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Investigation of Engine Emission with Diesel-Palm Biodiesel-Antioxidant Blend

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Abstract

Similar properties of biodiesel to conventional diesel have made biodiesel as a promising fuel. However, its NOx emission was reported higher by most researchers in the world. In this study, antioxidants are used in the effort of improving the oxidation stability of biodiesel and reducing the NOx emission while maintaining the engine performance. *p*-Phenylenediamine (PPD) and *N*,*N*'-diphenyl-*p*-phenylenediamine (DPPD) are added in 0.025 wt% and 0.15 wt% concentrations, respectively into palm oil methyl ester-diesel blend. The performance characteristics of biodiesel blends are tested on a single cylinder engine with an attached emission analyser. The addition of the PPD and DPPD antioxidants improved the oxidation stability of biodiesel without affecting much in the density and kinematic viscosity. For B20 (20% biodiesel + 80% Euro 5 diesel), the addition of DPPD showed the best results by reducing NO (0.8% lower on average), CO (10.8% lower on average) and HC emission (32.9% lower on average), as compared to B7 blend. However in terms of engine performance, B20+DPPD showed higher BSFC and lower brake power when compared to B7 blend.

Keywords: PPD antioxidant; DPPD antioxidant; palm oil methyl ester-diesel blend; emission characteristics

Introduction

Currently, Malaysia's diesel is a B7 blend which contains 7% of palm biodiesel and 93% of conventional diesel. Malaysian Biodiesel Association (MBA) is pushing for the implementation of B10 with the cooperation from the Ministry of Plantation Industries and Commodities as well as Malaysian Palm Oil Board (MPOB). On the other hand, in November 2014, Malaysia introduced Euro 5-grade diesel, which results in lower exhaust emission and improved air quality.

Meanwhile, many researchers reported that biodiesel improved the exhaust emission components of particulate matter (PM), carbon monoxide (CO), unburned hydrocarbon (HC) and smoke compared to conventional diesel [Li et al., 2015, Millo et al., 2015]. In addition, biodiesel is useful to reduce CO_2 emission through the life cycle. However, higher NOx emission than conventional diesel has been reported by the past studies [Li et al., 2015, Millo et al., 2015].









Furthermore, the engine performance from biodiesel fuel was reported to be lower than that of conventional diesel, in terms of brake power output and brake thermal efficiency (BTE).

Therefore, a lot of innovative solutions either through engine enhancements or fuel enhancements had been conducted by researchers in order to improve physicochemical properties and emission characteristics of biodiesel. In this regard, addition of antioxidants to biodiesel blend has the potential to improve physicochemical properties and exhaust emission of biodiesel blend [Barrios et al., 2014, Palash et al., 2014]. Although many studies have been experimentally done with various antioxidants [Barrios et al., 2014, Palash et al., 2014], the present study uses p-Phenylenediamine (PPD) and N,N'-diphenyl-*p*-phenylenediamine (DPPD) with B10 and B20 of palm biodiesel blend in the conventional diesel engine.

Material and Methods

Euro 5 diesel is chosen as a baseline fuel to evaluate its performance and emission characteristics in a diesel engine. All diesel sold in Malaysia consists of 7% blend of biodiesel (B7). Biodiesel, PPD antioxidant and DPPD antioxidant are purchased from local suppliers. Based on the research by Varatharajan et al. [2011] and Varatharajan et al. [2013], the optimal concentrations to reduce NOx emission for DPPD and PPD are 0.15 wt% and 0.025 wt%, respectively. These concentrations will be adapted in the present study.

The Rancimat instrument is used to determine the oxidation stability of biodiesel (B100). Stabinger viscometer is used to measure the kinematic viscosity and density of the fuels. For engine performance test, B10 and B20 blends were used and benchmarked with B7 blend. The engine performance test was carried out on a 0.6L single-cylinder, 4-stroke, direct injection diesel engine. The test engine is directly coupled to a 20kW eddy current dynamometer. BOSCH BEA150 emission analyzer is used to analyze the exhaust gases such as carbon monoxide (CO), hydrocarbon (HC) and nitric oxide (NO). All the tests were conducted at Energy Efficiency and Heat Engine Laboratory of Mechanical Engineering Department, University of Malaya.

Results and Discussions

The addition of antioxidant into biodiesel slightly increased the kinematic viscosity by 0.6% for DPPD and 0.1% for PPD. Higher kinematic viscosity implies that the fuel receives higher resistance during the flow in the fuel line, which leads to higher delay in the start of ignition [Hoekman et al., 2012]. Oxidation stability of B100 showed 18.6 hours of induction period, which meets both ASTM D6751 and EN 14214 standard specifications. The addition of both DPPD and PPD into B100 increased the oxidation stability up to more than 23 hours of induction period.

Highest reduction in engine brake power can be observed with B10+PPD and B20+DPPD, with 4.4% and 4.3% reductions, respectively compared to B7 at an engine speed of 1900 rpm (Figure 1.1). Generally, the addition of antioxidants reduces the engine brake power. The possible reason is the higher density and kinematic viscosity which leads to poor atomization and low combustion efficiency [Haşimoğlu et al., 2008].









At 1100-1900 rpm, BSFC increased between 3.1% and 8.9% for B10+PPD and B20+DPPD as compared to B7 (Figure 1.2). The possible reason of the increment is the lower heating value of biodiesel, in which more fuel is needed to produce the same amount of power. However, at higher engine speed (2300rpm), all biodiesel+antioxidant blends caused reductions in BSFC within the range of 10.2% to 20.3% in contrast to B7. The reduction in BSFC might be due to the friction reduction properties of the aromatic amine based antioxidants [Varatharajan et al., 2011].

At 1100 rpm, the NO emissions of biodiesel blends are comparatively higher than B7. However, the difference reduced with increasing engine speed (Figure 1.1). The NO emission eventually reduced at 2300 rpm, with B10+PPD and B20+DPPD showed reduction in NO emission by 4.5% and 7.1%, respectively. The reductions in NO emission from biodiesel+antioxidant mixtures are mainly due to the suppression of peroxyl free radical formations by reaction with aromatic amine antioxidants [Varatharajan et al., 2013].

Besides that, B20+DPPD showed the best CO reduction among the biodiesel blends, within the range of 3.1% to 22.8% as compared to B7 (Figure 1.2). The possible reason is due to its higher oxygen content and higher cetane number [Kivevele et al., 2011]. B20+DPPD also reduced the HC emission by 19.1% to 50% in contrast to B7 (Figure 1.3). This is due to the antioxidant that increases the cetane number of the fuel, in which HC emission is reduced [Kivevele et al., 2013].

Conclusions

DPPD antioxidant showed better emission characteristics than PPD. As the Malaysian Biodiesel Association pushes the government to implement B10 and B20 in stages, DPPD can be considered to improve emission characteristics of biodiesel in the future.

Acknowledgments

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Figure 1.1 Variation in engine brake power and NO emission at different engine speeds at full load condition.



Figure 1.2 Variation in engine brake specific fuel consumption (BSFC) and CO emission at different engine speeds at full load condition.



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Figure 1.3 Variation in engine unburned hydrocarbon (HC) emission at different engine speeds at full load condition.











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INTRODUCTION

- Malaysia's diesel is a B7 blend (7% palm biodiesel + 93% diesel blend).
- Malaysia Biodiesel Association is pushing for the implementation of B10 and B20 gradually, with the cooperation from the Ministry and Malaysian Palm Oil Board (MPOB)
 - Benefits our economy in terms of energy security (reducing dependence on foreign oil)

Euro 5 Diesel / Clean Diesel



In November 2014, Malaysia introduced Euro 5-grade diesel, which results in lower exhaust emission and improved air quality.

Euro 2-grade standard Diesel is also available



Priced at RM2.27 per litre (upd. 1st Nov 2017) Only RM0.10 higher than Euro 2 Diesel 8th Nov 2017 – RM0.03 increase. (BHPetrol, 2015; Shell, 2016)

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PROBLEM STATEMENT

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- Many researchers reported that biodiesel improved the PM, CO, HC and smoke emission compared to petroleum diesel. However, the NO_x emission is higher.
- 2. The addition of biodiesel into clean diesel increases the viscosity of the fuels and may cause fuel filter clog.
- 3. A lot of innovative solutions had been taken to improve the emission characteristics. Addition of antioxidants (additive) to biodiesel blend shows a strong potential.

OBJECTIVE

- To investigate viscosity, density and oxidation stability of diesel-Palm biodiesel-antioxidant fuel blend
- To investigate the engine performance at full load condition using diesel-Palm biodiesel-antioxidant fuel blend

SCOPE OF STUDY

- Euro 5-grade diesel was used in this study
- Biodiesel: Palm biodiesel/ Palm Methyl Ester (PME)
- Antioxidants additives (aromatic amines):
 - p-Phenylenediamine (PPD)
 - N,N'-diphenyl-p-phenylenediamine (DPPD)



LITERATURE REVIEW

Optimum concentration of antioxidant additives
PPD: 0.025% (m) (Varatharajan et *al.*, 2011)
Reduced NO_x emission by 43.55%, compared to B100

DPPD: 0.15% (m) (Varatharajan et al., 2013)

Biodiesel blends	B 5	B10	B15	B20
Reduction of NOx (compared to B100)	8.03%	3.50%	13.65%	16.54%

Both concentration are adapted in this project.

VARATHARAJAN, K., CHERALATHAN, M. & VELRAJ, R. 2011. Mitigation of NOx emissions from a jatropha biodiesel fuelled DI diesel engine using antioxidant additives. Fuel, **90**, 2721-2725.

METHODOLOGY

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Consumables

 Euro 5 Diesel, Palm biodiesel, additives - all purchased from local suppliers

- Palm biodiesel & diesel blend investigated B10 (10% Palm biodiesel + 90% diesel) and B20
- Results will be compared with B7 blend
- Antioxidant PPD 0.025% and DPPD 0.15%

Fuel Blends



Electronic shaker was used to blend the fuel.

> 350 rpm for 1 hour.

Euro 5 B7					
Euro 5 B10					
Euro 5 B10 + 0.025% PPD	Euro 5 B10 + 0.15% DPPD				
Euro 5 B20					
Euro 5 B20 + 0.025% PPD	Euro 5 B20 + 0.15% DPPD				

Equipment



Viscosity/ density



Oxidation stability



(SVM3000 Stabinger Viscometer)

(873 Biodiesel Rancimat)

Technical Specification of Diesel Engine



Yanmar TF 120M **Direct injection** 4-stroke single-cylinder diesel engine Cylinder bore x stroke: 92 x 96mm Displacement: 0.638 L Compression ratio: 17.7 Maximum engine speed: 2400 rpm

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Technical Specification of Dynamometer



Max. Power: 20 kW Max. Speed: 10,000 rpm Max. Torque: 80 Nm Water flow rate: 14 L/min Water pressure: 23 lbf/in² Electricity: 220 V, 50/60 Hz, 0.5 A



Bosch Emission Analyser



Main instrument to measure emission components of:

NO CO HC

Running Conditions

Engine is first run with clean diesel

For flushing & warm-up

Fuel flow rate and exhaust emission are measured at the same time. Run with biodiesel blends for five minutes.

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• To remove residual diesel in fuel line

The same blends are repeated twice for an average results.

The same procedure are repeated for other blends. DAQ is started.

- Engine conditions:
 Full Load
- 1100 to 2300rpm with interval of 400rpm

Calculation

Brake power, $BP = \frac{2\pi NT}{60}$

Brake specific fuel consumption, $BSFC (g/kWh) = \frac{m_f}{BP}$ where, m_f = mass flow rate of fuel (g/h) BP = brake power (kW)



RESULTS & DISCUSSION

Viscosity, Density and Oxidation Stability 19

Parameter	s B100	B100 + 0.15% (m) DPPD	B100 + 0.025% (m) PPD	ASTM D6751	EN 14214		
Density @40°C (kg/m ³)	857.3	857.7 +0.05%	857.4 +0.01%	N/S	860 – 900 (@15°C)		
Kinematic viscosity @40°C (mm²/s)	4.5490	4.5767 +0.6%	4.5534 +0.1%	1.9 – 6.0	3.5 – 5.0		
Induction time (hour	18.57	>23	>23	>3	>6		
Addition of DPPD and PPD slightly increased density and							

kinematic viscosity, but improved oxidation stability of B100



Engine Performance



Brake power (antioxidant additives)



Highest reduction in engine brake power can be observed with B10+PPD and B20+DPPD, with 4.4% and 4.3% reductions, respectively compared to B7 at 1900 rpm

Generally, addition of antioxidant additives to biodiesel blends reduces BP.

May be due to combined effect of lower energy content (lower calorific value and higher viscosity) (Rizwanul Fattah et al., 2014).

BSFC (g/kWh) vs engine speed



Brake specific fuel consumption (antioxidant additives)



At 1100-1900 rpm, BSFC increased between 3.1% and 8.9% for B10+PPD and B20+DPPD as compared to B7.

May be due to lower heating value of biodiesel compared to diesel fuel (Palash et al., 2014).

At 2300rpm, all biodiesel+antioxidant blends caused reductions in BSFC within the range of 10.2% to 20.3% in contrast to B7.

> Due to friction reduction properties of amines (Varatharajan et al., 2011).



Emission Characteristics

NO Emission (ppm) with engine speed 26 700 **B**7 **B10 + DPPD B10 + PPD B20 B20 + DPPD** B20 + PPD **B**10 600 500 400 300 200 DPPD DPPD B20 + DPPD B20 + DPPD DPPD B20 + DPPD DPPD B10 + DPPD DPD DPD 4 PPD B20 + PPD DPD DPD PPD DPD 100 + + + B10 + B10 + B10 + + + + + **B20 B20 B20** 20 **B10 B10 B10 B20 B20** B20 **B20 B10 B10 B10 B10 B10 B**₇ B7 B7 B7 Ω 0

1100

1500

1900

2300

NO emission (antioxidant additives)



- At 1100 rpm, the NO emissions of biodiesel blends are comparatively higher than B7.
- ► However, the difference reduced with increasing engine speed.
- At 2300 rpm, B10+PPD and B20+DPPD showed reduction in NO emission by 4.5% and 7.1%, respectively.
- The reductions in NO emission from biodiesel+antioxidant mixtures are mainly due to the suppression of peroxyl free radical formations by reaction with aromatic amine antioxidants [Varatharajan et al., 2013].







B20+DPPD showed the best CO reduction among the biodiesel blends, within the range of 3.1% to 22.8% as compared to B7.

The possible reason is due to its higher oxygen content and higher Cetane number [Kivevele et al., 2011]



HC emission (antioxidant additives)



B20+DPPD reduced the HC emission by 19.1% to 50% in contrast to B7

This is may be due to the antioxidant that increases the Cetane number of the fuel, in which HC emission is reduced [Kivevele et al., 2013]



CONCLUSION

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- The addition of the PPD and DPPD into biodiesel blends improved oxidation stability with slight increase in the density and kinematic viscosity.
- DPPD antioxidant showed better emission characteristics than PPD
- As the Malaysian Biodiesel Association pushes the government to implement B10 and B20 in stages, DPPD can be considered to improve emission characteristics of biodiesel in the future

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THANK YOU FOR YOUR KIND ATTENTION!

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ABSTRACT PROCEEDINGS

THE 10th AUN/SEED-NET REGIONAL CONFERENCE ON ENERGY ENGINEERING

Yangon, Myanmar November 9 - 11, 2017









RAID IN SHIELD



ABSTRACT PROCEEDINGS

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