Synthesis gas by catalytic steam reforming of bio-oil.

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Hydrogen economy:

- Increasing interest in Hydrogen economy:
  - Several chemical uses.
  - Utilization as clean fuel in high energetic efficiency systems like fuel cells in stationary, mobile or portable applications that can be used in vehicles.
Steam reforming of pyrolysis liquids (Bio-oil):

**Pyrolysis**

**Bio-oil**

- Complex mixture of organic compounds and water*.
- Are unstable and suffer from aging.

Steam reforming:

- Vegetable oils:
  - Sunflower
  - Soya
  - Rapeseed
  - Palm
  - ...

- Trap grease

- Bioethanol
Steam reforming:

- Bioethanol
- Biobutanol
Steam reforming:

- Important increasing in biodiesel production

Glycerol prices decrease, so it is necessary to find new ways to convert glycerol into valuable added products $\rightarrow \text{H}_2$
Steam reforming of pyrolysis liquids (Bio-oil):

Aqueous fraction

Lignin fraction

Higher stability

High valuable coproducts from bio-oil*

OBJECTIVES:

- Experimental work with model compounds and with the aqueous fraction of bio-oil both at micro and bench scales.

- Development of suitable catalysts for the process:
  - Adequate catalytic activity and selectivity towards $\text{H}_2$.
  - Resistance to deactivation by coking deposition.
  - Resistance to attrition to work at fluidized bed.

- Development of the process at a bench-scale fluidized-bed facility and scale up to a demonstration plant.
**CHARACTERISTICS OF BIO-OIL**


- Heterogeneous properties (feedstock)
- Colour: Dark red / brown
- Odour: smoke like
- Quite viscous at room temperature
- Thermally unstable (polymerization)
- High oxygen content (ca. 40 % dry wt.)
- pH: 2.3 – 2.8

**ORGANICS / WATER (85/15 w/w)**

**WATER ADDITION:**

- AQUEOUS FRACTION
  - Alcohols
  - Carboxylic acids
  - Sugars
  - Aldehydes
  - Ketones
  - Complex carbohydrates
  - Lignin derived materials

- WATER INSOLUBLE FRACTION (Pyrolytic lignin)

- Catalytic Steam Reforming *(Czernik et al., 1997)*

- Fine Chemicals *(Kelley et al., 1997; Shabtai et al., 1997)*
CHARACTERISTICS OF BIO-OIL*

(*Oasmaa and Meier, J. Anal. Appl. Pyrol. 73, (2005), 323)

Great complexity!

- Alcohols
- Carboxylic acids
- Sugars
- Aldehydes
- Ketones
- Complex carbohydrates
- Lignin derived materials

Experimental work with model compounds:
- Acetic acid
- Acetol
- 1-Butanol
- D-Fructose
CATALYSTS PREPARED AT INCREASING pH

Ni(NO$_3$)$_2$·6H$_2$O

Al(NO$_3$)$_3$·9H$_2$O

pH=7.9

NH$_4$OH

T = 40ºC

COPRECIPITATION

FILTERING

DRYING

HYDRATED PRECURSOR

3h, T = 750ºC

CALCINATION

CALCINED PRECURSOR

ACTIVATED CATALYST

10 % H$_2$, T = 650ºC 1 hour

REDUCTION
Characterization: Catalysts prepared at increasing pH

**XPS**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni 2p$_{3/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 %</td>
<td>856.6 (2.9)</td>
</tr>
<tr>
<td>28 %</td>
<td>856.0 (2.8)</td>
</tr>
<tr>
<td>33 %</td>
<td>856.0 (2.9)</td>
</tr>
<tr>
<td></td>
<td>854.3 (1.8)</td>
</tr>
</tbody>
</table>

**XRD**

**BET:**
- 23 % Ni → $S_g = 205 \text{ m}^2/\text{g}$
- 28 % Ni → $S_g = 205 \text{ m}^2/\text{g}$
- 33 % Ni → $S_g = 180 \text{ m}^2/\text{g}$

**ICP – OES:**

<table>
<thead>
<tr>
<th>Theoretical</th>
<th>Real</th>
</tr>
</thead>
<tbody>
<tr>
<td>23 %</td>
<td>22.0 %</td>
</tr>
<tr>
<td>28 %</td>
<td>26.9 %</td>
</tr>
<tr>
<td>33 %</td>
<td>32.1 %</td>
</tr>
</tbody>
</table>
CATALYSTS PREPARED AT CONSTANT pH

- **CATALYSTS**
  - **Ni(NO₃)₂·6H₂O**
  - **Al(NO₃)₃·9H₂O**
  - **Mg(NO₃)₂·6H₂O**
  - **Cu(NO₃)₂·3H₂O**

- **Hydration**
  - **FILTERING**
  - **Drying**
  - **Reduction**
  - **Calcination**

- **Coprecipitation**
  - pH = 8.5
  - NaOH
  - Na₂CO₃

- **Aging**
  - T = 80°C, 15h

- **Calcined Precursor**
  - T = 600°C, 6h

- **Activated Catalyst**
  - T = 650°C, 10% H₂, 10 hours
Study with Microactivity plant*:

- **Microactivity plant:**
  - Micro-scale fixed bed

- **Experiments with different model compounds:**
  - Acetic acid
  - Acetol
  - 1-Butanol
  - D-Fructose

- **Optimized experimental conditions:**
  - 650°C
  - 1 h previous reduction
  * Nickel content of the catalyst: 23, 28 and 33 % (Ni/(Ni+Al) relative at. %)
    * Ni/Al modified with Cu and Mg: Collaboration with the Norwegian University of Science and Technology (NTNU, Trondheim (Norway)).

Fixed bed microactivity setup
Experimental Conditions

- Atmospheric pressure, reaction temperature set at 650°C.

- Liquid feeding rate: 0.15 mL/min of acetic acid aqueous solution (23% w/w)

- 0.05 g of catalyst and ca. 1.5 g sand (particle size: 160-320 µm)

- $W/m_{HAc} \sim 1.46 \, g_{catalyst \cdot min}/g_{acetic \ acid}, \ S/C \ molar \ ratio = 5.58$

- $G_{c1 \ HSV} \sim 28500 \, h^{-1}$

- 1 h reduction time

- 2 h reaction time
Catalytic steam reforming of ACETOL: Influence of the nickel content and reaction temperature

\( \frac{W}{m_{Ac}} = 0,88 \text{ g cat·min/g Ac} \)

650 ºC: Better performance: 28 % Ni. 23 % y 33 % display similar performances.

650 ºC: Better performance: 28 % Ni.
ACETIC ACID VS ACETOL

Non catalytic reforming, 650 °C

*Significant non catalytic reforming for acetol.*

Catalytic Reforming. W/\( m_{\text{org}} \) = 1.46 g·min/g, 650 °C

*Slower decrease of the catalytic activity for acetol.*
ACETIC ACID VS ACETOL

ACETOL:
✓ Better catalytic reforming:
  · Much higher carbon conversion.
  · Greater gas yields.
✓ CH₄, C₂H₄ and C₂H₆ detected.
✓ Product gas compositions:
  · similar H₂
  · higher CO
  · lower CO₂
Fluidized bed plant:
**Experimental conditions**

- Atmospheric pressure and 650°C temperature
- Liquid flow rate: 0.75-0.77 ml/min acetic acid aqueous solution
- 7 cm height bed: 1.1 g catalyst and ~38 g sand (particle size of 160-320 µm)
- \( \frac{W}{m_{HAc}} \sim 6 \frac{g_{catalyst} \cdot min}{g_{acetic acid}}, S/C \) molar ratio = 5.58
- \( \frac{u}{u_{mf}} = 10 \) \( G_{c1}SHV \sim 6800 \text{ h}^{-1} \)
- 2 h reaction time

Experimental method
Screening of catalysts. Attrition tests.

- Fluidization attrition requirements: % weight loss/h < 0.5 % weight/h*
- Maximum resistance to attrition for D catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A*</th>
<th>A2*</th>
<th>B</th>
<th>B2</th>
<th>C</th>
<th>C2</th>
<th>D</th>
<th>D2</th>
<th>E†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative atomic % (Ni/(Ni+Al))</td>
<td>15</td>
<td>15</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>33</td>
</tr>
<tr>
<td>Calcination temperature (°C)</td>
<td>750&amp;750</td>
<td>900&amp;750</td>
<td>750</td>
<td>850</td>
<td>750</td>
<td>900</td>
<td>750</td>
<td>900</td>
<td>850</td>
</tr>
<tr>
<td>Ca/Ni molar ratio</td>
<td>0.32</td>
<td>0.32</td>
<td>0</td>
<td>0</td>
<td>1.29</td>
<td>1.29</td>
<td>0.31</td>
<td>0.31</td>
<td>5.00</td>
</tr>
<tr>
<td>Ca/Al molar ratio</td>
<td>0.06</td>
<td>0.06</td>
<td>0</td>
<td>0</td>
<td>0.50</td>
<td>0.50</td>
<td>0.12</td>
<td>0.12</td>
<td>2.50</td>
</tr>
<tr>
<td>Attrition (% weight loss/h)</td>
<td>0.62</td>
<td>0.46</td>
<td>1.16</td>
<td>0.99</td>
<td>1.47</td>
<td>0.69</td>
<td>0.22</td>
<td>0.16</td>
<td>3.25</td>
</tr>
</tbody>
</table>

*Prepared by impregnation. Support calcined at 900°C and impregnated precursor calcined at 750°C.

†Prepared by coprecipitation method at constant pH (precipitating agent: NaOH and NaNO₃ solution).
Catalysts:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method</th>
<th>wt% Ni</th>
<th>Mg/Al molar ratio</th>
<th>Ca/Al molar ratio</th>
<th>Attrition rate (wt%/h)*</th>
<th>Sustainable fluidizable catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl</td>
<td>Coprecipitation</td>
<td>28.5</td>
<td>0</td>
<td>0</td>
<td>1.16</td>
<td>No ✓</td>
</tr>
<tr>
<td>NiMgAl0.26</td>
<td>Coprecipitation</td>
<td>29.3</td>
<td>0.26</td>
<td>0</td>
<td>0.27</td>
<td>Yes ✓</td>
</tr>
<tr>
<td>NiCaAl0.12</td>
<td>Coprecipitation</td>
<td>26.3</td>
<td>0</td>
<td>0.12</td>
<td>0.22</td>
<td>Yes ✓</td>
</tr>
<tr>
<td>NiCaAl0.03</td>
<td>Impregnation</td>
<td>7.5</td>
<td>0</td>
<td>0.03</td>
<td>0.46</td>
<td>Yes ✓</td>
</tr>
</tbody>
</table>

* wt%/h: weight of catalyst lost per hour.
Sustainable fluidizable catalyst when attrition rate < 0.5 wt%/h.

Butanol steam reforming:

- Complete carbon conversion at $G_{C1}\text{HSV}$ of around 6000 h$^{-1}$

- $W/m_{\text{butanol}} = 6\ g_{\text{catalyst}} \cdot \text{min/g}_{\text{butanol}}$
- $W/m_{\text{butanol}} = 2\ g_{\text{catalyst}} \cdot \text{min/g}_{\text{butanol}}$

- $G_{C1}\text{HSV} \sim 6000\ h^{-1}$
- $G_{C1}\text{HSV} \sim 33800\ h^{-1}$

- 650°C, 1 atm, S/C = 14.7, $u/u_{mf} = 10$
Butanol steam reforming:

- Except with the impregnated catalyst CaAl 0.03 imp, low activity.

  Its catalytic activity is lower in butanol steam reforming than in acetic acid or acetol steam reforming where 99% and 88% carbon conversion were obtained respectively.

\[ W_{\text{butanol}} = 6 \text{ g catalyst} \cdot \text{min/g butanol} \]

\[ W_{\text{butanol}} = 2 \text{ g catalyst} \cdot \text{min/g butanol} \]

- 650°C, 1 atm, S/C = 14.7, \( u/u_{mf} = 10 \)
Butanol steam reforming:

- Mg and Ca modified coprecipitated catalysts can perform with a good activity and with a higher resistance to attrition than the non-modified Ni/Al catalyst.

\[
\begin{align*}
\text{NiAl} & \quad \text{NiMgAl 0.26} \\
\text{NiCaAl 0.12} & \quad \text{NiCaAl 0.03 imp}
\end{align*}
\]

\[
\begin{align*}
W/m_{\text{butanol}} = 6 \text{ g}_{\text{catalyst}} \cdot \text{min/g}_{\text{butanol}} \\
W/m_{\text{butanol}} = 2 \text{ g}_{\text{catalyst}} \cdot \text{min/g}_{\text{butanol}}
\end{align*}
\]

\[
\begin{align*}
G_{C1} \text{HSV} & \sim 6000 \text{ h}^{-1} \\
G_{C1} \text{HSV} & \sim 33800 \text{ h}^{-1}
\end{align*}
\]

650°C, 1 atm, S/C = 14.7, u/u_{mf} = 10
Butanol steam reforming:

Butanol

--- Equilibrium

NiAl

NiMgAl 0.26

NiCaAl 0.12

NiCaAl 0.03 imp

---

650°C, 1 atm, S/C = 14.7, \( \frac{u}{u_{mf}} = 10 \), \( W/m_{\text{butanol}} = 2 \text{ g}_{\text{catalyst}} \cdot \text{min}/g_{\text{butanol}} \)

\[\begin{align*}
0.30 & \quad 0.35 & \quad 0.40 \\
\text{g/g} & \quad \text{Butanol} & \\
\end{align*}\]

\[\begin{align*}
0.3 & \quad 0.4 \\
\text{Butanol} & \\
\end{align*}\]

\[\begin{align*}
\text{— Equilibrium} \\
\text{NiAl} \\
\text{NiMgAl 0.26} \\
\text{NiCaAl 0.12} \\
\text{NiCaAl 0.03 imp} \\
\end{align*}\]

\[\begin{align*}
0.00 & \quad 0.05 & \quad 0.10 & \quad 0.15 & \quad 0.20 & \quad 0.25 & \quad 0.30 & \quad 0.35 & \quad 0.40 \\
\text{Hydrogen yield (g/g} \text{Butanol)} & \quad \text{Time (min)} & \\
\end{align*}\]

\[\begin{align*}
0.00 & \quad 0.05 & \quad 0.10 & \quad 0.15 & \quad 0.20 & \quad 0.25 & \quad 0.30 & \quad 0.35 & \quad 0.40 \\
\text{CO yield (g/g} \text{Butanol)} & \quad \text{Time (min)} & \\
\end{align*}\]

\[\begin{align*}
\text{Mg and Ca modified catalysts showed close} \\
\text{hydrogen yields to the non modified} \\
catalysts.. \\
\end{align*}\]
Butanol steam reforming:

650°C, 1 atm, S/C = 14.7, u/u_{mf} = 10, W/m_{butanol} = 6 \text{ g}_{\text{catalyst} \cdot \text{min}/g_{\text{butanol}}}

Equilibrium hydrogen yields are reached with all the catalysts.

W/m_{butanol} from 2 to 6
Aqueous fraction of bio-oil

- Bio-oil supplied by BTG (technology based on rotating cone reactor)
- Aqueous fraction prepared by dropwise water addition with continuous stirring
- Elemental analysis: $C_{1.4} \, H_{3.4} \, O_{1}$.
- $S/C = 7.64$
- $pH = 2.52$
- Water/organic mass ratio: 85/15
Steam reforming of the aqueous-phase of bio-oil:

- 73.5% carbon conversion
- 63.3% H2 (%mol, N2 and H2O Free)

NiAl catalyst

28.5 wt% Ni

650°C, 1 atm, S/C = 7.64, u/u_{mf} = 10

W/m_{Aqueous Fraction of Bio-Oil} \approx 4, \quad G_{C1SHV} \approx 11800 \text{ h}^{-1}
Catalytic steam reforming of the aqueous fraction

- Experimental conditions: 2 h reaction at 650 °C, \( G_{C1}HSV = 19000 \ h^{-1} \)
- No operational problems detected
- Recovery (liquid+gas) = 97.5 %
- Carbon conversion averages 70 % during the first hour of reaction
- 28 % Ni catalyst reduced in diluted H\(_2\) (H\(_2\):N\(_2\) 1:10 vol.) at 650 °C for 1 h
- Other catalysts tested: 23 % and 33 % Ni (increasing pH method) and 0, 1, 3, 5 and 10 % Cu (constant pH method)

Average gas composition (vol. %):
- \( H_2 = 67.4 \)
- \( CO = 6.3 \)
- \( CO_2 = 25.5 \)
- \( CH_4 = 0.5 \)

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![Graph showing gas composition over time](image-url)
Synthesis gas by catalytic steam reforming of bio-oil.

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