Synthesis and Characterization of Nanoparticle Enhanced Biodiesel using Azadirachta Indica (Neem) leaf extract

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Abstract: Diesel fuel demand is rising globally but its direct combustion possesses many adverse health and environmental impacts. Biodiesel production has emerged as a promising substitute for commercial diesel. Biodiesel is usually prepared from edible or non-edible vegetable oils. Using edible oils for biodiesel production raises many issues such as availability, food security and cost. While in case of non-edible oils, main issues arise in terms of land use change. Fortunately, waste vegetable oils (WVO) are excellent options to solve all these problems, except for trivial costs associated with their collection and recycling. Despite several scientific breakthroughs, the biofuel production process is a slow process and there are various side reactions which inhibit the transesterification reaction. In the recent decade, nanotechnology has vastly expanded. The unique characteristics of nanoparticles such as high chemical stability, adsorption capacity and catalytic activity makes it attractive for enhancing the biofuel production process. In the present work, silver and copper oxide nanoparticles (Ag-NP and CuO-NP) were prepared using a green synthesis method. Three samples of biodiesel were prepared from WVO, one using Ag-NP catalyst, one using CuO-NP catalyst and one without nanoparticles. Prepared biofuel showed a remarkable yield of 72.9% and 64.6%, for Ag-NP biodiesel and CuO-NP biodiesel respectively. Acid values of both the prepared samples of NP biodiesels were decreased by over 7% ensuring a better quality.

Keywords: biodiesel, transesterification, nanoparticles, yield, characterization

Introduction

The need for transition to cleaner sources of energy is becoming increasingly evident. However, one of the main hurdles in the way of switching over to completely renewable sources of energy is the abrupt nature of the transition [1]. This is due to the current infrastructure being heavily dependent on hydrocarbon-based fuels [2]. One way of easing this change would be by incorporating biodiesel into the current energy economy [3]. This has an advantageous middle ground between both renewable and non-renewable sources of energy. This is because it is sourced in an environmentally friendly manner while being compatible with conventional diesel engines [4]. Biodiesel can also be used in mixtures with diesel in varying proportions. Furthermore, it was found to be a very good substitute for petroleum diesel [5]. Biodiesel is typically
synthesized through catalyzed transesterification of vegetable oils[6]. Here, alcohol and vegetable oil react along with catalytic activation which leads to the formation of crude glycerol and fatty acid methyl esters (FAME) [7]. These esters are also called biodiesel. In the present era where food security is a major concern, it would be impractical to use edible vegetable oils for biodiesel production [8]. High demand of plantation for these oils will also be a cause for rapid deforestation and disruption of plant and animal ecosystem [9]. Using leftover cooking oil or waste vegetable oils (WVO) from kitchens to produce biodiesel is a promising solution to this problem which also helps in waste management issues [10].

Homogeneous metallic hydroxide bases are the most commonly used catalyst for biodiesel production. Merits of these catalysts are their easy availability, less production time and higher yield [11]. However, homogeneous catalysts have certain limitations such as high energy consumption, low wastewater yield, catalyst separation problem, more wastewater [12]. Numerous studies have been conducted to find an ideal heterogeneous catalyst with high strong active sites, good recyclability, more stability and low cost [13, 14].

Nanotechnology, which is a rapidly growing field of science, presents unique approaches at various levels of research. The remarkable applications of nanotechnology are mainly because of the large surface-area-to-volume ratio of nanoparticles (NP) as well as their small size, which leads to distinct chemical and physical properties [15]. This technology also holds potential for considerable advancements in biodiesel production. Recently, NP have gained vast attention as heterogeneous catalysts owing to their unique properties in major areas of science [16]. Industrial NP are usually prepared by synthetic chemical or physical processes which are not very environmentally friendly. Numerous efforts were also done to explore biological methods for synthesis of NP, known as green synthesis. Biomolecules such as plant extracts, enzymes and amino acids are utilized in green synthesis of nanoparticles due to their abundant OH groups [17]. Among these biomolecules, plant extracts are gaining more recognition as reducing agents in NP synthesis, primarily due to their simplicity [18].

Azadirachta indica tree belonging to the mahogany family Meliacea, also commonly known as neem, has been used by many researchers for green synthesis of NP. Sohail et. al [19], produced zinc oxide (ZnO) NP employing neem leaf extract and found favourable enhancement in its properties. Manimaran [20] observed that using neem leaf extract to prepare cerium oxide (CeO) NP provided better yield. Its application in biofuel also enhanced the physico-chemical properties of the fuel. Kumaravel et. al [21], synthesized NP in biodiesel using neem leaf extract and dispersed in biodiesel blends. The testing of prepared biodiesel blends in diesel engines showed improved performance and emission characteristics. Sontakke [22] reviewed several studies concerning green synthesis of NP for biodiesel production and reported it to be an effective method for improving biodiesel performance. Due to the previous studies mentioned above, in this work, silver nanoparticles (Ag-NP) and copper(II) oxide nanoparticles (CuO-NP) were synthesized using neem leaf extract and employed as a stabilizing and reducing agent. Afterward, the Ag-NP and CuO-NP were used and evaluated as a catalyst for converting WVO into biodiesel.

Methodology

Materials

All of the reagents and standards used for this study were analytical grade. Neem leaves were sourced locally from the United Arab Emirates. Silver nitrate (AgNO₃), and Copper sulphate (CuSO₄) was procured from Loba Chemie. Methanol (CH₃OH 99%), Carbon tetrachloride (CCl₄), Wijs solution, potassium iodide (KI), Sodium thiosulphate (Na₂S₂O₃), Starch, isopropyl alcohol (C₃H₈O), Phenolphthalein, Potassium hydroxide (KOH), were purchased from Nice Chemicals. All the solutions were made using double distilled water.
Nanoparticle Synthesis

Neem leaves were collected, washed and air-dried for around a week. The dried leaves were further dehydrated in an oven for 2 hours. The dehydrated leaves were then crushed to form a fine powder, from which 5 grams was then mixed with 100 mL of distilled water to form a solution of neem leaf extract. This solution was then boiled and magnetically stirred at 100°C for 30 minutes, after which it was filtered into a conical flask using 2 sheets of tissue paper as the filter.

For preparing silver nanoparticles, 1 mM AgNO₃ solution was readied in a volumetric flask by dissolving around 0.017 g of AgNO₃ powder in 100 mL of distilled water. The flask was then wrapped with aluminium foil and kept in the dark to prevent the reaction of the silver with light. 10 mL of the prepared AgNO₃ solution was mixed with 10 mL of the neem leaf extract solution in a 1:1 ratio. The contents are magnetically stirred for around an hour after the flask is completely covered with aluminium foil. The flask is then incubated in a dark chamber for around 24 hours for nanoparticle formation, after which it is sonicated for 30 minutes. For preparing copper(II) oxide nanoparticles, 0.1596 g of copper sulphate salt was dissolved in 10 ml water, forming 0.1 M CuSO₄ solution. This CuSO₄ solution was then mixed with 30 ml of the prepared neem leaf extract, forming a mixture of 1:3 proportions. This solution was also magnetically stirred and kept for an hour. Figure 1 depicts the prepared silver and copper solutions. Preparation of the silver and copper nanoparticles was confirmed by using PG Instruments T80+, UV-VIS Spectrophotometer. The prepared silver and copper nanoparticles’ size was determined by the CILAS Nano DS Dual Scattering, Particle Size Analyzer.

Biofuel preparation

200 ml of waste vegetable oil (WVO) was taken for one batch of biodiesel. Two batches were prepared, one incorporated with Ag nanoparticles, and the other incorporated with CuO nanoparticles. Potassium methoxide is prepared by dissolving KOH in 80 ml of methanol (to be used for both batches). The acid value test was conducted to determine the amount of base required to neutralize the fatty acids in the oil. 1 ml of the oil was measured into a conical flask, to which 20 ml isopropyl alcohol was added, along with 2–3 drops of phenolphthalein. This was titrated against 0.1% KOH solution. Tests were run on both batches of nanoparticle-dispersed WVO as well as a blank for reference. WVO, potassium methoxide and the prepared nanoparticle solution are combined in a separator flask and shaken vigorously for around 5 minutes. The separator flask is then left undisturbed for ten days, after which the bottom layer containing glycerin is discarded, leaving behind the top layer containing biodiesel, which is then subjected to further analysis. The image of separator flasks containing the solutions of Ag-NP and CuO-NP biodiesel are presented in Fig. 2.
Characterization

The iodine value (IV) test serves to evaluate the degree of unsaturation in the biodiesel. For this, 0.5 g of oil and 10 mL of carbon tetrachloride (CCl₄) were added together in an iodine flask. 25 mL of Wijs solution was then added to the flask, after which the flask was energetically shaken and then kept in the dark for 30 minutes. Then, 10 mL of potassium iodide solution was mixed in. The contents of the flask were then titrated with sodium thiosulphate solution (0.1 N). When the sample turned light yellow, 2–3 drops of the starch indicator were added, upon which the solution’s color changed to blue. Titration was continued until the contents of the flask became colourless. The flasks used for conducting the iodine value test are shown in Fig. 3.

The hydroxide ions present in the biodiesel tend to form soap or metal salt through a process known as saponification. To determine the saponification value (SV) of the prepared biodiesel, 2 g
of the biodiesel was weighed into a conical flask to which 25 ml of 0.5 N potassium hydroxide was introduced. The contents of the flask are then heated for 10 minutes and then titrated with 0.5 N hydrochloric acid using phenolphthalein as the indicator. The endpoint is characterized by the sustained pink color of the flask’s contents. Tests were run on both batches of biodiesel as well as a blank for reference. The flasks used for conducting the saponification test are shown in Fig. 4.

![Flasks for saponification test](image)

**Fig. 4. Flasks for saponification test**

To determine the moisture content, the volume of biodiesel produced from each of the batches was recorded. Then, both batches were individually heated at 60°C for 10 minutes. The temperature was selected based on literature [23] to avoid boiling water but expedite the evaporation process. After allowing them to cool, the volumes of both batches were recorded.

The yield percentage was calculated using the following equation:

$$Yield = \frac{\text{Volume of biodiesel produced (ml)}}{\text{Volume of oil used (ml)}} \times 100 \quad (1)$$

To determine the completion of the transesterification reaction, a test known as the Methanol 27/3 test was conducted. The ratio used was 3 parts of Biodiesel dissolved in 27 parts of methanol was set aside for 24 hours, with tests being run on samples from both batches of biodiesel. A clear solution indicates that the transesterification reaction is complete and no residual glycerol remains. If any unreacted glycerol remains in the form of tri-, di-, or mono-glycerides, they would settle down as precipitate.

Flash and fire point tests were conducted using closed-cup Pensky-Martens apparatus from Controlab. The brass oil cup of the Pensky-Martens apparatus was filled with biodiesel to the mark and then placed inside the apparatus. It was then heated at a constant rate, with a test flame being introduced into it at regular intervals. The flash point was characterized by a flash when the test flame was introduced, while the fire point was characterized by sustained burning of the biodiesel, even after the test flame was removed.
Results and Discussion

The partial spectrums for the AgNP solution and the CuO solution obtained from the UV-VIS spectrophotometer are presented in Fig. 5. The Ag-NP solution displayed an absorption peak between 400 and 450 nm. While for CuO-NP solution, the absorption peak was observed between 200 and 250 nm. These values are consistent with those in the recent literature [24, 25].

![Fig. 5. UV-Vis spectra of AgNP & CuONP solution](image)

The results of the nanoparticle size analyser using the DLS instrument are presented in Fig. 6. It can be understood from Fig. 6 (a) that the mean diameter the synthesized Ag nanoparticles was found to be 67.5 nm. Fig. 6 (b) reveals that for synthesized CuO nanoparticles, the mean diameter was 209.9. These values are quite close to the ones seen in previous literature [26, 27]. It was observed that the prepared Ag particles were in the dimension range of 1–100 nm. However, the size of formed CuO particles was slightly larger.
The acid value of WVO biodiesel was determined to be 11.4 mg KOH/g. The acid values of Ag-NP biodiesel and CuO-NP biodiesel were both found as 10.5 mg KOH/g. This indicates that the presence of nanoparticles will in fact increase the rate of reaction by reducing the number of unsaturated fatty acids. The iodine value of Ag-NP biodiesel and CuO-NP biodiesel were found to be 35.81 and 38.1 respectively, which were found to be significantly low compared to the ones observed in previous literature [28]. The comparatively low iodine values indicate low levels of unsaturation as well as low concentrations of unsaturated carbon-carbon double bonds, which is advantageous with regard to its applications. The moisture content of simple biodiesel produced from WVO was found to be 1.02%. The moisture content of Ag-NP biodiesel was 1.14%, while for CuO-NP biodiesel, the moisture content was 3.23%. The saponification value for WVO biodiesel was 137.6, while for Ag-NP biodiesel and CuO-NP biodiesel, saponification values were 18.23 and 15.43 respectively. The findings of the Methanol 27/3 test revealed that, after leaving them undisturbed for 24 hours, the samples of all batches of biodiesel were clear with no residual glycerine. It indicated the completion of the transesterification reaction. The specific gravity of WVO biodiesel was measured to be 0.8519. The specific gravity of Ag-NP biodiesel was found to be 0.8927, while that of CuO-NP biodiesel was 0.8919. The similar values further indicate the type of nanoparticle utilized does not drastically impact biodiesel quality. The yield from the batch of Ag-NP biodiesel and CuO-NP biodiesel were 175 ml and 155 ml, respectively. This corresponds to a yield percentage of 72.9% and 64.6%, respectively. The yield of biodiesel from WVO was also in the similar range. For Ag biodiesel, the flash point was observed at 76°C, while the fire point was observed at 86°C. Similarly, for CuO-NP biodiesel, the flash point was observed at 81°C and the fire point at 92°C. This was in the range of results previously found in the literature [29].

Figure 7 depicts the FTIR peaks for Ag-NP biodiesel and CuO-NP biodiesel, respectively. The FTIR graphs of both the biodiesels are strikingly similar, with both exhibiting sharp peaks around 2800–2900 cm\(^{-1}\) and 1750 cm\(^{-1}\). The stretching vibrations of CH\(_2\) and CH\(_3\) can be observed at 2923 cm\(^{-1}\) and 2853 cm\(^{-1}\), while the stretching vibrations of C–O and C=O bonds of ester can be observed at 1742 cm\(^{-1}\). Both of these peaks show the presence of chain fatty acids [30]. They also share almost identical fingerprint regions. This is similar to previous literature, where strong peaks
are observed around 3000 cm\(^{-1}\) and 1750 cm\(^{-1}\)[31, 32]. Table 1 presents the comparison of parameters for the three sets of prepared biodiesel.

![FTIR spectra of Ag-NP and CuO-NP biodiesel](image)

**Fig. 7. FTIR spectra of Ag-NP and CuO-NP biodiesel**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>WVO biodiesel</th>
<th>Ag Biodiesel</th>
<th>CuO Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield (ml)</td>
<td>195</td>
<td>175</td>
<td>155</td>
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<tr>
<td>Yield (%)</td>
<td>81.25</td>
<td>72.92</td>
<td>64.58</td>
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<td>Moisture content (%)</td>
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<td>3.23</td>
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<tr>
<td>Acid value (mg)</td>
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<td>10.5</td>
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<tr>
<td>Iodine value (%)</td>
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<td>38.1</td>
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<tr>
<td>Saponification value</td>
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<td>18.23</td>
<td>15.43</td>
</tr>
<tr>
<td>Flash point (°C)</td>
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<tr>
<td>Fire point (°C)</td>
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<td>86</td>
<td>92</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.8519</td>
<td>0.8927</td>
<td>0.8919</td>
</tr>
</tbody>
</table>

**Table 1. Comparision of parameters of different batches of prepared biodiesel**

**Conclusion**

Waste vegetable oil (WVO) from the hospitality laboratory of the university was used to prepare the biofuel from methanol using a transesterification reaction. This biofuel was compared with two different samples of nanoparticle enhanced biofuels. The performance of Ag and CuO nanoparticles as catalysts in the field of biodiesel production was evaluated. These two nanoparticles were prepared using a green synthesis method employing neem leaf extract. The prepared nanoparticles were characterized using UV-VIS spectrographs and DLS. The dispersed Ag and CuO nanoparticles provided increased surface area for catalytic activity which was validated by remarkably reduced saponification values, better acid values and optimized yield percentage. Various characterization tests were conducted on the prepared samples of nanoparticle enhanced biofuels and the results of those tests were found to be in agreement with previous literature. A further study on different nanoparticles and amount of nanoparticles using neem leaf extract can be appraised to optimize the amount of catalyst used for the biofuel production.

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References


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