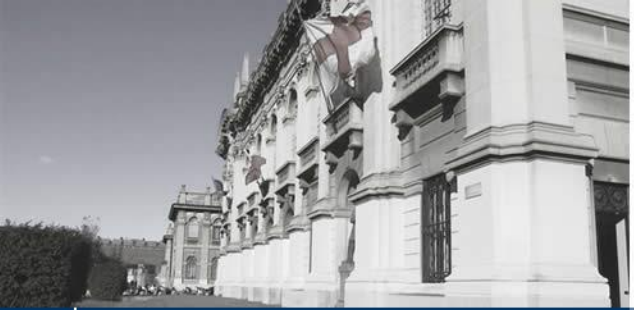


School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

Energy: Non Renewable (Fossil) Resources

Prof. Attilio Citterio

Dipartimento CMIC “Giulio Natta”

https://iscamapweb.chem.polimi.it/citterio/education/course-topics/

Energy.

The capacity to do work - **Energy is the common currency of all aspects of physical life.** Cannot be created nor destroyed, but can be converted from one form to another.

Two main forms: **Heat** and **Motion**

Fundamental SI unit of energy : joule (*J*) = *N·m* = *kg·m²·s⁻²*

Joule is a very small number;

1 *J* is required to raise the temperature of 1 *mL* of water by ~0.25°C

Calorie (*cal*) is an optional unit; 1 *cal* = 4.18 *J*

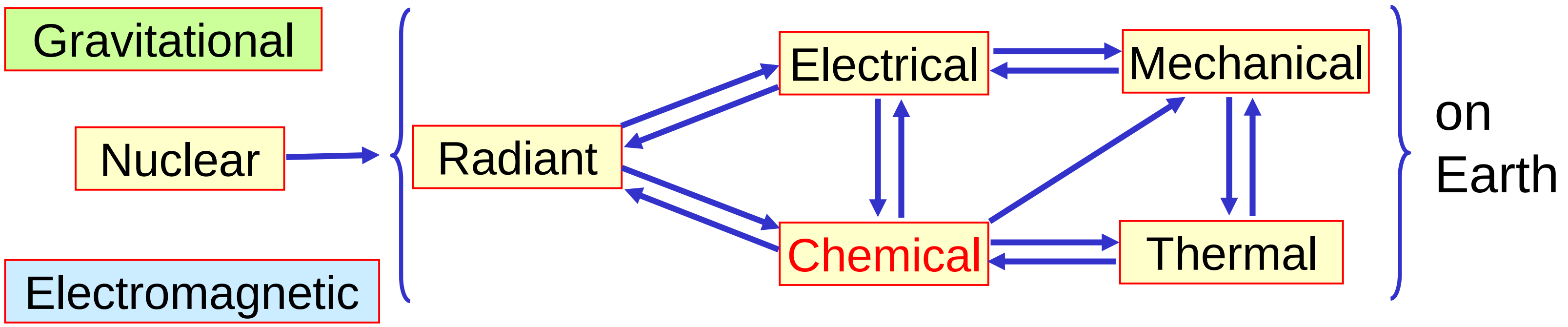
3000 *kcal* for a day diet = 1.25×10^7 *J* = 12.5 *MJ*

All sorts of other physical activities can be evaluated in terms of energy:

- Burning of a Fuel — 1 m^3 of natural gas = 3.7×10^7 *J*
- Man physical work — 1 hour of an hard work = 2.5×10^6 *J*
- Product manufacture — Embodied energy content for vehicles = $7 \times 10^7\ J \cdot kg^{-1}$

Energy Forms.

The energy occurs in different forms:

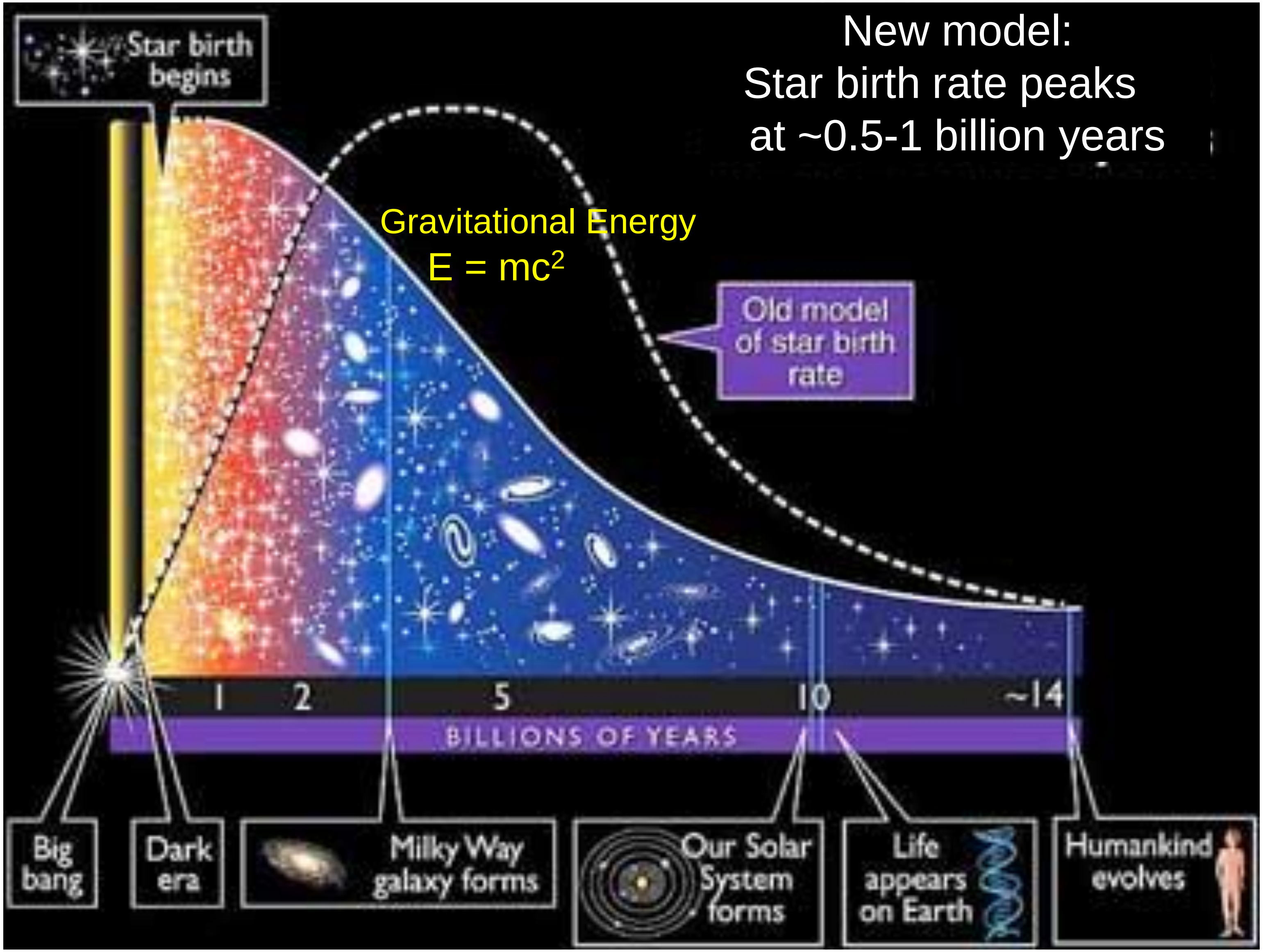


The **chemical energy** (produced by bond breaking and forming between atoms through chemical reactions) is the one which hold the main influence on human activities. Curiously, compared to others form of energy, its presence in the Universe is negligible.

The energy involved in chemical processes depend on:

- Selected route
- Process thermodynamic (ΔH and ΔG >,=,< 0)
- Kinetics (E_{att})
- Involved activities (heating, mixing, separations, purifications, …)

Energy and Universe Evolution.



Energy and Spontaneous Degradation of Energy.

Each energy form is characterized by a quality index, termed entropy S, which measures the dispersion probability of the system.

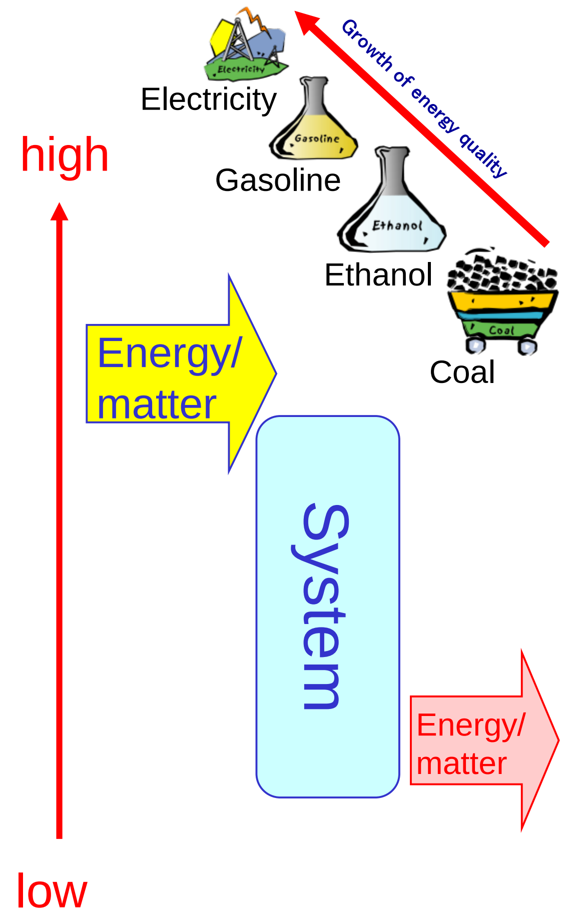
The economic value of the different forms of energy is, approximately, inversely proportional to their entropy content.

In an isolated system the energy is conserved and its different forms can transform each other according to II^ thermodynamic law, for which :

- Spontaneous processes evolve in the direction in which, total amount of energy being constant, the entropy increases.
- The natural direction of transformations is associated to a decline of the energy quality.

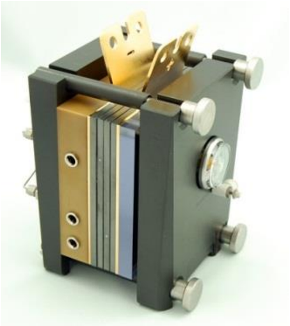
Quality of Different Forms of Energy.

	Energy Form	*Quality Index (% of exergy)*
Extra Superior	Potential Energy	100
	Kinetic Energy	100
	Electric Energy	100
Superior	Nuclear Energy	~ 100
	Solar Radiation	95
	Chemical Energy	95
	Hot Steam	60
	Thermal Cycle	30
Inferior	Waste Heat	5
without value	Heat irradiated from Earth	0



The quality is spent in the conversion of matter and energy

Energy Efficiency of some Common Energy Conversion Devices.

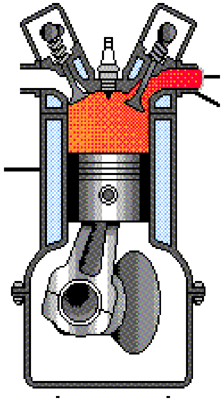


Fuel cell
60%

Steam turbine
45%

Human body
20-25%

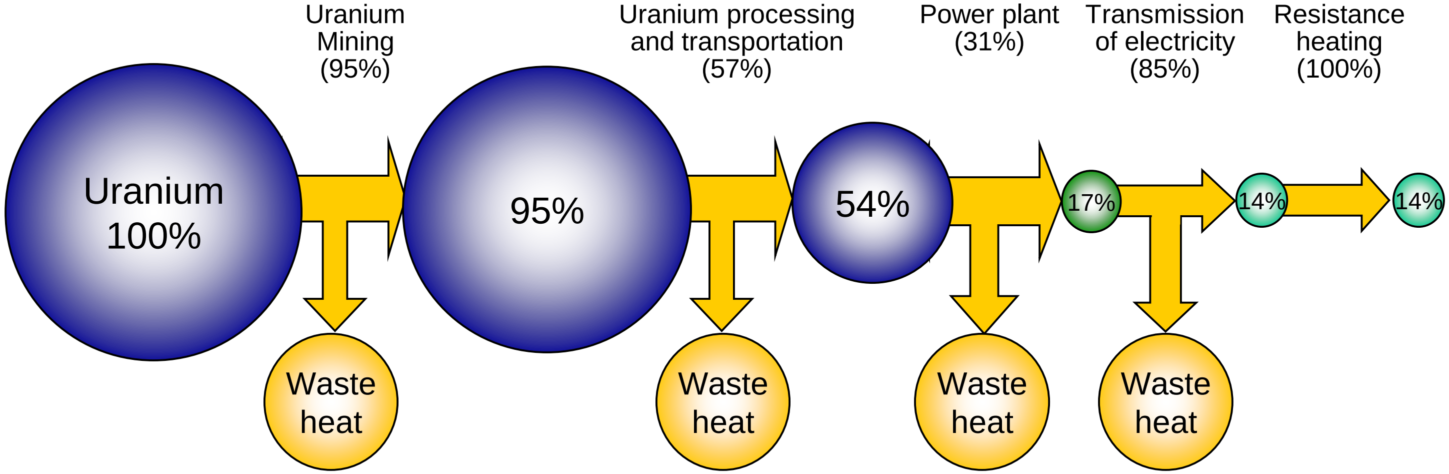
Fluorescent light
22%



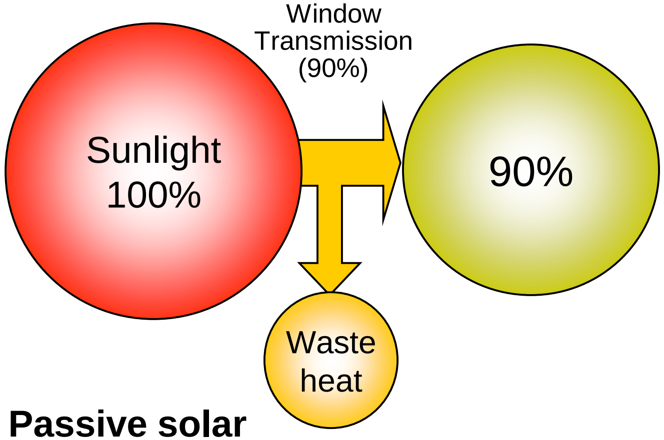
Internal combustion engine (gasoline)
10%

Incandescent light
5%

Comparison of Net Energy Efficiency for Two Types of Space Heating.



Electricity from Nuclear Power Plant



Passive solar

The cumulative net efficiency is obtained by multiplying the percentage shown inside the circle for each step by the energy efficiency for that step (shown in parenthesis). Because of the second law of thermodynamics, in most cases the greater the number of steps in an energy conversion process, the lower the net energy efficiency. About 86% of the energy used to produce space heating by electricity produced at a nuclear power plant is wasted. By contrast, with passive solar heating, only about 10% of incoming solar energy is wasted. If the additional energy needed to deal with nuclear wastes and to retire highly radioactive nuclear plant at the end of their useful life is included, then the net energy yield is only about 8% (or 92% waste)

Definition of *Power* in science:

Power is a Flux of Energy:

$$\textbf{Power} = \frac{\textbf{Energy}}{\textbf{Time}}$$

The energy unit converts to power unit dividing by time.

For example**,**

Cal per hour **BTU per min.** **Joule per sec. = watt**

The reference unit for Power is the watt, generally used as multiple

– **kilowatt = *kW***, **megawatt = *MW***.

The amount of energy can be obtained from power multiplying by time, therefore a typical unit of energy is the *kW·hour*.

$$1\ hp = 0.7547\ kW = 2.717 \times 10^{6}\ J \cdot h^{-1}$$

Annual Energy Consumption per Capita.

Home Heating Average 7 m^3 natural gas per day

- Total Energy = $7\ m^3 \times 365 \times 3.7 \times 10^7\ J{\cdot}m^{-3} = 9.5 \times 10^{10}$ J

Electricity 900 *kwh* per month

- Total Energy = $900\ kwh \times 12 \times 3.6 \times 10^6\ J{\cdot}kwh^{-1} = 3.2 \times 10^{10}\ J$

Car 12 000 *km* at 18 $km\ L^{-1}$ (gasoline)

- Total Energy = $(12\,000\ km / 18\ km{\cdot}L^{-1}) \times 4.8 \times 10^7\ J{\cdot}L^{-1}$
  $= 3.2 \times 10^{10}\ J$

per capita energy consumption per year in Italy

$$\cong \mathbf{1.2 \times 10^{11}\ J = 120\ GJ}$$

Global energy consumption per year

$$= \mathbf{340 \times 10^{18}\ J = 340\ EJ}$$

kilo	k	10^3	thousand
Mega	M	10^6	million
Giga	G	10^9	billion
Tera	T	10^{12}	trillion
Peta	P	10^{15}	
Exa	E	10^{18}	

Heating Values for Combustibles.

$$C_nH_mO_x + t\,O_2 \rightarrow n\,CO_2 + m/2\,H_2O$$

- Upper heating value (**UHV**), or gross calorific value (**GCV**):

  The heating value for the dry fraction of the fuel. Heat of evaporation for water formed from H is not taken into account.

  $UHV = 0.3491 \cdot \chi_C + 1.1783 \cdot \chi_H + 0.1005 \cdot \chi_S - 0.0151 \cdot \chi_N - 0.1034 \cdot \chi_O - 0.0211 \cdot \chi_{ash}$ [MJ·kg^{-1}, dry basis], ***χ_i in wt.%***

- Lower heating value (**LHV**):

  LHV = UHV minus heat of evaporation for water (2.447 MJ·kg^{-1} water) formed from H [MJ·kg^{-1}, dry basis]

- Effective heating value (**EHV**), or Net calorific value (**NCV**):

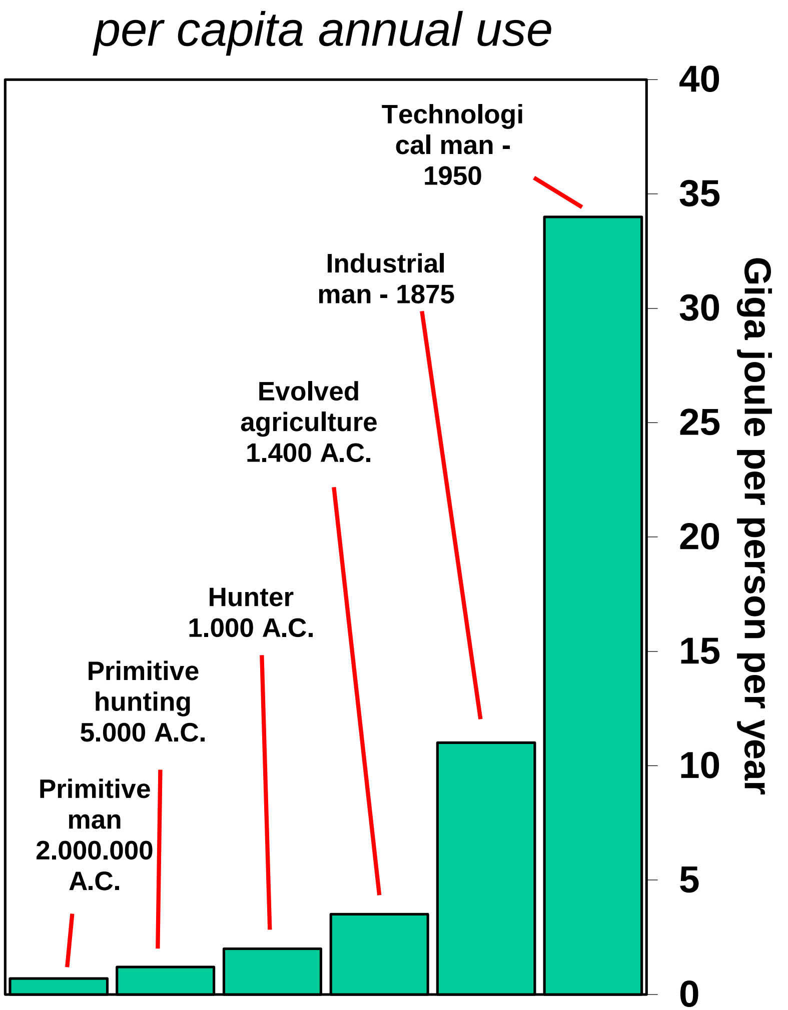
  EHV = LHV minus heat of evaporation for water in the fuel [MJ·kg^{-1}, wet basis]

Energy was Essential in Human Development.

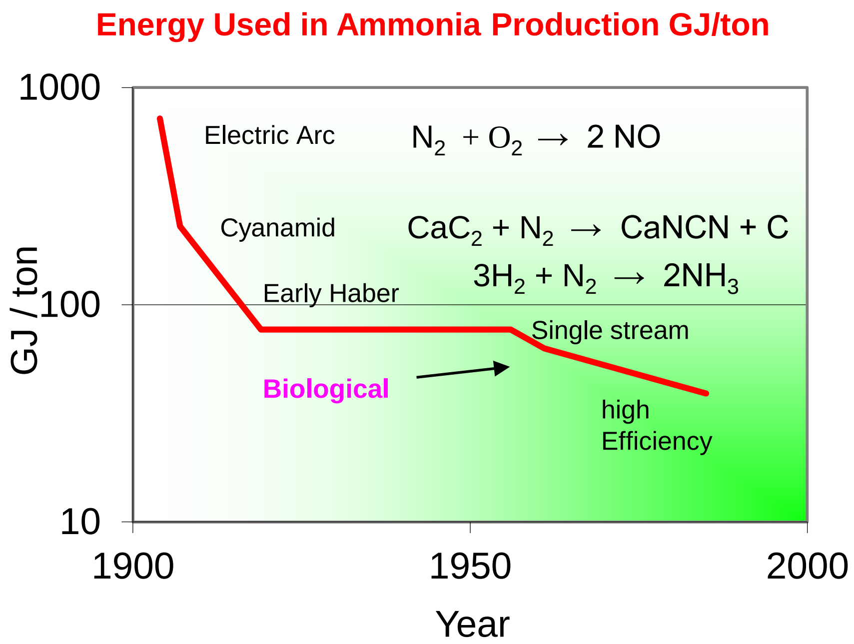
Modern society uses large amount of energy.

In the last 4000 years, man use of energy is enormously grown. Energy consumed by man for living was the only one produced using its work. After, the use of energies of different sources (animal, wood, water, solar energy, fossil fuels) made possible to sustain more complex needs.

Nowadays we use energy for heating, cooking, light up, play music, travelling, etc., in amount up to 35 times what necessary to human life. That is, if only the energy produced by man is used, 100 persons active during 24 hours are needed to produce the energy necessary for the life of only one person with a modern life style.



Energy Saving in Chemical Manufacturing: Improvements in Ammonia Synthesis.



- Insufficient natural sodium nitrate – ammonia synthesis needed
- Catalytic Haber process transformed energy requirements
- Production volumes increased 150 fold from 1930 to 2000
- Incremental increase in the last 40 years have reduced energy requirements to below biological process.

Energy Sources.

Most of the energy used by humans is obtained from several sources, some primary, other derived from them:

Primary Sources:

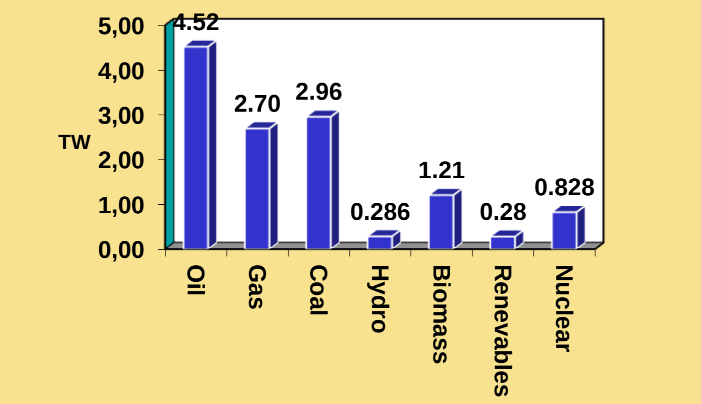
- Solar Energy
- Lunar Energy
- Geo Energy
  - Geothermal
  - Nuclear

Derived Sources:

- **First order**
  - Fossil fuels
  - Biomass
  - Flowing water
  - Tides
  - Wind
  - Waves
- **Second order**
  - Electricity
  - Animal
  - Human

Distribution of average values of energy use (in *TW*)

Total: 13.0 ,
U.S.A.: 3.3 ,
Italy : 0.25
(TW = Terawatt)



Energy Conversion Factors.

To fuel

Multiply by

From fuel

	tce	***GJ***	***MMBtu***	***bbl. oil***	***MWh***
tce	1.00	25.8	24.5	4.38	7.18
GJ	0.039	1.00	0.948	0.169	0.278
MMBtu	0.0408	1.06	1.00	0.179	0.293
bbl. oil	0.229	1.06	5.59	1.00	1.64
MWh	0.139	3.60	3.41	0.609	1.00

tce = tons of coal equivalent

K kilo = 10^3
M mega = 10^6
G giga = 10^9
T tera = 10^{12}
P peta = 10^{15}

A wider range of energy conversions is also possible by using the tool available at: http://www.processassociates.com/process/convert/cf_ene.htm

Energy Units for Different Sources.

Energy source	Unit	(abbreviation)	Equivalent in joules
Natural Gas	cubic meter	(m^3)	3.7 □ 10^{7}
Petroleum	**barrel**	**(bbl.)**	**5.8 □ 10^{9}**
	ton	**(t)**	**3.9 □ 10^{10}**
Tar sand oil	**barrel**	**(bbl.)**	**6.1 □ 10^{9}**
Shale oil	**ton**	**(t)**	**4.1 □ 10^{10}**
Coal **anthracite**	**ton**	**(t or TCE)**	**3.0 □ 10^{10}**
bituminous	**ton**	**(t or TCE)**	**3.0 □ 10^{10}**
sub-bituminous	ton	(t or TCE)	2.0 □ 10^{10}
lignite	ton	(t or TCE)	1.5 □ 10^{10}
charcoal	ton	(t or TCE)	2.8 □ 10^{10}
Biomass (all on a dry weight basis)			
general	ton	(t)	1.5 □ 10^{10}
misc. farm wastes	ton	(t)	1.4 □ 10^{10}
animal dung	ton	(t)	1.7 □ 10^{10}
assorted garbage	ton	(t)	1.2 □ 10^{10}
wood	ton	(t)	1.5 □ 10^{10}
	cubic meter	(m^3)	5 □ 10^{9}
Fission natural U	ton	(t)	8 □ 10^{16}
Electricity	kilowatt hour	(kwh)	3.6 □ 10^{6}
	terawatt year	(Twy)	3.2 □ 10^{19}
General Units	**erg**	**(erg)**	**1 □ 10^{-7}**
	calorie	**(Cal)**	**4.18**
	British thermal unit	**(BTU)**	**1.05 □ 10^{3}**
	horsepower hour	**(hp·h)**	**2.7 □ 10^{6}**

Chart of Energy Units by Source.*

Cubic Feet of Natural Gas	Barrels of Oil	Tons of Bituminous Coal	Kilowatt Hours of Electricity	Joules
1	0.00018	0.00004	0.293	1.55×10^{6}
1000	0.18	0.04	293	1.55×10^{9}
5556	1	0.22	1628	5.9×10^{9}
25,000	4.50	1	7326	26.4×10^{9}
1×10^{6}	180	40	293,000	1.05×10^{12}
3.41×10^{6}	614	137	1×10^{6}	3.6 □ 10^{12}
1×10^{9}	180,000	40,000	293×10^{6}	1.05×10^{15}
1×10^{12}	180×10^{6}	40×10^{6}	293×10^{9}	1.05×10^{18}

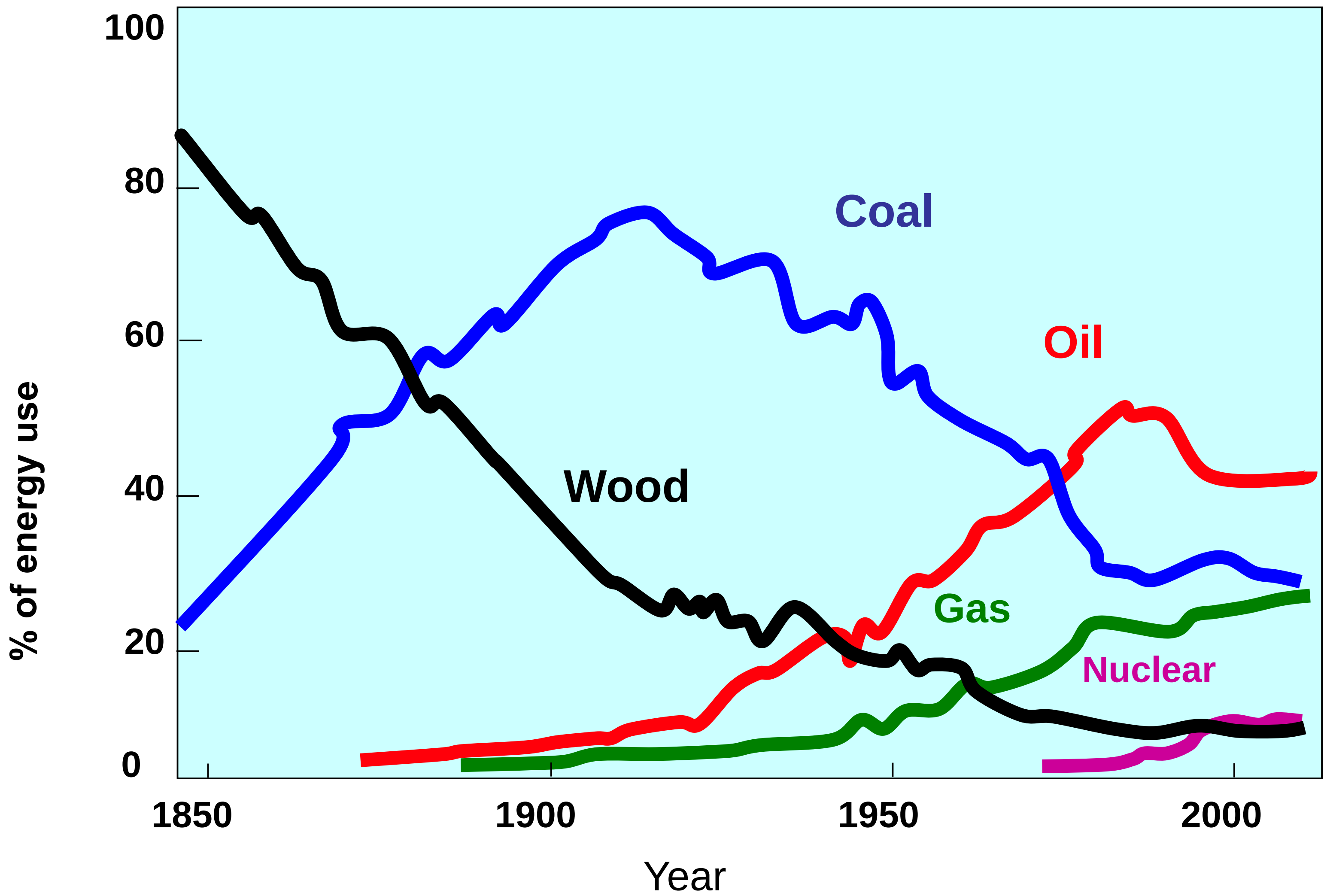
* Based on the common heat value of fuels.

Which Energy Sources are More Desirable?

1. Applicability and convenience

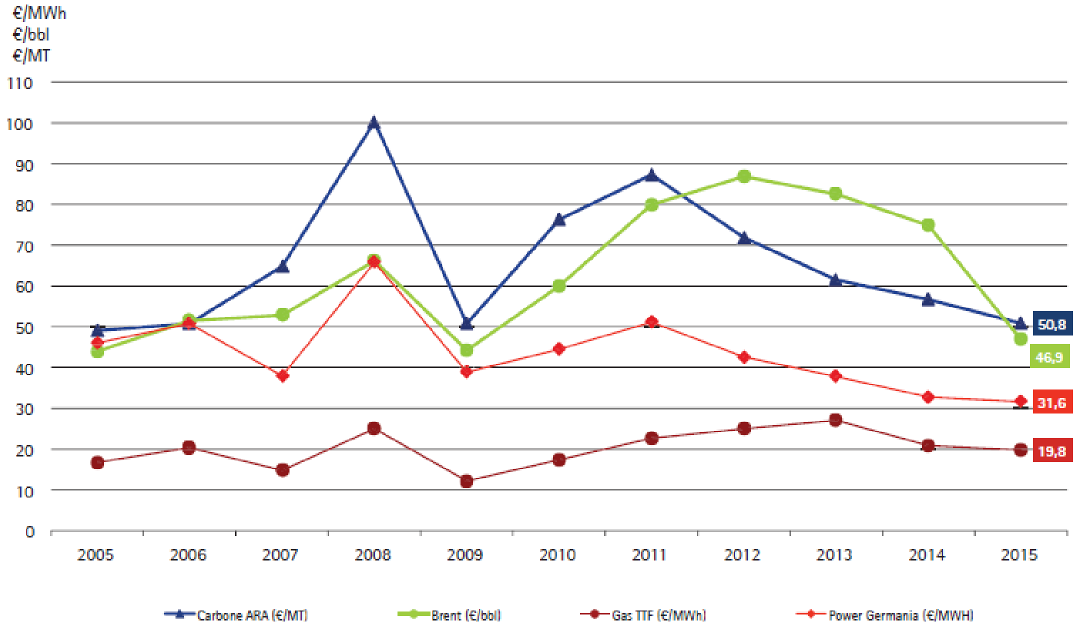
- Extraction
  - Technical and economic feasibility
  - Safety
- Transport
  - Gases, liquids, solids
- Conversion
  - Separation, upgrading
- Use

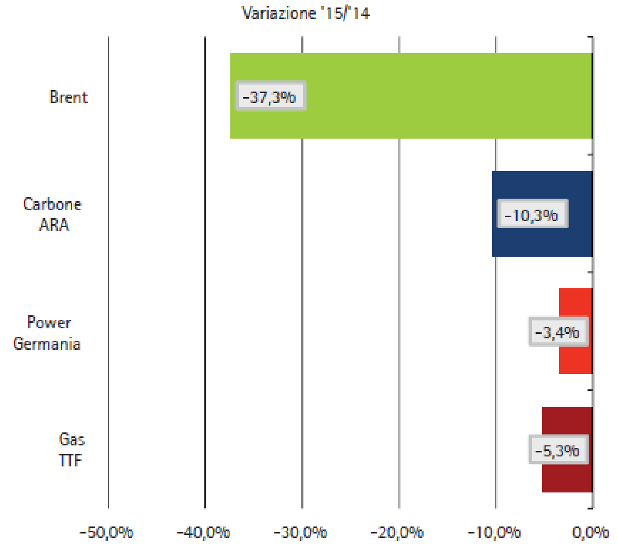
Energy Sources Used by Humans – Historical Trend.



Source: N. Nakicenovic (IIASA),

Price (in €) of Main Energy Commodities (2015).





Which Energy Sources are More Desirable?

2. Resource supply

- Economics, politics, reserves/renewability
- Global annual consumption = 340 EJ

kilo	k	10^3	thousand
Mega	M	10^6	million
Giga	G	10^9	billion
Tera	T	10^{12}	trillion
Peta	P	10^{15}	
Exa	E	10^{18}	

Reserves of non-renewable supplies

Coal	3.1×10^{22} J	=	31 000 EJ	=	92 y
Petroleum	6.0×10^{21} J	=	6000 EJ	=	17 y
Tar sands oil	1.0×10^{22} J	=	10 000 EJ	=	29 y
Natural Gas	5.2×10^{21} J	=	5200 EJ	=	15 y
Uranium	2.0×10^{23} J	=	200 000 EJ	=	590 y

Which Energy Sources are More Desirable? (2)

Global annual consumption = 340 EJ

- *Renewable resources*
  - Hydroelectricity 8.5 EJ
  - Biomass ~40 EJ
  - Solar 1.9 EJ
  - Wind 0.8 EJ (installed)
    [x ~0.2 (wind factor)]
  - Tidal 0.1 EJ
  - Geothermal 1.8 EJ

For appropriate discussion on renewable energy sources see the appropriate chapter.

Chemical Energy: Solid fuels.

- **Coal**
  - Coke
  - Lignite
  - Bituminous
  - Anthracite
- **Peat**
- **Biomass**
  - Virgin biomass:
  - Wood (softwood & hardwood)
  - Nonwoody biomass
  - Agricultural residues
  - Grasses
  - Animal residues: Manure
  - Charcoal
  - Refined solid biomass fuels (pellets, briquettes)
- **Waste**
  - Municipal solid waste (MSW)
  - Industrial waste
  - Wastewaters

3. Environmental consequences

Atmosphere

- CO_2 Emissions
- an inevitable fate of fossil fuels combustion

		ΔH / kJ·mol^{-1}
Coal	$C + O_2 \rightarrow CO_2$	-393.5
Heavy oil	$C_{20}H_{42} + 30.5\ O_2 \rightarrow 20\ CO_2 + 21\ H_2O$	-13,300.0
Natural gas	$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$	-890.3
Biomass	$\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O$	-440.0

CO_2 Emissions and Sequestration.

CO_2 emissions in the atmosphere

Combustion

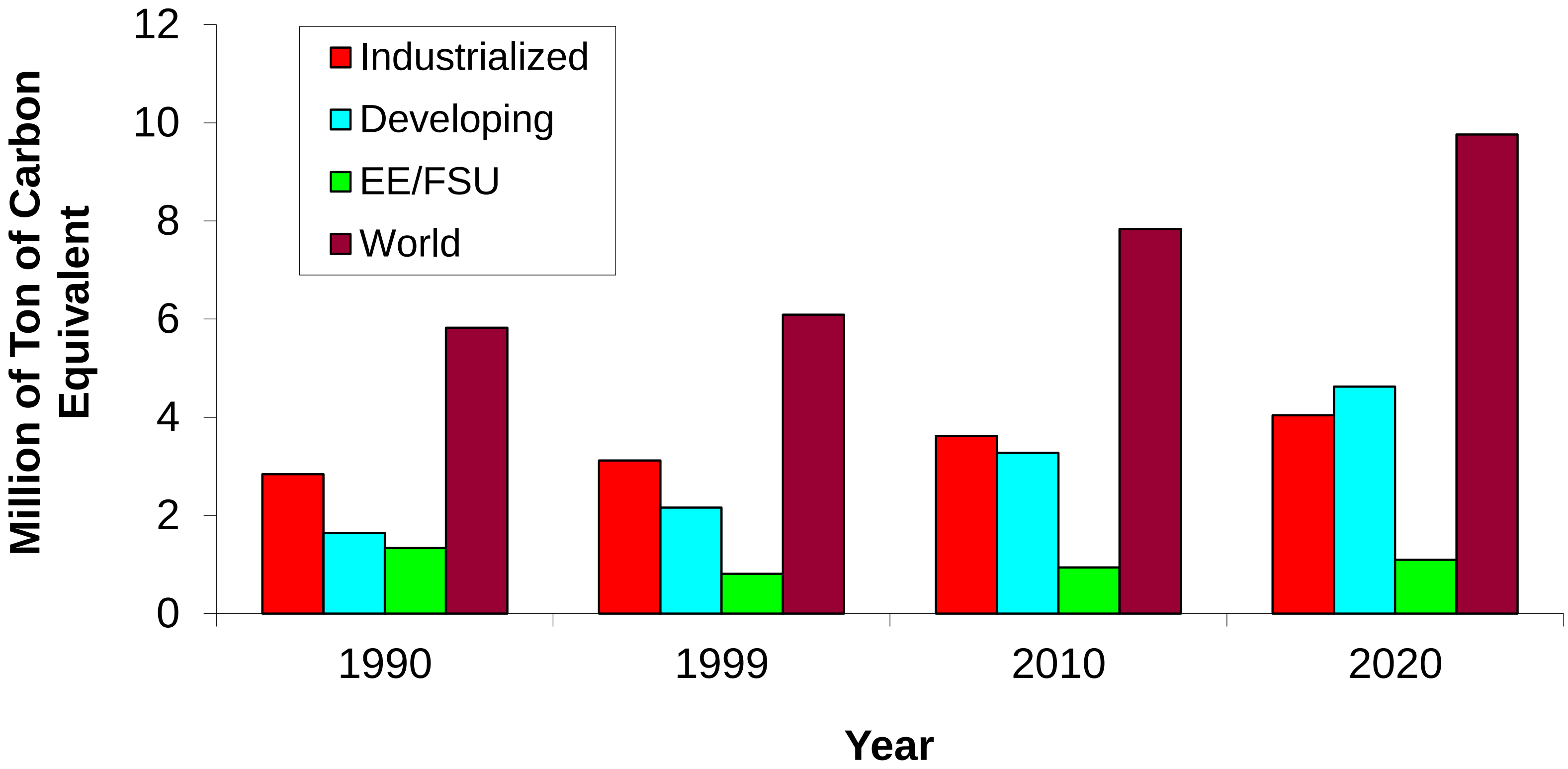
$$\{CH_2O\} + O_2 \longrightarrow CO_2 + H_2O \qquad \Delta H = -440\ kJ$$

Photosynthesis

$$CO_2 + H_2O \xrightarrow{h\nu} \{CH_2O\} + O_2 \qquad \Delta H = +440\ kJ$$

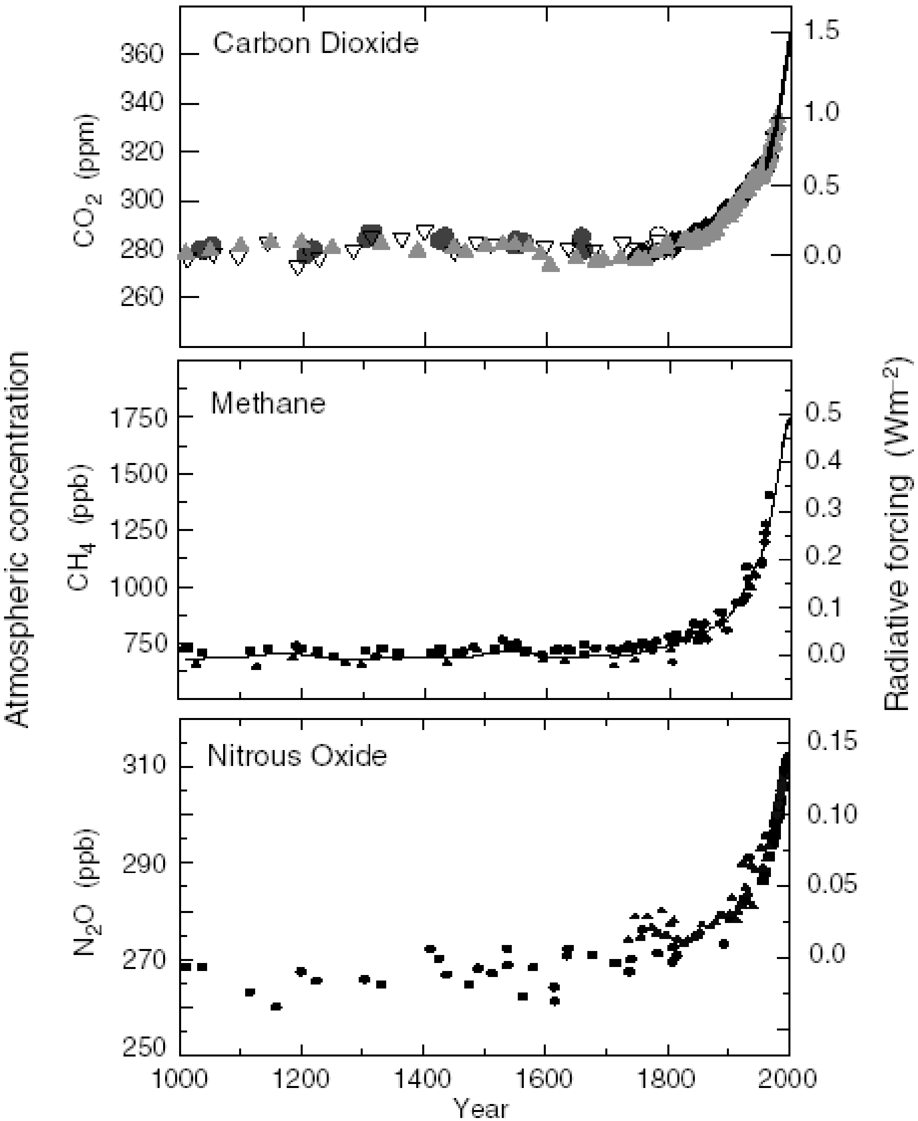
A closed loop - but efficiency?

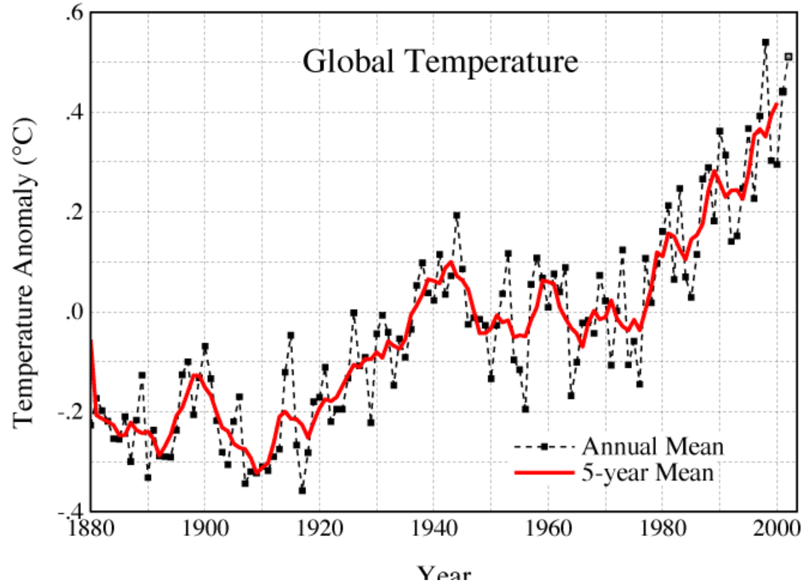
Carbon Emissions.

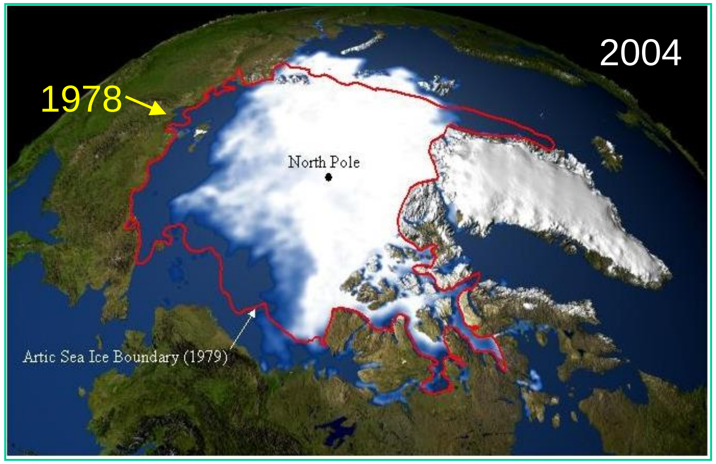


EE/FSU, Eastern Europe and the Former Soviet Union

Atmospheric Concentrations of CO_2, Methane (CH_4), and Nitrous Oxide (N_2O) from 1000 ac.



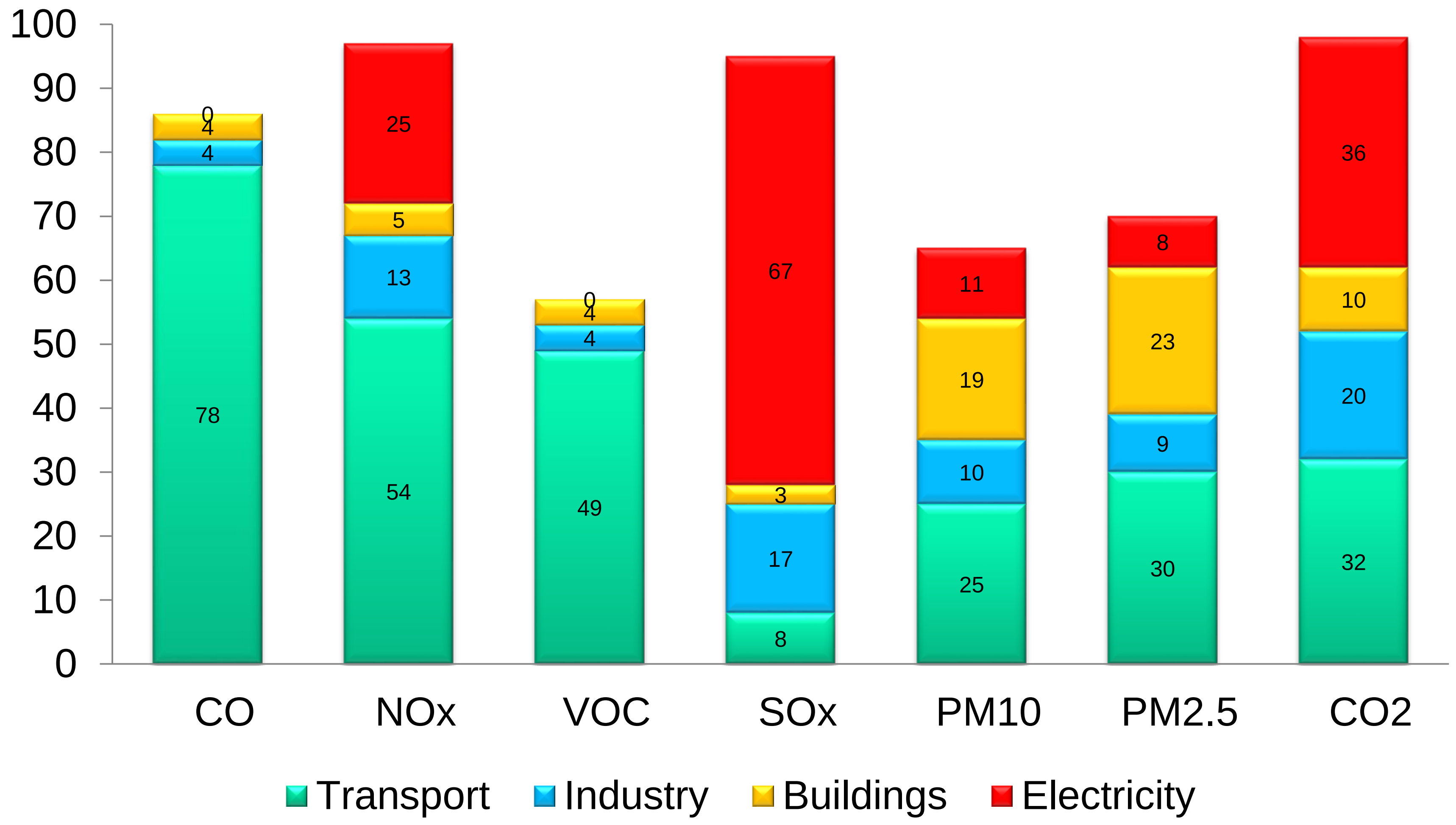




3. Environmental consequences

- *Atmosphere*
  - Emission of toxic compounds (NO_x , SO_2, PM, VOC, heavy metals)
- *Water*
  - Contaminated extraction and refining discharges
  - Scrubber wastes
  - Thermal pollution
  - Spills
- *Soil*
  - Production / transport / storage spills
  - Mine wastes
  - Fly-ash and bottom-ash

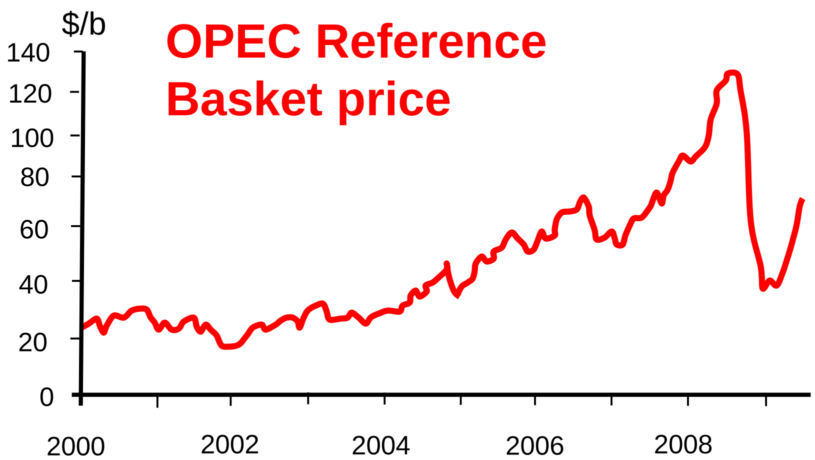
U.S. 1998 Energy-Linked Emissions as Percentage of Total Emissions.

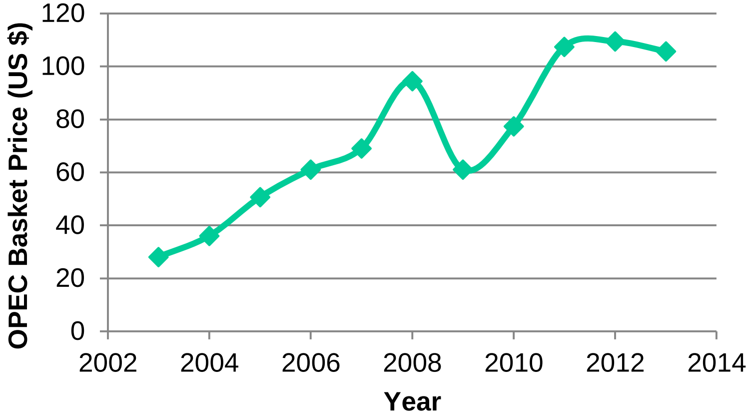


Desirable Energy Sources.

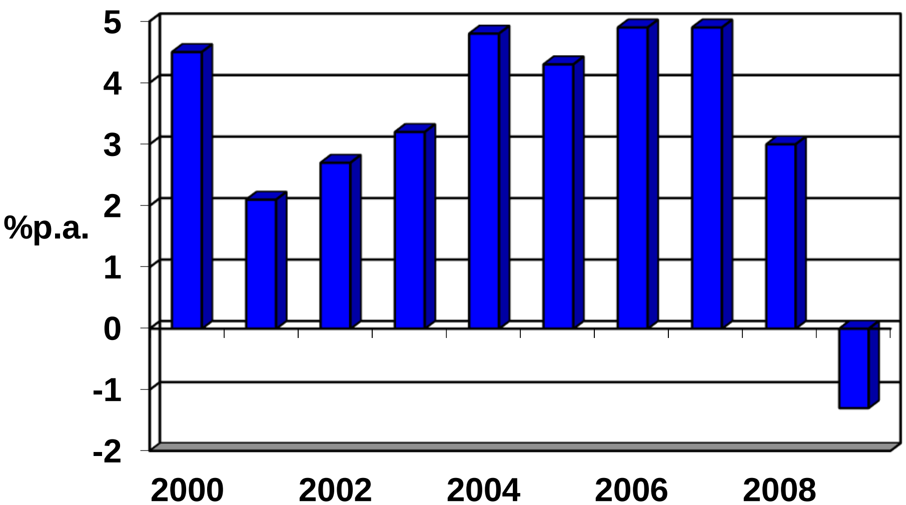
4. Cost

OPEC Reference Basket price

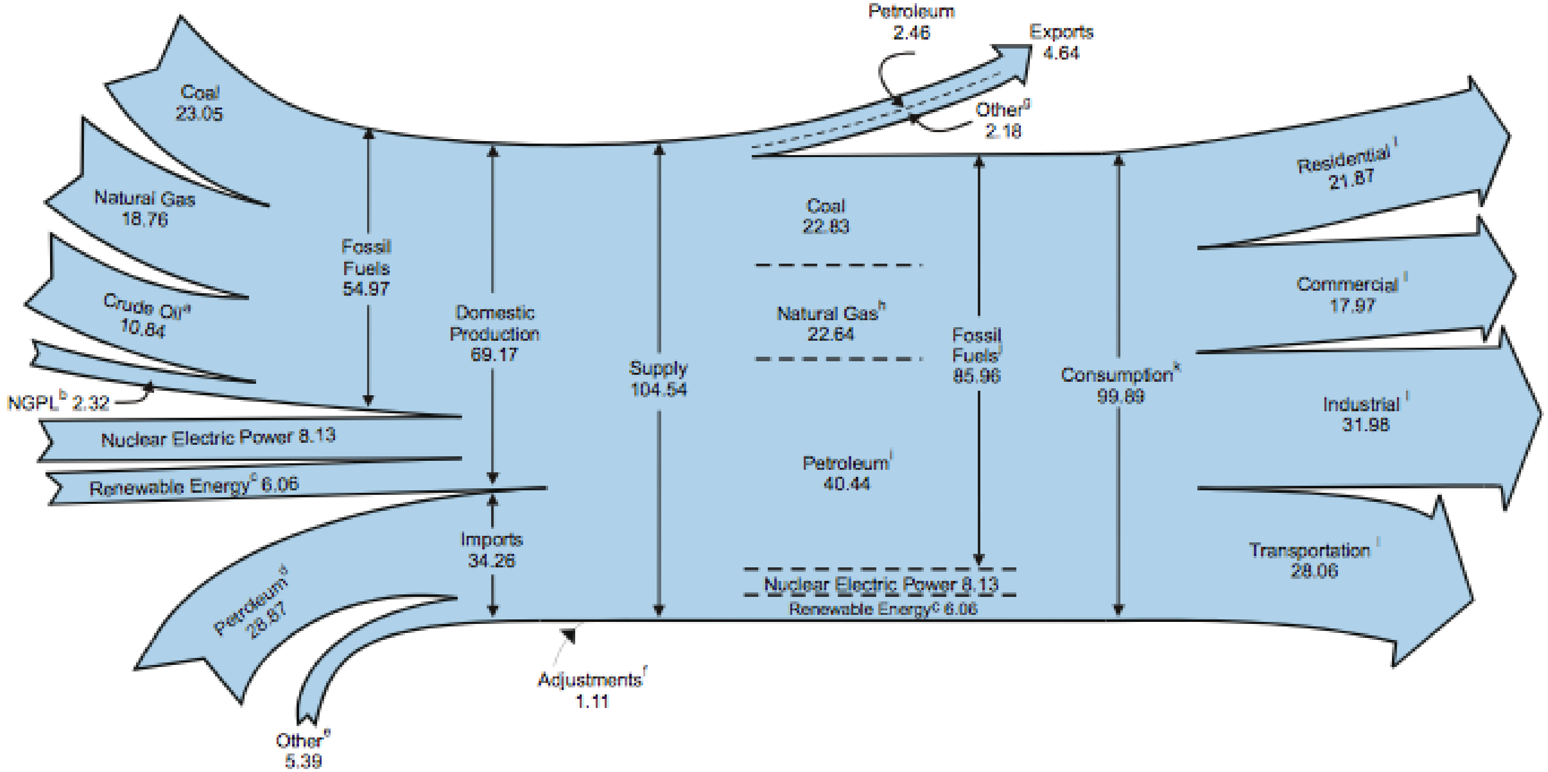




Annual global real GDP growth



Energy Flow (USA) 2005 (quadrillion BTU).

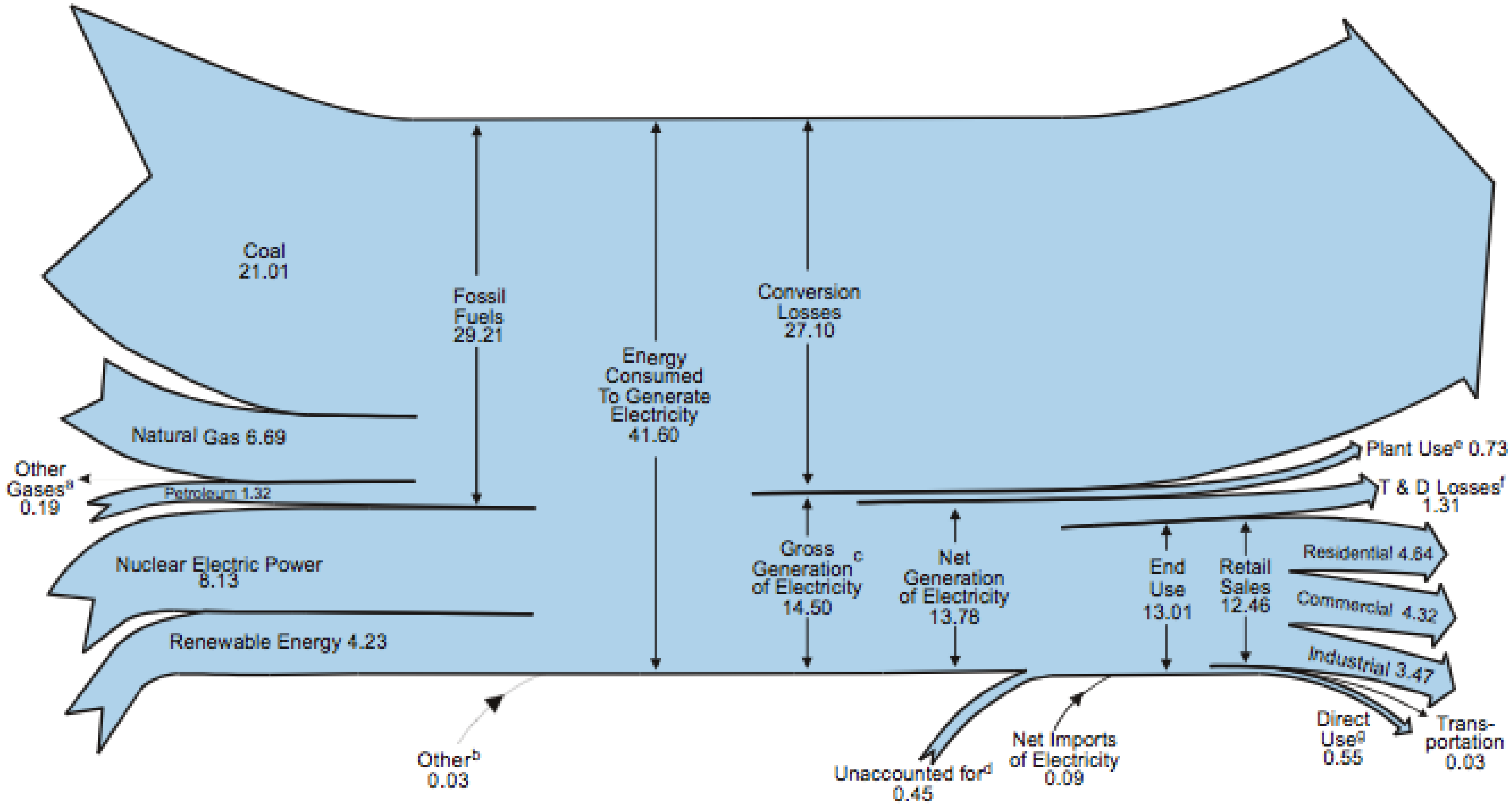


[a] Includes lease condensate.
[b] Natural gas plant liquids.
[c] Conventional hydroelectric power, wood, waste, ethanol blended into motor gasoline, geothermal, solar, and wind.
[d] Crude oil and petroleum products. Includes imports into the Strategic Petroleum Reserve.
[e] Natural gas, coal, coal coke, and electricity.
[f] Stock changes, losses, gains, miscellaneous blending components, and unaccounted-for supply.
[g] Coal, natural gas, coal coke, and electricity.
[h] Includes supplemental gaseous fuels.
[i] Petroleum products, including natural gas plant liquids.
[j] Includes 0.04 quadrillion Btu of coal coke net imports.
[k] Includes, in quadrillion Btu, 0.34 ethanol blended into motor gasoline, which is accounted for in both fossil fuels and renewable energy but counted only once in total consumption; and 0.08 electricity net imports.
[l] Primary consumption, electricity retail sales, and electrical system energy losses, which are allocated to the end-use sectors in proportion to each sector's share of total electricity retail sales. See Note, "Electrical Systems Energy Losses," at end of Section 2.

Notes: • Data are preliminary. • Values are derived from source data prior to rounding for publication. • Totals may not equal sum of components due to independent rounding.

Sources: Tables 1.1, 1.2, 1.3, 1.4, and 2.1a.

Electric Flow (USA) 2005 (quadrillion BTU).



[a] Blast furnace gas, propane gas, and other manufactured and waste gases derived from fossil fuels.

[b] Batteries, chemicals, hydrogen, pitch, purchased steam, sulfur, and miscellaneous technologies.

[c] Estimated as net generation divided by 0.95.

[d] Data collection frame differences and nonsampling error.

[e] Electric energy used in the operation of power plants, estimated as 5 percent of gross generation.

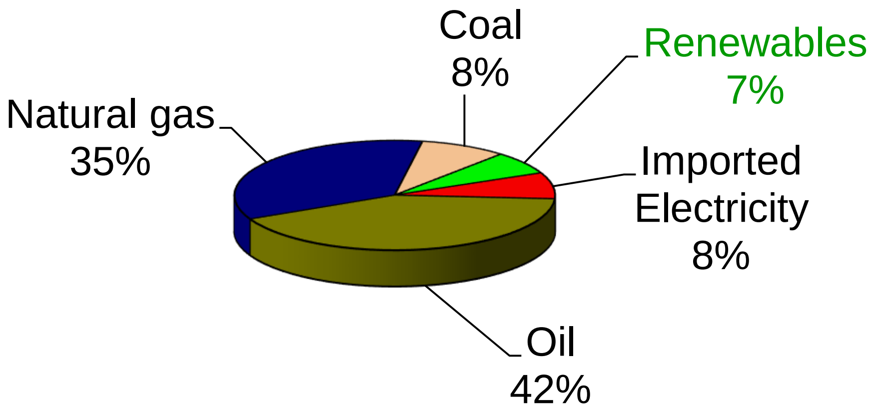
[f] Transmission and distribution losses (electricity losses that occur between the point of generation and delivery to the customer) are estimated as 9 percent of gross generation.

[g] Use of electricity that is 1) self-generated, 2) produced by either the same entity that consumes the power or an affiliate, and 3) used in direct support of a service or industrial process located within the same facility or group of facilities that house the generating equipment. Direct use is exclusive of station use.

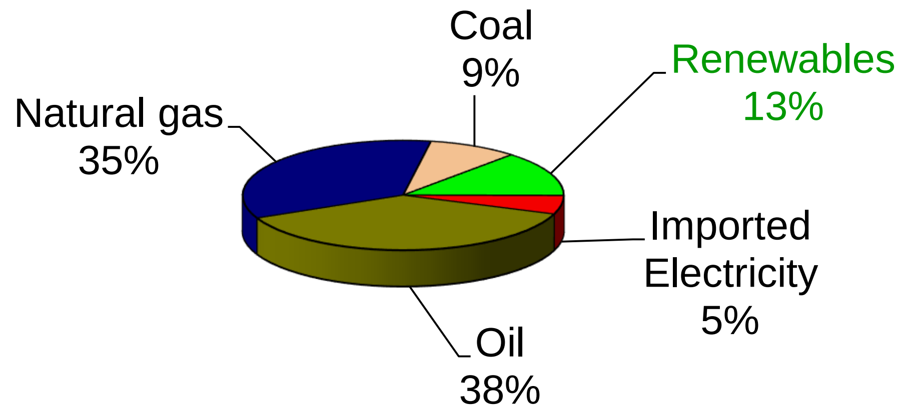
Notes: • Data are preliminary. • See Note, "Electrical System Energy Losses, at the end of Section 2. • Values are derived from source data prior to rounding for publication. • Totals may not equal sum of components due to independent rounding.

Sources: Tables 8.1, 8.4a, 8.9, and A6 (column 4).

Primary Energy and Electricity in Italy (2008-2012).

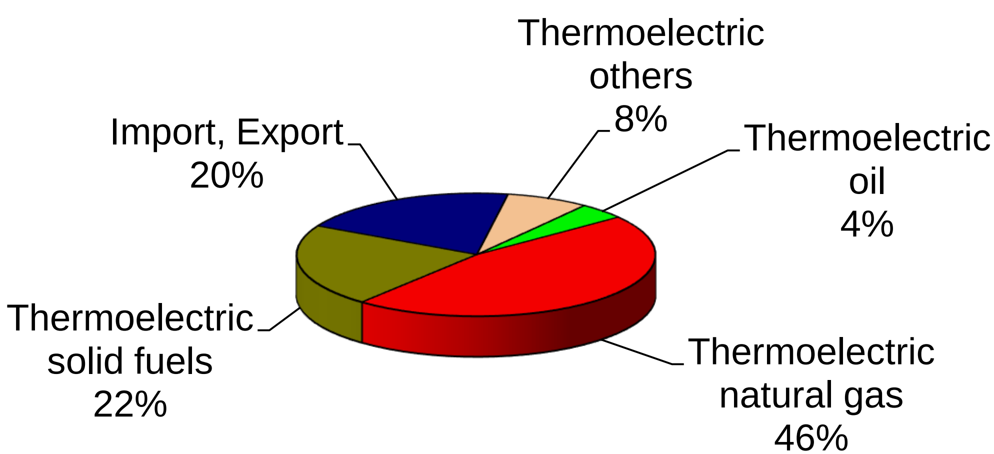


Primary Energy 2008



Primary Energy 2011

(30% in 2015)



Electricity Use 2012

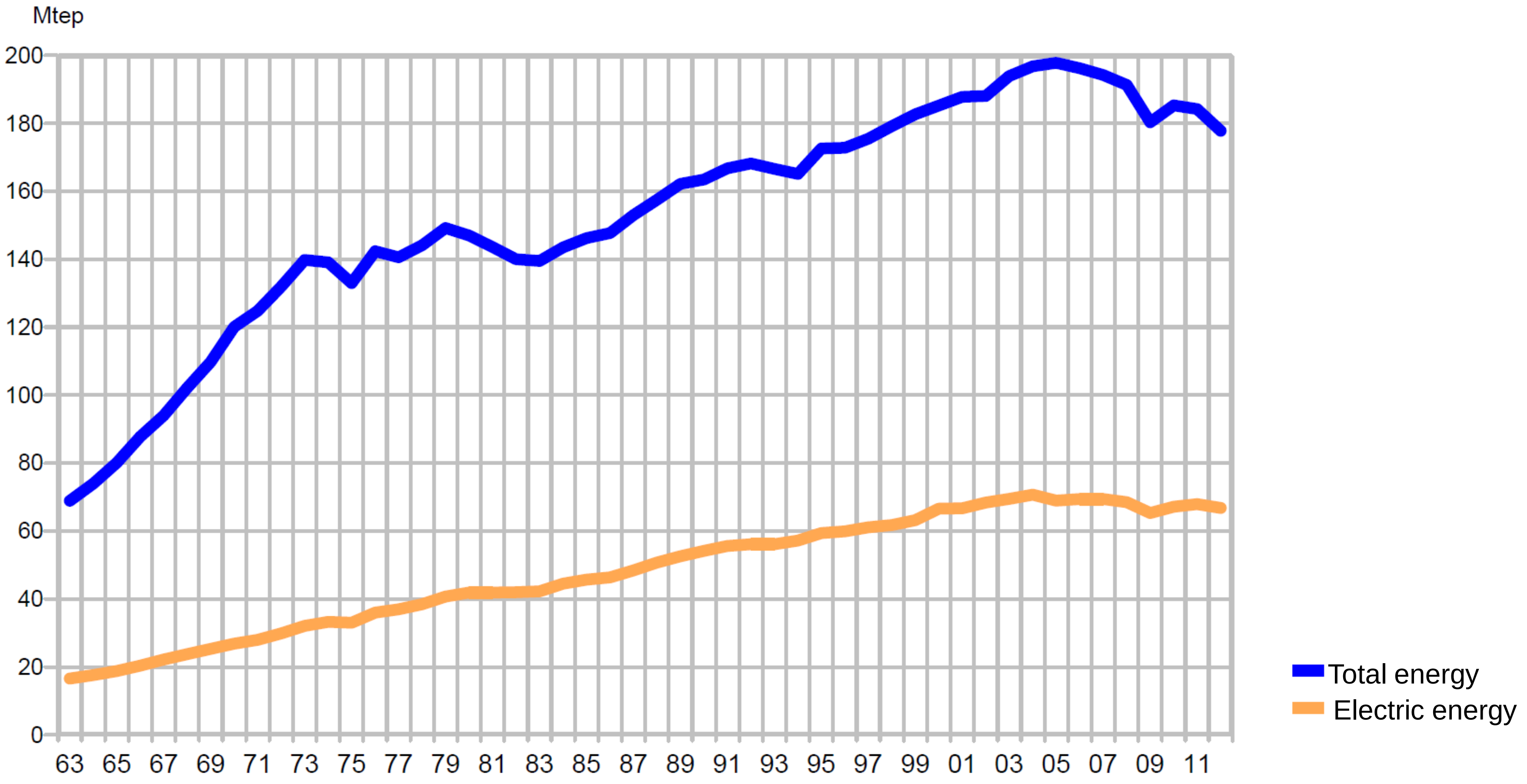
Summary of Some Numbers of Energy in Italy.

	2010	2011	2012
Primary energy demand	187.7 Mtep	184.2 Mtep	178 Mtep
Oil Import	78.6 Mt	72 Mt	
Oil Demand	73.7 Mt	71.9 Mt	63.9 Mt
Coal Import	22.1 Mt	23.5 Mt	
Gas Import	75.2 Gm^3	70 Gm^3	67.4 Gm^3
Gas Demand	83 Gm^3	77.9 Gm^3	74.9 Gm^3
Electric	330.5 TWh	334,6 TWh	325.3 TWh
Production of renew. electricity	77 TWh	83 TWh	92 TWh
PUN	64.12 €/MWh	72.23 €/MWh	75.48 €/MWh

Sources: UP, Mse, Terna, GSE, Snam Rete Gas.

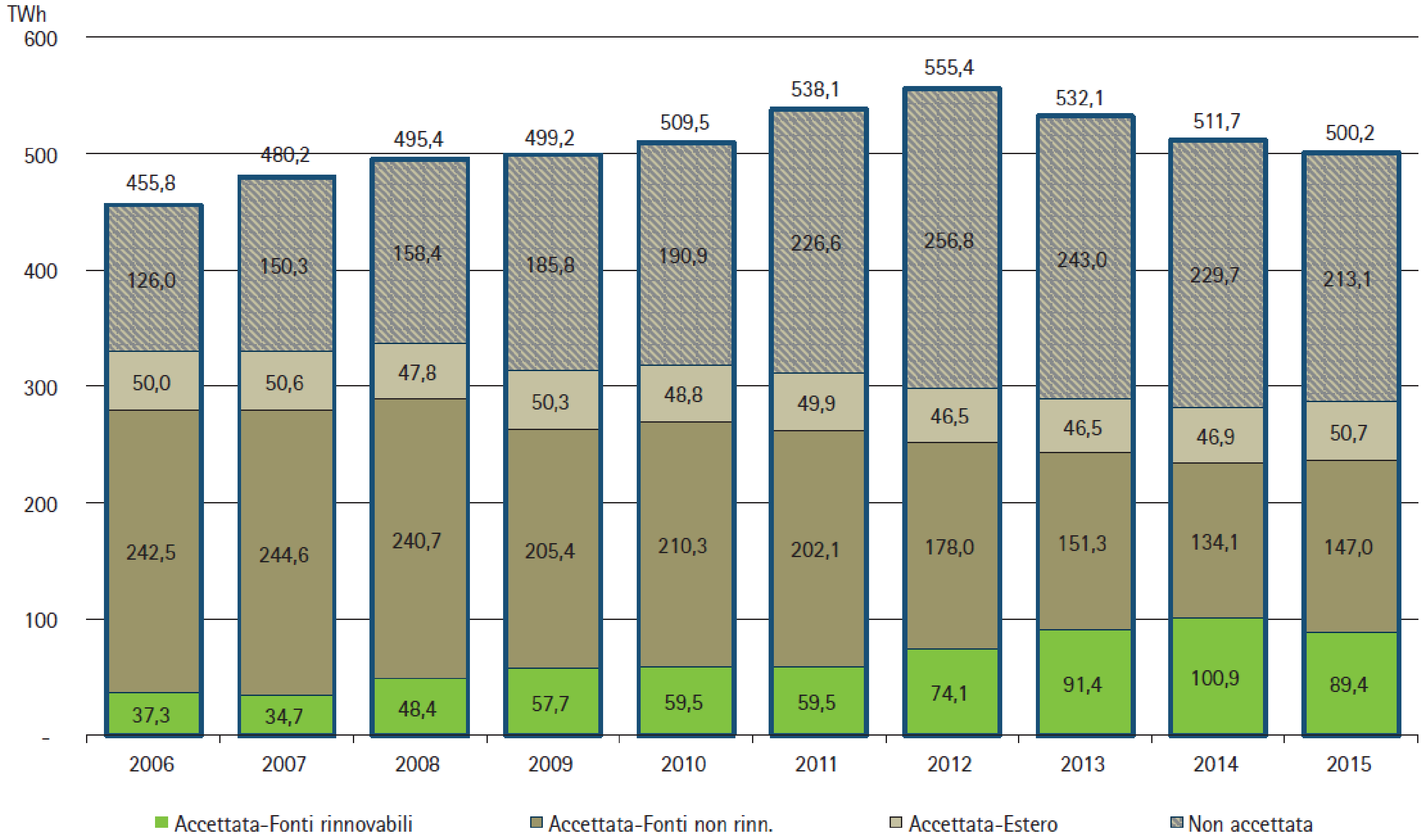
Mt = millions tons
Gm^3 = billions cubic meters
TWh = Terawatt
MWh = Megawatt

Use of Energy in Italy in Primary Sources.

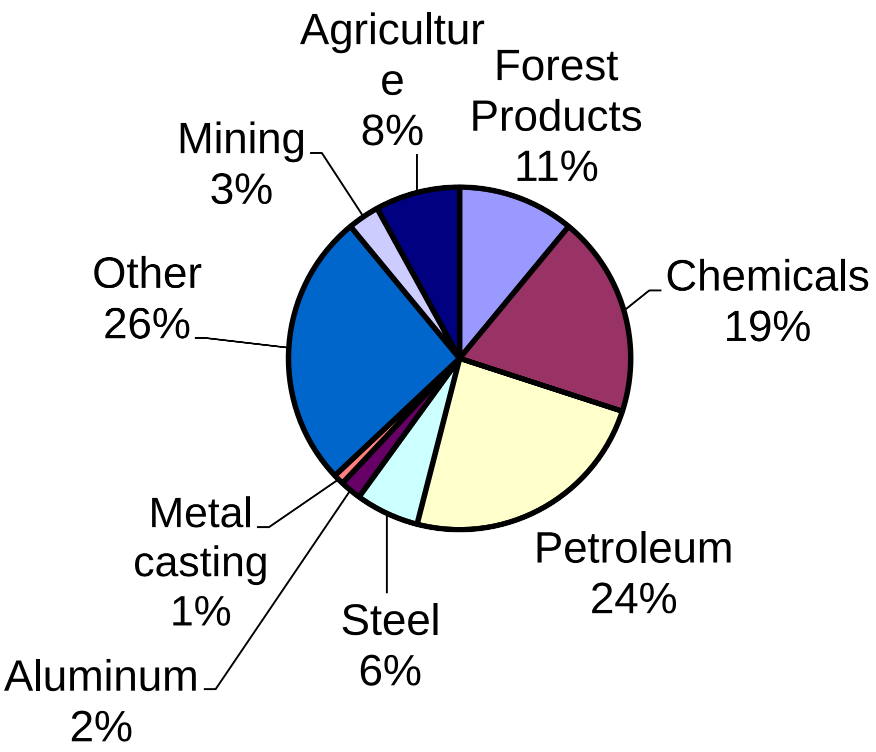


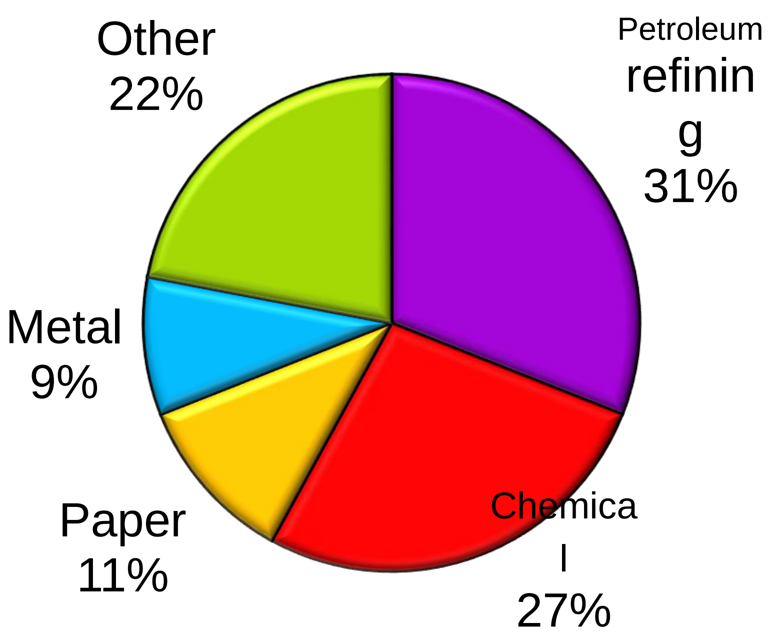
Source: Terna

Trends in Supply and Consumption of Electrical Energy in Italy (GME – 2015).



Industrial Energy Use in U.S.
(35 Quads, 1999) and by type of Industry (2010).

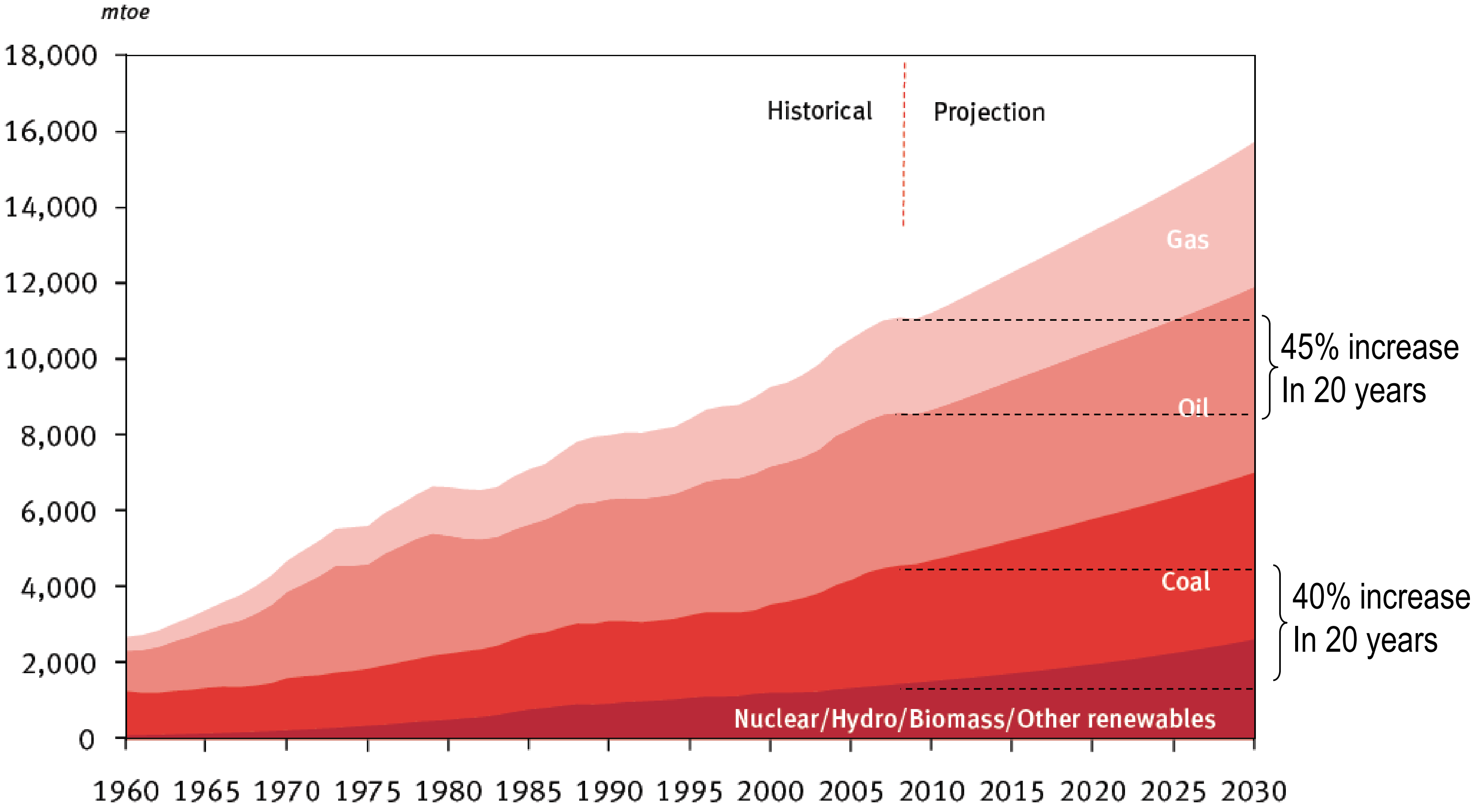




From EIA Annual energy Outlook 2001, for US Transport in 19991%

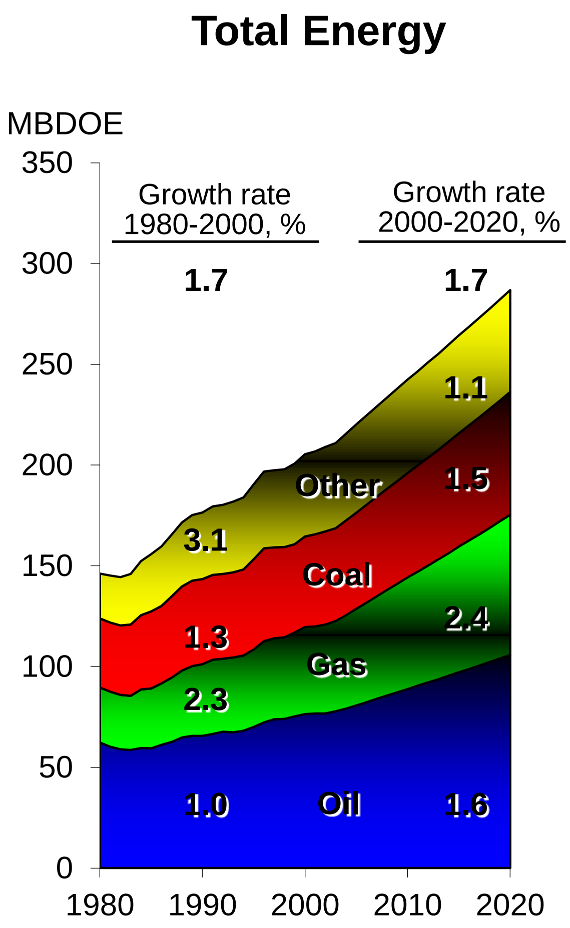
Source: U.S. Energy Information Administration , Manufacturing Energy Consumption Survey 2010, Table 1.2 (March 2013)

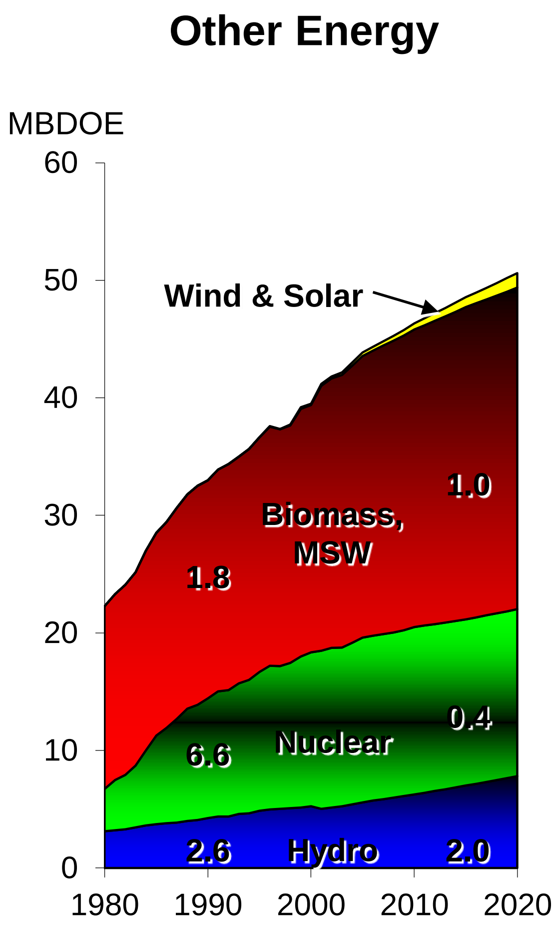
World Supply of Primary Energy by Fuel Type.

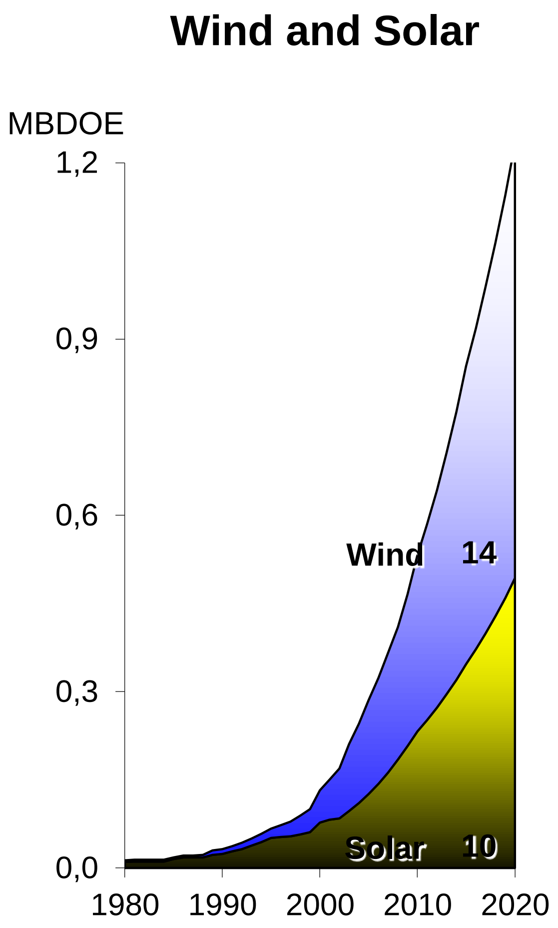


Source: World Oil Outlook, 2009 - OPEC

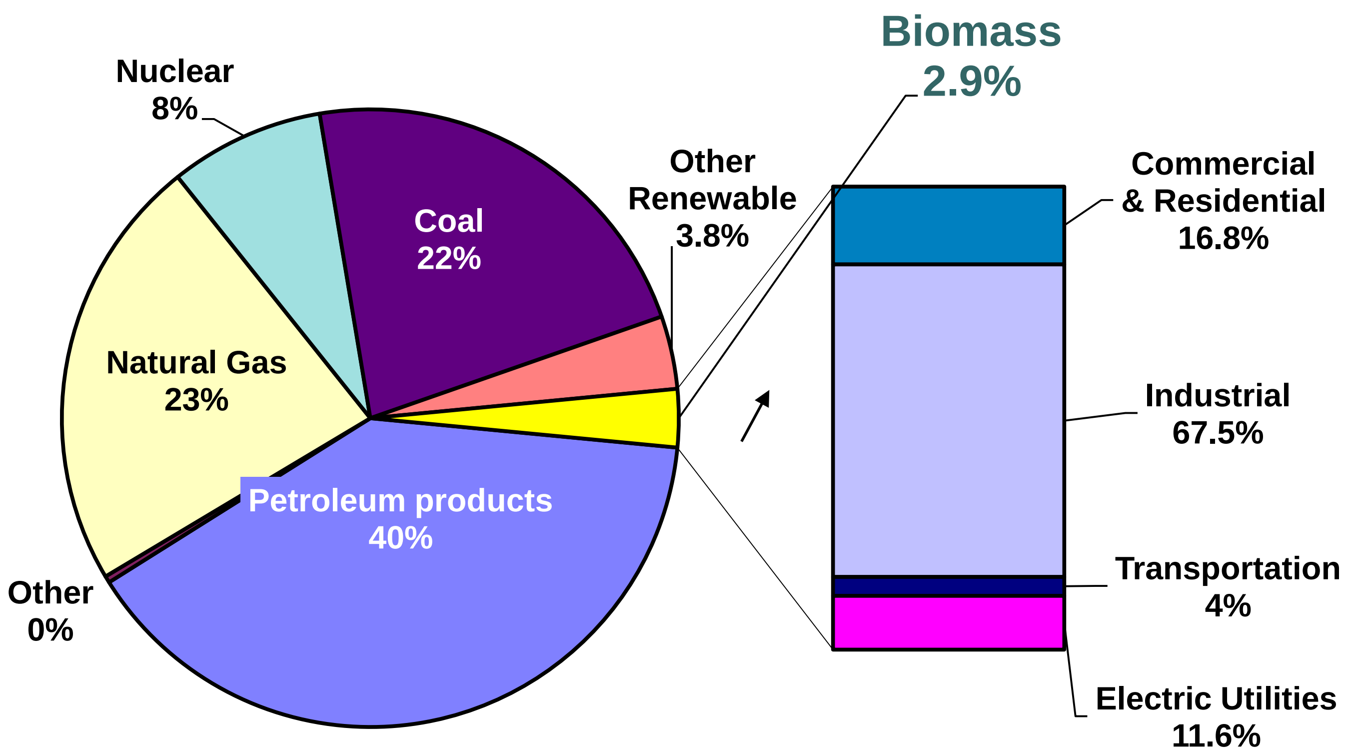
Energy Sources – Recent Years and Expected Trend.







Bioenergy (2010).



Total Consumption = 96 Quads
Biomass = 2.9 Quads

Science in Bioenergy & Bioproducts.

Feedstock production

- Plant growth and response to stress (and marginal lands use)**;**
- Higher productivity at lower input (water, fertilizer, etc.)
- Production of certain components and/or new components

=> Functional genomics; biochemistry; physiology; cellular control mechanisms; respiration; photosynthesis, metabolism, nutrient use, disease response

Biochemical pathways

=> Biocatalysis: enzyme function and regulation; enzyme engineering; catalyst reaction rates and specificity

Thermochemical pathways

=> Product-selective thermal cracking of biomass; CFD modelling

Bio products

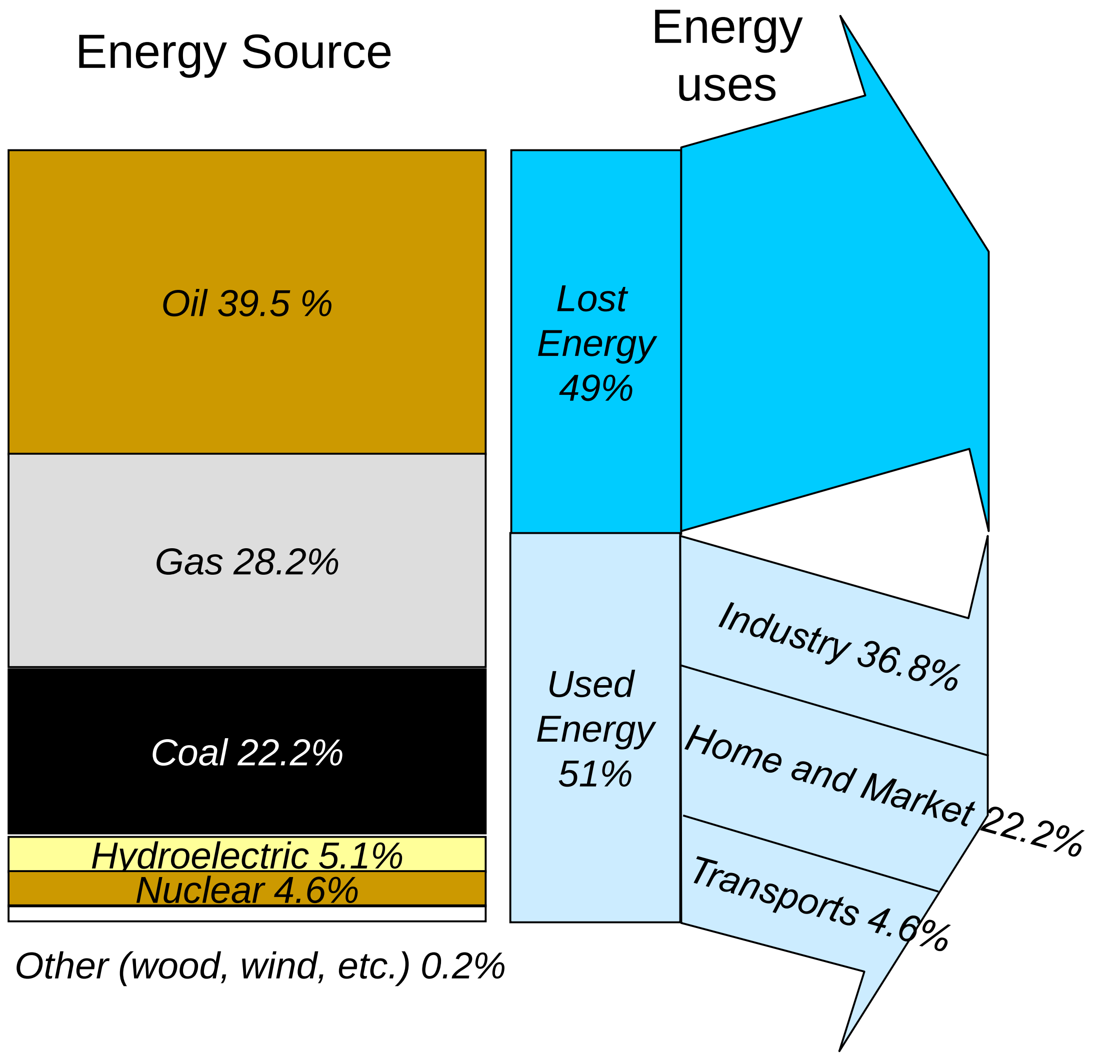
=> New and novel monomers and polymers;

- Biomass composites; => adhesion/surface science

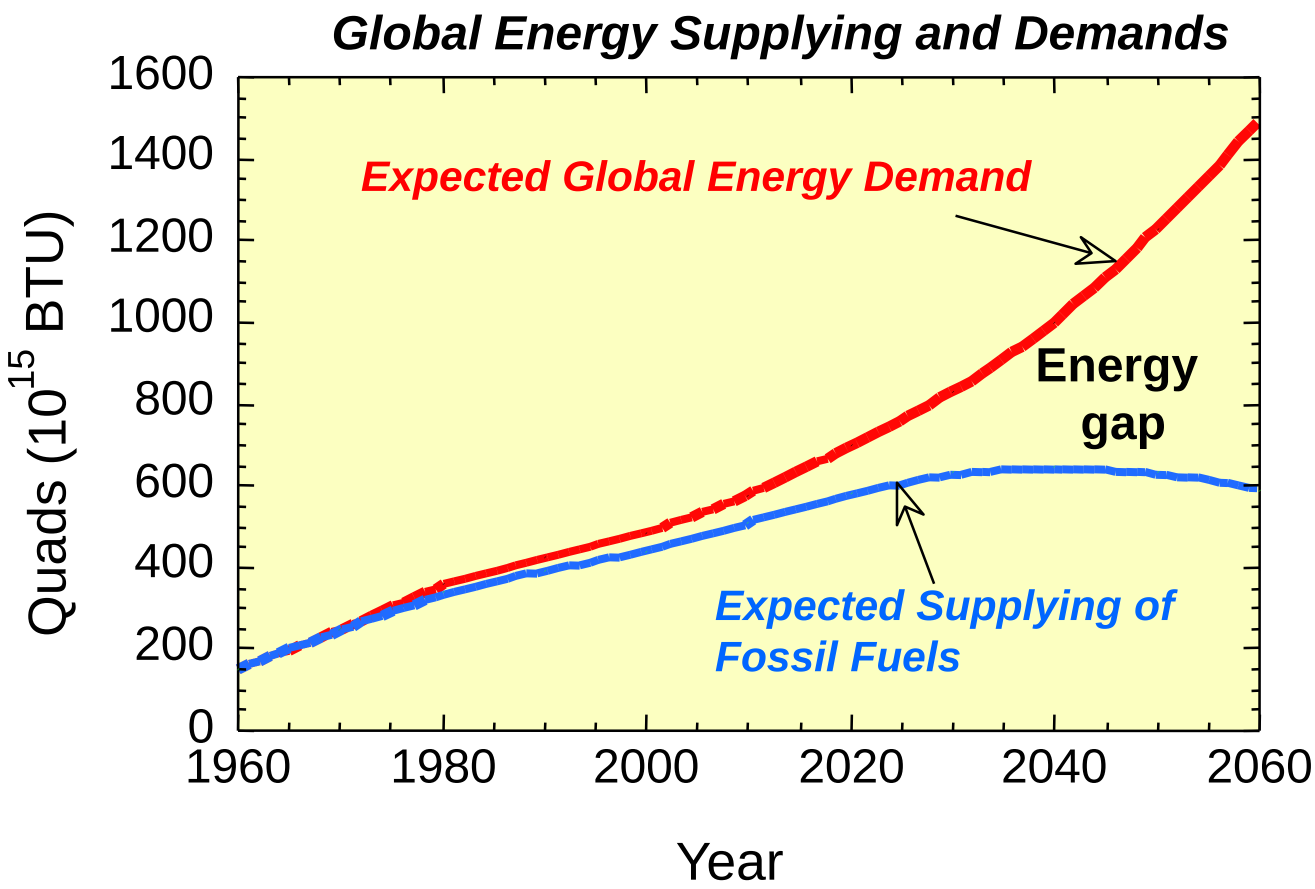
Combustion

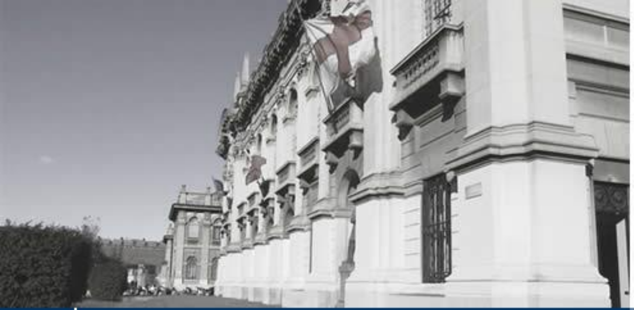
=> NOx chemistry; CFD modelling

Energy Lost from Energy Sources (2010).



The Future Energy Gap.





POLITECNICO DI MILANO

Fossil Fuels.

Non Renewable Energy Sources – Fossil Fuels.

- The term **fossil fuels** refers to the remains of plants and animals trapped in sediments which can be used as source of energy (fuels).
- The kind of sediment, the kind of organic matter, that take place as a result of burial and diagenesis, determine the kind of fossil fuel that forms
- In the ocean, microscopic phytoplankton and bacteria are the principal sources of trapped organic matter that are transformed (mainly by heat) into oil and gas.
- On land, trees, bushes, and grasses contribute most of the trapped organic matter, forming coal rather than oil or natural gas.

Fossil Fuels.

- In many marine and lake shales, burial temperatures never reach the levels at which the original organic molecules are converted into oil and natural gas.
  - Instead, an alteration process occurs in which wax-like hydrocarbon substances containing large molecules are formed.
  - This material, which remains solid, is called **kerogen**, and it is the substance in so-called oil shale.
- *Main kind of Fossil fuels*:
  - Petroleum
  - Natural Gas
  - Coal
  - Oil Shale and Tar Sands
  - Peat

Natural Gas

- 5.8×10^{7} J·kg^{-1} $\Rightarrow$ $0.6 \cdot 10^{15}$ m^{3}

Petroleum

- 4.4×10^{7} J·kg^{-1} $\Rightarrow$ $285 \cdot 10^{9}$ bbl.

Coal

- $(1.4 - 3.5) \times 10^{7}$ J·kg^{-1} $\Rightarrow$ $1490 \cdot 10^{9}$ ton

Fossil Fuels

- 1 litre of petroleum = 1 kg of coal = 1 m^{3} of natural gas

Compare this to nuclear fuels:

- 1 gram deuterium = 3 grams U-235 = 500 litres gasoline = 6 cubic meters of natural gas

N.B. Nuclear energy in 1kg of U-235 = 2,000,000 × chem. energy in 1kg of coal.

History of Automotive Engines.

1859 - Oil discovered at Drake's Well, Titusville, Pennsylvania (20 barrels per day) - 40 year supply

1876 - Premixed-charge 4-stroke engine - Otto

- 1^{st} practical ICE
- Power: 2.68 kW; Weight: 567 kg
- Comp. ratio = 4 (knock limited), 14% efficiency (theory 38%)
- Today CR = 9 (still knock limited), 30% efficiency (theory 55%)

1897 – Non premixed-charge engine - Diesel - higher efficiency due to:

- Higher compression ratio (no knock problem)
- No throttling loss - use fuel/air ratio to control power

1901 - Spindletop Dome, east Texas - Lucas #1 gusher produces 100,000 barrels per day - ensures that "2^{nd} Industrial Revolution" will be fuelled by oil, not coal or wood - 40 year supply

The Beginning of Petroleum/Biofuel Era.

First kerosene distilled from petroleum

Paris exposition – diesel engine working with peanut oil

"…the use of vegetable oils for engine fuels can appear insignificant now, but these oils can become, in future, equally important as the present petroleum and coal products." - Rudolf Diesel -

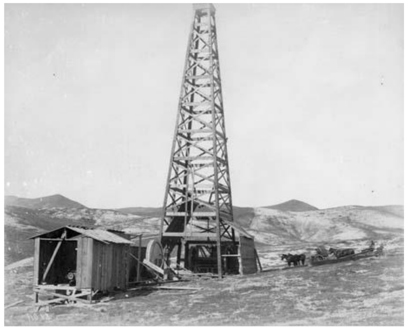
1853

First oil company formed

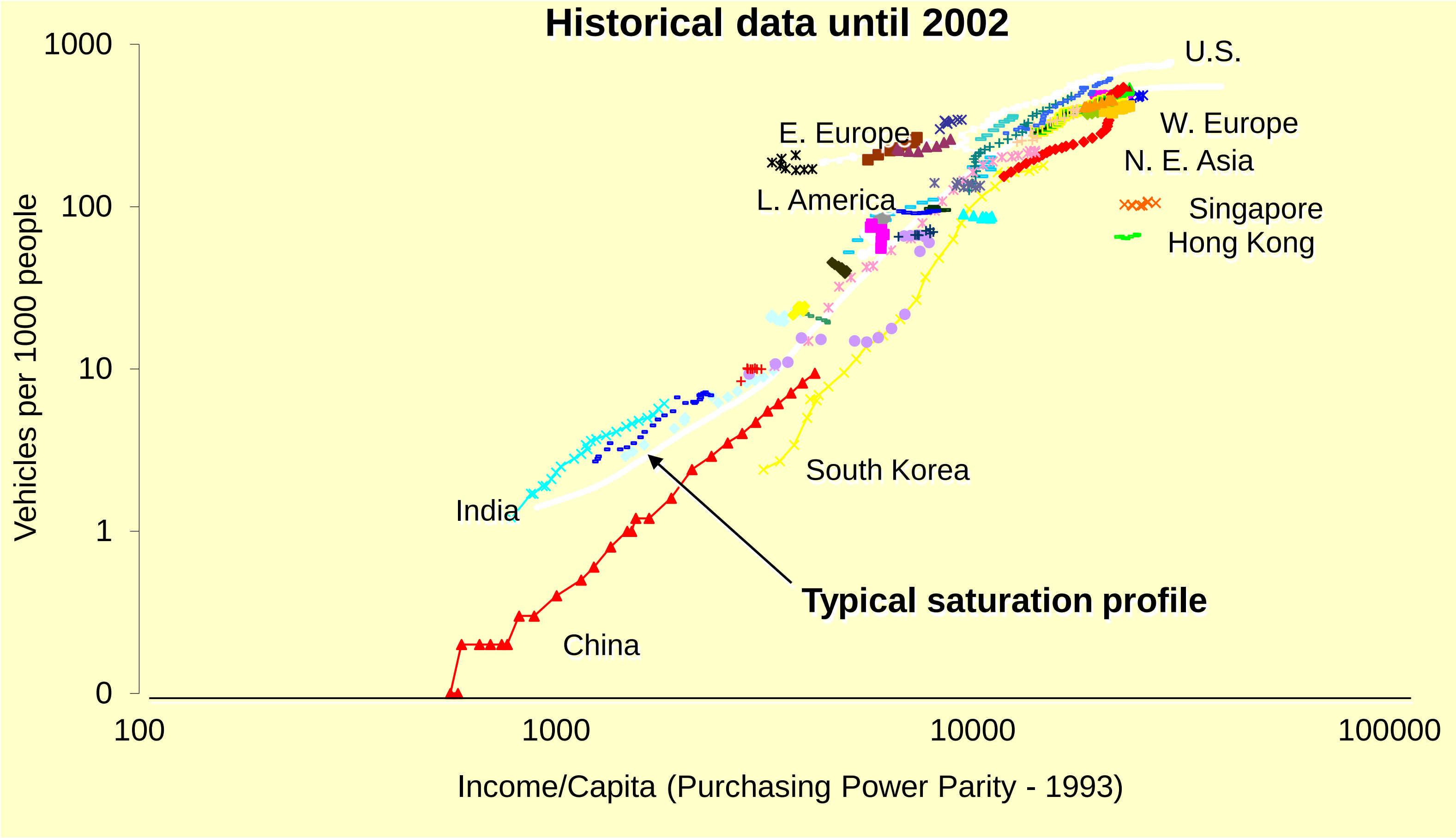
1898

1912

Brocken the monopoly of Standard Oil

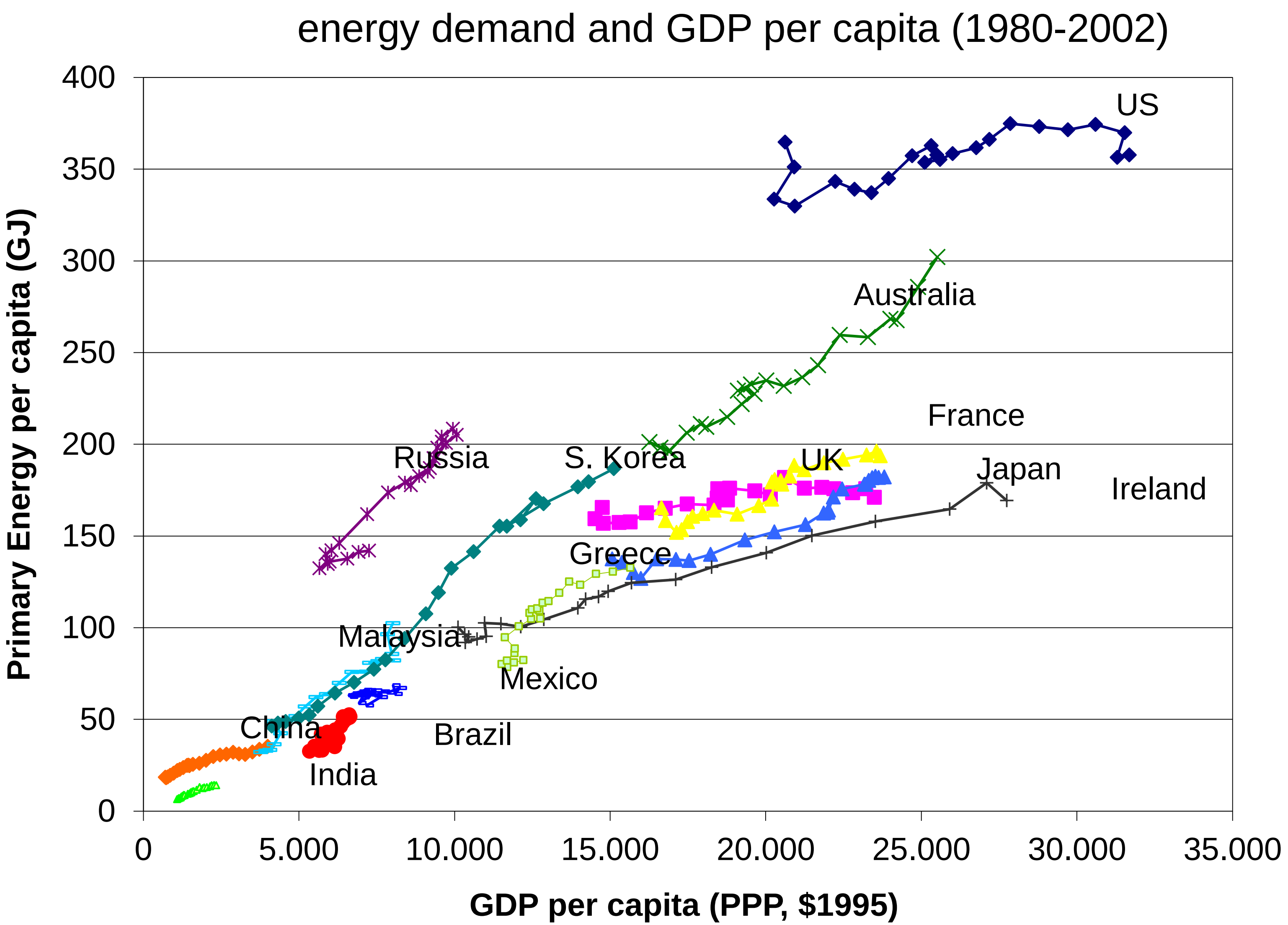


Vehicle Penetration on Market.



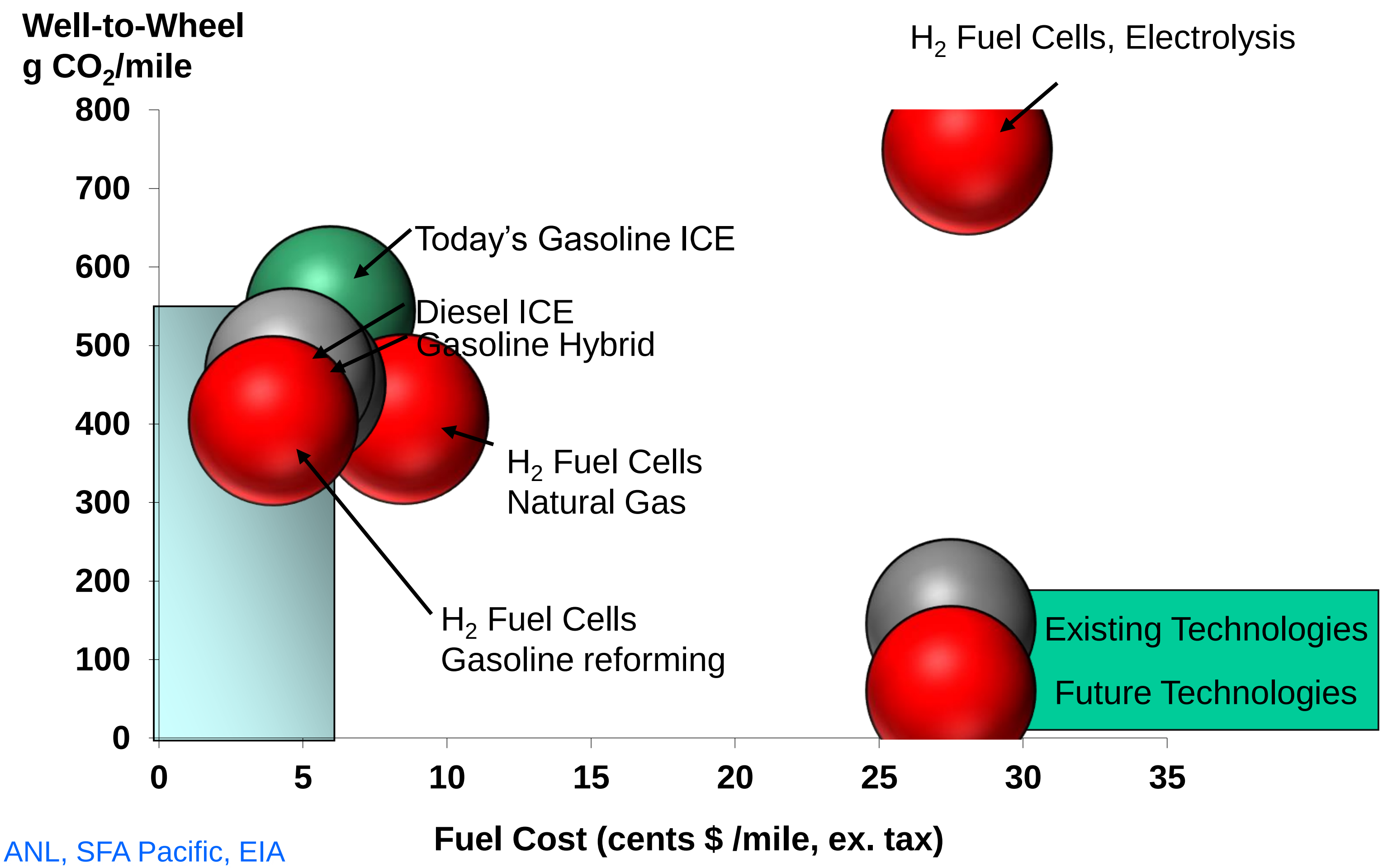
Data from Exxon

Energy Use Grows with Economic Development.



Source: UN and DOE EIA

Advanced Vehicles - Lifecycle Analyses / Operating Costs.



Source: ANL, SFA Pacific, EIA

Coal.

- Coal is the most abundant fossil fuel.
- It is the raw material for a multitude of organic chemicals, plastics, and materials.
- Through coalification, peat is converted to lignite, subbituminous coal, and bituminous coal.
    - Anthracite is a metamorphic rock.

Anthracite

- Oldest (350 million years), Highest quality (95% carbon), the cleaner coal

Bituminous

- 300 million years, Medium quality (50-80% carbon)

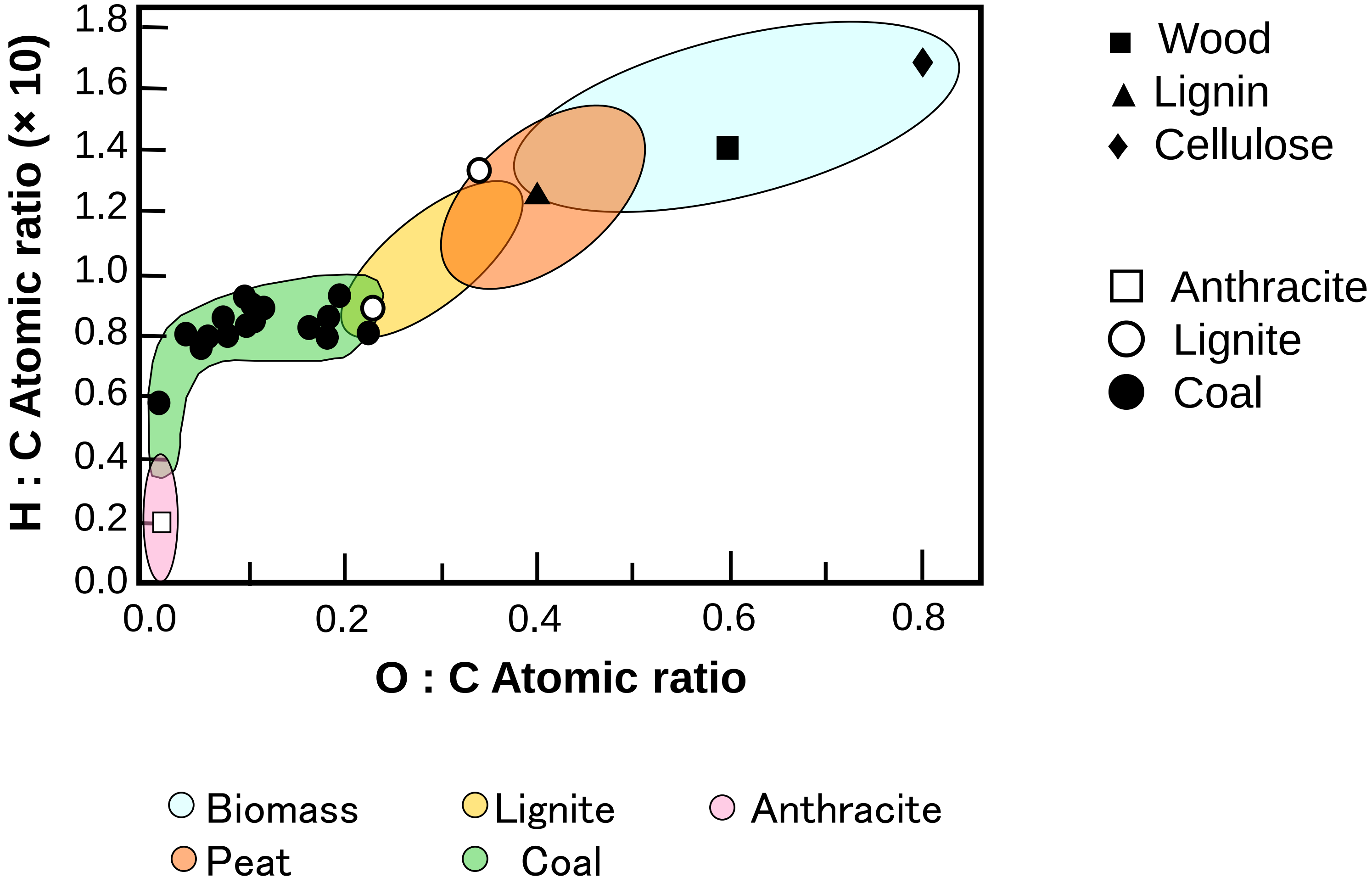
Lignite

- 150 million years, Low quality (<50% carbon)

Peat

(mix. of coals of different ranks such as brown coal, lignite, bituminous)

H:C:O Composition of Solid Fuels.



Peat.

- Peat is the partially decomposed remains of plant material, especially sphagnum moss. It is found in a wetlands environment where the addition of new plant material is faster than the decomposition of the accumulated plant material. Essential conditions to peat formation is provided in a wetlands: the plant material remains waterlogged, the temperature is low and there is a lack of oxygen both inducing a slow decomposition. “Wetlands” include floodplains, marshes, swamps, and coastal wetlands.
- Peat is the first material formed in the process that transforms plant matter into coal. As coal formation progresses, volatile materials like water are driven off, and the carbon % content of the material increases, making it increasingly dense and hard.
- The majority of the peat harvested is called reed-sedge peat. The other harvested forms are sphagnum moss, humus and hypnum moss. Formed from decaying woody plants and mosses in moist environments, usually in northern climates
- Cellulose is converted to peat by bacterial action in the absence of air (humification).
- Rate of formation: 3 cm per 100 years.
- Fresh peat contains 80 to 90% moisture, and dry peat contains 1 to 10% ashes.

Coal Formation.

- Coal is formed when peat is altered physically and chemically ("coalification“). In this process, peat undergoes several changes as a result of bacterial decay, compaction, heat and time. Peat deposits are quite varied and contain everything from pristine plant parts (roots, bark, spores...) to decayed plants, decay products and charcoal if the peat caught fire during accumulation.
- For the peat to become coal, it must be buried by sediment. Burial compacts the peat and, consequently, much water is squeezed out during the first stages of burial. Continued burial and the addition of heat and time cause the complex hydrocarbon compounds in the peat to break down and alter in a variety of ways. The gaseous alteration products (methane is one) are typically expelled from the deposit, and the deposit becomes more and more carbon-rich as the other elements disperse. The stages of this trend proceed from plant debris through peat, lignite, sub-bituminous coal, bituminous coal, anthracite coal to graphite (a pure carbon mineral).
- Because of the amount of squeezing and water loss that accompanies the compaction of peat after burial, it is estimated that it took 3 meter of original peat material to produce 0.3 meter of bituminous coal. The peat-to-coal ratio is variable and dependent on the original type of peat.

http://www.uky.edu/KGS/coal/coalform.htm

Coal Formation (2).

Dead plants

- Slow decomposition by aerobic bacteria yielding CO_2, CH_4, etc.
- Anaerobic decomposition when covered by mud for long time and slow chemical changes due to high pressure and temperature.

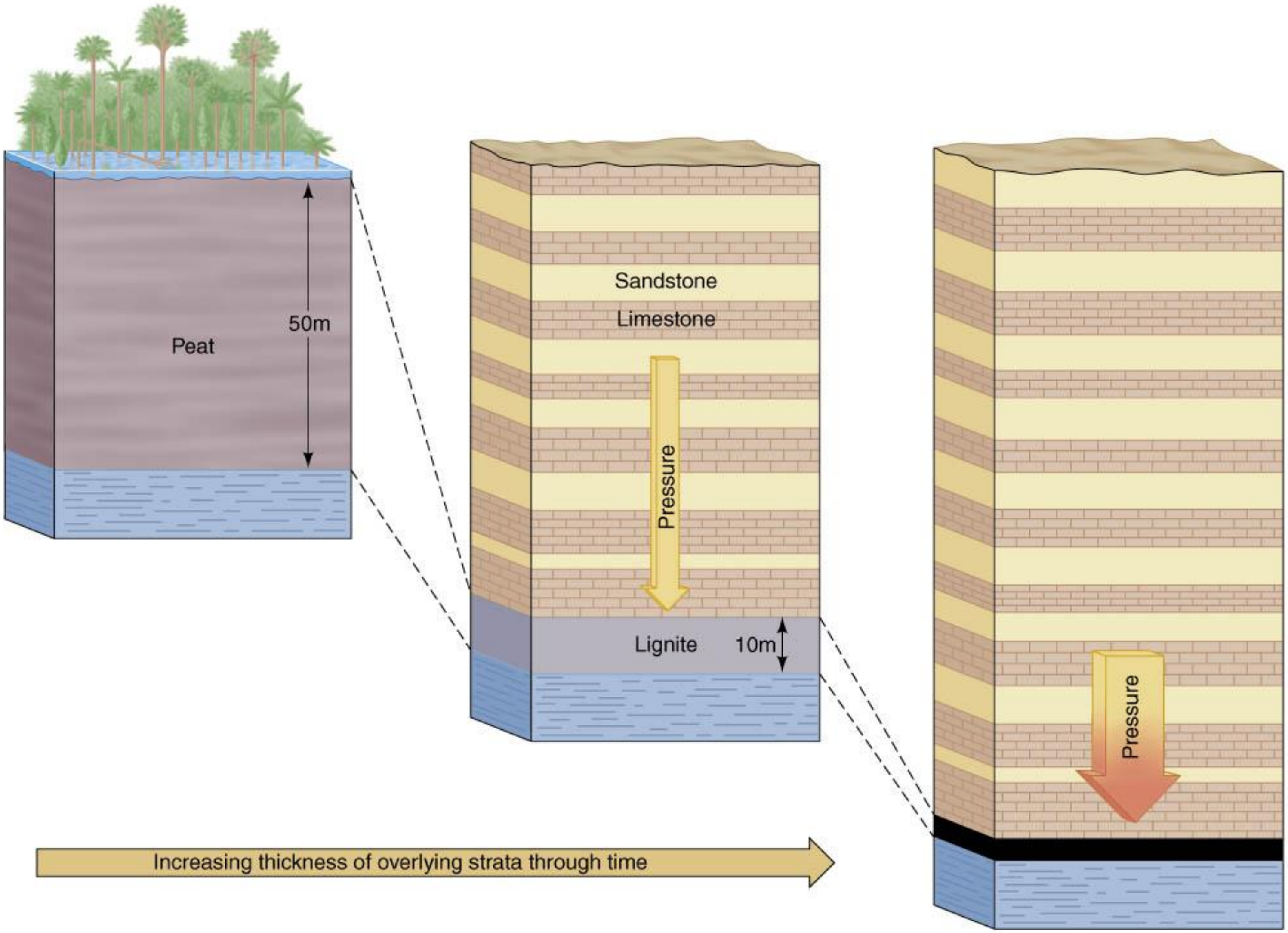
Occurs in stratified deposits, 0.7-33 m thick in average depth of about 100 m. A coal seam is a flat, lens-shaped body having the same surface area as the swamp in which it originally accumulated.

Peat formation has been widespread and more or less continuous from the time land plants first appeared about 450 million years ago, during the Silurian Period.

The greatest period of coal swamp formation occurred during the Carboniferous and Permian periods, when Pangaea existed.

The second great period of coal deposition peaked during the Cretaceous period but commenced in the early Jurassic and continued until the mid-Tertiary.

Coal Formation (3).



Non Renewable Energy Sources – Shale Oil.

In several rocks of marine and lake origin, the contact temperatures does not reach levels at which the original organic molecules are converted in oil and natural gas.

- An alteration process take instead place in which carbon bearing mudstone or marlstone containing organic **kerogen** (HC wax-like substance) are formed.
- 40 - 140 litters of petroleum can be recovered from a ton of rock, but the extraction costs are high.

Reptile: Notosaurus

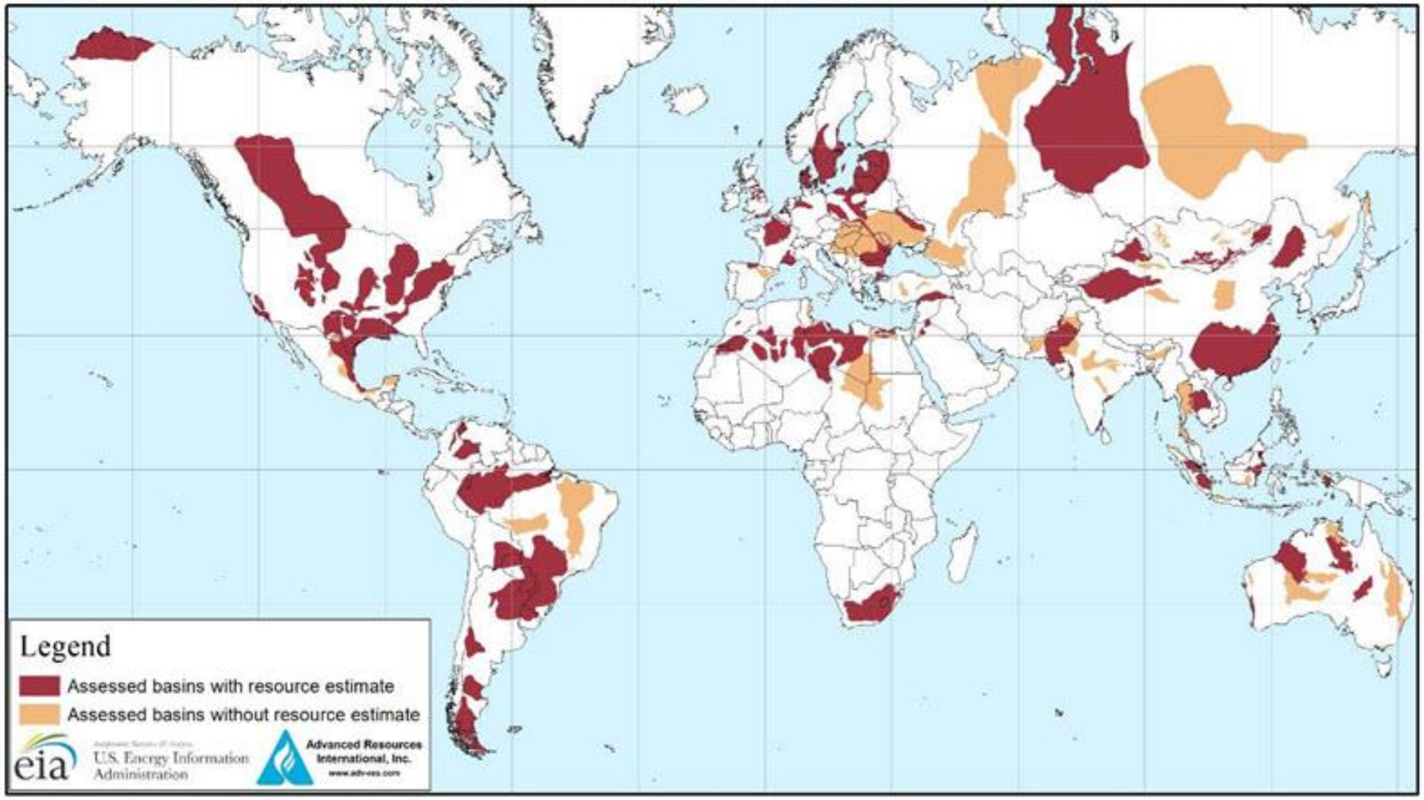
From Besano Bituminous Shale

Shale Oil – Problems.

- **Oil shale** was formed millions of years ago by deposition of silt and organic debris on lake beds and sea bottoms. Over long periods of time, heat and pressure transformed the materials into oil shale in a process similar to the oil; however, the heat and pressure were not as great.
- Oil shale generally contains enough oil that it will burn without any additional processing, and it is known as "the rock that burns".
- Relatively common all around the word, their reserves are higher than petroleum
- Must be extracted, retorted (heated to 540°C to drive out the HC) and refined.
  - High sulfur content
  - Requires a lot of water for processing
  - Disposal of spent shale a problem
  - Cost is high, except for the best quality shale oil, but now mined in growing amount.

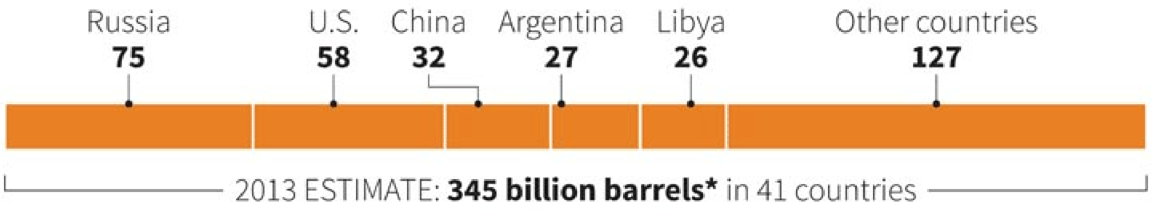
Recently Assessed Shale Oil Reserves.

Figure 1. Map of basins with assessed shale oil and shale gas formations, as of May 2013



Source: United States basins from U.S. Energy Information Administration and United States Geological Survey; other basins from ARI based on data from various published studies.

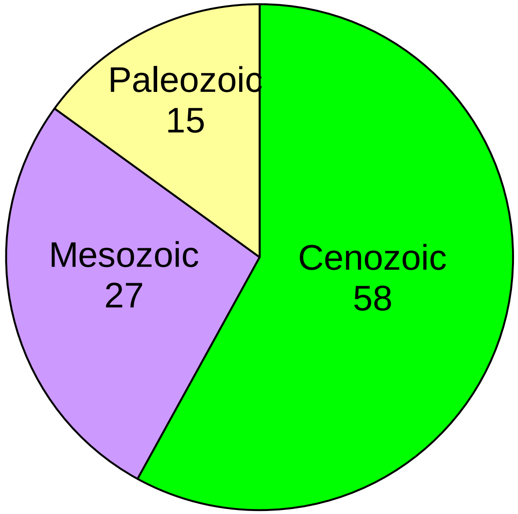
Source: US EIA



Tar Sands.

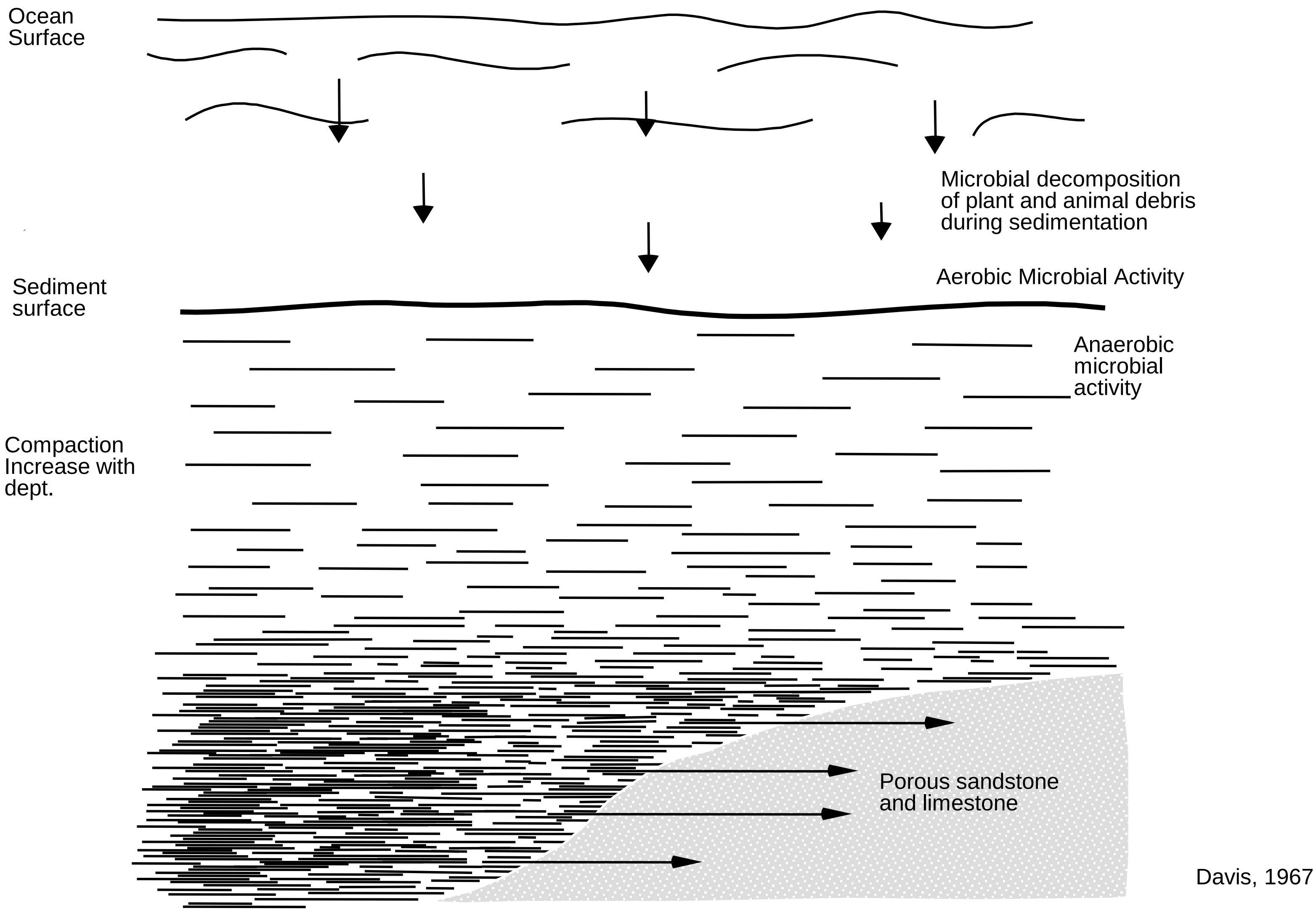
- **Tar sands** (also referred to as oil sands) are a combination of clay, sand, water, and **bitumen**, a heavy black viscous oil.
- Tar sands can be mined and processed to extract the oil-rich bitumen, which is then refined into oil. Only oil shale that produces 40 litters of oil per ton are worth mining.
- The bitumen in tar sands cannot be pumped from the ground in its natural state; instead tar sand deposits are mined, usually using strip mining or open pit techniques, or the oil is extracted by underground heating with additional upgrading. Must be mined and transported for processing.
- Processing involves extraction of bitumen by steam and hot water followed by refining.
- Main deposits in Alberta, Canada
- Production prices started to be comparable to that of crude oil.

Petroleum Origin.

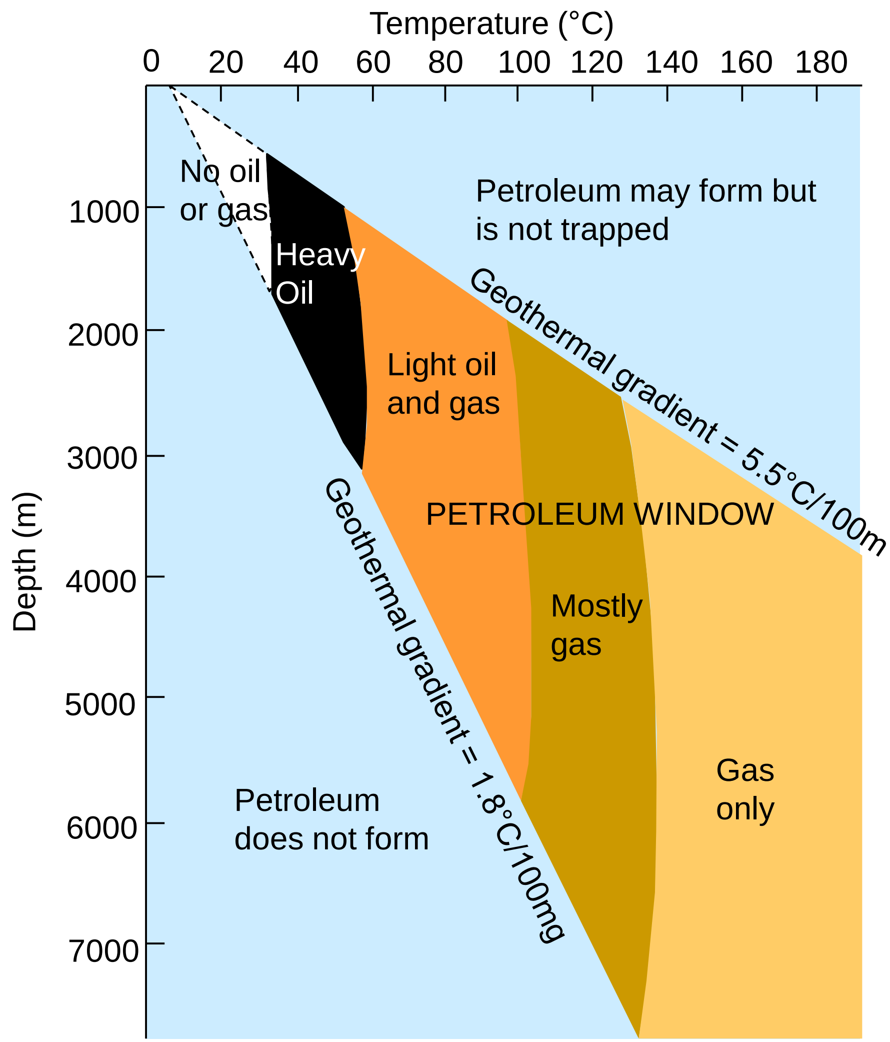


- Crude oil is found in sedimentary rock and is the product of the decomposition of the organic matter trapped in sediments, much of it is adsorbed to inorganics.
- Because it is lighter than water, the oil tends to glide upward, until it encounters a trap.
- Petroleum migration is analogous to groundwater migration. When oil and gas are squeezed out of the shale in which they originated and enter a body a sandstone or limestone, they can migrate easily.
- Nearly 60 percent of all the oil and gas discovered so far has been found in strata of Cenozoic age.
- Ultimate crude reserves estimated to be 8×10^8 barrels (or approximately 120 km^3)
- The amount of sedimentary rock is estimated at 80,000,000 km^3

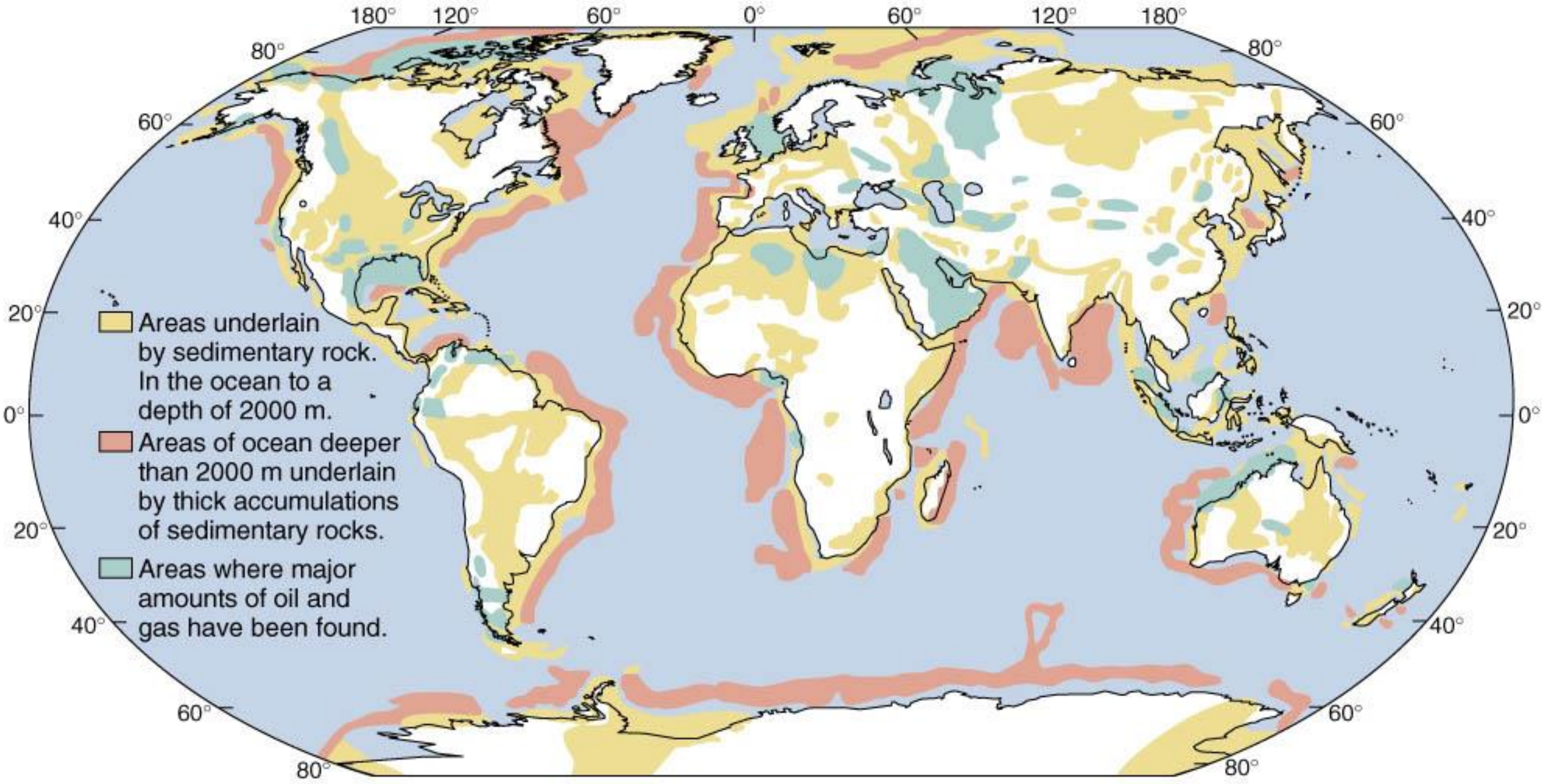
Description of Crude Oil Formation.



Origin of Crude Oil.



Distribution of Sedimentary Rocks and Hydrocarbon Deposits.

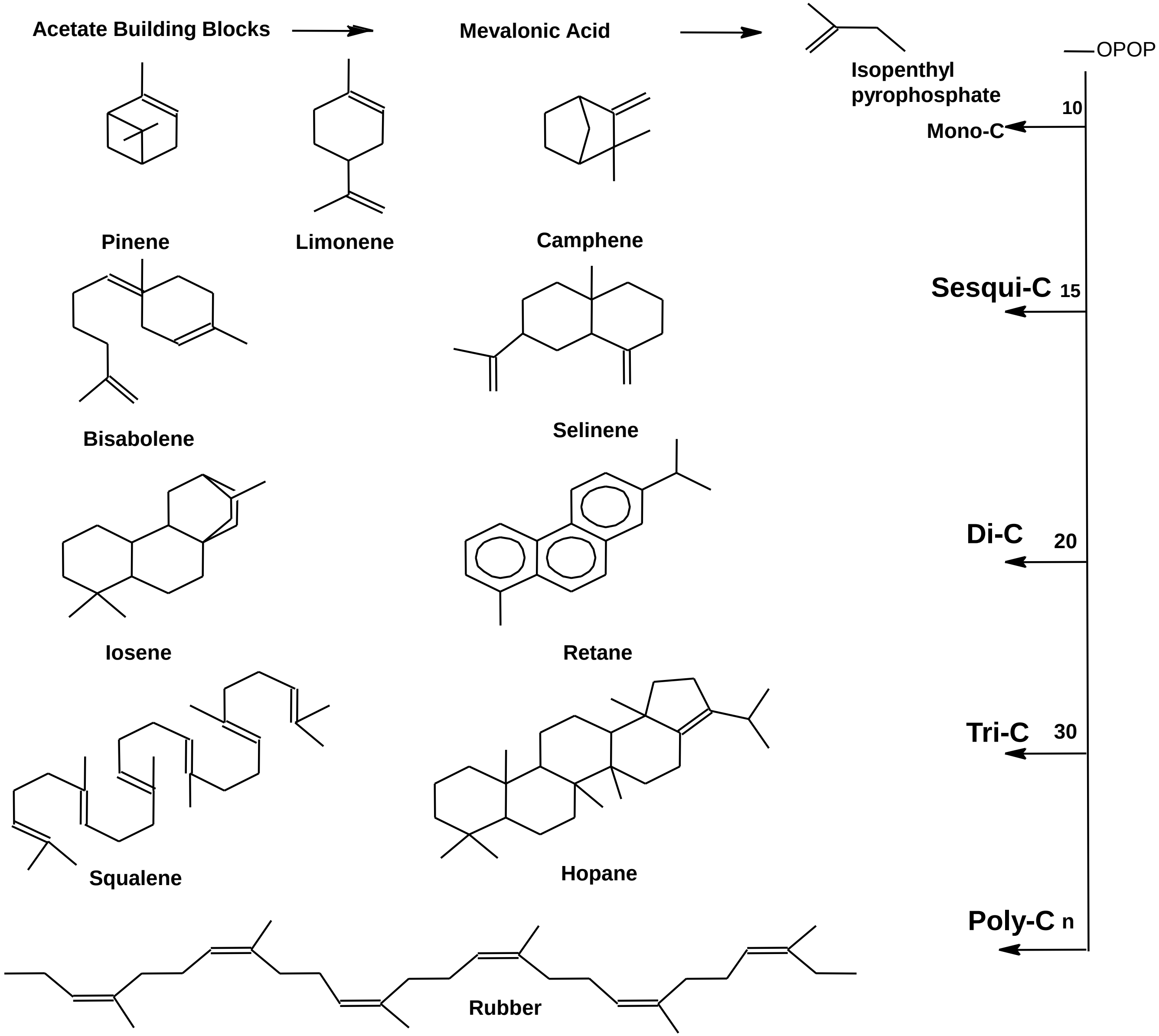


Oil Formation Process.

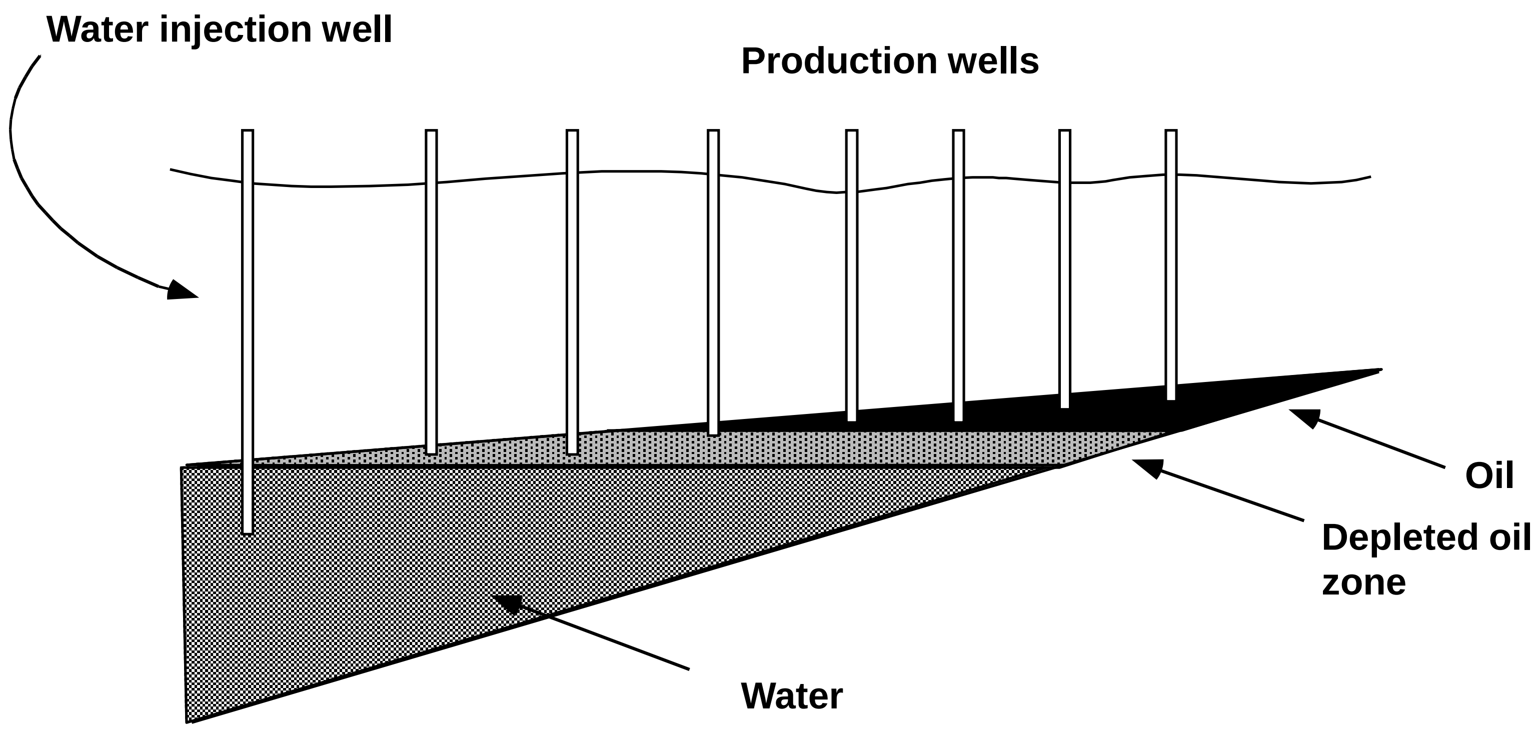
BIOPOLYMERS	Carbohydrates, Proteins Lipids, Lignin ↓	↑
	MICROBIAL ALTERATION, HYDROLISIS ↓	**DIAGENESIS**
BIOMONOMERS	Sugars, Amino acids, Fatty acids, Phenols ↓	↓
	CONDENSATION, MAILLARD REACTION, DEAMINATION, REDUCTION, CYCLIZATION, POLYMERIZATION ↓	
GEOPOLYMERS	Nitrogenous and humic complexes ↓	**50°C (122°F)** ↑
	THERMOCATALYTIC CRACKING, DECARBOXYLATION, HYDROGEN DISPROPORZIONATION ↓	**CATAGENESIS** ↓
GEOMONOMERS	**Petroleum Hydrocarbons and low molecular weight Organic Compounds** ↓	**200°C (392°F)** ↑
	TERMOCRACKING ↓	**METAMORPHISM** ↓
END PRODUCTS	**Gas and Pyrobitumens**	

Hunt, 1979

Terpene Biomarkers.

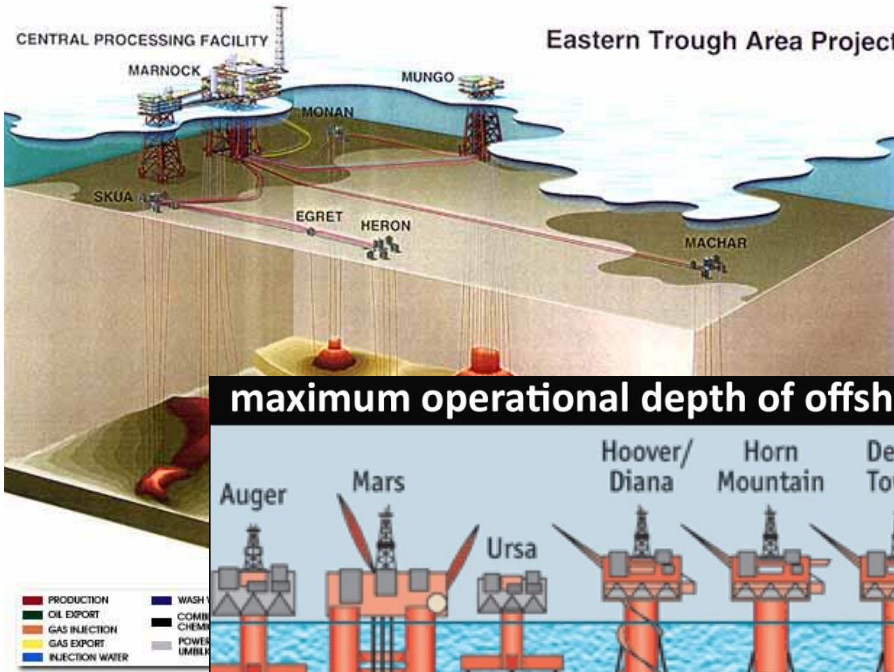


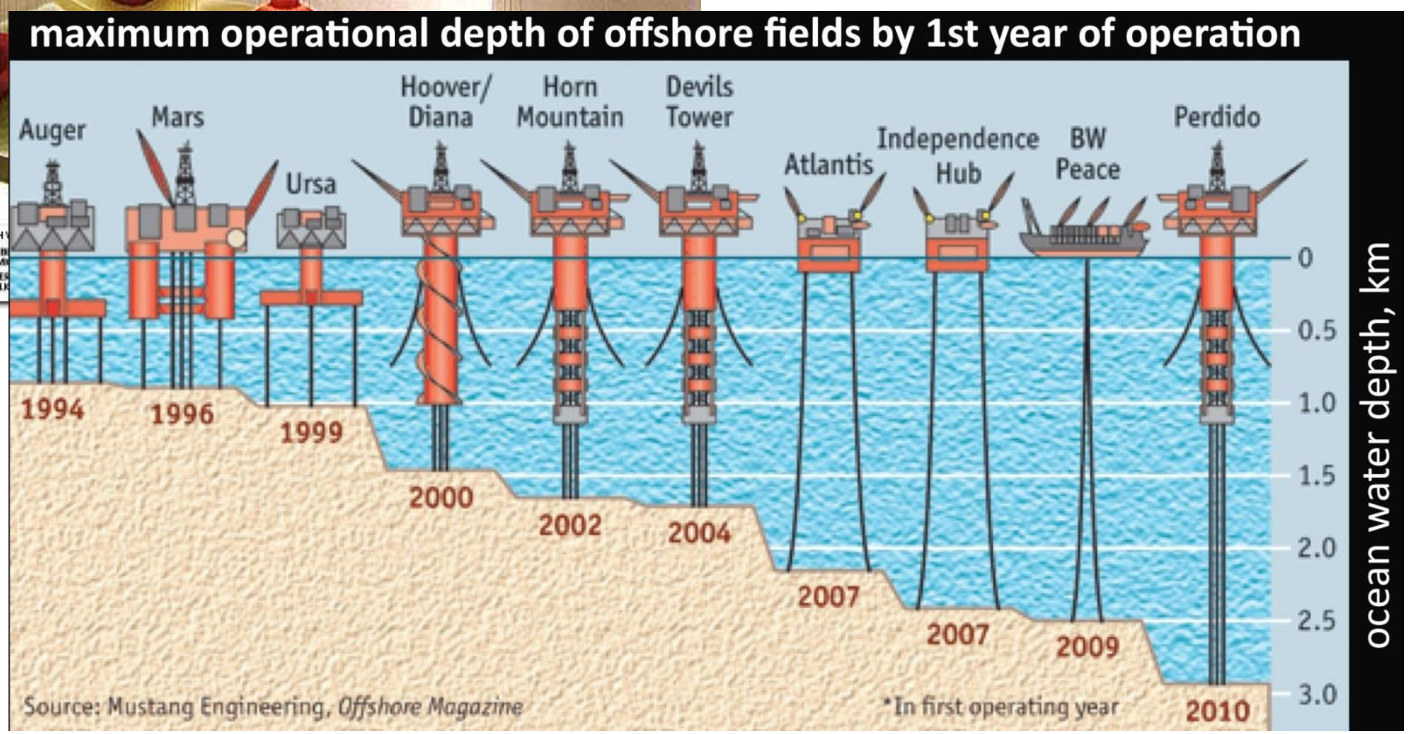
Crude Production.



Davis, 1967

Offshore Process.

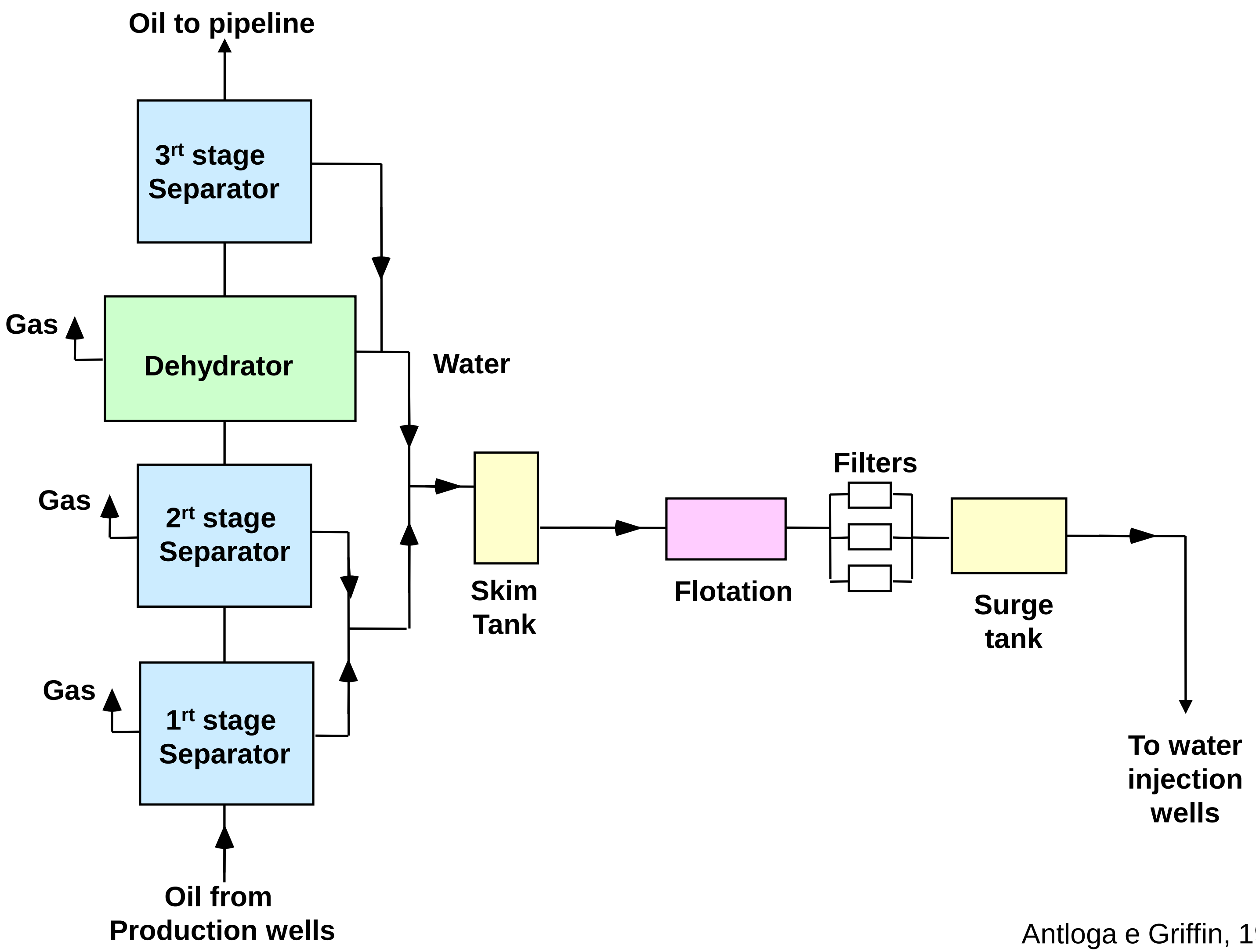




Gas Transformation Technology.

Petronas/Shell B11 Platform - First commercial application of the revolutionary Twister Supersonic Gas Processing technology.

Crude Processing.



Antloga e Griffin, 1985

Transportation and Refining.

Transportation:

- Pipelines
- Shipping
- Trucks

Refining

- Distillation
- Cracking
- Gasoline, Fuel Oils, Lube Oils, Asphalts

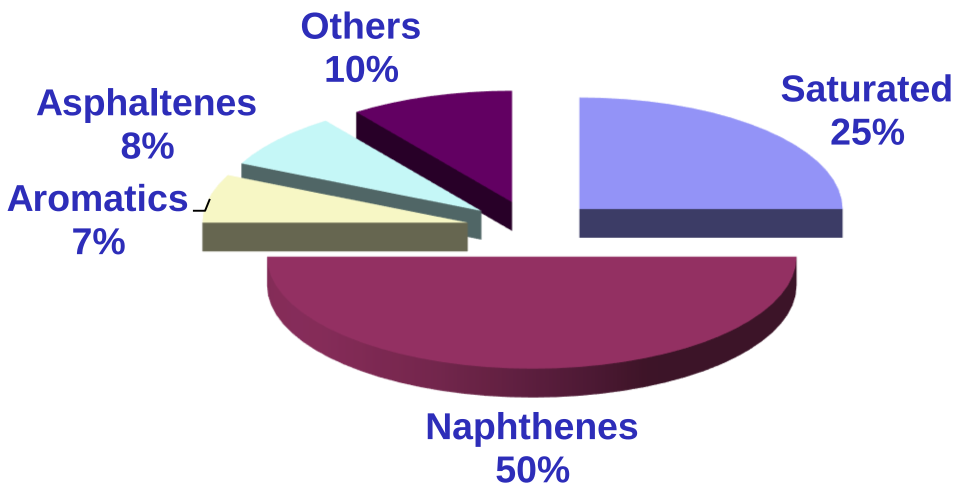
Crude Oil Classification.

OIL

SATURATED
- n-alkanes C_5 - C_{44}
- branched alkanes
- cycloalkanes (naphthenes)

AROMATICS
- Light aromatics
- Condensed aromatics

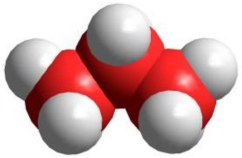
ASPHALTENES
- compound containing: nitrogen, oxygen, sulfur

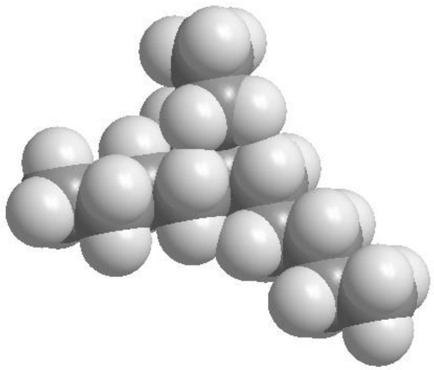


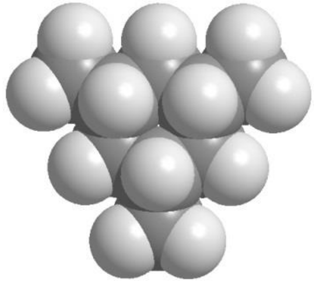
Gravity API = 35°

Saturated (or aliphatic) fraction

- n-alkanes (biodegradation up to C44)
- branched alkanes (more branching more resistant)
- cycloalkanes (naphthenes) (very resistant)
  - complex alicyclic compounds are the most persistent components in an environmental release



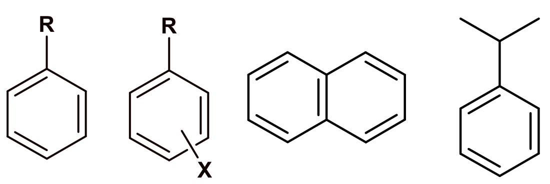


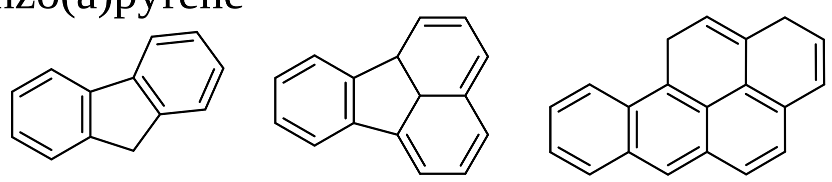


Aromatic Fraction

- light aromatics are subject to evaporation and microbial degradation in the dissolved state
  - condensed ring aromatics are subject to degradation by a similar mechanism as the aromatics
    - more rings more resistance
    - naphthalene degrades 1000 times faster than benzo(a)pyrene

Aromatici	
EC6 – EC8	Benzene, toluene, ethybenzene, xilenes
EC9 – EC16	Isopropylbenzene, naphthalene
EC16 – EC30	Fluorene, Fluoranthene, benzo(a)pyrene



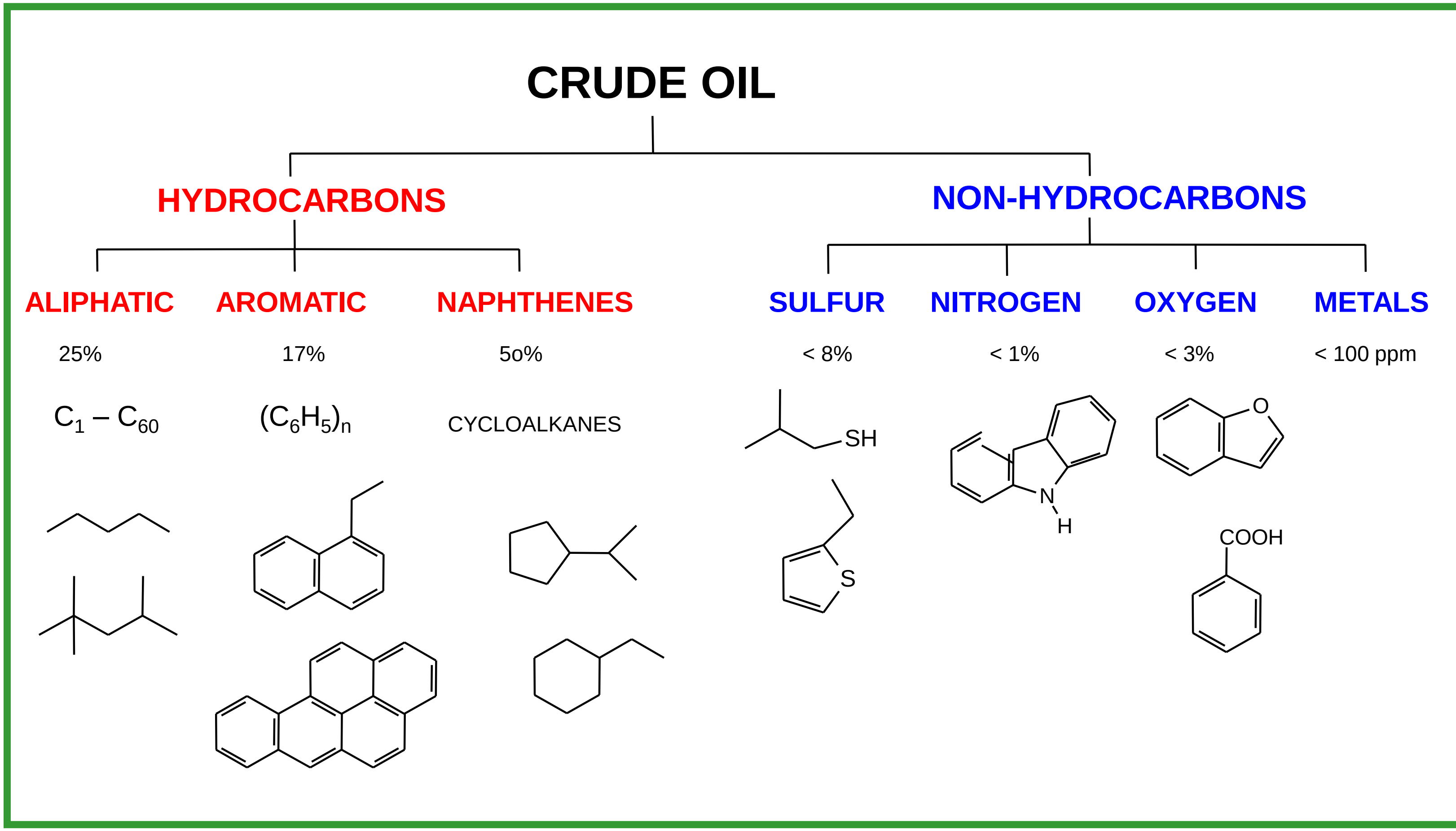


Gross Composition of Crude Oil – III.

Asphaltic or polar fraction

- Little is known about this fraction because of poor analytical techniques
- Several high molecular weight compounds containing heteroatoms and also metals are present
- A similar material can be extracted from bituminous shale (porous rocks) oil-soaked made by highly boiling fraction of complex hydrocarbons (bitumen).

Crude Oil Composition.



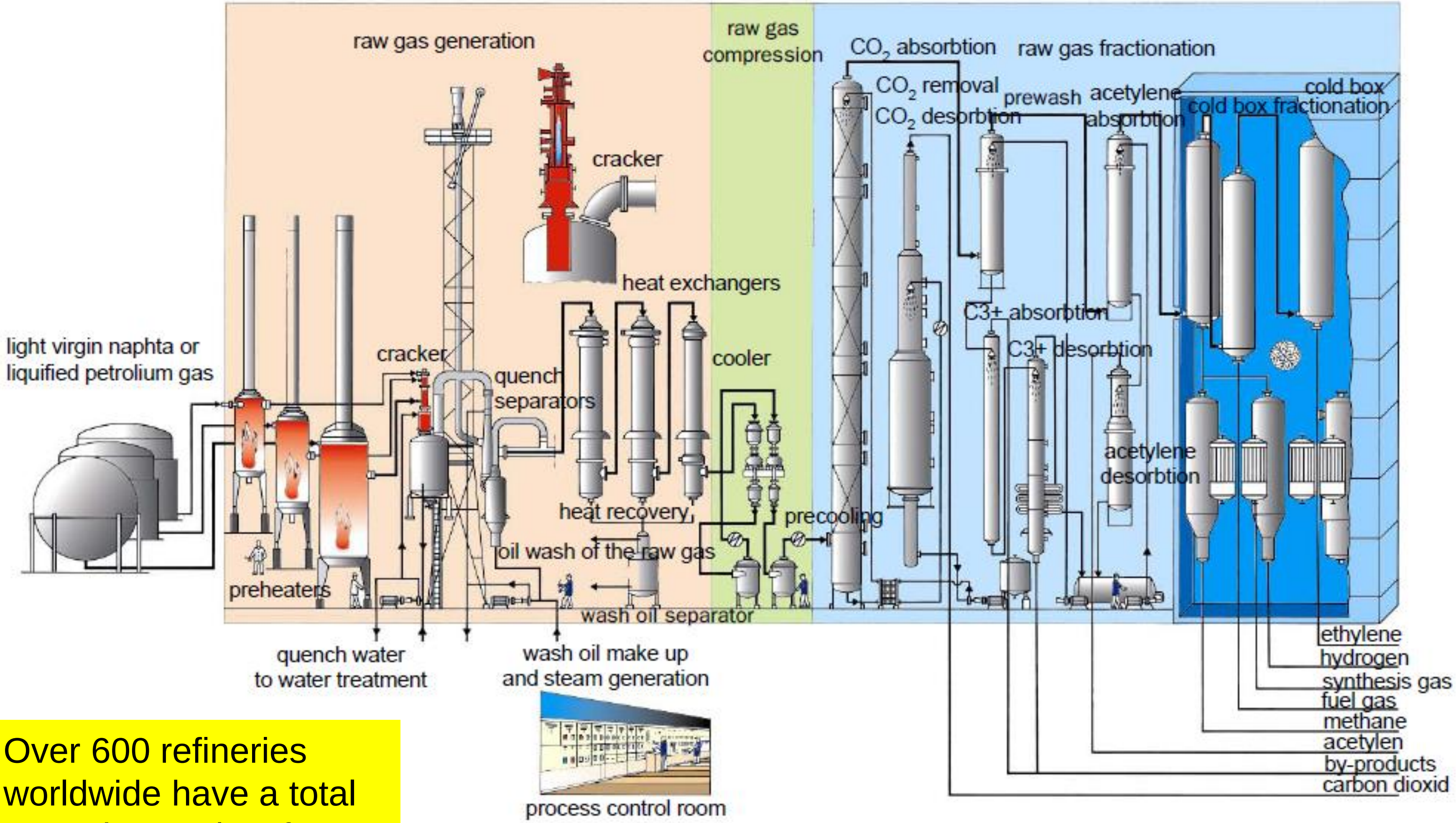
Composition of a 35° API Gravity Crude Oil.

Molecular Size	Volume percent
Gasoline (C_5 to C_{10})	27
Kerosene (C_{11} to C_{13})	13
Diesel fuel (C_{14} to C_{18})	12
Heavy gas oil (C_{19} to C_{25})	10
Lubricating oil (C_{26} to C_{40})	20
Residuum (>C_{40})	18
Total	100

Molecular type	Weight percent
Paraffins	25
Naphthenes	50
Aromatics	17
Asphaltics	8
Total	100

Hunt, 1979

The Petrochemical Feed Stock (flow sheet).



Over 600 refineries worldwide have a total annual capacity of more than $3500 \cdot 10^6$ tones

http://lorien.ncl.ac.uk/ming/distil/distil0.htm
http://science.howstuffworks.com/oil-refining.htm

Refining Operations.

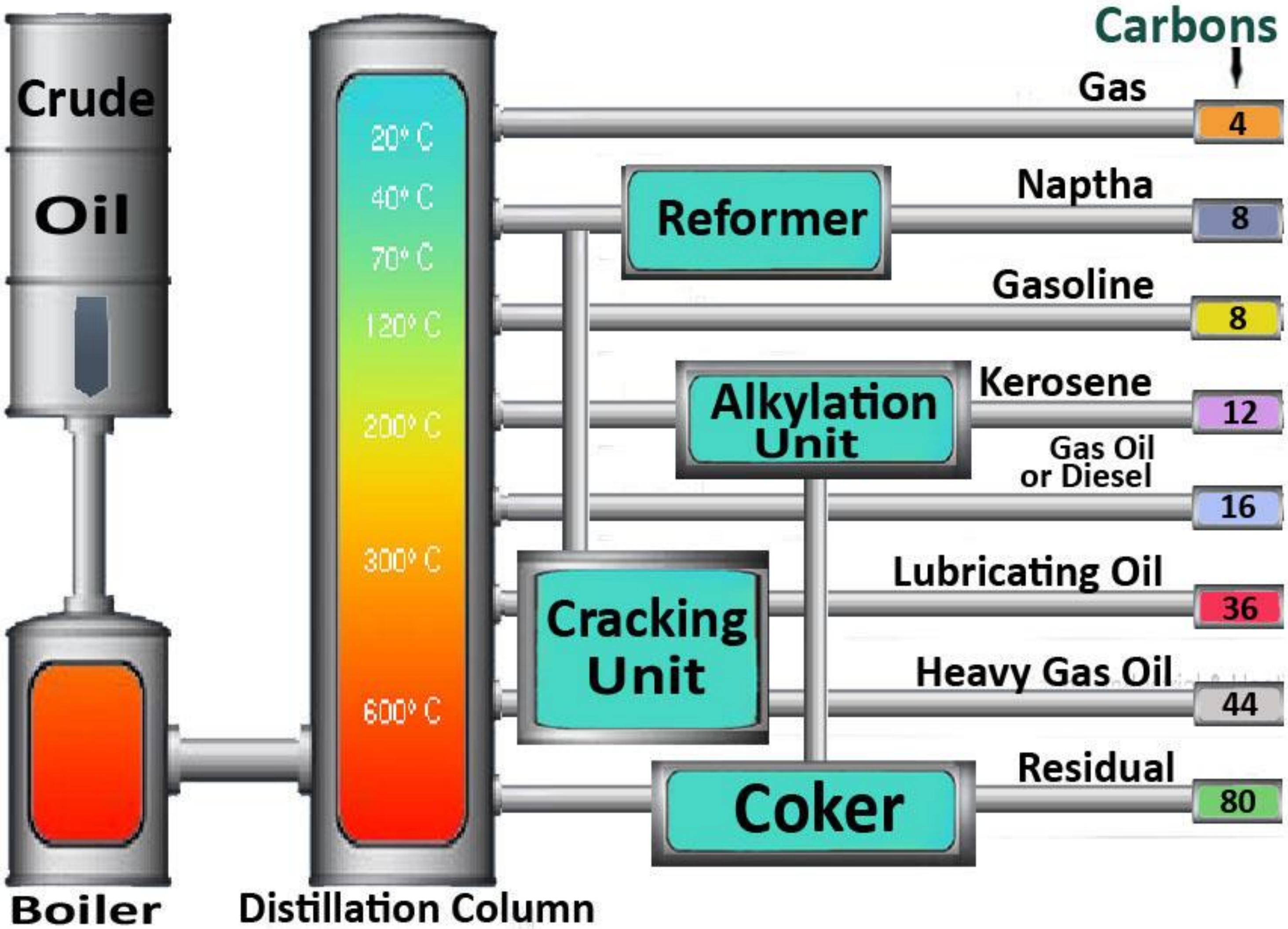
Petroleum refining processes and operations can be separated into five basic areas:

- **Fractionation** (distillation): separation of crude oil in distillation towers (atmospheric and vacuum) into groups of hydrocarbon compounds of differing boiling-point ranges called “fractions”; or “cuts”.
- **Conversion Processes :** change the structure of hydrocarbon molecules and include: :
  - Decomposition (fragmentation) by thermal and catalytic cracking;
  - Unification (combination) through alkylation and polymerization; and
  - Alteration (rearrangement) with isomerization and catalytic reforming.
- **Treatment Processes** to prepare hydrocarbon streams for additional processing or finished products. Treatment may include removal or separation of aromatics and naphthenes, impurities and undesirable contaminants. Treatment may involve chemical or physical separation e.g. dissolving, absorption, or precipitation using a variety and combination of processes including desalting, drying, hydrodesulfurizing, solvent refining, sweetening, solvent extraction, and solvent dewaxing.

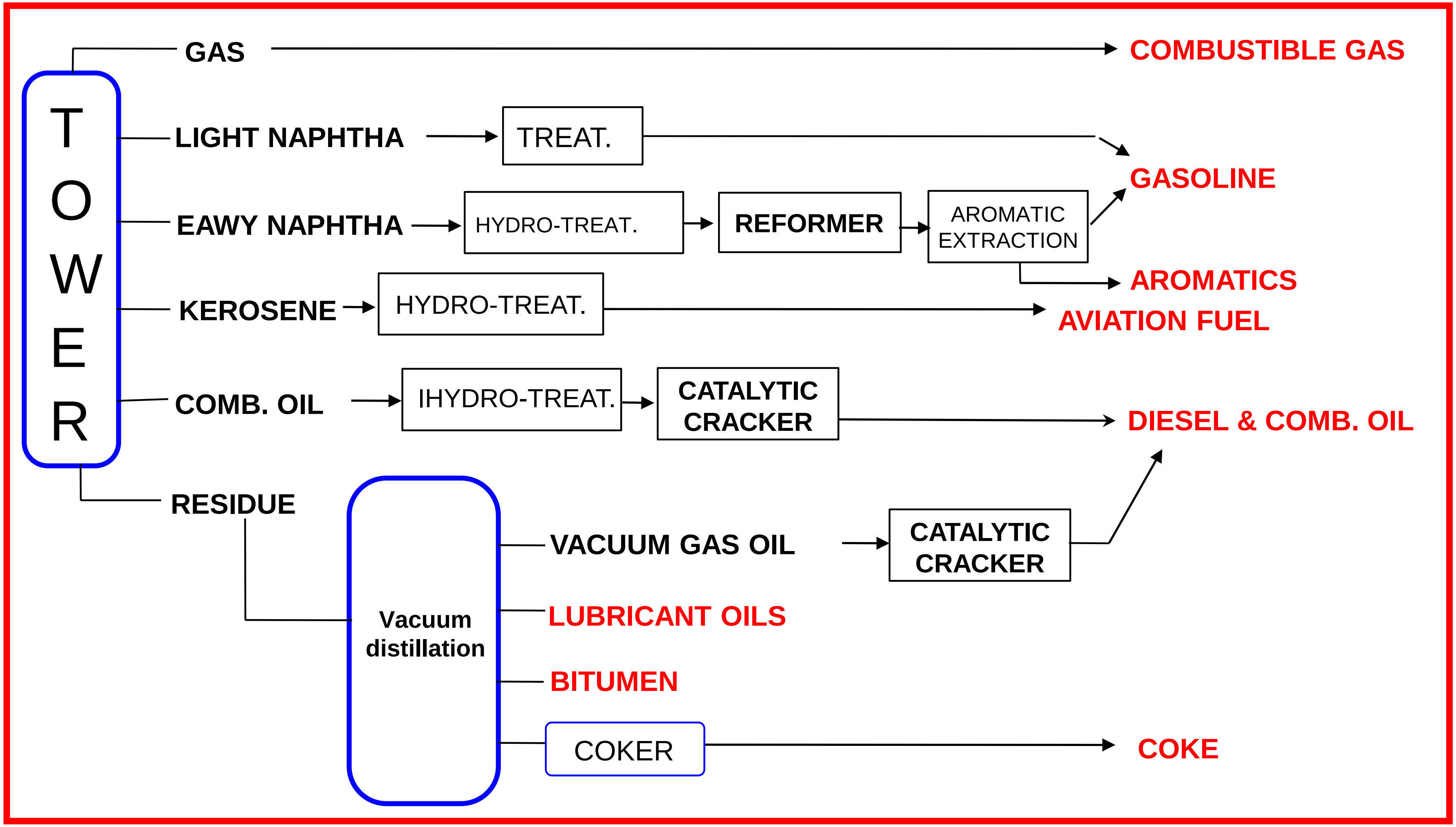
Refining Operations (2).

- **Formulating and Blending** is the process of mixing and combining hydrocarbon fractions, additives, and other components to produce finished products with specific performance properties.
- **Other Refining Operations** include:
  - light-ends recovery;
  - sour-water stripping;
  - solid waste, process-water and wastewater treatment;
  - cooling, storage and handling and product movement;
  - hydrogen production;
  - acid and tail-gas treatment;
  - sulfur recovery.
- **Auxiliary Operations and Facilities** include:
  - light steam and power generation;
  - process and fire water systems;
  - flares and relief systems;
  - furnaces and heaters;
  - pumps and valves;
  - supply of steam, air, nitrogen, …
  - alarms and sensors;
  - noise and pollution controls;
  - sampling, testing, analyses, Lab.;
  - control room;
  - maintenance; and
  - administrative facilities.

Crude-oil Refining.



Crude Oil Reforming.



Conversion Reactions.

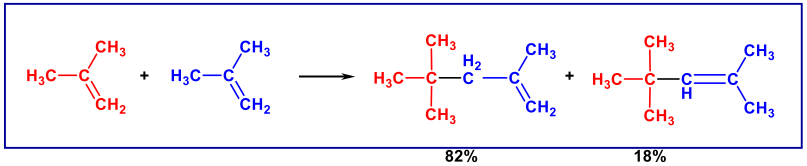
- **BREAKING**
  - THERMAL
  - CATALYTIC

$$C_7H_{15}\text{-}C_{15}H_{30}\text{-}C_7H_{15} \longrightarrow C_7H_{10} + C_7H_{14} + C_{15}H_{30}$$

C_7H_{10}: gasoline; C_7H_{14}: gasoline additive; $C_{15}H_{30}$: recycle

- **COMBINAT.**
  - ALKYLATION
  - POLYMERIZATION

$$CH_3\text{-}CH_2\text{-}CH_3 + CH_2\text{=}CH\text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{--}CH_2CH_2CH_2CH_3$$

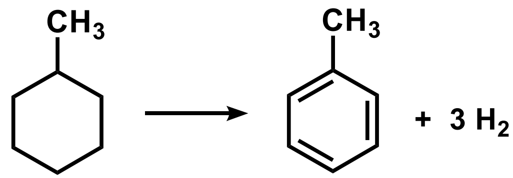


- **REARRANGEMENT**
  - REFORMING
  - ISOMERIZATION

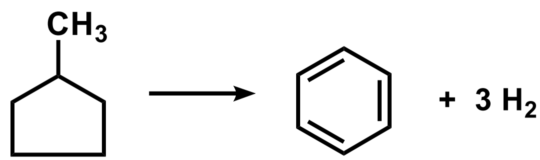
Dehydrogenation
Dehydroisomerization
Isomerization
Dehydrocyclization
Hydrocracking

Catalytic Reforming – Conversion Reaction.

Dehydrogenation of cycloalkanes and aromatics



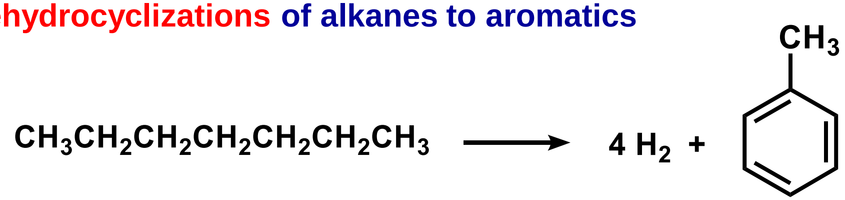
Dehydroisomerizations of cyclopentanes to aromatics



Isomerization to branched alkanes

$$CH_3CH_2CH_2CH_2CH_3 \longrightarrow H_3C{-}CH(CH_3){-}CH_2{-}CH_3$$

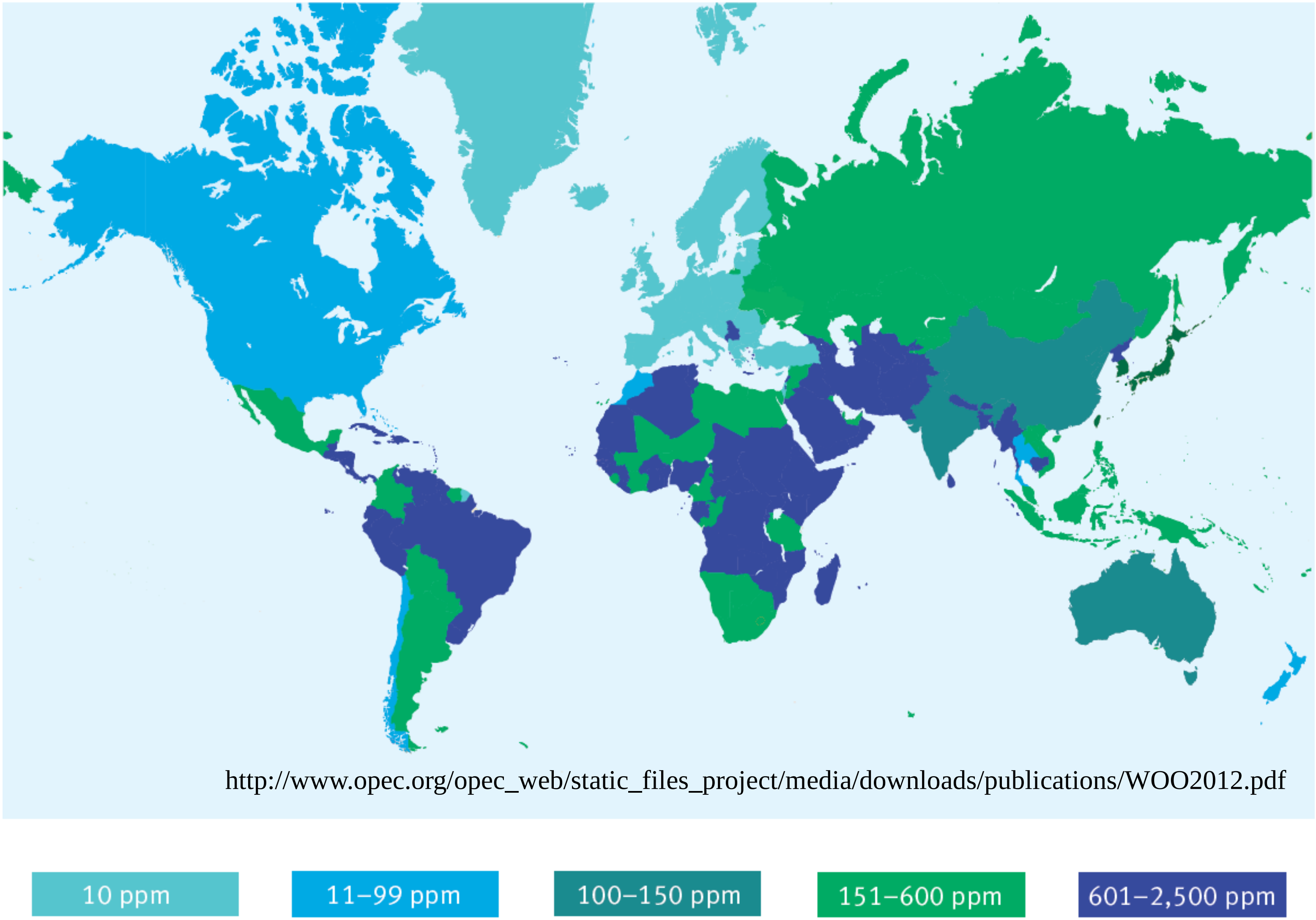
Dehydrocyclizations of alkanes to aromatics



Hydrocracking of alkanes

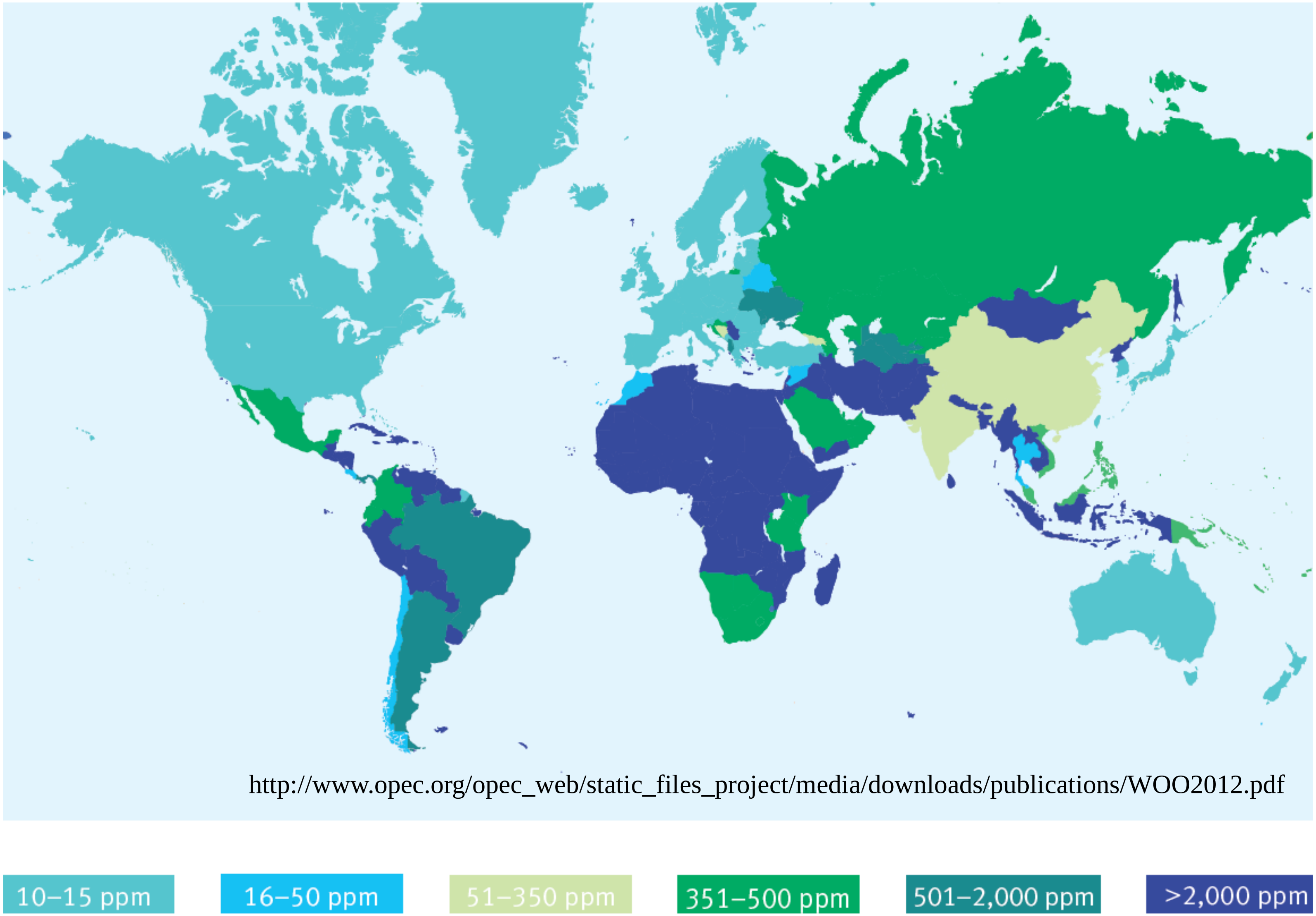
$$CH_3CH_2CH_2CH_2CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_3 + CH_3CH_2CH_2CH_3$$

Oil Desulphurization: Maximum gasoline sulphur limits, September 2012.



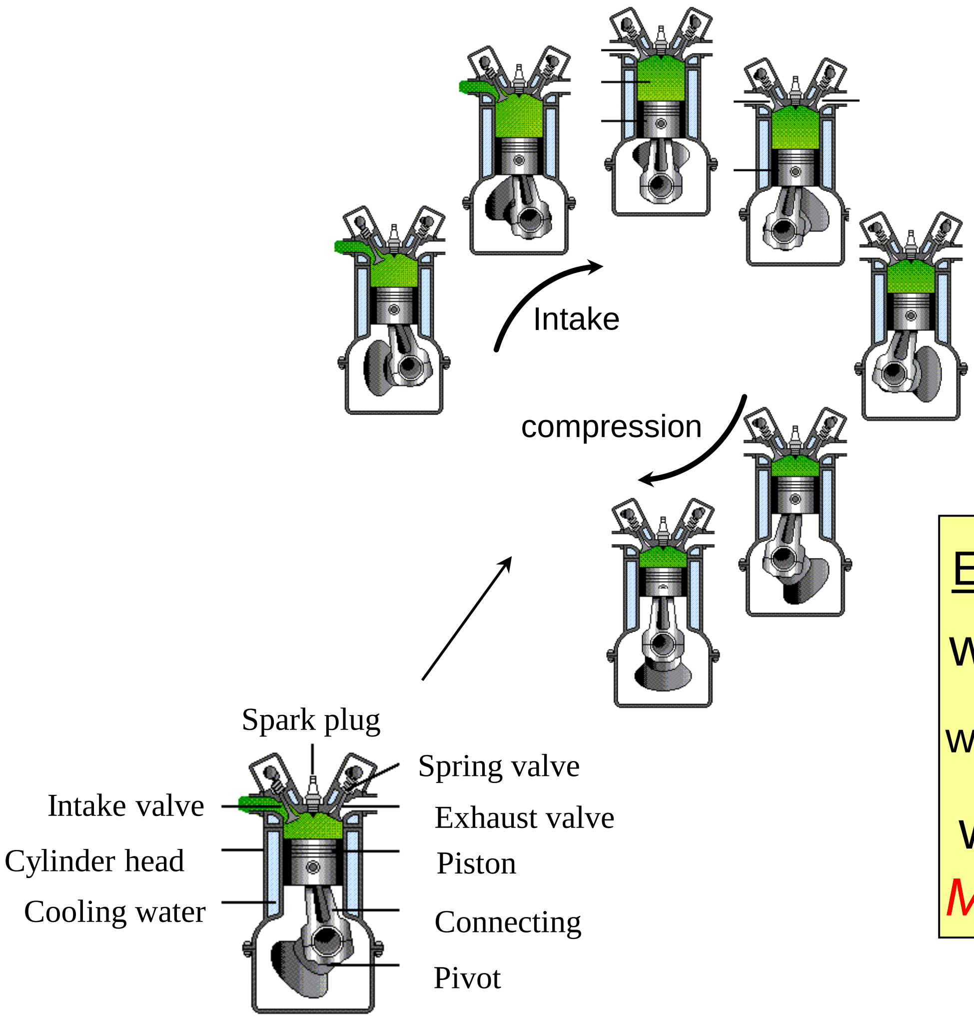
http://www.opec.org/opec_web/static_files_project/media/downloads/publications/WOO2012.pdf

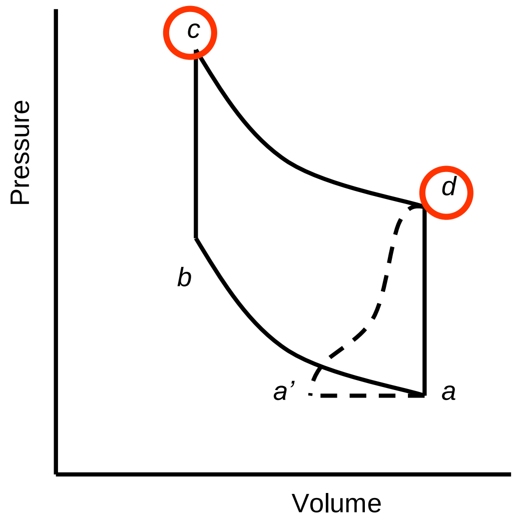
Oil Desulphurization: Maximum on-road diesel sulphur limits, September 2012.



Gasoline and the Otto Cycle (four-stroke).

Refined Fuel (C_7-C_8)





<u>Efficiency</u>:

$$w_{cycle}/Q_{heat} = 1 - T_d/T_c = 1 - (V_c/V_d)^{R/Cv}$$

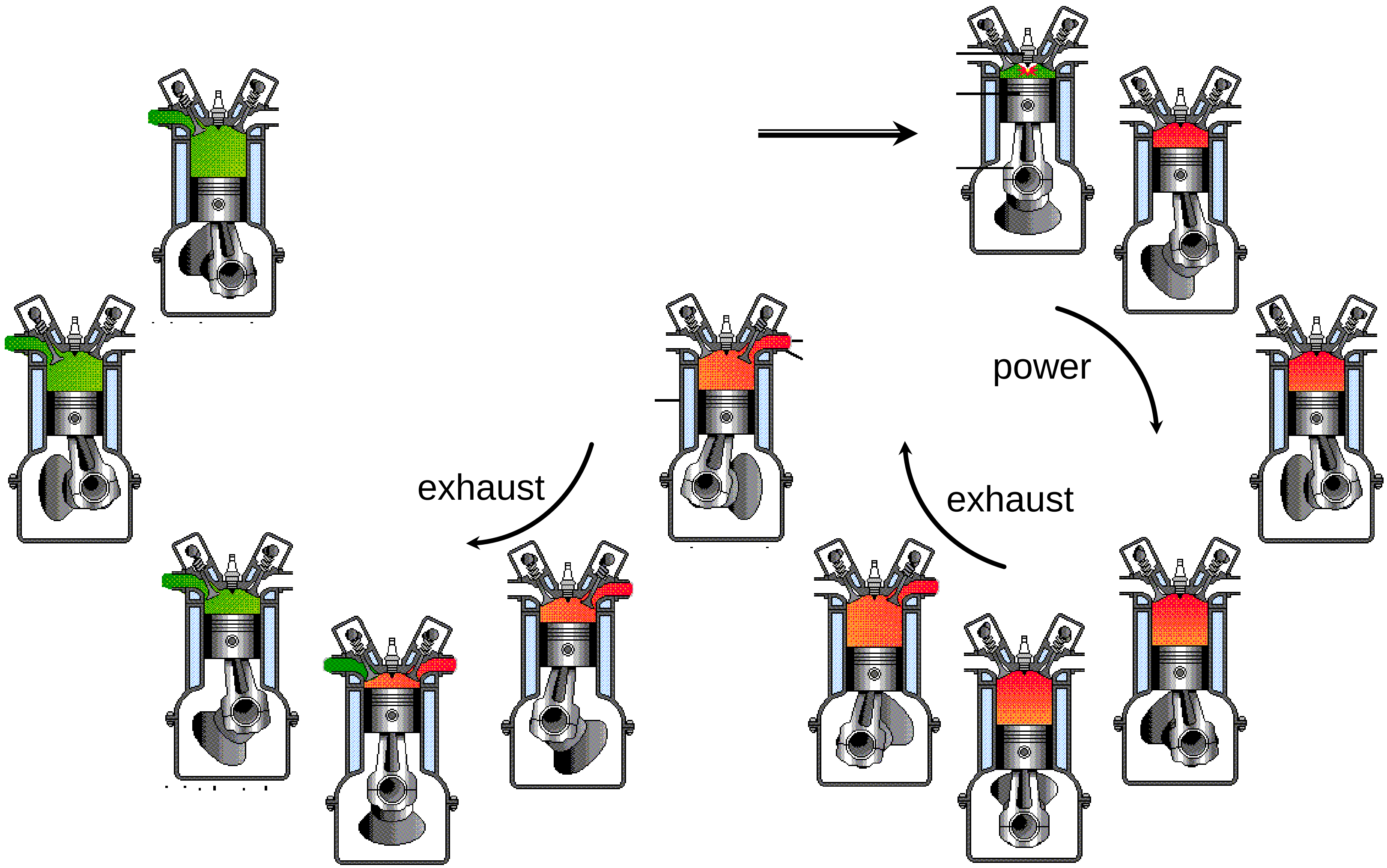
where V_d/V_c = compression ratio, r_c

$$w_{cycle}/Q_{heat} = 1 - (1/r_c)^{R/Cv}$$

Max ↑ ← *Max*

Gasoline and the Otto Cycle (four-stroke - 2).

$$C_nH_{2n+2} + (3n + 1)/2\ O_2 \rightarrow n\ CO_2 + (n+1)\ H_2O \qquad \Delta H << O$$

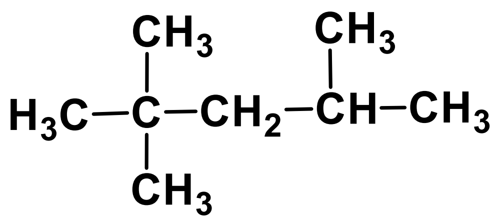


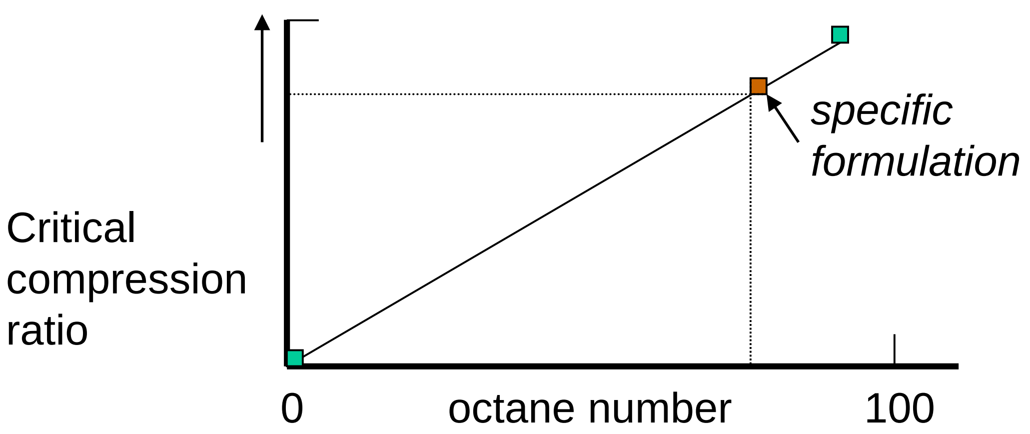
Fuel Formulation - Anti knocking.

- Knocking – premature ignition of the fuel, in the part of the cylinder remote from the spark plug, before the arrival of the flame front, resulting in a mechanical shock to the engine. A problem with straight chain hydrocarbons

n-octane $CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2CH_3$

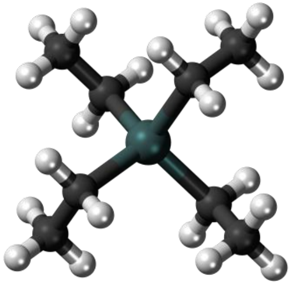
iso-octane





Fuel Additives (1).

Metal-containing octane boosters



Tetraethyl lead [an organic form of tetravalent Pb(IV)]

$Pb(C_2H_5)_4$ $(C < 0.74\ g \cdot L^{-1})$

$Pb(C_2H_5)_4 \rightarrow Pb^0_{(g)} + 4\ C_2H_5^{\bullet}$ (ethyl radical serves to prevent premature combustion)

Pb^0 would deposit in cooler parts of the engine. Additional additives are ethylene dibromide and ethylene dichloride:

$Pb^0 \rightarrow PbBrCl \rightarrow PbO \rightarrow$ atmospheric aerosol and deposition in soil/water

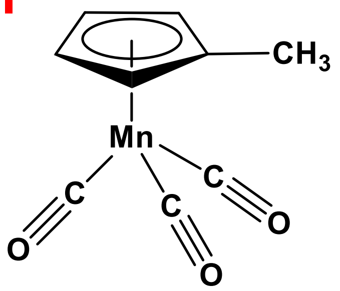
$Pb(C_2H_5)_4$ is quite volatile; some is present in the atmosphere in gaseous forms. Being lipophilic it can enter the body through the skin.

Banned in EU from 2000 year.

Fuel Additives (2).

η⁵-Cyclopentadienyl Compounds : MMT and Ferrocenes

MMT — Methylcyclopentadienylmanganesetricarbonyl

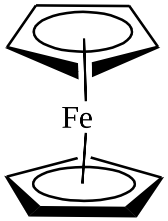


$CH_3(C_5H_4)Mn(CO)_3$

$< 0.1\ g\cdot L^{-1}$

MMT is toxic, but combustion is complete, and only significant emission product is Mn_3O_4 and other Mn oxides. These do not add significantly to the amount of Mn ingested in normal situations.

Ferrocene – Dicyclopentadienyl iron



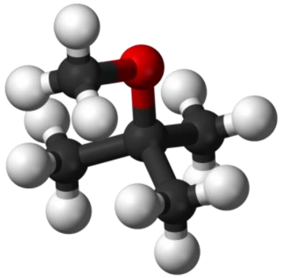
$(C_5H_4)_2Fe$ ($< 0.1\ g\cdot L^{-1}$)

Less toxic than MMT, suggested as diesel additive, limited by low solubility.

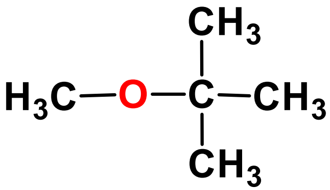
Fuel Additives (3).

Other octane boosters (10-20% v/v)

	Octane number	
Benzene	106	Adverse environmental (smog) and health (leukaemia) effects
Toluene	118	
p-xylene	116	
Methanol	116	Add oxygen to the fuel, therefore minimizing emissions of CO and other unoxidized or partially oxidized hydrocarbons
Ethanol	112	
MTBE	116	



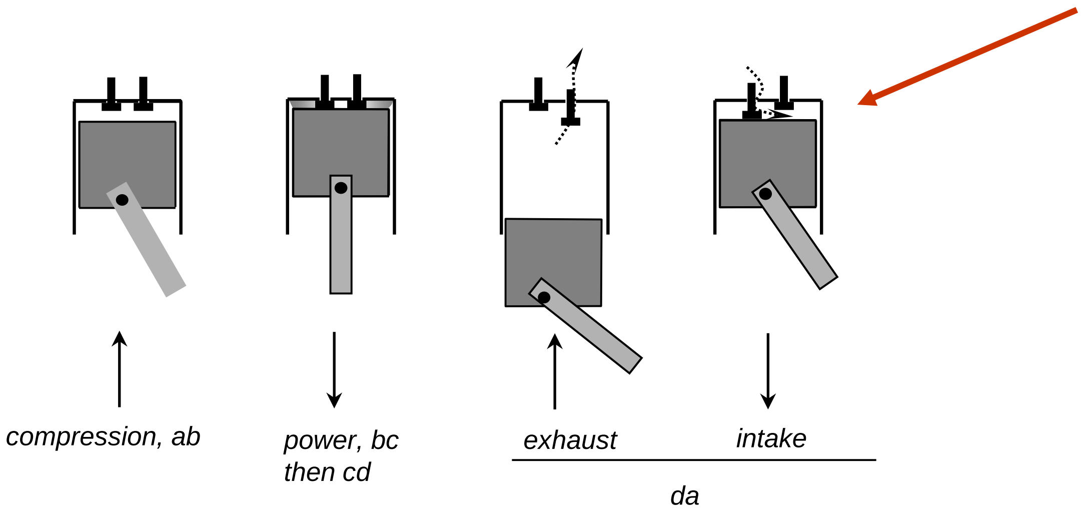
MBTE (methyl *tert*-butyl ether) is water soluble, and leakage into groundwater is a problem. Potential carcinogenic and aesthetic issues.



Methanol id toxic and induces blindness if ingested.

Diesel Fuel (Diesel Engine).

- Higher compression engine
- No spark plug
- Lower grade fuel (C_{16}-C_{18})
- Injection of fuel at the end of the compression stroke



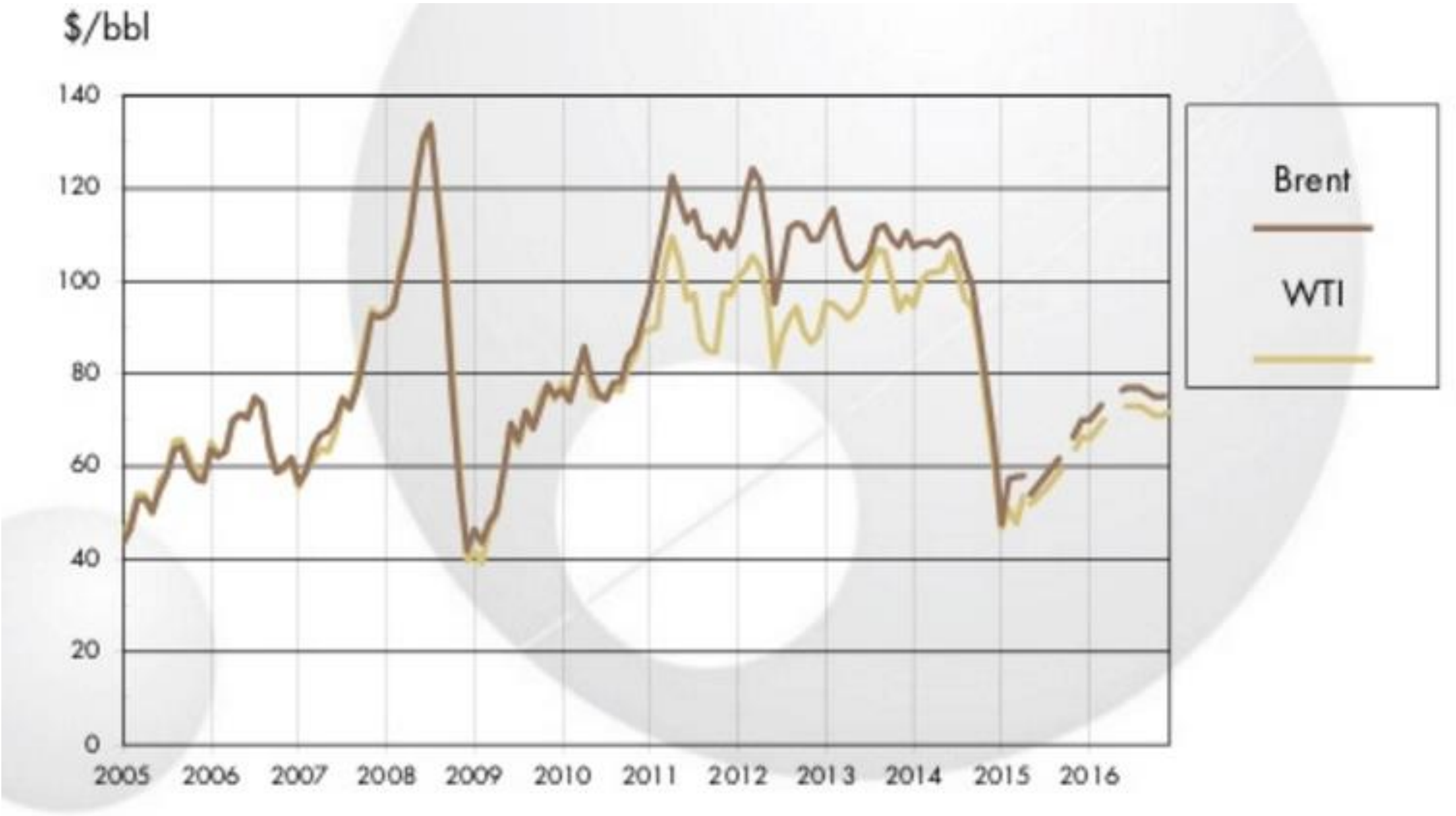
Environmental Concerns of Diesel Engines.

- High fuel efficiency
- Poor fuel / air mixing, resulting in increased release of unburned or partially burned hydrocarbons – solid and liquid rather than gaseous
- Sulfur compounds in the emissions is typical (~0.2 % S in fuel but deep desulphurization in now mandatory)
- NO_x due to high combustion temperatures
- Comprise 28% NO_x and 20% PM mobile source emissions worldwide
- Diesel exhaust has been implicated in an increased risk in human health and is implicated in serious air quality problems
- EPA has concluded that diesel exhaust is a likely human carcinogen

Diesel Fuel Additives.

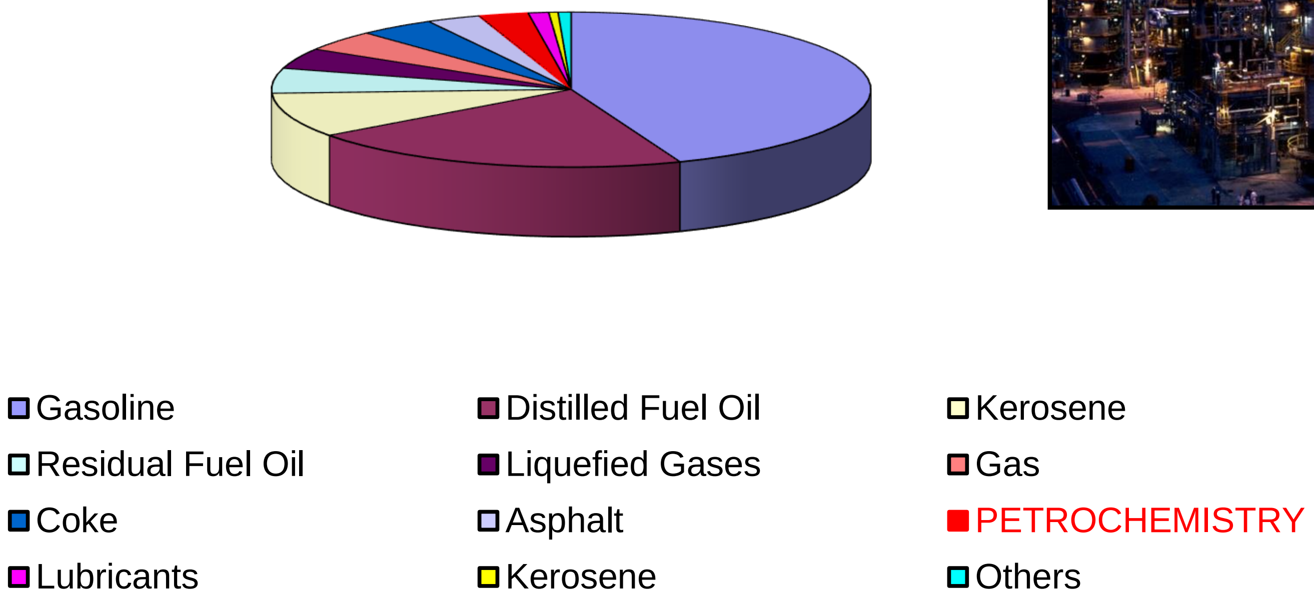
- Cetane number improvers (nitro alkanes)
- Lubricants (hydrocarbons C_{24}, polyol esters, etc.)
- Anticorrosion (sulphides, succinimides, paraffins, salicylates, etc.)
- Metal deactivators (benzothiazoles and derivatives)
- Thixotropic agents (PIB)
- Solubilizing agents (fatty alcohols and acids)
- Etc…..

WTI & Brent Crude Oil Prices 2005-2015.



(US EIA Short Term Forecast

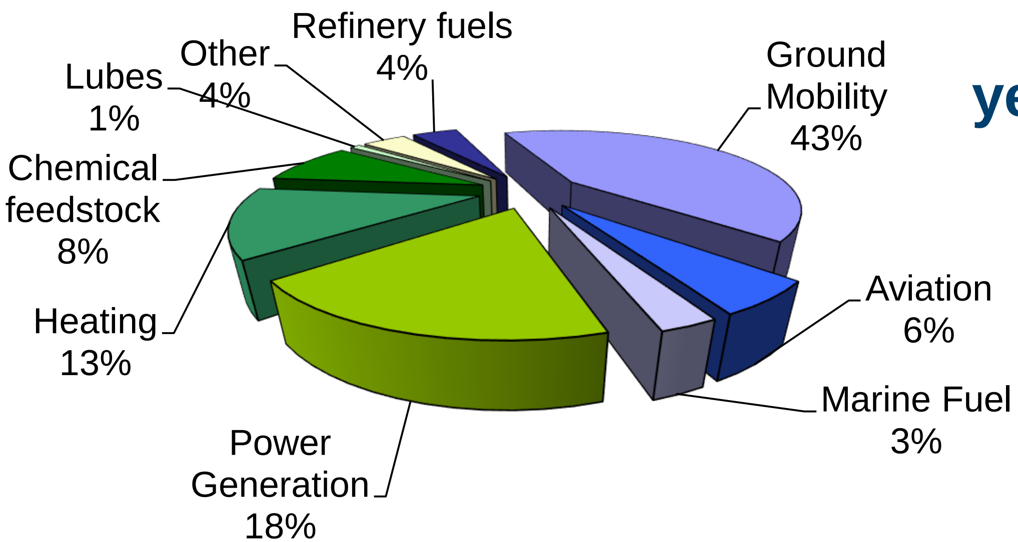
Crude Oil Uses.

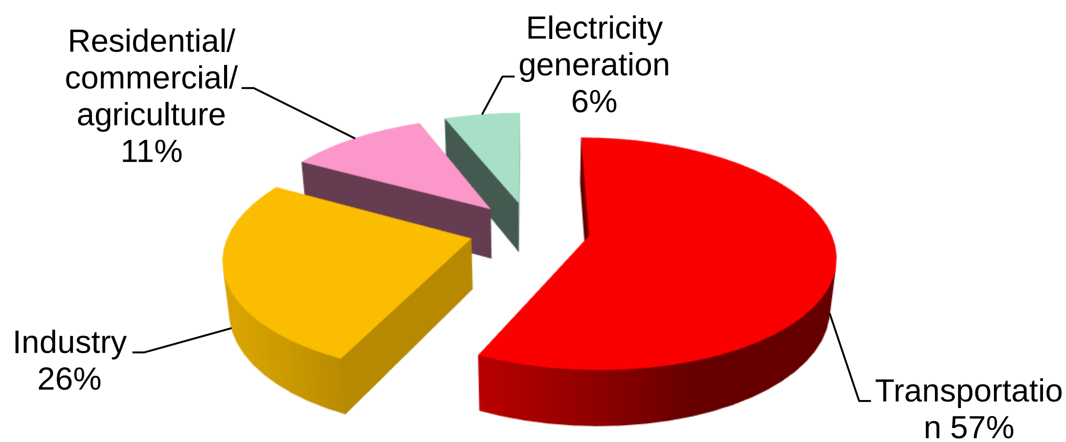


Source: API

Global Oil Consumption.

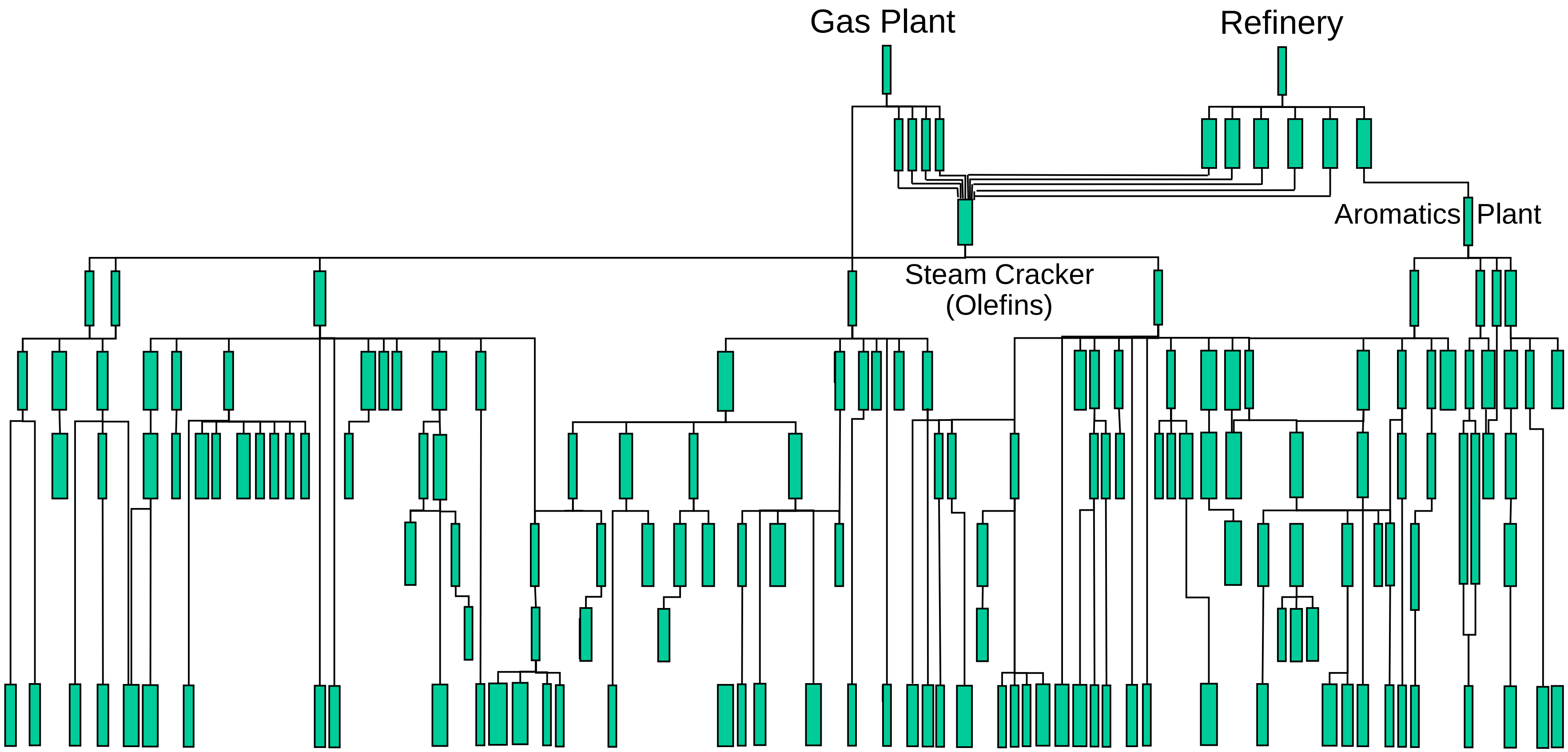
years 2000-2005





year 2012

Organic Product Tree from Petroleum and Natural Gas.



Derivatives Tree:
Products from Benzene.

Starting Material	Intermediate	Product
C_8H_{10}	Styrene	Polystyrene Plastics Styrene-butadiene Rubber
$C_6H_5SO_3H$	Phenol 2,4-Dichlorophenol Salicylic acid	 2,4-D Aspirin
C_6H_5Cl		DDT
$C_6H_5NO_2$	Aniline Acetanilide	Aniline dyes Analgesic drugs
$C_6H_4Cl_2$	p-Dichlorobenzene o-Dichlorobenzene	Insecticides Industrial solvents
C_6H_{12}	Caprolactam Adipic acid	Nylon 6 fibre Nylon 6,6 fibre Polyurethanes
C_6Cl_6		Insecticides
$C_4H_2O_3$	$C_4H_4O_2N_2$	Agrochemical compounds
$C_{18}H_{30}$	$C_{18}H_{31}O_4SNa$	Anionic Surfactants

Classification of ICEs.

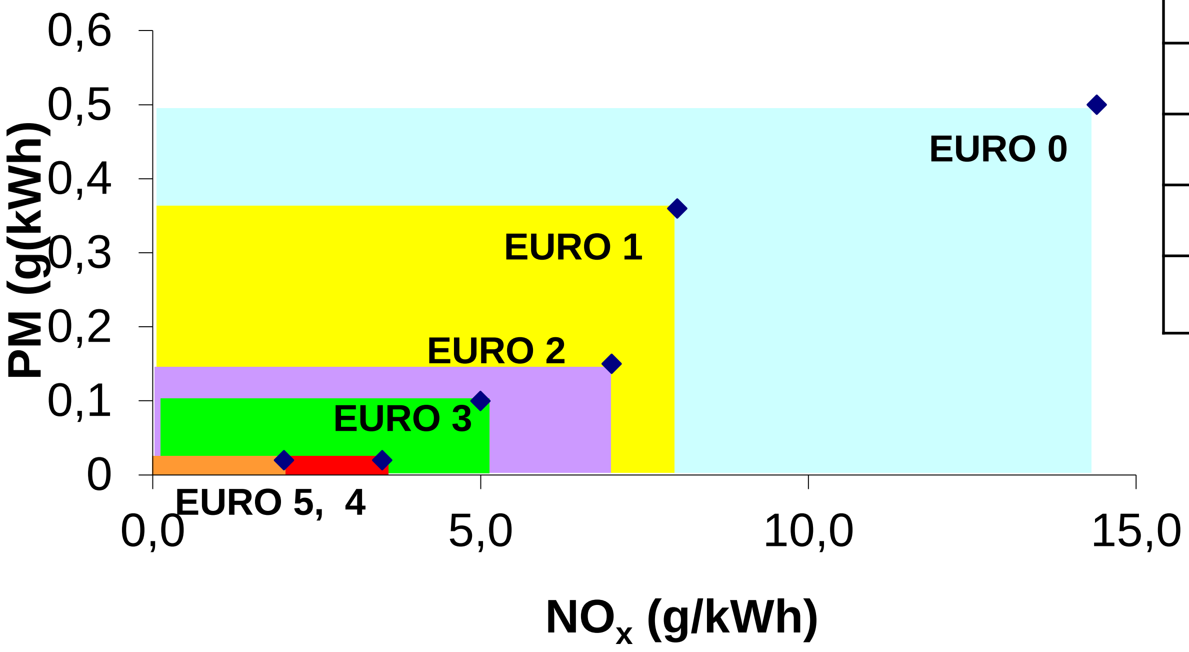
- Internal combustion engine (ICE) is a “heat engine“ in which the heat source is a combustible mixture that also serves as the working fluid
- They are generally used for vehicle (car, aircraft, etc.) propulsion
- The working fluid in turn is used either to
  - Produce shaft work by pushing on a piston or turbine blade that in turn drives a rotating shaft or
  - Creates a high-momentum fluid that is used directly for propulsive force
- By this definition, ICEs include also gas turbines, supersonic propulsion engines, and chemical rockets

What is an ICE.

Internal Combustion Engines

- **Steady**
  - **Gas Turbine** – Uses compressor and turbine, not piston-cylinder
    - **Turboshaft** – All shaft work to drive propeller, generator, rotor (helicopter)
    - **Turbofan** – Part shaft, part jet - "ducted propeller"
    - **Turbojet** – All jet except for work needed to drive compressor
  - **Ramjet** – No compressor or turbine. Use high Mach no. ram effect for compression
  - **Rocket** – Carries both fuel and oxidant. Jet power only, no shaft work
    - **Solid fuel** – Fuel and oxidant are premixed and put inside combustion chamber
    - **Liquid fuel** – Fuel and oxidant are initially separated and pumped into combustion chamber
- **Non-steady**
  - **Premixed-charge** – Fuel and air are mixed before/during compression. Usually ignited with spark after compression
    - **Two-stroke** – One complete thermodynamic cycle per revolution of engine
    - **Four-stroke** – One complete thermodynamic cycle per two revolutions of engine
  - **Non-premixed charge** – Only air is compressed, fuel is injected into cylinder after compression
    - **Two-stroke** – One complete thermodynamic cycle per revolution of engine
    - **Four-stroke** – One complete thermodynamic cycle per two revolutions of engine

EU-Regulations for Emissions of Exhaust Gas from Diesel Cars.



Euro	Year	PM	NO_x
0	1990	0.5	14.4
1	1992	0.36	8.0
2	1995	0.15	7.0
3	1999	0.1	5.0
4	2005	0.02	3.5
5	2008	0.02	2.0
6	2015	0.005	0.08

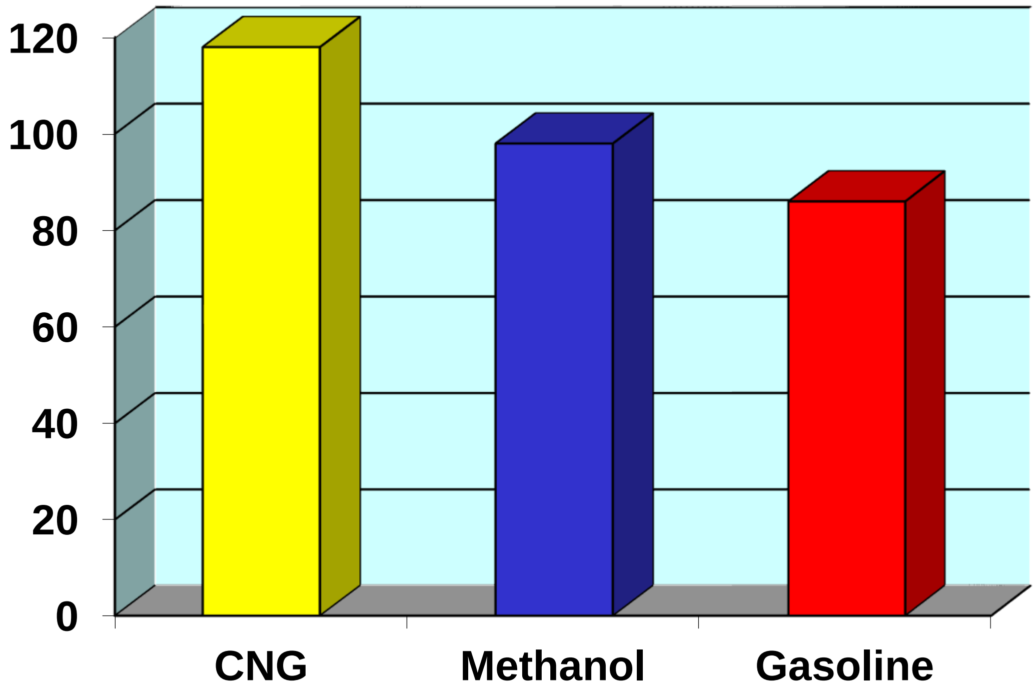
OPEC.

- Organization of Petroleum Exporting Countries
- Formed in 1960
- Current Member states are Algeria, Ecuador, Gabon, Indonesia, Iran, Iraq, Kuwait, Libya, Nigeria, Qatar, Saudi Arabia, Venezuela, and the United Arab Emirates
- OPEC's mission is to coordinate and unify the petroleum policies of Member Countries and ensure the stabilization of oil markets in order to secure an efficient, economic and regular supply of petroleum to consumers, a steady income to producers and a fair return on capital to those investing in the petroleum industry

Natural Gas.

- Primary constituent methane (CH_4).
- Lighter than air (specific gravity 0.55 to 0.65).
- Tasteless and odourless. Odorant is added for safety.
- Non-toxic. Simple asphyxiant. In sufficient concentrations, the oxygen in air is displaced.
- Flammable in concentrations of 5% to 15% by volume in air.
- Boiling point is -161.5°C. Above that temperature it is gaseous.
- Ignition temperature 580°C to 590°C.
  - With full combustion, natural gas burns with a pale blue flame.
  - Approximately 1.37 cm^3 for gram.
  - Approximately 1 kg of natural gas provides the same energy as 1.48 litres of gasoline.
  - Approximately 1 kg of natural gas provides the same energy as 1.64 litres of diesel

Octane Value of Natural Gas.



NG has a higher octane rating than gasoline or methanol. This allows optimized natural gas engines to use higher compression ratios for increased fuel efficiency.

Source of Methane.

- Sufficient gas and water molecules
- Correct temperature and pressure
- Not fully understood and is dependent on methane source

Biogenic origin*

- microbial alteration of Organic Matter - methane produced in anaerobic sediments
- $\delta^{13}C$ from -34 to -53 per km
- predominantly methane (C1/(C2 + C3)) > 1000
- mainly permafrost and gas idrates

Thermogenic origin

- produced by catagenesis
- $\delta^{13}C$ from -22 to -37 per km
- C1/(C2 + C3) < 100
- mainly marine

*Montello S.p.A., Montello (BG) Italy

Gas Hydrates.

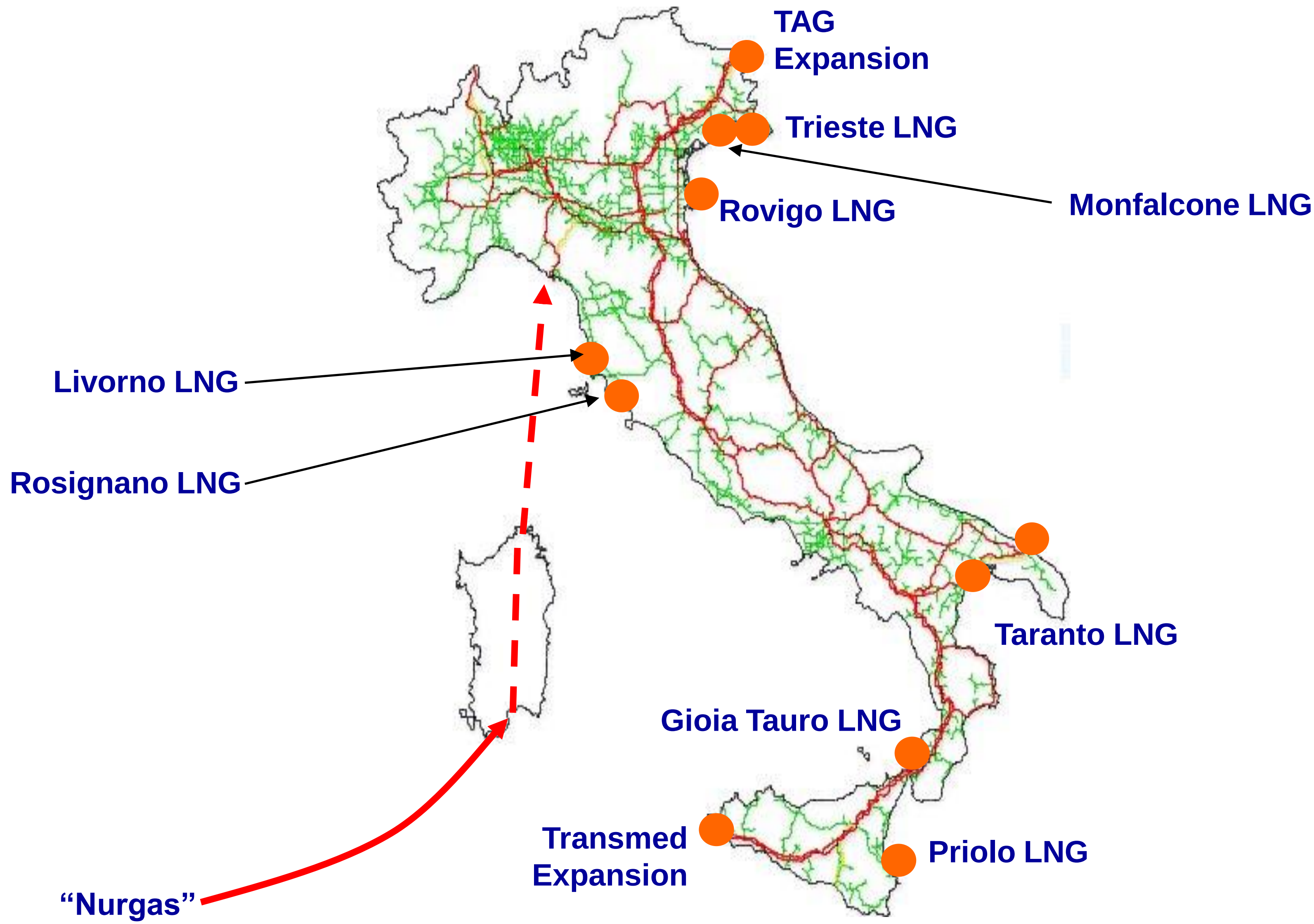
See the related presentation

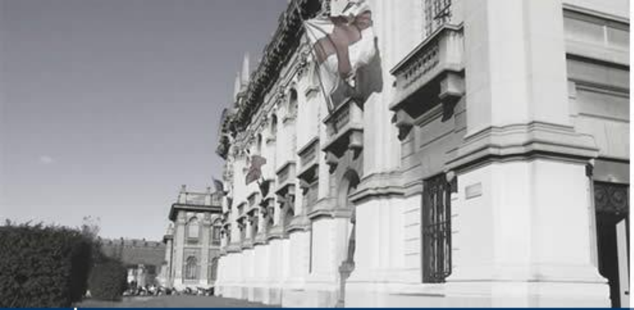
Liquefied Natural Gas (LNG).

- **LNG is natural gas that has been cooled to -160ºC and liquefied**
- **In its liquid state, there is no need for pressurization**
- **Only occupies 1/600th of the space of vaporized gas**
- **Transported thousands of miles in special ocean-going ships to onshore. Vaporization converts the LNG back to natural gas**
- **LNG flows are expected to quadruple by 2020 and account for 13% of world gas demand**

LNG Facility - Qatar

Projects for new LGN infrastructures (Italy).





School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

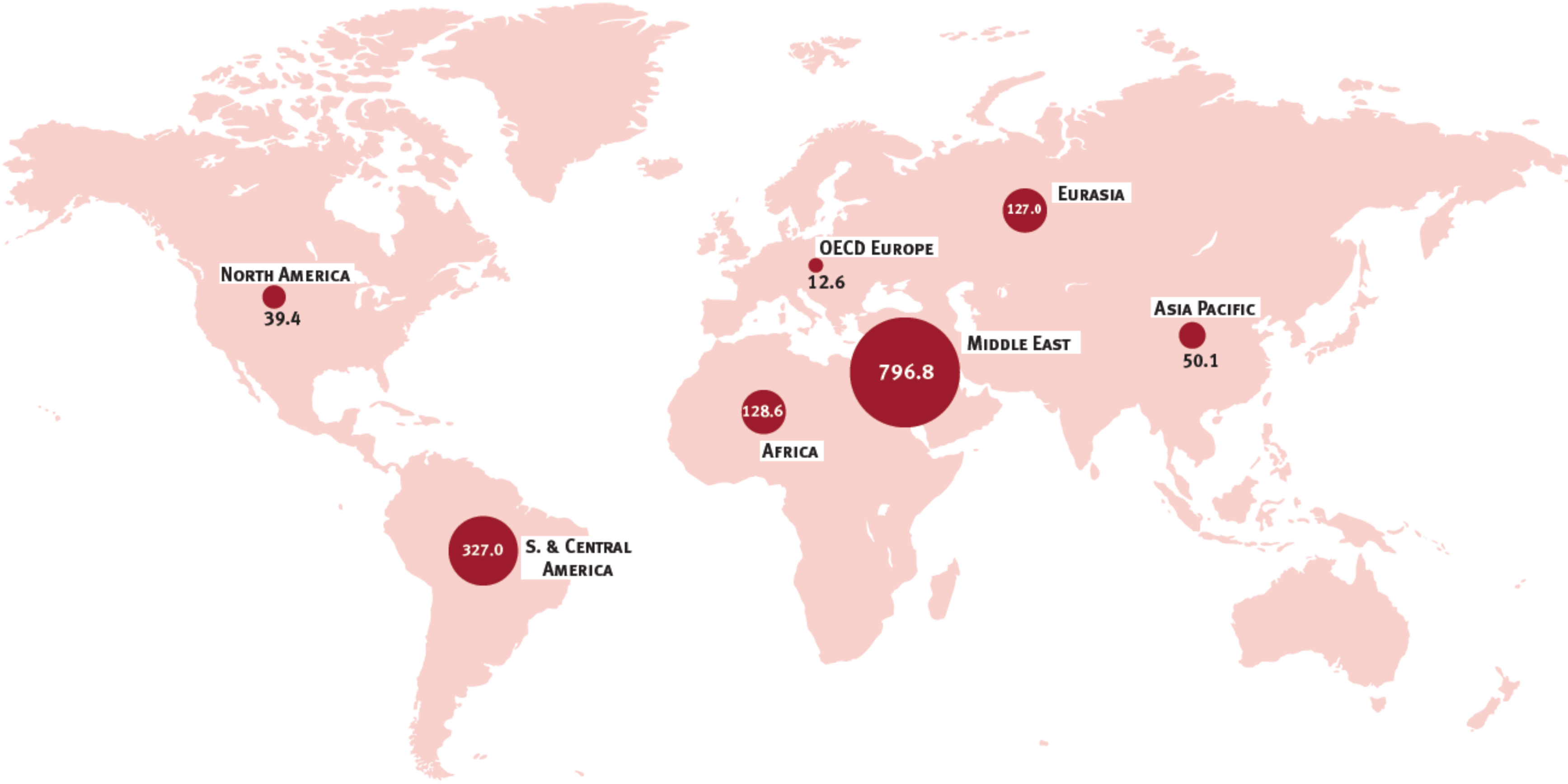
Reserves and Perspectives of Fossil Fuels.

Carbon Fuel Reserve Worldwide.

Type	Q_{inf}	Used until 1995	Remaining	Energy remaining (Btu)	%
Oil	$285 \cdot 10^9$ bbl.	$171 \cdot 10^9$ bbl.	$113 \cdot 10^9$ bbl.	$6.2 \cdot 10^{17}$	1.5
Natural Gas	$0.6 \cdot 10^{15}$ m^3	$0.3 \cdot 10^{15}$ m^3	$0.3 \cdot 10^{15}$ m^3	$1.2 \cdot 10^{18}$	2.7
Coal	$1490 \cdot 10^9$ ton	$80 \cdot 10^9$ ton	$1410 \cdot 10^9$ ton	$4,1 \cdot 10^{19}$	95.8

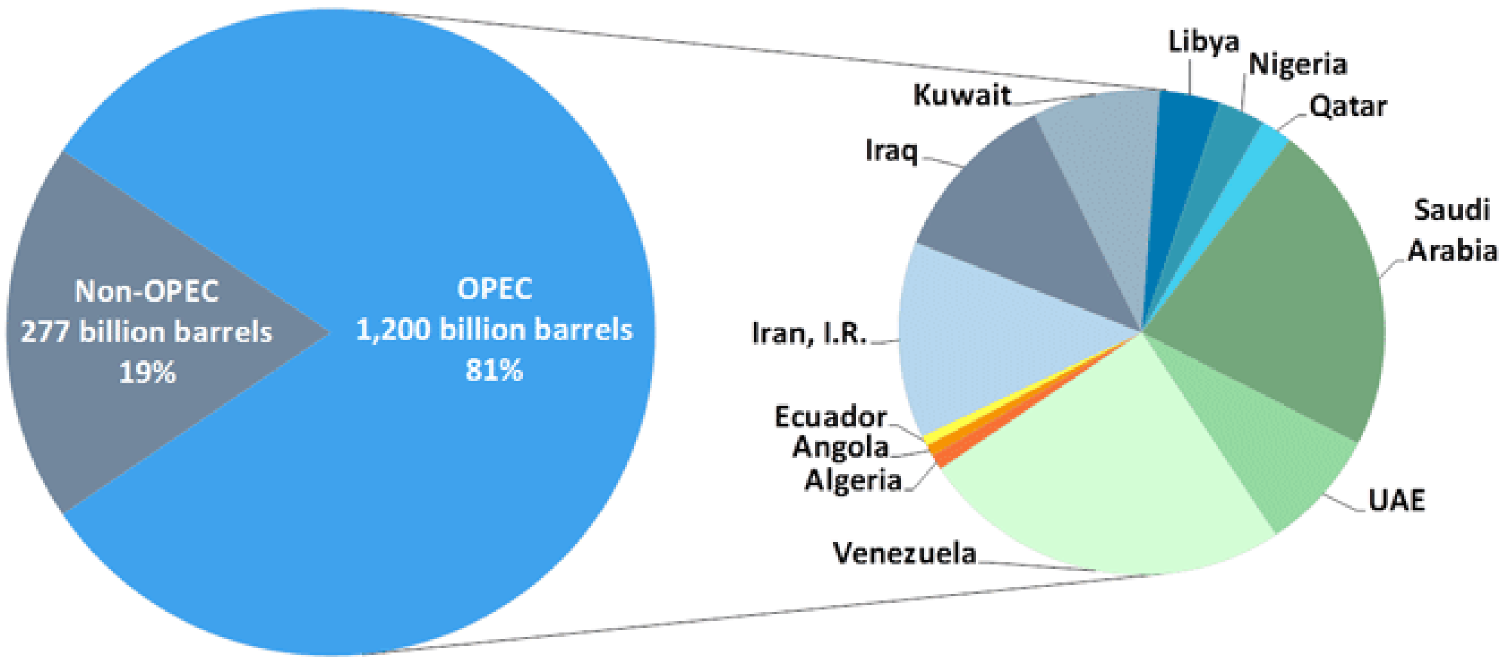
Proven Oil Reserves at End 2011.

billion barrels



Source: BP Statistical Review of World Energy 2012

OPEC Share of World Crude Oil Reserves 2012.



OPEC proven crude oil reserves, end 2012
(billion barrels, OPEC Share)

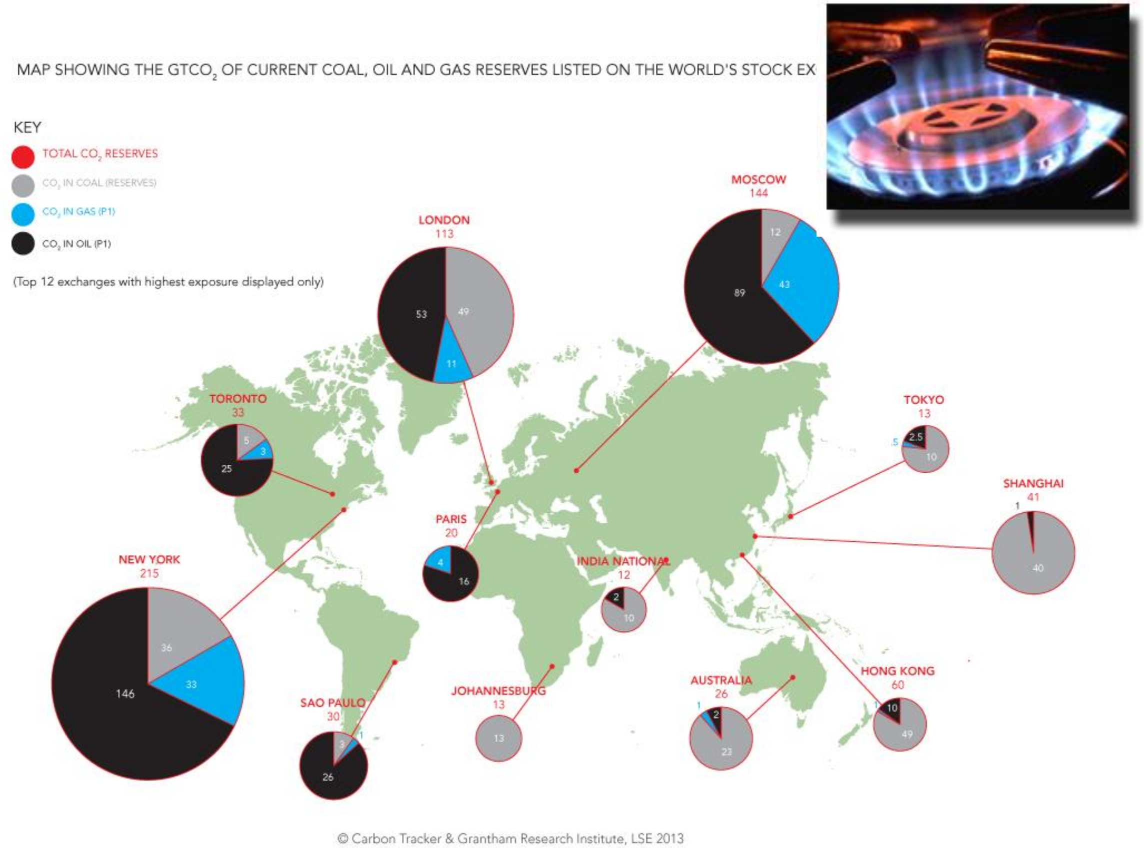
Venezuela	297.7	24.8%	Iraq	140.3	11.7%	Libya	48.5	4.0%	Algeria	12.2	1.0%
Saudi Arabia	265.9	22.1%	Kuwait	101.5	8.5%	Nigeria	37.1	3.1%	Angola	9.1	0.8%
Iran, I.R.	157.3	13.1%	United Arab Emirates	97.8	8.1%	Qatar	25.2	2.1%	Ecuador	8.2	0.7%

Source: OPEC Annual Statistical Bulletin 2013

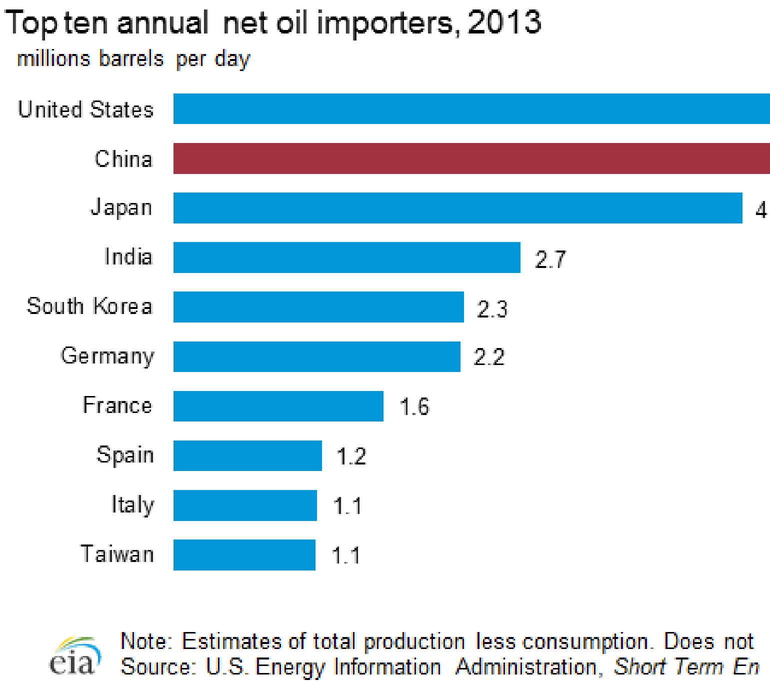
Gas Reserves.

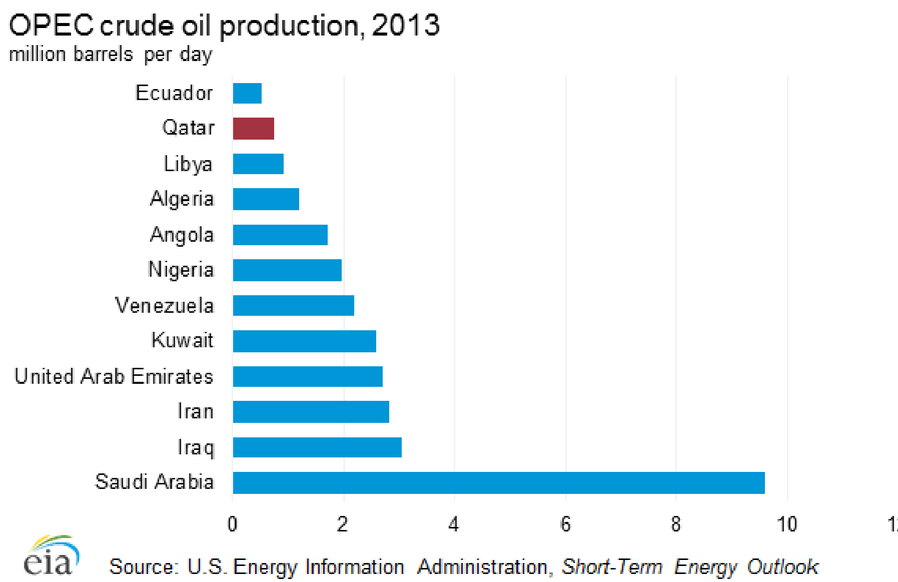
- **Natural gas proven reserves amounts to ~ 158,000 billion m^3.**
- **“Stranded” natural gas amount to 16% of this value. If converted to synthetic fuels, generate around 90 billion barrels a quantity equal to one third of Saudi Arabia’s proven oil reserves.**

The exploitation of the huge amount of stranded gas calls for a diversified portfolio of technologies: GTL can therefore provide an additional valuable route to bring natural gas to the market.

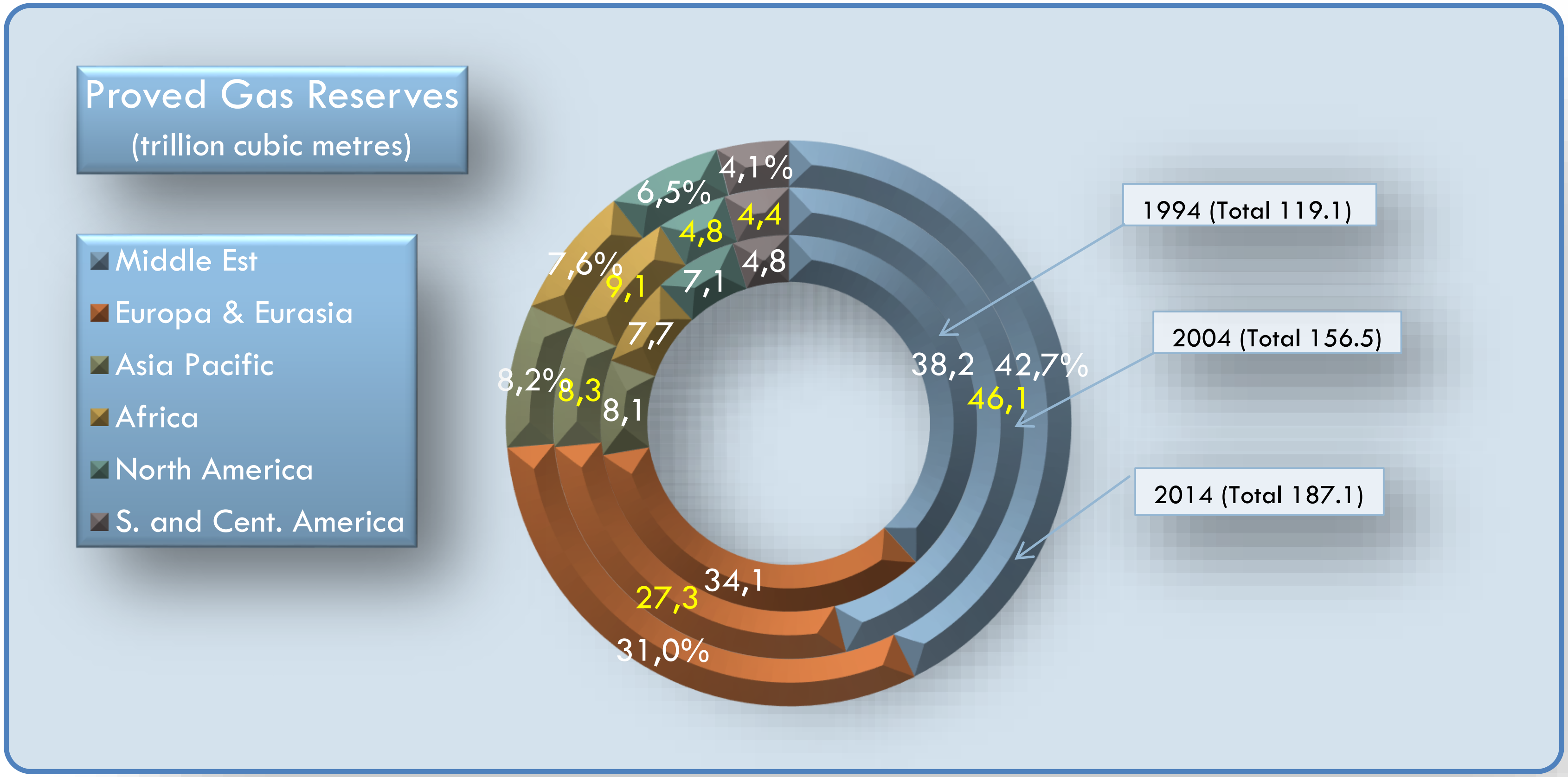


OPEC Oil Production and Importer (2013).



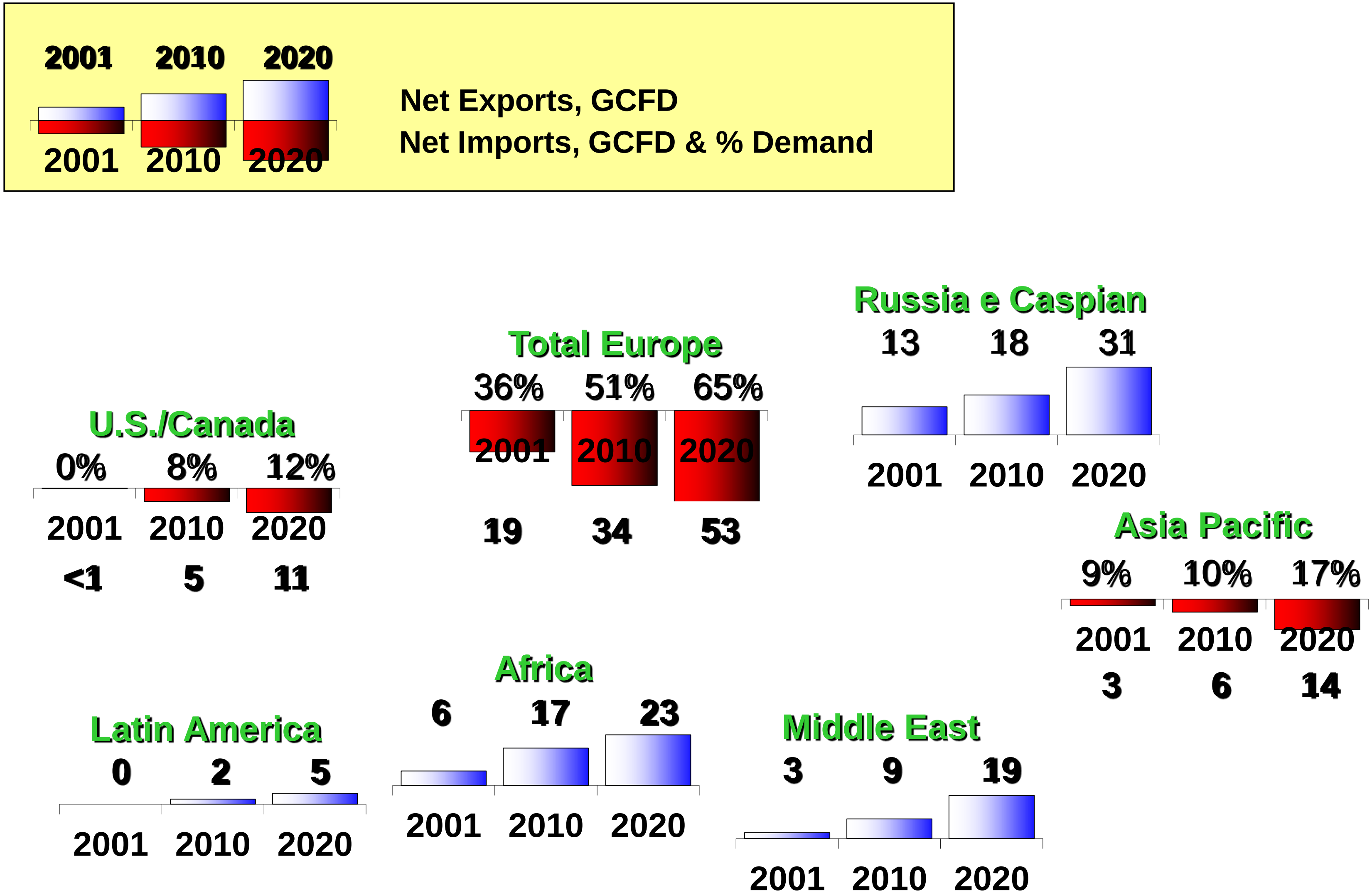


Distribution of proved gas reserves: 1994, 2004 and 2014 (%).



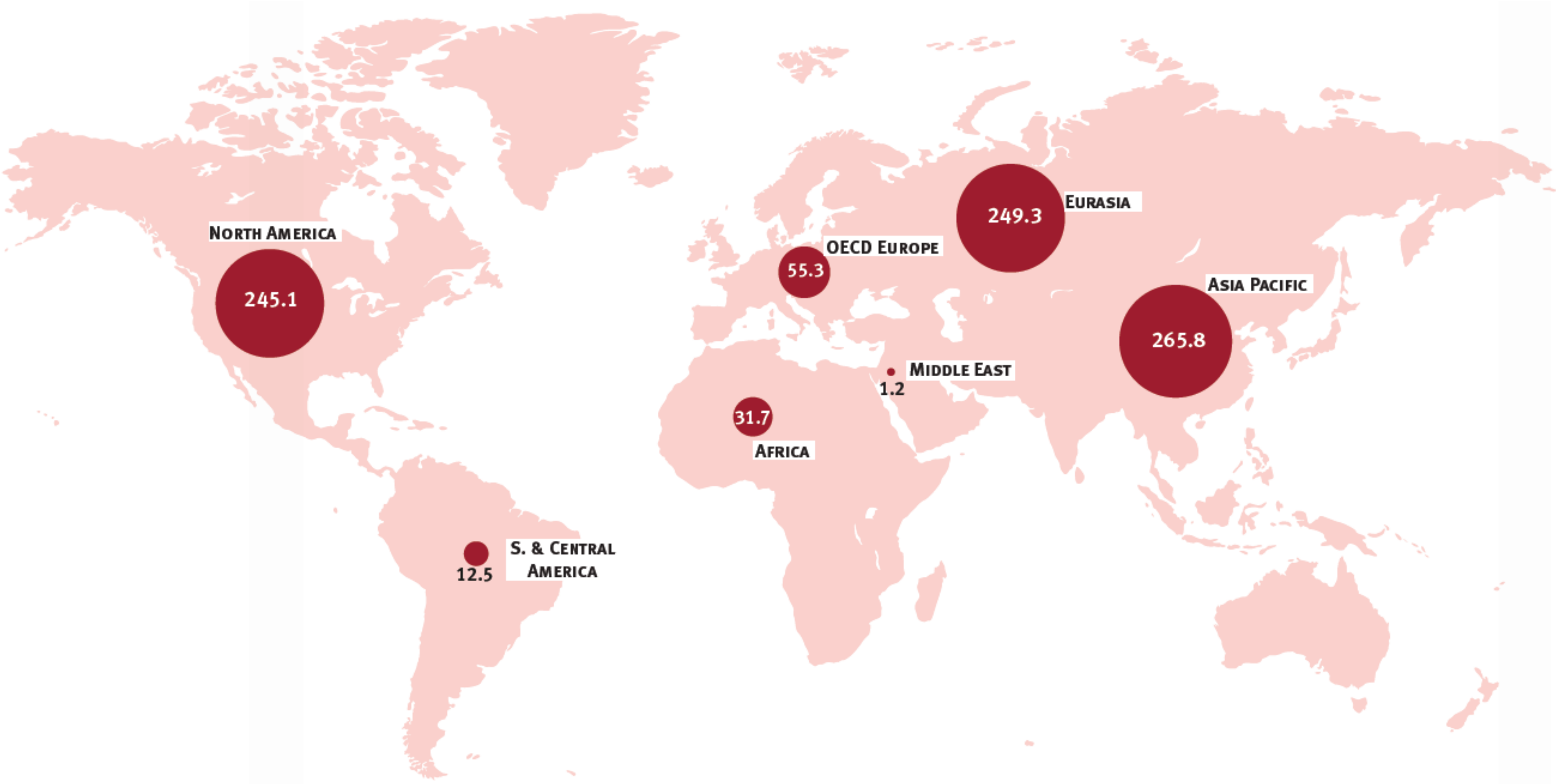
BP Statistical Review of World Energy 2015

Gas is now Global.



Coal: Proven Reserves at End 2011.

million tons



Source: BP Statistical Review of World Energy 2012

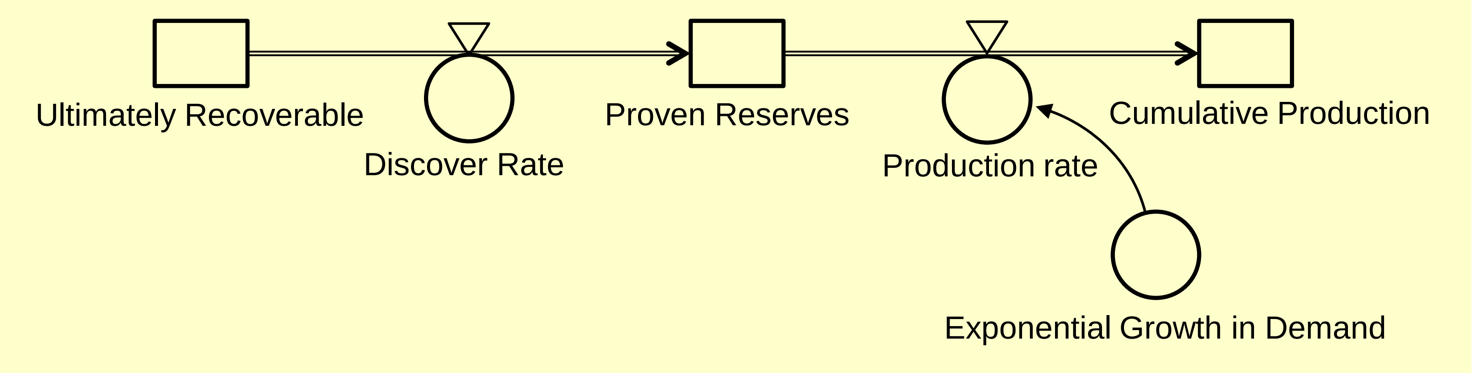
Renewables Consumption at End 2011.

million tons

Source: BP Statistical Review of World Energy 2012

Hubbert Model (1956) on non-Renewable Resources Life.

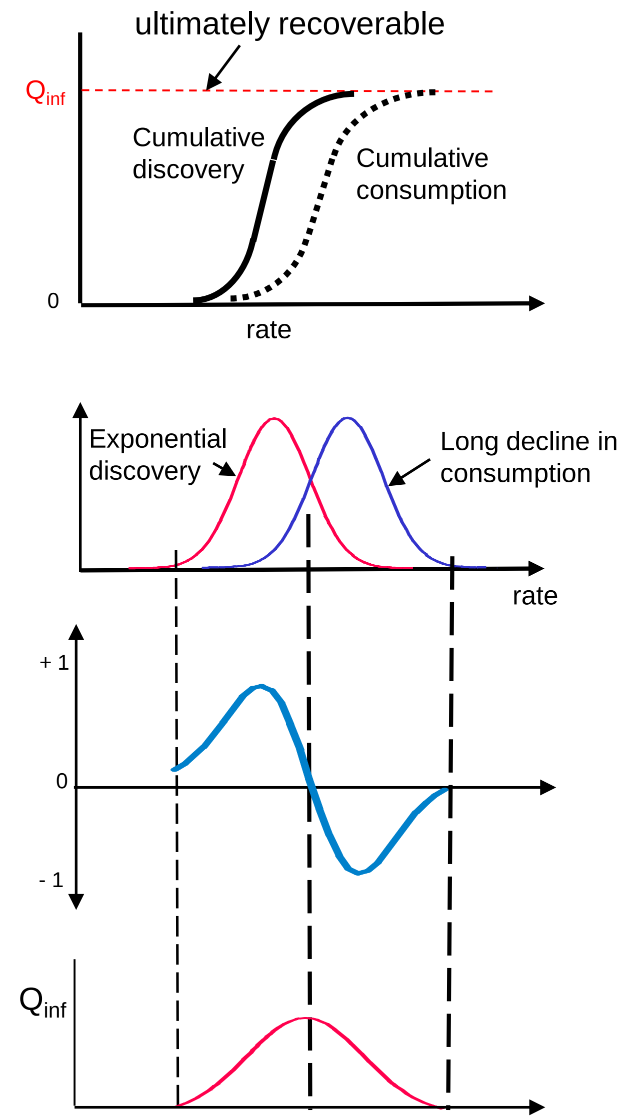
- All non-renewable resources (fossil fuel, minerals) have a finite life time.
- The peak production occurs at a point where 50% of all resource has been depleted.
- The distribution is symmetrical about the peak point.
- The overall amount of resource (ultimately recoverable) is indicated as Q_{inf}). The following stock-flow structure represents the basis of the Hubbert model.



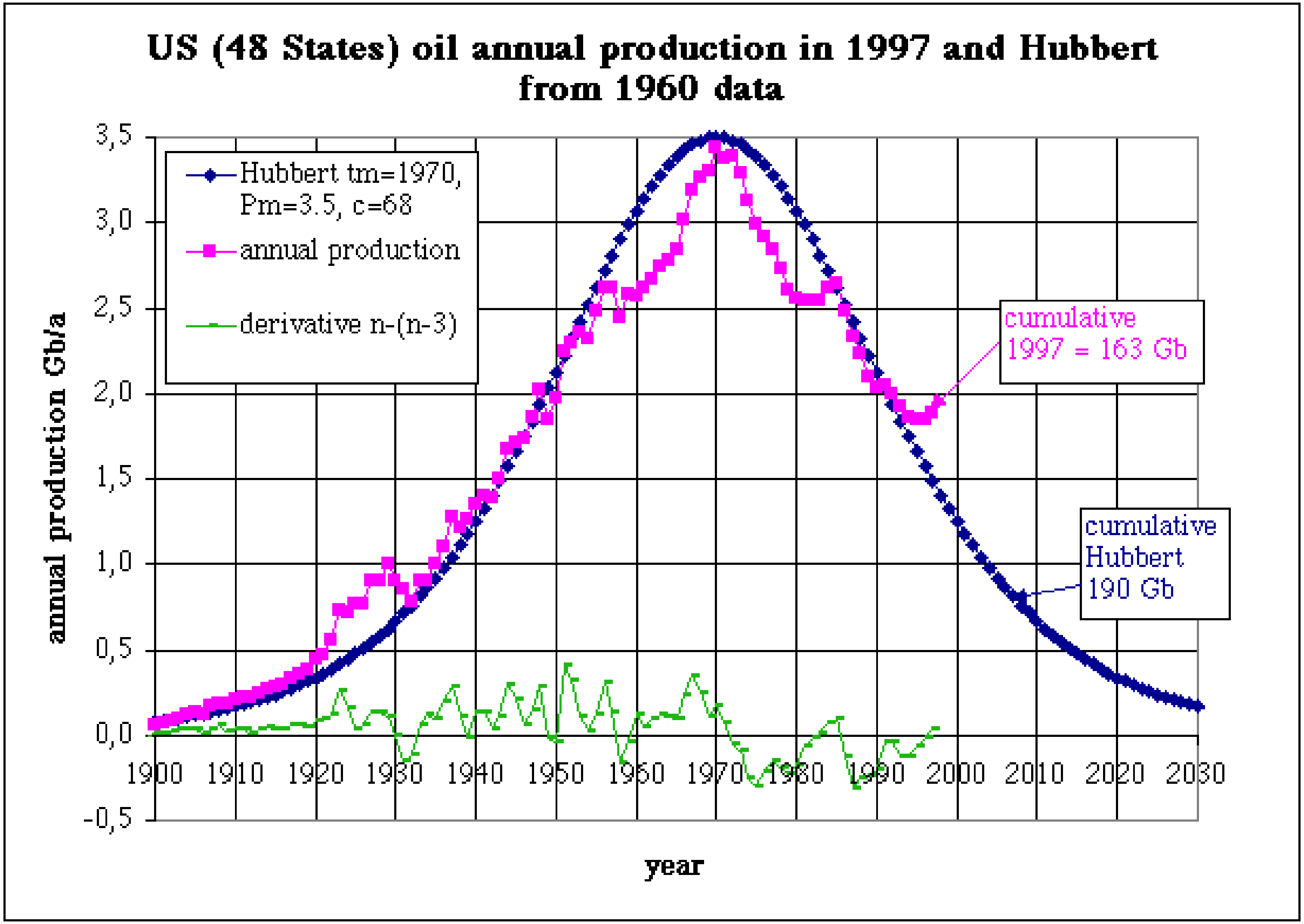
Stock-Flow Structure Representing Hubbert's View Resource Discovery and Production

Hubbert Model: Q_{inf}.

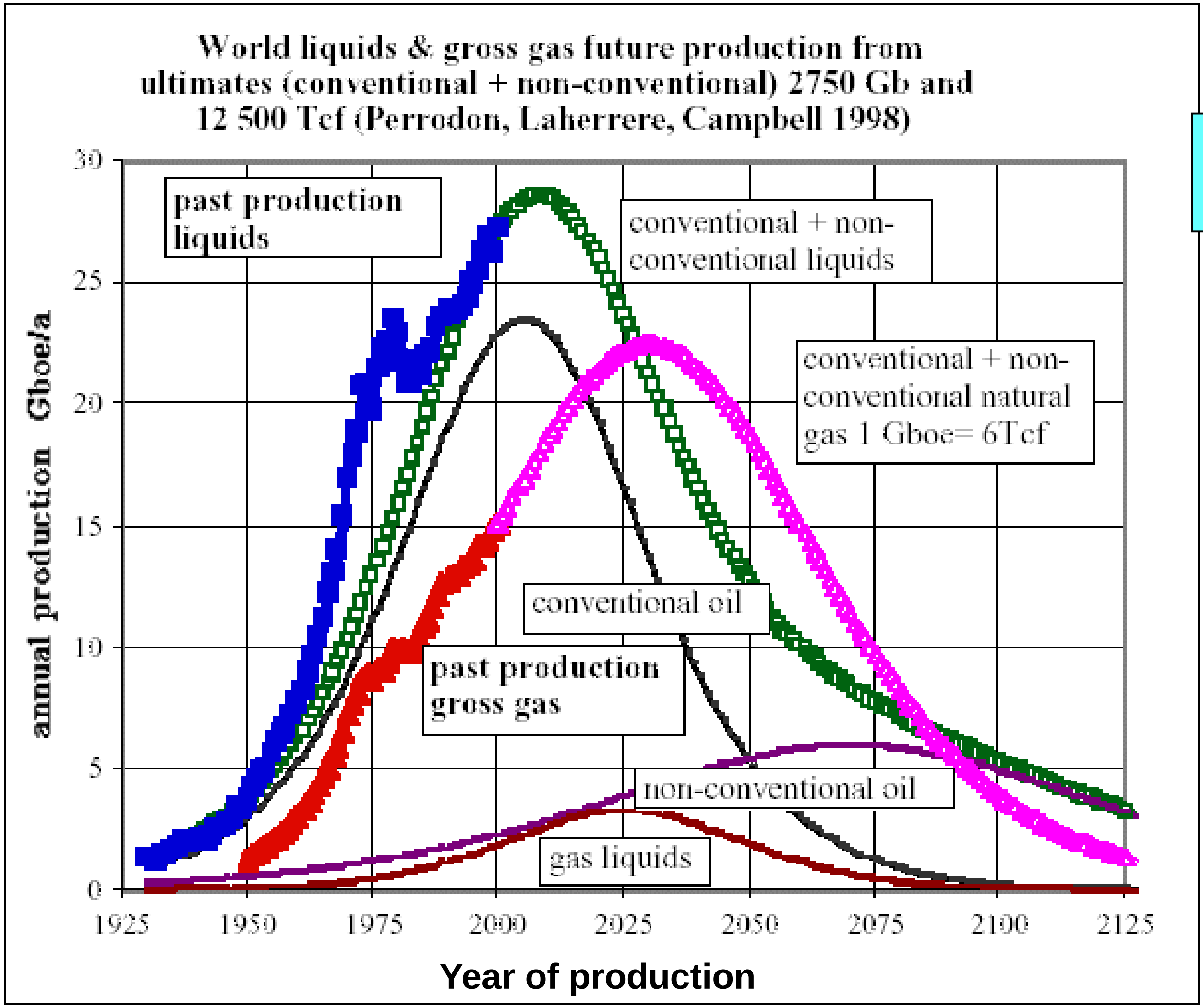
- Cumulative discovery follows a s-shape curve
- Production (Extraction, Refining) and consumption follows the discovery by a few years.
- Rate of discovery, production and consumption peaks.
- Total reserves are continuously built up until the point where production and consumption are equal. After this point we are digging into our reserves.
- Total cumulative resources (or ultimately recoverable) is termed Q_{inf}.



Example of Hubbert Model Application: US Oil Production.

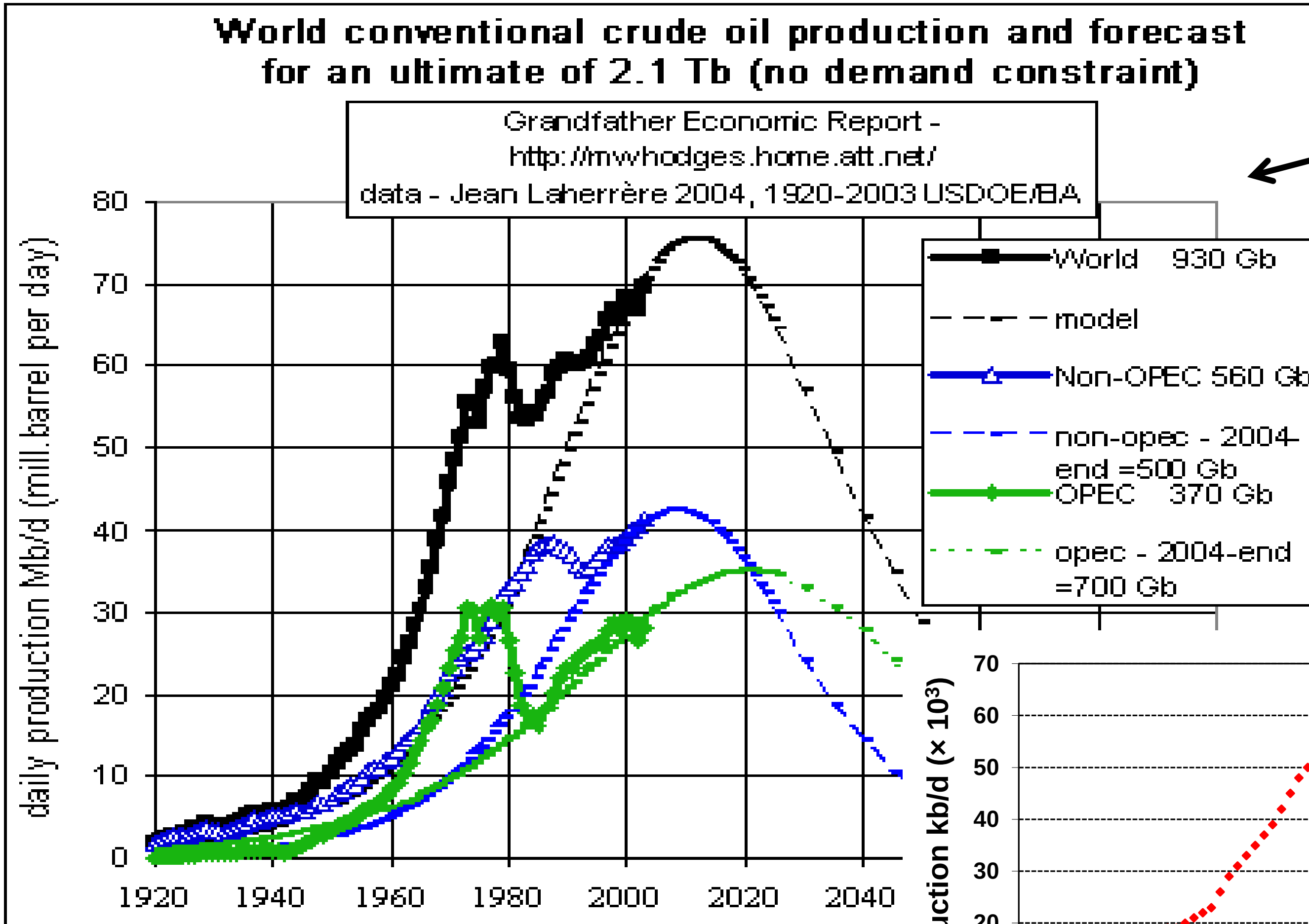


Laherrere's Oil Production Forecast (1930-2150).

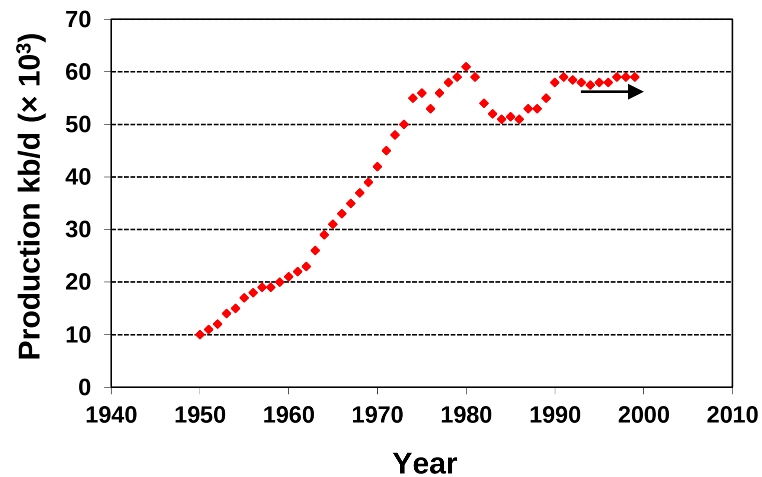


Production peak 2010

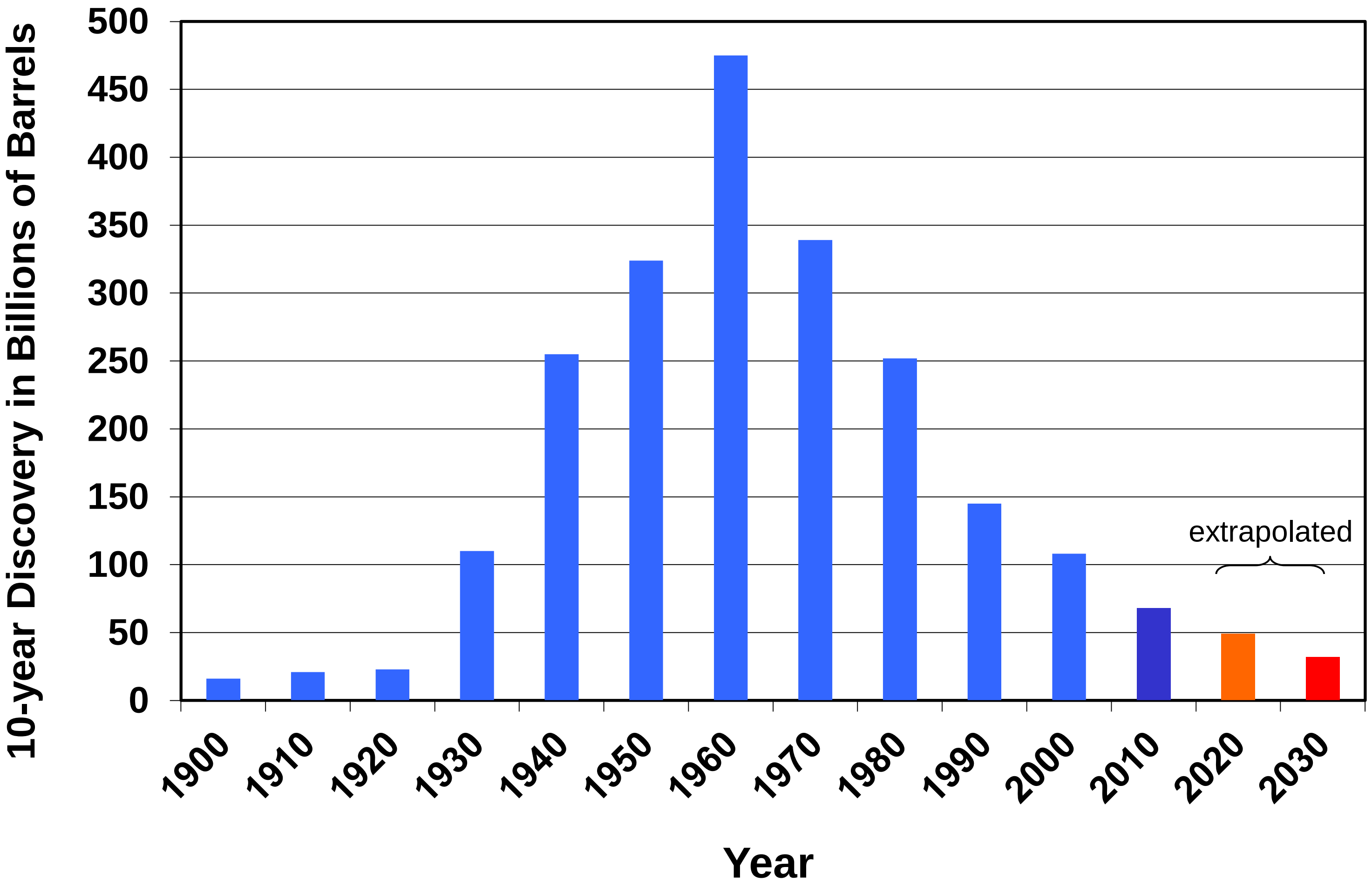
Word Production of Fossil Fuels.



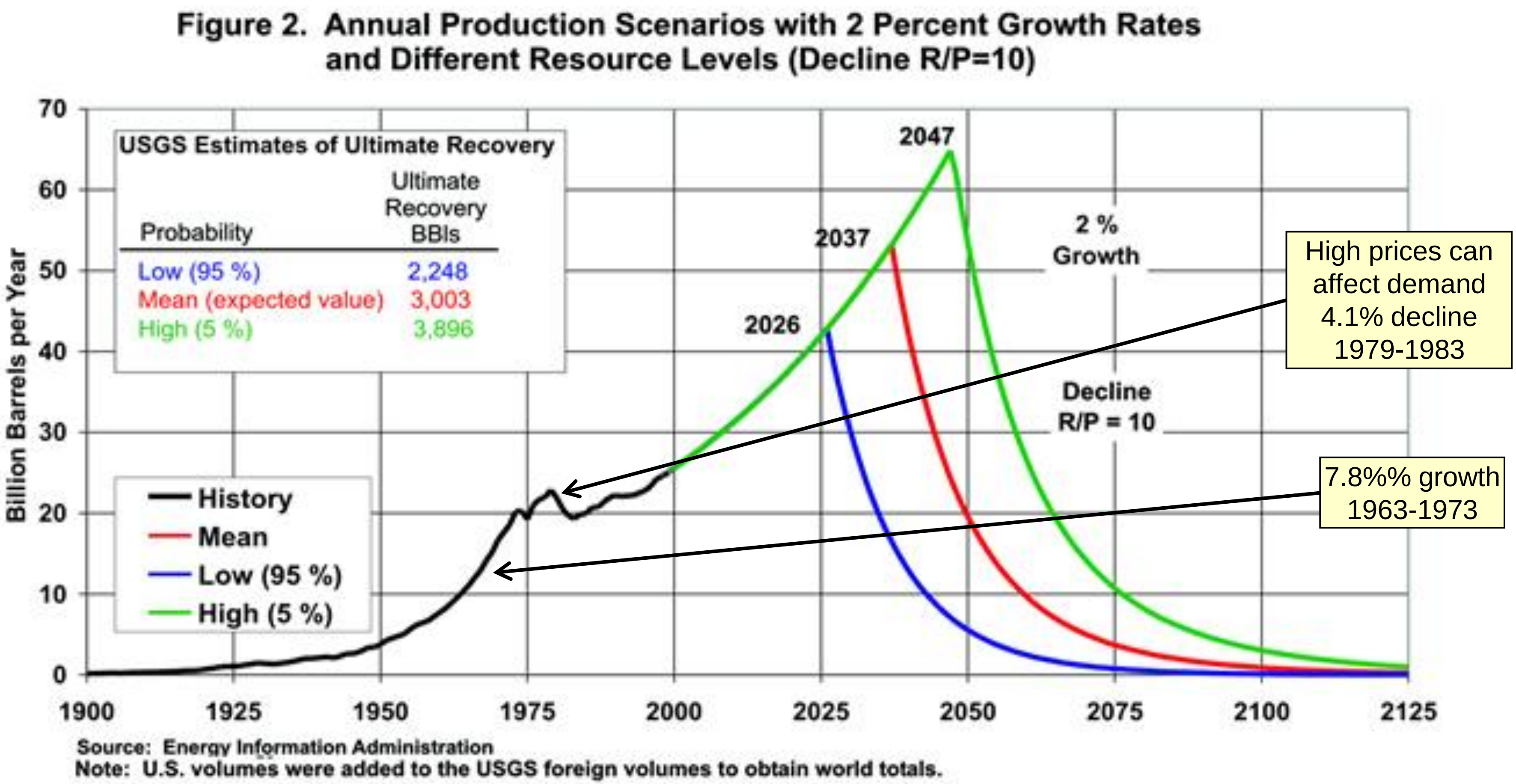
Production peak in 2004



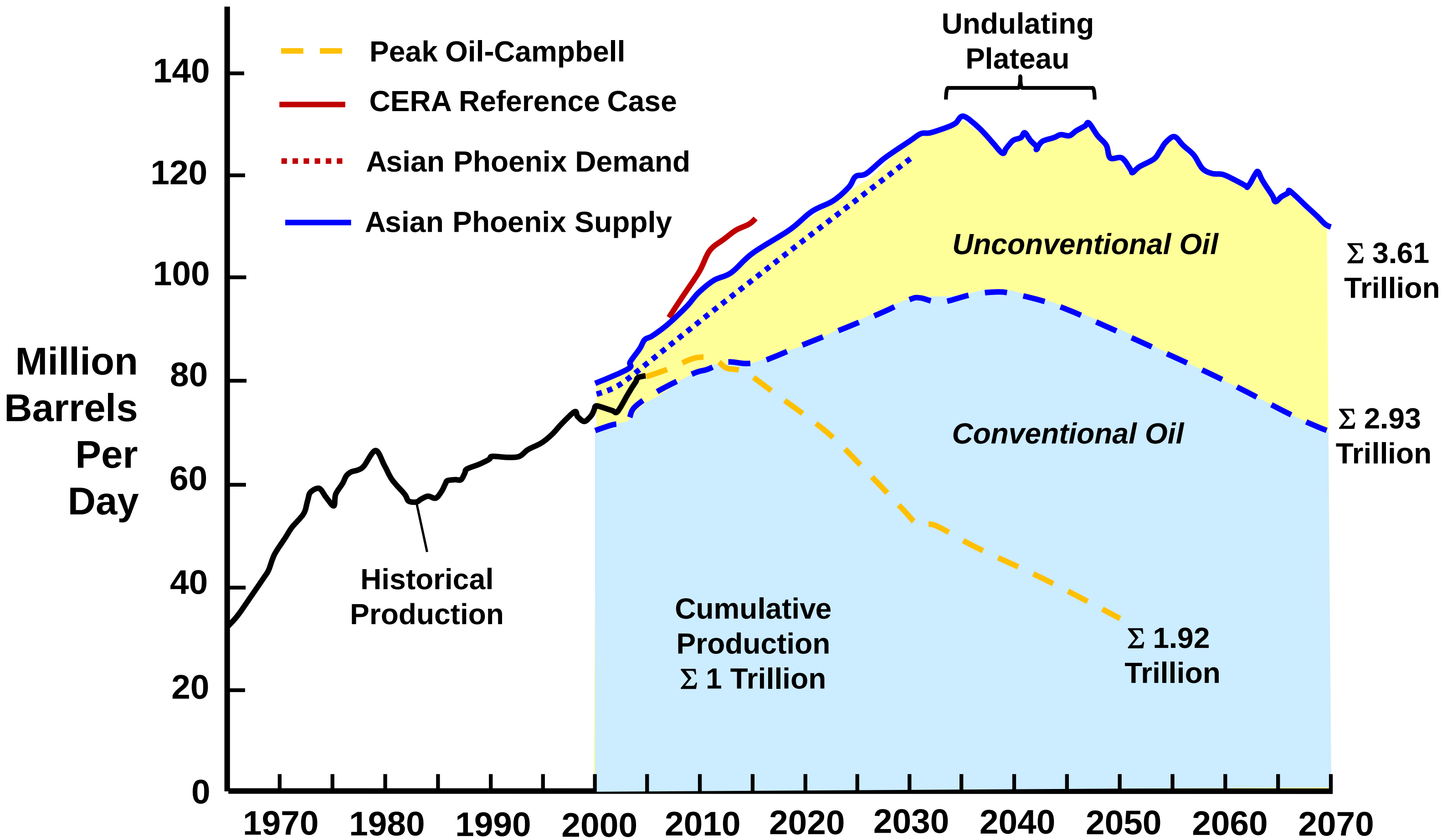
Oil Discoveries Declining Since 1964.



Annual Production with 2% Annual Growth & Decline.



Unconventional Oil to Improve the Plateau.



Source: Cambridge Energy Research Associates
60907-9

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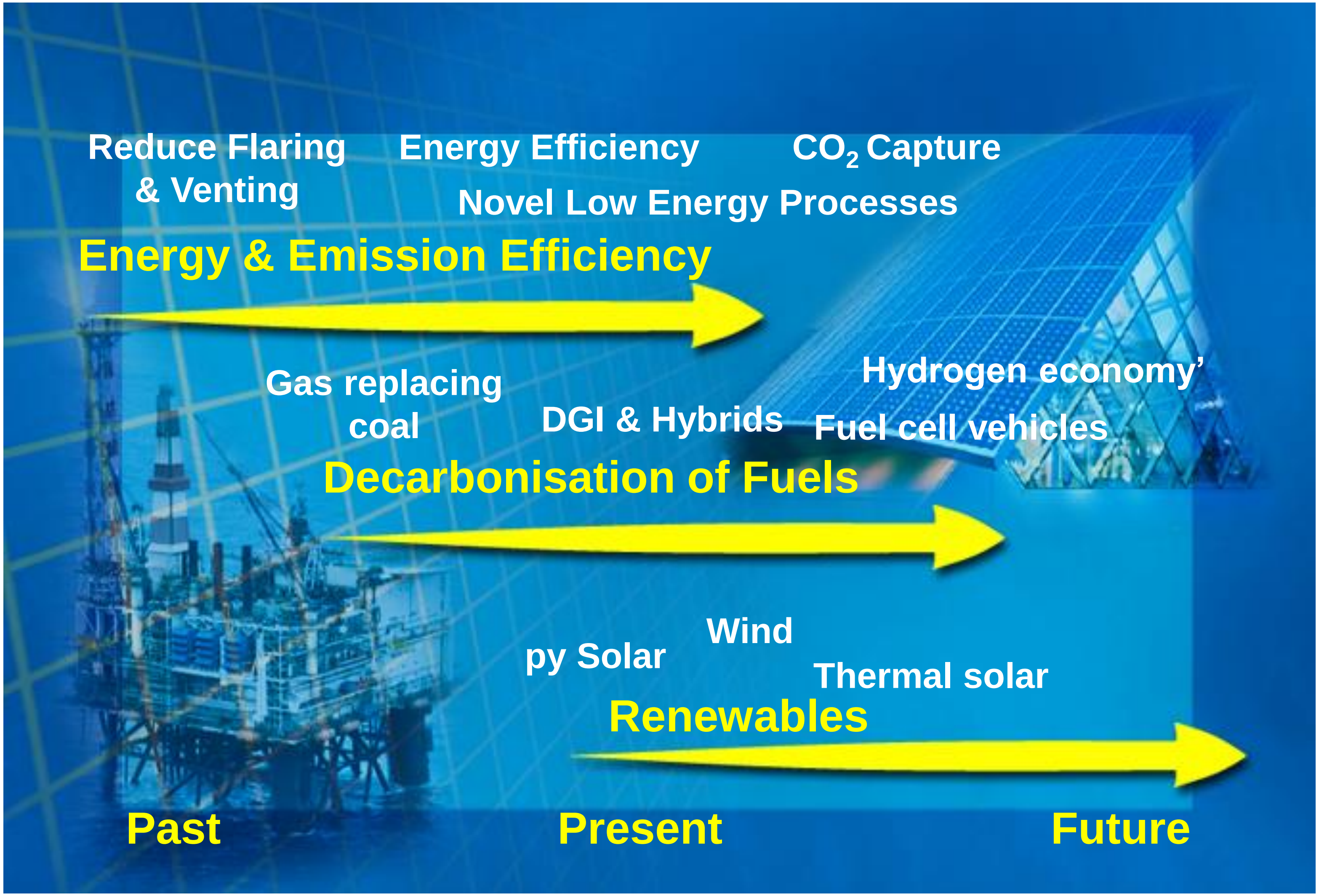
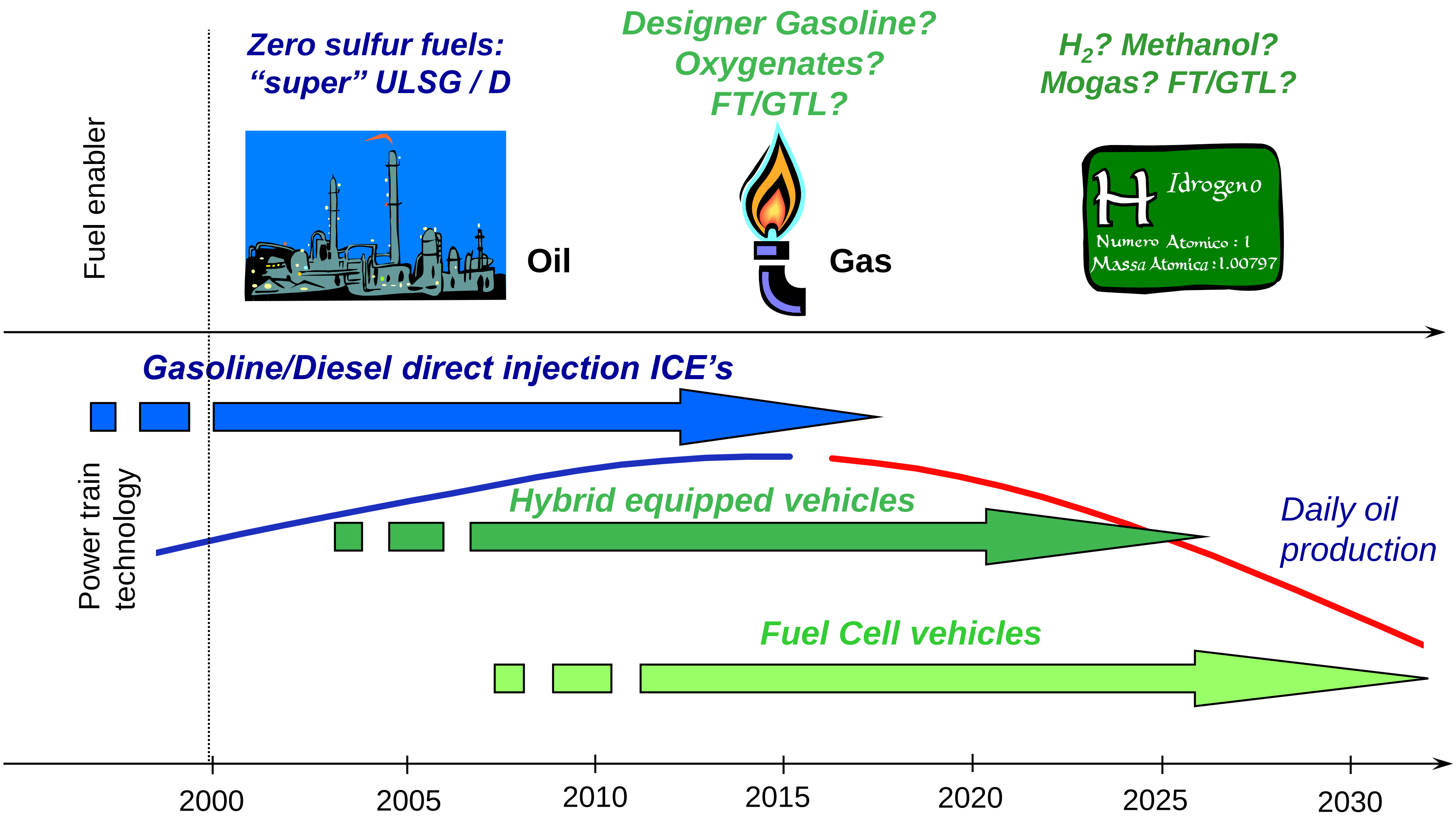
Developments in Chemical Sources for Energy and Chemicals.

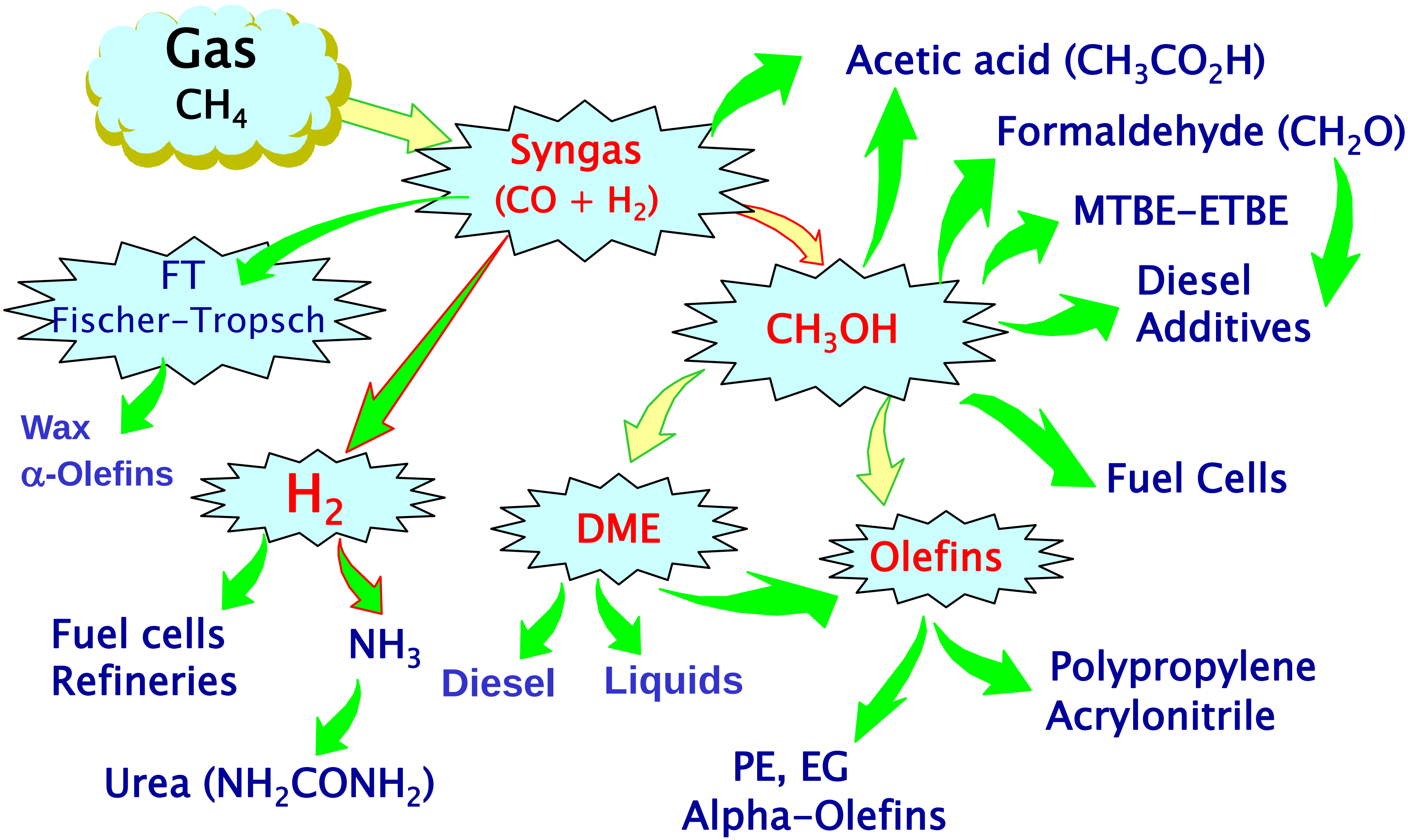
Lower Carbon Energy.



Expected Technology Developments.

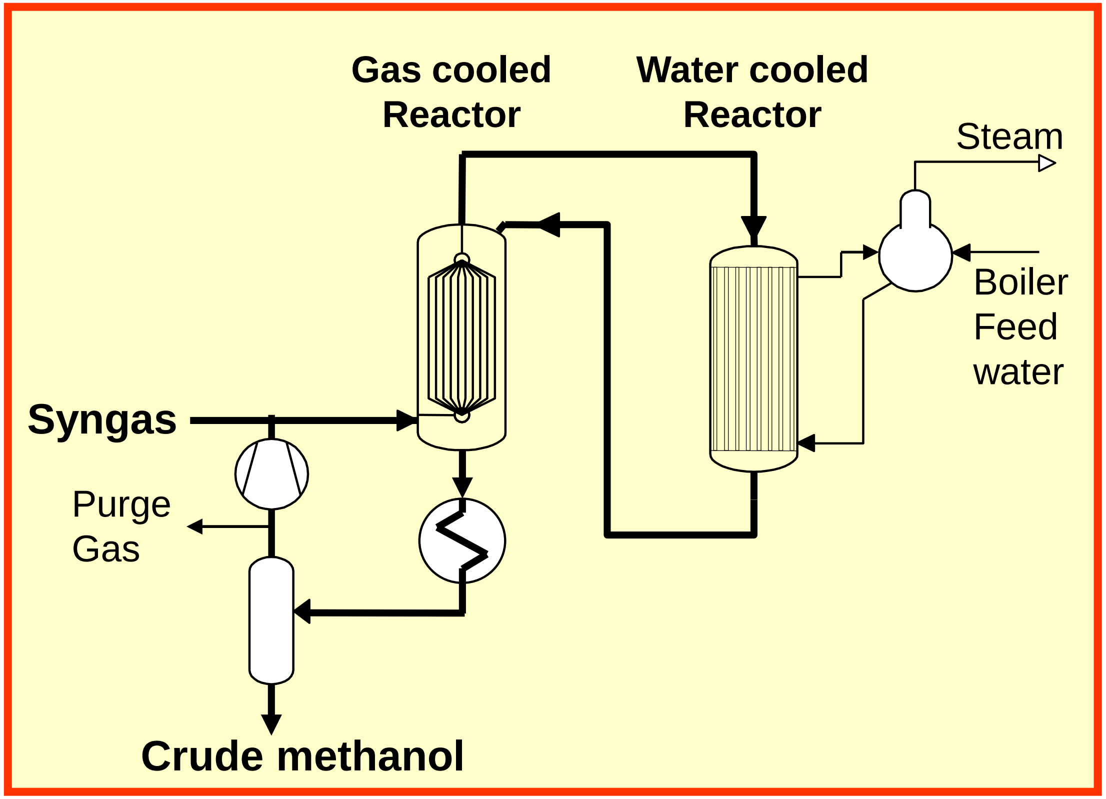


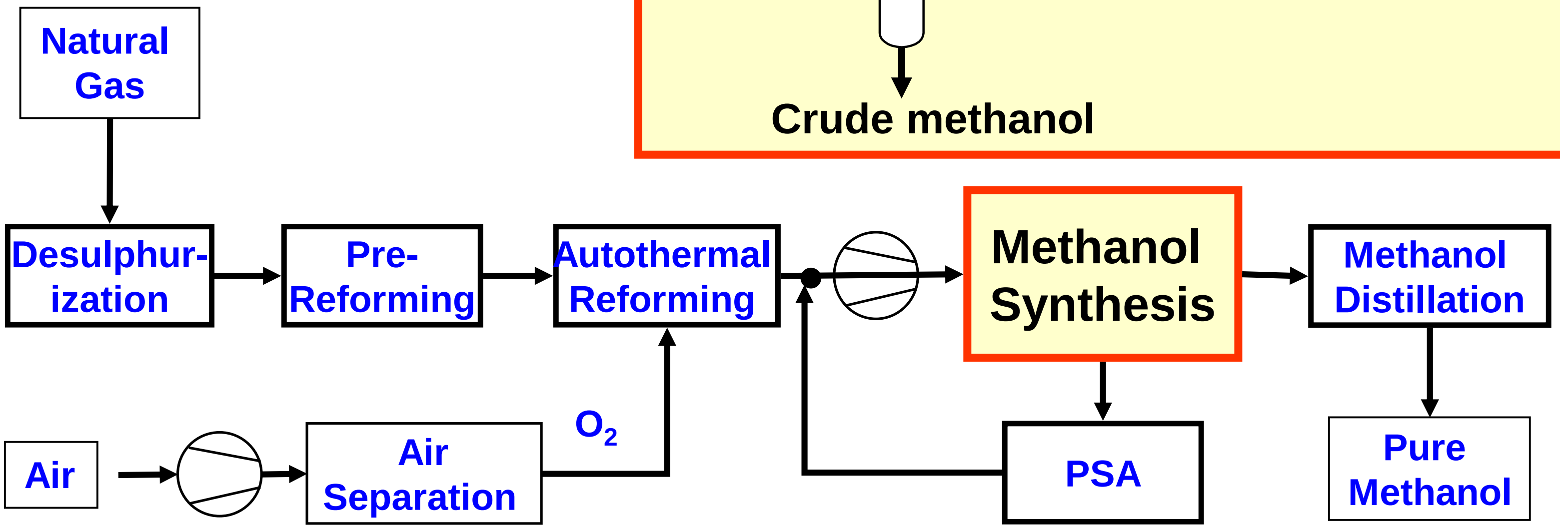
Future of Energy Markets: Gas to Chemicals & Fuels.



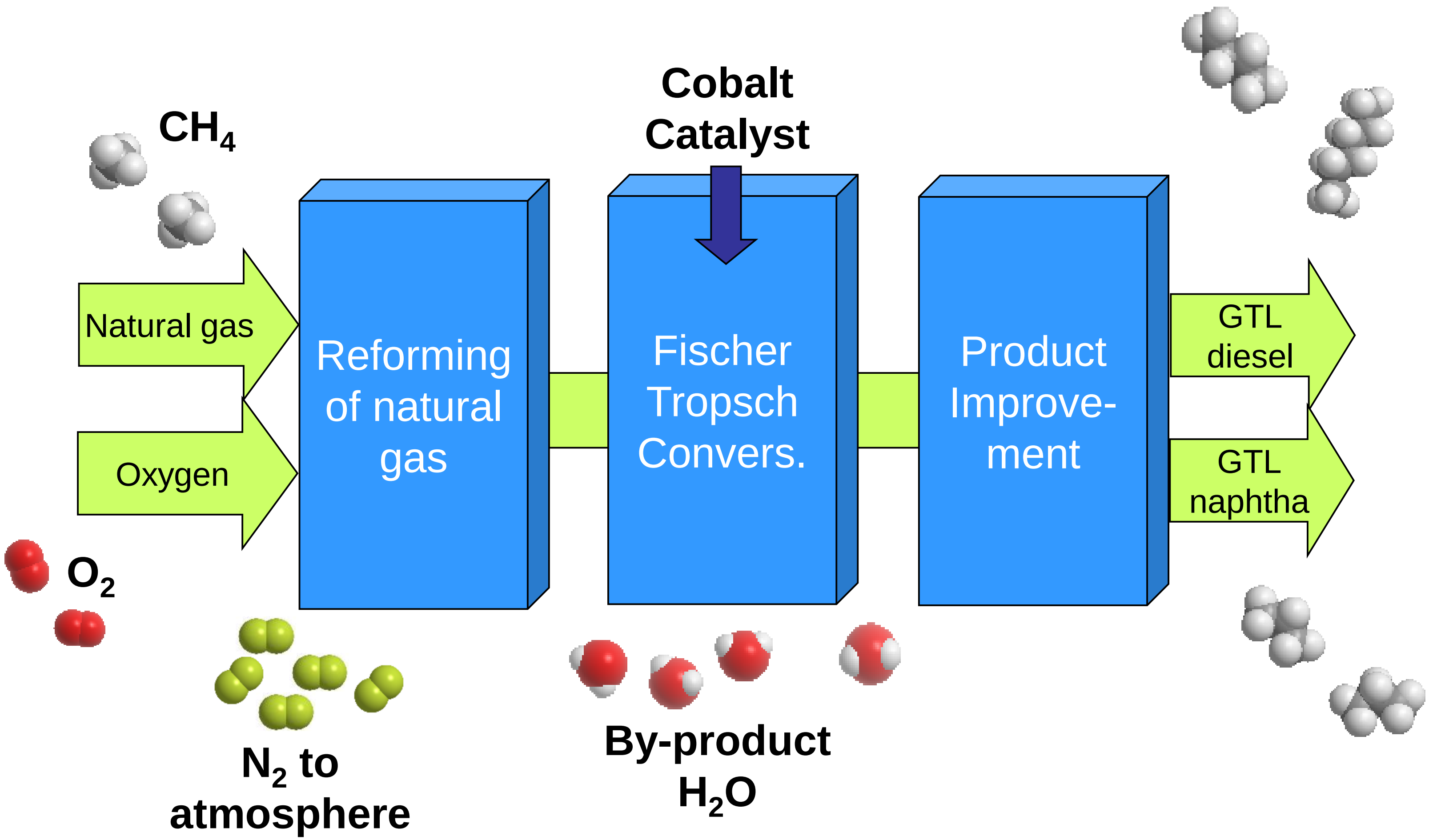
Simplified Diagram of Lurgi‘s MegaMethanol Technology.

- Improved gasification
- high energy efficiency in MeOH synthesis
- low investment costs
- large single-train capacity
- **MeOH production price cost of less than 50 \$/t!**

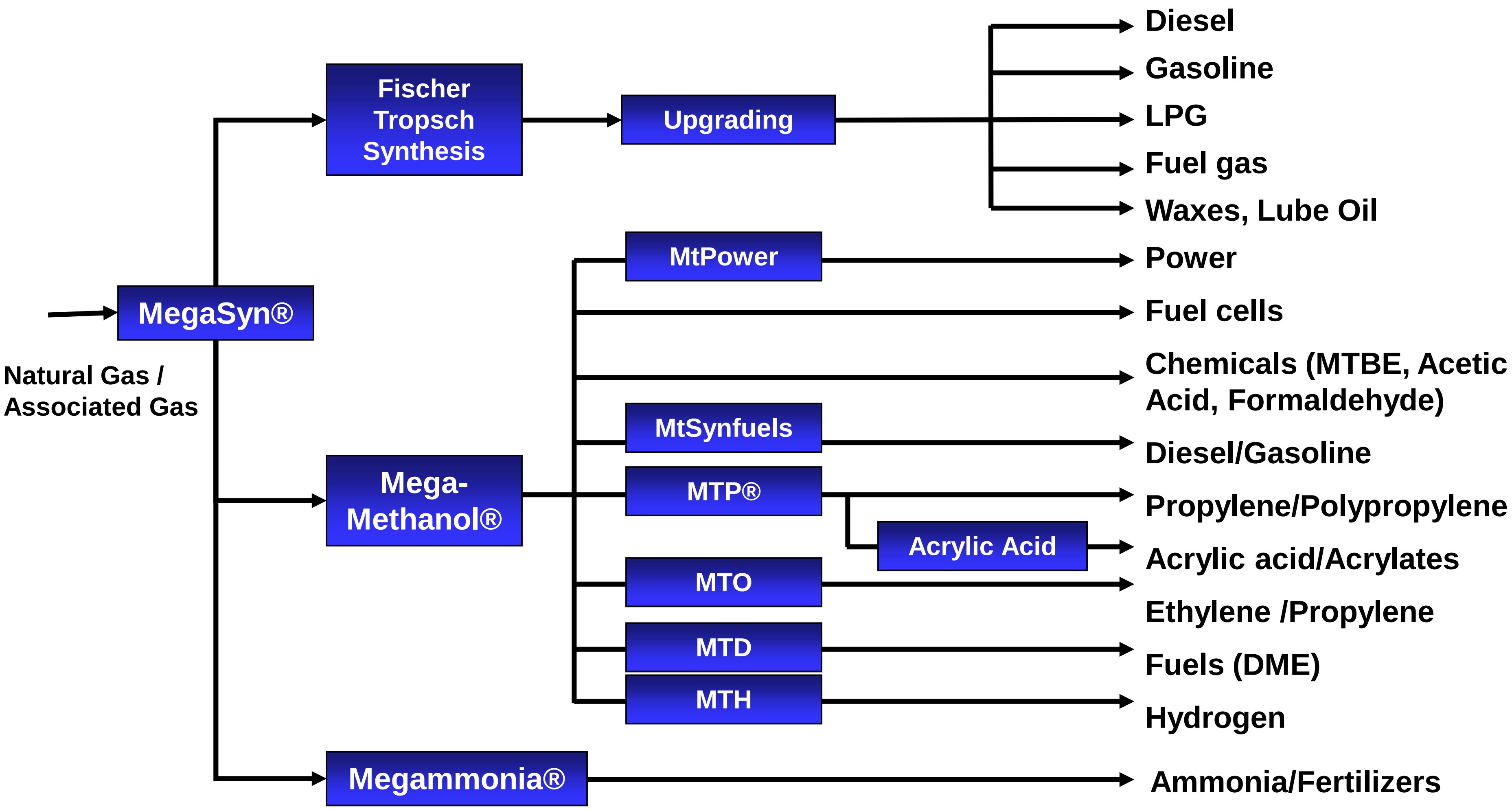




Gas to Liquid Technology.



Gas to Chemical Processing Route.



DME Synthesis: Alternatives.

Direct Synthesis of DME

DME Direct synthesis $$4\,H_2 + 2\,CO \longrightarrow CH_3OCH_3 + H_2O$$

Water gas shift reaction* $$CO + H_2O \longrightarrow CO_2 + H_2$$

*carbon loss by CO_2 formation

DME Synthesis via MegaMethanol®

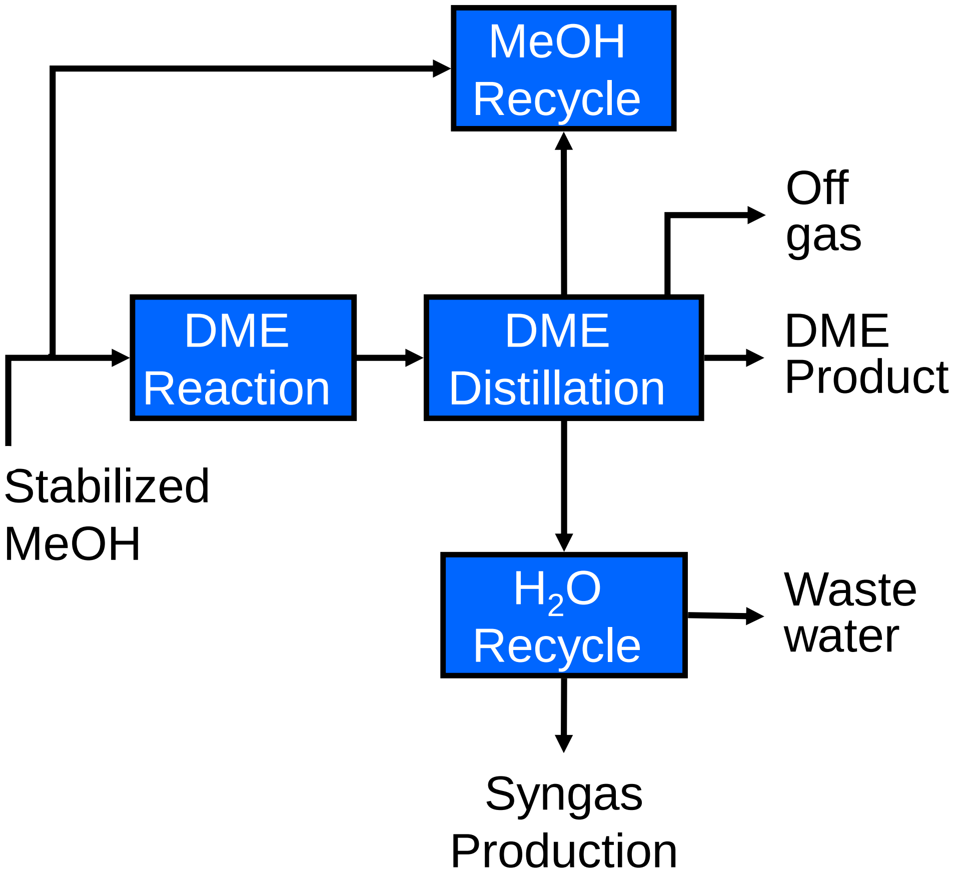
MegaMethanol® Synthesis** $$CO + CO_2 + 5\,H_2 \longrightarrow 2\,CH_3OH + H_2O$$

** CO_2 consumption = “sequestration”!

Methanol dehydration $$2\,CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

Dimethyl Ether (DME) – An Alternative Fuel.

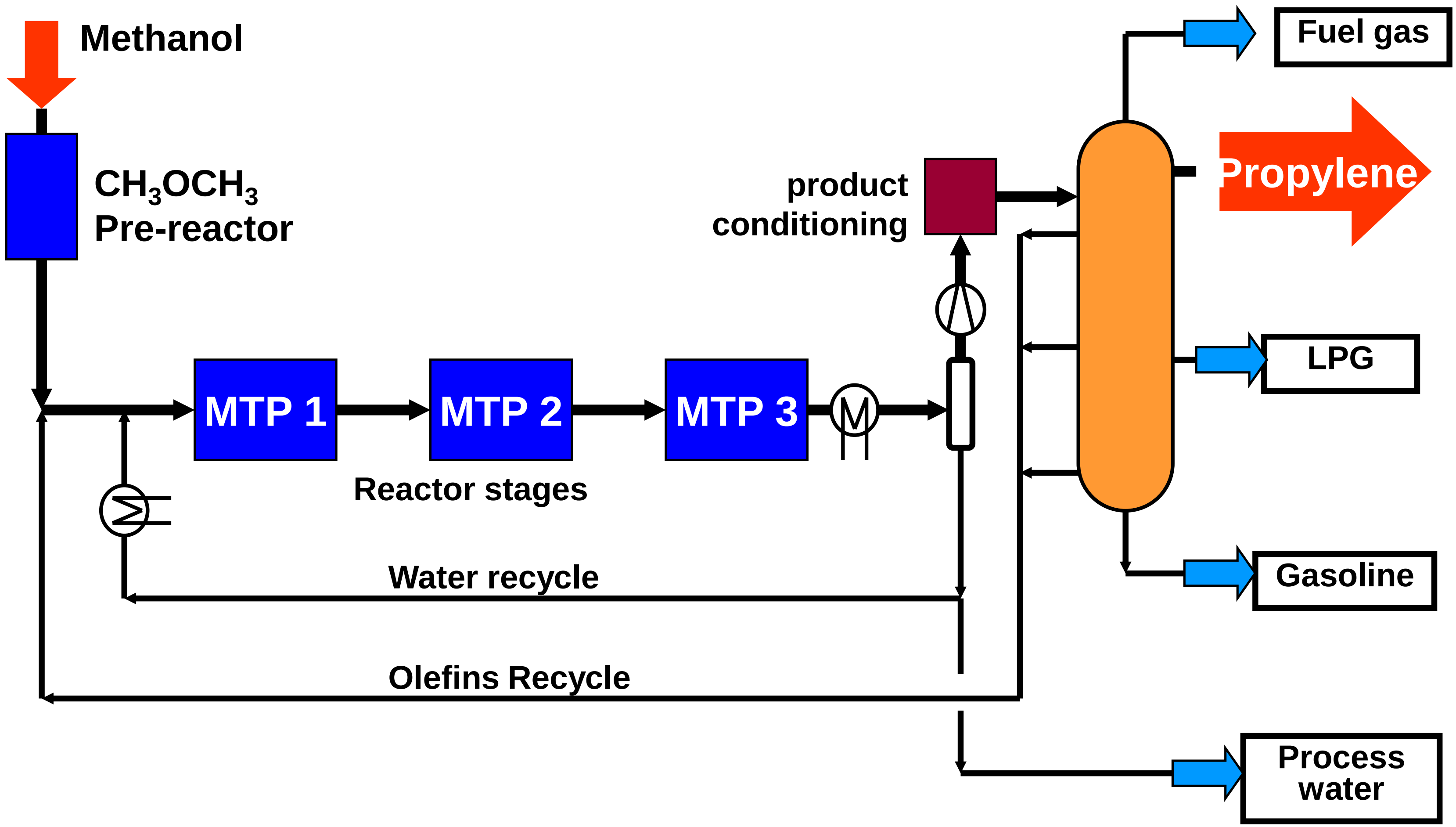
- **Reactor: Adiabatic Fixed Bed Reactor**
- **High Conversion Rate**
- **Zero emission**
- **Clean and efficient power generation**
- **Highly efficient Heat Integration Systems**
- **Low utility consumption**
- **Easily transported fuel ("better than diesel")**
- **Properties similar to LPG (stock, transport)**



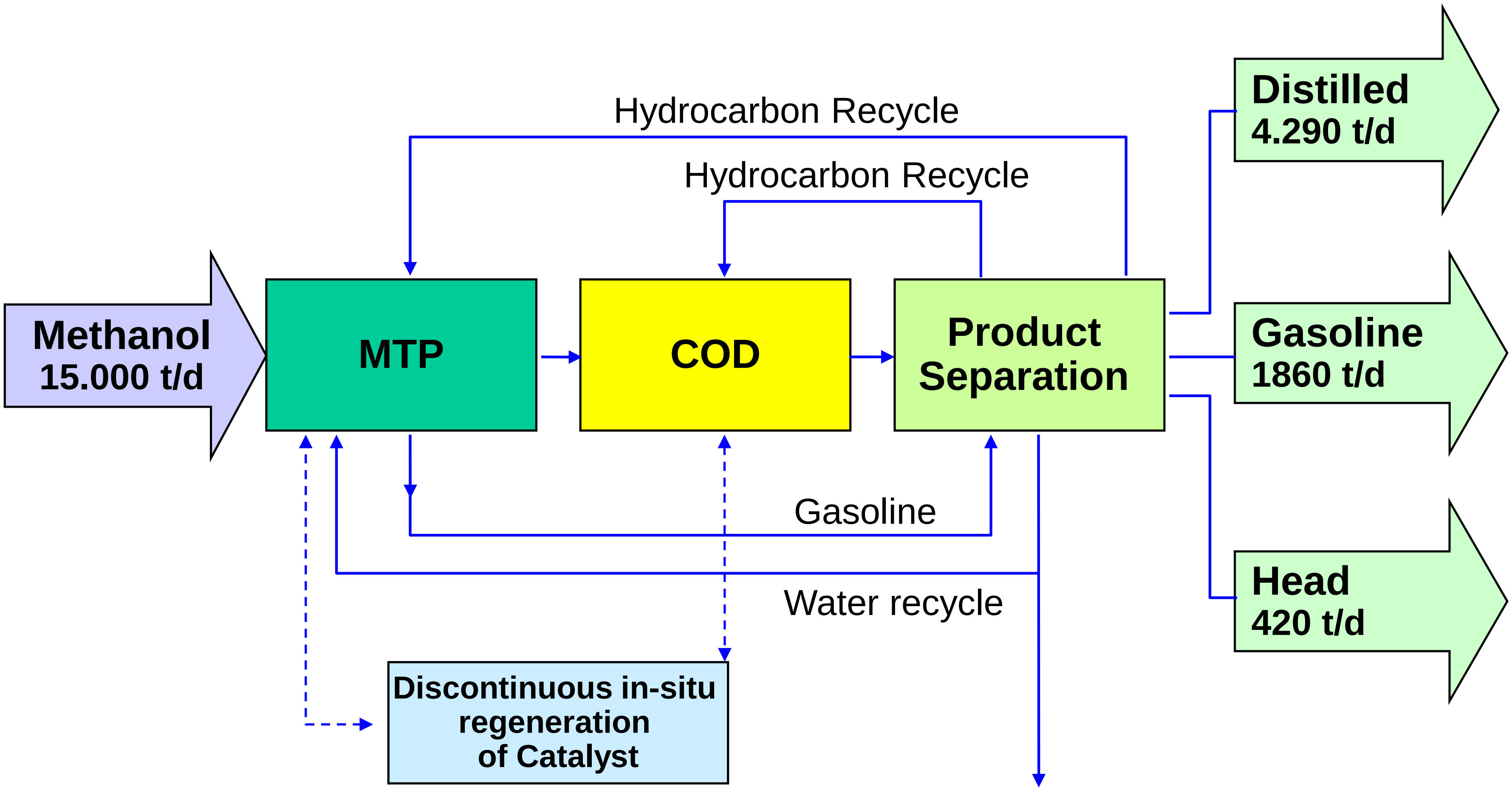
DME Properties vs. Other Fuels.

Name	DME	Propane	Methane	Methanol	Diesel
Chemical formula	CH_3OCH_3	C_3H_8	CH_4	CH_3OH	
Molecular weight	46.07	44.1	16.04	32.04	
Boiling point at 0.1MPa, °C	-24.8	-42.1	-161.5	64.7	150-370
Liquid density, kg·m^{-3} (20°C)	666	501	-	792	<845
Relative density (gas, air =1)	1.59	1.52	0.55	-	-
Vapor pressure, MPa (20°C)	0.51	0.85	-	-	-
Explosive limit (vol.% in air)	3-17	2.1-9.4	5-15	5.5-44	0.6-6.5
Cetane number	55-60	5	0	5	40-55
Net calorific value (MJ·kg^{-1})	28.84	46.3	50	19.9	~42.5

MTP® - Simplified Flow Diagram.



Gas Refinery via Methanol.



Lurgi's MtSynfuel® (MTS)

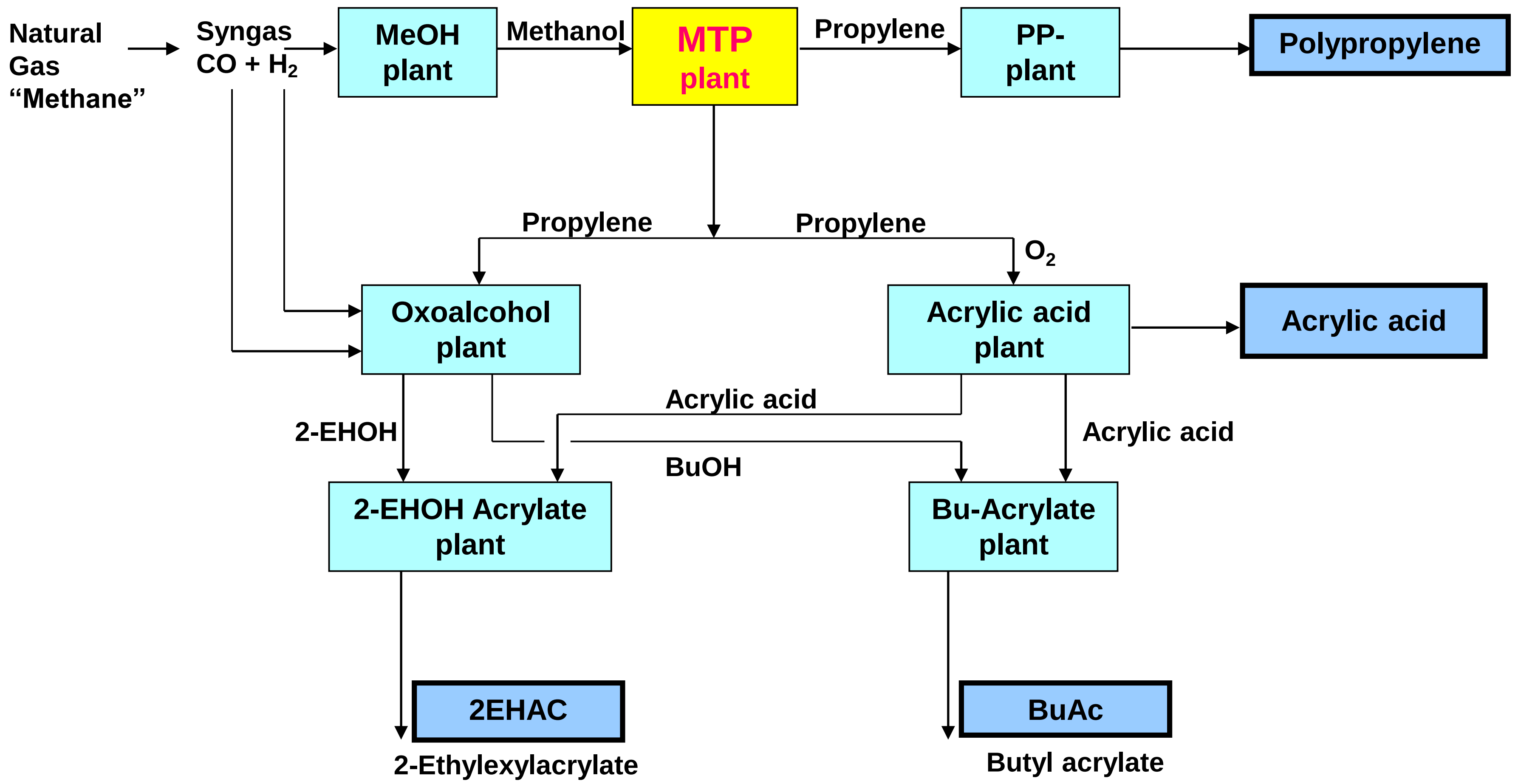
Comparison Lurgi MTS Process - FT Synthesis.

Product Slate	Lurgi Route	FT Synthesis
Naphtha : Diesel (max.)	1 : 4	1 : 2.3 – 1 : 5.4

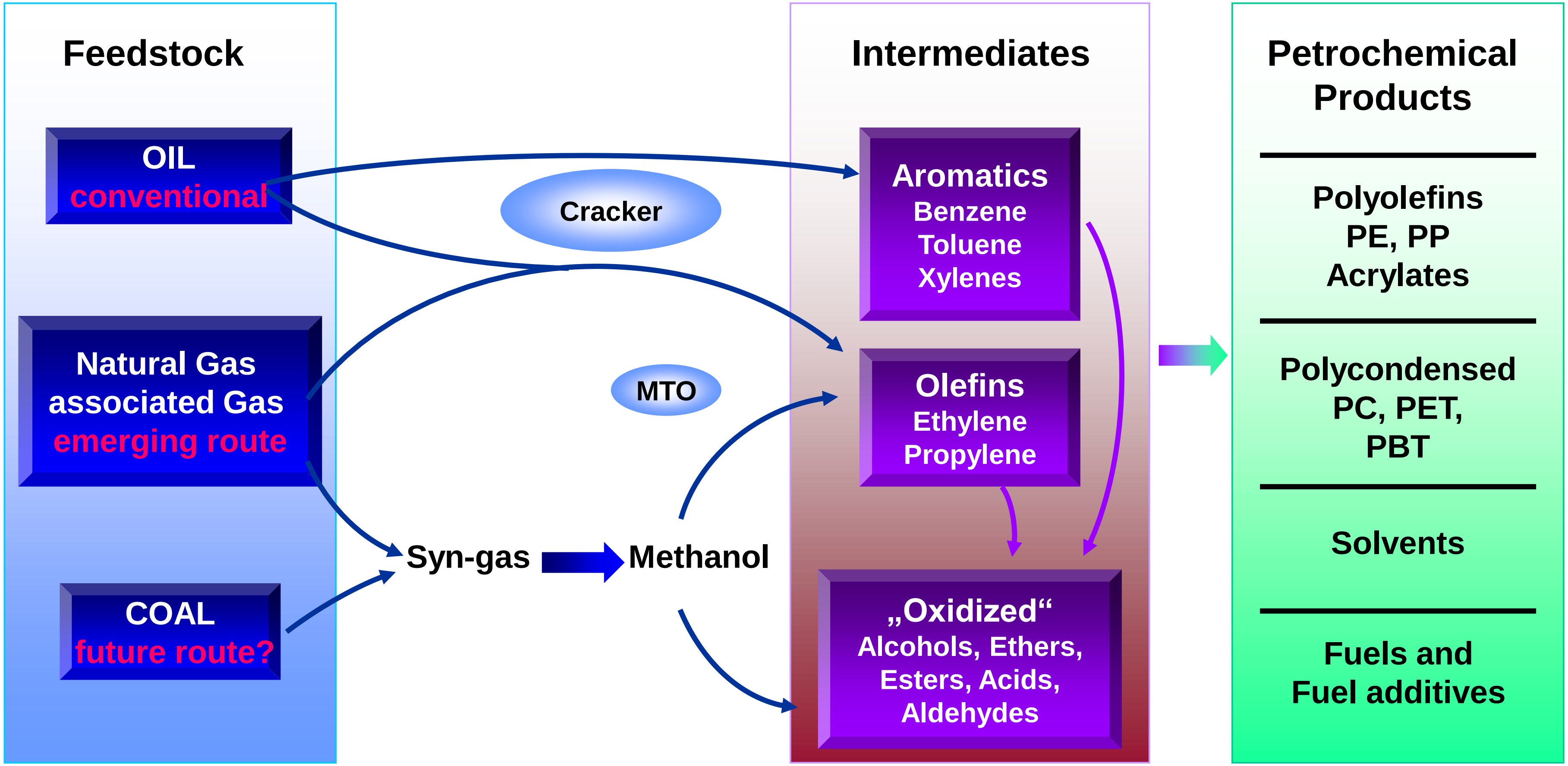
Product Properties				Lurgi Route[3)]	FT Synthesis [3)]
	Spec. (Europe after 2005)				
Gasoline					
- Aromatics	vol.%	max.	35	3	< 1
- Benzene	vol.%	max.	1	<< 1	<< 1
- Sulphur	wpp	max.	50/10 [1)]	0	0
- Olefins	m	max.	18	44	> 30
- RON [2)]	vol.%		91/95/98	80	< 40
- MON [2)]			82.5/85/88	75	< 40
Diesel					
- Polyaromatics	vol.%	max.	11	< 1	< 1
- Sulphur	wpp	max.	50/10 [1)]	< 1	< 5
- Cetane N°	m	min.	51	55	> 70

[1)] Diesel with 10 wppm of sulfur is required by the EU regulations
[2)] RON / MON fir Normal Gasoline/ Euro-Super / Super-Plus
[3)] Properties after the refinering of naphtha

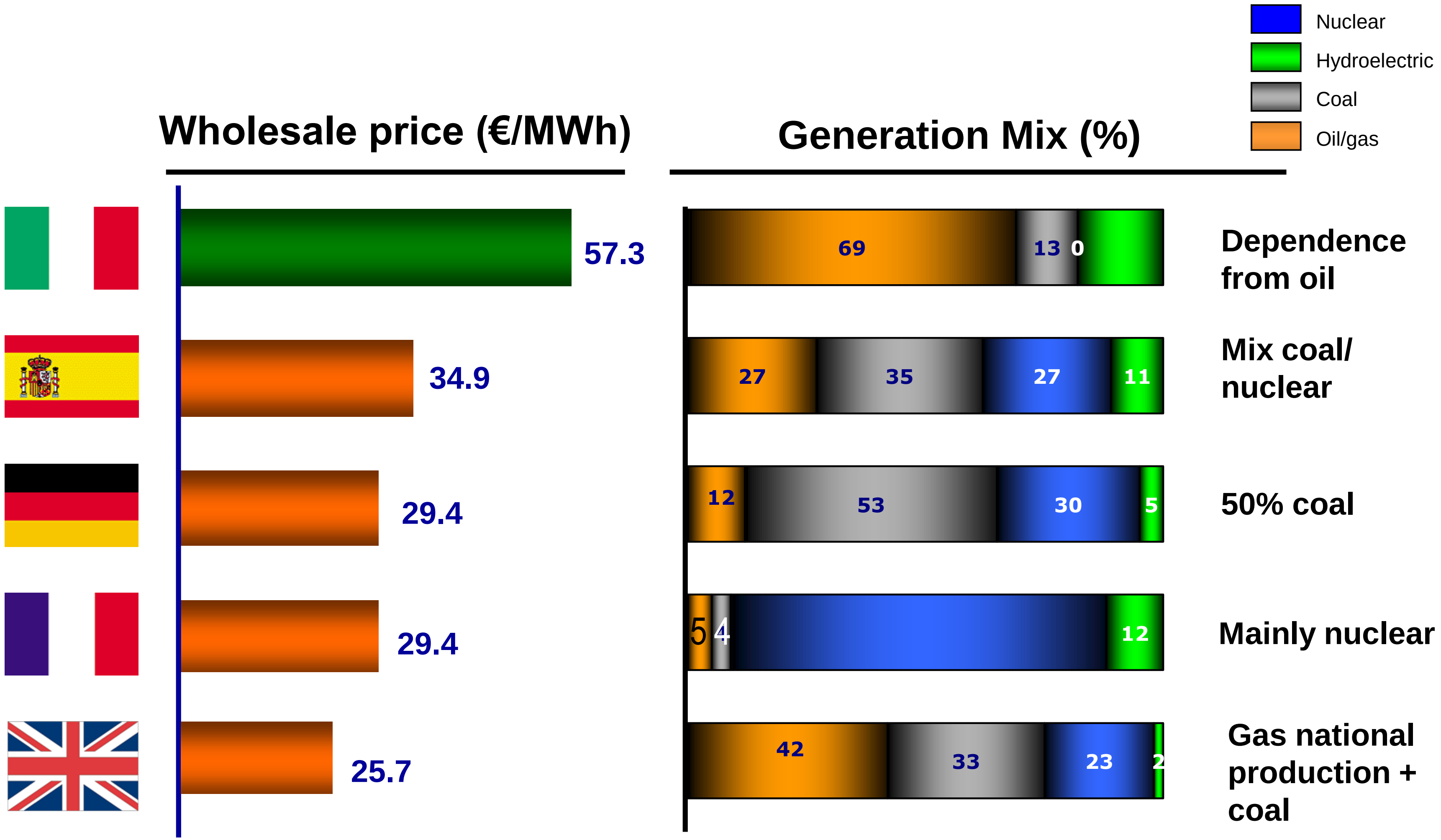
Petrochemistry Based on Natural Gas.



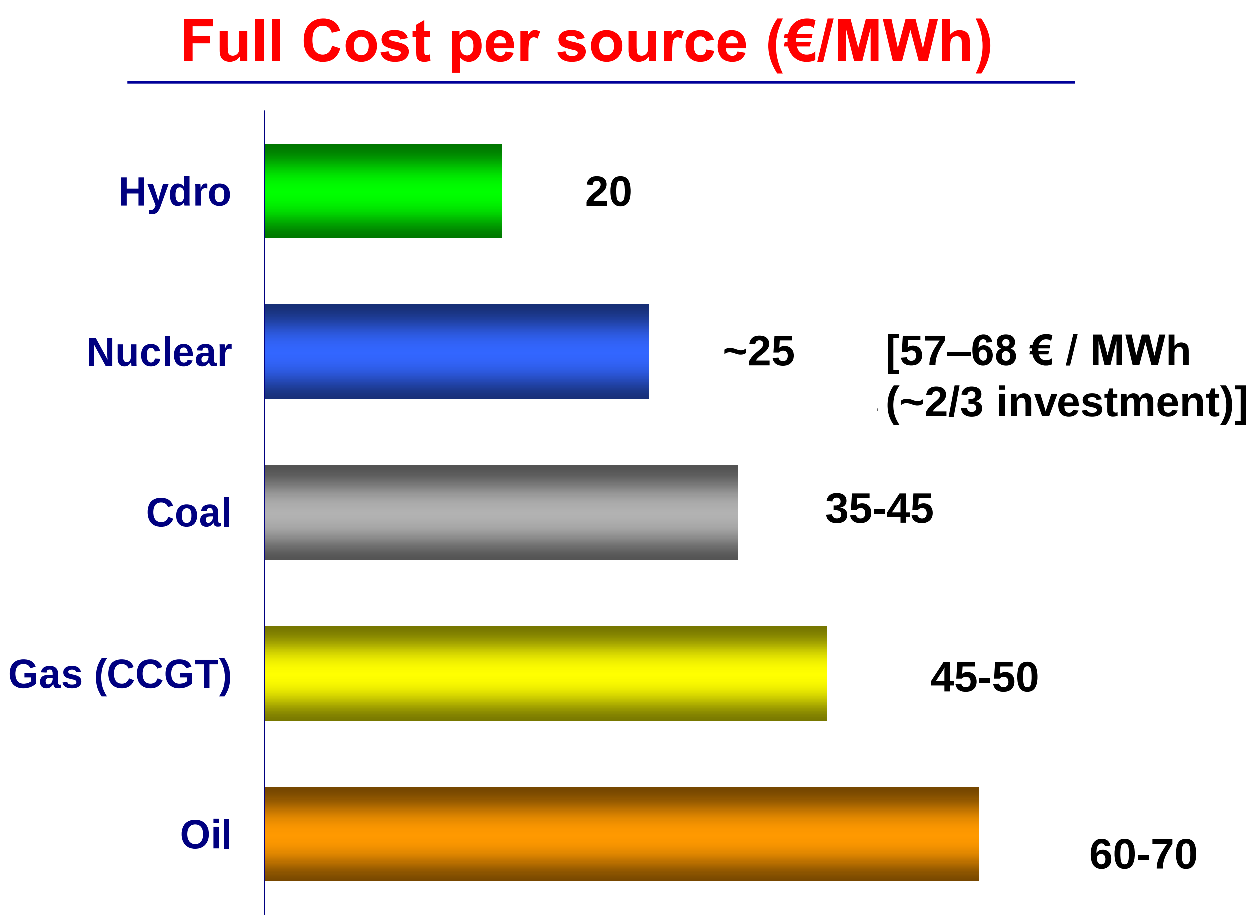
Gas based Petro-Chemistry.



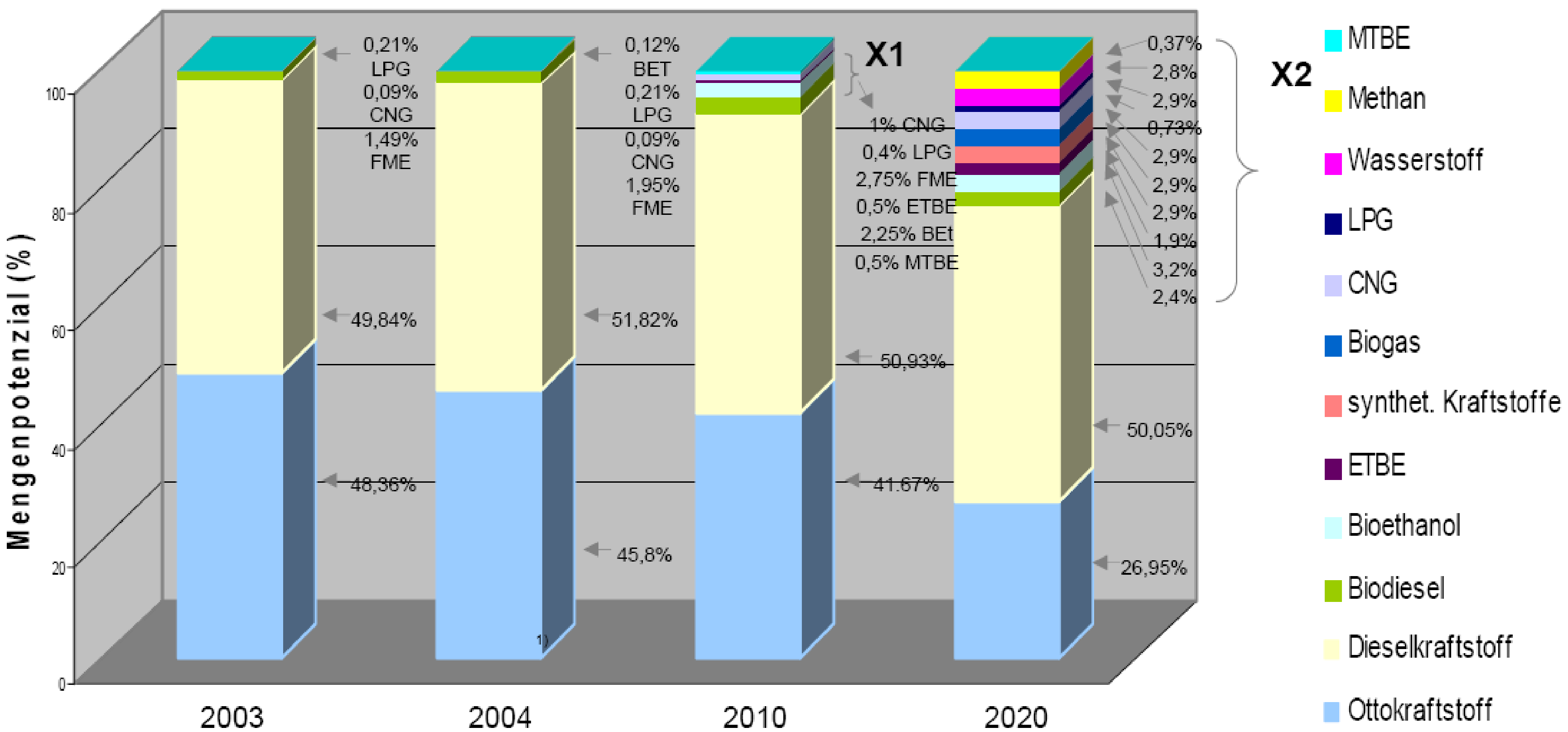
Electric Energy Composition and Production Prices in Some Countries.



Production Costs (Italy).



Relative Potential of Fuel Market (German Evaluation).



X_1 : According to report there is a theoretical potential for biofuels of up to 9%.

X_2 : According to report there is a theoretical potential for biofuels of up to 1/3 of the present fuels market.

To complete the Energy Topic, You must see also the chapters:

a) Renewable Energy Sources
b) Biofuels
c) Hydrogen
d) Pollution Prevention

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Examples of Energy Questions.

Problem - 1

What is Italy's contribution to total global energy consumption?

per capita consumption × population =

$1.6 \cdot 10^{11}$ J × $56 \cdot 10^{6}$ = $0.89 \cdot 10^{19}$ J

= 8.9 EJ

Global consumption = 340 EJ

Italy's contribution ~ 2.6 %

Problem - 2

The total global output of carbon dioxide emissions from all anthropogenic (human) sources is estimated to be 29 Gt CO_2 per year. Italian sources report a total CO_2 emissions value of 135 Mt per year, but the Italian sources are reported in terms of carbon (C) output. What is the ratio of release of carbon dioxide per capita for the Italian population compared to the total global population?

PM (CO_2) = 44 **PA (C) = 12**

CO_2 emissions in Italy = 135 Mt × 44/12 = 495 Mt

Ratio = $495 \cdot 10^6$ t / $29 \cdot 10^9$ t = 0.017 (1.7 %)

Problem - 3

To heat a home in Lombardia region, it may require approximately 2000 m^3 of natural gas per year.

Calculate the amount of carbon dioxide released from the furnace over this period.

		ΔH (kJ)
Natural Gas	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-890.3

$12 + 4 \times 1 = 16$ g

$12 + 2 \times 16 = 44$ g

$1\ m^3\ (CH_4) = 3.7\cdot10^7$ J ⟹ $2000\ m^3 = 7.4\cdot10^{10}$ J

1.0 GJ of heat produced by methane, 49 kg di CO_2 are released in air

74 GJ release: $49 \times 74 = 3626$ kg di CO_2

Problem - 4

The energy content per gram for biomass is between one third and one half that of fossil fuels. Considering the general structures of these materials, what is the reason?

Combustions

biomass $CH_2O + O_2 \rightarrow CO_2 + H_2O$ **ΔH = -440 kJ / 30 g (14.7)**

Natural Gas $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ **-890.3 kJ /16 g (55.6)**

Coal $C + O_2 \rightarrow CO_2$ **-393.5 / 12 g (32.8)**

Heavy oil $C_{20}H_{42} + 30.5O_2 \rightarrow 20CO_2 + 21H$ **-13 300 / 282 g (47.1)**

For 1.0 GJ of heat produced by biomass, 100 kg of CO_2 are released

Value very close to coal!

Problem - 5

In Italy the upper 'safe limit' for MTBE in water supplies has been set at 1.6×10^{-7} M. What is the concentration in the most convenient pp? unit?

For water (freshwater) solutions, 1 mL weighs 1 g (1 L = 1000 mL, weighs 1 kg)

$1\ m^3$ = 1000 L, weighs 1 t

1 ppm	**1 ppb**
$1\ \mu g \cdot mL^{-1}$	$1\ ng \cdot mL^{-1}$
$1\ mg \cdot L^{-1}$	$1\ \mu g \cdot L^{-1}$
$1\ g\ m^{-3}$	$1\ mg \cdot m^{-3}$

Mercury in a water sample is present at a concentration of $3.6 \times 10^{-8}\ mol \cdot L^{-1}$. This concentration is equal to:

7.2 ppm   1.8 ppm   3.6 ppb   14.4 ppb   none of these

Problem - 6

In some countries, the oxygen content of gasoline is requested to be almost 2.7 %. Determine the mass of ETBE (ethyl *tert*-butyl ether) for kg of gasoline to end up with a fuel with a 2.7 % content in oxygen by mass.

Problem - 7

What is the energy benefit of growing corn for ethanol production?

Energy output per liter

ethanol fuel value	19.0×10^6 J
co-production products	8.2×10^6 J
total output	27.2×10^6 J

Energy input

Corn production	5.4×10^6 J
Processing	9.1×10^6 J
total output	14.5×10^6 J

Total energy gain = $[(27.2 – 14.5) / 14.5] \times 100$ = **87 %**

Fuel energy gain = $[(19.0 – 14.5) / 14.5] \times 100$ = **31 %**

(energy from sum not evaluated!!!)

Problem - 8

The densities of methanol, ethanol, and octane are approximately 0.79, 0.79, and 0.77 g·mL^{-1},respectively. Use this and other information to comment on the relative sizes of fuel tanks required to contain fuel that will generate 1 GJ of energy.

Problem - 9

A natural gas-fired 10 MW power plant produces electricity with an average of 29 % efficiency. Assume that it is in operation on average 20 hours every day, estimate the amount of carbon dioxide released in a one month period.

Explain the environmental consequences associated with releasing the waste heat into a lake like Como Lake.

Suggest options for more constructive use of the 'waste heat'.

Problem 11

The enthalpy value for the combustion of one mole of methane is –890.3 kJ. The reported heat value for 1 m^3 of natural gas is 3.7×10^7 J. Assuming that natural gas is pure methane, calculate the pressure of the gas used for the calculation of its heat value. Assume 25^{o}C.

Problem 12

1. What is the energy content of 1 g of methane, 1 g of hydrogen?

2. How much energy from 1 m^3 of methane, 1 m^3 of hydrogen?

$\Delta H_{combustion}$ (methane) = -890.3 $kJ \cdot mol^{-1}$

$\Delta H_{combustion}$ (hydrogen) = -242 $kJ \cdot mol^{-1}$

molar mass methane = 16.04

$\Delta H_{combustion}$ on a mass basis = -890.3/16.04 = - 55.5 $kJ \cdot g^{-1}$

molar mass hydrogen = 2.016

$\Delta H_{combustion}$ on a mass basis = -242 / 2.016 = -120 $kJ \cdot g^{-1}$

Problem – 12 bis

1. What is the energy content of 1 g of methane, 1 g of hydrogen?

2. How much energy from 1 m^3 of methane, 1 m^3 of hydrogen?

1 m^3 of any gas at P^o and 25°C contains $n = PV / RT$ mol of gas

$$n = (101\,325 \times 1) / (8.314 \times 298.3) = 40.9 \text{ mol}$$

For methane, energy for combustion of 1 m^3 = 890.3×40.9 = 36 400 kJ

For hydrogen, energy for combustion of 1 m^3 = 242×40.9 = 9900 kJ

Problem - 13

a) Take in consideration the table of energy equivalent and other data in reference material. Compare the energy density of various fossil fuels (using anthracite, oil and natural gas as examples), and fresh biomass, hydrogen and uranium. Which are the environmental and practical consequences of differences?

b) Compare CO_2 emissions per GJ of energy from the same sources. Which are the environmental consequences of differences? Which other environmental issues must be taken in consideration in evaluating the quality of the energy source?