CCUS as a Tool for Sustainable Development

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ÁTOMO
ponte a nuestro servicio,
y en vez de las cenizas
mortales
de tu máscara,
en vez de los infiernos desatados
de tu cólera,
en vez de la amenaza
de tu terrible claridad, entréganos
tu sobrecogedora
rebeldía
para los cereales,
tu magnetismo desencadenado
para fundar la paz entre los hombres,
y así no será infierno
tu luz deslumbradora,
sino felicidad,
matutina esperanza,
contribución terrestre.

ATOM
put yourself to our service,
and instead of the mortal ashes of your mask,
instead of the unleashed Hells of your spite,
instead of the threat of your terrible clarity,
deliver us your overwhelming rebellion for the grains,
your unleashed magnetism to found peace between men,
and thus your dazzling light will not be a Hell,
but rather happiness, morning hope,
terrestrial contribution...

Pablo Neruda

Decarbonization as a route towards sustainable circularity

Eduardo Falabella de Sousa-Aguiar, Magdalena Ramirez Corredores, Mireya Goldwasser.

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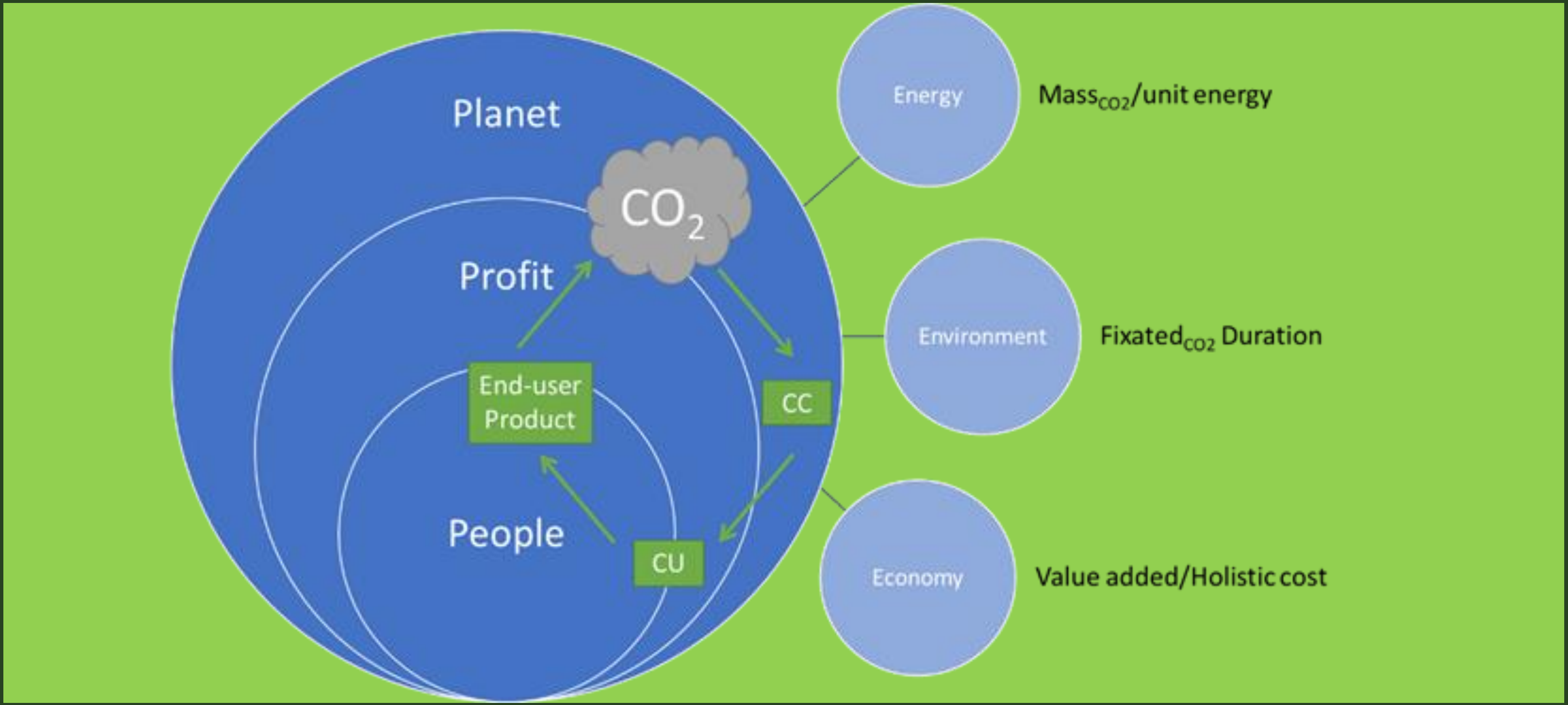
- **Our Society is facing the urgent need of a deep change of its lifestyle, stepping away from the consumerism that has characterized the entire 20th Century.**

- **The Linear Economy model is not sustainable anymore, for both the aspects of overexploitation of natural resources and the large production of waste that have a strong impact on environment and climate.**

- **The Circular Economy, that implements the concepts of reducing waste by giving several lives to a good, is a more conservative approach to the use of natural resources that are finite.**

Carbon Capture and Utilization-CCU is at the heart of the Circular Economy.



The basis of corporate social responsibility is a strategy that seeks a balance between the social, environmental and economic aspects.

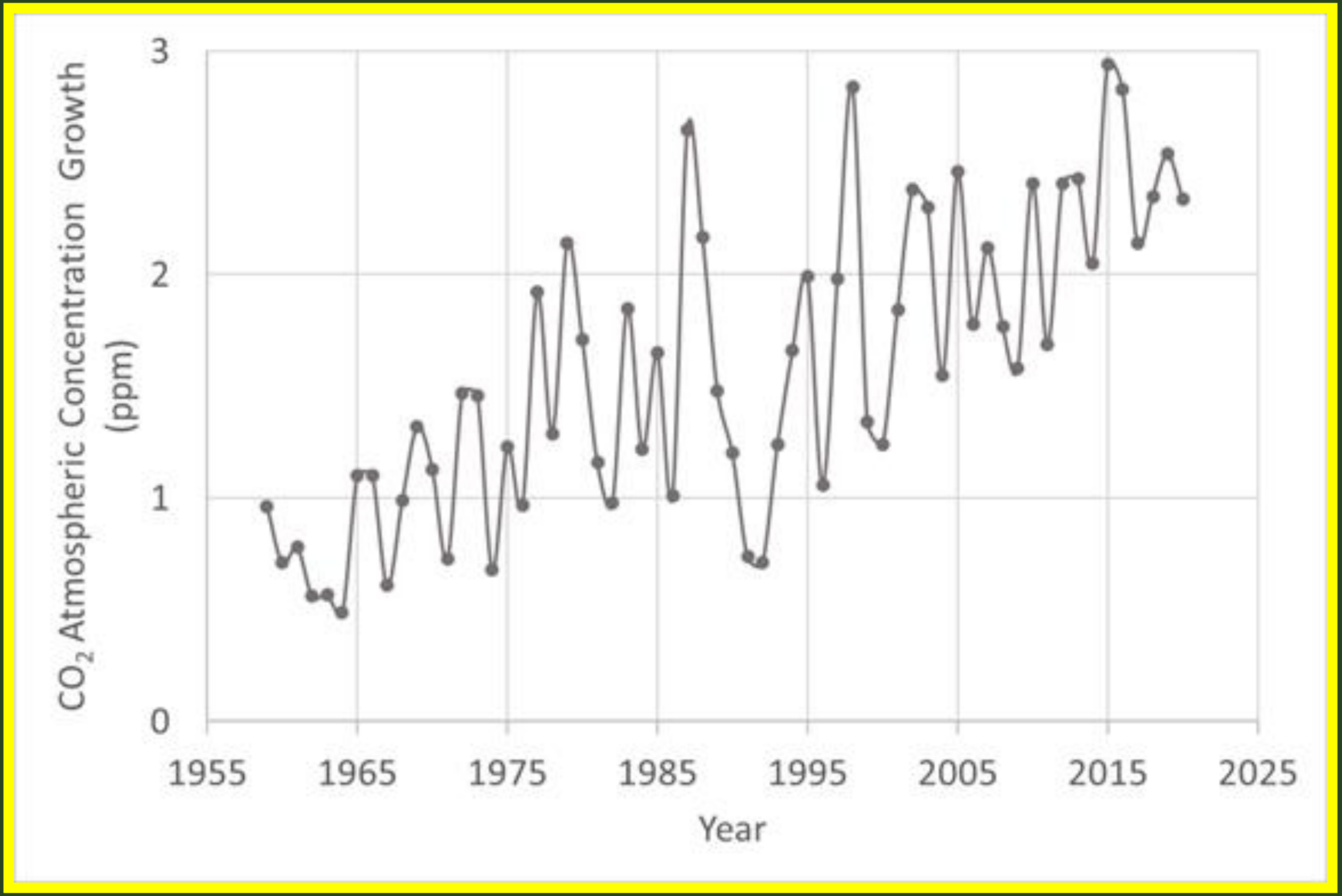
These three aspects provide the basis for the 3 Ps: People, Planet & Profit. It is an art to ensure that the 3 Ps in daily business activities are and remain in balance.

The problem regarding CO_2

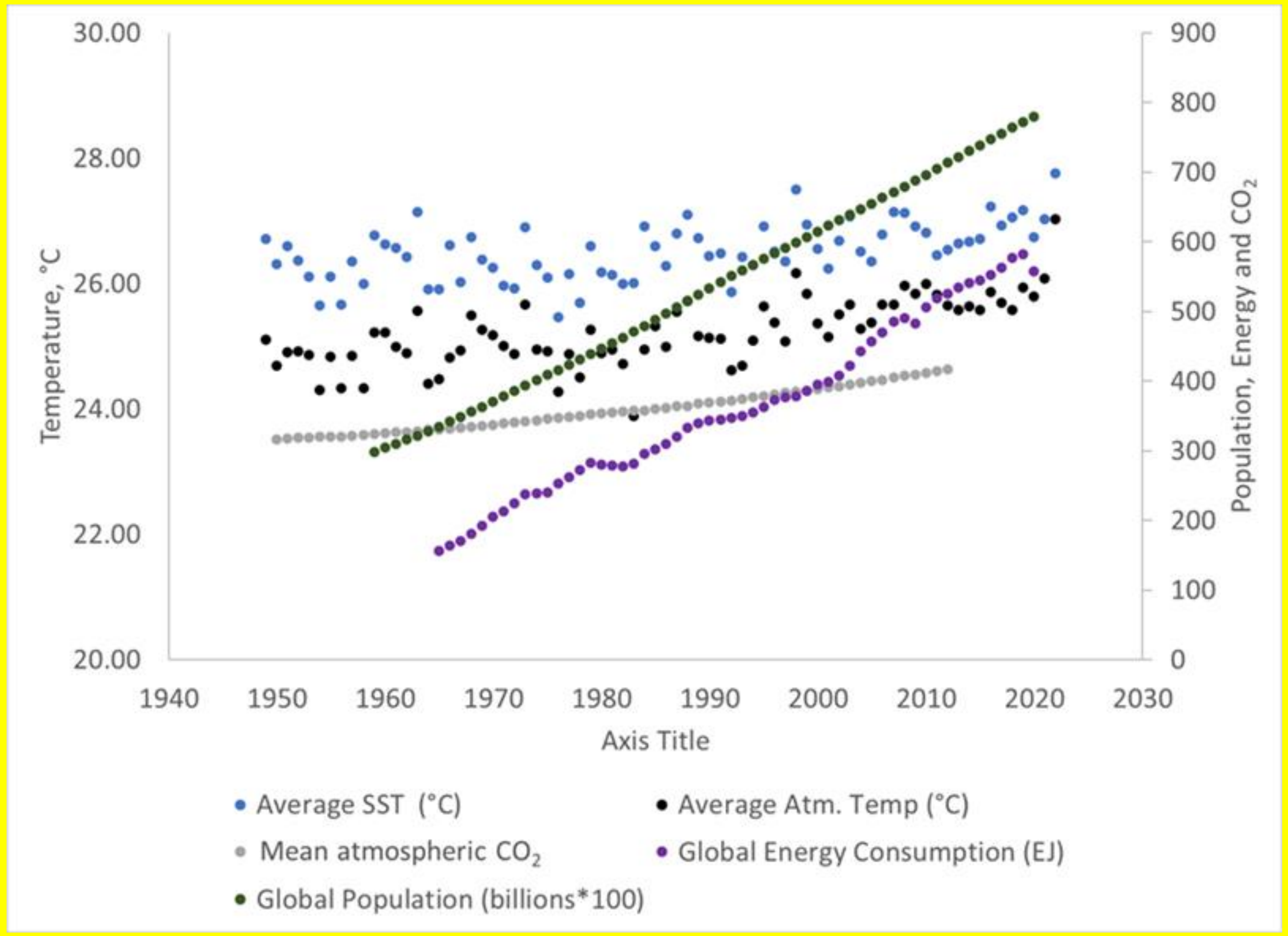
- **Certain gases i.e., greenhouse gases (GHGs) can absorb energy (radiative efficiency), during their effective time in the atmosphere (lifetime) causing a warming effect known as Global Warming Potential (GWP).**

- **Among the high-GWP GHGs, CO_2 is the most abundant with its concentration growing at a rate of more than 2 ppm/y.**

- **Therefore, the concept of Radiative Forcing (RF) was introduced to explain the net change in the energy balance of the Earth system due to some imposed perturbation, such as the increase of GHGs atmospheric concentration.**



CO_2 emissions growth since second half XX century


30.00
28.00
26.00
24.00
22.00
20.00
Temperature, °C
900
800
700
600
500
400
300
200
100
0
Population, Energy and CO_2
1940
1950
1960
1970
1980
1990
2000
2010
2020
2030
Axis Title
Average SST (°C)
Average Atm. Temp (°C)
Mean atmospheric CO_2
Global Energy Consumption (EJ)
Global Population (billions*100)

(i) The Earth's average surface temperature was 0.8°C warmer during the first decade of the 21st century than it was during the first decade of the 20th century,
(ii) Most of the warming has been attributed to human activities that release heat-trapping GHGs into the atmosphere, especially CO_2,
(iii) Natural climate variability can explain short-term climate changes, as well as regional differences; however it cannot account for the long-term warming trend,
(iv) Climate changes also include increases in frequency of intense rainfall, decreases in Northern Hemisphere snow cover and Arctic-sea ice, more frequent warmer days and nights, rising sea levels, and widespread ocean acidification,
(v) Human and natural systems at risk include freshwater resources, the littoral environment, ecosystems, agriculture, fisheries, human health, and national security, among others,
(vi) The magnitude of climate change and the severity of its impacts depend strongly on the measures taken and implemented.

United Nations Framework Convention on Climate Change (UNFCCC)

- **An initiative known as the “Net-Zero” is introduced.**

- **The main goal of such initiative is to achieve a temperature increase that does not exceed 1.5 °C by 2050 .**

Emphasis is placed on the need for reduction of CO_2 emissions.

		Time scale (y)
R. 1	$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^-$	$10 - 10^3$
R. 2	$6CO_2 + 6H_2O$ + photons $\rightarrow C_6H_{12}O_6 + 6O_2$ $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ + heat	$1 - 10^2$
R. 3	$CO_2 + CaSiO_3 \rightarrow CaCO_3 + SiO_2$	$10^4 - 10^6$
R. 4	$CO_2 + CaCO_3 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$	$10^3 - 10^4$

Examples of reactions involved in the natural CO_2 cycle

R.1 - solubility in sea water (buffering)
R.2 - photosynthesis and respiration
R.3 – mineralization
R.4 - carbonate dissolution

The concept of CCUS (Carbon Capture, Utilization and Storage)

Carbon Capture, Utilization, and Storage (CCUS) encompasses methods and technologies to remove CO_2 from the flue gas and from the atmosphere, followed by recycling the CO_2 for utilization and determining safe and permanent storage options.

In order to achieve Decarbonization it is necessary to develop new technologies that:

(i) capture and store or sequester the produced CO_2 (CS),

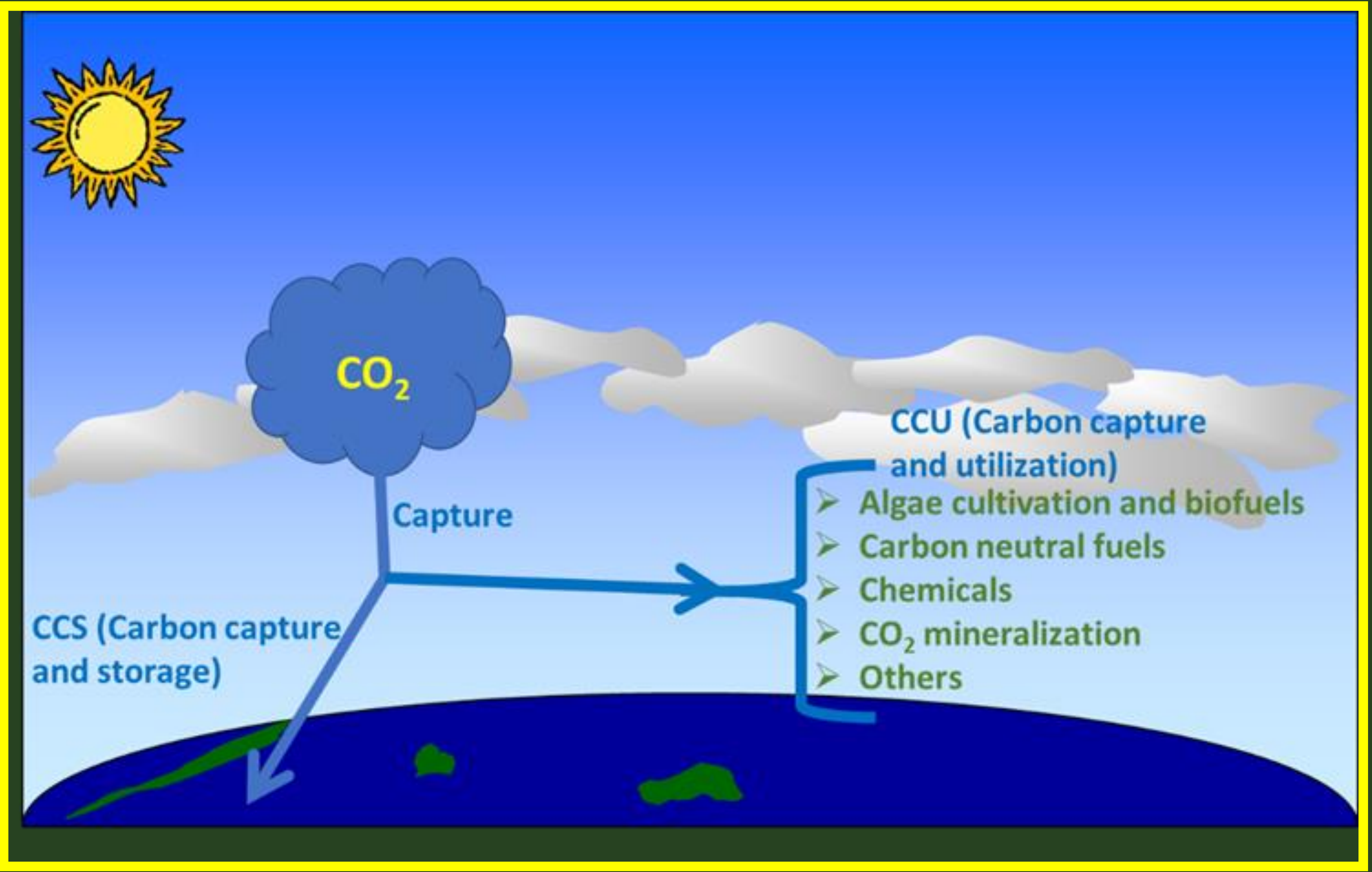
(ii) convert the produced CO_2 into more valuable chemical feedstock (CU),

carbon avoidance through:

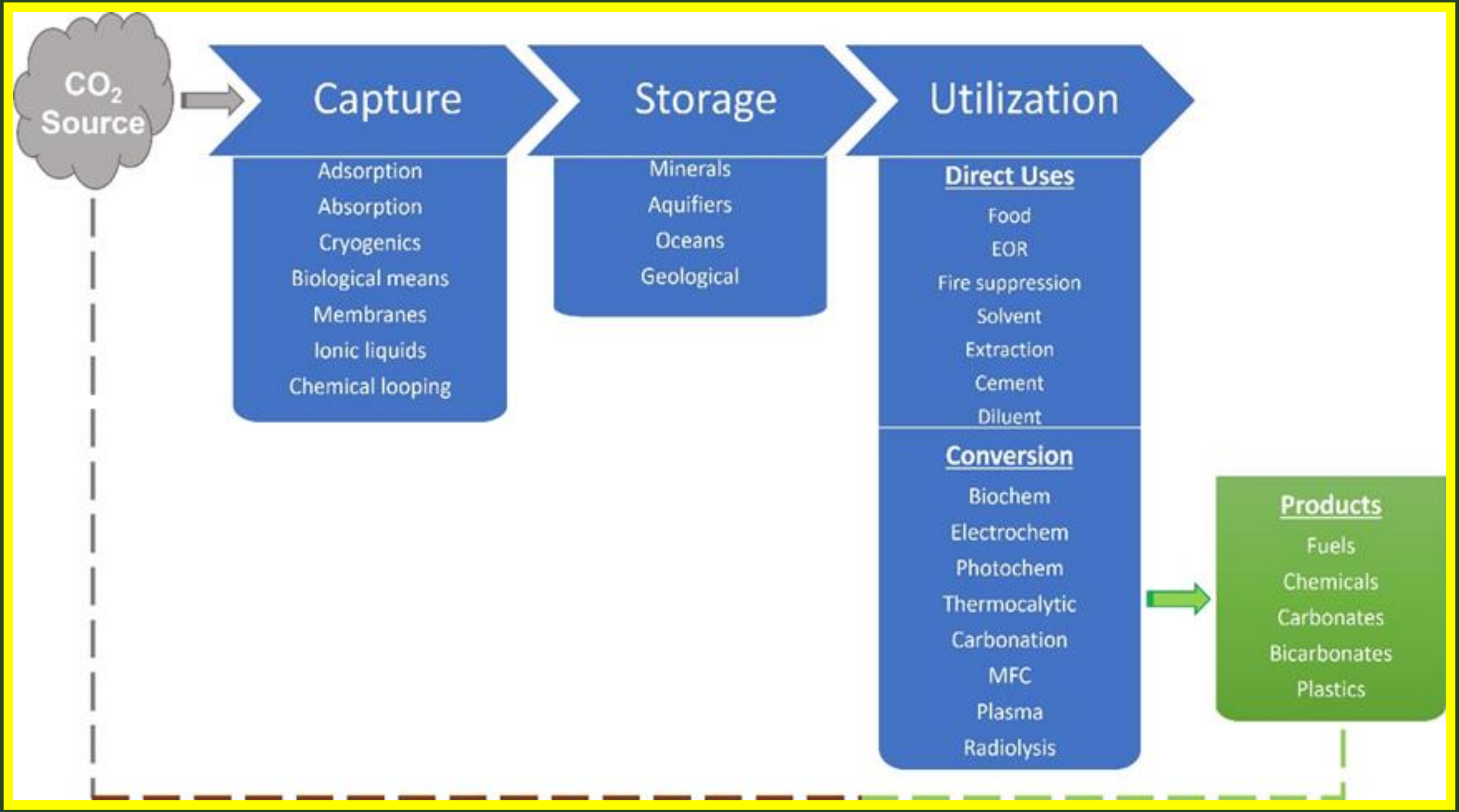
(iii) recycle the produced CO_2, and/or

(iv) eliminate the use of any process that generates CO_2 emissions.

DECARBONIZATION



DECARBONIZATION



Methods to promote CO_2 removal and utilization

CO_2 VALORIZATION VIA INORGANIC PROCESSES

CARBONATION

Mineralization or mineral carbonation (MC) refers to the process for capturing CO_2 into alkaline or alkaline earth carbonates, bicarbonates, or carbamates. MC refers to conversion processes mimicking some of the natural fixation reactions occurring between atmospheric gases and earth surface minerals.

Carbonates may have several types of application.

Current uses and applications of carbonates

Carbonate	Uses
Alkaline	
Lithium Carbonate	drug development
Sodium Carbonate (soda ash)	glass making, pulp and paper industry, sodium chemicals (silicates), soap and detergent production, paper industry and water softener
Potassium Carbonate	glass making, soft soap production, textile, and photography chemicals
Rubidium Carbonate	glass making, short-chain alcohol production
Cesium Carbonate	production of other cesium salts
Alkaline Earth	
Beryllium Carbonate	processing ores and in chemical and nuclear applications
Magnesium Carbonate	skin care products, cosmetic, anti-fire products, climbing chalk
Calcium Carbonate	glass, textile, paint, paper and plastic production, caulks industry, to produce ink and sealant, non-toxic food additive, as a drug development and chalk production
Strontium Carbonate	fireworks, magnets, and ceramic manufacture
Barium Carbonate	glass, cement, ceramic, porcelain, rat poison manufacture
Boron family	
Aluminum Carbonate	drug development
Thallium Carbonate	fungicides manufacture
Others	
Lead Carbonate	glass, cement, ceramic, porcelain, rat poison manufacture

DECARBONATION REACTIONS

R. 7

$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$ $\Delta H_{298\ K}$= -89 kJ/mol

R. 8

$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$ $\Delta H_{298\ K}$= -64 kJ/mol

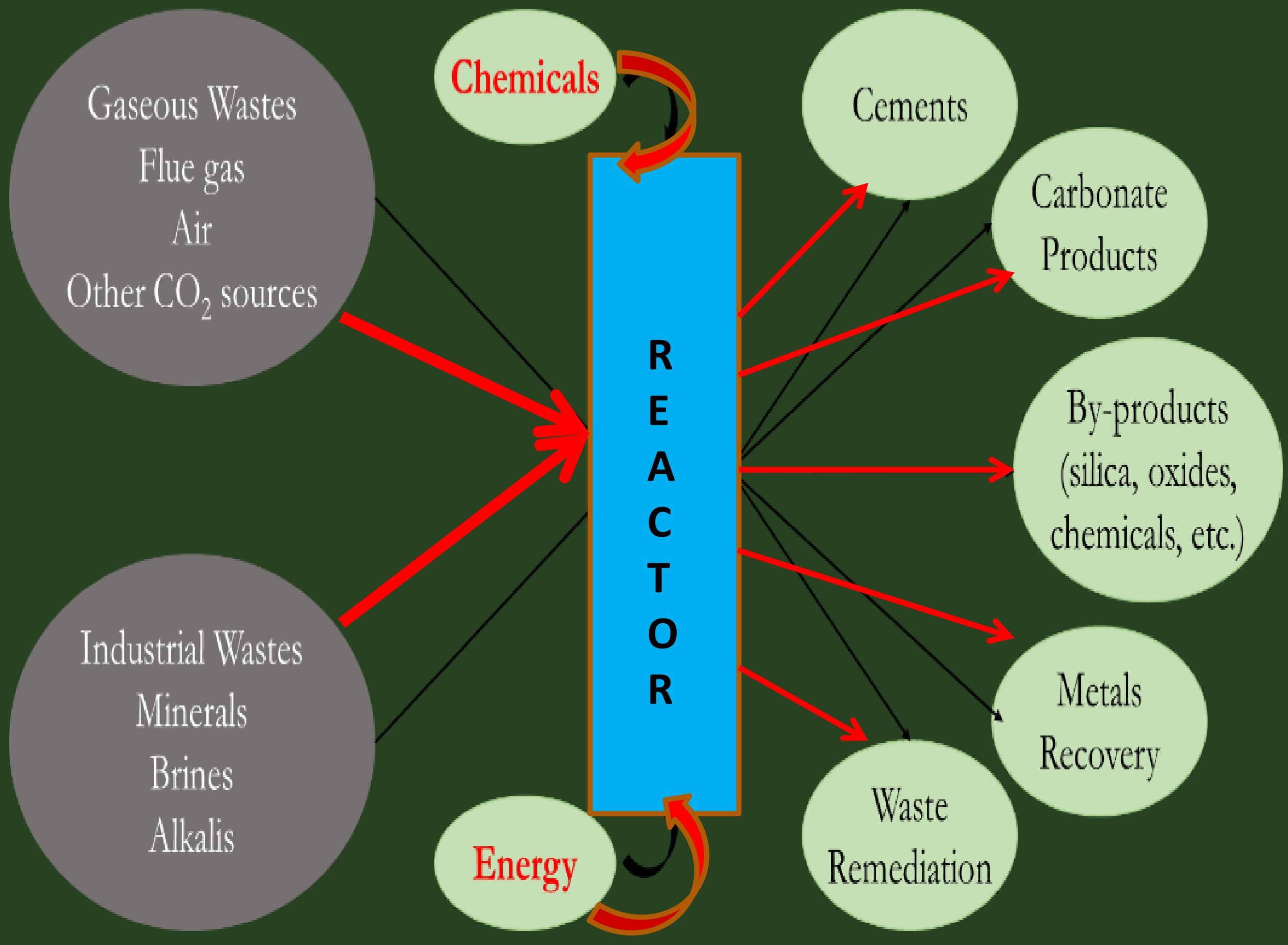
R. 9

$Ca_2SiO_4 + 2CO_2 \rightarrow 2CaCO_3 + SiO_2$ ΔH298 K= -90 kJ/mol

Although thermodynamically favored as an exothermic process (see reactions R. 7 through R. 9), Mineral Carbonation is kinetically limited (very slow).

Natural carbonation of silicate rocks is very slow. Hence, the addition of a mineral dissolution step using chemicals is an efficient technique to shorten reaction times and enhance the reaction extent. Among other chemical routes, MC using recyclable ammonium salts pH swing processes is considered a very promising MC technique to store CO_2 permanently.

The process comprises 5 steps: (1) CO_2 capture using ammonia ($NH_3 + CO_2 \leftrightarrow NH_4HCO_3$); (2) the leaching of the Mg/Ca cations from the mineral resource using acid ammonium bisulfate solution (NH_4HSO_4 + Mg/Ca rich silicate $\leftrightarrow$ MgSO4 + SiO_2 + unreacted silicate + $(NH4)_2SO_4$); (3) pH-regulation (to swing the pH from pH 1–2 caused by unreacted NH4HSO4, to pH 8–9, at which carbonation reaction occurs); (4) the MC of CO_2 (as NH_4HCO_3) ($MgSO_4 + NH_4HCO_3 + H_2O \leftrightarrow MgCO_3{\cdot}3H_2O + (NH_4)_2SO_4 + CO_2$); (5) the regeneration of the used chemicals .



Mineralization pathways

Methods to promote CO_2 removal

INORGANIC PROCESSES

UREA SYNTHESIS

Urea is an amide being widely used in fertilizers as a source of nitrogen (N); also, it is an important raw material for the chemical industry. Besides its use as fertilizer, urea is a raw material for the manufacture of two main classes of materials: urea-formaldehyde resins and urea-melamine-formaldehyde . In the health area, urea-containing creams are used as topical dermatological products to promote rehydration of the skin

Methods to promote CO_2 removal

INORGANIC PROCESSES

UREA SYNTHESIS

Urea is industrially produced from NH_3 and CO_2 . The synthesis of urea is currently the largest CO_2 conversion process by volume in the industry. Although urea is an organic compound, the synthesis thereof involves inorganic molecules, namely CO_2 and NH_3

$2NH_3 + CO_2 \rightleftharpoons H_2N\text{-}COONH_4$	$\Delta H_{298\,K}$= -117 kJ/mol
$H_2N\text{-}COONH4 \rightleftharpoons (NH_2)_2CO + H_2O$	$\Delta H_{298\,K}$= 15.5 kJ/mol
$CH_4 + H_2O \rightarrow CO + 3H_2$	$\Delta H_{298\,K}$= 206 kJ/mol
$CO + H_2O \rightarrow CO_2 + H_2$	$\Delta H_{298\,K}$= -41.15 kJ/mol

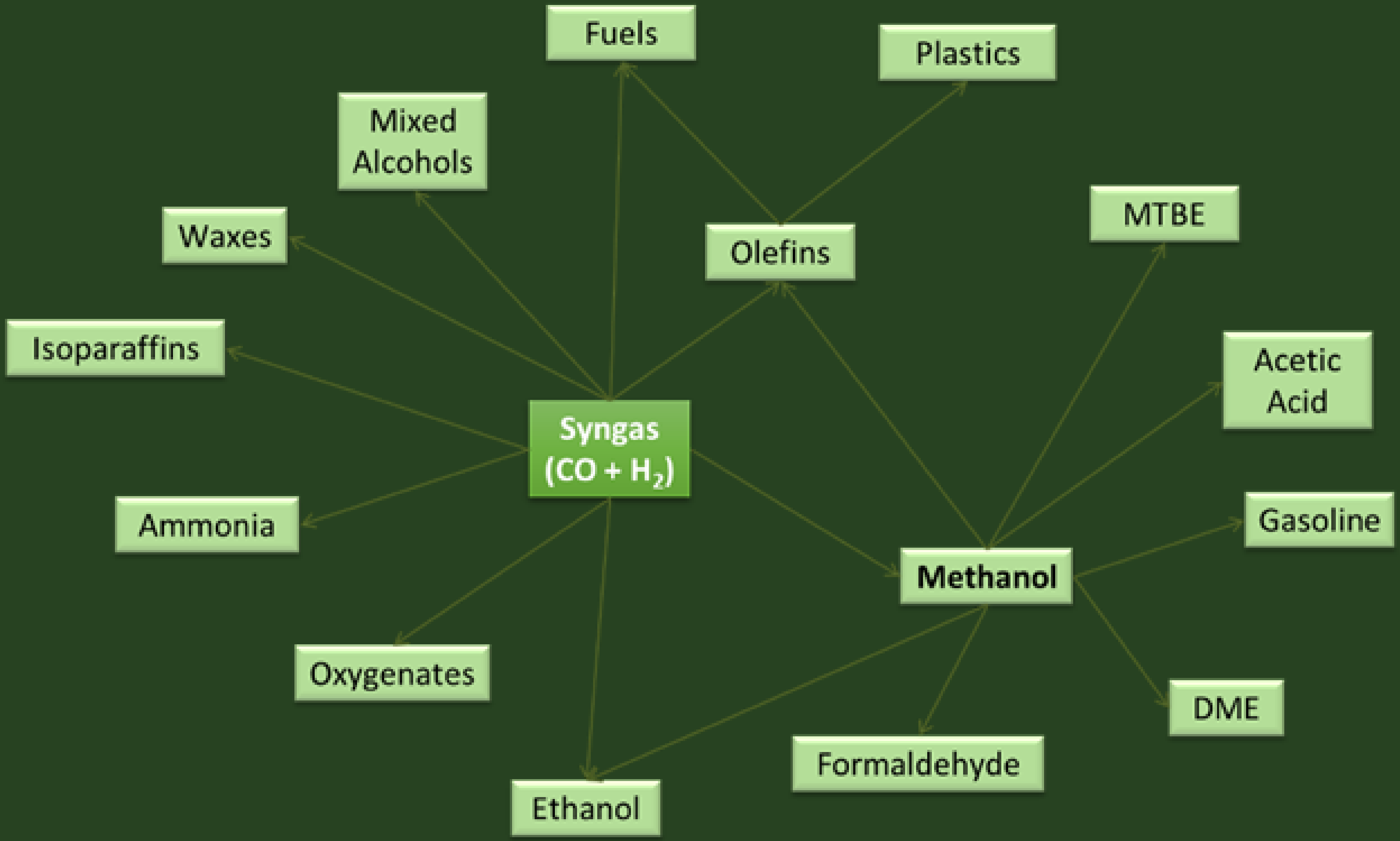
Methods to promote CO_2 removal and utilization

CO_2 VALORIZATION VIA ORGANIC PROCESSES

SYNTHESIS GAS (SYNGAS) PRODUCTION

Syngas is the name given to a mixture of carbon monoxide (CO) and hydrogen (H_2) since it is a useful intermediate, from which a wide range of chemicals, fuels and products can be synthesized. Among the products, olefins and methanol are of more significant importance as these are also intermediates and/or building blocks for some other products.

DECARBONIZATION



Methods to promote CO_2 removal and utilization

CO_2 VALORIZATION VIA ORGANIC PROCESSES

SYNTHESIS GAS (SYNGAS) PRODUCTION

CO_2 Reforming of methane

CO_2 reforming of methane, also known as methane dry reforming (MDR reaction), produces synthesis gas ($CO + H_2$). There are abundant reserves of natural gas with significant proportions of CO_2, which can serve as raw material to the process of MDR without the need to carry out costly gas separation or additional processes, including renewable sources such as biogas.

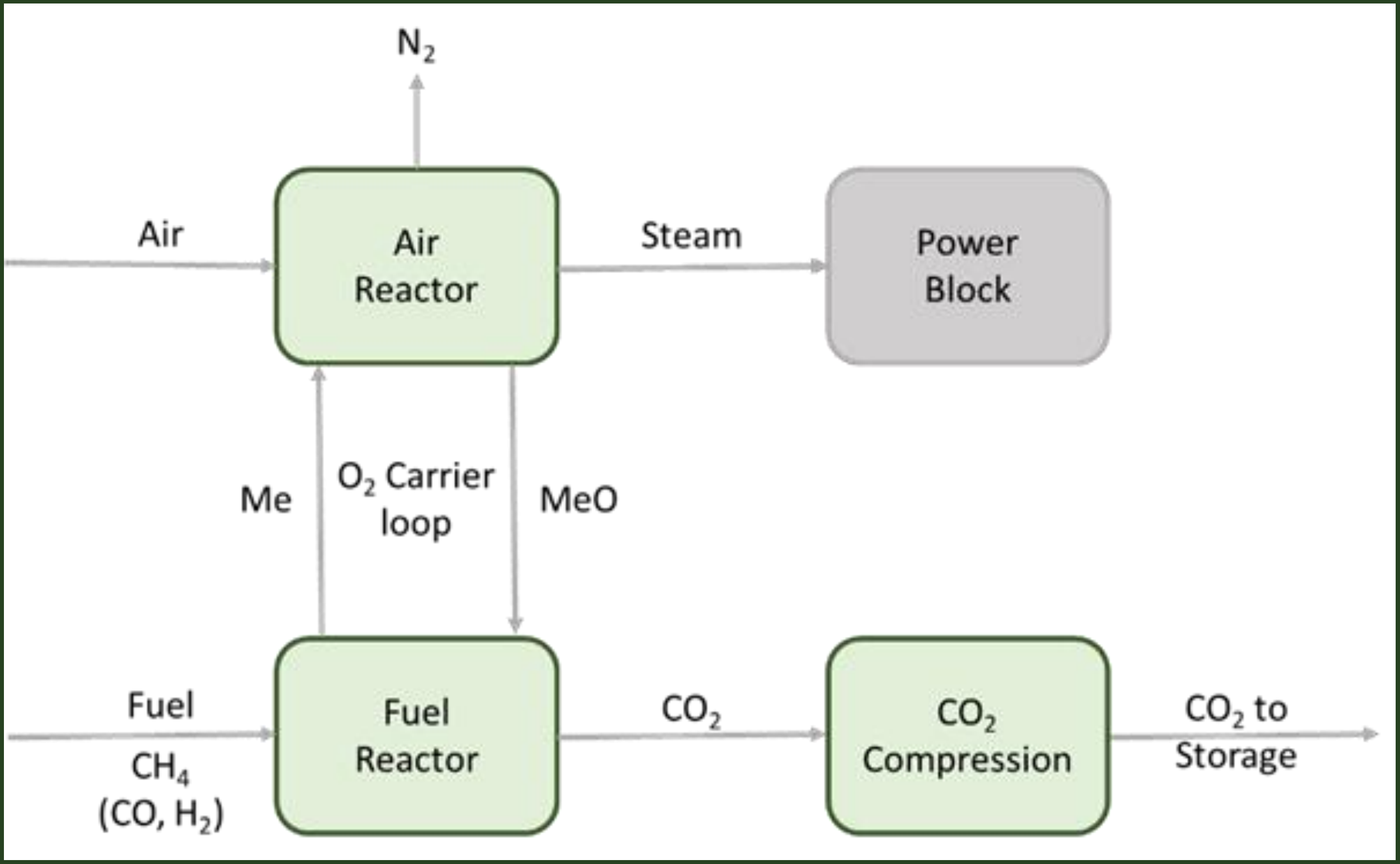
$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2 \qquad \Delta H_{298K} = 247\ \text{kJ/mol}$$

Thermochemical cycles

Chemical looping is a good example of a thermochemical cycle, originally conceived as a set of reactions that enabled oxygen transport within the reacting system.

		Hemi-cycle 1	Hemi-cycle 2
A	Chem. - Redox	Me + Oxidant → MeO + Reductant	MeO + Reductant → Me + Oxidant
B	Therm. - Redox	Me + Oxidant → MeO + Reductant	MeO + Heat → Me + ½O_2
C	Carbonation	MeO + Diluted CO_2 → $MeCO_3$ + Diluent	$MeCO_3$ + Heat → MeO + Pure CO_2

Chemical looping is a very promising CC method that reduces energy and cost penalties. The Chemical Looping Combustion (CLC) concept concerns the transfer of oxygen from the combustion air to the fuel by means of an oxygen carrier in the form of a metal oxide, thereby avoiding the direct contact between fuel and air



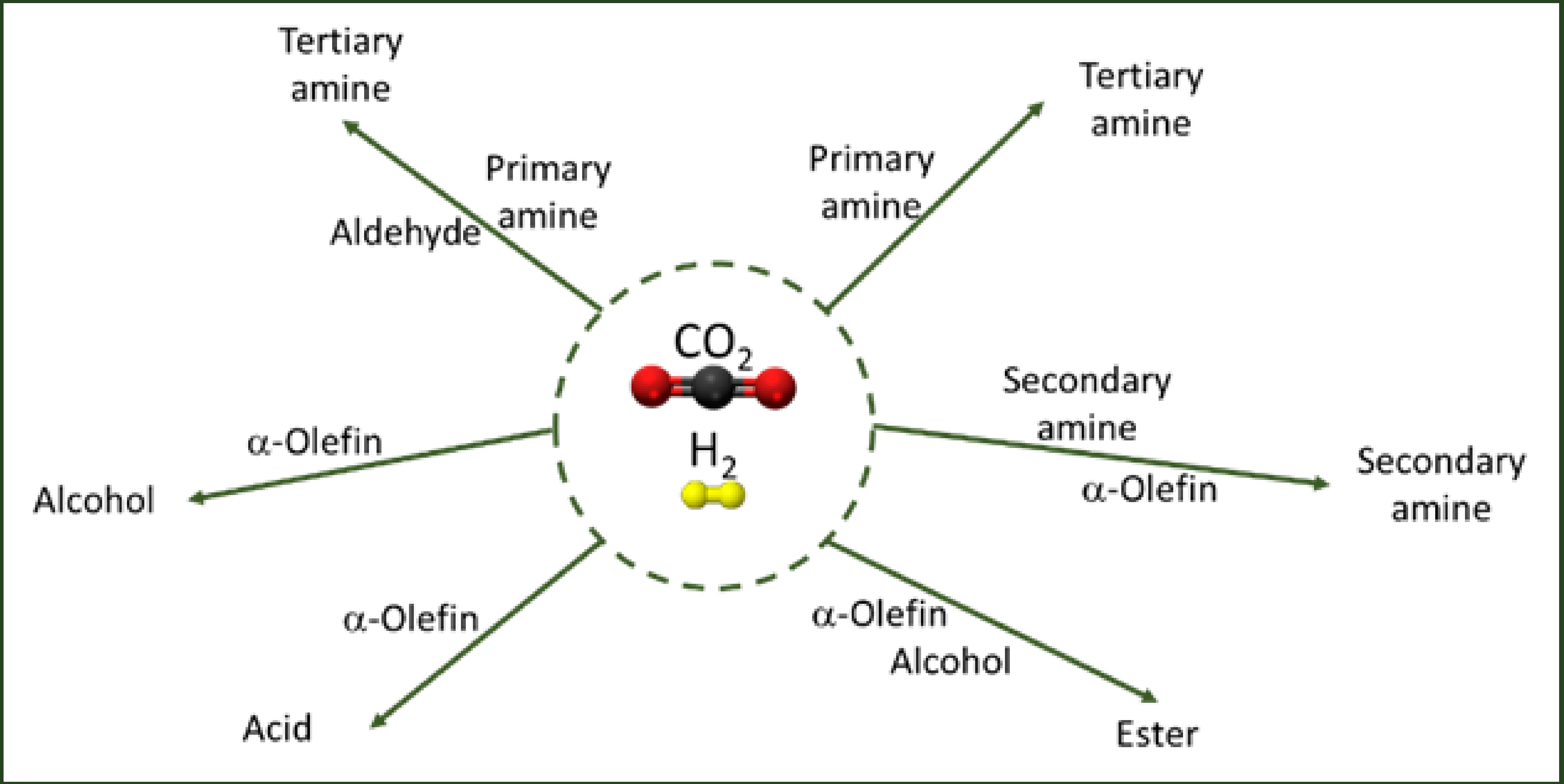
Methods to promote CO_2 removal and utilization

CO_2 VALORIZATION VIA ORGANIC PROCESSES

CARBOXYLATION REACTIONS

Similarly, to the inorganic valorization, the whole CO_2 moiety can be directly incorporated in organic molecules to form acids, esters, lactones, carbamates and carbonates.

Also, carboxylic acids can be synthesized directly from olefins or alcohols, CO_2, and H_2, via hydrocarboxylation which consists of a combination of the RWGS reaction and a hydroxycarbonylation step.



Examples of synthetic pathways from the CO_2/H_2 pair

CO_2 Hydrogenation

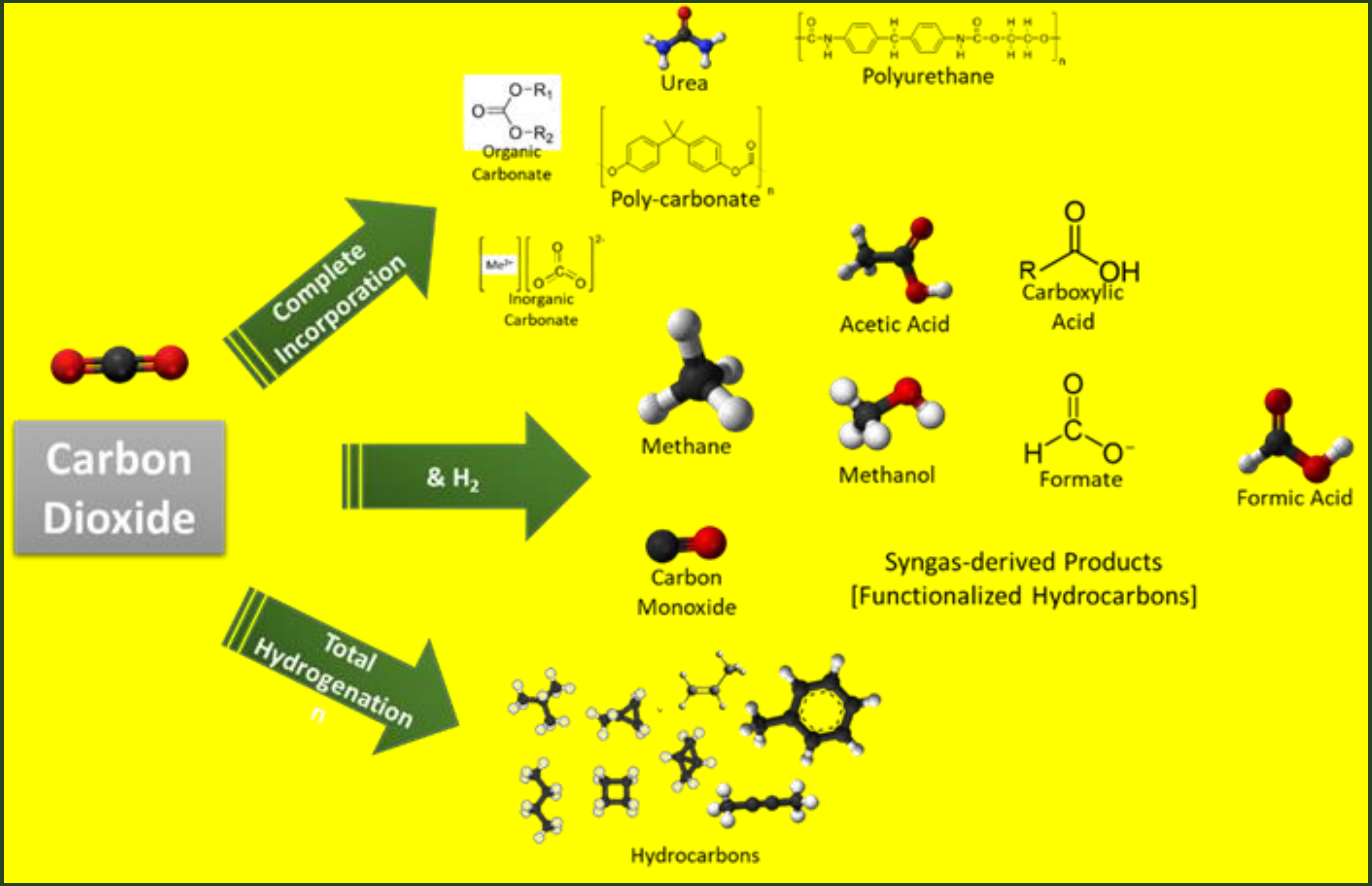
Hydrogenation of CO_2 not only contributes to reduce CO_2 in the atmosphere, but it also results in production of fuels and valuable chemicals.

Among CO_2 hydrogenation products, methanol and hydrocarbons are excellent fuels in internal combustion engines and are easily stored and transported

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H_{298\ K} = -11.8$ kcal/mol

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H_{298\ K} = -165$ kJ/mol

Examples of value-added products rendered from the conversion of CO_2



Methods to promote CO_2 removal and utilization

END-PRODUCTS AND END-USERS

Industries with profiles characterized by being energy-intense, C-intense or both, such as steel, cement, chemicals, oil and gas, health, etc. are directly involved in the definition, planning or implementation of decarbonization strategies. These industries employed the most energy-intensive processes, accounting for around 60% of industrial energy demand and an even higher share of direct CO_2 emissions.

By 2019, the industry contributed to 30% of the global CO_2 emissions (~11Gton), associated with an energy demand of more than 175 EJ. CC plays a vital role to convert such carbon into value-added products.

Methods to promote CO_2 removal and utilization

END-PRODUCTS AND END-USERS

Examples of end-products and end-users

- Steel and metallurgical sector
- Cement industry
- Oil & Gas Industry / Fossil fuels

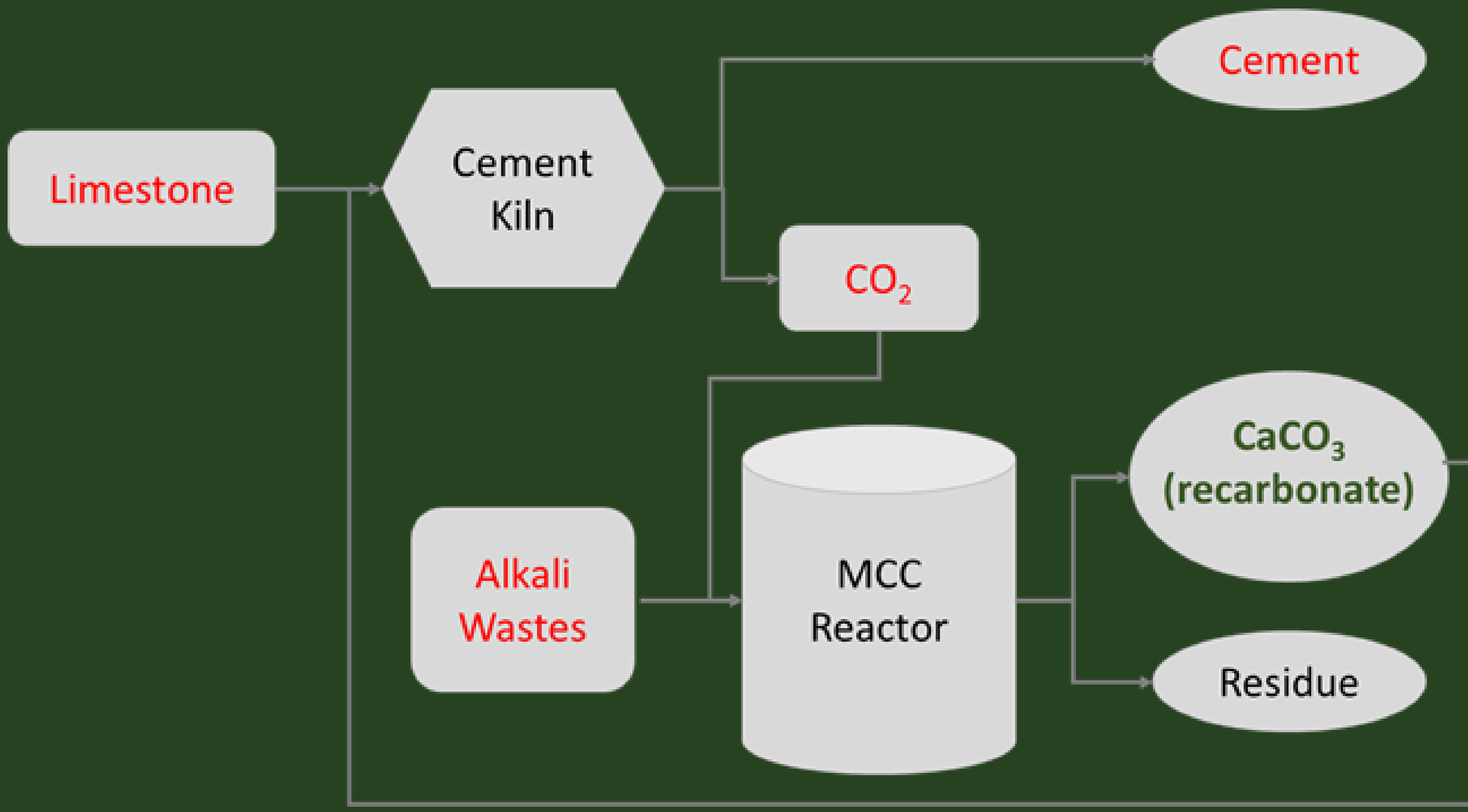
END-PRODUCTS AND END-USERS

Cement industry

- The high energy intensity involved in cement production accounts for approximately 7% of global anthropogenic greenhouse gas (GHG) emissions in CO_2 equivalents .

- The rising global population along with infrastructure development needs will augment the demand for cement and concrete. As a matter of fact, the cement production is expected to increase 12% by 2050.

- An innovative technology entitled mineral carbon capture and utilization (MCCU) has been proposed to reduce CO_2 emissions, particularly from the cement sector.



Main steps of cement production with the MCC technology

END-PRODUCTS AND END-USERS

Oil & Gas industry/ Fossil fuels

- The use of fossil fuels in the transportation sector and the application of fossil resources in energy generation are collectively responsible for more than the 80% of the global emissions.

- CCUS technologies in the Oil & Gas industry are a politically sensitive topic. At any rate, several actions are being carried out in many countries, aiming at implementing CCUS in their respective Oil & Gas industries.

- Although several technologies for CCUS have been proposed, there is no consensus on which is the most recommendable technology. In fact, there is no U.S. EPA endorsement of any particular control strategy

Oil & Gas industry/ Fossil fuels

- Shell's CANSOLV CO_2 Capture System (for capturing CO_2 from low-pressure streams, including flue gas) and Shell's ADIP ULTRA technology (for capturing CO_2 from high-pressure process streams).

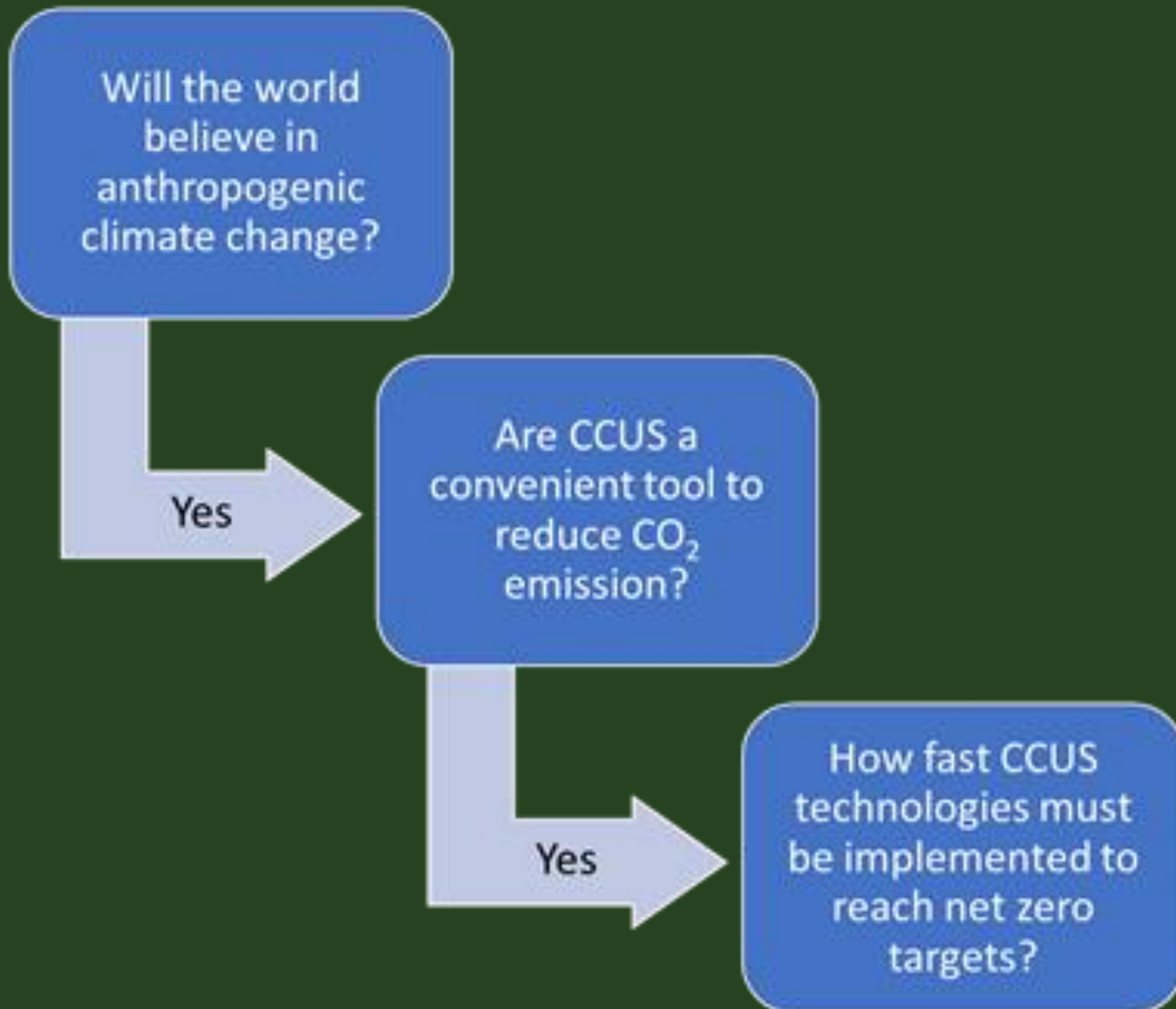
- Alternative fuels that could be produced from CO_2, using the concept of modified Fischer-Tropsch synthesis represent drop-in or replacement fuel options, for the transport sector to alleviate its dependence on fossil-carbon based fuels.

- As far as terrestrial transportation vehicles are concerned, the use of biofuels seems to be a good alternative solution for Net-zero carbon dioxide emissions. On the other hand, the case of both maritime and aviation sectors is much more complex.

Oil & Gas industry/ Fossil fuels

It must be highlighted that as far as the Oil & Gas industry is concerned, CCUS is not a universal panacea. Indeed, a rapid reduction in GHGs emissions, necessary to achieve the net-zero goal can only be undertaken through a radical cultural transformation that involves the way we produce and consume energy.

CONCLUSIONS



Todo lo arreglaremos
poco a poco:
te obligaremos, mar,
te obligaremos, tierra,
a hacer milagros,
porque en nosotros mismos,
en la lucha,
está el pez, está el pan,
está el milagro.

We’ll slowly
solve everything:
we’ll force you, sea,
we’ll force you, earth
perform miracles,
because in our very selves,
in the struggle,
is fish, is bread,
is the miracle.

ODA AL MAR
PABLO NERUDA