



## Corrosion monitoring of fuel system materials resulting from the use of bio heavy oil

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**Abstract:** To achieve the 2050 carbon neutrality goal, bio heavy oil is being explored as a substitute for conventional fossil fuels. Although bio heavy oil can reduce carbon emissions and serve as a sustainable energy source, its distinct chemical and physical properties may lead to unique corrosion issues in fuel oil systems. This study monitors the surface corrosion of fuel system materials over time due to the use of bio heavy oil, elucidates the corrosion mechanisms, and proposes effective corrosion prevention measures. Key findings include the increase in oxygen content on the surfaces of both untreated and nitrided carbon steels, as shown by SEM and XRD analyses. Over time, corrosion products such as FeO, Fe<sub>3</sub>O<sub>4</sub>, and FeS were identified on the material surfaces. Despite the nitride carbon steel known superior corrosion resistance, it exhibited similar oxygen bonding strength to iron under the same conditions, suggesting the influence of surface conditions, bio heavy oil environment, and corrosion product types. Additional data is required for accurate analysis, considering factors such as acidity, sulfur content, and moisture content of the bio heavy oil. This comprehensive analysis will aid in understanding corrosion mechanisms and developing effective corrosion prevention strategies.

**Keywords:** Bio heavy oil, Corrosion, Fuel system materials, Oxidation

### 1. Introduction

To achieve the 2050 carbon neutrality goal, the introduction of bio heavy oil as a substitute for conventional fossil fuels is being actively discussed [1][2]. Bio heavy oil has the potential to significantly reduce carbon emissions and be utilized as a sustainable energy source [3]. As an eco-friendly fuel based on renewable raw materials, it is increasingly being recognized as a viable alternative to traditional fossil fuels. Bio heavy oil is primarily produced from raw materials such as vegetable oils, animal fats, and waste oils. The utilization of these materials not only contributes to the reduction of carbon dioxide emissions but also alleviates the issue of fossil fuel depletion, thereby promoting environmental sustainability and resource conservation.

Moreover, bio heavy oil has found applications in various industrial sectors both domestically and internationally. It is particularly used as fuel for maritime vessels, power plants, and industrial boilers [4]-[6]. The adoption of bio heavy oil in these sectors underscores its versatility and effectiveness as a renewable energy source. As countries and industries strive to meet stringent

environmental regulations and reduce their carbon footprints, the role of bio heavy oil becomes increasingly critical. It provides a practical solution to energy needs while supporting global efforts to combat climate change and achieve sustainability goals.

However, the introduction and widespread use of bio heavy oil are not without challenges. One of the primary concerns is the potential for different types of corrosion issues compared to conventional fuel oils, necessitating further research and investigation. The chemical and physical properties of bio heavy oil differ significantly from those of traditional fossil fuels. These differences can lead to a high potential for corrosion problems in fuel oil systems [7][8]. The main materials used in fuel oil systems, such as iron and iron nitrides, are particularly susceptible to corrosion due to the acidity, moisture content, and impurities present in bio heavy oil [9]. These corrosion issues can result in performance degradation of fuel oil systems, increased maintenance costs, and safety concerns, making it a critical area for research and development.

This study aims to address these challenges by monitoring the

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surface corrosion of fuel system materials over time resulting from the use of bio heavy oil. Additionally, the study seeks to elucidate the corrosion mechanisms and establish effective corrosion prevention measures. The specific objectives of the study are as follows:

**Analyze the Chemical Properties of Bio Heavy Oil**, examining how characteristics such as acidity, moisture content, sulfur content, and impurities affect corrosion. A clear understanding of these properties is essential to evaluate corrosion potential and identify contributing factors.

Evaluate the Corrosion Characteristics of Fuel System materials, by experimentally assessing how key materials—such as iron and nitrided iron—respond to exposure to bio heavy oil. This includes analyzing the types and extent of corrosion observed in each material.

**Elucidate the Corrosion Mechanisms**, using analytical techniques such as SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-ray Spectroscopy), and XRD (X-ray Diffraction) to observe oxide formation and surface changes. These methods provide detailed insights into how corrosion develops over time.

**Propose Corrosion Prevention Measures**, by identifying effective strategies based on the research findings to minimize corrosion in fuel system materials. The goal is to implement practical solutions that improve the longevity and safety of systems using bio heavy oil. Special focus is placed on areas within internal combustion engines that are particularly vulnerable to corrosion.

**Fuel Storage Tanks and Supply Piping**, which are vulnerable to accelerated corrosion due to the high acidity and water content of bio heavy oil. Continuous monitoring and appropriate mitigation strategies are essential to maintain the integrity and reliability of these systems.

**Fuel Pumps and Injection Systems**, including components like pump plungers, barrels, injection valve internals, and high-pressure pipes, are susceptible to corrosion. Maintaining their durability and functionality is critical for the efficient operation of internal combustion engines.

**Sealing Components Inside the Engine** require materials with high corrosion resistance. For example, evaluating the compatibility of FKM (fluoroelastomer) seals with bio heavy oil is essential. Proper selection of sealing materials helps prevent leaks and ensures stable engine performance.

Through this comprehensive research, we aim to develop a thorough understanding of the corrosion issues associated with bio heavy oil and propose viable solutions to enhance the

longevity and safety of fuel oil systems. By addressing these challenges, we can facilitate the broader adoption of bio heavy oil as a sustainable and environmentally friendly energy source, contributing to the global efforts to achieve carbon neutrality by 2050.

## 2. Experimental Procedure

### 2.1 Characteristics of Bio Heavy Oil

Bio heavy oil, an eco-friendly fuel derived from renewable raw materials, exhibits distinct physical and chemical properties compared to conventional fossil fuels. These characteristics significantly influence the performance, storage stability, and corrosiveness of bio heavy oil as a fuel. Understanding these properties is essential for optimizing its use and addressing potential issues. The following are the main physical and chemical properties of bio heavy oil:

#### 2.1.1 Physical Properties

**Viscosity:** The viscosity of bio heavy oil is generally higher than that of conventional fossil fuels, and it varies depending on the raw materials and production methods used. Viscosity is a critical parameter as it changes significantly with temperature, increasing at lower temperatures. This can affect fuel flow, atomization, and combustion efficiency, particularly in colder climates or during storage. The higher viscosity necessitates modifications in fuel handling and injection systems to ensure optimal performance.

**Density:** The density of bio heavy oil is typically slightly higher compared to fossil fuels. This variation in density depends on the molecular structure and components of the bio heavy oil. Higher density influences the fuel's energy density and combustion characteristics, impacting engine performance and fuel consumption. Accurate measurement and control of density are crucial for achieving consistent energy output and efficient combustion.

**Water Content:** Bio heavy oil can contain water introduced during the production process. High water content is detrimental as it decreases combustion efficiency and can lead to corrosion and oxidation problems during storage and transportation. Water presence in fuel can also cause phase separation, microbial growth, and filter clogging. Therefore, effective water removal and management strategies are essential to maintain fuel quality.

**Color and Appearance:** The color of bio heavy oil can vary widely (yellow, brown, green, etc.) depending on the raw

materials and production methods. The appearance of bio heavy oil may also include impurities that require refining processes for removal. The visual inspection of color and clarity can serve as preliminary quality indicators, but detailed chemical analysis is necessary for comprehensive assessment.

## 2.1.2 Chemical Properties

### 2.1.2.1 Acidity (pH)

Bio heavy oil is generally mildly acidic due to organic acids formed during the production process. This acidity can affect storage stability and increase the risk of metal corrosion in fuel systems. Monitoring and controlling the pH levels are essential to prevent corrosion-related failures and ensure long-term storage stability.

### 2.1.2.2 Oxidative Stability

Bio heavy oil is susceptible to oxidation, which may reduce its oxidative stability during storage. Oxidation can lead to the formation of gums and sediments, adversely affecting fuel quality and engine performance. Antioxidant additives and proper storage conditions can help mitigate oxidation risks.

### 2.1.2.3 Sulfur Content

Bio heavy oil typically has a low sulfur content, resulting in lower emissions of sulfur oxides (SOx) during combustion. This low sulfur content is an environmental advantage, contributing to reduced air pollution and compliance with stringent emission regulations. However, the absence of sulfur also affects lubricity, necessitating the use of lubricity additives.

### 2.1.2.4 Fatty Acid Methyl Esters (FAME)

Bio heavy oil mainly consists of fatty acid methyl esters (FAME), which influence fuel combustion characteristics and engine performance. The types and proportions of FAME vary based on the raw materials used. FAME content impacts the fuel's cold flow properties, cetane number, and compatibility with engine materials.

### 2.1.2.5 Degree of Unsaturation

Bio heavy oil may contain unsaturated fatty acids, affecting its oxidative stability. Higher levels of unsaturation make the oil more prone to oxidation, leading to potential storage and handling issues. Hydrogenation or blending with more saturated oils can improve stability.

### 2.1.2.6 Calorific Value

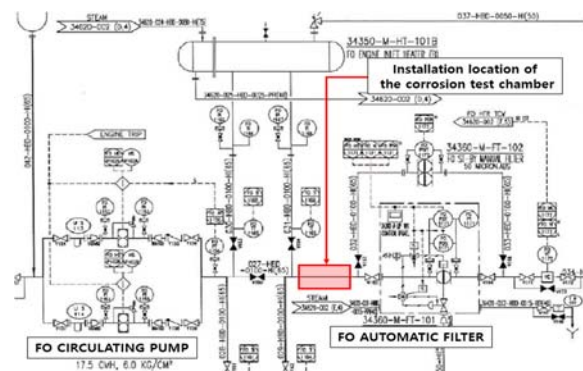
The calorific value of bio heavy oil is lower than that of fossil fuels, meaning more bio heavy oil may be required to obtain the

same energy output. This lower energy density necessitates adjustments in fuel metering and combustion systems to achieve desired performance levels.

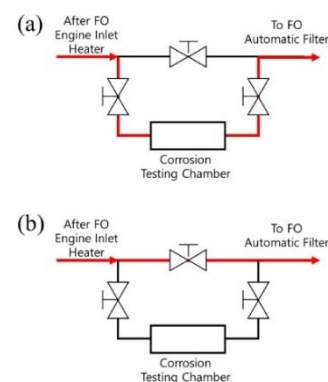
Among these properties, acidity (pH), water content, impurities, oxidative stability, and FAME content are particularly critical as they can cause different corrosion issues compared to conventional fossil fuels. Addressing these factors is essential for ensuring the reliable and efficient use of bio heavy oil in various applications.

## 2.2 Installation Location of the Corrosion Test Chamber

Figures 1 and 2 illustrate the location of the corrosion test chamber and the system diagram of the fuel oil supply line. The test chamber is strategically designed to avoid directly affecting the engine and is installed between the Fuel Oil (FO) Engine Inlet Heater and the FO Auto back washing filter. This placement ensures that the test chamber accurately simulates the operating conditions of the fuel system while isolating the engine from potential test-induced disruptions.



**Figure 1:** Location of the test chamber for corrosion evaluation in the engine room layout



**Figure 2:** System diagram of the fuel oil supply line: (a) configuration where fuel passes through the corrosion test chamber, (b) configuration where fuel bypasses the test chamber.

The test chamber's installation location is crucial for obtaining representative data on corrosion phenomena under real-world conditions. By situating the chamber in the fuel supply line, the study can monitor the interactions between bio heavy oil and fuel system materials, capturing the effects of temperature, flow dynamics, and fuel composition. This setup allows for a comprehensive evaluation of corrosion mechanisms and the development of effective prevention strategies.

A corrosion test chamber was installed between the FO engine inlet heater and the FO auto back washing filter (**Figure 1**) to simulate typical fuel supply conditions in marine diesel engines. During testing, bio heavy oil was maintained at 90–110 °C and 3–5 bar, reflecting standard preheating and supply conditions for high-viscosity fuels. Test specimens consisted of typical internal components used in marine fuel systems, including metal and sealing elements exposed to fuel in actual operations. These were installed in the flow path within the chamber to ensure continuous exposure. After 1, 3, and 6 months of exposure, specimens were analyzed using SEM, EDS, and XRD to evaluate surface changes and corrosion products.

In conclusion, the detailed examination of bio heavy oil's physical and chemical properties, coupled with the strategic installation of the corrosion test chamber, provides a robust framework for understanding and mitigating corrosion issues. This research aims to enhance the longevity and safety of fuel systems, promoting the broader adoption of bio heavy oil as a sustainable and environmentally friendly energy source.

### 2.3 Analysis and Evaluation of Specimens

In this experiment, scanning electron microscopy (FE-SEM, Mira3 LM, TESCAN) and energy-dispersive spectrometry (EDS) were employed to examine and elemental composition of the specimens following the composite corrosion test.

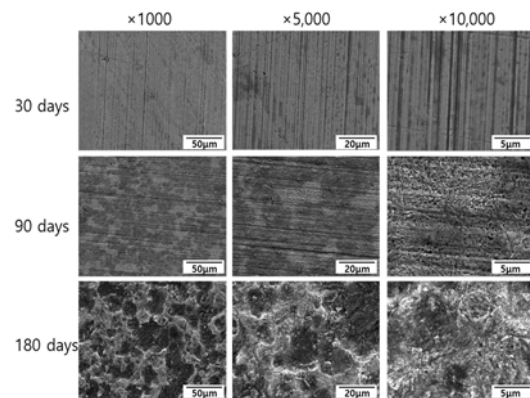
## 3. Results and Discussion

### 3.1 SEM Image Analysis

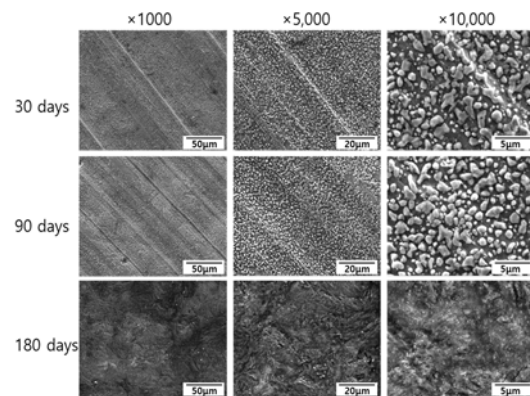
**Figures 3** and **4** present a detailed examination of the surface morphologies of untreated and nitrided carbon steels, as observed using SEM. The SEM images in **Figure 3** and **4**, depict the progression of surface changes over a period of 1 month, 3 months, and 6 months of exposure in the corrosion test chamber. This analysis provides insights into the corrosion mechanisms and the morphological evolution of the materials under the influence of bio heavy oil.

#### 3.1.1 Microstructural observations of Untreated Carbon Steel

At the onset of the experiment, the surface of untreated carbon



**Figure 3:** SEM images showing time-dependent changes in the surface morphology of untreated carbon steel after immersion in bio heavy oil



**Figure 4:** SEM images showing time-dependent changes in the surface morphology of nitrided carbon steel after immersion in bio heavy oil

steel, exhibited a relatively smooth and uniform structure. The SEM images revealed a homogeneous surface with minimal irregularities, indicating a pristine state with no significant signs of corrosion or deposition.

Three months into the exposure, noticeable changes began to appear on the surface of the iron. The SEM images showed the formation of island-shaped deposits distributed across the surface. These deposits contributed to an increase in surface roughness, indicating the initial stages of corrosion. The roughened texture suggested localized corrosion activities, possibly due to the interaction of iron with acidic components and impurities in the bio heavy oil.

By the six-month mark, the surface morphology of untreated carbon steel had undergone substantial transformation. The initial island-shaped deposits had grown into more complex, layered crystal structures. Under high magnification, the SEM images revealed that these deposits were composed of irregularly

arranged polyhedral particles, forming a porous structure. The disordered arrangement and increased porosity indicated advanced stages of corrosion, with significant material degradation and the formation of corrosion products.

### 3.1.2 Microstructural Observations of Nitrided Carbon Steel

Initially, the surface of nitrided carbon steel, displayed small, rounded deposits. These deposits were sparsely distributed and did not significantly alter the overall smoothness of the surface. The presence of these initial deposits suggested the onset of minor corrosion or reaction with the bio heavy oil components.

After three months of exposure, the SEM images of Material B showed a noticeable growth in the size and number of the deposits. The once small and rounded deposits had expanded, indicating progressive corrosion. The increased deposition suggested that the nitrided steel surface was actively reacting with the corrosive agents present in the bio heavy oil.

Six months into the experiment, the surface of nitrided carbon steel was entirely covered by the deposits. The SEM images revealed a complete transformation, with the deposits forming a continuous layer over the entire surface. This extensive coverage indicated severe corrosion, with the nitrided carbon steel surface being heavily compromised. The uniform deposition layer suggested a widespread and aggressive corrosion mechanism in progress.

The SEM analysis of untreated and nitrided samples highlights the distinct corrosion behaviors and progression patterns influenced by bio heavy oil. The untreated sample exhibited a gradual transition from a smooth surface to a porous, layered crystalline structure, indicative of localized and advanced corrosion processes. In contrast, the nitride sample showed an initial formation of small deposits that expanded and eventually covered the entire surface, suggesting a more uniform and aggressive corrosion mechanism.

These observations demonstrate the importance of understanding the specific interactions between bio heavy oil and different fuel system materials. The differences in corrosion patterns between the untreated and nitrided carbon steel highlight the need for tailored corrosion prevention strategies based on the material composition and the operational environment.

In conclusion, the SEM images provide valuable insights into the corrosion mechanisms and surface morphology changes of materials exposed to bio heavy oil. This detailed analysis is crucial for developing effective corrosion mitigation measures and ensuring the reliability and longevity of fuel systems utilizing bio

heavy oil as an alternative fuel source.

## 3.2. Changes in Elemental Composition

We present the results of the elemental composition analysis conducted using EDS. **Figure 5** illustrate the changes in elemental composition on the surfaces of untreated and nitrided carbon steel, respectively, after immersion in bio heavy oil over different periods. The analysis focuses on the variations in oxygen and sulfur content, which are key indicators of corrosion and oxidation processes.

### 3.2.1 EDS Analysis of Untreated Carbon Steel

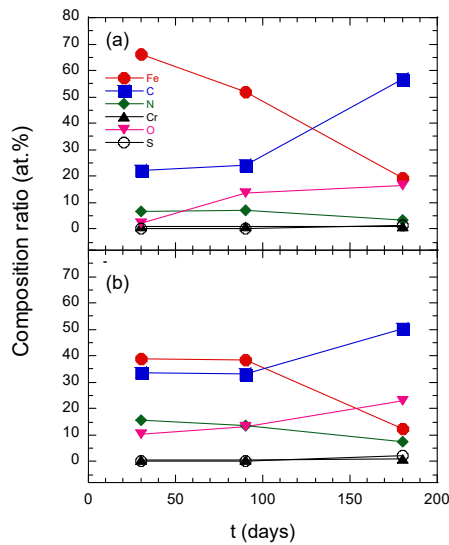
Regarding the oxygen content, the EDS analysis for Material A revealed a significant increase in oxygen content over time. Initially, the oxygen content was measured at 2.01% after 1 month of exposure. The value increased markedly to 13.74% after three months of exposure and continued to rise, reaching 16.48% at the six-month mark. The progressive rise in oxygen content indicates the ongoing formation of oxides on the iron surface, which is a hallmark of corrosion. The correlation between the oxygen content and the duration of exposure suggests that the rate of oxidation accelerates over time, likely due to the continuous interaction between the iron and the oxygen present in the bio heavy oil.

In addition to oxygen, sulfur content was also detected on the surface of Material A. The presence of sulfur compounds is indicative of sulfur-induced corrosion, which can occur due to the sulfur impurities present in bio heavy oil. The formation of iron sulfides alongside iron oxides contributes to the overall degradation of the material, exacerbating the corrosion process.

### 3.2.2 EDS Analysis of Nitrided Carbon Steel

Regarding the oxygen content, the EDS analysis for nitrided sample showed a different initial oxygen content compared to the untreated one. After 1 month of immersion, the oxygen content was already relatively high at 10.33%. This content increased to 13.14% after 3 months and further rose significantly to 23.12% after 6 months. The higher initial oxygen content suggests that nitrided one is more reactive to oxygen in the early stages of exposure. The substantial increase over time confirms that the oxidation process is vigorous and persistent, leading to the extensive formation of oxides on the surface.

Similar to the untreated carbon steel, sulfur content was detected on the surface of nitride one. The presence of sulfur compounds indicates that nitrided carbon steel is also susceptible to sulfur-induced corrosion. The combined effects of oxidation and sulfurization contribute to the complex corrosion phenomena



**Figure 5:** Changes in elemental composition of (a) untreated and (b) nitrided carbon steel after immersion in bio heavy oil

observed in nitrided carbon steel, affecting its structural integrity and performance.

The EDS results, as depicted in **Figure 5**, provide a quantitative understanding of the elemental changes occurring on the surfaces of untreated and nitride samples. The marked increase in oxygen content over time for both materials signifies the formation of oxides, which are typical corrosion products. The SEM images presented in Figures 3 and 4 further support these findings, as the surface deposits are presumed to be oxidation products formed through interactions with moisture and oxygen contained in the bio heavy oil.

The presence of sulfur content on both materials further demonstrates the complexity of the corrosion processes. Sulfur compounds can accelerate corrosion by forming iron sulfides, which weaken the material structure. The dual presence of oxygen and sulfur compounds indicates that both oxidation and sulfurization are contributing to the overall material degradation.

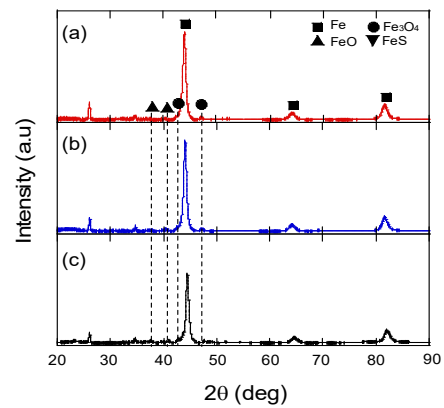
The temporal increase in the amount of corrosion products, as evidenced by the rising oxygen and sulfur content, confirms that the corrosion process intensifies with prolonged exposure. This progressive nature of corrosion highlights the importance of continuous monitoring and the development of effective corrosion prevention strategies.

The comprehensive analysis using EDS has provided valuable insights into the elemental composition changes on the surfaces of untreated and nitride samples immersed in bio heavy oil. The significant increase in oxygen and sulfur content over time indicates that the aggressive nature of the corrosion processes

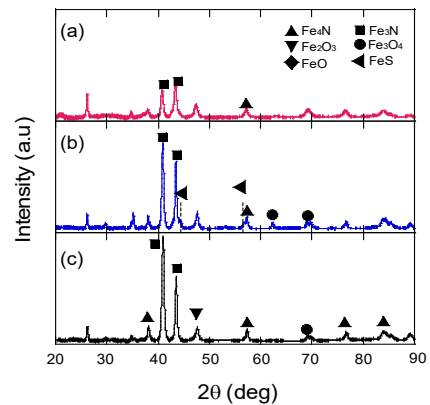
affecting both untreated and nitrided carbon steel. These findings are crucial for understanding the long-term effects of bio heavy oil on fuel system materials and for devising effective measures to mitigate corrosion. By addressing these challenges, we can enhance the durability and reliability of fuel systems using bio heavy oil, thereby supporting its broader adoption as a sustainable energy source.

### 3.3 XRD Analysis

We present the results of the X-ray Diffraction (XRD) analysis conducted on the untreated and nitrided after immersion in bio heavy oil. **Figures 6** and **7** illustrate the XRD patterns, which provide insights into the crystalline structures and the composition of corrosion products formed over time. This analysis complements the findings from the FE-SEM and EDS studies, offering a comprehensive understanding of the corrosion mechanisms.



**Figure 6:** Time-dependent changes in XRD peak intensity of untreated carbon steel after immersion in bio heavy oil: (a) 30 days, (b) 60 days, and (c) 180 days



**Figure 7:** Time-dependent changes in XRD peak intensity of nitrided carbon steel after immersion in bio heavy oil: (a) 30 days, (b) 60 days, and (c) 180 days

### 3.3.1 XRD Analysis of untreated carbon steel

For Material A, the XRD analysis revealed the initial formation of iron oxides such as FeO and Fe<sub>3</sub>O<sub>4</sub> after just 1 month of exposure, with the intensity of these peaks significantly increasing as the exposure time extended to 3 months and 6 months. By the end of the 6-month period, the emergence of FeS bonds was also detected, indicating that sulfur from the bio heavy oil had reacted with the carbon steel. This progression highlights the combined effects of oxidation and sulfurization, driven by the continuous interaction with both oxygen and sulfur present in the bio heavy oil. These findings suggest that the iron surface undergoes complex corrosion processes, resulting in the formation of both oxide and sulfide corrosion products, which contribute to significant material degradation over time.

### 3.3.2 XRD Analysis of Nitrided Carbon Steel

For Material B, the XRD analysis initially showed peaks corresponding to the crystalline structure of nitrided carbon steel, indicating a stable surface at the beginning of the experiment. However, as the exposure time increased, new peaks corresponding to iron oxides (FeO, Fe<sub>3</sub>O<sub>4</sub>, and Fe<sub>2</sub>O<sub>3</sub>) began to appear and their intensity grew significantly over the 3-month and 6-month periods. Additionally, the formation of FeS was observed after 6 months, confirming that sulfur from the bio heavy oil had also reacted with the nitrided steel surface. These findings demonstrate that the nitrided steel surface is susceptible to both oxidation and sulfurization processes during prolonged exposure to bio heavy oil. The combined effects of these processes result in significant structural changes and the development of various corrosion products, which further compromise the integrity and performance of the material over time.

The XRD analysis results, as depicted in **Figures 6 and 7**, provide valuable insights into the crystalline structure and composition of corrosion products formed on untreated and nitride carbon steel. The detection of iron oxides (FeO, Fe<sub>3</sub>O<sub>4</sub>, and Fe<sub>2</sub>O<sub>3</sub>) and iron sulfides (FeS) confirms the dual corrosion mechanisms of oxidation and sulfurization.

For untreated sample, the progressive increase in the intensity of iron oxide peaks over time indicates a continuous oxidation process. The formation of FeS after six months underscores the significant impact of sulfur in the bio heavy oil, contributing to the overall material degradation. Similarly, for the nitride carbon steel, the presence of nitrided carbon steel peaks initially, followed by the emergence of iron oxides and sulfides, highlights the complex interactions between the material and the corrosive

agents in the bio heavy oil.

The findings from the XRD analysis support the observations from the FE-SEM images and the EDS results. The formation of oxide and sulfide layers observed in the SEM images aligns with the elemental composition changes detected by EDS and the crystalline structure changes identified by XRD.

The comprehensive analysis using XRD has provided a detailed understanding of the corrosion products formed on the untreated and B after immersion in bio heavy oil. The identification of iron oxides and sulfides highlights the aggressive nature of the corrosion processes, involving both oxygen and sulfur. These findings are crucial for developing effective corrosion prevention strategies and ensuring the long-term reliability of fuel systems utilizing bio heavy oil. By addressing these challenges, we can promote the broader adoption of bio heavy oil as a sustainable and environmentally friendly energy source.

## 4. Conclusion

This study investigated the corrosion behavior of iron and nitrided iron when exposed to bio heavy oil (BHO) over a six-month period. Using SEM, EDS, and XRD analyses, we identified the progressive formation of iron oxides (FeO, Fe<sub>3</sub>O<sub>4</sub>, and Fe<sub>2</sub>O<sub>3</sub>) and iron sulfides (FeS) on both materials. These corrosion products intensified with time, indicating that BHO induces both oxidation and sulfurization processes, which degrade material integrity.

Although nitrided iron is generally considered more corrosion resistant due to the formation of stable nitrides such as Fe<sub>4</sub>N and Fe<sub>3</sub>N, our results showed comparable oxidation behavior between the two materials under identical test conditions. This suggests that factors such as surface condition, chemical composition of the BHO (e.g., acidity, sulfur, and moisture), and the nature of the corrosion products significantly influence the overall corrosion resistance.

To develop effective corrosion prevention strategies, further investigation is needed to quantify the morphology and structure of corrosion products and analyze peak shifts in XRD patterns. Comprehensive data that accounts for environmental and material-specific variables will be essential to improve the long-term durability and safety of fuel system components operating with BHO. Ultimately, these findings support the broader adoption of bio heavy oil as a sustainable alternative, provided that appropriate materials and protection strategies are employed.

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## Author Contributions

Conceptualization, J. Yang; Methodology, C. Kim; Software, C. Kim; Formal Analysis, C. Kim; Investigation, C. Kim; Resources, J. Yang; Data Curation C. Kim; Writing-Original Draft Preparation, Y. Kim; Writing-Review & Editing, Y. Kim; Visualization, Y. Kim; Supervision, J. Yang; Project Administration, J. Yang; Funding Acquisition, J. Yang.

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