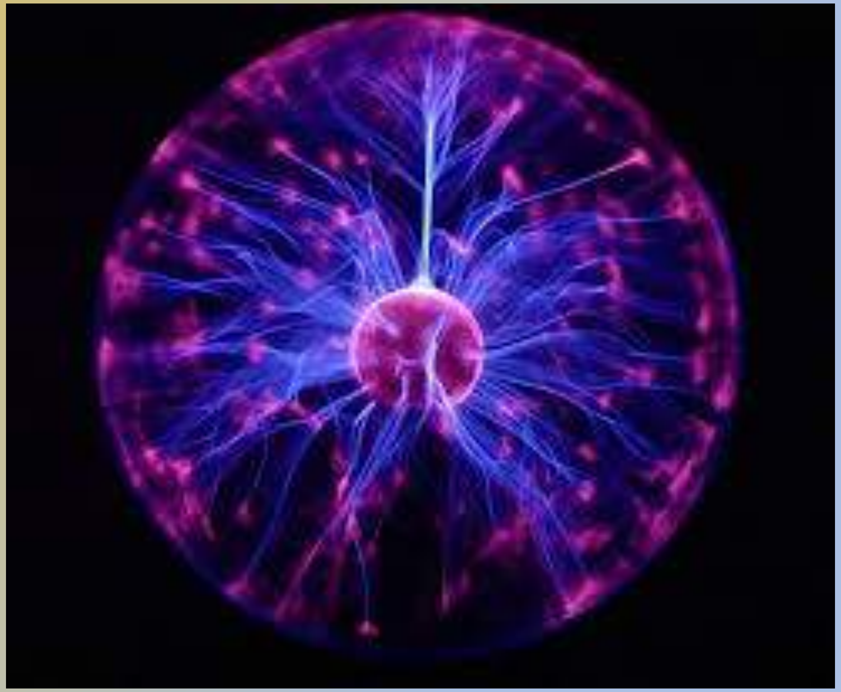
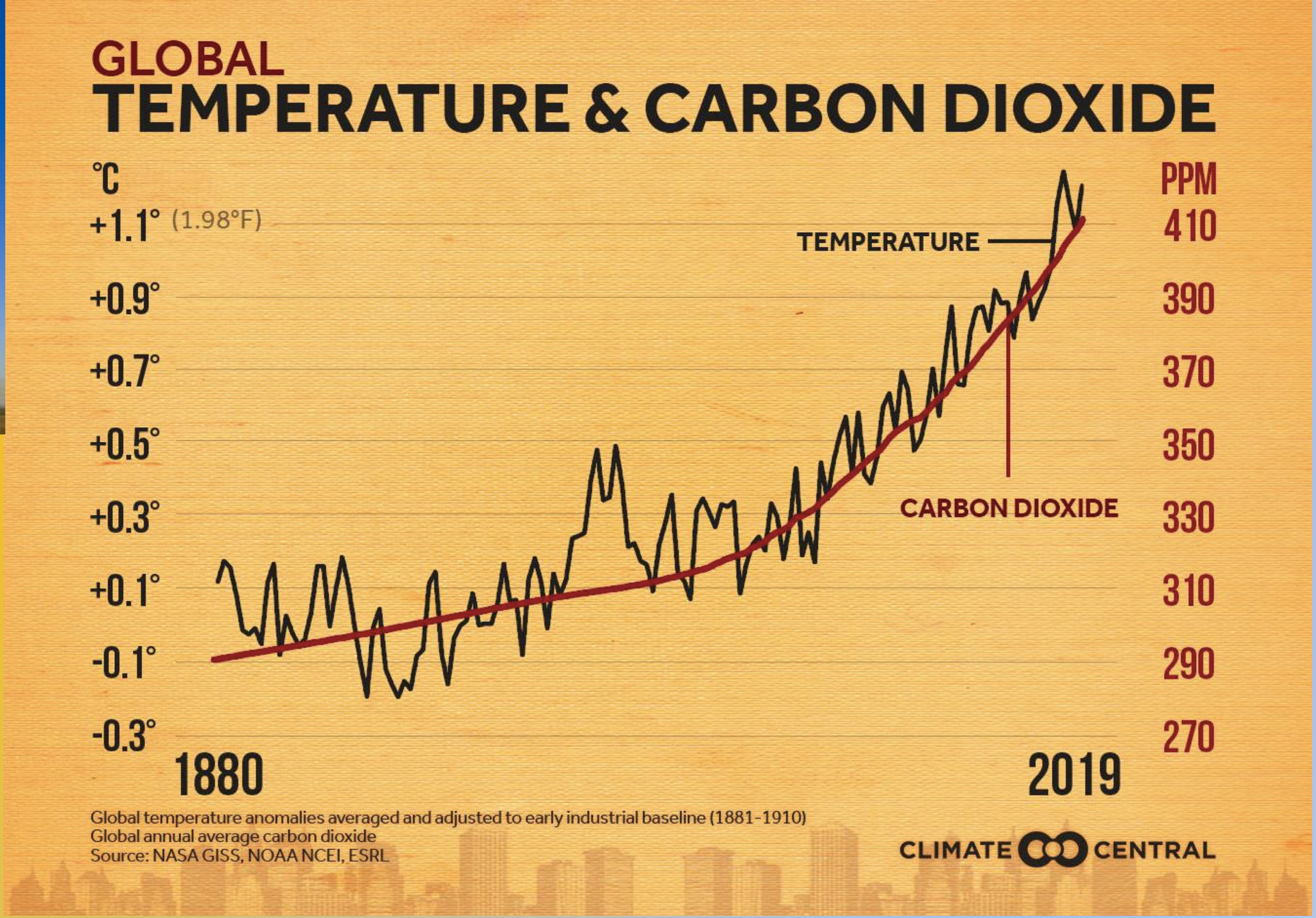
PLASMA PROCESSES FOR CO_2 RECYCLING



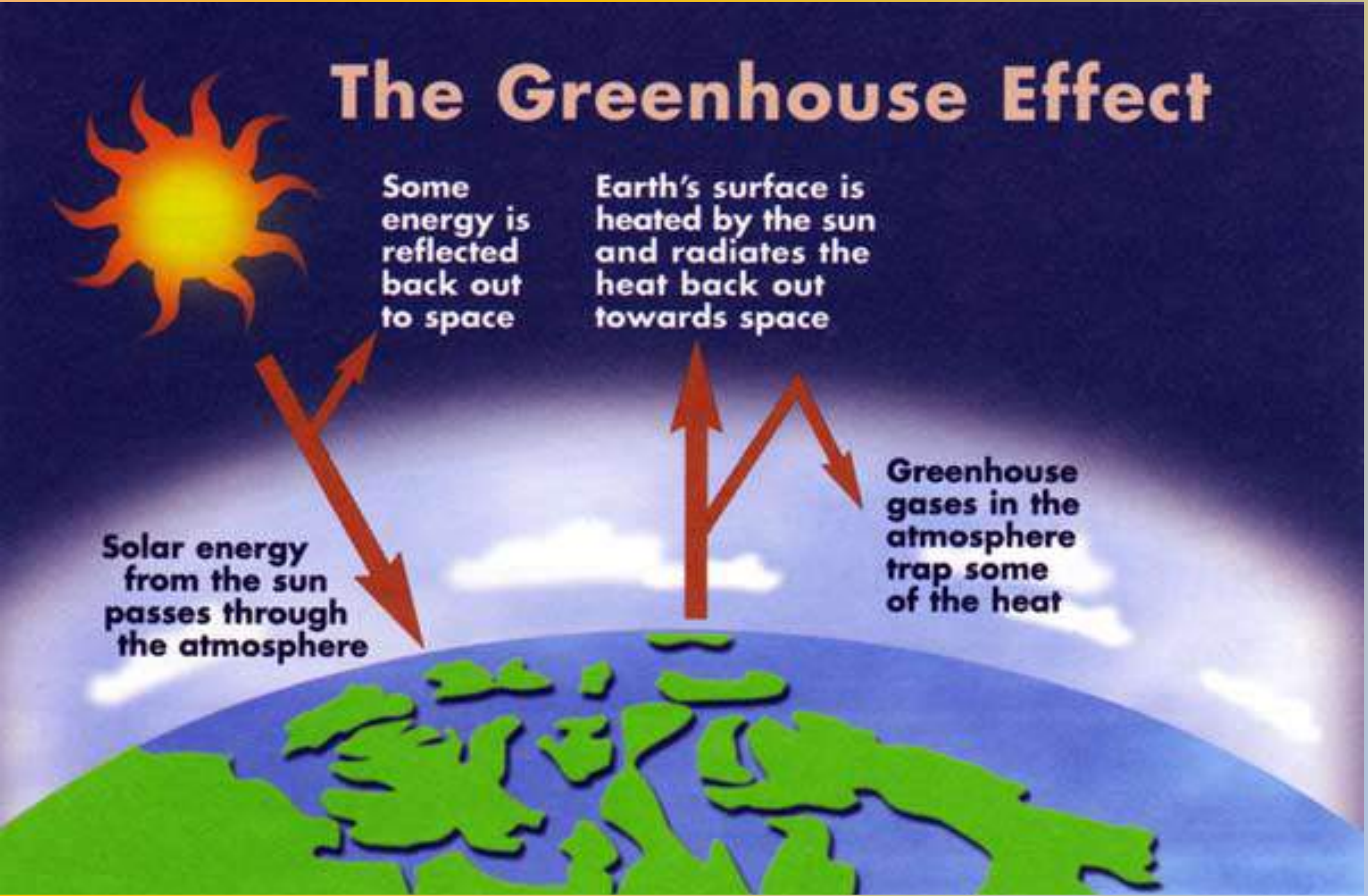
P I John

Online Talk given to IIT, Delhi on 4 October 2020



- Anthropogenic CO2 emissions outpace natural carbon cycle
- Atmospheric CO2 increased from 280 ppm in 1880 to 420 ppm in 2019.
- 3 Trillion tones already accumulated

CO2 AND GLOBAL WARMING



Sunlight falls on earth; scattered back as infrared light

CO_2 + GHG layer in the atmosphere absorbs IR and gets heated.

Hot CO_2 radiates, increasing atmospheric temperature.

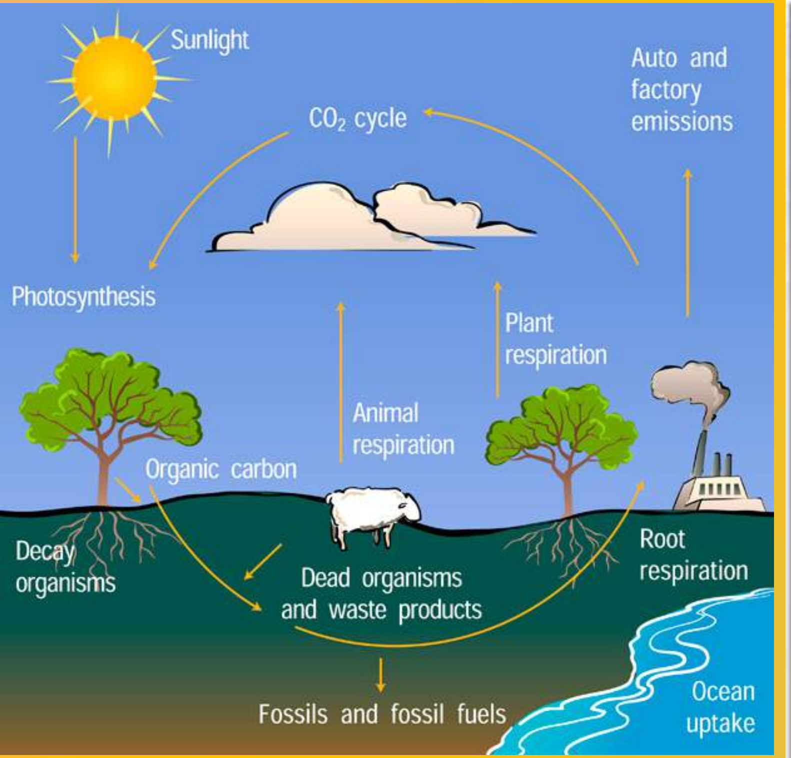
Beyond 1.5 deg C, the risks of extreme climatic events like floods, drought etc would be too high

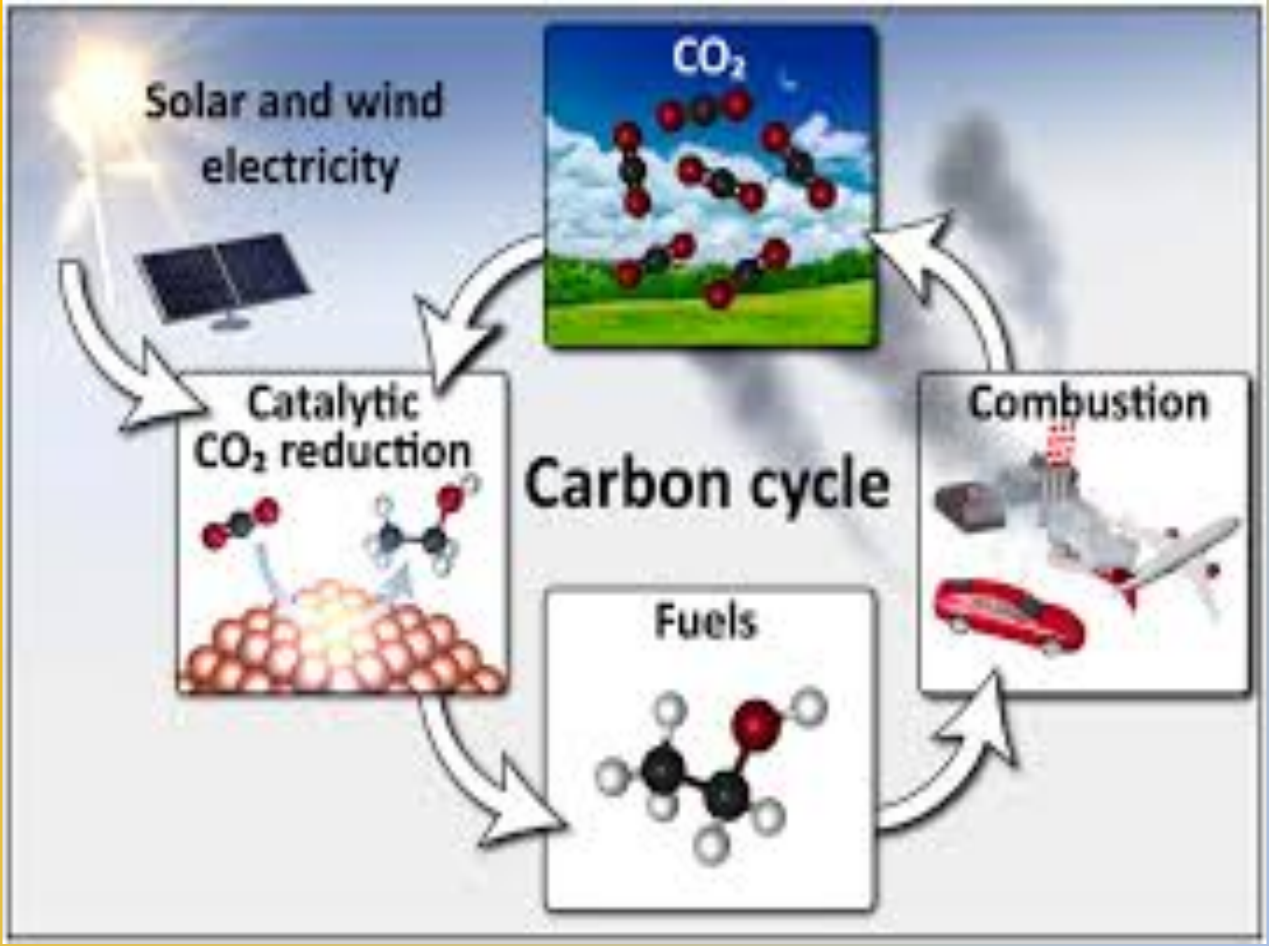
For 1.5 degree rise limit

CO_2 emissions should be cut by half by 2030 and brought down to zero by 2055.

Source: IPCC website www.ipcc.ch

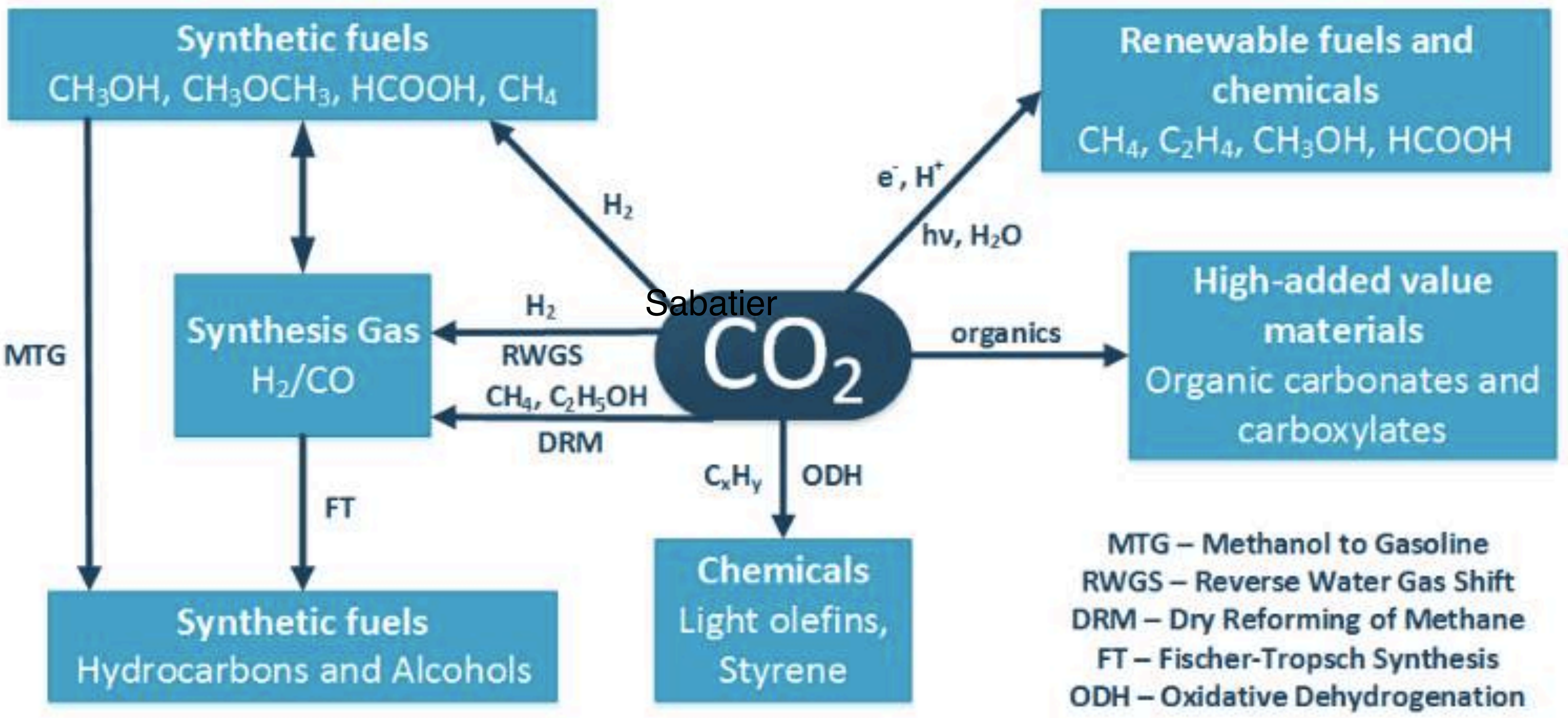
A NEW SUSTAINABLE CARBON CYCLE



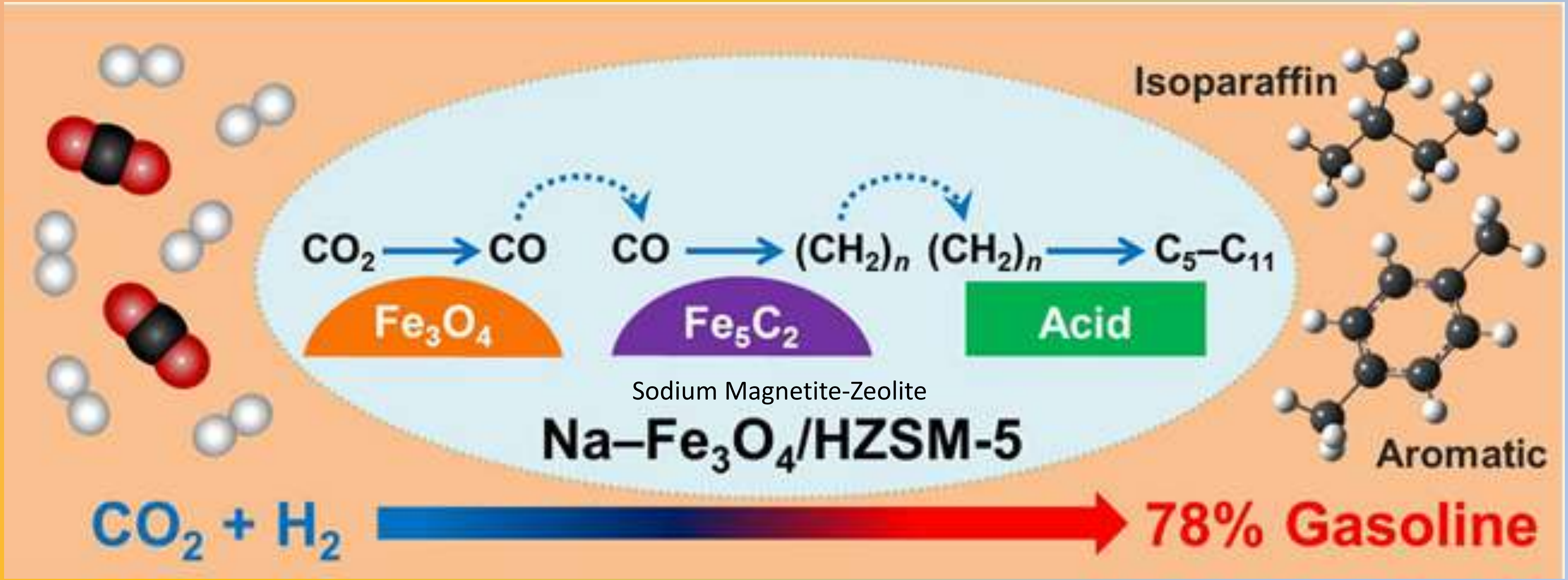


- High energy density, compact and safe storage, easy transportation
- Existing hydrocarbon infrastructure can be used
- (Hydrogen, Electric)
- Can transform to net carbon negative system reversing atmospheric CO2 levels

CO2 Recycling by Photosynthesis
+ Oceans
Too slow



Critical Step: CONVERT CO2 INTO CO



CO2 Methanation (Sabatier Process) 1897

CO2+4H2=CH4+2H2O (-165)

At 320 deg

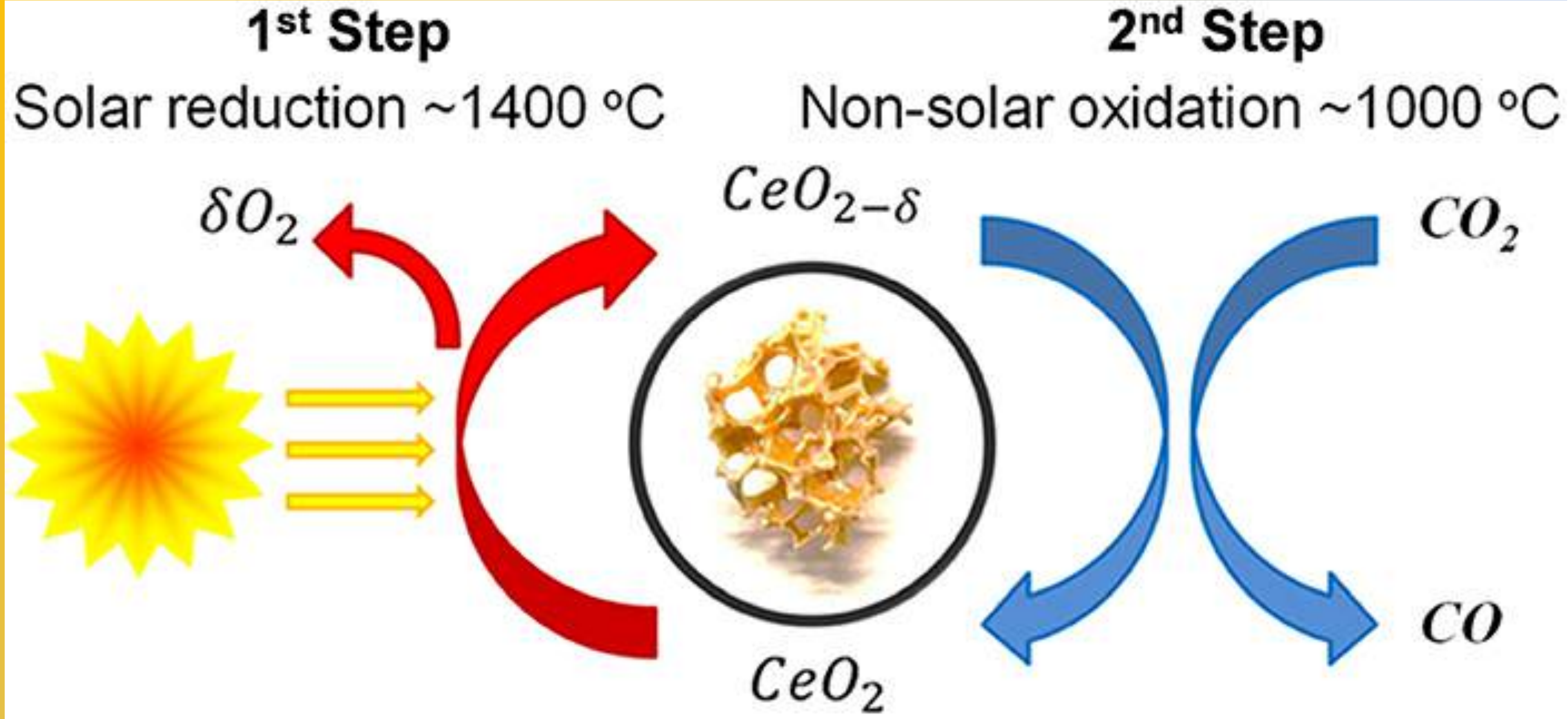
Louisa Rui Lin Ting, Oriol Piqué, Si Ying Lim, Mohammad Tanhaei, Federico Calle-Vallejo, and Boon Siang Yeo
ACS Catalysis **2020** *10* (7), 4059-4069

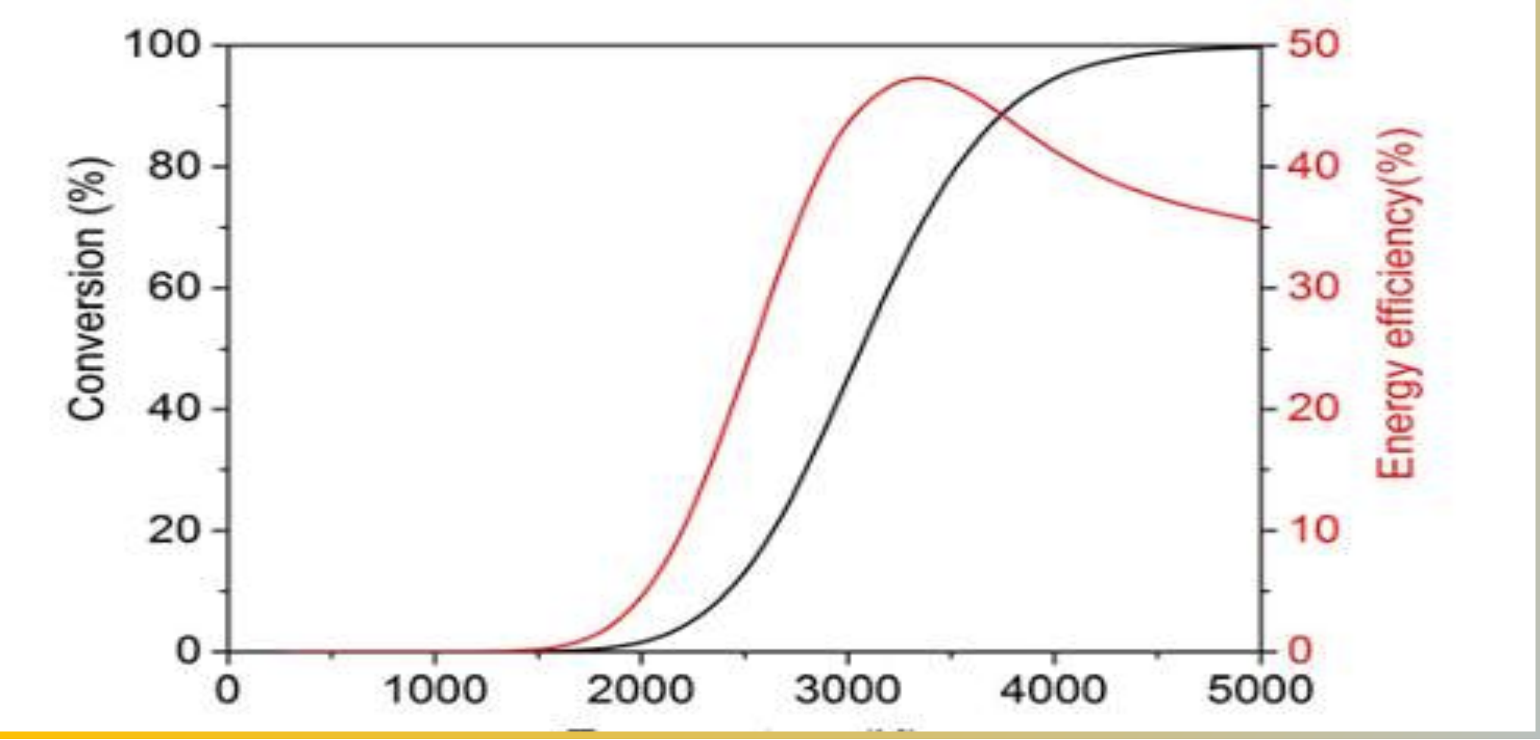
New Technologies!

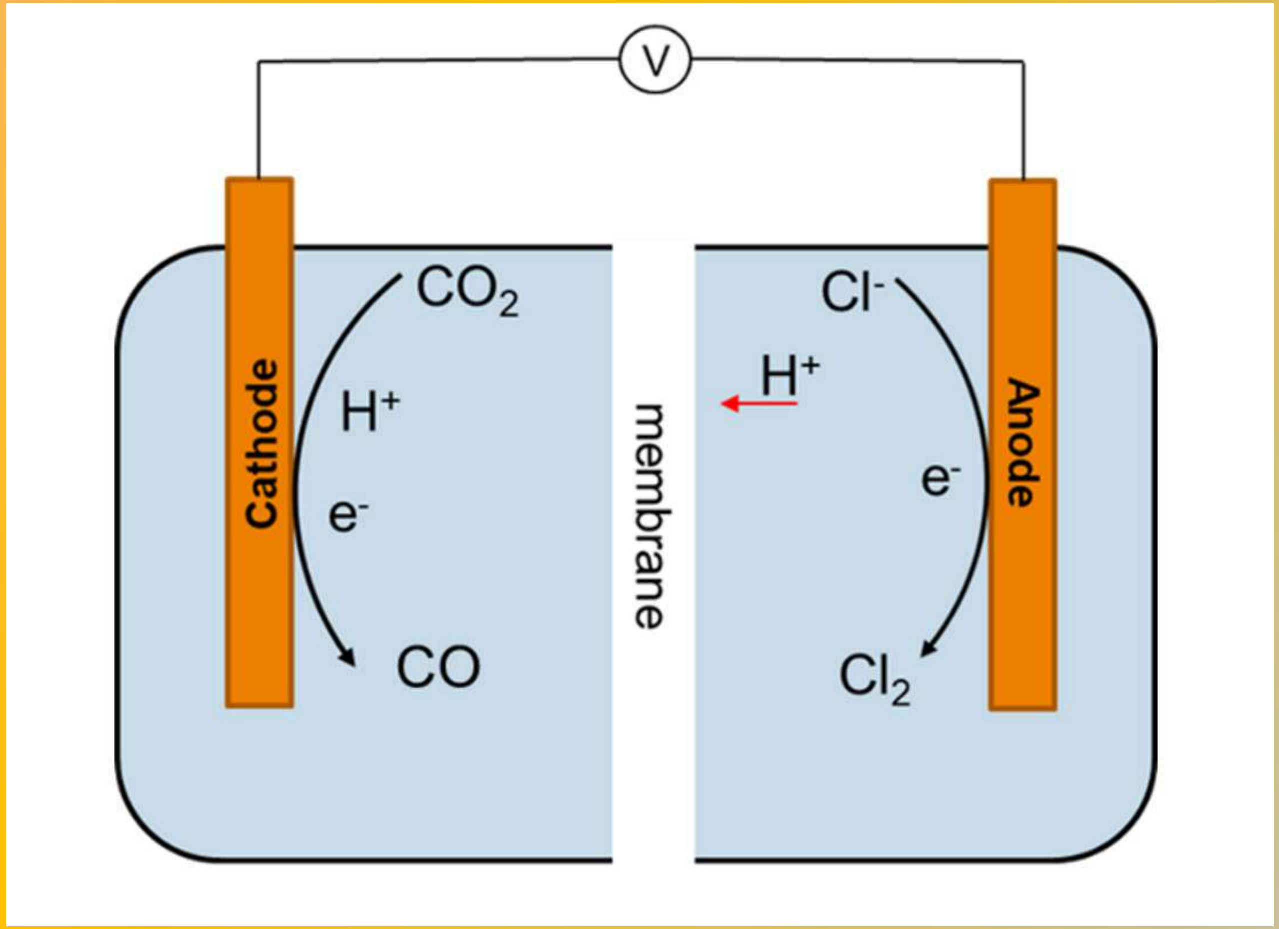
3000 deg For direct thermal splitting

Catalyst (Ceria)

Solar Thermochemical







Electrochemical reaction

$$CO_2 + 8e^- + 8\,H^+ = CH_4 + 2H_2O$$

H+ ions from electrolysis
H ions migrate to Cathode through membrane

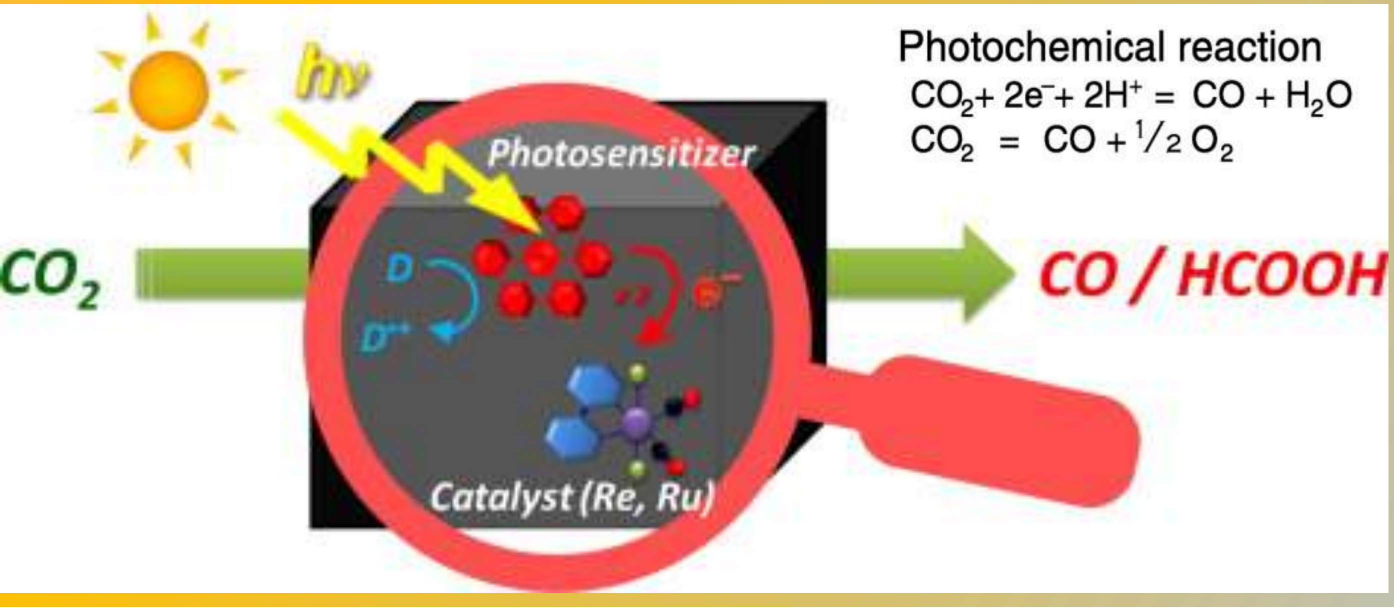


Photo excited electrons in the conduction band
of a semiconductor


Most of the matter in the Universe exists as Plasma. Sun, solar wind, stars.

Fluid made of electrons, ions and neutrals, interacting through Coulomb forces and exhibiting collective properties: Waves, Self-organisation


Energetic electrons ionize atoms

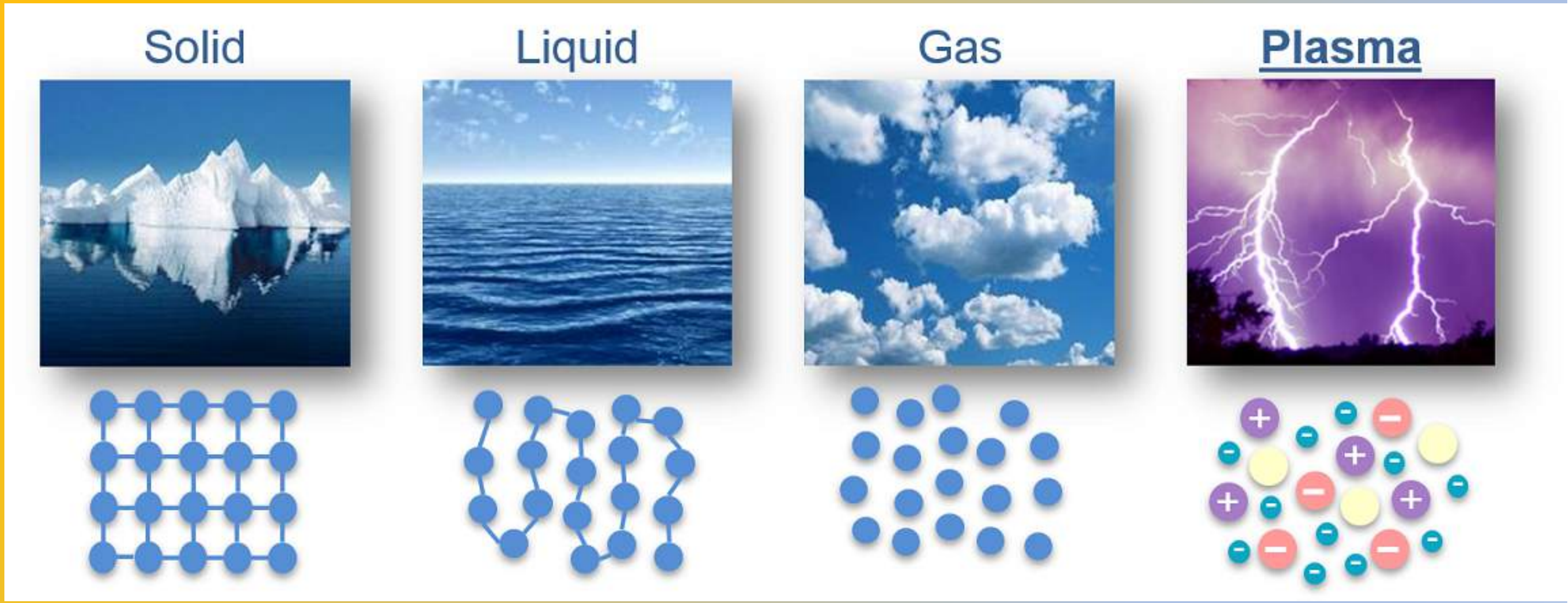
electron-ion pairs.

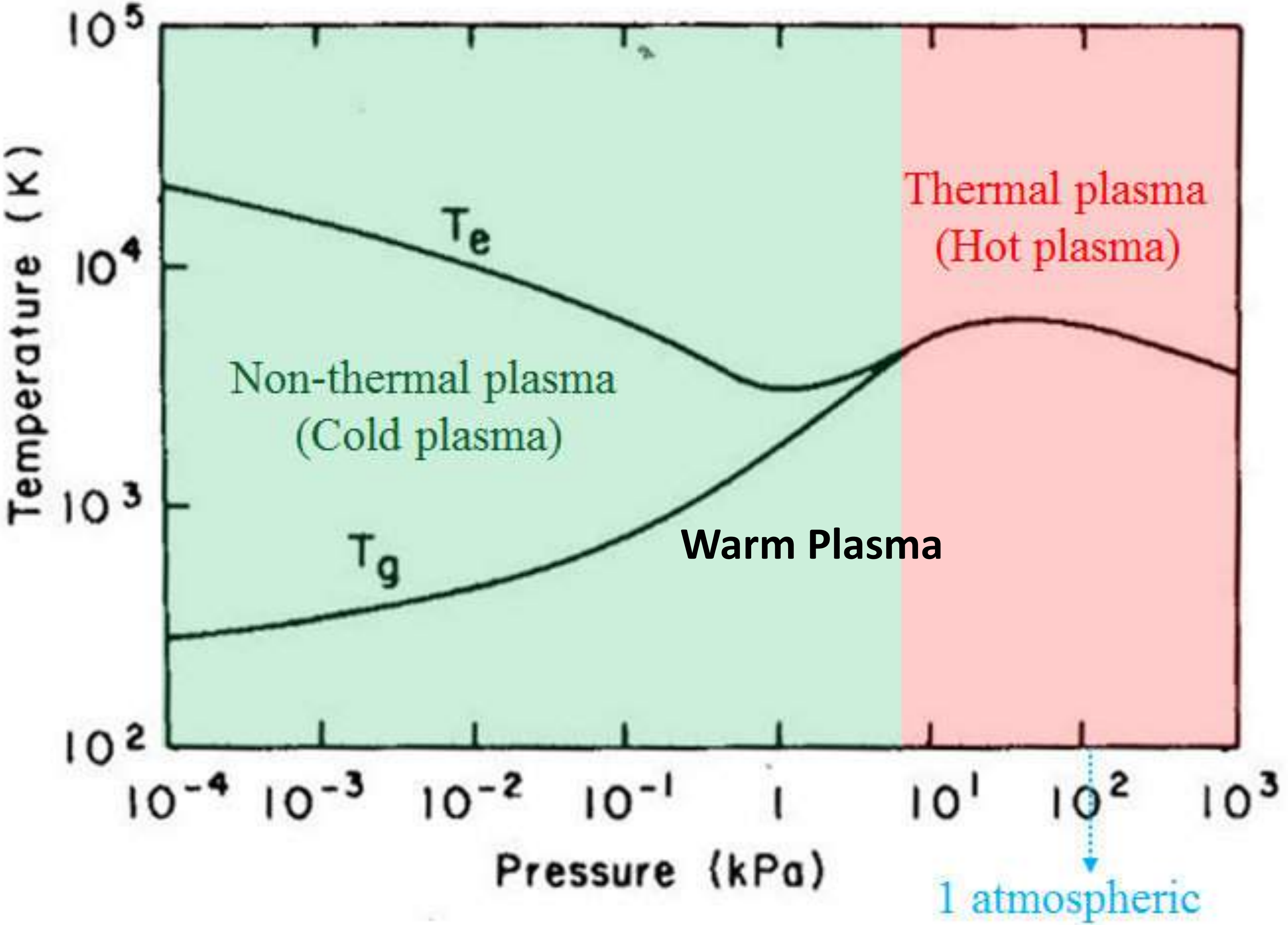
product electrons gain energy

more ionization

Avalanche of ionization

Plasma

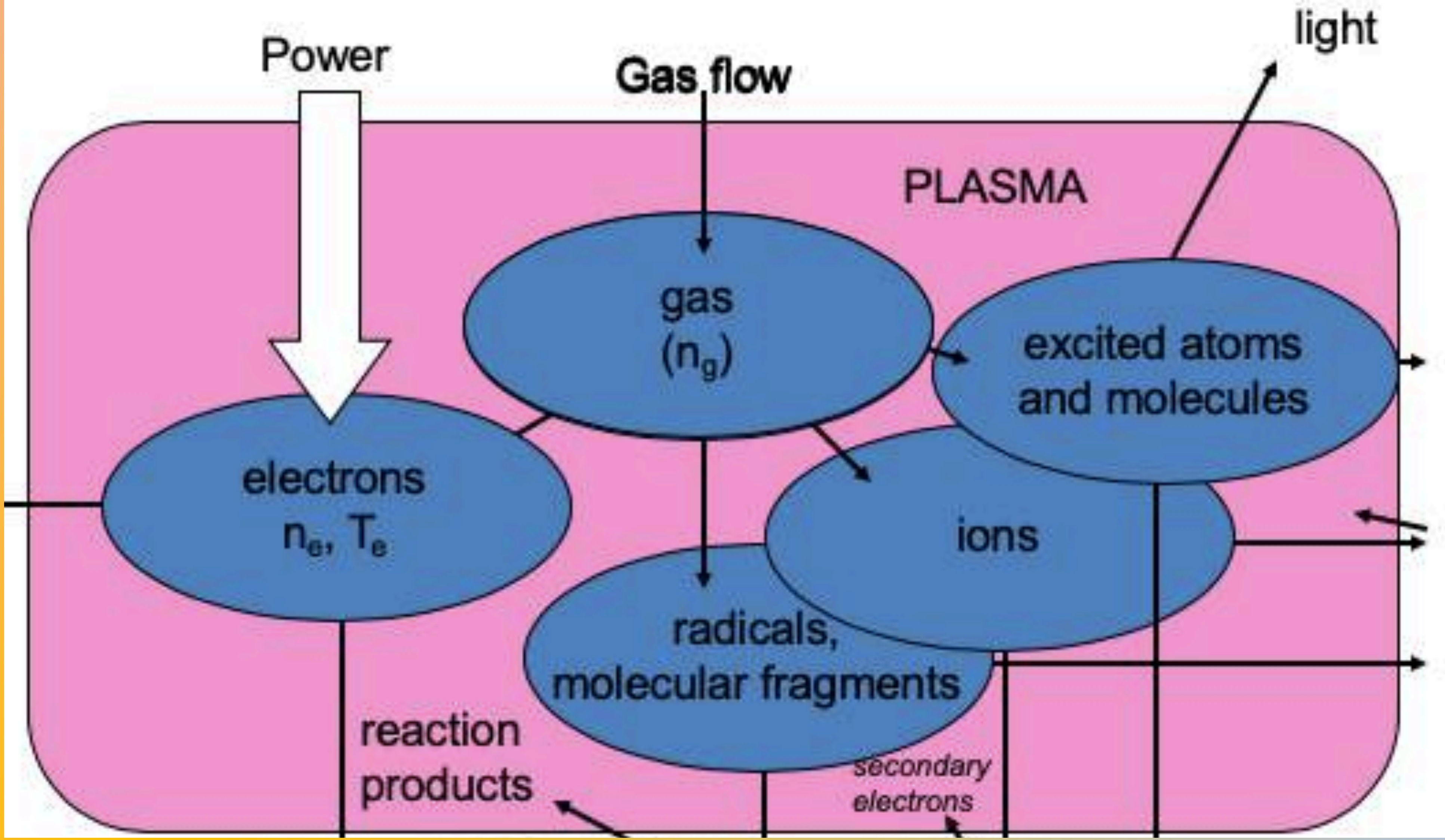




Drives thermodynamically unfavourable chemical reactions

NTP has low density: poor Conversion

Transitional plasma with high Temp and density



High chemical reactivity: free electrons/radicals.

Plasma chemistry

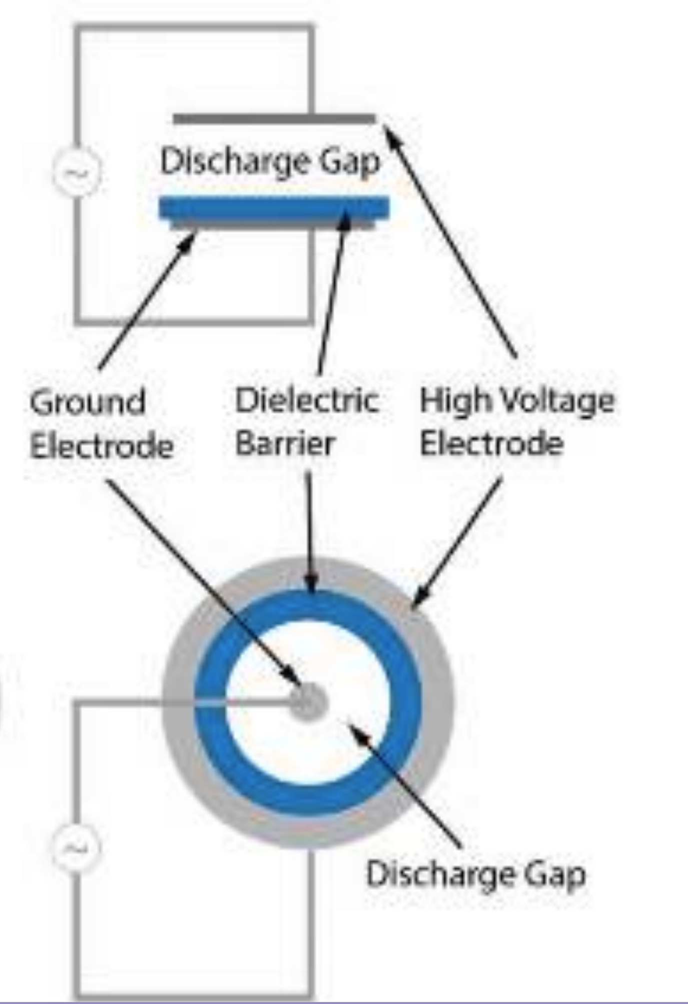
Reactivity depends on plasma parameters like density, temperature, E/p.

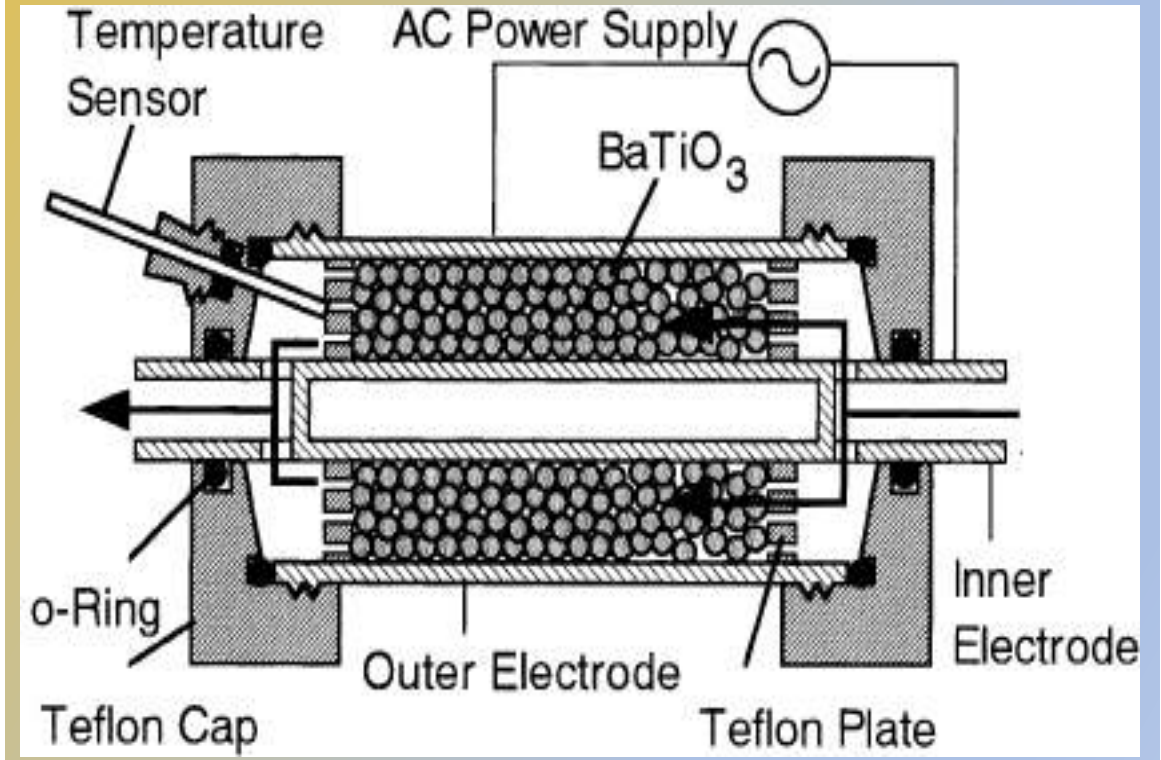
Each plasma source has a unique set of plasma parameters

Many types of plasma sources are required to do process optimization

DIELECTRIC BARRIER DISCHARGE

- Plane-parallel or concentric metal electrodes
- Dielectric barrier to prevent arcs.
- 'Non-thermal plasma' (streamers)
- Gas is at room temperature
- Electrons at temperatures of 20 000–30 000 K
- Pack with catalysts

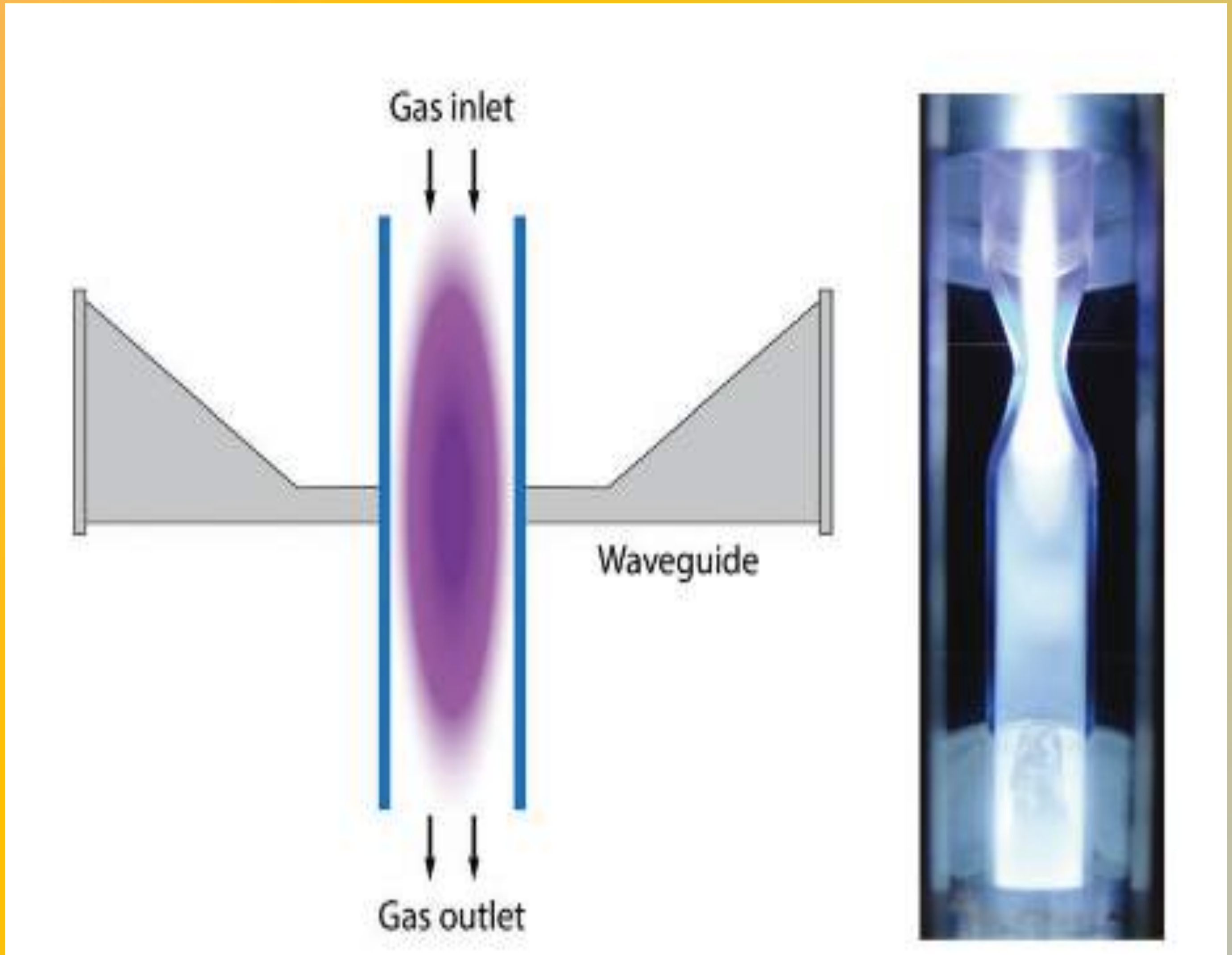


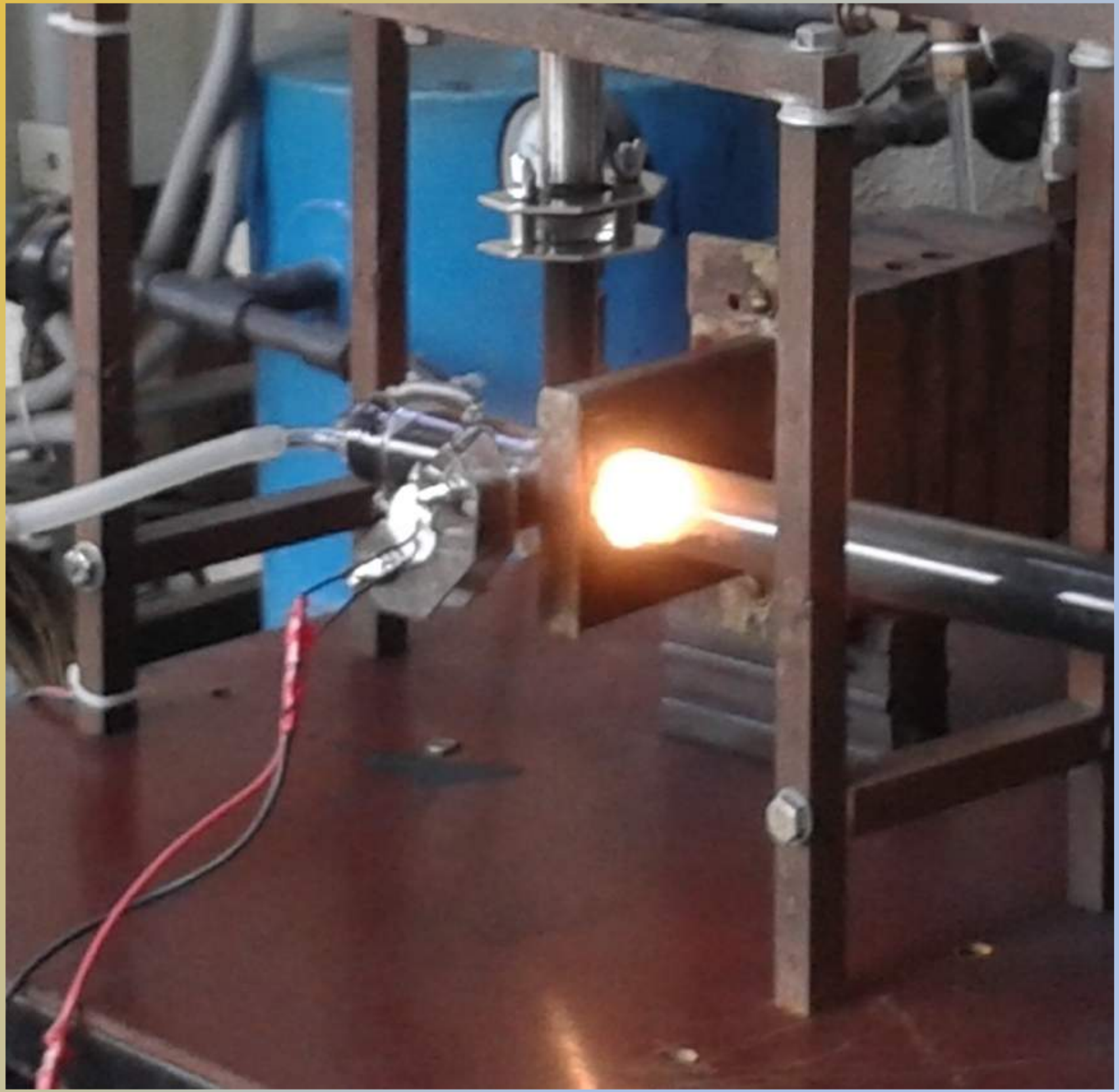


MICROWAVE DISCHARGE

300 MHz to 10 GHz.

Gas flows through a quartz tube.
Intersects with a wave guide (taper)
E-field starts discharge



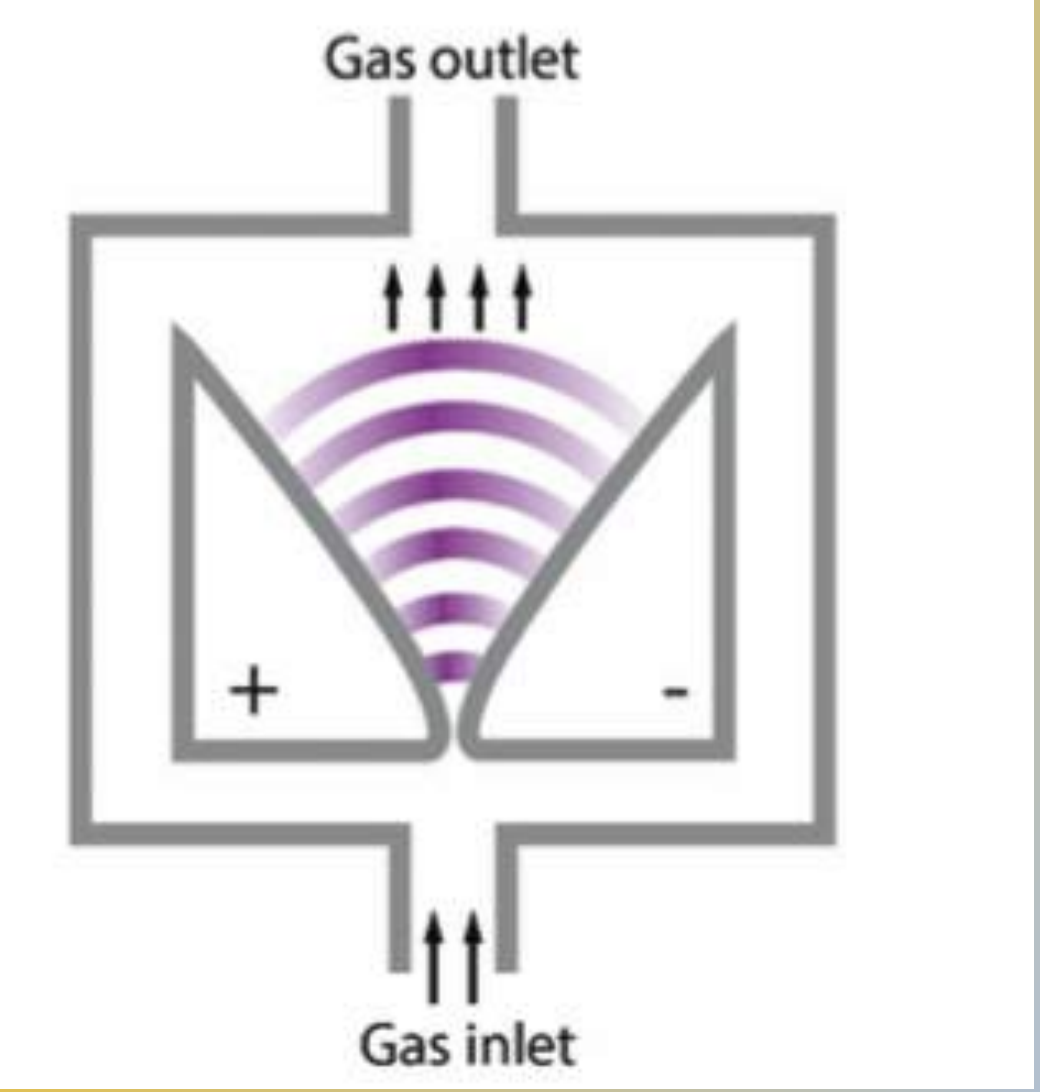


Gas flows between two diverging electrodes with a voltage across it.

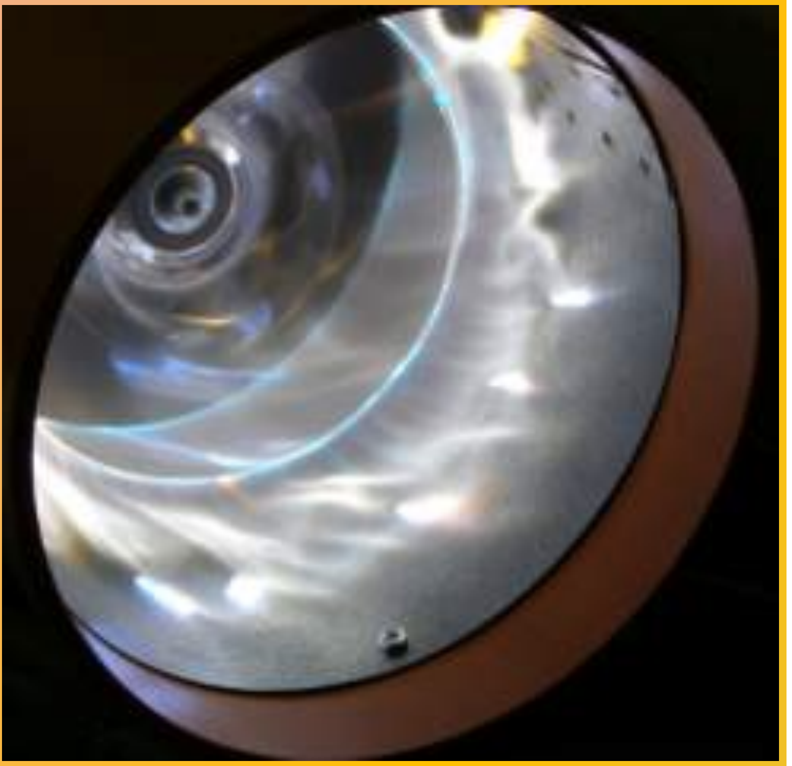
Arc plasma formed at the narrow gap

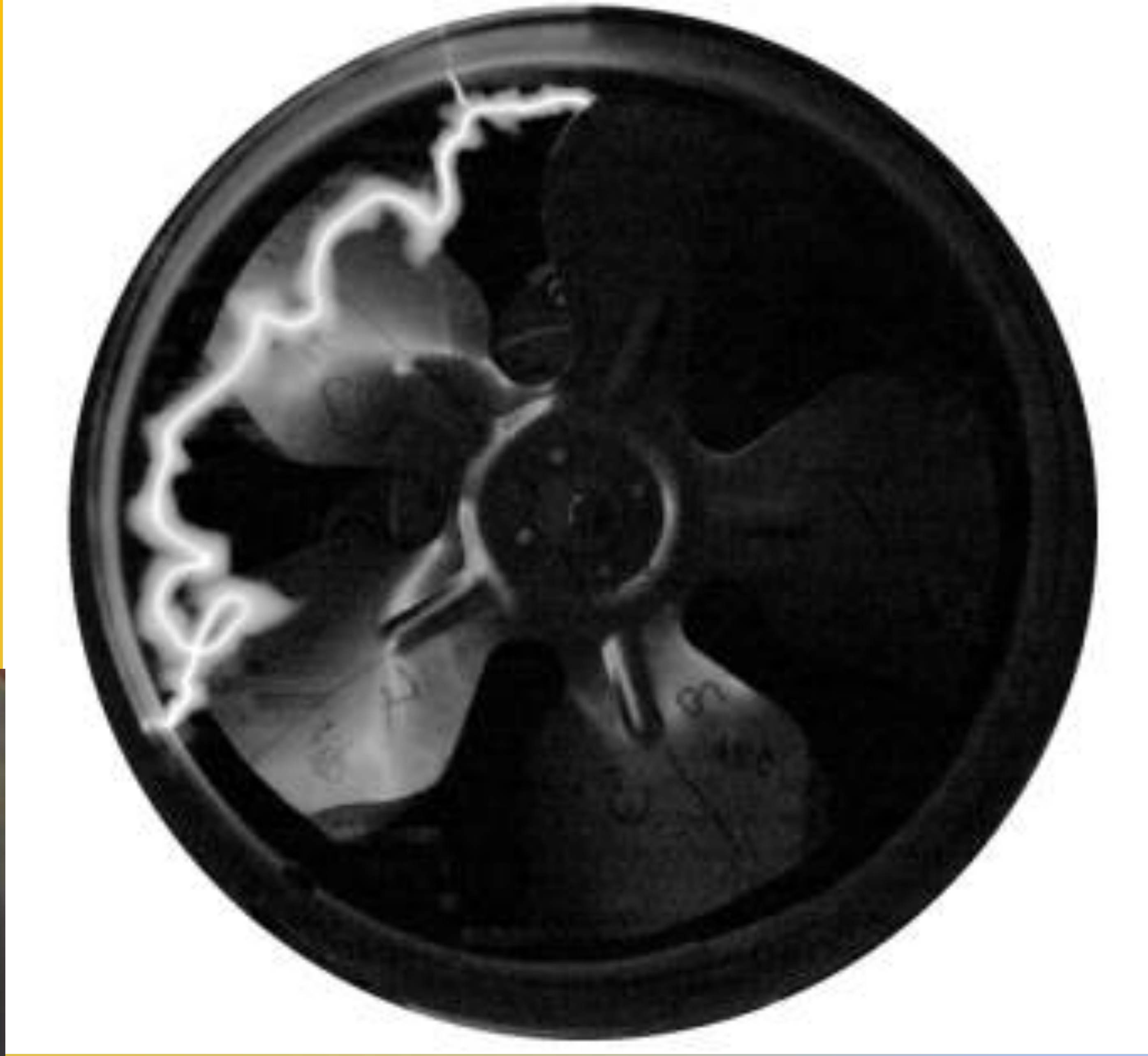
dragged by the gas flow towards a rising interelectrode gap, until it extinguishes.

A new arc is ignited at the shortest interelectrode gap.



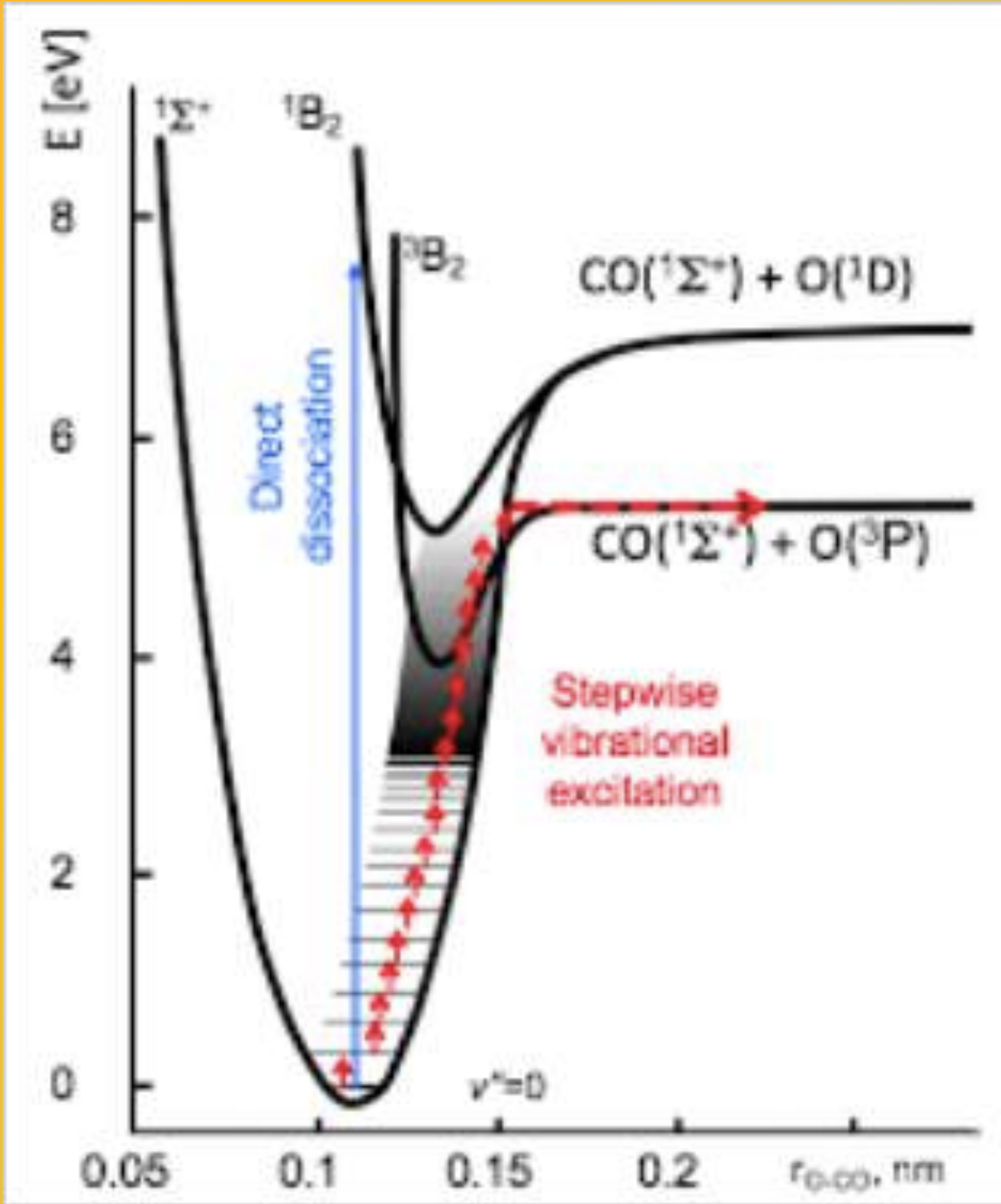
GLIDING ARC DISCHARGE





Rotating GD Arc Plasma

CO2 Dissociation in Plasma



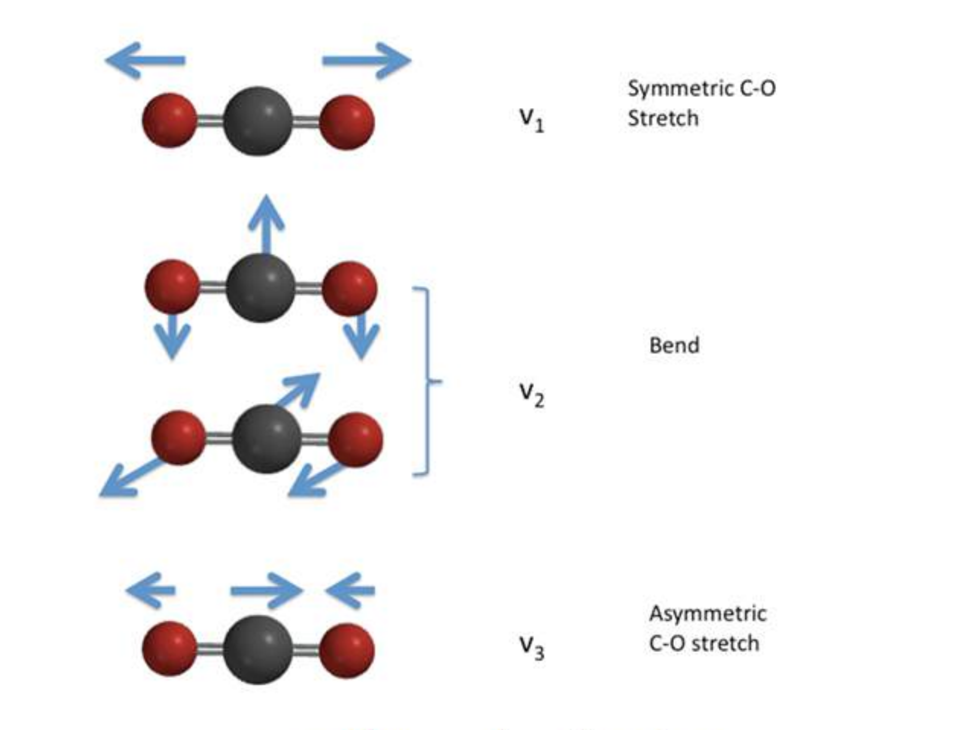


Fig. 1 Vibrational modes of CO_2

Electron impact dissociation
$CO_2 \rightarrow CO + O$, $\Delta H = 5.5$ eV/mol

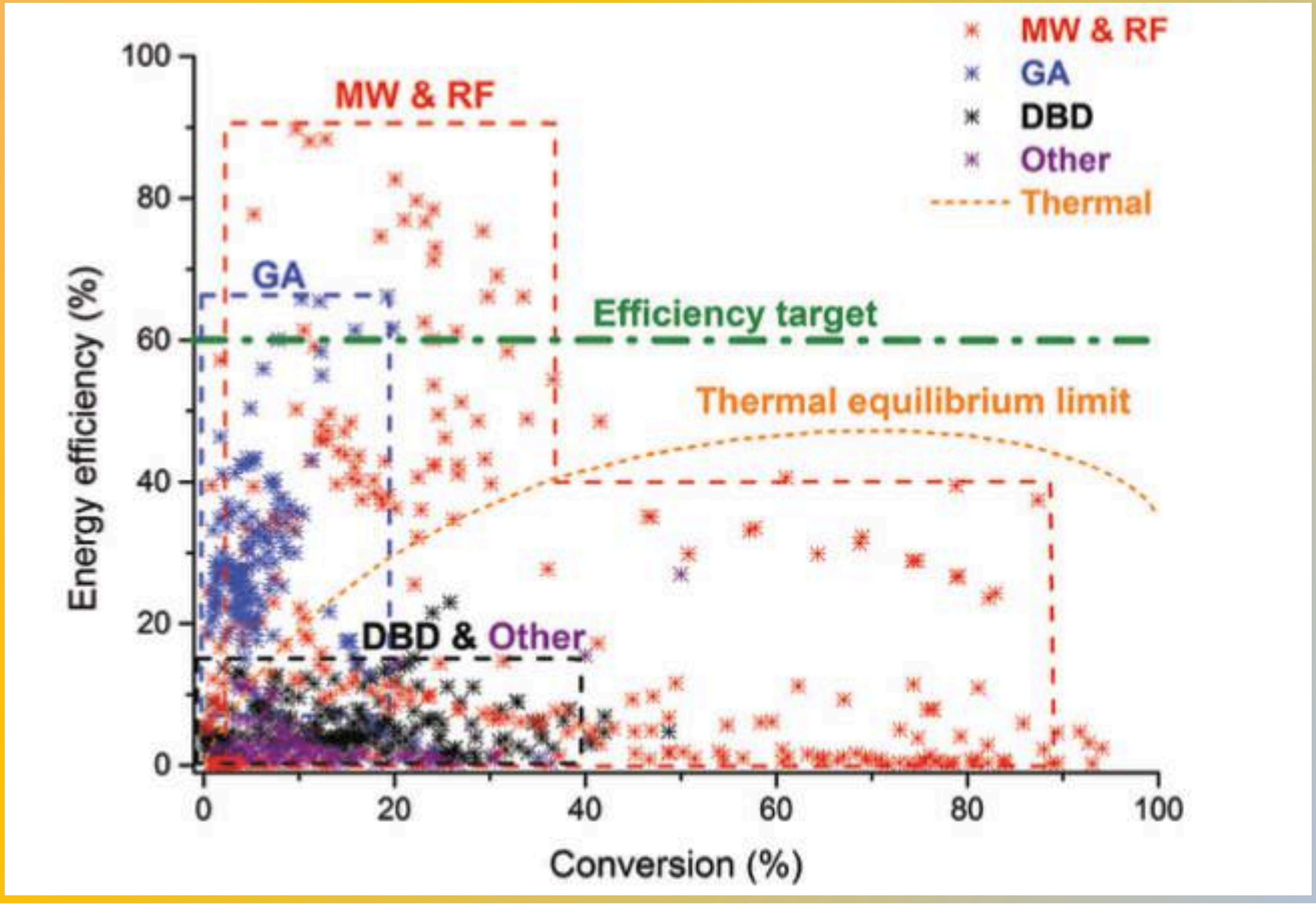
Vibrational excitation at 0.29 eV:

Ladder climbing

Dissociation

Source: Annemie Bogaerts,
Ramses Snoeckx
Chem. Soc. Rev., 2017, 46, 5805

PLASMA DISSOCIATION RESULTS



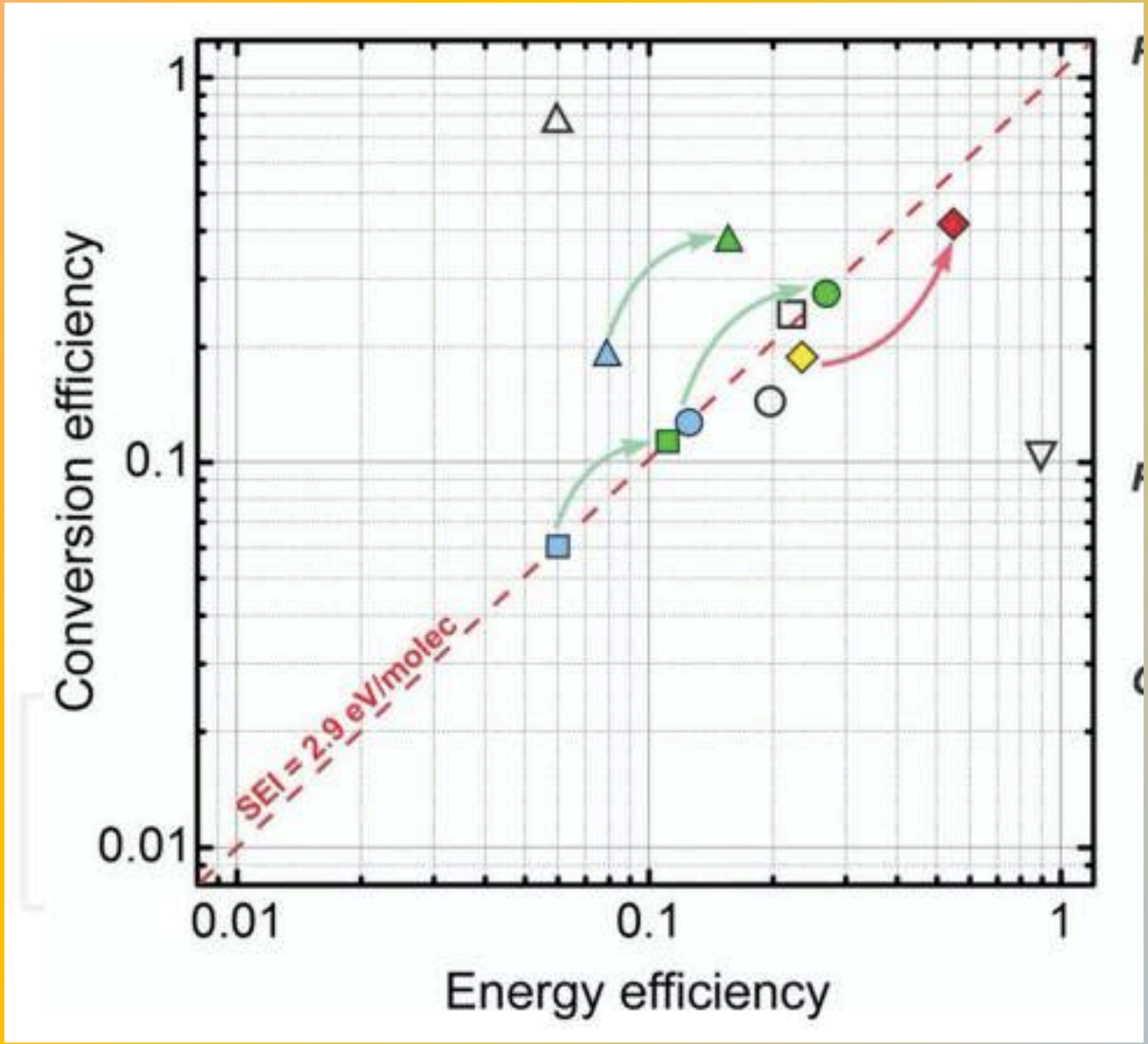
The energy efficiency is a measure of how efficiently the process performs compared to the standard reaction enthalpy

efficiency target of 60% is based on comparison with electrochemical Conversion

MW/GA high performance

DBD results

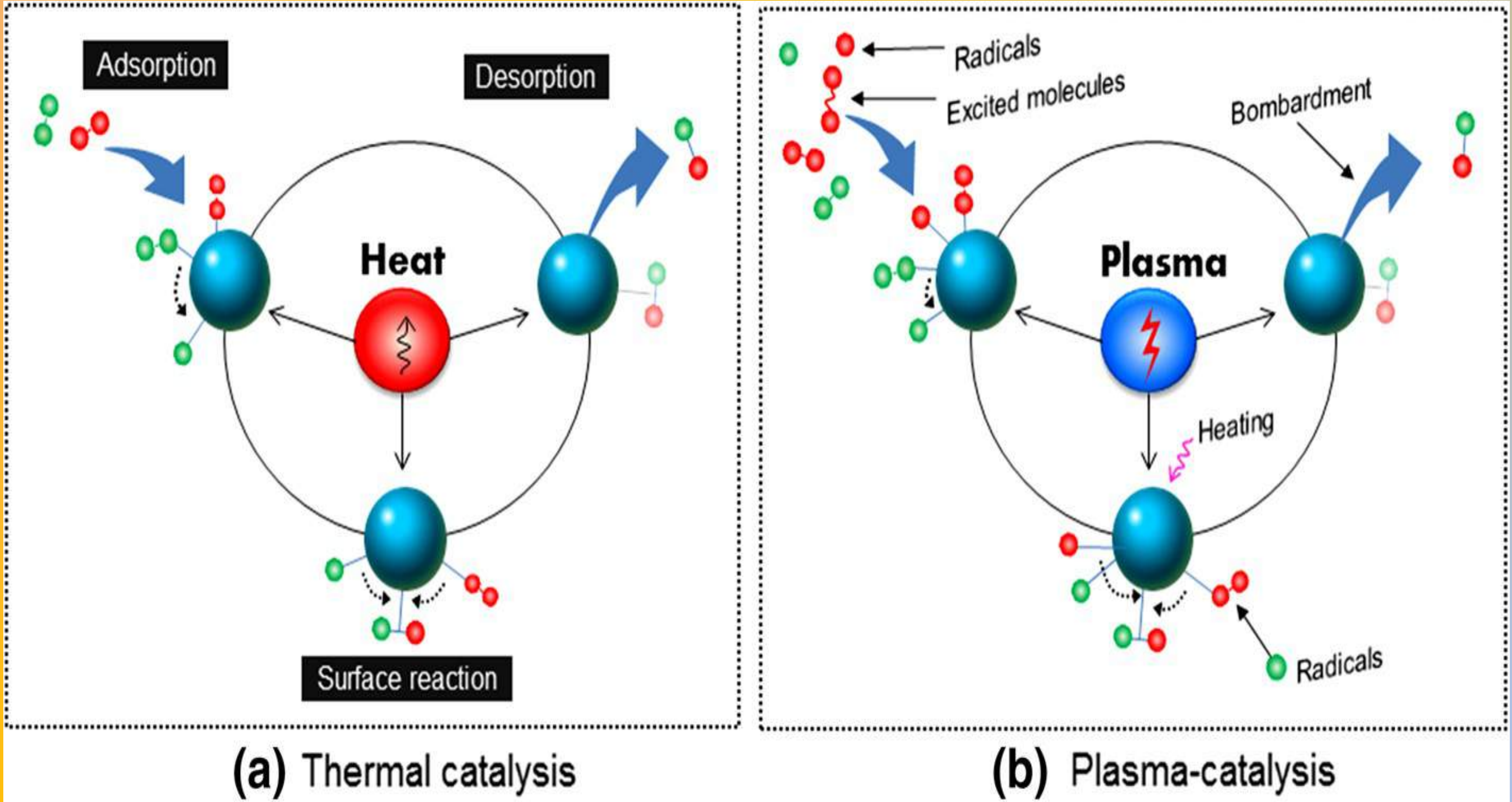
Low thermal equilibrium results



Supersonic gas flow
Power Interruption-Red
Catalysis-Green

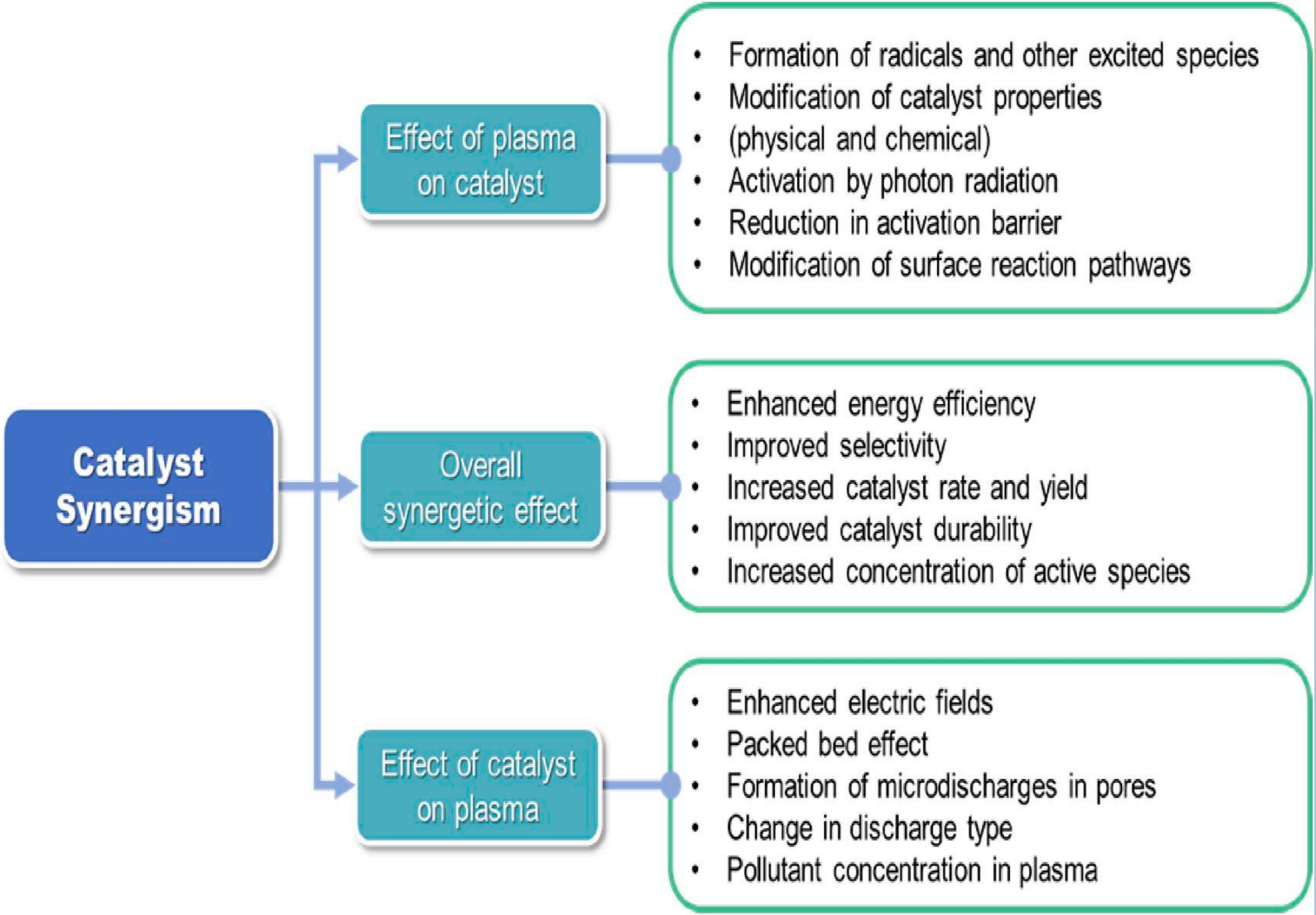
Fine tuning

Plasma Catalysis



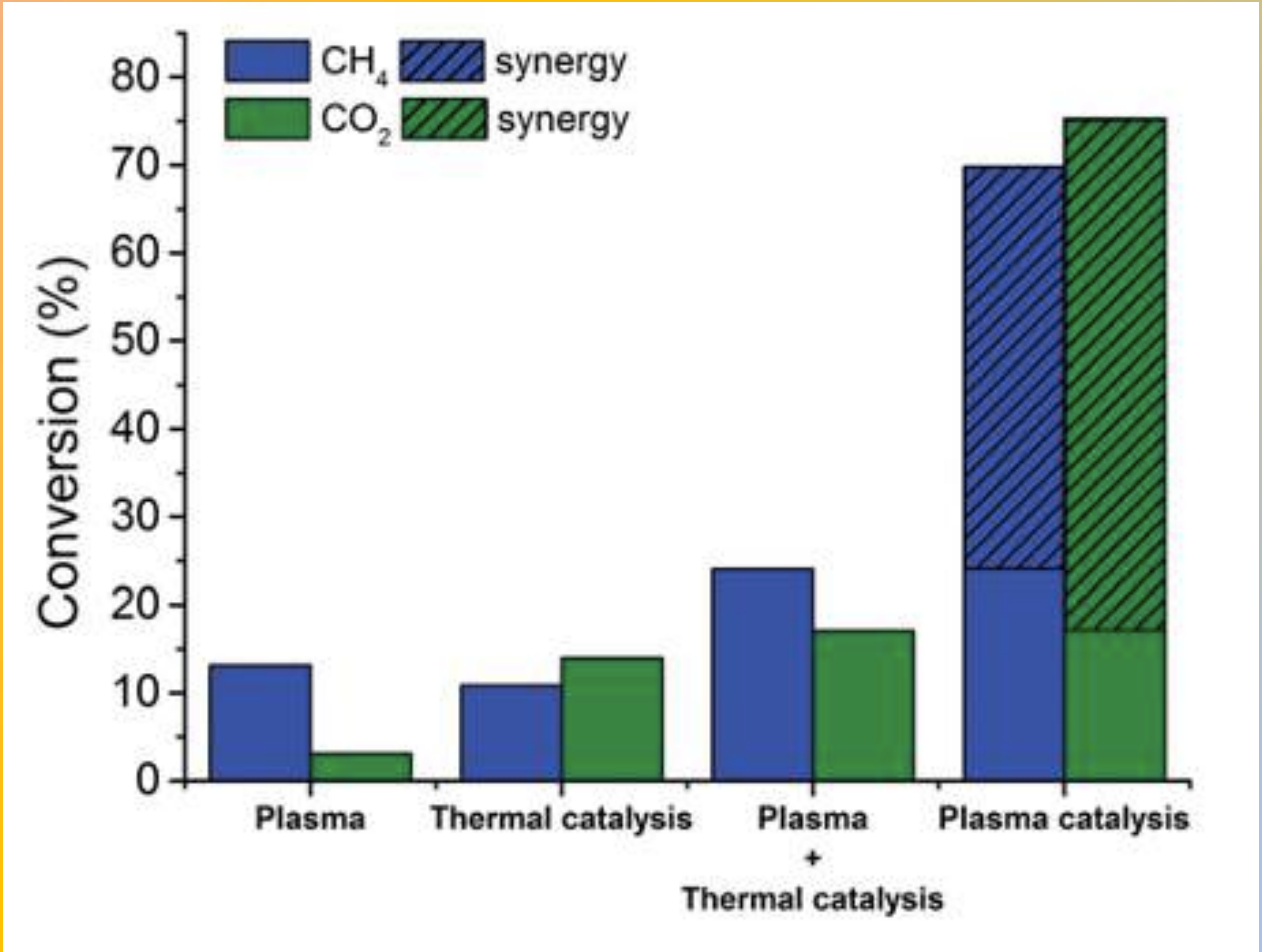
Vibrationally excited
Molecules provide
more reactivity at a
catalyst surface

lower barriers
for dissociation at the surface.



Renewable and Sustainable Energy Reviews
Vol 135, Jan 2021

Plasma Catalysis Synergy

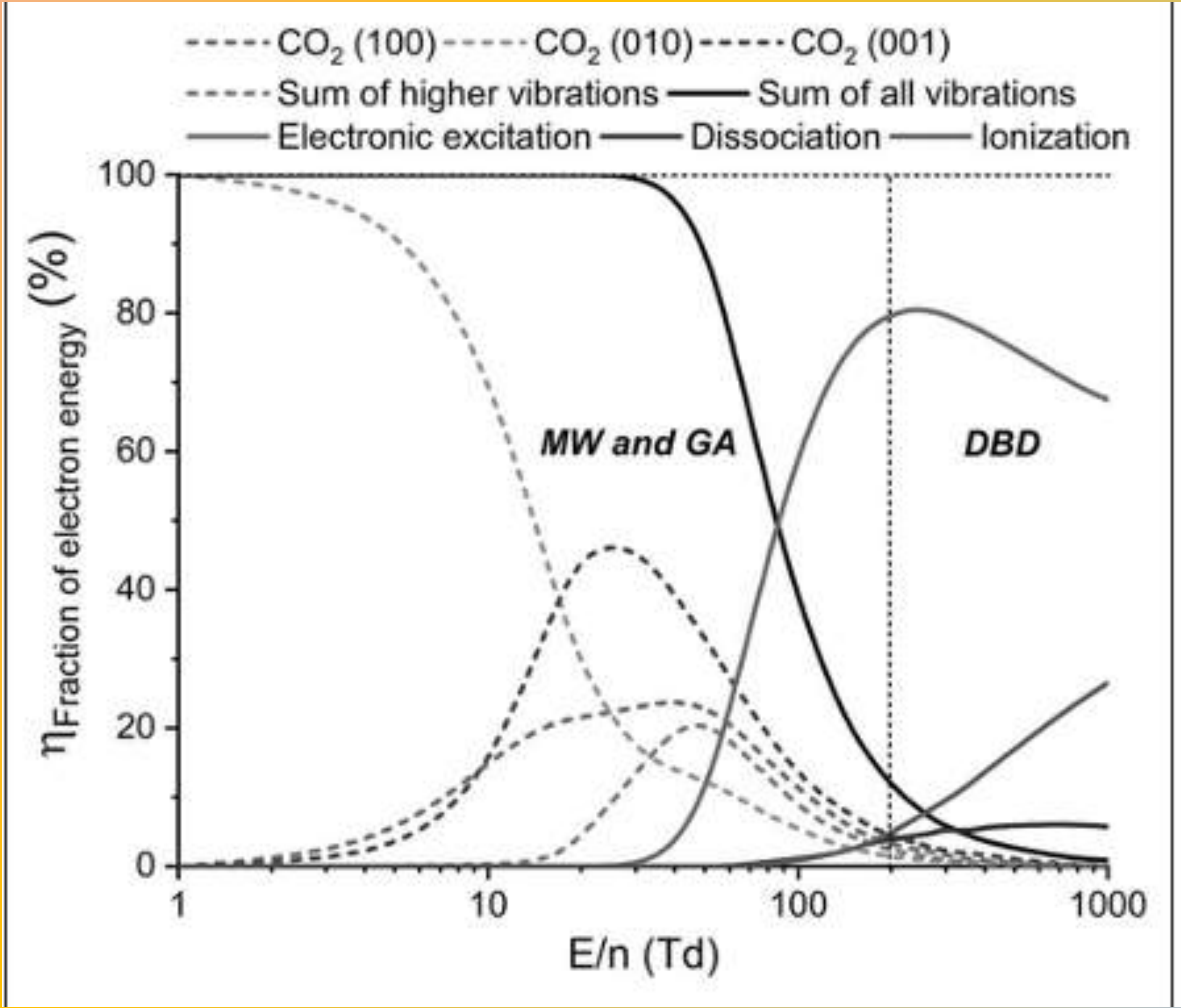


Versatility of Plasma Processes

	CO_2 splitting	CO_2/CH_4	CO_2/H_2	CO_2/H_2O
Catalysis	X	X	X	NA
Electrochemical	X	NA	NA	X
Solar thermochemical	X	NA	NA	X[a]
Photochemical	NA	NA	NA	X
Biochemical	NA	NA	NA	X[b]
Plasmachemical	X	X	X[c]	X[c]

PLASMA DISSOCIATION OF CO2: Advantages

- **On demand capability**
- **High energy efficiency (~60% demonstrated)**
- **High power density (45W/cm^3)**
- **Rapid ramping up and down (wrt high temperature SOEC)**
- **No scarce materials employed (Pt catalyst in PEM)**

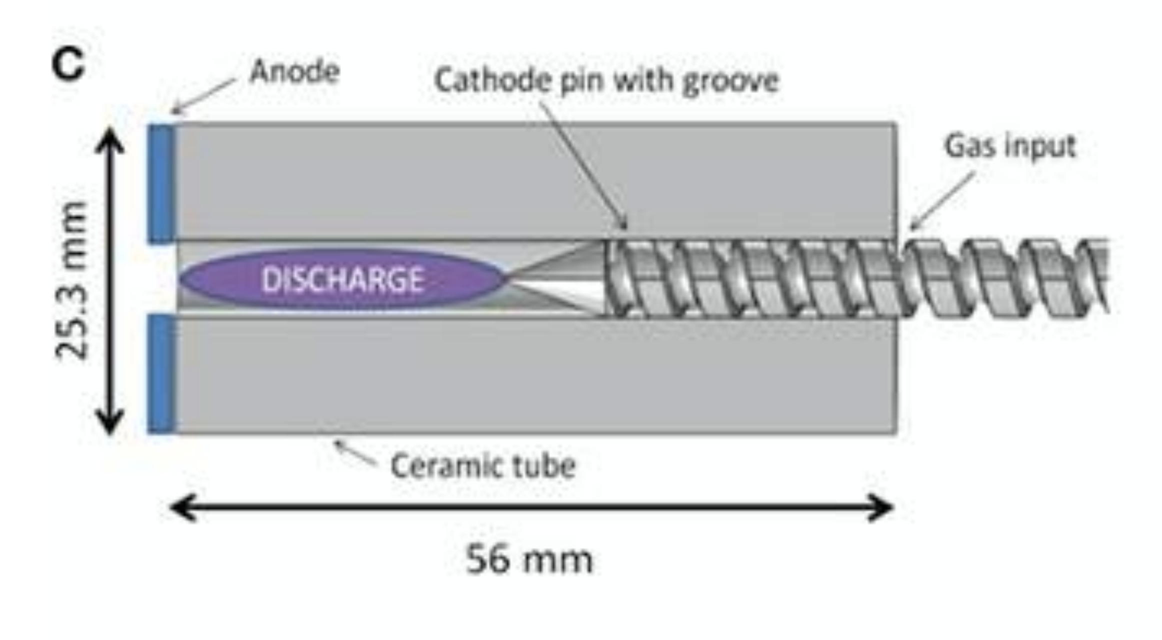


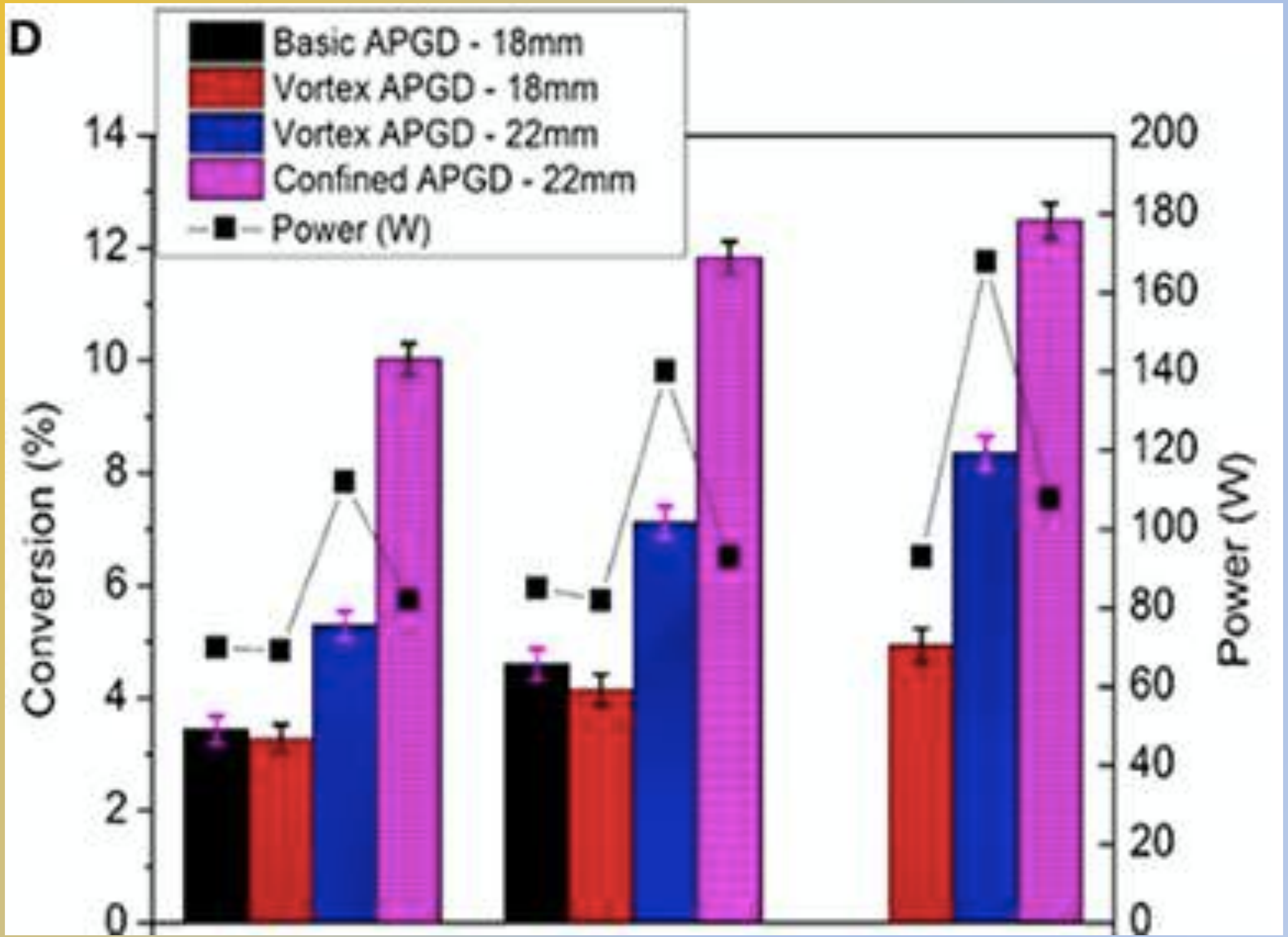
Designer Plasmas for optimizing conversion

E/n ~ 50Td

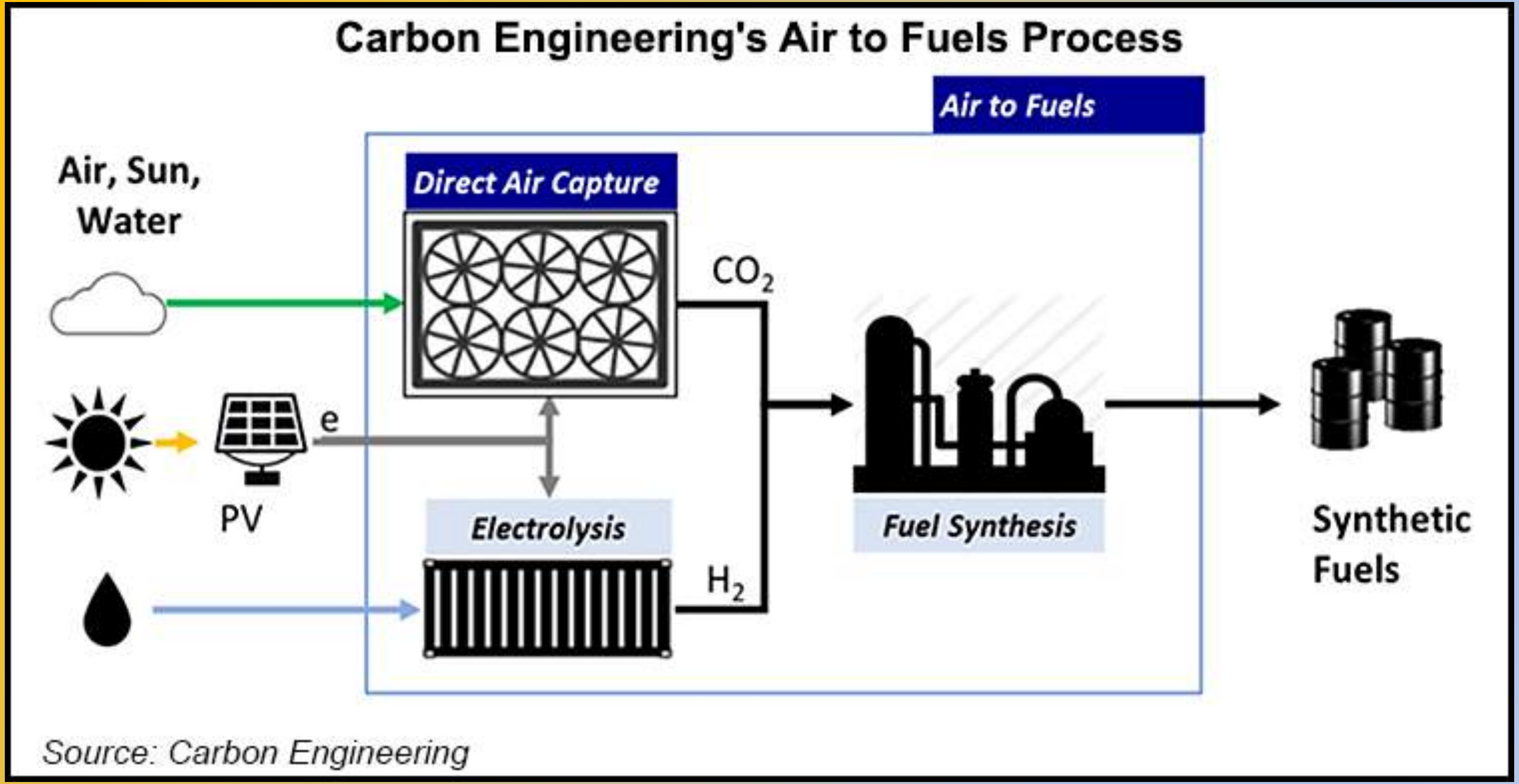
Source: Annemie Bogaerts, Ramses Snoeckx Chem. Soc. Rev., 2017, 46, 5805

Appropriate plasma devices





Annemie Bogaerts 1 and Gabriele Centi , Frontiers Energy Research July 2020*



Carbon Engineering

$20 MILLION

Prize Purse

The $20M NRG COSIA Carbon XPRIZE develops breakthrough technologies to convert CO_2 emissions into usable products.

Carbon8

Aljadix

Dioxide Materials™
The CO_2 Recycling Company™

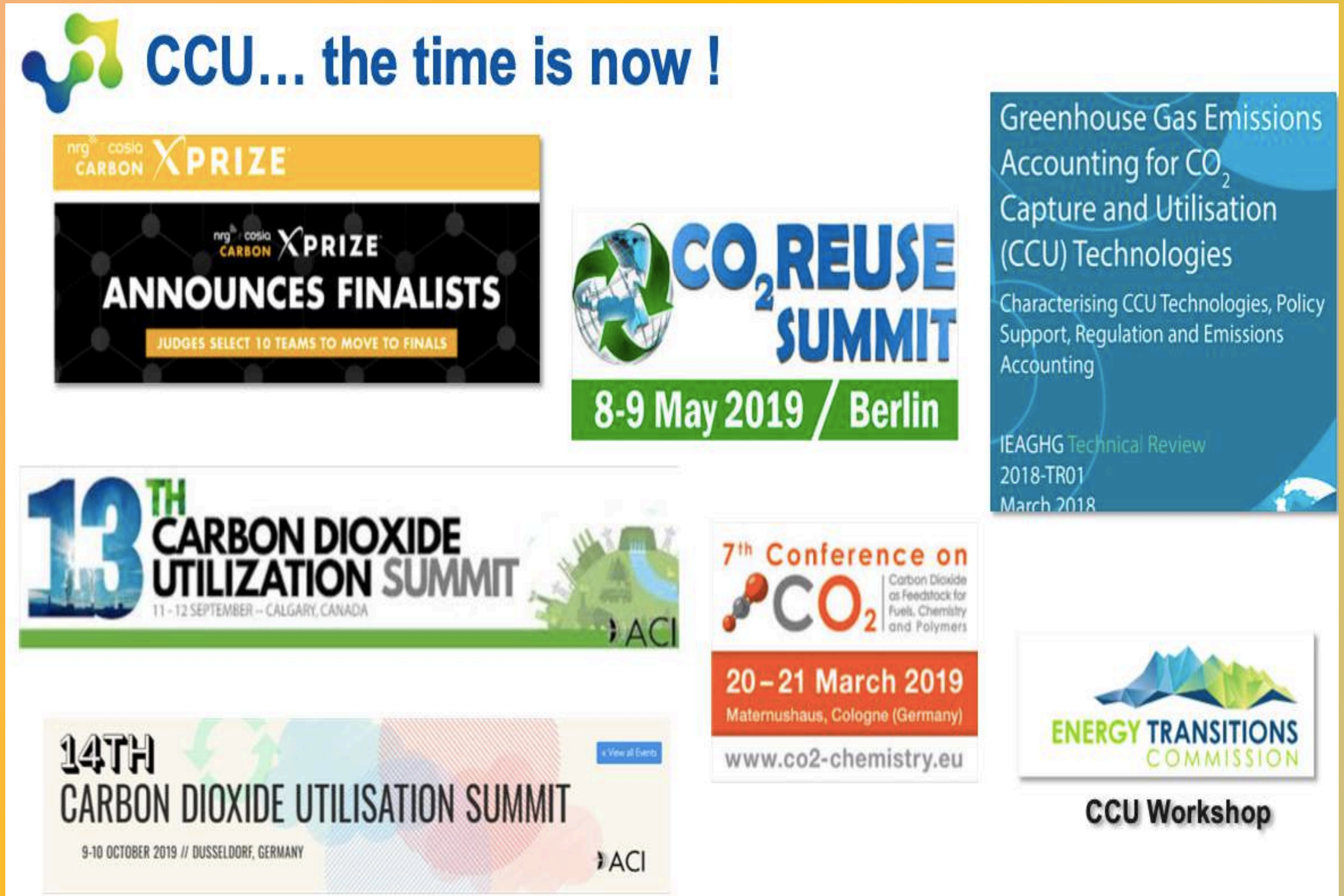
C2CNT

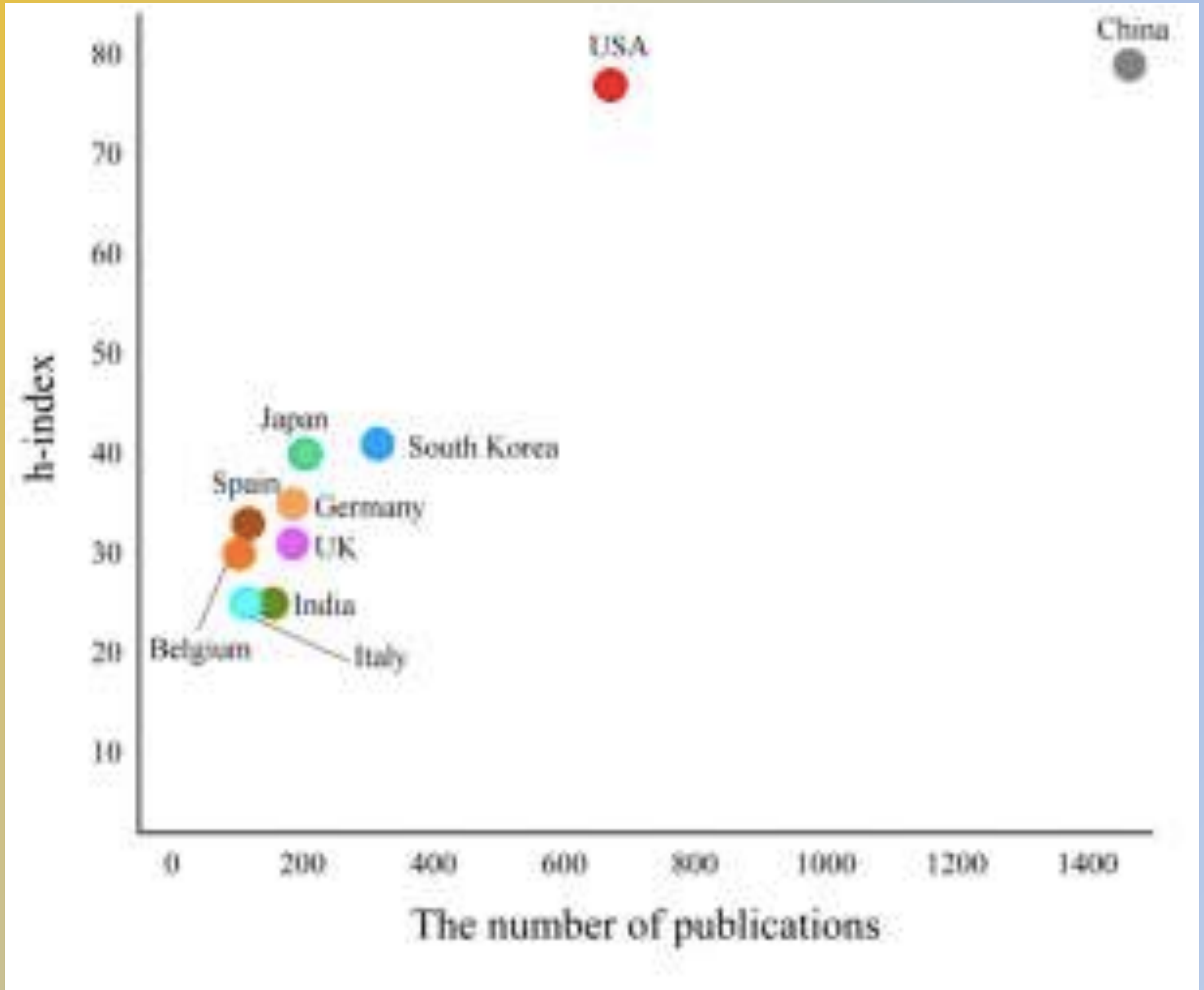
CARBON RECYCLING INTERNATIONAL

CCS Carbon Clean Solutions

covestro

nrg | cosia CARBON XPRIZE®

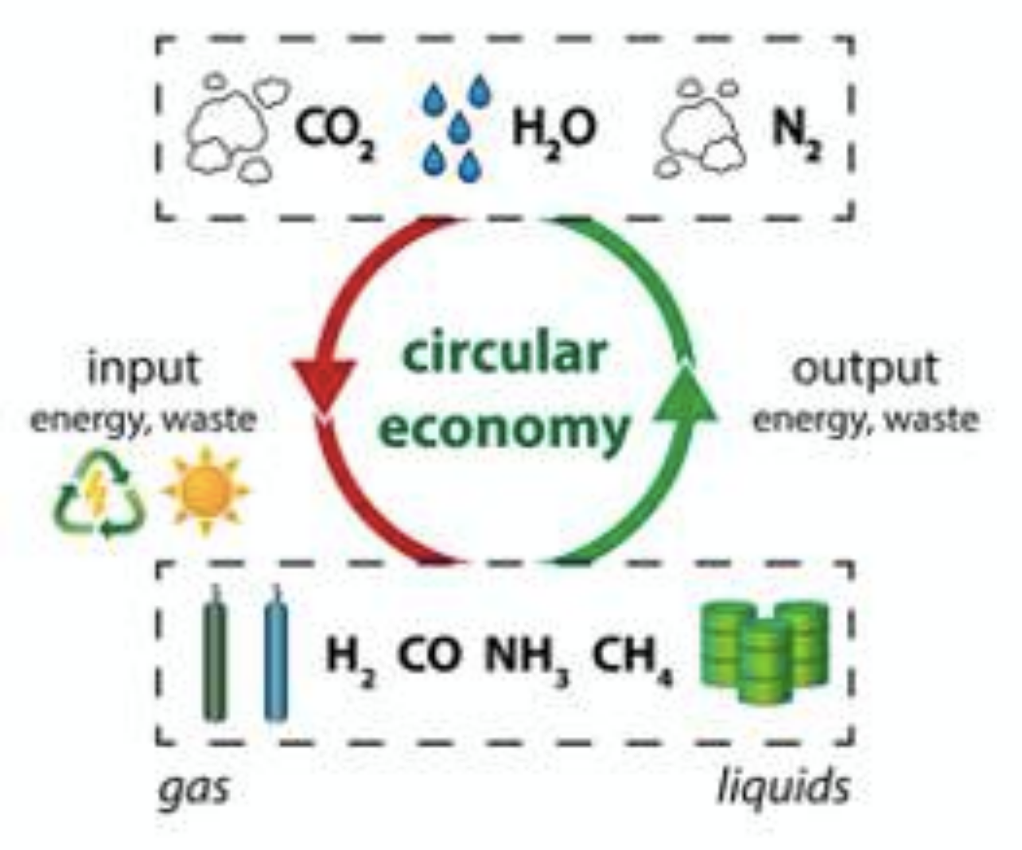


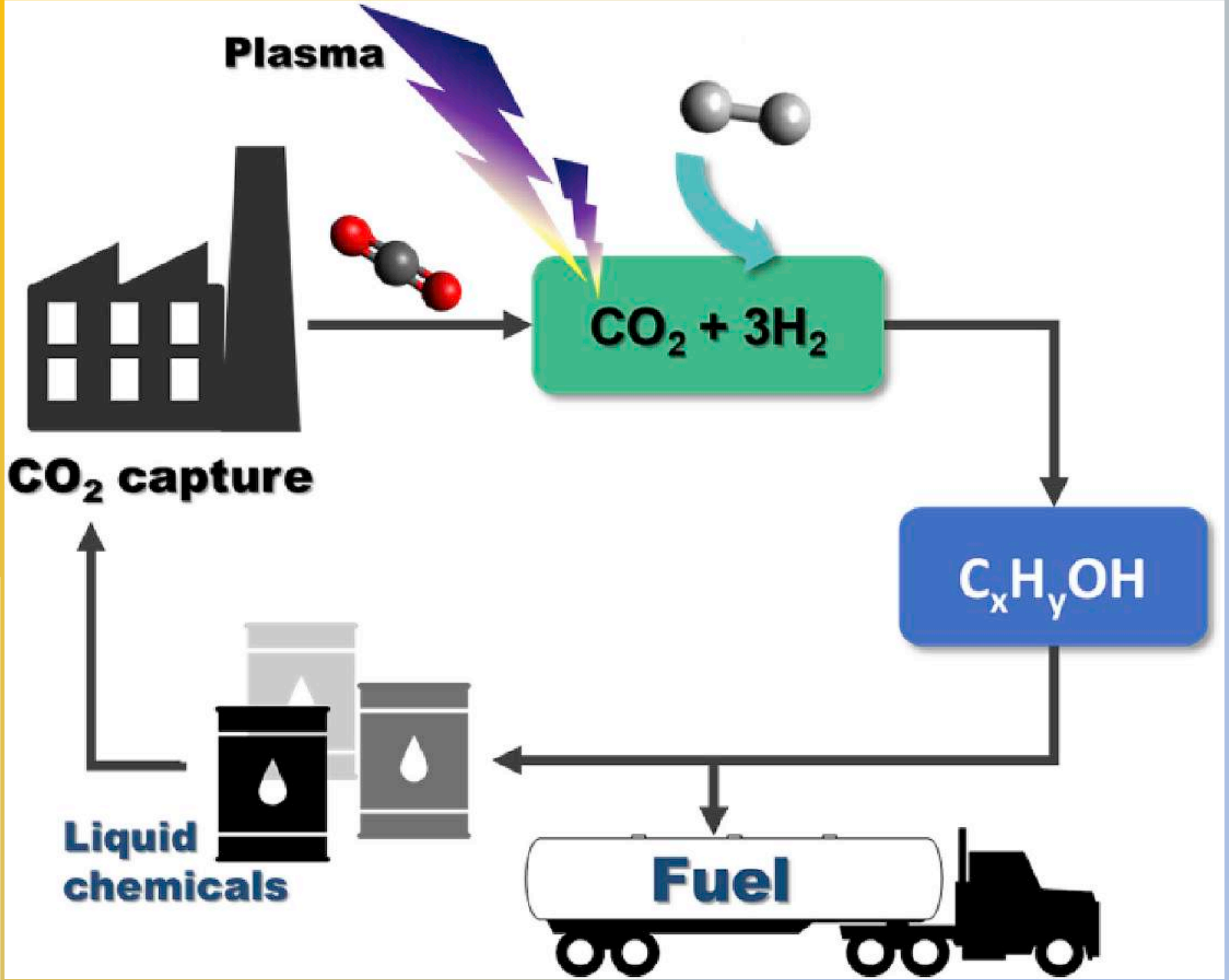


- **A new Industrial Revolution based on Circular concepts in waste to value is emerging.**
- **Europe is the epicentre**
- **Intellectual fervour and entrepreneurial effervescence.**
- **Many Startups: including one from India**

- **CO2 recycling with solar energy**
- **Storing electricity as chemical energy in gas grids**

CO2-Neutral Fuels.





Summary

New plasma processes to convert CO_2 into fuels enable a sustainable fuel cycle.

It will allow us to continue using the abundant Hydrocarbon resources and existing infrastructure

Plasma Catalysis may further increase the energy efficiency and throughput of the Plasma Process.

More research is needed to improve (i) energy efficiency, (ii) conversion, and (iii) product selectivity (iv) plasma sources

More insight in the plasma-catalyst interactions is crucial for designing catalysts most suited to the plasma environment.