Research article

Valorization of indigenous *Millettia ferruginea* seed oil for biodiesel production: parametric optimization, physicochemical characterization, engine performance and emission characteristics

Lekidelu Asrat Ayalew, Belachew Zegale Tizazu*

Department of Chemical Engineering, Addis Ababa Science and Technology University, Addis Ababa – 16417, Addis Ababa, Ethiopia

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**A B S T R A C T**

The current investigation aimed to synthesis the biodiesel from an indigenous *Millettia ferruginea* seed oil (MFO) using methanol with alkali catalyst (NaOH). The factors affecting the oil extraction viz., extraction time, kernel size, solvent: solid, extraction temperature) was optimized via the parametric study. Response surface methodology was utilized to improve the transesterification reaction. The optimum temperature, catalyst concentration, and methanol to oil molar ratio to achieve maximum biodiesel production of 98.1 wt.% were 52.3 °C, 1.3 wt.%, and 8:1, respectively. FTIR, NMR, and GC-MS analyses have been used for extracted oil and fatty acid methyl ester (FAME). From the $^1$H NMR analysis, the conversion of MFO to FAME was 97.5%. Moreover, engine performance and emission characteristics of biodiesel blends and diesel were investigated using a single-cylinder diesel test engine. The specific fuel consumption of biodiesel blends was higher than diesel fuel whereas the thermal efficiencies were found to be lower. The results showed that the blend B5 provided superior performance next to diesel fuel. Besides, the CO and HC emissions of B5 at 80% load condition were 7.28 and 8.56% lesser than diesel, respectively. However, in comparison to diesel, CO$_2$ and NO$_x$ emissions were higher for the biodiesel blends.

1. Introduction

The rapid increase in global energy demand, as well as the continuous rise in fuel consumption, CO$_2$ emissions, and the progressive exhaustion of fossil fuel has prompted an extensive search for sustainable sources of clean and renewable energy [1]. In regard to this, biodiesel is considered as a promising discretionary fuel due to its enhanced lubricity, superior flash point, improved biodegradability, low exhaust emissions, and toxicity in comparison to fossil fuels [2]. Though biodiesel renewability is an enormously encouraging fact, food prices and biodiversity issues should not be ignored. Not amazingly, concerns about the latter issues have sparked the innovation for biodiesel derived from non-edible sources due to their accessibility, eco-friendliness, low production cost, reduced food versus fuel debate, and lesser farming land requirements [3].

*Millettia ferruginea* is a beneficial endemic plant species in Ethiopia and it is widely distributed within the agro-climatic zones [4]. The powdered and crushed seeds are non-edible, commonly utilized as fish poisons and insecticides for scabies and chiggers owing to the presence of a mild toxic substance (Rotenone). Moreover, the seed possesses a high oil content (30–49%), with 80.7% unsaturated, and 19.3% saturated fatty acids that can further be used as a prospective substrate for biodiesel production [5]. Even though this seed can be available in large quantities in Ethiopia and its oil can be used as a possible feedstock for biodiesel production, from the author's point of view there are few reports on biodiesel production and no reports on engine performance and emission characteristics from *Millettia ferruginea*.

Among the various methods to reduce the viscosity of vegetable oils, transesterification reaction is the most widely used method in which the triglycerides react with an alcohol in the presence of a catalyst to produce biodiesel and by-product, glycerol [6]. In comparison to the heterogeneously catalyzed transesterification reaction, homogeneous reactions are relatively faster and require low catalyst loading [7]. Nowadays, owing to the low temperature and pressure requirements, high conversion rate and yield, no intermediate steps involved and low material processing costs, the majority of biodiesel is produced by using a base-catalyzed transesterification reaction [7].

Biodiesel and diesel being advantageous and disadvantageous in their respective terms, blending them would yield a fuel with an intermediate property which may improve the combustion and emission characteristics. Although fossil fuels have excellent engine performance such as
brake power output, air pollution is one of their prime snags [8]. Many researchers have explored that the burning of biodiesel generates a lower emission of carbon monoxide (CO), unburned hydrocarbons (UHC) and some increases in oxides of nitrogen (NOx) [9]. On contrary, the utilization of biodiesel leads to a reduction in engine brake power and thermal efficiency along with a rise in specific fuel consumption [10].

According to the Uyumaza et al. [11] experiment on a single-cylinder diesel engine fueled with poppy oil biodiesel blends, brake thermal efficiency, CO, and HC emissions were lower while NOx and specific fuel consumption was higher as compared to diesel fuel. Abed et al. [12] have also compared the performance and emissions of biodiesel blends of Jatropha, waste cooking oil, algae, and palm to diesel fuel. The experimental results revealed that CO, HC and CO2 emissions were significantly lower than diesel, but NOx emissions for all biodiesel blends were slightly higher. Nair et al. [1] evaluated performance and emissions characteristics using Neem biodiesel with different compositions at 10%, 20% and 30% ratio, extraction temperature, time, and particle size) on the yield of oil and NOx emissions were 23%, 8.5% and 22% lesser than that of diesel.

In this study, the effect of extraction parameters (viz. solvent to solid ratio, extraction temperature, time, and particle size) on the yield of oil from Milletia ferruginea seeds was investigated. RSM-CCD was used to optimize the transesterification reaction parameters (reaction temperature, catalyst concentration, and methanol to oil molar ratio). Moreover, physico-chemical properties of Milletia ferruginea seed oil and its methyl ester were investigated and compared with ASTM standards. 1H NMR, 13C NMR, GC-MS and FTIR analysis were performed for the confirmation of methyl ester formation from Milletia ferruginea seed oil. Further, engine performance parameters and emission characteristics of produced fatty acid methyl ester (FAME) blending with diesel fuel at various blending ratios were evaluated using a single-cylinder, four-stroke diesel test engine.

2. Materials and methods

2.1. Chemicals

n-Hexane (99%), NaOH (99.8), methanol (99.8), potassium hydroxide (85%), diethyl ether (99.7%), ethanol (99.5), hydrochloric acid (37%), and phenolphthalein were of analytical grade and procured from Sigma–Aldrich. All the chemicals were used without any modification.

2.2. Seed collection and preparation

Milletia ferruginea seeds utilized in the present study were collected from local market in Dejen, Ethiopia. Initially, the collected seeds were thoroughly washed with distilled water, followed by decortication manually to remove the outer shell of the seeds. Subsequently, the kernel was kept in a hot air oven at 105 °C for drying until the constant weight was achieved. Finally, using a mechanical grinder the dried kernels were crushed to enhance the interfacial area during extraction and then sieved using a set of sieves to get particle size within a specified range.

2.3. Milletia ferruginea seed oil (MFO) extraction

Extraction of the MFO was performed by following the AOAC standard method using the soxhlet apparatus [13]. 30 g of powdered Milletia ferruginea seed kernel was packed in a thimble and placed for the extraction, whereas n-hexane was charged into the round bottom flask. Further, the extraction process was performed by varying different extraction parameters. The parametric effects of four different extraction parameters namely (i) solvent to solid ratio (3.1–7.1 ml/g); (ii) extraction temperature (40–80 °C), (iii) time (2–6 h), and (iv) particle size (0.2–1.8 mm) on the yield of oil were studied. The levels of each extraction parameter were selected based on the preliminary experiment that was done at different values of extraction temperature, particle size and solvent to solid ratio. The extracted oil was separated from n-hexane using a rotary evaporator at 70 °C and the percentage yield of the oil was determined using Eq. (1).

\[
\text{Yield of oil} = \frac{\text{mass of crude oil extracted}}{\text{mass of total seed used}} \times 100\% \quad (1)
\]

2.4. CCD for parametric optimization of FAME production

The experiment was designed using RSM based on CCD to determine the interaction effects of independent variables on the yield of fatty acid methyl ester (FAME) production. During this study, the measured response was the yield of FAME. Three-levels along with the three-factors of CCD were employed in the experimental study \((2^3 + 2\times3 + 6)\), including 20 experimental runs (Table 1). In addition, to correlate the output variables, the experimental values were fitted using a polynomial quadratic equation. Further, the model predicting the yield of FAME at the particular given process variable combination (reaction temperature, catalyst concentration, and methanol to oil molar ratio) was developed using the general form of the polynomial quadratic equation.

2.5. Transesterification reaction

50 ml of oil was measured and transferred to a 500 ml three-necked round bottom flask on a stirring mantle equipped with a temperature controller and condenser. For the initial 30 min, the oil was pre-heated to 80 °C. Consequently, the mixture containing methanol and sodium hydroxide was poured into pre-heated oil followed by mechanical stirring to start the reaction. To obtain the optimum conditions for maximum FAME production, the reaction temperature that ranges from (45–65 °C), catalyst concentration (1–2 wt.%), MFO and methanol: oil molar ratio of (6:1–12:1) were investigated as reaction parameters. The levels of each reaction parameter were selected based on the preliminary experiment that was done at different values of each reaction parameter. Whereas the reaction time (2 h) and agitation speed (500 rpm) were both kept constant. Lastly, the reaction mixture was poured into a separating funnel and kept for 24 h until two distinguished layers were formed. The bottom layer (glycerol and other impurities) was removed and the top layer (obtained FAME) was purified even further to remove the impurities including unreacted alcohol and catalyst, and an excessive amount of soaps and glycerides. Further, it was washed with distilled water (50 °C). PH meter was utilized for ensuring the complete removal of the catalyst. Lastly, the produced FAME was dried for 30 min to evaporate any remaining moisture and the percentage yield of biodiesel was determined according to Eq. (2).

\[
\text{Yield of FAME (\%)} = \frac{\text{mass of FAME produced}}{\text{mass of oil used}} \times 100\% \quad (2)
\]

2.5.1. Model validation

The model validation was carried out in triplicates with the predicted optimum values as the experimental conditions and the average values obtained were reported.

2.6. MFO and FAME characterization

Various spectroscopic and physicochemical properties of extracted MFO and Milletia ferruginea seed oil methyl ester (FAME) were determined under
the optimal process conditions viz., density, kinematic viscosity, acid value, iodine value, saponification value, ash content, calorific value, cetane number and flash point were examined via the ASTM standard.

2.6.1. Fourier transform infrared spectroscopy (FTIR) analysis

Different functional groups associated with the raw material *Millettia ferruginea* seed, oil and its methyl ester were determined using FT-IR spectroscopy (Nicolet iS50 Spectrometer) equipped with potassium bromide (KBr) beam splitter. The infrared spectrum was recorded by passing a beam of infrared light through the sample. Each spectrum was taken within a few seconds at the resolution of 16 cm⁻¹, in the region of 4000–500 cm⁻¹ and not more than 0.5 ml per sample was taken.

2.6.2. Nuclear magnetic resonance (NMR) spectrometer analysis

To determine the conversion of *Millettia ferruginea* oil to fatty acid methyl ester both ¹H NMR and ¹³C NMR were performed using a 600 MHz ¹H NMR spectrometer (Bruker) and a 5 mm diameter ¹H NMR tube. Deuterated chloroform was used as the solvent with tetramethylsilane (TMS) as the internal standard. The samples (MFO and FAME) 10–15 mg to be analyzed were poured into NMR tube and then it was diluted with 500–600 μl denatured chloroform (CDCl₃). Main parameters such as a number of scan (NS), 6; spectra width, 8278.146 Hz; line broadening for exponential window function, 0.0Hz; relaxation delay, 5 s; temperature, 291.2 K were set for scanning. Further, the conversion of MFO to FAME was determined from ¹H NMR analysis using Eq. (3).

\[ C = 100 \times \frac{2A_{\text{Me}}}{3A_{\text{CH₂}}} \]  

where C = Conversion, \( A_{\text{Me}} \) = integration value of methoxy protons, \( A_{\text{CH₂}} \) = integration value of α-methylene protons.

2.6.3. Gas Chromatography–Mass spectroscopy (GC–MS) analysis of *Millettia ferruginea* oil

The FAME composition of the extracted *Millettia ferruginea* oil was determined using gas chromatography–mass spectroscopy (GC–MS) (Agilent 7890B/5977A). The oven’s initial temperature was 80 °C, which was raised gradually to 280 °C at a heating rate of 10 °C/min and held for 5 min. The injection temperature was 250 °C, with a 50:1 split ratio. Helium was utilized as the carrier gas with a column flow rate of 1 ml/min and an ion-source temperature of 230 °C.

2.6.4. Engine performance test and emission characteristics of FAME blends

To evaluate the engine performance and emission characteristics of FAME blends, experiments were carried out using a single-cylinder, 4-stroke, water-cooled, along with the maximum power output of a 7.5 kW diesel engine (Figure 1, Table 2). The experiment was carried out with variable engine loads (0, 20, 40, 60, and 80%) at a continuous engine speed and a compression ratio of 1500 rpm and 21:1, respectively. The load variation was carried out with the help of an eddy current dynamometer. In this study, the blends were represented as B₅, B₁₀, B₁₅, and B₂₀ which were produced by mixing 5%, 10%, 15%, and 20% of FAME (B₁₀₀) with pure diesel, respectively. Initially, the test engine was operated at 1500 rpm rated speed with diesel for 30 min without any load conditions till it reached the steady-state condition.

The concentration of gaseous emissions was measured using an exhaust gas emission analyzer (Kane AUTOplus 5-2 UK) for carbon dioxide CO₂ (%v), CO (%v), NOₓ (ppm), and unburned hydrocarbon UHC (ppm). Table 3 shows the detailed specifications of the exhaust gas analyzer.

2.6.4.1. Uncertainty analysis

The main purpose of the uncertainty analysis is to evaluate the errors that occur during the experiment. Choice and calibration of instruments, ambient factors and data collection methods can all contribute to uncertainties and errors. To avoid deviation...
and ensure the precision of experimental reading the ambiguity for the particular experiment has to be estimated. By employing the root mean square method, uncertainty was conducted. The uncertainty of different measured end calculated parameters is presented in Table 4.

Overall uncertainty = \( \sqrt{\text{uncertainty of time}^2 + \text{uncertainty of engine speed}^2 + \text{uncertainty of exhaust gas temperature}^2 + \text{uncertainty of air flow}^2 + \text{uncertainty of load}^2 + \text{uncertainty of fuel flow}^2 + \text{uncertainty of pressure sensor}^2 + \text{uncertainty of BF}^2 + \text{uncertainty of BT}^2 + \text{uncertainty of BSFC}^2} \)

\[
= \sqrt{(0.1)^2 + (0.3)^2 + (0.62)^2 + (0.31)^2 + (0.05)^2 + (0.08)^2 + (0.59)^2 + (0.92)^2 + (1.4)^2 + (0.5)^2}
= 1.99
Thus, from Eq. (4) the overall uncertainty of the experiment was found to be \( \pm 1.99 \).

3. Results and discussion

3.1. MFO yield

The oil extracted from Millettia ferruginea kernel (MFK) using \( n \)-hexane yielded 46.2 \( \pm 0.59 \)% of oil content, which is greater than the previous studies for rubber seed [14] and Morinda olfera seed [15]. However, Berhanu and Amare [5] reported 48.3 \( \pm 0.99 \)% oil yield from this seed kernel obtained from Addis Ababa region. It was slightly higher than the value obtained from this study. The variation in oil yield might be related to factors viz., geographical location, environmental and climatic factors, seed variety, and harvest period [16].

3.2. Effect of extraction parameters on MFO yield

The extraction parameters have a substantial influence on the percentage yield of MFO. Figure 2(a) shows the effect of extraction time on the oil yield of MFO at the fixed particle size (0.6), temperature (70 \(^\circ\)C), and solvent to solid ratio (6:1 ml/g). In this experiment, as the contact time increases, the oil yield increased up to 5 h followed by negligible change thereafter. Since the oil concentration in the solvent is lower at the initial stage of the extraction process, the oil disperses easily from the kernel powder to the solvent medium because of the mass transfer effect, further allowing the oil to be extracted rapidly. With the increase in time, the occurrence of high oil concentration in the solvent leads to a lower diffusional rate and constant oil yield.

The effect of various particle sizes (0.2 mm–1.8 mm) on MFO yield is illustrated in Figure 2(b). As can be observed in Figure 2(b), the yield of oil extracted using 0.6 mm particle size was 17% higher than the yield of 1.8 mm particle size, further attributing to a larger contact surface area leading to enhanced solvent diffusivity within the kernel powder. Larger particles, on contrary, have a smaller interfacial area and can resist solvent entry and oil diffusion towards the solvent, resulting in poor oil yield [16]. Extraction of Jatropha curcas seed [17] and Neem seed [18] oils was also consistent with the present study. Even though smaller particles are assumed to have higher contact surface area than that of larger particles, only 34% of the oil could be extracted from 0.2 mm particle size. This could be due to finer particle agglomeration, which decreases the surface area accessible for the flow of free solvent to solid [19].

In addition, the oil yield was also affected via the extraction temperature in the range of 40–80 \(^\circ\)C. With the increase in temperature, a higher yield of oil was obtained until the boiling point of \( n \)-hexane (\(~69 \, \text{\textdegree C})\) and then dropped further beyond it as shown in Figure 2(c). Apparently, at higher extraction temperatures, the oil solubility was improved and mass transfer was accelerated, resulting in a high oil extraction yield [17]. In general, by raising the temperature near the boiling point of \( n \)-hexane, both the diffusional rate and oil solubility were enhanced, resulting in an improved rate of extraction. This observation is analogous to the finding of Yusuff and Ewere [20]. Similarly, Sepidar et al. [19] also reported an increase in oil yield with the rise in temperature until the boiling point of hexane is reached.

Figure 2(d) indicates the yield of extracted MFO by hexane at five different solvent to solid ratios (ml/g). When the ratio was raised from 3:1 to 7:1, the total amount of oil extracted using \( n \)-hexane was increased from 27 to 44%. Increasing the solvent to solid ratio up to a defined value has increased the yield as the concentration gradient between solid-liquid phases is raised, promoting good mass transfer. According to the finding of this study, the solvent to solid ratio of 6:1 would be adequate to extract a high amount of oil. Further, an insignificant increase in the oil yield was observed by raising the ratio to 7:1.

3.3. Optimization fatty acid methyl ester transesterification process

The second-order polynomial equation in Eq. (5) described the model that linked the response to process variables (independent parameters) (Table 5). A positive indication with respect to the terms implies the rise in the FAME yield is positively affected by variables, and vice-versa [21]. Further, the quadratic model was selected as the finest fitted model possessing the highest order polynomial along with the significance of additional terms.

\[
Y = +96.56 - 5.59A - 5.41B + 0.2463C + 0.7312AB + 0.7562AC - 2.98BC - 10.22A^2 - 8.51B^2 - 5.24C^2
\]  
(5)
where \( Y \) represents the FAME yield (wt.%); \( A \) represents the reaction temperature (\(^\circ\)C); \( B \) represents catalyst concentration (wt.%); and \( C \) represents the methanol to oil molar ratio (mol/mol).

| Parameters                  | Accuracy | Percentage of uncertainties |
|-----------------------------|----------|----------------------------|
| Time                        | ± 1 s    | ± 0.1                      |
| Engine speed                | ± 5 rpm  | ± 0.3                      |
| Exhaust gas temperature     | ± 0.9 \(^\circ\)C | ± 0.62                     |
| Air flow                    | ± 1.2%   | ± 0.31                     |
| Load                        | ± 0.05%  | ± 0.05                     |
| Fuel flow                   | ± 0.5 l/h| ± 0.08                     |
| Pressure sensor             | ± 0.4 bar| ± 0.59                     |
| Brake power                 | ± 0.8%   | ± 0.92                     |
| Brake thermal efficiency    | ± 1.92%  | ± 1.4                      |
| Brake specific consumption  | ± 0.7%   | ± 0.5                      |

| Pollutant Range Percentage of uncertainties |
|----------------------------------------------|
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| Carbon dioxide (CO₂) CO₂: 0–16% ±0.5         |
| Carbon monoxide (CO) CO: 0–10% ±0.2          |
| Unburned hydrocarbon (UHC) UHC: 0–5000 ppm  ±3 |
| Oxides of nitrogen (NOₓ) NOₓ: 0–5000 ppm    ±2 |

Table 3. Exhaust gas analyzer range and percentage uncertainties.

Table 4. Uncertainty values of calculated and measured parameters.
To verify the experimental values with the suggested model, the model's adequacy, the determination coefficient ($R^2$), adjusted $R^2$ and predicted $R^2$ have been used. With the $R^2$ value of 0.9985, the predicted and experimental values were fairly close each other. This result shows that the studied variables describe 99.85% of the total variations and only about 0.15% of the variations are not explained. This is also supported by Figure 3. Moreover, the “Predicted $R^2$” of 0.9948 is reasonably consistent with the “Adjusted $R^2$” of 0.9972; that is, the difference is less than 0.2 [21]. Besides, “adequate precision” assesses the signal-to-noise ratio, with a ratio greater than 4 being preferred. The ratio of 76.1571 implies that the signal is also adequate.

The statistical significance of each model term, along with their interactions, was assessed using ANOVA which reflects the significant strength of each process variable. The statistical analysis of variance indicated that the model F-value of 749.56 and its associated p-value was less than 0.0001 which revealed the model was statistically significant (Table 6). On the other hand, the lack of fit having F-value of 0.5004 and its p-value of 0.5064 indicates that the models are well fitted to all experimental data. The ANOVA table also shows that the two independent linear variables (A and B) terms and all the three quadratic terms were significant to the model with P-values less than 0.05. The linear variable C (methanol to oil molar ratio) is insignificant in the ANOVA analysis which means the effect of the factor is very low when compared to the other two parameters. The reason for this might be explained as the effect of alcohol may vary with catalyst used, i.e. when we use alkali catalyst the reaction requires low ratio of alcohol to catalyze the transesterification of oils. Moreover, it might also relate with the viscosity and the polar component of oil, hence the viscosity of MFO was low compared with other non-edible oils like castor oil. Nevertheless, from the three interaction effects, only BC had a statistically significant (p < 0.05) effect on FAME yield.

Based on the generated data, the three-dimensional surface plots which are the graphical representation of the response as a function of reaction temperature, catalyst concentration, and methanol: oil molar

Table 5. The experimental design matrix and the response function value (coded and real values).

| Run | Temperature (ºC)(A) | Catalyst (Wt. %)(B) | Methanol: oil molar ratio (mol/mol)(C) | FAME yield % (w/w) | Experimental value | Predicted value |
|-----|---------------------|---------------------|---------------------------------------|---------------------|--------------------|-----------------|
| 1   | 45                  | 1                   | 12                                    | 86.70               | 86.79              |
| 2   | 55                  | 0.66                | 9                                     | 82.20               | 81.59              |
| 3   | 65                  | 2                   | 6                                     | 64.10               | 64.30              |
| 4   | 55                  | 1.5                 | 9                                     | 97.20               | 96.56              |
| 5   | 72                  | 1.5                 | 9                                     | 58.90               | 58.24              |
| 6   | 38                  | 1                   | 9                                     | 76.80               | 77.05              |
| 7   | 55                  | 1.5                 | 9                                     | 96.50               | 96.56              |
| 8   | 55                  | 1.5                 | 9                                     | 96.30               | 96.56              |
| 9   | 45                  | 2                   | 6                                     | 75.80               | 75.53              |
| 10  | 55                  | 1.5                 | 4                                     | 81.50               | 81.33              |
| 11  | 55                  | 1.5                 | 9                                     | 95.60               | 96.56              |
| 12  | 55                  | 2.3                 | 9                                     | 63.20               | 63.39              |
| 13  | 55                  | 1.5                 | 9                                     | 97.80               | 96.56              |
| 14  | 55                  | 1.5                 | 9                                     | 95.90               | 96.56              |
| 15  | 65                  | 2                   | 12                                    | 60.20               | 60.34              |
| 16  | 65                  | 1                   | 6                                     | 67.25               | 67.70              |
| 17  | 45                  | 1                   | 6                                     | 81.70               | 81.85              |
| 18  | 55                  | 1.5                 | 14                                    | 82.40               | 82.16              |
| 19  | 55                  | 2                   | 12                                    | 68.70               | 68.55              |
| 20  | 65                  | 1                   | 12                                    | 75.10               | 75.66              |

To verify the experimental values with the suggested model, the model's adequacy, the determination coefficient ($R^2$), adjusted $R^2$ and predicted $R^2$ have been used. With the $R^2$ value of 0.9985, the predicted
ratio and their interaction within the range of experimental values, are displayed in Figure 4(a)–(c). The effect of reaction temperature and catalyst concentration on the yield of FAME at fixed methanol to oil molar ratio is shown in Figure 4(a). As easily observed from the 3D surface plot, the effect of both process variables has a promising outcome on the FAME yield till the prime values. Further, the rise in reaction temperature or catalyst concentration did not enhance the FAME yield. The maximum conversion was obtained at 55 °C reaction temperature, a significant rise in the FAME yield up to an optimal point was attained, but variation in methanol to oil molar ratio has a low effect on FAME yield when compared to reaction temperature. The effect of methanol to oil molar ratio on the FAME yield was almost constant with a slight decrease beyond the molar ratio of 9:1. Excessive methanol may enhance the glycerol solubility, further complicating the separation of FAME and glycerol, and causing foam formation and a decrease in FAME yield [25]. This result is in concurred with the research reported by Musa [6] based on neat vegetable oils.

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Figure 4(c) depicts the response for the combined effect of catalyst concentration and methanol to oil molar ratio at constant reaction temperature (55 °C). It has been discovered that higher catalyst concentration and methanol to oil molar ratio cause the occurrence in a reduction of FAME yield due to soap formation, which tends to make difficulties during the separation. In conclusion, the reaction temperature and catalyst concentration have a substantial effect on the FAME production, whereas methanol to oil molar ratio has a minor impact.

Using the design-expert software (version 12), a numerical optimization method was applied to optimize the FAME production process. The optimized values for the FAME production were obtained at various reaction temperatures, catalyst concentrations, and methanol to oil molar ratio. The optimum conversion of 98.13% was predicted by the model with the desirability of 1.00 at 52.3 °C reaction temperature, 1.3%
The optimum results predicted by the model have been verified by conducting the triplicate experiments under the optimum conditions (52 °C, 1.3 wt.% catalyst concentration and 8.8:1 methanol to oil molar ratio). The deviation between experimental and model-predicted values was 0.08% of FAME yield (Table 7), justifying that the fitted model is consistent and significant for all the predicted responses.

### 3.4. Physico-chemical properties of MFO, FAME, and its blends

After transesterification, the density of refined *Milletia ferruginea* oil was reduced from 896 to 872 kg/m³, which is well within the range found in ASTM D 6751 (Table 8). Moreover, the density of the diesel fuel that was taken as a reference was found to be 837 kg/m³. According to the Evangelos [26] report, biodiesel fuels have a greater density than fossil fuels, which implies that volumetrically operating fuel pumps will inject a higher volume of biodiesel than conventional diesel fuel. The values obtained in this study are fairly consistent with the values obtained for *Jatropha curcas* methyl ester and palm oil methyl ester [11, 27].

The MFO with lower FFA content (0.56 wt. %) and acid value (1.12 mg KOH/g) in this study can be converted into FAME through a one-step transesterification reaction. These values are in line with the value reported for Kariya seed oil (1.941 mg KOH/g oil) [27] and it is lower than the value of rubber seed oil (13.02 mgKOH/g of oil) [28].

The saponification value obtained from this study was 166.9 and 151.7 mg KOH/g for MFO and FAME, respectively, which represent a relation of how much (weight) of alkali is needed to saponify a fixed mass of oil and measure the tendency of oil to form soap during transesterification reaction [29]. The Iodine value of oil and biodiesel, which is a measure of the degree of unsaturation that affects the oxidation stability of oil/biodiesel when exposed to air, was found to be 102.36 ± 0.11 and 96.4 ± 0.15 g I₂/100 g oil, respectively. This indicates the presence of a high amount of unsaturated fatty acids (C=–C) in the oil. The obtained value is in agreement with the Jatropha seed oil and *Terminalia catappa* L. oil [17, 30]. This value was within the range for semi-drying oils (100–150 g I₂/100 g oil). In compression ignition engines, low values of viscosity are preferable for allowing faster atomization of the fuel spray, which minimizes the ignition delay period [30].

### Table 7. Optimal conditions for maximum FAME yield by numerical optimization.

| Parameters | Temperature (°C) | Catalyst concentration (wt. %) | Methanol: oil molar ratio | FAME yield (%) |
|------------|-----------------|---------------------------------|--------------------------|----------------|
| Ultimate goal | In range | In range | In range | Maximize |
| Predicted | 52.3 | 1.3 | 8.8:1 | 98.13 |
| Actual | 52 | 1.3 | 8.8:1 | 98.05 |

Figure 4. 3D surface plot for percentage yield of FAME (wt.%) as a function of catalyst concentration and temperature (a), temperature and methanol: oil molar ratio (b), and catalyst concentration and methanol: oil molar ratio (c).
The value for FAME was found within the range (1.9–6.0 mm²/s) as endorsed by ASTM D 6751. Its value was significantly higher than diesel fuel at 3.1 mm²/s. Nevertheless, the obtained value further clarifies that the transesterification reaction has effectively declined the viscosity of oil from 41.29 mm²/s to 4.5 mm²/s, leading to an increase in its tendency to flow. It was also found that the calorific value of the FAME is 41.76 MJ/kg which is lower than that for diesel (43.15 MJ/kg). Owing to the presence of 10–12% per weight oxygen in methyl esters, the calorific values of methyl esters are lower than the diesel fuel. This depicts that for achieving similar engine power, the injected fuel quantity should be higher [26]. This result is comparable to Jatropha biodiesel (41.5 MJ/kg) [31]. The FAME has a flash point of 185.4 °C, which is slightly higher than the minimum values mentioned in both standards. Interestingly, the flash point of sunflower biodiesel obtained by Rizwana et al. [32] (183 °C) is comparable to the present study.

### 3.4.1. GC–MS analysis

GC–MS analysis was utilized to evaluate the fatty acid composition in the extracted Millettia ferruginea oil sample. The observed chromatogram is depicted in Figure 5 and the identified fatty acids, along with their profile are enlisted in Table 9. The extracted MFO showed the occurrence of 8 different triglycerides at various retention times having a molecular weight ranging between 172 and 417. Linoleic (41.99%), oleic (37.77%), palmitic (9.29%), and eicosenoic (3.60%) acids are predominant in MFO extracted using n-hexane. The obtained results revealed that the oil sample contained 85.96% unsaturated fatty acids. But the linoleic acid concentration was found to be lower when compared with the research carried out by Berhanu and Amare [33]. The variation in the oil’s fatty acid compositions could be because the seeds were from different geographical origins, growth conditions and retention times during GC–MS analysis.

### 3.4.2. FTIR analysis

Figure 6 shows the FTIR spectra of Millettia ferruginea seed (MFS), Millettia ferruginea oil (MFO), and Millettia ferruginea oil methyl ester (FAME) with several functional groups with their corresponding bending and stretching vibration. By detecting the transmission of IR, the response of the functional groups was evaluated and compared with known standards. The weak absorption band detected at 3284.13 cm⁻¹ in MFS sample corresponds to the presence of alcohol (–OH) while alkene groups (=C–H) by the peak at 3008.01 cm⁻¹ with stretching vibration are present in MFO.

![Figure 5. Chromatogram of Millettia ferruginea oil extracted with n-hexane.](image-url)

| Table 8. Physico-chemical properties of Millettia ferruginea oil, FAME and its blends. |
|----------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Physicochemical property          | MFO            | FAME (B100)    | B5             | B10            | B15            | B20            | Diesel        | ASTM D6751    |
| Density@25 °C (kg/m³)             | 896            | 872            | 843            | 849.7          | 856.8          | 862.4          | 837           | 870–900       |
| Kinematic Viscosity@40 °C (mm²/s) | 41.29          | 4.5            | 3.45           | 3.7            | 3.89           | 4.01           | 3.1           | 1.90–6        |
| Acid value (mg KOH/g of oil)      | 1.12 ± 0.02    | 0.39 ± 0.05    | –              | –              | –              | –              | –             | 0.8 max       |
| Free fatty acid (%)              | 0.56           | 0.19           |                |                |                |                |               |               |
| Iodine value (g I₂/100 g oil)    | 102.36 ± 0.11  | 96.4 ± 0.15    | 111.6          | 107.4          | 105            | 103.9          | 114           | <120          |
| Saponification value (mg KOH/g of oil) | 166.9 ± 0.09 | 151.7 ± 0.21   | 181.3          | 174            | 169.5          | 153.4          | 192.6         | 120           |
| Ash content (% w/w)              | 0.036          |                |                |                |                |                | 0.050         |               |
| Flash point (°C)                 | –              | 185.4          |                |                |                |                | 130 min       |               |
| Cetane number (%)                | –              | 61.5           | 51.29          | 53.5           | 54.8           | 58.52          | 49            | 47 min        |
| Calorific value MJ/kg            | 39.98          | 41.75          | 42.6           | 42.2           | 41.9           | 41.81          | 43.15         |               |

![Table 8. Physico-chemical properties of Millettia ferruginea oil, FAME and its blends.](image-url)

| Table 9. Fatty acid composition of Millettia ferruginea oil. |
|---------------------------------------------------------------|
| Fatty acid          | Chemical structure | Retention time (min) | Composition (%) |
| Palmitic acid       | C16:0             | 34.023               | 9.29            |
| Stearic acid        | C18:0             | 36.838               | 2.92            |
| Arachidic acid      | C20:0             | 39.837               | 1.17            |
| Capric acid         | C10:0             | 15.752               | 0.66            |
| Linoleic acid       | C18:2             | 36.461               | 41.99           |
| Oleic acid          | C18:1             | 36.53                | 37.77           |
| β-Sitosterol        |                   | 40.971               | 2.60            |
| Eicosenic acid      | C20:1             | 39.383               | 3.60            |
| Saturated fatty acid|                   |                      | 14.04           |
| Unsaturated fatty acid |               |                      | 85.96           |

![Table 9. Fatty acid composition of Millettia ferruginea oil.](image-url)
and FAME samples. In addition, the very sharp peak with stretching vibration in the range of 2928–2915 cm⁻¹ attributed to the presence of methyl (CH₃) and methylene (CH₂) groups. The prominent presence of carbonyl group (C=O) in the MFS, MFO, and FAME samples was confirmed by the peaks obtained at 1743.53, 1743.07, and 1741.33 cm⁻¹ with strong stretching vibration [15]. The main spectrum allowing for chemical structure differences between oil and FAME fell in the range of 1500–900 cm⁻¹. The occurrence of O–CH₃ group (monoglyceride, diglyceride, triglyceride) shows the peak at 1373 cm⁻¹ in MFO [34]. The formation of fatty acid methyl esters in the Millettia Ferruginea oil biodiesel can be identified by observing a shift of intensified peaks from 1743, 1460 and 11589 cm⁻¹ to 1741, 1438 and 1169 confirming the asymmetric stretching of –CH₃. The FT-IR spectra found in this study concurred with the research reported by Gupta et al. [35].

3.4.3. Multi-nuclear analysis of MFO and FAME

The ¹H NMR of MFO and its synthesized methyl ester are represented in Figure 7(a) and (b), respectively. The formation of FAME from MFO was confirmed from this analysis. The peak that exists at 3.6 ppm is a characteristic peak of methoxy protons, whereas the peak at 2.24 ppm indicates α-methylene protons. A terminal peak at 0.8 and 1.2 ppm due to (–CH₃) methyl protons was noticed. Aliphatic and β-methylene protons represented at the peak of around 2 and 1.6 ppm. The absence of glyceridic protons signals while the emergence of methoxy protons signal confirms the conversion of Millettia ferruginea oil into FAME. The

![Figure 6. FT-IR spectrum of MFS, MFO, and FAME.](image)

![Figure 7. ¹H NMR spectra of Millettia ferruginea oil (a) and Millettia ferruginea methyl ester (b).](image)
integration values of these two separate peaks were used to determine the conversion of MFO to corresponding methyl esters, which was found to be 97.5%. It is clear that FAME produced from MFO using NaOH as a catalyst gives a comparable conversion when compared to the other works reported in the literature.

$^{13}$C NMR spectra of MFO and its methyl ester are depicted in Figure 8(a) and (b), respectively. In $^{13}$C NMR spectrum of MFO, the characteristic peaks of the carbonyl methylene groups (HC–O–) and (CH$_2$–C–O–) are detected at 69 and 62 ppm. Further, the characteristic signal of each functional group such as carbon–carbon single and double bond due to saturated and unsaturated fatty acids of triglycerides was found between 20–35 ppm and 127–132 ppm, respectively. The terminal of –CH$_3$ for free fatty acid and triglycerides appeared at 14 ppm in $^{13}$C NMR. On the other hand, the glyceride proton signal of triglyceride is clearly missing in the FAME sample. The methoxy proton of methyl esters and the key peaks of ester carbonyl (–COO–) are illustrated at the signal of 51.45 and 174.5 ppm. The peaks at 128 and 131.5 ppm exhibit the unsaturated methyl esters, whereas the peaks at 76.74–78.1 ppm are related to chloroform carbon used as a solvent. Another peak at 14 ppm is allocated to methyl terminal and signals at 22.5–34.7 ppm is associated with methylene carbons of long carbon chain in FAME. These findings are comparable with results reported for Jatropha oil [36].

3.4.4. Performance evaluation

Figure 9(a) illustrates the comparison in brake power (BP) of biodiesel blends and diesel fuel as a function of different values of engine load and a compression ratio of 21:1. It is observed that less power is generated from biodiesel–diesel blends as compared to diesel fuel because of its lower heating value (41.75 MJ/kg) in comparison to diesel fuel (43.15 MJ/kg). With the rise in engine load, the brake power of all experimental fuels increased. The average engine brake power for B$_5$, B$_{10}$, B$_{15}$, and B$_{20}$ was reduced by 1.4%, 2.02%, 2.4%, and 3.27% when compared with diesel fuel. The values obtained herein concurred with the values reported for sheep skin biodiesel at the same blending ratio as in this study [37].

Figure 9(b) depicts the brake specific fuel consumption (BSFC) values of all test fuels against engine load at a constant engine speed of 1500 rpm. With increasing engine load, the BSFC of diesel, as well as biodiesel blends, decreases. This is because as the load increases, the air reaches the combustion chamber and the fuel–air mixture ratio also increases which causes in reduction of BSFC [37]. Moreover, BSFC is higher for all blended fuel than pure diesel under different loading conditions. This might be due to the high viscosity, density, and lower heating value of biodiesel blends. For the same energy output more mass of fuel is consumed. Since the BSFC was determined on a weight basis; higher
densities resulted in higher BSFC. Generally, at higher loads, all fuel exhibited minimal BSFC due to an increased in combustion efficiency and peak in-cylinder pressure. It is noticed that the mean BSFC values for blends such as B5, B10, B15, and B20 are 0.40, 0.43, 0.49, and 0.53 kg/kWh, respectively, whereas 0.38 kg/kWh for diesel.

Figure 9(c) displays the comparison of brake thermal efficiency for biodiesel blends and standard diesel fuel. Biodiesel blends have lower brake thermal efficiency than diesel due to the lower heating value and higher viscosity of the fuel blends. This condition leads to a decrease in atomization and fuel vaporization, poor combustion characteristics, and hence, reducing the BTE [38]. Thermal efficiencies for diesel and biodiesel blends of B5, B10, B15, and B20 are 32, 31.02, 30, 29.5, and 28.8%, respectively at 80% full condition load. The mean BTE for B5, B10, B15, and B20 was less than that of diesel fuel by about 3.31%, 7.2%, 11.12%, 10.67, and 17.06%, respectively. This result shows that B5 has a higher value of BTE which is relatively close to diesel (i.e. 3.31% lower than diesel) when compared to other tested biodiesel fuels. This result is similar to the research performed by Gad et al. [10] and Jayaprakash et al. [37] using a four-stroke single-cylinder diesel engine.

The change in exhaust gas temperatures (EGT) as a function of engine load is shown in Figure 9(d). When compared to all other blended fuels, diesel has the least EGT at all loads. The lower thermal efficiency of biodiesel blends compared to diesel fuel increased heat loss in exhaust gases. This could be due to a higher temperature inside the engine cylinder caused by more fuel being burned to satisfy the increased load demand [10]. In general, the exhaust gas temperature upturns with a rise in engine load for both diesel fuel and biodiesel blends. In comparison with diesel, B20 has the extreme EGT at a higher load. Compared with diesel fuel, the maximum deviation for B20 is 17.72% and for B5 is 4.1% at a higher engine load. These findings have concurred with Gad et al. [10] and Harish et al. [39].

3.4.5. Emission characteristics of biodiesel blends and diesel

The experimental test of engine exhaust gas emissions was performed for CO (%v), CO2 (%v), unburned HC (ppm), and NOx (ppm) for B5, B10, B15, B20, and standard diesel at 0, 20, 40, 60 and 80% loads. Figure 10(a) shows that carbon monoxide emissions for blended and diesel fuel alone due to incomplete combustion. It was observed that when biodiesel blends were used instead of diesel fuel, CO emissions were significantly reduced across the engine load range. This is because the presence of oxygen in the biodiesel blends, kinematic viscosity and density may have decreased, which could be another cause of the CO reduction. This might lead to improved fuel particle atomization throughout the burning phase, ensuring full combustion [12]. Moreover, for all tested fuels, CO emission declined with the rise in engine load up to 40% and then increased at a higher load. This is because the volume of the fuel consumed increases...
with higher load, resulting in a significant decrease in combustion efficiency and higher CO emissions. The least CO emissions have been obtained for the B20. CO emissions were reduced by 7.28%, 17.33%, 29.76%, and 35.4% when the engine was fuelled with B5, B10, B15, and B20 as compared with diesel fuel. The significant decrease in CO emissions has a positive influence on the environment. The results were fairly agreed with the results reported by Gad et al. [11] using IC engine-fueled palm oil methyl ester blended with diesel fuel. Moreover, dual biodiesel blends of Rapeseed and Mahua mixed with diesel fuel at different blending ratios and algal biodiesel blends also show a comparable result with this study [40].

Figure 10(b) illustrates the disparity in CO2 emissions of biodiesel blends and diesel fuel at different engine loads. Complete combustion inside the combustion chamber increases CO2 emissions. The figure clearly indicates that biodiesel blends emit more CO2 than diesel fuel. This is because biodiesel contains a significantly high amount of oxygen and has a lower C:H ratio in comparison to diesel [41]. On average 13.7%, 22.69%, 34.6%, and 38.3%, increase in CO2 emissions were achieved for B5, B10, B15, and B20 as compared to diesel fuel [37]. Besides, the values obtained in this study were also significantly lower than poppy oil biodiesel–diesel blends [11].

The change in NOx emissions at different engine loads for various blends of biodiesel and pure diesel is shown in Figure 10(c). Oxides of nitrogen mainly compose nitric oxide (NO), nitrogen dioxide (NO2) and nitrous oxide (N2O) in which NO is generated in major concentration. It is also termed as thermal NOx since it is produced during the in-cylinder combustion process by oxidation of molecular nitrogen [42]. In the present experiment, NOx emissions were found to increase with engine load for both diesel fuel and biodiesel blend combustion. Diesel fuel and B20 produced the lowest and highest NOx emissions, respectively. This increasing trend may be caused by the presence of oxygen in biodiesel, which improves the combustion process and promotes the formation of nitrogen oxides. Another cause of such emission behavior could be the engine's cylinder temperature. The NOx emissions for all blends at 80% engine load are noticed as 484 ppm, 492 ppm, 506, and 517 ppm for B5, B10, B15, and B20, respectively, and 452 ppm for diesel fuel. The NOx emission variation for B20 means value is 21.07% when compared to diesel [12]. Instead, this value was lower than the research performed on Tung oil biodiesel–diesel blends by Harish et al. [39].

Figure 10(d) depicts the variation in unburned hydrocarbon emissions of all the tested fuels along with the different engine load conditions. One of the primary causes of HC emission is the accumulation of fuel particles near the crevice volume inside the combustion chamber. It also shows the percentage of unburnt fuel coming out through the exhaust. Compared to diesel fuel, with the increase in biodiesel blending percentage, there is a reduction in the UHC emissions under all load conditions. This decrease could be explained by a lower heating value of biodiesel that leads to the injection of more fuel for the same load condition. A high amount of biodiesel leads to more oxygen availability which improves the quality of combustion and the oxidation of CO to CO2 [43]. At 80% engine load, HC
emissions for B5, B10, B15, and B20 were recorded as 40.5 ppm, 36.2 ppm, 31 ppm, and 25.3 ppm, while 43 ppm was recorded for diesel fuel. In accordance with the recorded mean values, the emission for the B20 blend was 40.55% lower than diesel. The efficient combustion process within the cylinder is responsible for the reduction in HC emission for the B20 blend. The results agreed with this reference [38].

4. Conclusions

The results of the study showed that Millettia ferruginea oil (MFO) is a sustainable feedstock for the FAME production with oil yield ranged from 29.8% to 46.2% by weight. Physico-chemical properties of extracted oil and produced FAME were comparable with ASTM standards. The Fourier transform infrared spectroscopy (FTIR) analysis showed that several functional groups were present in MFS, MFO and FAME. 1H NMR and GC-MS analysis showed that the conversion of MFO to FAME was acceptable and the fatty acids composed in MFO include Linoleic, Oleic, Palmitic and Eicosenoic acids predominantly. The results of emission analysis revealed that the use of B5 biodiesel test blend as a diesel fuel substitute gave an acceptable result in decreasing CO and HC emissions up to 35.4% and 40.55%. Nevertheless, the emission of NOx was 21.07% higher than diesel. With respect to specific fuel consumption, diesel fuels had lower specific fuel consumption among all tested biodiesel blends. The methyl ester of Millettia ferruginea oil can be utilized as a substitute fuel with an aim of reducing the exhaust gas emissions of diesel engines and can provide a comparable engine performance.

Declarations

Author contribution statement

Lekidelu Asrat Ayalew, MSc: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
Belachew Zegale Tizazu, PhD: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

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