# Methane as a feedstock in plasma processes

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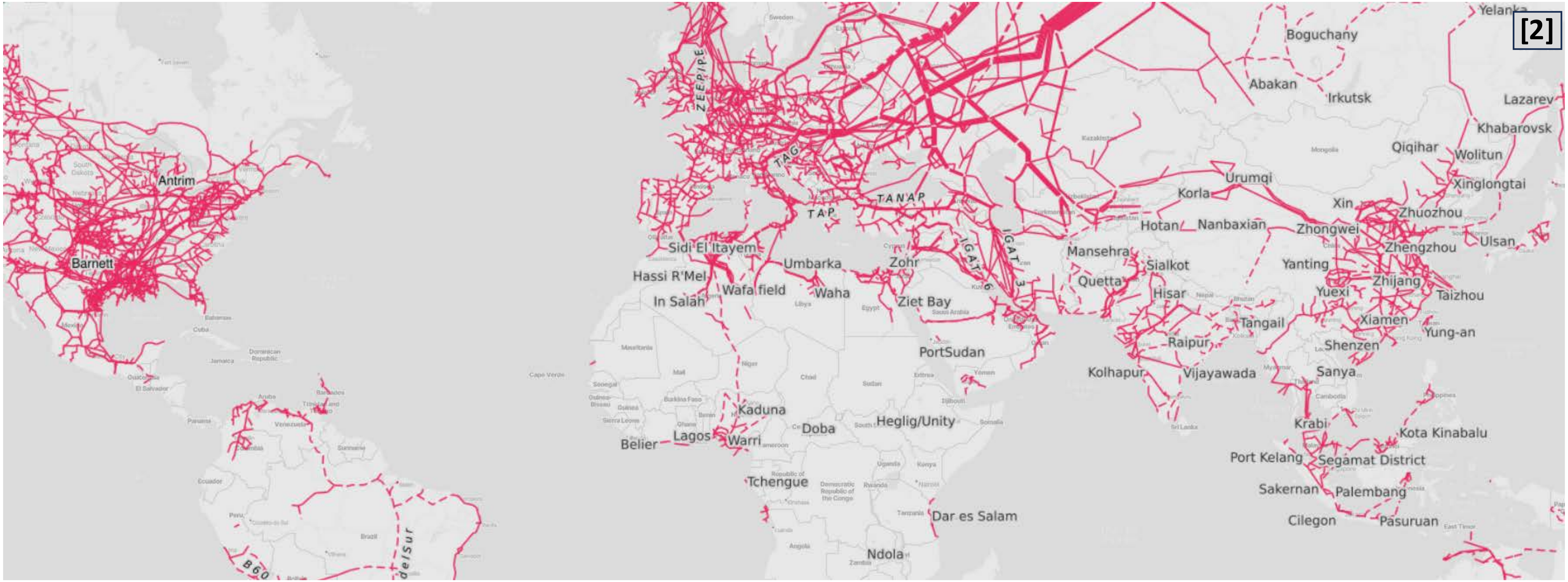
# Methane – $CH_4$



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[1] CIA Factbook 2014.

[2] http://www.snamatlas.it/index

# $CH_4$ - Major uses

- Steam-methane reforming

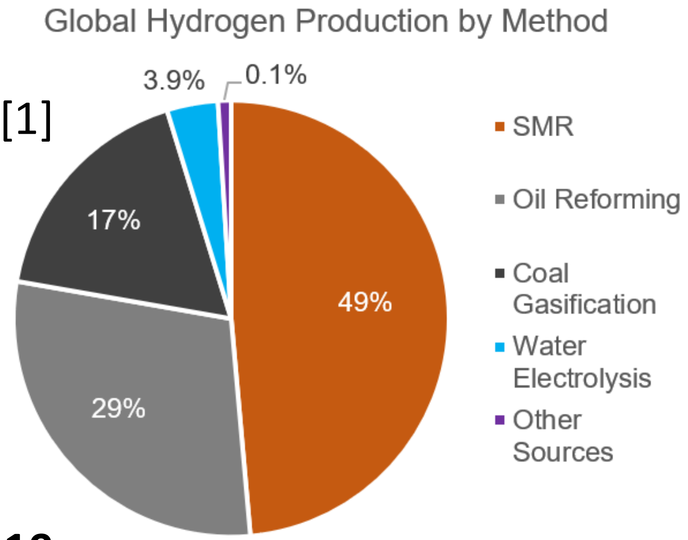
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2,$$
$$\Delta H_r = 206\,\text{kj/mol}$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2,$$
$$\Delta H_r = -41\,\text{kj/mol}$$

  - Produces 2-3% of $CO_2$ emissions.
- Partial oxidation into syngas and then into methanol, formaldehyde, formic acid etc.
- Chlorination, fluorination

# $CH_4$ and $H_2$ and $NH_3$

- $CH_4$ is used to make $H_2$.
- $H_2$ is used to $NH_3$, which is
  - The major starting feedstock in nitrogen chemistry.
  - Starting molecule for nitrogen-based fertilizers ($NH_4NO_3$, $CO(NH_2)_2$).
  - Easily transportable and storable fuel.

[1]



"Less than 0.1% of global dedicated hydrogen production today comes from water electrolysis." [2]

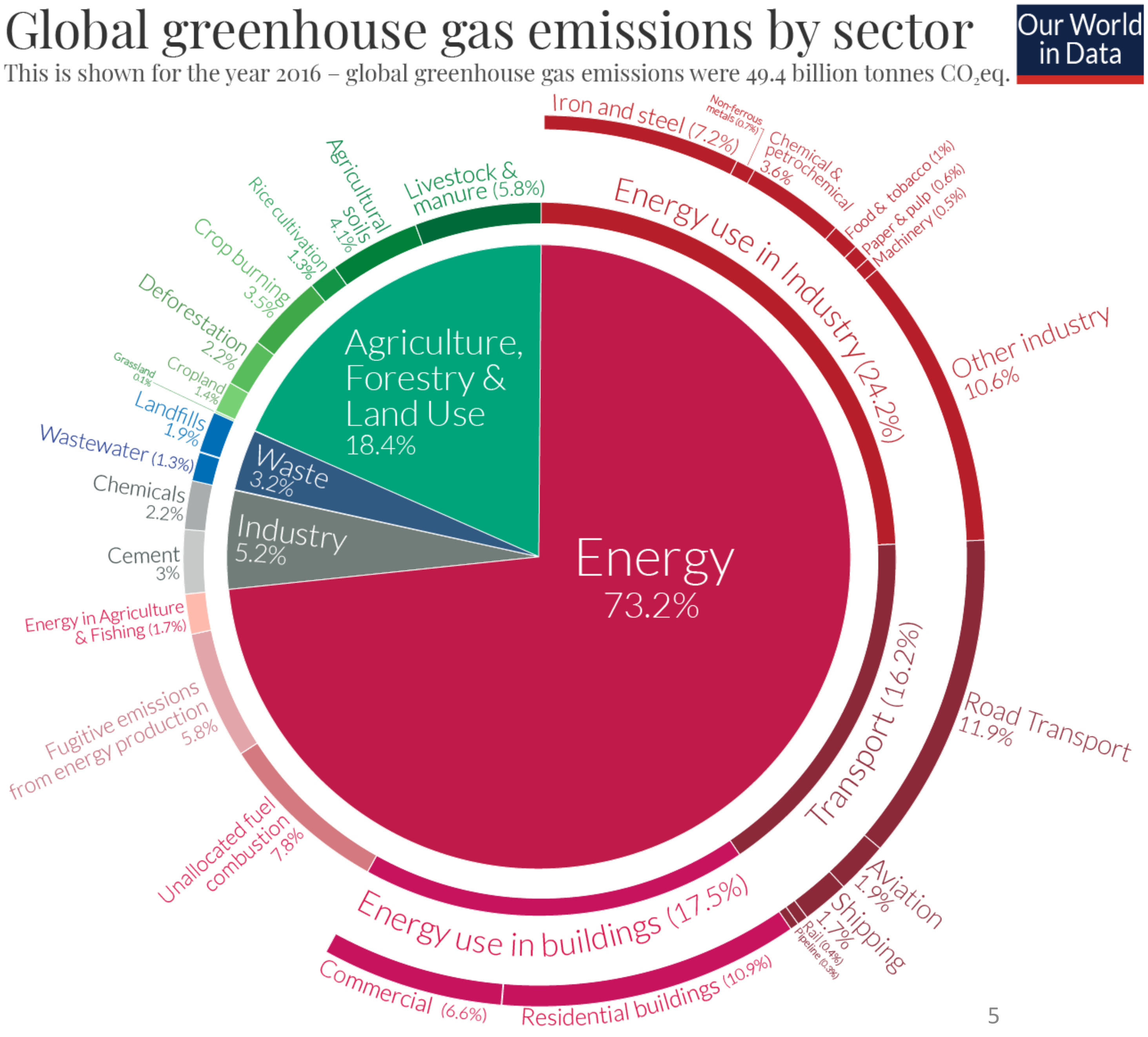
[1] İ. Dinçer & C. Acar, *Int. J. Hydrogen Energy*, 40, **2015.**
[2] International Energy Agency, The Future of Hydrogen, **2019**.

# Cutting down on $CO_2$

1) Clean hydrogen for the chemical and metallurgical industry.

2) Clean ammonia as the chemical energy carrier (requires clean hydrogen).

3) Electric cars for transport.



Global greenhouse gas emissions by sector

This is shown for the year 2016 – global greenhouse gas emissions were 49.4 billion tonnes $CO_2$eq.

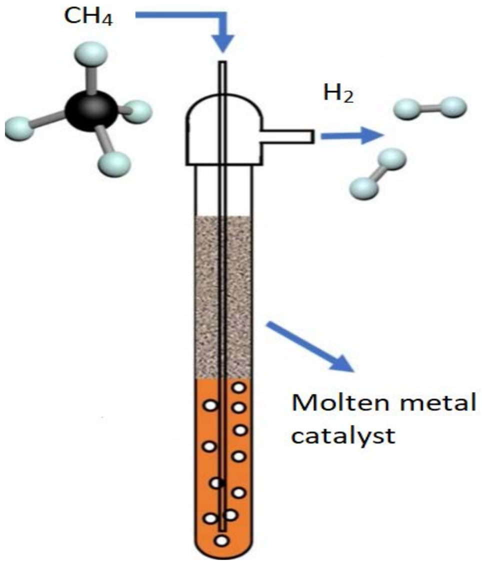
# Clean hydrogen

**Water electrolysis**

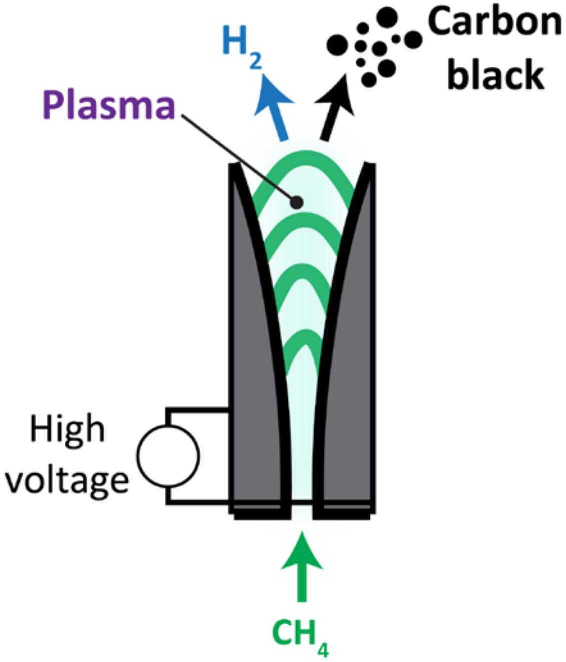
PEM cells

**Methane pyrolysis**

Thermal pyrolysis



Molten metal catalysis



Plasma pyrolysis

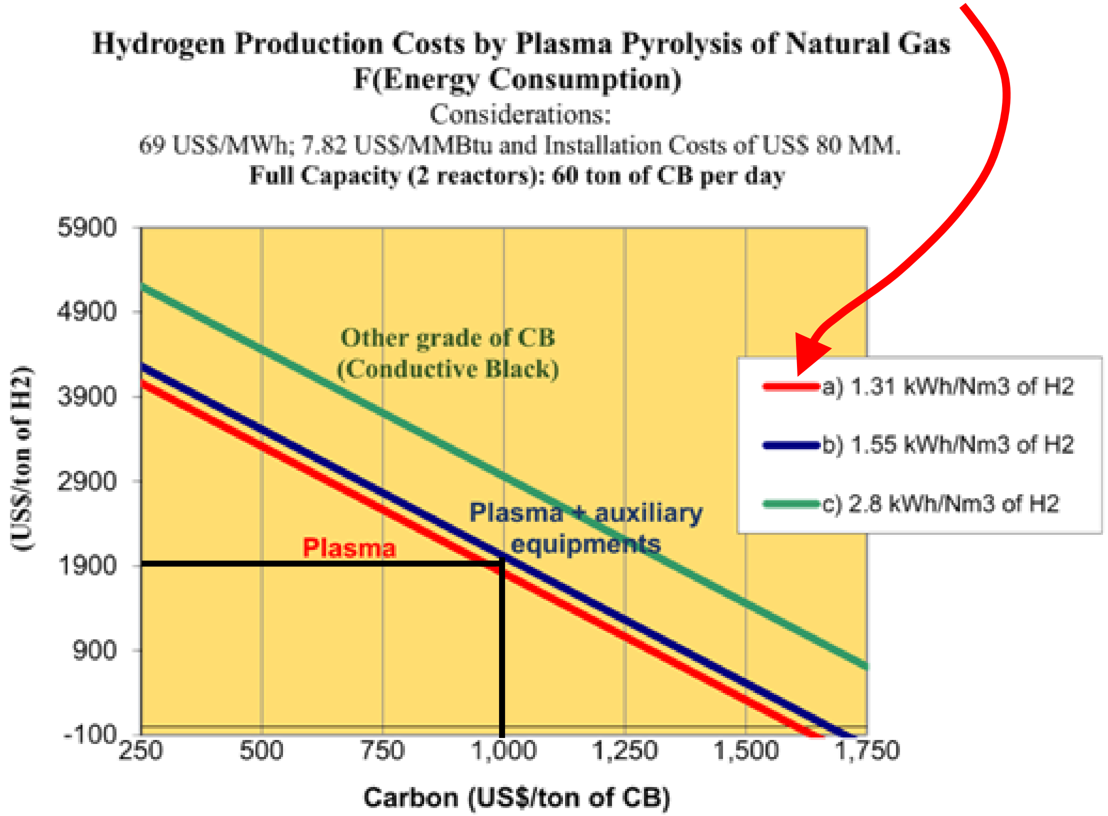
# Industrial work – Plasma pyrolysis

- Kvaerner* Karbomont Plant, 1998-2003.
- Atlantic Hydrogen New Brunswick pilot plant, 2015-2016.
- Monolith Inc. Nebraska plant, 2020-…

*now Aker Solutions

# $H_2$ or C? Which one is valuable?

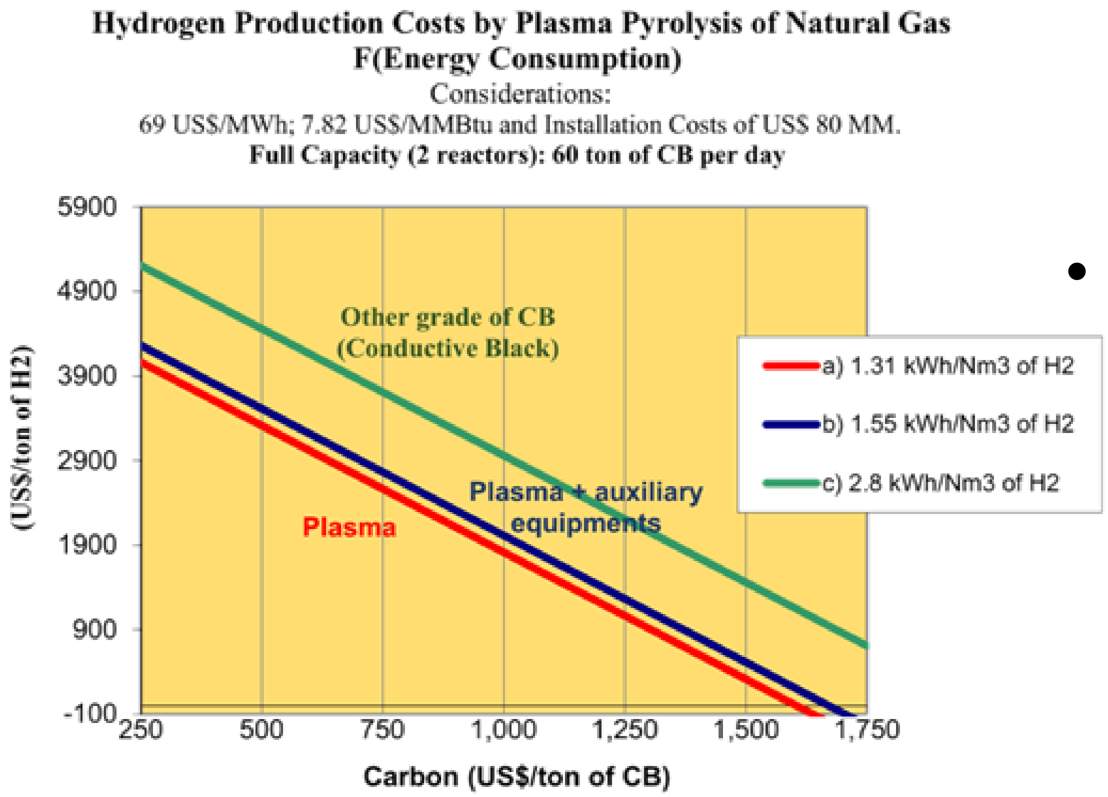
**14.6 kWh/kg $H_2$**



- Theoretical methane pyrolysis efficiency: **5.2 kWh/kg $H_2$**
- Kvaerner [1]: **15 kWh/kg $H_2$**
- Fulcheri and coworkers [2]: **14 kWh/kg $H_2$**
- Natural gas feed increases energy efficiency: as low as **11.8 kWh/kg $H_2$** according to Kvaerner [1]

[1] A.R. De Costa Labanca, *Int. J. Hydrogen Energy,* 45, **2020**.
[2] L. Fulcher and Y Schwob, *Int. J. Hydrogen Energy,* 20, **1995**.

# $H_2$ or C? Which one is valuable?



- Pure methane gas (Ankara Gaz): 8000 TL*
  - 50 L cylinder, grade 2.5, 200 bar
  - Total moles: 406
  - Unit price: **0.72 $/mol $CH_4$**
- Pure hydrogen gas (Ankara Gaz): 7250 TL
  - 50 L cylinder, grade 5.0, 200 bar
  - Total moles : 406
  - Unit price: **0.66 $/mol $H_2$**

Gain with full conversion through methane pyrolysis ($CH_4 \rightarrow 2H_2 + C$) (excluding carbon value): **0.6 $/mol $CH_4$** (or 0.05 $/g $CH_4$ carbon)

A.R. De Costa Labanca, *Int. J. Hydrog. Energy,* 45, **2020**.

*Gas costs only include refill.

# Carbon’s worth in small scale

**Carbon materials and their prices.** Materials were picked from the online catalog of Sigma-Aldrich’in on 24/08/2023. Only the materials that are available to Türkiye and the ones that consist of predominanyl carbon were listed. Product IDs were taken from the website of Sigma-Aldrich. Euro/Dollar parity was 1.08.

| Material | Type/Property | Product ID | Amount (g) | Price (€) | Unit Price ($/g) |
|---|---|---|---|---|---|
| **Graphite** | Anode powder | 907154 | 500 | 94.9 | 0.20 |
| | Powder, <20 µm | 282863 | 1000 | 75.1 | 0.08 |
| | flakes | 332461 | 2500 | 125 | 0.05 |
| | Powder, <45 µm, >99.95% | 496596 | 113.4 | 387 | 3.67 |
| | Nanopowder, Al, Ti, Fe, Ni, Cu & Zn content lower than 100 ppm | 699640 | 25 | 685 | 29.6* |
| **Graphene** | Powder, electrical conductivity >$10^3$ S/m | 900561 | 0.5 | 495 | 1069 |
| | Nanoplates | 900407 | 250 | 260 | 1.12** |
| **Graphene oxide** | 15-20 plates, 4-10% edge oxidation | 796034 | 1 | 186 | 201 |
| **Nanodiamond** | Nanopowder, <10 nm, >97% metal purity | 636428 | 5 | 662 | 143 |
| | Functionalized, 65 nm | 901770 | 1 | 481 | 520 |

*The unit price decreases to $25.6 when metal impurity increases to 500 ppm. (~15%)

** Decreases when surface area decreases. Graphene with lowest surface area on Sigma Aldrich costs $1.01 per gram. (~10%)

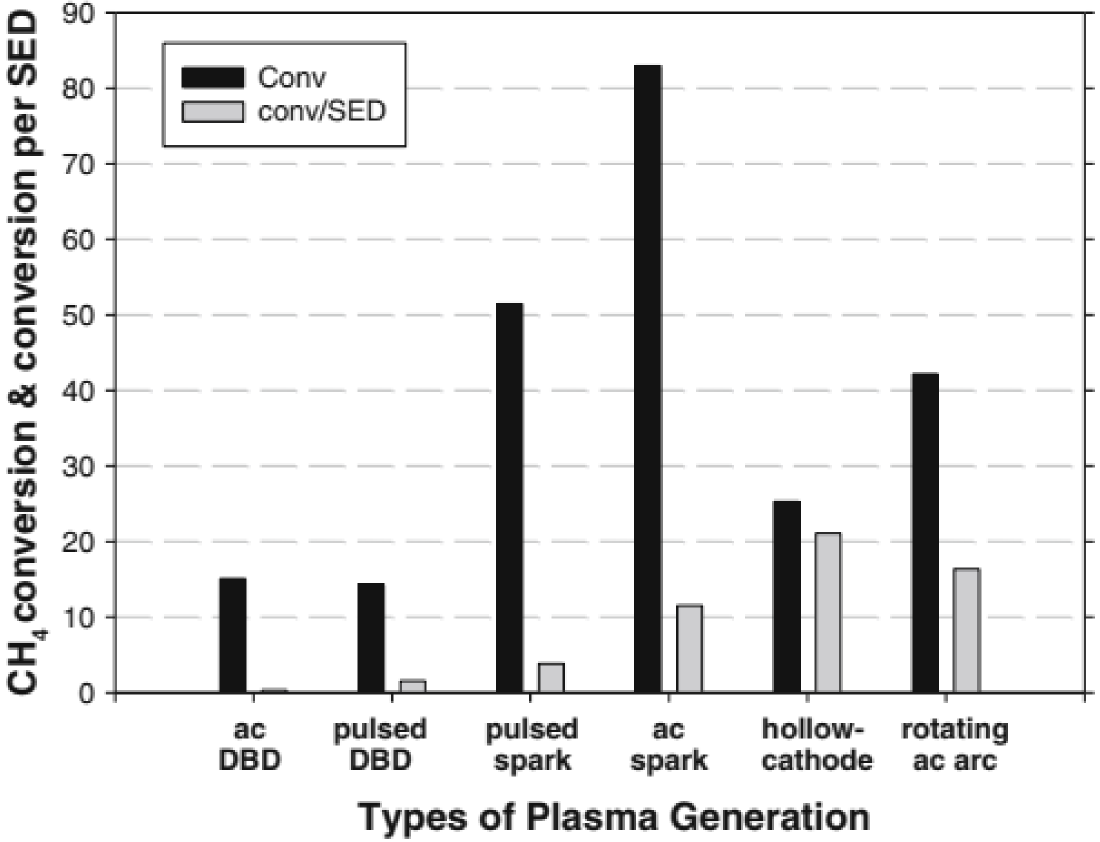
# Where will the carbon go? An example

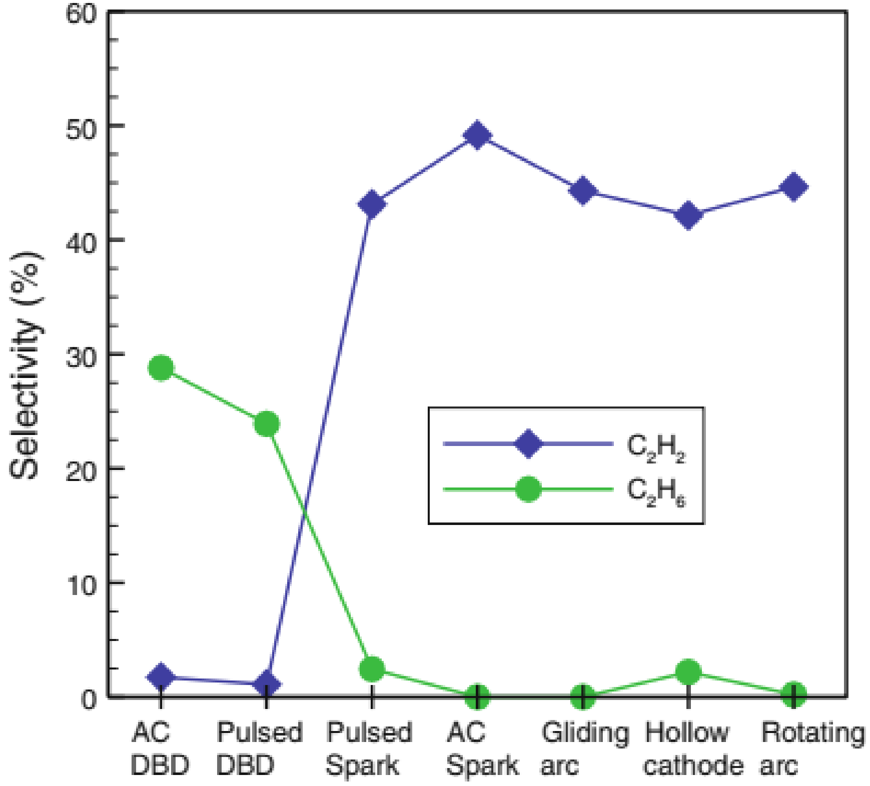
Most valuable materials → Electronics, composite materials

Least valuble materials → Agriculture (*biochar*)

- Total of **~1.5 billion cars** in the world.
- Considering the **massive $CO_2$ emission due to personal cars**, most of them will be need to be replaced with electric cars.
- Each electric car has **50-100 kg of graphite** in its Li-ion battery as the anode material.
- That makes **113 Mtons**.
- Taking the capacity of the Monolith plant as **250 tons/day**, to provide this much carbon in **20 years**, we need **61 more plants**.

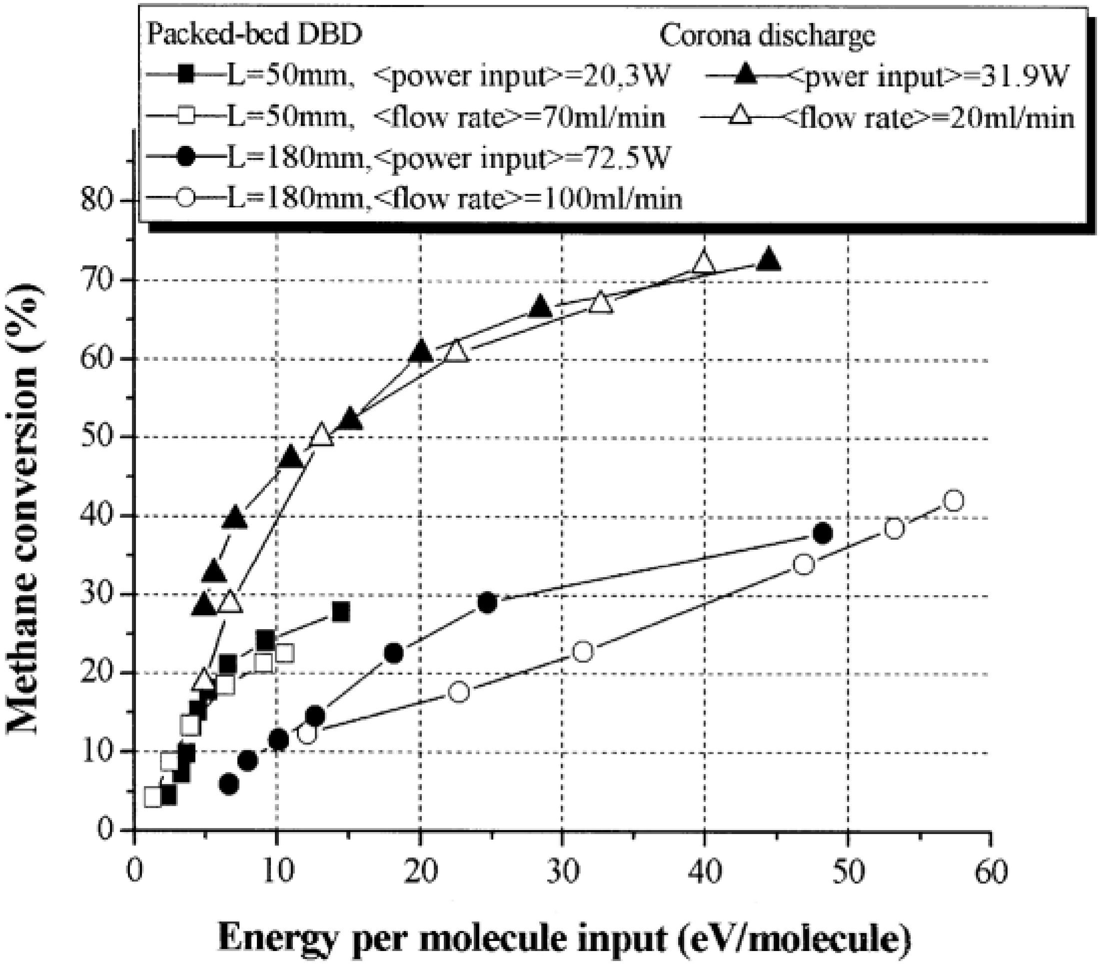
# Academic work – Gas yield

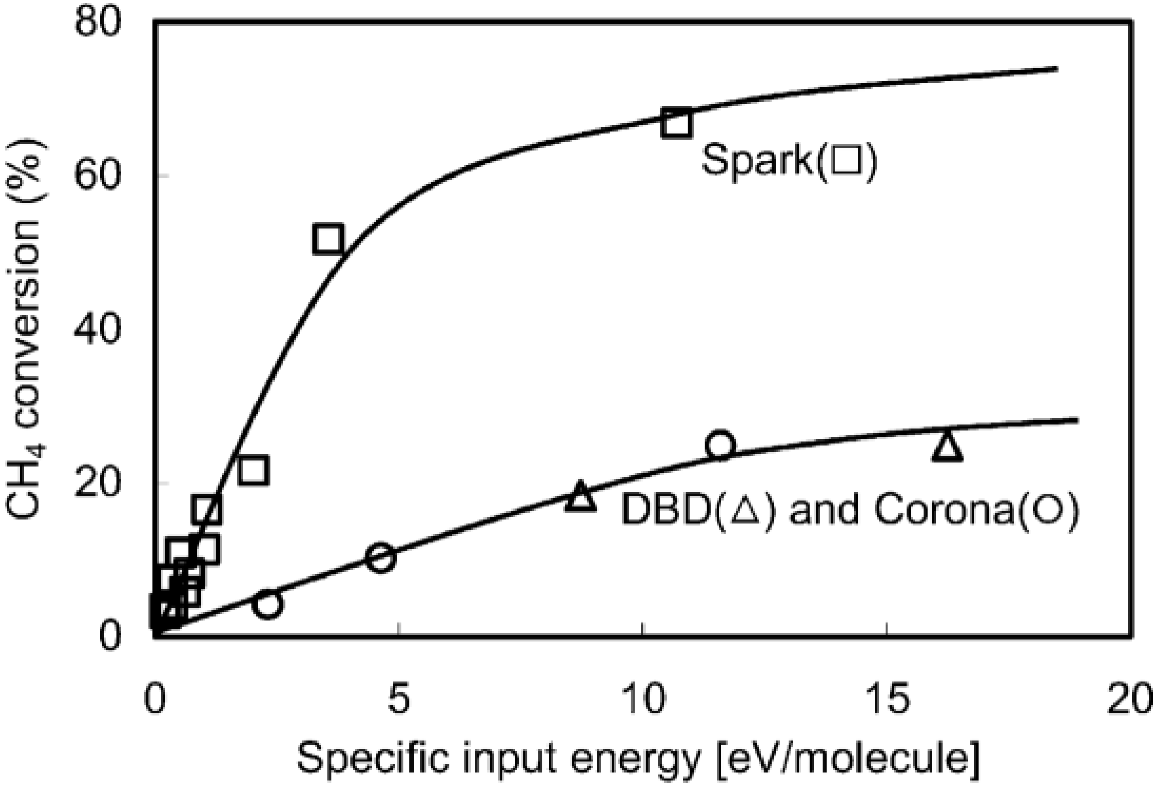




D.H. Lee et al, *Plasma Chem Plasma Process*, 33, **2013**.

# Academic work – Gas yield



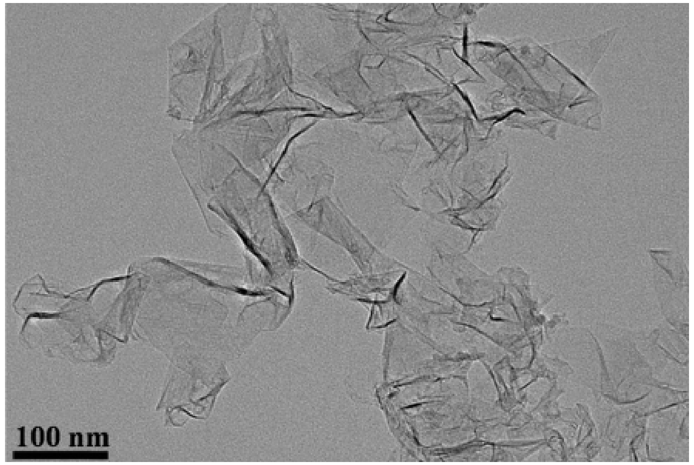


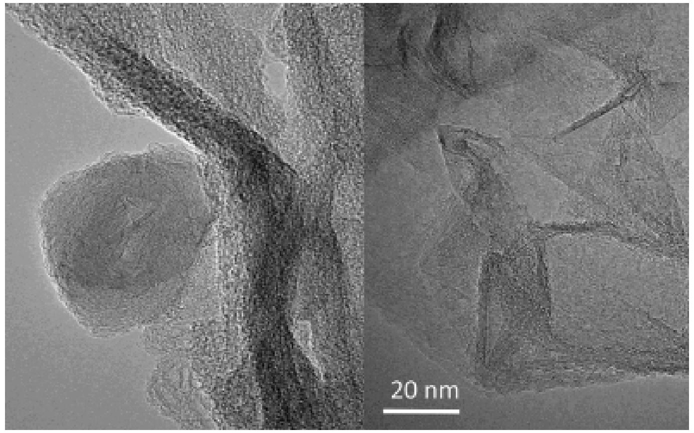
Y. Yang, *Plasma Chem Plasma Process*, 23, **2003**.
Kado et al, *Catal. Today*, 89, **2004**.

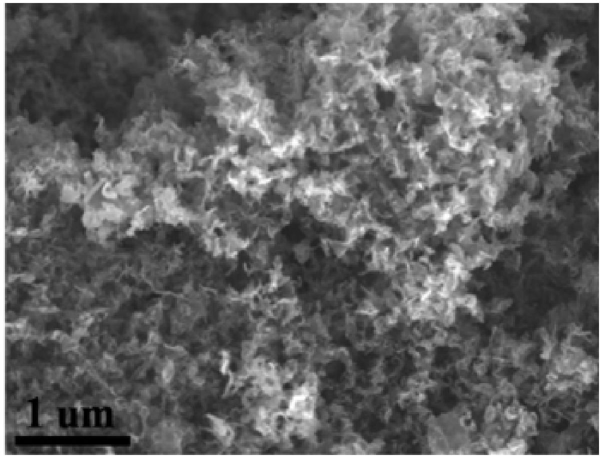
# Academic work – Carbon yield

- Microwave plasma – graphene [1]
- Microwave plasma – graphene and graphite particles [2]
- Nonthermal plasma – particles & graphene sheets [3]
- Thermal plasma – carbon particles [4]
- Gliding arc – graphene [5]

[1] E. Tatarova et al, *Appl. Phys. Lett,* 103, **2013**.
[2] M. Singh et al, *Carbon*, 143, **2019**.
[3] C Wang et al, *Chem. Eng. Sci.*, 227, **2020**.
[4] F. Fabry, G. Flamant, L. Fulcheri, *Chem. Eng. Sci*, 56, **2001**.
[5] D. Li et al, *Fuller. Nanotub.*, 28, **2020**.







**1) Product yield**
**2) Product characterization according to standards**
**3) Absence of inert gases**

# $CH_4$ in a plasma

Cracking the code of $CH_4$

1) $CH_3$, $CH_2$ abundant → oligomerization ($C_2H_6$, $C_2H_4$) and coupling into larger chain paraffins and olefins ($C_xH_y$).
2) CH abundant → oligomerization into acetylene ($C_2H_2$).
3) Complete cracking into C → highest hydrogen yield and carbon black.

***How do we control this?***

$RTD$

$f$

$E/N$

$T_e$

$P$

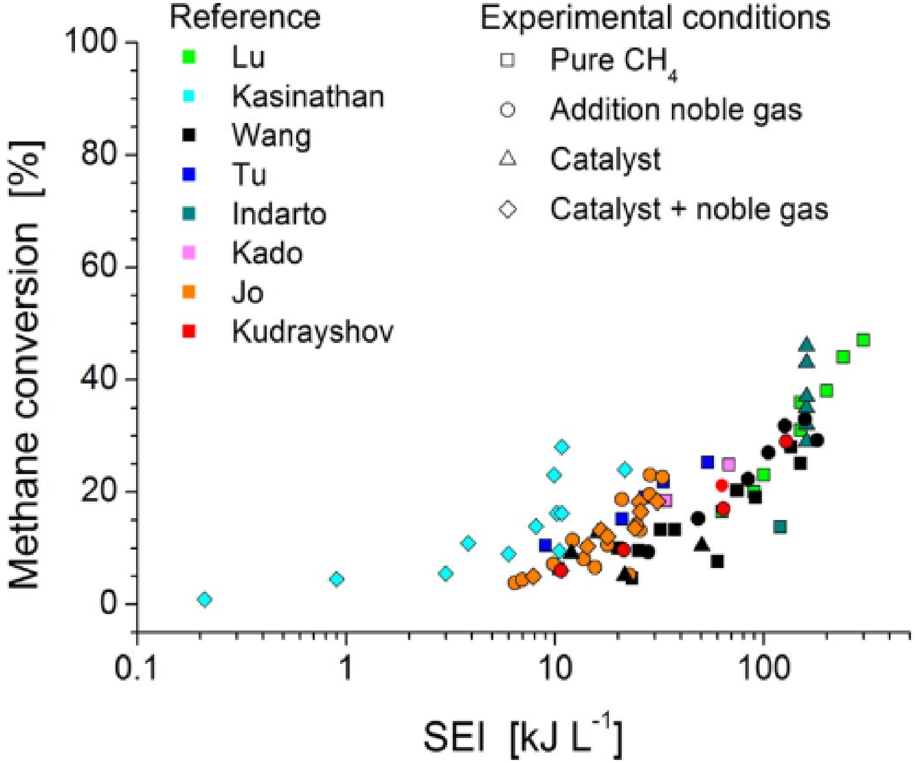
$T_g$

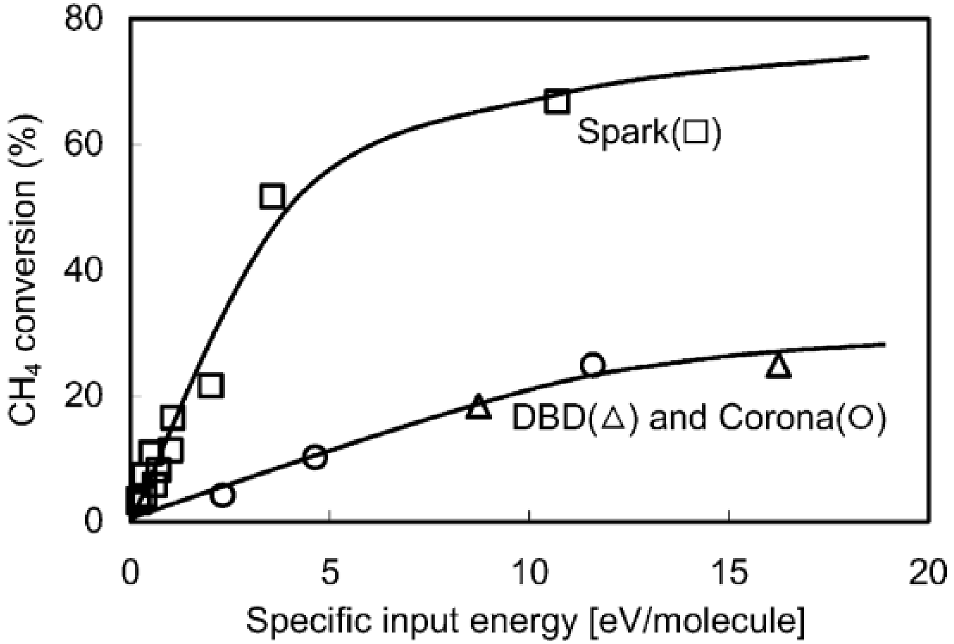
$n_e$

# Comparison of performance - Pyrolysis

## Important factors in chemical reaction engineering

1) Conversion 2) Selectivity 3) Energy efficiency 4) Scale

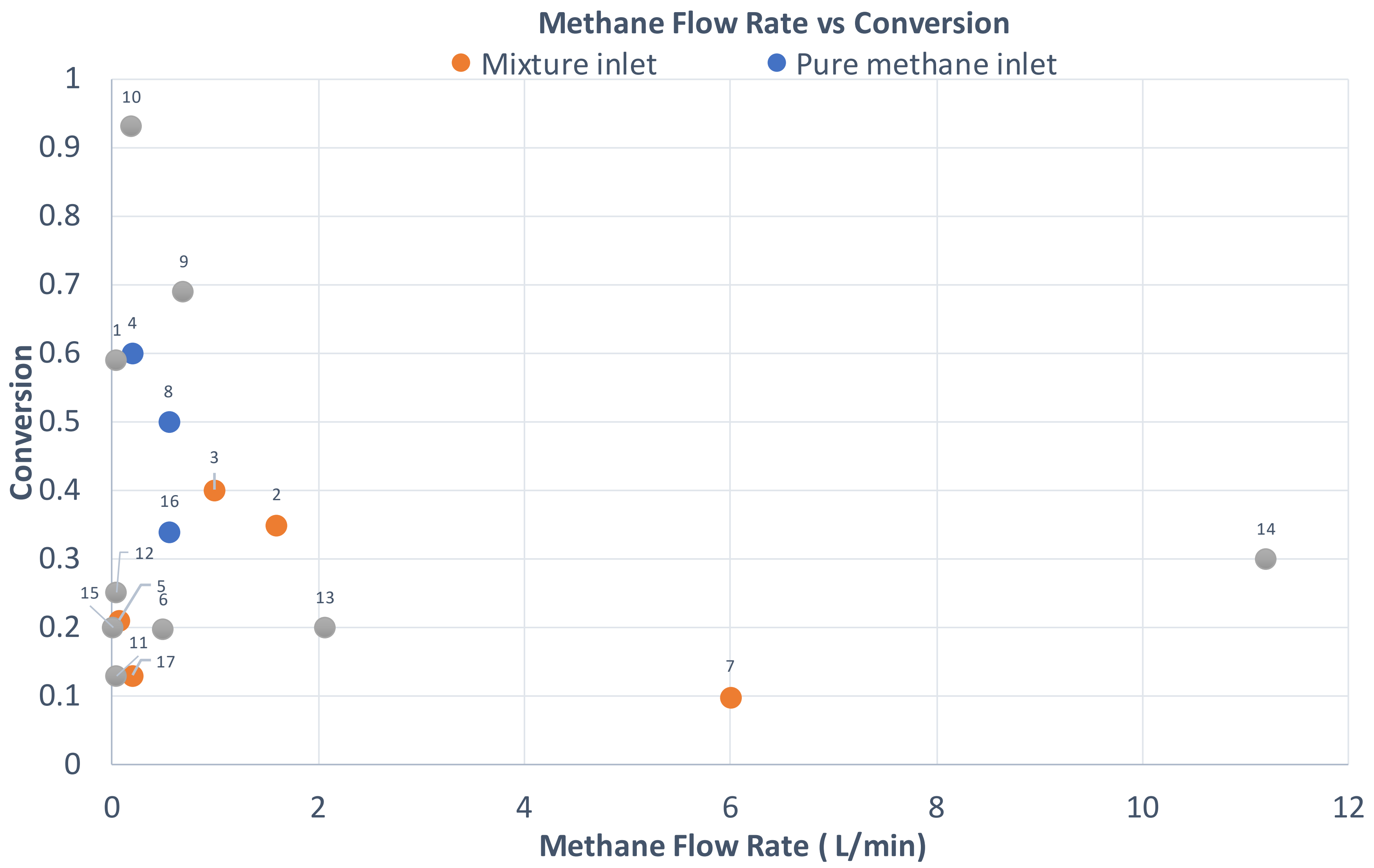




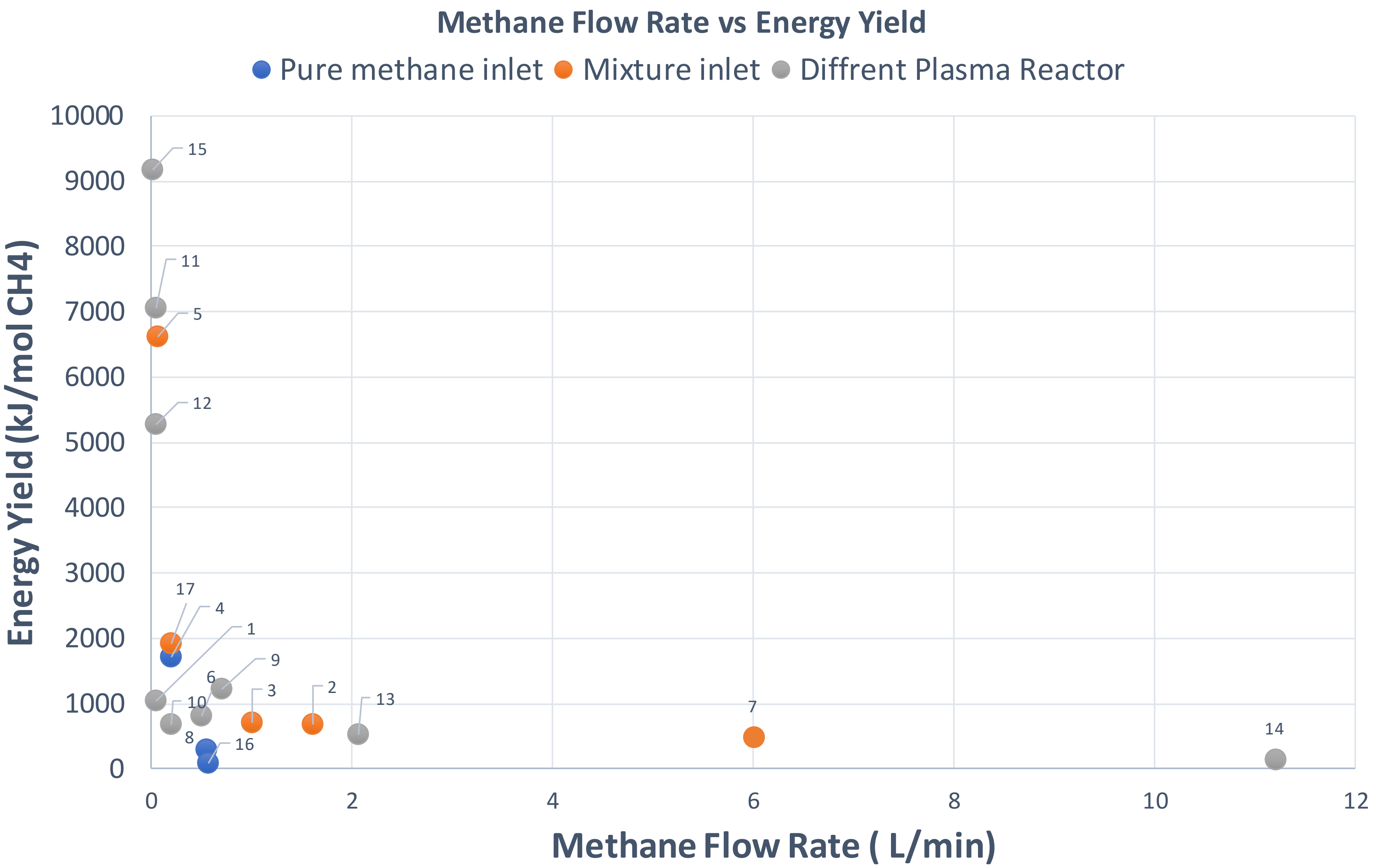
M.Scapinello, E. Delikonstantis, G.D. Stefanidis, *Chem. Eng. Process.: Process Intensif.,* 117, **2017**.
Kado et al, *Catal. Today*, 89, **2004**.

$$SEI = \frac{\text{Power}}{\text{Flow rate of } CH_4}$$

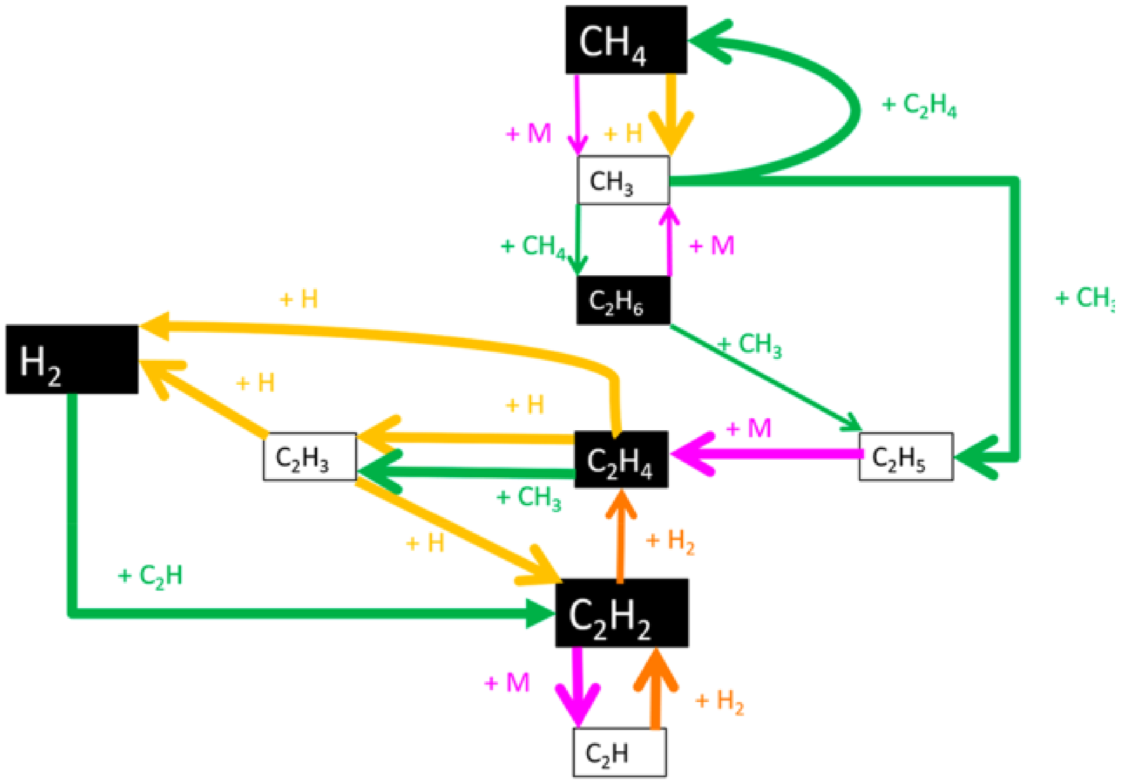
# Pyrolysis – Metrics - I

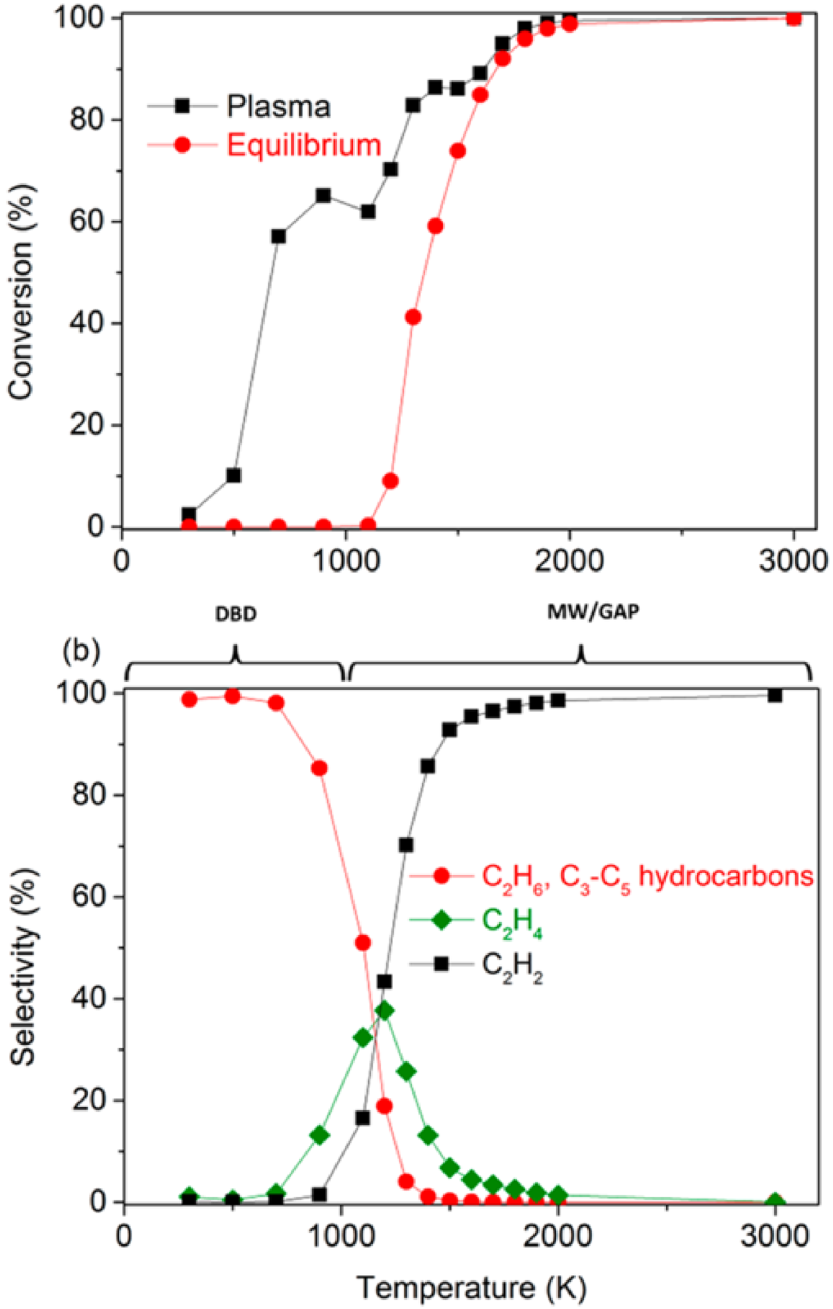


# Pyrolysis – Metrics - II



# Computation





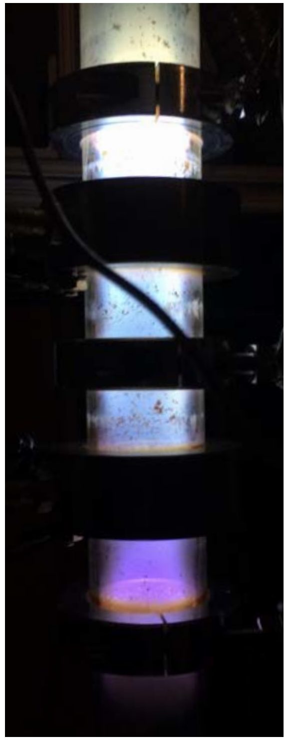
*‘Vibrational-translational nonequilibrium is negligible. Thermal conversion plays a major role.’*

S. Heijkers, M. Aghaei and A. Bogaerts, *J.Phys. Chem. C*, 124, **2020**.

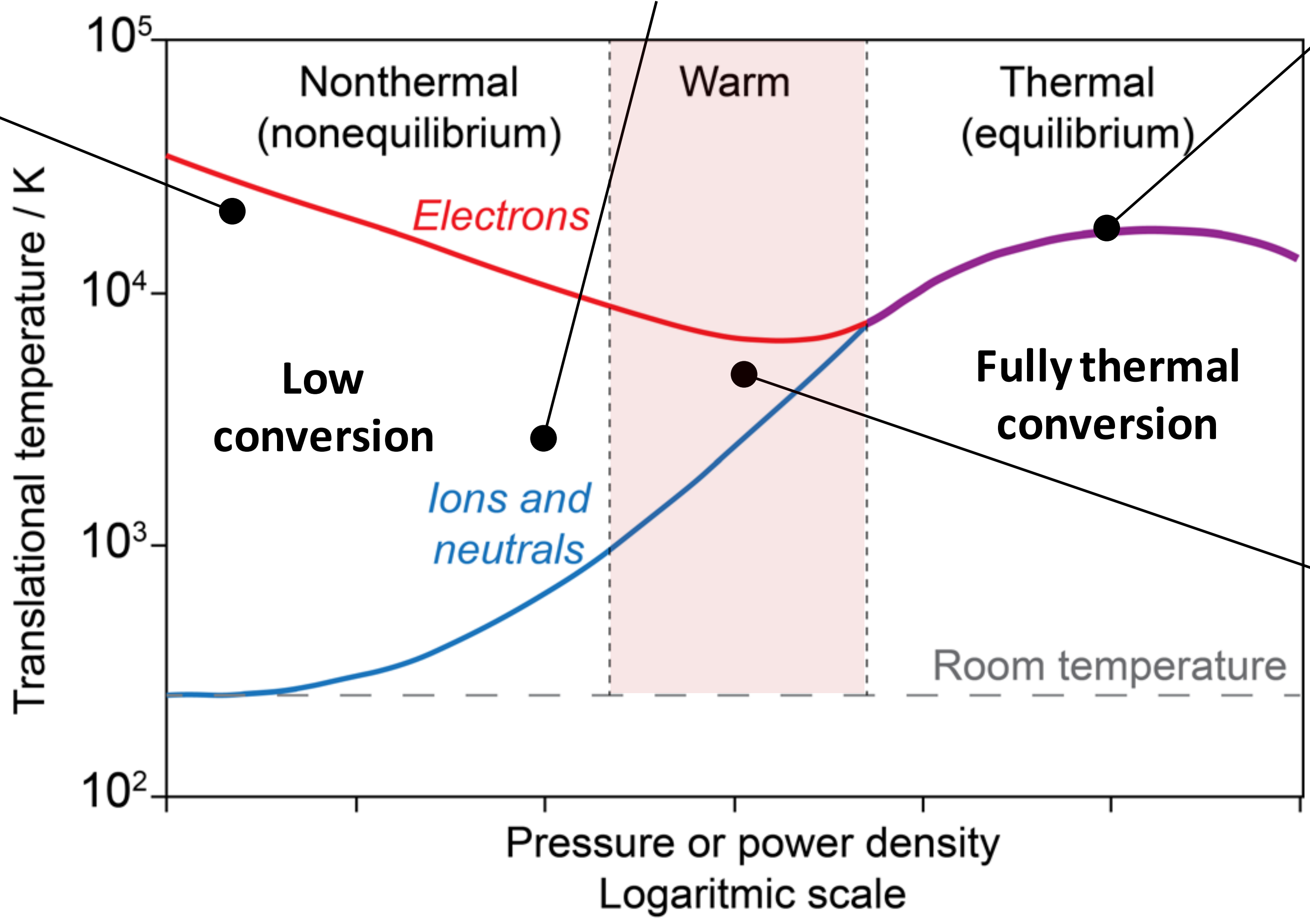
# Thermal + nonthermal processing

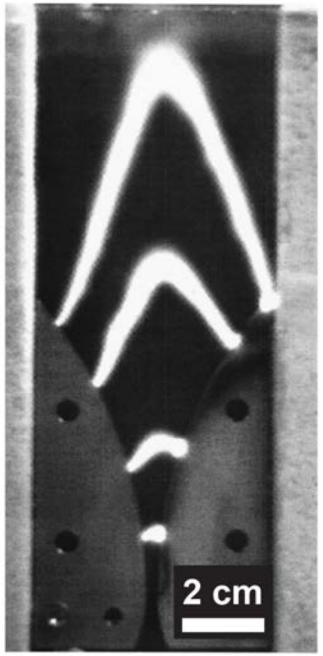
Dielectric barrier discharge (DBD)

Plasma torch



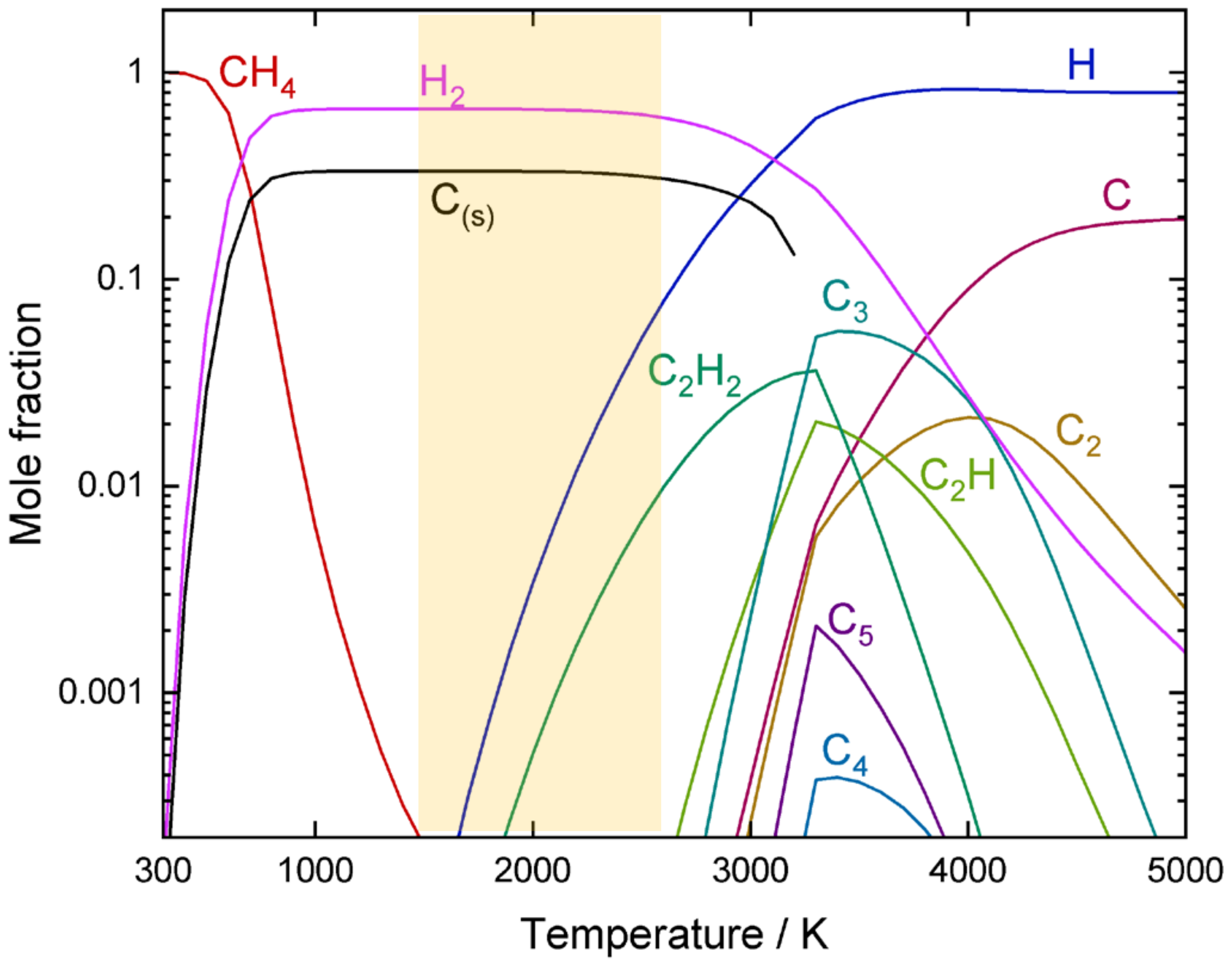
Low pressure radio-frequency plasma



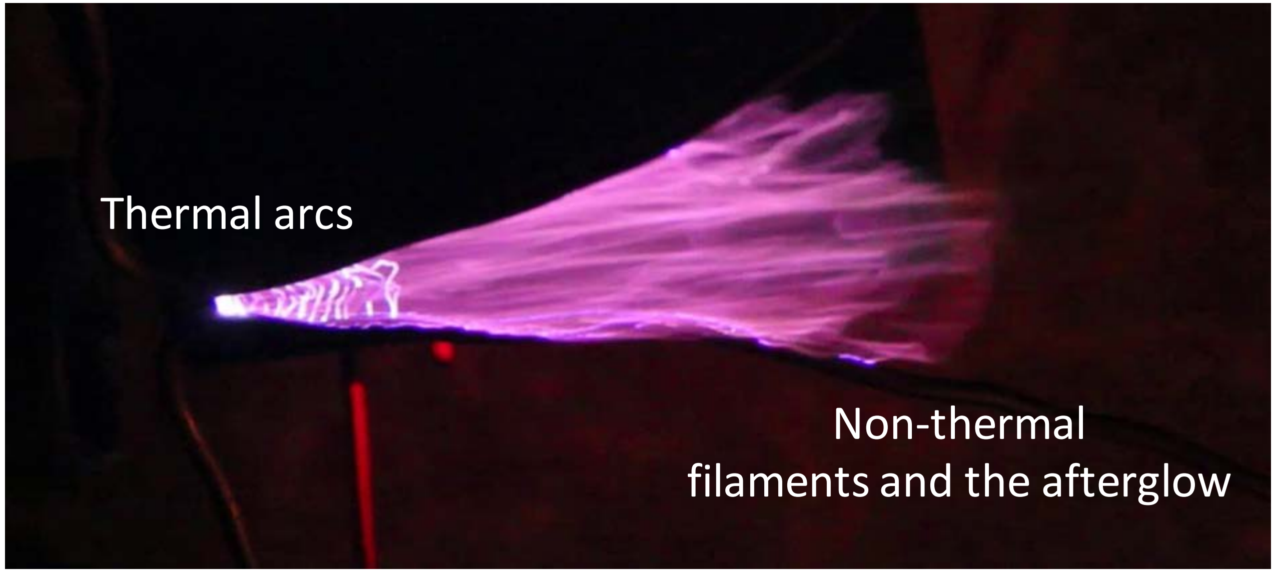


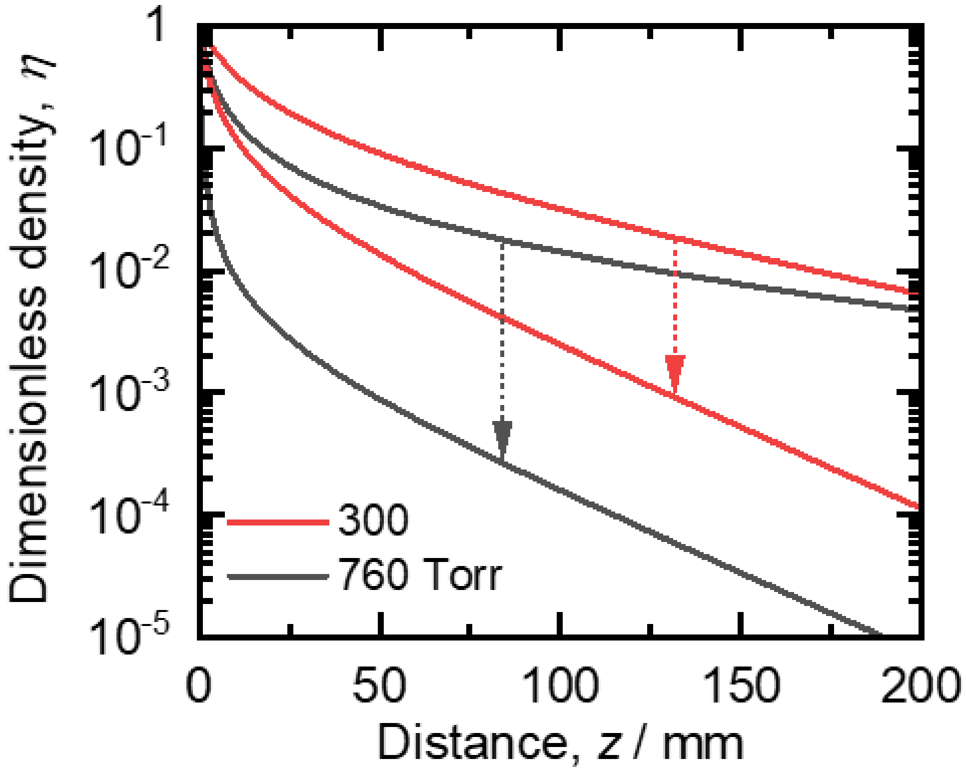
Gliding arc

# $CH_4$ conversion - Thermodynamics



# Quenching and the spatial afterglow





N.H. Abuyazid, N.B. Uner, S.M. Peyres & R.M. Sankaran, *Nat. Comms.*, **2023** *(to be published)*

# A possible scenario on $H_2$ production

**Can not satisfy the entire $H_2$ demand**

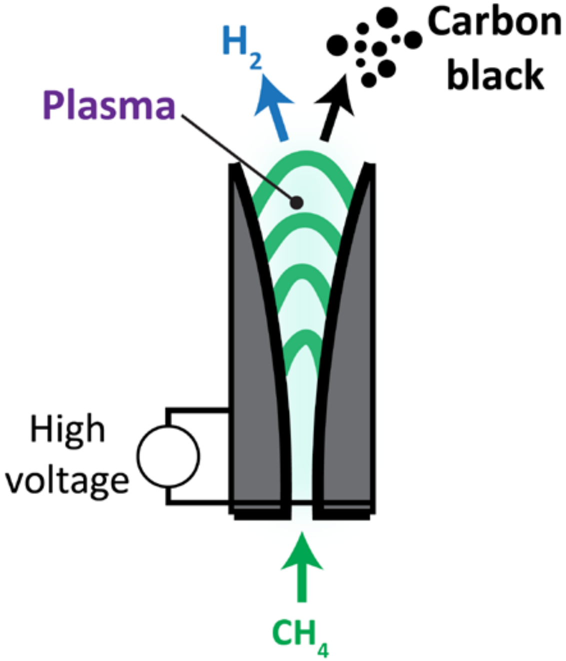
**Water electrolysis**

PEM cells

**Carbon sequestration**

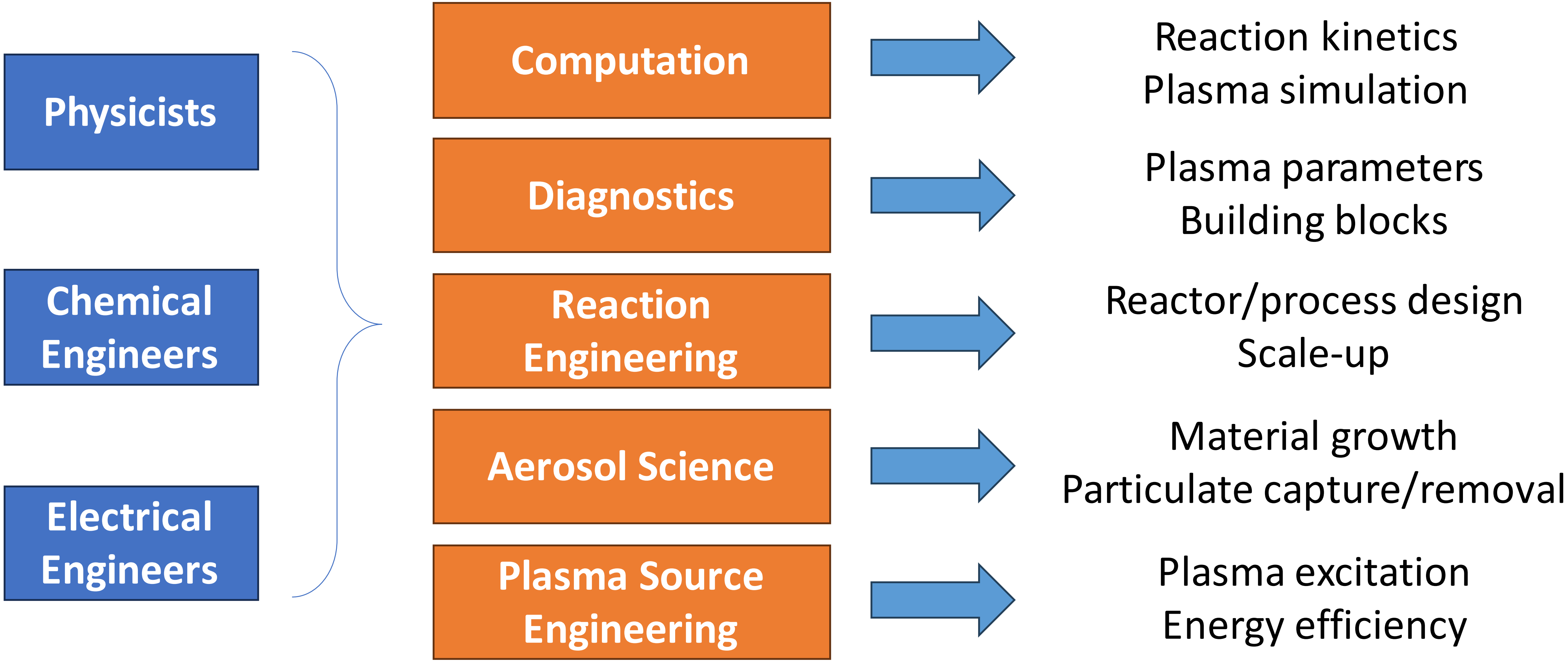
**Methane pyrolysis**

Thermal pyrolysis



Plasma pyrolysis

# What do we need?



Physicists

Chemical Engineers

Electrical Engineers

Computation → Reaction kinetics, Plasma simulation

Diagnostics → Plasma parameters, Building blocks

Reaction Engineering → Reactor/process design, Scale-up

Aerosol Science → Material growth, Particulate capture/removal

Plasma Source Engineering → Plasma excitation, Energy efficiency

# Acknowledgements

SOCAR