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Evaluation of MWCNT as fuel additive to diesel–biodiesel blend in a direct injection diesel engine

Hamit Solmaz[a], Alper Calam[b], Emre Yılmaz[c], Fatih Şahin[a], Seyed Mohammad Safieddin Ardebili[d] and Fatih Aksoy[e]

[a]Department of Automotive Engineering, Faculty of Technology, Gazi University, Ankara, Turkey; [b]Department of Machinery and Metal Technologies, Technical Sciences Vocational High School, Gazi University, Ankara, Turkey; [c]Department of Automotive Technology, Sakarya University of Applied Science, Arifiye Vocational High School, Sakarya, Turkey; [d]Department of Biosystems Engineering, Shahid Chamran University of Ahvaz, Ahvaz, Iran; [e]Department of Automotive Engineering, Faculty of Technology, Afyon Kocatepe University, Afyon, Turkey

ABSTRACT

In this study, effects of multi-walled carbon nanotube (MWCNT) addition to waste frying oil biodiesel (B20) on performance, combustion, and exhaust emissions in a direct-injection compression ignition engine were investigated. Experiments were carried out at maximum engine torque speed and four different engine loads. The results show that engine performance has deteriorated somewhat by using B20 fuel without MWCNT additive compared with neat diesel. The addition of MWCNT to B20 improved fuel properties. This occurred because MWCNT additive improved engine performance. By using 100 ppm additive to B20 fuel, the combustion duration has been shortened compared to neat diesel, indicating that thermal efficiency has increased with the decrease of heat losses. The highest indicated thermal efficiency was recorded as 33.16% at 15 Nm engine load using 100 ppm additive to B20 test fuel. Also, 100 ppm additive to B20 test fuel reduced hydrocarbon, CO and soot emissions by 41, 36.4 and 31.8%, respectively, compared to reference neat diesel fuel. The MWCNT additive improved the in-cylinder combustion reactions, thereby increasing engine performance. With the improvement of combustion, in-cylinder gas temperatures increased. For this reason, higher NO_x emissions were obtained using MWCNT additive fuels compared to neat diesel.

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KEYWORDS
Nanoparticles; nanotube; MWCNT; additive; performance; combustion

Introduction

Industrial and economic growth is directly affected by the use of energy resources. Especially in the automotive industry, fossil fuels fulfill the energy demand significantly. However, the atmosphere, water and soil are polluted very rapidly and permanently because of these fossil-based fuels. Moreover, petroleum, which is the raw material of fossil fuels, is rapidly depleted [1–5]. Researchers are currently working on high-efficiency alternative combustion modes [6,7], alternative fuels with lower exhaust emissions [7–10], and electric vehicle technologies [11,12].

Homogeneous charge compression ignition (HCCI) and reactivity-controlled compression ignition (RCCI) engines developed as alternative combustion models have lower nitrogen oxide (NO_x) and soot emissions than spark ignition (SI) and compression ignition (CI) engines. Thermal efficiency is very high in these combustion modes. However, the operation range of HCCI and RCCI engines is narrow in terms of engine speed and engine load, and there is no physical mechanism controlling the combustion process. The combustion that occurs in HCCI and RCCI combustion modes is dependent on the chemical kinetics of the fuels used [13–16]. Electric vehicle technology is planned to be replaced by internal combustion engines in the automotive industry soon. However, electric vehicles have issues preventing them from being used widely very soon, such as problems with the battery technology, driving range of the vehicle, charging durations, and insufficient charging stations. In addition, when electric vehicles completely replace those with internal combustion engines, how to produce the electricity needed for these vehicles is an additional problem as well [17–20].

CI engines have higher efficiency and lower fuel consumption values than SI engines. However, their NO_x and soot emissions are quite high due to heterogeneous combustion. CI engines having emission troubles are planned to be abandoned entirely in the passenger vehicle sector by eliminating the existing problems of electric vehicles. However, it is predicted that CI engines can be used for a long time in heavy-duty vehicles on the roads, in the public transportation sector and marine transportation [21–24]. Therefore, researchers are still working to resolve the emission problems of CI engines [25–28]. It has been demonstrated in previous studies that the soot, carbon monoxide (CO) and unburned hydrocarbon (HC) emissions can be reduced in CI engines by using low-carbon-number alcohols (ethanol and methanol) as fuel [29–32]. However, the use of fuels such as ethanol and methanol in internal combustion engines requires some engine modifications [33,34]. By using alcohol with high carbon numbers (butanol and pentanol), high thermal efficiency can be achieved in CI engines without any engine modification [32,35,36].

CONTACT Alper Calam acalam@gazi.edu.tr Department of Machinery and Metal Technologies, Technical Sciences Vocational High School, Gazi University, Ankara, Turkey

However, the use of pure alcohol in internal combustion engines may present a cold starting problem, a high fuel consumption rate due to the lower heating value, low lubrication properties, and corrosive effects in the fuel system [37–39].

The high amounts of NO_x and soot emissions caused by diesel engines must be reduced simultaneously. Different methods can be used for this purpose, such as modification in engine design, improvement of combustion, and after-treatment equipment used in the exhaust system. The most preferred approach to reducing exhaust emissions is improving combustion in the cylinder instead of developing new designs or using additional after-treatment systems. This method could be successful in reducing emissions by improving fuel properties, improving fuel's close injection, or using fuel additives. The use of oxygen-containing biodiesel fuel may be an alternative to diesel fuel [40–42].

Biodiesel fuel from vegetable oils is a quickly produced, non-toxic, environmentally friendly, low-sulfur, and oxygenated alternative energy source for CI engines [43,44]. Many properties of biodiesel are similar to those of diesel fuel. Biodiesel use is also considered one of the best methods to reduce the noise and emission problem of CI engines. Therefore, the production and use of biodiesel from vegetable oils is a clever way to overcome these difficulties [45,46]. In addition, the oxygen content of biodiesel improves combustion [47]. The main disadvantage of using biodiesel as fuel is the use of cooking oil as raw material for the production of biodiesel. This problem will adversely affect both the food and biodiesel markets, resulting in increased costs. Therefore, in order to overcome problems related to food requirements, the raw material to be used for biodiesel production should not increase competition in the food market [48–50]. Non-edible oils may be preferred to reduce raw material costs in biodiesel production. Biodiesel produced from plants that can be grown with wastewater, do not need much water, and can grow on inefficient agricultural lands, will not threaten the food market [51]. However, producing biodiesel from waste cooking oil will avoid the environmental impact of waste oils. It will be also more economical compared to raw oil [52,53].

While biodiesel fuels have diesel-like properties, the most significant difference is that they contain oxygen. Therefore, combustion into the cylinder improves. Also, the cetane number of biodiesel, in general, is at the desired level for use in diesel engines [54,55]. Biodiesel is also biodegradable; it does not contain sulfur and does not have toxic effects [56,57]. Biodiesel has excellent lubrication properties [34,40]. From a safety perspective, the higher flash point of biodiesel compared with conventional fuels, including diesel, reveals that it is one of the safest fuels on the market [58,59]. Despite these advantages, the energy content of biodiesel is low compared to diesel fuel. Also, it has a cold start problem and high NO_x emissions [60–62]. Therefore, biodiesel fuel properties need to be improved to overcome these difficulties.

The fuel economy and emission characteristics of internal combustion engines are closely related to the physical and chemical properties of the fuel used. Various additives can be used as catalysts to improve fuel quality, provide better combustion and reduce exhaust emissions. During combustion, catalysts eliminate instability in mixing fuels and improve engine performance [63–65]. In recent years, it has been revealed that nano additives improve the flashpoint, kinematic viscosity, and other properties of diesel, biodiesel, and their mixture [66,67]. Most nano additives are produced from ceramic, polymeric, and metallic materials. The most commonly used nano additives are organic-based additives and metal oxides such as titanium, carbon, and iron [65]. The high energy level and high surface area/volume ratio of the metallic nano additives can improve combustion by increasing the thermal conductivity [68,69]. Also, improved kinematic viscosity can help to reduce the ignition delay [70]. There are some studies on the use of metal-based nano additives in diesel–biodiesel fuel mixtures. Boutonnet *et al.* [71] conducted the first study promoting the use of metal-based nano additives. Palladium, platinum, rhodium, and iridium metals were reduced after dissolution in organic solvents in ionic form. Monodispersed metal particles in the form of microemulsions were studied first. That study was a pioneer in the use of metal-based additives to improve engine performance by improving fuel properties. Saxena *et al.* [65] investigated the effect of metal-based additives on performance and exhaust emissions of the CI engine in the use of diesel–biodiesel blend fuels. It was reported that the addition of nanoparticles to blended fuels improved engine performance and exhaust emissions. However, it was concluded that more research is needed to understand the behavior of nanoparticles in the combustion process.

Basha *et al.* [72] examined the effects on engine performance and exhaust emissions of adding 25 and 50 ppm alumina and carbon nanotubes (CNT) to jatropha biodiesel. The highest thermal efficiency was 28.9%, with 25 ppm alumina and CNT additive (JBD25A25CNT) fuel. Thermal efficiency was recorded as 27.1% and 27.9% with the use of biodiesel with 50 ppm CNT (JBD50CNT) and 50 ppm alumina (JBD50A) additive, respectively. Thermal efficiency was 24.9% with the use of pure jatropha biodiesel. Also, with the use of nanoparticle-added jatropha biodiesel, NO_x and soot emissions decreased compared to pure jatropha biodiesel.

Sajith *et al.* [73] investigated the effects of adding 40 and 80 ppm cerium oxide (CeO_2) to jatropha biodiesel on engine performance and emissions at different engine loads. The highest thermal efficiency was recorded as 29% with 80 ppm CeO_2 nanoparticle additive fuel. HC emissions decreased by an average of 25% and 40%, respectively, in the use of fuels compounded with 40 and 80 ppm CeO_2. NO_x emissions decreased by approximately 30% with the use of fuel compounded with 80 ppm CeO_2. No significant change in CO emissions was observed with CeO_2 addition. Ghafoori *et al.* [74] investigated the effects of 2.5–30 ppm multi-walled carbon nanotube (MWCNT) addition to a 20% waste frying oil biodiesel/80% diesel fuel mixture (B20). The results were compared with diesel fuel. They observed that B20 fuel reduced the torque and power due to the low heating value of the fuel. However, the addition of MWCNT to B20 fuel increased engine performance. With the addition of 30 ppm MWCNT to B20 fuel, power increased by 17%, and engine torque increased by 18% compared to diesel fuel. The greatest improvement in specific fuel

Table 1. Specifications of the CI engine.

Engine parameters	Specification
Number of cylinders	1
Bore, mm	85
Stroke, mm	90
Displacement, cm^3	510
Compression ratio	17.5/1
Rated power, kW/rpm	9/3000
Maximum torque, Nm/rpm	32.8/1800
Type of injection	Direct injection
Nozzle opening pressure, bar	190
Type of cooling	Water cooling

consumption was recorded as 55% in the case of using 20 ppm MWCNT additive. The addition of MWCNT to B20 fuel resulted in the improvement of CO and HC emissions depending on the MWCNT ratio in the mixture. Mirzajanzadeh *et al.* [75] studied the effects of hybrid nano-catalyst additive containing MWCNT and CeO_2 nanoparticles on performance and exhaust emissions of a CI engine. The biodiesel used in the study was produced from waste frying oil; 30, 60 and 90 ppm nanocatalysts were added to B5 and B20 fuels. The addition of a 90 ppm nano-catalyst increased engine torque by 3.51% compared to B5 fuel. Similarly, the addition of 90 ppm nanocatalyst increased the engine torque by 4.91% compared to B20 fuel. The lowest specific fuel consumption was achieved by adding a 90 ppm nanocatalyst to B20 fuel. The results obtained revealed that the high surface area of the nano-catalyst particles and their proper distribution, together with the catalytic oxidation reaction, led to significant improvements in combustion reactions, especially by adding 90 ppm additive to the B20 fuel. The addition of 90 ppm nanocatalyst to B20 reduced NO_x, CO, unburned HC, and soot emissions by 18.9%, 38.8%, 71.4% and 26.3%, respectively. Tewari *et al.* [76] examined the effect of adding 25 and 50 ppm MWCNT to honge biodiesel on performance and exhaust emissions in a single-cylinder diesel engine. Experimental results were compared with pure diesel (neat diesel) and pure honge biodiesel. Adding MWCNT to the biodiesel increased thermal efficiency due to its high surface area and, consequently, high chemical reactivity properties. Also, CO, UHC and soot emissions for biodiesel fuels blended with MWCNTs were lower than those of pure biodiesel fuel. This was due to the catalytic activity of MWCNTs that improve the combustion process.

In order to reduce exhaust emissions of CI engines, carbon nanotubes can be more effective than base metal additives such as titanium and molybdenum due to their superior thermal and chemical properties. For example, thanks to the high combustion temperature of carbon nanoparticles (high exothermic heat release), high surface area/volume ratio and various oxygen functional groups, they can provide the proper conditions for complete combustion in the cylinder [77]. Current MWCNT-related studies were carried out on air-cooled engines. It is known that air-cooled engines have instability problems. Accordingly, experimental studies were carried out on a water-cooled test engine in the present study. On the other hand, studies in the literature show that a maximum amount of 90 ppm MWCNT was used. In this study, biodiesel was produced from waste cooking oil and blended with 80% pure diesel by volume to obtain B20 fuel; 25, 50, 75 and 100 ppm MWCNT was added to B20 fuel, and combustion

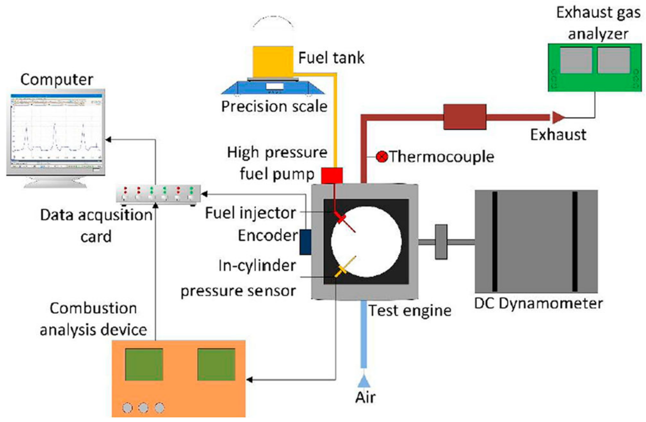

Figure 1. Layout of the experimental test rig.

characteristics, engine performance, and exhaust emissions were compared in a single-cylinder, water-cooled CI test engine. Experiments were carried out at an engine speed of 1800 rpm and engine loads of 20, 15, 10 and 5 Nm. As a result of the experimental study, internal pressure, rate of heat release (ROHR), combustion duration (CA90-10), CA50, indicated thermal efficiency, brake specific fuel consumption (bsfc), CO, HC, NO_x, and soot emissions were comparatively analyzed.

Experimental setup and procedures

Testbed

In this study, a single-cylinder, water-cooled and direct injection Lombardini-Antor brand model LD510 CI engine was used in the experiments. The technical specifications of the test engine are given in Table 1. A Cussons brand P8160 DC dynamometer, which can brake up to 10 kW at 4000 rpm engine speed, was used to load the test engine. In order to measure the in-cylinder pressure, an AVL brand model 8QP500c pressure sensor with a sensitivity of 11.96 Pc/bar and measuring range of 0–150 bar was used. The cylinder volume variation and location of the piston in the cylinder were determined using a 1000 pulse encoder that was connected to the crankshaft. In-cylinder raw pressure signals were amplified with the Cussons P4110 combustion analyzer. Amplified analog pressure signals were converted to digital signals with a NI USB6259 data acquisition card. Digital pressure signals and encoder data were stored on the computer with a crank angle resolution of 0.36°. The data obtained over 50 consecutive cycles for each test condition were averaged. A schematic view of the testbed is illustrated in Figure 1.

A Bosch BEA350 exhaust gas analyzer was used to measure exhaust emissions. AVL DiSmoke 400 device was used to determine soot emissions. Technical characteristics of the exhaust gas analyzer and soot opacimeter are shown in Table 2 and Table 3, respectively.

Preparation of waste cooking oil biodiesel

Production of biodiesel from edible vegetable oils is one of the threats to the food industry. Therefore, waste cooking oils are widely preferred for biodiesel production. In this study, biodiesel was produced by the transesterification method using waste cooking oils obtained from Gazi

Table 2. Specifications of the Bosch BEA350.

	Operating range	Accuracy
Lambda	0.5 to 9.999	0.001
Nitrogen oxide(ppm vol)	0 to 5000	1
Carbon monoxide(% vol)	0 to 10	0.001
Oxygen (% vol)	0 to 22	0.01
Hydrocarbon(ppm vol)	0 to 9999	1

Table 3. Specifications of the smoke meter.

	AVL DiSmoke 4000	
Analyzer	Opacity	K-value
Operating range, %	0–100	0.1
Accuracy, m^{-1}	0–99.99	0.01

University refectory. The waste oil was filtered before the biodiesel production process, and the particles in it were removed. Then, it was heated to 120 °C and left for 1 h to extract the water. For transesterification, 99.5% purity Merck brand methanol was used with a percentage of 20% by mass, and 0.5% sodium hydroxide (NaOH) catalyst was used. These components were used for biodiesel production by transesterification at a reaction temperature of 60 °C. The produced biodiesel was washed five times to remove glycerin. The produced biodiesel was blended with diesel fuel at 20% biodiesel by volume and 80% diesel fuel to obtain reference B20 fuel.

MWCNT–B20 mixture preparation and fuel properties

The MWCNT used in this study is a solid powder, dark black in color. Its purity is higher than 96%. The outer diameter of each tube is 4–16 nm, inner diameter is 2–6 nm, and length is 15–35 µm. The specific surface area is 240 m2/g. MWCNT was obtained from Nanografi. A scanning electron microscope (SEM) image of MWCNT is shown in Figure 2. The image shows that the surface of the MWCNTs is smooth.

An IsoLAB brand ultrasonic bath (homogenizer) was used to mix MWCNT and B20 fuel: 25, 50, 75 and 100 ppm MWCNT were mixed for 60 min with B20 fuel in a homogenizer with a maximum capacity of 10 L and a frequency of 40 kHz. The color of B20 fuel is light yellow. As the MWCNT ratio in the blend fuels increased, the fuel color turned to dark gray. The blended fuels were left for 24 h, and no precipitation was observed. The composition of the test fuels is given in Table 4. In addition, the properties of the test fuels are shown in Table 5.

Stability of the mixtures was determined by Zeta potential test with Malvern Nano ZS90 test equipment. Zeta potentials were determined as 41.5, 43, 50.3, and 55.8 mV for the blends B20MWCNT25, B20MWCNT50, B20MWCNT75, and B20MWCNT100, respectively. Zeta potential stability behavior of colloidal matters is classified in the 5 range and a potential above 40 mV indicates a good stability [78].

Combustion analysis

In-cylinder pressure was calculated by averaging the data obtained over 50 consecutive cycles. The combustion analysis was carried out using the mean in-cylinder pressure trace. An algorithm was prepared using MATLAB programming code. Cylinder pressure, heat release rate, the start of the combustion (CA10), combustion duration (CA90-10), and the crank angle at which 50% of cumulative heat release is realized (CA50) were calculated by thermodynamic analysis. The first law of thermodynamics was used to determine the rate of heat release. Therefore, mass and gas leaks were neglected during one cycle. The heat transfer from the cylinder to the cylinder wall was calculated to determine the heat release rate. The heat release rate, depending on the crank angle, was calculated with Equation (1):

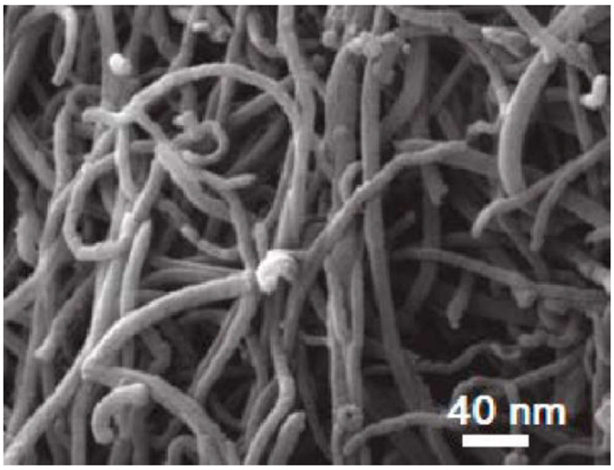

Figure 2. SEM image of MWCNT.

Table 4. Composition of the fuel types.

Fuel type	Composition
Diesel	Neat diesel
B20	80% diesel + 20% biodiesel by volume
$B20_{MWCNT25}$	B20 + 25 ppm MWCNT
$B20_{MWCNT50}$	B20 + 50 ppm MWCNT
$B20_{MWCNT75}$	B20 + 75 ppm MWCNT
$B20_{MWCNT100}$	B20 + 100 ppm MWCNT

$$\frac{dQ}{d\theta} = \frac{k}{k-1} P \frac{dV}{d\theta} + \frac{1}{k-1} V \frac{dP}{d\theta} + \frac{dQ_{1s1}}{d\theta} \quad (1)$$

In the equation above, dQ, P, V, $d\theta$, k and $\frac{dQ_{1s1}}{d\theta}$ represent net heat release, in-cylinder pressure, cylinder volume, differentiation of crank angle, rate of specific heats and heat transfer to the cylinder wall, respectively. Thermal efficiency was calculated using Equation (2):

$$\eta_{th} = \frac{W_{net}}{\dot{m}_{biodiesel} \times Q_{LHV\,biodiesel} + \dot{m}_{diesel} \times Q_{LHV\,diesel}} \quad (2)$$

In Equation (2), W_{net}, $\dot{m}_{biodiesel}$, $\dot{m}_{diesel}$, $Q_{LHV\,biodiesel}$ and $Q_{LHV\,diesel}$ represent net work, cyclic fuel consumption for biodiesel and diesel, and lower heating values of biodiesel and diesel, respectively. In order to calculate the network,

$$W_{net} = \int P dV \quad (3)$$

was used.

Results and discussion

In-cylinder pressure and rate of heat release

Figure 2 shows the variation of the in-cylinder pressure and heat release rate depending on the crank angle for different engine loads and test fuels. In the use of B20 fuel, the pressure in the cylinder increased by 2% for all engine

Table 5. Properties of the test fuels.

	Lower heating value [kJ/kg]	Density [kg/m^3 at 15 °C]	Flash point [°C]	Kinematic viscosity [cSt at 40 °C]	Cetane number
Diesel	44,343	831.9	65	2.76	55
B20	43,325	843.2	76	3.19	52.5
B100	39,253	888.4	120	4.9	42.5
B20MWCNT25	43,369	843.9	74	3.15	52.9
B20MWCNT50	43,401	845.2	71	3.09	53.4
B20MWCNT75	43,448	846.9	69	2.97	54.1
B20MWCNT100	43,616	848.1	67	2.95	55.3

loads compared to pure diesel, and the location of the peak pressure was delayed. The thermal value of B20 fuel is lower than that of pure diesel. However, the oxygen it contains improves combustion [44]. As can be seen in Figure 3, the maximum in-cylinder pressure is retarded by increasing the engine load for all test fuels. As more fuel is injected into the cylinder with increased engine load, more time is needed to complete the combustion. Therefore, the combustion phase is delayed at high engine loads. Figure 3d shows that the maximum in-cylinder pressure is obtained at the highest engine load compared to other engine loads. In order to achieve the highest indicated thermal efficiency, the maximum in-cylinder pressure must be obtained 7–11°CA after the top dead center (TDC) [79]. Injecting more fuel into the cylinder results in higher cylinder pressure.

It is shown in Figure 3 that higher cylinder pressure and heat release rate values were obtained by adding MWCNT to B20 fuel. MWCNT has high thermal conductivity. In addition, MWCNT is an additive used to increase the cetane number [64]. Adding MWCNT to B20 fuel increases the evaporation rate of fuel droplets. This shortens the ignition delay. However, the large surface area/volume ratio of MWCNTs increases the heat transfer between the particle and the fuel droplet; as a result, the MWCNT additive improves fuel atomization and combustion. The MWCNT additive increased the reaction temperature inside the cylinder and the peak pressure values. In experiments carried out at the engine speed of 1800 rpm and 20 Nm engine load, cylinder pressure of 59.1 bar was obtained with B20 fuel, while it was recorded as 59.3, 59.6, 60.1, and 60.6 bar for B20MWCNT25, B20MWCNT50, B20MWCNT75, and B20MWCNT100 fuels, respectively.

The variation of bsfc

The variation of bsfc for different engine loads is shown in Figure 4. Compared to the results for pure diesel at both full load and partial loads, bsfc values of B20 were higher. In diesel engines, bsfc values are directly affected by the fuel injection system, the specific gravity of the fuel, and the relationship between the viscosity and the thermal value of the fuel [80]. Due to its higher specific gravity and lower thermal value compared to pure diesel fuel, more fuel is needed when B20 fuel is used to achieve the same amount of output torque. When using B20 fuel under full load conditions, bsfc worsened by 11.7% compared to pure diesel fuel. At partial loads, the bsfc variations in B20 fuel are higher than in pure diesel. Adding MWCNT to B20 fuel improves combustion and increases the in-cylinder pressure, and as a result of that bsfc decreases. The addition of 100 ppm MWCNT to B20 fuel under full load conditions led to a 9.52% improvement in bsfc. As the MWCNT ratio in mixture fuels increased, bsfc values decreased and approached those of pure diesel. The increase in the amount of MWCNT in the fuel mixtures allowed the viscosity and cetane index to be regulated simultaneously [81]. This is an indication that the addition of MWCNT improves fuel quality. The decrease in bsfc might also be caused by the improved surface area/volume ratio [82]. A similar decreasing bsfc trend with the increase of MWCNT addition was reported by Ghafoori *et al.* [74].

The variation of combustion duration

Figure 5 shows the variation of the combustion duration depending on the crank angle for all test fuels. It can be seen that combustion is completed at a longer crank angle with increasing engine load. With the increase of engine load, the higher amount of fuel being sprayed into the combustion chamber extends the combustion duration. In this study, CA90-10 was defined as the combustion duration. CA10 defines the crank angle at which combustion starts and CA90 the angle at which combustion ends. Adding biodiesel to pure diesel fuel improves chemical oxidation reactions. B20 fuel provides higher oxygen content and better oxidation reactions. In addition, the higher cetane number of biodiesel causes the combustion duration to decrease compared to that of pure diesel. Combustion with B20 fuel was completed in 46.8°CA under full load conditions, while combustion in pure diesel use was completed in 48.96°CA. Adding MWCNT to B20 fuel caused the combustion duration to be shortened even more. Combustion was completed at smaller crank angles as the MWCNT ratio in the blend fuels increased. MWCNT is a metal-based fuel additive that stands out because of its high thermal conductivity. Therefore, by adding MWCNT to B20 fuel, fuel droplets can evaporate more easily. In addition, the high oxygen content of biodiesel improves combustion and ensures earlier combustion. However, the high surface area/volume ratio of MWCNT improves fuel atomization. Combustion was completed at 45, 42.84, 41.76, and 39.24°CA with the use of B20MWCNT25, B20MWCNT50, B20MWCNT75, and B20MWCNT100 fuel, respectively, under full load conditions.

The variation of CA50 and indicated thermal efficiency

Thermal efficiency is one of the most crucial motor performance parameters. Thermal efficiency refers to how fuel energy is converted into effective power. CA50 refers to the crank angle at which 50% of the cumulative heat release occurs. The fact that CA50 takes place 7–11°CA after TDC provides maximum thermal efficiency [79]. Therefore, CA50 and the indicated thermal efficiency are closely related. In Figure 6,

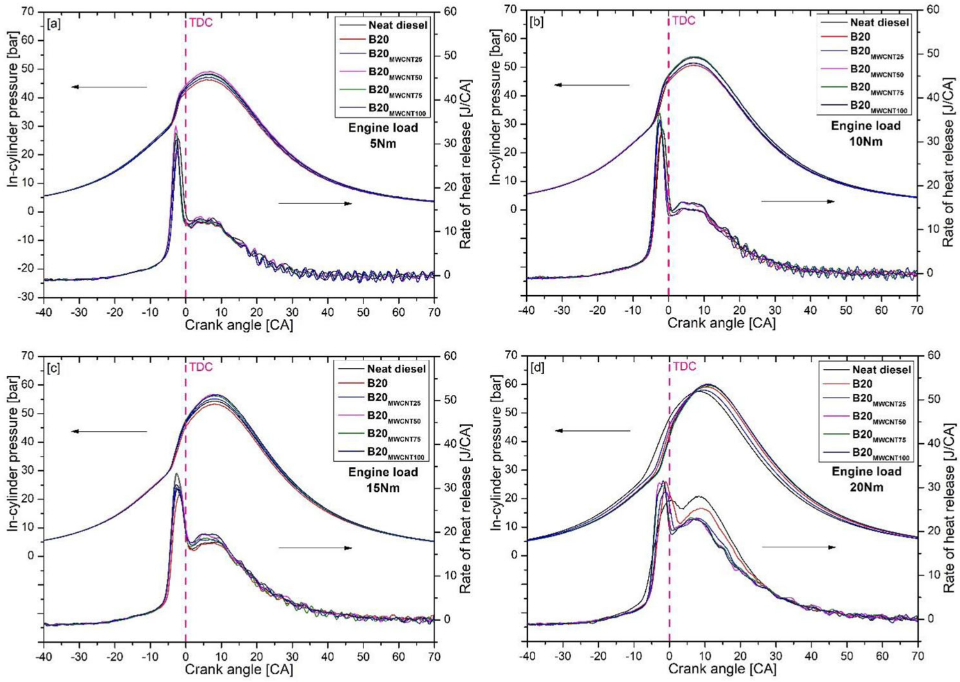

Figure 3. The variation of in-cylinder pressure and rate of heat release at different engine loads.

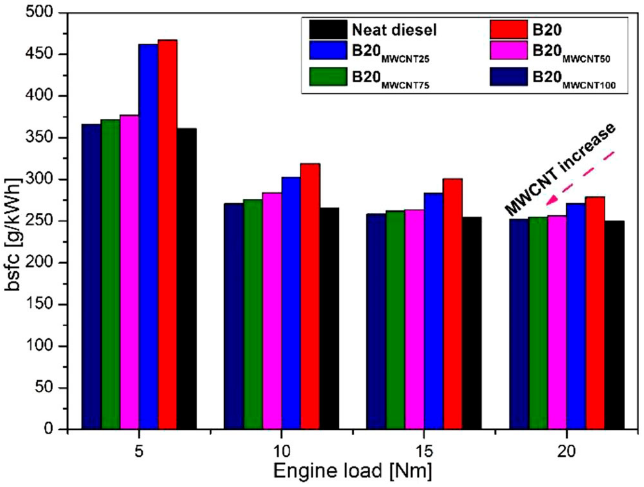

Figure 4. The variation of bsfc.

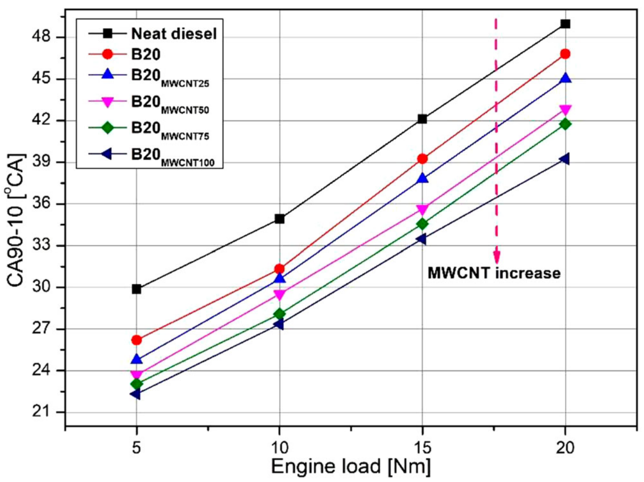

Figure 5. The variation of combustion duration.

the change in the indicated thermal efficiency and the CA50 depending on the engine load can be seen. Figure 6a shows that the CA50 was delayed in the use of all test fuels with increasing engine load. The most shifted CA50 was obtained with B20 fuel in all engine loads, because of the high viscosity of biodiesel which causes larger droplet diameter during the injection. With the addition of MWCNT to B20 fuel, the thermal conductivity of the fuel increased. Thus, the ability to blend fuels to evaporate was increased. Also, the high surface area/volume ratio of MWCNT enabled the droplet diameter to decrease during fuel injection of B20 fuel. As the rate of MWCNT added to B20 fuel increased, this enabled the CA50 to be advantageous at all engine loads. Figure 6b shows the variations in the indicated thermal efficiency. Indicated thermal efficiency increased up to 15 Nm engine load in all test fuels but decreased again under full load conditions. Under full load conditions, the amount of fuel injected into the cylinder is at the maximum level. Therefore, the combustion duration is extended, and CA50 is delayed. In addition, the fact that the location of the peak pressure occurs long after the TDC reduces the peak pressure values. To delay the CA50 too much causes the volume of the cylinder to increase. This increases the heat losses from the cylinder walls, and the thermal efficiency decreases. The highest indicated thermal efficiency was recorded as 33.16% in B20MWCNT100 fuel usage at 15 Nm engine load. Under the same conditions, the indicated thermal efficiency in the use of pure diesel, B20, B20MWCNT25, B20MWCNT50, and B20MWCNT75 fuel was recorded as 32.81%, 31.32%, 30.82%, 31.2%, and 32.7%, respectively. Compared to pure diesel fuel, while the indicated thermal efficiency in B20 usage decreased, adding MWCNT to B20 improved combustion and increased thermal efficiency. The thermal efficiency results are compatible with the results of the study conducted by Basha and Anand [72], in which the best thermal efficiency was obtained with CNT addition.

The variation of CO emissions

The main reasons for the formation of CO emissions in internal combustion engines are the in-cylinder oxygen concentration and post-combustion gas temperatures. Low temperatures after combustion increase CO emissions

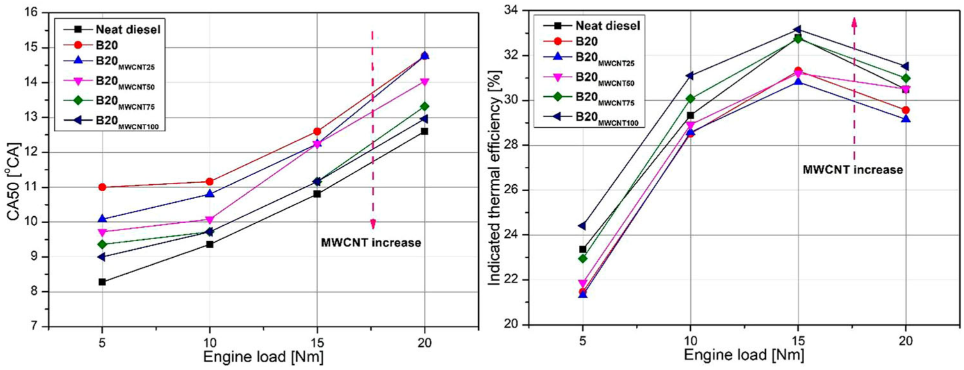

Figure 6. The variation of (a) CA50 and (b) indicated thermal efficiency.

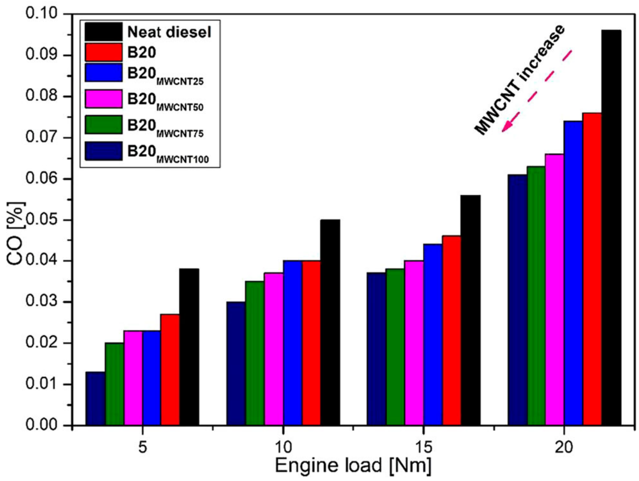

Figure 7. The variation of CO.

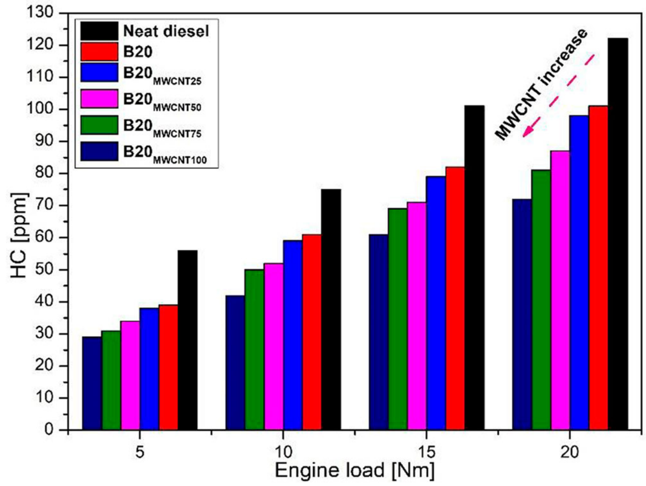

Figure 8. The variation of HC.

because oxidation reactions are disrupted. However, biodiesel, which has an oxygen content, ensures CO emissions are reduced. Figure 7 shows the variation of CO emissions depending on the engine load. CO emissions increase with increasing engine load. However, compared to pure diesel fuel, B20 and MWCNT-added fuels achieved lower CO emission values for all engine loads. Injecting more fuel into the cylinder at high engine loads causes a decrease in the oxygen concentration in the combustion chamber because of the increased average engine temperature at high loads. Low oxygen content causes less fuel oxidation. Thus, hydrocarbon and oxygen molecules cannot perform a good reaction, and CO emissions increase. CO emissions decreased when using B20 fuel compared to pure diesel fuel, due to the oxygen content of the biodiesel. Additionally, adding MWCNT to B20 fuel further reduced CO emissions. MWCNT improved combustion and increased the indicated thermal efficiency for all engine loads. Gas temperatures at the end of combustion increased with the contribution of MWCNT, and CO emissions decreased. In the use of B20, B20MWCNT25, B20MWCNT50, B20MWCNT75, and B20MWCNT100 fuels compared to pure diesel fuel, CO emissions decreased by 20.8%, 22.9%, 31.25%, 34.4%, and 36.4%, respectively.

The variation of HC emissions

HC emissions result from the fuel not being oxidized due to low temperature or a lack of oxygen in the cylinder [25,43,47]. The variation of HC emissions at different engine loads is shown in Figure 8. HC emissions increase with increasing engine load, because the amount of fuel injected into the cylinder increases and the oxygen concentration decreases accordingly. The oxygen content of B20 fuel improves combustion and contributes to the reduction of HC emissions. In addition, as mentioned, the high cetane number of biodiesel causes the combustion duration to be shortened. The combustion completed in smaller crank angles reduces heat losses from the cylinder wall, reduces HC emissions and increases thermal efficiency. The highest HC emission for all engine loads was recorded with the use of pure diesel fuel. It is shown in Figure 8 that HC emissions were significantly reduced by adding MWCNT to B20 fuel. A similar trend was also presented in the study conducted by Ghafoori *et al.* [74]. MWCNT additive improved the atomization properties of the fuel. The high surface area/volume ratio accelerated proper air–fuel mixture. Thus, oxidation reactions were accelerated, and HC emissions were reduced further. Compared to pure diesel fuel, HC emissions decreased by 17.2%, 19.67%, 28.69%, 33.6%, and 41% with the use of B20, B20MWCNT25, B20MWCNT50, B20MWCNT75, and B20MWCNT100 fuels, respectively, at full load conditions.

The variation of NO_x and soot emissions

High combustion temperature in CI engines causes NO_x emissions to be high. At high cylinder gas temperatures, nitrogen and oxygen molecules react chemically, and NO_x emissions occur. In-cylinder gas temperature, sufficient oxygen concentration, and reaction time are the main factors

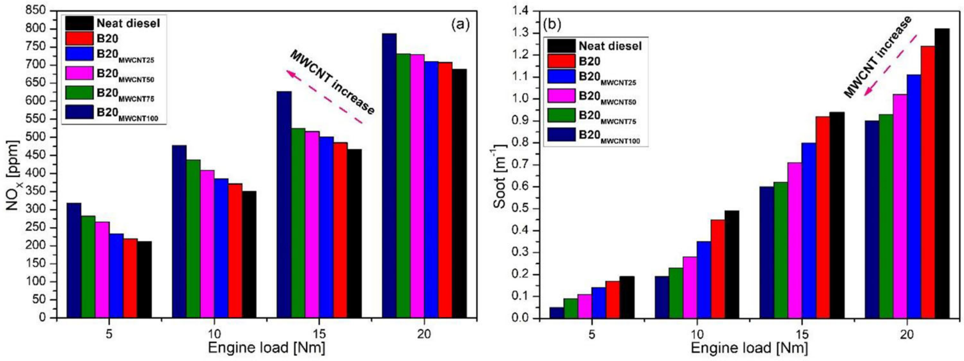

Figure 9. The variation of (a) NO_x emissions and (b) soot emissions.

in NO_x emissions. Figure 9a shows that NO_x emissions increase with increasing engine load. As the engine load increases, the amount of fuel oxidized in the combustion chamber increases, and higher gas temperatures are obtained. The lowest NO_x emission was recorded with the use of pure diesel fuel. NO_x emission increased with the use of B20 and MWCNT-added fuels compared to pure diesel. The presence of oxygen in the biodiesel content improves oxidation reactions. As a result, the gas temperatures at the end of the combustion increase, and NO_x emission increases. The addition of MWCNT to B20 improved combustion, thereby increasing thermal efficiency at all engine loads. Accordingly, post-combustion gas temperatures increased, and NO_x emissions increased. The highest NO_x emissions were recorded with B20MWCNT100 fuel for all engine loads. B20MWCNT100 fuel provided minimum bsfc and minimum HC emissions at all engine loads. The maximum indicated thermal efficiency was also obtained with B20MWCNT100 fuel. Under full load conditions, NO_x emission was recorded as 786 ppm with B20MWCNT100 fuel. NO_x emissions worsened with the use of B20, B20MWCNT25, B20MWCNT50, B20MWCNT75, and B20MWCNT100 fuels under full load conditions compared to pure diesel fuel, by 2.7%, 3.1%, 5.6%, 5.9%, and 12.4%, respectively.

Figure 9b shows the variation of soot emissions with the engine load. The figure clearly shows that the soot emissions increase due to the increase in engine load. More fuel injection with increased engine load will result in more regionally rich mixing zones in the combustion chamber. Especially in combustion areas where oxygen is insufficient, soot emissions occur as a result of the thermal cracking of long-chain HC molecules. However, oxygenated biodiesel increases the concentration of oxygen in the combustion chamber, thereby reducing soot emissions. With the use of MWCNT-added fuels, soot emissions were reduced for all engine loads compared to pure diesel, because MWCNT additive improves the air/fuel mixture rate and reduces work emissions. The soot emissions of B20MWCNT25, B20MWCNT50, B20MWCNT75, and B20MWCNT100 fuels decreased by 15.9%, 22.7%, 29.5% and 31.8%, respectively, compared to pure diesel at full load conditions.

Conclusion

In this study, the effect of MWCNT addition to biodiesel fuel on engine performance, combustion and exhaust emissions in a single-cylinder, water-cooled, direct-injection CI engine was investigated. Pure diesel was used as a reference fuel. In addition, biodiesel produced from waste cooking oil was blended with 80% pure diesel by volume. Test fuels were prepared by adding 25, 50, 75, and 100 ppm MWCNT to B20 fuel. Experiments were carried out at four engine loads (20, 15, 10, and 5 Nm) and an engine speed of 1800 rpm, which is the maximum torque speed of the engine. The experimental results showed that the addition of MWCNT to B20 fuel eliminates the disadvantages of biodiesel compared to pure diesel. The indicated thermal efficiency decreased by 3.05% at full load with B20 fuel compared to pure diesel, while the thermal efficiency of B20MWCNT100 increased by 3.3% compared to pure diesel. It can be said that pure diesel, B20, and MWCNT additives did not cause a significant change in the in-cylinder pressure. Nevertheless, MWCNT-added biodiesel blend fuels provide better performance than pure diesel. B20 and MWCNT-added blended biodiesel fuels showed significant improvements in HC, CO, and soot emissions. The most important improvement was achieved with B20MWCNT100 fuel. In the use of B20MWCNT100 fuel, HC, CO and soot emissions decreased by 41, 36.4 and 31.8%, respectively, under full load conditions, compared to pure diesel fuel. The addition of MWCNT to B20 fuel improved fuel atomization, increased combustion efficiency, and shortened combustion time due to a high surface area/volume ratio and high thermal conductivity. Therefore, NO_x emissions of MWCNT-added fuels increased under all engine load operating conditions compared to pure diesel. The highest increase was recorded as 12.4% with the use of B20MWCNT100 fuel compared to pure diesel.

In conclusion, this study reveals that metal-based MWCNT-added biodiesel could be used in conventional CI engines instead of pure diesel fuel to retain high engine performance. However, the increase in NO_x when MWCNT was used should be eliminated by an after-treatment system. For this reason, the effects of the metallic MWCNT particles on after-treatment systems such as selective catalytic reduction (SCR) and diesel particulate filter (DPF), which have very narrow flow channels coated with noble metals, must be investigated.

Disclosure statement

No potential conflict of interest was reported by the authors.

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ORCID

Alper Calam http://orcid.org/0000-0003-4125-2127

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