Greenhouse Gases Mitigation CO_2 Capture and Utilization

Topic No: 1

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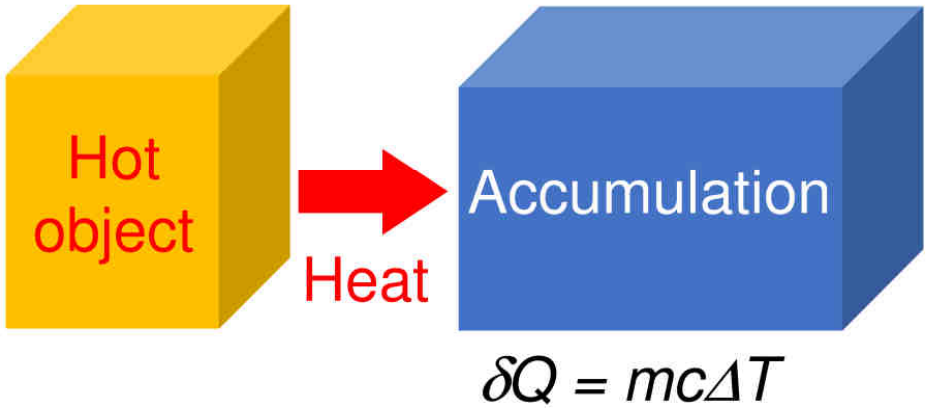
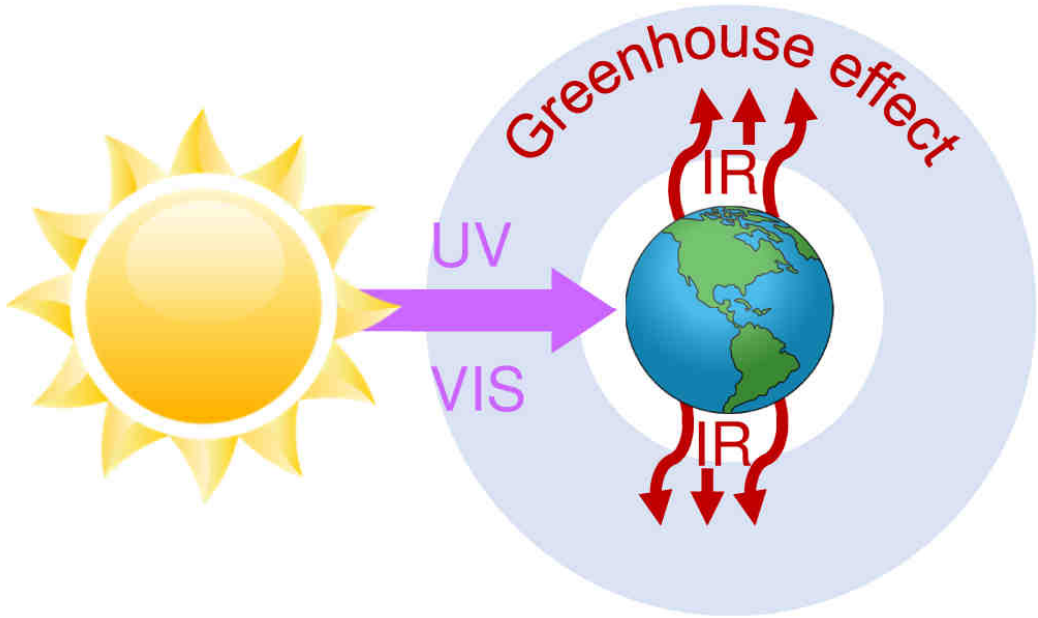
What is greenhouse effect?

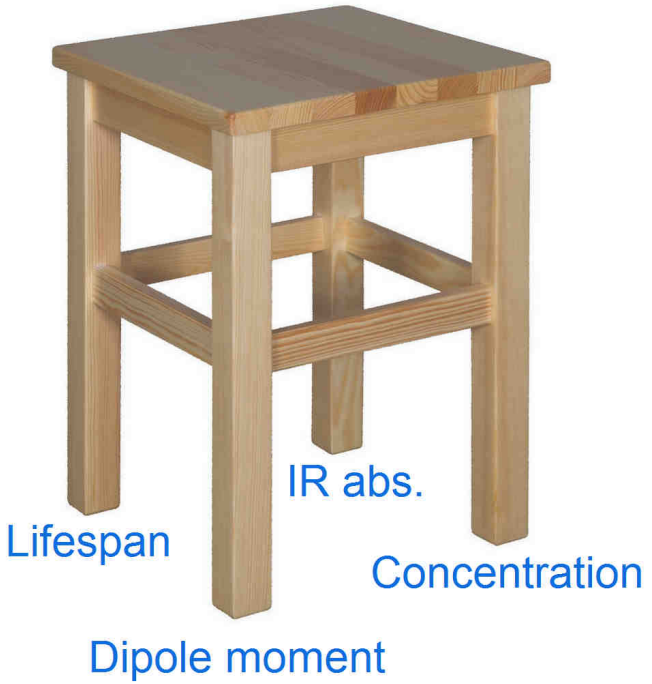
- The greenhouse effect **is not** simply the accumulation of heat.
- Principle: The Earth absorbs UV and VIS and emits IR, but specific gases retain it in the atmosphere.
- Gases capable of this process = greenhouse gases (GHGs).





Which gases are classified as GHG?

- GHG must absorb radiation in IR part of spectrum.
- Molecules of GHG must change their dipole moment due to IR absorption
  - Symmetric di-atomic molecules (H_2, N_2, O_2) do not change their dipole moment ⇒ IR inactive;
  - Molecules with different partial charges on the atoms (CO, CO_2, N_2O…) change the dipole moment ⇒ IR active.
- GHG molecules must have sufficient lifetime in the atmosphere.
  - e.g. CO_2 50 – 200 years, CH_4 12 – 17 years etc.
- GHG must be present at sufficient concentrations
  - e.g. CO_2 > 400 ppmv, H_2O ≅ 0.4 % vol.



Reference(s): -

The most important GHGs

Hundreds of compounds … the main are:

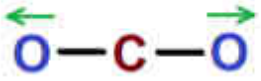
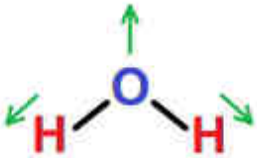
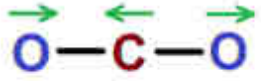
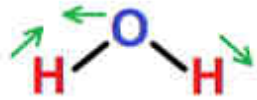
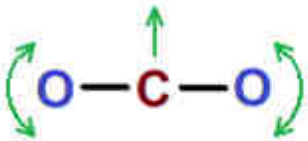
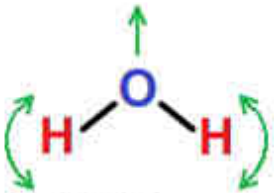
- H_2O (vapor)
- CO_2
- C_xH_y (especially CH_4)
- N_2O
- F-gases a ClF-gases:
  - CFCs (chlorofluorocarbons)
  - HFCs (hydrofluorocarbons)
  - PFCs (perfluorocarbons)
  - SF_6 (sulfur fluoride)
- O_3

The most important GHGs

	What is their origin:	
H_2O (vapor)	NATURAL	
CO_2	NATURAL	ANTHROPOGENIC
C_xH_y (especially CH_4)	NATURAL	ANTHROPOGENIC
N_2O	NATURAL	ANTHROPOGENIC
F-gases a ClF-gases:		
▶ CFCs (chlorofluorocarbons)		ANTHROPOGENIC
▶ HFCs (hydrofluorocarbons)		ANTHROPOGENIC
▶ PFCs (perfluorocarbons)		ANTHROPOGENIC
▶ SF_6 (sulfur fluoride)		ANTHROPOGENIC
O_3	NATURAL	ANTHROPOGENIC

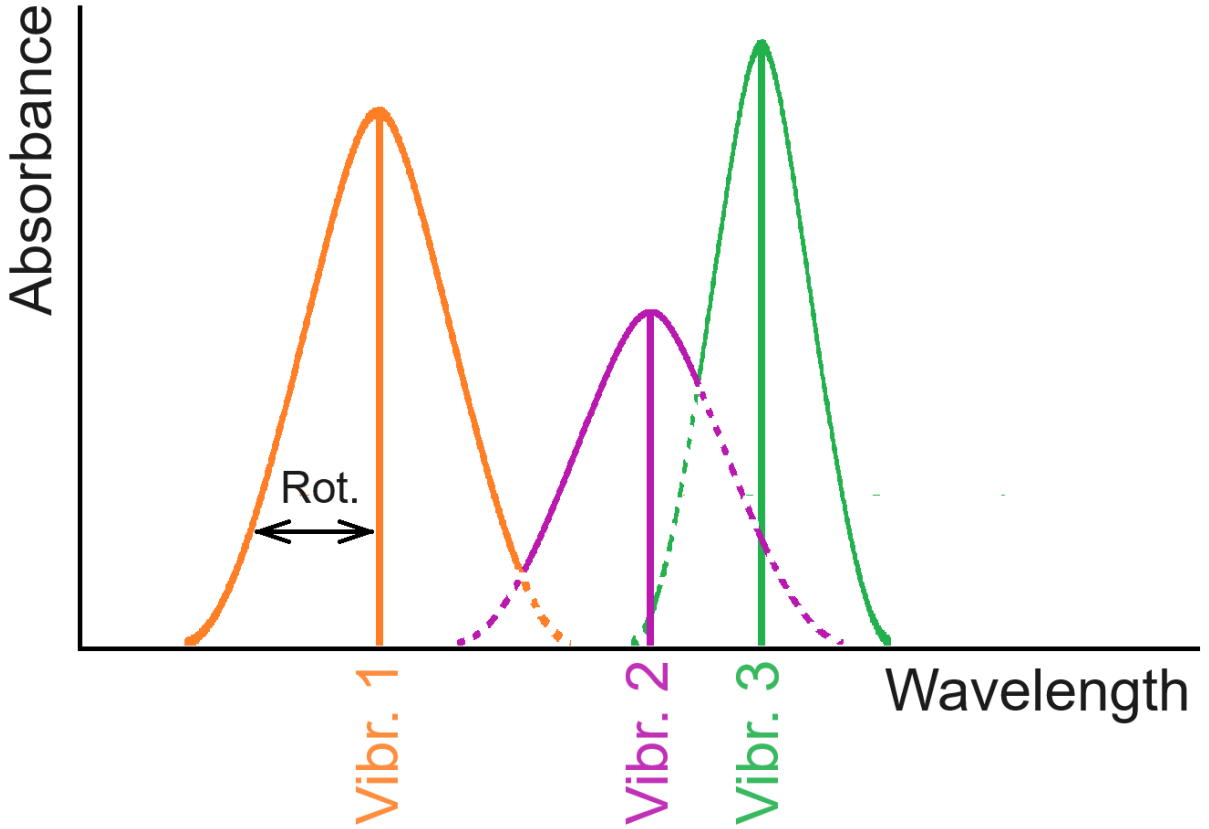
How GHGs retain IR?

- Absorption of light induces molecular vibrations.
- Quantum transition during IR absorption = values of molecular vibrations
  - Each molecular vibration has its specific wavelength value

	Carbon dioxide	Water
Symmetric stretch (ν_s)		
	7,490 nm	2,738 nm
Asymmetric stretch (ν_{as})		
	4,257 nm	2,656 nm
Bend (δ)		
	14,992 nm	6,269 nm

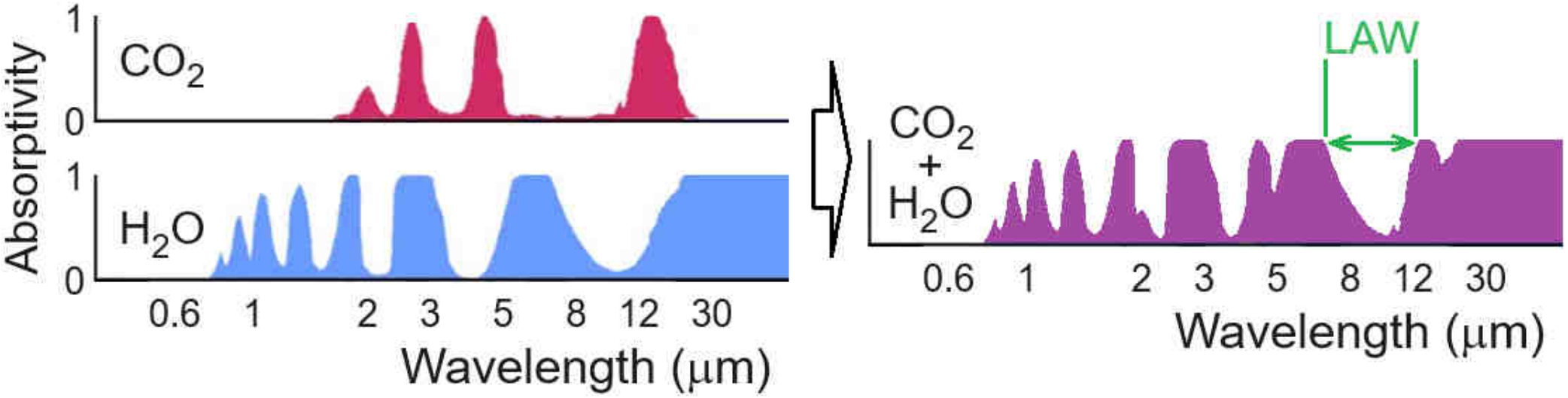
How GHGs retain IR?

- Absorption of light induces molecular vibrations.
- Quantum transition during IR absorption = values of molecular vibrations
  - Each molecular vibration has its specific wavelength value
  - But 1 molecular vibration induces high number of various rotation levels ⇒ extension of absorption belt width ⇒ continuous spectrum



What is the **L**arge **A**tmospheric **W**indow?

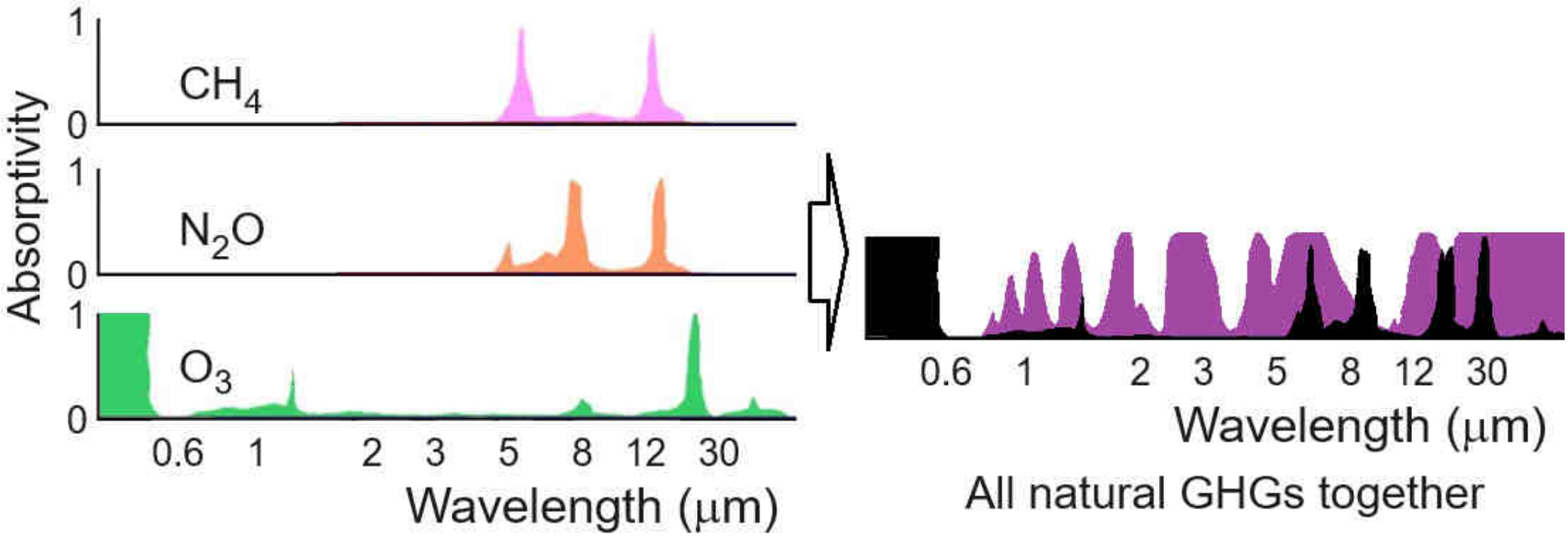
- CO_2 and H_2O – the most concentrated GHGs in the atmosphere
  - e.g. CO_2 concentration more than 200 times higher than CH_4
- Cooling of the atmosphere strongly limited by the CO_2 + H_2O absorption bands.
- Where neither CO_2 nor H_2O absorbs, the Earth well radiates IR into space.



Could the **LAW** be closed?

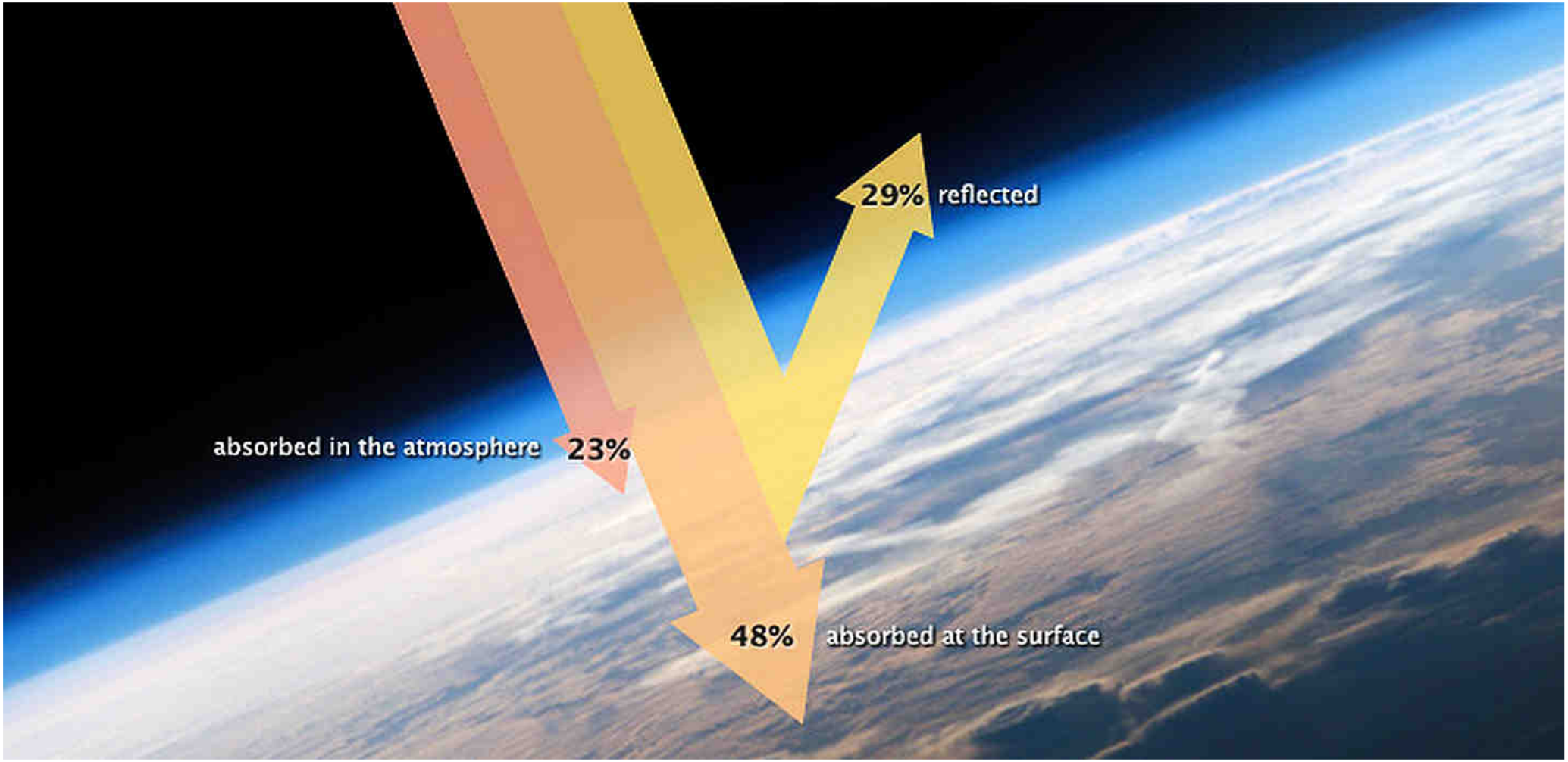
- YES: among natural GHGs, e.g. N_2O shows maximum within the LAW.
- Especially solely anthropogenic CFC_s, HFC_s, PFC_s absorb inside the LAW.

A compound absorbing within the LAW is more dangerous than CO_2 and H_2O.



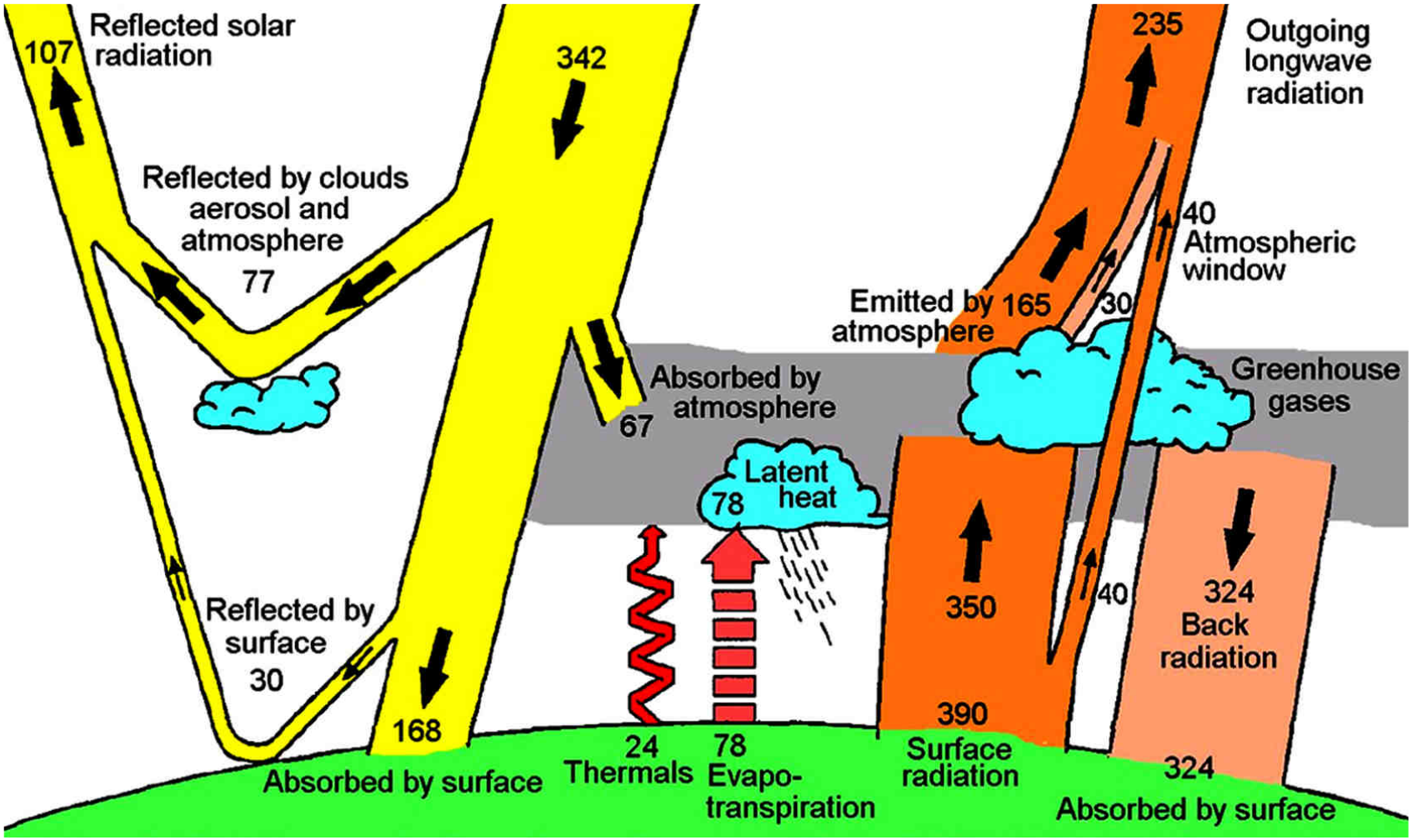
Energy balance of the atmosphere

- Balance of incoming solar radiation (UV + VIS)
  - Total incoming energy flux ≅ 340 W m^{-2} (defined in tropopause)
  - 29% reflected (98.6 W m^{-2}), 23% (78.2 W m^{-2}) absorbed in the atmosphere



Energy balance of the atmosphere

- The overall energy balance of the Earth
  - The atmospheric window shown at 38% proportion of clear sky
  - 30 W m^{-2} = radiative energy of clouds in longwave area



What the Climatologic theory says

- There is the equilibrium between UV and visible radiation absorbed by the planet and reflection of IR radiation back to the space.
- Due to absorption of IR radiation, GHG gases change this ratio ⇒ accumulation of energy.
  - Since the beginning of the industrial era: Of all the investigated factors, only the concentration of GHGs changed along with the rise in temperature.

How we can express the GHG impact

- Several possible parameters, which the most widespread are:
  - Radiative Forcing Capacity (RFC)
  - Global Warming Potential (GWP)
- RFC = the amount of energy per unit area per unit time, absorbed by greenhouse gases, which would otherwise be radiated into space
  - Do not confuse with „Radiative Forcing“ = difference between the solar energy absorbed by the Earth and the energy radiated back to outer space.
- GWP is a relative measure of how much heat is retained in the atmosphere by a gas;
  - GWP compares the amount of heat, retained by the certain amount of the particular gas, relative to the same amount of the reference gas - CO_2
  - GWP is a dimensionless factor
  - GWP is related to CO_2, thus GWP(CO_2) = 1

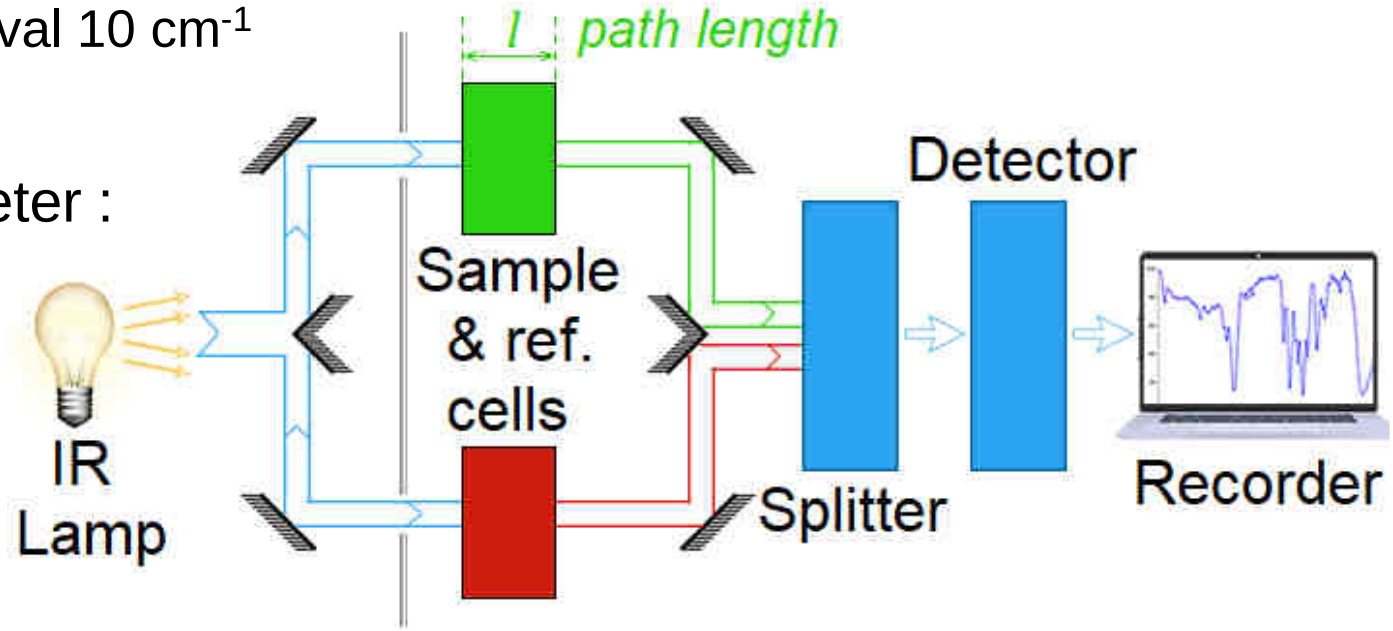
Radiative Forcing Capacity (RFC)

- RFC expressed by the formula (Beer's law) :

$$RF = \sum_{n=1}^{100} \frac{Abs_i \cdot F_i}{l \cdot n}$$

  - Abs_i = integrated infrared absorbance in i^{th} interval
  - F_i = radiative forcing in i^{th} interval
  - l = path length of the IR measuring cell (cm)
  - n = number density of GHG molecules (cm^{-3})
  - Subscript i = interval 10 cm^{-1}

- RFC determined using the IR spectrometer :



Reference(s): 5

Global Warming Potential (GWP)

- GWP values published by the Intergovernmental Panel on Climate Change (IPCC)
- GWP changed several times between 1996 and 2001.
- In 2001, the exact formula published in the third IPCC report:

$$GWP(x) = \frac{\int_0^{TH} a_x \cdot [x(t)]dt}{\int_0^{TH} a_r \cdot [r(t)]dt}$$

  - *TH* = time horizon, for the calculation (20, 100 or 500 years)
  - a_x = radiative efficiency for unit increase of atmospheric abundance of the selected substance (W m^{-2} kg^{-1})
  - *[x(t)]* = time-dependent decay of the substance (decrease of its abundance from its release in the time t = 0 until t = TH)
  - Denominator of the fraction includes the same variables for the reference gas.

Global Warming Potential (GWP)

- GWP depends on the following factors:
  - The rate of absorption of IR radiation by the substance;
  - Position of wavelengths, absorbed by the substance, in the solar spectrum;
  - Lifetime of the substance in the atmosphere.
- GWP calculation meets problems:
  - Radiative efficiencies a_x, a_r not constant within the whole-time horizon
  - For the majority of gases IR absorbance increases linearly with their abundance in the atmosphere
  - Several important GHGs show non-linear dependence, e.g. **CO_2**, CH_4, N_2O
  - Increase of CO_2 concentrations has lower impact on overall IR absorption (saturation of corresponding wavelengths) TOO HIGH CONCENTRATION
  - Calculation for H_2O almost impossible: Unequal H_2O distribution in troposphere (average ca. 0.4 % vol., but up to 1.8 % vol. near the sea level.)

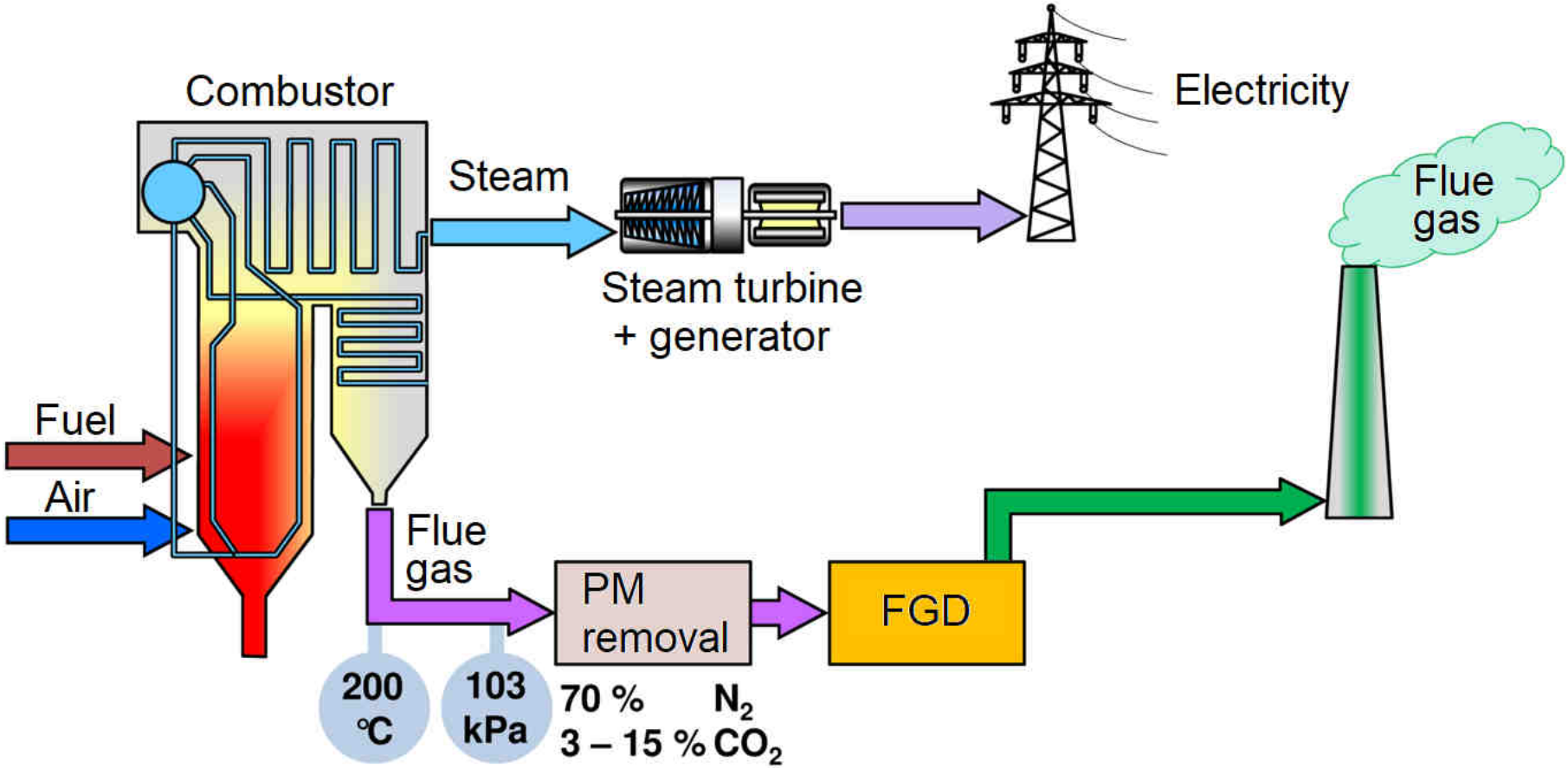
GHG emitted by different economical sectors

- Statistical values given by the National Greenhouse Gas Inventory
- Based on international agreement United Nations Framework Convention on Climate Change (UNFCCC)
- Mandatory IPCC methodology (Guidelines for National Greenhouse Gas Inventories etc.)
- UNFCCC parties collect data from 5 sectors:
  - Energy
  - Industrial processes
  - Agriculture
  - Land-Use, Land-Use Change and Forestry (LULUCF)
  - Waste

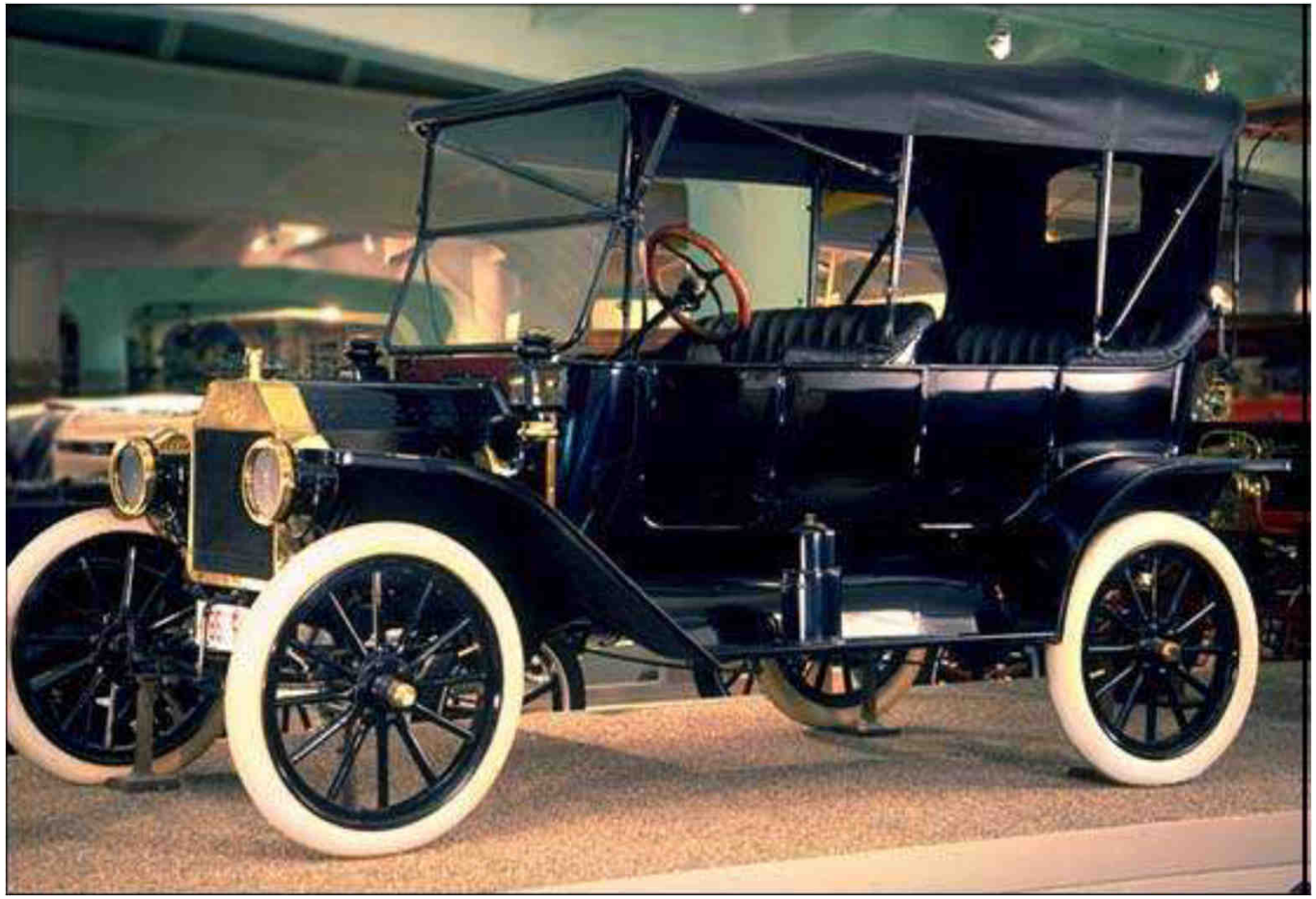
Sector ENERGY

- The most significant category
- In central Europe > 85 % of the overall emissions of GHGs (mostly CO_2)
- Combustion processes (coal, biomass, petroleum, natural gas)
- Processes joined with mining, conversion and manufacturing of fuels and energy (refineries, fugitive emissions of CH_4 from coal mining etc.)
- Emissions from local transport and other mobile sources (NOT international and air transport)
- Part of the fuel consumptions reported in other categories, or not taken into account:
  - non-energetic utilization of fuels for production of lubricants, asphalt etc.
  - coke as reducing agent for Fe production
  - Fuels as raw materials in chemical production, e.g. of NH_3

- Coal/biomass-fired power station
- Huge flue gas flow – e.g. 200 MW unit produces:
  - Lignite: 1.0 – 1.2 10^6 m^3 h^{-1}
  - Heavy fuel oil: 0.5 – 0.6 10^6 m^3 h^{-1}



- Local transport vehicles
- According to the National Greenhouse Gas Inventory within ENERGY sect.
  - In 2016: 2016: 1,32 10^9 (personal cars + truck + buses)

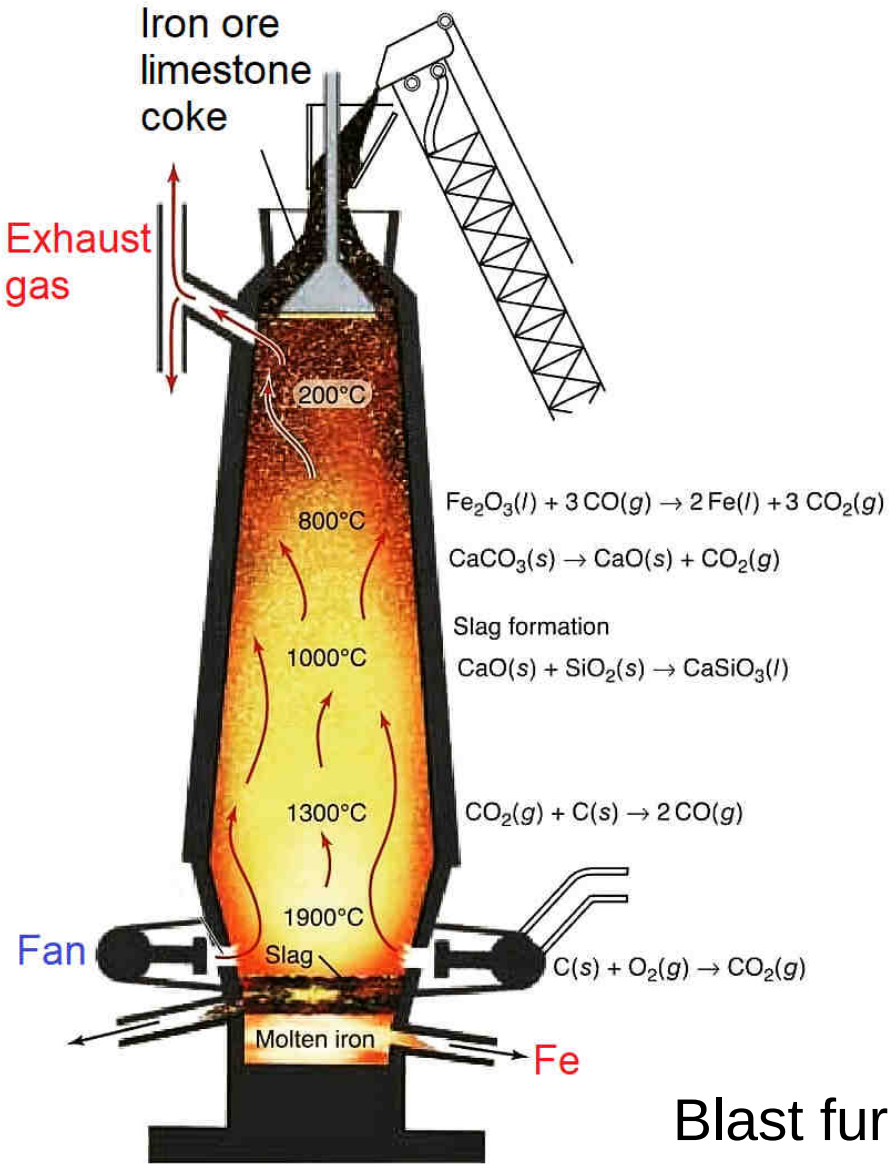


Ford model T (1908)

Sector INDUSTRIAL PROCESSES

- Metallurgical and chemical processes
  - CO_2 from application of coke for reduction of iron ores to Fe
  - N_2O from production of HNO_3
  - CO_2 from production of ammonia (Haber-Bosch process) …… etc.
- Processes of decomposition of carbonate minerals:
  - CO_2 from production of cement and lime
  - CO_2 from manufacture of glass and ceramics
  - CO_2 from limestone flue gas desulfurization (FGD)
- Application of F-gases:
  - HFC and PFC and (particularly in cooling and chilling processes).
  - SF_6 from high voltage circuits (insulating gas)
  - SF_6 from inert protective atmospheres (Al, Mg metallurgy)

- Examples of technologies emitting GHGs:



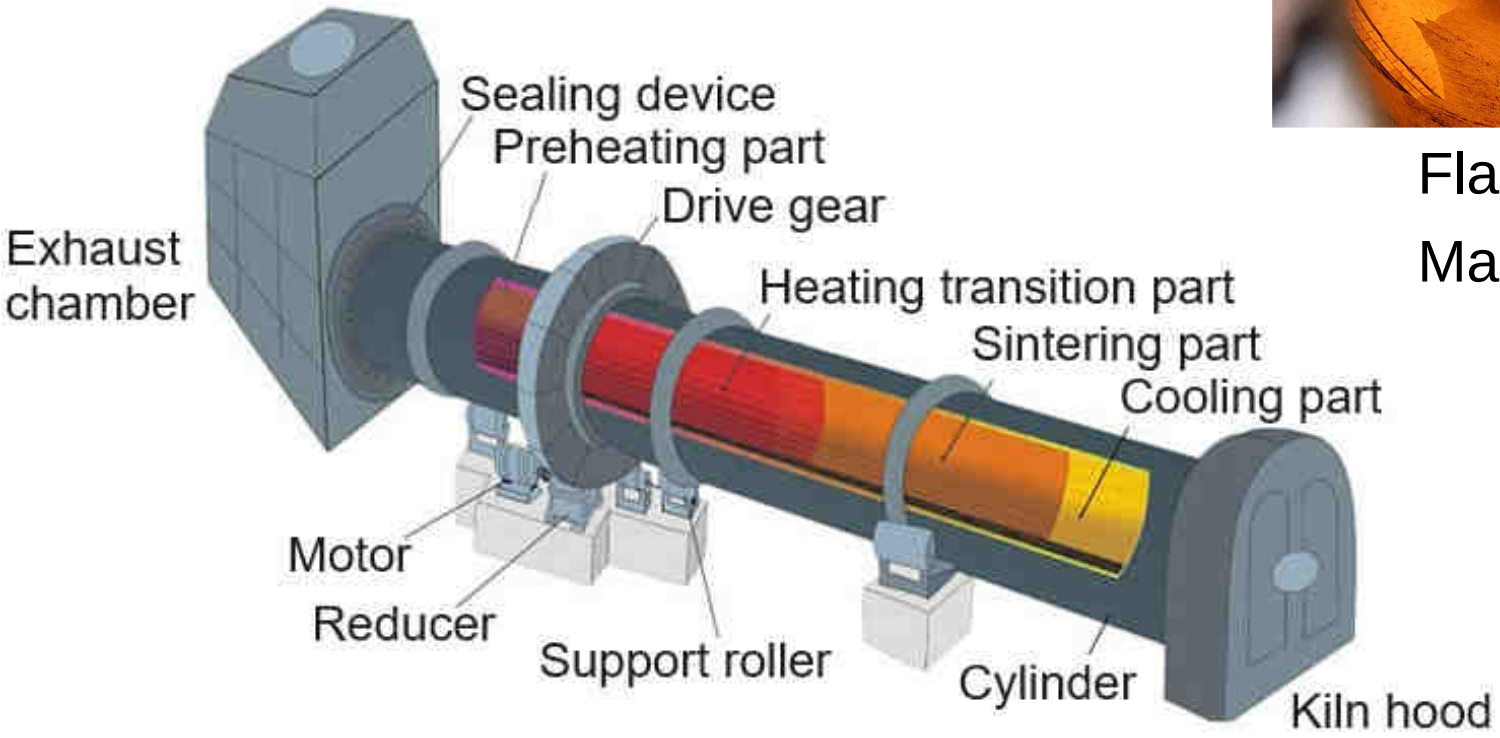
Blast furnaces emitting CO_2

SF_6 used in wind turbines

- Examples of technologies emitting GHGs:

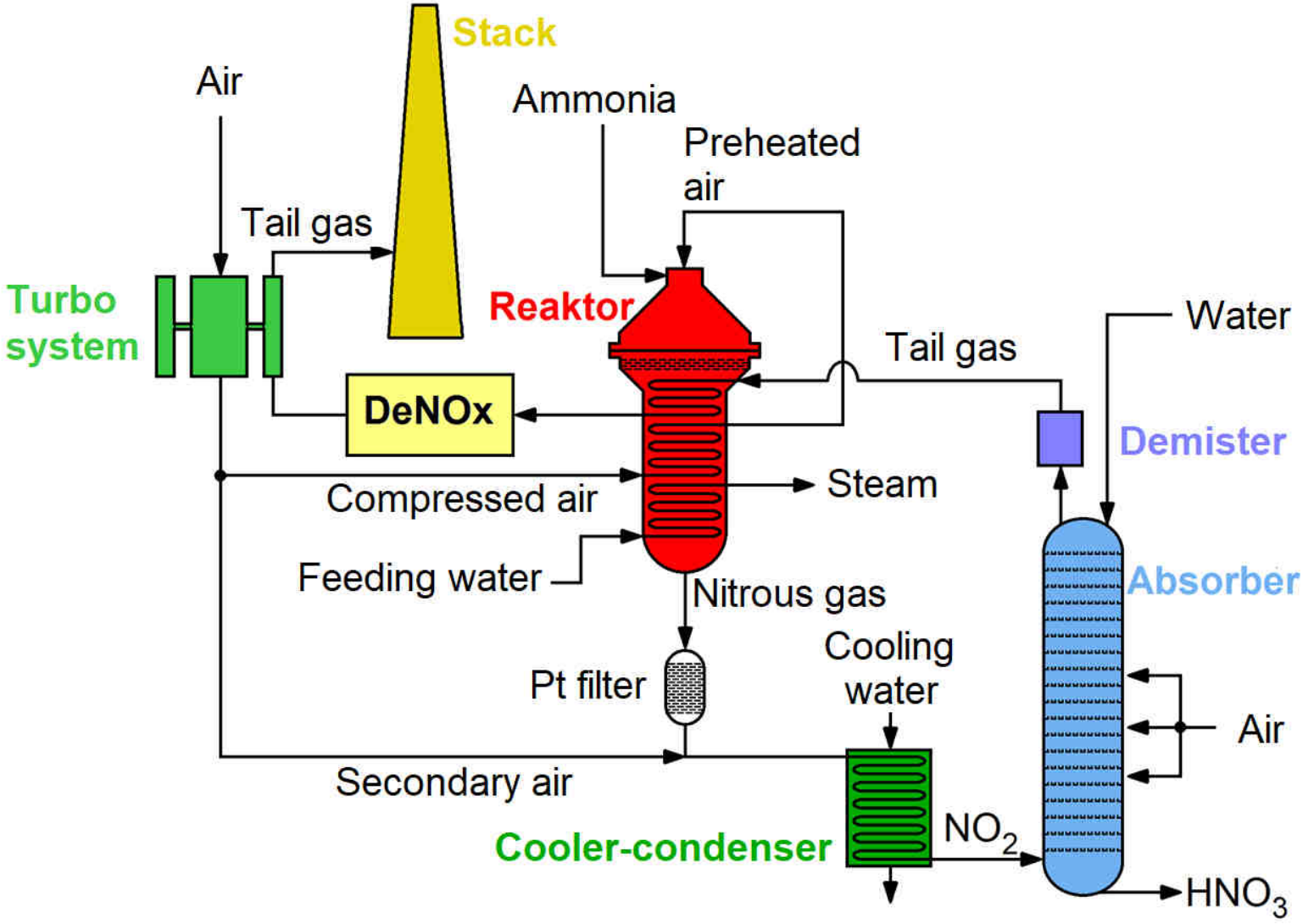
Flame: up to 2,000 ℃

Material: up to 1,450 ℃



Cement rotary kiln (combusting NG , emitting CO_2)

- Examples of technologies emitting GHGs:



Nitric acid production plant (combusting NH_3, emitting N_2O)

Sector AGRICULTURE

- In central Europe mostly emissions of CH_4 and N_2O
- Breeding of animals (anaerobic decomposition of animal manure and CH_4 from enteric fermentation = digestion of vegetal aliment
  - especially breeding of bovine animals
  - CH_4 emissions ca. 65 - 100 mil. t/year
  - less from swine breeding
- Rice cultivation (170 mil. t/year):
  - CH_4 emissions ca. 170 mil. t/year
- N_2O emissions from bacterial denitrification in soil

Reference(s): 11, 12

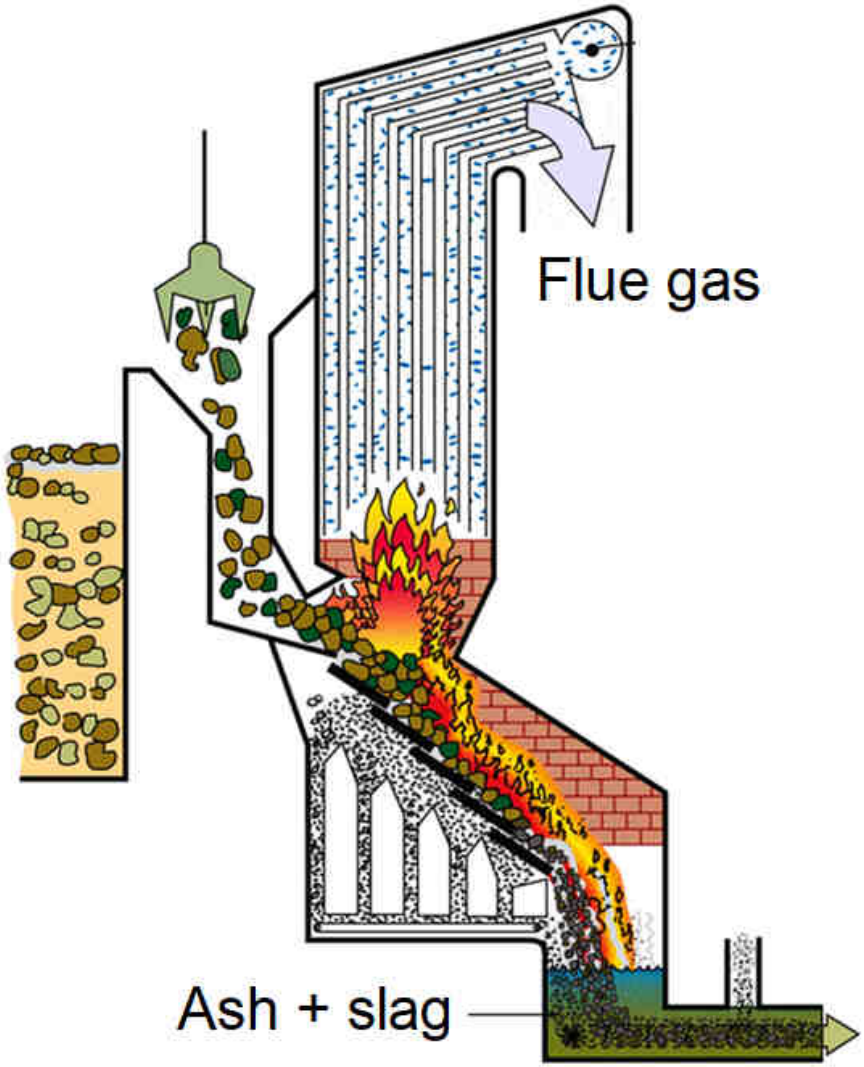
Land-Use, Land-Use Change and Forestry

- Emissions of CO_2
- Inventory based on the analysis of total quantity of wood in forests and its annual changes
- For example in the Czech Republic this sector showed higher CO_2 capture than it emitted
  - negative CO_2 balance till 2018 diminished overall emissions from other sectors
  - at present …… forests damaged due to dry seasons ⇒ **CO_2 emissions**

Sector WASTE

- In central Europe mostly emissions of CH_4, CO_2, N_2O;
- Treatment of municipal and industrial wastewater (CH_4, N_2O):
  - reported emissions of CH_4 reduced by collected and energetically exploited biogas
- Municipal waste dumps (CH_4) – landfills:
  - reported emissions of CH_4 reduced by collected and energetically exploited biogas
  - 2 methods for evaluation of CH_4 emissions:
    - carbon compounds converted to CH_4 within the year of deposition
    - mathematic model of slower, gradual decomposition

- Waste incinerators - emissions of CO_2
  - example: waste-to-energy plant



How to get the GHG emissions data?

- National Inventory Report – complete data for each country
- Administrator: United Nations Framework Convention on Climate Change (UNFCCC)
- Link:
  - https://unfccc.int/ghg-inventories-annex-i-parties/2010 ..... 2021, 2022 etc.
- Complete reports sorted by years and in alphabetic order:

Party	Date of CRF original submission	Latest submitted NIR	Latest submitted CRF [1]	Latest submitted SEF	Status Report
Australia	15 April 2021	NIR 15 Apr 2021	CRF 15 Apr 2021	SEF-CP1-2020 15 Apr 2021 SEF-CP2-2020 15 Apr 2021	SR/AUS 10 Jun 2021
Austria	15 April 2021	NIR 15 Apr 2021	CRF 15 Apr 2021	SEF-CP1-2020 20 May 2021 SEF-CP2-2020 15 Apr 2021	SR/AUT 10 Jun 2021

References (figures)

1. https://ossarchive.adm.ntu.edu.sg/2016-17/cm8001-group-30/index.html_p=103.html
2. http://earthobservatory.nasa.gov/Features/EnergyBalance/page4.php
3. https://climate-woodlands.extension.org/radiative-forcing/
4. Kiehl and Trenberth, 1997
5. https://www.priyamstudycentre.com/2022/12/infrared-spectroscopy-ir-spectrophotometer.html
6. https://g.cz/galerie/dedecek-automobil-slavi/?back=/budvar-fordt/&img=2
7. https://www.metallics.org/pig-iron-bf.html
8. https://newatlas.com/energy/mingyang-myse-18x-28x/
9. https://www.cementplantequipment.com/products/rotary-kiln/
10. https://www.flukeprocessinstruments.com/en-us/service-and-support/knowledge-center/infrared-technology/temperature-monitoring-rotary-kiln-shell
11. https://www.ochranazvirat.cz/2020/04/14/chov-skotu/
12. https://farm-cs.desigusxpro.com/posadka/ogorod/zlaki/ris/gde-i-kak-rastet.html

References (figures)

13. https://www.drevoastavby.cz/vse-o-drevostavbach/jak-na-drevostavbu/na-co-si-dat-pozor/5333-ohrozuje-kurovec-i-drevostavby

14. https://www.nazeleno.cz/energie/energetika/spalovani-odpadu-kolik-vyrobime-tepla-a-elektriny.aspx