COMPARATIVE ASSESSMENT OF THE EMISSION CHARACTERISTICS OF FIRST, SECOND AND THIRD GENERATION BIODIESELS AS FUEL IN A DIESEL ENGINE

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ABSTRACT

The present study aims to investigate emission characteristics with the B20 blend level of first, second and third generation biodiesels. The engine, a naturally aspirated, single cylinder, diesel engine, was operated at 1500 rpm engine speed and at different engine loads with intervals of 25%. Also, the engine is analyzed by Diesel-RK mathematical tool and emission characteristics such as smoke, carbon dioxides (CO2), particulate matter (PM), nitric oxide (NO) and summary of emission (SE) were obtained. Numerical simulation is performed using pure diesel (D100), first, second and third generation B20 (80% diesel + 20% biodiesel). Results of reduction in emissions for biodiesel blend were found to be lower than diesel fuel as smoke (BSN) by 54.68% for jojoba, PM by 4.8% for coconut, 52.0% for jojoba and 7.1% for fish oil, NO by 38.2% for jatropha curcas, and SE by 8.8% for soybean, 12.9% for jatropha curcas and 8.8% for spirulina but carbon dioxides was found to be higher by 0.38% for rapeseed, 0.61% for fish oil. The blend of B20 shows a decrease in emissions at 1500 rpm with 100% engine load. The numerical results are verified against experimental results conducted under the same operating conditions.

Keywords: Compression ignition engine; Biodiesel; Emission; Numerical

INTRODUCTION

Biodiesel is an alternative and renewable fuel for compression ignition engine, can be formed from different categories of edible and non-edible vegetable oils from first, second and third generation renewable fuel. The special effects on exhaust gas emissions such as smoke, unburnt hydrocarbon (UHC), carbon monoxide (CO), carbon dioxides (CO2), Nitric oxide (NO) and particulate matter (PM) emissions and slightly reduced engine performance using biodiesel as an alternative fuel in place of petroleum fuel [1-3]. The effect of emission parameter on a direct injection diesel engine using five different categories of biodiesel is investigated. The results show reduction in NO_X by 31.2% of chicken fats, PM emission by 93.78% for poultry fats and reductions in smoke emission by 93.8% for sunflower at full load condition [20]. The effect of microalgae Chlorella protothecoides with diesel is evaluated and compared on a 4-stroke, single-cylinder air-cooled diesel engine at different engine speeds. Results found are reduction in performance with brake power by 7.0%, torque by 4.9%, exhaust gas temperature by 6.1% and emission of CO by 28%, CO2 by 4.2% and NOX by 7.4%, but increase in fuel consumption by 10.2% and O2 by 15.8% for microalgae chlorella protothecoides (B100) as compared to diesel (D0) [21].

Investigated the effect of ternary blends (diesel + cotton oil + n-butanol) as a volume basis at different engine speed (1800 rpm to 4400 rpm) on a direct injection turbocharged diesel engine. The results show that reduction in thermal brake efficiency (BTE), brake power (BP), brake torque (BT), and exhaust gas temperature (EGT), but increase of fuel consumption with increasing blend ratio of n-butanol. The emission parameters show the reduction in CO, UHC, but increase in oxides of nitrogen (NO and NO2). Higher reduction in CO and UHC emissions in 30% diesel + 10% cotton oil + 60% n-butanol and 20% Diesel +20% cotton oils + 60% n-butanol blends and increase of fuel consumption [22]. The utilization of 10%, 15%, and 20% pentanol and Calophyllum inophyllum (CI) biodiesel blend on a water-cooled, direct-injection diesel engine is investigated for performance, emission, and combustion parameters at different engine speeds (1200 rpm to 2400 rpm). The results show that the addition of pentanol with CI 20 in blend improved fuel properties. Also, thermal efficiency and engine power are higher and fuel consumptions lowered by using 15% and 20% blends of pentanol as compared to CI20. The emission parameters are slightly increase, such as NO, CO and UHC for 15% and 20% blends of pentanol and a significant *This paper was recommended for publication in revised form by Regional Editor Yasin Karagöz*

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reduction in smoke emission but better than CI 20 blend ratio [23]. Evaluated effects of water (5, 10 and 15%) and biodiesel (10, 20, 30 and 40%) addition with diesel at engine speeds (1000, 2100 and 3000 rpm) with a load of 20%, 50% and 80%. The thermal efficiency, fuel consumption, carbon monoxide emissions increase and exhaust gas temperature, smoke emission and NOX are reduced emission with increasing water percentage [25].

A number of studies was carried out investigating the blend ratio of diesel and biofuels on CI engine combustion, performance and emission at different operating conditions. In this respect, the present study carried out to investigate the emission characteristics and comparison of emulsion B20 (80% diesel+20% biodiesel) of a diesel engine by using three different categories of biofuels from first, second and third generation. Thus, the primary ambition of present investigation is to emphasize the enormous potential of biodiesel as the renewable energy source in the transport industry and potential to avoid the energy and environment crisis.

MATERIAL AND METHOD

Fuel Properties

The Alternative fuel properties (first, second and third generation) are one of the key reasons responsible for the quality of fuel mixing rate and burning procedure. Fuel density, viscosity, fuel calorific value, cetane number, and flash point are the properties dependably emphasized by researchers to define the effects of an alternative additive on emission characteristics of a diesel engine [1-17, 29]. Properties of the first (coconut, palm, rapeseed, and soybean), second (cottonseed, jatropha, jojoba, and Karanja), and third (fish oil, microalgae spirulina, waste oil and animal fats) generation biodiesel feedstocks are shown in Table 1, Table 2 and Table 3. The blended fuel properties as shown in Table 4.

 Table 1. First generation biodiesel [1-7]

Properties	Coconut	Palm	Rapeseed	Soybean
Density (kg/m ³) at 40 °C	872.1 at 303K	860-900	874 - 920.9	887 at 15 °C
Viscosity (mm ² /s) at 40	2.80 at 313K	4.42	6.92-34.32	4-4.63
Calorific value (MJ/kg)	37.785	34-36.77	36.7-40.5	37.53
Cetane number	60	62-63	49.5–54.4	51
Flash point (°C)	391	174	236	> 120

Table 2. Second generation biodiesel [2, 8-11]

Properties	Cottonseed	Jatropha	Jojoba	Karanja
		curcas		
Density (kg/m ³) at 40 °C	874–911	863.6-873	863-866	876–890
Viscosity (mm ² /s) at 40	4-6.37	4.78-6.71	19.2–25.4	4.37–9.60
Calorific value (MJ/kg)	39.5-40.1	39.8–42	42.76-47.38	36–38
Cetane number	41.2–59.5	57.2-63	63.5	52–58
Flash point (°C)	210-243	238	292	163–187

 Table 3. Third generation biodiesel [1, 12-17]

Properties	Fish oil	Spirulina	Waste	Animal fats
			cooking oil	
Density (kg/m ³) at 40 °C	870-885	860	871 at 20 °C	882.5
Viscosity (mm ² /s) at 40	4.14-4.74	5.66	4.6	6.3
Calorific value (MJ/kg)	40.05-41	41.36	37.5	39.93
Cetane number	51.5-52.6	-	51	52.34
Flash point (°C)	114-173	130	453	-

Fuel	Density (kg/m ³)	Viscosity (mm ² /s)	Calorific	Cetane	Flash
	at 40 °C	at 40 °C	value	number	point
			(MJ/kg)		(°C)
D100	830	2.8	42.5	48	74
BC20	838.75	2.8	41.51	50.49	137.4
BPA20	836.24	3.06	40.73	50.91	94
BRA20	839.2	3.35	41.3	49.33	106
BSO20	841.85	3.0	41.46	48.47	83.2
BCO20	839.2	3.0	41.87	50.4	101.2
BJA20	836.98	3.12	41.93	49.92	106.8
BJO20	836.86	4.12	42.55	51.22	117.6
BKA20	839.56	3.06	41.14	48.83	91.8
BFA20	833.2	3.03	41.9	48.95	82
BSP20	836.24	3.22	42.26	-	85.2
BWC20	838.52	3.1	41.46	48.62	149.8
BAF20	840.92	3.29	41.96	48.91	-

Table 4. B20 blend for first, second and third generation of biodiesels

Experiment Method

The engine was operated with different engine load with a step of 25% and regular diesel at 1500 rpm constant speed to achieve an engine steady state condition. After achieving the steady-state condition and with three- times repeatability of readings, data were recorded into the data-acquisition system. After completing the test for one test fuel, the engine was run after a few minutes to ensure the achievement the steady-state condition and prediction of test results considering average of three times reading for diesel fuel. Test engine is illustrated in Fig. 1 and Test conditions are shown in Table 5. The single cylinder diesel engine connected eddy current dynamometer in present study for proposed tool validation. An eddy current dynamometer of 10 kg capacity with maximum output of 3.5 kW is used for this study.



Figure 1. Test engine

Parameter	Value
Initial pressure	1.0 bar
Cylinder/type	single cylinder/four strokes
Initial temperature	300 K
Piston temperature	530 K
Liner temperature	420 K
Head temperature	500 K
Compression ratio	17.5
Bore & stroke	80 mm & 110 mm
Connecting rod length	235.0 mm
Fuel injection timing	23.5° CA b TDC
Fuel spray angle	70°
Fuel injection pressure	220 bar
Inlet valve open/closed	4.5° before TDC/35.5° after BDC
Outlet valve open/closed	35.5° before BDC/4.5° after TDC
Piston	bowl shape
Cooling system	water
Fuel	Diesel, biodiesel

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Uncertainty Analysis Of Experiment And Numerical Results

The uncertainty of instruments and impact of the varying environmental condition. The uncertainties of the instruments are temperature sensor (± 0.15), pressure sensor (± 0.5), speed sensor (± 1.0), crank angle encoder (± 0.2), load cell (± 0.2), burette for fuel measurement (± 1.0), smoke (± 1.0), CO2 (± 1.0), NOX (± 0.5), CO (± 0.3), HC (± 0.1) and O2 (± 0.3). The total percentage of uncertainty in experimental and numerical results depends on magnitude the uncertainties of all the sensors as shown in Table 6. The overall uncertainty in the experimental setup measurement is 2.2% of the measured value.

Table 6. Uncertainty of instruments		
Instruments	Uncertainty (%)	
Temperature sensor	±0.15	
Pressure sensor	±0.5	
Speed sensor	±1.0	
Crank angle encoder	±0.2	
Load cell	±0.2	
Burette for fuel measurement	±1.0	
Smoke	±1.0	
Exhaust gas analyzer		
СО	±0.3	
CO ₂	± 1.0	
HC	±0.1	
O ₂	±0.3	
NO _X	± 0.5	

Table 6. Uncertainty of instruments

Governing Equation Of Diesel-Rk Model

The governing equation for numerical simulation tool of Diesel-RK model are energy, species, heat release rate, NOX formation, smoke formation using in equation (1-12) [5, 19, 20, 27, 28]:

Conservation Of Species

In The species conservation equation considering the evaluation and destruction of each species has been considered on mass fraction basis, which is described in the following equations (1-2) [39]:

$$\frac{\mathrm{dm}}{\mathrm{dt}} = \sum_{j} \dot{m}_{j} \tag{1}$$

$$Y_i = \frac{m_i}{m} \tag{2}$$

Conservation Of Energy

General conservation of energy equation written by Fivelend and Assanis for a thermodynamic system is shown in equation (3):

$$\frac{d(mu)}{dt} = -P \frac{dv}{dt} + \frac{dQ_{ht}}{dt} + \sum_{j} \dot{m}_{j} h_{j}$$
(3)

Heat Model

Multi-zone combustion model used in Diesel-RK model where combustion cylinder heat release rate is defined in four phases are in equation (4-7):

Ignition delay period model

$$\tau = 3.8 \times 10^{-6} (1 - 1.6 \times 10^{-4} . n) \sqrt{\frac{T}{P}} \exp\left(\frac{E_a}{8.312T} - \frac{70}{CN + 25}\right)$$
(4)

Premixed combustion period model

$$\frac{dx}{d\tau} = \varphi_o \times \left(A_0 \left(\frac{m_f}{V_i} \right) \times (\sigma_{ud} - X_0) \times (0.1 \times \sigma_{ud} + X_0) \right) + \varphi_1 \times \left(\frac{d\sigma_u}{d\tau} \right)$$
(5)

Controlled combustion period model

$$\frac{dx}{d\tau} = \varphi_1 \times \left(\frac{d\sigma_u}{d\tau}\right) + \quad \varphi_2 \times \left(A_2\left(\frac{m_f}{V_c}\right) \times (\sigma_u - X) \times (\alpha - X)\right) \tag{6}$$

Burning period model

$$\frac{dx}{d\tau} = \varphi_3 A_3 K_T (1 - X) \left(\xi_b \alpha - X\right) \tag{7}$$

No_x Formation Model

 NO_X emission produced within the combustion chamber in diesel engine are grouped in form of nitric oxide (NO) and nitrogen dioxide (NO2) using equation (8-12):

$$\begin{bmatrix} \mathbf{O}_2 \end{bmatrix} \longleftrightarrow \begin{bmatrix} 2\mathbf{O} \end{bmatrix} \tag{8}$$

$$[N_2] + [O] \leftrightarrow [NO] + [N]$$
⁽⁹⁾

$$\begin{bmatrix} N \end{bmatrix} + \begin{bmatrix} O_2 \end{bmatrix} \longleftrightarrow \begin{bmatrix} NO \end{bmatrix} + \begin{bmatrix} O \end{bmatrix}$$
(10)
$$\frac{d[NO]}{d\theta} = \frac{P \times 2.333 \times 10^{-7} . e^{-\frac{38020}{T_b}} \begin{bmatrix} N_2 \end{bmatrix}_e . \begin{bmatrix} O \end{bmatrix}_e . \left\{ 1 - \left(\begin{bmatrix} NO \end{bmatrix} / \begin{bmatrix} NO \end{bmatrix}_e \right)^2 \right\} }{R . T_b . \left(1 + \frac{2365}{T_b} . e^{-\frac{2365}{T_b}} . \begin{bmatrix} NO \end{bmatrix} \\ \begin{bmatrix} O \end{bmatrix}_e \right) } . \frac{1}{\omega}$$
(11)

Smoke (Bsn) Model and Particulate Matter (Pm) Formation Model

PM emission by Alkidas method is selecting for calculation of particulate matter emission which is given in equation (12). PM emission consists of list of species. Soot has a dominant fraction. PM emission as a function of soot emission [15]:

$$[PM] = Z_{PM} 565 \left(\ln \frac{10}{10 - \text{Bosch}} \right)^{1.206}$$
(12)

RESULTS AND DISCUSSION

The comparison of the in-cylinder pressure, heat release rate (HRR), smoke emission between experimental results and numerical results are demonstrated in Figure (2-4). In the experiment and numerical analysis the same operating conditions as shown in Table 5. The trend of results curve was similar during the intake, compression, combustion and exhaust processes and percentage of error deviation between experiment and numerical results as shown in Table 7. The numerical analysis performed using commercial solver Diesel-RK results show that higher cylinder pressure by 4.3%, reduction in maximum heat release rate by 5.9% and smoke emission by 4.6%. The numerical results and experimental results percentage difference acceptable range. The necessary changes are made in the manuscript at section 3.1 validation simulation tool.



Figure 2. Shows cylinder pressure versus crank angle

Figure 3. Shows cylinder heat release rate versus load



Figure 4. Shows smoke emission versus load

Table 7	Experimental	results and	numerical	results
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Characteristics	Experimental	Numerical	Error (%)
Cylinder Pressure (MPa)	8.8	9.2	4.3
Maximum heat release rate (J/CA)	85.3	80.2	5.9
Smoke emission (BSN)	3.1	3.25	4.6

Emission Parameters

The numerical results in this paper shows the effects of biodiesels (B20) as characterized by, first, second and third generation biofuels, on the emission characteristics when used as fuel for a direct-injection diesel engine. This section details the related emission characteristics for diesel engine such as smoke, PM, CO₂, NO and summary of emission.

Smoke Emission

Figure 5 shows the variation of smoke emissions with load for first, second and third generation biodiesel. The smoke emission is affected by advancing injection timing, fuel mixing rate, viscosity, oxygen contents, incomplete combustion, the temperature of the combustion zone, engine load, speed, injection pressure [2, 12, 20, 23, 25]. At full load, smoke emission (BSN) is found to be 3.2 for diesel, 3.05, 3.1, 3.12, 3.1 for first-generation biodiesels coconut, palm, rapeseed, and soybean, respectively, 2.85, 3.45, 1.45, 2.89 for second generation biodiesels cottonseed, jatropha, jojoba, and Karanja respectively and 3.05, 3.08, 3.1, 3.06 for third generation biodiesel fish oil, microalgae spirulina, waste oil and animal fats respectively. The minimum smoke emission observed, is 1.45 BSN for jojoba biodiesel, and is about 54.68% as compared to diesel fuel and other biodiesels. For all the tested biodiesels lesser smoke emissions are obtained as compared to regular diesel fuel. Well, it is the cause due to advanced injection timing and a higher percentage of oxygen contents within biodiesel [30-33]. The fuel-air mixture preparation is good in premixed combustion phase due to oxygen contents, which results in better combustion and low smoke emission [42].

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Figure 5. Comparison of variation of smoke emission from first, second and third generation biodiesel at different engine load for B20

Carbon Dioxide Emission

Figure 6 shows the variation of carbon dioxide (CO2) with load for first, second and third generation biodiesels. The CO2 emission is affected by the heating value of fuel, exhaust gas temperature, oxygen contents, complete combustion, engine load, speed [13, 19, 21]. At CR17.5 on full load condition, CO2 emissions (g/kWh) are found 825.5 for diesel, 839.5 for coconut, 844.57 for palm, 828.65 for rapeseed, 836.1 for soybean of the first generation biodiesels, respectively, 846.7 for cottonseed, 823.46 for jatropha, 883.7 for jojoba, 857.6 for Karanja, of the second generation biodiesels respectively and 830.55 for fish oil, 836.24 for microalgae spirulina, 835.46 for waste oil and 834.87 for animal fats of the third generation biodiesel respectively. The CO2 emissions are obtained higher by 0.38% for rapeseed, and 0.61% for fish oil, but are reduced for jatropha curcas by 0.27% within blend of B20 as compared to diesel fuel. For all tested biodiesel obtained CO2 emissions are higher as compared to regular diesel fuel, but lesser only for jatropha curcas, due to complete combustion and higher oxygen percentage within the combustion chamber, as compared to diesel fuel. The fuel-air mixture preparation is good in premixed combustion phase due to oxygen contents which results in better combustion and higher CO2 emission [34-36].

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Figure 6. Comparison of variation of CO₂ emission from first, second and third generation biodiesel at different engine loads for B20

Particulate Matter Emission

Figure 7 shows the specific particulate matter (PM) emission changes at different load for three tested generation biodiesel (B20) samples and diesel. The PM emission is affected by oxygen contents, engine load and speed, injection timing, improper combustion, combustion temperature, and air-fuel mixing rate [1, 5, 19, 20, 27]. The PM emission produced in the combustion chamber due to the improper combustion process. High combustion flame temperature, injection timing, percentage of oxygen, speed and load lead to lower PM emission [37-41]. At CR17.5 with high fuel injection pressure of 220 bar on full load condition, the PM (g/kWh) was found to be 0.798 for diesel, 0.759 for coconut, 0.776 for palm, 0.772 for rapeseed, 0.767 for soybean (first generation), 0.698 for cottonseed, 0.891 jatropha curcas, 0.383 for jojoba, 0.72 Karanja (second generation) and 0.742 from fish oil, 0.767 spirulina, 0.772 for waste oil, and 0.756 for animal fats (third generation). The minimum PM emission were found to be 4.8% for coconut (first generation), 52.0% for jojoba (second generation) and 7.1% of fish oil (third generation) within a blend of B20 compared to diesel fuel. For all tested biodiesels, lower PM emissions are obtained as compared to regular diesel fuel, due to complete combustion and higher oxygen percentage, compared to diesel fuel.

The fuel-air mixture preparation is good in premixed combustion phase due to oxygen contents which results in better combustion and lowered PM emission.



Figure 7. Comparison of variation of PM emission from first, second and third generation biodiesel at different engine load for B20

Nitric Oxide Emission

Figure 8 shows the specific nitric oxide (NO) emission changes at different loads for the three generation biodiesel (B20) samples and diesel. The NO emission is affected by engine load and speed, in-cylinder peak pressure and temperature, calorific value of fuel, viscosity, injection timing, oxygen content, and cetane number [3, 12, 13, 18, and 27]. The NO emission is produced within the cylinder due to high temperatures during the combustion process. At CR17.5 with the full load condition, the NO (g/kWh) was found to be 16.65 for diesel, 16.63 for coconut, 15.68 for palm, 16.4 for rapeseed, 14.64 for soybean (first generation), 23.4 for cottonseed, 10.3 for jatropha curcas, 28.3 for jojoba, 22.64 for Karanja (second generation) and 18.2 for fish oil, 14.65 for spirulina, 16.12 for waste oil, and 17.81 for animal fats (third generation). The minimum NO emission was found to be 12.0% for soybean (first generation), 38.2% for jatropha curcas (second generation) and 12.01% for spirulina (third generation) within a blend

of B20, compared to diesel fuel. The NO emission was found higher 41.16% for jojoba and 8.5% for fish oil, compared to diesel, due to higher oxygen and viscosity, compared to diesel [43-45].



Figure 8. Comparison of variation of NO emission from first, second and third generation biodiesel at different engine load for B20

Summary of Emissions

Figure 9 shows the changes in summary of emission (SE) at different loads for three biodiesel generation (B20) samples and diesel. The SE is affected by engine load, combustion temperature, viscosity, oxygen contents. At CR17.5 with the full load condition, the SE was found 5.1 for diesel, 4.91 for coconut, 4.83 for palm, 4.92 for rapeseed, 4.65 for soybean (first generation), 5.66 for cottonseed, 4.44 jatropha curcas, 5.32 for jojoba, 5.63 for Karanja (second generation) and 5.1 for fish oil, 4.65 for spirulina, 4.87 for waste oil, and 5.1 for animal fats (third generation) respectively. The minimum SE emissions were found to be 8.8% for soybean (first generation), 12.9% for jatropha curcas (second generation) and 8.8% for spirulina (third generation) within a blend of B20, compared to diesel, due to higher oxygen and complete combustion, as compared to diesel. Should be clarified from figure 9, the SEs decrease with increase in engine load, shown at the right hand side of 25%.

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Figure 9. Comparison of variation of SE emissions from first, second and third generation biodiesels at different engine loads for B20

CONCLUSION

The effects of first, second and third generation biodiesel blends and diesel on the emission characteristics is investigated. The proposed Diesel-RK model will reproduce the smoke, PM CO2, NO and SE trends of different fuels obtained in the single cylinder diesel engine. The critical decisions are as follows.

- Similar numerical and experimental results for tool validation, the numerical results show that reduction in heat release rate and smoke emission, but higher cylinder pressures as compared for diesel.
- The smoke emission is observed to be lower for biodiesel than diesel and increases with an increase in engine load.
- NO emission is lower by 12.0%, 38.2% and 12.01% for soybean, jatropha curcas and spirulina biodiesel, respectively, but higher by 41.16% for jojoba and 8.5% of fish oil, as compared to diesel. It is also observed that the increase of engine load increases the NO emissions at 1500 rpm and CR17.5.

- Similarly, PM and SE emissions were also lower for testing of first, second and third generation biodiesel than diesel. Engine load can further decrease these emissions.
- Biodiesels showed higher CO2 emissions by 0.38% for rapeseed, 0.61% of fish oil, but the reduction for jatropha curcas about by 0.27% within a blend of B20, compared to diesel fuel due to complete combustion as compared to diesel.

The numerical analysis results show that soybean (first generation), jatropha curcas (second generation) and spirulina (third generation) biodiesel superior fuel for compression ignition engine due to lower NO emission obtained.

NOMENCLATURE

τ	time (second)
Ea	Activation energy of fuel
$dx/d\tau$	Heat release rate (J/sec)
dx/dt	Heat release rate (J/deg.)
b TDC	Before top dead center
BDC	bottom dead center
BSN	Bosch smoke number
CR	Compression ignition
PM	Particulate matter
rpm	Revolution per minute
MPa	Mega Pascal
NO	Nitric oxide
TDC	Top dead center
D100	Pure diesel
B20	80 diesel + 20 biodiesel
BC20	Coconut oil biodiesel
BPA20	Palm biodiesel
BRA20	Rapeseed biodiesel
BSO20	Soybean biodiesel
BCO20	Cottonseed biodiesel
BJA20	jatropha curcas biodiesel
BJO20	Jojoba oil biodiesel
BKA20	Karanja biodiesel
BFA20	fish oil biodiesel
BSP20	microalgae spirulina biodiesel
BWC20	Waste cooking oil biodiesel
BAF20	animal fats biodiesel
CO_2	Carbon dioxide

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