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Supercritical water gasification of glucose and aqueous biomass for the production of CH$_4$ and H$_2$

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2$^{\text{nd}}$ year MESc

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Joint Supervisor: Dr. Paul Charpentier
1. Introduction and background:

✓ Supercritical water (SCW):

Water above its critical point ($T=374^\circ C$, $P=22.1$ MPa) acquire special thermal and physical properties in comparison with normal water:

- Higher diffusivity
- Higher solubility for organics
- Less viscosity
- Less solubility for inorganics
- Less polarity, makes it a good solvent for non-polar compounds.

✓ **NO drying** is needed for SCWG of biomass even for water content > 90% in contrast with other hydrothermal processes.

✓ The gas product mostly contains: $\text{CH}_4$, $\text{H}_2$, $\text{CO}_2$, $\text{CO}$. 
2. Motivations:

- Based on **thermodynamic** equilibrium:
  
  Low SCWG temperatures - \( \text{CH}_4 \)
  
  Higher temperatures - \( \text{H}_2 \)

- SCW act both as a media and a reactant.
  
  **shorter residence times**
  
  **smaller reactor volume**

- SCWG can be applied for:
  
  **gas reforming of organic biomasses**
  
  **treatment of hazardous waste for the waste water treatment industry**

- At relative low SCWG temperature zone (600 °C \( >T>374 \) °C) suitable catalyst is essential:
  
  **Decline char and tar formation**
Gas products:

**Methane rich gas:** This synthetic natural gas (SNG) can be injected into gas grids to be used for households. This high-pressure methane can also be transferred for CNG purposes to be burned as a fuel in car’ engines.

**Hydrogen rich gas:** Syngas can be used for fuel cell.

Main possible reaction pathways are suggested by many research groups

**Steam-reforming:**

\[ C_6H_{12}O_6(l) + H_2O(g) \rightarrow 6CO + 6H_2 + H_2O(g) \]

\[ \Delta H_{298}^0 = 607.82 \text{ kJ/mol} \]

**Methanation:**

\[ CO(g) + 3H_2(g) \rightarrow CH_4 + H_2O(g) \]

\[ \Delta H_{298}^0 = -206.19 \text{ kJ/mol} \]

**Water-gas shift**

\[ CO(g) + H_2O(g) \rightarrow CO_2 + H_2 \]

\[ \Delta H_{298}^0 = -41.16 \text{ kJ/mol} \]
3. Methodology:

5 wt% Glucose-water solution
Or
Aqueous fraction of pyrolysis oil

Catalyst
(prepared by impregnation method)

T=400-600 °C
P=4000 psi=27.5 MPa

SCWG

Effluent
Analysis:
- TOC
- ICP

Gas Products
Analysis:
- Micro-GC
Main Gases:
- H₂, CH₄, CO₂, CO

Used Catalyst
Analysis:
- TPR
- Pulse chemisorption
- TGA
- XRD
- SEM-EDX
- TPD
4. Materials and methods:

SCWG of model compound:

- Feedstock: **5 wt% glucose-water** solution
- Operational condition:
  - **T=500 °C** (400, 500, and 600 °C) **P=4000 psi= 27.5 Mpa**
  - Feeding rate= 1 ml/min   WHSV= 3 h⁻¹
- Fixed-bed catalyst with considering pre-heating effect
- Catalyst prepared by **impregnation method**, and was reduced in-situ at 600 °C.

SCWG of aqueous fraction of pyrolysis oil:

- Operational condition: **T=500-700 °C** **P=4000 psi= 27.5 Mpa**
  - Feeding rate= 1 ml/min   WHSV= 3 h⁻¹ in presence of the screened catalyst in the model test
- Different feed concentration: 0.7 wt% - 2.9 wt% carbon
4.1. Bench-scale Flow type reactor:

- Continuous flow reactor
- Tube: *Inconel 625* with 9.55mm OD X 6.34mm ID X 472mm Length
- In-situ catalyst reduction
- Maximum operation condition: T= 800 ºC, P=6000 psi, 41.3 Mpa
- Fixed-bed catalyst inside
- HPLC pump
4.2. Schematic diagram of the reactor:
## 5. Key Results:

### 5.1. Catalyst Characterization:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal content (wt%)</th>
<th>Support</th>
<th>BET surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₃₀Ru₂/γ-Al₂O₃</td>
<td>30%Ni+2%Ru</td>
<td>γ-Al₂O₃</td>
<td>106.32</td>
<td>0.27</td>
<td>9.88</td>
</tr>
<tr>
<td>Ni₂₀Ru₂/γ-Al₂O₃</td>
<td>20%Ni+2%Ru</td>
<td>γ-Al₂O₃</td>
<td>126.47</td>
<td>0.29</td>
<td>9.23</td>
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<tr>
<td>Ni₁₀Ru₂/γ-Al₂O₃</td>
<td>10%Ni+2%Ru</td>
<td>γ-Al₂O₃</td>
<td>139.45</td>
<td>0.36</td>
<td>10.4</td>
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<tr>
<td>Ni₂₀/γ-Al₂O₃</td>
<td>20%Ni</td>
<td>γ-Al₂O₃</td>
<td>113.18</td>
<td>0.31</td>
<td>10.82</td>
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<tr>
<td>Ru₂/γ-Al₂O₃</td>
<td>2%Ru</td>
<td>γ-Al₂O₃</td>
<td>146.02</td>
<td>0.44</td>
<td>11.54</td>
</tr>
<tr>
<td>Ni₂₀Ru₂/TiO₂</td>
<td>20%Ni+2%Ru</td>
<td>TiO₂</td>
<td>27.88</td>
<td>0.14</td>
<td>20.6</td>
</tr>
</tbody>
</table>
5.2. Catalyst Screening (SCWG 5wt% glucose-water solution)

T=500°C, P=27.7MPa, WHSV=3h⁻¹
5.3. Catalyst Stability test (Ni$_{20\%}$Ru$_{2\%}$/γ-Al$_2$O$_3$):

Gas composition distribution

**Volume fraction %**

- **H$_2$**
- **CH$_4$**
- **CO$_2$**

**Time (hr)**

**T=500°C, P=27.7MPa, WHSV=3h$^{-1}$**
5.4. Pre-heating effect on SCWG of 5% glucose–water solution:

![Diagram showing gas composition and production yield with and without pre-heating.](image)

**Gas Composition**

- L1: without pre-heating
- L2: with pre-heating

**Gas Production Yield**

- Product (mol) / C in feedstock (mol)

H₂, CO₂, CH₄ concentrations are shown for both L1 and L2.
5.5. Nickel loading effect on SCWG of model compound:

![Graph showing gas products' yields for different nickel loading conditions.](image)

- **Gas products’ yields**

- **Yields** for:
  - H₂
  - CH₄
  - CO₂
  - Total carbon in gas

- **Conditions**:
  - Ni₁₀Ru₂/γ-Al₂O₃
  - Ni₂₀Ru₂/γ-Al₂O₃
  - Ni₃₀Ru₂/γ-Al₂O₃
5.6. SEM image of Ni$_{20\%}$Ru$_{2\%}$/γ-Al$_2$O$_3$ (the best catalyst):  

**Fresh Ni$_{20\%}$Ru$_{2\%}$/γ-Al$_2$O$_3** 
Prepared by impregnation method 
Calcined at 600 °C 
Heating rate 10 °C/min 

**Used Ni$_{20\%}$Ru$_{2\%}$/γ-Al$_2$O$_3** 
Operated at T=500 °C for 20hr, P=27.7 MPa, WHSV=3 h$^{-1}$ 
Feed: glucose solution 5wt%
5.7. Temperature effect on SCWG of 5 wt% glucose-water solution in presence of Ni$_{20\%}$Ru$_{2\%}$/γ-Al$_2$O$_3$ catalyst:

![Graph showing yield (mol/mol of Carbon in the feed) for H2, CH4, CO2, and Total conversion at different temperatures (T=400°C, T=500°C, T=600°C).]

Ni$_{20\%}$Ru$_{2\%}$/γ-Al$_2$O$_3$, T=500 °C, P=27.7 MPa, WHSV=3 h$^{-1}$
5.8. SCWG of aqueous fraction of pyrolysis oil (2.9 wt% carbon) in presence of Ni_{20\%}Ru_{2\%}/\gamma-Al_2O_3 catalyst:

Ni_{20\%}Ru_{2\%}/\gamma-Al_2O_3, P=27.7 MPa, WHSV=3 h^{-1}
6. Conclusion:

- The novel nickel catalyst prepared by the authors, Ni$_{20}$Ru$_2$/$\gamma$-Al$_2$O$_3$, is the most active catalyst for methane production via SCWG of glucose and aqueous fraction of pyrolysis oil.

- 98% carbon conversion to gas was achieved in glucose SCWG test at 500 °C.

- 90% carbon conversion to gas was obtained in Aq-PO SCWG test at 700 °C.

- 20% nickel loading produced the highest methane yield, but 10% nickel loading resulted in the highest hydrogen production.

- At 500 °C we already achieved almost 100% carbon conversion to gas. A higher temperature resulted in lower methane but higher hydrogen production.

- Ruthenium is an effective catalyst promoter which may promote nickel dispersion, prevent sintering of catalyst and increase nickel reducibility.
7. Acknowledgment and sponsors:
Thank You!

Question?