HYDROGEN PRODUCTION BY AQUEOUS-PHASE REFORMING OF GLYCEROL FROM THE BIODIESEL MANUFACTURING

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Bioenergy III: Present and New Perspectives on Biorefineries, Lanzarote (Spain), May 25th, 2011
OUTLINE

1. INTRODUCTION AND OBJECTIVES
2. EXPERIMENTAL METHOD
3. EXPERIMENTAL RESULTS
   • Effect of the feedstock and the glycerol content
   • Effect of the catalyst composition
4. CONCLUSIONS
OUTLINE

1. INTRODUCTION AND OBJECTIVES

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1. Introduction and objectives

**THERMOCHEMICAL CONVERSION**

- **STEAM REFORMING**
  - Reforming + Shift
  - $T \sim 500-850^\circ C$
  - $P = 1$ atm
  - $S/C = 2-4$
  - Me/CeO$_2$/Al$_2$O$_3$

- **AUTOTHERMAL REFORMING**
  - Air + Reforming
  - $T \sim 500-800^\circ C$
  - $C/O = 0.3$
  - $S/C = 3$
  - Pt-Ni/Al$_2$O$_3$

- **AQUEOUS PHASE REFORMING (APR)**
  - Reforming + Shift
  - $T \sim 227^\circ C$
  - $P = 25-50$ bar
  - No catalyst
  - $C/O = 0.3$
  - $S/C = 3$
  - Pd/Ni/Al$_2$O$_3$

- **SUPERCritical WATER REFORMING**
  - $T \sim 374^\circ C$
  - $P = 221$ bar
  - $C/O = 0.43$
  - Pt/Al$_2$O$_3$

- **PARTIAL OXIDATION**
  - Air
  - $T \sim 800-1000^\circ C$
  - $C/O = 0.43$
  - Pt/Al$_2$O$_3$

1. Introduction and objectives

Chemical reaction:

\[
\begin{align*}
\text{CH}_3\text{OH} + 3 \text{CO}_2 & \rightarrow \text{CH}_2\text{OH} + 3 \text{CO}_2 \\
\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{OH} + 3 \text{CO}_2 \\
\text{CH}_2\text{OH} & \rightarrow \text{CH}_2\text{OH} + 3 \text{CO}_2
\end{align*}
\]

Valuable products:

- USES: • CO + H\(_2\)
- • fuel cells

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Synthesis of biodiesel in the laboratory:

**Reagents:**

- **Pure glycerol (chem)**
- **Glycerol from biodiesel manufacturing (co-prod):**

  Average of organics:
  - MeOH: 4%
  - Acetic Acid: 38%
  - Glycerol: 58%

**Reaction Conditions:**

- $T = 60^\circ C$
- Time: 3h

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1. Introduction and objectives

Methanation on and Fisher and Fisher-Tropsch reaction

Water-gas-shift

H₂ + CO → H₂O + CO₂

Cleavage C-C

Alkanes

Cleavage C-O

Organics acids

C-CH₃ + H₂O → C₂H₅OH

Alcohol

Methanation and Fisher-Tropsch reaction

OBJECTIVES

- Experimental work with glycerol as a waste of biodiesel process at micro-scale reactor.

- Development of suitable catalysts for the process:
  - Adequate catalytic activity and selectivity towards H₂.
  - Resistance to deactivation.
2. EXPERIMENTAL METHOD
2. Experimental method

Experimental conditions:
- \( T = 500 \) K
- \( P = 33 \) bar
- Glycerol aqueous solution 2-10 wt%
- Liquid flow rate: 1 mL/min
- \( \text{WHSV} = 3 \) (g glycerol/ g catalyst h)
- Run time: 5 h

Characteristics:
- Micro-scale reactor test.
- Fixed bed (sand + catalyst)
- Particle sizes: 320-160 \( \mu \)m.
- Upward flow.
- Stainless steel reactor (9mm i.d.).
2. Experimental method

Experimental system
Catalysts prepared by a coprecipitation method

28 and 41% Ni/(Ni+Al)

\[
\begin{align*}
\text{Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \\
\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}
\end{align*}
\]

\(\text{pH} = 7.9\)

\(T = 40^\circ\text{C}\)

\(\text{COPRECIPITACION}\)

\(T = 750^\circ\text{C}\)

140 cm\(^3\)/min air, 3 h

\(\text{REDUCTION}\)

100 cm\(^3\)/min \(\text{H}_2\), 1 h, \(T=650^\circ\text{C}\)

\(\text{ACTIVATED CATALYST}\)

3. EXPERIMENTAL RESULTS

- Effect of the feedstock and the glycerol content
Effect of the feedstock and the glycerol content:

3. Results

The co-prod glycerol showed higher hydrogen selectivity and smaller alkane selectivity.

Constant gas yield values were obtained with time, no deactivation was observed.

↓ $H_2$ and $CO_2$ yields when the co-prod glycerol is fed.
3. Results

- Organic conversion is similar between both feedstock. However, an improvement was observed with the highest glycerol content.

- Higher carbon conversion to gas is obtained in glycerol from chemical reagent compared to co-product in biodiesel manufacturing.
### 3. Results

**Effect of the feedstock and the glycerol content:**

<table>
<thead>
<tr>
<th>Product</th>
<th>2% chem</th>
<th>2% co-prod</th>
<th>5% chem</th>
<th>5% co-prod</th>
<th>10% chem</th>
<th>10% co-prod</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>0.0574</td>
<td>0.0617</td>
<td>0.0256</td>
<td>0.0382</td>
<td>0.0167</td>
<td>0.0180</td>
</tr>
<tr>
<td>EtOH</td>
<td>0.0213</td>
<td>0.0280</td>
<td>0.0181</td>
<td>0.0244</td>
<td>0.0482</td>
<td>0.0042</td>
</tr>
<tr>
<td>Acetol</td>
<td>0.1305</td>
<td>0.1250</td>
<td>0.0800</td>
<td>0.0873</td>
<td>0.0502</td>
<td>0.0480</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>0.1435</td>
<td>0.4110</td>
<td>0.0618</td>
<td>0.6092</td>
<td>0.0289</td>
<td>0.2869</td>
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<tr>
<td>Propylene glycol</td>
<td>0.0535</td>
<td>0.1529</td>
<td>0.0954</td>
<td>0.0711</td>
<td>0.1488</td>
<td>0.0118</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>0.0951</td>
<td>0.0592</td>
<td>0.0615</td>
<td>0.0460</td>
<td>0.0580</td>
<td>0.0155</td>
</tr>
</tbody>
</table>

Product yields ↓ when the glycerol content ↑
3. EXPERIMENTAL RESULTS

- Effect of the catalyst composition
3. Results

Effect of the catalysts composition:

- 28% Ni chem (■) 41% Ni chem (●)
- 28% Ni co-prod (□) 41% Ni co-prod (○)

- 41 wt% Ni catalyst tested showed a slightly deactivation in co-prod glycerol.
- Co-prod glycerol: H\textsubscript{2} and CO\textsubscript{2} yields are similar for both catalysts, after deactivation period of 41 wt% Ni catalyst.
- Chemical glycerol: H\textsubscript{2} and CO\textsubscript{2} yields ↓ when %Ni ↓
3. Results

- The organic conversion is similar for both feeds and catalysts except for the 41% Ni catalyst and co-product feeding, that is higher.

- Higher carbon conversion to gas is obtained in glycerol from chemical reagent.
### Effect of the catalysts composition:

<table>
<thead>
<tr>
<th></th>
<th>Yield (g chemical/g organics):</th>
<th>28% Ni 5% chem</th>
<th>28% Ni 5% co-prod</th>
<th>41% Ni 5% chem</th>
<th>41% Ni 5% co-prod</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>0.0256</td>
<td>0.0382</td>
<td>0.0280</td>
<td>0.0316</td>
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<tr>
<td>EtOH</td>
<td>0.0181</td>
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<tr>
<td>Acetol</td>
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<td>0.0873</td>
<td>0.0607</td>
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</tr>
<tr>
<td>Acetic acid</td>
<td>0.0618</td>
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<td>0.0591</td>
<td>0.2924</td>
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</tr>
<tr>
<td>Propylene glycol</td>
<td>0.0954</td>
<td>0.0711</td>
<td>0.0878</td>
<td>0.0390</td>
<td></td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>0.0615</td>
<td>0.0460</td>
<td>0.0887</td>
<td>0.0408</td>
<td></td>
</tr>
</tbody>
</table>

3. Results
OUTLINE

4. CONCLUSIONS
CONCLUSIONS

- The co-prod glycerol showed higher hydrogen selectivity and smaller alkane selectivity.

- Organic conversion is similar between both feedstock. However, an improvement was observed with the highest glycerol content.

- Higher carbon conversion to gas is obtained in glycerol from chemical reagent compared to co-product in biodiesel manufacturing.

- Co-prod glycerol showed a slightly deactivation in 41 wt % Ni catalyst tested.

FUTURE WORK

- Upgrade of waste biomass aqueous streams from several industrial processes; cheese whey and black liquor in a bench scale.
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