World Energy Council, 1991; (b) British Petroleum, 1992. (*Annual Energy Review 1993*)

Table 4. Potential shale oil in place in the oil shale deposits of the United States (billions of barrels).

	Range of shale oil yields (gallons per ton[a])		
Location	5–10	10–25	25–100
Colorado, Utah, and Wyoming (the Green River formation)	4,000	2,800	1,200
Central and eastern states (includes Antrim, Chattanooga, Devonian, and other shales)	2,000	1,000	(?)
Alaska	Large	200	250
Other deposits	134,000	22,000	(?)
Total	140,000+	26,000	2,000(?)

[a]Order of magnitude estimate. Includes known deposits, extrapolation and interpolation of known deposits, and anticipated deposits.
Source: Reference 1 as reported in Reference 2.

Table 8.2.
World Resources of Heavy Oil, Tar Sands, and Oil Shale, 1990

Heavy Oil

	Billion Barrels		
	Proved Reserves	*Undiscovered Resources*	*Total Recoverable*
North America	23	30	65
Central and South America	280	16	309
Western Europe	8	0	9
USSR and Eastern Europe (former)	7	21	33
Africa	4	1	5
Middle East	115	22	169
Far East and Oceania	13	4	19
World total	450	94	609*

Tar Sands

	Billion Barrels		
	Measured Resources	*Speculative Resources*	*In-Place Resources*
United States	21	41	~60
Canada			~1,700
Venezuela			~700
World total			~4,000

Oil Shale

		*Billion Barrels of Oil**
United States		630
Western	460	
Eastern	170	
South America (Brazil)		300
USSR (former)		40
Africa (Zaire)		40

Source: Data from compilation by Kulp 1990.
* Recovery = 38% of estimated in-place resource.