

FOSSIL FUELS' ENERGY AND THEIR ENVIRONMENTAL IMPACT

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FOSSIL FUELS:

We love to hate ...

- The Big Picture, Revisited, why do we care?
- Types, amounts, how long and what are the trends?
- Combustion and reforming, why some chemistry headache?
- Combustion phenomena, where do they fit?
- Burners and Combustors, some hardware?
- Power Cycles, conventional and advanced, what are the trends?
- Emissions and their control, successes or failures?
- Fuel Cell; what do they have to do with fossil?
- Biomass, what is the connection?

THE GLOBAL PICTURE

The Terawatt Challenge

R. Smalley*

Rice University

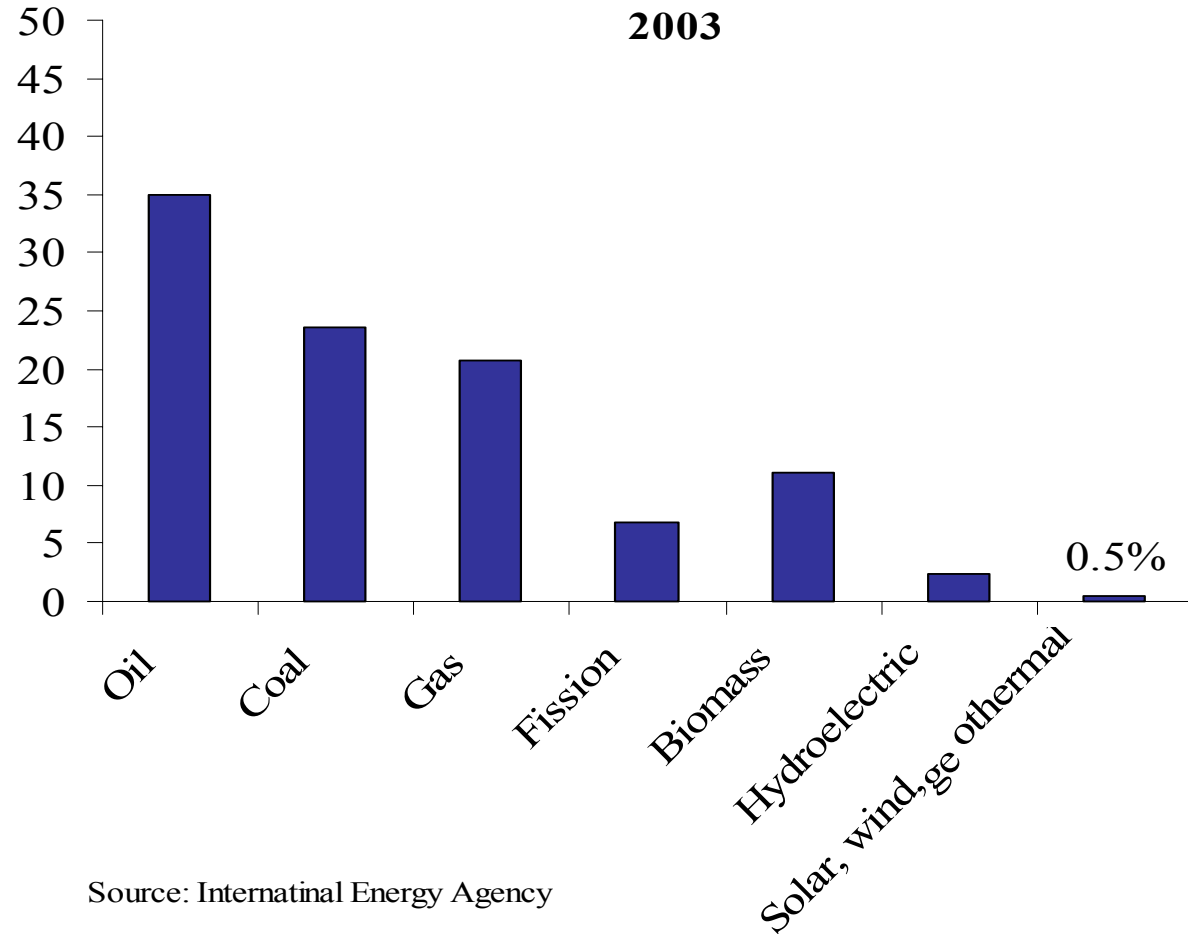
1. ENERGY
2. WATER
3. FOOD
4. ENVIRONMENT
5. POVERTY
6. TERRORISM & WAR
7. DISEASE
8. EDUCATION
9. DEMOCRACY
10. POPULATION

12 Terawatts World wide

(3.3 TW in US)

~ 80% fossil, ~ 90% with biomass

2003



Energy Sources and Demand

Source: M.I. Hoffert et. al., *Nature*, **1998**, 395, 881

Graph removed for copyright reasons.

Wigley, Richels and Edmonds, ppmv of CO₂,
pre-industrial concentration is 280 ppmv

CO₂ emissions and Global Temperature!

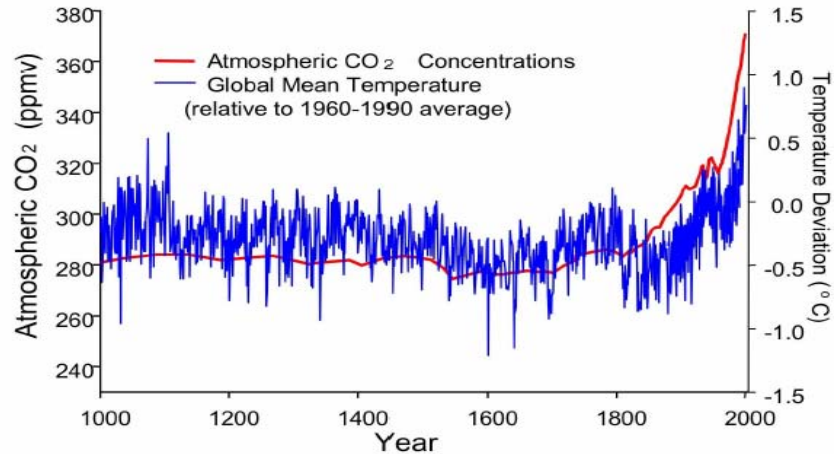


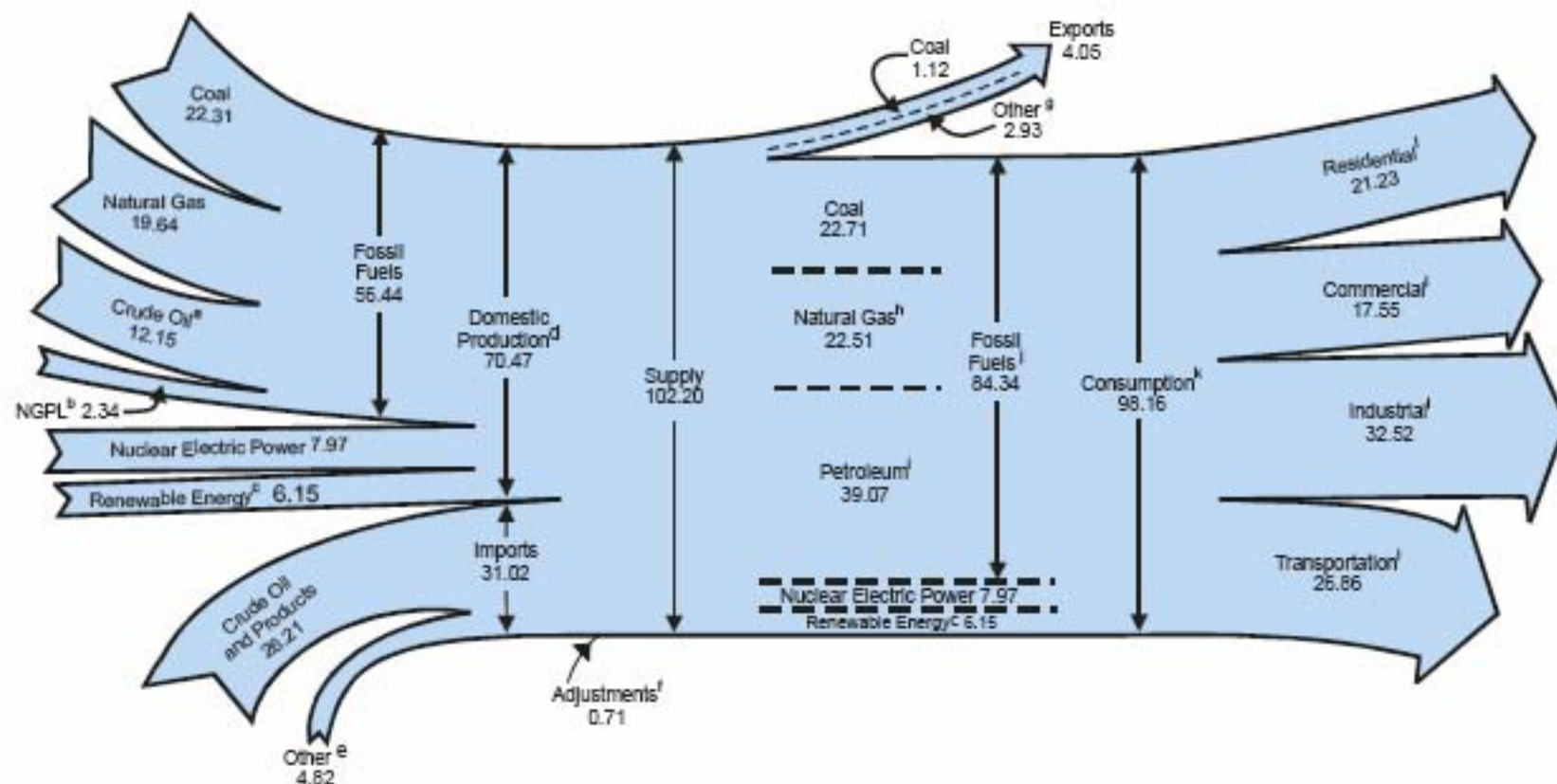
Figure 1b Increased CO₂ Emissions Causing a Rise in Atmospheric CO₂ Associated with a Rise in Global Temperature (Sources: CO₂ data from Ethrige et al. 2001, Keeling and Whorf 2002; temperature data from Jones et al. 1998, Peterson and Vose 1997)

From “Basic Research Need for a Hydrogen Economy”,
Report of DOE BES Workshop, May 13-15, 2003

Predictions are always wrong! But it is good to have a plan ...

THE DOMESTIC PICTURE

Diagram 1. Energy Flow, 2003
(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 Includes -0.09 quadrillion Btu hydroelectric pumped storage.

^e Natural gas, coal, coal coke, and electricity.

^f Stock changes, losses, gains, miscellaneous blending components, and unaccounted-for supply.

^g Crude oil, petroleum products, natural gas, electricity, and coal coke.

^h Includes supplemental gaseous fuels.

ⁱ Petroleum products, including natural gas plant liquids.

^j Includes 0.05 quadrillion Btu of coal coke net imports.

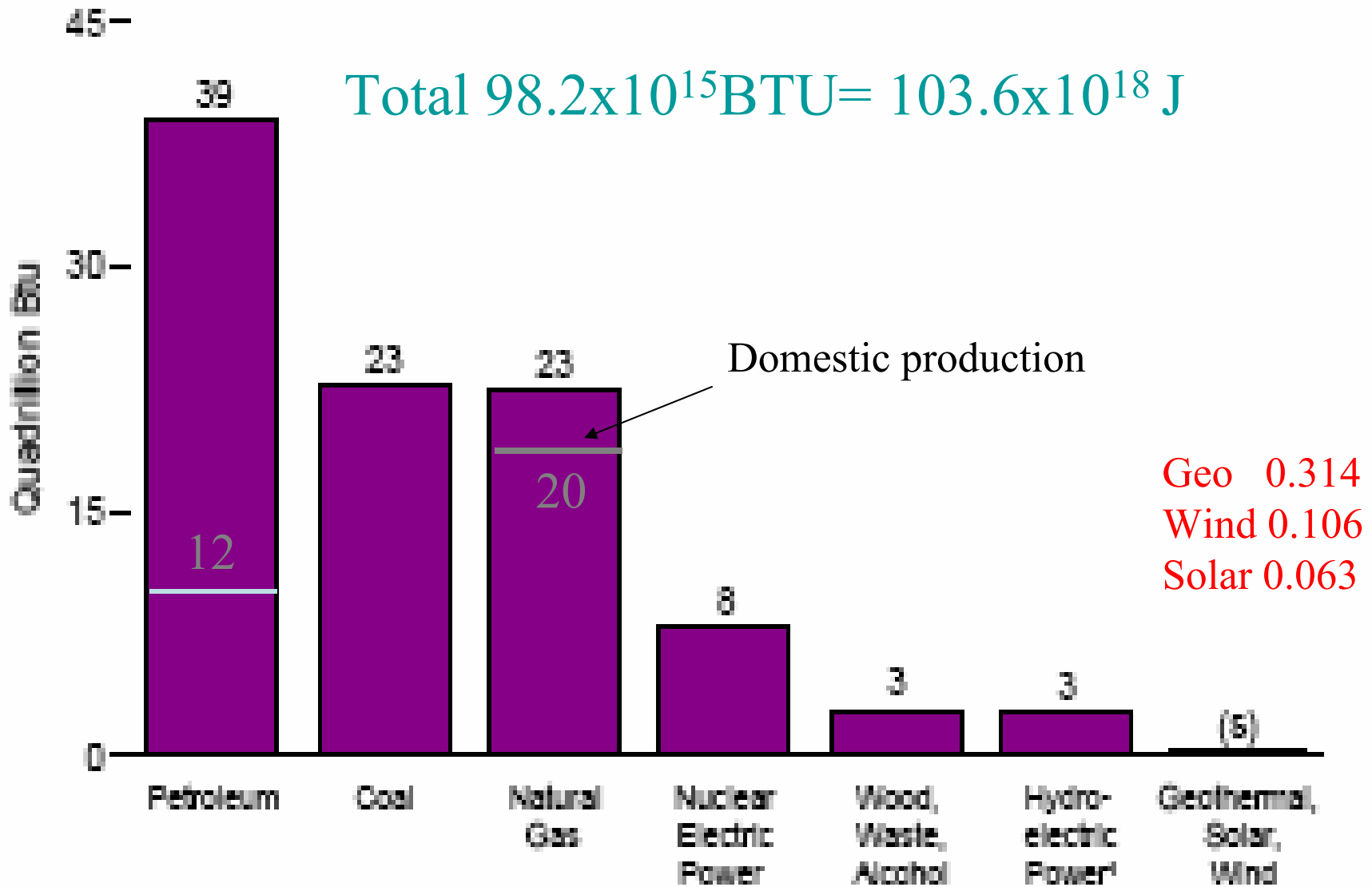
^k Includes, in quadrillion Btu, -0.09 hydroelectric pumped storage; -0.24 ethanol blended into motor gasoline, which is accounted for in both fossil fuels and renewable energy but counted only once in total consumption; and 0.02 electricity net imports.

^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 at end of Section 2.

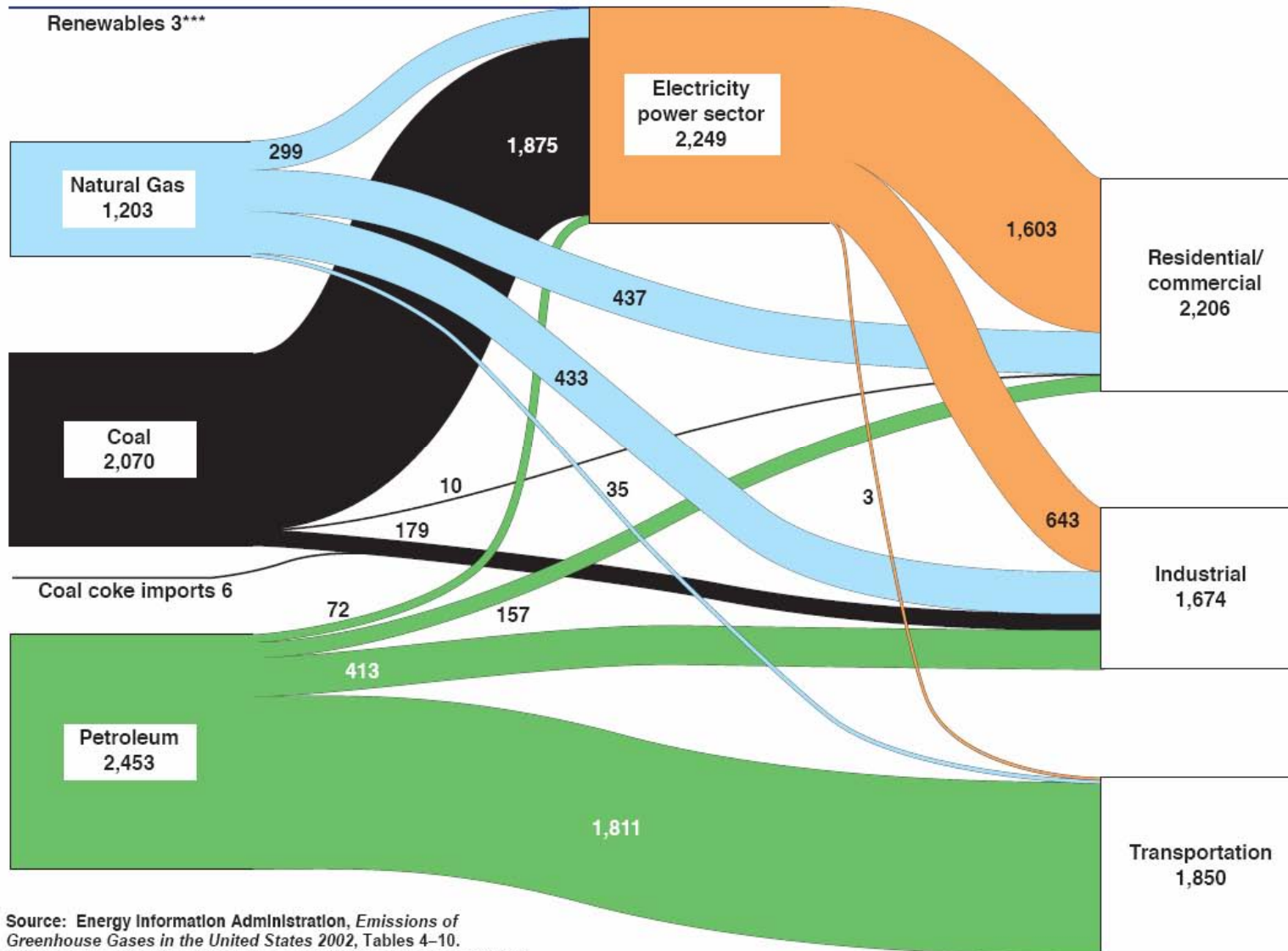
Notes: • Data are preliminary. • Totals may not equal sum of components due to independent rounding.

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

By Source, 2003



U.S. 2002 Carbon Dioxide Emissions from Energy Consumption – 5,682* Million Metric Tons of CO₂**



Source: Energy Information Administration, *Emissions of Greenhouse Gases in the United States 2002*, Tables 4–10.

*Includes adjustments of 42.9 million metric tons of carbon dioxide from U.S. territories, less 90.2 MtCO₂ from international and military bunker fuels.

**Previous versions of this chart showed emissions in metric tons of carbon, not of CO₂.

***Municipal solid waste and geothermal energy.

Note: Numbers may not equal sum of components because of independent rounding.

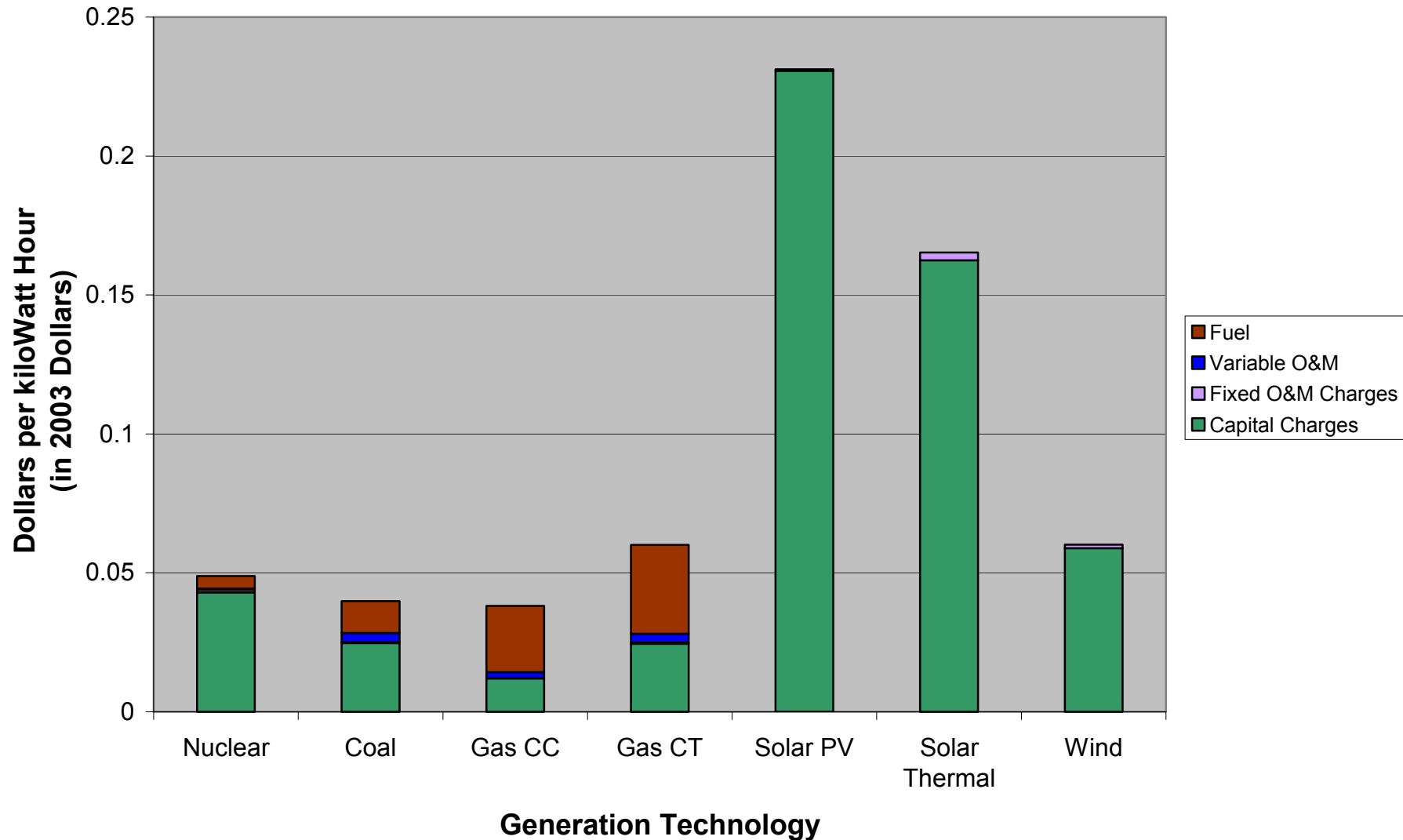
**Figure 2. Energy consumption by fuel, 1970-2025
(quadrillion Btu)**



87-89% fossil based

Annual Energy Outlook 2003, Energy Information Agency,
Office of Integrated Analysis and Forecasting, DOE

Levelized Cost Comparison for Electricity



Source: John Weyant, Stanford Energy Modeling Forum

Edwards, C., ME Seminar, December, 2004

FOSSIL FUEL TYPES

FOSSIL/ORGANIC FUELS

COAL, OIL, NATURAL GAS.

OIL SHALE, TAR SAND, PEAT.

“BIOMASS” .. Young, “renewable”.

- Formed due to the fossilization of *organic* matter, under ground (although evidence of earth mantle inorganic methane is rising).
- All formed of carbon and hydrogen, some with little oxygen, plus sulfur, mercury and other minerals, and non combustibles.
- Most require some form of processing: sulfur removal, grinding and washing, oil refining, gas desulfurization.

COAL

(fossilized vegetations)

lignite, subbituminous, bituminous, anthracite.

- Coal is carbon + hydrogen (CH_m , $m < 1$) + sulfur (up to 10% by weight) + nitrogen + ash (non combustibles).
- Some sulfur can be washed away before combustion, but mostly is scrubbed from combustion products using limestone.
- In fluidized bed combustors, pulverized coal is mixed with limestone and burned at lower temperature in blowing air.
- In gasification, rich burning in oxygen and water forms syngas ($\text{CO} + \text{H}_2$), desulfurization before combustion or gas separation.

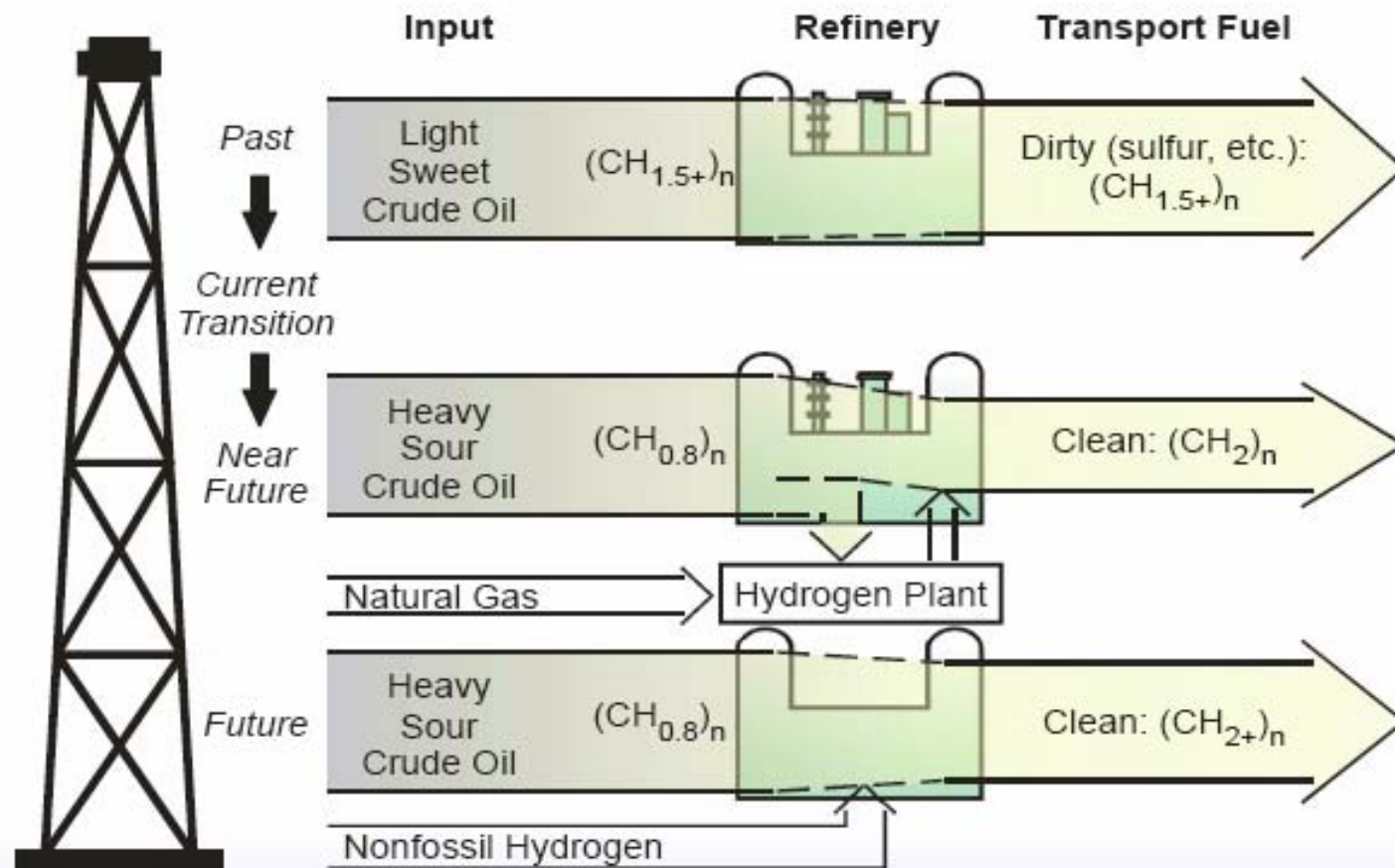
OIL

(or petroleum, liquid rock, fossilized marine life. algae)

- Made up of many organic compounds + hydrogen + nitrogen + sulfur. Sweet and sour refer to the amount of sulfur. CH_m , $1 < m < 2$.
- “Light oil” is generally composed of three hydrocarbon families:
 - Saturated hydrocarbons: paraffins (or normal alkanes), $\text{C}_n\text{H}_{2n+2}$, with gas, $n = 1-4$, liquid, $n = 5-15$, and solids, $n > 15$.
 - Unsaturated hydrocarbons, or aromatics, like benzene, C_6H_6 , toluene, C_7H_8 and naphthalene, C_{10}H_8 .
 - Resin and asphaltenes, heavier hydrocarbons rich in nitrogen, oxygen, sulfur and vanadium.
- Refining: distillation (separation of lighter components), catalytic cracking (heating) and reforming (with steam or hydrogen). Products are typically refinery gas, LPG, gasoline (mostly octane C_8H_{18}), aviation fuels (JPx) diesels, heating and lube oils

A Large Demand for Hydrogen is due to the Declining Quality of Available Crude Oil

ORNL DWG 2001-107R2



Non-Conventional “Heavy” Oil

(all require intensive processing)

Oil Shale:

impermeable hard rock containing (organic, non petroleum) kerogen (pre-oil), which pyrolyzes into oil + (organic, petroleum) bitumen that liquifies with heating.

Tar and Tar Sand:

a mixture of sand and bitumen (coal-like) can be reformed into oil components.

Peat:

“Duff” material in forests and woodland ..

NATURAL GAS

- Mostly methane, CH_4 , ethane C_2H_6 , some propane, C_3H_8 , and little butane, C_4H_8 , with small fractions of higher hydrocarbons, may contain sulfur, oxygen, CO_2 at small quantities.
- Requires least processing.
- Biogenic Gas: near surface, difficult to exploit.
- **Methane hydrides/hydrates**, found in deep oceans, and permafrost, encapsulated in water (estimated to exceed 2 orders of magnitude of proven gas reserves) in ice like structures.

One way to classify fuels is through their heating value, In this table it is the *LHV*, in MJ/kg fuel.

Commercial Fuels

Natural gas			36-42
Gasoline			47.4
Kerosene			46.4
No. 2 oil			45.5
No. 6 oil			42.5
Anthracite coal			32-34
Bituminous coal			28-36
Subbituminous coal			20-25
Lignite			14-18

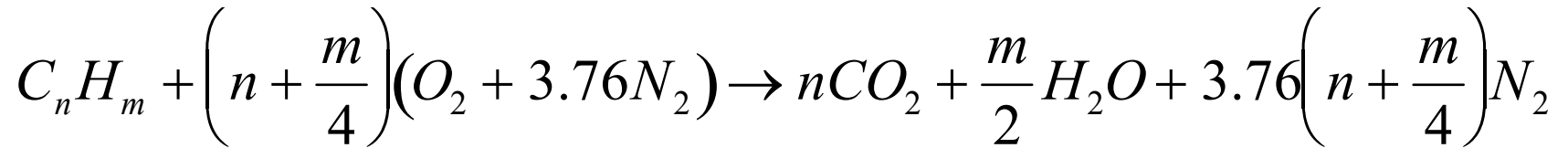
Biomass Fuels

Wood (fir)			21
Grain			14
Manure			13

Some Combustion Fundamentals: Chemical Thermodynamic

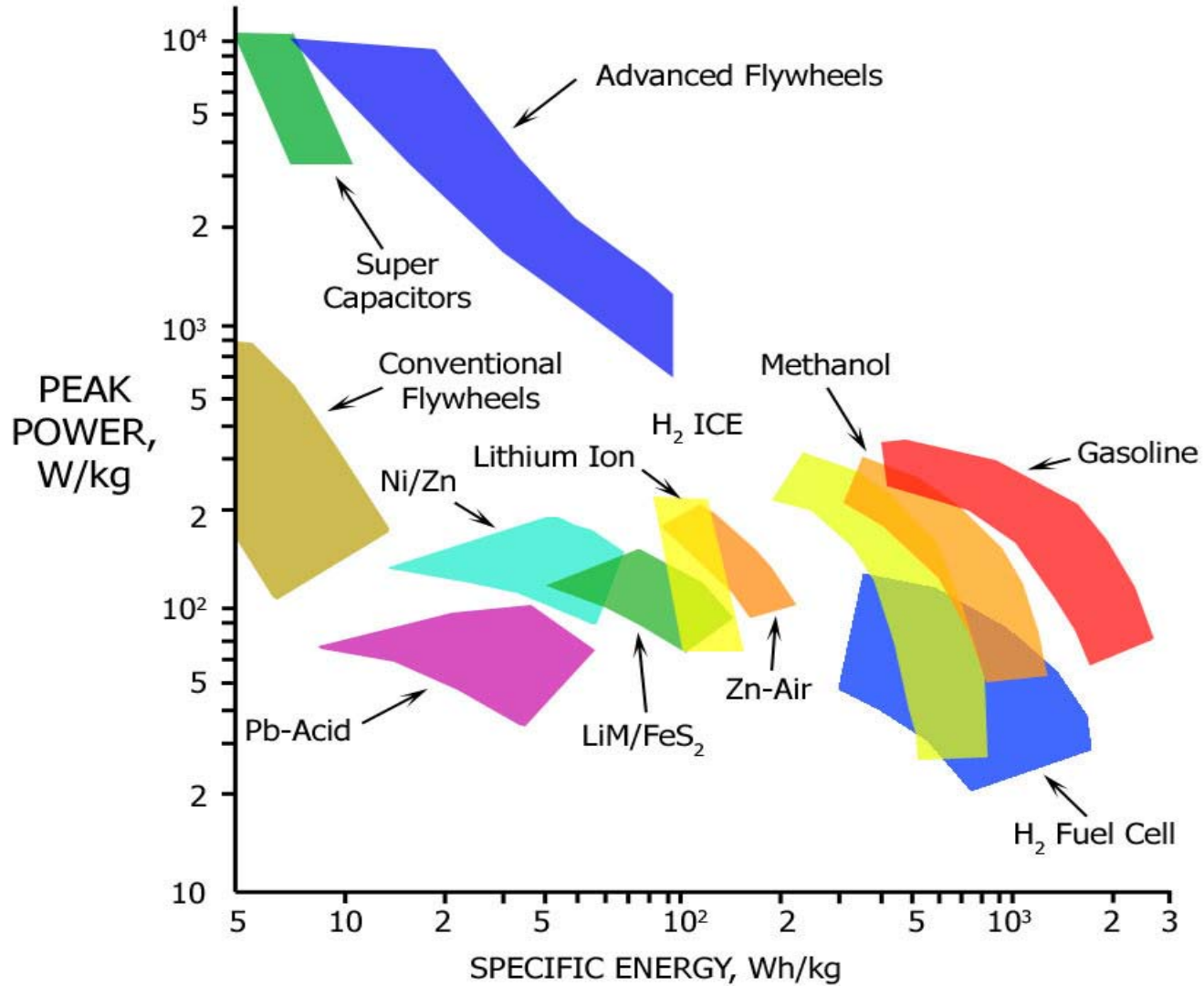
“Classical Thermodynamics is the only physical theory of universal content which within the framework of its basic notions, will never be toppled.” **Albert Einstein.**

HYDROCARBON COMBUSTION IN AIR

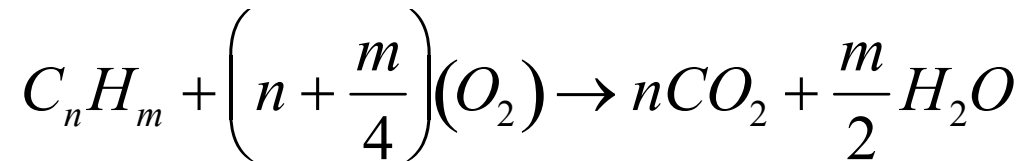


- Hydrocarbons store energy in their chemical bonds. Highest energy storage per unit mass or unit volume (in liquid form).
- Chemical Energy is converted into thermal energy during combustion, or other chemical energy in refining and reforming (processes that require energy).
- In complete, *stoichiometric* combustion of hydrocarbons, the products are water and carbon dioxide.

Ragone plot of Energy Storage

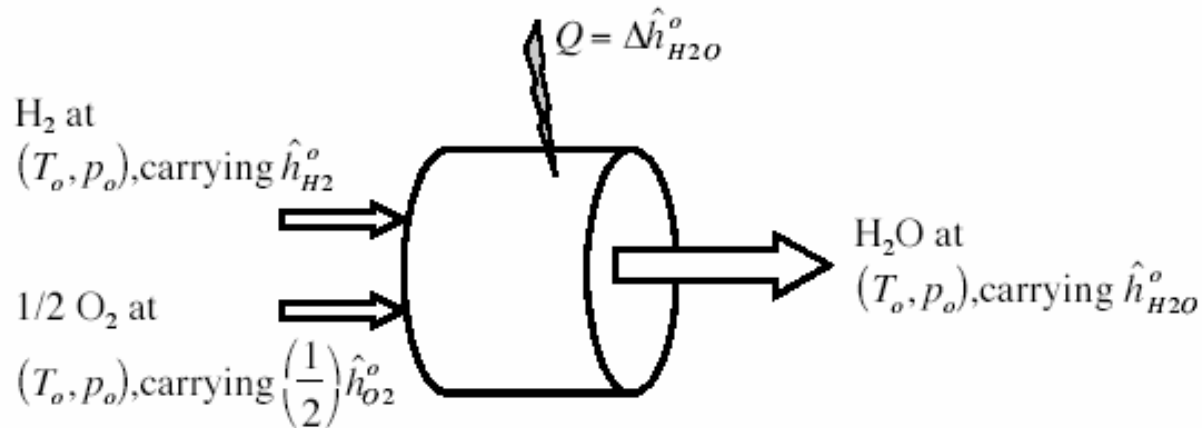
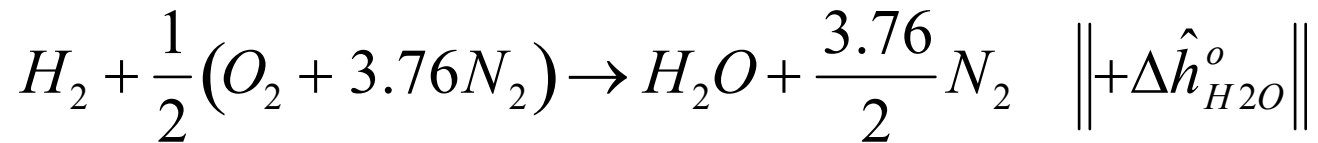


- *Oxyfuel combustion*, that is burning in pure oxygen, is also used to further raise the products temperature, in gasifiers (reformers), or to avoid the formation of nitric oxides.

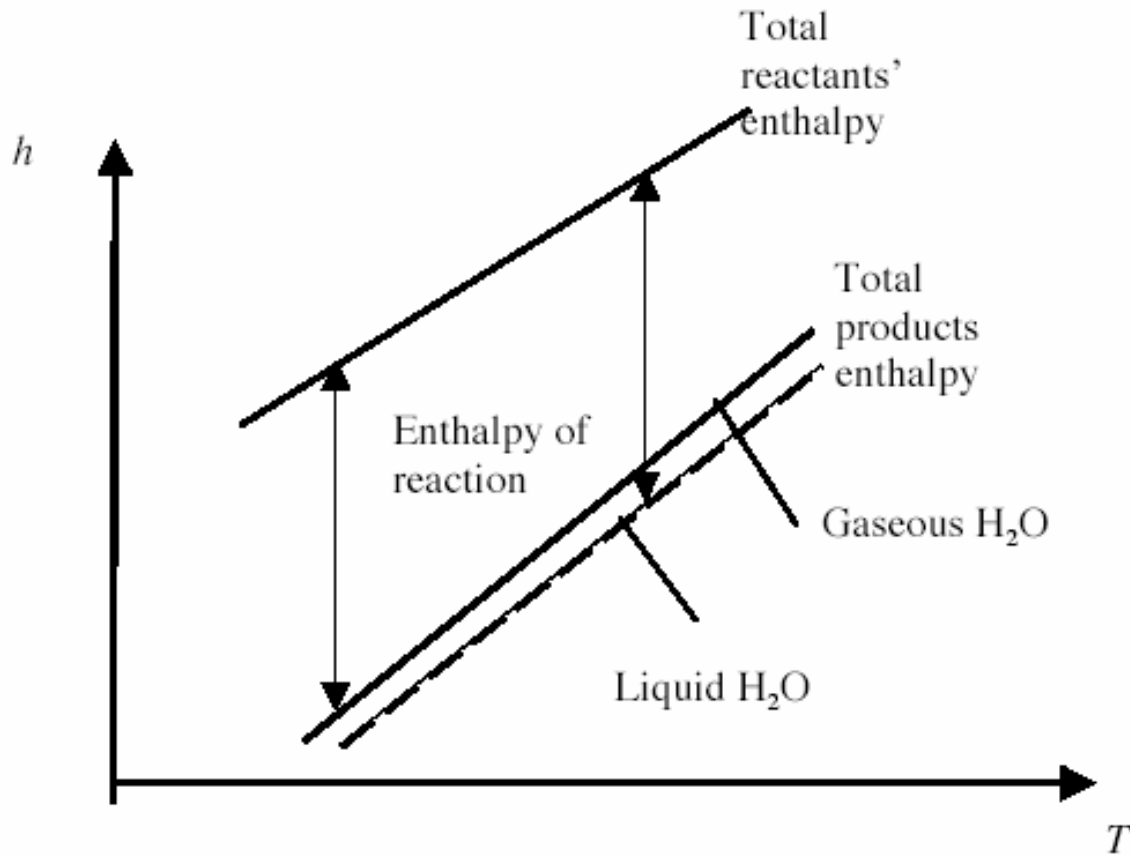


- Even with stoichiometric combustion, carbon monoxide and nitric oxides form, as well very small amounts of hydrocarbons and their fragments (PAH).
- The amount of CO, NO_x and “CH” in the products depend on the fuel, combustion conditions, nature of the combustion process, and how fast the products are cooled.

- The amount of heat transferred out this reaction, when burning at constant pressure is known as *the enthalpy of reaction*.



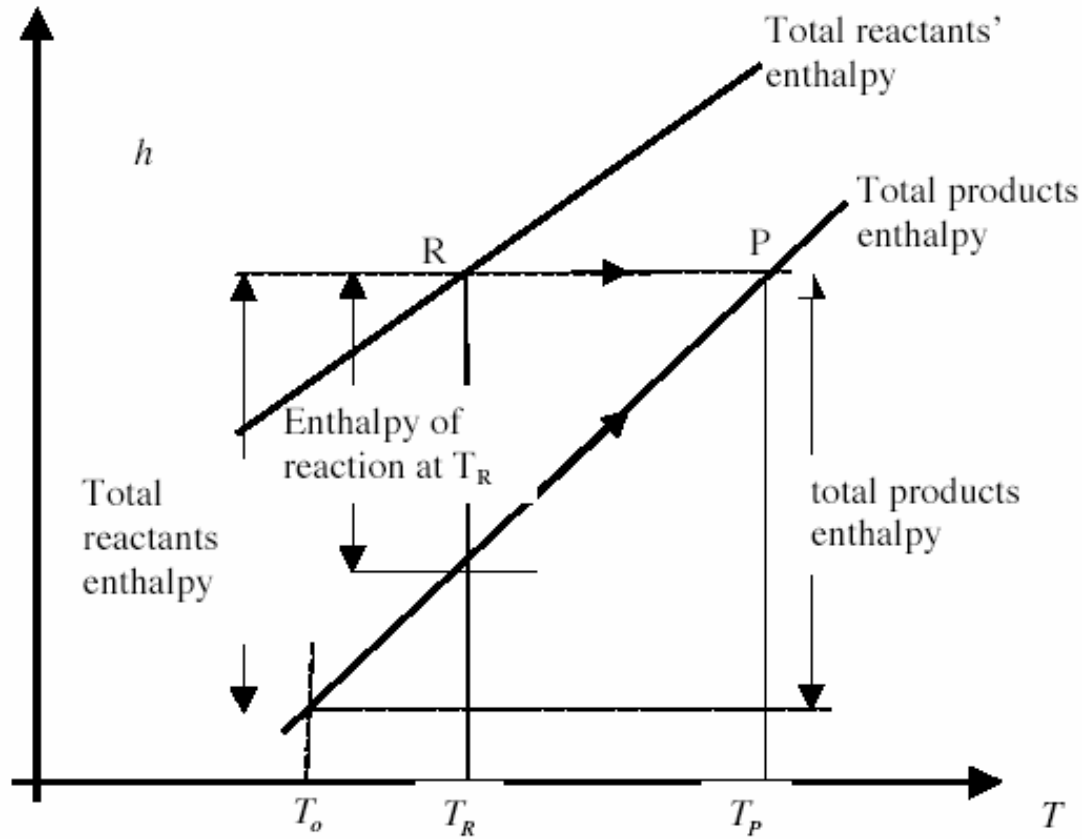
- For most hydrocarbon the enthalpy of reaction per unit mass of fuel is 45 - 50 MJ/kg, for hydrogen it is 123 MJ/kg.



This is also the *Higher Heating Value*, if water in the products is in the liquid phase, or the *Lower Heating Value*, if it is in the gaseous phase (getting either depends on T and p of the process).

Thermodynamic Properties of Fuel Combustion at 25°C and One Atmosphere Pressure^a

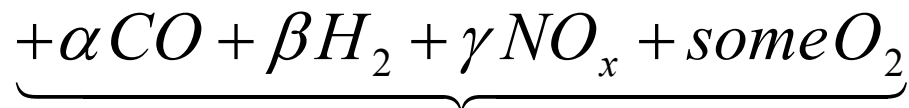
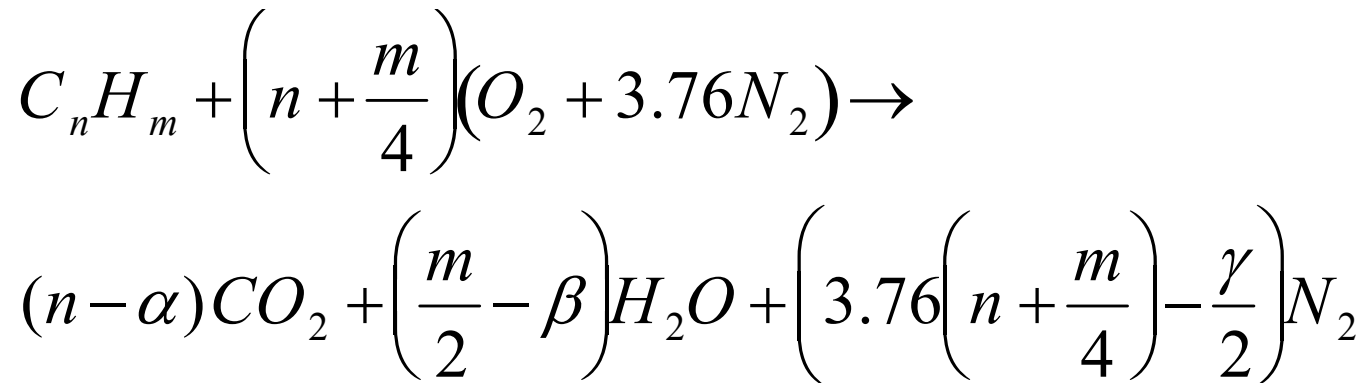
Fuel	Symbol	Molecular Weight (g/mol)	FHV^b (MJ/kg fuel) ^c	$(A/F)_d$	$(h_r - h_p)^*$ (MJ/kg product)	Δf (MJ/kg fuel)	FHV^b (MJ/kg C)
Pure Compounds^d							
Hydrogen	H ₂	2.016	119.96	34.28	3.400	117.63	NA ^e
Carbon (graphite)	C _(solid)	12.01	32.764	11.51	2.619	32.834	32.764
Methane	CH ₄	16.04	50.040	17.23	2.745	51.016	66.844
Carbon monoxide	CO	28.01	10.104	2.467	2.914	9.1835	23.564
Ethane	C ₂ H ₆	30.07	47.513	16.09	2.780	48.822	59.480
Methanol	CH ₃ O	32.04	20.142	6.470	2.696	22.034	53.739
Propane	C ₃ H ₈	44.10	46.334	15.67	2.779	47.795	56.708
Ethanol	C ₂ H ₆ O	46.07	27.728	9.000	2.773	28.903	53.181
Isobutane	C ₄ H ₁₀	58.12	45.576	15.46	2.769		53.142
Hexane	C ₆ H ₁₄	86.18	46.093	15.24	2.838		54.013
Octane	C ₈ H ₁₈	114.2	44.785	15.12	2.778		53.246
Decane	C ₁₀ H ₂₂	142.3	44.599	15.06	2.778		52.838
Dodecane	C ₁₂ H ₂₆	170.3	44.479	15.01	2.778		52.567
Hexadecane	C ₁₆ H ₃₄	226.4	44.303	14.95	2.778		52.208
Octadecane	C ₁₈ H ₃₈	254.5	44.257	14.93	2.778		52.102



Under adiabatic conditions, the products' temperature is high ~ 2000 C (depending on the initial temperature and the process). It is called the *Adiabatic Flame Temperature*.

Products Composition in Equilibrium Combustion

There is no complete combustion!



equilibrium dissociation and NOx formation

Impact of Equivalence Ratio and Initial Temperature On Flame Temperature

Graph removed for copyright reasons. Figure 11 in Docquier, N., and S. Candel.
"Progress in Energy and Combustion." *Science* 28 (2002) 107-150.

- COMBUSTION PROCESSES
- COMBUSTION DEVICES
- COMBUSTORS
- BURNERS

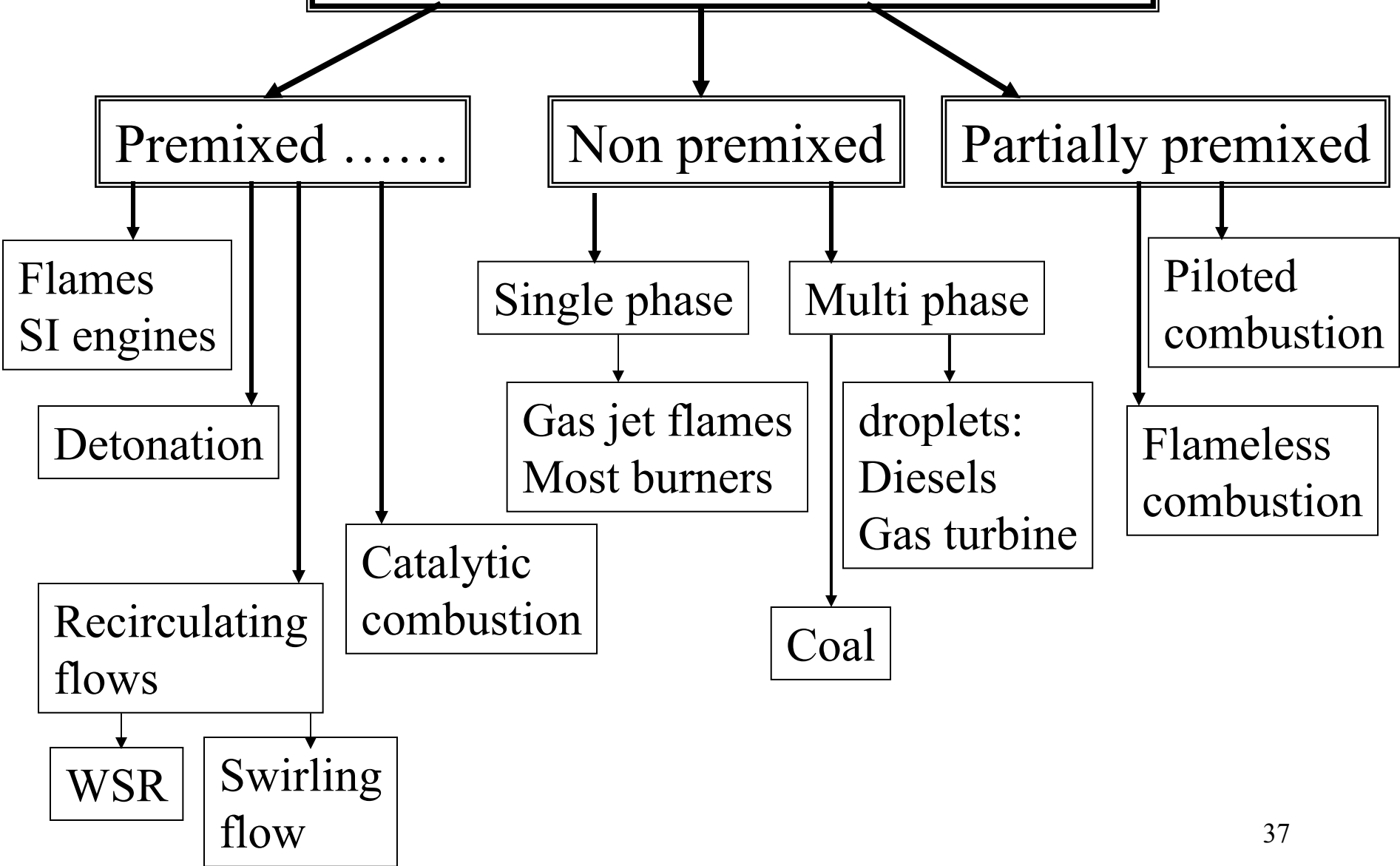
Power, what is it and what controls it ..

Two photos removed for copyright reasons. Donkeys pulling cart and a fuel cell car.

Power Density in Combustion Processes

Coal: pulverized	0.01 GW/m ³
fluidized bed	0.04
SI engine	0.1
Gas boiler	0.2
Aero engine (overall)	2.0
(primary)	4.0
<u><i>Vehicle brakes</i></u>	<u>5</u>
Premixed flame (peak)	6
<u><i>Spark</i></u>	<u>10</u>
WSR (at T*)	10-50

Practical Combustion Processes



Flame Types

A rich, long, sooty, jet diffusion flame, heavy HC or coal, strong radiation, typical in boiler burners

Photos removed for copyright reasons.

A well mixed (swirling) compact flame of a lighter HC, typical of modern burners, gas turbines, etc.

FOSSIL BASE ENERGY CONVERSION: ADVANCED POWER SYSTEMS

The fuel does not matter much!!

Do we have an Energy or an *Entropy Crisis*?

$$\eta_{carnot} = 1 - T_L / T_H$$

“Nature, in providing us with combustibles on all sides, has given us the power to produce, at all times and in all places, heat and the impelling power which is the result of it. To develop this power, to appropriate it to our uses, is the object of heat engines. The study of these engines is of greatest interest, their importance is enormous, their use is continually increasing, and they seem destined to produce a great revolution in the civilized world.”

Sadi Carnot, *Reflection On The Motive Power Of Heat And On Machines Fitted To Develop That Power*, 1824.

Gas turbine Open (Brayton) Cycles

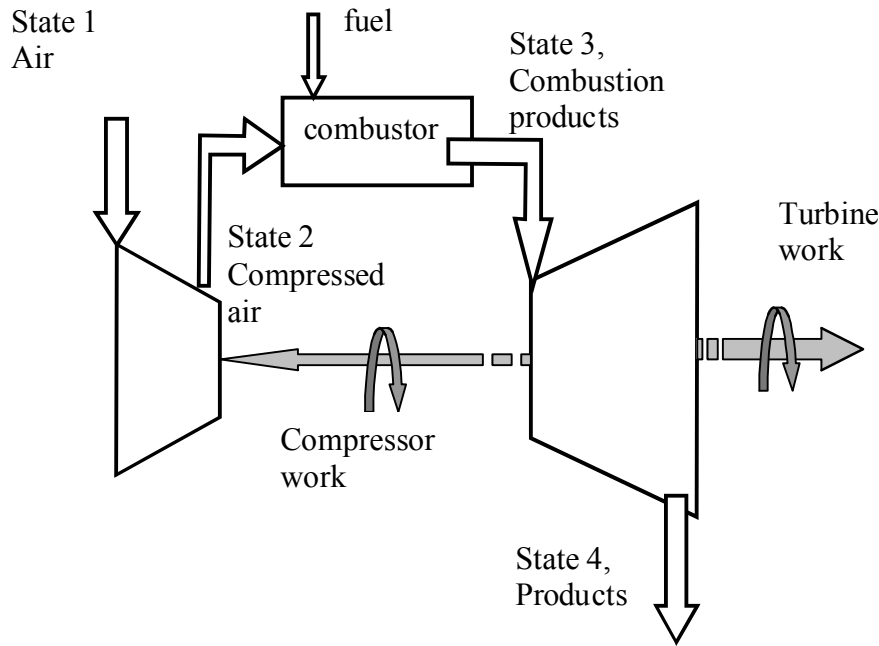


Figure 1. The components and states in a Brayton combustion gas turbine cycle.

$$\frac{T_{2s}}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \quad \frac{T_3}{T_{4s}} = \left(\frac{p_3}{p_4} \right)^{\frac{k-1}{k}} = \left(\frac{p_2}{p_1} \right)^{\frac{k-1}{k}}$$

$$\eta_C = \frac{h_{2s} - h_1}{h_2 - h_1} \quad \eta_T = \frac{h_3 - h_4}{h_3 - h_{4s}}$$

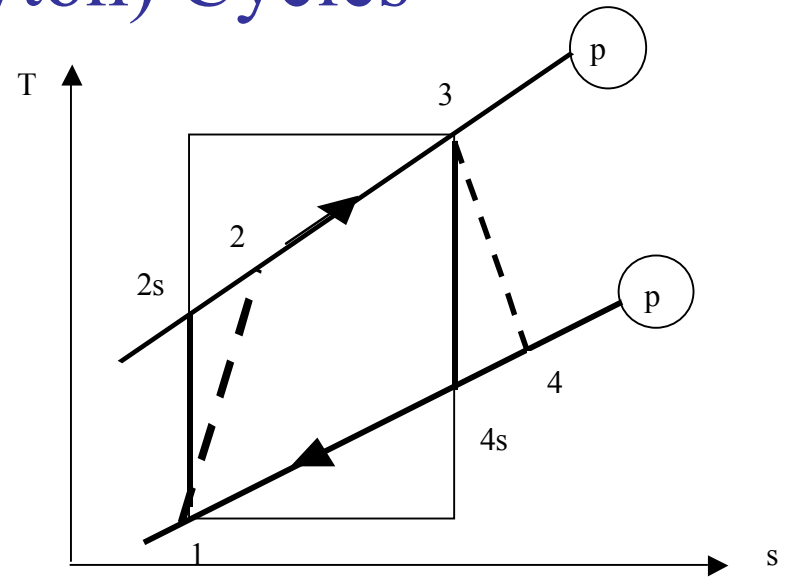


Figure 2. the temperature entropy diagram of an ideal Brayton cycle, and one with finite isentropic efficiencies for the work transfer components. A Carnot cycle is superposed between the two extreme temperatures.

$$Q_{in} = h_3 - h_2 = c_p(T_3 - T_2)$$

$$W_{net} = (h_3 - h_4) - (h_2 - h_1) \\ = c_p[(T_3 - T_4) - (T_2 - T_1)]$$

$$\eta_{cycle} = \frac{\text{net mechanical work out}}{\text{heat transfer in}} \quad 43$$

Gas turbines have advantages in electric power generation:

1. They operate at high temperatures.
2. They can are capable of meeting peak load demands.
3. They are compact and easy to operate, and take advantage of aerospace propulsion applications.
4. They operate at relatively low pressures.
5. Many installations burn natural gas, or in dual fuel mode burning NG and/or oil.
6. They do not handle wet gases, and are not as vulnerable to corrosion as steam turbines.
7. Combustion gas turbines do not require heat transfer equipment on the low-temperature side, and no coolant either.

However, gas turbines suffer from several limitations:

1. They have relatively low efficiency since their maximum temperature is limited by material.
2. Their efficiency is low because of the high compressor work, and low efficiency of compressors.
3. Open cycle turbines are limited by the high exhaust temperature, which limits the turbine work.
4. They cannot be used with “dirty” fuels, such as coal, since sulfur oxides can damage their blades.

Steam, or vapor Rankine cycles overcome some of these limitations, and hence have been very popular in electric power generation.

Rankine (Vapor) Cycles:

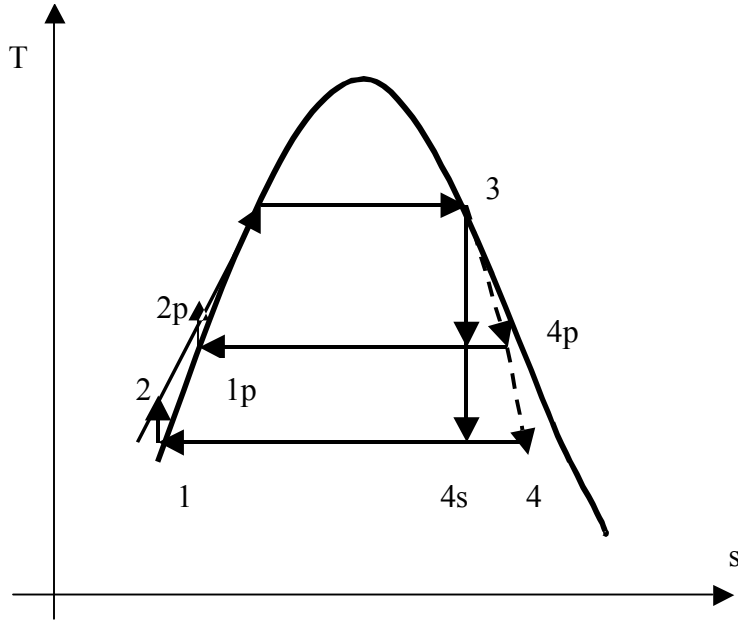


Figure 12. the T-s diagram of an open Rankine cycle, 1p-2p-3-4p, and a closed Rankine cycle, 1-2-3-4, with subatmospheric pressure

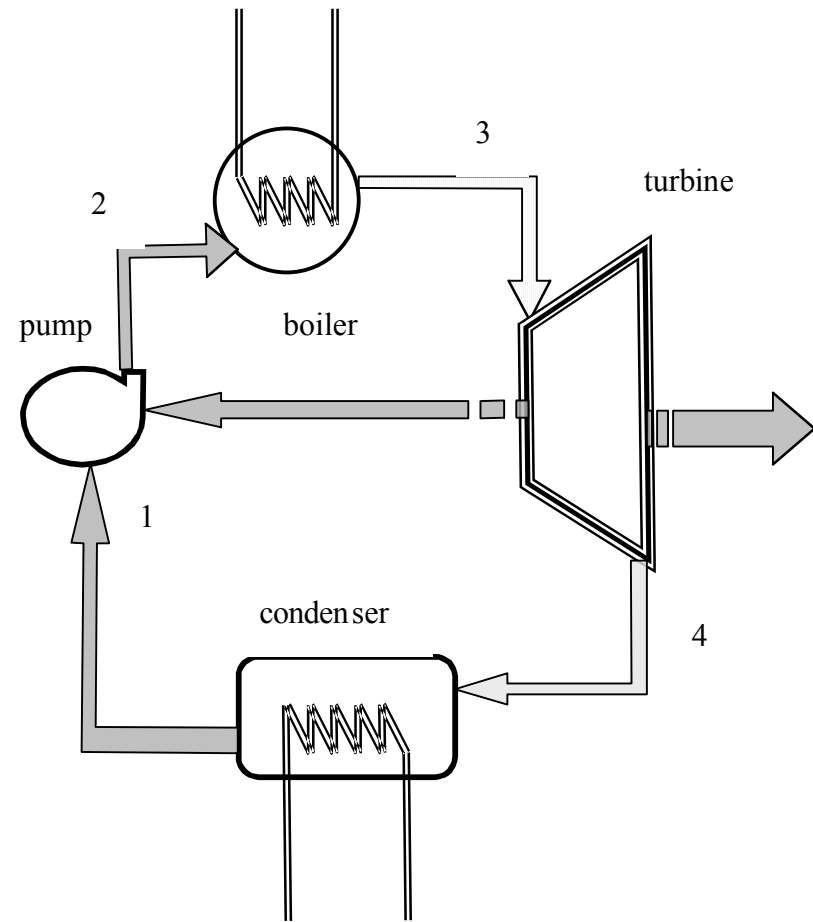


Figure 12. The components of a Rankine cycle.

Critical point: $T_c = 374 \text{ C}$, $P_c = 22.088 \text{ MPa}$

Cooling available at: $T = 15 \text{ C}$, where $P_{\text{sat}} = 5.63 \text{ kPa}$

Rankine cycles:

1. Fuel flexible, works well with coal (closed cycle).
2. High efficiency, low pumping power.
3. Lower flow rate (latent enthalpy).
4. Run at low T (works with geothermal and solar), but high p.
5. Works well with nuclear energy:

Pressurized WR: $T = 350 \text{ C}$

Boiling WR: $T = 400\text{-}500 \text{ C}$

Gas Cooled R: $T = 600\text{-}800 \text{ C}$

High Temperature GR $T > 800 \text{ C}$

BUT

1. High inertia, good for base load but not for load following.
2. Require cooling, big condensers, .. Water ...

COMBINED CYCLES:

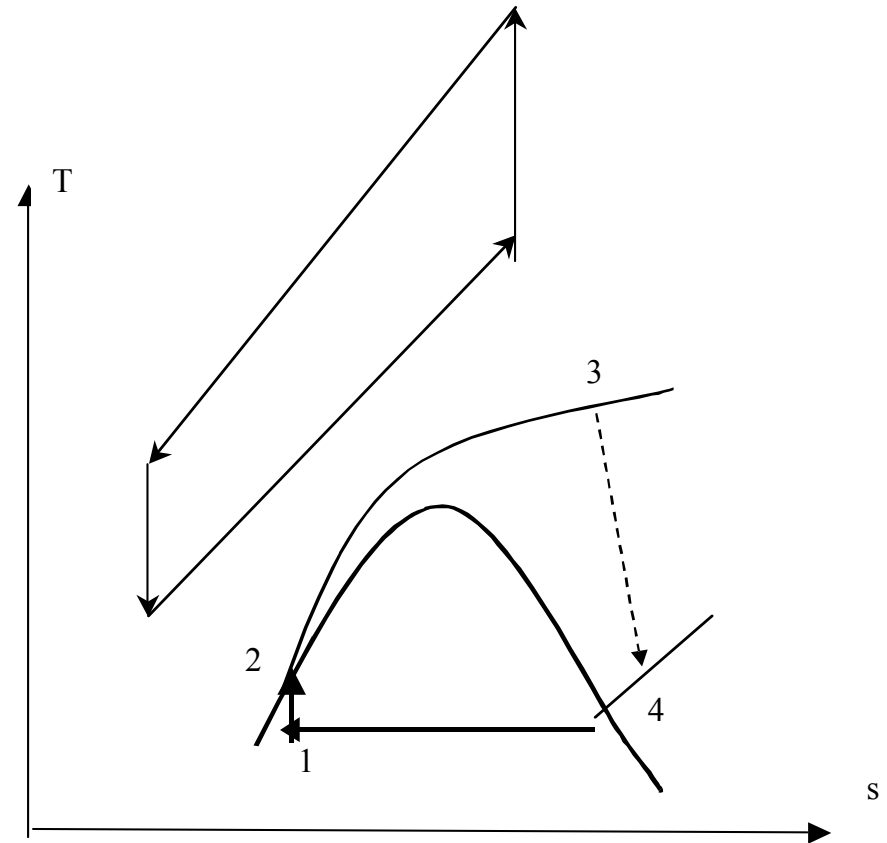


Figure 18. A supercritical steam cycle, and a “matching” gas turbine cycle for use in a combined cycle plant.

Combined cycles take advantage of high T gas turbine exhaust.

Combined cycle efficiency: $\eta_{com} = \eta_{top} + \eta_{bot}(1 - \eta_{top})$.

For: $\eta_{top} = 0.25$ and $\eta_{bot} = 0.4$, $\eta_{com} = 0.55$

Table 2.1: Efficiency of current power plant types and efficiency potential stemming from possibilities for improvement and for future power plant cycles [22]⁴

Year of Initial Operation	Example	Operating Characteristics	Efficiency in %
Natural Gas-Fired Power Plant Cycles			
1998	Gas turbine simple cycle	TIT approx. 1190°C (ISO 2314) ⁵	approx. 38-40
1997	GT with reheat		approx. 38
1998	GT with recuperation		approx. 40
1996	GT with steam injection (STIG/Cheng)		<45
>1998	Humid Air GT (HAT)		approx. 58-59
>>2000	GT with chemical recuperation (CRGT)		55-62
1998	Gas / steam turbine combined cycle power plants	TIT approx. 1190°C (ISO 2314) ⁵	58-59
1995 / >2000	Fuel cells, natural gas-fired: PAFC / PEMFC	[23, 24]	approx. 40
>2000 / >2005	MCFC / SOFC combined cycle plant	[23, 24, 25]	55 ... >60

Courtesy of U.S. DOE.

Source: Gottlicher. "The Energetics of Carbon Dioxide Capture in Power Plants." *DOE*, 2004.

Coal-Fired Steam Power Plants			
Operational since 1998	Coal-fired steam power plant (seawater cooling system) Nordjyllandsvaerket [26]	Steam: 285 bar/580°C/580°C/580°C Feedwater preheating: 300°C Condenser pressure: 0.023 bar 10 feedwater preheating stages	47
Planned for 1999 (adjusted)	Coal-fired steam power plant (wet cooling tower system) Gelsenkirchen-Hefiler[27]	Steam: 275 bar/580°C/600°C Feedwater preheating: 300°C Condenser pressure: 0.037 bar 9 feedwater preheating stages	45 to 45.5
Planned for 2001-2005	Coal-fired steam power plant (seawater cooling system) Avedoere 2 [28, 29]	Steam: 300 bar/580°C/600°C Condenser pressure: 0.023 bar	50

Courtesy of U.S. DOE.

Source: Gottlicher. "The Energetics of Carbon Dioxide Capture in Power Plants." *DOE*, 2004.

Coal-Fired Combined Cycle			
1994	Pressurized Fluidized Bed Combustion (PFBC) combined cycle	Gas turbine: 860°C/12 bar	36-40 (1999: >45)
>2010	Pressurized Pulverized Coal-Fired combined cycle power plant (with hot gas clean up or warm gas clean up according to heat exchanger)		>50
	Magneto Hydro Dynamic generator (MHD) + steam cycle		50-60
1993	IGCC Power plant Buggenum (NL)	TIT 1050°C (ISO 2314) ⁵	43.2
1998	Puertollano (E)	TIT 1120°C -"	45
>1998	Study, ready for construction in 1998 [21]	TIT >1190°C -"	51.5
≥1998	IGFC (IGCC with fuel cells): PAFC (split fuel stream) / GT combined cycle plant	[31]	approx. 50
>2000	MCFC combined cycle plant	[32]	> 55
>2005	SOFC combined cycle plant	[32]	> 55
	Multiple steam cycles		50-51
	Kalina cycle		>47

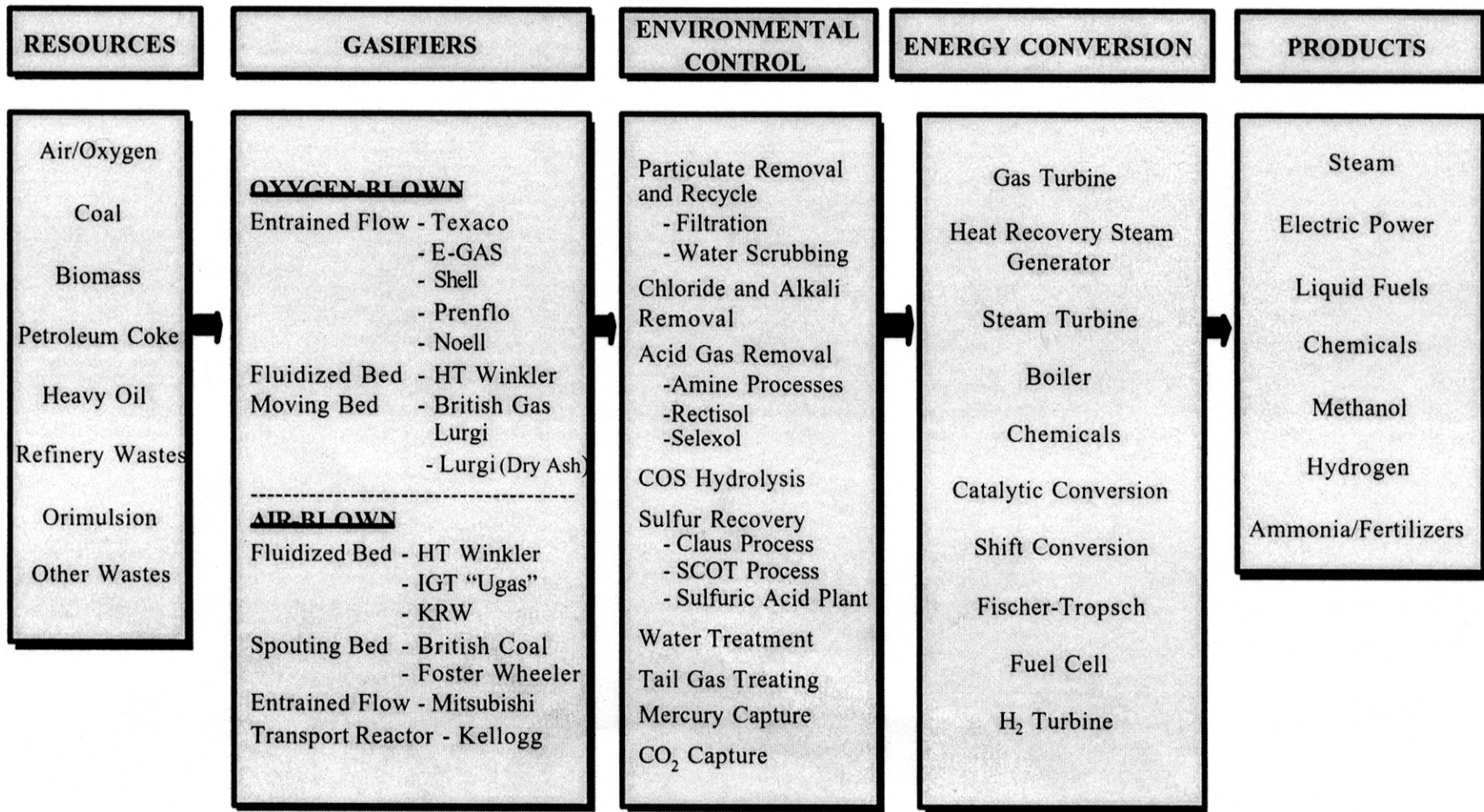
Courtesy of U.S. DOE.

Source: Gottlicher. "The Energetics of Carbon Dioxide Capture in Power Plants." *DOE*, 2004.

TEMPA ELECTRIC POLK IGCC POWER PLANT

250 MW, 35.3 % efficiency, 2500 TPD coal, 200 TPD sulfuric acid, built 1996, \$600M

Facility schematic diagram removed for copyright reasons.

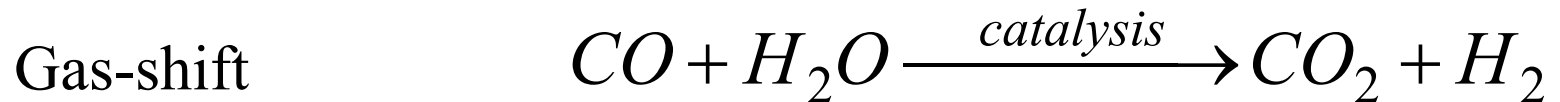
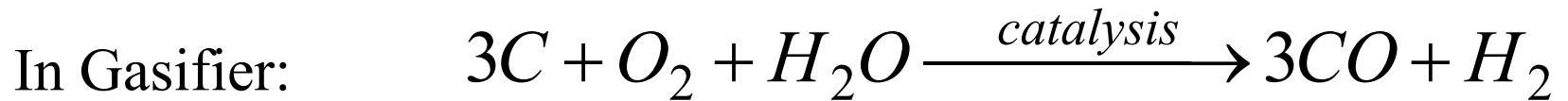


- Tampa Electric 250 MW, Florida
- PSI energy (Cinergy) 262 MW, Indiana
- Dow Chemical 160 MW, Louisiana
- S. Cal Edison 100 MW, California

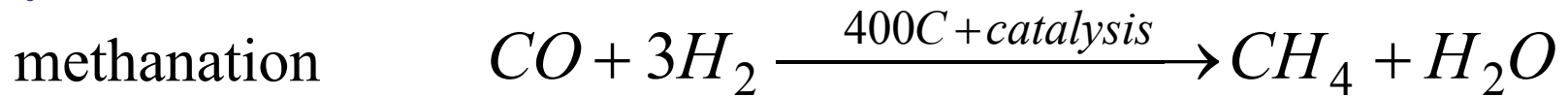
- MHI built 250MW in Japan, 56.5%
- They are building a 500 MW coal.
- China market ..
- India ..

Reforming, Gasification & Synthesis

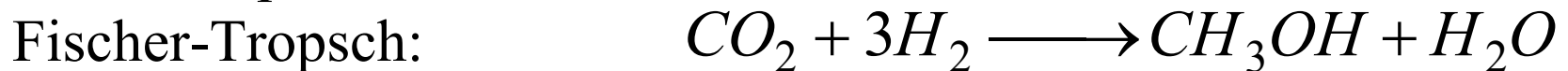
From Fossil: Coal/Tar Sand/Biomass



Synthesis



Synthesis+Liquefaction



Fuel Reforming and Synthesis: Efficiencies, and Fuel life Cycle Analysis

Thermal Efficiencies of Synthetic Fuel Production

FUEL	PRODUCT	EFFICIENCY* (%)
Coal	Synthesis	72-87
Coal	Methane	61-78
Coal	Methanol	51-59
Coal	Hydrogen	62
Oil	Hydrogen	77
Methane	Hydrogen	70-79
Coal, Oil, or Gas	Hydrogen (Electrolytic)	20-30
Oil Shale	Oil and Gas	56-72
Methanol	Oil and Gas	86
Wood	Gas	90
Corn	Ethanol	46
Manure	Gas	90

*Thermal efficiency is the ratio of the heating value of the synthetic product divided by the heating value of the parent fuel.