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

9th International Conference On Sustainable Solid Waste Management
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CRC - Process intensification for advanced catalysts and sustainable energy
Overview

- Université de Sherbrooke
- Research group
- Process intensification
- Nonthermal plasma assisted reactions
- New approaches for CO₂ Hydrogenation
- Clean biofuels production from contaminated biomass
- Conclusion
UDS in numbers

3 CAMPUS: THE MAIN CAMPUS IS SITUATED AT SHERBROKE

8 FACULTIES

HOST TO MORE THAN 33,000 STUDENTS

22 RESEARCH CENTRES

78 RESEARCH CHAIRS

6 RESEARCH INSTITUTES
Université de Sherbrooke

Group of Research on technologies and processes (GRTP)

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

Research topics
- Catalysis, nanoparticles
- Biofuels, Fuel cells
- Process Intensification
- Alternative energy

Impact sectors
- Energy
- Environment
- Process Engineering
- Pharmaceutical industry

Achievements
- Technology transfer (Spinoff)
- Publications (science & technology)
- Patents
- Int. and national networks

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Process intensification

Benefits of process intensification

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

Process:
- Higher reaction rates.
- Improved product properties.
- Improved process safety.
- Wider processing conditions.
-Continuous processing.

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

Responsive processing
Faster, safer, and greener processing
Sustainable processing

H. Wang, et al., A review of process intensification applied to solids handling 2017, Chemical Engineering and Processing: Process Intensification
Targeted projects

Nonthermal plasma assisted reactions

New approaches for CO₂ Hydrogenation

Clean biofuels production from contaminated biomass
Project 1: Nonthermal plasma catalysis

Methane dry reforming
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: CO₂ 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)
Carbon Capture & Storage (CCS):
- reported as an attractive solution for the temporary storage of large volumes of CO₂ (Gao, J. Y., 2011)
- has the potential risk of leakage (Li W. W., 2018)

Carbon Capture & Utilization (CCU):
- consider CO₂ as a source to produce value-added chemicals and fuels (de La Fuente, 2016)
- there are several routes to utilize CO₂ such as beverage carbonation, food packaging, water desalination, EOR (70-80Mton of CO₂ is consumed per year), biomass gasification, construction and building materials, and renewable energy systems (for instance, CO₂ based geothermal energy systems)
CONVENTIONAL METHANE DRY REFORMING REACTIONS:

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO} \quad 247 \text{ kJ mol}^{-1} \quad (1)
\]

Side reactions:

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{C(s)} + 2\text{H}_2 \quad 75 \text{ kJ mol}^{-1} \quad (2) \\
2\text{CO} & \rightarrow \text{C(s)} + \text{CO}_2 \quad -171 \text{ kJ mol}^{-1} \quad (3)
\end{align*}
\]

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 ($T_e >> T_h$) 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.
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

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>DBD</th>
<th>CD</th>
<th>SD</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme</td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
<td><img src="image" alt="Diagram" /></td>
</tr>
<tr>
<td>Electron energy [eV]</td>
<td>1 - 30</td>
<td>= 5</td>
<td>-</td>
<td>1 - 2</td>
</tr>
<tr>
<td>Electron density [cm^{-3}]</td>
<td>(10^{12} - 10^{15})</td>
<td>(10^9 - 10^{13})</td>
<td>(10^{14} - 10^{15})</td>
<td>(10^{13})</td>
</tr>
<tr>
<td>Current [A]</td>
<td>1 - 50</td>
<td>10 - 5</td>
<td>20 - 30</td>
<td>-</td>
</tr>
<tr>
<td>Gas Temperature [K]</td>
<td>300 - 500</td>
<td>= 400</td>
<td>400 - 1000</td>
<td>100 - 2000</td>
</tr>
<tr>
<td>Break down voltage [kV]</td>
<td>5 - 25</td>
<td>10 - 50</td>
<td>5 - 15</td>
<td>-</td>
</tr>
</tbody>
</table>
Evaluation of cold plasma discharge in DRM

\[
\text{CH}_4 + 2\text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}
\]

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$_2$

Performance/collection of data of energy efficiency vs conversion under different plasma discharge in CO2 splitting
Advantages of MW plasma

- High Plasma Density
- Electode Free Configuration
- Better Energy Efficiency
- Potentially Easy Scale-up

Current and future applications of MW plasma

Present Applications
- Stripping Etching
- High rate chemical vapor depositions
- Biomass gasification
- UV desinfections
- Waste gas treatment

Future Applications
- Chemical synthesis
- Methane reforming
- Natural gas conversion to value-added products
- Carbon dioxide utilization

Microwave Plasma in industries

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<table>
<thead>
<tr>
<th>Plasma</th>
<th>Power</th>
<th>Frequency</th>
<th>Pressure</th>
<th>Year</th>
<th>CH₄/CO₂</th>
<th>Conversion</th>
<th>Selectivity (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>6 kW</td>
<td>2.45 GHz</td>
<td>Atmospheric pressure</td>
<td>2017</td>
<td>1:1</td>
<td>68.4 %  96.8 %</td>
<td>H₂ Production rate g/H = 240 And H₂:CO = 0.9:1.1</td>
<td>[20]</td>
</tr>
<tr>
<td>MW</td>
<td>6.5 kW</td>
<td>915 MHz</td>
<td>Atmospheric pressure</td>
<td>2019</td>
<td>2:3</td>
<td>- 86.5 %</td>
<td>H₂ (73.3)</td>
<td>[21]</td>
</tr>
<tr>
<td>MW</td>
<td>2 kW</td>
<td>2.45 GHz</td>
<td>Atmospheric pressure</td>
<td>2021</td>
<td>1:1</td>
<td>90.7 %  96.4 %</td>
<td>H₂ (97.3) CO (85.7)</td>
<td>[22]</td>
</tr>
<tr>
<td>MW</td>
<td>700</td>
<td>-</td>
<td>Atmospheric pressure</td>
<td>2019</td>
<td>1:2</td>
<td>19 %  83 %</td>
<td>H₂ (99) CO (19)</td>
<td>[23]</td>
</tr>
<tr>
<td>MW</td>
<td>700</td>
<td>-</td>
<td>Atmospheric pressure</td>
<td>2018</td>
<td>1:2</td>
<td>44.40 % 84.91%</td>
<td>H₂ (51.31) CO (61.17)</td>
<td>[24]</td>
</tr>
<tr>
<td>MW</td>
<td>1.0 kW</td>
<td>2.45 GHz</td>
<td>atmospheric pressure</td>
<td>2010</td>
<td>- -</td>
<td>91.6 %</td>
<td>H₂ (92.7)</td>
<td>[25]</td>
</tr>
</tbody>
</table>
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

\[
SEI = \frac{\text{Plasma power (kW)}}{[\text{CO+H2}] \text{ produced (l/min)}}
\]

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

\[
\text{Energ efficiency (\%)} = \frac{\Delta H_R (\frac{\text{kJ}}{\text{mol}}) \times X_{\text{total}}(\%)}{SEI}
\]
Optimization of Process Parameters

- Energy Cost
- Specific Energy Input
- Feed ratio
- Energy Efficiency
- conversion & selectivity
- flow rate

the importance of control over process parameters
Conclusion

Elements needed to advance the MW plasma field
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 ...)

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Experimental section
Synthesis of catalysts

Catalyst preparation by the wetness incipient impregnation method

- Precursors
  - Ni(NO$_3$)$_2$.6H$_2$O
  - Co(NO$_3$)$_2$.6H$_2$O

- H$_2$O

- Catalytic support

- Bimetallic Homogeneous Solution
Experimental set-up for the dry reforming reaction
Experimental conditions:

- Temperature: 800 °C
- Pressure: atmospheric
- A ratio of CH₄/CO₂=1
- GHSV is chosen (1000) (ml.h⁻¹.g⁻¹_cat).
Conversion of CH$_4$

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

![Conversion Graph]

- 10%Ni/HAP
- 10%Ni-10%Co/HAP
Yields

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

![Graph showing hydrogen yields over time for 10%Ni and 10%Ni-10%Co/HAP](image-url)
characterization of catalysts
XRD Characterization of fresh and used catalysts

XRD for 10%Ni/Hap

XRD for 10%Ni-10%Co/Hap

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Project 2: 
CO$_2$ direct hydrogenation

PhD student: Farbod Farzi
Thermal catalysis of CO₂

Considering the CO₂ limitations of being soluble in water and its thermodynamic stability, CO₂ conversion to commercial products is deemed to be highly energy intensive as thermal decomposition of pure CO₂ commences at 2500-3000 K (Kozák, 2014).

CO₂ reduction can be catalyzed via:

- Photo catalysis
- Thermal catalysis
- Electro catalysis

**Thermal catalysis:**
- fast Rxn kinetics
- flexible components
Thermal catalysis of CO$_2$ (Cont’d)

CO$_2$ is thermodynamically stable;
Activation and more importantly reduction of CO$_2$ is energy-intensive

Addition of a higher Gibbs energy component such as H$_2$ will make the conversion more favorable from the thermodynamic point of view (Li W. W., 2018)
CO$_2$ hydrogenation products

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

(Li, 2018, 10.1039/C7RA13546G)
Experimental section

Study of thermal catalysis of CO$_2$ 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:**
- Al₂O₃,
- SiO₂,
- TiO₂,
- CeO₂,
- ZrO₂,
- Ce-ZrO₂,
- Zeolites (Hbeta, HZSM-5, SAPO-34, …)
- Ca₁₀(PO₄)₆(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
- Ni/ZrO₂-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)
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:

<table>
<thead>
<tr>
<th>Item</th>
<th>Desc.</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Temp.</td>
<td>500 °C</td>
</tr>
<tr>
<td>2</td>
<td>Press.</td>
<td>3 bar</td>
</tr>
<tr>
<td>3</td>
<td>Flow composition</td>
<td>50 vol% H₂/N₂</td>
</tr>
<tr>
<td>4</td>
<td>Flow rate</td>
<td>500 mL/min</td>
</tr>
<tr>
<td>5</td>
<td>TOS</td>
<td>2 h</td>
</tr>
</tbody>
</table>

Temperature (280-400 °C)
Pressure (10-40 bar)
GHSV (700-50,000 mLrxn/gr. hr)
Solvent type (various organic solvents)
Effect of reactor configuration on CO2 Conversion & product Selectivity

CO2 Conversion (%), Ni/ZrO2-HAp, 340 C, 10 bar, GHSV=25,200

Selectivity (%), Ni/ZrO2-HAp, 340 C, 10 bar, GHSV= 25,200
Effect of GHSV on CO2 Conversion & product Selectivity

CO2 Conversion (%), Ni/ZrO2-HAp, 340 C, 10 bar

Selectivity (C5+), Ni/ZrO2-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
GOLD – route 1: Biofuels production

Contaminated biomass → Torrefaction Pre-treatment → EF Gasification → Gas Cleaning → Syngas Fermentation → Ethanol, Butanol, Hexanol

- Slow Pyrolysis Pre-treatment
- Torrefaction Pre-treatment
- TorWash® Pre-treatment
- CO and CO₂ rich gas
- Slag containing heavy elements in vitrified form (Cu, Ni)
- Fly ash containing condensed residue trace elements
- Liquid by-product with humic acids and main parts of Cd, As, Pb, etc.
- Clean water (for recycling)
- Humic acids (bio stimulants)
- Liquid handling

GOLD – route 2 biofuels productions

Contaminated biomass

Solid phase evaluation for EF gasification (Route 1)

Syngas evaluation for gasfermentation (Route 1)

BFB - Autothermal Pyrolysis Udes

Liquid by-product with humic acids and main parts of: Cd, As, Pb, etc.

Catalytic Reforming

FT-Synthesis

Renewable synthetic waxes and fuels

Liquid by-product with humic acids and main parts of: Cd, As, Pb, etc.

Catalytic reforming

Bio oil-catalytic hydrotreatment

to conventional refineries

Concentrated pollutants (heavy metals)

Bio-oil catalytic cracking

Ash/slag containing heavy elements in vitrified from (Cu, Ni) solid and liquid

GOLD Project at UDS

Contaminated biomass → Pyrolysis → Char concentrated with heavy metals → Steam reforming → Syngas → Biofuels and waxes

Biogas → Liquids
What is the behavior of heavy metals during the pyrolysis of naturally and artificially contaminated biomass?

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?

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

Heavy metal-Contaminated biomass

Pyrolysis
- Thermochemical conversion
- System optimization

Bio-oil production
Clean biofuels
Low ILUC risk

Upgrading process

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.


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PhD 3 - Steam reforming and Fischer-Tropsch Synthesis

CH₄, CO₂, CO, C₂H₆, C₂H₄

Ni-Co/HAp

H₂, CO₂, CO

Ni-Co/HAp

• Hydrocarbons
• Olefins
Reactor design for steam reforming
### Operation conditions of the experiment

<table>
<thead>
<tr>
<th>Run</th>
<th>P (atm)</th>
<th>T (°C)</th>
<th>H$_2$O/CH$_4$</th>
<th>GHSV (ml.h$^{-1}$.g$^{-1}$ cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>800</td>
<td>2</td>
<td>1656</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>800</td>
<td>1.5</td>
<td>1656</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>700</td>
<td>2</td>
<td>1656</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>800</td>
<td>2</td>
<td>4140</td>
</tr>
</tbody>
</table>
Effect of H$_2$O/CH$_4$ ratio on catalyst activity

T=800 °C, P=1 atm, GHSV=1656 ml.h$^{-1}$.g$^{-1}$cat

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Effect of temperature on catalyst activity

\[ \text{CH}_4 \text{ conversion} \]

\[ \text{H}_2 \text{ Selectivity} \]

\[ \text{H}_2\text{O}/\text{CH}_4=2, \ P=1\text{atm}, \ \text{GHSV}=1656 \text{ ml.h}^{-1}.\text{g}^{-1}\text{cat} \]

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Effect of GHSV on catalyst activity

CH$_4$ conversion

H$_2$ SELECTIVITY

H$_2$O/CH$_4$=2, P=1atm, T=800 °C

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Fischer-Tropsch Synthesis

I. Fischer-Tropsch reactions and products

Main reactions
1. Paraffins\( (2n+1)H_2 + n\text{CO} \rightarrow C_nH_{2n+2} + nH_2O \)
2. Olefins\( 2nH_2 + n\text{CO} \rightarrow C_nH_{2n} + nH_2O \)
3. WGS\( \text{CO} + H_2\text{O} \rightleftharpoons \text{CO}_2 + H_2 \)

Secondary reactions
4. Alcohols\( 2nH_2 + n\text{CO} \rightarrow C_nH_{2n+2}O + (n-1)H_2O \)
5. Boudouard reaction\( 2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2 \)

II. Catalyst formulation used for Fischer-Tropsch Synthesis

- Metals: Fe, Ni, Co
- Supports: Zeolites, metallic oxides, Carbon(NT, NF, AC)
- Promoters: Ru, Au, Ni, Mo, Zr, Mn, K, Na

Main parts of FTS project

- CO2 in the feed
- Low H2/CO ratio

The feed

Reactor design

- Fixed bed reactor
- Slurry reactor
Reactor design for Fischer-Tropsch Synthesis

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

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Thanks for listening!
References


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17. Zhu, F.; Zhang, H.; Yan, X.; Yan, J.; Ni, M.; Li, X.; Tu, X. Plasma-catalytic reforming of


34. Bogaerts, A.; Tu, X.; Whitehead, J.C.; Centi, G.; Lefferts, L.; Guaitella, O.; Azzolina-Jury,