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Biodiesel production from oleander *(Thevetia Peruviana)* oil and its performance testing on a diesel engine

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Abstract−Oleander oil has been used as raw material for producing biodiesel using ultrasonic irradiation method at the frequency of 20 kHz and horn type reactor 50 watt. A two-step transesterification process was carried out for optimum condition of 0.45 v/v methanol to oil ratio, 1.2% v/v H_2SO_4 catalyst, 45 °C reaction temperature and 15 min reaction time, followed by treatment with 0.25 v/v methanol to oil ratio, 0.75% w/v KOH alkaline catalyst, 50 °C reaction temperature and 15 min reaction time. The fuel properties of Oleander biodiesel so obtained confirmed the requirements of both the standards ASTM D6751 and EN 14214 for biodiesel. Further Oleander biodiesel-diesel blends were tested to evaluate the engine performance and emission characteristics. The performance and emission of 20% Oleander biodiesel blend (B20) gave a satisfactory result in diesel engines as the brake thermal efficiency increased 2.06% and CO and UHC emissions decreased 41.4% and 32.3% respectively, compared to mineral diesel. Comparative investigation of performance and emissions characteristics of Oleander biodiesel blends and mineral diesel showed that oleander seed is a potential source of biodiesel and blends up to 20% can be used for realizing better performance from an unmodified diesel engine.

Keywords: Biodiesel, Oleander Oil, Ultrasonic Cavitation Method, Performance Testing

INTRODUCTION

The decline in fossil fuel resources along with high crude oil prices has generated attention towards the development of fuel from alternate sources. One of the best alternatives is biodiesel obtained from different vegetable oils. Biodiesel is defined as monoalkyl esters of vegetable oils or animal fats, obtained by transesterification of an oil or fat with an alcohol [1]. It is a biodegradable, renewable and nontoxic fuel, and its application as a diesel engine fuel improves exhaust emissions, with great potential to decrease environmental pollution [2]. Biodiesel is generally produced through a three-step process, a consecutive and reversible reaction called "transesterification." Low mass transfer due to immiscible nature of reactants is the main weakness of transesterification [3]. Various techniques have been introduced to overcome the mass transfer resistance of immiscible reactants. Some of the recently developed biodiesel production technologies are power ultrasound and hydrodynamic cavitation [4-6,9,10]. Among the techniques, ultrasonic is preferred due to its capability to intensify the transesterification reaction. Many authors have reported that low-frequency ultrasound accelerates reaction rate in which higher conversion is achieved in transesterification within shorter reaction time compared to the other approaches [4-6]. Kumar et al. [7] developed a new biodiesel from Manilkara zapota (L.) seed oil and optimized the influencing parameters of transesterification using the Taguchi method. The experimentally determined optimum conditions for the production of Manilkara zapota methyl ester are 6 : 1 methanol to oil molar ratio, 1% (w/w) concentration of catalyst, 90 min time of reaction and 50 °C temperature of reaction and the corresponding yield rate is 94.83%. Federica et al. [8] carried out a pilot-scale trial of biofuel production from sunflower and found that sunflower oil obtained from high-oleic hybrids fulfilled most of the quality requirements for the use of vegetable oils as engine fuels, and also reported that direct use of crude oil seemed to be a more suitable option than its conversion to biodiesel. Kakati et al. [11] reported maximum BTE and ITE for biodiesel blends compared to neat diesel, and it was the maximum for B20 at all BMEPs. Similarly, Ong et al. [12] found the comparable performance of Calophyllum inophyllum biodiesel and its blends with petroleum-based diesel. Other findings include emissions reduction, increased brake power, and BSFC. The BSFC, for all biodiesel-diesel blends increases with increasing blending ratio and decreases with increasing engine speed [13]. Khiari et al. [14] reported a maximum increase of 3.1% in BTE at full engine load condition for Pistacia lentiscus biodiesel, and a significant reduction in CO and HC emission than that of mineral diesel, but higher NOx levels.

It is apparent from the above literature that most of the work has been done on edible oils and a limited amount of work has been done on non-edible oils for biodiesel production and its consequent utilization. It is also important to note that amongst the non-

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edible oils, Jatropha, Karanja, Castor and some other feedstocks were mostly used. However, oleander (Thevetia Peruviana), which is an underutilized non-edible vegetable oil in India, is not sufficiently considered. The present work deals with the production and performance of biodiesel from novel feedstock oleander oil.

MATERIALS AND METHODS

The oleander fruits (Fig. 1) were collected from plants grown in Delhi Technological University Campus, Delhi, India. Mature fruits were collected two times a year (summer and winter seasons), pulps removed, seeds dried in sunlight, deshelled and the kernel crushed using a grinder prior to oil extraction. Solvents and other chemicals used were of analytical grade, and they were procured from commercial sources and used as such without further treatment.

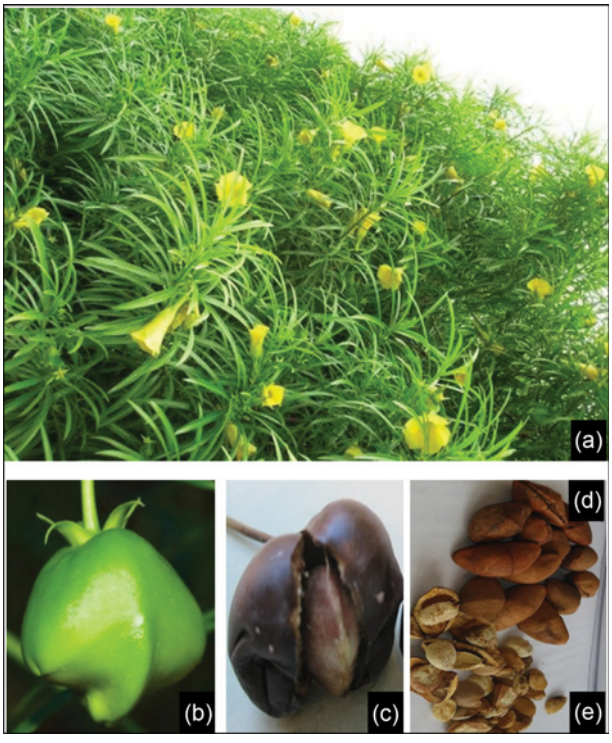


Fig. 1. (a) Oleander plant (b) raw fruit (c) ripe fruit (d) kernels (e) deshelled seeds and cake.

1. Oleander Seed (Thevetia Peruviana)

The oleander (Thevetia Peruviana) tree is a very drought resistant poisonous plant found throughout India. It is most abundant in the north Indian plains of India, especially in Assam. It contains 52-60% of oil; hence it can be used to produce bio-diesel in large scale. It is widespread in the American, Asian and African continents. It grows to about 10-18 feet high, the leaves are linear and about 13-15 cm in length arranged spirally and the flowers are funnel-like and yellow. An oleander tree can produce about 800-1,000 fruits all the year-round depending on the climatic conditions and age of the plant. The fruits are usually green and become black on ripening. Each fruit contains one to four seeds in its kernel and the oil content in the seed is high (60-65%) [15], which makes it a suitable naturally occurring renewable source of non-edible oil. A normal tree produces an average of 40-50 Kg of fruit every season.

From the earliest time, in India, this plant has been proved to be worthwhile in several ways. The latex from leaves can be used to make rubber, though the amount is too small for commercial deployment. The wood is suitable for firewood and furniture. The oil is not considered to be edible as it is bitter in taste, but the oil is commonly used for making of soaps, paints, and cosmetic. The cake can be used as a source of animal feeds and fertilizer, etc. It is also used in traditional medicine for numerous symptoms. The oleander has been used in the treatment of cancer [18].

2. Oil Extraction Method

Oil can be extracted from oleander by mechanical and solvent extraction, with solvent extraction preferred when oil is extracted in commercial quantity. A Soxhlet apparatus and n-hexane as extraction solvent were used for this work. The apparatus was initially charged with powdered oleander kernels, which was packed in a cloth. A round bottom flask was filled with the extraction solvent and the whole setup was heated in a heating mantle at 50-70 °C. The extraction solvent in the solvent-oil mixture was recovered and recycled by distillation. The oil was extracted with petroleum ether from the crushed kernel in a Soxhlet extractor. The solvent was then removed at 45 °C.

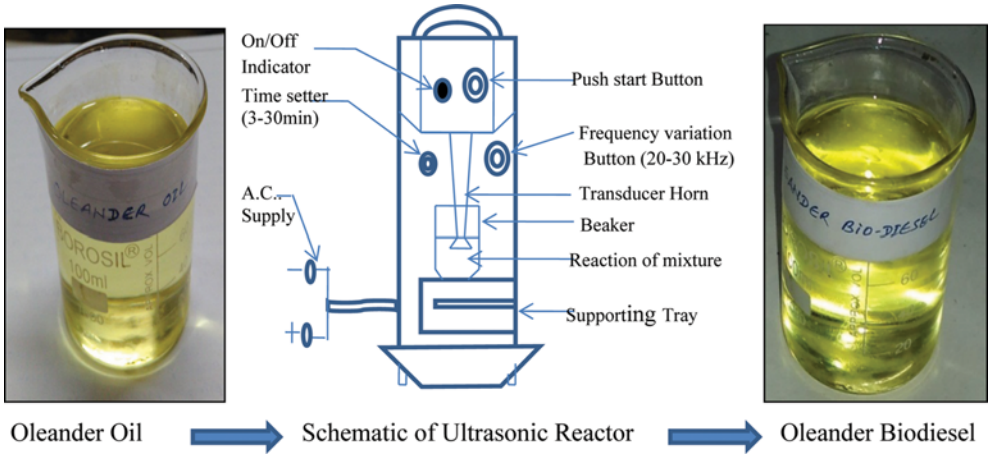


Fig. 2. Oleander biodiesel production through ultrasonic horn type reactor.

3. Biodiesel Production by Ultrasonic Cavitation Method

An ultrasonic processor with a working frequency of 20-30 kHz and an output power of 50 watts was used in this experiment (Fig. 2). A 250-ml-glass beaker loaded with the mixture was directly exposed to the ultrasonic sound. Both esterification and transesterification were carried out for a period ranging from 10-15 min.

4. Acid-catalyzed Esterification Process

The oleander oil extracted had FFA 7.5%, which was far above the 2% limit for satisfactory transesterification reaction using an alkaline catalyst. Thus, there is the need to reduce the FFA of the oil to about 2% or less via esterification reaction prior to transesterification reaction. 100 ml of preheated oleander oil was measured into a 250 ml flask and mixed with 45 ml of methanol and 1.2% v/v of concentrated H_2SO_4. The resulting mixture was heated to 45 °C and for 15 minutes. The esterification and transesterification chemical reactions are shown in Eq. (1) and Eq. (2), respectively.

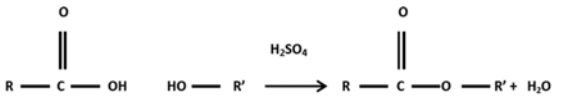
5. Alkaline Catalyzed Transesterification Process

The pre-treated oleander oil was mixed with alcohol at the ratio of 0.25% v/v along with 0.75% w/v KOH Catalyst. The mixture was heated to 50 °C and for 15 min reaction time. The transesterified oil was transferred into a separating funnel and allowed to settle under gravity for four hours. A biodiesel layer was formed at the top and the glycerol layer at the bottom of the separating funnel. The upper layer of the biodiesel was removed and washed with distilled water three to four times and dried over anhydrous sodium sulfate.

6. Yield of Biodiesel (% Y)

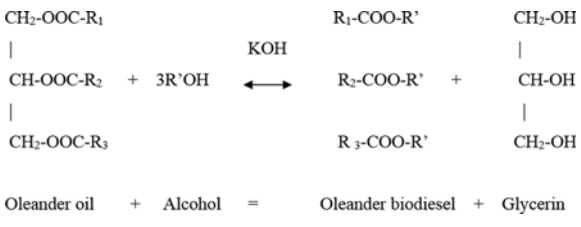
The yield of oleander biodiesel using ultrasonic method was determined by using the following formulae

$$\%\ Y_{BD} = \frac{\text{Weight of biodiesel produced} \times 100}{\text{Weight of raw oil}} = \frac{W_{BD} \times 100}{W\ oil}$$



(1)

Acid + Alcohol ⟷ Ester + Water



(2)

Oleander oil + Alcohol = Oleander biodiesel + Glycerin

7. Experimental Setup for Performance and Emission Testing

The experimental setup consisted of a single cylinder, four strokes, water cooled diesel engine with 3.5 kW maximum power, 110 mm stroke and 87.5 mm bore connected to eddy current type dynamometer for loading. Oleander biodiesel blends were prepared with diesel fuel. The blends were prepared on a volume basis. 10%, 20% and 30% biodiesel blends with diesel were used and are named as B10, B20, and B30. Different parameters were measured with varying the load from 0.5 kW to 3.5 kW in steps of 0.5 kW at a compression ratio of 18 and a constant speed of 1,500 rpm. The performance characteristics were measured by using the software "Engine soft." Table 1 shows the technical details of the engine.

Table 1. Technical details of the engine

S. no	Component	Specification
1	Engine make	Kirloskar
2	Engine type	1 Cylinder, 4 stroke, water cooled
3	Rated Power	3.5 kW at ,1500 rpm
4	Cylinder volume	661 cc
5	Compression ratio	Variable (12 to 18)
6	Dynamometer	Eddy current, water cooled
7	Piezo Sensors	Range 5000 PSI
8	Crank Sensor	Resolution 1 Deg, Speed 5500 RPM
9	Load Sensor	Load cell, type strain gauge
10	Software	"Engine soft," Engine Performance analysis software

The NOx, HC, and CO emissions were measured with AVL DIX, Emission Diagnostic System. The range and accuracy of measurements of AVL DIX emission diagnostic system are shown in Table 2. The performance and emission characteristics for different test fuels were compared with the result of baseline diesel operation. All experiments were repeated thrice in order to determine the range and reproducibility of the results.

RESULTS AND DISCUSSION

1. Fatty Acid Composition

Gas chromatography analysis (GC-FID) of oleander seed oil revealed that it contains main acids as oleic acid (44.23±.74%), palmitic acid (23.28±0.32%) and linoleic acid (21.82±.24%) (Table 3).

2. Physico-chemical Properties of Oleander Seed Oil

Various physico-chemical properties of oleander oil, its biodiesel and mineral diesel were determined according to standard methods shown in Table 4. Experiments were repeated thrice in order to determine the range and reproducibility of the results.

The density of oleander biodiesel was found to be 0.87±.03 g/cc, which is closer to the density of diesel. The viscosity of oleander oil

Table 2. AVL DIX emission diagnostic systems specification

Measured variables	Measurement range	Resolution	Accuracy
CO	0-10 vol%	0.01 vol%	<0.6% vol.: ±0.03% vol.
HC	0-20,000 ppm	<2000: 1 ppm vol.	<200 ppm vol.: ±10 ppm
		>2000: 10 ppm vol.	P 200 ppm vol.: ±5% of ind. val.
CO_2	0-20 vol%	0.1 vol%	<10% vol.: ±0.5% vol.
NO	0-5,000 ppm	1 ppm vol.	<500 ppm vol.: ±50 ppm vol.

Table 3. Fatty acid composition of oleander oil

Fatty acids	Chemical formula	Degree of unsaturation	Values (wt%) (mean±standard deviation)
Palmitic	$C_{16}H_{32}O_2$	16 : 0	23.28±0.32
Stearic	$C_{18}H_{34}O_2$	18 : 0	7.46±.29
Oleic	$C_{18}H_{32}O_2$	18 : 1	44.23±.74
Linoleic	$C_{20}H_{40}O_2$	18 : 2	21.82±.24
Arachidic	$C_{20}H_{38}O_2$	20 : 0	1.8±.02
Lignoceric	$C_{18}H_{34}O_2$	24 : 1	2.66±.03

Table 4. Physico-chemical properties of oleander oil and biodiesel in comparison with biodiesel specification standards

Properties	Mean value±Standard deviation			Test methods	ASTM D6751 limit of acceptance	EN 14214 limit of acceptance
	Oleander oil	Oleander biodiesel	Mineral diesel			
Density at 15 °C (g/cc)	0.89±.05	.87±.03	0.83±.02	D 1298	0.86-0.90	0.85
Viscosity at 40 °C (cSt)	35±1.4	4.1±0.25	2.9±0.2	D 445	1.9-6.0	3.5-5.0
Flash point (°C)	190±4	174±3	55±2	D 93	Min. 130	min 120
Pour point (°C)	−2±1	−8±1	−15±1	D97	−15 to −16	-
Cloud point (°C)	2±1	−5±1	−10±1	D 2500	−3 to −12	-
CFPP (°C)	8±1	6±1	−9±1	D 6371	-	-
Calorific value (MJ/kg)	39.8±.05	42.69±.04	44.23±.03	D240	-	-
Acid value (mg KOH/gm.)	15±0.6	.62±.03	.08±.01	D 664	Max 0.5	Max 0.5
Iodine value (g I_2/100 g)	85±.44	76.9±.32	4.5±0.2	EN 14214	-	Max. 120
Cetane number	61±1	72±1	49±1	D 613	Min 47	Min 51
Oxidation stability (h)	-	8±1	-	EN 14112	Min 3	Min 6

was reduced from 35±1.4 to 4.1±0.25 cSt after the transesterification process. The flash points of oleander biodiesel are higher than the fossil diesel (55±2 °C). The higher flash point of oleander biodiesel ensures safe handling and storage. The cloud and pour point of oleander biodiesel were almost within the specified range. The calorific value of oleander biodiesel obtained in the study (42.69± .04 MJ/Kg) is quite comparable with the conventional diesel. The properties of biodiesel obtained in this study are in good agreement with other researchers [15-17]; hence, oleander biodiesel can be used as an alternate fuel.

3. Performance and Emission Characteristics

3-1. Brake Thermal Efficiency (BTE)

Thermal efficiency is the ratio of power output to the energy of injected fuel. Fig. 3 shows the variation of brake thermal efficiency (BTE) with BP. The values of BTE were increased with increasing load in all cases. This was due to a reduction in heat losses at higher load [20]. From Fig. 3 it can be observed that the average BTE values for 10%, 20%, and 30% oleander biodiesel blend were 21.02%, 23.71%, and 20.82% compared to diesel fuel, which was about 22.25%. An average increase in BTE compared to diesel fuel was found as 2.06% for B20 blend, while other blends B10 and B30 showed a reduction in BTE by 5.5% and 6.4%, respectively, compared to diesel fuel. Lower calorific value and higher viscosity might have been the dominating factor for lower brake thermal efficiency. In comparison to B10, B30, and diesel, the slight increase in brake thermal efficiency of B20 may be observed due to higher oxygen content causing proper combustion and slightly lesser heating value than that of diesel. Higher BTE with biodiesel blends was also reported by previous researchers [10,14,19-21].

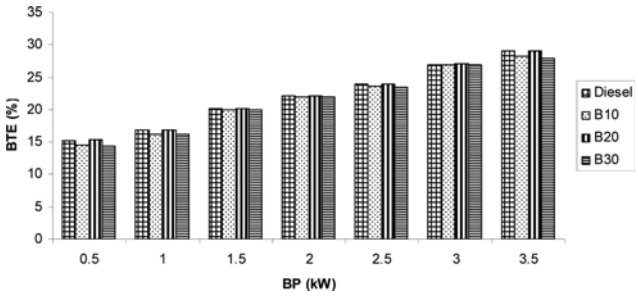


Fig. 3. Variation of brake thermal efficiency with brake power.

3-2. Unburned Hydrocarbon Emission (UHC)

Incomplete combustion of fuels is the major cause for the for-

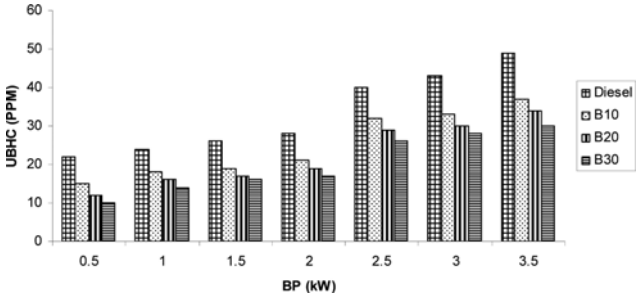


Fig. 4. Variation of unburned hydrocarbon emission with brake power.

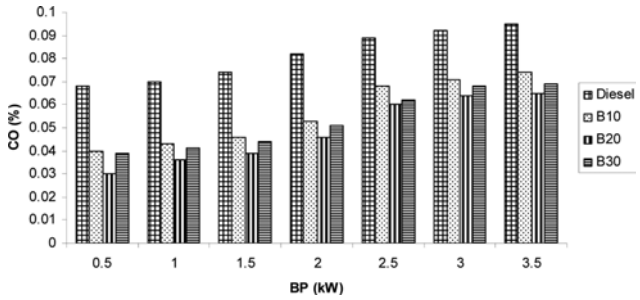


Fig. 5. Variation of carbon monoxide emission with brake power.

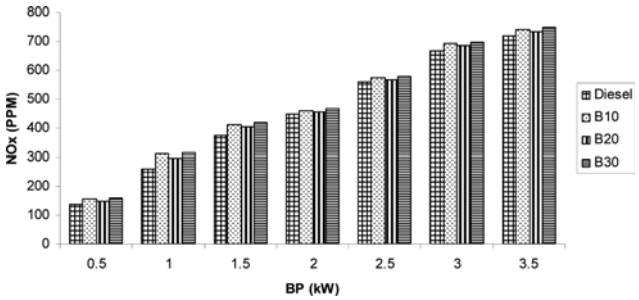


Fig. 6. Variation of Nitrogen oxide emission with brake power.

mation of hydrocarbon emission. Fig. 4 shows the variation of unburned hydrocarbon emission (UHC) with the BP. It was observed that the increasing the load increases HC emission due to relatively less oxygen available for the reaction when more fuel injected into the engine cylinder at higher engine load. Also, oleander biodiesel blended fuels exhibited lower UHC emissions as compared to mineral diesel. This reduction in emissions of UHC with increasing volume fraction of biodiesel in the fuel may be attributed to the combined effects of higher in-cylinder temperature, higher cetane rating and reduced ignition delay [27]. At full load, diesel fuel showed highest HC emission (49 ppm), whereas B30 blend showed lowest (30 ppm). The 10%, 20%, and 30% blends showed an average reduction of 24.8%, 32.3% and 40.6% respectively compared to diesel fuel. Similar trends of reducing HC emission for biodiesel blended fuel are reported by Satyanarayana et al. [22] and Chuah et al. [9].

3-3. Carbon Monoxide Emissions (CO)

Fig. 5 shows the variation of carbon monoxide (CO) emission with brake power for blends of oleander biodiesel and diesel. The 10%, 20%, and 30% blend showed an average reduction of 31.7%, 41.4%, and 34.4%, respectively, compared to diesel fuel. Minimum emission of carbon monoxide is observed for B20, which may be due to its higher thermal efficiency and proper combustion. All biodiesel blends emit lesser carbon monoxide emission as compared to diesel. This is attributed to increasing in-cylinder temperature at higher engine load and presence of oxygen in biodiesel fuel, which improves fuel combustion and, consequently, reduces CO emissions [23]. The oxygen in biodiesel prevents the possibility of fuel-rich zones formation and also creates a more homogeneous distribution, which leads to complete combustion. Higher CN makes short ignition delay, which results in better combustion. Furthermore, the increase in saturation level of biodiesel leads to a significant reduction in CO emissions [26]. These results are in agreement with results of previous researchers [12-14]; even higher reduction levels (up to 87%) were recorded by Ozsezen et al. [24].

3-4. Nitrogen Oxide Emissions (NO_X)

Fig. 6 shows the variation of nitrogen oxide emission with brake power. The average NOx values for B10, B20 and B30 were 467 ppm, 460 ppm, and 473 ppm, respectively, as compared to 445 ppm for diesel. An average increase in NOx in these blends compared to diesel fuel was found to be 5% (B10), 3.3% (B20) and 6.2% (B30), respectively. Biodiesel blends emit a higher amount of nitrogen oxide emission as compared to diesel, and this may be attributed to the inherent presence of oxygen in biodiesel. Similar results were obtained by Engin et al. [21]. It is also observed that B20 has slightly lesser NOx emission as compared to B10 and B30. This may be due to higher exhaust gas temperature of B10 and B30 in comparison to B20. The NOx emission level increases with engine load for all fuels. This may be attributed to the higher peaks of pressure and temperature resulting from an increase in the injected fuel amount. Also, notice that all biodiesel blends exhibit higher NOx emissions than diesel fuel over the entire power range. This trend can be explained by the high cetane number and the oxygen content of biodiesel, both of which result in rapid combustion and an increase of combustion pressure and temperature maximum. In addition, other studies have shown that the double bonds contained in biodiesel are likely to result in higher levels of radicals that promote NOx emissions [25].

CONCLUSIONS

Good quality biodiesel has been prepared in high yield (97.1%) from oleander seed oil using ultrasonic transesterification process. The results of experimental studies are concluded as given below:

- The ultrasonic transesterification process is a highly efficient and time-saving process.
- An average increase in BTE compared to diesel fuel was found as 2.06% for B20 blend, while other blends B10 and B30 showed a reduction in BTE by 5.5% and 6.4%, respectively, compared to diesel fuel.
- All biodiesel blends emitted lesser carbon monoxide as compared to diesel. The 10%, 20%, and 30% blends showed an average reduction of 24.8%, 32.3% and 40.6% respectively compared to diesel fuel.
- All biodiesel blends emitted lesser carbon monoxide as compared to diesel. The 10%, 20% and 30% blend showed average reduction of 31.7%, 41.4% and 34.4%, respectively, compared to diesel fuel.
- As compared to diesel, all biodiesel blends emitted a higher amount of nitrogen oxide. The 10%, 20% and 30% blend showed an average increase of 5%, 3.3% and 6.2%, respectively, compared to diesel fuel.

After analyzing the above performance and emission parameters, it may be concluded that B20 Oleander biodiesel fuel can be used in an unmodified diesel engine effectively. The present investigation has established the oleander seed oil as highly promising feedstock for the biodiesel industry.

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