

**OPTIMIZATION OF PHYSIOCHEMICAL PROPERTIES FOR CLEANER
DIESEL WITH ALCOHOL FROM OIL PALM BIOMASS AS ADDITIVE**

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**A report submitted
In fulfillment of the requirements for the degree of
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DECLARATION

I declare that this project report entitled “Optimization of Physiochemical Properties for Cleaner Diesel with Alcohol from Oil Palm Biomass as Additive” is the result of my own work accept as cited in the references

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APPROVAL

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DEDICATION

To my beloved mother and father, family and friends

ABSTRACT

Diesel-biofuel / biochemical blend (cleaner diesel blend) is a promising solution to reduce the impact on the environment while enhancing diesel performance. A comprehensive computer-aided approach can easily address the design problems of green diesel blends and replace the iterative, complex and time-consuming approach to experimental trial and error. The main objective of this research is to determine the optimal composition of cleaner diesel (GD) blends by determining the most feasible diesel / biodiesel / alcohol that satisfies the ASTM D975, Standard diesel Specification. The engine performance related fuel properties (density, kinematic viscosity, cetane number and calorific value) as well as cost are being analyzed. This research involved utilisation of software such as General Algebraic Modelling System (GAMS) and Multi Criteria Decision Analysis software, Expert Choice. The blend is proposed to contain at least 70% of diesel while the remaining will consist a maximum value of 20% of biodiesel content and each of the blend are blended with four different types of alcohol which is methanol, ethanol, propanol and butanol. A systematic methodology involving of six key tasks were developed in order to achieve the objective. Simple mixing rules for predicting the basic properties of diesel / biodiesel blends are the Linear Kay and Arrhenius mixing rules. Twenty feasible blend candidates were simulated using GAMS which have different physiochemical properties and cost but only ten candidates are further analyzed as it meets the target properties. Then, the model was validated using statistical analysis by conducting manual calculations. All the physiochemical properties of all mixture candidates was analyzed in Expert Choice software, where all measurements with AHP were performed by a pairwise graphical comparison. A synthesis with respect to the goal are conducted on the entire model to obtain the most optimal cleaner diesel blend and it is found that the blend consists of diesel, biodiesel and methanol are the most promising candidates.

ABSTRAK

Diesel-biodiesel-alkohol (campuran diesel yang lebih bersih) adalah penyelesaian yang menjanjikan untuk mengurangkan impak terhadap alam sekitar sambil meningkatkan prestasi diesel. Pendekatan berbantuan komputer yang komprehensif dapat dengan mudah mengatasi masalah reka bentuk campuran diesel bersih dan menggantikan pendekatan berulang, kompleks dan memakan masa untuk percubaan berulang kali secara eksperimen. Objektif utama penyelidikan ini adalah untuk menentukan komposisi campuran diesel yang lebih bersih dan optimum dengan menentukan diesel / biodiesel / alkohol yang paling sesuai yang memenuhi ASTM D975, Standard Spesifikasi diesel.. Sifat bahan api yang berkaitan dengan prestasi enjin (ketumpatan, kelikatan kinematik, bilangan cetane dan nilai kalori) serta kos sedang dianalisis. Penyelidikan ini melibatkan penggunaan perisian seperti Sistem Pemodelan Algebra Umum (GAMS) dan perisian Analisis Keputusan Multi Kriteria, Expert Choice. Campuran dicadangkan mengandungi sekurang-kurangnya 70% diesel sementara selebihnya akan terdiri daripada nilai maksimum 20% kandungan biodiesel dan sebilangan campuran dicampur dengan empat jenis alkohol yang berbeza iaitu metanol, etanol, propanol dan butanol. Metodologi sistematik yang melibatkan enam tugas utama dikembangkan untuk mencapai objektif. Peraturan pencampuran sederhana untuk meramalkan sifat asas campuran diesel / biodiesel adalah peraturan pencampuran Linear Kay dan Arrhenius. Dua puluh calon campuran yang layak disimulasikan menggunakan GAMS yang mempunyai sifat dan kos fisiokimia yang berbeza tetapi hanya sepuluh calon yang dianalisis lebih lanjut kerana memenuhi sifat sasaran. Kemudian, model tersebut disahkan menggunakan analisis statistik dengan melakukan pengiraan manual. Semua sifat fisiokimia dari semua calon campuran dianalisis dalam perisian Pilihan Pakar, di mana semua pengukuran dengan AHP dilakukan dengan perbandingan grafik berpasangan. Satu sintesis berkenaan dengan tujuan dilakukan pada keseluruhan model untuk mendapatkan campuran diesel pembersih yang paling optimum dan didapati bahawa campuran terdiri daripada diesel, biodiesel dan metanol adalah calon yang paling menjanjikan.

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LIST OF ABBREVIATIONS

AHP	Analytic Hierarchy Process
ASTM	American Society Of Testing Material
CN	Cetane Number
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CR	Consistency Ratio
EU	European Union
CD	Cleaner Diesel
GAMS	General Algebraic Modelling System
GHG	Green House Gaseous
IEA	International Energy Agency
MCDA	Multi Criteria Decision Analysis
MILP	Mixed Integer Linear Programming
NO _x	Nitrogen Oxide
OC	Oxygen Content
PM	Particulate Matter
SO ₂	Sulphur Dioxide
UHC	Unburned Hydrocarbon

CHAPTER 1

INTRODUCTION

1.1 Research Background

Fossil fuel retains its reputation as the primary energy resource for the transportation sector (mainly gasoline and diesel); however, it is the largest source of significant greenhouse gas (GHG) emissions: carbon dioxide (CO₂) after coal (IEA, 2015). Regarding to Figure 1.1, CO₂ emissions from gasoline and diesel increased in the European Union (EU) nation steadily from 1990 to 2008 without signs of decrease. The transportation sector alone is projected to contribute about 24 per cent of world CO₂ emissions in the year 2035, as shown in Figure 1.2 and road transport was the largest contributor to CO₂ relative to other transports (International Energy Agency, 2015). In the foreseeable future, CO₂ emissions are unlikely to decrease as transportation fuel demand is expected to rise to nearly 40 percent in 2035, with the rising population (International Energy Agency, 2013). Global emissions also have no sign of a peak while they are rising slower than the global economy.

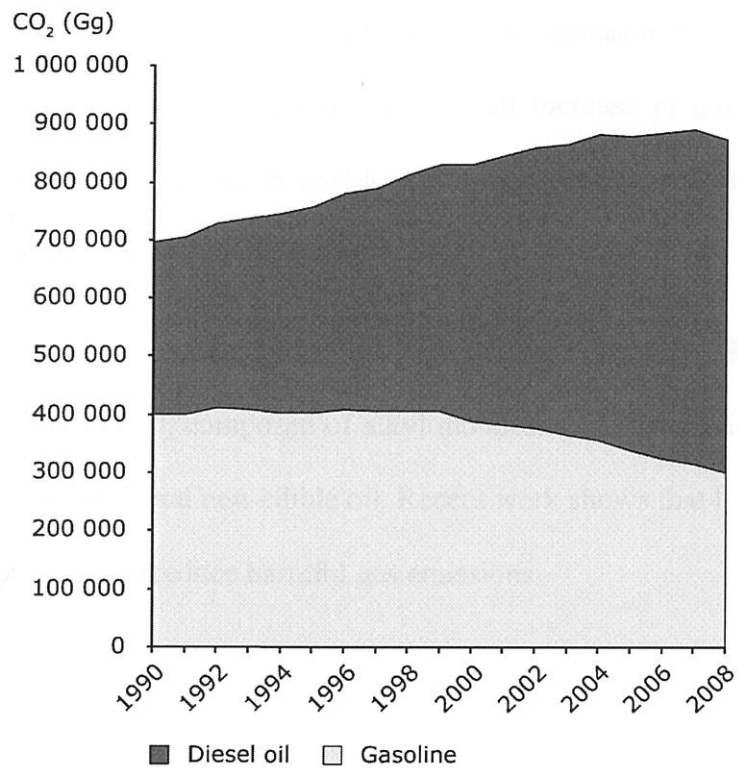


Figure 1.1: CO₂ emissions from diesel and gasoline in the EU, 1990 – 2008

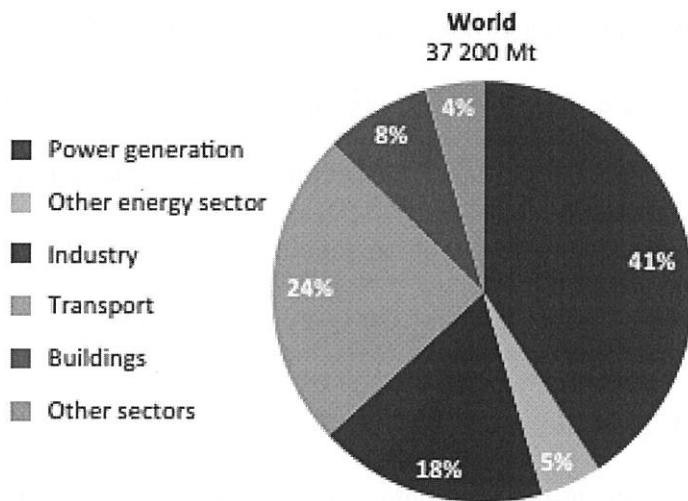


Figure 1.2: Expected World CO₂ Emissions in 2035

Despite the extraordinary growth in renewable fuels over the last decade, fossil fuel sources still dominate the global energy system. The annual increase in global energy consumption is greater than the increase in renewable energy, meaning the use of fossil fuel continues to increase. This growth must stop forthwith.

A greener alternative fuel is necessary for this problem to be mitigated. Biodiesel is considered an alternative diesel fuel, composed of alkyl monoesters of fatty acids derived from vegetable oils or animal fats, and non-edible oil. Recent work shows that biodiesel, in essence, is sustainable and helps to reduce harmful gas emissions.

1.2 Problem Statement

Malaysia's National Biofuel Policy was formulated in 2005 and implementation is expected to minimize fossil fuel reliance, mobilize local biofuel capital and harness existing biofuel development technologies (Chin, 2011). Malaysia's goal of reaching Euro 5 emission level diesel fuel by 2020 to slash carbon footprint by 40 per cent in 2020 compared to 2005 (Begum and Pereira, 2011). Unfortunately, biodiesel use also results in higher NO_x emissions and this rise will become important as more biodiesel is combined with diesel (Man *et al.*, 2016). Moreover, high reliance on edible palm-oil based diesel will induce the conflict between food and fuel and increase the price of food (palm oil).

Cleaner Diesel (CD) blend, which is defined as blending diesel with oxygenated biofuel / bio-chemical such as bio-ester, bio-ether and bio-alcohol, is efficient in reducing toxic emissions while maintaining or even enhancing engine efficiency at an reasonable cost of implementation. The key issue relating to the Cleaner Diesel mix, however, is to obtain the correct blending agent for desired target products. A conventional experimental approach to trial and error is time- and cost-consuming, as multiple attempts are required to achieve

the desired outcome. Moreover, it might exacerbate the situation because there could be enormous potential blend candidates. Therefore, a systematic model-based optimization utilizing computer-aided tools such as the General Algebraic Modeling Method (GAMS) and Expert Choice is necessary for this work to be carried out effectively.

1.3 Research Objective

The aim of this research is to propose an integrated systematic **computer-aided** formulation in obtaining a cleaner diesel. To achieve this goal, the sub-objectives are listed as follows:

- a) To study the effect of oxygenates on the biodiesel
- b) To analyze the performance and characteristics of fuel using **computer-aided** Tool such as General Algebraic Modelling System (GAMS)
- c) To design an optimization model for the optimal diesel formulation using Multi Criteria Design Analysis (MCDA) tools such as Analytic Hierarchy Process (AHP) to obtain the most optimal cleaner diesel.

1.4 Research Scope

In order to attain the aforementioned objectives, the research scopes have to include the followings:

- a) Optimize the cleaner diesel blends containing biodiesel with oxygenates such as alcohol using GAMS software.
- b) Retrieve and analyze the target fuel physiochemical properties and determine the optimal cleaner diesel formulation.

1.5 Significant of Research

To determine the model-based formulation for cleaner diesel blending and obtain the optimal cleaner diesel product that consider important attributes which is the best performance, environmental friendly and the least cost.

1.6 Thesis Outline

This thesis is divided into 5 chapters. Chapter 1 introduces the research background, problem statement, research objectives, scopes and significant of research. A comprehensive literature review is provided in Chapter 2. Chapter 3 describes the research methodology that comprises of the model based optimization to obtain optimal cleaner diesel. In Chapter 4, it presents a complete account of the results obtained in the study and the best fuel candidates. Chapter 5 chapter contains a brief summary of the entire work, including methods, results and major conclusions /recommendations arising from this work.

CHAPTER 2

LITERATURE REVIEW

2.1 Diesel

Diesel fuel continues to drive the global economy. From consumer goods transported across the globe to power production, to improved farm output, diesel fuel plays a crucial role in improving the global economy and living standards. Diesel is a fuel obtained from crude oil refining in a petroleum refinery as shown in Figure 2.1 that is used in diesel or compression ignition (CI) engines. For diesel engines the air is heated to a sufficiently high temperature until the fuel is pumped into the cylinder to ignite or detonate when a piston is actuated by combustion and expansion (Hsu, 2000). It converts the chemical energy contained in the fuel into mechanical energy that can be used to power cars, marine vessels, locomotive trains, and trucks. A diesel engine is much more cost-effective compared with spark ignition engines due to its operating advantages, higher reliability, high power output and fuel economy under all loads.

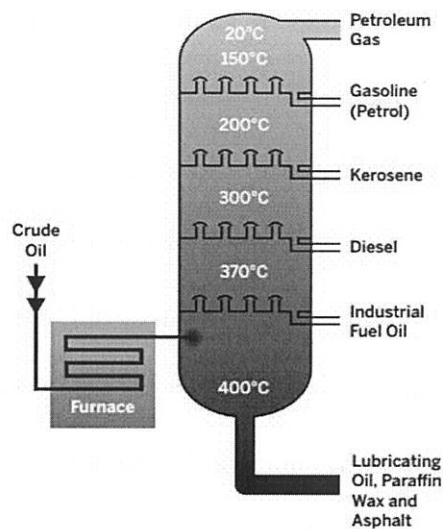


Figure 2.1: Crude Oil Refining Process Diagram

2.1.1 Drawback of Diesel

Diesel itself does have disadvantages which should be considered when evaluating its use. Since the diesel cycle has a high working pressure which is 1.5 times higher than the gasoline engines, it needs a heavier and costlier part of the engine to withstand the operation (Lloyd and Cackette, 2001). The lean combustion ratio features of the diesel result in less power being produced per unit displacement compared to that provided by gasoline engines. In addition, diesel engines emit equal quantities of nitrogen compounds and particulate matter when fuel is burned.

2.2 Biodiesel as diesel alternative

Biodiesel is a substitute for safe, clean burning fuel that can be used without modification in existing diesel engines. Various studies have shown that emission such as Carbon Monoxide (CO), Hydrocarbon (HC), Particulate Matters (PM) and others can be substantially reduced with biodiesel. According to Srinivasnaik, Sudhakar, & Naik (2015) The use of biodiesel in diesel engines does not require any alteration of the systems, because vegetable oils have cetane numbers close to diesel.

Compared with other biofuels such as alcohol, biodiesel is the main biomass renewable fuel generated for the diesel alternative. Biodiesel is primarily produced by the transesterification with alcohol of vegetable oil, mainly methanol (Aransiola *et al.*, 2014). World biodiesel production is still primarily dependent on edible oil and this biodiesel is recognized as the first generation of biofuels because it comes from edible sources. Malaysia is one of **Asian countries ' leaders** for the manufacture of biodiesel using palm oil. Today, the second generation of biofuel generated from non-edible resources and waste biomass (lignocellulosic material) has become more essential. The common processing routines for

transforming lignocellulosic material into useful biofuel are thermochemical (pyrolysis, gasification) and biochemical (fermentation) processes (Schlichter, and Montes, 2011), for example alcohols (e.g. bioethanol, biomethanol, biobutanol and linear bioalcohol mixed).

2.2.1 Current Status of Biodiesel Industry

Oil palm tree was first introduced in Malaysia in 1875 and the early interest in oil palm was as an ornamental plant and from 1917 till now, the palm sector began its development into what is witnessed today as a Multibillion Ringgit industry (Obad M. Ali *et al.*, 2015). Currently, biodiesel industry in Malaysia shows a bright future as 10% of biodiesel have been mandatory blended in the diesel fuels and the biodiesel percentage is expected to increase over years as Malaysia are looking for sustainable and greener fuel alternative.

2.2.2 Drawback of Biodiesel

Biodiesel could efficiently reduce harmful emissions, but being able to fully replace diesel with biofuel is undesired. Biodiesel have higher viscosity compared to diesel fuel where it will cause engine filters clogging thus it requires engine modification in order to run diesel engine with biodiesel (Sorate and Bhale, 2015).

Moreover, increment in NO_x emissions has been a major drawback in biodiesel. Besides, the high viscosity of the vegetable oil leads to poor fuel atomization, which in turn may lead to poor combustion, ring sticking, injector cocking, injector deposits, injector pump failure and lubricating oil dilution by crank-case polymerization (Rakopoulos, 2006).

2.3 Cleaner Diesel

Due to increasing demand for fuel, alternative energy production from bio sources are being developed. Cleaner Diesel is one of the alternative energy products, where it is a second generation of biofuel, which has a similar molecular structure as diesel but provide better diesel properties (Kittisupakorn *et al.*, 2016).

2.4 Biodiesel-Diesel Blends

Blends of biodiesel and conventional hydrocarbon-based diesel are produced by mixing biodiesel and petroleum diesel in suitable proportions under appropriate conditions. Biodiesel – diesel blended fuel usually utilized with a limit of 20% blending ratio mainly due to higher viscosity and lower energy content which is lesser than diesel which might affect the engine power (Obad M. Ali *et al.*, 2015).

2.5 Biodiesel-Alcohol-Diesel Blends

The blend of alcohol with diesel and biodiesel which is also known as Cleaner Diesel is superior in reducing harmful emission while maintaining or even improving engine performance with acceptable implementation cost. The alcohol plays a vital role as an oxygenate to enhance a complete combustion to be achieved. The presence of alcohol leads to significant increase in cetane number, reduce viscosity and density of biodiesel concentration (Yasin *et al.*, 2013) .

2.6 Oxygenates

Oxygenates are hydrocarbons that contain one or more oxygen atoms and alcohol is the most adopted oxygenates (EIA, 2000). Oxygenates are added to motor vehicle fuels to make them burn more cleanly hence reducing emission, particularly Carbon Monoxide (CO). The oxygenates can alter and further enhance the fuel properties and engine performance due to its thermos-chemical properties (Zhang and Balasubramanian, 2018) Some of the example of alcohol as an oxygenates are methanol, ethanol, propanol and butanol.

2.7 Cetane Number

Cetane number refers to the measure of diesel fuel ignition quality in an engine as the ability to readily active combust under the temperature and pressure conditions inside the engine combustion chamber. A higher cetane number indicates the better ability for cold start, engine noise reduction as well as shorter ignition delay and better ignition quality (ASTM D975, Information, 2017).

2.8 Flash Point

Flash point of a liquid petroleum product is defined as the lowest temperature at which the fuel must be heated to produce sufficient vapors that ignite spontaneously in the present of a flame (Crowl and Louvar, 2002).

2.9 Industrial Standards for Diesel, Biodiesel and Biodiesel-Diesel Blends

As biodiesel is gaining considerable global attention and market, standards are vital for its commercialization and market introduction as shown in Table 2.1. The authorities need to assess the safety risks and the impact on the environment while providing users with

quality assurance. Manufacturers of cars would also need a standard to allow the use of biodiesel for automobiles. It is therefore essential for manufacturers, retailers and consumers to have an accepted biodiesel standard.

Table 2.1: European, American and Malaysian standard for Diesel, Biodiesel and Biodiesel-Diesel Blends

Fuel	European Standard	American Standard	Malaysian Standard
Diesel	EN 590	ASTM D975	MS 123-3:2016 (EURO 5)
Biodiesel (B100)	EN 14214	ASTM D6751	MS 2008:2014 (Palm Methyl Ester)
Biodiesel-diesel blends	EN 590 (up to B7) EN 16709 (B20 and B30)	ASTM D975 (up to B5) ASTM D7467 (B6 to B20)	Not available

2.10 Exhaust Emissions Gaseous

Diesel engines are recognized as one of the greatest contributors to pollution caused by harmful exhaust emissions. Although they have many advantages, they have a significant impact on environmental pollution problems around the world.

2.10.1 Nitrogen Oxide (NO_x)

Nitrogen Oxides (NO_x) are one of the pollutants causing photochemical smog and brings negative effects on human health (Tan *et al.*, 2017). When a fuel combustion occurs, a nitrogen is released and combines with oxygen atoms to create nitric oxide (NO). Later, it further combines with oxygen to create Nitrogen Dioxide (NO₂). Nitric oxide is not considered to be hazardous to health at typical ambient concentrations but Nitrogen Dioxide can be. Nitrogen dioxide and nitric oxide are referred together as oxides of Nitrogen (NO_x).