URCA-Luke webinar #2

J n 17th 2023

Institut de Thermique, Mécanique, Matériaux

UNIVERSITÉ DE REIMS CHAMPAGNE-ARDENNE

VALORIZATION OF BIOMASS INTO HYDROGEN OR SYNGAS BY A THERMAL PROCESS

Speakers :

A/Prof. Jaona RANDRIANALISOA

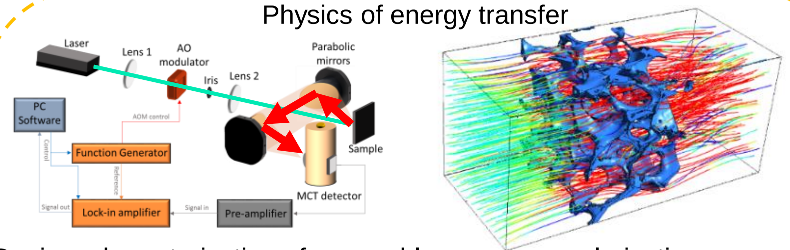
Dr. MSc. Mira ABOU RJEILY

Outline

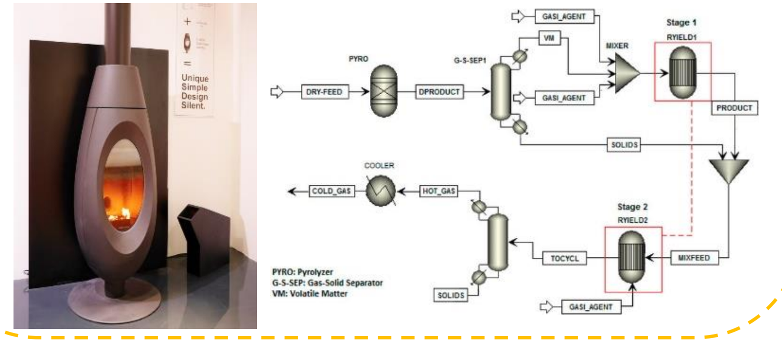
The Institute

Team 1: Energy and Heat Transfer Physics

Physics of energy transfer



Design, characterization of renewable resources valorization processes



18 Researchers

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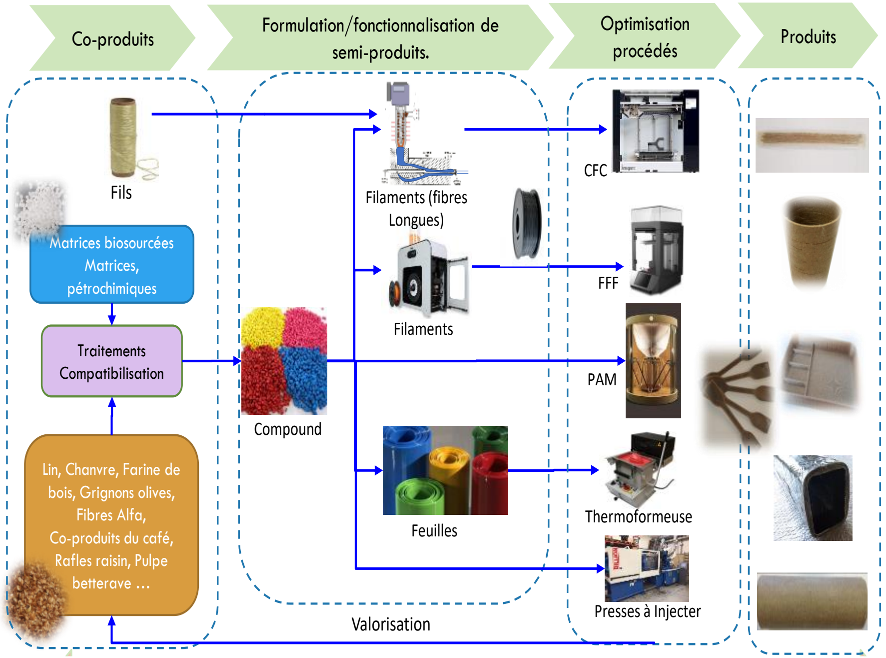
Institut de Thermique, Mécanique, Matériaux
53 Researchers

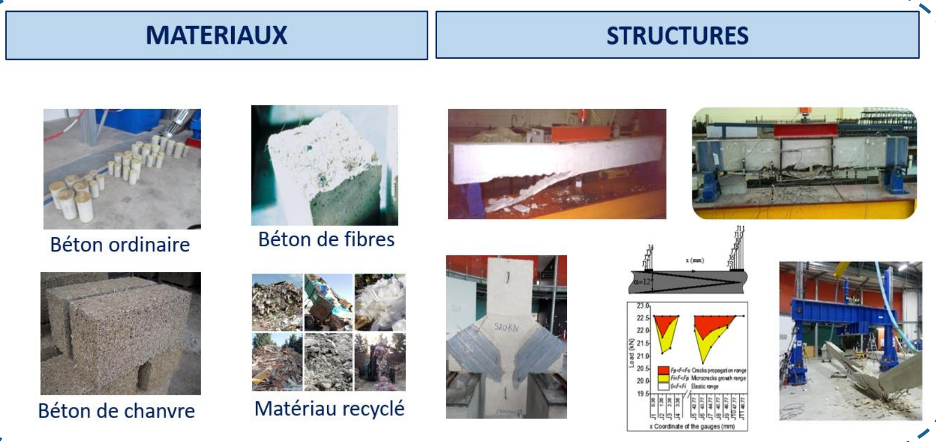
Team 2: Materials and Innovative Processes



18 Researchers

Team 3: Mechanics applied to Civil Engineering

17 Researchers



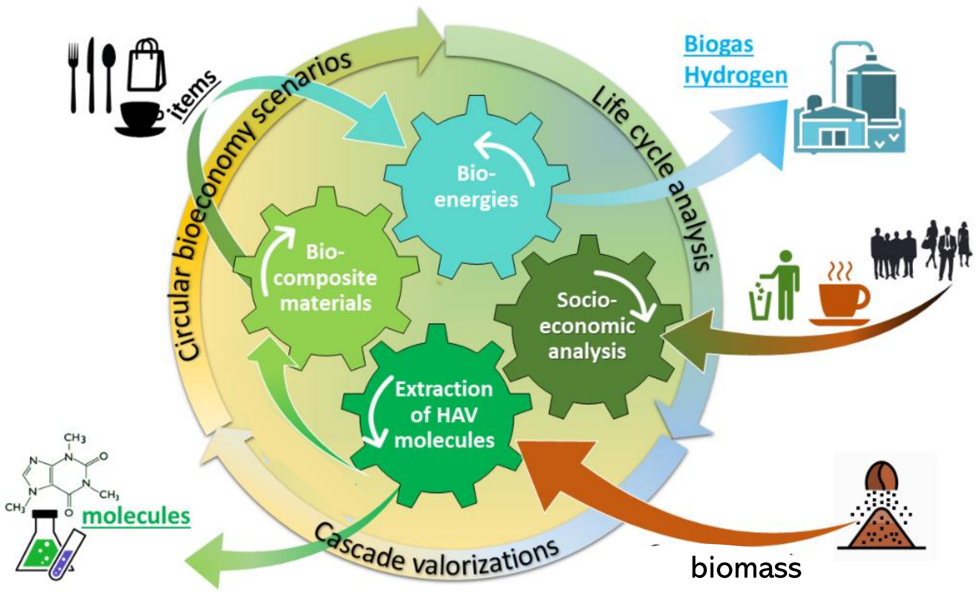
The Institute

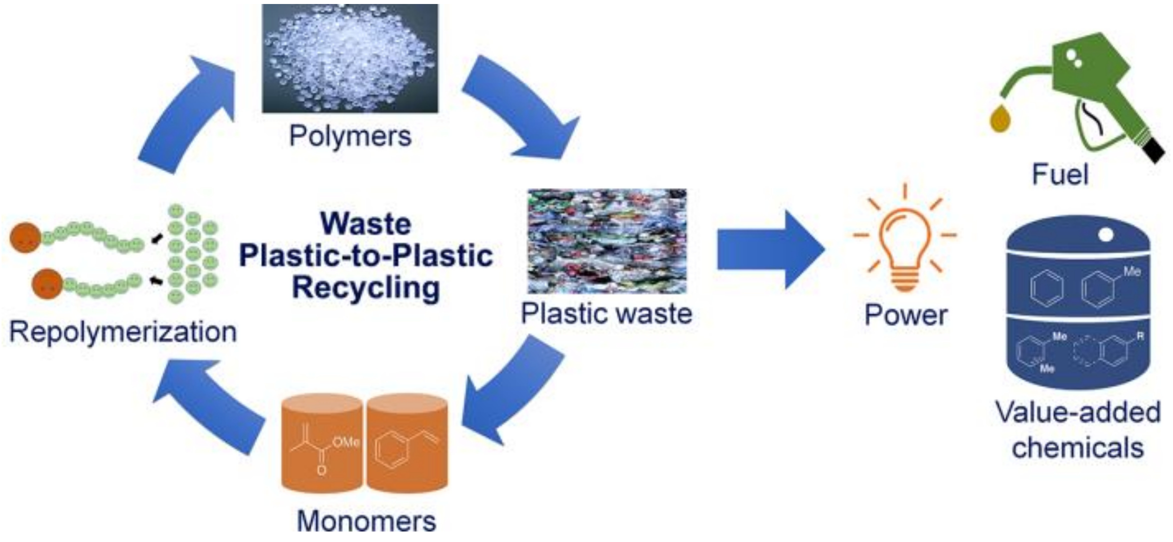
Team 1: Energy and Heat Transfer Physics

Overall objective of Team 1 > axis #3:

Valorization of Renewable resources (biomass, sun, waste ...) for Energy purposes

- Develop efficient approaches
- (Bio sourced) wastes reaching the end of *circular economy cycle*
- High added value energy vectors (syngas, hydrogen…)





Introduction

Pollution

Growing carbon emission

Fossil fuel depletion

Global warming

Climate change

Alternative renewable sustainable energy (solar, wind, hydro, tidal, geothermal biomass…)

Provide the global energy demand for electricity, fuels and H_2 (transportation and power generation)

Introduction

Present and future hydrogen applications

Industry feedstock

- **Petroleum refinery (38.2 MT)**: water treatment, hydrocracking
- **Ammonia production (31.5 MT)**

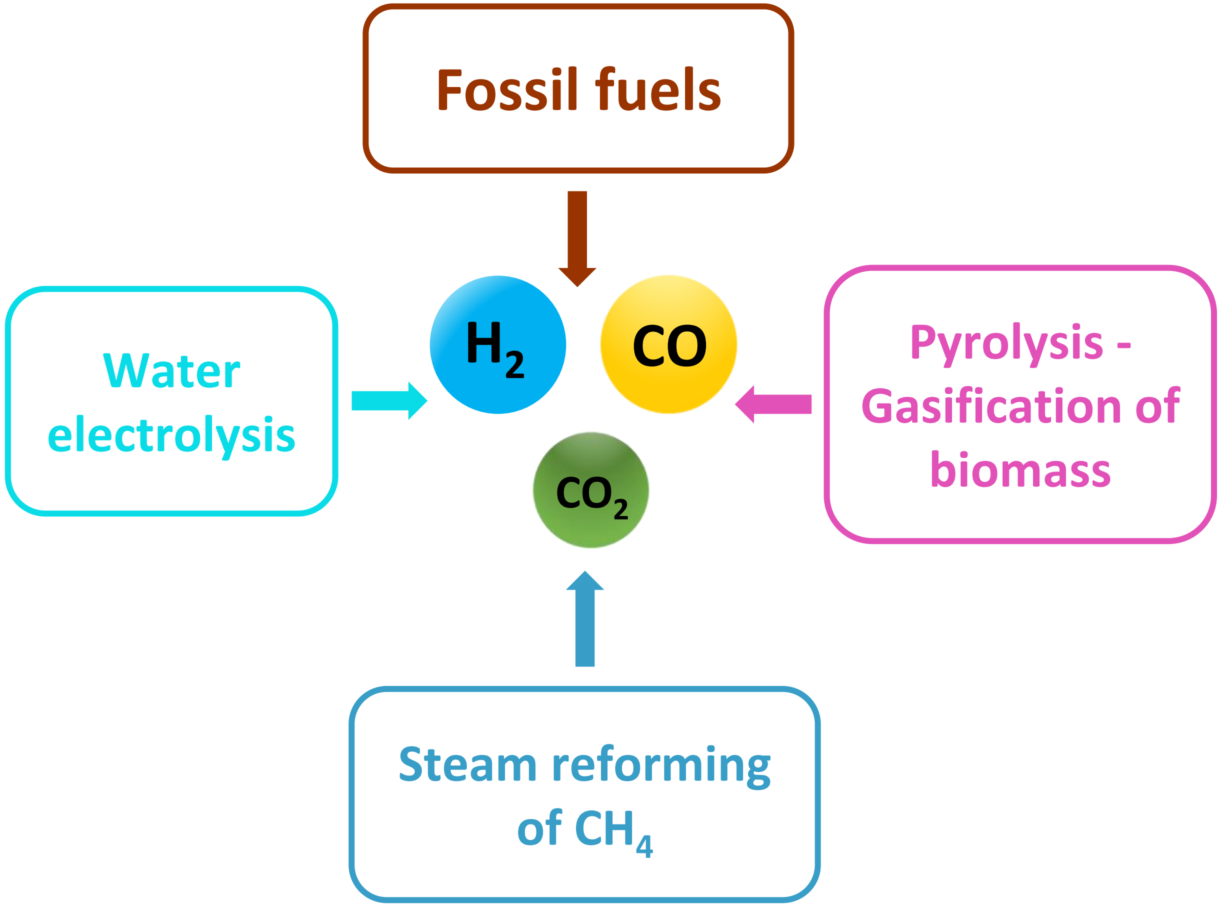
Power and heat generation

- Power generation for grid
- Heat/power for building and industry
- H_2 addition to natural gas

Transportation

- H_2 powered vehicles, trains, aircraft, shipping
- Fuel cell forklifts

Overview of syngas production

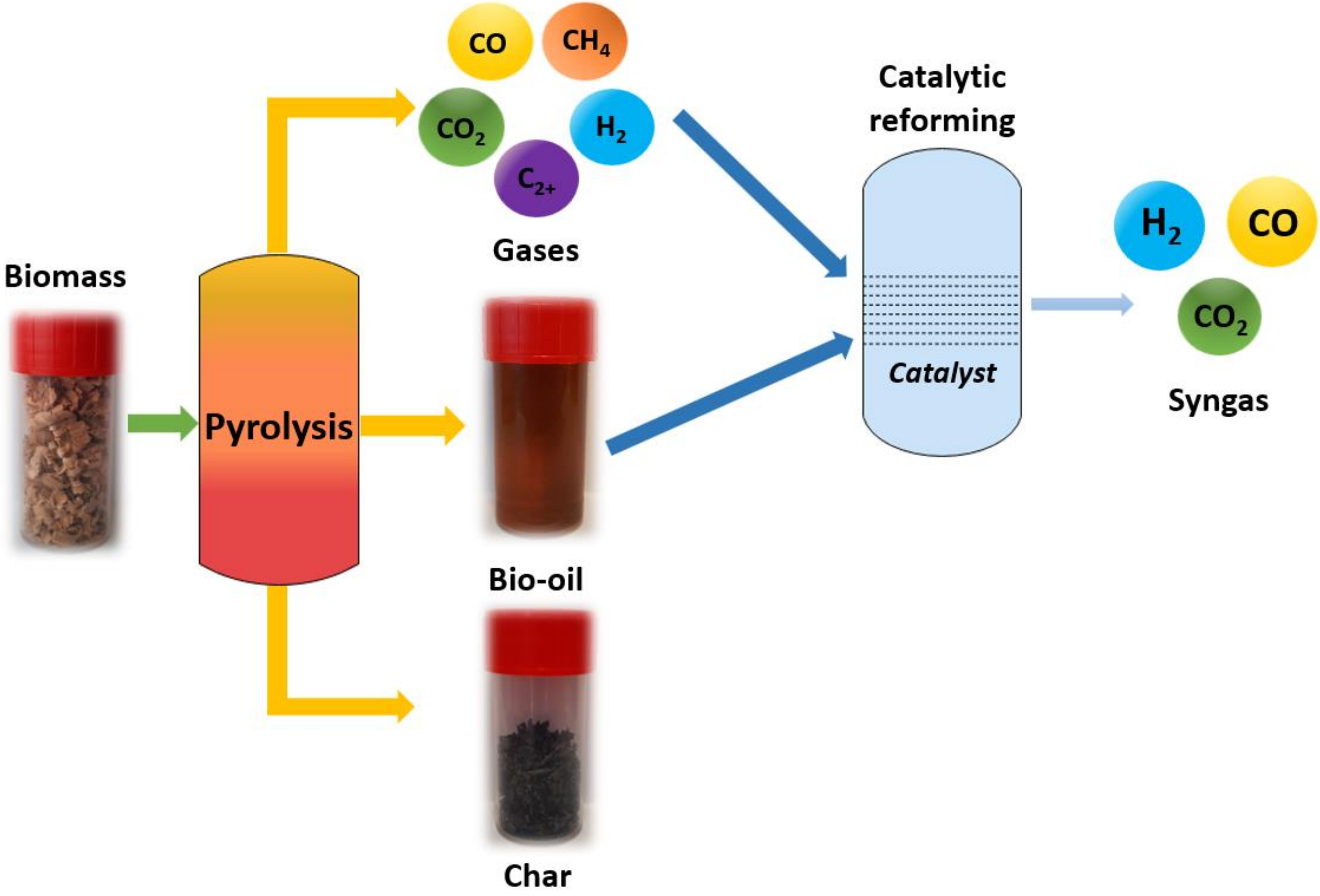


Introduction

Improve the production of syngas (H_2) while reducing CO_2 and CH_4 (greenhouse gases) by valorizing the biomass (pyrolysis/catalytic reforming)

Parameters:
- Catalyst active phase
- Temperature
- External steam feed

Products:
- Gas, bio-oil, char
- Conversion rates
- Syngas production



Introduction

Dry reforming (CO_2)

- **Methane:**

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$$

- **Bio-oil:**

$$C_nH_x + nCO_2 \rightarrow \left(\frac{x}{2}\right) H_2 + 2nCO$$

Steam reforming (H_2O)

- **Methane:**

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO$$

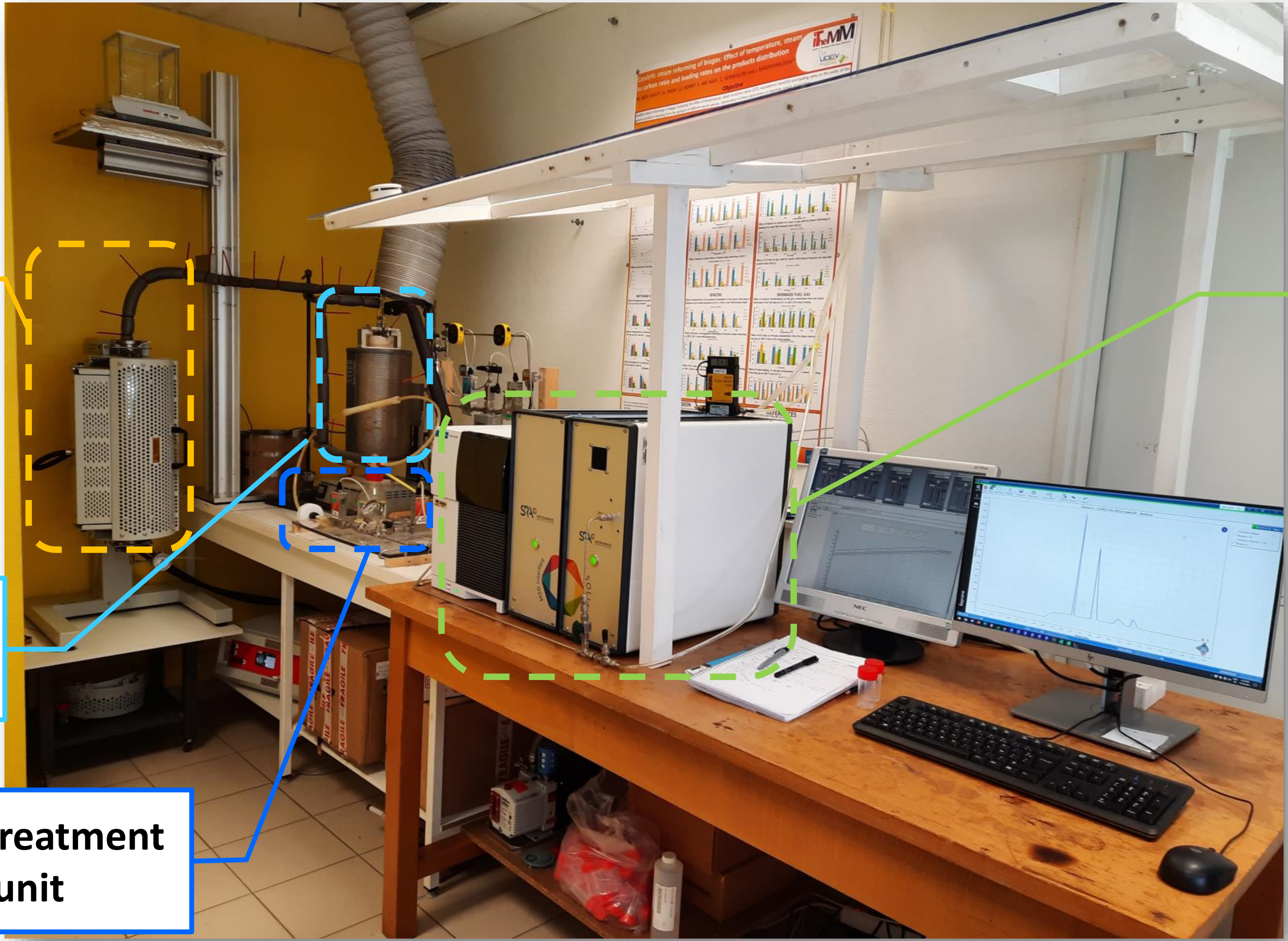
- **Bio-oil:**

$$C_nH_x + nH_2O \rightarrow \left(n + \frac{x}{2}\right) H_2 + nCO$$

Hybrid reforming:

CO_2 et H_2O vapor produced by the biomass pyrolysis → reactants for the reforming of the pyrolysis volatiles

Materials and Methods



Pyrolysis unit

Reforming unit

Post-treatment unit

Gaseous products analysis (µGC/MS)

Materials and Methods

Parameter ranges:

Pyrolysis unit:

- Biomass: up to **10g**
- Temperature: **300 – 800°C**
- Heating rate: **5 – 100°C/min**
- Volatiles residence time: **50 – 250 s**

Catalytic reforming unit:

- Gas and bio-oil volatiles
- Temperature: **600 – 800°C**
- GHSV: **900 - 25000 h^{-1}**
- Volatiles residence time: **10 – 120 s**

Carrier gas:

- Nature: **nitrogen, air or water vapor**
- Flowrate: **25 – 300 mL/min**

Catalyst:

- Type: **bulk or supported on alumina**
- Active phase: **Nickel, Cobalt, Cobalt-Nickel**
- Metal loading: **0 – 30%**

Materials and Methods

Characterizations:

Biomass

- Elemental analysis (C, H, O, N, S…)
- Chemical composition (cellulose, hemicellulose, lignin)
- Physical properties (density, size, porosity)

Bio-oil

- Chemical composition:
  BTEX,
  phenols,
  PAH (polycyclic aromatic hydrocarbons),
  others (furfural)

Catalyst

- TGA (Thermogravimetric Analysis)
- DTA (Differential Thermal Analysis)
- Porosimetry analysis, BET surface area
- XRD (X-ray diffraction)
- SEM (Scanning Electron Microscopy) images
- EDX (Energy-dispersive X-ray spectroscopy)

Materials and Methods

Biomass

Oak wood chips

Flax shives

Catalysts

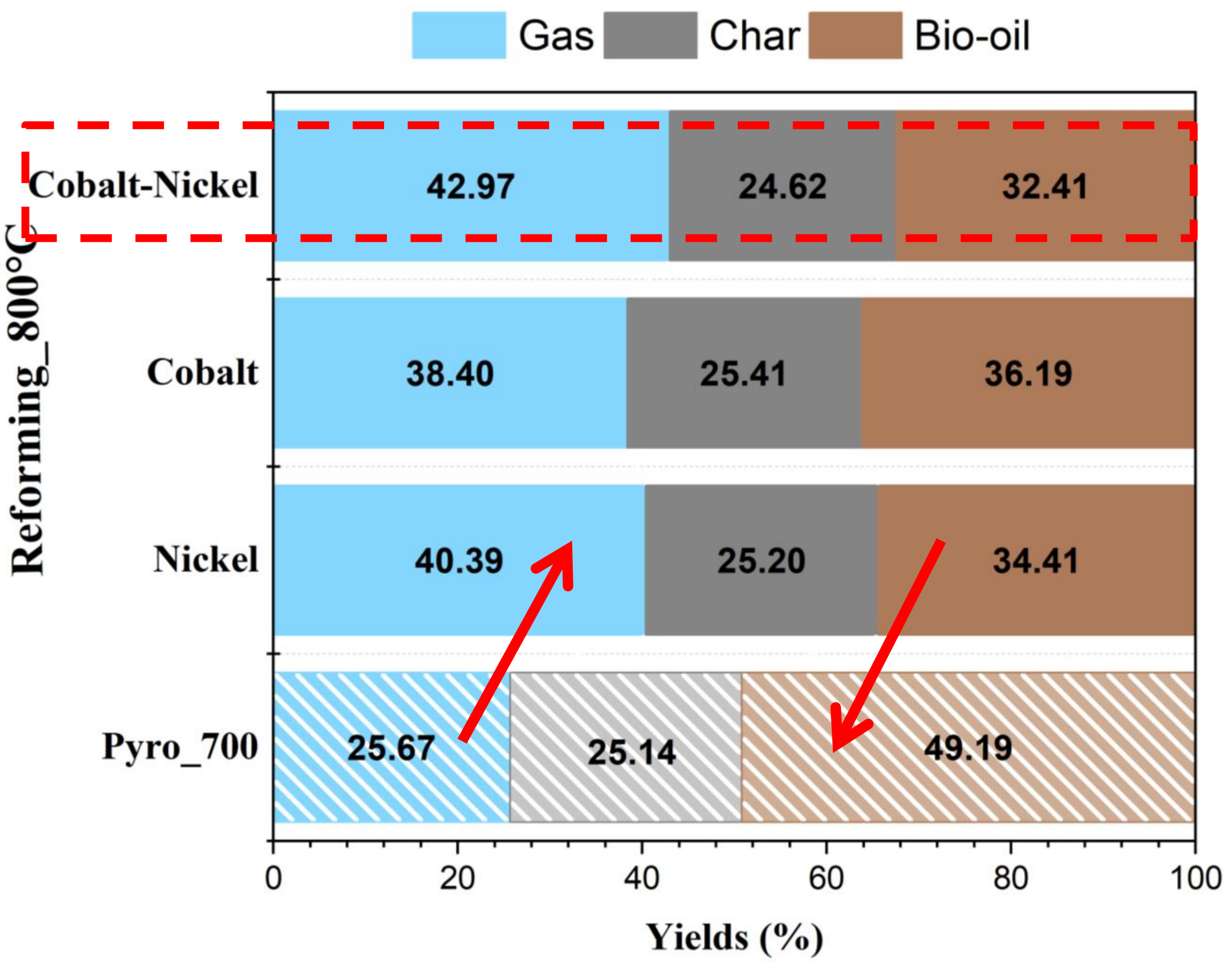
Bulk catalysts

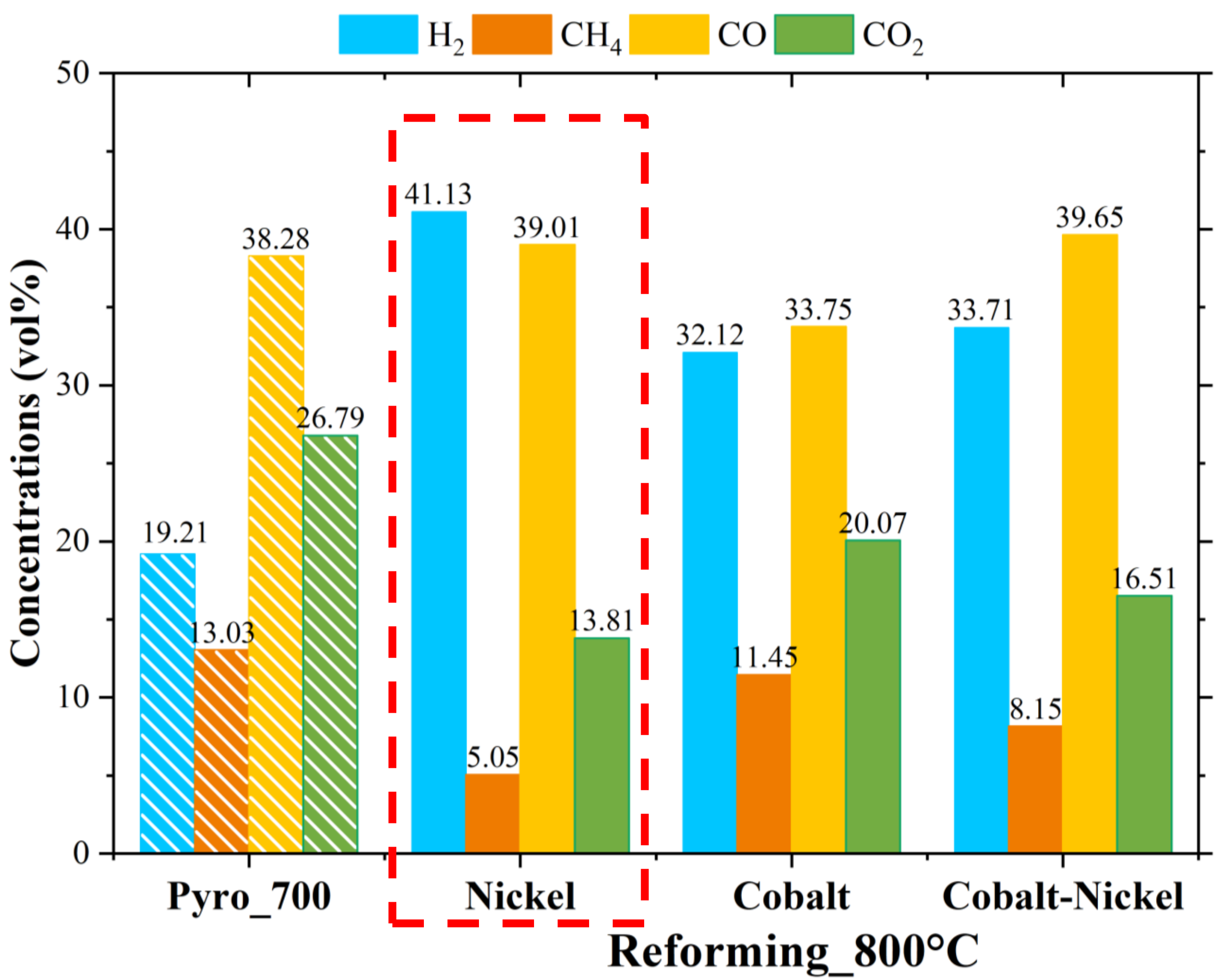
Supported catalysts

Cobalt, Nickel and Cobalt-Nickel

Results and discussions

1) Effect of the active phase of bulk catalysts with oak wood chips as biomass





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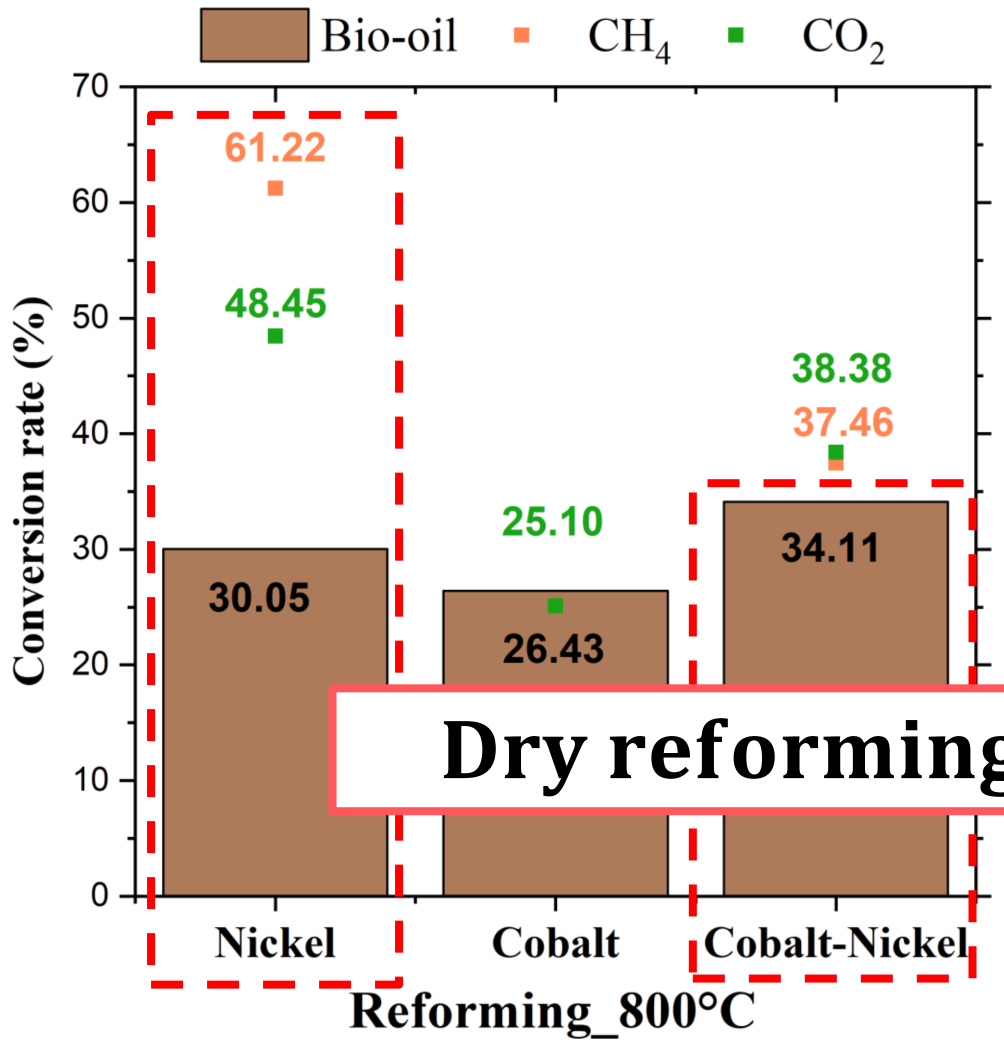
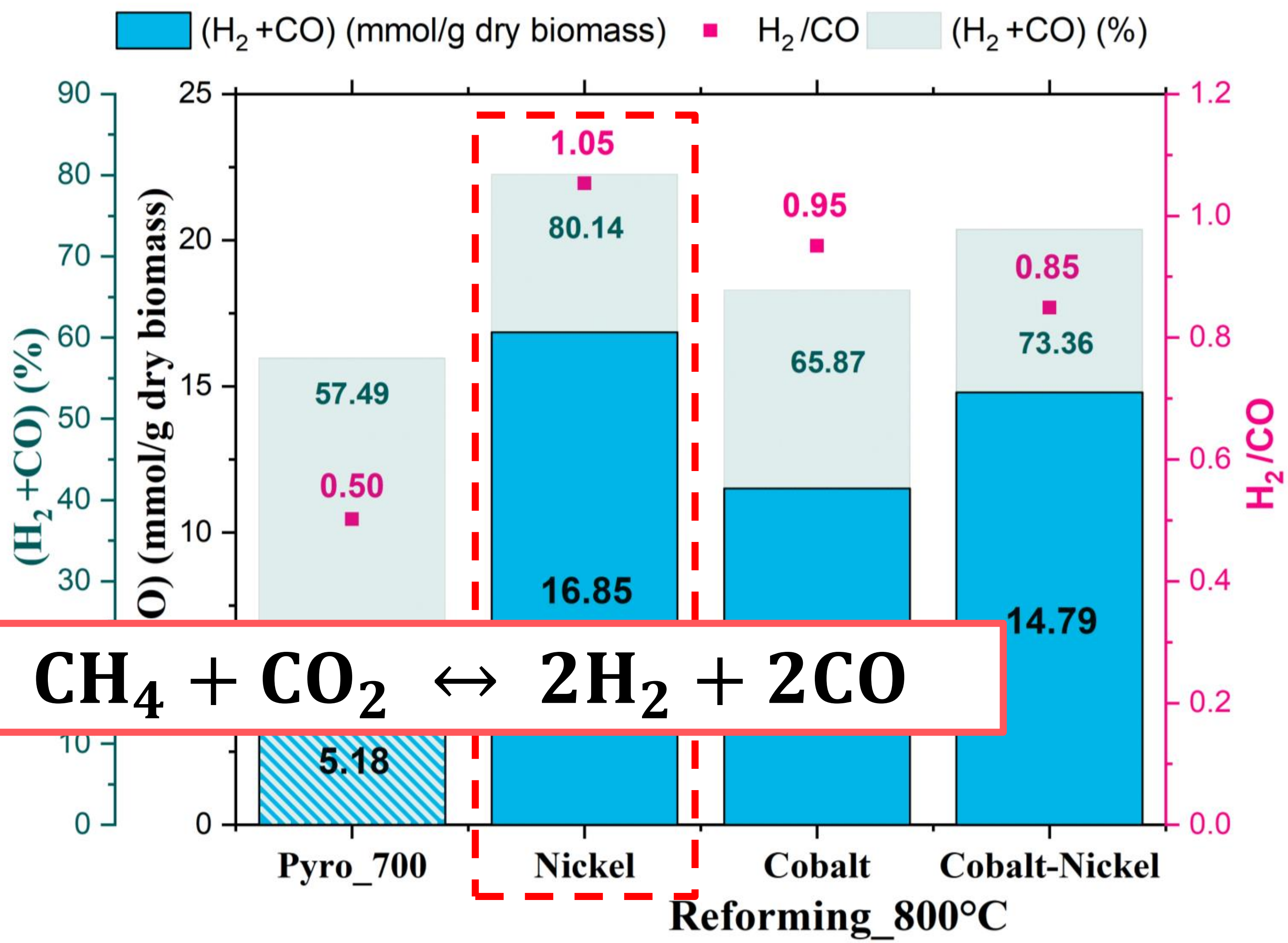




Dry reforming: $CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$

Materials and Methods

Biomass

Oak wood chips

Flax shives

Catalysts

Bulk catalysts

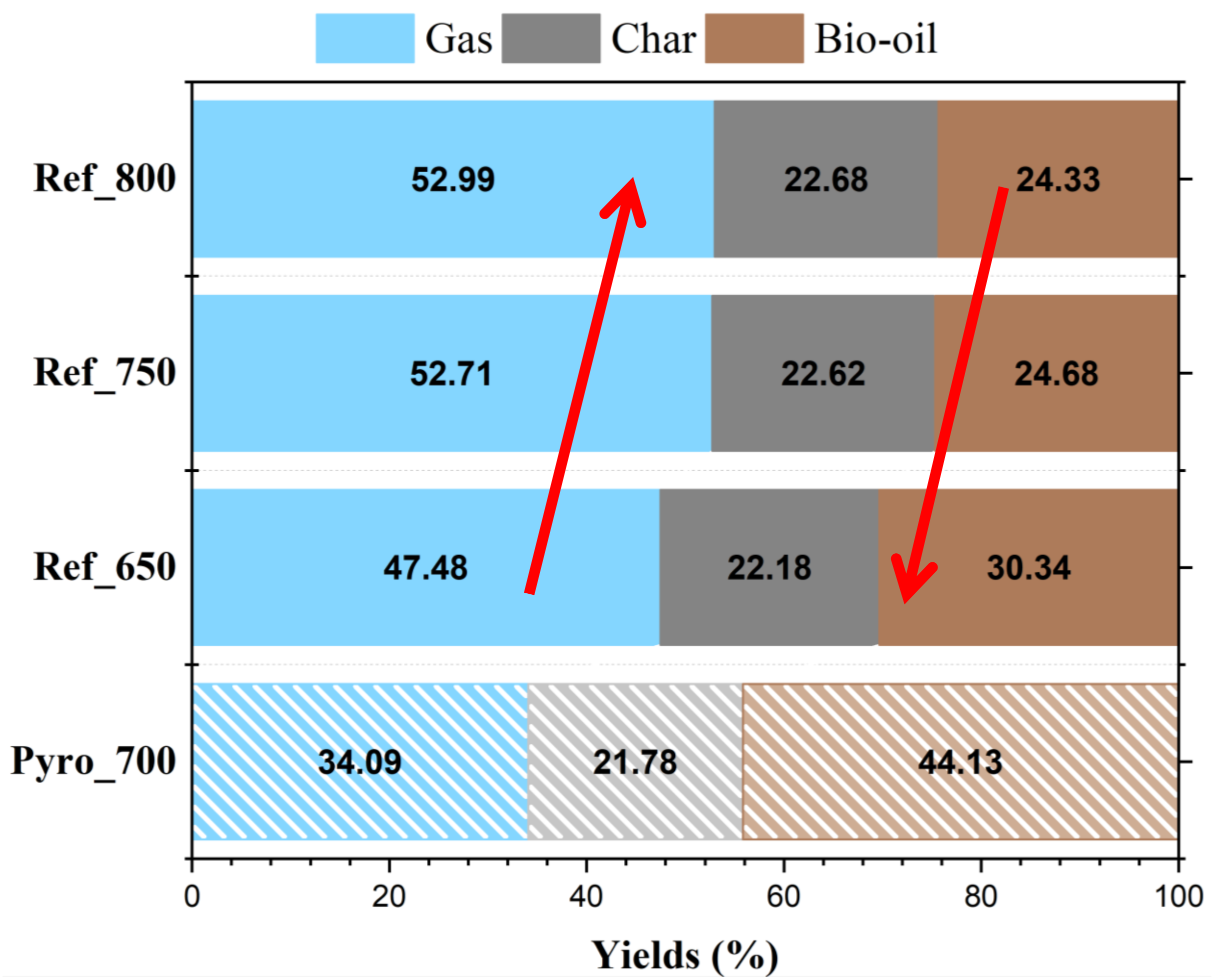
20%Ni/Al_2O_3

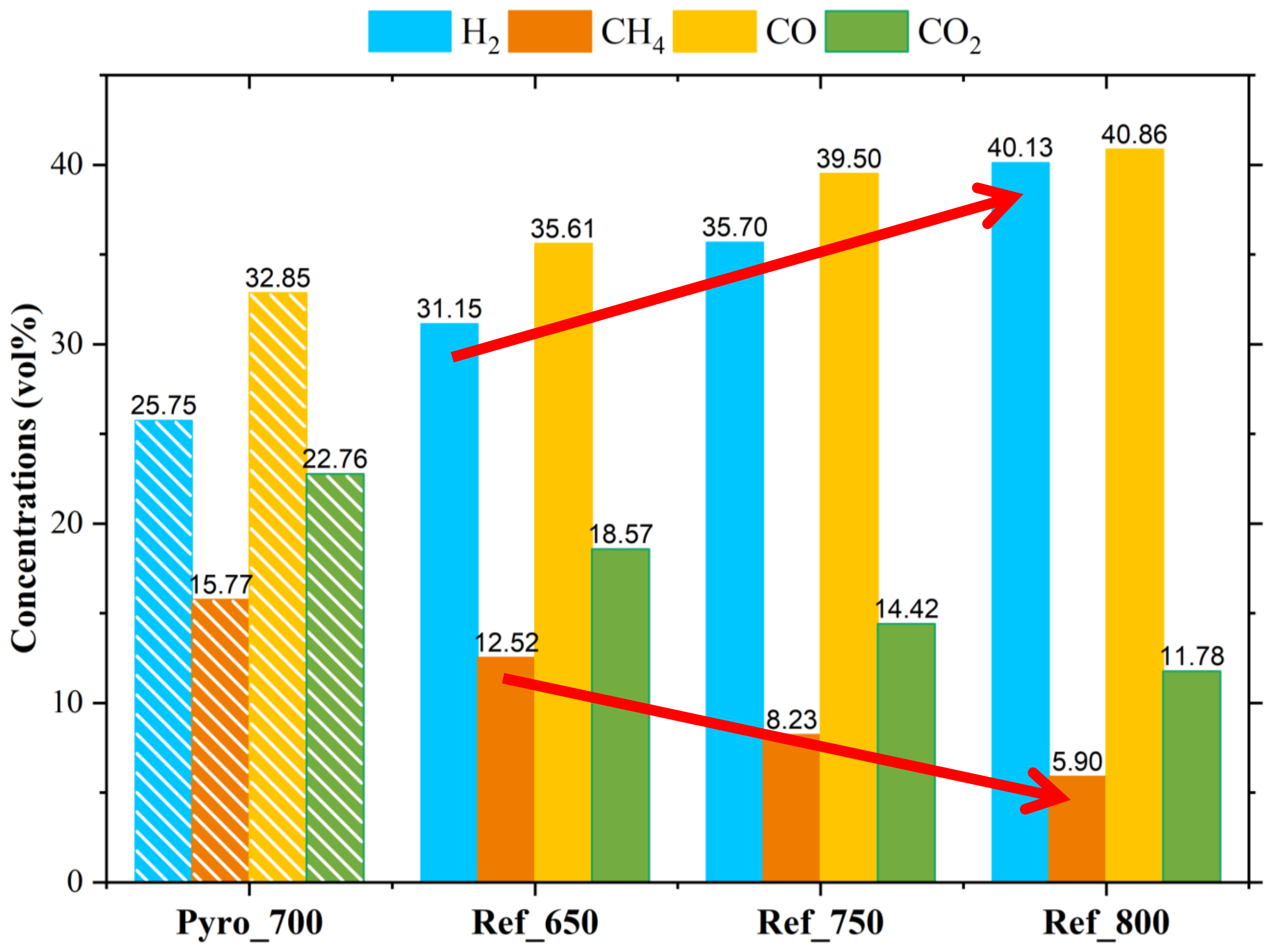
Supported catalysts

Cobalt, Nickel and Cobalt-Nickel

Results and discussions

2) Effect of reforming temperature (flax shives and 20%Ni/Al_2O_3)





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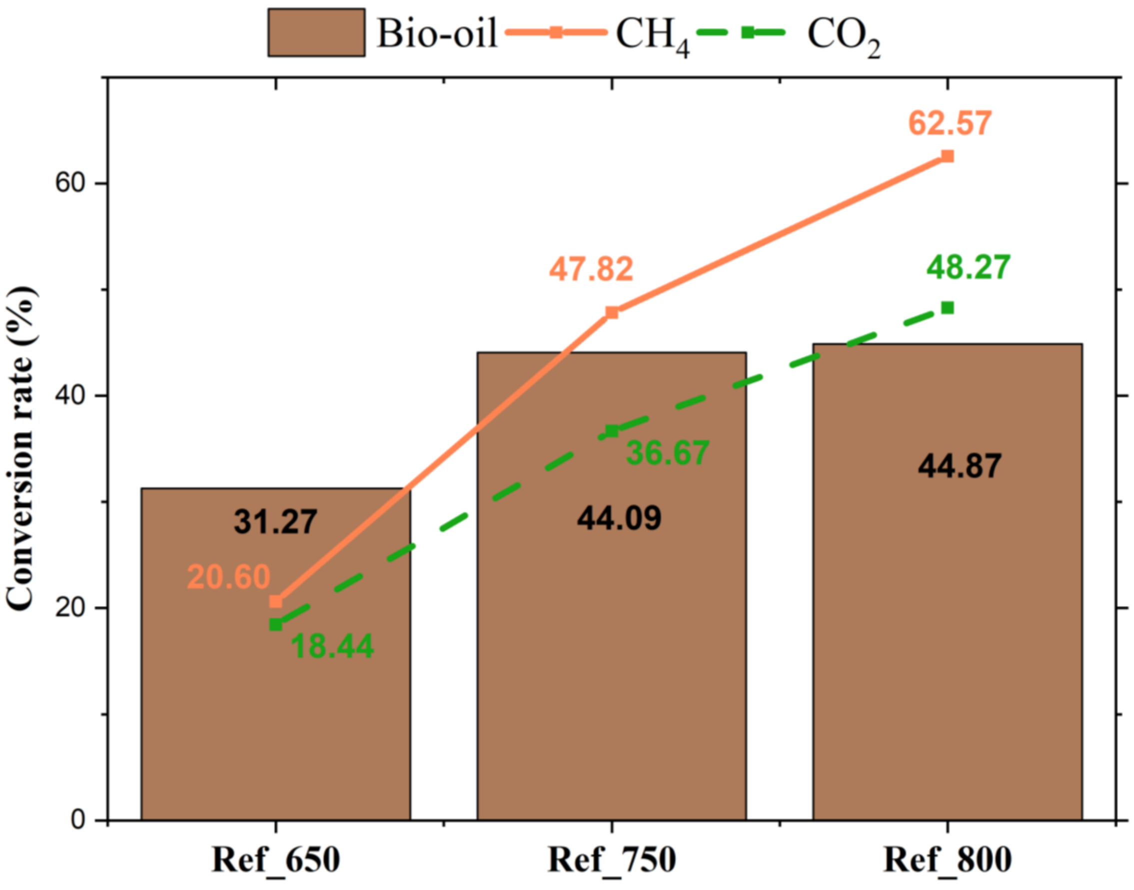
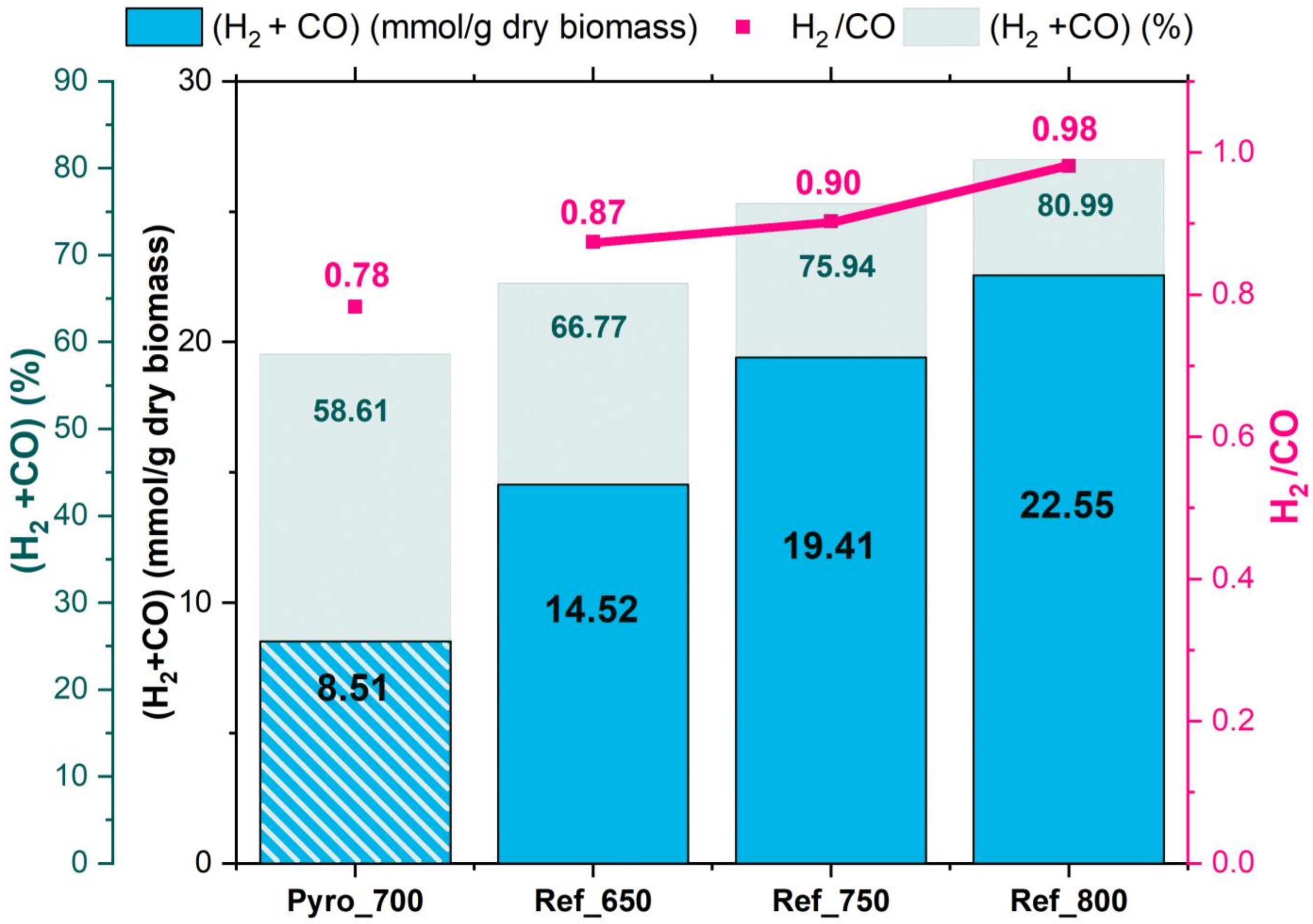


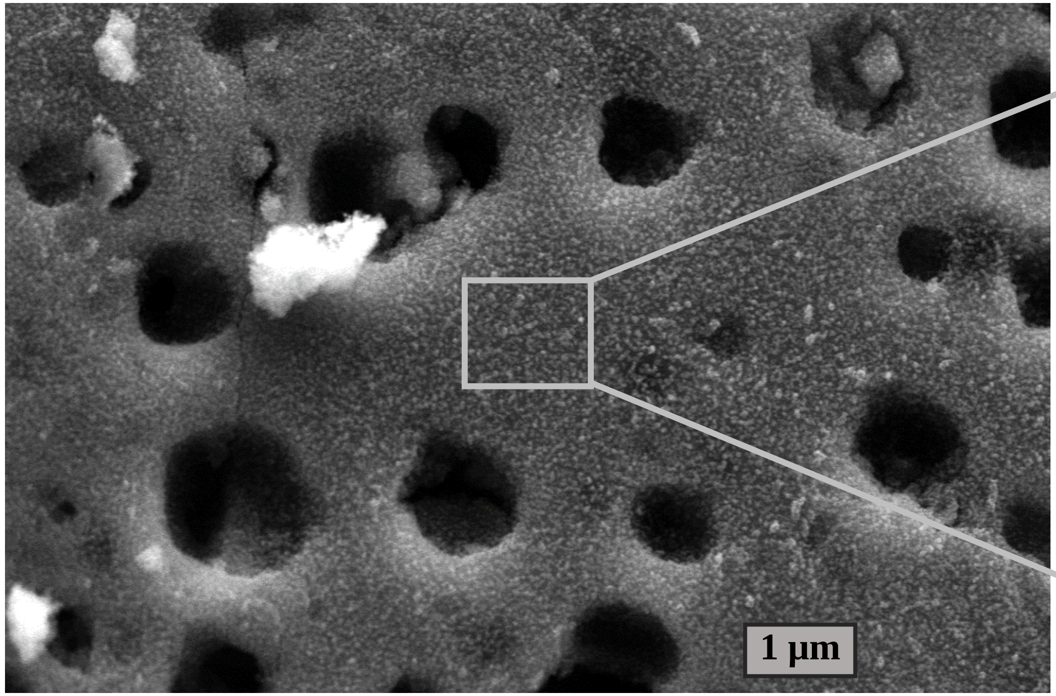


Reforming at 800°C favors the bio-oil conversion and improves the syngas production **(H_2)**

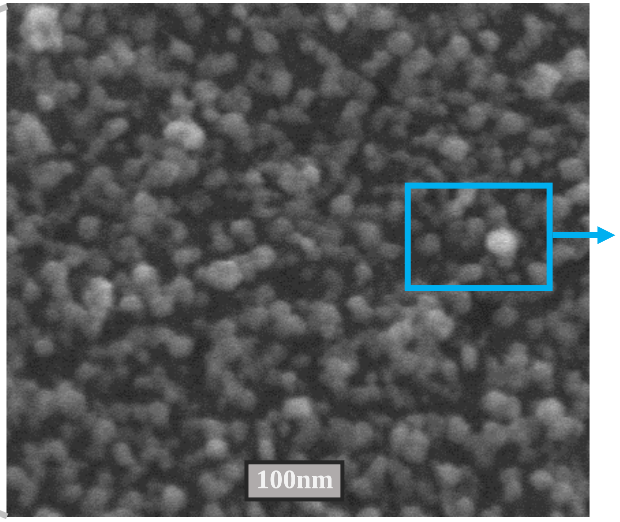
Results and discussions

Characterization of catalysts by SEM images and EDX analysis

Initial catalyst 20% Ni/Al_2O_3



× 10 000



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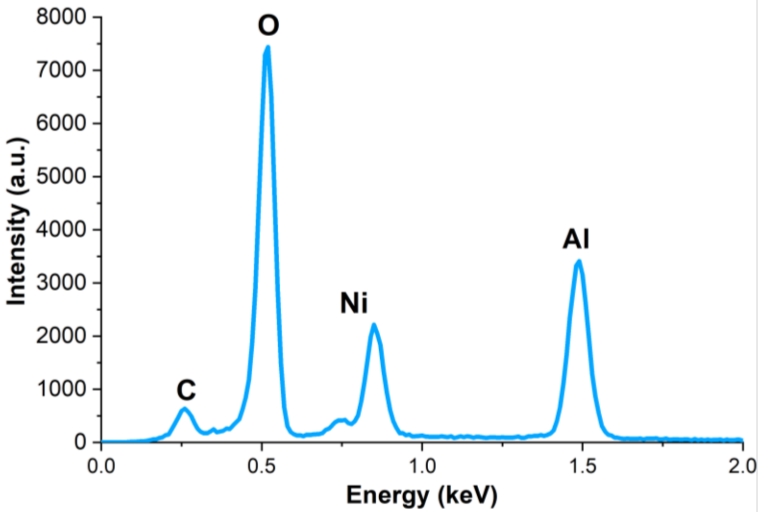
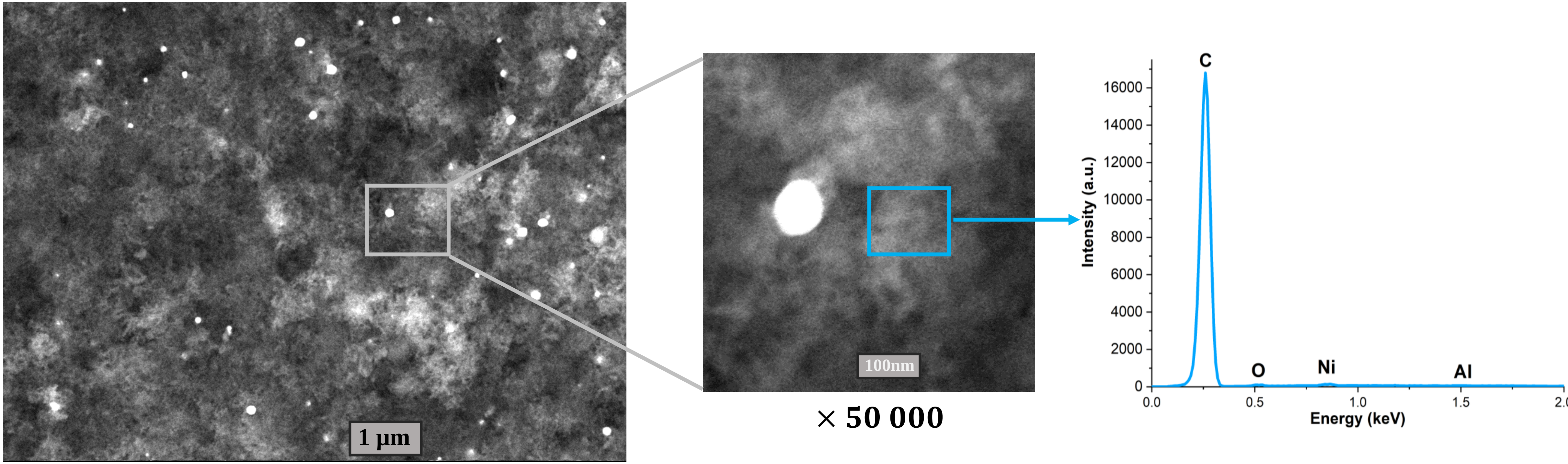


- Nickel particles (~30-40nm) → proven by the EDX analysis (Ni, Al, O et C)
- Pores (~7 nm) between the particles de Ni
- Large pores (1 µm)→ initial pores present in the alumina beads non covered by Ni

Results and discussions

Characterization of catalysts by SEM images and EDX analysis

20% Ni/Al_2O_3 after reforming at <u>800°C</u>



× 10 000

- Large Ni particles (~100 nm) → Agglomeration of the Ni → Sintering of the catalyst
- Presence of filamentous carbon (~50 nm) (confirmed by EDX) → carbon deposition → deactivation of active Ni sites

Materials and Methods

Dry reforming (CO_2) of methane:

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$$

$\rightarrow$ **$H_2/CO = 1$**

Objective: intensify steam reforming for H_2 production

Steam reforming (H_2O) of methane:

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO$$

$\rightarrow$ **$H_2/CO = 3$**

Materials and Methods

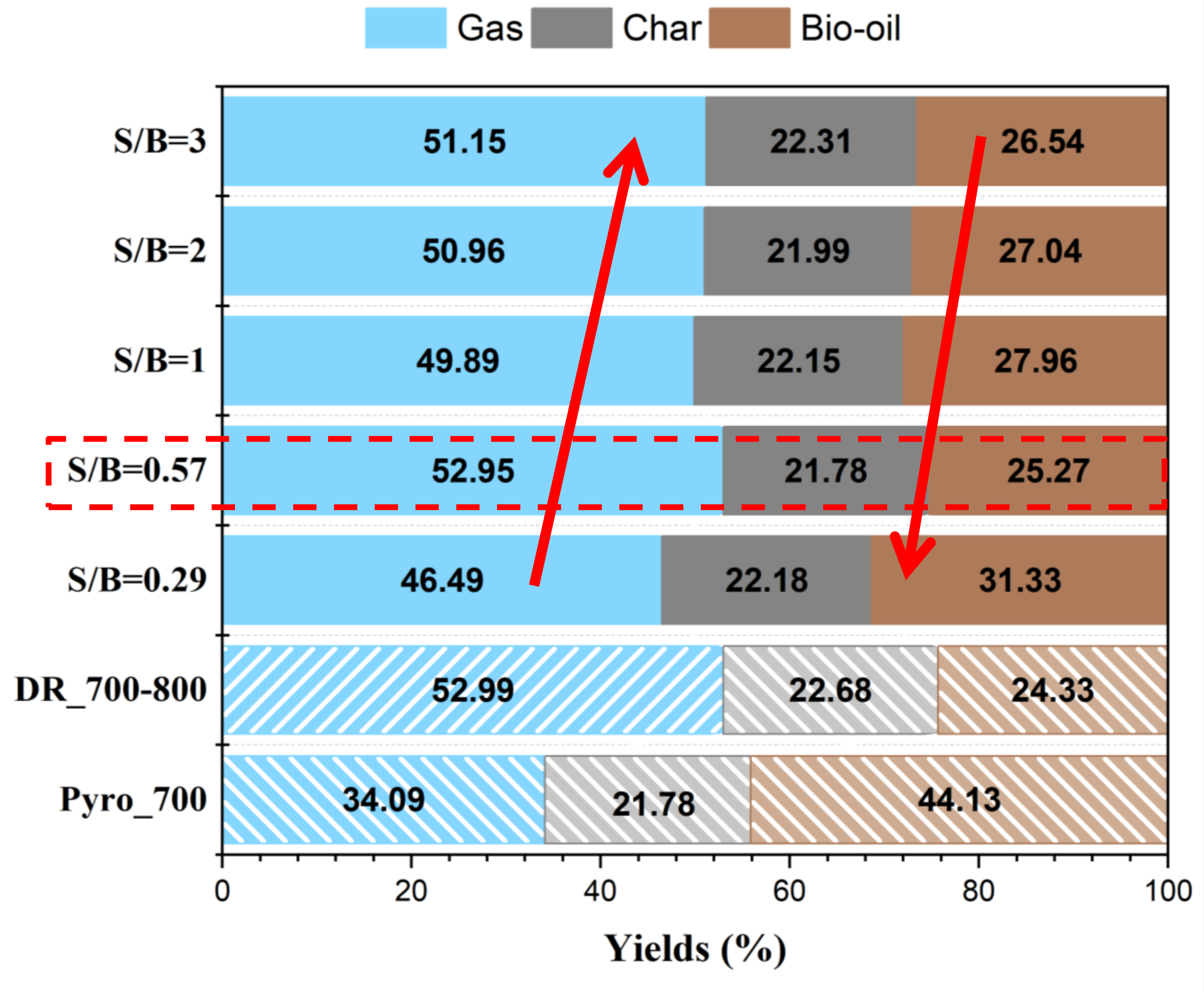
Steam to biomass ratio S/B

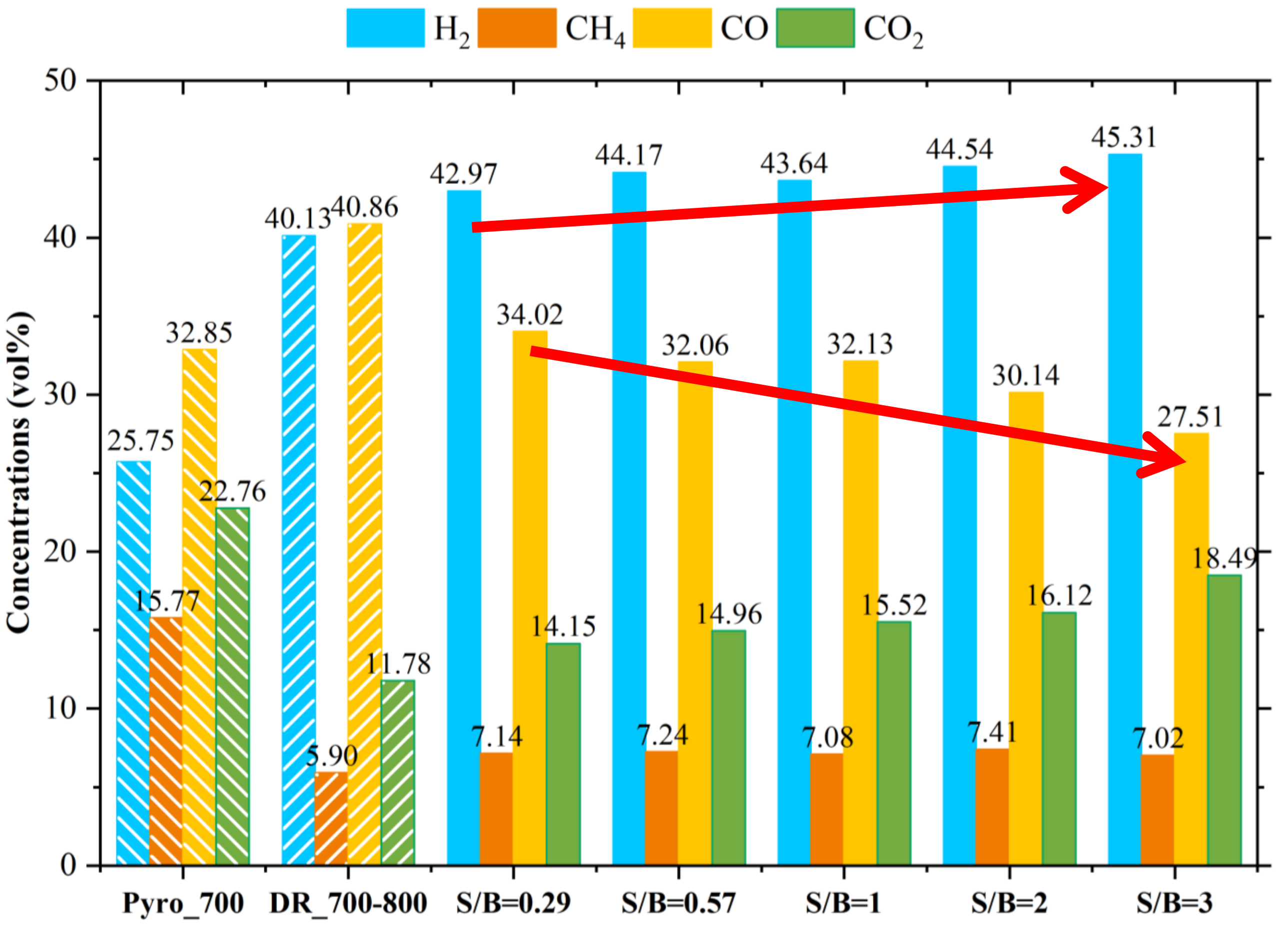
Steam to biomass ratio: $S/B = \frac{\text{Water vapor flow rate}}{\text{biomass flow rate}}$

Steam feed (g.h^{-1})	**0.5**	**1**	**1.75**	**3.5**	**5.25**
S/B ratio	0.29	0.57	1	2	3

Results and discussions

3) Effect of S/B ratio on steam reforming (T_{ref}=800°C, 20%Ni/Al_2O_3)





Results and discussions

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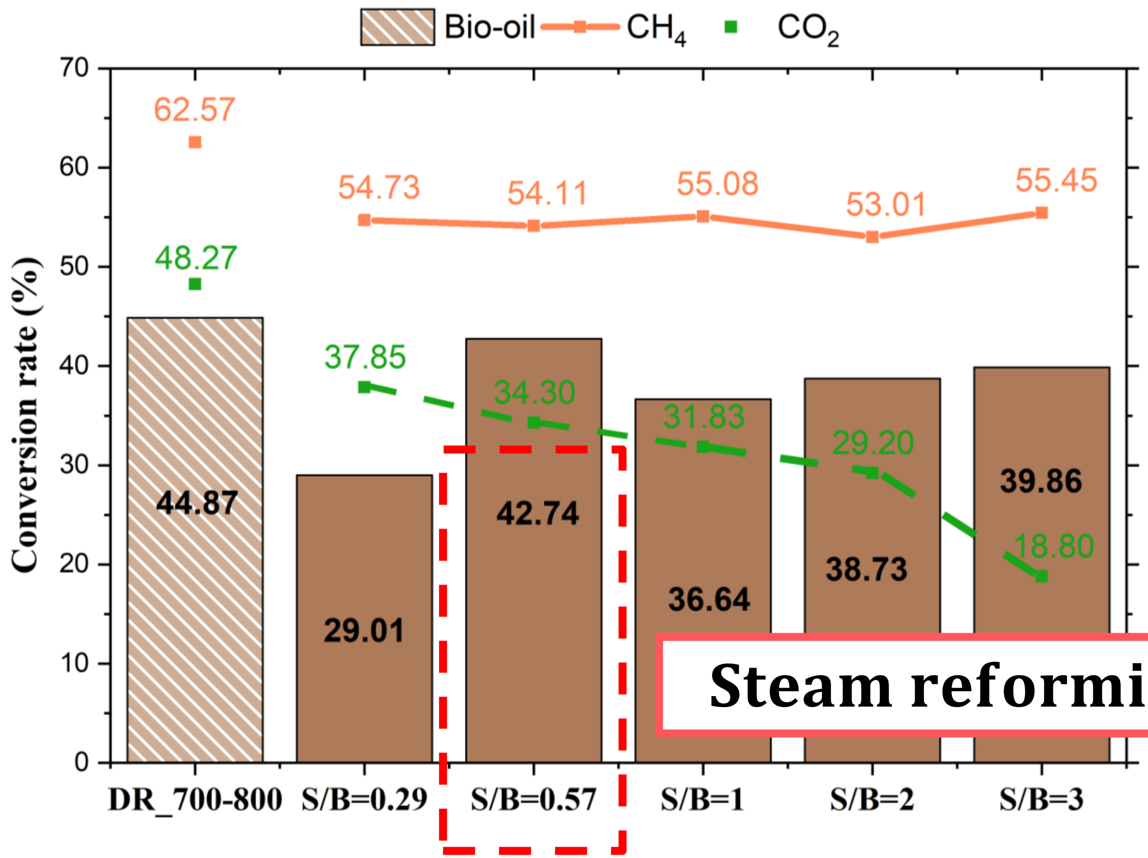

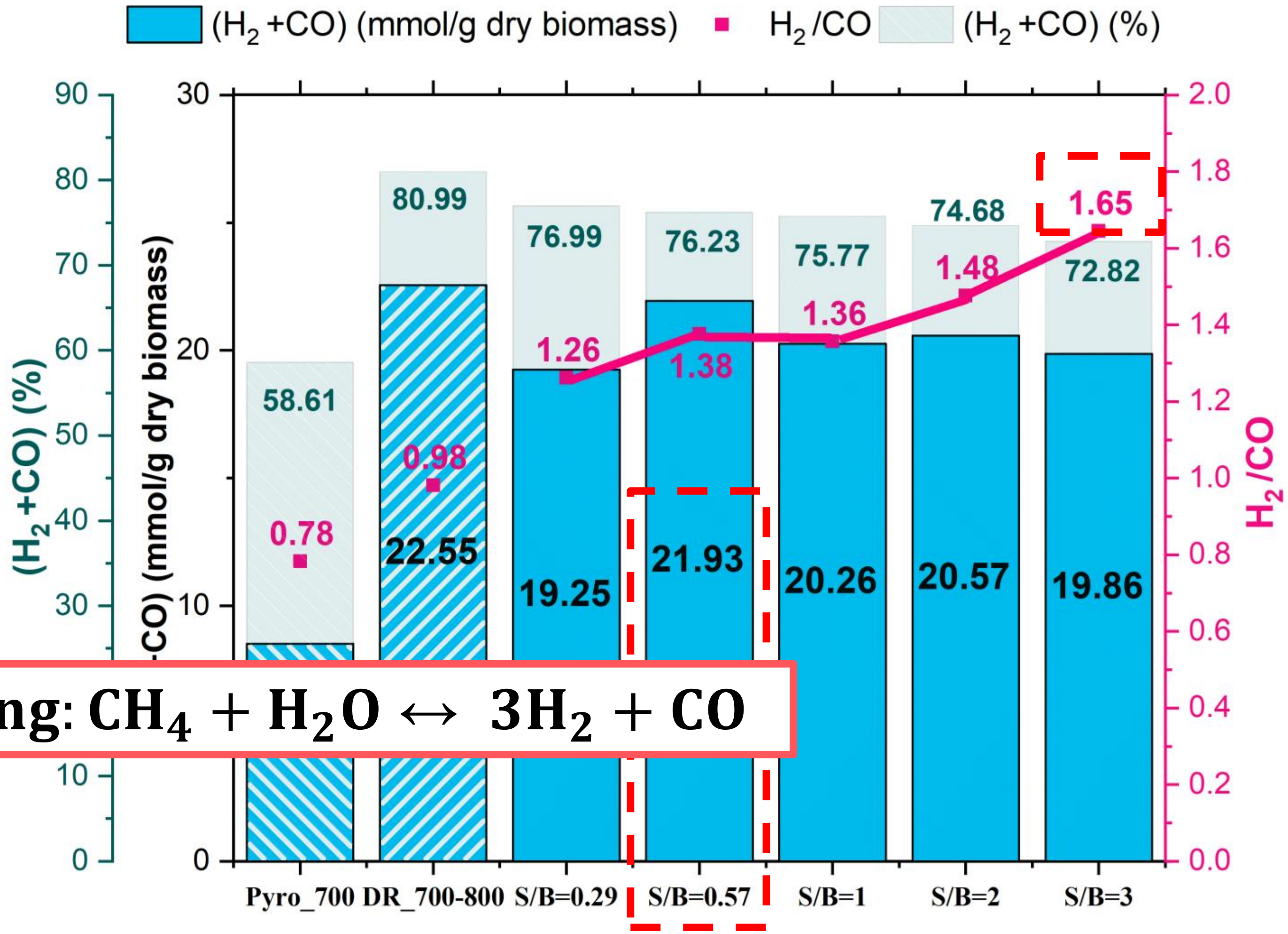

Steam reforming: $CH_4 + H_2O \leftrightarrow 3H_2 + CO$

Conclusion

Pyrolysis/ reforming

- **Valorization of biomass** into high added value products such as syngas

Nickel

- Low cost, high availability, strong activity and stability
- Suffers from carbon deposition and sintering leading to its deactivation

Cobalt-Nickel

- Increases gas production and improves bio-oil conversion
- Reduces carbon deposition

Temperature [650 – 800°C]

- Increasing the temperature **improves the syngas** production
- Optimal conditions: **800°C (reduces carbon deposition)**

Steam reforming S/B = [0.29-3]

- Adding water vapor poorly impacts the products distribution but strongly enhances H_2 production
- Optimal conditions: **S/B = 0.6 for max syngas; S/B = 3 for max H_2**

Perspectives

Improve the catalyst by alloying Ni with others **noble metals** (Ru, Rh…)

Valorize other feedstock materials such as **plastic wastes, biocomposites…**

Upscale the experimental set-up to reach pilot or semi-industrial level (TRL > 6)

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Université de Reims Champagne-Ardenne

Our recent publications on the topic

Environmental Chemistry Letters (2021) 19:2825–2872
https://doi.org/10.1007/s10311-021-01190-2

REVIEW

Pyrolysis-catalytic upgrading of bio-oil and pyrolysis-catalytic steam reforming of biogas: a review

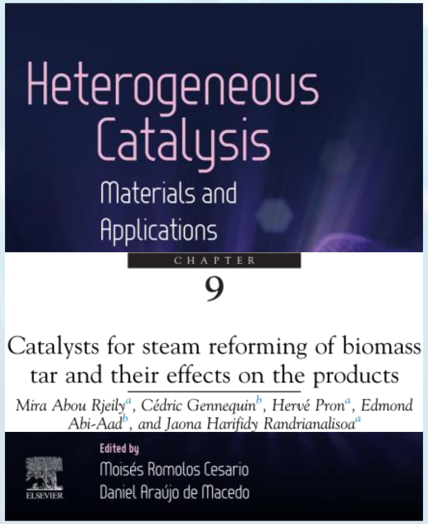
Mira Abou Rjeily[1] · Cédric Gennequin[2] · Hervé Pron[1] · Edmond Abi-Aad[2] · Jaona Harifidy Randrianalisoa[1]

Waste and Biomass Valorization
https://doi.org/10.1007/s12649-022-01848-0

ORIGINAL PAPER

Detailed Analysis of Gas, Char and Bio-oil Products of Oak Wood Pyrolysis at Different Operating Conditions

Mira Abou Rjeily[1,4] · Fabrice Cazier[2] · Cédric Gennequin[3,4] · Jaona Harifidy Randrianalisoa[1,4]



Waste and Biomass Valorization
https://doi.org/10.1007/s12649-022-02012-4

ORIGINAL PAPER

Biomass Pyrolysis Followed by Catalytic Hybrid Reforming for Syngas Production

Mira Abou Rjeily[1,3] · Muriel Chaghouri[2,3] · Cedric Gennequin[2,3] · Edmond Abi Aad[2,3] · Herve Pron[1,3] · Jaona Harifidy Randrianalisoa[1,3]

Jan 17th 2023

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Thank you for your attention

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