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A POTENTIAL STUDY ON CLOVE OIL, EUGENOL AND EUGENYL ACETATE AS DIESEL FUEL BIO-ADDITIVES AND THEIR PERFORMANCE ON ONE CYLINDER ENGINE

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Abstract. Research on the potency of essential oils as diesel fuel bio-additives has been reported. It also has been found out that clove oil has a better performance than turpentine oil on decreasing Break Specific Fuel Consumption (BSFC) and reduces the exhaust emissions of the engine. Clove oil is essential oil the content of which is made of eugenol acting as the main component. Eugenol has a bulky structure, two oxygen atoms and can form eugenyl acetate from ester reaction. Eugenyl acetate has a bulkier structure and higher oxygen content than eugenol which leads to optimizing the process of fuel combustion. This experiment can give information about the potency of the bio-additive based on clove oil and eugenol and about the influence of oxygen enrichment with eugenol on the performance of the diesel fuel bio-additive. In general, this experiment covered three stages. The first step is the characterization of the diesel fuel bio-additive using a GCMS and FTIR spectrophotometer. The second step is the characterization of the diesel fuel bio-additive and composition optimization. The final step is conducting a diesel fuel bio-additive performance test on one cylinder engine on a laboratory scale. The results of the carried out experiment show that clove oil, eugenol and eugenyl acetate can decrease Break Specific Fuel Consumption (BSFC) and reduce the exhaust emissions of the engine as well as oxygen enrichment can help in reaching optimal fuel combustion.

Keywords: clove oil, eugenol, eugenyl acetate, diesel fuel, bio-additive, engine.

1. Introduction

A number of researches on an increase in diesel fuel quality have been conducted. Gupta *et. al* (2007) studied the effect of Di-tertiary Butyl Peroxide (DTBP) on Primary Reference Fuels (PRFs) in Homogeneous Charge Compression Ignition (HCCI) engines and the results of the performed experiment show that a DTBP predominant mode of action on low Octane Number (ON) fuels is thermal while for high ON fuels it is chemical. Shih (1998) examined the influence of fuel additives such as EHN, DTBP, MTBE, DMC, diglyme, monoglyme and ethanol on the exhaust emissions of the diesel engine. The overall results of the carried out experiment show that fuel additives have a substantial effect on the engine's fuel spray penetration, fuel-air mixing processes, ignition delay, chemical reaction rates, total heat release and have a positive impact on reducing exhaust emissions; however, it is not necessary that these effects are all positive and significant on every type of emissions (temperature, NO_x, HC and smoke). Johnson (2008) analyzed the oxidation behavior of SI primary reference fuels with propionaldehyde and DTBP as an additive. The conducted experiment shows an addition of propionaldehyde or a negative temperature coefficient (NTC) of DTBP effects during HCCI combustion. Research into the quality of fuels and their biocomponents also presented by another researchers, for example: Al-Hasan and Al-Momany (2008); Butkus *et al.* (2007); Chen *et al.* (2008); Kwanchareon *et al.* (2007); Lebedevas and Lebedeva (2009); Lebedevas *et al.* (2009); Lebedevas *et al.* (2007); Lingaitis and Pukalskas (2008a, 2008b); Matijošius and Sokolovskij (2009); Mittelbach and Remschmidt (2004); Pukalskas *et al.* (2009); Raslavičius and Bazaras (2009); Raslavičius and Markšaitis (2007); Shi *et al.* (2006); Török (2009); Yao *et al.* (2008).

Fuel oxygen content (oxygenates) is one of parameters for determining the quality of diesel fuel. Song *et al.* (2002) has considered that blending oxygen-containing compounds with diesel fuel leads to an increase in cetane number and the process of fuel combustion can be completed. It is in accord with research published by Kadarohman *et al.* (2008) at the International Seminar on Chemistry who reported that a clove oil bio-additive

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had a better performance than turpentine oil to increase the process of fuel combustion reactivity.

The detailed mechanisms of the oxygenated fuels reducing the exhaust emissions of the engine are not properly understood. Mueller and Martin's (2002) experiment has shown that the overall oxygen content is not the only important parameter in determining the potential of reduction in exhaust emissions of the oxygenated fuel.

Clove oil is the essential oil containing eugenol as the main component. Eugenol allows splash blending in a solution possibly used for the first time. Analysis shows that eugenol has two oxygen atoms (Kadarohman 2003). The oxygenated molecular structure also plays a significant role. The bulky structure of eugenol can decrease the strength of Van der Walls bond in diesel fuel and the chain of carbon. Oxygen content and the molecular structure can lead to an increase in the efficiency of the fuel combustion process. The structure of eugenol is displayed in Fig. 1.

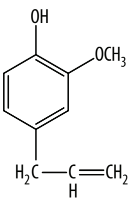
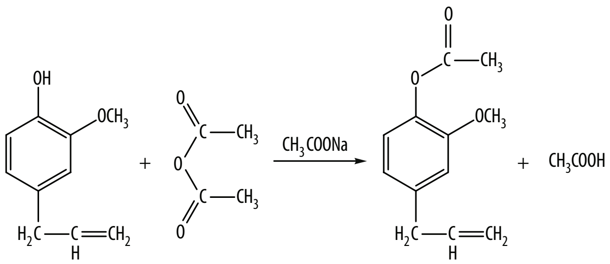


Fig. 1. The structure of eugenol



Eugenol Eugenyl asetat

Fig. 2. The ester reaction of eugenol forms eugenyl acetate

Eugenol can form eugenyl acetate from ester reaction. Eugenyl acetate has a bulkier structure and higher oxygen content than eugenol. Such enrichment with oxygen can optimize the process of fuel combustion. The caused reaction is presented in Fig. 2.

2. Methods of Research

The experiment included three stages:

1. Diesel fuel and bio-additive characterization.

At this stage, diesel fuel, clove oil, eugenol and eugenyl acetate were characterized using a FTIR and GCMS spectrophotometer.

2. The physical characterization and composition of bio-additive fuel blends were optimized.

According of Callahan *et al.* (1987), the quality parameter of diesel fuel is influenced by specific gravity, viscosity, aniline point and diesel index, and therefore this experiment covered physical characterization obtained by specific gravity parameter, viscosity, aniline point, flash point, API gravity and diesel index. The received data was compared with diesel fuel specifications for DIRJEN MIGAS. An optimum composition was determined by a test on fuel consumption flow in one cylinder engine (using KUBOTA engine).

3. Performance test in one cylinder engine.

Performance test was done on a laboratory scale using one cylinder engine HATZ 667 cc 1D81Z with testing parameters for fuel consumption flow and exhaust emissions.

3. Results

3.1. Diesel Fuel and Bio-additive Characterization

First, the characterization of diesel fuel, clove oil, eugenol, and eugenyl acetate was done using the GCMS and FTIR spectrophotometer.

a. Diesel Fuel Characterization

GC analysis of diesel fuel has shown that diesel fuel used in this experiment contains 66 alkane compounds with the number of carbon which is about 14–19 (Fig. 3). Based on the MS analysis of the reached peaks, some compounds of diesel fuel can be identified (Table 1).

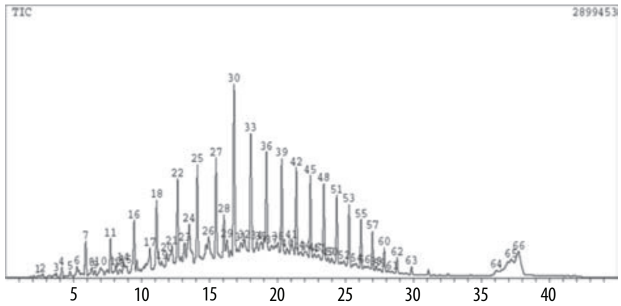


Fig. 3. GC spectra of diesel fuel

Table 1. Some compounds of diesel fuel.

No	Molecular Formula	Name	Retention time (minutes)	Conc. (%)
1	$C_{14}H_{30}$	Tetradekane	14.278	3.60
2	$C_{15}H_{32}$	Pentadekane	16.071	4.18
3	$C_{16}H_{34}$	Heksadekane	17.770	4.67
4	$C_{17}H_{36}$	Heptadekane	19.428	9.28
5	$C_{18}H_{38}$	Oktadekane	20.925	6.95
6	$C_{19}H_{40}$	Nonadekane	22.363	5.03

b. Clove Oil Characterization

This experiment used clove oil taken from MITRA PALA MAS, Kampung Krajan Wanayasa, Purwakarta. Clove oil was characterized using the GCMS and IR spectrophotometer to know the content of compounds in clove oil. GC and IR spectra of clove oil are shown in Figs 4 and 5 respectively.

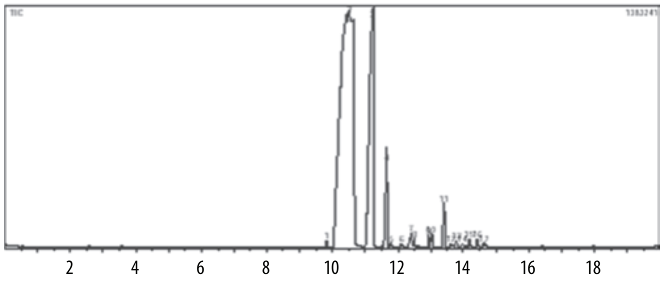


Fig. 4. GC spectra of clove oil

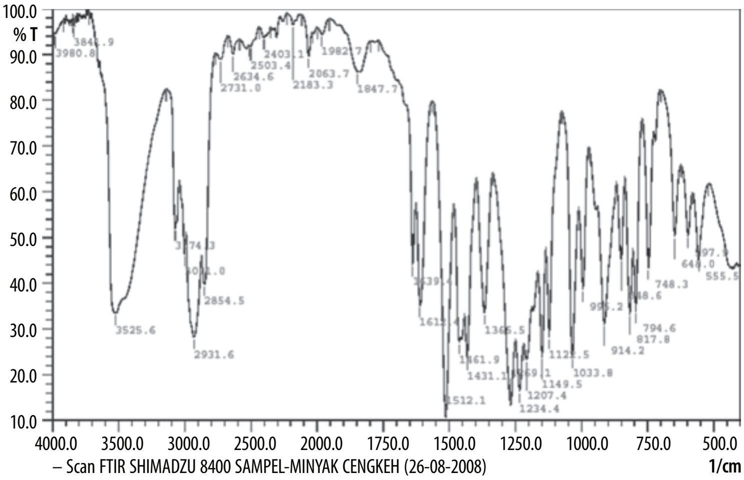


Fig. 5. IR spectra of clove oil

The chromatogram in Fig. 4 shows there are two peaks having high concentration. They are the second and third peaks making 70.54% and 21.54% respectively. The second peak has the retention time of 10.515 minutes while the third peak has that of 11.223 minutes. Both peaks were analyzed using MS and the results of the carried out analysis are shown in Figs 6 and 7.

On the basis of the MS database, these peaks can be identified. The first peak is eugenol, whereas the second one is cariofilena.

c. Eugenol Characterization

Eugenol used in this experiment came from PT. Indesso Aroma Cilengsi Bogor. The chromatogram of GC analysis on eugenol shows there is one peak with 100% concentration at the retention time of 10.552 minutes (Fig. 8).

MS analysis of the peak displayed in Fig. 9 and IR analysis in Fig. 10 show that the peak is eugenol which means it is of 100% purity.

d. Eugenyl Acetate Characterization

Eugenyl acetate used in the experiment was taken from PT. Indesso Aroma Cilengsi Bogor. GC and IR analysis on this raw material is shown in Figs 11 and 12 respectively.

Two peaks within GC spectra are displayed in Fig. 11. The first peak has a concentration of about 0.59% with the retention time of 10.064 minutes and the second peak has a concentration of about 99.412%

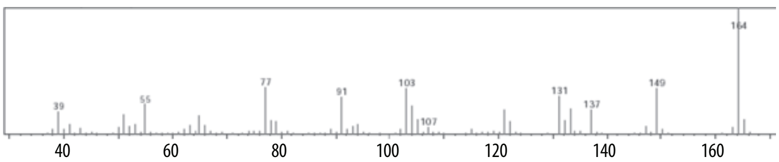


Fig. 6. MS spectra of the second peak

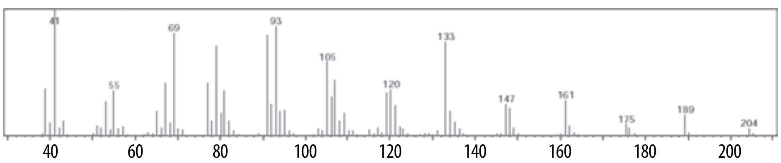


Fig. 7. MS spectra of the third peak

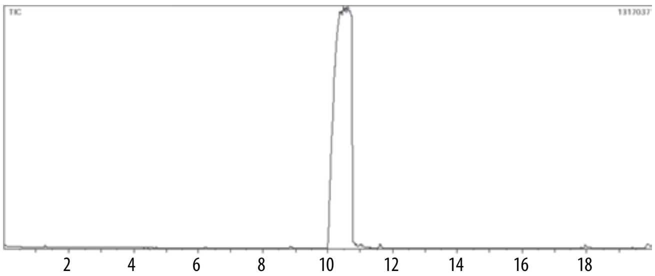


Fig. 8. GC spectra of eugenol

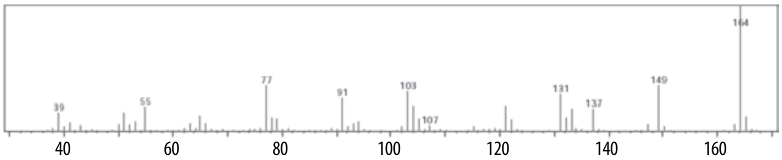


Fig. 9. MS spectra of the first peak

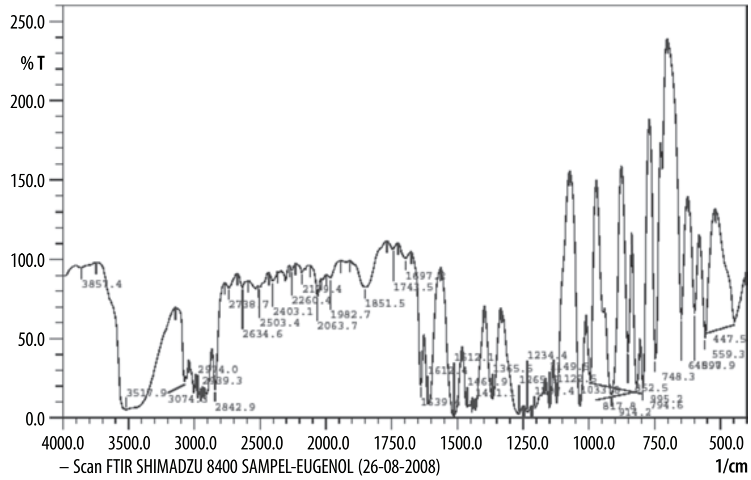


Fig. 10. IR spectra of eugenol

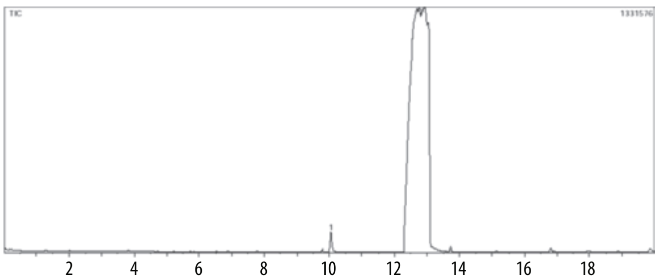


Fig. 11. GC spectra of eugenyl acetate

with the retention time of 21.816 minutes. Based on MS analysis (Figs 13 and 14), the identified peaks are eugenol and eugenyl acetate respectively.

3.2. Physical Characterization and Composition Optimization of Bio-additive Fuel Blends

a. Clove Oil Fuel Blends

The optimization of clove oil fuel blends was determined by the fuel consumption flow rate.

Fig. 15 shows that the optimum composition of clove oil is 0.6% and the fuel consumption rate is 251.91 mL/hour.

In 0.6% reformulation of clove oil, diesel fuel has the following physical characteristics which displayed in Table 2.

A comparison of these physical characteristics with DIRJEN MIGAS specification shows that the physical characteristics of clove oil fuel blends still complied with diesel fuel specifications for DIRJEN MIGAS which means that the essential oil is safe to be used as a bio-additive.

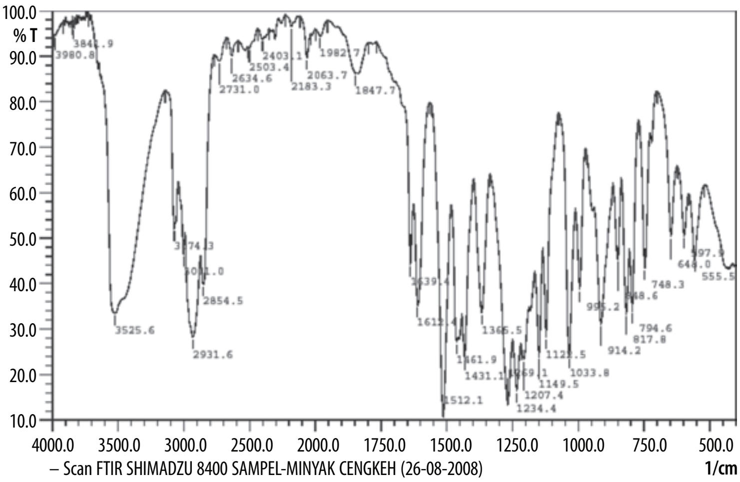


Fig. 12. IR spectra of eugenyl acetate

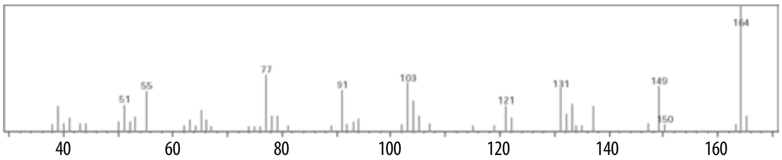


Fig. 13. MS spectra of the first peak

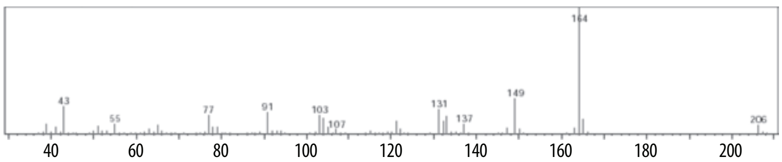


Fig. 14. MS spectra of the second peak

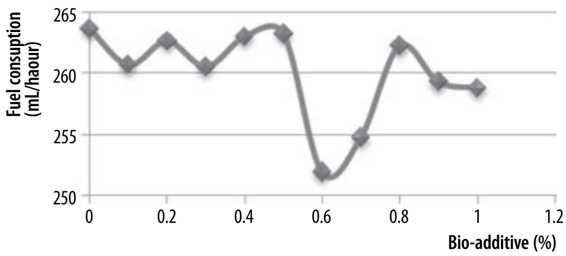


Fig. 15. The influence of clove oil fuel blends on the fuel consumption flow rate

Table 2. Physical characteristics of diesel fuel and diesel fuel + 0.6% clove oil

Parameters	Diesel fuel	Diesel fuel + 0.6% clove oil	DIRJEN MIGAS specification	
			Min	Max
Fuel consumption (mL/hour)	263.58	251.91	–	–
Specific gravity at 25°C (g/mL)	0.8452	0.8473	–	–
Specific gravity at 15.6°C (g/mL)	0.8522	0.8536	0.82	0.87
API gravity	34.5408	34.2685	–	–
Aniline point (°F)	156.2	149.9	129.6	–
Diesel index	53.9527	51.3685	–	–
Viscosity (cSt)	3.7215	3.6718	1.6	5.8
Flash point (°C)	73	72	60	–

b. Eugenol Fuel Blends

The influence of eugenol fuel blends on the fuel consumption flow rate is presented in Fig. 16.

A chart in Fig. 16 shows that the optimum number is 0.2% for eugenol having fuel consumption rate 252.21 mL/hour. The physical characteristics of this composition are displayed in Table 3.

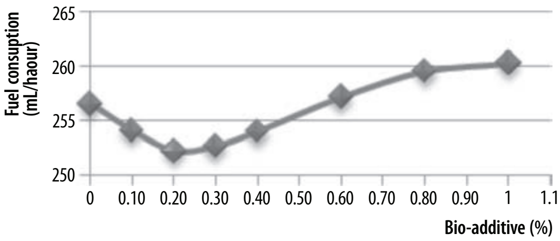


Fig 16. The influence of eugenol fuel blends on the fuel consumption flow rate

Physical parameters for the blends of 0.2% eugenol are still in the upper minimum limit of DIRJEN MIGAS specification.

c. Eugenyl Acetate Fuel Blends

An addition of eugenyl acetate considers the composition of eugenol fuel blends (0.2%). The process is caused by eugenyl acetate which is a product of oxygen enrichment with eugenol producing ester reaction. It offers the possibility of oxygen enrichment that can optimize the fuel combustion process.

An addition of eugenyl acetate to diesel fuel must be similar to the composition of eugenol fuel blends in order to identify the effectiveness of oxygen enrichment with bio-additive blends.

3.3. Bio-additive Fuel Blends Performance Test on One Cylinder Diesel Engine

The performance test was investigated using one cylinder engine HATZ 667 cc 1D81Z with speed torque and weight variation.

The performance test covered the experiment with clove oil, eugenol and eugenyl acetate in 0.2% composition respectively. The use of clove oil was different from the experiment results of the optimized composition. It considers a eugenol addition because it is the main component of clove oil. The performance of all bio-additives can be compared in the same composition. The performance of bio-additives was shown applying BSFC (Break Specific Fuel Consumption) parameter. Good performance has a low number of BSFC the bio-additives of which are shown in the below Fig. 17.

At 1500 rpm, 2000 rpm and 2500 rpm, diesel fuel and fuel blends with bio-additives have quite the same BSFC. However, at the high speed of 3000 rpm, all bio-additives have lower BSFC than unreformulated diesel fuel which means that all bio-additives can increase engine performance by increasing fuel combustion reactivity, especially eugenyl acetate, because eugenyl acetate has the lowest BSFC. Volumetric efficiency can show the effectiveness of the fuel combustion process.

The highest volumetric efficiency was achieved using eugenyl acetate at 3000 rpm which proves that the bulky structure and content of oxygen atoms in eugenyl acetate lead to an increase in combustion reactivity with supplying oxygen internally (Fig. 18).

3.4. Exhaust Emissions

a. CO and CO_2

In general, all bio-additives can decrease CO emission rate at various speeds and variation in weight. Containing high oxygen atoms in the bio-additives leads to the next oxidizing reaction of CO to form CO_2. Nevertheless, a decrease in CO emission and consequently CO_2 emission is going to increase. In this case, the reaction is as follows:

$2C + O_2 \rightarrow 2CO;$

$2CO + O_2 \rightarrow 2CO_2.$

A decrease in CO concentration is shown in Fig. 19.

An increase in CO_2 is presented in Fig. 20.

b. Hydrocarbon (HC)

HC emission is unburned fuel. The Fig. 21 show that each bio-additive has optimum performance to decrease HC concentration in exhaust emissions. However, at the high speed of 3000 rpm, reformulating diesel fuel using eugenyl acetate reaches the lowest hydrocarbon emission rate.

Table 3. Physical characteristics of diesel fuel and diesel fuel + 0.2% clove oil

Parameters	Diesel fuel	Diesel fuel + 0.2% eugenol	DIRJEN MIGAS Specification	
			Min	Max
Fuel consumption (mL/hour)	263.58	252.21	–	–
Specific gravity at 25°C (g/mL)	0.8452	0.83929	–	–
Specific gravity at 15.6°C (g/mL)	0.8522	0.83931	0.82	0.87
API gravity	34.5408	37.1311	–	–
Aniline point (°F)	156.2	184.5	129.6	–
Diesel index	53.9527	68.56060	–	–
Viscosity (cSt)	3.7215	3.67130	1.6	5.8
Flash point (°C)	73	69	60	–

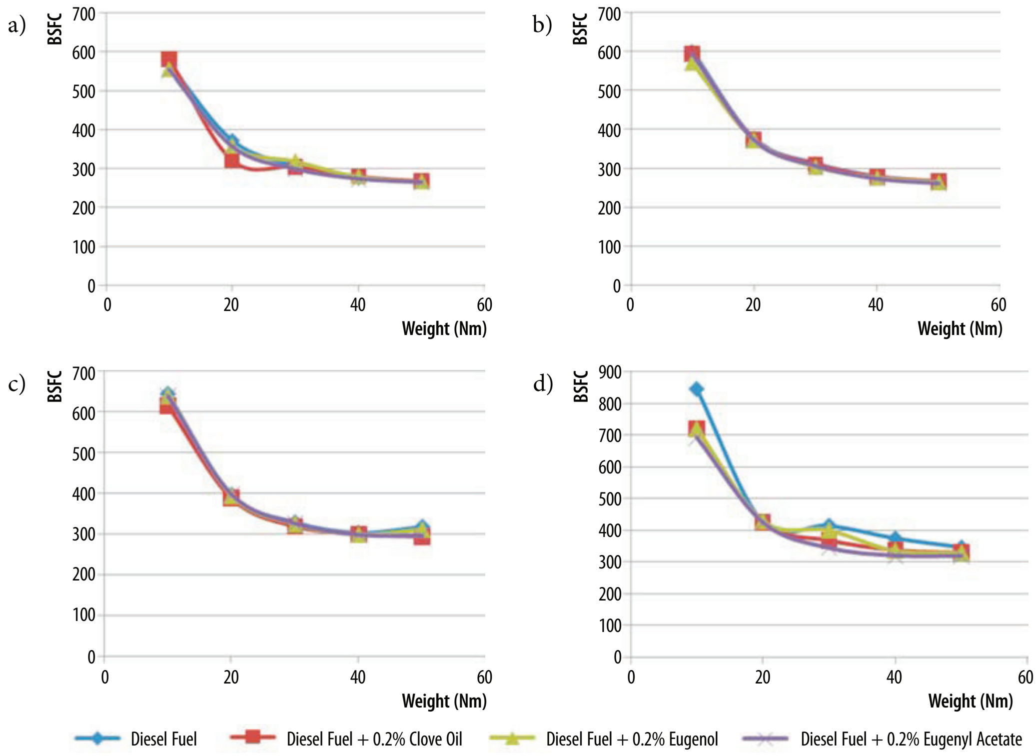


Fig. 17. BSFC of diesel fuel, diesel fuel+0.2% clove oil, diesel fuel+0.2% eugenol and diesel fuel+0.2% eugenyl acetate at: a – 1500 rpm; b – 2000 rpm; c – 2500 rpm; d – 3000 rpm

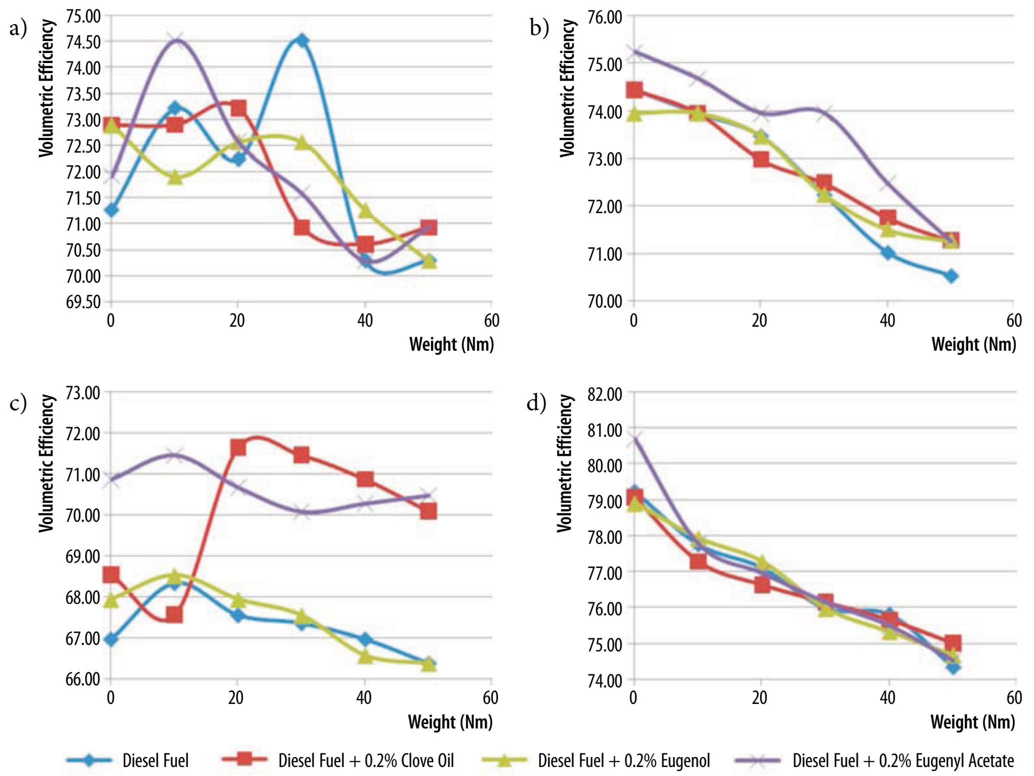


Fig. 18. Volumetric efficiency of diesel fuel, diesel fuel+0.2% clove oil, diesel fuel+0.2% eugenol and diesel fuel+0.2% eugenyl acetate at: a – 1500 rpm; b – 2000 rpm; c – 2500 rpm; d – 3000 rpm

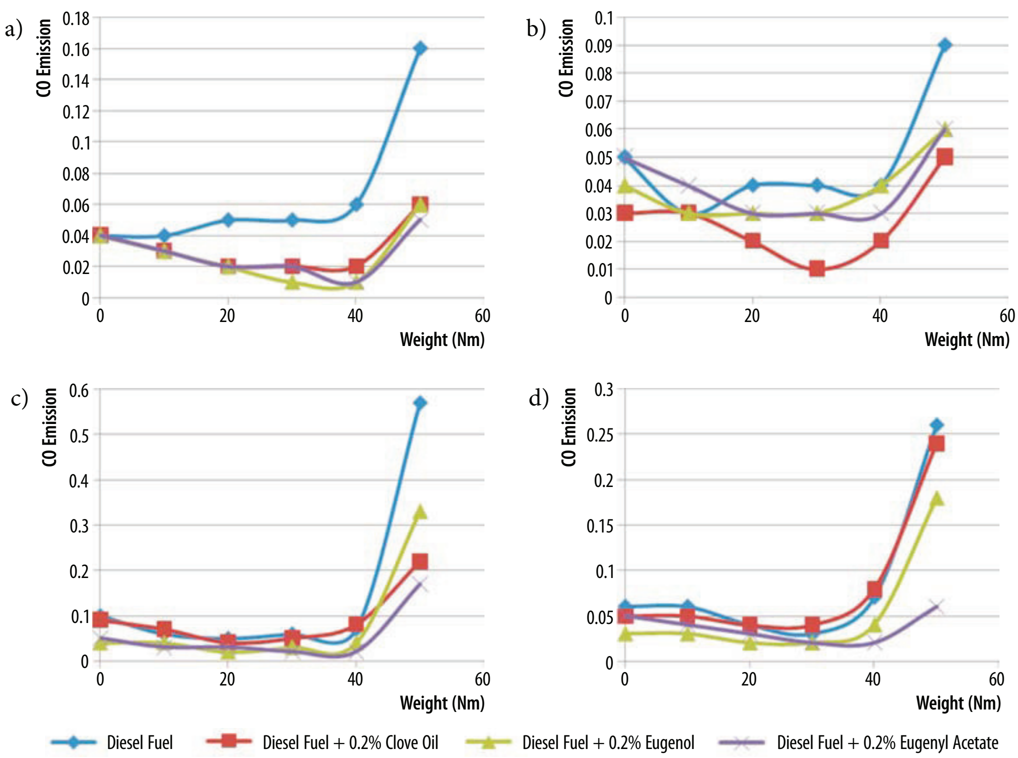


Fig. 19. CO emission of diesel fuel, diesel fuel+0.2% clove oil, diesel fuel+0.2% eugenol and diesel fuel+0.2% eugenyl acetate at: a – 1500 rpm; b – 2000 rpm; c – 2500 rpm; d – 3000 rpm

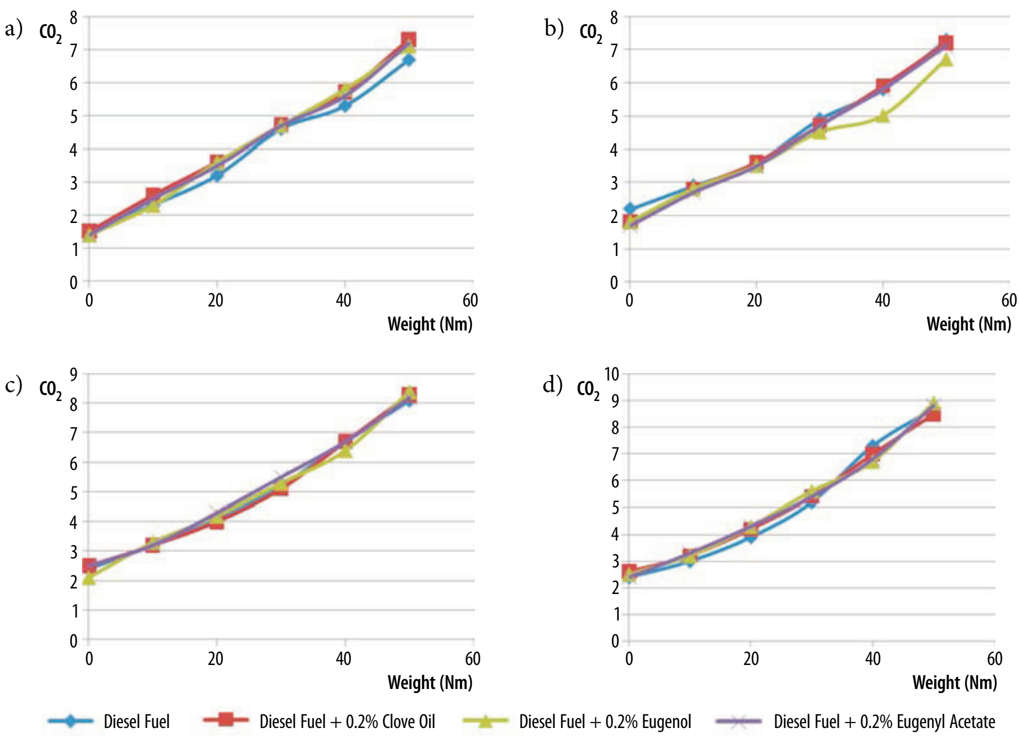


Fig. 20. CO_2 emission of diesel fuel, diesel fuel+0.2% clove oil, diesel fuel+0.2% eugenol and diesel fuel+0.2% eugenyl acetate at: a – 1500 rpm; b – 2000 rpm; c – 2500 rpm; d – 3000 rpm

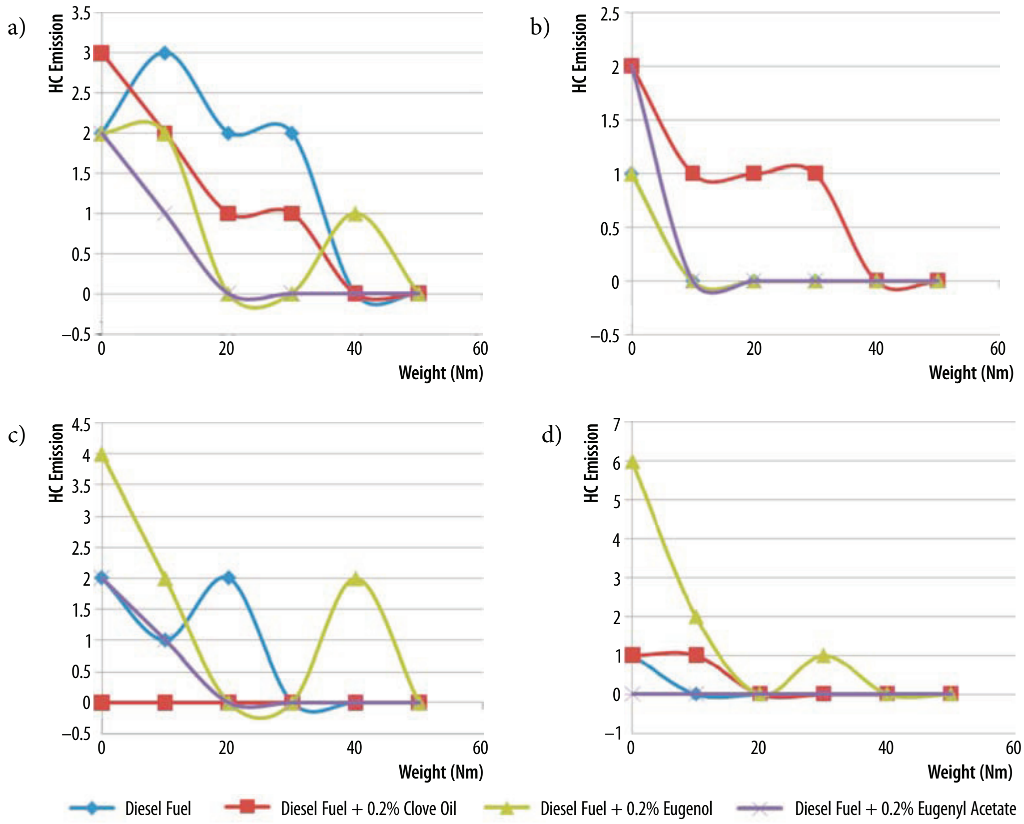


Fig. 21. HC emission of diesel fuel, diesel fuel+0.2% clove oil, diesel fuel+0.2% eugenol and diesel fuel+0.2% eugenyl acetate at: a – 1500 rpm; b – 2000 rpm; c – 2500 rpm; d – 3000 rpm

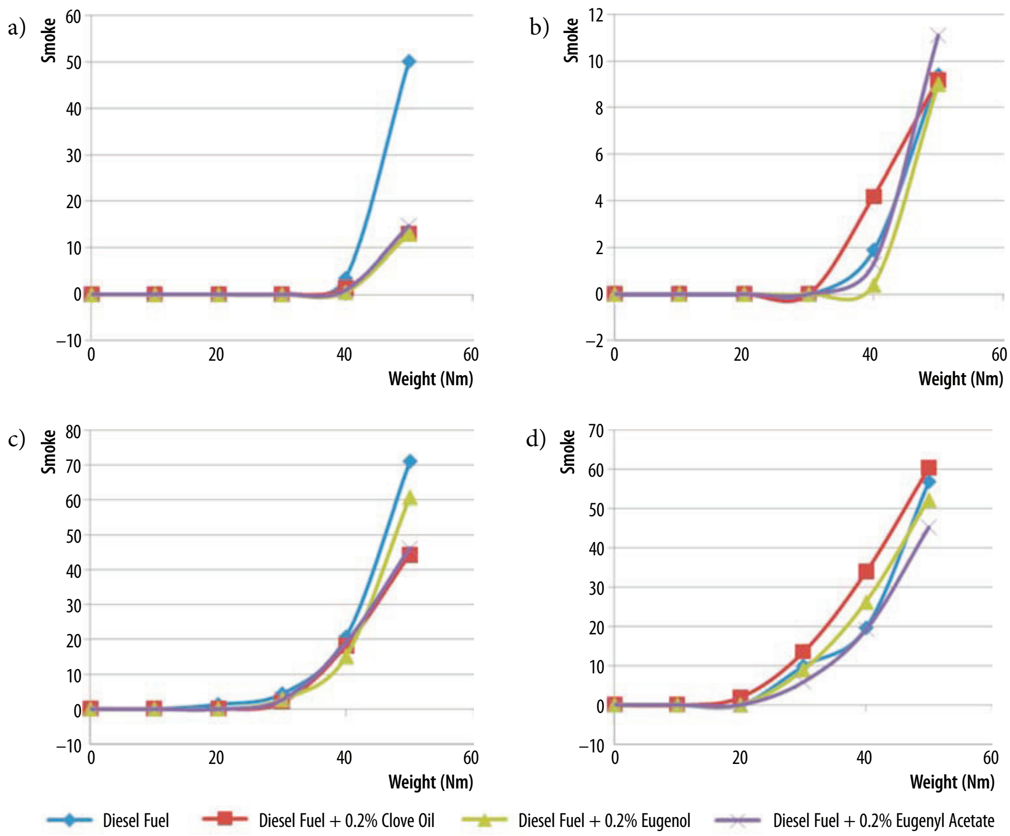


Fig. 22. Smoke emission of diesel fuel, diesel fuel+0.2% clove oil, diesel fuel+0.2% eugenol and diesel fuel+0.2% eugenyl acetate at: a – 1500 rpm; b – 2000 rpm; c – 2500 rpm; d – 3000 rpm

c. Smoke (Particulates)

At 0–20 Nm, smoke was not detected, whereas at 40–50 Nm, an increase in smoke was noticed. Generally, the reformulation of diesel fuel using bio-additives still gives a lower concentration of smoke than unreformulated diesel fuel (Fig. 22). This result is in accord with Choi and Reitz (1999) who proposed that the oxygen atoms contained in the additive lead to oxidize particulates.

d. NO_x

If CO, HC and smoke emission decrease, consequently, the concentration of NO_x is going to increase (Fig. 23). This result is in accord with Klell theory (1998)

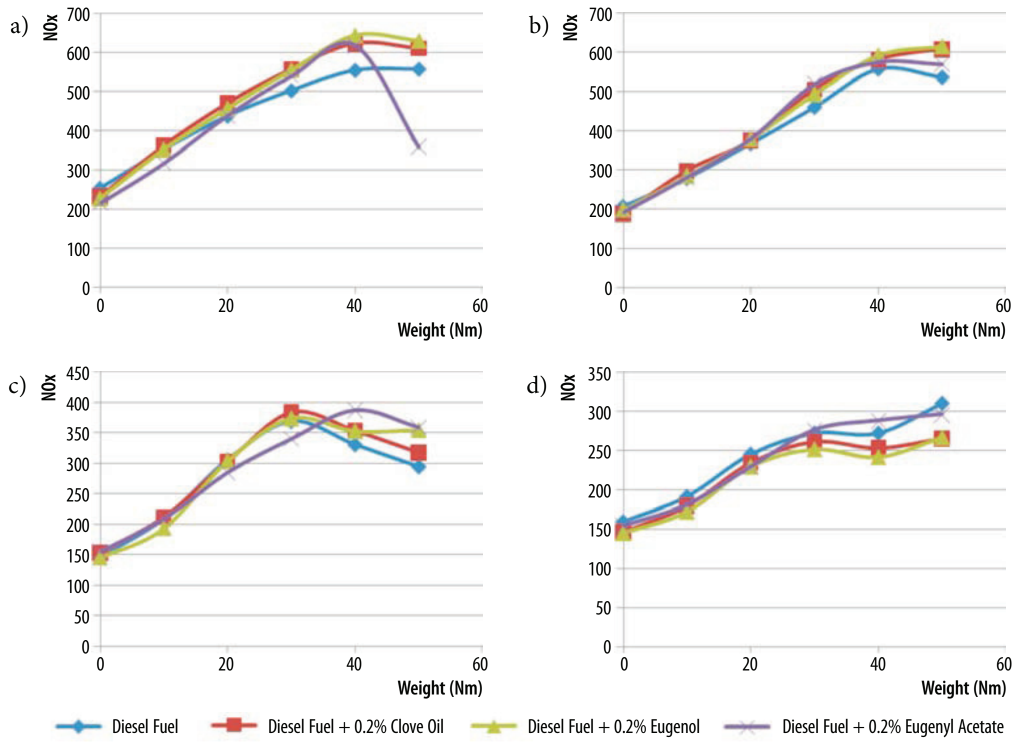


Fig. 23. NO_x emission of diesel fuel, diesel fuel+0.2% clove oil, diesel fuel+0.2% eugenol and diesel fuel+0.2% eugenyl acetate at: a – 1500 rpm; b – 2000 rpm; c – 2500 rpm; d – 3000 rpm

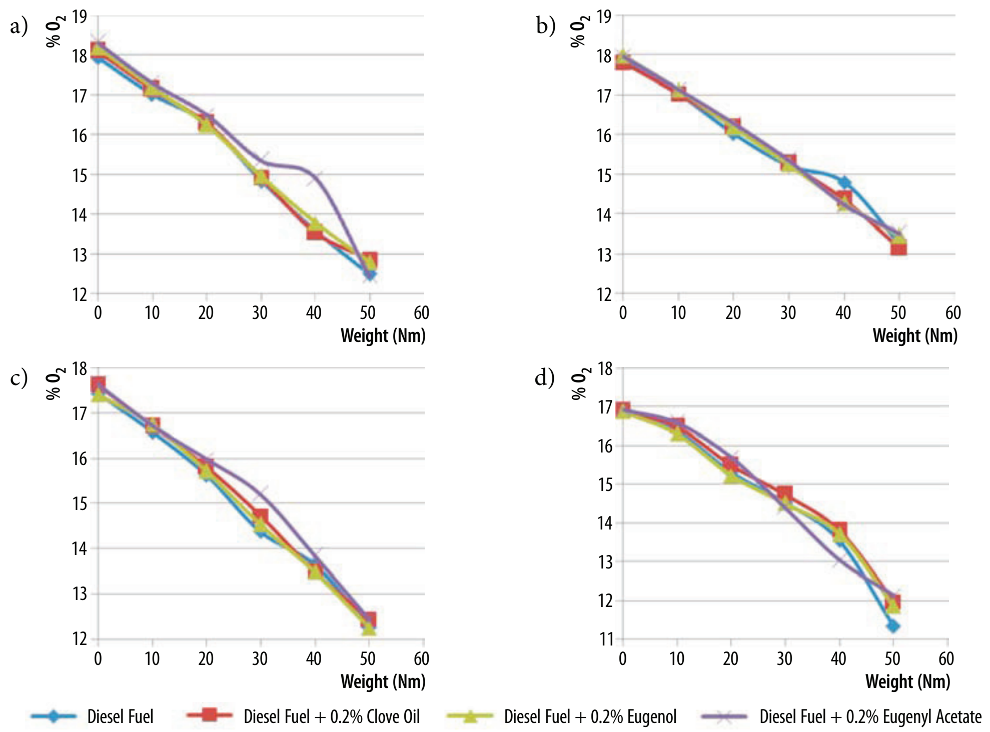


Fig. 24. The concentration of oxygen atoms in the exhaust emission of diesel fuel, diesel fuel+0.2% clove oil, diesel fuel+0.2% eugenol and diesel fuel+0.2% eugenyl acetate at: a – 1500 rpm; b – 2000 rpm; c – 2500 rpm; d – 3000 rpm

who proposed that a decrease in CO and HC emission rate would follow with an increase in NO_x concentration. An increase in NO_x emission is caused by the use of the air, so at high temperature, N_2 and O_2 can react into NO:

$$N_2 + O_2 \rightarrow 2\ NO.$$

The next reaction of NO in the air leads to NO_2.

e. O_2

As oxygen atoms are supplied internally, fuel blends with bio-additives lead to an increase in the high content of oxygen in exhaust emissions.

At 2500 rpm and 3000 rpm, a high concentration of oxygen content accords with the results of the conducted experiment which has shown that at high speed, the reformulation of the bio-additives give effectiveness to the fuel combustion process (Fig. 24).

4. Conclusions

1. In general, clove oil, eugenol and eugenyl acetate lead to a decrease in the BSFC of diesel fuel, CO, HC and smoke emissions.
2. The oxygenated molecular structure and its high oxygen content play a significant role in the mechanism responsible for the performance of these fuel blends with bio-additives and decreasing emissions.
3. Eugenyl acetate has the best performance as a diesel fuel bio-additive which is expressed by the highest volumetric efficiency.

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