Levi Cases

Università degli Studi di Padova

CENTRO STUDI
DI ECONOMIA E TECNICA DELL’ENERGIA
“GIORGIO LEVI CASES”

evento: «Le ricerche del Levi Cases»

10 anni di Levi Cases: la transizione energetica al centro

ALBERTO BERTUCCO

Centro «Levi Cases» per l'economia e la tecnica dell'energia

Università di Padova

Corte Benedettina, Sala Agricoltura, Via Roma 34, 35020 Legnaro PD

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Qui Houston, abbiamo un problema

1. La concentrazione dei gas serra nell'atmosfera aumenta molto velocemente (rispetto al tempo caratteristico di risposta dell'ecosistema)
2. Tale fenomeno crea un riscaldamento globale dell'atmosfera e degli oceani, altrettanto veloce e preoccupante
3. Questo riscaldamento ha due effetti fisici principali:
   i. scioglie i ghiacci, innalzando i livello del mare
   ii. fa aumentare il contenuto di acqua nell'atmosfera per evaporazione (per 1°C, il 6% in più!)

Che cosa fare per trovare una soluzione?

1. azzerare le emissioni di gas serra nell'atmosfera causate dalle attività dell'uomo
2. ripulire l'atmosfera dei gas serra che vi si sono accumulati
3. adattarsi alle trasformazioni in atto («prenderla nel fiocco»)

oppure: BAU (la «peste» non c'è), far finta di nulla, e…

4. …sperare che l'ecosistema sia capace di reagire da solo. («who knows?», cioè «non possiamo escluderlo»)

Analisi del problema: perché si sono accumulati i gas serra?

1. La differenza fra gas ad effetto serra e CO_2
2. L'emissione di CO_2 è la conseguenza del nostro modo di produrre energia degli ultimi 200 anni: la combustione di carburanti fossili
3. Lo sbilanciamento fra la portata (tonn/anno) con cui viene emessa CO_2 e quella con cui viene catturata e fissata (sequestrata) dall'ecosistema attraverso:
    1. L'assorbimento da parte delle piante (fotosintesi, processo biologico)
    2. L'assorbimento da parte degli oceani (processo chimico-fisico)
    3. L'adsorbimento da parte delle rocce (mineralizzazione, processo chimico-fisico)
4. L'effetto netto è il trasferimento di carbonio dal sottosuolo all'atmosfera, dove la CO_2 permane per lungo tempo

Che cosa possiamo fare concretamente?

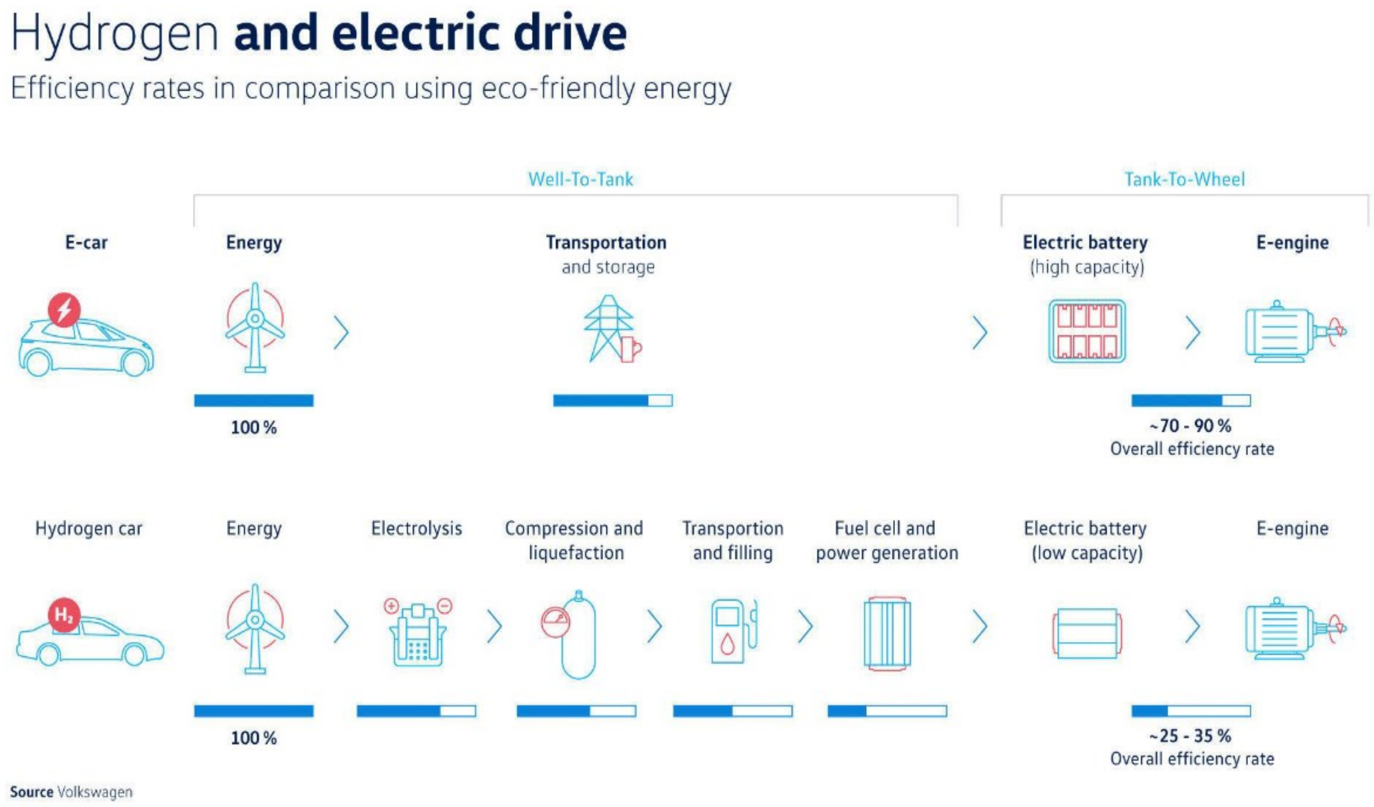
1. Sono disponibili (sul mercato) le soluzioni tecniche per produrre l'energia necessaria senza bruciare combustibili?
    1. PV, WT, Hydro, hydro Storage: TECNOLOGIE PRONTE!
    2. Electrochemical Batteries, Gas Insulated Transmission Lines, new energy markets regulations: MANCA POCO! (diamoci una mossa)
    3. Energy from waves: CI VUOLE PIÙ TEMPO…
    4. Hydrogen: NON CI SIAMO! (e forse non ci saremo…)
    5. Nuclear fusion: A NIGHTMARE!
    6. Nuclear fission: NO COMMENT!
2. Concentrare i finanziamenti sulle soluzioni disponibili o quasi
3. Fare qualcosa da subito, prima che la situazione causata dal riscaldamento globale si aggravi ulteriormente!

About hydrogen, which burns without producing CO_2

Is hydrogen (H_2) a renewable or NON renewable energy source?

- H_2 is NOT an energy source! Similarly to electricity it might be a way of transferring energy (but also of storing energy!)
- No mineral deposits of H_2 are available, H_2 must be industrially produced!
- H_2 is renewable if produced by using renewable energy only (green hydrogen. What about blue hydrogen or turquoise hydrogen?)
- H_2 is a (very) hazardous material, it diffuses through steel and you cannot see a hydrogen flame. A tiny question: is it worth to bet on hydrogen as a broad spectrum solution, or it is better to restrict its use to specific and well controlled applications?
- my opinion as a chemical engineer is that hydrogen should be used in the same place where it is produced
- Hydrogen for terrestrial mobility is a nonsense

Comparison of overall energy efficiency between hydrogen-fuelled and e-cars



A tiny question:

1. Perché non applichiamo le tecnologie già disponibili per realizzare la transizione energetica verso fonti che non emettono CO2?
   1. costano troppo (MA STIAMO USANDO UN SACCO DI QUATTRINI PER RIPARARE I DANNI CAUSATI DALLE FONTI FOSSILI!)
   2. siamo alla ricerca di alternative migliori (MA NON C'È TEMPO!)
   3. ci sono inerzie «di sistema», rendite di posizione difficili da ridimensionare
   4. chi dovrebbe prendere decisioni importanti ha altre priorità (il consenso?, le prossime elezioni?)
2. Comunque, è un problema che ci tocca molto da vicino, soprattutto in senso temporale

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Greenwashing of the Oil companies

News IN NUMBERS

BIG GREEN CLAIMS

A report by independent think tank *InfluenceMap* says that although big oil companies are spending hundreds of millions of dollars each year promoting their climate-positive actions, little is actually being spent on green investments.

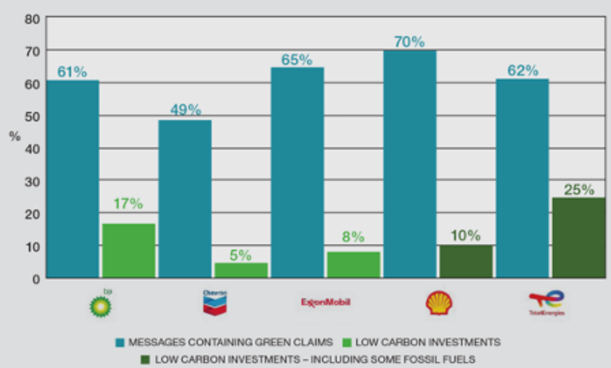
As much as 60% of the public messages from BP, Shell, Chevron, ExxonMobil, and TotalEnergies contain "green" claims, says the report, while 23% promote oil and gas. But in reality only 12% of the five companies' 2022 capital expenditure (CAPEX) is forecasted to be dedicated to "low carbon" activities.

Of these, Shell tops the list for having the most messages with green claims – 70%, compared with 49% for Chevron.

Furthermore, none of the big five's forecasted oil production appears in line with the IEA's Net Zero Emissions by 2050 (as of Q4 2021), and none have aligned their climate policy engagement activities with the goals of the Paris Agreement, *InfluenceMap* said.

https://bit.ly/3RZtr3D

BIG OIL'S CLAIMS VS GREEN INVESTMENTS



Graph comparing the percentage of Big Oil's 2021 public communications promoting pro-climate messaging vs the percentage of projected low carbon investments in 2022 CAPEX per company

Source: InfluenceMap

Ørsted

WIND POWER

The world's largest offshore wind farm, Hornsea 2, has officially entered full operation.

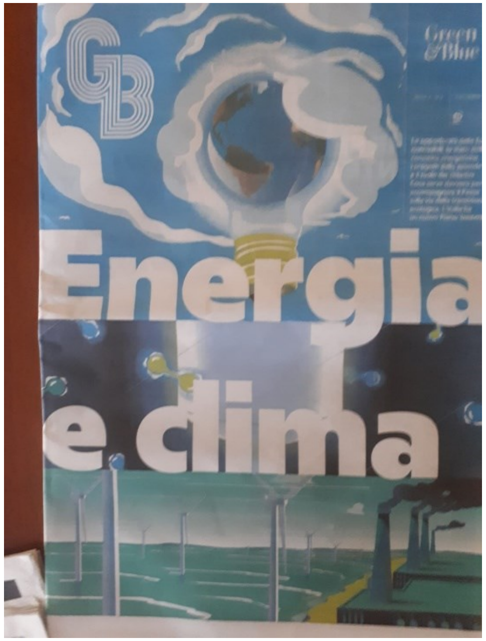
Situated roughly 89 km off the coast of Yorkshire, the facility has a capacity of more than 1.3 GW and can help power in excess of 1.4m UK homes with its 165 turbines, says its Danish owner, Orsted.

The site stretches across an area of 462 km² – more than half the size of New York City – and just one revolution of the wind turbine blades can power an average UK home for 24 hours, the company says.

https://bit.ly/3RADmge

Nel 2023 tutti si rendono conto della necessità di mitigare il riscaldamento globale…

1. i medici (articolo del Presidente dell'ordine dei Medici della Provincia di Verona)
2. i giornalisti (inserto de La Repubblica 7/9/23)
3. i cittadini (mah??)



4. Gli scienziati.
Come ricercatore mi chiedo: ma di che cosa mi dovrei occupare se non di questo problema?

Giorgio Levi Cases (1882-1969)

IL Centro Levi Cases:

1. Una grande realtà dell'Università di Padova, in largo anticipo rispetto ai tempi
   1. istituito grazie al lascito dell'Ing. Giorgio Levi Cases, 50 anni fa
   2. non restringe il problema agli aspetti tecnologici, ma lo inquadra in un contesto multidisciplinare e trasversale
2. un'opportunità sprecata dalla «governance» dell'Università, anche per l'incapacità del direttore precedente (che è chi vi parla)
3. un «asset» a disposizione dei giovani (i ricercatori A e B) per analizzare i vecchi problemi con mente fresca, ed escogitare nuove soluzioni

a few key points

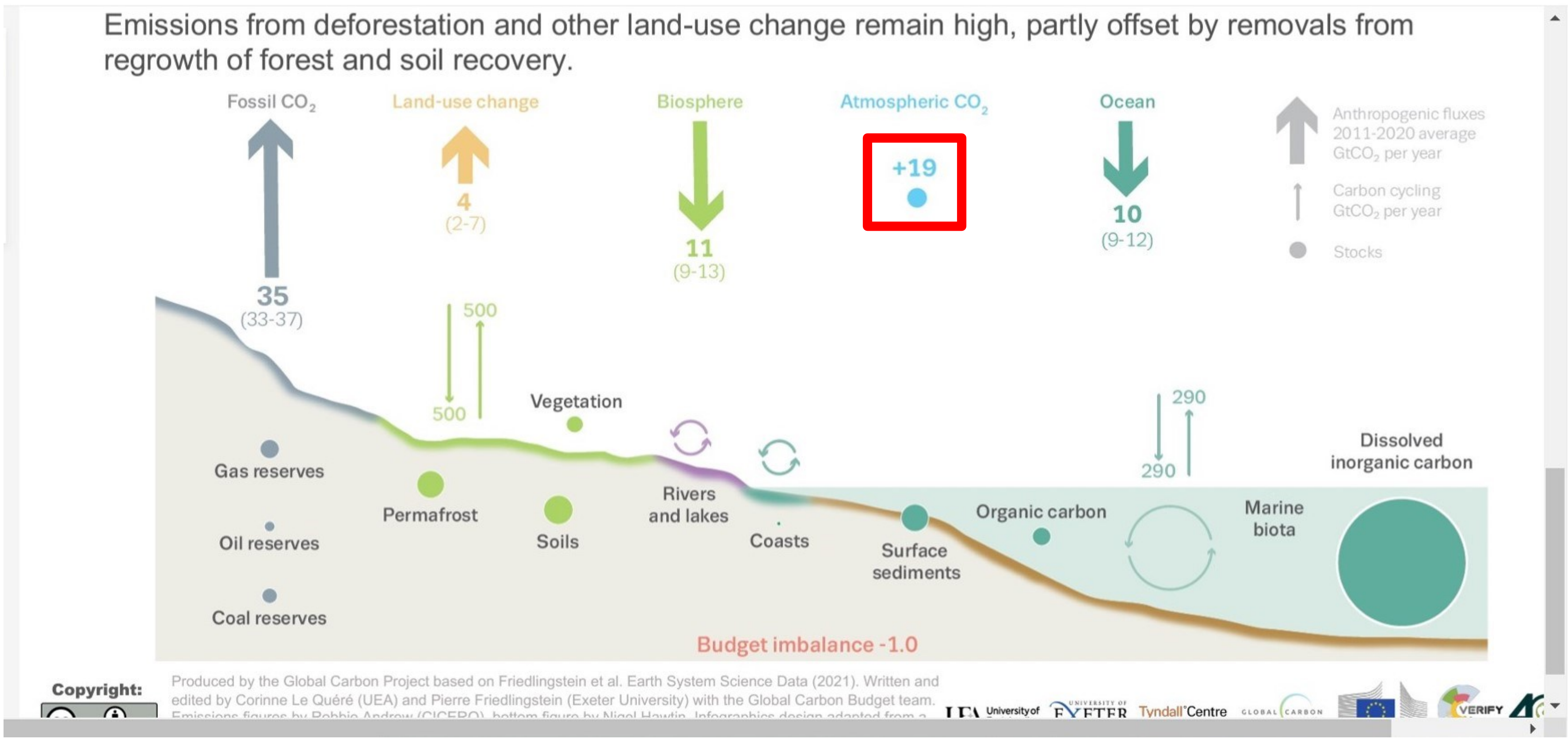
1. The strongest constraint and challenge for mankind nowadays is reducing the concentration of greenhouse gases in the atmosphere in the shortest time (i.e. to BOTH reduce new emissions of CO_2, methane and GHG, AND lowering the atmospheric concentration of CO_2 as the result of emissions in the past)
2. Enough technology is already availale to deploy renewables (PV, WT) as energy sources in order to achieve a Fossil Fuel Free world, except for energy storage technologies. It is essential to find the best storage system integration ASAP.
3. Achieving Clean Energy Transition is not just a matter of technology. Economical, financial and regulatory aspects, as well as individual and societal issues, must be accounted for in order to ensure that the process of fossil fuels phase out will be economically, environmentally and socially sustainable

Energy production and global CO_2 emissions (not only for energy)

- Unbalanced CO_2 emissions add up to about 19 Gton/year
  They are mainly due to the huge energy demand for energy supply, to the combustion of fuels for transportation purposes, and to industrial production processes for the remaining part
- The earth ecosystem is unluckily NOT able to absorb and fix these emissions fast enough
- So, that the concentration of GHGs in the atmosphere increases, and also its rate of growth is increasing!

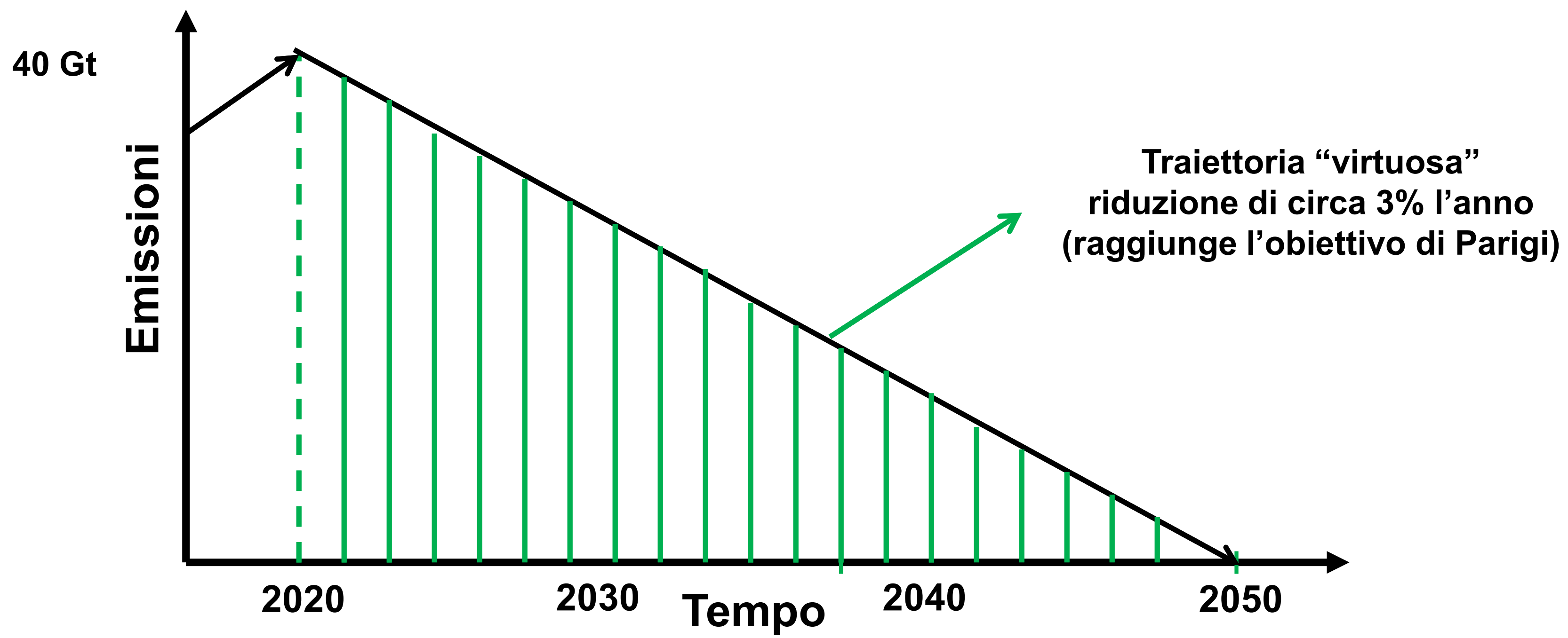
bilancio globale di emissioni di GHG (in CO2 equivalente)

secondo Global Carbon Project CSIRO



Perché non possiamo perdere tempo?*

- Quello che conta non é il valore dell'obiettivo di emissioni per un certo anno (e.g. il mantra "0 emissioni nel 2050"), ma la traiettoria che si adotta per raggiungere questo obiettivo



*Filippo Giorgi, IPCC, personal communication

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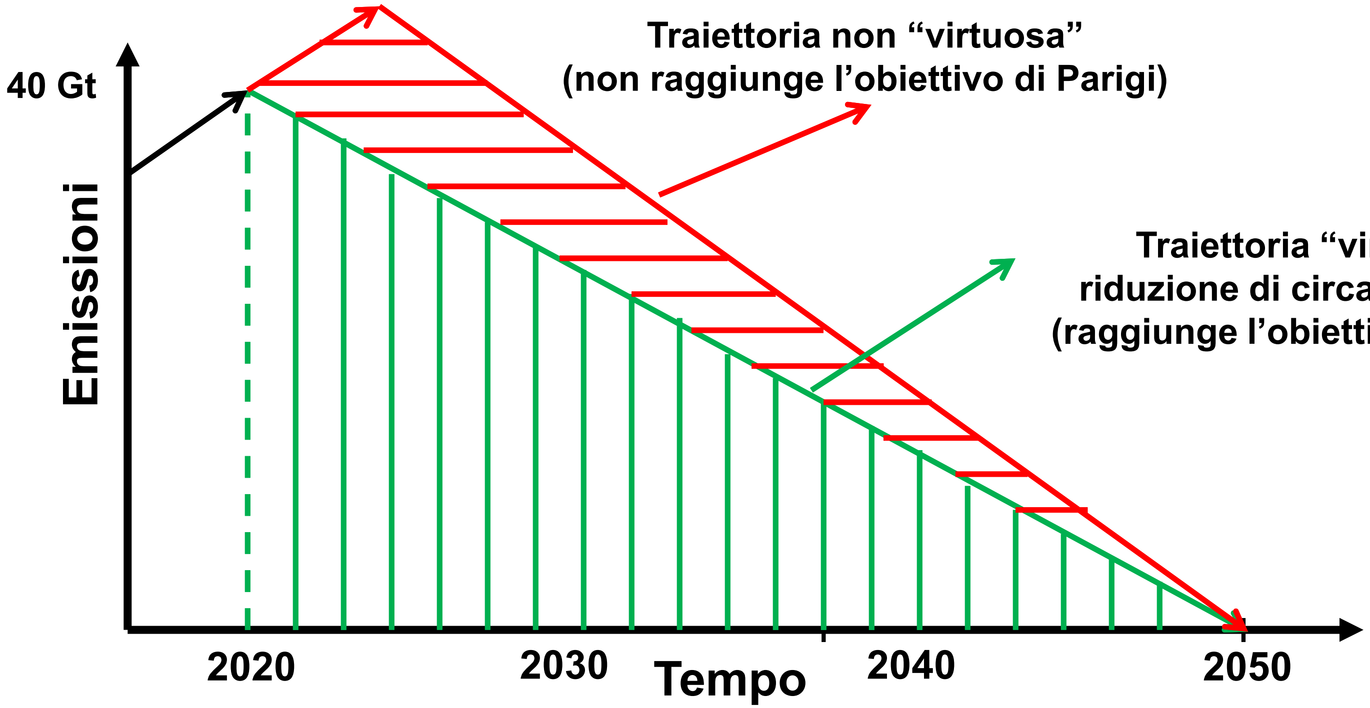

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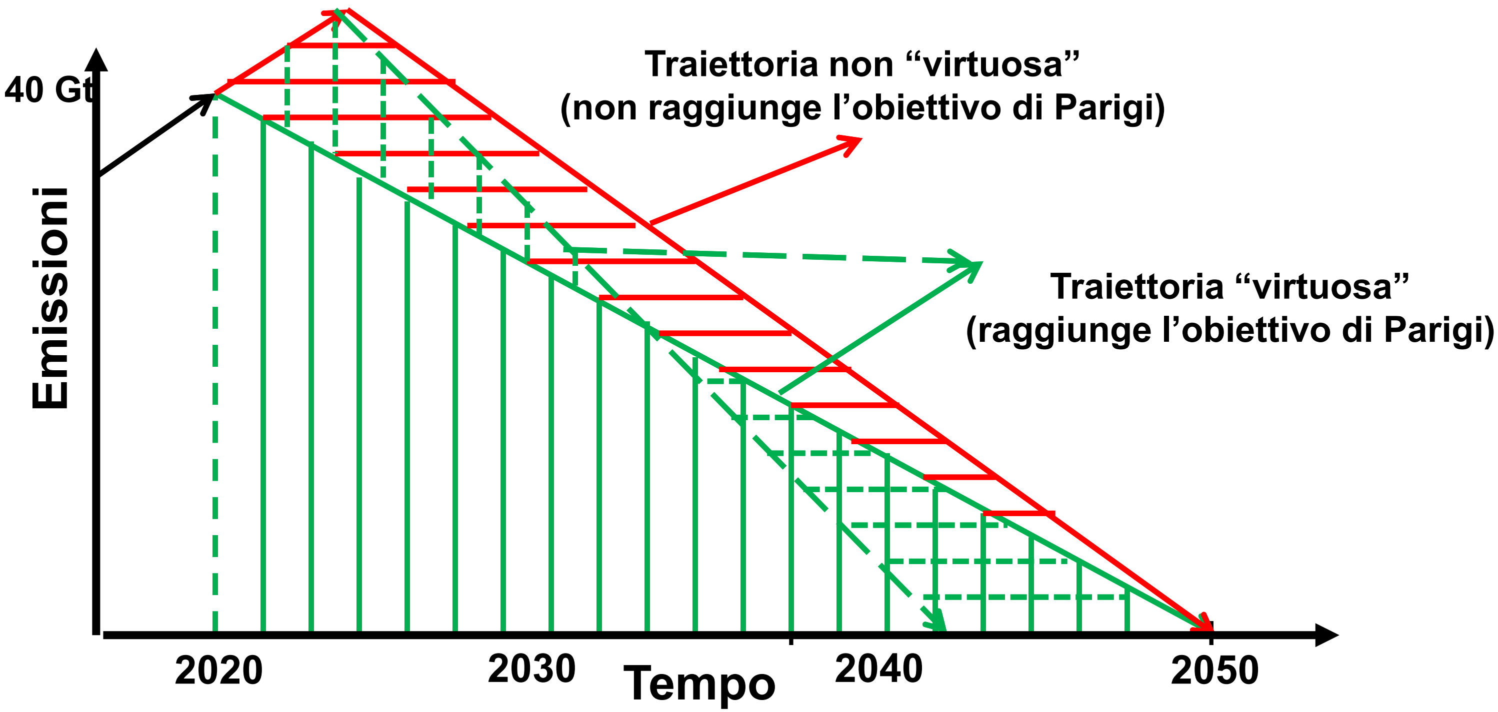

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We must reduce both CO_2 emissions and CO_2 atmospheric concentration

Two are the process steps:

- a **first** step: CO_2 capture
- a **second** step: chemical reduction of C by means of H^+
- chemically speaking: **how can CO_2 as a molecule be reduced**?

Are there any technologies available (i..e. on the market) **for the first step? Yes!**

Are there any technologies available (i..e. on the market) **for the second step? No!**

Comparing fuel energy content and CO_2 emissions

1. **The energy balance: LHV, Lower Heating Value, and HHV, Higher Heating Value**
   - **LHV: energy released per unit fuel mass, excluding water condensation (HHV*)**
   - **on mass basis (MJ/kg), and on volume basis (MJ/litre): see table**
2. **The material balance: stoichiometry of combustion**

   every C-in-the-fuel + $O_2 \rightarrow CO_2 + H_2O$
   - **kg of CO_2 emitted from burning coal: 3.5 kg/kg; oil 3.1 kg/kg; NG*: 2.8 kg/kg**
   - **if atoms other than C, H are in the fuel, other emitted pollutants are NOx, Sox**
   - **micro and nanoparticles of carbon are always produced («soot»)**
3. **Why is so much energy released?**
   - **the ΔH of formation of CO_2 from C + O_2 is -393.5MJ/kmol (highly exothermic)**
   - **the same amount of energy must be supplied to reduce CO_2 to solid C**

Comparing fuel energy content and CO2 emissions

table of LHV values

Hydrogen:	**143 MJ/kg**	**or**	**0.013 MJ/L**
Natural gas:	**54 MJ/kg**	**or**	**0.039 MJ/L**
Diesel fuel:	**46 MJ/kg**	**or**	**39.1 MJ/L**
Gasoline:	**44 MJ/kg**	**or**	**32.6 MJ/L**
Ethanol:	**30 MJ/kg**	**or**	**23.5 MJ/L**
Coal*:	**35 MJ/kg**	**or**	**28.0 MJ/L**
Wood*(dry weight):	**18 MJ/kg**	**or**	**6.0 MJ/L**

HOWEVER, for transportation the volume basis is most important!

Wait a minute: do we need fuels or services?

1. **For transportation:**
   - ground, people: electrical cars and vehicles (GAME OVER for endothermic engines)
   - ground goods freight: electric, H2 fuel cells, or liquid fuels (GAME ON)
   - ship transport: sustainable (carbon neutral) liquid fuels, liquid fuels (GAME ON)
   - air transport: synthetic liquid fuels and biofuels (to be developed) + reduce (Zoom?)*

2. **For heating/cooling:**
   - heat pumps, geothermical heat pumps (GAME OVER for Natural Gas. Burning H2?*)
   - solid biomass when available (but with proper systems to avoid pollutant emissions)
   - reduce needs by energy savings and near-zero emission buildings

3. **For industrial production and agriculture**
   - locally produced green hydrogen to be used at the same site (industry)
   - biofuels, mainly biogas (agriculture). Also fertilizers should be made carbon neutral

How to deal with CO_2 (and CH_4) emissions

1. For methane: ensure and check there are no leaks in production and transportation
   - CH_4 is significantly present in all oil fields: which is its final destination?
   - seals/leaks are currently an issue in gas pipelines and in gas plant connections
   - this issue is even greater at the local distribution level
   - anyway, the lifetime of CH_4 in the atmosphere is much less than the one of CO_2
2. Carbon Capture and Sequestration (CCS)
   - technologies are industrially available for capture from flue gases, NGas, Biogas,…
   - technology is NOT industrially available for sequestration (yes Enhanced Oil Rec.)
   - technology is NOT suitable for capturing CO_2 from the atmosphere («air washing»)
3. Carbon Capture and Utilization (CCU)
   - it means converting CO_2 into a valuable, or useful, or at least safe material
   - CCU allows to use CO_2 twice (or more times) before emission to the atmosphere
   - the time between the CO_2 into an e-fuel and its combustion is quite relevant

How to reduce CO_2 by chemical/biochemical reaction

1. **Biochemical/biological route: photosynthesis by plants and «oceans»**
   - **CO_2 fixed into biomass by a process, which has to be «enforced» (industrialized)**
   - **high amount of light energy needed to run these photobioreactors**
   - **low reaction rate, resulting in large photobioreactor volume (or area) required**
   - **«artificial photosynthesis» NOT an option in the energy transition timeframe (NF*)**
2. **Chemical routes:**
   - **catalytic chemical and/or electrochemical reactors required**
   - **high amount of energy needed (it might be thermal one as well as electrical one)**
   - **H_2 is most suitable as both electron donor and energy supplier**
3. **Geological routes and inorganic mineralization:**
   - **metal oxides needed: not enough oxides available to fix CO_2 are available**
   - **maybe basalts under the oceans are enough?**

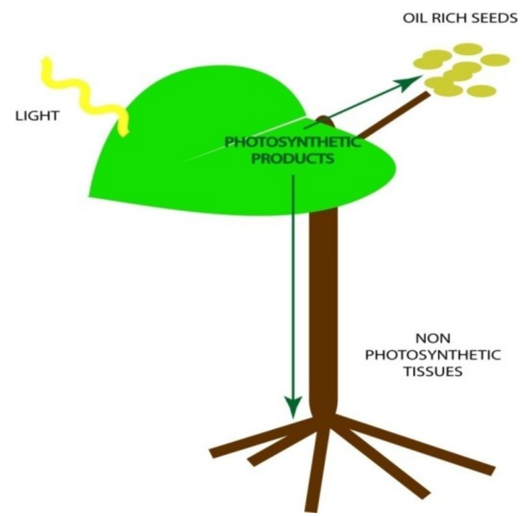
Recalling thermodynamic and kinetic fundamentals

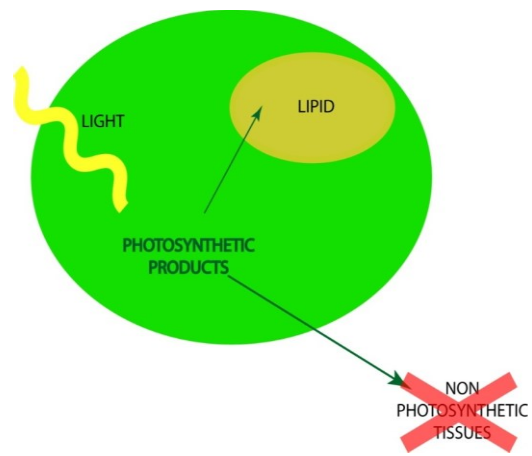
1. **Enthalpy of formation**
   - **it defines the energy demand to perform the CO2 reduction proces**
   - **effective energy transfer to the reactor is needed**
2. **Free Gibbs energy of formation (related to the equilibrium constant value):**
   - **it decides about the possibility to pursue any idea (MF)**
   - **it depends on the selected CO2 fixation reaction: i.e.** $C + O_2 \Leftrightarrow CO + \frac{1}{2}O_2 \Leftrightarrow CO_2$
   - **if unfavourable, suitable downstream separation units needed**
3. **CO2 bond strength energy:**
   - **its value is 532 MJ/kgmol**
   - **suitable catalysts are needed to reduce the activation energy, to speed up reactions**

1. Industrial Photosynthesis

1. **Energy is supplied by sunlight**
   - amount of light energy is huge but its superficial density is too low (1 kW/m^2)
   - photosynthetic efficiency is maximum 11.5%, usually more than ten times lower (PV)
2. **Harvesting of photons and CO2 fixation are ensured by photosynthetic systems I & II**
   - these systems have been set up thanks to a two-billion year evolution
   - this is a biocatalyst which operates around room temperature
   - the turnover frequency is indeed regrettably low ($days^{-1}$)
3. **Biomass production requires not only CO2:**
   - other components are involved in the feed as «nutrients»
   - consider also nitrogen fixing cyanobacteria

Microalgae are the best for Industrial Photosynthesis





In terrestrial plants not all plant tissues contribute to photosynthesis. Lipid content is maximum 5% (in seeds)

Microalgae are like a plant which is entirely photosynthetically active. Sunlight energy may be stored in the cells as lipids and carbohydrates, which can be as much as 40-80%.
About 2 kg of CO2 are fixed per kg of microalgae

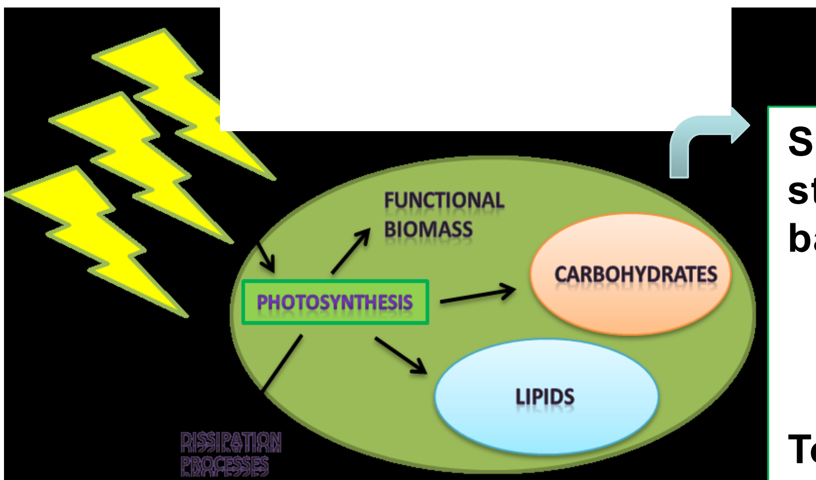
Microalgae LHV (dry mass basis): 20-22 MJ/kg

Industrial Photosynthesis by Microalgae

Simplified stoichiometry of photosynthetic organisms:

$$6CO_2 + 12\,H_2O + \text{LIGTH} \longrightarrow C_6H_{12}O_6 + 6O_2 + 6H_2O$$

oxidized state → ***reduced state***



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So, other atoms are involved, with additional stoichiometric conditions. For instance, on a molar basis the composition of microalgae could be:

$$C_{1.852}\,N_{0.132}\,O_{0.403}\,P_{0.005}$$

To grow microalgae, basically C, N and P must be supplied. However, other "micronutrients" (Fe, S, …) are needed.

Industrial Photosynthesis by Microalgae: pros

- **they are not in competition with food for land use**
- **non-seasonal growth enables continuous production**
- **they require only photons, CO_2 and a few nutrients to grow**
- **their growth rate is «remarkable» (up to three duplication per day)**
- **they can contain very high fractions of lipids and carbohydrates (up to 80% of dry mass, both)**
- **they are able to «acclimate», i.e. to grow also in a "difficult" environment**
- **flue gas CO_2 and nutrients from wastewaters are suitable to grow them**
- **it is a way to fix CO2 into a solid which can be stored underground with long-term stability**
- **they enrich the carbon content of soils, improving soil characteristics**

Industrial Photosynthesis by Microalgae: cons

- **atmospheric CO_2 concentration is low! It limits biomass growth rate**
- **light energy availability is the major limit to growth rate, i.e. to the achievable production they grow in water, at very high dilution (1 kg/m^3): downstream processing is required**
- **transforming them into biofuels requires downstream processing which is quite energy intensive (hydrotreatment to HC)**
- **as a result, at present biofuels from microalgae are not economically competitive (>7 $/liter**)**
- **Forecasts to predict the development of a viable industrial processes were completely wrong***

**Elia Armandina Ramos Tercero, Giacomo Domenicali, Alberto Bertucco (2014). Autotrophic production of biodiesel from microalgae: An updated process and economic analysis. Energy, 76, 807-815

Industrial Photosynthesis by Microalgae: the cost

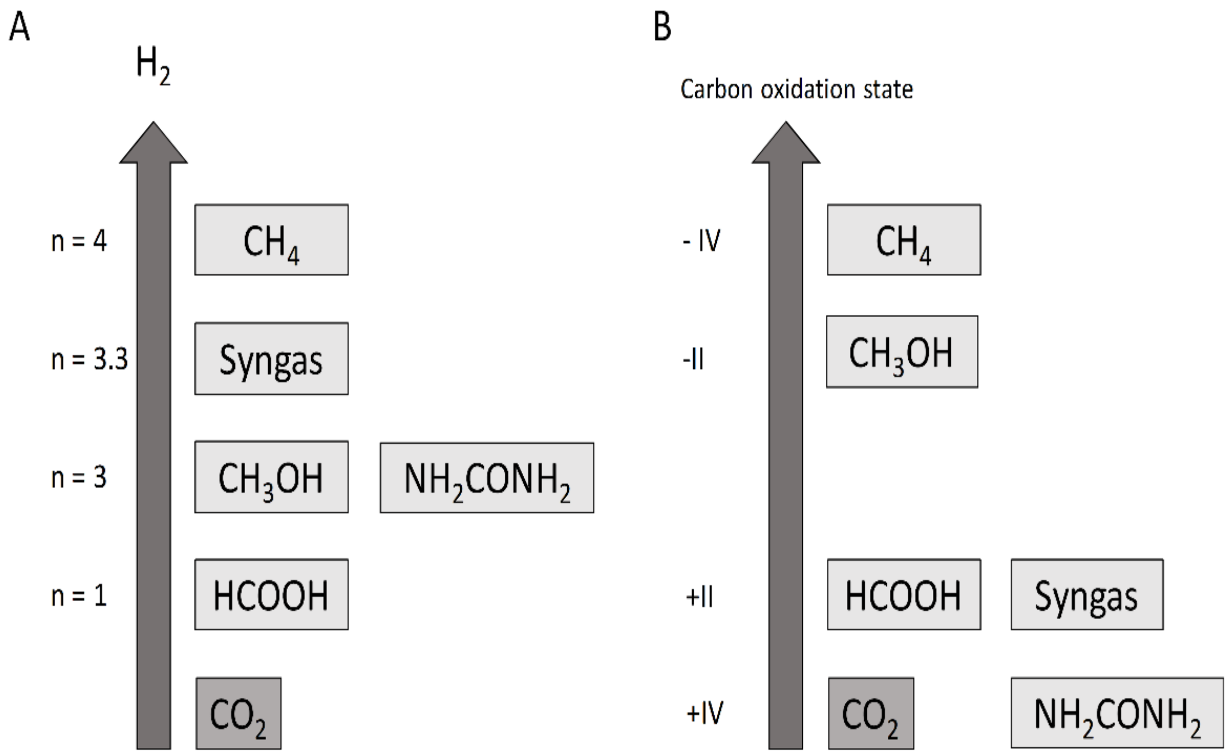
Photo.eff	5%	10%	15%	20%	25%
€/kWh	€/ton$_{CO2}$	€/ton$_{CO2}$	€/ton$_{CO2}$	€/ton$_{CO2}$	€/ton$_{CO2}$
0.025	1363	682	454	341	273
0.05	2727	1363	909	682	545
0.075	4090	2045	1363	1022	818
0.1	5453	2727	1819	1363	1091

High is the cost for fixing CO2 by Photosynthesis!
It must be compared to the value of an ETS allowance

2. Chemical reduction of CO_2 to fuels (e-fuels*)

1. **Syngas synthesis (a gaseous fuel)**
   - the feed is CO_2 and H_2, the product is a mixture of CO and H_2 (dry reforming)
   - a reverse water-gas shift reaction: $CO_2 + nH_2 \Leftrightarrow CO + (n-1)H_2 + H_2O$
2. **Methane synthesis (Synthetic Natural Gas, a gaseous fuel)**
   - the feed is CO_2 and H_2, the product is a mixture of CH_4 and water
   - the Sabatier reaction: $CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O$
3. **Formic Acid* synthesis (liquid fuel, or better a liquid vector to store energy)**
   - homogeneous catalytic reaction of CO_2 with H_2 in the presence of a tertiary amine
4. **Methanol* synthesis (liquid fuel, or better a liquid vector to store energy)**
   - by syngas catalyic conversion: or by direct catalytic CO_2 hydrogenation:
   $CO_2 + 2H_2 \Leftrightarrow CH_3OH$ $CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$

2. Chemical reduction of CO2 to fuels (e-fuels)

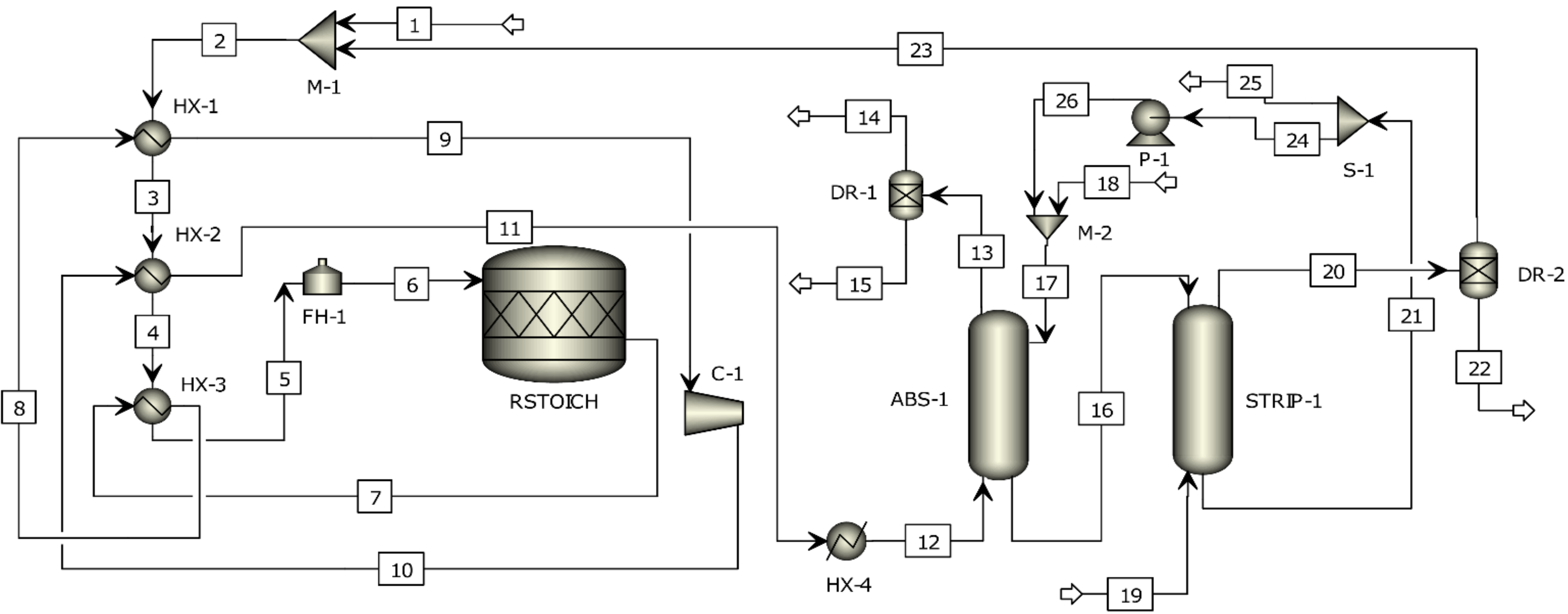


2. Chemical reduction: proposed methodology**

1. Conceptual design by Process Simulation (material+energy balances)
   - definition&optimization of process flowsheet and operating variables of the units
   - pinch analysis for heat integration
2. Thermodynamic data to fit parameters of adequate thermodynamic models
   - model selection very important, consistent VLE data essential
3. Kinetic experimental data from literature or patents
   - indispensable
4. Hydrogen always needed: it must be obtained from renewable sources
   - from water electrolysis powered by renewables (145 MJ/kg with 70% efficiency)

**Elena Barbera, Fabio Mantoan, Alberto Bertucco, Fabrizio Bezzo (2020). Hydrogenation to convert CO2 to C1 chemicals: Technical comparison of different alternatives by process simulation. Can. J. Chem. Eng. 98, 1893-1906

2. Chemical reduction: results /PFD of syngas synthesis



2. Chemical reduction: some conclusions

- **Conceptual design and rigorous (i.e. correct) process simulations developed for the e-fuel synthesis processes considered**
- **All the processes investigated achieved high overall CO_2 conversion**
- **Production of syngas, methane and methanol are all characterized by acceptable energy ratios**
- **Techno-economic analysis and life cycle assessment are necessary for a comprehensive comparison of e-fuel (fuel-from-CO2-reduction using green hydrogen) processes**

2. Chemical reduction: next step

- **Rigorous (i.e. correct) process simulation is the starting point to assess any e-fuel synthesis process under investigation. They provide inlet and outlet mass and energy flows of the industrial process**
- **Results of process simulation can be used for *a priori* estimation (prediction) of relevant indicators to compare the processes of interest from the energetic, economic and environmental standpoints**
- **A multicriteria methodology is needed! Main indicators are the Energy Return on Energy Invested (EROEI), the Levelized Cost of Energy (LCOE), the Levelized Cost of Fuel (LCOF), and environmental indicators evaluated by the Life Cycle Assessment Analysis (LCA)**
- **These indicators are valuable in order to define long-term strategies aimed to the development of national and international energy systems (Decision Support Tool)**

CONCLUSIONE

Di che ca…volo ci dovremmo occupare se non di risolvere il problema del riscaldamento globale prima che si raggiunga il punto di non ritorno?

Vi ringrazio molto del vostro tempo e della vostra attenzione