Progress in Corrosion Research on Alternative Liquid Fuels

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Abstract: In the current context of fossil energy depletion and the requirement for low carbon emissions, the efficient use of energy and a diversified energy mix have become increasingly important. The use of cleaner and low-carbon alternative fuels is rapidly growing. However, corrosion remains a key issue limiting the large-scale application of alternative fuels. This paper describes the corrosion characteristics of different alternative fuels. Also, the mechanisms of fuel corrosion, corrosion measurement methods, and the future of corrosion inhibitor applications are discussed. Corrosion causes changes in material weight and surface morphology and generates electrical signals as it progresses. Although there are well-established methods to characterize corrosion by recognizing these changes, there is still a need to identify a universal standard signal for their detailed description. For the foreseeable future, corrosion in fuels will continue to be mitigated by the addition of corrosion inhibitors. The research on corrosion inhibitors focuses on green corrosion inhibitors and multifunctional corrosion inhibitors. However, further analysis is needed to understand the active ingredients in green corrosion inhibitors, and the mechanism of corrosion inhibition for different types of corrosion inhibitors needs further research.

Keywords: biofuel; corrosion mechanism; corrosion testing and standards; corrosion inhibitor

1. Introduction

Fossil fuels have been the main source of energy for human society, and they provide about 80% of the current global energy demand [1]. Solar and wind energy, the main sources of alternative energy, are also not promising in terms of their extraction potential, and researchers have calculated that both should be lower than the final energy consumption of current fossil fuels [2,3]. The fossil energy crisis and pressures to reduce carbon emissions are driving the search for new alternative fuels.

Alternative fuels derived from biomass are non-polluting and renewable resources. Liquid fuels derived from renewable biomass offer several advantages: they are abundant, renewable, and produce minimal environmental pollution [4]. These liquid fuels derived from biomass are effective in reducing emissions [5]. Researchers are constantly looking for biomass sources for liquid fuels, such as palm oil, rapeseed oil, and sunflower oil. Additionally, blending a certain percentage of methanol or ethanol with gasoline and diesel is a popular focus for future fuels. Such fuel blends already exist in many countries and are performing well. However, further large-scale applications need to consider factors such as the energy density, viscosity, ignition performance, and industry chain integration of liquid fuels. Another important issue to address is corrosion. Each new alternative fuel must overcome corrosion challenges as it transitions from the laboratory to large-scale production. Corrosion problems continue to cause significant economic losses, safety issues, environmental pollution, and resource depletion in various settings.
A cited report by the World Bank indicates that the cost of corrosion consumes 3.4% of the global gross domestic product (GDP) [6]. Corrosion by liquid energy sources affects production equipment, transportation pipelines, storage vessels, and, most importantly, engines. Researchers are increasingly concerned about engine sensitivity to fuel corrosion, which is becoming more pronounced [7]. Accidents associated with liquid fuel corrosion are frequent and result in significant losses, posing a key constraint to the further development of alternative fuels. To date, more than two thousand articles have addressed this issue, providing substantial insight into the problem (see Section 2 for details). However, a clear mechanism and comprehensive solution have not yet been developed. Therefore, it is necessary to review the previous research results to identify key research directions and unresolved problems. The present situation of fuel corrosion is reviewed in this paper. On the one hand, it can help researchers more easily discover unsolved problems involving corrosion in alternative fuels. On the other hand, it can help reveal more effective ways to reduce corrosion in the practical application of fuel, thereby reducing economic losses, safety risks, and environmental pollution caused by corrosion.

This paper provides an overview of the corrosion of metallic materials by liquid fuels. Utilizing bibliometric tools (Section 2) and the author’s research, this paper aims to identify key directions and questions of interest to researchers in the field of liquid fuel corrosion. Key areas of concern include the extent to which corrosion occurs between different fluids and materials, which materials corrode more intensely, the reasons for varying levels of corrosion, and strategies to mitigate the effects of corrosion. Additionally, the methods used to study corrosion problems are discussed. These concerns are addressed in this paper in separate chapters.

In short, oils derived from biomass exhibit the greatest corrosion potential, mainly because they contain organic acids or chemicals that can spontaneously oxidize and turn into organic acids. The corrosion potential of different biodiesels can be predicted based on their acidity; higher acidity correlates with higher corrosion. Considering the cost and effectiveness, corrosion inhibitors—especially imidazole-type organic corrosion inhibitors—offer the best performance in preventing corrosion. Observing changes in the material’s surface and measuring its weight change are the easiest and most intuitive ways to recognize corrosion. A more accurate method involves probing the electrical characteristics of corrosion. Looking to the future, researchers are mainly concerned with two issues: identifying alternative fuels that balance combustion performance with minimal corrosion and developing efficient, low-cost, and nontoxic corrosion inhibitors to mitigate corrosion when it occurs.

2. Bibliometric Analysis of Studies on Corrosion in Alternative Liquid Fuels

A bibliometric approach was used to assess the current research direction on corrosion in alternative liquid fuels. The search was based on data from the Web of Science (WoS) database operated by Clarivate Analytics. The WoS database is widely accepted for bibliometrics, providing consistent and standardized records on more than 100 topics across different research fields. The statistical value of bibliometrics for publications has been widely accepted. This paper utilizes this statistical approach to find directions of interest to researchers. It is also used later to validate and elaborate on the issues revealed therein in a traditional review. Using the WoS database on 15 April 2024, we searched for and retrieved key documents based on the following search strategy: “TOPIC”: “(Corrosion*) AND (Biofuel* or alcohols* or diesel* gasoline* or petrol* or alternative fuel* or biodiesel*) NOT (Cavitations* or battery*)”. This produced 2630 results. The characteristics of liquid fuel corrosion research were determined by analyzing these 2630 results, which were mainly in the form of articles. Of these, 2103 articles accounted for 79.96% of the total search results.

From the publications obtained through the WoS search, we can gather information about the authors and their locations, titles, document types, publication years, publication institutes, abstracts, subject categories, and references. Data from these 2630 publications were exported to Microsoft Excel 2021, where aspects such as the document type, language, subject category, journal, country, institute, and author keywords were analyzed. We
used VosViewer_1.6.18 (an open-licensed software) to analyze the information related to countries, authors, and keywords.

Based on the publication year data, researchers began systematically exploring the hazards of and solutions to liquid fuel corrosion after 1999. Since then, the articles have shown an increasing trend year by year. The columnar section of Figure 1 shows the number of articles published on this topic from 1999 to 15 April 2024. Among these results, articles published in English dominate, with 2538 articles accounting for 96.50% of the total. Chinese follows with 21 articles (0.80%), and Portuguese with 20 articles (0.79%). English is the most widely used language in the world and the most advantageous language for scientific research, including the study of liquid fuel corrosion. In addition, seven countries produced more than 100 articles: China with 490 articles (18.63%), the United States with 306 (11.63%), India with 293 (11.14%), Brazil with 234 (8.90%), Egypt with 135 (5.13%), Saudi Arabia with 122 (4.64%), and Malaysia with 113 (4.30%).

The research directions of these 2630 papers are mainly related to engineering, with overlaps among different research areas. One paper can belong to different research directions simultaneously, indicating that solving corrosion problems requires collaborative research across various disciplines. Four major research directions account for more than 20% each: Engineering with 1012 articles (38.48%), Materials Science with 667 articles (25.36%), Chemistry with 574 articles (21.83%), and Energy & Fuels with 572 articles (21.75%). Table 1 shows the specific number and proportion of major research directions.

Among the journals in which these articles were published, as shown in Figure 2, Fuel published the most articles with 92 articles, followed by Energy & Fuels with 82 articles (3.12%), Corrosion Science with 34 articles (1.29%), and Engineering Failure Analysis with 32 articles (1.22%). In the following graph of source publications versus time, the two categories with the most numerous articles, Engineering and Energy & Fuels, have
similar publication numbers, with significant differences compared to other categories. However, over time, the publication numbers in other journals have been catching up. While the number of studies is increasing, the research appears to be dispersed across different fields. This trend confirms that the understanding of corrosion problems results from the collaborative efforts of multiple research directions, as shown in Table 1.

Table 1. Top 16 most productive research directions based on number of publications.

<table>
<thead>
<tr>
<th>Research Directions</th>
<th>Number of Publications</th>
<th>TP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engineering</td>
<td>1012</td>
<td>38.48</td>
</tr>
<tr>
<td>Materials Science</td>
<td>667</td>
<td>25.36</td>
</tr>
<tr>
<td>Chemistry</td>
<td>574</td>
<td>21.83</td>
</tr>
<tr>
<td>Energy &amp; Fuels</td>
<td>572</td>
<td>21.75</td>
</tr>
<tr>
<td>Metallurgy &amp; Metallurgical Engineering</td>
<td>263</td>
<td>10.00</td>
</tr>
<tr>
<td>Science, Technology, and Other Topics</td>
<td>220</td>
<td>8.37</td>
</tr>
<tr>
<td>Environmental Sciences and Ecology</td>
<td>159</td>
<td>6.05</td>
</tr>
<tr>
<td>Physics</td>
<td>148</td>
<td>5.63</td>
</tr>
<tr>
<td>Electrochemistry</td>
<td>101</td>
<td>3.84</td>
</tr>
<tr>
<td>Biotechnology &amp; Applied Microbiology</td>
<td>84</td>
<td>3.19</td>
</tr>
<tr>
<td>Geology</td>
<td>56</td>
<td>2.13</td>
</tr>
<tr>
<td>Thermodynamics</td>
<td>54</td>
<td>2.05</td>
</tr>
<tr>
<td>Agriculture</td>
<td>43</td>
<td>1.64</td>
</tr>
<tr>
<td>Polymer Science</td>
<td>42</td>
<td>1.60</td>
</tr>
<tr>
<td>Mechanics</td>
<td>40</td>
<td>1.52</td>
</tr>
<tr>
<td>Microbiology</td>
<td>34</td>
<td>1.29</td>
</tr>
</tbody>
</table>

TP (%): Individual items as a percentage of the total.

The number of documents is accumulated every four years

Figure 2. Top 6 most frequently assigned Web of Science categories in 4-year intervals.
A citation analysis provides the number of times a publication on a topic has been cited by other publications listed in the Web of Science Core collection. A total of 2630 articles or publications were used 55,069 times as references in other publications. The average citation number per publication is 20.94. Among them, 433 publications (16.46%) were cited 0 times at the time of the extraction of data. A total of 266 publications (10.11%) were cited 50 times or more, and 103 publications (3.92%) were cited 100 times or more. The h-index of 101 was seen. Figure 1 shows that the number of document citations increased from 1999 to 2023, with 7375 citations in 2023. As of 15 April 2024, 1604 citations have been reported this year.

Table 2 displays the top 10 most frequently cited publications on this topic. The most cited paper is “Synthesis of Biodiesel via Acid Catalysis” by Lotero, E. et al. [8], which has been cited 1270 times since its publication in 2005, averaging 63.5 citations per year. This paper, along with the third and seventh most cited articles, addresses significant corrosion problems in alternative liquid fuels, particularly those caused by organic acids and sulfides.

<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Authors</th>
<th>Journal</th>
<th>Publication Year</th>
<th>Total Citations</th>
<th>Average per Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Synthesis of biodiesel via acid catalysis</td>
<td>Lotero, E; Liu, YJ; et al. [8]</td>
<td>Industrial &amp; Engineering Chemistry Research</td>
<td>2005</td>
<td>1270</td>
<td>63.5</td>
</tr>
<tr>
<td>4</td>
<td>Chemical properties of solid biofuels—significance and impact</td>
<td>Obernberger, I; Brunner, T; et al. [11]</td>
<td>Biomass &amp; Bioenergy</td>
<td>2006</td>
<td>569</td>
<td>29.95</td>
</tr>
<tr>
<td>6</td>
<td>Chemical reactions on rutile TiO2(110)</td>
<td>Pang, CL; Lindsay, R; et al. [13]</td>
<td>Chemical Society Reviews</td>
<td>2008</td>
<td>458</td>
<td>26.94</td>
</tr>
<tr>
<td>7</td>
<td>Resolution and identification of elemental compositions for more than 3000 crude acids in heavy petroleum by negative-ion microelectrospray high-field Fourier transform ion cyclotron resonance mass spectrometry</td>
<td>Qian, KN; Robbins, WK; et al. [14]</td>
<td>Energy &amp; Fuels</td>
<td>2001</td>
<td>385</td>
<td>16.04</td>
</tr>
<tr>
<td>10</td>
<td>Gas diffusion barriers on polymers using multilayers fabricated by Al2O3 and rapid SiO2 atomic layer deposition</td>
<td>Dameron, AA; Davidson, SD; et al. [17]</td>
<td>The Journal of Physical Chemistry C</td>
<td>2008</td>
<td>341</td>
<td>20.06</td>
</tr>
</tbody>
</table>

The second and fourth most cited articles highlight researchers’ concerns about damage occurring during combustion. Meanwhile, the sixth, seventh, eighth, ninth, and tenth articles focus more on the production process of alternative fuels. Understanding how new fuels are obtained and produced on a large scale is considered more fundamental than studying their use and combustion processes.
Figure 3 shows the primary keywords for this problem. In the picture, the circle and font of the label represent the number of occurrences, the color represents the category of groups, and the distance between two labels indicates the degree of correlation. The high-frequency keywords include the aspects described below.

![Term analysis with time information.](image)

It is unsurprising that the keyword describing this type of fuel is “conventional fossil fuels”, given the prevalent use of liquid fuels today, including oil, petroleum, gasoline, coal, and diesel. The term “liquid fuel” is primarily defined as liquid petroleum products used on a large industrial scale. Corrosion issues have been a challenge for centuries, and significant progress has been made, such as implementing zero-sulfur requirements for diesel and gasoline, developing corrosion-resistant alloys and coatings, and utilizing corrosion inhibitors that can be added directly to the fuel. Despite these advancements, much work remains to be carried out. Biofuels, alcohols, methanol, palm biodiesel, vegetable oils, rapeseed oil, and hydrogen indicate a new direction in the development of alternative fuels, emphasizing environmental protection and low carbon emissions. Among these, biofuels present the most severe potential corrosion problems. Alcohols are currently less corrosive than diesel and gasoline. Corrosion remains a critical issue that all fuels must address as they transition from laboratory research to practical applications. It is evident that an increasing number of researchers aim to achieve breakthroughs in the search for low-carbon, low-emission, and widely available fuels on a large scale. The corrosivity of these fuels is discussed in more detail below.

The key to understanding the corrosion problem is to explore how fuel corrosion affects various materials. Among the keywords related to different materials, steel is the most prominent. Terms like iron, carbon steel, and mild steel all refer to it. Steel is the most widely used material in industrial production and serves as an important indicator of the industrial production capacity of a country or region. In the context of liquid fuel corrosion, whether for pipes or engines, the materials with the most applications need the
most research. Other materials frequently mentioned include aluminum and copper. These metals are commonly used in the petrochemical and machinery industries due to their strong corrosion resistance.

Some keywords reflect the knowledge of the corrosion environment, including water, chlorine, naphthenic acid, sulfuric acid, bacteria, biodegradation, CO₂ corrosion, and combustion. Corrosion is associated with, or exacerbated by, these environments. Researchers believe that the main culprits of corrosion are sulfides, organic acids [18], and microorganisms [19]. The presence of water creates an ideal environment for microbial activity, chemical reactions, and electrochemical reactions, all of which contribute to material damage. In addition to the corrosion caused by the composition of the fuel itself, researchers have found that corrosion resulting from the reaction of liquid fuel with CO₂ and H₂S in the air is another key factor. This phenomenon is well known in the petrochemical industry and is discussed and analyzed in this paper. Section 4 of this paper summarizes the environments prone to corrosion and the mechanisms of corrosion in these environments to help readers better understand the specific dangers of corrosion in such conditions.

The identified keywords, including corrosion resistance, corrosion inhibitor, model, coating, and alloy, reflect the efforts made by researchers to solve the corrosion problem. The lowest-cost and most efficient way to solve the corrosion problem is to add a corrosion inhibitor. Corrosion inhibitors can be divided into organic and inorganic corrosion inhibitors [20], anodic reaction corrosion inhibitors, and cathodic reaction corrosion inhibitors [21]. However, in this field of research, the study of inorganic corrosion inhibitors, acid environmental corrosion inhibitors, common organic corrosion inhibitors, and green corrosion inhibitors is conducted independently. Inorganic and green corrosion inhibitors have not been used on a large scale due to their poor efficiency. The mainstream imidazole-based inhibitors, which are the most commonly used, will be discussed separately.

Liquid fuels go through a complex chain of production, transportation, storage, and use. In this process, production equipment and plant facilities, pipelines, dedicated storage tanks, and engine or other fuel contact parts in vehicles are directly exposed to this corrosion hazard. We can see that researchers are most interested in pipelines, followed by engines. Overall, in terms of the frequency of vocabulary occurrences, the fuel types chosen by researchers are concentrated around the few oil-related keywords mentioned earlier, with only minor differences in their prevalence. However, the choice of materials is overwhelmingly dominated by various types of steel, with aluminum being mentioned less frequently. The approach to recognizing and addressing the corrosion problem is fragmented and multi-directional. Researchers explore various aspects, such as the microbiological aspects of corrosion, the movement of ions and electrons during corrosion, and the relationship between corrosion and oxidation reactions. Their goals are also diverse, ranging from developing corrosion inhibitors and identifying corrosion mechanisms to creating corrosion-resistant alloys and addressing emission problems. This dispersion of research aims highlights the complexity and interdisciplinary nature of corrosion research.

The coloration of the nodes in the graph indicates when specific terms appeared with high frequency. Dark-blue nodes represent issues that were of greater interest to researchers ten years ago (until 2024), while yellow nodes highlight topics that have gained recent interest. Due to the continuity and persistence of research questions over time, no nodes appear and disappear suddenly within the last decade. Nodes with colors in between generally indicate topics that have been consistently relevant throughout the study of corrosion. Three clear trends emerge along the timeline: (1) Influence of Environmental and Low-Carbon Elements: Researchers are increasingly focused on the environmental impact and emission characteristics of new fuels, such as palm oil, which is considered a more sustainable option. (2) Improved Research Methods: Advances in research techniques have enhanced the study of corrosion. For instance, surface characterization now often involves sophisticated and expensive equipment like the scanning electron microscope (SEM) and atomic force microscope (AFM). Additionally, advanced electrochemical methods, such as impedance spectroscopy, are commonly used. This indicates that more researchers are
now equipped to perform these studies, emphasizing that future results should be based on a deeper understanding of findings rather than merely relying on advanced instrumentation or characterization methods. (3) Deeper Understanding of Corrosion Mechanisms: Researchers are delving deeper into the mechanisms of corrosion and developing more effective application-end solutions. The lighter-colored nodes represent terms like bacteria, resistance, kinetics, ionic, and mechanical, indicating an increased focus on these advanced factors and solutions.

3. Current Status of Corrosion in Alternative Liquid Fuels

Since the beginning of liquid fuel use two centuries ago, corrosion has persisted, causing significant economic losses. Frequent pipeline damage and related accidents have been a recurring issue. Additionally, modern, more sophisticated engines are highly sensitive to the quality and purity of fuel, making the problem of corrosion even more critical [7]. With the global focus on low-carbon issues, new low-carbon fuels are being developed, and their use is accompanied by a variety of additives and blending issues. All of this makes the problem of corrosion even more difficult.

Researchers are now seeking lower-carbon, cleaner, more efficient, and more economical liquid fuels as alternatives or complements to gasoline and diesel. The relevant keywords identified in the metrics, including biofuel, alcohol, methanol, palm biodiesel, vegetable oil, canola oil, and hydrogen, indicate a strong interest in this direction. This paper suggests two possibilities. One is the development of biofuels from vegetable oils and animal fats, which are readily available in large quantities in nature [22]. The second is to find eligible chemical products that can be manufactured in large quantities by industrial methods, including alcohols and esters. Esters and ketones are generally used to make fragrances, essential oils, and other similar applications. They are expensive and not likely to be used as fuels [23, 24]. Of course, as we know, the blended fuel of ethanol and gasoline has been used on a large scale [25].

This section describes the corrosion issues for each of the above liquid fuels individually and describes the corrosion when the fuels are blended for use. Then, it describes the possible corrosion caused by liquid fuels from manufacturing to emission.

3.1. Corrosion Study of Single Fuels

Diesel and gasoline are the most widely used liquid fuels and have been the primary power sources for human transportation since the Second Industrial Revolution. Over time, it has been recognized that these fuels cause corrosion and damage to various materials. Researchers have investigated the corrosion of copper by diesel, highlighting the role of sulfides and copper in this process [26–28]. Similarly, various materials, including aluminum [29,30], zinc [31,32], steel [33,34], lead [26,35], and rubber [36], have shown corrosion in gasoline and diesel. These experiments also reveal that liquid fossil fuels are particularly damaging to rubber due to their tendency to cause swelling. Researchers continue to devote significant time and effort to exploring the processes by which these types of corrosion occur (which will be introduced in the next chapter) and comparing the strengths and weaknesses of different metals affected by corrosion. The literature cited represents only a small, yet representative, portion of the research. From these studies, we know that, among metal materials, copper alloys are relatively prone to corrosion, while metals like aluminum are more resistant due to the protective oxidizing substances that form on their surfaces.

Biodiesel is a hot spot with the potential to replace traditional fossil fuels on a large scale [37]. Studies have shown it to be far more corrosive than gasoline and diesel. A series of experiments proved that biodiesel and biodiesel blends corrode metals such as copper, aluminum, cast iron, and steel to a higher degree than diesel [38]. It has been suggested that biodiesel is more prone to water absorption and consequent microbial contamination than fossil fuels or provides a reaction solvent for various solutes that enhance electrochemical corrosion. In addition, the generally higher acidity of biodiesel is responsible for more
intense corrosion [39]. There are some related experiments. Researchers found that there was a glitch in the biofuel production process and investigated it. They found that the problem came from the acid in the biofuel production, and the damage to AISI 316L steel resulted in the ultimate economic loss [40]. Similarly, other researchers have demonstrated that austenitic stainless steels will crack under stress corrosion during the process of converting municipal solid waste into biofuel [41]. Biodiesel from Schizochytrium sp. microalgae also showed strong corrosive effects on the copper materials tested [42]. In storage, the strong corrosion of stainless steel, carbon steel, and aluminum by biofuels has also been confirmed experimentally. Experiments have also shown that this corrosion is mainly caused by microorganisms in storage [43].

Biodiesel, derived from the transesterification of vegetable oils or animal fats, is composed of saturated and unsaturated long-chain fatty acid alkyl esters. Recently, it has been considered one of the most promising alternative fuels for internal combustion engines [22]. Biofuel sources mainly include soybean, jatropha, rapeseed, palm, sunflower, etc. There has been a lot of work to determine the characteristics of biofuel from different sources. A 256 h long-term durability test was successfully conducted on a diesel engine to investigate the damage caused by a pongamia oil methyl ester–diesel blend to the diesel engine’s health and life, and it was found that pongamia biodiesel (PME 20) has inferior lubricity properties due to its corrosiveness, hygroscopic nature, autooxidation, and deposit formation [44]. Some researchers improved the engine based on the fuel B40 (40% jatropha biodiesel + 60% diesel) and conducted 512 vanishing long-term durability tests. They paid more attention to lubricating oil dilution, deposit formation, and oxidative stability, and all of the performance results indicated that their improvements were successful [45]. But it is also worth thinking about whether, in engineering, we need to change the type of engine for a particular biofuel. In a palm oil study, some researchers reported some positive news. They found that the friction and wear characteristics of palm biodiesel are better than those of diesel. This is more likely attributed to the presence of oxygenated moieties, the degree of unsaturated molecules, free fatty acid components, etc., in biodiesel. This may indicate that biodiesel is more corrosive because of its chemical properties [46]. Another study about palm biodiesel evaluated the effects of palm biodiesel dissolved oxygen and conductivity on metal corrosion and elastomer degradation under standard and novel immersions. And both biodiesel dissolved oxygen and conductivity adversely affected fuel delivery materials’ degradation. In the course of this study, the more severe corrosion of copper by palm diesel was confirmed again [47]. As we all know, coating is an important way to protect metals from corrosion. Some researchers reached the conclusion that vanadium carbide coating protects gray cast iron against corrosion by biodiesel [48]. Similarly, other researchers drew the conclusion that NbC coatings on gray iron provide protection against corrosion by palm biodiesel. This paper also mentioned that niobium carbide coatings offer high anticorrosive properties for protection from degradation in environments of palm biodiesel [49]. Of course, the corrosion strength is also related to the material of the specimen. In the case of a blend of palm kernel oil and ethanol fuel, the aluminum material showed excellent corrosion resistance. The researchers analyzed this corrosion resistance in terms of the fuel’s fatty acid concentration, total acid number, and capacity to attract and hold water [50]. And sunflower biodiesel has also been shown to be more corrosive to metals [51].

Alcohols and ethers meet the requirements for low-carbon, clean, and low-cost liquid fuel substitute substances, and many researchers have explored their corrosion properties. In fact, compared to conventional fossil fuels, we can even think of them as non-corrosive. Many of these types of substances are even added to liquid fuels as corrosion inhibitors [52,53], which are described in the Corrosion Inhibitors Section of this article. But some researchers have still found a risk of corrosion when there is a place for corrosion reactions to occur. This risk has been assessed for corrosion in ethanol–gasoline products due to water absorption and the separation of the water and oil phases [54] or the ability of
microbes to multiply and damage the material they come in contact with. This process is described in the principles of corrosion section of this article [55].

Neither methanol nor ethanol can be directly immiscible with diesel or gasoline, and the use of low-carbon alcohol as fuel faces the problem of insufficient power, so it is necessary to add a cosolvent in the mixing process of fossil fuel and low-carbon alcohol [56]. The biodiesel–diesel–ethanol (BDE) blend represents an important alternative fuel for diesel engines, and this blending method is also the main way that biodiesel is going to be used in engineering. To ensure proper fuel performance, ethanol and biodiesel combined should add up to no more than 30 percent. Some researchers suggest using 20 percent biodiesel and 10 percent ethanol to ensure excellent combustion performance after mixing [57]. Work on BDE’s corrosivity has shown it to be somewhere between that of diesel and biodiesel. Experiments by different researchers have demonstrated this [58,59]. Experiments also show that the higher the biodiesel content in BDE, the more corrosive the fuel mixture. Based on the fact that biodiesel is more corrosive than regular diesel and that low-carbon alcohols are non-corrosive, this result is very consistent with our understanding. In addition, BDE corrodes copper the most, followed by mild steel and aluminum. The use of methanol as fuel also requires cosolvent mixing, and its corrosion characteristics are similar to those of BDE in that the corrosion mainly comes from the content of diesel oil or the selection of the cosolvent [60–62]. In the blending of fuel-grade ethanol with gasoline, the higher the ethanol content, the stronger the corrosive effect on X70 steel parts. The corrosion will be more pronounced if the steel parts have undergone a welding process [63]. Butanol of biological origin shows similar corrosive effects when blended with gasoline. More butanol in the blend caused higher corrosion of automotive parts such as pistons and valves [64]. Butanol–gasoline blends are more corrosive than ethanol–gasoline blends when steel is used as a specimen to test the degree of corrosion of the blended material [65]. The use of high-carbon alcohols as fuel does not have the same phase separation and stability problems as low-carbon alcohols, but the disadvantage is that there is no mature technology for their cheap production in large quantities [66,67]. Experimental support for corrosion characteristics caused by mixing high-carbon alcohols with diesel or using high-carbon alcohols as fuel alone is still lacking. Similarly, there are many attempts to add ethers to gasoline as fuel, and it is an important direction to follow in the future [68–71]. This work shows that many ethers can not only be added to fossil fuel for combustion but can also be used as corrosion inhibitors, and combined with their chemical properties, we can think of ethers as non-corrosive, just like alcohols. But more direct experiments are lacking.

3.2. Blending of Liquid Fuels

Liquid fuels are generally used as blends of multiple components rather than as single substances. For instance, ethanol is added to gasoline to promote complete combustion, improve emission performance, and save energy. In diesel production, different blends are created based on specific usage requirements. Blending involves mixing various fuels to achieve an optimal fuel ratio, such as using ethanol–gasoline and biodiesel (BDE) fuel.

New fuels, including biodiesel and low-carbon alcohols, often begin their use by being blended with established fossil fuels rather than being used alone. Additionally, fuels may require the addition of functional additives to enhance certain properties. For example, cosolvents can improve mutual solubility, corrosion inhibitors can mitigate corrosive properties, antioxidants can delay oxidation and extend service life, and lubricants can reduce wear on metal materials during use.

Some researchers have explored the results of studies on corrosion in some new blended liquid fuels. Many of the results are promising. Some researchers have explored corrosion in diesel fuel containing 5–30 wt% soybean oil methyl ester. It was found that the soybean oil content increased the level of copper corrosion. However, the blended content was low and had little effect on the corrosion performance of the blended fuel after blending. In addition, the sulfur content of soybean oil was low, which would reduce corrosion [72]. Another fuel, palm fatty acid distillate, is blended with commercial diesel
fuel. A copper strip corrosion test showed that, despite the high acid value of the mixture, the corrosion properties were similar to those of diesel fuel [73]. Similarly, some researchers have studied the production pathway of green gasoline, jet, and diesel biofuels from waste greases and then proved that these new fuels blended with diesel pass the copper corrosion (D130) test and silver metal corrosion (D7681) test [74]. Diglycidyl ether ester derived from hempseed oil has also been tested for copper corrosion, and it was proved that its corrosion is low enough to be used as an alternative to diesel fuel [75]. Similarly, oil products obtained by the rapid pyrolysis of Yang (Dipterocarpus alatus) hard resin (HY) as feedstock are also in the same class as diesel fuel in ASTM tests [76]. The high corrosiveness of biodiesel also lies in the fact that it is significantly reduced by methanol blending [77].

However, it is not all good news. Some researchers have added rapeseed oil methyl ester to ultra-low-sulfur diesel fuel. It was found that the more rapeseed oil methyl ester in it, the more corrosive the performance [78]. Another similar fuel, an oil obtained by the pyrolysis of wood, is proven to be adequate as an alternative to diesel in all respects except corrosive properties. To use it in a diesel engine, one must choose a corrosion-resistant material or use a corrosion inhibitor [79]. Crude mixed alcohols obtained from syngas as a raw material do not have the corrosion characteristics required for their use, even when mixed with gasoline. It is necessary to add corrosion inhibitors to ensure corrosion safety in use [80].

It is clear that the corrosive properties of blended fuels are intermediate between the corrosive properties of the individual fuels before blending. However, these properties do not vary linearly with the blending ratio. The phase behavior of the two fuels plays a key role. Fuels with similar polarity can easily form a stable emulsion. When oily and aqueous fuels do not mix well, an emulsifier must be added to create a homogeneous and stable phase. At the microscopic level, emulsions can exhibit two situations based on the number of components: oil-in-water (O/W), where water is the continuous phase with oil dispersed within it, and water-in-oil (W/O), where oil is the continuous phase with water dispersed within it [81].

According to the general mechanism of corrosion (described in Section 4 of this paper), water-based blended emulsions tend to have higher corrosion rates. This paper argues that when the water phase increases to the point where there is a shift in the micro-morphology of the emulsion, there is a corresponding jump in corrosion. Some researchers have measured the conductivity of emulsions with different morphologies after blending methanol and palm oil and found that the conductivity of water-in-oil (W/O) emulsions is significantly greater [82,83]. This can also be used as a side example of corrosivity.

Of course, the corrosiveness of the emulsifier itself is also a source of corrosion risk. For example, some researchers have found that PODE is significantly more corrosive than tetrahydrofuran and n-butanol, also used as emulsifiers. When an emulsifier is added in larger proportions, its corrosiveness should also be taken into account [84].

4. Corrosion Mechanism in Alternative Liquid Fuels

Corrosion results from chemical or electrochemical reactions between the corroded material and the fuel. For example, Figure 4 illustrates the microchemical process of iron corrosion in a humid environment. Through redox reactions, iron transforms into a hypervalent oxide, leading to material failure and associated losses. The corrosion process is accompanied by redox reactions that produce hydrogen in acidic environments and OH$^-$ in neutral or alkaline environments. However, simply knowing this is not sufficient to address the engineering challenges posed by corrosion. This chapter will explain the mechanism of corrosion from two perspectives. First, to clarify and summarize the corrosion behavior of different liquid fuels, it is necessary to identify which fuel components undergo these reactions or which parts of the fuel cause damage to the materials they contact. Second, in the petrochemical industry, there is a distinction between acid corrosion and sweet corrosion, illustrating different characteristics of corrosion in this field. In Section 2, we identified key terms related to researchers’ understanding of corrosion mechanisms through bibliometrics,
including water, chlorine, naphthenic acid, sulfuric acid, bacteria, biodegradation, CO\textsubscript{2} corrosion, and combustion. This chapter will elaborate on the role of these factors in the corrosion process in more detail.

Figure 4. Corrosion of iron in air.

4.1. Corrosive Components in Liquid Fuels

The copper corrosion test is now an important standard to identify the corrosion degree of petroleum products. The corrosion degree of petroleum products can be judged by the color state of copper after soaking in petroleum products for three hours. This standard identifies the sulfur element in petroleum products, especially active sulfide, which is the most important component in fuel corrosion. Some researchers found that the presence of hydrogen sulfide, sulfide ions, or other sulfides increases corrosion dramatically [84,85]. Some researchers found that, in drinking water containing sulfide, the corrosion efficiency instantly increases to 5–50 times that without sulfide [85]. Some researchers found that corrosion can occur quickly if sulfide is present in pipeline transport [86]. In the petrochemical industry, oil taste is mainly judged by the sulfur content. On the one hand, people are constantly seeking to produce higher-grade oil with lower sulfur content. On the other hand, people are trying to realize desulfurization technology for petroleum. The current crude oil desulfurization technologies include biological desulfurization, hydrogenation-bacterial catalysis, microwave catalytic hydrogenation, oxidative desulfurization, ultrasonic/microwave catalytic oxidation, alkali washing, dry gas desulfurization, hydrodesulfurization, and so on [87,88]. Now, the use of hydrogen sulfide is prohibited in petroleum products, and other sulfides, such as mercaptans, are also under strict control, but the hazards caused by sulfides are unavoidable due to the presence of sulfur-containing gases in the air.

Organic acids are an important threat to corrosion in fuel systems. Corrosion-causing organic acids in fossil fuels mainly include naphthenic acid, carbonic acid, and carboxylic acid. Naphthenic acid is left over as a by-product produced during the processing of crude oil [89,90]; carbonic acid is mainly produced from contact with carbon dioxide in the air during production, transportation, and storage; and carboxylic acid is mainly produced from the oxidation of small molecules of organic matter in fossil fuels. Other organic acids containing sulfur and nitrogen may also be involved but are too small to be considered. Among them, acid corrosion caused by carbonic acid corrosion and H\textsubscript{2}S in the air is the most harmful to metal.
Microorganisms, mainly bacteria, are an important source of corrosion of liquid fuel metals. Microbiologically influenced corrosion (MIC) is an important aspect of global infrastructure erosion, causing continuous damage to fuel production, processing, transportation, and storage systems [91]. Because of the complexity of colonies and the variability of the corrosion environment, it is difficult to draw definitive conclusions about which species of bacteria are responsible for the corrosion. In the last century, some people documented the destruction of metal by microbial activities. At that time, people mainly focused on biofilms formed on a relatively large scale [92]. Now, with greater understanding, people tend to think that bacteria damage materials in two ways. On the one hand, they make related microorganisms react with the damaged metal. Like the corrosion of steel by giant bacillus [93], sulfate-reducing bacteria (Desulfotomaculum geothermicum) have proved to be hugely disruptive in the refinery [94]. Corrosion by Bacillus subtilis and Bacillus circosus was observed in aircraft fuel tanks [95]. Bradyrhizobium, Sphingomonas, Bacillus, Pseudomonas, Methylobacterium, and Lelliottia genera have been proven to cause corrosion [96]. On the other hand, the effect can be indirect, as the sulfate and organic acid substances generated by microbial activities create a more easily corrosive environment, and sulfate-related bacteria are the most damaging. Firmicutes, Deltaproteobacteria (primarily sulfate-reducing bacteria), Chloroflexi, and Lentisphaerae are involved in the production of sulfides that damage carbon steel [97]. Sulfur-producing bacteria have also been linked to corrosion in diesel storage tanks [98]. The genus Bacillus and the fungi Aureobasidium and Penicillium have been confirmed to cause damage to aluminum in aircraft fuel tanks [99]. There are many more experiments demonstrating microbial corrosion in fuels [100–111]. Of course, other microorganisms besides bacteria can also increase the corrosiveness of fuel. Researchers have identified a fungal strain present in diesel that oxidizes ferrous ions to iron oxide. The paper says that this is the first time that a fungus involved in diesel corrosion has been identified [112]. Other researchers found that storing B20 biofuel (which is 20% biofuel mixed with diesel fuel) was degraded by one of the filamentous fungi of the genus Paecilomyces and caused more corrosion. The authors confirmed that the fungi degraded the fatty acid methyl esters and alkanes into acidic substances in the fuel and further provided an effective quantitative measure for the corrosion intensification of fungus-contaminated types [113]. In another article, the author described filamentous fungi in the genus Trichocomaceae as a new species of fungi that increases corrosion in liquid fuels. This article also emphasized bacteria with corrosive effects that were already known, such as Acetobacteraceae, Clostridiaceae, Proteobacteria, and Saccharomycetaceae [101]. Of course, the complexity of microbial taxa in the storage and transportation units of fuels and methods for the rapid detection of microbial contamination levels require more in-depth work [114].

In environments containing sulfur ions, the ions added by sulfate-reducing bacteria (SRB) corrode metallic aluminum. A researcher found a novel metal–phenolic supramolecular film that kills SRB to stop the continuation of corrosion. He demonstrated the effectiveness of this metal–phenolic supramolecular film in his experiments and obtained pictures of sulfate-reducing bacteria corroding aluminum, as shown in Figure 5 [115]. The high bacterial mortality illustrates the effectiveness of the product.

Water is a good solvent and an important factor that cannot be ignored when facing fuel corrosion problems. Microorganisms multiply rapidly in water; acidic and alkaline substances from the oil phase released into the water phase will become more active and stimulate various chemical and electrochemical reactions. An increase in water content will lead to an increase in corrosion [116]. Although water does not directly damage the material structure, it has been accepted that the water content should be controlled in order to control corrosion.
4.2. Sour Corrosion and Sweet Corrosion

Sweet corrosion and acid corrosion have led the petrochemical industry to describe different types of corrosion. Sweet corrosion is mainly caused by CO$_2$, accompanied by CO$_2$ dissolved in water caused by carbonic acid corrosion. Sour corrosion describes corrosion caused by sulfides at H$_2$S concentrations of less than 0.010 Mpa, primarily sulfuric acid. Sour and sweet corrosion exist at the same time, and which corrosion is mainly determined by the partial pressure of H$_2$S. Acid corrosion is more severe and more destructive than sweet corrosion [117].

The degree of sweet corrosion is weaker than that of acid but stronger than that of inorganic acid. The reason is that carbonic acid is a weak acid, with pH < 4, and H$^+$ is transferred slowly to the metal surface. Carbonic acid causes more H$_2$ to be produced on the surface of the electrode, where electrochemical corrosion occurs. In the presence of a conductive medium, such as salt water, CO$_2$ corrosion is more intense [118–120].

Its cathode reaction is generally as follows:

$$2H^+ + 2e^- \rightarrow H_2$$
$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^-$$
$$2HCO_3^- + 2e^- \rightarrow 2CO_3^{2-} + H_2$$

Its anodic reaction is generally (iron, for example)

$$Fe \rightarrow Fe^{2+} + 2e^-$$

The nature of sour corrosion is a hydrogen evolution reaction. Acid corrosion is caused by salts and sulfides dissolved in crude oil. These result in the formation of corrosive aqueous solutions whose chemical composition involves the presence of hydrochloric acid (HCl) and hydrogen sulfide (H$_2$S). Previous studies showed that H$_2$S significantly accelerated the dissolution of anode iron and precipitation on the cathode.

5. Standard and Analytical Methods

The occurrence of corrosion alters the mass, resistance, magnetic flux, and mechanical properties of the corroded material. Theoretically, corrosion can be detected by monitoring these changes, and the extent of these changes can indicate the severity of the corrosion. Internationally, the copper testing method is commonly used to characterize the corrosion.
strength of a given fuel. Additionally, changes in mass resulting from corrosion are also used to quantify the degree of corrosion.

In addition, other methods can be divided into two broad categories. One is based on electrical changes, given that corrosion is a chemical reaction, or a flow of electrons. In the detection of the corrosion process based on current changes, or the applied voltage, the characteristics of the current caused by material in the liquid can reflect the corrosion characteristics of liquid fuels. The second method is based on corrosion-induced changes in the surface of the material. Intuitive surface observations, such as the rust condition and color, can indicate the degree of corrosion that has occurred. After the corrosion of the material surface, if viewed at a magnification of dozens of times to hundreds of times, tiny traces of corrosion can be observed, from which the characteristics and strength of the corrosion can be inferred. And we can use scanning electron microscopy, which provides greater magnification, to look for microscopic mechanisms of corrosion or the mechanism of action of corrosion inhibitors.

This paper argues that a significant problem remains in the development of standards for corrosion: the lack of a more accurate and universal quantification method. Existing copper sheet experiments are not precise enough and only provide vague gradations. Experiments that yield precise data are typically those in which the researcher controls variables and gathers data that are only comparable within that specific study. Consequently, we cannot combine data from different experimental articles to form a cohesive opinion. Identifying a characteristic that can serve as a precise quantitative basis for corrosion criteria is still an issue that requires further exploration.

5.1. Copper Strip Test

In the petrochemical industry, petrochemical products are typically evaluated using methods such as ASTM D130-83 [121] in the USA or GB/T 5096 [122] in China. Figure 6 shows the colorimetric card in the ASTM D130-83 standard. These methods are used to test products like aviation gasoline, aviation turbine fuel, automotive gasoline, standard solvent, kerosine, diesel fuel, distillate fuel oil, lubricating oil, natural gasoline, and other hydrocarbons.

![Standard colorimetric card for copper testing][1]

**Figure 6.** Standard colorimetric card for copper testing [121].
The specific test method involves submerging a piece of polished copper in a certain amount of liquid fuel, heating it to a specified temperature, as required by the product standard, and maintaining it at that temperature for a certain period. After the test, the copper sheet is removed, washed, and compared with a standard colorimetric plate to determine the corrosion level. The time and temperature are determined according to the specimen characteristics and requirements; for example, industrial lubricants are typically tested at 100 °C for 3 h. This test method is designed to target reactive sulfides, which are among the most corrosive substances found in liquid fuels.

As an industry standard, petrochemical industry practitioners can easily use it to describe the strength of corrosion caused by petroleum products. But in the laboratory, researchers generally expect more accurate corrosion data. And copper is not the only material that researchers are interested in. When corrosive conditions originate primarily from components other than active sulfides, changes in copper flakes may not be accurately revealed by color.

5.2. Weight Loss Measurements

It is also common to measure the loss of material mass due to corrosion processes. This method requires simple experimental conditions, but the error is large, and can present quantitative data in some less demanding corrosion measurements. The method involves putting the weighed metal into the fuel to be tested for a period of time and then taking it out and weighing it again to calculate the weight loss. Of course, the debris should be cleaned before both weighing steps, rinsed with ethanol, and dried.

\[
R_1 = \frac{W_1 - W_2}{W_1}
\]

\[
R_2 = \frac{W_1 - W_2}{(t_1 - t_2)\rho}
\]

where \(W_1\) and \(W_2\) are the initial and final masses (g), \(t_1\) and \(t_2\) are the starting and ending times, and \(\rho\) is the density. \(R_2\) accounts for different materials and different times. For example, some researchers have used the weight loss rate to prove that the corrosion rate of metal increases with the increase in corrosion time [123].

This measurement method is less costly and is commonly used by researchers to determine the rate and degree of rusting when corrosion primarily manifests as rust. However, when the weight change caused by short-term corrosion is minimal, the method’s error margin increases. Furthermore, the structural damage caused by corrosion is often more significant than the weight loss. This method does not provide detailed information about the corrosion, such as its precise location and microscopic characteristics.

5.3. Potentiodynamic Galvanostatic Polarization

This method is based on monitoring the corrosion potential and corrosion current density. It measures the current corresponding to the change in potential from the free corrosion potential by applying a working electrode voltage. Care must be taken during the scanning process to ensure that the scanning speed does not allow a large capacitance to form on the surface. Researchers analyze the resulting current curves to determine the strength of the ongoing corrosion. The Tafel curves generated by this applied current scheme have been demonstrated to accurately describe corrosion and are applicable to various corrosion scenarios. These curves provide valuable insights into the corrosion process, allowing for a more detailed and precise assessment compared to other methods, [124,125]. The article further demonstrates how currents under conditions of pitting and crevice corrosion exhibit different responses due to microscopic electrochemical reactions.

Figure 7 shows a set of polarization curves obtained by a researcher exploring the corrosion inhibition effect of 4-phenylbutyric acid (PBA) on copper in a NaCl solution using the polarization curve method. PBA was electrodeposited on the copper surface for 30 s
and 300 s, respectively. The figure shows the logarithm of the current as the applied voltage changes. The more PBA electrodeposition, the more the Tafel curve shifts toward lower currents, indicating reduced corrosion. This confirms the effectiveness of PBA in inhibiting copper corrosion in NaCl.

![Tafel polarization curves](image)

**Figure 7.** Tafel polarization curves for corrosion of copper electrode covered with 4-phenylbutyric acid (PBA) in 3.5% NaCl: 30 s and 300 s [126].

The application of this method is relatively broad, providing accurate results and fast measurement times, making it a popular choice among researchers. However, while this method is useful for monitoring electrochemical corrosion, it cannot be applied in cases of chemical corrosion. Additionally, if the electrode surface is not in a non-activated state, such as when covered with a dense oxide film, the measurement of polarization resistance can show significant deviations. Furthermore, additional redox reactions during the measurement may affect its accuracy.

5.4. **Electrochemical Impedance Spectroscopy (EIS)**

This method is characterized primarily by monitoring the condition of the naturally occurring passivation film on the surface of the metal or alloy. Changes in this passivation film, both its formation and destruction, are important microscopic features for corrosion behavior to proceed [127,128]. Because of its characteristics, this method is very suitable for studying the corrosion mechanism and corrosion inhibition mechanism.

Figure 8 shows the Electrochemical Impedance Spectroscopy (EIS) diagram obtained with the addition of different concentrations of a 4-methyl pyrazole corrosion inhibitor when iron is corroded in hydrochloric acid. The impedance of the corroded material is measured by applying an external AC voltage. The horizontal axis represents the real part of the impedance, while the vertical axis represents the imaginary part of the impedance. The charge transfer resistance is calculated from the difference in impedance at lower and higher frequencies. From the charge transfer resistance, the inhibition efficiency of the corrosion inhibitor on iron can be determined. This figure effectively demonstrates the corrosion inhibition effect of 4-methyl pyrazole, highlighting its potential as an effective corrosion inhibitor in hydrochloric acid environments.
parameter indicating corrosion intensity. The greater the number of charges, the more

The charge transfer resistance is calculated from the difference in impedance, while the vertical axis represents the imaginary part of the impedance. The data collection time of this method is relatively long (in hours), and changes in the system, such as temperature or stability during the collection process, can lead to measurement failure. It takes quite some time to learn the principles of impedance spectroscopy. The equivalent circuit in the measurement is not well defined and relies on the understanding of the researchers [131]. Some researchers have performed metrological comparisons in the field of corrosion measurements and found that the present method has fewer applications [132].

5.5. Electrochemical Noise Method

This method allows for measuring corrosion without the need for an applied current and voltage. The strength of corrosion is determined by directly monitoring the weak current generated during the corrosion process. Some researchers studied the corrosion inhibition properties of two similar heterocyclic compounds, benzotriazole (BTA) and benzothiazole (BNS), on copper in a 1.0 M H_2SO_4 solution using electrochemical techniques. In this study, the electrochemical noise method proved to be more accurate than both the EIS and electrochemical polarization methods [133]. In principle, this method provides a direct, non-destructive response to the original corrosion potential without the capacitive interference generated by applied potentials, which contributes to its accuracy. The noise impedance of electrochemical noise is a crucial parameter obtained by this method; a larger noise impedance indicates less corrosion. Additionally, the number of charges in the frequency domain generated from the current noise signal is another important parameter indicating corrosion intensity. The greater the number of charges, the more intense the corrosion.

Figure 9 shows an image of the electrochemical noise signature of stainless steel as it corrodes by immersion in FeCl_3, with subsequent changes in the anode. Because the signal is often too weak, corrosion products around the electrode are frequently in a flowing state. Data processing needs to remove these disturbances to obtain more stable current and voltage readings. The method of judging the strength of corrosion is simpler than the previous two methods: a stronger voltage or current signifies stronger corrosion.
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![Figure 9.](image)

This method does not use an applied current or voltage; instead, it measures and analyzes the current generated during the corrosion process. It does not damage the corroding electrode or require a series of electrochemical conditions to meet measurement prerequisites, making it advantageous for engineering practice. It can also measure corrosion in real time through measurement systems and monitoring connections. However, this method is time-consuming because obtaining data related to corrosion requires low-frequency measurements, which take a long time. Additionally, the tiny currents generated by corrosion test the accuracy of the device. Some researchers have noted that electrode asymmetry and trends caused by DC drift may negatively affect the reliability of the results [135].

5.6. Surface Analytical Methods

Corrosion will occur from the outside to the inside. The occurrence of corrosion in a material will definitely change the surface morphology of the material. Observing the changes and characteristics of the surface morphology is also an important way for researchers to understand corrosion.

Figure 10 shows the corrosion process of gray cast iron material in methanol containing methyl microorganisms. Pits appeared on the smooth surface after 30 days of corrosion. The electron scanning microscope visualizes the damage to the surface of the material by corrosion.
Inorganic corrosion inhibitors mainly inhibit corrosion by participating in the chemical reaction of the anode or cathode [141]. Inorganic corrosion inhibitors are cheaper and can provide anti-corrosion protection. Keywords in the bibliometrics, such as cathodic protection [136], organic coating [137], and corrosion-resistant alloy application [138,139], can provide anti-corrosion protection.

Figure 10. Gray cast iron is corroded in methanol containing methyl microorganisms: (a) initial morphology of corrosion, (b) appearance after 30 days of corrosion.

Figure 11 shows a three-dimensional image of the corrosion of a gray cast iron test piece in methanol. It is evident that the surface roughness is increasing, and the holes in the surface are getting deeper. This image was obtained using an atomic force microscope, which determines the nanoscale surface morphology and the mechanical and electrical characteristics of the sample by measuring the force between the probe and the test sample.

Figure 11. The three-dimensional surface morphology of gray cast iron was obtained by atomic force electron microscopy after corrosion in methanol for 7 days, 14 days, and 28 days.
Since there is no specific information on data and extent, researchers generally do not use this method independently as the primary method for studying corrosion. Instead, it serves as a supplement to measuring electrical signal characteristics in corrosion. Visual inspection is the most intuitive way for people to obtain information. By observing corrosion-induced changes on the surface, such as the shape of grooves and differences in various parts, researchers can gain insights into the corrosion process. This method is particularly suitable for studying stress corrosion and localized corrosion. Additionally, the high magnification provided by the atomic force microscope can help determine the mechanisms of corrosion, as illustrated in the example above.

6. Corrosion Inhibitors

In the use of liquid fuel, faced with different corrosion conditions, many technologies, such as cathodic protection [136], organic coating [137], and corrosion-resistant alloy application [138,139], can provide anti-corrosion protection. Keywords in the bibliometrics, including corrosion resistance, corrosion inhibitor, model, coating, and alloy, demonstrate researchers’ quest to solve the corrosion problem. However, the use of a corrosion inhibitor is the most economical and reliable method to control corrosion in liquid fuel [140]. Corrosion inhibitors can be classified according to their chemical composition into non-polar corrosion inhibitors, organic corrosion inhibitors, and polymer corrosion inhibitors. Based on their mode of action, they can be divided into anode corrosion inhibitors and cathode corrosion inhibitors, which passivate and prevent reactions in the anode and cathode regions, respectively. They can also be classified according to their use in acidic or alkaline environments. However, researchers do not always strictly follow these classification methods in their studies. Consequently, some corrosion inhibitors may belong to two or three categories simultaneously. In this paper, we will elaborate on the multifaceted nature of corrosion inhibitors, acknowledging that they may overlap across different classification categories.

6.1. Inorganic Inhibitors

Inorganic corrosion inhibitors mainly inhibit corrosion by participating in the chemical reaction of the anode or cathode [141]. Inorganic corrosion inhibitors are cheaper and are used in less acidic and more stable environments. Inorganic corrosion inhibitors mainly include chromate, nitrite, silicate, molybdate, tungstate, polyphosphate, and zinc salt [142–146]. Some researchers found that a special case is the ability to control corrosion caused by sulfide by poisoning sulfide bacteria with toxic inorganic substances, but these substances are obviously also a potential threat to the human body and cannot be used on a large scale [147]. Because of its low corrosion inhibition efficiency and weak adaptability, it has the risk of heavy metal pollution and precipitation, which can block pipelines in specific acid–base environments [142], so it is seldom used in industrial production.

6.2. Imidazole Compounds

Imidazoles are the most widely used commercial and industrial corrosion inhibitors and can be used as a representative of current corrosion inhibitors with stable effects in a variety of environments. Imidazole (IMD) compounds are heterocyclic aromatic compounds consisting of three carbon atoms and two nitrogen atoms and are highly soluble in water and oil phases. They have both acid and basic functional groups, so they have both properties [148]. They attach to the surface of the metal and form a protective complex to prevent further corrosion of the metal [149]. The representative of this kind of substance is imidazoline, which has a nitrogen-containing heterocyclic ring, which is composed of a hydrophilic side group, an imidazoline ring, and a substituent group. Among them, the hydrophobic part is the most important part that plays an inhibition role [150]. Given the negative effects of its bioaccumulation, much work has been carried out to address this problem [151]. In addition, the corrosion inhibition of similar products
has been studied, such as 2-mercaptobenzimidazole [20,152,153], thiazole, thiazole, and tetrazole [154–158].

In view of the advantages of such a mature corrosion inhibitor, we need a corrosion inhibitor with at least several characteristics: it can be manufactured in large quantities at a low cost, it is chemically stable, and it can adapt to a variety of corrosive environments. Additionally, in the future, its ecological damage and biological accumulation need to be considered.

6.3. Other Organic Corrosion Inhibitors

Organic-compound-type corrosion inhibitors are considered to be effective industrial corrosion inhibitors, and the efficiency of corrosion inhibition is greatly increased compared to that of inorganic corrosion inhibitors [159]. In addition to the most popular imidazoles, there are some organic compounds with corrosion inhibition capability.

In acidic environments, alcohols have excellent corrosion inhibition effects on metals. Propargyl alcohol is an important corrosion inhibitor for alcohol. Researchers studied the corrosion inhibition process of aluminum in a 0.5 M H₂SO₄ solution in the presence of propargyl alcohol (PA) and zinc sulfate at room temperature. Then, the study found that PA attenuated the corrosion of metals in acidic environments by adsorbing on metal surfaces. The higher the concentration is, the better the inhibition effect is. The synergistic effect of PA and zinc sulfate greatly enhances the inhibition effect [160]. Similarly, 2-butyn-1-ol, another alkyne alcohol, also shows excellent corrosion inhibition in acidic environments. The researchers found that the two alkyne alcohols adhere to the same adsorption rules. The key to inhibiting corrosion is through the adsorption of the triple-bond carbon atoms [160,161]. Dimethyl 2-(2–hydroxy phenyl amino)-3-(triphenyl phosphoranimidin) butane dioate (L-OH) has been shown to inhibit corrosion in acidic environments. L-OH is adsorbed to the surface of the metal through a double bond of carbon atoms and a lone pair of electrons present on nitrogen and oxygen in the conjugated system. The adsorption capacity of L-OH varies with temperature, and its corrosion inhibition ability is consistent [162]. In addition, other researchers have demonstrated the inhibition effect of crotyl alcohol [163]. Some researchers have proved the effectiveness of papaya leaf as a corrosion inhibitor and extracted the part that can effectively reduce corrosion, proving that it inhibits corrosion by blocking the reaction of the cathode [164]. Three ethoxylated fatty alcohols with different ethylene oxide unit numbers have been proved to be effective in reducing the corrosion of carbon steel in an acidic environment, and the related thermodynamic parameters have been calculated [165].

6.4. Inhibitors in Acidic Environments

In general, acidic or chloride-containing environments are the most aggressive, and most corrosion problems occur in these environments, so it is necessary to describe this aspect of corrosion inhibitor research separately. In spite of the fact that natural products, extracts, and pharmaceutical drugs can act as corrosion inhibitors because of their nontoxicity and relatively low cost, they cannot be widely used in industrial systems due to their low corrosion inhibition efficiency. The most widely used corrosion inhibitors in salt and weak-acid environments are the azole compounds that were introduced before, and then there are three more widely used corrosion inhibitors: amine-based, polymer-based, and Gemini-surfactant-based inhibitors [140].

Amines are organic compounds containing basic nitrogen atoms with characteristic electron pairs. They are divided into primary amines, secondary amines, and tertiary amines according to the number of substituents on the nitrogen atoms. Cyclic substituent organic compounds become cyclic amines [166]. They are important organic corrosion inhibitors in acidic environments. Amine inhibitors inhibit corrosion by forming protective films. The mechanism of amine film formation on carbon steel was demonstrated by X-ray photoelectron spectroscopy. Figure 12 shows the mechanism of this corrosion inhibitor. In an acidic environment, HS⁻ reacts with the N atoms of amines and forms
coordination bonds on metal through lone-pair electrons of N and a vacant orbital of the metal, forming an oil layer to prevent the metal surface from being corroded by acid gas [18,167]. A relatively new exploration of amine corrosion inhibitors includes the testing of Di-ethylenetriamine (DETA) for corrosion inhibition in ethanol and diesel blends. The results demonstrate the excellent corrosion inhibition properties of DETA [168]. There are mature commercial products of amine inhibitors, such as CORTRON AR-505 and Fentacare 1227 [169]. New amine substances continue to prove excellent in reducing corrosion [170–172].

![Adsorption mechanism of amine inhibitor.](image)

Gemini-surfactant-based inhibitors are active organic compounds that can reduce the surface tension between the two interfaces. It has both hydrophilic and hydrophobic parts and forms a film at the two interfaces to protect metal materials from erosion [173]. They are sensitive to pH changes and are mainly used in acid–base-stable environments. Their adsorption behavior in the process of corrosion inhibition has been described in detail. Hydrophilic and hydrophobic attraction and hydrogen bonds play key roles [174]. Their difficulty in biodegradation and high toxicity limit their use. Different corrosion inhibitors of this class are being discovered [175], such as N⁺-((ethane-1,2-diylbis(oxy))bis(2oxoethane-2,1-diyl))bis(N,N-dimethyl-4-((E)-2-((E)-octadec-9-enoyl)hydrazineylidene)methyl)-benzenaminium) dichloride [176], counterion-coupled surfactant (RBOS-12) [177], novel cocogem surfactants [178], and quaternary ammonium dicationic surfactant with phenyl linker [179].

Polymers are also widely used as corrosion inhibitors in the petrochemical industry. They are insoluble in water, cannot withstand high temperatures, are not clean, and are high in carbon, which limits their range of application. They have the advantage of usually having a high caloric value and a high viscosity that allow them to be used as thickeners while limiting corrosion [180]. Because of their specificity, their range of application is very fixed, and they are being used less and less with the advent of the low-carbon era. Typical polymer inhibitors include water-based Acrylic terpolymer [181] and butyl-capped Aniline Tetrarmers [182].
6.5. Green Inhibitors

The extraction of corrosion inhibitors from renewable biomass is an important research direction of corrosion inhibitors. Although existing corrosion inhibitors can effectively reduce the corrosion in the application, their toxicity and non-biodegradability when used in this process have become new problems. Now, researchers are looking for green corrosion inhibitors with little or no toxicity that can be obtained from renewable energy sources [183,184]. Green corrosion inhibitors have been obtained from a wide range of sources; all natural sources and derivatives of natural sources that can inhibit the corrosion behavior of metals can be classified into this category [185]. For example, honey has been shown in various experiments to inhibit the corrosion of CuNiFe alloy, Q235 steel, mild steel, and stainless steel in acidic and neutral environments [186–188]. However, green corrosion inhibitors are mainly plant extracts and derivatives of plant extracts, and it has been confirmed that there are corresponding green corrosion inhibitors that function at any environmental pH [189].

Many plant extracts have been shown to inhibit corrosion. Previous extracts experimentally investigated include Marine algae [190,191], baicalin derivatives [192], Angelica sinensis [193], vernonia amygdalina [194], citrus aurantium [195], nicotiana tabacum [196], African breadfruit [197], combretum bracteosum [198], and buddleia perfoliata [199]. Some researchers concluded that since most plant chemical synthesis occurs in leaves, the main sources of corrosion inhibitors also converge in leaves. And the absorbability component is complex, as it is a combination of actions [189]. Similar results have been found for plant derivatives. Some researchers synthesized two chitosan derivatives to reduce carbon dioxide corrosion of P110 steel and proved their excellent performance in reducing corrosion. Experiments have proved their efficiency. The mechanism of the corrosion inhibitors was analyzed theoretically. They are compounds with a carbonyl group and primary amine, which can provide lone-pair electrons. Through these electrons, organic inhibitors can easily be adsorbed on the metal surface and form a barrier to prevent corrosion, playing the role of a corrosion inhibitor for steel. And the inhibition efficiency is much higher than that of the corresponding aldehyde [183,200].

The different mechanisms of action of different corrosion inhibitors are mentioned in Table 3. In fact, the mechanism of action of all types of corrosion inhibitors, including green corrosion inhibitors, is a key factor when considering their use. In environments where galvanic corrosion is predominant, such as those containing acids or bases, it is best to choose a corrosion inhibitor with a chemisorption mechanism. When the corrosion resistance of the material at the cathode or anode is relatively poor, special protection of the material should be considered, for example, by using a cathode or anode hybrid inhibitor.

<table>
<thead>
<tr>
<th>Source of Extract</th>
<th>Experimental Environment</th>
<th>Material</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>H. clathratus</td>
<td>1.0 M hydrochloric acid and 1.0 M sulfuric acid</td>
<td>mild steel</td>
<td>physical absorption</td>
</tr>
<tr>
<td>baicalin derivatives</td>
<td>1.0 M hydrochloric acid</td>
<td>aluminum</td>
<td>physical absorption, complex formation</td>
</tr>
<tr>
<td>angelica sinensis</td>
<td>1.0 M sulfuric acid</td>
<td>mild steel</td>
<td>cathode and anode hybrid inhibitor</td>
</tr>
<tr>
<td>bitter leaf root</td>
<td>1.5 M sulfuric acid</td>
<td>mild steel</td>
<td>physical adsorption</td>
</tr>
<tr>
<td>citrus aurantium leaves</td>
<td>1.0 M hydrochloric acid</td>
<td>carbon steel</td>
<td>chemical adsorption</td>
</tr>
<tr>
<td>nicotiana tabacum leaves</td>
<td>2.0 M sulfuric acid</td>
<td>mild steel</td>
<td>physical adsorption</td>
</tr>
<tr>
<td>ficus sycomorus leaves</td>
<td>1.0 M hydrochloric acid</td>
<td>mild steel, aluminum</td>
<td>physical adsorption</td>
</tr>
<tr>
<td>combretum bracteosum</td>
<td>2.0 M sulfuric acid and 5.0 M sulfuric acid</td>
<td>mild steel</td>
<td>physical adsorption</td>
</tr>
<tr>
<td>buddleia perfoliata</td>
<td>0.5 M sulfuric acid</td>
<td>1018 carbon steel</td>
<td>adsorption of tannins and Fe²⁺ ions</td>
</tr>
</tbody>
</table>

Table 3. Some green corrosion inhibitor studies.
For now, green corrosion inhibitors are confined to the laboratory, where their ability to reduce corrosion is clearly proven, but not for commercial or practical use. Their corrosion inhibition efficiency is the most important problem, as it is far from that of the common organic corrosion inhibitors. In addition, more extreme environments that are more acidic or alkaline are less stable. It is also generally impossible to extract the specific molecular components of corrosion inhibition [183]. I believe that the corrosion inhibition efficiency of products directly extracted from natural ingredients or derivatives after simple treatment can reach the level of widely used corrosion inhibitors. Even if the cost increases, it still has advantages. The difficulty is how to determine the exact components of corrosion inhibition.

7. Prospects

Liquid fuels will play a crucial role in the long term, and corrosion caused by traditional fossil fuels will continue to cause significant damage. Efforts to mitigate this damage will require substantial work. Alternatives, supplements, and additives to fossil fuels must be rigorously tested for corrosion. The understanding of future corrosion problems presented in this paper includes the following insights:

(1) The addition of alcohols to conventional fossil fuels offers significant advantages in terms of reducing corrosion problems. Biofuels, however, urgently need further research due to their high potential for causing corrosion. If researchers can creatively solve the corrosion issues associated with biofuels, it could lead to an epoch-making breakthrough in the energy industry.

(2) There is a lack of systematic exploration of material selection for specific corrosive environments. For example, it is unclear what materials or coatings are best suited for environments containing reactive sulfides, which materials are most resistant to corrosion in humid environments, and whether certain materials are sensitive to specific components while being resistant to others.

(3) The mechanism of the microbial corrosion of metals deserves in-depth study. While it is known that the presence of microorganisms intensifies corrosion, the detailed processes and mechanisms of microbial corrosion are not fully understood. Researchers in the biological field could make significant contributions to other disciplines by uncovering specific roles of certain microorganisms or discovering new mechanisms of microbial metabolism that impact corrosion.

(4) From an electrochemical perspective, a quantifiable corrosion criterion should be developed. By establishing standardized calibration and measurement conditions, researchers could accurately determine and express the “standard corrosion value” of a material in a specific solution.

(5) Solving the corrosion problem by developing new materials and transforming the production, transportation, and use processes of fuel is challenging. Significant progress has been made in controlling water and sulfur contents in fuels, leading to substantial results. However, further reducing these indicators is currently difficult. In the future, corrosion control will likely focus on the development and use of corrosion inhibitors.

(6) The ideal corrosion inhibitor of the future will likely be an additive that provides multiple benefits to fuel oil, such as reducing corrosion, enhancing oxidation resistance, improving anti-wear properties, and adjusting viscosity and calorific value. Collaborative research and development across different additive fields should be strengthened to identify intersections and synergies, striving to create multifunctional additives that can address various challenges simultaneously.

(7) Organic corrosion inhibitors remain the first choice for addressing fuel corrosion problems. However, their toxicity and environmental impact present new challenges. Currently, there are no products that can replace them entirely. It is important to identify environmentally friendly alternatives or to improve the environmental performance of mainstream organic corrosion inhibitors.
Green corrosion inhibitors are an important research direction, but their corrosion inhibition efficiency and economic cost remain significant challenges. Currently, most efforts are focused on confirming that natural extracts can reduce corrosion. However, there is a lack of further research on the interactions and mechanisms between different green corrosion inhibitors. This gap limits the potential for improving their corrosion inhibition efficiency.

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