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Non thermal plasma-assisted catalysis for methane abatement.

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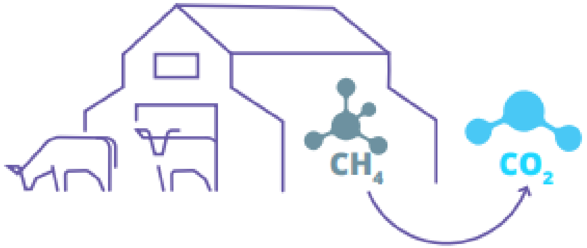
Introduction: CANMILK project

- **CA**rbon **N**eutral **MILK** (CANMILK):
  - EU project.
  - 7 different organizations from across Europe.
- Methane from dairy barns/meat farms.
  - 5.4% of total greenhouse gases.
  - 28 times more potent than CO2.
  - Takes 10 to 12 years to decompose.
- Goal: develop a simple, efficient and innovative technology based on **plasma** to capture **methane emissions from dairy barns and convert them into carbon dioxide.**

Consortium partners

- **VTT Technical Research Centre of Finland** – www.vttresearch.com – Finland
- **Valio** – www.valio.com – Finland
- **University of Antwerp** – www.uantwerpen.be – Belgium
- **Maastricht University** – www.maastrichtuniversity.nl – The Netherlands
- **Steinbeis Europa Zentrum** – www.steinbeis-europa.de – Germany
- **Johnson Matthey** – www.matthey.com – United Kingdom
- **Durham University** – www.durham.ac.uk – United Kingdom



For more information, please visit: *canmilk.eu*

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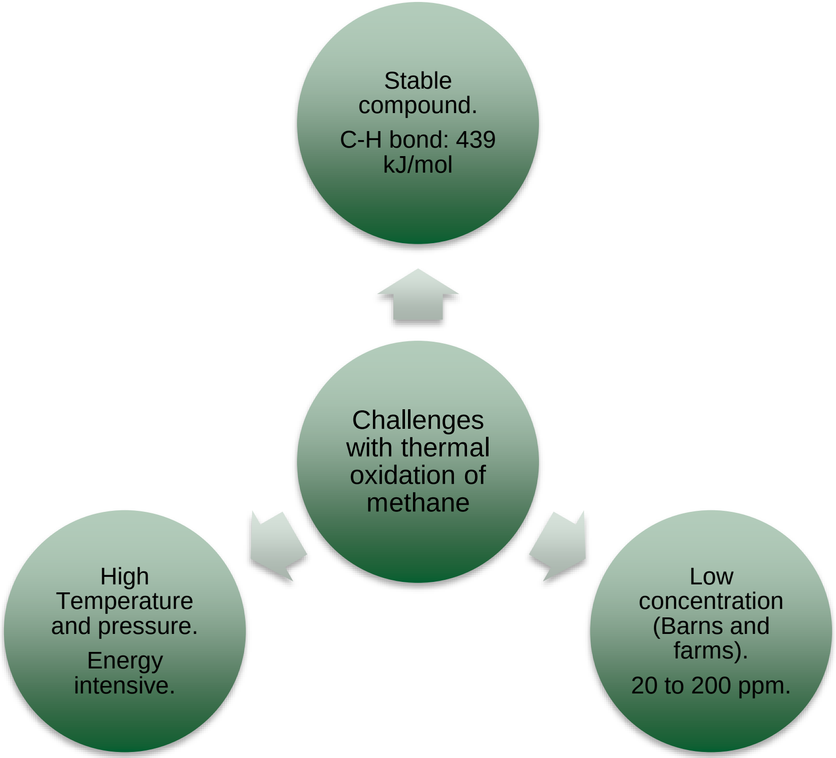
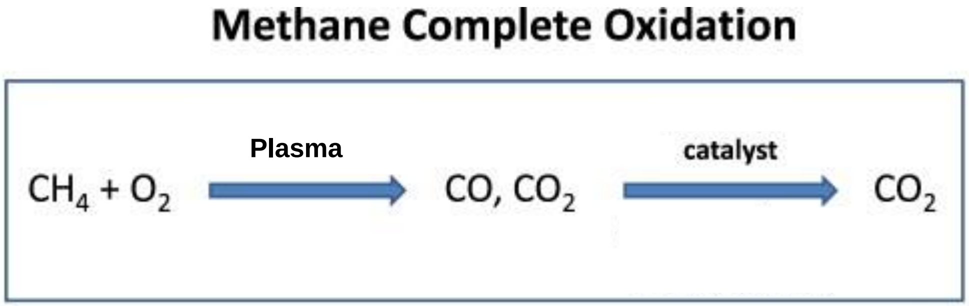
Introduction





Plasma oxidation scheme (Graphical abstract). Original from:
Lee, H. et al. (2015) "Complementary effect of plasma–catalysis hybrid system on methane complete oxidation over non-PGM catalysts," Catalysis communications. DOI: https://doi.org/10.1016/j.catcom.2015.07.001

- ❑ Plasma produces highly reactive species, and radicals which can undergo gas phase reaction.
- ❑ However, gas phase plasma reaction is highly **nonselective**.
- ❑ The use of oxidation catalysts can improve **complete oxidation of methane into CO2.**

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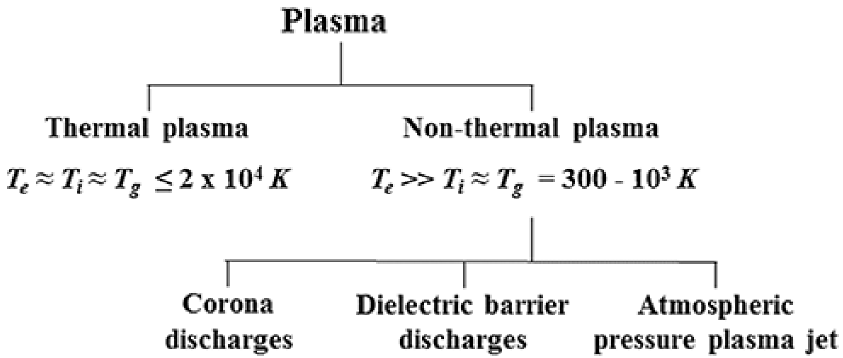
Introduction: Plasma

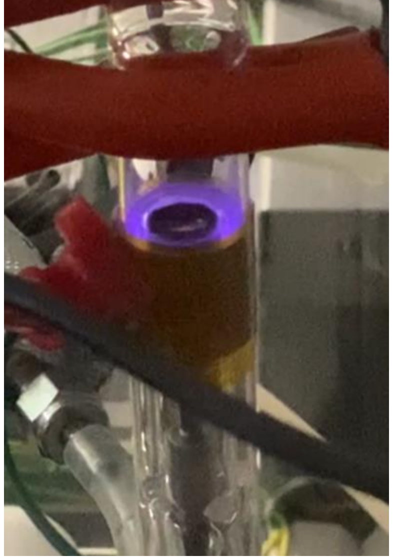
- **Plasma**: fourth state of matter, partially or completely ionized.
- Types of plasma:
  - **Thermal plasma:** Thermal equilibrium, gas is heated to high temperature, using high energy source such as laser or microwave.
  - **Non-thermal plasma** (NTP): cold plasma or non-equilibrium plasma, electrons and ions are not in thermal equilibrium. generated at atmospheric pressure by passing the gas through the electric field.



Classification of plasma.
Original from: Lee, J. et al. (2017) "Use of Atmospheric Pressure Cold Plasma for Meat Industry," Korean Journal for Food Science of Animal Resources. Korean Society for Food Science of Animal Resources. DOI: https://doi.org/10.5851/kosfa.2017.37.4.477

Experimental set up

- Reactor: **Coaxial Dielectric barrier discharge** (DBD) reactor.
  - Two concentric quartz tubes.
  - Discharge length: 2 cm.
  - Discharge gap: 2 mm.
- Gases: 1 vol % CH4 in air (0,99 % CH4, 20,89 % O2 and 78,12 % N2) and volumetric flow of **200 mL/min.**
- Ambient conditions: atmospheric temperature and pressure.



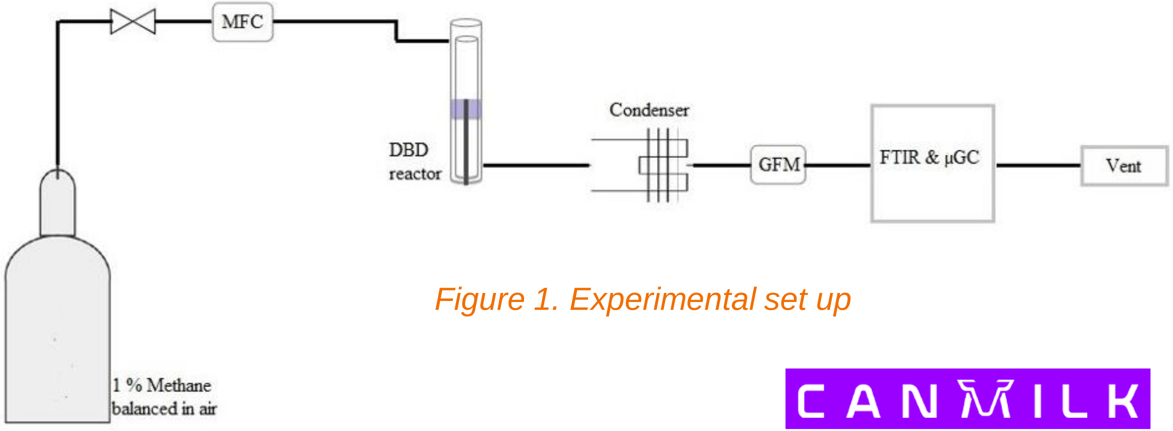


Figure 1. Experimental set up

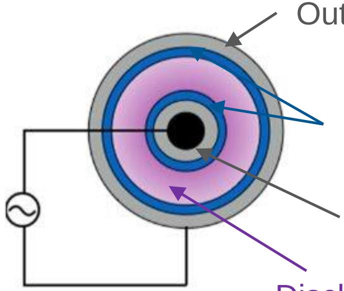


Figure 2. A co-axial DBD set up.

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Experimental set up

- Catalyst was placed inside the plasma discharge zone.
- 6 different catalysts were studied.

	Catalyst
1	γ-Al2O3
2	1% Cu/ γ-Al2O3
3	1% Pd/ γ-Al2O3
4	1% Pt/ γ-Al2O3
5	1% Pd – 0.5% Cu/ γ-Al2O3
6	3% Pd/ γ-Al2O3

In plasma catalyst reactor configuration. A. Side view, ground electrode is moved lower for better visualization B. Top view

- Catalysts were prepared by incipient wetness vacuum impregnation.

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Results: N2 physisorption

Fresh catalyst	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
γ-Al_2O_3	231	0,60	10
1 % Pd/γ-Al_2O_3	263	0,63	10
3 % Pd/γ-Al_2O_3	228	0,59	10
1 % Cu/γ-Al_2O_3	227	0,60	10
1 % Pd-0.5 % Cu/γ-Al_2O_3	225	0,60	10
1 % Pt/γ-Al_2O_3	228	0,59	10
Spent catalyst			
1 % Pd/γ- Al_2O_3	259	0,63	10
1 % Cu/γ- Al_2O_3	224	0,60	10

- The BET surface area, pore volume, and pore size of all materials are in the same order of magnitude.
- 1% Pd/Al2O3 catalyst had slightly higher BET surface area.
- The pore volume and BET surface are of the catalysts **did not change upon plasma exposure.**

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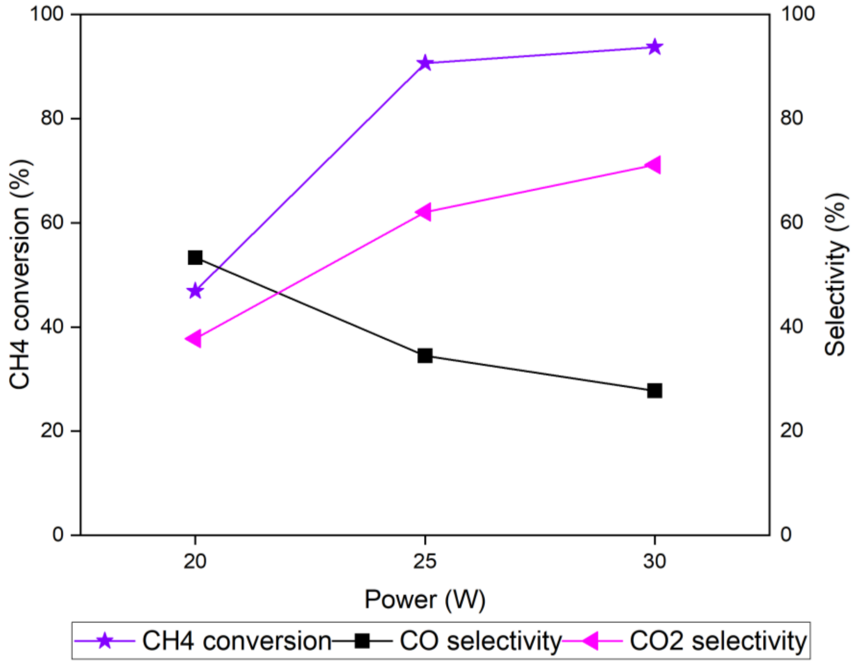
Results: Plasma alone system



- Non-thermal plasma (NTP) achieved a 92% conversion of methane.
- The methane conversion increased with increase in plasma power.
- Methane was mostly converted into CO and CO2.
- The selectivity of CO2 increased with higher plasma power while CO declined.

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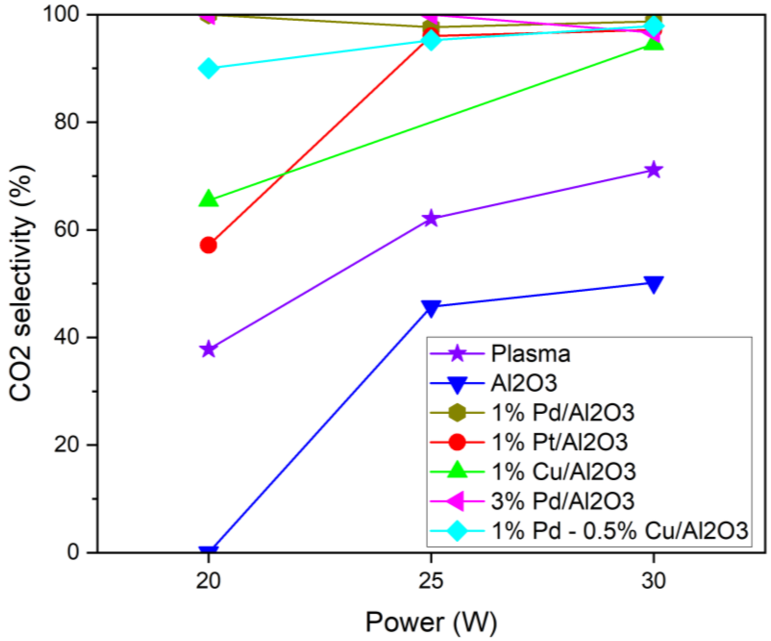
Results: CO2 selectivity



- The **complete oxidation of methane into carbon dioxide** was achieved in plasma-catalyst system.
- Pd based catalyst exhibited no CO selectivity across varying power levels.
- The Al2O3 support demonstrated lower CO2 selectivity compared to the plasma only system.

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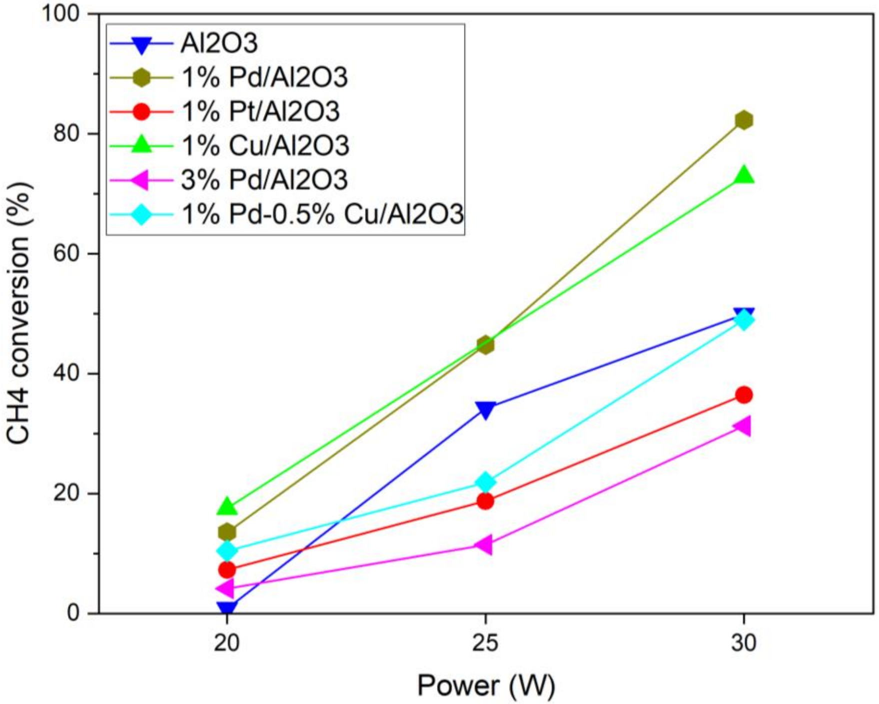
Results: Plasma-catalyst system



- The order of activity is

  1 % Pd/Al2O3 > 1 % Cu/Al2O3 > y-Al2O3 > 1 % Pd – 0.5 % Cu/Al2O3 > 1 % Pt/Al2O3 > 3 % Pd/Al2O3.
- The conversion increased with increase in plasma power.
- The Al2O3 support did not show any activity at 20 W plasma power.

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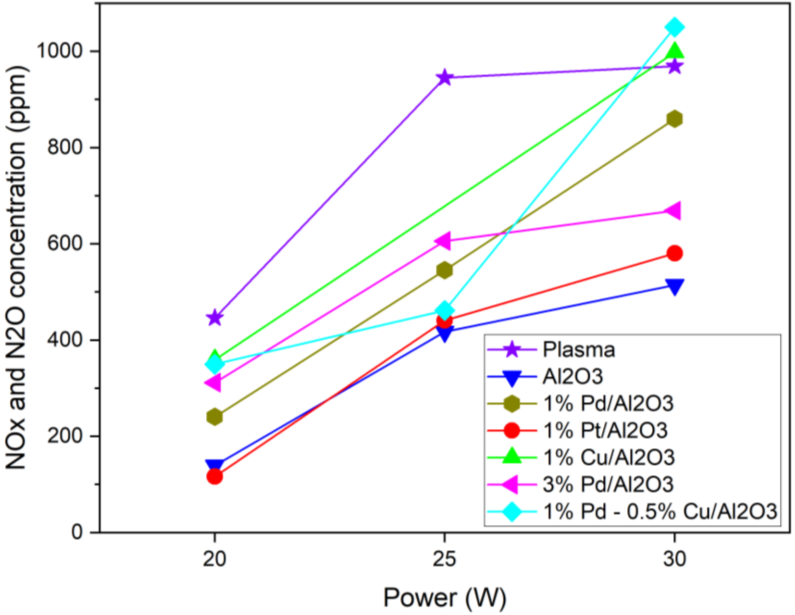
Results: NOx and N2O formation



- The formation of undesirable NOx and N2O is unavoidable.
- The NOx formation is the function of catalytic activity.
- The NOx formation increases with increase in plasma power.
- The presence of catalyst did not suppress NOx and N2O formation.

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Conclusions

- NTP was able to achieve the highest methane conversion of 92% and CO_2 selectivity of 70%.
- 1% Pd/Al_2O_3 catalyst showed the highest methane conversion of 84% and **CO_2 selectivity of 99%.**
- Combining NTP with catalysts proves to be an efficient method for **converting methane to carbon dioxide**, making it a promising technology for application in dairy barns and meat farms.

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Thank you for your attention!

For more information, please visit: *canmilk.eu*

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References and credits:

- Slide 1: Picture by Ramon Salinero, from **unsplash.com**
- Slide 3: Graphical abstract: Lee, H. et al. (2015) "Complementary effect of plasma–catalysis hybrid system on methane complete oxidation over non-PGM catalysts," Catalysis communications. DOI: *https://doi.org/10.1016/j.catcom.2015.07.001*
- Slide 4: Thunderstorm picture taken by Melody P, from **unsplash.com**
- Slide 4: Northern lights picture taken by Jon Anders Dalan, from **unsplash.com**
- Slide 4: Classification of plasma. Original schematic from: Lee, J. et al. (2017) “Use of Atmospheric Pressure Cold Plasma for Meat Industry,” Korean Journal for Food Science of Animal Resources. Korean Society for Food Science of Animal Resources. DOI: *https://doi.org/10.5851/kosfa.2017.37.4.477*

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