Biodiesel Synthesis from Waste Cooking Oil using Heterogeneous Catalyst from Corncob Ash Impregnated with KOH

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Abstract. Biodiesel was usually synthesized by transesterification with aid of a catalyst. In this research, corncob ash was utilized as a heterogeneous catalyst and treated waste cooking oil (TWCO) was used as the raw material. The objective of this study was to assess the ability of corncob ash impregnated with KOH as a heterogeneous catalyst in biodiesel synthesis. Prior to use, the corncob ash/KOH catalyst was calcined and characterized to determine its physical and chemical properties. Transesterification was carried out at 60°C for 3 hours. Effects of process variables, such as amount of catalyst, and methanol to TWCO molar ratio (MTR), were observed. The maximum yield of 96% biodiesel was obtained at MTR of 12:1 and 4% w/w catalyst. The obtained biodiesel was analyzed for its ester content, density, viscosity, and flash point. It was then compared to European standard EN 14214. The results confirmed that corncob ash/KOH was very suitable as heterogeneous catalyst in biodiesel synthesis.

1. Introduction

The use of waste cooking oil (WCO) as a feedstock for biodiesel synthesis will not only reduce environmental problems, but also increase added value and lower production costs. Use of a heterogeneous catalyst in biodiesel synthesis will also reduce the energy requirement, since the catalyst is easily separated and reused. The use of heterogeneous catalysts derived from agricultural waste can further reduce the cost of producing biodiesel.

Corncob waste can be utilized as a heterogeneous catalyst for biodiesel synthesis. The metal oxide content of the corncobs will act as a catalyst when the corncob is calcined. Calcination will result in form of ash with silicon dioxide (SiO₂) as main content at up to 62.01%. The use of pure SiO₂ as a catalyst in biodiesel synthesis has not been reported because SiO₂ absorbs water easily making the activation difficult. Thus, SiO₂ is more likely to serve as a catalyst support. In essence, a heterogeneous catalyst consists of two main components, the active site and support. The active site is generally a metal oxide which serves to accelerate and direct the reaction, whereas the support is generally a porous solid which provide a larger surface area for the active site.

Aside of the components, another important aspect in catalyst production is the preparation method, one of which is by impregnation. The use of an alkaline catalyst is better than that of an acid catalyst, as evidenced by the more methyl ester formation for same reaction time. Impregnating alkali metals into SiO₂ will increase the number of active site of catalyst, increasing conversion and yield. SiO₂ is stable at high temperatures and capable of expanding contact area, increasing stability, porosity and activity.
The use of SiO$_2$ as a catalyst support had been reported by some researchers, but limited to raw husk rice\(^1\),\(^4\),\(^9\). So far, the use of corncob derived SiO$_2$ as a catalyst support for biodiesel synthesis had not been conducted.

2. Materials and Methods

2.1. Pre-Treatment of WCO

Pre-treatment of WCO adopted the procedure reported by Kheang et al\(^10\). Before usage, WCO was measured for its density, viscosity, and free fatty acid (FFA) content. Activated carbon at 10 wt.% of WCO was mixed with WCO and stirred for 30 min. The mixture was left to allow the impurities to settle. The solids were separated using Whatman filter paper no.1. The filtrate was taken as treated waste cooking oil (TWCO) and analyzed for its density, viscosity, composition, and FFA content. TWCO was stored in a sealed container as a feedstock in biodiesel synthesis.

2.2. Catalyst Preparation

2.2.1. Corncob Ash Calcination

Silica ash was extracted from corncob using procedure reported by Owoeye et al\(^3\) with slight modification. Corncob was washed with aqua dest to remove impurities, dried for 2 weeks under the Sun, and further dried in oven at 110°C for 3 h. Dry corncob was crushed with ball mill for 4 h, then sieved to 200 meshes. Sieved corncob was calcined in a furnace at 700°C for 3.5 h to yield corncob ash. The corncob ash was analyzed for its SiO$_2$ content using Scanning Electron Microscopy - Energy Dispersive Spectroscopy (SEM-EDS). It was then stored in a closed container for further usage.

2.2.2. Impregnation with KOH

Corncob ash was impregnated with KOH using the procedure reported by Hindryawati et al\(^1\). A total of 10 g ash was submersed in 60 ml HCl 0.1M for 1 hour then washed with aqua dest to neutrality and dried in oven at 105°C for 2 h. Dry ash was mixed with KOH at KOH to SiO$_2$ molar ratio of 2:1. The mixture was stirred at 95°C for 2 h followed by dehydration in oven at 200°C for 30 min. The dehydrated mixture was recalcined in a furnace at 500°C for 2 h. The catalyst was stored in a sealed container and ready for use. The catalyst was morphologically analyzed using SEM.

2.3. Transesterification

Transesterification followed procedure reported by Chen et al\(^4\). As much as 50 g TWCO was added into a three-neck flask. TWCO was heated with hot plate to 60°C. Methanol, at methanol to TWCO molar ratio (MTR) of 8:1, 10:1; 12:1, and catalyst, at 2-5% w/w of TWCO, were added into the flask. The mixture was stirred using a magnetic stirrer at 350 rpm for 3 h. The transesterification product was separated from the catalyst by means of a vacuum pump. The mixture was placed in a separator funnel and left for 18 hours to form two layers. The lower layer was removed. The crude methyl ester (top layer) was washed by adding hot water (±80°C) then shaken gently and left for 5 min to form two layers, after which, the lower layer was removed again. The washing step was repeated until the water became clear. The methyl ester was reheated at 105°C using hot plate and stirred using a magnetic stirrer then cooled to room temperature. Finally, it was weighed and analyzed for its density (OECD 109), viscosity (ASTM D-445), composition of methyl ester (AOCS Official Method Ce 1b-89), and flash point (closed cup flash point tester). Iodine value (IV) of the methyl ester was calculated from its fatty acids composition using the following equation\(^11\),

\[
IV = \frac{\sum (254 \times D \times A_i)}{MW_i}
\]  

where $A_i$ is the percentage, $D$ is the total number of double bonds, and $MW_i$ is the molecular weight of each fatty acid.
3. Experimental Result

3.1. Characteristics of WCO

The results of WCO characterization were as follows: the density at 25°C was 889 kg/m³, the kinematic viscosity was 42 mm²/s, and FFA content was 0.2%. The chemical composition of WCO was analyzed using gas chromatography (GC), and the results are presented in Table 1.

| Fatty Acid                     | Composition (%) |
|--------------------------------|-----------------|
| Lauric acid (C12:0)            | 0.3367          |
| Miristic acid (C14:0)          | 0.9504          |
| Palmitic acid (C16:0)          | 39.2308         |
| Palmitoleic acid (C16:1)       | 0.4023          |
| Stearic acid (C18:0)           | 3.9442          |
| Oleic acid (C18:1)             | 44.2491         |
| Linoleic acid (C18:2)          | 10.0192         |
| Linolenic acid (C18:3)         | 0.2148          |
| Arachidic acid (C20:0)         | 0.4244          |
| Eicosenoic acid (C20:1)        | 0.2020          |

3.2. Characteristics of WCO

3.2.1. Calcination

Calcination at high temperatures will convert corncob powder into oxide elements, some of which are Al₂O₃, SiO₂, K₂O, Na₂O, MgO, and CaO. In this study SiO₂ in corncob ash will be used as heterogeneous catalyst support. Table 2 shows the elemental composition of corncob powder by SEM-EDS.

| No. | Component | Percentage (%) |
|-----|-----------|----------------|
| 1.  | C         | 49.55          |
| 2.  | O         | 45.23          |
| 3.  | K         | 5.02           |
| 4.  | Si        | 0.20           |

Table 3. Elemental Composition of Corncob Ash

| No. | Component | Percentage (%) |
|-----|-----------|----------------|
| 1.  | K         | 37.90          |
| 2.  | Si        | 27.35          |
| 3.  | In        | 14.75          |
| 4.  | O         | 14.20          |
| 5.  | C         | 4.38           |
| 6.  | Cl        | 1.25           |

From Table 2 and 3, the content of K and Si increased after calcination. Si in corncob ash corn was 27.53% or in SiO₂ form, equal to 58.99%. This increase might be due to phase changes in the structure of K and Si at high temperature, resulting in direct carbon reduction in corncob ash³. Calcination also increases diffraction intensity in which crystalline phase is more orderly¹. Calcination at higher temperatures will result in decreased catalytic properties and active surface area on the catalyst¹².
Figure 1 shows the surface of corncob powder before calcination by SEM. In Figure 1, corncob surface morphology was sharp, irregular, and partially lumped.

In Figure 2, corncob ash surface morphology was rather sharp, more orderly, distributed uniformly, and had many impurities and small pores compared to before calcination. The purpose of calcination is to remove volatile substances, oxidize a portion of mass and render the calcined materials friable. Calcination decreased particle size and increased number of pores thus increased surface area of the corncob ash.

3.2.2. Impregnation with KOH

Corncob ash was impregnated with KOH before recalcination. When calcination was carried out at 500°C, crystalline silica will form\(^1\). The structure of silica can be describe as follows\(^13\):

![Structure of silica](image)

Figure 3. Structure of silica

Because the energy of Si-O bonds is higher, Si tends to bond with oxygen (O\(_2\)) to form a compound than with other Si. To form the octet state of this complex silica crystal, each O atom requires an electron. Alkali metals can donate one electron to achieve stability of silica crystals, one example is K\(^+\). The K\(^+\) can come from KOH. During the impregnation with KOH, potassium silica is formed\(^14\). Figure 4 shows the potassium silica structure formed through impregnation with KOH to SiO\(_2\) in corncob ash.
Figure 4. Structure of potassium silica after KOH impregnation\textsuperscript{14}.

Result of composition analysis of KOH/SiO\textsubscript{2} catalyst from corncob ash by SEM-EDS is shown in table 4. After impregnation, metal salt will tend to diffuse in the pore of catalyst support. Thus, impregnated samples are recalcined or subjected to thermal activation to remove moisture and volatile compounds, and assist metal salt attachment to catalyst surface. The catalytic activity of catalyst with support is higher than that without one due to increase in the strength of catalyst base.

| No. | Component     | Percentage (%) |
|-----|---------------|----------------|
| 1.  | K             | 68.54          |
| 2.  | Si            | 0.56           |
| 3.  | In            | 22.00          |
| 4.  | O             | 7.20           |
| 5.  | C             | 1.70           |

Table 4. Elemental composition of KOH/SiO\textsubscript{2} catalyst from corncob ash

Figure 5 shows the potassium silicate catalyst having diminishing flat surface morphology. KOH was orderly and uniformly dispersed on catalyst. There were also no impurities as in the morphology of corn cob ash. The KOH/SiO\textsubscript{2} catalyst obtained from this study was 1-20 µm. The pore size appeared smaller. This pore size reduction leads to reduced pore surface area. Similar results had also been reported in some literature\textsuperscript{4,15}. A decrease in pore surface area will lower catalyst activity due to smaller pore volume in which fewer accessible active sites on catalyst surface\textsuperscript{15}. This decrease of catalyst surface area is due to structural changes such as the formation of silica oxide (SiO\textsubscript{2}) and potassium oxide (K\textsubscript{2}O) during calcination.

Figure 5. SEM of KOH/SiO\textsubscript{2} catalyst from corncob ash at 1000 times magnification

3.3. Transesterification

Figure 6 shows the effect of catalyst amount on biodiesel yield at various MTR for reaction temperature of 60°C and 3 h reaction time. At fixed MTR, use of catalyst amount from 2 to 4% increased biodiesel yield. In this state, the odds of contact between catalyst and reactants are high. However, further increasing amount of catalyst decreased biodiesel yield. The same phenomenon was also reported by
other researchers\textsuperscript{1,9}. Large amount of catalyst causes the catalyst and reactants mixture to become viscous, resulting in resistance during mixing and requiring considerable energy for efficient mixing\textsuperscript{16,17}.

Figure 6 shows that for a fixed amount of catalyst, an increase in MTR increased biodiesel yield. Higher MTR leads to better contact between methanol and TWCO, resulting in increased yields of biodiesel. However, too much use of methanol can cause difficulties in the separation of methyl esters and glycerol, as well as in methanol removal\textsuperscript{16}. The highest biodiesel yield of 96\% was obtained at MTR of 12:1 and 4\% catalyst.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure6.png}
\caption{Effect of catalyst amount on biodiesel yield at reaction temperature of 60\textdegree C and 3 h reaction time}
\end{figure}

3.4. Biodiesel Properties

Table 5 lists several biodiesel properties from this study and their comparison with the EN 14214 standard. From the test results of some biodiesel properties, the synthesized biodiesel met the established standards. The results show that KOH/corncob ash catalyst can be used as a heterogeneous catalyst in the manufacture of biodiesel from WCO.

\begin{table}[h]
\centering
\caption{Comparison of the properties of biodiesel produced from WCO with KOH/corncob ash catalyst with European Standard (EN 14214).}
\begin{tabular}{|c|c|c|}
\hline
Properties & Biodiesel produced & EN 14214 \\
\hline
Methyl ester content, \% & 99.70 & >96.5 \\
Density, kgm\textsuperscript{-3} & 870.00 & 860-900 \\
Viscosity, mm\textsuperscript{2}s\textsuperscript{-1} & 4.22 & 3.5-5.0 \\
Flash point, °C & 150.00 & 101 (min) \\
Iodine value & 59.09 & 120 ax) \\
\hline
\end{tabular}
\end{table}

The biodiesel properties shown in table 5 match the biodiesel obtained by other researchers using silica catalysts derived from rice husk\textsuperscript{1,9}. Each value in table 5 represents the mean of five measurements.

4. Conclusion

Biodiesel can be produced from WCO using heterogeneous KOH/corncob ash catalyst. The highest biodiesel yield of 96\% was obtained at MTR of 12:1 and 4\% w/w catalyst. The resulting biodiesel properties met the European standard. Results of this study resembled those obtained by other researchers who used KOH/rice husk ash catalyst.
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