The NanoF-PoRes Process for the production of NanoFilaments from Waste Plastic

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Keynote address from
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Partners

CRD/NSERC; PRIMA-Quebec; UdeS; KWI; Soleno

Overview

- Deliverables
- Methodology
- R&D description
- Pilote (kg-lab)

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Deliverables at kg-lab scale

- Convert efficiently low-cost feedstock (waste plastic) into a fluid stream using a proprietary autothermal pyrolysis + reforming process
- Synthesize the carbon nanofilaments (CNF) at kg-lab scale using a proprietary mobile bed reactor (MBR)
- Separate and collect the so-produced CNF
- Introduce the CNF in the recycled polymers matrix
- Measure the properties of the composite polymers

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Methodology

- 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.
- Use of the KFusion^{TM} process developed by KWI to incorporate nanosolids in polymers.

Scientific challenges of ATP unit

- Mixed residual plastics thermal reactivity: role of composition, size and wetness
- Inert or Catalytic fluidized bed?
- Bubbling Fluidized bed operation
  - Optimal bed and upper zone temperature profile
  - Optimize residence time and mass and heat transfer coefficients for the targeted feedstock
  - Solids feed position
  - Bed expansion and disengagement zone
- Condensable and non-condensable components in the producer gas
- Minimize solid products and carbon loss
- Estimate bed replacement rate
- Evaluate the effect of heteroatoms in the products which is feedstock in the CNF production reactor

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Scientific challenges of CNF unit

- MBR geometry as function of the catalytic bed and feed properties
- Study, adapt and validate catalyst pretreatment protocol; namely, surface partial oxidation phenomenological kinetics and surface changes over TOS
- Validate CNF production mechanism under the new reactor configuration
- Mobile bed reactor operation
  - Study feed conversion to CNF efficiency as function of the operating conditions
  - Study properties of the produced CNF as function of the operating conditions: diameter and length size distributions
  - Evaluate catalyst particles size distribution as function of TOS: the MBR is considered as a continuous reactor but, it is rather a transient state system with a long time constant
  - Evaluate quantity vs quality of the CNF and optimize operating protocol
- Evaluate the effect of heteroatoms in CNF productivity
- Evaluate the catalyst consumption rate for this configuration

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

Where this idea is generated from?

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The DRIVE^2 Process

DRY REFORMING INDUCED VALORIZATION OF ENVIRONMENTALLY FRIENDLY ENERGY CARRIERS

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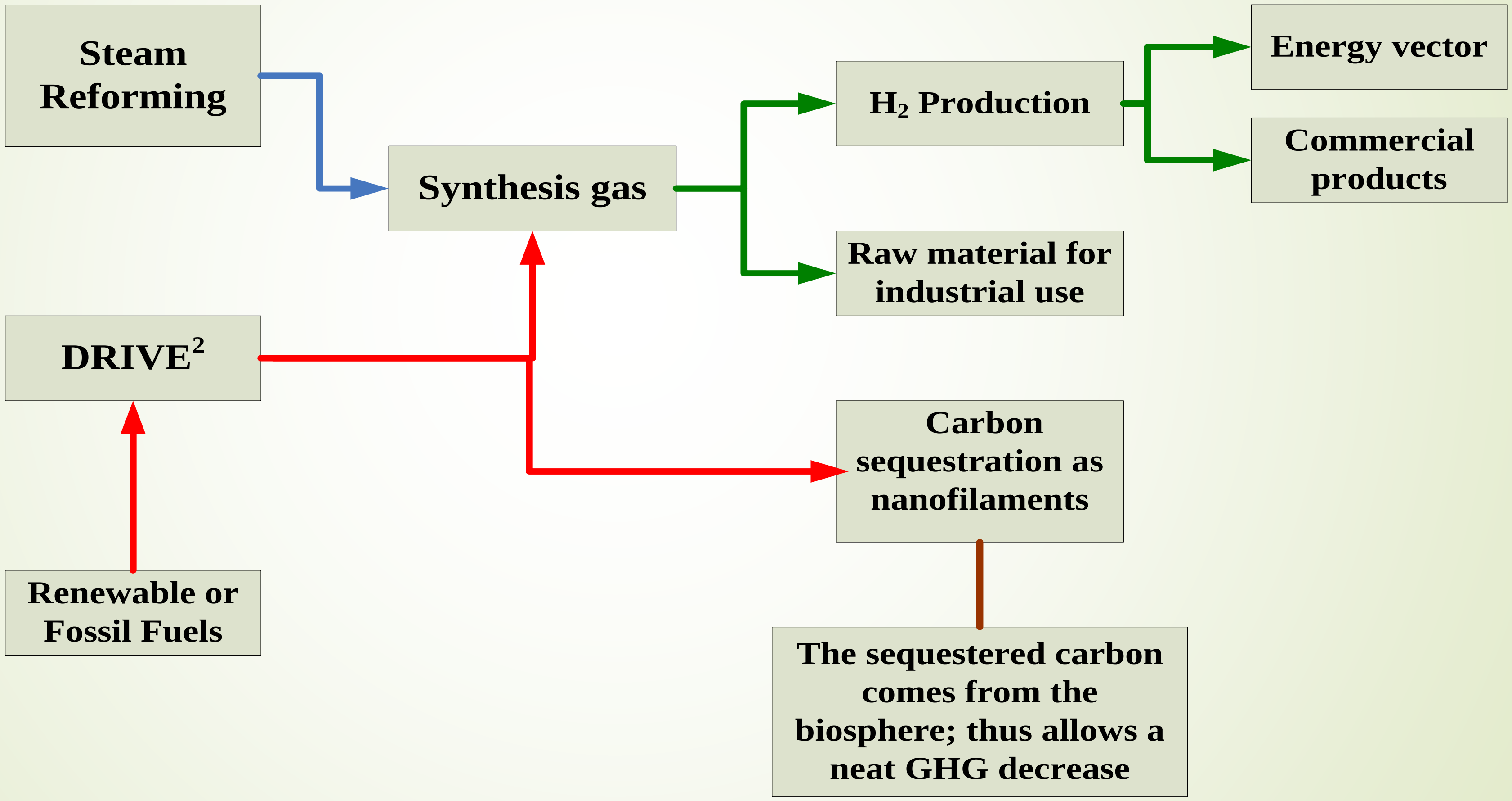
Rationale : GHG Sequestration?



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Literature (1)

- In published work the authors had shown that:
  - Low internal surface iron alloys are both cracking and dry reforming effective catalysts
  - Such catalytic reactions lead to formation of nanocarbons (nanofilaments and multi-wall nanotubes)
  - These nanocarbons contain nanograins of iron carbides

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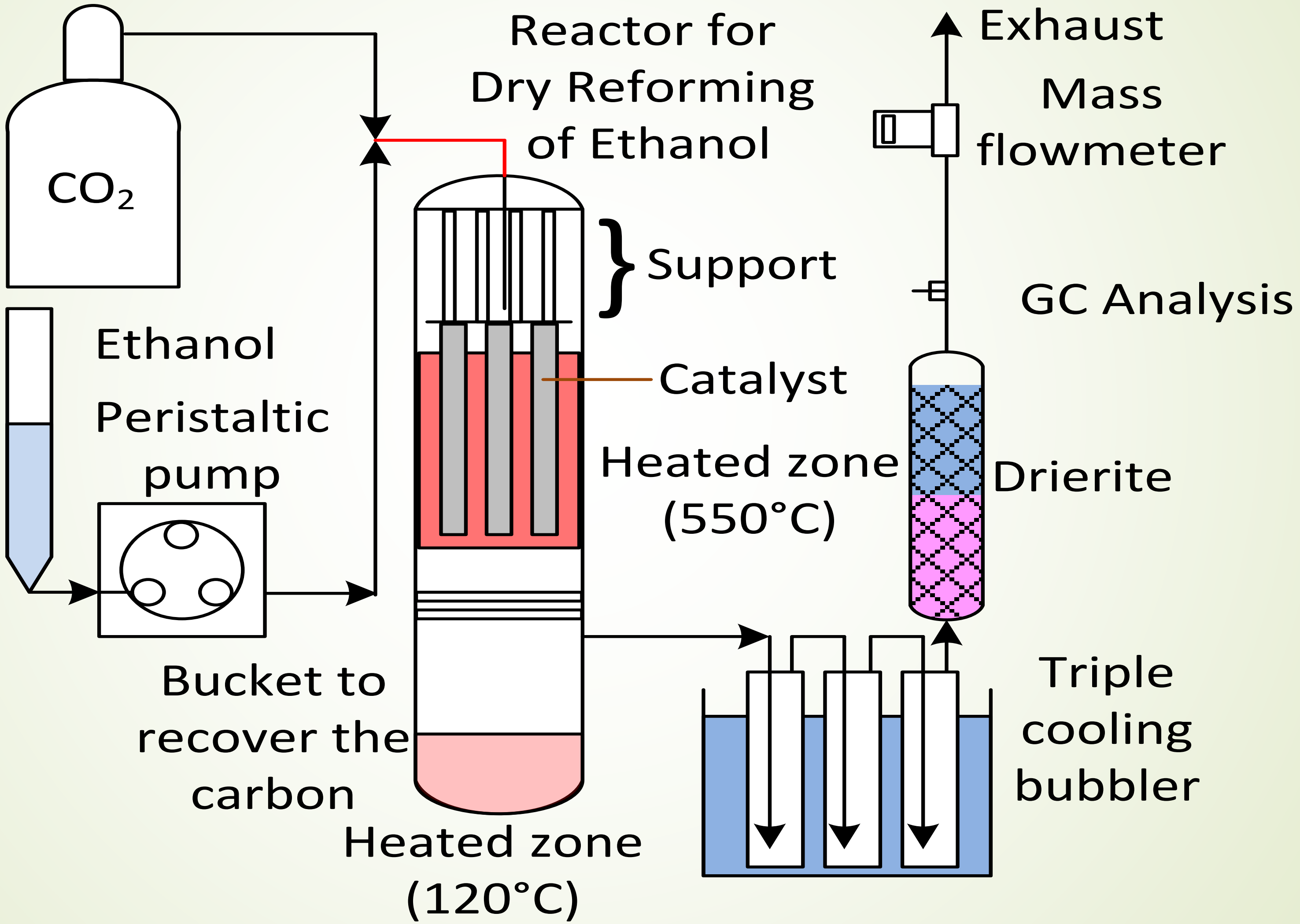
Literature (2) : Mechanism

- Formation of magnetite particles via the thermal-oxidative treatment; improves the specific surface
- Ethanol/CO_2 adsorb and react on magnetite
- Reduction of the magnetite to iron
- Transformation of iron into cementite
- Reforming of ethanol on cementite
- Growth of nano-filaments from the cementite particles

Experimental Set-Up



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Experimental Conditions

- **Quartz, bench-scale, fixed-bed reactor (BSFBR)**
- **Diameter of 4.6 cm and length of 122 cm**
- **T = 550°C and barometric pressure**
- **Liquid ethanol (98%-99.9%v/v) pumped and then vaporized before entering the reactor**
- **CO_2 or Ar gases (purity of 99.99%) were added to the ethanol vapour upstream of the reactor**
- **t = 2h**
- **Molar Ethanol/CO_2 = 1**
- **Overall GHSV of 2 300ml/h/g = 1.15 $m^3/(h*m^2)$**

The initial Fe catalyst

- Catalyst : Carbon steel (AISI 1010)
  - Max of 0.13% C
  - 0.3-0.6% Mn
  - Max of 0.04% P
  - Max of 0.05% S
  - Sheet thickness of 0.13 mm (+/- 10%)
- Thermally pretreated (partial oxydation)

Products Analysis

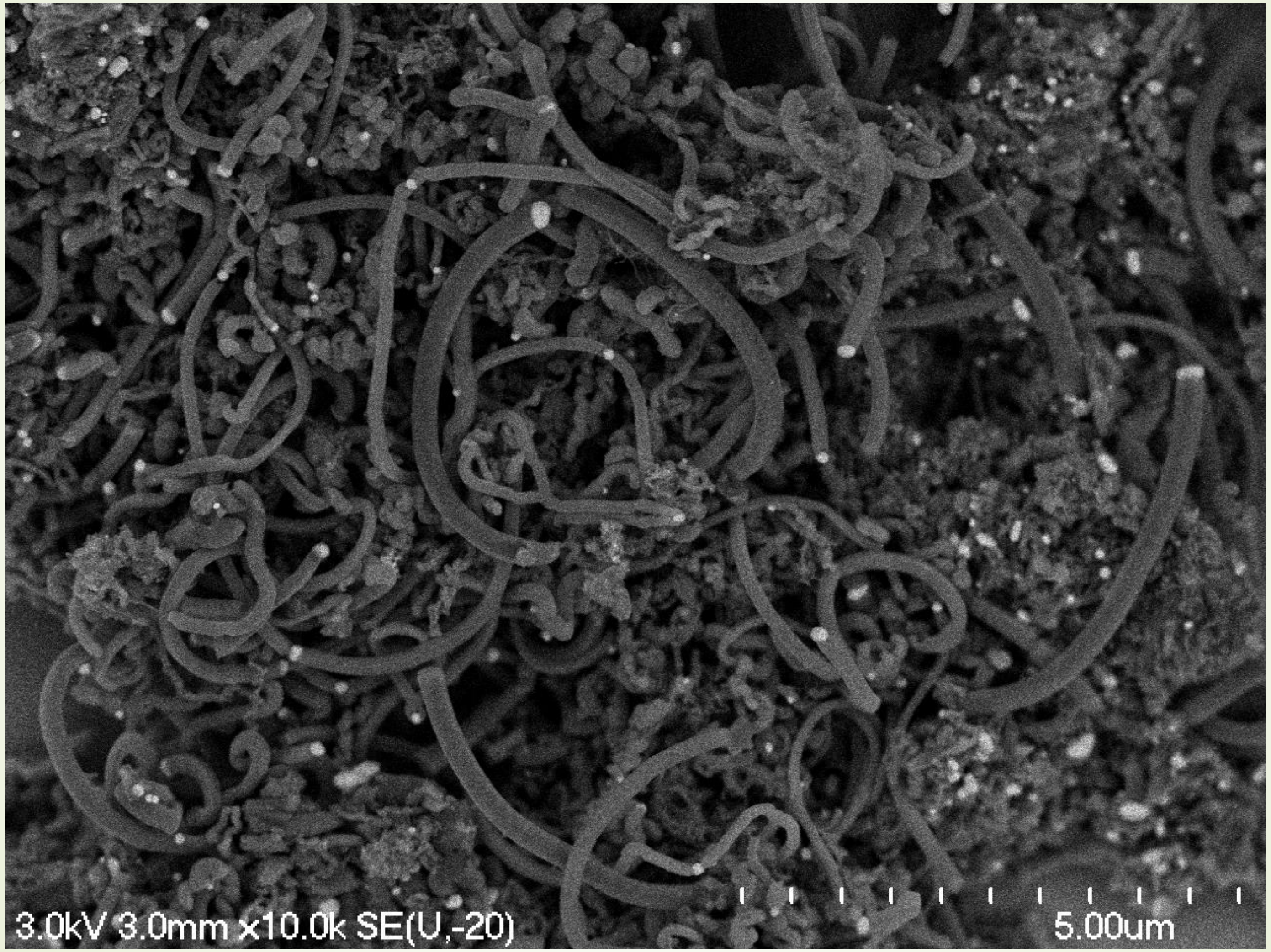
- **Exit gas is dried, using a cold trap and a molecular sieve column; then analyzed**
  - GC Model Varian CP3800 (HayeSep Q CP81073, HayeSep Q 81069, and HayeSep T CP81072 columns and Molsieve 13X CP81071 and Molsieve 5A CP81025)
- **CNF Analysis**
  - SEM Hitachi S-4700 for high quality imaging and for elemental analysis
  - XRD (Panalytical X'pert Pro diffractometer), for the crystalline phases in the CNF
  - AA (Varian SpectrAA-50/55 Spectrometer) for iron quantification. The analysis of each CNF sample was repeated three times, and the average Relative Standard Deviation (RSD) percentage was of 0.6%.

CNF as reforming catalysts

- Step 1 : Dry reforming of ethanol, using low carbon steel as the catalyst; this step produced the tested CNF

- Steps n (n=2-4) : Ethanol Cracking and Dry reforming tests, using the produced in step (n-1) CNF as catalyst

FEG/SEM – CNT Step 1



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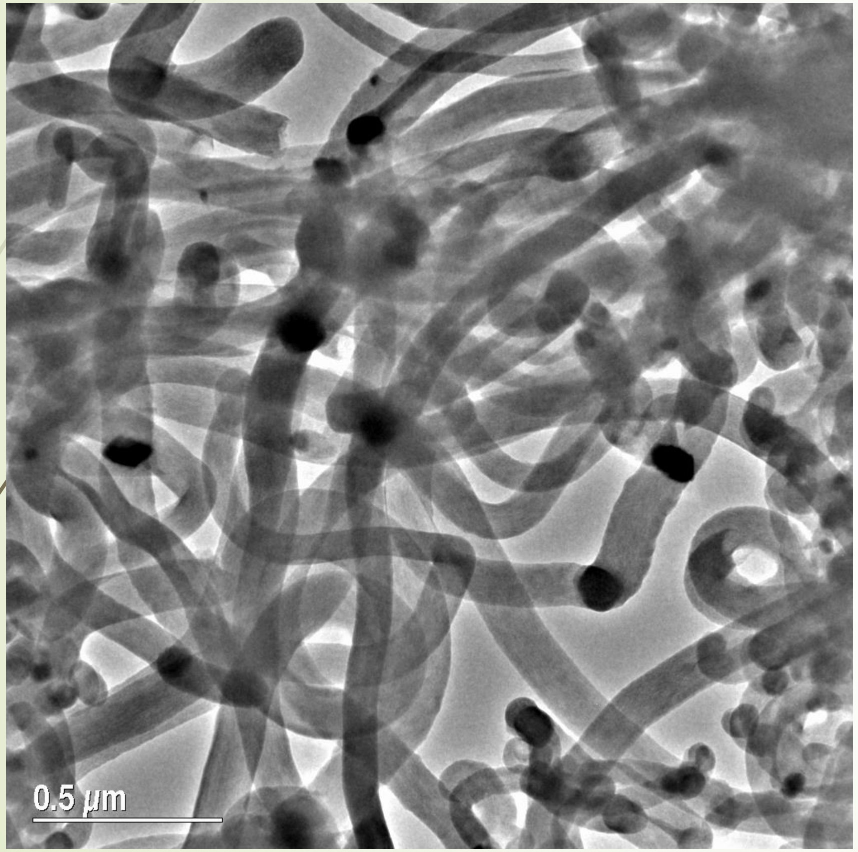
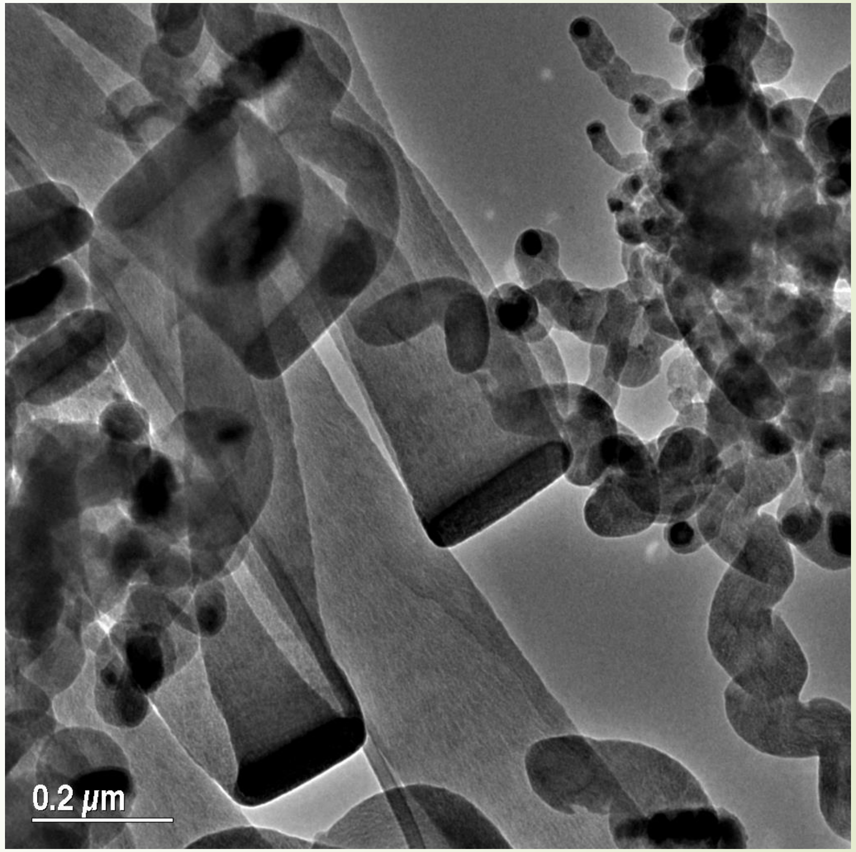
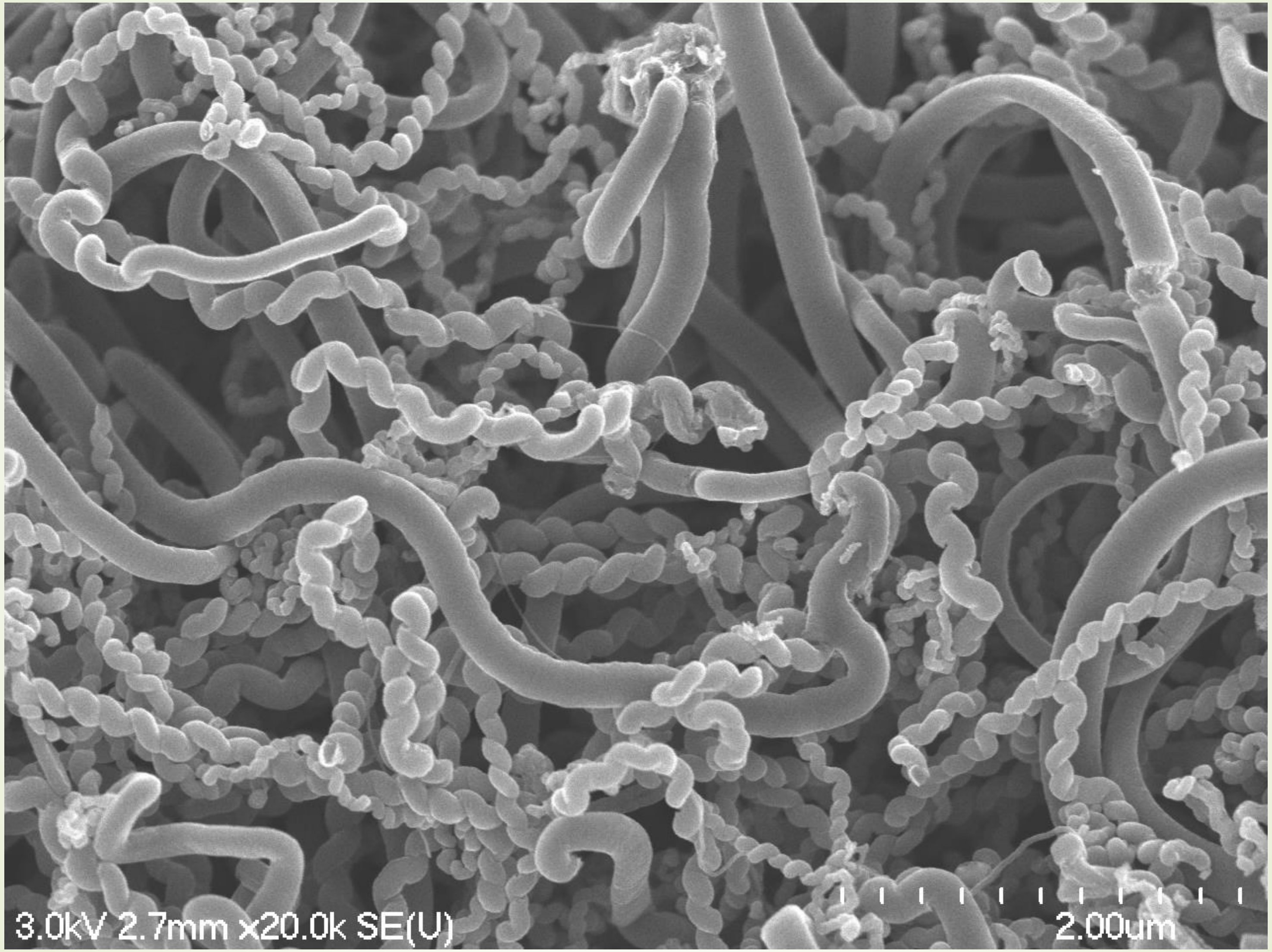
TEM nanograph of Carbon Nano-Filaments



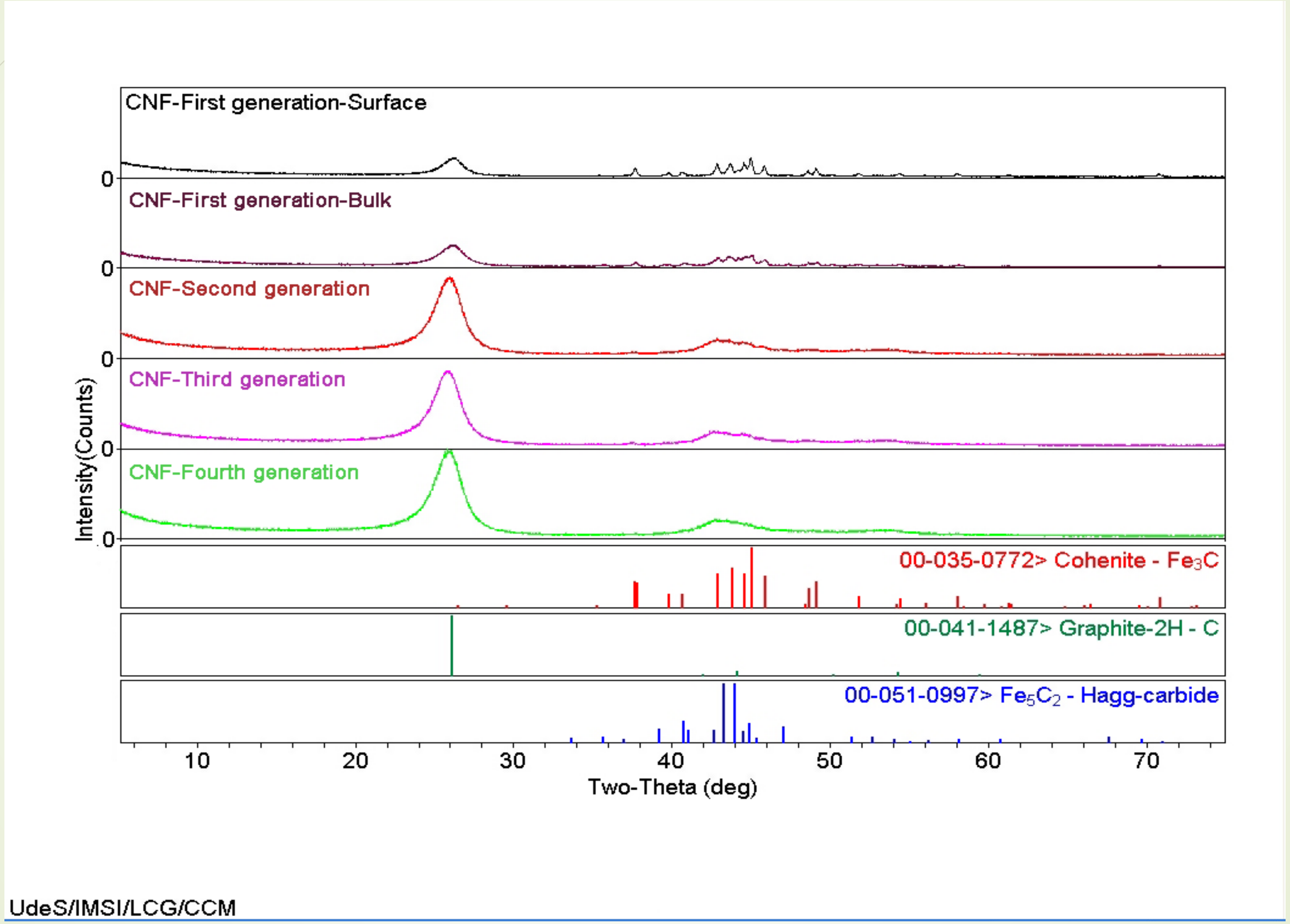


SEM - CNT 2nd generation



SEM - CNT 3rd generation

XRD – All 4 generations CNT



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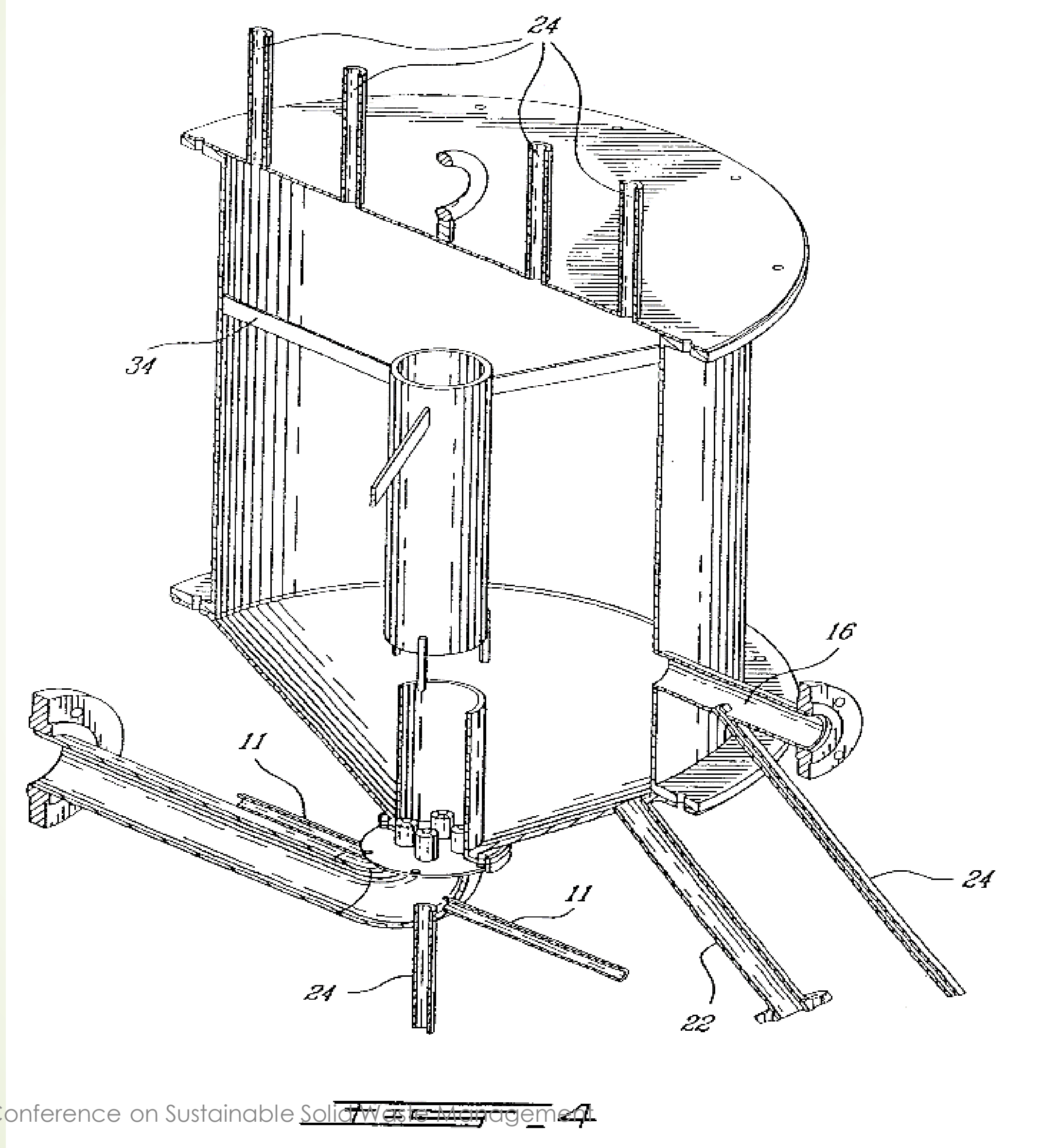
Results

CNF catalyst	2nd generation CNF catalyst	3rd generation CNF catalyst	4th generation CNF catalyst
Fe in Catalyst (g)	0.38	0.13	0.06
GHSV(ml/h/g)	120 955	348 155	789 367
GHSV Ratio	n.a.	2.88	2.27
TOF (H_2) (s^{-1})	0.00099	0.00267	0.00424
TOF (H_2) Ratio	n.a.	2.70 !	1.59
TOF (CO) (s^{-1})	0.00777	0.01984	0.0339
TOF (CO) ratio	n.a.	2.55 !	1.71

The extended DRIVE² Process: The HyFMBR



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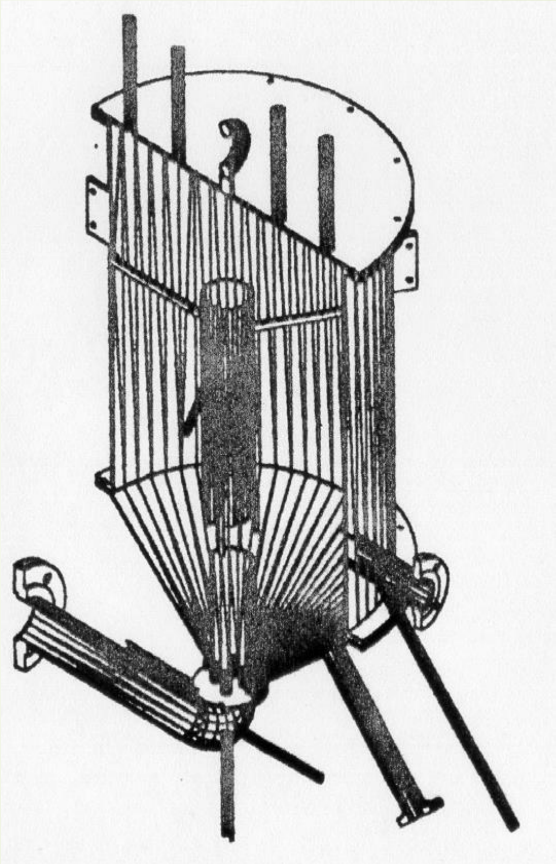
Principle of the HyFMBR

- **Central entrained bed**
- **The pyrolysis product is the fluidizing agent**
- **The fluid bed is situated in the middle of a quasi-static mobile bed (concentric cylinders configuration)**
- **The movement of the granular media renews continuously the surface and prevails a rigid cake formation. CNF formed are skimmed off and transported by the gas flow**
- **The flux of the granular media back to the fluidized bed area insures continuity**



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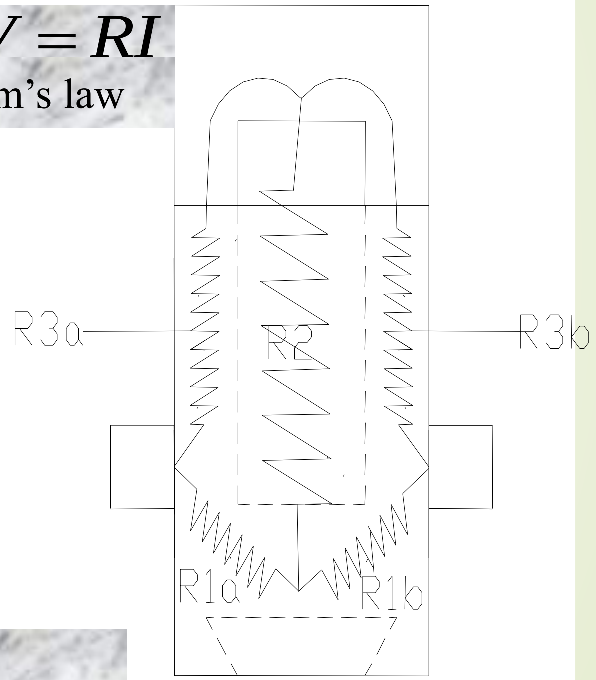
Flow Resistances in the HyFMBR

Darcy's Law ⟷ $\Delta V = RI$ Ohm's law

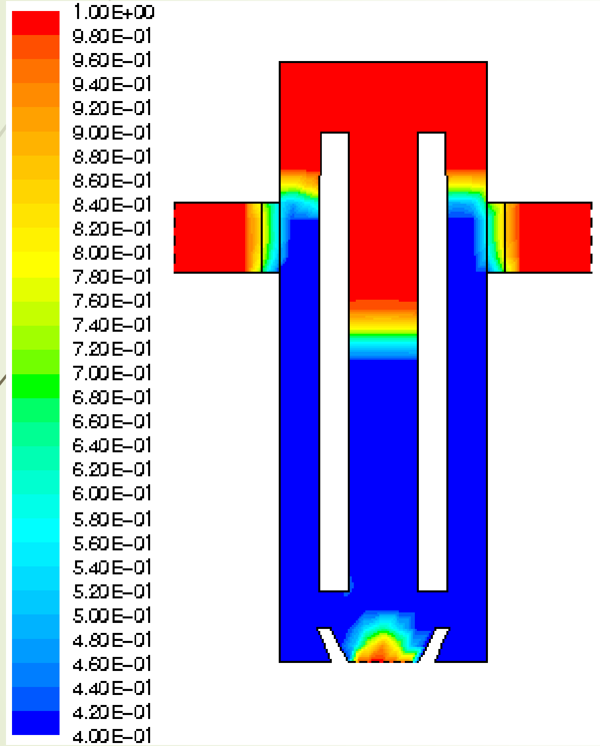
$$\Delta P = (Rtot) * (U_{0inlet} * \mu_f)$$

$$Rtot = \left(\frac{1}{R1a} + \frac{1}{R1b} + \frac{1}{R2 + \frac{R3a * R3b}{R3a + R3b}}\right)^{-1}$$

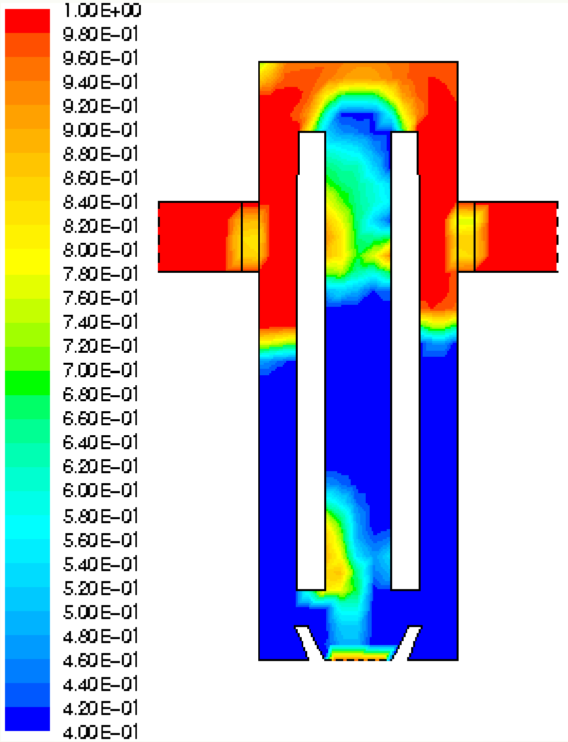
$$Q1a = Q1b = \frac{\Delta P}{R1a * \mu_f} * A = \frac{\Delta P}{R1b * \mu_f} * A$$



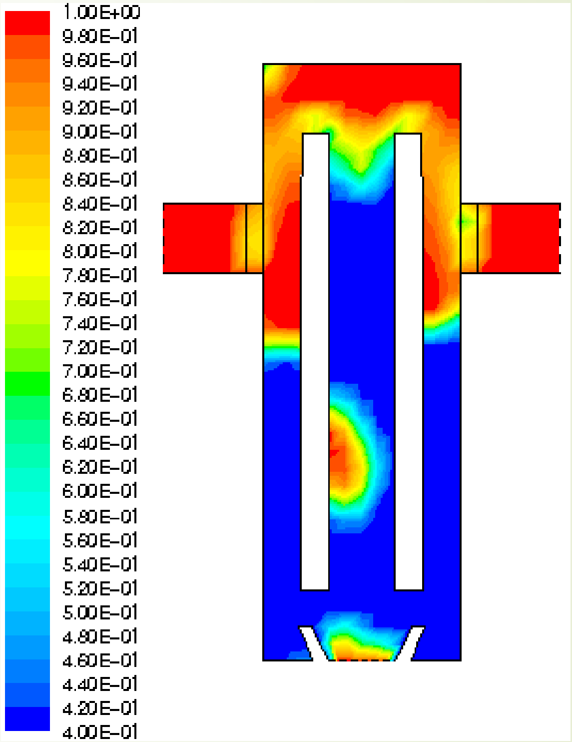
CFD simulation



Bubble formation



Bubble rising



Bubble explosion

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Addition of CNF in polymeric matrices

Storage modulus & Glass transition T vs CNF conc.

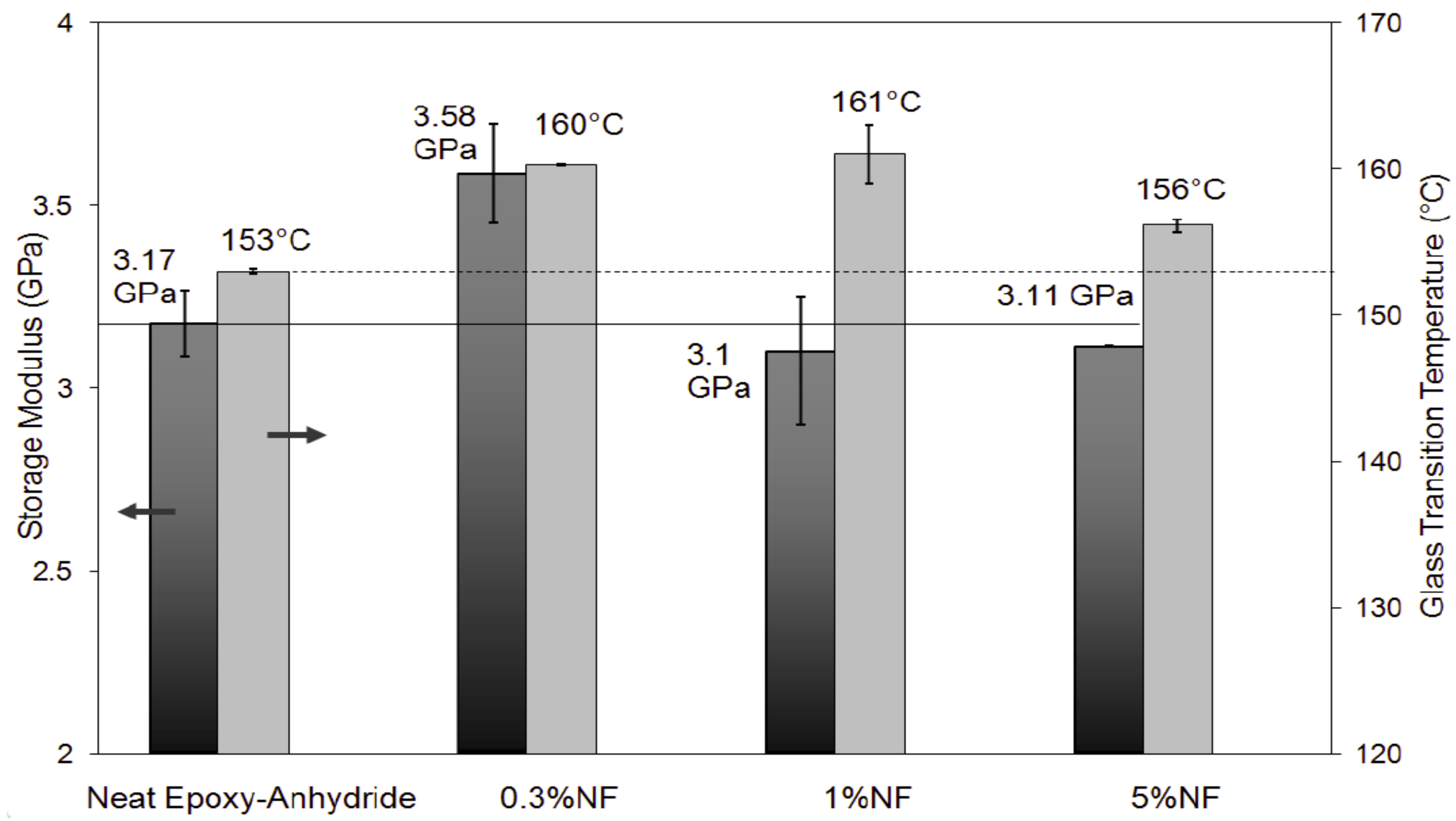

Figure 4. 4: Storage Modulus and *Tg* values of *CNFs*/epoxy-anhydride cured for various concentrations (*DMA* flexural test).

Source: Master Thesis of Isabelle Ortega, École Polytechnique de Montréal

Storage modulus vs CNF conc.

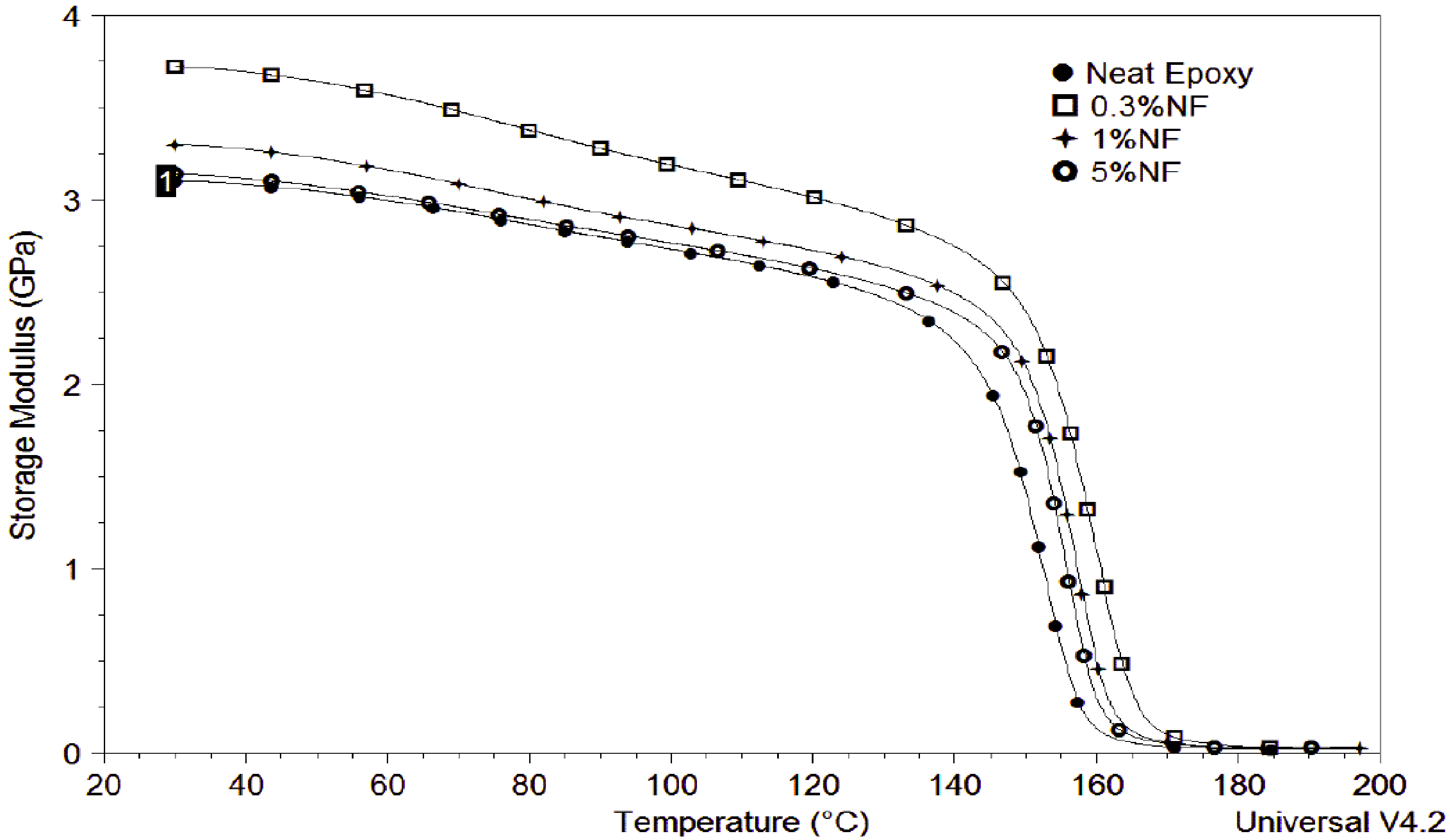

Figure 4. 3: ***DMA*** **flexural tests of** ***CNFs*****/epoxy-anhydride cured nanocomposites for various concentrations of** ***CNFs*****.**

Source: Master Thesis of Isabelle Ortega, École Polytechnique de Montréal

Conductivity vs CNF concentration without and with US

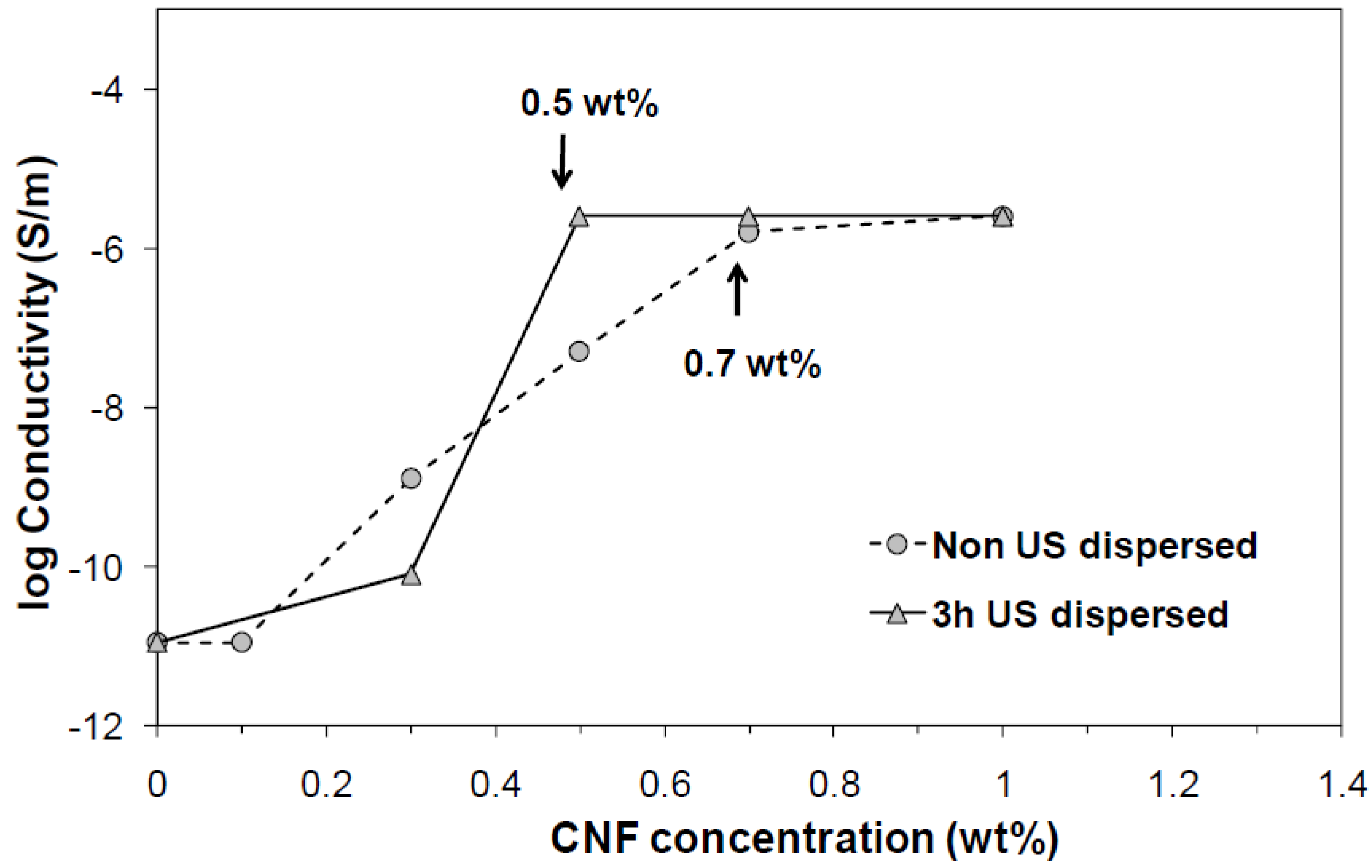

Figure 4. 12: Dielectric conductivity of CNFs/epoxy-anhydride cured nanocomposites with and without ultrasonication.

Source: Master Thesis of Isabelle Ortega, École Polytechnique de Montréal

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.

Fluidized bed pyrolyzer

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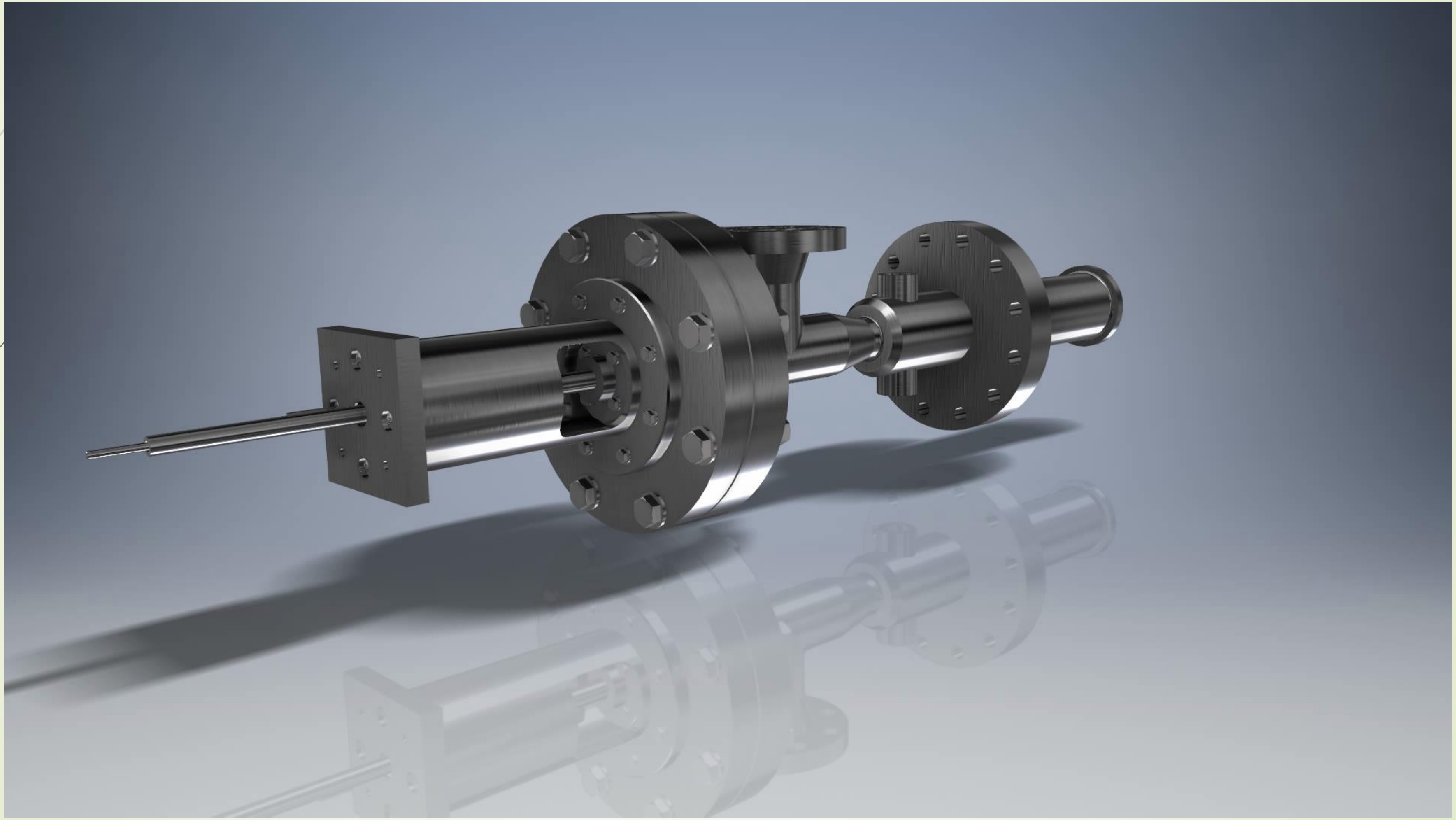
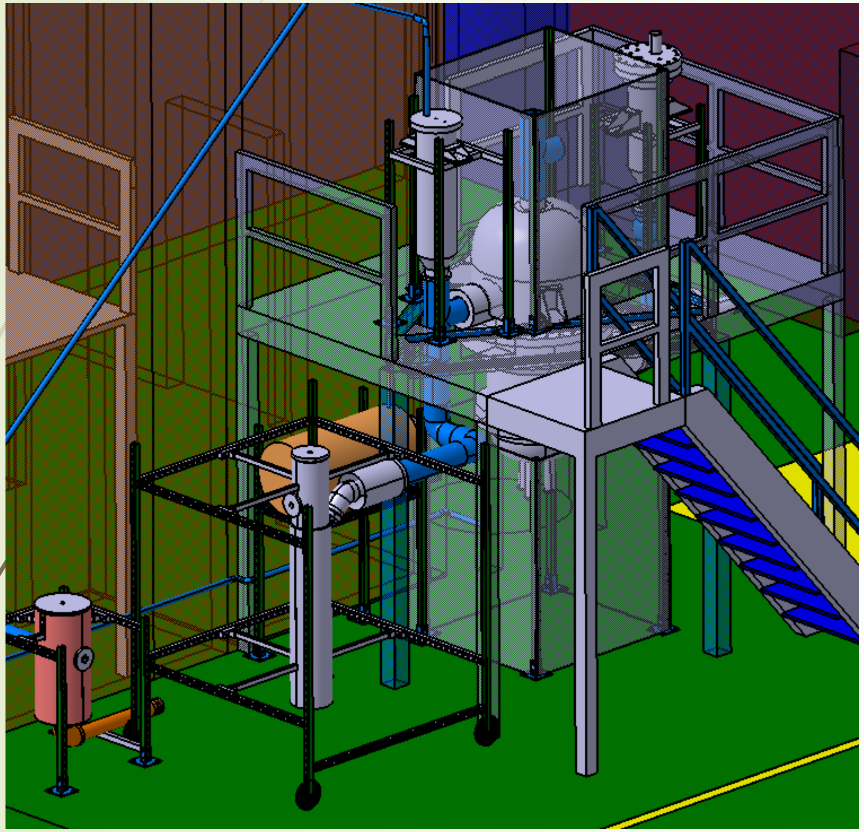
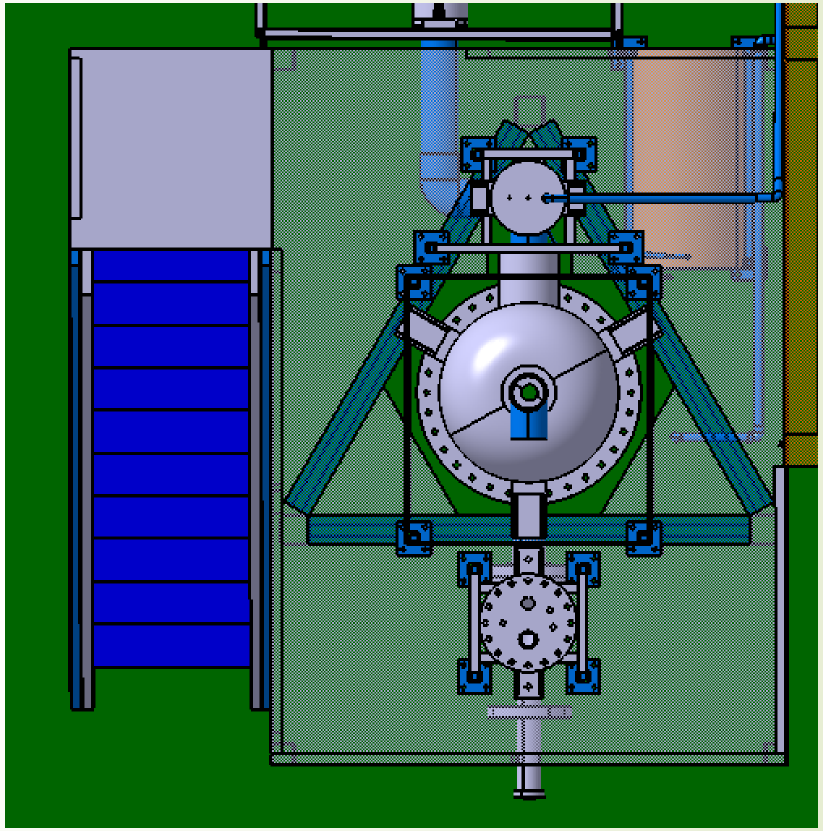
Screw feeder



Pyrolyzer & Peripherals

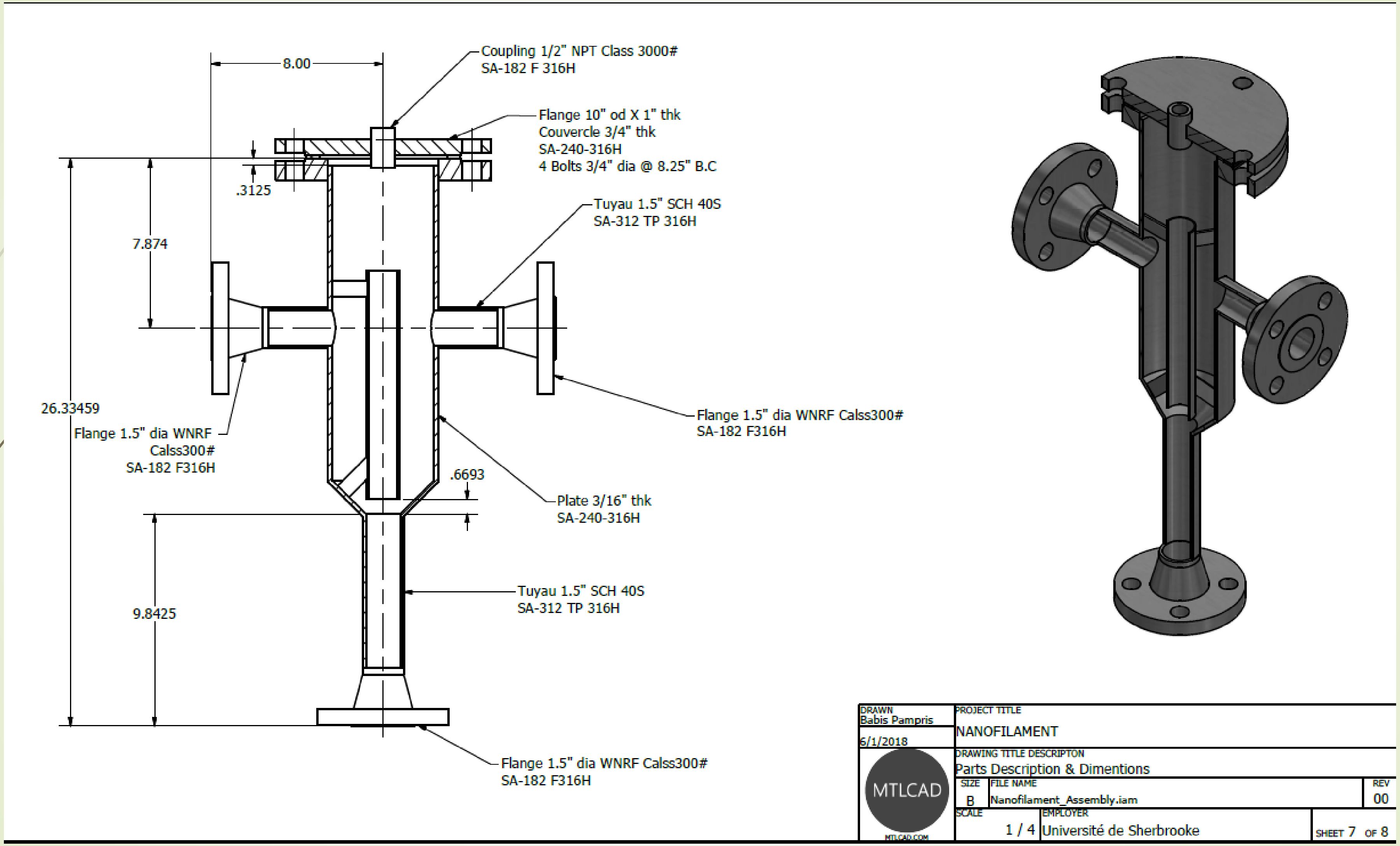


Isometric view



View from the top

CNF Reactor



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Coupling 1/2" NPT Class 3000#
SA-182 F 316H
Flange 10" od X 1" thk
Couvercle 3/4" thk
SA-240-316H
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.3125
7.874
Tuyau 1.5" SCH 40S
SA-312 TP 316H
26.33459
Flange 1.5" dia WNRF
Calss300#
SA-182 F316H
Flange 1.5" dia WNRF Calss300#
SA-182 F316H
.6693
Plate 3/16" thk
SA-240-316H
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Tuyau 1.5" SCH 40S
SA-312 TP 316H
Flange 1.5" dia WNRF Calss300#
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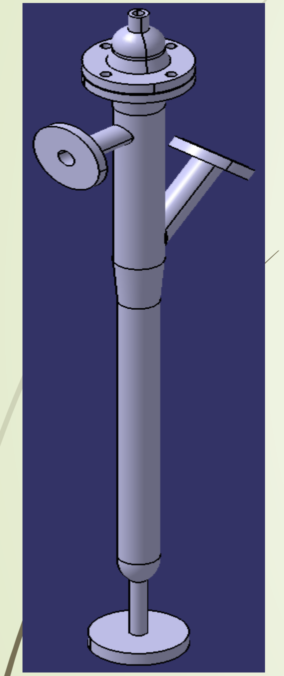
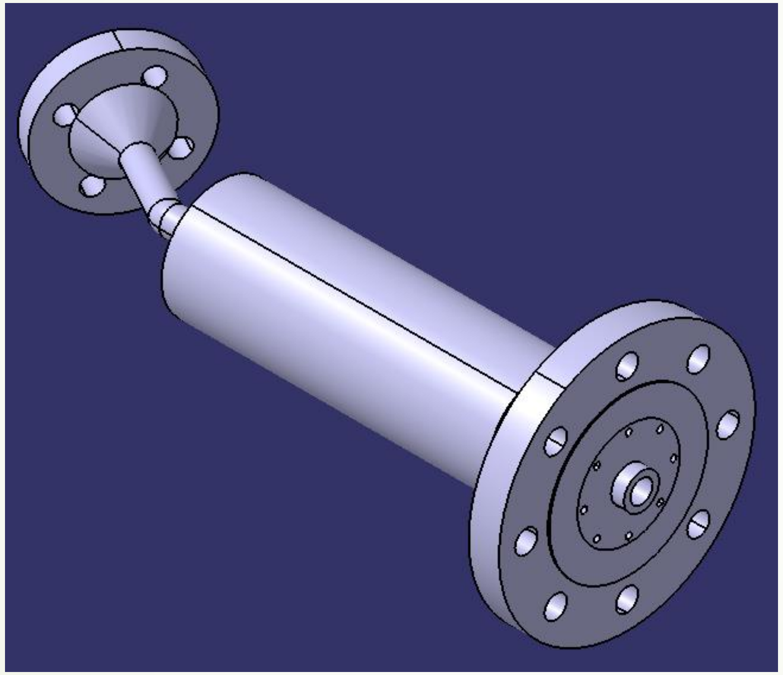
Université de Sherbrooke
SHEET 7 OF 8

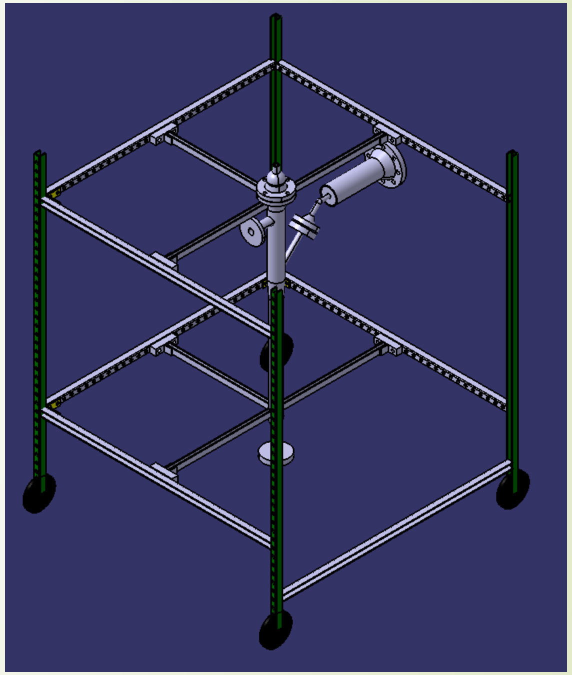
Reformer and Preheater



Reformer

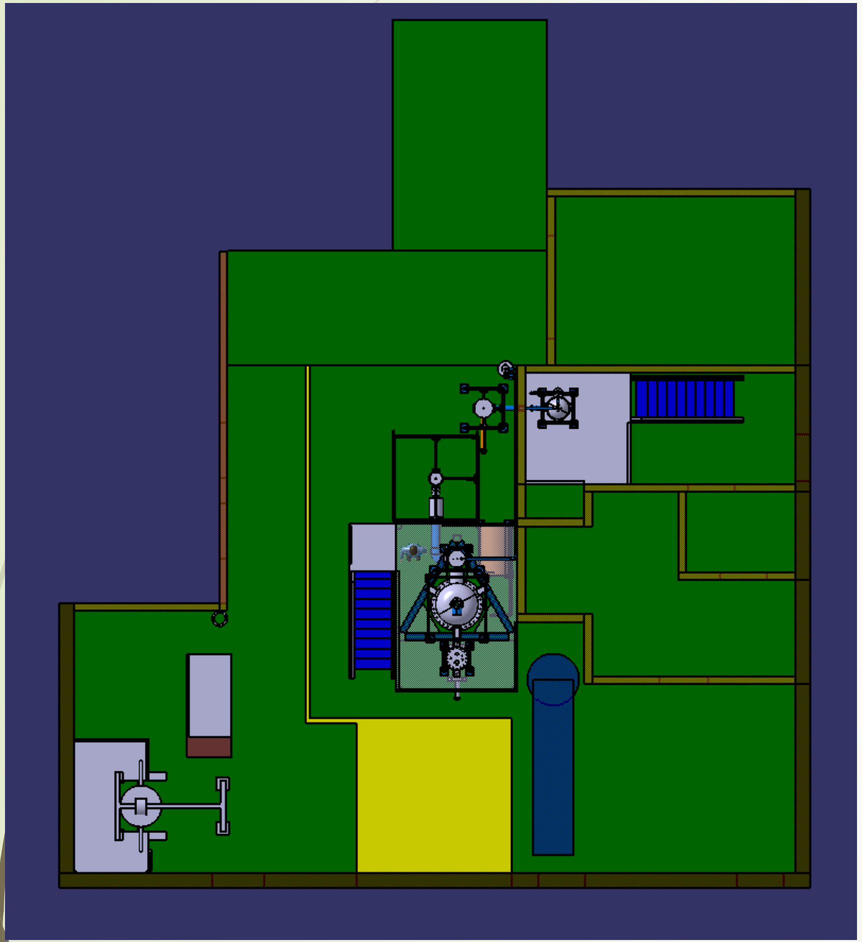


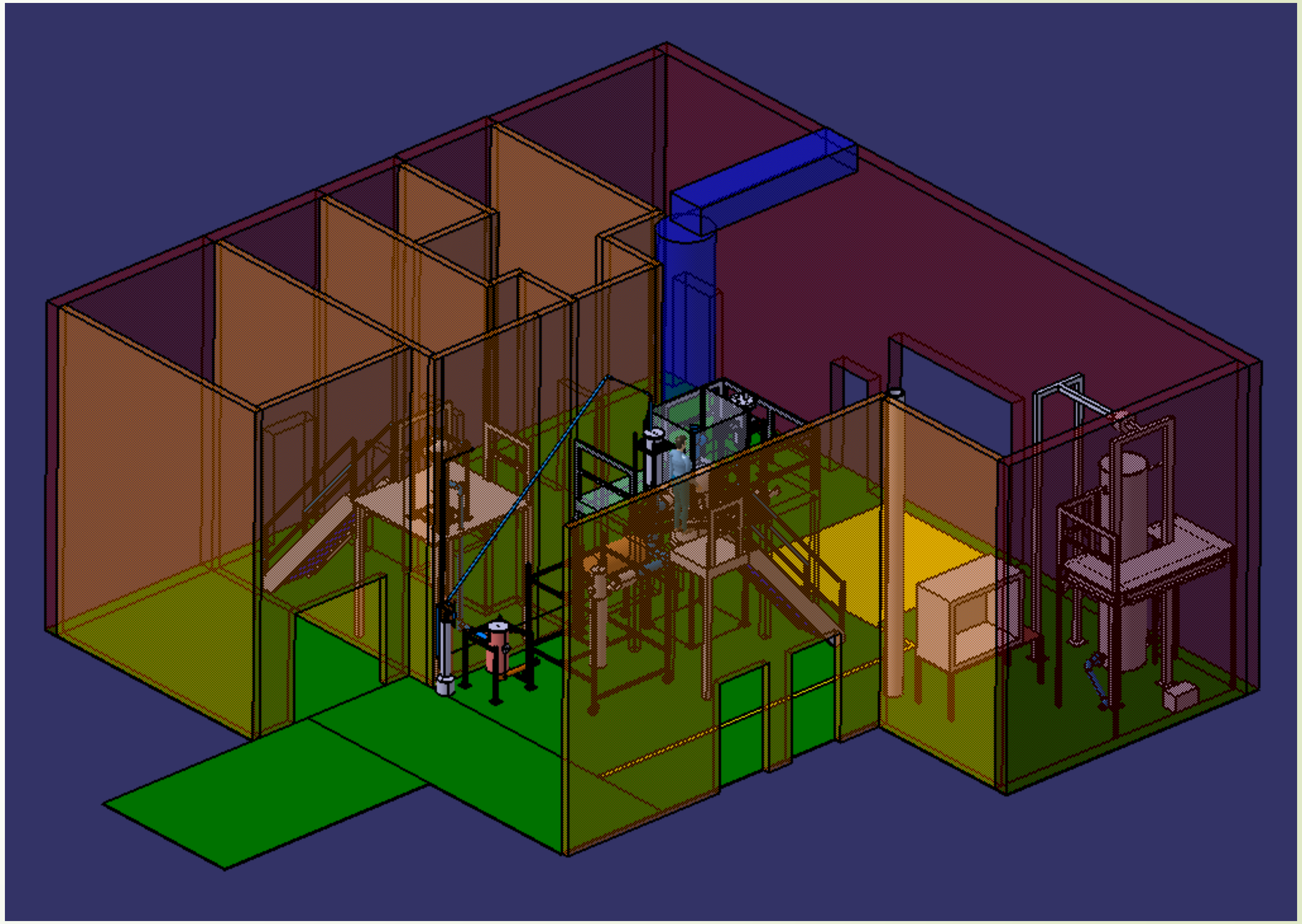
Preheater



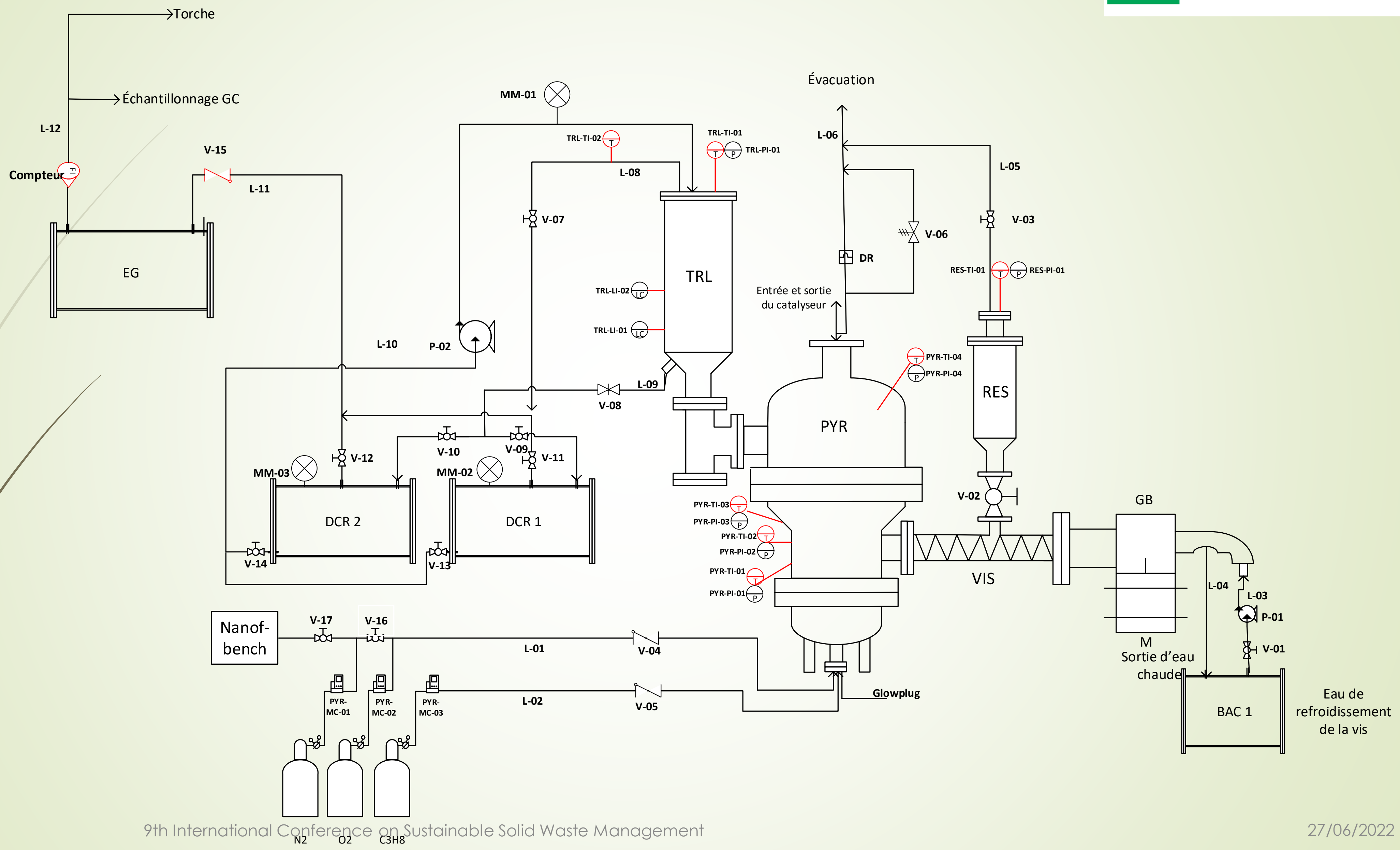
Installed

Isometric view in new building





ATP Pilot P&ID



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ATP reactor setup

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ATP Reactor

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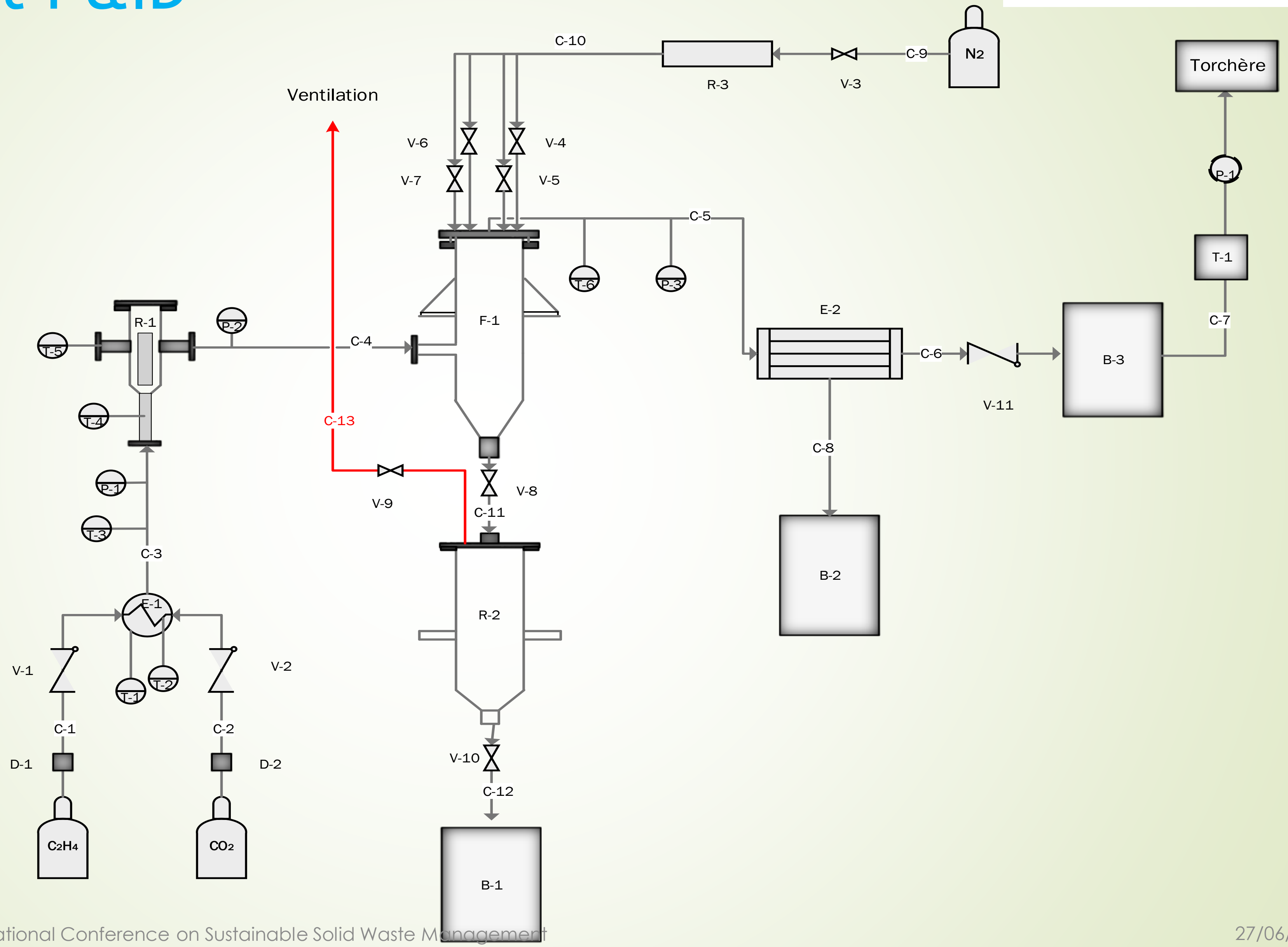
CNF Pilot P&ID



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- Filter
- CNF recovery vessel
- Gas dehydration

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Gas Flare

Process parameters & experimental results of the nanocarbons production

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RESULTS	Test A	Test B
Carbon (g)	615	291
Carbon production rate ($kg_C.kg_{cat}^{-1}.h^{-1}$)	0.21	0.15
Carbon yield (%)	53.2	37.3
Hydrogen yield (%)	46.4	43.1
Total HC conversion (%)	73.0	48.5
Total CO_2 conversion (%)	69.9	57.2
Mass balance error for C (%)	6.3	7.6
Mass balance error for H (%)	4.0	5.3
Mass balance error for O (%)	9.6	4.9
Temperature (°C)	550	600

Contributions

- HQP
  - Dr Mostafa Chamoumi, PDF
  - Abir Azara, PhD student
  - Salma Belbessai, PhD student
  - Dr Frank Dega
  - Martin Gagnon
- Technicians and Drafters
  - Henri Gauvin
  - Stéphane Guay
  - MTLCAD and François-Niels Meillot, 3D Drawings
- KWI & Soleno
  - Dr Jasmin Blanchard, KWI
  - Yves Laroche, MBA, KWI
  - Dr Pierre Breton, KWI
  - Carl Diez, Soleno
- Centre de caractérisation des matériaux de l'UdeS
- Prof. Edu Ruiz, École Polytechnique de Montréal
- UdeS for new buildings
  - Prof. Patrik Doucet, Dean of Engineering
  - Prof. Jean-Pierre Perrault, Vice-Rector, Research and Graduate studies

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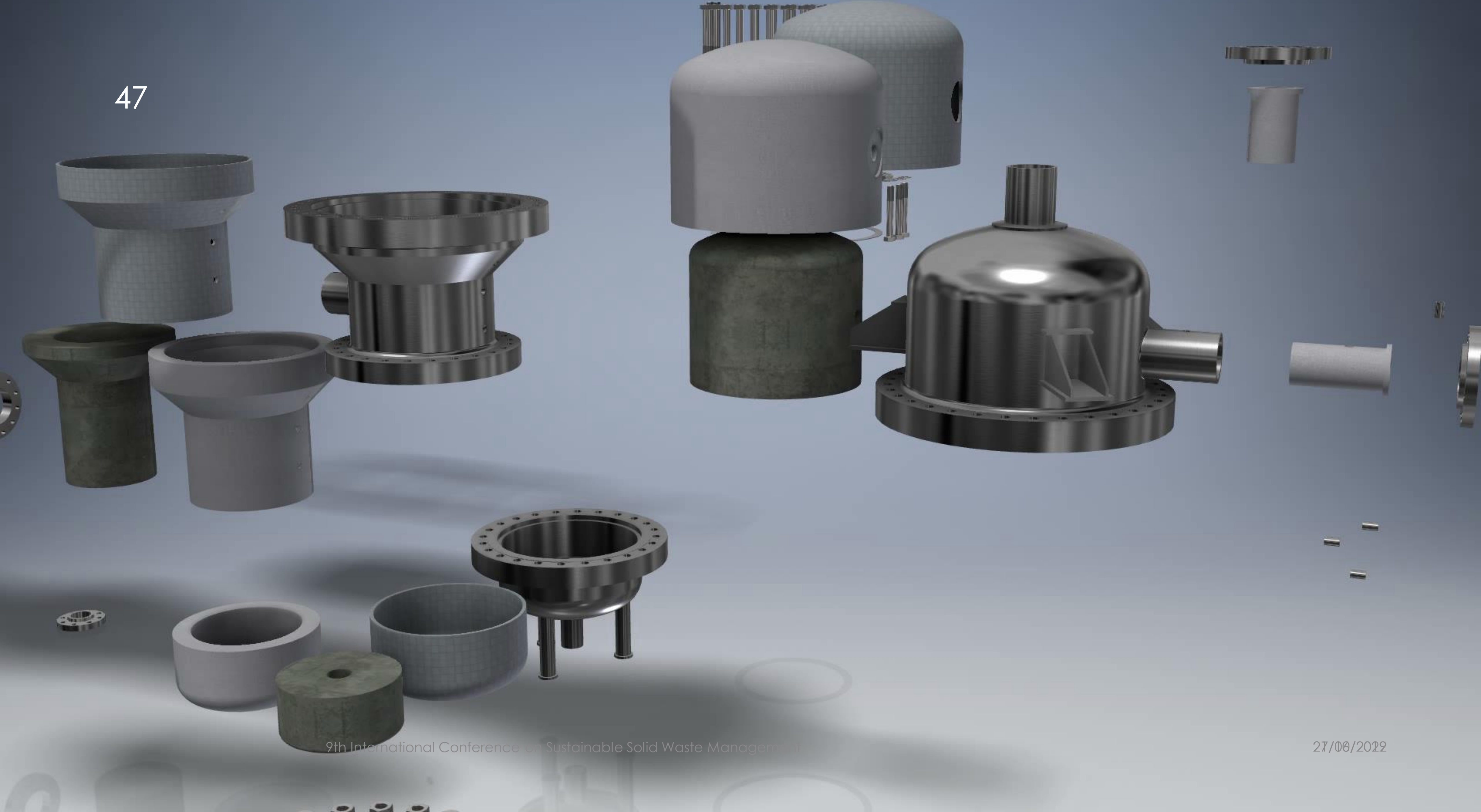
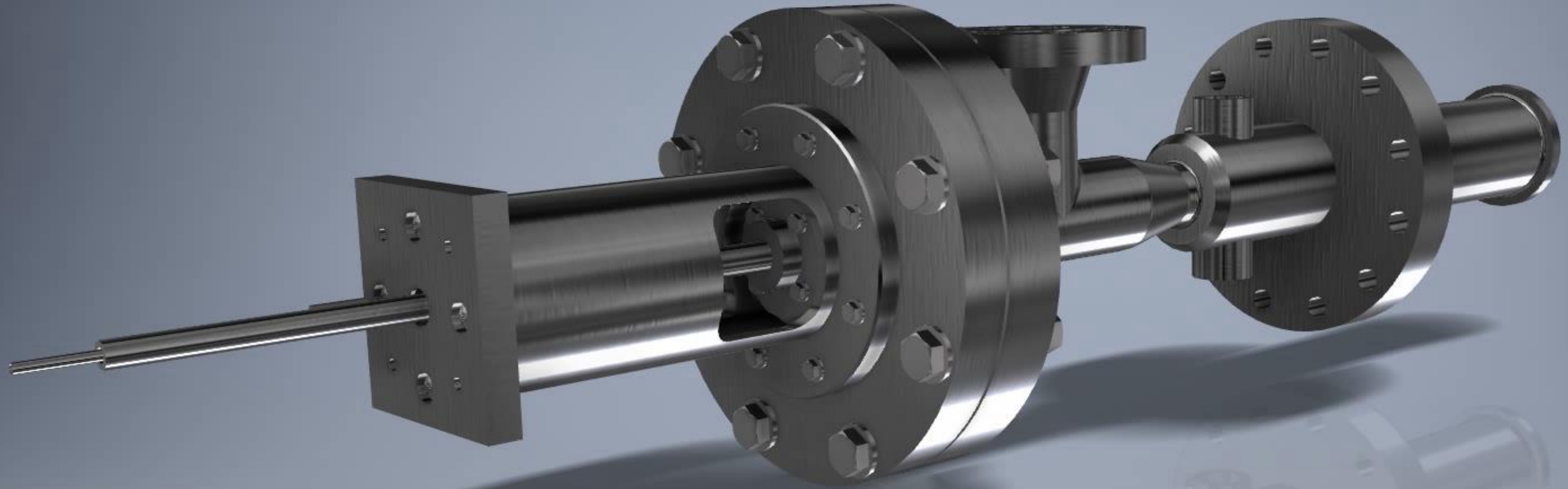




Fluidisation Relationships

Thonglimp:

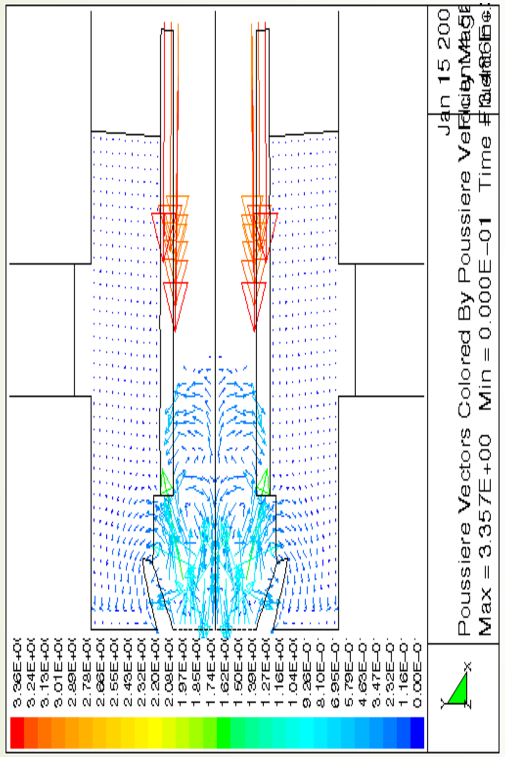
$$U_{mf} = \frac{Re_{mf} * \mu_f}{D_p * \rho_f}$$

$$GaMv = 1.75\frac{Re_{mf}^2}{\psi\varepsilon_{mf}^3} + 150\frac{(1-\varepsilon_{mf})}{\psi^2\varepsilon_{mf}^3}Re_{mf}$$ (Ergun)

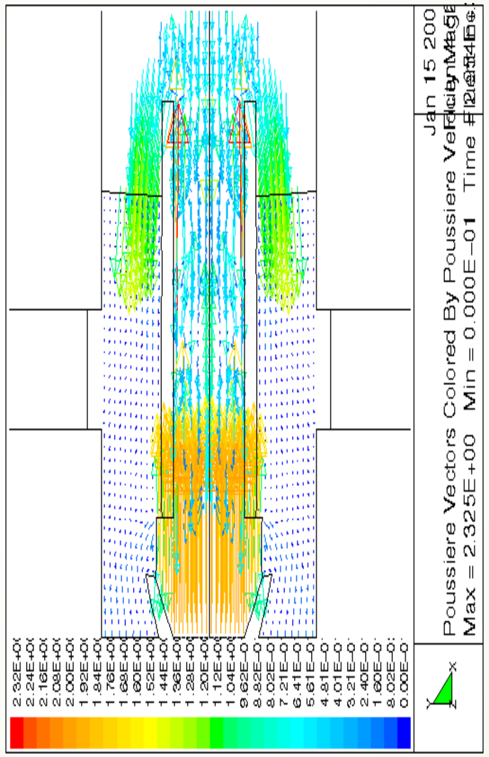
$$Re_{mf} = 7.54e^{-4}(GaMv)^{0.98}$$

$$\varepsilon_{mf} = 1 - \frac{M}{\rho_S S H_{mf}}$$

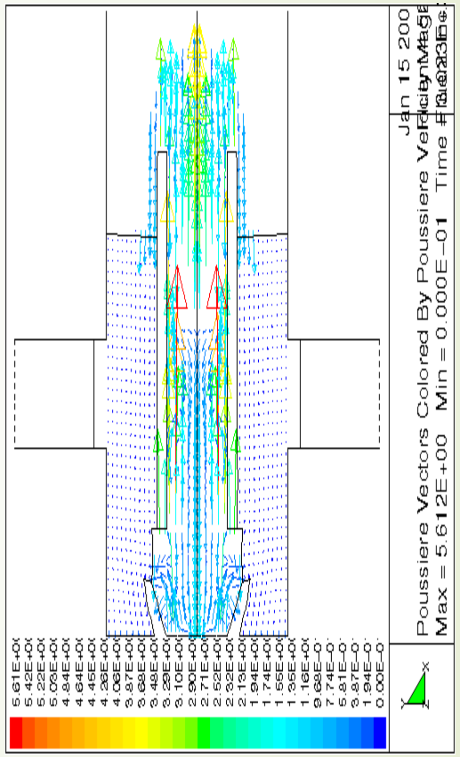
CFD simulation



Plugging Period



Expansion Period



Falling Period

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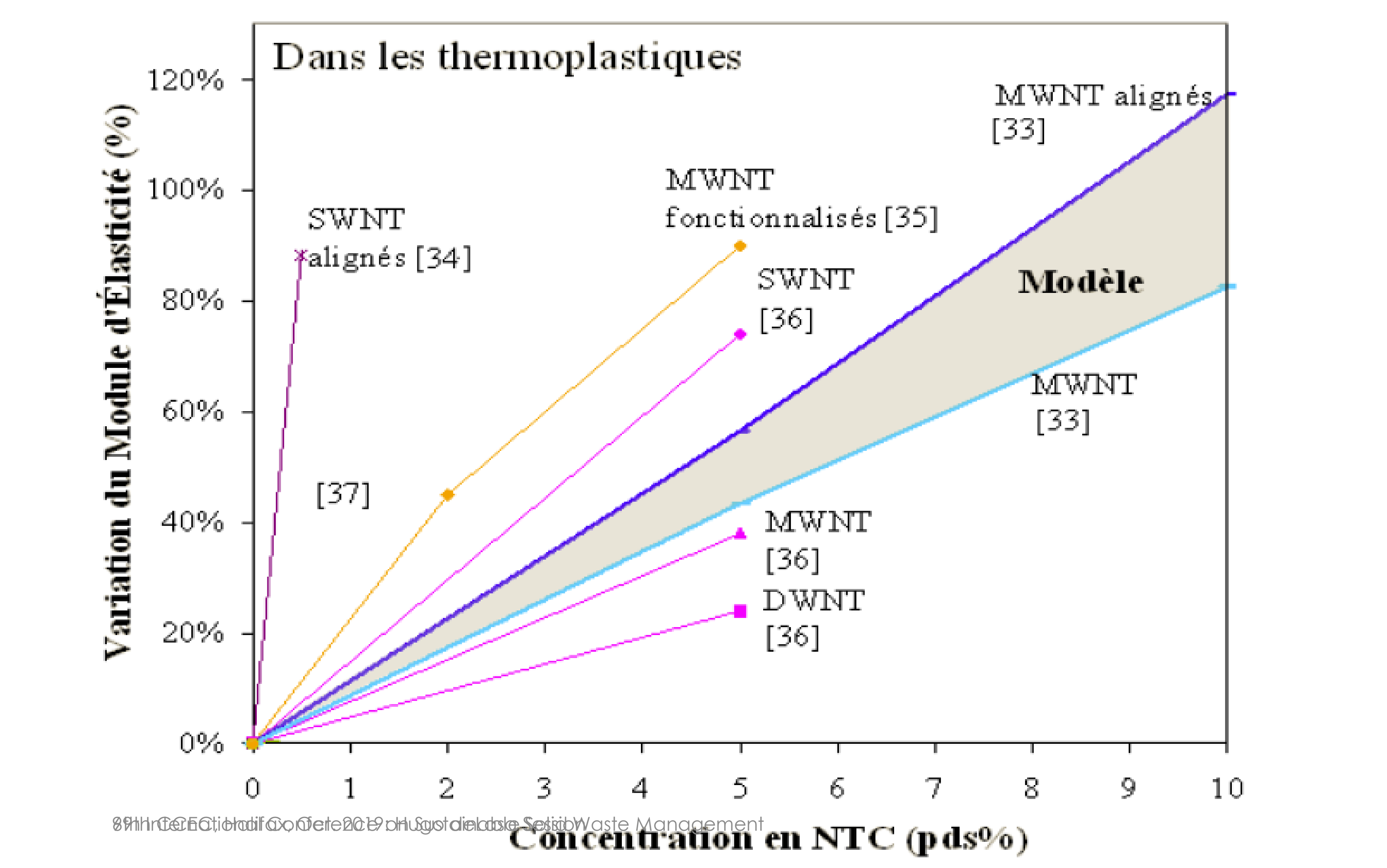
Young Modulus vs CNT concentration in thermoplastics



EPOXY used in the tests

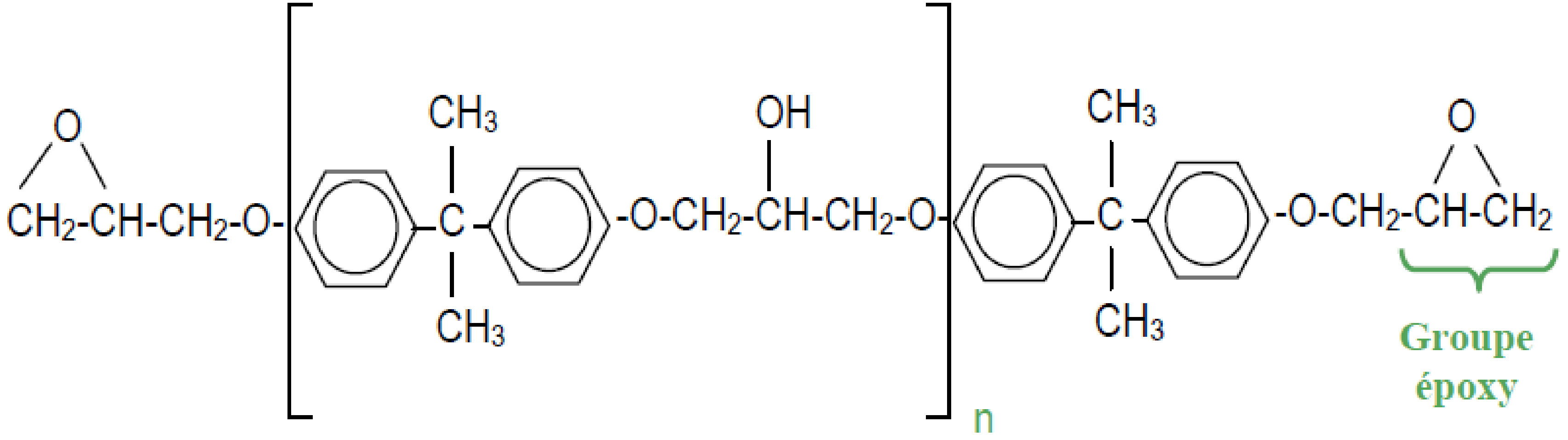
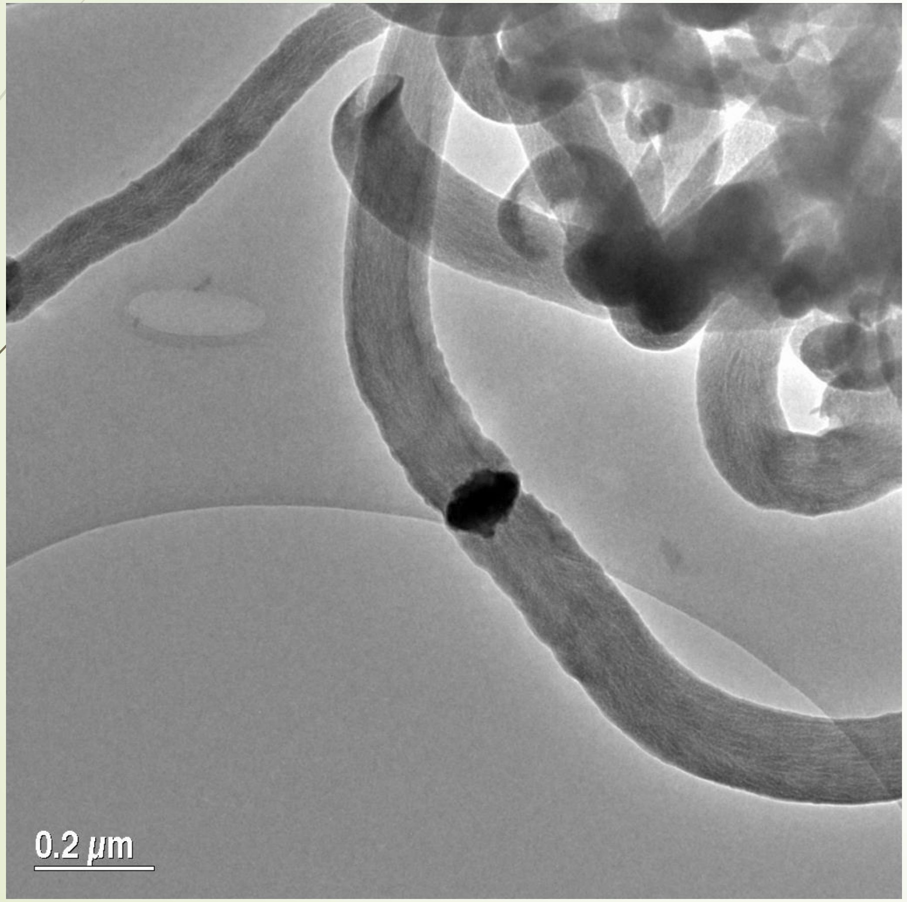
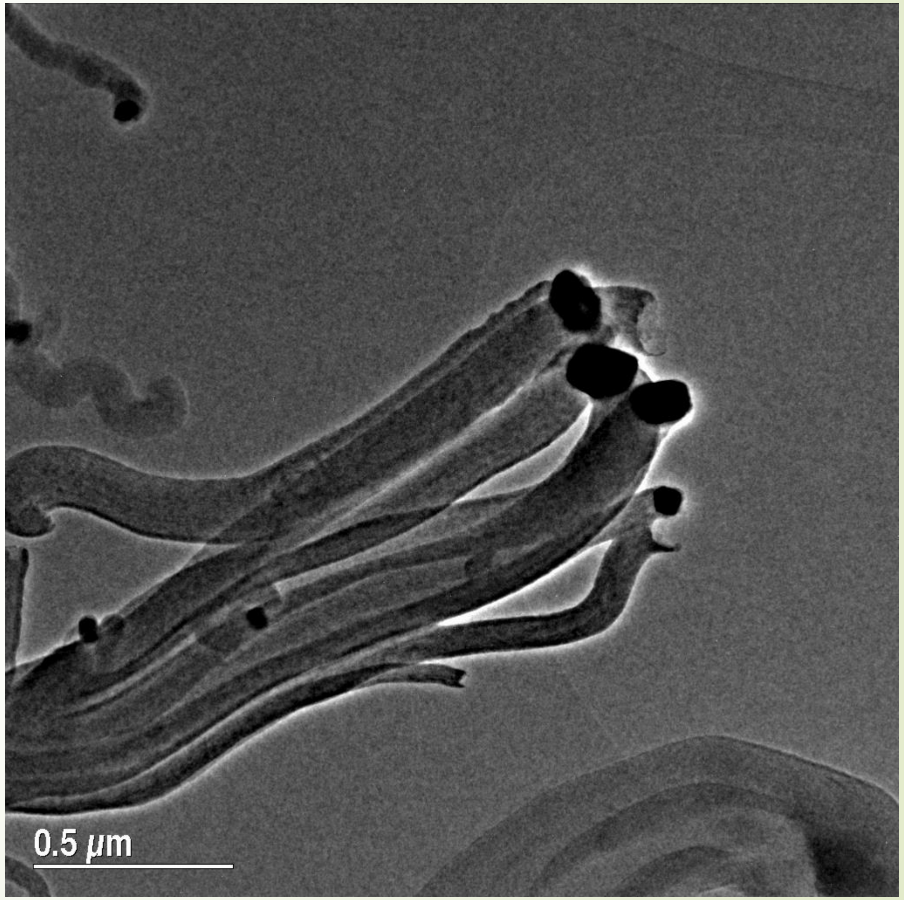


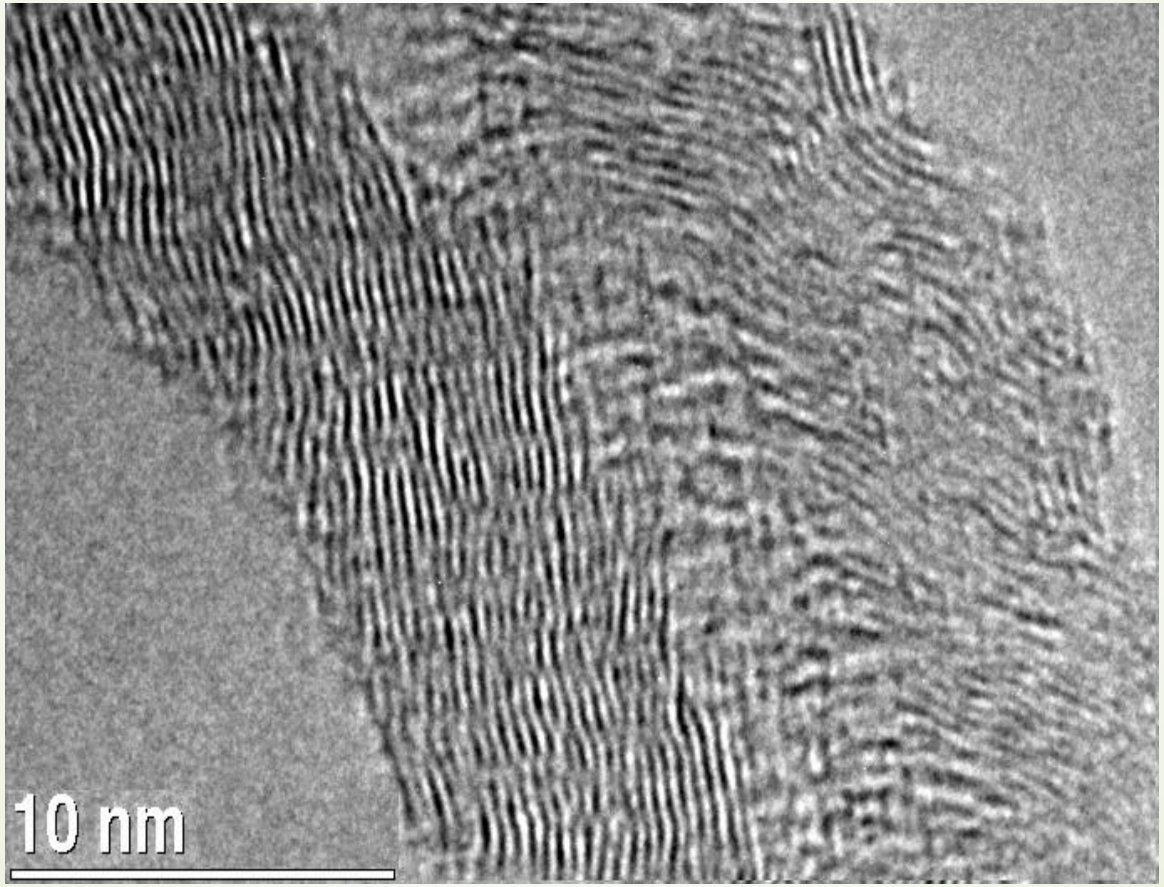
Figure 2. 5 : Structure chimique d'une époxy de type DGEBA.

TEM nanograph of Carbon Nano-Filaments





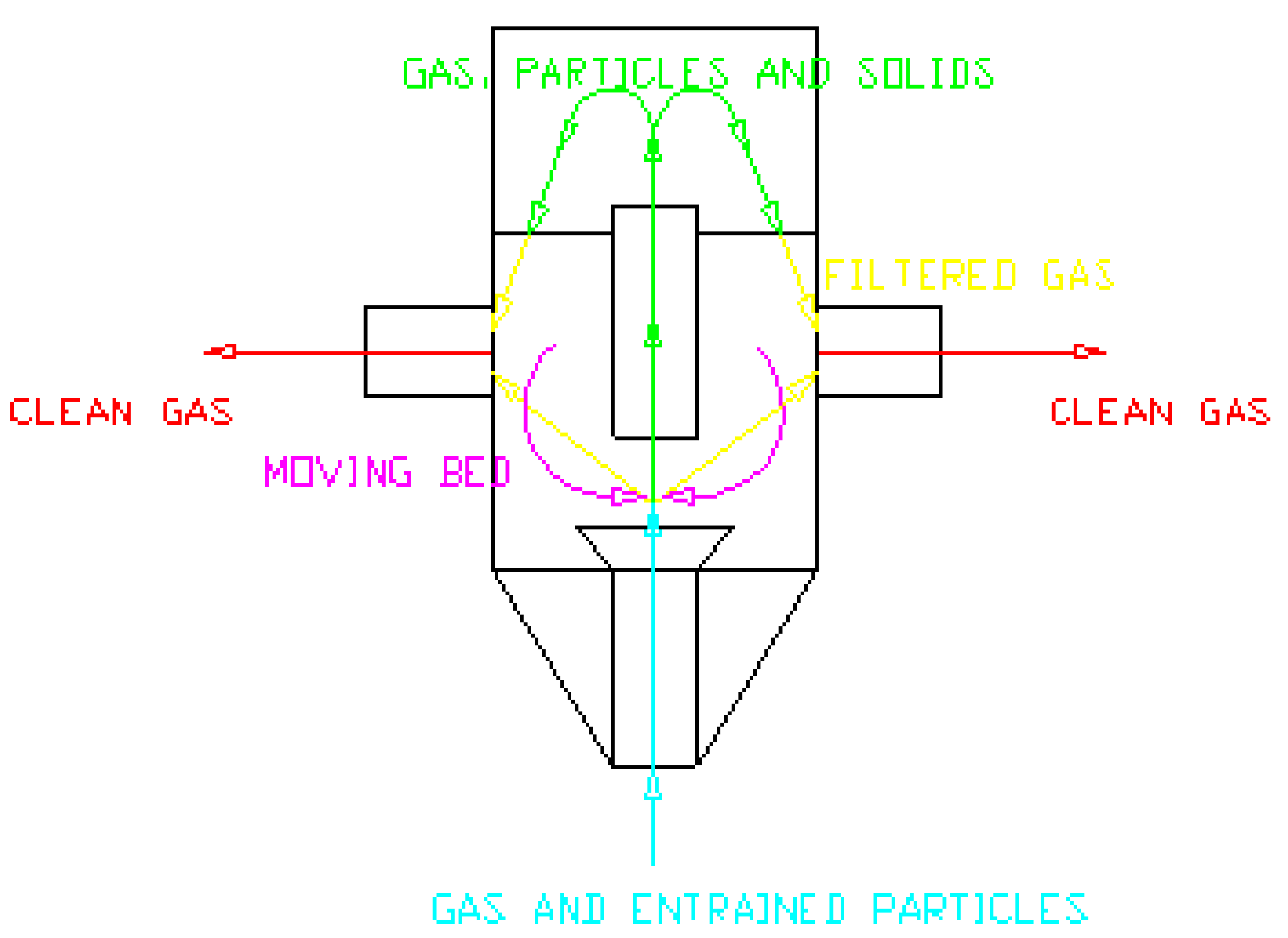
TEM nanograph of Carbon Nano-Filaments



System Definition for CFD

- Three-phase flow (g-s_1-s_2)
- s_1 is the filtering media phase (average of 500μm)
- Eulerian multiphase flow
- Kinetic theory for dense (frictional) granular flow
- K-ε model for turbulence
  - Kinetic energy and dissipation
  - Contribution to the viscosity
- Exits permeable for gas flow (g) and filtered particles (s_2) at atmospheric pressure
- No spatial heterogeneity at time zero

MBR phase movements



Storage modulus & Glass transition T at 1% CNF vs US treatment time

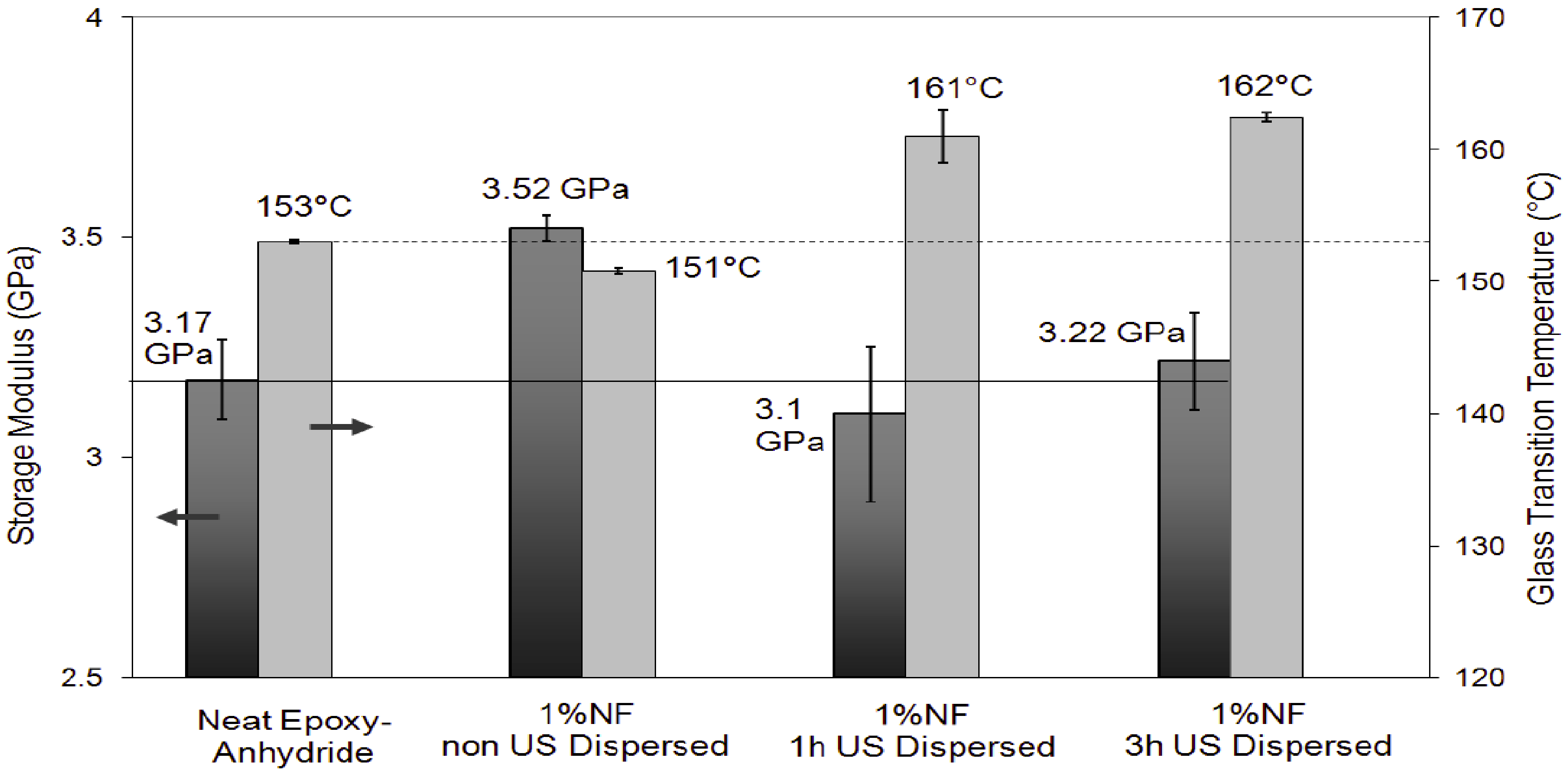


Figure 4. 5: Storage Modulus and *Tg* values of *CNFs*/epoxy-anhydride cured for various dispersion times in ethanol (*DMA* flexural test).

Source: Master Thesis of Isabelle Ortega, École Polytechnique de Montréal