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.
THERMOCHEMICAL CONVERSION

Supercritical conditions
- $\text{CH}_4/\text{CO}_2$
  - Reforming + Shift
  - $\text{H}_2/\text{CO}_2$

GASIFICATION
- $\text{CH}_4/\text{CO}_2$
  - Reforming + Shift
  - $\text{CH}_3\text{OH}/\text{CO}_2$
  - $\text{H}_2/\text{CO}$
  - Synthesis
  - Shift

PYROLYSIS
- Flash
  - Bio-oil
  - Reforming + Shift
  - $\text{H}_2/\text{C}$

Severe
Steam reforming of pyrolysis liquids (Bio-oil):

Pyrolysis

Bio-oil

BTG process (fast pyrolysis)

- 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 $\rightarrow H_2$
Steam reforming of pyrolysis liquids (Bio-oil):

Aqueous fraction

Ligninic 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 $H_2$.
  - 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*

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

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

Fine Chemicals (Kelley et al., 1997; Shabtai et al., 1997)

Catalytic Steam Reforming (Czernik et al., 1997)
**CHARACTERISTICS OF BIO-OIL**

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

### Table 15
**Determination of acids (wt.% based on wet liquid)**

<table>
<thead>
<tr>
<th>No.</th>
<th>9^-</th>
<th>12^-</th>
<th>3^-</th>
<th>5^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>6.29</td>
<td>9.35</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>1.7</td>
<td>7.84</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>0.05</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propionic acid</td>
<td>0.17</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyric acid</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Butyric acid</td>
<td>0.07</td>
<td>1.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lactic acid</td>
<td>0.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glycolic acid</td>
<td>6.34</td>
<td>6.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td>0.04</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Valeric acid</td>
<td>0.01</td>
<td>0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Methylpentanoic acid</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Hydroxypropanoic acid</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Oxopentanoic acid</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lactic acid</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butyric acid</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignin derived materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>4.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Laboratory No.

### Table 17
**Determination of aldehydes, ketones, and alcohols (wt.% based on wet liquid)**

<table>
<thead>
<tr>
<th>No.</th>
<th>9^-</th>
<th>12^-</th>
<th>3^-</th>
<th>5^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>0.84</td>
<td>8.92</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.14</td>
<td>1.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydroxyacetaldehyde</td>
<td>3.52</td>
<td>6.42</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>0.54</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetol</td>
<td>2.07</td>
<td>7.62</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td>1-Hydroxy-2-butanone</td>
<td>0.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Hydroxy-2-cyclopentanone-1-one</td>
<td>0.46</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Hydroxy-2-methyl-2-cyclopentanone-3-one</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pinacolaldehyde</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>0.06</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paraldehyde</td>
<td>0.49</td>
<td>0.2</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>5-Hydroxy-2-pentanone</td>
<td>0.17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-Hydroxy-2-pentanone-1-one</td>
<td>0.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Laboratory No.

### Table 18
**Determination of sugars (wt.% based on wet liquid)**

<table>
<thead>
<tr>
<th>No.</th>
<th>12^-</th>
<th>3^-</th>
<th>5^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-arabinose</td>
<td>0.04</td>
<td>4.03</td>
<td>7.6</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xylose</td>
<td>0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arabinose</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>4.1</td>
<td>4.8</td>
<td>9.8</td>
</tr>
</tbody>
</table>

---

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

T = 40°C

COPRECIPITATION

FILTERING

DRYING

3h, 3h, 3h, 3h,

REDUCTION

10 % H$_2$, T = 650°C

1 hour

HYDRATED PRECURSOR

NH$_4$OH

3h, T = 750°C

CALCINATION

ACTIVATED CATALYST

CALCINED PRECURSOR

COPRECIPITATION

CALCINATION

T = T = T =

40ºC 40ºC 40ºC 40ºC

COPRECIPITATION

CALCINATION
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>
</tbody>
</table>

XRD

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

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

FILTERING

DRIYING

Mg(NO₃)₂·6H₂O

Ni(NO₃)₂·6H₂O

Al(NO₃)₃·9H₂O

Cu(NO₃)₂·3H₂O

HYDRATED PRECURSOR

6h, T = 650ºC

10% H₂, 10 hours

REDUCTION

ACTIVATED CATALYST

CALCINATION

6h, T = 600ºC

CALCINED PRECURSOR

COPRECIPITATION

pH=8.5

NaOH

Na₂CO₃

Aging:
T = 80ºC, 15h

Aquatization

pH=8.5

NaOH

Na₂CO₃
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)).

*Results reported by Bimbela, F. et al., J. Anal. Appl. Pyrol., 79 (2007) 112*
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)
- \( W/m_{\text{HAc}} \sim 1.46 \, g_{\text{catalyst}} \cdot \text{min}/g_{\text{acetic acid}}, \) \( S/C \) 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

\( \text{W/m}_{\text{Ac}} = 0.88 \text{ g cat} \cdot \text{min/g Ac} \)

**650 °C:** Better performance: 28 % Ni. 23 % y 33 % display similar performances.
ACETIC ACID VS ACETOL

Non catalytic reforming, 650 °C

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

↓ Significant non catalytic reforming for acetol.

↓ 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)
- $W/m_{HAc} \sim 6 \frac{g_{catalyst \cdot min}}{g_{acetic \ acid}}$, $S/C$ molar ratio = 5.58
- $u/u_{mf} = 10$ \quad $G_{c1 \ SHV} \sim 6800 \ h^{-1}$
- 2 h reaction time
**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 imp</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:

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

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

- Complete carbon conversion at \( G_{C_1} \) HSV of around 6000 h\(^{-1}\)

- \( G_{C_1} \) HSV \( \sim 6000 \text{ h}^{-1} \)

- \( G_{C_1} \) HSV \( \sim 33800 \text{ h}^{-1} \)

650ºC, 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. 😞

**FLUIDIZED BED PLANT**

**NiAl**  □ □
**NiMgAl 0.26**  □ □
**NiCaAl 0.12**  □ □
**NiCaAl 0.03 imp**  □ □

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

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

- \( G_{C_1} \text{HSV} \approx 6000 \text{ h}^{-1} \)
- \( G_{C_1} \text{HSV} \approx 33800 \text{ h}^{-1} \)

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.

| Catalyst               | Activity
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NiAl</td>
<td></td>
</tr>
<tr>
<td>NiMgAl 0.26</td>
<td></td>
</tr>
<tr>
<td>NiCaAl 0.12</td>
<td></td>
</tr>
<tr>
<td>NiCaAl 0.03 imp</td>
<td></td>
</tr>
</tbody>
</table>

---

650°C, 1 atm, S/C = 14.7, \( \frac{u}{u_{mf}} = 10 \)

\( G_{ClHSV} \approx 6000 \, \text{h}^{-1} \)

\( G_{ClHSV} \approx 33800 \, \text{h}^{-1} \)
Butanol steam reforming:

650°C, 1 atm, S/C = 14.7, u/u_{mf} = 10, \ W/m_{butanol} = 2 \ g_{catalyst} \ min/g_{butanol}

- Equilibrium
- NiAl
- NiMgAl 0.26
- NiCaAl 0.12
- NiCaAl 0.03 imp

- Mg and Ca modified catalysts showed close hydrogen yields to the non modified catalysts.
Butanol steam reforming:

650ºC, 1 atm, S/C = 14.7, \( u/u_{mf} = 10 \), \( W/m_{\text{butanol}} = 6 \text{ g}_{\text{catalyst}} \cdot \text{min/g}_{\text{butanol}} \), \( W/m_{\text{butanol}} \) from 2 to 6

Equilibrium hydrogen yields are reached with all the catalysts.
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/umf = 10
W/m Aqueous Fraction of Bio-Oil ~ 4, GC1SHV ~ 11800 h⁻¹
Catalytic steam reforming of the aqueous fraction

- Experimental conditions: 2 h reaction at 650 ºC, $G_{C_1HSV} = 19000 \text{ h}^{-1}$
- 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 ºC 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
Synthesis gas by catalytic steam reforming of bio-oil.

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