Exergy analysis of a diesel engine with Waste Cooking Biodiesel and Triacetin

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Abstract

This study uses the first and second laws of thermodynamics to investigate the effect of oxygenated fuels on the quality and quantity of energy in a turbo-charged, common-rail six-cylinder diesel engine. This work was performed using a range of fuel oxygen content based on diesel, waste cooking biodiesel, and a triacetin. The experimental engine performance and emission data was collected at 12 engine operating modes. Energy and exergy parameters were calculated, and results showed that the use of oxygenated fuels can improve the thermal efficiency leading to lower exhaust energy loss. Waste cooking biodiesel (B100) exhibited the lowest exhaust loss fraction and highest thermal efficiency (up to 6% higher than diesel). Considering the exergy analysis, lower exhaust temperatures obtained with oxygenated fuels resulted in lower exhaust exergy loss (down to 80%) and higher exergetic efficiency (up to 10%). Since the investigated fuels were oxygenated, this study used the oxygen ratio (OR) instead of the equivalence ratio to provide a better understanding of the concept. The OR has increased with decreasing engine load and increasing engine speed. Increasing the OR decreased the fuel exergy, exhaust exergy and destruction efficiency. With the use of B100, there was a very high exergy destruction (up to 55%), which was seen to decrease with the addition of triacetin (down to 29%).

Keywords: Energy analysis; exergy analysis; waste cooking biodiesel; fuel oxygen content; exergetic efficiency.

1. INTRODUCTION

The world's energy demand, which is driven by population and economic growth, is continuously increasing, with a 48% energy growth projection between 2012 and 2040, while fossil fuel has been forecast to meet approximately three-quarters of the total energy demand in 2040 [1]. This growth is potentially problematic, owing to diminishing non-renewable reserves, large-scale environmental degradation in the form of global warming, and atmospheric pollution due to the products of combustion of these fuels. To overcome the challenges posed by fossil fuel, renewable and alternative energy sources are being sought now, more than ever.

Biodiesel offers many advantages as an alternative fuel because it is renewable, energy efficient, sulphur free and biodegradable [2, 3]. This alternative energy source can satisfy strict emission rules in some applications and can potentially be used in existing diesel engines. However, it performs differently and has different combustion characteristics compared to diesel fuel, and thus, requires analysis from different points of view to fully appraise its utility as an alternative. The chemical and physical properties of the biofuels such as the biodiesel chain are the key parameters on engine performance and emissions [4, 5].

The effect of these fuels on engine performance has been mainly considered using the first law of thermodynamics (energy analysis), as it quantitatively evaluates the energy in the process [6]. However, further clarification with the use of the second law of thermodynamics (exergy analysis) can be achieved for the system inefficiencies. Exergy analysis involves the application of exergy concepts, balances and efficiencies to evaluate and improve the system performance. It qualitatively and quantitatively determines losses in a system and locations where they occur as sources of irreversibilities, and provides more accurate information about engine efficiencies [7, 8]. This has rekindled interest in the second law of thermodynamics (exergy analysis), as the use of the first law of thermodynamics (energy analysis) only to evaluate engine performance has the limitation of not being able to evaluate some features of energy degradation [9, 10].

With the rationale of better understanding the performance and sensitivity of various operating parameters of internal combustion engines when operating with biodiesel, some studies have considered the use of energy and exergy analysis to evaluate engine performance [11-13]. Karthikeyan et al. [14] compared three blends of rice bran biodiesel with pure diesel using energy and exergy analysis. As reported by Cavalcanti et al. [12], engine at higher load with biodiesel blends operates with higher exergetic efficiency. Rakopoulos and Giakoumis [15] used computer analysis to study the energy and exergy performance of a diesel engine operating under transient engine operating conditions, and they revealed how exergy properties vary with different operating parameters. The first and second law analysis of a four-cylinder direct injected diesel engine fuelled with diesel and peanut oil biodiesel blend were considered in another study [16]. Using a Fortran-based code, Jafarmadar and Nemati [17] studied the performance of diesel/biodiesel blends in a homogenous charge compression ignition engine using a three-dimensional model. The exergy analysis showed the improvement of exergy efficiency with an increase in volume percentage of biodiesel. Meisami and Ajam [18] performed both energy and exergy analysis on a diesel engine using castor oil biodiesel with a 190 kW SHENCK engine dyno when operated at full load. From the result of their analysis, the brake thermal efficiency and exergetic efficiency of the 15% castor oil blend was seen to equal the diesel fuel (0% blend) with low exhaust gas efficiency. A single-cylinder, water-cooled diesel engine was tested by Sayin Kul et al. [19] with varying quantities of biodiesel-diesel blends containing 5% bioethanol operated at different speeds. It was seen that the pure diesel fuel had slightly higher thermal and exergetic efficiencies when compared to the biodiesel blend. However, a study by Zare et al. [20] with the engine used in current research showed that using 100% waste cooking biodiesel increases the thermal efficiency by up to 5% for the engine used in this study.

Fuel oxygen content has been introduced as an influential factor in engine performance and emissions [20-25]. Song et al. [23] investigated the effect of oxygen content on combustion in single- and multi-cylinder diesel engines using rapeseed biodiesel to vary the oxygen content of the diesel used. From the results obtained, using oxygenated fuel was associated with a subsequent increase in NOx emissions. Effect of the fuel oxygen content on hydrocarbon formation in diesel engine has been studied recently [26]. It was found that in oxygen-rich condition, combustion temperature was the main influencer on the hydrocarbon formation. Jena and Misra [24] used two different biodiesels separately - palm and karanja. The biodiesels had differing oxygen content and they compared the energetic and exergetic efficiencies in a compression ignition engine. The palm biodiesel, which had higher oxygen content, gave a higher thermal efficiency with less associated irreversibility. Given the thermal efficiency as the ratio of the output power to the input energy from the fuel, with the same output power during the test, lower calorific value of the palm biodiesel was reported to be the reason for the higher thermal efficiency of palm biodiesel. It also concluded that better combustion with less irreversibility was possible with a further increase in the oxygen content of the fuel. This is seen in a further study by Zare et al. [20], considering the performance and emissions of waste cooking biodiesel blends whose oxygen content was increased with the addition of triacetin. In previous studies with the same engine and fuels, engine performance and emissions (such as NOx and PM) has been reported during modal cycles [22], steady-state and transient operation [21, 29] and cold start operation [30]. Compared to diesel with no oxygen content, when it comes to alternative fuels in the market, fuel oxygen content will be an important fuel properties which significantly affects the engine performance and emissions. With a reduction in most exhaust emissions and little insight to the exergy analysis in previous studies conducted by this research group, an exergy-based performance analysis can provide insight to the losses associated with the system [27, 28]. As a result, a detailed evaluation of fuel efficiency as well as irreversibility can be developed.

To the knowledge of authors, the effect of fuel oxygen content on exergetic parameters of diesel engine performance in such a wide range has not been studied in the past. In this study, the first and second laws of thermodynamics are used to analyse the quantity and quality of energy produced by diesel and biodiesel blends operated at three different engine speeds and four different loads. The experiments aimed to study the increase in the oxygen content of the blends with the use of triacetin, which has a high oxygen content. Performance parameters were analysed, including the power produced by the engine, brake specific fuel consumption (BSFC), brake thermal efficiency (BTE), fuel energy and exergy, exergetic efficiency, exergy destruction heat and exhaust losses, as well as other irreversibilities associated with operating the engine at different loads and speeds, and with different biodiesel blends. These performance parameters were graphically represented to establish the relationships between the aforementioned variables.

As the aim of this manuscript is to study the effect of oxygen content on exergy-related parameters, there is no intention to introduce a new fuel/mixture in this study. However, this aspect has been analysed on European Stationary Cycle (ESC) and non-road transient cycle (NRTC) in this research group [21, 22] to evaluate the possibility of using such fuels for Euro III engines.

2. MATERIALS AND METHODS

2.1 Engine specification, experimental setup and design of experiment

The engine used for this experimental study was a turbo-charged, common-rail, six-cylinder after-cooled diesel engine whose specification is shown in Table 1. The engine load was controlled using an electronically controlled water-brake dynamometer which was coupled with this engine.

Table 1. Specification of experimental engine setup

Model	Cummins ISBe220 31
Emission standard	Euro III
Cylinders	6 in-line
Aspiration	Turbocharged
Capacity	5.9L
Compression ratio	17:3:1
Bore x Stroke	102 x120 (mm)
Maximum torque	820 Nm @ 1500 rpm
Maximum Power	162 kW 2500 rpm
Dynamometer type	Hydraulic
Fuel injection	High pressure common rail

The schematic diagram for the experimental setup is presented in Fig. 1. A small fraction of diesel exhaust was passed through a HEPA filter and then gas analysers to measure the gaseous emissions. For CO_2 and NOx measurement, CAI-600 CO2 and CAI-600 CLD NO/NOx were used in this study. A Testo 350 XL Portable Emissions Analyser was also used to measure HC and CO. The exhaust was passed through a dilution tunnel before measuring the particle emissions. PM measurement was done with DustTrak II Aerosol Monitor 8530 (TSI) While a

SABLE CA-10 was used to measure CO_2 for calculating the dilution ratio. Table 2 shows the accuracy of the measurement systems used for this study.

Table 2. The accuracy of instruments

Measurement instruments	Types of exhaust gases	Range	Accuracy	Flow rate (L min-1)
CAI-600 CLD NO/NOxChemiluminescence (CLD) Photodiode (thermally stabilized with Peltier Cooler)	NO/NOx	0-1 to 3,000 ppm	RESPONSE TIME: T90 < 2 Seconds to 60 Seconds Adjustable RESOLUTION=10 ppb NO/NOX (Displays 5 significant digits) REPEATABILITY > 0.5% of Full Scale LINEARITY > 0.5% of Full Scale NOISE < 1% of Full Scale	0.3-3.0
CAI-600 CO2 Non-Dispersive Infrared (NDIR)	CO2	0-1000/2000/3000 ppm	RESPONSE TIME (IR): T90 < 2 Seconds to 60 Seconds Adjustable (Depending on configuration) RESOLUTION Displays Five Significant Digits REPEATABILITY > 1.0% of Full Scale LINEARITY > 0.5% of Full Scale NOISE < 1% of Full Scale	0.25 to 2.0
Sable CA-10 CO2 Analyser	CO2	0 – 5% standard 0 – 10% optional	1% of reading	5-500(x 10-3)
Testo 350 XL Portable Emission Analyser	SO2 CO CO2 O2 NO NO2 HC	0 – 5000 ppm 0 – 10,000 ppm 0 – CO_2 max 0 – 25% 0 – 3000 ppm 0 – 500 ppm 0 – 60,000 ppm	5% of mv 5% of mv - 0.8% of fv 5% of mv 5 ppm 60 ppm	1.2
DustTrakTM II Aerosol Monitor 8530 (TSI)	PM1 PM2.5 PM10	0.001 – 400 mg m-3	5%	3.0

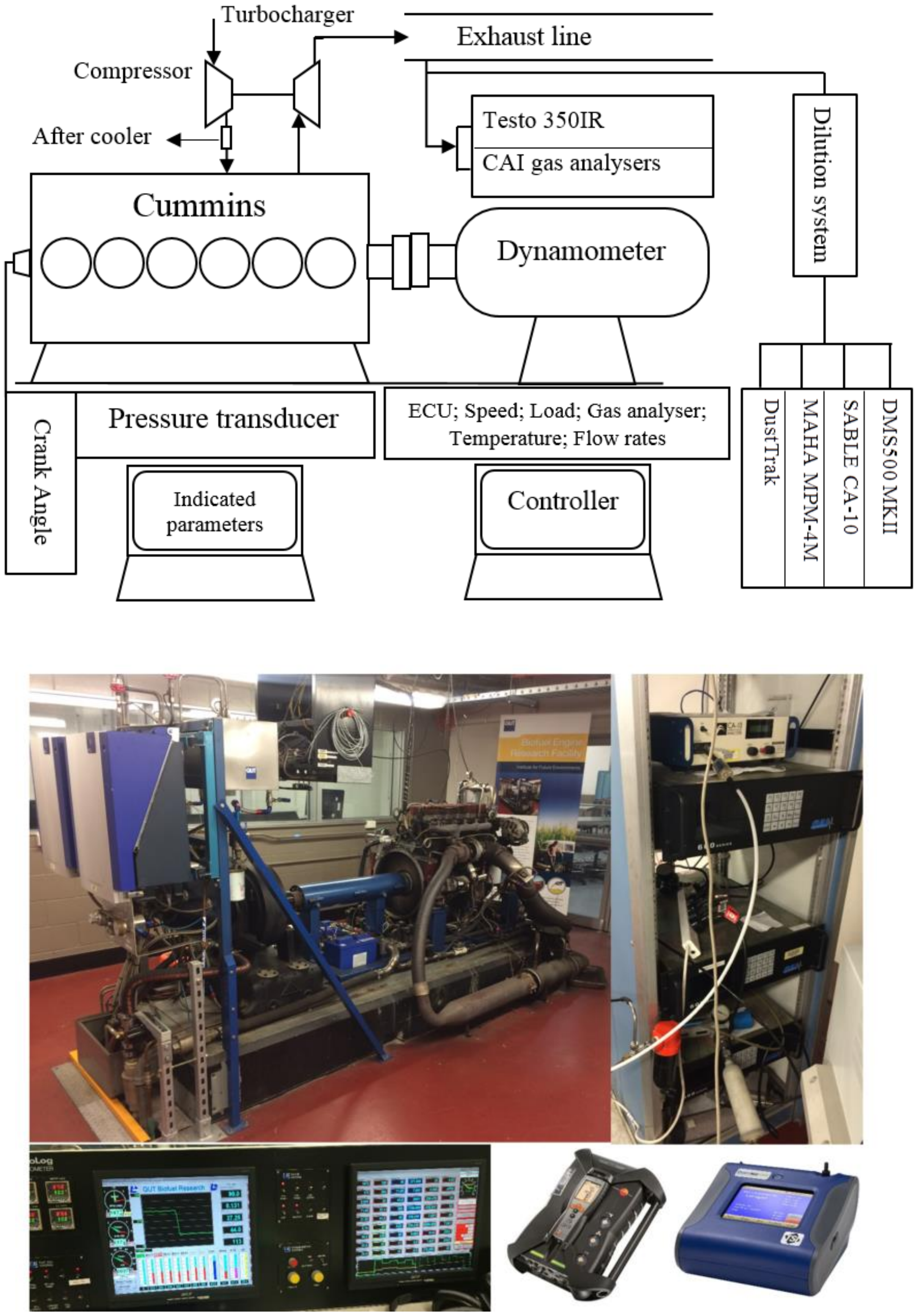

Fig. 1. Experimental setup

Since the engine used in this study was a Euro III engine, the operating modes were selected from the European Stationary Cycle (ESC) schedule. This cycle is a legislated test cycle for heavy-duty engines in the Euro III jurisdiction. In this experiment, 12 engine operating modes from the ESC comprising three engine speeds (1472, 1865 and 2257 rpm) and four engine loads (25, 50, 75 and 100 %) were used.

2.2 Fuel properties

Diesel (D100), waste cooking biodiesel (B100), and varying proportions of both/either diesel and/or waste cooking biodiesel served as the primary fuel, with triacetin (T). Triacetin was added to waste cooking biodiesel in order to study a wide range of fuel oxygen content. A total of six different fuels were used in this experiment and are denoted by the portion of each fuel in the final fuel, as displayed in the first row of Table 3. For example, T5B35D60 stands for 5% (by volume) triacetin, 35% (by volume) biodiesel and 60% (by volume) diesel. That there was no phase separation as the blends were tested at room temperature for 96 hours to ensure miscibility and stability. It was observed that there was no phase separation. Readers can refer to ref. [20] for more specific information about the fuels used in this study and their effects on engine performance and exhaust emission parameters under different engine operating conditions.

It should be noted that beside oxygen, hydrogen and carbon, fuel also contains small trace of sulfur, nitrogen and metals [31]. Our main concern in this investigation was to know the fuel oxygen, as it influences significantly to suppress diesel emissions. We did not account for nitrogen and sulfur to cope up with 100%.

Table 3. Properties of tested fuels

Fuel	D100	T5B35D60	B100	T4B96	T8B92	T10B90	T100
O (wt%)	0	6.02	10.93	12.25	13.57	14.23	44.00
C (wt%)	85.1	80.46	76.93	75.81	74.73	74.19	49.53
H (wt%)	14.8	13.47	12.21	11.97	11.74	11.63	6.42
Density @15°C (g/cc)	0.84	0.866	0.87	0.882	0.893	0.898	1.159
HHV (MJ/kg)	44.79	41.74	39.9	39.02	38.15	37.72	18.08
LHV (MJ/kg)	41.77	38.92	37.2	36.38	35.57	35.16	16.78
KV@40°C (mm^2/s)	2.64	3.66	4.82	4.94	5.06	5.12	7.83
Stoichio-metric air (kg_a/kg_f)	14.89	13.64	12.59	12.33	12.07	11.94	6.02
Formula	$C_{7.09}H_{14.8}$	$C_{6.71}H_{13.47}O_{0.38}$	$C_{6.41}H_{12.21}O_{0.68}$	$C_{6.32}H_{11.97}O_{0.77}$	$C_{6.23}H_{11.74}O_{0.85}$	$C_{6.18}H_{11.63}O_{0.89}$	$C_9H_{14}O_6$
H/C	0.17	0.167	0.159	0.158	0.157	0.156	-
O/C	0	0.0749	0.142	0.162	0.182	0.192	-
S/C	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-

The biodiesel used in this study was provided by Eco Tech Biodiesel Pty Ltd. in Australia. Table 4 shows the fuel technical specification.

Table 4. Fuel technical specification, Fuel technical specification, Eco Tech Biodiesel, SPECCHECK LABORATORIES P/L, Mittagong, NSW 2575, Australia

METHOD	TEST	RESULT	SPECIFICTION		UNITS
EN12662	Total contamination	11.1	24	max	mg/kg
ASTM D664	Total Acid Number	0.25	0.8	max	mgKOH/g
ASTM D7501	Cold soak filterability	201	360	max	sec
ASTM D874	Sulphated Ash	<0.01	0.02	max	%
ASTM D4350	Carbon Residue (10% res)	0.108	0.3	max	%
ASTM D6584	Free glycerol	0.01	0.02	max	%
EN14110	Alcohol content	0.02	0.2	max	%
ASTM D93	Flash point	>130	120	min	°C
ASTM D130	Copper Corrosion	1A	1	max	-
ASTM D6304	Moisture content	312	500		ppm
EN14112	Oxidation stability	9.52	9	min	h
EN14103	Ester content	97.4	96.5	min	%
ASTM D6584	Monoglycerides	0.246	0.8	max	%
ASTM D6584	Total glycerol	0.089	0.25	max	%
ASTM D6371	Cold filter plugging point	-2	-	-	°C
ASTM D2068	Filter blocking tendency (B100)	1.05	2	max	-
ASTM D1160	Distillation temp @90% rec	316	360	max	°C

2.3 Combustion analysis

The number of moles (n) of each individual reactant required for a chemical reaction can be obtained through the knowledge of the mass of the compound set to undergo the reaction. From the knowledge of the moles of the chemical reactant, the reaction equation can be balanced when some of the emission concentrations of individual products have been measured. In this study, the measured emission products found in the emission data include CO, O_2, CO_2, HC and NO. From these measured compounds, N_2, H_2O, and H_2 can be obtained by balancing the chemical equation. Concentrations of other substances such as nitrogen dioxide (NO_2) and particulate matter (PM) were sufficiently low compared to others and were neglected in this analysis. The combustion equation can be written as Equation (1):

$$aC_\alpha H_\beta O_\gamma + b(O_2 + 3.76N_2) \rightarrow X(dO_2 + eCO_2 + fCO + jHC + hNO) + gH_2O + iN_2 + kH_2 \quad (1)$$

where the coefficients a, b, d, e, f, g, h, i, j, k are the mole fractions of the respective components and X is the number of moles of the measured products. It is assumed that no trace of water vapour is contained in the intake air and the calculations assumed that the air was dried, thus the air contains 21% oxygen and 79% nitrogen. The coefficients of both the reactant and exhaust product are important in the energy and exergy analysis of the combustion system, as it is needed to carry out further analysis [24]. The values of α,β and γ are identified from fuel properties as they have been measured and presented in Table 3 for each fuel (C, O and H (wt%)). Air and fuel flow rates are available from experimental data, so “a” and “b” are known. Emission concentrations in exhaust are also measured experimentally and the remaining coefficients has been calculated using experimental emission data and material balance from the combustion equation.

2.4 Oxygen ratio

The equivalence ratio has been a more widely-used term to show the ratio of fuel and air to that of its stoichiometric ratio. This may be misleading in the case of oxygenated fuels, which have oxygen molecules in their chemical formulae. Pham et al. [32] considered the use of an equivalent parameter to the equivalence ratio termed the oxygen ratio (OR). This is because OR gives a more appropriate measure of stoichiometry for oxygenated fuels. OR which considers the oxygen content in fuel is defined as the ratio of total atoms in the mixture to the total required oxygen atoms for the stoichiometric combustion and is given by Equation (2):

$$OR = \frac{O_{2,fuel} + O_{2,air}}{Stoichiometric\ oxygen\ requirement} \quad (2)$$

where $O_{2,fuel}$ and $O_{2,air}$ are the masses of oxygen in the fuel and intake air ,respectively. Therefore OR changes during the experiment by changing the engine load and speed as under different engine operating condition, the intake air amount is different.

2.5 Energy analysis

For the energy analysis to be carried out, some simplifying assumptions are made [33]:

- The entire engine, which excludes the dynamometer, is considered to be a control volume running at steady-state.
- The combustion air and exhaust gas each form ideal gas mixtures.
- Changes in the potential and kinetic energy of the air, fuel and exhaust gases are negligible.
- The lower heating value (LHV) of the fuel is used due to the vapour state of water in the exhaust product.

With the aforementioned assumptions, the fuel input energy rate (Q_f) into the control volume is given by Equation (3):

$$\dot{Q}_f = \dot{m}_f \,.\, LHV \quad (3)$$

where $\dot{m}_f$ and LHV are the mass flow rate (kg/s) and the lower heating value (kJ/kg) of the fuel respectively.

The brake power ($\dot{W}$) generated by the engine can be obtained from the engine torque (T) and speed (N) as shown in Equation (4):

$$\dot{W} = \frac{2\pi NT}{60}\,(\text{kW}) \tag{4}$$

where N is in rpm and T is in kNm. The mass and energy balance for the control volume can be represented by the continuity equation and the first law of thermodynamics [33]. The mass balance which equates the mass inflow to the mass outflow is represented in Equation (5):

$$\sum m_i = \sum m_e \tag{5}$$

The energy balance is given in Equation (6) using the brake power from Equation (4).

$$\dot{Q}_{cv} - \dot{W} = h_p - h_R \tag{6}$$

$$h_p = \sum_p n_e\left(h_f^0 + \Delta\bar{h}\right)_e, \qquad h_R = \sum_R n_i\left(h_f^0 + \Delta\bar{h}\right)_i$$

where subscripts *p*, *R*, *cv*, *i* and *e* represent the product, reactant, control volume, inlet and exit states, respectively. *n* denotes the number of moles while h_f^0 and Δh represent the standard enthalpy of formation and enthalpy change due to a change of state. Standard Tables of thermodynamic [34] properties are used to extract the standard enthalpy and the enthalpy change at the exit temperature of the gases. To obtain the enthalpy of the reactant (h_R), the formation enthalpy is determined from complete combustion of the fuel when the theoretical quantity of air is supplied [18]. This is mathematically stated as shown in Equation (7):

$$C_xH_yO_z + \left(x + \frac{y}{4} - \frac{z}{2}\right)(O_2 + 3.76N_2) \rightarrow xCO_2 + \frac{y}{2}H_2O + 3.76\left(x + \frac{y}{4} - \frac{z}{2}\right)N_2 \tag{7}$$

The standard enthalpy of formation for the fuel can be obtained utilising the first law of thermodynamics; the heat released from the reaction equals the lower heating value of the fuel. The enthalpy of the fuel can be obtained from Equation (8):

$$(h_f^o)_{Fuel} = x(h_f^o)_{CO_2} + 0.5y(h_f^o)_{H_2O} + (3.76x + 0.94y - 1.88z)(h_f^o)_{N_2} + \overline{LHV} \tag{8}$$

The heat loss through the exhaust gases can be calculated as the difference between the energy input rate from the air/fuel mixture and the control volume, which consists of the mechanical work (brake power) and the heat transfer. The amount of energy brought into the system by the combustion air can be ignored, as it enters the system having the same temperature as the reference environment. The heat loss through the exhaust is mathematically represented as shown in Equation (9):

$$\dot{Q}_{exh} = \dot{m}_f . LHV - \left(\dot{W} + \left|\dot{Q}_{CV}\right|\right) \tag{9}$$

To evaluate how well the engine converts heat to work, the brake thermal efficiency (BTE) is introduced, and is the ratio of the brake power $\dot{w}$ to the fuel energy input rate $\dot{Q}_f$, as shown in Equation (10):

$$BTE = \frac{\dot{W}}{\dot{Q}_f} \tag{10}$$

Another important engine characteristic is the brake specific fuel consumption (BSFC), which is a measure of the amount of fuel needed to produce a kilowatt of power in one hour, and it is given by Equation (11):

$$BSFC = \frac{\dot{m}_f}{\dot{W}} 3600 \tag{11}$$

2.6 Exergy analysis

In order to effectively carry out the exergy analysis, assumptions used in energy analysis are still valid. The reference environment in this study corresponds to an environment temperature (T_0) of 298.15 K and atmospheric pressure of 1 bar. Based on this assumption, the exergy balance for the control volume can be stated as Equation (12):

$$\dot{E}_Q + \dot{E}_W = \sum \dot{m}_{in} e_{in} - \sum \dot{m}_{out} e_{out} - \dot{E}_{dest} \quad (12)$$

where $\dot{E}_Q$ is the exergy flow rate accompanying the heat leaving the control volume to the environment through the cooling water; $\dot{E}_W$ is the exergy flow accompanying work, $\dot{E}_{dest}$ is the exergy destruction rate due to irreversibility in the control volume; also, $\sum \dot{m}_{in} e_{in}$ *and* $\sum \dot{m}_{out} e_{out}$ represent the rate of exergy entering and leaving the control volume. e_{in}, and e_{out} are the specific exergies of the fuel and exhaust gases, and $\dot{m}_{in}$ and $\dot{m}_{out}$ are the mass/molar flow rate of the fuel and exhaust gases.

The exergy flow rate leaving the control volume through the cooling water can be represented as shown in Equation (13):

$$\dot{E}_Q = \sum Q_{cv} \left(1 - \frac{T_o}{T_{cw}}\right) \quad (13)$$

Where Q_{cv} is the heat leaving the control volume through the engine cooling water, T_o and T_{cw} are the temperatures of the reference environment and the cooling water respectively. Also, the exergy associated with the work transfer for the defined control volume is equal to the brake power. It is mathematically represented as shown in Equation (14):

$$\dot{E}_W = \dot{W} \quad (14)$$

The input exergy rate, which is the rate of exergy entering the control volume, can be represented with the chemical exergies of the fuel and combustion air, which can be neglected due to the air entering the engine at the temperature of the reference environment. The input exergy rate can be represented as shown in Equation (15):

$$\sum \dot{m}_{in} e_{in} = \dot{m}_f \phi \, |LHV| \quad (15)$$

where $\dot{m}_f$ is the mass of fuel consumed, and ϕ is the chemical exergy factor of the fuel in unit mass as given in Equation (16) [35]:

$$\phi = \left[1.0401 + 0.1728\frac{h}{c} + 0.0432\frac{o}{c} + 0.2169\frac{s}{c}\left(1 - 2.0628\frac{h}{c}\right)\right] \tag{16}$$

where *h, c, o, and s* are the mass fractions of hydrogen, carbon, oxygen and sulphur contents of the fuels from Table 3. The chemical exergy of liquid fuel, is related to its LHV by using an empirical coefficient (ϕ) calculated based on atomic compositions [36, 37].

The exhaust gas exergy, which is the rate of exergy leaving the control volume, can be represented by the sum of two constituents: thermomechanical ($\bar{\bar{e}}_{tm}$) and chemical ($\bar{\bar{e}}_{th}$) exergies of the fuel. The exhaust gas exergy is represented by Kotas [35] as shown in Equations 17 and 18:

$$\sum \dot{m}_{out} e = n_f(\bar{\bar{e}}_{tm} + \bar{\bar{e}}_{th})$$

$$\bar{\bar{e}}_{tm} = \sum_i a_i\left[\bar{h}_{i,T} - \bar{h}_{i,T_O} - T_O\left(\bar{s}^O_{i,T} - \bar{s}^O_{i,T_O}\right)\right] + \bar{R}T_O\, In\, \frac{P}{P_o} \tag{17}$$

$$\bar{\bar{e}}_{ch} = \bar{R}T_O \sum_i a_i \left(ln\frac{y_i}{y_{i,00}}\right) \tag{18}$$

where h and s are the specific enthalpy and absolute entropy of the exhaust gases, n is the molar flow rate, R is the general gas constant, To is the temperature of the reference environment, p and po are the exhaust gas pressure and reference pressure, y_i is the molar fraction of the exhaust gas component i, and $y_{i,00}$ is the molar fraction of gases in the reference environment tabulated below. The mole fractions are obtained by balancing the chemical equation of each combustion process. In addition, the exhaust gas pressure is considered to be the same as the atmospheric pressure as it is discharged to the environment, thus causing the pressure term of the thermomechanical exergy to equate to zero. Thermophysical properties of gases can be obtained from [34]. Experimental data (such as air and fuel mass flow rates, emission data etc.)

which varies for each operating condition is used to find the component coefficients in the combustion equation and used with exhaust temperature for each operating condition to obtain the exergy from Eq. 17 and 18.

Table 5: Definition of Environment [38]

Reference environment	Mole fraction
O_2	20.35
CO	0.0007
CO_2	0.0345
Others	0.91455
H_2O	3.03
N_2	75.67
SO_2	0.0002
H_2	0.00005

From Equations 12-18, the irreversibility associated with the combustion process can be obtained. If the exergy balance equation is rearranged (Equation 12), the exergy destruction can be mathematically stated as:

$$\dot{E}_{dest} = \sum \dot{m}_{in}\varepsilon_{in} - \dot{E}_Q - \dot{E}_W - \sum \dot{m}_{out}\varepsilon_{out} \tag{19}$$

The ratio of each of the exergy components to the input exergy rate is an important indication of exergy analysis, as it shows the fraction of the fuel exergy carried away through the different processes. These fractions obtained from the combustion of a particular fuel can be compared with similar fractions obtained from the combustion of a different fuel whose heating value varies from the other fuel. In order to determine the fraction of the fuel exergy converted to work, second law efficiency is considered. Second law efficiency (also known as exergetic efficiency) is the fraction of the fuel exergy converted to the desired product (work), and is mathematically stated in Equation (20):

$$\eta_{ii} = \frac{\dot{E}_W}{\dot{E}_f} = \frac{\dot{E}_W}{\dot{m}_f e_f^{ch}} \tag{20}$$

3. RESULTS AND DISCUSSION

In this section, parameters such as brake specific fuel consumption, thermal efficiency, fuel energy and heat loss, as well as the exergetic efficiency and the exergy loss accompanying the exhaust gas are presented. In all figures, the six fuels are differentiated by using different colours; the three engine speeds are shown with three different shapes, and four engine loads are displayed with four shape sizes (the higher the load, the bigger the shape size). For the exergy analysis, the exergy parameters are analysed according to engine operation parameters, i.e. the exergy content of the fuel (fuel exergy) converted to work (brake power), and losses through the exhaust (exhaust exergy) or destruction due to the irreversibilities (exergy destruction). Relationships between energy and exergy parameters were also discussed in details

3.1 Energy analysis

As the main objective of this work is to look at the exergy parameters, just two main parameters of energy analysis (i.e., BTE and exhaust loss) which are more relevant to exergy analysis will be presented firstly. From the experimental data, brake thermal efficiency (BTE) was obtained and presented in Fig. 2. BTE is a good indicator of how well the chemical energy of the fuel is transformed into useful work as it depends on the brake power, heating value and mass of fuel. From Fig. 2, it is seen that with increasing load, BTE increases. In this study, by increasing the speed, the BTE is seen to be decreased. Considering the variation in BTE among fuels, it is seen that the BTE is higher for B100 in this study, which shows a different trend to the literature. This higher thermal efficiency is a good indication that higher energy input in the form of heat is converted to work. However, it will be discussed further in exergy analysis. It is seen that using oxygenated fuels improves the thermal efficiency when compared with diesel fuel. Improved combustion owing to better mixture formation with oxygen-rich fuels and lower exhaust temperatures [39]. The lower exhaust temperature with the oxygenated fuels could be due to the lower calorific value of the fuels, which leads to lower in-cylinder pressure and temperature.

Heat loss through the exhaust discharge t is one of the greatest sources of inefficiency. Exhaust energy loss can be looked at as the ratio of the exhaust energy to the fuel input energy to indicate the proportion of the fuel energy carried away by the exhaust gases as presented in Fig. 2. At low loads and high RPMs, over 40% of the fuel energy is wasted by exhaust discharge. It is seen that increasing the load reduces the proportion of fuel energy carried away by the exhaust gas. The decrease in the proportion of fuel energy carried out by the exhaust gas at full load shows that more energy has been converted to work (causing an increase in BTE), with a slight increase in heat transfer loss. Also, an increase in exhaust energy loss is observed as the speed increases. Considering the fuels, it is observed that the highest proportion of fuel energy wasted as the exhaust gas is for D100 at all operating modes, while B100 had the least exhaust energy loss. This high/low exhaust loss causes a corresponding decrease/increase in other energy forms to which the fuel energy is converted.

From Fig. 2, it is seen that operating the engine at low speed and high load yields higher BTE and lower exhaust energy loss, with B100 having the highest BTE and lowest exhaust energy loss. This indicates a better energy-to-work conversion at high load. Also, it is seen that the values obtained when the engine is operated at 75% and 100% load at 1472 rpm are almost the same for the exhaust loss and brake thermal efficiency showing the same order of energy converted to useful work is wasted by exhaust discharge. It is worth noting that increasing the speed at constant load reduces the brake thermal efficiency and heat transfer rate, with a corresponding increase in the proportion of the fuel energy leaving the combustion chamber as exhaust gas. This is true as the increase in speed increases the amount of fuel taken into the combustion chamber, resulting in improper mixing and incomplete combustion.

Load% (Shape Size): 100(9) – 75(7) – 50(5) – 25 (3) -------- Speed (rpm): 1472 (∆) 1865 (O) 2257 (x)

D100(0%) T5B35D60(6.02%) B100(10.93%) T4B96(12.25%) T8B92(13.57%) T10B90(14.23%)

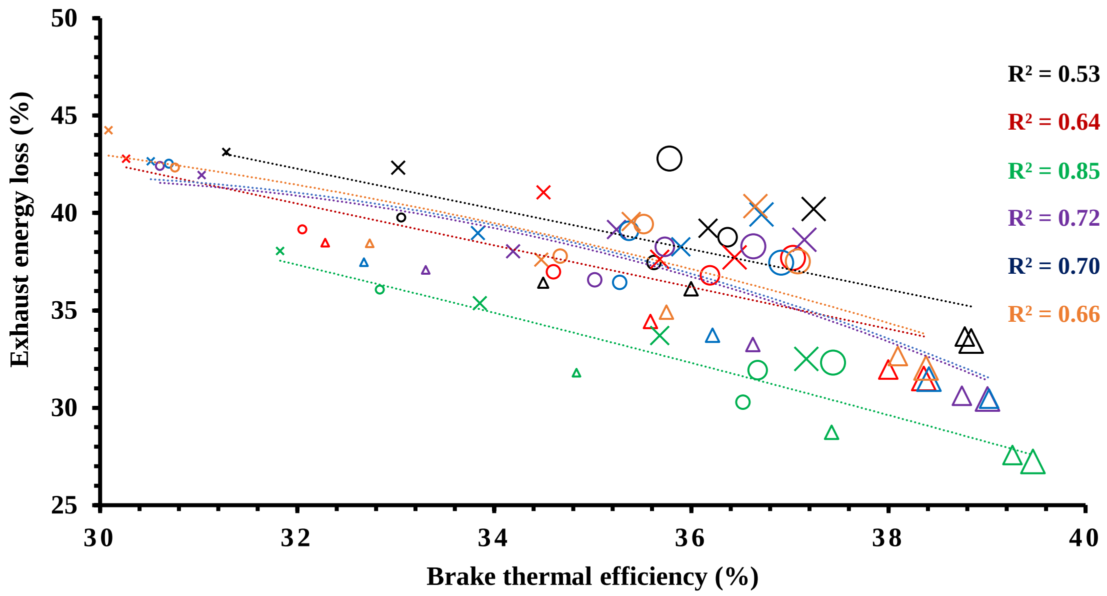

Fig. 2: Exhaust energy loss vs. brake thermal efficiency at 12 engine operating modes for the 6 tested fuels

3.2 Exergy analysis

From the second law of thermodynamics, the fuel exergy converted to work is calculated for different fuels and engine operating conditions. Unlike fuel energy, fuel exergy does not only depend on the mass and heating value of the fuel, but also on the chemical exergy factor of the fuel (Equation 15) [19]. From Table 3, it is seen that LHV decreases with an increase in the oxygen content of the fuel, thus causing a decrease in fuel exergy among oxygenated fuels. D100, which has no oxygen content, is expected to have the highest fuel exergy at all operating modes, while T10B90, with the highest oxygen content, should present the least fuel exergy.

Regarding the effect of engine operating condition on exergy and energy analyses, the air-fuel and equivalence ratio can be used. However, these two parameters cannot consider the effect of fuel oxygen content when oxygenated fuels are used, especially given that the fuel oxygen content has a significant effect on engine performance and emissions [20, 22-24]. Therefore, it is more representative to consider the OR in this work [20].

From Fig. 3, it is seen that the OR decreases by increasing the engine load. It is also shown that increasing the engine speed is associated with an increased OR. As can be seen in Fig. 3., at three different engine speeds, there is a strong correlation between fuel exergy and OR, which confirms the strong correlation between fuel exergy and engine load. Increase in load and speed cause an increase in the mass of injected fuel, which increases the fuel exergy. This increase in fuel exergy causes a corresponding increase in the ways by which energy is converted into various forms. Also, from Fig. 3, it is seen that at a specific load and speed, an increase in fuel oxygen content decreases the fuel exergy. This is due to the reduction in LHV of fuels by increasing the oxygen content as discussed before.

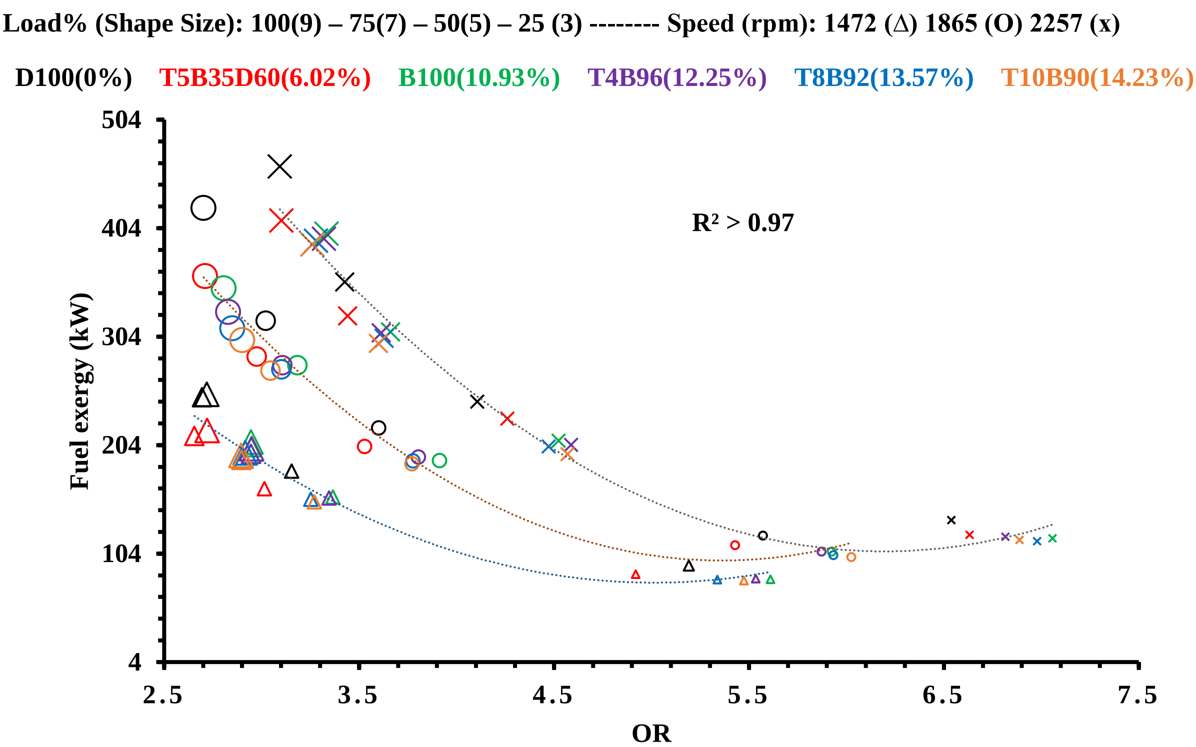

Fig. 3. Fuel Exergy vs. OR at 12 engine operating modes for the 6 tested fuels

Brake power is the parameter to present the exergy of the useful work produced by the engine at different speeds and loads for the various fuels is shown in Fig. 4. It is seen that D100 has the highest brake power compared to the oxygenated fuels used at all operating conditions. For the oxygenated fuels, it is seen that the power produced decreases with an increase in oxygen content and is largely attributed to the low heating value of oxygenated fuels. This decrease in heating value of the fuel owing to the increase in oxygen content also significantly influences the fuel energy as shown before. Increasing either the speed or the load causes a corresponding increase in the power produced as more fuel is injected into the chamber, thus increasing the energy input rate.

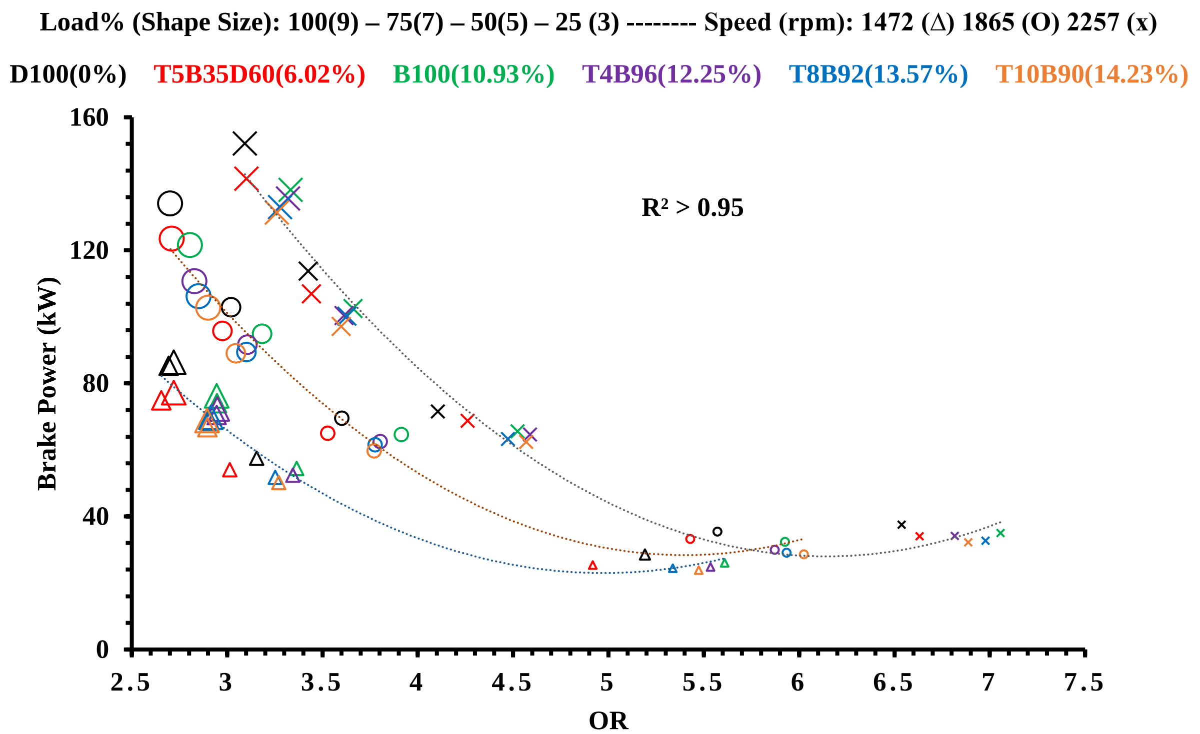

Fig. 4. Brake power vs. OR at 12 engine operating modes for the 6 tested fuels

With a fraction of the fuel exergy converted to the brake power, the remaining is lost in varying proportions through the exhaust gas or cooling water losses, or destroyed as a consequence of a number of irreversible processes, such as mixing, combustion and friction. Considering the fuel exergy lost through the exhaust, Fig. 5 shows the variation of the exhaust exergy loss with OR at different speeds and loads. The effect of increase in speed at a constant load on exhaust exergy loss can clearly been observed in this figure. With the increase in speed, the exhaust exergy loss increases as the time available for complete combustion decreases [40]. This increase in exhaust exergy loss leads to a corresponding decrease in all other fuel exergy values.

As the exhaust temperature is the key indication of the exergy loss, a plot of the exhaust exergy against the exhaust temperature is presented in Fig. 6. The fraction of the fuel exergy lost through the exhaust for the different fuels used is seen to follow similar trendlines, as shown in Fig. 6. However, B100 followed a different path and it is represented by a separate trendline. These trendlines, which are polynomials of order 2, have a very high regression of above 0.99 for all speeds. The exhaust exergy loss decreases by decreasing the exhaust gas temperature as shown in this figure. It is seen that increasing the load increases the temperature of the exhaust gas as expected. From the analysis carried out, it is seen that diesel fuel has the highest exhaust exergy loss owing to its high exhaust temperature, at all operating modes [41]. Lower exhaust temperature and exergy loss are seen with oxygenated fuels due to their lower heating values. This indicates a decrease in combustion temperature which has a positive effect on the exhaust exergy loss as it occurs in the lean flame zone [42].

Load% (Shape Size): 100(9) – 75(7) – 50(5) – 25 (3) -------- Speed (rpm): 1472 (∆) 1865 (O) 2257 (x)

D100(0%) T5B35D60(6.02%) B100(10.93%) T4B96(12.25%) T8B92(13.57%) T10B90(14.23%)

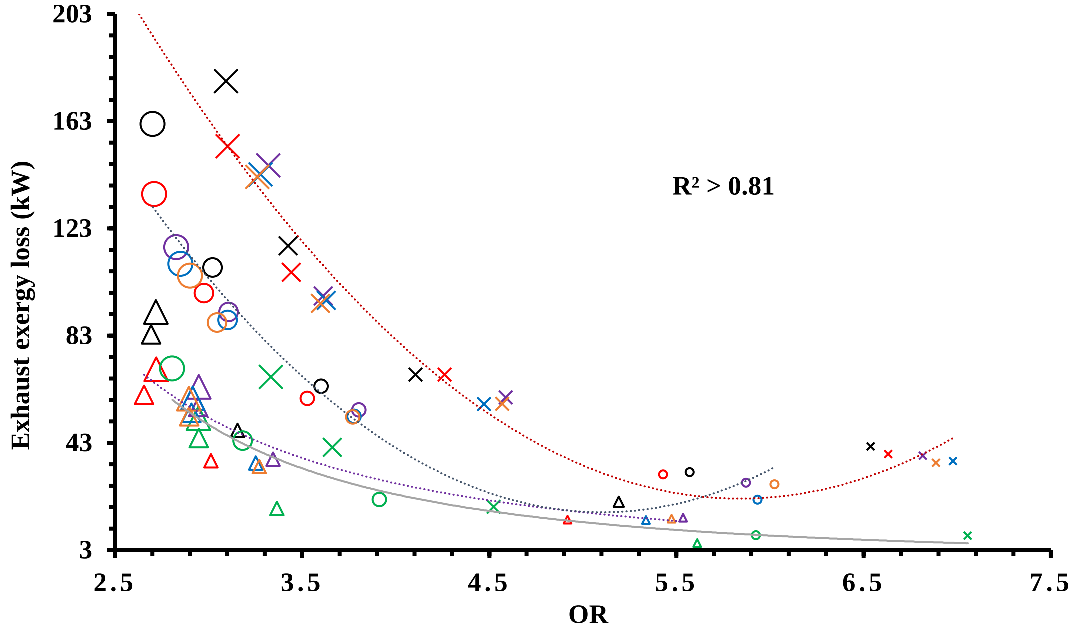

Fig.5: Exhaust exergy loss vs. OR at 12 engine operating modes for the 6 tested fuels

Load% (Shape Size): 100(9) – 75(7) – 50(5) – 25 (3) -------- Speed (rpm): 1472 (∆) 1865 (O) 2257 (x)

D100(0%) T5B35D60(6.02%) B100(10.93%) T4B96(12.25%) T8B92(13.57%) T10B90(14.23%)

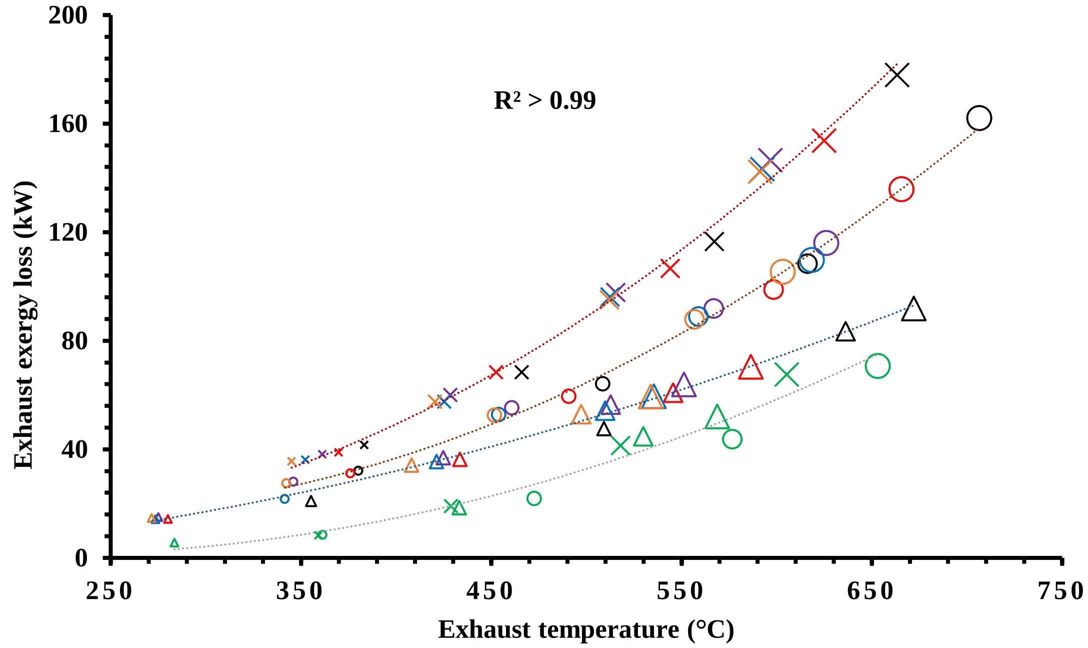

Fig.6. Exhaust exergy loss vs. exhaust gas temperature at 12 engine operating modes for the 6 tested fuels

Factors such as combustion, turbulence, flow losses and mixing are sources of irreversibility and are accounted for as exergy destruction. Since fuel exergy varies with different fuels, exergy destruction ratio, which represents the proportion of fuel exergy destroyed during the combustion, would be an important parameter for comparing different fuels in this study. From Fig. 7, it is seen that the exergy destruction is lower at high loads showing the combustion is happening in condition closer to the ideal with less destruction of exergy. As can be seen, exergy destruction decreases with an increase in both engine load and speed in general. Considering the fuels at all modes, it is seen that the variation in exergy destruction is higher at low loads between the fuels while in high loads all fuels (except B100) are performing more similar. D100 has the lowest destruction ratio and B100 shows the highest destruction ratio at all modes. It is seen that at full load, the lowest destruction is achieved with D100 yielding a destruction ratio of 23.9%, occurring at the highest speed, but with a corresponding high exhaust exergy loss of 38.6%, owing to its high temperature.

Load% (Shape Size): 100(9) – 75(7) – 50(5) – 25 (3) -------- Speed (rpm): 1472 (∆) 1865 (O) 2257 (x)

D100(0%) T5B35D60(6.02%) B100(10.93%) T4B96(12.25%) T8B92(13.57%) T10B90(14.23%)

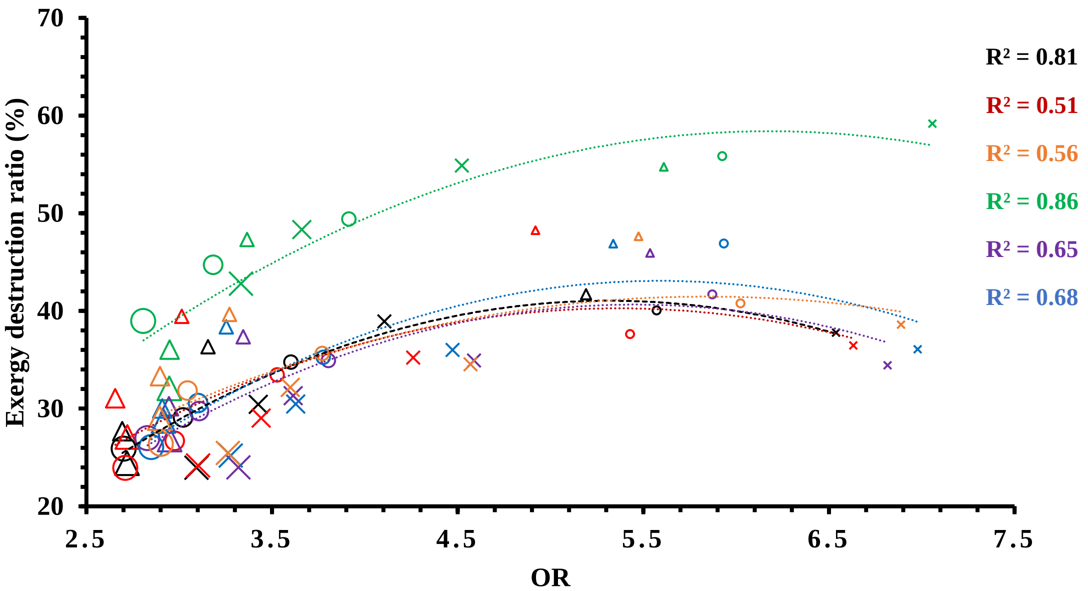

Fig.7. Exergy destruction ratio vs. OR at 12 engine operating modes for the 6 tested fuels

As exergy loss and destruction are sometimes interpreted similarly by mistake, they are presented separately in Fig. 8. This figure shows the variation of exergy destruction and the exhaust exergy loss for different fuels at different engine operating modes. A reverse trend between exhaust exergy loss and exergy destruction is found from this figure showing that the parameters affecting exergy destruction are affecting the exergy loss in opposite way. D100 maintaining the highest exhaust exergy loss at all operating modes. This is largely attributed to high exhaust gas temperature for diesel as shown before. This is contrary to B100, as the proportion of fuel exergy lost through the exhaust is seen to be the lowest in all operating modes and exergy destruction is the highest. B100 showed a very high destruction and on the other hand a low exergy loss, thus shifting slightly from the path taken by other fuels tested. This fuel exhibits the highest cetane number (lowest ignition delay) meaning the lowest level of premixed combustion with this fuel which leads to more incomplete combustion condition and more exergy destruction. Exergy destruction ratio is seen to be increased with an increase in engine speed with significant reduction in exhaust exergy loss. Also, with load increase, the proportion of the fuel exergy destroyed reduces and a corresponding increase in the exhaust exergy loss is observed. This increase in exhaust exergy loss at increasing load (and also speed) is caused mainly by the increase in temperature at which the gases leave the combustion chamber.

Load% (Shape Size): 100(9) – 75(7) – 50(5) – 25 (3) -------- Speed (rpm): 1472 (Δ) 1865 (O) 2257 (x)

D100(0%) T5B35D60(6.02%) B100(10.93%) T4B96(12.25%) T8B92(13.57%) T10B90(14.23%)

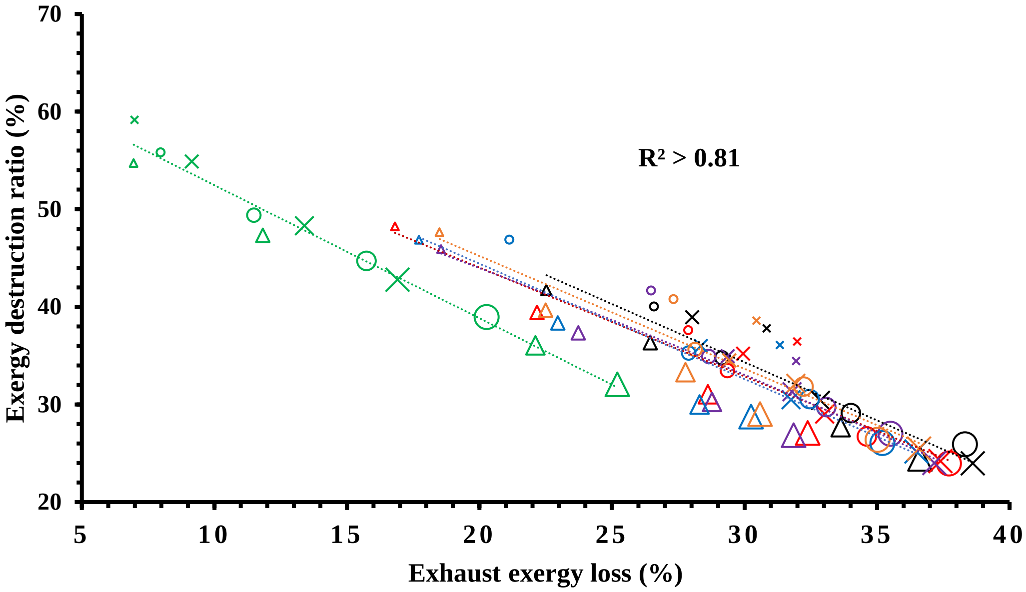

Fig. 8. Exergy destruction ratio vs. Exhaust exergy loss at 12 engine operating modes for the 6 tested fuels

Fig. 9 shows the exergetic efficiency, which defined as the ratio of brake power to the fuel exergy, for different conditions. The proportion of extracted useful work is seen to be increased with an increase in load and the maximum values happen at the lowest speed and 100% load for all the fuels. This is similar to its energy counterpart, but has a lower efficiency, whose percentage difference with the BTE ranges from 6.56% for D100 and increases with an increase in oxygen content to 7.02% in T10B90. The exergetic efficiency gives a better idea of engine operation as it takes into account both the first and second laws of thermodynamics as well as the exergy destructions and exergy losses. At a constant load, the exergetic efficiency is seen to be decreased by increasing speed causing the minimum exergetic efficiency to be seen at 25% load operated at 2257 rpm. This is attributed to the decrease in volumetric efficiency of the combustion chamber as less time is required to fill the cylinder [43].

The other important finding is the exergetic efficiency improvement with the use of oxygenated fuels, with the exception at 25% load. This increase in exergetic efficiency is primarily due to the better combustion of these oxygenated fuels and less losses, compared to D100. The highest exergetic efficiency is exhibited by B100 at all operating modes, and thus can be considered a better quality fuel than other fuels used, if we assume the exergetic efficiency as the measure of fuel quality. At low loads, the lower exergetic efficiency was observed by some of the oxygenated fuels (T4B96, T8B92 and T10B90) when compared with D100. It could be attributed to low in-cylinder pressure and also low combustion temperature, as an increase in load provides an appropriate condition for combustion for this fuels [43]. This is seen to be reversed with an increase in load, as higher combustion temperatures with the oxygenated fuels were obtained, thus converting more heat into useful work.

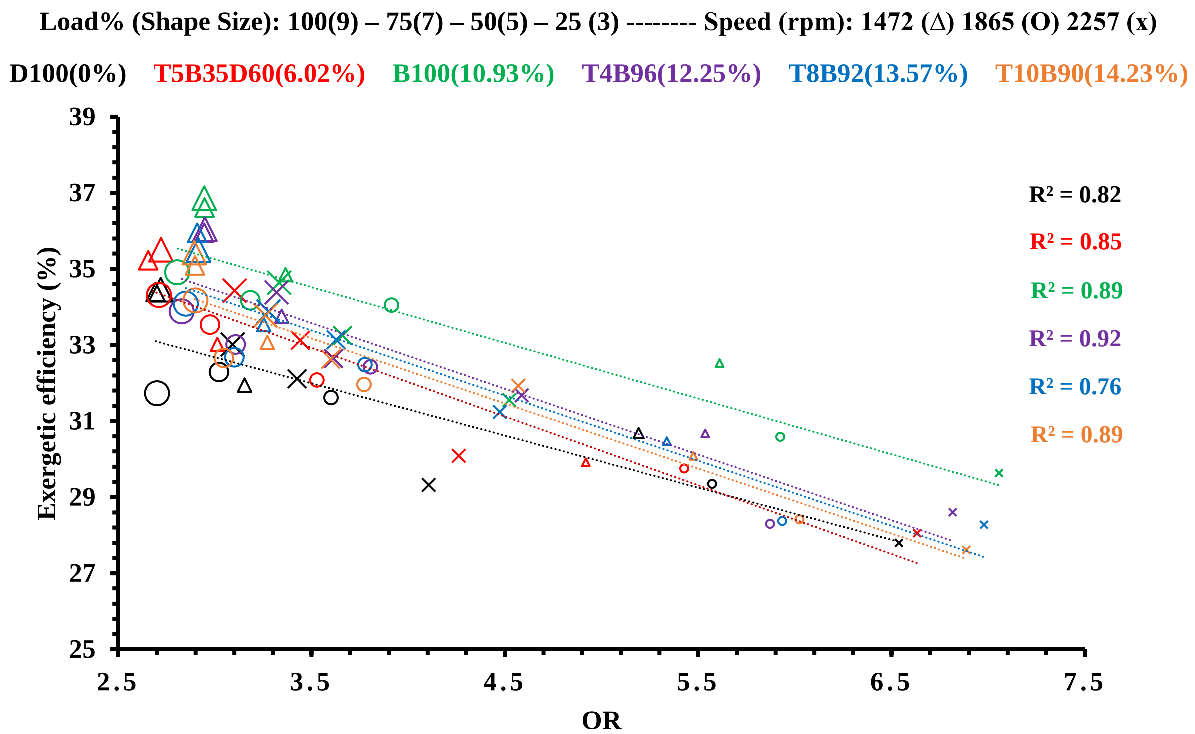

Fig. 9. Exergetic efficiency at 12 engine operating modes for the 6 tested fuels

3.3 Exergy and fuel consumption relationships

The correlation between exergetic efficiency and BSFC for fuels at different speeds and loads shows a linear trend and is presented in Fig. 10. Considering the BSFC, it is seen that at all three speeds, by increasing the engine load the BSFC reduces and the minimum BSFC was obtained at full load. Also, at any given load, an increase in speed causes an increase in BSFC. As can be seen, the BSFC increases with an increase in oxygen content. This is because an increase in the oxygen content of the fuel causes a decrease in the lower heating value [44]. The oxygen content of the fuel is a good indicator of the loss of heating value and increased fuel consumption [39]. It is seen that D100 had the lowest BSFC at all modes, owing to its high heating value. The minimum BSFC was 0.22 g/kWh at full load and 1475 rpm belongs to D100, while the maximum BSFC was observed at 0.342 g/kWh with the higher oxygenated fuel (T10B90) operating at 25% load and 2257 rpm.

Considering BSFC against exergetic efficiency, maximum exergetic efficiency can deliver the lowest BSFC. Values of BSFC decrease with decreasing speed and increasing load, causing a corresponding increase in the exergetic efficiency and operating the engine at low speed (1472 rpm) and high load yields the lowest possible BSFC and the highest exergetic efficiency for each individual fuel considered. It is seen that D100 has the lowest BSFC and exergetic efficiency, while B100 shows the highest exergetic efficiency with moderate BSFC. As can be seen, maximum exergetic efficiency is for B100 and addition of triacetin to biodiesel (which results in a lower heating value) increases the BSFC and decreases the exergetic efficiency [20]. From the plot the increase in diesel content of the oxygenated fuel, causes a decrease in BSFC, as observed for T5B35D60.

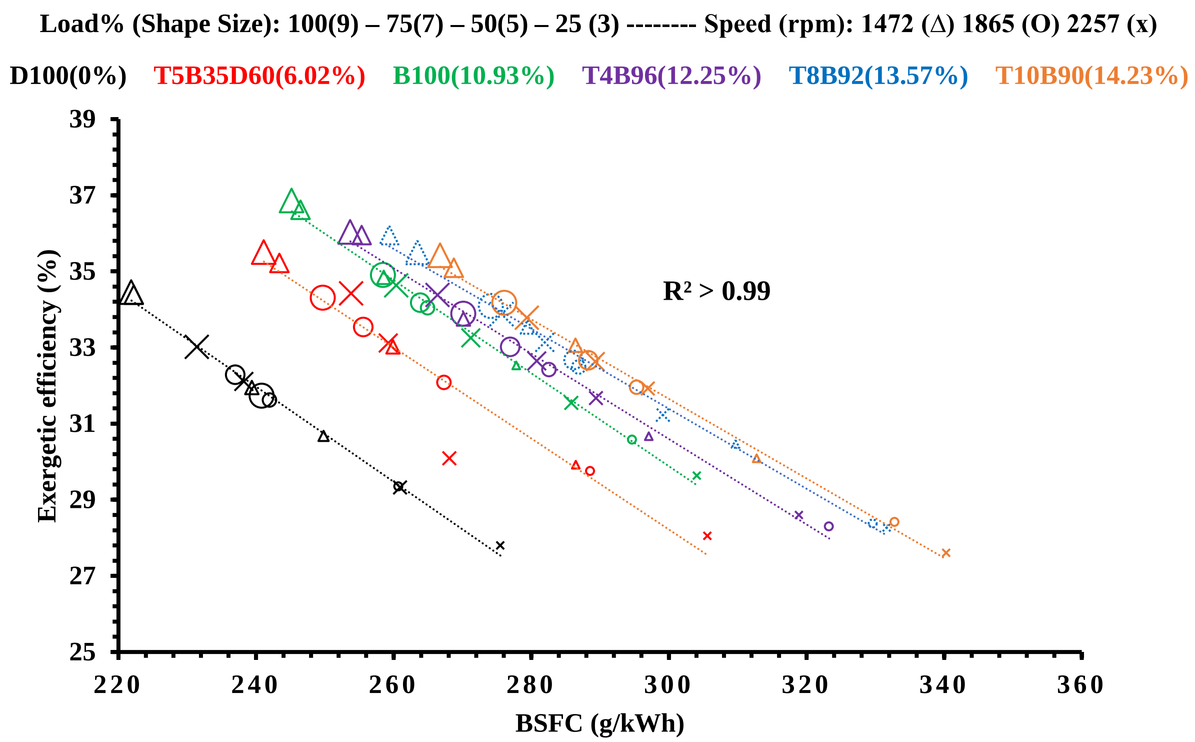

Fig.10. Exergetic Efficiency vs. BSFC at 12 engine operating modes for the 6 tested fuels

As the LHV is different for the fuels used in this study, $BSFC_{equivalent}$ is calculated to develop a further analysis of the results presented in Fig. 11. Equivalent brake specific fuel consumption $BSFC_{equivalent}$ represents the amount of diesel fuel equivalent for producing the same amount of power and it is defined as follow [45]:

$$BSFC_{equivalent} = BSFC \times LHV_{blend}/LHV_{diesel} \quad (21)$$

The results of exergetic efficiency vs. $BSFC_{equivalent}$ are presented in Figure 11. All the biofuels are following almost the same trendlines, however, the trend is still similar to Figure 10. As can be seen, improving the exergetic efficiency means achieving lower $BSFC_{equivalent}$ for each fuel as presented on this figure. Among all the tested fuels, the $BSFC_{equivalent}$ for B100 is the lowest at different operating conditions making it a better alternative fuel. At low load and high speed, the $BSFC_{equivalent}$ of all the tested fuels are higher than diesel (except for B100). This trend changes by increasing the load and speed for different fuels.

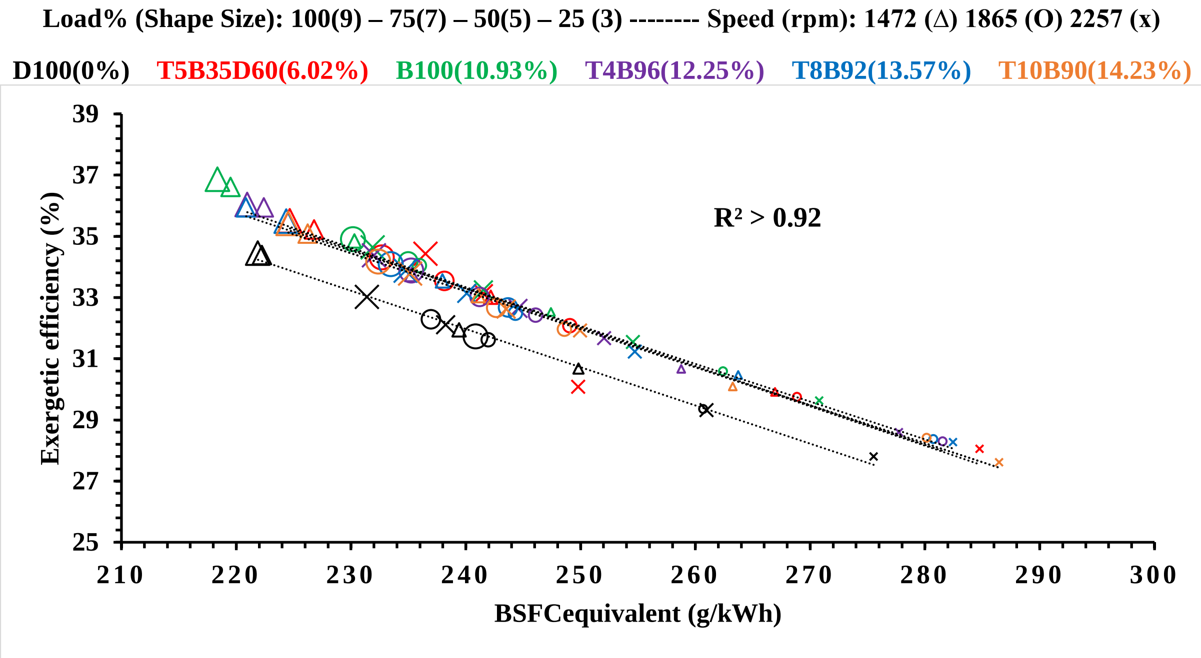

Fig.11. Exergetic Efficiency vs. BSFCequivalent at 12 engine operating modes for the 6 tested fuels

A linear trend can be obtained when the BTE is plotted against the exergetic efficiency in Fig. 12. This is because the BTE and exergetic efficiency are both used to measure the quantity of the heat converted to work with respect to first and second law analysis. Comparing the exergetic efficiency against BTE, it is seen that the BTE is higher for all operating conditions than the exergetic efficiency owing to the lower value of energy input rate when compared to the high chemical exergy of the fuel used in the exergy analysis. Also, the exergetic efficiency combines both first and second law efficiency to account for the usefulness of the energy being supplied.

From both efficiencies, it is seen that they depend on the lower heating value of the fuel. The lower heating value of D100 is seen to be the highest, and decreases with an increase in fuel oxygen content while T10B90 has the lowest heating value. From Fig. 12, it is seen that D100 clearly distinguishes itself from the other fuels owing to the low fuel consumption and high heating value (minimum difference with the oxygenated fuels used in this study is approximately 4800 kJ/kg). This high heating value of D100, which produces less power with respect to the energy input, causes a visible decrease in the exergetic efficiency of the diesel fuel as it moves below the other fuels' line. It is also seen that the oxygenated fuels are closely packed and increase linearly. This cluster is mainly attributed to the closeness of their respective heating value and fuel consumption. With respect to oxygenated fuels, it is seen that T10B90 (with the lowest heating value) had the lowest BTE and exergetic efficiency.

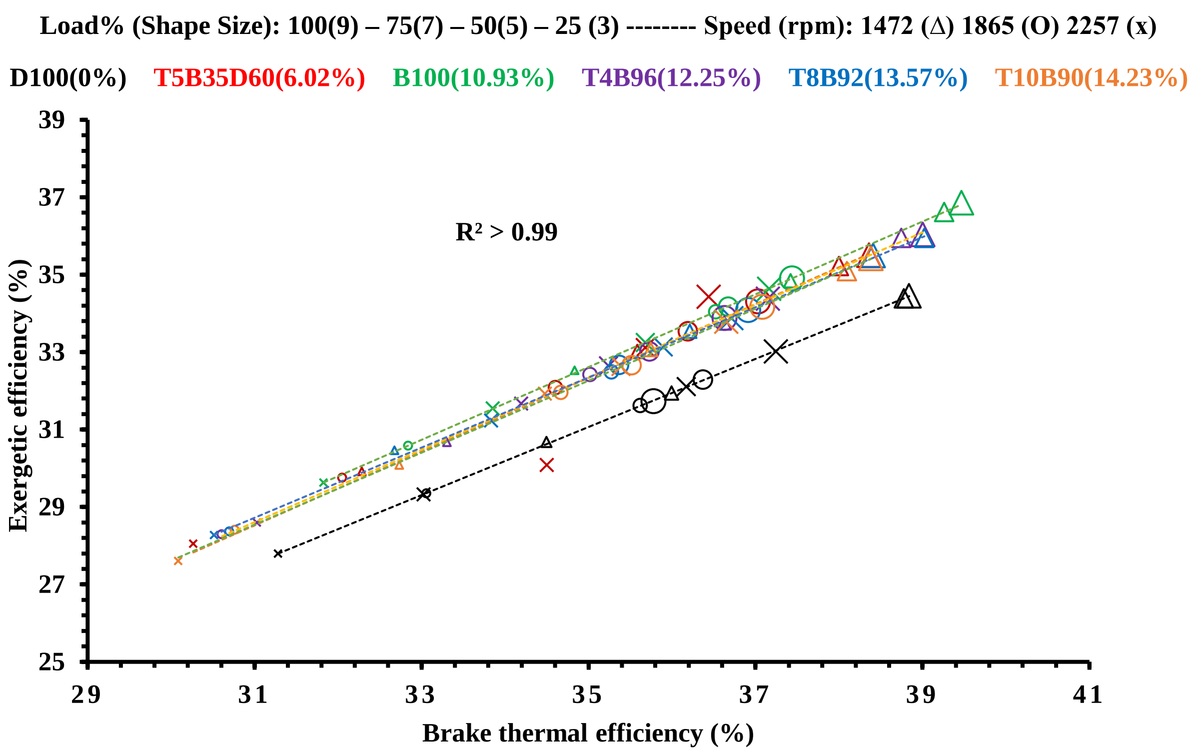

Fig. 12: Exergetic Efficiency vs. Brake thermal efficiency at 12 engine operating modes for the 6 tested fuels

4. Conclusion

This investigation used the first and second laws of thermodynamics to analyse the influence of oxygenated fuels on the quality and quantity of energy in a diesel engine using diesel, waste cooking biodiesel, and a highly oxygenated additive, triacetin. The six fuels used in this study had a range of fuel oxygen content from 0 to 14 wt%. The experimental engine performance and emission data were collected at 12 different engine operating modes (three different speeds and four engine loads), and were used to calculate and analyse the energy and exergy parameters, such as: fuel energy, thermal efficiency, exhaust energy loss, exergetic efficiency, destruction efficiency and exhaust exergy. The following conclusions were obtained from this study:

- Since the investigated fuels were oxygenated, this study used the oxygen ratio (OR) instead of the equivalence ratio.
- OR increased with decreasing engine load and increasing engine speed.
- OR showed strong correlations (with a high R^2) for different energy and exergy parameters.
- Increasing the OR decreased the fuel exergy, exhaust exergy, destruction efficiency and exergetic efficiency, while it increased the exergy destruction.
- Strong correlations with high R^2 was found between exhaust energy loss and brake thermal efficiency, exhaust exergy and exhaust temperature, destruction efficiency and exhaust efficiency, exergetic efficiency and brake specific fuel consumption, exergetic efficiency and thermal efficiency.
- Using oxygenated fuels resulted in higher brake thermal efficiency, OR, exergy destruction and exergetic efficiency; and lower exhaust energy loss, fuel exergy, engine power, exhaust exergy, exhaust temperature and brake specific fuel consumption.
- Increased in oxygen content resulted in better combustion, as irreversibilities were seen to be reduced with the addition of triacetin, but with a corresponding loss in heating value.
- Lower exhaust temperature obtained with oxygenated fuels resulted in lower exhaust exergy losses and higher exergetic efficiency.

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