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High Vacuum Fractional Distillation (HVFD) Approach for Quality and Performance Improvement of *Azadirachta indica* Biodiesel

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Abstract: Biodiesel offers an advantage only if it can be used as a direct replacement for ordinary diesel. There are many reasons to promote biodiesel. However, biodiesel cannot get wide acceptance until its drawbacks have been overcome including poor low temperature flow properties, variation in the quality of biodiesel produced from different feedstocks and fuel filter blocking. In the present study, a much cheaper and simpler method called high vacuum fractional distillation (HVFD) has been used as an alternative to produce high-quality refined biodiesel and to improve on the abovementioned drawbacks of biodiesel. The results of the present study showed that none of biodiesel sample produced from crude *Azadirachta indica* (neem) oil met standard biodiesel cetane number requirements. The high vacuum fractional distillation (HVFD) process improved the cetane number of produced biodiesels which ranged from 44–87.3. Similarly, biodiesel produced from fractionated *Azadirachta indica* oil has shown lower iodine values (91.2) and much better cloud (−2.6 °C) and pour point (−4.9 °C) than pure *Azadirachta indica* oil. In conclusion, the crude oil needs to be vacuum fractioned for superior biodiesel production for direct utilization in engine and consistent quality production.

Keywords: biodiesel; vacuum fractionation; transesterification; fuel; fatty acids composition

1. Introduction

Biodiesel is getting the attention of policy makers to overcome serious concerns about climate change and maintain the security of the energy supply. Biodiesel has several advantages, such as being non-toxic, sustainable, non-explosive, environmentally friendly and biodegradable, which lessens toxic emissions and productions when used in a diesel engine [1–8]. Many observers consider biodiesel to be the one of the feasible options for the substitution of fossil diesel in the transport sector [9–19].

Increasing biodiesel supplies helps to reduce fuel imports and to cut down the emission of greenhouse gases (GHG). There is a downside of biodiesel as well. The fuel performance in in the engine depends upon the derived cetane number, total acid number, viscosity, and oxidative stability, etc. Biodiesels usually have higher viscosity than petroleum diesel. The engine will not operate well when the viscosity of the fuel is too high. The derived cetane number (CN) is "the measure of the ignition delay from the time the fuel injected and the start of combustion". The higher the CN, the shorter the ignition delay and, therefore, the better the quality of the fuel [5,8,20–22].

Most importantly, food crop production for biodiesel often requires massive acreage and may lead to land-use conflicts in food production. Despite these using non-edible oil seed crops such as *Pongamia glabra, Jatropha curcas* and *Azadirachta indica* prove best suitable for the biodiesel synthesis. Several other disadvantages include higher cost, poor low temperature, flow properties, variation in ignition quality of biodiesel produced from different feedstocks and clogging in engine etc. Biodiesel is unusable in cold areas. This is one of the major drawbacks of biodiesel use. If it gets below −1 °C, it will be solidifying in the engine and fuel tank. Usually, the temperature of congelation is relatively high for biodiesel. However, biodiesel can still be used in winter, if it is mixed with some sort of winterized diesel to remain a liquid. Biodiesel cold-flow properties are characterized by three temperature measures: cloud point (CP), "the temperature at which the fuel shows a haze from the formation of crystals"; cold filter plugging point (CFPP), "the temperature at which the crystals formed will cause the plugging of the filters"; and pour point (PP), "the lowest temperature at which the liquid will flow" [23].

The crude oils usually contains moisture, gums (lecithins), solids (insoluble), waxes, free fatty acids (FFA), and compounds of Na, K, Mg, Ca and other metals, which must be removed to make high-quality biodiesel more efficient and stable against rancidity upon storage. A series of steps are used to remove these impurities, including degumming (to remove gums), neutralizing (to remove FFA), bleaching (to remove color), deodorizing (to remove odor and taste), and dewaxing or winterization (to remove waxes). The alternative methodology to improve quality of biodiesel adopted in this study was fractionation of *Azadirachta indica* seed oil followed by its transesterification for production of biodiesel. The high demand for biodiesel in replacing fossil fuels has driven many researchers to come out with new ideas and inventions. Neem (*Azadirachta indica*) belongs to the Maliaceae family. *Azadirachta indica* seed oil is a non-edible feedstock to produce biodiesel. *Azadirachta indica* seed contains up to 40% lipid contents [24]. The main purpose of the present study was to remove the components from the source oil that deteriorate the quality of the produced biodiesel. Biodiesel quality can be directly related to type and percentage amount of various fatty acids present in the source oil. The presence of fatty acids with short chains or overlong chains could have negative effects on biodiesel fuel standard parameters. Hence, it is possible to control and improve the quality of the produced biodiesel by controlling and maintaining the fatty acid composition of the source oil. In the present study, *Azadirachta indica* seed oil is separated into several fractions using high vacuum fractional distillation (HVFD) to produce biodiesel with superior flow and burning proprieties. The present study is based on the hypotheses that biodiesel produced from a specific oil fraction show more consistent fatty acid composition, low cloud point and low pour point.

2. Materials and Methods

2.1. Sample Collection and Oil Extraction

The *Azadirachta indica* seeds (10 kg) were collected from the University of Agriculture Faisalabad, Pakistan. A sample cleanup using deionized distilled water (DDW) was carried out to eliminate impurities and dirt. The cleaned samples were dried at 40 °C in an electric oven until a constant weight was attained. The *Azadirachta indica* seed oil extracted using a cold press.

2.2. Vacuum Fractional Distillation of Azadirachta Indica Oil

Vacuum fractionation distillation of *Azadirachta indica* oil was carried out to separate out different isolates based on boiling points. Vacuum fractional distillation apparatus consisted of an electric heater (operation range: room temperature to 375 °C), boiling flask (500 dm^3), condenser with vacuum adapter, one-stage vacuum pump (10 Pa, power = $\frac{1}{4}$, oil capacity = 250 dm^3, Model TW-1A), short-path distillation receiver, cow shaped (with four 50 dm^3 flasks). In a single run, 300 dm^3 of *Azadirachta indica* oil was separated into fractions under a constant vacuum of −760 mmHg at varied temperatures. A digital thermometer was used to record temperature of vapors of boiling fractions (Figure 1). Table 1 present fractions obtained after the distillation of 650 g of *Azadirachta indica* oil. The oil left after fractionation consist of impurities that severely affect biodiesel properties. This oil can be further processed to produce lubricating liquid, *Azadirachta indica*-based antiseptic soap or in monoacylglycerol production as done previously in the literature [25]. The *Azadirachta indica* oil was distilled using vacuum fractions to isolate fraction F1 (120–150 °C), fraction F2 (180–190 °C), fraction F3 (202–230 °C) and fraction F4 (235–240 °C).

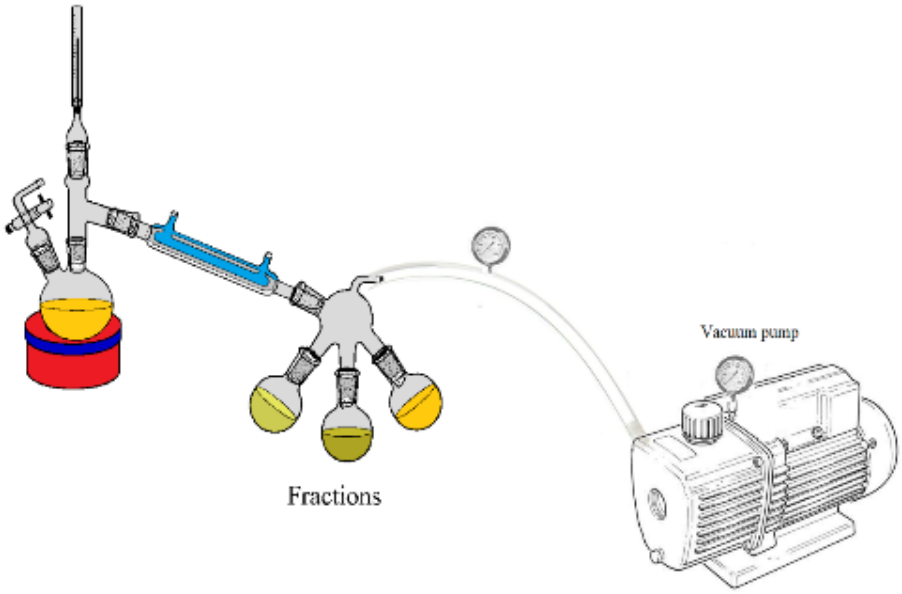

Figure 1. High vacuum fractionation distillation (HVFD) setup of *Azadirachta indica* oil.

Table 1. *Azadirachta indica* seed oil fractions separated using vacuum fractionation at −760 mmHg.

Fraction	Temperature Range (°C)	Wt. (g)	% of Total *Azadirachta indica* Oil
F1	120–150	156.48	24.06 ± 0.87
F2	180–190	69.54	10.68 ± 0.67
F3	202–230	111.35	17.12 ± 0.54
F4	235–240	144.61	22.24 ± 0.97

2.3. Transesterification

Transesterification is a cheaper way of converting the branched, large molecules of oil to smaller molecules [26]. The extracted *Azadirachta indica* oil and its fractions were converted into biodiesel and glycerol (byproduct) using methanol through the catalytic transesterification process. The transesterification process was carried out by base (potassium hydroxide), enzyme (lipase Novozymes) and acid (hydrochloric acid) catalysts. Each catalyst was used at five different concentration levels for the optimization of the catalyst dose required for the transesterification process. The concentration of catalyst was measured in percentage (weight of catalyst/weight of oil). The base catalyst (KOH) was used at five different concentrations levels (0.2%, 0.4 %, 0.6%, 0.8% and 1% of the

Azadirachta indica oil weight). The mixture of KOH (of respective concentration), *Azadirachta indica* oil or its fractions (10 g) and methanol (3 g) was stirred at 60 °C for 150 min. For the acid-catalyzed transesterification, HCl concentrations were 20%, 40%, 60%, 80% and 100% of oil weight. The used concentration of methanol was 5%. A mixture of oil, methanol and acid was stirred at 75 °C for 270 min. Five concentrations (1%, 2%, 3%, 4% and 5%) of lipase were added to the mixture of oil (10 g) and methanol (50 g) under constant stirring at 100 rpm for 24 h. The water insoluble biodiesel layer and glycerol (water soluble) layer were separated using a 250 dm^3 separatory funnel. The biodiesel layer was washed with an excess quantity of warm deionized distilled water (DDW) to remove soap and other water-soluble contaminants. Biodiesel was dried over anhydrous sodium sulfate before further use.

2.4. Biodiesel Quality Testing

The chemical composition of *Azadirachta indica* oil and its fractions was analyzed by gas chromatographic and mass spectrometric (GC-MS) analysis. A Perkin Elmer Clarus 600 GC System was used for the GC-MS analyses fitted with a capillary column (30.0 m–0.25 mm) at the 350-°C optimum temperature. As carrier gas, ultra-high (99.99%) pure helium was used with 0.2 dm^3/min constant flow. The transfer line, ion source and injection temperatures were 200, 200 and 220 °C, respectively. There was 70 eV ionization energy in the system for the breakdown of fragments. The data collection was done by mass spectra ranging from 10 to 600 m/z. Then, 0.1 dm^3 of the injected sample was used with 50:1 split ratio. The identification of obtained compounds was done by comparison with mass spectrum libraries (Wiley, 9th edition) and retention times.

The physico-chemical properties such as densities (kg/lit), saponification values (mg KOH/g), iodine values, cetane number, cloud and pour points were tested by following standard procedures [2,27]. The cold filter plugging point (CFPP) was determined in accordance with the EN 116 standard procedure for CFPP testing, as specified in the EN 590 standard [28]. Biodiesel pH was measured using a Hanna pH meter (model, HI 8010), and a densitometer (Wilnos LCD 51) was used for density (gram per dm^3) determination. The oxidation stability was measured by the Induction Period (IP) according to EN14112 [29].

For iodine value (I.V) determination, 0.05 g of *Azadirachta indica* biodiesel was taken in an iodine flask with a capacity of 250 dm^3. Then, 12.5 dm^3 of Wijs solution and 10 dm^3 of carbon tetrachloride were dissolved in biodiesel. Subsequently, contents of mixture were shaken vigorously and kept in a dark place for almost 30 min followed by the addition of 10 dm^3 of potassium iodide solution (15%) and 50 dm^3 of DDW. The obtained mixture was titrated against $Na_2S_2O_3.5H_2O$ (0.1 N) until the disappearance of the color of the iodine using starch as an indicator. For the blank sample, a similar procedure was adopted. The following formula (Equation (1)) was used for the determination of the iodine value of biodiesel samples [2]:

$$\text{Iodine value} = \frac{(\text{Blank titration} - \text{Sample titration}) \times \text{Normality of } Na_2S_2O_3.5H_2O \times 12}{\text{Sample weight (g)} \times 100} \quad (1)$$

To determine the saponification value, 10 dm^3 KOH (alcoholic) solution and 0.25 g *Azadirachta indica* oil were taken in a round bottom flask of 250 dm^3 capacity. A condenser was attached with this flask and heated smoothly till transparent solution was obtained. The appearance of a transparent solution indicates the completion of the saponification reaction. After cooling the reaction mixture to room temperature, a phenolphthalein indicator (2–3 drops) was added to it and the whole mixture was titrated against HCl (0.5 N) until the disappearance of the pink color. An appropriate reagent blank sample was also prepared, and a reading was determined for it. Using the following formula (Equation (2)), the saponification value in mg KOH/g of oil sample was calculated [2,30]:

$$\text{Saponification value (SV)} = \frac{(B - S) \times N \times 56.1}{w} \quad (2)$$

where S is the volume used of titrant for biodiesel sample, B is the volume used of titrant for the blank sample, 56.1 is MW of KOH in mg per mmol, N is the normality of HCl in mmol per dm^3 and w shows sample mass (gm).

For the determination of acid value, 1g of *Azadirachta indica* oil, 20 dm^3 of ethanol and 2–3 drops of phenolphthalein were added to a 250-dm^3 titration flask. This solution was titrated against NaOH (0.1 N) solution until there was a pink appearance. Using the following equation (Equation (3)), free fatty acid contents (oleic acid) were determined [2]:

$$\text{Free fatty acid (FFA), \%} = \frac{(\text{V} \times \text{N} \times 282)100}{\text{w}} \quad (3)$$

where V stands for volume of titrant sodium hydroxide (dm^3), N for Normality of sodium hydroxide (mol/1000 dm^3), 282 is the molecular weight of oleic acid in gram per mole. The obtained value was converted into acid value using the following equation (Equation (4)):

$$\text{Acid value (AV)} = 1.989 \times \text{\% FFA} \quad (4)$$

The following formula (Equation (5)) was used to determine the Cetane number (CN) of all biodiesel samples:

$$\text{Cetane number (CN)} = 46.3 + \frac{5458}{\text{SV}} - 0.225 \times \text{IV} \quad (5)$$

3. Results and Discussion

3.1. Effect of Various Catalysts on the Biodiesel Yield Percentage (%)

The effect of different catalysts (acid, base and enzyme) on the percentage yield of biodiesel is shown in Figure 2a–c. Transesterification using base catalysts is found to be cost effective because of its reusability, wide availability, easy separation from product and longer lifetime [31,32]. In base-catalyzed transesterification of *Azadirachta indica* oil and its fractions, the maximum biodiesel yield of 99.9% was shown by fraction F4. In another study, the biodiesel yield obtained by whole date seed oil using base catalysts was approximately 80% [2]. The optimized catalyst level for pure oil, F1 and F4, was 1% KOH (wt. of catalyst/wt. of oil) and for F2 and F3 was 0.2% KOH (wt. of catalyst/wt. of oil). Thus, the result obtained clearly indicated that, for better biodiesel yields, higher alkaline catalyst doses are required in the case of *Azadirachta indica* oil, F1 and F2. However, fractions F2 and F3 produced the highest quantity of biodiesel at the lowest KOH dose of 0.2% KOH (wt. of catalyst/wt. of oil). This indicates that after fractionation biodiesel could be produced at much lower levels of base catalyst using some specific fractions. This will be helpful in cutting costs on base catalysts and will also be helpful in reducing environmental pollution caused by base catalysts. The maximum biodiesel yields of acid catalyzed transesterification reactions were 99%, 85%, 97.25%, 76.25% and 94.25%, respectively, for *Azadirachta indica* oil, fraction F1, fraction F2, fraction F3 and fraction F4. The most suitable level of HCl for obtaining maximum biodiesel from *Azadirachta indica* oil, F3 and F4 was 80% (wt. of HCl/wt. of oil). However, F1 and F2 have shown maximum biodiesel yields at 100% and 60%, respectively. The acid catalysis reaction rate was much slower than base catalysis. The acid-catalyzed transesterification reaction was completed in 4.5 h as compared to the 1.5 h taken by the base-catalyzed reaction. Transesterification is the replacement of original ester groups into desired esters. The best way for transesterification is base-catalyzed as it is a very facile reaction. The enzyme is inhibited in the presence of methanol. Acidic catalysts have low acid site concentration, low micro porosity, and high cost compared with basic types. Acids catalyzes both esterification and transesterification simultaneously and is insensitive to FFA and water. In a previous study, biodiesel productivities of used vegetable oils by acidic catalysis at 25 and 100 °C, respectively, were as follows: Safflower (84.7% and 94.3%), Soybean (85.9% and 94.2%), Sunflower (83.4% and 95.2%), Canola (80.8%

and 93.7%), Corn (83.2% and 83.3%), Olive (84.3% and 85.3%), Hazelnut (82.5% and 83.4%) and Waste sunflower (84.3% and 90.4%) [33].

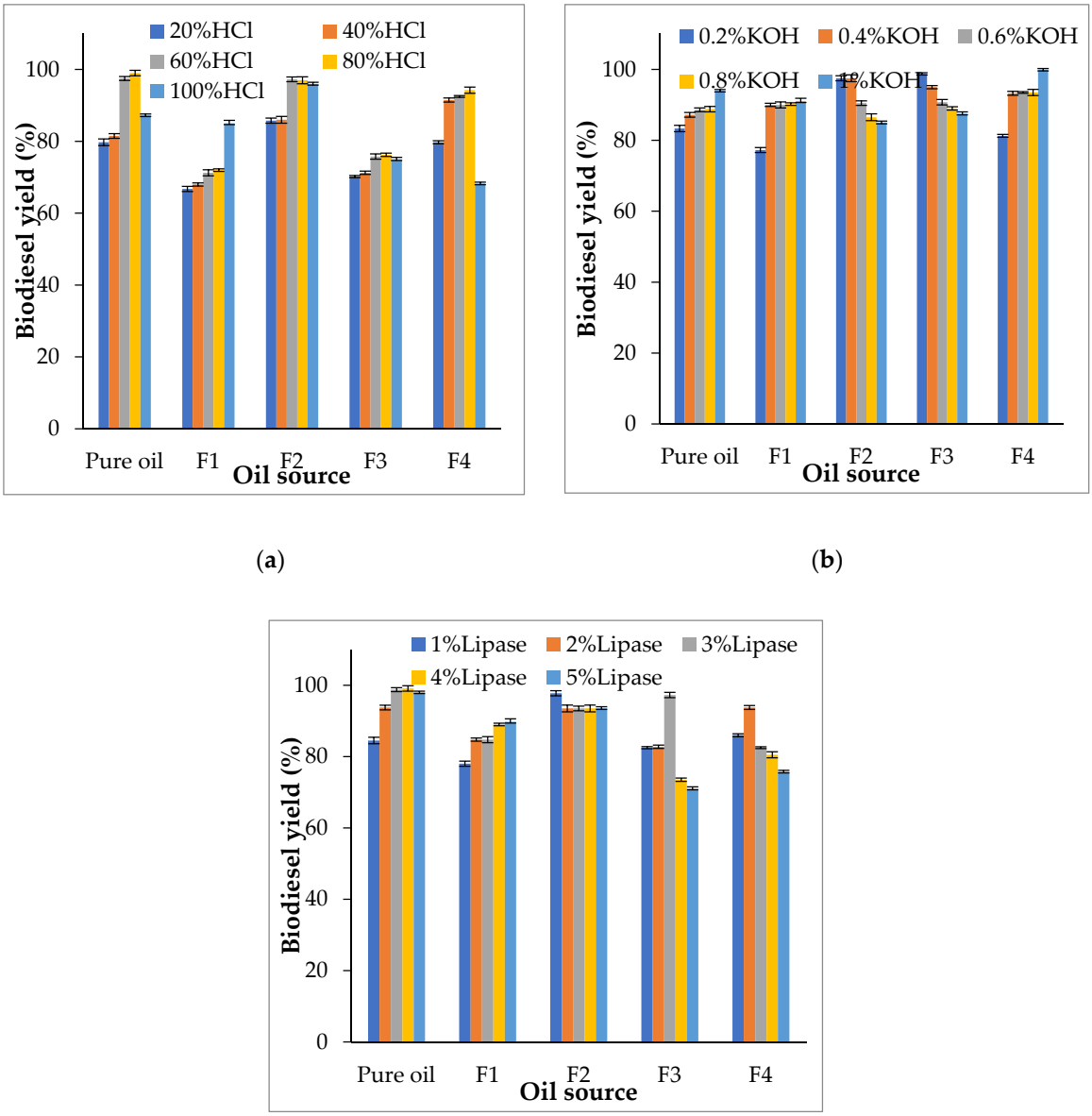

Figure 2. (**a**) Biodiesel yield using HCl as the catalyst; (**b**) biodiesel yield using KOH as the catalyst; (**c**) biodiesel yield using lipase enzyme as the catalyst.

Enzyme-catalyzed biodiesel production was completed in 24 h. For the biodiesel synthesis, five different lipase concentrations (1–5%) were used. The results obtained show that *Azadirachta indica* oil and its four fractions have the highest biodiesel yield at different enzyme concentrations. F2, F4, F3, pure oil and F1 produced the maximum quantity of biodiesel at 1%, 2%, 3%, 4% and 5% of lipase, respectively, and the respective maximum yields were 97.75%, 93.75%, 97.25%, 99.1% and 89.75%. The *Azadirachta indica* oil fractionation process yielded distillates with a variable composition as confirmed by gas chromatographic and mass spectrometric analysis. The variance in composition of fractions and *Azadirachta indica* oil was responsible for the variable optimized yield. Enzymes have a three-dimensional structure and are large protein biomolecules that can take part in many

chemical reactions. Enzymes are highly specific; they function with only one reactant to produce specific products. Comparing acid, base and enzyme catalyst-optimized yields, it is apparent that the highest biodiesel yield was shown by base-catalyzed transesterification. The biodiesel yields of acid and enzyme-catalyzed reactions were comparable.

3.2. Gas Chromatographic and Mass Spectroscopic (GC-MS) Analysis

The identification and quantification of the fatty acids present in biodiesel was conducted by GC-MS. The major fatty acids present in *Azadirachta indica* oil were found to be oleic acid (67%), palmitic acid (14.7%) and lignoceric acid (8.23%). The fuel and physical properties of biodiesel are dependent on chain length, degree of unsaturation, and branching of the chain. In a previous study, the quality of biodiesel produced from shorter fatty acids was superior than longer chain fatty acids [34]. The longer carbon chain length leads to decreased ignition delay. Longer chain fatty acids are present in all oils. However, their percentages in various oils widely differ. Lignoceric acid, or tetracosanoic acid, is the saturated fatty acid with the formula $C_{23}H_{47}COOH$. It is present in almost 8.23% of *Azadirachta indica* oil. Its removal from *Azadirachta indica* oil was necessary to avoid its negative effects on the biodiesel centane number, cloud point, pour point and freeze point. The vacuum fractional distillation process was used to carry out lignoceric acid removal from biodiesel. Lignoceric acid was removed from oil and collected in the first fraction F1. The other major components of F1 were erucic acid (22.4%), oleic acid (20.9%), phthalic acid (13.4%) and linoleic acid (11.7%). Fraction F2 contained oleic acid (C18, 61.3%) as a major fatty acid and all other fatty acids were present at less than 10%. Capric acid (C10) was 43.6% present in the fraction F3. Fraction F4 was found to have highest quantities of oleic acid (71.8%). Linoleic acid (C18) was present 16.91% in F4 (Table 2).

Table 2. Fatty acid composition of *Azadirachta indica* oil and its fractions.

No.	Fatty Acid	Percentage (%)				
		F-1	F-2	F-3	F-4	*Azadirachta indica* Oil
1	Phthalic acid (C6)	13.4	3.9	0	0	2.6
2	Caprylic Acid (C8)	1.45	0	0	0	1.44
3	Capric acid (C10)	0	0	43.6	0	0
4	Dichloroacetic acid, undec-2-enyl ester (C13)	0	0	26.0	0	0
5	Palmitic Acid (C16)	5.3	2.32	18.5	1.3	14.7
6	Linoleic Acid (C18)	11.7	0	0.60	16.91	1.30
7	Oleic Acid (C18)	20.9	61.3	5.1	71.8	67.0
8	Stearic Acid (C18)	2.72	4.8	0	1.7	0.87
9	Arachidic Acid (C20)	4.2	8.38	0	3.1	1.88
10	Behenic Acid (C22)	5.9	8.6	0	0	0.98
11	Erucic Acid (C22)	22.4	9.4	0	1.7	0.93
12	Lignoceric acid (C24)	10.6	0	0	0	8.23

3.3. Assessment of Fuel Quality Parameters

The acid value (AV) is defined as "the weight of KOH in mg needed to neutralize the organic acids present in 1 g of fat and it is a measure of the free fatty acids (FFA) present in the fat or oil" [31]. An increment in the amount of FFA in a sample of oil or fat indicates hydrolysis of triglycerides. The acid value (AV) of *Azadirachta indica* oil, F1, F2, F3 and F4 were 1.23, 2.91, 6.61, 8.89 and 3.36, respectively. The results obtained show that there was breakdown of fatty acids from triglyceride chains during the molecular distillation process of fractionation. The observed density of all biodiesel samples is given in Table 3. According to American standards (ASTM), there is no specified range of density of produced biodiesel. However, in European standards (EN), the recommended range of densities of biodiesel should range from 0.86 to 0.90 kg/liter. The density of *Azadirachta indica* oil and fraction biodiesel samples ranged from 0.70–0.91 kg/liter. The density value has great influence on some properties of the biodiesel concerning the engine efficiency including injection timing, injection

system and spray properties. Lower density biodiesel has lower engine efficiency and higher density value exhibits greater mass of biodiesel introduced into the injection system [35].

Table 3. Densities (kg/dm^3) of biodiesel produced from *Azadirachta indica* seed oil and its fractions.

Catalyst	Conc. of Catalyst (%)	Densities (kg/dm^3)				
		Azadirachta indica oil	F-1	F-2	F-3	F-4
HCl	20	0.90	0.89	0.87	0.81	0.84
	40	0.89	0.86	0.87	0.76	0.83
	60	0.86	0.80	0.81	0.75	0.82
	80	0.85	0.81	0.79	0.75	0.81
	100	0.84	0.80	0.78	0.74	0.81
KOH	0.2	0.86	0.85	0.82	0.82	0.90
	0.4	0.84	0.84	0.80	0.81	0.90
	0.6	0.83	0.82	0.78	0.78	0.88
	0.8	0.82	0.80	0.75	0.78	0.76
	1.0	0.80	0.79	0.75	0.77	0.70
Lipase	1	0.86	0.90	0.89	0.86	0.85
	2	0.80	0.90	0.89	0.76	0.84
	3	0.80	0.88	0.87	0.76	0.84
	4	0.80	0.86	0.87	0.75	0.82
	5	0.79	0.84	0.81	0.75	0.75

The saponification value or saponification number of *Azadirachta indica* biodiesel synthesized by using several catalyst concentrations is given in the Table 4. The saponification value or number relies on fatty acid concentration present in the biodiesel and the molecular weight. The existence of fatty acids with short chains of alkyl groups in biodiesel is also indicated by the saponification number. Using a KOH catalyst, higher saponification values of *Azadirachta indica* biodiesel were observed. This indicated high volatilities of the synthesized biodiesel. This might be supportive in burning *Azadirachta indica* biodiesel easily and efficiently to avoid the backfire. This happens in diesel engines when unburned fuel meets hot parts that are close enough to the tip, where oxygen is present, to explode spontaneously. However, it is quite rare for this to happen. This property is reflected in the existence of the small chained fatty acids or methyl esters.

Table 4. Saponification values (mg KOH/g) of biodiesel from *Azadirachta indica* seed oil and its various fractions.

Catalyst	Conc. of Catalyst (%)	Saponification Number				
		Azadirachta indica oil	F-1	F-2	F-3	F-4
HCl	20	270.2 ± 4.5	202.9 ± 4.1	270.2 ± 4.7	202.9 ± 4.1	270.2 ± 4.7
	40	270.2 ± 4.5	214.1 ± 4.2	146.8 ± 2.6	191.9 ± 2.9	158.0 ± 2.5
	60	171.9 ± 2.5	158.0 ± 2.6	191.7 ± 2.9	101.9 ± 2.1	158.0 ± 2.5
	80	202.9 ± 4.1	214.1 ± 2.1	180.5 ± 2.8	101.9 ± 2.1	202.9 ± 4.2
	100	281.4 ± 4.8	124.4 ± 2.2	191.7 ± 2.9	146.4 ± 2.4	109.7 ± 2.9
KOH	0.2	308.5 ± 5.3	249.0 ± 4.5	270.2 ± 4.7	281.4 ± 4.8	214.1 ± 4.1
	0.4	341.5 ± 5.5	204.9 ± 4.1	281.4 ± 4.8	276.8 ± 4.7	259.0 ± 4.5
	0.6	360.0 ± 5.6	156.1 ± 2.5	281.4 ± 4.8	270.2 ± 4.7	136.6 ± 2.3
	0.8	371.2 ± 5.7	185.8 ± 2.8	191.7 ± 2.9	270.2 ± 4.7	270.2 ± 4.7
	1	376.1 ± 5.8	178.5 ± 2.7	214.1 ± 4.2	259.5 ± 4.5	225.3 ± 4.2
Lipase	1	214.1 ± 4.2	158.0 ± 2.5	202.9 ± 4.3	226.3 ± 4.2	124.4 ± 2.2
	2	202.9 ± 4.1	180.5 ± 2.8	124.4 ± 2.4	157 ± 2.5	169.2 ± 2.6
	3	191.7 ± 2.9	146.8 ± 2.4	191.7 ± 2.9	124.4 ± 2.2	101.9 ± 2.1
	4	191.7 ± 2.9	135.6 ± 2.3	169.2 ± 2.6	134.6 ± 2.3	101.9 ±2.1
	5	180.5 ± 2.8	158.0 ± 2.5	214.1 ± 4.1	134.6 ± 2.3	124.4 ± 2.2

Furthermore, a high saponification number also articulates the presence of carboxylic groups in high amounts in the biodiesel. In the present study, the maximum saponification value was 376 mg KOH/g of biodiesel sample synthesized by the pure *Azadirachta indica* oil using 1% KOH catalyst (w/w of oil), while the minimum saponification value (136.6 mg KOH/g) of biodiesel sample produced by the F4 fraction. Using the HCl catalyst, a maximum saponification value (281.4) of pure *Azadirachta indica* oil biodiesel was shown using 100% HCl catalyst (w/w of oil) and the minimum value (101.9) for the F3 fraction was observed using 60% and 80% HCl catalyst w/w of oil. Using the lipase enzyme catalyst, a maximum saponification value (226.3) was observed for the F3 fraction using 1% lipase enzyme catalyst (w/w of oil), while the minimum SP value (101.9) was observed for the F4 fraction using 3% and 4% lipase enzyme catalyst (w/w of oil).

The iodine values (IV) of *Azadirachta indica* biodiesel are shown in Table 5. The minimum iodine value (37.2) for the *Azadirachta indica* biodiesel was found for the biodiesel synthesized using 20% HCl catalyst w/w of oil, while the maximum iodine value (218.4) was shown by pure *Azadirachta indica* oil transesterified using KOH 0.8% w/w of oil. Iodine value relies on the unsaturated fatty acid and indicate double bound present in biodiesel sample [36]. According to European standards, iodine values equal to or less than 120 is preferable for biodiesel produced for consumption. However, in American standards, no iodine value is specified. Unsaturation represented by the iodine value reflects the chance of biofuel solidification [37]. The greater the unsaturation, the greater the iodine value will be. High unsaturation in the biofuel may cause deposition as breakage of some weak bonds results in polymerization or leads to epoxide formation in the engine at high temperatures. A careful examination of Table 5 shows that biodiesel produced from *Azadirachta indica* oil had higher iodine values. However, fractionation of *Azadirachta indica* oil into various components was useful for producing better quality biodiesel with lower iodine values. The production of biodiesel from oil fractions (F1–F4) as compared to whole oil was advantageous, as evidenced by the great oxidative stabilities of oil fractions (F1–F4). Cloud point and pour point are important physical properties of any liquid fuel. Some fractions produced under vacuum produced high-quality biodiesel with comparatively much better cloud, pour points and Cold Filter Plugging Point than *Azadirachta indica* oil (Table 6). In fractionation, oil was separated into various fractions. It was expected that some fractions will have better properties than oil and others. As oil comprises all components so it displayed intermediate properties.

Cetane number (CN) is a biofuel quality parameter. CN is one of the factors that determines the ignition capability and depends on the fatty acid or methyl ester composition in the biodiesel. It influences the engine efficiency and ignition power after injection of biofuel [38]. In the present study, the CN value ranged from 9.1–87.3 (Table 7). None of biodiesel sample produced from pure *Azadirachta indica* oil met standard biodiesel cetane number requirements. However, the fractionation process improved the centane number of produced biodiesels. Cetane number of all biodiesel samples produced from *Azadirachta indica* oil fractions was in the recommended range. Biodiesel offers the advantage of a direct replacement for ordinary diesel. In the present study, we propose a much cheaper and simpler method named high vacuum fractional distillation as an alternative to refining to produce high quality biodiesel with desired fuel properties. The cetane number of commonly occurring fatty acids methyl esters are as follows: palmitic (85.9), palmitoleic (51.0), stearic (101.0), oleic (59.3), and linoleic (38.2).

Table 5. Iodine values of biodiesel from *Azadirachta indica* seed oil.

Catalyst	Conc. of Catalyst (%)	Iodine Value					Oxidative Stability at 110 °C (Induction Time/h)				
		Azadirachta indica oil	F-1	F-2	F-3	F-4	*Azadirachta indica* oil	F-1	F-2	F-3	F-4
HCl	20	115.2 ± 2.5	51.2 ± 1.1	66.3 ± 1.3	44.1 ± 0.9	37.2 ± 0.5	11.4	28.8	21.3	18.7	13.4
	40	129.6 ± 2.1	52.4 ± 1.1	69.6 ± 1.4	44.3 ± 0.9	40.2 ± 0.6	11.8	28.7	22.4	19.4	13.2
	60	126.4 ± 2.2	60.4 ± 1.3	70.0 ± 1.8	48.4 ± 0.8	41.8 ± 0.4	11.7	27.9	23.1	19.3	13.3
	80	110.4 ± 3.1	61.2 ± 1.3	71.2 ± 1.9	49.2 ± 0.5	43.6 ± 0.6	11.6	26.9	22.7	19.2	13.5
	100	118.0 ± 1.2	61.4 ± 1.4	72.1 ± 2.5	49.3 ± 0.4	45.2 ± 0.4	11.8	29.8	22.5	19.1	13.9
KOH	0.2	192.0 ± 2.7	62.0 ± 1.3	63.2 ± 1.9	25.2 ± 0.5	41.2 ± 0.4	11.3	28.4	22.6	19.4	13.8
	0.4	103.2 ± 1.9	66.0 ± 1.6	64.0 ± 1.7	43.6 ± 0.4	46.4 ± 0.6	11.4	28.3	22.5	18.9	13.8
	0.6	184.8 ± 2.6	67.3 ± 1.6	65.2 ± 1.5	55.2 ± 0.4	47.5 ± 0.6	11.3	27.7	22.8	18.7	13.7
	0.8	218.4 ± 3.1	68.1 ± 1.7	71.2 ± 1.5	79.2 ± 2.1	48.2 ± 0.7	11.7	27.5	21.8	18.9	13.6
	1	201.6 ± 3.5	69.6 ± 1.7	71.4 ± 1.6	91.2 ± 2.6	48.8 ± 0.6	11.8	27.3	22.6	18.7	13.8
Lipase	1	110.4 ± 2.5	67.2 ± 1.6	62.0 ± 1.5	55.2 ± 1.8	38.0 ± 0.5	11.3	28.9	22.8	18.6	13.5
	2	109.9 ± 2.6	68.1 ± 1.6	66.3 ± 1.7	55.2 ± 1.6	38.4 ± 0.7	11.8	28.1	22.7	18.8	13.2
	3	113.9 ± 1.6	69.1 ± 1.7	68.0 ± 1.8	55.2 ± 1.7	43.2 ± 0.7	11.6	28.2	22.8	18.9	13.8
	4	114.6 ± 1.7	69.2 ± 1.5	69.2± 1.8	58.4 ± 1.9	45.2 ± 0.8	11.8	28.5	22.7	18.6	13.4
	5	129.6 ± 1.9	69.8 ± 1.5	68.8 ± 1.5	59.3 ± 1.8	47.2 ± 0.9	11.6	28.4	22.6	18.8	13.6

Table 6. CP, PP and CFPP (°C) of various biodiesel samples.

SR.	Catalyst	Conc. %	*Azadirachta indica* Oil			F-1			F-2			F-3			F-4		
			CP	PP	CFPP	CP	PP	CFPP	CP	PP	CFPP	CP	PP	CFPP	CP	PP	CFPP
1		20	2.1	0.2	−3.1	0.1	−4.5	−10.1	1.2	0.4	−6.2	6.3	1.2	−5.3	2.3	0.5	−3.3
2		40	1.5	−1.3	−2.9	1.4	−1.2	−10.2	1.1	−0.7	−6.2	5.4	0.9	−5.2	0.4	−0.4	−3.2
3	HCl	60	1.1	−1.8	−3.0	2.1	−1.9	−10.0	−0.3	-2.5	−6.3	4.3	0.8	−5.0	0.8	−1.2	−3.0
4		80	1.0	−1.1	−2.9	2.3	−3.2	−10.3	3.8	0.1	−6.3	4.7	0.9	−5.3	0.1	−0.3	−3.2
5		100	0.9	−0.4	−2.8	2.7	−0.7	−10.4	1.3	−0.5	−6.1	5.9	1.1	−5.4	1.2	−0.7	−3.1
6		0.2	−0.4	−4.6	−5.1	−0.1	−4.5	−11.1	−2.6	−4.9	−7.1	1.6	−1.3	−5.1	−0.9	−4.6	−4.1
7		0.4	−0.6	−4.8	−5.0	−0.3	−3.4	−11.0	0.1	−1.1	−6.0	9	4.5	−5.0	0.4	−1.3	−4.0
8	KOH	0.6	−0.4	−4.2	−5.0	−2.1	−4.5	−11.1	0.4	−1.2	−6.2	8.4	4.7	−5.2	0.6	−2.3	−4.1
9		0.8	−0.5	−4.7	−5.8	−2.5	−4.8	−11.2	0.1	−1.1	−6.2	2.7	−0.3	−5.2	0.7	−2.5	−4.2
10		1	−0.3	−4.4	−5.6	−2.4	−4.4	−11.3	0.3	−1.0	−6.3	10	6.6	−5.2	0.8	−2.7	−4.3
11		1	1.1	−3.1	−3.4	7.2	3.8	−12.0	5.0	3.5	−6.0	15	11	−5.0	1.7	−2.8	−4.0
12		2	2.1	−0.1	−2.9	5.2	3.5	−12.2	5.2	3.0	−6.2	14	10	−5.1	2.3	−0.2	−4.2
13	Lipase	3	2.8	−3.1	−3.3	8.2	3.4	−12.0	5.4	2.8	−6.0	15	13	−5.0	1.3	−3.1	−4.0
14		4	3.8	2.9	−2.9	6.2	3.5	−12.9	8.4	5.2	−6.9	15	12	−4.9	1.1	−0.7	−4.7
15		5	5.6	5.1	−2.7	5.1	3.2	−12.3	9.2	5.0	−6.3	13	11	−5.1	3.5	2.3	−4.6
			Diesel oil (CP, °C)			Diesel oil (PP, °C)						Diesel oil (CFPP, °C)					
			−15 to −5			−35 to −15						−8					

Table 7. Cetane numbers of biodiesel produced from *Azadirachta indica* seed oil and its various fractions.

Catalyst	Conc. of Catalyst (%)	Cetane Number 47 Minimum (ASTMD6751)					Kinematic Viscosity at 40 °C (mm^2/s) 3.5–5.0 (ASTMD6751)					Calorific Value (MJ/kg)				
		Azadirachta indica oil	F-1	F-2	F-3	F-4	*Azadirachta indica oil*	F-1	F-2	F-3	F-4	*Azadirachta indica oil*	F-1	F-2	F-3	F-4
HCl	20	37.8	58.9	48.8	60.5	55.3	4.8	4.3	4.4	4.5	4.7	37.13	36.52	37.37	38.31	39.48
	40	34.5	57.2	65.0	61.9	68.9	4.8	4.3	4.4	4.5	4.7	37.15	36.52	37.41	38.36	39.53
	60	46.8	64.4	56.2	86.1	68.6	4.8	4.3	4.3	4.5	4.6	37.15	36.59	37.41	38.38	39.56
	80	45.5	55.2	57.7	85.9	60.6	4.7	4.2	4.3	4.4	4.6	37.20	36.60	37.43	38.39	39.58
	100	36.3	73.5	55.7	69.6	83.1	4.7	4.2	4.2	4.4	4.5	37.21	36.60	37.49	38.45	39.59
KOH	0.2	17.9	51.5	49.5	57.2	59.7	4.8	4.3	4.4	4.5	4.7	37.25	36.50	37.31	38.33	39.45
	0.4	36.3	55.3	48.5	53.4	54.1	4.7	4.2	4.4	4.4	4.6	37.28	36.51	37.32	38.35	39.51
	0.6	17.1	63.3	48.2	51.3	72.8	4.7	4.2	4.4	4.4	4.6	37.29	36.53	37.38	38.36	39.54
	0.8	9.1	57.5	55.9	45.9	52.8	4.7	4.2	4.3	4.4	4.6	37.31	36.55	37.39	38.38	39.56
	1	12.6	58.4	52.9	44.0	56.7	4.7	4.2	4.3	4.3	4.4	37.34	36.56	37.40	38.41	39.56
Lipase	1	44.1	62.9	56.5	55.2	78.8	4.8	4.3	4.4	4.5	4.7	37.19	36.57	37.40	38.32	39.47
	2	46.7	58.4	72.5	65.8	67.1	4.8	4.3	4.2	4.5	4.7	37.21	36.57	37.41	38.32	39.51
	3	46.3	65.1	56.7	74.9	87.3	4.7	4.2	4.2	4.4	4.6	37.24	36.59	37.46	38.35	39.52
	4	46.1	68.2	60.2	70.9	86.9	4.7	4.1	4.2	4.4	4.5	37.25	36.59	37.48	38.35	39.55
	5	44.6	62.3	53.5	70.7	76.7	4.7	4.1	4.2	4.3	4.5	37.26	36.60	37.48	38.39	39.56
		Diesel oil					Diesel oil					Diesel oil				
		46					2.0–4.5 (mm^2/s) at 40 °C					44.80 MJ/kg				

A previous study [39] was undertaken with similar objectives such as development of cost-effective processing technology, and elimination of degumming, esterification and dehydration steps from the oil purification processes by conducting a supercritical extraction using CO_2 [39].

However, when capital investment and processing cost of high vacuum fractional distillation (HVFD) used in the present study is compared with a supercritical extraction using CO_2, HVFD is a much cheaper and simpler alternative. HVFD does not add to the cost of biodiesel as it is an alternative route for oil purification. In another previous study [40], supercritical fluid carbon dioxide was used to separate out biodiesel fraction from impure fatty acid methyl ester (FAME) solution mixes. The disadvantage of doing fractionation after production of methyl esters is the production of a number of useless byproducts, which does not happen in HVFD. Secondly, the prior methodology does not bring any significant improvements in the cetane number, cloud point or pour point of biodiesel.

4. Conclusions

The following important conclusions can be drawn from the present study:

- *Azadirachta indica* seed oil can be explored as a renewable and reliable source for biodiesel production.
- High vacuum fractional distillation (HVFD) process was very effective in producing such fractions of *Azadirachta indica* oil which produced better quality biodiesel.
- A superior quality biodiesel was produced from some fractions as presented by oxidative stabilities, iodine values, cloud points, pour points and cetane numbers.
- Biodiesel produced after fractionation of crude oil offers the advantage that it can be used as a direct replacement for ordinary diesel.

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