Characterization of methyl ester compound of *Carica papaya* seed oil through Transesterification using CaO Catalyst from *Strombus canarium* shells

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**Abstract.** Biodiesel is an alternative fuel that is included in renewable energy. Various problems of the source of raw materials for making biodiesel create an opportunity to find alternative sources of raw materials from plant oils, one of which is papaya seeds. Extraction of papaya seeds into oil is carried out by soxhletation and distillation methods. GCMS analysis showed that papaya seed oil contained oleic acid. Biodiesel transesterification has been carried out using CaO catalyst from the Strombus canarium shells. The reaction was carried out at the papaya seed oil to methanol molar ratio of 1: 6, presence catalyst 5% wt relative to oil and temperature reaction of 65 °C for 2 h. GC/MS analysis result showed that the content of methyl esters is 50.35% with the highest abundance is 10-Octadecenoic acid and the smallest abundance is 9-Octadecenoic acid.

1. **Introduction**

The most widely considered alternative fuel lately is biodiesel (methyl ester). The production of biodiesel from plant oils (such as palm oil and jatropha oil) is constrained because palm oil is used for cooking oil. Based on data from Badan Pusat Statistika (2015) on papaya production in Bangka Belitung, which was 1843 tons/year. Generally, people make papaya as a snack and a mixture of spices in cooking. On the other hand, the high processing of papaya fruit-based products causes its problems. The processed products of papaya produce waste that is not optimized for papaya seeds. The oil content in papaya seeds varies from 15.3 to 30% [1] one alternative to processing papaya seed oil is as a raw material for synthesis of biodiesel [2].

Generally, biodiesel preparation is carried out through transesterification reactions using alkaline catalysts (NaOH and KOH) [3], enzymes (lipases) [4], and through the esterification process using a liquid acid catalyst (H₂SO₄ and H₃PO₄) [5]. The use of liquid catalysts is considered inefficient in a process. Therefore, it is necessary to develop solid (heterogeneous) catalysts that can help in transesterification reactions that are more environmentally friendly, easier to separate, and can be reused. One solid catalyst that can be used for biodiesel is a mixture of calcium compounds (CaO, Ca(OH)₂, CaCO₃) [6]. Many sources of CaO are found in the shells of soft animals such as shellfish and snails. Shellfish are rich in calcium carbonate (CaCO₃), around 98.5% [7,8].
One of the soft animals found on the coast of Bangka Island is *Strombus canarium*, so far the *Strombus canarium* is processed by the community as local food, and the shell is thrown away, so it becomes unoptimized waste. The *Strombus canarium* shell has a CaO content of 97.8% and has been used as a catalyst in the production of biodiesel from waste cooking oil [9].

In this study transesterification of papaya seed oil into biodiesel using CaO catalyst from *Strombus canarium* shell, the reaction was carried out with a 1:6 mole ratio of oil to methanol, 5% CaO catalyst, 65 °C for 2 hours. The biodiesel produced was then analyzed by Gas Chromatography Mass Spectrometry (GC/MS).

2. Research methods

2.1 Preparation of CaO catalyst

The *Strombus canarium* shell were dried and then roughly ground using mortar. The *Strombus canarium* shell is then calcined in a furnace at 900 °C for 4 h. After calcination is complete, the snail shell were crushed and sifted using 200 mesh sieve and stored in a desiccator. The catalyst used for biodiesel synthesis is a 200 mesh catalyst. The CaO catalyst was then characterized using XRD to calculate the degree of crystallinity and phase of CaO.

2.2 Extraction of papaya seed

Papaya seeds were washed with 3 rinses to make sure the papaya seeds are clear of the gelatin layer. Papaya seeds were dried in the sun for ± 3 days. Papaya seeds are put into the oven to reduce the remaining water remaining at 105 °C for ± 4 hours. The dried papaya seeds are then mashed into powder. Extraction of papaya seeds was carried out by the socletation method using n-hexane at a temperature of 69 °C for 3 hours. The socletation results were distilled at 69 °C for 2 hours to get papaya seed oil.

2.3 Transesterification process

Transesterification of biodiesel from papaya seed oil was carried out at optimum conditions according to previous research [9], the mole ratio of oil: methanol (1:6), 5% CaO catalyst, reaction temperature of 65 °C for 2 hours. The reaction mixture is then allowed to stand and a small amount of Na₂SO₄ is added to bind the remaining water molecules. Furthermore, the synthesis product was analyzed for the content of methyl esters by GC/MS analysis

3. Result and Discussion

3.1 The catalyst characterization

Characterization of CaO catalyst was carried out by X-ray diffraction analysis (XRD).

![Figure 1. Diffractogram of CaO samples (red) and CaO standard (blue)](image-url)
The diffraction pattern from the calcination of the *Strombus canarium* shell in Figure 1 shows the suitability of the pure CaO diffraction pattern based on the International Center for Diffraction Data (ICDD) database where calcined CaO has a value of $2\theta = 32.16^\circ; 37.31^\circ; 53.82^\circ; 64.11^\circ; 67.33^\circ; 91.42^\circ$, while the value of $2\theta$ on the ICDD is $2\theta = 32.19^\circ; 37.35^\circ; 53.85^\circ; 64.14^\circ; 67.36^\circ; 91.45^\circ$. Based on the diffraction pattern, it can be concluded that the calcination of the gonggong snail shell at 900 °C for 4 hours succeeded in producing pure CaO [8].

### 3.2 GC/MS analysis

The characteristics of biodiesel were observed by Chromatography Mass Spectrometry (GC/MS). GC/MS analysis was carried out to determine the content of methyl esters (biodiesel) contained in the sample.

![Figure 2. GC chromatogram](image)

The chromatogram of GC/MS analysis in Figure 2 shows that there are 10 peaks with retention time (RT) and peak area (%) which indicate the presence of methyl ester compounds as presented in Table 1. Based on these data, it can be concluded that the transesterification of papaya seed oil into biodiesel using CaO catalyst from *Strombus canarium* shells was successfully carried out.

**Table 1. Components identified in biodiesel**

| Retention times (min) | Peak area (%) | Molecular weight | Molecular formula | Compounds                                                                 |
|-----------------------|---------------|------------------|------------------|---------------------------------------------------------------------------|
| 1                     | 16.929        | 0.18             | 228              | C_{13}H_{30}O_{2} Tridecanoic acid, methyl ester (CAS) Methyl tridecanoate |
| 2                     | 20.283        | 0.50             | 242              | C_{13}H_{30}O_{2} Tetradecanoic acid, methyl ester (CAS) Methyl myristate  |
| 3                     | 23.020        | 0.58             | 270              | C_{17}H_{32}O_{2} 9-Hexadecenoic acid, methyl ester, (Z)-(CAS) Methyl palmitoleate |
| 4                     | 23.333        | 15.58            | 270              | C_{17}H_{32}O_{2} Hexadecanoic acid, methyl ester (CAS) Methyl palmitate   |
| 5                     | 23.400        | 0.40             | 292              | C_{19}H_{35}O_{3} Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester |
| 6                     | 24.408        | 0.10             | 296              | C_{19}H_{36}O_{2} 9-Octadecenoic acid, methyl ester, (E)-(CAS) Methyl elaidate |
| 7                     | 25.658        | 6.09             | 294              | C_{19}H_{36}O_{2} 9,12-Octadecadenoic acid, methyl ester                  |
| 8                     | 25.767        | 24.57            | 296              | C_{19}H_{36}O_{2} 10-Octadecenoic acid, methyl ester                     |
| 9                     | 26.100        | 2.19             | 298              | C_{19}H_{36}O_{2} Octadecanoic acid, methyl ester (CAS) Methyl stearate    |
| 10                    | 28.325        | 0.16             | 296              | C_{19}H_{36}O_{2} 9-Octadecenoic acid, methyl ester, (E)-(CAS) Methyl elaidate |
Based on Table 1, the content of methyl esters obtained at 50.35% with the highest abundance is 10-Octadecenoic acid and the smallest abundance is 9-Octadecenoic acid. The methyl ester compounds found in the biodiesel formed are methyl tridecanoate, methyl myristate, methyl palmitoleate, methyl palmitate, methyl elaidate, methyl stearate and methyl octadecanoic. These result are in accordance from previous study which is the fatty acid composition of Carica papaya seed oil to be oleic acid (74.3%); palmitic acid (16.2%); lauric acid (0.4%); stearic acid (5.0%); hexadecenoic acid (0.8%); linoleic acid (0.4%); myristic acid (0.4%) [11].

4. Conclusion
The transesterification process will produce methyl ester (biodiesel) was obtained at the papaya seed oil to methanol molar ratio of 1:6, presence catalyst 5% wt relative to oil and temperature reaction of 65 °C for 2 h. This methyl ester was confirmed to find out its functional groups. GC/MS analysis result showed that the content of methyl esters is 50.35% with the highest abundance is 10-Octadecenoic acid and the smallest abundance is 9-Octadecenoic acid.

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