
Corrosiveness of Fuels During Storage Processes

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1. Introduction

Corrosion, or destruction of materials in consequence of chemical or electrochemical interactions between the material and its environment, has been a major problem in industry for years. The petrochemical industry being no exception, corrosiveness has been blamed, as the major perpetrator, for costly failures of equipment. Knowing well and understanding the process of corrosion enables its effective control and prevention of the problems caused by corrosion. Bear in mind that corrosion attacks a variety of materials, not just metals alone: the destructive effect of the environment on ceramics, plastics, as well as composites is also observed.

In a more complex environment, it is more difficult to investigate and find a solution to the corrosive effect. Paradoxically, corrosion is a common problem wherever petroleum products are in contact with metal parts and alloys, whether during production, distribution, operation, or storage – even though non-polar hydrocarbons contained in the fuel do not cause corrosion. Corrosion changes are caused by certain constituents of the fuel: sulfur compounds, organic acids, and water-soluble inorganic acids and bases. Among the aforementioned compounds, the most aggressive ones, having the highest corrosive effect are active sulfur compounds (e.g., free sulfur, hydrogen sulfide), especially in the presence of water. The content of water in the refinery fuels is usually very low (30-80 ppm) and its effect on corrosion rate is insignificant. If increased (for instance, due to the penetration of steam into storage tanks), it does have an effect on corrosion processes. In gasoline with a water content of 80 ppm or less, the rate of corrosion on carbon steel is 0.001 mm/year; in those with a water content of 200 ppm – corrosion rate is as high as 0.4 mm/year [1]. Part of the steel or metal surface is wetted with water, which forms thin (from 3-10 μm), interrupted water films between the metal and the organic phase. Since oxygen has different solubilities (higher for the organic and lower for the aqueous phase), anode or cathode regions are formed on the steel or metal surface. This creates favorable conditions for electrochemical corrosion in a given environment. Also microbial growth in fuels causes corrosion damage during the storage and transport of fuels. Above a certain limit,

which usually is low, the presence of each of the aforementioned factors of corrosion is unacceptable. Bear in mind that fuel ageing and corrosion are coexistent processes. According to certain reports, the presence in fuels of metal ions originating from corrosion processes accelerates the formation of deposits and gums [2] which, in turn, lead to problems in the fuel distribution system, such as filter plugging or damage to engine parts. Therefore, it is very important to determine the corrosive effect of fuels on the construction materials, widely used in automobile engines or storage tanks.

2. Corrosion in storage tanks

Corrosion is also a problem during fuel storage in storage tanks. Corrosion leads to the formation of products which are likely to cause changes in the quality of fuels (affecting their physical and chemical properties), may accelerate oxidation of hydrocarbon ingredients of the fuel – this leads to higher acid values and to the development of gum and sludge in the fuel. Carbon-steel storage tanks, intended for long-term (5 years a minimum) storage of fuels, may affect the chemical stability of fuels (increased content of oxidation products) [1].

Any sludge developed in the fuel will promote microbiological corrosion. Steam and atmospheric oxygen may dissolve in the fuel during storage. Water and atmospheric oxygen may penetrate into the storage tanks during their evacuation and during what is called “tank breathing”. As temperature fluctuates between day and night, water with its contaminants may be separated from a fuel being stored in aboveground tanks, forming a thin aqueous electrolyte film. Typically, the film is formed on the tank walls and travels downwards, to reach the bottom. This creates conditions in which electrochemical corrosion processes are likely to occur. In storage tanks, there are several corrosion zones with different susceptibilities to corrosion:

- Zone 1 – Top of the tank (inner surfaces of the roof and side walls), which contacts the fuel vapors.
- Zone 2 – Splashing zone: a border between the gas phase and liquid phase. The size of it is variable and depends on how much fuel is in the tank and how the tank is filled/evacuated.
- Zone 3 – Liquid zone: that part of the storage tank which is permanently in contact with the liquid fuel; same as above, its size depends on how much fuel is in the tank.
- Zone 4 – Bottom of the tank and, optionally, its immediately adjacent region. That part of the aboveground tanks is most exposed to contact with water, any salts that may be dissolved in it and its organic and inorganic deposits. The organic deposits are composed of hydrocarbons and bio-films, whereas the inorganic deposits may comprise corrosion products, salts, and sand [1].

The mechanisms of corrosion taking place on the inner parts of the tank are more complex, compared with those describing the corrosion processes that may occur on its outer surface. The rate and type of corrosion taking place in aboveground tanks depends on what petroleum

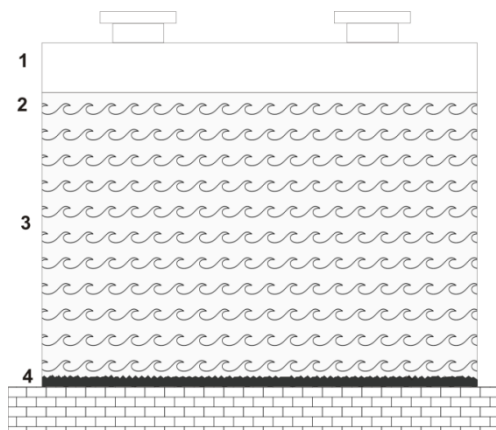


Figure 1. Corrosion zones in storage tanks

product is stored, on solubility of water and oxygen in that kind of fuel, tank capacity, filling/evacuation frequency, and on temperature. Also important are the design features of the tank itself, such as roof type (floating or fixed), the presence of pontoons, tank breathing solutions, as well as its location. Typical tanks for storing gasoline or petroleum are provided with floating roofs and pontoons which limit fuel evaporation and losses through safety valves [1].

Depending on the type of fuel, corrosion processes may take place in different tank zones. In aboveground storage tanks for gasoline, corrosion is observed usually on the south-facing part of the tank. This is probably due to the fact that the day and night temperature fluctuations are higher on the south-facing surface. The south part of the storage tank is more exposed to sunlight, this causes a local temperature increase in daytime and improves the solubility of water in the fuel. In the night, the temperature goes down, again, causing separation of water and its adsorption on the steel surface of the tank walls. Such circumstances, combined with the presence of oxygen, lead to electrochemical corrosion. During the storage of gasoline, the bottom surfaces of storage tanks are less exposed to corrosion.

2.1. The mechanism of corrosion taking place in fuels

With the exception of noble metals, all metals are thermodynamically unstable under normal conditions and it is natural for the system (comprising metals and their alloys) to achieve a form with a better thermodynamic stability (oxidized form). Although a number of types and mechanisms of corrosion are known, it is believed that in the case of fuels there occur electrochemical corrosion (in the presence of electrolytes) and chemical corrosion (in the absence of electrolytes). Compounds which are formed as the result of corrosion, also called corrosion products, may accelerate or inhibit corrosion, or may have no effect on the further course of the metal destruction process. In the case of certain metals, weakly soluble metal compounds (usually oxides) are formed, creating a protective film on its surface, it reduces the rate of corrosion to negligible values – the metal then remains passive. The presence of such naturally

formed surface films has an effect on the corrosion resistance of such construction materials as alloy steels, titanium alloys, or aluminum. The oxide layer significantly inhibits corrosion of the metal on which it is formed. This enables designing of components and storage tank fittings without any extra safety devices against corrosions. For instance, in alloy steels, the formation of a thin passive film is connected with a suitable content of chromium in the steel. Under certain conditions, a chromium-rich oxide film on the surface will practically prevent general corrosion. A problem appears as soon as the passive film is destroyed locally and its continuity is interrupted, leading to the formation of active-passive galvanic cells and to the development of corrosion pits. In such galvanic cells the area which is devoid of the passive film becomes the anode where the metal is oxidized while the passivated metal area functions as the cathode. This is very dangerous because the anode/cathode surface area ratio is often unfavorable, very much accelerating metal digestion. For certain conditions, this may have serious consequences, for instance, perforation of the tank walls. The Figure below illustrates the idea of how the galvanic cell works, on the example of iron.

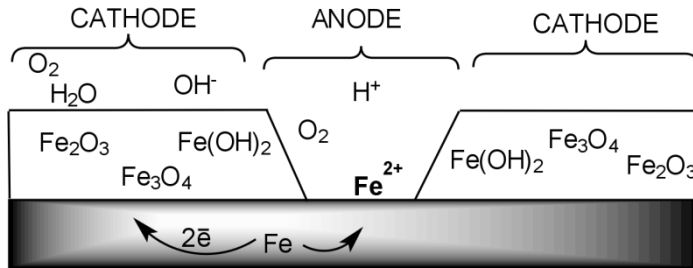


Figure 2. Galvanic cell – the principle of operation

The rate of electrochemical corrosion depends on the nature of the protective film being formed on the metal or alloy surface, the presence of polar solvents (especially water) in the environment of the metal (fuel), the presence of electrolytes (salts, acids, bases), as well as temperature. For a given material, corrosion resistance depends on its structure, composition and the various forces acting upon it. In the case of metal, its electrochemical potential is important as well. Metals having a positive electrochemical potential in relation to hydrogen will undergo oxidation more readily and the process is the more intensive the higher the potential.

To explain the mechanisms of corrosion is a great challenge because fuels are very complex mixtures and corrosion processes are complicated. Corrosion interactions remain to be the subject of studies globally. Studies are carried out to investigate the details of the mechanism of corrosion – both in order to fill some gaps in our knowledge of the problem, and to find better ways to prevent corrosion and minimize corrosion damage. Understanding corrosion processes is important both for economic and safety reasons. One must not forget that losses caused by corrosion involve not only damaged or destroyed tanks, pumps, engines, but also loss of energy, utilities, or the human effort involved in the manufacturing of materials or products. In the case of fuel storage, on the one hand, the ongoing corrosion processes may

destroy tanks or fittings, generating high costs of maintenance or even creating a necessity to replace the damaged parts, posing realistic environmental hazard (leakage of fuel); on the other hand, the products of corrosion may affect the quality of fuel during storage, intensifying the process of fuel ageing as well as vehicle engine problems.

Corrosion of metals while in contact with the fuels occurs under the influence of products which are formed by oxidation of gasoline, diesel fuel or biofuels. Such factors cause morphological changes taking place on metal parts, which is manifested by changes in coloration of the fuel, among other things. In the case of biofuels and alternative fuels, the problem of their corrosive effect is not very well known yet; this is because of the variability of raw materials and progress in the production technology of such fuels.

2.2. Corrosive effect of biodiesel on copper, aluminum, carbon steel and stainless steel

Biodiesel is perceived as a novelty fuel, based on renewable sources, having a potential to replace the conventional diesel fuel. From the point of view of chemistry, biodiesel is a combination of fatty acid methyl or ethyl esters. In spite of its numerous advantages, it does have certain drawbacks. Test reports indicate that biodiesel causes more corrosion, compared with the petroleum-based diesel fuel, especially in the presence of water [3]. Corrosive effect on metals is one of the major parameters of biofuels, determining their usefulness as engine fuels.

Studies on the corrosive effect of *Jatropha* biodiesel were carried out before, using such materials as copper, zinc, lead, tin, bronze. It was found that the rate of oil degradation was increased by oxidation which, in turn, was catalyzed by the presence of the metal (the most pronounced catalytic effect was recorded for copper) [4, 5].

Reported in [6] are findings of studies concerning the effect of biodiesel and bioethanol on corrosion for selected materials. Immersion tests were carried out at room temperatures which demonstrated that copper and aluminum are susceptible to corrosion both in biodiesel and in bioethanol. Corrosion pits were also observed on carbon-steel and cast-iron surfaces. A research team of Fazal reported, in [7], their findings on the effect of palm-oil biodiesel on the structural materials of engine components, and compared their findings with similar tests on the conventional diesel fuel. Their findings indicate that the extent of corrosion was higher for biodiesel, compared with diesel fuel. Copper and aluminum appeared to be quite readily corroded in biodiesel and stainless steel was found to resist corrosion.

The corrosive effect of biodiesel and bioethanol on copper, aluminum, carbon steel and stainless steel was also investigated in [8]. Immersion corrosion tests were carried out in accordance with ASTM G32-72 at 43°C for two months. For comparison, similar tests were carried out for a petroleum-based diesel fuel. The results indicate that corrosion rate of copper in biodiesel was roughly 6 times as high as that in diesel fuel. A similar phenomenon occurred when carbon steel plates were immersed in biodiesel: corrosion rate was 12 times as high as that in diesel fuel. On the other hand, corrosion rate of stainless steel and aluminum in biodiesel was only slight, in the same range as that found for diesel fuel. In the case of aluminum, its surface was covered with a thin, strongly sticking layer of oxides (passive film). The passive

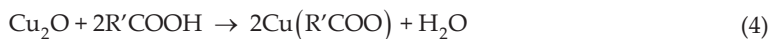
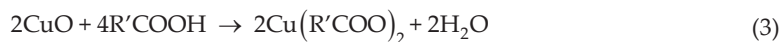
film forms a barrier between the metal surface and the fuel, preventing also any access of oxygen of which the presence is essential in corrosion processes; this results in lower corrosion rates. Materials such as copper or carbon steel are readily oxidized. When exposed to biodiesel, metal oxides are formed, including: CuO , Cu_2O , Fe_2O_3 etc., which adhere less strongly to metal surfaces, compared with aluminum [8]. Later in the tests, surface analyses were carried out using SEM, EDS, XPS, and the concentrations of the respective ions in biodiesel before and after the corrosion tests were measured using AAS. Based on their findings, the authors proposed a possible mechanism of the reaction for copper and iron, which could have been working during the corrosion processes taking place. Initially, at room temperatures, copper slowly reacts with oxygen, forming the red copper(I) oxide according to the following reaction:



At elevated temperatures, the black copper(II) oxide may be formed directly (reaction 2).



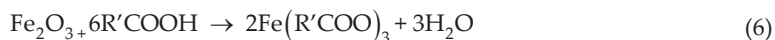
If water is present in the biodiesel, processes may take place which result in its degradation. The presence of water leads to hydrolysis of esters and, eventually, to the formation of free fatty acids and glycerol. Each of the oxides formed in reactions 1 and 2 may react with fatty acids, forming organic salts (reactions 3 and 4) and water, which accelerates corrosion.



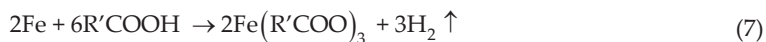
Similar reactions take place for iron, exposed to biodiesel. Initially, metallic iron is oxidized to form iron oxide (reaction 5).



In the next step, the iron oxide may react with the fatty acids being formed in the biodiesel (reaction 6).



Another possibility is that iron reacts directly with fatty acids, forming organic salts which are adsorbed on the metal surface, in addition to hydrogen (reaction 7).



The corrosion processes taking place were also indicated by changes in the fuel's coloration after exposure of the test metal samples. Its color depended on what kind of ions were released from the test samples. Specifically, a greenish shade of biodiesel after exposure of copper plates was attributed to the presence of Cu^{+2} ions in the fuel. A brownish shade after testing the carbon steel plates may indicate the presence in the fuel of Fe^{+2} or Fe^{+3} ions. Discoloration of biodiesel after immersion tests with aluminum samples is attributed to Al^{+3} ions, whereas a slightly yellowish shade after exposure of the stainless steel samples – to Fe^{+3} or Cr^{+3} ions. In addition to discoloration, sufficient evidence confirming the passage of the metal ions into the solution was that the weight of the test samples was reduced after the corrosion tests.

With the exception of stainless steel, metal surfaces tend to change coloration when reacting with biodiesel, for instance, the copper plate was coated with some black material. Examination indicates [8] that the black deposit may be composed of oxides or organic salts. On the other hand, the presence of organic salts and no iron oxide was observed on the carbon steel plate. Organic salts may also be present on aluminum surfaces. Compared with copper surfaces, aluminum showed only slight discoloration though the entire surface grew a little darker. Certain products of oxidation of the surface of metal or metal alloys, such as ions or deposits, may penetrate into the biodiesel fuel, causing changes in its physico-chemical properties, other products may react with free fatty acids leading, eventually, to the formation of fatty acid organic salts on metal surfaces. This is potentially the main cause of diversification in the appearance of biodiesel and metal surfaces. Examinations were carried out using atomic absorption spectroscopy (AAS), which confirmed that the content of copper and iron ions in biodiesel was high after corrosion.

The carbon steel surface in biodiesel was found to have a higher content of carbon and oxide after the corrosion test. This was caused by the reaction between metal oxides and fatty acids to form salts, which strongly stick to the metal surfaces.

Also traces of carbon, oxygen, nitrogen and sulfur were detected on non-corroded metal surfaces. This was caused by exposure of the metal to the influence of air, and its reaction with atmospheric oxygen whereby metal oxides are generated and certain organic contaminants are absorbed on the surface. Literature reports indicate that, after corrosion, the content of carbon was higher on copper, carbon steel and aluminum and lower on stainless steel. This indicates the formation of organic deposits, such as fatty acid salts, and oxides. The deposits strongly adhere to metal surfaces and are hard to remove with a solvent such as acetone. No significant changes were noticed on stainless steel, indicating the absence of organic deposits on the metal surfaces. Spectral analysis of stainless steel suggested the presence of carbon complexes, including organic deposits and amorphous carbon. The formation of carbon complexes reduces the carbon content on steel, compared with other metal surfaces, where such complexes are not formed.

Certain organic deposits tend to develop on metal surfaces only after exposure to atmospheric air; this was observed for such metals as copper, carbon steel, or aluminum. In such tests, the

metal surfaces had a higher carbon content and the level of $-\text{COOH}$ carboxylic groups also was higher after corrosion in biodiesel. The increased content of carboxylic groups indicates oxidation of the biodiesel and the formation of carboxylic acids. Reactions between carboxylic acids and metal oxides produce organic salts which deposit upon the metal surfaces [8].

Such conclusions are confirmed by IR spectral analysis. After the corrosion tests, the intensity of the peaks corresponding to iron oxides (Fe_3O_4 and Fe_2O_3) was higher, indicating the presence of such oxides; at the same time the iron peak intensity was lower. This explains why organic salts are present on the steel surface, while the content of iron is lower. The same phenomenon was observed for the aluminum surface. A higher intensity of the Al_2O_3 peak and lower intensity of the aluminum peak indicates the formation of organic salts. Aluminum reacts quite readily with atmospheric oxygen, generating Al_2O_3 , and tends to adsorb organic compounds. It is safe to say that the formation of an aluminum oxide film inhibits corrosion reactions with the metal surface. Oxygen, dissolved in biodiesel induces further formation of the aluminum oxide film, preventing access to the surface.

From among copper, aluminum, carbon steel and stainless steel, the rate of corrosion in biodiesel was the highest for copper (0.02334 mm/year), second highest for carbon steel (0.01819 mm/year), 0.00324 mm/year for aluminum and 0.00087 mm/year for stainless steel. The corrosion products included mainly fatty acid salts, and metal oxides. It was also demonstrated that decomposition of biodiesel is catalyzed by elements such as copper and iron, creating an environment for corrosion of engine components [8].

2.3. Corrosive effect of biodiesel on copper and brass

Copper and copper alloys undergo corrosion in fuels probably according to the same mechanism as iron and iron alloys. However, the corrosion processes taking place on copper are less destructive and slower – corrosion pits, if present all, are limited to extreme conditions; corrosion is usually manifested by discoloration of the metal or alloy surface. It was demonstrated that even the lowest concentrations of sulfur present in the fuel will take part in corrosion reactions taking place on copper, forming sulfides on its surface. Destructive oxidation reactions are catalyzed by Cu^{2+} ions which pass into the fuel due to corrosion processes. According to literature, the effect is observed when the concentration of copper ions in the fuel is between 100 and 3000 ppm [2].

Oxidation of biodiesel leads to the formation of various products such as peroxides and hydroperoxides. During degradation, these products transform into shorter-chain compounds such as low-molecular weight acids, aldehydes, ketones, and alcohols [9]. Moreover, oxidative polymerization may lead to the formation of macromolecular chemical compounds [10]. Thus, oxidation of biodiesel intensifies its corrosive effect, affecting the physico-chemical properties of the fuel [7]. The corrosiveness of biodiesel is also connected with the presence in it of contaminants, such as: water, alcohol, free fatty acids.

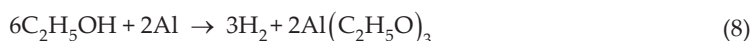
Studies on the effect of light, temperatures, and selected metals on corrosiveness and degradation of biodiesel are reported in [11]. The corrosiveness studies were carried out for copper and brass using the immersion method according to the standards ASTM G31 and ASTM G1.

The experiment was continued for 5 days at room temperatures (ASTM G1) in the presence or absence of light. The studies were also carried out at 55°C for comparison with the findings of tests according to ASTM G31 (with air bubbling). In the tests referred to in ASTM G31, the test samples were placed at 3 different levels (totally immersed in fuel, partly immersed in fuel, exposed to fuel vapors only). The copper and brass plates had more corrosion-induced changes after being immersed in biodiesel, compared with the test plates exposed to fuel vapors only. The corrosion processes were accelerated by bubbling with air, leading to larger weight losses in the copper and brass plates. After 5 days of exposure, a slightly higher corrosion rate was recorded for the plates exposed to light at room temperatures, compared with those tested in the absence of light. Interestingly enough, in the tests carried out in the dark, corrosion rate was much slower for copper and for brass after increasing the temperature to 55°C; presumably, this was caused by the fact that oxygen is less soluble at higher temperatures. Moreover, biodiesel samples were found to have higher viscosities and higher water contents after the corrosion tests according to ASTM G31.

2.4. Corrosive effect of bioethanol on aluminum

The presence of alcohols in the fuel has a significant effect on its corrosion behavior. The alcohol itself is a corrosive medium, additionally, it is able to dissolve in and be mixed with water at any ratio. Studies on the effect of bioethanol on corrosion for an aluminum alloy (A348) were described in [12]. Corrosive properties were tested by its immersion in fuel blend samples, made of unleaded gasoline with various concentrations of bioethanol (10, 15 and 20% (v/v)). The tests were carried out at temperatures 60, 80 and 100°C, by immersing the test metal samples in the prepared blends for 24 hours. The test results indicate the presence of local corrosion pits on the surface of the aluminum alloy plates after continuing the tests for 24 hours at a temperature of 100°C. The extent of corrosion was higher for higher concentrations of ethanol in the blends, as indicated by the higher number of corrosion pits on the surface of the test alloy samples. No corrosion damage was observed at lower temperatures (60 and 80°C).

Presumably, a protective film of hydrated aluminum oxide was formed on the aluminum alloy surface during the tests at temperatures below and including 80°C. Only after increasing the temperature to 100°C was the reaction triggered between aluminum and bioethanol (reaction 8).



The reaction involves substitution of the aluminum atom originating from the metal or from the oxide film with a hydrogen atom originating from bioethanol; hydrogen and aluminum acetate are formed.

Reported in [13] are results of studies, intended to determine the effect of oxygen present in the fuel on the corrosive properties of aluminum alloy. The test fuel blend was composed of 80% unleaded gasoline and 20% of 99.9% pure ethanol. The fuel blends were heated up to 100°C after being subjected to bubbling with nitrogen or gaseous oxygen for 2 hours. This

provided fuels with different concentrations of oxygen. The effect of oxygen, dissolved in the fuel, on a high-temperature corrosion of aluminum alloy was investigated in electrochemical tests, using impedance spectroscopy and by evaluating the condition of the surface of the aluminum alloy samples before and after the tests. It was shown that corrosion resistance was increased with the increasing concentration of oxygen dissolved in the fuel, indicating the passive film formation on the test sample surface. On the other hand, it was demonstrated that bioethanol may be oxidized by the oxygen dissolved in the fuel, generating acetic acid and water. Each of the products is able to have an effect on corrosion of aluminum alloys. In further tests, the authors attempted to determine the effect of those factors on aluminum alloy destruction processes: to achieve this, specified amounts of acetic acid and/or water (0, 0.1, 0.5, 1.0 % v/v) were added to a fuel blend comprising 80% unleaded gasoline and 20% bioethanol after passing nitrogen through the blend. The test alloy plates were immersed for 6 hours in the prepared fuel blends after heating the blends to 100°C. It was demonstrated that water had a beneficial effect on the corrosion resistance of the aluminum alloy, having formed a hydrated aluminum oxide film on the metal surface, which acted as a protective film. Changes on the surface of the alloy sample were not observed for blends with a water content of more than 0.5 % v/v. Addition of acetic acid worked quite differently: it had a harmful effect, destroying the protective film and causing corrosion pits even at as low concentrations as 0.1 % v/v, and the process was intensified by addition of more acetic acid.

3. Corrosion processes in fuels during storage

Storage of fuels is accompanied by various processes, including oxidation, condensation, and polymerization. Contaminants which were detected during long-term storage of fuels included products of corrosion, organic particulate matter, and deposits. Part of such impurities tended to settle at the tank bottom and side walls, although most of them remained in the fuel and were present in the engine chamber during its operation. Such impurities were not flammable, they tended to escalate soot formation during combustion, affecting the engine's performance. Certain components and impurities (iron oxides, sulfides) also had an effect on the fuels tribology, causing increased wear and tear of the surfaces of the engine's major components. That is why investigating the influence of the storage process on the durability of the selected materials and on the quality of the fuel itself seemed so important. That fuels have a corrosive effect on materials they contact in at every step of their life cycle, is an established fact. What remains to be provided is the findings of studies describing the influence of the degree of fuel ageing on its corrosiveness – both to the materials applied in design solutions for storage tanks, and to the materials applied in vehicle engines. It is the objective of this paper to find out whether and how, if at all, the corrosive effect of various fuels varies in time during storage.

3.1. Corrosiveness tests of gasoline and diesel fuels

The gasoline and diesel fuels which are the national strategic reserve have a zero content of bio-components. The content of bio-components in fuels is known to affect the kinetics of

corrosion processes. In order to determine the actual effect of bio-components on the rate of corrosion, and on fuel ageing processes, tests were carried out using fuels with and without a content of bio-components.

The following fuels were used in the tests:

- 95 octane gasoline containing a maximum of 5% (V/V) of bioethanol (E5);
- 98 octane gasoline containing a maximum of 15% ETBE and no bioethanol (E0);
- diesel fuel containing a maximum of 7% (V/V) of FAME (B7);
- diesel fuel containing no FAME (B0).

The above-mentioned fuels were stored in underground storage tanks to cause their ageing in field conditions. Samples were collected from the storage tanks at certain intervals in order to find out how the physico-chemical properties of the stored fuels were changing and to test the fuels for their corrosive effect. The fuel samples were collected after 6 and 12 months of storage. Tests of the corrosive effect of fuels during storage were carried out using test samples of the following metals or alloys:

- aluminum with an aluminum content of max. of 99.5%;
- copper with a copper content of max. of 99.9%;
- lead with a lead content of a max. of 99.9%;
- brass (copper and zinc alloy, with a copper content of 60%, and a zinc content of 40%);
- C45 steel with a carbon content from 0.42 to 0.5%;
- S235JR steel with a carbon content of max. of 0.2%.

The above-mentioned materials are commonly used as structural materials for vehicle engines. For instance, aluminum alloys are used for making engine blocks, cylinder heads, oil sumps, drive shafts, and rocker arms. Owing to its good conductive properties, copper is used for making windings for alternators, starters, or ignition coils. Brass is used for tubes in fuel distribution systems, tubing for coolers, electrical connections. Steel is used for making major components, including connecting rods, timing gear, and piston pins. Moreover, each of the selected metals and alloys has a different corrosion resistance (different electrochemical potential), which adds to the comprehensiveness of evaluation of the corrosive behavior of fuels. If a fuel contains factors of corrosiveness, such as sulfur compounds, organic acids, and water soluble inorganic acids and bases, in the presence of water and oxygen, each of the above-mentioned metal/alloy plates will be affected by electrochemical corrosion, although the process will be running at different rates. A copper plate with an electrochemical potential of 0.337 V in relation to the hydrogen electrode is classified as a semi-noble metal. In theory, its electrochemical corrosion resistance is high although, if water soluble acids are present (pH below 6.5), it may be corroded in oxygen depolarization conditions. The corrosion resistance of steel depends on its chemical composition. Higher carbon concentrations have an adverse effect on corrosion resistance (C45 grade steel is expected to be corroded sooner than S235JR grade).

Test samples of the selected materials in the form of 15 x 50 x 2 mm plates were sanded with abrasive paper with different grain-sizes, so as to obtain smooth and scratch-free test surfaces. The resulting plates were then defatted with acetone and dried.

3.2. Corrosiveness tests of fuels by the immersion method

The tests were carried out by immersion, using a dedicated, custom-made glass connected vessel which is illustrated in Figure 3. One part of the glass vessel was filled with 100 ml of the test fuel and the other remained empty. The vessel was heated for about 2 minutes to remove any air therefrom, so that the volume just above the fuel was filled with fuel vapors. Both parts of the vessel were then plugged with stoppers having plates of a same kind attached to them. The plates were weighed previously to an accuracy of 0.0001 g, using an analytical balance. The length of the threads was selected so as to enable one plate to be fully immersed in the fuel in one part of the vessel. The other plate, attached in the other part of the vessel, was suspended at the same height. The resulting measuring vessel was placed in a Binder KBF/KBF-ICH chamber in an oxygen free environment.

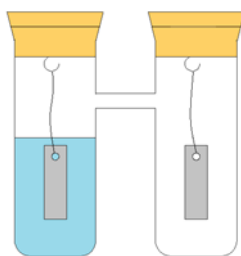


Figure 3. Measuring vessel diagram

The tests were carried out in mixed cycles of ambient temperature and elevated temperature, as follows, respectively:

- 40°C for diesel fuel containing up to 7% (V/V) FAME (B7) and with no FAME (B0),
- 25°C for 95 octane gasoline containing a maximum of 5% (V/V) bioethanol (E5) and for 98 octane gasoline containing a maximum of 15% ETBE and no bioethanol (E0).

The duration of a single cycle was 24 hours, including 8 hours at an elevated temperature and the other 16 hours at an ambient temperature. The tests were completed after 16.5 cycles. The vessel remained at elevated temperatures for a total of 100 hours. The conditions simulated temperature fluctuations between day and night, prevailing in storage tanks.

After the tests were completed, the plates were taken out from the vessels, cleaned with acetone, dried, and weighed to the same accuracy as before the measurements.

Corrosion was measured in terms of the sample weight changes before and after exposure in fuels with different degrees of ageing. In addition, the condition of the plate surfaces was

visually examined and evaluated with regard to the size, distribution, and type of changes on the plate surfaces.

4. Corrosive effect on metals

The corrosive effect of petroleum products was tested by two groups of methods: visual evaluation of samples of materials after exposure in fuels – this only enabled finding out whether corrosion did or not take place. If corrosion changes have taken place, the method provides no information on the rate of the process, therefore, it is important to add to the information a specific quantitative description of the changes taking place.

Changes in the weight of the test material before and after exposure in the given fuel were adopted as the criterion of the evaluation of the corrosive effect of the test fuels. To enable a comparison of the changes taking place in the test metals and steels, it was necessary to use a parameter, taking into account the different densities of the test materials. This purpose is served by linear corrosion rate, defined as the cross-sectional loss per year [mm/year]. The linear corrosion rate was found from the following formula:

$$K_L = \frac{(m_1 - m_2) \times 24 \times 365}{\rho TS \times 1000} = 8.76 \times \frac{\Delta m}{\rho TS}$$

wherein:

m_1 – sample weight before corrosion [g],

m_2 – sample weight after corrosion [g],

Δm – change in sample weight [g],

ρ – density of material [g/cm³],

T – time of exposure at elevated temperatures [hr],

S – surface area of sample [m²].

Findings for each of the test fuels after 6 and 12 months of storage are given below.

4.1. Corrosive effect of 95 octane gasoline containing ethanol

In the corrosive-effect tests for commercial 95 octane gasoline (containing a maximum of 5 % V/V of ethanol) after 6 months of storage, weight changes were observed for all of the exposed metal and steel plates. Such weight changes were recorded after exposure to liquid gasoline and to gasoline vapors. The linear rate of the process of corrosion was found from weight changes and density of the metal (steel), taking into account the duration of exposure of the test samples at elevated temperature (Figure 4).

Based on the test results, it was found that such corrosion rates are rather insignificant, and fall in the range from 0.001 to 0.004 mm/year. The highest corrosion rate was recorded in the

case of lead samples, both for the plate immersed in the liquid gasoline, and for the one exposed to its vapors. The lowest corrosion rates in the test gasoline were recorded for the plates made of S235JR (constructional steel), which indicates its optimum corrosion resistance. For the other materials, such as copper, brass, aluminum and C45 carbon steel, corrosion rates were similar. None of the materials was affected by corrosion to a significant degree, which was assessed as corrosion resistance grade 2 – materials with high corrosion resistance – Table 1.

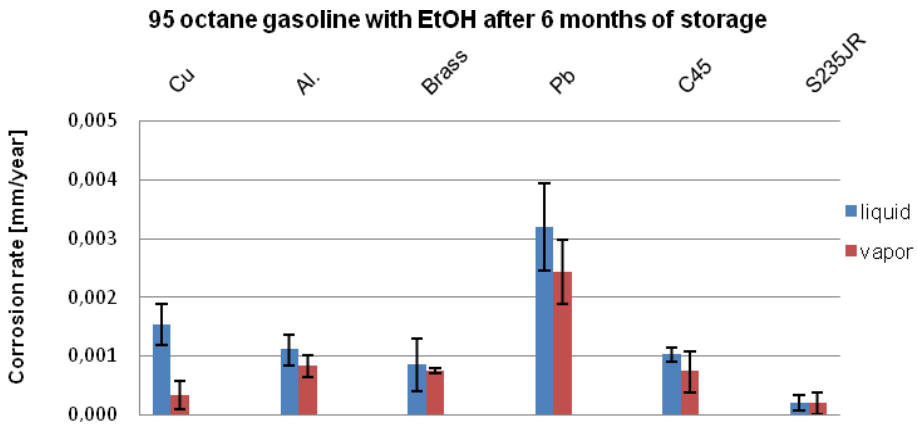


Figure 4. Linear corrosion rate for the test metals and steel, obtained for 95 octane gasoline after 6 months of storage

| Corrosion resistance group | Symbol | Corrosion resistance grade | V_p [mm/year] |
|----------------------------|--------|----------------------------|-----------------|
| Entirely resistant | I | 1 | > 0.0001 |
| | | 2 | 0.001- 0.005 |
| Highly resistant | II | 3 | 0.005 - 0.01 |
| | | 4 | 0.01 - 0.05 |
| Resistant | III | 5 | 0.05 - 0.1 |
| | | 6 | 0.1 - 0.5 |
| With reduced resistance | IV | 7 | 0.5 -1.0 |
| | | 8 | 1.0 - 5.0 |
| With low resistance | V | 9 | 5.0 - 10.0 |
| | | 10 | > 10.0 |
| Non-resistant | VI | | |

Table 1. Corrosion resistance groups

Figure 5 shows the appearance of the plates after the tests. Only the copper plate was slightly discolored after being immersed in gasoline. Its discoloration was uniform and present all over the surface.

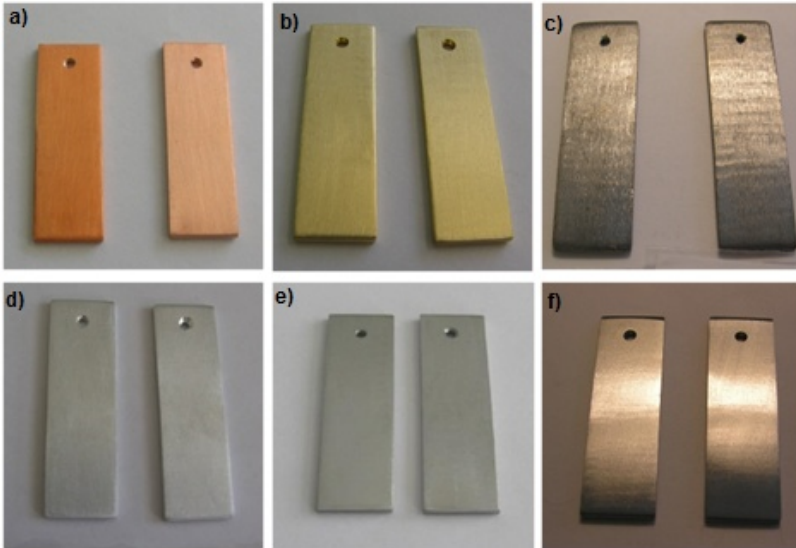


Figure 5. Appearance of samples after corrosion tests for 95 octane gasoline after 6 months of storage a) copper, b) brass c) lead, d) aluminum, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

A similar phenomenon was observed for the same gasoline after 12 months of storage: exposure did not cause any significant changes in the test materials. Here again, the highest corrosion rate was observed for lead, although it was slightly lower, compared with that for gasoline after 6 months of storage (Figure 6).

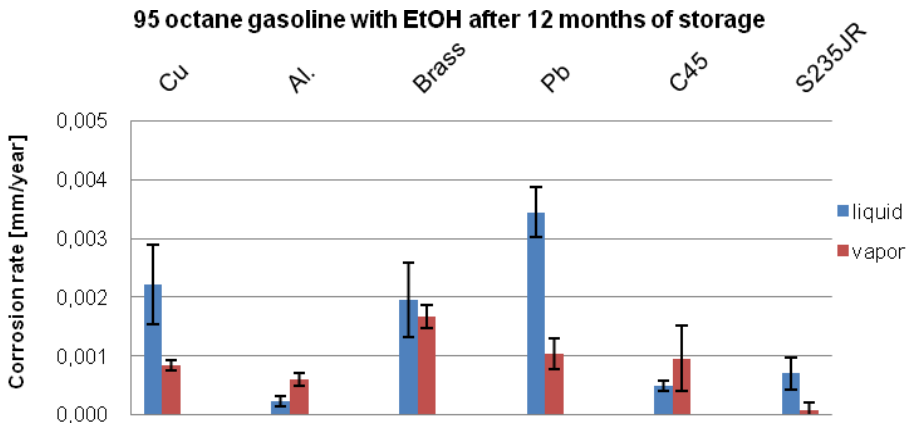


Figure 6. Linear corrosion rate for the test metals and steel, obtained for 95 octane gasoline after 12 months of storage

Interestingly enough, the calculated corrosion rate in the case of aluminum appeared to be much lower than that for gasoline after 6 months of storage. This is probably due to the formation, on the surface of aluminum, of a passive film (the metal is capable of self-passivation). This is connected with the presence of a thin film of oxygen or other compounds on the metal surface. The film is a specific barrier to the environment. Hence, passivation is accompanied by a decrease in the rate of degradation of the substrate. In the case of copper, brass, and the S235JR steel, corrosion rates after 12 months were roughly twice as high, compared with the tests for gasoline after 6 months of storage. On the other hand, one must bear in mind that the results are burdened with a rather serious error, which may be connected both with the fact that the plates were not uniform, and with the complexity of the processes leading to corrosiveness.

The above results were confirmed also by observation of the plates after exposure in the test fuel and its vapors. No changes were visible to the naked eye either on the plates exposed to the liquid gasoline or to its vapors. All of the test materials after exposure in a gasoline containing bioethanol after 12 months of storage were rated as materials with corrosion resistance grade 2.

4.2. Corrosive effect of 98 octane gasoline containing ETBE

For 98 octane gasoline containing ETBE after 6 months of storage, the highest corrosion rate was recorded for lead (Figure 7). Interestingly enough, in this case, a higher corrosion rate was noted for the plate exposed to the gasoline vapors. The lowest corrosion rate after exposure in gasoline was recorded for brass. For the other metals and steels, the rates were comparable. One should bear in mind that the ranges of linear corrosion rate for all of the test materials were rather not large, indicating their good corrosion resistance in a given environment (corrosion resistance grades 1-2).

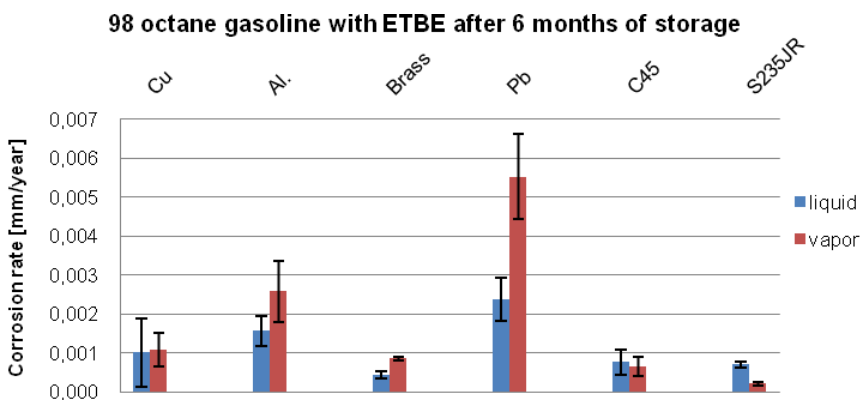


Figure 7. Linear corrosion rate for the test metals and steel, obtained for 98 octane gasoline after 6 months of storage

No significant changes were noted by observation of the plate surfaces, their condition after the test was similar to that before the test. The appearance of the plates after the tests for gasoline after 6 months of storage is shown in Figure 8.

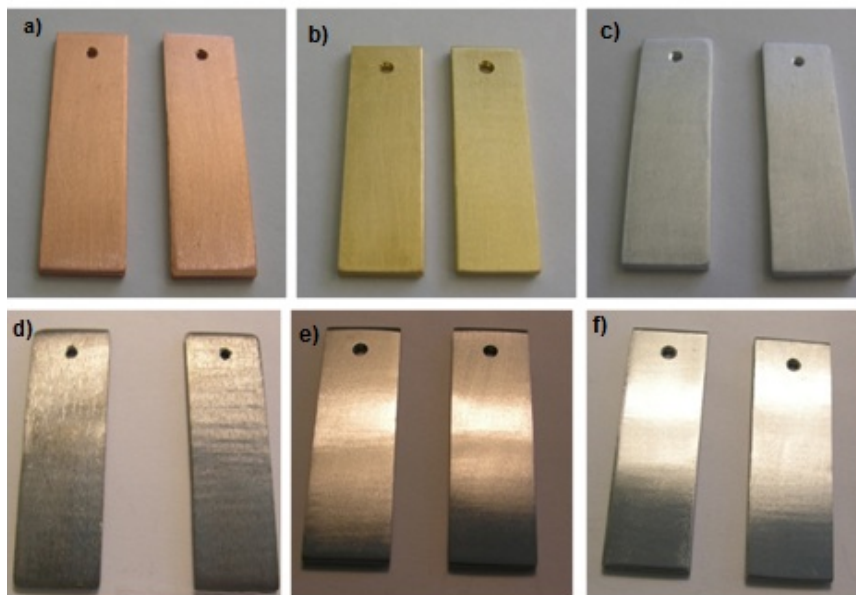


Figure 8. Appearance of samples after corrosion tests for 98 octane gasoline after 6 months of storage a) copper, b) brass c) aluminum, d) lead, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

Tests for 98 gasoline containing ETBE indicate that, after 12 months of storage, corrosion rates were lower (for aluminum, lead, C45 steel and S235JR steel) or remained at a similar level (copper, C45 steel and S235JR steel), which is a desirable phenomenon (Figure 9).

In the case of brass plates immersed in gasoline, corrosion rates after 12 months and after 6 months of storage were similar. In the case of brass, a difference was noted for exposure to vapors – corrosion rate was 3 times as high after 12 months of storage. The calculated corrosion rates for all the metals and alloys were very low, indicating that the test materials demonstrate good resistance. A decrease in corrosion rates after 12 months may be connected with changes in the fuel taking place during storage, which promote passivation of metal surfaces (formation of thin film of metal oxides or organic salts).

No changes were observed on the test plate surfaces for gasoline after 12 months of storage (Figure 10).

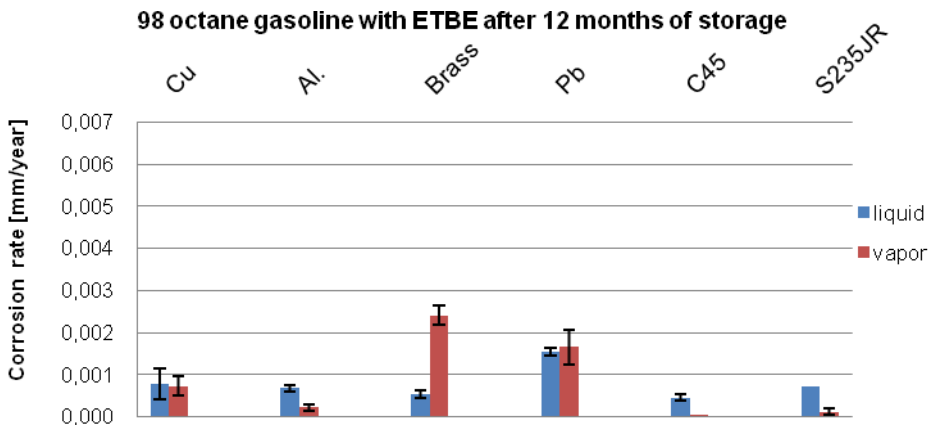


Figure 9. Linear corrosion rate for the test metals and steel, obtained for 98 octane gasoline after 12 months of storage

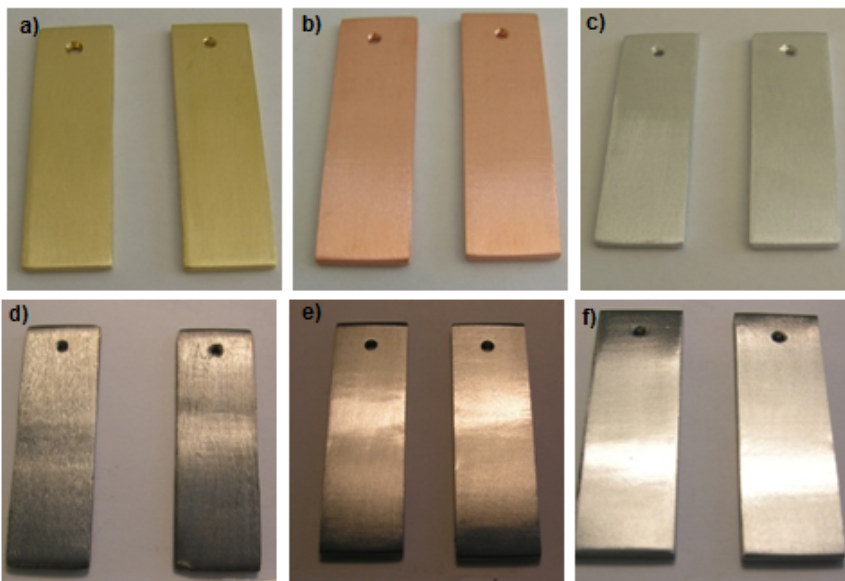


Figure 10. Appearance of samples after corrosion tests for 98 octane gasoline after 12 months of storage a) copper, b) brass c) aluminum, d) lead, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

4.3. Corrosive effect of diesel fuel containing up to 7% FAME

For lead samples after exposure in the diesel fuel containing up to 7% FAME, corrosion rate was very high after just 6 months of storage (Figure 11).

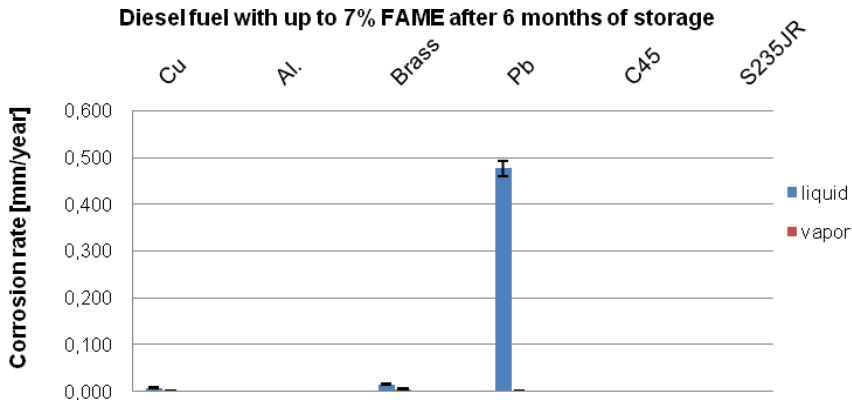


Figure 11. Linear corrosion rate for test samples of metals and steel, obtained for a diesel fuel containing up to 7% FAME after 6 months of storage

Corrosion rate for lead was more than 33 times as high as that for brass. According to the data shown in Table 1, lead may be classified as a material with corrosion resistance grade 7 (out of 10 grades). The other test metals and steels showed better corrosion resistance: copper and brass were classified as materials with corrosion resistance grade 4, aluminum, C45 steel and S235JR steel – as materials with corrosion resistance grade 2.

For a better illustration of their corrosion rates, Figure 12 shows the test results obtained for the test materials with the exception of lead.

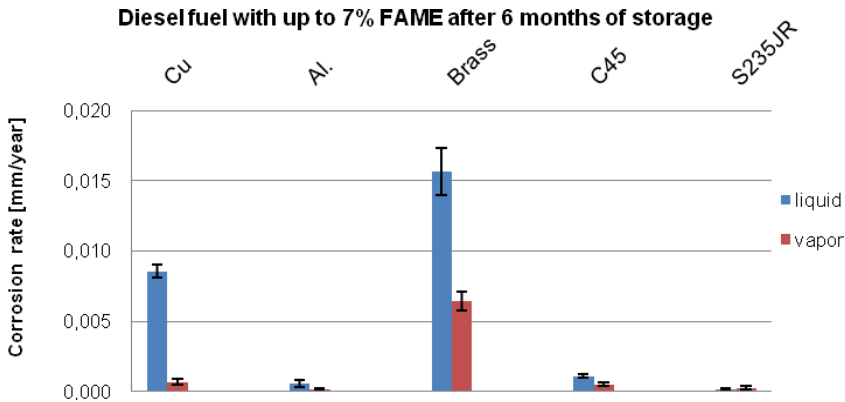


Figure 12. Linear corrosion rate for test samples of metals and steel, obtained for a diesel fuel containing up to 7% FAME after 6 months of storage

Among these test materials, the highest corrosion rate was observed for brass, the lowest was observed for the S235JR steel.

The appearance of the samples after subjecting them to the corrosive effect tests is shown in Figure 13. Significant changes were observed in the case of lead, following its direct exposure to diesel fuel (Figure 13 d)), as confirmed by the calculated corrosion rates. The lead plate is coated with corrosion products. No changes were detected in the lead plate after exposure to the fuel vapors. The copper and brass plates showed discoloration after exposure in the test fuel.

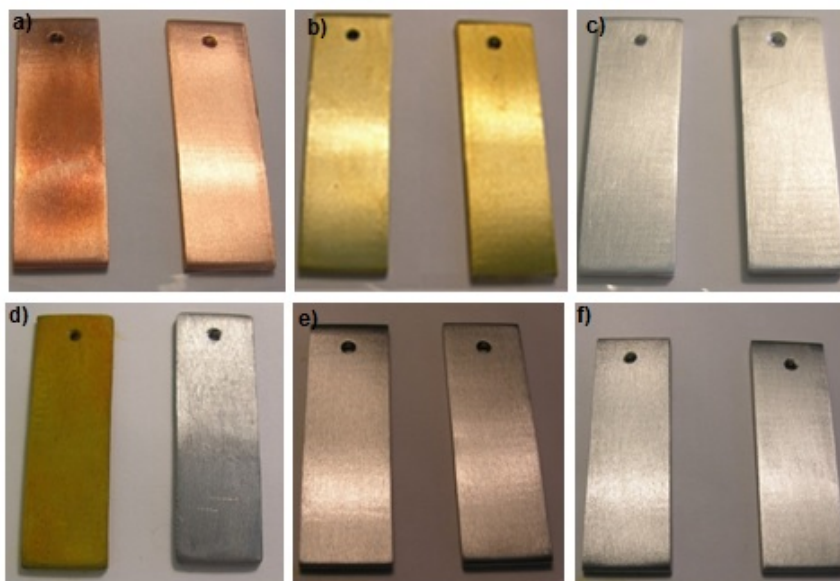


Figure 13. Appearance of samples after corrosion tests for diesel fuel containing up to 7% FAME after 6 months of storage: a) copper, b) brass c) aluminum, d) lead, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: – after exposure in vapors)

In corrosive effect tests after storing diesel fuel for 12 months, lead appeared to be the material with the highest susceptibility to corrosion. The calculated linear corrosion rate for lead was approx. 0.450 mm/year, which is slightly lower than that obtained after exposure in diesel fuel after 6 months of storage. In the case of copper and brass, corrosion rate was much reduced (Figure 14).

Corrosion rates for aluminum, C45 steel and S235JR steel were comparable and very low, indicating their good resistance to the effect of diesel fuel as early as in the initial period of its storage.

Figure 15 shows the appearance of copper, brass, and aluminum plates after exposure in commercial diesel fuel after 12 months of storage. Macroscopic examination of the plates indicates no corrosion changes on their surface.

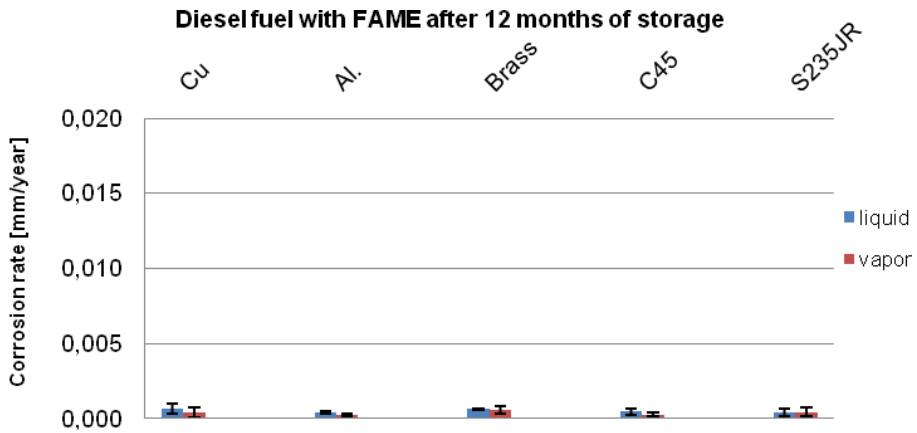


Figure 14. Linear corrosion rate for test samples of metals and steel, obtained for a diesel fuel containing up to 7% FAME after 6 months of storage

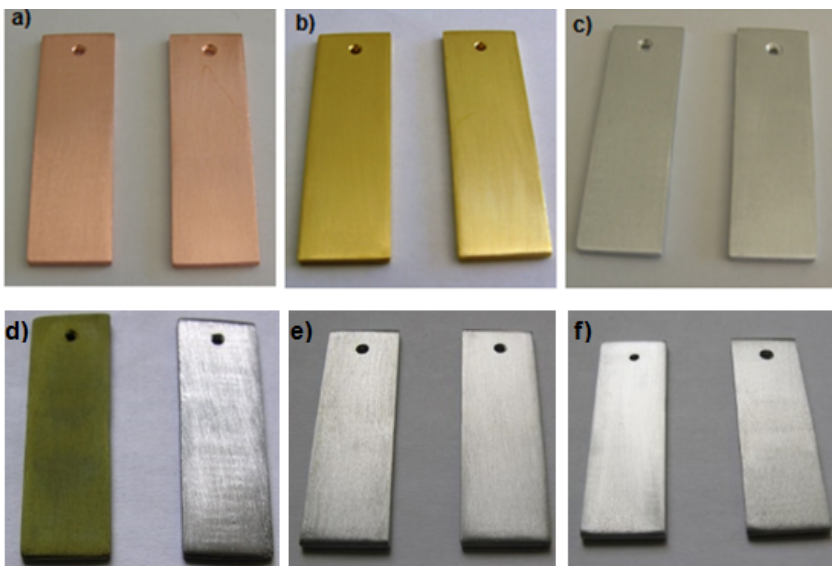


Figure 15. Appearance of samples after corrosion tests for diesel fuel containing up to 7% FAME after 6 months of storage: a) copper, b) brass c) aluminum d) lead, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

4.4. Corrosive effect of diesel fuel containing no FAME

The same kind of tests were carried out for a diesel fuel containing no FAME. Also in this case, the highest susceptibility to corrosion in a fuel stored for 6 months was found for lead (linear

corrosion rate of about 0.170 mm/year) (Figure 16). Such rate was much higher, compared with the other test metals and steels. The second highest corrosion rate was recorded for brass; moreover, corrosion rate was higher for the brass samples immersed in the liquid fuel, compared with those obtained for the plates exposed to vapors.

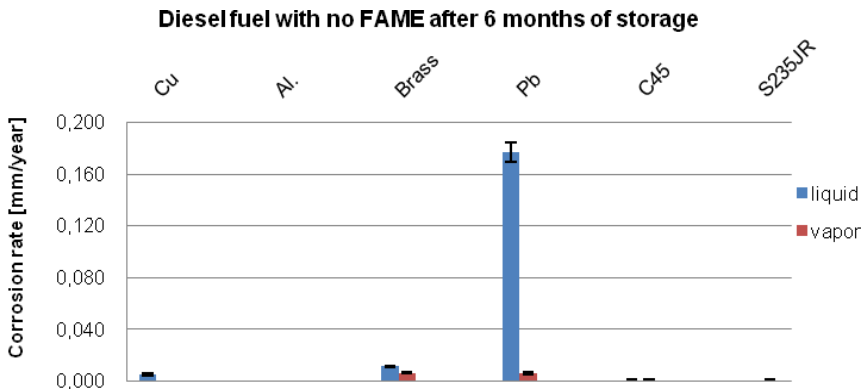


Figure 16. Linear corrosion rate for the test metals and steels, obtained for diesel fuel containing ETBE after 6 months of storage

Same as in the case of the previous diesel fuel, high corrosion resistance was observed for the aluminum and the steel samples (Figure 17).

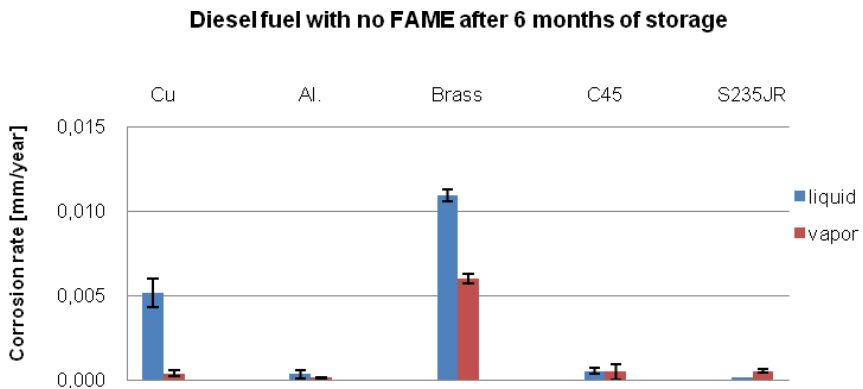


Figure 17. Linear corrosion rate for copper, aluminum and brass after exposure in diesel fuel with no FAME after 6 months of storage

Figure 18 shows the appearance of the plates after immersion tests for diesel fuel, after 6 months of storage.

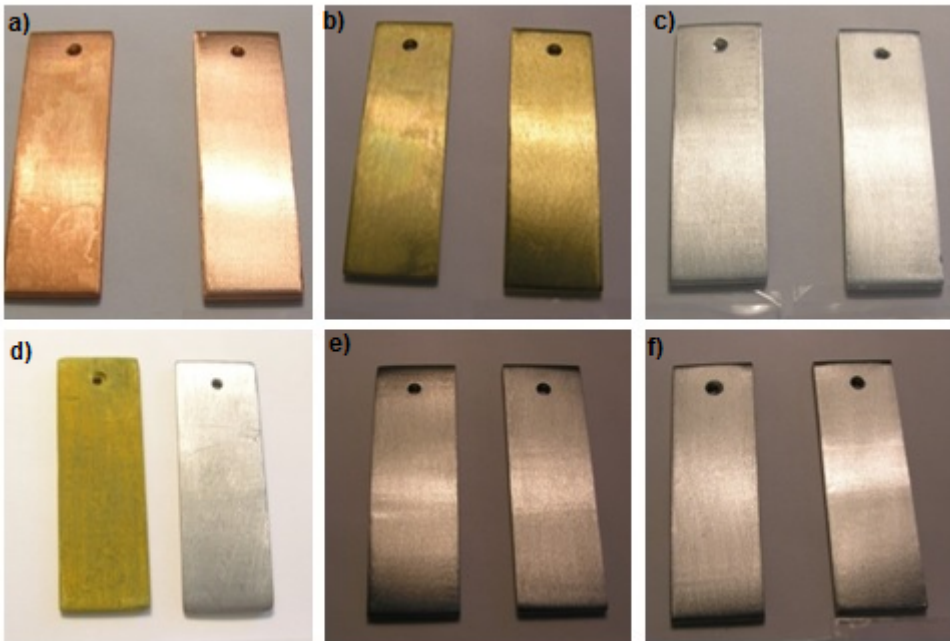


Figure 18. Appearance of samples after corrosion tests for a diesel fuel containing no FAME after 6 months of storage: a) copper, b) brass c) aluminum, d) lead, e) C45 steel and f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

Changes were detected in the appearance of the plate surfaces for copper, brass, and lead which were exposed to the test fuel. Such changes were not observed in the case of plates after their exposure to the effect of vapors.

After storing the diesel fuel with no FAME for 12 months, the highest corrosion rate was recorded for lead (0.165 mm/year). The other test metals and steels showed high corrosion resistance (grade 2) (Table 1), and linear corrosion rate did not exceed 0.001 mm/year (Figure 19).

The appearance of the test samples after corrosion tests for a diesel fuel collected after 12 months of storage is illustrated in Figure 20. The surface of the copper plate after direct exposure to the fuel had not changed, which was the case for diesel fuel after 6 months of storage. This is confirmed by the value of linear corrosion rate, which is 4 times as low for the tests in the fuel after 1 year of storage.

Changes in the appearance of the plate surfaces were detected only for lead, which was exposed to the diesel fuel.

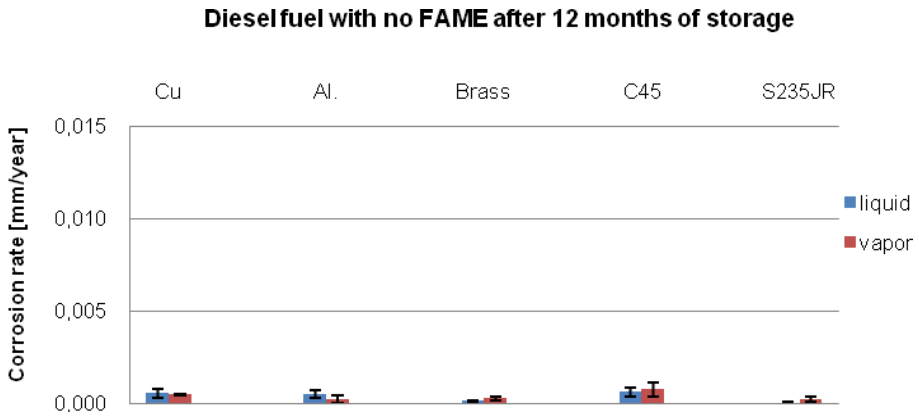


Figure 19. Linear corrosion rate for copper, aluminum, brass, C45 and S235JR steel after exposure in diesel fuel with no FAME after 12 months of storage

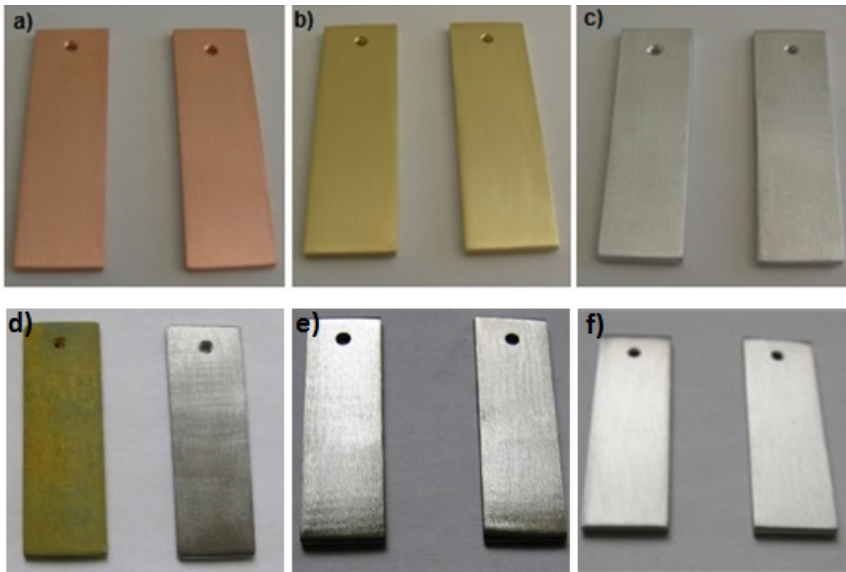


Figure 20. Appearance of samples after corrosion tests for a diesel fuel containing no FAME after 12 months of storage: a) copper b) brass c) aluminum d) lead e) C45 steel f) S235JR steel (left: sample exposed to liquid, right: sample exposed to vapors)

5. Conclusion

The present studies indicate that the test samples of gasolines showed a lower corrosive effect on the materials, selected for the corrosion tests, compared with diesel fuels. Regardless of the

type of fuel, the highest rate of corrosion among the test samples of steel and other materials was observed for lead, both after 6 and after 12 months of storage. In the case of diesel fuels after 6 months of storage, a more pronounced effect on degradation of the test lead sample was observed for diesel fuel with FAME. Corrosion rate for lead in the diesel fuel with FAME was 3.5 times as high as that for the diesel fuel without FAME. For the other metals and alloys, tested in diesel fuel with FAME, corrosion rate was also higher, compared with the oil without the bio-component; this confirms literature reports relating to the adverse effect of the bio-component on the durability of structural materials. A macroscopic examination of the condition of the plate surfaces, tested in diesel fuels, indicated changes in the surface of copper, brass, and lead samples. For gasolines, the highest weight losses were recorded, again, for lead; in the case of gasoline with ETBE, higher losses were observed for the plates exposed to the gasoline vapors, compared with those directly immersed in the fuel. This may be attributed to the different composition and higher vapor pressure of the gasoline with ETBE. Compatibility with the test fuel samples was the highest in the case of steel and aluminum. Considering the duration of fuel storage time, corrosion rate was reduced for both test samples of diesel fuel after 12 months of storage, which is a beneficial phenomenon. On the other hand, the plates were exposed to the fuel for a rather short duration (approx. 17 days). In the aspect of the fuel blends' complexity and their storage for a relatively short period of time, the aforementioned tests ought to have been carried out in fuels, exposed to storage for even longer durations. It seems that it would be beneficial to test the corrosiveness of the test fuel samples also with the use of other methods, such as impedance spectroscopy, techniques enabling a microscopic examination of the surface condition and composition, as well as measuring the rate of the corrosion, initiated in the early phase of storage.

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