Synthesis of Calcium Oxide from River Snail Shell as a Catalyst in Production of Biodiesel

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Abstract
This research studied synthesis of calcium oxide from river snail shells by calcination at 700, 800 and 900 °C for 4 h, and its subsequent use as a catalyst for biodiesel production. The calcium oxide fraction in calcined river snail shell was analyzed by X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRF result showed calcium oxide levels of 59.499 %, 70.113 % and 73.88 1%, respectively, at corresponding calcination temperatures of 700, 800 and 900 °C. The SEM images revealed porous, rough, and fragile surfaces which became agglomerated at elevated temperatures. The calcium oxide obtained from each calcination temperature was utilized as a catalyst in production of biodiesel. The process used waste cooking oil and methanol in a molar ratio of 6:1, reaction temperature 60-65 °C for 3 h and 1-3 % by weight of catalysts. The transesterification reaction using calcined river snail shell as catalyst was compared at three temperature ranges. They results revealed that a calcination temperature of 800 °C, a catalyst amount of 1 % resulted in maximum biodiesel yield, at 95.91 %. The properties of biodiesel, flash point, heat of combustion, acid value and methyl ester content were analyzed. The results found biodiesel from this research was qualified according to the standards of the Department of Energy Business. In conclusion, river snail shell is considered effective as a source of calcium oxide catalyst for commercial biodiesel production in the future.

Keywords: Calcination; Calcium oxide; Biodiesel; Calcined river snail shell

Introduction
Increasing global energy demand imposes increasing pressure on dwindling oil reserves [1-3]. Biodiesel is emerging as a viable renewable alternative fuel that is environmentally friendly, helps to prevent global warming and reduces air pollution [4]. Biodiesel can be produced from a wide range of biomass, including vegetable oils, animal fats and waste cooking oils [5]. Transesterification is the most commonly
popular production method, using homogeneous catalysts such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) [6-7]. These catalysts are inexpensive and result in short reaction times and high yield. However, these catalysts generate toxic wastewater from washing during the process and are also prone to contamination with methoxide resulting from reaction with methanol used in the process [3, 6, 8].

To address this problem, this study investigated other potential catalysts for biodiesel production. Heterogeneous catalysts such as chicken egg, river snail egg, and crab shell are promising due to the ease of catalyst separation and reduction in wastewater consumption [6, 9-10]. Calcium oxide (CaO) is one such heterogeneous catalyst that can be obtained from river snail shells. This research studied the viability of calcium oxide from river snail shells for biodiesel production from waste cooking oil using the transesterification process.

Materials and methods
1) Catalyst preparation and analysis

The river snail (Viviparidae) belongs to a family of large operculated freshwater snails. It is classified in the group of Architaenioglossa, and adults are commonly found in waterways as illustrated in Figure 1 [11].

A sample of 1 kg of river snail shells was collected and cleaned by washing thoroughly with water several times and then dried in a hot air oven at 105 °C. The resulting material was calcined in a muffle furnace under static air conditions at designated temperatures (700, 800 and 900 °C) for 4 h, then crushed to powder and filtered through a 60 mesh stainless steel sieve. The resulting calcined river snail shell powder (CRSP) weighed 0.5 kg and was stored in a desiccator before use.

The chemical composition of the CRSP sample was determined by X-ray fluorescence (Philips, Netherlands) spectroscopy under vacuum conditions, while the structural characterization was determined by X-ray diffraction (XRD; Philips, Netherlands) coupled with Cu ka radiation (λ = 0.154 nm) generated at 40 kV and 30 mA, over a 20 range from 5º to 90º with a step size of 0.05º at a scanning speed of 3º min⁻¹. The microstructure of the material was determined by scanning electron microscope (SEM). The SEM images and surface elemental analysis were recorded on a Quanta 400 (Czech Republic).

Waste cooking oil was filtered and boiled at 105 °C for 30 min to remove moisture. Then, free fatty acid analysis (FFA) was assayed by titration with standard solutions. A 5 g sample of oil was placed in flask, to which 25mL of 2-propanol and 3-5 drops of phenolphthalein were added. Hydroxide solution (KOH) was used as a standard for titration, and the volume of KOH used was recorded to calculate total FFA in the waste cooking oil and thereby estimate the amount of catalyst needed.

2) Transesterification reaction

A sample of 200 mL waste cooking oil was placed in a 500-mL flask together with methanol at a molar ratio of 6:1. CRSP was added as a catalyst, prepared at temperatures of 700, 800 and 900 °C. The amount of catalyst ranged from 1-3 %. The reaction temperature was maintained at 60-65 °C, with stirring at 300 rpm for 3 h, using a hot plate controlled by a thermoregulator. The experiments were repeated 3 times. After completion of the transesterification reaction, the calcium oxide catalyst was separated by
centrifugation and excess methanol was removed by evaporation at 100 ºC. The percentage yield was calculated using Eq. 1 [12].

\[
Yield(\%) = \left( \frac{\text{Weight of biodiesel}}{\text{Weight of oil}} \right) \times 100 \quad \text{(Eq. 1)}
\]

3) Biodiesel production properties

The properties of the biodiesel produced was analyzed by acid value (ASTM D664), density (ASTM D1298), flash point (ASTM D93), heat of combustion (ASTM D4809) and fatty acid methyl ester (FAME), using a gas chromatograph (Agilent 7890A) by method (EN 14103), equipped with a flame ionization detector and a capillary column (DB-WAX, 30 m × 0.25 mm × 0.25 µm). Methyl heptadecanoate was used as an internal standard to quantify the biodiesel content.

The FAME of biodiesel samples was identified and the peak areas utilized to quantify the FAME content, using Eq. 2 [13].

\[
C = \left( \sum A \right) - A_{EI} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \quad \text{(Eq. 2)}
\]

Where \( C \) = fatty acid methyl content (%); \( \sum A \) = total peak area; \( A_{EI} \) = peak area corresponding to the methyl heptadecanoate; \( C_{EI} \) = concentration of methyl heptadecanoate solution in heptane (mg mL\(^{-1}\)); \( V_{EI} \) = volume of methyl heptadecanoate solution (mL); \( m \) = mass of biodiesel sample (mg).

Results and discussion

1) Catalyst characterization

1.1) XRF analysis

Chemical compositions was determined with the XRF technique in CRSP at 700, 800 and 900 ºC for 4 h. It was found that at a temperature of 700 ºC, 59.4 9 % of the calcium carbonate in the shells was transformed into active calcium oxide catalyst. When the calcined temperature was increased to 800 ºC, the rate increased to 70.11 %. The result indicated that transformation of calcium carbonate (CaCO\(_3\)) to calcium oxide (CaO) is temperature-dependent [14]. The reaction produces carbon dioxide as illustrated in Eq. 3 [14].

\[
\text{CaCO}_3 (s) \rightarrow \text{CaO} (s) + \text{CO}_2 \quad \text{(Eq. 3)}
\]

The optimal calcination temperature was found to be 800 ºC. The XRF spectroscopy showed that the CRSP material derived from the shells was composed of CaO, magnesium oxide (MgO), aluminium oxide (Al\(_2\)O\(_3\)) and silicon dioxide (SiO\(_2\)) as shown in Table 1.

1.2) XRD analysis

In order to study the crystalline structure at different calcination temperatures, XRD was used. At 700°C, the calcium carbonate contained in the shell was partially converted to calcium oxide. X-ray diffraction found many peaks for CaCO\(_3\), at 2θ = 29.43º, 39.46º, 43.23º, 47.46º, and 48.53º as illustrated in Figure 2, while calcination temperature at 800 and 900ºC showed CaO as the major peaks. The peaks at 2θ = 32.23º, 37.41º, 53.93º, 64.26º, 67.48º, 79.1º and 88.56º were the characteristic as similar to the standard XRD pattern of CaO. As a result, it was concluded that a high temperature over 800°C is required to completely convert calcium carbonate into calcium oxide [3, 14].

<table>
<thead>
<tr>
<th>Element (%)</th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO (%)</td>
<td>59.499</td>
<td>70.113</td>
<td>73.881</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>0.271</td>
<td>0.362</td>
<td>0.329</td>
</tr>
<tr>
<td>Al(_2)O(_3) (%)</td>
<td>0.237</td>
<td>0.159</td>
<td>0.162</td>
</tr>
<tr>
<td>SiO(_2) (%)</td>
<td>0.123</td>
<td>0.109</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 1 XRD patterns of the river snail shell catalysts calcined at 700-900 °C for 4 h.

1.3) SEM analysis

The scanning electron microscope (SEM) was used to determine the external structure of the calcined river snail shell, as illustrated in Figure 3 (a-c). The catalysts, which had a particle size of 5 µm at 6000 imaginable, had a porous on the surface and the particles of size 2 µm at 20,000 imaginable as shown in Figure 3 (d-f) the calcination temperature 700-800 °C, the structure had more rough and many surface cracks. At the higher calcination temperature of 900 °C, particles were small and agglomerated. The smaller particle size resulted in higher surface area for catalysis [3, 15]. However, calcination at higher temperature thus fragile, easily brittle fractures can be easily crushed to calcination at a lower temperature [14-15].

2) Transesterification reaction

Analysis revealed that the waste cooking oil contained 0.49 % free fatty acids (FFA). From the transesterification reaction using CRSP as catalyst, at 800 °C, catalyst amount of 1 % for a 6:1 methanol:oil ratio resulted in the maximum biodiesel yield (95.91 %) as shown in Figure 4. Increasing the amount of catalyst to 2 % reduced the yield to 94.67 % because of incomplete distribution [16]. In addition, an excess amount of catalyst would increase biodiesel viscosity and reduce the mass transfer of reactant, reducing the yield [15]. The effect of calcination temperature of the catalyst (700-900 °C) on biodiesel yield is shown in Figure 4.
Figure 3 SEM images of the river snail shell catalysts calcined at 700-900 °C for 4 h; (a-c) with magnification of approximately 5 µm, and (d-f) with magnification of approximately 2 µm.

Figure 4 Effect of different designated temperature catalyst to biodiesel yield.

3) Biodiesel production properties

Biodiesel yield from all treatments were above 85 %. The specific properties of biodiesel produced by transesterification from waste cooking oil using CRSP at 700-900 °C were determined, including flash point, acid value, density, and heat of combustion as shown in Table 2.

Density of the biodiesel ranged from 880-910 kg m⁻³ while acid value ranged from 0.33-0.88 mg KOH g⁻¹. Under the ASTM D1298 standard, biodiesel density should be in the range of 860-900 kg m⁻³, while acid value under the ASTM D664 standard should be below 0.5 mg KOH g⁻¹ [17]. The results indicate that increasing the amount of catalyst resulted in lower density of the biodiesel, but higher acid values, which would increase engine corrosion.

The flash point of biodiesel was close to the standard value. The standard ASTM D93 specifies a flashpoint of not less than 120 °C [17]. The flash points of biodiesel from all treatments were higher than 150 °C. The heat of combustion values of biodiesel under ASTM D4809 is specified at 40,000 kJ kg⁻¹, which is slightly lower than that of petroleum diesel fuel [18]. The heat of combustion properties of biodiesel from all treatments were 31,000-42,000 kJ kg⁻¹. Thus, proper conditions are needed to ensure compliance with specified
standards for density, acidity, flash point and heat of combustion.

The treatment samples were also analyzed for the amount of methyl ester by gas Chromatograph. From Table 2, biodiesel properties of treatments 4 and 5 complied with all the standard requirements for biodiesel as specified by the Department of Energy Business. They were chosen to analyze the methyl ester content using gas chromatography, as shown in Table 3.

As shown in Table 3, the treatment using CRSP 800 °C at 1 % generated methyl ester at 81.34 %, whilst the treatment using CRSP 800 °C at 2 % catalyst resulted in a higher yield of methyl ester (97.95 %), which was compliant with the Department of Energy Business standard determination value (more than 96.5 %) [17]. The other properties of both treatments (density, acidity value, flash point, heat of combustion and methyl ester) complied with the Department of Energy Business standard requirements.

<table>
<thead>
<tr>
<th>Temp (ºC)</th>
<th>Catalyst (%)</th>
<th>Yield (%)</th>
<th>Density (kg m⁻³)</th>
<th>Acid value (mg KOH g⁻¹)</th>
<th>Flash points (ºC)</th>
<th>Heat of combustion (kJ kg⁻¹)</th>
<th>Methyl ester (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1%</td>
<td>92.63</td>
<td>920</td>
<td>0.55</td>
<td>&gt; 230</td>
<td>31,760</td>
<td>81.34</td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>91.56</td>
<td>910</td>
<td>0.33</td>
<td>&gt; 230</td>
<td>32,891</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>85.52</td>
<td>905</td>
<td>0.86</td>
<td>&gt; 230</td>
<td>35,627</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>1%</td>
<td>95.91</td>
<td>900</td>
<td>0.45</td>
<td>157</td>
<td>31,170</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2%</td>
<td>94.67</td>
<td>890</td>
<td>0.46</td>
<td>157</td>
<td>41430,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>95.16</td>
<td>880</td>
<td>0.56</td>
<td>165</td>
<td>43,022</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>1%</td>
<td>88.86</td>
<td>910</td>
<td>0.55</td>
<td>&gt; 230</td>
<td>35,925</td>
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<td>94.86</td>
<td>880</td>
<td>0.88</td>
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<tr>
<td></td>
<td>3%</td>
<td>92.89</td>
<td>880</td>
<td>0.77</td>
<td>158</td>
<td>31,940</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 Properties of biodiesel product using different percentage of catalyst (CRSP at 800°C)

<table>
<thead>
<tr>
<th>Catalyst (%)</th>
<th>Yield (%)</th>
<th>Density (kg m⁻³)</th>
<th>Acid value (mg KOH g⁻¹)</th>
<th>Flash points (ºC)</th>
<th>Heat of combustion (kJ kg⁻¹)</th>
<th>Methyl ester (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>95.91</td>
<td>900</td>
<td>0.45</td>
<td>175</td>
<td>31,170</td>
<td>81.34</td>
</tr>
<tr>
<td>2%</td>
<td>94.67</td>
<td>890</td>
<td>0.46</td>
<td>157</td>
<td>41430,</td>
<td>97.95</td>
</tr>
</tbody>
</table>

Conclusions

This research studied the synthesis of calcium oxide from calcined river snail shells, and determined an optimal calcination temperature of 800 ºC. Because of the amount of CaO catalysts that are balanced with the transesterification reaction. The result shows that using CRSP at 800 ºC at 2 % as a catalyst in biodiesel production was optimal for production of biodiesel by transesterification using calcined river snail shell powder, and that the resulting biodiesel product was compliant with the Department of Energy Business standards. Therefore, the catalyst produced from calcined river snail shell carries potential as a catalyst, replacing NaOH or KOH in the process, and reducing health and environmental burdens in biodiesel production.

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References


