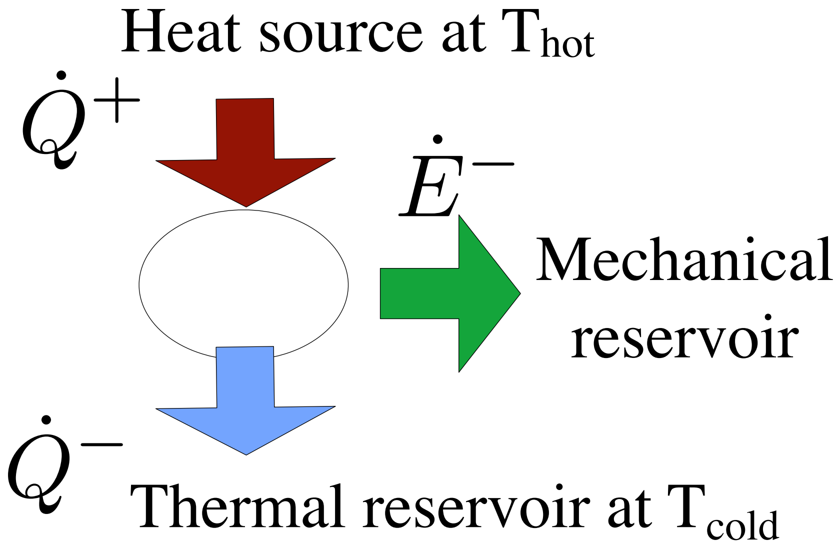
Fossil fuels and Combustion

Emanuela Peduzzi, François Maréchal
Industrial Process and Energy Systems Engineering (IPESE)
École Polytechnique Fédérale de Lausanne

ME-409 ENERGY CONVERSION AND RENEWABLE ENERGY

Recall : work production requires a heat source


Heat source at T_{hot}

$\dot{Q}^+$

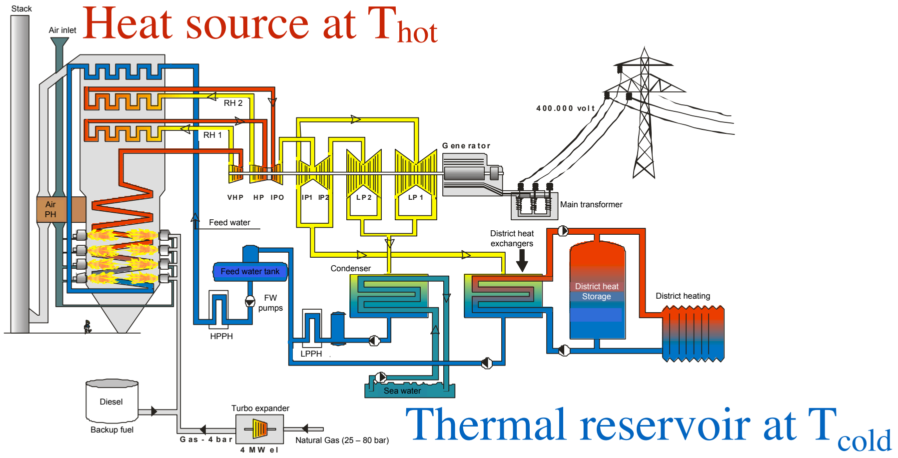
$\dot{E}^-$

Mechanical reservoir

$\dot{Q}^-$

Thermal reservoir at T_{cold}

Steam Rankine Cycle


Heat source at T_{hot}

Thermal reservoir at T_{cold}

With current technologies, one can expect 55% of the best efficiencies calculated from thermodynamics

1st principle: Heat balance

$$\dot{E}^- = \dot{Q}^+ - \dot{Q}^-$$

$$\eta_e = \frac{\dot{E}^-}{\dot{Q}^+}$$

2nd principle: Carnot

If reversible process

$$\dot{E}^-_{max} = \dot{Q}^+ * (1 - \frac{T_{cold}}{T_{hot}})$$

$$\theta_{Carnot} = \frac{\dot{E}^-_{max}}{\dot{Q}^+} = (1 - \frac{T_{cold}}{T_{hot}})$$

$$\dot{E}^- = \eta_{Carnot} * \theta_{Carnot} * \dot{Q}^+$$

$$\eta_{Carnot} \approx 0.55$$

What are the typical heat sources ?

- **Combustion gases**
  - –Coal, fuel, gas combustion
  - –Waste combustion
  - –Biomass combustion
  - –Gas turbines outlet gases
  - –Internal combustion engine

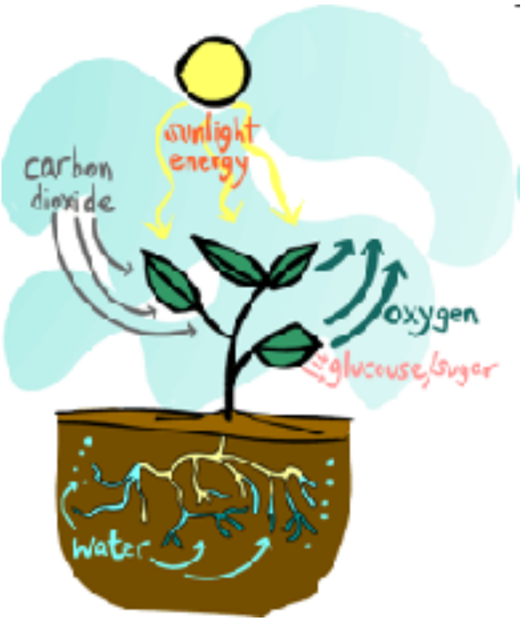
Combustion of fuel

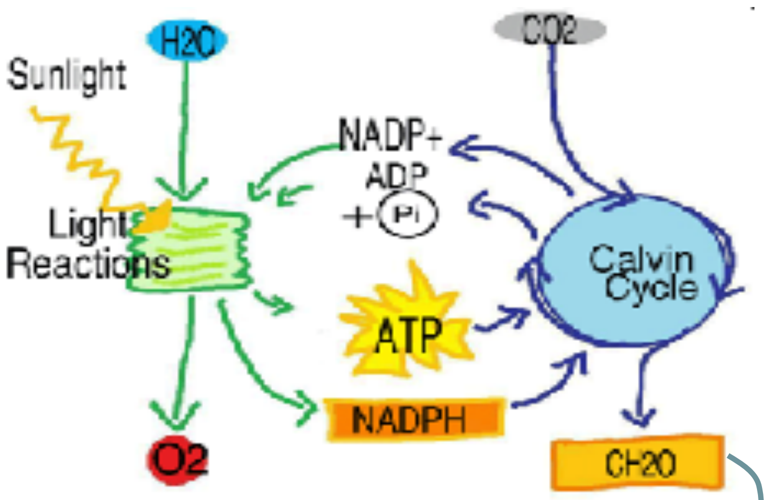
- **Industrial Waste Heat**
  - –Cement
  - –Steel industry
  - –Industrial sites
  - –Refineries

Combustion of fuel

- Nuclear reaction
- Solar heat
- Geothermal heat

The origin of fuels in Nature – biomass – Photosynthesis

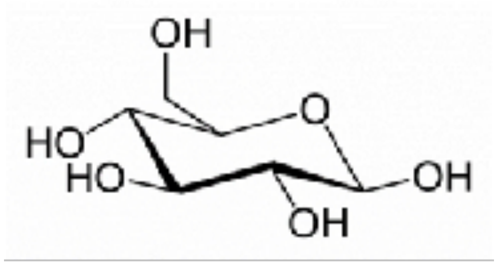




carbohydrates

$$nCO_2+mH_2O + \text{sunlight} \rightarrow C_n(H_2O)_m+nO_2 \quad \Delta H^o=+470 \text{ kJ/mol}$$

1961 Nobel Prize in Chemistry
Calvin cycle, Calvin–Benson-Bassham (CBB) cycle



glucose

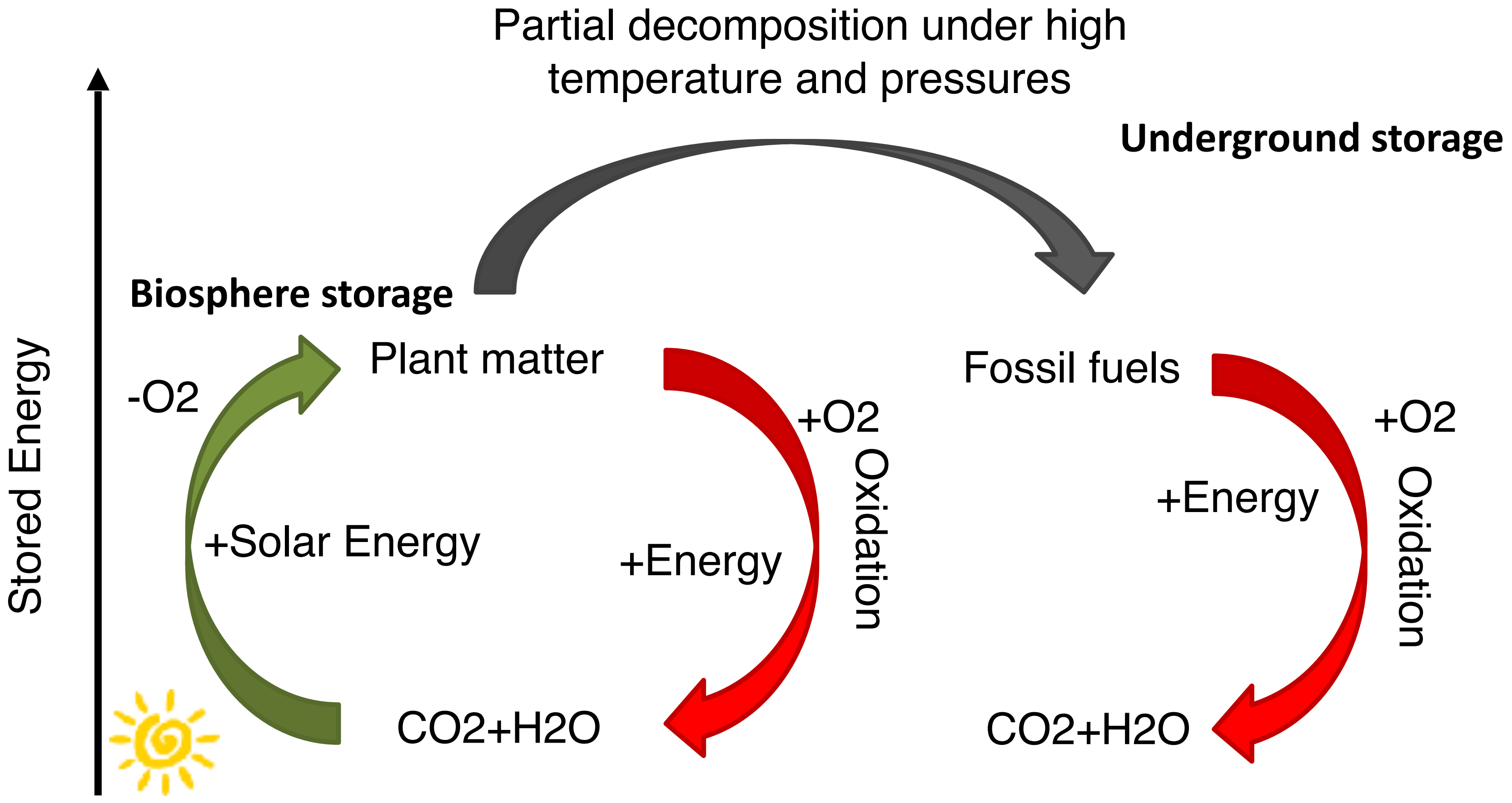
The efficiency of photosynthesis (kJ stored/kJ irradiation) is about 1%

(ATP) Adenosine-5'-triphosphate

(NADP+) Nicotinamide adenine dinucleotide phosphate

www.sheppardsoftware.com
www.the-simple-homeschool.com

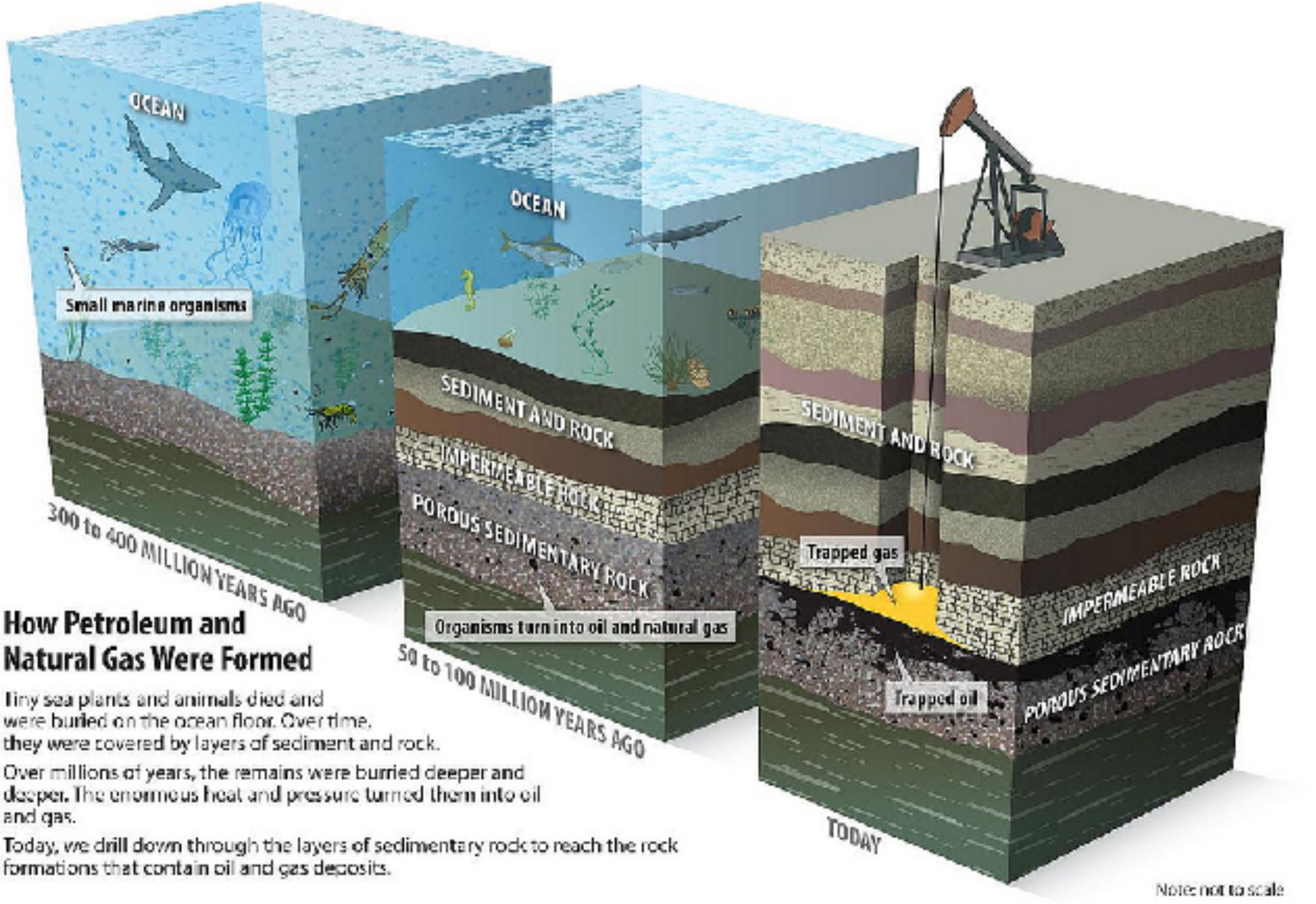
The origin of fuels in Nature



Adapted from: http://web.mnstate.edu/marasing/

The energy stored in fossil fuels is the sun's energy captured Millions of years ago by plants

The origin of fuels in Nature – petroleum and natural gas



How Petroleum and Natural Gas Were Formed

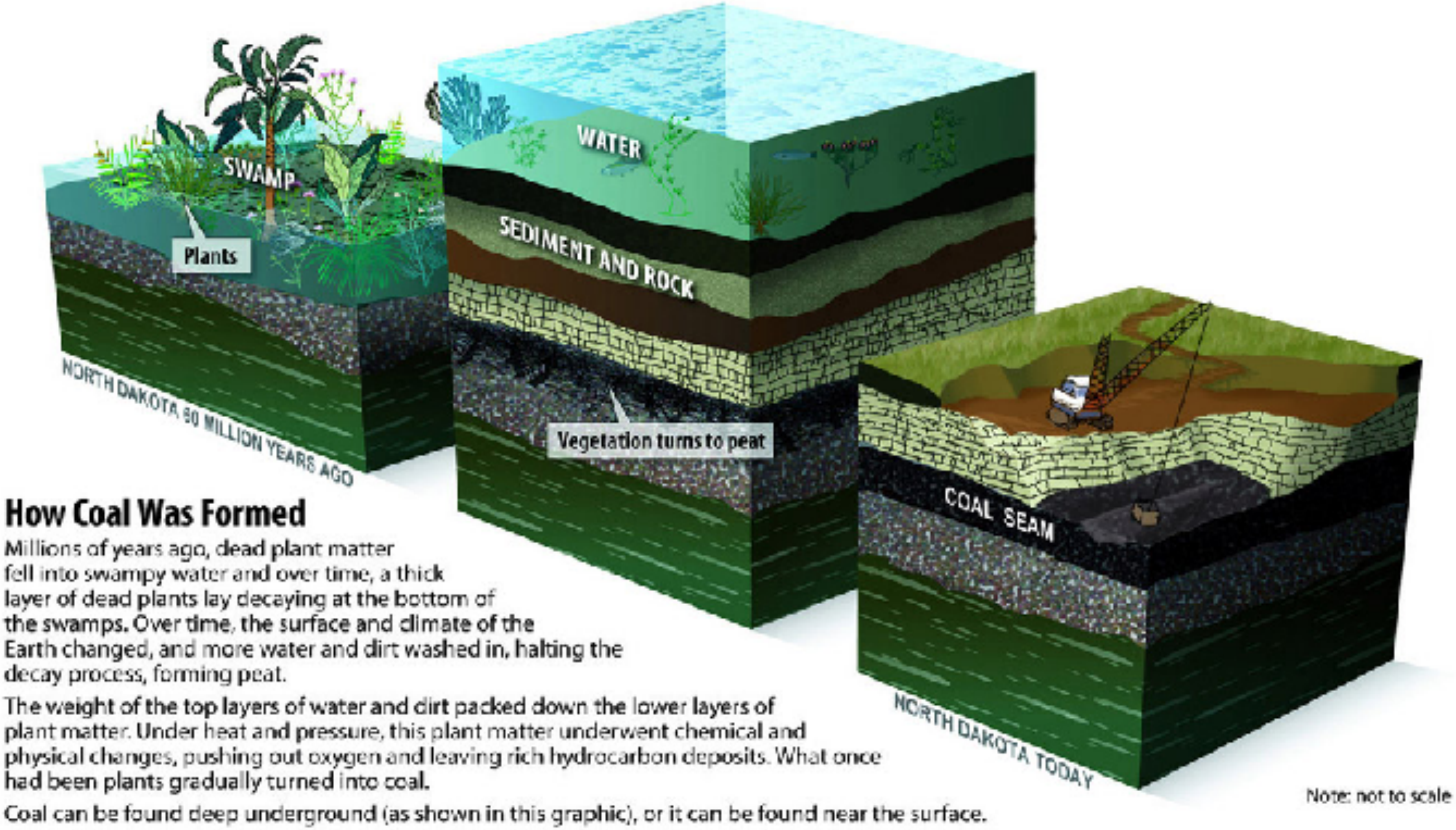
Tiny sea plants and animals died and were buried on the ocean floor. Over time, they were covered by layers of sediment and rock.

Over millions of years, the remains were burried deeper and deeper. The enormous heat and pressure turned them into oil and gas.

Today, we drill down through the layers of sedimentary rock to reach the rock formations that contain oil and gas deposits.

http://ndstudies.gov/gr8/content/unit-i-paleocene-1200-ad/lesson-1-changing-landscapes/topic-2-geology/section-2-williston-basin

The origin of fuels in Nature – coal



How Coal Was Formed

Millions of years ago, dead plant matter fell into swampy water and over time, a thick layer of dead plants lay decaying at the bottom of the swamps. Over time, the surface and climate of the Earth changed, and more water and dirt washed in, halting the decay process, forming peat.

The weight of the top layers of water and dirt packed down the lower layers of plant matter. Under heat and pressure, this plant matter underwent chemical and physical changes, pushing out oxygen and leaving rich hydrocarbon deposits. What once had been plants gradually turned into coal.

Coal can be found deep underground (as shown in this graphic), or it can be found near the surface.

http://ndstudies.gov/gr8/content/unit-i-paleocene-1200-ad/lesson-1-changing-landscapes/topic-2-geology/section-2-williston-basin

Combustion

Rapid **oxidation** of chemical compounds generating heat, or both light and heat; also, slow oxidation accompanied by relatively little heat and no light -

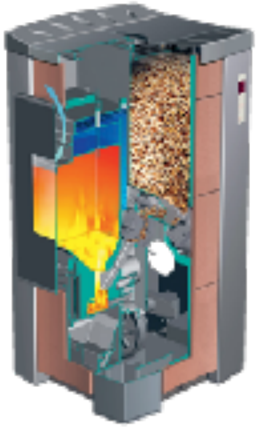
Combustion releases by oxidation reaction the chemical energy stored in the chemical bonds of the fuels

Known since more than **400.000** years

Fuel + Air => Combustion gases + Heat

boiler = combustion in a BOX (boiler)

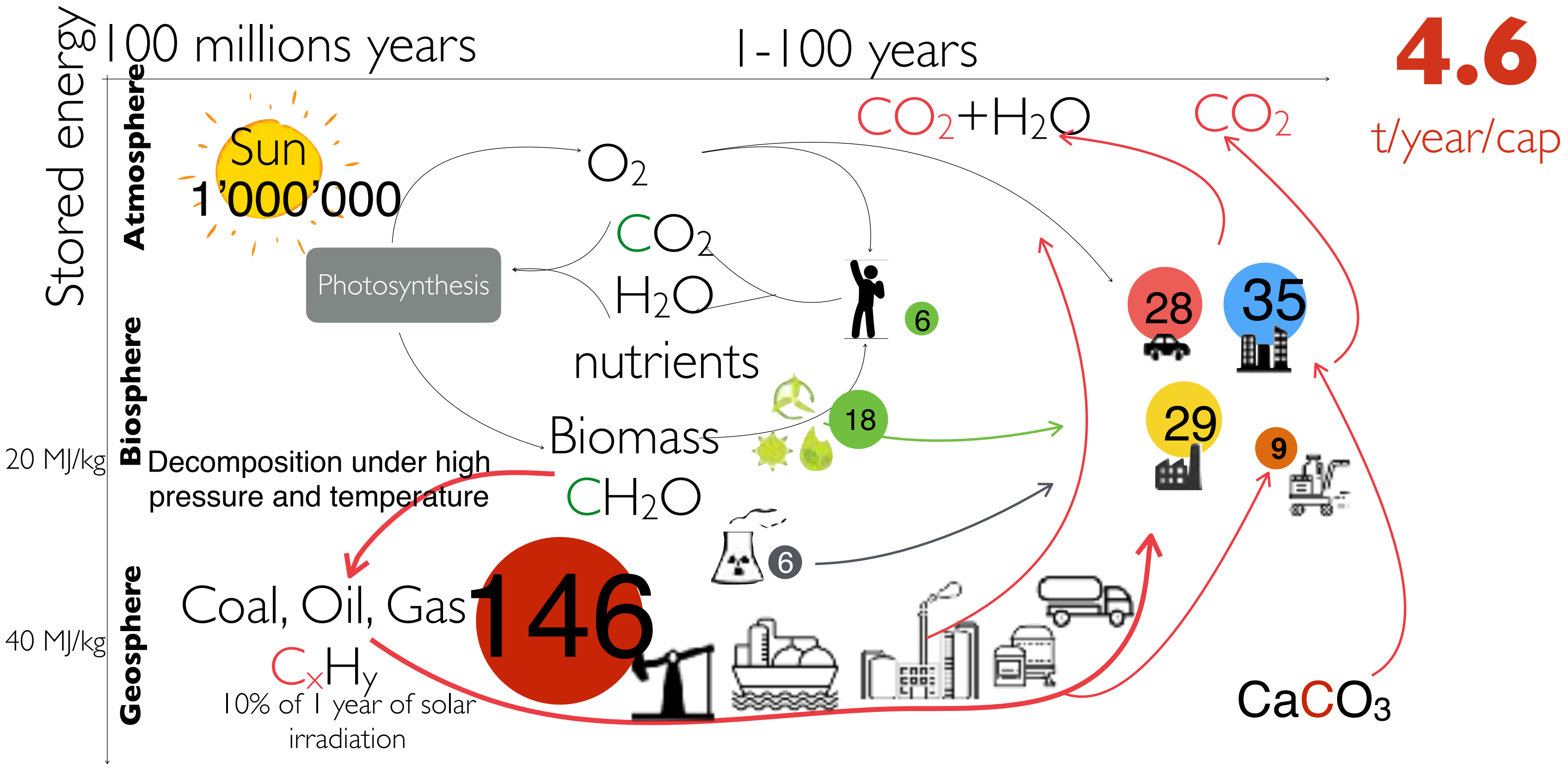
1^{st} law efficiency : 92%
2^{nd} law efficiency : 16%
(LHV, Theat=60°C)



www.auldtonstoves.co.uk

Current applications:
- Heating
- Electricity
- Cogeneration
- Mobility
- Military/Space (rockets, missiles, etc.)
- Hazards (fires,explosion,detonations)
- Catalytic combustion, Metal combustion, particle synthesis

Fossil fuels supply up to 85% of the world energy consumption and 75 % of the electricity production



Stored energy

100 millions years

1-100 years

Atmosphere

Biosphere

Geosphere

Sun

1'000'000

Photosynthesis

O_2

CO_2

H_2O

nutrients

6

18

Biomass

CH_2O

20 MJ/kg

Decomposition under high pressure and temperature

40 MJ/kg

Coal, Oil, Gas

146

C_xH_y

10% of 1 year of solar irradiation

6

CO_2+H_2O

CO_2

28

35

29

9

$CaCO_3$

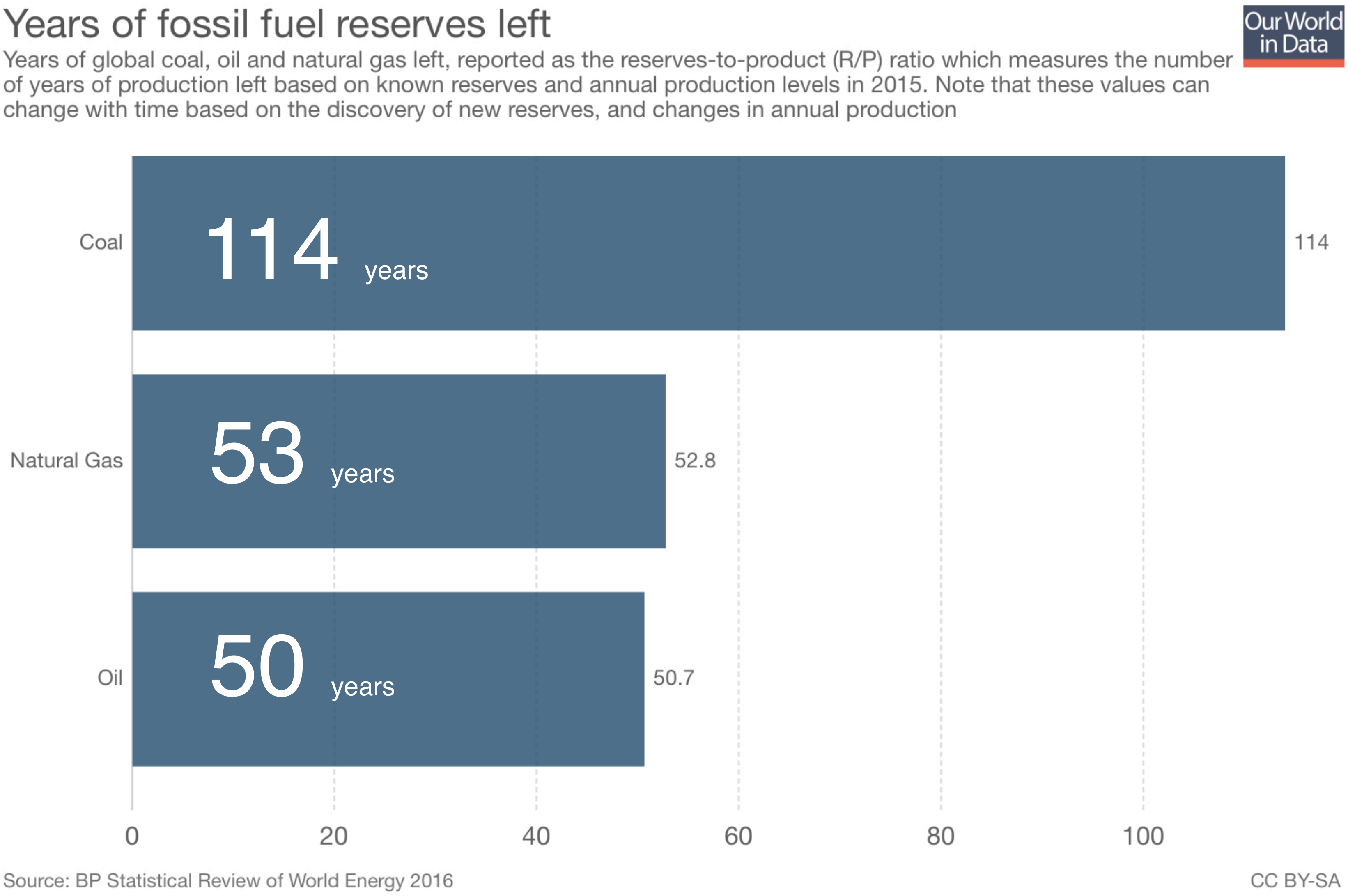
4.6

t/year/cap

100 = 390 EJ/y

World balance 2013, adapted from http://sankey.iea.org

Fossil fuel reserves



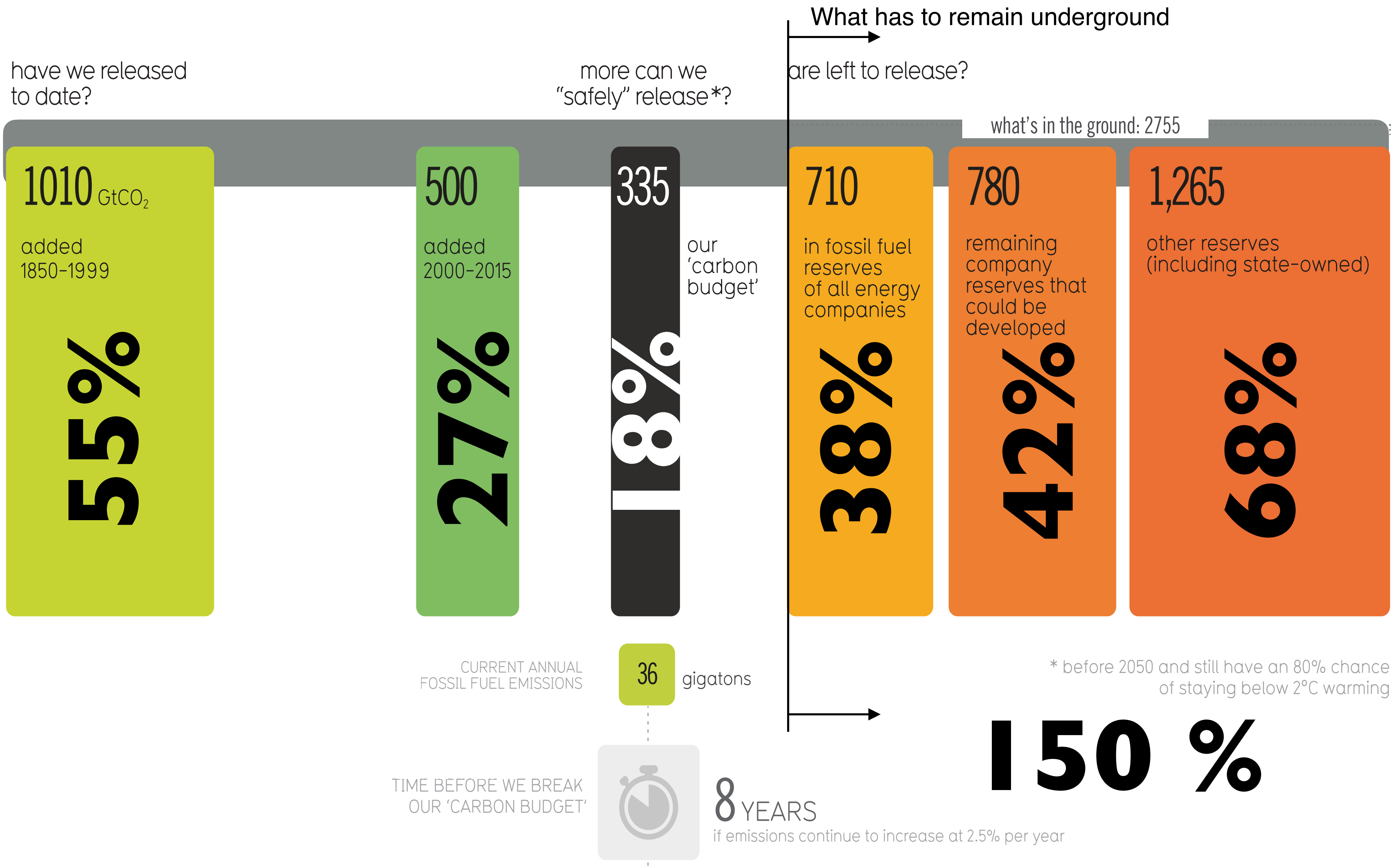
Years of fossil fuel reserves left

Years of global coal, oil and natural gas left, reported as the reserves-to-product (R/P) ratio which measures the number of years of production left based on known reserves and annual production levels in 2015. Note that these values can change with time based on the discovery of new reserves, and changes in annual production

Source: BP Statistical Review of World Energy 2016

But the stone age has not ended due to the lack of stones …

The capacity of atmosphere to absorb CO2 is limited : our carbon budget



What has to remain underground

have we released to date?

more can we “safely” release*?

are left to release?

what’s in the ground: 2755

1010 $GtCO_2$ added 1850-1999 55%

500 added 2000-2015 27%

335 our ‘carbon budget’ 18%

710 in fossil fuel reserves of all energy companies 38%

780 remaining company reserves that could be developed 42%

1,265 other reserves (including state-owned) 68%

CURRENT ANNUAL FOSSIL FUEL EMISSIONS 36 gigatons

TIME BEFORE WE BREAK OUR ‘CARBON BUDGET’ 8 YEARS if emissions continue to increase at 2.5% per year

* before 2050 and still have an 80% chance of staying below 2°C warming

150 %

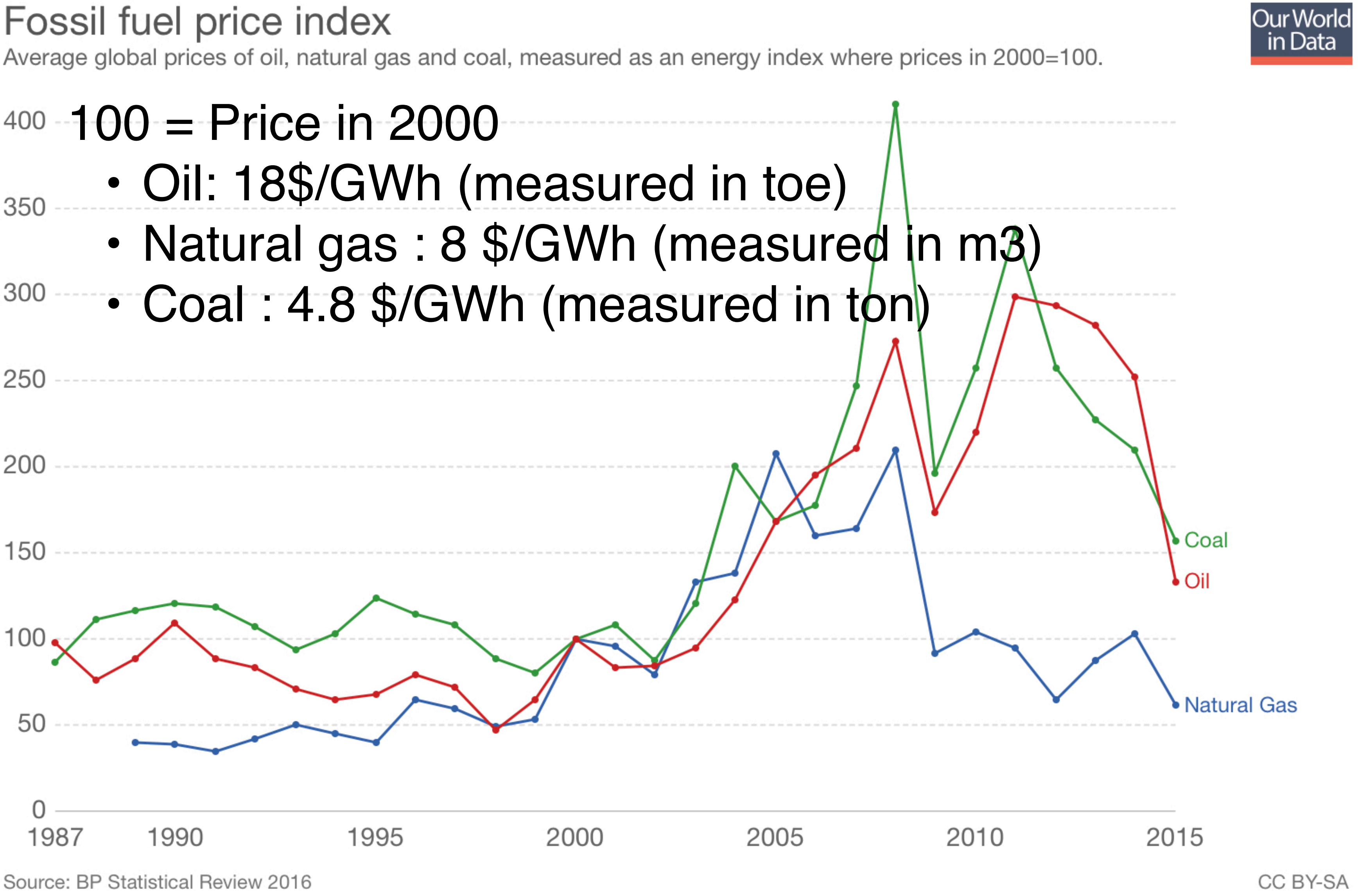
The fossil age will not end due to the lack of fossil resources …

Fuel Characterization

- **Availability**
  - Storage tanks
  - Distribution grid
- **Price (for industry CH - 2017 (IEA))**
  - Coal : 4 $/GJ
  - Natural Gas : 17 $/GJ
- **Energy or Heating value (kJ/kg)**
  - Lower (LHV)
  - Higher (HHV)
- **Chemical composition (atoms)**
- **Oxygen requirements**
- **Adiabatic temperature of combustion**

Fossil fuel cost : harvesting oil has a cost

800 bUSD invested each year for fossil resources extraction and distribution



Fossil fuel price index

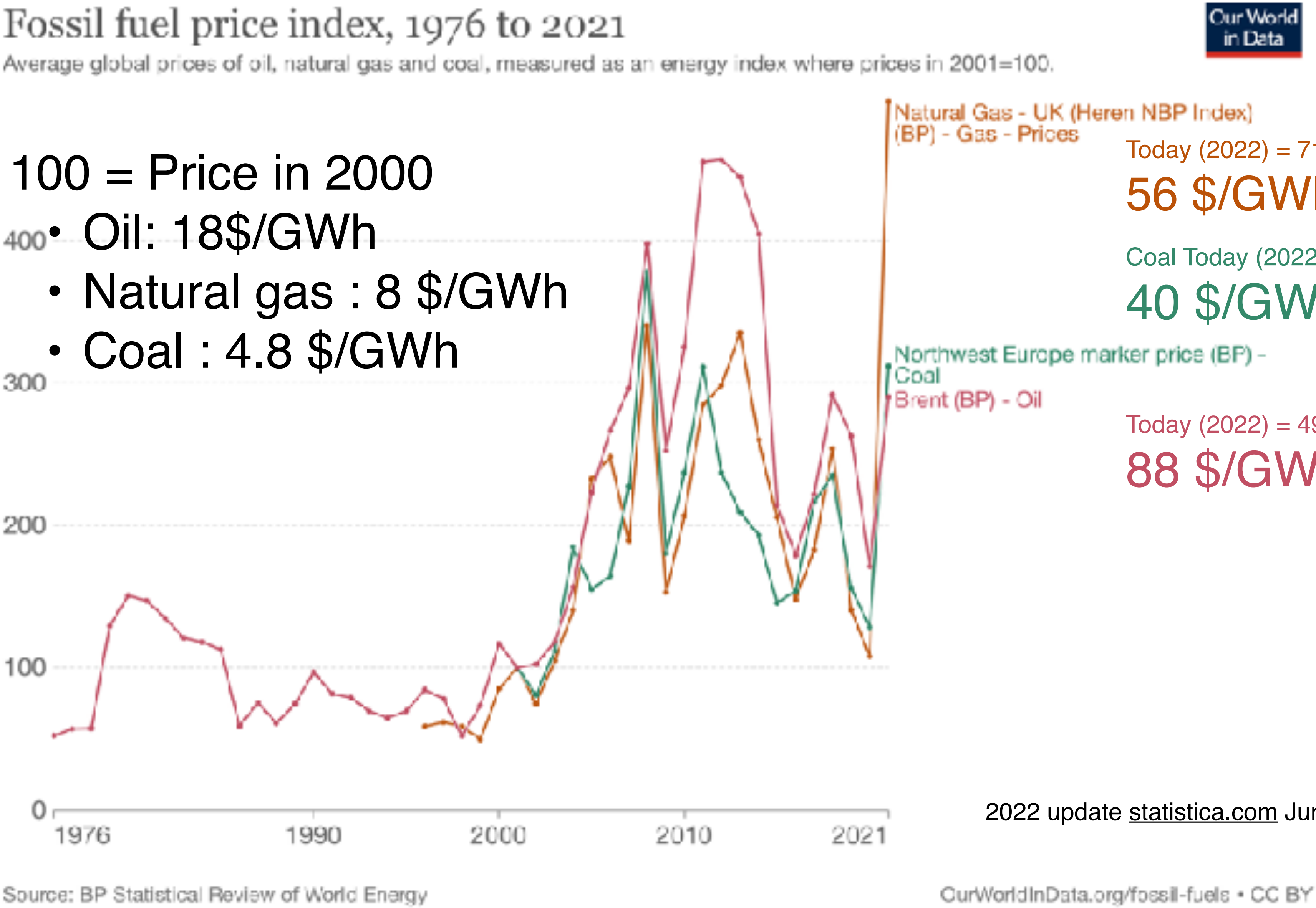
Average global prices of oil, natural gas and coal, measured as an energy index where prices in 2000=100.

100 = Price in 2000

- Oil: 18$/GWh (measured in toe)
- Natural gas : 8 $/GWh (measured in m3)
- Coal : 4.8 $/GWh (measured in ton)

Source: BP Statistical Review 2016

Prices change - order change



Fossil fuel price index, 1976 to 2021

Average global prices of oil, natural gas and coal, measured as an energy index where prices in 2001=100.

Source: BP Statistical Review of World Energy

OurWorldInData.org/fossil-fuels • CC BY

100 = Price in 2000

- Oil: 18$/GWh
- Natural gas : 8 $/GWh
- Coal : 4.8 $/GWh

Today (2022) = 710

56 $/GWh

Coal Today (2022) = 843

40 $/GWh

Today (2022) = 491

88 $/GWh

2022 update statistica.com June 2022

Chemical composition of a fuel

Atoms

1 molecule — $C_vH_wS_xO_yN_z$

Stoechiometric coefficient : v atoms/molecule

1 kmol of a compound corresponds to $6{,}022 \cdot 10^{26}$ molecules or atoms (Na = number of Avogadro, universal constant).

Element/Atoms	Symbol	Molar mass in kg/kmol
Carbon	C	12.0112
Hydrogen	H	1.008
Nitrogen	N	14.0067
Oxygen	O	15.9994
Sulfur	S	32.046

Molecule => Mass : kg/kmol

$$\tilde{M}_f = v \cdot \tilde{M}_C + w \cdot \tilde{M}_H + x \cdot \tilde{M}_S + y \cdot \tilde{M}_O + z \cdot \tilde{M}_N$$

Fuels are mixtures – chemical composition

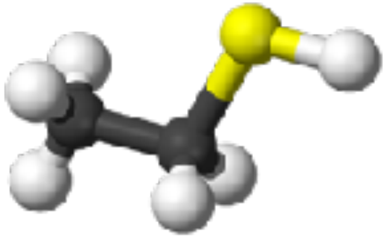
example Natural gas - Grid

Compound	Formula	% vol
Methane	CH_4	**89.16**
Ethane	C_2H_6	3.42
Propane	C_3H_8	0.93
n-butane	C_4H_{10}	0.14
I-butane	C_4H_{10}	0.2
n-pentane	C_5H_{12}	0.09
I-pentane	C_5H_{12}	0.07
Nitrogen	N_2	5.13
Carbon dioxide	CO_2	0.86

$pV=nRT$

Volume composition
equivalent to
Molar composition

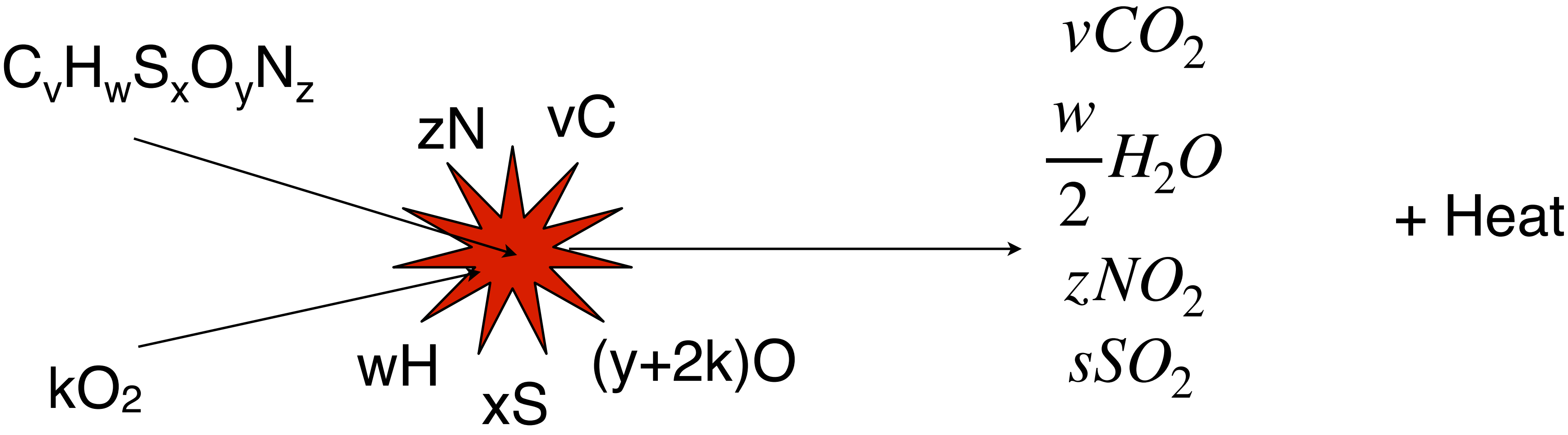
Mercaptans:
ppb levels to serve as an "odorizer"



Ethyl- mercaptan

http://www.spentcaustic.com/introduction.htm

Combustion is an oxidation reaction



$C_vH_wS_xO_yN_z$

kO_2

zN vC wH xS $(y+2k)O$

vCO_2

$\frac{w}{2}H_2O$

zNO_2

sSO_2

+ Heat

$$vC + vO_2 = vCO_2$$

$$wH + \frac{w}{4}O_2 = \frac{w}{2}H_2O$$

$$zN + zO_2 = zNO_2$$

$$xS + xO_2 = xSO_2$$

Minimum Oxygen needed

Stoechiometric oxygen

$$k = v + \frac{w}{4} + z + x - \frac{y}{2}$$

In combustion, the oxygen is breaking the chemical bounds between atoms in the fuel molecule
Atoms are conserved but form new molecules with higher oxidation level.
Note that combustion needs an energy of activation (spark !)

The oxidant : air

The air is composed of **78,09%**-vol. nitrogen (N_2), **20,95 %**-vol. oxygen (O_2), 0,93 %-vol. argon (Ar) and 0,04 %-vol. CO_2, neon (Ne), helium (He), CH_4 and other gases. However, it is in practice sufficient to consider a composition of **79,05%-vol. N_2 and 20,95 %-vol. d'O_2**. In this case, the molar ratio if nitrogen over oxygen is equal to **3,773 kmol N_2/kmol O_2**

Example $$CH_4 + 2\left(O_2 + 3.773N_2\right) \rightarrow CO_2 + 2H_2O + 7.546N_2$$

$$\nu_f C_v H_w S_x O_y N_z + \nu_{O_2}\left(O_2 + 3.773N_2\right) \rightarrow \nu_{CO_2} CO_2 + \nu_{H_2O} H_2O + \nu_{SO_2} SO_2 + \nu'_{N_2} N_2$$

Amount of N_2 $$\frac{\nu'_{N_2}}{\nu_f} = \frac{z}{2} + 3.773\frac{\nu_{O_2}}{\nu_f} \quad \text{en} \quad \frac{\text{kmol N}_2}{\text{kmol C}_v\text{H}_w\text{S}_x\text{O}_y\text{N}_z}$$

Volume increase ratio $$f_v = \frac{\nu_{CO_2} + \nu_{H_2O} + \nu_{SO_2} + \nu'_{N_2}}{\nu_f + 4.773\cdot\nu_{O_2}}$$

Air is used as the oxidant : combustion gases composition

$C_vH_wS_xO_yN_z$

fuel

air

$$\left(\frac{v+\frac{w}{4}+z+x-\frac{y}{2}}{0.21}\right)*(1+\lambda_a)*(0.21O_2+0.79N_2)$$

$$vC+vO_2=vCO_2$$

$$wH+\frac{w}{4}O_2=\frac{w}{2}H_2O$$

$$zN+zO_2=zNO_2$$

$$xS+xO_2=xSO_2$$

λ_a : air excess

All the expressions are **molar** expressions

1 kmol of a compound corresponds to 6,022·10^{26} molecules or atoms (number of Avogadro, universal constant).

fumes/ combustion gases

$$\left(\frac{v+\frac{w}{4}+z+x-\frac{y}{2}}{0.21}\right)*(1+\lambda_a)*(0.79N_2)+\left(\frac{v+\frac{w}{4}+z+x-\frac{y}{2}}{0.21}\right)*(\lambda_a)*(0.21O_2)$$
$$+vCO_2+\frac{w}{2}H_2O+zNO_2+xSO_2$$

Oxygen is delivered by air from the atmosphere, to be sure that a molecule of oxygen meets the atoms of the broken fuel, one typically adds an excess of oxygen and therefore an excess of air.

The combustion gases therefore are the mix of the combustion gases, the unreacted oxygen and the nitrogen from the air used.

Heat of combustion

$C_vH_wS_xO_yN_z$

fuel

air

$$\left(\frac{v+\frac{w}{4}+z+x-\frac{y}{2}}{0.21}\right)*(1+\lambda_a)*(0.21O_2+0.79N_2)$$

$$vC+vO_2=vCO_2$$

$$wH+\frac{w}{4}O_2=\frac{w}{2}H_2O$$

$$zN+zO_2=zNO_2$$

$$xS+xO_2=xSO_2$$

Enthalpy of formation of the fuel molecule is used to reconstruct the combustion gases molecules

The balance is the heat of reaction (kJ/kg)

The remaining heat of reaction is used to heat the combustion gases to T_{ad} the adiabatic temperature of combustion that will release the heat when being cooled down to ambiant conditions by heat exchange

fumes @Tad

$$\left(\frac{v+\frac{w}{4}+z+x-\frac{y}{2}}{0.21}\right)*(1+\lambda_a)*(0.79N_2)+\left(\frac{v+\frac{w}{4}+z+x-\frac{y}{2}}{0.21}\right)*(\lambda_a)*(0.21O_2)$$

$$+vCO_2+\frac{w}{2}H_2O+zNO_2+xSO_2$$

The adiabatic temperature is never existing because it assumes that the heat of formation only heats the combustion gases which means that no heat is leaving the system boundaries (adiabatic system). In reality, heat transfer using radiative and convective heat exchange occurs simultaneously to the combustion reactions reducing therefore the temperature at which the reactions take place.

Heating value

- **Amount of heat recovered by cooling the hot gases from the adiabatic temperature of combustion to the reference conditions (25°C, 1 atm), considering that both air and fuel are taken in reference conditions.**

combustion gases

$$LHV_{fuel} = \int_{T_0}^{T^o_{ad}} \frac{\dot{m}^o_{cg}}{\dot{m}_{fuel}} cp^o_{cg}(T)dT = \int_{T_0}^{T_{ad}} \frac{\dot{m}_{cg}}{\dot{m}_{fuel}} cp_{cg}(T)dT$$

$$\frac{\tilde{\dot{m}}_{cg}}{\dot{m}_{fuel}} cp_{cg} \approx \frac{LHV_{fuel}}{T_{ad} - T_0}$$

T$_{ad}$: **Adiabatic Temperature of Combustion** : temperature reached by the fumes heated by the release of the heat of reaction

Heating value

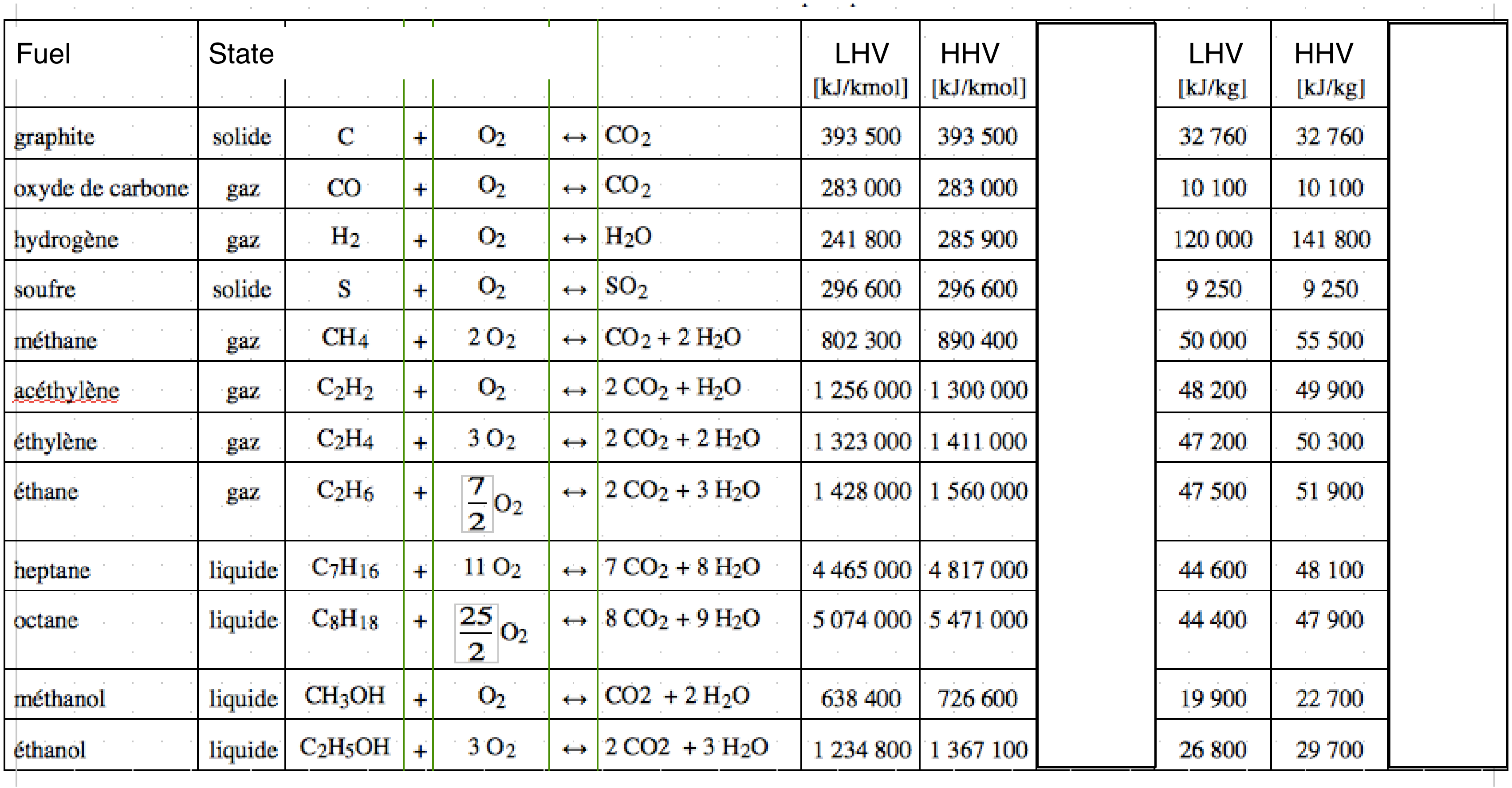
- **Higher Heating Value : HHV (kJ/kg) or PCS**
  - Amount of energy obtained by cooling to 25°C at standard conditions (1 atm) the fumes obtained by the combustion of one unit of fuel with stoichiometric air (air excess = 0) both taken at 25°C and 1 atm.
  - With higher heating value, the water produced during the combustion is condensed, i.e. released in the liquid form.
- **Lower Heating Value : LHV (kJ/kg) or PCI**
  - assumes that the water formed in the combustion will not condense
    - **LHV = HHV - (heat from the condensation of the water formed during the combustion at 25°C)**

$$LHV = HHV - \Delta H^0_{vap} \Delta m_{H_2O_{comb^*}}$$

$$\Delta H^0_{vap} = 44332 (kJ/kmol_{H_2O}), T = 25^\circ C, P = 1 bar$$

$\Delta m_{H_2O_{comb^*}} [kmol_{H_2O}/kg]$ water produced by combustion

Heating values = Energy of formation of molecules



Fuel	State						LHV [kJ/kmol]	HHV [kJ/kmol]		LHV [kJ/kg]	HHV [kJ/kg]	
graphite	solide	C	+	O_2	↔	CO_2	393 500	393 500		32 760	32 760	
oxyde de carbone	gaz	CO	+	O_2	↔	CO_2	283 000	283 000		10 100	10 100	
hydrogène	gaz	H_2	+	O_2	↔	H_2O	241 800	285 900		120 000	141 800	
soufre	solide	S	+	O_2	↔	SO_2	296 600	296 600		9 250	9 250	
méthane	gaz	CH_4	+	$2\ O_2$	↔	$CO_2 + 2\ H_2O$	802 300	890 400		50 000	55 500	
acéthylène	gaz	C_2H_2	+	O_2	↔	$2\ CO_2 + H_2O$	1 256 000	1 300 000		48 200	49 900	
éthylène	gaz	C_2H_4	+	$3\ O_2$	↔	$2\ CO_2 + 2\ H_2O$	1 323 000	1 411 000		47 200	50 300	
éthane	gaz	C_2H_6	+	$\frac{7}{2} O_2$	↔	$2\ CO_2 + 3\ H_2O$	1 428 000	1 560 000		47 500	51 900	
heptane	liquide	C_7H_{16}	+	$11\ O_2$	↔	$7\ CO_2 + 8\ H_2O$	4 465 000	4 817 000		44 600	48 100	
octane	liquide	C_8H_{18}	+	$\frac{25}{2} O_2$	↔	$8\ CO_2 + 9\ H_2O$	5 074 000	5 471 000		44 400	47 900	
méthanol	liquide	CH_3OH	+	O_2	↔	$CO2\ + 2\ H_2O$	638 400	726 600		19 900	22 700	
éthanol	liquide	C_2H_5OH	+	$3\ O_2$	↔	$2\ CO2\ + 3\ H_2O$	1 234 800	1 367 100		26 800	29 700	

Heating values of typical fuels (mixture of molecules)

	Tad K	mO2 kg air/kg	LHV kJ/kg	
Gaz naturel	2270	13,879	39680	Natural gas
Belgique	2290	15,693	44945	Belgium year 2000
Mer du Nord	2292	16,735	47900	Nord sea
Gaz de charbon	2373	8,557	27270	Coal gas
Essence	2431	15,003	47798	gasoline
Vaporizing oil	2389	15	46105	vaporising oil
Diesel	2426	14,583	45867	Diesel
Kérozène	2429	14,826	46924	Kerosene
Fuel léger	2425	14,454	45316	Light fuel oil
Fuel lourd	2423	14,264	44500	Heavy fuel oil
Anthracite	1819	11,53	33220	Anthracite coal
Bitume	1954	10,21	31520	Bitume
Lignite	2111	7,23	25450	Coal lignite

Estimating Heating Values

- **Solid fuels**
  - Higher heating value from final composition (% mass)

$$HHV = 35.17 c_C + 116.26 c_H - 11.10 c_O + 10.47 c_S + 6.28 c_N \quad [MJ/kg_{dry}]$$

$$c_i [\% mass]$$

  - Lower heating value :

$$LHV_{dry} = HHV - \frac{\tilde{m}_{H_2O}}{2} \Delta h_{vap}$$

$$\Delta h_{vap} = 2441 [kJ/kg]$$

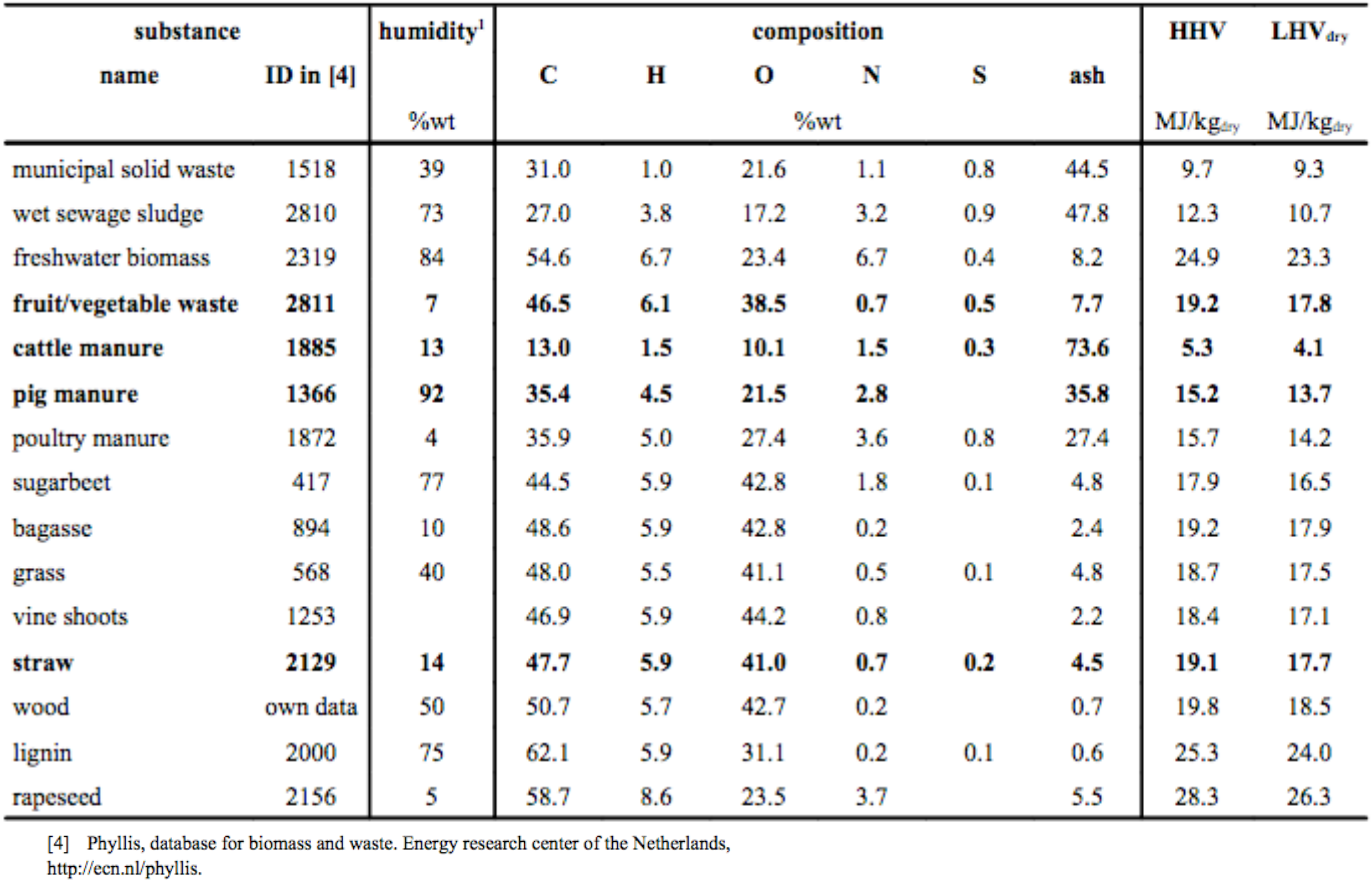
  - Humidity (ar : as received ; db dry basis)

$$LHV_{ar} = LHV_{db} \cdot \left(1 - \frac{MC}{100}\right) - \frac{MC}{100} \cdot \Delta H_{vap} \qquad \text{MJ/kg}$$

MC Moisture content on a wet basis (kg/kg in %)

The heat of reaction is first used to evaporate the humidity, this decreases the heat available in the combustion gases and therefore the adiabatic temperature of combustion. This heat can only be recovered at low temperature when condensing the water that is in the combustion gases.
A reduction of the adiabatic temperature of combustion may prevent the activation energy to be reached and therefore the combustion will be stopped or high quality fuel needs to be used,

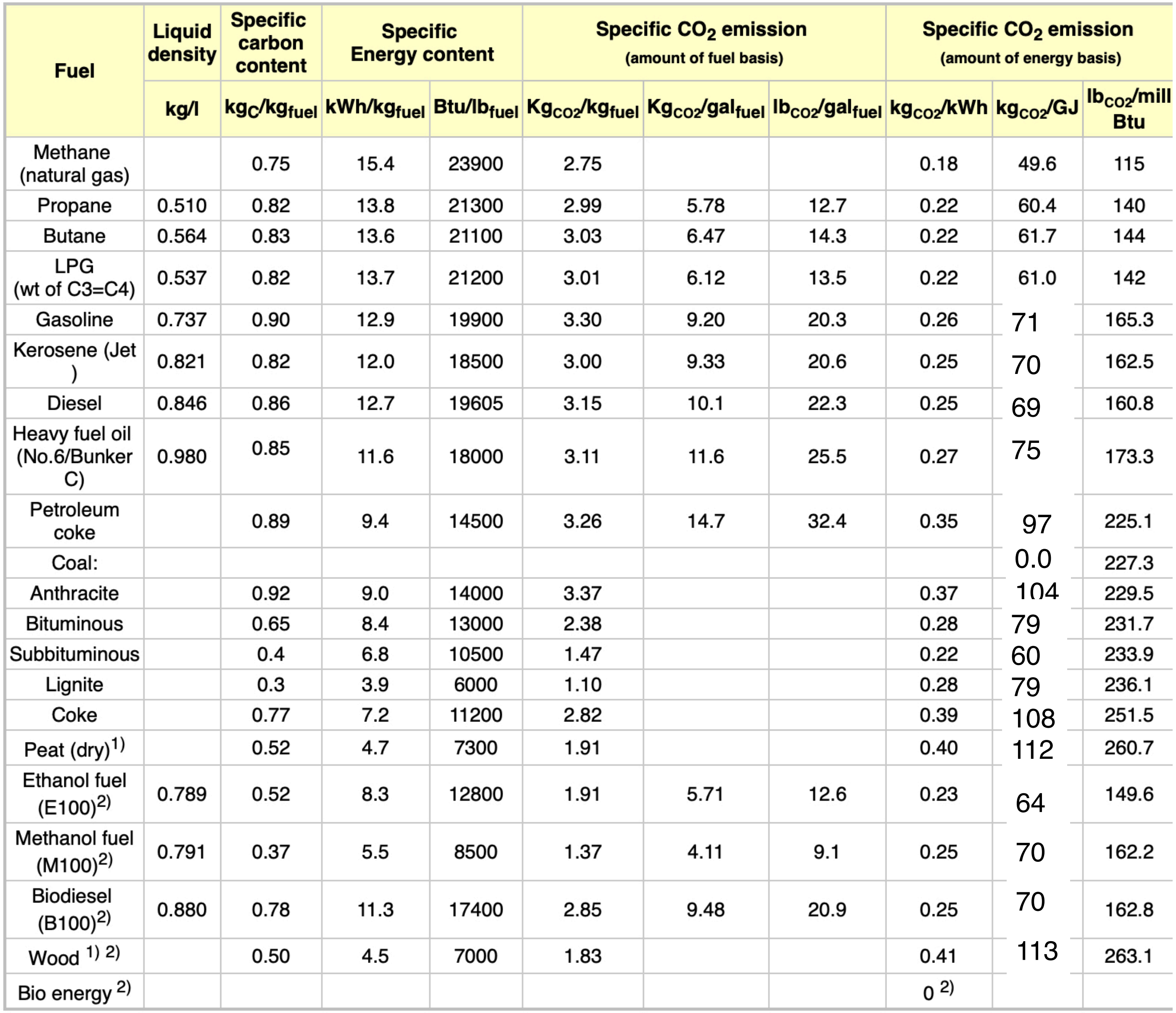
BIOMASS : Typical heating value



substance name	 ID in [4]	humidity[1] %wt	composition C	 H	 O	 N	 S	 ash	HHV MJ/kg$_{dry}$	LHV$_{dry}$ MJ/kg$_{dry}$
municipal solid waste	1518	39	31.0	1.0	21.6	1.1	0.8	44.5	9.7	9.3
wet sewage sludge	2810	73	27.0	3.8	17.2	3.2	0.9	47.8	12.3	10.7
freshwater biomass	2319	84	54.6	6.7	23.4	6.7	0.4	8.2	24.9	23.3
fruit/vegetable waste	**2811**	**7**	**46.5**	**6.1**	**38.5**	**0.7**	**0.5**	**7.7**	**19.2**	**17.8**
cattle manure	**1885**	**13**	**13.0**	**1.5**	**10.1**	**1.5**	**0.3**	**73.6**	**5.3**	**4.1**
pig manure	**1366**	**92**	**35.4**	**4.5**	**21.5**	**2.8**		**35.8**	**15.2**	**13.7**
poultry manure	1872	4	35.9	5.0	27.4	3.6	0.8	27.4	15.7	14.2
sugarbeet	417	77	44.5	5.9	42.8	1.8	0.1	4.8	17.9	16.5
bagasse	894	10	48.6	5.9	42.8	0.2		2.4	19.2	17.9
grass	568	40	48.0	5.5	41.1	0.5	0.1	4.8	18.7	17.5
vine shoots	1253		46.9	5.9	44.2	0.8		2.2	18.4	17.1
straw	**2129**	**14**	**47.7**	**5.9**	**41.0**	**0.7**	**0.2**	**4.5**	**19.1**	**17.7**
wood	own data	50	50.7	5.7	42.7	0.2		0.7	19.8	18.5
lignin	2000	75	62.1	5.9	31.1	0.2	0.1	0.6	25.3	24.0
rapeseed	2156	5	58.7	8.6	23.5	3.7		5.5	28.3	26.3

[4] Phyllis, database for biomass and waste. Energy research center of the Netherlands, http://ecn.nl/phyllis.

Fuels and CO2 emissions



Fuel	Liquid density	Specific carbon content	Specific Energy content		Specific CO_2 emission (amount of fuel basis)			Specific CO_2 emission (amount of energy basis)		
	kg/l	kg_C/kg_{fuel}	kWh/kg_{fuel}	Btu/lb_{fuel}	Kg_{CO2}/kg_{fuel}	Kg_{CO2}/gal_{fuel}	lb_{CO2}/gal_{fuel}	kg_{CO2}/kWh	kg_{CO2}/GJ	lb_{CO2}/mill Btu
Methane (natural gas)		0.75	15.4	23900	2.75			0.18	49.6	115
Propane	0.510	0.82	13.8	21300	2.99	5.78	12.7	0.22	60.4	140
Butane	0.564	0.83	13.6	21100	3.03	6.47	14.3	0.22	61.7	144
LPG (wt of C3=C4)	0.537	0.82	13.7	21200	3.01	6.12	13.5	0.22	61.0	142
Gasoline	0.737	0.90	12.9	19900	3.30	9.20	20.3	0.26	71	165.3
Kerosene (Jet)	0.821	0.82	12.0	18500	3.00	9.33	20.6	0.25	70	162.5
Diesel	0.846	0.86	12.7	19605	3.15	10.1	22.3	0.25	69	160.8
Heavy fuel oil (No.6/Bunker C)	0.980	0.85	11.6	18000	3.11	11.6	25.5	0.27	75	173.3
Petroleum coke		0.89	9.4	14500	3.26	14.7	32.4	0.35	97	225.1
Coal:									0.0	227.3
Anthracite		0.92	9.0	14000	3.37			0.37	104	229.5
Bituminous		0.65	8.4	13000	2.38			0.28	79	231.7
Subbituminous		0.4	6.8	10500	1.47			0.22	60	233.9
Lignite		0.3	3.9	6000	1.10			0.28	79	236.1
Coke		0.77	7.2	11200	2.82			0.39	108	251.5
Peat (dry)$^{1)}$		0.52	4.7	7300	1.91			0.40	112	260.7
Ethanol fuel (E100)$^{2)}$	0.789	0.52	8.3	12800	1.91	5.71	12.6	0.23	64	149.6
Methanol fuel (M100)$^{2)}$	0.791	0.37	5.5	8500	1.37	4.11	9.1	0.25	70	162.2
Biodiesel (B100)$^{2)}$	0.880	0.78	11.3	17400	2.85	9.48	20.9	0.25	70	162.8
Wood $^{1)\ 2)}$		0.50	4.5	7000	1.83			0.41	113	263.1
Bio energy $^{2)}$								0 $^{2)}$		

https://www.engineeringtoolbox.com/co2-emission-fuels-d_1085.html

Using the heat of combustion : heat exchange

Boilers

$$\dot{Q}_b = \dot{Q}_{rad} + \dot{Q}_{conv} = \dot{m}_{cg} \int_{T_{ch}}^{T_{ad}} cp_{cg} dT - \dot{Q}_{loss}$$

Heat exchange

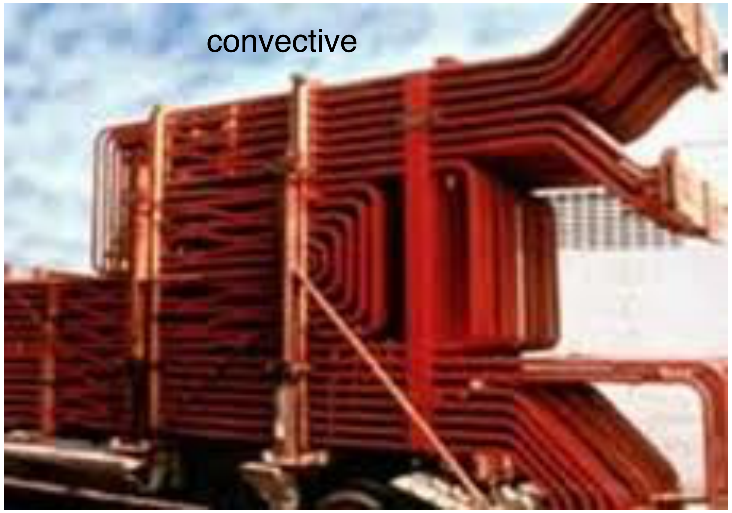
Burners

Radiative exchange (T > 850 C)

$$\dot{Q}_{rad} = GS(T_{gas}^4 - T_{water}^4)$$

Convective exchange

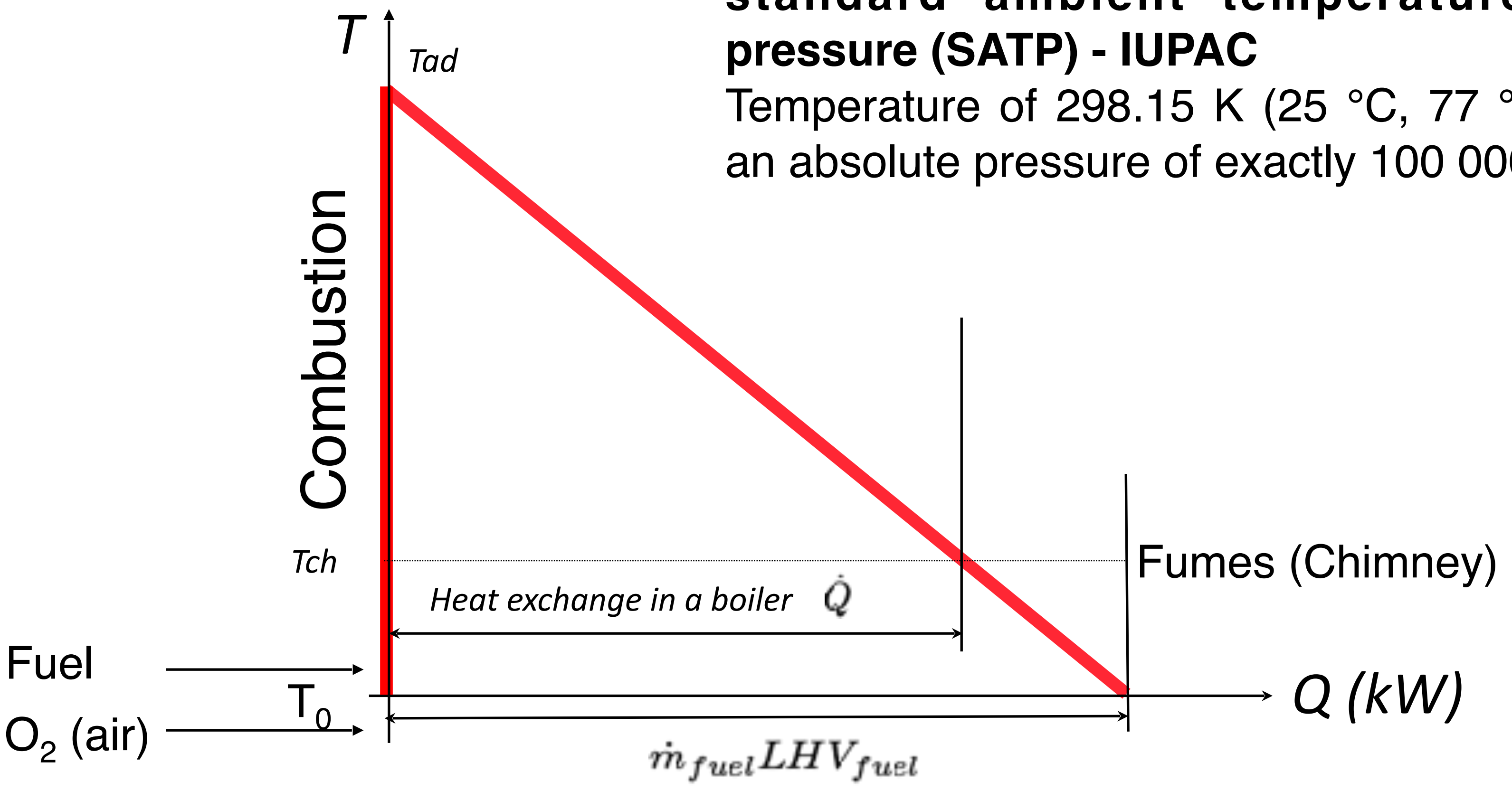
$$\dot{Q}_{conv} = UA\Delta T_{lm}$$



Heat of combustion is exchanged via heat exchangers to a fluid that is heated (e.g.. steam). There are two mechanisms for the heat transfer : the radiative at high temperature and the convective at low temperature. After the heat exchange, the combustion gases leave the boiler in the chimney.

- http://www.industrial-lima.com.pe/web/images/stories/sobrecalentador.jpg http://www.cleaverbrooks.com/templates_products/

Heat recovery



standard ambient temperature and pressure (SATP) - IUPAC
Temperature of 298.15 K (25 °C, 77 °F) and an absolute pressure of exactly 100 000 Pa.

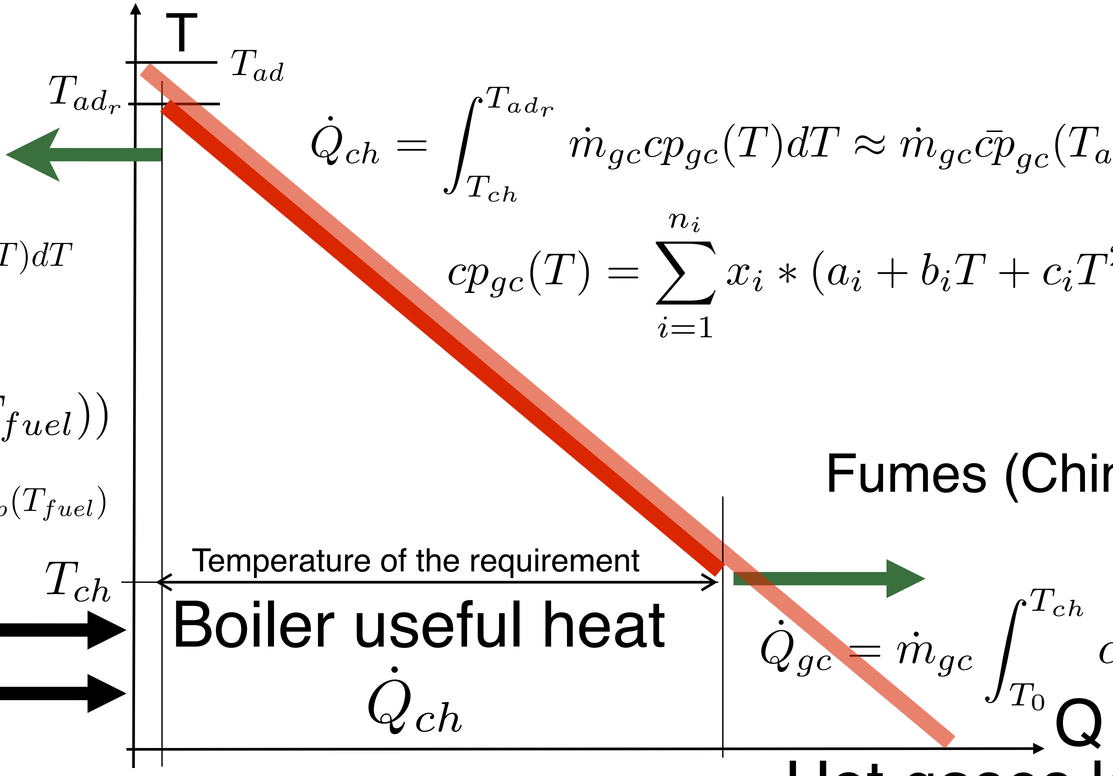
$$\dot{Q} = \int_{T_{ch}}^{T_{ad}} \dot{m}_{cg} cp_{cg}(T) dT \approx \dot{m}_{cg} \bar{cp}_{cg} (T_{ad} - T_{ch})$$

$$kW = \frac{kJ}{s} = \frac{kg}{s} * \frac{kJ}{kgK} * K$$

Boiler efficiency calculation

Useful heat depends on the temperature of the heat requirement

$$\dot{Q}_{ch} = \dot{Q}_{fuel} + \dot{Q}_{air} - (\dot{Q}_r + \dot{Q}_{gc})$$



Radiative losses (1-2%) $\dot{Q}_r$

$$\dot{Q}_r = \int_{T_{ad_r}}^{T_{ad}} \dot{m}_{gc} cp_{gc}(T)dT \approx 2\% \cdot \int_{T_0}^{T_{ad}} \dot{m}_{gc} cp_{gc}(T)dT$$

$$\dot{Q}_{ch} = \int_{T_{ch}}^{T_{ad_r}} \dot{m}_{gc} cp_{gc}(T)dT \approx \dot{m}_{gc} \bar{cp}_{gc}(T_{ad_r} - T_{ch})$$

$$cp_{gc}(T) = \sum_{i=1}^{n_i} x_i * (a_i + b_i T + c_i T^2 + d_i T^3)$$

$$\dot{Q}_{fuel} = \dot{m}_{fuel}(LHV_{fuel} + \hat{h}_{fuel}(T_{fuel}))$$

$$\hat{h}_{fuel}(T_{fuel}) = \int_{T_0}^{T_{fuel}} cp_{fuel}(T)dT + \alpha_{fuel} \Delta h_{vap}(T_{fuel})$$

Fuel

O2 (air)

Fumes (Chimney)

$$\dot{Q}_{gc} = \dot{m}_{gc} \int_{T_0}^{T_{ch}} cp_{gc}(T)dT$$

Hot gases losses

Air inlet

$$\dot{Q}_{air} = \dot{m}_{air}(\hat{h}_{air}(T_{air}))$$

$$\dot{Q}^{+}_{air} = \dot{m}^{+}_{air}(h_{air}(T_{air}) - h_{air}(T_0))$$

In a boiler fuel and air can be at another temperature or conditions than the standard conditions

Boiler efficiency

Boiler Losses

$$\dot{Q}_p = \dot{Q}_r + \dot{Q}_{gc}$$

Heat loss at the stack $\dot{Q}_{gc} = \dot{m}_{gc} \int_{T_0}^{T_{ch}} cp_{gc}(T)dT$

Radiative losses $\dot{Q}_r = \int_{T_{ad_r}}^{T_{ad}} \dot{m}_{gc} cp_{gc}(T)dT \approx 2\% \cdot \int_{T_0}^{T_{ad}} \dot{m}_{gc} cp_{gc}(T)dT$

Useful heat

$$\dot{Q}_{ch} = \dot{Q}_{fuel} + \dot{Q}_{air} - (\dot{Q}_r + \dot{Q}_{gc})$$

Energy from the fuel $\dot{Q}_{fuel} = \dot{m}_{fuel}(LHV_{fuel} + \hat{h}_{fuel}(T_{fuel}))$

Heat from the air $\dot{Q}^+_{air} = \dot{m}^+_{air}(h_{air}(T_{air}) - h_{air}(T_0))$

Boiler efficiency : typical values are from 85% to 90%

$$\eta_{ch} = \frac{\dot{Q}_{ch}}{\dot{Q}_{fuel} + \dot{Q}_{air}} = 1 - \frac{\dot{Q}_p}{\dot{Q}_{fuel} + \dot{Q}_{air}}$$

In a boiler the losses are the radiative losses and the heat released in the environment by releasing hot gases at the stack

Water condensation

When temperature decreases, there is a point where water starts condensing.

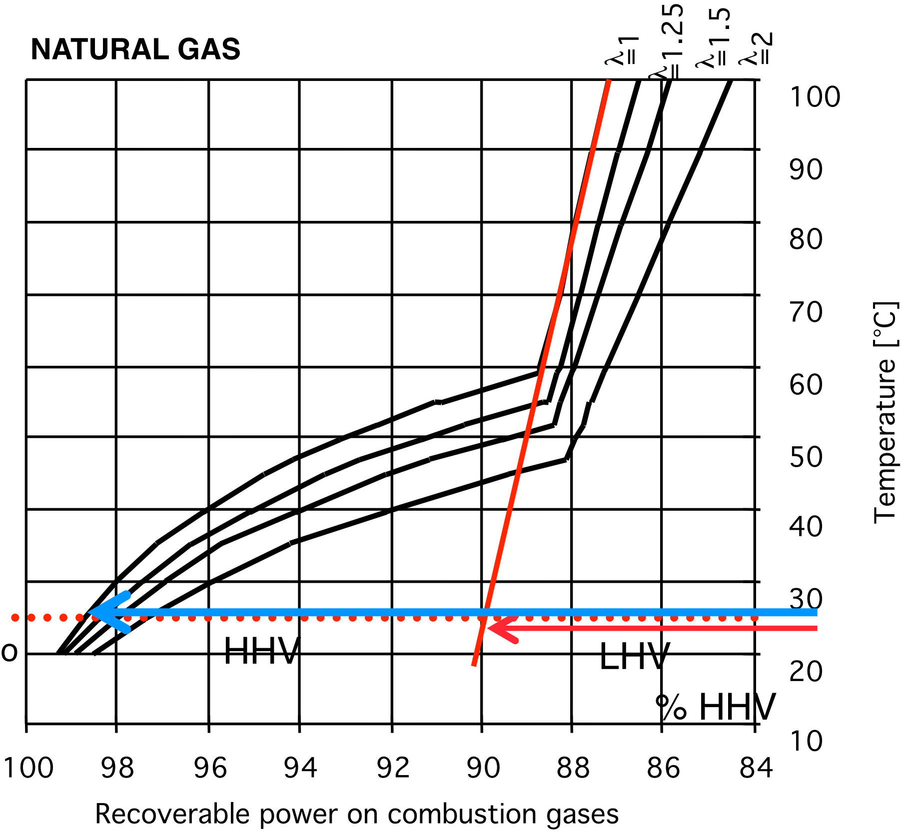
Water partial pressure :

$$T_{sat}\left(\frac{\nu_{H_2O} * P}{\sum_{i=1}^{n_s} \nu_i}\right)$$

Saturation temperature is the temperature at which the partial pressure of water is equal to the saturation pressure

$$x^{sat} = \frac{P^{sat}}{P}$$

$$P^{sat}[atm] = 0.001315 \cdot 10^{\left(8.07131 - \frac{1730.63}{233.426 + T[^oC]}\right)}$$



The heat that can be recovered by condensing the water is equal to

$$\dot{Q}_{H_2O} = 327.6(374 - T)^{0.3425}[kJ/kg]$$

In the combustion gases, the water does not occupy the whole space, therefore it sees a pressure (the partial pressure) that is different from the total pressure. The partial pressure is calculated knowing the molar concentration of the water in the mixture.

The water will condense if its partial pressure is below the saturation pressure for the temperature of the mixture.

The water condenses when it sees a cold part with a temperature lower than its saturation temperature in the heat exchanger or outside

As the gas contains CO2, the produced water is acidic and therefore creates corrosion. Low temperature heat exchangers in condensing boilers have to be protected from corrosion by using special materials. Due to the corresponding cost increase, condensations is typically avoided.

The temperature of condensation is lower than 100 °C which means that the combustion gases have to see tubes with temperatures lower than the saturation temperature. The liquid is forming on the tubes meaning that the temperature of the combustion gas flow will not be saturated in water.

Pollutants that can be produced in addition

Sulphur : kinetic control

$$0.95 * sS + 0.95 * sO_2 = 0.95 * sSO_2$$

$$0.05 * sS + 0.05 * \left(\frac{3}{2}\right) sO_2 = 0.05 * s * SO_3$$

$$0.05 * s * SO_3 + 0.05 * s * H_2O = 0.05 * s * H_2SO_4$$

Affinities with water (production of H2SO4 in the liquid phase) is increasing the saturation temperature of water in the presence of sulphur in the gas phase => higher chimney temperatures are needed to avoid highly corrosive gases (+70°C) This is penalising the efficiency of the boiler.

NO_x = NO, N_2O, NO_2 Nitrogen is coming from the fuel or from the air the oxidation of N2 occurs at high temperature (>1500°C) and is frozen (do not go back to N2 + O2) at lower temperatures

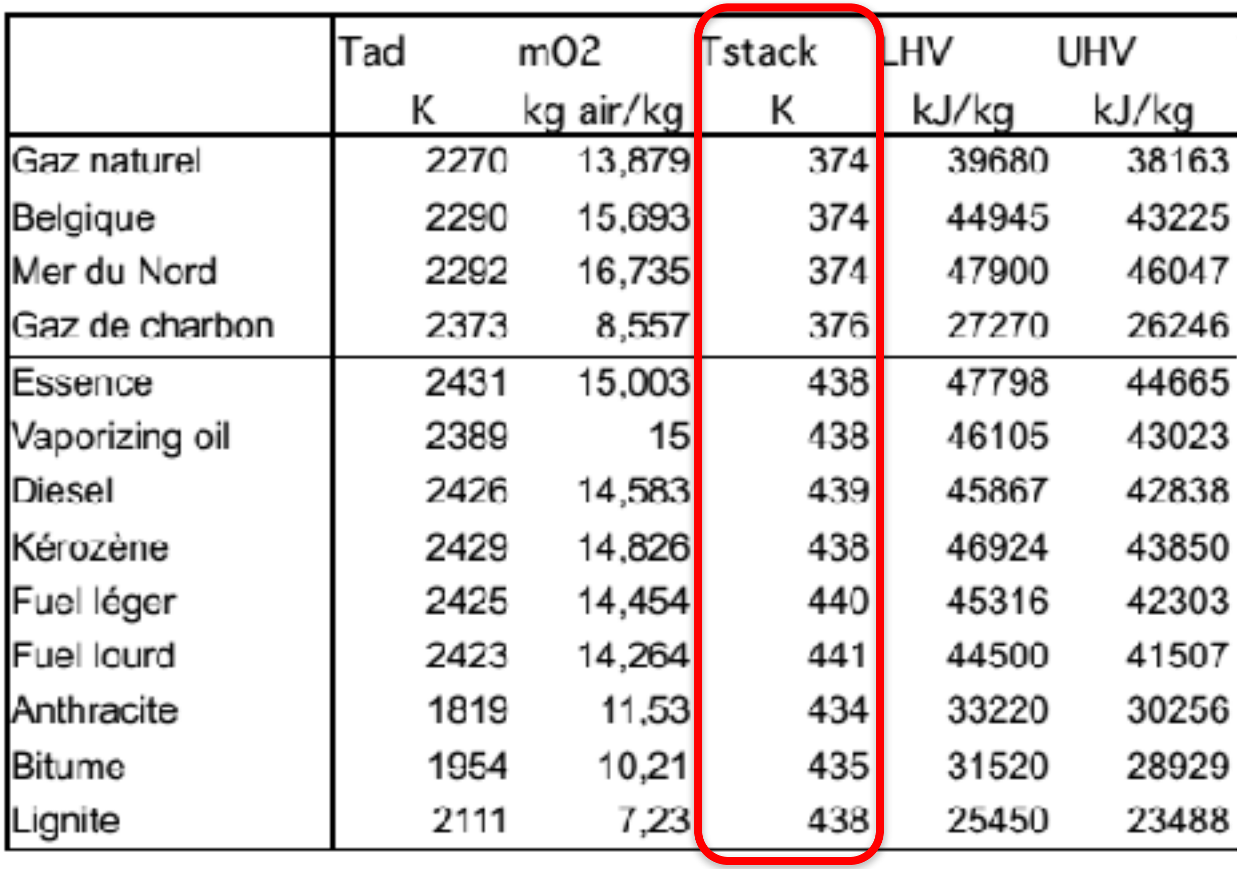
Unburnt = unburnt fuel (CO, tars) when the combustion is no complete or goes to fast

Ashes and dust for solid fuels (wood, coal, waste) which contains minerals in this composition

Importance of Tstack

UHV = useful heating value

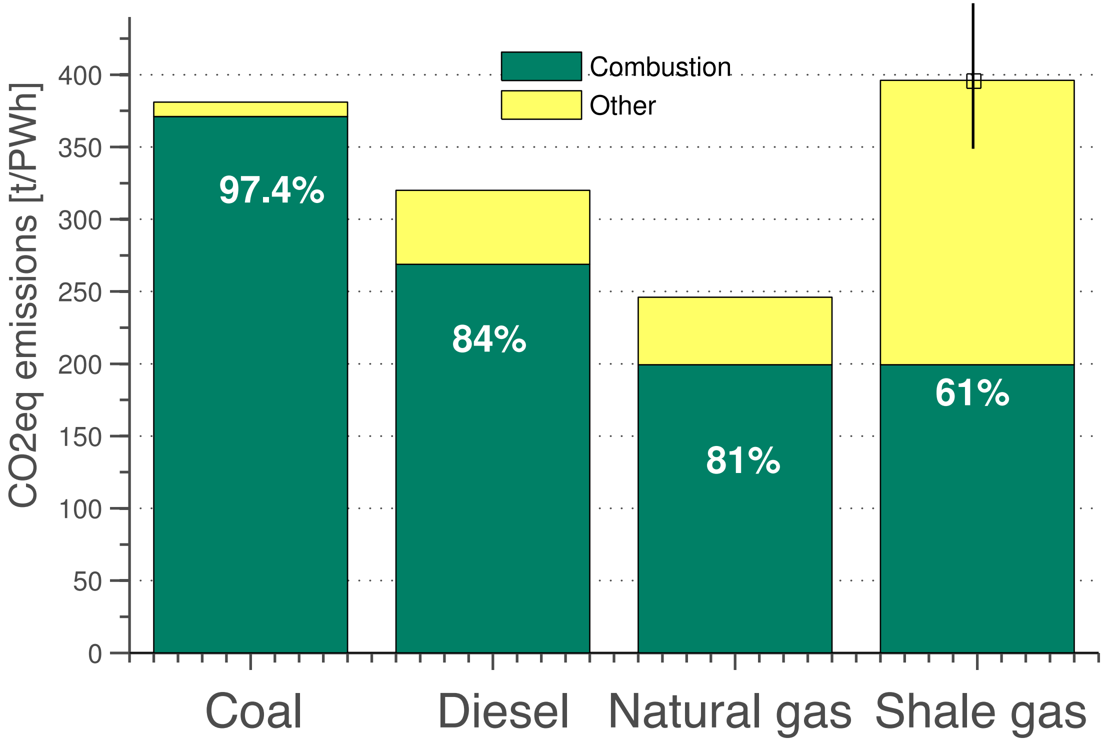
$$UHV[kJ/kg_{fuel}] = \int_{T_{ad}}^{T_{stack}} m_{cg}[kg_{cg}/kg\,fuel] \cdot cp_{cg}[kJ/kg_{cg}/C] \cdot dT$$



	Tad K	m02 kg air/kg	Tstack K	LHV kJ/kg	UHV kJ/kg	
Gaz naturel	2270	13,879	374	39680	38163	Natural gas
Belgique	2290	15,693	374	44945	43225	Belgium year 2000
Mer du Nord	2292	16,735	374	47900	46047	Nord sea
Gaz de charbon	2373	8,557	376	27270	26246	Coal gas
Essence	2431	15,003	438	47798	44665	gasoline
Vaporizing oil	2389	15	438	46105	43023	vaporising oil
Diesel	2426	14,583	439	45867	42838	Diesel
Kérozène	2429	14,826	438	46924	43850	Kerosene
Fuel léger	2425	14,454	440	45316	42303	Light fuel oil
Fuel lourd	2423	14,264	441	44500	41507	Heavy fuel oil
Anthracite	1819	11,53	434	33220	30256	Anthracite coal
Bitume	1954	10,21	435	31520	28929	Bitume
Lignite	2111	7,23	438	25450	23488	Coal lignite

Environmental impact of the use of combustion

- **Importance of the life cycle**
  - Extraction
  - Conditionning
  - Transport
  - Refining
  - Distribution
  - Combustion



CO2 eq : is a measure of the global warming potential of the emissions over the overall conversion chain up to combustion. The global warming potential is considering not only the CO2 emissions but also other emissions like CH4 (that has a GWP of 20 CO2 eq), NOx and other gases in the complete life cycle chain.

Life cycle assessment : emissions before the use

15 to 40% of the CO2 emissions have been made to prepare the fossil fuels

		Natural gas	**Wood**	**Gasoline**	**Diesel**
	kg/Nm3	0.7	240	0.8	0.8
LHV	MJ/kg	50	17.8	44.4	43.4
	GJ/Nm3	0.0359	5.3-9.6	35.5	34.7
CO2	g CO2/MJ	49.3	0	67	72
supply eq CO2	g CO2/MJ	11.6	1.4-1.8 (production) 0.19 (20 MW) -1.1(320 MW) 1.6 - 2.9	16.7	13.4
	g CO2/MJ	60.9	1.6-2.9	83.7	85.4
		19%	-	20%	16%
Cost	cts/kWh	10	3 - 7.5	18.6	19.2
industry	cts/kWh	3.4			