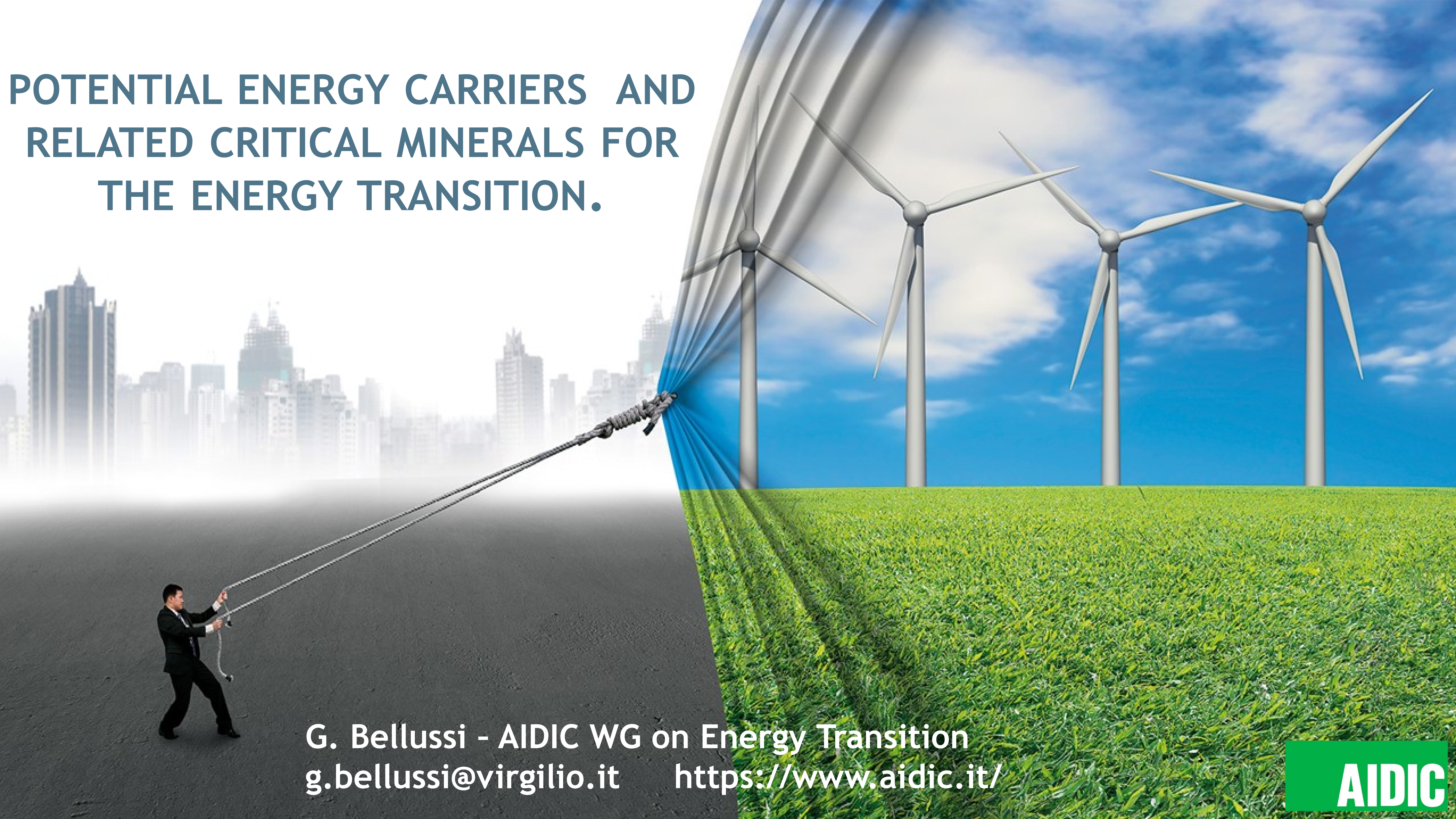
POTENTIAL ENERGY CARRIERS AND RELATED CRITICAL MINERALS FOR THE ENERGY TRANSITION.



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Introduction

- The pressure due to the fear about climate change is accelerating actions for the reduction of CO_2 emissions and the replacement of fossil fuels with renewable ones.
- The main renewable sources, wind and photovoltaic supply energy in a variable way, therefore the adoption of these sources requires the use of storage systems such as lithium batteries.
- Even the use of the energy carriers most likely to support mobility, i.e. electricity and hydrogen, have some important limitations that could make them not as pervasive as is generally assumed
- In this presentation, derived from the AIDIC position papers on critical metals and the use of methanol as an energy carrier, the main critical issues for the use of hydrogen and electricity as energy carriers will be highlighted, and this will lead us to the topic of critical materials.

The energy carriers for the mobility: hydrogen and electricity

https://www.cnbc.com/2022/05/12/tesla-ceo-elon-musk-dismisses-hydrogen-as-tool-for-energy-storage.html

https://www.ilsole24ore.com/art/il-ceo-toyota-l-auto-elettrica-business-immaturo-costi-energetici-e-sociali-insostenibili-AD6XQ38

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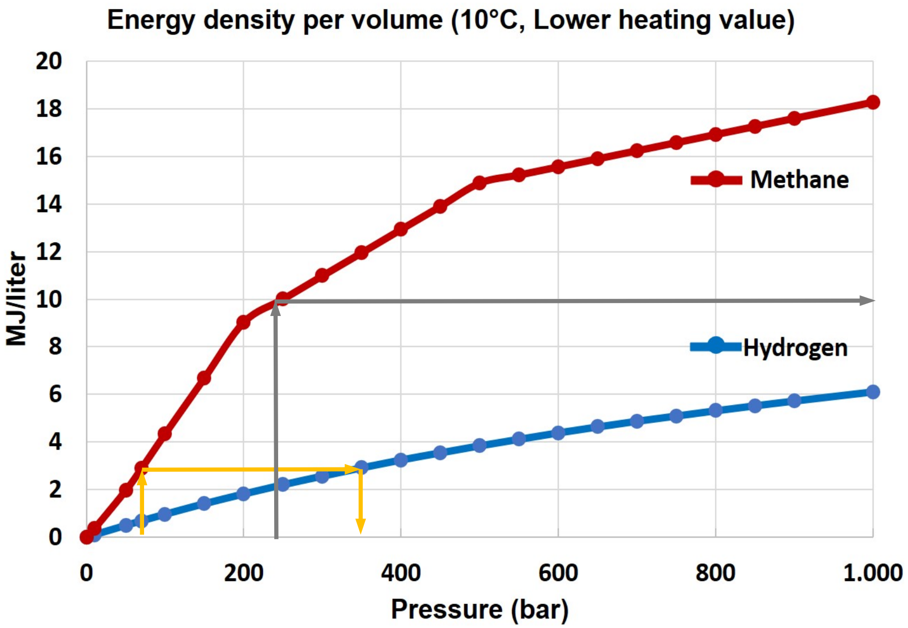
The energy carriers for the mobility: hydrogen



http://www.peacesoftware.de/einigewerte/methan_e.html
https://webbook.nist.gov/cgi/fluid.cgi?Action=Page&ID=C1333740

The energy density per unit volume of hydrogen is very low. For a practical comparison we can compare the energy densities of methane and hydrogen (10°C) at different pressures. For example, to have the same energy density as a high pressure pipeline (70 bar), the hydrogen would have to be compressed to over 320 bar. Hydrogen cannot be transported using existing pipelines. The addition of small quantities of hydrogen to methane in current pipelines reduces the energy content per unit volume of the gaseous mixture.

Furthermore, again due to the low density, the costs of hydrogen compression are very high. A comparison with methane is reported alongside.

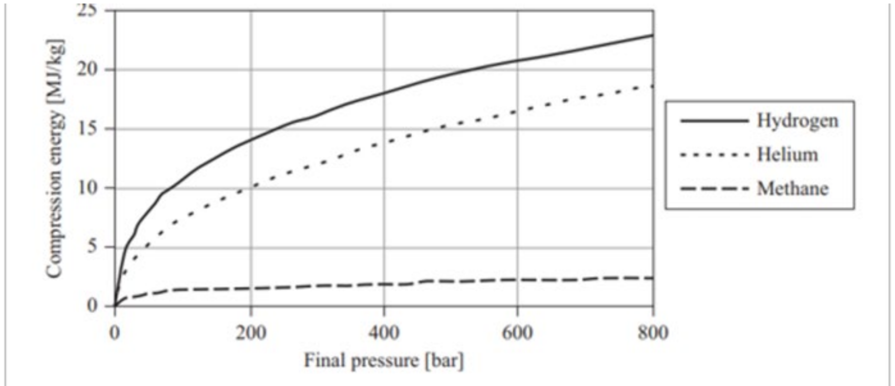


Figure 1.3 Adiabatic compression work for hydrogen, helium and methane [22]

https://afdc.energy.gov/files/pdfs/hyd_economy_bossel_eliasson.pdf

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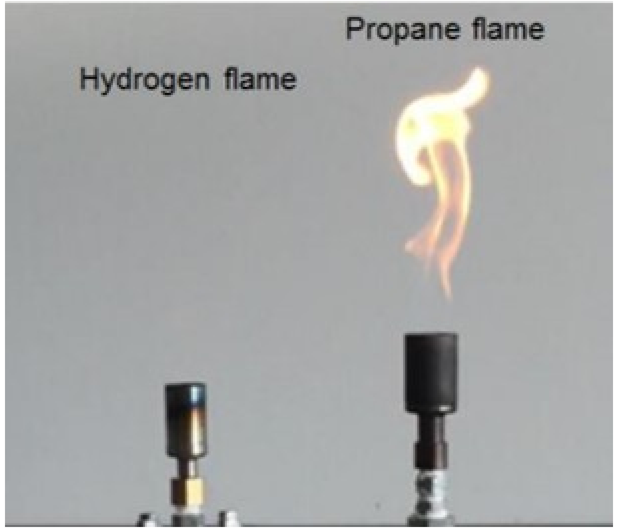
The energy carriers for the mobility: hydrogen

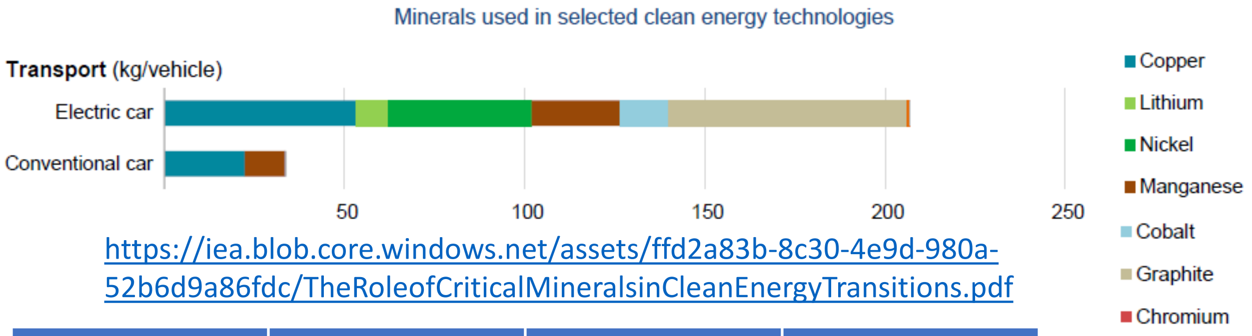


Flame images of hydrogen (left) and propane (right) taken by an ordinary CIS showing entirely invisible characteristics of the hydrogen flame.
T. Okino et al., https://www.imagesensors.org/Past%20Workshops/2017%20Workshop/2017%20Papers/P34.pdf

Unlike hydrocarbon flames, the hydrogen flame is invisible and this amplifies the safety measures necessary for handling this gas when compressed to high pressures.

Energy and the Hydrogen economy: https://afdc.energy.gov/files/pdfs/hyd_economy_bossel_eliasson.pdf

The energy carriers for the mobility: electricity



https://iea.blob.core.windows.net/assets/ffd2a83b-8c30-4e9d-980a-52b6d9a86fdc/TheRoleofCriticalMineralsinCleanEnergyTransitions.pdf

	World reserves 10^6 t	Cars EU ($258\ 10^6$) 10^6 t	Cars World ($1.4\ 10^9$) 10^6 t
Copper	890(1)	13.5	73.5
Lithium	89(2)	2.3	12.6
Nickel	100(3)	10.2	55.3
Manganese	1700(4)	6.2	33.7
Cobalt	7.5(5)	3.5	18.8
Chromium	560(6)	0.3	1.4
Grafite		16.9	91.7

(1) https://www.statista.com/statistics/1070228/global-copper-reserves/#:~:text=As%20of%202022%2C%20the%20total,as%20high%20conductivity%20and%20malleability.
(2) https://natural-resources.canada.ca/our-natural-resources/minerals-mining/minerals-metals-facts/lithium-facts/24009
(3) https://www.statista.com/statistics/273634/nickel-reserves-worldwide-by-country/
(4) https://www.statista.com/statistics/247609/world-manganese-reserves/#:~:text=In%202022%2C%20the%20total%20global,to%20iron%20and%20steel%20production.
(5) https://natural-resources.canada.ca/our-natural-resources/minerals-mining/minerals-metals-facts/cobalt-facts/24981
(6) https://www.statista.com/statistics/1040749/reserves-of-chromium-worldwide-by-country/#:~:text=Global%20chromium%20reserves%202022%2C%20by%20country&text=The%20total%20global%20reserves%20of,its%20hardness%20and%20corrosion%20resistance.

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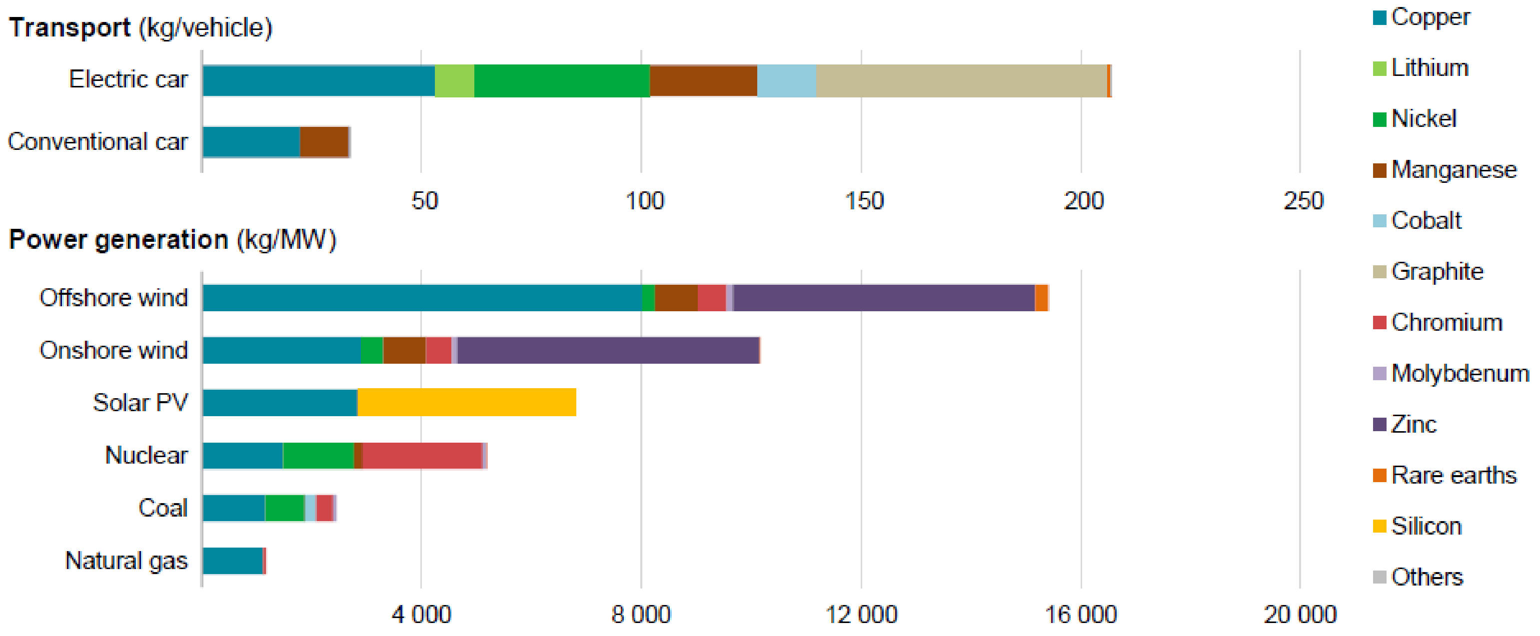
The critical minerals

The rapid deployment of clean energy technologies as part of energy transitions implies a significant increase in demand for minerals

Minerals used in selected clean energy technologies



Notes: kg = kilogramme; MW = megawatt. Steel and aluminium not included. See Chapter 1 and Annex for details on the assumptions and methodologies.

https://iea.blob.core.windows.net/assets/ffd2a83b-8c30-4e9d-980a-52b6d9a86fdc/TheRoleofCriticalMineralsinCleanEnergyTransitions.pdf

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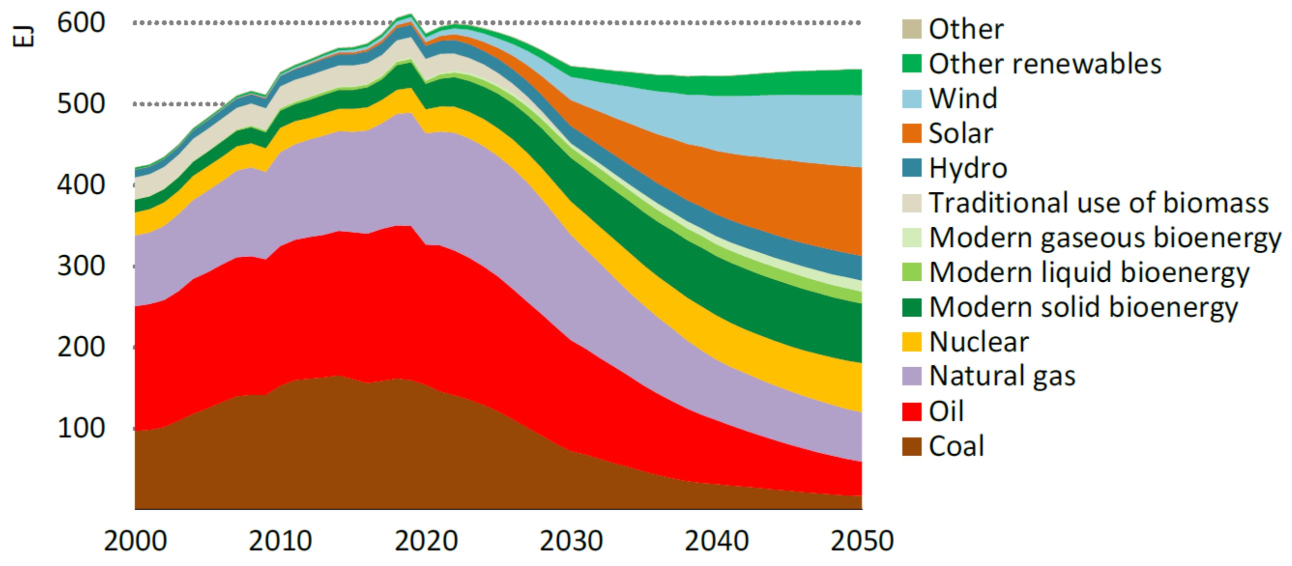
The critical minerals

Figure 2.5 ▷ **Total energy supply in the NZE**



According to what is reported in the IEA's NetZero By 2050 (https://www.iea.org/reports/net-zero-by-2050) by 2050 the contribution of discontinuous renewable energies (Solar and Wind) will have to be 203.3 EJ corresponding to 5.6 10^4 TWh. Conservatively assuming that the need for storage is 50%, we would need to store 2.8 10^4 TWh.

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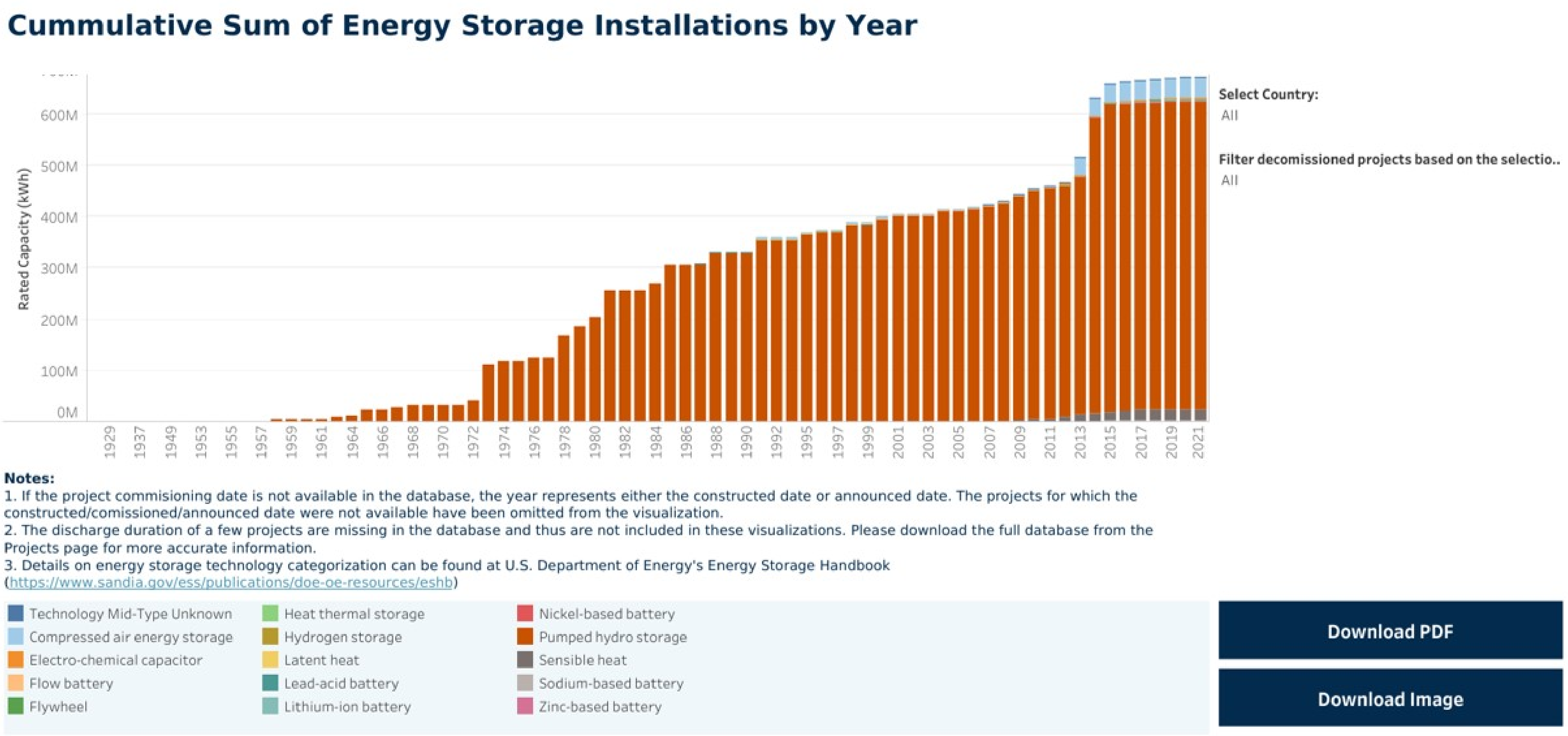
The critical minerals



By the DOE's Energy Storage DataBase, the amount of electricity stored in 2021 was 0.67 TWh, of which 90% pumped hydro storage, 3.2% sensible heat, 0.65% Li Ion Batteries, 6.06% Compressed air, 0.09% Unknown sources.
https://sandia.gov/ess-ssl/gesdb/public/statistics.html

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The critical minerals

- ✓ The amount of storage needed by 2050 (2.8 10^4 TWh assumptions based on IEA data) is much higher than the current installed storage capacity of 0.67 TWh and could not be based on pumped hydro storage.
- ✓ Energy storage in a system powered by renewables will require a very high storage capacity based on Li-ion Batteries and therefore will require very large quantities of metals.
- ✓ By the table reported above on the estimate of metals available worldwide, it can be deduced that in a scenario dominated by a renewable energy supply and electric mobility, there could be competition on the supply of metals to be allocated to transport and to be allocated to the energy storage.

The geopolitical situation

https://www.iea.org/reports/the-role-of-critical-minerals-in-clean-energy-transitions

The transition to a clean energy system brings into play new energy business models, countries and geopolitical considerations. It therefore appears prudent to seek alternative solutions to electric transport for mobility, which do not require the use of large quantities of metals and which do not expose us to the monopoly control of renewables by few nations.

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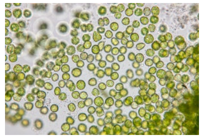
Alternative energy carriers: the biomass

From several sources



Microalgae

Microbial

Vegetables

Biomass Wastes

Biomethane

Castor

BioGas

Animals

Municipal Solid Wastes

Through known processes

- Hydrogenation Cracking Isomerization
- Steam reforming
- Gasification
- Fermentation

Different biofuels can be obtained

- Methanol
- Ethanol
- Gasoline
- Jet fuel
- Diesel

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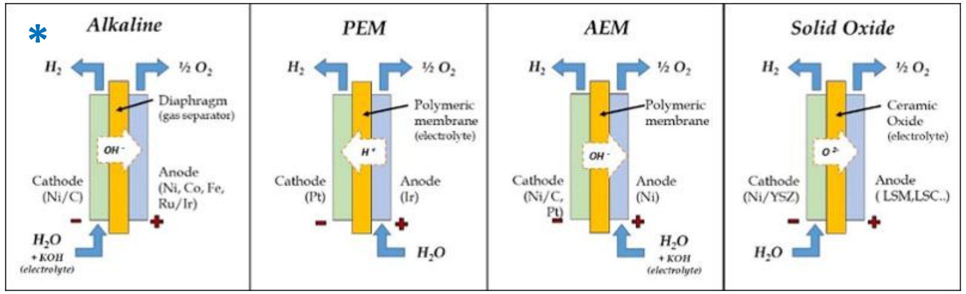
Alternative energy carriers: the e-fuels

Renewable e.e.



55 (45) KWh x 1 Kg H_2

(1 Kg H_2 ≈ 36 KWh)

H_2

CO_2

Fischer-Tropsch

Methanol synthesis

Methanol

Jet fuel

Diesel

* https://rienergia.staffettaonline.com/articolo/34856/Elettrolisi:+le+tecnologie+che+trasformano+l%E2%80%99elettricit%C3%A0+in+idrogeno/S.+Campanari,+P.+Colbertaldo,+G.+Guandalini

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Alternative energy carriers: the methanol

Of all the alternative energy carriers, methanol has several attractive aspects:

- ✓ Boiling point: 64.7 °C, it is liquid at room temperature.
- ✓ Octane number: 113÷120 [(RON+MON)/2], it is a high-octane component and when blended with petrol it allows to reach high octane values. A high octane number makes it possible to increase the compression ratio and therefore the efficiency of the endothermic engine.
- ✓ Low CO_2 emissions per unit of energy produced:

	Rapporto C/H	Pot Cal Sup (kJ/g)	CO_2 rilasciata (moli/MJ)	CO_2 rilasciata (Kg/MJ)	CO_2 rilasciata (Kg/Kg)
Carbone	1/1	39.3	2.0	0.088	3.5
Petrolio	1/2	43.6	1.6	0.070	3.1
Metano	1/4	51.6	1.2	0,053	2.7
Metanolo	1/4	22.7	1.4	0.061	1.4

- ✓ Methanol, like ethanol, is soluble in water unlike hydrocarbons and in case of dispersion, it is rapidly degraded in the environment.

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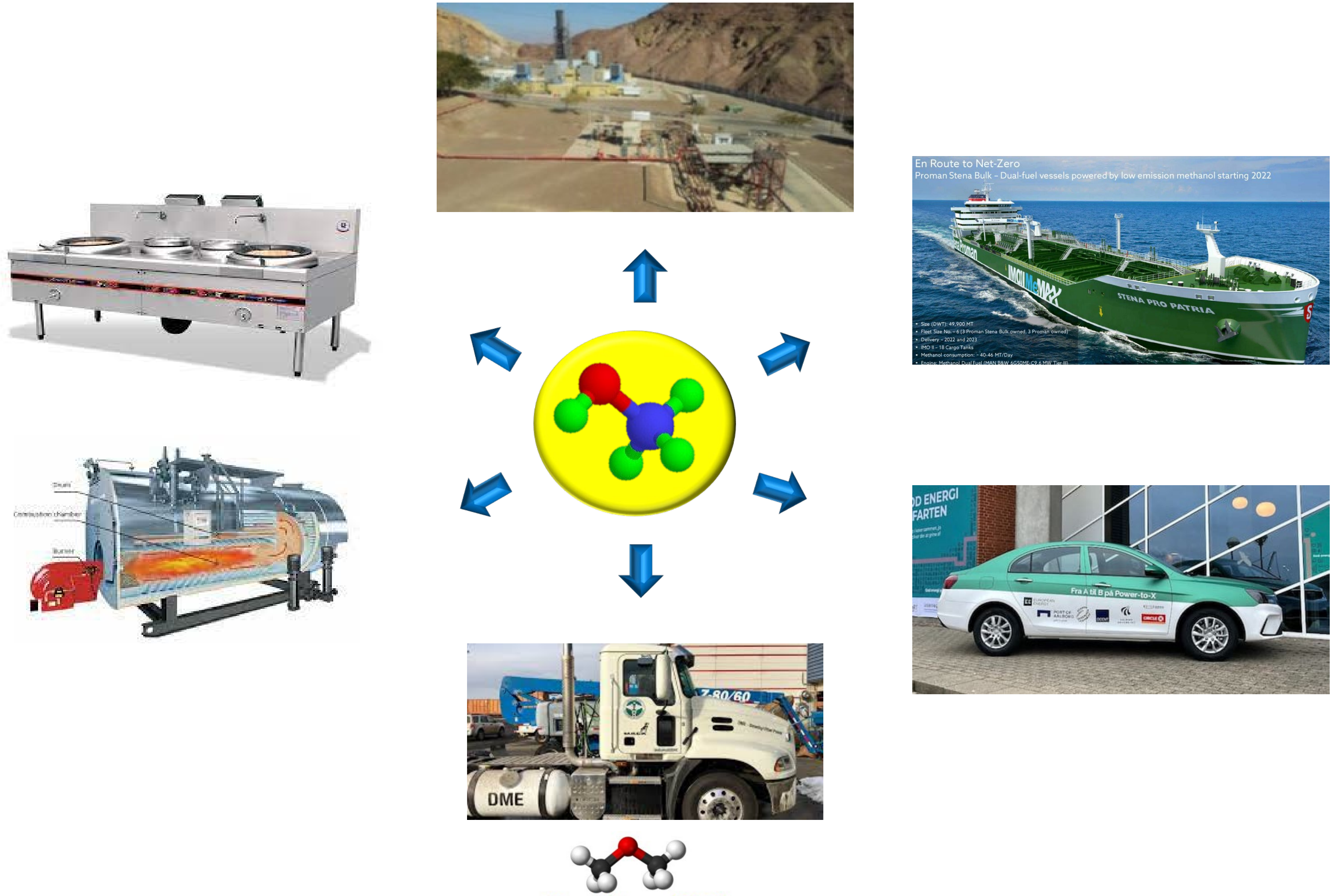
Alternative energy carriers: the methanol

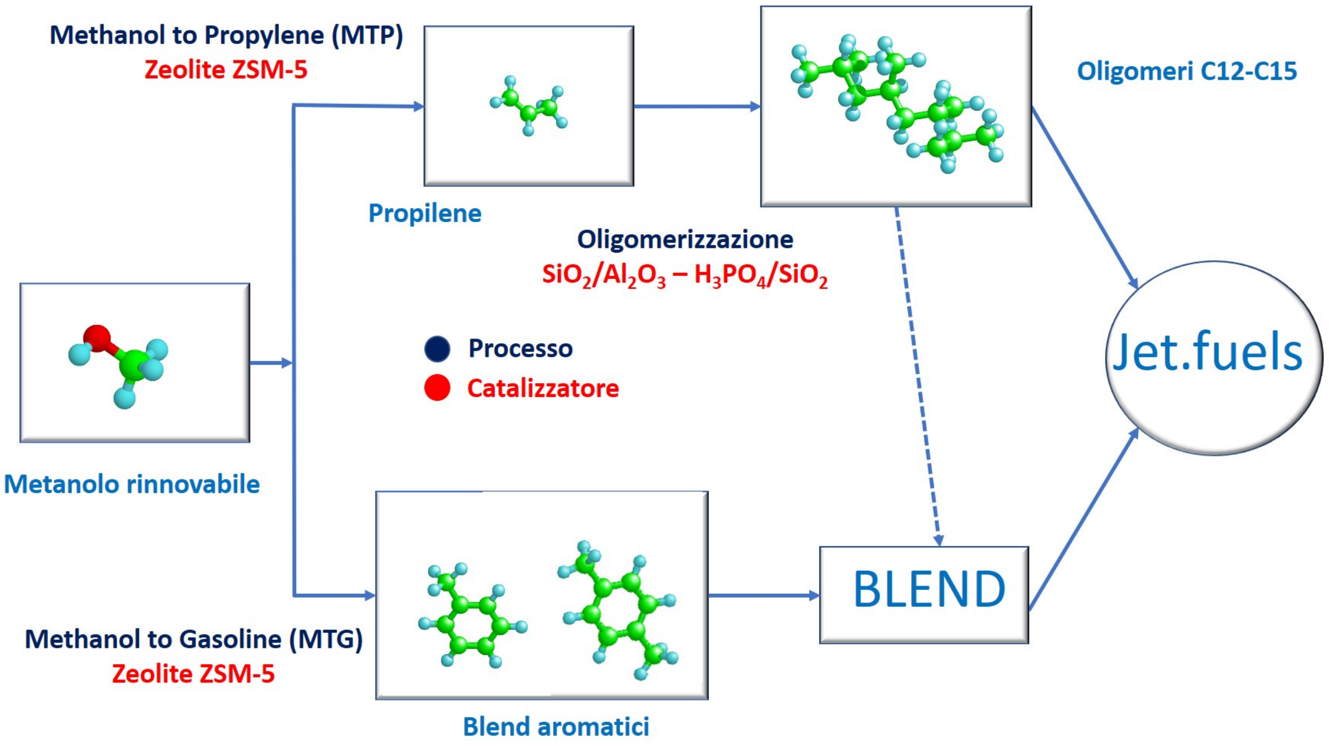


Dimetiletere (DME)

Alternative energy carriers: methanol as a raw material for the production of jet-fuel

Methanol cannot be used directly as jet fuel, but it can be used as a raw material for the production of high quality jet fuel. The processes available for the transformation are:

- ✓ Methanol to Gasoline (MTG) to produce a mixture of aromatics with a fraction suitable for use in jet-fuels,
- ✓ Methanol to Olefins oriented to the production of propylene (MTO – MTO) followed by oligomerization of propylene to a mixture of C12-C16 iso-olefins, which can then be hydrogenated. The streams of the two processes can then be mixed to produce a Jet-A1. All the processes mentioned are well known and already implemented on an industrial scale.



J. Ruokonen et al. , Processes **2021**, 9, 1046. https://doi.org/10.3390/pr9061046

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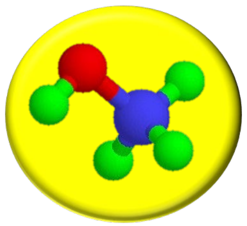
Alternative energy carriers: methanol as a raw material for the production of chemicals

Ethylene and propylene production

MTO – MTP (ZSM-5 – SAPO-34)

Production of sulfur and nitro derivatives

Sulfo-nitration of oxygenated hydrocarbons



Aromatics production

MTG (ZSM-5)

Production of aliphatics and Aromatics oxygenates

Selective oxidations (TS-1/H_2O_2)

Ethylbenze and cumene production

Alkylation (Zeolites Beta or MCM-22)

Jet fuel and solvents production

Propylene oligomerization (SiO_2/Al_2O_3 – H_3PO_4/Kieselgur SiO_2)

Starting from methanol it is possible to build all the chemistry derived from petroleum.

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Conclusions

- Actions aimed at containing Climate Change must also consider the use of the various energy carriers available, especially with respect to the mobility.
- Hydrogen, while being attractive for end-of-pipe emissions, has strong limitations due to its low density.
- The electric vehicles seem the most attractive solution, above all for its ability to locally reduce harmful NOx and particulate emissions.
- The most advanced batteries (Li-ion) for this application still have cost, technological (Production and distribution of e.e., recharging times, distance limits) and environmental (Availability and supply of metals, recovery of used batteries, and emissions correlates of greenhouse gases) drawbacks.
- A situation of almost monopolistic control of the production and processing of the metals needed for batteries by China is emerging.
- It is therefore prudent to look for a solution that can be an alternative, in the worst case, or complementary to the electric one.
- Methanol seems to be a particularly attractive energy carrier to meet the present, but above all the future needs for environmentally compatible energy distribution and mobility.