

The Impact upon Applicability of Metal Fuel Tank Using Different Biodiesel

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ABSTRACT

With the development of world economy, the shortage in the supply of oil energy as well as the greenhouse effect have become a public concern around the world. The application of biodiesel on vehicle transportation has become the focus of development in many countries. Biodiesel, Fatty Acid Methyl Esters (FAME), is made during the process of transesterification of the animal and vegetable oils. Compared with fossil diesel, biodiesel has some characteristics, such as organic acid, higher water saturation, and oxygen content. From the results of the literatures [1] to [5], it showed that biodiesel would cause the inflation of some plastic and flexible products and the corrosion of metal materials.

Metal fuel tanks have the characteristics of high flammability, high impact resistance, and good workability and are often used in commercial vehicles. The corrosion of metal materials is a natural chemical change and it can be influenced by the environment. The metal materials soaked in biodiesel will show different rates of corrosion and phenomenon, influenced by the factors such as water content, PH value, dissolved oxygen, temperature, conductivity, microorganism attachment and so on. Therefore, nine different oils (D100, B2, B5, B10, B20, B40, B60, B80, and B100) and four different samples of metal fuel tanks (Zn, ZnSn, SUS 304 and SUS 316) were used in this study under the conditions of room temperature, and high humidity. With the samples soaked for 2400 hours, the visual investigation was used for surface observation, the film thickness gauge was used to measure the thickness of Zn coating, SEM & EDS qualitative analysis were conducted, and the conductivity of the oils was analyzed periodically to study the impacts of biodiesel on fuel tanks.

The results of this study showed that after being soaked for 2400 hours, on the surfaces of the four different metal fuel tank samples, rust or corrosion were not found. There were some color changes found on the Zn coated samples soaked in B40 and above, but the thickness of Zn coating was not reduced. Using the SEM & EDS element analysis, it was found that there was some oxidization on the Zn coated samples with the increase of the percentage of the biodiesel. As for the stainless steel samples, little oxygen was measured. However, for the quality of biodiesel, the performances on conductivity, oxidation stability and the amount of dissolved Zn from the Zn coated samples using high percentage biodiesel (B20 and above) were poor. If the fuel tank was made of Zn coated material, it might increase the deterioration of high percentage biodiesel. Therefore, it is suggested that when using or transporting low percentage biodiesel (B20 and below), the material of the equipment should be coated with Zn or stainless steel. However, when storing high percentage biodiesel for long hours, the storage equipment should be made of stainless steel to avoid speeding the deterioration of the quality of the oils.

KEYWORDS: Biodiesel, Fuel Tank, Durability

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1. INTRODUCTION

The corrosion of metal materials is a natural chemical change and it can be influenced by the environment. It will also be affected by soaking in different fluids. The metal materials soaked in biodiesel

will show different rates of corrosion and phenomenon, influenced by the factors such as water content, PH value, dissolved oxygen, temperature, conductivity, microorganism attachment and so on



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1. Temperature

The change of the temperature of the fuel tanks was affected by fuel return flow and the temperature of the environment. The variation of temperature is closely related with the chemical property, physical property and the growth of microorganism of biodiesel. Therefore, the change of temperature is a very complicated variant of the metal material corrosion reaction mechanism. Generally speaking, temperature affects the reaction speed and mass delivery of dynamics. According to the theory of dynamics, when the temperature of fluids arises 10 K, the corrosion speed doubles. When temperature arises, the reduction potential of metal materials becomes lower. It means steel materials react to corrosion more easily.

2. PH Value

Biodiesel was produced by animal or vegetable oils or discarded edible oils during the chemical process of transesterification. (It is generally referred as the organic chemical reaction of alcohols and acid interaction to produce ester and water). It contained the organic acids, such as linolenic acid methyl ester, fatty acid methyl ester and so on, and these will affect the PH value of biodiesel. Acid value will be changed during the process of oxidation. The researches showed [6,7] that the variation could be the index of the stability of B100. If biodiesel is not used immediately after purchasing, the purchasers should monitor the variation of acid value of biodiesel as the index of oil degradation. If the fuel oil contains acid, it could harm the injection system and other metal components.

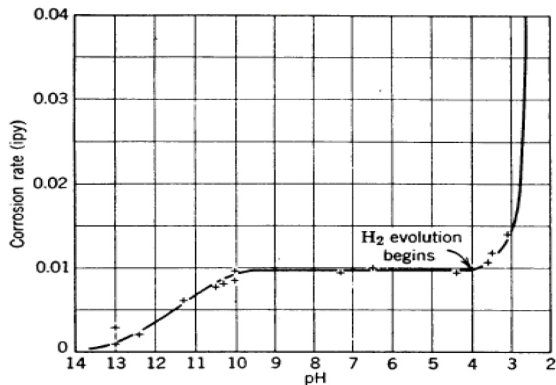


Figure 1-1. Relation of the Corrosion Rate of the Steel Material and the PH Value [8]

The corrosion reaction speed of the metal materials in the fluids is closely related with the PH value. When the PH value is between 4 and 10, the corrosion speed of the metal remains at certain rate and is only related with the speed of oxygen spreading to the surface of the metal, as shown in Figure 1-1. Usually, when the steel materials are eroded in the fluids, a membrane of $\text{Fe}(\text{OH})_2$ will be formed on the surface of the metal to block the expansion of oxygen. During the process of corrosion, the membrane will be formed continuously and contact with the alkaline fluids. When the PH value of the fluids is under 4, the $\text{Fe}(\text{OH})_2$ on the surface of steel material will be dissolved and the rate of corrosion will increase. However, when the PH value is over 10, with the increase of alkalinity, the PH value of the surface of the steel is also increased. The passive protection membrane will not be dissolved easily and therefore, the rate of corrosion will be lowered hugely.

3. Dissolved Oxygen

Biodiesel is composed with the chemical compounds such as methyl ester. Methyl ester contains higher oxygen content, which is about 11 %. Oxygen is the main assistant for the corrosion of metal. It is mainly because during the process of the electrochemical reaction of the metal corrosion, oxygen reacts with the fluids to form OH^- in the cathode half-reaction and OH^- reacts with the Fe^{+2} dissolved during anode half-reaction to create the corrosion product, $\text{Fe}(\text{OH})_2$. If the supply of oxygen is sufficient, $\text{Fe}(\text{OH})_2$ will form various kinds of rust products. The corrosion rate of the steels in the fluids depends on the dissolved oxygen on the surface. If the dissolved oxygen in the fluids increases, the oxygen contacted with the surface of the steel also increases, so the corrosion rate will increase, too. The relative relation is shown as Figure 1-2.[9]

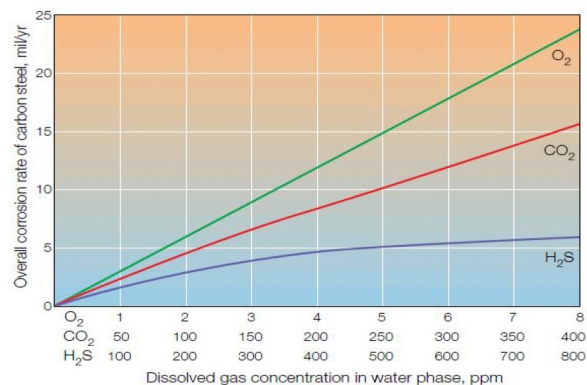


Figure 1-2. Relation of the Corrosion Rate of the Steel Material and the Dissolved Oxygen [9]

4. Conductivity

Compared with fossil fuel, biodiesel has higher conductivity. According to the research of National Biodiesel Board, NBB[7], the conductivity of biodiesel of different percentages differed hugely and rose exponentially with the percentage of the biodiesel, as shown in Table 1-1. The conductivity of the fluids is an important factor to determine the degree of metal corrosion, especially with the Galvanic coupling effect or partial gap on the metal surface. The aqueous solution of higher conductivity will easily cause huge area of the metal surface for corrosion reaction. When the anode area is smaller and the cathode area is bigger on the metal surface, the corrosion is especially serious and will form partial pitting corrosion or crevice corrosion. The inverse of the conductivity is resistivity, which is one of the main factors affected the waste of anode material in the cathode anti-corrosion design.

Table 1-1. Relation of the Conductivity of the Biodiesel with Different Percentages [10]

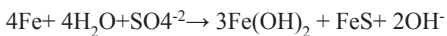
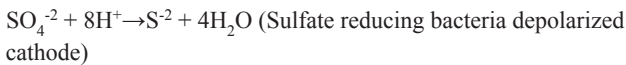
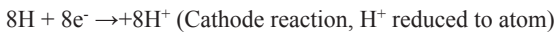
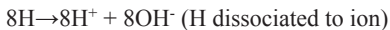
The conductivity of different biodiesel blend (pS/m)						
Biodiesel -%	0%	2%	20%	40%	60%	100%
conductivity	2	4	75	358	775	1209

*Results Courtesy of the National Biodiesel Board.

5. Microorganism Attachment

Microorganism attachment is not one of the general corrosion forms for the steel corrosion. It deteriorates the metals by attaching organic microorganism. The common microorganism in the oils will increase by the amount of water contained. There are various kinds of organism in water. The microorganism exists in the water but can obtain nutrition from the interface between oil and water and creates deposits sinking to the bottom of the fuel tanks. The kinds and growth of the organism will be affected by the factors of the temperature, luminosity and nutrition in the fluids. The processes of corrosion due to microorganism attachment are described as follows:

- Cause the depolarization of cathode to influence the characteristics of corrosion or speed the corrosion rate.
- Because metabolism or excretions of organic acids create the environment for easy corrosion, steel will react with acidity to cause serious partial corrosion.
- Destroy the passive protection membrane on the surface of the metal.
- Cause the oxygen concentration cell on the surface of the metal.
- The product of sulfides in the fluids or around the surface of the metal will cause sulfate reducing bacteria becoming more corrosive. The corrosive mechanism of sulfate reducing bacteria to the steel material is as the followings:



2. EXPERIMENTAL METHODS

This study mainly analyzed the impacts of fossil diesel (D100), pure biodiesel (B100), and different percentages of biodiesel on the fuel tanks coated with Zn, ZnSn, SUS 304 and SUS 316. The testing items are shown in [Table 2-1](#).

The tests mainly analyzed the corrosion of the samples of the fuel tanks, including the corrosion of the appearance of the metal, the thickness of the Zn coating, the metallographic analysis of the Zn coating, the degree of oxidization, the amount of Zn deposited, the degree of oxidization of the oil and the conductivity of the oil. The time of soaking in the entire study was 2400 hours, the temperature was set at 27°C to 30°C, and the humidity was around 72% to 78%, (referred to the annual average temperature and humidity of the summer in Taiwan). The samples were placed indoor and devoid of

sun light. Under the long-time soaking, the corrosion impacts of testing oils on the fuel tanks were observed. The procedure of the experiment is shown in [Figure 2-1](#).

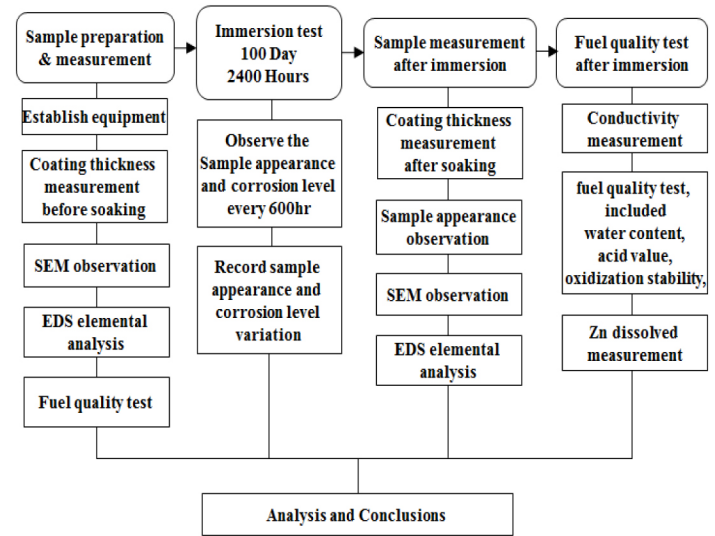


Figure 2-1. Description of the Procedure of the Experiment

Table 2-1. Testing Items of the Durability Verification of the Long-Time Soaking of Fuel Tanks

Testing Items	Testing Methods	Descriptions
Appearance	The Degree of Corrosion of Appearance	Use visual investigation to observe the corrosion of the surface
Thickness of the Zn Coating	Measure the Thickness of Zn Coating	Use the film thickness gauge to measure the thickness of Zn coating before and after soaking
Metallographic Analysis of the Zn Coating	SEM Scanning Electron Microscope	Use SEM to take pictures of the samples to observe if there was any special change of the metallogenesis
Degree of Oxidization	EDS Spectrum Component Analysis	Use the EDS spectrum component analysis to observe if the soaking would influence the samples
Amount of Zn Deposited (Dissolved Zn)	ICP-MASS	Examine the oils with different percentages before and after soaking to observe if the soaking would influence the oils. Analysis items included water, acid value, oxidization stability, the amount of Zn deposited, conductivity and so on.

3. EXPERIMENTAL RESULTS

There were four kinds of metals used in this study, including Zn, ZnSn, SUS 304 and SUS 316, with nine oils of different percentages. It means that there were 36 samples, but because there were too many samples, this study mainly focused on the analysis of the durability of using D100, B5, B20, and B100 on the material coated with Zn and SUS 304.