Towards hybrid biorefineries: Waste plastics and Me-contaminated biomass as sources of nanocarbons, synthesis gas, hydrogen and liquid biofuels

Keynote address from

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Partners

CRD/NSERC; PRIMA-Québec; UdS; KWI; Soleno; GOLD/HORIZON 2020; NFRF

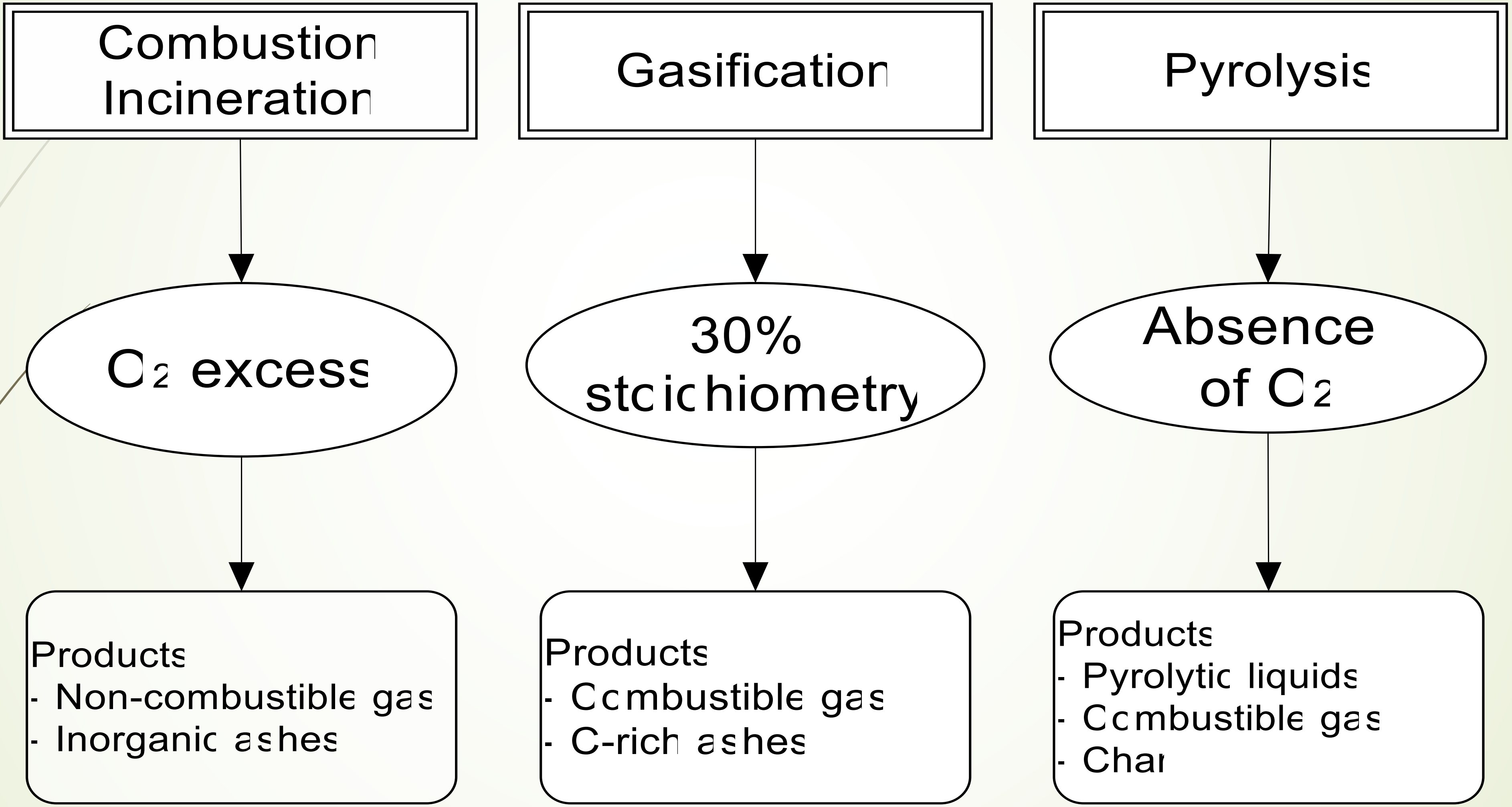
Overview

- Biorefineries: Reality or Chimera?
- Technological platforms
- The GRTP ATP platform
  - g-lab and kg-lab scale
  - The projects underway
- Past and present projects
  - Nano-F-PoRes
  - GOLD/HORIZON 2020
- Results
- Take-home message

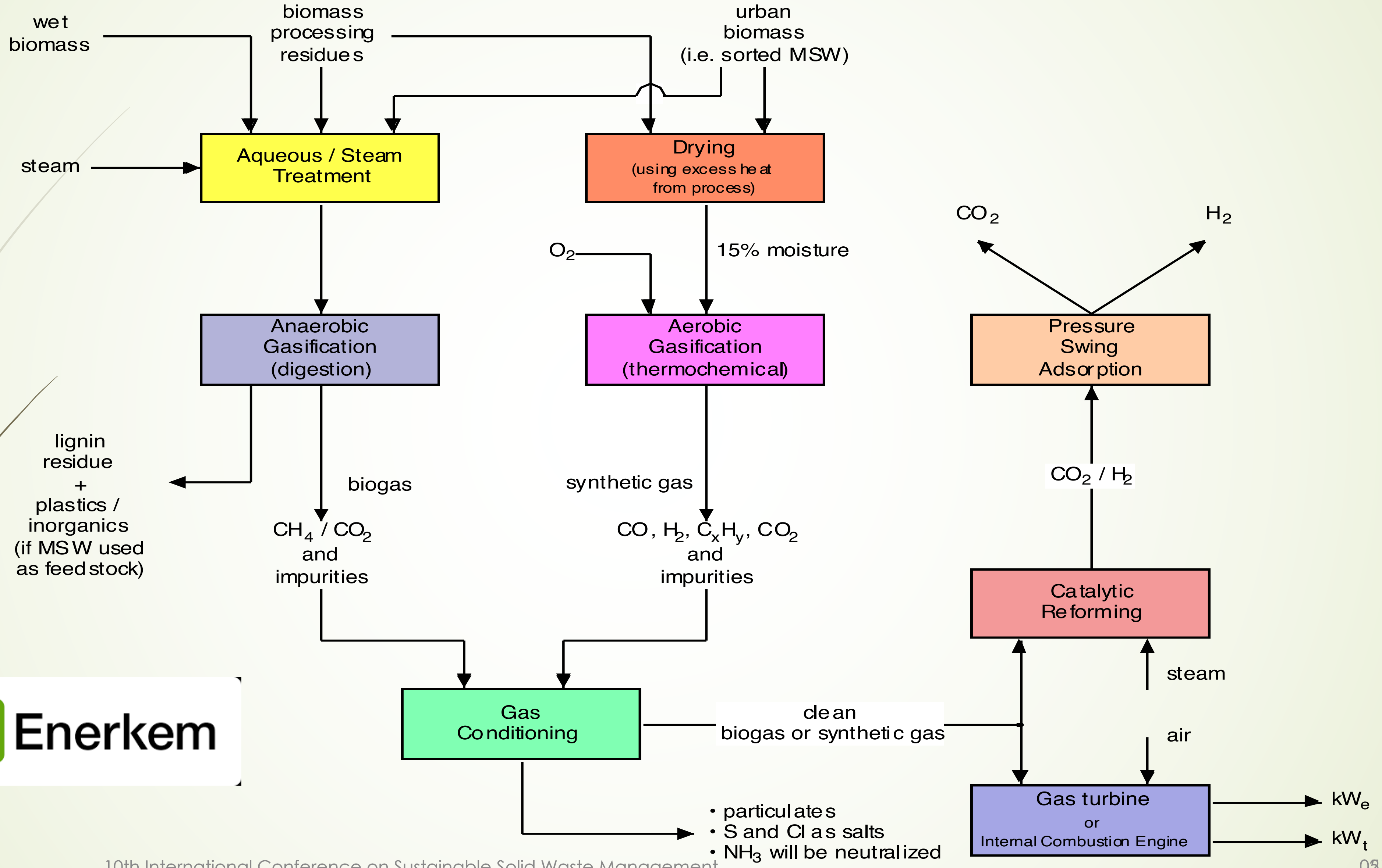
Biorefineries: Reality or Chimera?

- Sustainable production paradigm is here to stay
- Although renewable energy vectors are many, only waste and biomasses are renewable products resources
- Biorefinery is an alternative under development but in a not so far future (some generations ahead) will be the only remaining alternative
- Today's 'chimera' will be tomorrow's 'lion king'

Technological platforms

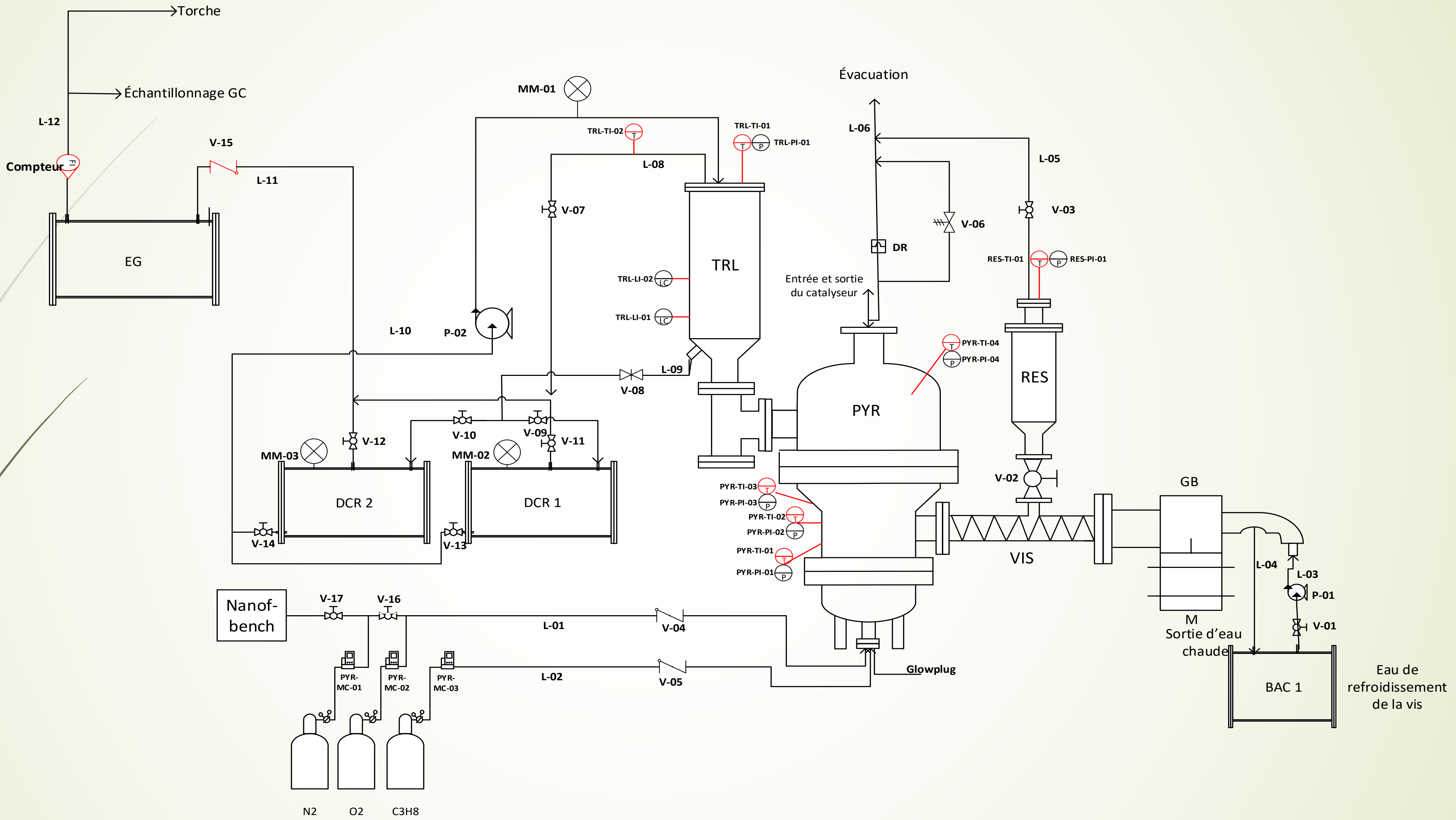


Biogas, Syngas and Hydrogen from Biomass

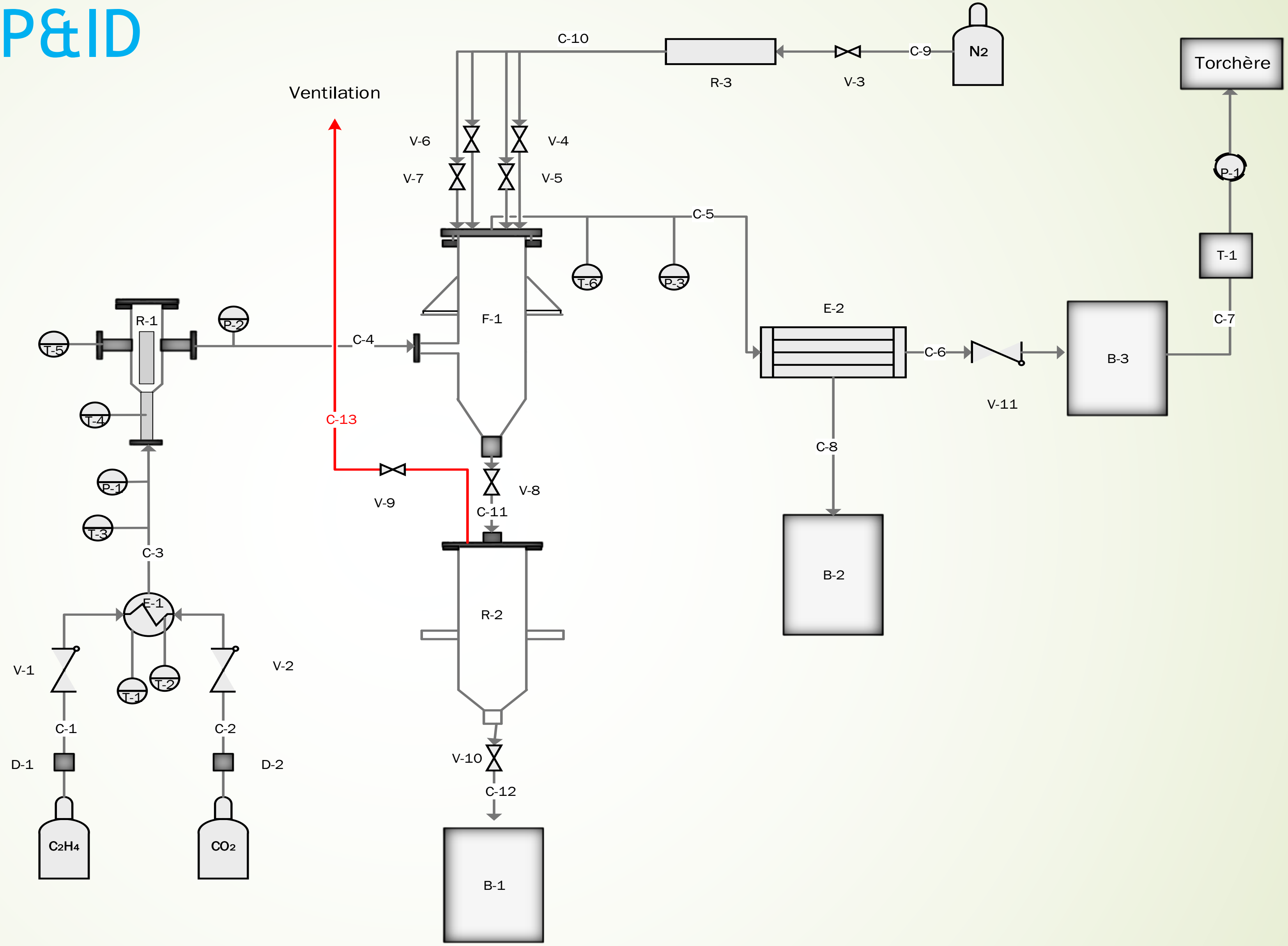


The ATP platform of the GRTP

ATP Pilot P&ID



CNF Pilot P&ID



The Nano-F-PoRes project

- Bubbling fluidized bed ATP : the lower part of the bed serves as exothermal POX vessel producing the necessary thermal energy for the endothermic thermolysis (thermal cracking) taking place at the upper part of the vessel.
- Combination of a bubbling fluid bed and a mobile catalytic bed in a reactor vessel: this vessel was patented [Abatzoglou et al., 2002] as a mobile bed filter and it is now tested as a reactor vessel for the production of CNF.
- The fluid product of the ATP is composed of gases and condensable components.
- The synthetic fluid stream can be used as it is produced after the solids retention. If it is too heavy for the CNF production reactor, there are two options:
  - Increase the catalytic cracking inside the ATP.
  - Add a Steam reforming reactor just before the CNF production reactor. Our patented catalyst (Ni-UGSO) [2016], known for its carbon-formation resistance as well as its high reforming ability even under low H_2O/C ratio, is used.

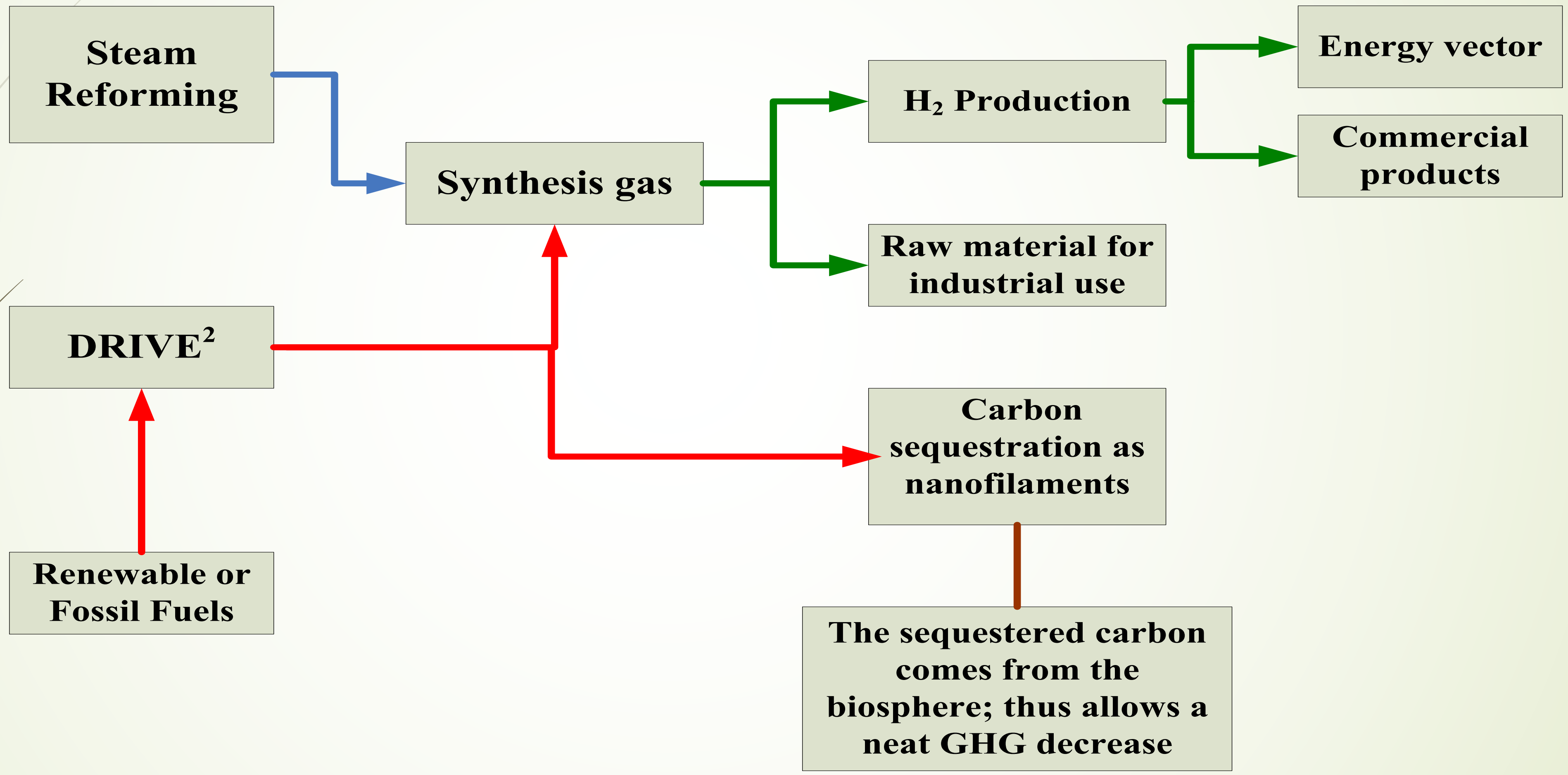
Production of carbon nanofilaments from waste streams and their use as polymers additives

Where this idea is generated from?

The DRIVE^2 Process

DRY REFORMING INDUCED VALORIZATION OF ENVIRONMENTALLY FRIENDLY ENERGY CARRIERS

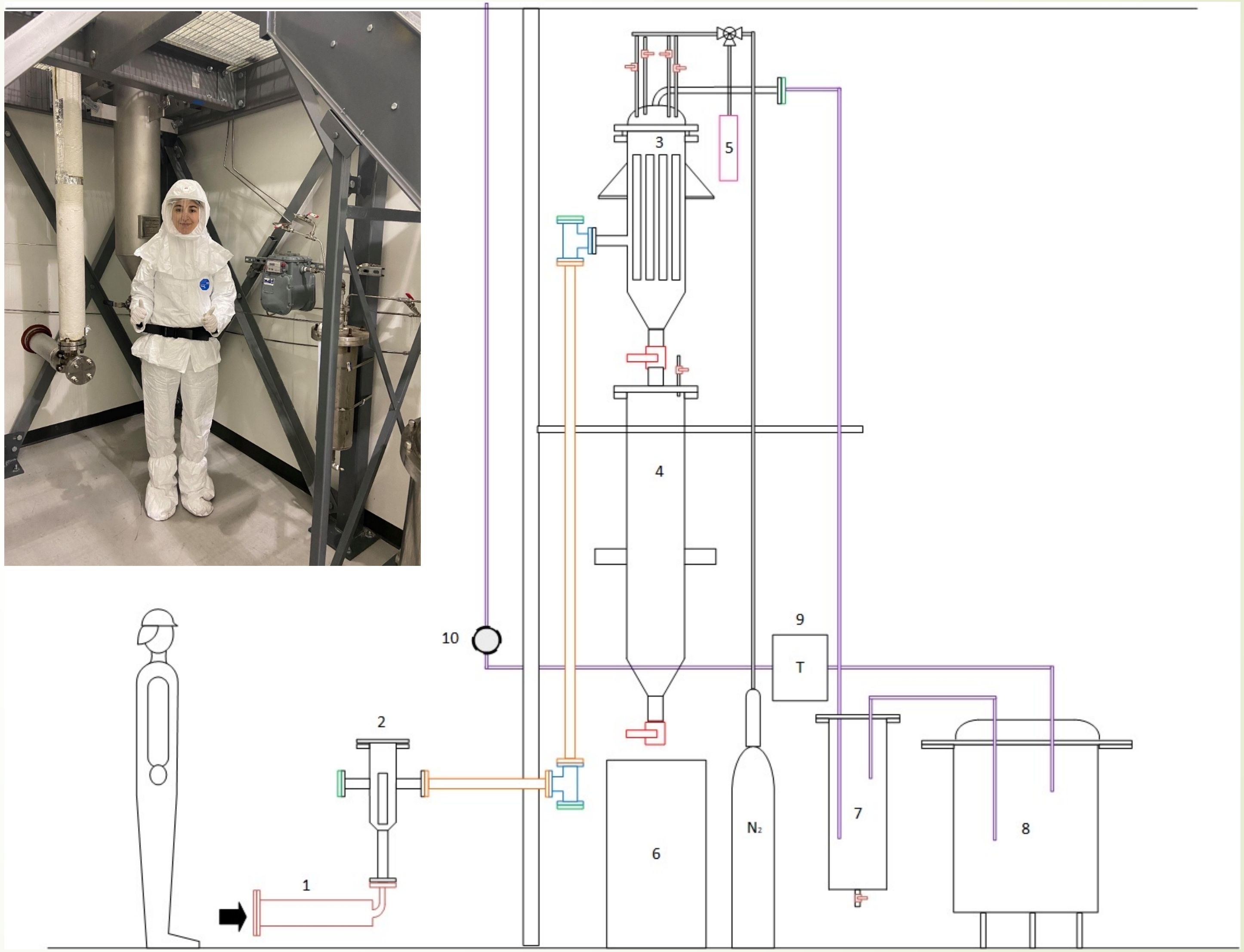
Rationale : GHG Sequestration?



CNF collection setup

Process diagram

1-Preheater
2-Reactor
3-Filter
4-NFC collection tank
5-Cylinder
6-NFC Recovery Barrel
7-Condenser
8-Glycol bath
9-Totalizer
10-Sampling point



Experimental Conditions

Activation

Catalyst	H_2 Flow rate (SLPM)	Ar Flow rate (SLPM)	Catalyst mass (kg)	Reaction time (h)	$GHSV_{STP}$ ($l.h^{-1}.kg^{-1}$)	T(°C)
$Fe\text{-}Al_2O_3$ 10 wt%	1	3	0.5	0.5	480	550

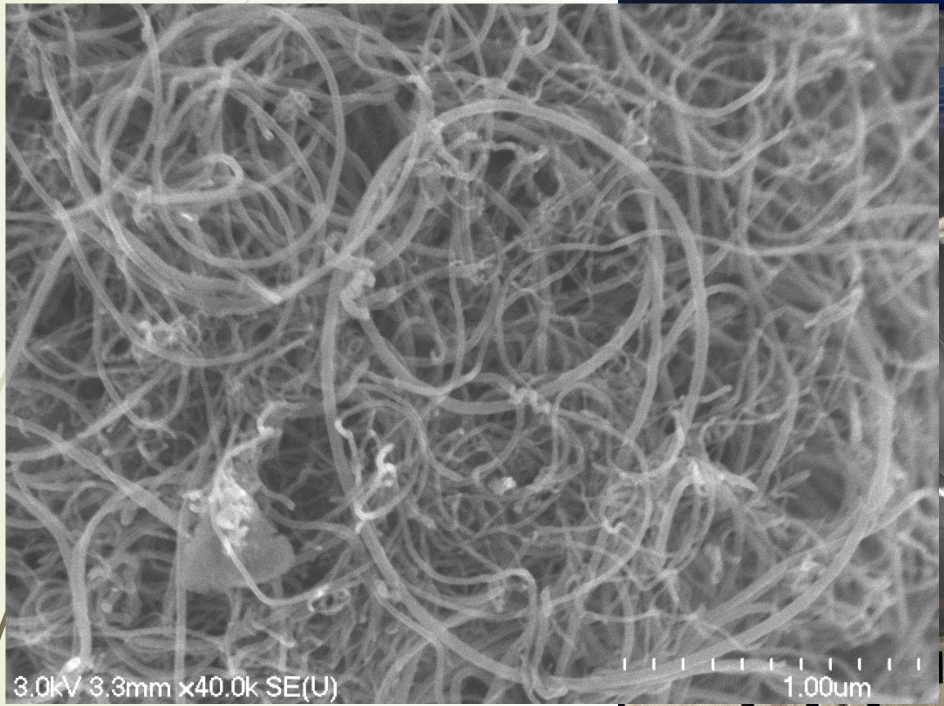
Reaction (duplicated)

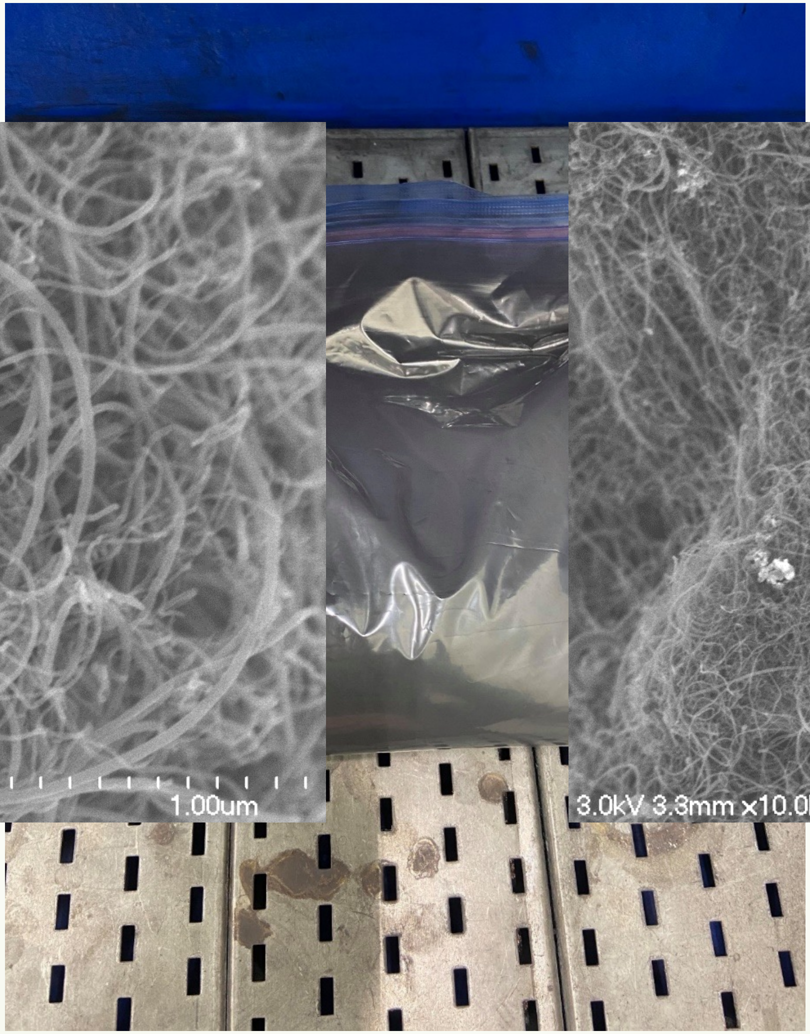
Catalyst	H_2 Flow rate (SLPM)	Ar Flow rate (SLPM)	Catalyst mass (kg)	Reacti on time (h)	$GHSV_{STP}$ ($l.h^{-1}.kg^{-1}$)	T(°C)
$Fe\text{-}Al_2O_3$ 10 wt%	3	1	0.5	6	480	600

Experimental results

Carbon mass (g)	615
Carbon Production rate ($kg_C.kg_{cat}^{-1}.h^{-1}$)	0.2
C Yield (%)	53.2
H_2 Yield (%)	46.4
C_2H_4 conversion (%)	73.0
CO_2 conversion (%)	69.9
C balance closure (%)	6.3
H balance closure (%)	4.0
O balance closure (%)	4.3

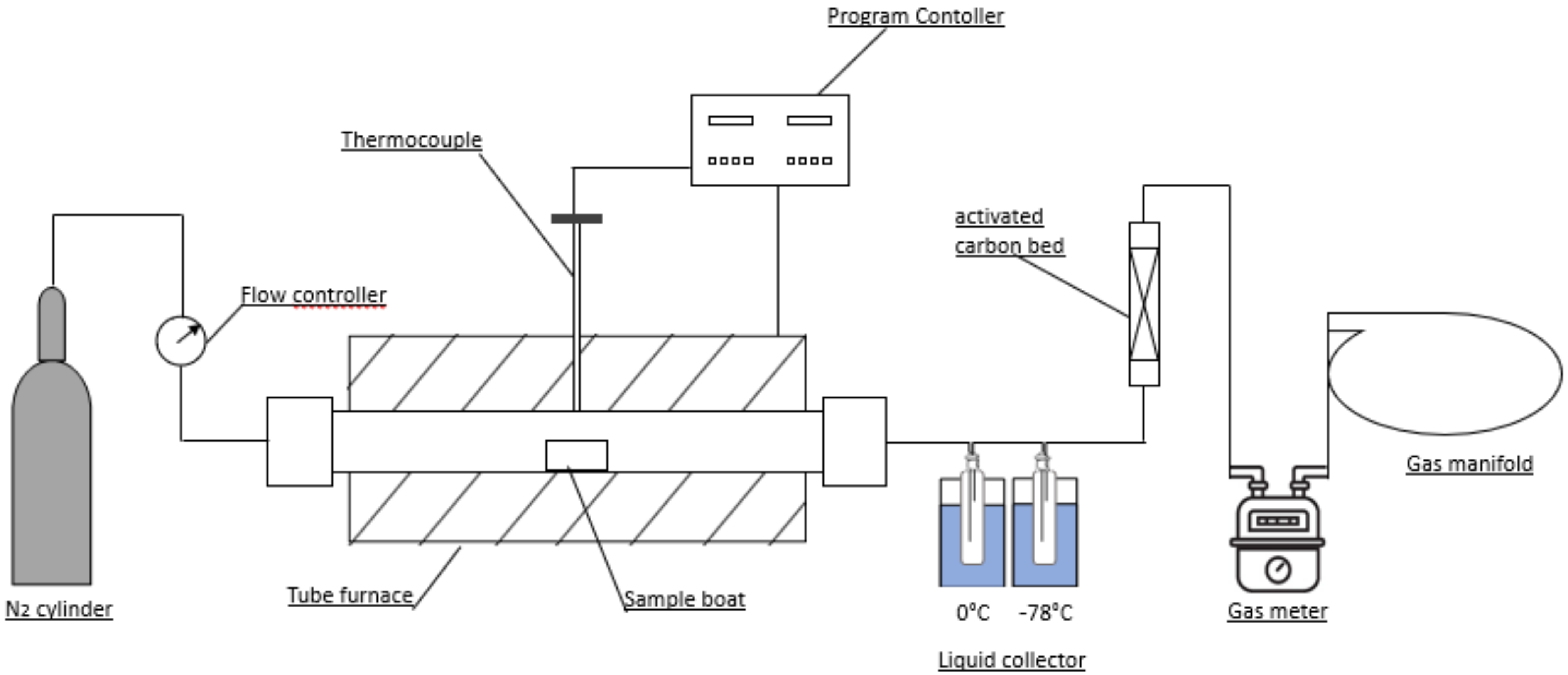
SEM Carbon characterization





Catalytic pyrolysis at g-lab scale

Batch Catalytic Pyrolysis Setup



Catalysts tested

Catalyst	Ni-UGSO	Fe/Al_2O_3
BET surface area ($m^2 \cdot g^{-1}$)	4.86	1.84
Pore volume ($mm^3 \cdot g^{-1}$)	23	10
Average pore size (nm)	7.9	8.5
H_2 chemisorption ($ml \cdot g^{-1}$)	566	206

Catalytic pyrolysis results – Post-consumer HDPE Semi-Batch at 700 °C for 2 h

Parameters \ Catalyst	Ni-UGSO	Fe/Al_2O_3
Solid yield (wt%)	57.2	7.4
Gas yield (wt%)	34.4	63.7
Liquid yield (wt%)	8.4	29
Average carbon production rate ($g_C \cdot g_{cat}^{-1} \cdot h^{-1}$)	2.26	0.13
Total filamentous carbon yield (wt%)	68	3.7
Total H_2 yield (wt%)	79.4	58.4

Catalytic pyrolysis results – Various feedstoch Semi-Batch at 700 °C for 2 h

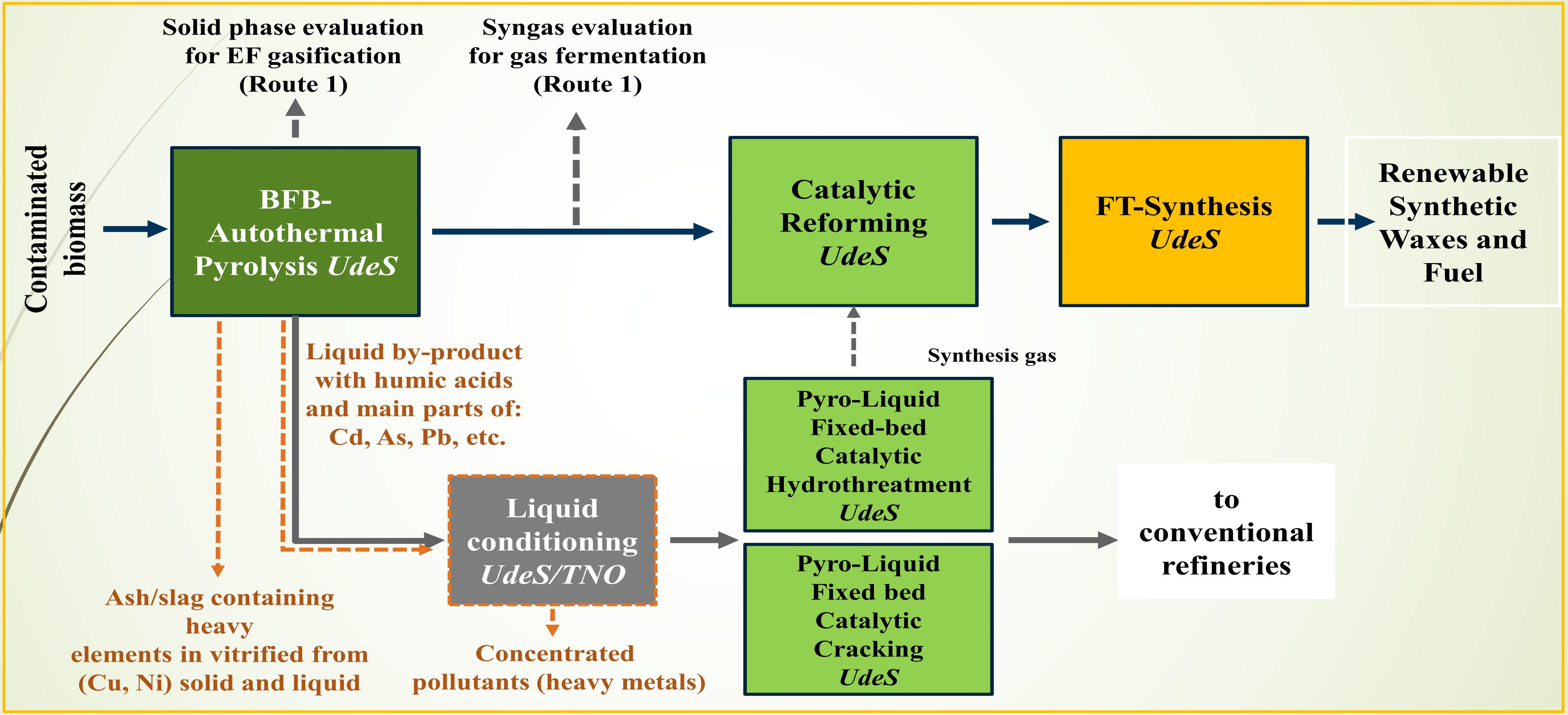
Parameters \ Plastic type	Virgin HDPE	Used HDPE	Mixed plastics
Solid yield (wt%)	56.5	57.2	61.8
Gas yield (wt%)	33.1	34.4	36.1
Liquid yield (wt%)	10.4	8.4	2.1
Average carbon production rate ($g_C \cdot g_{cat}^{-1} \cdot h^{-1}$)	2.3	2.3	2.0
Total filamentous carbon yield (wt%)	67.8	67.9	58.6
Total H_2 yield (wt%)	75.6	79.4	70.4

Call: H2020-LC-SC3-2020-RES-RIA: Combined clean biofuel production and phytoremediation solutions from contaminated lands worldwide

'Bridging the gap between phytoremediation solutions
on growing energy crops on contaminated lands and clean biofuel production'
Acronym: GOLD

EU H2020 grant no. 101006873, 1/5/2021 – 30/4/2025

GRTP's Role in GOLD Project (WP2.5)



Me-Contaminated biomass for Pyrolysis tests

- About 13g of previously washed, dried and ground biomass are used for each pyrolysis test.
- An experimental plan (Box-Behnken optimization plan) was established varying the temperature (between 500 and 800°C), the heating rate (between 2 and 10°C/min) and the residence time at the maximum temperature (between 20 and 60 min) for the pyrolysis of switchgrass biomass.
- The biomass used contains 43.5 ± 2.21% carbon (elemental analysis SC632) and has an ash content of 1.4% (ASTM-e1755 method).
- According to our ICP the level of contamination of this biomass is:
  - 35 ppb Cu
  - 500 ppb Fe
  - 60 ppb in Sb
  - Other heavy metals in trace.

Results of preliminary pyrolysis tests

- **The mass yields of biochars are between 21% for high heating rates and 26% for low heating rates.**

- **Elemental analysis of chars gives a carbon content of 85-90%. Metals are captured by more than 95% in the solids.**

- **The bio-oil yields are around 30% for average temperatures (650°C) and average heating rates (6°C/min).**

- **The quantity of gas increases with T, and it is favored with low heating rates.**

Take-home message

- Hybrid biorefineries development is to become the basis of renewable resources-based products.
- The under-development autothermal pyrolysis technological platform is the equivalent of the fossil carbon-based resources pretreatment step (i.e.; heavy crude oil).
- The g-lab scale results are highly promising and scaled-up runs are underway.
- The combination of residual (waste) plastic with biomass (i.e.; me-contaminated biomass from phytoremediation) adds a significant flexibility to the proposed technology.

Contributions

- Funding: PRIMA Québec & FRQ-SC (Québec); NSERC & NFRF (Canada); KWI; Soleno
- Professor: François Gitzhofer and Inès Esma Achouri
- HQP
  - Abir Azara, PhD student
  - Salma Belbessai, PhD student
  - Khadija Olivia Ogoula Igouwe, PhD student
- Professionals & Technicians
  - Jacques Gagné
  - Marc G. Couture
- KWI & Soleno
  - Dr Jasmin Blanchard, KWI
  - Yves Laroche, MBA, KWI
  - Dr Pierre Breton, KWI
  - Carl Diez, Soleno
- Plateforme de recherche et d'analyse des matériaux: PRAM/UdS
- UdS for new buildings
  - Prof. Patrik Doucet, ex-Dean of Engineering
  - Prof. Jean-Pierre Perrault, Vice-Rector, Research and Graduate studies

Patents

Abatzoglou, N., Fauteux-Lefebvre, C., Blanchard, J., Gitzhofer, F. (2011) Steam reforming of hydrocarbonaceous fuels over a Ni-alumina spinel catalyst, Application number: WO2010CA01284 20100819

Abatzoglou, N., Fauteux-Lefebvre, C. (2015) Metal-Functionalized Carbon Nanofilaments And Process For Removing Sulfur From Gaseous Fuels, provisional patent application, USPTO No 61894033.

Abatzoglou, N., Gitzhofer, F., Gravelle, D., Blanchard, J., De Oliveira-Vigier, K., Oudghiri-Hassani, H., Gauvin, H. (2010) Carbon sequestration and dry reforming process and catalysts to produce same, US Patent 7,794,690.

Abatzoglou, N., Bureau, J., Mincic, A., Chornet, E., (2002) Mobile granular bed filtration apparatus for hot gas conditioning, UStates Patent 6,436,161.