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Synthetic phenolic antioxidants to biodiesel: path toward NO_x reduction of an unmodified indirect injection diesel engine

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ABSTRACT

Biodiesel is a green alternative fuel produced from renewable resources. The major disadvantage of biodiesel is the substantial increase in NO_x emission. This study examined the effects of antioxidant-treated coconut biodiesel on the performance and exhaust emission characteristics of an indirect injection diesel engine. Coconut biodiesel was produced by transesterification using potassium hydroxide as a catalyst. Two low-cost synthetic antioxidants, 2(3)-tert-butyl-4-methoxyphenol (BHA) and 2,6-di-tert-butyl-4-methylphenol (BHT), were added at 2000 ppm to 20% coconut methyl ester in diesel (CB20). Tests were conducted on a 55 kW 2.5 L four-cylinder diesel engine at a constant load varying speed. Results showed that the antioxidants significantly reduced NO_x emission with a slight effect on brake thermal efficiency. The addition of BHA and BHT to CB20 reduced the average NO_x emission by 7.78% and 3.84%, and the average brake specific fuel consumption by 1.77% and 1.46%, respectively. The antioxidant addition increased CO, HC, and smoke opacity, but the extent of increase was still below the diesel level. Thus, the addition of antioxidants presents a promising option for NO_x reduction.

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1. Introduction

Energy consumption is globally increasing because of lifestyle progress and substantial population growth. The transportation sector is one of the top energy consumers. The increasing need for energy in this sector was previously catered with fossil resources, such as coal, gasoline, and diesel alone. Fossil fuel combustion in transport vehicles results in serious ecological changes, including increase in global surface temperature (global warming), changes in rainfall patterns, and changes in the frequency of extreme weather events. Hence, substantial effort is being exerted globally to explore renewable energy sources that can replace fossil fuels. Biomass-based fuels or biofuels are advantageous over fossil fuels that are predominantly used for liquid fuels in the transportation sector (Balat, 2011). Biofuels include biomethanol, bioethanol, vegetable oils, biodiesel, biogas, biosynthetic gas (bio-syngas), bio-char, Fischer–Tropsch liquids, and biohydrogen. However, biodiesel, bioethanol, and biohydrogen are the most widely studied fuels that have potential for sustainable production as clean energy resources. Significant research has focused on the production of these biofuels using low-cost and efficient methods (Balat, 2011; Leung et al., 2010; Show et al., 2012). Not only the sustainable production but also the efficient separation and end use of these biofuels are of concern for energy researchers (Atadashi et al., 2011; Bakonyi et al., 2013; Huang et al., 2008). Many researchers have explored the use of these clean alternatives of fossil fuels in internal combustion engine, on which the transportation sector is exclusively dependent (Agarwal, 2007; Verhelst, 2014). Biodiesel refers to mono-alkyl esters of long-chain fatty acids; it is usually composed of renewable lipid feedstock and biological resources, such as vegetable oil, animal fat, used cooking oil, and algae (Farooq et al., 2013; Liew et al., 2014). Different types of biodiesel have different properties depending on fatty acid composition. Automotive fuel combustion produces NO_x that causes lung irritation and deteriorates resistance to respiratory infection. NO_x is also an important precursor to acid rain that disturbs both aquatic and terrestrial ecosystems.

NO_x can be formed by two major pathways during diesel fuel combustion: the Zeldovich ("thermal") mechanism and the Fenimore ("prompt") mechanism (Palash et al., 2013). The formation

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Nomenclature

ASTM	American Society for Testing and Materials
ACS	American Chemical Society
BHA	2,6-di-tert-butyl-4-methylphenol
BHT	2(3)-tert-butyl-4-methoxy phenol
BSFC	Brake Specific Fuel Consumption
BTE	Brake Thermal Efficiency
CME	Coconut Methyl Ester
CN	Cetane Number
CO	Carbon monoxide
DPPD	N,N′-diphenyl-1,4-phenylenediamine
DTBP	Di-tert-butyl-peroxide
EDA	Ethylenediamine
EHN	2-ethyl-hexyl nitrate
FAC	Fatty acid composition
GC	Gas Chromatography
HC	Hydrocarbon
IDI	Indirect Injection
NPPD	N-phenyl-1,4-phenylenediamine
NO_x	Nitrogen oxides (NO + NO_2)
PPDA	p-phenylenediamine
TBHQ	tert-butyl-hydroquinone
TDI	Turbocharged Direct Injection
CB20	20% CME + 80% diesel
CB20 BHA	20% CME + 80% diesel + 2000 ppm BHA
CB20 BHT	20% CME + 80% diesel + 2000 ppm BHT

rate of Zeldovich NO_x rapidly increases with temperature, whereas that of Fenimore NO_x is complex. In this mechanism, free radicals such as CH and CH_2 formed from the fuel react with N_2 to form NO_x. Prompt NO_x is prevalent in rich flames. This mechanism occurs immediately in the combustion process and is partly dependent upon fuel radical concentration and establishment (Hess et al., 2004). Graboski et al. (2003) reported "fuel chemistry effects in the flame region" as a precursor of prompt NO_x formation because of sensitivity to radical concentrations at the flame front. Fuel chemistry can account for 30% or more of the total NO_x emission. Thus, the generation of free radicals from biodiesel combustion can be attributed to the increase in NO_x emission and addition of free radical quenching agents that may reduce NO_x elevation. Antioxidants are examples of free radical quenching agents. Thus, higher amount of antioxidants can result in higher NO_x reduction.

McCormick et al. (2003) also reported that antioxidants, such as ethylhexyl nitrate (EHN), di-tert-butylphenol, and tert-butyl hydroquinone (TBHQ), are effective in NO_x emission reduction from biodiesel. During the long-term storage of biodiesel, antioxidants significantly delay biodiesel degradation (Rizwanul Fattah et al., 2014b). Phenolic antioxidants possess −OH group that scavenges reactive radicals, such as peroxyl radicals, resulting in the poor and limited oxidative reaction of phenoxyl radicals (Varatharajan et al., 2011).

Previously published articles on the effects of various antioxidants on NO_x emission with different feedstock (e.g., canola, jatropha, and soybean) supported the inference of McCormick et al. İleri and Koçar (2014) studied the effect of adding four antioxidants on the emission characteristics of a turbocharged four-cylinder diesel engine. The antioxidants EHN, 2(3)-tert-butyl-4-methoxyphenol (BHA), 2,6-di-tert-butyl-4-methylphenol (BHT), and TBHQ were added to 20% canola biodiesel at concentrations of 0, 500, 750, and 1000 ppm. They reported that the addition of these antioxidants can reduce the average NO_x emission by 1.21%–4.05%. They also found that EHN is the most viable NO_x-reducing additive that exerts negative effects on CO and HC emission. Varatharajan and Cheralathan (2013) investigated the effects of adding two aromatic amine antioxidants [N,N′-diphenyl 1,4-phenylenediamine (DPPD) and N-phenyl-1,4-phenylenediamine (NPPD)] to soybean biodiesel on engine criteria emissions in a single-cylinder diesel engine. They found a 9.35% reduction in NO_x with a 9.09% increase in CO and a 10.52% increase in HC for DPPD added to 20% soybean biodiesel (B20).

Another study (Varatharajan et al., 2011) investigated the effects of antioxidants on the NO_x emission of jatropha biodiesel fuel containing 0.025%-m of different additives in a single-cylinder diesel engine. Among the different antioxidants used, p-phenylenediamine produced the greatest NO_x reduction with a mean value of 34.55%. However, the addition of antioxidants increased HC and CO emission compared with neat biodiesel and blends. Hess et al. (2005) studied the effect of different antioxidants on NO_x emission to B20 and found that the addition of EHN, BHA, and BHT reduces NO_x emission by (4.5 ± 1)%, (4.4 ± 1.0)%, and (2.9 ± 1.5)%, respectively. However, the addition of TBHQ at 2000 ppm confirmed an increase in NO_x emission for 1000 ppm TBHQ-treated B20. Our previous study on palm biodiesel showed that adding BHA and BHT at 1000 ppm to 20% palm biodiesel helps reduce NO_x emission (Rizwanul Fattah et al., 2014c). The report showed 12.6% and 9.8% reduction in average NO_x emission relative to the level of B20 for these antioxidant-blended fuels.

The literature provided insights into the potential of antioxidants to reduce NO_x emission when coconut biodiesel is used. Coconut biodiesel is mostly composed of short-chain fatty acid esters, making it a superior feedstock for countries with cold climate. Coconut biodiesel also shows superior ignition quality, similar performance, and lower exhaust emissions compared with biodiesel from other feedstock; this finding can be attributed to the higher (14%) oxygen content of the former than the latter (Eiji Kinoshita et al., 2006; Yusuke Soma et al., 2007). Researchers have also shown a strong positive correlation with NO_x emission for coconut biodiesel and its blends (Liaquat et al., 2013; Satyanarayana and Muraleedharan, 2011). Even though CBD has high OS attributed to high saturation level, long storage may affect the oxidation stability. Thus, adding antioxidants to biodiesel is necessary. The current study aims to demonstrate the NO_x reduction potential of antioxidants with 20% coconut methyl ester (CME) in diesel (CB20) blends in an IDI diesel engine.

2. Materials and methods

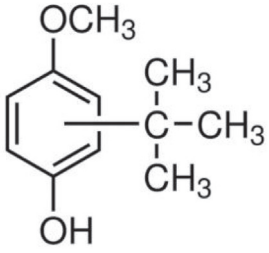
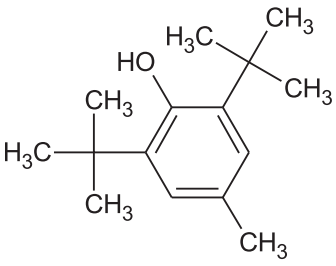
2.1. Materials

Crude coconut oil purchased from a local market was used to produce biodiesel. The antioxidants used in the study were BHA and BHT. These antioxidants possess moderate inhibitory effect on biodiesel. Methanol, sulfuric acid, potassium hydroxide, anhydrous sodium sulfate, and qualitative filter papers were used for biodiesel production. Table 1 shows the properties of used chemicals.

2.2. Biodiesel production

Biodiesel or CME was produced through alkali-catalyzed transesterification. Crude coconut oil with methanol (25% v/v of oil) and potassium hydroxide (1% w/w of oil) was processed in a jacket reactor at 60 °C using circulating water bath for 2 h, and the

Table 1
Properties of used chemicals.

Chemical	Chemical structure	CAS number	Assay (%)	Molecular weight (g/mol)	Melting point (°C)	Grade
BHA	 2(3)-*tert*-butyl-4-methoxyphenol	25013-16-5	≥98.5%	180.24	58–60	
BHT	 2,6-di-*tert*-butyl-4-methylphenol	128-37-0	≥99.0%	220.35	69–73	
Methanol	CH_3OH	67-56-1	≥99.9%	32.04	−98	ACS
Potassium Hydroxide	KOH	1310-58-3	≥85.0%	56.11	360	ACS
Sodium Sulphate (Anhydrous)	Na_2SO_4	7757-82-6	≥99.0%	142.04	884	ACS

ACS: American Chemical Society.

mixture was stirred at 1200 rpm using a motor stirrer. Subsequently, a separation time of 12 h was given to this mixture to separate glycerin from methyl ester. The methyl ester separated from glycerol was washed with distilled water to remove the entrained impurities and glycerin. In this process, 50% (v/v) of distilled water at 60 °C was sprayed over ester, and the mixture was shaken gently. The opaque lower layer containing water and impurities was removed. Then, methyl ester was distilled under vacuum distillation at 65 °C for 1 h using a rotary evaporator to remove water and methanol. Finally, methyl ester was dried using anhydrous Na_2SO_4 for 3 h and filtered using qualitative filter papers. Table 2 shows a summary of the equipment used in this study to measure the physicochemical properties of coconut biodiesel and its blends. The saponification number (SN), iodine value (IV), and cetane number (CN) of the produced biodiesel were calculated as follows (Rizwanul Fattah et al., 2014e):

$$SN = \sum\left(\frac{560*A_i}{MW_i}\right) \quad (1)$$

$$IV = \sum\left(\frac{254*D*A_i}{MW_i}\right) \quad (2)$$

$$CN = \left(46.3 + \left(\frac{5458}{SN}\right) - (0.225*IV)\right) \quad (3)$$

where A_i is the percentage of each component, D is the number of double bonds, and MW_i is the mass of each component. Table 3 shows the molecular mass of each component.

Table 2
List of equipment used in the characterization of fuels.

Property	Equipment	Manufacturer	Standard method	ASTM D6751 limit[a]	Accuracy
Kinematic viscosity	SVM 3000-automatic	Anton Paar, UK	D7042	1.9–6.0	±0.35%
Dynamic viscosity	SVM 3000-automatic	Anton Paar, UK	D7042	N/S	±0.35%
Viscosity Index	SVM 3000-automatic	Anton Paar, UK	D2270	N/S	
Flash Point	Pensky-martens flash point – automatic NPM 440	Normalab, France	D 93	130 min	±0.1 °C
Oxidation stability	873 Rancimat – automatic	Metrohm, Switzerland	D 675	3 h min	±0.01 h
Density	SVM 3000-automatic	Anton Paar, UK	D7042	N/S	±0.1 kg/m^3
Calorific value	C2000 basic calorimeter - automatic	IKA, UK	D 240	N/S	±0.1% of reading
Cloud Point	Cloud and Pour point tester – automatic NTE 450	Normalab, France	D 2500	Report	±0.1 °C
Pour Point	Cloud and Pour point tester – automatic NTE 450	Normalab, France	D 97	N/S	±0.1 °C
CFPP	Cold filter plugging point – automatic NTL 450	Normalab, France	D 6371	N/S	

N/S ≡ not specified in ASTM test method.
[a] Data obtained from Ref. (Pullen and Saeed, 2012).

Table 3
Fatty acid profile (wt. %) of CME.

Fatty acid ester	Structure	Molecular mass	Formula	Fraction in CME
Methyl octanoate	8:00	158.24	$CH_3(CH_2)_6COOCH_3$	6.6
Methyl decanoate	10:00	186.29	$CH_3(CH_2)_8COOCH_3$	5.6
Methyl Laurate	12:0	214.34	$CH_3(CH_2)_{10}CO_2CH_3$	47.2
Methyl Myristate	14:0	242.40	$CH_3(CH_2)_{12}COOCH_3$	19
Methyl Palmitate	16:0	270.45	$CH_3(CH_2)_{14}CO_2CH_3$	10
Methyl Palmitoleate	16:1	268.43	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOCH_3$	N/D
Methyl Stearate	18:0	298.50	$CH_3(CH_2)_{16}CO_2CH_3$	2.9
Methyl Oleate	18:1	296.49	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3$	7.1
Methyl Linoleate	18:2	294.47	$CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7CO_2CH_3$	1.5

N/D = Not detected.

Table 5
Detailed engine specification.

Description	Specification
No. and arrangement of cylinders	4 in-line, longitudinal
Rated Power	55 kW at 4200 rpm
Combustion chamber	Swirl chamber
Total displacement	2477 cc
Cylinder bore x stroke	91.1 × 95 mm
Valve mechanism	SOHC
Compression ratio	21:1
Valve timing	IVO: 20°BTDC IVC: 49°ABDC EVO: 55°BBDC EVC: 22°ATDC
Lubrication system	Pressure feed, full flow filtration
Fuel system	Distributor type injection pump
Air flow	Turbocharged
Fuel Injection Pressure	157 bar

2.3. Fatty acid composition

A 1 μL biodiesel sample was injected into a gas chromatograph (Shidmadzu, GC-2010A series) equipped with a flame ionization detector and a BPX70 capillary column of 30 m × 0.25 μm × 0.32 mm inner diameter. An initial temperature of 140 °C was held for 2 min, which was then increased to 165 °C at 8 °C/min, 192 °C at 3 °C/min, and 220 °C at 8 °C/min. The column was held at the final temperature for another 5 min. The oven, injector, and detector ports were set at 140 °C, 240 °C, and 260 °C, respectively. The carrier gas was helium with a column flow rate of 1.10 ml/min at a 50:1 split ratio. Each peak was identified by comparing with an external standard reference mixture of fatty acid methyl esters. The concentrations of the identified peaks were added as an absolute value. The percentage of each methyl ester was calculated based on this value. Table 3 shows the composition of the produced CME. CME contains 91.4% and 8.6% of saturated and unsaturated methyl esters, respectively, respectively. Table 4 shows the properties of crude oil, produced biodiesel, and all tested fuels.

2.4. Engine test

The experimental investigation was carried out at the Heat Engine Laboratory of the Mechanical Engineering Department, University of Malaya on a 2.5 L naturally aspirated four-cylinder diesel engine. Table 5 describes the details of this engine. The test engine was directly coupled to a Froude Hofmann AG250 eddy current dynamometer. Fuel flow was measured using a KOBOLD ZOD positive-displacement type flow meter. Engine oil, cooling water, exhaust gas, and inlet air temperatures were measured using K-type thermocouples. A REO-dCA data acquisition system was used for data collection. The engine fuel system was modified by adding separate tanks with a two-way valve, which allowed rapid switching of fuels. The exhaust gas composition of CO, HC, and NO_x emissions was measured by a gas analyzer (AVL DiCom4000). In this equipment, the CO and HC measuring instrument used non-dispersive infrared detectors, and the NO_x analyzer used the electrochemical method. Smoke opacity was measured by a continuous flow smoke meter (AVL DiSmoke 4000) working on Hartridge principle.

To carry out tests using biodiesel blends, the engine was run with diesel until steady operating conditions were achieved. The fuel was then changed to a biodiesel blend. After consumption of sufficient blend fuel, data acquisition was started to ensure the removal of residual diesel in the fuel line. After each test, the engine was run again with diesel to drain out all the blends in the fuel line. This procedure was followed for all the blends. The test fuels were fossil diesel (B0) and CB20. To determine the effects of antioxidants, 2000 ppm of BHA and BHT was added to CB20 (CB20 BHA and CB20 BHT). The test fuels were blended using a homogenizer device at a speed of 3000 rpm for 10 min. The engine was operated between 1000 and 4500 rpm with a step of 500 rpm at 100% load condition.

2.5. Accuracies and uncertainties

Uncertainties in the experiments can arise from instrument selection, experimental condition, equipment calibration, ambient environment, observation, reading, and test preparation. Uncertainty analysis is needed to establish the accuracy of the experiments. The uncertainties of measured quantities, such as torque, CO, HC, NO_x, and smoke, were calculated using those of the various

Table 4
Fuel characteristics of crude oil, biodiesel, biodiesel blends and fossil diesel.

Property	Crude oil	Biodiesel CME	Diesel	B20	B20 BHA	B20 BHT	ASTM D7467[a]
Calorific value (MJ/kg)	37.806	38.026	45.395	43.813	43.781	43.776	
Kinematic viscosity at 40 °C (mm^2/s)	27.420	3.0741	3.0738	2.9746	2.9835	2.9946	1.9-4.1
Dynamic viscosity at 40 °C (mPas)	24.908	2.6439	2.5501	2.4833	2.4922	2.5008	
Density at 40 °C (kg/m^3)	891.7	858.1	829.6	834.8	835.2	835	
Oxidation stability (h)	6.01	11.25	59.1	73.16	96.13	94.47	6
Flash point (°C)	264.5	122.5	69.5	80.5	81.5	81.5	52 (min)
Saponification number		267.4					
Iodine value		9.12					
Cetane number		64.7	52				40 (min)
Viscosity index	167.4	236.6					
Cloud point	17	−5	8	7	7	7	Report
Pour point	19	−4	7	−15	−15	−15	
Cold filter plugging point	23	−1	8				

[a] Data obtained from Ref. (de Guzman et al., 2010).

Table 6
The accuracies and uncertainties of the measured quantities.

Measured qty.	Measuring range	Accuracy	Uncertainty
Torque	0–1200 Nm	±3 Nm	
Fuel flow measurement	0.5–36 l/h	±0.089 l/h	
Speed	0–6000 rpm	±1 rpm	
Smoke opacity	0–100%	0.1%	±0.5%
CO	0–10%vol	0.01 %vol.	±0.01 %vol.
HC	0–20,000 ppm vol	1 ppm vol.	±1 ppm
NO_x	0–5000 ppm vol	1 ppm vol.	±5 ppm
Calculated Results			
Power			±0.1 kW
BSFC			±0.35 g/kWh

instruments used in the experiment. The relative uncertainty of calculated brake specific fuel consumption (BSFC) was determined using the linearized approximation method of uncertainty. Table 6 shows the accuracies and uncertainties of the measured and calculated parameters.

3. Results and discussion

3.1. Engine performance analysis

3.1.1. Brake specific fuel consumption (BSFC)

The BSFC values for all fuels at different speeds at full load condition is shown in Fig. 1. The average BSFC values for diesel, CB20, CB20 BHA, and CB20 BHT were 331.8, 353.6, 347.4, and 348.5 g/kWh, respectively. CB20 produced approximately 6.59% higher BSFC than diesel; this result can be primarily attributed to the lower heating value of the former than the latter (Kannan and Anand, 2011; Muralidharan et al., 2011). The addition of the antioxidants to CB20 further reduced the calorific value (Table 4). However, this phenomenon helped reduce BSFC. This result is consistent with previous reports (Kivevele et al., 2011; Ryu, 2010). The addition of BHA and BHT to CB20 reduced the average BSFC by 1.77% and 1.46%, respectively. This result can be attributed to the volumetric effect of constant fuel injection rate and the higher viscosity of antioxidant-treated biodiesel blends, which produce slightly higher power than CB20 (Gumus and Kasifoglu, 2010). However, the average BSFC values of the BHA- and BHT-added blends were 4.71% and 5.03% higher than those of diesel, respectively.

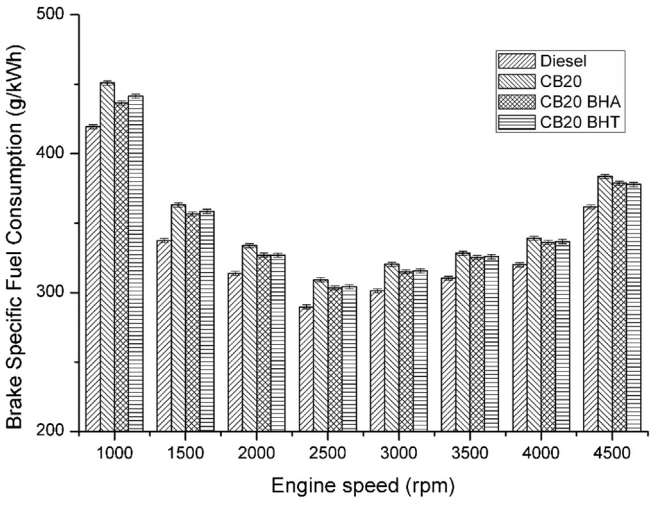


Fig. 1. Variation of BSFC for the test fuel at different speeds.

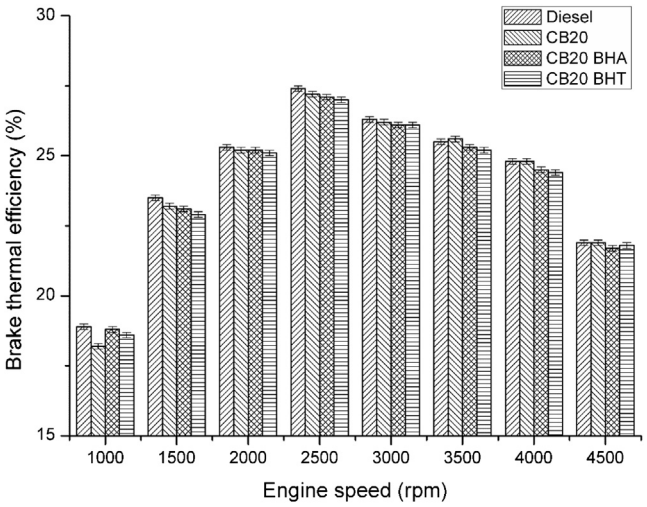


Fig. 2. Variation of BTE for the test fuel at different speeds.

3.1.2. Brake thermal efficiency (BTE)

Thermal efficiency is the ratio of power output and energy introduced through fuel injection. The energy introduced is the product of the injected fuel mass flow rate and the lower heating value. Fig. 2 shows the comparison of BTE with engine speed for different fuels. The maximum BTE rates observed at 2500 rpm for diesel, CB20, CB20 BHA, and CB20 BHT were 27.4%, 27.2%, 27.1%, and 27.0%, respectively. However, the average BTE rates for diesel, CB20, CB20 BHA, and CB20 BHT were 24.20%, 24.04%, 23.97%, and 23.90%, respectively. Thus, CB20 reduced BTE by 0.68% compared with diesel. This result can be attributed to the combined effect of low heating value and low power output (Devan and Mahalakshmi, 2009). The addition of BHA and BHT to B20 further reduced BTE by 0.28% and 0.57%, respectively. This result can be attributed to the slight reduction in cylinder pressure with the addition of antioxidants (Varatharajan and Cheralathan, 2013).

3.2. Engine emission analysis

3.2.1. NO_x emission

Fig. 3 illustrates the effect of antioxidant addition on NO_x emission for the different fuels tested. NO_x is the most deleterious

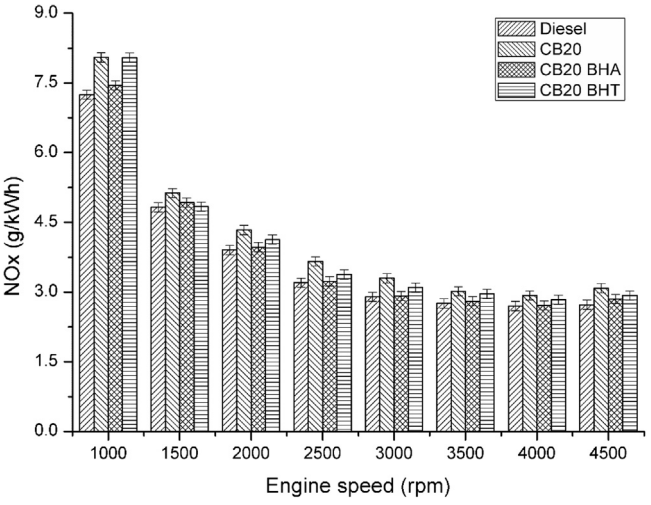


Fig. 3. Variation of NO_x emission for the test fuels at different speeds.

Table 7
Summary of NO_x reduction activity of antioxidants from various studies.

Study	Feedstock	Fuels	Engine type and test condition	Antioxidant	Concentration	Effect on NO_x compared to base blend (On avg.)	Suggested reason
(İleri and Koçar, 2014)	Canola	B20	4 cyl. TDI Full load with variable speed	BHA, BHT, TBHQ and EHN	1000 ppm	−4.05% (EHN) −2.73% (BHA) −1.8% (BHT) −1.21% (TBHQ)	Antioxidants quench the free radical which take part in prompt NO formation within the flame of biodiesel combustion
(İleri and Koçar, 2013)	Canola	B20	4 cyl. TDI Full load with variable speed	BHA, BHT, TBHQ and EHN	500, 750 and 1000 ppm	ppm↑ NO_x↓ (EHN) ppm↑ NO_x↑(BHT) EHN > BHT > BHA > TBHQ (NO_x reduction potential) Engine speed↑ NO_x↓	Shorter ignition delay due to higher CN of antioxidant treated blend resulted in lower NO_x
(Palash et al., 2014)	Jatropha	B5, B10, B15 and B20	4 cyl. IDI full load variable speed	DPPD	0.15% (by mass)	(NO emission) −8.03% (B5) −3.50% (B10) −13.65% (B15) −16.54% (B20)	Peroxyl radicals ($ROO^{\bullet}$) react with p-phenylenediamine radical to form primary amine radicals which further react with primary amine radicals resulting in benzoquinonediimine and nitroxyl radicals. These constrain the free radicals from reacting further.
(Hess et al., 2005)	Soybean	B20	1 cyl. NA DI constant speed and constant load	EHN, BHA, BHT and TBHQ	2000 ppm for TBHQ 1000 ppm for rest	−4.5% (EHN) −2.9% (BHT) −4.4% (BHA) +2.7% (TBHQ)	Shorter ignition delay due to higher CN and accelerated formation of free radicals at usage of antioxidant treated blend resulted in lower NO_x (EHN) Phenolic hydroxyl groups present in antioxidants interfere with the prompt NO_x formation (BHA and BHT)
(Kivevele et al., 2011)	Croton megalocarpus	B100	4 cyl. TDI constant speed and varying load	PY	1000 ppm	+1.5%↑ (full load) NO_x↓ (partial load)	n/e
(Ryu, 2010)	Soybean	B100	4 cyl. IDI constant speed varying load	TBHQ and PG	300, 500, 1000 and 2000 ppm	Insignificant change	n/e
(Varatharajan and Cheralathan, 2013)	Soybean	B20 and B100	1 cyl. NA DI constant speed variable load	NPPD and DPPD	50, 100, 250, 500, 750, 1000, 1500 and 2000 ppm	(NO emission) ↓ (≤1500 ppm DPPD in B20 and up to 75% load) ↑ (≥1500 ppm DPPD in B20 and all load) ↓ (all ppm NPPD and all load) DPPD gave more than 25% NO_x reduction at all load.	Peroxyl radicals ($ROO\bullet$) react with p-phenylenediamine radical to form primary amine radicals which further react with primary amine radicals resulting in benzoquinonediimine and nitroxyl radicals. These constrain the free radicals from reacting further.
(Varatharajan et al., 2011)	Jatropha	B100	1 cyl. NA DI constant speed full load	EDA, PPDA, BHT, Vit. E, Vit. C	0.005, 0.015, 0.025, 0.035, 0.05 %-m	↓ (all antioxidants) −34.55% (PPDA at 0.025 %-m) −22.50% (EDA at 0.05 %-m) −12.00% (BHT at 0.035 %-m)	Reduction of formation of free radicals by antioxidants

(*continued on next page*)

Table 7 (*continued*)

Study	Feedstock	Fuels	Engine type and test condition	Antioxidant	Concentration	Effect on NO_x compared to base blend (On avg.)	Suggested reason
						−19% (Vit. E at 0.05 %-m)	
						−9% (Vit. C at 0.05 %-m)	
(Rizwanul Fattah et al., 2014c)	Palm	B20	4 cyl. IDI full load variable speed	BHA and BHT	1000 ppm	−12.6% (BHA)	Phenolic hydroxyl groups present in antioxidants interfere with prompt NO_x formation
						−9.8% (BHT)	
(Rizwanul Fattah et al., 2014d)	Calophyllum inophyllum	B20	4 cyl. IDI full load variable speed	BHA, BHT and TBHQ	2000 ppm	−3.6% (BHA)	Phenolic hydroxyl groups interfere with prompt NO_x formation
						−1.6% (BHT)	
						−1.9% (TBHQ)	
This study	Coconut	B20	4 cyl. IDI full load variable speed	BHA and BHT	2000 ppm	−7.78% (BHA)	
						−3.84% (BHT)	

TDI: Turbocharged Direct Injection, DPPD: N,N′-diphenyl-1, 4-phenylenediamine, NPPD: N-phenyl-1,4-phenylenediamine, EDA: Ethylenediamine, PPDA: p-phenylenediamine, Vit. E: α tocopherol acetate, Vit. C: L-ascorbic acid, NA: Naturally Aspirated, n/e: no explanation.

gas from engine emissions. NO_x reduction is a frequent target for engine research and car manufacture. As stated earlier, "thermal" and "prompt" mechanisms predominate NO_x formation in biodiesel combustion. The average NO_x values for diesel, CB20, CB20 BHA, and CB20 BHT were 3.78, 4.19, 3.86, and 4.03 g/kWh, respectively. CB20 increased the mean NO_x emission by 10.68% compared with diesel. Biodiesel is an oxygenated fuel with a short ignition delay caused by high CN; thus, CB20 can improve combustion, increase local peak temperatures, and promote NO_x formation (Kannan et al., 2012). Antioxidant addition to the blends helped reduce NO_x emission. BHA was the more effective antioxidant between the two antioxidants studied; it reduced the average NO_x emission by 7.78% compared with B20. BHT decreased the average NO_x emission by 3.84% NO_x compared with B20. Therefore, the phenolic hydroxyl groups present in these antioxidants can interfere the prompt NO_x mechanism (Hess et al., 2005). These results validate the hypothesis on the free radical quenching action of antioxidants and hence on the reduction of NO_x emission compared with the base blend CB20. By contrast, CB20 BHA and CB20 BHT increased the average NO_x by approximately 2.07% and 6.43%, respectively, compared with diesel. Table 7 provides a summary of the NO_x reduction activity of different antioxidants for different feedstock. Despite the high oxygen content, the addition of high antioxidant concentrations reduced NO_x emission for coconut B20.

3.2.2. CO emission

CO is formed during combustion whenever charge is burned with an insufficient air supply with low flame temperature (Rizwanul Fattah et al., 2013). Fig. 4 shows the variation in CO emission as a function of engine speed with diesel, CB20, and antioxidant-treated CB20. The average CO emission values for diesel, CB20, CB20 BHA, and CB20 BHT were 12.74, 9.64, 10.52, and 10.40 g/kWh, respectively. Thus, CB20, CB20 BHA, and CB20 BHT reduced the average CO emission by 24.32%, 17.44%, and 18.39%, respectively, compared with diesel. This result can be attributed to the combined effect of oxygen content and high CN (Hirkude and Padalkar, 2012). High CN exhibits short ignition delay and prolongs combustion duration. The oxygen content of biodiesel enhances combustion. It ensures that high in-cylinder combustion temperature promotes complete combustion and CO-to-CO_2 conversion compared with diesel fuel (Kivevele et al., 2011). The addition of BHA and BHT increased the average CO emission by 9.09% and 7.84%, respectively, compared with B20. These findings

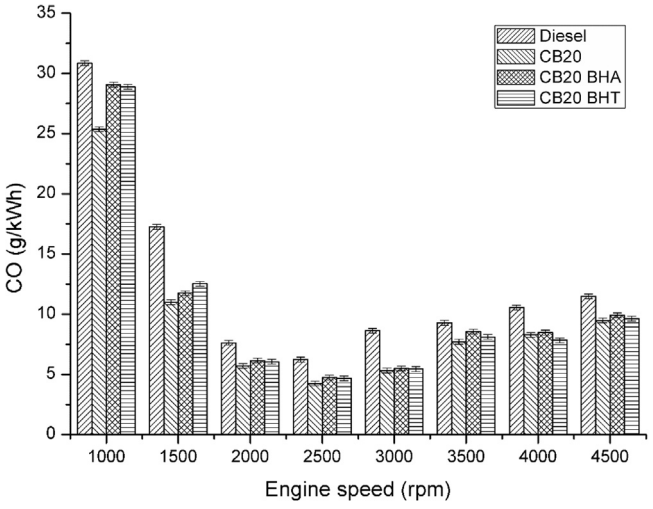


Fig. 4. Variation of CO emission for the test fuels at different speeds.

can be attributed to the hindrance created by the antioxidants in CO conversion (Palash et al., 2014). During oxidation, peroxyl and hydrogen peroxide radicals are formed successively. These species further convert to hydroxyl radicals by absorbing heat from the combustion chamber. Treating biodiesel with the antioxidants reduced the concentration of peroxyl and hydrogen peroxide radicals, which significantly affected CO conversion.

3.2.3. HC emission

HC emission is affected by engine operating conditions, fuel properties, and fuel spray characteristics (Valente et al., 2012). Two major causes of HC emission in diesel engine are (1) fuel mixed to leaner than the lean combustion limit during the delay period and (2) mixing of fuel that leaves the fuel injector nozzle late in the combustion process at a low velocity. Fig. 5 illustrates the HC emission of the different test fuels at various speeds. The average HC emission values for diesel, CB20, CB20 BHA, and CB20 BHT were 0.145, 0.086, 0.101, and 0.110 g/kWh, respectively. Thus, CB20 reduced the mean HC emission by 40.47% compared with diesel. The oxygen content of biodiesel can provide some advantageous conditions (post flame oxidation, higher flame speed, etc.) during air–fuel interactions, particularly in fuel-rich regions, which enhanced the oxidation of unburned HC and thus significantly reduced HC (Ozsezen et al., 2009). The addition of antioxidants clearly increased HC emission compared with CB20 at all speeds, which may be attributed to the reduction in oxidative free radical formation (Varatharajan et al., 2011). However, the level of HC emission was still lower than that of diesel. CB20 BHA and CB20 BHT reduced the mean HC by 30.67% and 24.37%, respectively, compared with diesel.

3.2.4. Smoke opacity

Fig. 6 shows the exhaust smoke opacity of the tested fuels. The average smoke opacity values for diesel, CB20, CB20 BHA, and CB20 BHT were 39.24, 26.51, 30.25, and 31.95 HSU, respectively. Thus, CB20, CB20 BHA, and CB20 BHT reduced the average smoke opacity by 32.43%, 22.91%, and 18.57%, respectively, compared with diesel. The smoke opacity in all blends was lower than that in diesel. The lower smoke opacity can be explained by the reduction of probability of rich zone formation (high local fuel–air ratio) in the presence of fuel borne oxygen and oxidation of soot nuclei during fuel combustion (Rizwanul Fattah et al., 2014a). The increase in smoke opacity caused by antioxidant addition compared with CB20

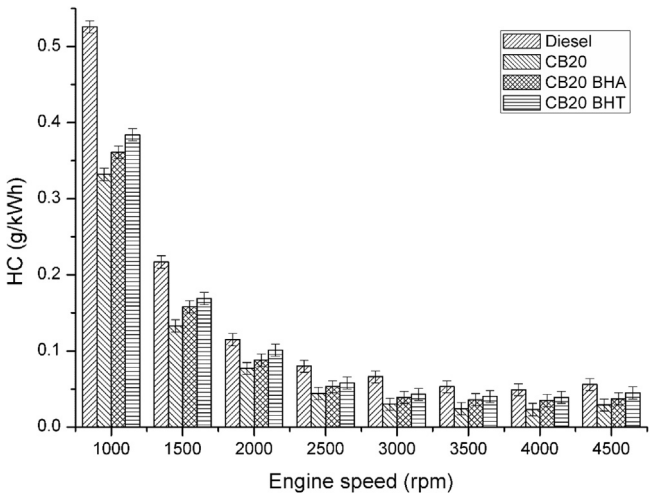


Fig. 5. Variation of HC emission for the test fuels at different speeds.

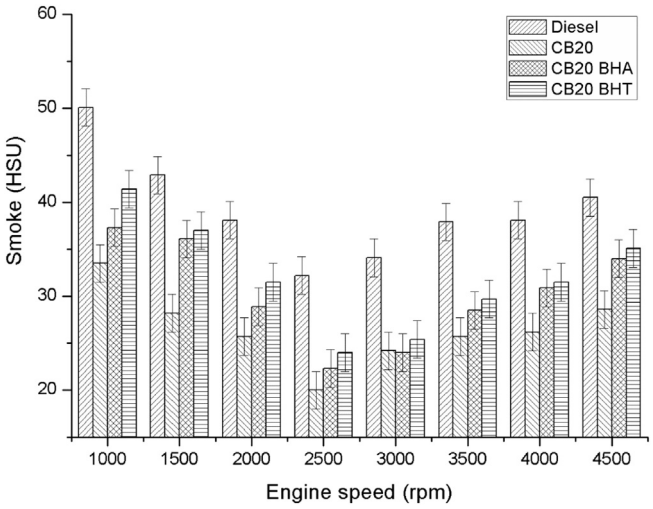


Fig. 6. Variation of smoke opacity for the test fuels at different speeds.

can be attributed to the reduction in oxygen availability, increase in C–C bonds, and increase in aromatic content. This finding is similar to the suggestions of other researchers (Varatharajan and Cheralathan, 2013)

4. Conclusions

This study investigated the effects of phenolic antioxidants BHA and BHT on the performance and emission characteristics of an engine fueled with coconut biodiesel blends. The following conclusions can be drawn based on the experimental results.

- Blending of 20% CME with diesel met the ASTM specification for blends.
- BHA produced better stabilization than BHT in CB20.
- CB20 produced approximately 6.59% higher BSFC than diesel. The addition of BHA and BHT to CB20 reduced the mean BSFC by 1.77% and 1.46%, respectively.
- CB20 increased the mean NO_x emission by 10.68% compared with diesel. The addition of BHA and BHT reduced the mean NO_x emission by 7.78% and 3.84% relative to CB20 because the phenolic hydroxyl groups in these antioxidants interfered with the prompt NO_x mechanism.
- CB20, CB20 BHA, and CB20 BHT reduced the average CO emission by 24.32%, 17.44%, and 18.39%, respectively, compared with diesel. CB20 BHA and CB20 BHT increased the mean CO emission by 7.84%–9.09% compared with CB20. This result can be attributed to the hindrance caused by the antioxidants in CO conversion.
- CB20 reduced the mean HC emission by 40.47% compared with diesel. CB20 BHA and CB20 BHT increased the mean HC emission by 16.45%–27.04% compared with CB20 because of the reduction in oxidative free radical formation.
- CB20, CB20 BHA, and CB20 BHT reduced the average smoke by 32.43%, 22.91%, and 18.57%, respectively, compared with diesel. The increase in smoke opacity for the treated blends can be attributed to the reduction in oxygen availability, increase in C–C bonds, and increase in aromatic content.

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