

Performance and Emission Characteristics of Green Diesel Blends containing Diethyl-Succinate and 1-Octanol

Li Yee Phoon^a, Azizul A. Mustaffa^{*,a,b}, Haslenda Hashim^{a,b}, Ramli Mat^b

^aProcess Systems Engineering Centre (PROSPECT), Research Institute for Sustainable Environment (RISE), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

^bDepartment of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
 azizulazri@utm.my

Further enhancing the oxygen content (OC) of the conventional B5 palm oil biodiesel is the key to attain greener emissions in future. Diethyl succinate (DES) and 1-octanol (OCT) is designed to blend with B5 to address this issue. In this study, the optimum binary and ternary blend (with higher OC) of B5 with DES and/or OCT is obtained using a computer-aided decomposition-based optimisation. Subsequently, the engine performances including fuel efficiency: brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC) and emissions of nitrogen oxides (NO_x), carbon monoxide (CO) and un-burnt hydrocarbon (UHC) of these optimum blends are evaluated experimentally. Ternary blend of B5 with DES and OCT could attain higher OC than binary blends with satisfied target fuel properties. The designed optimum blends generally have greener emissions than B5 while having similar fuel efficiency with B5. T1 ternary blend (B5 = 70.0 %; OCT = 24.1 %; DES = 5.9 %) appear as the most promising green diesel blend owing to its greener emissions and similar fuel efficiency with B5.

1. Introduction

Blending biofuel or bio-chemicals with the conventional diesel fuel is one of the most promising solutions to mitigate the air pollution issues while retaining or even improve the performance of the conventional diesel fuel. B5 palm oil biodiesel, which is containing 5 vol% of palm oil biodiesel and 95 vol% of petrodiesel is a conventional diesel fuel to address the environmental issues. Further increasing the oxygen content (OC) of B5 is essential as the harmful emissions, especially the emissions of carbon monoxide (CO) and un-burnt hydrocarbon (UHC), could be further reduced by increasing the OC of the blended fuel (Shahir et al., 2015). Utilisation of lignocellulosic bio-chemicals with high OC and excellent combustion characteristics is the key to obtain green diesel blends with high OC and excellent performance.

Diethyl succinate (DES) with high OC has been proposed as a potential blending agent with diesel fuel (Jenkins et al., 2013). Alcohol with longer carbon chain (higher alcohol), such as 1-octanol (OCT), which shows better combustion characteristics over lower alcohols (for example methanol and ethanol), is getting more attention now (Campos-Fernández et al., 2012). In order to obtain green diesel blends with highest OC by using DES and/or OCT, computer-aided decomposition-based optimisation approach is preferred.

Computer-aided approach can efficiently narrow down the search space of the feasible blends before the costly and time consuming trial and error approach. The most promising blends with maximum OC could be identified computationally, while the experimental work is only applied to the shortlisted blend candidates for further evaluation (Phoon et al., 2015).

On the other hand, there are limited studies evaluating the engine performances of the blends of B5 with DES and/or OCT. This information is essential to validate the feasibility of using DES and OCT in a diesel engine. This study is presented to experimentally study the engine performances of the optimum blends of B5 with DES and/or OCT with the highest OC and satisfied target fuel properties.

This study is divided into two phases. The first phase is to obtain the optimum solution of the binary and ternary blend of B5 with DES and/or OCT by using the tailor-made green diesel blend design algorithm, which

is proposed in the previous study (Phoon et al., 2015). Subsequently, the fuel efficiency such as brake thermal efficiency (BTE) and brake specific fuel consumption (BSFC) and the emissions of nitrogen oxides (NO_x), UHC and CO of these optimum binary and ternary blends are experimentally evaluated in the second phase. A conclusion is presented at the end of this study to summarise the significant contributions of this study.

2. Methodology

2.1 Green Diesel Blend Optimisation

The OC of the binary and ternary blend of B5 with DES and/or OCT is optimised to enhance fuel combustion, by using the computer-aided technique. The optimum blends with maximum oxygen content designed in this study should have at least 1.00 % by mass of DES and/or OCT while the maximum amount allowed for bio-chemicals used in the blends is 30.00 % by mass. Only 5 % loss of higher heating value compare to B5 is preferred to ensure they have compatible engine performances with B5. The property constraints used are set according to Malaysian EURO 4M diesel standard. The optimisation problem is mathematically formulated and summarised in Table 1. This problem is solved by using a decomposition-based optimisation approach, which is proposed in the previous study (Phoon et al., 2015). The search space of the feasible binary and ternary blends of DES and/or OCT is solved to match the linear property constraints using Eqs(2) to (5). Subsequently, the non-linear properties constraint: flash point is analysed using Liaw model (Eq(6)) (Liaw et al., 2002) and this model had been study to apply for green diesel blends containing B5 and alcohol (Phoon et al., 2016). In Table 1, x and x_m is mass fraction and mole fraction; γ_{VLE} is liquid phase activity coefficient calculated using UNIFAC group contribution method, in which the group interaction parameters for B5-DES blend and the blends containing OCT are retrieved from Fredenslund et al. (1975) and Phoon et al. (2016).

$$\text{Objective function: } F_{obj} = \min \sum x_i OC_i \quad (1)$$

Table 1: Optimisation design problem in mathematical form

Constraint	Equation	Lower Bound	Upper Bound	
Product property constraints				
a) Linear Property Constraints				
Density at 15 °C, ρ (kg/m ³)	$\rho_{mix} = \sum_{i=1}^n x_i \cdot \rho_i$	810	870	(2)
Kinematic Viscosity at 40 °C, η (mm ² /s)	$\ln \eta_{mix} = \sum_{i=1}^n x_i \cdot \ln \eta_i$	1.5	5.8	(3)
Cetane Number, CN	$CN_{mix} = \sum_{i=1}^n x_i \cdot CN_i$	4.9	-	(4)
Higher Heating Value, HHV (MJ/kg)	$HHV_{mix} = \sum_{i=1}^n x_i \cdot HHV_i$	43	-	(5)
b) non-Linear Property Constraints				
Flash Point, T_{FP} (°C)	$\sum_i \frac{x m_i \cdot \gamma_{VLE,i}(T_{FP}) \cdot P_i^{sat}(T_{FP})}{P_{i,FP}^{sat}} = 1$	60	-	(6)
Process model constraint				
Mass balance	$\sum_i x_i - 1 = 0$	-	-	(7)
Total blending agent allowed, mass fraction	$\sum x_{bio,i}$	-	0.30	(8)
DES and OCT composition, mass fraction	$x_{bio,i} \geq 0.01$	0.01	-	(9)

2.2 Material and Experimental Method

The engine performances and emissions of the optimum blends obtained in Section 2.1 are experimentally evaluated. B5 is supplied by Petrolia Nasional Berhad (PETRONAS) through their petrol station in Malaysia. The blending agent used: DES and OCT with purity $\geq 99\%$ were purchased from Merck Millipore (Malaysia).

The green diesel blends are prepared by splash blending at room temperature using a hotplate stirrer and stir bar. The stirrer speed is control carefully to avoid excessive vortex and the mixture is stirring for 10 min to allow homogenous solution form. Aluminium foil is used to cover the mixing beaker when stirring to avoid the light compounds from evaporate and escape to the open air.

A four stroke-cycle, vertical cylinder, air-cooled Yanmar L70N diesel engine with the specification listed in Table 2 is used to evaluate the fuel efficiency: BTE and BSFC and emissions: NO_x , UHC and CO of the green diesel optimum blends. The emissions are measured by using an EMS emission analyser. The testing was done at steady state condition, constant speed test (1,500 rpm, 2,000 rpm and 2,500 rpm) at variable load setting. The engine testing is performed at Automotive Development Centre, University Teknologi Malaysia.

Table 2: Specification of Yanmar L70N diesel engine

Parameter	Value
Number of cylinder	1
Bore, mm	78
Store, mm	67
Displacement, L	0.320

3. Results and Discussion

3.1 Optimum Green Diesel Blends

The optimum binary and ternary blends are ranked according to OC as showed in Table 3 together with the experimental B5 fuel properties to allow for comparison. Ternary blend of B5 with 5.9 % of DES and 24.1 % of OCT (T1) has the highest OC compared to the binary blends. This result revealed that blend with higher OC and satisfied target properties is easier to attain by using both DES and OCT when compared to the blend that only using one blending agent (either DES or OCT). On the contrary, binary blend design is strongly dependent to the fuel property and OC of the bio-chemical used. DES (OC = 36.7 %) has higher OC than OCT (OC = 12.3 %); hence, G1 (B5 + 11.1 % of DES) has higher OC than G2 (B5 + 30.0 % OCT) although G2 containing higher bio-chemical content. The performances of these top two blends: T1 and G1 in a diesel engine are further evaluated by studying their fuel efficiency and emissions.

Table 3: Optimum green diesel blends

Fuel Blends (wt%)	Predicted Property					
	OC, %	ρ , kg/m ³	η , mm ² /s	CN	HHV, MJ/kg	FP, °C
Main Ingredient: B5	0.62	838.90	3.085	57.8	45.25	344.65
T1: B5 + 5.9 DES + 24.1 OCT	5.57	849.08	3.408	51.1	43.00	343.52
G1: B5 + 11.1 DES	4.62	861.79	2.872	53.7	43.00	343.87
G2: B5 + 30.0 OCT	4.12	836.35	3.666	52.2	43.94	343.07

3.2 Fuel Efficiency

Fuel efficiencies of T1 and G1 were analysed in the form of BTE and BSFC. These efficiencies were compared to B5 at different engine loads (indicated by brake mean effective pressure (BMEP)) as shown in Figure 1. BTE is inversely proportional with BSFC; as the engine speed and load increases, BTE is increased while BSFC is decreased. This phenomenon indicates that higher combustion temperature is attained at higher engine speed and load, more efficient work is produced and less fuel is consumed (Kakati and Gogoi, 2016).

B5 has lower BTE compared to T1 and G1 as more chemical bonded oxygen is present in T1 and G1 to enhance complete fuel combustion. T1 and G1 have lower cetane number than B5; and longer ignition delay results in better air-fuel premixed for the subsequent combustion occur. High combustion temperature is attained and resulting T1 and G1 have higher BTE than B5 (Zhang and Balasubramanian, 2014).

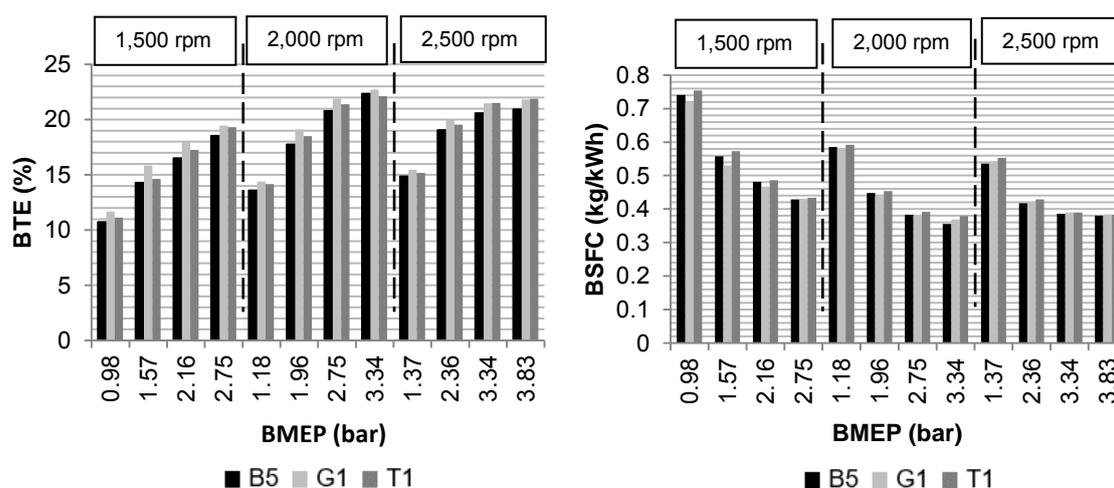


Figure 1: Comparison of engine performance of BTE and BSFC

G1, which has higher CN and lower OC than T1, always has higher BTE when compared to T1. This happened could be attributed to the density of green diesel blend. G1 is denser than T1; more fuel (by mass) is injected into combustion chamber and produces more energy than (with the same fuel volume) T1. As a result, G1 gained higher BTE among the tested fuel.

BSFC obtained for G1 and T1 are similar with B5 in most cases or just slightly higher than B5, although G1 and T1 have lower HHV than B5 (45.25 MJ/kg). BSFC of these lower HHV fuel blends were recovered by their high fuel density as more fuel (by mass) is injected into combustion chamber and burned to produce similar power with the same volume of B5 (Zhang and Balasubramanian, 2014). G1 has slightly lower BSFC than T1 as G1 is denser than T1 while their predicted HHVs are similar.

3.3 Emissions

The emissions of NO_x , UHC and CO of different tested fuels are illustrated in Figure 2. Generally, all the green diesel blends have lower emissions than B5 with some exceptions at lower engine speed: 1,500 rpm and loads. This happened might due to the higher density and kinematic viscosity of G1 and T1. Larger droplets were form for these high density and viscosity fuels and this leads to poor atomisation and slower fuel vaporisation at lower engine speed (Atmanli et al., 2015). As results, poor fuel combustion occurred at low engine speed (1,500 rpm) and load and this leads to poor emissions, especially for the emissions of NO_x and CO of the denser G1 fuel blends. The effects of high density and viscosity to NO_x and CO emissions are eased at higher engine speeds (2,000 and 2,500 rpm) and loads because of the temperature at the engine combustion chamber wall is increased (Guido et al., 2013). G1 (OC = 4.62 %), which have lower oxygen content than T1 (OC = 5.57 %), normally has higher emissions than G1 except NO_x . Higher oxygen content enhances more complete combustion to reduce CO and UHC emissions (as a result of high local combustion temperature) of G1 and T1. Their high self-provided oxygen tends to produce more thermal NO_x , where more nitrogen from fresh air is oxidised at high temperature. This NO_x emission happens more readily at higher engine speed (2,000 and 2,500 rpm) as higher temperature is at the combustion chamber wall (Chuaha et al., 2016). T1 has lower cetane number than G1; longer ignition delay results in more homogenous air-fuel premixed. Higher temperature combustion region was generated and this situation was induce more NO_x emission (Atmanli et al., 2015). B5, which has lowest OC (0.62 %), has higher NO_x emission than G1 and T1. This is because blending DES and or OCT with B5 could lowering the overall combustion temperature and in-cylinder temperature as a result of higher heat of vaporisation of G1 and T1 (Guido et al., 2013). NO_x emissions could be further reduced by decreasing the fuel HHV (Chang et al., 2013) (G1 and T1 have lower HHV than B5).

The emissions of UHC and CO at higher engine speeds (2,000 and 2,500 rpm) and loads are more depending to the OC of fuel used. G1 and T1 combust more efficiently with sufficient self-provided oxygen; more complete combustion is attained and these by-products generated from incomplete combustion (UHC and CO) are reduced. More oxygen present in G1 and T1 have lower carbon/hydrogen ratio than B5 and this lowers the emissions of UHC and CO (Aransiola et al., 2014).

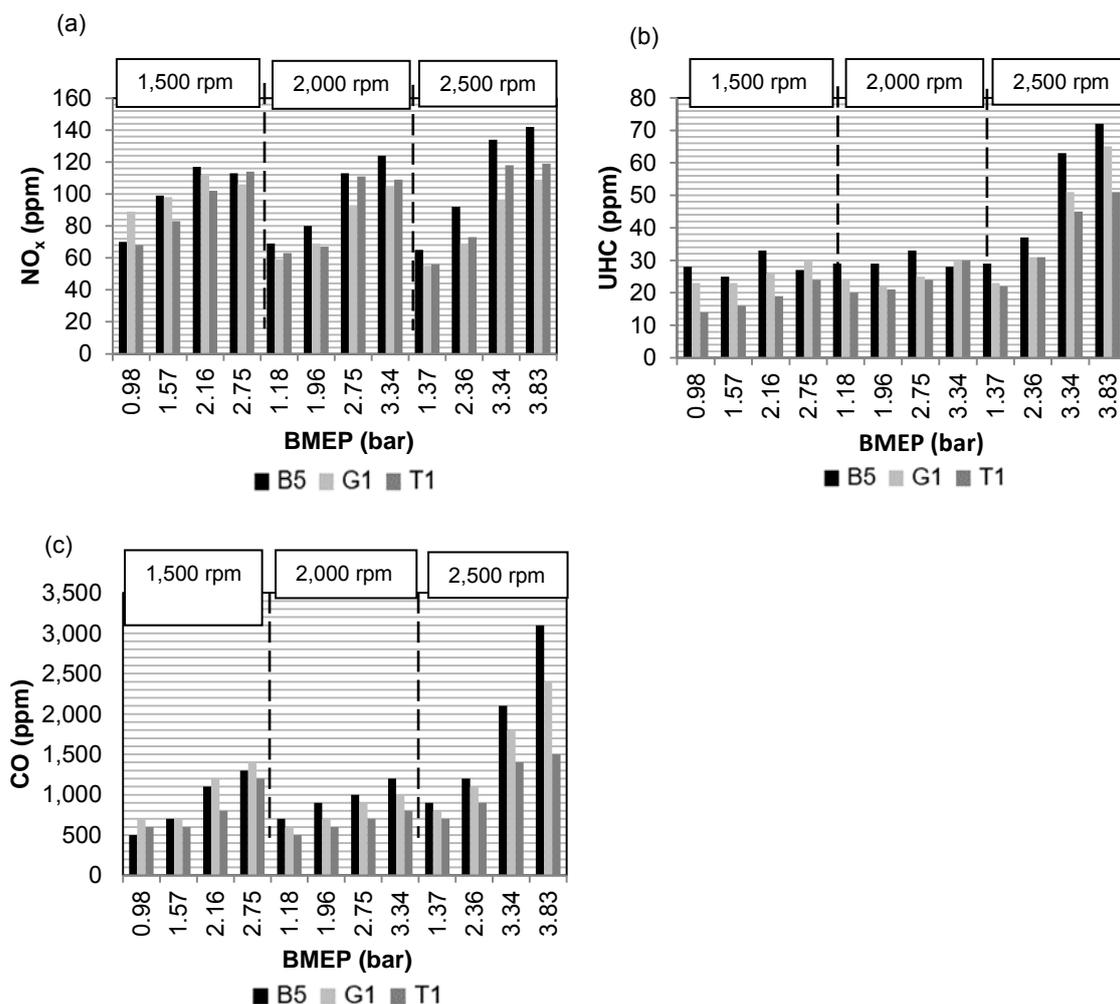


Figure 2: Comparison of the emissions of a) NO_x, b) UHC and c) CO

4. Conclusions

The optimum blends of B5 with DES and/or OCT were obtained by optimising the OC using a computer aided decomposition-based optimisation approach. The engine performances of these optimum blends obtained were experimentally analysed. T1 containing 0.59 % of DES and 24.1 % of OCT (by mass) have the highest OC (OC = 5.57 %) while the binary blends of B5 with 11.1 % of DES (OC = 4.62 %) have better OC than the optimum blend of B5 with 30.0 % OCT (OC = 4.12 %). Generally, G1 and T1 have similar BSFC, slightly higher BTE and greener emissions when compared to B5 with some exception at lower engine speed (1,500 rpm). G1, which has similar HHV but higher density than T1, showed slightly better fuel efficiency than T1; but, its emissions of UHC and CO are much higher when compared to T1. T1 gained higher NO_x when compared to G1 owing to its high OC. Overall, satisfied engine performances are obtained by using DES and OCT as a blending agent to B5. T1 is suggested as the best green diesel blends thanks to its greener emissions. The NO_x emissions problem of T1 could be further reduced by increasing its cetane number using cetane enhancer and it will be a part of further work.

Acknowledgments

The authors would like to appreciate the financial support from the Ministry of Higher Education (MoHE) Malaysia and the Universiti Teknologi Malaysia (UTM) under the Vote No. R.J130000.7844.4F670 to perform this research work. The valuable guidance and advice provided by the Automotive Development Centre at University Teknologi Malaysia to perform engine performance testing is highly acknowledged.

Reference

- Aransiola E.F., Ojumu T.V., Oyekola O.O., Madzimbamuto T.F., Ikhu-Omoregbe D.I.O., 2014, A review of current technology for biodiesel production: State of the art, *Biomass Bioenergy* 61, 276-297.
- Atmanli A., Ileri E., Yuksel B., Yilmaz N., 2015, Extensive analyses of diesel–vegetable oil–n-butanol ternary blends in a diesel engine, *Applied Energy* 145, 155-162.
- Campos-Fernández J., Arnal J.M., Gómez J., Dorado M.P., 2012, A comparison of performance of higher alcohols/diesel fuel blends in a diesel engine, *Applied Energy* 95, 267-275.
- Chang Y.-C., Lee W.-J., Lin S.-L., Wang L.-C., 2013, Green energy: Water-containing acetone–butanol–ethanol diesel blends fueled in diesel engines, *Applied Energy* 109, 182-191.
- Chuah L.F., Aziz A.R.A., Yusup S., Klemeš J.J., Bokharia A., 2016, Waste cooking oil biodiesel via hydrodynamic cavitation on a diesel engine performance and greenhouse gas footprint reduction, *Chemical Engineering Transactions* 50, 301-306.
- Fredenslund A., Jones R. L., Prausnitz J. M., 1975, Group-contribution estimation of activity coefficients in nonideal liquid mixtures, *AIChE Journal* 21, 1086-1099.
- Guido C., Beatrice C., Napolitano P., 2013, Application of bioethanol/RME/diesel blend in a Euro5 automotive diesel engine: Potentiality of closed loop combustion control technology, *Applied Energy* 102, 13-23.
- Jenkins R.W., Munro M., Nash S., Chuck C. J., 2013, Potential renewable oxygenated biofuels for the aviation and road transport sectors, *Fuel* 103, 593-599.
- Kakati J., Gogoi T.K., 2016, Biodiesel production from Kutkura (*Meyna spinosa* Roxb. Ex.) fruit seed oil: Its characterization and engine performance evaluation with 10% and 20% blends, *Energy Conversion Management* 121, 152-161.
- Liaw H.-J., Lee Y.-H., Tang C.-L., Hsu H.-H., Liu J.-H., 2002, A mathematical model for predicting the flash point of binary solutions, *Journal of Loss Prevention in the Process industries* 15, 429-438.
- Phoon L. Y., Hashim H., Mat R., Mustafa A.A., 2015, Tailor-Made Green Diesel Blends Design using a Decomposition-Based Computer-Aided Approach, *Computer Aided Chemical Engineering* 39, 487-505
- Phoon L.Y., Hashim H., Mat R., Mustafa A. A., 2016, Flash point prediction of tailor-made green diesel blends containing B5 palm oil biodiesel and alcohol, *Fuel* 175, 287-293.
- Shahir V.K., Jawahar C.P., Suresh P.R., 2015, Comparative study of diesel and biodiesel on CI engine with emphasis to emissions—A review, *Renewable and Sustainable Energy Reviews* 45, 686-697.
- Zhang Z.-H., Balasubramanian R., 2014, Influence of butanol addition to diesel–biodiesel blend on engine performance and particulate emissions of a stationary diesel engine, *Applied Energy* 119, 530-536.