

Comparative Evaluation of Madhuca Longifolia and Jatropha Curcas Extracted Biodiesel.

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Abstract

In order to fulfil the growing need to replace fossil fuels, investigations exploring the production of biodiesel from agricultural biomass have gained attention. The purpose behind this study is to examine the efficiency of biodiesel extracted from *Madhuca longifolia* and *Jatropha curcas* by means of pre-treatment followed by two step acid-base homogeneous catalyst method. The *Madhuca* and *Jatropha* biodiesels were blended with diesel at different percentages. Fourier Transform Infrared Spectroscopy (FTIR) showed a strong presence of fatty acid profile, and triglyceride ester linkage at 1744 cm^{-1} . UV-Vis spectra confirmed the presence of conjugated dienes in the extracted biodiesels. UV absorbance at 320 nm decreases linearly with blend percentage. ^1H NMR and ^{13}C NMR confirmed the presence of methyl ester moiety at 3.6 ppm and methoxy carbon at 51.2 ppm in biodiesel distinguishing it from diesel. Raman spectra exhibited C = O stretching at 1725 cm^{-1} indicating conversion of *Madhuca* and *Jatropha* oil into biodiesel. The engine performance and emission tests of these biodiesels were evaluated. In the engine performance tests, the variations of brake specific fuel consumption (BSFC), exhaust gas temperature (EGT), and brake thermal efficiency (BTE) versus brake power were studied. The emission tests of different blends were done in terms of carbon mono-oxide, nitrous oxide, and unburnt hydrocarbon (UHC). The *Jatropha* biodiesel exhibited less mean BSFC, EGT and emitted less CO and UHC than *Madhuca* biodiesel. The average decrease in BTE was more in *Jatropha* biodiesel than *Madhuca* biodiesel.

1. Introduction

Biodiesel as an alternative fuel is non-toxic, renewable, biodegradable, and carbon-neutral fuel (Chatterjee et al.2015). Earlier research indicates that biodiesels emit lesser CO, and particulate matter but higher NO as compared to diesel (Joshi and Pegg 2007). Kannan (2019) revealed that oxidation catalysts decrease oxidation temperature, which reduces NOx emission. Addition of nano additives enhances thermal efficiency and lowers fuel consumption (Ganesan et al. 2020). In the combustion process biodiesel exhibits no efficiency loss, despite its heat of combustion being slightly lower than that of diesel (Raheman and Ghadge 2007).

During the storage process biodiesel undergoes oxidative degradation because of the presence of reactive unsaturated fatty acid esters mainly oleate, and linoleate (Pantoja et al. 2013). This degradation leads to alteration in peroxide value, decomposing hydroperoxides to ketones, and oligomers (Bondioli et al. 2003). The degradation further leads to poor performance like seal swelling of the elastomer, and dilution of engine (Karavalakis and Stournas 2010). Fourier transform infrared spectroscopy (FTIR) is mainly used to observe oxidative degradation of biodiesel (Bacha et al. 2015). Its absorption at around 1745 cm^{-1} is due to the existence of ester carbonyl group (Zhou et al. 2017). Faragun et al. (2019) observed high linearity correlation between concentration and FTIR absorption (R^2 above 0.998). Shimamoto and Tubino (2016) explored the presence of conjugated dienes in oxidized biodiesel and

found positive correlation between peroxide value and the UV absorbance and having two intense absorption bands along the 230–260 nm wavelengths (Shimamoto and Tubino 2016).

Several authors studied Raman spectra for the estimation of transesterification reaction, and ester composition of biodiesel. Several researchers also studied the intensity and position of C = O of carbonyl group. Authors observed high correlation (R^2 above 0.99) between biodiesel concentration and Raman spectra (Ghesti et al. 2007).

Nuclear Magnetic Resonance (NMR) technique is applied to determine the chemical structure of compounds associated in biodiesel synthesis (Ghesti et al. 2007).

It is also used for quantifying biodiesel in diesel-biodiesel blends, and changes in the fatty acid content (Shimamoto and Tubino 2016). Knothe (2001) reported olefin protons (5.3–5.4 ppm), methyl ester peaks (3.6–3.7 ppm), and methyl protons of the hydrocarbon moieties in biodiesel in establishing biodiesel-diesel blends.

Monteiro et al. (2009) analysed the effectiveness of ^1H NMR in influencing the blend of methyl biodiesel in diesel fuels, using castor oils, soybean biodiesel and three diesel fuels.

Anderson (2012) exhibited NMR spectra for studying formation of triacylglycerol, and FAME in biodiesel production. Satyarthi et al. (2009) utilized NMR spectroscopy to establish free fatty acid value (FFA). Authors estimated FFA content using R-CH_2 of FFA and ester.

The shifting of paraffin hydrocarbon and O_2 content reduces the effect of biodiesel (Schmid and Gerpen 1996). Tat et al. (2004) found cetane number (CN) and NO_x emissions are inversely correlated. Several researchers revealed biodiesels emit less NO_x and have higher degree of saturation (Knothe et al. 2006). Pinzi et al. (2013) pointed NO_x , HC, and CO emissions increase with an increased chain length of unsaturated FAME. NO_x emission increases with decreasing chain length of fully saturated fatty acids.

The present work uses for the first-time treatment of ortho phosphoric acid (H_3PO_4) and toluene (C_7H_8), to produce biodiesel followed by two step homogeneous acid-base catalyst method. The efficiency of this method is evaluated by using two variants of biodiesels: *Madhuca longifolia* and *Jatropha curcas*. This treatment drastically reduces the FFA value which in turn increases the performance of the biodiesels.

2. Production

The novelty in the production method is pre-treatment of oil by addition of C_7H_8 , and H_3PO_4 , which removes impurities. C_7H_8 is also added both in transesterification and esterification steps, which removes impurities, and results in the addition of less catalyst. The acid- base two-step process enhances the yield and reduces the FFA value. The reduction of FFA is the indicator of efficient fuel exhibiting high performance tests. Figure 1 represents the production of biodiesel from *Madhuca* and *Jatropha*.

FFA of pure *Madhuca* oil was 19%, which was reduced to 2% by pre-treatment with C_7H_8 , and H_3PO_4 , subsequently reduced to 0.91 % by transesterification step and 0.3% by three step production method. The yield was 97.6%. Similarly, in *Jatropha* oil FFA was reduced from 20–1.45% in the first step of pre-treatment, which was further reduced to 0.8% by transesterification by acid H_2SO_4 catalyst and finally to 0.2% by base catalyst. The yield was also 98%.

2.1. Experiment details

Both *Madhuca* and *Jatropha* oils were obtained commercially from Uttar Pradesh, India. NMR solvent $CDCl_3$ (99%) was obtained from Sigma Aldrich, n-Heptane (99%), NaOH pellets from Thermo Fisher, H_3PO_4 , and H_2SO_4 from Rankem, CH_3OH from Fisher Scientific.

The produced *Jatropha curcas* (JB) and *Madhuca longifolia* (MB) biodiesels were blended with diesel at varying proportions ranging within 0–95% characterization.

The characterization of all blended samples of JB and MB was performed by FTIR (Make- Shimadzu Corp, spectrometer, wave number ranging from 7500– 350 cm^{-1}). The absorption spectra of all samples were obtained by using UV-vis spectrophotometer (Make- Perkin Elmer Lambda 25 UV/Vis spectrometer) in the wavelength range of 190 nm-1100 nm with a 10 mm quartz cuvette at room temperature. All the blended JB and MB samples were diluted with n- Heptane to bring the absorbance to the measurable range of the spectrophotometer. Again, each spectrum was recorded 3 times. 9.9 ml of n- Heptane was mixed with 0.1 ml of the sample to prepare the final sample. The dilution of JB and MB with aromatic compounds i.e., diesel resulted in decrease in absorbance wavelength. NMR analysis was conducted by using JEOL JNM spectrometer, at 298 K. NMR spectra for all samples were obtained using 1 ml $CDCl_3$ as solvent, mixed with 0.1ml of each sample. Raman Spectra was performed by using Renishaw InVia Raman Spectrometer. The 785 nm laser line was employed, and grating has 1200 l/mm.

The engine was made to run on pure diesel, and its various blends of MB and JB. The performance was studied at four different loads (%) at constant 1500 rpm. AVL Di-Gas analyser was used to measure the exhaust gases i.e., carbon monoxide (CO), Oxides of nitrogen

(NO_x), and unburnt hydrocarbon (UHC) of the engine. The inlet manifold of the analyser was connected to the exhaust valve of the engine to measure the emission gases. Table 1 depicts engine specifications.

Table 1
Engine specifications

S. No.	Item	Units	Specifications
1.	Manufacturer		Kirloskar Oil Engines Ltd
2.	Engine Capacity	hp	10
3.	Cylinder		1
4.	Stroke		4
5.	Compression Ratio		17.5:1
6.	Bore	mm	102
7.	Stroke	mm	116
8.	Ignition		Compression
9.	Max. Power @ rpm	kW	6.7kW@ 3000 rpm
10.	Cooling System		Water Cooled
11.	No. of Valves / Cylinder		1

3. Result And Discussion

3.1. Characterization

3.1.1. Physical Characterization

All physio-chemical properties namely viscosity, calorific value, density, flash point, and fire point of different blends of *Jatropha* and *Madhuca* biodiesels are provide in the supplementary sheet. Figure 2 shows the variation of kinematic viscosity of biodiesel blends as a function of blend percentage. It is observed the kinematic viscosity increases linearly with the blending ratios of biodiesel both in JB and MB. This increase in kinematic viscosity arises due to lower density of diesel than biodiesel. Both JB and MB have showed similar linear behaviour. However, their slope and starting point is relatively different from other literature (Acharya et al. 2017, 2019; Jain and Sharma 2011; Raheman and Ghadge 2007; Rashed et al.2016; Shahabuddin et al. 2012). It may be stated that initial diesel viscosity would decide the rate of which other blends changes. The lower the viscosity greater is the linearity. Viscosity increases with increase in carbon chain length in biodiesel (Shahabuddin et al. 2012). The variation observed by Shahabuddin et al. (2012) is non-linear and is not similar with other literature studies (Fig. 2).

The calorific value of various biodiesel blends decreases linearly as a function of blending percentage (Fig. 3). The increase in biodiesel percentage in biodiesel-diesel blend reduces the calorific value due to

lower calorific value of biodiesel than diesel. Both JB and MB have showed similar behaviour. However, their slope is different from other literature.

3.1.2. Raman Spectra

Figure 4a-b represents Raman spectra of all blending samples of JB and MB with diesel and pure diesel. All blends of JB) and MB show peak at around 2935 cm^{-1} , which corresponds to ν_{CH_2} . The peak at around 1739 cm^{-1} represents $\nu_{\text{C=O}}$ band. The spectra band at 865 cm^{-1} corresponds to $\nu_{\text{R-C=O}}$ and $\nu_{\text{R-C-O}}$. The band at around 378 cm^{-1} represents $\nu_{\text{C-O-C}}$. Both bands at 865 and 378 are due to the formation of ester (Ghesti et al. 2006). The different blends of JB and MB blends show peak at about 1725 cm^{-1} and 1740 cm^{-1} . The spectra at 1725 cm^{-1} and 1740 cm^{-1} represents $\text{C}=\text{O}$ and $\text{C}=\text{C}$ respectively. In almost all blends of JB and MB spectrum between $800\text{--}900\text{ cm}^{-1}$ is present. It is due to $\text{C}_1\text{-C}_2$, C-O stretching and CH_3 rocking (Miranda et al. 2014).

The peak around $1030\text{--}1090\text{ cm}^{-1}$ is due to weak C-C stretching present in all biodiesel blends. The peak scissoring around 1240 cm^{-1} and 1250 cm^{-1} , is seen in higher biodiesel blends and is due to $=\text{C-H}$ bending. Again, CH_2 bending is seen twisting between 1295 and 1300 cm^{-1} and also flapping between 1355 cm^{-1} and 1385 cm^{-1} in all JB and MB blends. The peaks around $1480\text{--}1500\text{ cm}^{-1}$ indicates bending of CH_2 and CH_3 . Again peak at $1650\text{--}1690\text{ cm}^{-1}$ is due to $\text{C}=\text{C}$ stretching. $\text{C}=\text{O}$ stretching is also seen between $1740\text{--}1750\text{ cm}^{-1}$ confirming biodiesel production. The vibration of C-H stretching is present at nearly $2800\text{--}3000\text{ cm}^{-1}$. The peak at $3000\text{--}3050$ is due to the stretching of olefinic $=\text{C-H}$ as per the literature (Miranda et al. 2014).

3.1.3. Fourier transform infrared spectroscopy

The FTIR spectra of pure diesel, JB and MB and their blends with diesel are depicted in Fig. 5a and 5b. The spectral pattern of diesel, all blends of JB with diesel (J5 to J100) and all blending samples of MB with diesel (M5 to M100) lies between the spectral ranges from 500 cm^{-1} to 4000 cm^{-1} . FTIR spectral region from $1688\text{--}1810\text{ cm}^{-1}$ is $\text{C}=\text{O}$, which determines methyl in biodiesel-diesel blends. The spectra area from $1700\text{--}1800\text{ cm}^{-1}$ is owing to stretching of $\text{C}=\text{O}$. This peak is present in fatty acid methyl ester (FAME), J100, M100 and in all blends of JB and MB, which is ester. The absorption from $1300\text{--}1470\text{ cm}^{-1}$ presents in all blends of JB and MB relates to bending of $-\text{CH}_3$ asymmetric stretching.¹⁴ Fig. 5a-b depicts that OH spectra is absent in the absorption range from $3600\text{--}3500\text{ cm}^{-1}$ in diesel and in all blends of JB and MB, indicating the absence of residual alcohol or un-reacted methanol (Shah 2013). A peak present at all blends of MB and JB at 1743.65 cm^{-1} shows the presence of strong ester carbonyl bond ($\text{C}=\text{O}$) signifying FAME or biodiesel. This is one of the major differences of biodiesel from diesel, where peak in the range of $1740\text{--}1755\text{ cm}^{-1}$ is missing (Fig. 5a-b). Infrared spectrum from all samples of both JB and MB at 1745 cm^{-1} depicts the triglyceride ester linkage. The aromatic hydrocarbon is present in the spectrum range from 722 cm^{-1} to 1095 cm^{-1} , whereas spectrum ranging from 1175 to 1245 cm^{-1} indicates C-O absorption (Chatterjee et al. 2015); absorption ranging from $1362\text{--}1373\text{ cm}^{-1}$ designates

the CH₃ group whereas the peak at 1458 cm⁻¹ is the bending absorption of CH₂. Each sample spectrum ranging from 2800 cm⁻¹ to 3000 cm⁻¹ corresponds to C-H. The IR spectra of all blends of JB (J5-J100) and MB (M5-M100) show strong ester linkage at 1752.31 cm⁻¹. IR spectra of blends of JB (J10, J20, J40, J50, J85, J90, J95, J100) and blends of MB (M5, M15, M20, M50, M85, M90, M100) show strong ester peak (C-O vibrations) around 1173–1230 cm⁻¹. No interference was detected in the 1750 cm⁻¹ region, but diesel signals interfered in the region of 1170–1200 cm⁻¹.

The peaks at 2935 – 2931 cm⁻¹ in JB blends (J5-J20, J40, J50, J80-J100), MB blends (M5-M20, M40, M50, M80-M100) and in diesel is due to –C-H₂ stretching; also, spectra ranging from 3100 cm⁻¹ until 2700 cm⁻¹ is absorption for C–H (Bardley 2007). The spectra of all JB and MB blends exhibited –C-H₂ symmetric stretching at 2854 cm⁻¹. The absence of peak in spectra ranging from 3110 cm⁻¹ – 3500 cm⁻¹, in JB and MB indicates low water content. The absorption ranging from 964–1018 cm⁻¹ of all blends of JB and MB is due to –C = C- bending. The characteristics absorption spectra at 1242–1246 cm⁻¹ (J50-J100, M40-M80, M90-M100); 1195 cm⁻¹ (J40, J60-J85,100); and 1167 cm⁻¹(J5-J100, M5-M100) is due to –C-O-C- stretching as per previous literature (Berman et al. 2016).

The calibration model was plotted using Magic Plot Student and Origin 8.2 software. The linearity was determined at selected peak at 1745 cm⁻¹ using base points from 1800 cm⁻¹ to 1600 cm⁻¹. The peak height was correlated against half width half maximum (HMWM). The linearity over the selected peak at 1745cm⁻¹ showed high co-efficient R² = 0.9243 in case of JB and its blends (Fig. 6a) and R² = 0.9184 in case of MB and its respective blends (Fig. 6b).

3.1.4. UV spectroscopic analysis

Figure 7a and 7b show the UV-vis spectra of MB and JB biodiesels. UV spectroscopy indicates the occurrence of conjugated dienes in pure diesel, JB and MB and their blends (J5 to J100 and M5 to M100) with diesel. In the present study all JB and MB blends with diesel were diluted with n-heptane to bring the absorbance to the measurable range of spectrophotometer. The dilution of JB and MB with aromatic compounds i.e., diesel resulted in decrease in absorbance wavelength. The mono and fully saturated FFAE in the UV region are not absorbed with linoleic acid methyl ester and with linolenic methyl ester, but poly-unsaturated samples are absorbed strongly having a unique characteristic spectrum (Chuck et al. 2010).

In blended percentages of JB and MB with diesel, no change was indicated in the characteristic shape of absorbance curve except in the magnitude of absorbance.

The double bonds unsaturated FAME would isomerize to form the more stable conjugated C = C-C = C or C = C-C = O in the degradation of blended biodiesel (Vega-Lizama et al.2015). The oxidative products possessing conjugated double bonds absorb energy both in visible and ultra-violet regions.

The decreasing absorption trend was observed in MB blends from 80M to 100M in the spectral band of 245–275 nm, where M100 has the lowest coefficient (Fig. 7b). The linearity of absorbance declines with the augmentation in biodiesel blending with biodiesel and diesel due to the decreased concentration of aromatic compounds (Fig. 8a-b). The linear line fitted for absorbance versus the different blended percentages of JB and MB biodiesels at 320 nm showed a high coefficient of determination ($R^2 = 0.906$ and 0.963).

3.1.5. Nuclear Magnetic Resonance

^1H NMR spectra of blending samples of JB (J5 to J100) with diesel and MB (M5 to M100) with diesel showed a characteristic singlet peak of methyl ester moiety at 3.6 ppm (Fig. 9a-b). The existence of the peaks has been observed in the spectrum of within 3.59–3.63 ppm in all biodiesel blends. This confirms the production of biodiesel. The decrease trend or absence of the peak at 4.00 ppm indicates the production of biodiesel i.e., assigned to hydrogen of glycerol moiety of *Jatropha* and *Madhuca* oil.

The presence of triplets in the blends of JB (J10, J15, J40, J80, J90) and MB (M5-M20, M40, M60, M80-M100) at 0.8 ppm is methyl hydrogen which makes them distinct from diesel.

In J100 and M100 spectra, peaks situated at 2.1, 2.78 and 5.33 ppm are allylic, bis-allylic and olefinic hydrogen, respectively. The NMR spectra of J100 and M100 showed peak at 1.3, 1.57 ppm and 1.57 ppm are methylene of carbon chain and from beta- carbonyl methylene. The peak at 2.27 ppm confirms the presence of carbonyl group of the ester moiety (Monteiro et al. 2015).

NMR spectrum of diesel showed a group of peaks at 0.8–2.8 ppm which is from aliphatic hydrogen and quite a few peaks at 6.79–7.25 range from aromatic hydrogen (Fig. 10a-b). Table 2 depicts the functional group of the JB and MB samples peaks in ppm of ^1H NMR.

Table 2

Functional group and its respective ppm of the sample's peaks in ^1H NMR.

Sample's where peaks are present	Functional Group	ppm
J10, J15, J40, J80, J90, M5-M20, M40, M60, M80-M100, Diesel	$-\text{CH}_2-\text{CH}_3$	0.84–0.90
J5-J100, M5-M100	$-\text{CH}_2-\text{CH}_3$	0.92–1.29
J15, J20, J90, J95, J100, M15, M100	$-\text{OCO}-\text{CH}_2-\text{CH}_2$	1.54–1.71
J5-J100, M5-M100	$-\text{CH}_2-\text{C}=\text{C}-$	1.96–2.15
J100	$-\text{OCO}-\text{CH}_2$	2.27
J5-J100, M15, M20, M40, M50	$-\text{OCO}-\text{CH}_2$	2.10–2.52
J5-J90, J100	$\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}$	2.75–2.83
J5-J100, M5-M100	$-\text{COOCH}_3$	3.59–3.68
M5-M100, J5-J100	$-\text{CH}=\text{CH}-$	5.24–5.42

^{13}C NMR spectrum shows the presence of methoxy carbon at 51.20 ppm in JB and MB and its blends, confirming the conversion of *Jatropha* and *Madhuca* oils to methyl ester. The characteristic peak of carbonyl carbon at 173.92 is present in all blends of MB and JB. The peaks around 129.8 ppm present in all mixtures of JB and MB with diesel indicates olefinic carbon (unsaturation in methyl esters). The signal at 14.21 present in all blends is due to methyl carbon and peaks around 33 – 21 ppm are due to methylene carbon of long chain FAME. All these peaks are assigned as per literature (Tariq et al. 2011). Table 3 depicts the functional group of the JB and MB samples peaks in ppm of ^{13}C NMR. The different blends of JB and MB ^1H NMR and ^{13}C NMR graphs are provided in supplementary sheet.

Table 3

Functional group and its respective ppm of the sample's peaks in ^{13}C NMR.

Sample's where peaks are present	Functional Group	ppm
J5-J100, M5-M100	methoxy carbon	51.2
J5-J100, M5-M100	methylene and methyl carbons	33.98–14.21
J5-J100, M5-M100	olefinic carbon	129.8–128.03
J15-J100, M5-M100	carbonyl carbon	173.92

3.2 Engine Performance and Emission Characteristics

3.2.1. Brake specific fuel consumption

Figure 11a-b depicts the variation in BSFC with different loads (%) for *Jatropha* (JB) and *Madhuca* (MB) biodiesels. The BSFC of diesel and all JB and MB blends have a decreasing trend with increasing load and an increasing trend with the increase in the proportion of JB and MB in the fuel blends with diesel. The reason behind is percent increase in fuel required to operate engines, is less, as compared to percent increase in brake power, since less proportion of heat is lost at higher loads. Biodiesels having poor spray characteristics, and thus having differences in mixture formation, owing to their higher kinematic viscosity and density, as compared to diesel fuel. Thus, more biodiesel is required to produce the same torque.

The mean BSFC for the JB was higher than that of diesel by 1.65% (J5), 2.51% (J10), 3.45% (J15), 3.50% (J20), 17.5% (J40), 20.4% (J60), 29.01% (J80), and 36.5% (J100). Similarly, in MB mean BSFC with respect to diesel was higher by 4.62% (M5), 7.01% (M10), 8.86% (M15), 8.66% (M20), 13.5% (M40), 21.5% (M60), 32.22% (M80) and 37.2% (M100). Thus, the mean BSFC of JB is better than MB.

Higher biodiesel densities result in higher BSFC values. The densities of M100 and J100 was 3.5% and 4.1% respectively higher than diesel, indicating that consumption of the same fuel on volume basis resulted in 3.5% and 4.1% higher BSFC in case of M100 and J100, respectively. Blends of biodiesel with higher densities at same pressure injection create greater mass injection for the same volume (Raheman and Ghadge 2007).

3.2.2. Brake Thermal Efficiency

Figure 12a-b depicts the change in BTE as a function of load variation for compression ratio 17.5:1 for JB and MB. BTE decreases with increasing concentration of JB and MB blends. The increasing trend of efficiency was also seen for diesel as well as for JB and MB. The maximum BTE for JB and MB were 24.12% for J5 and 24.01% for M5 at full load (100%) as against 24.2% in diesel. The thermal efficiency for JB and MB blends were less than that of diesel. It is due to slow-burning rate, lower calorific values, poor volatility, and high viscosity. It was also observed that variations in BTE was less for various JB and MB blends at full load (100%) conditions than that of part load. It is because at higher load more amount of fuel gets burnt due to the increase in temperature (Dutta and Mandal 2018).

The average decrease in BTE for JB blends was 0.9% (J5), 1.59% (J10), 3.2% (J15), 16.8% (J20), 14.7% (J40), 16.8% (J60), 18.9% (J80), and 23.5% (J100) than diesel. Similar trend was also observed in MB.

3.2.3. Exhaust gas temperature

Figure 13a-b indicates EGT variations with load (%) for different JB, MB blends and diesel. EGT increases with an increase in load because more amount of fuel is needed to generate extra power to resist extra loading. The average increase in EGT for JB blends was 1.07% (J5), 1.29% (J10), 4.39% (J15), 6.42% (J20), 10.25% (J40), 14.93% (J60), 16.17% (J80), and 19.17% (J100) higher than diesel. Similarly, mean increase trend was also obtained in MB as 4.63% (M5), 5.82% (M10), 7.01% (M15), 13.55% (M20), 15.33% (M40), 15.9% (M60), 20.09% (M80), and 27.46% (M100). Thus, JB exhibits better EGT than MB. The higher concentration of biodiesel exhibits higher EGT due to more heat losses, and a higher CN.

The higher CN of the fuel displays lower ignition delay, thus resulting in a shorter premixed combustion period. At higher load (%), both J100 and J20 and diesel have comparable EGT. The mean difference between diesel and J20 was not much at 100% load, probably due to more injection of fuel, resulting in more heat losses.

3.2.4 Carbon Monoxide

CO emissions variation with respect to load for diesel, different blends of JB, MB is illustrated in Fig. 14a-b. CO decreases with an increase in JB and MB blends because higher biodiesel blends result in complete oxidation as against diesel. At the time of biodiesel combustion, the produced CO is perhaps converted to CO₂ by taking a molecule of O₂ from the biodiesel chain. CO initially decreases with full load initially and then again increases swiftly up to full load both in case of JB and MB along with their respective blends. At first in the low load condition, the cylinder temperature was low and later it increased swiftly with increase in load. It is because of more injection of fuel inside the cylinder. The cylinder was initially low in the low load condition, and subsequently, with increase in load, it increased swiftly, on account of the availability of more injection of fuel inside the cylinder. At a higher temperature, engine performance improves with comparative enhancement in the burning rate of fuel thus resulting in decreased CO.

Again, additional loading, requires more fuel leading to formation of smoke. It might prevent oxidation of CO into CO₂ resulting in increment of CO emission. The average decrease in CO for JB blends were 6.66% (J5), 15% (J10), 16.6% (J15), 18.3% (J20), 21.6% (J40), 41.6% (J60), 51.6% (J80), 68.3% (J100) lower than diesel. Similarly, mean decrease trend was also obtained in MB as 10% (M5), 11.6% (M10), 16.6% (M15), 16.6% (M20), 26.66% (M40), 26.66% (M60), 45% (M80), and 58.33% (M100). Thus, CO emissions was less in JB than MB.

3.2.5. Nitrous oxide (NO_x)

Emission of NO_x increases with increase in respective blends of JB and MB with diesel (Fig. 15a-b). It is due to increased EGT, and presence of O₂ content in JB and MB resulting in NO_x formation. At a lower temperature, atmospheric nitrogen exists as a stable diatomic molecule, with a small amount of NO_x, but at a higher temperature, in the combustion chamber of an engine, some diatomic nitrogen breaks down to mono atomic nitrogen, which is reactive. NO_x varies linearly with increase in percentage of load. At a higher load percentage, the fuel-air ratio increases, consequently increasing the average gas temperature in the combustion chamber, thus resulting in NO_x formation on account of its susceptibility to temperature increment.

The average increase in NO_x of JB blends were 4.47% (J5), 12.6% (J10), 8.96% (J15), 0% (J20), 14.17% (J40), 17.1% (J60), 20.14% (J80), 20.14% (J100) lower than diesel. A similar increase in trend was also observed in MB blends. Biodiesel contains more oxygen content than diesel, which leads to higher emissions of NO_x because of complete high combustion temperature (Cheng et al.2009; Devan et al. 2009). Kalam et al. (2011) indicated higher fuel viscosity, which is due to bigger droplet size injection which enhances higher NO_x emissions.

3.2.6. Unburnt Hydrocarbon (UHC)

Figure 16a-b depicts a decrease of UHC emissions with increasing blends of JB and MB. It is due to higher CN of biodiesels which results in delayed combustion. Fuel atomization enhances ignition and mixing resulting in efficient combustion. Fuel properties affect mixing, and the CN plays a major role in combustion. JB and MB made from vegetable oil have higher CN than diesel, thus leading to HC emissions. The average reduction of HC is 6.94% (J5), 11.58% (J10), 16.6% (J15), 25.86% (J20), 43.62% (J40), 46.71% (J60), 49 % (J80), and 48.4% (J100) lower than diesel. Similar decrease in trend was also observed in MB blends as 3.8% (M5), 7.33% (M10), 13.51% (M15), 20.46% (M20), 27.33% (M40), 35.13% (M60), 44.08% (M80), and 49.03% (M100). Thus, JB emits less UHC than MB. With an increase in the concentration of oxygen in blended fuels, more molecules get burnt and thus resulting in the completion of combustion process (Ashraful et al. 2014). Higher oxygen content results in complete efficient combustion, which in turn decreases the concentration of HC emissions concentration. Again, the delay in burning is due to decrease in HC as the biodiesel has greater CN than that of diesel.

Conclusions

The comparative study of MB and JB biodiesels and their respective blends were conducted to assess the engine performance, emissions and the characterization of biodiesels and their blends.

It was observed that BTE decreases with increasing concentration of JB and MB blends. The increasing trend of efficiency was also seen for diesel, JB and MB. The BTE for JB and MB blends were less than that of diesel due to their slow-burning rates, lower calorific values, poor volatility, and high viscosity. It was also observed that the average reduction of HC in MB was less than that in the case of JB as against diesel because of the higher oxygen content in JB. Similarly, the average reduction in CO was observed to be lower in JB than MB as compared to diesel because of higher oxygen content in biodiesel resulting in complete combustion. All blends of JB exhibited less mean BSFC, EGT than MB. The average decrease in BTE was more in JB than MB. JB exhibited less CO and UHC emissions than MB.

Raman spectra showed C=O stretching between 1740-1750 cm^{-1} confirming biodiesel production. FTIR confirms the presence of ester carbonyl group at 1743 cm^{-1} in all blends of JB and MB. The linearity over the selected peak at 1745 cm^{-1} showed a high co-efficient $R^2 = 0.924$ in case of JB and its blends and $R^2 = 0.918$ in case of MB.

The UV-vis linearity for both JB and MB showed a high coefficient of determination ($R^2 = 0.9064$ and 0.9635); again, ^1H NMR and ^{13}C NMR spectra exhibited signal at 3.6 ppm and 51.2 ppm due to the methyl ester moiety and methoxy carbon respectively confirming production of biodiesel. Thus, the characterization techniques showed the quantification of different JB and MB blends of biodiesel.

On the basis of the analysis of performance and emission and characterization results analysis it is concluded that JB was better fuel than MB.

Declarations

Ethics approval and consent to participate: Not Applicable

Consent for publication: Not Applicable

Availability of data & material: Biodiesels were produced, and experiments were performed in IC Engine lab and Central Institute of Technology at Birla Institute Technology, Mesra. Data and materials comply with field standard. All data generated or analysed during this study are included in this article (and supplementary sheet).

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