

**STUDY OF FORMULATION AND
PERFORMANCE CHARACTERISTICS OF
HYBRID BIOFUEL FOR COMPRESSION
IGNITION ENGINE APPLICATION**

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**STUDY OF FORMULATION AND
PERFORMANCE CHARACTERISTICS OF
HYBRID BIOFUEL FOR COMPRESSION
IGNITION ENGINE APPLICATION**

by

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LIST OF SYMBOLS

ΔL	Burned fuse wire
π	Pi radian
ρ	Density of substance
μ	Dynamic viscosity
ν	Kinematic viscosity
C	Viscometer constant
C_p	Specific heat of water
g	Gravity acceleration
m	Mass of sample
R^2	Coefficient of determination
S	Surface tension
T	Torque
T_{10}	10% distillation recovery temperature
T_{50}	50% distillation recovery temperature
T_{90}	90% distillation recovery temperature
v/v	Volume percentage
w/w	Weight percentage

LIST OF ABBREVIATIONS

32RPO68CMO	32% RPO + 68% MCO
35RPO50MCO15HX	35% RPO + 50% MCO + 15% HX
AFR	Air-fuel ratio
AN	Acid number
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
BHB	Binary hybrid biofuel
BP	Brake power
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
CAD	Crank angle degree
CCI	Calculated cetane index
CI	Compression ignition
CO	Carbon monoxide
CO ₂	Carbon dioxide
CV	Calorific value
DOE	Design of Experiment
EGT	Exhaust gas temperature
EISA	Energy Independence and Security Act
EN	European Standards
EU	European Union
FAME	Fatty acid methyl ester
GC-MS	Gas chromatography mass spectrometry
HC	Hydrocarbon
HX	1-Hexanol
HBB	Hybrid biofuel blend
HRR	Heat release rate
ID	Ignition delay
IEA	International Energy Agency
IOP	Injection opening pressure
MCO	Melaleuca cajuputi oil

Mtoe	Million tonnes of oil equivalent
NO _x	Nitrogen oxides
RFS	Renewable Fuel Standard
RPM	Revolution per minute
RPO	Refined palm oil
SDS	Sustainable Development Scenario
SOC	Start of combustion
SOI	Start of injection
SVO	Straight vegetable oil
THB	Ternary hybrid biofuel
TDC	Top death centre
WOT	Wide open throttle

**KAJIAN KE ATAS FORMULASI DAN CIRI-CIRI PRESTASI BAHAN
API-BIO HIBRID UNTUK APLIKASI PADA ENJIN
NYALAAAN MAMPATAN**

ABSTRAK

Bahan api-bio dari produk seperti minyak sayur tulen (SVO), bio-alkohol dan minyak dari daun tumbuhan yang kaya dengan terpenes telah dilihat sebagai bahan bakar alternatif yang berpotensi tinggi untuk menggantikan bahan api fosil. Walau bagaimanapun, setiap bahan api-bio ini mempunyai kelebihan dan kekurangan tersendiri yang menghalang mereka dari terus digunakan sebagai bahan api enjin. Oleh itu, kajian ini bertujuan untuk memformulasi, mengoptimum, membangunkan dan menganalisa prestasi enjin, pencemaran asap serta ciri-ciri pembakaran untuk campuran dua bahan dan campuran tiga bahan api-bio hibrid sebagai sumber bahan api alternatif untuk enjin pembakaran mampatan. Kajian ini memperkenalkan bahan api-bio yang berkelikatan rendah yang baharu, iaitu minyak dari daun tumbuhan yang kaya dengan terpenes dikenali sebagai minyak *Melaleuca cajuputi* (MCO) yang akan diadun dengan minyak kelapa sawit bertapis (RPO) dan hexanol (HX) untuk menghasilkan bahan api-bio hibrid bagi menggantikan sepenuhnya bahan api diesel. Sifat-sifat fizikal-kimia MCO, RPO dan HX telah dikaji secara mendalam untuk menganalisis potensi bahan api-bio ini sebagai bahan api enjin diesel. Pendekatan reka bentuk eksperimentasi (DOE) menggunakan kedah reka bentuk campuran telah digunakan untuk membina sebuah set eksperimen dan seterusnya membangunkan model ramalan baru untuk mendapatkan campuran bahan api-bio hybrid yang optimum. Ciri-ciri semburan untuk bahan api-bio yang optimum dianalisis dan dibandingkan dengan bahan api diesel. Seterusnya, sistem sel ujian telah dibangunkan

bagi menganalisa prestasi enjin, ciri-ciri pembakaran dan kadar pencemaran asap bahan api-bio hibrid. Campuran 32RPO68MCO dan 35RPO50MCO15HX didapati memiliki ciri-ciri kelikatan, kepadatan dan nilai kalori (CV) mengikut piawaian ASTM D6751 / EN14214. Ciri-ciri semburan campuran 32RPO68MCO menunjukkan penembusan semburan setanding dengan bahan api diesel dengan perbezaan maksimum kurang daripada 5% secara keseluruhan. Kuasa maksimum enjin yang menggunakan campuran 32RPO68MCO didapati sedikit rendah sebanyak 8.9% berbanding bahan api diesel. Penggunaan bahan api spesifik (BSFC) dari campuran 32RPO68MCO menunjukkan persamaan yang rapat dengan bahan api diesel dengan perbezaan terendah sebanyak 3.6% berlaku pada bebanan enjin paling maksimum. Pada keseluruhan ujian, campuran 35RPO50MCO15HX menghasilkan NO_x dan asap yang lebih rendah berbanding bahan api diesel dengan pengurangan maksimum sebanyak 56.0% dan 41.6%. Secara keseluruhannya, kajian ini menunjukkan bahawa campuran bahan api-bio hibrid telah berjaya menghidupkan enjin diesel dengan prestasi enjin dan pelepasan ekzos yang setara dengan bahan api diesel. Ini menunjukkan bahawa bahan api-bio hibrid ini amat berpotensi sebagai sumber bahan api-bio yang baharu.

**STUDY OF FORMULATION AND PERFORMANCE
CHARACTERISTICS OF HYBRID BIOFUEL FOR COMPRESSION
IGNITION ENGINE APPLICATION**

ABSTRACT

Biofuel from bio-based products such as straight vegetable oil (SVO), bioalcohol and terpenes-rich light biofuel were marked as promising fuel alternative to the fossil fuel. However, each of this biofuel has their own limitation that hinder them from directly been used as an engine fuel. Therefore, this study aims to formulate, optimise, develop and investigate the engine performance, emissions and combustion characteristics of binary and ternary blend of hybrid biofuel as an alternative fuel source for stationary compression ignition (CI) engine. This study introduces a new terpenes-rich light biofuel that is Melaleuca cajuputi oil (MCO) to be blended with refined palm oil (RPO) and hexanol (HX) to produce hybrid biofuel that fully substitute diesel fuel for CI engine applications. The physicochemical properties of neat MCO, RPO and HX were extensively studied to analyses the potential of these biofuel as CI engine fuel. The design of experiments (DOE) approach in the form of mixture design method was adopted to construct the set of experimental runs and to subsequently develop a new prediction model to obtain the optimal hybrid biofuel blend. Spray characteristics of optimise blends were analysed and compared to the diesel fuel. This was followed by developing a test cell system to analyse the performance, combustion, and emission characteristics of optimised hybrid biofuel. Optimised blend of 32RPO68MCO and 35RPO50MCO15HX was found to have the key properties of viscosity, density and calorific value (CV) in accordance to the ASTM D6751/EN14214 standards. Spray characteristics of 35RPO50MCO15HX

blend demonstrated comparable spray penetration with maximum difference is less than 5% as compared to diesel fuel. Maximum brake power of the engine running with 32RPO68MCO blend were found slightly lower by 8.9% as compared to the baseline diesel fuel. The brake specific fuel consumption (BSFC) of the 32RPO68MCO blend has shown a close resemblance to diesel fuel with the lowest difference of 3.6% occurring at maximum engine load. Notably, at the entire range of test, 35RPO50MCO15HX blend produced lower NO_x and smoke opacity as compared to diesel fuel with the maximum reduction of 56.0% and 41.6%, respectively. Overall, this study has shown that hybrid biofuel blend has successfully operated in a diesel engine with a comparable engine performance and exhaust emissions to those of diesel fuel. This shows that the blend is marked as a potential new source of biofuel.

CHAPTER 1

INTRODUCTION

1.1 Present and Future of Biofuel

The decline of global oil reserves and concerns over environmental pollution caused by the burning of fossil fuels, have stimulated the research on alternative renewable biofuels. At present, the world is heavily dependent on fossil fuel for industrialisation, generation of electricity, transportation and agriculture (Darda et al., 2019). In the event of oil price upsurges, countries without oil resources will face energy and economic crises. Thus, it is important to seek for new sources of renewable and environmentally-friendly biofuels that can be obtained and produced locally within the country.

The exponential growth of global energy demand and concern on the effect of fossil fuel on the greenhouse gas emissions are the key factors leading to the search for renewable and sustainable energy. Figure 1.1 shows the global biofuel production and projection by International Energy Agency's (IEA) Sustainable Development Scenario (SDS) policy. Based on the IEA report (International Energy Agency (IEA), 2019), biofuel production in 2017 was 81 Mtoe and the production was forecasted to reach 284 Mtoe by 2030. Significant increase in biofuel demand is expected by 2025 based on the actions of some European countries such as Paris, Madrid and Athens that will ban the sale of diesel-powered vehicles from 2025 onwards (Hooftman et al., 2018). To achieve the 2030 forecast, the production of biofuels needs to triple the current production.

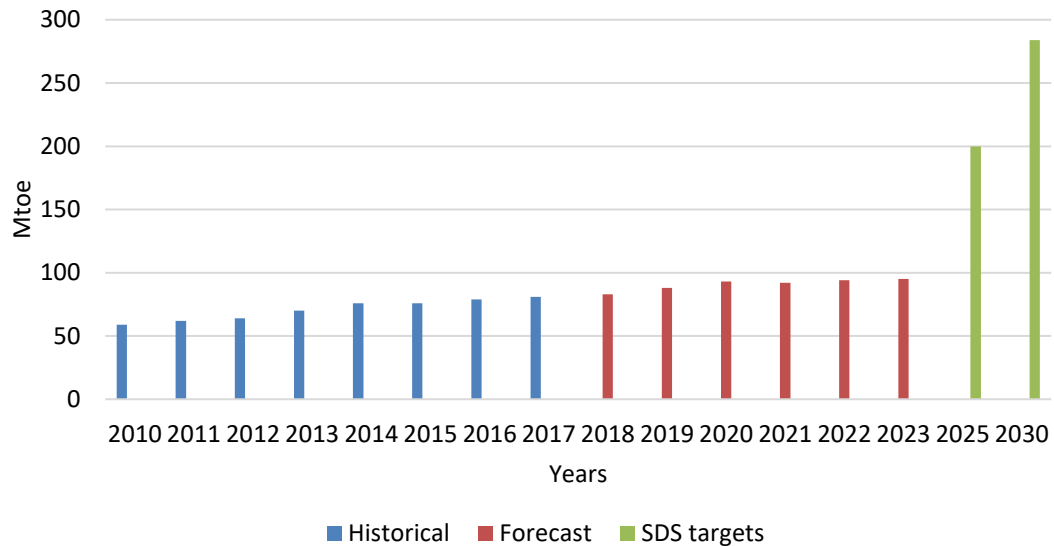


Figure 1.1 Global biofuel production and projection (International Energy Agency (IEA), 2019)

The European Union has taking a proactive step where in their 2020 framework (Directive 2009/28/ec) has targeting 20% of energy consumption in the Europe is from the renewable energy sources by 2020. A renewables deployment in transport was targeted at least by 10% of the energy consumption (Giuliano Albo et al., 2017). In the United States, the Energy Independence and Security Act (EISA) of 2007 has mandates the Renewable Fuel Standard (RFS) to use 36 billion gallons of renewable fuels per year by 2022 (U. S. Department of Energy, 2007). At the meantime, Asian countries like India, China, South Korea, Thailand, Taiwan, Malaysia and Philippines also have set national mandates to blend biofuels. China has targeted to produce 12 million tons of biofuels by 2020 forecasting to replace 15% of transportation energy needs (Scarlat et al., 2011). In this regard, Malaysia also has implementing biofuel policy by introducing B5 (5 % palm biodiesel and 95 % diesel) biodiesel in 2011, B7 in 2014 and B10 effective by 2019 (Ministry of Primary Industries, 2019). Figure 1.2 shows biofuel consumption in 2017 for major countries in the world. It is apparent that United States, Brazil and the EU are the countries with major biofuel consumption.

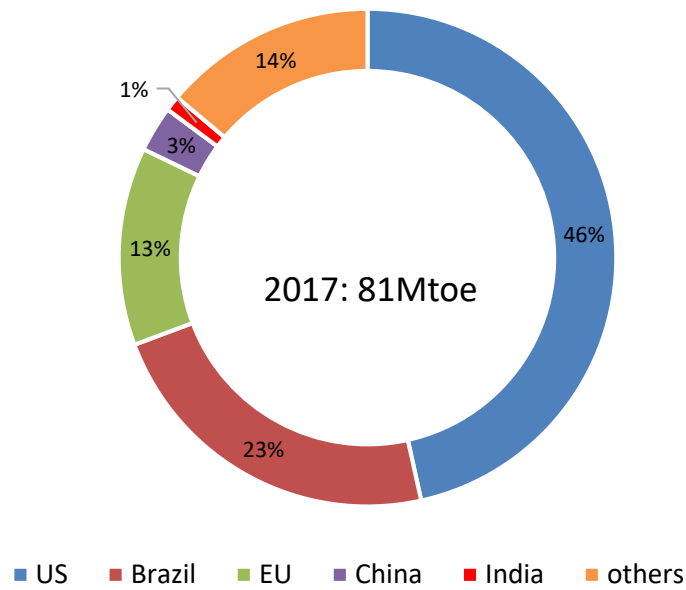


Figure 1.2 Biofuel consumption in 2017 around the globe (International Energy Agency (IEA), 2019)

1.2 Alternative Sources of Promising Biofuel

Recent studies have identified few sources of biofuels as the most promising alternative biofuel for diesel engine application. Researches have marked that plant oils such as straight vegetable oils (SVOs) (S. Y. No, 2017), bioalcohols (Rajesh Kumar et al., 2016), and terpenes-rich light biofuels (Mewalal et al., 2017) are the most promising alternative biofuels as a replacement for current diesel fuel.

Today, the production of vegetable oil has expanded all over the world. Different countries produce different types of vegetable oil depending on their climate. Rapeseed and sunflower oils are largely produced in the European Union, soybean oil in the United States, palm oil in South East Asia and coconut oil in the Philippines (Barnwal et al., 2005). Vegetable oil is mainly extracted from the seeds and also from the kernel of food crops. Vegetable oil can be divided into two categories, which are edible and non-edible oils, as listed in Table 1.1. Rapeseed, sunflower, corn, soybean and palm oil are examples of edible oil, while jatropha, mahua, karanja, linseed and

cottonseed oils are examples of non-edible oil. The presence of toxic components in non-edible oils makes it unsuitable for human food (Ahmad et al., 2011). Among edible oils, palm oil has the highest oil yield around 5000 kg per hectare, while jatropha and karanja (*pongamia pinnata*) are among the highest oil yield for non-edible oil.

Table 1.1 Example of edible and non-edible vegetable oil

Edible oil	Non-edible oil	References
Sunflower oil, Corn oil, Soybean oil, Rapeseed oil, Palm oil, Rice Bran oil, Coconut oil, Olive oil, Peanut oil, Sesame seed oil	Jatropha oil, Pongamia oil, Neem oil, Jojoba oil, Cottonseed oil, Linseed oil, Mahua oil, Sea mango, Poon oil, Polanga oil	(S.-Y. No, 2011; Russo et al., 2012; Silitonga et al., 2013)

Currently, Malaysia is the world's second largest producer of palm oil after Indonesia. In 2017 Malaysia has produced more than 20 million tonnes oil (Iskandar et al., 2018) and the palm oil production is projected to rise to 26.6 million tonnes by 2035 (Gan et al, 2014). With such a huge production capacity, Malaysia has the potential to play a major role in the world biofuel market. As shown in Figure 1.3, Malaysia has produced 34% of total worldwide palm oil production. In view of these advantages, the Malaysian government through the Malaysian Palm Oil Board (MPOB) and Palm Oil Research Institute of Malaysian (PORIM) have established national biofuel strategies to develop comprehensive biofuel programs in accordance with the National Biofuel Policy (NBP) and the Biofuel Industry Act (BIA). This policy is intended to make Malaysia a leading player in the global biodiesel industry (Johari et al., 2015). To date, palm oil has become the main biodiesel feedstock in Southeast Asia due to its suitability to regional climate conditions and high oil yield rate. Palm oil yields the highest oil compared to soybean, sunflower, rapeseed or even other non-edible vegetable oils. Palm oil can produce an average of 4 to 5 tons of oil

every year for every hectare of land (Ong et al., 2012a). Obviously, palm oil is the most productive crop compared to other non-edible or edible oils. The high yield of palm oil is making it a promising feedstock for an alternative biofuel. Besides, with lower production costs than other oil crops, palm oil provides higher returns on land, labour and manufacturing capital (Mukherjee et al., 2014).

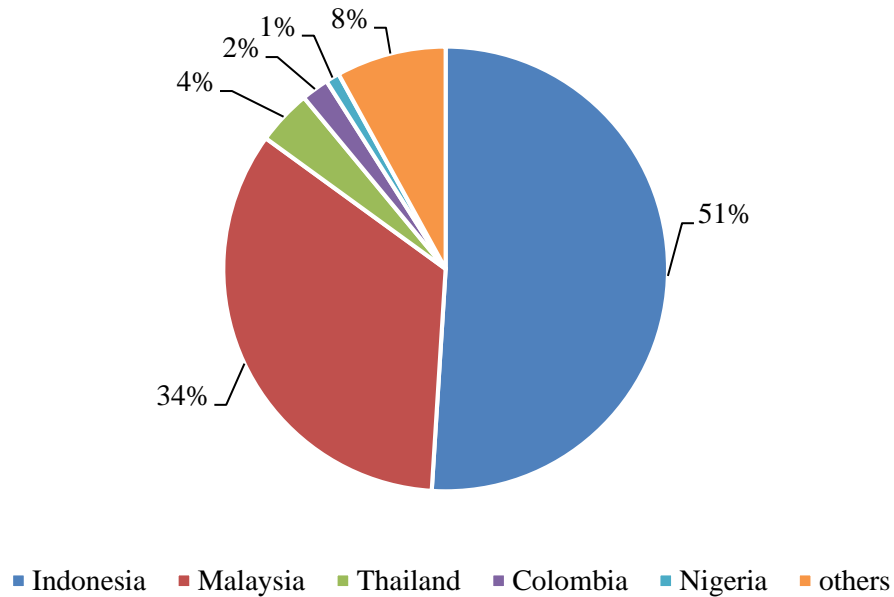


Figure 1.3 Major palm oil producers worldwide (Mosarof et al., 2015).

However, due to the concern over competition between food supply and fuel, extensive studies on non-edible vegetable oil have been carried out for the past decade. Jatropha, mahua, linseed, rubber, karanja, and cottonseed oil are among the non-edible oils that receive attention from many researchers (Adam et al., 2018; Chauhan et al., 2016; Dash et al., 2018; Deepanraj et al., 2017). Various blends of non-edible oil with diesel or biodiesel were found to have comparable engine performance and combustion as compared to diesel fuel. In addition, it was reported that biodiesel fuels have demonstrated a better tribological performance than diesel fuels (Rahman et al., 2017). Despite numerous researches conducted on non-edible oils, those non-edible oils are still unable to compete with palm oil in terms of oil yielded.

Vegetable oils do not contain sulphur, non-toxic, and have no aromatic hydrocarbon. The absence of Sulphur reduces the severity of corrosion in the engine crankcase caused by the accumulation of sulphuric acid and lessens the exhaust of sulphur dioxide into the air that can cause acid rain (Dwivedi et al., 2014). However, the direct use of SVO as fuel is largely constrained by its high viscosity. This high viscosity results in poor atomisation, low volatility, incomplete combustion, and other related long-term problems such as carbon deposit build-up and clogged fuel injector in diesel engines (Yilmaz et al, 2014). In addition, high viscosity fuel can lead to rapid wear in the fuel pump components and injector.

At present, transesterification is a broadly used method to convert SVO into vegetable oil methyl ester (biodiesel). However, this method involves chemical processes and high energy input which increases the production cost. Additionally, crude glycerol is produced as a by-product requires further expensive purification processes (Zhang et al., 2015). Thus, many researches have proposed and studied alternatives to transesterification for reducing the viscosity of SVO such as by preheating, blending, and micro-emulsion methods (Atmanli et al., 2015; Bari et al., 2002; Nwafor, 2004; Qi et al., 2013).

Bioalcohol is another promising biofuel as an alternative to fossil fuel. Many studies have been done in order to realise the replacement of diesel fuel is by using the SVO-alcohol blending. Usually, ethanol and methanol are the most common lower alcohols used in this study. However, due to limited solubility of SVO in lower alcohol, additional surfactants are required as an additive to increase the miscibility and stability of the blends (Bhimani et al., 2013). Recent studies have proposed the use of higher alcohols such as butanol and pentanol, which have closer properties to diesel and have better solubility and stability as compared to the lower alcohols. Furthermore,

SVO can be blended with higher alcohols without the need for additional surfactants. These higher alcohols have low viscosities, which reduces the effect of high viscosity of the SVO in the blend. Coupled with its high oxygen content, these characteristics can reduce emissions of particulates (Laza et al., 2011).

Recently, light biofuels, such as lemongrass, pine, camphor and eucalyptus oils, are recent additions to the family of promising renewable fuel. Several studies have used these light biofuels in blends of diesel or biodiesel, and have reported improved performance, combustion and emission characteristics (Cho et al., 2018; Mewalal et al., 2017; Sathiyamoorthi et al., 2016; Vallinayagam et al., 2014a). Lemongrass and eucalyptus oil are extracted from the leaves and twigs mostly by using the steam distillation process while pine oil is synthesized from the resins of pine trees. As compared to SVO, these light biofuels have relatively lower viscosity, which are comparable to alcohols and diesel fuels. However, unlike alcohols, they have better calorific value (CV) as compared to diesel fuel (Vallinayagam, Vedharaj, Yang, & Lee, 2014).

Notably, regardless of any biofuel, the key properties, such as viscosity, density and CV, have a significant effect on the fuel atomisation, emissions, and engine performance. These factors have a major influence on the fuel injection spray characteristics such as quality of the fuel atomisation, spray tip penetration, spray cone angle, spray-wall interaction, and spray development (Melo-Espinosa et al., 2015). These spray characteristics can affect the performance and emissions of diesel engines. Besides, high viscosity will lead to poor cold flow characteristics especially during cold weather (Hassan et al., 2013). Therefore, these key properties should form the initial selection criteria in determining the suitability of any potential biofuel for use in diesel engine applications.

1.3 Problem Statement

Biofuel production from plant oils were seen as promising alternative to current fossil diesel. Among those plant oils, SVO, bioalcohol and light biofuel were marked as the most promising alternative biofuels. These biofuels are readily available, renewable and bio-degradable which make them an attractive source of biofuel. Many studies have been done to evaluate the potential application of these biofuel as a fuel for diesel engine. However, each of this biofuel has their own limitation that hinder them from directly been used as an engine fuel.

SVO is renewable, non-toxic, biodegradable and contain no sulphur that make it as an attractive candidate to replace diesel fuel (Sidibé, et al., 2010). However, the direct use of SVO in diesel engine will lead to severe carbon deposit, fuel injector clog and rapid wears of fuel pump components. These issues are primarily associated with a high viscosity of SVO that dramatically alters fuel spray characteristics, atomisation quality and volatility (Meher et al., 2006).

There are several methods used to reduce the viscosity of SVO, such as micro-emulsion, preheat, blending, and transesterification. Among these different methods, the transesterification process is the most widely used to reduce the viscosity of SVO and convert triglycerides into fatty acid methyl ester (commonly known as biodiesel) and glycerol. Generally, the produced biodiesel has viscosity and other key properties close to petroleum diesel fuel. However, transesterification process involved a complex yet expensive process where a specific equipment and instrumentation are required. Besides, the process also leads to a by-product formation of glycerol. This crude glycerol requires further expensive purification process to produce pure glycerol which has better value-added product instead of crude glycerol (Zhang et al., 2015).

Meanwhile, Blending of SVO with other lower viscosity fuel was found to be an effective and economical method to reduce its viscosity. This strategy has been studied by many researchers (Atmanli et al., 2015; Devarajan et al., 2017; Hazar et al., 2010; Yusaf et al., 2011). Generally, it was reported that engine fuelled with this blended fuel has comparable performance characteristics to those of diesel fuel, but with some penalties in brake specific fuel consumption (BSFC). Most of the authors have concluded that this is mainly associated with the low calorific value (CV) of the blend, which resulted in the reduction of engine performance and increase in BSFC. Meanwhile, on the bright side, NO_x emission was reported to be slightly lower compared to diesel fuel.

Bioalcohol is another biofuel that receiving much attention among researchers. Alcohol can be produced from fermentation of ligno-cellulosic biomass feedstock (Rajesh Kumar et al., 2016). Lower alcohol likes methanol and ethanol were much suitable for spark ignition engine due to their high octane but not suitable for diesel engine owing to the lower cetane number. Lower cetane number will leads to longer ignition delay (ID) and short combustion period. Therefore, higher HC emissions are formed. In general, CO and HC increase with the increase of engine load. Even, most of their properties are comparable to gasoline fuel (Santosh Kumar et al., 2010). However, blend of lower alcohols with diesel or vegetable oil have successful run on the diesel engine (Bhimani et al., 2013; Jamrozik, 2017; Lei et al., 2012; Senthil Kumar et al, 2003; P. J. Singh et al., 2010). Generally, lower alcohols-diesel or alcohol-vegetable blend manage to improve some exhaust emissions and reduce smoke opacity. Increase in alcohol fraction would improve the volatility and fuel atomisation however it will reduce the CV and cetane number of the blend. Thus, the performance of the engine would slightly reduce. Moreover, short chain alcohols also have mixing

stability issues where surfactant is required for higher fraction blend to avoid phase separation (Attaphong et al., 2013; Senthil Kumar et al., 2003).

Besides vegetable oils and alcohols, a new biofuel termed as light biofuel has also received attention among researchers. Some of the examples are pine, camphor, lemongrass and eucalyptus oils. These light biofuels possess low viscosity similar to alcohol. But, contrasting to alcohol, they have comparable CV to those of diesel fuel. These light biofuels also have viscosity, density, flash point and boiling point similar to fossil diesel fuel. However, these light biofuels have low cetane number which is not favourable to be used directly as diesel fuel. Instead, blends of its with diesel or biodiesel was found to enhance the engine performance and combustion characteristics (Kasiraman et al., 2012; Kommana et al., 2015; Sathiyamoorthi et al., 2016; Subramanian et al., 2018; Vallinayagam et al., 2014). Moreover, the presence of lipophilic compounds enables light biofuels to dissolve in vegetable oil and various liquid hydrocarbons without the presence of surfactants (Southwell et al., 1999).

Notably, each of this biofuel have their own pros and cons if there were directly been used as a fuel for diesel engine. Generally, SVO is considerably have high cetane number and energy content but, its high viscosity and density hinder it from directly used as diesel fuel. Meanwhile, alcohol have viscosity, flash point and density close to diesel fuel. In addition, alcohol provide more clean combustion as compared to diesel fuel. However, alcohol contain low CV and cetane number which limits its application as a direct fuel for diesel engine. On the other hand, terpenes-rich light biofuel was seen as promising biofuel due to their viscosity, density, flash point, boiling point, and CV are closed to diesel fuel. However, its low cetane number is the main properties that is lack that hinder this light biofuel to directly used as fuel for diesel engine. Thus, the blend of these biofuels is seen as a method to overcome their shortcomings to

produce a hybrid biofuel that has properties comparable to those of fossil diesel. Therefore, in this study SVO, higher alcohol and light biofuel will be used as main ingredient to develop a so-called hybrid biofuel blend (HBB) as a fuel for diesel engine. Table 1.2 present the comparison of the key properties between SVO, light biofuel and bioalcohol.

On the other hand, working with new compositions of biofuel blends usually requires voluminous amounts of experimental runs to analyse and optimise the final mixture. In the past, many researchers have employed the traditional methods of experimentation such as one-factor-at-a-time and expert trial-and-error to determine the best combination of biofuel blends. However, in this study, a design of experiments (DOE) approach in the form of mixture design method was adopted to construct the set of experimental runs and to subsequently develop a new prediction model of HBB blend. Using statistical approach in conducting the experiments allows efficient use of limited resources and help to save time, cost, and waste of materials during the experiments (V. F. De Almeida et al., 2015). Therefore, this study aims to formulate, develop, optimise and investigate the physicochemical properties, spray characteristics, engine performance, emissions and combustion characteristics of binary and ternary blend of hybrid biofuel as an alternative fuel source for stationary compression ignition (CI) engine.

Table 1.2 Comparison of the key properties between SVO, light biofuel and bioalcohol.

Biofuel	Kinematic viscosity (mm/s ²)	Density (kg/m ³)	Calorific value (MJ/kg)	Cetane number	References
SVO					
Jatropha	24.5-52.7	901.0	38-42	33.7-51	(S.-Y. No, 2011)
Palm oil	39.6	910.0	39.6	42	(Misra et al., 2010)
Sun flower	33.9	916.1	39.6	37.1	(Murugesan et al., 2009)
Rapeseed	37.0	911.5	39.7	37.6	
Light Biofuel					
Camphor	1.9	890.0	38.2	5	(Subramanian et al., 2018)
Eucalyptus	2	890-895	43.3	15	(Vallinayagam et al.,
Pine	1.3	875	42.8	25	2015)
Bioalcohol					
Ethanol	1.1	789.4	26.8	8	(De Pours et al., 2017)
1-Butanol	2.5	809.7	33.1	17	
Pentanol	2.89	814.8	34.65	20	
1-Hexanol	5.32	821.8	39.10	23	
Diesel	2.72	835	42-50	45-50	

1.4 Objectives

The objectives of this research are as follows:

- i. To characterise the physicochemical properties of neat and hybrid biofuel blends.
- ii. To optimise the binary and ternary hybrid biofuel blend ratio having kinematic viscosity, density and calorific value within allowable limits of ASTM D6751 standard.
- iii. To analyse the macroscopic spray characteristics of the optimum binary and ternary hybrid biofuel blends.
- iv. To analyse and compare the engine performance, emissions and combustion characteristics of the optimum binary and ternary hybrid biofuel blends with baseline diesel fuel.

1.5 Research Questions

The research questions of this study are as follows:

- i. What are the physicochemical properties of neat RPO, HX and MCO and their binary and ternary blends?
- ii. What are the optimal binary and ternary biofuel blends and the key properties that have significant effects on the blends?
- iii. What are the similarities and differences of fuel injection spray of optimal binary and ternary hybrid biofuel blend as compared to diesel fuel?
- iv. What effects do optimal binary and ternary hybrid biofuel have on the diesel engine?

1.6 Scopes of Study

The scope of this research work is as follows:

- i. Characterisation of physicochemical properties of neat and newly introduced hybrid biofuel blend according to ASTM D6751/EN14214 standard. The properties analysed include chemical constituent, elemental analysis, viscosity, density, calorific value, flash point, boiling point, cetane index, acid value, water content and surface tension. These physicochemical properties were analysed and compared to diesel fuel.
- ii. The key properties of hybrid biofuel blend were optimised using design of experiment (DOE) software to save time, cost, and waste of materials during the experiments. The mixture design, a special type of DOE, was applied to analyse the correlation between the variables of the factors and the response variables.
- iii. Investigation on macroscopic spray characteristics of the optimum hybrid biofuel blends in comparison with diesel spray characteristics.
- iv. Engine test cell design and setup. This includes the engine dynamometer, data acquisition system and data post-processing set up.
- v. Analysing the effect of hybrid biofuel blends on engine performance, exhaust emissions and combustion characteristics.

1.7 Structure of Thesis

This thesis is comprised of five chapters. The thesis is organised with the following section:

Chapter 1 highlight the scenario of present and future of biofuel followed by overview on alternative sources of promising biofuel from plant oil as a replacement for fossil diesel. This chapter also emphasise the problem statement and the objectives of the study.

Chapter 2 comprise of literature review on previous and recent studies related to the present work. The literature discusses on the potential of plant oil as a fuel for CI engine as well as the methods used to improve their properties to suit for CI engine application. Moreover, the literature also deeply looks into the effect vegetable oil and its blends on the engine performances and exhaust emissions. This chapter also covers on DOE used to formulate and optimised hybrid biofuel blend related to present study.

Chapter 3 describes the materials and the methodology used in this study. This chapter explain the methods and equipment used to characterise the physicochemical properties of the samples. Moreover, the process of hybrid biofuel formulation and optimisation using DOE were also described. The experimental setup for gravitational phase stability, macroscopic spray characteristics and engine test bed setup were also described in detail. Last but not least, the methods used to analyse the engine performance, combustion and exhaust emissions also been described.

Chapter 4 is specifically discussed on the results obtained from the experiments conducted. Details discussion on physicochemical properties, formulation and development, spray characteristics, engine performance, combustion and emissions of hybrid biofuel were presented in this chapter.

Chapter 5 summarise and conclude all the finding from this work. Recommendation for future research also included in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The rising demand for global energy, depletion of fossil fuel, and concern over environmental issues has led to an intensive search for renewable and reliable biofuel. The fluctuation of crude oil price and currency exchange rate could affect the energy supply and economics of those countries that solely depend on imported oil from others. Continuous effort in the search for new energy resources is very important to ensure energy security for the future. Thus, it is important to seek biofuel which is available locally and renewable throughout the year. Biofuel production from plant oil was seen as promising alternative to current fossil fuel. Vegetable oil, alcohols and terpenes-rich biofuel are marked to be a potential source of energy from plant oil that can substitute fossil fuels because of its comparable properties to diesel fuel, renewable and readily available. In this review, the effects of plant oils and its blends on engine performance and emissions are comprehensively studied. Research on the direct use of SVO and several blends such as vegetable oil-diesel blend, vegetable oil-alcohol blend and vegetable oil-alcohol-diesel blend on diesel engine over the last decade are discussed. Furthermore, DOE method used to analyse and optimise the optimal blend of hybrid biofuel is discussed.

2.2 Strategies to Enhanced SVO Properties as Engine Fuel Application

Rapidly diminishing fossil fuels has encouraged research and development on alternative renewable biofuels. Under this circumstance, vegetable oils are found to be a potential source of energy that can substitute fossil fuels (Misra et al., 2010; S.-Y. No, 2011; Nwafor, 2004; Ramadhas et al., 2004). The oil has been gaining popularity

as an alternative fuel for diesel engines as its properties are very similar to those of diesel fuel (Esteban et al, 2012; Sidibé et al., 2010). However, there is a limitation in using neat vegetable oil as a fuel for internal combustion engines. Direct use of vegetable oil will lead to the formation of carbon deposit in the combustion chamber, incomplete combustion and some problems such as clogging injector and sticking piston ring (S. C. A. de Almeida et al., 2002; Hassan et al., 2013; Mosarof et al., 2015). These problems mainly occur because of the high viscosity and low volatility of SVO compared to those of ordinary diesel fuel (Dwivedi et al., 2014; Q. Li et al., 2015; F. Lujaji et al, 2010). To enhance the properties of vegetable oil, chemical or thermal methods are employed to reduce its viscosity. Those chemical methods are transesterification, dilution, pyrolysis, and microemulsion, while the thermal method preheats the fuel to reduce its viscosity (Abbaszaadeh et al, 2012; Pandey et al., 2012; Qi et al., 2013; Russo et al., 2012; Uddin et al., 2015; Yilmaz et al., 2014).

Transesterification is the most common method currently used to convert vegetable oil into biodiesel. Unfortunately, this method has a longer reaction time and high energy consumption during the biodiesel purification process (Deng et al., 2010). Furthermore, there is by-product formation in the form of glycerol. Approximately 1 kg of glycerol is produced for the production of every 10kg biodiesel. Crude glycerol is usually disposed, especially in small or medium scale biodiesel plants, due to expensive purification process (Zhang et al., 2015). However, glycerol is harmful to the environment if it is not properly disposed. Figure 2.1 shows the flow of transesterification process.

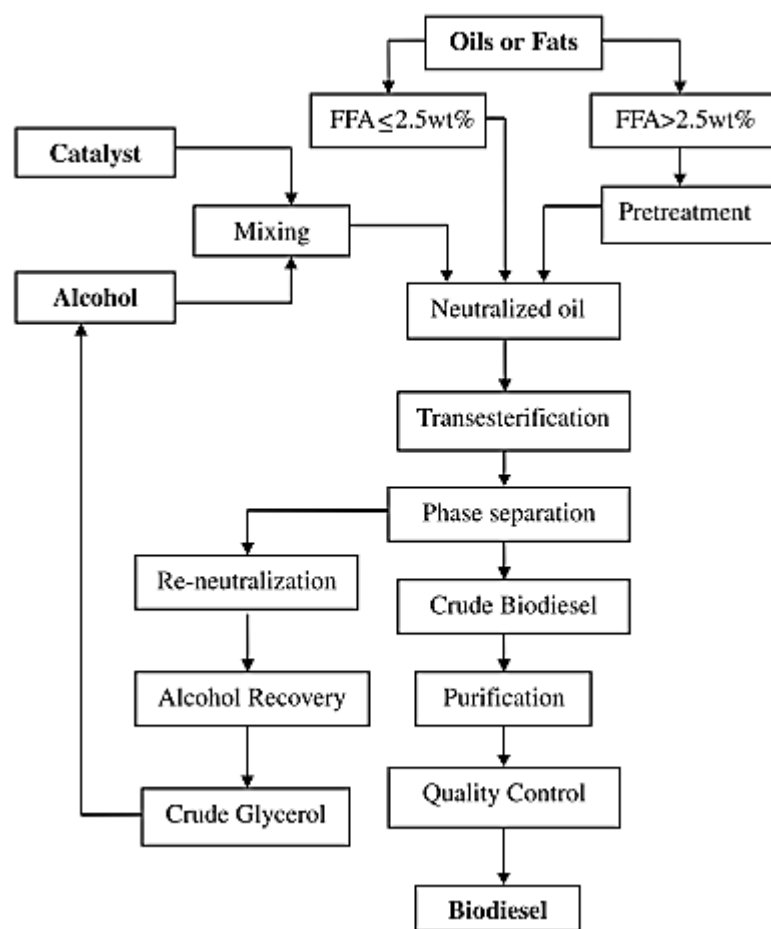


Figure 2.1 Transesterification process to produce biodiesel (Leung et al., 2010).

Several studies have reported that preheating of SVO was found to help reduce the viscosity similar to the diesel fuel (Acharya et al., 2014; Esteban et al., 2012; Franco et al., 2011). Galle et al. (Galle et al., 2013) studied the influences of fuel properties on the injection process. They found that the viscosity and density are strongly temperature dependent. The viscosity and density were decreased with the increased in temperature. Slight change in temperature significantly influences the injection pressure thus improved the spray atomisation. Attempts have been made by preheating the vegetable oil (palm oil) to reduce its viscosity. Obviously preheating of vegetable oil lowers the viscosity comparable to that of diesel fuel (Bari et al., 2002; Kalam et al., 2004). In term of performance, preheated crude palm oil (CPO) is comparable to fossil diesel, however its NO_x emission is higher than that of fossil

diesel. Nevertheless, an external heating system is required, which increases the cost and is not practical for the current diesel engine (Melo-Espinosa et al., 2015). Even though preheating can offer similar viscosity to those of diesel but in practice this will increase the design complexity and increase in cost.

Microemulsion is another method employed to improve the properties of SVO mainly associated with high viscosity and low volatility. Microemulsion is formed by mixing of two or more immiscible liquid in each other to form homogenous mixture. Certain surfactant is required as an additive to enhance the miscibility and stability of the blend. Generally, microemulsion containing high volatile water or alcohol droplets trapped inside less volatile and high viscosity SVO is able to exhibit a micro-explosion effect during combustion. Micro-explosion will enhance combustion efficiency and reduce exhaust emissions (Abedin et al., 2016). Even though, microemulsion provide simple and fast process, the present of surfactant in the blend would increase the cost of formulation (Sangeeta et al., 2014).

Alternatively, the blending method was found to be effective, simple and economical to reduce the viscosity of the SVO. Blending of SVO with low viscosity fuel, such as diesel and alcohol were found to reduce the viscosity and have comparable engine power as compared to diesel fuel (Gad et al., 2018; Ileri, 2016; Jamuwa et al., 2016; N. Kumar et al., 2018). This allows the vehicle fuel system to handle the blend without any difficulty. Testing of different SVO–diesel fuel blends have been found to be successful as engine fuels (A. K. Agarwal et al., 2009; Fontaras et al., 2011; Huzayyin et al., 2004; Pant et al., 2014; D. C. Rakopoulos et al., 2011).

2.3 Potential Biofuel for Diesel Engine Application

2.3.1 Straight vegetable oil

The history of using vegetable oil as a fuel for diesel engine has long begun when Rudolf Diesel ran his first engine with vegetable oil over ten decades ago. However, soon, fossil fuel took over and only during the 20th century, vegetable oil was used once in a while when fossil fuel availability was limited (Hossain et al., 2010; Karmakar et al., 2010). Recently, vegetable oil has regained attention due to depleting fossil fuel. Its properties are close to diesel, it is renewable and domestically produced, and it has a simple production process (Altın et al., 2001; Laza et al., 2011) which has drawn the attention of researchers around the globe.

In the biodiesel industry, oil crops with higher oil yield can reduce the production cost. Nowadays, most biodiesel is produced from edible vegetable oil, which has raised the concern of biodiesel feedstock competing with food supply in the future. This has led to intensive research on non-edible oils as a biodiesel feedstock (Chhetri et al., 2008). Even though non-edible oils have the potential as an alternative to edible oil, they are yet to reach commercial scales for feedstock production. As a comparison, palm oil yielded an average 4000–5000 kg/hectare/year, while oil yielded for jatropha and karanja is less than 2500 kg/hectare/year (Gui et al., 2008). The oil yielded for major non-edible and edible oil are summarised in Table 2.1. Obviously, high yield of palm oil is making it a promising feedstock for an alternative biofuel.

Table 2.1 Oil yielded for major non-edible and edible oil.

Type of oil	Vegetable oil	Oil yield (kg oil/ha)	Oil content (wt %)	References
Non-edible oils	Jatropha	741-1590	Seed:20-60, kernel :40-60	(Ahmad et al., 2011; S.-Y. No, 2011)
	castor	1188-1307	45-53	(Ahmad et al., 2011; S.-Y. No, 2011)
	Karanja / Honge	225-2250	Seed:25-50, kernel:30-50	(S.-Y. No, 2011)
Edible oils	Palm oil	4000-5366	20-36	(Ahmad et al., 2011; Habibullah et al., 2014)
	Sunflower	460-1070	40	(Ahmad et al., 2011)
	Soybean	375-636	18-20	(Ahmad et al., 2011)
	rapeseed	680-1000	37-50	(Ahmad et al., 2011)

Most vegetable oil is extracted from the seed and some from kernels. Oil extraction can be done either via mechanical extraction or chemical extraction using solvent. For commercial application, vegetable oil is commonly extracted using solvents, which produces higher yield and faster compared to mechanical extraction (Atabani et al., 2013).

Straight vegetable oils are mainly composed of triglycerides which contain three fatty acids and one glycerol. Triglyceride contributes to the high viscosity of vegetable oil, compared to fatty acid methyl ester (FAME). Figure 2.2 shows the typical structure of a triglyceride molecule. The composition of fatty acids determines the physiochemical properties of vegetable oil. Fatty acid is characterised by the length of carbon chain and numbers of double bonds. Commonly found fatty acids in vegetable oils are palmitic, stearic, oleic, linoleic and linolenic acid (Anand et al., 2010). Table 2.2 shows the common fatty acid found in vegetable oil.

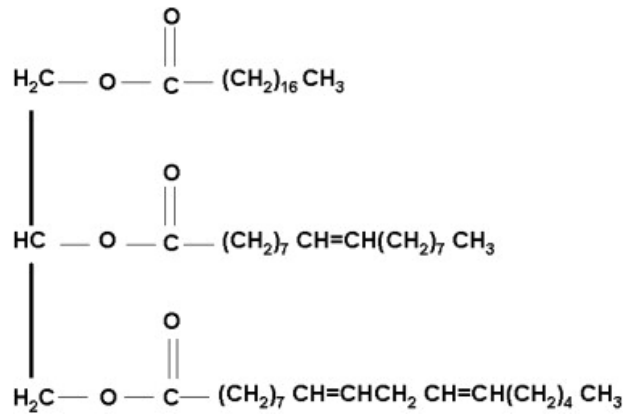


Figure 2.2 Typical triglyceride molecule structure (Chauhan et al., 2010)

High viscosity of SVO causes incomplete combustion and carbon deposit in the combustion chamber. Table 2.3 shows a range of vegetable oil properties. It can be seen that the viscosity of vegetable oil is in the range 30 – 40 mm²/s at 38 °C, which is more than 10 times higher than fossil diesel fuel. Cetane number of vegetable oil is slightly lower than that of diesel, however still comparable. Interestingly, the heating value of vegetable oil is close to diesel, where the value is in the range 39 – 41 MJ/kg compared to diesel at around 44 MJ/kg.

Moreover vegetable oil has negligible sulphur content (Lin et al., 2011), non-toxic (Khalid et al., 2014), contains no aromatic hydrocarbons, metals or crude oil residues. The absence of sulphur reduces the risk of acid rain caused by sulphur dioxide emissions. Besides, it will also reduce the level of sulphuric acid accumulating in the engine oil over the time (Peixoto et al., 2017). Additionally, it is eco-friendly, non-toxic, and has the potential to significantly reduce pollution.

Table 2.2 Common fatty acid found in edible and non-edible vegetable oils (Attaphong et al., 2013; Dwivedi et al., 2014; Esteban et al., 2012; Hellier et al., 2015; Shahabuddin et al., 2013)

Fatty Acid	Carbon Number	Mol. formula	Edible				Non-edible		
			Palm	Rapeseed	Soybean	Sunflower	Jatropha	Karanja	Castor
Lauric (dodecanoic)	C12:0	C ₁₂ H ₂₄ O ₂	0.1-0.2	-	<0.1	-	-	-	-
Myristic (tetradecanoic)	C14:0	C ₁₄ H ₂₈ O ₂	0.8-0.9	<0.1	<0.1	<0.1	0.15	-	-
Palmitic (hexadecanoic)	C16:0	C ₁₆ H ₃₂ O ₂	39.5-47	3.3-6	8-13.3	5.6-7.6	14.4-15.6	10.9	1.4-2.0
Palmitoleic (hexadecenoic)	C16:1	C ₁₆ H ₃₀ O ₂	<0.6	0-3.0	0.2-13.3	<0.3	0.69	-	-
Stearic (octadecanoic)	C18:0	C ₁₈ H ₃₆ O ₂	3-6	1.3-6	3-5	3-6	5.8-10.5	7.9	1.1-2.0
Oleic (octadecenoic)	C18:1	C ₁₈ H ₃₄ O ₂	36-44	52-65	18-26	14-40	42-43	53.6	3.4-6.0
Linoleic (octadecadienoic)	C18:2	C ₁₈ H ₃₂ O ₂	6-12	18-25	49-57	48-74	30.9-35.4	21.3	4.0-4.8
Linolenic (octadecatrienoic)	C18:3	C ₁₈ H ₃₀ O ₂	<0.5	8-11	5-9	<0.2	0.2	2.1	<0.6
Ricinoleic (OH)	C18:1	C ₁₈ H ₃₄ O ₃	-	-	-	-	-	-	86-88

Table 2.3 Properties of various edible and non-edible vegetable oils (Hellier et al., 2015; Misra et al., 2010; Murugesan et al., 2009; Sidibé et al., 2010)

Property	Edible					Non-edible					Diesel
	Palm	Rapeseed	Soybean	Sunflower	corn	Jatropha	Karanja	Mauha	Rubber seed	Castor oil	
Kinematic viscosity (mm ² /s)	39.6 ^a	37 ^a	32.6 ^a	33.9 ^a	34.9 ^a	24.5-53 ^b	27-56 ^b	24-37.6 ^b	34-76.4 ^b	29.7 ^a	1.3-4.1
Calorific value (MJ/kg)	36.9	37.4-39.7	37.3-39.6	37.7-39.6	39.5	38-40	34-38.8	35-41.8	37.5	39.5	42-43.8
Cloud point (°C)	31	-3.9	-3.9	7.2	-1.1	8-16	13-15	12-13	14	-11.6	-15 to -5
Pour point (°C)	31	-31.7	-12.2	-15	-40	-3 to 5	-3 to 6	12-15	-1	-31.7	-33 to -15
Flash point (°C)	267-330	246-320	254-330	274-316	277	180-280	198-263	212-260	144-198	229	60-80
Density at 20°C (kg/m ³)	910	915	920	925	915	901-940 ^b	870-928 ^b	891-960 ^b	910-930 ^b	970	834-855

^a Data at 38 °C

^b Data at 40 °C