CORROSION OF PHOSPHOR BRONZE IN DIFFERENT BIODIESEL BLENDS

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ABSTRACT

Biodiesel fuel is gaining rapid recognition around the globe as a reliable alternative to the use of petroleum fuel in the automotive industry. This safer, greener, renewable energy source originates from naturally forming feedstocks such as animal fats and vegetable oils. Biodiesel blends consist of mixtures of biodiesel with diesel at different composition. Biodiesel fuel is much more corrosive when compared to petroleum fuel, thus giving rise to many compatibility issues with the material construction of a typical combustion ignition engine. This research studies the effects of Tert-butylamine and Benzotriazole additive on the corrosion behaviour of phosphor bronze in different diesel/biodiesel blends. The biodiesel feedstock used in the research originates from palm oil. The corrosion behaviour of phosphor bronze was studied through immersion test in B0, B20 (20% biodiesel and 80% diesel), B50 (50% biodiesel and 50% diesel) and B100 for 1440 hours. Similar test was carried out with the addition of additive Tert-butylamine and Benzotriazole in B20 and B100. The test coupons were weighed before and after the immersion test to determine the weight loss measurement and calculate the corrosion rate. The metal surface was characterized by Scanning Electron Microscopy and Energy Dispersive X-Ray, while fuels was analysed by measuring Total Acid Number and density. The test result indicates that biodiesel is more corrosive to phosphor bronze sample when compared to diesel. Increasing biodiesel volume in the immersion solution increases the corrosion attack on phosphor bronze. The presence of additive Tert-butylamine and Benzotriazole, retards the corrosion attack and protects the phosphor bronze from further deteriorating. Benzotriazole was found to be a more efficient and effective corrosion inhibitor for phosphor bronze in biodiesel environment.

ABSTRAK

Bahan api biodiesel semakin mendapat pengiktirafan pesat di dunia sebagai alternatif yang boleh dipercayai untuk menggantikan bahan api petroleum dalam industri automotif. Bahan api ini selamat, mesra alam, dan merupakan sumber tenaga yang boleh diperbaharui. Ia berasal daripada bahan semualjadi seperti lemak haiwan dan minyak sayur-sayuran. Bahan api biodiesel lebih menghakis berbanding bahan api petroleum serta menimbulkan isu-isu ketidakserasian dengan bahan pembinaan enjin pembakaran biasa. Kajian ini menyelidik kesan penambahan perencat kakisan Tert-butylamine dan Benzotriazole terhadap tahap kakisan bahan phosphor bronze dalam campuran diesel/biodiesel yang berlainan. Larutan biodiesel yang digunakan dalam kajian ini berasal dari minyak kelapa sawit. Phosphor bronze direndam dalam campuran B0, B20 (20% biodiesel dan 80% diesel), B50 (50% biodiesel dan 50% diesel) dan B100 untuk 1440 jam. Ujian yang sama diulang dengan menambah perencat kakisan Tert-butylamine dan Benzotriazole pada campuran B20 dan B100. Phosphor bronze ditimbang sebelum dan selepas ujian rendaman untuk menentukan penurangan berat bahan dan menghitung kadar kakisan. Ujian Scanning Electron Microscopy dan Energy Dispersive X-Ray dijalankan pada phosphor bronze manakala ujian Total Acid Number dan ketumpatan dijalankan pada larutan campuran. Keputusan ujian menunjukkan bahawa biodiesel lebih mengakis kepada phosphor bronze berbanding diesel. Peningkatan biodiesel dalam campuran, meningkatkan kadar kakisan terdadap sampel. Kehadiran Tert-butylamine dan Benzotriazole bertindak sebagai perencat kakisan yang melambatkan serangan kakisan dan melindungi sampel phosphor bronze daripada terus merosot. Kajian menunjukkan Benzotriazole adalah lebih cekap dan berkesan sebagai perencat kakisan untuk bahan phosphor bronze dalam biodiesel.

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LIST OF SYMBOLS AND ABBREVIATIONS

CI	-	Combustion-ignition
SEM	-	Scanning Electron Microscopy
EDX	-	Energy Dispersive X-Ray
TAN	-	Total Acid Number
FAME	-	Fatty acid methyl esters
FFA	-	Free fatty acids
TBA	-	Tert-butylamine
BTA	-	Benzotriazole
R&D	-	Research and Development
Na	-	Sodium
NaOH	-	Sodium hydroxide
KOH	-	Potassium hydroxide
PP	-	Pour point
CP	-	Cloud point
CFPP	-	Cold filter pluggin point
PB	-	Phosphor bronze
Cu	-	Copper

BS	-	Brass
Al	-	Aluminnium
EDA	-	Ethylenediamine
TBHQ	-	Tert-butylhydroquinone
BHT	-	Butylated hydroxytoluene
BHA	-	Butylated hydroxyanisole
nBA	-	n-butylamine
PEG	-	Polyethylene glycol
NaCl	-	Sodium chloride
PPy	-	Polypyrrole film

CHAPTER 1 : INTRODUCTION

1.1. Biodiesel

Biodiesel fuel is rapidly gaining its place as an effective and reliable alternative compared to the use of petroleum based fuels around the globe. Biodiesel is being widely researched and developed in order to improve its fuel properties and also to adapt its properties for many other applications and industries. One of the main advantages of the use of biodiesel fuel is its cleaner-burning efficiencies and eco-friendly combustion properties when compared to petroleum diesel (Balat & Balat, 2008). Other than that, biodiesel fuel also serves as a renewable energy, which helps to overcome the concerns related to depletion of petroleum or fossil fuels in the coming future. The continuous and unfavourable impact of utilising petroleum fuels has led to the vast and extensive development of biodiesel fuel and its blends in many developing countries.

Biodiesel is produced domestically from naturally forming fatty acid feedstock. These feedstocks includes animal fats, vegetable oils and also recycled oils and grease from cooking waste. Vegetable oils are more commonly used as biodiesel feedstock due to its renewable stock that can be obtained through continuous plantation (Jaichandar & Annamalai, 2011; Ong, Mahlia, Masjuki, & Norhasyima, 2011). The most commonly used vegetable oils are coconut, rapeseed, sunflower, palm, peanut, cotton seed and soybean oil. Malaysia, as one of the leading countries in palm oil production is also actively involved in introducing and promoting the utilization of biodiesel fuels for many application and industries in the country. Biodiesel is generally produced through transesterification reaction method. This method involves the chemical reaction between vegetable or animal oils with short chain alcohols such as methanol or ethanol. Figure 1.1 shows the chemical reaction of one mole tri-glyceride with three mole of alcohol forming one mole of glycerol and three moles of fatty acid methyl esters (FAME). The presence alcohol acts as a catalyst that tends to increase the transesterification reaction rate (Jaichandar & Annamalai, 2011). The glycerol is the by-product of the reaction, while esters are known as biodiesel.

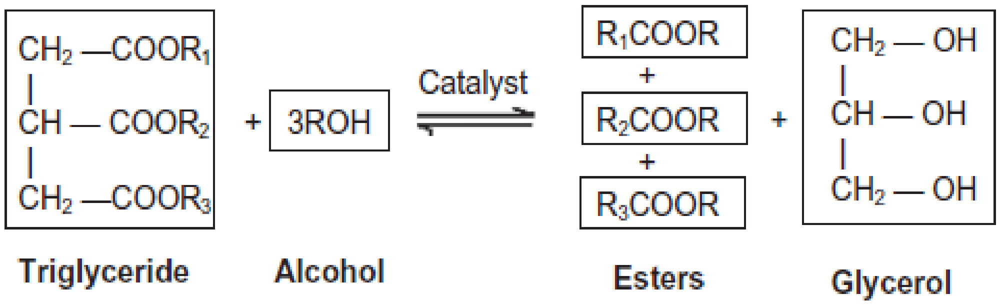


Figure 1.1: Chemical reaction of the Tri-glyceride with alcohol forming glycerol and fatty acid methyl esters (Haseeb, Fazal, Jahirul, & Masjuki, 2011)

Neat biodiesel in its pure and unblended form is indicated as B100. However, B100 is hardly used as fuel because of its higher viscosity and incompatibility with engine components. Therefore, in most cases, biodiesel are usually used in the forms of blends, whereby the composition of the blend consist of controlled mixture between biodiesel and petroleum fuels. Common biodiesel blends such as B20 consist of 20% biodiesel and 80 % diesel (Tyson & McCormick, 2006). Biodiesel blends are primarily formulated in order to improve the chemical and physical properties, thus making it suitable for automotive application. The physical and chemical properties of biodiesel fuel, also depends on the type of biodiesel feedstock and its FAME composition (Hoekman, Broch, Robbins, Ceniceros, & Natarajan, 2012). The variation in these factors, gives both advantages and disadvantages to the overall use of biodiesel fuel as an alternative in automation fuel. Therefore, it is highly necessary to analyse and research on the impact of biodiesel blends towards the fuel properties and also the operating environment.

1.2. Biodiesel: An Alternative Automation Fuel

The inconsistent hike in petroleum fuel prices and fluctuation in the supply and demand chain of petroleum fuel causes many disruption and interference in the automation industry. This mainly affects the operation of travel and transportation business in the country. As a result, many countries are now venturing into the prospects and potentials of biodiesel fuel as an alternative for conventional petroleum fuel. Countless designs experiments together with innovation ideas are being researched and developed in order to stabilize, improve and optimise the properties and compatibility of biodiesel fuel when operating in conventional compression- ignition (CI) engines.

Some of the main concerns involving the use of biodiesel fuel in CI engines are the level of compatibility of the fuel to the components and materials of the conventional CI engine, together with the combustion quality and performance of the engine. Research has shown that there are certain downfalls in the properties of biodiesel fuel such as low volatility, high viscosity and its cold flow properties that can lead to various problems, such as reduced atomization of fuel, partial combustion with heavy smoke discharge, carbon deposition, and injector chocking within the CI engine (Karmakar, Karmakar, & Mukherjee, 2010). Therefore, it is essential to conduct further research and improvement in order to rectify and minimise these impacts prior complete use of biodiesel fuel in CI engine.

Biodiesel fuel is generally instable, whereby its properties and composition can degrade over time and under selective operating conditions, causing it to deviate from the standard properties (Jakeria, Fazal, & Haseeb, 2014). There are certain factors that can affect the stability and performance of biodiesel as automation fuels. These include oxidation stability, thermal decomposition, storage stability, corrosion and contamination together with wear and friction properties of biodiesel fuel (Jakeria et al., 2014; K. A. Sorate & Bhale, 2015). Depending on the percentage of unsaturated fatty acid components within various biodiesel feedstock, palm and coconut biodiesel exhibits the least amount of unsaturated fatty acid, thus making them much more stable when compared to other biodiesel feedstock such as peanuts, rapeseed, soybean and sunflower (Jakeria et al., 2014).

It is essential to address and refine these factors in order to boost the performance and stability of the operating environment and its components in contact with biodiesel fuel. The economic capability of biodiesel fuel also plays a vital role in guaranteeing its potential as an alternative automation fuel. The cost of primary feedstock, processing and mass production of biodiesel fuel are primary factors that needs to be considered in order to ensure the sustainability of utilising biodiesel fuel in the automation industry (Atabani et al., 2012).

1.3. Material Compatibility to Biodiesel Fuel

The material technologies of CI engine has evolved greatly throughout the years, introducing many more complex materials and alloys that is proven to be well suited and able to improve the performance and durability of the engine. Therefore, it is highly necessary to study the compatibility of biodiesel fuel with the typical materials composed in the CI engine system. Much research has shown that biodiesel fuel exhibits higher corrosion, contamination and wear tendencies when compared to petroleum fuel (K. A. Sorate & Bhale, 2015). This is due to auto-oxidation or instability of biodiesel together with the presence of moisture in the operating environment. The fuel coming in contact with the engine components also varies according to its operating condition, in terms of temperature, velocity, load and pressure (Singh, Korstad, & Sharma, 2012). In such events, different engine parts and components in contact with biodiesel fuel will undergo different corrosion rates, thus giving rise to problems such as metal thinning, sediment and corrosion product formation, clogging of filters and injector pumps, and reduced durability and lifespan of CI engine. The biodiesel fuel properties and composition could also be off specification or degraded.

The common materials in a typical CI engine can be divided into metallic and non-metallic materials, comprising ferrous alloys, non-ferrous alloys and elastomer material (Haseeb et al., 2011). Ferrous alloys such as stainless steel tends to show greater resistance to corrosion in the biodiesel environment, due to the presence of a regenerating passive layer that acts as a barrier to corrosion activity on the metal surface. Similar corrosion protection mechanism was also exhibited by aluminium alloy in the non-ferrous alloy category (Ortega et al., 2013). Research by Ortega et al., (2013) has also shown that copper alloys are more susceptible to corrosion than aluminium alloys and ferrous alloys. Upon exposure in biodiesel, materials such as copper, brass and bronze tend to accelerate biodiesel degradation, leading to weight loss and formation of pitting on the metal surface. This leads to the formation of deposits and sedimentation in the biodiesel fuel. Copper acts as a strong catalyst in driving palm oil oxidation (Ortega et al., 2013).

1.4. Biodiesel Blending and Additive Additions

The poor corrosion resistance of copper and copper alloy in contact with biodiesel fuel gives a major impact to the use of biodiesel fuel in CI engines. This is because fuel system components such as fuel feed pumps and fuel pumps within the CI engine are constructed with copper based alloys (Haseeb et al., 2011). Therefore, it is highly essential to analyse and study the behaviour of copper and copper alloys towards biodiesel fuel in depth in order to improve its corrosion resistance and compatibility when in service. Fuel blending is one of the alternatives that have been proposed to improve the corrosion resistance of metals in contact with biodiesel fuel. The formation of fuel blending can decrease metal corrosion while similarly improving the physical and chemical properties of the biodiesel blended automation fuel.

The corrosion behaviours of metals in contact with biodiesel can also be improved by the addition of additives. These include chemicals such as antioxidants and also corrosion inhibitors. Antioxidants play a key role in improving the stability of biodiesel blend by reducing the oxidation rate of biodiesel when in operating condition. Research shows that oxidised biodiesel is more corrosive when compared to as-received biodiesel (Haseeb et al., 2011). This is due to the mechanism involved in the oxidation process, which increases the fatty acid content in the biodiesel, making it highly corrosive. Elements like copper, brass and bronze has higher tendencies to accelerate the oxidation of biodiesel when compared to elements like stainless steel, aluminium and carbon steel. Therefore, it is highly necessary to retard oxidation reaction of biodiesel by the addition of antioxidants especially when in contact with copper and copper alloys. Some of the commonly used antioxidants include tertbutylated hydroquinone (TBHQ), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA) (Yaakob, Narayanan, Padikkaparambil, Unni K, & Akbar P, 2014).

Corrosion inhibitors are also another group of additives that can be used to reduce the corrosion activity at the metal surface. Corrosion inhibitors form a protective layer on the metal surface, reducing the contact points between the metals and its environment. This action reduced the corrosion rate and corrosion product discharged into the environment. Tert-butylamine (TBA) is an amine base compound used as corrosion inhibitors for diesel system. Research has shown that TBA is effective in retarding corrosion activity through the formation of protective layer on the metal surface (Fazal, Haseeb, & Masjuki, 2011b). The formation of iron nitrite hydrate layer, shields oxygen and moisture contact with the metal surface, and decreases the corrosion effects. Benzotriazole (BTA) is also a well-known and effective corrosion inhibitor for copper and copper alloys. The presence of BTA in the biodiesel solution minimises the copper dissolution rate, thus preventing the formation of corrosion deposits and sediments in the fuel. However, research has shown that the performance of BTA addition is also dependent on factors such as pH and flow velocity of the solution (Khan, Shanthi, Babu, Muralidharan, & Barik, 2015). Therefore, it is necessary to study and understand the operating condition of the CI engine to optimise the effects of BTA addition towards improving the corrosion protection for copper and copper alloy based components (Khan et al., 2015).

1.5. Objective

The specific objectives of the present study are as listed below:

1. To analyse the corrosion behaviour of phosphor bronze in contact with petroleum fuel (B0), biodiesel fuel (B100) and different diesel-biodiesel fuel blends (e.g. B20, B50).

2. To investigate the effect of corrosion inhibitor on the corrosion behaviour of phosphor bronze and properties of the investigated fuels.

1.6. Scope of Studies

The scope of this research is to analyse and investigate the corrosion behaviour of phosphor bronze in contact with biodiesel fuel and its blends when used as automotive fuel. It also studies the effects of corrosion inhibitor on the corrosion behaviour of phosphor bronze in contact with biodiesel fuel and its blends. The research primarily focuses on the corrosion rate calculation obtained through weight loss of the sample before and after immersion test. Other than that, experiments to determine metal surface properties and composition using Scanning Electron Microscopy (SEM) and

Energy Dispersive X-Ray (EDX) was also conducted. The Total Acid Number (TAN) and density properties of the respective fuels was also measured and analysed to determine the changes in the fuel properties in contact with phosphor bronze.

1.7. Structure of Thesis

The organization of the report is as follow:

Chapter 1 provides a brief introduction of the research. In Chapter II, a complete literature review on biodiesel, its properties, the drawbacks and improvement methods for its future in the automotive industry is provided. In Chapter III, design of the experiment, implementation, tools, materials and process flow were discussed. Chapter IV focuses on discussions of the obtained results and comparison with some of previous research work. Meanwhile, the final chapter which is Chapter V concludes the research with some future recommendations and improvements.

CHAPTER 2 : LITERATURE REVIEW

2.1. Introduction to Biodiesel

Biodiesel fuel has grown as a valuable alternative to the use of petroleum based fuel for many industries. Biodiesel can be defined as fuel consisting of mono-alkyl esters of long chain fatty acids obtained and processed from any natural or used feedstock that contains fatty acids. Biodiesel feedstock includes vegetable fats and oils, animal fats and also used or waste oils. The first test involving biodiesel was initiated in the early years by Rudolph Diesel, using peanut oil. The development of biodiesel has then grown steadily by research in many countries, such as France and Belgium, involving the use of other type vegetable oils and also palm oil ethyl ester. The widespread production of biodiesel (mono alkyl esters) took place in 1990s as a substitute to the growing demand of energy levels (Balat & Balat, 2008)

Biodiesels are predominantly produced from vegetable oils. The common source of biodiesel feedstock comes from coconut, rapeseed, sunflower, palm, peanut, cotton seed, soybean oil and Jathropa. Vegetable oils (triglycerides) consist of a major portion of triglycerides (98%) and small portion of mono- and diglycerides. It is seen that different vegetable oils varies from one another based on the types of the fatty acid present in terms of the length of its carbon chains and the presence and numbers of double bonds within the molecule (Balat & Balat, 2008; Ong et al., 2011). The feedstock of biodiesel and its production is highly depending on the availability of the feedstock in the region. Figure 2.1 shows the comparison of productivity per unit hectares for various types of vegetable oil feedstock. Based on this comparison, palm oil is seen as most potential to cater for a higher production of biodiesel. Palm oil provides the highest oil productivity when compared to other highly used feedstock in the European Union such as rapeseed oil and soybean. One of the advantages of palm oil is its continuous availability and productivity throughout the year without interruption, thus giving a higher yield when compared to other crop such as soybean and rapeseed.

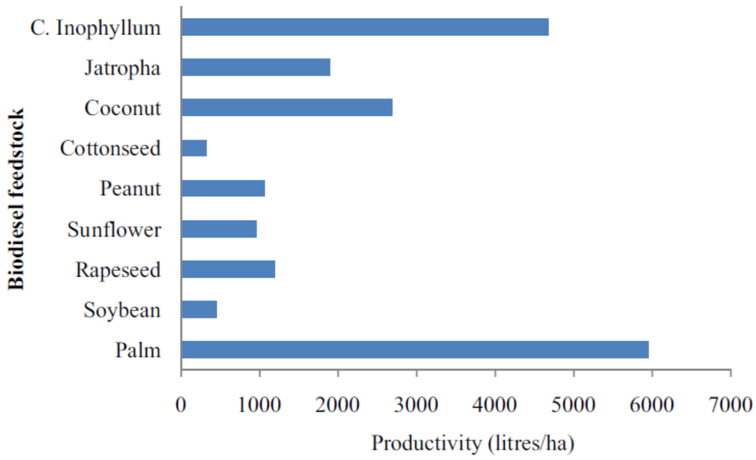


Figure 2.1: Production yield for various source of biodiesel feedstock (Ong et al., 2011)

As a major producer of palm oil, Malaysia is also greatly developing through extensive Research & Development (R&D) on the application of palm oil biodiesel products and production quality since 1980s. South East Asia provides the highest palm oil output, which is a total of 89% from the world production. Malaysia, having 4.5 million hectares of palm oil plantation contributes to 40% of the world production (Ong et al., 2011). It is now a growing demand in Malaysia to research and develop biodiesel as a new fuel alternative that also serves as a renewable energy for the depletion of traditional petroleum fuels. In this scenario, the utilization of palm oil feedstock in biodiesel production serves as an efficient and reliable yield in terms of productivity per hectar.

2.2. Disadvantages of Petroleum Fuel

The production and utilization of biodiesel from vegetable oils, animal fats and waste or used cooking oil have been found to provide greater advantage in terms of environmental and also cost aspects to daily users. The main concerns involving the use of petroleum fuel involves the constant and unpredictable hike in the petroleum fuel price, which affects the need for daily use of petroleum fuel by the people. Fossil fuel is also not a renewable energy and faces depletion over time when compared to the increasing need in the fuel demand for the transportation industry. Other than that, the increase in environmental pollution and also the greenhouse effect by the use of petroleum fuel has led to serious global warning crisis. The impact of reduction in fossil fuel and environmental degradation has led to the successive research and development of biodiesel to be introduced as a much safer, cleaner and reliable alternative for fossil fuel (Balat & Balat, 2008; Ong et al., 2011).

2.3. Biodiesel: Fuel for the Future

The active search for a reliable and renewable fuel has led to the drastic growth of research and development of biodiesel fuel. In comparison with all other means of alternative fuels, biodiesel from on vegetable oil feedstock has proved to be the most promising alternative with many advantages. Vegetable oils are widely available around the globe, thus making it readily available for processing and production. Vegetable oils are also renewable, whereby the source can be obtained through ongoing plantation throughout the year. Other than that, the combustion of biodiesel based from vegetable oils is also more environmental friendly, with less or no contamination such as sulphur element, aromatic hydrocarbons, and crude oil residue in the source.

The CO_2 emission form the combustion of biodiesel fuels is also well-balanced whereby the emitted gas is reabsorbed by the plants planted for the production of biodiesel feedstock. Biodiesel is also much safer for use and is classified as non-flammable fluid. The use of biodiesel fuels also provides better lubrication properties, thus providing better performance and life span extension for the combustion-ignition (CI) engine (Jaichandar & Annamalai, 2011).

However, research has also shown that there are known disadvantages to the use of biodiesel based from vegetables oils. The use of vegetable oil has a tendency to exhibit higher viscosity that can lead to many problems in the injection and combustion process of the biodiesel. The viscosity of vegetable oil based biodiesel is 10 to 20 times greater than that using petroleum fuels (Balat & Balat, 2008). Viscosity is an essential property that affects the fuel injection equipment in the compression- ignition (CI) engine. Operating at low temperature condition also has a tendency to increase the biodiesel viscosity, leading to failures such as clogging and choking that can affect the engine performance and durability (Balat & Balat, 2008; Jaichandar & Annamalai, 2011). Therefore, it is highly necessary that the viscosity properties of biodiesel to be monitored and controlled in order to improve its performance as a vehicular combustion fuel.

2.4. Biodiesel Production

The most common method of biodiesel production is through transesterification of vegetable oils and also animal fats. Transesterification is well-known and economical biodiesel processing method in which the vegetable oils and animals fats are reacted with alcohol such as methanol, leading to the formation of ester and glycerol. Research shows that transesterification process of biodiesel is able to lower the viscosity of the fuel and also increase combustion properties (Jaichandar & Annamalai, 2011; Ong et al., 2011). The main variable affecting this process includes the type of alcohol utilized, the type and amount of catalyst, the reaction condition such as temperature and time together with the amount of free fatty acids (FFA) and water content of the origin base biodiesel.

Catalytic transesterification with methanol, (methanolysis) is a common production method in which catalyst such as sodium hydroxide or sulfuric acid is used to escalate the reaction and improve the biodiesel synthesis (Balat & Balat, 2008). Figure 2.2 shows a typical catalytic transesterification production method using vegetable oil as the feedstock.

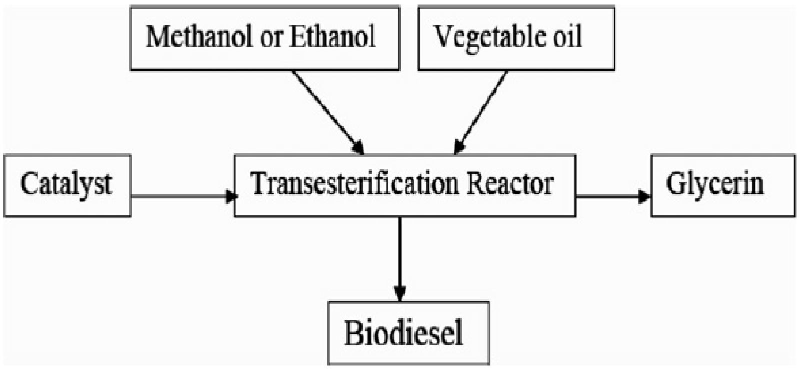


Figure 2.2: Catalytic transesterification production diagram (Balat & Balat, 2008)

One of the advantages of this process is that the methanol used in the processing is highly recoverable by distillation method, while the by-product formed by the reaction, that is glycerin, which has a higher density than that of biodiesel, can be used in the pharmaceutical and cosmetics industries (May, 2004). It was reported that it is possible to obtain 80 -85% pure glycerol after the removal of excess methanol. This approach is highly necessary to reduce the cost and maximize the utilization of the reaction products. The research on the transesterification of palm oil shows that Na, NaOH and KOH are effective catalyst that is able to produce a higher yield of biodiesel, within the shortest reaction time (May, 2004).

The concentration of the type of catalyst used is also essential to determine the rate of transesterification (May, 2004). The research shows that increasing the concentration of catalyst NaOH on the transesterification of RBD palm oil using methanol up to 2 weight% based on oil, can decrease the completion time of the reaction up to 1 minute. Therefore, it is highly essential to conduct a proper selection of type and concentration of catalyst in the catalytic transesterification process, which can lead to a higher yield of processed biodiesel within the shortest reaction time (May, 2004).

2.5. Biodiesel Blends

Biodiesel is commonly used as blends with petroleum diesel. Biodiesel blends consist of mixtures of biodiesel with diesel at different composition. Biodiesel blends are indicated with the letter B and the consequent numbers to the letter B indicates the biodiesel percentage. The typical industrial standard biodiesels found in the market are B2, B5, B10 and B20. Concentration up to 5% biodiesel, B5 in conventional diesel fuel is considered to be as pure petroleum diesel (Tyson & McCormick, 2006). Concentrations beyond that value, which is from 6 to 20% biodiesel, can be used with little or no modification requirement for any application that currently utilizes petroleum fuel. The common biodiesel blend used in the United States is B20 as it provides a well-balanced and suitable combination that is able to sustain the material selection, engine performance and cost benefits of biodiesel (Tyson & McCormick, 2006).

Some examples of application utilising B20 are CI engines, turbines and oil boilers. The B20 blend has been successfully used in low-temperature climates in the US, in order to reduce the cloud point (CP) that is the temperature at which fuel starts to visually form crystals when cooled (Tyson & McCormick, 2006). On the other hand, biodiesel blends with higher combination such as B50 and B100 will require careful handling and also major modification to the contact equipment or process, in order to ensure the safety and compatibility of the blend to the operating system and its surroundings (Tyson & McCormick, 2006).

2.6. Biodiesel Properties

The property of biodiesels varies from the type of feedstock involved in the biodiesel production. The physical and chemical properties of biodiesel are tied up to the specific composition of the fatty acid methyl esters (FAME) present in the biodiesel (Hoekman et al., 2012). The major characters such as the number of FFA and its composition in the feedstock influence the biodiesel production and final properties (Karmakar et al., 2010). FFA can be defined as the amount of fatty acid in the feedstock (wt %) that is not chemically bonded to the triglyceride molecule. Therefore, it is essential to compare the general properties of biodiesel to that of petroleum diesel, in order to achieve similar or improved performance for the automation fuel system.

Biodiesel has a higher oxygen content when compared to diesel, giving it a lower carbon and hydrogen content. This leads to a lower mass energy content in biodiesel (Hoekman et al., 2012). Chemically bonded oxygen has the tendency to lower the heating value and also reduce the CO emission content during combustion (Jaichandar & Annamalai, 2011). Biodiesel also exhibits higher fuel density when compared to diesel. The density factor is essential in the process involving fuel injector pumps and determines the energy level and air-fuel ratio within the CI engine.

In terms of cetane number, biodiesel shows an excellent value compared to diesel, in particular, No 2 diesel fuel. Cetane number represents the combustion or ignition properties of a fuel. A higher cetane number indicates a shorter delay period in ignition time and thus the fuel easily combustible. Higher speed diesel engine can operate much efficient and effectively with higher cetane number in fuels (Hoekman et al., 2012; Tyson & McCormick, 2006). The chain length and its saturation level can influence the cetane number in a particular feedstock (Karmakar et al., 2010). Biodiesel blends tend to exhibit a higher cetane value due to the increase in B-level of the blends.

Some of the downfall in the biodiesel properties when compared to diesel properties is due to the higher viscosity of biodiesel. Viscosity represents the level of resistance in a fluid by friction within the surrounding and its fluid. A review conducted by Hoekman et al., (2012) comparing the kinematic viscosity in 12 types of biodiesel shows that more than 80% of biodiesel exhibits a viscosity range between 4–5 mm^2/s. This comparison is also made clear by Tyson & McCormick, (2006) proving that the higher viscosity of biodiesel when compared to diesel can be an impact to the performance and durability of the conventional CI engine. The viscosity of biodiesel is higher than that of diesel, usually by a factor of two. Higher viscosity leads to performance deterioration in terms of fuel injection volume and atomization. This problem is more significant in cold climate and low temperature operating conditions where the fuel viscosity is also highly affected by the surrounding temperature.

Cold flow peoperties of biodiesel is also one of the concern when utilizing biodiesel fuels in CI engine. Review conducted by Sorate & Bhale, (2015) highlights that the crystallization of FAME in biodiesel at low or cold temperature can lead to clogging and choking of fuel injector pump and filters and is capable to deteriorate engine performance. The cold flow properties of biodiesel is tied to the CP and pour point (PP) of the feedstock. The CP is generally higher than the PP, which is the lowest temperature at which the fuel will crease to flow and solidify to form gel like substance (Tyson & McCormick, 2006). The CP and PP of biodiesel is generally higher when compared to diesel, typically, No 2 diesel fuel. The fuel selected for cold or low temperature condition is best recommended to have the lowest cold flow properties. It is seen that the low temperature flow properties of biodiesel and its higher blends is affeted by the hydrocarbon chain length and also the amount or presence of unsaturated bonds (K. A. Sorate & Bhale, 2015).

Another property of biodiesel that is considered under cold flow properties is the cold filter pluggin point (CFPP) (Hoekman et al., 2012). This point is defined as the the minimum temperature at which fuel form crystallization or gels and causes the filters to plug (Dwivedi & Sharma, 2014). The CFPP of biodiesel varies according to the content of fatty acid in the feedstock, whereby the CFPP is directly proportional to the fraction of saturated fatty acid in the biodiesel. The CFPP tends to be lower then the CP in which, upon cooling to CP temperature of the biodiesel, the methy ester molecules within the fluid tends to precipitate and crystallize, leading to the clogging of fuel filters (Karmakar et al., 2010). Dwivedi & Sharma, (2014) informed that the criticality of cold flow properties is seen especially during winter season, where decreasing temperature in the surroundings is unavoidable and prolonger over a period. Fuels with higher CFPP points will lead to faster malfunction of the vehicles during these critical times. In such scenarios, further alternative steps such as addition of additive and blending of fuels needs to be implemented to reduce the freezing points of fuels (Dwivedi & Sharma, 2014).

The value of CP, PP and CFPP are interrelated to one another and thus can be used as an indication to determine or assess on the cold flow properties of the biodiesel feedstock (Hoekman et al., 2012). Biodiesel exhibits a much higher flash point when compared to diesel, and is considered as less hazardaous in terms of flammability (Hoekman et al., 2012; Tyson & McCormick, 2006). Flash point can be defined as the lowest temperature in which a fluid is able to evaporate and ignite in the presence of a heat source. Flash point is the inverse of fuel volatility, whereby biodiesel exhibits low volatility. Many research has shown that the low volatility of biodiesel can lead to poor combustion quality in diesel engines, thus affecting the performance of the CI engine (Balat & Balat, 2008; Jaichandar & Annamalai, 2011; Tyson & McCormick, 2006).

2.7. Factors Affecting the Performance and Stability of Biodiesel as Automation Fuel

The widespread use and application of biodiesel in the transportation industry is greatly expanding among the developing countries around the world. Therefore, it is highly necessary that research in understanding and classifying the properties of biodiesel be conducted in order to maximize the development of biodiesel fuel as automation fuel. There are many factors that are able to affect the stability and quality of biodiesel used as automation fuel. These factors include oxidative stability, thermal decomposition, corrosion and contamination, wear and friction, microbial growth, combustion and emissions and also storage capabilities of biodiesel. These factors can cause the instability of biodiesel which will eventually lead to the alteration of biodiesel properties and composition (Jakeria et al., 2014).

2.7.1 Oxidation Stability

Oxidation stability is one of the main concerns in evaluating the performance of biodiesel as automation fuel. One of the main reasons of rapid oxidation in biodiesel is due to the level of unsaturated fatty acid components together with the higher number of carbon-carbon double and lower number of hydrogen molecules in the feedstock (Jakeria et al., 2014). This gives biodiesel much lower oxidation stability when compared to petroleum diesel leading to the formation of decomposition products such as acid, alcohol, peroxides and ester as sediments in the biodiesel. Oxidation stability can be determined by evaluating the concentration of antioxidant together with the total glycerine and fatty acid content. Jakeria et al., (2014) also mentions that other factors such as light intensity, temperature, metallic traces within the biodiesel can also affect the rate of oxidation.

There are two mechanisms in which biodiesel oxidation can take place that is auto-oxidation and photo-oxidation. Auto-oxidation is much more common in biodiesel feedstock and occurs readily when exposed to oxygen through a series of chain reactions involving initiation, propagation and termination (Yaakob et al., 2014). The UV light acts as an initiator that breakdown the compound such as peroxides, carbonyl and hydroperoxides into free radical that act as an initiator in the for subsequent auto-oxidation reaction (Yaakob et al., 2014). The level of oxidation susceptibility can affect basic properties such as cetane number, CP, PP and viscosity of the biodiesel feedstock. Beyond that, a drastic rate in the oxidation degradation of biodiesel can lead to the formation of insoluble high molecular weight polymers that can be harmful when in used in application.

2.7.2. Thermal Decomposition

Thermal decomposition or disintegration is also one of the major concerns in the application of biodiesel fuels. Temperature plays a key role in the stability of biodiesel whereby it is able to increase the rate of thermal deterioration (Jain & Sharma, 2011). Thermal stability is defined as the capability of fuel to form asphaltenes when exposed to elated temperature conditions. This decomposition products are tar like resinous matter that can lead to the clogging and plugging of injector pumps and fuel filters within the internal CI engine (Jain & Sharma, 2011). Jakeria et al., (2014) stated that the chemical properties of biodiesel such as viscosity, density, oxidation, lubrication and corrosion can be influenced by the temperature exposure.

Biodiesel feedstock from vegetable oils consists of natural antioxidants that in general improve the stability of biodiesel. However, when exposed to high temperature condition, degradation of antioxidants takes place at a higher rate, thus making the biodiesel less stable. This condition is unsavoury especially in the application of CI engine, where high temperature condition is unavoidable (Jain & Sharma, 2011). A study on the oxidative and thermal stability of biodiesel during frying was conducted by comparing the quality of soybean oil (SO) and a blend of soybean: palm (6:4) (MO) at a temperature of 180°C for 12 hours. The results indicated that the increase in the temperature led to the formation of higher weight molecules that causes an increase in the viscosity of biodiesel for both types of feedstock. However, it is seen that SP biodiesel exhibits a higher viscosity when compared to SO biodiesel. This could be due to the lower level of anti-oxidants present in the MO biodiesel blend, leading to a higher decomposition rate of biodiesel (Nzikou et al., 2009).

The result also shows a decrease in linoleic acid content, with an increase in polar compounds within the biodiesel for both types of feedstock as the frying temperature increase. Linoleic acid contributes to the highest percentage of polyunsaturated fatty acids in the feedstock and is more susceptible to oxidation degradation. Polar compounds on the other hand represent the oxidation products due to high temperature exposure (Nzikou et al., 2009). It was concluded that the decrease in linoleic acid content as a results of lipid oxidation, and increase in the percentage of polar compound is correlated with the increasing temperature of biodiesel. The results show that higher degradation rate is exhibited by MO feedstock when compared to SO feedstock (Nzikou et al., 2009).

Many other researches have also gained similar findings, concluding that the increase in the operating temperature affects the viscosity, peroxide and acid value within the biodiesel (Jain & Sharma, 2011; Jakeria et al., 2014; Nzikou et al., 2009). Therefore, it is highly necessary to analyse and understand the effects of temperature towards the performance and stability of biodiesel as automation fuel.

2.7.3. Storage Stability

Storage stability of biodiesel is a concern where prolonged duration of biodiesel storage can affect the primary composition of the fuel. Research has reported biodiesel is not be used as fuel after 6 months storage period due to deterioration in the biodiesel stability and may be detrimental in use. There is an increase in properties such as peroxide and acid value, density and viscosity of biodiesel with increasing storage time (Jakeria et al., 2014). The storage stability of biodiesel is affected by the level of air exposure and water content in the feedstock. The degradation rate of biodiesel stored for a prolonged time at lower temperature is much lower when compared to biodiesel stored for the same duration of time, at higher temperature. This is due to the induction period of biodiesel that decreases with the increase in temperature (K. A. Sorate & Bhale, 2015).

A research on the effect of storage time and condition on biodiesel from vegetable oils and used frying oil after a period of 12 months indicates that there is an increase in the peroxide value and acid value of all the biodiesel samples (Bouaid, Martinez, & Aracil, 2007). The increase in acid and peroxide value is due to the hydrolysis of FAME to fatty acids. The viscosity of all the biodiesel blends also shows an increment with increase in storage time, whereby initial increment in viscosity only takes place when the peroxide value has reached a critical level. It was mentioned that factors such as the water content and level of exposure to air can affect the rate of biodiesel degradation. In conclusion, a significant deterioration in biodiesel fuel quality after a period of 12 months. Therefore, precautionary steps such as limiting oxygen, light and moisture excess during storage of biodiesel and also addition of additives such as antioxidants and stabilizers can improve the storage life and quality of biodiesel (Bouaid et al., 2007).

2.7.4. Corrosion

Corrosion is one of the major deterioration faced by engine components when in contact with biodiesel. Biodiesel is seen to exhibit higher corrosive tendencies when compared to petroleum diesel due to the presence of unsaturated molecules that is prone to oxidation and decomposition (Singh et al., 2012). The CI engine consists of main parts that come in contact with the biodiesel fuel. Figure 2.3 shows a typical CI diesel fuel engine system and its commonly material selection for the components. The critical parts comprises of the fuel assembly that includes fuel tank, pump, lines, filters and its injector cylinder. The level of corrosion within the CI engine depends on the type of alloy in contact with the biodiesel fuel and also the biodiesel composition such as level of unsaturation, FFA content, and also hygroscopic nature of the biodiesel (Singh et al., 2012).

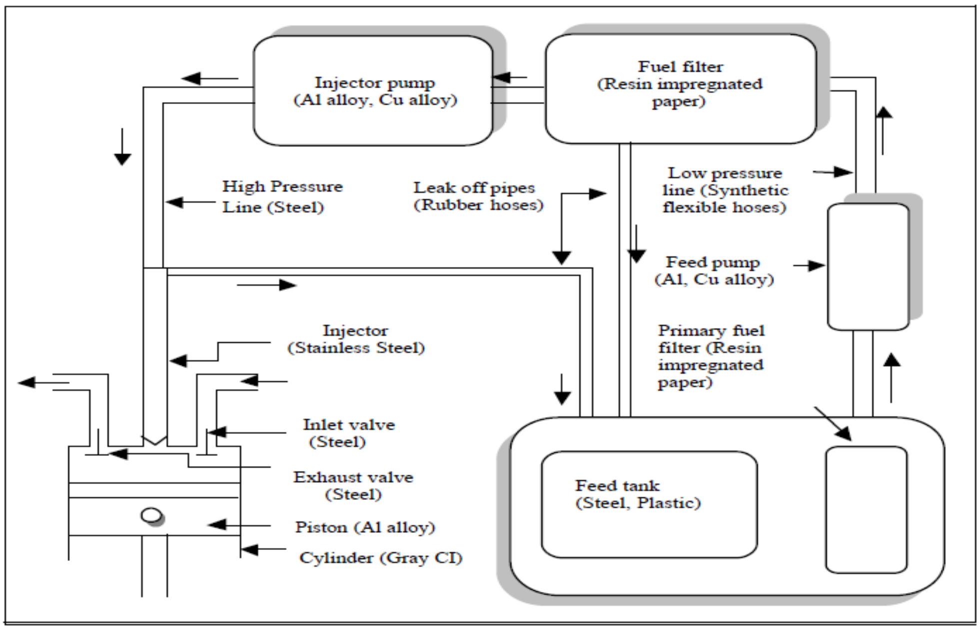


Figure 2.3: CI fuel engine system with common material selection (K. Sorate & Bhale, 2013)

Corrosion is an important aspect of assessment for the widespread use of biodiesel as automation fuel as many of the components in the existing CI engine configuration consist of metal such as cast iron, stainless steel, aluminium, copper and copper alloys and also elastomers (Singh et al., 2012). Therefore, it is important to monitor effects of factors such as water retention, auto-oxidation, and microbial activity during storage that can lead to increase in corrosion rate of the exposed components. Other than that, the hygroscopic nature of biodiesel that is prone to water absorption and retention can lead to increased hydrolysis of the ester chemical bonds, this forming a higher amount of FFA (K. Sorate & Bhale, 2013).

2.7.5. Wear and Friction

Wear is defined as the material degradation or loss in thickness due to friction when sliding motion between two surfaces (Fazal, Haseeb, & Masjuki, 2014). The combination effect of wear and corrosion in biodiesel fuel leads to an inter-related effect and is commonly known as tribo-corrosion. The deposit formed from the action of corrosion activity over time is capable to reduce the lubrication characteristics of biodiesel at sliding points, thus increasing abrasion action, leading to engine component damage (Fazal, Haseeb, et al., 2014). It is known that biodiesel exhibits better lubricity properties when compared to diesel, however factors such as auto-oxidation, corrosion and hygroscopic nature of biodiesel, can influence the wear and friction characteristics, thus altering the chemical properties of biodiesel (Fazal, Haseeb, & Masjuki, 2011a). It has been reported that biodiesel shows better lubrication and wear resistance during short term test, but it tends to lose its lubrication characteristics under long term condition, thus making it more susceptible to wear and friction. Therefore, it is important to study and understand the tribo-corrosion phenomena of biodiesel fuel for both long and short term condition in a typical CI engine. Engine components that are commonly effected by tribo-corrosion action are cylinder liners, pistons and piston pins and the valve assembly (Fazal et al., 2011a).

Many researches have shown that there is no significant change in wear characteristics when compared between biodiesel and diesel fuel (Fazal et al., 2011a; Fazal, Haseeb, et al., 2014). It is seen that biodiesel with appropriate level of FFA, monoglycerides, and polyglycerides can improve the lubrication and wear resistance properties; however, an increase beyond that level can lead to deterioration due to oxidation and corrosion. A distinct decrease of wear was seen at the range of 10–20% biodiesel (Fazal, Haseeb, et al., 2014). Research has shown that biodiesel blend B20 is capable to demonstrate physical wear reduction up to 30% lesser when compared to diesel fuel engine. Injector cocking and carbon deposit accumulation was also seen to be much lesser in the biodiesel fuelled engine (Agarwal, 1999). The lower increase in density of biodiesel fuel when compared to the density of diesel fuel also indicates that lesser degradation and wears contamination in the biodiesel fuel. Based on this research, it can be concluded that the wear and friction characteristics of biodiesel is correlated to the lubrication properties of its fuel, which is tied up to the level of unsaturated molecules and FFA content in the biodiesel feedstock (Agarwal, 1999).

2.7.6. Economical Capability and Acceptance of Biodiesel

Biodiesel exhibits its own advantages and also disadvantages when considered to be applied as automation fuel. Certain detrimental properties such as its high viscosity and FFA content, polymerisation tendencies, moisture absorption and oxidation instability together with its high corrosive nature of biodiesel leads to the requirement for detailed and precise assessment on the short and long term durability to the CI engine prior utilization. The economic viability of biodiesel is also a factor that leads to the limitation use of biodiesel. Biodiesel is known to be more expensive than conventional petroleum diesel (Atabani et al., 2012; Balat & Balat, 2008). The cost of biodiesel in developing countries is 1.5 to 3 times higher when compared to the prices of petroleum diesel, thus making it less practical in terms of economic viability (Atabani et al., 2012).

Atabani et al., (2012) stated that costs of primary feedstock and its processing to biodiesel comprise the two main segments of cost expenditure. Approximately 80% of the total production cost of biodiesel is allocated for the feedstock (Balat & Balat, 2008). Additional production cost is then required for the use of methanol, catalyst and labour in the biodiesel processing technology. Therefore, it was emphasised that proper selection of biodiesel feedstock is crucial in order to ensure low capital expenditure. Non-edible oils as feedstock has been recommended as a better choice in terms cost value. Other than that, the production cost due to biodiesel transesterification technology can be reduced by practising continuous transesterification process, thus providing a higher production capability with reduced reaction time. It is also recommended for biodiesel plants to have its own glycerol recovery service line, in order to ensure recovery of high quality glycerol that acts as an additional income to the main processing facility (Atabani et al., 2012).

In conclusion, more research and development emphasising on biodiesel feedstock cost, production and processing technology, properties and its effects to CI engine needs to be conducted in order to improve its economic feasibility and also to ensure the continuous growth and widespread expansion of biodiesel and it's blends as automation fuels.

2.8. Material Selection for a Typical CI Engine System

A typical CI engine system consist of three sub-assembly that is the fuel feed, combustion and the exhaust system (Haseeb et al., 2011). The basic scematic of a CI engine process flow is as shown in Figure 2.4. The fuel flowing in the CI engine comes in contact with various types of material selected for the internal emgine components.

These material can be divided into metallic and non-metallic materials that includes ferrous materials such as carbon steel, stainless steel and cast-iron together with non-ferrous material such as aluminium, copper and copper aloys. Elastomers and plactics are classified under non-metallic material.

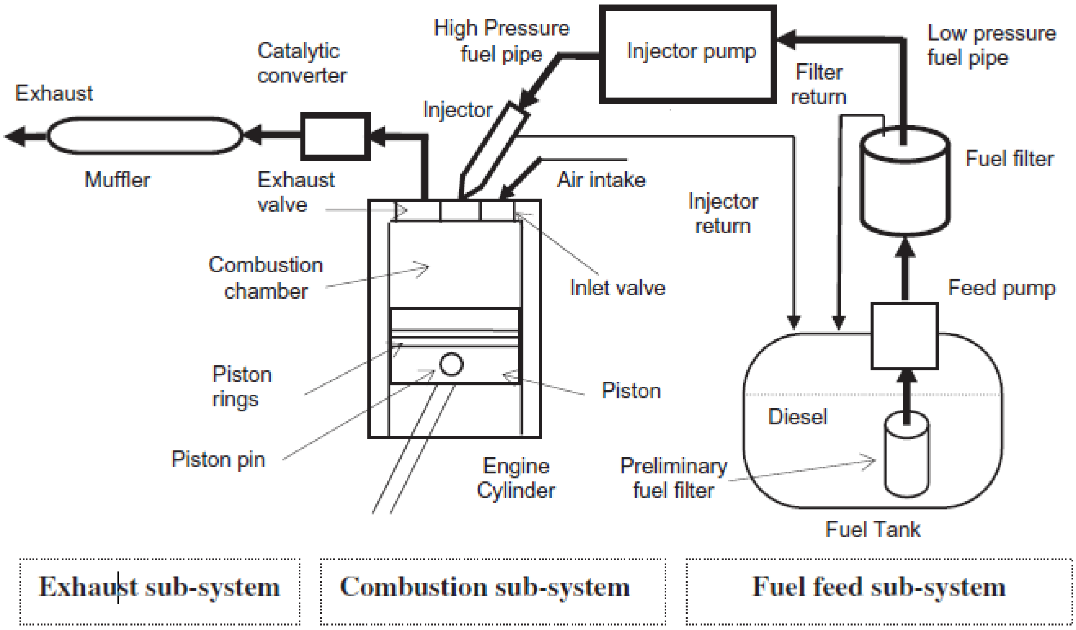


Figure 2.4: Typical process flow of CI engine (Haseeb et al., 2011)

Table 2.1 shows the common materials selected for the respective components and systems in a CI engine. Based on the selected materials, it is seen that the fuel comes in contact with these materials at different stages and process in the CI engine and will be with different chemical properties due to the changes in the operating condition and process based on the respective sub-section (Haseeb et al., 2011). Therefore, it is important to understand the effects of biodiesel towards respective material categories in the CI engine. In general, it is seen that various materials react differently in terms of corrosive characteristics and wear degradation when in contact with biodiesel fuel. It is also important to determine the most compatible biodiesel blends that is able give the excellent corrosion properties by reducing metal loss and preventing degardation of biodiel fuels when in contact with the respective metals.

Table 2.1: Material selection in the construction of typical CI engine components and systems (Haseeb et al., 2011)

Main parts	Components	Materials
Fuel tank	Housing	Steel, plastic, paint, coating
	Gasket	Elastomer, paper, cork, copper
Fuel feed pump		Aluminum alloy, iron based alloy, copper based alloy
Fuel lines	High pressure	Steel
	Low pressure	Plastics, rubber
Fuel filter	Filter cartridge	Paper
	Housing	Aluminum, plastic
Fuel pump		Aluminum alloy, iron based alloy, copper based alloy
Fuel injector		Stainless steel
Cylinder	Cylinder head	Gray cast iron, cast aluminum, forged aluminum
	Cylinder barrels	Gray cast iron, steel, cast aluminum
	Cylinder liner	Gray cast iron, aluminum
	Valves	Steel casting
Piston assembly	Piston	Sand-cast aluminum, die-cast aluminum, forged aluminum, gray cost iron
	Piston pin	Steel
	Piston ring	Special cast iron, steel
	Bearing	Copper alloy
	Connecting rod	Steel, aluminum alloy
Exhaust system	Exhaust manifold	Cast iron
	Exhaust pipe	Steel
	Catalytic converter	Stainless steel, ceramic fiber, aluminum fiber
	Muffler	Steel

2.9. Corrosion of Ferrous Metal in Different Biodiesel Blends

An experiment testing the integrity of carbon steel specimens was conducted by using standard 1 in. by 1 in. of low carbon steel (ASTM 36) immersed in two B100 biodiesel blends derived from soy oil and animal fat and two types of petroleum diesel consist of 7 ppm and 4000 ppm sulfur content respectively (Grainawi, Jakab, Westbrook, & Hutzler, 2008). The corrosion behaviour was measured through the use of an electrochemical impedance spectroscopy (EIS) whereby the samples were partially immersed in the fuel blends to measure the corrosion activity at the air/fuel interface. The impedance signal is used to measure the conductivity of cell across two electrodes, whereby one electrode acts as the reference electrode while the other acts as the working electrode. The impedance spectrum was recorded weekly for a 90-days exposure period. The test involves various fuel blends and combination of biodiesel and petroleum diesel.

The results upon 90-day period indicated that there was no significant corrosion activity measurement. The visual inspection indicated small traces of surface rusting due to the reaction between the surface oxide layer and the fuel blend. The results also indicated that the corrosion activity was more significant in carbon steel specimen immersed in animal-fat biodiesel when compared to soybean biodiesel blend. Substantially higher corrosion rate was also observed in fuel blend with 5% animal-fat biodiesel and 95% petroleum diesel with 7ppm sulfur content (Grainawi et al., 2008). This is due to animal fats and waste cooking oils that contain larger amount of FFA when compared to vegetable oils, thus making the biodiesel feedstock more instable and susceptible to corrosion. It was mentioned that crude vegetable oil contains 0.3 to 0.7% of FFA content while animal fat contains 5-30% FFA content (Karmakar et al., 2010).

An experiment studying the corrosion properties of carbon steel grade A765, and stainless steel grade SS 304 under the influence of microorganisms was conducted using diesel fuel (B0), biodiesel fuel (B100) and biodiesel blends, B5, B20, B35 and B50 (Kamiński & Kurzydłowski, 2008). The finding shows that there is a significant effect with the addition of microorganism on the total acid number (TAN) of fuels with increasing biodiesel content. In other word, it is seen that the microbiological activity is highly affected by the content of FAME in the fuel whereby there is a drastic increase in the TAN number for B35, B50 and B100 biodiesel blends. It was also seen that the viscosity of the biodiesel fuel is not influenced by the addition of microorganisms to the fuels. This shows that the viscosity factor of the fuel mainly depends on the FAME content where the viscosity for fuels with and without addition of microorganism, shows an increasing trend from B 20 to B100 (Kamiński & Kurzydłowski, 2008). The comparison is as shown in Figure 2.5.

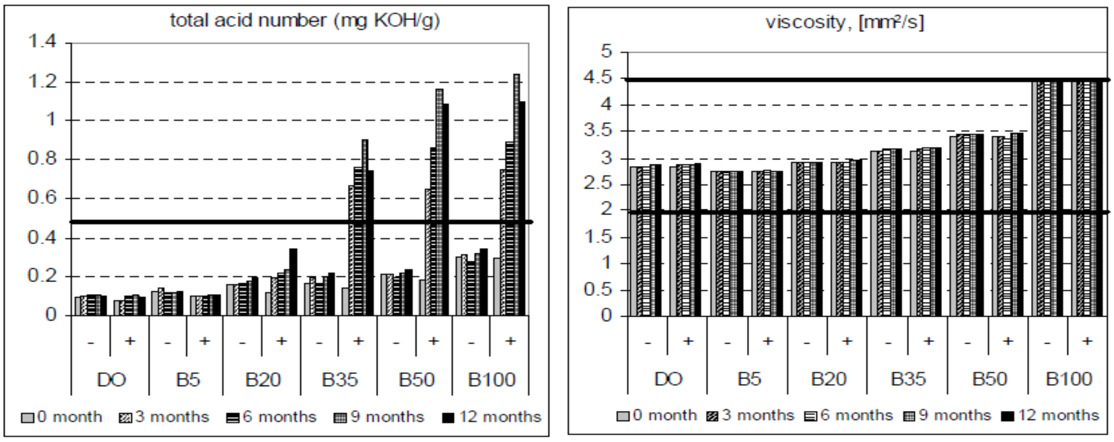


Figure 2.5: Comparison of TAN and viscosity of fuels with (+) and without (-) additon of microorganism (Kamiński & Kurzydłowski, 2008)

Maru et al., (2009) tested the corrosion behaviour of 3 different types of fuels, that is petroleum diesel with 870 ppm sulfur content (D), soybean (SB) and sunflower (SF) derived biodiesel when in contact with carbon steel and high density polyethylene (HDPE). The immersion test was carried out for a period of 60 and 115 days with carbon steel specimen and 75 and 125 days for polymer specimen. The test temperature was manintained at a temperature of 60 °C (Maru et al., 2009). The weight loss measurement after 115 days indicated that the weight reduction of carbon steel exposed to biodiesel is higher when compared to diesel. Furthermore, it is also seen that the sunflower biodiesel is much more reactive to the metal when compared to the soybean biodiesel. It was said that the difference in the corrosion activity of biodiesel feedstock is higly due to the variation in the primary chemical composition of the feedstock. Similar findings by other researchers also shows that carbon steel is highly reactive and not compatible in the biodiesel environment (Ortega et al., 2013).

The storage stability of soybean biodiesel in contact with carbon steel and galvanised steel has been studied by Fernandes et al., (2013). The experiment also measured the effects of additions, tert-butyl-hydroquinone (TBHQ) that functions as antioxidants to overcome the low oxidation stability of biodiesel. The findings indicated that the peroxide value of biodiesel in contact with carbon steel increased throughout the immersion period, but the peroxide value of galvanised steel only shown increment upon 84 days of exposure. Increasing exposure time also tends to increase the TAN in the biodiesel fuel, proving that corrosion activity increases with the formation of organic compound. Analysis on galvanised steel shows that there is a substantial amount of zinc in the diesel exposed to galvanised steel recorded since the first day of immersion (Fernandes et al., 2013). This indicates the occurrence of corrosion activity due to the presence of free-water content in the biodiesel feedstock. On the other hand, the addition of antioxidant TBHQ has shown to decrease the corrosion rate of galvanised steel with no zinc indicated in the biodiesel feedstock even after a period of 12 weeks. It was concluded that antioxidant TBHQ was being consumed in the biodiesel environment thus preserve the metal from deterioration during immersion period (Fernandes et al., 2013).

An experiment studying the corrosion characteristics of copper, aluminium, and stainless steel in the presence of palm oil biodiesel and diesel have been conducted at 80°C for 600 and 1200 hours (Fazal, Haseeb, & Masjuki, 2010). The results, as per shown in Figure 2.6, indicates that the corrosion activity in stainless steel is the least when compared to aluminium and copper samples, while copper exhibits the highest corrosion rate in both diesel (B0) and palm oil biodiesel (B100). There is also no significant change in the surface morphology of the 316 stainless steel sample when observed under microscopy. Stainless steel generates an invisible, exceedingly thin, passive film of chromium oxide that is formed on the surface of the material to protect it against the onset of corrosion and also other forms of contamination such as leaching. The protective oxide layer causes stainless steel to undergo very little leaching when compared to carbon steel. Therefore, stainless steel, namely Type 304L is very compatible in the biodiesel environment (Torsner, 2010). Other research has also mentioned that stainless steel and aluminium are metallic materials that is compatible and recommended in the use with biodiesel, partly due to the formation of protective passive film on the metal surface (Ortega et al., 2013).

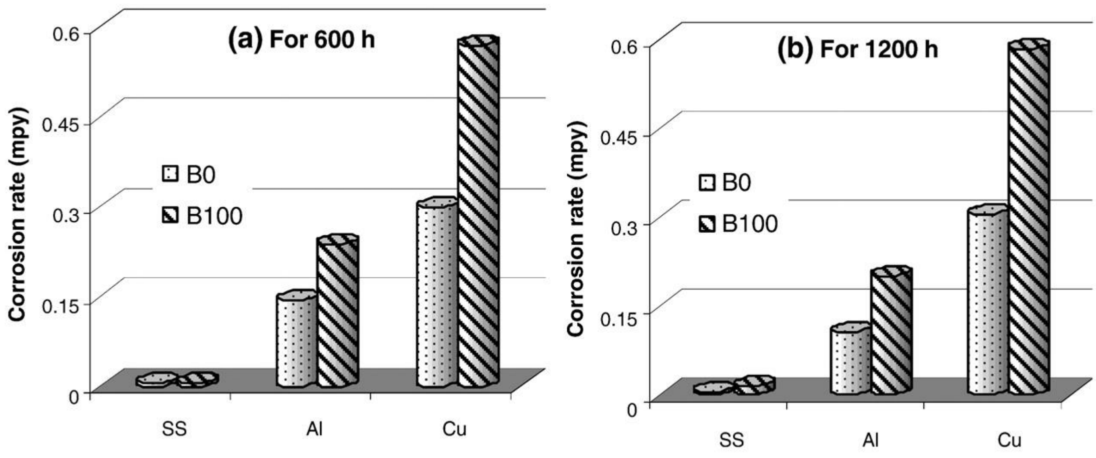


Figure 2.6: Corrosion rate (mpy) for SS, Al and Cu sample immersed in biodiesel (B100) and diesel (B0) for (a) 600 hours and (b) 1200 hours (Fazal et al., 2010)

An experiment assessing on the corrosion rates of carbon steel together with aluminum, copper and bronze was conducted by immersing the sample material for a period of 100h in 200 ml of biodiesel (B100), biodiesel (B99) and NaCl (1%) solution and NaCl (3%) solution individually (Meenakshi, Anisha, Shyamala, Saratha, & Papavinasam, 2010). Figure 2.7 shows the corrosion rate measurement (mpy) comparison between all the three immersion samples for the first 24 hours. The results indicate that carbon steel shows lower corrosion rates in biodiesel when compared to that in NaCl solution. The addition of 1% NaCl was also found to increase the corrosion rate of the sample, while the highest corrosion rate was seen in the sample with NaCl medium. A commercial conductivity meter was also used to measure the conductivity of the solutions before and after exposure of carbon steel coupons. The measurements indicate that the conductivity of biodiesel blend solutions in contact with carbon steel increases after upon complete immersion period (Meenakshi et al., 2010).

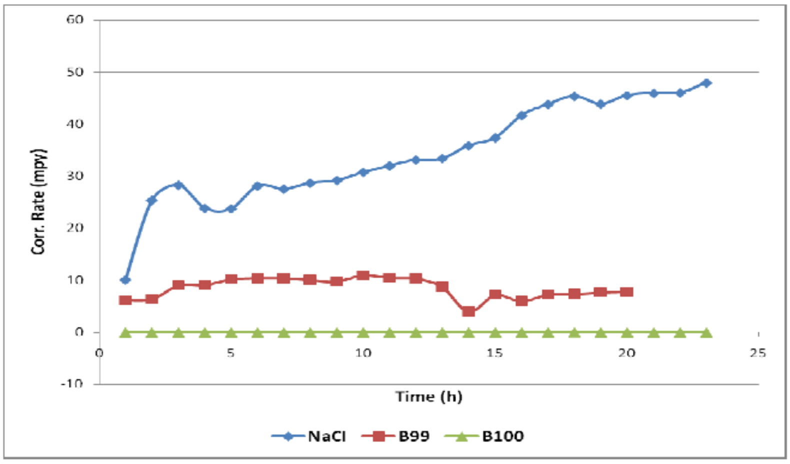


Figure 2.7: Deterioration trend of carbon steel as a function of time measured by LPR Method (Meenakshi et al., 2010)

The effect of temperature on the corrosion activity of biodiesel in contact with mild steel was experimented at three temperatures that is room temperature, 50°C and 80°C (Fazal, Haseeb, & Masjuki, 2011c). The mild steel samples were immersed in a solution of B0, B50 and B100 for 1200 hours, upon which the corrosion rate was calculated through weight loss measurements. The findings indicated that the corrosion rate of in each fuel increases with increasing temperature, however, biodiesel (B100) shows the highest corrosion rate followed by biodiesel blend B50 and least corrosion was seen in diesel (B0) solution (Fazal et al., 2011c).

Elemental analysis on the samples, before and after immersion also shows that there is an increase in the oxygen content with the increase in immersion temperature. The presence of oxygen was not detected on the as received sample but sample exposed to biodiesel (B100) at room temperature increases the oxygen content to 5.33 wt%, while the sample exposed to biodiesel at 80°C shows the highest content of oxygen with 10.04 wt% (Fazal et al., 2011c).The hygroscopic nature of biodiesel tends to increase with increasing temperature. The as-received biodiesel solution does not show any presence of water; however, there was an indication of increasing percentage of water in biodiesel solution from immersion temperature 27°C to 80°C that is 0.30% to 0.36% respectively. The increasing temperature also has the tendency to increase the oxidation rate and TAN of the sample. It was concluded that exposure of mild steel in biodiesel leads to oxidation instability, with higher corrosion activity and is further accelerated with increasing temperature of the immersed solution (Fazal et al., 2011c).

2.10. Corrosion of Non-Ferrous Metal in Different Biodiesel Blends

Copper is one of the highly applied materials in automotive components especially for the fuel pump components. However, many published research shows that biodiesel causes enhanced corrosion activity and rapid degradation in copper base components within the CI engine (Fazal et al., 2010; Ortega et al., 2013). An experiment investigating the behavior of copper in palm biodiesel was carried out by immersing copper (99.9%, commercially pure) in palm biodiesel (B100) for 200, 300, 600, 1200 and 2880 h of immersion period (Fazal, Haseeb, & Masjuki, 2013).

The experiment results for an immersion periods of 200 to 2880 hours shows that there is an increase in the corrosion rate up to a maximum rate at 600–1200 h immersion time and decreases gradually. This decrease is due to the increasing thickness of corrosion products on the copper surface, tends to decrease the area of contact for corrosion activity, thus reducing the corrosion rate of the sample. An interesting finding in this research also shows that there is a difference in the appearance of test coupons before and after exposure to biodiesel for different periods. As shown in Figure 2.8, the appearance if the bluish-green colour is firstly seen around the edges of the sample. It is found to increases upon increase in the immersion time of the sample, which finally covers the entire surface of the sample in a strong greenish colour. This is due to the conversion of copper compound on the surface of the sample, whereby the increase in the immersion time increases the thickness of the corrosion product (Fazal et al., 2013).

The SEM micrograph results shows that there are formations of small pits randomly on the surface of the sample exposed in the biodiesel environment for 200h. The pits are also found to increase in size with the increase in immersion time. Elemental analysis through EDS also shows that there is an increase in the oxygen and carbon content with the increase in immersion time of copper in biodiesel due to oxidation reactions (Fazal et al., 2013).

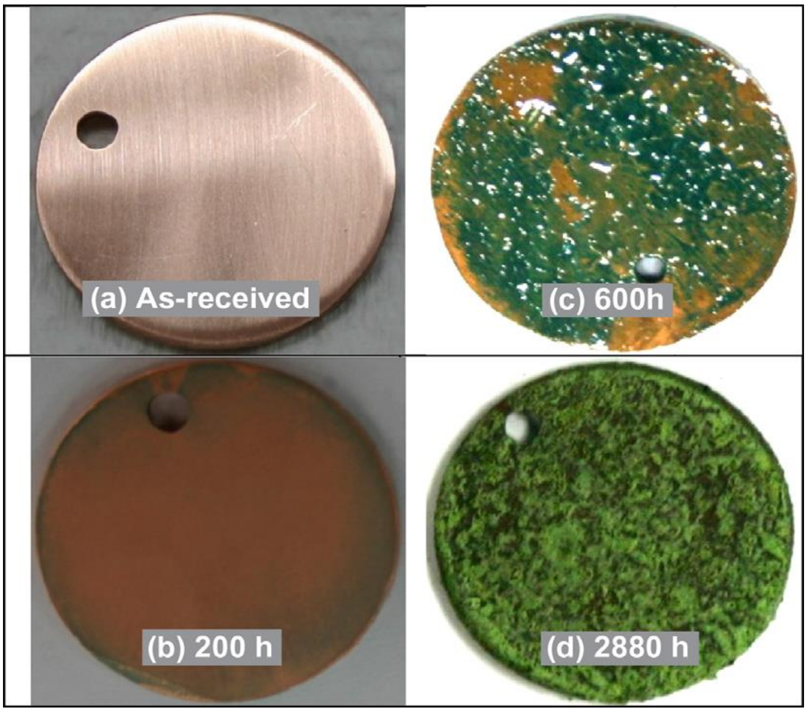


Figure 2.8: Deterioration trend of copper sample exposed to palm biodiesel for different immersion time (Fazal et al., 2013)

Copper and copper alloys are highly reactive and more prone to degrade in the biodiesel environment. Copper and copper alloys are susceptible to pitting and also discoloration due to the formation of oxide species (Fazal et al., 2013; Geller, Adams, Goodrum, & Pendergrass, 2008). Brass coupons show a lesser extent of corrosion rate in comparison to copper yet with similar corrosion patterns. Copper coupons in contact with 20% biodiesel solution shows a higher percentage of weight loss, that is 0.71%, while increasing biodiesel content to 80% gives a slight increment in the weight loss, that is 0.74% (Geller et al., 2008). Brass coupons are less reactive in lower concentration of biodiesels where weight loss of the samples exposed to 20% biodiesel was an average of 0.46% while those exposed to 80% biodiesel lost approximately 0.74% weight. Therefore, it was mentioned that copper and /or brass components should be replaced with steel based materials as it may affect the storage, transport, quality and utilization of the biodiesel (Geller et al., 2008).

The performance of leaded bronze in comparison to copper in palm oil solution was investigated by immersing of copper (99.99% commercially pure) and leaded bronze (87% Cu, 6% Sn, 6% Pb) in three solution, B0, B50 and B100 at two different immersion temperatures that is room temperature and 60 °C. Figure 2.9 shows the corrosion rate measurement, for the respective samples at different immersion temperature (Haseeb, Masjuki, Ann, & Fazal, 2010). Based on the results, it is seen that the corrosion rate of copper and leaded bronze in biodiesel is higher when compared with diesel in all solutions (Haseeb et al., 2010).

It is also seen that leaded bronze is less reactive and more compatible in diesel and biodiesel environment as compared to copper. Further analysis also shows that copper tends to form oxide on its surface in B100 at room temperature, while it turns into black at 60 °C. For leaded bronze, test coupons at 60 °C is cleaner and more shining compared with those tested at room temperature. The TAN assessment also shows that there is an increase in the TAN value of biodiesel upon exposure, whereby the increment is found to be similar in both copper and leaded bronze immersed solution. It was also found that the oxidation product increases with increasing biodiesel percentage in the solution (Fazal et al., 2013; Haseeb et al., 2010).

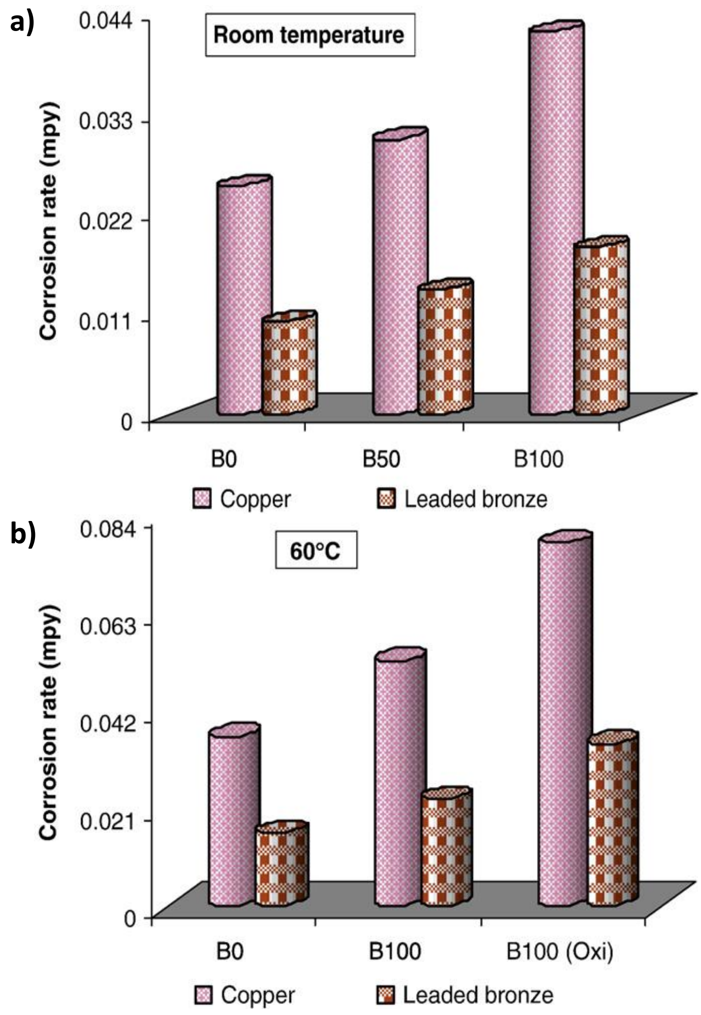


Figure 2.9: Corrosion rate of copper and leaded bronze at (a) room temperature and (b) 60°C (Haseeb et al., 2010)

The use of copper alloys not only causes corrosion problems but also the possibility of fuel pollutions by copper ions which may eventually affect the reagent used in the chemical reactors of the fuel processors within the CI system (Sgroi, Bollito, Saracco, & Specchia, 2005). Pitting corrosion was also seen in bronze filter of oil nozzles after several hours of exposure to biodiesel at 70°C. Based on these findings, it was recommended that the use of copper-free components should be emphasized especially in oil pumps and filters in contact with biodiesel environment (Sgroi et al., 2005).

Edible oils face the problem of high feedstock cost and affect the food storage, supply and demand trend when is increased in utilization as biodiesel production feedstock. Therefore, non-edible oils such as Pongamia pinnata, Calophyllum inophyllum, Madhuca indica and Jatropha curcas are widely investigated as a replacement for biodiesel feedstock (Karmakar et al., 2010; Meenakshi et al., 2010; Ong et al., 2011). An experiment comparing corrosion rate of copper and brass in contact with Pongamia pinnata oil (B100) shows that the corrosion rate of copper is much higher when compared to brass in contact with biodiesel for an immersion period of 100 hours. It was explained that brass is mainly the alloy of copper and zinc, making it more resistant to corrosion activity. The conductivity measurement of solution upon complete immersion also shows that brass exhibits lower conductance value as compared to copper. This indicates that there is a higher increase in the ionic content in copper biodiesel solution as a result of the increased corrosion activity (Parameswaran, Anand, & Krishnamurthy, 2013).

An experiment evaluating the influence of light intensity and temperature on the corrosion activity of brass and copper samples was conducted by immersing the samples for duration of 5 days in commercial biodiesel (B100) at room temperature, in the presence and absence of light. The immersion was also carried out in an oven set to 55°C, in order to simulate the condition of no light (Aquino, Hernandez, Chicoma, Pinto, & Aoki, 2012). The results shows that the condition with presence or absence of light incidence at room temperature gives similar corrosion rate to both copper and brass, with a slightly higher indication of corrosion under the presence of light. However, it was seen that the condition in the absence of light and higher temperature (55°C), shows a drastic decrease in the corrosion rate measured for both copper and brass sample. It was explained that the limitation to oxygen absorption and replenishment at higher temperature limits the corrosion rate activity in the immersed sample (Aquino et al., 2012). Induction period measures the duration leading to oxidative degradation of biodiesel. The optimum condition with least corrosion rate however contradicts with the optimum condition for storage stability of biodiesel. It is seen that based on the induction period and viscosity measurement, the absence of light and at room temperature is most suitable condition for the storage of biodiesel (Aquino et al., 2012).

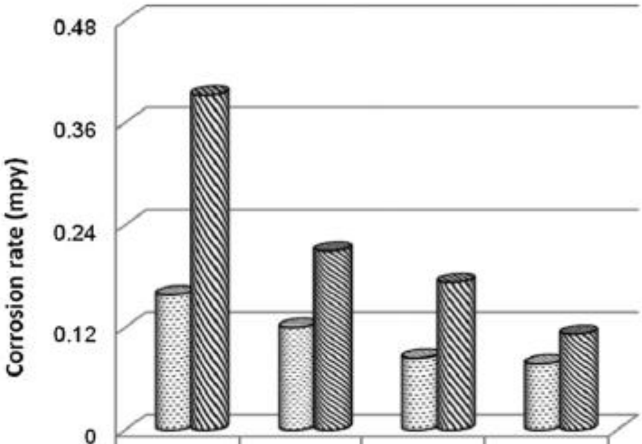
Further study on the relationship between immersion time and fuel stability was conducted by comparing the fuel properties and palm oil composition after immersion of mild steel and copper sample for a period of 20, 40 and 60 days (Fazal, Jakeria, & Haseeb, 2014). The GC (gas chromatography) analysis of the fuel upon immersion shows that methyl oleate is the major constituent of palm oil biodiesel. However, it is seen that there is a drastic and continuous reduction of methy oleate in copper exposed solution, within the 20 to 60 days duration, giving a final amount of 24.62% methy oleate in the solution when compared to the initial 46.16% methy oleate before immersion. Mild steel however shows a much lesser reduction with a final amount of 42% methy oleate after 60 days of immersion. Methyl oleate is an unsaturated component providing oxidation sites such as double bonds that offers more reaction sites for a metal ion leading to oxidation degradation of biodiesel. It is seen that copper has a higher tendency to react with these sites when compared to mild steel, thus leading to reduction of methy oleate in the solution (Fazal, Jakeria, et al., 2014).

It was also seen that copper affects the instability of the biodiesel solution giving it a lower induction period when compared to mild steel biodiesel solution. It was stated that the induction period decreases with the decrease in the methy oleate content, thus affecting the fuel properties of copper in biodiesel. Copper immersed biodiesel also shows a higher kinematic viscosity, water content and TAN of the solution when compared to mild steel immersed biodiesel. This is associated with the higher corrosion rate exhibited by copper in comparison to mild steel. The EDS analysis also shows that there is a higher content of oxygen detected on the copper sample surface than that of mild steel. This implies that there are more oxides in the copper surface, and also inside the corrosion pits. The increase in immersion time also tends to increase the oxygen content detected on the sample surface (Fazal, Jakeria, et al., 2014).

A research studying the effect of biodiesel fuel made from rapeseed oil and methanol on common automotive materials was conducted on copper, mild carbon steel, aluminum and stainless steel material (Hu, Xu, Hu, Pan, & Jiang, 2012). The findings are in line with other researches in the field, stating that corrosions of copper and mild carbon steel were more severe than those of aluminum and stainless steel in biodiesel. This is attributed to the reactivity and oxidation of both copper and mild steel. Minor corrosion effects were seen in aluminum and stainless steel, similar to those of diesel. This may be due to the formation of films of metal oxide, which prevents metal oxidation, thus giving lower corrosion rates.

However, the corrosion rates of all four metals are still lower in diesel when compared to biodiesel environment. This is attributed to the higher amount of saturated fatty acids in diesel, giving it a better stability when compared to biodiesel. It was also seen that there is a higher percentage of oxygen and carbon elements on the corrosion oxide layer of biodiesel. It was stated that the reaction between metal oxides and fatty acids of biodiesel leads to the production and adherence of reaction salts on the surface of the exposed metals. This leads to the increase in oxygen and carbon content detected on the biodiesel immersed samples (Hu et al., 2012).

Much research comparing the overall performance of various material in contact to biodiesel has been conducted across the globe. This is an essential comparison as the components within a CI engine consist of both ferrous and non-ferrous metals, with different corrosion reaction and stability towards biodiesel. A study comparing the corrosion deterioration and oxidation stability of common automotive component materials such as aluminum, copper and stainless steel, brass and cast iron in both petroleum diesel and palm biodiesel shows that aluminum is the most compatible material among the non-ferrous materials showing the least difference in corrosion rates between diesel (B0) and biodiesel (B100) environment. The corrosion measurement of the tested sample is as shown in Figure 2.10. The decomposition of biodiesel produces copper and iron ions that tend to further activate various other chemical reactions (Fazal, Haseeb, & Masjuki, 2012).



	Cu	BS	Al	CI
B0	0.158296	0.120122	0.084055	0.077402
B100	0.39278	0.209898	0.173055	0.112232

Figure 2.10: Corrosion rate of copper and leaded bronze at (a) room temperature and (b) 60°C(Fazal et al., 2012)

An experiment evaluating the corrosion behaviors of aluminum, copper and mild carbon steel exposed to sunflower biodiesel (B100), biodiesel blend (B20) and conventional petroleum diesel (B0) was conducted at room temperature and 60◦C for 3000 hours (Cursaru, Brănoiu, Ramadan, & Miculescu, 2014). It is noted that the increase in temperature, increase the corrosion rate. This can be attributed to the TAN factor. High TAN factor in biodiesel is due to the formation of free fatty acid in the solution. The experimental research indicates that increase in the immersion temperature, causes the TAN factor to increase in the biodiesel and consequently, the oxidation of metal in the biodiesel environment increases (Cursaru et al., 2014). Figure 2.11 shows the experimental results indicating that the corrosion activity increase from aluminum to mild carbon steel to copper.

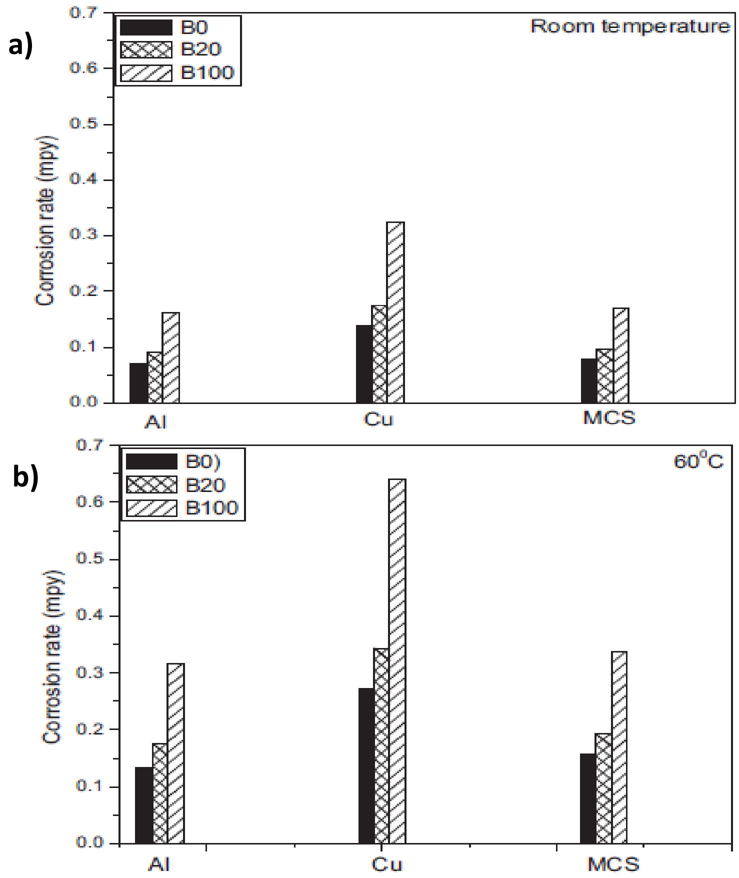


Figure 2.11: Corrosion rate for aluminum (Al), copper (Cu) and mild carbon steel (MCS) (a) at room temperature and (b) at 60 ◦C (Cursaru et al., 2014)

The increase in temperature leads to higher oxygen content and moisture adsorption which eventually gives a higher corrosion rate. The SEM observation indicates the formation of pits on the surface of copper and mild steel upon exposure to biodiesel at room temperature and intensifies at exposure of 60◦CThe corrosion rate of all metals shows similar observation in regards of lower corrosion rate in diesel when compared to biodiesel. As seen in various researches, copper tends to exhibit higher corrosion rate when compared to other materials under the same condition (Fazal et al., 2012; Geller et al., 2008; Haseeb et al., 2010). The present research studies the behaviors of copper based alloy phosphorus bronze in the presence of biodiesel and its blends. However, significant and published research on this scope is not available yet.

2.11. Additives and its Effects on Biodiesel Blends

Many research has shown that the compatibility of biodiesel to the selected materials, namely ferrous and non-ferrous materials within a conventional CI engine is still very much poor in performance when compared to diesel fuel. Therefore, it is highly necessary to develop an alternative method in order to improve the performance and quality of biodiesel as a suitable replacement for diesel fuel in the automation industry. The addition of additives is one of the alternatives that is able to improve the properties and stability of fuel (Rashedul et al., 2014). There is a vast selection of additives can be added according to improve specific limits and enhance the properties of automotive biodiesel. Commonly used additives can be further divided in terms of the purpose of its addition.

One of the major drawbacks in the use of biodiesel is the deterioration of oxidation stability of the fuel. Oxidation of biodiesel cannot be completely eliminated but can be reduced by the addition of antioxidants (K. A. Sorate & Bhale, 2015). Antioxidants are one of the common additives that functions to inhibit the oxidation process of biodiesel fuel by intercepting the formation of free radicals, thus, preventing the initiation of oxidation chain reaction. The oxidation process leads to the formation of free radical and peroxides within the fuels. The addition of antioxidants tends to decompose the peroxide formed and acts as free radical traps to retard the biodiesel fuel oxidation process. Antioxidants are also used to improve the flash point and cetane number of the biodiesel fuel properties (Rashedul et al., 2014). The naturally formed antioxidant in the biodiesel only partially exists and transferred to the final product after the transesterification processing technology. Therefore, it is highly necessary to re-introduce the presence of antioxidants to improve the stability of biodiesel fuels (Domingos, Saad, Vechiatto, Wilhelm, & Ramos, 2007).

A research was conducted to study effects antioxidant tert-butylhydroquinone (TBHQ) towards the storage stability of biodiesel (Almeida et al., 2011). The storage stability of biodiesel with and without the addition of antioxidant was evaluated through static immersion test with copper corrosion coupons. The result shows that the addition of antioxidant TBHQ shows higher induction time for the biodiesel fuel of 24 hours during initial exposure condition. The oxidation stability of biodiesel without the addition of TBHQ antioxidant shows a period of 6.5 hours. However, both samples shows similar oxidation trend with prolonged exposure to pro-oxidative condition, giving an approximate induction period of 2.42 hours after 24 hours. This shows that the presence of antioxidants retards the corrosion process, by protecting the coupon surface from corrosion activation sites (Almeida et al., 2011).

Corrosion inhibitors are also considered as effective additives to improve the corrosion reactivity of biodiesel when in contact with CI engine components (Almeida et al., 2011). The corrosion protection mechanism involves the formation of an enduring, resistive layer on the metal surface, thus reducing contact point at the metal/solution interface (Fazal et al., 2011b). It has been reported that amine based compounds such as primary amines, diamines, aminoamines, and oxyalkylated amines are effective corrosion inhibitors in diesel. An experiment investigating the performance of three common corrosion inhibitors, ethylenediamine (EDA), n-butylamine (nBA), tert-butylamine (TBA) was conducted on cast iron in contact with palm oil biodiesel (Fazal et al., 2011b). The results of corrosion rate calculation shows that all three addition of corrosion inhibitor is able to reduce the corrosion of cast iron, when compared to corrosion rate of cast iron in biodiesel without corrosion inhibitor additive. The effectiveness of corrosion inhibitor is as shown in Figure 2.12, with decreasing performance from EDA>TBA>nBA (Fazal et al., 2011b).

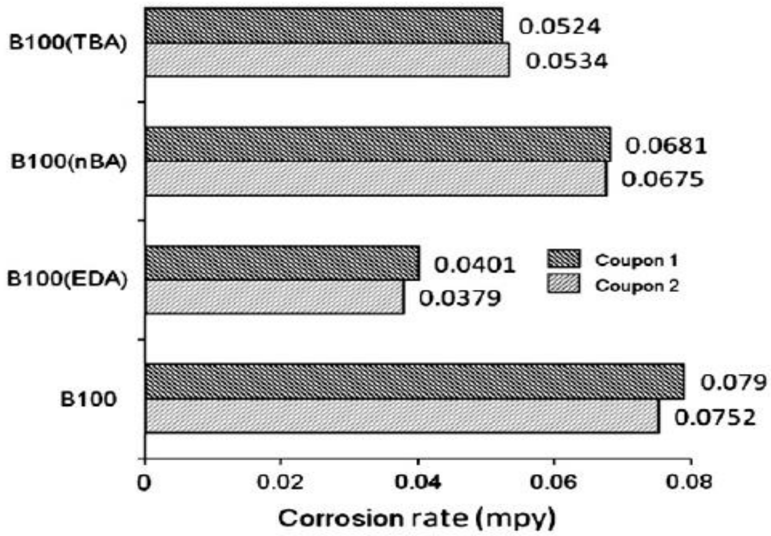


Figure 2.12: Corrosion rate of cast iron in the presence of palm oil biodiesel with and without addition of corrosion inhibitor (Fazal et al., 2011b)

However, further analysis on fuel samples shows that the fuel properties of biodiesel with EDA addition undergoes greater degradation when compared to fuels with addition of other corrosion inhibitors. Based on this assessment, it was found that TBA is most effective in reducing corrosion activity whereby the formation of protective layer iron nitrite hydrate, prevents oxygen or water contact on the metal surface, thus eliminating the formation and dissolution of metal oxides. In comparison of fuel TAN and density, TBA added biodiesel shows an optimum performance due to the lower amount of corrosion products and sediments formation (Fazal et al., 2011b).

Benzotriazole (BTA) is a well-known corrosion inhibitor used to inhibit corrosion activity of metals, especially of copper and its alloys (Allam, Nazeer, & Ashour, 2009). The chemical structure of BTA consist of benzene and triazole rings, $C_6H_5N_3$. The structure of BTA with free electrons enables itself to bond on the copper surface, thus preventing the occurrence of corrosion. Many researches has been conducted to understand the effects of BTA in copper and its alloys exposed to various condition and environments such as strongly acidic, alkaline and neutral solutions. It was stated that the performance of BTA is most effective in clean environments, whereby the presence of pollutants such as sulfide ions, is able to not only retard the performance of BTA against corrosion of copper and its alloys but also increase the corrosion rate to a greater level leading to faster metal degradation (Allam et al., 2009).

The inhibition of copper corrosion by addition of BTA mentions that a protective barrier film, mainly composed of copper and BTA complex, is formed as the copper surface is penetrated by BTA (Finšgar & Milošev, 2010). This mechanism prevents the discoloration and staining of copper surface. A study was conducted to understand the performance of BTA as corrosion inhibitor of archaeological polished copper and archaeological copper covered with corrosion products exposed to aqueous polyethylene glycol (PEG) (Guilminot, Rameau, Dalard, Degrigny, & Hiron, 2000). The result shows that the addition of BTA was less significant for polished copper samples, whereby the presence of PEG was sufficient to limit the dissolution current of the polished copper sample. On the other hand, samples covered with corrosion products were highly affected by PEG, whereby corrosion products degradation increases with time. Here, the presence of BTA was able to reduce the dissolution current of the corrosion product, thus protecting the corrosion layer of the copper. It was seen that the higher protection was achieved with increasing BTA concentration and immersion time (Guilminot et al., 2000).

An experiment was conducted to study the effect of BTA of various concentration and velocity towards providing corrosion protection to copper samples (Khan et al., 2015). The samples were immersed in 3.5% NaCl test solution with and without the presence of BTA at different concentrations and velocities. The results as shown in Figure 2.13, proves that BTA provides sufficient protection to the copper sample, whereby increasing BTA concentration in the solution reduces the weight loss of the sample. It was also seen that increasing the velocity of the sample rotation increases the weight loss of the sample.

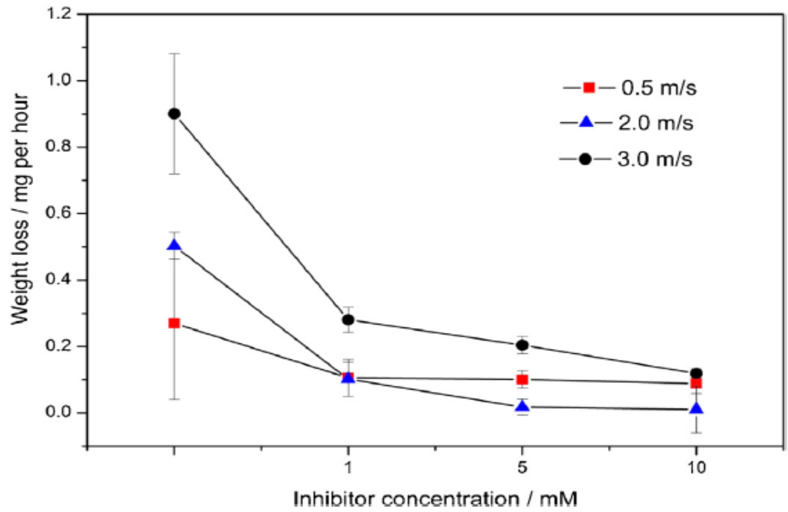


Figure 2.13: Effects of BTA concentration and sample rotating velocity to the weight loss of copper sample (Khan et al., 2015)

The effects of BTA addition on the formation of Polypyrrole film (PPy) on copper was investigated for corrosion protection purposes (Lei, Sheng, Hyono, Ueda, & Ohtsuka, 2014). The corrosion inhibitor was added into the oxalic acid aqueous solution that consists of pyrrole monomer. The results of the experiment indicated that the addition of BTA in the solution caused the initial formation of BTA-Cu complex layer followed by the anodic polymerisation of PPy layers. Analysis on the copper sample showed that the adhesion of PPy film was more homogeneous and stronger due to the presence of BTA-Cu complex layer on the copper surface, that support to coordinate the systematic adhesion of the PPy monomers. The presence of the BTA-Cu film acts as a second barrier that supports to inhibit corrosion activity if the PPy layer was damaged locally. It was also seen that the presence of BTA in the oxalic acid solution reduces the corrosion effects to the copper sample. The dissolution of cipper immersed in 3.5wt %

NaCl for 480h was retarded with 80% inhibition efficiency when compared to bare copper (Lei et al., 2014).

Experiment was also conducted to study the effects of BTA addition as corrosion inhibitors for brass in chloride solution (Kosec, Milošev, & Pihlar, 2007). The tested samples includes copper, zinc and copper-zinc alloy, Cu-10Zn and Cu-40Zn. It was seen that the addition of BTA decreases the corrosion current for all metals tested, however, highest inhibition efficiency was seen in sample Cu-10Zn. The higher inhibition efficiency of the sample was due to the formation of copper based alloy having a better resistance in chloride containing solution. It was concluded that BTA is an effective corrosion inhibitor for zinc metal as well. The formation of a mixed copper-zinc protective oxide surface acts as an effective barrier for both metal components in the copper alloy (Kosec et al., 2007).

Similar conclusion was drawn by other researchers stating that BTA and BTA derivative corrosion inhibitors such as N,N-dibenzotriazol-1-ylmethylamine (DBMA), and 2-hydroxy ethyl benzotriazole (HEBTA) are excellent additions for improving corrosion protection and reducing dezincification of brass. The solution analysis of brass immersed in NaCl solution, with and without the presence of BTA, shows that the dissolution of copper and zinc in the solution is lesser when compared to the bulk alloy. The formation of BTA-Cu complex protective layer controls the rate of metal dissolution, thus inhibiting corrosion activity on the metal surface and reducing the rate of metal leaching into the solution (Ravichandran, Nanjundan, & Rajendran, 2004).

CHAPTER 3 : METHODOLOGY

3.1. Introduction

The research experiment was carried out in different stages that comprise of sample preparation and immersion, weight loss measurement and corrosion rate calculation followed by metal and fuel characterization study. The detailed methodology is explained in this chapter.

3.2. Material

3.2.1. Phosphor Bronze

Phosphor bronze was produced by Morgan Bronze Products, Inc, and purchased from a local company. The phosphor bronze (92% Cu, 6% Sn, 0.35% P, 0.30% Zn) were cut to a size of 29.0 mm diameter and 2.0 mm thickness. The properties of the coupon are as shown in Table 3.1.

Table 3.1: Properties of Phosphor Bronze

Properties	**Value**
Liquidus Melting Point (ºC)	1049
Solidus Melting Point (ºC)	954
Density at 20 ºC (g/cm^3)	8.86
Specific Gravity	8.86
Thermal Conductivity at 20 ºC (W/m · °K)	69.2

3.2.2. Biodiesel

The commercial palm oil biodiesel used in this research was purchased from Weschem Technologies Sdn. Bhd. in Batang Kali, Selangor. Biodiesel is used in its pure form, B100 and also to produce biodiesel blends, B20 and B50. The properties of the commercial biodiesel are as shown in Table 3.2.

Table 3.2: Properties of Commercial Biodiesel

Properties	Value
Density at 15 ºC (kg/l)	0.8754
Kinematic Viscosity at 40 ºC (cSt)	4.53
Flash Point (ºC)	125
Sulfur content (ppm)	3
Ester Content (%)	98.0

3.2.3. Diesel

The commercial diesel used in this research was purchased from Petron Malaysia. Diesel was used in its pure form, B0 and also in biodiesel blends, B20 and B50. The properties of the commercial diesel are as shown in Table 3.3.

Table 3.3: Properties of Commercial Diesel

Properties	Value
Density at 15 ºC (kg/l)	0.8296
Kinematic Viscosity at 40 ºC (cSt)	3.400
Flash Point (ºC)	62
Sulfur content (ppm)	358
Ester Content (%)	0.0

3.2.4. Tert-Butylamine (TBA)

TBA is one of the four isomeric amines of butane, containing carbon, hydrogen and nitrogen atoms. This chemical compound is used as an effective corrosion inhibitor in the diesel environment. The chemical for this research was purchased from R & M Chemicals in Semenyih, Selangor. It is commercially available in a colourless liquid form, with a strong amine odour. The properties of TBA are as shown in Table 3.4.

Table 3.4: Properties of TBA

Properties	Value
Molecular Formula	$C_4H_{11}N$
Molecular Weight (g/mol)	73.14
Melting Point (ºC)	-67.50
Boiling Point (ºC)	43 - 47

3.2.5. Benzotriazole (BTA)

BTA is a heterocyclic compound commonly used as CI in the presence of copper and its alloys (Finšgar & Milošev, 2010). It contains carbon, hydrogen and nitrogen atoms. BTA for this research was purchased from a local company where it was produced by Alfa Aesar. It is commercially available in a white to light tan, crystalline powder form. The properties of BTA are as shown in Table 3.5.

Table 3.5: Properties of BTA

Properties	Value
Molecular Formula	$C_6H_5N_3$
Molecular Weight (g/mol)	119.12
Melting Point (ºC)	100
Boiling Point (ºC)	350

3.3. Equipment

3.3.1. Metallography Grinding & Polishing Machine

This machine is used to grind the phosphor bronze coupon prior immersion test. This step is essential in order to remove the scratches and oxide layer. The coupon is grinded on its entire exposed surface. These layers need to be removed in order to ensure the accuracy of the weight loss and corrosion rate measurement of the phosphor bronze coupon. The silicon carbide grinding paper grade goes from 800 to 1200.

3.3.2. Analytical Balance

This machine is used to measure smaller masses in sub-milligram scale, such as the weight of phosphor bronze coupon, before and after immersion testing together with the weight of chemicals and additives added to the fuel. The equipment is shielded in a transparent enclosure, also known as draft shield with doors to prevent the collection of dust, contaminants and air current to affect the accuracy of the measurements and its deviance.

3.3.3. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) Machine

This machine is used to analyse the image of the phosphor bronze coupon upon complete immersion and also to study the elemental composition or chemical characterization of the coupons. The model of the equipment is Hitachi SU1510 SEM & Horiba EMAX EDX. The SEM analysis was carried out at a magnification of 3000X. The similar coupon was then subjected for EDX analysis.

3.3.4. Acid Value Tester

This machine is used to determination of the free fatty acid content of animal and vegetable oils and fats. The model of the machine is G20 Compact Titrator by Mettler Toledo It quantifies the amount of potassium hydroxide (KOH) in milligrams that is needed to neutralize one gram of the test solution. The testing takes place by titration of the test solution with KOH solution, which is a strong basic solution. The result determines the amount of KOH utilised in the neutralization process thus indicating the level of acidity in the fuel.

3.3.5. Density Meter

This tester is used to determine the density of the fuel. This is a portable density meter that is lightweight and suitable for on-site measurement. The model of the tester is DMA 35 by Anton-Paar. The density is measured in units g/cm^3 @15 ºC.

3.4. Methodology

3.4.1. Sample Preparation

The phosphor bronze coupons (29.0 mm diameter and 2.0 mm thickness) was abraded with 800, 1000 and 1200-grit silicon carbide papers in order to remove scratches and oxide layer. A hole of diameter 0.002 m was drilled near the edge of each coupon. The cross section of the coupon upon grinding is shown in Figure 3.1.

Figure 3.1: As-received phosphor bronze coupon

Coupons were then washed by deionised water and degreased with acetone. The initial weight measurement of phosphor bronze coupons was measured prior immersion using an analytical balance to four decimal points accuracy. The immersion fuels consist of pure biodiesel, pure diesel and biodiesel blends. Biodiesel blends are indicated with the letter B and the consequent numbers to the letter B indicates the biodiesel percentage. In this experiment, the biodiesel blends refers to B20 and B50 fuels. B0 represents pure diesel, while B100 represents pure biodiesel. B20 and B50 on the other hand consist of 20:80 and 50:50 ratio of biodiesel-diesel fuels respectively. The biodiesel blends were prepared by measuring the specific amount of biodiesel and diesel required to form a 500ml solution. The specific amount for biodiesel blend is as shown in Table 3.6. A similar setup of fuels was prepared with biodiesel blends B20 and B100 doped with 500ppm of TBA and BTA corrosion inhibitors respectively.

Table 3.6: Biodiesel Blend Components

Biodiesel Blend	**Biodiesel (ml) Composition**	**Diesel (ml) Composition**	**Total (ml)**
B0	0	500	500
B20	100	400	500
B50	250	250	500
B100	500	0	500

3.4.2. Immersion of Coupons in Different Fuels

The phosphor bronze coupons that has been weight for initial weight measurement is labelled and tied to thin bamboo sticks using a tie string. The tie is secured in a hole (diameter 0.002 m) that was drilled in the coupons edge with sellotape to ensure that the coupons is always in a vertically upright position, while being immersed completely in the fuel. Sufficient distance is ensured between each coupon to prevent overlapping. This can reduce the exposed surface area of the coupons. The setup involves three phosphor bronze coupons tied in a horizontal line, in a single stick and fitted into the immersion beaker. Three coupons are immersed to obtain a more precise and accurate averages in the weight loss of coupons upon complete immersion. The beaker is then tightly closed with aluminium foil to prevent contamination and moisture from the environment to affect the experimental procedure and results. The experimental setup is as shown in Figure 3.2.

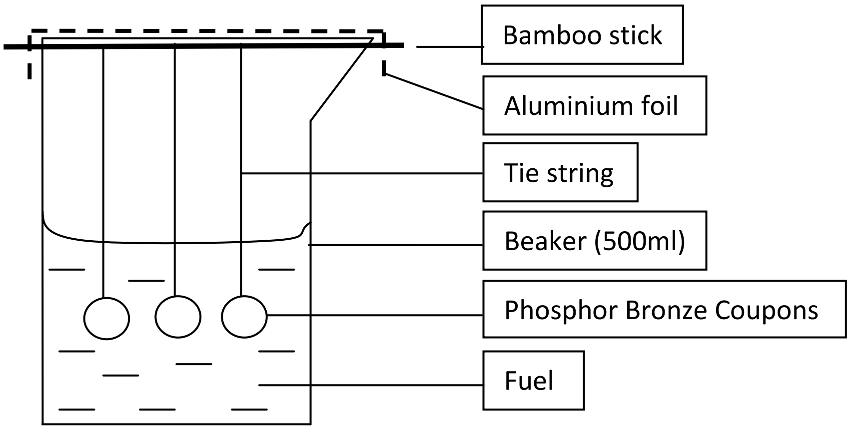


Figure 3.2: Experimental setup for immersion of phosphor bronze coupons

The coupons were immersed in their respective solution for a period of 1440 hours. The experimental setup was stored at room temperature, approximately 25ºC to 27 ºC and relative humidity, approximately 82%.

3.4.3. Weight Loss Measurement and Corrosion Rate Calculation

Upon completion of immersion test, the coupons were inspected visually to gauge the variation in the physical appearance. The coupons were then cleaned carefully in a water stream by using a polymer brash in order to remove the corrosion products. The coupons were dried under a blower and the weight of each coupon after immersion test was recorded by using an analytical balance to four decimal points accuracy. The weight loss measurement is applied to determine the corrosion rate of the coupons.

Corrosion rate measurement determines the analytical measurement and extent of corrosion on the phosphor bronze coupons. The obtained data from weight loss will be converted into corrosion rate (mpy) by using Equation 1 (Fazal et al., 2010)

$$\text{Corrosion rate (mpy)} = \frac{W \times 534}{D \times T \times A} \qquad (1)$$

where corrosion rate in units 'mpy' stands for mils (0.001 in.) per year, W is the weight loss (mg), D is the density (g/cm^3), A is the exposed surface area (square inch) and T is the exposure time (h).

3.4.4. Characterization Study of Metals and Fuels

The characterization study of phosphor bronze coupons and fuels was carried out upon complete immersion test. The characterization study can be divided into metal and fuel characterization test. The metal characterization includes SEM and EDX study, while the fuel analysis was conducted by measuring TAN and density.

3.4.4.1. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX) Testing

The phosphor bronze coupons were subjected to SEM and EDX at Quasi-S Sdn. Bhd, UKM-MTDC Smart Technology Center, Universiti Kebangsaan Malaysia. The coupons were stored in an air-tight container prior testing. The coupons were placed in the test compartment and the testing was initiated. The SEM working principal involves the scanning of the sample through a focused beam of electron in order to obtain the sample image. The various signal obtained through electron interaction with the atoms on the samples is converted to obtain information on sample's surface topography and composition. Each coupon was tested for SEM and EDX at three different locations in order to obtain an average result when analysing the image and elemental composition.

3.4.4.2. Total Acid Number (TAN) Testing

The test fuels were measured up to 10g in a 250 ml flat bottom flask using an analytical balance. The test solution was then mixed with 80mL Ethanol 95% reagent solution. The flask was fixed to the acid value tester and the testing was initiated. The titration of the free fatty acids in the solution of potassium hydroxide takes place, and the amount of KOH solution used in the neutralization process is recorded. The final result indicates the total amount of KOH required to neutralise the fuels. A higher TAN value indicates a more acidic fuel, with higher number of free fatty acid within the solution. Therefore, a higher amount of KOH solution is necessary to neutralise the test solution.

3.4.4.3. Density Testing

The filling tube is connected to the density meter. The pump level on the density meter is pressed down and held, while the filling tube is submerged in the fuel. The pump level is then slowly released, as fuel is drawn into the density meter. The density measurement appears on the meter screen and is recorded. The pump level is then rapidly and repeatedly pumped down to ensure that all fuels are removed from the filling tube before preceding the density test for the next fuel.

CHAPTER 4 : RESULTS AND DISCUSSION

4.1. Visual Inspection

Figure 4.1 shows the physical appearances of phosphor bronze before and after exposure in fuels for 1440 hours. It is seen that the colour of the corrosion compounds formed on the coupons upon exposure in biodiesel or its blends is greenish in colour. The appearance of coupons exposed to diesel fuel was not significantly changed. Similar findings were reported by Haseeb et al., (2010) when experimenting on copper and leaded bronze in B100. Figure 4.1 also shows that the greenish corrosion product seems to be darker with the increase of biodiesel concentration in the blends.

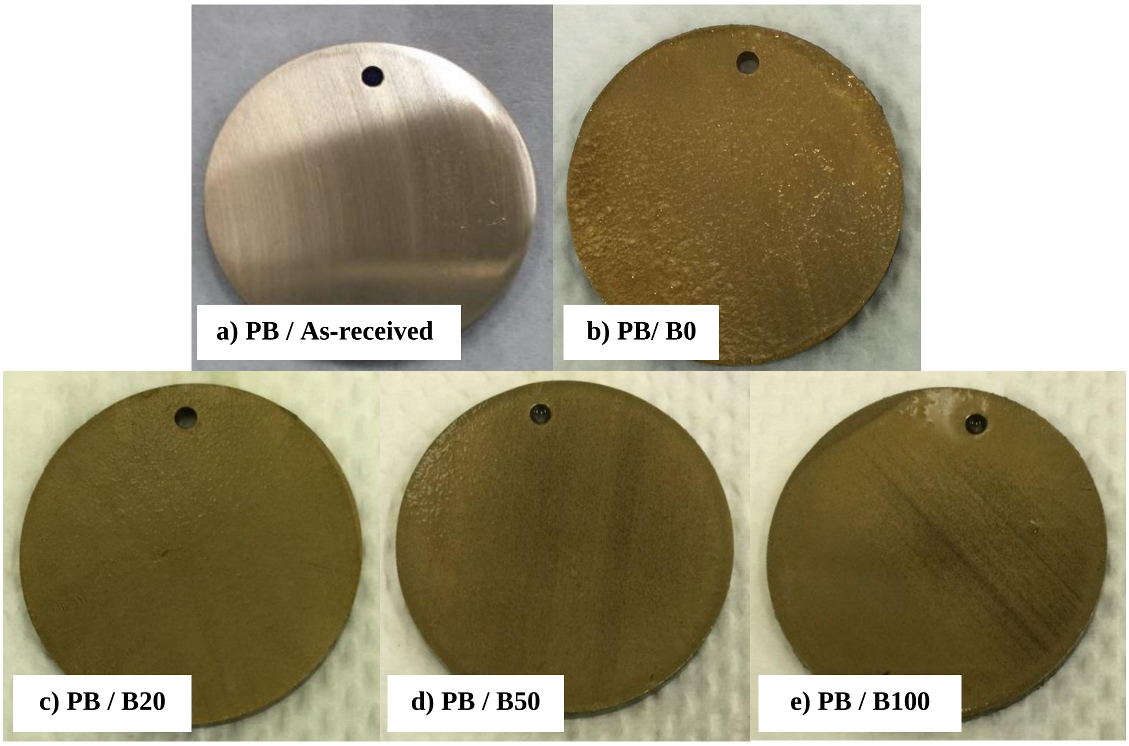


Figure 4.1: Appearance of phosphor bronze (PB) coupons (a) before and (b-e) after exposure in (b) B0, (c) B20, (d) B50 and (e) B100 fuels for 1440 hours

Figure 4.2 shows the effects of additives on the appearance of phosphor bronze immersed in B20 and B100. It is seen that the addition of TBA and BTA in the fuels caused the formation of greenish corrosion product to be highly reduced. This demonstrates that additives are effective in reducing corrosion of phosphor bronze. Coupons immersed in BTA doped fuels do not show any discolouration on the exposed surface. Therefore, BTA seems to be more effective than TBA in inhibiting corrosion attack for both B20 and B100.

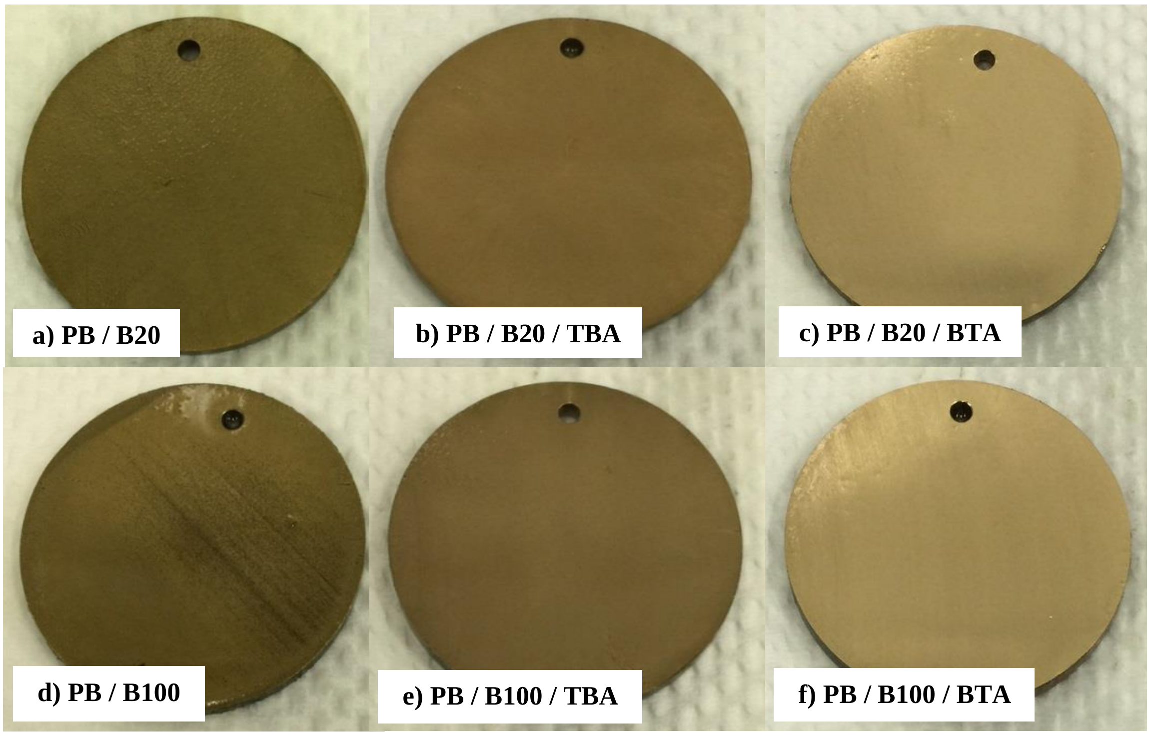


Figure 4.2: Effect of additives TBA and BTA on the appearance of phosphor bronze (PB) upon exposure in B20 and B100

Figure 4.3 shows the colour changes of B20 and B100 before and after exposure to phosphor bronze for 1440 hours. It is seen that the colour of both B20 and B100 turned to yellowish upon exposure of phosphor bronze. The addition of TBA in B20 and B100 in the presence of phosphor bronze does not significantly prevent the change in the fuel colour. The change in colour may suggest the compositional change in the fuel. However, BTA doped fuel for both B20 and B100 does not show a significant change in the fuel colour even after exposure to phosphor bronze when compared to the as-received diesel and biodiesel fuels. This suggests that the addition of BTA may control the change in fuel composition when exposed to phosphor bronze.

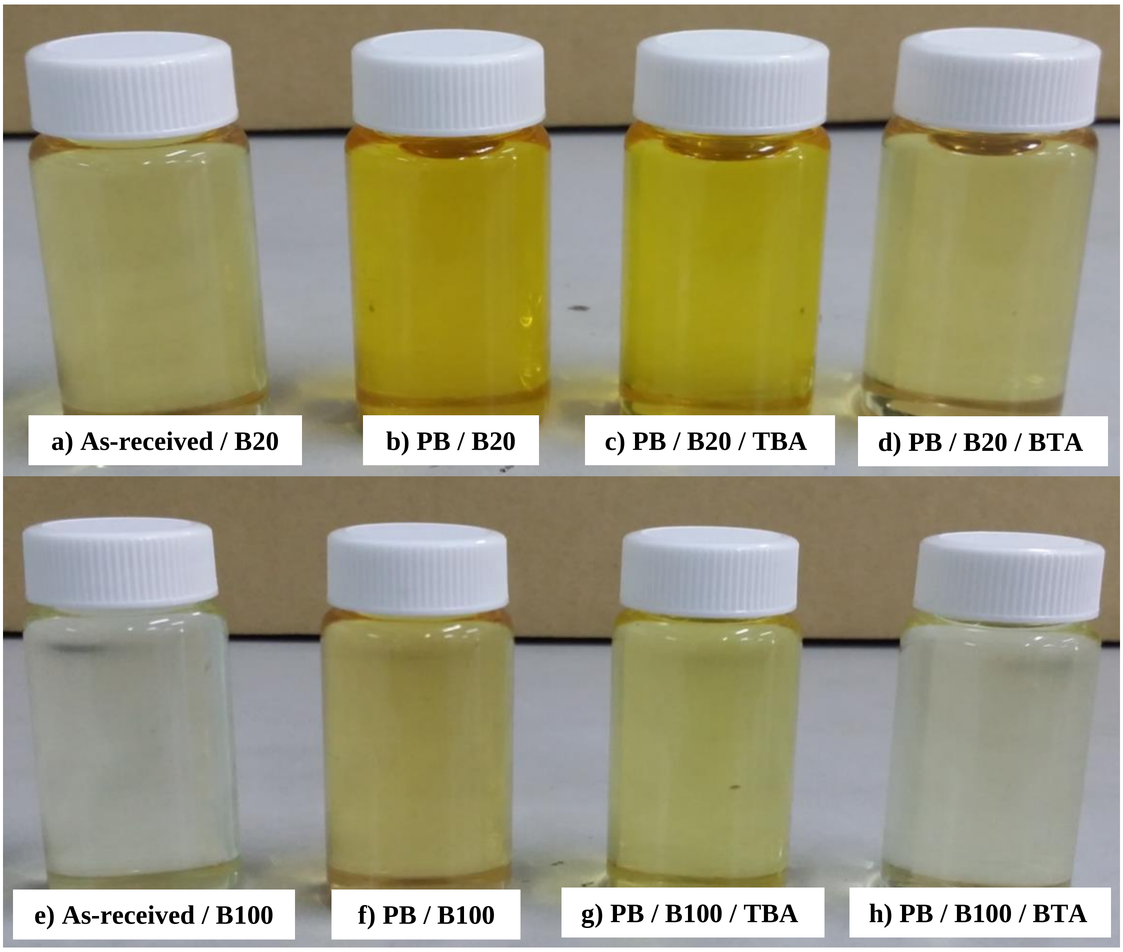


Figure 4.3: Colour of B20 and B100 before (a,e) and after exposure (b-d, f-h) to phosphor bronze (PB) in the absence and presence of additives (TBA and BTA)

4.2. Weight Loss Measurement and Corrosion Rate Calculation

The weight loss measurement of the respective phosphor bronze coupons was recorded and applied to calculate the corrosion rates. Figure 4.4 shows the corrosion rate of phosphor bronze coupons in different fuels. The result shows that increasing biodiesel content in blend increases the corrosion rate of the coupon. However, it does not indicate a significant change in terms of weight loss measurement and corrosion rate calculation in between B50 and B100. Corrosion rates of phosphor bronze in diesel and biodiesel are 0.0063 mpy and 0.0101 mpy respectively. This finding proves that biodiesel fuel is much more corrosive than diesel fuel. Figure 4.5 shows the corrosion rate of phosphor bronze in the absence and presence of TBA and BTA additive.

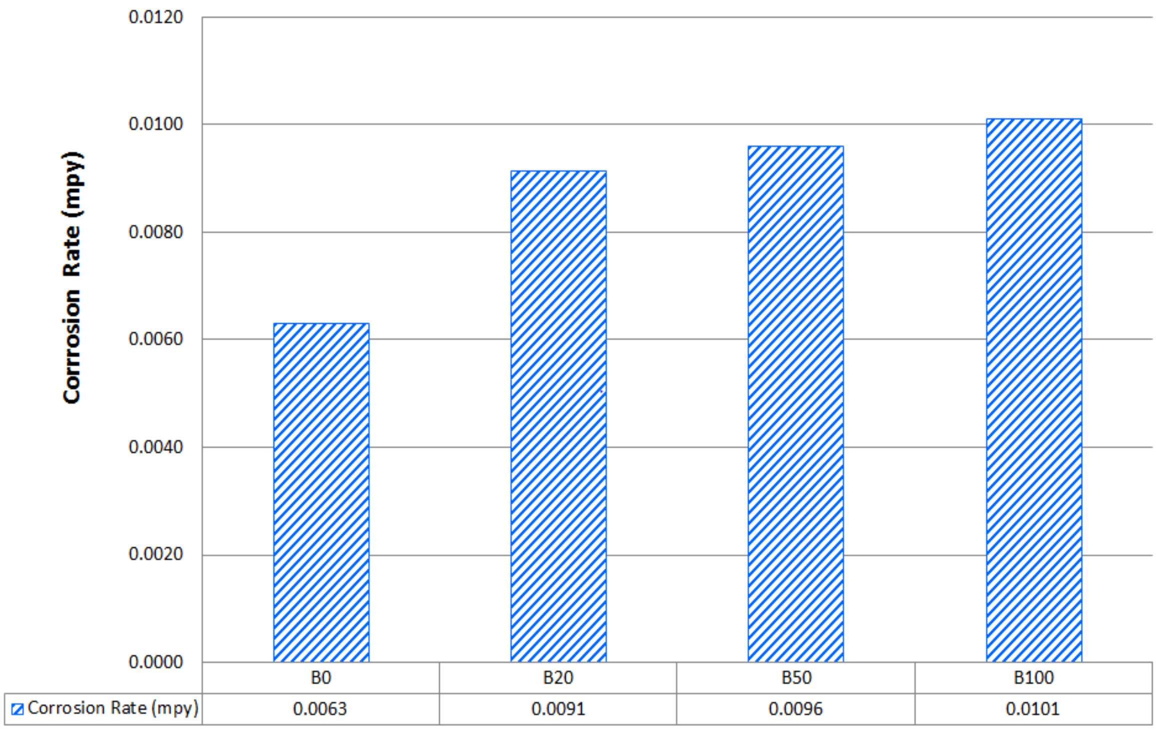


Figure 4.4: Corrosion rate of phosphor bronze in different fuels

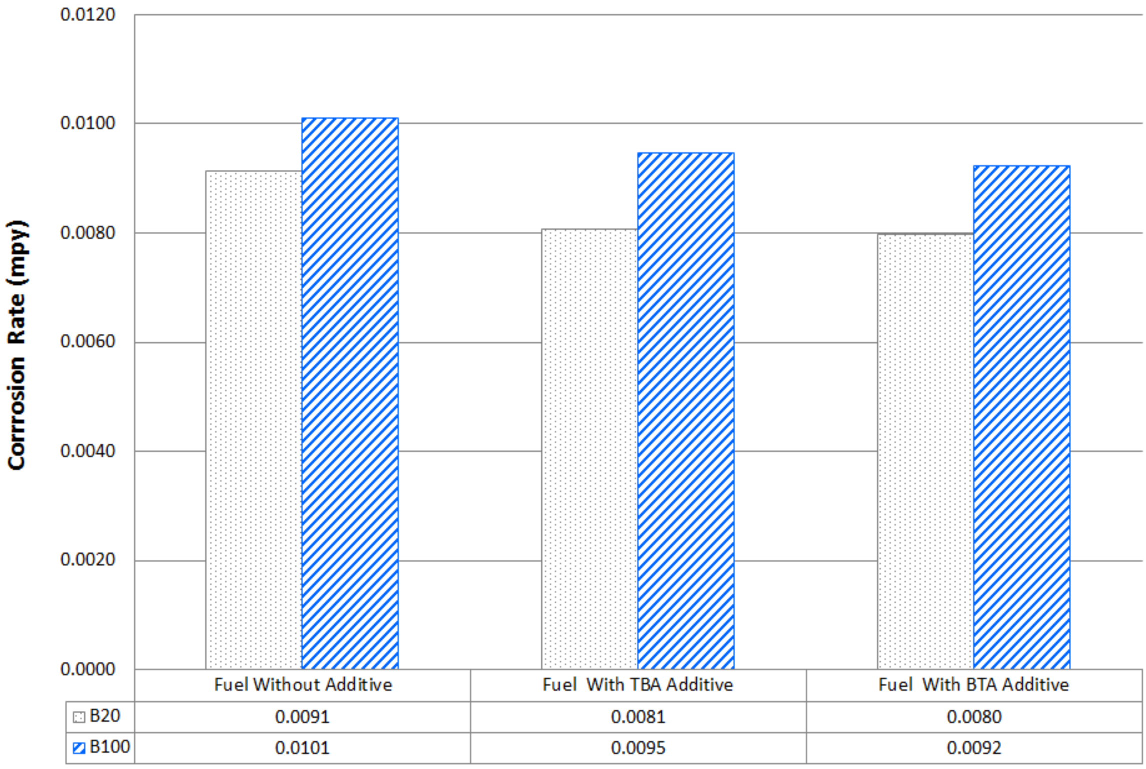


Figure 4.5: Corrosion rate of phosphor bronze in B20 and B100 in the presence of TBA and BTA additive

The results prove that the addition of corrosion inhibitor is capable to retard and provide better corrosion protection to the test sample. It is also seen that BTA acts more effectively in retarding corrosion activity and sample deterioration when compared to the TBA. Corrosion rates of phosphor bronze in B100 fuel doped with TBA and BTA 0.0095 and 0.0092 respectively. Although a significant change is not recorded in terms of corrosion rate, the trend still proves that the addition of corrosion inhibitors improves the corrosion resistance of phosphor bronze.

4.3. Scanning Electron Microscopy (SEM)

Figure 4.6 shows the scanning electron micrographs of phosphor bronze in different fuels. It is seen that diesel is much more resistant to corrosion attack when compared to biodiesel. Localised corrosion takes place on the sample surface. The as-received sample shows a clean and scratch free appearance. Sample B0 shows the least corrosion attack when compared to sample B100. Similar trend was seen in the experimental research conducted by Fazal et al., (2012), proving that increasing biodiesel volume in the immersion solution tends to increase the corrosion rate of the sample. It was also stated that copper and brass tends to exhibit a higher corrosion attack in the biodiesel environment.

Figure 4.7 shows the scanning electron micrographs of phosphor bronze in B20 and B100 fuels in the presence of TBA and BTA additive. The results supports the findings that increasing biodiesel percentage in the immersion solutions tends to increase the corrosion attack on the sample. The corrosion attack on sample B100 in the presence of TBA additive is visibly more severe when compared to the corrosion attack on sample B20 in the presence of TBA additive. The result also shows that the addition of TBA in B20 and B100 in the presence of phosphor bronze does not provide significant corrosion protection to phosphor bronze sample.

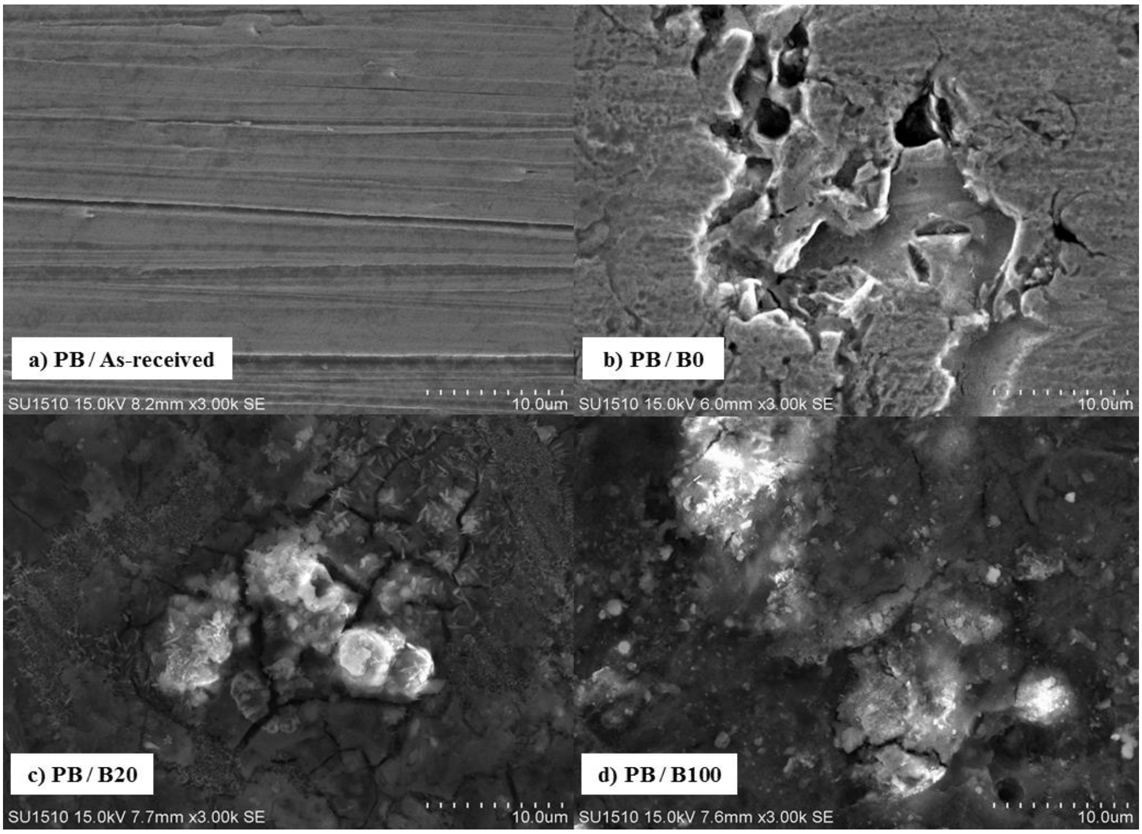


Figure 4.6: SEM micrographs of phosphor bronze (PB) in different fuels

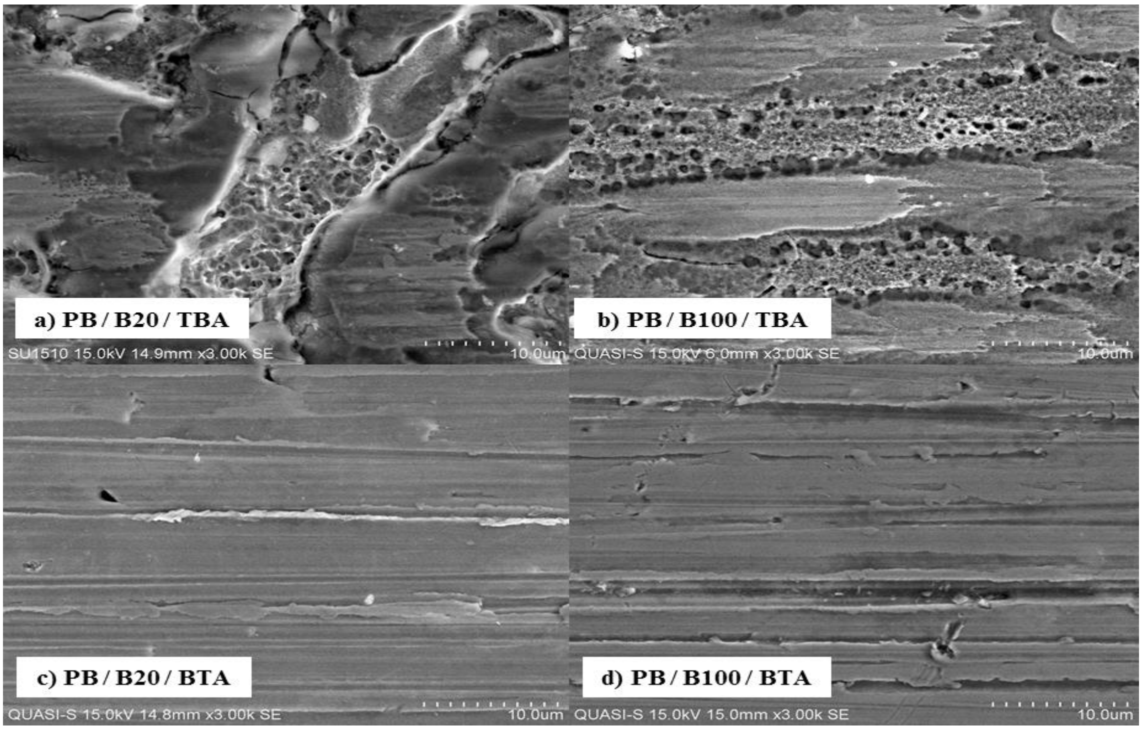


Figure 4.7: SEM micrographs of phosphor bronze (PB) in B20 and B100 in the presence of TBA and BTA additive

BTA addition is seen to be more effective in corrosion inhibition of copper and copper based alloys. The least physical variation in terms of corrosion attack can be noted when comparing the SEM micrographs in between as-received phosphor bronze (Figure 4.5) and sample immersed in biodiesel in the presence of BTA (Figure 4.6). This finding is in line with a review conducted by Finšgar & Milošev, (2010) stating that BTA forms a protective barrier film when in contact with copper and copper alloys. BTA is more effective at higher pH values, leading to the formation of Cu(I)BTA surface complex that is responsible for corrosion protection.

It was reported that thickness of the Cu(I)BTA layer is dependent on the transport of Cu(I) ions from the copper metal to the surface layer, whereby the transferred cuprous ions will then react with the physisorbed BTA molecules and form Cu(I)BTA protective layer. It was concluded that the increasing thickness of Cu(I)BTA layer, tends to increase the inhibitory effectiveness of the layer. However, the actual theory on the corrosion inhibition mechanism of BTA on copper and its alloys is still not well defined and requires more clarification and in depth research (Finšgar & Milošev, 2010). Based on these findings, BTA is seen to be the most efficient and effective corrosion inhibitor for phosphor bronze in biodiesel environment.

4.4. Energy Dispersive X-Ray (EDX)

The elemental study was conducted on phosphor bronze immersed in different fuels. Figure 4.8 shows the elemental study of phosphor bronze before and after immersion test. It is seen that there is increasing oxygen content on the sample surface, with increasing biodiesel content in the blend. The as-received phosphor bronze does not indicate the presence of any elements of oxygen on the metal surface. Sample immersed in pure diesel, B0, contains the least amount of oxygen, that is 6.90 wt% while sample immersed in pure biodiesel contains the most amount of oxygen content, that is 20.07 wt%. There is also an increase in the carbon content when comparing between B0, B20 and B100.

Similar findings were reported through research stating that the higher concentration of oxygen drives to increase the reaction between metal and metal compounds (Fazal et al., 2012). This eventually increases the weight loss and corrosion rate of the metal. It is also seen that the copper content decreases with increasing biodiesel content in the immersion solution. The oxidation of metal to form different oxides and metal compound in the presence of oxygen, leads to the dissolution and decrease in the copper content of the metal.

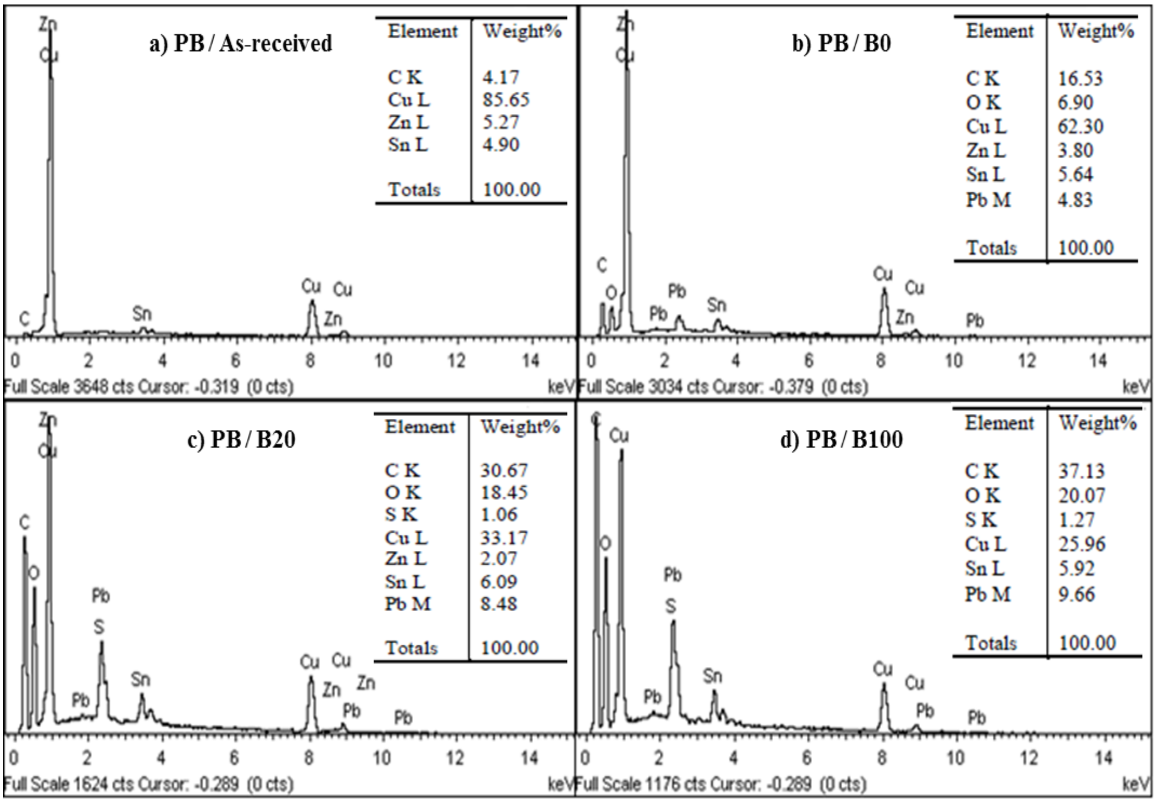


Figure 4.8: EDX of phosphor bronze (PB) in different fuels

The increasing metal oxidation is also due to the hygroscopic nature of biodiesel, which causes water retention. Water is available through condensation or dissolution in the air. Excessive water retention can also promote microbial growth and contamination within the biodiesel fuel. These factors are also able to increase metal dissolution and corrosion attack on the sample (Jakeria et al., 2014). There are also traces of Lead (Pb) element detected on the test sample immersed in solution B0, B20 and B100. This element was however not detected on the as-received sample. The actual theory regarding the corrosion mechanism and chemical reaction of phosphor bronze is not clearly defined and requires further in-depth research. Figure 4.9 shows the elemental study of phosphor bronze in B20 and B100 fuels in the presence of TBA and BTA additive.

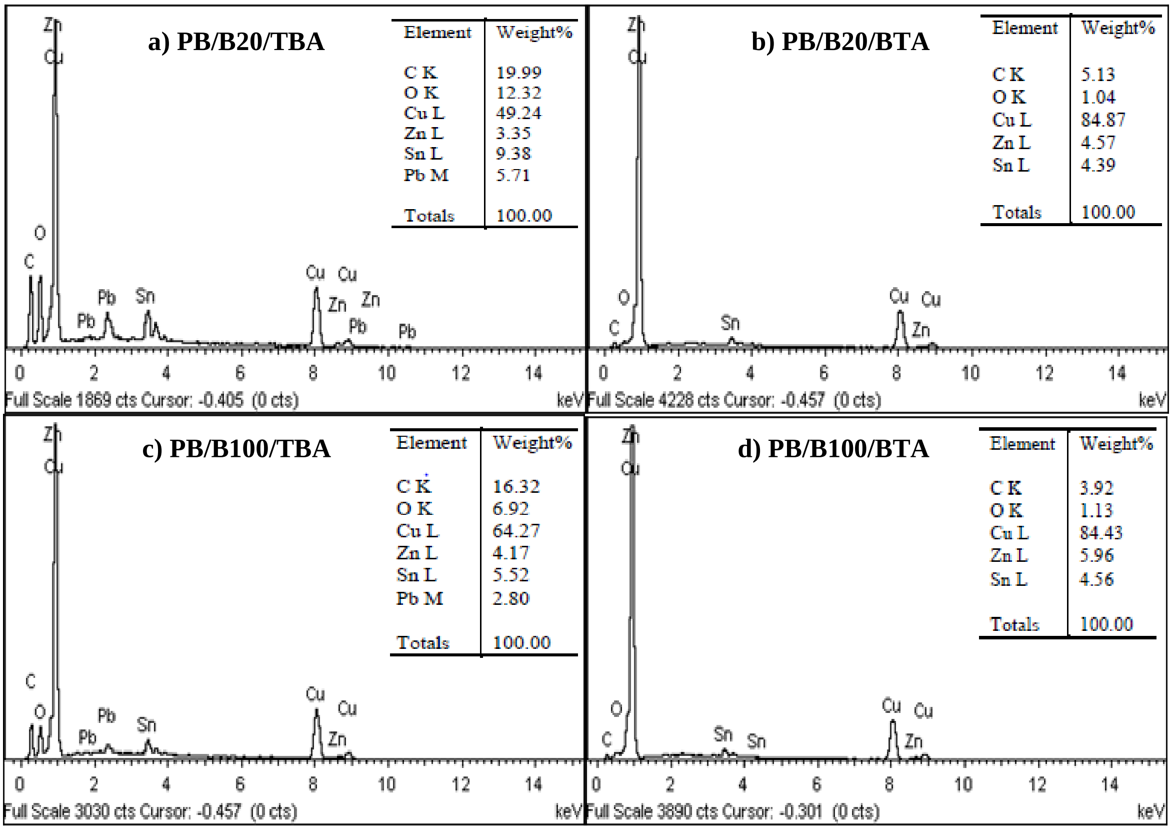


Figure 4.9: EDX on phosphor bronze (PB) in B20 and B100 in the presence of TBA and BTA additive

The comparison of elemental analysis in the presence of additive shows that the corrosion inhibitor works in favour to retard the corrosion activity on the metal surface. Based on the results, there is a decrease in the oxygen content accordingly from 18.45 wt % in B20 fuel in the absence of additive to 12.32 wt% in B20 fuel with TBA additive to finally 1.04 wt% in B20 fuel with BTA additive. The similar trend was seen when comparing the elemental analysis in B100 fuels, in the presence and absence of TBA and BTA additive respectively.

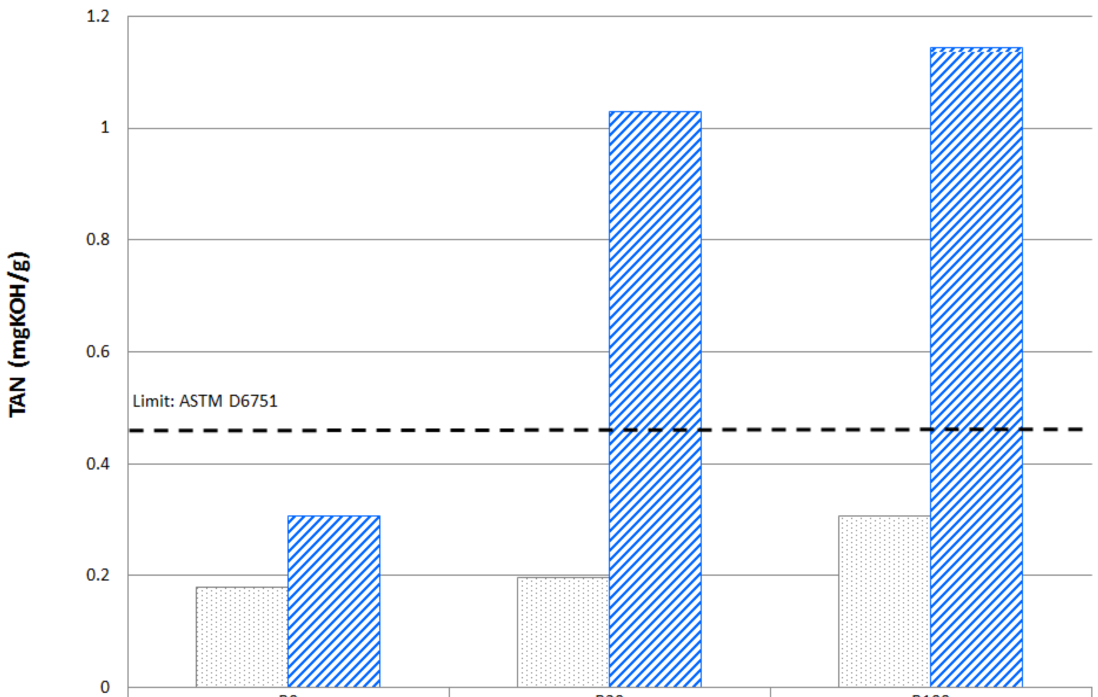
The results show that BTA acts as the most effective inhibitor addition for copper and copper alloy. The low oxygen and carbon content and high copper content show that metal oxidation and dissolution reaction is not significant. It is also noted that lead element is present in the samples immersed in TBA doped fuels, but not present in samples immersed in BTA doped fuels. The addition of BTA corrosion inhibitor increases the protection against corrosion and metal deterioration, thus making the material suitable to be used in the biodiesel environment.

However, the velocity control within the operating condition is an important factor to be considered when attempting the use of BTA additive addition in biodiesel environment. A review by Khan et al., (2015) explains that the increasing velocity subjected to the sample causes the more damage to the copper surface, leading to increased exposed area for corrosion activity. Copper samples undergo passivation and depassivation of protective film with increasing rotating velocity, leading to the formation of pitting corrosion. However, it was seen that the effects of flow on copper decreases with the increase of BTA concentration, proving that BTA with appropriate concentration is able to provide sufficient protection to copper when under constant flow or rotating condition (Khan et al., 2015).

4.5. Total Acid Number (TAN)

The standard limit of TAN value in biodiesel blend stocks is 0.5mg KOH/g, as per ASTM D6751. This represents the content of fatty acid within the solution. Figure 4.10 shows the TAN value recorded before and after immersion for B0, B20 and B100. The TAN analysis shows that the as-received fuel of B0, B20 and B100 is well and below the standard limit of 0.5mg KOH/g (Yaakob et al., 2014). However, there is an increase in the overall TAN value after immersion test. It is seen that pure diesel (B0), undergoes an increase in the TAN value after immersion, but still exhibits an acceptable TAN value of 0.305mg KOH/g, that is below the standard limit.

B20 and B100 show a drastic increase in the TAN, far exceeding the standard limit, giving a value of 1.028mg KOH/g and 1.142 mg KOH/g respectively. The trend shows that the TAN value increases with increasing biodiesel in the fuel. In other words, there is an increase in the free fatty acid content within the fuels, thus requiring a higher volume of KOH to neutralise the fuel. The increasing TAN value is due to the increasing level of biodiesel oxidation to form free fatty acids in the fuel. The presence of corrosive acids in the fuel can also lead to the increase in TAN value (Fazal et al., 2012).



	B0	B20	B100
Before Immersion	0.178	0.196	0.306
After Immersion	0.305	1.028	1.142

Figure 4.10: Change in TAN of different fuels, before and after immersion test

Figure 4.11 compares the TAN value recorded for B20 and B100 in the absence and presence of TBA and BTA additive. Based on the results, it is seen that there is a decrease in the TAN value for both B20 and B100, in the presence of corrosion inhibitor. It is also noted that fuels doped with BTA shows the least increment in TAN value when compared to the as-received fuels.

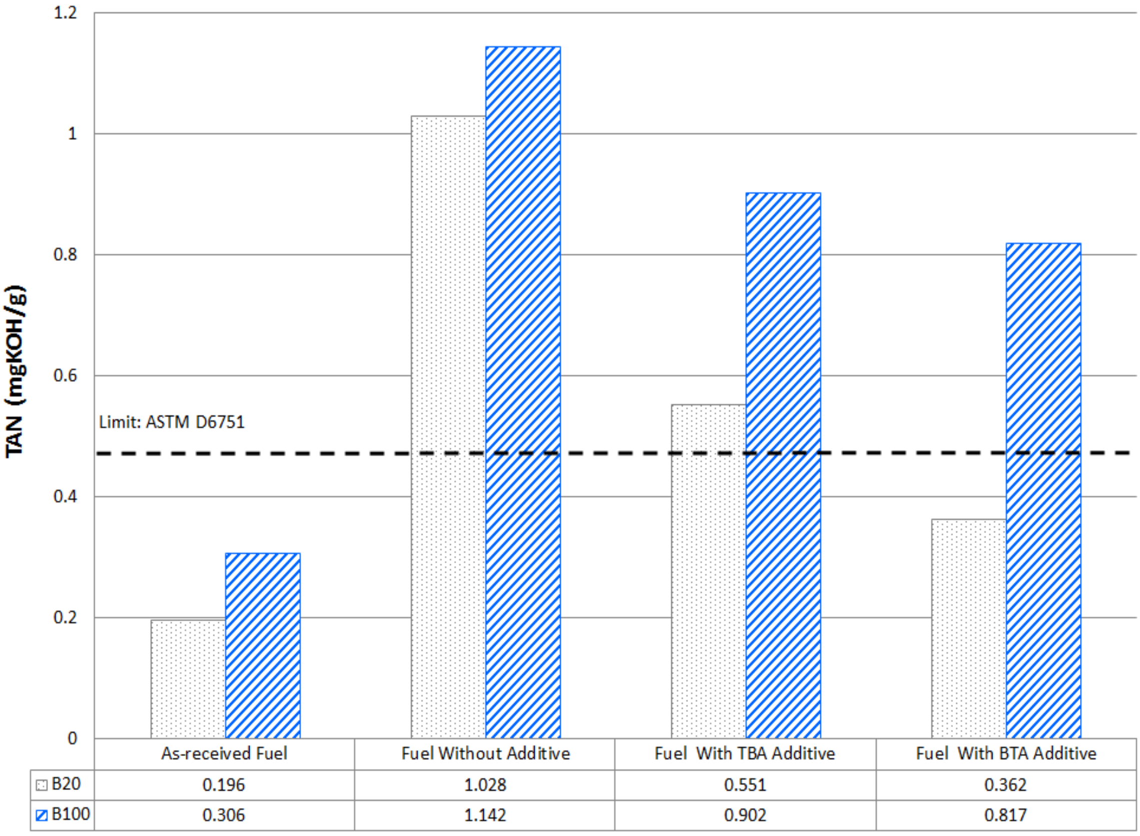
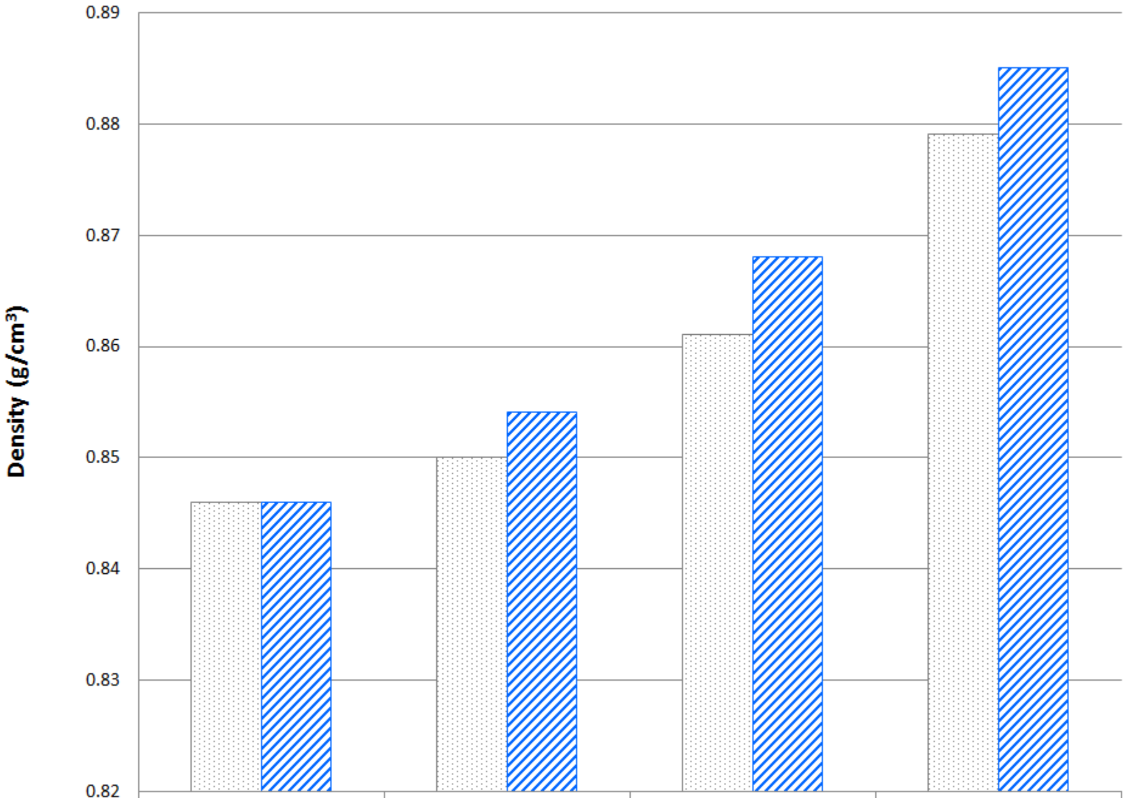


Figure 4.11: Comparison of change in TAN of B20 and B100 in the absence and presence of TBA and BTA additive

4.6. Density

The standard density of as-received diesel is 0.842 g/cm^3, while the standard density of as-received biodiesel is 0.875 g/cm^3. Figure 4.12 shows the density of B0, B20, B50 and B100 before and after immersion test. The results indicate that the increasing biodiesel from B0 to B100 increases the density of the fuel. B0 that is pure diesel shows the least increase in the density of fuels. This result is in line with much research, stating that the density of biodiesel is higher than that of diesel (Hoekman et al., 2012), whereby increasing biodiesel content in the blend increases the density of the fuels. The increase in density of biodiesel can be due to the increase in higher molecular weight compound in the solution (Fazal, Jakeria, et al., 2014). This is supported by the increase in the free fatty acid number as shown through TAN analysis.



	B0	B20	B50	B100
Before Immersion	0.846	0.85	0.861	0.879
After Immersion	0.846	0.854	0.868	0.885

Figure 4.12: Change in density of different fuels exposed to phosphor bronze

The hygroscopic nature of biodiesel that is capable for water retention, can lead to the increase in the overall density of the fuel. This is because the density of water that is 1 g/cm^3 is much higher when compared to the initial density of biodiesel used in this research. Other than that, increasing oxidation rate, metal dissolution and corrosion products can also increase the density of the fuel (Yaakob et al., 2014). Increasing density can lead to lower viscosity properties, resulting in the formation of precipitation compounds and sediments that can plug and damage the filters and pumps in the CI engine (Hoekman et al., 2012).

Figure 4.13 shows the density measurement of B20 and B100 in the presence of TBA and BTA additive. Based on the results, it is seen that there is a decrease in the density of the fuels. BTA doped fuels tends to be more effective in reducing the density of the fuel when compared to the addition of TBA. This finding is supported by the similar decreasing trend seen through TAN analysis, thus proving that corrosion inhibitors, particularly BTA is a practical solution for corrosion prevention of phosphor bonze in the biodiesel.

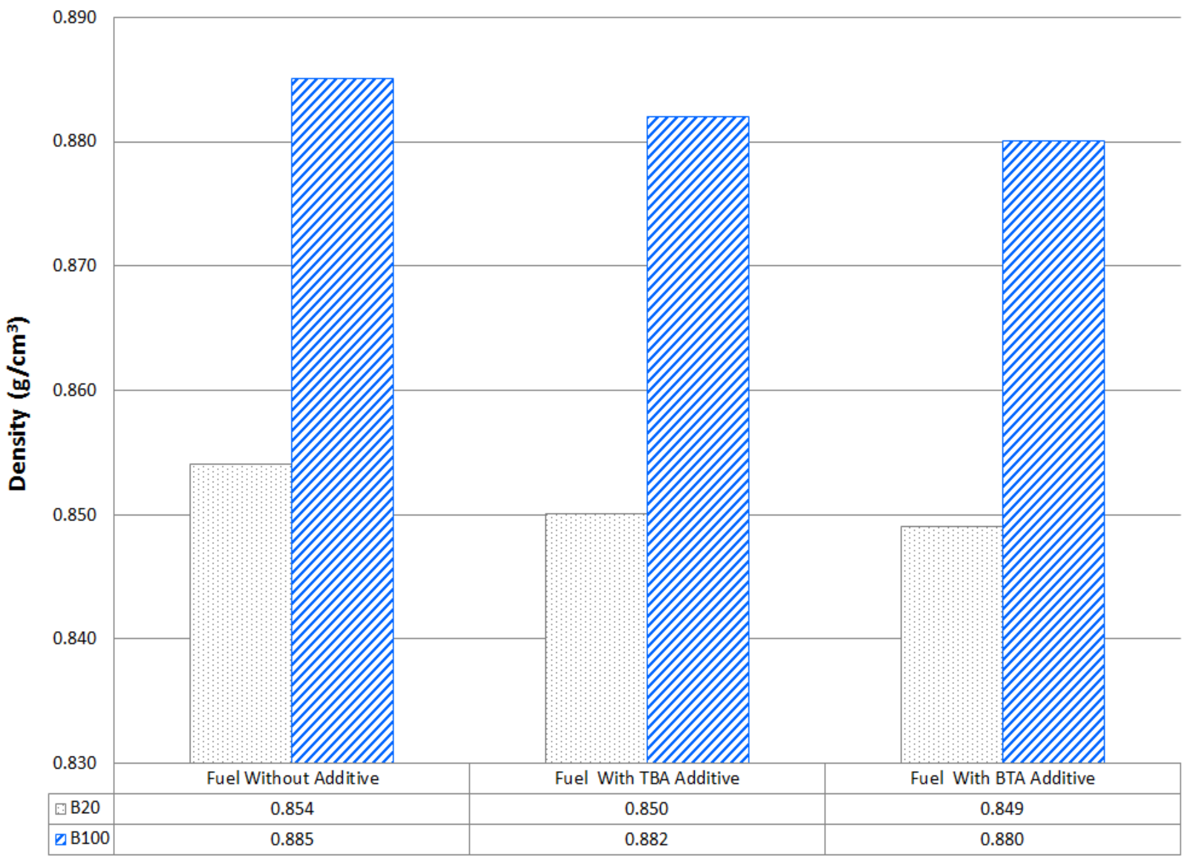


Figure 4.13: Comparison of density of fuels in the absence and presence of TBA and BTA additive

CHAPTER 5 : CONCLUSION

5.1. Introduction

This research has shown that biodiesel fuel is much more instable when compared to diesel fuel. This is due to variation of characteristic in the basic composition of biodiesel, especially the level of saturated and unsaturated fatty acid esters. The conclusions drawn from this research are:

I. There is an increasing greenish colour appearance on phosphor bronze with increasing biodiesel in the fuel. The lowest corrosion activity was recorded in the B0 while the highest corrosion rate was recorded in the B100. The presence of corrosion inhibitors was seen to reduce the corrosion rate of phosphor bronze. The addition of BTA is most effective in reducing the corrosion rate of phosphor bronze when compared to the addition of TBA.

II. The SEM micrographs results show phosphor bronze immersed in B100 has the highest corrosion attack with localised thinning on the surface. B0 shows the least corrosion attack. TBA doped fuel does not provide sufficient protection to phosphor bronze when compared to BTA doped fuels that shows minimum corrosion attack with almost similar appearance to the as-received test sample prior immersion.

III. There is an increase in the oxygen and carbon content with increasing biodiesel in the fuel. This indicates that there is an increase in the corrosion compound formed on the sample surface. The addition of TBA and BTA reduces the oxygen and carbon elements detected on phosphor bronze. BTA is seen to be more effective in reducing the formation of corrosion compounds when compared to TBA.

IV. There is an increase in the acid value of the test solution with increasing biodiesel content. B100 solution shows the highest TAN value among the different fuels. The addition of BTA additive gives the lowest TAN value for both B20 and B100 solution that is 0.362 mg KOH/g and 0.817 mg KOH/g respectively. It is seen that increasing biodiesel content leads to the dissolution and oxidation of biodiesel to form free fatty acids, thus resulting in the instability of biodiesel.

V. The density of biodiesel fuel is higher that diesel fuel. Increasing biodiesel content in the test solution tends to increase the overall density of the blend. Biodiesel solution B100 shows that highest density of 0.885 g/cm^3. The addition of corrosion inhibitor is seen to reduce the density of both B20 and B100 immersion solution. The addition of BTA additive acts as an effective corrosion inhibitor giving the lowest density of 0.848 g/cm^3 and 0.880 g/cm^3 for both B20 and B100 fuels.

VI. The performance of phosphor bronze test sample is highly affected by the content of biodiesel in the immersion solution. Increasing biodiesel content in the solution tends to increase rate of metal dissolution and corrosion attack on the test sample. The addition of corrosion inhibitors is capable to improve the corrosion resistance of phosphor bronze. BTA additive serves as a better and more efficient corrosion inhibitor in reducing the corrosion attack on phosphor bronze.

5.2. Future Recommendations

I. In-depth research and further experiment can be conducted to understand the mechanism of BTA additive in reducing corrosion of phosphor bronze in biodiesel.

II. X-Ray Diffraction (XRD) study on the test coupon can be performed to analyse the crystalline material and determine the composition of the corrosion product, to better understand the corrosion mechanism that takes place when dealing with phosphor bronze. This will also support in understanding the origin of Lead (Pb) element detected on phosphor bronze upon complete immersion, except for sample immersed in B20 and B100 fuels with BTA additive.

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