Potential of papaya seeds as a heterogenous catalyst in biodiesel synthesis

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Abstract. A biomass based low-cost catalyst production has been attempted. This study evaluated papaya seeds as the catalyst precursor for biodiesel synthesis. Dried papaya seed powder was calcined at 500°C for 3 hours to produce papaya seed ash. Then, papaya seed ash was applied as catalyst for transesterification of palm oil and methanol. Catalyst load and reaction time was varied. Papaya seed ash was analyzed by SEM-EDX and biodiesel physical properties was analyzed according to the European standards (EN 14214). SEM-EDX results indicated that papaya seed ash contains a number of minerals such as K₂O, MgO and CaO which can function as catalysts in biodiesel synthesis. The produced biodiesel also met European standards. Highest biodiesel yield of 95.6% was obtained for reaction temperature of 60°C, reaction time of 2 hours, catalyst load of 2%, methanol to oil ratio of 12:1. Preliminary research revealed that PSA may be applied as a catalyst in biodiesel synthesis.

1. Introduction

Alternative fuels have garnered attention of various parties due to growing energy demands and subsiding fossil fuel reserve. Various efforts have been made to find renewable, sustainable, environmentally benign alternative fuels and reduce greenhouse gases production. One of these alternative fuels is biodiesel. Biodiesel has many advantages such as having high flash point, low viscosity, high cetane number, high lubricating performance, easy decomposition and is environmentally benign because of its lower carbon footprint compared to fossil fuels [1]. Biodiesel consists of fatty acid methyl esters which can be produced by transesterification of vegetable oils such as palm oil and alcohol using certain catalyst. The catalyst can either be homogeneous or heterogeneous. The use of heterogeneous catalysts is preferred over homogeneous catalysts because of easier product and catalyst separation, lower H₂O consumption, and lesser environmental contamination. In addition, heterogeneous catalysts are reusable [2,3].

Heterogeneous catalysts derived from biomass have been studied recently because of their potential to reduce biodiesel production costs. Usually, the biomass was converted to carbon to be used as catalyst support and desired active components were added. However, biomass with high mineral content can be directly applied as catalyst after calcination [4,5]. Utilization of biomass waste for catalyst synthesis will not only reduce catalyst cost, but also serve as a partial solution for biomass waste disposal produced by humans and agricultural activities. It is known that every year, over 5 billion metric tons of biomass waste will be generated from the agricultural sector [6].
One source of easily obtained biomass is papaya seed. In general, the seeds of ripe papaya are about 16% of the fresh fruit and are considered as by-product. The availability of papaya seeds throughout the year and its low economic value suggest that papaya seeds need to be utilized. Papaya seeds are rich in elements such as K, Ca, Mg, Na, Fe, P, S, Zn, Cu and Pb. A hundred grams of papaya seeds contain 681 mg Ca, 424 mg Mg, 2.116 mg P, 5.80 mg Fe, and 23.4 mg Na [7]. Due to the high mineral content, papaya seeds can be utilized as catalyst for biodiesel synthesis.

Biomass calcination generally requires high temperatures. The choice of temperature is influenced by type of biomass used [6]. During calcination, pores and active sites are formed as result of biomass constituent material decomposition [5]. Formation of pores and active sites is strongly influenced by calcination temperature. If the temperature is too high, it may reduce the active sites on catalyst surface and consequently reduce catalyst activity.

Previous studies on solid catalysts derived from biomass have been reported in several literatures, such as banana peduncle [4], moringa leaves [5,8], banana peel [9], and cacao peel [10]. To the authors’ knowledge, till the time this paper was written, no research on catalysts from papaya seeds had ever been attempted, even though papaya seeds are rich in minerals. Therefore, this study aimed to evaluate papaya seeds as a catalyst precursor, and apply it in biodiesel synthesis.

2. Materials and Methods

2.1. Materials
Papaya seeds were obtained from local merchants in Medan Selayang. Chemicals such as methanol, and ethanol were purchased from local supplier. Palm oil (RBDPO) was supplied by PT Salim Ivomas Pratama, Indonesia. Density, kinematic viscosity and moisture content of the palm oil was 918 kg/m³; 24.15 mm²/s, dan 0.2 % respectively.

2.2. Preparation of catalyst
Papaya seeds were washed with water to remove impurities, dried for 1 day under the sun and further dried in an oven at 105°C to constant weight [11]. Dried papaya seeds were crushed using a ball mill, and sieved using a 100 mesh sieve. Papaya seeds powder (PSP) was calcined using a furnace at 500°C for 3 h to produce papaya seed ash (PSA). PSP and PSA were analyzed using Scanning Electron Microscope-Energy Dispersive X-Ray (SEM-EDX). PSA was stored in a closed container and ready to be used as catalyst.

2.3. Transesterification
As much as 50 g palm oil was placed into a three neck flask equipped with heater, magnetic stirrer, condenser, and thermometer. Methanol (methanol to oil ratio of 6:1, 9:1, 12:1) and catalyst (1, 2, 3, 4% load) was mixed and stirred for 30 min in a glass beaker and then put into the three-neck flask. The reaction was carried out at 60°C at a stirring speed of 300 rpm. The reaction time was varied from 90-150 min. The product was separated from the catalyst by filtration and purified by washing with hot water. After purification, the obtained biodiesel was analyzed for its physical properties.

3. Results and Discussion

3.1. SEM-EDX analysis
Surface morphology of PSP and PSA were analyzed using SEM. SEM results are depicted in Figure 1. In Figure 1(a), PSP was agglomerated with non-uniform pore morphology and particle size. In Figure 1(b), PSA was still agglomerated albeit with smaller particle size, and more pores. Similar phenomenon was also observed by other researchers [8].
EDX results indicated that PSP and PSA contained metal oxides as in Table 1. The levels of these metal oxides (K₂O, MgO and CaO) increased after calcination. These metal oxides act as catalyst in biodiesel synthesis [12,13]. During calcination, thermal decomposition leads to removal of volatile fractions, and formation of pores which increases the surface area. Calcination also increased the active site on the surface of the material [5]. Catalysts with large porosity and many active sites are needed in the transesterification reaction in biodiesel synthesis.

| No. | Component | Composition (%) |
|-----|-----------|-----------------|
|     |           | PSP             | PSA             |
| 1   | C         | 92.34           | 48.07           |
| 2   | Na₂O      | -               | 0.78            |
| 3   | MgO       | 0.97            | 6.63            |
| 4   | P₂O₅      | 2.62            | 7.85            |
| 5   | SO₃       | 1.36            | 6.49            |
| 6   | Cl        | 0.16            | 2.59            |
| 7   | K₂O       | 1.48            | 22.50           |
| 8   | CaO       | -               | 2.71            |
| 9   | CuO       | 0.57            | 1.19            |
| 10  | ZnO       | 0.49            | 1.20            |

### 3.2. Transesterification

In Figure 2, catalyst load greatly affects biodiesel yield. Catalyst load was varied at 1, 2, 3 and 4% (w/w) of oil, while reaction temperature, methanol to oil molar ratio, and reaction time were fixed at 60°C, 12:1, and 2 h respectively. Increasing catalyst load also increases alkaline sites, resulting in better contact with the reactants. Biodiesel yield increased to 95.6% when catalyst load increased from 1% to 2%. Further increase in catalyst load decreased biodiesel yield. Excess catalysts render the reaction mixture more viscous so that mixing between reactant molecules becomes harder and requires greater energy [11]. In addition, separation of the catalyst from the mixture was harder as soap was formed. Catalyst leaching occurred in which metal-oxide in the catalyst reacted with triglycerides to form soap [14]. Meanwhile, at 1% catalyst load, transesterification did not proceed well enough because of lacking alkaline sites. In this state, contact between reactants and alkaline sites are inadequate, resulting in lower yield.
Figure 2. Effect of catalyst load on biodiesel yield

Transesterification is also affected by temperature as in Figure 3. Reaction temperatures were varied at 55, 60 and 65°C, while catalyst load, methanol to oil molar ratio, and reaction time were fixed at 2%, 12:1, and 2 h, respectively. Biodiesel yield increased as temperature was increased from 55°C to 60°C, then decreased upon further increase of temperature. Higher temperature stimulates collisions between reactant molecules, hence reaction becomes more prevalent. At higher temperature, reaction rate also accelerates due to lower oil viscosity [15]. At 65°C, methanol reaches its boiling point and begins evaporating. This reduces contact between reactants, thus the yield was lower at this temperature compared to that at 60°C. The optimum temperature in this study was 60°C with yield reaching 95.6%. The optimum temperature in this study is similar to that of previous researchers [5,13].

Figure 3. Effect of reaction temperature on biodiesel yield

3.3. Biodiesel Properties
Biodiesel quality is determined from the physical properties as in Table 2. Several physical properties were compared with the European standard (EU 14214) and the results have met the standards.
| Physical properties | Unit    | Biodiesel produced | EN 14214 |
|---------------------|---------|--------------------|----------|
| Methyl ester content| %       | 98.7               | >96.5    |
| Density             | kg/m³   | 876                | 860-900  |
| Kinematic viscosity | mm²/s   | 4.4                | 3.5-5.0  |

4. Conclusion

Papaya seeds can be used as precursor for sustainable and environmentally benign catalysts through calcination. Calcination produces papaya seeds ash which is composed of metal oxides (K₂O, MgO and CaO). These oxides act as catalysts during biodiesel synthesis. From this preliminary study, the highest biodiesel yield of 95.6% was obtained at reaction temperature of 60, reaction time of 2 h, and methanol to oil molar ratio of 12:1.

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