Biofuel Production from Waste Cooking Oils and its Physicochemical Properties in Comparison to Petrodiesel

Ganesh Lamichhane1,2*, Sujan Khadka*, Sanjib Adhikari*, Niranjan Koirala3*, Dhruba Prasad Poudyal1,4,5

1Department of Chemistry, Birendra Multiple Campus, Tribhuvan University, Bharatpur Chitwan, 44200, Nepal
2Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, 44613, Nepal
3Department of Microbiology, Birendra Multiple Campus, Tribhuvan University, Bharatpur Chitwan, 44200, Nepal
4Department of Environment and Energy Research, Dr. Koirala Research Institute for Biotechnology and Biodiversity, Kathmandu, 44613, Nepal.
5Department of Civil and Environmental Engineering, Faculty of Science and Technology, University of Macau, Macau SAR, 999078, China

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Abstract

Haphazard mining and consumption of fossil fuels have reduced petroleum reserves causing fossil fuel depletion and environmental degradation; thus, reflecting the need for the cheaper, renewable and eco-friendly alternative source of petroleum to meet the fuel demand. A million liters of edible oil used for cooking foods and date expired oils from oil manufacturers are discarded into sewage. This study primarily intends to study the feasibility of biodiesel production using such waste oils. In this work, biodiesel was prepared from waste cooking oils by a process called transesterification with NaOH as a catalyst. Our results showed that methyl ester (biodiesel) (92.67±0.90%), soap materials (1.33±0.224%), and glycerol (6±0.68%) were obtained after the transesterification of waste cooking oil. The physicochemical properties of biodiesel such as density, viscosity, volatility, surface tension, and flashpoint were analyzed, which were found to be 0.86±0.006 g/cm³, 2.23±0.021 cP, 0.327×10⁻⁴±4.5×10⁻⁶ g/s, 32.0±1.138 dyne/cm, 169.67±0.810°C, respectively. These properties were compared with that of commercial diesel as well as with the values specified by the American Society for Testing and Materials (ASTM) D6751. The density and the surface tension of the biodiesel were found similar to that of petrodiesel but its volatility was 3 times lower. Fourier-transform infrared spectroscopy (FTIR) spectra of the biodiesel showed methyl ester functional group at 1,243 cm⁻¹. Based on the cost of the materials used for production, the cost of biodiesel was estimated to be about 81 Nepalese rupees (0.67 USD) per liter. The properties of biodiesel also met the standard values of ASTM D6751. These findings indicate that waste oil is one of the feasible biodiesel sources and it can be used as a suitable alternative to petrodiesel.

Keywords: Waste cooking oils; Transesterification; FTIR spectra; Methyl ester; Biodiesel

Introduction

A sharp population increase and the lifestyle changes in the world today have gradually increased the enormous demand for fuel [1]. Alternative sources of petroleum fuel are a serious topic of discussion since petroleum fuel has an ever-increasing price, non-renewable nature, and exerts a negative effect on the global climate [2]. Several sources of alternative energy (solar, wind, hydropower, geothermal, biogas, biodiesels, etc.) have been identified and are being used. Among them, biodiesel is of special interest due to its ubiquitous demand, cheaper price, and eco-friendly properties [3]. Biodiesel, a sulfur-free, oxygenated, renewable, non-toxic, and eco-friendly biodegradable oil, is chemically alkyl esters of long-chain fatty acids derived from renewable sources, such as vegetable oil, animal fat, and is used or waste cooking oil [4, 5]. Attempts to obtain biodiesel from waste cooking oil have been done from antiquity [6], and even today, plethora of researches are going in the same direction for identifying and synthesizing biofuel of higher efficiency and feasibility [6, 7, 8, 9, 10]. In early 1853, scientists E. Duffy and J. Patrick conducted the first transesterification process to synthesize biofuel from waste cooking oils [11]. In 1900, Rudolf Diesel, an inventor of a diesel engine, demonstrated the engine powered by peanut oil as biofuel at the world fair in Paris, France [6]. These discoveries have motivated the scientific communities to accomplish the search for alternatives to drastically vanishing petroleum products. Inspired by this, waste oil has already been re-used by other industries such as animal feed and cosmetics [8], but the quantity is still being wasted [12] and the production sites are very small in number. Synthesizing biodiesel from waste cooking oil is the forthcoming means of preserving energy and meeting our requirements without depending on anyone [13].
Different processes such as micro-emulsion, thermal cracking, and transesterification have been applied to synthesize biodiesel. In particular, the most convenient way is the transesterification process, as it can reduce the viscosity of the vegetable oils (substrate), thereby making it closely similar to the petrodiesel (commercial diesel), and the process is relatively straightforward. In addition, fatty acid methyl or ethyl esters obtained by the transesterification process may be directly burned in unmodified diesel engines, with very low deposit formation [9, 14, 15]. In this process, triglyceride reacts with an alcohol in the presence of strong acid or strong base, producing a mixture of fatty acid alkyl esters and glycerol [14]. The triglycerides are fatty acid molecule which is further broken into methyl esters molecules and glycerin (Figure 1) [16]. Unlike petrodiesel, biodiesel is eco-friendly and has a much higher lubricating property; this means that it is essentially “slipperier” than normal diesel fuel with the added lubricity. Due to the lubricating properties, biodiesel reduces the wear of vital engine parts [17]. However, it also has some disadvantages. It has variations in quality due to its feedstock [18]. The fatty acid composition of the feedstock varies among and within species, and the main determinant of biodiesel quality also varies [19].

![Figure 1: Chemical reaction of synthesis of biodiesel from waste cooking oils (transesterification process) [16]](image)

In recent days, the search for the economic, feasible, and efficient raw materials for biodiesel production has extensively excelled. Cooking oil is found to be one of the best raw materials for biodiesel due to its portability, availability, renewability, lower sulfur content, lower aromatic content, and biodegradability. Furthermore, it is cheaper, gives more yield, and is a feasible option for the production of biodiesel [20]. Despite having plenty of research on biodiesel synthesis from waste cooking oil all over the world, very few of them have revealed the feasible biodiesel product for potential applications. In light of this background, this study aimed at producing biodiesel from waste cooking oils and studying its physicochemical properties in comparison to petrodiesel.

**Materials and Methods**

**Waste cooking oil collection and preparation**

Waste oil was collected from a restaurant located in Bharatpur, Chitwan, Nepal. As the oil sample was taken to the lab, it was filtered and heated up to 120 °C to remove unwanted moisture present in it.

**Processing method**

Biodiesel production process involved the collection of oil, heating, mixing with sodium hydroxide (NaOH), settling, separating, and washing for purification [21]. Several physicochemical parameters were tested with appropriate methods and instruments. The processing method is mentioned briefly in Figure 2 [22].

![Figure 2: Simplified flow chart of biodiesel production through transesterification [22]](image)

**Transesterification of waste cooking oil**

One liter of waste oil sample was taken in an Erlenmeyer flask and mixed with 3.5 g NaOH and 200 mL methanol mixture, i.e., 6:1 molar ratio of alcohol (methanol) to oil [8]. The catalyst used here was NaOH.

\[
\text{CH}_3\text{OH} + \text{NaOH} \rightarrow \text{CH}_3\text{ONa} + \text{H}_2\text{O}
\]

Methanol Sod. hydroxide Sod. methoxide Water

The temperature of the waste cooking oil was around 55-60 °C while mixing with the catalyst. The mixing solution was settled for 72 h. After this, three-layer varying colors (yellow, brown, white) were formed which was observed through our naked eyes. The layers were separated by a separating funnel. Among the layers, the yellow layer was biodiesel which was methyl fatty ester and was purified by washing with hot water to remove unreacted catalyst (\(\text{CH}_3\text{COONa}\)). Then, the volume of obtained biodiesel and glycerol were estimated with the help of a measuring cylinder [23, 24].

**Physicochemical properties analysis**

Several parameters such as density, viscosity, surface tension, volatility, flash point, etc. were analyzed by
specific methods to see whether the products fulfill the ASTM D6751 specifications [25]. Density was determined by using the following formula, and measured by weighing specific gravity bottle containing biodiesel with respect to water [26]:

\[
\text{Density of oil} = \frac{M_1}{V_1} / \frac{M_2}{V_2}
\]

where, \(M_1 = \text{mass of oil (oil + sp. gravity bottle – empty sp. gravity bottle)}\), \(V_1 = \text{volume of oil/biodiesel/commercial diesel (25 mL)}\), \(M_2 = \text{mass of water (water + sp. gravity bottle – empty sp. gravity bottle)}\), and \(V_2 = \text{volume of water (25 mL)}\).

Viscosity was analyzed by Ostwald’s viscometer by using the following formula [27, 28]:

\[
\frac{\eta_l}{\eta_w} = \frac{d_l}{d_w} \frac{t_l}{t_w}
\]

where, \(\eta_l = \text{coefficient of viscosity of liquids}\), \(\eta_w = \text{coefficient of viscosity of water}\), \(d_l = \text{density of liquids}\), \(t_l = \text{time required to flow of liquid}\), \(d_w = \text{density of water}\), and \(t_w = \text{time required to flow of water}\).

The surface tension of fuel was found out by drop number methods using Taube stalagmometer [27]:

\[
Y_l = \frac{n_l \times d_l}{n_w \times d_w} \frac{Y_w}{Y_l}
\]

where, \(Y_l = \text{surface tension of the liquid}\), \(Y_w = \text{surface tension of water}\), \(d_l = \text{density of the liquid}\), \(d_w = \text{density of water}\), \(n_l = \text{mean number of liquid drops}\), and \(n_w = \text{mean number of waterdrops}\).

Volatility was checked out by using the waste loss method as described by Võ and Morris [29] with some modifications. Three grams of each sample was weighed in a watch glass and placed at room temperature i.e. 29 °C. At each 5 mins. interval time, the sample was weighed, and the result was recorded. The flashpoint of these samples was analyzed by using flash point tester (GD-261 PMCC, Chongqing Gold Mechanical and Electrical Equipment Co. Ltd, China).

Fourier Transfer Infrared Spectroscopy (FTIR) spectra were recorded on an Infrared (IR) Tracer 100 Shimadzo, FTIR apparatus at Nepal Academy of Science and Technology (NAST). The method suggested by Ullah et al. [30] was used for sample preparation in IR with slight modifications. A drop of each sample (waste cooking oils disc of the instrument and spectra were recorded from 4000 to 500 cm\(^{-1}\) with a 4 cm\(^{-1}\) resolution.

**Cost analysis of Biodiesel**

The probable cost of final biodiesel product was estimated based on the laboratory cost including the cost of materials (such as CH\(_3\)OH, NaOH, waste cooking oils) used during the experiments.

**Data analysis**

Data analysis were performed by using International Business Machines (IBM) Statistical Package for the Social Sciences (SPSS) Statistics Version 21 [31]. All the experiments were performed in triplicates and their mean values and standard deviations were also determined which are mentioned in the results.

**Results**

**Yield analysis**

The products obtained after transesterification of waste cooking oil was methyl ester (biodiesel) (92.67±0.90%), soap materials (1.33±0.224%) and glycerol (6±0.68%) (Figure 3).

**Physicochemical properties analysis of biodiesel**

The density, viscosity, surface tension and flash point of biodiesel was found to be 0.862±0.006 g/cm\(^3\), 2.23±0.021 cP, 32.03±0.138 dynes/cm and 169.67±0.810 °C, respectively. Detailed information is presented in Table 1. Figure 4 showed that the rate of the volatility of

| Fuel types                        | Density (g/cm\(^3\)) | Surface tension (dyne/cm) | Viscosity (centipoise) | Flashpoint (°C) | Volatility (g/s) |
|-----------------------------------|-----------------------|---------------------------|------------------------|-----------------|------------------|
| Petro-diesel                      | 0.83±0.017            | 31.83±0.140               | 1.08±0.015             | 54.66±0.449     | 1.083×10\(^3\)±1.99×10\(^4\) |
| Waste cooking oil                 | 0.89±0.005            | 34.12±0.085               | 3.63±0.006             | 195.33±0.224    | -                |
| Biodiesel                         | 0.86±0.006            | 32.03±0.138               | 2.23±0.021             | 169.67±0.810    | 0.327×10\(^3\)±4.5×10\(^6\) |
| ASTM D6751 Standard               | 0.86-0.9              | -                         | 1.9-6                  | >130            | -                |
commercial diesel was higher than the biodiesel as the commercial diesel vaporizes and loses higher amount of mass (more volatile) than biodiesel when left for the same interval of time at room temperature.

Figure 4. Rate of the volatility of commercial diesel and Biodiesel (the X and Y error bars are also shown in the figure).

Figure 5. FTIR spectra of waste cooking oil

Figure 6. FTIR spectra of biodiesel from waste cooking oil

FTIR analysis
FTIR results of waste cooking oils and biodiesel are shown in Figure 5 and Figure 6. The functional group changes before and after the transesterification process as clearly shown in Figure 7 at 1435 cm⁻¹ of methyl ester (biodiesel) and 1377 cm⁻¹ is the glycerol group O-CH₂ of waste oil. In addition, spectra results are tabulated in Table 2 and Table 3.

Cost analysis per liter biodiesel
Based on the cost of laboratory materials used, the cost of biodiesel is estimated to be about 81 Nepalese rupees (0.67 USD) per liter [32] (Table 4).

Discussion
Biodiesel from waste cooking oils was produced and the results are consistent with the previous studies by Thirumarimurugan et al [33]. The study showed 80% biodiesel yield by using 1% base. Slightly higher, i.e., 87% biodiesel was obtained in a study conducted by Shrestha
and Ghimire using Jatropha oil as a raw material [34]. Likewise, some studies reported 85% [8] and 95% [35] biodiesel yields from waste oils using NaOH catalyst which resembles our findings. Using methanol and waste oil in the ratio of 6:1.8:1, with KOH catalyst, Kawentar and Budiman obtained 92.76% of biodiesel from waste oils at temperature 66.5 °C, which is closely similar to the findings of the present study [36].

The physicochemical properties are the main characteristics of biodiesel that determine its applicability. Here, the density of biodiesel was found to be 0.862±0.006 g/cm³ (Table 1), which is near to the standard value (0.86-0.9 g/cm³) [6, 37]. In addition, the density of the obtained biodiesel was found to be 0.862±0.006 g/cm³ which is slightly higher than the density of commercial diesel (0.83±0.017 g/cm³) (Table 1). The density of biodiesel was comparatively higher than commercial diesel which means that biodiesel has a high-energy potential to drive an engine. The findings of our study reiterate the study of Shrestha and Ghimire who demonstrated that the density of waste oil (0.9098 g/cm³) was higher than the petrodiesel (0.832 g/cm³) [34]. Similarly, Karunanithi found the densities of waste cooking oil, biodiesel, and commercial diesel to be 0.9240 g/cm³, 0.8966 g/cm³, and 0.84g/cm³, respectively [8]. Likewise, Phan and Phan found the values as 0.88 g/mL, 0.92 g/mL, 0.83 g/mL for biodiesel, waste cooking oil, and commercial diesel, respectively [38].

Viscosity, the measure of the ability of fluid to flow, affects the injector’s lubrication and fuel atomization [6]. The dynamic viscosity of biodiesel was 2.23±0.021 cP, which is slightly higher than that of commercial diesel (1.08±0.015 cP) but less than that of waste cooking oil (3.6±0.006 cP) (Table 1). Since the fuels with low viscosity may not provide sufficient lubrication resulting in leakage or increased wear in an engine, biodiesel can be preferred over petrodiesel [39]. These results are comparable to the standard ASTM D6751 specifications and other literatures as well [25]. Phan and Phan obtained the viscosity of five different waste oil samples in the range of 27-55 mm²/s. In their study, the viscosities for biodiesel and petrodiesel were found to be 4.89 mm²/s and 3.53 mm²/s, respectively [38]. Similarly, Hossain and Boyce [23] found the viscosities of pure sunflower cooking oil, waste cooking sunflower oil, and biodiesel to be 5.8 mm²/s, 9.5 mm²/s and 4.1-4.3 mm²/s, respectively. Comparing this study’s results with the study conducted by Phan and Phan, it can be concluded that the biodiesel produced can be used in diesel engines with a little bit of modification by blending technique [38]. The viscosity of biodiesel from waste cooking oil was found to be higher than that of petrodiesel. Since various properties of obtained biodiesel resemble the commercial petrodiesel, it could be used directly in existing engines with slight modifications like blending with petrodiesel [4, 38, 39].

Surface tension directly affects fuel atomization and causes the formation of small droplets on the engine combustion chamber [40]. Surface tension, though plays a greater role in atomization, lacks attention compared to other properties. In the present study, surface tensions of waste cooking oil, biodiesel and petrodiesel were studied and found to be 34.12±0.085 dyne/cm, 32.03±0.138 dynes/cm and 31.83±0.140 dyne/cm, respectively (Table 1). The result shows that the surface tension of biodiesel is slightly higher than petrodiesel which means biodiesel can be easily atomized and combusted. To compare the finding of this study, Watts and Chhetri found surface tension for Jatropha oil (30.1 mN/m), soapnut oil (29.5 mN/m) and biodiesel (28.50 mN/m), respectively [41]. Melo-Espinosa et al. study results revealed surface value tension of 33.83 mN/m for sunflower oil and 33.75 mN/m for Jatropha oil, which are consistent with our study [42]. The flashpoint of the biodiesel obtained was found to be 169.67±0.810 °C, which is quite high compared to petrodiesel (54.66±0.449 °C) and lower than waste cooking oil (195.33±0.224 °C) (Table 1). This indicates that biodiesel is safer to handle. This finding is supported by a number of previous studies. Kawentar and Budiman found the flashpoint of biodiesel obtained from waste cooking oil was 180.5 °C [36]; Karunanithi found it 196 °C [8]; Phan and Phan found it 120 °C [38]; Saddu et al. found it 164 °C [37] and Kumar and Pal found it 187 °C [4]. The finding of the present study is also in tune with the ASTM standard which recommends it to be ≥ 130 °C [15, 43].

Although the volatility is a feebly studied parameter, it is very important to fuel property referring to how easily a fuel vaporizes and how easily a car can be started, warmed up, and run well [44]. The volatility of the biodiesel sample was 0.327×10⁻³±4.5×10⁻⁶ g/s which is nearly one-third of petrodiesel (1.083×10⁻²±1.999×10⁻⁵ g/s) at room temperature (27 °C) (Figure 4) (Table 1). The volatility increases with the increase in temperature and

**Table 4: Estimated cost per liter of biodiesel**

| SN | Materials          | Amount | Cost  |
|----|--------------------|--------|-------|
| 1  | Methanol           | 200 mL | 64 rupees |
| 2  | Sodium hydroxide   | 3.5 g  | 2 rupees |
| 3  | Waste oil          | 1 lit  | 10 rupees |
| 4  | Processing cost    | -      | 5 rupees |
| Total |                   | -      | 81 rupees/L |

Source: Experimental estimation (2018)
these results are based on the presence of aromatic compounds in diesel fuel. Biodiesel contains methyl esters which lack the aromatic compounds and other volatile compounds. Thus, our study showed that petrodiesel has higher volatility than biodiesel, which is also supported by a study by Traviss et al. [45]. Transesterification is a major step in the production of biodiesel from waste oils in which a large molecule of triglycerialdehyde is converted into a certain fraction of glycerol molecule and fatty acid methyl ester molecule. Since glycerol—the existing byproduct of the transesterification process—can be used as a plasticizer in biopolymer-based films, it can be separated from biodiesel and used as a raw material in biopolymer industries [46]. To observe this structural entity, FTIR is a crucial technique. Often FTIR spectra of biodiesel fuel are measured for two proposes: the first is the qualitative determination of obtained characteristics bands, and the second is for the quantitative determination by monitoring the transesterification reaction [47, 48]. The difference was visible in the spectra of waste oils (Table 2, Figure 5) and biodiesel (Table 3, Figure 6), which is to say different spectra were found at 1436 cm$^{-1}$. The different spectra obtained from waste cooking oil and biodiesel are summarized and discussed below with reference to a few previous studies [30, 48]. The peak analysis of both spectra shows significant differences. The ester groups affect the differences. The change from ester groups to methyl ester has the strongest impact in the infrared spectrum. The ester group is commonly described as $R_1-C-(OR)=O$ in waste cooking oils and as $R_1-C(OCH_3)=O$ in biodiesel. $R_1$ represents long chains of hydrocarbons and the functional group (CH$_2$-O-) is reduced, and new signals are visible belonging to CH$_2$-O vibrations in biodiesel. The most influencing result from transesterification is in the new signal at 1435 cm$^{-1}$ (Table 3). The peak observed at 1377 cm$^{-1}$ is the glycerol group O-CH$_2$ (mono-, di- and triglycerides) which should be present in the refined oil spectrum and should be absent in the FAME (fatty acid methyl ester) spectrum (Table 2). The next visible transformation is in the ester control area approximately 1159 cm$^{-1}$. The strong, broad signals at 1169 cm$^{-1}$, 1170 cm$^{-1}$, and 1195 cm$^{-1}$ show that the ester group in waste oil has a lower wavenumber. The oil separates into two concrete signals at 1163 cm$^{-1}$ and 1195 cm$^{-1}$ called the ester group, which is present in both waste oil and biodiesel (Figure 5, Figure 6 and Figure 7). A signal at 966 cm$^{-1}$ is the CH$_2$ wagging frequency which is a deformation vibration of the RO-CO$-$ group. Some previous researches summarized the different spectra of waste cooking oils and biodiesel, and obtained similar results confirming that the obtained biodiesel effectively contained methyl ester groups and the transesterification process can be effectively done [30, 47, 48]. The cost of biodiesel is estimated to be about 81 Nepalese rupees (0.67 USD) per liter [32]. This price is based on lab-scale production. Industrial/large scale production will require a huge quantity of raw materials; it might in turn decrease the overall price of raw materials (when bought in large quantity) and increase the production of biodiesel. Hence, the resulting costs of final biodiesel products might decrease accordingly, which is lower compared to the current price of petrodiesel in the Nepalese market, that is, 89.73 rupees (0.75 USD) per liter [49].

**Conclusion**
The physicochemical properties of biodiesel from waste cooking oils obtained from the transesterification process in the lab were compared with commercial diesel. The density, surface tension, and viscosity of biodiesel from the waste oil were closer to that of the density of commercial diesel. Given this density, no engine modification is required. The flashpoint of biodiesel met the standard value. The volatility rate of commercial diesel was also higher than biodiesel, which indicates that biodiesel is safer than commercial diesel for handling or storage process. Further researches are mandatory to detect cetane number, calorific value, and particulate matter. The emission test should be performed and compared to the standard fuels for the analysis of fuel quality.

**Authors’ Contributions**
GL performed the experiment in the lab. GL and SK contributed equally to research, original draft preparation and during revision. SK and SA contributed significantly in editing, revising, and rendering the write-up. SA and NK further edited the manuscript, and DPP supervised this research. All authors have read and approved the final manuscript.

**Competing Interests**
All authors declare that they have no competing interests.

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Ethical Approval and Consent
Not required.

Data Availability
All data that are used to support the results of this research are included in the article.

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