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An investigation into galvanic corrosion within compression ignition (CI) fuel systems caused by the increased conductivity of hydrocarbon diesel when doped with biodiesel

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Abstract

Biodiesel is derived from plant or animal fats, through the use of a transesterification reaction which converts long-chain fatty acid alkyl esters into smaller ester molecules with a glycerine by-product. This results in a fuel that is more electrically conductive compared to regular diesel. This paper has collected and analysed research data for corrosion caused by the properties of biodiesel doped regular diesel in fuel systems. Data is analysed, causes investigated and then solutions are explored. Research into the corrosion potential at the material-fuel interface between biodiesel and components compared to regular oil diesel is an important part of bio-fuel development and application feasibility in automobiles.

1. Introduction

An international trend shift away from hydrocarbon fuel due to increasing resource scarcity, public and political pressure, pollution and certainly desire for an eco-friendly image from oil corporations has led scientists and engineers to study alternate fuels. It is important to understand any corrosion issues with new fuels in current fuel systems to achieve longer service life and better safety performance in the automotive industry. Biodiesel can be produced from plant or animal fats, chemically these fats are viscous triglycerides, composed of three long-chain fatty acids, a transesterification reaction using monohydric alcohol [3] is employed to break each fat molecule into three smaller molecules called esters [1]. Excessive viscosity can be an issue; this is resolved by retaining a percentage of regular diesel, usually up to 50:50, described industrially as B50: B denoting bio then 50% volumetric content. Having properties very close to that of regular diesel, a higher cetane number and containing no sulphur or aromatics, [4] biodiesel appears to be an excellent additive to reduce fossil fuel consumption and emissions. It is noted that impurities such as glycerol, free fatty acids, alcohol and catalyst remaining in the biodiesel cause deposits to accumulate in the engine which also causes corrosion of the fuel system; this has been studied [4]. This method of corrosion has been studied to occur most notably on components manufactured from or contain the metals: copper, aluminium, zinc and to a lesser extent steel [1].

Those many dissimilar metals within a fuel system also pose a different corrosion problem; that of galvanic corrosion caused by dissimilar metals submerged in an electrolyte and electrically connected to each other through earth straps from component to vehicle chassis or monocoque, in this case the biodiesel itself. There are three conditions that must exist for galvanic corrosion to occur. First there must be two electrochemically dissimilar metals present (e.g. copper and steel). Second, there must be an electrically conductive path between the two metals (e.g. steel fuel pipe). And third, there must be a conductive path for the metal ions to move from the more anodic metal to the more cathodic metal (e.g. biodiesel). If any one of these three conditions does not exist, galvanic corrosion will not occur. Where an engineering task requires dissimilar metals come in contact, the galvanic corrosion potential is usually managed by applying finishing or plating, or electrical isolation as previously mentioned. The finishing or plating protection will facilitate the dissimilar materials being in contact whilst protecting the base materials from corrosion, such as paint or plating with an electrochemically similar metal. However this resolution is complicated by some materials having incompatibility with long term fuel exposure and also obviously not solving the problem of biodiesel in vehicles already in use.

To understand the extent of the corrosion problem potentially faced, first the component constituent materials must be identified and analysed. In order from fuel filler to injector in the engine, the materials which are in constant contact with fuel are listed in table 1. Looking at the periodic table, the metals can be listed in their order of nobility to calculate their proximity in the galvanic series which is as follows: Stainless steel, bronze, brass, copper, and steel including tool steel then aluminium [5].

Component	Material
Filler neck, fuel cap	Mild steel, aluminium
Fuel tank	Mild steel, HDPE
Fuel lift pump	Aluminium, brass, stainless steel
Fuel feed/return lines	Mild steel
Diesel injection pump	Tool steel, aluminium, copper, bronze
Injection lines	Mild steel
Injectors	Tool steel, mild steel, aluminium
Fuel filter, pre filter	Stainless steel, mild steel, brass, aluminium

Table 1: Component materials of a typical automobile fuel system

2. Experimental

Before each experiment the apparatus was degreased with alcohol and rinsed with deionised water. Each experiment was repeated three times and the mean figure used for comparison. The apparatus was setup as figure 1, from a rectangular polycarbonate tray (X 13 x Y 50 x Z 30 cm) and was fitted with copper electrodes glued to each end of the long sides with epoxy (Figure 2) to contain the biodiesel blends. The fuel was filled to 2cm depth during each experiment. All equipment and fuels used were at room temperature of 25^{o}C. The apparatus was washed with ethanol before and after each experiment and each experiment was repeated three times and the results for each blend averaged.

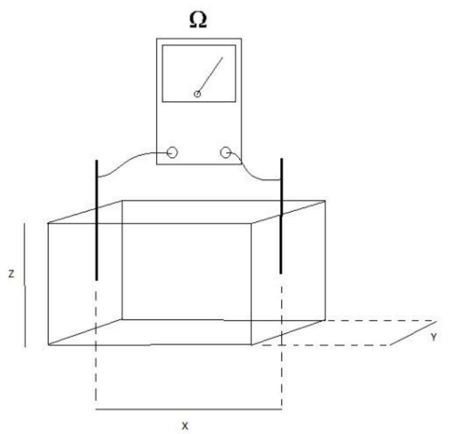

Figure 1: Liquid conductivity testing apparatus

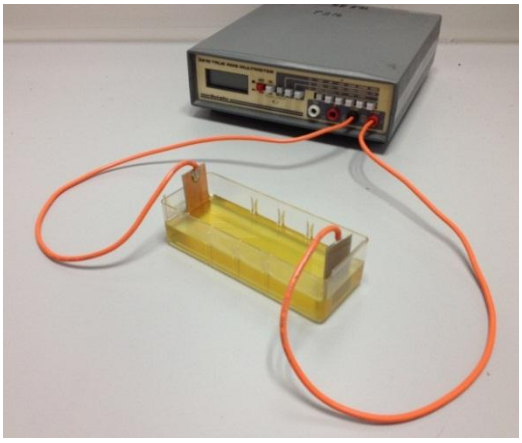

Figure 2: Apparatus used for experiment

2.1 Fuel used to experiment

The biodiesel used in the investigation for this paper was prepared from waste vegetable oil (WVO) sourced from local catering businesses including restaurants and takeaways, typically containing palm, soybean, rapeseed, corn and sunflower oil, as well as contaminants from use such as a wide variety of animal fats, water and tallow, drastically lowering the quality over virgin produced biodiesel. (Bio Solutions, Holton Heath Industrial Estate, UK). This may not be a suitable biodiesel to use for this analysis because most commercially available biodiesels and current biodiesel research focus on virgin biodiesel produced from the above plant oils. The regular diesel used was purchased from a local fuel filling station outlet (Low sulphur diesel, Texaco Ltd, Dorset, Bournemouth, UK).

2.2 Methodology

The electrical conductivity of the liquid (SI unit: S/m) was determined by measuring the resistance between two electrodes of 11.35cm^2 surface areas, submerged in the liquid in a non-conductive vessel, a rectangular dish of given dimensions, and separated by a fixed distance. A digital multi-meter set to AC (50Hz UK) was used, Black Star: 3210. The cross-sectional area was then calculated with the liquid 0.02m deep. And the resistance multiplied by this area, and then the length divided by this figure to obtain the conductivity. After each experiment was set up it was left for 30 seconds to stabilise before each figure was recorded.

3. Results

Table 2 and figure 3 shows the data from the experiment converted into picosiemens per meter (pS/m) where the conductivity of the fuel reduces from a mean 1209.3pS/m with 100% biodiesel down to 1pS/m for neat diesel. This change seems drastic however the microscopic value of picosiemens per meter which is x10^{-12} is unlikely to cause galvanic corrosion between the dissimilar metals within a fuel system due to the distances of some metals from each other. For example: using the most dissimilar metals, fuel tank mounted pump made from aluminium, itself a reactive metal in the galvanic series, which when it comes into contact with other more cathodic metals, it acts as a sacrificial anode and becomes susceptible to corrosion, and the brass (containing copper) pre-filter mounted to the inlet of the injection pump, there is a potential difference of 2.01V (Table 3) which when distance is over 2 meters due to the components mounted at opposite ends of the vehicle and the

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fuel being replaced on average every 12 hours due to storage during the night will not cause any corrosion. However the now proved low conductivity of biodiesel relative to mineral diesel and components mechanically connected to each other may exhibit galvanic corrosion if prolonged contact with stagnant fuel occurs such as spilt fuel collecting in the fuel tank filling recess of the vehicles bodywork.

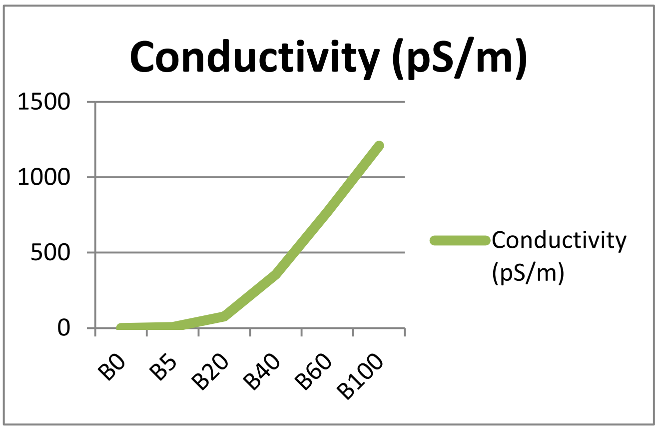

Figure 3: *Graphical representation of conductivity of diesel when doped with increasing levels of biodiesel*

Concentration	B100	B60	B40	B20	B5	B0
Experiment 1	1209	775	358	75	7	2
Experiment 2	1180	768	350	75	5	0
Experiment 3	1239	770	357	79	11	1
Mean	1209.3	771	355	76.3	7.6	1

Table 2: *Results from experiment on conductivity of biodiesel in pS/m. (Repeated 3 times).*

Element	Electrode potential (V)
iron	0.45
Aluminium	-1.67
Copper	0.34
Zinc	-0.76
Chromium	-0.74
Tin	-0.14

Table 3: *Values showing the potential difference in volts of elements found in a typical diesel automobile fuel system relative to that of a hydrogen electrode.*

A more likely outcome would be from excessive hydrolysis of the biodiesel due to its large water absorption capacity, Singh et al. [4] causing rust in the steel components which are usually protected by the corrosion-inhibiting properties of mineral diesel. This rust may form sediment on the bottom creating an environment where a differential aeration cell is formed causing localised pitting corrosion leading to a perforation in the fuel tank. Differential aeration cells may form at the fuel-air boundary due to sufficient water saturation.

The only remaining scenario where electrochemical corrosion may occur is at the water-biodiesel boundary within the water separator fitted in the fuel line between fuel tank and engine. Here, a water-fuel boundary may exist for over a year between service intervals and impurities in biodiesel including sulphuric acid and methanol left over from the transesterification reaction causing trace salts to combine with the water in the separator to cause a mild brackish water environment which can cause a cathodic zone to form at the boundary [6].

This scenario is more likely to occur with a car using biodiesel as the saturation level of water in biodiesel is in the order of 20 times more than mineral diesel (1395ppm vs. 62ppm)[7]. Also aerobic and anaerobic groups of microorganisms methanogens, and sulphate- and nitrate-reducing bacteria in the aerobic rich biodiesel metabolise the mixture and change the ph increasing conductivity possibly to galvanic-corrosion inducing levels [7].

4. Discussion

One method to prevent galvanic corrosion in micro-environments that may occur due to stagnated biodiesel and especially in the presence of water is by stopping electron sink at the cathodic metal, this allows the anode to remain in contact with the electrolyte without requiring a protection method that would compromise its operating capability e.g. plating with a more noble metal. Several methods can be employed for this to happen. A sacrificial anode method cannot come into contact with the electrolyte as its dissolution will lead to metal particulates being deposited into the fuel. This cannot be allowed to happen, before or after the fuel filter(s) [9].

5. Conclusions

It is the conclusion of this paper that under normal operating conditions the likelihood of a pair of dissimilar metals experiencing galvanic corrosion due to being electrically connected through

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biodiesel acting as an electrolyte will cause insignificant corrosion problems compared to mineral diesel. Even under laboratory conditions, when different types of biodiesels are subjected to different temperatures over extended periods of time (115 days) a negligible difference in their properties took place suggesting that prolonged exposure will not induce corrosion in the fuel system [7]. Interestingly the corrosion potential of pure aluminium exposed to biodiesel after a different number of wash cycles does increase however the corrosion current density decreases [8] (figure 4) indicating correct, thorough cleaning (washing) of biodiesel will further reduce the negligible electrolytic corrosion potential of biodiesel.

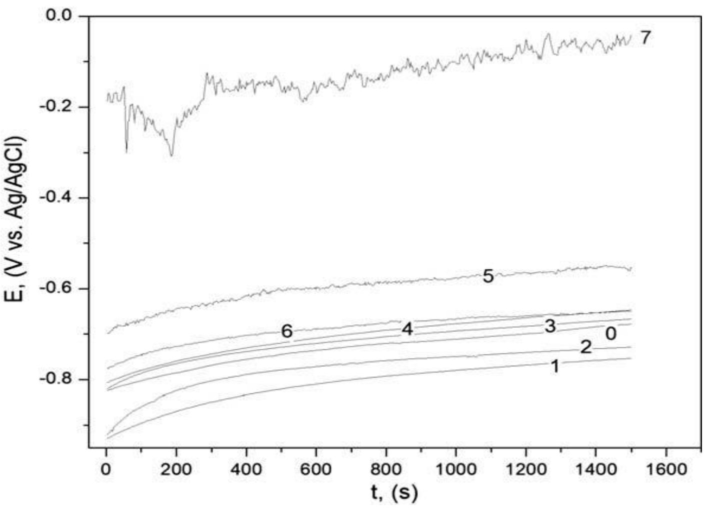

Figure 4: *Open circuit potential of pure aluminium exposed to biodiesel after a different number of wash cycles [8]*.

Lateral research has suggested that biodiesel induced corrosion has been attributed to compounds present or formed over time within the biodiesel solution such as sulphur, and oxidisation of the biodiesel caused by contact with metals like bronze, brass, copper, tin and zinc causing sediments leading to micro-environments where further corrosion may take place such as pitting corrosion on components [10]. Haseeb et al. [11] observed that copper alloys are significantly more prone to corrosion by biodiesel as compared with ferrous alloys suggesting that corrosion due to the method focused on in this paper is not of concern to designers of future biodiesel fuelled engines or fuel systems nor should be considered when converting a current vehicle to biodiesel fuelled operation.

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