

# Lecture 3

## Fossil fuels

PHY 555 – Energy & Environment

Erik Johnson, Mathieu de Naurois, Daniel Suchet



# Advertisement



## Coriolis Seminars

at Ecole polytechnique for the Environment

Energy Research  
& Innovation



Alain  
**CHARDON**

Energy Transition,  
Capgemini Invent



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**WYKA**

Sustainable IT offer,  
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# Sustainable IT / IT for Sustainability

Thursday October 14, 2021

6 pm - Amphi. Becquerel

All details on <https://www.e4c.ip-paris.fr/#/fr/education/conferences/Coriolis>

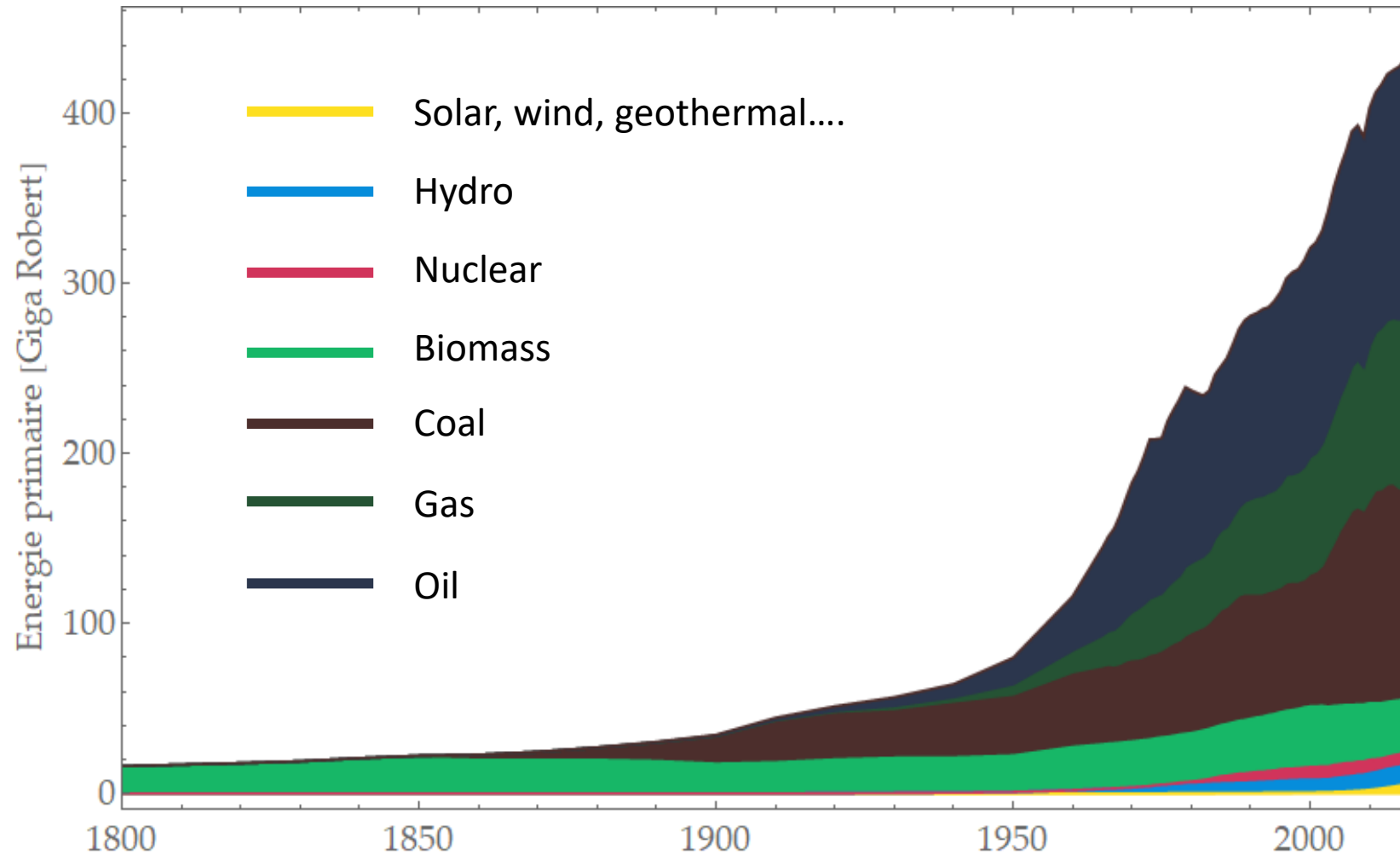


Départements de Mécanique & Physique • [www.e4c.ip-paris.fr/#/fr/education/conferences/Coriolis](https://www.e4c.ip-paris.fr/#/fr/education/conferences/Coriolis)

# Why discuss fossil fuel?



1. Because fossil fuels cover 85% of our primary energy



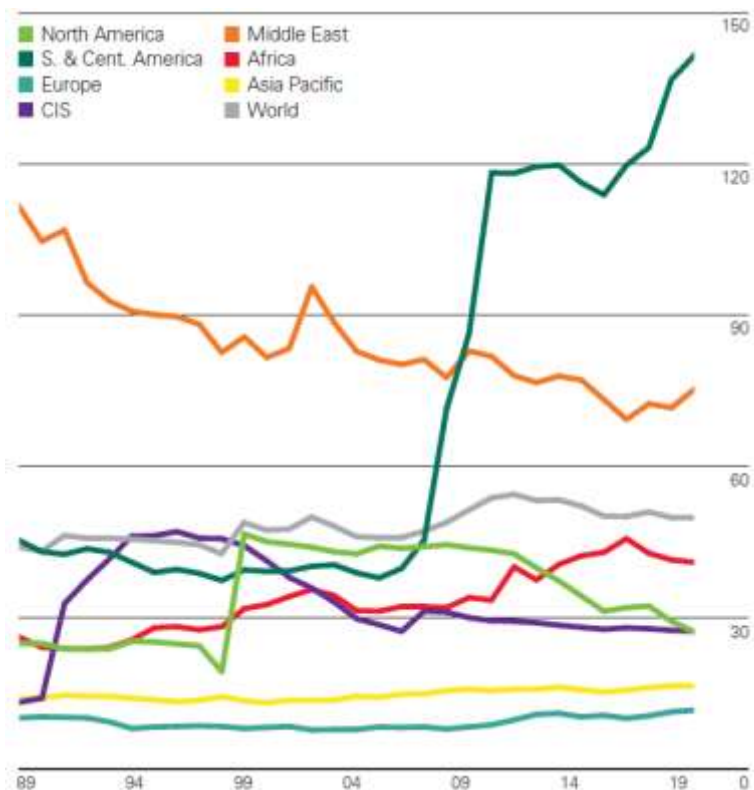


# Why discuss fossil fuel?

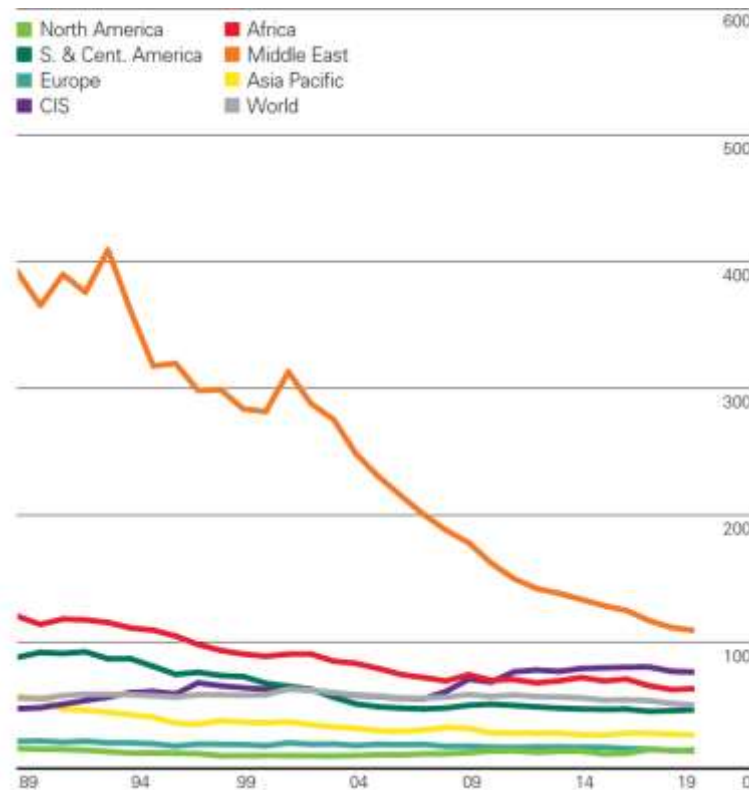
1. Because fossil fuels cover 85% of our primary energy
2. Because fossil reserves are limited

Source: BP Statistical Review of World Energy (2020)

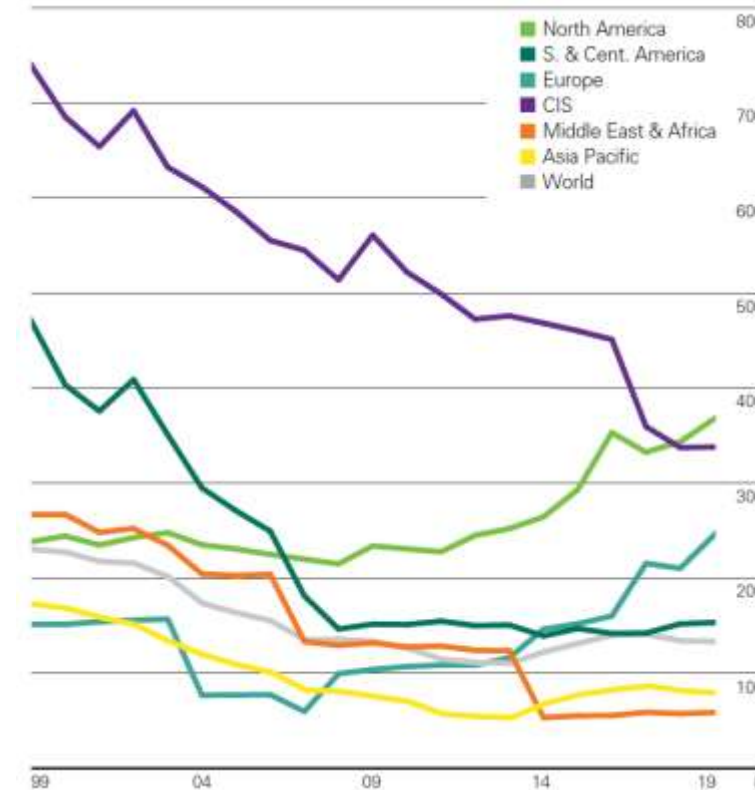
Reserve – to – production ratios



Oil : 50 years



Gas: 50 years

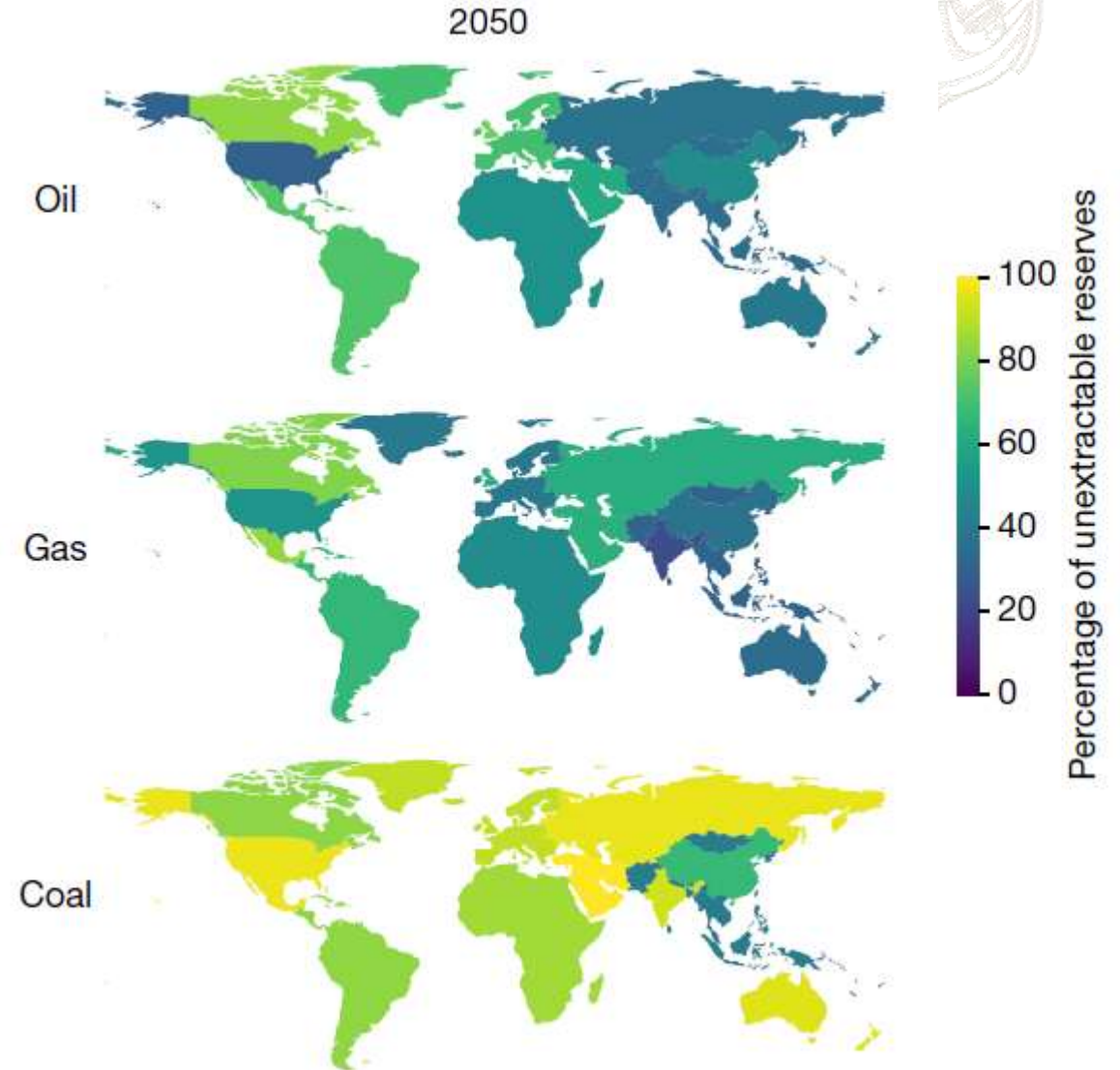


Coal: 130 years

# Why discuss fossil fuel?

1. Because fossil fuels cover 85% of our primary energy
2. Because fossil reserves are limited
3. Because we'd better not reach this limit

*“By 2050, we find that nearly 60 per cent of oil and fossil methane gas, and 90 per cent of coal must remain unextracted to keep within a 1.5 °C carbon budget”*



# Lecture 3 Fossil fuels

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What, Who, What for, Why ?

Thermo toolbox : the chemical potential

Oil, gas and coal formation: in and out the organic carbon cycle

Oil (and gas) production: conventional and unconventional sources

Oil refining: from crude oil to the gas station

Perspectives

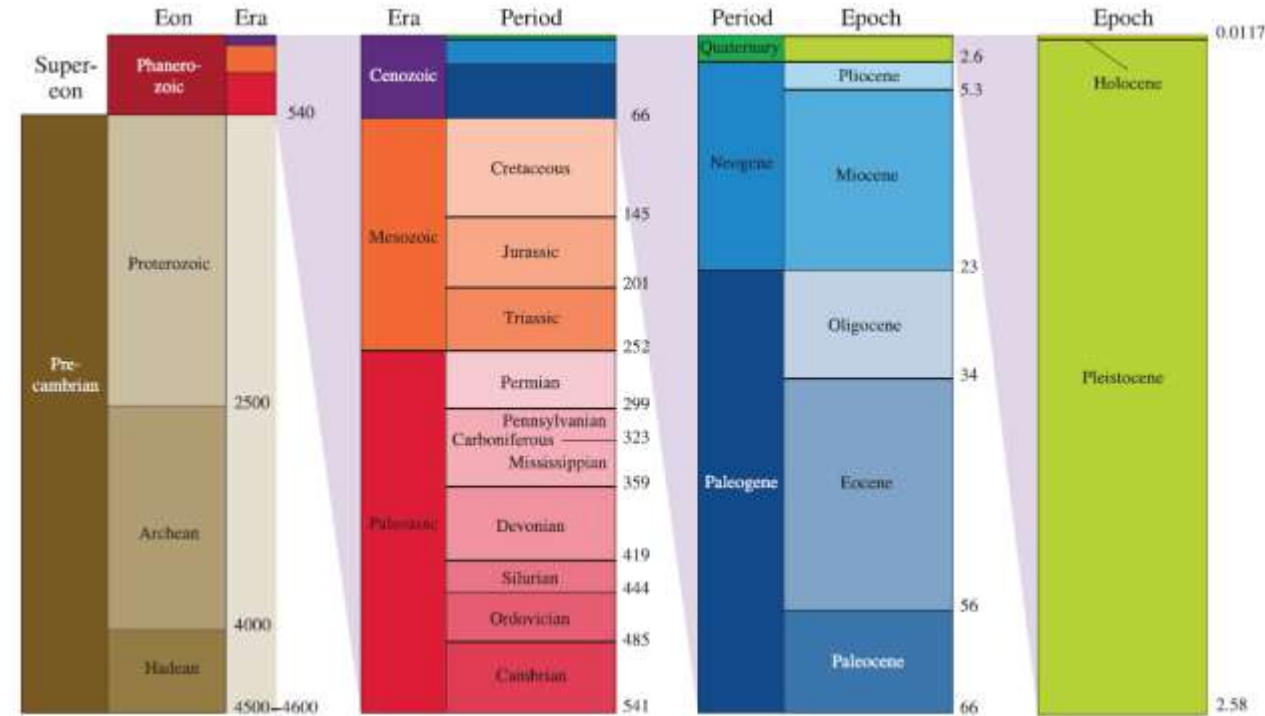
# Dino's juice



**Table 26.2** Average Chemical Composition of Biochemicals as Compared to Petroleum.

	Elemental Composition in Weight Percent				
	C	H	S	N	O
Carbohydrates	44	6			50
Lignin	63	5	0.1	0.3	31.6
Proteins	53	7	1	17	22
Lipids	76	12			12
Petroleum	85	13	1	0.5	0.5

Source: From Hunt, J. M. (1996). *Petroleum Geochemistry and Geology, 2nd edition*. W. H. Freeman and Co., New York, p. 63.



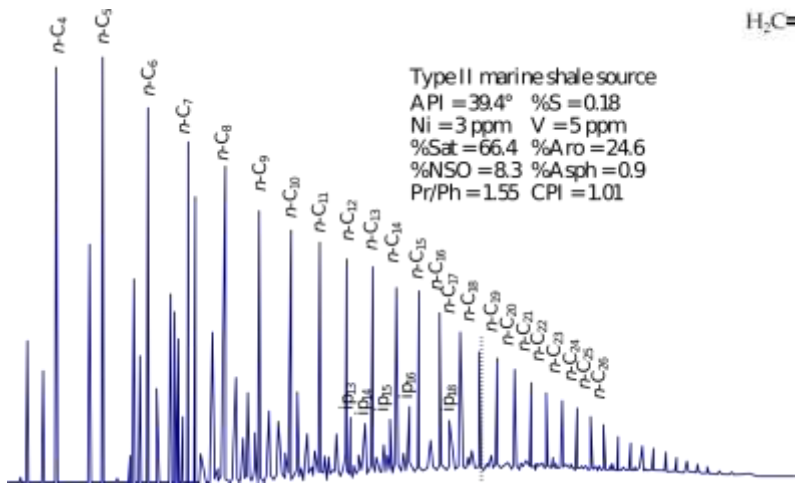
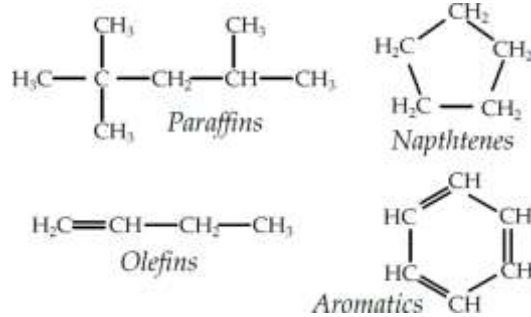
Petroleum ← lipids ← plankton ← sea environment (Mesozoic era, 66 to 252 Myr)

Coal = lower H/C ratio ← lignin ← vascular plants ← terrestrial environment (Carboniferous, 320 Myr)



# What? Petroleum (=crude oil)

A broad mixture of hydrocarbons

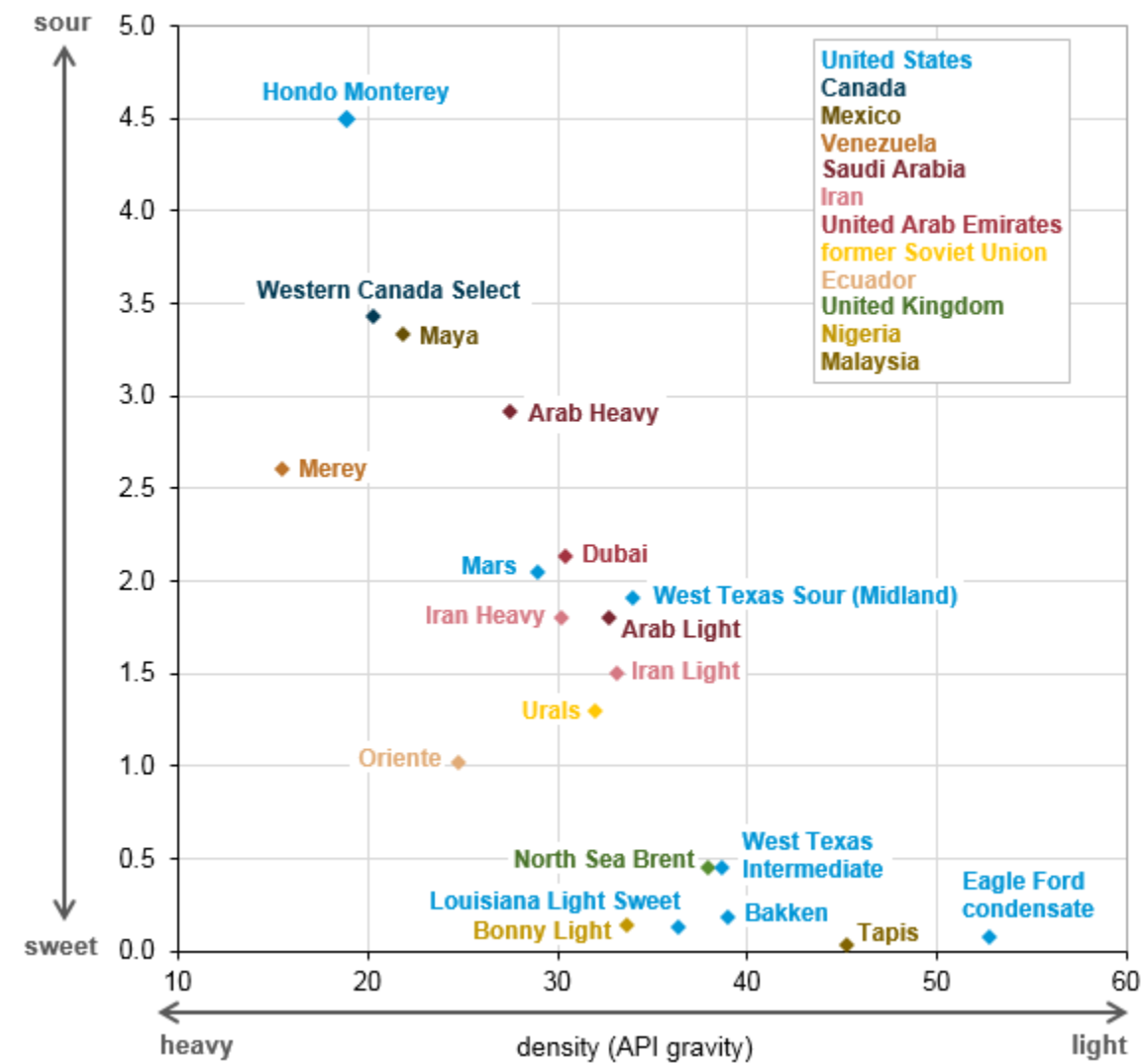


Hsu, Robinson (Eds), Springer Handbook of Petroleum Technology



<https://kimray.com/>

Density and sulfur content of selected crude oils  
sulfur content (percent)



Typical characterizations

Heavy versus light

$$\text{API gravity} = \frac{141.5}{\rho_{\text{oil}} / \rho_{\text{water}}} - 131.5$$

Sour versus sweet

% of sulfur content

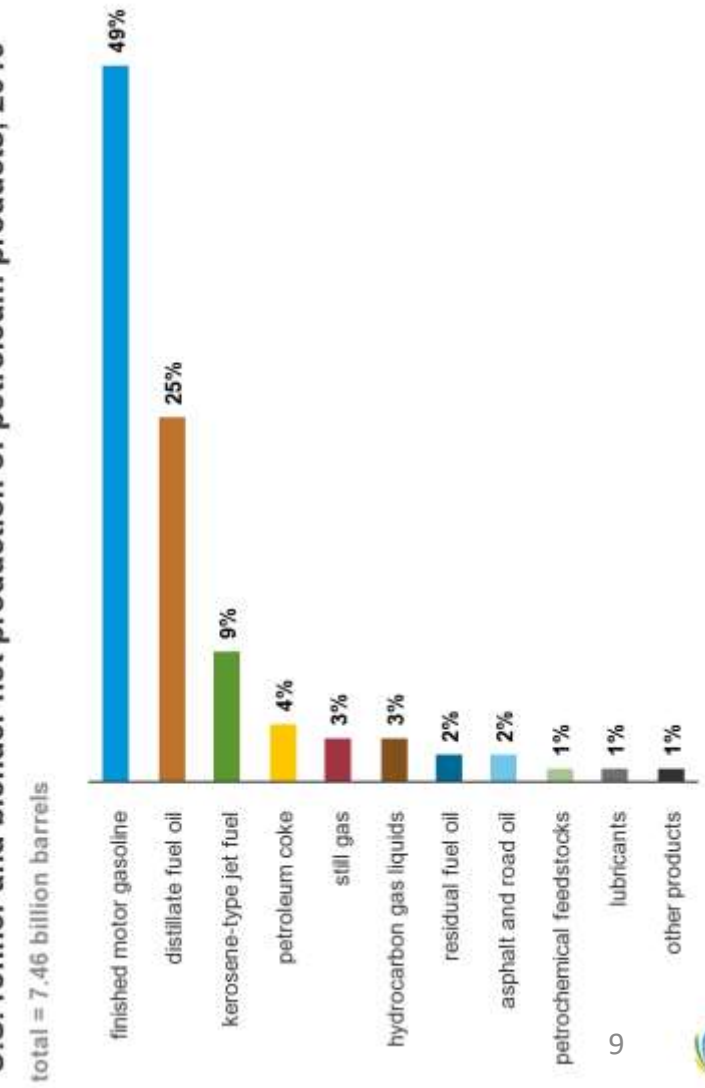




# What? Oil products

	Number of carbons	Boiling point range	Uses	
· Gases	1–4	0–30°C	Bottled and natural gas	Light distillates
· Naphthas	5–10	30–180°C	Gasoline	
· Kerosenes	10–16	180–260°C	Kerosene for home heaters, jet fuel	Middle distillates
· Gas oils	16–60	260–350°C	Diesel fuel, feedstock for cracking	
· Lubricants	>60	350–575°C	Motor oil, feedstock for cracking	Heavy distillates
· Fuel oil	>70	>490°C	Candles, fuel oil for ships and power stations	
· Asphalt	>80	>580°C	Roofing tar, road tar	Residuum

U.S. refiner and blender net production of petroleum products, 2019



Source: U.S. Energy Information Administration, Petroleum Supply Annual, August 2020

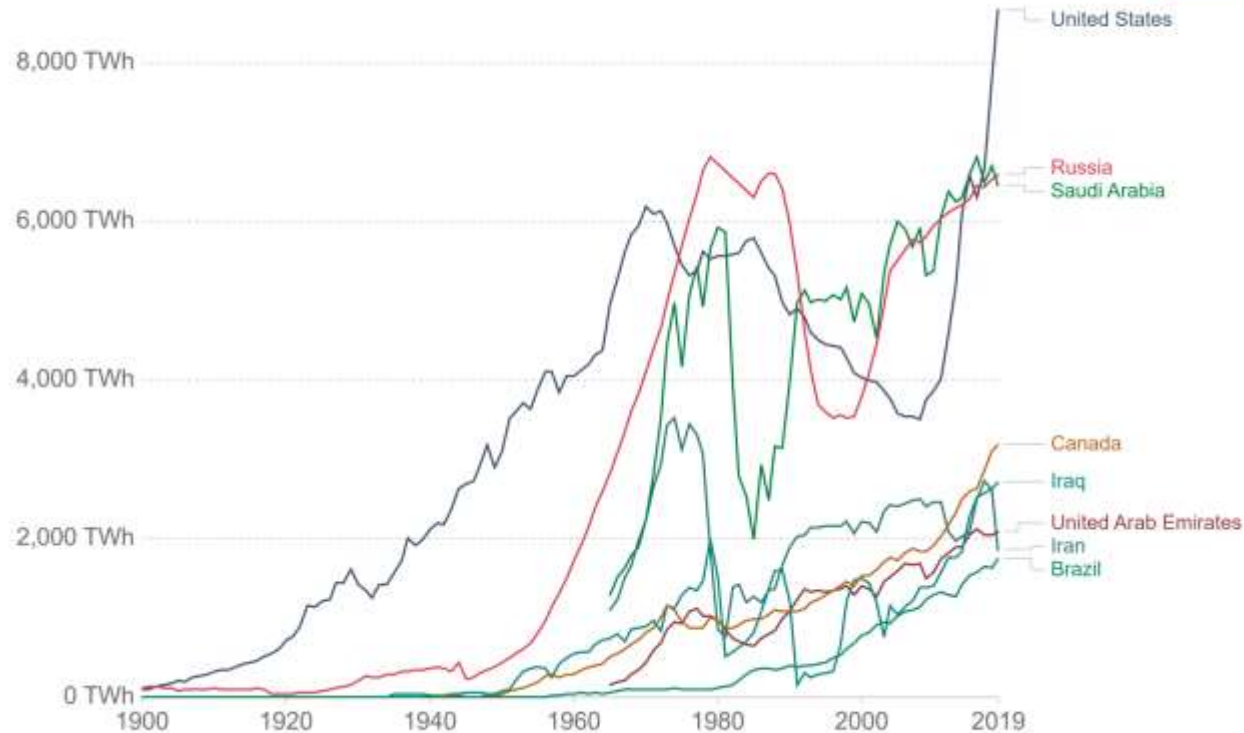


# Who? Oil



## Oil production

Our World  
in Data



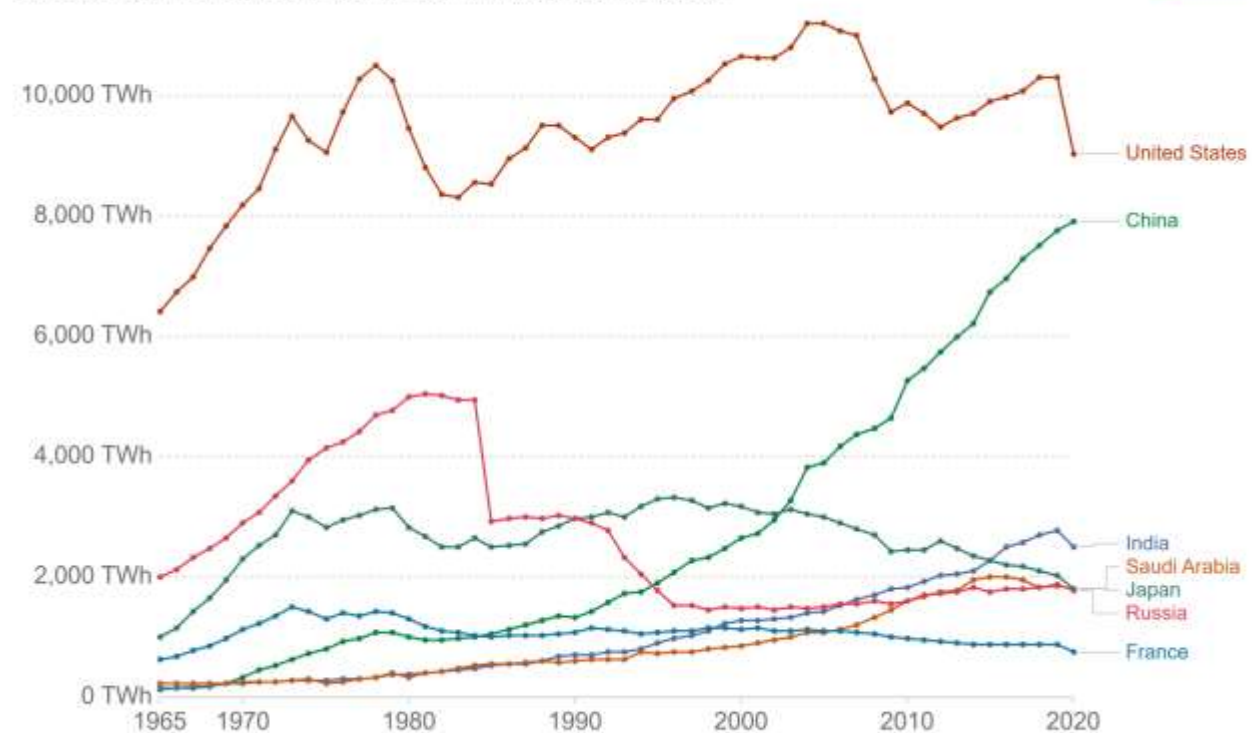
Source: BP Statistical Review of World Energy; the Shift Project

OurWorldInData.org/fossil-fuels/ • CC BY

## Oil consumption

Our World  
in Data

Oil consumption is measured in terawatt-hour (TWh) equivalents per year.



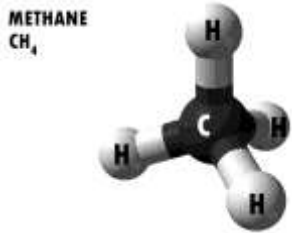
Source: Statistical Review of World Energy - BP (2021)

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# What? Gas

Light hydrocarbon (#C < 5) are gaseous at ambient (T,p)

- Natural Gas  $\approx$  95% Methane =  $\text{CH}_4$

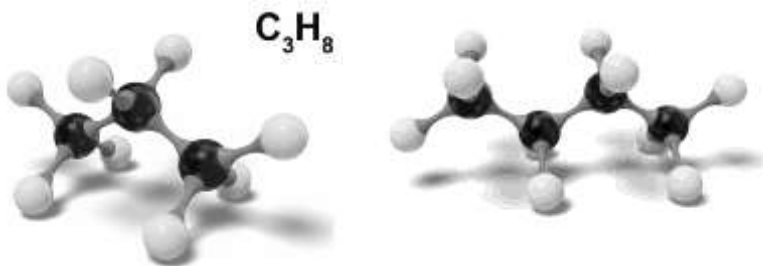


Extracted together with oil, or dedicated production

Liquified Natural Gas (LNG) : ambient p,  $-160^\circ\text{C}$

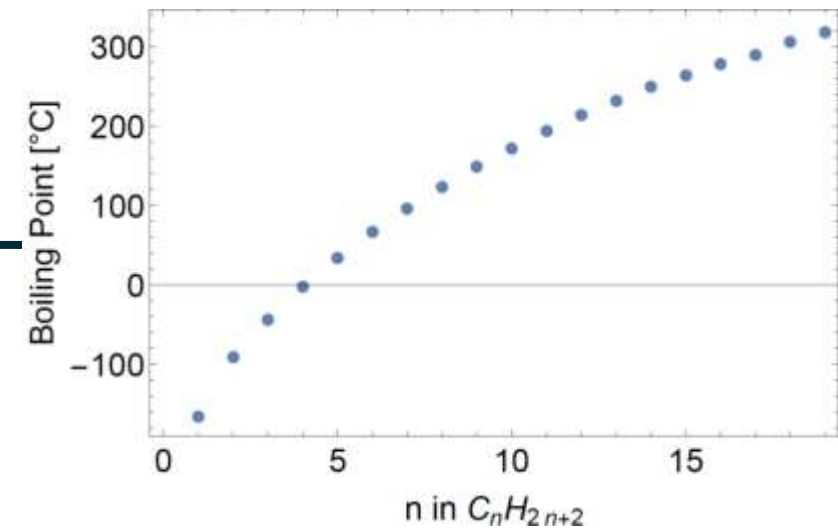
Compressed Natural Gas (CNG) : 200-250 bar, ambient T

- Liquified Petroleum Gas (LPG) = propane & butane mix



Much easier to handle: 17,5 bar ambient T

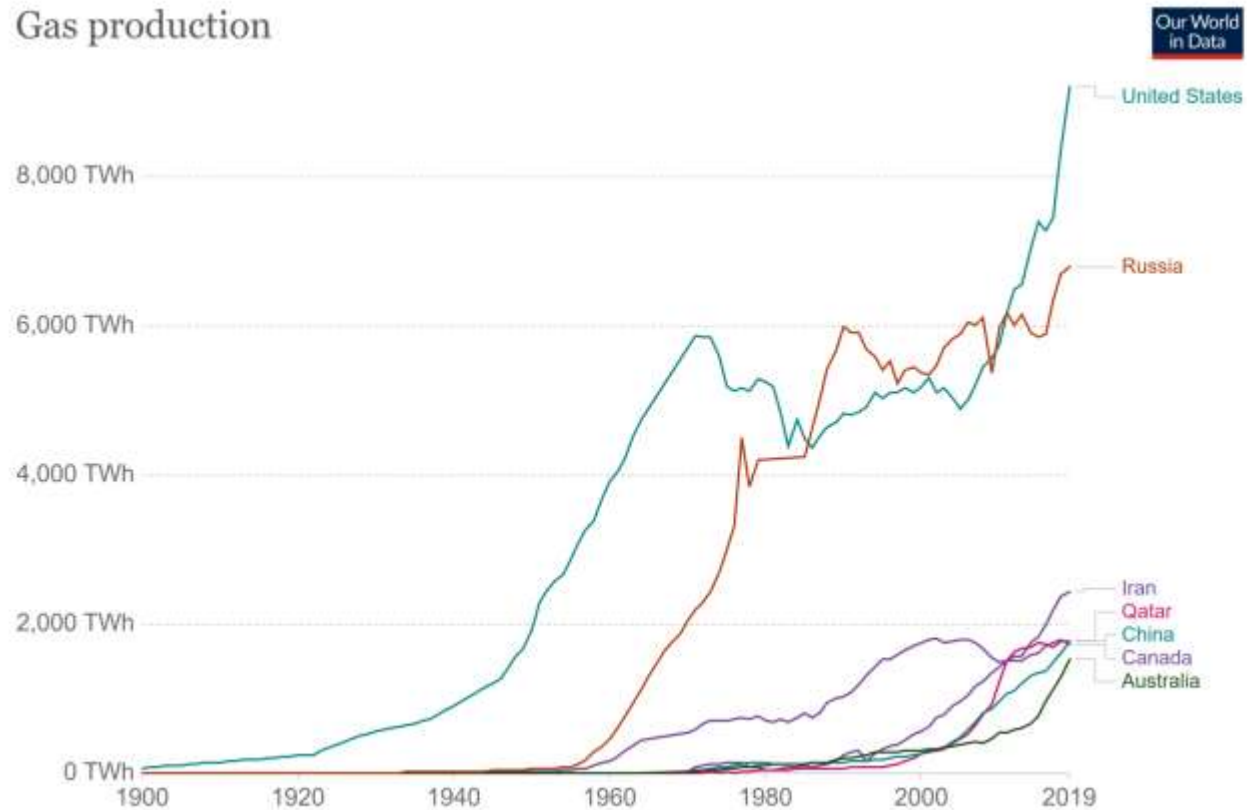
Smaller energy densities



# Who? Gas



## Gas production



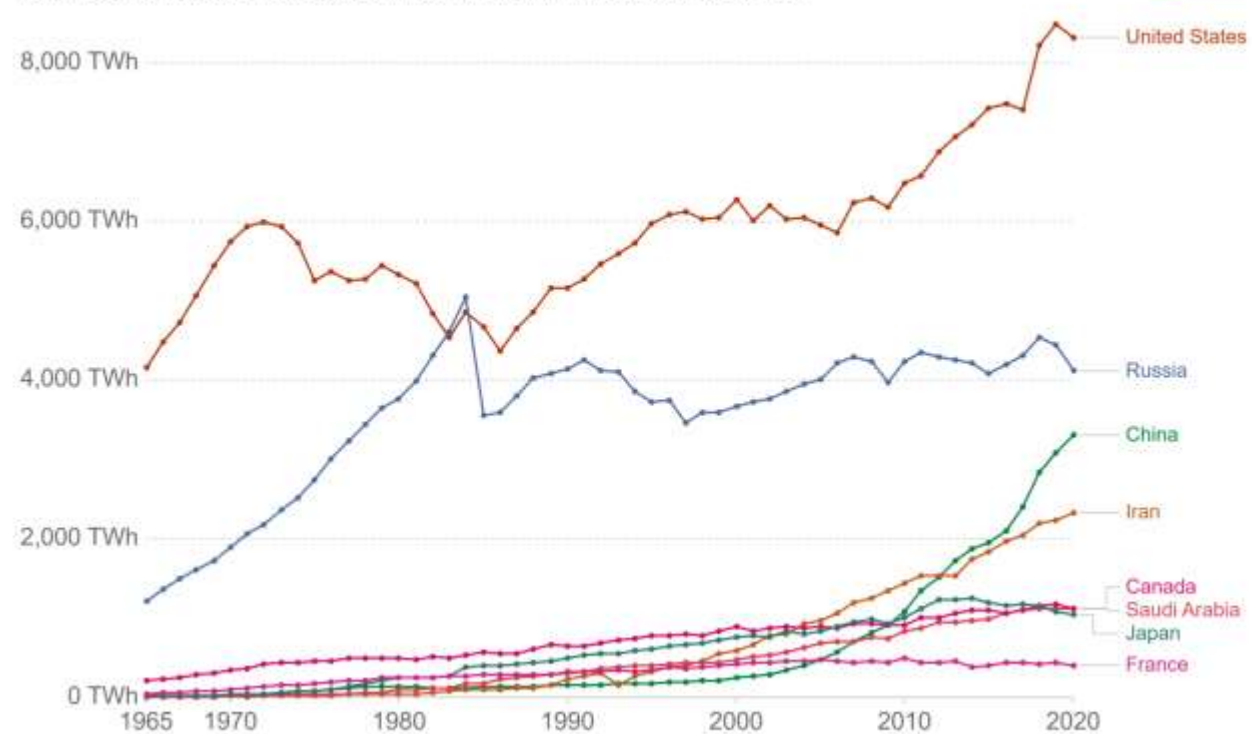
Our World in Data

Source: BP Statistical Review of World Energy; the SHIFT Project

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## Gas consumption

Natural gas consumption is measured in terawatt-hour (TWh) equivalents per year.



Our World in Data

Source: BP Statistical Review of Global Energy

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# What? Coal

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Peat [=tourbe]

Carbon content 50%, energy density 10-20 MJ/kg



Lignite

Carbon content 60-80%, energy density 20 MJ/kg



Bituminous coal [=houille]

Carbon content 80-90%, energy density 30 MJ/kg



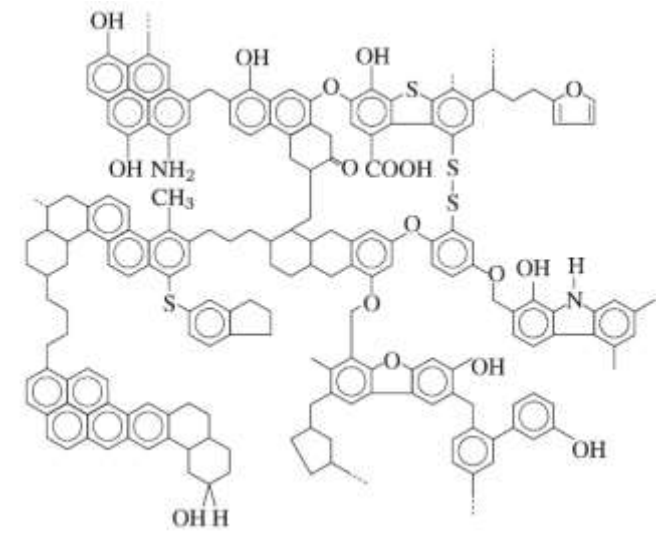
Coking coal

Used to produce coke by pyrolysis → industrial applications



Anthracite

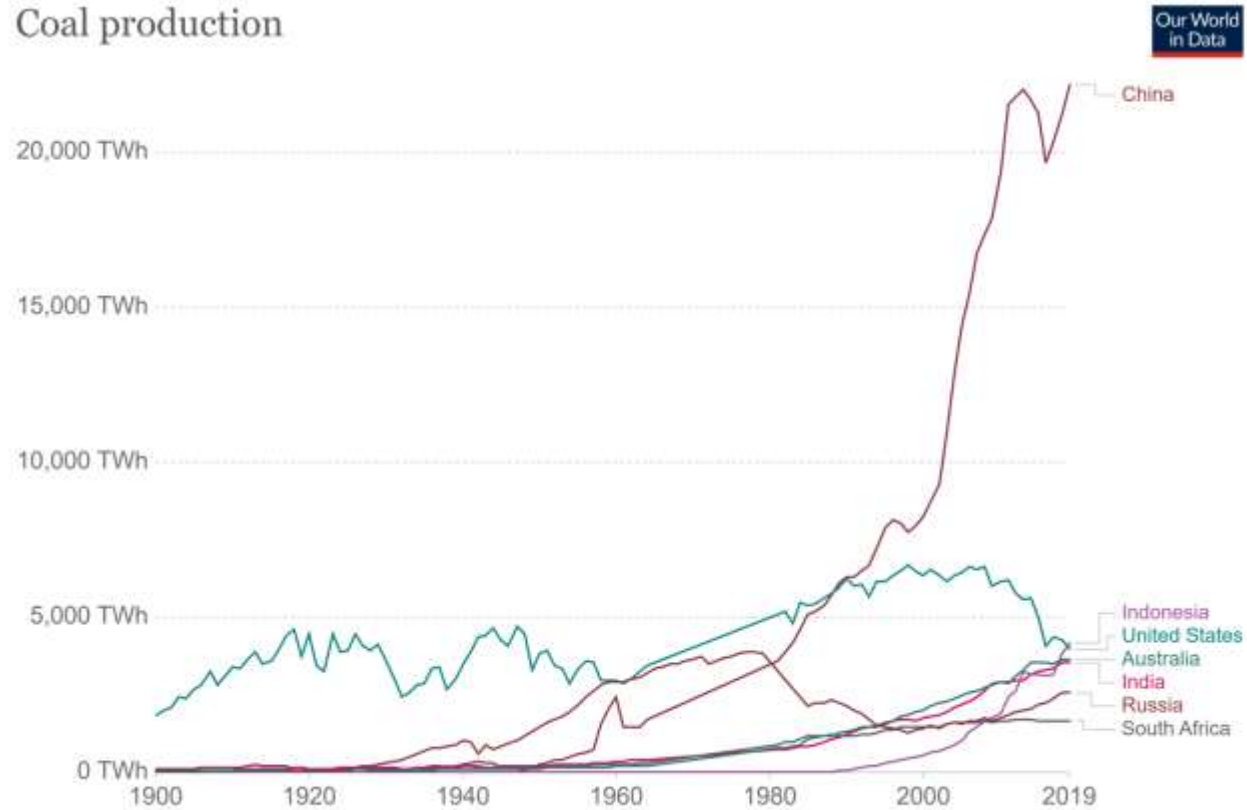
Carbon content 98%, energy density 36 MJ/kg



# Who? Coal



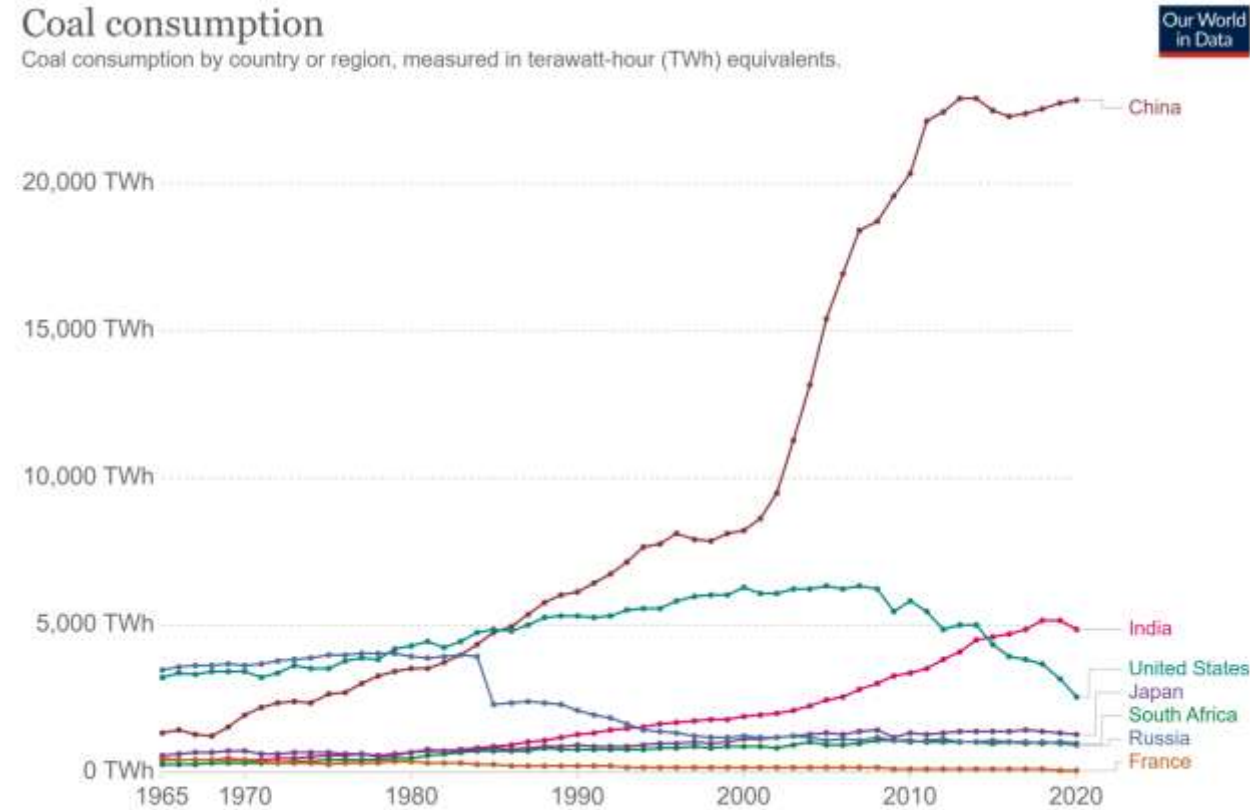
## Coal production



Source: BP Statistical Review of World Energy; and Shift Data Portal

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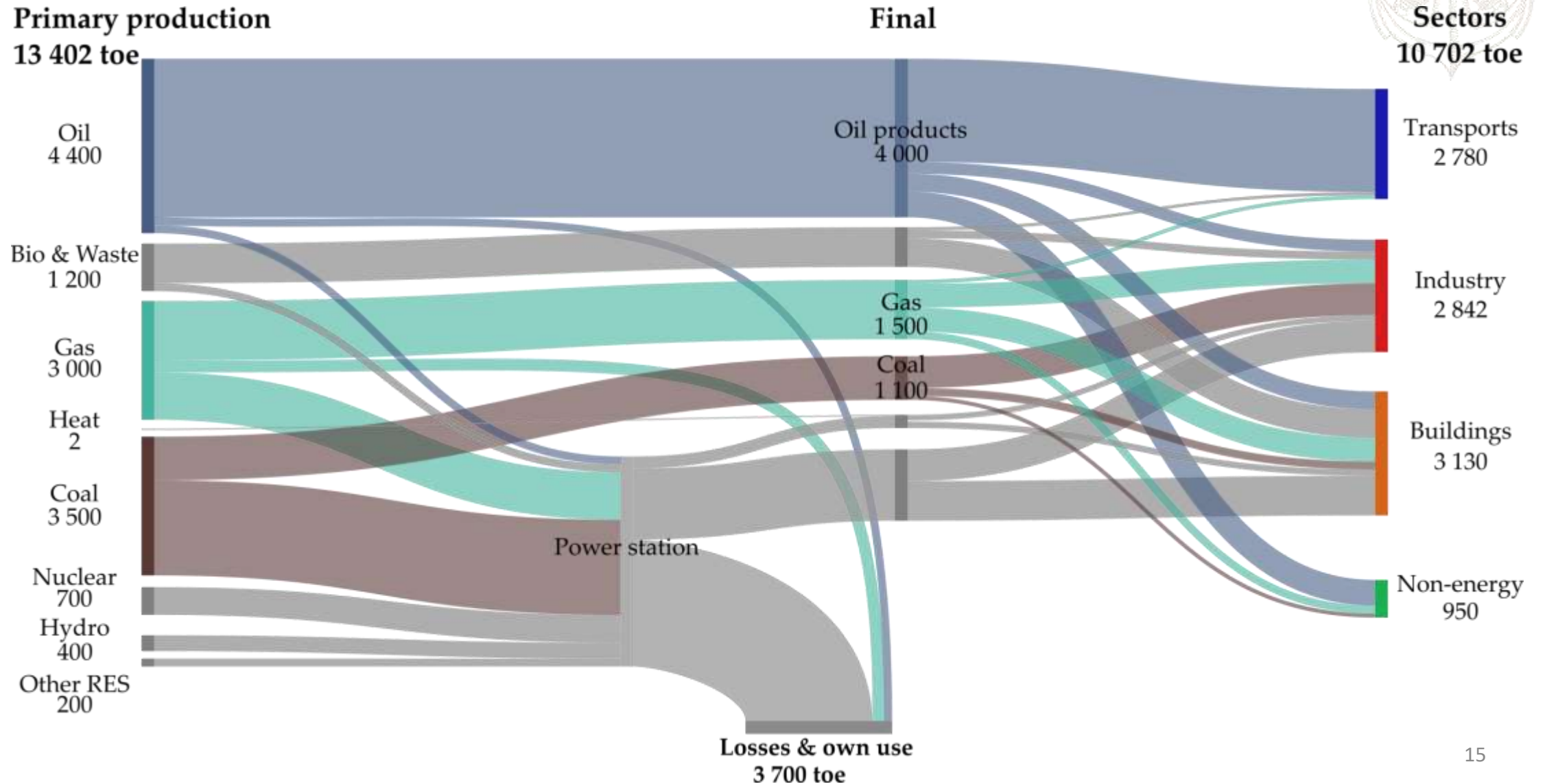
## Coal consumption



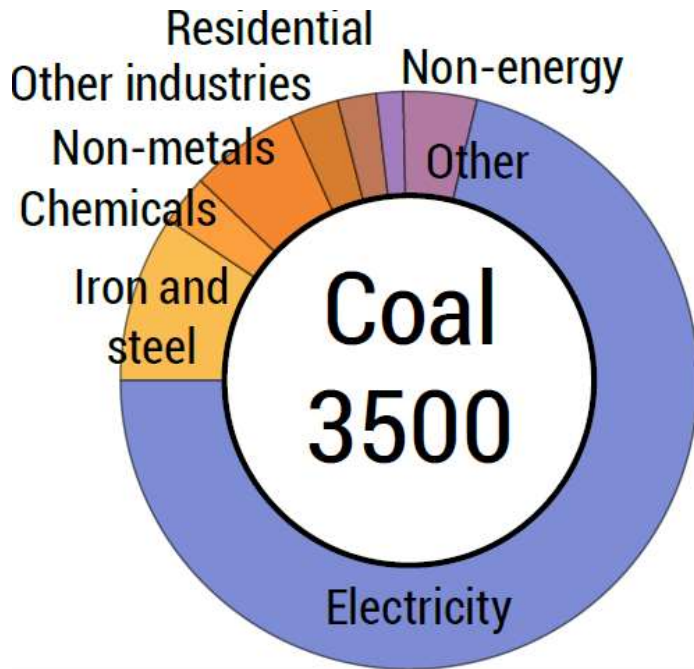
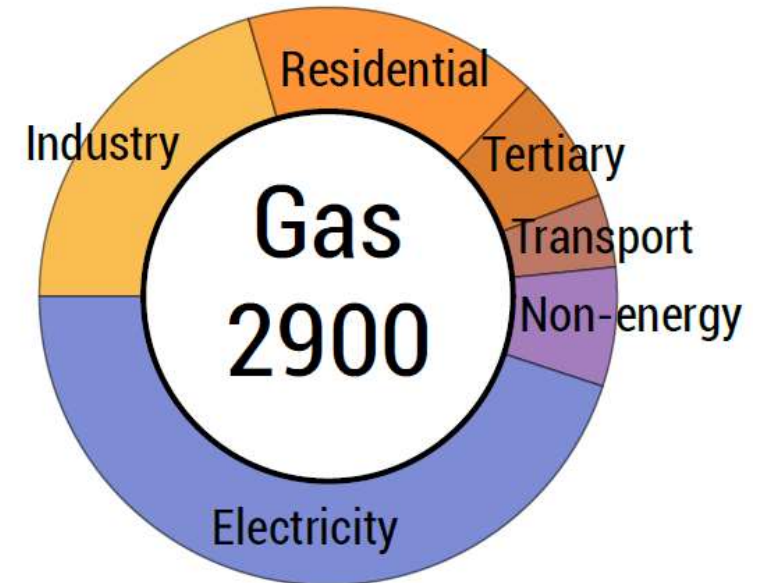
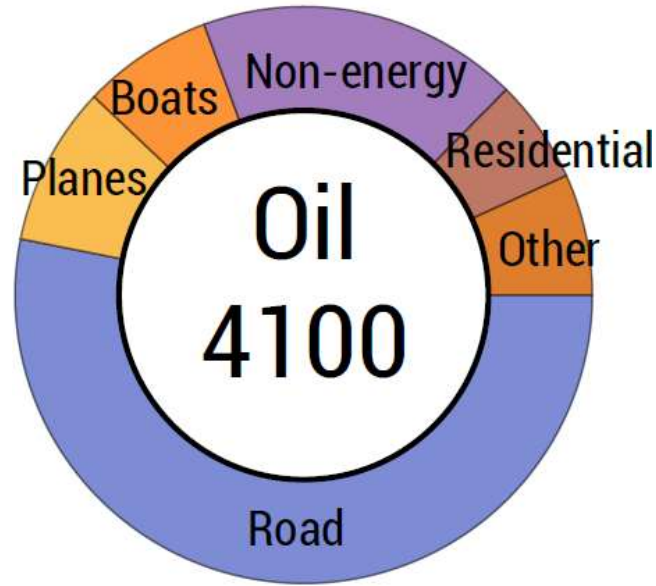
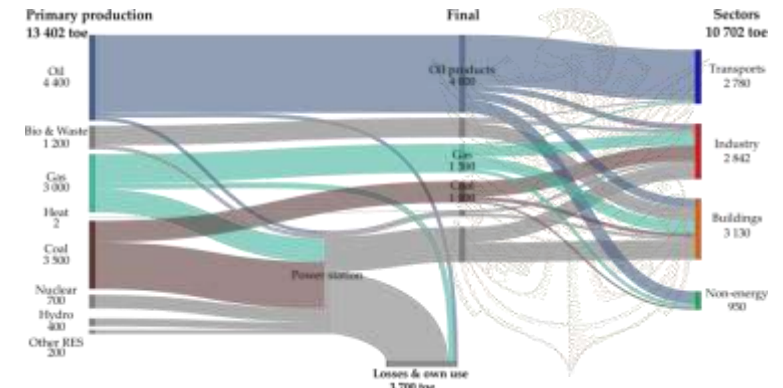
Source: Statistical Review of World Energy - BP (2021)

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# What for?



# What for?

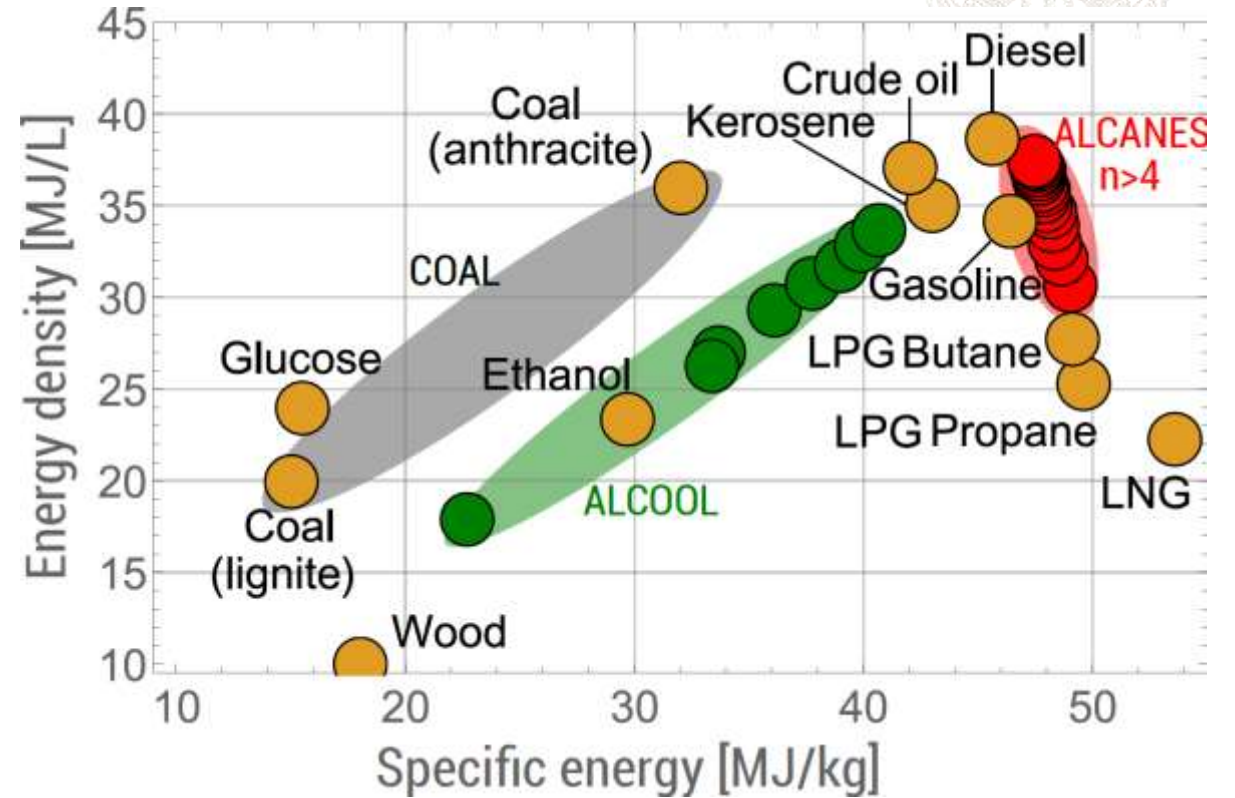
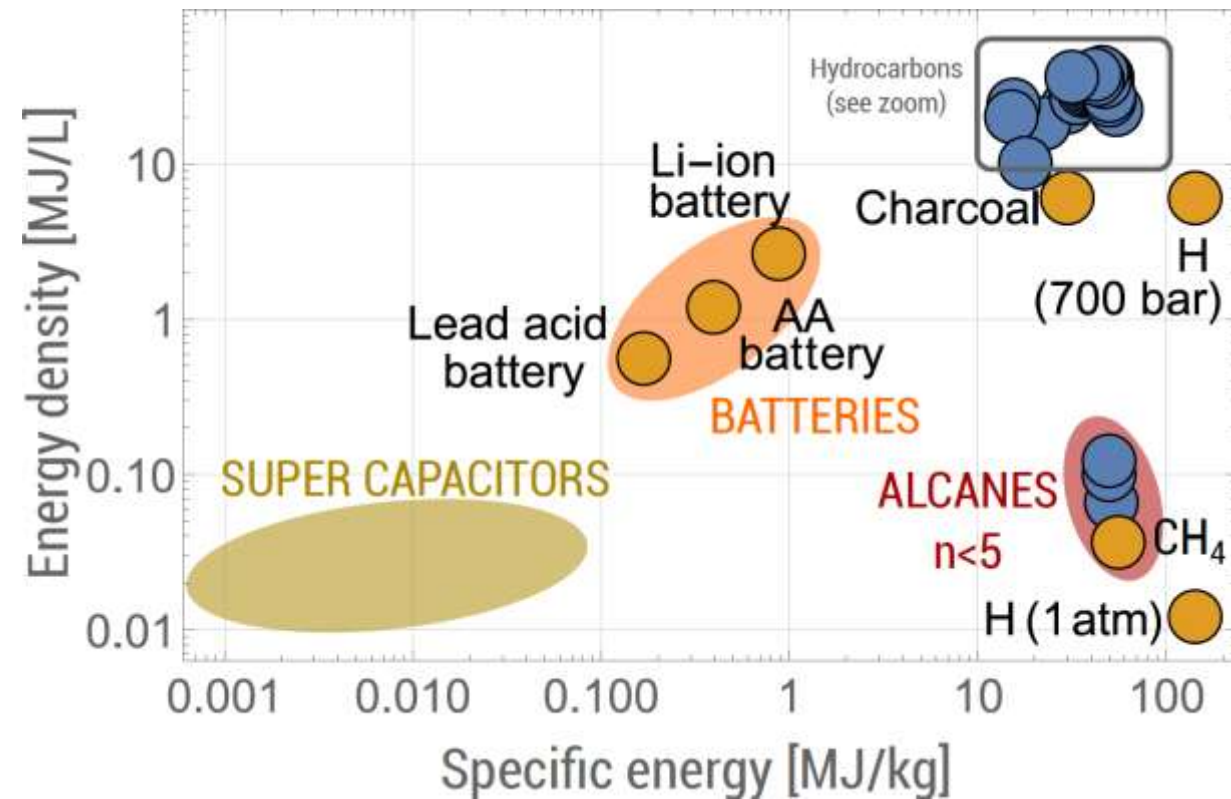




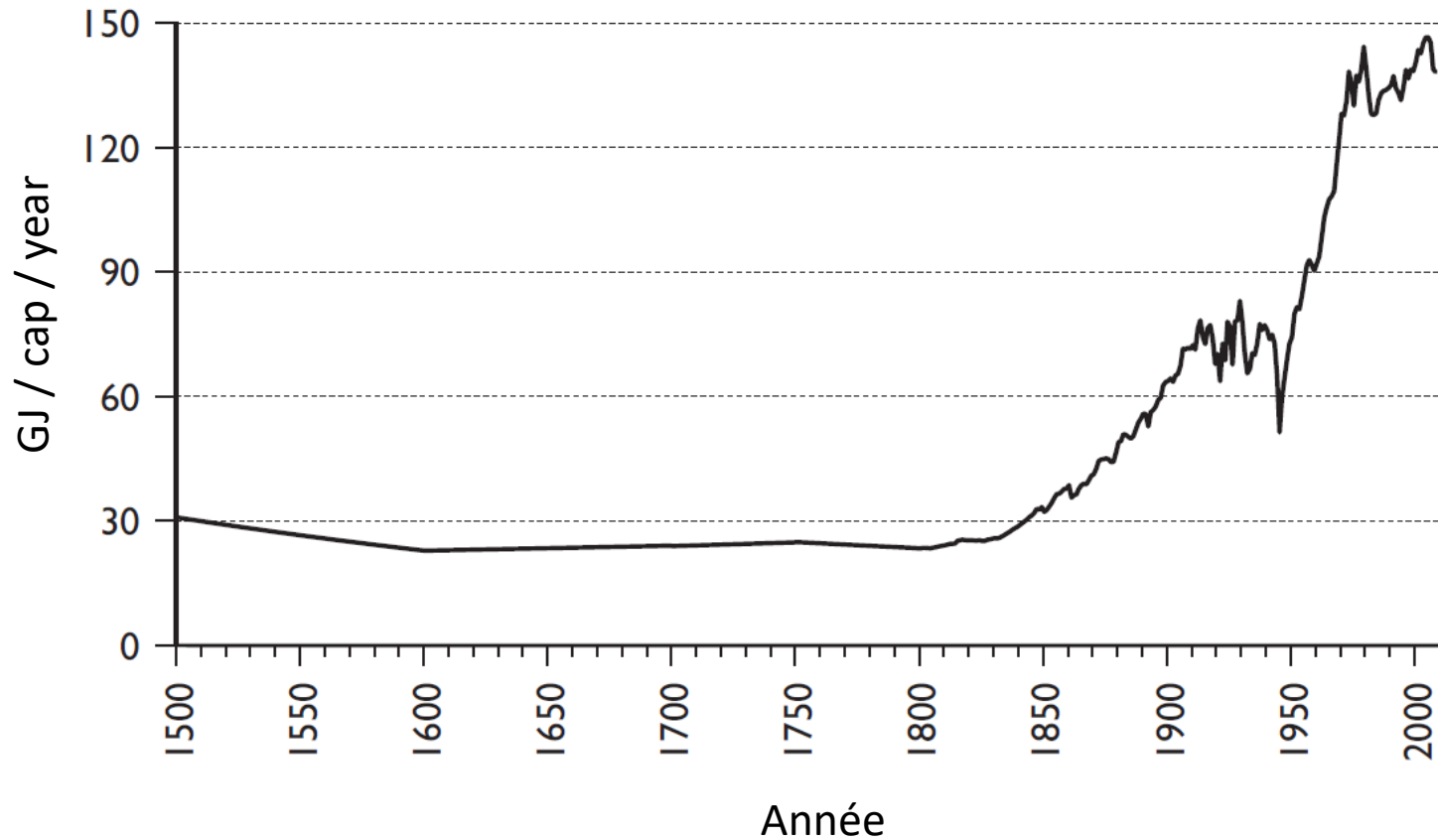
# Why? Energy density



Fossil fuels  
= solar energy accumulated over millions of year released in a second



# Why? Energy availability



For 1€,  
30 000 J



For 1€,  
30 000 000 J

Source Astrid Kander et al, *Power to the People* (2013)

# Lecture 2 Fossil fuels

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What, Who, What for, Why ?

**Thermo toolbox : the chemical potential**

Oil, gas and coal formation: in and out the organic carbon cycle

Oil (and gas) production: conventional and unconventional sources

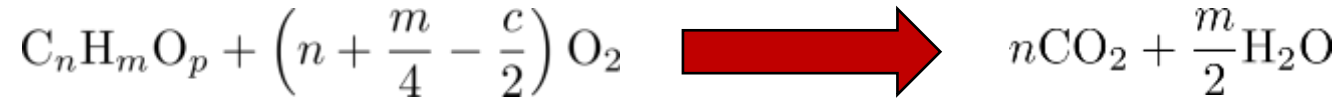
Oil refining: from crude oil to the gas station

Perspectives

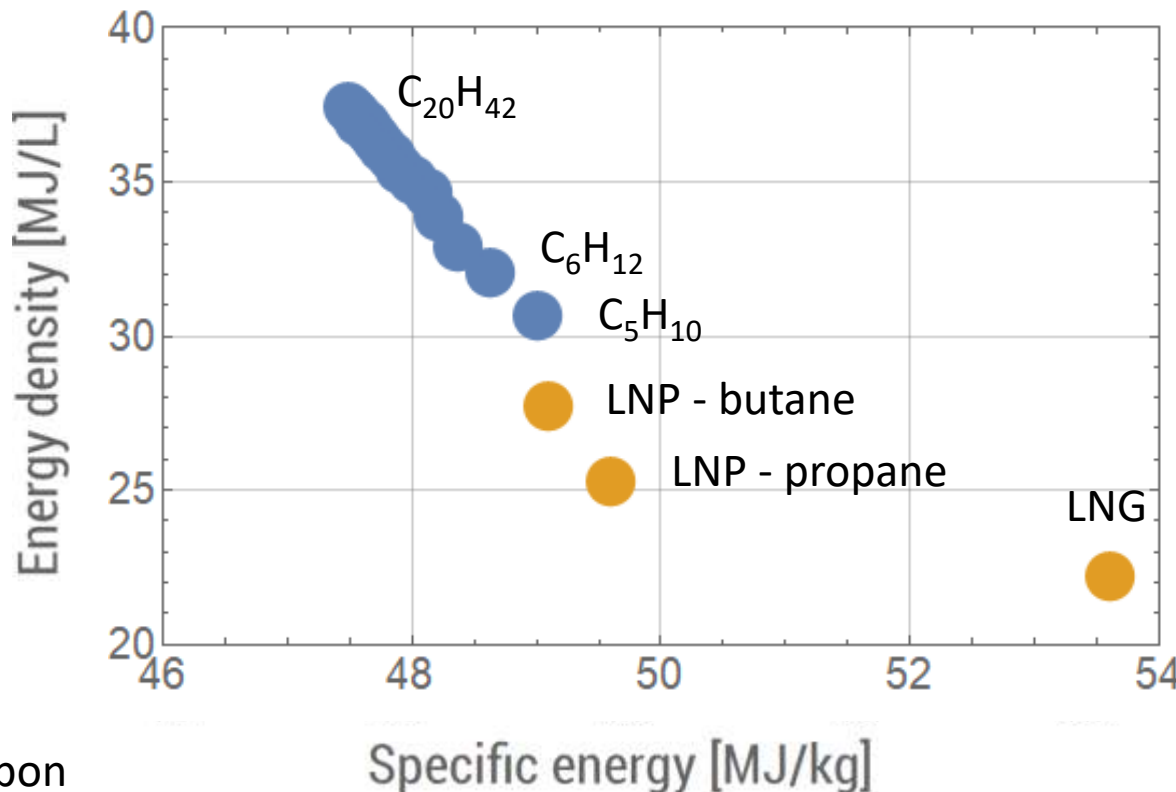


# Combustion: redox reaction

Reduced carbon



Combustion = carbon oxidation from reduced form to CO<sub>2</sub>



Largest energy per carbon atom

= most reduced carbon = CH<sub>4</sub>

→ also per MJ/kgCO<sub>2</sub>, per MJ/kg

Problem :

gas → very small density (kg/L)

LNG → heavy logistics (T,p)

Heavier hydrocarbons

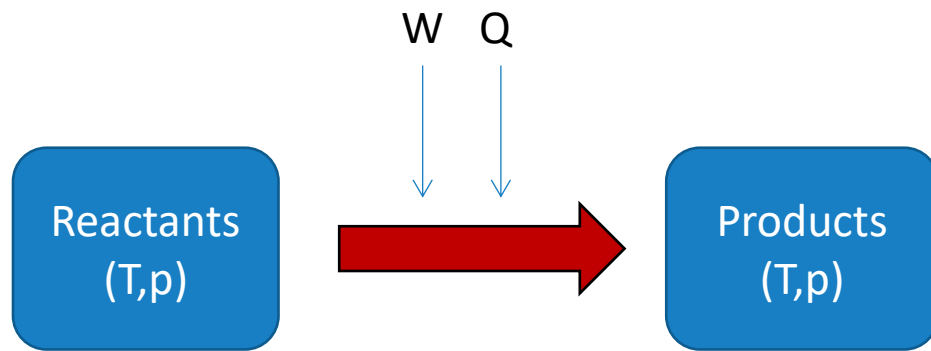
→ less MJ/#C (MJ/kg, MJ/kgCO<sub>2</sub>)

→ much larger density (liquid)

Oxidized carbon

# Combustion: Hess' law

How to estimate the released energy?



$$\Delta H = Q = H_{\text{prod}} - H_{\text{react}}$$

$$\Delta H < 0 \quad \text{Exothermal}$$

$$\Delta H > 0 \quad \text{Endothermal}$$

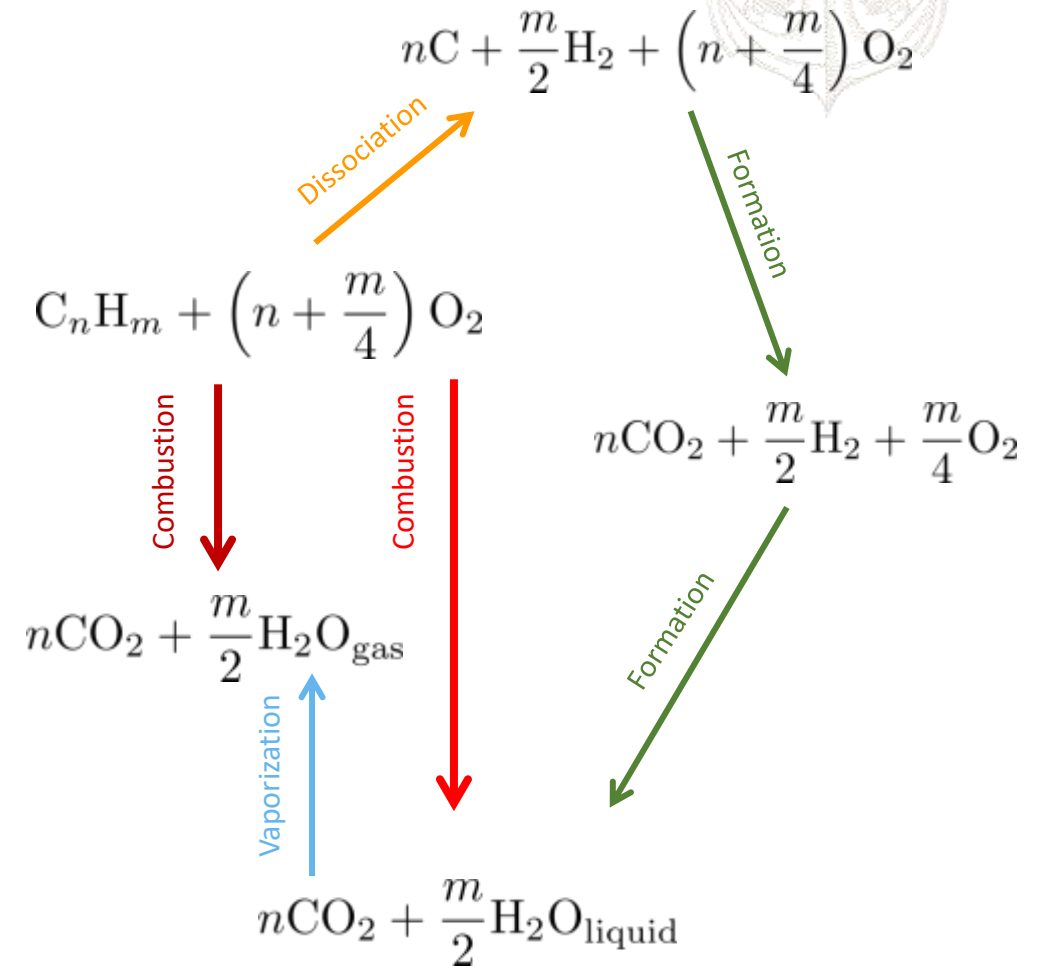
Lower heating value: water vapour still gaseous

Higher heating value: condensed water vapour

Enthalpy



State Variable !



$$\Delta_{\text{comb}} H_{\text{HHV}} = \underbrace{-\Delta_f H (\text{C}_n\text{H}_m) + n\Delta_f H (\text{CO}_2) + \frac{m}{2}\Delta_f H (\text{H}_2\text{O})}_{\Delta_{\text{comb}} H_{\text{LHV}}} + \frac{m}{2}\Delta_{\text{liq}} H (\text{H}_2\text{O})$$



# Nature's nature

## General idea

Take a system out of equilibrium with the environment (T,p,μ...),  
Let it relax towards environmental conditions (dead state),  
Collect work along the ride !

What is the spontaneous evolution?

*Energy?* Some spontaneous reactions are endothermic (ex: water evaporation)

*Entropy?* Some spontaneous reactions decrease entropy (ex:  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ )

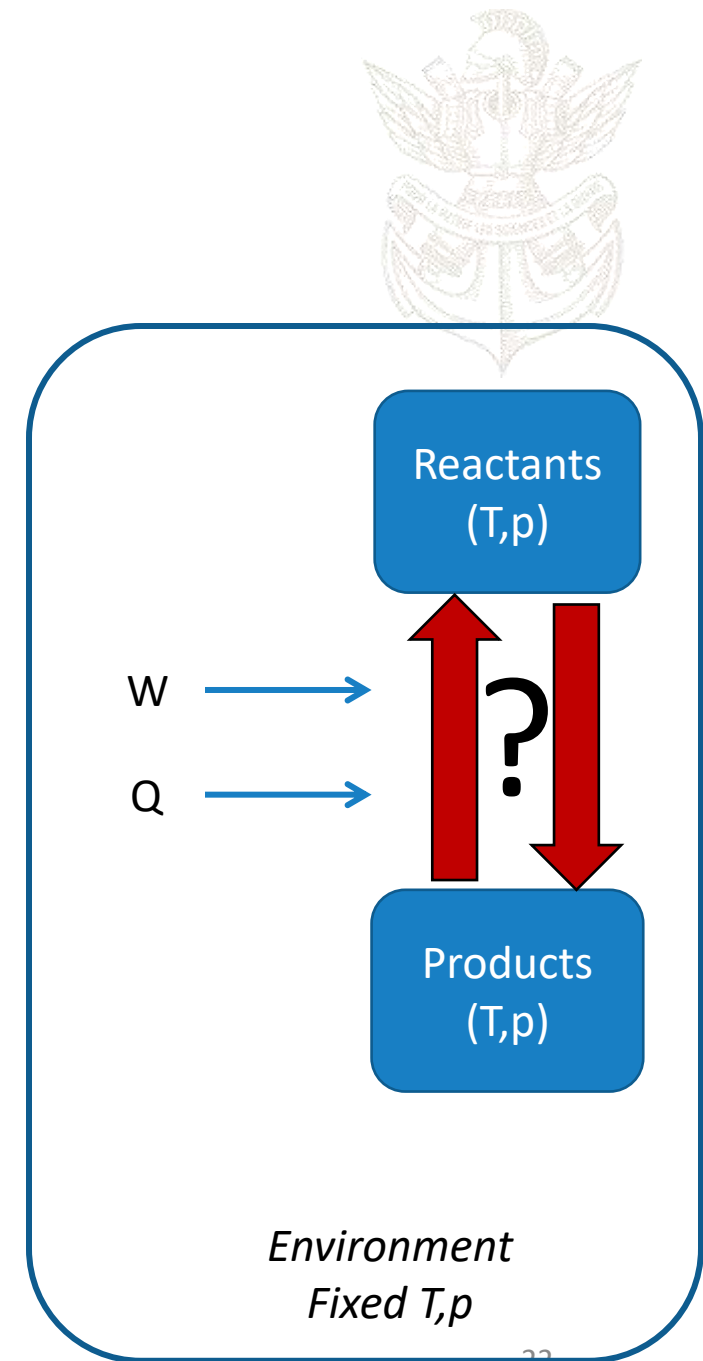
**Global** entropy must increase

$$dS_{\text{tot}} = dS_r - \frac{dH_r}{T} \geq 0$$

Spontaneous evolution:

$$dG_r = dH_r - TdS_r \leq 0$$

*Lazy Sloppy*



# Gibbs energy and chemical potential

Gibbs (Free) Energy

$$G(N, T, p) = H - TS = N \mu(T, p)$$

➤ Thermo identity

$$dG = -SdT + Vdp + \mu dN$$

➤ What is  $\mu$  ?

“Energy required to add a particle” **at fixed S and V !**

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} = \left( \frac{\partial F}{\partial N} \right)_{T,V} = \left( \frac{\partial G}{\partial N} \right)_{T,p} = -T \left( \frac{\partial S}{\partial N} \right)_{U,V}$$

$\mu$  for particle exchange  $\leftrightarrow$  T for energy exchange



*Josiah Willard Gibbs*



# Two major consequences

$$G(N, T, p) = H - TS = N \mu(T, p)$$



For a closed system at fixed (T,p),  
spontaneous evolution = minimize G

*Application*

$\Delta H < 0$

$\Delta H > 0$

$\Delta S > 0$

Always

At high  
temperatures

*Application*  $\Delta G = (\mu_2 - \mu_1)\Delta N$

$\Delta S < 0$

At low  
temperatures

Never

*Particles flow spontaneously from high  $\mu$  to low  $\mu$*

*Two systems exchanging particles reach the same  $\mu$*

$\mu$  for particle exchange  $\leftrightarrow$  T for energy exchange



Maximal recoverable heat:  $-\Delta H$

Maximal recoverable work:  $-\Delta G = -\Delta H + T\Delta S$



$-\Delta G > -\Delta H$  if  $\Delta S > 0$

System drains heat from environment





# The many lives of $\mu$

Pure body



$$\mu_{A,0}(T, p)$$

Gibbs Duhem relation

$$d\mu = -sdT + vdp$$

Non reacting mixture



$$\begin{aligned} \mu_A(T, p, x) \\ \mu_B(T, p, x) \end{aligned}$$

Activity

$$\mu_i = \mu_{i,0} k_B T \log x_i$$

Phase change

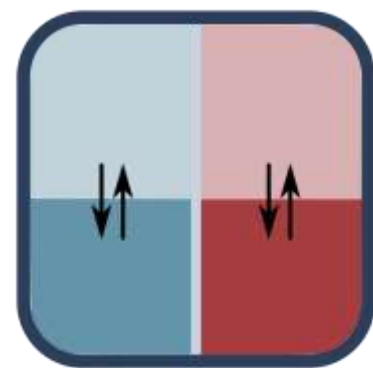


$$\mu_{A,0}^{gas}(T, p) = \mu_{A,0}^{liq}(T, p)$$

Clapeyron relation

$$\frac{dp_{sat}}{dT} = \frac{\Delta_{vap}H}{T \times (v_{gas} - v_{liq})}$$

Binary system



$$\begin{aligned} \mu_A^{gas}(T, p, x_A^g) &= \mu_A^{liq}(T, p, x_A^l) \\ \mu_B^{gas}(T, p, x_B^g) &= \mu_B^{liq}(T, p, x_B^l) \end{aligned}$$

Binary diagram

Chemical reaction



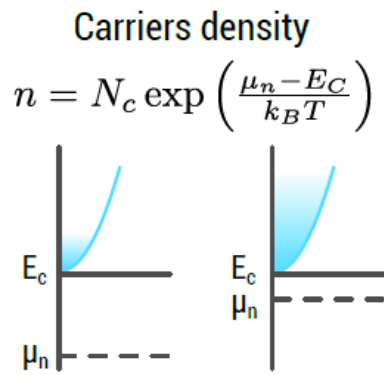
$$\begin{aligned} a\mu_A(\xi) + b\mu_B(\xi) \\ = c\mu_C(\xi) + d\mu_D(\xi) \end{aligned}$$

Law of mass action

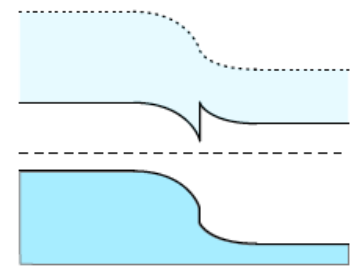
Equilibrium displacement  
(Van't Hoff, Le Chatelier...)



# The many (many) lives of $\mu$

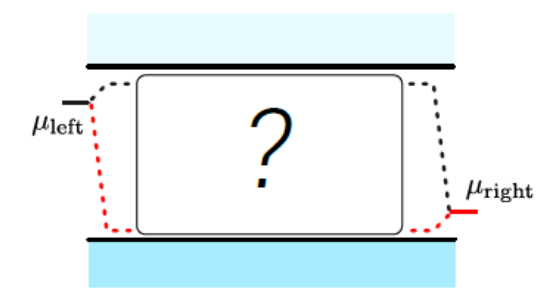


**Band alignment**

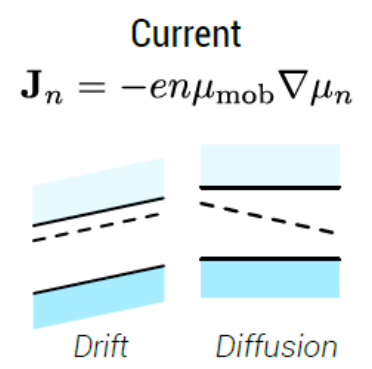


**Voltage**

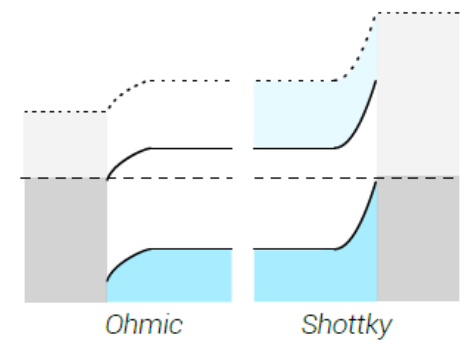
$$qV = \mu_{\text{left}} - \mu_{\text{right}}$$



**Chemical potential ( $\sim$  Fermi level) in a semi conductor**

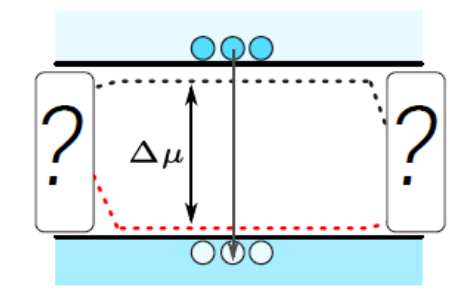


**Contact**



**Photoluminescence**

$$PL(E) = C \times \frac{A(E)E^2}{\exp\left(\frac{E - \Delta\mu}{k_B T}\right) - 1}$$



# Lecture 3 Fossil fuels

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What, Who, What for, Why ?

Thermo toolbox : the chemical potential

**Oil, gas and coal formation: in and out the organic carbon cycle**

Oil (and gas) production: conventional and unconventional sources

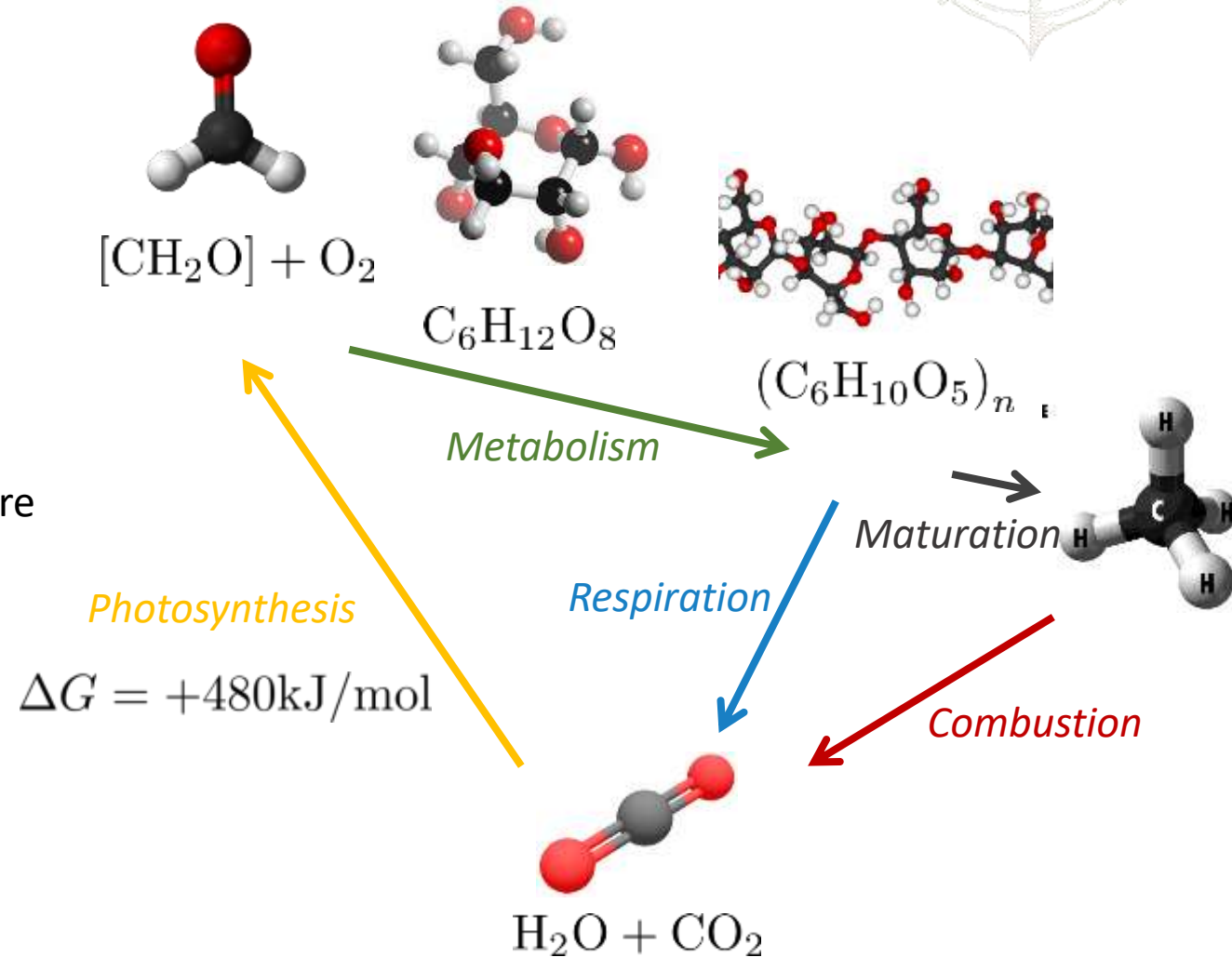
Oil refining: from crude oil to the gas station

Perspectives

# Fossil fuel formation - outline



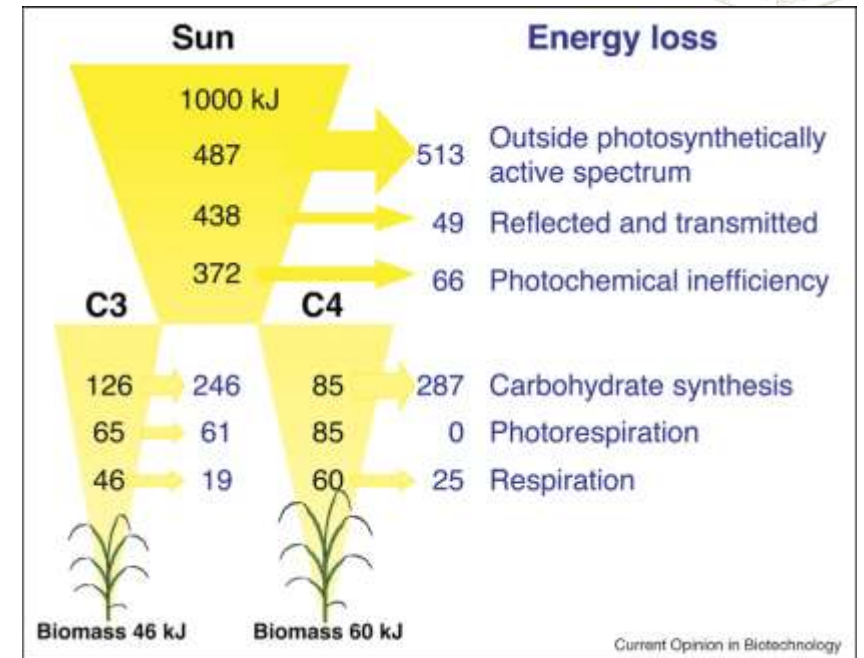
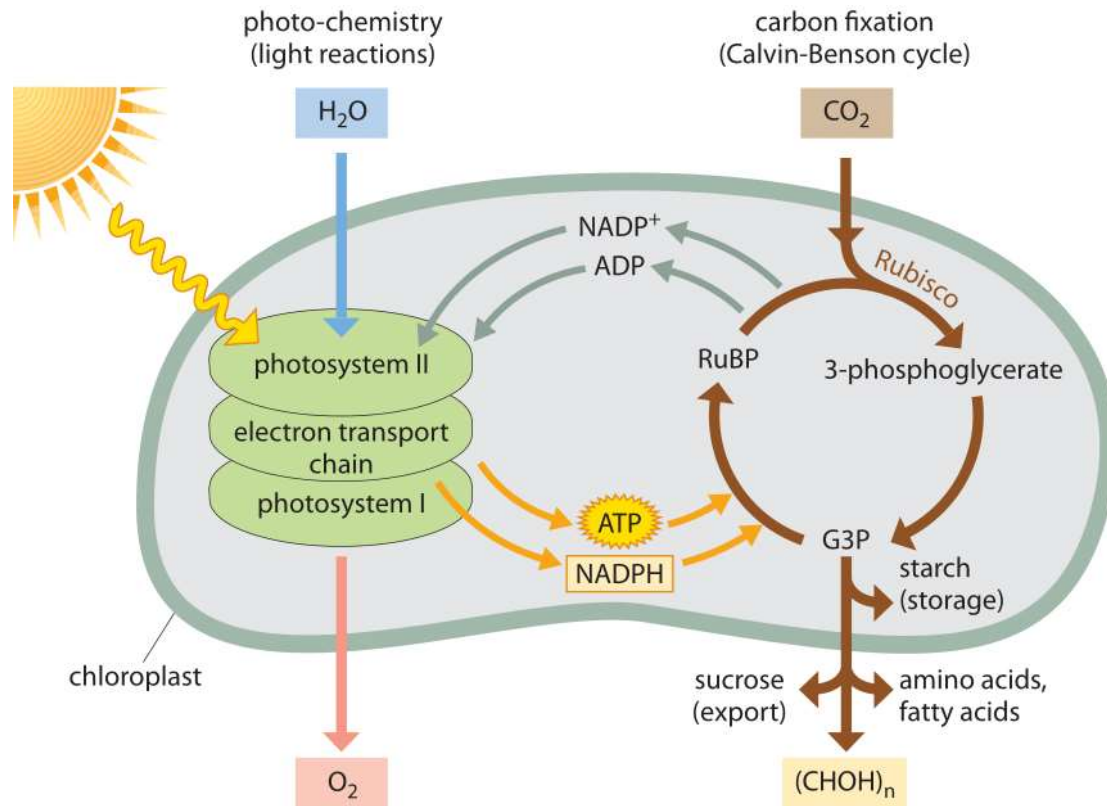
- |              |  |
|--------------|--|
| <b>Step1</b> | Turn atmospheric CO <sub>2</sub> into biomass          |
|              | <i>Plankton</i> <i>Plants</i>                          |
| <b>Step2</b> | Prevent biomass from oxidizing back to CO <sub>2</sub> |
|              | <i>Sediments</i> <i>Peat</i>                           |
| <b>Step3</b> | Let biomass mature at high temperature and pressure    |
|              | <i>Source rock</i> <i>Coal</i>                         |
| <b>Step4</b> | Migrate to a trap                                      |
|              | <i>Reservoir rock</i> -                                |
| <b>Step5</b> | Extraction   |



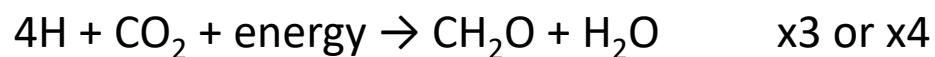
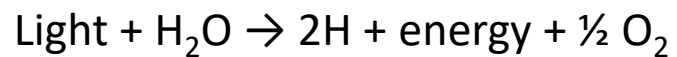




# Photosynthesis: carbon cycle's engine



Zhu et al. Current Opinion in Biotechnology 2008, 19



~ 8 red photons per CO<sub>2</sub> molecule

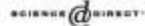
Overall efficiency (light to chemical energy) : 0.1-1%

→ Power density : 1 W/m<sup>2</sup>

# Thermo clash – round 1



Available online at [www.sciencedirect.com](http://www.sciencedirect.com)



Biochimica et Biophysica Acta 1589 (2005) 293–298



<http://www.sciencedirect.com/locate/bba>

## Photosynthesis and negative entropy production

Robert C. Jennings<sup>a,\*</sup>, Enrico Engelmann, Flavio Garlaschi, Anna Paola Casazza, Giuseppe ZaccHELLI

<sup>a</sup> Istituto di Biologia del Consiglio Nazionale delle Ricerche-Istituto di Milano, Dipartimento di Biologia Orientata degli Istituti di Milano, Via Celoria 26, 20133 Milano, Italy

Received 9 June 2005; received in revised form 4 August 2005; accepted 11 August 2005  
Available online 25 August 2005

### Abstract

The widely held view that the maximum efficiency of a photosynthetic pigment system is given by the Carnot cycle expression  $(1 - T_c/T_h)$  for energy transfer from a hot bath (radiation at temperature  $T_h$ ) to a cold bath (pigment system at temperature  $T_c$ ) is critically examined and demonstrated to be inaccurate when the entropy changes associated with the microscopic process of photon absorption and photochemistry at the level of single photosystems are considered. This is because entropy losses due to excited state generation and relaxation are extremely small ( $\Delta S \sim k_B^{-1}$ ) and are essentially associated with the absorption–fluorescence Stokes shift. Total entropy changes associated with primary photochemistry for single photosystems are shown to depend critically on the thermodynamic efficiency of the process. This principle is applied to the case of primary photochemistry of the isolated core of higher plant photosystem I and photosystem II, which are demonstrated to have maximal thermodynamic efficiencies of  $\sim 0.98$  and  $> 0.92$ , respectively, and which, in principle, function with negative entropy production. It is demonstrated that for the case of  $(1 - T_c/T_h)$  entropy production is always negative and only becomes positive when  $T_c < 11 - T_c/T_h$ .  
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Keywords: Carnot cycle; Entropy; Photosynthesis; Photosystem I core; Photosystem II core

### 1. Introduction

Over the past five decades, a considerable literature has accumulated on thermodynamic aspects of primary photosynthetic processes, and quite widely contrasting views have been published. Following the initial suggestion by Dreyers [1] many people have accepted the view that the photosynthetic conversion of electromagnetic energy, which is the internal energy of the photon ( $h\nu$ ), into the free energy of chlorophyll excited states (G) is described by the Carnot cycle equation  $G = (h\nu - T_c/T_h)$ , where  $G = h\nu_0$ , the purely electronic transition of the lowest excited singlet state ( $S_1$ ), and  $T_h$  and  $T_c$  are the temperatures of the chlorophyll system (approximately 300 K) and the radiant energy, respectively (e.g. [2–4]). This point is interesting for two main reasons.

Firstly, in the interpretation of the above cited authors, this is understood to place an upper limit on the maximal photochemical work obtainable from an absorbed photon. For values

of  $T_c = 1100$  K, as suggested by Dreyers [1], the Carnot cycle efficiency  $(1 - T_c/T_h) = 0.71$  and thus according to this point of view the Gibbs free energy of a chlorophyll molecule in the first singlet excited state could not exceed this value. Thus, the maximum chemical work associated with charge separation was not expected to exceed 1.3 eV, even though  $h\nu_0 = 1.8$  eV. However, this point of view was criticized by Porco [5], who pointed out that this misunderstanding arose from the incorrect application of the concept of chemical potential to photosynthetic systems Eq. (1):

$$\mu = h\nu_0 + kT \ln Z \quad (1)$$

$\mu$  is the chemical potential associated with chlorophyll in the excited state,  $h\nu_0$  is the photon energy for frequency  $\nu_0$  which is taken as that of the  $S_1$  purely electronic transition,  $Z$  is some factor related to the relative concentrations of  $S_0$  and  $S_1$ ,  $T$  is the temperature of the chlorophyll system. This author pointed out that the concept of chemical potential was applicable only to molecular ensembles and not to single chlorophyll molecules, or single molecular complexes, which absorb photons and perform photochemistry with in single photosystems. Thus, Eq. (1) is applicable to "systems containing large numbers of

[...]the Carnot cycle concept for photosynthetic energy conversion is based on the assumption that the second law of thermodynamics is necessarily applicable to photosystem function. [...] If the overall quantum efficiency is high enough, negative or zero entropy changes are able to be contemplate

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# Thermo clash – round 2



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Review  
Commentary on: "Photosynthesis and negative entropy production"  
by Jennings and coworkers

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**Abstract**  
This commentary agrees against the view that photochemical energy conversion violates the second law of thermodynamics, as expressed in a recent paper [R.C. Jennings, E. Rappaport, F. Gauthier, A.P. Castéra, G. Zaccarello, Photosynthesis and negative entropy production, *Bioscience, Biophys., Acta* 1509 (2005) 250–255]. The basic principle of free energy conversion by a photo-electrochemical cell are outlined, emphasizing the fact that the potential depends on the relative population of the excited state and thus on the photochemical intensity.  
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**Keywords:** Photosynthesis; Thermodynamic; Energy yield; Second law; Entropy; Energy; Photochemical energy conversion; Solar energy conversion

**1. Introduction**  
Over the accelerated thermic process published, I worry people conversion energy of its excited state  $(E^* - E_0) - E_1$  of the leaves temperature and the main interesting is finally, in understood chemical way

**1.1. Introduction**  
"The general struggle for existence of living beings is therefore not a fight for energy, which is plentiful in the form of heat, uniformly transformable, in every body. Rather, it is a struggle for entropy that becomes available through the flow of energy from the hot Sun to the cold Earth. To make the fullest use of this energy, the plants spread out the immensurable area of their leaves and harness the Sun's energy by a process as yet unexplored, before it sinks down to the temperature level of our Earth, to drive chemical synthesis of which one has no inkling as yet in our laboratories." This 1888 quotation from Boltzmann (cited in Ref. [1]) gives a remarkably lucid overview of what photosynthesis is all about. Whereas things have drastically changed concerning our understanding of the mechanisms (we do have some inkling nowadays), the thermodynamic insight remains valid. A point of semantics must be made, however: the fight for entropy should be rather understood as a fight against entropy or more accurately, for Gibbs' free energy. The modern understanding of the thermodynamics of photochemical conversion dates back from the 1958 paper by Dismuss [2], who showed, to a particular but enlightening case, how the process could be viewed as a heat engine (in line with Boltzmann's view). As such, the efficiency of energy conversion is subject to the upper limit expressed by the Carnot yield. This means that under normal levels of illumination, less than ~75% of the absorbed energy is available for performing work. This approach was even since generalized and developed by a number of authors (e.g., [3–7]).  
In a recent paper, Jennings and coworkers [8] discussed this subject and concluded, at variance with previous literature, that the photochemical process in photosynthesis is likely to produce negative entropy, violating the second law of thermodynamics. I believe this view is unwarranted. Although probably most readers have received Jennings' claims with the skepticism, I would like to take the opportunity for presenting in a concise and (I hope) simple way the basic notions concerning this issue.  
Since the question under debate is the amount of work that can be retrieved from the absorption of light, it is useful to consider some conceptually simple device: a photo-electrochemical cell where work appears in the familiar form of an electric current. The processes that take place in the electrochemical part of such a cell are isothermal and can approach reversibility as closely as desired by adjusting the load, so that the free energy losses in this section become vanishingly small. Thus, this part of the setup can be viewed

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[...] the authors ignore the statistical essence of the problem. There is no justification for excluding the interaction of matter with light from common thermodynamics: the theory of black body emission, which was at the origin of the quantum revolution, was precisely elaborated to meet this demand.

Another precursor of second law violation in photosynthesis, according to Jennings, is Parson [6], who would have argued against "the incorrect application of the concept of chemical potential to photosynthetic systems". This is again an obvious misunderstanding of what this author really said. Parson was by no means an opponent to the application of chemical potential in this field.



# Thermo clash – round 3



Robert C.

doi

Abstract

The yield for energy for photosynthesis is estimated to be of the order of 1% (1-7) (15-17) (18-20) (21-23) (24-26) (27-29) (30-32) (33-35) (36-38) (39-41) (42-44) (45-47) (48-50) (51-53) (54-56) (57-59) (60-62) (63-65) (66-68) (69-71) (72-74) (75-77) (78-80) (81-83) (84-86) (87-89) (90-92) (93-95) (96-98) (99-101) (102-104) (105-107) (108-110) (111-113) (114-116) (117-119) (120-122) (123-125) (126-128) (129-131) (132-134) (135-137) (138-140) (141-143) (144-146) (147-149) (150-152) (153-155) (156-158) (159-161) (162-164) (165-167) (168-170) (171-173) (174-176) (177-179) (180-182) (183-185) (186-188) (189-191) (192-194) (195-197) (198-200) (201-203) (204-206) (207-209) (210-212) (213-215) (216-218) (219-221) (222-224) (225-227) (228-230) (231-233) (234-236) (237-239) (240-242) (243-245) (246-248) (249-251) (252-254) (255-257) (258-260) (261-263) (264-266) (267-269) (270-272) (273-275) (276-278) (279-281) (282-284) (285-287) (288-290) (291-293) (294-296) (297-299) (300-302) (303-305) 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# Thermo clash – round 4



ELSEVIER

Robert C. Co

Reply to

R.C.

**Abstract**

The work by Jennings et al. (2007) is a strong flow of energy from a small (ΔS ≈ 7) photochemical reaction applied to the same reaction production. In 2008, we published a paper in which we demonstrated the level of a small (ΔS ≈ 7) photochemical reaction applied to the same reaction production. In 2008, we published a paper in which we demonstrated the level of a small (ΔS ≈ 7) photochemical reaction applied to the same reaction production.

**1. Introduction**

Over the past few years, there has been a renewed interest in the Second Law of Thermodynamics. In particular, there has been a renewed interest in the Second Law of Thermodynamics. In particular, there has been a renewed interest in the Second Law of Thermodynamics.

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Journal of Bioenergetics and Biomembranes

## Entropy production and the Second Law in photosynthesis

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**Abstract**

An assertion that the primary photochemistry of photosynthesis can violate the Second Law of thermodynamics in certain efficient systems has been put forward by Jennings et al., who maintain their position strongly despite an argument to the contrary by Lavergne. We identify a specific omission in the calculation of Jennings et al. and show that no violation of the Second Law occurs, regardless of the photosynthetic efficiency. © 2007 Elsevier B.V. All rights reserved.

**1. Introduction**

Application of thermodynamics to the determination of photosynthetic efficiency has a long history, whose description may be found in the many sources cited in references [1–11]. Its principal origin is the treatment by Debye [1]. In a recent publication, Jennings et al. [4] claim that in certain circumstances the initial reaction of photosynthesis violates the Second Law of thermodynamics. This claim has been challenged by Lavergne [5], whose arguments are clearly not accepted by the former authors [6]. We point out here that Jennings et al. omitted a significant contribution to the entropy production, namely that which accompanies the initial photoexcitation. Restoring this term brings the process into accord with the Second Law.

**2. Entropy changes associated with photoexcitation**

The Second Law, in asserting that entropy production must be positive or zero, refers either to total entropy production within an isolated system or to internally-generated entropy production in an open system [7–14]. Consider the radiation ( $\nu$ ), an ensemble of one or more pigments ( $i$ ), and the surroundings ( $s$ ) as an isolated system undergoing the process of absorption. We interpret “pigment” broadly to include whatever molecular components are involved in the initial photoexcitation prior to charge separation. The entropy change in the system when the pigment absorbs a photon is

$$\Delta S_{\text{tot}} = \Delta S_s + \Delta S_i + \Delta S_\nu \quad (1)$$

where the subscripts refer respectively to the three mentioned subsystems. Jennings et al. correctly evaluate  $\Delta S_s$  as  $-\ln p_i/T_s$ , where  $\ln p_i$  is the photon energy and  $T_s$  is the radiation temperature. They also evaluate  $\Delta S_i$  as a positive contribution given by  $(1-\xi) \ln p_i/T_s$ , where  $\xi$  is the fraction of the photon energy that goes into charge separation, i.e., does photochemical work, and  $T_s$  is the ambient temperature. We are left to evaluate the pigment contribution,  $\Delta S_i$ , which can be separated temporally into two components, one accompanying the initial photoexcitation and the second accompanying the period of a fraction  $1-\xi$  of the absorbed energy to the surroundings. We first treat the photoexcitation.

Consider an ensemble of  $N$  distinguishable pigments illuminated among a set of eigenstates, the number of pigments in state  $i$  being  $n_i$ . The statistical entropy of such an ensemble is given by Boltzmann’s expression,

$$S_i = k_B \ln(D_i) = k_B \ln \left( \frac{N!}{\prod_i n_i!} \right) \quad (2)$$

where  $k_B$  is Boltzmann’s constant and  $D_i$ , the statistical weight or multiplicity of the distribution, is the number of ways of assigning the pigments to the microscopic states consistent with

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 Tel.: +1 509 335 1181.  
 Fax: +1 509 335 1181.

An assertion that the primary photochemistry of photosynthesis can violate the Second Law of thermodynamics in certain efficient systems has been put forward by Jennings et al., who maintain their position strongly despite an argument to the contrary by Lavergne.

We identify a specific omission in the calculation of Jennings et al. and show that no violation of the Second Law occurs, regardless of the photosynthetic efficiency.

# Thermo clash – round 5



ELSEVIER

Robert C. Jennings

Reply to

R.C. Jennings

Abstract

The work by Jennings et al. (2007) is a reply to the article by Kruys and Pagan (2007) on the thermodynamic considerations of the Law of Thermodynamics in the context of primary photosynthesis. The article by Jennings et al. (2007) is a reply to the article by Kruys and Pagan (2007) on the thermodynamic considerations of the Law of Thermodynamics in the context of primary photosynthesis.

1. Introduction

Over the past few years, the thermodynamic considerations of the Law of Thermodynamics in the context of primary photosynthesis have been a topic of debate. In his article, Jennings et al. (2007) present a new perspective on this issue, arguing that the thermodynamic considerations of the Law of Thermodynamics in the context of primary photosynthesis should be re-examined. In this article, we will discuss the arguments presented by Jennings et al. (2007) and provide our own perspective on the issue.

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Entropy consumption in primary photosynthesis

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Available online 23 August 2007

Abstract

Kruys and Pagan have objected to our previous conclusion on possible negative entropy production during primary photosynthesis, i.e., from photon absorption to primary charge separation, by considering a pigment system in which primary photosynthesis is not specifically considered. This approach does not address our proposal. They suggest that when a pigment absorbs light and passes to an excited state, its entropy increases by  $k_B \ln 2$ . This point is discussed in two ways: (1) from considerations based on the energy gap law for excited state relaxation, (2) using classical thermodynamics, in which the energy is transferred into the pigment (antenna) system by photon absorption. Both approaches lead us to conclude that the excited state and the ground state are isentropic, in disagreement with Kruys and Pagan. A discussion on total entropy change specifically during the charge separation process itself indicates that the process may be almost isentropic and thus our conclusion on possible negentropy production associated with the sequence of reactions which go from light absorption to the first primary charge separation event, due to its very high thermodynamic efficiency, remains unchanged.

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1. Introduction

We have recently suggested that, contrary to the generally accepted view, primary photosynthesis in plants can, in principle, proceed with negative entropy production (Jennings et al., 2007). Based on straightforward energy balance considerations for the total entropy change ( $\Delta S_{\text{tot}}$ , system plus environment) in a photochemical system, the following expression was presented:

$$\Delta S_{\text{tot}} = h\nu_p(T_e - T) + \Delta S_p \quad (1)$$

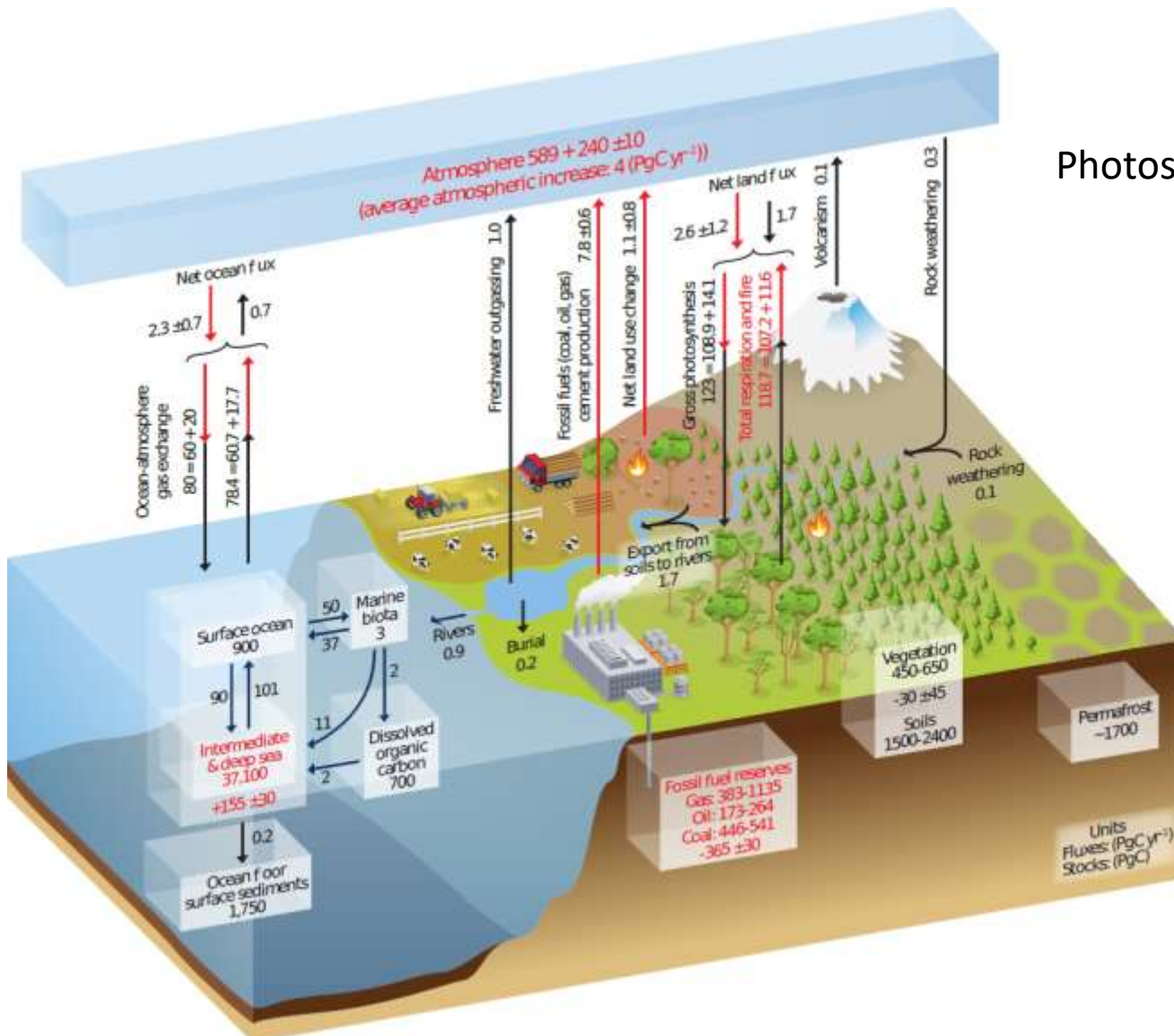
where  $h\nu_p$  is the energy of a photon absorbed by a photosystem;  $T_e$  is the radiation temperature, i.e., the black body temperature which emits a certain, temperature dependent, photon density at frequency  $\nu$ . Values in the literature for different energy flux densities considered are 1000 K  $\leq T_e \leq$  5500 K.  $\zeta$  is the thermodynamic efficiency of primary photochemistry and encompasses all energy losses from photon absorption to primary charge separation, i.e., the Stokes shift, the quantum efficiency, the free energy changes during primary charge separation,  $T$  is the environmental bath temperature, in which the photosystems are embedded, and is taken as 300 K.  $\Delta S_p$  is the small entropy decrease associated with primary photochemical production of charge asymmetry. As already discussed in our earlier reply (2) to a paper by Lavergne (3), this conclusion refers to primary processes in a system of single photosystems, such of which absorbs a photon  $h\nu$ , in other words, to a system of photochemical photosystems in the excited state. At high values of  $\zeta$ ,  $T_e - T$ , may be less than  $T$  and thus  $\Delta S_{\text{tot}}$  has a negative value. This possibility is implicit in the earlier study by Yougou and van der Meer (4) in their Eq. (1), in physical terms, this conclusion is largely based on the entropy loss by the light flux upon absorption ( $-h\nu/T_e$ ) not being compensated by entropy release into the environmental bath at very high values of  $\zeta$ . In our initial reasoning it was

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our conclusions on possible negentropy production [...] remain unchanged.



# From the atmosphere to the atmosphere



Photosynthesis

Organic matter

Respiration  
Degradation

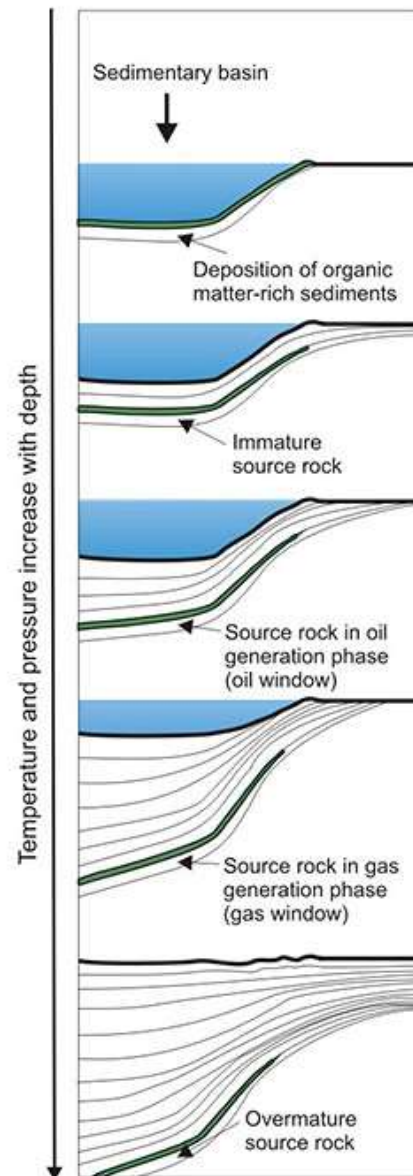
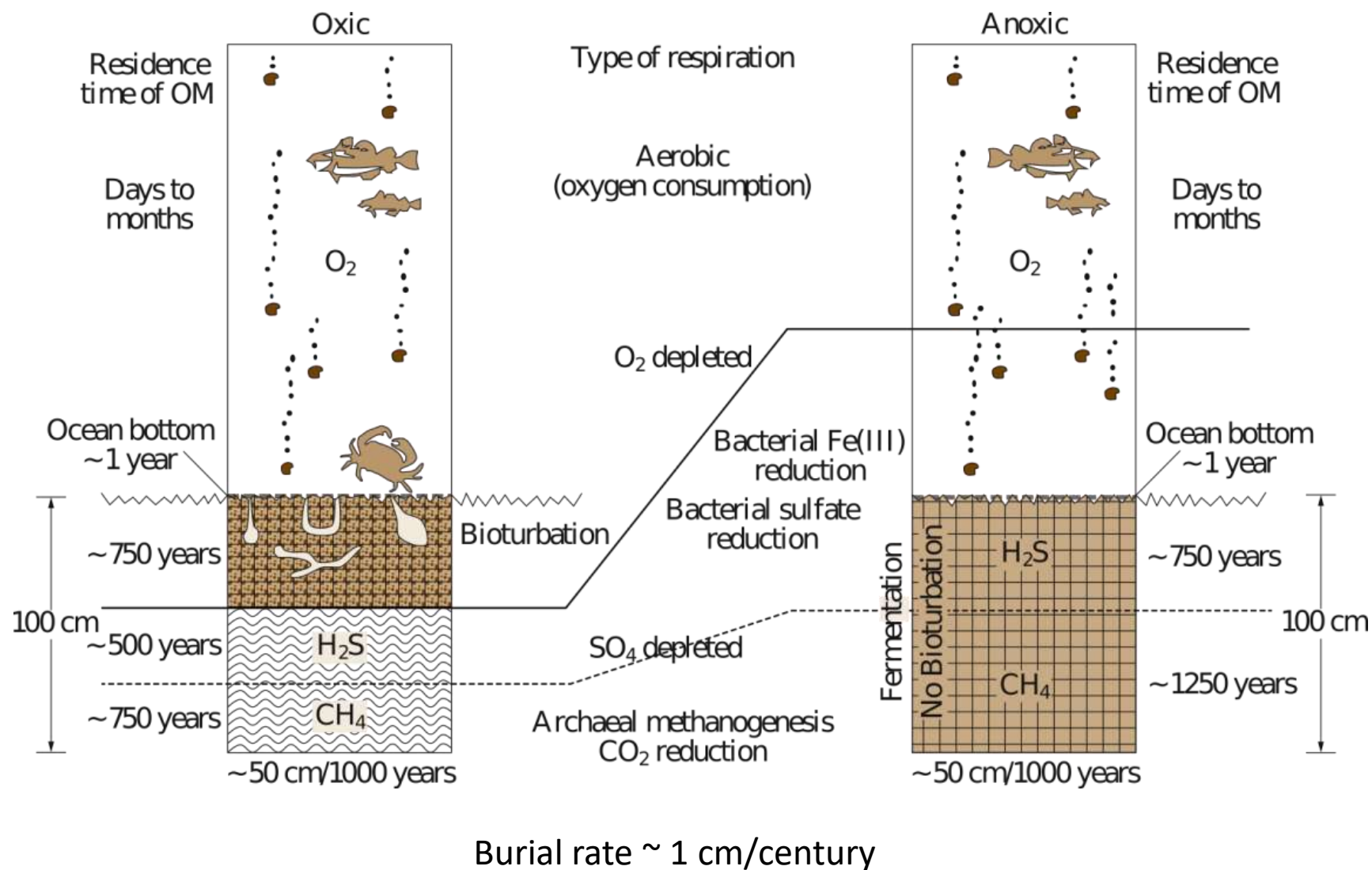
CO<sub>2</sub>

Photosynthesis requirements:

- Sunlight
- Water
- CO<sub>2</sub>
- Nutriments

Surface waters close to shore  
Adequate land areas

# Escaping the carbon cycle



# Maturation – oil & gas

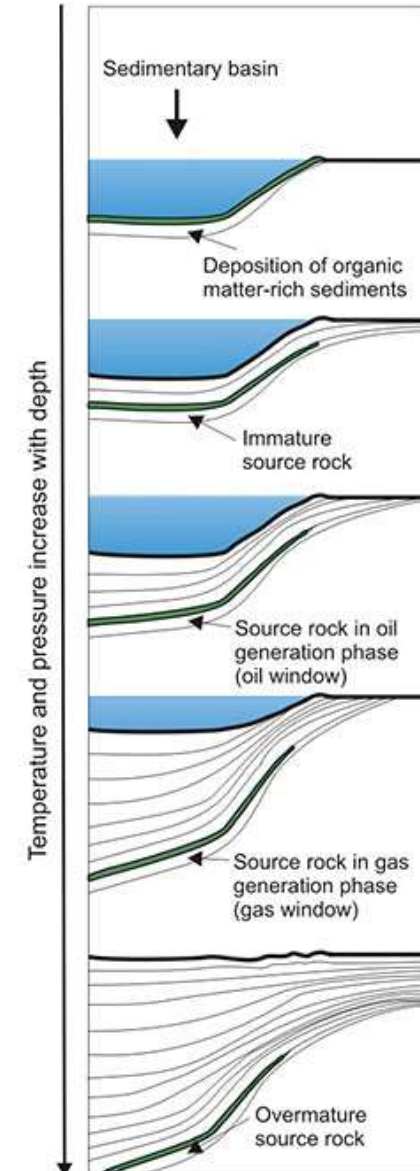
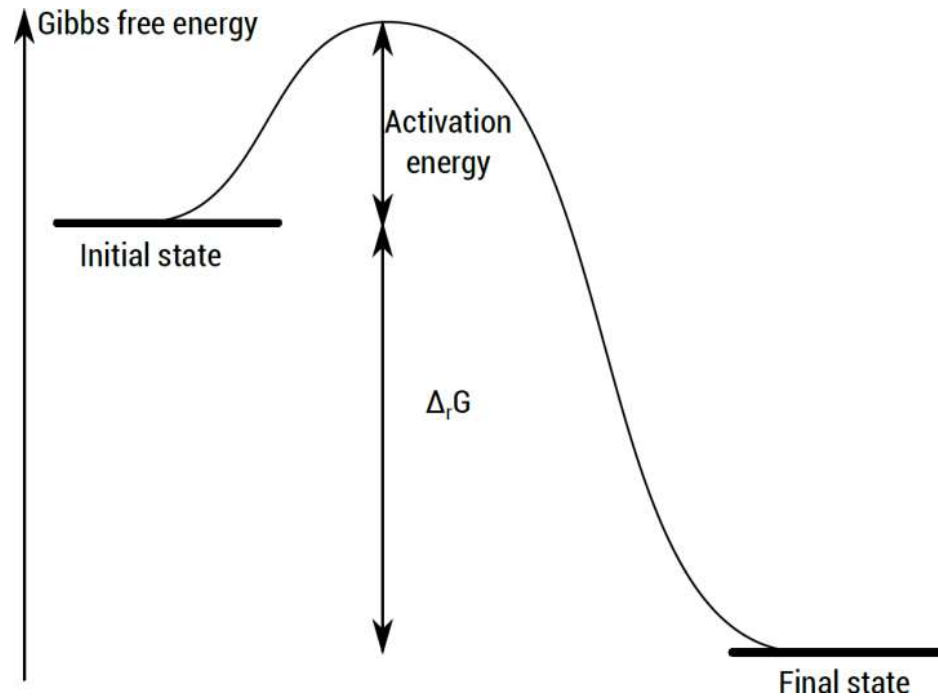
Burial rate  $\sim 1$  cm/century



Increasing pressure (100 bar/km)  
& temperature (15-50 K/km)



- Displace chemical equilibriums
- Accelerate thermal clock

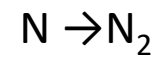
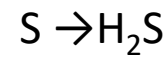
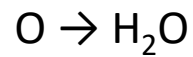




# Maturation – oil & gas

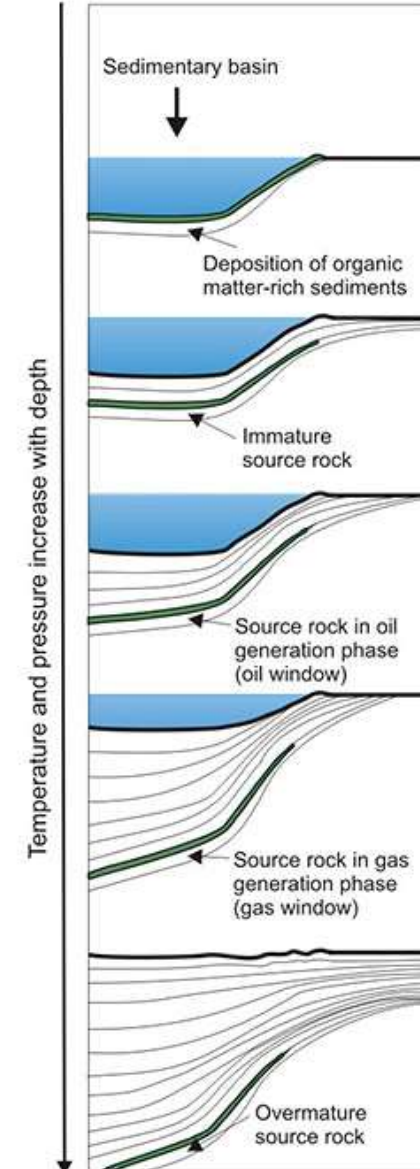
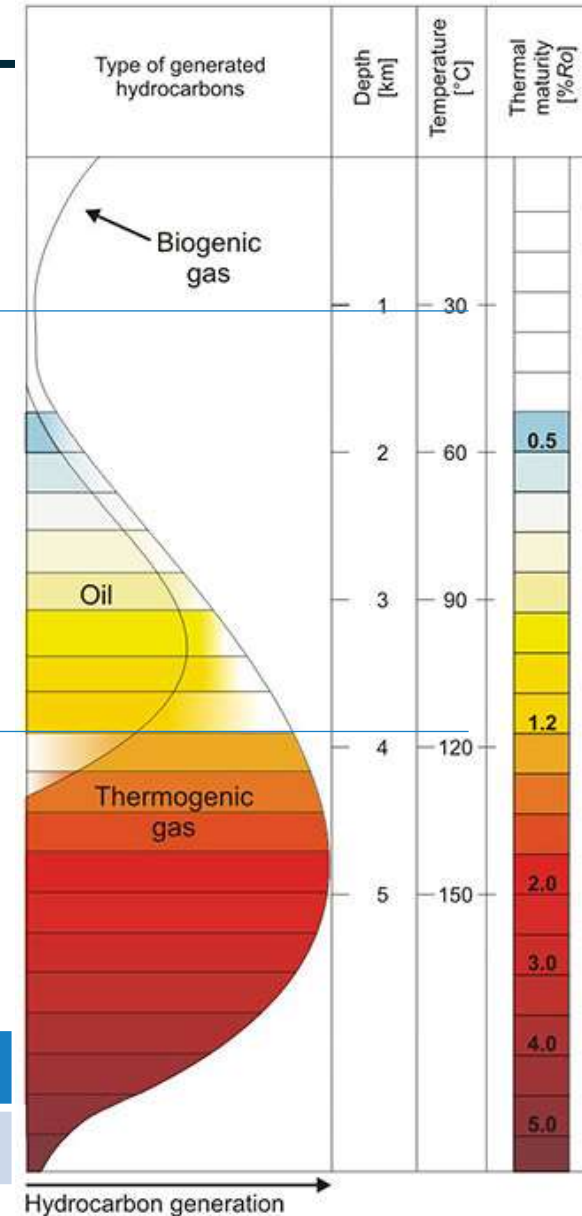
*Diagenesis* (Mostly) biotic degradation of organic matter into kerogen

*Catagenesis* Thermal degradation of kerogen into hydrocarbons



*Metagenesis* Further carbonisation → graphite

Organic matter → kerogen → hydrocarbons in a source rock



Total Organic Carbon [%]	< 0.5	<1	<2	<4	>4
Source rock quality	Poor	Fair	Good	Very good	Excellent

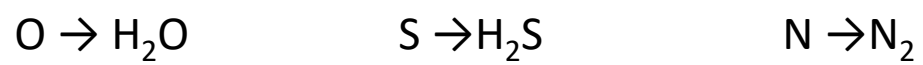




# Maturation – oil & gas

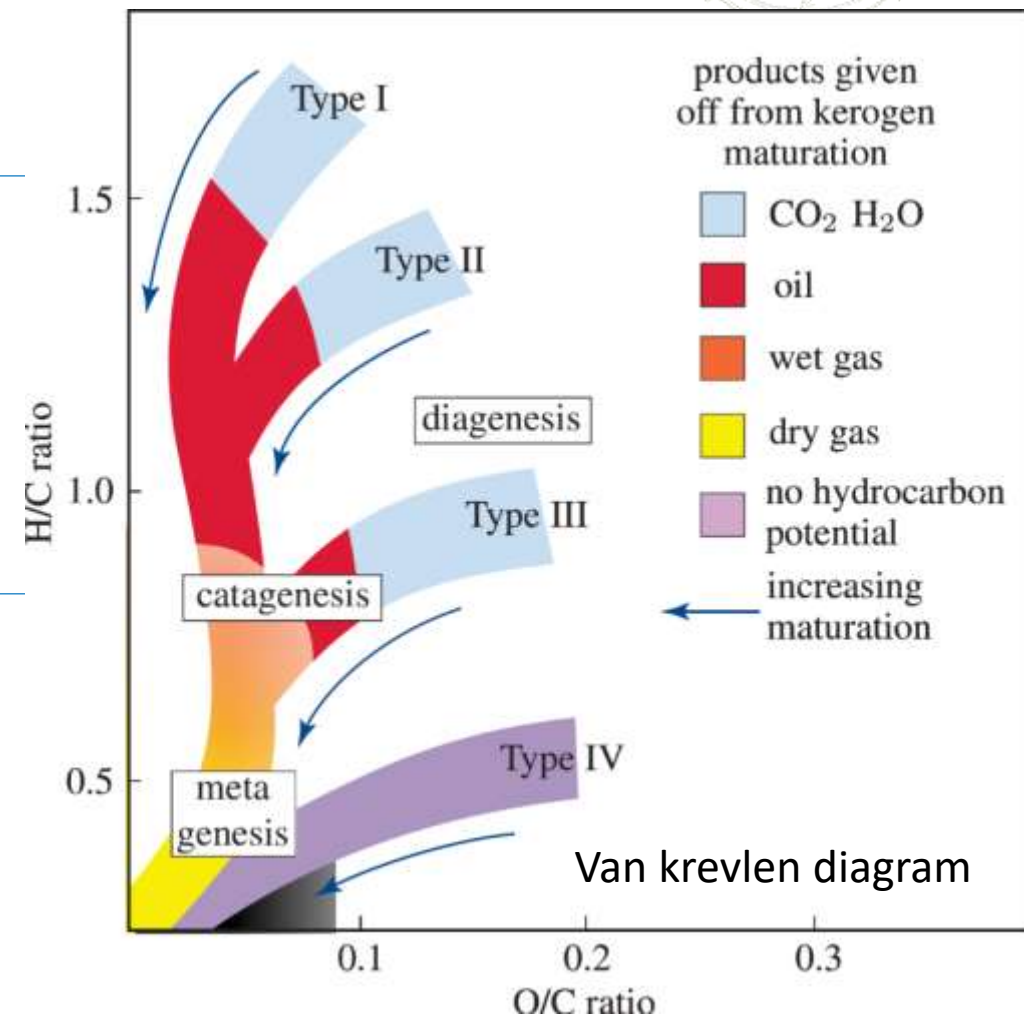
*Diagenesis* (Mostly) biotic degradation of organic matter into kerogen

*Catagenesis* Thermal degradation of kerogen into hydrocarbons



*Metagenesis* Further carbonisation  $\rightarrow$  graphite

Organic matter  $\rightarrow$  kerogen  $\rightarrow$  hydrocarbons in a source rock

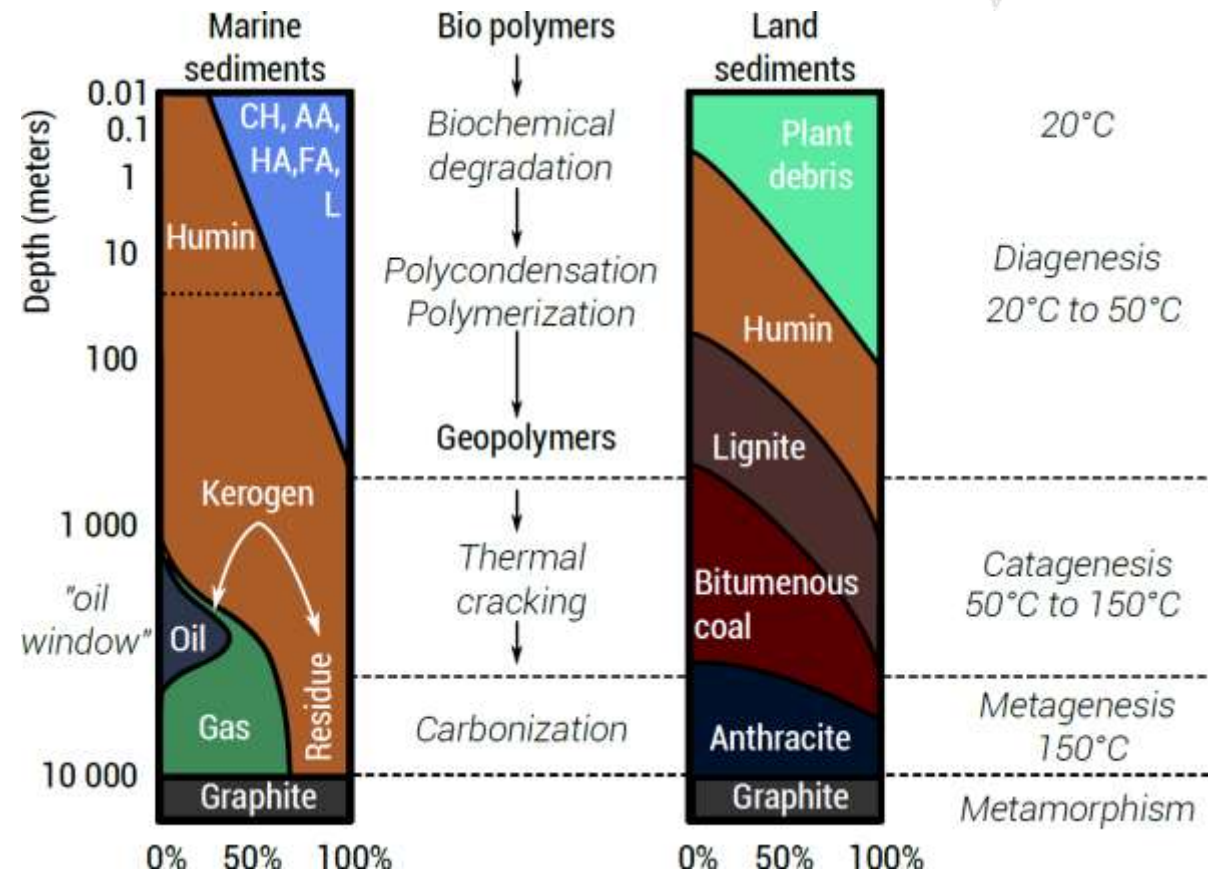
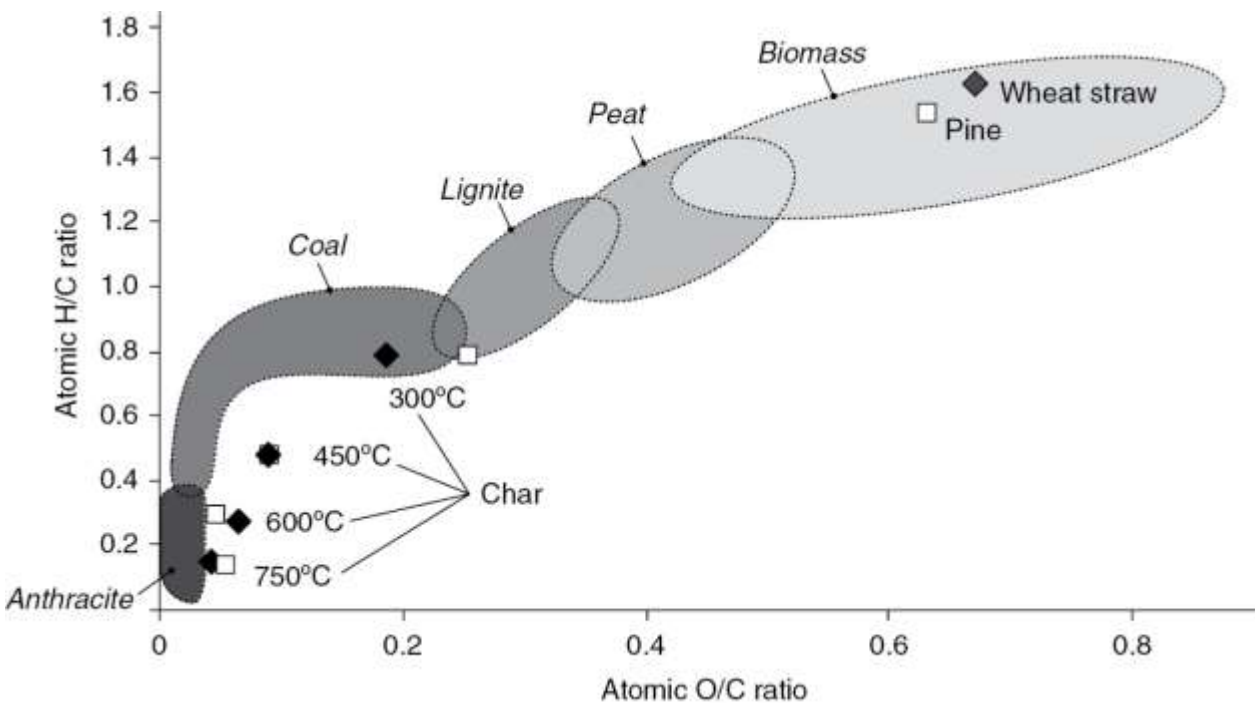


Total Organic Carbon [%]	< 0.5	<1	<2	<4	>4
Source rock quality	Poor	Fair	Good	Very good	Excellent



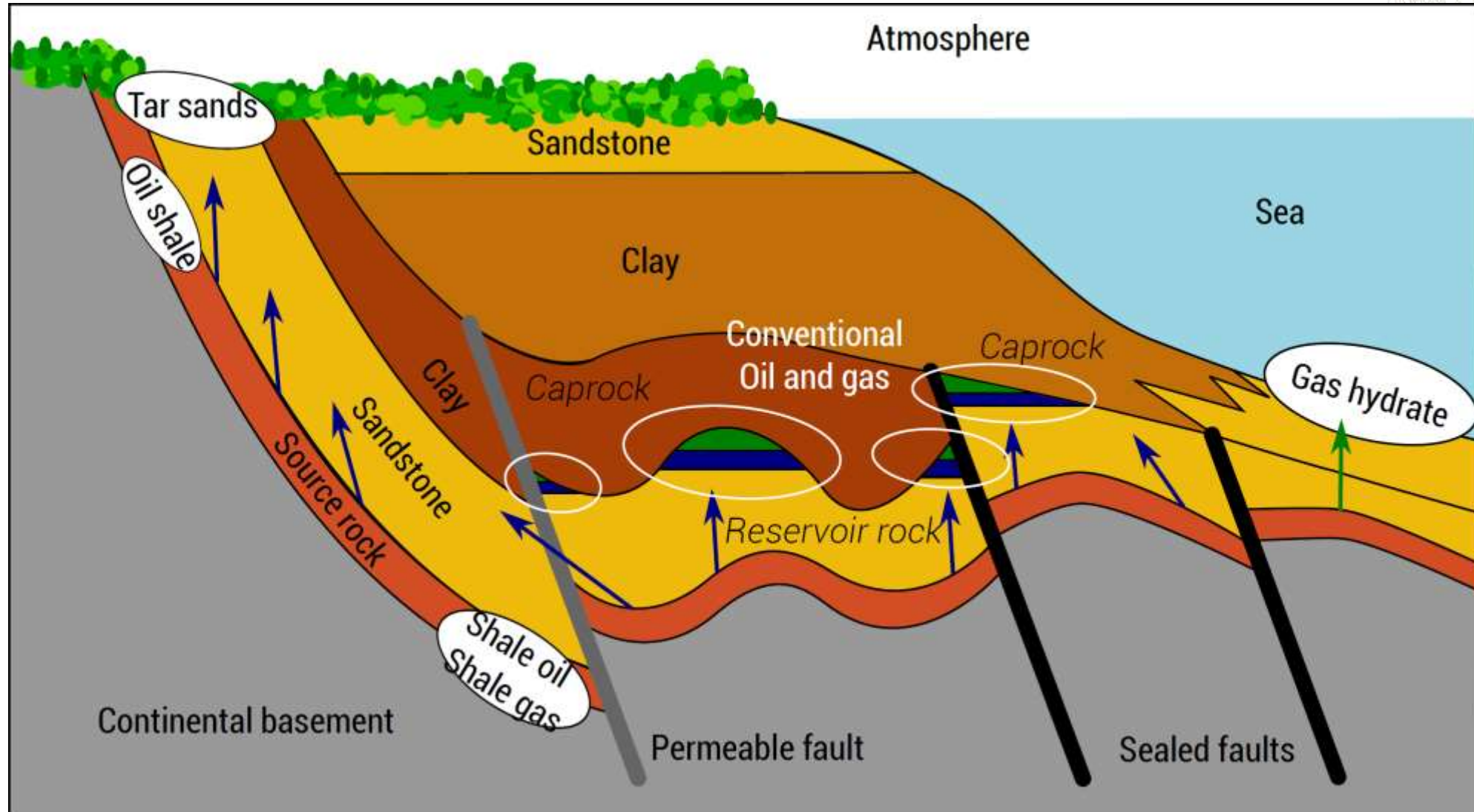
# Maturation – coal & gas

Similar story for coal:



Gas is formed together with coal → firedamp [=grisou]

# Migration



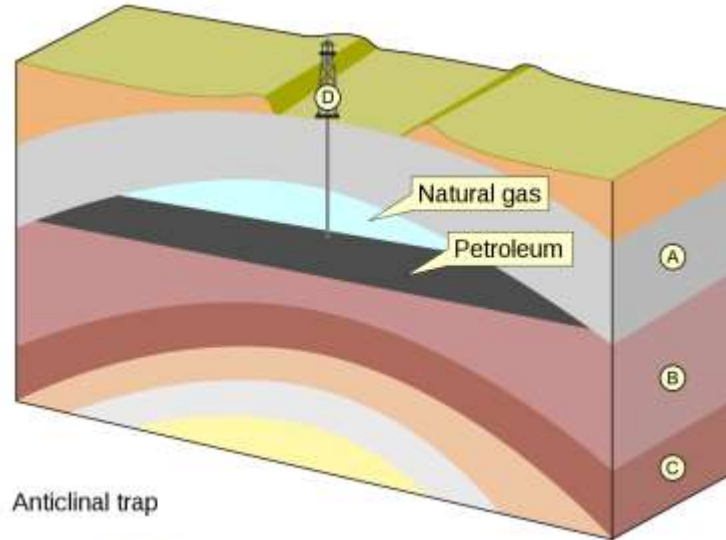
# It's a trap



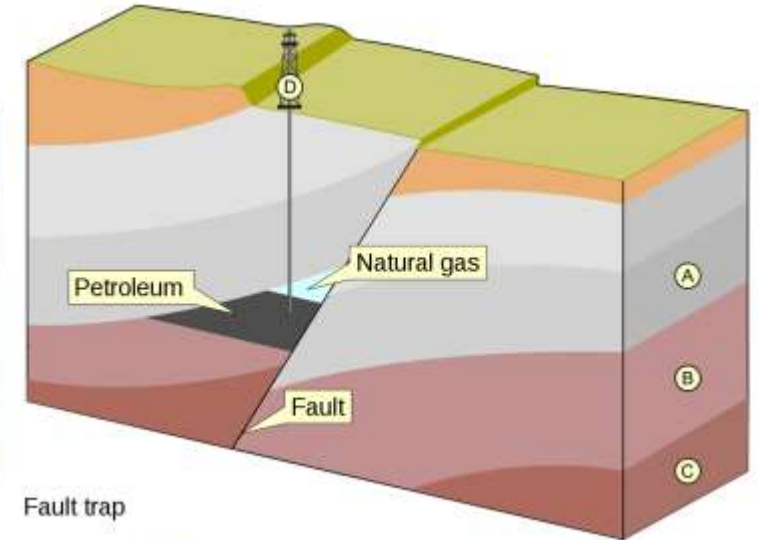
Sometimes gas without oil

Water !

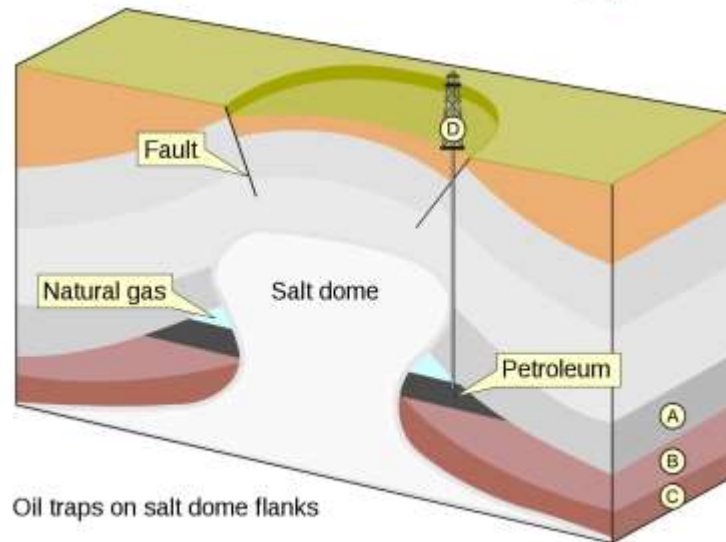
Resource vs reserve



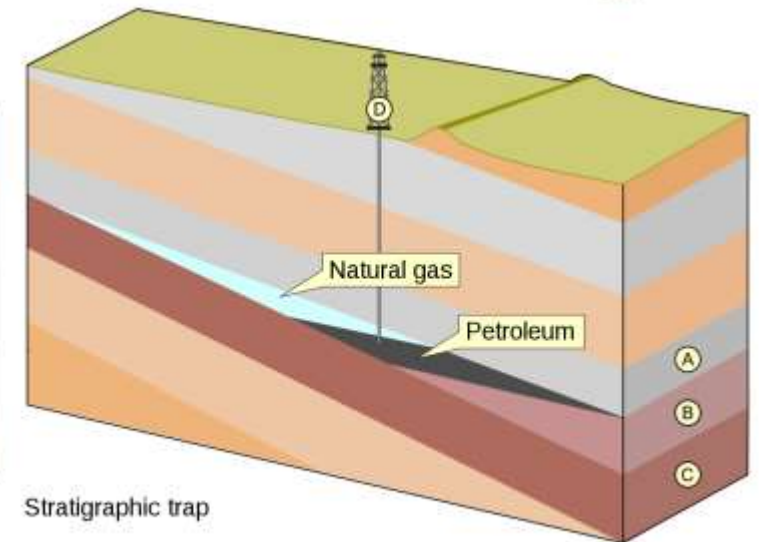
Anticlinal trap



Fault trap



Oil traps on salt dome flanks



Stratigraphic trap

(A) = Impermeable shale

(B) = Porous reservoir rock

(C) = Source rock

(D) = Oil well

# Lecture 2 Fossil fuels

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What, Who, What for, Why ?

Thermo toolbox : the chemical potential

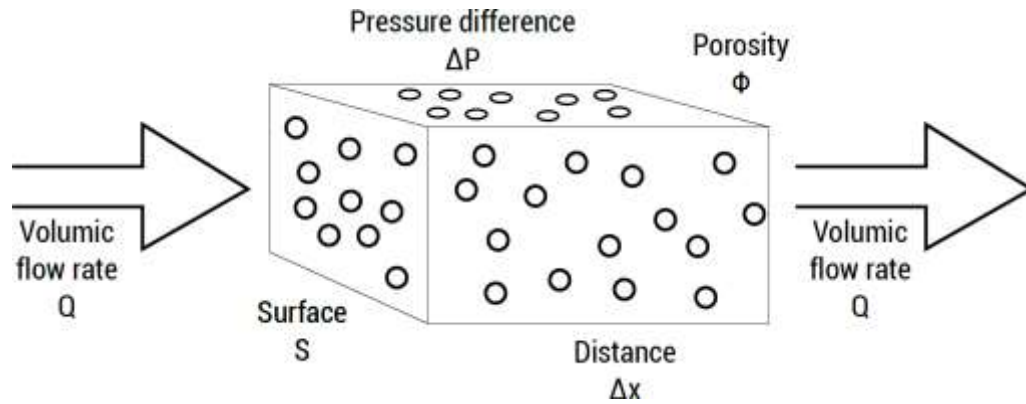
Oil, gas and coal formation: in and out the organic carbon cycle

**Oil (and gas) production: conventional and unconventional sources**

Oil refining: from crude oil to the gas station

Perspectives

# Conventional oil



Porosity

$$\phi = \frac{\text{Empty volume}}{\text{Total volume}}$$

Permeability (Darcy's law)

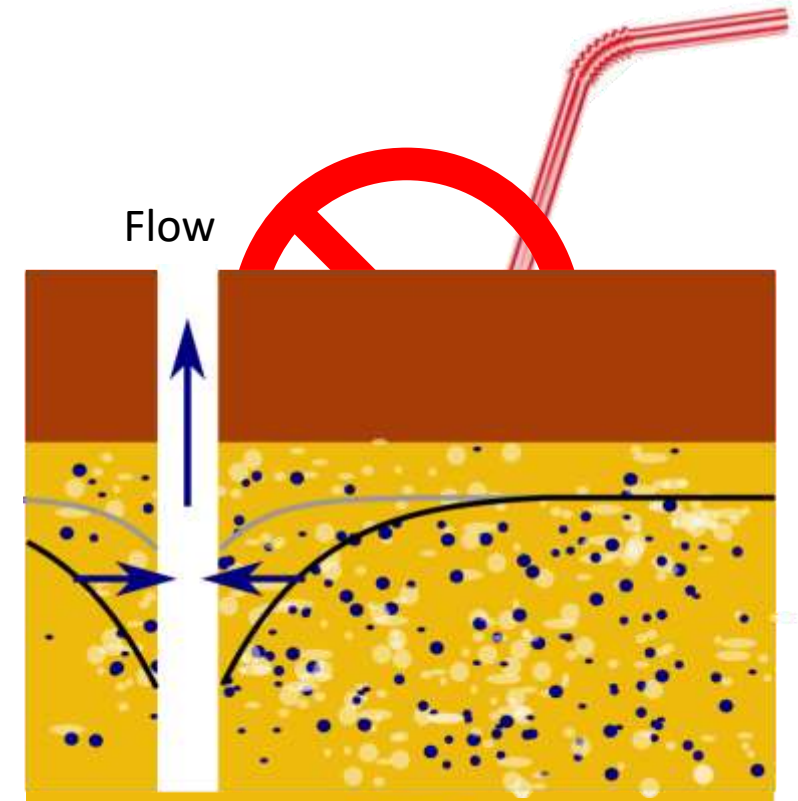
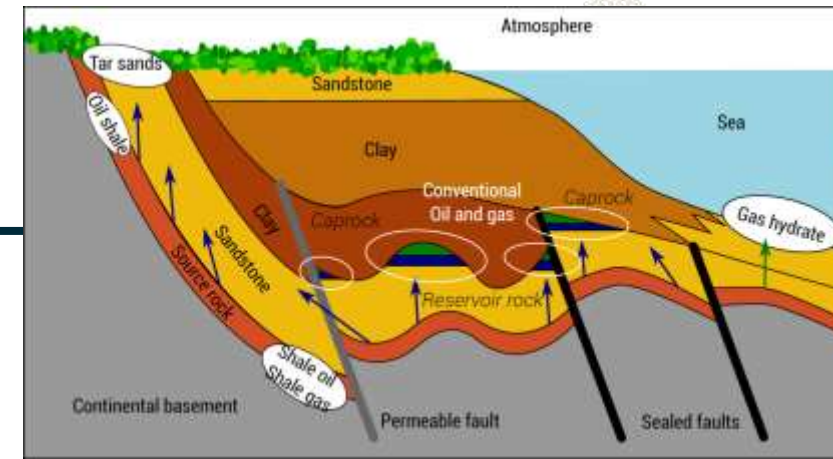
$$Q = k \times \frac{S}{\eta} \frac{\Delta p}{\Delta x}$$

Drill a well  $\rightarrow$  pressure gradient  $\rightarrow$  oil flow

(to bring the oil up, push, don't pull !)

Oil flow  $\rightarrow$  decrease pressure gradient

$$\partial_t p = \frac{k}{\bar{\chi} \eta} \Delta p \quad \longrightarrow \quad R(t) \sim 4 \sqrt{\frac{k}{\bar{\chi} \eta} t}$$



# Consequences

Darcy's law

$$Q = k \times \frac{S}{\eta} \frac{\Delta p}{\Delta x}$$

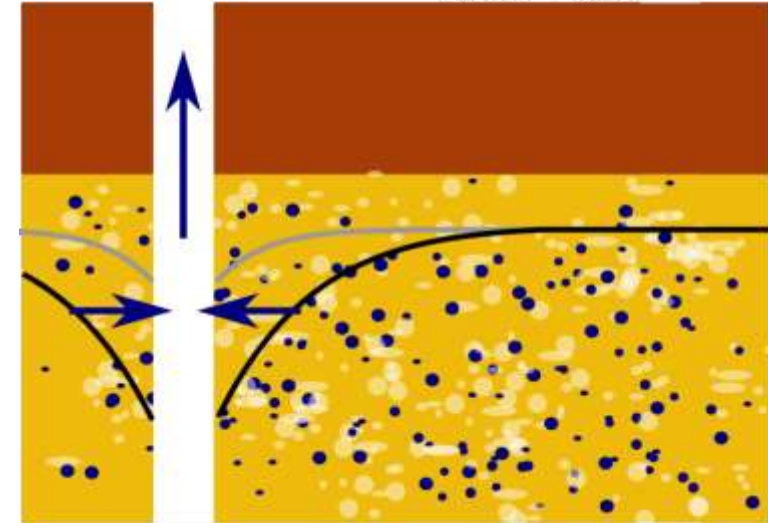


Pressure relaxation

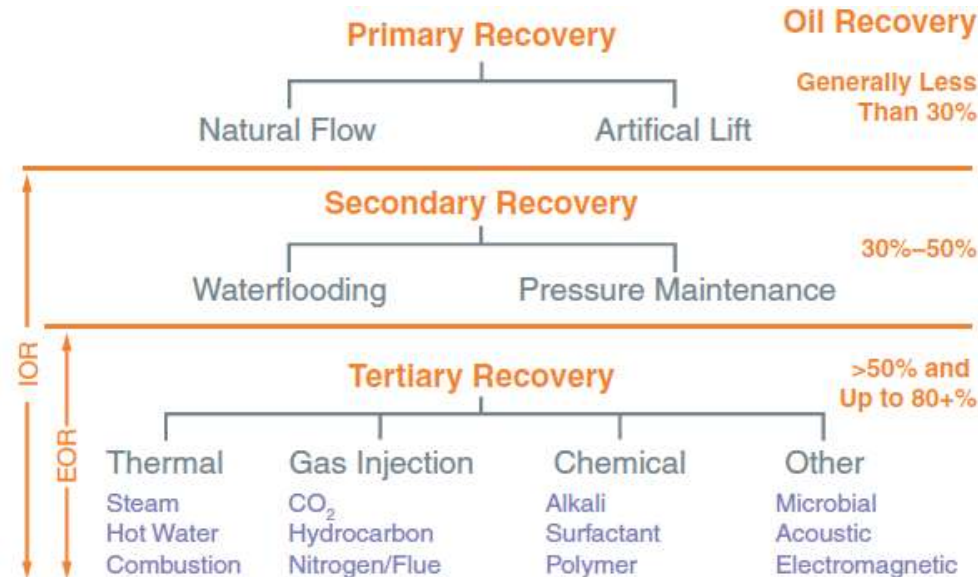
$$R(t) \sim 4 \sqrt{\frac{k}{\bar{\chi} \eta} t}$$

Competition between wells

Don't drill too close to the neighbour !



Exploitation phases



Source: SPE Papers 84908 and 87864

Fig. 2—Defining improved oil recovery (IOR) and enhanced oil recovery (EOR).



100% recovery is impossible

# Unconventional petroleum



*Shale oil = tight oil* [pétrole de schiste, de roche mère]

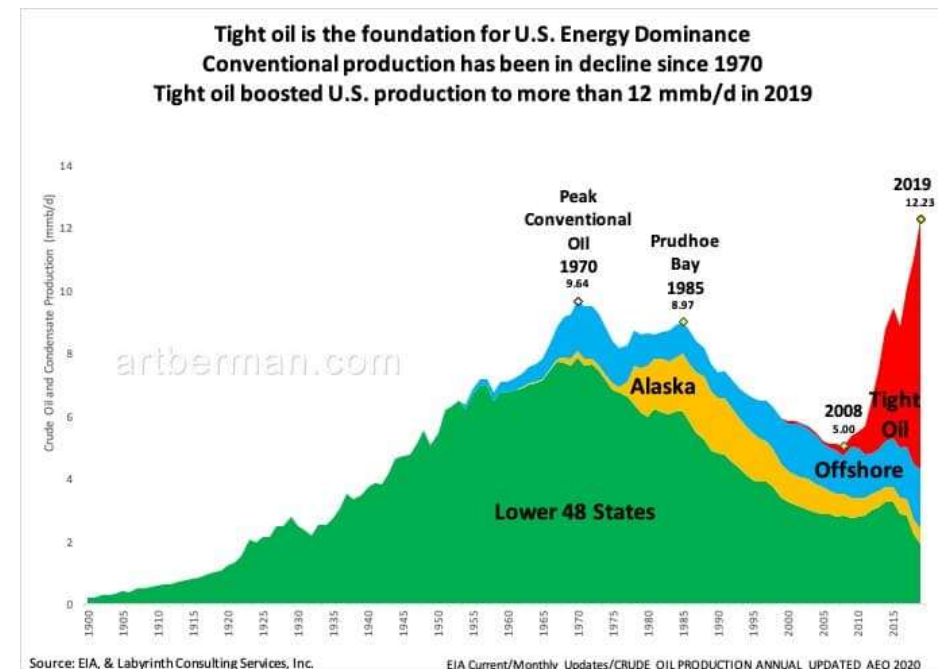
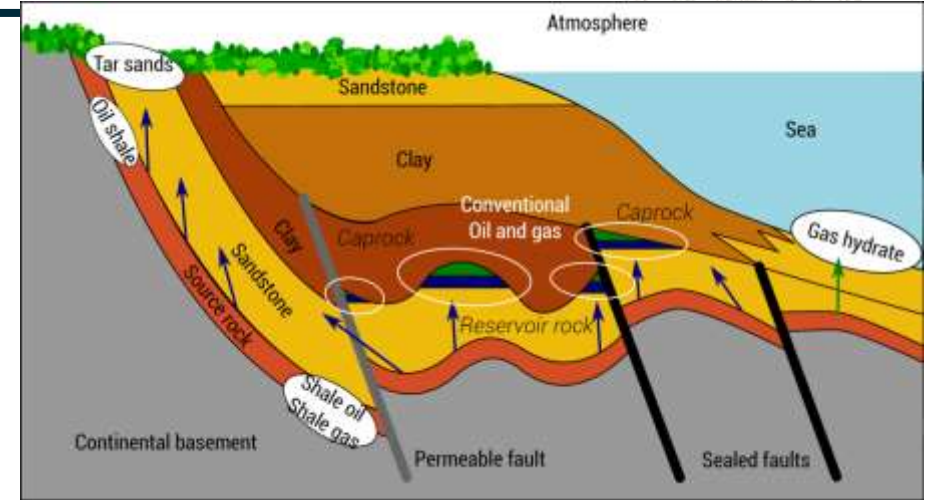
*Shale gas* [gaz de schiste]

Fracture low permeability source rocks to recover hydrocarbons



*Oil shale* [schistes bitumineux] → oil shale oil [huile de schiste].

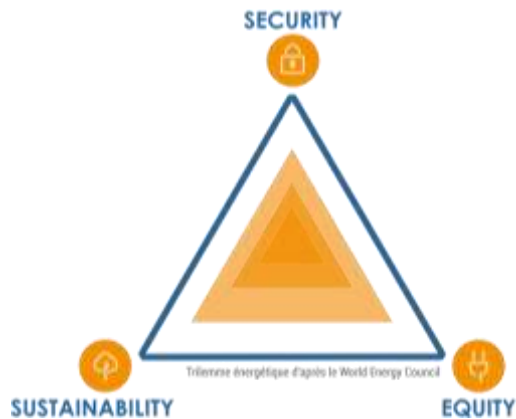
Immature source rock, requires treatment to process kerogen into synthetic fossil fuels.



Fracking techniques?

Energy return on investment?

Economic viability?





# Lecture 3 Fossil fuels

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What, Who, What for, Why ?

Thermo toolbox : the chemical potential

Oil, gas and coal formation: in and out the organic carbon cycle

Oil (and gas) production: conventional and unconventional sources

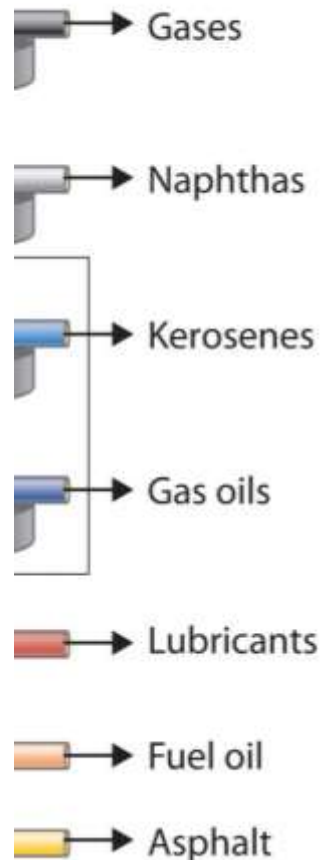
**Oil refining: from crude oil to the gas station**

Perspectives

# Refining oil – what, why?



Crude oil in, oil products out



Costly and complicated operation  
*(15% of industry consumption in the US !)*

*Why bother?*

Specific properties for specific applications

You can eat everything but the oink



# Application: diesel and gasoline (1/2)

Otto cycle efficiency (see next lecture)

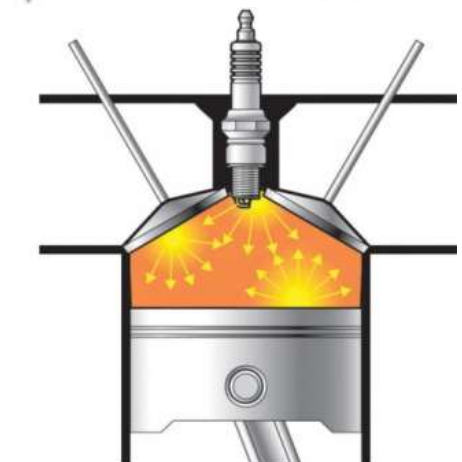
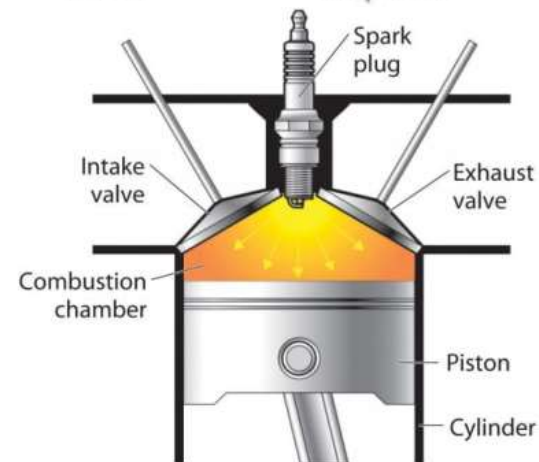
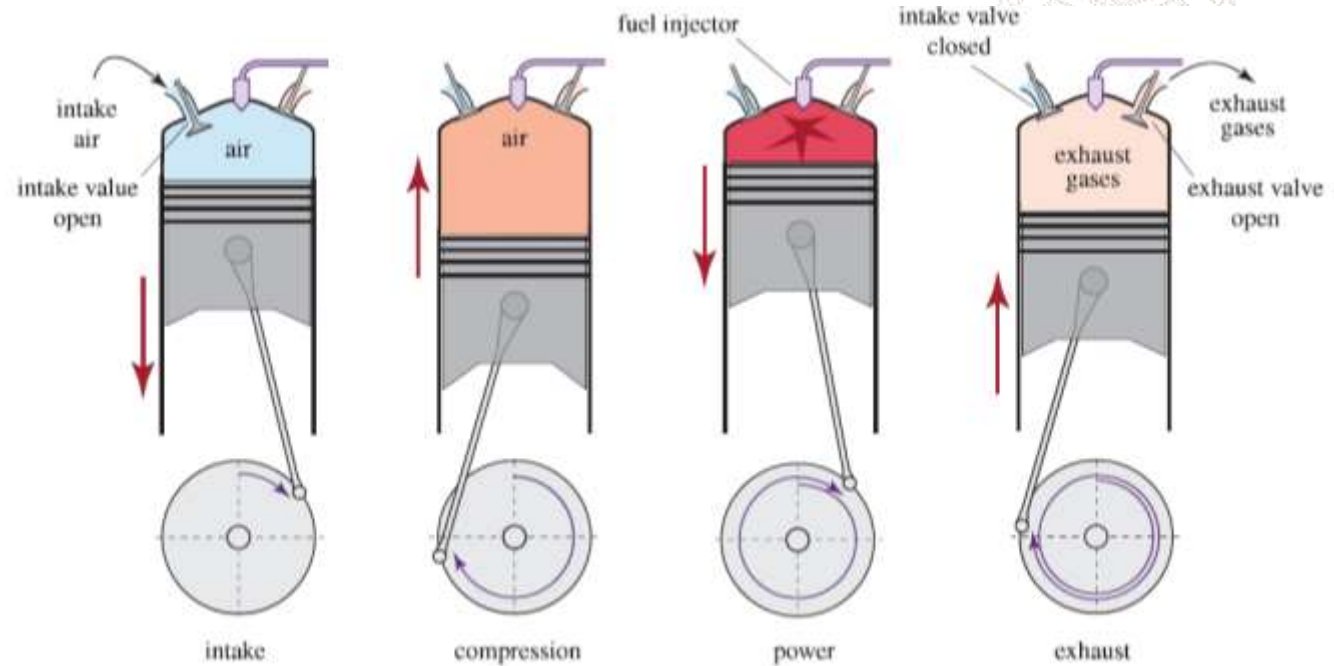
$$\eta = 1 - \frac{1}{r^{\gamma-1}}$$

*compression ratio*

Higher compression ratio

→ more work recovered from fuel

Problem: self ignition (knocking)



(a) Normal combustion

(b) Premature combustion

# Application: diesel and gasoline (2/2)

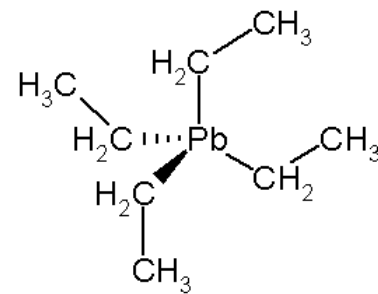
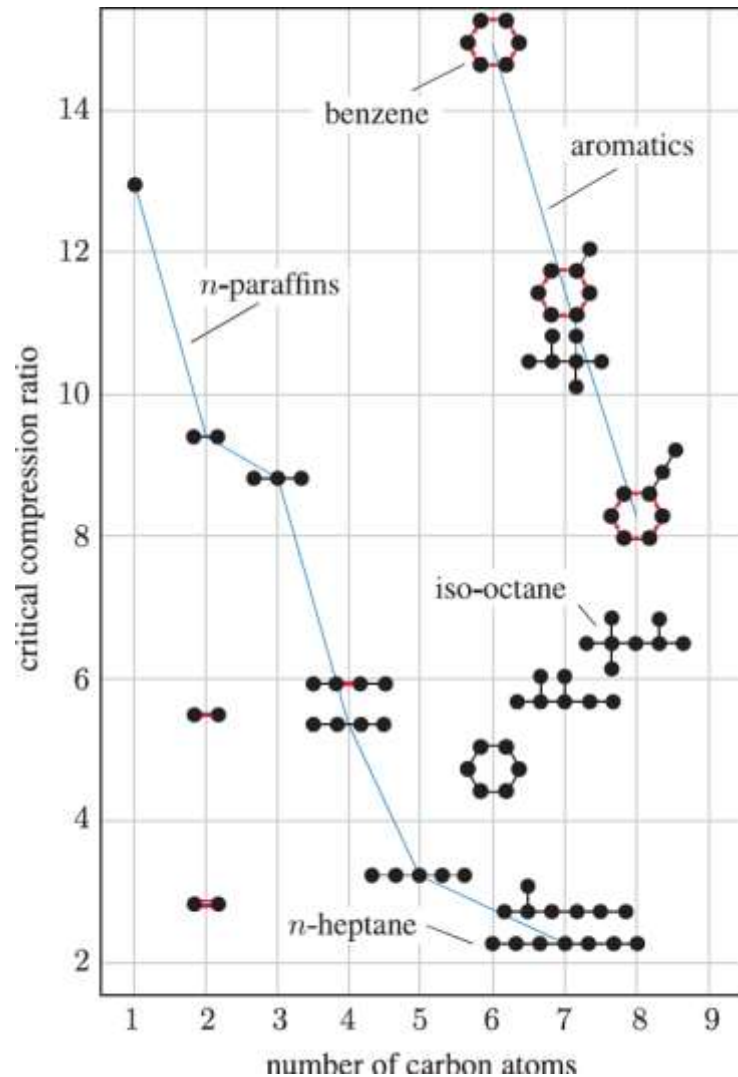


Knock resistance: Octane Number

0 = n-heptane

100 = iso octane

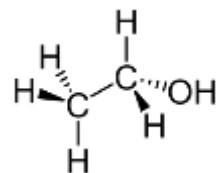
- Don't compress too much (if your car don't need so much power)
- Select fuels with high critical compression ratio  
*Iso octane, aromatics*
- Add antiknock agent
- Self ignition proof design



Tetraethyllead

Banned due to toxicity

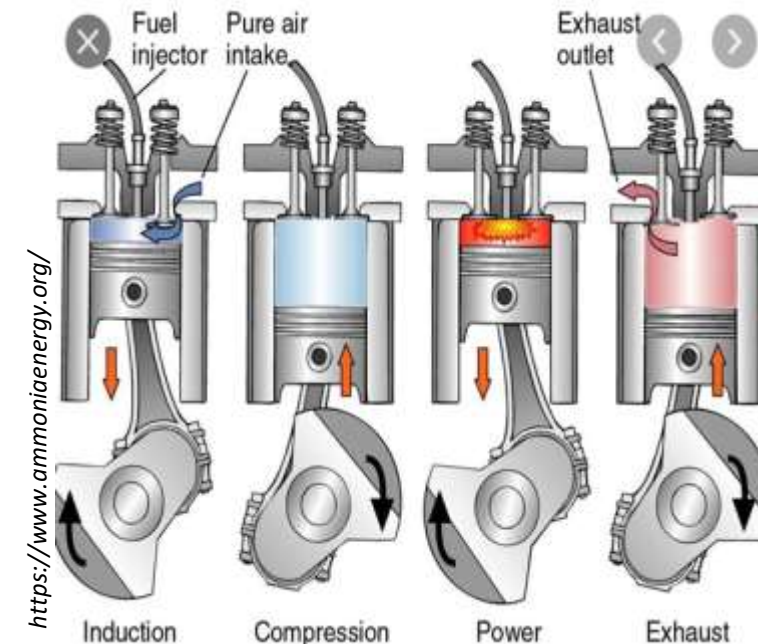
Unleaded fuels  
[=*sans plomb*]



Ethanol

Ethanol / gasoline mix :

$$x 21.2 + (1 - x) 35 \text{ [MJ/L]}$$





# Application: diesel and gasoline (2/2)

➤ Don't compress too much (if your car don't need so much power)

➤ Select fuels with high critical compression ratio

➤ Add antiknock agent

➤ Self ignition proof design



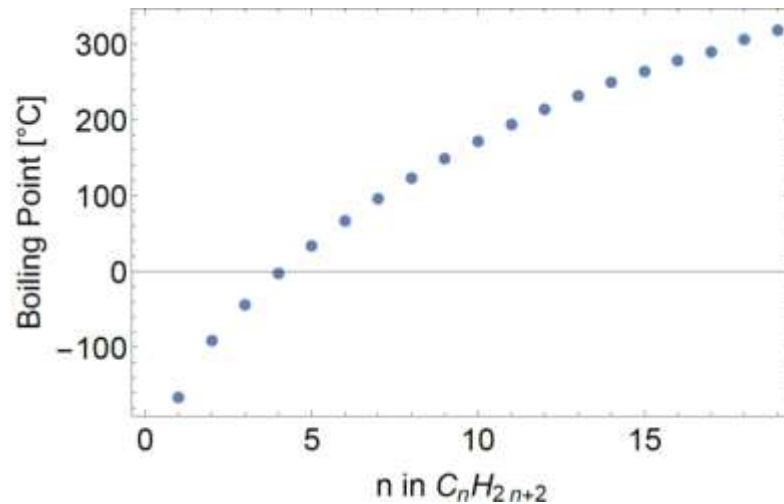
# Boiling a mixture



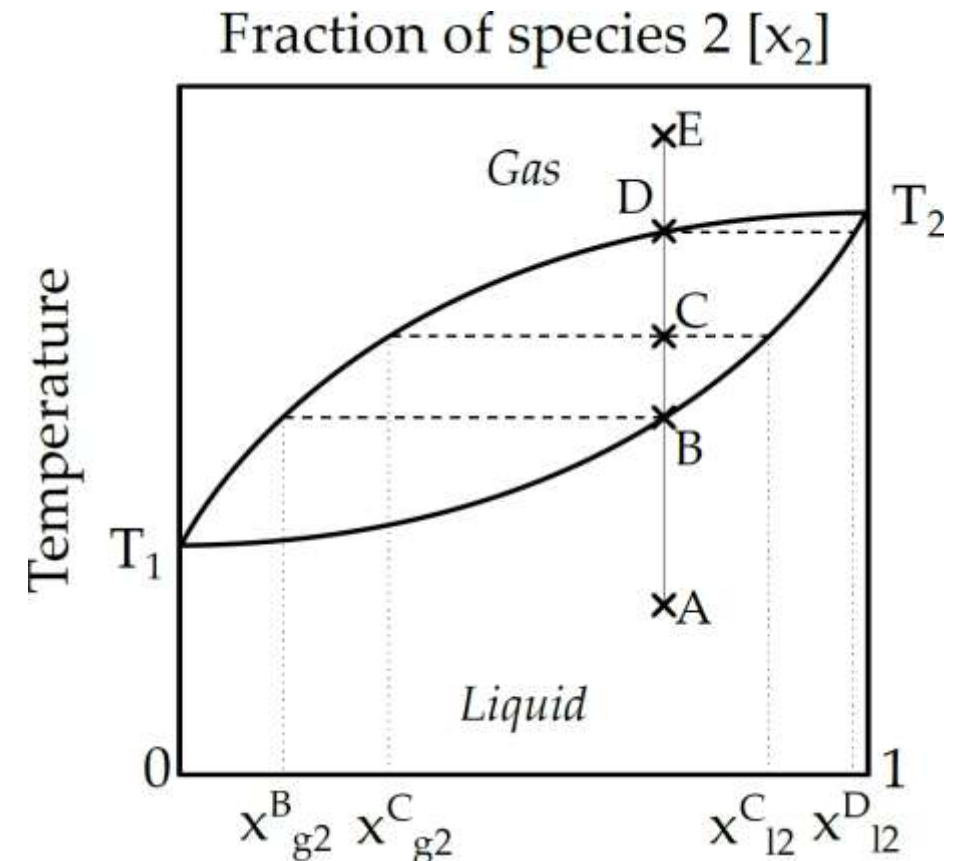
Different hydrocarbons have different boiling temperatures



Distillation

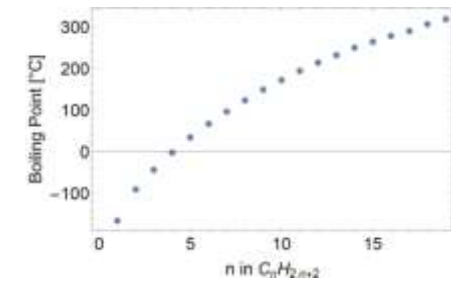
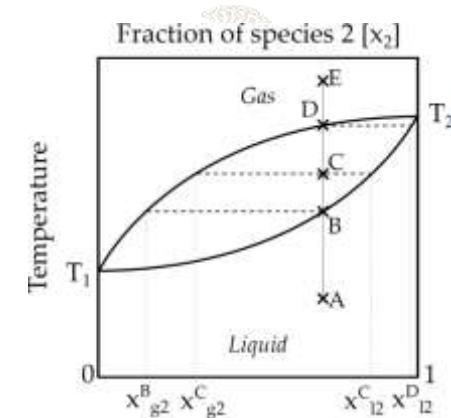
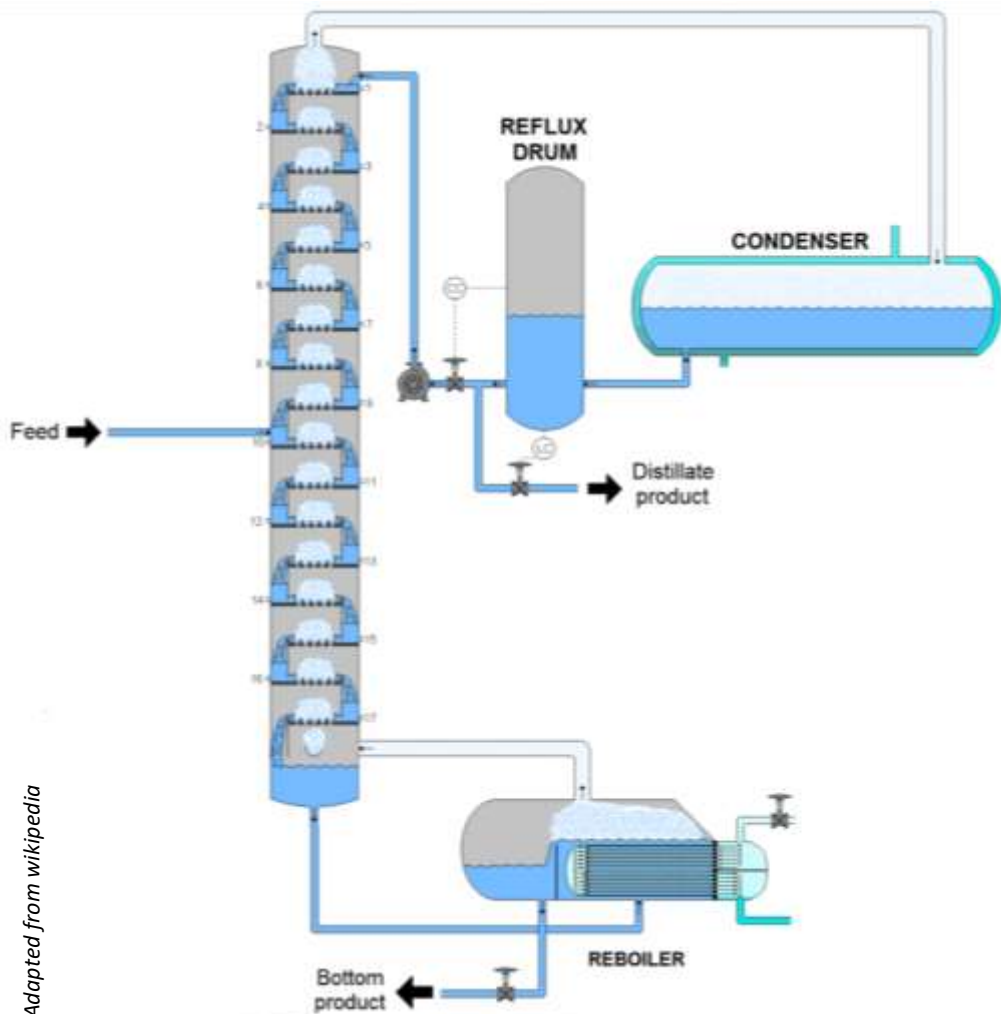


- A: Heat up a mixture of species 1 and 2 with two different boiling temperatures ( $T_1 < T_2$ )
- B: The mixture starts boiling. The first bubble of gas is enriched in species 1
- D: All the mixture turned into a gas. The last droplet is enriched in species 2



(calculated from chemical potentials !)

# Distillation - principle



Introduce pre heated feedstock of crude oil

At a given tray

- Gas phase enriched in lighter species  
→ moves up to the next tray
- Liquid phase enriched in heavier species  
→ falls down to the previous tray

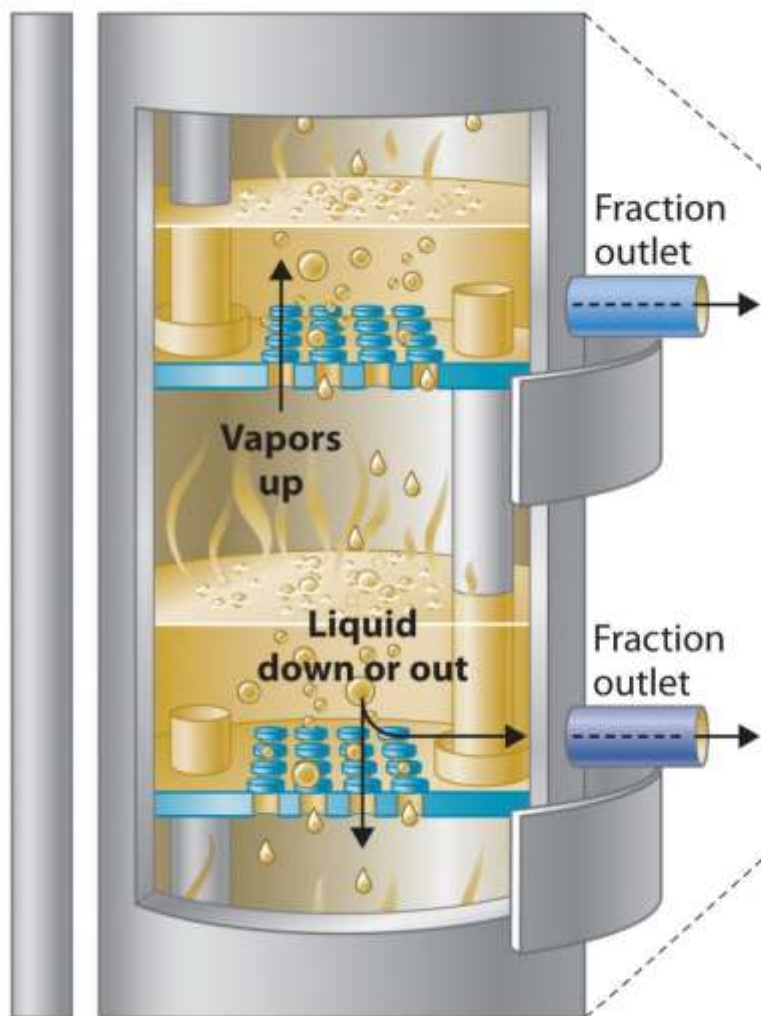
Cuts @ given locations

⇔ given temperatures

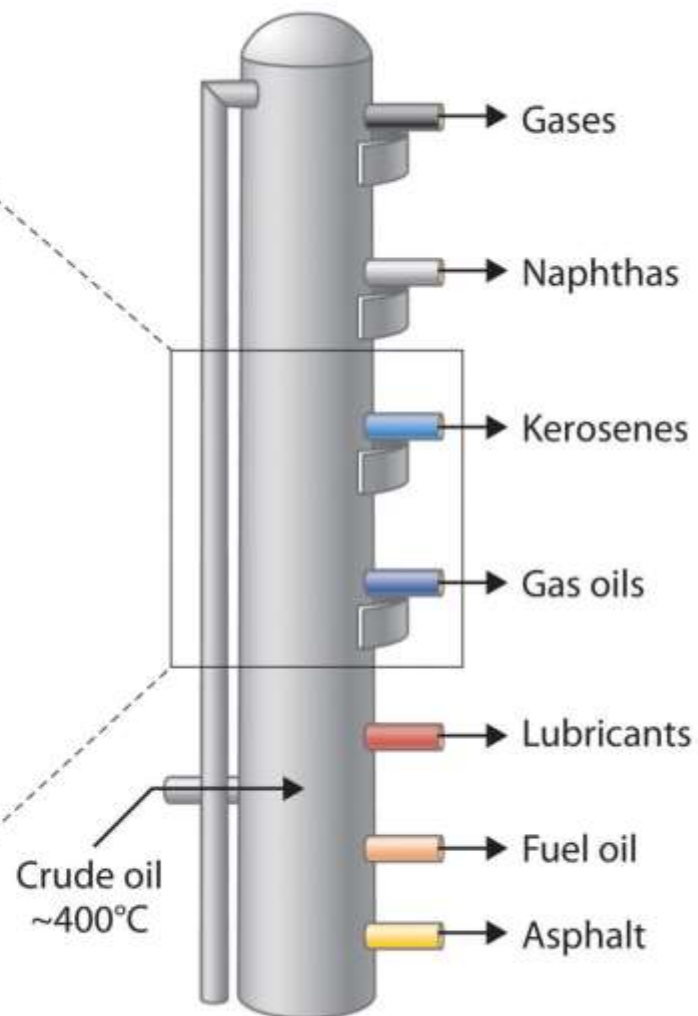
⇔ given compositions



# Distillation tower



(a) Petroleum distillation tower



(b) Petroleum fractions

	Number of carbons	Boiling point range	Uses
Gases	1-4	0-30°C	Bottled and natural gas
Naphthas	5-10	30-180°C	Gasoline
Kerosenes	10-16	180-260°C	Kerosene for home heaters, jet fuel
Gas oils	16-60	260-350°C	Diesel fuel, feedstock for cracking
Lubricants	>60	350-575°C	Motor oil, feedstock for cracking
Fuel oil	>70	>490°C	Candles, fuel oil for ships and power stations
Asphalt	>80	>580°C	Roofing tar, road tar





# Refining chemistry

## Cracking / polymerization

Turn large / small chains into small / large chains

Change an oil product into another

## Reforming

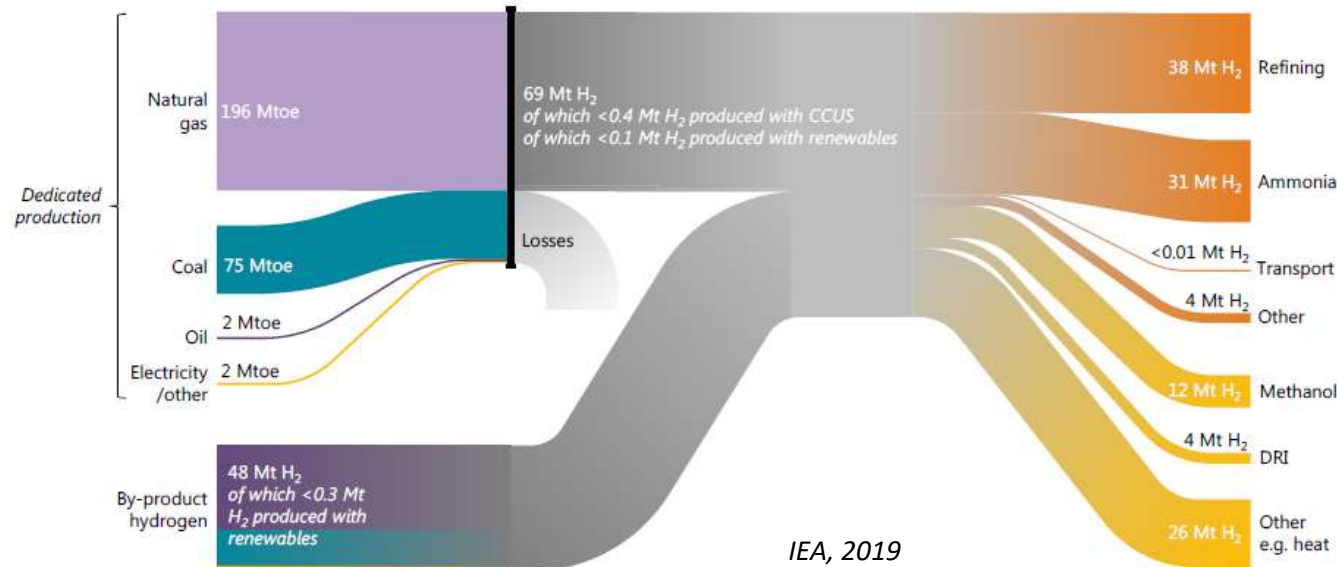
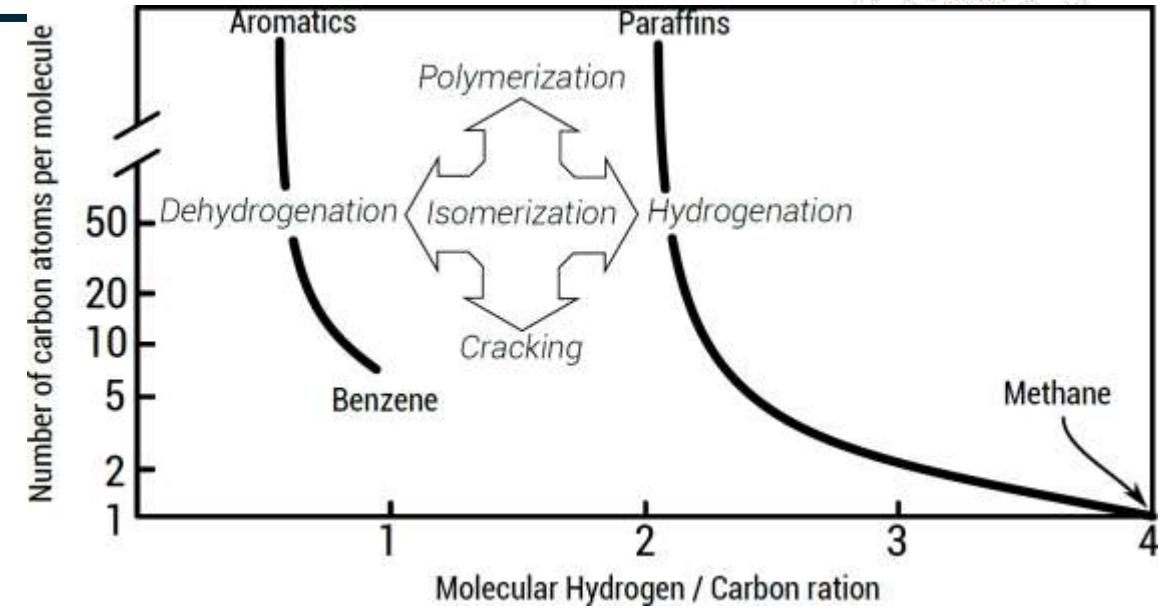
Create double bonds → produces H

Increase octane number

## Purifying

Separate different molecules

Remove heteroatoms (N,S) → requires H

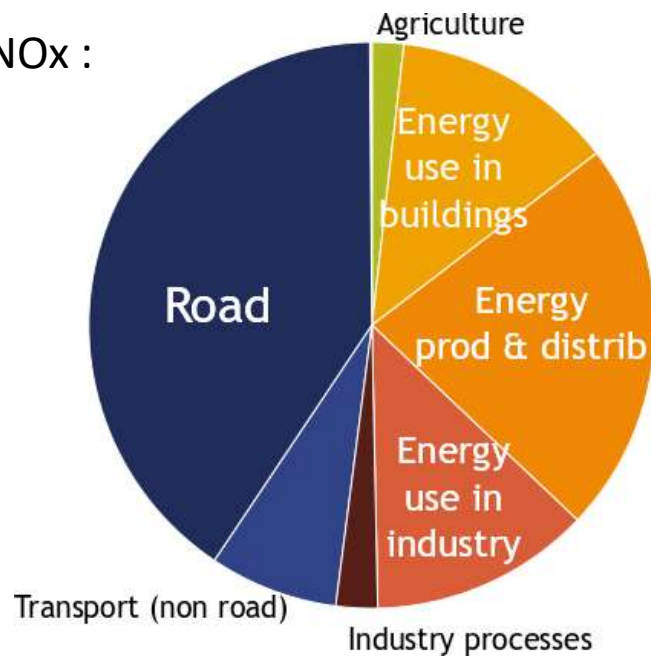


# Nitrogen and sulfur oxides



SOx : fossil fuels combustion

NOx :

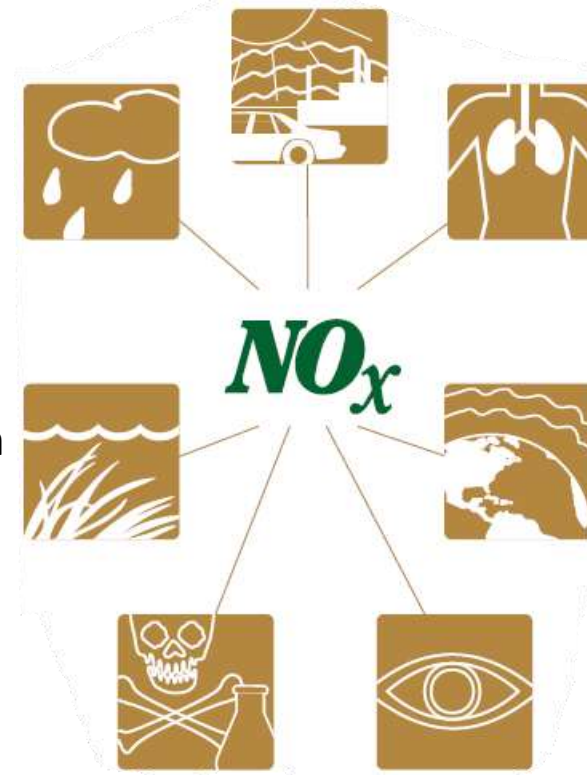


European Environment Agency



NOx + volatile compounds + sunlight  
Ground-level Ozone (Smog)

Acid rain



NOx + ammonia  
Particles

Water Quality Degradation  
Eutrophication

Global warming  
GWP N<sub>2</sub>O = 250

Toxic chemicals

Fog



# Lecture 3 Fossil fuels

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What, Who, What for, Why ?

Thermo toolbox : the chemical potential

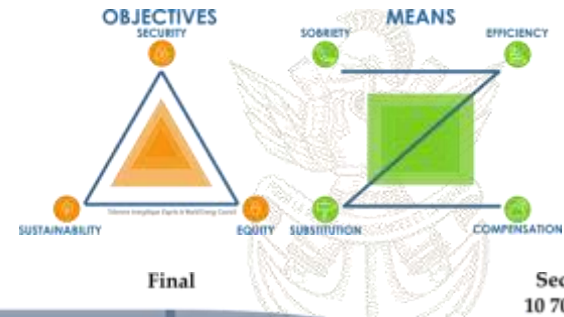
Oil, gas and coal formation: in and out the organic carbon cycle

Oil (and gas) production: conventional and unconventional sources

Oil refining: from crude oil to the gas station

**Perspectives**

# Alternatives to fossile fuels?



Restraint

Yes !



Compensation

CCS (PC 3)



Efficiencies

Lecture 4 (heat engines)

Lecture 8 (heating)

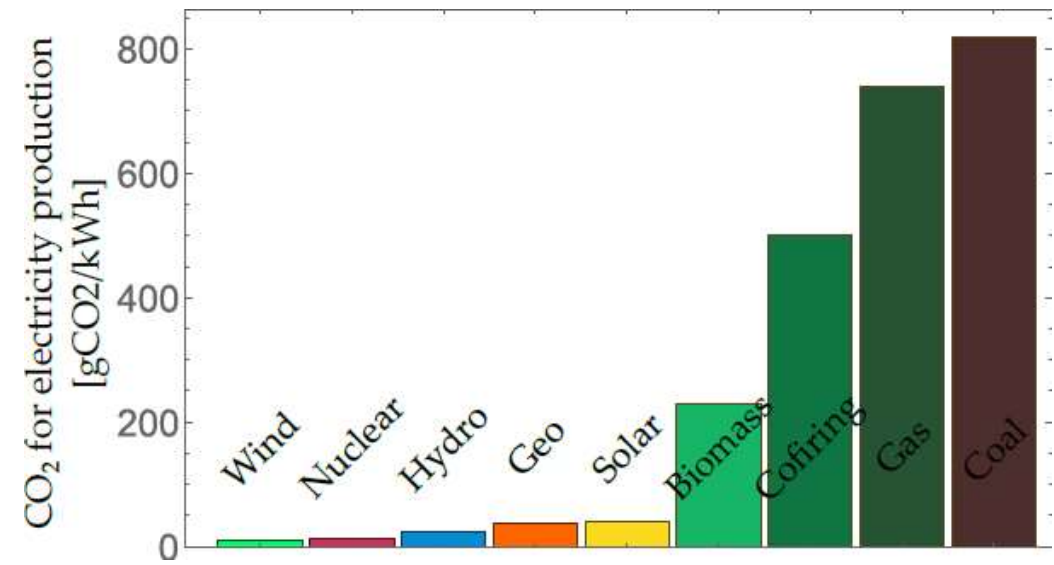
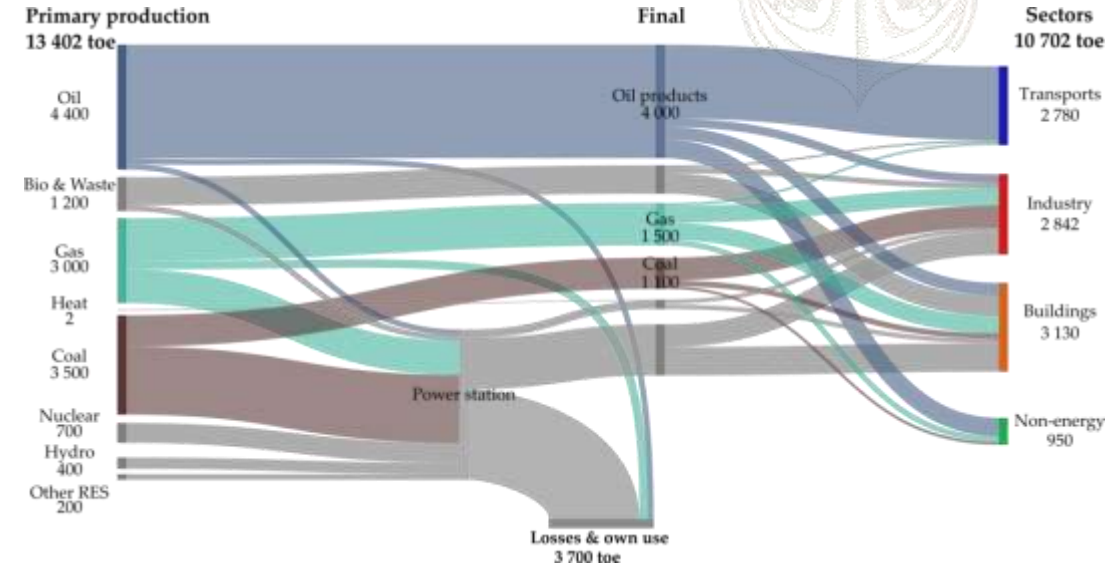


Substitution

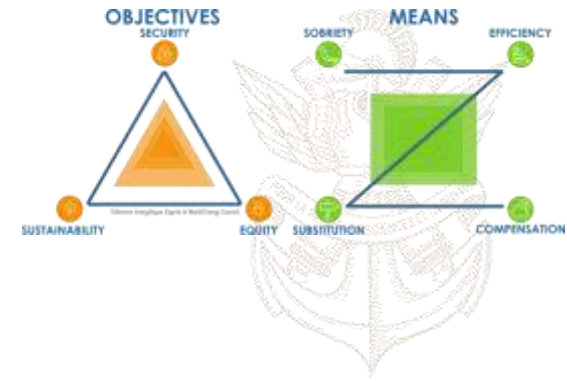
Electricity (lectures 5,6,7,9)

Heating (lectures 8)

Transport (lecture 9)



# Alternative fuels



## Biomass based

Conventional  
1st generation

(Edible) crops → Bioethanol, biodiesel

Advanced  
2<sup>nd</sup>, 3rd generation

Non competing with food & feed  
Residue, municipal wastes, used cooking oil, algae...



## Electricity based

Electric battery

(loaded with low carbon electricity !)

Fuel cell

Hydrogen flow to electricity current



## Hydrogen based

Ammonia

Hydrogen combined with atmo nitrogen

e-fuels

Hydrogen to reduce CO<sub>2</sub> into hydrocarbon

# Alternative questions



Technical specificities?

*power density, freezing point...*

Costs?

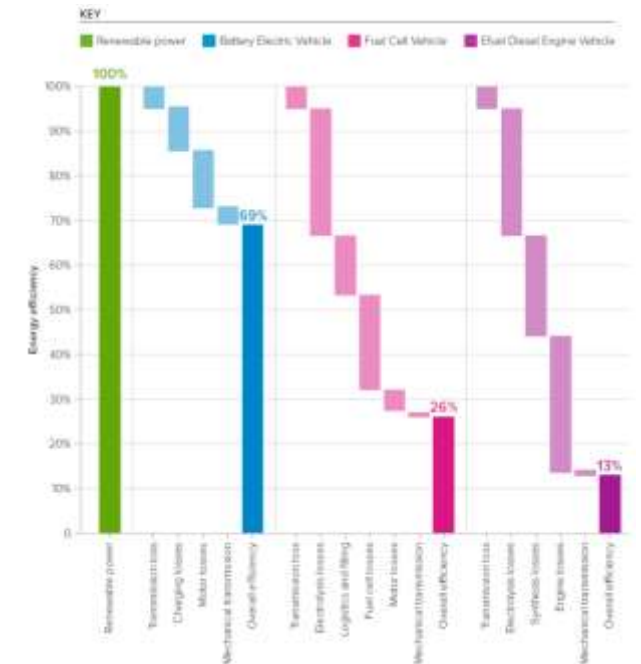
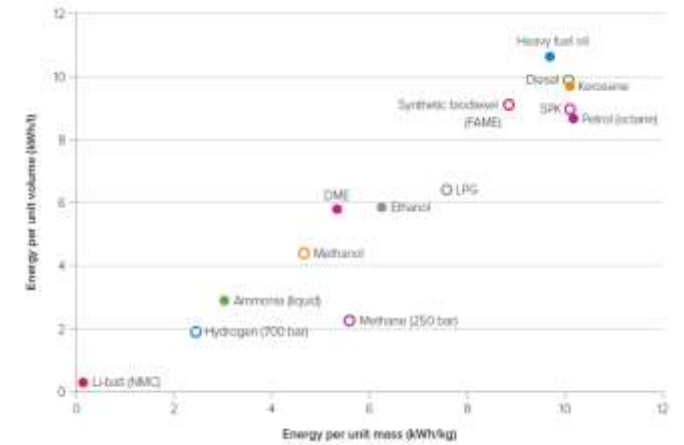
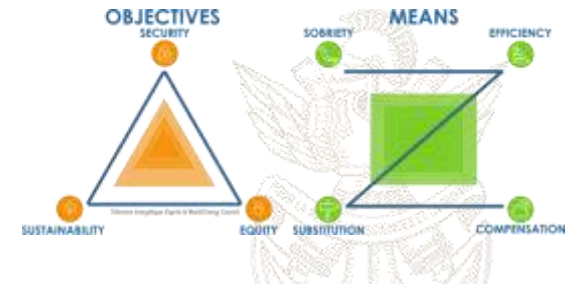
*Overall efficiency, feedstock availability...*

Supply chain?

*Compatible with current infrastructures?*

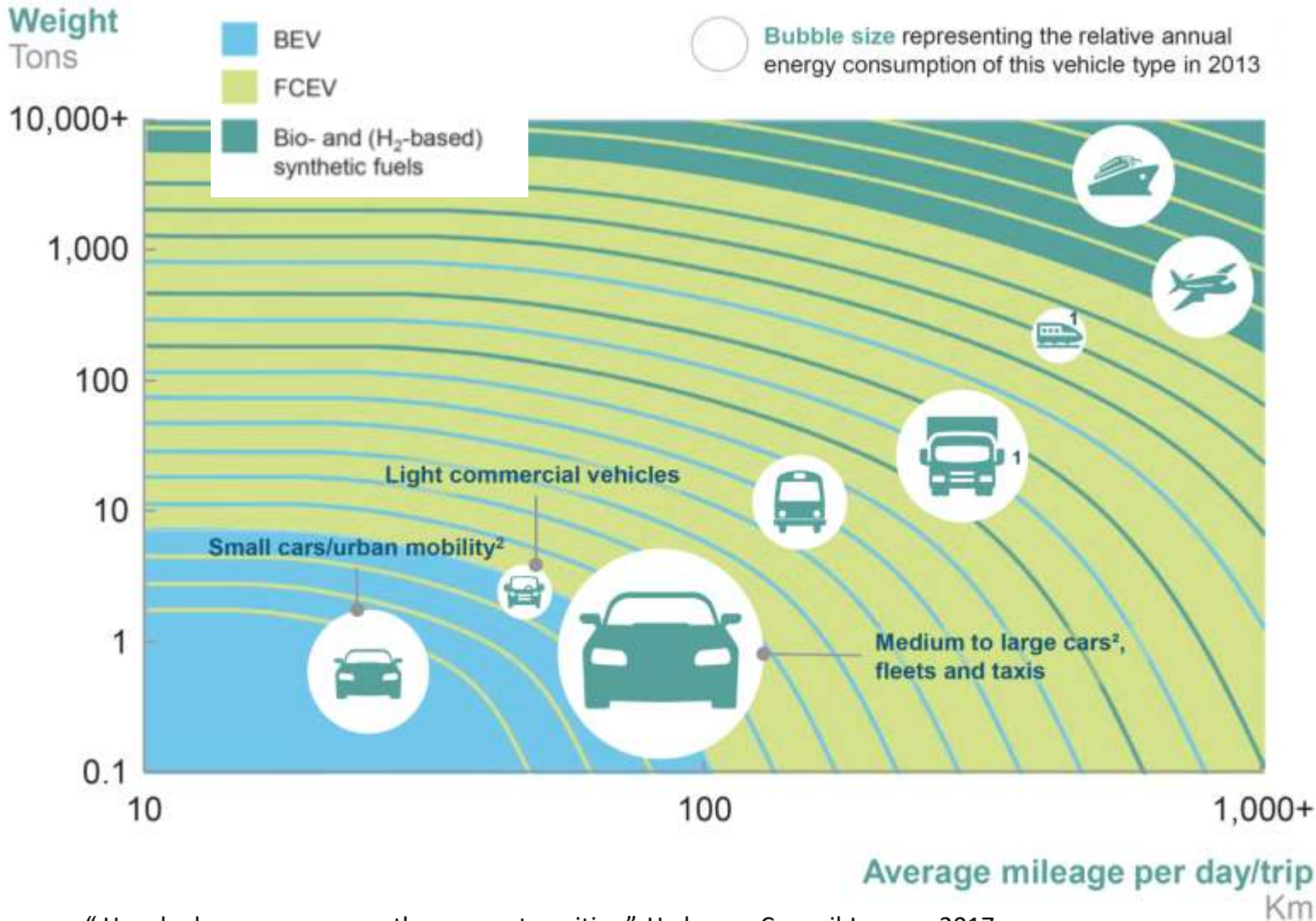
Environmental impacts?

*Sustainability besides CO<sub>2</sub>*





# The right fuel for the right transport

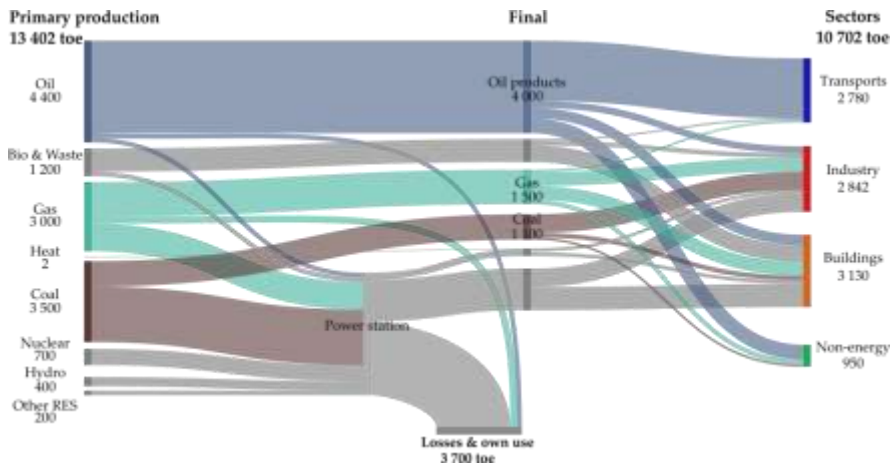


Vehicle and duty cycle compatibility	Synthetic efuels	Biomethane	Hydrogen	Electricity
City car		CNG		
Long distance car		CNG		
Urban van		CNG		
Heavy-duty truck		LNG		
Aviation Short haul				
Aviation Long haul				
Marine Short journey		LNG		
Marine Long journey		LNG		

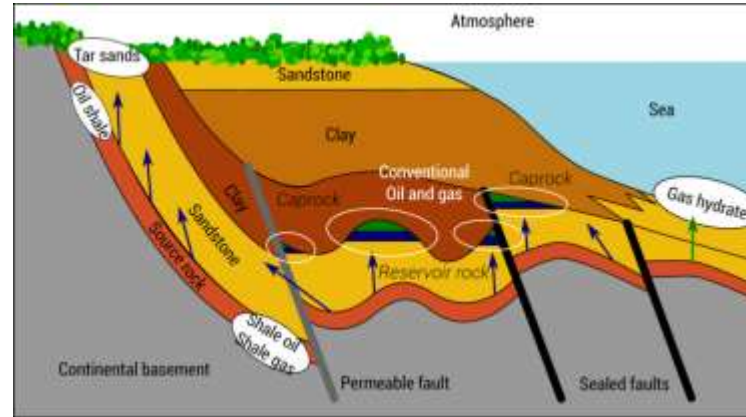
# Take home message



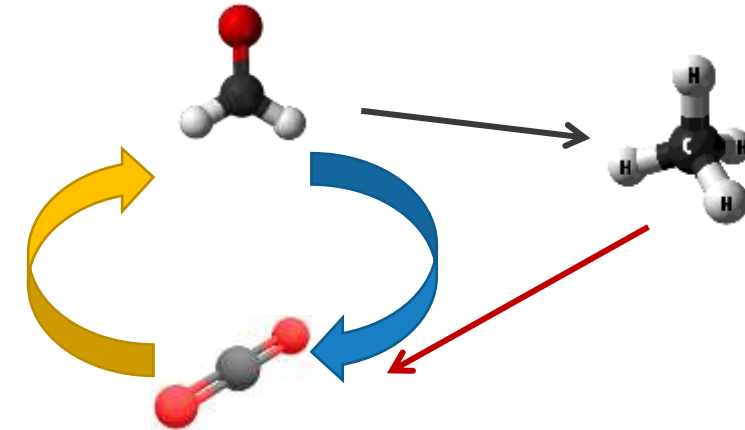
## Oil, coal and gas: what, why?



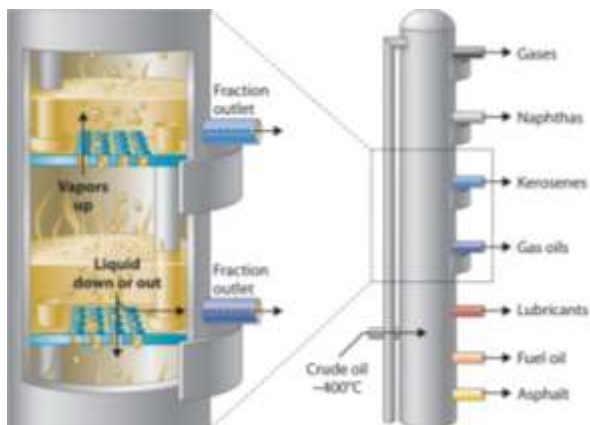
## Basic petroleum vocabulary



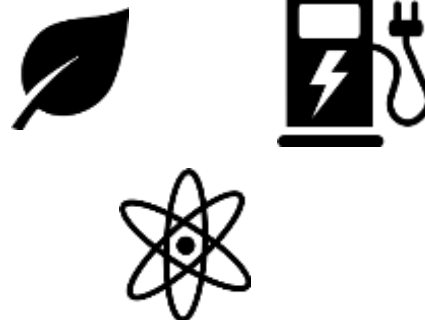
## In and out the organic carbon cycle



## Refining 101



## Alternative fuels



It's all about the chemical potential !

$$G(N, T, p) = H - TS = N \mu(T, p)$$