Chapter 4: Energy from Combustion

The primary means of generating energy for human endeavors is the combustion of fuels.

Fuels:
Coal - burned in power plants
Gasoline - burned in automobiles
Natural gas - heating
Heating oil – heating
.
Propane, charcoal, wood, candles, …

Combustion (burning in air) releases the *chemical energy stored in the chemical bonds* of the fuels.

The rate of use/consumption of fuels is unsustainable.

The fossil fuels supply is not infinite.

Fossil fuels took millions of years to produce and are nonrenewable.

The products from the burning of fuels adversely affect the environment.

Coal
$\Rightarrow$soot, CO, Hg, SO_x, NO_x
$\Uparrow$
$\Downarrow$
global warming, acid rain, poor air and water quality.

Laws governing energy transformation from fuels.

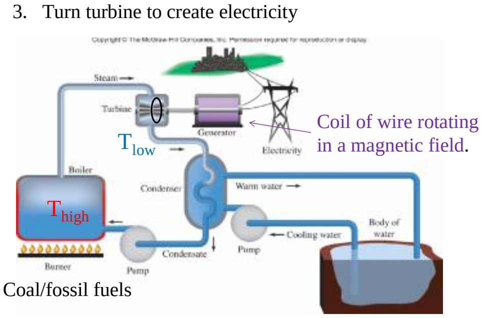
Practical limitation of converting ‘all’ energy in a fuels to usable energy.

Energy ‘content’ of different fuels (made up of different chemical compounds).

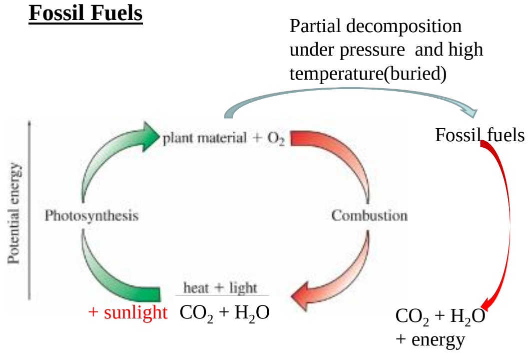
Recent attempts at using ‘Biofuels’.

Coal (70% in US) generates electricity in power plants:

1. Combustion of coal produces heat
2. Use heat to boil water in a closed, *high pressure system*
3. Turn turbine to create electricity



Fossil Fuels



The potential energy stored in fossil fuels are the sun's energy captured, millions of years ago by plants.

Definitions:

Energy is the capacity to do work.

Work is movement against a force (w = f × d).

Heat is energy that flows from a hotter to a colder object.

Heat is a consequence of motion at the molecular level; **temperature** is a measure of the average speed of that motion.

Temperature determines the direction of heat flow.

First Law of Thermodynamics

Potential/Kinetic energy

First Law: The energy of the universe is constant,

or, energy can neither be created nor destroyed; but it can be converted from *one form to another*.

Potential energy (PE) is energy due to position and/or composition of matter.

Fuels with higher PE are better fuels.

Kinetic energy (KE) is energy due to movement of matter. = ½ mv^2

Potential energy (chemical bonds - fuel)

↓ Burner - heat

Kinetic energy (steam)

↓ gas turbine

Mechanical energy Turbine

↓ generator

Electrical energy

The First Law of Thermodynamics
Energy is neither created nor destroyed, but may be transformed from one form to another.

Taking random, thermal energy and transforming it into ordered work goes against the Second Law of Thermodynamics.

The Second Law of Thermodynamics
The entropy of the universe is increasing.

Power plants are inevitably inefficient.

Power Plant Efficiency:

No electric power plant can completely convert one type of energy into another. Efficiency is always <100%
Some of the energy is transferred into unusable heat.

$$\%\text{Net efficiency} = \frac{\text{electrical energy produced}}{\text{heat from fuel}} \times 100$$

$$\%\text{Net efficiency} = \frac{T_{high} - T_{low}}{T_{high}} \times 100$$

The higher the temperature of the steam, the more efficient the power plant but other issues such as ability to withstand high temperatures and pressures arise.

The Second Law of Thermodynamics

The entropy of the universe is increasing.

Unusable heat dissipates to the environment. The molecules in the environment picks up the heat, their kinetic energy rises.

Such molecules move faster and disperses the energy gained and that energy can never be recaptured.

Such energy raises the degree of random movement of molecules – termed Entropy. Overall the entropy of the universe increases

***Units* of heat**

The joule (J): 1 J is the amount of energy required to raise a 1-kg object 10 cm against the force of gravity.

The calorie (cal): 1 cal is the amount of heat required to raise the temperature of 1 g of water by 1 ^{o}C.

1 calorie = 4.184 J
1 kcal = 1000 cal = 1 Cal (1 dietary cal)

So that 450 Cal doughnut is really 450,000 calories!

4.2

Raw Materials for Energy: Coal

- Coal is a complex *mixture* of substances.
- Better energy source (low %O, high %C) and exists in many grades.
- 92% coal in US – power industry
- Although not a single compound, coal can be *approximated by the chemical formula* $C_{135}H_{96}O_9NS$. Some S, Si, Na, Ca, Al, Ni, Cu, Zn, As, Pb, Hg.

4.3

Not all coal is created equal!

Table 4.1 Energy Content of U.S. Coals

Type of Coal	State of Origin	Energy Content (kJ/g)
anthracite	Pennsylvania	30.5
bituminous	Marylan	0.7
sub-bituminous	Washingto	4.0
lignite (brown coal)	North Dakot	6.2
peat	Mississipp	3.0
wood	variou	0.4–14.1

Anthracite - Nearly exhausted.

4.3

Drawbacks of Coal:

1. Mining – underground, dangerous and expensive; respiratory diseases.

2. Ground water flooding of abandoned mines in contact with S rich coal generates acids. Acids dissolves Fe and Al, - fish habitat and drinking water adversely affected.

3. Mines closer to surface – mountaintop mining – massive rubble – overburden – dumped into rivers and valleys –and eco systems and drinking water adversely affected.

Drawbacks of Coal:

4. "Dirty fuel". Soot – buildings and lungs; NO_x, SO_x. Hg gets concentrated in flyash – PM in atmosphere. Bottom ash – storage problems!!

5. CO_2 more per kJ vs. petroleum or natural gas. 40% global emissions of CO_2.

"Clean Coal"

A collection of methods to increase efficiency of coal fired power plants while decreasing harmful emissions. Selected plants.

- Coal washing, to remove S and minerals before combustion.
- Gasification. Coal + $H_2O \Rightarrow CO + H_2$ (water gas; burns at lower T, no NO_x)
- Wet scrubbing. Remove SO_2 (with limestone + water)

Does not address emission of greenhouse gases. (Carbon capture and storage).

Coal, to be made more usable as a fuel needs a change of phase to gas or liquid state.

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$
(water gas, both components are fuels)

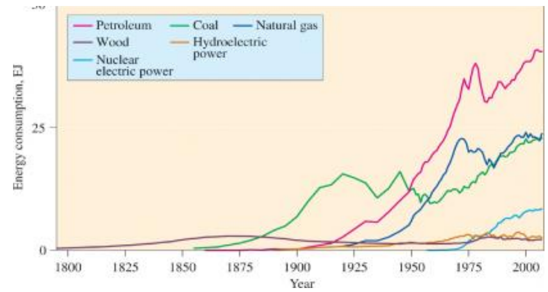
Liquefaction/Gasification of coal: Fisher-Tropsch Process

$$n\,CO(g) + (2n+1)\,H_2(g) \xrightarrow{\text{Catalyst (Fe/Co)}} C_nH_{2n+2}(g, l) + nH_2O(g)$$

n=1, methane, n=2,3 (g)
n= 5-8, gasoline components(l)

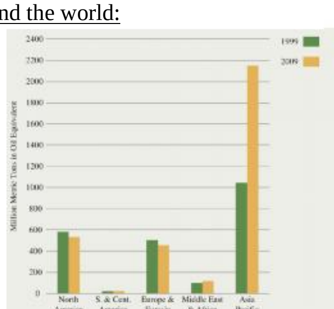
In the end coal still produces CO_2 ! Also the production and use produces more CO_2 than petroleum.

History of U.S. Energy Consumption by Source 1800–2008



1 EJ = 10^{18} J

Coal use around the world:



Green = 1999
Gold = 2009

The unit is million metric tons oil equivalent, the approximate energy released in burning a million metric tons of oil.

Distillation Tower:

Crude – mixture of thousands of compounds.

Petroleum must be refined before use.

48kJ/g vs. 30kJ/g (high grade coal.

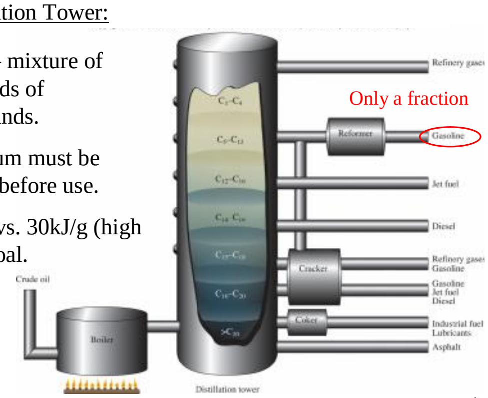


Table 04.02

Alkanes; C-C and C-H bonds only.

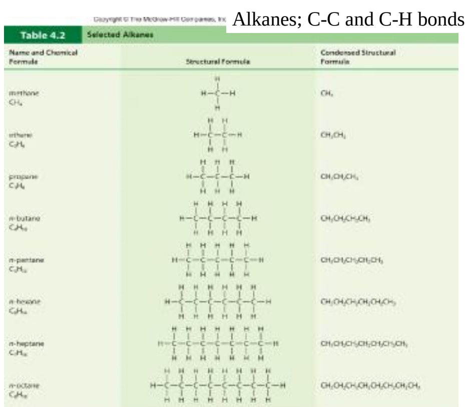
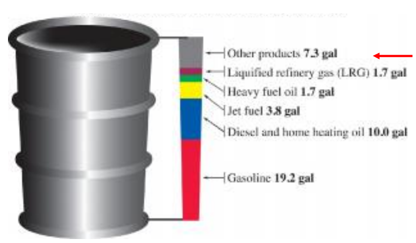


Table 4.2 Selected Alkanes

Name and Chemical Formula	Structural Formula	Condensed Structural Formula
methane CH_4		CH_4
ethane C_2H_6		CH_3CH_3
propane C_3H_8		$CH_3CH_2CH_3$
n-butane C_4H_{10}		$CH_3CH_2CH_2CH_3$
n-pentane C_5H_{12}		$CH_3CH_2CH_2CH_2CH_3$
n-hexane C_6H_{14}		$CH_3CH_2CH_2CH_2CH_2CH_3$
n-heptane C_7H_{16}		$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$
n-octane C_8H_{18}		$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

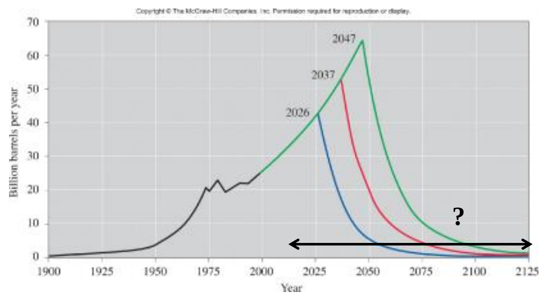
How do we use each barrel (42 gal) of petroleum?



This 7.3 gal includes nonrenewable feedstocks for all plastics, pharmaceuticals, fabrics and other carbon-based products.

Over 87% of each barrel is used for transportation and heating.

Peak Oil (Recoverable) Scenarios:



Assumption 2% increase per year of consumption.

Natural Gas:

Raw: Methane, 2-6% ethane, small hydrocarbons, water vapor, CO_2 H_2S and He.

Used in homes, electricity production, vehicles.

Cleaner burning ('S' removed at refinery, unburned material low. No ash.

Produces CO_2 and lesser energy per unit mass.

Measurements involving energy

The absolute (potential) energy of any reactants and products (fuel or oxidant) cannot be measured.

Only the difference in (potential) energy of reactants and products can be measured.

The energy from a reaction is the difference in potential energy between product and reactants, after all.

The potential energy of reactants and products are stored in their chemical bonds.

The reactions of importance are combustion reactions.

Heat of Combustion - definition and measurement

Definition: The heat given off when a specified amount (1 mole) of a substance (reactant) burns in oxygen gas.

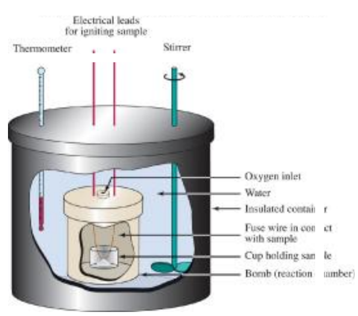
e.g.

CH_4 (g) + 2 O_2 (g) $\longrightarrow$ CO_2 (g) + $2H_2O$ (l) + Energy

Bomb calorimeters can be used to determine the heat of combustion.

Bomb calorimeters

If you test a reaction that releases heat, the temperature of the water will increase.



$$\text{mass fuel} = m(g)$$

$$\text{Heat capacity of calorimeter} = C_{cal}(kJ/^oC)$$

$$\text{Temperature rise} = \Delta T(^oC)$$

$$\text{energy per gram} = \frac{C_{cal}(kJ/^oC) \times \Delta T(^oC)}{m(g)}$$

Hydrocarbon fuels like methane (CH_4) burn in the presence of oxygen to produce carbon dioxide and water. This process of **combustion releases energy.**

CH_4 (g) + 2 O_2 (g) ⟶ CO_2 (g) + $2H_2O$ (l) +ENERGY

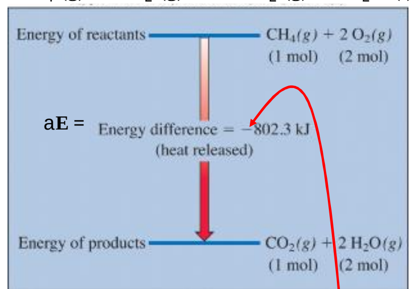
When <u>energy is released</u> during the course of a chemical reaction, it is said to be an <u>*EXOTHERMIC*</u> <u>*reaction*</u>.

The combustion of of methane gas releases 50.1 kJ/g. This is the equivalent of 802.3 kJ/mol CH_4.

50.1 kJ/~~g~~ × (12.01 + 4× 1.00)~~g~~/mol = 802.3 kJ/mol

<u>Energy Diagram</u>

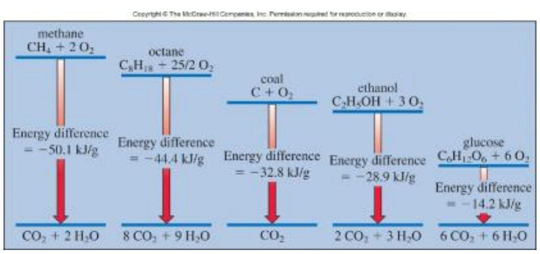
CH_4 (g) + 2 O_2 (g) ⟶ CO_2 (g) + $2H_2O$ (l) + ΔE



Exothermic reaction

The products are lower in energy than the reactants.
Exothermic reaction: **aE** is a negative value.

<u>Are all fuels are not created equal</u>



<u>Endothermic</u> reactions will have products higher in energy, (ΔE *will be positive*) than the reactants; there will still be a required activation energy.

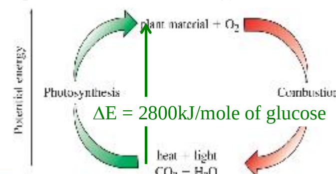
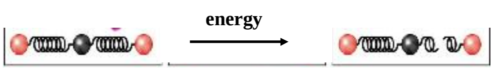


Table 4.3 Endothermic Versus Exothermic Reactions	
Endothermic Reaction	**Exothermic Reaction**
$Energy_{products} > Energy_{reactants}$	$Energy_{products} < Energy_{reactants}$
Net energy change is positive.	Net energy change is negative.
Energy is absorbed.	Energy is released.

<u>Energy Changes at the Molecular Level</u>

The energy changes are due to the rearrangement of the atoms during reaction. The energies involved in breaking and forming of bonds dictates if a reaction will be endothermic or exothermic.

<u>**Bond**</u> <u>**energy**</u> is the amount of energy that must be absorbed to break a chemical bond.



<u>Breaking</u> bonds demands/requires energy!
<u>Forming</u> bonds releases energy!

Table 4.4 Covalent Bond Energies (in kJ/mol)

(for gas phase reactions)
(Average values)

	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	
C≡C	813			C≡N	866		C≡O	1073	
N=N	418			O=O	498				
N≡N	946								

<u>Breaking</u> bonds demands/requires energy!

overall it is H, Bond Breaking Energies

<u>Forming</u> bonds releases energy!

overall it is J, Bond Forming Energies

Net energy change for the reaction

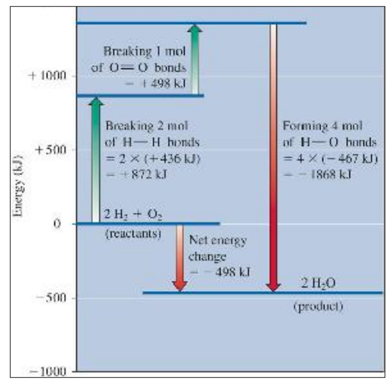
= **Bond Breaking Energies + Bond Forming Energies**

Consider: $2\ H_2 + O_2 \longrightarrow 2\ H_2O$

<u>Bonds breaking</u>	<u>Bonds forming</u>
2 H–H + O=O	4 O–H i.e. (2 H–O–H)

2×(+436) + (+498) + 4×(– 467) kJ = - 498 kJ

Consider: $2\ H_2 + O_2 \longrightarrow 2\ H_2O$



<u>Bonds breaking</u>

2 H–H + O=O

<u>Bonds forming</u>

4 O–H

(2 H–O–H)

4.6

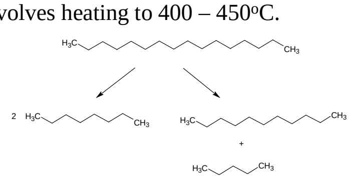
<u>Gasoline</u>

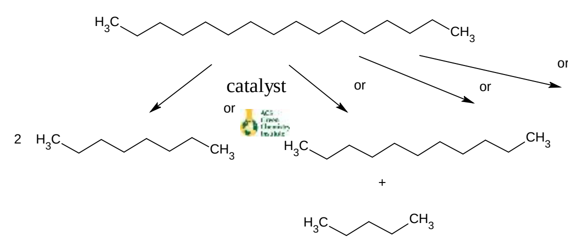
Only a fraction of distilled crude oil is gasoline jet fuel and diesel. Higher boiling fractions are in less demand.

Thermal Cracking:

Conversion of high (mol.wt.) boiling compounds to low (mol.wt.) boiling ones.

Process involves heating to 400 – 450^{o}C.

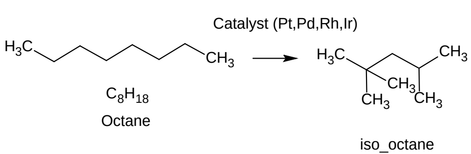




Catalytic Cracking: lower temperatures employed, thus less energy used. Can break into different fragments (selective breaking of bonds) with different catalysts.

Catalytic Reforming

Linear molecules changed to branched molecules by rearrangement reaction, aided by catalysts.



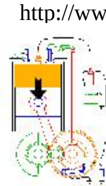
Isomers, same molecular formula but different compounds.

Branched hydrocarbons burn smoothly.

Car Engine

Movement of the piston is primary in the movement of cars.

Watch video at:
http://www.animatedengines.com/otto.html



Premature ignition can occur before the spark, lower efficiency, high fuel consumption.

After spark violent uncontrolled reaction, **Knocking**, can occur leading to loss of power, overheating engine damage.

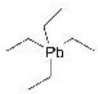
Knocking depend on the composition of fuel.

Octane – superior performance, no knocking at all.

Octane rating: Fuel rating basis – isooctane assigned a octane rating of 100. n-heptane assigned octane rating of 0

Octane rating of 90% *means* the fuel blend ***behaves*** as a mixture of 90% isooctane and 10% n-heptane.

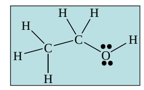
An early additive used as an anti-knocking agent was Tetraethyl lead.



Gasoline Additives

Elimination of octane enhancing tetraethyl lead (TEL) created a need to find substitutes.

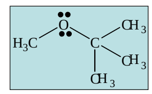
Ethanol (ethyl alcohol)



"Oxygenated gasolines"

O makes cleaner burning (less CO)

MTBE, methyl tertiary-butyl ether



MTBE
Problematic; toxicity and leaches into ground water

4.7

Reformulated gasoline RFG (Clean Air Act Amendment 1990) – for regions with high ground level O_3.

Oxygenated gasoline with a lower percentage of more volatile hydrocarbons (<1% benzene and at least 2% O), less evaporation and produces less CO.

Coal, to be made more usable as a fuel needs a change of phase to gas or liquid state.

$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$
(water gas, both components are fuels)

Liquefaction/Gasification of coal: Fisher-Tropsch Process

$$n\,CO(g) + (2n+1)\,H_2(g) \xrightarrow{\text{Catalyst (Fe/Co)}} C_nH_{2n+2}\,(g, l) + nH_2O(g)$$

n=1, methane, n=2,3 (g)
n= 5-8, gasoline components(l)

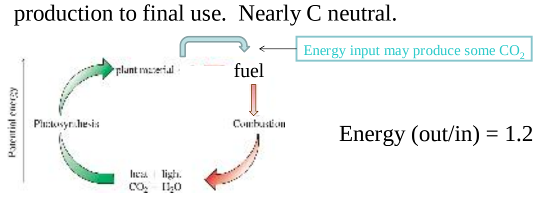
In the end coal still produces CO_2 ! Also the production and use produces more CO_2 than petroleum.

Biofuels

Ethanol, Biodiesel, Garbage, Biogas

Renewable fuels derived from biological materials; plant matter. (grasses, trees crops and other biological material).
A more sustainable energy future?

Less net CO_2 release from raw material through the production to final use. Nearly C neutral.



Energy (out/in) = 1.2

Ethanol (from corn)

Grains + water → Starch → Glucose → Ethanol

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2\,C_2H_5OH + 2CO_2 \quad \text{(in water)}$$

Distill off

Ethanol however produces less energy per unit mass. 29.7kJ/g (ethanol) vs. 47.8 kJ/g (octane). Nearly C neutral.

Sustainability? READ: Sections 4.9 and 4.10

Ethanol (Cellulosic)

From corn stalks, switch grass, wood chips – non edible materials.

Potential – 60 billion gallons/year in US.

Biodiesel

Vegetable oils and animal fats (triglycerides) – raw material

$$\text{triglyceride} + 3\,CH_3OH \longrightarrow \underbrace{3\,CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CO_2CH_3}_{\text{Biodiesel}} + \underbrace{C_3H_8O}_{\textit{glycerol}}$$

Energy (out/in) = 3.2

Develop possible by *product*s to assist economic heath.

Fuel Alternatives

Biodiesel fuel use is on the rise. Made from natural, renewable sources (vegetable oils, animal fats), it can be used as pure fuel or blended with petroleum.

Ethanol is renewable, but more expensive than gasoline.

Some believe it takes more energy to produce a gallon of ethanol than you will obtain from burning it.

4.9

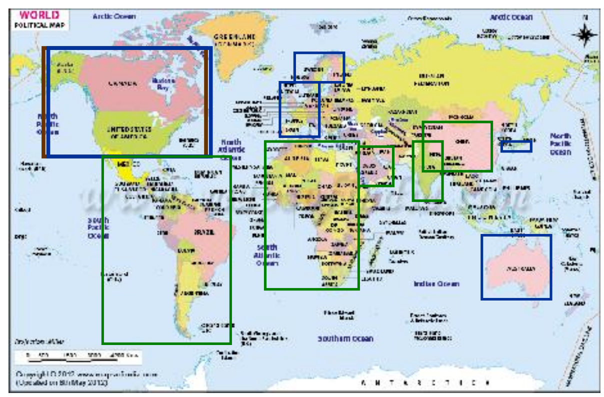
Resource Recovery – Incineration of Garbage.

Biogas generation: Organic matter decomposed into methane and CO_2 and small amounts of water, H_2S and CO.

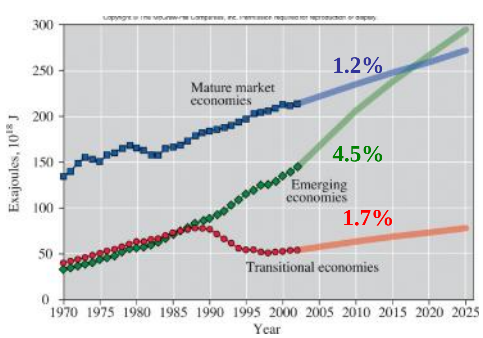
Used for cooking, heating, lighting etc.

Raw material : Sewage and manure.

Energy use: 25% of world energy used by 5% of worlds population.



Historic and projected energy consumption worldwide:



Note: All three projections slope upward.

4.11

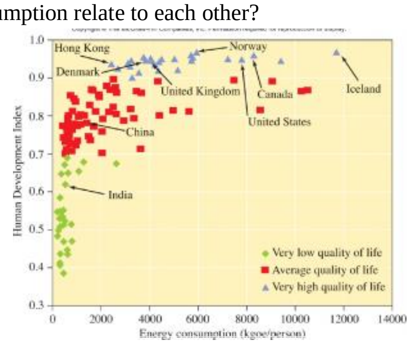
The energy consumption and GDP (~economic growth) are correlated.

However the GDP alone is not a good measure of the quality of life of average citizens in a country.

Human Development Index (HDI) is considered an advanced measure of the quality of life of an average citizen.

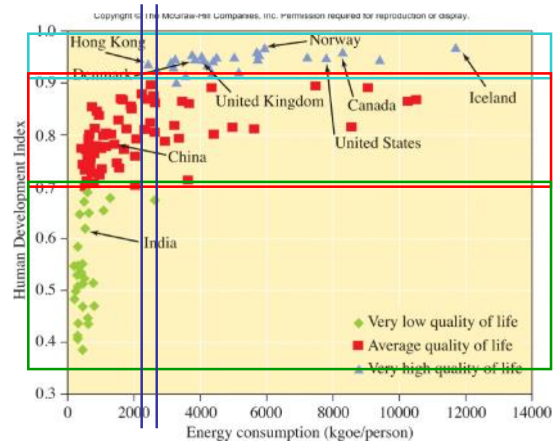
HDI ⟷ { GDP; Public Health (life expectance); Education (literacy rates) }

How do the Human Development Index and energy consumption relate to each other?



Note: All three projections slope upward.

4.11



There is not enough conventional energy sources for everyone in the planet to live at HDI ≥ 0.9. Population increase exacerbates the situation.

Develop new sources of energy, preferably renewable; hydro, solar, wind, tidal and geothermal.

Conservation – inherent <100% efficiency of energy conversion is inevitable. Develop efficient technologies.

Public policy: CAFÉ standards, public transportation, safety technologies, better materials.

Reading assignment: 4.9, 4.10, 4.11.