



Effect of unsaturated fatty acid esters of biodiesel fuels on combustion, performance and emission characteristics of a DI diesel engine

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Abstract

Many studies have reported that exhaust from biodiesel fuel gives higher oxides of nitrogen or lower, while HC and smoke emissions are significantly lower than that of diesel fuel. Possible explanations are: the physical properties and fatty acid composition of biodiesel affecting the spray and the mixture formation with reduced heat losses. The aim of this present investigation is to study the effect of unsaturated fatty acid composition of biodiesel on combustion, performance and emissions characteristics of a diesel engine. For this experiment thirteen different biodiesel fuels with different fatty acid compositions were selected. The performance and emissions tests on a single cylinder DI diesel engine were conducted using same biodiesel fuels. The results showed that biodiesel having more unsaturated fatty acids emit more oxides of nitrogen and exhibit lower thermal efficiency compared to biodiesel having more saturated acids. No significant differences in HC and smoke emissions among the biodiesel fuels were noticed. Thermal efficiency and NO_x emission of saturated biodiesel is comparatively better than other biodiesel. Combustion analysis results show that high unsaturated fatty acid biodiesel has longer premixed combustion and high peak pressure compared to that of high saturated fatty acid biodiesel.

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Keywords: Biodiesel fuel, Pollutant emissions, DI diesel engine, Unsaturated fatty acid esters.

1. Introduction

Biodiesel is a domestically produced renewable fuel capable of strengthening India's energy security by reducing dependence on imported oil. The use of vegetable oil as a fuel for the compression ignition engine is not a new idea. Rudolph Diesel used peanut oil to fuel the diesel engine during the late 1800's. Petroleum based diesel fuel has been the fuel of choice for the diesel engine for many years due to abundant supply and low fuel prices. However, methyl esters of animal and vegetable oils (biodiesel) are again being re-evaluated for use as a fuel for diesel engines due to their cleaner burning tendencies, environmental benefits, and energy security reasons. Several researcher reported that high viscosity and low volatility of pure vegetable oil reduces fuel atomization and increases fuel spray penetration [1,2]. Higher spray penetration and polymerization of unsaturated fatty acids at higher temperatures are partly responsible for the difficulties experienced with engine deposits and thickening

of the lubricating oil [2]. Several approaches have been undertaken to improve the physical properties of vegetable oil e.g. a) addition of chemicals (additives) to improve the air-fuel mixture by decreasing the surface tension, b) preheating to diminish the viscosity for improving the internal formation of the mixture and the combustion, c) mixture with other fuels, to give a better internal formation of the air-fuel mixture as a consequence of a lower viscosity of the blends or to initiate better burning by easier burning components. These techniques are not suitable for a long run test. Later it was realized that the derivatives of vegetable oils in the form of alkyl esters and blends with diesel were more attractive as biodiesel [3]. A number of studies [4 -11] have been carried out on preparation of biodiesel from soybean, Canola, sunflower, rape, palm, and waste cooking oil.

Different biodiesels derived from different sources have been tested in diesel engines for several years. All these biodiesels perform differently in diesel engine in terms of performance, emissions and combustion. Because the physical and chemical properties of biodiesel derived from different sources are not same, those properties have strong relation with the fatty acid composition of biodiesel. The structure of the fatty compounds can also affect other properties of biodiesel such as density, cetane number, heating value and low temperature properties. On the other hand, the need for standardization of biofuels physical and chemical properties has been widely recognized. In fact, it is widely recognized that only the existence of standards and norms may allow engine manufacturers to endorse the use of biofuels in vehicle engines and provide consumer confidence. Currently, several European countries have defined their own norms. It is worth noticing that the majority of existing norms point towards iodine numbers below 115. The index reflects the degree of unsaturation of the oil, i.e., the number of bonds available for oxygenation (the higher the iodine index, the higher the number of bonds suitable for hydroperoxides generation). The presence of hydroperoxides increases the risk of polymerization and acidification and of the appearance of insoluble sediments and gums, which can lead to filter plugging and deposits in the fuel systems.

Esterified soybean oil was tested in a diesel engine by Leo et al [12] and concluded that the engine output was increased by 3 % with HC, CO, smoke and particulate matter showing lesser values whereas NO_x emission was higher for biodiesel operation. Combustion parameters of soybean oil methyl ester namely ignition delay, peak pressure and rate of pressure rise were closer to that of diesel fuel [13]. A DI diesel engine running with olive oil shows same efficiency and engine performance as that of diesel. And a reduction in emission of CO, CO₂, NO_x and SO₂ by 59 %, 8.6 %, 32 % and 57 % respectively was noticed [14]. It was observed that advance in injection timing due to fuel compressibility could lead to a longer premixed burning phase and an increase in the production of NO_x [15]. The advance in injection timing was further investigated and concluded that a carbon-carbon double bond introduces a kink into, and thereby distorts the linearity of, a run carbon-carbon single bonds. It may be that this kinked configuration fosters intra- or inter- molecular interactions in the fuel that reduces compressibility, leading to earlier injection [16]. Earlier injection of biodiesel fuel due to high compressibility leads to higher NO_x. Even then some biodiesel emits lower NO_x. Biodiesel from recycled corn oils containing approximately 75 % methyl oleate, produced significantly lower NO_x than the base line diesel fuel [17]. The objective of this experiment is to investigate the effect of biodiesel unsaturation on engine combustion, performance and emissions characteristics.

2. Experimental methods

2.1 Fuel preparation

Good Quality ($\leq 1\%$ Free Fatty Acid and $\leq 0.5\%$ moisture Content) oil (5L) was taken in a glass reactor fitted with a stirrer, an external heater and a condenser for transesterification process. The oil was heated to 50 °C in the glass reactor and NaOH dissolved with alcohol was added. The contents were heated to the required temperature (60°C). Reflux condenser condenses the evaporated alcohol back into the reactor. Stirring helps to achieve uniformity of reactants, and helps the reaction go faster. Methanol, ethanol and butanol (20, 30, 40 vol % of oil) were taken for the study. Reaction temperature was fixed in the range 60 and 65°C at the boiling temperature of the alcohol. Reaction duration was fixed as 2 hrs under reflux condition. After two hours, the reaction was stopped and the product was allowed to settle in two layers. The upper layer consisted of ester and alcohol and was separated from the bottom layer (glycerin). The upper layer was distilled to remove and recover excess alcohol and the esters were washed with hot water to remove traces of glycerin and alkali. Finally the product was dried for 1 hour in hot air oven at 105 °C. The product was analyzed for fuel properties as per the ASTM standard test methods and subsequently used for engine test.

2.2 Engine test procedure

Figure 1 shows the schematic diagram of the experimental setup. The test engine used was a single cylinder four-stroke air-cooled diesel engine developing 4.4 kW at 1500 rpm. The specifications of the engine are given in Table 1. This engine was coupled to a dynamometer with control system. Time taken for fuel consumption was measured with the help of a digital stopwatch. Chromel alumel thermocouple in conjunction with a digital temperature indicator was used for measuring the exhaust gas temperature. An orifice meter attached with surge tank measures air consumption of an engine with the help of a U tube manometer.

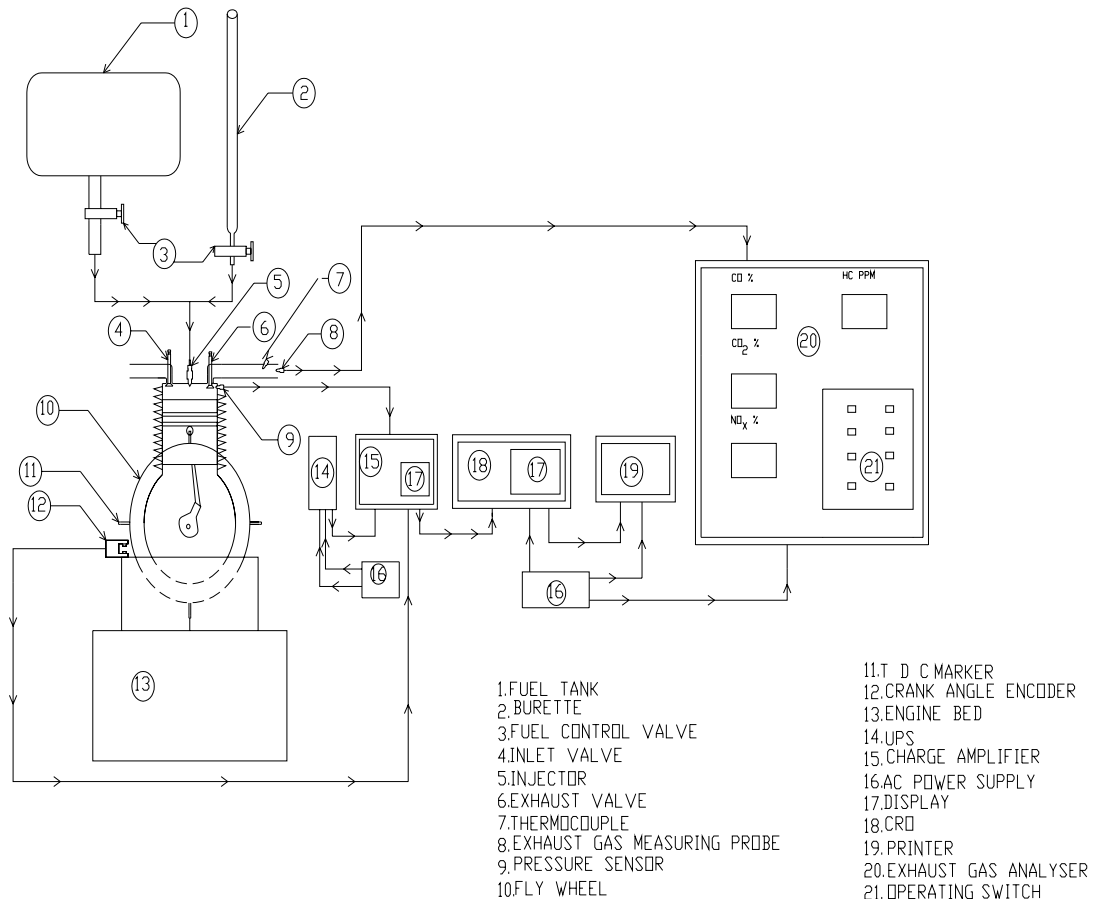


Figure 1. Schematic of experimental set up

Table 1. Engine specifications

Parameter	Description
Model	Kirloskar TAFI
Type	Single cylinder, four stroke, direct injection, bowl-in-piston
Capacity	661 cm ³
Bore & stroke	87.5 mm x 110 mm
Compression ratio	17.5:1
Speed (constant)	1500 rpm
Rated power	4.4 kW
Cooling system	Forced air cooling by flywheel fan
Injection timing	23° bTDC
Injection pressure	200 bar

The surge tank fixed on the inlet side of an engine maintains a constant airflow through the orifice meter. Exhaust emission from the engine was measured with the help of a QROTECH, QEO-402 gas analyzer. Smoke intensity was measured with the help of a Bosch Smoke meter. Bosch Smoke meter usually consists of a piston type sampling pump and a smoke level measuring unit. Two separate sampling probes were used to receive sample exhaust gases from the engine for measuring emission and smoke intensity. A 2-inch as diameter filter paper was used to collect smoke samples from the engine, through smoke sampling pump for measuring Bosch Smoke Number.

3. Results and discussions

3.1 Properties of biodiesel fuels

The results of fuel tests on different biodiesel fuels are summarized in Table 2 and Table 3. A correlation analysis was made to find out the degree of linear association between different biodiesel properties and percentage of unsaturation. The pearson product moment correlation coefficient between different properties and percentage of unsaturation shown in Table 4. The formula used to find out the Pearson correlation coefficient (r) is shown in equation (1).

$$r = \frac{\left(X - \bar{X} \right) \left(Y - \bar{Y} \right)}{\sqrt{\left(X - \bar{X} \right)^2 \left(Y - \bar{Y} \right)^2}} \quad (1)$$

Where, X (% of unsaturation) and Y (properties) are the two variables.

Table 2. Properties of different biodiesel fuels and blend

Biodiesel	Density (kg/m ³) @ 40 °C	Kinematic Viscosity (mm ² /s) @ 40 °C	Cetane Number	Heating Value (MJ/kg)	Iodine Value (g Iodine / 100 g oil)	Saponification Value (mg KOH / g oil)
Sunflower	841	4.87	47.8	39.5	136	193
Rubberseed	839	4.88	51	39.3	120	196
Jatropha	836	4.91	54	39.7	105	198.8
Cottonseed	837	4.95	52.1	39.4	113.2	202.7
Karanja	837	5.00	52	39.5	92	198
JT 80:20	834	5.04	59.2	39.6	88	197.5
JP 50:50	834	5.10	59	39.6	84	198
Neem	832	5.16	58.7	39.8	83.2	201
JT 50:50	835	5.21	62.2	39.9	83	214
SFCt 50:50	834	5.27	54.6	39.9	81.5	210
Mahua	830	5.33	61.4	40.5	80	187
Palm	830	5.39	64	41.0	59	205
JCt 50:50	829	5.45	58	40.2	69.2	215

Where, JT 80:20 = Blend of 80 % of jatropha oil methyl ester and 20 % of tallow oil methyl ester by volume, JP 50:50 = Blend of 50 % of jatropha oil methyl ester and 50 % of palm oil methyl ester by volume, JT 50:50 = Blend of 50 % of jatropha oil methyl ester and 50 % of tallow oil methyl ester by volume, SFCt 50:50 = Blend of 50 % of sunflower oil methyl ester and 50 % of coconut oil methyl ester by volume, JCt 50:50 = Blend of 50 % of jatropha oil methyl ester and 50 % of coconut oil methyl ester by volume

Table 3. Fatty acid methyl composition of different biodiesel fuels

Biodiesel	Fatty acid methyl ester composition (FAME) in wt %								% of US
	Lauric	Myristic	Palmitic	Stearic	Oleic	Lino-leic	Lino-lenic	Others	
Sunflower	0.00	0.10	6.00	5.90	16.00	71.40	0.60	0.00	88.00
Rubberseed	0.00	0.24	12.46	8.32	27.78	37.65	13.44	0.11	78.87
Jatropha	0.00	0.10	14.90	9.50	40.50	34.70	0.30	0.00	75.50
Cottonseed	0.00	0.80	22.90	3.10	18.50	54.20	0.50	0.00	73.20
Karanja	0.01	0.05	9.94	7.83	53.19	19.09	0.04	9.85	72.32
JT 80:20	0.12	0.64	16.58	11.48	40.88	28.34	0.42	1.54	68.18
JP 50:50	0.13	0.48	28.06	7.70	42.66	20.06	0.17	0.74	62.89
Neem	0.83	0.47	18.20	20.10	43.70	16.40	0.30	0.00	60.40
JT 50:50	1.22	1.72	19.94	15.44	41.64	15.62	0.66	3.76	57.92
SFCt 50:50	20.28	10.47	9.34	4.31	19.38	32.63	0.04	3.55	52.05
Mahua	0.00	0.00	24.20	25.80	37.20	12.80	0.00	0.00	50.00
Palm	0.21	1.30	43.90	4.90	39.00	9.50	0.30	0.89	48.80
JCt 50:50	20.88	10.40	13.71	7.16	26.11	18.21	0.12	3.41	44.44

Where, % of US = % of unsaturated fatty acid esters in the respective biodiesel

Table 4. Pearson correlation coefficient (r) between biodiesel properties and percentage of unsaturation

	Density @ 40°C	Kinematic viscosity @ 40°C	Cetane number	Heating Value	Iodine Value	Saponification value
% of US	0.933	- 0.979	- 0.796	- 0.796	0.927	- 0.496

3.2 Analysis of combustion parameters

In this section, the influence of biodiesel unsaturation in relation with properties on different combustion parameters would be discussed in a richer manner. The experimental values of all the above parameters at 100 % load for various biodiesel fuels are listed in Table 5 and Table 6. Using equation (1) correlation analysis between biodiesel properties and combustion parameters was done. The correlation coefficients are listed in Table 7.

Table 5. Experimental results of ignition delay and premixed combustion duration at 100 % load for different biodiesel fuels

Biodiesel	Start of Dynamic Injection (CA deg)	Ignition Delay (CA deg)		Maximum Heat Release Rate (J/ CA deg)	Location of Maximum Heat Release Rate (CA deg)	Premixed Combustion (CA deg)	
		From-To	Duration			From-To	Duration
Sunflower	343	343-356	13	69.98	368	356 - 369	13
Rubberseed	344	344-357	13	71.00	366	357 - 367	10
Jatropha	347	347-359	12	72.10	365	359 - 366	7
Cottonseed	345	345-357	12	73.20	359	357 - 363	6
Karanja	344	344-355	11	72.28	362	355 - 363	8
JT 80:20	342	342-353	11	71.36	365	353 - 368	15
JP 50:50	344	344-355	11	73.27	366	355 - 367	12
Neem	343	343-353	10	83.16	365	353 - 366	13
JT 50:50	345	345-355	10	63.16	366	355 - 367	12
SFCt 50:50	343	343-353	10	75.20	365	353 - 366	13
Mahua	346	346-355	9	77.82	368	355 - 370	15
Palm	347	347-357	10	71.12	364	357 - 368	11
JCt 50:50	346	346-355	9	71.20	367	355 - 368	13

Table 6. Experimental results of total combustion duration and cumulative heat release at 100 % load for different biodiesel fuels

Biodiesel	Peak Pressure (bar)	Location of Peak Pressure(bar)	Diffusion Combustion (CA deg)		Total Combustion Duration (CA deg)	Cumulative Heat Release (J)
			From - To	Duration		
Sunflower	66	373	369 - 405	36	49	1147
Rubberseed	66	372	367 - 406	39	49	1151
Jatropha	66	374	366 - 409	43	50	908
Cottonseed	66	370	363 - 407	44	50	935
Karanja	63	371	363 - 407	44	52	1018
JT 80:20	67	371	368 - 407	39	54	1061
JP 50:50	68	371	367 - 410	43	55	1072
Neem	68	375	366 - 409	43	56	1273
JT 50:50	67	372	367 - 412	45	57	1155
SFCt 50:50	68	370	366 - 410	44	57	1007
Mahua	68	373	370 - 413	43	58	959
Palm	67	375	368 - 415	47	58	1329
JCt 50:50	68	372	368 - 415	47	60	1192

Table 7. Pearson correlation coefficient (r) between biodiesel properties and combustion parameters

"X" variable	"Y" variable	Correlation coefficient
% of Unsaturation	Start of dynamic injection bTDC	0.360
	Ignition delay	0.948
	Maximum heat release rate	-0.180
	Premixed combustion duration	-0.440
	Peak pressure	-0.654
	Diffusion combustion duration	-0.777
	Total combustion duration	-0.969
	Cumulative heat release	-0.283
Density	Start of dynamic injection	0.405
	Ignition delay	0.912
	Maximum heat release rate	-0.332
	Premixed combustion duration	-0.440
	Peak pressure	-0.628
	Diffusion combustion duration	-0.705
	Total combustion duration	-0.909
	Cumulative heat release	-0.288
Cetane number	Ignition delay	-0.779
Heating value	Maximum heat release rate	0.083
	Cumulative heat release	0.398
Iodine value	Start of dynamic injection bTDC	0.323
	Ignition delay	0.899
	Maximum heat release rate	-0.147
	Premixed combustion duration	-0.357
	Peak pressure	-0.474
	Diffusion combustion duration	-0.787
	Total combustion duration	-0.916
	Cumulative heat release	-0.338

From Table 7, it can be observed that the fuel dynamic injection timing is positively correlated with percentage of unsaturation and density. That is the fuel injection timing is faster for higher density fuels. The fuel injection timing is mainly influenced by the fuel properties, such as its bulk modulus and

viscosity. The higher the bulk modulus and viscosity is, the faster the injection timing is. The bulk modulus of unsaturated FAME is higher than that of saturated FAME and increases with increase in density. But still, the injection timing of JT 80:20 is faster than that sunflower oil methyl ester, though the density of JT 80:20 is lower than that of sunflower oil methyl ester. The faster injection timing of JT 80:20 may be believed due to the higher viscosity of JT 80:20 than that of sunflower oil methyl ester. Eventually, it may be stated that the dynamic injection timing would be faster for more unsaturated and for higher density biodiesel fuels. Figure 2 illustrates the variation of start of dynamic injection with percentage of unsaturation.

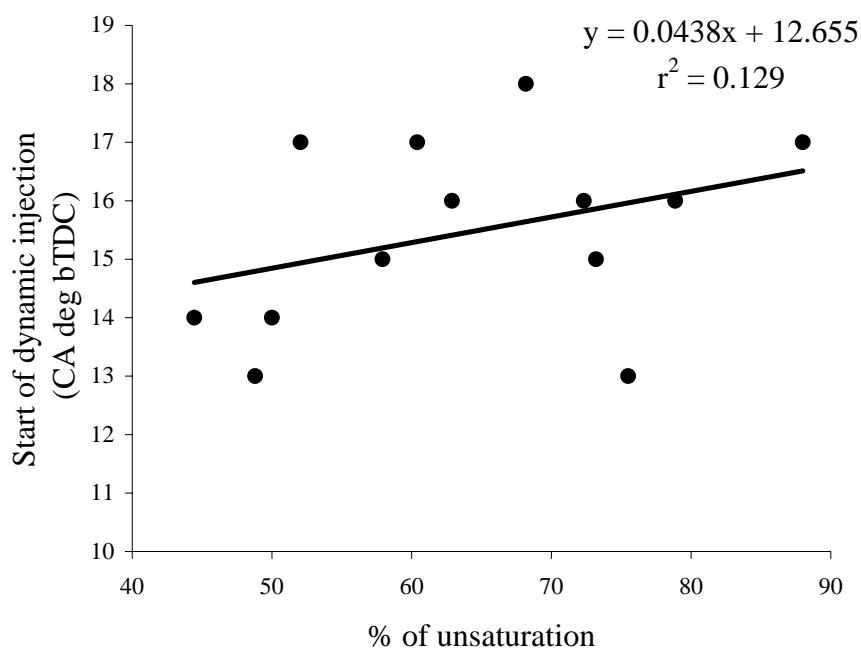


Figure 2. Variation of start of dynamic injection with percentage of unsaturation

The ignition delay of JcT 50:50 is shorter and of sunflower biodiesel is longer as compared to other biodiesel fuels. This result may direct to an idea that the ignitability order of sunflower biodiesel and JcT 50:50 are matched with the order of their cetane number. This may not be true since the JT 50:50 has a higher cetane number than the other candidates but has a longer ignition delay than palm oil methyl ester and JcT 50:50. In reality, the ignitability of an ester fuel depends not only upon the cetane number, but also upon the FAME composition, the residual glycerides, methanol and water in ester fuels. However in the present work only the FAMEs structure and the fuel properties would be discussed. The correlation analysis reveals that the ignition delay exhibits a good correlation with percentage of unsaturation, density, cetane number, and with iodine value.

During the investigation on the relationship between fatty acid ester composition and ignition delay, it was found that the ignition delay increases with increase in unsaturation. By observing Table 3 and Table 5, the above statement can be justified. Biodiesel of palm has a lower percentage of unsaturation, but still has a longer ignition delay as compared to biodiesel of mahua. This may be due to the contribution of stearic acid which is relatively higher in mahua biodiesel than that of biodiesel of palm. In addition to unsaturation, ignition delay increases with fuel density and iodine value. The effect of unsaturation on ignition delay is shown in Figure 3.

A first order differential equation can give the slope between the ignition delay and percentage of unsaturation. By differentiating the slope equation $0.0962x + 4.6838$ (from Figure 3), the gradient between ignition delay can be found as 0.0962. For every single percentage increase in unsaturation may result in an increase of 0.0962 units (in terms of degree crank angle) in ignition delay.

It was found complex to relate the fatty acid ester composition and properties of biodiesel with heat release rate very precisely. Prior to the further discussion, paying attention to the following points may offer a successful understanding on investigation findings.

- Generally, a fuel that has a longer ignition delay should have a higher value of maximum heat release rate as compared fuels those have a shorter ignition delay. However the value of maximum heat release rate not only depends on the ignition delay, but also upon the heating value and the mass fraction burnt for a given crank angle duration.
- Sauter mean diameter (SMD) has shown to increase with increasing surface tension (and hence density) and with increasing viscosity.
- An increases droplet size can reduce the fraction of fuel burned in the premixed combustion phase.
- Density (and hence surface tension) increases with increase in unsaturation.

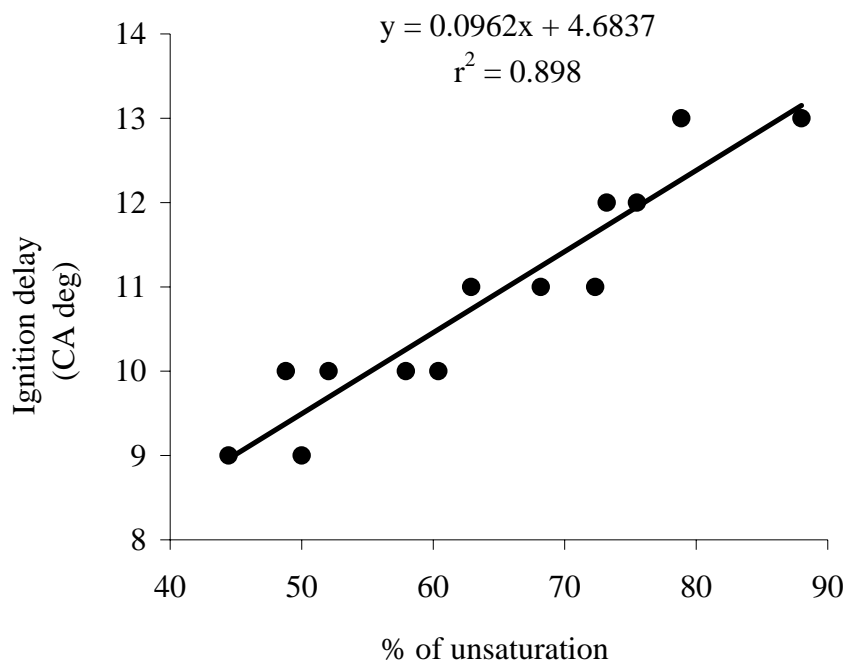


Figure 3. Variation of ignition delay with percentage of unsaturation

From the aforesaid points it may be declared that a fuel with more density may lead to an increased droplet size which in turn reduces the mass fraction burnt in the premixed combustion phase as compared to a lower density fuel. Therefore, a higher density fuel may expect to have a lower value of maximum heat release rate. Also, it was already found that heating value decreases with increase in unsaturation. Hence for given value of mass fraction burnt, the fuel with lower heating value may release lesser heat energy as compared to the fuel with higher heating value. From the above discussion it may be concluded that the value of maximum heat release rate tend to decrease with increase in unsaturation.

From Table 7, it can be observed that the maximum heat release rate is negatively correlated with percentage of unsaturation, density and iodine value; however the correlation coefficients are not so significant. From Table 4, it can be observed that biodiesel of JT 50:50 has a lower value of maximum heat release rate than that of sunflower biodiesel, though the percentage of unsaturation is lower in JT50:50 biodiesel as compared to sunflower biodiesel. The reduction in maximum value of heat release rate may be due to the higher viscosity of JT 50:50. In spite of increase in unsaturation, the differences in maximum value of heat release rate between the various test biodiesel fuels are not so significant. Figure 4 depicts the variation of maximum heat release rate value with percentage of unsaturation. Due to the poor r^2 value, the gradient between maximum heat release rate value and percentage of unsaturation could not be proposed.

Unlike maximum heat release rate, the peak cylinder pressure showed better correlation with biodiesel properties. From Table 7, a good correlation coefficient can be observed between peak pressure and fuel properties (percentage of unsaturation, density, and iodine value). Biodiesel of neem and JcT 50:50 have a higher peak pressure value (68.49 bar) as compared to other biodiesel fuels. The increase in peak

pressure values of neem biodiesel and JcT 50:50 biodiesel are believed to be higher value of maximum heat release rate and lower percentage of unsaturation respectively. On the other hand it was found strange while investigating the relationship between percentage of unsaturation, maximum heat release rate and peak pressure for karanjia biodiesel. Biodiesel of karanjia has a lower percentage of unsaturation and has a higher value of maximum heat release rate than those of sunflower biodiesel, but still has a lower value of peak pressure than that of it. Nevertheless this odd relationship could not be justified very precisely. But still it can be proposed that the cylinder peak pressure decreases with increase in percentage of unsaturation of biodiesel fuels. The variation of peak cylinder pressure with percentage of unsaturation is presented in Figure 5.

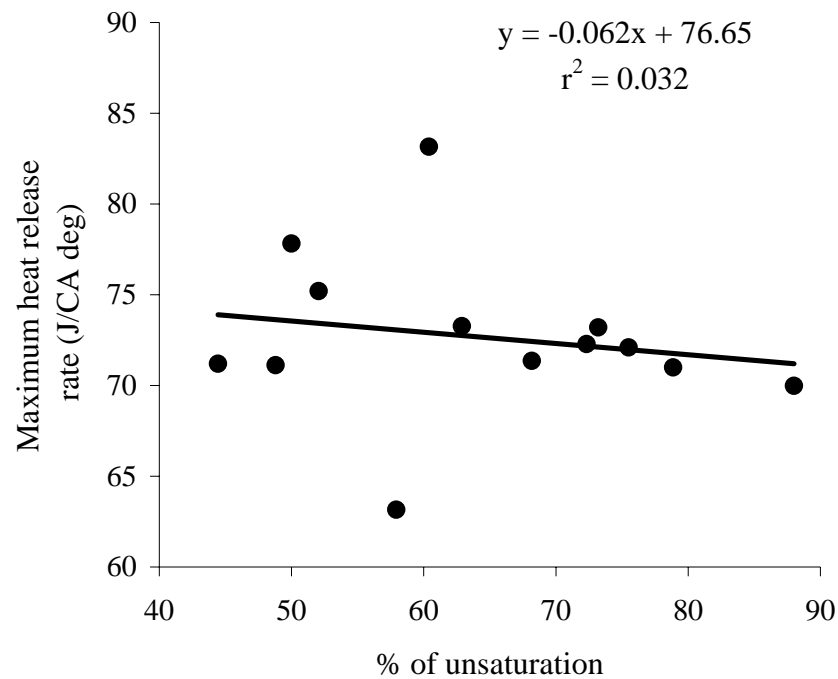


Figure 4. Variation of maximum heat release rate with percentage of unsaturation

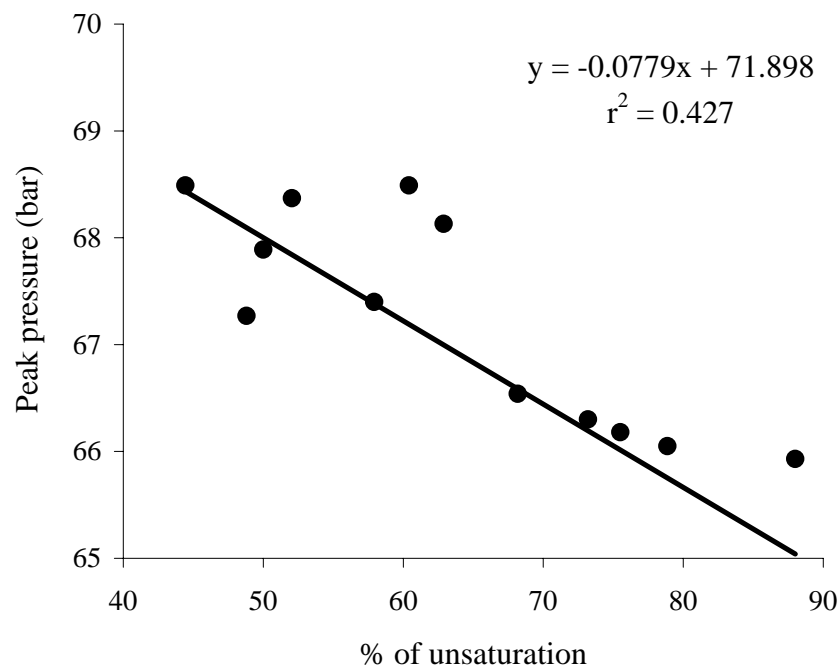


Figure 5. Variation of peak cylinder pressure with percentage of unsaturation

From the equation “ $y = - 0.0624x + 71.209$ ” (from Figure 5), the gradient between peak cylinder pressure and percentage of unsaturation may be proposed as $- 0.0624$. For each unit increase in percentage of unsaturation, a decrease of 0.0624 units (bar) in peak cylinder pressure may be expected. From the correlation analysis it was found that the premixed combustion duration was moderately negatively correlated with percentage of unsaturation, density, and iodine value. The diffusion and the total combustion duration were highly negatively correlated with percentage of unsaturation, density, and iodine value (the correlation coefficients can be seen from Table 7). That is the total combustion duration decreases with increase in percentage of unsaturation (and hence with density, and iodine value). The percentage contribution of premixed and diffusion combustion in total combustion duration for different biodiesel fuels are listed in Table 8.

Table 8. Percentage contribution of premixed and diffusion combustion in total combustion duration

Biodiesel	Total Combustion Duration (CA deg)	% Contribution	
		Premixed combustion	Diffusion combustion
Sunflower	49	27	73
Rubberseed	49	20	80
Jatropha	50	14	86
Cottonseed	50	12	88
Karanja	52	15	85
JT 80:20	54	28	72
JP 50:50	55	22	78
Neem	56	23	77
JT 50:50	57	21	79
SFCt 50:50	57	23	77
Mahua	58	26	74
Palm	58	19	81
JCt 50:50	60	22	78

From Table 8, it can be observed that even for a same total combustion duration, the percentage contribution of premixed and diffusion combustion are different for different fuels. For example, sunflower biodiesel and rubber seed biodiesel are having the same value (49 CA deg) of total combustion duration in terms of crank angle degrees. But the percentage contribution of premixed and diffusion combustion in total combustion duration is different for these two biodiesel fuels. The above finding can be explained by interpreting Figure 6 that illustrates the variation of percentage of premixed and diffusion combustion with start of dynamic injection.

The interpretation on Figure 6 reveals that if the start of dynamic injection before TDC increases (i.e. dynamic injection timing becomes faster), the percentage of premixed combustion increases with a corresponding decrease in percentage of diffusion combustion. In other words, the percentage of diffusion combustion increases with slower dynamic injection timing. Therefore, more unsaturated biodiesel can have faster dynamic injection timing (due to higher density) and result in a decrease in diffusion combustion duration. It may therefore be concluded that the diffusion and total combustion duration decreases with increase in percentage of unsaturation, density and iodine value. The variation of total combustion duration with percentage of unsaturation is shown in Figure 7 along with fitted line equation.

From the fitted line equation $y = - 0.2806x + 72.202$, it can be proposed that every one per cent increase in unsaturation may result in a decrease of 0.2806 units (CA deg) in total combustion duration.

The cumulative heat release showed a similar trend as that of total combustion duration with percentage of unsaturation, density, and iodine value. From Table 6, it can be observed that the cumulative heat release is negatively correlated with percentage of unsaturation, density and iodine value. The total combustion duration decreases with increase in unsaturation and therefore, it is obvious that the cumulative heat release tend to decrease with increase in unsaturation. Figure 8 depicts the variation of cumulative heat release with percentage of unsaturation.

Due to very poor R^2 value, slope between cumulative heat release and percentage and percentage of unsaturation may not be proposed.

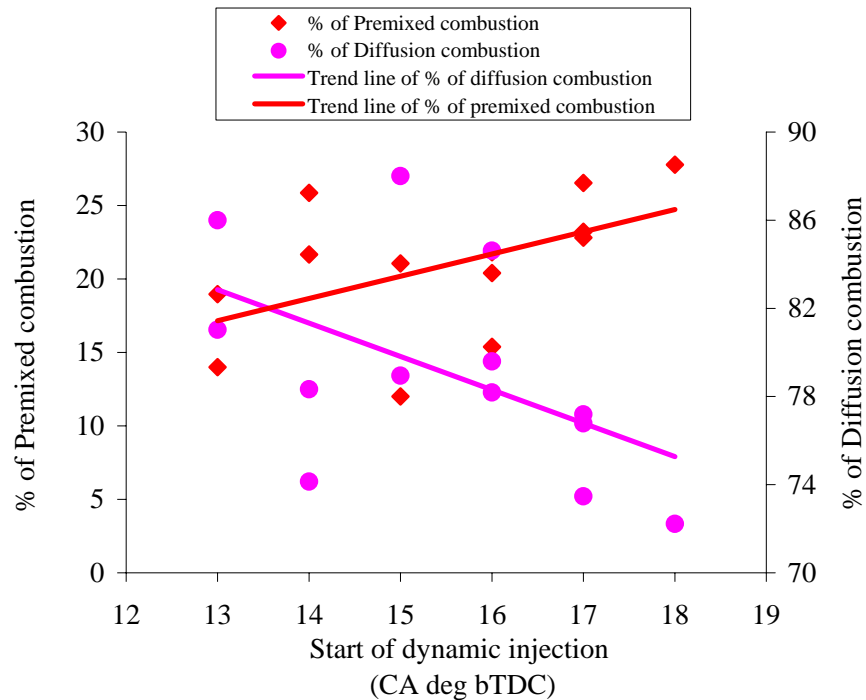


Figure 6. Variation of percentage of premixed and diffusion combustion with start of dynamic injection

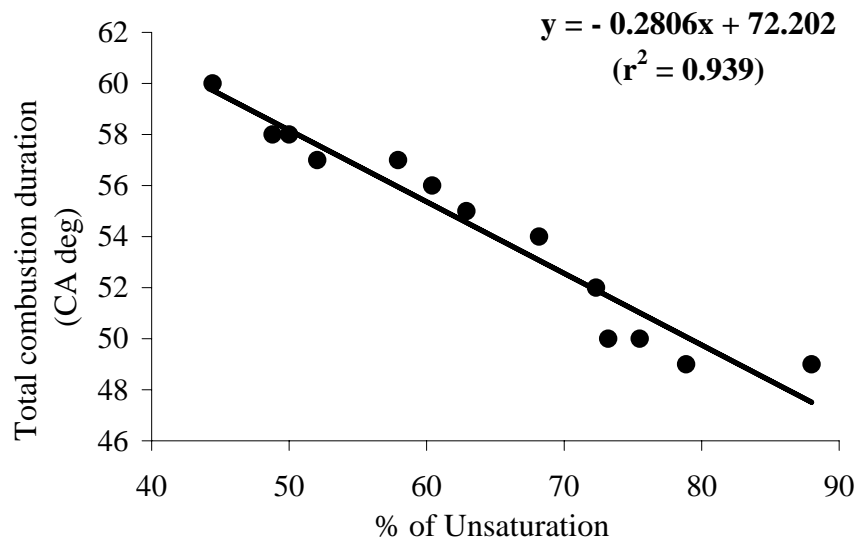


Figure 7. Variation of total combustion duration with start of dynamic injection

3.3 Analysis of performance and pollutants emission parameters

In this section, the influence of biodiesel properties on the test engine's performance and emissions will be discussed in a richer manner. The following parameters are considered for the investigation.

- Brake Specific Fuel Consumption (BSFC)
- Brake Specific Energy Consumption (BSEC)
- Brake Thermal Efficiency
- Exhaust Gas Temperature (EGT)
- Oxides of Nitrogen (NO_x)
- Carbon Monoxide (CO)
- Hydrocarbons (HC)
- Smoke

The experimental values of all the above parameters at 100 % load for various biodiesel fuels are listed in Table 9. The correlation coefficient between percentage of unsaturation and performance parameters are listed in Table 10.

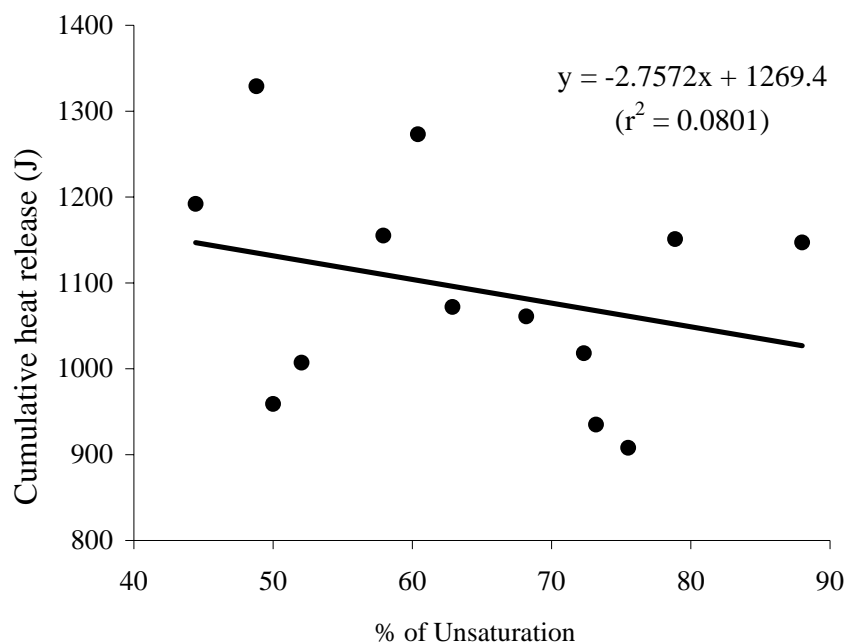


Figure 8. Variation of cumulative heat release with percentage of unsaturation

Table 9. Experimental values of performance and emission parameters of test engine with various biodiesel fuels at 100 % load

Biodiesel	% of US	BSFC (kg/kWh)	BSEC (MJ/kWh)	Brake Thermal Efficiency (%)	Exhaust Gas Temp. (°C)	NO _x (g/kWh)	CO (g/kWh)	HC (g/kWh)	Smoke (BSU)
Sunflower	88.00	0.3342	13.20	27.27	365	14.378	3.618	0.389	0.8
Rubberseed	78.87	0.3345	13.15	27.38	360	14.137	2.583	0.374	0.9
Jatropha	75.50	0.3305	13.12	27.44	358	13.644	3.099	0.331	1.2
Cottonseed	73.20	0.3293	12.98	27.74	355	13.317	2.582	0.345	0.9
Karanja	72.32	0.3276	12.94	27.82	350	13.400	2.583	0.345	1.2
JT 80:20	68.18	0.3259	12.91	27.89	348	12.940	2.581	0.316	1.3
JP 50:50	62.89	0.3254	12.89	27.93	343	12.675	2.065	0.288	1.3
Neem	60.40	0.3235	12.88	27.96	342	12.593	2.064	0.345	1.4
JT 50:50	57.92	0.3236	12.91	27.88	339	12.517	2.063	0.316	1.4
SFCt 50:50	52.05	0.3225	12.87	27.98	338	12.342	2.579	0.287	1.5
Mahua	50.00	0.3162	12.81	28.11	335	11.932	1.545	0.344	1.3
Palm	48.80	0.3110	12.75	28.23	334	11.700	1.061	0.287	1.4
JCt 50:50	44.44	0.3150	12.66	28.43	330	11.495	2.061	0.287	1.6

The engine performance parameters could highly be influenced by the fuel properties such as mass based heating values and density. From Table 9, it can be observed that for a given operating conditions the engine consumes higher quantity of rubber seed oil methyl ester as compared to the other biodiesel fuels. That is BSFC for rubber seed oil methyl ester is more than that of other biodiesel fuels. The investigation

on the influence of fuel properties on engine's performance reveals that the increase in BSFC may be believed due to the increase in density. Increasing density may increase BSFC because the fuel injector injects a constant volume, but larger mass, of the more dense fuels.

When compared to sunflower oil methyl ester, rubber seed oil methyl ester has a lower density but results in a higher BSFC. The possible reason for this increase may be due to the lower mass based heating value of rubber seed oil methyl ester. Because, as compared to sunflower biodiesel, the lower mass based heating value of rubber seed biodiesel requires larger mass of fuel to maintain constant energy input to the engine. The effect of fatty acid ester composition on BSFC is easily understandable. It can be stated that BSFC increases with increase in percentage of unsaturation, since an increase in percentage of unsaturation will result in an increase in density and in a decrease in heating value. From Table 10, a strong positive correlation can be observed between BSFC and percentage of unsaturation. Figure 9 depicts the variation of BSFC with percentage of unsaturation.

Table 10. Pearson correlation coefficient (r) between performance parameters and biodiesel properties

	BSFC	BSEC	Brake Thermal Efficiency	Exhaust Gas Temperature
% of US	0.938	0.939	-0.940	0.989
Density	0.937	0.926	-0.926	0.924
Heating value	-0.921	-	-	-

Where, BTE = Brake Thermal Efficiency

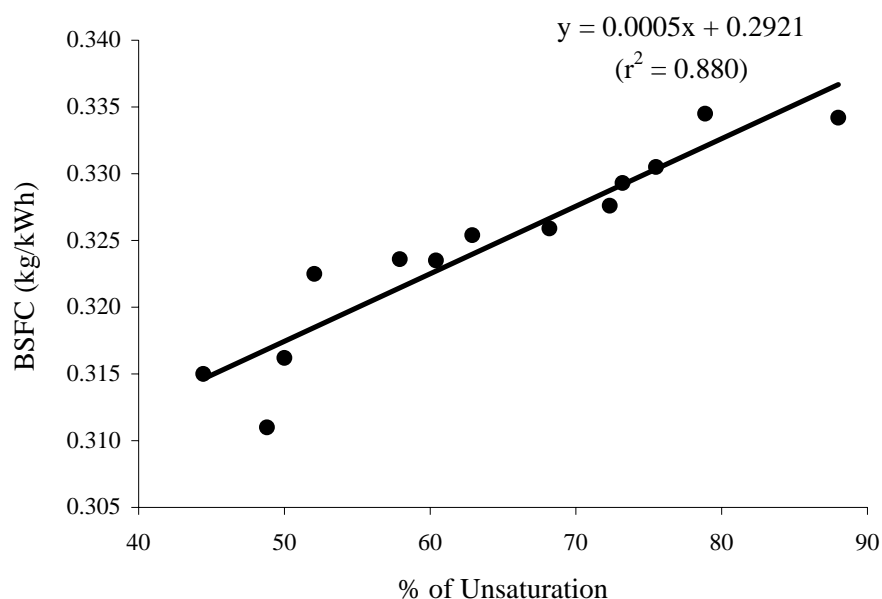


Figure 9. Variation of BSFC with percentage of unsaturation

From the slope equation ($0.0005x + 0.2921$), every one per cent increase in unsaturation may result in an increase of 0.0005 units (g/kWh) in BSFC.

In order to compare the performance of a given engine that is operated with different fuels, the term BSEC could provide clearer picture than the term BSFC. The BSEC can be obtained by multiplying the heating value with BSFC. From Table 9, it can be observed that the BSEC is higher for sunflower biodiesel and lower for JcT 50:50 biodiesel as compared to other biodiesel fuels. It is obvious that the trend of BSEC should follow the same as that of BSFC. It can also be noted that the BSFC for sunflower biodiesel is lower than that for rubber seed biodiesel, but still the BSEC for sunflower biodiesel is higher

than that for rubber seed biodiesel. Similarly the engine has a higher BSFC and a lower BSEC when it is operated with JcT 50:50 biodiesel as compared to palm biodiesel. The possible cause for the above findings may be due to the lower heating value of rubber seed biodiesel as compared to sunflower biodiesel and lower heating value of JcT 50:50 biodiesel as compared to palm biodiesel. From the correlation analysis, it was found that the BSEC was highly positively correlated with density and percentage of unsaturation (from Table 10). It is due to the fact the BSFC increases with increase in percentage of unsaturation and with density. It can also be noted that the BSFC increases with decrease in heating value. Figure 10 depicts the variation of BSEC with percentage of unsaturation.

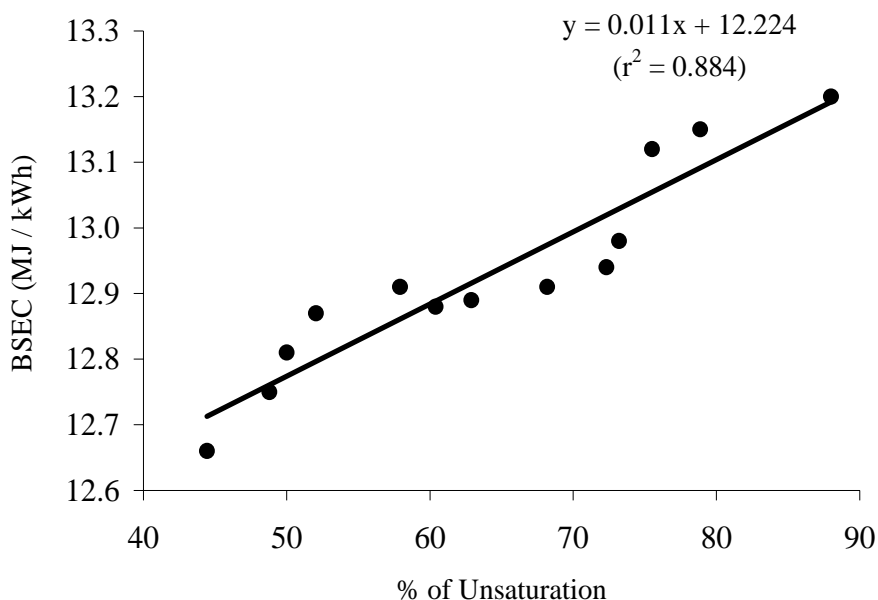


Figure 10. Variation of BSEC with percentage of unsaturation

From the slope equation $y = 0.011x + 12.224$, the gradient between BSEC and percentage of unsaturation can be proposed as 0.01. Every one per cent increase in unsaturation may result in an increase of 0.011 units (MJ/kWh) in BSEC.

Brake thermal efficiency shown in Table 9 is higher for JcT 50:50 blend and is lower for sunflower biodiesel. This shows that the order of magnitude of brake thermal efficiency for the biodiesel fuels are matched exactly with the reverse order of BSEC. From the correlation analysis, it was found that the brake thermal efficiency decreases with increase in percentage of unsaturation and density. This is due to the fact that the BSEC decreases with increase in percentage of unsaturation and density. The variation of brake thermal efficiency with percentage of unsaturation is illustrated in Figure 11.

From the slope equation $y = -0.0236x + 29.366$, a decrease of 0.0236 units (%) could be predictable for every one per cent increase percentage of unsaturation.

The exhaust gas temperature shown in Table 9 is higher for sunflower biodiesel and lower for JcT 50:50 blend. The order of magnitude of EGT matched with order of percentage of unsaturation. That is a more unsaturated biodiesel can produce higher value of EGT as compared to a less unsaturated one. This is believed due to the more afterburning stage for higher unsaturated biodiesel fuels which may increase the exhaust gas temperature. A high degree of positive correlation was found to exist between exhaust gas temperature and percentage of unsaturation from the correlation analysis. The variation of exhaust gas temperature with percentage of unsaturation is shown in Figure 12.

From the slope equation $y = 0.825x + 293.15$, the gradient between EGT and percentage of unsaturation could be predictable. In other words, every one per cent increase in unsaturation may result in an increase of 0.825 units ($^{\circ}\text{C}$) in exhaust gas temperature.

Once again a correlation was performed (using equation (1)) to allow a determination as to whether the measured emission values are correlated with biodiesel properties and unsaturation. The correlation coefficients are shown in Table 11.

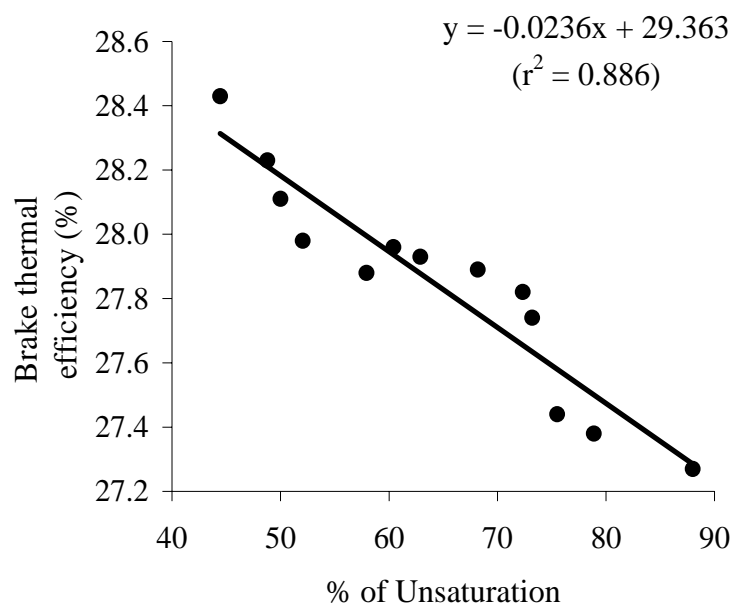


Figure 11. Variation of brake thermal efficiency with percentage of unsaturation

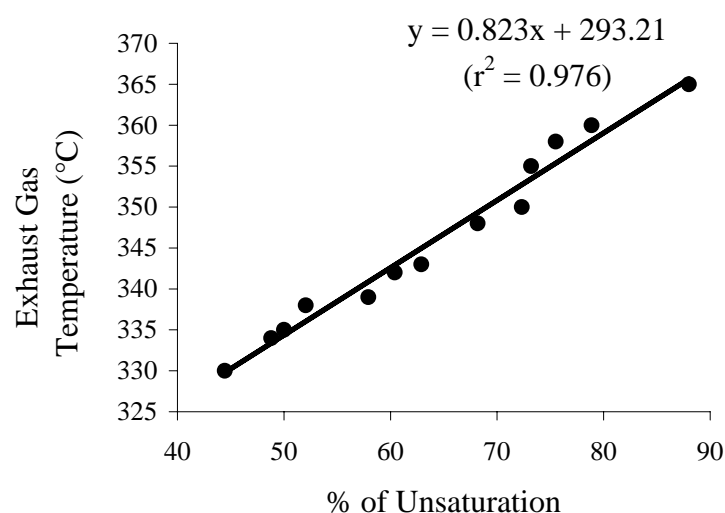


Figure 12. Variation of exhaust gas temperature with percentage of unsaturation

The effect of fatty acid ester composition on emissions is implicit in density, cetane number or in iodine value. NO_x was found to be highly positively correlated with density, iodine value and percentage of unsaturation. Table 9 shows that the NO_x for sunflower biodiesel is higher and for JcT 50:50 is lower than the other biodiesel fuels. From the investigation, it was found that the NO_x concentration in the exhaust emissions increases with increase in biodiesel density, iodine value and percentage of unsaturation. This can be explained as follows.

- Increasing density may increase NO_x because the fuel injector injects a constant volume, but larger mass, of the more dense fuels. Since a larger mass of the fuel is burned more NO_x is produced.
- Another possibility is that the higher density which results in higher bulk modulus can advance the effective injection timing and thereby cause NO_x to increase. The injection advance results in longer ignition delay since the fuel is injected in air at lower temperatures and pressure.
- It could also be noted that the iodine value which is a direct measure of unsaturation is highly inversely correlated with cetane number. Thus, excessive ignition delay and poor combustion performance may also be proposed as a cause of the higher NO_x .

It may be expected that the lean flame region (LFR) is one of the major contributing regions to nitric oxide (NO) formation since it is first part of the spray to burn and has the longer post-flame residence time. With lower cetane number fuel, the ignition delay is longer and more fuel is present in the LFR when combustion starts. The larger ignition delay produces a higher gas temperature upon combustion early in the cycle, and more NO could be formed in the LFR. It can be recalled that the cetane number decreases with increase in unsaturation. Hence, it may be concluded that, NO_x concentration in the exhaust emissions increases with increase in biodiesel density, iodine value, and percentage of unsaturation. Figure 13 depicts the variation of NO_x with percentage of unsaturation.

Table 11. Pearson correlation coefficient (r) between emission parameters and biodiesel properties

"X" variable	"Y" variable	Correlation coefficient
% of US	NO _x	0.986
	CO	0.817
	HC	0.773
	Smoke	- 0.887
Density	NO _x	0.957
	CO	0.822
	HC	0.700
	Smoke	- 0.844
Cetane number	NO _x	- 0.830
	CO	- 0.864
	HC	- 0.659
	Smoke	0.739
Iodine value	NO _x	0.940
	CO	0.841
	HC	0.831
	Smoke	- 0.917

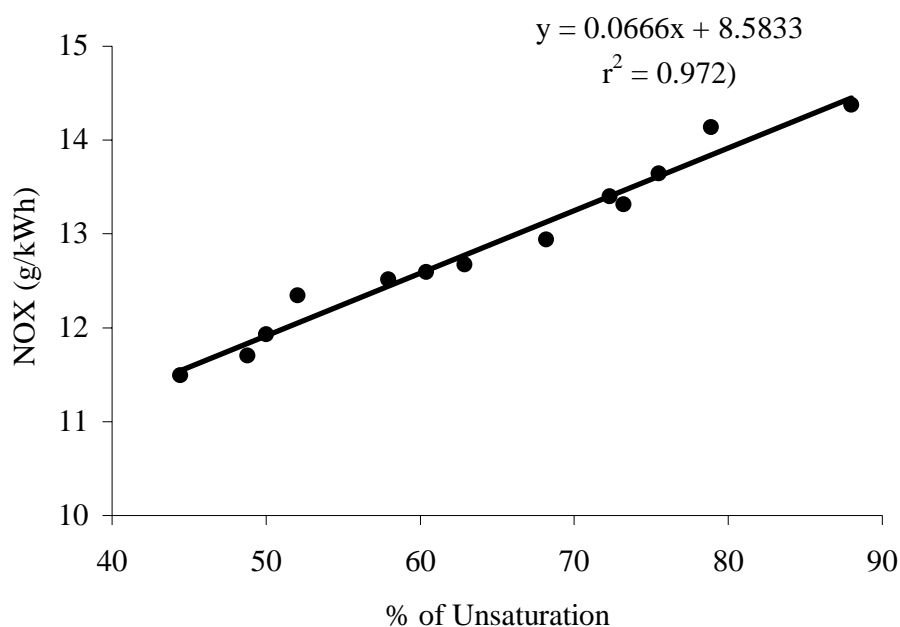


Figure 13. Variation of NO_x with percentage of unsaturation

From the proposed slope equation $y = 0.0666x + 8.5833$, an increase of 0.0666 units (g/kWh) in NO_x might be expected for every one percent increase in unsaturation.

The carbon monoxide (CO) and hydrocarbon (HC) emission levels in diesel engines are small in absolute terms, so that they are of no real concern. But still it is fairly reasonable to discuss the effect of biodiesel

properties and fatty acid composition on CO and HC emissions. The correlation analysis reveals that the CO and HC emissions are positively correlated with percentage of unsaturation. That is CO and HC emissions are increases with increase in unsaturation. This may be believed due to the lower oxygen concentration in higher unsaturated biodiesel fuels. The oxygen content decreases with increase in unsaturation. Carbon monoxide is believed to be formed at the borders between the LFOR and LFR during the early stages of spray combustion. At this stage, primary reaction can take place and the initial hydrocarbons may reduce to CO, H₂, and H₂O. As the local temperature is not enough at this stage, very little oxidation reactions take place. Increase in unsaturation may tend to decrease the gas temperature. The reduced gas temperature may not provide a positive situation for complete oxidation reaction thereby increase the CO concentration.

On the other hand, it may be believed that the lean flame out region (LFOR) is one of the main contributors to the HC concentration in the exhaust. LFOR is the region that is nearer to the leading edge of the spray (downwind). In this region the mixture is too lean to ignite or support the combustion. If the ignition delay is larger, the droplets and vapour will be carried farther away from the centre line of the spray in the downward direction, resulting in a wider LFOR. If unsaturation increases, the ignition delay increases which result in an increased width of LFOR. Increased width of LFOR eventually increases the HC concentration in the exhaust. The variations of CO and HC with percentage of unsaturation are illustrated in Figure 14 and Figure 15.

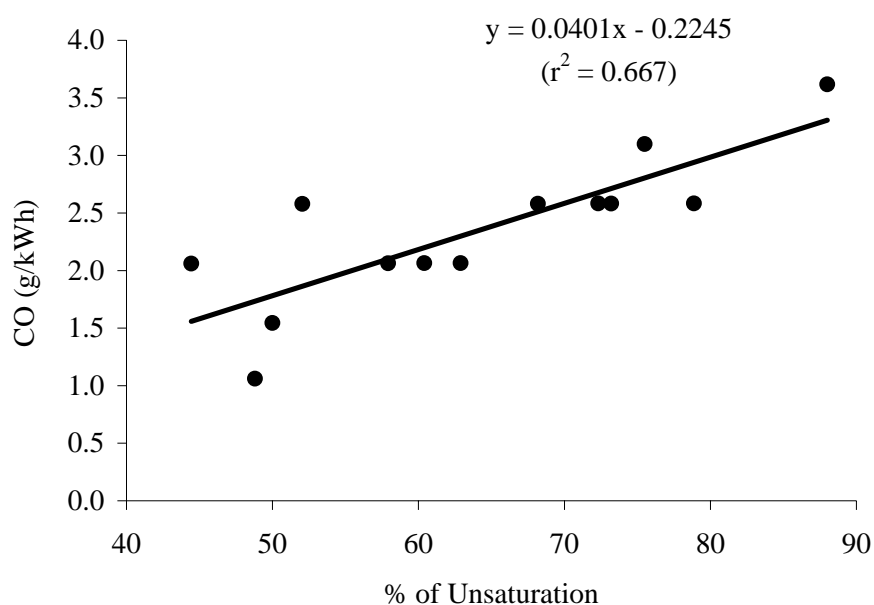


Figure 14. Variation of CO with percentage of unsaturation

From the equation $y = 0.041x - 0.2245$, the probable increase in CO may proposed as 0.0401 units (g/kWh) for every one per cent increase in unsaturation.

The equation $y = 0.002x + 0.2001$ provides the gradient between HC emission and percentage of unsaturation as 0.002. An increase of 0.002 units (g/kWh) may be expected for every one per cent increase in unsaturation.

Smoke is emitted as a product of the incomplete combustion process, particularly at maximum loads. Smoke particles are formed from the fuel deposited on walls or in the spray core, especially under elevated loads. It was found from the investigation that the smoke intensity for biodiesel fuels decreases with increase in percentage of unsaturation. It is necessary to discuss the mechanism of smoke formation to justify the investigation findings. The smoke formation mechanism can be explained as follows.

- The evaporation, ignition and combustion of a fuel droplet begin at its outermost layer.
- As the outer layer of the fuel droplet burns, heat is produced and transferred to the inner layers. Therefore, the availability of oxygen for reaction is lesser at the interior layers.

- Hydrogen molecules have greater affinity towards oxygen compared to carbon molecules. As such hydrogen molecules combine with oxygen molecules more quickly leaving little or no oxygen for carbon molecules to react.
- The carbon molecules, therefore fail to burn within the limited time that is available for combustion. These unburned carbon molecules appear as smoke in the exhaust gases.

It must be noted that the unsaturation is nothing but the deficiency of hydrogen atoms. Greater unsaturation represents the greater deficit of hydrogen atoms. Therefore, for a given supply of air (and oxygen) to the engine, if unsaturation is more, carbon molecules could find more oxygen molecules to react with due to the less number of hydrogen molecules. Therefore, the biodiesel with more unsaturation can have a higher degree of oxidation process than that of the biodiesel with less unsaturation. Hence, it can be stated that the smoke intensity decreases with increase in unsaturation. Figure 15 illustrates the variation of smoke with percentage of unsaturation.

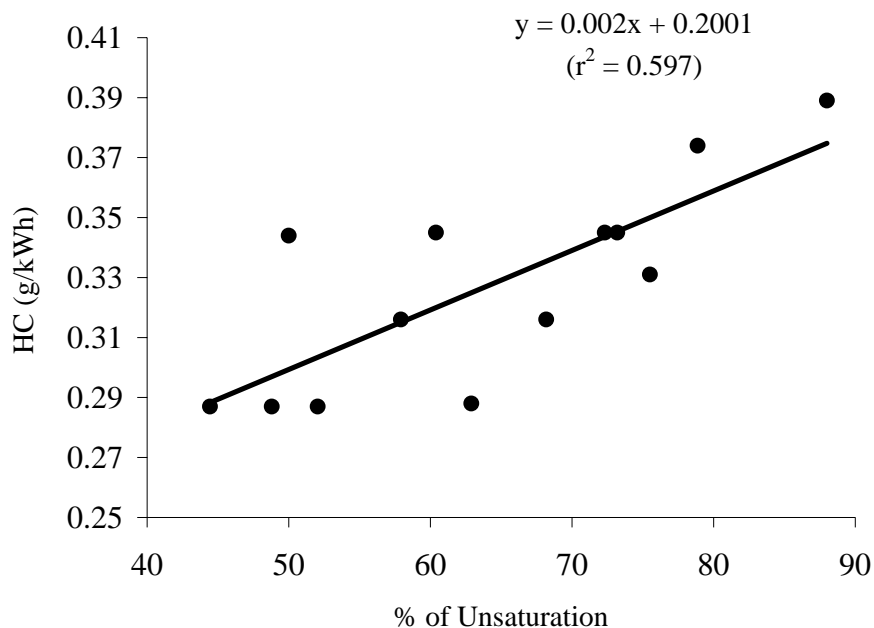


Figure 15. Variation of HC with percentage of unsaturation

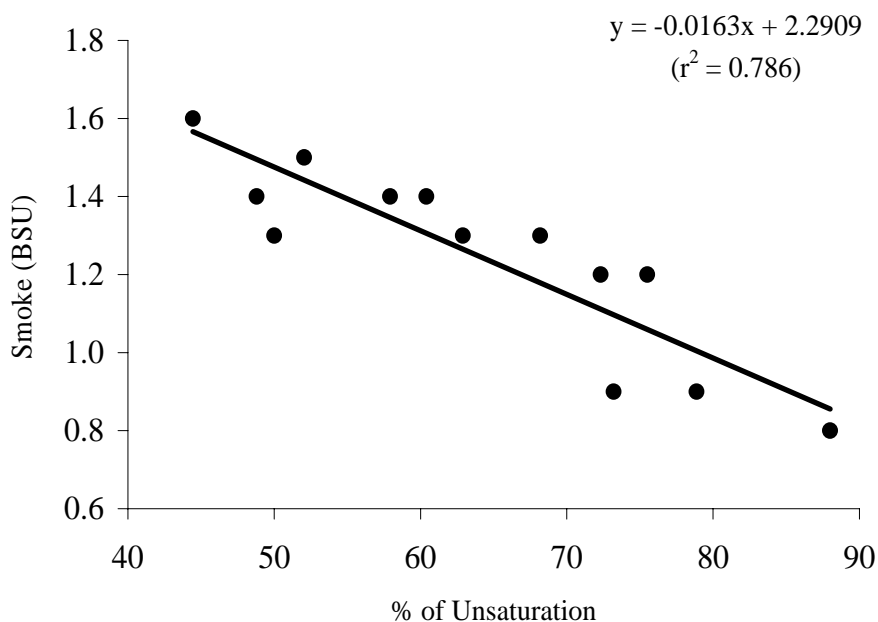


Figure 16. Variation of smoke with percentage of unsaturation

Where, BSU = Bosch Smoke Unit in Figure 16. The gradient between smoke and percentage of unsaturation can be found as -0.0163 (from the equation $y = -0.0163 + 2.2909x$). It can be proposed that for one per cent increase in unsaturation may result in a decrease of 0.0163 units (BSU) in smoke.

4. Conclusions

An experimental investigation was conducted to evaluate and compare the Combustion, performance and exhaust emission levels of different biodiesel fuels in a fully instrumented, single cylinder, direct injection diesel engine. A series of tests were conducted using different biodiesel fuel, with the engine working at 1500 r.p.m. The following conclusions are drawn from the experimental study

1. Biodiesel fuel with more unsaturated fatty acid composition has more density but less viscosity.
2. Biodiesel with more unsaturated has lower cetane number and heating value respectively.
3. Biodiesel with high-unsaturated fatty acid composition shows lower thermal efficiency compared to high saturated fatty acid composition.
4. More unsaturated biodiesel fuels emits lower HC, CO and Smoke emissions compared to highly saturated biodiesel fuel as .
5. More NO_x was observed in case of high unsaturated biodiesel, The biodiesel having 50/50 saturated and unsaturated fatty acid composition like MOME proves a better fuel in terms of thermal efficiency and NO_x emission. The data observed as 27.91 % and 12.34 g/ kWh, which is a NO_x neutral fuel with penalty of 1.75 % efficiency compared to diesel fuel.
6. Maximum gas pressure and exhaust gas temperature was observed in case of high unsaturated biodiesel.
7. Heat release rate and cumulative heat release rate is lower in case of high- unsaturated biodiesel fuel.
8. A general conclusion is that all the tested bio-diesel fuels can be used safely and advantageously in the present engine. All the biodiesel fuels tested can be used in forms of blends to compromise the NO_x emissions and thermal efficiency.

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