

Biodiesel Production of Waste Cooking Oil through Ultrasound Cavitation

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Abstract

This paper presents the comparative details of biodiesel production process using low frequency ultrasonic energy (28-33 kHz) and conventional mechanical stirrer method. For this purpose, Waste Cooking Oil (WCO) is used as the biodiesel feedstock. The experiments have been performed for molar ratio (alcohol/oil) 6:1 and 4.5:1, with three different catalyst percentages (0.5%, 0.75% and 1%) of Potassium Hydroxide. The important chemical and physical properties of Waste Cooking Oil biodiesel were determined and compared with diesel. It is observed that the density and viscosity values of the biodiesels produces are within the permissible limits but still higher than petroleum diesel. Further an experimental investigation has been carried out on a four cylinder, diesel engine operating on diesel and biodiesel blends [B10, B20, and B30]. It can be concluded from present study that: (i) Biodiesel production through ultrasound energy seems to be a relatively simple, efficient, time saving, eco-friendly and industrially viable process. (ii) The trends for percentage variations of performance parameters for biodiesel blends (in reference to diesel as baseline) do not show any deterioration. (iii) There is tremendous improvement in smoke reduction while operating with biodiesel as compared to petroleum diesel.

Keywords: Biodiesel; Ultrasonic energy; Waste Cooking oil; Performance tests; Engine emissions.

1. Introduction

Majority of the world's energy needs are supplied through petrochemical sources, coal and natural gas, with the exception of hydroelectricity and nuclear energy, all these sources are finite and at current usage rates will be consumed shortly^[1]. Economic growth is always accompanied by commensurate increase in the transport. Diesel fuel play important role in the industrial economy of developing countries and commonly used in transports, industrial and agricultural goods, etc. Compared to rest of the world, India's demand for diesel fuel is six times higher than gasoline^[2]. Also, petroleum fuels are currently the dominant global source of CO₂ emissions and their combustion is posing stronger threat to clean environment. This has stimulated the recent interest in alternative sources for petroleum-based fuels.

A viable alternative fuel should be easily available, environment friendly and techno-economically competitive. Bio-diesel is an alternative to petroleum-based fuels derived from vegetable oils or animal fats^[3]. It is named biodiesel because it is derived from biological products and matches petro diesel in performance. Vegetable oils are widely available from different kind of plants and the glycerides present in the oils can also be separated and used as by-product^[4]. Bio-diesel production is a very modern and technological area for researchers due to its environmental advantages the increase in the price of petroleum fuels^[5]. The most common way of producing bio-diesel is the transesterification of vegetable oils and animal fats. Vegetable oils have good heating power and provide exhaust gas with almost no sulphur and aromatic polycyclic compounds. It possesses high biodegradability and lubricating property which makes it even better fuel. As vegetable oils are produced from plants, their burning is completely recyclable as it produces carbon dioxide (CO₂), which is consumed by the plants in photosynthesis^[6]. Vegetable oils can be directly used as fuel for diesel engines, but their viscosities are much higher (10 to 20 times) than usual diesel fuel and require modifications of the engines^[7]. The injection and atomization characteristics of the vegetable oils are significantly different than those of petroleum-derived diesel fuels, mainly due to their high viscosities^[8].

In a country like India, having huge agricultural potential vegetable oils proves a promising alternate for petroleum (diesel oil) fuel. In recent years systematic effort have been made by several researchers to use vegetable oils like sunflower, peanut, soybean, rapeseed, palm, olive, cottonseed, linseed, jatropha, coconut, pongamia, rubberseed, jojoba etc. as alternative for diesel. Many of the vegetable oils are edible in nature; therefore their continuous use may cause shortage for food supply and prove far expensive to be used as fuel at present. So far a very few of non-edible vegetable oils have been tried on diesel engine leaving a lot of scope in this area. Different countries are looking for different types of vegetable oils as substitutes for diesel fuels that further depending upon the climate and soil conditions. For example; soya-bean oil in U.S., Rapeseed and Sunflower oils in Europe, Palm oil in Southeast Asia and Coconut oil in Philippines are being used^[9].

India is a developing country and its energy demand is increasing day by day. Vegetable oils are good alternative source in Indian context because India is

agriculture based country. Vegetable oil consists edible and non-edible oil, edible oil demand being higher than its domestic production, there is no possibility of diverting these oils for production of bio-diesel. Non-edible oil plants can be planted on understocked forest lands, farmer's field boundaries to provide protective hedge, fallow lands, public lands along railway tracks, highways, canals and community and government land in villages. Therefore biodiesel production through non-edible oil is major concerned field for India. The by-products of Bio-diesel from non edible oil are oil cake and glycerol which have good commercial value.

Basic reaction carried out in the biodiesel production is transesterification. In this reaction different catalysts can be used to enhance the transesterification reaction which is namely alkali catalyst, acid catalyst and lipase catalyst^[10]. Different technique has been developed so far for biodiesel production like mechanical stirring, hydrodynamic cavitation, ultrasonic cavitation [11] and supercritical methanol^[12].

Ji et al.^[11], prepared biodiesel through Power Ultrasonic (PU) (19.7 kHz), Hydrodynamic Cavitation (HC) and Mechanical Stirring (MS). The yield of PU and HC are found to be almost similar and are better than MS. Power ultrasonic gave the shortest reaction time and the highest yield. It is found that the PU and HC processes require approximately a half of the energy that was consumed by the MS method. Stavarache et al.^[13], studied low frequency ultrasound (40 kHz) with the aim of gaining more knowledge on intimate reaction mechanism with the KOH (potassium hydroxides). it was concluded that by Stavarache et al.^[14] that using ultrasounds the reaction time is much shorter (10–40min) than for mechanical stirring and the quantity of required catalyst is 2 or 3 times lower.

Gogate et al.^[15] performed the similar experiment on hydrodynamic cavitation, ultrasonic cavitation and mechanical stirring technique for biodiesel production under optimum operating conditions. Production of fatty acid ethyl ester (FAEE) from oleic acid (FFA) with short-chain alcohols (ethanol, propanol, and butanol) under ultrasonic irradiation was investigated by Hanh et al.^[16] and it was concluded that Ultrasonic irradiation condition is efficient, time saving and economically functional for esterification of free fatty acid with short-chain alcohols to produce biodiesel fuel. The esterification of fatty acid with ethanol under ultrasonic irradiation provides a possibility for producing cheap alternative fuels, which could reduce air pollution and protect the environment. Hanh et al.^[17] also investigated the biodiesel production through transesterification of triolein with various alcohols under ultrasonic irradiation (40 kHz) and mechanical stirring (1800 rot/min) conditions. It was found that the rate of the alkyl ester formation under the ultrasonic irradiation condition was higher than that under the stirring condition. Santos^[18], evaluated the production of methyl esters from *Oreochromis niloticus* (Nile tilapia) oil and methanol. The reaction was carried out applying low-frequency high-intensity ultrasound (40 kHz) under atmospheric pressure and ambient temperature. The optimal operating condition was obtained applying an alcohol to oil molar ratio of 9.0 and a catalyst concentration of 2.0% w/w and temperature of 30 °C.

In the open literature, experimental studies on application of ultrasound energy for biodiesel production of non-edible oils are not available. Therefore, the objectives of present experimental study are to explore the possibility of production of biodiesel from non-edible oils using ultrasound energy in comparison to mechanical stirring method, followed by engine performance testing.

2. Materials

Raw *Citrullus colocynthis* (Thumba) oil, and waste cooking oil have been used for biodiesel production. These Non-edible oils are purchased from the Jodhpur district of western Rajasthan (India), whereas waste cooking oil (WCO) was obtained from Maurya Sheraton the five star hotel in Delhi and commercially available diesel oil was purchased from the nearby IOCL petrol pump.

3. Experimental work

3.1 Test rig for ultrasonic cavitation technique

The transesterification reactions were carried out in the horn type ultrasonic reactor (Figures 1 and 2). In horn type reactor the horn is attached with the transducer which produces ultrasonic irradiation in the mixture. Ultrasonic processor frequency is ranging from 25 kHz to 30 kHz and time limit is ranging from 3 min to 30 min. There is an integrated arrangement for supporting the beaker (100 ml) so as the transducer horn should be submerged at the separating boundary of two immiscible liquids. The horn of the transducer was submerged approx. 2 cm in the reactive mixture of methanol and fatty acid oil. The temperature of the reaction mixture was controlled by a water bath. Heated fatty acid oil (50 gm, 50° C) was poured into the reactor at the beginning. The reaction started when a mixture consisting of desired amount of KOH was dissolved in methanol liquor KOH was poured into the heated reactor.

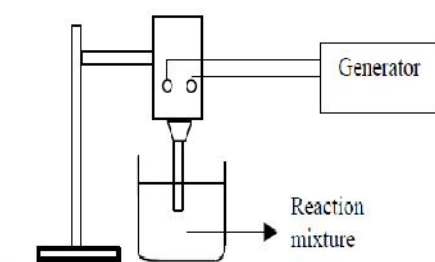
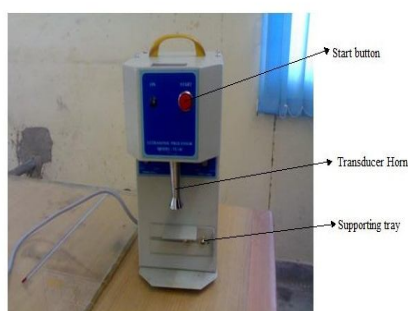


Figure 1: Photograph of ultrasonic horn type processor (TU-50) **Figure 2:** Schematic diagram of ultrasonic horn type reactor

The reaction is carried out by ultrasonic irradiation from the acoustic rod horn incorporated with the transducer. Cavities are created by the irradiation of power ultrasonic with sufficient energy in immiscible liquid (oil and alcohol are not miscible with each other) as a result micro fine bubbles are formed and these bubbles are collapsing at various place of the reactor and disturb the phase boundary between two immiscible liquid and resulted in emulsification of mixture.

3.2 Fuel properties

Biodiesel properties in comparison to diesel are shown in Table 1. Density is almost same for the Thumba and WCO biodiesel but higher than the diesel. Kinematic viscosity of thumba biodiesel is higher than WCO and diesel has the lowest kinematic viscosity. Flash point of WCO biodiesel is much higher than the thumba oil and diesel. Water content (0.005 w/w %) is much lower in case of diesel oil. Sulphur content in all biodiesel is lower than diesel.

Table 1: Comparison of the property of biodiesel and diesel as per BIS: 2796.

Property	Biodiesel from		Unit	Limit	Diesel
	Thumba oil	WCO			
Appearance	clear	clear	----	----	clear
Color	Brownish	Yellowish	----	----	----
Density at 15 0C	890	886	kg/m ³	860-900	840
Kinematic viscosity at 40 0C	5.86 x 10 ⁻⁶	4.3 x 10 ⁻⁶	m ² /sec	3.5-5 x 10 ⁻⁶	4.86 x 10 ⁻⁶
Flash point	>66	>110	0C	Min 100	51
Sulphur contents	0.01	>0.012	w/w%	Max 0.05	0.35-0.55
Water content	0.05	>0.04	w/w%	0.02-0.05	0.005

3.3 Preparation of biodiesel blends

Biodiesel blends of thumba and WCO biodiesel with diesel oil has been prepared for engine performance testing. From the literature it is evident that dilution or blending of non edible oil with other fuels like alcohol or diesel fuel would bring the viscosity close to a specified range. Therefore thumba and WCO biodiesel blends with diesel in varying proportion to reduce its viscosity. Engine experiments are performed with different blends of biodiesel (pure diesel, B-10, B-20, and B-30).

3.4 Experimental setup for performance testing

The setup consists of four cylinder, four stroke, Tata Indica diesel engine connected to eddy current type dynamometer for loading. It is provided with necessary instruments for combustion pressure and crank-angle measurements. The signals are interfaced to

computer through engine indicator for p - θ diagrams. Provision is also made for interfacing airflow, fuel flow, temperatures and load measurement. The set up has stand-alone panel box consisting of air box, fuel tank, manometer, fuel measuring unit and transmitters for air and fuel flow measurements. The setup enables study of engine performance for various engine parameters. The main aim of this experiment is to investigate the suitability and effect on performance of blending of biodiesel (produced through power ultrasound) in comparison to the gasoline diesel fuel.

4. Result and Discussion

4.1 Experimental data of biodiesel production

Vegetable oil (50g) is taken in a 100 ml beaker and filtered it to remove impurities and heated up to 120 °C in order to remove water content of oil to avoid soap formation. This oil is allowed to cool up to 60 °C temperature. Methyl alcohol (CH₃OH) with a molar ratio of (1:4.5 & 1:6) and Catalyst KOH is taken as (0.5%, 0.75% and 1%) by weight of oil. Then mixer of methyl alcohol and KOH stirred until KOH dissolve in methyl alcohol. This mixture is mixed with vegetable oil. The mixture of oil, methanol and catalyst come in contact with ultrasonic processor transducer (model TU-50) which works at the ultrasonic frequency of 28.5 kHz. During the reaction the temperature of mixture is kept between 40 -55 °C. When reaction is completed the beaker is kept for the separation. Fatty acid has higher specific weight therefore it will settle at bottom. Separation of methyl ester and glycerol will take 2 to 3 hr duration. After complete separation bio-diesel (methyl Ester) is visible in the upper layer and the lower layer as glycerol. Bio-diesel is separated from beaker for purification process. To remove the catalyst, water at around 60 °C is mixed with the methyl ester and left for settling down. Water due to its higher specific gravity collected at bottom. Excess methanol present in biodiesel has been removed by distillation process. The experiments are performed with alcohol to oil molar ratio as 6:1 and 4.5:1. The amount of oil, alcohol and catalyst taken is shown in Table 2.

Table 2: Oil, alcohol and catalyst during the experimentation.

Molar ratio (alcohol/oil)	Quantity of non- edible oil (gm)	Quantity of methanol (gm)	Catalyst (KOH)		
			0.5%	0.75%	1.0%
6:1	50 g	11 g	0.25 g	0.375 g	0.5 g
4.5:1	50 g	8.28 g	0.25 g	0.375 g	0.5 g

Time and yield produced for the different vegetable oils

Experiments have been performed to prepare biodiesel from vegetable oil (Thumba and waste cooking oil) by ultrasonic cavitation method and conventional magnetic stirring method. Main aim of this experiment to calculate reaction time, catalyst percentage and molar ratio (alcohol/oil) for biodiesel production with maximum yield

in comparison to the conventional method. Our emphasis in the present study is to reduce the use of catalyst (KOH) and alcohol because catalyst (KOH) is pollutant for the water and land. If biodiesel produce on industrial scale, large amount of catalyst will be discharged in river or land causing harm to environment. The results obtained from experiments are discussed below:

Experimental Data for Ultrasonic Cavitation Method

Experimental data are collected by performing ultrasonic cavitation on the sample which is a mixture of vegetable oil (thumba and waste cooking oil), methanol (CH₃OH) and catalyst (KOH). For every sample reaction time required for biodiesel production and yield of methyl ester is calculated. Time and yield for every sample is shown in Table 3.

Table 3: Time (Min) and yield (%) of thumba and waste cooking oil for different molar ratio and catalyst (%).

% of catalyst	Molar ratio (alcohol/oil) 6:1				Molar ratio (alcohol/oil) 4.5:1			
	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
0.5%	20	92.8	16	91.6	21	95.2	18	94.2
0.75%	14	90.7	15	88.7	18	93.4	16	91.3
1%	9	90	10	84	15	87.7	15	87.5

Experimental Data for Magnetic Stirring Method

For comparison purpose experiment has also been performed with magnetic stirrer. Time and yield of methyl ester for three different oil and catalyst (%) of oil is shown in table 4.

Table 4: Time (Min) and yield (%) of jatropha, thumba and waste cooking oil for different molar ratio and catalyst (%).

% of catalyst	Molar ratio (alcohol/oil) 6:1				Molar ratio (alcohol/oil) 4.5:1			
	Thumba		Waste cooking oil		Thumba		Waste cooking oil	
	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)

0.5%	38	87	38	87.1	42	88.7	42	89.8
0.75%	34	84.2	36	85.8	39	86.3	37	87.2
1%	30	79.8	30	84.8	36	84.1	35	85.3

5. Discussion on experiment data

With the help of experimental data shown in Tables 4 and 5, graphs have been plotted to compare the power ultrasound and mechanical stirring methods applied for these non-edible oils.

5.1 Comparison for thumba oil

Comparison of ultrasonic and mechanical stirring method for molar ratio 6:1 (alcohol and oil) for different catalyst (%) is shown in Figure 3(a) and 3(b). Thumba biodiesel also exhibit lower reaction time and more yield than conventional method. Maximum yield in case of ultrasonic method for thumba biodiesel is 92.8% and lower reaction time is 9 minutes for 1% catalyst. Comparison of these two techniques for molar ratio 4.5:1 is shown in Figure 3(c) and 3(d). For this molar ratio and same catalyst (%) yield and reaction time is optimum for the ultrasonic cavitation method. It can be seen that using ultrasonic method reaction time is almost half compare to conventional method which is beneficial for industrial applications.

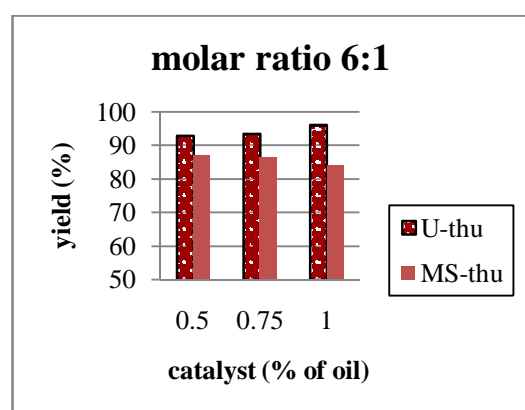


Figure 3(a): Comparison of yield for thumba biodiesel and molar ratio 6:1

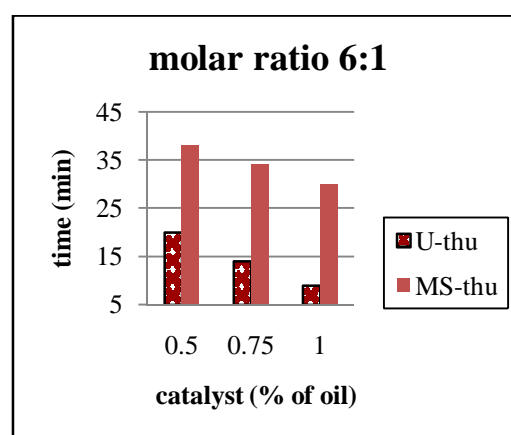


Figure 3(b): Comparison of time for thumba biodiesel and molar ratio 6:1

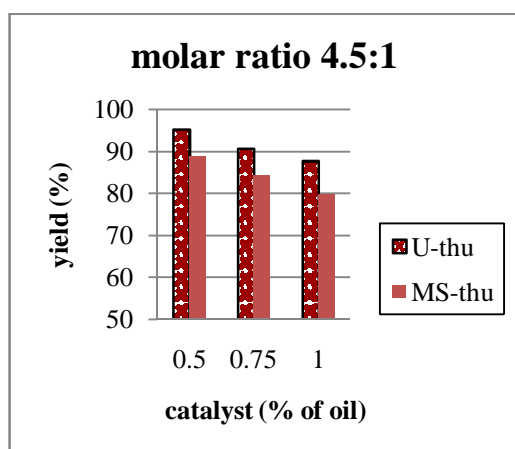


Figure 3(c): Comparison of yield for thumba biodiesel and molar ratio 4.5:1

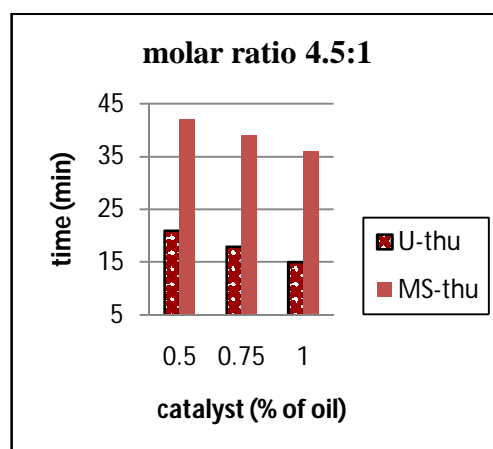


Figure 3(b): Comparison of time for thumba biodiesel and molar ratio 4.5:1

Comparison with waste cooking oil (WCO)

Similar comparison has also been performed for the waste cooking oil for molar ratio 6:1 and different catalyst (%) which is shown in Figure 4(a) and 4(b). Yield is almost same for both method for all catalyst (%) but time is much lower in case of ultrasonic cavitation method.

For molar ratio 4.5:1 (alcohol to oil) comparison between ultrasonic and magnetic stirring method is shown in Figure 4(c) and 4(d). Yield in case of ultrasonic method higher for 0.5% and 0.75% catalyst of oil and it is lower for 1% compared to conventional method. Reaction time show similar pattern as above.

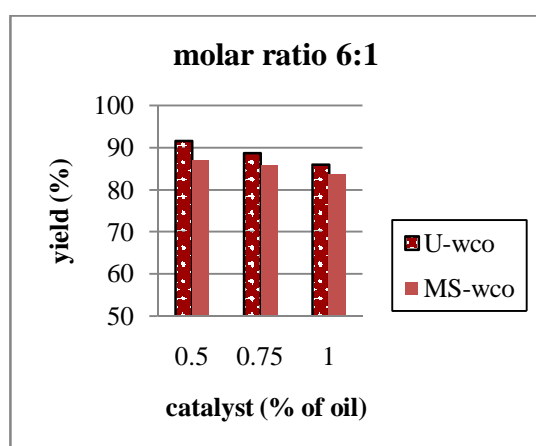


Figure 5(a): Comparison of yield for WCO biodiesel and molar ratio 6:1

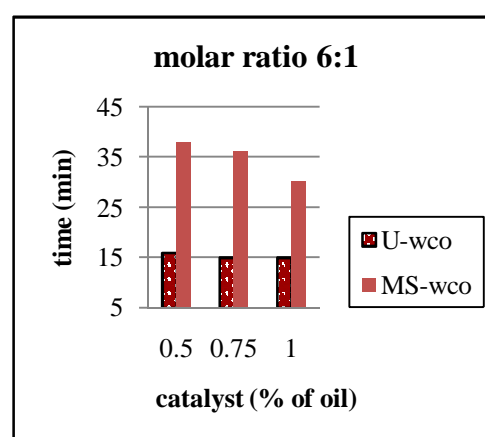


Figure 5(b): Comparison of time for WCO biodiesel and molar ratio 6:1

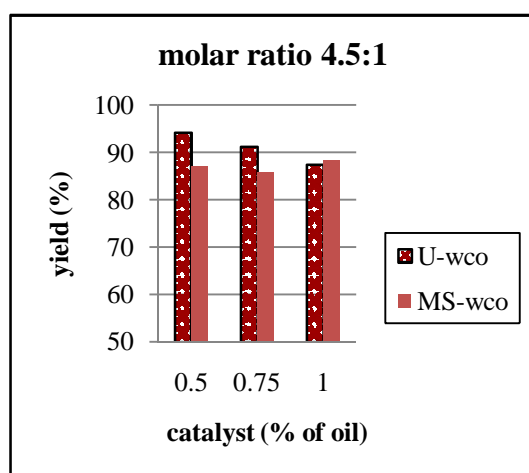


Figure 4(c): Comparison of yield for WCO biodiesel and molar ratio 4.5:1

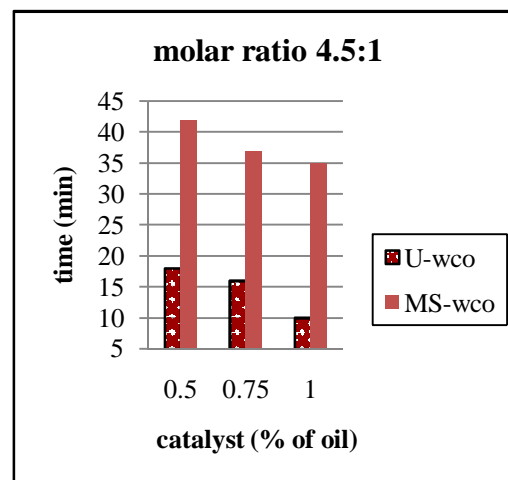


Figure 4(d): Comparison of time for WCO biodiesel and molar ratio 4.5:1

6. Performance and Emission Studies

6.1 Experimental Setup of single cylinder kirloskar Engine

The setup consists of a diesel kirloskar engine single cylinder, water cooled, direct injection, naturally aspirated, four stroke, 87.5 mm bore, 110 mm stroke and compression ratio (17.5). Diesel engine connected to eddy current type dynamometer for loading as shown in Figure 5.

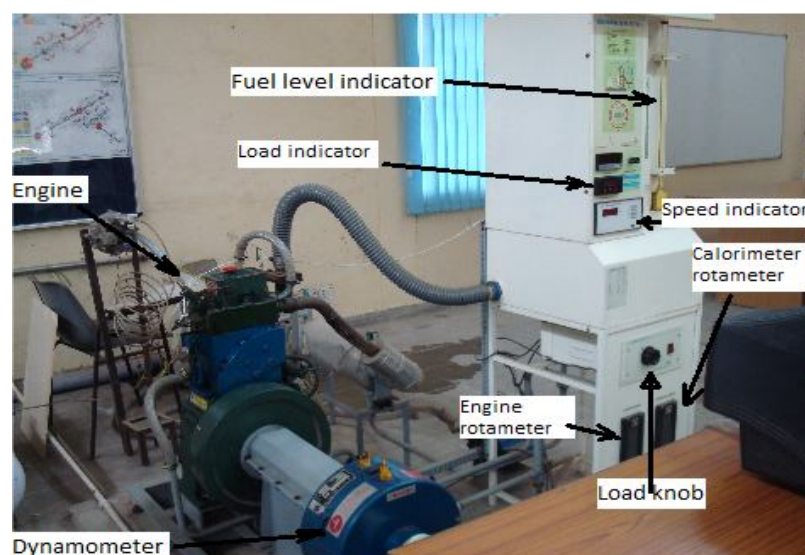


Fig. 5: Engine setup for performance and emissions test.

Variation of brake thermal efficiency w.r.t brake power

Figure 6 (a-c) shows the variation of BTE v/s brake power and % variation of BTE for thumba and WCO blends of B20, B40, B60, respectively compared with diesel. For all blends BTE increases with increases power output. The maximum percentage deviation of BTE for all blends of WCO and thumba is $\pm (3-10)$ % w.r.t. diesel operation, this narrow range of variation for wide range of brake power output shows that WCO and thumba can be similar alternative of diesel petroleum. The biodiesel produced from WCO and thumba have good combustion quality due to presence of oxygen and higher lubricity than diesel.

Variation of smoke opacity W.R.T. brake power

Shown in figures 7 (a-c) represents the variation of the smoke opacity with brake power for different blends of WCO and thumba biodiesel blends compared with diesel. Smoke opacity is usually found to significantly decrease with biodiesel as compared to diesel with increase in load. The smoke emissions were also sensitive to the oxygen content of the fuel and good combustion characteristics. Because of the heterogeneous nature of diesel combustion, fuel-air ratios, which affect smoke formation, tend to vary within the cylinder of a diesel engine. Smoke formation occurs primarily in the fuel-rich zone of the cylinder, at high temperatures and pressures. If the applied fuel is partially oxygenated, locally over-rich regions can be reduced and primary smoke formation can be limited. Percentage reductions is up to 40 % , higher reductions were observed with higher loads.

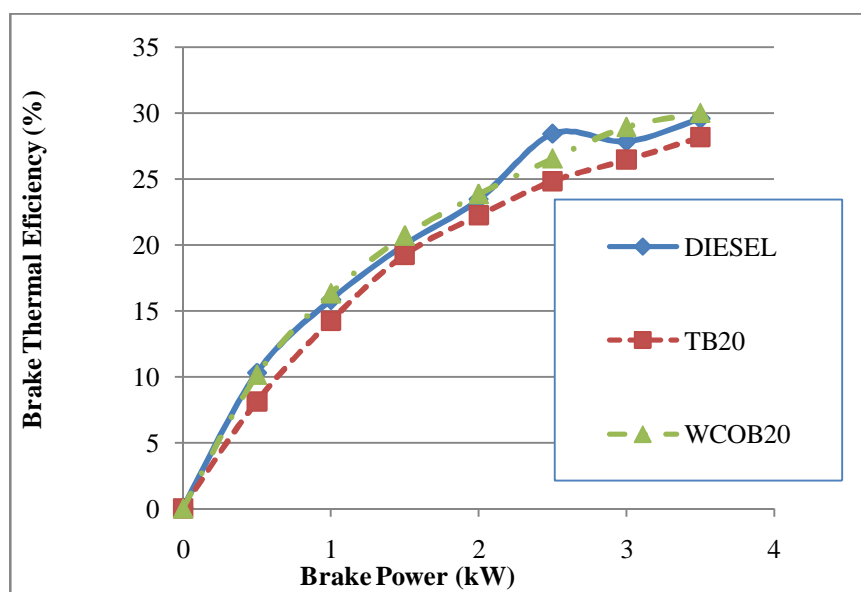


Fig. 6(a): BTE V/s Brake power of WCOB 20,TB.

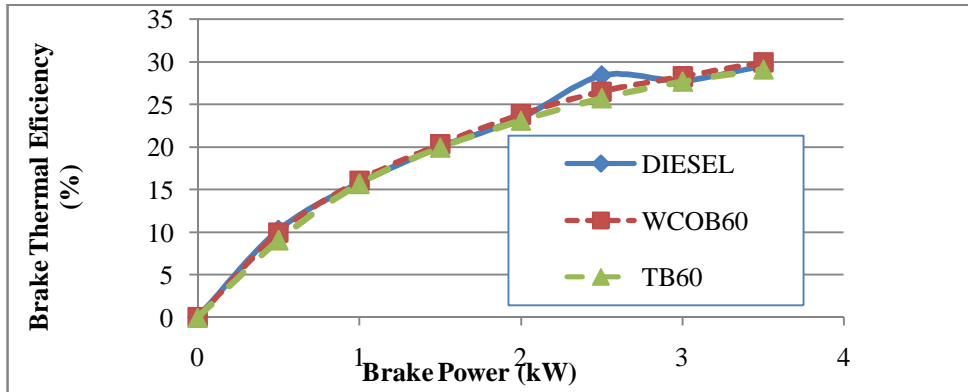


Fig. 6 (c): BTE v/s Brake power of WCOB60, TB60.

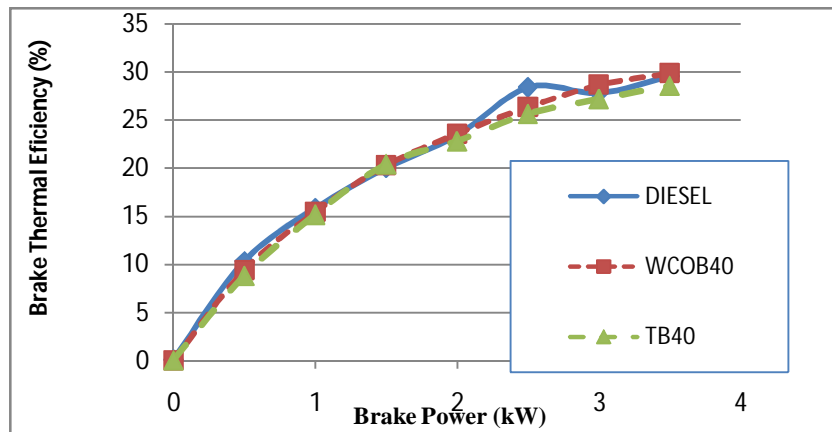


Fig. 6(b): BTE v/s Brake power of WCOB 40, TB 40.

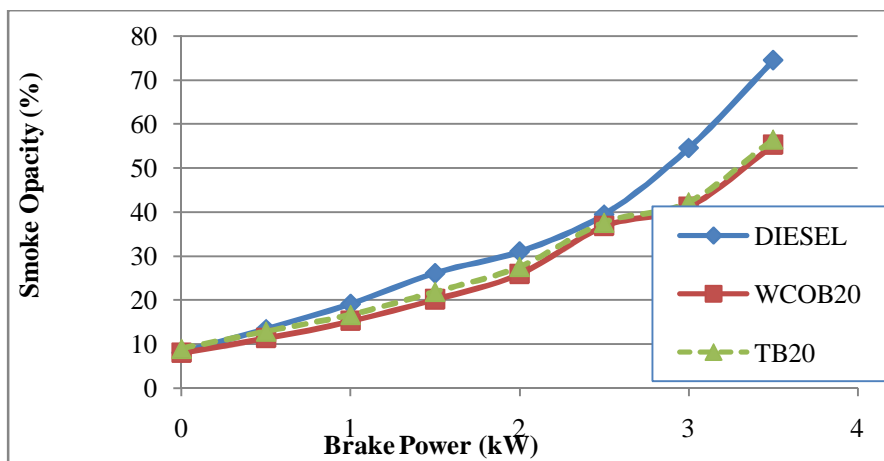


Fig. 7(a): Smoke opacity v/s Brake power of WCOB 20, TB 20.

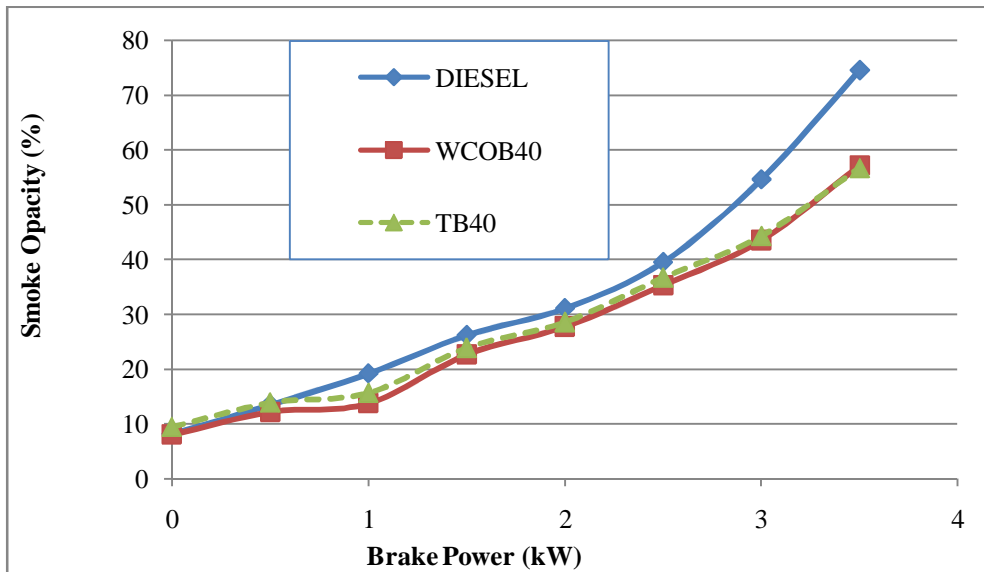


Fig. 7(b): Smoke opacity v/s Brake power of WCOB 40, TB 40.

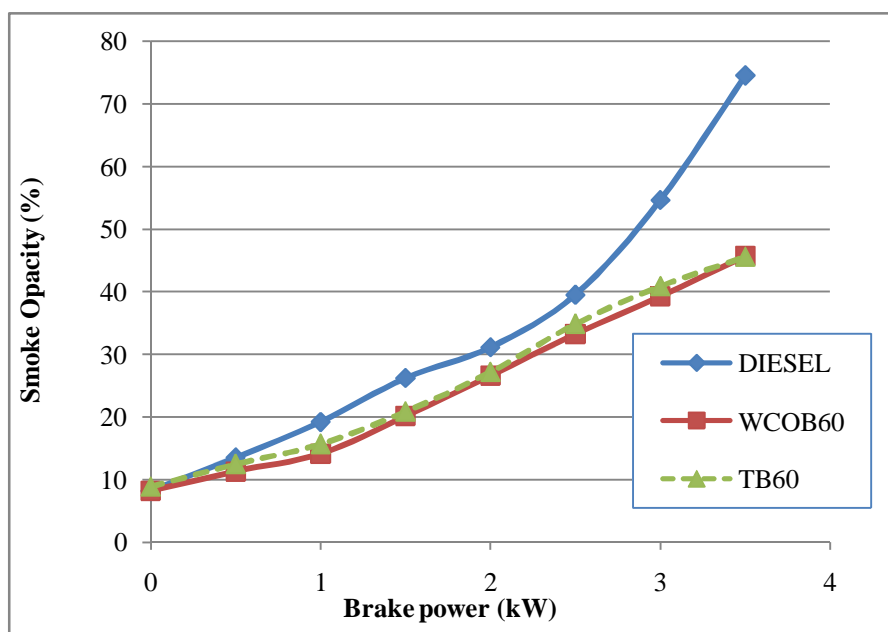


Fig. 7(c): Smoke opacity v/s Brake power of WCOB60, TB 60.

7. Conclusion

Ultrasonic cavitation method is energy efficient, environmental friendly and industrially viable alternative for the biodiesel production. Following conclusions have been made from the experiments:

1. The reaction time required for methyl ester formation is much shorter for ultrasonic cavitation method compare to conventional magnetic stirring method.
2. Relatively better yield has been obtained by ultrasonic cavitation technique compare to convention method of biodiesel production.
3. Thumba and jatropa biodiesel are potential alternative to diesel.
4. From the engine performance testing it can be concluded that the thermal efficiency parameter for both biodiesel (thumba and jatropa) have better results than the diesel oil.

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