

Evidence Synthesis Report 5

Study of the Increased Risk of Corrosion with the Use of Fatty Acid Methyl Ester (FAME) as a Diesel Additive



Authors: Carmel Breslin, Gillian Collins, Tara Barwa and Daniele Alves

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Government of Ireland

Environmental Protection Agency

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3. Office of Evidence and Assessment
4. Office of Radiation Protection and Environmental Monitoring
5. Office of Communications and Corporate Services

The EPA is assisted by advisory committees who meet regularly to discuss issues of concern and provide advice to the Board.

EPA RESEARCH PROGRAMME 2021–2030

**Study of the Increased Risk of Corrosion with
the Use of Fatty Acid Methyl Ester (FAME) as a
Diesel Additive**

(FTP-2023-02)

EPA Research Evidence Synthesis Report

Prepared for the Environmental Protection Agency

by

Maynooth University

Authors:

Carmel Breslin, Gillian Collins, Tara Barwa and Daniele Alves

ENVIRONMENTAL PROTECTION AGENCY

An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353 53 916 0600 Fax: +353 53 916 0699

Email: info@epa.ie Website: www.epa.ie

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This report is based on research carried out/data from April 2024 to November 2024. More recent data may have become available since the research was completed.

The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Project Partners

Carmel Breslin

Department of Chemistry
Maynooth University
Maynooth
Co. Kildare
Ireland
Email: Carmel.Breslin@mu.ie

Gillian Collins

Department of Chemistry
Maynooth University
Maynooth
Co. Kildare
Ireland
Email: Gillian.Collins@mu.ie

Tara Barwa

Department of Chemistry
Maynooth University
Maynooth
Co. Kildare
Ireland
Email: Tara.Barwa@mu.ie

Daniele Alves

Department of Chemistry
Maynooth University
Maynooth
Co. Kildare
Ireland
Email: Daniele.Alves@mu.ie

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Executive Summary

Biodiesels, and especially fatty acid methyl ester (FAME)-based biodiesels, have emerged as a family of biofuels in Ireland that have the potential to decarbonise our environment. These FAME-based additives are derived from feedstocks of animal fats and waste cooking oils, which have no food value. Using these additives is therefore perfectly aligned with the “food versus fuel crisis” and serves as an environmentally efficient manner of treating waste cooking oils. The fats and oils are treated chemically through a reaction called transesterification to produce the FAME product. The FAME product is then blended with petroleum-based diesel to produce the final FAME-based biodiesel. The FAME levels in these biodiesels in Ireland are generally between 5% and 7%, giving blends referred to as B5, B6 and B7.

Safe bulk fuel storage is an essential element in the management of all petroleum-based fuels. As FAME-based biodiesels have become more established, challenges related to storage have emerged. FAME is not compatible with all materials, and corrosion issues have been reported during longer-term storage. These corrosion reactions can give rise to the perforation of metallic storage tanks, potentially leading to fuel release, a safety and environmental hazard.

The aim of this project was to gain a more thorough understanding of these corrosion reactions and how they might be inhibited and managed. The available literature on FAME-induced corrosion was reviewed and assessed. In terms of corrosion, these reactions are complex in nature, involving both metallic corrosion and microbial-induced corrosion, and are connected with the FAME added to the fuel. FAME-based biodiesel is hygroscopic and can absorb high levels of water and oxygen from the environment. This leads to oxidation of the fuel, and as a result the fuel becomes more acidic. It is this combination of water, oxygen and

acidity that leads to the corrosion of metallic storage tanks. Furthermore, microbial contamination of the fuel can occur, and the microbes can further induce corrosion reactions. Following a review on the nature of the corrosion reactions, approaches that could be used to inhibit these reactions were considered. Several options were identified: (1) the addition of corrosion inhibitors to inhibit the onset of the reaction, (2) the addition of antioxidants to stabilise the FAME-based biodiesel, (3) the addition of biocides to inhibit the microbial contamination of the fuel, (4) the use of storage tank liners to isolate the steel tank from the stored FAME-based biodiesel and (5) the regular removal of any water that collects in the storage tank. Currently available antioxidants can also serve as corrosion inhibitors and inhibit antimicrobial growth, making them one of the best additives to use with FAME-based biodiesels.

We conclude by providing guidelines and policies on the general protocols to follow when managing and storing FAME-based biodiesels. Different guidelines are recommended for low- and high-level FAME blends. The low-level blends (up to and including B10) are relatively stable over short storage periods; however, when storing for longer terms, lined storage tanks, antioxidants, monitoring acidity and antimicrobial contamination levels, and removal of accumulated water are recommended. The higher-level blends are more susceptible to oxidation with increases in acidity and viscosity, and more regular monitoring is essential. A risk matrix is developed by considering the management of FAME-based biodiesel as a function of the probability of corrosion, with the consequences varying from negligible to very severe. Finally, a decision tree is provided, which outlines the main management protocols recommended for the mitigation of corrosion risks during the storage of FAME-based biodiesels.

1 Introduction

In the search for alternative sustainable energy sources, biodiesel has emerged as a suitable candidate (Nabgan *et al.*, 2022). Its success is already evident, with biodiesel plants with large fatty acid methyl ester (FAME) production capacity operating in several EU Member States (Tender No. ENER/C2/2013/628). Biodiesel is considered a renewable fuel, as it is derived from biodegradable feedstocks, including vegetable oils, animal fats and cooking oils (Singh *et al.*, 2020), and its use was highlighted in the *State of Renewable Energies in Europe: 19th EurObserv'ER Report* (EurObserv'ER, 2019). The use of cooking oil as a feedstock (Uçkun Kiran *et al.*, 2014) is particularly attractive, as most cooking oil ends up as waste, creating environmental issues. Furthermore, there are no issues related to the “food versus fuel crisis”, as cooking oil has no food value. This sets it apart from edible oils, which are an essential food source. Feedstocks in this category, that is, those based on used cooking oils, non-edible food crops (jojoba oil, tobacco seed, cotton seeds, etc.) and animal fat, are commonly known as FAME additives (Singh *et al.*, 2020). Pure biodiesel is rarely used, and instead the pure biodiesel is blended with petroleum-based diesel, to give blends consisting of, for instance, 5% biodiesel (B5) or 20% biodiesel (B20). In Ireland, the current blend levels are B5 and B7.

Much research has been focused on the optimisation, formation and purification of biodiesel, aiming to improve efficiency and cost while reducing any

environmental impacts. The commonly used reaction to convert waste cooking oil and animal fats into biodiesel is termed transesterification (Rezania *et al.*, 2019). This involves the reaction between the feedstock oil and an alcohol, usually methanol, in the presence of a catalyst (depicted in Figure 1.1). However, when the fatty acid content is high, the oil is typically treated with a base to reduce the fatty acid content, as many of the catalysts employed in the transesterification step are very sensitive to the presence of fatty acids. Again, much research has been devoted to purification technologies, with developments in membrane separation (Emmanouilidou and Kokkinos, 2022) showing promising results in removing some of the impurities, such as glycerol and fatty acids, thereby enhancing the overall quality of the biodiesel.

Like any petroleum-based fuel, biodiesel must be stored safely. Recently, evidence has emerged suggesting that the metallic tanks used to store FAME-based biodiesel can suffer from corrosion reactions (Rocha *et al.*, 2019). This has been traced to the presence of water, oxygen and acidic conditions that facilitate the dissolution and corrosion of the steel tanks. These corrosion reactions can lead to damage and perforation of the steel tanks, with the potential release of the biodiesel into the environment. Blends with higher biodiesel levels (> B20) are more prone to corrosion issues, while the lower-level blends, such as B2, are considerably less affected by corrosion

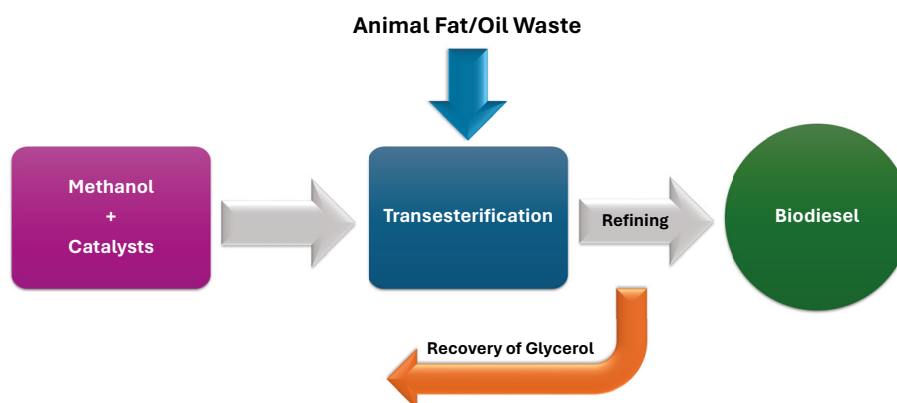


Figure 1.1. Schematic representation of the formation of biodiesel.

reactions and can be stored in largely the same way as petroleum-based diesel.

Therefore, the primary objective of this study was to analyse the available data on the nature of these corrosion reactions and identify possible mitigation strategies that could be employed in this developing

sector. This is discussed in Chapter 3, "Examination of the Findings". Likewise, a list of recommendations, which are based on the available data, is provided in Chapter 4, "Conclusions, Guidelines and Policy Recommendations".

2 Overview of the Research

2.1 Objectives of the Research Project

The overall objective of this literature study is to assess and summarise the current developments and understanding of the corrosion induced by FAME additives when present in biodiesel. The specific aims and objectives are listed below, and each objective is discussed in turn in Chapter 3. The specific aims and objectives are to determine the following:

- The overall properties and quality of FAME-based biodiesels.
- The nature of the corrosion events and the types of corrosion induced with FAME-based biodiesel, including the role of the FAME, water and dissolved oxygen in the development of an environment that promotes the corrosion of the storage tank when in contact with FAME-based biodiesel.
- The conditions that lead to microbial contamination and microbial-induced corrosion, and the nature of the microbial colonies and their growth in FAME-based biodiesel.
- The potential risk of fuel release due to a corrosion event.
- Possible control measures that could be used to inhibit the onset of corrosion reactions and microbial growth, and the identification of regimes for monitoring and maintaining storage tanks, so that the early onset of corrosion, or indeed the conditions that will induce corrosion, can be identified.
- Suitable monitoring strategies that could be employed to mitigate the onset and progression of corrosion during storage.

2.2 Approach Used to Collect the Data and Information

The information presented in Chapter 3 was compiled and analysed using a combination of literature resources, including (1) Scopus, Google Scholar, SciFinder and Web of Science; (2) published reports and policy documents; (3) ASTM International standards (formerly known as American Society for Testing and Materials) and European standards; and (4) general web-based searches to find other relevant documents. When searching for corrosion studies, the main keywords used were “fatty acid”, “biodiesel” and “corrosion”. The Scopus search returned 154 entries (on 31 October 2024), with one of the earliest papers (published in 2005) mentioning the potential for corrosion from the fatty acids (Lotero *et al.*, 2005). The paper by Lotero *et al.* mainly focuses on the quality and processing of FAME-based biodiesel but suggests that the acids would cause corrosion. Information on the nature of FAME-based biodiesel was also obtained using search terms such as “biodiesel” and “fatty acid”. This returned a total of 13,903 papers, with most published from 2010 to 2024, indicating a clear interest in and increasing focus on FAME-containing biodiesel. Literature searches using the keywords “biodiesel” and “cooking oil” returned 3895 papers, highlighting the increasing interest in biodiesel derived from waste cooking oils.

A breakdown of relevant papers published from 2005 to 2024 that specifically mention corrosion is illustrated in Figure 2.1. This figure clearly shows that several cases of corrosion have been reported, and corrosion can indeed occur when metals or alloys are in contact with FAME-based biodiesels.

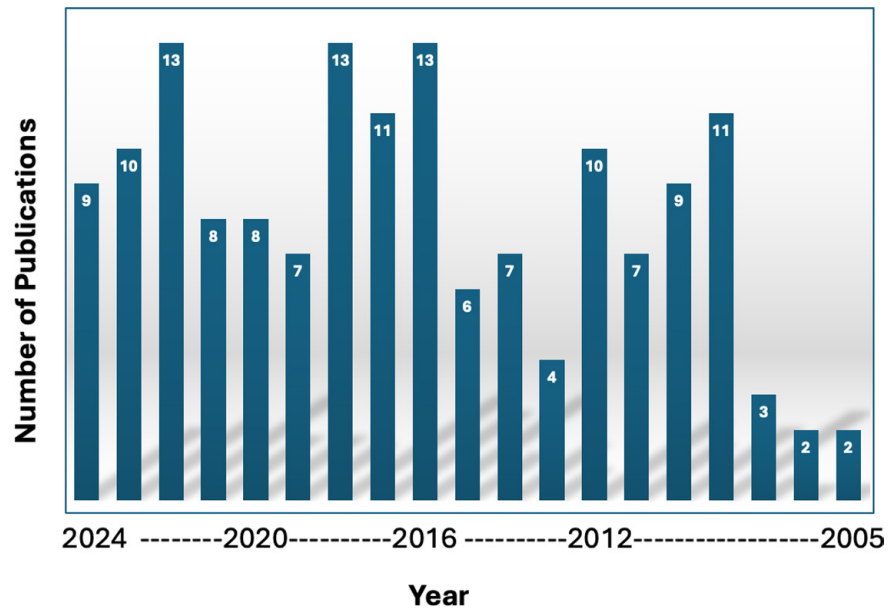


Figure 2.1. Number of papers published that mention the corrosion of biodiesel in the presence of FAME additives, taken from Scopus.

3 Examination of the Findings

3.1 The Overall Quality and Stability of FAME-based Biodiesels

Vegetable oils are a major feedstock for biodiesel production, providing a high-quality product. Nevertheless, waste oils, such as yellow grease from used cooking oils and animal fats, are widely available and cost-effective, and their conversion into FAME-based biodiesels provides a convenient route to recycle these waste oils/grease, having a positive impact on the environment. FAME-based biodiesels typically have a higher concentration of fatty acids than vegetable oils. Accordingly, FAME-based biodiesels are considered low quality compared with the biodiesels formed using refined vegetable oils. Although more processing steps are required to generate FAME-based biodiesels, the low price of the waste oils/grease feedstocks is attractive (Foo *et al.*, 2022). Nevertheless, stability and corrosion issues have emerged with FAME-based biodiesels (Rocha *et al.*, 2019). These have been traced to the relatively high FAME content, relatively high water content and the oxidation and degradation of the biodiesel (Floyd *et al.*, 2021). Moreover, these effects become more of an issue when the biodiesel is stored for extended periods (Ai *et al.*, 2024).

FAME-based biodiesels have high levels of fatty acids. Figure 3.1 shows the typical acids that are present in cooking oils, indicating that a large variety of acids are present. Lauric, myristic, palmitic and oleic acids are present at concentrations ranging from about 10% to 30% (by weight) (Estrada *et al.*, 2024). The other acids are normally at much lower concentrations, ranging from about 1% to 5%.

Pre-esterification is normally required to reduce the fatty acid content. However, in recent years, a one-step methodology has been developed, whereby bifunctional acid-base catalysts (Fu *et al.*, 2024) can serve for both the pre-esterification reaction (converting the acids to esters) and the transesterification reaction (conversion of the alcohol to the ester; see Figure 3.2). Nevertheless, the final biodiesel will contain some unreacted acids. One of the biggest challenges facing the use of FAME-based biodiesels is related to the long-term storage of the fuel, with higher amounts of FAME additives posing greater storage issues. The fuel, especially blends with higher FAME content (higher B values), due to its biodegradability, is easily oxidised in the presence of oxygen (Speidel *et al.*, 2000) in the air/environment, and this gives rise to the development of acidity that promotes the corrosion reaction.

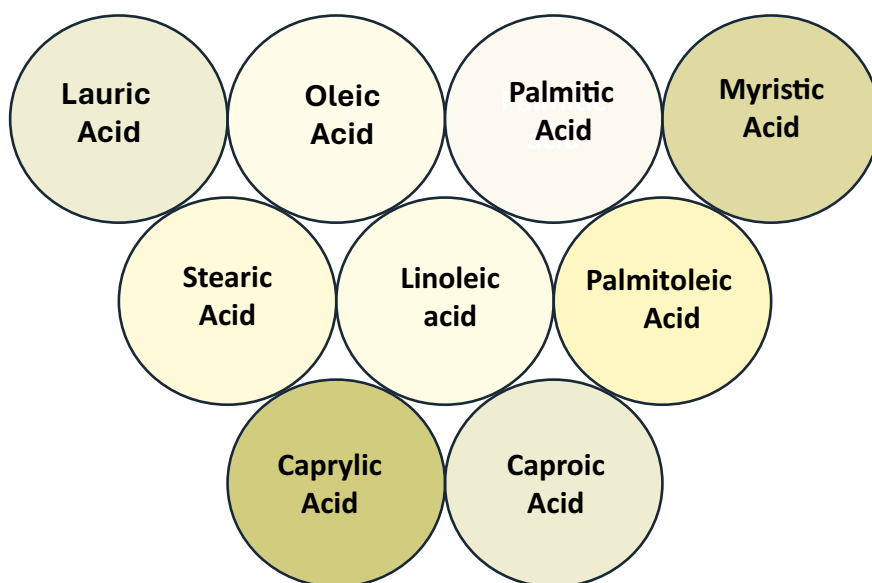


Figure 3.1. Summary of the main acids in cooking oils.

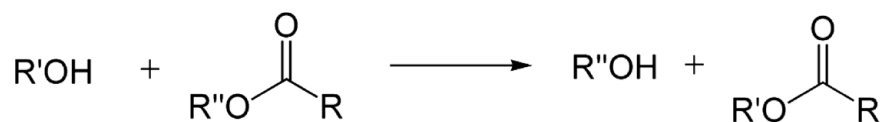


Figure 3.2. Transesterification reaction where an alcohol (ROH) is reacted with an ester (ROOR) to give the exchange of R' with R''.

3.2 Corrosion Reactions in the Presence of Biodiesel

Metals and alloys, such as iron, various steels, aluminium, copper and bronze, are all prone to corrosion. The corrosion reaction requires the metal or alloy to be exposed to an electrolyte, with the presence of oxygen that will serve as the reduction reaction. These conditions are easily met when the FAME-based biodiesel is stored in a metallic tank (Ai *et al.*, 2024). As the biodiesel is oxidised and absorbs water, it becomes acidic, and the perfect electrolyte is generated. The oxygen dissolved in the biodiesel provides the necessary reduction reaction, and, accordingly, the exposed metal or alloy undergoes corrosion, as illustrated in Figure 3.3. As this corrosion reaction proceeds, the metallic tank is weakened and eventually perforation may occur due to pitting attack with the escape of the biodiesel into the environment. The corrosion rate increases with increasing FAME content. For example, a corrosion rate of 8.1 $\mu\text{m}/\text{year}$ has been reported for B10 FAME-based biodiesel, increasing to 15.3 $\mu\text{m}/\text{year}$ for B30 and 38.7 $\mu\text{m}/\text{year}$

for B100, indicating considerable loss of the metal at the highest FAME content (Ateeq *et al.*, 2022). There is also clear evidence that metals such as copper, zinc and tin, and alloys such as bronze, are very prone to corrosion when exposed to biodiesels (Serqueira *et al.*, 2021). However, stainless steels, and to a lesser extent carbon steel, are more stable and are therefore more suitable materials for the storage of biodiesels. The overall stability of some commonly used metals and alloys is summarised in Table 3.1, where the nature of the corrosion reaction and the corrosion products are provided. It is also well known that the rate of corrosion depends on the composition and processing of the biodiesel (Kugelmeier *et al.*, 2021), and there is clear evidence to show that the rate of corrosion increases with increasing storage times (Deyab and Keera, 2016).

The total acid number (TAN) is used to give an indication of the acidity levels in biodiesels. Typically, the TAN should fall below 0.5, in accordance with ASTM International standard specifications (ASTM D664). The TAN of petroleum-based diesel in contact

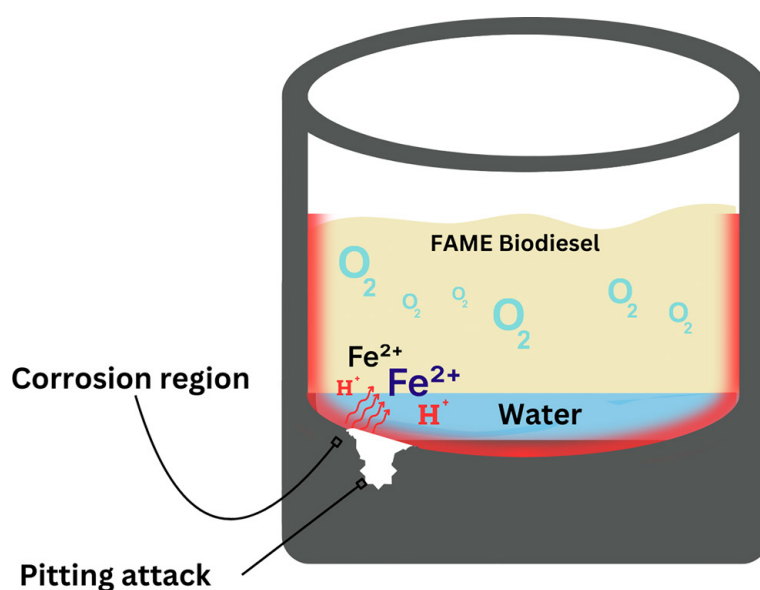


Figure 3.3. Schematic representation of pitting corrosion in a storage tank with FAME-based biodiesel, showing the accumulation of water and oxygen and the onset of pitting attack.

Table 3.1. Corrosion characteristics of various materials in biodiesel

Material	Corrosion resistance	Nature of corrosion	Corrosion products
Copper	Very poor	Uniform corrosion	CuCO_3 , $\text{Cu}(\text{OH})_2$
Carbon steel	Poor/good	Uniform corrosion and pitting attack	Fe_2O_3 , Fe_3O_4
Aluminium	Good	Pitting attack	Al_2O_3 , $\text{Al}(\text{OH})_3$
Stainless steel	Good	Pitting attack	Fe_2O_3 , Cr_2O_3 , NiO

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with different metals falls well below the TAN limit. However, much higher values have been recorded with biodiesel, reaching values of 1.5 when in contact with stainless steel and about 1.8 when in contact with copper after a 1200h period (Fazal *et al.*, 2010).

Compared with diesel, biodiesel is more hygroscopic and absorbs more moisture and water, which can occur during its production, transport and storage. The solubility of water depends on the temperature, humidity and composition of the biodiesel. It has been shown that about 10 to 15 times more water is absorbed by biodiesel than by diesel. Water uptake over a 24 h period was shown to vary between 1500 mg/kg (at 10°C) and 1980 mg/kg (at 50°C), indicating a considerable uptake of water (Fregolente *et al.*, 2012).

This moisture condenses onto the metallic surface, providing a layer of moisture that facilitates the corrosion reaction. As the corrosion reaction is initiated and the metal or alloy corrodes, metal ions are released, and this gives rise to the further modification of the biodiesel. Indeed, it has been shown that the metal ion concentration increases in the biodiesel. For example, copper ion concentration in biodiesel increased from 0 to 41.088 mg/L following corrosion of copper, while the iron content increased from 0 to 3.544 mg/L following the corrosion of carbon steel when exposed to biodiesel (Hu *et al.*, 2012). The presence of these metallic ions can lead to instability and further degradation of the biodiesel. Therefore, not only does the metallic tank corrode once a corrosion event is initiated, but the purity and stability of the biodiesel is also affected.

There is clear evidence that corrosion results in the further degradation of the biodiesel by increasing the metal ion content and viscosity, while reducing the oxidation stability. In terms of viscosity changes, relatively high viscosity changes from 4.15 to 4.48 mm²/s have been observed for biodiesel samples

following the immersion and corrosion of brass over a relatively short 5-day period (Aquino *et al.*, 2012).

Other environmental conditions, such as temperature and light, can have a significant effect on the overall stability of biodiesel (Aquino *et al.*, 2012). In general, the corrosion rate increases with an increase in temperature, and it also appears that light exerts an effect. Biodiesel contains natural pigments, such as carotenoids, that can absorb light energy. This, in turn, can generate oxygen species that attack the FAME, resulting in the formation of hydroperoxides (Jemima Romola *et al.*, 2021). These hydroperoxides are unstable and decompose into smaller molecules, such as ketones, and acids, altering further the composition of the biodiesel.

3.3 Microbial Contamination and Microbial-induced Corrosion

The combination of water and the availability of organic esters and their oxidation products can serve as a nutrient source and accordingly an ideal environment for the growth of microbes is generated. The ambient temperature and the availability of dissolved oxygen contribute further to the development of an environment that facilitates the growth and propagation of microbes (Surger *et al.*, 2023). The nature of the microbial contamination in biodiesel tanks is complex and is very dependent on the biodiesel constituents, such as the carbon source (esters, acids, etc.), the presence of sulfur, storage conditions and environmental conditions, such as temperature and humidity. The different strains of microbes found to contaminate biodiesel are summarised in Table 3.2, highlighting the complexity of the microbial contaminants that can persist, multiply and contaminate biodiesels (Komariah *et al.*, 2022). As the microbes continue to multiply and consume the organic esters, secondary metabolites are formed in large amounts. These new metabolites

Table 3.2. Typical microorganisms detected in biodiesel storage tanks

Microbe	Microbial diversity	
Bacteria	Sulfate-reducing bacteria, <i>Flavobacterium</i> , <i>Acinetobacter</i> and <i>Micrococcus</i>	<i>Acinetobacter</i> , <i>Bacillus</i> sp., <i>Clostridium sporogenes</i> , <i>Flavobacterium diffusum</i> , <i>Micrococcus</i> sp., <i>Pseudomonas</i> sp., <i>Pseudomonas aeruginosa</i> , <i>Serratia marcescens</i> , <i>Sarcina</i> sp., <i>Hydrogenomonas</i> sp., <i>Clostridium</i> sp., <i>Gordonia</i> sp.
Yeasts	<i>Candida</i> , <i>Saccharomyces</i> , <i>Torula</i> and <i>Hansenula</i>	<i>Candida</i> sp., <i>Candida famata</i> , <i>Candida lypolytica</i> , <i>Candida silvicola</i> , <i>Candida tropicalis</i> , <i>Rhodotorula</i> sp., <i>Saccharomyces</i> sp.
Fungi/moulds	<i>Hormoconis resinae</i> , <i>Cladosporium resinae</i> , <i>Aspergillus</i> , <i>Penicillium</i> , <i>Fusarium</i> and <i>Botrytis</i>	<i>Acremonium</i> sp., <i>Aspergillus</i> sp., <i>Aspergillus fumigatus</i> , <i>Cladosporium</i> sp., <i>Fusarium oxysporum</i> , <i>Penicillium</i> sp., <i>Penicillium citrinum</i> , <i>Penicillium funiculosum</i> , <i>Trichiderma</i> sp., <i>Paecilomyces</i> sp., <i>Moniliella</i> and <i>Byssochlamys</i> , <i>Phyla</i> sp., <i>Pseudallescheria boydii</i> , <i>Hormoconis resinae</i> , <i>Fusarium</i> sp., <i>Aureobasidium pullulans</i> , <i>Moniliella wahieum</i>

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and by-products can further affect the quality of the biodiesel, contributing to its further oxidation and reduced stability. Furthermore, metabolites can accumulate as deposits at the bottom of the storage tanks.

Several studies show that the microbial contamination of biodiesel-containing fuels is related to the proportion of biodiesel in the blend. However, other factors are also very important, including the availability of nutrients (FAME additives) and storage conditions, including temperature, humidity, oxygen levels and the nature of the storage tank material, making this a very complex issue. In addition to microbial contamination, microbial-induced corrosion of metals and alloys is a significant issue in biodiesel tanks (Miller *et al.*, 2020; Pusparizkita *et al.*, 2022). The biodiesel is hygroscopic and can absorb water. This in turn creates an interface between the aqueous (water) and non-aqueous (oil) organic layers. Extensive bacterial and fungal growth has been observed in biodiesel storage tanks at this interface (Speidel *et al.*, 2000). In the presence of oxygen, the microbes metabolise the FAME to yield acids, which in turn provides an acidic environment that accelerates the corrosion of the biodiesel storage tank.

3.4 The Potential Risks of Biodiesel Release

The potential risks of fuel release can be considerable given the combinations of higher water uptake, oxidation and acidification of the biodiesel, corrosion, microbial growth and microbial-induced corrosion, as illustrated in Figure 3.4.

This becomes more of an issue when the biodiesel has a high content of FAME additives (e.g. B20 or B50) and is stored for longer periods, enabling both microbial contamination and the accumulation of metal ions from corrosion reactions. The release of petroleum-derived fuels can have an impact on natural ecosystems and human health (Bento *et al.*, 2005). These petroleum-based fuels have high toxicity and are resistant to biodegradation. The environmental impact of biofuels and the role of FAME additives are less well studied (Lancheros *et al.*, 2024). However, biodiesel does have a clear advantage in terms of being more biodegradable. Indeed, it has been shown that biodiesel derived from animal fat is rapidly biodegraded by soil microorganisms and has less of an impact on seed development than petroleum-derived diesel (Cruz *et al.*, 2019). However, if the biodiesel is released following long-term storage, the release of metal ions from corrosion of the storage tank and microbes from the microbial contamination of the biofuel becomes possible. Furthermore, as the FAME-based biodiesel blends used in Ireland tend to have relatively low FAME levels (B5 or B7), high levels of petroleum-based diesel could enter the environment.

3.5 Possible Corrosion Control Measures

As illustrated in the previous sections, FAME-containing biodiesels are susceptible to oxidation during storage. These oxidation processes are accelerated in the presence of oxygen (from air) and water, and this leads to changes in the physical and chemical characteristics of the biodiesel. Two quality

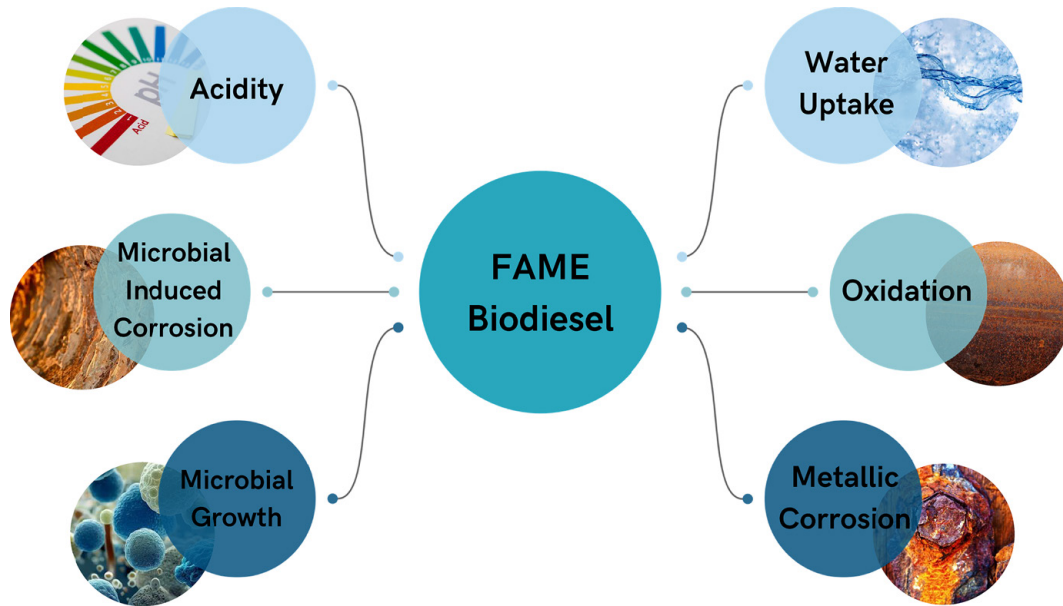


Figure 3.4. Summary of events that occur over time with FAME-based biodiesels.

control measures used in the production of biodiesels are very relevant to corrosion, and these are (1) oxidation stability and (2) TAN.

The standard test used for oxidation stability is termed the Rancimat test. This is specified by the EU standard EN 14112 and the US standard ASTM D7462. The test is an accelerated oxidation test carried out at 110°C, and an induction period is obtained that corresponds to the time required for the appearance of the oxidation products. The minimum induction period set by the EU (EN 14112) is 6h, while a more relaxed period of 3h has been set by the USA. However, there has been some discussion on these time frames and the temperatures used, and modifications are expected soon. For example, in EN 14214, the EU has increased the minimum induction period to 8h. TAN refers to the acidity of the biodiesel. This is typically determined using titrations. Both ASTM D6751 and EN 14214 stipulate a maximum TAN of 0.5, which corresponds to the consumption of 0.5 mg potassium hydroxide/g of biodiesel.

Various approaches have been employed to enhance the oxidative stability of biodiesel, including low-temperature storage and storage in the presence of nitrogen (to remove the oxygen). In terms of storage, low temperatures are too expensive to maintain. Likewise, the use of nitrogen is difficult to maintain for longer-term storage. Nevertheless, the use of nitrogen is very effective in ensuring the stability of FAME-based biodiesels over shorter periods. The most

feasible and cost-effective approaches for longer-term storage are introduced and discussed in the following sections.

3.5.1 Antioxidants

Using antioxidants that can inhibit the oxidation of biodiesel (David and Kopac, 2023) is considered one of the best approaches, combining feasibility, cost-effectiveness and the ability to stabilise the biodiesel. Naturally occurring antioxidants are attracting much attention, and this stems from the fact that biodiesels derived from unrefined vegetable oils possess a high concentration of natural antioxidants, and generally exhibit high stability. As most of these inherent antioxidants are removed during the transesterification and/or refining processing steps, much of the recent research has focused on naturally occurring antioxidants (Kongolo *et al.*, 2024). Nevertheless, more is known about synthetic antioxidants, and they have been tested more thoroughly in biodiesel blends.

Currently, the leading synthetic antioxidants are tertiary butylhydroquinone (TBHQ), butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), propyl gallate (PG), octyl gallate, dodecyl gallate, ethoxyquin and pyrogallol. An evaluation of these antioxidants showed that the synthetic antioxidants pyrogallol, PG, TBHQ and BHA were highly effective with biodiesel made from rapeseed oil, sunflower oil, used frying oil and beef tallow (Mittelbach and Schober, 2003). To be

effective in stabilising the biodiesel, the antioxidants must have a minimum concentration, and this is typically about 200 to 1000 parts per million (ppm) (Jain and Sharma, 2010). However, this minimum concentration depends on the quality of the biodiesel, including the FAME level in the blend, and the nature of the antioxidant. For example, 1000 ppm BHT is recommended in EN 14214 as the concentration needed to inhibit the oxidation of biodiesel. When the fuel is stored for longer periods of time, the antioxidant is consumed and may need to be replenished. This period will depend on the FAME level in the biodiesel blend. As the antioxidants are exhausted, oxidation of the biodiesel will occur, resulting in a decrease in pH. Therefore, antioxidant levels can be indirectly monitored through pH measurements.

There is good evidence that antioxidants exert positive effects when combined with biodiesels and used as a fuel. For example, it has been shown that antioxidants added to biodiesel blends inhibit the build up of carbon in the exhaust from engines (Bhangwar *et al.*, 2024), and when used in boilers they enhance the combustion process (Zelege and Haile, 2024). Generally, the addition of antioxidants to biodiesel enhances oxidative stability (which inhibits corrosion and microbial contamination) and increases the flash point and cetane number but somewhat reduces the calorific value of the fuel (Rashedul *et al.*, 2014).

3.5.2 Inhibition of microbial growth

Biocides can be very effective in controlling the growth of microbes, and they have been added to biodiesels to inhibit microbial growth. Examples of well-known biocides include isothiazolinone, thiocyanate, oxazolidine and morpholine. However, they also present human health risks and environmental concerns (Luz *et al.*, 2018). Some antioxidants that are commonly added to biodiesels have been evaluated in the inhibition of microbial growth, and evidence suggests that some of these, for example TBHQ, can inhibit the growth of various microorganisms, at least to some extent. They are not as effective as biocides but are considerably more environmentally acceptable.

3.5.3 Inhibition of corrosion reactions

The research field of corrosion inhibitors is very well established, and there has been much progress in

recent years in the development of green corrosion inhibitors. Many of these green corrosion inhibitors are derived from plant extracts, making them very well suited to and compatible with FAME-based biodiesels. An example of a plant-derived corrosion inhibitor is *Psidium guajava* L. leaf extract (Fernandes *et al.*, 2021). Other plant-derived systems, such as IONAL (a mixture of phenolic compounds) and a natural phenolic antioxidant derived from cashew nut shells, have been shown to exhibit bi-functionality, by acting as both antioxidants and corrosion inhibitors (Rangel *et al.*, 2021).

In addition, the dual action of antioxidants has been demonstrated (Serqueira *et al.*, 2021), with antioxidants being found to both increase the stability of biodiesel and inhibit corrosion reactions. The antioxidant TBHQ has been shown to inhibit the corrosion of various metals in biodiesel (Joumaa *et al.*, 2024). Other antioxidants, such as BHT and PG, have also been studied. Indeed, the corrosion inhibition efficiency of carbon steel in the presence of antioxidants varied in the order BHT > curcumin > PG > TBHQ, while for copper the order was slightly different (i.e. PG > BHT > TBHQ > curcumin) (Serqueira *et al.*, 2021).

3.5.4 Water content

While antioxidants can certainly enhance the stability of FAME-based biodiesels, act as corrosion inhibitors and inhibit microbial growth to some extent, they function by delaying these unwanted events and cannot prevent or eliminate them. Therefore, other control measures need to be considered. The water content in FAME-based biodiesels is linked to the corrosion of the storage tank, the growth of microbial populations and the resulting microbial-induced corrosion or biocorrosion of the storage tank. Therefore, the management of the water content is essential for controlling these unwanted corrosion reactions and the contamination of the biodiesel with microbes. The removal of accumulated water from the bottom of storage tanks at regular intervals is one method that can be employed to maintain FAME-based biodiesels and limit the onset and propagation of corrosion reactions.

3.5.5 Liners for storage tanks

Storage tank liners can be very effective in corrosion protection by preventing the biodiesel from coming in contact with the metallic storage tank. The quality of the liner is important, as any defects or voids in the lining will allow solution to collect and corrosion to occur between the liner and the metallic storage tank. Epoxy-based liners are commonly used and are available commercially, and these are very well suited to blends with lower FAME levels (up to B20).

3.6 Risk Analysis

The corrosion of FAME-based biodiesel storage systems is an unintended consequence in the development of biofuels for renewable energy applications. It has emerged as an issue over recent years. Using the available information on the stability of FAME-based biodiesels, a risk analysis was performed of the potential risks of a biodiesel fuel release due to a corrosion event. This analysis, provided as a risk matrix, is shown in Figure 3.5. A risk matrix is a tool that can be used to visually assess and categorise risks. Here, a 5 × 5 risk matrix was employed by considering the likelihood of corrosion, based on both the FAME content of the biodiesel and the management of the fuel storage system.

In this approach, the risks are grouped under four categories, based on their level of probability and risk of corrosion: (1) low, (2) moderate, (3) high and (4) very high. Each of these levels is given an additional score, with a score of 1 indicating that corrosion is highly unlikely to occur under the specified conditions and a score of 25 indicating a very high probability of corrosion, or that corrosion will certainly occur at some stage. The categories used for the probability of occurrence and their significance in terms of the management of the stored biodiesel are described in Table 3.3. The consequences in Figure 3.5 are divided into five categories:

1. Negligible oxidation of the fuel and corrosion of the fuel storage system, resulting in minimal chemical changes in the fuel with no significant impact on storage.
2. Water build-up in the tank, indicating some changes in the stored FAME-based biodiesel. This water can act as a breeding ground for microbes and accelerate fuel degradation and the onset of microbial-induced corrosion.
3. Increased acidity, indicating oxidation of the biodiesel combined with the generation of acidic conditions, which can promote tank corrosion.

RISK MATRIX		Consequences				
		Very short storage time <i>Negligible</i>	Some water build-up <i>Minor</i>	Increase in Acidity <i>Significant</i>	Microbial contamination <i>Severe</i>	Tank corrosion and microbes <i>Very Severe</i>
Management	High level Blends Almost Certain	Moderate (6)	High (10)	High (15)	Very High (20)	Very High (25)
	Poor management Likely	Moderate (4)	Moderate (8)	High (12)	Very High (16)	Very High (20)
	Maintenance, but no liners Possible	Low (3)	Moderate (6)	Moderate (9)	High (12)	High (15)
	Higher blends Liners/anti-oxidants Unlikely	Low (2)	Moderate (6)	Moderate (6)	Moderate (8)	High (10)
	Low Blends/Liners Very unlikely	Low (1)	Low (2)	Low (3)	Moderate (6)	Moderate (6)

Figure 3.5. A risk matrix for FAME-based biodiesels.

Table 3.3. Summary of the probabilities of occurrence for the categories used in Figure 3.5

Category	Management and storage conditions	Probability of occurrence
Very unlikely	Very low-level blends (B2)	Corrosion is unlikely to occur and is awarded the lowest risk level of 1 when the low-level blends are stored for short periods of time
Unlikely	Liners and antioxidants, but blend with higher FAME levels (B5–B10)	Corrosion is unlikely to occur with a risk level of 2 for short storage times, but it may occur under exceptional circumstances
Possible	Maintenance and monitoring in place, but a tank liner is not employed (B5–B10)	Corrosion is now possible, as the FAME-based biodiesel is in direct contact with the metallic tank. There is a risk level of 3 for very short storage times, increasing to 9 when a decrease in pH is observed
Likely	Poor management of the stored FAME-based biodiesel (B5–B10) – for example no antioxidants, liners, pH measurements	Corrosion is now likely to occur, with a risk level of 4 at short periods of time, increasing to 12 when a pH decrease occurs, indicating the oxidation of the FAME-based biodiesel
Almost certain	High-level blends (B50–B100)	Corrosion is certain to occur, with a risk level of 5 for shorter periods of time, increasing to 15 when a pH change is first observed

4. Detection of microbes, indicating microbial contamination and possibly microbial-induced corrosion.
5. Corrosion of the fuel tank and the release of the stored fuel, posing significant environmental and safety risks.

By considering the fuel storage conditions of the FAME blends (management) as a function of the probability of corrosion (consequences), a risk matrix (as shown in Figure 3.5) can be generated. This shows that the risks of corrosion are highest for blends

with higher FAME levels and when management and monitoring of the stored fuel are poor. The risk of corrosion increases further following a build-up of water, an increase in the acidity of the biodiesel and the detection of microbial contamination, and finally corrosion of the storage tank occurs. It is evident from this analysis that good management and routine testing protocols coupled with lower-level blends are essential in minimising the consequences and keeping the risks of corrosion and fuel release low or at moderate levels.

4 Conclusions, Guidelines and Policy Recommendations

Increasing energy demands and environmental concerns have placed much focus on cleaner and more sustainable energies. Biodiesel blends have emerged as a replacement for petroleum diesel and have been proven to be more beneficial in terms of emissions and renewability. In addition, their good biodegradability is a key advantage. Biodiesel is not only considered for transport and heating, but also as a marine fuel (CIMAC, 2024). Nevertheless, it is clearly evident that FAME-based biodiesels are less stable than petroleum-based biodiesel. These effects become more pronounced with increasing storage times and with higher FAME contents or higher-level blends (i.e. higher B values).

Accordingly, additional policies and guidelines regarding the handling, use and storage of FAME-based biodiesels are needed within Ireland. Currently, the biodiesel blends in Ireland typically have a 5–7% biodiesel content (B5 to B7). This needs to be increased further to have a real and lasting impact on the renewable energy sector in Ireland. However, as shown in Chapter 3, increasing the biodiesel content of fuels comes with increasing risks of corrosion, depending on the composition of the biodiesel blends used and the fuel storage system materials and management (National Renewable Energy Laboratory, 2008).

The development of policies, such as (1) fuel excise tax reduction/exemption on FAME-based biodiesel blends, (2) biodiesel mandates, with annual volume targets, (3) biodiesel blending mandates for different sectors and (4) rebates and/or tax incentives on research and development in FAME-based biodiesels, could increase the use of FAME-based biodiesel within Ireland. Nevertheless, with increased usage, additional guidelines and recommendations that are specific to the unwanted corrosion reactions are essential, and these are discussed below.

Guidelines and recommendations for minimising the risks of corrosion are outlined below and are divided into the following:

- General guidelines and steps to follow when first managing, using and storing FAME-based biodiesel.
- Additional considerations when handling and storing low-level blends, up to and including B10.
- Additional guidelines when dealing with B100 and other high-level blends.

Developing guidelines for B100, as well as for the lower-level blends that are commonly used as fuel, was considered important, because pure biodiesel is stored before blending, and therefore a good understanding of how it should be handled and stored is important. If not handled correctly, and corrosion and antimicrobial contamination occur, then this could have a significant impact on the stability of the blends derived from the B100.

4.1 General Guidelines and Steps to Follow When Managing FAME-based Biodiesels

Biodiesels come in many different forms, including those derived from highly refined vegetable oils and FAME additives. They can be blended with petroleum-based diesel at different levels and their compositions can vary with time. Therefore, when first working with biodiesel, it is important to establish the following:

- What biodiesel is stored – a FAME-derived biodiesel or a more stable highly refined vegetable oil combination?
- Has an inspection programme been set up to monitor the storage tanks and other metallic materials in contact with the FAME-based biodiesel?
- When was the FAME added to the diesel?
- What is the FAME level in the blend (e.g. 5% (B5), 7% (B7))?
- How long will the FAME-based biodiesel be stored?
- Is the storage tank modified with a suitable liner?
- Have antioxidants been added to the biodiesel?

- Has consideration been given to corrosion issues (pitting corrosion attack of the storage tanks) and microbial contamination that could occur during storage? These are more relevant if the storage time, or the contact time between the FAME-based biodiesel and the storage tank or pipelines, increases.
- Has consideration been given to equipment that may be more prone to corrosion when in contact with FAME additives? Copper, brass, tin and zinc are easily corroded in the presence of FAME additives and are not recommended. Likewise, polymers, such as polyethylene, polypropylene, polyurethane and polyvinylchloride, are not recommended. The recommended metals and alloys are stainless steel, carbon steel and aluminium, while nylon and Teflon also have reasonably good stability when in contact with FAME-based biodiesels.
- Has consideration been given to the possibility of microbial contamination of the FAME-based biodiesel? This microbial growth can, in turn, lead to microbial-induced corrosion (also termed biocorrosion).

4.2 Additional Recommendations for Low-level FAME Blends

- Low-level blends (e.g. B2 to B10) have adequate stability for normal use and short storage times, requiring no additional steps when compared with petroleum-based diesel.
- If stored for more than a few months, then antioxidants (stability additives) are recommended.
- Lined storage tanks are recommended; however, corrosion can occur between the lining and the metallic storage tank if defects are present in the lining. This should be considered during the inspection and maintenance of the storage tanks.
- When stored, acidity should be measured regularly, approximately every 1 or 2 months.
- Minimising the water content is important, and any accumulated water at the bottom of the storage tank should be removed from tanks on a regular basis. It is also recommended that the pH of this water be tested (with litmus paper or a pH meter), to assess the level of acidity.
- When storing for longer terms, tanks should be kept as full as possible to prevent condensation,

which would eventually contribute to higher amounts of water in the storage tank.

- Finally, standing tanks should be sampled and tested for microbial contamination.

4.3 Additional Recommendations for B100 and Other High-level FAME Blends

- B100 oxidises quickly and increases in acidity and viscosity, and its storage should be monitored carefully. If it becomes degraded to the point where it is out of specification then it should not be used and blended with diesel to produce lower-level blends, as this would introduce acidity and oxidation products, and affect the stability and performance of the lower-level blends.
- If storing B100, consideration should be given to storing it under a nitrogen atmosphere, as this removes the presence of oxygen, which promotes its oxidation.
- B100 freezes at higher temperatures than most other diesel-based fuels. At temperatures of about 2–15°C, it begins to cloud, and its viscosity increases. This must be taken into account when handling B100 or when blending it with diesel to produce lower-level blends.
- B100 is aggressive to common plastics (e.g. polyethylene and polypropylene) and these should not be used for storing B100.

A decision tree for the mitigation of risks associated with FAME-based biodiesels is presented in Figure 4.1, summarising the main points discussed for the low- and high-level blends. This analysis clearly shows that one of the most important steps is establishing the FAME-content of the biodiesel, as this will dictate which storage, management and testing protocols should be used.

In conclusion, it is clear that FAME-based and other blended biodiesels contribute to the renewable energy sector in Ireland and that they could contribute further. However, a thorough understanding of the conditions that give rise to the corrosion of the materials in contact with these fuels is needed. This must also be combined with the routine monitoring and management of any stored fuel to minimise the risks of corrosion and the release of fuel into the environment.

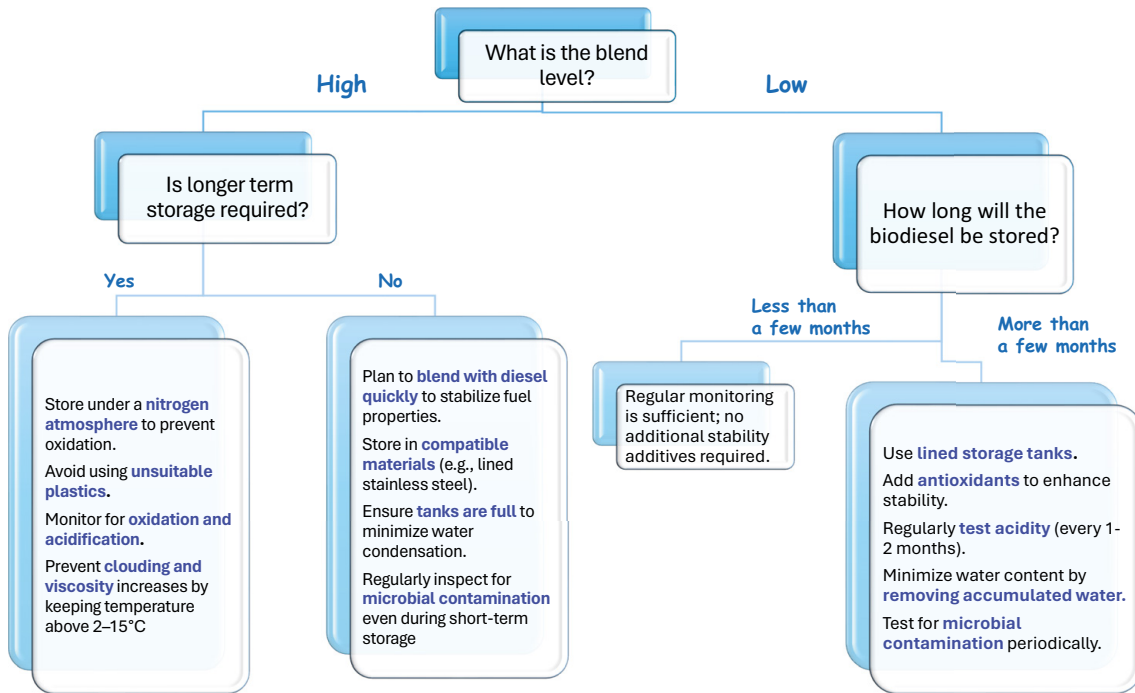


Figure 4.1. Decision tree for the mitigation of corrosion risks associated with high-level blends (equal to or higher than B50) and low-level blends (equal to or lower than B10) for FAME-based biodiesels.

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Abbreviations

BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
FAME	Fatty acid methyl ester
PG	Propyl gallate
TAN	Total acid number
TBHQ	Tertiary butylhydroquinone

An Gníomhaireacht Um Chaomhnú Comhshaoil

Tá an GCC freagrach as an gcomhshaoil a chosaint agus a fheabhsú, mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaoil a chosaint ar thionchar díobhálach na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialáil: Rialáil agus córais chomhlíonta comhshaoil éifeachtacha a chur i bhfeidhm, chun dea-thorthaí comhshaoil a bhaint amach agus díriú orthu siúd nach mbíonn ag cloí leo.

Eolas: Sonraí, eolas agus measúnú ardchaighdeán, spriocdhírthe agus tráthúil a chur ar fáil i leith an chomhshaoil chun bonn eolais a chur faoin gcinnteoireacht.

Abhcóideacht: Ag obair le daoine eile ar son timpeallachta glaine, táirgiúla agus dea-chosanta agus ar son cleachtas inbhuanaithe i dtaobh an chomhshaoil.

I measc ár gcuid freagrachtaí tá:

Ceadúnú

- > Gníomhaíochtaí tionscail, dramhaíola agus stórála peitрил ar scála mór;
- > Sceitheadh fuíolluisce uirbhig;
- > Úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe;
- > Foinsí radaíochta ianúcháin;
- > Astaíochtaí gás ceaptha teasa ó thionscal agus ón eitlíocht trí Scéim an AE um Thrádáil Astaíochtaí.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

- > Iniúchadh agus cigireacht ar shaoráidí a bhfuil ceadúnas acu ón GCC;
- > Cur i bhfeidhm an dea-chleachtais a stiúradh i ngníomhaíochtaí agus i saoráidí rialáilte;
- > Maoirseacht a dhéanamh ar fhreagrachtaí an údaráis áitiúil as cosaint an chomhshaoil;
- > Caighdeán an uisce óil phoiblí a rialáil agus údaruithe um sceitheadh fuíolluisce uirbhig a fhorfheidhmiú
- > Caighdeán an uisce óil phoiblí agus phríobháidigh a mheasúnú agus tuairisciú air;
- > Comhordú a dhéanamh ar líonra d'eagraíochtaí seirbhíse poiblí chun tacú le gníomhú i gcoinne coireachta comhshaoil;
- > An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaoil.

Bainistíocht Dramhaíola agus Ceimiceáin sa Chomhshaoil

- > Rialacháin dramhaíola a chur i bhfeidhm agus a fhorfheidhmiú lena n-áirítear saincheisteanna forfheidhmithe náisiúnta;
- > Staitisticí dramhaíola náisiúnta a ullmhú agus a fhoilsiú chomh maith leis an bPlean Náisiúnta um Bainistíocht Dramhaíola Guaisí;
- > An Clár Náisiúnta um Chosc Dramhaíola a fhorbairt agus a chur i bhfeidhm;
- > Reachtaíocht ar rialú ceimiceán sa timpeallacht a chur i bhfeidhm agus tuairisciú ar an reachtaíocht sin.

Bainistíocht Uisce

- > Plé le struchtúir náisiúnta agus réigiúnacha rialachais agus oibriúcháin chun an Chreat-treoir Uisce a chur i bhfeidhm;
- > Monatóireacht, measúnú agus tuairisciú a dhéanamh ar chaighdeán aibhneacha, lochanna, uiscí idirchreasa agus cósta, uiscí snámha agus screamhuisce chomh maith le tomhas ar leibhéal uisce agus sreabhadh abhann.

Eolaíocht Aeráide & Athrú Aeráide

- > Fardail agus réamh-mheastacháin a fhoilsiú um astaíochtaí gás ceaptha teasa na hÉireann;
- > Rúnaíocht a chur ar fáil don Chomhairle Chomhairleach ar Athrú Aeráide agus tacaíocht a thabhairt don Idirphlé Náisiúnta ar Gníomhú ar son na hAeráide;

- > Tacú le gníomhaíochtaí forbartha Náisiúnta, AE agus NA um Eolaíocht agus Beartas Aeráide.

Monatóireacht & Measúnú ar an gComhshaoil

- > Córais náisiúnta um monatóireacht an chomhshaoil a cheapadh agus a chur i bhfeidhm: teicneolaíocht, bainistíocht sonraí, anailís agus réamhaisnéisiú;
- > Tuairiscí ar Staid Thimpeallacht na hÉireann agus ar Tháscairí a chur ar fáil;
- > Monatóireacht a dhéanamh ar chaighdeán an aeir agus Treoir an AE i leith Aeir Ghlain don Eoraip a chur i bhfeidhm chomh maith leis an gCoinbhinsiún ar Aerthruailliú Fadraoin Trasteorann, agus an Treoir i leith na Teorann Náisiúnta Astaíochtaí;
- > Maoirseacht a dhéanamh ar chur i bhfeidhm na Treorach i leith Torainn Timpeallachta;
- > Measúnú a dhéanamh ar thionchar pleananna agus clár beartaithe ar chomhshaoil na hÉireann.

Taighde agus Forbairt Comhshaoil

- > Comhordú a dhéanamh ar ghníomhaíochtaí taighde comhshaoil agus iad a mhaoiniú chun brú a aithint, bonn eolais a chur faoin mbeartas agus réitigh a chur ar fáil;
- > Comhoibriú le gníomhaíocht náisiúnta agus AE um thaighde comhshaoil.

Cosaint Raideolaíoch

- > Monatóireacht a dhéanamh ar leibhéal radaíochta agus nochtadh an phobail do radaíocht ianúcháin agus do réimsí leictreamaighnéadacha a mheas;
- > Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as tasmí núicléacha;
- > Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta;
- > Sainseirbhísí um chosaint ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Ardú Feasachta agus Faisnéis Inrochtana

- > Tuairisciú, comhairle agus treoir neamhspleách, fianaise-bhunaithe a chur ar fáil don Rialtas, don tionscal agus don phobal ar ábhair maidir le cosaint comhshaoil agus raideolaíoch;
- > An nasc idir sláinte agus folláine, an geilleagar agus timpeallacht ghlan a chur chun cinn;
- > Feasacht comhshaoil a chur chun cinn lena n-áirítear tacú le hiompraíocht um éifeachtúlacht acmhainní agus aistriú aeráide;
- > Tástáil radóin a chur chun cinn i dtithe agus in ionaid oibre agus feabhsúchán a mholadh áit is gá.

Comhpháirtíocht agus Líonrú

- > Oibriú le gníomhaireachtaí idirnáisiúnta agus náisiúnta, údaráis réigiúnacha agus áitiúla, eagraíochtaí neamhrialtais, comhlachtaí ionadaíochta agus ranna rialtais chun cosaint comhshaoil agus raideolaíoch a chur ar fáil, chomh maith le taighde, comhordú agus cinnteoireacht bunaithe ar an eolaíocht.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an GCC á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóir. Déantar an obair ar fud cúig cinn d'Oifigí:

1. An Oifig um Inbhuanaitheacht i leith Cúrsaí Comhshaoil
2. An Oifig Forfheidhmithe i leith Cúrsaí Comhshaoil
3. An Oifig um Fhianaise agus Measúnú
4. An Oifig um Chosaint ar Radaíocht agus Monatóireacht Comhshaoil
5. An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tugann coistí comhairleacha cabhair don Gníomhaireacht agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair inmí agus le comhairle a chur ar an mBord.

Evidence Synthesis Report 5

**Study of the Increased Risk of Corrosion
with the Use of Fatty Acid Methyl Ester
(FAME) as a Diesel Additive**

Authors:

Carmel Breslin, Gillian Collins,
Tara Barwa and Daniele Alves

EPA Research: McCumiskey House,
Richiew, Clonskeagh, Dublin 14.

Phone: 01 268 0100

Twitter: @EPAResearchNews

Email: research@epa.ie

EPA Research Webpages

www.epa.ie/our-services/research/

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