CHEMICAL ENGINEERING TRANSACTIONS
VOL. 72, 2019
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jeng Shiun Lim, Azizul Azri Mustaffa, Nur Nabila Abdul Hamid, Jiří Jaromír Klemeš

ISBN 978-88-95608-69-3; **ISSN** 2283-9216
DOI: 10.3303/CET1972066

Optimisation of Ternary Green Diesel Blends for Diesel/Palm Methyl Ester/Alcohol using Product Design Optimization

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Among many alternative fuels, oxygenated fuels like biodiesel and biomass-based energy (biofuel) such as bioalcohol have greater potential to enhance engine performance and mitigate particulate exhaust emissions in compression-ignition (CI) engines. The main objective of this study is to determine the optimal ternary green diesel (GD) blends formulation by identifying the most feasible diesel/biodiesel/alcohol that meeting the ASTM D975, Standard Specification for petro-diesel. Three steps of product design optimization (PDO) has been performed, (1) specify the fuel target properties based on Euro5; (2) optimize the formulation for ternary GD blends; (3) rank and select the optimal ternary GD blends. The ranking and selecting the optimal ternary GD blends were focused on the correlation of the higher cetane number (CN) over the cost of fuel. The PDO model indicated the most cost-effective and environmentally friendly diesel/biodiesel/alcohol ternary GD blends shall contain 74 % Malaysia petro-diesel, 16 % palm methyl ester (PME) and 1 % of butanol. Notably, the higher CN, the shorter the fuel ignition and the better the combustion efficiency. High CN fuels can significantly burn faster and more completely and hence reduce the harmful exhaust emissions such as SO_2.

1. Introduction

Biofuels such as biodiesel and bioethanol are promising green alternative to fossil fuels in the transportation sector. Recently, numerous researchers claimed that biodiesel has gaining acceptance in automotive industry as a promising biofuel (Razak et al., 2017) because the fuel properties of biodiesel are extremely relative to petro-diesel. Henceforward, biodiesel permits a few technological advantages over petro-diesel such as having a higher cetane number (CN), ultra-low sulphur, enhanced lubricity, no sulfur or aromatics and containing 10-11 % more oxygen by weight (Hasan and Rahman, 2017), resulting substantial reduction of regulated pollution such as unburned hydrocarbons (HC), carbon monoxide (CO) and particulate matter (PM) and unregulated pollution, polycyclic aromatic hydrocarbons (PAHs) (Ribeiro et al., 2007). PAHs is the most serious problem associated with petro-diesel engine deposits because this aromatic HC are mutagenic carcinogenic toward humans.

Regardless of its many advantages, it has a depleted oxidation stability and higher nitrogen oxide (NO_x) emissions over the petro-diesel. Furthermore, the lower oxidation stability of biodiesel may lead to polymerization when oxidation occurred during combustion, hence further increasing the fuel viscosity and reduce the engine power output. Consequently, some modifications are required for the diesel/biodiesel (DB) blends fuel in order to run effectively in diesel engine (Sorate and Bhale, 2015). To remedy the problems of DB blends, oxygenates such as alcohol, esters and ethers has been explored for reducing the emission of PM, CO and toxic components from the engine exhaust. The oxygenates also known as fuel borne which can further enhance the fuel properties and upgrade the engine performance caused by their thermo-chemical properties

Paper Received: 26 September 2018; Revised: 11 October 2018; Accepted: 19 October 2018

Please cite this article as: Razak N.H., Hashim H., Yunus N.A., Klemeš J.J., Phoon L.Y., 2019, Optimization of ternary green diesel blends for diesel/palm methyl ester/alcohol using product design optimization, Chemical Engineering Transactions, 72, 391-396
DOI:10.3303/CET1972066

(Zhang and Balasubramanian, 2018). Oxygenates such as alcohols and biodiesel were determined as an effective way to improve the combustion chemistry and more importantly fuel economic (Phoon et al., 2015).
Oxygenates are used directly in an engine as a pure fuel, or they can be blended with diesel. The oxygenates primarily generate the O_2 required to compose CO_2 instead of carbon-rich particles. Therefore, the oxygenates blend with fuel, generally known as oxygenated fuel can significantly reduce harmful exhaust emissions as complete combustion can be achieved (Jamrozik et al., 2018). Prominently, oxygenates can offer an alternative to the fuel augmentation of petro-diesel. Considering these technical merits, infinite research on oxygenates such as biodiesel and cellulosic alcohol (bioalcohol) blend to petro-diesel, in the form of ternary blends, is currently obtaining an extensive focus. To conclude the benefits of oxygenate, the oxygen fuel borne in the oxygenated fuel generates more energy by providing an extra chemical energy during combustion and hence emit cleaner exhaust emissions.
On the other hand, there are limited studies evaluating the engine performances and emissions of GD blends consisted of bioalcohol derived from OPB. Most case studies concentrate on the traditional experimental approach, trial and error of different blends composition to diesel/biodiesel. This traditional approach is not economic and viable approach as numerous attempts are required. Henceforth, PDO as a systematic computer aided approach will be employed for determining the optimal ternary GD blends with a particular set of desired Eero5 fuel properties. Therefore, this work will establish the PDO model for ternary GD blends containing diesel/biodiesel blends (the base fuel) and the fuel additive, bioalcohol derived from OPB. In Malaysia, the biodiesel has been generated from oil palm, namely as palm methyl ester (PME).
In addition, many oxygenates are available and ready for GD blends; therefore, laboratory trial and error experimental approach is not economically practiced. However, prediction method such as PDO is preferable in order to narrow down the costly and time-consuming experimental validation process. Furthermore, computer aided method can very quickly identify the most feasible ternary GD blends via fuel properties prediction technique that meets ASTM D975.
In conclusion, the aim of this work is to develop a systematic computer aided PDO model for ternary GD blends formulation and consecutively to investigate a comparative evaluation of six types of alcohol, from short chain alcohol to long chain alcohol; methanol, ethanol, propanol, butanol, pentanol, and hexanol. Finally, the decisive aim is to generate an optimal ternary GD blends that can become a viable alternative to petro-diesel, in order to sustain the biodiesel demand availability and reduce the harmful exhaust emissions.

2. Methods

The PDO model of the diesel/PME/alcohol blends is formulated as a mathematical problem, which results in a Mixed Integer Linear Programming (MILP) problem. The oxygen content (OC) of the ternary blend of diesel/PME/alcohol was optimized to enhance fuel combustion efficiency that can lead to better engine performance and hence cleaner exhaust emissions. The PDO formulation aimed to optimize a specific performance index, subject to Euro5 diesel fuel properties as well as engine performance attributes that comply the diesel property standard, ASTM D975.

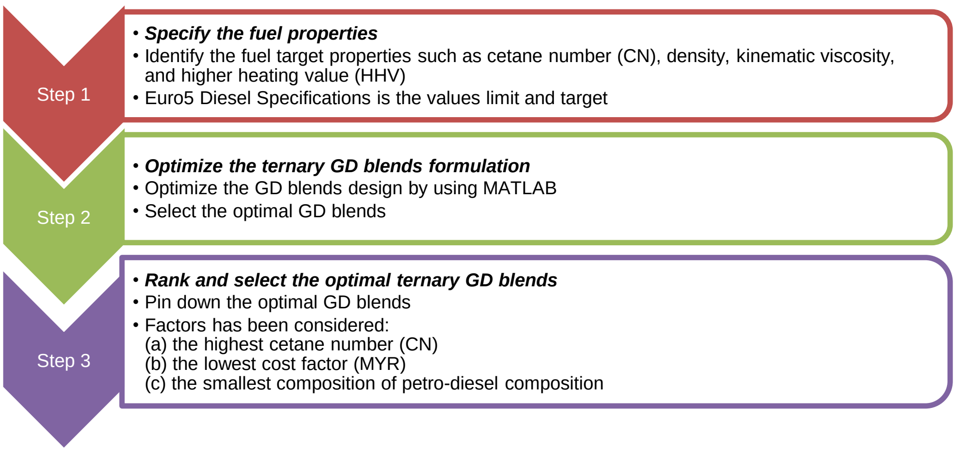

Figure 1: Product design optimization steps for ternary green diesel blend design

The optimal ternary GD blends with maximum oxygen content designed in this study should have at least 1 % by mass of alcohol and/or maximum at 10 % by mass. This is because, the higher energy content of 33 %

ethanol for example in diesel can lead to lower fuel economy. Furthermore, more alcohol content can absorb water which may lead to metal corrosion and phase separation. Mahmudul et al. (2017) also claimed that higher alcohol may lead to explosion because alcohol is highly flammable and explosive which need extra careful on the blending.

Meanwhile, in all ternary GD blends, the ratio of PME was maintained at maximum 20 % by mass due to their drawback fuel properties. Several studies have revealed that higher amount of PME may drive to higher viscosity which caused clogged car filters and nozzles and lower energy content, and hence degrade the engine power (Wan Ghazali et al., 2015). The fuel property constraints used are set according to Euro5 diesel standard. There are five fuel properties has been examined in this work; cetane number (CN), density, kinematic viscosity and higher heating value (HHV). Also, the sulfur content and the cost has been investigated. All the limitations are designated referring to the American Standard (ASTM) and Malaysia Standard (MS); Diesel fuel - Specification-Part 3: Euro 5 (MS 123-3:2016). The PDO model was mathematically formulated and summarized in Table 1. The objective function is to maximize the oxygen content in the ternary GD blends as presented in Eq(1).

$$F_{obj} = \max \sum x_i \tag{1}$$

Where, Fob_j is the objective function, x_i is the composition of the fuel and the function is subjected to the linear constraints below:

Table 1: Mathematical constraint models with target values

Constraints	Mathematical Equation	Lower Limit	Upper Limit	Referee Test Method
a) Product Property Linear Constraints				
				MS 123-3:2016 Diesel fuel - Specification - Part 3: Euro 5
Cetane Number, CN	$CN_{mix} = \sum_{i=1}^{n} x_i \cdot CN_i$	49	-	ASTM D6890
Density at 15 °C, ρ (kg/m^3)	$\rho_{mix} = \sum_{i=1}^{n} x_i \cdot \rho_i$	-	845	ASTM D4052
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	ASTM D445
Higher Heating Value, HHV (MJ/kg)	$HHV_{mix} = \sum_{i=1}^{n} x_i \cdot HHV_i$	-	-	Literature Database
b) Process Design Constraints				Limitation
Total mass balance of GD blend	$\sum_i x_i - 1 = 0$	-	1	
Total pure biodiesel (B100) allowed, mass fraction	$x_{B100,i} \geq 0.05$ $x_{B100,i} \leq 0.2$	0.05	0.2	Biodiesel limited to 20 % due to higher viscosity and lower energy content which can lead to degrade the engine power. Biodiesel (HHV = 39.8 MJ/kg) and Diesel (HHV = 43 MJ/kg) (Ali et al., 2015)
Lignocellulosic Biomass derived alcohol composition, mass fraction	$x_{cellulosicalcohol,i} \geq 0.01$ $x_{cellulosicalcohol,i} \leq 0.1$	0.01	0.1	Maximum 10 % of alcohol has been limited because: i. The higher energy content, such as 33 % ethanol in diesel can lead to lower fuel economy. Shorter combustion period of alcohol blended to DB blend induce to decrease cooling effect, which leads to higher NO_x emission (Zaharin et al., 2017) i. More alcohol can absorb water which may lead to metal corrosion and phase separation. ii. Alcohol is highly flammable and explosive which need extra careful on the blending (Mahmudul et al., 2016).

3. Results and discussion

3.1 Fuel properties

Table 2 tabulates the optimal composition of ternary GD blends, diesel/PME/alcohol that satisfy the desired petro-diesel target properties. Six types of alcohol have been considered for the PDO model formulated in MATLAB. The optimal composition of each fuel; diesel, PME and alcohol were successfully predicted. It can be seen from the data; the smallest petro-diesel composition is in GD2 (diesel/PME/ethanol) among the six candidates. Further analysis showed that the littles amount of petro-diesel can promote to cleaner emissions especially on reducing the harmful gases such as sulfur dioxide content (SO_2) and the greenhouses gases, carbon dioxide (CO_2) (Rajesh Kumar and Saravanan, 2016). Here, note that the oxygenates like alcohol and biodiesel can boost the fuel combustion emit ultra-low sulfur (Natarajan et al., 2011). This tabulated information is very significant to validate the feasibility of ternary GD blends; diesel/PME/alcohol.

Table 2: Fuel properties of ternary green diesel blends

Properties	GD1	GD2	GD3	GD4	GD5	GD6
Bio-Alcohol Used	Methanol	Ethanol	Propanol	Butanol	Pentanol	Hexanol
Malaysia Petro-Diesel, x_1	0.76	0.74	0.76	0.76	0.76	0.76
Malaysia Palm Methyl Ester, x_2	0.14	0.16	0.14	0.14	0.14	0.14
Bio-Alcohol, x_3	0.1	0.1	0.1	0.1	0.1	0.1
Density (kg/m^3)	840.6	845.6	840.6	840.63	840.74	840.88
Cetane Number, CN	49.91	50.22	49.9	49.91	49.94	49.98
Kinematic Viscosity at 40°C (mm^2/s)	1.2	1.2	1.2	1.2	1.2	1.2
Higher Heating Values (MJ/kg)	44.65	44.53	44.67	44.67	44.65	44.66
Sulfur Content (wt %)	0.76	0.74	0.76	0.76	0.76	0.76
Cost Factor (MYR)	17.06	14.58	18.95	21.27	22.63	24.04

3.2 Optimization of the most feasible ternary green diesel blends

Figure 2 demonstrates a 2-carbon alcohol (ethyl alcohol) known as ethanol, C2H5OH performed as the most feasible ternary GD blends among the six blends, as a result of higher CN with lower cost and petro-diesel composition. The CN experiences as the most critical fuel properties since the CI diesel engine is relying on compression ignition (Emiro and Mehmet, 2018). CN indicates the ignition delay time that promote the combustion efficiency. In short, the higher the CN, the shorter the ignition delay time, the better the combustion performance and hence promoting cleaner emissions and greater fuel economy.

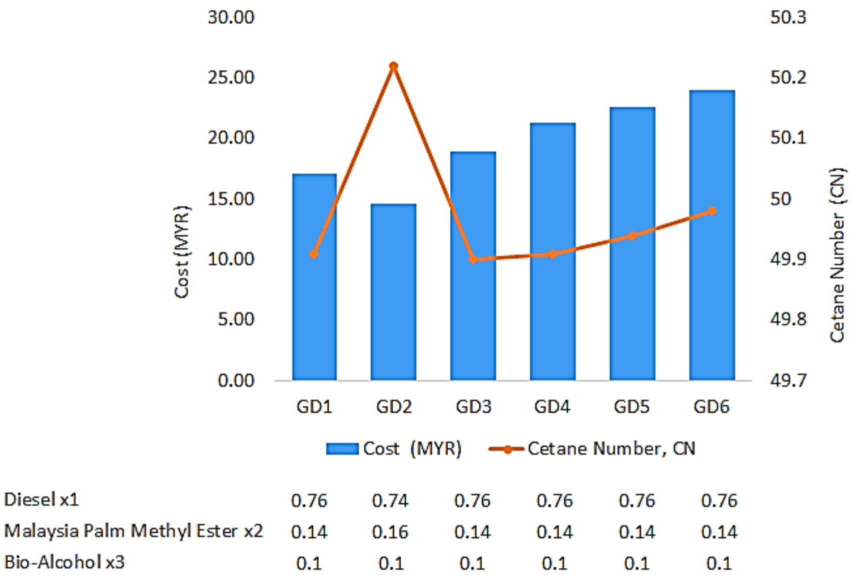

Figure 2: Comparison of six types of the ternary diesel/PME/alcohol green diesel blends considering cost and cetane number

Moreover, the highest CN value of GD2 (CN=50.22) concluded that the ethanol is the best oxygenate to these ternary GD blends; diesel/PME/alcohol. What is interesting in this data is that the highest CN value if GD2 was affected by the biggest composition of biodiesel in the ternary blends (16% by mass); diesel/PME/alcohol.
Strong evidence of the findings is consistent with Rahimi et al. (2009) who found the CN of 12 % bioethanol to petro-diesel and sunflower methyl ester have improved the CN to 54 compared to 40, the CN of bioethanol to petro-diesel only without any critical reduction in power. This result may be explained by the fact that the higher CN of biodiesel can ameliorate the CN of the diesel/biodiesel/ethanol blends up to the CN of petro-diesel (Barabás et al., 2010).
Furthermore, ethanol as an oxygenates (fuel additive) blended to DB profound to be a promising alternative fuel to petro-diesel without affecting the performance of the engine. The combination of these two oxygenates in CI diesel engines can successfully enhance the engine performance as this ternary GD blends, diesel/PME/ethanol has the similar fuel physiochemical properties like the commercial petro-diesel in the market. These findings further support the idea of in another major study, Yilmaz et al. (2014) highlighted that the ethanol cultivate cooling effect that resulting NOx decrease in exhaust gases. This is because, the lower heat value ethanol with results of cooling effect can reduce the combustion temperature and hence reducing the NO_x emission.

3.3 Ranking and selection of the optimal ternary green diesel blends

An enhancement of ternary GD blends ranking and selection can provide a better decision making. The ternary GD blends of diesel/PME/alcohol are ranked from the most feasible ternary GD blends to the least feasible ternary GD blends. This ranking statistical method is completed once performance of ternary GD blends is compared with that of other GD blends, from GD1 to GD6. Rank correlation is defined based on three selection criteria; (1) the highest cetane number (CN), (2) the lowest cost factor (MYR) and (3) the smallest composition of petro-diesel composition. This ranking statistical method provides a novel and unifying approach for hypotheses prediction. Table 3 depicts the final ranking to select the best ternary green diesel of diesel/PME/alcohol blends. The results determine that GD2, a ternary GD blends of diesel/PME/ethanol is the most feasible ternary GD blends followed by GD1, GD3, GD4, GD5, and the least feasible is GD6 that contain the highest primary alcohol type, hexanol.

Table 3: Final selection of the optimal ternary green diesel blends

Ternary GD Blends	Cetane Number (CN)	Cost (MYR)	Final Rank
diesel/PME/methanol, GD1	5	2	2
diesel/PME/ethanol, GD2	1	1	1
diesel/PME/propanol, GD3	6	6	6
diesel/PME/butanol, GD4	4	4	4
diesel/PME/pentanol, GD5	3	5	4
diesel/PME/hexanol, GD6	2	6	4

4. Conclusions

The ternary blend of diesel/PME/ethanol implicated as the most feasible ternary GD blends that has higher potential to enhance the engine performance and mitigating the harmful pollutants in the exhaust emissions. This is because the diesel/PME/ethanol offers the highest CN with the lowest cost plus accommodate the smallest petro-diesel composition. Also, the PDO concluded that the most cost-effective, better performance and environmentally friendly ternary GD blends are 74 % Malaysia petro-diesel, 16 % PME and 1 % of ethanol. Notably, the diesel/PME/ethanol proffer the higher CN which may lead to better CI engine performance, and it has also the smallest sulfur content than the commercial petro-diesel. The use of these ternary GD blends as an alternative biofuel can help cut down the harmful exhaust emission besides being a sustainable fuel for the future. In addition, the oxygenates as an alcohol can reduce significantly the dependence on fossil fuels.

Acknowledgement

The authors gratefully acknowledge the Universiti Teknikal Malaysia Melaka (UTeM) and Ministry of Higher Education (MOE) Malaysia for the SLAB scholarship award. A very special gratitude goes out to all down at High Impact Research Grant with grant number, QJ130000.2451.04G95 from Universiti Teknologi Malaysia (UTM) for helping and providing the funding for the work.

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