

THE LITHOSPHERE

*T*he **lithosphere**, including the internal structure below the earth's surface, is the part of the earth where all mineral resources originate. A number of illustrations will be used to introduce the lithosphere. From the continental crust down, the structure of the mantle always provides the necessary energy to form compounds from iron and the elements associated with iron above the upper mantle level (refer to Figure A-1). Different metamorphic facies are formed due to both the pressure and temperature gradients. Above the transition zone, especially in the continental margins, organic-rich sediments are formed, as shown in Figure A-2. All mineral deposits in veins and domes accumulate at the tectonic plate boundaries, as can be seen in Figure A-3. These can take the shape of belts or bands, as illustrated in Figure A-4.

All energy on earth comes from the sun and is called **stellar energy** (see Figure A-5). When stellar energy is absorbed by the atmosphere and hydrosphere, the net result is the energy in wind, waves, ocean currents, tidal currents, hydroelectric power, etc. When energy is absorbed by the biosphere and used in lifecycles by photosynthesis, the biomass produces decay that becomes buried in sediments, thereby producing fossil energy. Energy is

absorbed by the lithosphere and is used in geochemical cycles and the conduction and convection from the earth's interior. These are called **geothermal** and **nuclear energy**; the latter of these is known as **fissile fuels**.

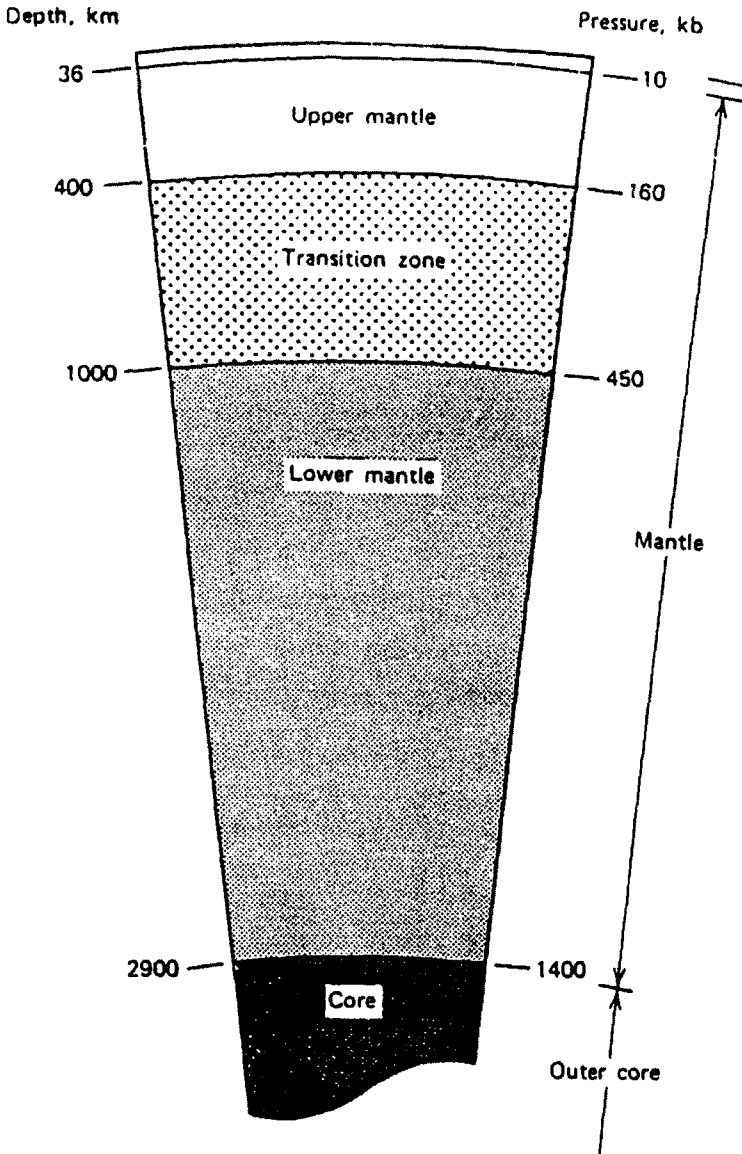


Figure A-1. The internal structure of the Earth. (After B. Mason, *Principle of Geochemistry*, 1966)

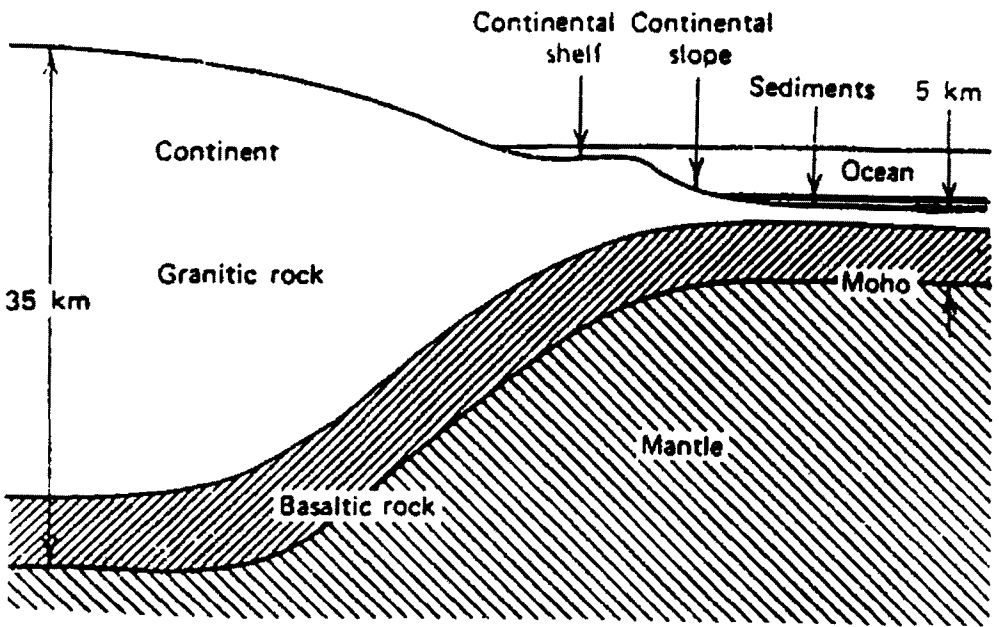


Figure A-2. The Earth's crust under the continents and oceans. The moho is Mohorovicic discontinuity which separates the highly heterogenous crust from the more homogenous upper mantle.

In the following chapters of this section, we will briefly discuss fossil fuels, followed by solar, wind, tidal, and other non-fossil fuels. In the last group, we will concentrate on nuclear power.

As the world has become increasingly industrialized and modernized, energy consumption has increased accordingly. After decades of careless exploitation of energy resources, the world has finally come to realize that the energy supplies that were once considered inexhaustible will shortly be nonexistent. Moreover, this increased energy consumption has resulted in an extremely adverse impact on the environment in the form of air, water, and other kinds of pollution. There are increasing conflicts between environmental conservationists, who are concerned with leaving a clean and healthy world for the future generations, and industrialists and businesspersons, who are pushing for a higher level of technological civilization and material consumption. In the following chapter, we will explore the background of energy production and consumption with an emphasis on fossil energy.

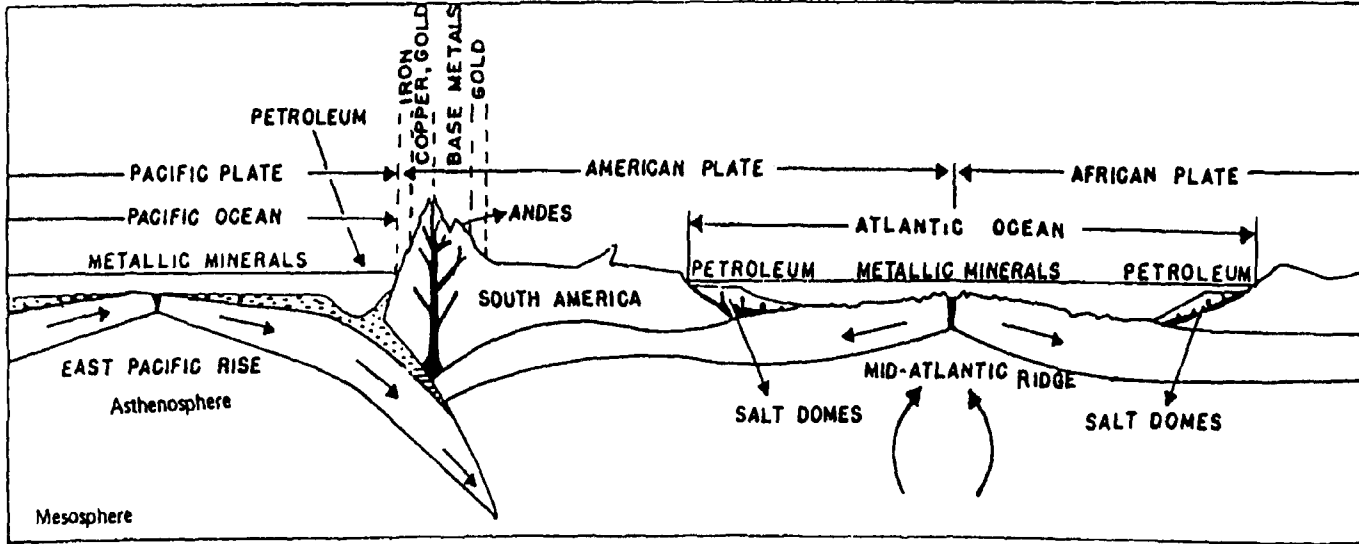


Figure A-3. The role of the plate boundaries in the accumulation of mineral deposits.

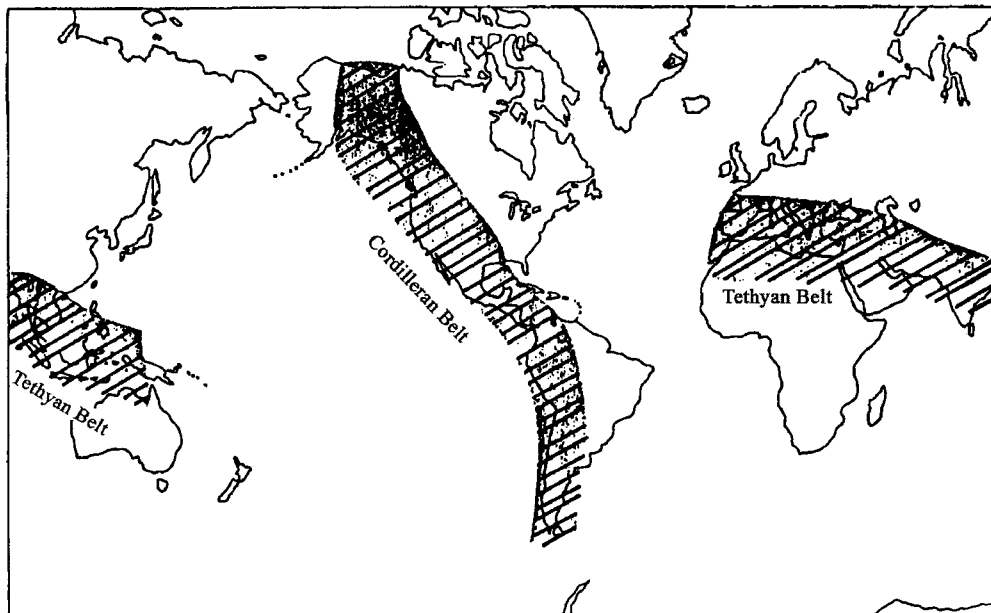


Figure A-4. Major world petroleum belts. [Source: T.F. Yen, *Genesis and Degradation of Petroleum Hydrocarbons in Marine Environments* in (T. M. Church ed.) *Marine Chemistry in the Coastal Environments*, ACS Symp. Series 18, Washington, DC, 1975 pp. 231-266.]

We will see that protecting the environment is not necessarily incompatible with meeting energy demands. We will begin with energy and power, and explain energy consumption. The introduction is followed by a brief classification of fossil fuels. Lastly, we will introduce some of the resource models used in energy technology. Energy conservation and the green process will be discussed briefly, as will alternative energy sources, mostly arising from indirect, inanimate sources as indicated by Figure A-5. The origin of fissile fuels is also discussed in succeeding chapters.

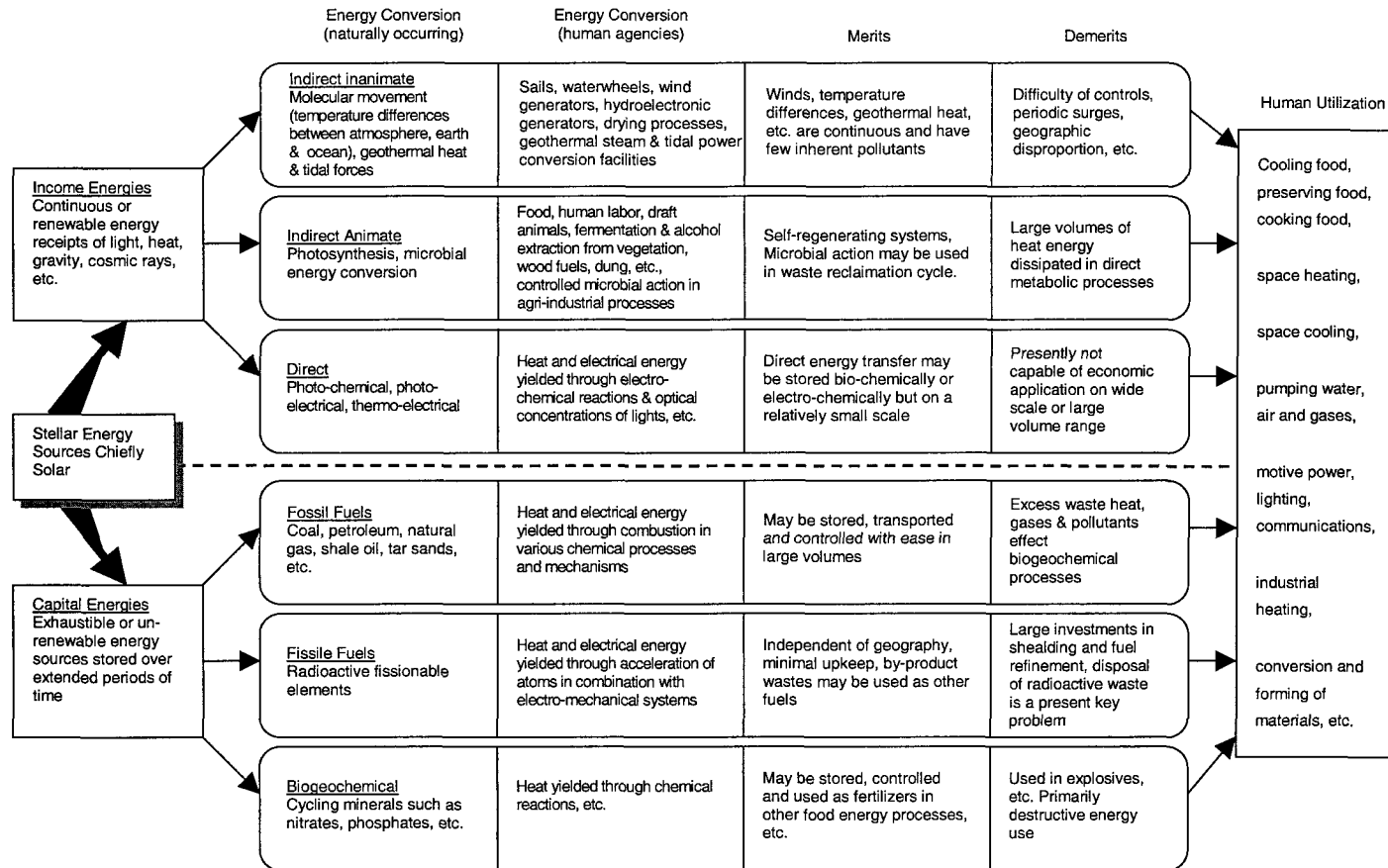


Figure A-5. Energy Systems. (Source: J. McHale, World Facts and Trends, Collier, New York, 2nd ed., 1972, p.61.)

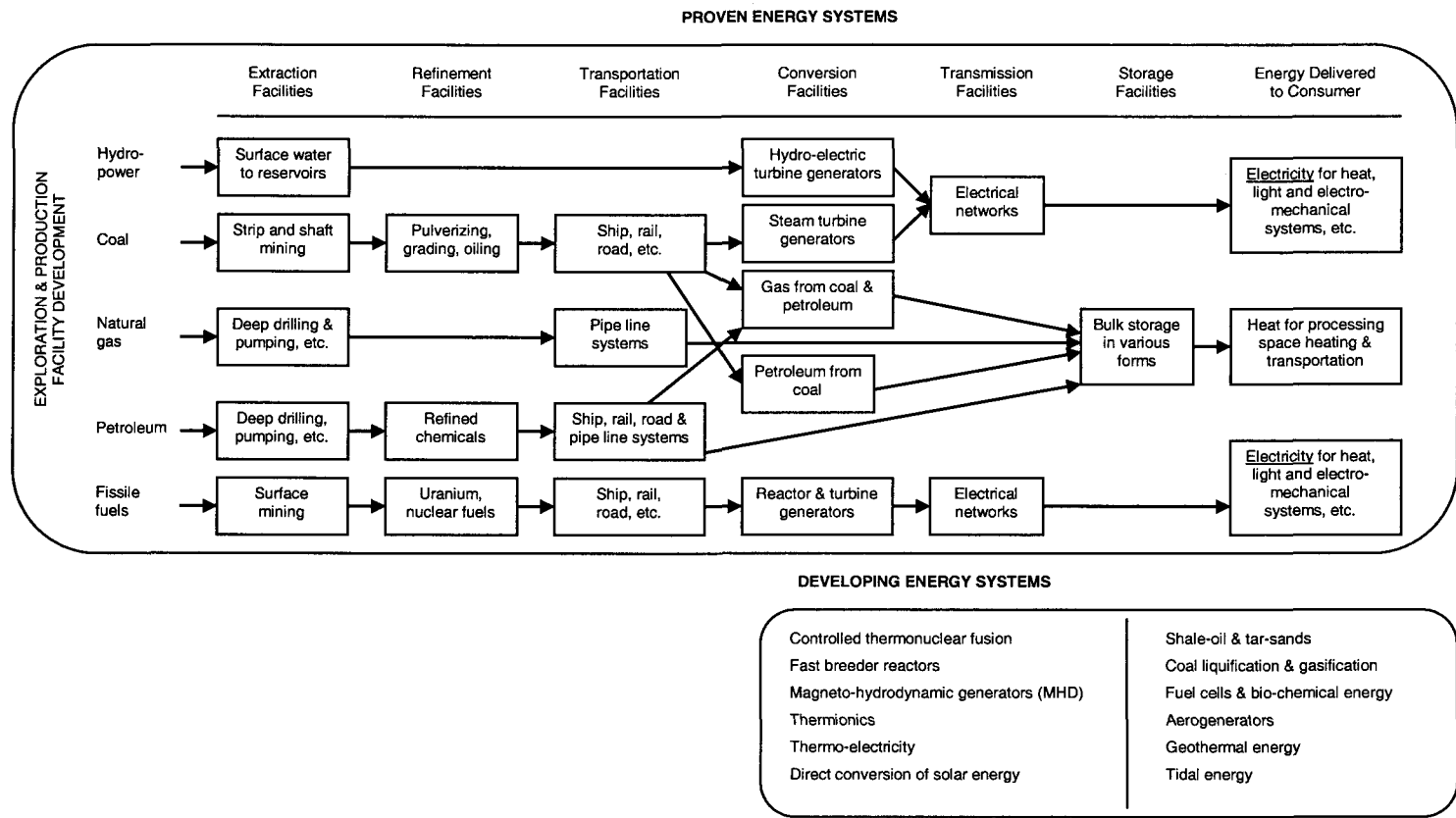


Figure A-5. Energy Systems. (Continued)

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FOSSIL FUELS

1.1 ENERGY AND POWER

Solar energy is the major source of the earth's energy system, in conjunction with two other small contributors: **tidal energy** and **geothermal heat**. The hydroelectric power we utilize results from rainfall, through a process in which sunlight provides energy to raise water up to the atmosphere. The food we eat is the end-product of food chains in which sunlight provides energy for photosynthesis. The fossil fuel we burn originates from these organic compounds created through the preceding process, to which solar power makes a great contribution. As shown in Figure 1-1, a quantity of $174,000 \times 10^{12}$ W of solar energy is intercepted by the earth. Of this quantity, about 30% is reflected or scattered back into space. This scattered fraction is called the **albedo**, and it determines the total energy balance of the earth. Another 47% of this solar energy is converted directly into heat. About 23% of the total energy intercepted is used to drive the **hydrologic cycle**, the massive evaporation and precipitation of water upon which we depend for our fresh water supplies. Only a very small fraction, 0.1%, is used by green plants and algae in photosynthesis, which are vital for our food supply.

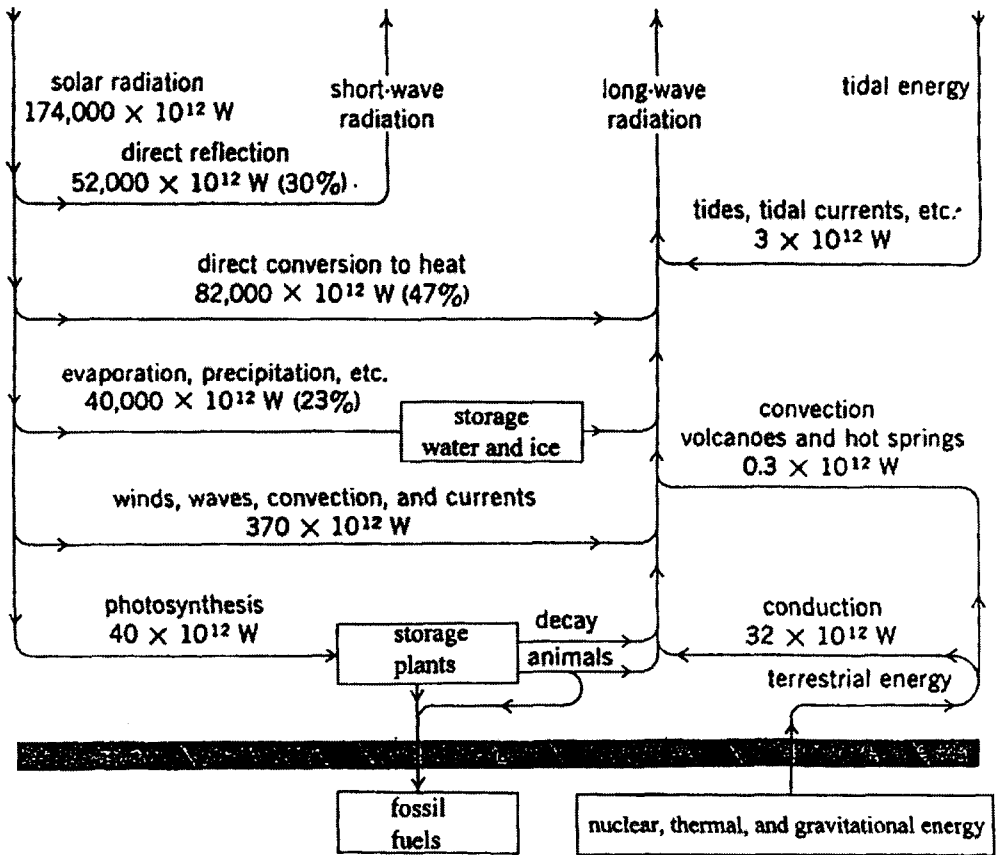


Figure 1-1. Energy flow-sheet for the Earth. [From M.K. Hubbert, U.S. energy resources: A review as of 1972, pt. 1, in A National Fuels and Energy Policy Study, U.S. 93rd Congress, 2nd Session, Senate Committee on the Interior and Insular Affairs, ser. no. 93-40 (92-75), 1974.]

Various energy unit systems have been adapted for use by different groups of people. It is troublesome, however, for people to convert a value from one unit to another. For convenience, Table 1-1 and Figure 1-2 provide some common energy equivalents and conversion factors.

For energy, it is useful to know some of the abbreviations that are commonly adopted. In addition to the units discussed in the Appendix 1, both **Quad** (10^{15}) and **Quin** (10^{18}) are used in large numbers. In the study of energy demands, various units (tons of coal, barrels of oil, cubic feet of gas, gigawatts, and so on) are often encountered. To be consistent with other studies, Btu is sometimes used as the common unit of energy. On that basis, one Quad is equal to 1×10^{15} Btu and one Quin is equal to 1×10^{18} Btu.

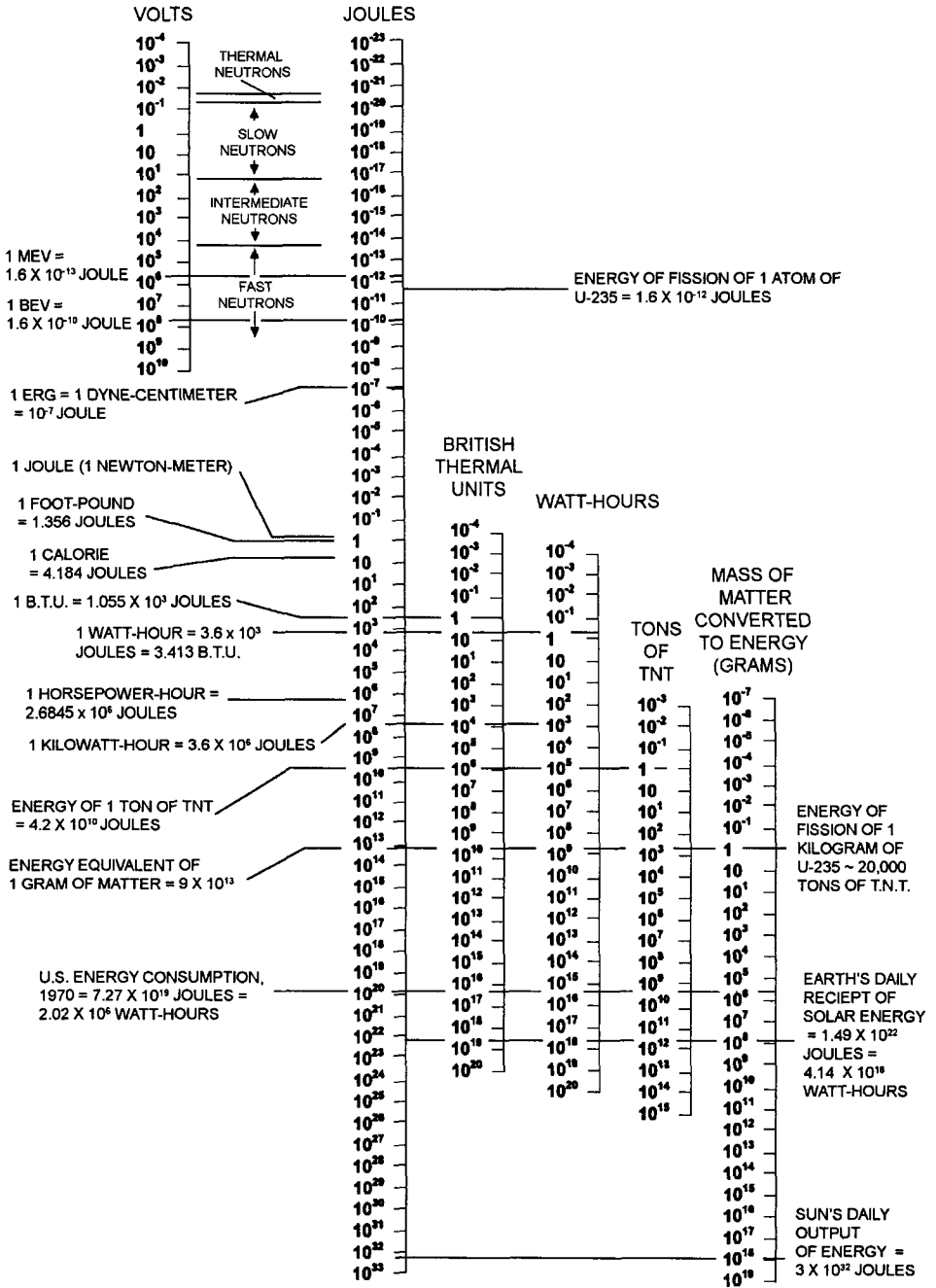


Figure 1-2. Energy Conversion Factors. (Modified after C. Starr, 1971)

Table 1-1. Energy Equivalents and Other Conversion Factors

Unit	Equivalent	Remarks
1 kcal	$= 1.162 \times 10^{-6}$	MWh
2 Hph (metric)	$= 7.355 \times 10^{-4}$	MWh
1 BTU	$= 0.293 \times 10^{-6}$	MWh
1 Q	$= 0.293 \times 10^{12}$	MWh 1 Q = 10^{18} BTU
1 t hard coal	= 8.134	MWh 1 kg hard coal equivalent = 7,000 kcal
1 t petroleum products	= 11	MWh varies according to raw material
10^3 m^3 natural gas	= 10	MWh varies according to raw material
1 t U	$= 2.25 \times 10^7$	MWh 200 MeV/U atom
1 t Th	$= 2.30 \times 10^7$	MWh 200 MeV/Th atom
1 t D	$= 6.69 \times 10^7$	MWh 5 MeV/D atom
1 short ton U_3O_8	= 0.7693	t U
1 kg U_3O_8	= 0.8480	kg U
1 lb U_3O_8	= 0.3847	kg U
1 short ton ThO_2	= 0.7972	1 Th
1 kg ThO_2	= 0.8788	kg Th
1 lb ThO_2	= 0.3986	kg Th
1 lb	= 0.4536	kg
1 short ton	= 0.9072	t
1 U.S. barrel (petroleum)	= 0.1590	m^3

Power is the rate at which energy is consumed or generated; for example, Joules are the energy unit, while Watts are Joules/sec, or the power unit.

$$P = \frac{dE}{dt} \quad [1-1]$$

$$E_{\text{year}} = \int_0^T P_{\text{inst}} dt \quad [1-2]$$

and

$$P_{\text{ar}} = \frac{1}{T} E_{\text{year}} = \frac{1}{T} \int_0^T P_{\text{inst}} dt \quad [1-3]$$

$$T = 3.15 \times 10^7 \text{ sec} \quad [1-4]$$

Present world energy consumption = 7.1×10^{12} W = 5.3×10^{19} cal/y. The United States alone consumes 1.8×10^{16} kcal/y, which is one-third of the world's total energy consumption. The metabolic consumption per capita is 3100 kcal/day, or 150 Watts. Thus, the United States non-metabolic per capita consumption rate equals 12 kW, which is about 80 times as great as the metabolic consumption.

1.2 TOTAL ENERGY CONSUMPTION

Humans are now consuming fossil energy faster than nature can produce it. We are living off the store of energy of past ages. Fossil fuel is an exhaustible resource, and the energy consumption by humans grows exponentially, as shown in Figure 1-3. This type of growth is inevitably unreasonable. It will double in 18 years even if energy consumption only increases by 4% per year. For an exhaustible resource, the cumulative production and rate production are shown in Figures 1-4 and 1-5.

Nothing in the natural world can grow through too many doubling periods before it runs into some constraint. Eventually all exponential growth curves have to level off, and the growth of energy consumption is no exception. In the long run, energy inputs and outputs for human society must be in a steady state. Because population grows exponentially, our energy consumption is exponential in nature.

$$Q = Q_0 \exp(\lambda T) \quad [1-5]$$

where $e = 2.718$, $T = \text{time AD}$, $\lambda = \text{constant (yr}^{-1}\text{)}$.

For example, our present total energy consumption is

$$Q^T = 1.85 \times 10^{-21} e^{0.0282T} \text{ (Quad/yr)} \quad [1-6]$$

The following are some properties from the above exponential equation.

a. **doubling time, T_2**

$$T_2 = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} \quad [1-7]$$

For example,

$$T_2 = \frac{0.693}{0.0282} = 25 \text{ yr}$$

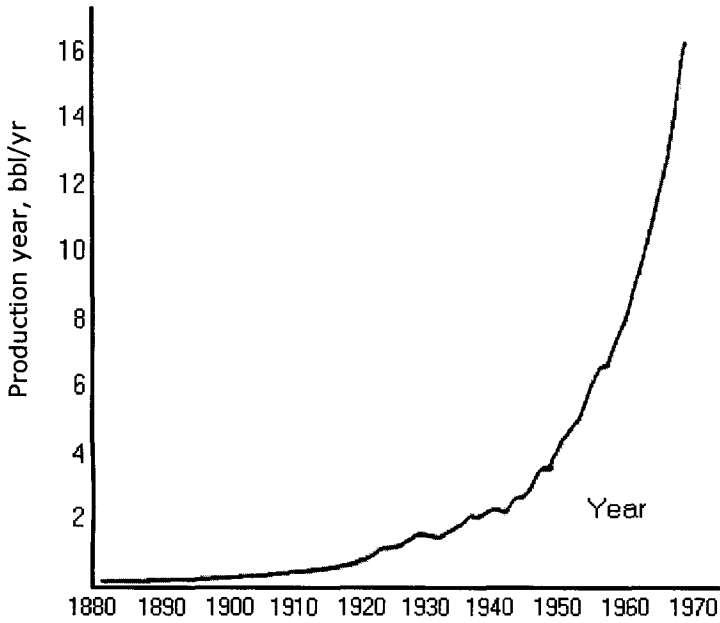


Figure 1-3. World crude oil production (From Hubbert, op. cit., 1974).

b. yearly fractional increase, R

$$R = e^{\lambda} - 1 \quad [1-8]$$

For example,

$$\% \text{ increase} = (e^{0.0282} - 1)(100) = 2.86\% \text{ per yr}$$

Derivation of R can be accomplished as follows:

$$R = \frac{dQ}{Q dt} \quad [1-9]$$

or

$$R = \frac{Q - Q_0}{Q_0 t} = \frac{Q}{Q_0} - 1$$

since $t = 1$, or

$$\frac{Q}{Q_0} = R + 1$$

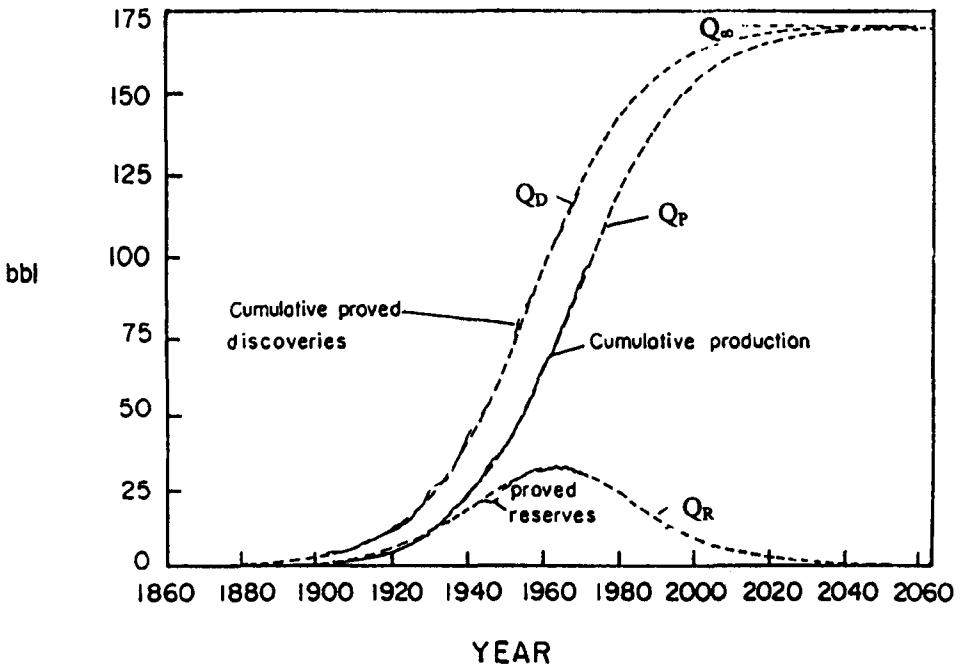


Figure 1-4. Logistic equations and curves of cumulative production, cumulative discoveries, and proven reserves of crude oil from the contiguous United States 1900-1971 (From Hubbert, op. cit., 1974).

$$\ln \frac{Q}{Q_0} = \ln (R+1)$$

since

$$\ln \frac{Q}{Q_0} = \lambda$$

Thus,

$$\ln (R+1) = \lambda \quad [1-10]$$

or

$$e^\lambda = R+1$$

or

$$e^\lambda - 1 = R$$

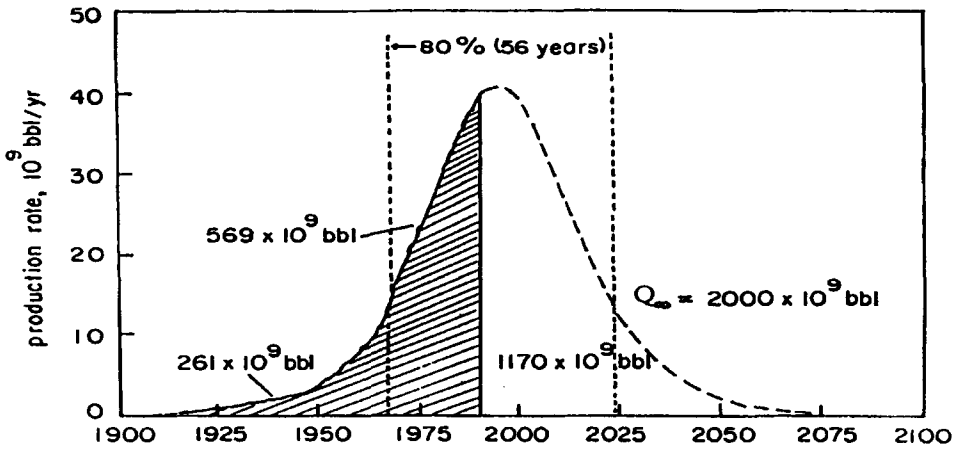


Figure 1-5. Estimate as of 1972 of complete cycle of world crude oil production (From Hubbert, op. cit., 1974).

c. crossover

$$Q_T = 1.85 \times 10^{-21} e^{0.0282T} \quad [1-11]$$

For example, gas consumption has become increasingly rapid in recent years. Gas consumption has the potential to exceed the total energy consumption, and at its current rate it has increased from 6 Q in 1960 to 23 Q in 1980.

Thus,

$$6 = Q_0 e^{1960\lambda}$$

$$23 = Q_0 e^{1980\lambda}$$

Solving,

$$\lambda = .067 \text{ y}^{-1}$$

$$Q_0 = 1.1 \times 10^{-56}$$

Hence,

$$Q_G = 1.1 \times 10^{-56} e^{0.067T}$$

Solving, when $Q_G = Q_T$, $T = 2090$, the crossover will take place.

1.3 FOSSIL ENERGY

The fraction of sunlight (0.1%) used by plants in photosynthesis is converted to chemical energy and stored in the form of carbohydrates such as glucose, sucrose, and starch. The reduced carbon can be reoxidized into carbon dioxide during the process of respiration, providing for the energy needs of biological organisms.

Plants themselves use up about 20% of their carbohydrates for their own energy needs. The remainder, which represents stored photochemical energy, is called the **net primary productivity**.

A small fraction of plant and animal matter, estimated at one part in 10,000, is buried in the earth and removed from contact with atmospheric oxygen. Some of these buried carbon compounds accumulated in deposits and were subjected to high temperatures and pressures in the earth's crust, becoming coal, petroleum, gas, oil shale, and tar sands. These are the **fossil fuels**. In the following sections, we will give some detailed descriptions of each of the fossil fuels.

1.3.1 Petroleum and Gas

Petroleum (rock-oil, derived from Latin "petra," meaning rock or stone, and "oleum", meaning oil) occurs widely in the earth as a gas and a liquid. Gas is a part of petroleum, and petroleum is classified as a mineral according to the U.S. Department of Interior. Chemically, any petroleum is an extremely complex mixture of hydrocarbon compounds, with a minor amount of nitrogen, oxygen, and sulfur impurities. The various fractions can be separated by distillation to determine the overall composition, as shown in Table 1-2. Nearly all petroleum occurs in sediments. These sediments are chiefly of marine origin, and it follows that the contained petroleum is also most likely marine, or related to marine conditions, as shown in Figure 1-6. The process occurs as follows: a small portion of reduced carbon resulting from photosynthesis in the oceans settles to the bottom, where oxidation is negligible. The biological debris is covered by clay and sand particles and forms a compacted organic layer in a porous clay or sandstone. Anaerobic bacteria digest the protein, fat, and carbohydrates, releasing most of the oxygen and nitrogen. As the sediment with the remains, mostly lipid material, becomes buried deeper, the temperature and pressure acting on it rise. Bacterial action decreases, and organic disproportionation reactions are thought to occur through geochemical transformation. Figure 1-8 shows the comparison between reservoir rock and source rock as a function of depth.

There are some other theories regarding the origin of petroleum, such as "inorganic theories," which state that the primary source material for petroleum

generation is inorganic. Theories that uphold the inorganic origin of petroleum have few supporters today. Solid proof of an organic origin came about when a C^{13} mass spectroscopy experiment confirmed that the lipid content of marine microorganisms and that of petroleum have very close values, as shown in Figure 1-7.

The most immediate constraint on energy growth is the availability of petroleum and natural gas. The Industrial Revolution was initially fueled by coal, but oil and gas were increasingly substituted because they were cleaner fuels and were transported more easily. Petroleum and gas now constitute nearly 80% of the total energy consumption in the United States.

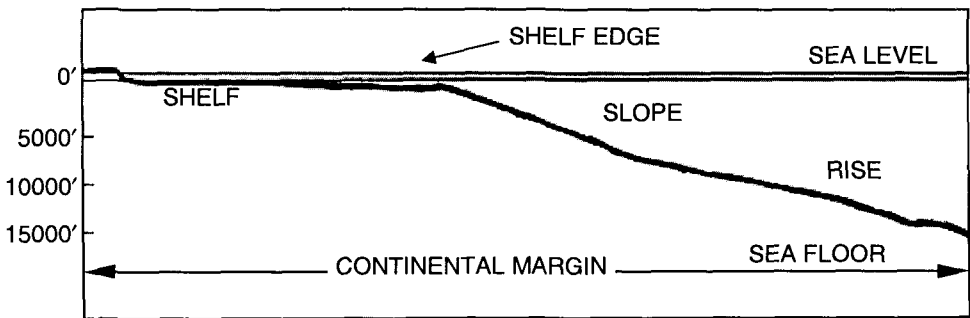


Figure 1-6. Schematics for continental margins. (Source, T. F. Yen, *Chemistry of Marine Sediments*, Ann Arbor Sci.Pub., 1977, p.4)

Table 1-2. Petroleum Components

Components	Distillation Temperature (°C)	Structure
Gas	20	C_p ; $C_1 - C_4$
Petroleum ether	20 - 60	C_p ; $C_2 - C_6$
Ligroin (light naphtha)	60 - 100	C_p ; $C_0 - C_7$
Natural gasoline	40 - 205	C_p , C_N ; $C_6 - C_{10}$
Kerosene	175 - 325	C_p , C_N , C_A ; $C_{12} - C_{18}$
Gas oil	Nonvolatile liquid	C_p , C_N , C_A ; $> C_{18}$
Lubricating oil	Nonvolatile semisolid	C_N , C_A , C_p , X ; $\sim C_{20}$
Asphaltic bitumens	Nonvolatile	C_N , C_A , C_p , X ; $C_{100} - C_{120}$

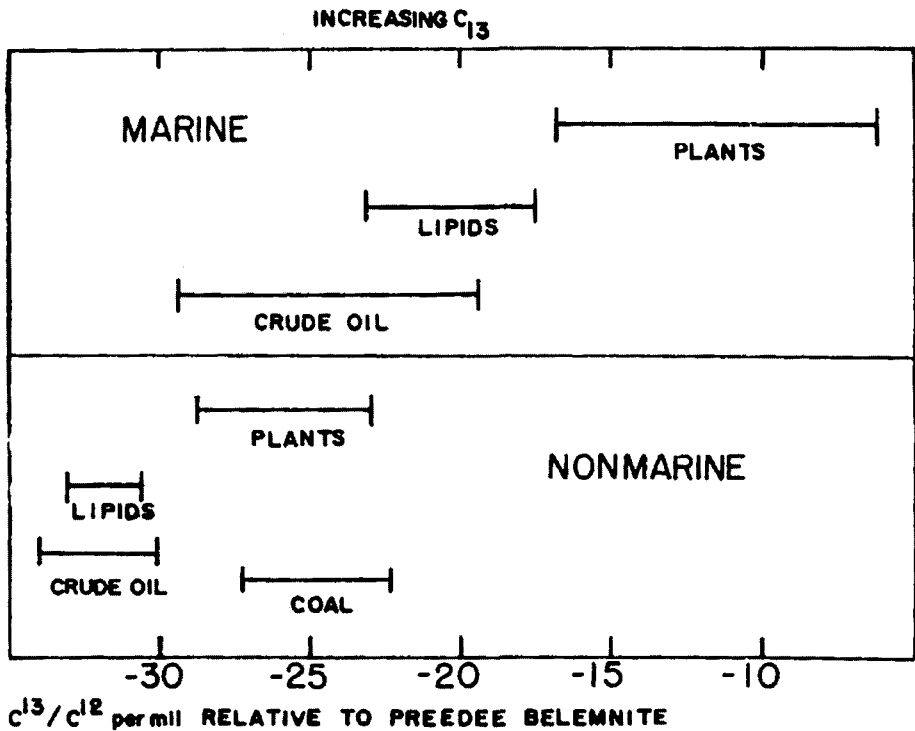


Figure 1-7. Carbon isotope range of natural materials. (Source: S. R. Silverman, 1971)

Estimates of the ultimate amount of recoverable liquid petroleum worldwide range from 10,440 to 21,170 Quads (one Quad is equal to 10^{15} Btu). The world oil production until 1983 was approximately 2,800 Quads. In 1982 alone, the world production was about 110 Quads, which is equivalent to 19 billion barrels. Based on the 1982 rate of oil consumption, in the year 2000 our world's reserves of conventional petroleum would have been exhausted. Fortunately, due to conservation measures, that rate has been reduced.

After production, petroleum is transported via pipeline and can be refined or upgraded into a lighter fraction called **gasoline** by the use of a cracking catalyst. Both production and recovery are termed upstream processes, and similarly, both refining and upgrading are termed downstream processes.

Asphalt (or bitumen), the heavy or involatile fractions of petroleum, virtually controls many parameters of the production as well as refining processes. The asphaltic system is comprised of (a) asphaltenes, the dispersed or micellar phase, (b) resins, the peptizing agent (or surfactant), and (c) gas oil, the dispersed phase or intermicellar medium. These fractions can be separated by sol-

vent cuts with appropriate Hildebrand's solubility parameters, as shown in Table 1-3.

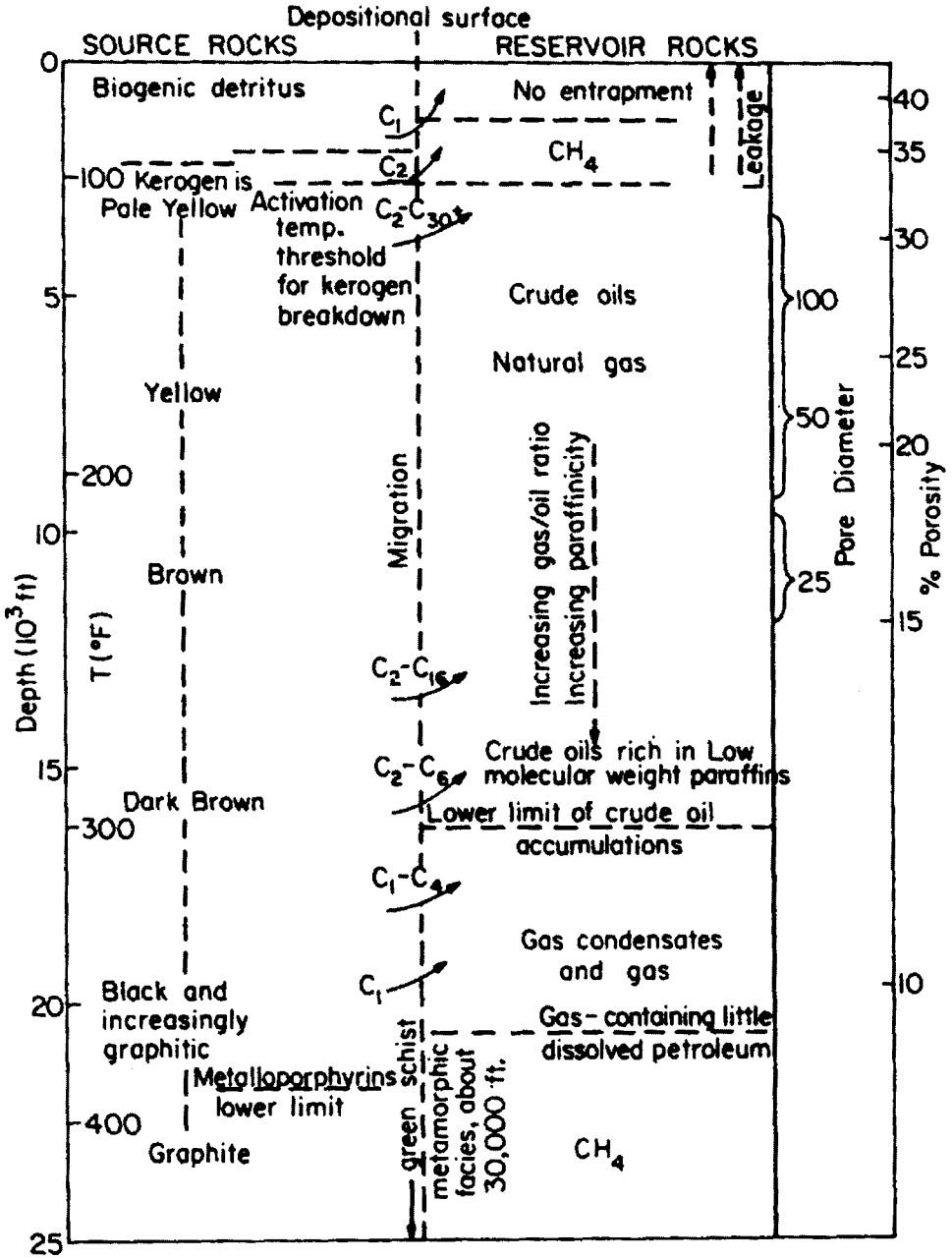


Figure 1-8. Comparison between reservoir and source rock as a function of depth.(Yen, *Energy Sources*, 1973)

Table 1-3. Solvent Fractions of Asphalt and Related Carbonaceous Material

Fraction		Solubility Parameter		
#	Designation	Solubility	δ in hildebrands	Remarks
1	gas oil	propane soluble	below 6	saturated and aromatic hydrocarbons
2	resin	propane insoluble pentane soluble	6 – 7	combined 1 and 2 are also called maltene or petrolene
3	asphaltene	pentane insoluble benzene soluble	7 – 9	ASTM uses CCl ₄ instead of benzene
4	carbene	benzene insoluble CS ₂ soluble	9 – 10	ASTM uses CCl ₄ instead of benzene
5	carboid	CS ₂ insoluble pyridine soluble	10 – 11	combined 4 and 5 are referred to as preasphaltene or asphaltol
6	mesophase	pyridine insoluble	above 11	

Volatile-free basis.

1 hildebrand = $2.04 \text{ J}^{1/2}/\text{cm}^{3/2} = 1 \text{ cal}^{1/2}/\text{cm}^{3/2}$.

Because of the flammability of CS₂, pyridine is preferred; fractions 4 and 5 can be combined.

Source: T. F. Yen in *Encyclopedia of Polymer Science and Engineering*, 1990, Wiley, New York.

1.3.2 Oil Shale

Oil shale is diverse fine-grained rock that contains refractory organic material that can be refined into fuels. The soluble fraction, called **bitumen**, constitutes about 20% of this organic material, whereas the remainder exists as an insoluble fraction, **kerogen**. However, most oil shales do contain inorganic minerals accounting for 20–80% of the bulk. All oil shales appear to have been deposited in shallow lakes, marshes, or seas that support a dense algal biota. The latter is a probable source for shale-bound organic precursors.

In Australia, France, and Scotland, oil shales have been the source of products similar to those obtained from petroleum for many years. In the United States, there are over 700 billion barrels of synthetic crude oil spread over the Green River Formation, located in Colorado, Utah, and Wyoming. The total world potential is estimated to be 30 trillion bbl of shale oil.

A typical composition of Green River oil shale is listed in Table 1-4. Kerogen, which can be viewed as a cross-linked organic polymer, constitutes the bulk (approximately 80%) of the available organic material in oil shale. Kerogen itself is 3,200 times richer in biomass than the total available bitumen and petroleum. The liberation of hydrocarbons depends on the degree to which

kerogen can be degraded into liquid fuel precursors. Because kerogen is the most abundant organic carbon source in the world, it may be a potential food precursor in an age of food shortages, just as single cell proteins have been.

Table 1-5 shows the elemental and ash analyses of a number of raw fuels.

Table 1-4. Composition of a Typical Green River Oil Shale

General scheme of the oil-shale components			
Inorganic matrix		Quartz Feldspars Clays (mainly illite and chlorite) Carbonates (calcite and dolomite) Pyrite and other minerals	
Bitumens (soluble in CS ₂)			
Kerogens (insoluble in CS ₂)			
(containing U, Fe, V, Ni, Mo)			
Average chemical composition of Green River oil shale, as determined by the writers for several samples from Rifle, Colorado.			
FeS ₂	0.86%		
NaAlSi ₂ O ₆ · H ₂ O (analcite)	4.3%		
SiO ₂ (quartz)	8.6%		
KAl ₄ Si ₇ AlO ₂₀ (OH) ₄ (illite)	12.9%		
Montmorillonite			
Muscovite			
KAlSi ₃ O ₈ (K-feldspar)	16.4%		
NaAlSi ₃ O ₈ –CaAl ₂ Si ₂ O ₈ (plagioclase)			
O	22.2%	CaMg(CO ₃) ₂ (dolomite)	
Ca	9.5%	And calcite	43.1%
Mg	5.8%		
C	5.6%		
S, N, O	1.28%	Bitumen	2.76%
H	1.42%		
C	11.1%	Kerogen	11.04%
		Mineral matter	86.2%
		Organic matter	13.8%
			Oil shale

Source: T.F. Yen and G.V. Chilingarian. *Oil Shale*, Elsevier Sci. Pub. Amsterdam, 1976, p.3

Table 1-5. Elementary and Ash Analyses of Raw Fuels.

Sample	C(%)	H(%)	N(%)	S(%)	O(%)	Mineral and ash(%)
Oil Shale (Colorado)	12.4		0.41	0.04		84.6
Oil Shale (Alaska)	53.9		0.30	1.50		34.2
Kerogen (Green River)	65.7	9.1	2.13	3.15	8.9	10.2
Lignite (Kincaid)	63.1	5.0	0.64	<0.04	21.5	9.3
Bituminous (Lower Freeport)	77.0	5.7	1.42	1.72	8.1	6.6
Anthracite (Pennsylvania)	87.1	3.8	0.60	<0.3	2.6	7.0
Gilsonite (Tarbor vein)	84.5	10.0	2.4	0.53	2.6	0.7
Residuum (Mid-continent)	87.7	6.6	0.90	0.75	1.6	1.3
Asphaltene (Baxterville)	84.5	7.4	0.80	5.60	1.7	0.5

1.3.3 Coal

Coal is composed of the remains of plant matter from the huge, thickly wooded swamps that flourished 250 million years ago during a period of mild, moist climate. Woody plants are made of lignin as well as cellulose and protein as shown in Figure 1-9. **Lignin** is a complex, three-dimensional polymer that contains aromatic groups. While aerobic bacteria rapidly oxidize cellulose when a plant dies, lignin is much more resistant to bacterial action. In swamps, lignin accumulates under water, compacting into a substance called **peat**. Over the geological ages, the peat layers of the primeval swamps were metamorphosed into coal. The first stage of coalification (the formation of coal) is termed **lignite**, where the %C value is 55-75 and the heating value in Btu/lb is 6300-8300.

The next stage is **subbituminous**, where both %C and heating values increase. Next is **bituminous**, which can be divided into high volatile and low volatile types. The last stage can reach **anthracite**, which has a %C value of 87-97. The different stages of coal formation and the corresponding properties can be found in Table 1-6. Figure 1-10 shows the structural representations of bitumen, coal, and kerogen.

The recoverable reserves of coal are estimated to be about 7.4×10^{12} metric tons, with the United States and the former Soviet Union owning about 75% of the supply. Coal is substantially more abundant than oil or gas on a world basis. The size of U.S. coal reserves is also substantially larger than those of oil and gas.

Table 1-6. ASTM Classification of Coals by Rank (in box) and Corresponding Bank Rank Parameters not Used in the ASTM Classification

ASTM Class	ASTM Group	Heating Value			Agglomerating	R	
		Btu/lb (moist, mmf)	MJ/kg (moist, mmf)	% VM (d, mmf)		Oil max. (vitrinite)	% Moisture (moist, mmf)
	Peat	3,000 – 4,000 ^a	7.0 – 9.3	No	62 – 72	0.2 – 0.4	50 – 95
Lignite	Lignite B	Undefined – 6,300 ^a	–14.6	No	40 – 65	0.2 – 0.4	45 – 60 ^b
	Lignite A	6,300 – 8,300 ^a	14.6 – 19.3	No	40 – 65	0.2 – 0.4	31 – 50 ^b
Subbituminous	Subbituminous C	8,300 – 9,500 ^a	19.3 – 22.1	No	35 – 55	0.3 – 0.7	25 – 38 ^b
	Subbituminous B	9,500 – 10,500 ^a	22.1 – 24.4	No	35 – 55	0.3 – 0.7	20 – 30 ^b
	Subbituminous A	10,500 – 11,500 ^a	24.4 – 26.7	No	35 – 55	0.3 – 0.7	18 – 25 ^b
Bituminous	High volatile C bit.	10,500 – 13,000 ^a	26.7 – 30.2	Yes	35 – 55	0.4 – 0.7	10 – 25 ^b
	High volatile B bit.	13,000 – 14,000 ^a	30.2 – 32.5	Yes	35 – 50	0.5 – 0.8 ^c	5 – 12 ^b
	High volatile A bit.	> 14,000	> 32.5	Yes	31 – 45	0.6 – 1.2 ^c	1 – 7 ^b
	Med. volatile bit.	> 14,000	> 32.5	Yes	22 – 31 ^b	1.0 – 1.7 ^b	< 1.5
Anthracitic	Low volatile bit.	> 14,000	> 32.5	Yes	14 – 22 ^b	1.5 – 2.0 ^b	< 1.5
	Semianthracite	> 14,000	> 32.5	No	8 – 14 ^b	1.8 – 2.6 ^b	< 1.5
	Anthracite	> 14,000	> 32.5	No	2 – 8 ^b	2.2 – 5.0 ^b	0.5 – 2
	Meta-anthracite	> 14,000	> 32.5	No	< 2	> 4.5 ^b	1 – 3

^a Air dried ^b Well-suited for rank discrimination in range indicated. ^c Moderately well-suited for rank discrimination.

After H.H. Damberger, R.D. Harvey, C.R. Ruch and J. Thomas in *Science and Technology and Coal Utilization*, Plenum Press, 1984.

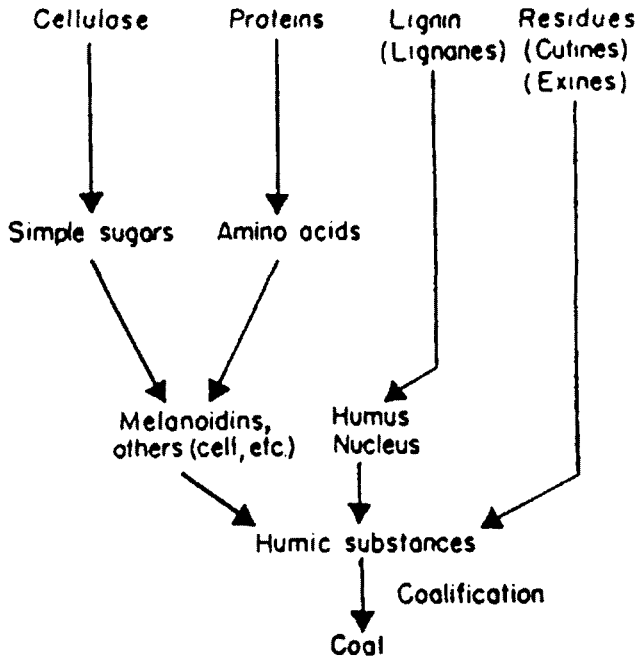


Figure 1-9. Relation of melanoidins to coal as derived from cellulose and protein. [T. F. Yen, ACS Symp. Ser. 18, 231-266 (1975)]

The major concern with coal is that it is a dirty fuel to burn. Of particular concern is the sulfur dioxide emitted, which causes serious health hazards in urban areas. In addition, being a solid, coal is much less convenient to use than petroleum or natural gas. Using the appropriate chemistry, it is possible to convert coal to liquid or gaseous fuels. The reduced carbon in coal, in which most of its energy content resides, can be transformed into hydrocarbon molecules that are either liquid or gaseous, depending on their molecular weight and structures. A simplified diagram for **interfuel conversion** is shown in Figure 1-11.

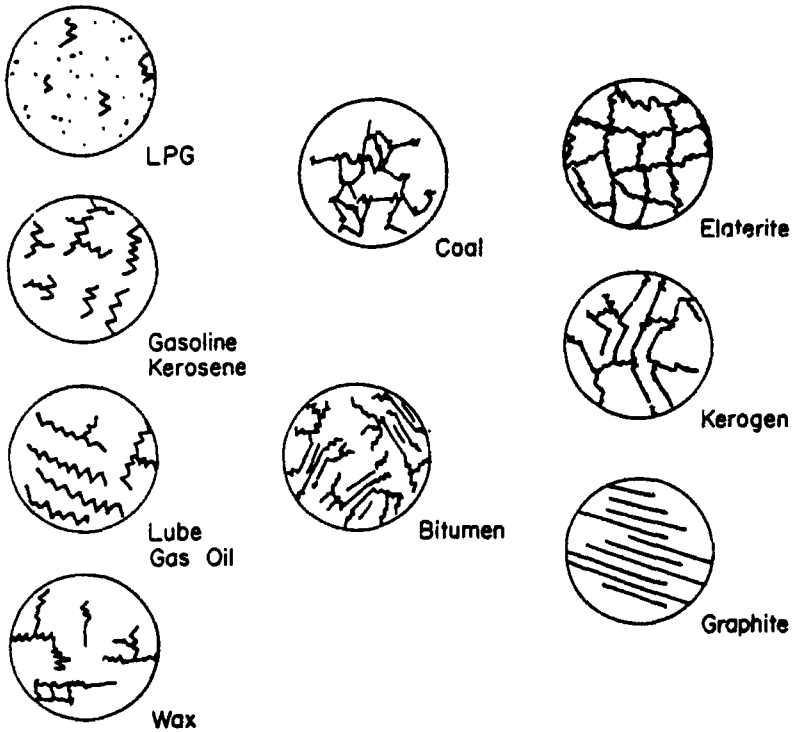


Figure 1-10. Structural representations of bitumen, coal and kerogen, and their relations with LPG (liquified petroleum gas), gasoline, gas oil, and wax. Their interrelations among elaterite and graphite are also indicated. [Source: T. F. Yen, *Chemical Aspects of Interfuel Conversion*, Energy Sources 1(1) 117-136 (1973)]

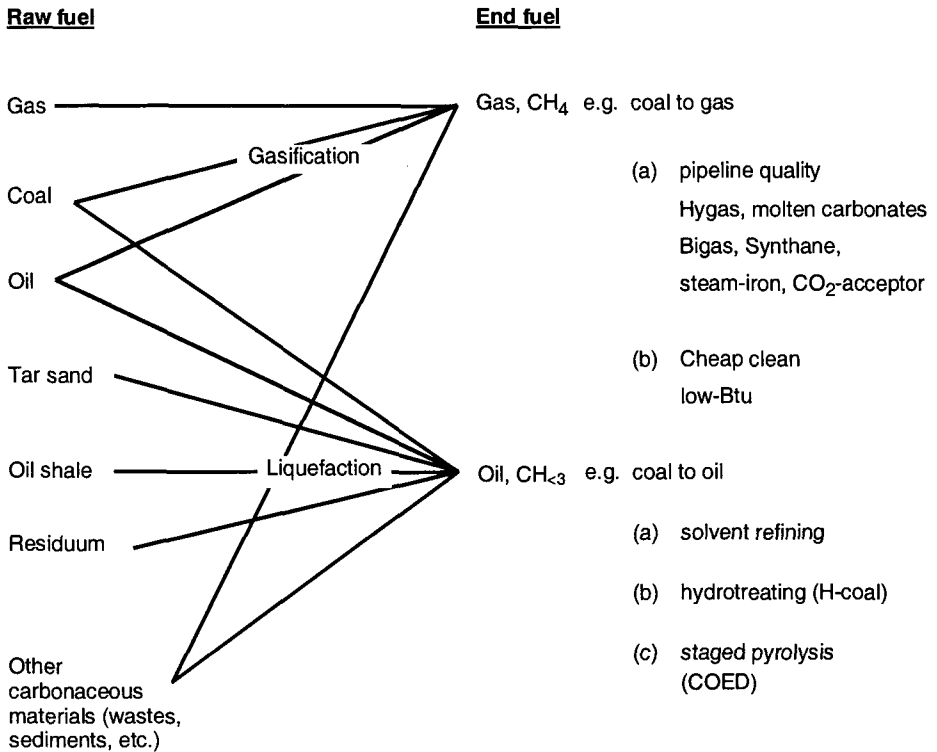


Figure 1-11. Interfuel conversion process

The main problem in converting coal to liquid (coal liquefaction) or gaseous fuel (coal gasification) is finding an efficient way to combine hydrogen with solid carbon, which is a hydrogen-enriched method. The H/C atomic ratio is 4 for methane and about 2 for gasoline, but in coal it ranges from 0.3 to 0.8. Figure 1-12 shows a simplified flow diagram of current coal conversion technologies, including the **Fischer-Tropsch synthesis**. This process represents the indirect conversion of coal in the synthetic fuel program of the United States Department of Energy.

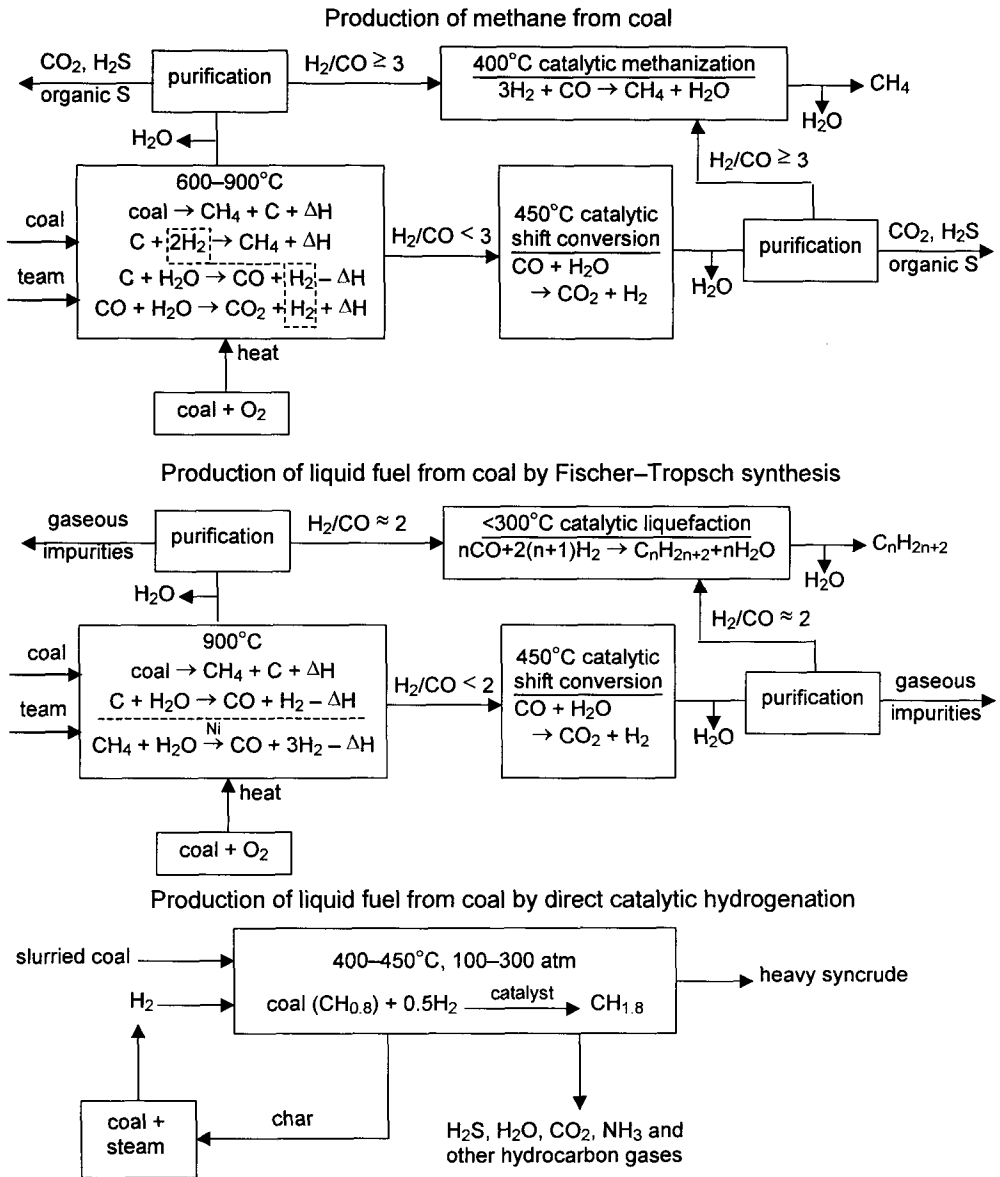


Figure 1-12. Coal conversion technology. (Source: Spiro and Stigliani, 1980)

1.3.4 Tar Sands

Tar sands are petroleum deposits and are distinctive in that their bitumen is so viscous that primary production is impossible. The “sands” refer to rock types including limestone, dolomite conglomerate, and shale in addition to consoli-

dated sandstone and unconsolidated sand. Estimates of reserves range from 2.5 to 6 trillion barrels of oil equivalence. The world's most well-known sand deposit is Athabasca, in Canada. In Alberta, the sands of the McMurray Formation of the lower Cretaceous age contain one billion barrels of oil in place. Next to this in size and recognition is the Orinoco heavy oil belt in eastern Venezuela. The biggest deposits of sand appear to be lodged in deltaic sediments. Mechanisms for turning migrating oil into heavy residue are still under debate, including bacterial degradation and meteoric water washing. Usually, these bitumen will have API gravities ranging from -10 to $+16$ degrees.

$$^{\circ}\text{API} = \frac{141.5}{\text{specific gravity at } 60^{\circ}\text{F}} - 131.5 \quad [1-12]$$

Viscosities range from 10,000 to more than one million centipoise (cp). Therefore, the bitumen cannot readily move through the carrying rock or the associated inorganic materials. The general methods for providing fuel from tar sands in-place are combustion and the injection of hot water or steam. Both methods are based on petroleum **enhanced oil recovery** (EOR) of the tertiary recovery schemes. The in-situ combustion method for tar sand recovery always encounters problems in formation permeability. Currently, commercial production of tar sands includes strip mining of the deposit and extraction with hot water (Suncor and Syncrude). One of the serious environmental problems is the gigantic volume of the tailing ponds containing the oily residues and the abrasive, quartz-like inorganic particulates that currently cannot be disposed of.

1.4 RESOURCES MODELS

Of the available evaluations of our energy and resources on Earth, there have been many attempts to point out that all forms of resources are limited. This will affect the suppliers as well as the users; it also has an impact on government policies. In the following sections, we will discuss four such types of models.

1.4.1 Macroscopic Approach by King Hubbert

The essential feature of this model is based on the record of past discoveries and production history records.

$$Q(\text{resource}) = \int_{t_1}^{t_2} P(\text{Production}) dt \quad [1-13]$$

Initially, there is exponential growth and leveling off (refer to Figs. 1-3 and 1-4).

$$P = P_0 e^{\lambda t}$$

$$Q = \int_0^T e^{\lambda t} dt = \frac{P_0}{\lambda} e^{\lambda t} \Big|_0^T = \frac{P_0}{\lambda} (e^{\lambda T} - 1) \quad [1-14]$$

At the point of leveling off, the maximum production (P_m) is reached, suggesting a bell-shaped curve that can easily be represented by a probability curve.

$$Q_\infty = \int_{-\infty}^{\infty} P dt = \int_{-\infty}^{\infty} P_m \exp \left[-\frac{1}{2} \left(\frac{t - t_m}{\sigma} \right)^2 \right] dt$$

$$Q_\infty = \sqrt{2\pi} \sigma P_m$$

$$P_0 = P_m \exp \left[\frac{1}{2} \left(\frac{t_m}{\sigma} \right)^2 \right]$$

or

$$t_m = \sigma \sqrt{2 \ln \frac{P_m}{P_0}} \quad [1-15]$$

where σ is standard deviation and t_m is the maximum time for production (notice also $t = 0$ for the preceding calculation). According to King Hubbert, energy resource and the proved reserves are equivalent as shown in Figure 1-13. If Q_D is from discovery and Q_P is from production, then $Q_D - Q_P = Q_R$ (resources). The rate of the increase of resources or approved reserves can be simply represented by a differential curve, as shown in Figure 1-14.

$$Q = \int_0^t \left(\frac{dQ}{dt} \right) dt = \text{resource} \quad [1-16]$$

$$\frac{dQ_D}{dt} - \frac{dQ_P}{dt} = \frac{dQ_R}{dt} \quad [1-17]$$

When Q_R is maximum,

$$\frac{dQ_R}{dt} = 0 \quad [1-18]$$

then

$$\frac{dQ_D}{dt} = \frac{dQ_P}{dt} \quad [1-19]$$

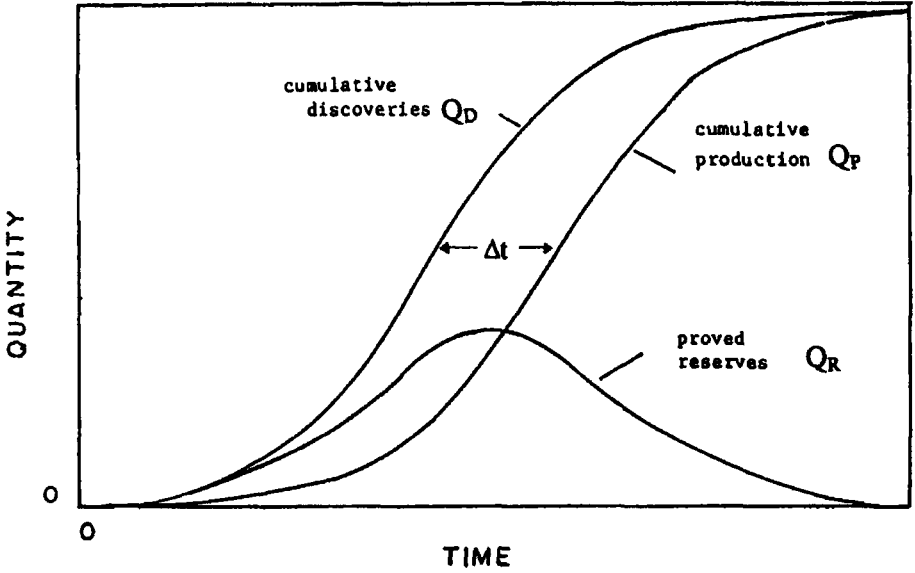


Figure 1-13. Variation of proved reserves Q_R , cumulative production Q_P , and cumulative proved discoveries Q_D , during a complete cycle of petroleum production. (Source: M.K. Hubbert, *Energy Resources: A Report to the Committee on Natural Resources*, Nat. Acad. Sci., Nat. Res. Council. Publ. 1000-D, 1962; and Hubbert, op. cit., 1974)

but

$$Q_D = \frac{Q_\infty}{1 + ae^{-bt}}$$

Q_∞ is ultimate discovery

$$t = 0, \quad Q_D = \frac{Q_\infty}{1 + a}$$

$$t = \infty, \quad Q_D = Q_\infty$$

$$\ln\left(\frac{Q_\infty}{Q_D} - 1\right) = \ln a - bt \tag{1-20}$$

a and b can be evaluated from

$$\ln\left(\frac{Q_\infty}{Q_D} - 1\right) \text{ vs. } t \text{ plot}$$

In this regard, the fossil utilization is finite, only occurring as a short time interval when one considers a ± 5000 year period. The fossil fuel use exploited by mankind is only a blink of time (Figure 1-15). Long-term reserves may come from nuclear fusion or solar power as indicated in Figure 1-16.

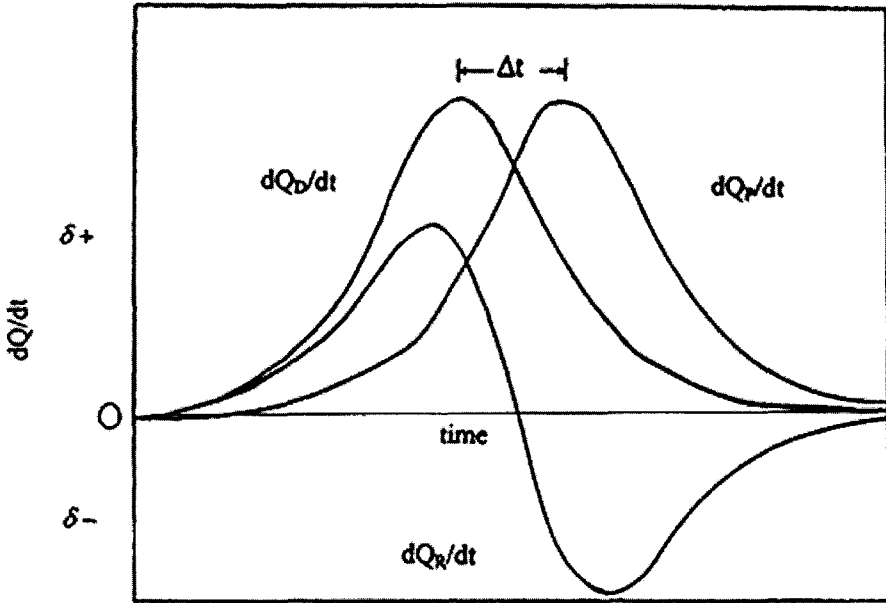


Figure 1-14. Variation of rates of production, of proved discovery, and of rate of increase of proved reserves of crude or natural gas during a complete production cycle. (After Hubbert, op. cit., 1962 and 1974)

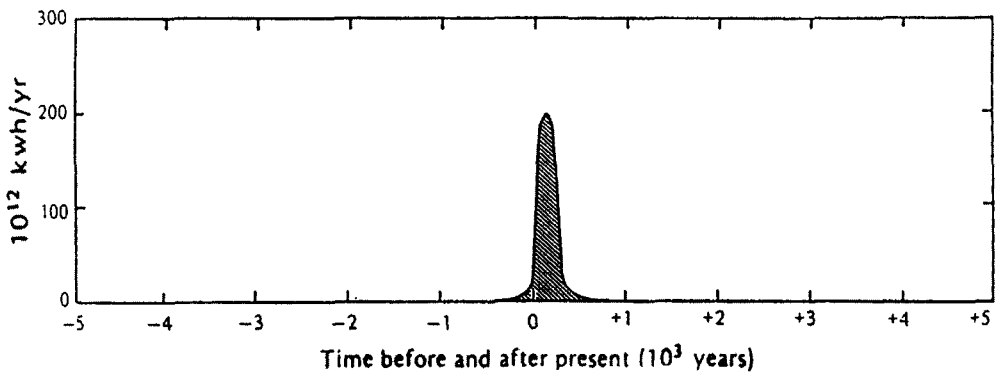


Figure 1-15. Epoch of fossil-fuel exploitation in perspective of human history from 5,000 years in the past to 5,000 years in the future. (Modified from Hubbert, 1962)

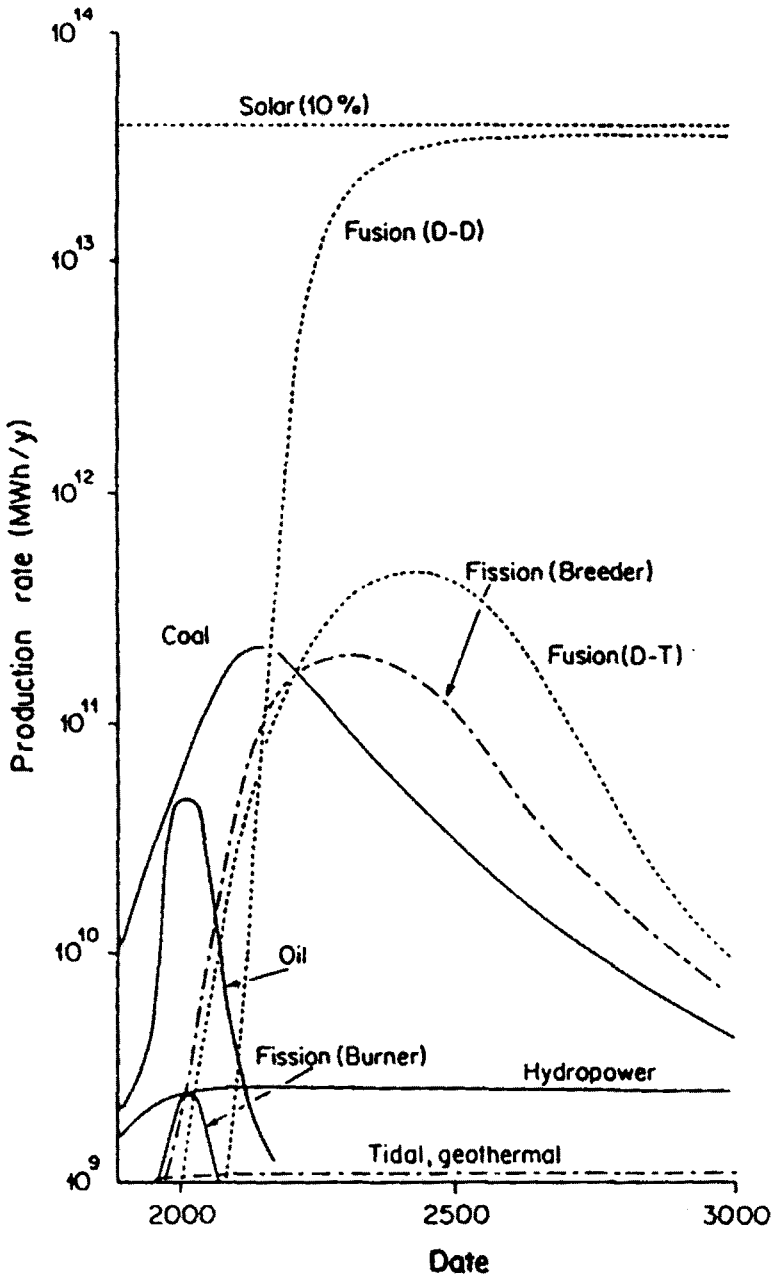


Figure 1-16. Possible fuel consumption levels and projected availability of reserves.

1.4.2 McKelvey's Microanalytical Model

This model is based on cost and geological factors by a stepwise analysis of the deposit domains in a specific region. The analytical methods involve statistical approximations including a regression analysis.

$$L = \frac{REI}{P} \quad [1-21]$$

Here:

L = living standard

R = resource

E = energy

I = ingenuity (socioeconomic, political, and technological)

P = capita

$$\frac{E}{P} = a + b \frac{G}{P} \quad [1-22]$$

G = GNP

$$E_t = \frac{E_m}{g} + E_s \quad [1-23]$$

Here:

E_t = total energy required

E_m = mining energy

E_s = smelting and refining energy

g = grade

Therefore, **resource** depends on an increasing degree of both **geological assurance** (measured, indicated, inferred, hypothetical, speculative, and so on) and **economic feasibility** (submarginal, paramarginal, and so on), as shown in Figure 1-17. For each mineral there is a separate mineralogical barrier and threshold above crustal abundance, as shown here:

<u>Metal</u>	<u>Percentage threshold above crustal abundance</u>
Fe	5
Al	8.13
Cu	0.007

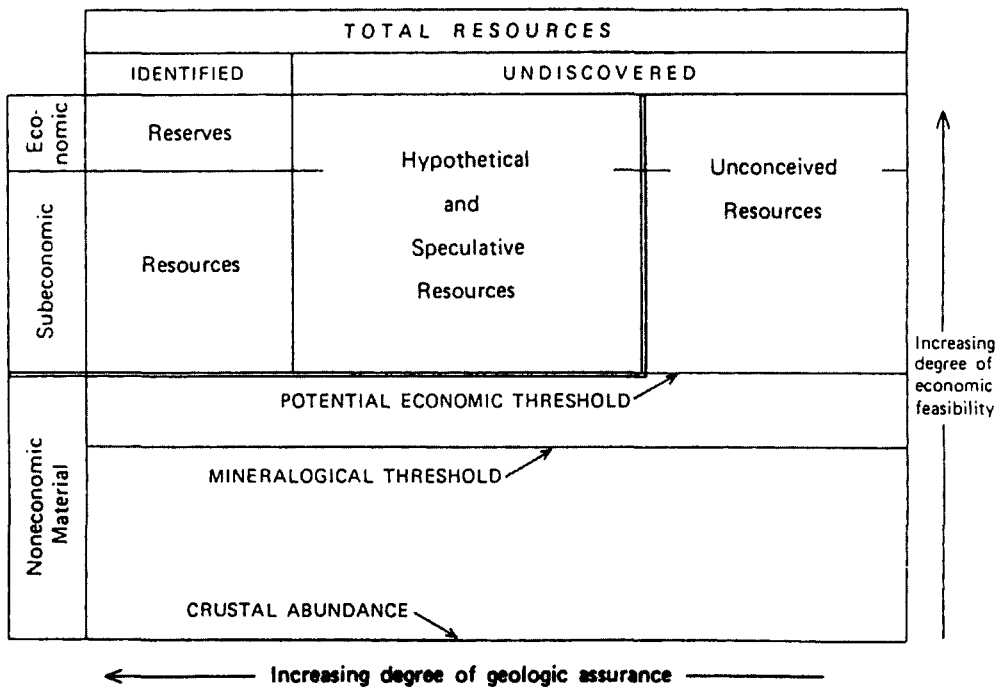


Figure 1-17. The relation of resources to non-economic mineral materials. (Source: Brobst, 1979)

Such a barrier is illustrated by Figure 1-18 for the copper ore. If the ore grade is below 0.007%, it is not economical to recover.

1.4.3 Dynamic Model of Meadows

Dennis Meadows' model concluded that reserves are finite, that usage rate will create substitution technology, and that recycling is minor. He suggested a static reserve life index (s) and an exponential reserve life index (e), where

$$e = \frac{\ln(Rs + 1)}{R} \tag{1-24}$$

where R = annual fractional growth rate.

	<i>s</i> (yr)	<i>e</i> (yr)
Coal	900	110
Fe	400	86
Al	175	60
Ni	140	55
Petroleum	70	35
Cu	40	26
Ag	20	16
Pb	15	12
Hg	13	11

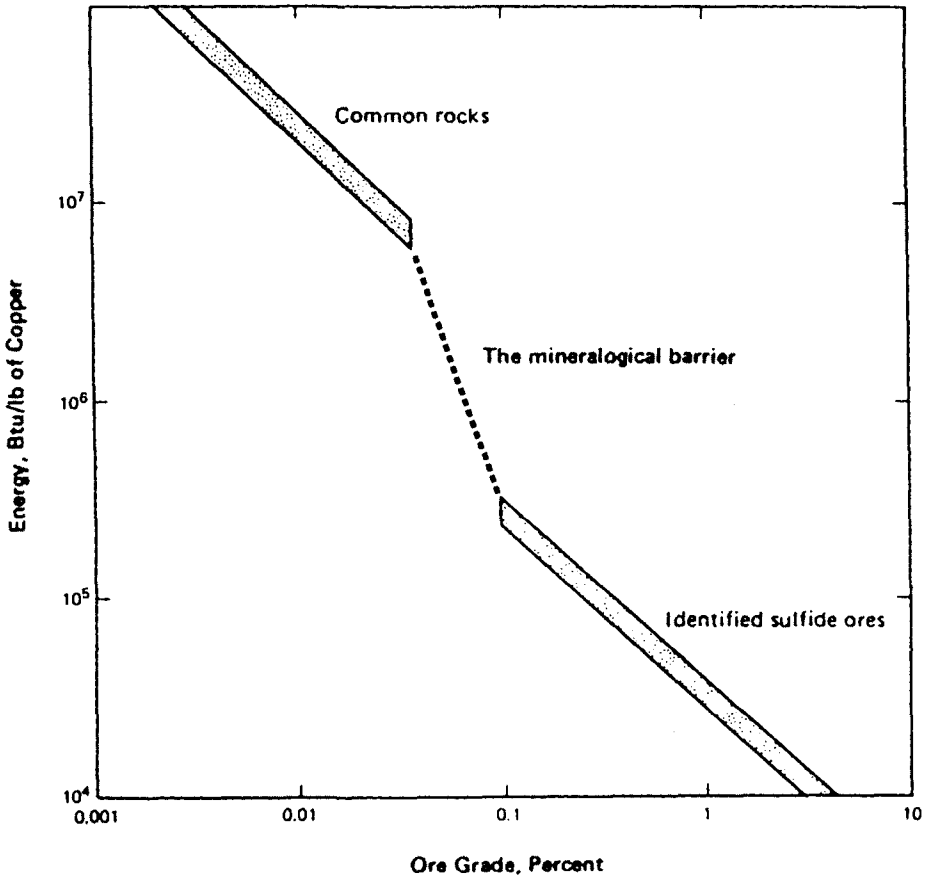


Figure 1-18. The mineralogical barrier.

All resources are limited from 1980 to 2050 as shown in Figure 1-19.

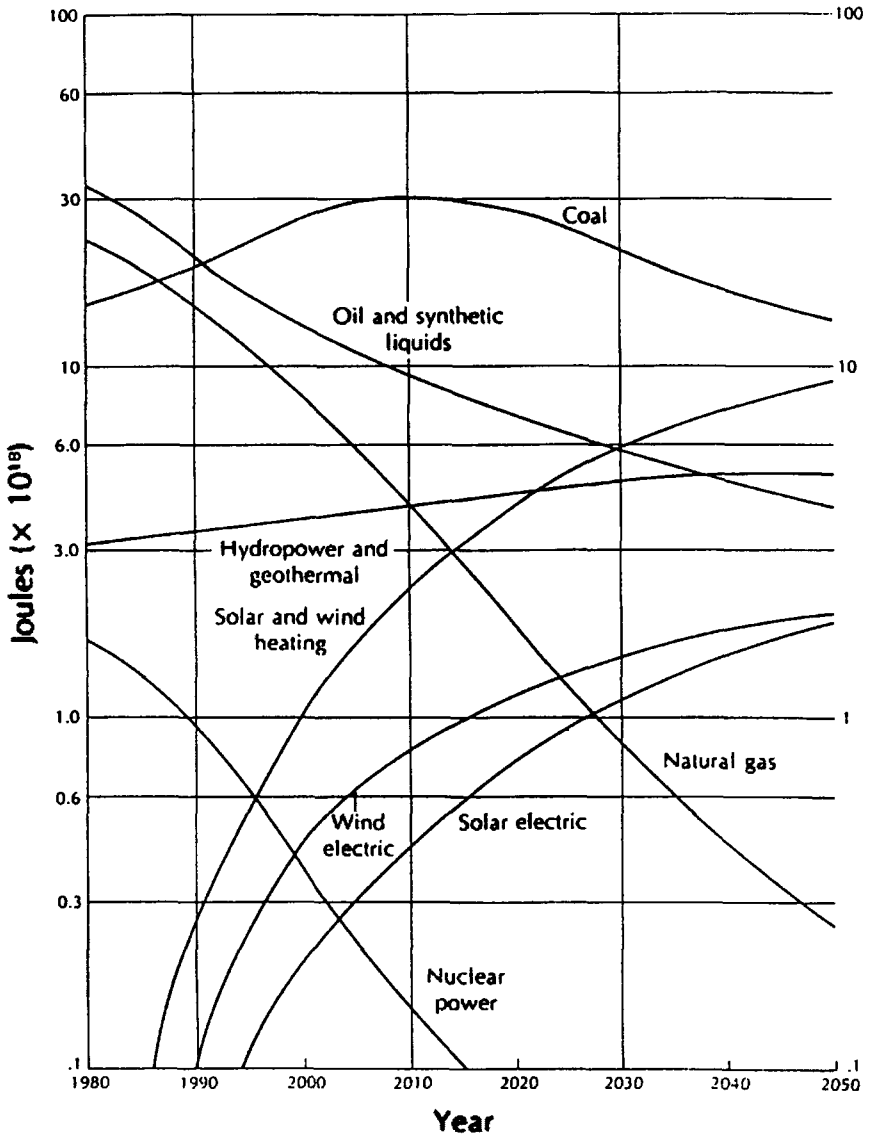


Figure 1-19. Energy supply 1980 - 2050.

1.4.4 Odum Ecological Model

Howard Odum proposed that the energy network is similar to electrical circuitry, as shown in Figure 1-20. All calculations can be performed as they would be in systematic engineering. The essential points are as follows:

- Energy flows in the complex forest ecosystem, which includes all humans, such that

$$n = 1 + \frac{\left(\frac{\log E}{NPP} \right)}{\log \eta} \quad [1-25]$$

where

n = trophic level

E = energy

NPP = net primary production

η = ecological efficiency

- Man's diverse work substitutes ecosystem variety in an agricultural system.
- Fossil fuel subsidized agriculture is a colonial member of technological society with maximum solar conversion.
- Energy is the organizing principle from which all economic, social, and political values are derived.
- Maximum power is in the middle of high rate and low efficiency, and vice versa for all competitors.

Finally, a diagram can illustrate the fossil energy flow in our ecosystem, as shown in Figure 1-21.

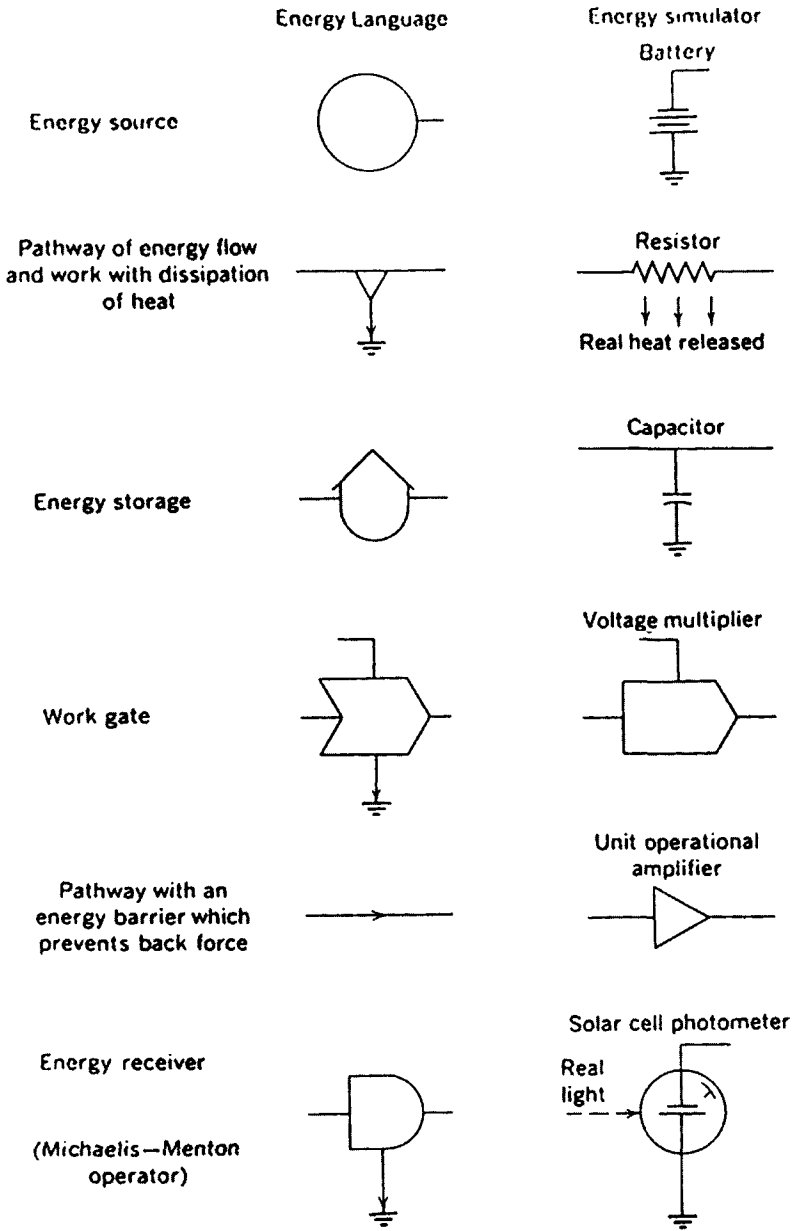


Figure 1-20. Symbols for electric hardware items which are substituted for parts of the energy network diagram in making an energy simulator. (Source: Odum, 1976, Ref. 1-9)

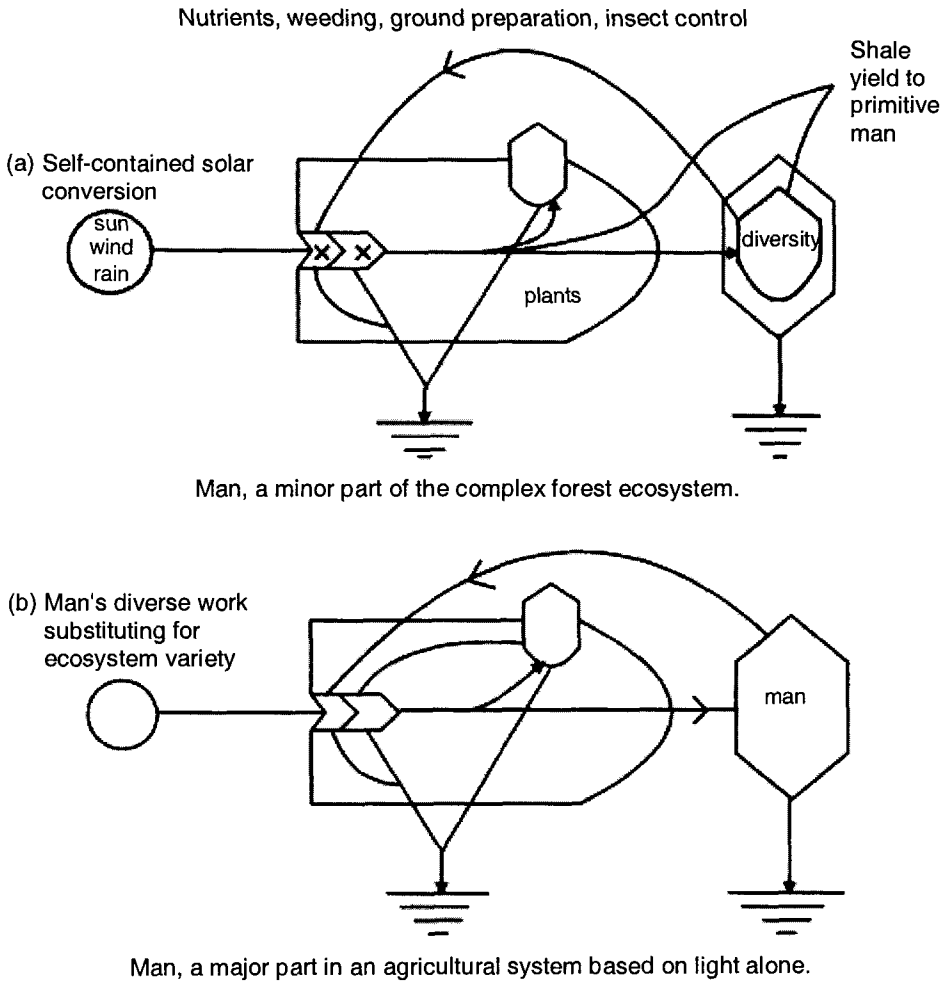


Figure 1-21. Forest ecosystem.

1.5 ENERGY CONSERVATION AND ITS CHEMICAL PERSPECTIVE

Following the 1973 Arab oil embargo, the United States developed technologies based on new and alternative sources. At the same time, social, economic, and political realizations had exerted influence on the public towards a **soft path** on energy policy instead of developing “hard” technology to accelerate the depletion of nonrenewable resources, as seen in the past. As defined by Lovins, the soft path consists of the following alternatives:

- relying heavily on renewable energy sources such as solar, and biomass
- being diverse and tailored for maximum effectiveness under specific circumstances
- being flexible and accessible to most of the public
- being matched in both geographic distribution and scale to prominent end use needs
- having a good agreement between energy quality and end use

In 1991, the Union of Concerned Scientists and other conservation organizations united and issued three other scenarios (soft path) other than the U.S. government analysis, which anticipates a one-time increase of energy consumption by 2030 based on 1988. Even the market driven scenario of a GNP 2.1% annual growth is better. The softest scenario is the climate stabilization scenario, which is designed to achieve a 25% reduction of CO₂ emissions by 2005 and a 50% reduction by 2030. Regardless, since the selection of the soft path, many technologies have been developed for the conservation of energy. They will be discussed in the following sections.

1.5.1 Intra, Inter and Combined Fuel Conversions

Intrafuel conversion signifies that a given raw fuel can produce more than one type of end-use fuel. For example, highly volatile bituminous B coal can be used for liquefaction as well as gasification; thus, it can produce coal gas as well as coal liquid. The optimum yield of either product will depend on the type of raw coal that is fed to a given process. Furthermore, direct conversion or indirect conversion (such as Fischer-Tropsch Synthesis) can be evaluated (refer to Fig. 1-10). **Interfuel conversion** is the use of two or more raw fuels as feedstocks to derive one type of end fuel. Petroleum has been used with coal for a liquefaction process. The use of spent nuclear fuel as a catalyst for petroleum refining is another example. The **combined fuel conversion** is intended for the end use for two or more usages from one type of fuel. A good example is **cogeneration** in which both electricity and space heating can be achieved. Magnetohydrodynamics is another example where coal is thermally decomposed to obtain energy; in the meantime, iodine vapor is conditioned in the magnetic field to increase the current to yield more electricity. The combined cycles for geothermal energy production to increase the efficiency is another example.

1.5.2 Enhanced Oil Recovery (EOR) and Ultimate Oil Recovery (UOR)

When a petroleum oil field is discovered, the natural stored energy (expansion of natural gas or volatile component) assisted by pumping will produce oil. This stage is usually referred to as a **primary recovery**. As the energy is depleted, production declines and water is injected to the reservoir and this is called **secondary recovery**. When the water-to-oil production ratio of the field approaches an economic limit of operation, the net profit diminishes because the difference between the value of the produced oil and the cost of water injection and treatment becomes too narrow. The **enhanced oil recovery (EOR)** or the **tertiary recovery** then begins. The combined total oil production of primary and secondary recovery is generally less than 40% of the original oil in place. The target setting for EOR is an additional 10–15%. In most cases, the oil well is shut down and about 50% of the oil can never be recovered.

Current EOR technology involves the following:

- **surfactant flooding** — reduction of interfacial tension assistance in emulsification
- **polymer flooding** — addition of water-soluble polymers such as polyacrylamide or polysaccharide to increase the viscosity of water for mobility control
- **miscible flooding** — use of CO₂ for oil swelling
- **steam or fire flooding** — thermal recovery to improve sweep efficiency
- **alkaline flooding** — injection of alkali to and from the in situ surfactant with the acid portion of the oil components

For recovery, either one or a combination of the preceding processes is used in the field. A good example is **microbial enhanced oil recovery (MEOR)**, which uses injected bacteria and nutrients for the production of surfactants, polymers, gases, solvents, and biomass simultaneously for recovery. The bacteria also can be used as a selective plugging agent for great heterogeneous distributions of the reservoir rocks in propensity and permeability. **Ultimate oil recovery (UOR)** is the employment of the final physical, chemical, and microbiological techniques for the recovery of the remaining residual oil in the reservoir. This technique has not been developed. At any rate, the EOR process is essential for the duration of the 21st century, as shown in Figure 1-22.

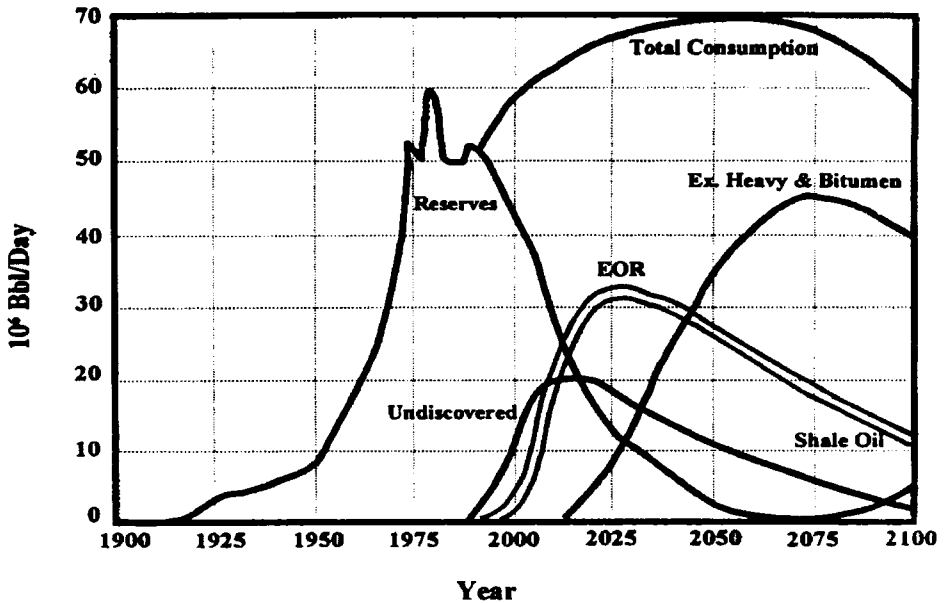


Figure 1-22. World Crude Oil Supply from 1900 to 2100. (Source: from DOE, *Energy Outlook to the Year 2000 an Overview*, 1990, p.3)

1.5.3 Substitution Technology

Because waste can be looked upon as a resource, recycling becomes important. The problem is that based on the constraints of materials, some resources cannot be recycled indefinitely; for example, paper can only be recycled up to four times — unless new technology is invented, such as ink that will fade after a fixed duration so that paper can be reused. The consideration of material is essential to proper recycling. This theory will be illustrated in the following example. In many communities, the use of Styrofoam food containers has been banned because the material is nonbiodegradable. Yet, in a careful study of a styrofoam cup versus a paper cup on a per cup basis, the styrofoam cup has less environmental impact as compared to a paper cup. This is due to the weight of the required raw material (polyfoam vs. paper cup, 1.59g vs. 10.1g). As resources deplete, especially for metals, new technology or substitution should be in place. Figure 1-23 demonstrates that chromium usage requires substitution. Recycling of metals plays an important role because it only requires a small fraction of energy compared to the energy used to extract and manufacture the metals from ores. Typically, the reprocessing of aluminum cans of soft drinks only requires 5% of the energy compared to the processing from aluminum ore. Some metals are higher; for example, steel requires 48%.

Due to the shortage and deprivation of nonrenewable resources, new substitution technology will be initiated. For example, carbon fibers will replace steel. In substitution, model economics becomes important. For example, the market share, F , of the introduction of new technology will rise exponentially in the beginning and reach a saturation lag phase.

$$\frac{dF}{dt} = \alpha F(1-F) = \alpha F - \alpha F^2 \quad [1-26]$$

Upon integration,

$$F(t) = \frac{1}{\{1 + \exp[-(\alpha t + c)]\}} \quad [1-27]$$

α determines the speed of the substitution process, and c is the integration constant. This case is for two competing commodities. From system dynamics, it can also be stated as:

$$\frac{dF}{dt} = \frac{\alpha F(1-F)^2}{[\gamma F + (1-F)]} \quad [1-28]$$

Now γ is time dependent to exogenous restrictions.

1.5.4 Environmentally-Benign Processing (Green Process)

In the 90s, energy efficiency is applicable to most industrial processes. For example, automobile energy intensities in the United States (mJ per vehicle per km) and fuel economy (L/100 km) have improved from 1970 to 1990. Improvement will be made by cutting the loss of efficiency due to aerodynamic drag and breaking. An effort will also be made to reduce the weight by (possibly) using carbon fiber composites (see Figure 1-24 for the “greener” vehicles). Research and development are centered on novel process designs and process improvement that would reduce the potential for environmental release. Also, for fossil fuel production, feedstock substitutions, and alternative synthetic and separation procedures with efficient catalysts, a new process that would minimize by-products formation and reduce waste at the source will be developed. Some areas are under consideration.

- more highly selective catalysts
- low temperature and pressure operations
- low-energy separation techniques
- synthesis that bypass toxic feedstock and solvents
- substitution of halogenated solvents

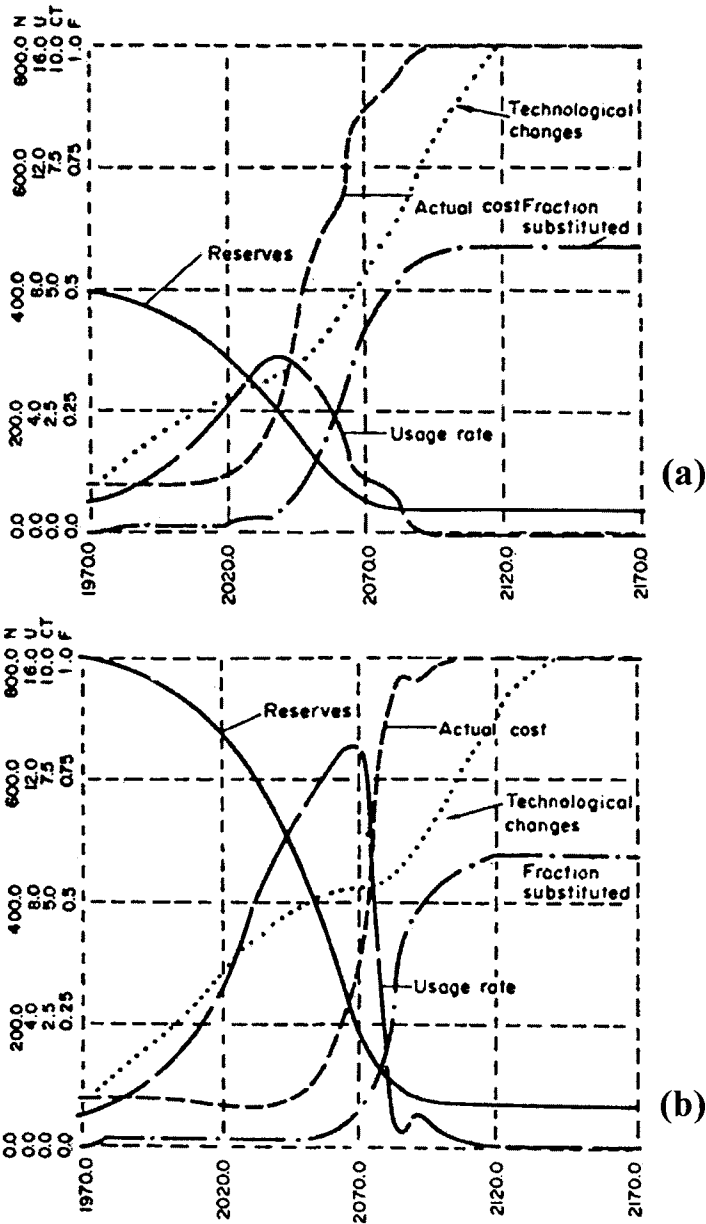


Figure 1-23. Chromium usage patterns (a) with 1970 reserve (b) double the reserve U (usage), N (reserves), C (cost), T (technology), F (fraction substituted). (After Meadows et al., Ref. 1-6)

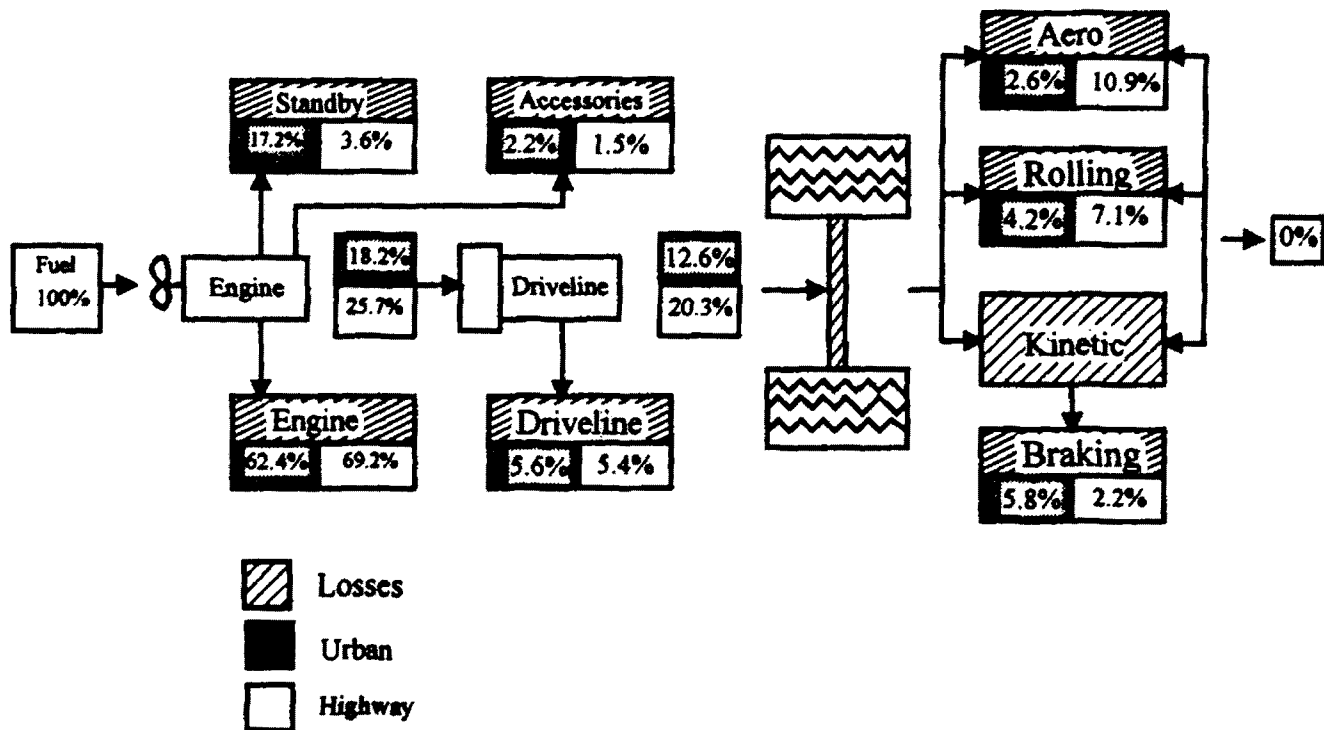


Figure 1-24. Energy losses in automobile transport point to strategies for improving fuel efficiencies in automobiles. (Source: D.L. Illman (1994). Auto-makers move toward new generation of "greener" vehicles. *Chemical and Engineering News* 72(31): 8-16. Copyright 1994 by American Chemical Society. Reprinted with permission)

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PROBLEM SET

1. Our energy consumption can be described as follows:

$$Q = Q_0 \exp(\lambda T)$$

Where $\lambda = 0.035$ per year.

- a) Define and calculate the doubling time T_2
b) Also calculate the yearly fractional increase R
2. a) Calculate the API gravity of water
b) If an oil has -3° API, what is the specific gravity at 60° F
3. Calculate the following for the daily output of the Hoover Dam
a) Power in Joules/sec
b) Energy in Joules

(Given power of Hoover Dam = 4.3×10^9 KW)