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

Keynote address from Prof. Nicolas Abatzoglou, Eng, PhD, FCAE, MCIC

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

- Deliverables
- Methodology
- R&D description
- Pilote (kg-lab)
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
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 H₂O/C ratio, is used.

- Use of the KFusion™ 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
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?
The DRIVE$^2$ Process

**DRY REFORMING INDUCED VALORIZATION OF ENVIRONMENTALLY FRIENDLY ENERGY CARRIERS**
Rationale: GHG Sequestration?

Steam Reforming → Synthesis gas → H₂ Production

DRIVE²

Renewable or Fossil Fuels

Energy vector
Commercial products

H₂ Production
Raw material for industrial use

Carbon sequestration as nanofilaments
The sequestered carbon comes from the biosphere; thus allows a neat GHG decrease

Energy vector
Commercial products

Synthesis gas

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27/06/2022
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
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

Reactor for Dry Reforming of Ethanol

Support

Catalyst

Heated zone (550°C)

Heated zone (120°C)

Bucket to recover the carbon

Exhaust

Mass flowmeter

GC Analysis

Drierite

Triple cooling bubbler
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
- CO₂ or Ar gases (purity of 99.99%) were added to the ethanol vapour upstream of the reactor
- t = 2h
- Molar Ethanol/CO₂ = 1
- Overall GHSV of 2 300ml/h/g = 1.15 m³/ (h*m²)
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
TEM nanograph of Carbon Nano-Filaments
SEM - CNT 2\textsuperscript{nd} generation
SEM - CNT 3rd generation

3.0kV 3.0mm x40.0k SE(U) 1.00um
XRD – All 4 generations CNT

- CNF-First generation-Surface
- CNF-First generation-Bulk
- CNF-Second generation
- CNF-Third generation
- CNF-Fourth generation

00-035-0772 > Cohenite - Fe₃C
00-041-1487 > Graphite-2H - C
00-051-0997 > Fe₃C₂ - Hagg-carbide
## Results

<table>
<thead>
<tr>
<th>CNF catalyst</th>
<th>2nd generation CNF catalyst</th>
<th>3rd generation CNF catalyst</th>
<th>4th generation CNF catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe in Catalyst (g)</td>
<td>0.38</td>
<td>0.13</td>
<td>0.06</td>
</tr>
<tr>
<td>GHSV (ml/h/g)</td>
<td>120 955</td>
<td>348 155</td>
<td>789 367</td>
</tr>
<tr>
<td>GHSV Ratio</td>
<td>n.a.</td>
<td>2.88</td>
<td>2.27</td>
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<tr>
<td>TOF (H₂) (s⁻¹)</td>
<td>0.00099</td>
<td>0.00267</td>
<td>0.00424</td>
</tr>
<tr>
<td>TOF (H₂) Ratio</td>
<td>n.a.</td>
<td>2.70 !</td>
<td>1.59</td>
</tr>
<tr>
<td>TOF (CO) (s⁻¹)</td>
<td>0.00777</td>
<td>0.01984</td>
<td>0.0339</td>
</tr>
<tr>
<td>TOF (CO) ratio</td>
<td>n.a.</td>
<td>2.55 !</td>
<td>1.71</td>
</tr>
</tbody>
</table>
The extended DRIVE² Process: The HyFMBR
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
Flow Resistances in the HyFMBR

Darcy's Law

\[ \Delta P = (R_{tot}) \times (U_{inlet} \times \mu_f) \]

\[ R_{tot} = \left( \frac{1}{R_{1a}} + \frac{1}{R_{1b}} + \frac{1}{\frac{R_2}{R_{3a} + R_{3b}}} \right) - 1 \]

\[ Q_{1a} = Q_{1b} = \frac{\Delta P}{R_{1a} \times \mu_f} \times \frac{A_{inlet}}{A_{outlet}} \]

\[ R_{inlet} = R_{inlet} \]

Ohm's Law

\[ \Delta V = RI \]
CFD simulation

Bubble formation

Bubble rising

Bubble explosion
Addition of CNF in polymeric matrices
Figure 4.4: Storage Modulus and $T_g$ values of CNFs/epoxy-anhydride cured for various concentrations (DMA flexural test).

Source: Master Thesis of Isabelle Ortega, École Polytechnique de Montréal
Figure 4.3: DMA flexural tests of CNFs/epoxy-anhydride cured nanocomposites for various concentrations of CNFs.
Figure 4.12: Dielectric conductivity of CNFs/epoxy-anhydride cured nanocomposites with and without ultrasonication.

Conductivity vs CNF concentration without and with US

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


Fluidized bed pyrolyzer
Screw feeder
Pyrolyzer & Peripherals

Isometric view

View from the top
CNF Reactor
Reformer and Preheater
Isometric view in new building
ATP Pilot P&ID

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ATP reactor setup
ATP Reactor
CNF Pilot P&ID
- Filter
- CNF recovery vessel
- Gas dehydration
Gas Flare
### Process parameters & experimental results of the nanocarbons production

<table>
<thead>
<tr>
<th></th>
<th>Test A</th>
<th>Test B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (g)</td>
<td>615</td>
<td>291</td>
</tr>
<tr>
<td>Carbon production rate (kg_{C}\cdot kg_{cat}^{-1} \cdot h^{-1})</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>Carbon yield (%)</td>
<td>53.2</td>
<td>37.3</td>
</tr>
<tr>
<td>Hydrogen yield (%)</td>
<td>46.4</td>
<td>43.1</td>
</tr>
<tr>
<td>Total HC conversion (%)</td>
<td>73.0</td>
<td>48.5</td>
</tr>
<tr>
<td>Total CO_{2} conversion (%)</td>
<td>69.9</td>
<td>57.2</td>
</tr>
<tr>
<td>Mass balance error for C (%)</td>
<td>6.3</td>
<td>7.6</td>
</tr>
<tr>
<td>Mass balance error for H (%)</td>
<td>4.0</td>
<td>5.3</td>
</tr>
<tr>
<td>Mass balance error for O (%)</td>
<td>9.6</td>
<td>4.9</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>550</td>
<td>600</td>
</tr>
</tbody>
</table>
Contributions

**HQP**
- Dr Mostafa Chamoumi, PDF
- Abir Azara, PhD student
- Salma Belbessai, PhD student
- Dr Frank Dega
- Martin Gagnon

**Technicians and Drafters**
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- Stéphane Guay
- MTL CAD and François-Niels Meillot, 3D Drawings

**KWI & Soleno**
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- 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**
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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)

\[ Re_{mf} = 7.54 \epsilon^{-4} (GaMv)^{0.98} \]

\[ \varepsilon_{mf} = 1 - \frac{M}{\rho_s SH_{mf}} \]
CFD simulation

- Plugging Period
- Expansion Period
- Falling Period
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

0.2 µm

0.5 µm
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 500\(\mu\)m)
- Eulerian multiphase flow
- Kinetic theory for dense (frictional) granular flow
- K-\(\varepsilon\) 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
Figure 4.5: Storage Modulus and $T_g$ 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