Synthesis, characterization and applications of carbon-based calcium catalysts deriving from avocado seeds for biodiesel production


7TH INTERNATIONAL CONFERENCE ON SUSTAINABLE SOLID WASTE MANAGEMENT
26-29 June 2019, Heraklion, Crete Island, Greece
Fossil fuels vs Biofuels

Fossil fuels
- Petroleum;
- Coal;
- Natural gas

Disadvantages
- Exhaustible resources;
- Greenhouse gases emission: CO$_2$, CO, SO$_x$, NO$_x$

Biofuels
- Vegetable oil
- Biodiesel
- Biogas
- Bioethanol

Eco-sustainable
Renewable resources
Biodiesel

Triglycerides + MeOH $\leftrightarrow$ Diglycerides + RCOOMe
Diglycerides + MeOH $\leftrightarrow$ Monoglycerides + RCOOMe
Monoglycerides + MeOH $\leftrightarrow$ Glycerol + RCOOMe

F. Ma, M. A. Hanna, Bioresource Technologies, vol. 70, pp. 115-118, 1999
Homogeneous basic catalysts

**Advantages**
- Lower ratio methanol to oil (18-30:1)
- Cost of catalysts
- Temperature (50-70 °C)
- Time of reaction (< 3h)

**Drawbacks**
- Production of water
- Lower concentration of FFAs (< 0.5%w)
- Production of waste

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Heterogeneous catalysis - Lower cost in plant management
- Recovery of the catalyst
- Thermal and chemical resistance of catalysts
- Easy purification of the products

Homogeneous catalysis - Corrosion of the plants used derived from the use of strong acids and bases
- Loss of the catalyst
- Neutralization and removal of water from chemical products

CaO
- Cheap
- Abundant
- Efficient
- Leaching
CaO

Why not supporting?
Part 1. Preparation of CaO-deposited on biochar

- Preparation of biochar
- Deposition of Ca onto the biochar
Preparation of biochar

900 °C, 2h under nitrogen flow
Deposition of Ca onto avocado-char

1.5 N NaOH solution

1h, 25 °C under stirring

Metal salts solution

Avocado seed carbon char

1) 1h, 80 °C

2) washing with water

3) dried in oven 100 °C, 24 h

900 °C, 2h under nitrogen flow

Activation

Calcium carbon-based materials

Metals supported
20%wt Ca
10%wt Ca
5%wt Ca

CaO
Ca(OH)$_2$

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Part 2. Characterization of Ca carbon-based materials

- Elemental analysis
- Determination of acid and basic sites, piezoelectric point
- FT-IR analysis
- XRD analysis
- SEM analysis
Elemental analysis

Table 1. Elemental analysis for determination of Ca content for pure and Ca-carbon supported materials.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Theoretical value (%wt)</th>
<th>Experimental Value (%wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%wt Ca carbon avocado seed</td>
<td>20</td>
<td>14.3 ± 0.5</td>
</tr>
<tr>
<td>10%wt Ca carbon avocado seed</td>
<td>10</td>
<td>7.9 ± 0.2</td>
</tr>
<tr>
<td>5%wt Ca carbon avocado seed</td>
<td>5</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>CaO</td>
<td>71.5</td>
<td>64.1 ± 2.1</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>54.1</td>
<td>52.7 ± 1.8</td>
</tr>
</tbody>
</table>
XRD analysis: calcium compounds (supported materials)

XRD analysis also confirm the presence of CaO in the supported materials.

20%wt Ca loaded
10%wt Ca loaded
5%wt Ca loaded
Carbon avocado seed
SEM analysis

Carbon avocado seeds  
5%wt Ca loaded  
10%wt Ca loaded  
20%wt Ca loaded

Carbon avocado seeds  
5%wt Ca loaded  
10%wt Ca loaded  
20%wt Ca loaded
Part 3. Catalyst reactivity for biodiesel production on refined oils

• Reactivity tests of pure metal compounds and supported catalysts
• Kinetic studies
• Optimization of reaction conditions
• Recycling tests
• Reactivity tests with other bio-oils
Trans-esterification using Ca-supported materials as catalysts. Reaction conditions: weight ratio catalyst to oil = 5%, molar ratio methanol to oil = 15:1, temperature = 100 °C, time = 3 h. Sunflower oil.

Reactivity of supported catalysts on refined oils

- Carbon avocado seed
- 5%wt Ca supported
- 10%wt Ca supported
- 20%wt Ca supported
- CaO

Yield FAMEs (%wt)

Complete dissolution of CaO
Kinetic studies

- Reaction conditions: weight ratio catalyst to oil = 5%, molar ratio oil to methanol = 15:1, temperature = 100 °C, time = 300 min. Sunflower oil

Effect of Temperature
TG + 3 MeOH $\leftrightarrow$ 3 FAMEs + Gly

Pseudo first-order

$$\ln[\text{TG}] - \ln[\text{TG}]_0 = - k_1 t$$
$$- \ln(1 - \alpha_{\text{TG}}) = k_1 t$$

Pseudo second-order

$$\frac{1}{[\text{TG}]} - \frac{1}{[\text{TG}]_0} = k_2 t$$
$$\frac{\alpha_{\text{TG}}}{1 - \alpha_{\text{TG}}} = k_2 t$$

Bioresource Technology 100 (2009) 1203–1210
Kinetic studies

\[ k_2 = \frac{A e^{-\frac{E_a}{RT}}}{k} \]

\[ \ln k_2 = \ln A - \frac{E_a}{RT} \]

**Kinetic constants**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( k_2 ) (L/mol min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>1.8*10^{-2}</td>
</tr>
<tr>
<td>353</td>
<td>5.3*10^{-3}</td>
</tr>
<tr>
<td>333</td>
<td>2.3*10^{-3}</td>
</tr>
</tbody>
</table>

80-100 \( \text{kJ K}^{-1} \text{mol}^{-1} \)

Ea = 39.94 \( \text{kJ K}^{-1} \text{mol}^{-1} \)

20-30 \( \text{kJ K}^{-1} \text{mol}^{-1} \)

Linear interpolation for Ea determination.
Optimization of reactive conditions

Box-Behnken design matrix for the four independent variables for the production of FAMEs (27 experiments).

Catalyst (%wt)= 2.5, 5, 10 (cat)
Methanol (molar ratio to oil): 10, 15
Temperature (°C) = 60, 80, 100 (T)
Time (h) = 1, 3, 5 (t)

Yield FAMEs = - 162.71 + 4.46733 cat + 4.50325 C + 1.82206 T + 7.69187 t - 0.230933 cat² - 0.139 cat C + 0.0362 cat T + 1.156 cat t + 0.00551667 C² - 0.03785 CT + 0.40475 Ct - 0.00518333 T² + 0.131688 T t - 2.97052 t²
Recycling tests and mechanism

Reactive conditions
Sunflower oil (Acidity = 0.21 mg KOH/g)
Weight ratio catalyst to oil = 7.3%
Molar ratio methanol to oil = 15.6:1
Temperature = 99.5 °C
Time = 5 h

Recovery and reuse of catalyst
- Separation from organic mixture by centrifugation
- Washing with methanol
- Dried in oven (100 °C, 3 h)

11.5 mg Ca lost = 16.1 mg CaO
Reacting an equivalent amount of the Ca lost during the 1° cycle under the same experimental conditions
Yield FAMEs = 31.4 ± 0.4 %wt

Catalysis occurred mainly onto the surface
XRD

- CaO
- Ca(OH)$_2$
- Ca(CO)$_3$

Starting material

After 3 cycles

FTIR

- 1744 cm$^{-1}$
- 3641 cm$^{-1}$
- 2800 - 3000 cm$^{-1}$

Starting material
After 3 cycles of reaction
1. Centrifugation
2. Washing with methanol
3. Dried in oven (100 °C, 3 h)

![Image of CaO](image1)

![Image of Ca(OH)₂](image2)

![Image of Ca(RCOO)₂](image3)

![Image of Ca(OR)₂](image4)

%wt FAMEs

<table>
<thead>
<tr>
<th>Cycles of reaction</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>%wt FAMEs</td>
<td>99.5</td>
<td>90.0</td>
<td>81.0</td>
</tr>
<tr>
<td>%wt FAMEs</td>
<td>99.5</td>
<td>99.4</td>
<td>99.3</td>
</tr>
</tbody>
</table>

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Use of waste cooking oil

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Waste cooking oil</th>
<th>Pretreated Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content (ppm)</td>
<td>701 ± 8</td>
<td>100 ± 6</td>
</tr>
<tr>
<td>Acid value (mg KOH/g)</td>
<td>8.05 ± 0.04</td>
<td>1.05 ± 0.03</td>
</tr>
<tr>
<td>FAMEs</td>
<td>Traces</td>
<td>3.5 ± 0.2</td>
</tr>
<tr>
<td>Monoglycerides</td>
<td>0.8 ± 0.1</td>
<td>0</td>
</tr>
<tr>
<td>Diglycerides</td>
<td>3.9 ± 0.1</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>Triglycerides (%wt)</td>
<td>90.9 ± 0.3</td>
<td>93.2 ± 0.4</td>
</tr>
<tr>
<td>SN (mg KOH/g)</td>
<td>194 ± 1</td>
<td>190 ± 1</td>
</tr>
<tr>
<td>Ashes (ppm)</td>
<td>100 ± 11</td>
<td>Nd</td>
</tr>
<tr>
<td>Metal content (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>13.3 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td>Mg</td>
<td>9.2 ± 0.3</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Conclusions

1. A new catalyst was prepared and characterized
2. Reaction conditions were optimised
3. Kinetics was studied
4. Procedures to recover and recycle were critically studied and optimized
5. Application to waste cooking oil was positively verified
Acknowledgements

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