# COMPATIBILITY OF BIODIESEL FUEL WITH METALS AND ELASTOMERS IN FUEL DELIVERY SYSTEM OF A DIESEL ENGINE

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**ABSTRACT**

*This article intends to evaluate available literature findings and determine if they are representative of the actual compatibility between fuel delivery materials (FDM) and biodiesel fuel in the physical system. The study will also evaluate current test standards on their effectiveness of representing the physical fuel delivery system. Although the compatibility of a number of materials with biodiesel fuel has been reported, there is a need to establish the exact materials present in the fuel delivery system. This is especially true for elastomers since their resistance is mainly dependent on their elemental compositions. While typical standards such as the ASTM G31 and ASTM D471 for metals and elastomers, respectively are deemed suitable for evaluating the effects of water content, total acid number and oxidised products in biodiesel on FDM degradation based on laboratory immersion studies, none of these standards resemble the actual engine operating conditions such as varying fuel pressure/temperature as well as presence of a wide range of materials in a typical diesel engine's fuel delivery system. As such, findings from existing studies so far are inadequate to conclusively determine the compatibility between FDM and biodiesel fuel in the actual fuel delivery system of a diesel engine.*

**Keywords:** biodiesel compatibility, fuel delivery materials (FDM), actual operating conditions, material composition in fuel line.

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## INTRODUCTION

Biodiesel (B100), also known as fatty acid methyl ester (FAME), is typically produced from vegetable (or animal) oil through the transesterification process. Under transesterification, vegetable oil molecules which consist of triglycerides are converted into three mono-alkyl esters, as shown in *Figure 1*. The main purpose of this process is to reduce the high viscosity of vegetable oil (40 $mm^2 s^{-1}$) to a much lower viscosity of approximately 5 $mm^2 s^{-1}$, to be suitable for diesel engine operation. To date, biodiesel is becoming an important alternative fuel in the global fuel market due to factors such as declining air quality, depleting energy reserves and price hike in fossil fuel. Furthermore, its ability to be used without general engine and infrastructure modification promotes its adoption level.

Utilisation of biodiesel was initiated in blended form with diesel, from a minimum of 1 vol% biodiesel. Today, the blending level has reached a maximum of 20 vol% of biodiesel in diesel (B20), as

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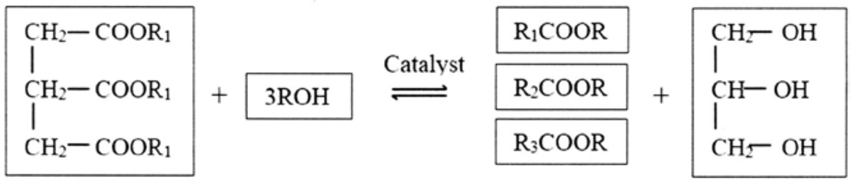


*Figure 1. Transesterification process for biodiesel production from vegetable oil.*

shown in *Table 1*. The B100 and B20 fuels here are typically expected to meet the specifications as per stipulated in the ASTM 6751-15a (ASTM D6751-15a, 2015) and the ASTM D7467-15a (ASTM D7467-15a, 2015) Standards, respectively. However, the use beyond B20 is typically not allowed as the level of FDM degradation becomes too severe. Other challenges include reduced lifespan of fuel delivery components such as filter, pump and injector, wax formation, sedimentation, poor atomization and injector choking (Ng *et al*., 2010; Van Gerpen *et al*., 2007; Mofijur *et al*., 2013).

The fuel delivery and storage system in a diesel engine typically consists of the fuel tank, fuel lines, fuel filter, fuel pump, fuel rail and fuel injectors as shown in *Figure 2*. The typical metals and elastomers present in the fuel delivery system are listed in *Table 2*. Metals were chosen due to their excellent compatibility with diesel, as well as for their suitability in the fabrication of fuel delivery components. The components are expected to last for an estimated lifespan of 10-15 years, depending on their function. Corrosion, a natural phenomenon of metal mass loss could reduce the lifespan. High corrosion rate would result in an accelerated metal mass loss leading to fuel leakage. Fuel leakage, critically between the fuel filter and the fuel pump, would result in fuel starvation. This phenomenon, could lead to fuel pump seizing, abruptly stalling the engine operation. Like metals, the compatibility of elastomers has long been established with diesel. The utilisation of incompatible fuel could however accelerate the degradation process, leading to significantly early failure. This could be observed in the form of seal breakage and hose rupture, culminating in fuel leakage and loss of compression.

Realising these implications, extensive studies have been conducted on the compatibility of biodiesel with FDM. Here, greater metal corrosion with biodiesel than diesel fuel have been reported (Kaul *et al*., 2007; Geller *et al*., 2008; Sgroi *et al*., 2005). The addition of even a small amount of biodiesel in diesel blend such as 2 vol% in terne cups at 80°C for 1000 hr increased the leaching of lead by 22 900% when compared with diesel (Tsuchiya *et al*., 2006). The corrosion rate is reported to increase with increasing biodiesel concentration in diesel (Haseeb *et al*., 2010a). The rise in copper corrosion rate in biodiesel when compared to diesel is typically within the range of 68% to 148% (Haseeb *et al*., 2010a; Fazal *et al*., 2010; 2012). The utilisation of corrosion inhibitors in controlling metal corrosion, despite being effective (Fazal *et al*., 2011b; Kalam and Masjuki, 2002), is not suitable since it adversely affects elastomers by inducing further crosslinks (Petrash, 2002). In addition, leached metal ions due to corrosion could adversely affect biodiesel's stability. These ions, acting as catalyst in promoting biodiesel oxidation, form undesirable oxidised products such as aldehydes and ketones (Sarin *et al*., 2009a, b;

**TABLE 1. LEVEL OF BIODIESEL ADOPTION IN SELECTED COUNTRIES/REGIONS**

| Nation | Current utilisation | Future target |
|---|---|---|
| Australia | B5-B20 ('Biodiesel in Australia,' 2014) | B20-B100 ('Biodiesel in Australia,' 2014) |
| Brazil | B5 (Rodrigues, 2009) | B7 (Lima, 2013) |
| Ecuador | B5 (Lane, 2013) | B10 (Lane, 2013) |
| Peru | B2 (Lane, 2013) | B5 (Lane, 2013) |
| Uruguay | B2 (Lane, 2013) | B5 (Lane, 2013) |
| United States | B10 (Lane, 2013) | B20 (Lane, 2013) |
| European Union | B5.75 (Lane, 2013) | B10 (Lane, 2013) |
| Malaysia | B7 (Zainal, 2014) | B10 (Adnan, 2013) |
| Philippines | B2 (Lane, 2013) | B5 (Lane, 2013) |
| South Korea | B2 (Lane, 2013) | B3 (Lane, 2013) |

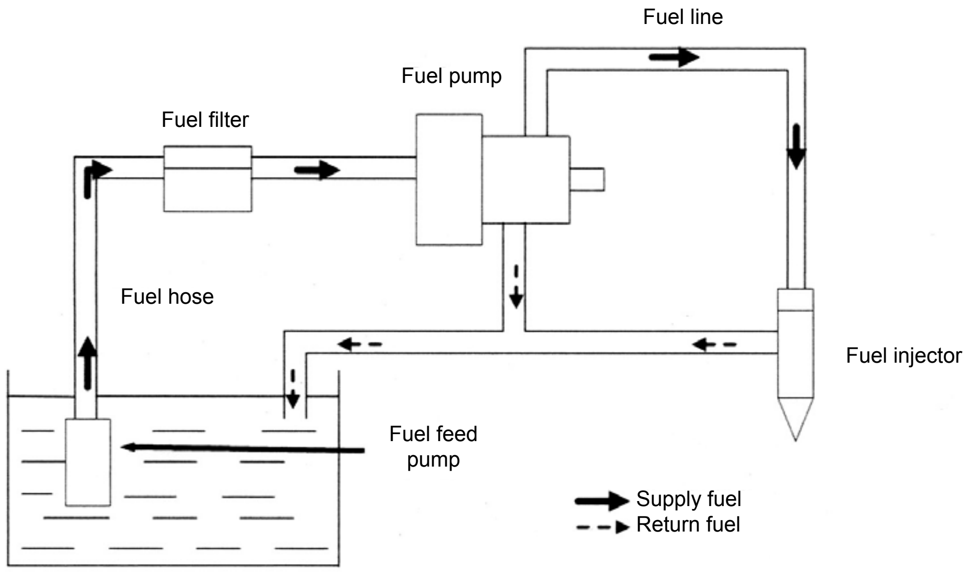


*Figure 2. Fuel delivery system in a typical diesel engine.*

**TABLE 2. MATERIALS USED FOR THE FABRICATION OF FUEL STORAGE AND DELIVERY COMPONENTS**

| Parts | Materials |
|---|---|
| Fuel tank | Steel, plastic |
| Fuel feed pump | Aluminum alloy, iron-based alloy, copper-based alloy |
| Fuel lines | Steel, plastic, rubber |
| Fuel filter | Aluminum, plastic, paper, resin impregnated paper |
| Fuel pump | Aluminum alloy, iron-based alloy, copper-based alloy |
| Fuel injector | Stainless steel |
| Nozzles | Steel |
| Gasket | Elastomer, paper, cork, copper |

Source: Abstracted from Yamagata (2005), Crouse and Anglin (1993), Bosch (2001), Haseeb *et al*. (2011a), Sorate and Bhale (2013).

Haseeb *et al*., 2011a). Oxidised biodiesel is reported to be more corrosive than un-oxidised biodiesel (Haseeb *et al*., 2010a). The corrosion rate of copper was found to increase by 59% when comparison was made between oxidised and un-oxidised palm biodiesel at 80°C for 840 hr of immersion.

Most of the elastomers which showed good compatibility with diesel fuel underwent significant degradation when tested with biodiesel fuel (Haseeb *et al*., 2010b; Zhang *et al*., 2009; Bessee and Fey, 1997). In a study by Hu *et al*. (2010) the authors determined the mass change of nitrile rubber immersed in diesel and *Jatropha curcas* biodiesel for 672 hr at 26°C. Here, the mass change was reported to be 250% higher in *Jatropha curcas* biodiesel than in diesel. In a separate study by Haseeb *et al*. (2011b) to evaluate the compatibility of poly-tetrafluoroethylene in diesel and palm biodiesel for 1000 hr at 26°C, the volume change of poly-tetrafluoroethylene was reported to be three times higher in palm biodiesel than in diesel. In general, carbon black and silica fillers serve to improve the hardness, abrasion resistance, tensile strength and tear strength properties of elastomers (Haseeb *et al*., 2010b). The addition of curing agents and accelerators creates cross-links between the polymer chains. The reaction caused by biodiesel fuel on the polymer chain, cross-links and filler system have been suggested as a cause of degradation to the elastomers (Haseeb *et al*., 2010b).

Majority of the studies agreed that FDM experienced greater degradation than the acceptable level with B20 and above. However, these studies were not investigated under actual diesel engine's fuel delivery system. Instead, a majority of the studies utilised immersion investigation such as the ASTM G31 and ASTM D471 for metal and elastomer, respectively. For metals, the mass loss is determined to calculate the corrosion rate. On the other hand, the degradation of elastomer is determined from volume, mass, tensile strength and hardness change. In terms of the samples preparation, ASTM G1 (ASTM G1-03, 2011) and ASTM D471 (ASTM D471-12, 2012) are usually employed for metal and elastomer specimens, respectively. Findings from these studies were utilised to assess the compatibility of FDM with biodiesel to determine the permissible biodiesel-diesel blend for utilisation (Singh *et al*., 2012; Haseeb *et al*., 2011a; Zuleta *et al*., 2012). Despite the significance of the findings, it is crucial to ensure the accuracy of existing compatibility studies in representing the compatibility of FDM with biodiesel fuel in the physical system. Accurate representation is necessary as it leads to accurate judgement which directly affects the allowable biodiesel-diesel blends for general utilisation in diesel engines. This review aims to evaluate the sufficiency of existing studies on assessing the compatibility of FDM with biodiesel in the actual fuel delivery system of a diesel engine. The focused aspects are the evaluated FDM and the standards utilised for the compatibility studies.

## EVALUATED MATERIALS IN EXISTING COMPATIBILITY STUDIES

A number of studies have evaluated the compatibility of metals and elastomers with biodiesel, diesel as well as biodiesel-diesel blends. *Table 3* shows the list of evaluated metals and elastomers. The majority of the studies agreed that copper and nitrile rubber are the most adversely affected metal and elastomer respectively, while stainless steel, aluminium and fluoroelastomer are the least (Meenakshi *et al*., 2013; Geller *et al*., 2008; Bessee and Fey, 1997; Zhang *et al*., 2009; Haseeb *et al*., 2011a; McCormick and Terry, 2006). An important point observed from these studies is that none investigated the exact materials present in the fuel delivery system prior to the study. Typical approach of evaluating common FDM such as those listed in handbooks (Crouse and Anglin, 1993; Yamagata, 2005) might not be sufficient as the compatibility of materials with fuels are very dependent on their elemental composition.

Determination of the exact material composition in fuel line is essential especially for elastomers as the chemical resistance is dependent on their elemental compositions. For example, higher percentage of acrylonitrile content in nitrile rubber contributes towards its higher resistance against fuel permeation/attack. In a study by Linhares *et al*. (2013), the authors evaluated the effects of coconut-based biodiesel on nitrile rubber with 28% and 45% acrylonitrile content. Here, the nitrile rubber with 28% acrylonitrile content experienced 90% reduction in tensile strength while the latter experienced only 10% reduction. Similarly, higher fluorine content in fluoroelastomers contributes towards the higher resistance against fuel permeation/attack. To date, the least resistant fluoroelastomer evaluated in biodiesel has 64% fluorine content by weight (Thomas *et al*., 2007). Based on this, biodiesel is said to have sufficient compatibility with fluoroelastomer only if the existing fluoroelastomer has a minimum fluorine content of 64 wt.%. Furthermore, since common rail direct injection is the current mainstream fuel delivery system, emphasis should be placed towards the fuel delivery materials of this particular set-up.

## STANDARDS USED IN EXISTING COMPATIBILITY STUDIES

To date, there are two analytical tests to determine the fuel's corrosive effect on metals: the ASTM D130 and ASTM D664. ASTM D130 (ASTM D130-12, 2012) evaluates the effects of immersed copper strip in fuel, with a standardised reference strip. The results are rated on a scale of slight tarnish 1A, B to heavy tarnish 4A-C. *Table 4* shows the experimental results conducted based on the ASTM D130. The 1A result (marginal corrosion) was obtained for all the tested samples, irrespective of diesel, biodiesel [from cottonseed methyl ester (CME), rapeseed methyl ester (RME) and soya methyl ester (SME)] and B20 biodiesel-diesel blend. This demonstrates that the analytical test is incapable of distinguishing the corrosive effects of diesel, biodiesel, biodiesel-diesel blends as well as different biodiesel feedstock towards copper (Haseeb *et al*., 2011a). Nevertheless, the test determines the corrosivity of the fuel based on the quantity of sulphur compound present (ASTM D130-12, 2012). Since biodiesel does not contain sulphur, this test is not able to measure its corrosivity.

ASTM D664 (ASTM D664-11, 2011) is the other analytical test utilised to determine the fuel's corrosive effect on metal. This test works by determining the required mass of bases solution (potassium hydroxide) in neutralising the acidity of the fuel. The acidity of the fuel could typically be correlated to the fuel's corrosivity. However, there is no general correlation between the acid number and the corrosive tendency of the biodiesel (ASTM D664-11, 2011). The varying corrosivity of the oxidation products and the organic acids which are naturally present in biodiesel fuels are believed to be the key parameters governing this observation. Therefore, this analytical test is also deemed unsuitable to determine the corrosion effect of biodiesel and biodiesel-diesel blends.

Apart from these two analytical tests, a number of standards have been utilised in evaluating the compatibility between biodiesel and metals. Among these are the immersion standard ASTM G31 (ASTM

**TABLE 3. EVALUATED FUEL DELIVERY MATERIALS AND THE CORRESPONDING STUDIES IN LITERATURE**

| | Metals |
|---|---|
| Type | Studies (Ref.) |
| Aluminium | Fazal *et al*. (2010; 2012), Norouzi *et al*. (2012), Anisha *et al*. (2011), Hu *et al*. (2012), Chew *et al*. (2013), Meenakshi *et al*. (2011) |
| Brass | Fazal *et al*. (2012), Aquino *et al*. (2012), Anisha *et al*. (2011), Meenakshi *et al*. (2011; 2013) |
| Bronze | Haseeb *et al*. (2010a) |
| Carbon steel | Fazal *et al*. (2011a), Maru *et al*. (2009), Anisha *et al*. (2011), Hu *et al*. (2012), Liu and Fang (2009), Grainawi *et al*. (2008), Meenakshi *et al*. (2011), Cursaru and Mihai (2012), Fernandes *et al*. (2013) |
| Cast iron | Fazal *et al*. (2012; 2011b) |
| Copper | Haseeb *et al*. (2010a), Fazal *et al*. (2010; 2012; 2013), Aquino *et al*. (2012), Norouzi *et al*. (2012), Anisha *et al*. (2011), Hu *et al*. (2012), Meenakshi *et al*. (2011; 2013) |
| Galvanized steel | Fernandes *et al*. (2013) |
| Magnesium | Chew *et al*. (2013) |
| Monel steel | Cursaru and Mihai (2012) |
| Stainless steel | Fazal *et al*. (2010), Hu *et al*. (2012), Cursaru and Mihai (2012) |

| | Elastomers |
|---|---|
| Type | Studies (Ref.) |
| Acrylic rubber | Trakarnpruk and Porntangjitlikit (2008) |
| Chloroprene | Haseeb *et al*. (2011b) |
| Ethylene-propylene-diene monomer | Hu *et al*. (2010), Zhang *et al*. (2009), Haseeb *et al*. (2011b) |
| Fluoroelastomer | Thomas *et al*. (2007), Hu *et al*. (2010), Micallef (2009), Zhang *et al*. (2009), McCormick and Terry (2006), Trakarnpruk and Porntangjitlikit (2008), Haseeb *et al*. (2010b) |
| Fluorosilicone | Micallef (2009) |
| Hydrogenated nitrile rubber | McCormick and Terry (2006), Trakarnpruk and Porntangjitlikit (2008) |
| Nitrile rubber | Hu *et al*. (2010), Zhang *et al*. (2009), McCormick and Terry (2006), Linhares *et al*. (2013), Trakarnpruk and Porntangjitlikit (2008), Haseeb *et al*. (2010b; 2011b) |
| Nylon | Choudhury and Mallick (2012) |
| Polychloroprene | Haseeb *et al*. (2010b) |
| Poly-tetrafluoroethylene | Haseeb *et al*. (2011b) |
| Synthetic rubber | Zhang *et al*. (2009) |
| Silicone rubber | Haseeb *et al*. (2011b), Zhang *et al*. (2009) |

G31-12a, 2012), rotating cage standard ASTM G184 (ASTM G184-12, 2012) and the linear polarisation resistance standard ASTM G59 (ASTM G59-97, 2014). *Table 5* describes the working principle of these standards and the respective studies based of these. Typically, metal deterioration is evident from mass loss. Therefore, the analysis which is given the most importance is corrosion rate.

The major difference between ASTM G31 and ASTM G184 is the flow condition. In ASTM G31, the fuel is in static condition while the fuel is travelling at a fixed speed in ASTM G184. Meenakshi *et al*. (2013) compared the corrosion rates of copper in *Pongamia pinnata* oil under ASTM G31 and ASTM G184 test standards for 100 hr at a rotational speed of 500 revolution per minute. The authors reported higher corrosion rate of copper by 12 times under ASTM G184 than ASTM G31. As such, higher metal corrosion is anticipated when the fuel travels through the fuel delivery system than when stored in the fuel tank. In terms of the ASTM G31 and ASTM G59, the earlier measures the duration averaged corrosion rate, while the latter measures the instantaneous corrosion rate. In a study by Anisha *et al.* (2011) the corrosion rate of copper, brass and carbon steel were compared under ASTM G31 and ASTM G59 test standards. Here, higher corrosion rate were reported under ASTM G31 than ASTM G59 for

**TABLE 4. RESULTS OF BIODIESEL'S CORROSIVENESS FROM ASTM D130 AND ISO 2160 STANDARDS**

| References | Standard | Fuel | Results |
|---|---|---|---|
| Barnitt *et al*. (2006) | ASTM D130 | Diesel<br>B20 (feedstock not mentioned) | 1A<br>1A |
| Mazzoleni *et al*. (2007) | ASTM D130 | B20 (feedstock not mentioned)<br>B100 (feedstock not mentioned) | 1A<br>1A |
| Rashid *et al*. (2009) | ASTM D130 | B100 (CME) | 1A |
| McCormick and Terry (2006) | ASTM D130 | B20 ( SME; oxidised) | 1A |
| Dinkov *et al*. (2009) | ISO 2160<br>(ISO 2160:1998) | B100 (RME) | 1A |
| Clark *et al*. (1984) | ASTM D130 | B100 (SME) | 1A |

Source: Abstracted from Haseeb *et al*. (2011a).

**TABLE 5. WORKING PRINCIPLES OF THE TEST STANDARDS AND THE CORRESPONDING REFERENCE STUDIES**

| Standards | Working principle | References |
|---|---|---|
| ASTM G31 | Determines the average corrosion rate by accelerating the metal deterioration by simulating the conditions of interest through immersion study (typically static) | Chew *et al*. ( 2013), Haseeb *et al*. (2010a), Fazal *et al*. (2011a) |
| ASTM G184 | Determines the corrosion rate by simulating pipeline flow under laboratory conditions (dynamic) | Meenakshi *et al*. (2013) |
| ASTM G59 | Determines the corrosion rate by monitoring the relationship between the electrochemical potential and current generated between electrically charged electrodes | Anisha *et al*. (2011) |
| ASTM D471 | Determines the effects on elastomers by accelerating the elastomer degradation by simulating the conditions of interest | Thomas *et al*. (2007), McCormick and Terry, (2006), Haseeb *et al*. (2010b) |

copper, brass and carbon steel by 698%, 262% and 426%, respectively. The higher corrosion rate under ASTM G31 than ASTM G59 nevertheless shows that the corrosion rate of metals in biodiesel increases with duration.

The most commonly utilised standard for the elastomers is the immersion standard ASTM D471 (ASTM D471-12, 2012). The working principle of this standard and the respective studies utilised this are shown in *Table 5*. ASTM D471 and ASTM G31 are similar in a way where both standards accelerate the material deterioration process by simulating the conditions of interest in evaluating the effects on the materials. Among the commonly evaluated conditions of interest include the effects of water content, total acid number and oxidised products present in biodiesel fuels on FDM degradation. For example, Haseeb *et al*. (2010a) utilised ASTM G31 to evaluate the effects of oxidised products present in palm biodiesel on copper's corrosion rate immersed at 60°C for 840 hr. In another study, McCormick and Terry (2006) utilised ASTM D471 to evaluate the effects of oxidised products present in B20 SME on nitrile rubber's degradation immersed at 60°C for 1000 hr.

All these standards are excellent in benchmarking the effects of biodiesel, diesel and biodiesel-diesel blends on FDM. However, the conditions employed in these standards do not resemble the actual operating conditions in the fuel delivery system of diesel engines. The conditions in the fuel delivery system are dependent on the varying speed-load, which instantaneously alters the fuel pressure and hence, directly affects the fuel temperature. The effects of varying fuel temperature, together with the presence of a variety of FDM, could not be simulated by any of these standards. As a result, the identified factors promoting material degradation such as water content, total acid number and oxidised products determined from these standards may not necessarily be present in the actual fuel delivery system.

Besides, there is also a possibility that the adverse effects observed on FDM especially using the immersion test could be influenced by secondary effects. The secondary effects here refer to the effects caused by the formed oxidation products such as aldehydes, ketones and short chain acids. The presence of these products is known to accelerate the FDM deterioration (Haseeb *et al*., 2010a).

## CONCLUSION

Based on the discussion above, the existing studies are deemed insufficient to comprehensively assess the compatibility of FDM in the fuel delivery system of a diesel engine with biodiesel fuel. This is mainly due to the lack of available studies in investigating the exact FDM present in the physical fuel delivery system. This is important as the elemental composition present in the FDM, especially elastomer, significantly determines the resistance towards biodiesel fuel. Furthermore, the current standards used in evaluating the compatibility between FDM and biodiesel do not resemble the actual conditions in the fuel delivery system in a typical diesel engine. This is especially true in terms of the varying fuel pressure/temperature and the various materials present in the fuel delivery system.

The identified factors promoting material deterioration from these studies may not necessarily be present under the actual operating conditions. Besides, there are also chances for the formed oxidation products to be influencing the findings observed mainly from immersion studies. All these suggest that a more systematic study is required to appropriately appraise the compatibility between the FDM and biodiesel fuel in the fuel delivery system.

Firstly, the exact materials present in the fuel delivery system should be systematically determined. This includes elemental composition for both metals and elastomers. Additional tests would be required for elastomers such as functional group determination to allow for the exact material identification. Here, FDM of the common rail fuel injection system should be given emphasis due to its popularity as the current mainstream fuel delivery set-up. Secondly, the deterioration of biodiesel under diesel engine operations, preferably common rail system should be determined. This is crucial in order to understand if biodiesel fuels actually oxidise under actual diesel engine operations, as well as to ascertain the presence of common factors promoting FDM degradation such as water content and total acid number. From here, the effects of oxidised biodiesel, water and total acid number on FDM degradation could be determined.

In conclusion, the compatibility of FDM with biodiesel in the actual fuel delivery system of a diesel engine could be sufficiently assessed only with the availability of all the identified information.

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