



› **INDUSTRY TRANSFORMATION**
CCU - CARBON CAPTURE AND UTILIZATION
DR. IR. F.E. WUBBOLTS

TNO - UNIT ENERGY & MATERIALS TRANSITION

Advisory Group for Economic Affairs
Energy Transition Studies

Biobased and Circular Technologies
Climate, Air & Sustainability

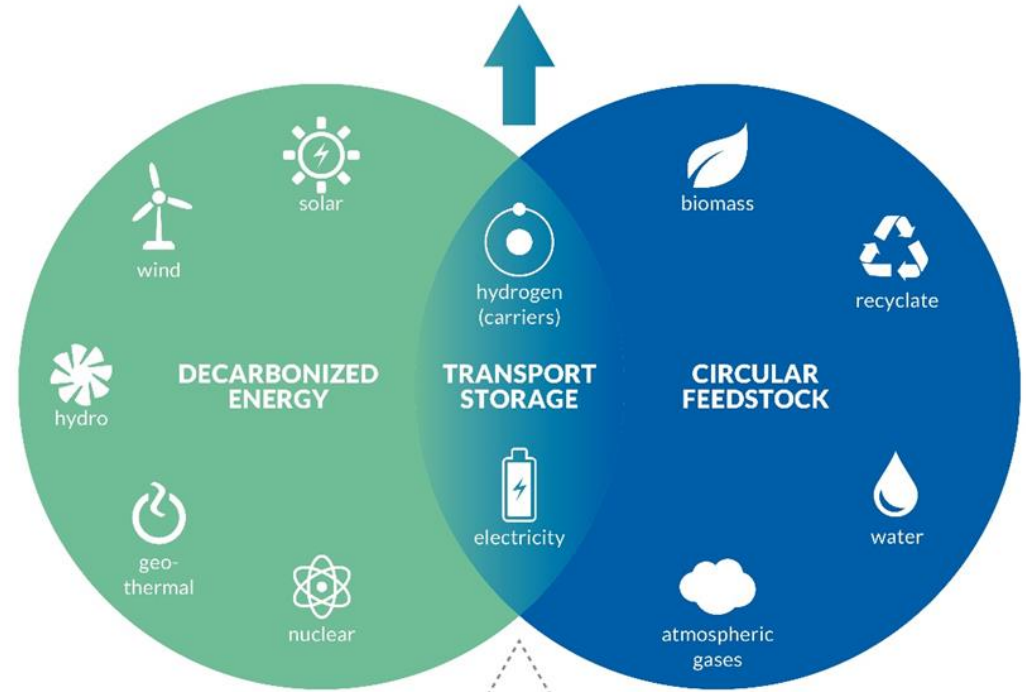
Applied Geosciences
Environmental Modelling, Sensing and Analysis
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Solar Energy
Solar Technologies & Applications
Wind Energy

Sustainable Process & Energy Systems
Sustainable Technologies for Industrial Processes
Heat Transfer & Fluid Dynamics



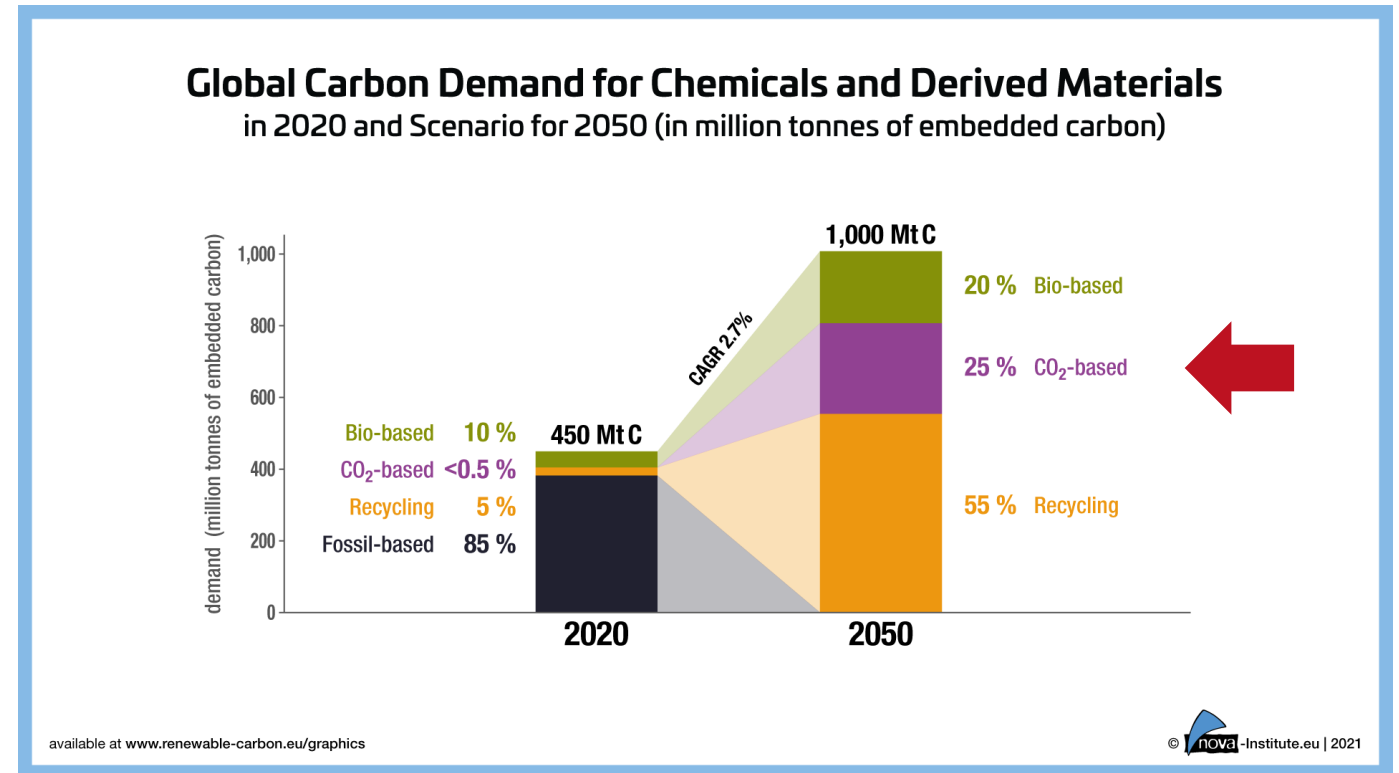
INDUSTRY TRANSFORMATION



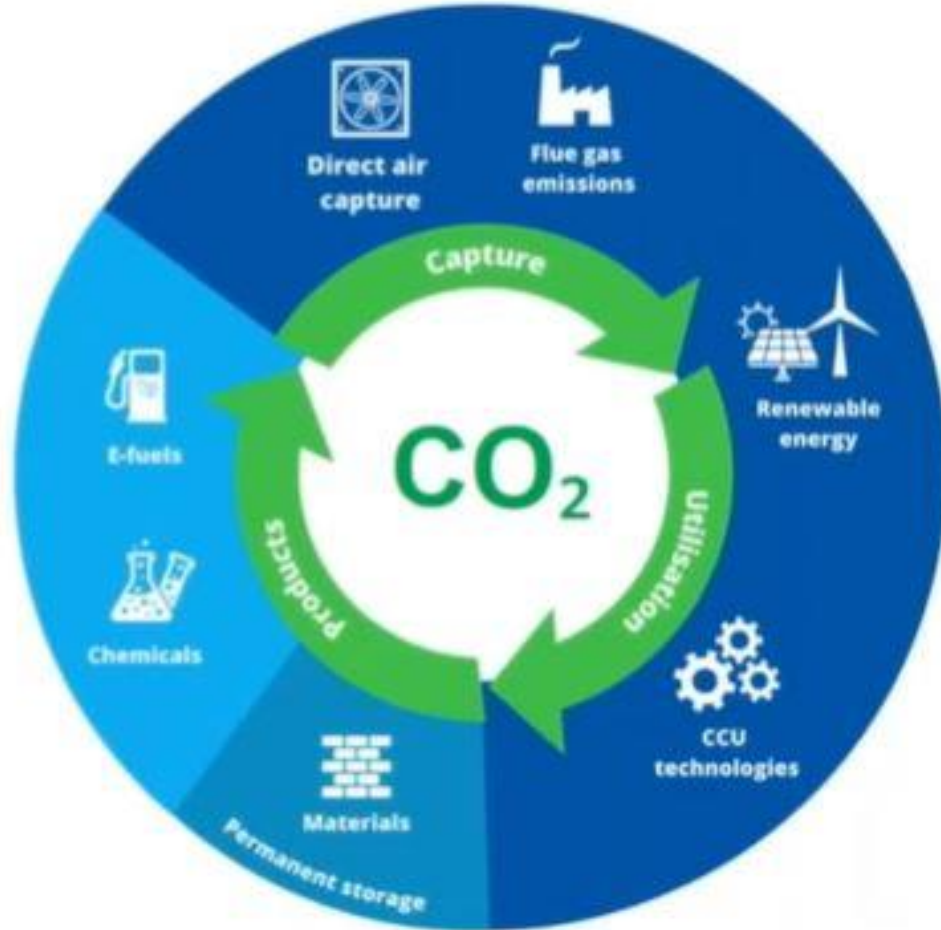
› CARBON SOURCES

CARBON CAPTURE & UTILIZATION - KEY TO CIRCULARITY

- › Without fossil resources, carbon must come from recycled materials
- › Whether bio-based or recycled, the carbon efficiency of processes will be limited
- › Hence there will be a parallel need for the capture and conversion of CO₂



CO₂ UTILIZATION



(1) Applications of CO₂

- Mineralization, greenhouses, enhanced oil recovery, ...
- CO₂ as a building block in organic synthesis
- CO₂ for synthetic fuels and feedstock

(2) Technology readiness

- Direct utilization
- Chemical conversion

(3) Performance comparison of CO₂ applications

- TRL, cost and volume
- Life cycle analysis
- Merit order for renewable electricity

APPLICATIONS OF CO₂

CO₂ AS BUILDING BLOCK IN ORGANIC SYNTHESIS

Table 1: Most advanced implemented plants for the synthesis of CO₂-based polycarbonates and polyols for polyurethanes

Companies	Countries	Capacity in tonnes per annum (t/a)	Final products	CO ₂ share (%)	CO ₂ -based carbon content (%)
Asahi Kasei and various under their licenses	various	750,000	Aromatic polycarbonates	17.3	4.7
Covestro	Germany	5,000	Polycarbonates polyols for polyurethanes	20	5.5
Empower Materials	United States	500	PPC, PEC, PCHC, PPCHC, PBC	ca. 40	ca. 11
Jiangsu Zhongke Jinlong-CAS Chemical	China	10,000	PPC polyols	40	11
Jilin Boda New Materials	China	50,000	PPC or PEC	ca. 40	ca. 11
Inner Mongolia Mengxi High-Tech Group	China	3,000	PPC, PEPC, PPCHC	ca. 40	ca. 11
Saudi Aramco (formerly Novomer)	United States	5,000	PPC, PEC	43	ca. 12
Taizhou BangFeng Plastic	China	30,000	PPC	ca. 40	ca. 11
Nanyang Zhongju Tianguan – Tianguan Group	China	5,000	PPC	ca. 40	ca. 11

<http://nova-institute.eu/press/?id=236>

- CO₂ reacts only with highly reactive chemicals
- 'Polymers' may bring significant volume

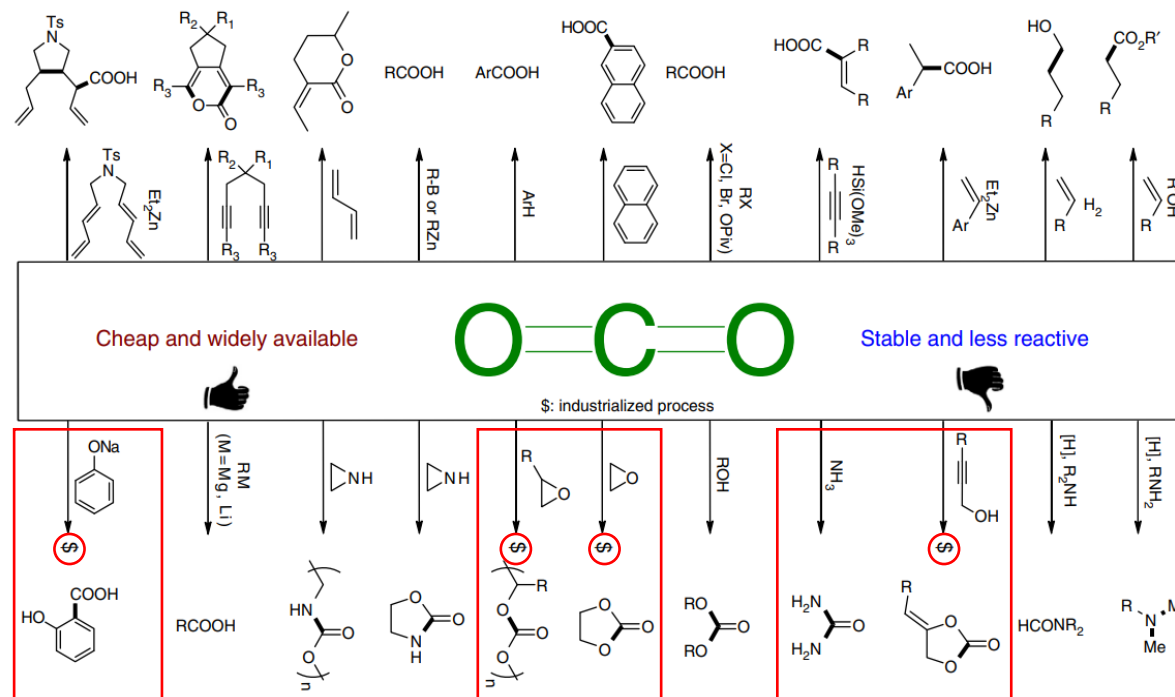


Figure 1 | Representative examples using CO₂ as C1 building block in organic synthesis. Along with the rapid development of organometallic chemistry and catalysis, various types of efficient CO₂ transformations were discovered in the past decades. However, in general, the substrate scope and efficiency of these reactions are still limited due to the requirement of reactive agents for CO₂ activation. As a result, only a few processes have been industrialized until now (marked by \$).

Source: Using carbon dioxide as a building block in organic synthesis; Qiang Liu, Lipeng Wu, Ralf Jackstell & Matthias Beller; DOI: 10.1038/ncomms6933, Nature communications

APPLICATIONS OF CO₂

PROCESS DEVELOPMENT FOR SYNTHETIC FUELS AND FEEDSTOCK

ENERGY TRANSITION IN INDUSTRY:

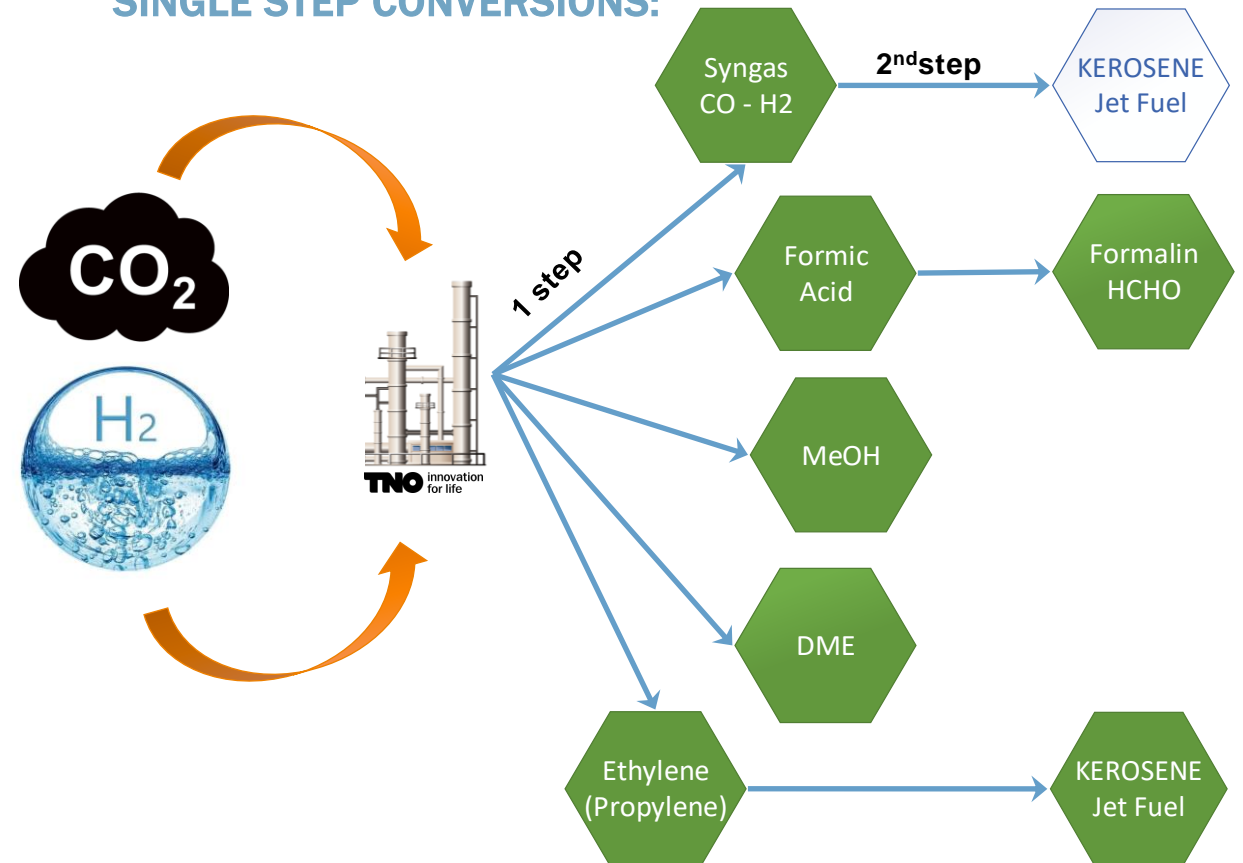
In a fossil-free future hydrocarbons will remain to be important in the products we use in everyday life.

With renewable energy, hydrogen can be produced from water by electrolysis. CO₂ can be captured from biogenic flue gasses or directly from ambient air.

- › TNO is recognized as expert on carbon capture processes in industry
- › TNO develops technology that converts CO₂ to commodity chemicals for use in industry and the transportation sector.
- › These conversion processes are based on process intensification and process integration technology.
- › With smart reactors, products can be made from H₂ and CO₂ in a single step, with high conversion and energy efficiency

Jan-Willem Könemann – “Synthetic fuels and Feedstock”, TNO 2022

SINGLE STEP CONVERSIONS:

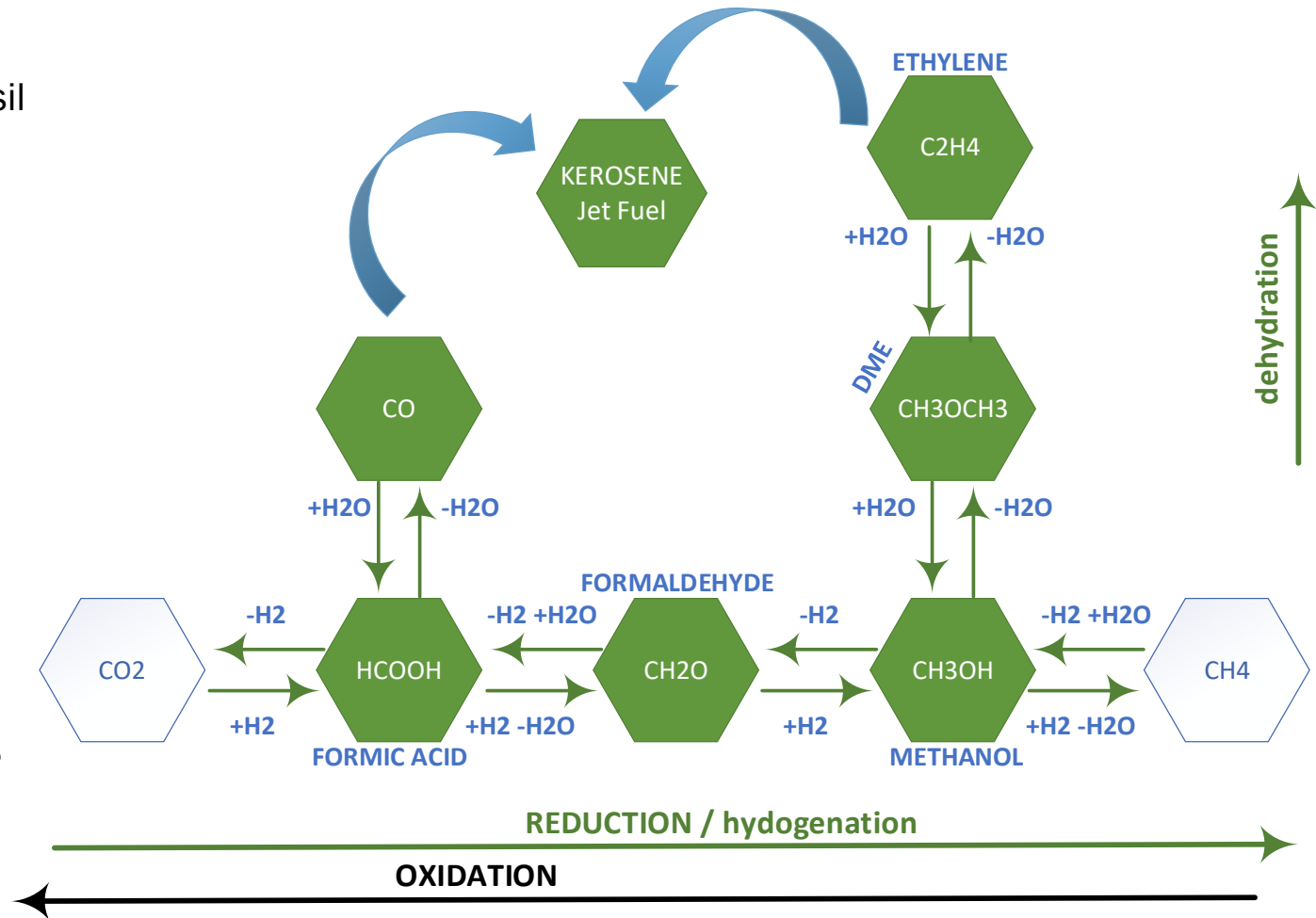


CO₂ FOR SYNTHETIC FUELS AND FEEDSTOCK

COST OF GREEN HYDROGEN DOMINATES SYNTHETIC FUELS COSTS

- › Bio and synthetic feedstock will replace fossil fuels in time
- › The future chemical commodity market is changing, oxygenates such as alcohols and ethers will become increasingly important
- › Synthetic products are made by reduction instead of oxidation processes

› Example: the current conventional way to produce formaldehyde is oxidation of methanol, with CO₂ as starting point, this is reversed



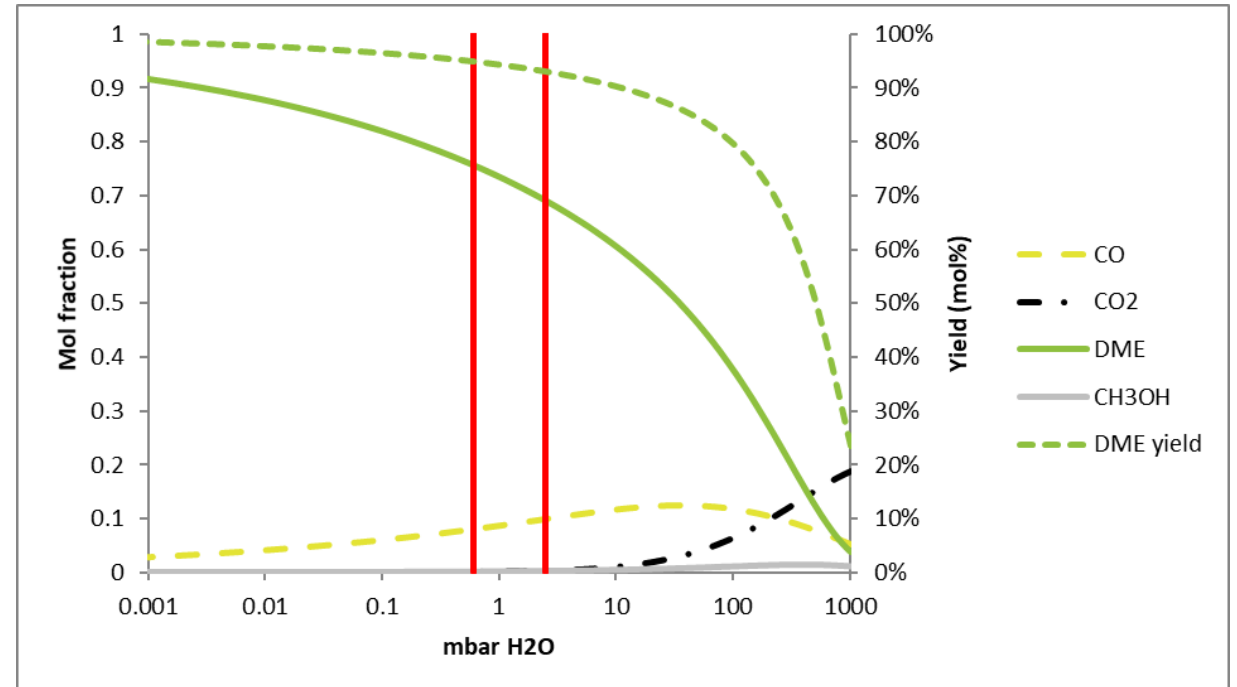
CO₂ FOR SYNTHETIC FUELS AND FEEDSTOCK

PROCESS DEVELOPMENT - CONVERSION IS HINDERED BY STEAM

THERMOCHEMICAL REACTIONS:

- › $\text{CO}_2 + 3\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ (hydrogenation to methanol)
 - › $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$ (reversed water gas shift, syngas)
 - › $\text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH}$ (hydrogenation to methanol)
 - › $2 \text{CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$ (dehydration to DME)
- › Removing steam pushes the reaction equilibrium to the product side, hence enhances single pass conversion (Le Chatelier's principle)

- › Two options are investigated by TNO
 - › Water removal by adsorbents (**SEDMES**)
 - › Water removal by membranes (**SIENNA**)



van Kampen et al. (2019) *Chemical Engineering Journal*.
<https://doi.org/10.1016/j.cej.2019.06.031>

CO₂ FOR SYNTHETIC FUELS AND FEEDSTOCK

TWO NEW TNO REACTOR CONCEPTS FOR DME (AND SYNGAS / METHANOL / ETHYLENE)

SEDMES (TRL 5 → 6)

› In-situ water separation by adsorption



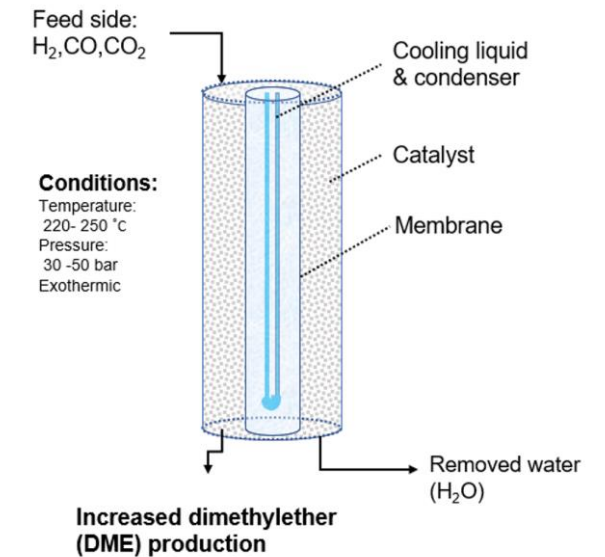
TRL 5 → TRL 6

SIENNA (TRL 3 → 5)

› In-situ water separation by a membrane & condensation

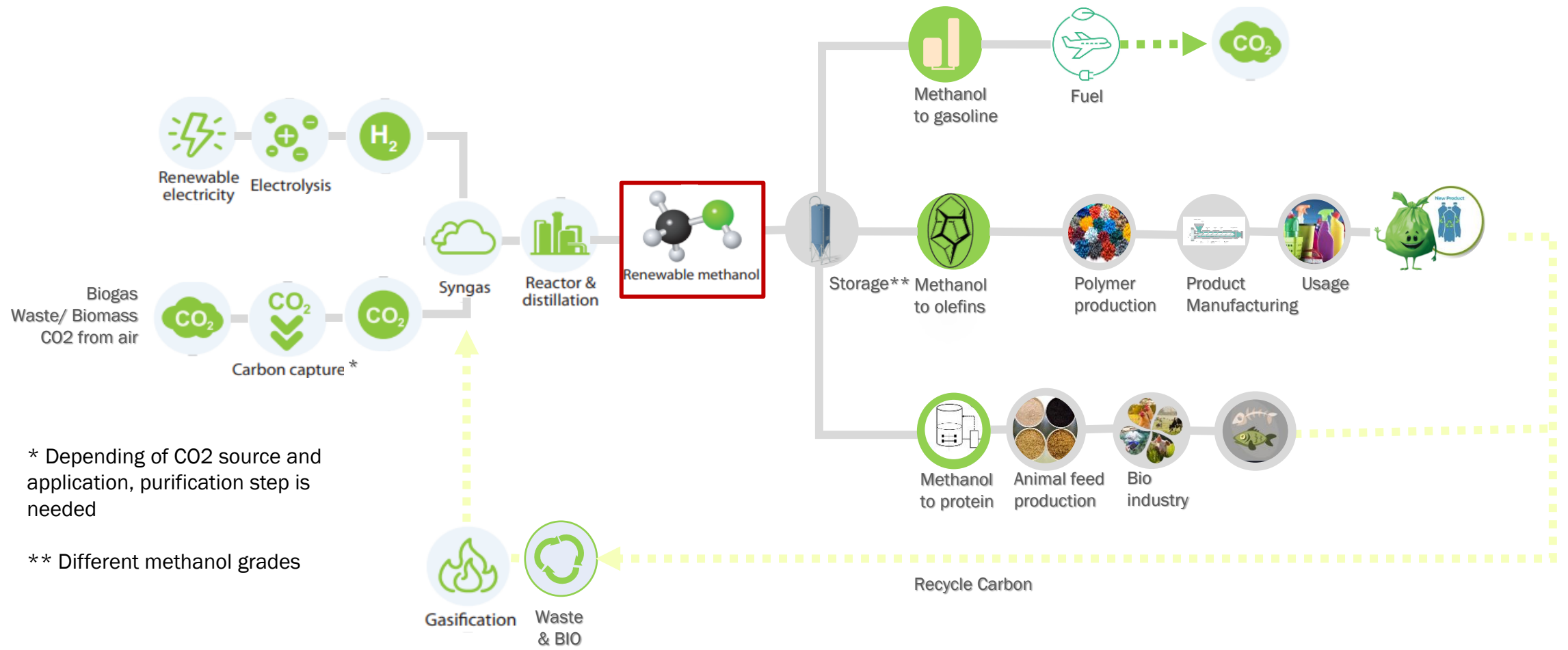


TRL 3 → TRL 5



CO₂ FOR SYNTHETIC FUELS AND FEEDSTOCK

METHANOL – THE FULCRUM MOLECULE?

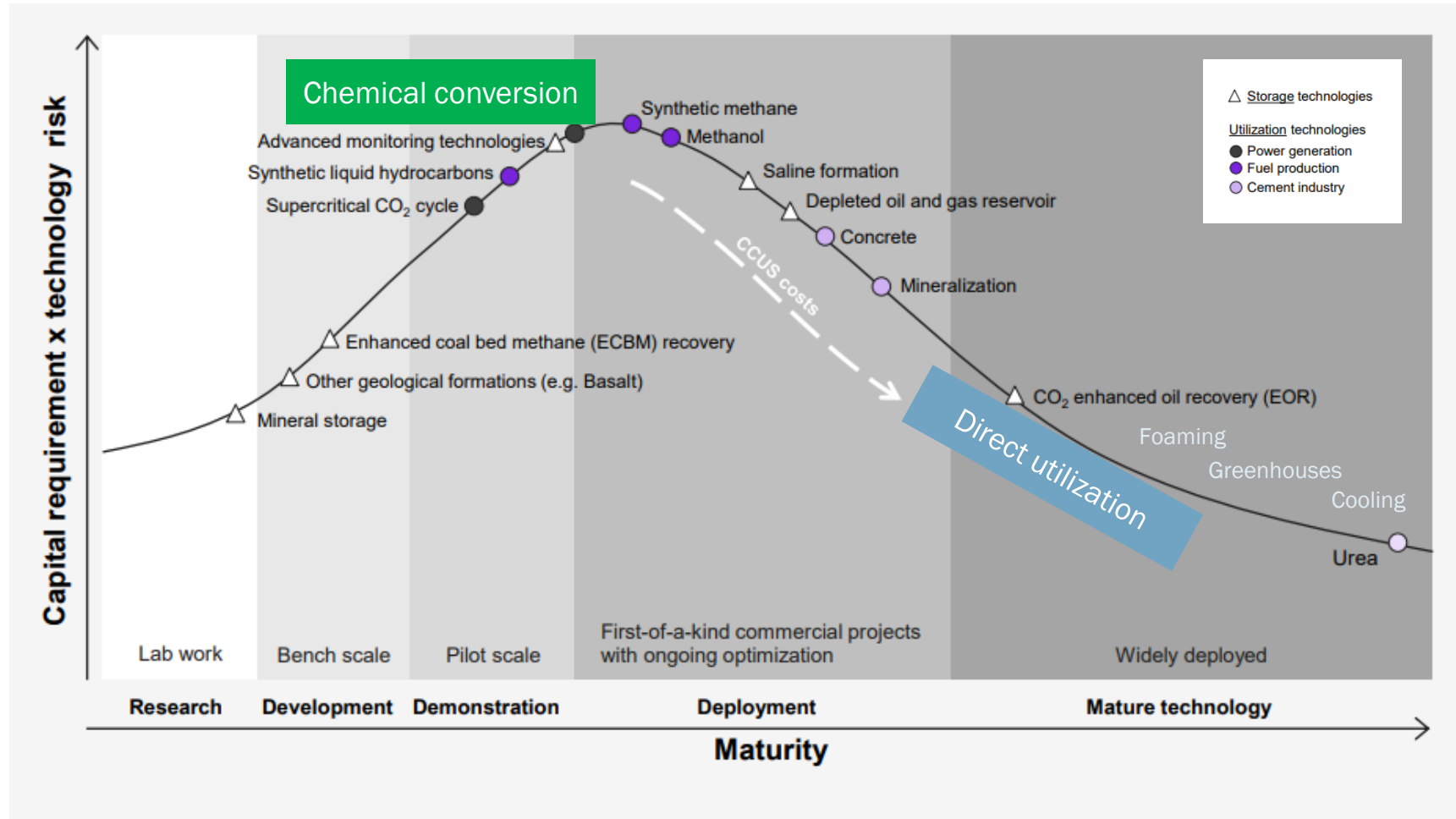


* Depending of CO₂ source and application, purification step is needed

** Different methanol grades

Bron: gedeeltelijk van Methanol institute and QAFAQ

TECHNOLOGY READINESS OF CO₂ UTILIZATION



Direct utilization

- Volume usually small
- Short cycle-time ('back in the air quickly')

Chemical conversion

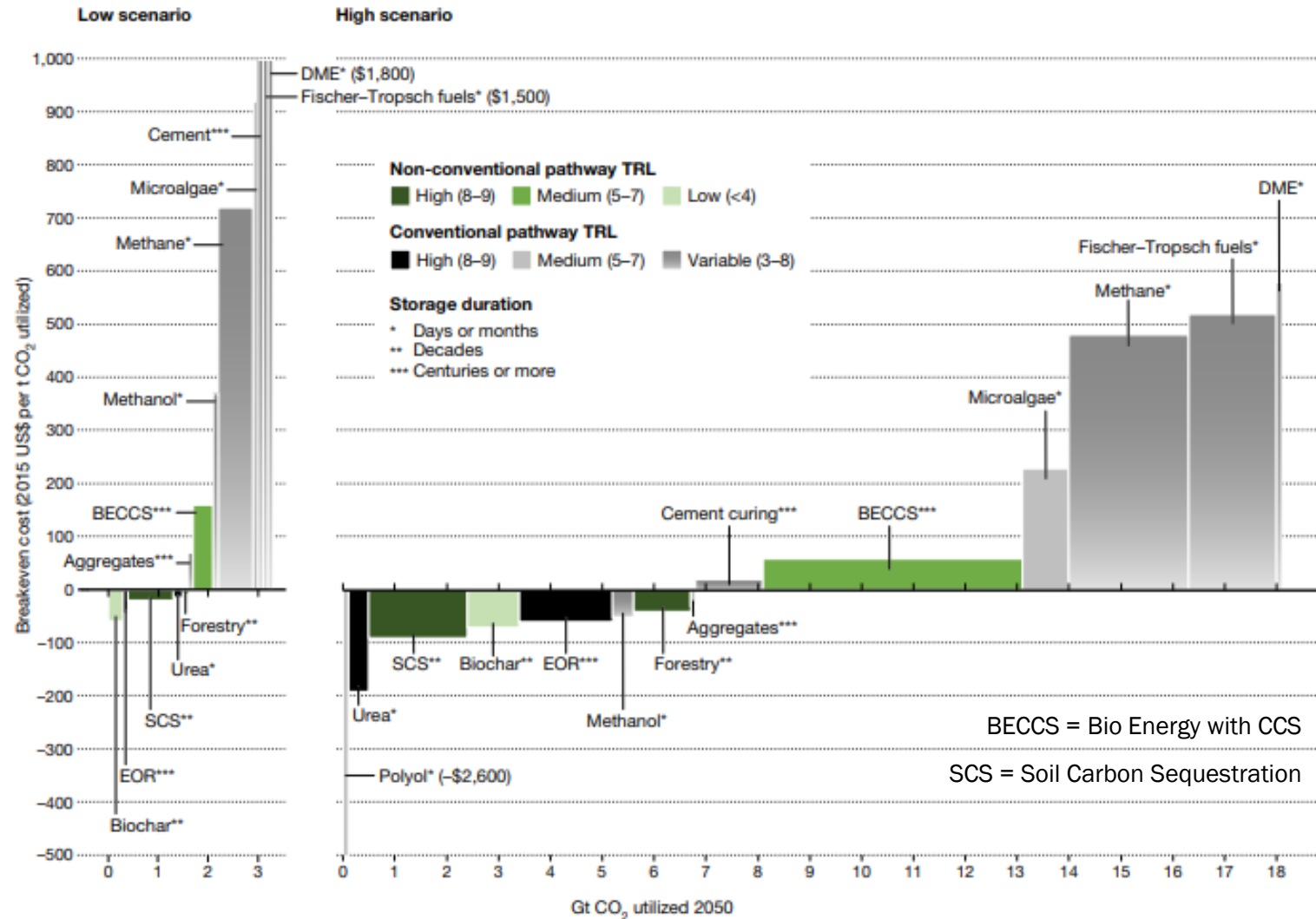
- Potentially high volume
- High energy cost
- Short cycle time (fuels)
- Long cycle time (materials)

Carbon Capture Utilization and Storage - Towards Net-Zero 2021 (Kearney institute)

Sources: IEA-ETP Clean Energy Technology Guide (2020); Kearney Energy Transition Institute analysis

PERFORMANCE COMPARISON OF CO₂ APPLICATIONS

TECHNICAL & ECONOMIC: TRL, COST AND VOLUME



Chemicals, fuels and micro-algae reduce emissions, but have limited potential to remove CO₂ for long duration.

(Construction) materials have volume and margin compared to conventional alternatives and potential for net removal.

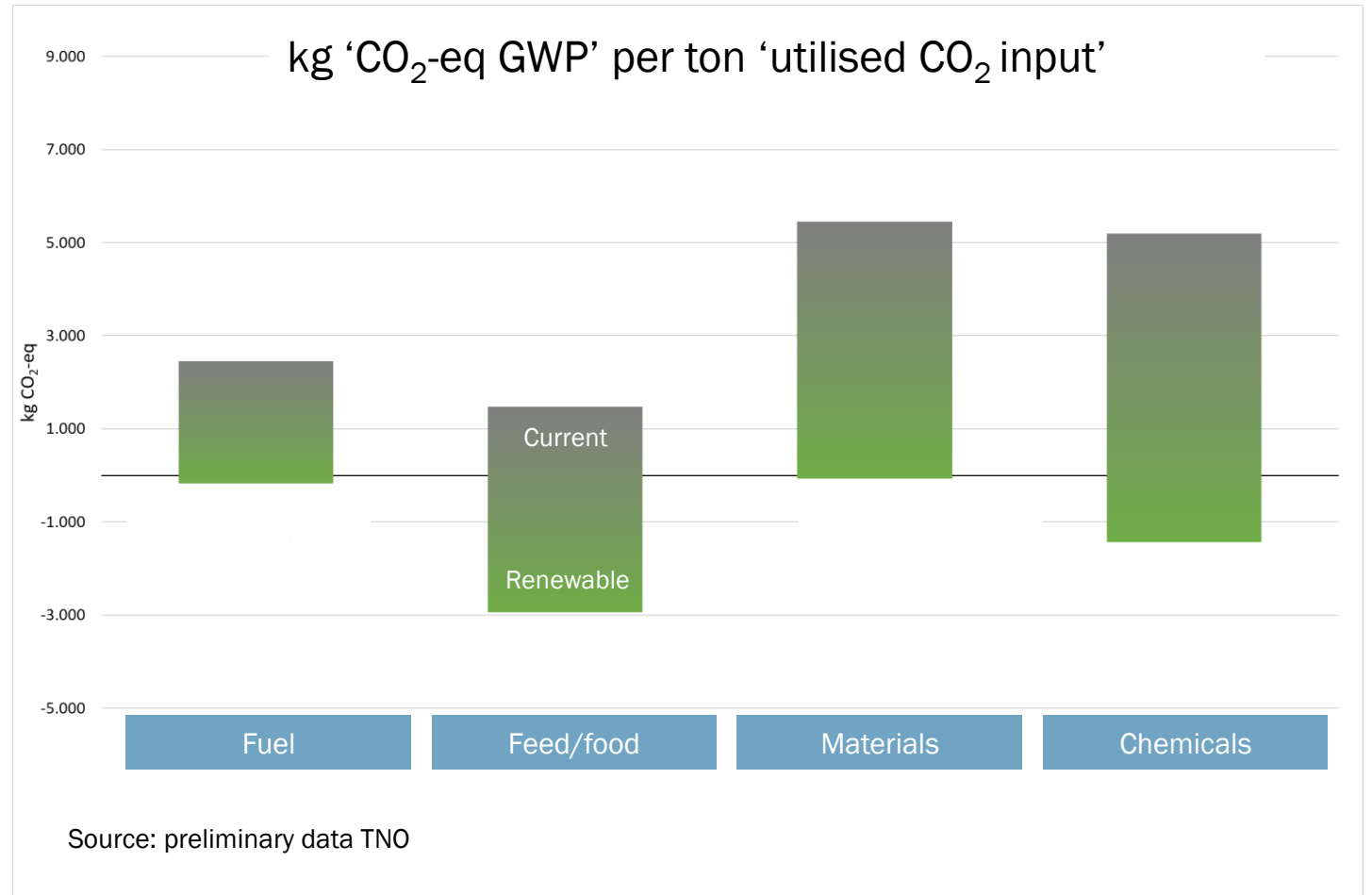
Caveat These are techno-economics only, *not* life-cycle.

Hepburn, C., Adlen, E., Beddington, J. et al. The technological and economic prospects for CO₂ utilization and removal. Nature 575, 87–97 (2019). <https://doi.org/10.1038/s41586-019-1681-6>

PERFORMANCE COMPARISON OF CO₂ APPLICATIONS

LIFE CYCLE ANALYSIS

- › LCA analysis assesses the full system impact on global warming
 - Duration of 'storage'
 - Net CO₂ (GHG) balance
 - Start 'today or tomorrow'
- › LCA is most relevant for deployment policy
- › The type of energy source ('current' or renewable) accounts for most of the difference

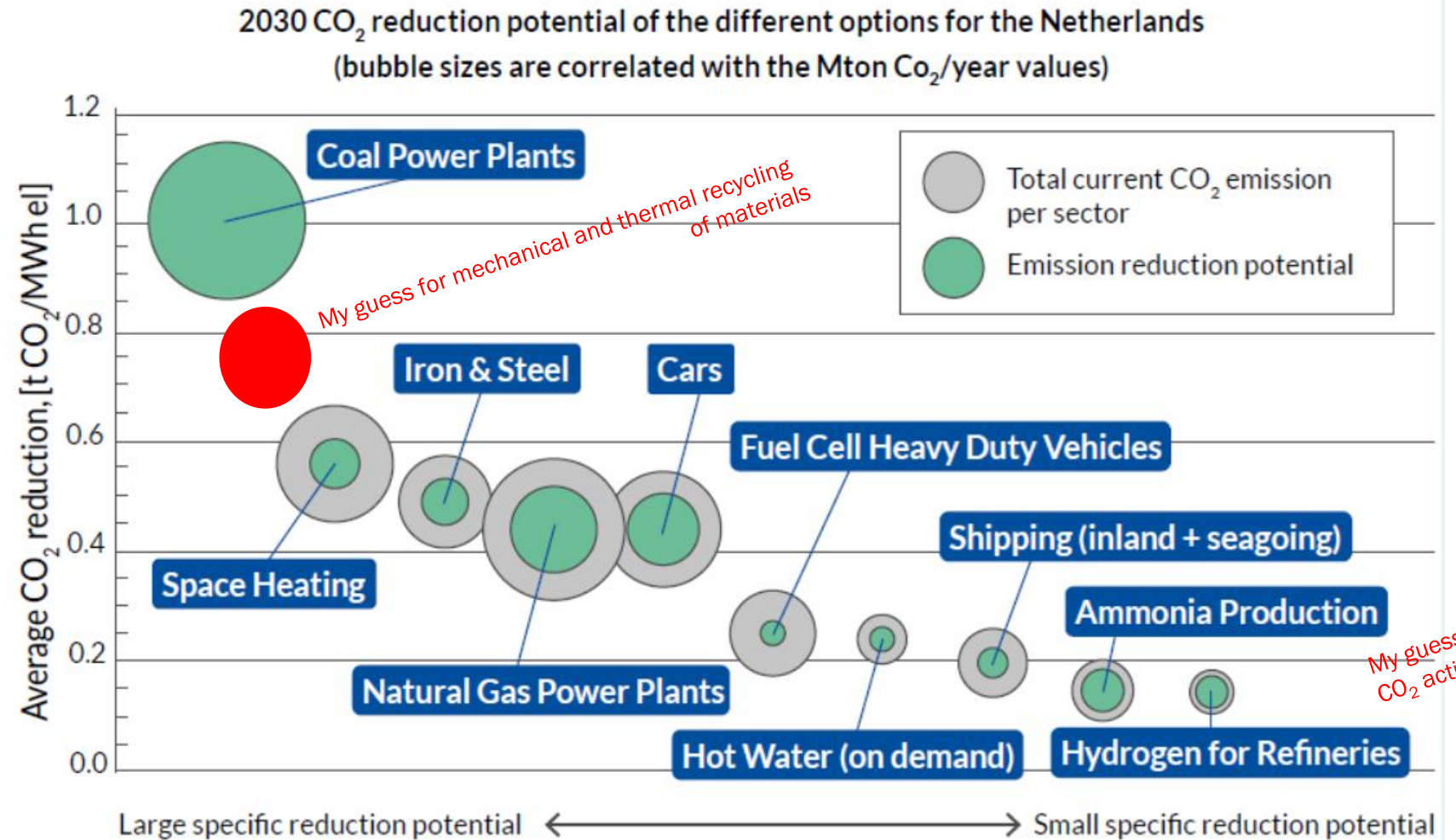


MERIT ORDER FOR RENEWABLE ELECTRICITY

IF (when)

renewable electricity is available

... how to use it most effectively to reduce CO₂ emission?



(Source: TNO-Voltachem whitepaper)

› CONCLUSIONS & REMARKS

CO₂ conversion to some materials is mature, yet requires energized ('reduced') co-reactants

CO₂ conversion to basic chemical intermediates has substantial volume potential and technology is maturing rapidly

Thorough Life Cycle Analysis of applications is needed to know net effects on the CO₂ emission to atmosphere

To lower net system CO₂ emissions through CO₂ conversion requires abundant low-carbon electricity

As the production of renewable electricity grows, prioritize its use for the:

- Electrification of processes and services that today lead to the production of CO₂
- Mechanical and thermal processing of biomass and waste
- CO₂ conversion processes that rank high by their life-cycle performance to reduce global warming

Abandoning oil and gas tackles CO₂ emission, but necessitates carbon circularity:

- CO₂ capture & conversion to intermediates needs much clean electricity, but enables pathways for basic chemicals
- *Carbon* capture & conversion through recycling and biomass conversion needs less clean electricity but more processing

For development & deployment

- Aim to build investable value chains
- Mature the more efficient CO₂ capture + utilization routes that require less energy and space



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