

# Catalytic Process Intensification Routes for the Production of Synthetic Fuels and Energy Vectors

9<sup>th</sup> International Conference On Sustainable Solid Waste Management  
5-18 JUNE 2022

Inès Esma Achouri, Eng., MSc., Ph.D.

CRC - Process intensification for advanced catalysts and sustainable energy



# Overview

- ▶ Université de Sherbrooke
- ▶ Research group
- ▶ Process intensification
- ▶ Nonthermal plasma assisted reactions
- ▶ New approaches for CO<sub>2</sub> Hydrogenation
- ▶ Clean biofuels production from contaminated biomass
- ▶ Conclusion



# UDS in numbers



3 CAMPUS: THE  
MAIN CAMPUS IS  
SITUATED AT  
SHERBROOKE



8 FACULTIES



HOST TO MORE  
THAN 33,000  
STUDENTS



22 RESEARCH  
CENTRES



78 RESEARCH  
CHAIRS

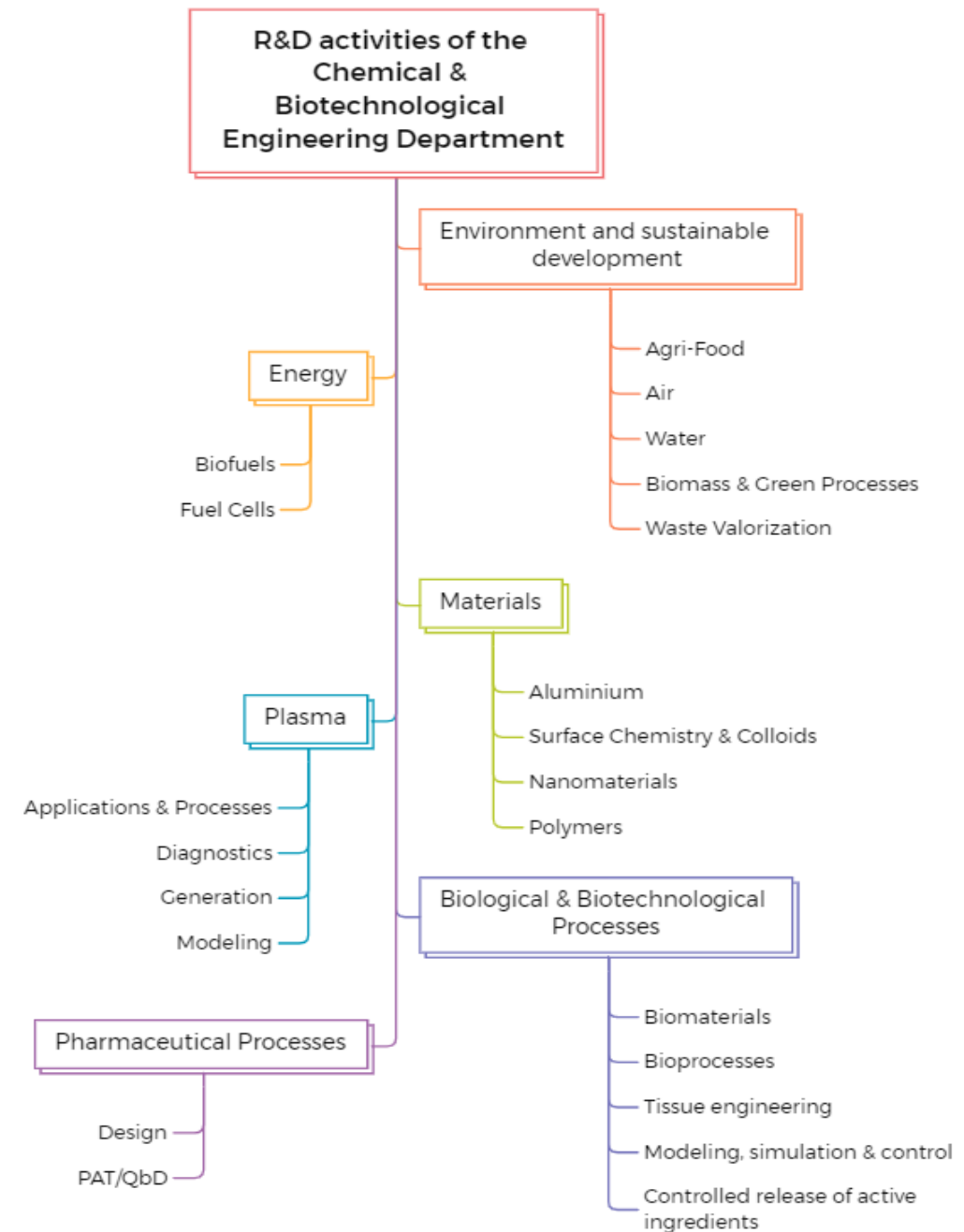


6 RESEARCH  
INSTITUTES



# Université de Sherbrooke

## – R&D Chem. Eng.



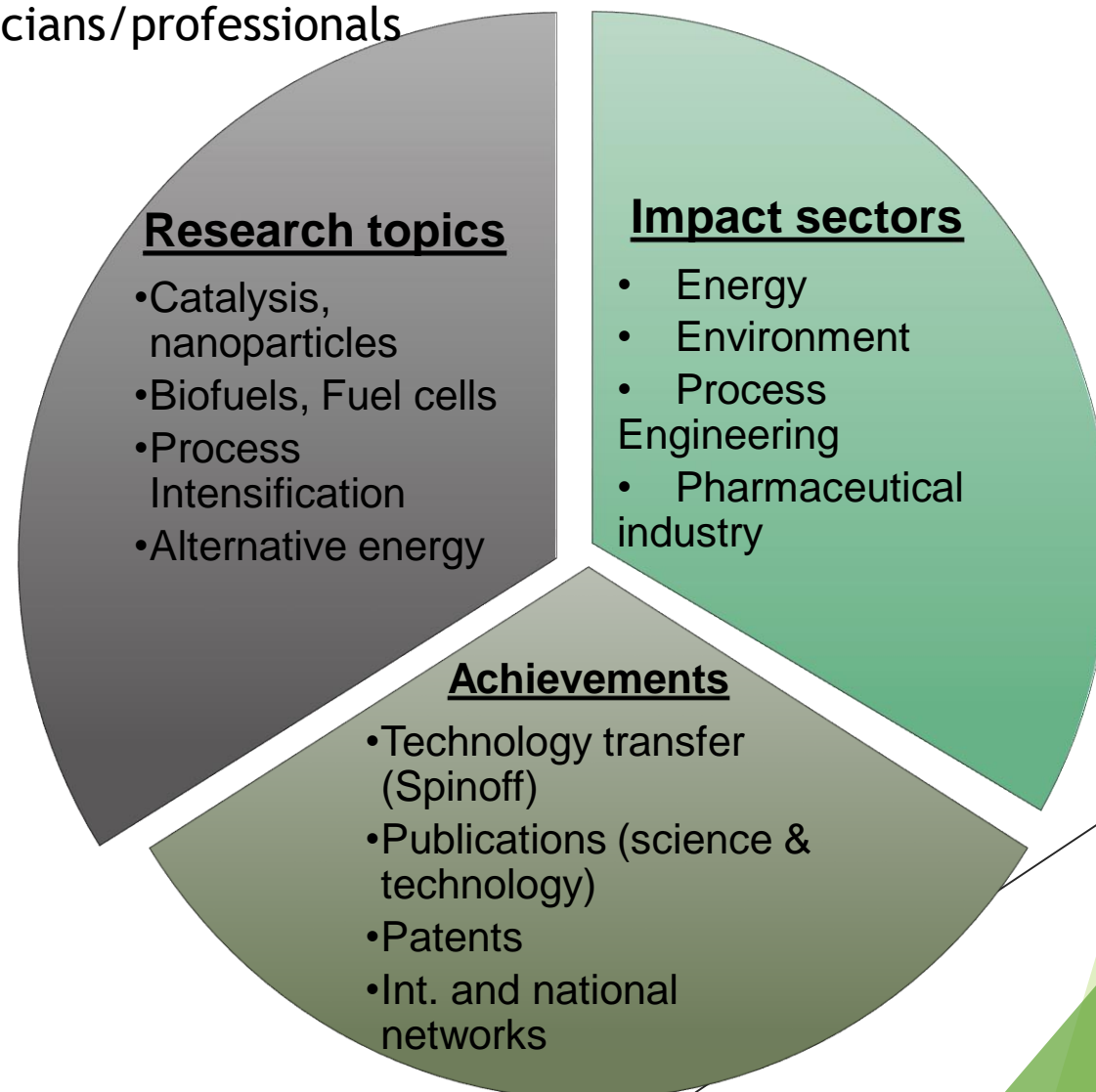




# Université de Sherbrooke

## Group of Research on technologies and processes (GRTP)

- ❑ 4 professors
- ❑ 20 graduate students
- ❑ 3 technicians/professionals



# Process intensification

## Benefits of process intensification

### Business:

- Miniaturized plant size.
- Reduced CAPEX and OPEX.
- Distributed manufacturing.
- Faster transformation from research to market.

Responsive  
processing

### Process:

- Higher selectivity/product purity.
- Higher reaction rates.
- Improved product properties.
- Improved process safety.
- Wider processing conditions.
- Continuous processing.

Faster, safer, and  
greener processing

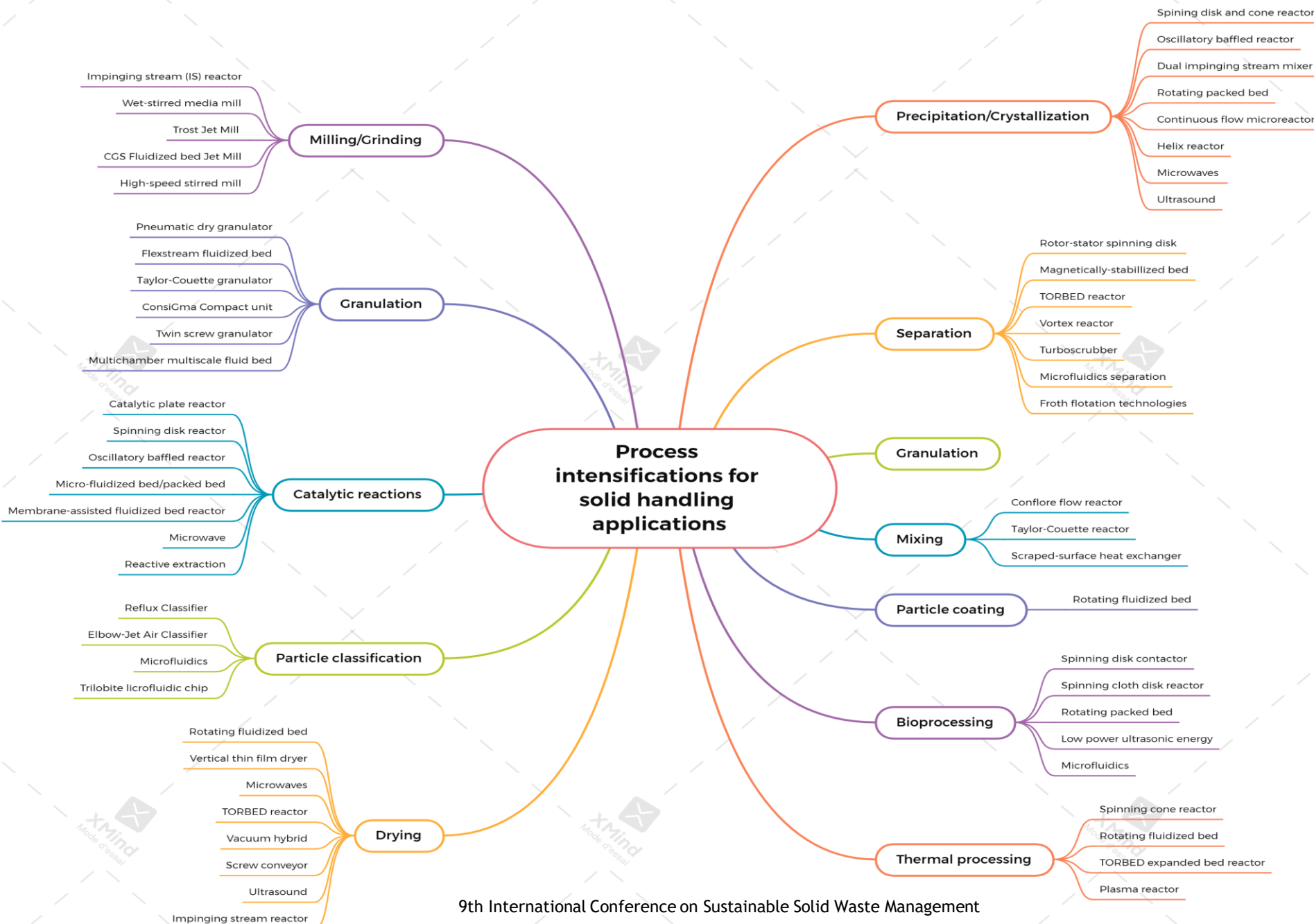
### Environment:

- Reduced energy usage.
- Reduced wastage.
- Reduced solvent usage.
- Smaller plants equal to less obstruction on landscape.

Sustainable  
processing



# PI for solid handling



# Targeted projects



CFI / FCI

Nonthermal plasma assisted reactions

Canada  
Canada Research  
Chairs



New approaches for CO<sub>2</sub> Hydrogenation



Clean biofuels production from contaminated biomass



New Frontiers in Research Fund  
Fonds Nouvelles frontières en recherche





CFI / FCI

# Non-thermal plasma assisted reactions

## Project 1: Nonthermal plasma catalysis Methane dry reforming



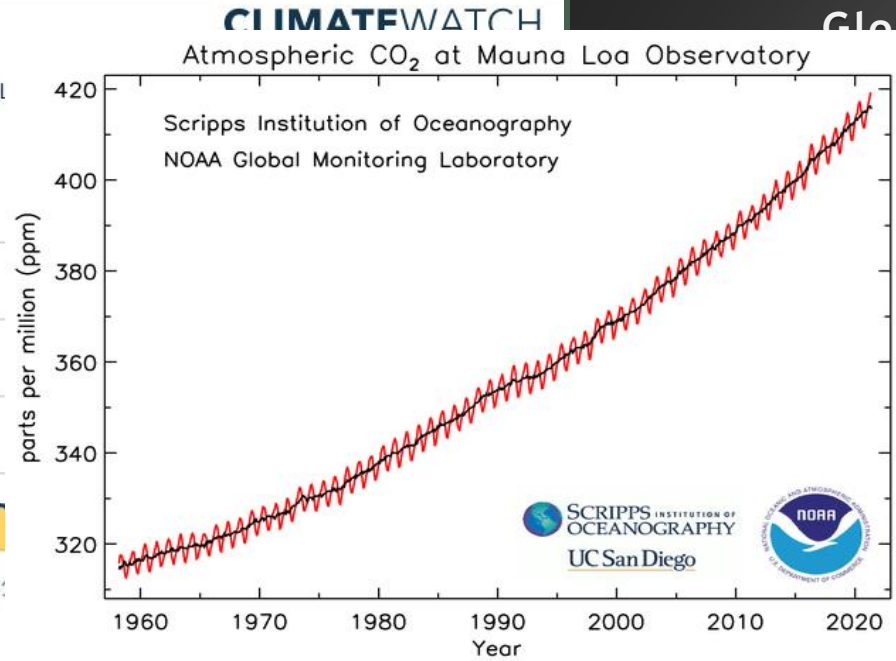
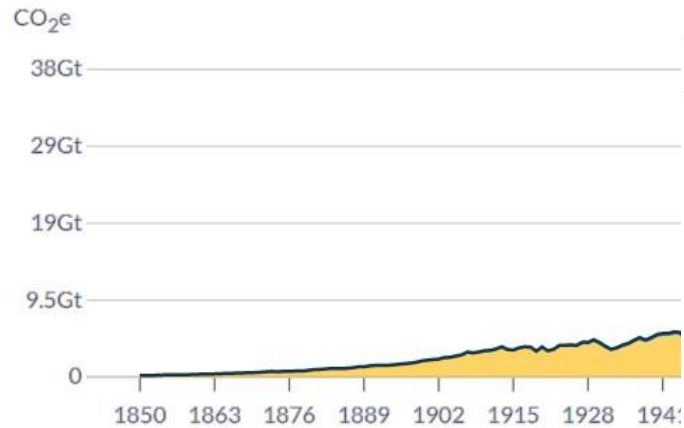
9th International Conference on Sustainable Solid Waste Management



# Global GHG emissions

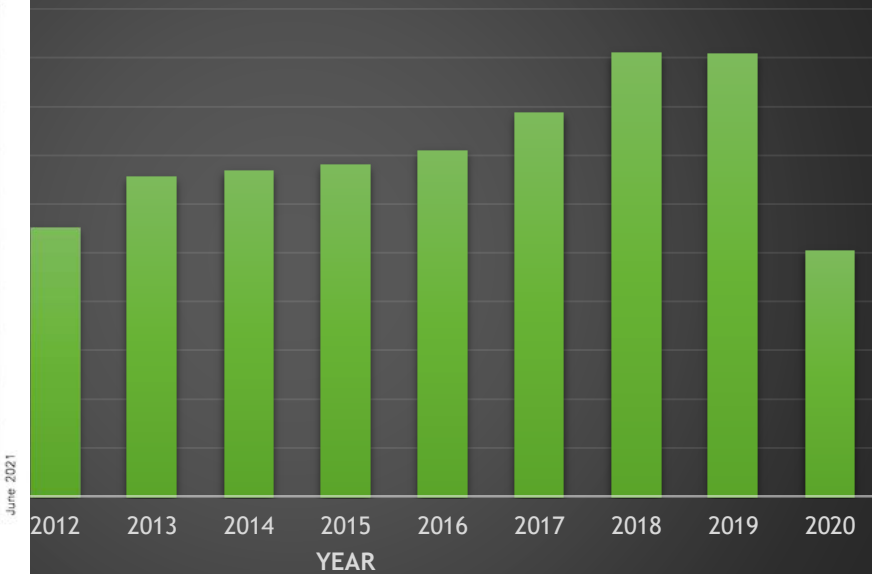
## Historical GHG emissions

Data source: PIK; Location: World; Sectors/Subsectors: Total excluding LUL Sectors.



Atmospheric CO<sub>2</sub> concentration at Mauna Loa Observatory, North flank of Mauna Loa Volcano, U.S. (GML, 2021)

## Global Carbon Dioxide Emissions



Statistical Review of World Energy 2021, (BP r., 2021)

<https://www.wri.org/insights/history-carbon-dioxide-emissions>, dated access: 09/05/2022

- Due to the Covid-19 pandemic, we experienced the largest falls in both energy demand and carbon emissions since World War II. However, The carbon budget is running out: CO<sub>2</sub> emissions have increased in every year since the Paris COP in 2015, except in 2020. Delaying decisive action to reduce emissions sustainably could lead to significant economic and social costs. (BP r., 2022)



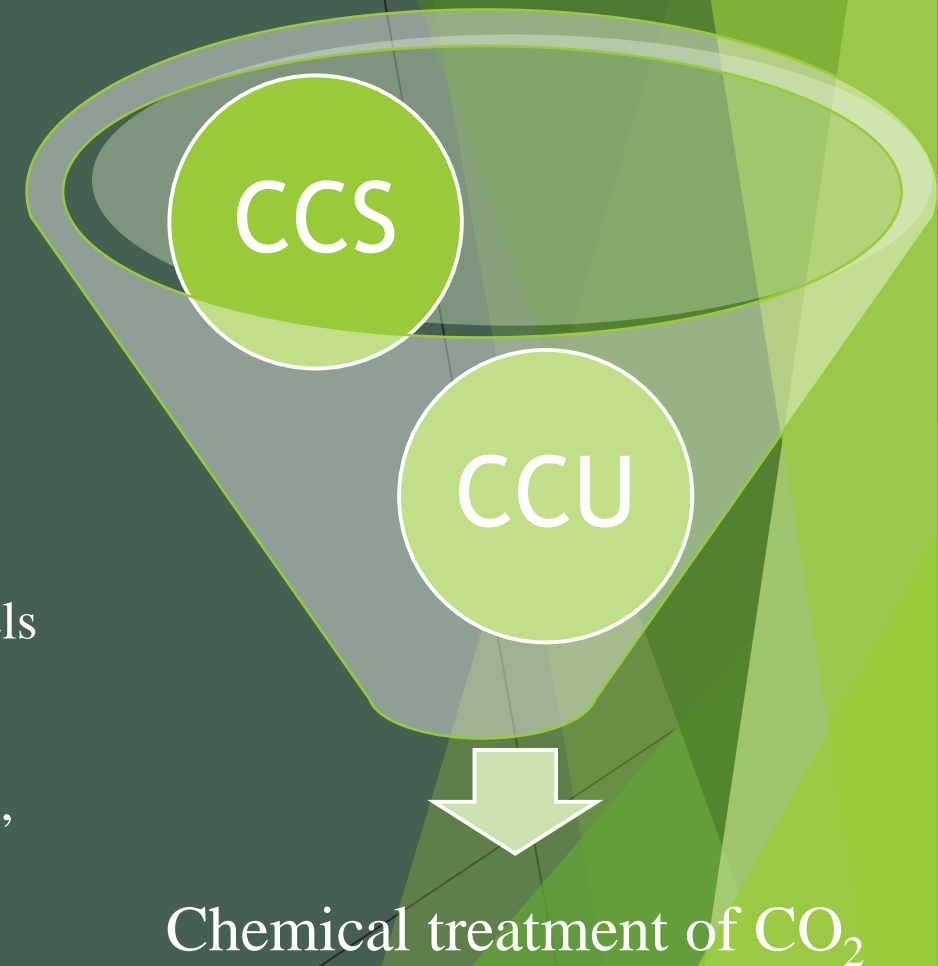
# Routes to CO<sub>2</sub> treatment

## ➤ Carbon Capture & Storage (CCS):

- reported as an attractive solution for the temporary storage of large volumes of CO<sub>2</sub> (Gao, J. Y., 2011)
- has the potential risk of leakage (Li W. W., 2018)

## ➤ Carbon Capture & Utilization (CCU):

- consider CO<sub>2</sub> as a source to produce value-added chemicals and fuels (de La Fuente, 2016)
- there are several routes to utilize CO<sub>2</sub> such as beverage carbonation, food packaging, water desalination, EOR (70-80Mton of CO<sub>2</sub> is consumed per year), biomass gasification, construction and building materials, and renewable energy systems (for instance, CO<sub>2</sub> based geothermal energy systems)



# CONVENTIONAL METHANE DRY REFORMING REACTIONS:



Side reactions:



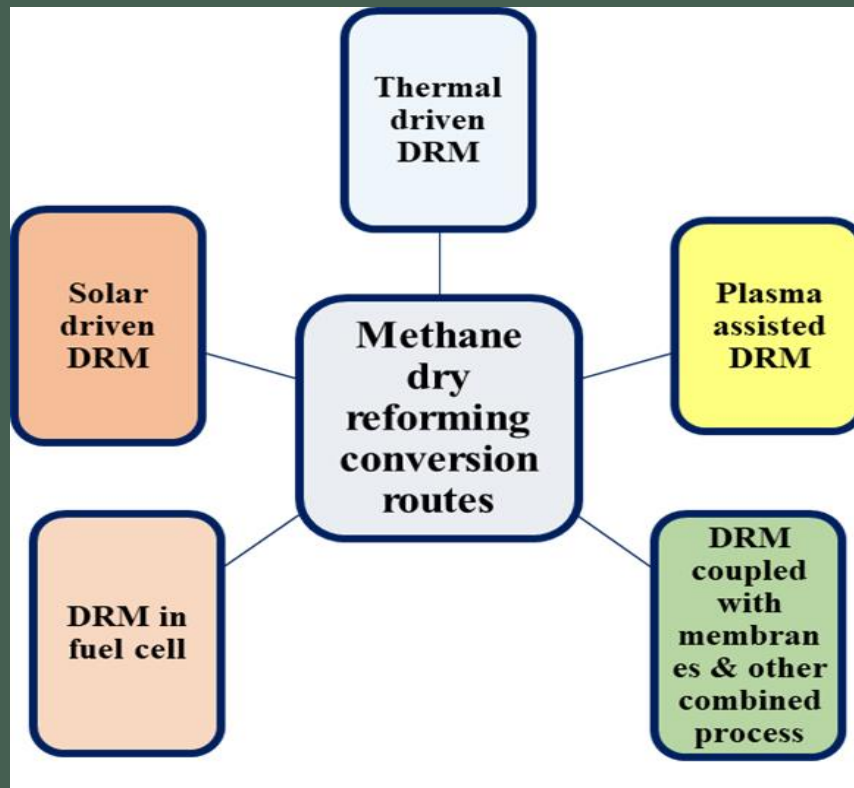
## Problems:

- 1) Intensive carbon deposition (Large Ni size)
- 2) Active metal sintering (weak interaction)
- 3) High temperature process

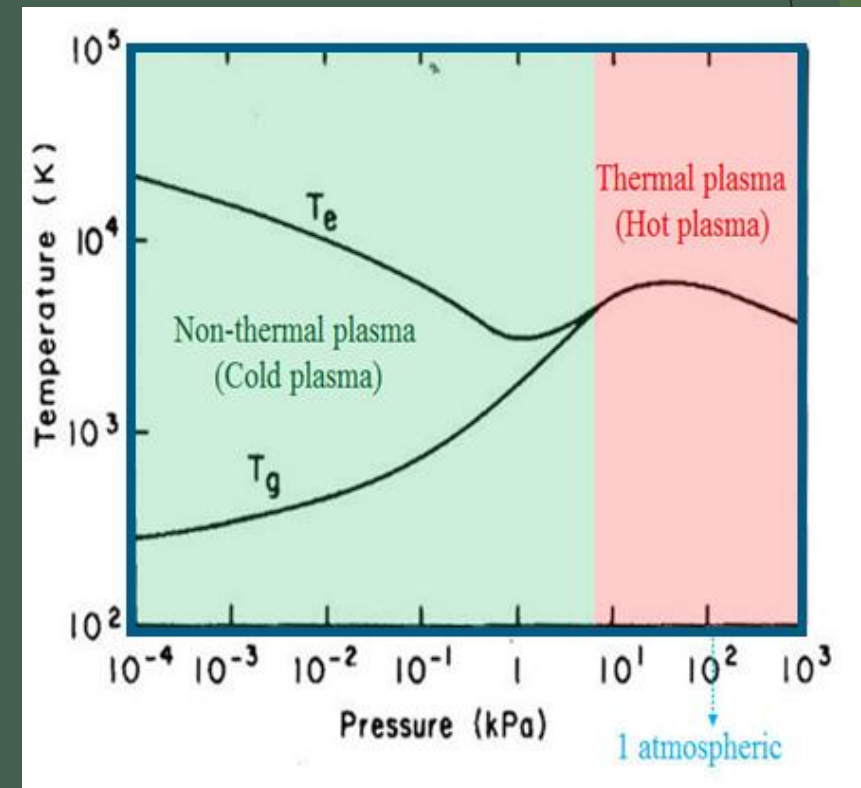


# DRM conversion routes

plasma deviation from the kinetic equilibrium ( $T_e \gg T_h$ ) where the electron temperature is sufficiently high compared to the heavy species with a high degree of non-thermodynamic equilibrium is classified as non-thermal plasma

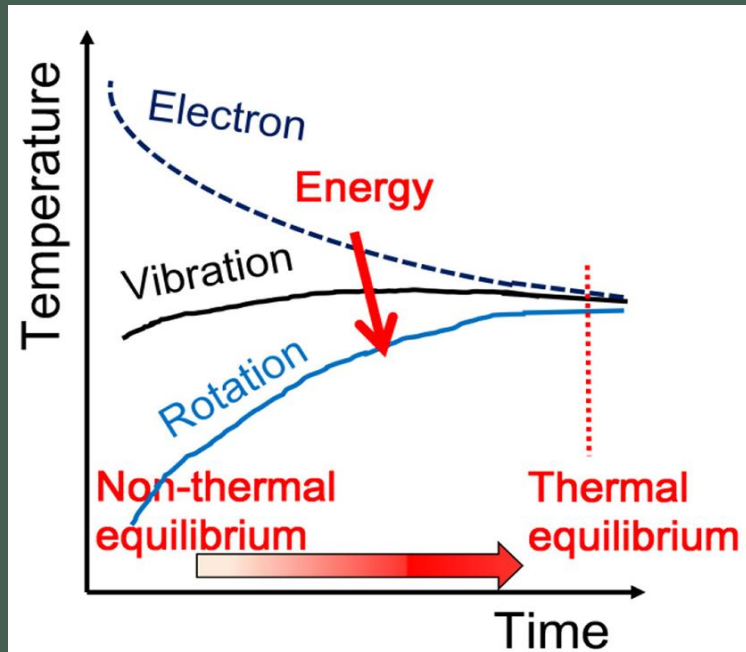


Current Dry reforming routes in cold plasma

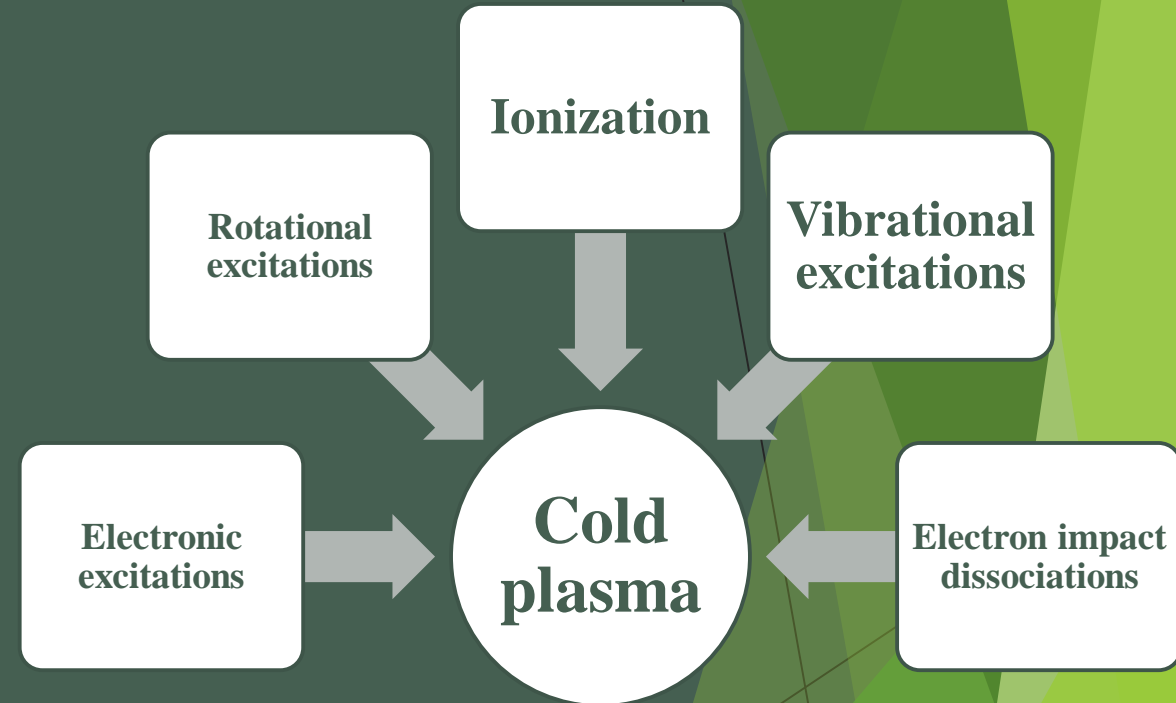


# Electron impact energy transfer in cold plasma

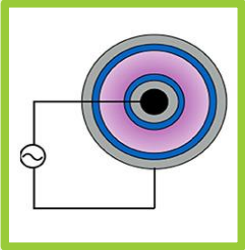
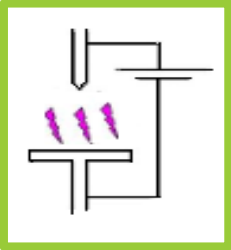
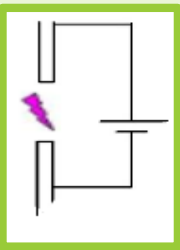
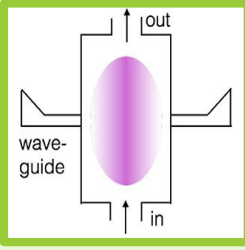
$$T_e \gg T_v > T_r \approx T_i \approx T_o$$



$T_v$  is the temperature of vibrationally excited molecules,  $T_r$  is the rotational degree of freedom,  $T_i$  is ion temperature, and  $T_o$  describes the gas temperature

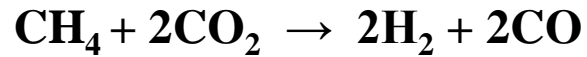


# Table 1. Use of different cold plasma discharge in DRM

Reactor type	DBD	CD	SD	MW
Scheme				
Electron energy [eV]	1 - 30	≈ 5	-	1-2
Electron density [cm <sup>-3</sup> ]	10 <sup>12</sup> - 10 <sup>15</sup>	10 <sup>9</sup> -10 <sup>13</sup>	10 <sup>14</sup> - 10 <sup>15</sup>	10 <sup>13</sup>
Current [A]	1 - 50	≈ 10-5	20 - 30	-
Gas Temperature [K]	300 - 500	≈ 400	400 -1000	100-2000
Break down voltage [kV]	5 - 25	10 - 50	5 - 15	-

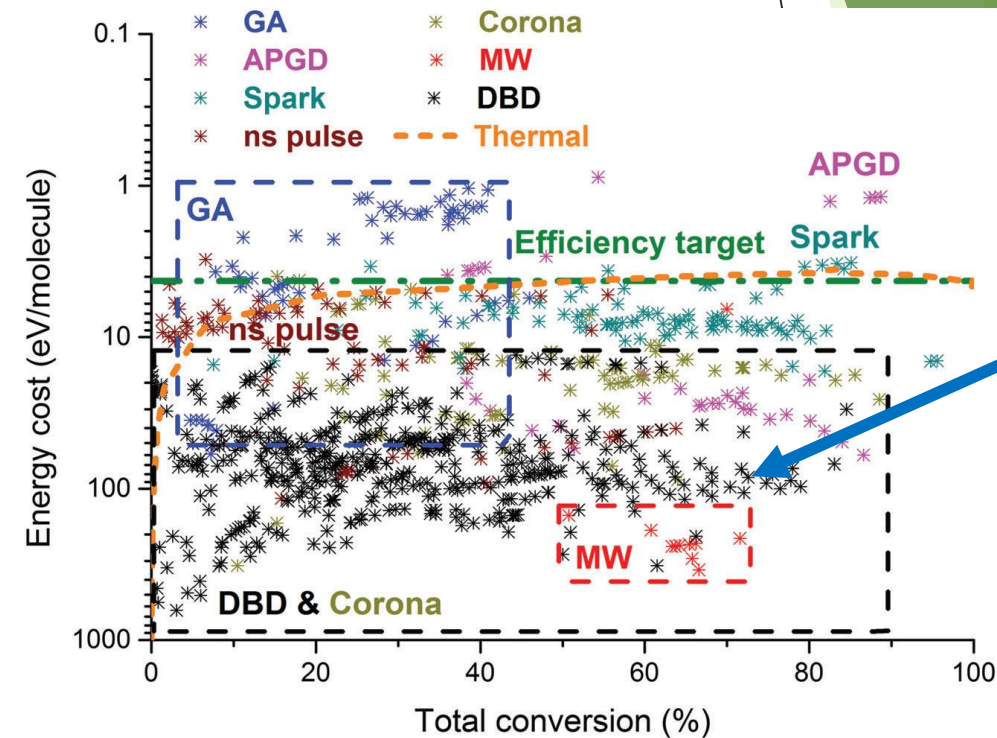


# Evaluation of cold plasma discharge in DRM



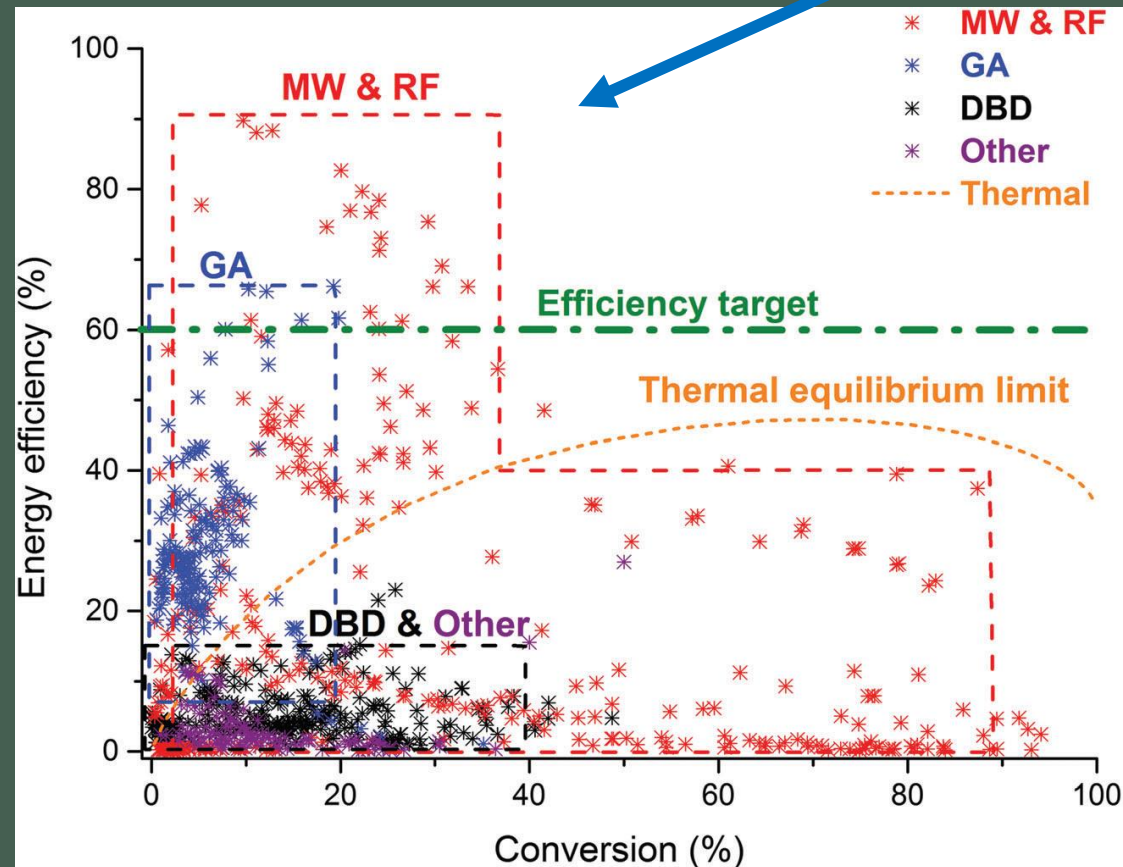
$$247 \text{ kJ mol}^{-1} \sim 2.57 \text{ eV}$$

It is worth mentioning that for a 100% energy-efficient dry reforming reaction, considering all the products, including gas and liquids, the energy cost per molecule conversion is 2.57 eV, equal to the reaction's standard enthalpy (247.3 kJ/mol)



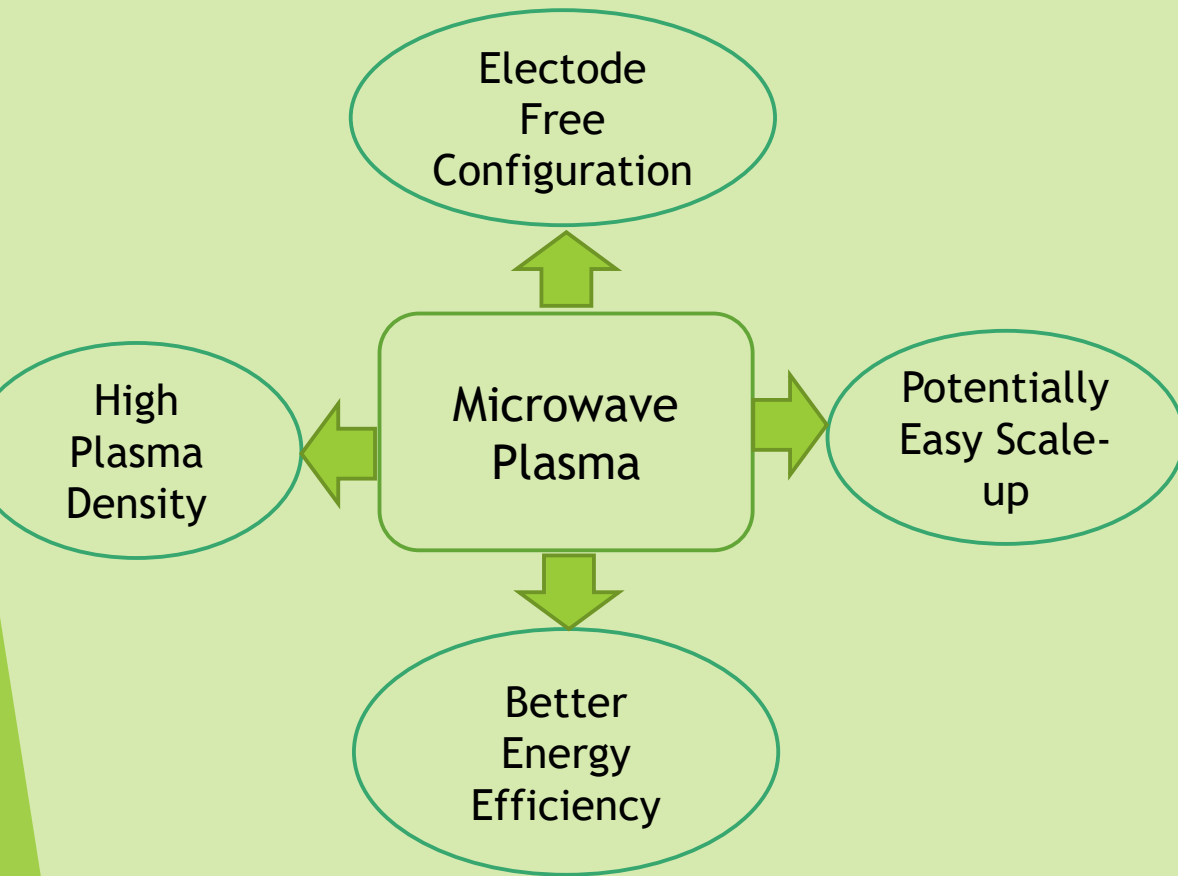
**Performance/collection of data of energy cost vs total conversion under different plasma discharge in DRM**

# Evaluation of cold plasma discharge in CO<sub>2</sub>

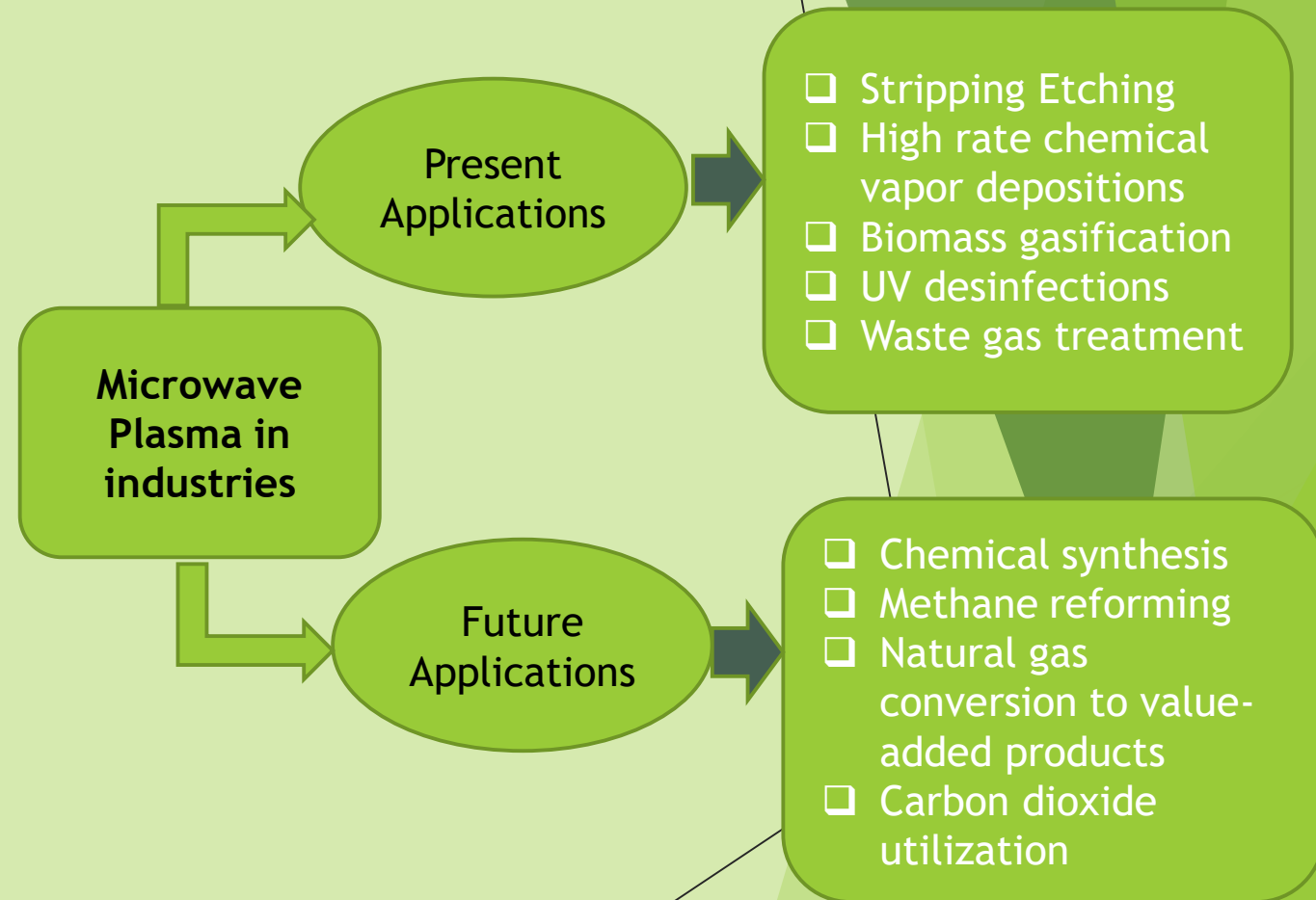


Performance/collection of data of energy efficiency vs conversion under different plasma discharge in CO<sub>2</sub> splitting

## Advantages of MW plasma



## Current and future applications of MW plasma

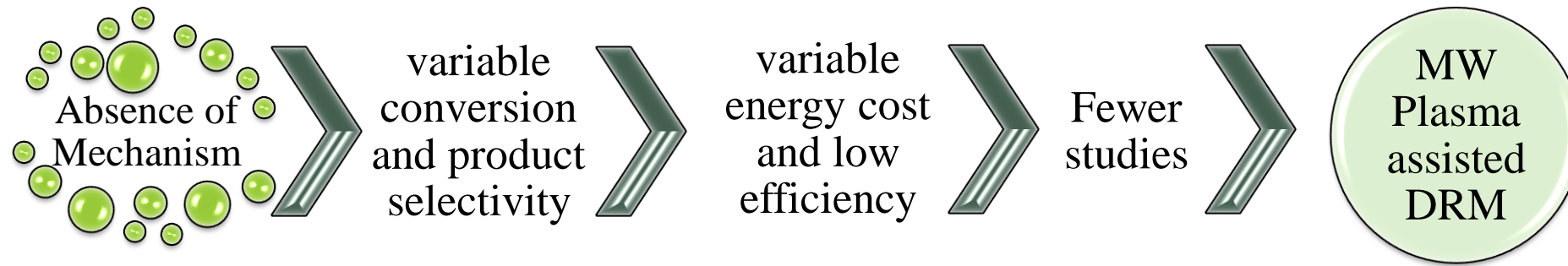




# Microwave plasma dry reforming

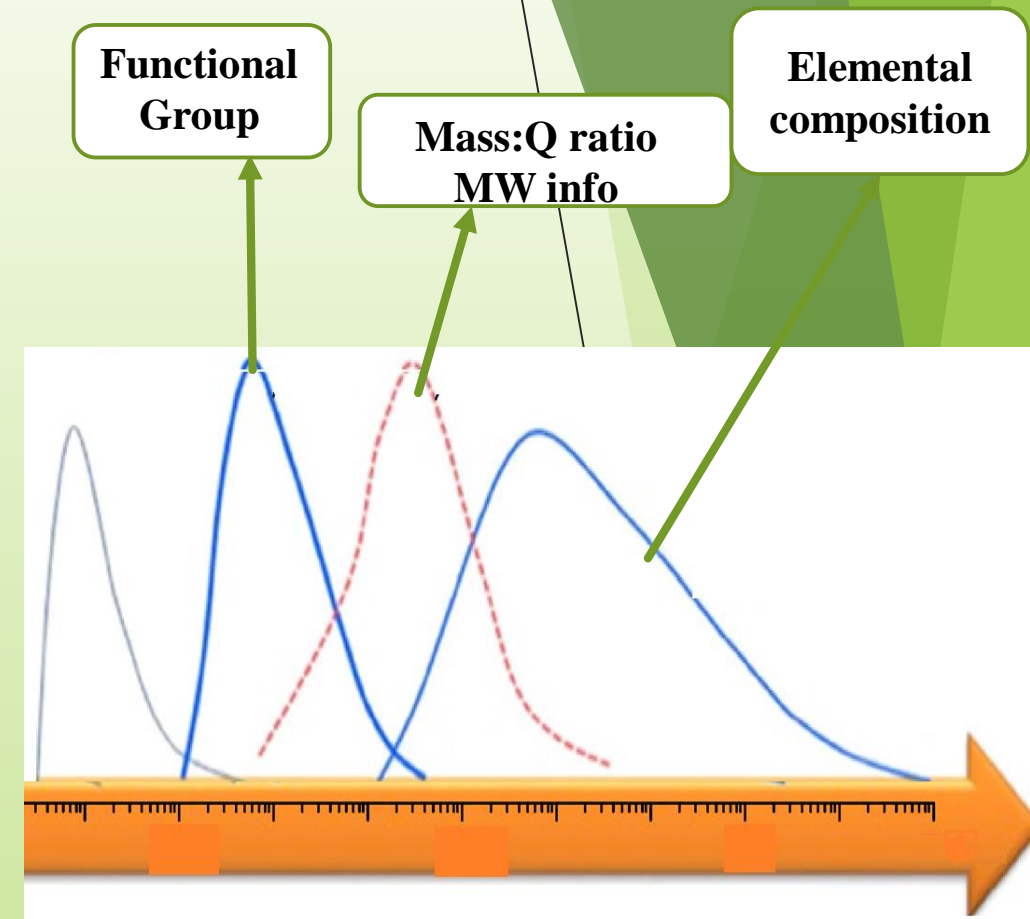
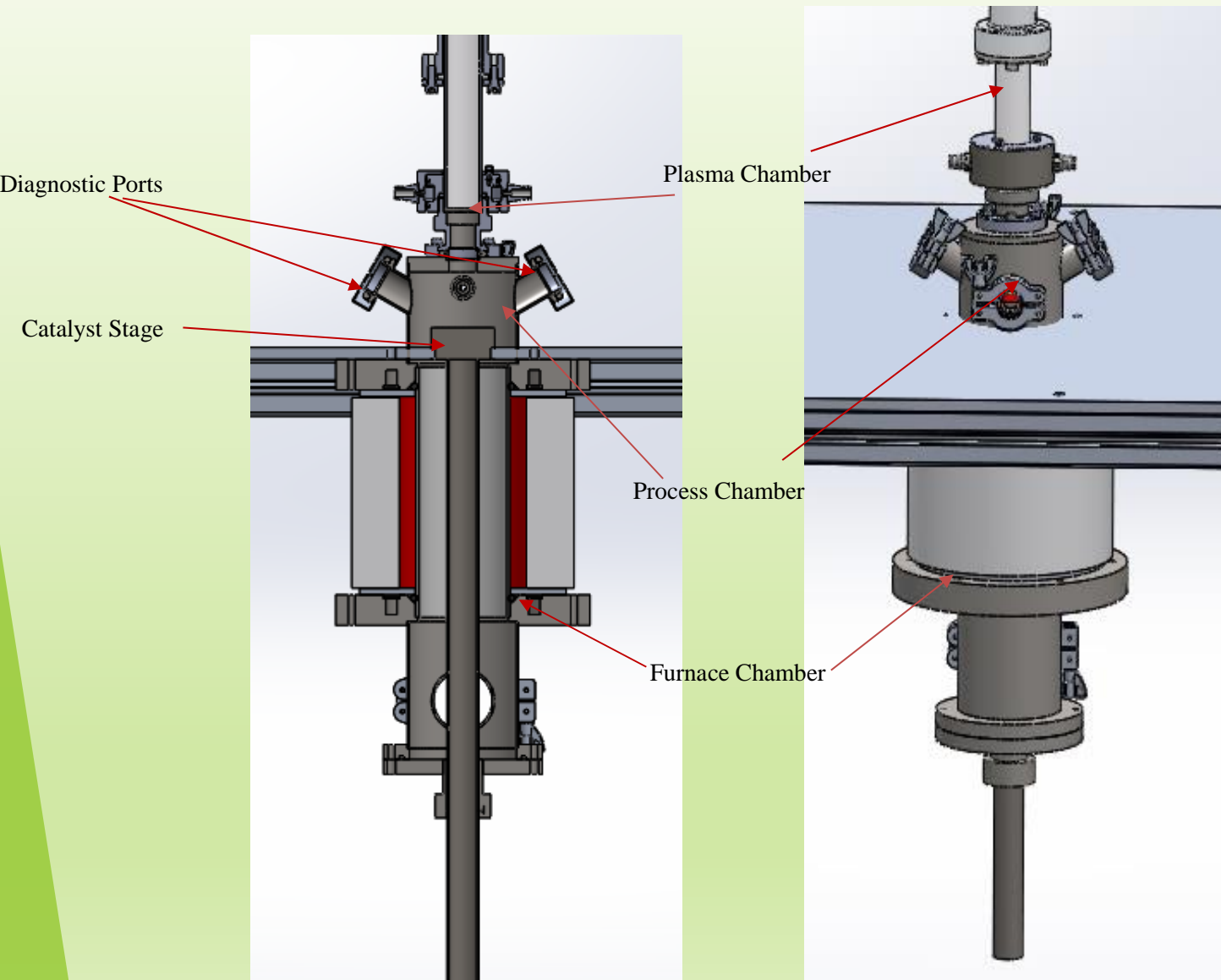
Plasma	Power	Frequency	Pressure	Year`	CH <sub>4</sub> /CO <sub>2</sub>	Conversion		Selectivity (%)	Ref.
	(W)					CO <sub>2</sub>	CH <sub>4</sub>		
MW	6 kW	2.45 GHz	Atmospheric pressure	2017	1:1	68.4 %	96.8 %	H <sub>2</sub> Production rate g/H = 240 And H <sub>2</sub> :CO = 0.9:1.1	[20]
MW	6.5 kW	915 MHz	Atmospheric pressure	2019	2:3	-	86.5 %	H <sub>2</sub> (73.3)	[21]
MW	2kW	2.45 GHz	Atmospheric pressure	2021	1:1	90.7 %	96.4 %	H <sub>2</sub> (97.3) CO(85.7)	[22]
MW	700	-	Atmospheric pressure	2019	1:2	19 %	83 %	H <sub>2</sub> (99) CO (19)	[23]
MW	700	-	Atmospheric pressure	2018	1:2	44.40 %	84.91%	H <sub>2</sub> (51.31) CO (61.17)	[24]
MW	1.0 kW	2.45 GHz	atmospheric pressure	2010	-	-	91.6%	H <sub>2</sub> (92.7)	[25]

# Challenges and Problems in MW assisted plasma DRM



**The gaps and areas to be improved in MW plasma assisted DRM**

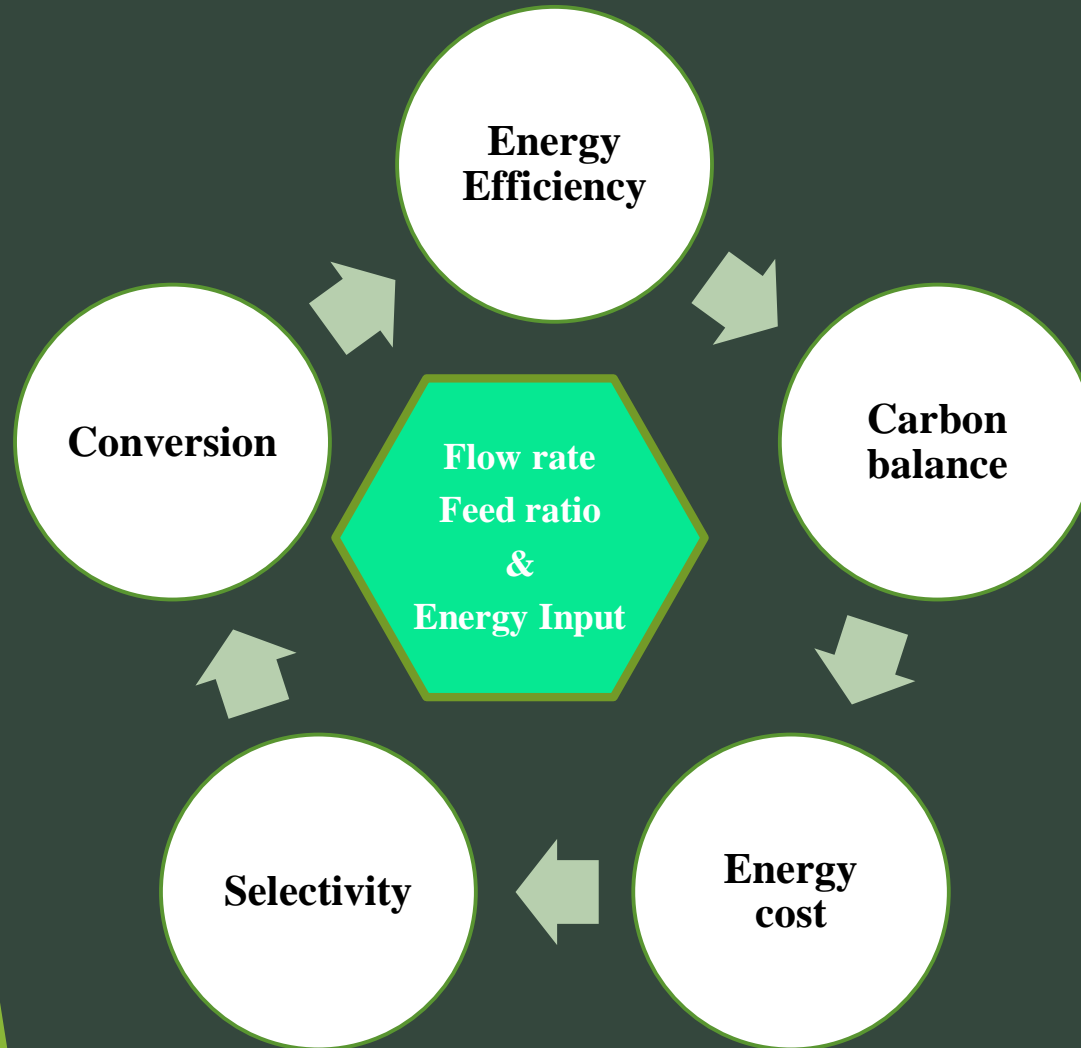
# Reactor configurations with *in situ* Characterization



**Elements needed to advance the field of plasma catalysis.**



# Correlations Process Parameters



Effect of flow rate , feed ratio and energy input on the reaction metrics

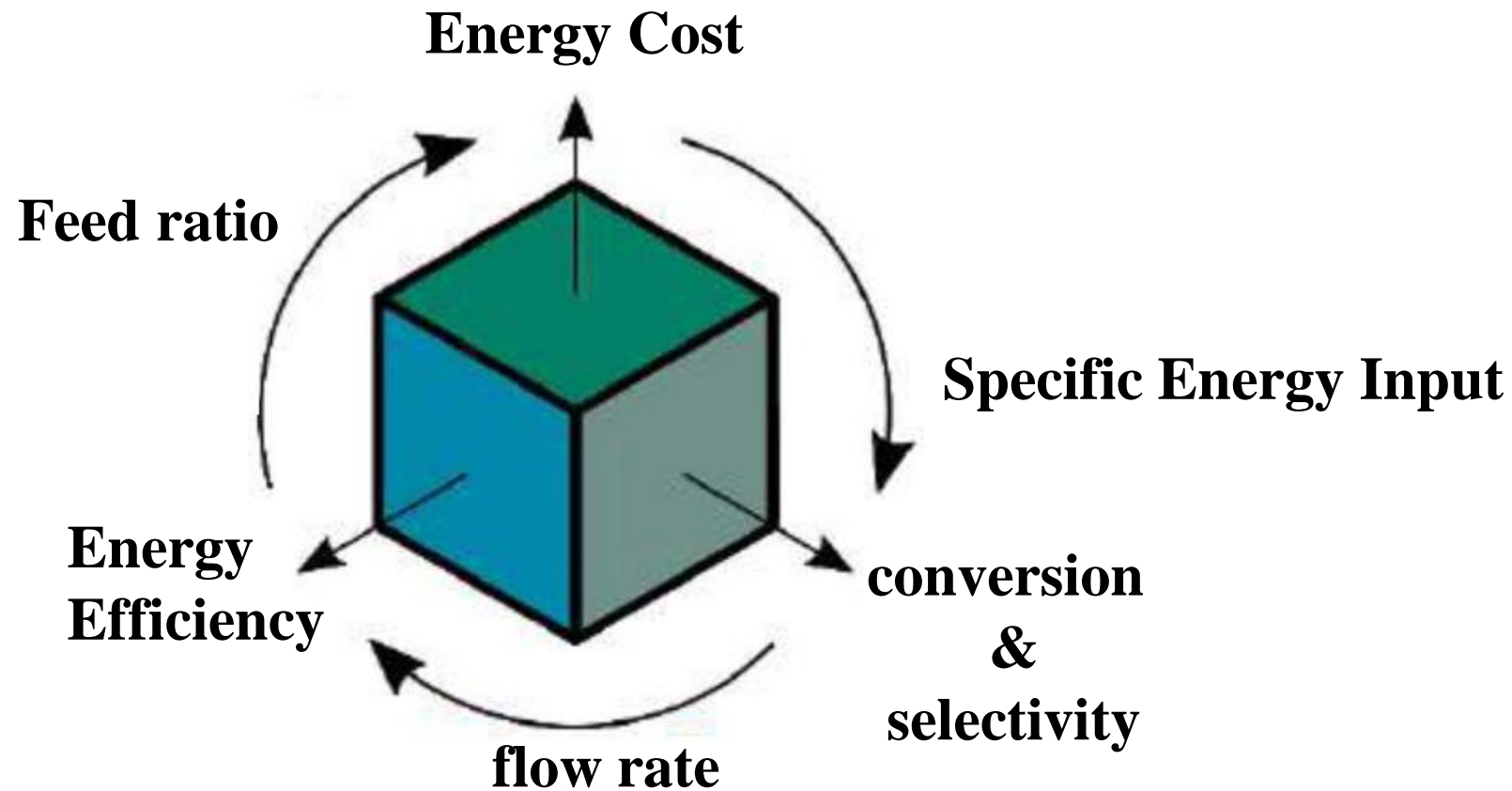
Specific energy input (SEI)  
the ratio of plasma power to the gas flow rate

$$\text{Energy cost} = \frac{SEI}{X_{total}(\%)}$$

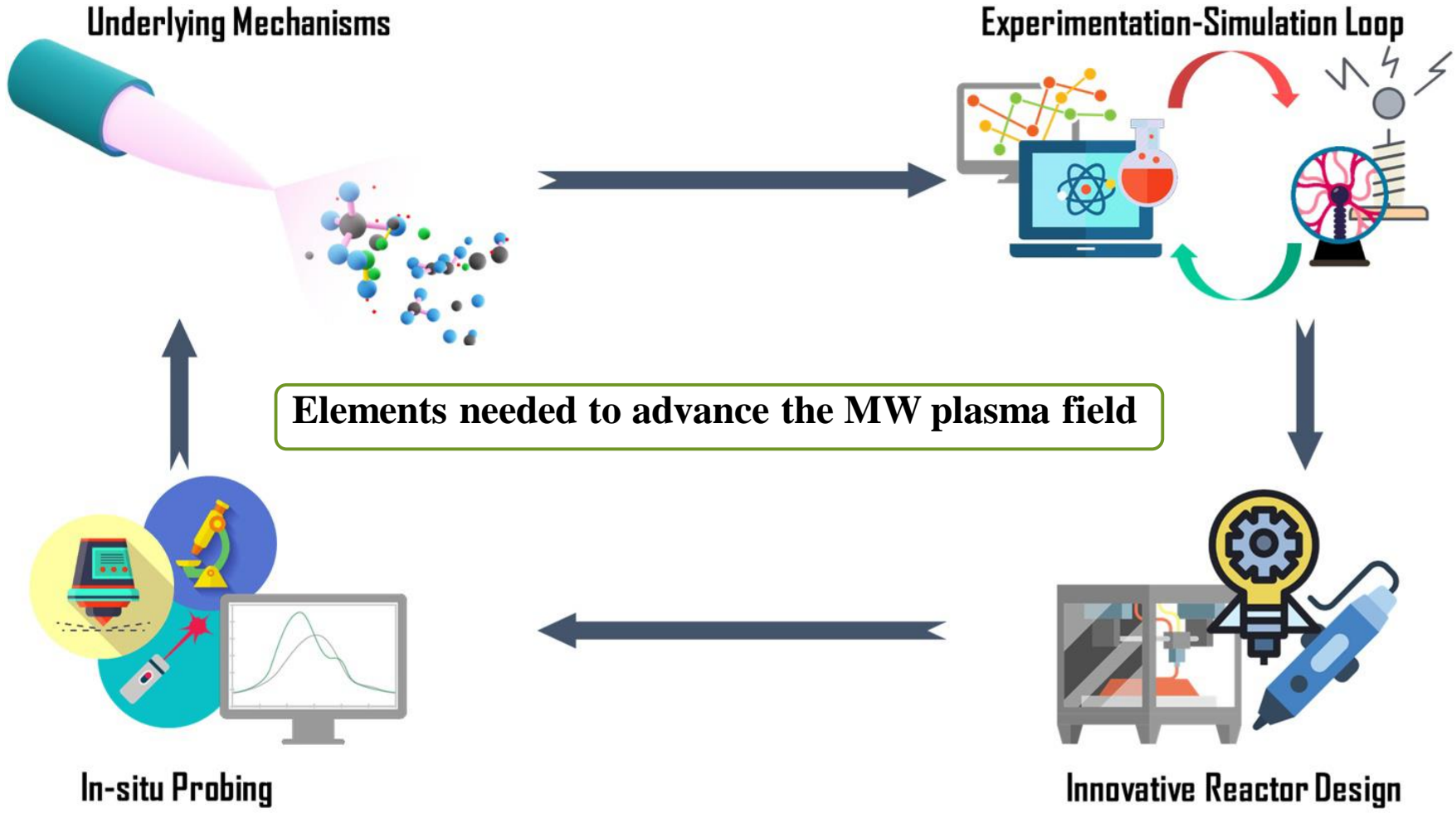
$$\text{Energy efficiency (\%)} = \frac{\Delta H_R \left( \frac{kJ}{mol} \right) \times X_{total}(\%)}{SEI}$$

$$SEI = \frac{\text{Plasma power (kW)}}{[CO+H_2]_{produced} (l/min)}$$

# Optimization of Process Parameters



**the importance of control over process parameters**





# Main objectives for drying reforming:

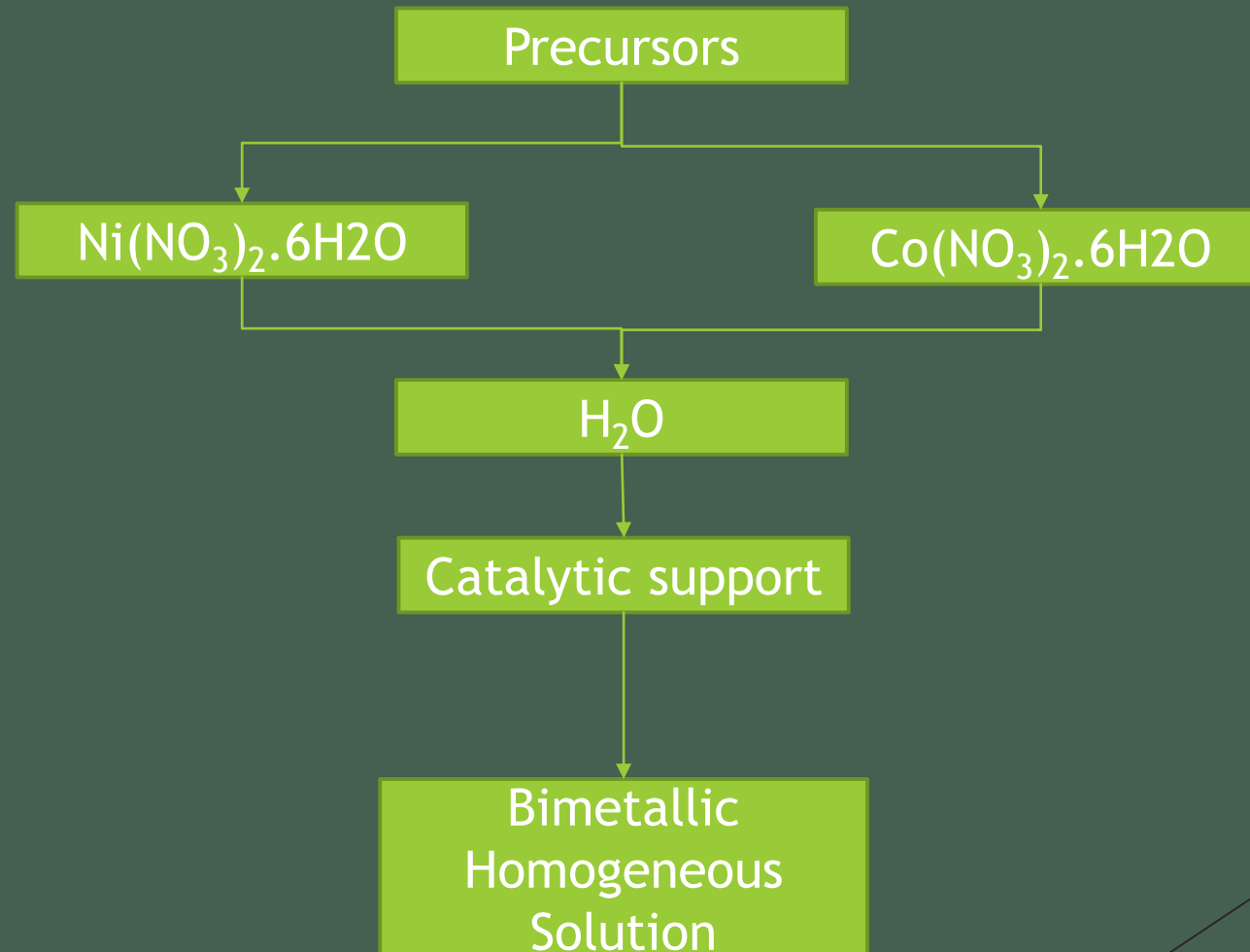
- ▶ Production of hydrogen together with carbon monoxide
- ▶ The use of catalysts mainly based on Nickel only or with other metals on several supports.
- ▶ Analysis and characterization of catalysts by different characterization techniques (XRD, SEM, BET ...)

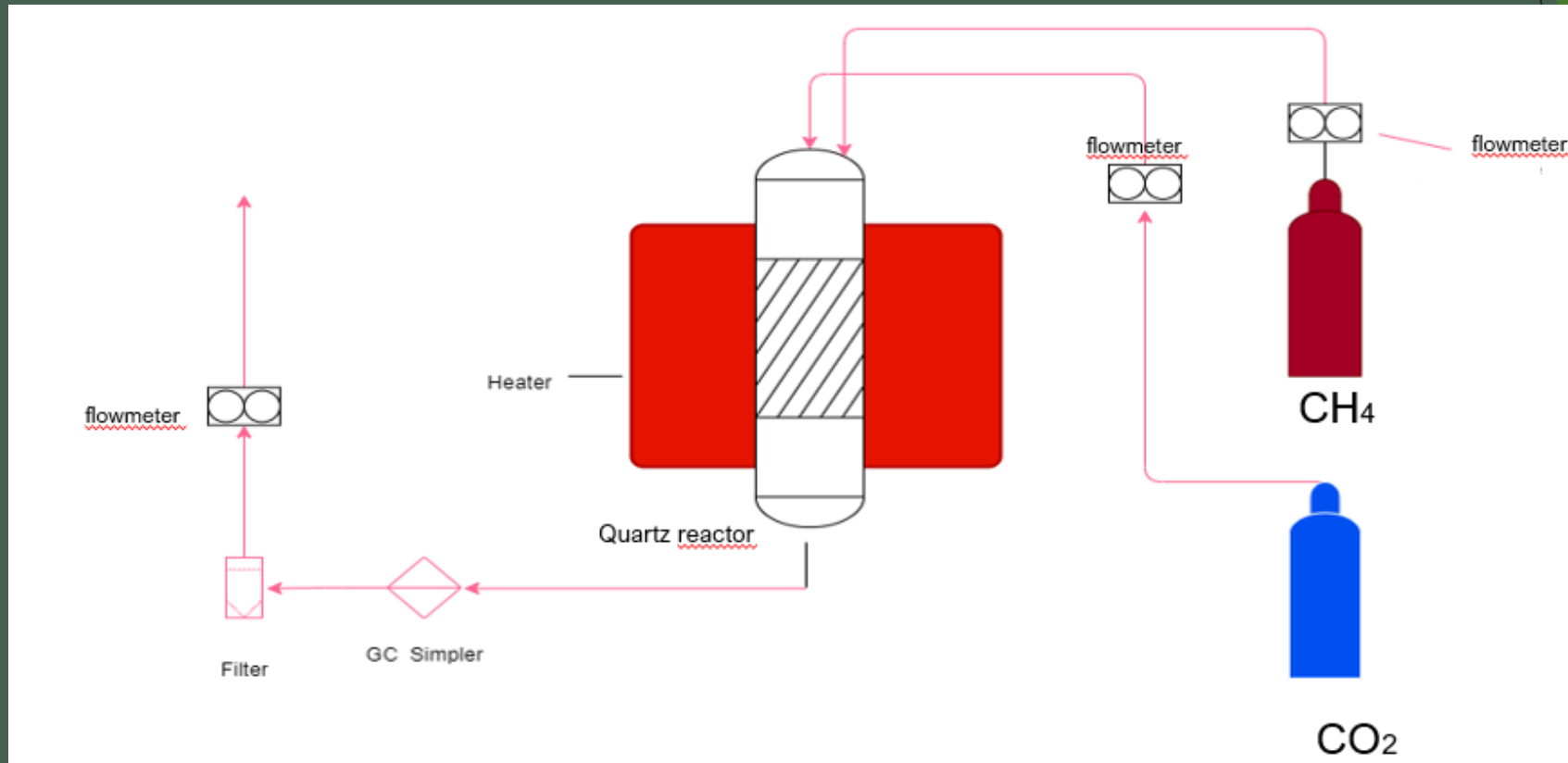


# Experimental section

# Synthesis of catalysts

Catalyst preparation by the wetness incipient impregnation method





## Experimental set-up for the dry reforming reaction

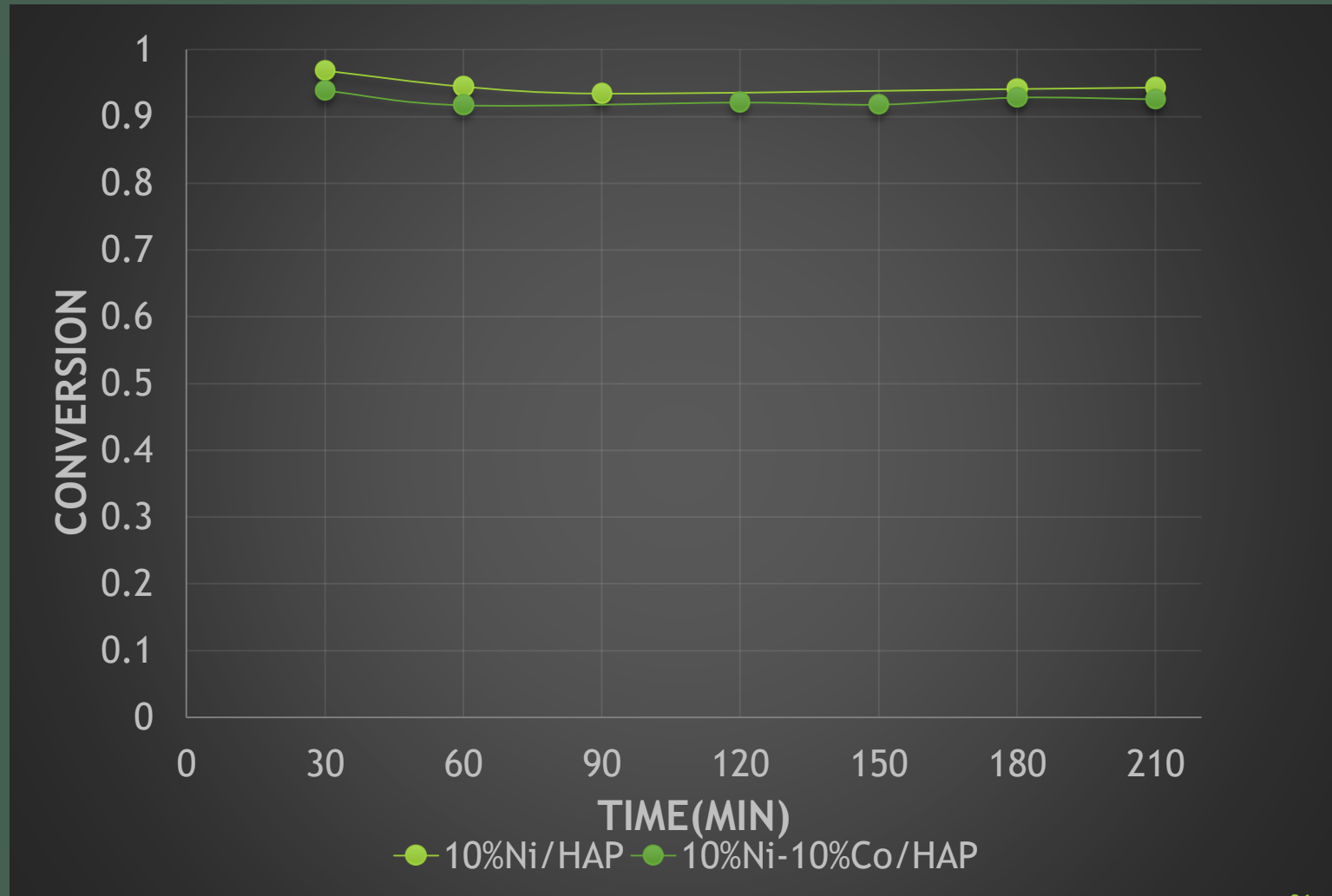


# Experimental conditions:

- ▶ Temperature: 800 °C
- ▶ Pressure: atmospheric
- ▶ A ratio of  $\text{CH}_4/\text{CO}_2=1$
- ▶ GHSV is chosen (1000) ( $\text{ml.h}^{-1}.\text{g}^{-1}_{\text{cat}}$ ).

# Conversion of CH<sub>4</sub>

Conversions of 10%Ni, 10%Ni-10%Co/HAP



36

# Yields

## Hydrogen yields of 10%Ni, 10%Ni-10%Co/HAP



# characterization of catalysts

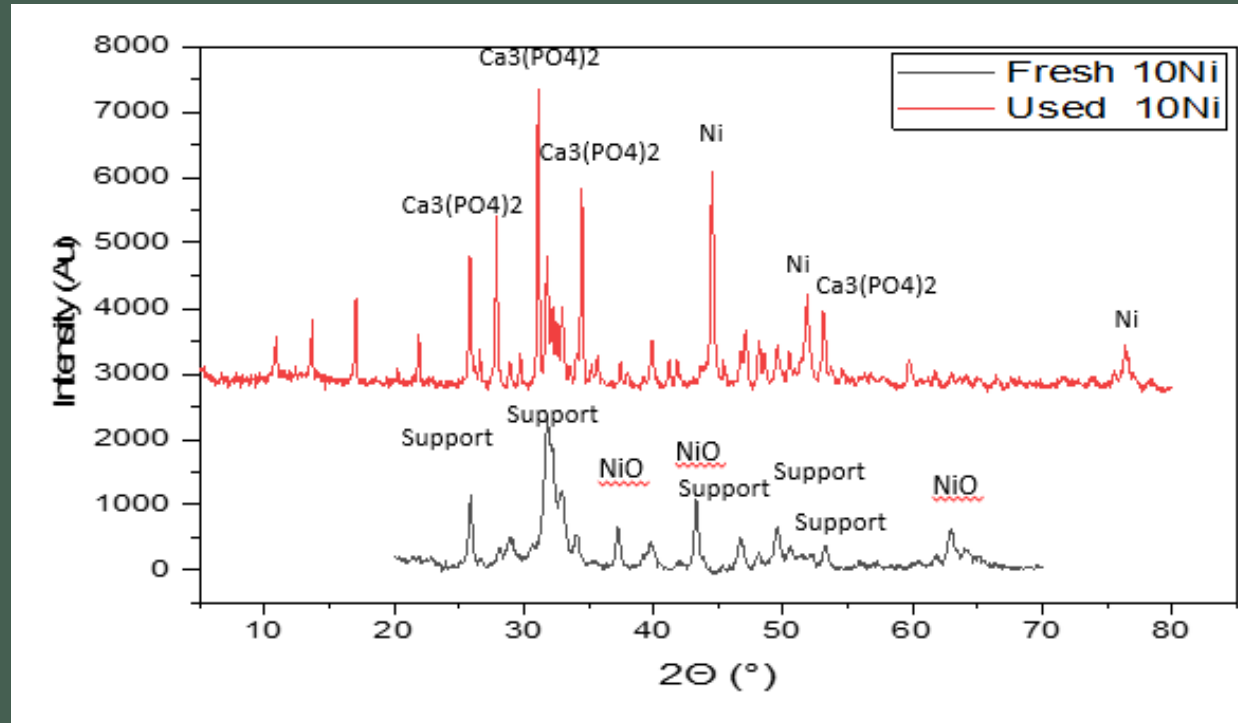


38

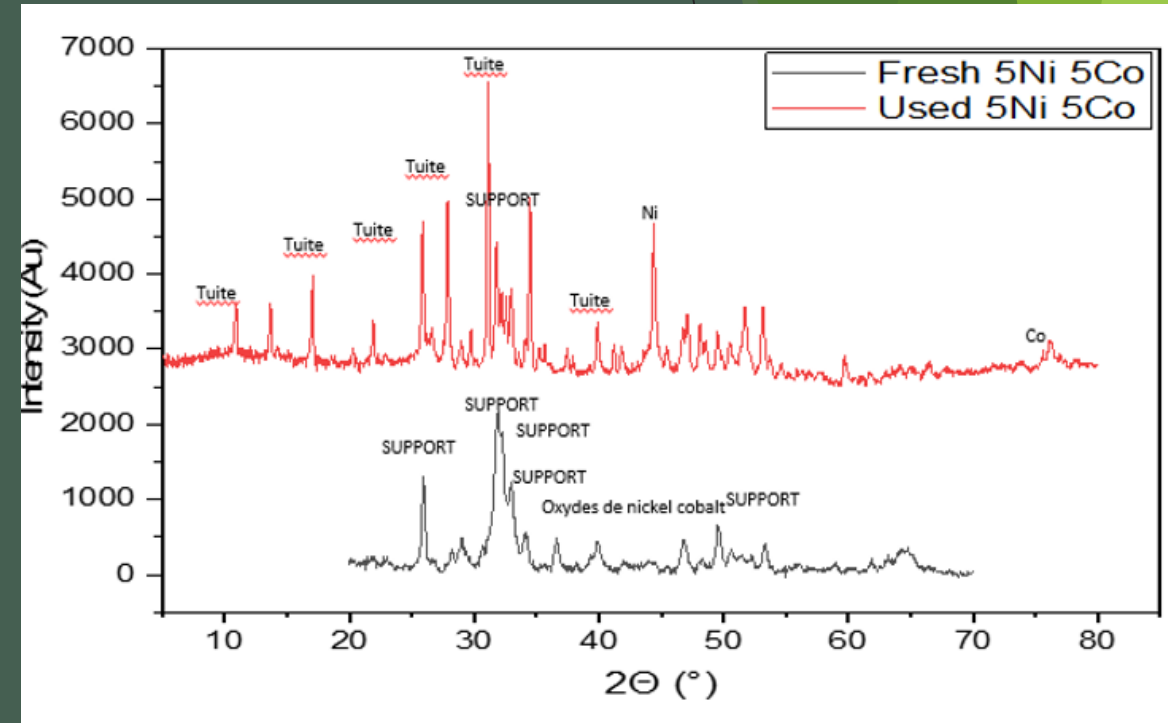
38



# XRD Characterization of fresh and used catalysts



XRD for 10%Ni/Hap



XRD for 10%Ni-10%Co/Hap

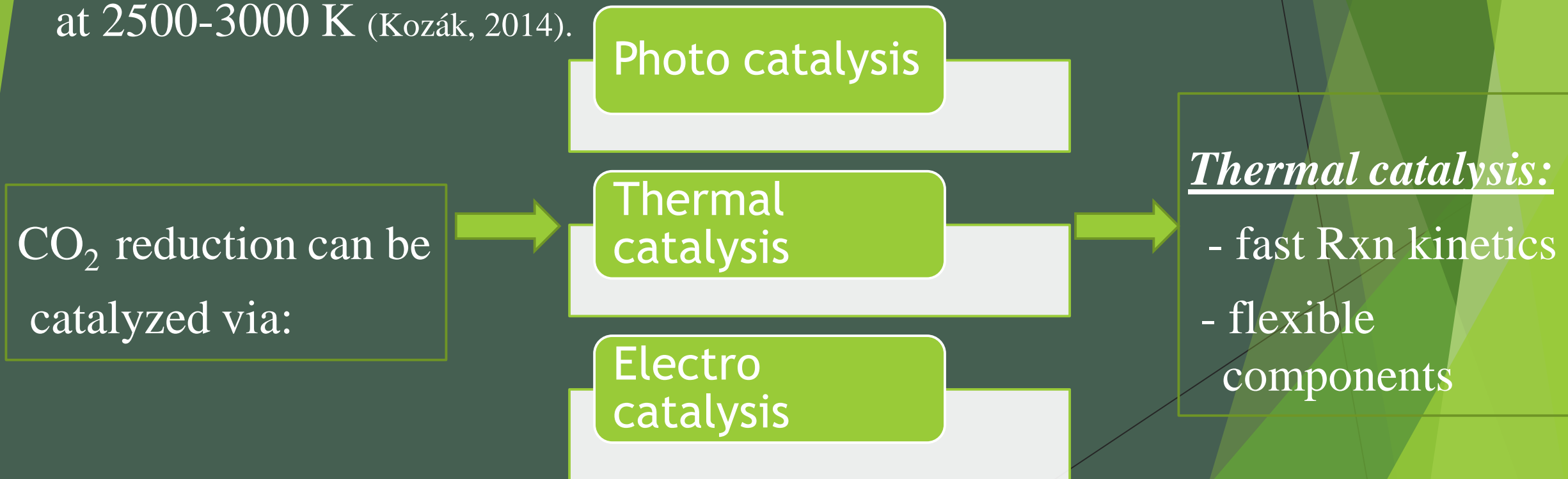
## Project 2: CO<sub>2</sub> direct hydrogenation

► PhD student: Farbod Farzi



# Thermal catalysis of CO<sub>2</sub>

➤ Considering the CO<sub>2</sub> limitations of being soluble in water and its thermodynamic stability, CO<sub>2</sub> conversion to commercial products is deemed to be highly energy intensive as thermal decomposition of pure CO<sub>2</sub> commences at 2500-3000 K (Kozák, 2014).



# Thermal catalysis of CO<sub>2</sub> (Cont'd)

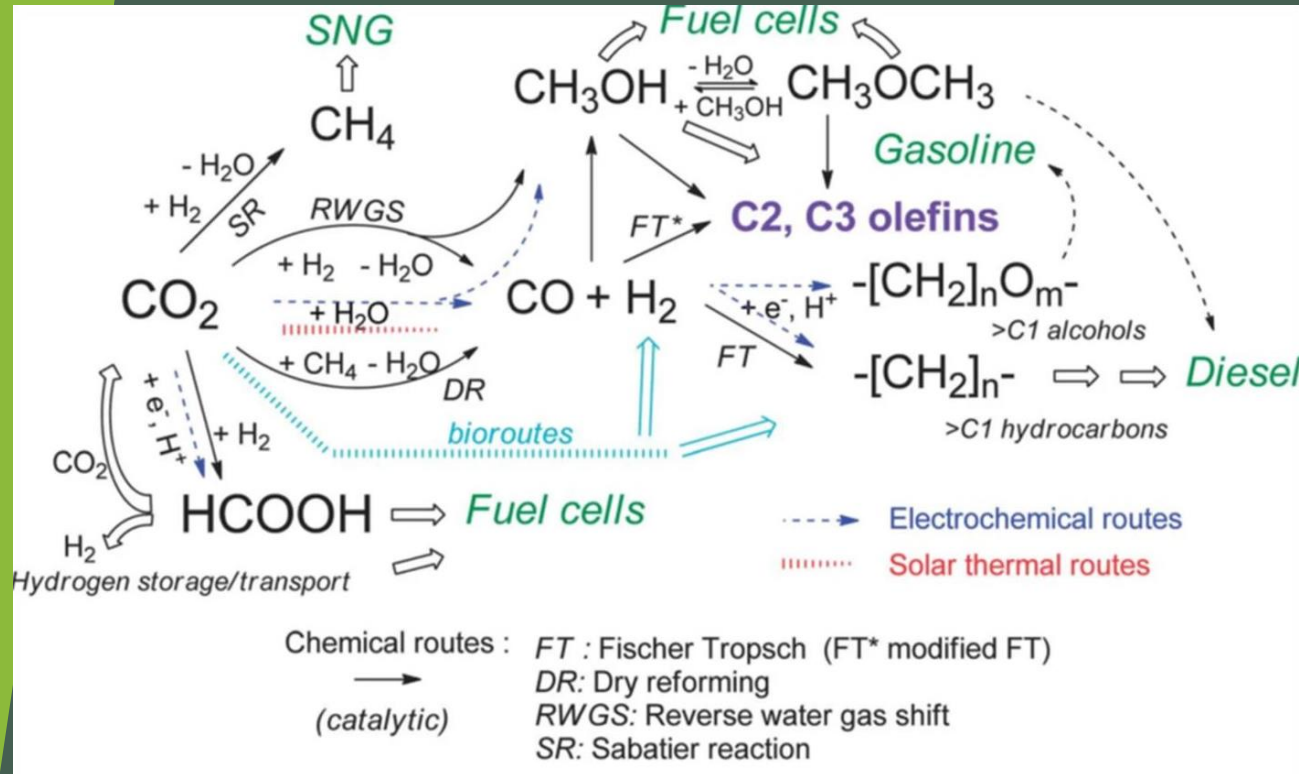
CO<sub>2</sub> is thermodynamically stable;  
Activation and more importantly reduction of CO<sub>2</sub> is energy-intensive



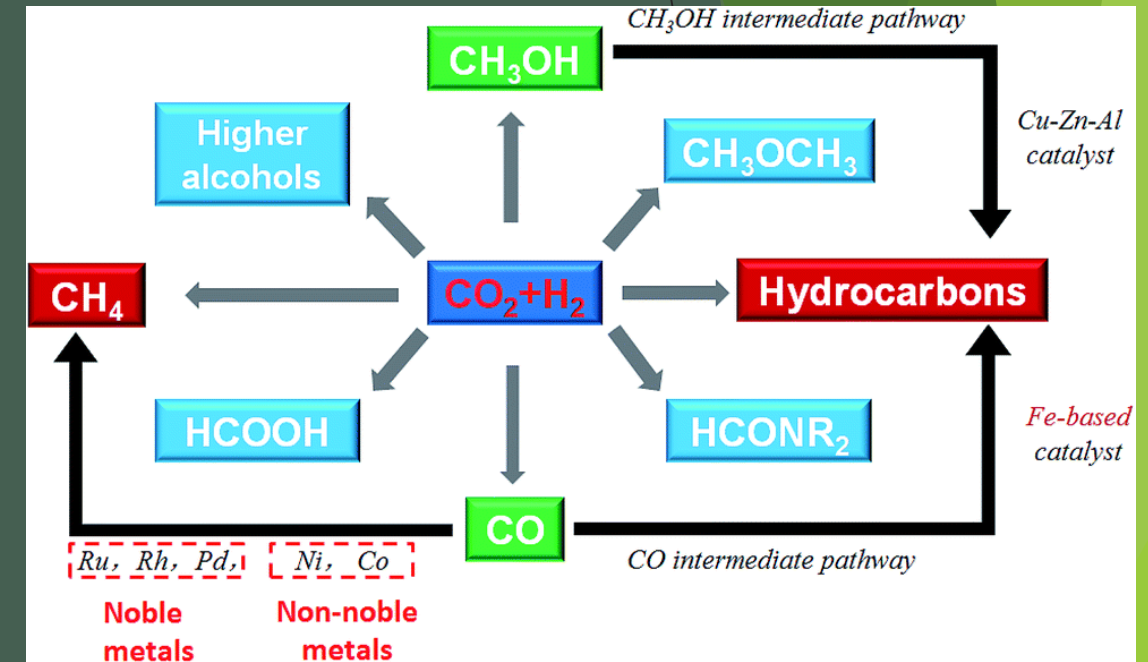
Addition of a higher Gibbs energy component such as H<sub>2</sub> will make the conversion more favorable from the thermodynamic point of view (Li W. W., 2018)



# CO<sub>2</sub> hydrogenation products



(Adamu, 2020, 10.1186/s42480-019-0026-4)



(Li, 2018, 10.1039/C7RA13546G)

# Experimental section

Study of thermal catalysis of CO<sub>2</sub> hydrogenation reaction towards liquid hydrocarbons



Catalyst  
formulation



Reactor Setup



Operating  
Conditions

# Experimental section (Cont'd)

## Catalyst Formulation

### Active metal:

#### Monometallic:

- ☐ Fe
- ☐ Co
- ☐ Cu
- ☐ Mn
- ☐ Ni, ...

#### Bimetallic:

- ☐ Ni-Co
- ☐ Co-Fe, ...

### Support:

- ✓  $\text{Al}_2\text{O}_3$ ,
- ✓  $\text{SiO}_2$ ,
- ✓  $\text{TiO}_2$ ,
- ✓  $\text{CeO}_2$ ,
- ✓  $\text{ZrO}_2$ ,
- ✓  $\text{Ce-ZrO}_2$ ,
- ✓ Zeolites (Hbeta, HZSM-5, SAPO-34, ...)
- ✓  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  commonly known as Hydroxyapatite (HAP) was used as a catalyst support for Dry Reforming of Methane (DRM)



### Our formulations:

- Cu/HAP
- Mn/HAP
- Ni-Co/HAP
- Co-Fe/HAP
- $\text{Ni/ZrO}_2\text{-HAP}$

# Experimental section (Cont'd)

## Catalyst Synthesize



### Synthesize methods:

-  precipitation
-  impregnation (dry & wet)
-  sol-gel
-  thermal
-  solvothermal
-  solvent-free methods
-  plasma decomposition
-  reverse microemulsion

### Our synthesize method:

- ✓ incipient wetness co-impregnation
- ☐ Simplicity of operation
- ☐ Controlled measures
- ☐ Proper way of fine distribution of metal over support shell
- ☐ Mixing & Solid handling solutions available for scale-up purposes

### Post-synthesize steps:

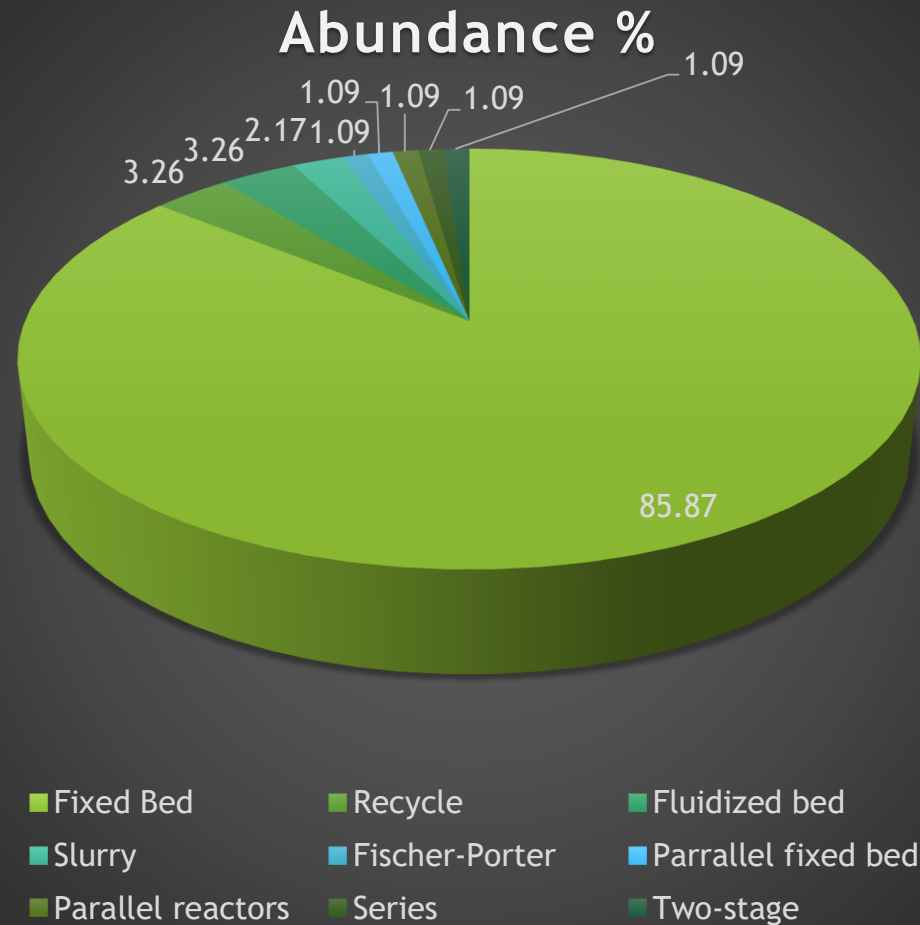
-  Drying at 105 °C, overnight
-  Calcination at 500 °C under static air atmosphere for 2h

(Park & McFarland, 2009),  
(Chew, et al., 2014),  
(Lu, Fatah, & Khodakov, 2017),  
(Jia, Zhang, Rui, Hu, & Liu, 2018)

(Teimouri, Z., 2021, 10.3390/catal11030330)



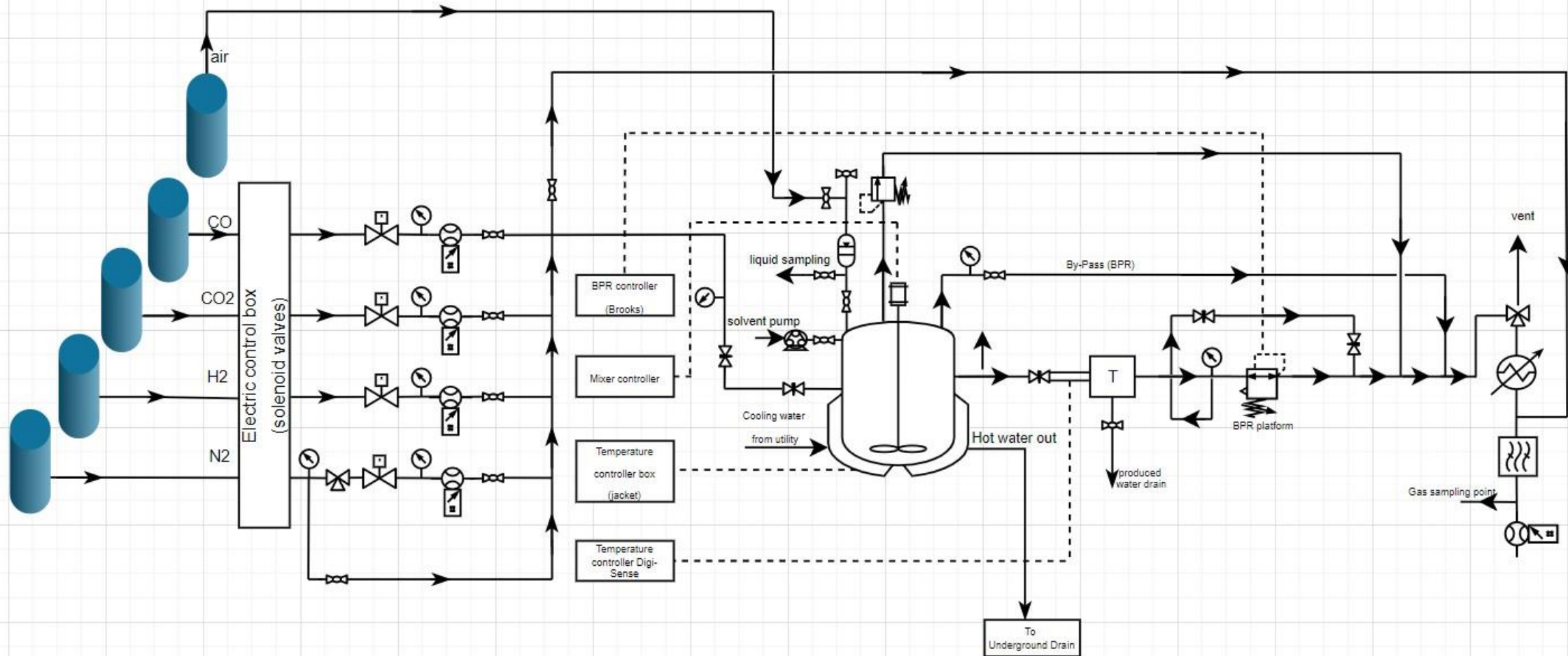
# REACTOR CONFIGURATION



Among the 92 investigations available in the recent literature, 79 were performed in a fixed bed reactor, revealing a huge potential to study other reactor configurations.

# Experimental section (Cont'd)

## Reactor Set-up

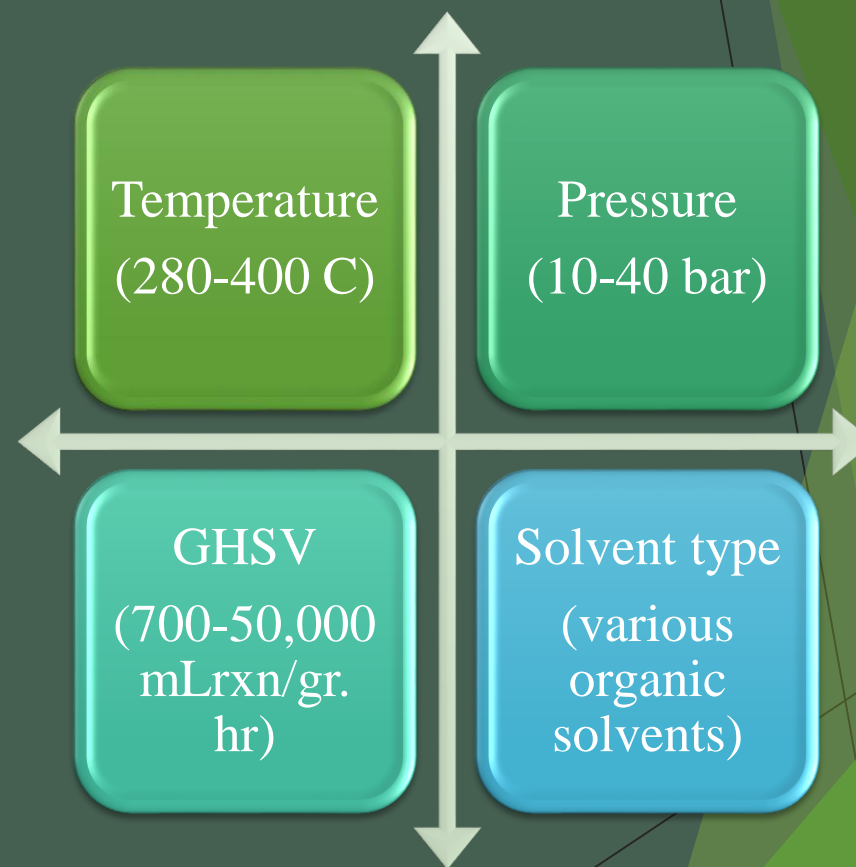


# Experimental section (Cont'd)

## Operating Conditions

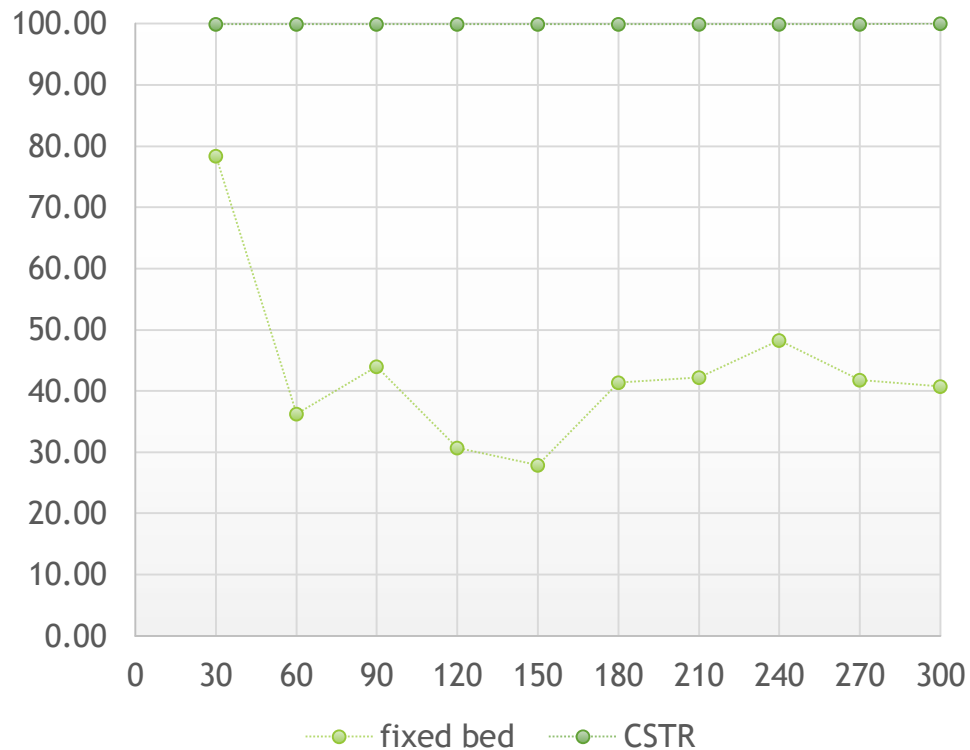
### Pre-treatment conditions:

Item	Desc.	Value
1	Temp.	500 °C
2	Press.	3 bar
3	Flow composition	50 vol% H <sub>2</sub> /N <sub>2</sub>
4	Flow rate	500 mL/min
5	TOS	2 h

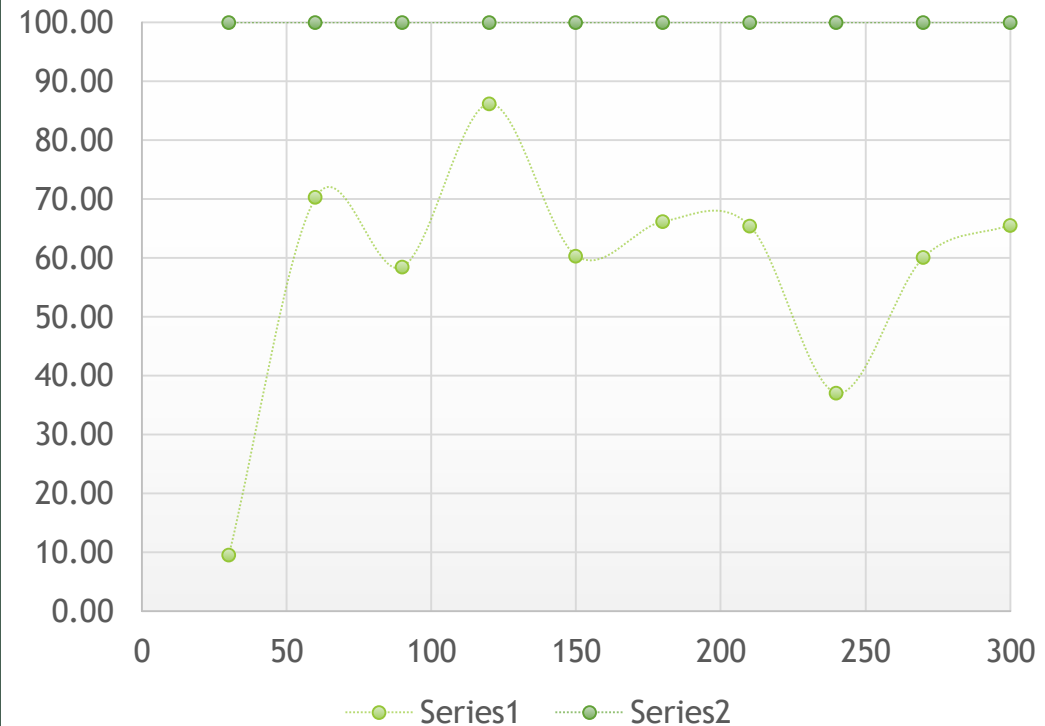


# Effect of reactor configuration on CO<sub>2</sub> Conversion & product Selectivity

CO<sub>2</sub> Conversion (%), Ni/ZrO<sub>2</sub>-HAp, 340 C, 10 bar, GHSV=25,200

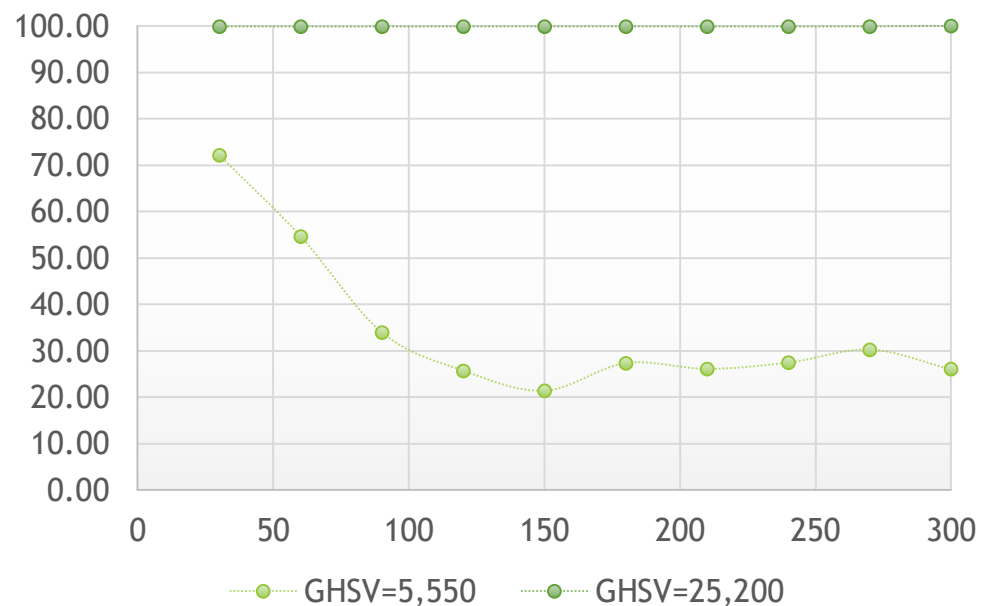


Selectivity (%), Ni/ZrO<sub>2</sub>-HAp, 340 C, 10 bar, GHSV= 25,200

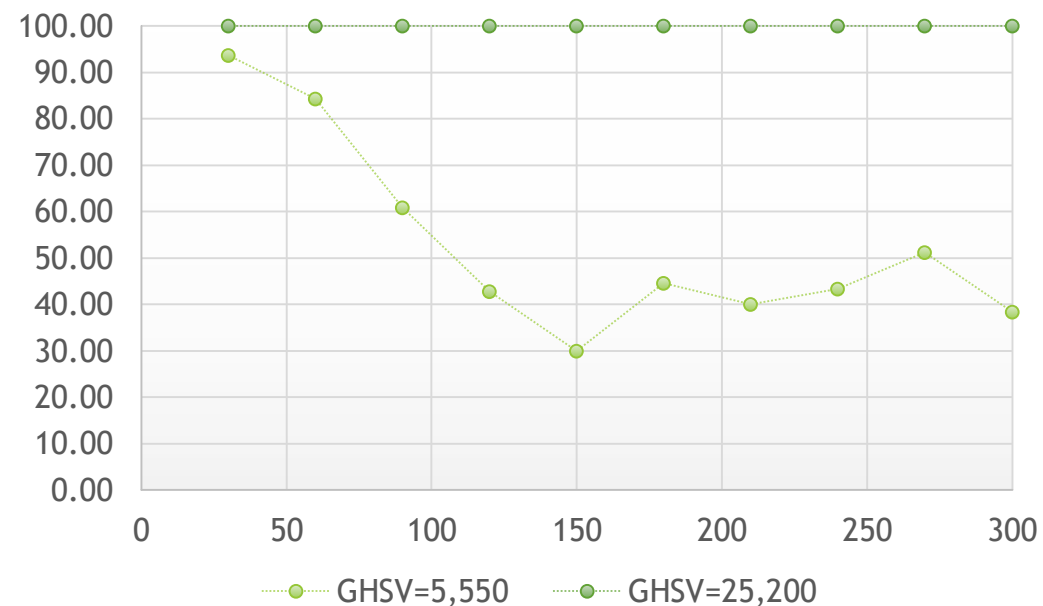


# Effect of GHSV on CO<sub>2</sub> Conversion & product Selectivity

CO<sub>2</sub> Conversion (%), Ni/ZrO<sub>2</sub>-HAp,  
340 C, 10 bar



Selectivity (C<sub>5</sub>+), Ni/ZrO<sub>2</sub>-HAp, 340  
C, 10 bar





## Project 3:

# Pyrolysis and FTS for clean low ILUC biofuels production

Horizon project: *Bridging the gap between phytoremediation solutions on growing energy crops on contaminated lands and clean biofuel production*

Collaborative project GRTP with 18 partners around the world



Growing energy crops on soils contaminated with organic and inorganic pollutants

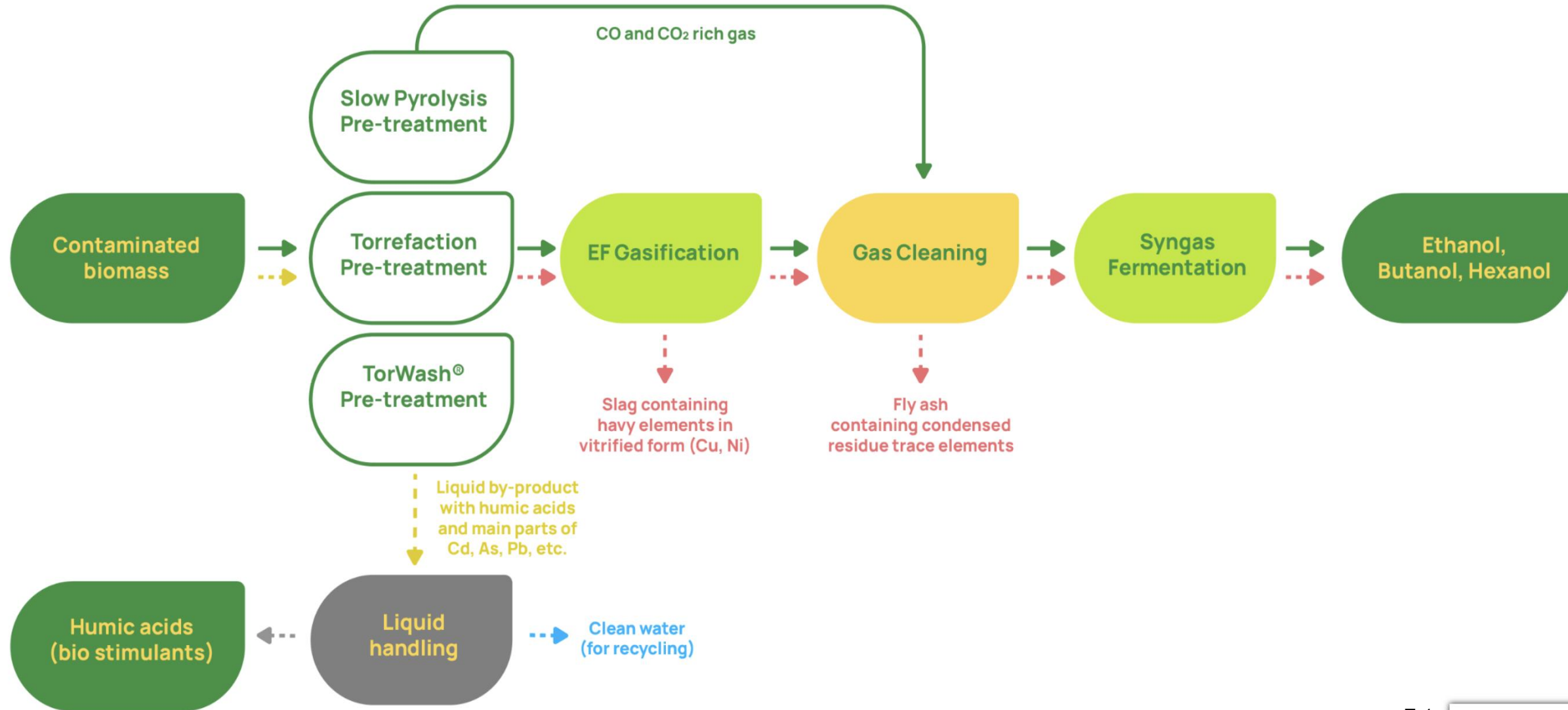


Biofuels with low ILUC risks and contaminants in a concentrated form

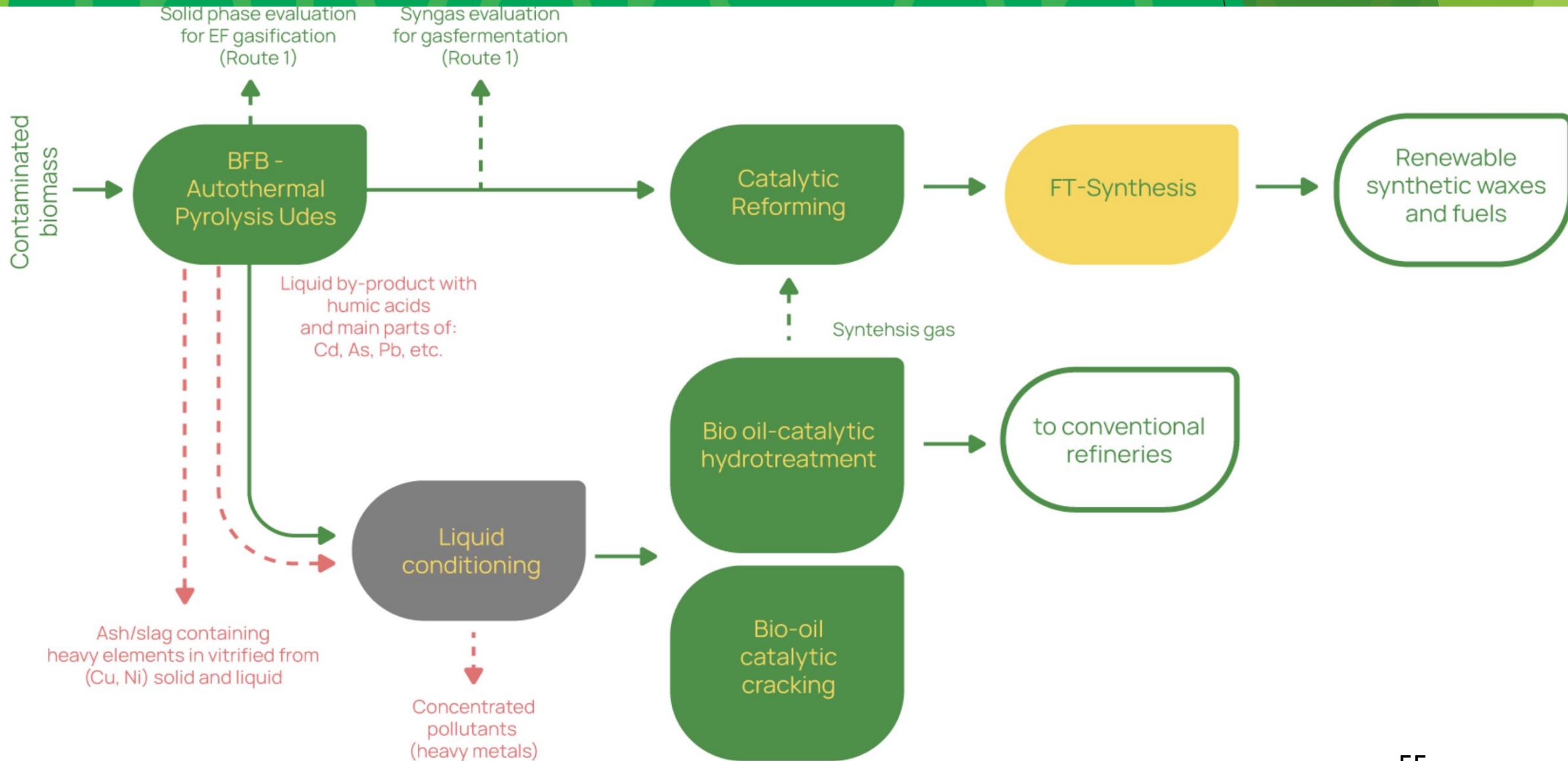


Optimized value chains in terms of cost, sustainability and SDGs

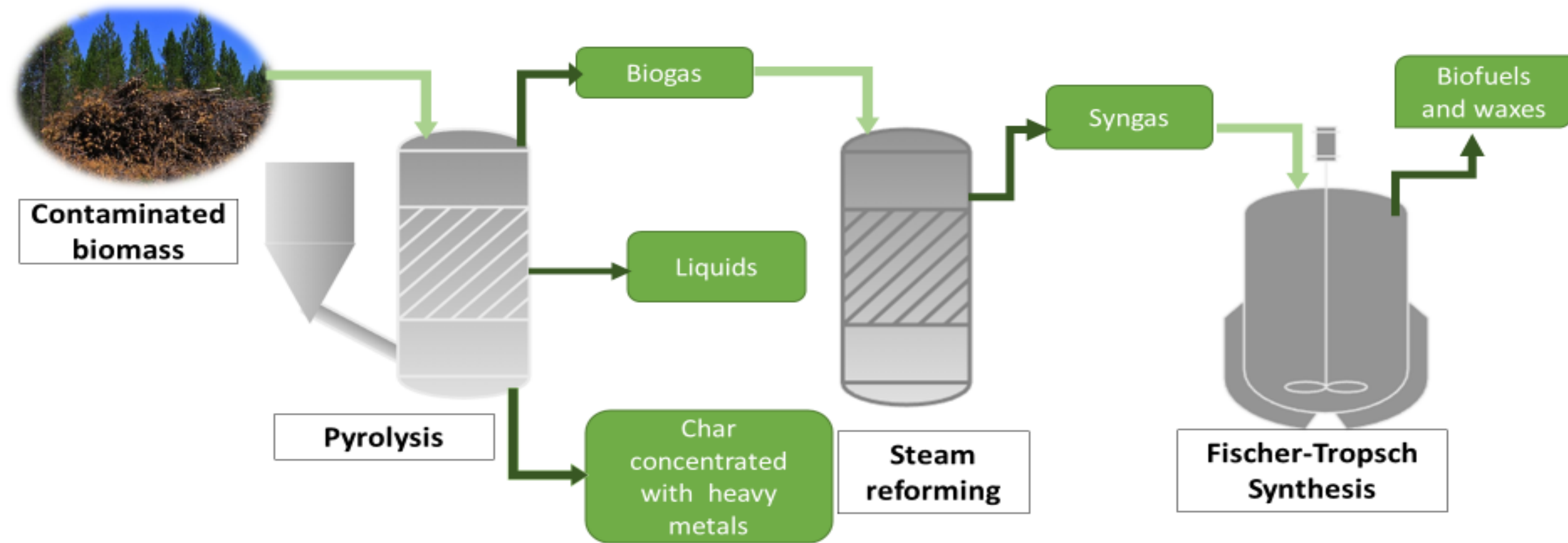
# GOLD –route 1: Biofuels productions



# GOLD –route 2 biofuels productions



# GOLD Project at UDS



# PhD 1 – Pyrolysis of contaminated biomass: Problematic

What is the behavior of heavy metals during the pyrolysis of naturally and artificially contaminated biomasses ?

What is the role of heavy metals during the pyrolysis of biomass

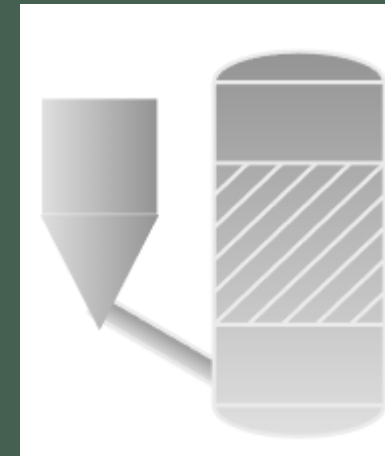
What are the optimal pyrolysis conditions to have an optimal yield of bio-oil with a minimum of heavy metal contamination?

Contamination  
sources

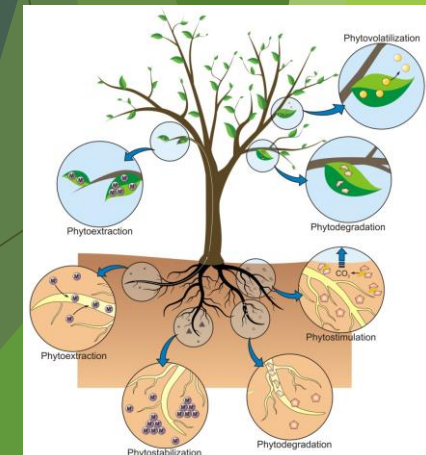


Fate of heavy  
metals

Thermochemical  
conversion



Phytoextraction





# PhD 2 Contaminated lignocellulosic biomass to pyrolysis oil: Analytical and Upgrading studies

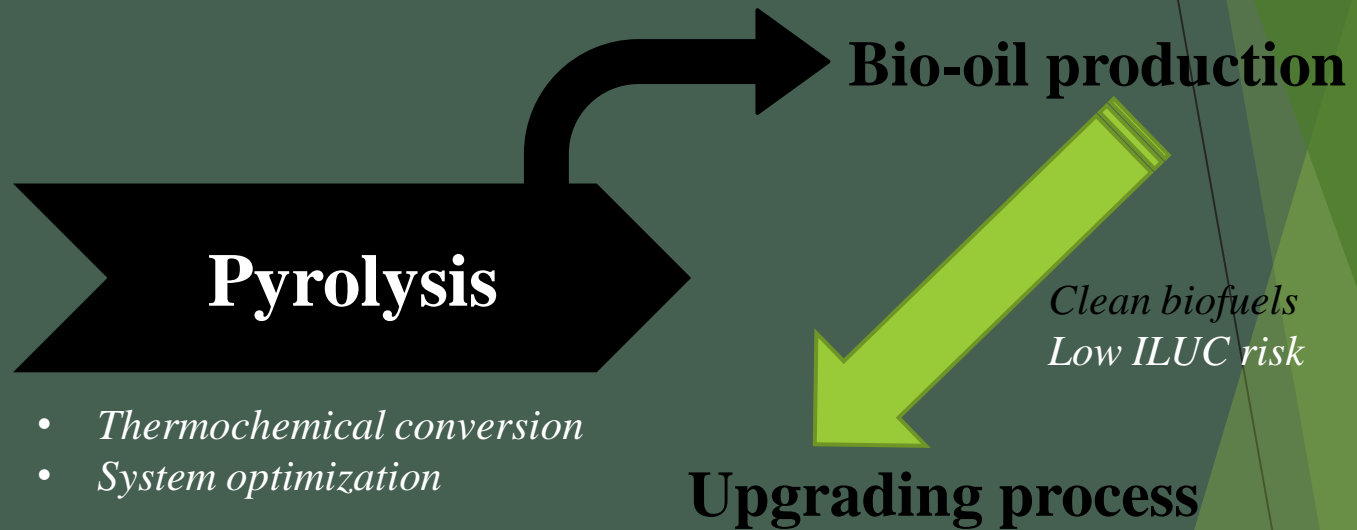
Heavy metal-Contaminated biomass



## Problematic



- How can we fully identify and quantify the chemical composition of the pyrolysis liquid?
- How can we achieve contamination-free bio-oil production



## Problematic



- What is the appropriate route to upgrade the pyrolysis liquid into biofuels and added value chemicals ?

# Phytoremediation to biofuel: Challenges and limitations



The **key challenge** in using biomass for bioenergy is the question of **pollution transfer** and **heavy metal content of biomass**.



**Emissions** that may be generated in the use of contaminated plants for bioenergy.



Bioenergy production with minimal environmental impacts  
*Management of by-products and residual products*



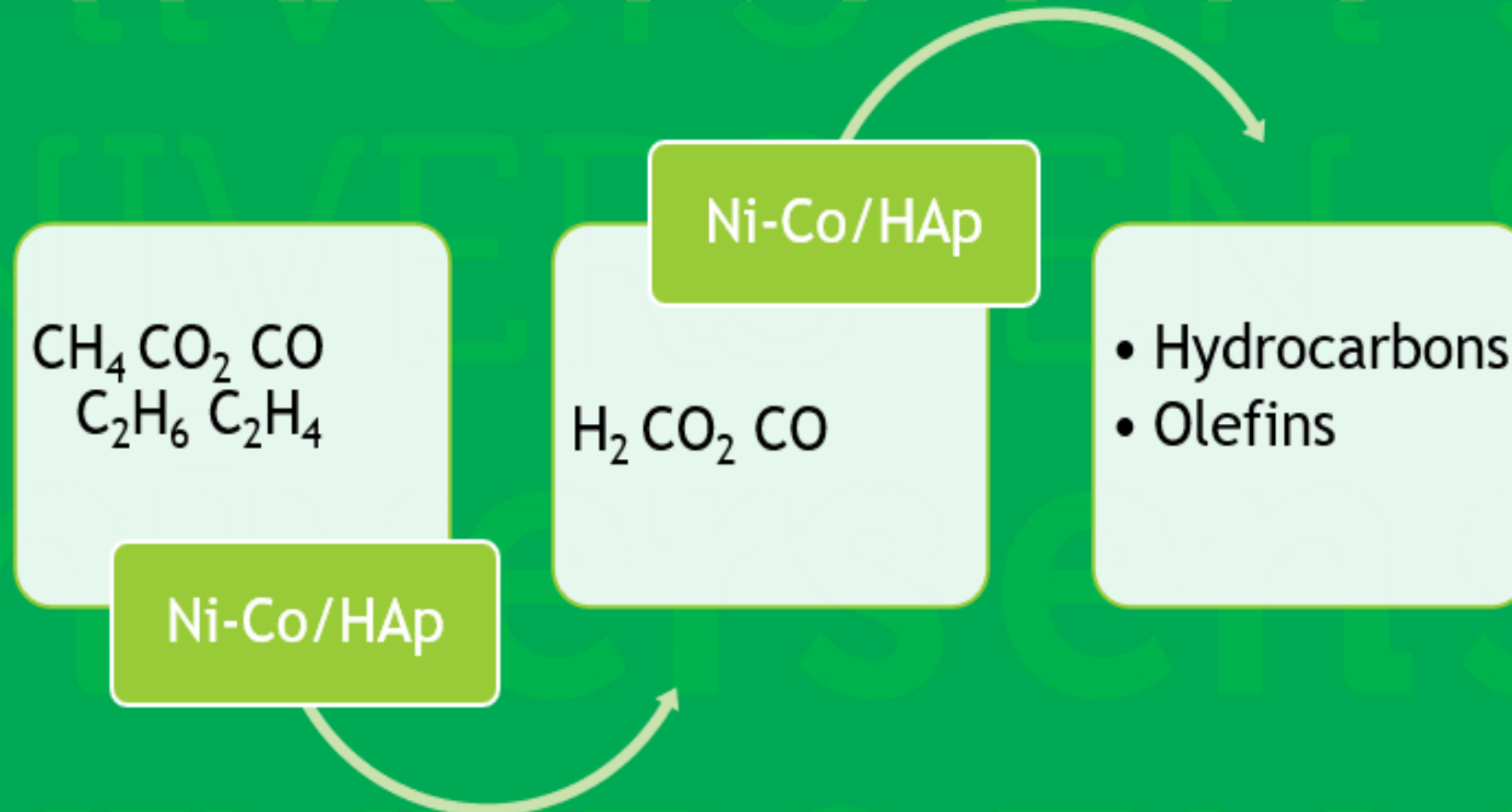
- Extraction of pollutants in concentrated form in the solid part (biochar).
- Valorization of biochar contaminated by heavy metals as a catalyst.



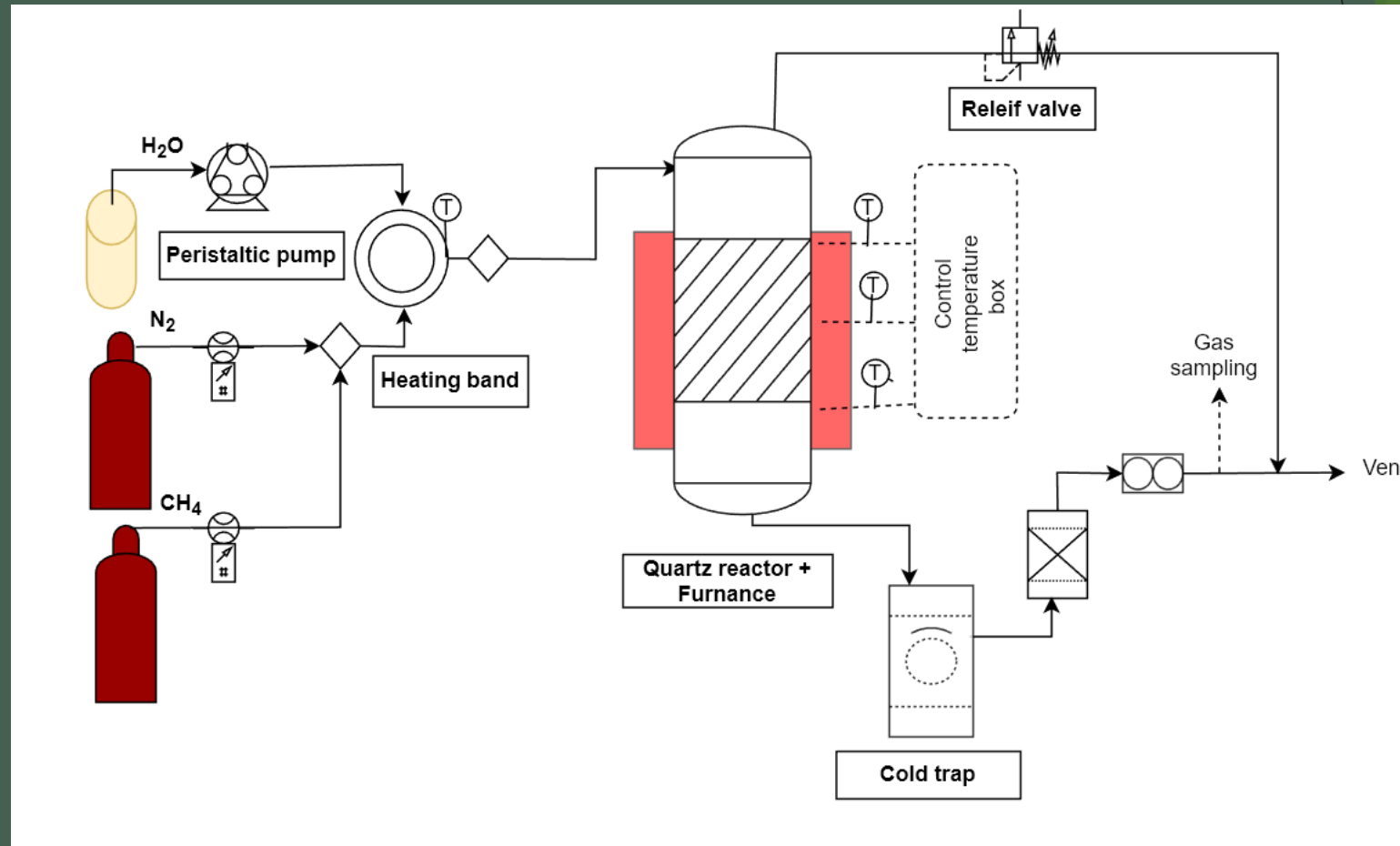
Feedstock for pyrolysis



## PhD 3- Steam reforming and Fischer-Tropsch Synthesis



# Reactor design for steam reforming



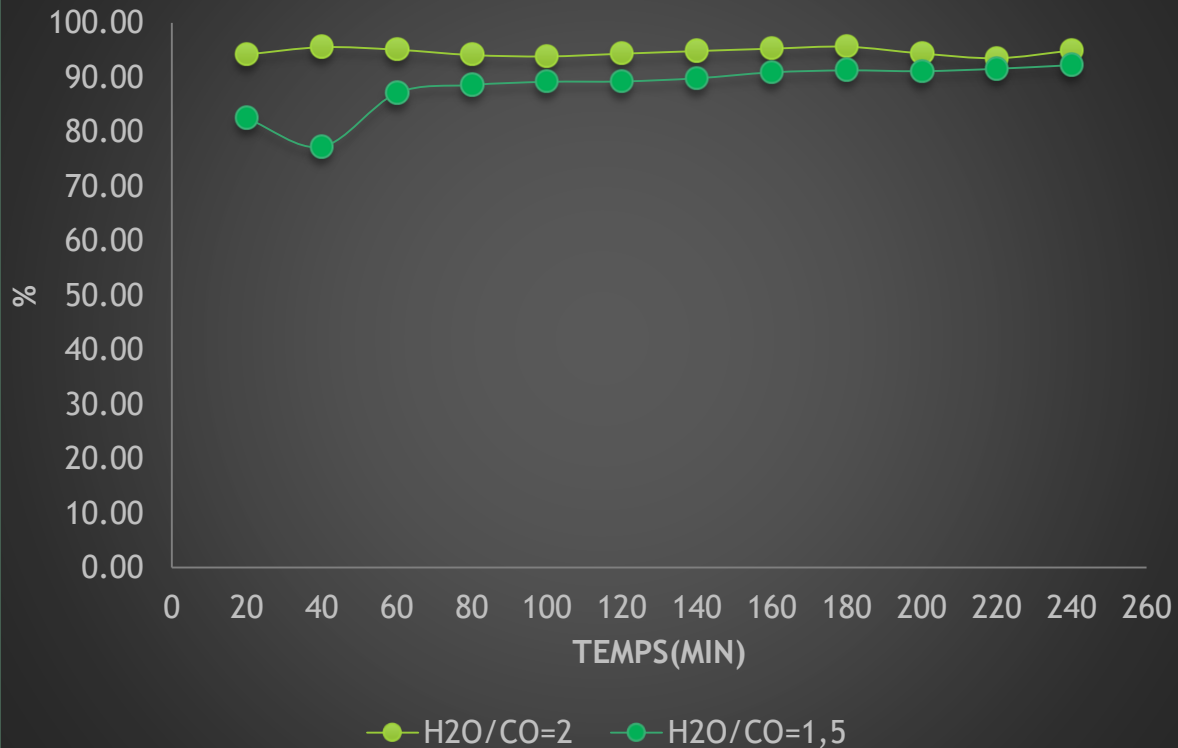
# Operation conditions of the experiment

Run	P (atm)	T (°C)	H <sub>2</sub> O/CH <sub>4</sub>	GHSV (ml.h <sup>-1</sup> .g <sup>-1</sup> <sub>cat</sub> )
1	1	800	2	1656
2	1	800	1,5	1656
3	1	700	2	1656
5	1	800	2	4140

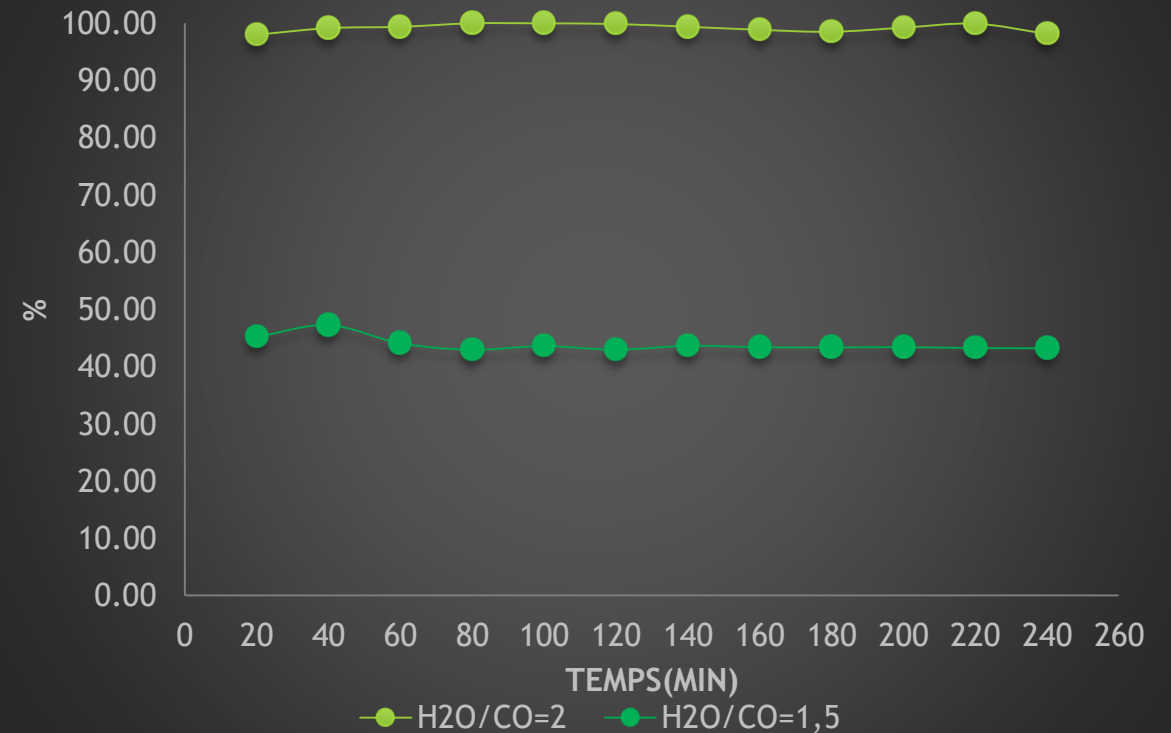


# Effect of H<sub>2</sub>O/CH<sub>4</sub> ratio on catalyst activity

## CH<sub>4</sub> conversion



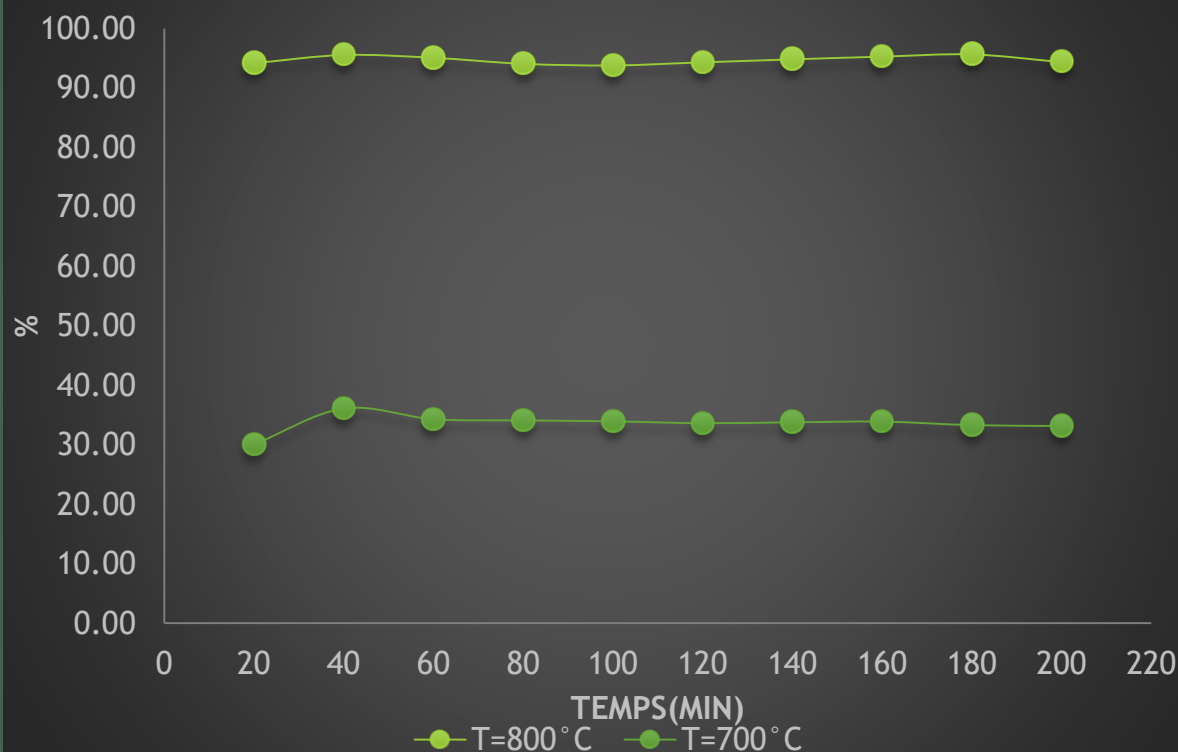
## H<sub>2</sub> selectivity



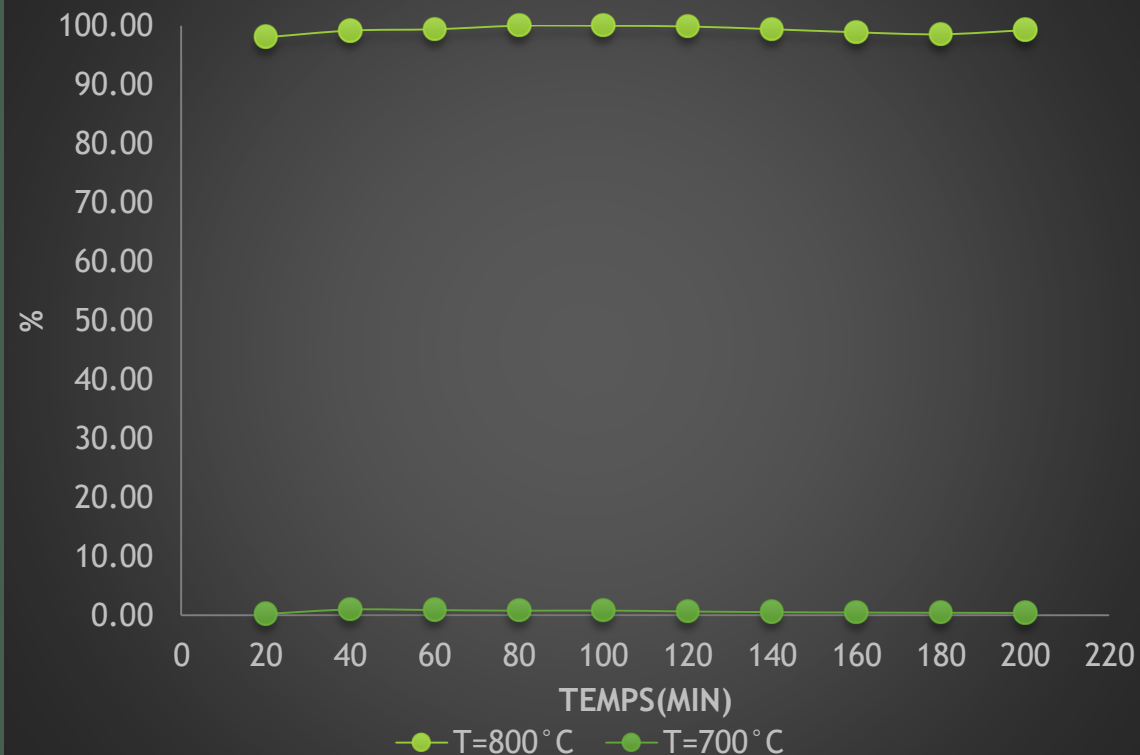
T=800°C, P=1atm, GHSV=1656 ml.h<sup>-1</sup>.g<sup>-1</sup><sub>cat</sub>

# Effect of temperature on catalyst activity

## CH<sub>4</sub> conversion



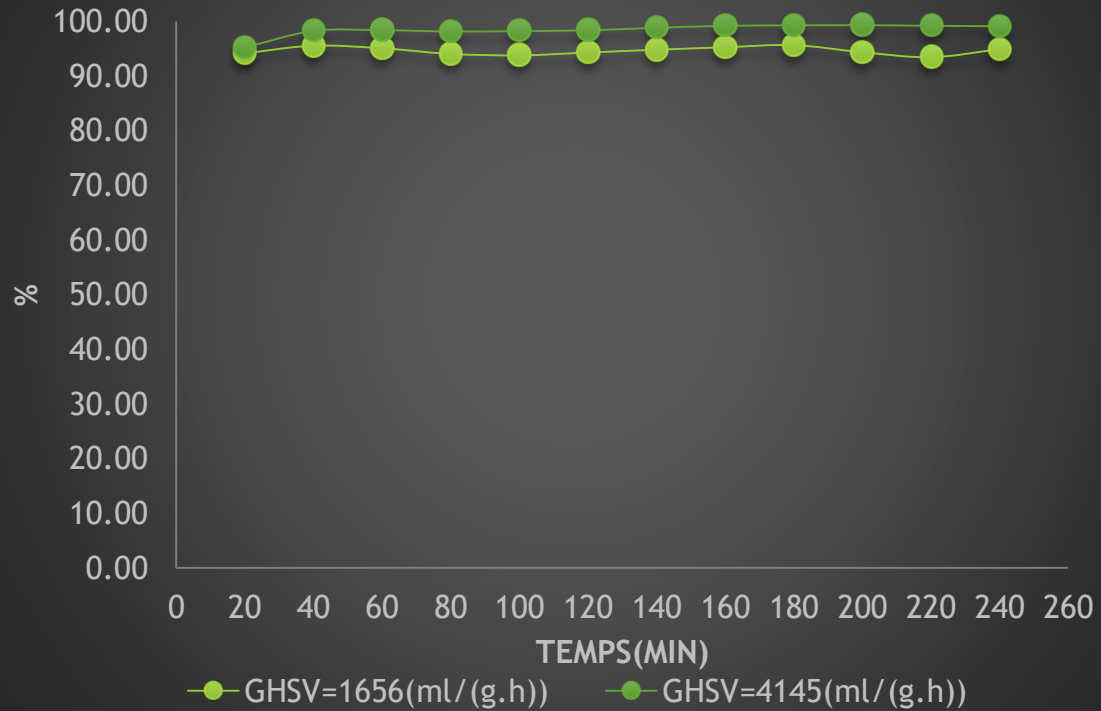
## H<sub>2</sub> Selectivity



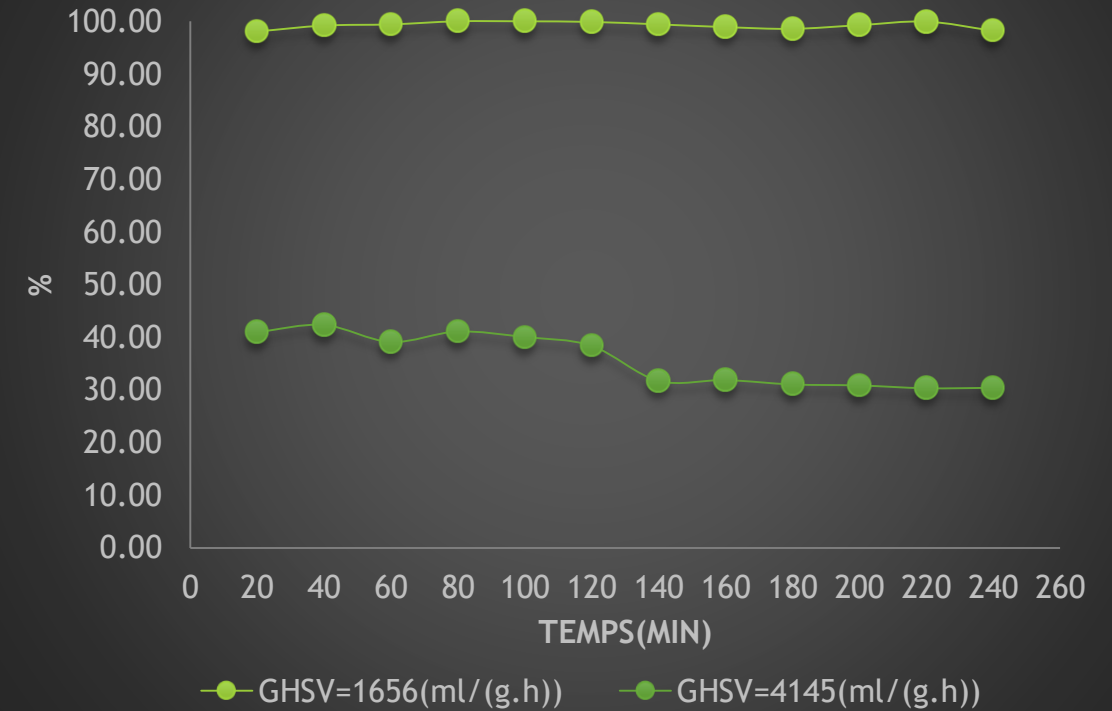
H<sub>2</sub>O/CH<sub>4</sub>=2, P=1atm, GHSV=1656 ml.h<sup>-1</sup>.g<sup>-1</sup><sub>cat</sub>

# Effect of GHSV on catalyst activity

## CH<sub>4</sub> conversion



## H<sub>2</sub> SELECTIVITY



H<sub>2</sub>O/CH<sub>4</sub>=2, P=1atm, T=800°C

# Fischer-Tropsch Synthesis

## I. Fischer-Tropsch reactions and products

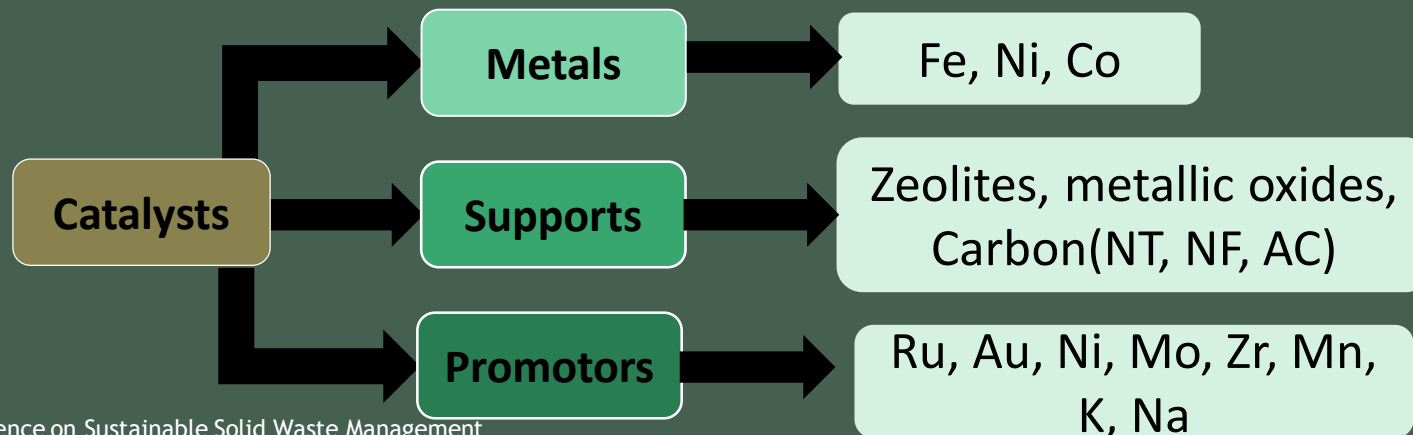
### Main reactions

- |              |   |
|--------------|---|
| 1. Paraffins | $(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$ |
| 2. Olefins   | $2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$       |
| 3. WGS       | $CO + H_2O \rightleftharpoons CO_2 + H_2$         |

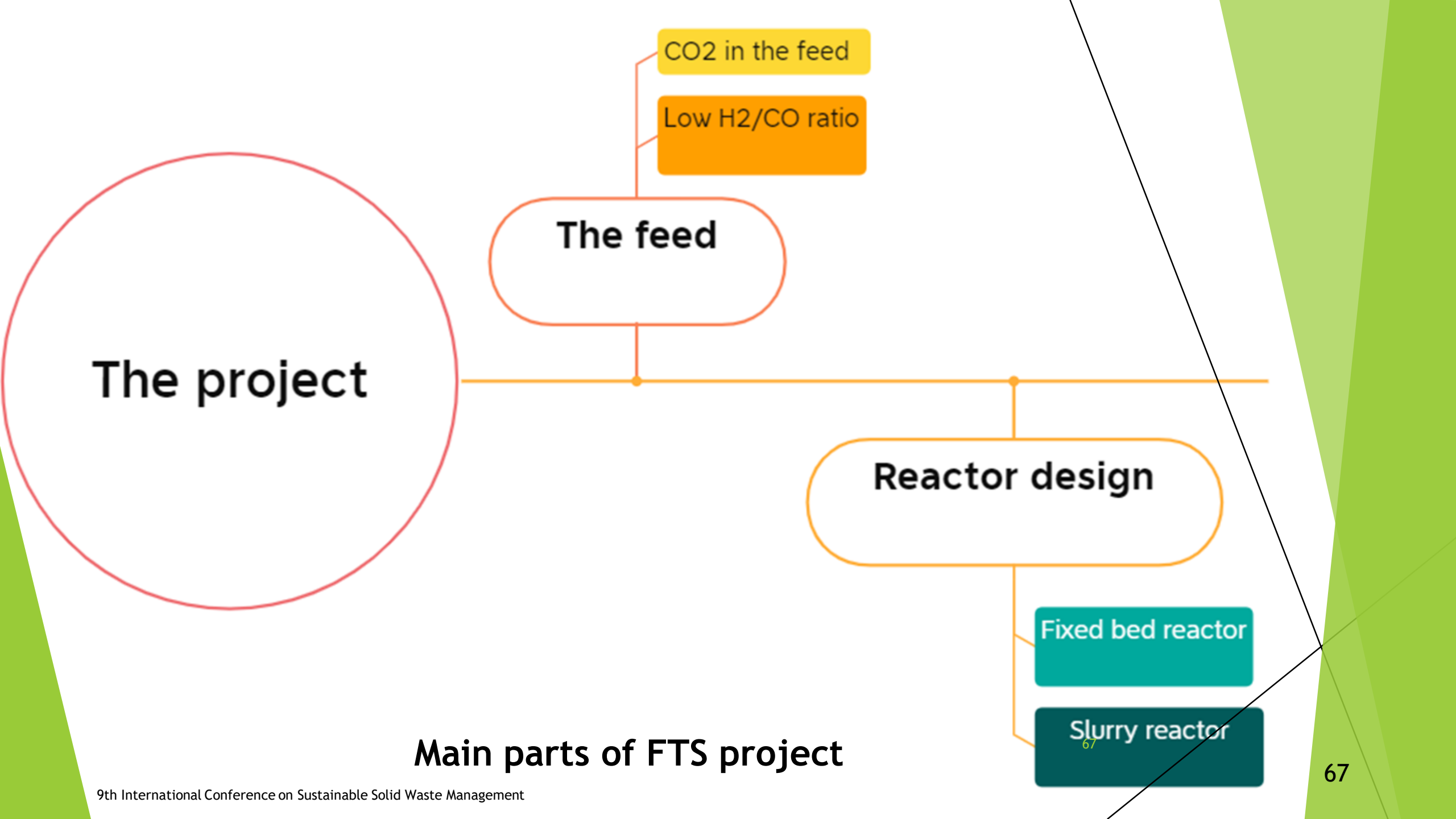
### Secondary reactions

- |                       |  |
|-----------------------|--|
| 4. Alcohols           | $2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n-1)H_2O$ |
| 5. Boudouard reaction | $2CO \rightleftharpoons C + CO_2$                  |

## II. Catalyst formulation used for Fischer-Tropsch Synthesis



9th International Conference on Sustainable Solid Waste Management



**The project**

**The feed**

CO2 in the feed

Low H2/CO ratio

**Reactor design**

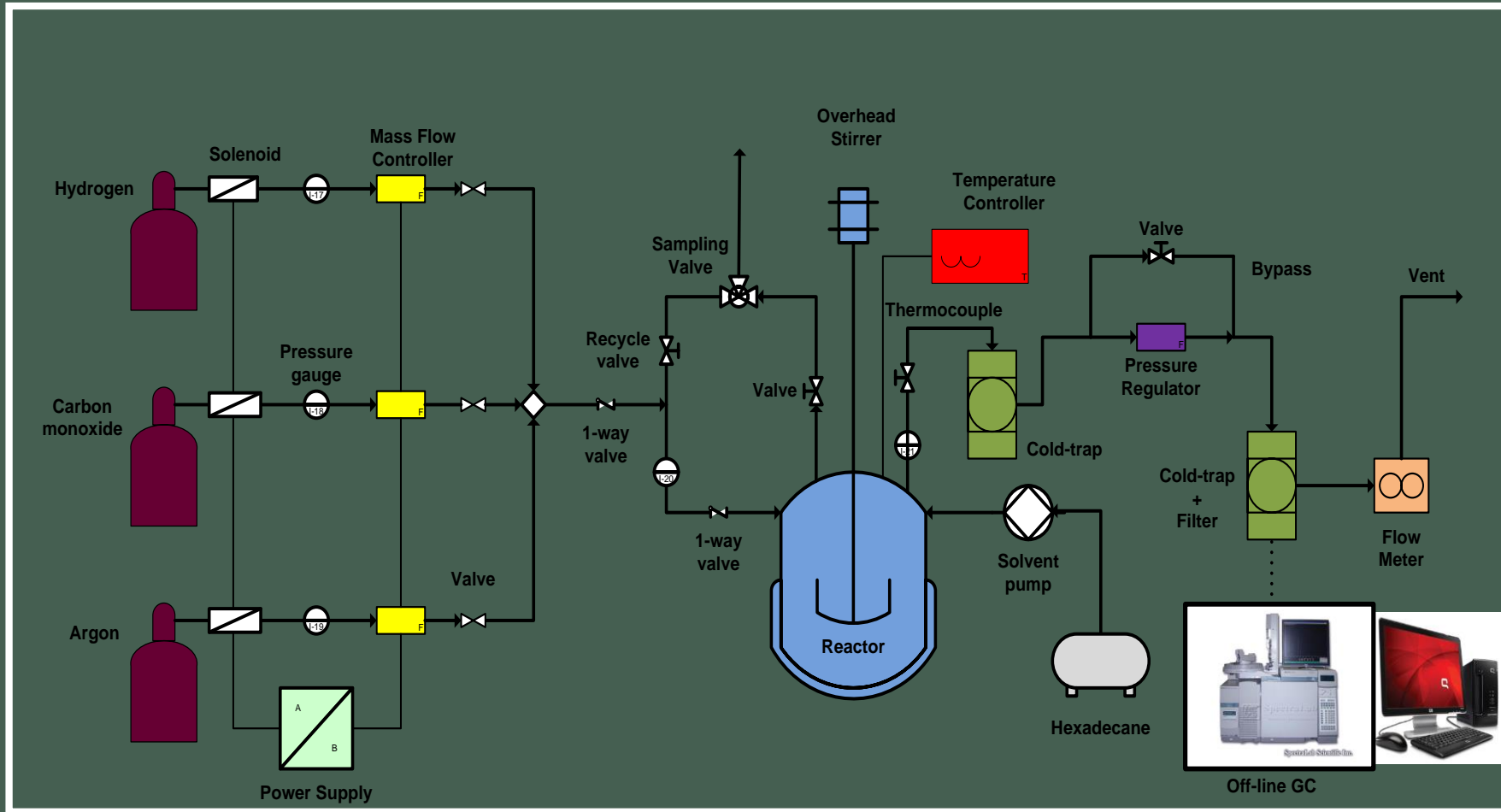
Fixed bed reactor

Slurry reactor

**Main parts of FTS project**



# Reactor design for Fischer-Tropsch Synthesis



*Basket of the reactor*

*Process flow diagram of the 3-φ Mahoney-Robinson slurry reactor-system set-up*



Catalyzing a Greener Future  
Vancouver, Canada, May 16-18, 2022

**CSC2022**

The 26th Canadian Symposium on Catalysis

Thanks for listening!



9th International Conference on Sustainable  
Waste Management  
Université de Sherbrooke



[Ines.Esma.Achouri@USherbrooke.ca](mailto:Ines.Esma.Achouri@USherbrooke.ca)



+1 819 821-8000 (EXT:62408)



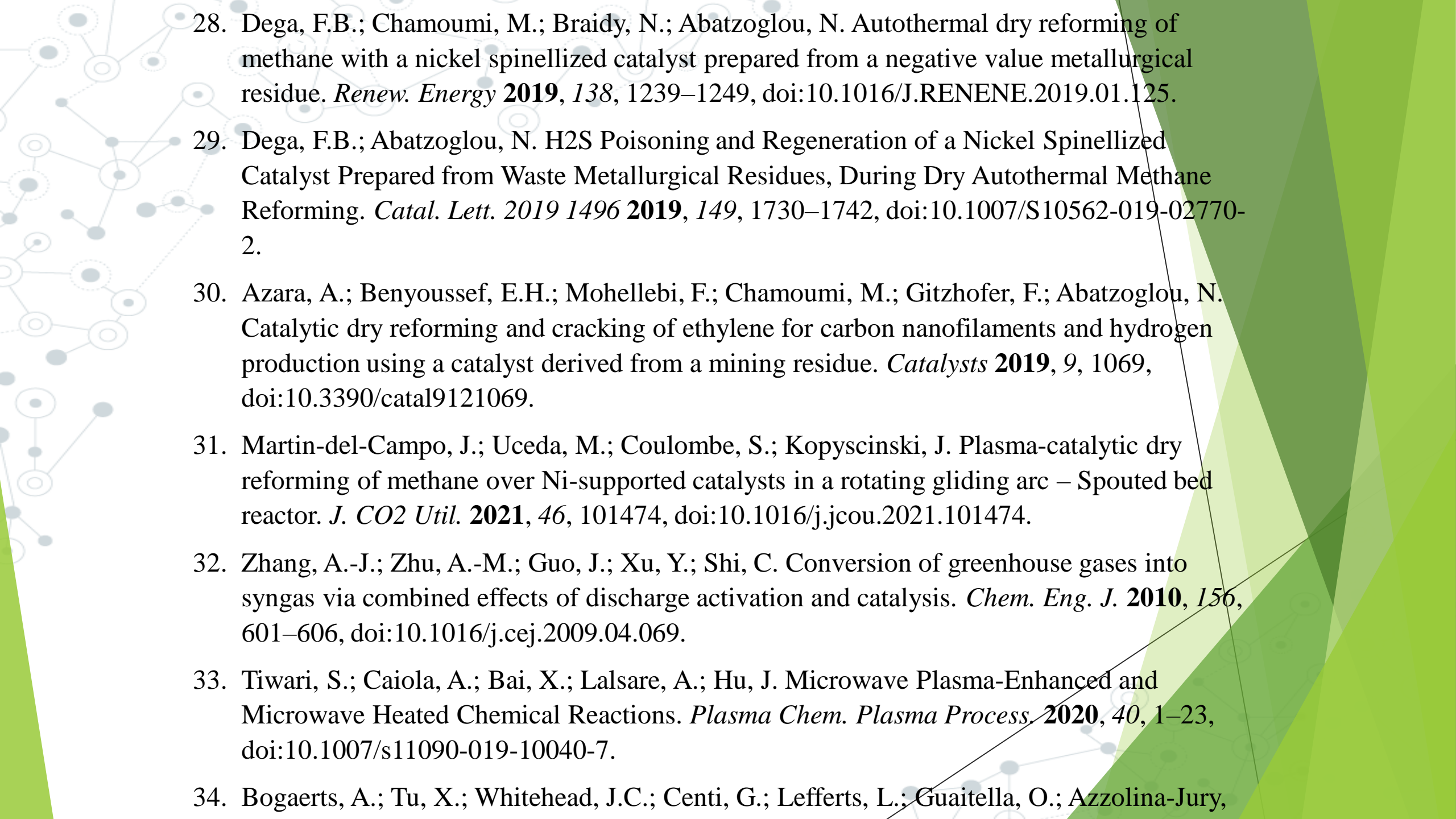
# References

1. Tomishige, K.; Li, D.; Tamura, M.; Nakagawa, Y. Nickel-iron alloy catalysts for reforming of hydrocarbons: Preparation, structure, and catalytic properties. *Catal. Sci. Technol.* 2017, 7, 3952–3979.
2. Li, Z.; Lin, Q.; Li, M.; Cao, J.; Liu, F.; Pan, H.; Wang, Z.; Kawi, S. Recent advances in process and catalyst for CO<sub>2</sub> reforming of methane. *Renew. Sustain. Energy Rev.* 2020, 134, 110312.
3. Terra Plasma.
4. Kinoshita, M.; Fuyuto, T.; Akatsuka, H. Measurement of vibrational and rotational temperature in spark-discharge plasma by optical emission spectroscopy: Change in thermal equilibrium characteristics of plasma under air flow. *Int. J. Engine Res.* **2019**, 20, 746–757, doi:10.1177/1468087418791684.
5. Puliyalil, H.; Lašič Jurković, D.; Dasireddy, V.D.B.C.; Likožar, B. A review of plasma-assisted catalytic conversion of gaseous carbon dioxide and methane into value-added platform chemicals and fuels. *RSC Adv.* 2018, 8, 27481–27508.
6. Snoeckx, R.; Bogaerts, A. Plasma technology-a novel solution for CO<sub>2</sub> conversion? *Chem. Soc. Rev.* 2017, 46, 5805–5863.
7. Morgan, W.L. A critical evaluation of low-energy electron impact cross sections for plasma processing modeling. II: Cl<sub>4</sub>, SiH<sub>4</sub>, and CH<sub>4</sub>. *Plasma Chem. Plasma Process.* **1992**, 12, 477–493. doi:10.1007/BF01447255

11. Andersen, J.A.; Christensen, J.M.; Østberg, M.; Bogaerts, A.; Jensen, A.D. Plasma-catalytic dry reforming of methane: Screening of catalytic materials in a coaxial packed-bed DBD reactor. *Chem. Eng. J.* **2020**, *397*, 125519, doi:10.1016/j.cej.2020.125519.
12. Wang, X.; Gao, Y.; Zhang, S.; Sun, H.; Li, J.; Shao, T. Nanosecond pulsed plasma assisted dry reforming of CH<sub>4</sub>: The effect of plasma operating parameters. *Appl. Energy* **2019**, *243*, 132–144, doi:10.1016/J.APENERGY.2019.03.193.
13. Chung, W.-C.; Pan, K.-L.; Lee, H.-M.; Chang, M.-B. Dry Reforming of Methane with Dielectric Barrier Discharge and Ferroelectric Packed-Bed Reactors. *Energy and Fuels* **2014**, *28*, 7621–7631, doi:10.1021/EF5020555.
14. Pan, K.L.; Chung, W.C.; Chang, M.B. Dry Reforming of CH<sub>4</sub> With CO<sub>2</sub> to Generate Syngas by Combined Plasma Catalysis. *IEEE Trans. Plasma Sci.* **2014**, *42*, 3809–3818, doi:10.1109/TPS.2014.2360238.
15. Esbah Tabaei, P. S., Ghoanneviss, M., & Bozorgzadeh, H. Reforming by Atmospheric Pressure Glow Discharge Plasma Reactor. In Proceedings of the APS March Meeting Abstracts; 2017; pp. G1-099.
16. LI, D.; LI, X.; BAI, M.; Tao, X.; SHANG, S.; Dai, X.; Yin, Y. CO<sub>2</sub> reforming of CH<sub>4</sub> by atmospheric pressure glow discharge plasma: A high conversion ability. *Int. J. Hydrogen Energy* **2009**, *34*, 308–313, doi:10.1016/j.ijhydene.2008.10.053.
17. Zhu, F.; Zhang, H.; Yan, X.; Yan, J.; Ni, M.; Li, X.; Tu, X. Plasma-catalytic reforming of

20. Chun, S.M.; Hong, Y.C.; Choi, D.H. Reforming of methane to syngas in a microwave plasma torch at atmospheric pressure. *J. CO2 Util.* **2017**, *19*, 221–229, doi:10.1016/j.jcou.2017.03.016.
21. Hrycak, B.; Czyrkowski, D.; Jasiński, M.; Dors, M.; Mizeraczyk, J. Hydrogen Production via Synthetic Biogas Reforming in Atmospheric-Pressure Microwave (915 MHz) Plasma at High Gas-Flow Output. *Plasma Chem. Plasma Process.* **2019**, *39*, 695–711, doi:10.1007/S11090-019-09962-Z.
22. Sun, H.; Lee, J.; Bak, M.S. Experiments and modeling of atmospheric pressure microwave plasma reforming of a methane-carbon dioxide mixture. *J. CO2 Util.* **2021**, *46*, 101464, doi:10.1016/J.JCOU.2021.101464.
23. Majd Alawi, N.; Hung Pham, G.; Barifcani, A.; Hoang Nguyen, M.; Liu, S. Syngas formation by dry and steam reforming of methane using microwave plasma technology. In *Proceedings of the IOP Conference Series: Materials Science and Engineering*; Institute of Physics Publishing, 2019; Vol. 579, p. 012022.
24. Alawi, N.M.; Barifcani, A.; Abid, H.R. Optimisation of CH<sub>4</sub> and CO<sub>2</sub> conversion and selectivity of H<sub>2</sub> and CO for the dry reforming of methane by a microwave plasma technique using a Box–Behnken design. *Asia-Pacific J. Chem. Eng.* **2018**, *13*, e2254, doi:10.1002/apj.2254.
25. Wang, Y.F.; Tsai, C.H.; Chang, W.Y.; Kuo, Y.M. Methane steam reforming for produced hydrogen in an atmospheric-pressure microwave plasma reactor. *Int. J. Hydrogen Energy* **2010**, *35*, 135–140, doi:10.1016/J.IJHYDENE.2009.10.088.



- 
28. Dega, F.B.; Chamoumi, M.; Braid, N.; Abatzoglou, N. Autothermal dry reforming of methane with a nickel spinellized catalyst prepared from a negative value metallurgical residue. *Renew. Energy* **2019**, *138*, 1239–1249, doi:10.1016/J.RENENE.2019.01.125.
29. Dega, F.B.; Abatzoglou, N. H<sub>2</sub>S Poisoning and Regeneration of a Nickel Spinellized Catalyst Prepared from Waste Metallurgical Residues, During Dry Autothermal Methane Reforming. *Catal. Lett.* **2019**, *149*, 1730–1742, doi:10.1007/S10562-019-02770-2.
30. Azara, A.; Benyoussef, E.H.; Mohellebi, F.; Chamoumi, M.; Gitzhofer, F.; Abatzoglou, N. Catalytic dry reforming and cracking of ethylene for carbon nanofilaments and hydrogen production using a catalyst derived from a mining residue. *Catalysts* **2019**, *9*, 1069, doi:10.3390/catal9121069.
31. Martin-del-Campo, J.; Uceda, M.; Coulombe, S.; Kopyscinski, J. Plasma-catalytic dry reforming of methane over Ni-supported catalysts in a rotating gliding arc – Spouted bed reactor. *J. CO<sub>2</sub> Util.* **2021**, *46*, 101474, doi:10.1016/j.jcou.2021.101474.
32. Zhang, A.-J.; Zhu, A.-M.; Guo, J.; Xu, Y.; Shi, C. Conversion of greenhouse gases into syngas via combined effects of discharge activation and catalysis. *Chem. Eng. J.* **2010**, *156*, 601–606, doi:10.1016/j.cej.2009.04.069.
33. Tiwari, S.; Caiola, A.; Bai, X.; Lalsare, A.; Hu, J. Microwave Plasma-Enhanced and Microwave Heated Chemical Reactions. *Plasma Chem. Plasma Process.* **2020**, *40*, 1–23, doi:10.1007/s11090-019-10040-7.
34. Bogaerts, A.; Tu, X.; Whitehead, J.C.; Centi, G.; Lefferts, L.; Guaitella, O.; Azzolina-Jury,