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# B20 Fuel Compatibility with Steels in Case of Fuel Contamination

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**Abstract:** This study evaluated the compatibility with steels for three B20 fuel samples blended from fossil diesel and used cooking oil methyl ester. One sample was untreated and its concentration of copper was analyzed as <1 ppm. Another sample was doped by adding Cu at a concentration of ≤2 ppm and the third sample by adding Cu at a concentration of ≤4 ppm. Steel samples (carbon steel, stainless steel and a special alloy) were then put into the fuel blends and stored at 50 °C for 692 h. After storing, the metal concentrations of the fuel blends were again analyzed, and signs of corrosion were evaluated visually. The aim of this study was to find out if the fuel already contaminated by copper will affect the corrosion of the chosen steel qualities. Additionally, fuel properties were measured for all three blend samples before the immersion of steels. Visual evaluation of the steels indicated that signs of corrosion were seen in all studied samples, but Cu doping did not increase the signs of corrosion notably. The results also showed that the copper content from 1 to 2 and 4 ppm reduced the oxidation stability and increased the acid number of the fuel samples.

**Keywords:** biodiesel; diesel fuel; fuel blending; metal contamination; corrosion of steels



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## 1. Introduction

Before achieving the green transition to 100% renewable energy, the transition period may be relieved by blending fossil fuels with sustainable renewable ones. One option for blending components lies in biodiesels, also called fatty acid methyl ester (FAME) fuels, which are mono alkyl esters made of vegetable oils or animal fats. FAME fuels have potential to replace fossil diesel fuel and promote the sustainability in many engine applications. The use of FAME fuels also reduces emissions of greenhouse gases (GHG), if their raw materials are used vegetable oils or nonedible wastewater-based microalgae, and the entire production process is sustainable [1]. When used in internal combustion engines, the combustion properties are quite similar to those of fossil diesel, and FAMEs do not require engine modifications [2].

Biodiesels usually produce fewer emissions of carbon monoxides, hydrocarbons and particulate matter than fossil diesel fuel [3]. Fuel blending results have shown that a relatively high content of biodiesel, 40 vol.%, leads to an optimum increase of brake thermal efficiency and decrease in NOx emissions [4].

Sustainably produced biodiesel is used at large quantities already today. To sustain this positive development, the fuel producers must still optimize the properties of these fuel options. Despite the good properties of biodiesels, using biodiesel has caused a number of practical problems in diesel engines. Among others, important issues to be considered are oxidation stability, chemical composition, ash formation in combustion and the compatibility with metallic structures. Many of the materials used in a diesel engine, especially in the fuel system, might not be compatible with biodiesel.

Most of the mentioned issues are related to the content of some metals in the fuel. Metals can end up in fuel in several ways. Large quantities of sustainable biodiesels are refined from nonedible plants. The elemental composition of seeds varies between different plant species [5] and can also depend on the soil quality in which the feedstock plants have grown [6]. Trace elements from the plant-derived oil can show in biodiesels [7] unless they are removed in the manufacturing process. Heavy metals can be transported from plants to fuel [8]. Trace elements, most of which are metals, can also end up in fuels as a result of fuel contamination. Additionally, metals may be found as a natural, intrinsic part of some lower-quality fossil fuels, which must be taken into account when looking at the blends of bio- and fossil diesels [9]. In biodiesels made of used cooking oils (UCOs), traces of metals may originate from packages. Nevertheless, according to the Cárdenas et al. study [10], for instance, the copper (Cu) contents in different used cooking oils are low, varying from 0.05 to 5 ppm. UCOs are usually pretreated before the biodiesel production process, and metals are removed with other solid impurities. However, metals can also dissolute to fuel from tanks or fuel systems. When in contact with steels, especially carbon steel, biodiesel or its blends may dissolve small traces of metals. In the Sirviö et al. study [11], it was found that a small amount of Cu was dissolved from carbon steel when a carbon steel bar was immersed in B20 fuel.

A fuel contaminated by metals can also threaten the oxidation stability of FAME. Especially high content of Cu seems to have a detrimental effect on the oxidation stability as the metals accelerate the fuel's oxidation [12–14]. A Kugelmeier et al. study [15] stated that metals have a catalytic effect on oxidation stability.

Biodiesels are less compatible with metallic structures and components than fossil diesel fuel. This has to be considered when biodiesels are in contact with the fuel system. The fuel system includes, e.g., fuel tanks, supply pumps and lines, fuel filters plus injection pumps and nozzles which are prone to possible corrosion caused by fuel. Also, the combustion products of biodiesel can affect the combustion chamber walls and valves, as well as the crank mechanism. Several types of steels are largely used in the components prone to these adverse effects [16,17].

The compatibility of steels in contact with biodiesel blends was studied by Kugelmeier et al. [15]. They used biodiesels made of soybean oil, beef tallow and swine lard and formed the blends of B7, B15 and B30 with fossil diesel. In these experiments, carbon steel, stainless steel and aluminum (Al) did not corrode. Cu instead corroded intensively, lost mass and consequently degraded the blends. Fazal et al. [18] found that metals corrode when they were immersed in palm biodiesel. They also stated that, of the studied metals, Cu was causing the highest corrosion rate.

Oni et al. [19] investigated corrosion behaviors of mild steel (MS), Al and Cu immersed in microalgae biodiesel and its blends. Of the studied metals, Cu was the most prone to corrode. They also found that neat biodiesel was more reactive with metals than its blends with fossil diesel fuel.

As seen above, several researchers have studied the material compatibility and corrosion effects of biodiesels. However, these phenomena have rarely been investigated with used cooking oil methyl esters (UCOMEs) and their blends. When assessing the overall compatibility of the fuels, storage and fueling infrastructure, additional knowledge of the stability and corrosivity of UCOMEs should be acquired. The present study increases the scientific knowledge about the UCOME blends for the manufacturers of engines and fuel systems.

The objective of the present study was to investigate the corrosion of carbon steel, stainless steel and a special alloy immersed in metal-doped biodiesel–diesel blends. B20 fuel was chosen to be studied instead of 100% biodiesel, because many engine manufacturers allow B20 fuel as drop-in fuel, while B100 is not generally allowed [20]. The aim of the study was to find out if the fuel, already contaminated by Cu, will affect the corrosion of the chosen steel qualities.

To make B20 fuel, UCOME readily treated with antioxidant and light fuel oil (LFO) were mixed on the volume basis. Three B20 fuel batches were prepared with three different concentrations of Cu (1 ppm, $\leq$2 ppm and $\leq$4 ppm). Steel samples were then put into the fuel blends and stored at 50 °C for more than 600 h. The temperature (of 50 °C) was chosen above the room temperature to accelerate the possible corrosion reactions. However, to make the sample handling convenient, the temperature was chosen not to exceed 50 °C. The Cu concentration was analyzed twice during the storing period to see if metals dissolve from steels to the fuel. Visual evaluations of samples were carried out five times during the immersion. The kinematic viscosity, density, distillation properties, oxidation stability and acid number were measured for the three batches of B20 fuel blends before steel immersion to see if the addition of Cu content from 1 to 2 and 4 ppm has an effect on the mentioned properties.

## 2. Materials and Methods

The experimental part of the present study was similar to the research by Sirviö et al. [11]. Three B20 fuel batches were prepared from fossil light fuel oil (80 vol.%) and used cooking oil methyl ester or UCOME (20 vol.%). Cu was added to the batches at concentrations of B20-1: 1 ppm, B20-2: ≤2 ppm and B20-3: ≤4 ppm. The metal additive used for doping was Conostan Cu Standard. The metal concentrations were checked by analyzing the samples B20-1, B20-2 and B20-3, being no more than 1 ppm, less than 2 ppm and less than 4 ppm, respectively.

One of the steels was carbon steel (CS; grade Imatra 550), the other stainless steel (SS; 1.4301/1.4307), and the third a special alloy steel called as MoC210M/25CrMo4+SH (CrMo). Ingredient certificates of the steels were available. The concentrations of metals originally found in the steels are listed in Table 1. The amount of Fe was above 70% according to the literature for all the steels [21].

**Table 1.** The concentration of the elements in the three steel types.

| | Carbon Steel | Stainless Steel | MoC210M/25CrMo4+SH |
|---|---|---|---|
| Cu (%) | 0.20 | 0.96 | 0.20 |
| Fe (%) | >70 | >70 | >70 |
| Mn (%) | 1.13 | 1.66 | 0.81 |
| Si (%) | 0.24 | 0.27 | 0.27 |
| V (%) | 0.06 | | 0.01 |
| Pb (%) | 0.0003 | | 0.0007 |
| C (%) | 0.13 | 0.023 | 0.27 |
| Cr (%) | 0.20 | 18.1 | 0.99 |
| Ni (%) | 0.15 | 8.01 | 0.19 |
| Mo (%) | 0.03 | 0.29 | 0.22 |

Fuel samples of 150 mL were taken, three from each batch, B20-1, B20-2 and B20-3. These samples were filled into borosilicate glass bottles. One round bar of each steel was immersed in one of each fuel sample, B20-1, B20-2 and B20-3, yielding altogether nine samples (Figure 1). The bars were 10 cm long and 2 cm in diameter. Half of the bar was immersed in the fuel blend liquid, and the other half was positioned in the air space above the blend in the glass bottle. The bottles were closed with polypropylene screw caps.

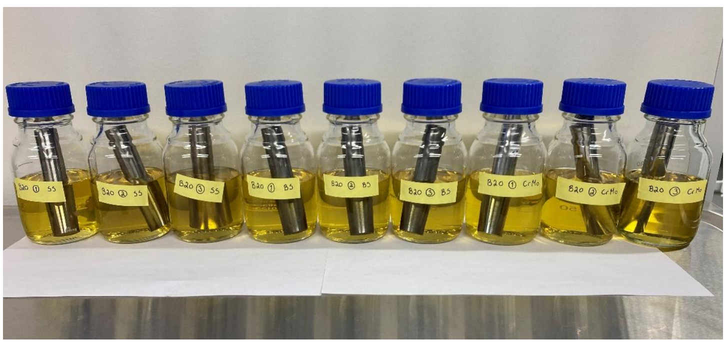

**Figure 1.** Steel bars immersed in fuel samples. Here, BS (black steel) is referring to CS (carbon steel).

The samples were stored in an oven at 50 °C for 692 h. The oven was a TIN-TN50 Phoenix Instrument, a device manufactured by Phoenix Instrument in Garbsen, Germany.

The Cu concentrations in the fuel blends were analyzed after 308 and 692 h of storing in the oven. The bottles were opened for sampling the fuel. The concentrations of Cu were measured with a PerkinElmer 7000 DV ICP-OES spectrometer, a device manufactured by PerkinElmer, Inc. in Waltham, MA, USA. The analysis procedure entailed diluting a weighed sample with kerosene in a weight ratio of 1:1 and injecting this solution into the spectrometer plasma. Calibration was performed with the known concentrations of the multielement standard which included Cu.

The method evaluates the presence and concentration of these elements by comparing the intensity of the light wavelength emissions with those from the known concentrations of the various elements. The analyses were performed by an in-house method based on Standards EN 14538 [22] and EN 14107 [23] and in accordance with the spectrometer manufacturer's advice.

The samples, fuels and metal bars, were also evaluated visually five times, after 140, 308, 500, 644 and 692 h.

Kinematic viscosity and density were measured with a Stabinger SVM 3000 rotational viscometer, which uses torque and speed measurements to determine viscosity. The device calculates the dynamic viscosity, η (in mPas), from the rotor speed.

The viscometer also has a density-measuring cell which utilizes the oscillating U-tube principle. The kinematic viscosity ($mm^2/s$), was calculated automatically based on these measurements [24] according to Standard ASTM D7042 [25]. The used device is manufactured by Anton Paar GmbH in Graz, Austria.

The oxidation stability index (OSI) was measured with a Metrohm 873 Biodiesel Rancimat instrument, a device manufactured by Metrohm Ltd. in Herisau Switzerland. This uses an accelerated method to determine the oxidation stability of biodiesel–diesel blends, blowing a stream of air through a heated fuel sample. Vaporizing compounds from the sample drift with air into water, and the consequential change in the water's conductivity is measured. The end point is achieved when the increase in conductivity is at its highest. This method is described in European Standard EN 15751 [26].

The distillation curve was measured with PAC's OptiPMD Micro distillation analyzer, a device manufactured by PAC LP in Houston, TX, USA. This uses a method for the determination of the distillation characteristics of light and middle distillates derived from petroleum and related products, as described in Standard EN ISO 3405 [27].

The acid number was analyzed with a Metrohm Titrando 888 titrator, a device manufactured by Metrohm AG in Herisau, Switzerland. This instrument utilizes the potentiometric titration method. The acid number is measured by a titrimetric method, whereby alkali neutralizes the free fatty acids present in the sample. The sample is diluted with isopropanol and titrated with potassium hydroxide (KOH). The results are expressed as mg KOH/g. The measurement was performed according to Standard EN 14104 [28].

The total ester content and fatty acid profile of neat UCOME were analyzed with a PerkinElmer Clarus 580 gas chromatograph. The method for analyzing total ester content is presented in European Standard EN 14103 [29], and methylheptadecanoate is used as an internal standard. The samples are diluted to heptane. The fatty acid profile is measured using an in-house method that is based on EN 14103.

All the presented results are arithmetic means of at least two replicants. The used methods for analyzing kinematic viscosity, density, oxidation stability and acid number are validated. The relative standard deviations for the measurements were: kinematic viscosity <1%; oxidation stability 4.5%; density <1%; acid number 7.9%; distillation 1.1%.

## 3. Results

Figure 2 presents the results of the Cu analysis. The results at time 0 h represent the blend batches before immersing the metal bars. As compared with the initial state, the concentration of Cu in the fuel increased in those B20-1 and B20-2 blends where CS was immersed. The increase in B20-1 CS was from 1 to 2 ppm, in B20-2 CS from 2 to 3 ppm and in B20-3 CS from 4 to 5 ppm. The concentration of Cu did not increase in the other samples, but it decreased in the B20-3 SS sample from 4 to 3 ppm. The doping itself did not have any impact on Cu dissolution from CS steel bars into the fuel, as the amount of Cu also increased in the sample which was not doped (B20-1 CS). The results of the B20-3 SS analysis showed slightly smaller concentrations (3 ppm) than the concentration before the steel immersion (≤4 ppm). All the measured changes were small and therefore within the measurement accuracy that was ensured by using the internal standard and a sample with a known concentration. A variation of 1 ppm in the results may still occur between the measurements series. However, the Cu content in all CS samples rose. The dissolution of Cu seems not to depend only on its concentration in the steel as the stainless steel contains more Cu (0.96%) than carbon steel (0.20%) (Table 1), yet Cu concentrations did not rise in fuel samples with stainless steel.

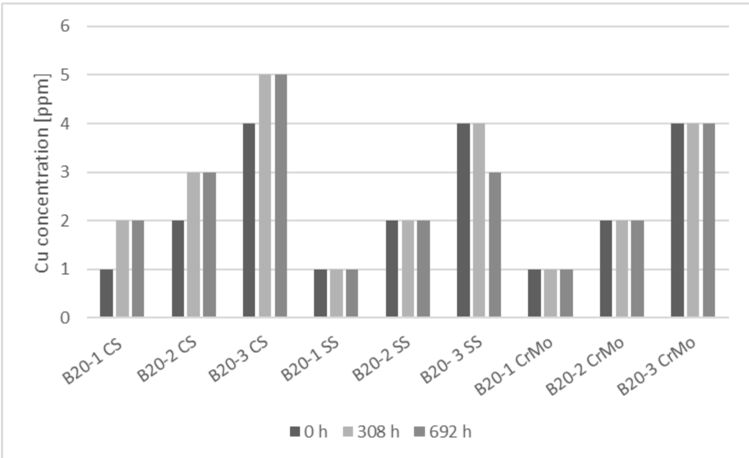


**Figure 2.** Results of Cu analysis of B20 fuels.

The samples, fuels and metal bars, were also evaluated visually after 140, 308, 500, 644 and 692 h. Notable signs of corrosion were not detected on the steel bars, only minor signs which were seen after 692 h. However, the color of the fuels containing 2 and 4 ppm of Cu changed from yellow to light yellow already after 140 h. The color change was clearer in later evaluations and was also seen after 692 h in B20- CS (which contained Cu less than 1 ppm). After 692 h, some sediment was seen in the bottom of the bottles which contained stainless steel and CrMo steel.

In addition to the immersion and corrosion tests, the present study also covered analyses of UCOME biodiesel and its blends with fossil diesel. These measurements were made before steel immersion. All the results of fuel analyses below are average values of at least two replicates. The total ester content and fatty acid profile of UCOME is given in Table 2.

**Table 2.** Total ester content and fatty acid profile of UCOME.

| Parameter | Method | UCOME | EN 14214 [30] |
|---|---|---|---|
| Total ester content (%) | EN 14103 | 96.9 ± 0.28 | min. 96.5 |
| Linoleic acid (%) | EN 14103 | 1.85 ± 0.003 | max. 12 |
| C14 (%) | EN 14103/in-house method | 0.93 ± 0.004 | |
| C16 (%) | EN 14103/in-house method | 26.2 ± 0.141 | |
| C18 (%) | EN 14103/in-house method | 7.28 ± 3.89 | |
| C18:1 (%) | EN 14103/in-house method | 35.3 ± 2.92 | |
| C18:2 n-6 (%) | EN 14103/in-house method | 23.8 ± 4.34 | |
| C20:2 n-6 (%) | EN 14103/in-house method | 0.1 ± 1.80 | |
| C22 (%) | EN 14103/in-house method | 0.21 ± 3.66 | |

The density, kinematic viscosity and distillation results of the B20-1, B20-2 and B20-3 samples complied with the limits set for diesel fuel in Standard EN 590 (Table 3). Cu doping did not affect the kinematic viscosity and density of the fresh samples. The density of B20-1 was 816 $kg/m^3$ and that of B20-2 and B20-3 was 815 $kg/m^3$. The kinematic viscosity of all three samples was 2.57 $mm^2/s$.

**Table 3.** Fuel properties measured for the B20 samples and UCOME used for blending. The LFO fulfilled the requirements of EN 590.

| Parameter | Method | B20-1 | B20-2 | B20-3 | UCOME | EN 590 [31] |
|---|---|---|---|---|---|---|
| OSI | EN 15751 | 22 | 1 | 1 | 5 | min. 20 (min. 8 *) |
| Density at 15 °C, $kg/m^3$ | ASTM D7042 | 816 | 815 | 815 | 878 | 800–845 (class 1) |
| Kinematic viscosity at 40 °C, $mm^2/s$ | ASTM D7042 | 2.57 | 2.57 | 2.57 | 4.29 | 1.50–4.00 (class 1) |
| Acid number (mg KOH/g) | EN 14104 | 0.12 | 0.13 | 0.15 | 0.24 | max. 0.50 * |
| Distillation, | EN ISO 3405 | | | | | |
| % recovered at 250 °C, vol. % | | 35 | 35 | 35 | 0 | max. 65 |
| % recovered at 350 °C, vol. % | | 100 | 100 | 100 | 99 | min. 85 |
| 95% recovered, °C | | 340 | 340 | 340 | 351 | 360 |

* EN 14214.

The acid number was compared to the limit set in the biodiesel standard EN 14214, and all the results of the B20 samples were clearly below the limit (max. 0.50 mgKOH/g). The acid number for B20-1 was 0.12, for B20-2 0.13 and for B20-3 0.15 mgKOH/g, showing a slightly increasing trend corresponding to increasing amount of Cu (Figure 3). However, it must be borne in mind that EN 14214 applies to 100% biodiesel, whereas the samples were B20 blends.

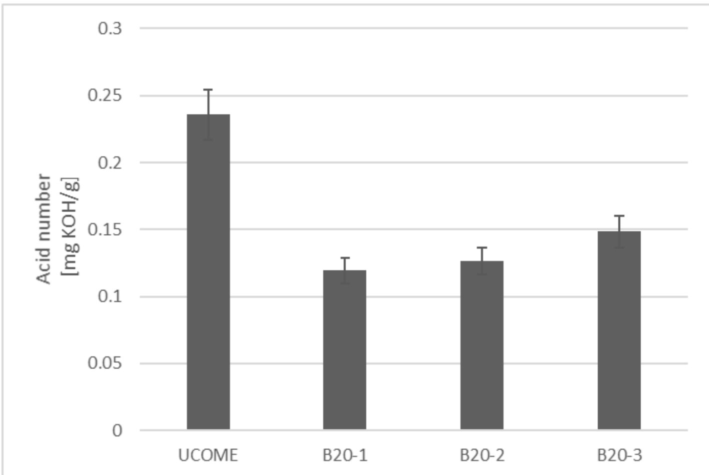


**Figure 3.** Acid number results of UCOME and the B20 samples.

The distillation results showed that the B20 fuels conformed to the limits set for diesel fuel distillation in Standard EN 590. This stipulates that a maximum of 65 vol.% has to be recovered at 250 °C, a minimum of 85 vol.% at 350 °C and at least 95 vol.% at 360 °C. For B20-1, B20-2 and B20-3, the recovery at 250 °C was approximately 35 vol.%. At 350 °C, 100 vol % was recovered.

A pronounced reduction in OSI was observed immediately after preparing the Cu-doped samples of 2 ppm and 4 ppm. The B20-1 sample, containing Cu at a concentration of less than 1 ppm, had an OSI result of 22 h. The samples B20-2 ($\leq$2 ppm of Cu) and B20-3 ($\leq$4 ppm of Cu) both showed results of 1 h, well below EN 590's minimum OSI value of 20 h. Furthermore, although the increment in metal content from 1 to 2 ppm was enough to weaken oxidation stability from 22 h to 1 h, the increase from 2 to 4 ppm did not cause any further deterioration in OSI.

## 4. Discussion

Fazal et al. [18] stated that neat biodiesel is corrosive when it is in contact with metals. They also stated that the corrosion rate is higher in contact with Cu than with other metals.

Oni et al. [19] studied corrosion behaviors of mild steel (MS), Al and Cu. According to them, neat biodiesel was more reactive with metals than its blends. The same statement was also made as in the study [18]: Cu was the most prone to corrode when it was immersed in biodiesel.

The study of Kugelmeier et al. [15] showed that biodiesel–diesel blends of B7, B15 and B30 did not cause corrosion in carbon and stainless steels, neither did aluminum corrode during the tests.

The corrosive effect of added Cu on steels was not clearly seen in our study. Nevertheless, the Cu content of all the blends increased in the case of the carbon steel, and the color of the B20 fuel changed.

These results also showed that even low concentrations of Cu—from 2 to 4 ppm—can notably cause a significant deterioration in the fuel quality. Doping with Cu did not have any effect on the kinematic viscosity, nor the density of the fresh samples. However, the addition of Cu had a major effect on fuel quality in terms of oxidation stability of the fresh B20 samples, with the OSI result decreasing from 22 h to 1 h. This is outside EN 590's OSI limit.

Acidity may restrict the uptake in the market of alternative fuels, especially biodiesels. It seems that the increased content of Cu in the B20-2 and B20-3 fuel samples slightly raised their acid numbers, but these were still well within the requirement for 100% biodiesel set in EN 14214 with <0.50 mg KOH/g.

The obtained results show that Cu may have a deleterious catalytic effect on the oxidation stability, and even minor metallic contamination may cause serious damage to the B20 fuel quality. Metals at a certain concentration initiate or accelerate the oxidation reaction but are not consumed in the reaction. The same observation was also made by Jain and Sharma [12] and Yang [14]. Jain and Sharma in particular showed that the higher the metal contents, the lower the oxidation stability. However, they concluded that metal concentrations higher than 2 ppm did not lead to further reductions of OSI. The present study supports that finding, but more detailed chemical analysis would be required to approve this statement. Kugelmeier et al. [15] studied corrosion behaviors of metallic materials in contact with biodiesel–diesel fuel blends. The authors found that the corrosion rate of Cu was higher than that of other studied materials. This was also shown by Fazal et al. [18]. At the same time, Kugelmeier et al. [15] found relatively low OSI values, notably less than 30 min for biodiesel blends in contact with Cu. In the present study, it is presumed that Cu had an effect on the marked reduction of oxidation stability, while it affected only one out of the three tested steel qualities.

The knowledge of biodiesel's corrosive effect on metals provides an opportunity to study antioxidants' effect on biodiesel stability in more detail. Serqueira et al. [32] studied the efficiency of corrosion inhibition of antioxidants for carbon steel and Cu. The main findings were that treating biodiesel with antioxidants forms protective layers of carbonaceous solids over metals, and propyl gallate increases the oxidation stability of residual cooking oil biodiesel exposed to carbon steel and Cu. On the other hand, copper oxide CuO, at a concentration of 100 mg/L, has also been used as an additive in biodiesel blends to improve diesel engine performance and cause a marginal emissions reduction [33]. Most probably, part of the enhancement of this additive in the combustion process is due to its oxygen content. Still, adding Cu to fuel may also have beneficial effects on its combustion properties.

## 5. Conclusions

The primary task of this study was to investigate the corrosion of carbon steel, stainless steel and a special alloy immersed in metal-doped biodiesel–diesel blends. UCOME, treated with antioxidant BHT, and LFO were mixed based on volume to make B20 fuel. Three B20 fuel batches were prepared with three different concentrations of Cu (1 ppm, ≤2 ppm and ≤4 ppm). Steel samples were then put into the fuel blends and stored at 50 °C for 692 h. The Cu analysis of fuels was conducted twice during the storing period to see if Cu will dissolute from steels to fuels. Visual evaluations of samples were carried out five times during the immersion. The kinematic viscosity, density, distillation properties, oxidation stability and acid number were measured for the three batches of B20 fuel blends to see if the addition of Cu content from 1 to 2 and 4 ppm will have an effect on the mentioned properties.

Based on the performed work, the following conclusions could be drawn:

- When the fuel is contaminated by Cu, it will not amplify the corrosion of the selected steels. The concentration of Cu increased slightly in all samples containing carbon steel, not only in those which were doped with metals.
- The Cu concentration rose in all three fuel blends when CS steel was present.
- The dissolution of Cu seems not to depend only on its concentration in the steel.
- Based on the visual evaluations, only minor signs of corrosion were seen in the studied steel qualities. However, the color of the fuel samples changed during the immersion.
- Even a minor metal contamination may cause serious damage to fuel quality in terms of the oxidative stability. An incremental increase in metal content from 1 to 2 ppm was sufficient to weaken oxidation stability from 22 h to 1 h. A further increment from 2 to 4 ppm did not additionally affect the results.
- The addition of Cu to the blend did not affect fuel density.
- The increased content of Cu slightly raised the acid numbers, but the results were still safely below the limits set for biodiesels, ranging from 0.12 to 0.15 mg KOH/g.

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