The perspective of plasma conversion within the Power-to-X initiative

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MAX PLANCK GESELLSCHAFT

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

Sector coupling with Power-To-X conversion technologies

Usage of surplus electric power for electricity conversion, energy storage, and reconversion pathways

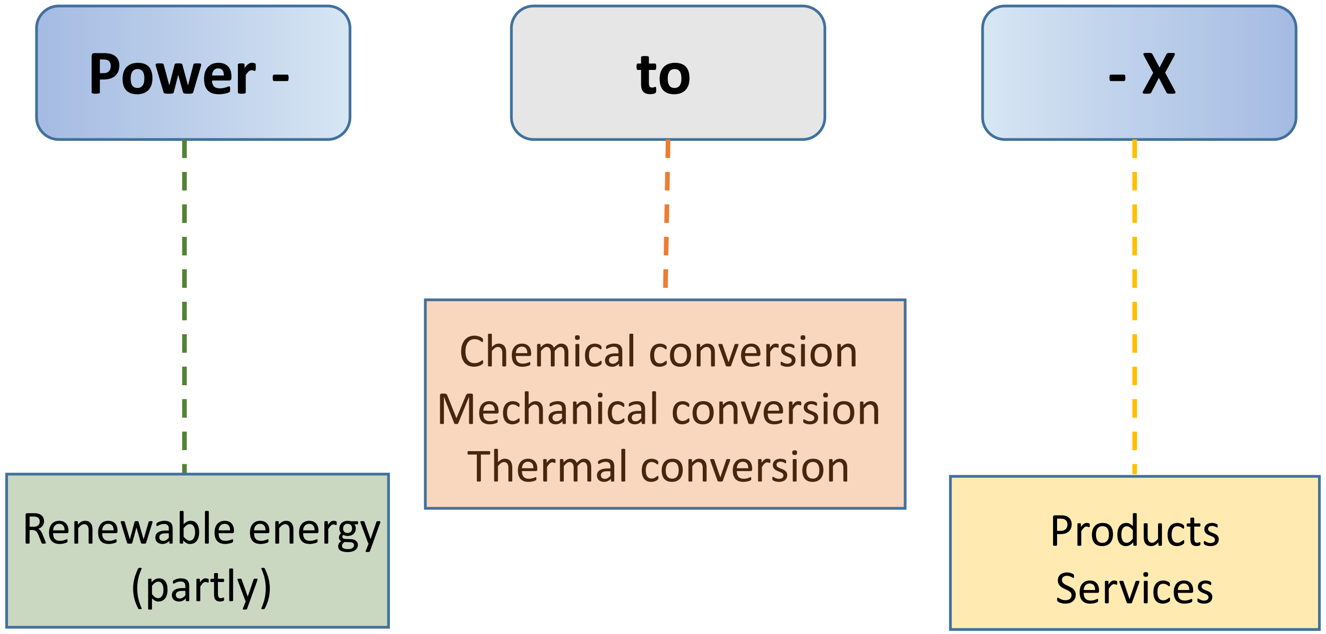


Figure adopted from: Berger et al. 2020 *Z Energiewirtsch* **44** 177

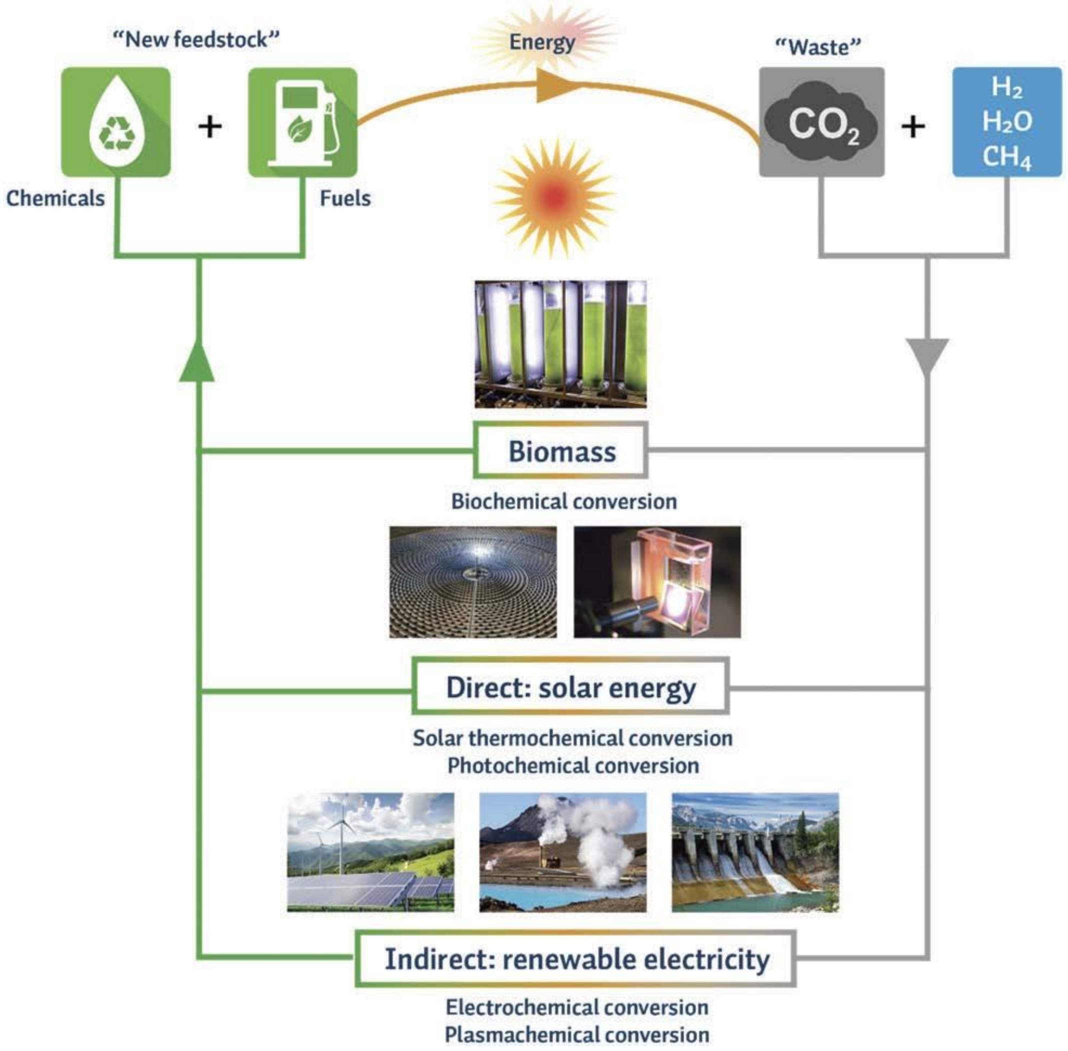
Energy conversion routes

- Power-to-Gas PtG
- Power-to-Heat PtH
- Power-to-Liquid PtL

Intendent use

- Power-to-Ammonia
- Power-to-Chemicals
- Power-to-Fuel
- Power-to-Syngas
- Power-to-Power

PtX: conversion of CO_2 in a carbon neutral cycle



Snoecks and Bogaerts 2017 *Chem. Soc. Rev.* ***46*** *5805*

Plasmas, complementary to established transformation routes

- Thermochemical
- Electro-catalysis
- Photo-electrochemical

Plasma properties

- Fast gas heating
- Fast response time (seconds)
- High throughput (~100 slm)
- Work with a manifold of gases
  CO_2, CH_4, C_xH_y, **N_2, H_2**, O_2, H_2O, …
- Scalable

PtM: synthetic fuels and chemicals
HGF, ENERGY Research Field, 2021-2027

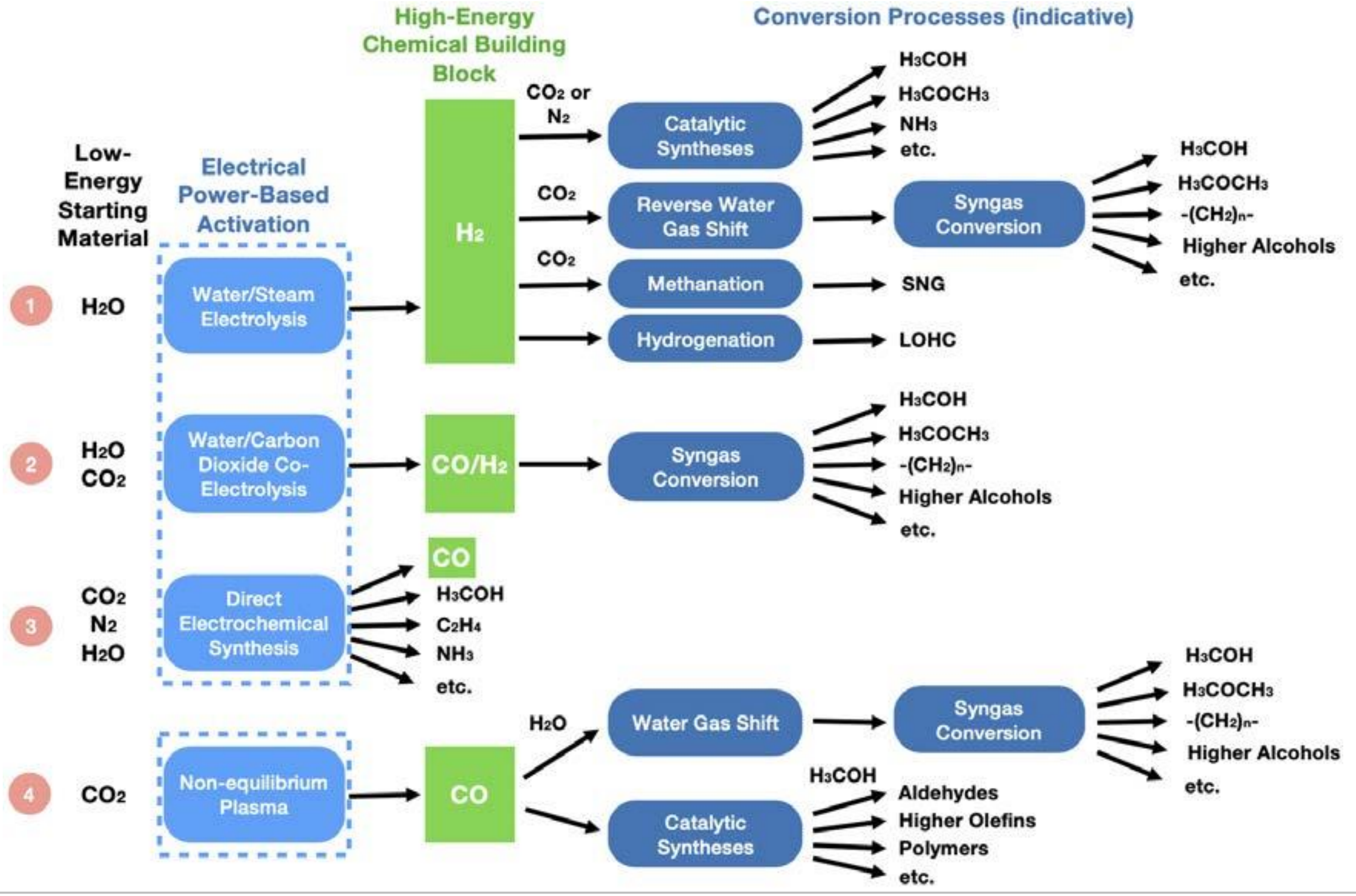
Initiative within HGF

HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

following

4 pathways

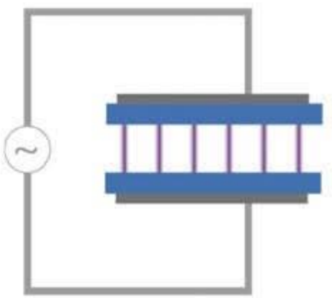
Plasma route



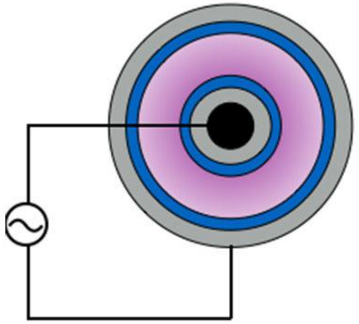
Typical plasma reactors for gas conversion

Dielectric Barrier Discharge

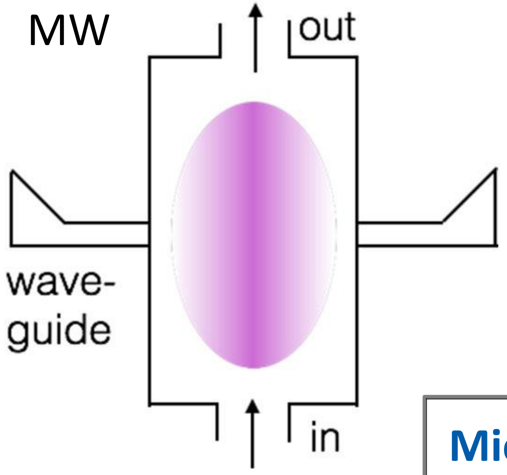
planar DBD



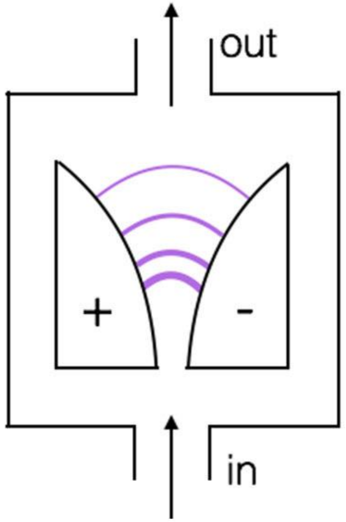
cylindrical DBD



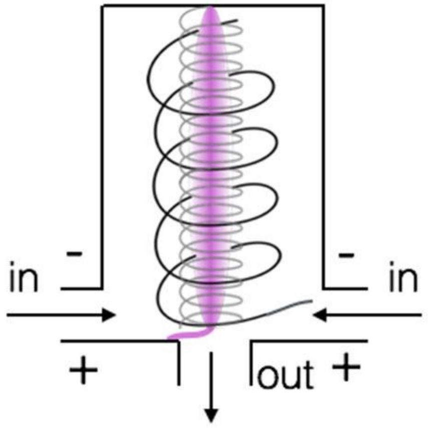
Microwave plasma



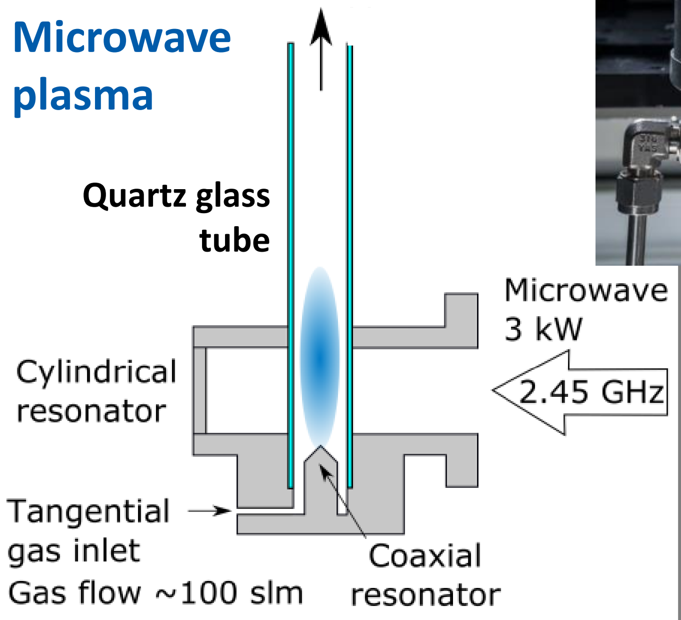
Gliding arc

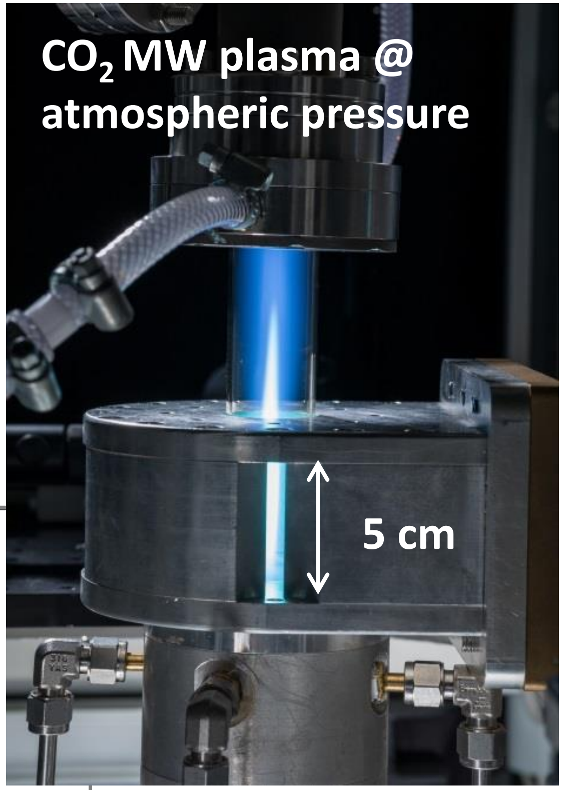


Gliding arc plasmatron



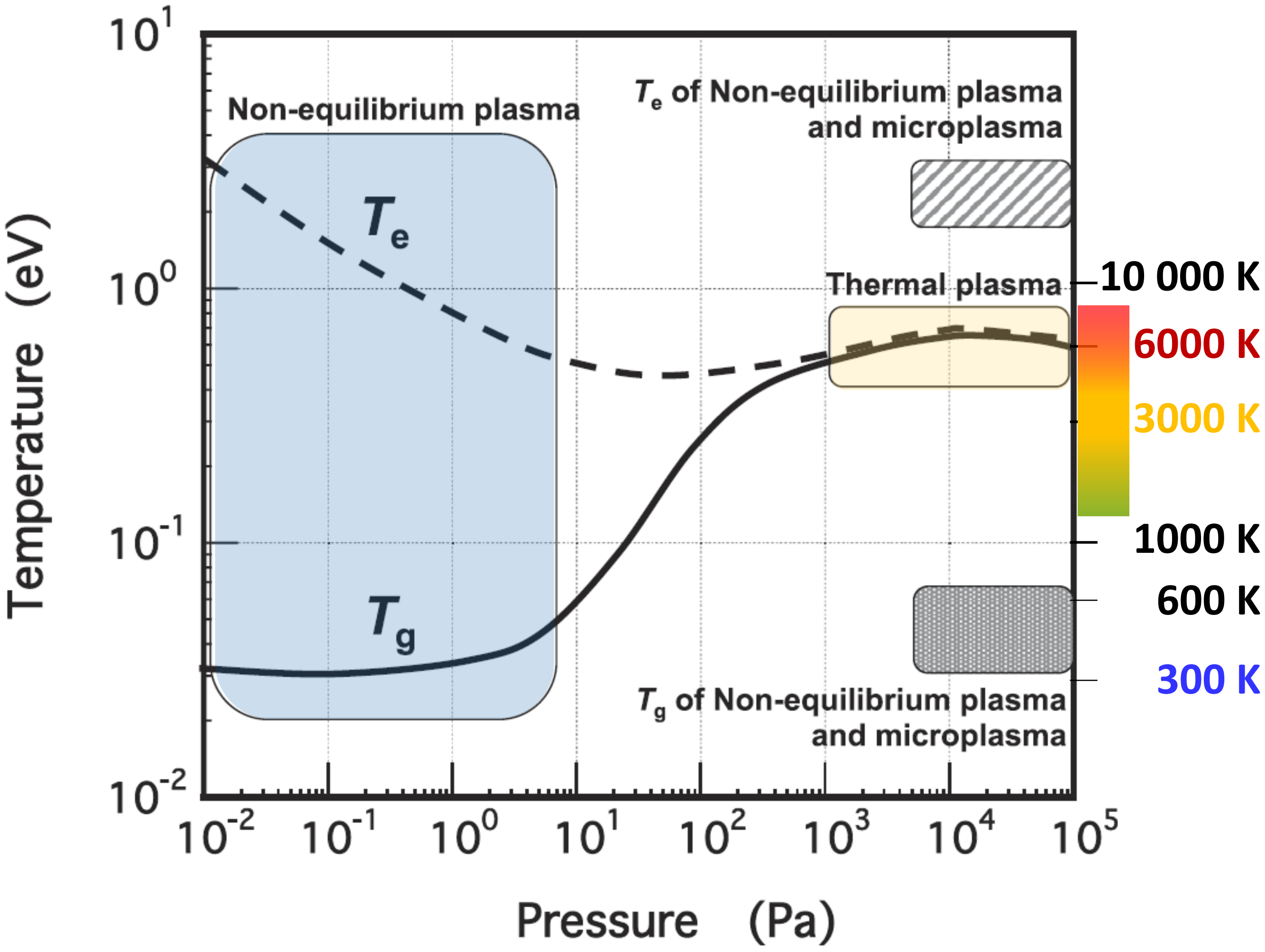
Microwave plasma





Bogaerts and Centi 2020 *Front. Energy Res.* **8** 111
Snoecks and Bogaerts 2017 *Chem. Soc. Rev.* **46** 5805

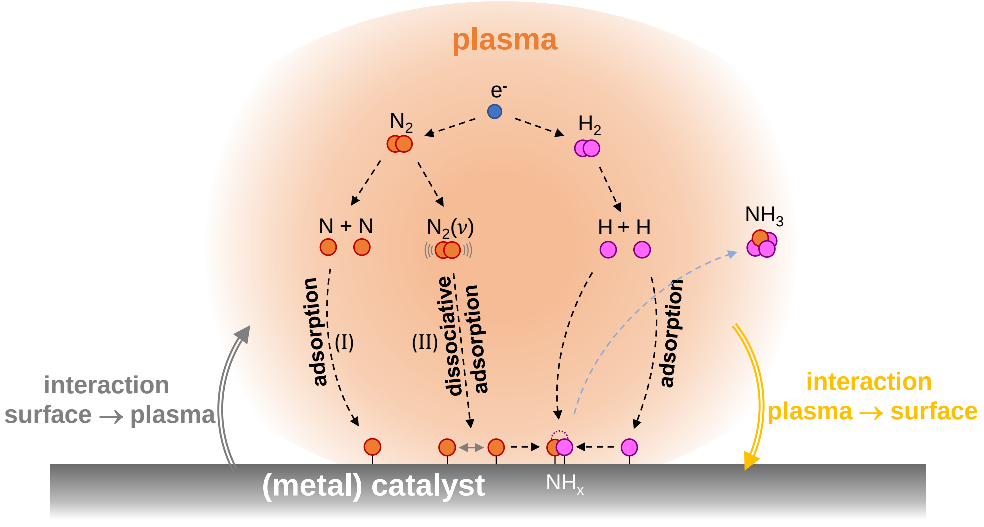
The typical temperature and pressure map of plasmas



Setsuhara 2016 *Archives of Biochemistry and Biophysics* 605 3

Plasma provides different particle species in addition to "heat"

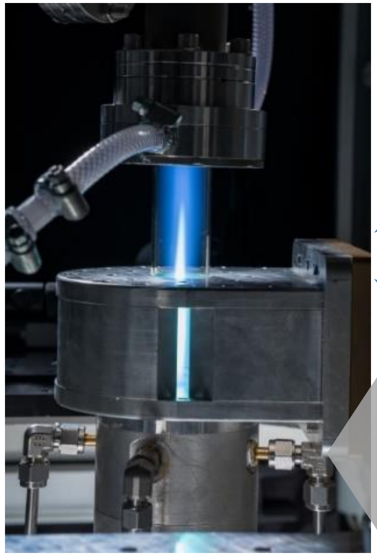
- Neutral species, radicals
- Ions (mostly singly ionized)
- Electrons



which interact also with surfaces

→ **plasma (assisted) catalysis**

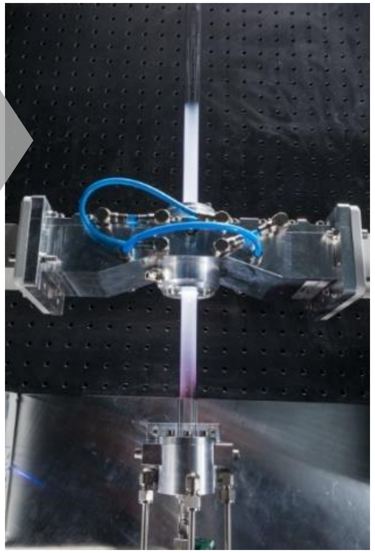
Microwave plasmas for gas conversion: Example CO_2



Fotos: Axel Griesch

Plasma torch
10-1000 mbar
Applications

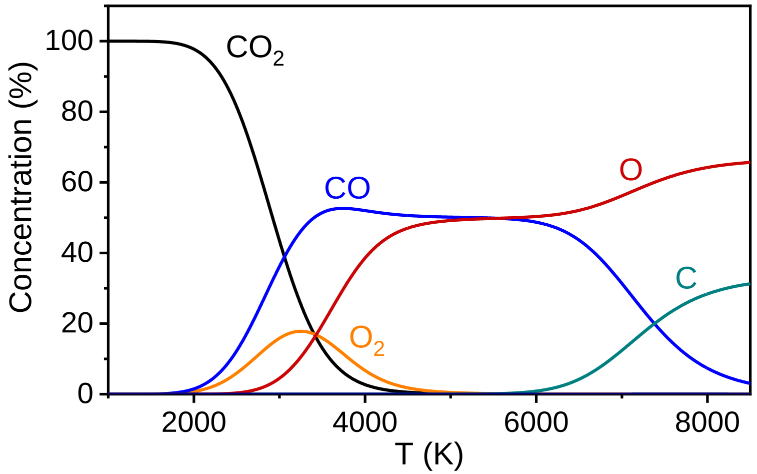
Surfaguide
0.3-100 mbar
Fundamental research



Pressure (mbar): 1000 … 1

T_{gas} > 3000 K

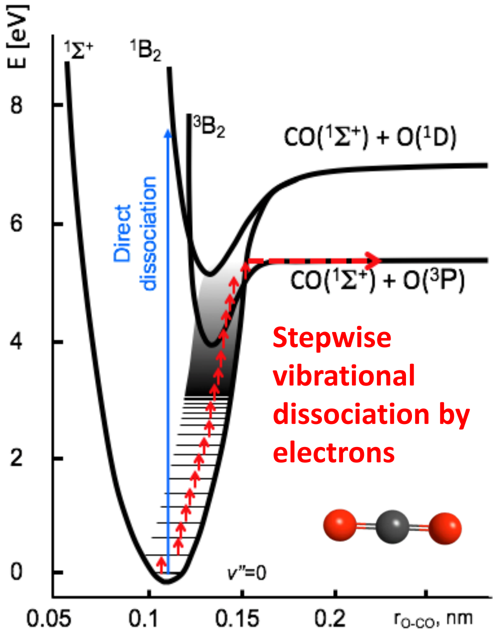
1. Thermal dissociation of CO_2



T_{gas} < 3000 K

Non-equilibrium plasma $T_{vib} \gg T_{gas}$

2. Electron impact dissociation [E > 7eV]
3. Stepwise vibrational dissociation [E > 5.5eV]



[A. Fridman *Plasma chemistry* (2008)]

Thermal conversion – one example

CO_2 conversion: $CO_2 \rightarrow CO + O$

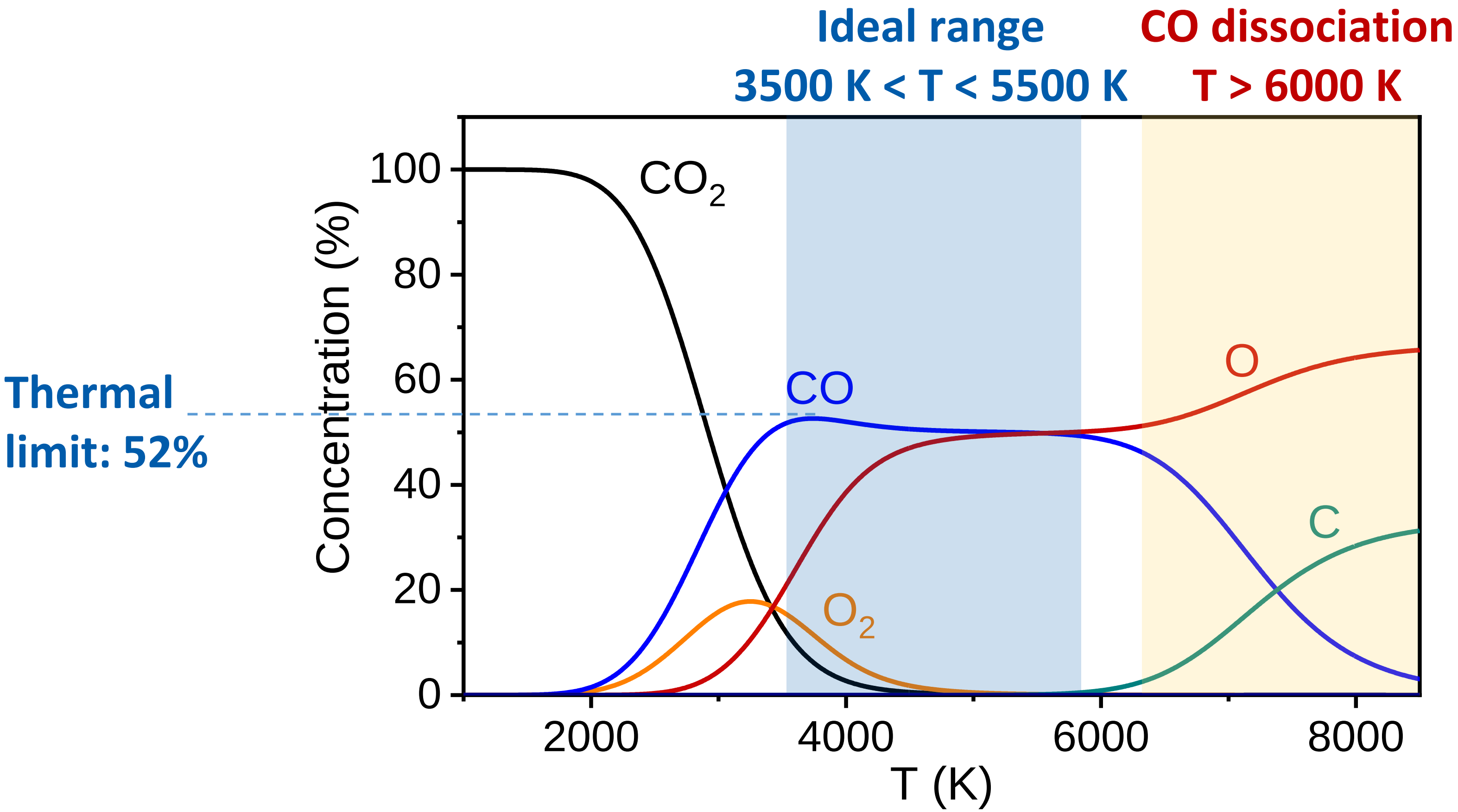
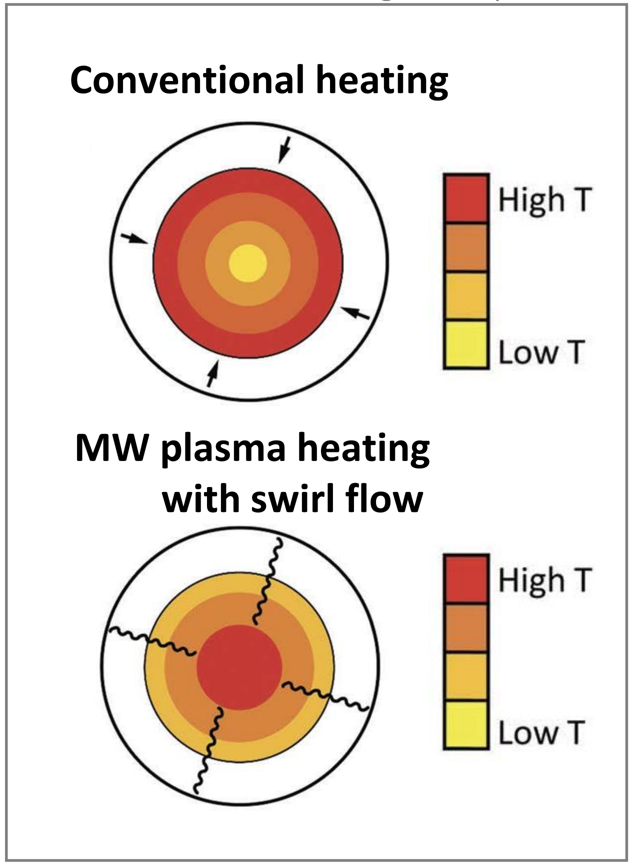


Figure adopted from:



Snoecks and Bogaerts 2017 *Chem. Soc. Rev.* ***46*** *5805*

Calculated with: NASA CEA code, Sanford and McBride 1994 *J. NASA reference publication* ***1311***

Figures of Merit: CO_2 conversion using plasmas

Energy efficiency and conversion

Conversion

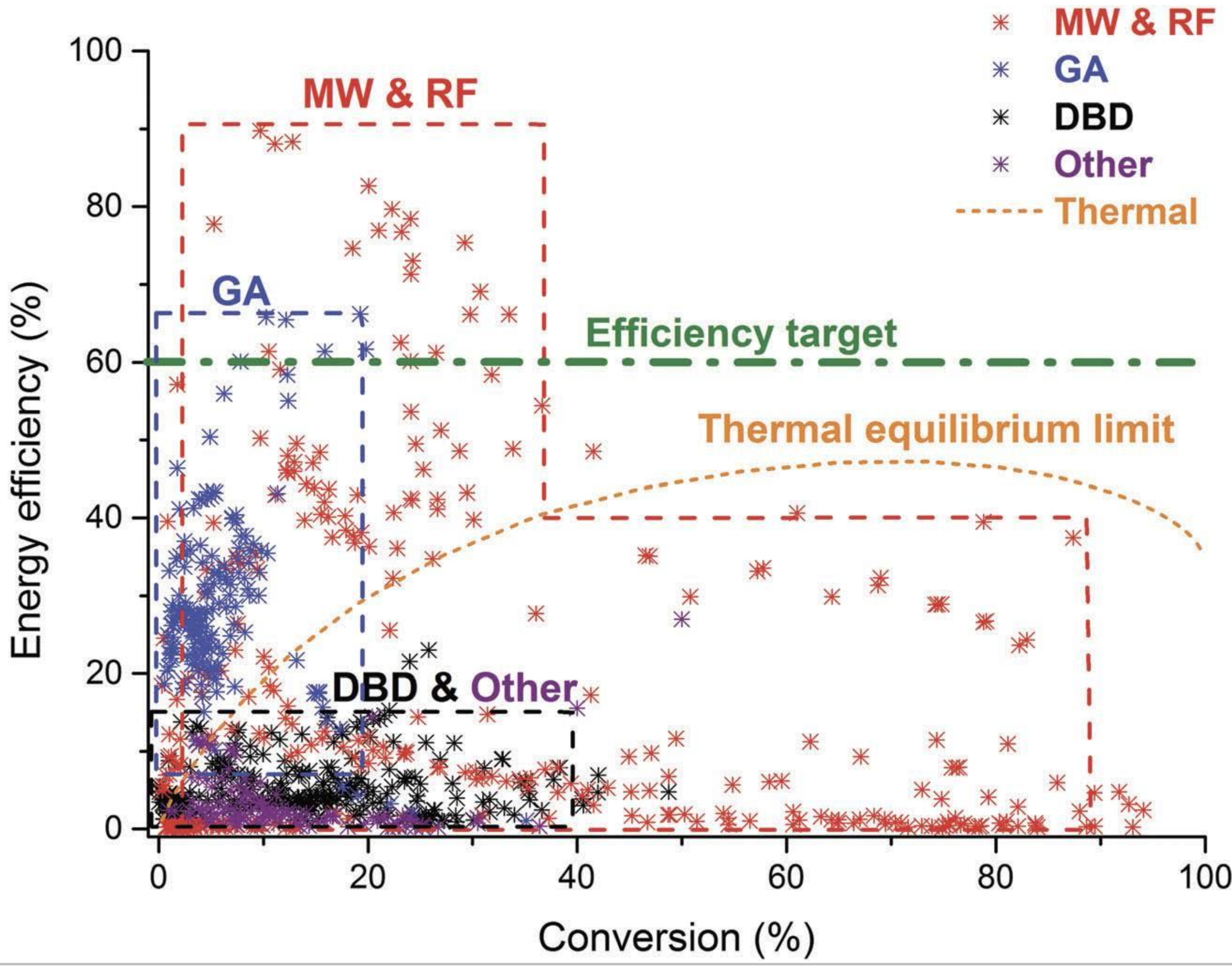
$$\chi = 1 - \frac{\dot{n}_{CO_2,out}}{\dot{n}_{CO_2,in}}$$

Energy efficiency

$$\eta = \chi \frac{\Delta H}{SEI}, \Delta H = 2.9\ eV,$$

with SEI ~ power/flow
Specific Energy Input

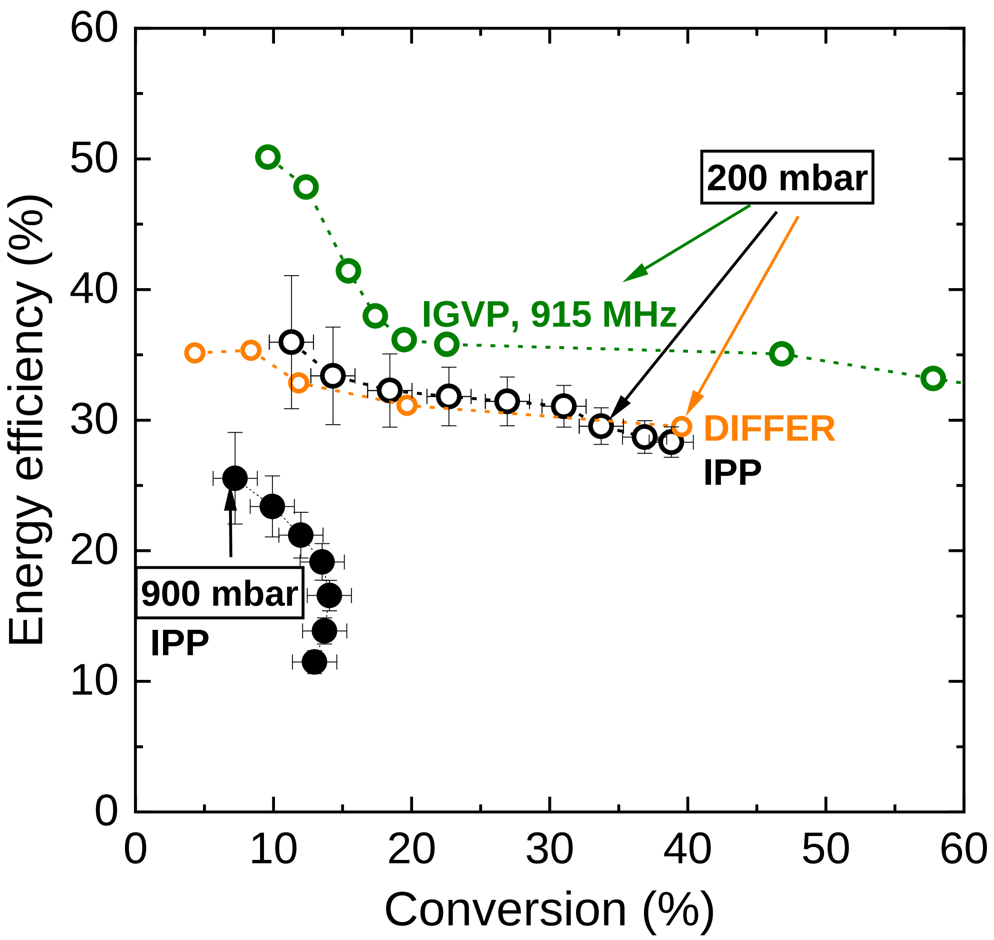
$CO_2 \rightarrow CO + O$	$\Delta H = 5.5\ eV$
$CO_2 + O \rightarrow CO + O_2$	$\Delta H = 0.3\ eV$
$CO_2 \rightarrow CO + ½\ O_2$	$\Delta H = 2.9\ eV$



Snoecks and Bogaerts 2017 *Chem. Soc. Rev.* **46** 5805

Energy efficiency and conversion for CO_2

The pressure effect demonstrated at the plasma torch



IGVP data: [Bongers 2017, Plasma Process Polym. 14]
DIFFER data: [Wolf 2020, J. Phys. Chem. C 124]

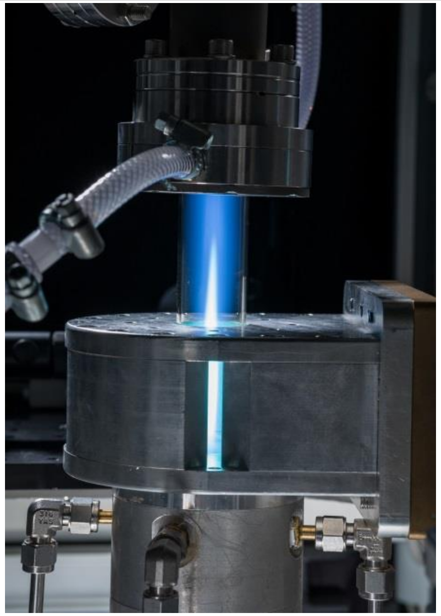
CO_2 dissociation

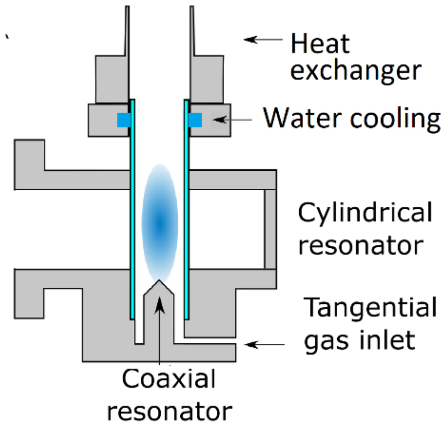
$CO_2 \rightarrow CO + O$

Reduce backward reactions:

$CO + O + M \rightarrow CO_2 + M$

$CO + O_2 \rightarrow CO_2 + O$





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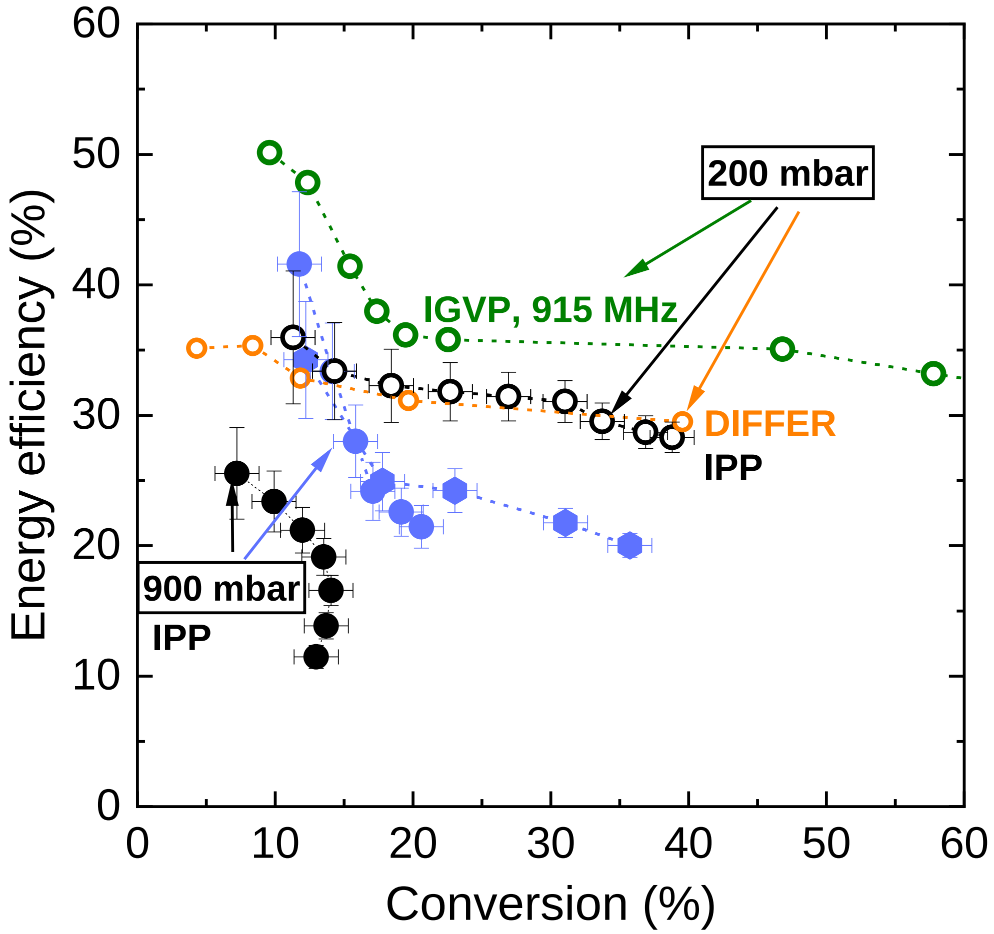


IGVP data: [Bongers 2017, Plasma Process Polym. 14]
DIFFER data: [Wolf 2020, J. Phys. Chem. C 124]

Hecimovic et al 2022 *Journal of CO2 Utilization* **57** *101870*

CO_2 dissociation

$CO_2 \rightarrow CO + O$

Reduce backward reactions:

$CO + O + M \rightarrow CO_2 + M$

$CO + O_2 \rightarrow CO_2 + O$

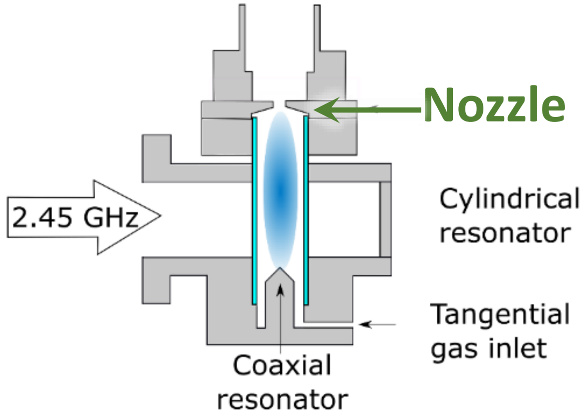
and foster

Quenching reactions

$O + O + M \rightarrow O_2 + M$

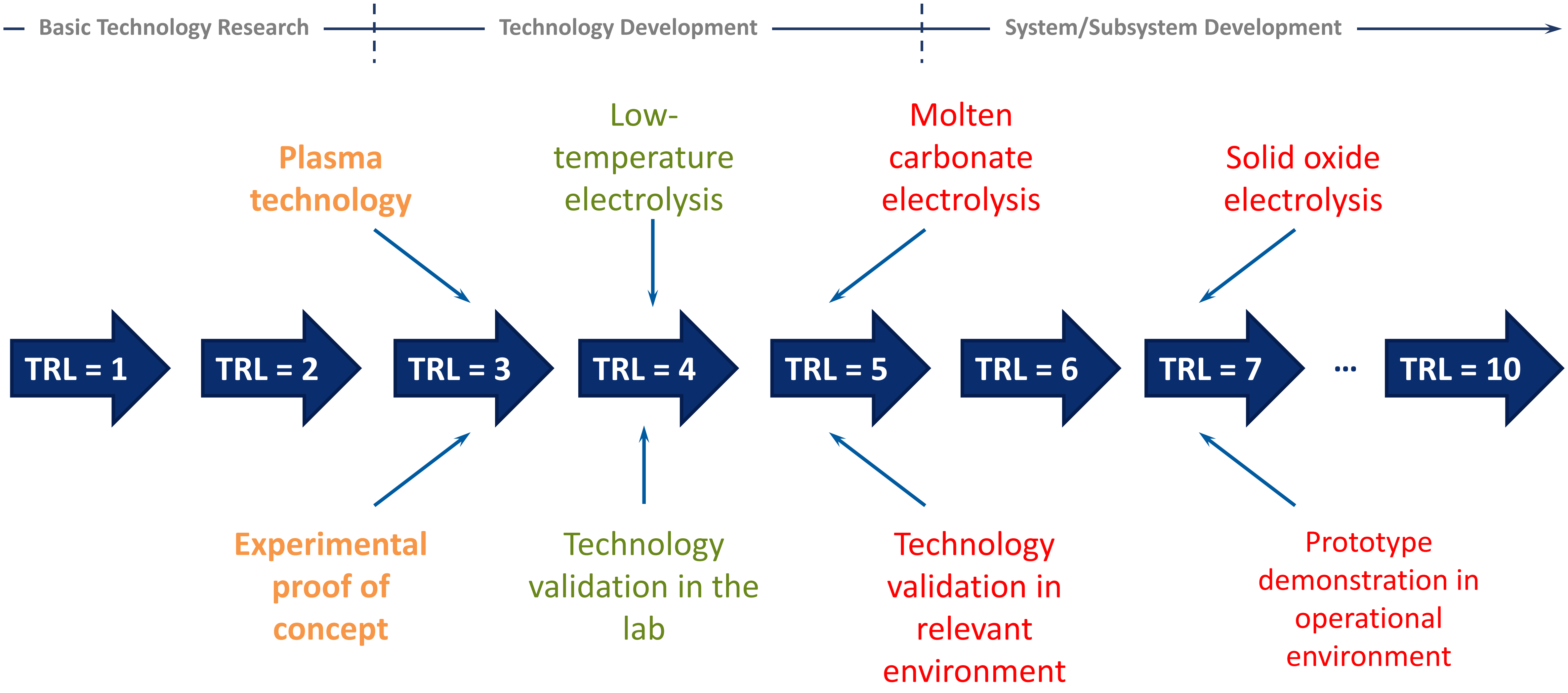
$O + CO_2 \rightarrow CO + O_2$

by fast cooling



Technology Readiness Level (TRL) compared to electrolysis

compiled from: Küngas et al 2020 *Journal of The Electrochemical Society* ***167*** *044508*



Plasma pathways for hydrogen production and utilization

Methane-based hydrogen production

$CH_4 \rightarrow C + 2H_2$ (pyrolysis)

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ (dry reforming)

$CH_4 + H_2O \rightarrow CO + 3H_2$ (steam reforming)

$CH_4 + ½O_2 \rightarrow CO + 2H_2$ (partial oxidation)

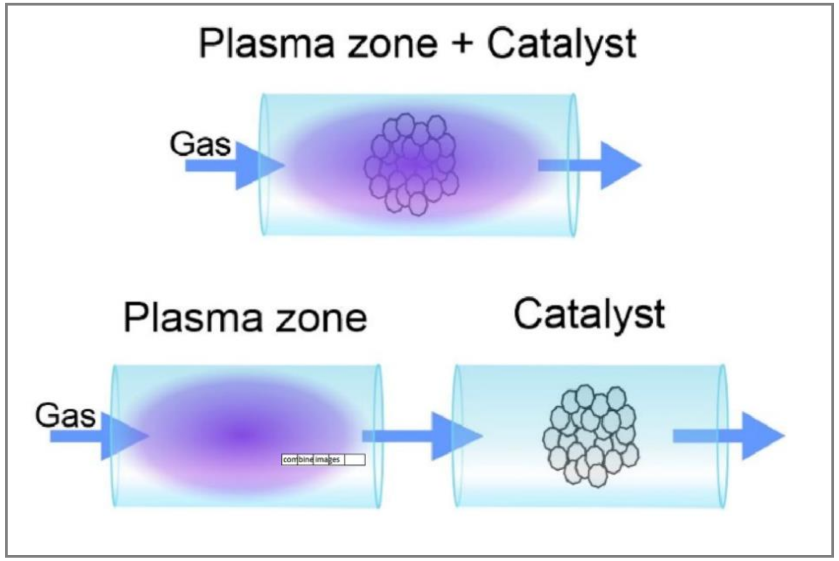
Challenges to overcome

- **Soot formation**
- (DBD) Efficiency
- Selectivity and scalability

Hydrogen storage

$N_2 + 3H_2 \rightarrow 2NH_3$ **Ammonia production**

Requires plasma catalysis



Ong et al 2022 *Journal of Cleaner Production* 336 130447

Assessment of plasma (assisted) processes with multiple gases

→ combined dry + steam reforming

→ methanol production

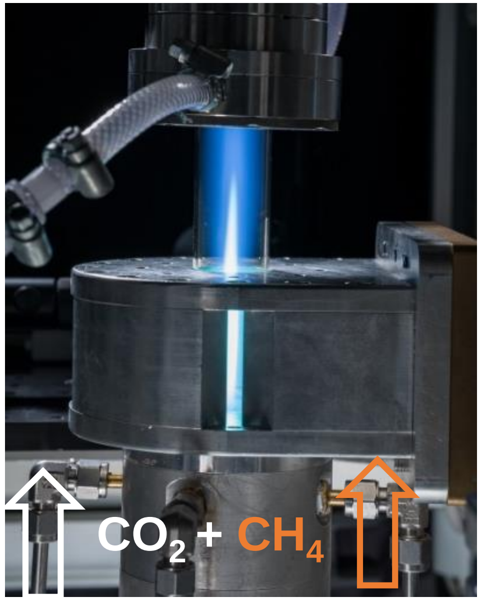
Plasma pathways for hydrogen production and utilisation

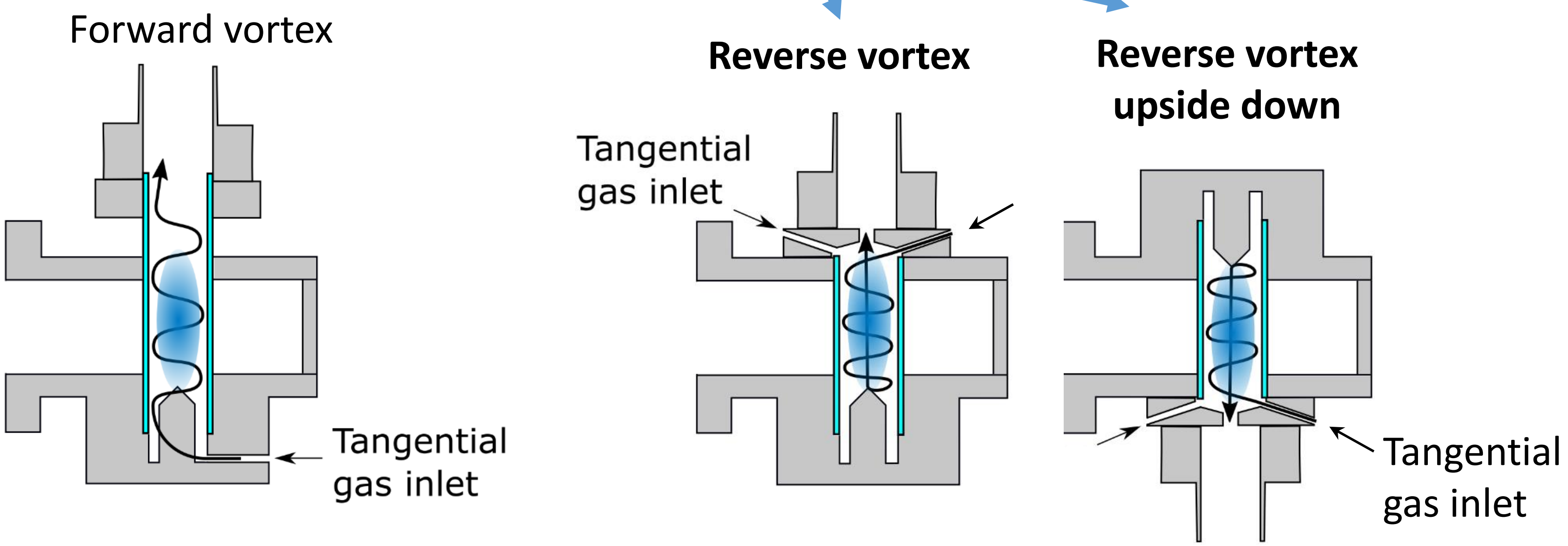
Methane-based hydrogen <u>production</u> e.g. via

$CH_4 \rightarrow C + 2H_2$ (pyrolysis) or $\mathbf{CH_4 + CO_2 \rightarrow 2CO + 2H_2}$ **(dry reforming)**

CH_4 challenge

Suppression of undesirable (back-)reactions → adapted **gas flow**





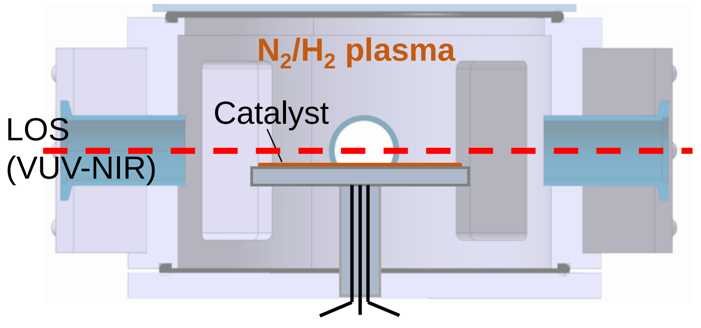
Plasma pathways for hydrogen production and utilisation

Hydrogen storage $N_2 + 3H_2 \rightarrow 2NH_3$

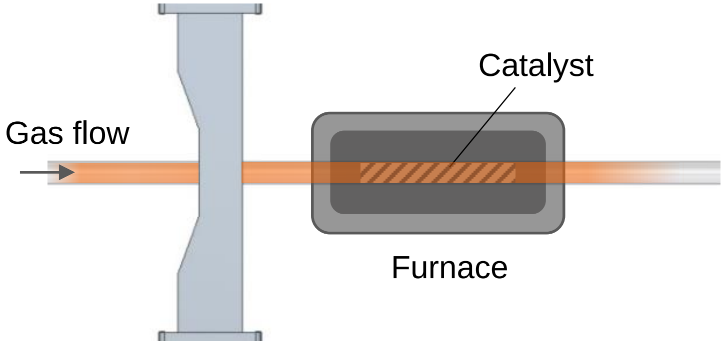
Ammonia production via plasma catalysis from nitrogen and hydrogen

pressure: < 0.1 mbar < 100 mbar 1000 mbar

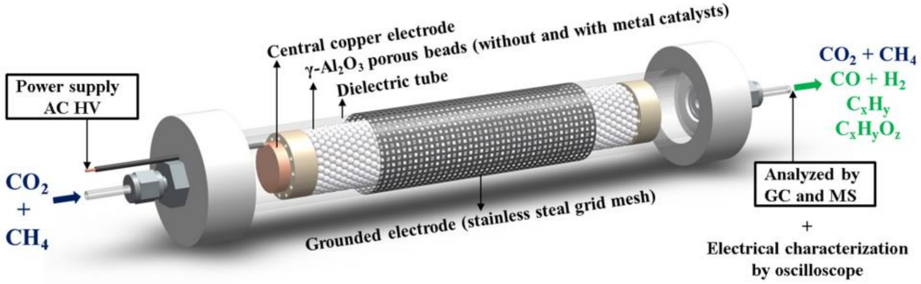
RF discharges
Planar ICP



Microwave discharges
Surfaguide



Dielectric Barrier Discharges
Packed-bed DBD



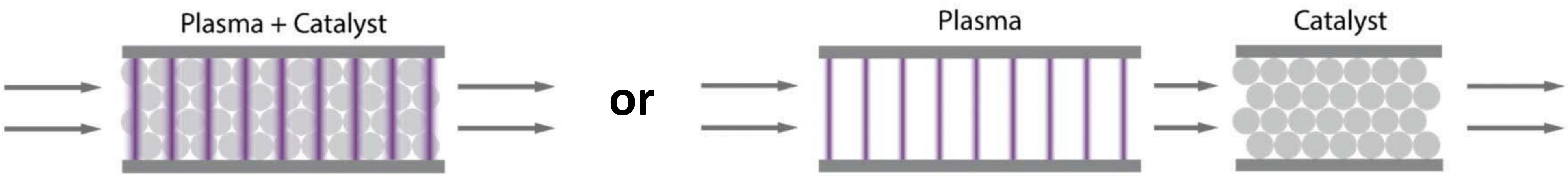
[L.Brune, J. Phys. D. 51 (2018)]

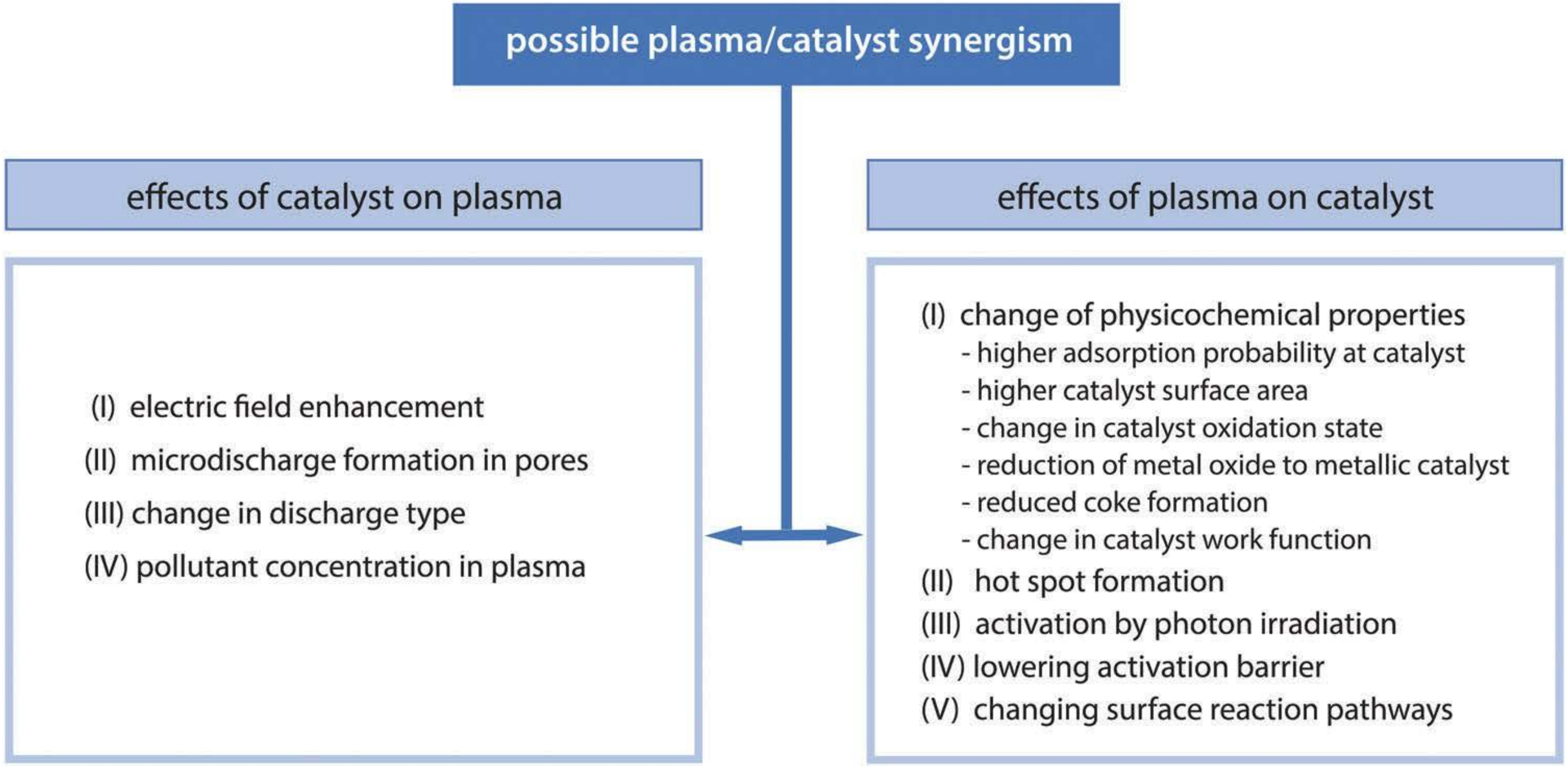
Fundamental research
plasma catalyst-interaction
(+ diagnostic accessibility)

Transition & extrapolation
towards atmospheric
conditions

Application at atmospheric conditions
(and beyond…) & reactor design

Plasma catalysis – plasma assisted catalysis



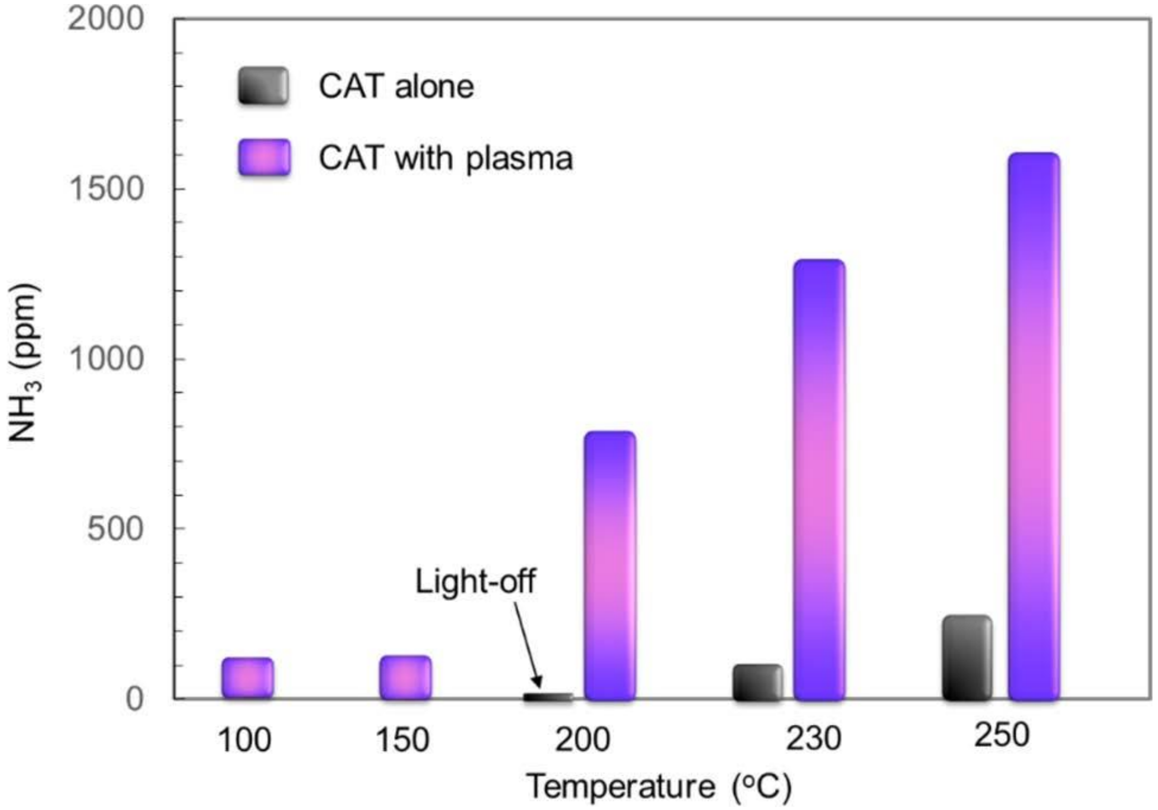


Snoecks and Bogaerts 2017 *Chem. Soc. Rev.* ***46*** 5805

Plasma catalysis – plasma assisted catalysis

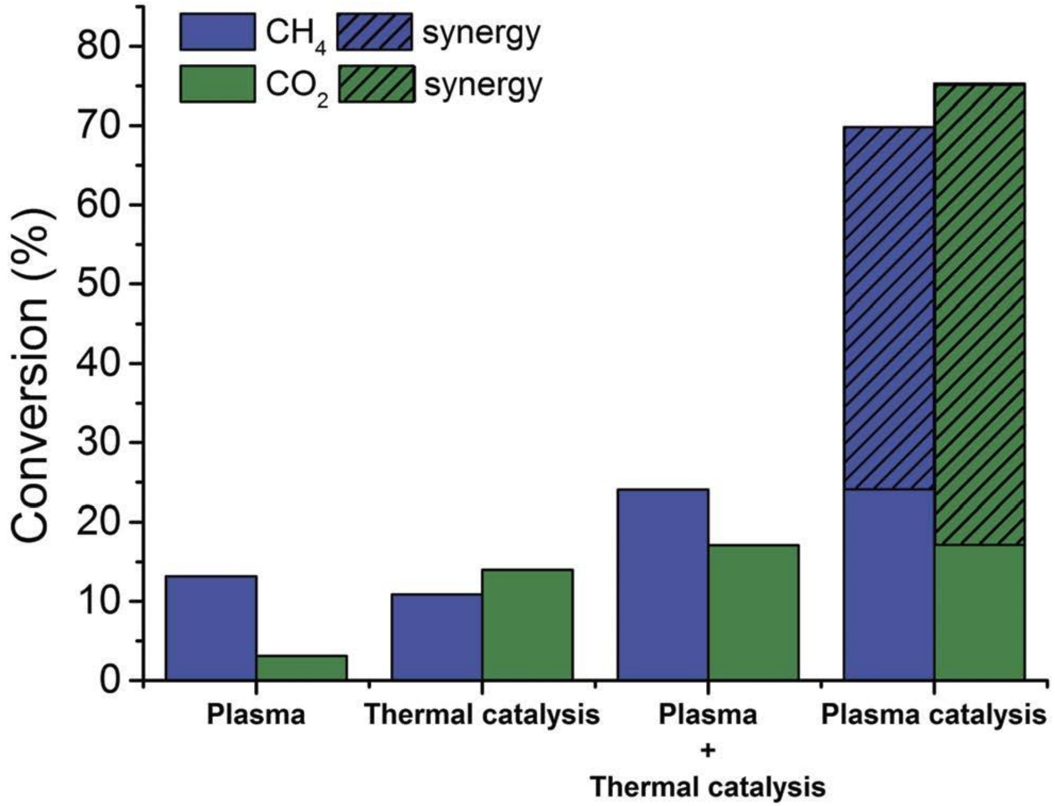
Synergy of plasma-catalysis for

Ammonia formation



Kim et al 2016 *Plasma Chem. Plasma Process.* **36** 45

Dry reforming of methane



Snoecks and Bogaerts 2017 *Chem. Soc. Rev.* **46** 5805, adopted from:
Zhang et al 2010 *Chemical Engineering Journal* **156** 601

Selection criteria beside efficiencies

Comparison of plasma conversion technology with other emerging technologies

	Traditional catalyst	Catalyst by MW heating	Electro-chemical	Solar thermo-chemical	Photo-chemical	Bio-chemical	Plasma-chemical
Use of rare earth materials	Yes	Yes	Yes	Yes	Yes	No	No
Renewable energy	-	Indirect	Indirect	Direct	Direct	Direct	Indirect
Turnkey process	No	No	No	N/A	Yes	No	Yes
Conversion and yield	High	High	High	High	Low	Medium	High
Separation step needed	Yes	Yes	Yes	No	Yes	Yes	Yes
Oxygenated products	Yes	Yes	Yes	No	Yes	Yes	Yes
Investment cost	Low	Low	Low	High	Low	High/low	Low
Operating cost	High	Low	Low	Low	Low	High	Low
Overall flexibility	Low	Low	Medium	Low	Low	Low	High

Additional sense of
Impact of the feature
- **negative**
- **undesirable/neutral**
- **positive**

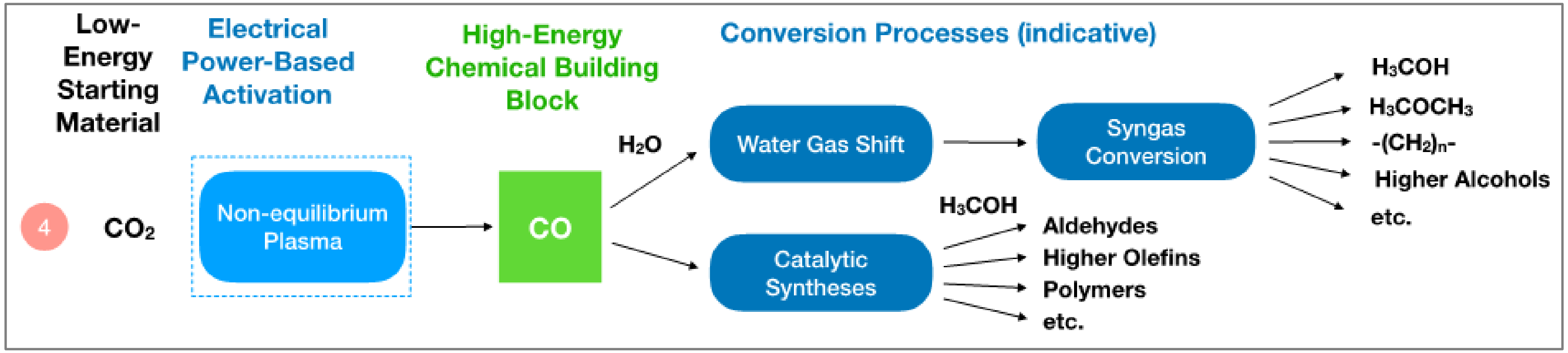
Figure adopted from: Snoecks and Bogaerts 2017 *Chem. Soc. Rev.* ***46*** *5805*

Activities in Germany within HELMHOLTZ RESEARCH FOR GRAND CHALLENGES (2021 – 2027)

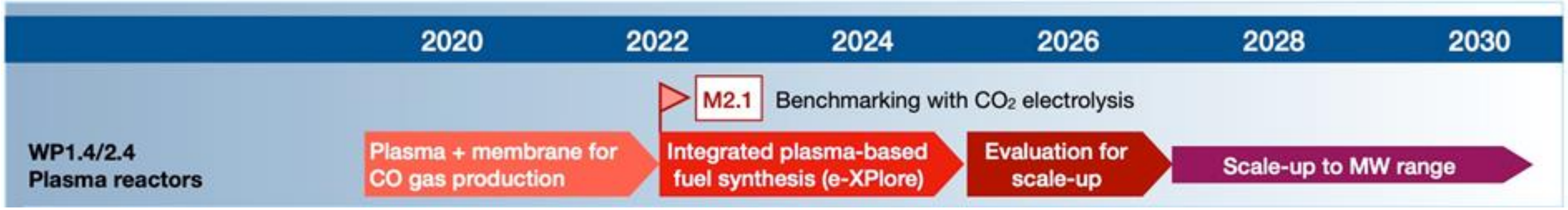
Research Field Energy → Materials and Technologies for the Energy Transition → Chemical Energy Carriers → Power-based Fuels and Chemicals → Syngas, Hydrogen Technology, Nitrogen Fixation

HGF consortium JÜLICH Forschungszentrum IEK-1, IEK-4, KIT Karlsruhe Institute of Technology IHM, IMVT, IPP with IGVP & EPP (Uni Stuttgart, Uni Augsburg)

Plasma route as forth path

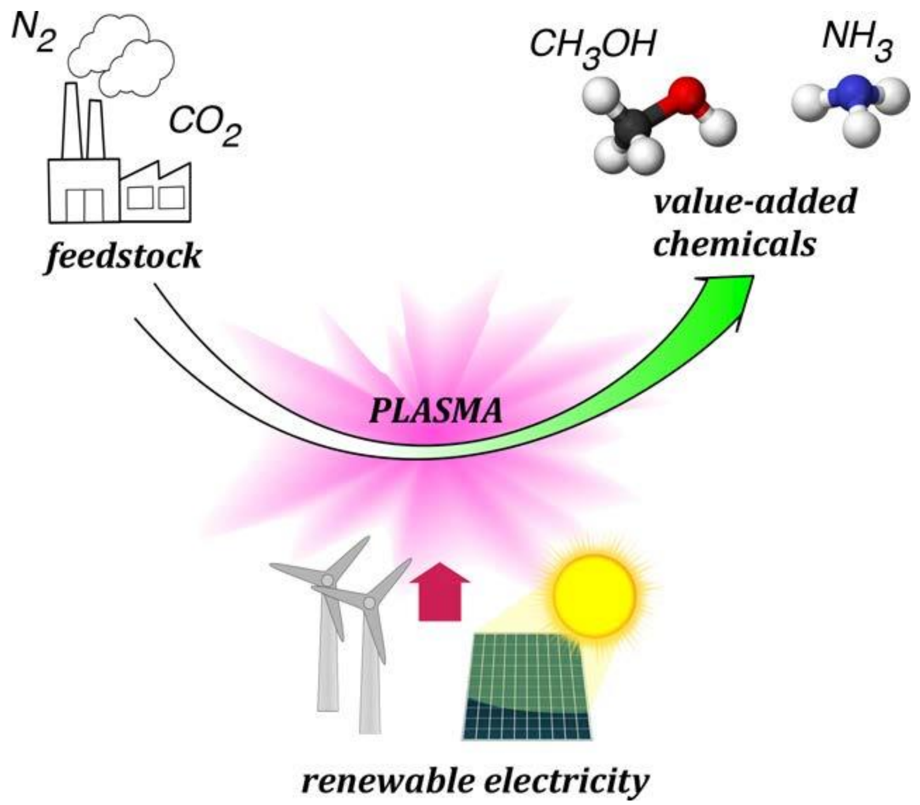


Roadmap, including gas separation and catalysis



Summary – Conclusion

Bogaerts and Neyts 2018 *ACS Energy Lett.* **3** 1013



Plasmas are an attractive route for conversion of molecules into value-added chemicals

Plasma technology

- Ideal for renewable energies due to fast response time (sec)
- Manifold of gases: **CO_2, CH_4, N_2, H_2**, H_2O, C_xH_y, …
- High throughput (~100 slm)
- Scalable

Challenges

- TRL of 3-4
- Selectivity for desired process
- Gas separation, membrane development
- Catalysis – interaction with material
- Integration in process chain

to be tailored to plasma environment (Gas separation, membrane development; Catalysis – interaction with material)