Corrosion Behaviour of Copper Alloys in RME

Affecting Parameters and Test of Alloys

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Corrosion behaviour of copper alloys in RME: affecting parameters and test of alloys
Korrosion av kopparlegeringar i RME: parameterstudie och legeringstester

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Looking back at the journey, from the start when I sat my foot in Stockholm that late Sunday evening a few hours before the start of my Master thesis to now the very end, I see that it was a journey I did not do alone and of that I am grateful.

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Stockholm, June 2015,

Martin Lindström
Abstract
Biodiesels are a hot topic and this includes the diesel replacement rapeseed methyl ester (RME). However, there is some concern because some metals may accelerate the degradation of RME. RME also causes corrosion of some metals. Copper, which accelerates degradation the most, can be found in engine system. Therefore, the aim of this Master’s thesis was to evaluate the corrosion of copper and different copper alloys in RME. In the experimental part, evaluation was made by analyzing water content, concentration of formic acid, acetic acid and propionic acid, metal concentrations in the fuel, oxidative stability (time until degradation with Rancimat method), macroscope of metallic surface and surface analysis by FTIR. The studied alloys included copper, brass, and aluminum alloyed with 3.2 weight % copper.

A stable period for copper corrosion was observed through the copper levels in the fuel. The stable period was confirmed to be related to the properties of the material. Most likely, a protective layer consisting of corrosion products was formed on the copper surface. Formic acid and free water addition increased corrosion and prevented a stable period. Salt formation was observed when decreasing copper and acid levels and was confirmed by FTIR analysis on exposed copper. Brass accelerated the aging of B100 fuel, but to a less extent than pure copper and indicated a stable period. Aluminum did not accelerate the aging of B100 fuel in this experiment.

The evaluation method proposed for copper involved measuring copper concentration as an indicator for when the corrosion has passed by the stable period. In these bench scale experiment which used 250 ml B100 and 40 cm² area copper, the threshold was 5 mg Cu/kg B100. This method may potentially also be used for copper alloys. The knowledge that there is a stable period can be used in field tests (engines) to understand the behaviour of corrosion of copper and to design a stable window. Important to remember is that copper corrosion behaviour can be drastically different in field tests (engines) compared to the lab scale experiments performed in this Master’s thesis. This because of different temperature, flow patterns, additional factors, etc.

The stable period of brass needs to be confirmed with longer aging times with B100 fuel. The additions of formic acid and free water to both brass and aluminum will need to be studied to see if they exhibit the same behaviour as copper. Other metals should be studied to see if the also exhibit a stable corrosion period similar to copper.
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**Abbreviations**

- CAPS: 3-(Cyclohexylamino)-1-Propanesulphonic acid
- CSTR: Continuous Stirred Tank Reactor
- FAME: Fatty Acid Methyl Ester
- PFR: Plug Flow Reactor
- RME: Rapeseed Methyl Ester
- SCFA: Short Chain Fatty Acid (includes formic acid, acetic acid and propionic acid)
- FTIR: Fourier Transform Infrared Spectroscopy
- IR: Infrared Light

**Glossary**

- Acid value: the mass in milligrams of KOH that is required to neutralize one gram of solution
- Alkali: a base
- B100: 100 % RME
- Biodiesel: fossil diesel replacement produced from renewable biomass
- Brazing: joining whereby metal is heated and put between joints by capillary action
- Elastomers: a polymer with viscoelasticity
- Esters: has the functional group $R_1$-COO-$R_2$ derived from a carboxylic acid and an alcohol
- Ferrous alloys: alloys containing iron
- Fossil diesel: diesel produced from crude oil
- Induction point: the point where secondary degradation products are detected
- Induction time: the time for secondary degradation products are detected
- Mono-unsaturated: has one double bond in the carbon chain
- Non-ferrous alloys: alloys not containing iron
- Poly-unsaturated: has at least two double bonds in the carbon chain
- Radical: an atom or a molecule that has unpaired valence electrons
- Soap: salt of a fatty acid
- Soldering: joining together by melting and putting a filler metal into the joint
1 Introduction

Biofuels are a hot topic today since they have the potential to both being more environmental friendly as a renewable resource and replacing oil and other non-renewable resources. Biofuels may therefore potentially make us independent of the world’s reserve of fossil resources. Biofuels are fuels derived from different sources of biomass as plants of different sorts, algae etc. Biodiesels are biofuels designed for replacement of fossil diesels. Biodiesels also have the advantage that they can be used in the existing infrastructure for fossil diesel. They have relatively similar properties compared to diesel, for example viscosity, and can therefore be used in conventional compression ignition engines with small or no modifications (Çelikten, Koca and Arslan 2010).

The chemical composition of biodiesels differs depending on the biomass source. Often it is produced from a vegetable oil source that is abundant in the production region. These vegetable oils are mixtures with varying composition, among these differences are the fraction of mono-unsaturated and poly-unsaturated carbon chains. In the United States and Europe rapeseed is one of the main sources used giving the biodiesel product rapeseed methyl ester, RME (Lang, et al. 2001). A picture of rapeseed can be seen in Figure 1 below.

![Rapeseed blooming](image)

**Figure 1. Rapeseed blooming (Bamford 2013).**

Rapeseed contains mainly mono-unsaturated carbon chains, a moderate amount of poly-unsaturated and a very small saturated fraction (Lang, et al. 2001). This large fraction of unsaturated carbon chains makes the fuel prone to oxidizing and therefore degrading. This process has been observed to be accelerated in contact with metals and especially copper (Jain and Sharma 2014) (Norouzi, et al. 2012). With respect to the metals, RME acts corrosive and the degradation products in the fuel will increase the corrosivity. This creates a vicious circle were the biodiesel degrades the metal and the copper degrades the fuel and makes the fuel even more corrosive.

This is a significant problem since the components in vehicles may contain copper in different alloys such as brass and aluminum alloys. The biofuel industry is aware of this problem and research activities in this area have been started. Copper alloys are presently used because of their advantageous properties, being easily joined by soldering or brazing, ductile, tough and corrosion resistant in aquatic environments.
2 Aim of study and scope

The aim of this Master’s thesis were to i) evaluate the corrosion of copper and different copper alloys in contact with RME, ii) to understand the mechanism of the corrosion behaviour and chemistry of RME fuel and iii) propose a method of evaluating the corrosion. Both a literature review and experimental testing were performed.

In the experimental part, the parameters studied were water, temperature and the concentration of formic acid. The evaluation were made by analyzing water content, concentration of formic acid, acetic acid and propionic acid, metal concentrations in the fuel, oxidative stability, macroscope of metallic surface and surface analysis by FTIR. The studied alloys included copper, brass and aluminum alloyed with 3.2 weight % copper.
3 Literature review

3.1 Production of biodiesel

Biodiesel can be produced from a number of different triglyceride sources such as vegetable oil or animal fats. In a chemical plant, these triglycerides react with an alcohol, producing new esters by a transesterification reaction. The alcohol used is often methanol, thus producing methyl esters (Gerpen 2005). FAME (Fatty Acid Methyl Esters) produced from renewable sources such as vegetable oil is called biodiesel as they can replace fossil diesel and is environmentally friendly, thus the prefix “bio”.

The transesterification is often performed at around 80°C and at this temperature a catalyst is needed, see reaction in Figure 2. The catalyst is often an alkali but it is also possible to use an acid catalyst or an enzyme. Alkali catalysts are mostly preferred since they give higher reaction rates than acid catalysts and enzymatic processes are considered too expensive (Gerpen 2005).

\[
\begin{align*}
\text{Triglyceride} & \quad \text{Methanol} & \quad \text{Mixture of fatty esters} & \quad \text{Glycerin} \\
\text{CH}_2 - \text{O} - \text{C} - \text{R}_1 & \quad \text{CH}_3 - \text{O} - \text{C} - \text{R}_1 & & \\
\text{CH} - \text{O} - \text{C} - \text{R}_2 + 3 \text{CH}_3\text{OH} & \quad \text{CH}_3 - \text{O} - \text{C} - \text{R}_2 + \text{CH} - \text{OH} \\
\text{CH}_2 - \text{O} - \text{C} - \text{R}_3 & \quad \text{CH}_3 - \text{O} - \text{C} - \text{R}_3
\end{align*}
\]

*Figure 2. Transesterification reaction of triglyceride and methanol with catalyst (Gerpen 2005).*

A schematic overview of a biodiesel process using an alkali catalyst is shown in Figure 3. The oil, methanol and catalyst are mixed in a chemical reactor. The outgoing stream from the reactor consists of methyl esters, glycerol and unreacted methanol.

The first separation step is done by settling or centrifugation since glycerol has higher density than methanol and methyl esters. Methyl ester is then distilled from methanol either in a vacuum flash process or falling film evaporator. Thereafter, acid is added in order to break up any soap that has formed to its respective free fatty acid and salt. The acid also neutralizes any remaining alkali catalyst. Water is used to wash the methyl esters from catalyst, salts, soap, methanol and free glycerol. The biodiesel is thereafter dried in a vacuum flash before being a finished product.

The glycerol also needs to be refined after the first separator. First, acid is added to break up soaps which are solved in the glycerol. The formed free fatty acids are not soluble and can be separated in a settler by their lower density. Methanol is thereafter separated from the glycerol by evaporation in for example a vacuum flash. The produced glycerol only has a purity grade of about 85% and is therefore sent to a glycerol refining process.
The type of chemical reactor used, will depend on the size of the plant’s production. Small producers often have batch reactors while large scale (>4 million liters/year) often use continuous. Preferred types of continuous reactors are continuous stirred tank reactor (CSTR) and plug flow reactors (PFR) (Gerpen 2005). An example of a continuous reactor can be seen below in Figure 4 (Fangrui and Milford 1999). This reactor also has an integrated first step separation process with an addition of acid and then settling of esters and glycerol. The alcohol is separated by evaporation, for warming, steam in a heat exchanger is used.
A study from Freedman, Pryde and Mounts (1984) shows how the degree of the reaction depends on methanol to oil ratio, see Figure 5. The study was performed with sunflower oil over an alkali catalyst at 60 °C. It was observed that the reaction reached equilibrium within 1 hour. At the same conditions but with a reaction temperature of 32 °C, equilibrium was not attained before 4 hours. As seen in Figure 5, a high alcohol to oil ratio is needed for high conversion equilibrium, with a 6:1 ratio needed for 98 % conversion. Lowering the ratio will consequently leave unreacted triglycerides, diglycerides and monoglycerides in the product stream.

![Figure 5. Product composition for transesterification depending on methanol to oil ratio (Freedman, Pryde and Mounts 1984).](image_url)

### 3.2 Composition of RME

Biodiesel from vegetable sources contain a large portion unsaturated fatty acid esters. The composition of fatty acid esters varies depending on the source but as previously mentioned RME has mainly mono-saturated carbon chains, with a moderate amount of poly-unsaturated and a very small saturated fraction (Lang, et al. 2001). The typical fraction saturated vs. unsaturated fats in RME can be seen below in Figure 6. RME contains fatty acid methyl esters (FAME) since the alcohol used in the production is methanol.
When comparing data from Lang, et al. (2001) and Norouzi, et al. (2012) it is clear that RME from different rapeseed sources and processes give different composition. The proportions of saturated, mono-unsaturated and poly-unsaturated does, however, seem to be essentially the same. RME supplied by Shell Global Solutions UK was analyzed by Norouzi, et al. (2012); the composition is shown below in Table 1.

### Table 1. Composition of commercial RME from Shell Global Solutions UK (Norouzi, et al. 2012).

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Relative content [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl laurate (12:0)</td>
<td>0.01</td>
</tr>
<tr>
<td>Methyl myristate (14:0)</td>
<td>0.10</td>
</tr>
<tr>
<td>Palminate (16:0)</td>
<td>4.35</td>
</tr>
<tr>
<td>Methyl stearate (18:0)</td>
<td>1.84</td>
</tr>
<tr>
<td>Methyl oleate (18:1)</td>
<td>68.83</td>
</tr>
<tr>
<td>Methyl linoeate (18:2)</td>
<td>19.55</td>
</tr>
<tr>
<td>Arachidic (20:0)</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Blending biodiesel with fossil diesel is common; the blend is then named after the content of biodiesel. For example B30 is a blend with 30 % RME and 70 % fossil diesel and B100 is pure RME. The biodiesel is RME if not otherwise stated in this Master’s thesis.

The solubility of water in B100 has previously been studied and is about 2000 ppm at 20 °C for B100. It increases with temperature and can increase with the degradation of the biodiesel (Bakhshandi 2014).

### 3.3 Instability of RME/biodiesels

A known fact is that biodiesels are less stable than fossil diesel. Factors and processes that can have negative effect are oxidation in the presence of air (oxygen), hydrolysis in the presence of water, thermal degradation, contamination with microorganisms etc. (Pullen and Saeed 2012). The one of most concern during long term storage is oxidation (Yaakob, et al. 2014). One reason is that some of the products formed by degradation give a more corrosive fuel. Examples of products are alcohols, organic hydroperoxides, asphaltenes, polymers, aldehydes and carboxylic acids (Pullen and Saeed 2012) (Yaakob, et al. 2014). Many external factors as temperature, contact with water and
microorganisms can affect a fuel and degrade it. The stability of a fuel is therefore essential when assessing it.

3.3.1 Oxidation mechanism of RME/biodiesels
The oxidation degradation is progressed by free radical chain reaction on mono-unsaturated and poly-unsaturated fatty acids (Pullen and Saeed 2012). The three main steps in free radical chain reaction are initiation, progression and termination. An overview can be seen in Figure 7 below. Polyunsaturated fatty acids, LH in Figure 7, are initiated by free radicals, X, to form fatty acyl radicals, L*. Then follows the radical chain reaction cycle in the propagations step between fatty acyl radical and the peroxyl radical. As seen in Figure 7 this cycle forms hydroperoxides when peroxyl radicals react with poly-unsaturated fatty acids to form fatty acyl radicals. Termination will occur when two free radicals react or an antioxidant react with a free radical as briefly described in section 3.3.1.5.

![Figure 7. Overview of oxidation degradation by free radical chain reaction (Fattah, et al. 2014).](image)

3.3.1.1 Initiation
Initiation is the first step and here free radicals are formed

\[ A - B \rightarrow A^* + B^* , \]

where \( A^* \) and \( B^* \) are free radicals. This can happen by primarily three different mechanisms in biodiesel; thermal dissociation of organic hydroperoxides, metal catalyzed decomposition of organic hydroperoxides and photo-oxidation (Pullen and Saeed 2012). It is believed that during storage the metal catalyzing radical reaction is the most relevant process, since trace metals always will be present (Pullen and Saeed 2012). Photo-oxidation is a process when UV-light initiates the oxidation and this occurs when the fuel is insufficiently shielded from UV-light sources, usually the sun. Thermal dissociation will normally be unlikely in storage at low temperatures but of concern if the temperature increases, see section 3.3.1.4 below.
Initiation by thermal dissociation of organic hydroperoxides and photo-oxidation of organic hydroperoxides reaction can be written

\[ ROOH \xrightarrow{\text{heat or UV light}} RO^* + OH^*, \]

where ROOH is organic hydroperoxide and * over species indicates a free radical. The initiation by metal catalyzed decomposition of organic hydroperoxides will take place by two-steps reaction

\[ ROOH + M^{2+} \rightarrow RO^* + OH^* + M^{3+}, \]

\[ ROOH + M^{3+} \rightarrow ROO^* + H^+ + M^{2+}, \]

where ROOH is an organic hydroperoxide, M is the active metal ion and * over species indicates formed free radical.

The radicals formed by reactions (2-4) are called initiator radicals because the initiate the chain reaction by

\[ RH + I^* \rightarrow R^* + IH, \]

where RH is a fatty acid, I* is a radical from reactions (2-4), R* is the formed fatty acyl radical and IH is a stable species. The fatty acyl radical, R*, proceeds to the propagation step. If the radical, I*, is a hydroxide, OH*, one of the formed product in reaction (5) will be water, \( H_2O \).

### 3.3.1.2 Propagation

The propagation step represents the chain reactions. The fatty acyl radical first react with oxygen which forms a fatty acid peroxide radical which further react with a new fatty acid. This creates a new organic hydroperoxide while giving a new fatty acid radical. The two connected reactions are

\[ R^* + O_2 \rightarrow ROO^*, \]

\[ ROO^* + RH \rightarrow ROOH + R^*, \]

where \( R^* \) is a fatty acyl radical, \( O_2 \) is molecular oxygen, \( ROO^* \) is an organic peroxy radical, \( RH \) is a fatty acid and \( ROOH \) is an organic hydroperoxide. These two reactions (6-7) can theoretically be repeated indefinitely.

### 3.3.1.3 Termination

If two fatty acid radicals encounter each other and react, the chain reactions (6-7) will be broken for those two radicals. This is called the termination step. The two radicals react with each other to form a stable non-radical species, this ends the cycle. This reactions is

\[ R^* + R^* \rightarrow R - R, \]
where R* is a fatty acyl radical and R-R the formed stable species or

\[ \text{ROO}^* + \text{ROO}^* \to \text{stable products}, \]

where ROO* is an organic hydroperoxide radical and stable product is different stable species.

### 3.3.1.4 Thermal dissociations dependence on temperature

At low temperature thermal dissociation as an initiation step in oxidation degradation is of low significance. However, increasing the temperature from normal room temperature will make thermal dissociation significant as depicted in Figure 8 (Jain and Sharma 2011). It shows that the acid value (AV) increases when storing biodiesel for 6 hours at different temperatures. Acid value increases when biodiesel is oxidized as described in the previous section 3.3.1.

![Figure 8. Acid values (AV) dependence on temperature when storing biodiesel for 6 hours (Jain and Sharma 2011).](image)

### 3.3.1.5 Antioxidants

Antioxidants are a wide concept and refer to the stopping or prevention of the radical chain reaction; antioxidants can by various means slow down oxidant degradation in biodiesel. They can be classified into free radical terminators, oxygen scavengers, and metal ion chelators. For example phenol antioxidants are free radical terminators; they terminate the radical reaction by donating hydrogen to the organic hydroperoxides (Fattah, et al. 2014).

Antioxidants are present in natural oil and can be present in the finished biodiesel product depending on production process. For example a distillation process will often result in little or no natural antioxidants in the biodiesel (Diwani, Rafie and Hawash 2009).

### 3.3.2 Temperature degradation of RME/biodiesels

Thermal degradation or decomposition of RME is mostly due to isomerization by a reaction termed “Diels Alder reaction” and occurs normally at 250-300 °C and above (Jakeria, Fazal and Haseeb 2014). The reaction can give source to asphaltenes that can clog filters in an engine system. This reaction is considered not to be of importance in this Master’s thesis experimental phase, since the used temperature is much lower (80 °C).
When the temperature is high enough, methylene-interrupted unsaturated olefin structures will begin to react and form more stable structures through isomerization (Figure 9).

![Figure 9. Example of methylene-interrupted unsaturated olefin structures. R is carbon chains and to the left is the double bond and to the right of it is a methylene.](image)

One Diels Alder reaction is when conjugated olefins from one fatty acid react with a mono olefin from another fatty acid to form a cyclohexene; a cyclohexane ring with the connected fatty acid chains of respective fatty acid (Figure 10).

![Figure 10. General Diels Alder reaction in RME, illustration redrawn from Jain and Sharma (2011).](image)

An example of a Diels Alder reaction in RME can be seen in Figure 11, where methyl lineolate (18:2) reacts and forms a dimer (example without a cyclohexane ring).

![Figure 11. Illustration of methyl lineolate (18:2) reacting in a Diels Alder reaction, modified figure from Yaakob, et al. (2014).](image)
3.3.3 Temperatures effect by the Arrhenius equation

The Arrhenius equation is an empirical relationship between temperature and chemical reaction rate. It describes the temperature dependence of the reaction rate.

\[ k = Ae^{-E_a/(RT)} \]

where \( k \) is the rate constant, \( A \) is the pre-exponential factor, \( E_a \) is the activation energy for the reaction, \( R \) is the ideal gas constant and \( T \) is the temperature.

The oxidative stability of biodiesel has been studied (Loyall, Zumbrägel and Kalcher 2011). Results show that at the temperature range 100-120 °C, a temperature increase of 10° gives twice as fast oxidative degradation of the biodiesel.

3.4 Reaction in RME/biodiesels with copper

There are many different kind of reactions possible between RME and copper, which make the system quite complex. Some reactions take place on the surface to the metal, some in the proximity and some in the bulk of the fluid. According to Fazal, Haseeb and Masjuki (2013), copper corrosion in acid environment advances through two reactions

\[ 2Cu (s) + \frac{1}{2}O_2(aq) + 2H^+ \rightarrow 2Cu^+ + H_2O \text{ (l)}, \]

\[ 2Cu^+ + \frac{1}{2}O_2(aq) + 2H^+ \rightarrow 2Cu^{2+} + H_2O \text{ (l)}. \]

The reactions (11-12) show that copper in an acidic environment with access to oxygen will corrode and form copper ions. The actual corrosion occurs in reaction (11) while reaction (12) shows further oxidation of the copper ion. Cu(I) is not stable in an aquatic environment so either it reacts further as in reaction (12) or is stabilized in a solid or a metal complex. Water is also produced as a by-product in the corrosion reactions (11-12).

Copper in contact with oxygen will in some conditions form a protective layer of corrosion products on the metal surface. In an aquatic solution, the more oxygen dissolved (more oxidative environment) the more oxidized products will be formed. If the pH is high enough a protective layer of Cu₂O or the more oxidized CuO will form. Cu₂O gives a semi-protective layer while CuO forms a protecting layer that prevents from further corrosion in an aquatic solution (Oliphant 2003). Other corrosion products are also formed in an aquatic environment which can act protectively.

Cu(II) can also give corrosion by (Fazal, Haseeb and Masjuki 2013)

\[ Cu^{2+} + Cu (s) \rightarrow 2 Cu^+. \]

By exposing copper to biodiesel and looking at the formed products at the surface some possible reactions are suggested. On the copper surface, reactions (14-22) below is suggested (Fazal, Haseeb and Masjuki 2013)
The reactions can be divided into three groups. Reactions (14-15) are formation of oxides, reactions (16-18) are formation of carbonates and reactions (19-22) are formation of hydroxides and carbonates. The reactions (14-22) can react independently and separately when exposing copper to biodiesel. The produced corrosion products forms different kind of greenish layers on the copper metal, this is widely known as patina. These can form a layer that fully or to some extent protect the copper metal. Some of the oxide products, Cu₂O and CuO, can dissolve in the fuel and react with free fatty acids forming fatty acid salts (Norouzi, et al. 2012)

\[
2 Cu (s) + \frac{1}{2} O_2(solv.) \rightarrow Cu_2O (s) ,
\]

\[
Cu_2O (s) + \frac{1}{2} O_2(solv.) \rightarrow CuO (s) ,
\]

\[
Cu^{2+} + 2 RCOO^- \rightarrow CuCO_3(s) + [R - R] (s) + CO (solv.) ,
\]

\[
Cu_2O (s) + 2 CO_2(solv.) + \frac{1}{2} O_2(solv.) \rightarrow 2 CuCO_3 (s) ,
\]

\[
CuO (s) + CO_2(solv.) \rightarrow CuCO_3 (s) ,
\]

\[
2 Cu (s) + H_2O (solv.) + CO_2 (solv.) + O_2(solv.) \rightarrow Cu(OH)_2 \cdot CuCO_3 (s) ,
\]

\[
2 Cu (s) + 2 H_2O (solv.) + O_2 (solv.) \rightarrow Cu(OH)_2 (s) ,
\]

\[
CuO (s) + H_2O (solv.) \rightarrow Cu(OH)_2 ,
\]

\[
2 Cu(OH)_2 (s) + CO_2(solv.) \rightarrow Cu(OH)_2 \cdot CuCO_3 (s) + H_2O (solv.) .
\]

"solv." denotes that the species are dissolved in the biodiesel phase.

Reactions (23-24) occur on the surface of the metal and therefore easily forms deposits on the metal surface.

As previously described, in section 3.3.1, metals can catalyze oxidation of RME/biodiesel. Of the metals common in motorized vehicles; copper gives the highest degradation (Fazal, Haseeb and Masjuki 2012). It has also been described that the copper oxides formed will react with the biodiesel (Norouzi, et al. 2012)

\[
2 RCOOH (solv.) + Cu_2O (s) \rightarrow 2 Cu(RCOO) (s) + H_2O (solv.) ,
\]

\[
4 RCOOH (solv.) + CuO (s) \rightarrow 2 Cu(RCOO)_2(s) + 2 H_2O (solv.) .
\]
The methyl esters, RCOOCH₃, react with copper oxides, CuO and forms organic hydroperoxides, RCOOH and HCOOH. This accelerates the oxidative degradation of the RME fuel as described in section 3.3.1.

A probable explanation to why copper gives higher degradation of biodiesel than aluminum, which is also common in motorized vehicles, is that aluminum oxide is more stable and copper oxide is a stronger oxidizer (Norouzi, et al. 2012). Reaction (25) for aluminum oxide is therefore not possible (Norouzi, et al. 2012). Reaction (25) also implies that any protective oxide layer on copper could be broken down, exposing the copper metal. Copper can therefore accelerate the degradation of the biofuel.

Copper surfaces exposed to biodiesels at room temperature for 200 h were analyzed, showing corrosion products as CuCO₃, CuCO₃·Cu(OH)₂, Cu(OH)₂·H₂O, Cu(OH)₂, CuO and Cu₂O in small amounts. However, after 2880 h the dominating product is solely CuCO₃ with only minor amount of the other products. (Fazal, Haseeb and Masjuki 2012). CuCO₃ is a common form of patina for copper and appears greenish for the eye in visible amounts. For a schematic overview of the formed layer see Figure 12.

<table>
<thead>
<tr>
<th>Metallic copper</th>
<th>Layer of corrosion products</th>
<th>Biodiesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>CuO</td>
<td>Fatty acid methyl esters (FAME)</td>
</tr>
<tr>
<td></td>
<td>CuO₂</td>
<td>Hydroperoxides</td>
</tr>
<tr>
<td></td>
<td>CuCO₃</td>
<td>Peroxyl radicals</td>
</tr>
<tr>
<td></td>
<td>CuCO₂·Cu(OH)₂</td>
<td>Carboxylic acids</td>
</tr>
<tr>
<td></td>
<td>Cu(OH)₂·H₂O</td>
<td>Other degradation products</td>
</tr>
<tr>
<td></td>
<td>Cu(OH)₂</td>
<td></td>
</tr>
</tbody>
</table>

Figure 12. Schematic representation of copper, corrosion layer and biodiesel.
3.5 Materials in a diesel engine system

In an ordinary car or truck there are many different materials used in the engine fuel system. In a diesel engine there are three main groups of materials that is in contact with the fuel; ferrous alloys, non-ferrous alloys and elastomers (Haseeb, et al. 2011). In Figure 13 below an overview of a generic diesel fuel engine system can be seen (Haseeb, et al. 2011).

As illustrated in the overview above, Figure 13, there are many different components in contact with the fuel. The typical materials used in components can be seen in Table 2 (Haseeb, et al. 2011).

![Figure 13. Overview of a generic diesel fuel engine system with exhaust, combustion and fuel feed systems (Haseeb, et al. 2011).](image)

Table 2. Normally used materials in components in contact with fuel in a diesel engine system (Haseeb, et al. 2011).

<table>
<thead>
<tr>
<th>Main part</th>
<th>Component</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel tank</td>
<td>Housing</td>
<td>Steel, plastic, paint, coating</td>
</tr>
<tr>
<td></td>
<td>Gasket</td>
<td>Elastomer, paper, cork, copper</td>
</tr>
<tr>
<td>Fuel feed pump</td>
<td></td>
<td>Aluminum alloy, iron based alloy, copper based alloy</td>
</tr>
<tr>
<td>Fuel lines</td>
<td>High pressure</td>
<td>Steel, plastic, paint, coating</td>
</tr>
<tr>
<td></td>
<td>Low pressure</td>
<td>Plastics, rubber</td>
</tr>
<tr>
<td>Fuel filter</td>
<td>Filter cartridge</td>
<td>Paper</td>
</tr>
<tr>
<td></td>
<td>Housing</td>
<td>Aluminum, plastic</td>
</tr>
<tr>
<td>Fuel pump</td>
<td></td>
<td>Aluminum alloy, iron based alloy, copper based alloy</td>
</tr>
<tr>
<td>Fuel injector</td>
<td></td>
<td>Stainless steel</td>
</tr>
<tr>
<td>Cylinder</td>
<td>Cylinder head</td>
<td>Gray cast iron, cast aluminums, forged aluminums</td>
</tr>
<tr>
<td></td>
<td>Cylinder barrels</td>
<td>Gray cast iron, steel, cast aluminum</td>
</tr>
<tr>
<td></td>
<td>Cylinder liner</td>
<td>Gray cast iron, aluminum</td>
</tr>
<tr>
<td></td>
<td>Valves</td>
<td>Steel casting</td>
</tr>
<tr>
<td>Piston assembly</td>
<td>Piston</td>
<td>Sand-cast aluminum, die-cast aluminum, forged aluminum</td>
</tr>
<tr>
<td></td>
<td>Piston pin</td>
<td>Steel</td>
</tr>
<tr>
<td></td>
<td>Piston ring</td>
<td>Special cast iron, steel</td>
</tr>
</tbody>
</table>
Field tests with fossil diesel and biodiesel showed different effect on different metals. Notably, in most cases the results showed higher corrosion and wear on copper with pure biodiesel from different sources (B100) in comparison to fossil fuel. In general, iron, lead and aluminum had less or equal wear for biodiesel in comparison to fossil fuel, when comparing results from several studies (Haseeb, et al. 2011).

Corrosion studies using biodiesel have given contradictory results as to whether the used biodiesel blend is more or less corrosive than fossil diesel on the studied metal. For example, one report recommended copper, different alloys with copper, lead, zinc and tin not to be used with biofuel in fuel systems; this since oxidation and corrosion is accelerated (Haseeb, et al. 2011). However, as previously discussed, lead had in generally less or equal wear for biodiesel compared to fossil fuel. Some studies however, showed higher wear of lead in biodiesel (Haseeb, et al. 2011). One explanation may be that the source of the biodiesel differs. Therefore, it is important to know the origin of the biodiesel. Metals and alloys used in the different studies may also differ in manufacturing process, chemical composition and microstructure which can affect the corrosion behaviour.

A review of commercially used elastomers show that many elastomers are not compatible with biodiesels. They are usually used in seals and hoses in the engine system. Many of these materials show swelling in contact with biodiesel, so much that it becomes a problem. Fully compatible elastomers are fluorocarbons, carbon-filled acetal, Hilfur, perfluoroelastomers, Chemraz, virgin and Teflon. Others like Viton, ethylene propylene, butyl, etc. exhibit some swelling and are considered as partially compatible. Not compatible are for example natural rubber, Nitrile and styrene-butadiene rubber (Haseeb, et al. 2011).

### 3.6 Corrosion and its types

The process when a metal chemically reacts with the surroundings, for achieving its lowest energy state possible, is called corrosion. The outcome is often destructive and the process itself is usually electrochemical (Sparr and Linder 2011). A short introduction to some corrosion types is presented in Table 3 but for a more thorough review the reader is referred to other sources as (Sparr and Linder 2011).

<table>
<thead>
<tr>
<th>Type of corrosion</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crevice corrosion</td>
<td>Localized corrosion within a crevice where the fluid has limited exchange with the bulk. This limited exchange creates after a time an aggressive environment.</td>
</tr>
</tbody>
</table>
Pitting corrosion  The effect of local loss of passivation and is promoted by slow bulk flow.

Under-deposit corrosion  This is corrosion under deposits on the metal surface. Either the deposit itself is aggressive or it acts as surface shielding and creates concentration cell corrosion.

Bimetallic corrosion  Also called galvanic corrosion and happens due to the difference in electrode potential when two metals are connected electrically in a conducting fluid.

Stress-corrosion cracking  The results from the combination of tensile stress, a susceptible material and a corrosive environment.

Corrosion fatigue  Altering stress creates cracking even though the stress is considerably lower than the yield strength. The cracking is accelerated because of corrosion.

The corrosion types common for copper and copper alloys are erosion corrosion, under-deposit corrosion, pitting corrosion, dezincification, bimetallic corrosion, stress-corrosion cracking and corrosion fatigue. For aluminum the most common corrosion types are pitting corrosion and erosion corrosion (Sparr and Linder 2011).

3.7 Previous studies

One previous study has been performed on B100 and its corrosion behaviour (Talus, Johansson, et al. 2014). From data obtained for corrosion on copper, it is indicated that copper concentration in B100 has a stable period as shown in Figure 14; the stable period seems to be around 24-48 h at 80 °C in open systems. Unexposed B100 (0 h) contains undetectable copper content (<0.1 ppm) which gives the graph below the look of a plateau. This may possibly be explained by the formation of a protective layer on the copper surface as described in section 3.4. However, only three data points were presented. Further studies are therefore of need in this system.

![Figure 14. Copper levels in aged B100 at different aging times. Done in open system at 80 °C (Talus, Johansson, et al. 2014).](image-url)
4 Methods and experiments

4.1 Analyzing methods

The experiments were evaluated by mainly six analyzing methods. The analyzed parameters was selected for their relevance. Water content changes with the aging of the B100 fuel, acids are formed during aging, oxidation stability can be affected by metal exposure, visual damage on the metal can occur, FTIR can identify chemical changes on the metal surfaces, and metal concentration in the B100 fuel changes during exposure and corrosion of metals.

The analyzing methods were chosen after consultation with corrosion experts at Swerea KIMAB. The water contents were analyzed by coulometric Karl Fischer titrations, acid content by ion chromatography, oxidation stability by the Rancimat method, visually by macroscope, surface analyses by FTIR, and metal concentration in fuel by ICP analysis. ICP analyses were performed by an external lab, Exova Materials Technology, the other analyses were done in-house at Swerea KIMAB AB as a part of the practical work within this thesis project. Coulometric Karl Fischer titration, ion chromatography, macroscope, the Rancimat method and FTIR are described below.

4.1.1 Karl Fischer titration

The method used for water content analysis in biodiesel in this Master’s thesis were coulometric Karl Fischer titrations. The original method uses methanolic solution of iodine together with sulfur dioxide and a basic buffer, the iodine is titrated into the solution. In a coulometric system, the iodine is directly and precisely generated in the electrolyte by electrochemical means. The alkylsulfite salt oxidizes to alkylsulfate salt and this reaction consumes water. When no water remains iodine will be in excess and the equivalence point is detected. The reactions is

\[ \text{H}_2\text{O} \text{solv.} + I_2 \text{solv.} + [RNH]SO_3CH_3 \text{solv.} + 2 RN \text{solv.} \rightarrow [RNH]SO_4CH_3 \text{solv.} + 2 [RNH]I \text{solv.} ,\]

and is principally the same today. "solv." : solved in a polar solvent as an alcohol or ether. Since the method has gone through development the actual reaction compounds differ, often with the use of a different alcohol to form the alkylsulfate salt. There are many variants which are used for different purposes as precision, kind of solutions analyzed and what range the water content is (756/831 KF Coulometer, Instructios for use 2003).

The titration system used was Metrohm 831 KF Coulometer and the setup can be seen in Figure 15. The autosampler was not used; instead the samples were manually injected. The solution which contains solvent, base and sulfite salt was Hydranal®-Coulomat AG-Oven.
4.1.2 Rancimat method

The oxidation stability of biodiesel and different blends can be analyzed with the Rancimat method. The measuring setup for the Rancimat method can be seen in Figure 16 (873 Biodiesel Rancimat, Manual 2007). A sample of the biodiesel is placed inside a glass tube which is in contact with a heating block. The sample is run through with a constant airflow at a specific temperature. If volatile compounds as formic acid have been formed, as a result from oxidation, they will be brought with the air stream (873 Biodiesel Rancimat, Manual 2007). See section 3.3.1 for description of oxidation in biodiesel. The air goes to a secondary vessel with distilled water. Organic acids products will increase the conductivity in the water thus creating a conductivity curve.

If the sample has any oxidation stability left it will show a constant conductivity. When the oxidative stability is gone, conductivity starts increasing. From the constant and increasing part of the conductivity curve, an induction point is calculated. The induction point is the breaking point between oxidation stability and instability i.e. when the conductivity curve goes from constant to increasing. The induction time is how long time the biodiesel has oxidation stability in the set conditions.
The used standard for biodiesel analysis was EN 157751 which specifies a temperature of 110 °C, sample amount of 7.5 g and air flow of 10 l/h.

4.1.3 Ion Chromatography
The SCFA (short chain fatty acids) propionic acid, acetate and formic acid were analyzed with ion chromatography. Such a system requires the acids in the biodiesels to be transferred to an aqueous phase, this is described in the next section.

Ion chromatography works principally by separating ions by their charge and size. The separation is done in a separation column. For example having positively charged materials in a column will retain negatively charged ions, anions. When a sample is pumped through the column, ionic species will be retained. Then by pumping through an eluent, the species will be released but different substances have specific retention time, and will be released from the column at different times. The conductivity of the outgoing liquid is measured and by calibrating the time different species exit the column, the area (voltage*time) can be related to the concentration.

4.1.3.1 Extraction of acids from biodiesel
The biodiesel cannot be analyzed directly in the ion chromatograph as previously mentioned. The acids will need to be transferred to a water phase. This can be done by extraction to a water phase and the used method is based on previous work (Strömberg and Sahlin 2012) and further developed on Swerea KIMAB (Talus and Ingelgård, Analysing chloride and organic acids in biofuels using ion chromatography 2015)

The biodiesel were weighted into a syringe to about 1.5 grams. 1 ml isooctane and 8 ml CAPS\(^1\) buffer were then pipetted in, see Figure 17. The syringe was closed and hand shaken for 30 s and the mixture left to settle for 1 hour. The water phase will settle below the oil phase, since it has a higher density. The water phase was then removed by tapping off the syringe from below and analyzed directly by ion chromatography. The method has been developed for this specific application, thus the exchange of acids to the water phase is well known and adjusted for (Talus and Ingelgård 2015).

![Figure 17. Illustration of adding in extraction method, modified and redrawn from (Ingelgård 2015).](image)

\(^1\) CAPS is short for 3-(Cylohexylamino)-1-propanesulphonic acid.
4.1.4 Visual analysis by macroscope
The metallic surfaces were analyzed visually; both by looking and taking images of the surfaces through a macroscope. A macroscope is used to look at objects near the naked eyes abilities. The total magnification of the macroscope was between 0.125-4. Images from the macroscope was captured with a digital sensor connected to a computer.

4.1.5 FTIR
Fourier Transform Infrared Spectroscopy (FTIR) uses infrared light (IR) to identify materials and compounds. Functional groups absorb the IR spectrum differently and thus create unique spectrums. The bonds between atoms have specific vibrations which correspond to the absorbed wavelengths in the IR spectrum. The analysis can be both qualitative and quantitative depending on references and setup (Introduction to Fourier Transform Infrared Spectrometry 2001).

4.2 Experimental setup – open system
For exposure of metal to B100 an open system setup with heating and magnetic stirring was selected. Heating was to get elevated temperature for accelerated aging, magnetic stirring was to have less gradients in the B100 fuel, and an open system was selected for free access to air (oxygen).

A schematic illustration can be seen in Figure 18. It was composed of a distillation flask of 500 ml with three openings. 250 ml fuel sample was placed in the distillation flask which was placed in a block heater combined with a magnetic stirrer. The stirrer speed was set to 700 rpm and the temperature to 80 °C if not otherwise stated. The left opening on the distillation flask was used for possibility of attachment of copper sample. The right opening was used for a thermometer with feedback to the block heater, to be able to set a specific temperature. The middle opening of the distillation flask was open to the surrounding air but went first to a gas cooler and then to an air dehumidifier.

Figure 18. Schematic illustration of experimental setup for open system.
In total, six identical setups of the opens system ran in parallel, see Figure 19. The only difference was that the gas coolers water was connected in two parallel series. Two cool water streams went to the gas cooler three and three. This made up for a slight difference in temperature of the gas cooler but it is considered negligible.

![Figure 19. Setup for open system aging which has a heating plate with magnetic stirrer, thermometer and gas cooling.](image19)

The magnetic stirrer rotated clockwise and a simple flow pattern illustration can be seen in Figure 20. When exposing two metal coupons, they were mounted in line with each other on a rod as also seen in Figure 20. The coupons had a gap between them of about 5 mm. The coupon closest to the rod was called the inner coupon and the coupon closest to the center of the distillation flask was called outer the coupon. The way the coupons were set up, the sides of each coupon would be exposed to a different liquid flow.

![Figure 20. Simple flow pattern in distillation flask from the magnetic stirrer. The left illustration shows from the side and the right from above.](image20)
4.2.1 Metal coupons preparation and dimensions
When exposing metal to aging B100 two metal coupons were simultaneously exposed and the total metal area was 40 cm$^2$. This gave a ratio of 6.25 ml B100/cm$^2$ metal. For example, the copper coupons were 20x50 mm which gives an area of 10 cm$^2$ on one side, four sides on the two copper coupons gives a total area of 40 cm$^2$.

All samples were grinded to P1200 to remove any previous protective layer and expose the underlying metal, and to attain a smooth surface. The grinding was performed three days before exposure in order to have the same layer on all samples that possibly comes from exposure to air.

4.3 Aging B100 fuel, 24-72 hours
Different chemical reactions take place in biodiesel over time as previously discussed. When elevating the temperature, the degradation and oxidation processes are accelerated. To understand this process, B100 was aged for three different aging times (Table 4).

Table 4. Test series with aging time at 80 °C.

<table>
<thead>
<tr>
<th>ID</th>
<th>C</th>
<th>B</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time [h]</td>
<td>24</td>
<td>48</td>
<td>72</td>
</tr>
</tbody>
</table>

4.4 Aging B100 fuel with copper, 8-140 hours
Studies on copper corrosion in B100 have been performed, see section 3.7, and a stable phase is indicated during aging. Confirmation of the stable period was a good starting point for understanding the corrosion behaviour of copper in B100. In order to study the copper corrosion as a function of aging time, an experiment was performed where copper coupons were exposed to B100 at 6 different times.

The experimental setup was an open system, see section 4.2. Two copper coupons of 20x50 mm were placed together with 250 ml of B100 in each distillation flask. In total six different sets were executed with different aging times, see Table 5.

Table 5. Test series with aging time at 80 °C with copper metal.

<table>
<thead>
<tr>
<th>ID</th>
<th>F</th>
<th>E</th>
<th>D</th>
<th>C</th>
<th>B</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time [h]</td>
<td>8</td>
<td>18</td>
<td>48</td>
<td>56</td>
<td>100</td>
<td>140</td>
</tr>
</tbody>
</table>

4.5 Changing copper and B100
Two possible explanations to the stable period were investigated; either the copper forms a protective layer after a while or the fuel is in a passive state. Three sets were aged for 20 h before placing the aged copper samples into fresh B100 and aged for additionally 20 h. At the same time, new copper specimens were placed in the aged B100 and also aged for another 20 h. See Figure 21 for illustration of the change.
4.6 Pre-studies acid and free water
To study the effect of free water and acid content on copper corrosion, experiments when adding respective compound to the fuel were performed. However, because of the high temperature (80 °C) which is close to the boiling temperature of both water (100 °C) and the SCFA (100-140 °C), pre-studies were performed to establish how long the respective substances would stay in the biodiesel.

4.6.1 Dissolved water
The evaporation rate of water from B100 was studied by dissolving water into B100, then aging the B100 in an open system. The dissolving of water was performed by mixing 1000 ppm in B100 for 24 hours. The water used was of Milli-Q purity.

4.6.2 Free water
Experiments to study how long time free water remained present in B100 was performed by adding 5 and 10 ml water in B100 and aging at both 60 °C and 80 °C in an open system. The aging was done for 48 hours with visual monitoring over the time. The water used was of Milli-Q purity.

4.6.3 Acid content
Experiments to look how long the formic acid stays in the biodiesel were performed. Formic acid was chosen since it has the lowest boiling point (100 °C) of the SCFA. Acid evaporation was studied by adding 150 mg/kg respective 300 mg/kg formic acid in B100 before aging the B100 at 80 °C over 24 hours in an open system. The formic acid used was of reagent grade (> 95 % purity).
4.7 Influence of acids on copper corrosion

From the results of the pre-study of acid evaporation it is apparent that one third evaporates quickly and then the concentration level stabilizes. Therefore 50% extra were added to get the desired amount for the longest time. To see how acid concentration affects copper corrosion, two different acid concentrations were added at the start of aging of B100 with copper, see Table 6.

Table 6. Added acid, aimed acid concentrations and aging times for the test series.

<table>
<thead>
<tr>
<th>ID</th>
<th>Added formic acid conc. [mg/kg]</th>
<th>$S_1$ 18h</th>
<th>$S_2$ 18h</th>
<th>$S_1$ 48h</th>
<th>$S_2$ 48h</th>
<th>$S_1$ 100h</th>
<th>$S_2$ 100h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>225</td>
<td>450</td>
<td>225</td>
<td>450</td>
<td>225</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>300</td>
<td>150</td>
<td>300</td>
<td>150</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>18</td>
<td>48</td>
<td>48</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

4.8 Influence of free water on copper corrosion

The results from the pre-study of free water showed that 10 ml water needs to be added to 250 ml B100 if free water levels should be enough for aging at 80 °C. The test series consist of 5 sets, see Table 7. The aging times were between 6-72 hours and to all sets 10 ml Milli-Q water were added at the beginning.

Table 7. Added water and aging time for the series.

<table>
<thead>
<tr>
<th>ID</th>
<th>Added water [ml]</th>
<th>W6</th>
<th>W16</th>
<th>W24</th>
<th>W48</th>
<th>W72</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Aging time [h]</td>
<td>6</td>
<td>16</td>
<td>24</td>
<td>48</td>
<td>72</td>
<td></td>
</tr>
</tbody>
</table>

After aging, a sample of 10 ml was taken from each set for analysis of acid. Then 240 ml Milli-Q water was then added; this was the same amount as the biodiesel phase left. The mixture was hand shaken for 1 min and then left to separate for 30 min. Samples of both the water phase and biodiesel phase were analyzed to determine their copper concentration.

4.9 Visual corrosion damage over time

The corrosion on copper in B100 progresses was studied by aging copper in B100 and photographing the copper sample in a macroscope during the aging. In Table 8 the different aging times where the copper coupons where photographed can be seen. The copper was removed from the B100 and rinsed with acetone before the photographing.

Table 8. Photograph series aging times.

<table>
<thead>
<tr>
<th>Photograph time [h]</th>
<th>0</th>
<th>68</th>
<th>92</th>
<th>116</th>
<th>140</th>
<th>164</th>
</tr>
</thead>
</table>

The coupon closest to the rod is called the inner coupon and the coupon closest to the center of the distillation flask is called outer coupon. The sides facing the other coupon are called inner inwards and outer inwards and the sides facing from the other coupon are called inner outwards and outer outwards, see Figure 22. The way the coupons are set up, the sides of each coupon will be exposed to a different liquid flow.
4.10 Changes of parameters after stable period (ASP)

Previous experiments were focused on how different additions affected corrosion at the start of the aging. To study the reactions at the end of the stable period, when the copper still has a protective layer; changes to the system were performed at this time. Table 9 below shows how the test series were executed. The temperature was set to 80 °C and stirrer speed to 700 rpm if not otherwise stated. The additions at the end of the stable period represent the introduction of potential contaminations in the system taking place during storage and use. Moist air was introduced by replacing the internal parts of the air dehumidifier with a moist cloth.

<table>
<thead>
<tr>
<th>ID</th>
<th>Time of change [h]</th>
<th>Change</th>
<th>End time [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference/Standard</td>
<td>-</td>
<td>-</td>
<td>140</td>
</tr>
<tr>
<td>W1 ASP</td>
<td>72</td>
<td>Addition of 10 ml MilliQ water</td>
<td>140</td>
</tr>
<tr>
<td>S1 ASP</td>
<td>72</td>
<td>Addition of 225 mg/kg formic acid</td>
<td>140</td>
</tr>
<tr>
<td>S2 ASP</td>
<td>72</td>
<td>Addition of 450 mg/kg formic acid</td>
<td>140</td>
</tr>
<tr>
<td>Moist ASP</td>
<td>72</td>
<td>Moist air</td>
<td>140</td>
</tr>
<tr>
<td>T60 ASP</td>
<td>72</td>
<td>Lowering temp to 60 °C</td>
<td>140</td>
</tr>
</tbody>
</table>

4.11 FTIR analyses on selected copper coupons and B100

To study the characteristics of the copper surfaces some selected samples was analyzed with FTIR. Also samples of B100 were analyzed. The analyzed samples can be seen in Table 10. The reference frequencies for the analysis are taken from (Socrates 2004).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 0h</td>
<td>Copper coupon</td>
<td>Grinded new Cu sample</td>
</tr>
<tr>
<td>B 100h</td>
<td>Copper coupon</td>
<td>Exposed to B100 for 100h</td>
</tr>
<tr>
<td>S2 18h</td>
<td>Copper coupon</td>
<td>Exposed to B100 with 450 mg/kg added formic acid for 18h</td>
</tr>
<tr>
<td>S2 100h</td>
<td>Copper coupon</td>
<td>Exposed to B100 with 450 mg/kg added formic acid for 100h</td>
</tr>
<tr>
<td>W1 72h</td>
<td>Copper coupon</td>
<td>Exposed to B100 with free water for 72h</td>
</tr>
<tr>
<td>B100 0h</td>
<td>B100 fuel</td>
<td>Unexposed B100 fuel</td>
</tr>
<tr>
<td>B100 72h</td>
<td>B100 fuel</td>
<td>B100 fuel aged 100h (without Cu)</td>
</tr>
</tbody>
</table>
4.12 Aging B100 with brass
The alloy brass was aged with B100 to investigate if it has similar behavior as copper. The brass alloy was of the grade CW614N and was supplied by Nordic Brass Gusum AB. The chemical analysis can be seen in Table 11.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Sn</th>
<th>Fe</th>
<th>Al</th>
<th>Ni</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>57.5385</td>
<td>38.8489</td>
<td>3.0663</td>
<td>0.1401</td>
<td>0.2323</td>
<td>0.039</td>
<td>0.0602</td>
<td>0.0035</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>As</th>
<th>Sb</th>
<th>B</th>
<th>Bi</th>
<th>P</th>
<th>Mg</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0104</td>
<td>0.0379</td>
<td>0.0085</td>
<td>0.0002</td>
<td>0.0061</td>
<td>0.0024</td>
<td>0.0012</td>
<td>0.0046</td>
</tr>
</tbody>
</table>

The aging times were chosen for B100 with aluminum (Table 12) to be the same as B100 with copper (Table 5) for comparable results.

<table>
<thead>
<tr>
<th>ID</th>
<th>Brass 140h</th>
<th>Brass 100h</th>
<th>Brass 56h</th>
<th>Brass 48h</th>
<th>Brass 18h</th>
<th>Brass 8h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time [h]</td>
<td>140</td>
<td>100</td>
<td>56</td>
<td>48</td>
<td>18</td>
<td>8</td>
</tr>
</tbody>
</table>

4.13 Aging B100 with aluminum
Aluminum with copper content of about 3.2 % was aged by contact with B100 to investigate its corrosion behaviour. The aluminum was supplied by Sapa Technology in Finspång. The full chemical analysis of the aluminum can be seen in Table 13.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Ni</th>
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<td>8.885</td>
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<td>3.229</td>
<td>0.4133</td>
<td>0.3298</td>
<td>0.00077</td>
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<table>
<thead>
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<th>Zn</th>
<th>Ti</th>
<th>Ag</th>
<th>As</th>
<th>B</th>
<th>Ba</th>
<th>Be</th>
<th>Bi</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.1086</td>
<td>0.1492</td>
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<td>0.00352</td>
<td>0.0004</td>
<td>0.00004</td>
<td>0.00001</td>
<td>&lt;0.0001</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Cd</th>
<th>Co</th>
<th>Ga</th>
<th>Hg</th>
<th>In</th>
<th>Li</th>
<th>Na</th>
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<tbody>
<tr>
<td></td>
<td>0.00047</td>
<td>0.0003</td>
<td>0.00013</td>
<td>0.0113</td>
<td>0.00006</td>
<td>0.00005</td>
<td>&lt;0.00001</td>
<td>&lt;0.00001</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>P</th>
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<th>Sb</th>
<th>Sn</th>
<th>Sr</th>
<th>V</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.00036</td>
<td>0.0007</td>
<td>0.00233</td>
<td>0.00113</td>
<td>0.0002</td>
<td>0.00347</td>
<td>0.00087</td>
</tr>
</tbody>
</table>

The aging times were chosen for B100 with aluminum (Table 14) to be the similar to B100 with copper (Table 5) for comparable results.

<table>
<thead>
<tr>
<th>ID</th>
<th>Alu 140h</th>
<th>Alu 124h</th>
<th>Alu 56h</th>
<th>Alu 48h</th>
<th>Alu 18h</th>
<th>Alu 8h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time [h]</td>
<td>140</td>
<td>124</td>
<td>56</td>
<td>48</td>
<td>18</td>
<td>8</td>
</tr>
</tbody>
</table>
5 Result and discussion

5.1 Aging B100 fuel, 24-72 hours

Aging B100 in an open system at 24, 48 and 72 hours was performed to study its degradation. The experimental method can be seen in section 4.3.

The oxidation stability of unaged B100 can be seen in Figure 23.

![Figure 23. Oxidation stability curve for unaged B100 with the Rancimat method. The induction point is marked with a red vertical line at 6.6 h.](image)

The result showed an approximate 6.6 hour long induction time for unaged B100.

The oxidative stability of aged B100 can be seen in Figure 24.

![Figure 24. Oxidation stability curves for aged B100 with the Rancimat method. The induction point is marked with respective colored sign.](image)

The results clearly showed that the stability decreased with aging time. Aging of B100 at 80 °C for 24 hours shortened the induction time to about 3.6 hours, a decrease by 3 hours from unaged B100.
Aging for 48 hours resulted in a decrease of about 2 hours from 24 hours. After 72 hours of aging the B100 fuel showed no remaining stability.

The acid concentrations over time can be seen in Figure 25.

![Acid concentrations in B100](image)

**Figure 25. Acid concentrations plotted vs. aging time, aging B100 at 80 °C.**

Only slight increases in acid concentration were seen from unaged B100 (0 hours) until 48 hours. From 48 hours to 72 hours there was a high increase in acid concentrations, with the highest increase in formic acid which went from 38 to 500 mg/kg. This high increase between 48 and 72 hours correlates with the expired oxidative stability between these two aging times. This, since after the induction point a high increase in acid concentrations should be expected.

The water content is displayed in Figure 26.

![Water content in B100](image)

**Figure 26. Water content plotted vs. aging time, aging B100 at 80 °C.**
The water content was constant from 0 to 48 hours. There was a high increase from 48 to 72 hours, from 400 ppm to 2200 ppm. This follows the acid concentration in Figure 25 and correlates with the induction point between these two aging times. When biodiesel is degraded by oxidation is one by-product water, as explained in section 3.3.1. This may explain the high increase in water content passing the induction point. The hygroscopy should also increase as the B100 fuel ages and therefore absorbs more water.

5.2 Aging B100 fuel with copper, 8-140 hours

Aging B100 with copper was performed to study the corrosion behaviour of copper in B100. The experimental method can be seen in section 4.4.

The copper concentration can be seen in Figure 27 below.

![Cu content in B100 with Cu](image)

Figure 27. Copper concentration plotted vs. aging time, aging B100 with copper.

Previous analyses showed, as expected, that the copper concentration in fresh B100 was below the detection limit of 0.1 mg/kg, see section 3.7. Copper content (Figure 27) had a stable period between 18-56 h which was followed by an exponential increase. This confirms the stable period for copper corrosion in aging B100 at around 18-56 h.

The results from the Rancimat method analysis can be seen below in Figure 28.
Figure 28. Oxidation stability curves for aged B100 with copper with the Rancimat method. Unaged B100 (red and cyan) has an induction time of about 6.6 hours.

Figure 28 shows that the induction point has been passed in all samples, except in the unaged reference samples. This means that copper has accelerated the degradation of B100 much faster than anticipated and the oxidative stability does not follow the data on copper content directly (Figure 27). Possibly, degradation products that give a more corrosive fuel needs time to form or a certain amount formed after the oxidative stability is gone.

The acid concentration in each sample is presented in Figure 29.

**Acid concentrations in aged B100 with Cu**

Figure 29. Acid concentrations plotted vs. aging time when aging B100 together with copper at 80 °C.

A stable concentration until 18 h was shown after which the concentration for all analyzed acids rose quickly, indicating that several substances are transpiring between 18 and 48 hours. At 140 h formic acid concentration decreased; this can possibly be caused by salt formation according to reactions (23-24).
The water content is displayed in Figure 30.

**Figure 30. Water content plotted vs. aging time when aging B100 together with copper at 80 °C.**

The water content showed an increasing trend over time. According to the analyses, the water content decreased from 48 to 58 hours but this may be due to uncertainties in the analysis method. Otherwise, water content followed the increase of the acid concentrations until 100 hours. Then, the water content remained constant at about 3800 ppm from 100 to 140 hours.

As previously described in section 3.2, the water content in unaged B100 was determined to be about 2000 ppm; thus the water concentration had increased during the aging of B100. The constant content between 100 and 140 hours can be explained by that the solubility of water in B100 had been reached and that the solubility of water in B100 was not increasing.

Sample images of the copper coupons after exposure can be seen in Figure 31.

**Figure 31. Sample images from macroscope after 140 h, 100 h, 56 h, 48 h, 18 h and 8 h time in B100 at 80 °C.**
Corrosion was not observed until 48 hours aging, see Figure 31 in the middle right. This is in agreement with the stable period and exponential increase observed in copper concentration and acid concentrations.

5.3 Changing copper and fuel

The theory of a protective layer forming on the surface of copper was tested by changing the copper and B100 fuel as described in section 4.5.

Copper concentration was analyzed after aging for 20 hours, 20 hours after placing the aged copper into unexposed fresh B100 and 20 hours after placing unexposed copper into aged B100. The copper concentrations can be seen below in Figure 32.

![Figure 32. Copper concentration in aged B100 with copper and changing to new copper respective new B100.](image)

Aging B100 with copper for 20 hours showed a copper concentration of 1.5-2 mg/kg. Replacing the exposed copper with unexposed copper and aging for another 20 hours showed more than a twofold increase in copper concentration. This suggests that the B100 in itself is not the reason for the stable period. If it had been, it should not show such a notable increase in copper concentration. Placing the exposed copper in unexposed B100 and aging for 20 hours showed upon a significantly lower copper concentration around 0.3-0.4 mg/kg. Comparing this to the aging unexposed B100 with copper (1.5-2 mg/kg) verifies that the copper gets some kind of protective layer. The protective layer can be different corrosions products as previous studies have shown, see section 3.4, for example CuCO₃, CuO and Cu₂O etc.

In Figure 33 below, the acid concentrations after aging for 20 hours, 20 hours after placing the aged copper into unexposed fresh B100 and 20 hours after placing unexposed copper into aged B100 can be seen.
The formic acid concentrations was in the range of 35-55 mg/kg, when aging unexposed fresh B100 in contact with unexposed copper for 20 hours. When exchanging the copper metal and aging for another 20 hours, it can be seen that the acid levels rose significantly. This is in agreement with previous results when aging B100 with copper. The acid concentrations between 18-46 hours, shown in Figure 29, revealed an exponential increase within this range. However, the unexposed copper seems not to have accelerated the degradation further; as acid levels were in level with when not exchanging the copper (Figure 29). This suggests that the copper at a certain level in B100 fuel is not a limiting factor and consequently, an increase will not further accelerate the degradation.

Placing the aged copper in fresh B100 and aging for 20 hours resulted in significantly lower acid concentrations (15-25 mg/kg formic acid) than when aging fresh B100 in contact with unexposed copper (35-55 mg/kg formic acid). This indicates that some kind of protective layer may have been formed preventing corrosion and thereby also degradation of the fuel to an extent.

Water contents can be seen in Figure 34.
The water contents were 500-600 ppm after 20 hours with unexposed copper and unexposed fresh B100. After aging the exposed copper with unexposed fresh B100 in 20 hours, water contents had slightly lower levels at 350-400 ppm. This suggested that the biodiesel has not aged as much when having pre-aged copper because of its protective layer, preventing the copper to accelerate the aging of biodiesel. The difference in levels was however too low to draw any definite conclusions. Aging unexposed copper in exposed B100 for another 20 hours showed a doubling in water content (except one sample) to about 1200-1600 ppm compared when aging unexposed copper and unexposed fresh B100. This shows that the unexposed copper sample have not further accelerated the degradation of biodiesel when comparing with data when not exchanging the copper (Figure 30). Therefore, the copper at a certain level is not a limiting factor and further increase will not accelerate the degradation more.

Picture samples of the copper coupons can be seen in Figure 35.

![Figure 35. Copper coupons exposed to B100. The three copper coupons on the left have been exposed to 20 hours of B100 already aged 20 hours. The three copper coupons on the right have been exposed to 20 hours of new B100 and then placed in new B100 for another 20 hours.](image)

The three copper coupons to the left in Figure 35 have been placed in the B100 that has been aged for 20 hours. They show significant corrosion after 20 hours with multiple dark areas. Compare this to the copper coupons to the right which has been in B100 for 20 hours and then placed in new B100 for another 20 hours. By visual inspection these showed some smaller corrosion damage but it was significantly less. However the corrosion seemed to be the same kind as they were visually similar.
5.4 Pre-studies acid and free water

Experiments to see how long dissolved water, free water, and formic acid were performed to establish how long respective substance would stay in the biodiesel. The method is described in section 4.6.

5.4.1 Dissolved water

How fast water solved in B100 evaporates can be seen in Table 15.

<table>
<thead>
<tr>
<th>Table 15. Solved water in B100 evaporation.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Before adding water</strong></td>
</tr>
<tr>
<td>260 ppm</td>
</tr>
</tbody>
</table>

After adding 1000 ppm water and mixing for 18 hours the water content was 1330 ppm. When heating the B100 in an open system the water level dropped instantly. The 0.5 hours in Table 15 was the 0.5 hours it took to heat the B100 from room temperature up to 80 °C. This means that the water escaped quickly and faster than accurate measurement could be done. This also points at the high water levels when aging B100 for longer times without and with copper (Figure 26 and Figure 30) were because either water was produced in the degradation and/or the hygroscopy increased with the aging.

5.4.2 Free water

The remaining water after adding 5 ml and 10 ml water and then aging for 48 hours, both in 80° and 60 °C, can be seen in Table 16.

<table>
<thead>
<tr>
<th>Table 16. Remaining solved and free water after 48 hours.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ID</strong></td>
</tr>
<tr>
<td>Free water [ml]</td>
</tr>
<tr>
<td>Solved water in B100 [ppm]</td>
</tr>
</tbody>
</table>

All sets except 5 ml at 80 °C showed a great deal of water remaining. The free water amount analysis was very uncertain because of separation problems between the small amount of water and the B100. 5 ml at 80 °C also showed that B100 is not saturated with water as unaged B100 has a solubility of water around water 2000 ppm; solved water in W5 at 80 °C was only 1240 ppm.

From visual inspection during the aging a lot of condensation was observed on the distillation flasks and the lower part of the gas coolers. This was probably the reason for that free water was still available in all of the sets; water condensed and dripped back into the B100. 5 ml at 80 °C was deemed to have too low free water levels (0.5 ml) after 48 hours for experiments to be done. The others seemed good and preferably for the free water study was to use the same temperature as in previous experiments. Therefore the free water study was using 10 ml at 80 °C.

5.4.3 Acid content

In Figure 36 the pre-study results for acid evaporation are presented.
Figure 36. Formic acid concentration over time after addition of acid in B100 at 80 °C.

300 mg/kg respectively 150 mg/kg formic acid were added in B100; at 0 hours the B100 fuel showed similar concentrations as the added amounts. Aging the B100 in an open system showed that the concentration decreased at the start but quickly stabilized. Both concentrations stabilized at roughly on two thirds of the original concentration. Therefore 50 % extra of the aimed amount would need to be added to get the aimed amount. The reason for the decrease in formic acid concentration could be an equilibrium adsorption on the glass in the distillation flask or equilibrium with compounds in B100.

5.5 Acids influence on copper corrosion
The effect of formic acid addition on corrosion was studied, see method in section 4.7.

The copper concentration over time can be seen in Figure 37.

Figure 37. Copper concentration over time when adding formic acid.
The copper levels (Figure 37) were much higher (approx. 4-10 times) than when not adding formic acid (Figure 27). This means that presence of formic acid increases copper corrosion in B100. Interestingly, the copper concentration was the same for both levels of addition of formic acid, S1 (225 mg/kg) and S2 (450 mg/kg). This suggests that formic acid addition above a certain threshold before any protective layer is formed gives high and the same amount of corrosion; further increase of formic acid does not increase corrosion at the levels added (225 and 450 mg/kg).

The copper concentrations between 48-100 hours decreased, from 75 down to 50 mg/kg, which suggest that copper has reacted with something that has formed during the aging of B100. Most probably have copper formed salts together with carboxylic acids.

No stable period was observed between these data points (18-100 h). However, there are only three which give less certain conclusions. There could be a stable period in between or before the first aging time (18 h) but this seems unlikely since the copper levels were very high. The initial formic acid concentration was so high the protective layer was never able to form.

In Figure 38 the acid concentrations at 24 hours for the sets that was longer than 24 hours are shown.

![Acid concentration at 24 hours](image)

Figure 38. Acid concentrations at 24 hours when adding formic acid at start.

The samples that had an aimed concentration of 150 mg/kg formic acid (S1 in Figure 38) showed a concentration of 75-80 mg/kg formic acid. This was much lower than the aimed concentration. The same trend was for the samples that had an aimed concentration of 300 mg/kg formic acid (S2). They showed a concentration of about 105 mg/kg formic acid. This could be due to salt formation as described in section 3.4. The copper concentrations were high (Figure 37) and could therefore drive the reaction to form more salts according to Le Châtelier's principle.

In Figure 39 the acid concentrations at the end of each set are shown.
The formic acid concentration (Figure 39) was low at the end of each set, comparing when not adding formic acid (Figure 29). For example, formic acid concentrations were 150 and 175 mg/kg (S1 and S2 respectively) at 100 hours. Compare this to the formic acid concentration when not adding formic acid at the start (Figure 29), which was substantially higher at 670 mg/kg. The increase between 18 to 48 hours when not adding formic acid was about 300 mg/kg but the increase when adding formic acid was 20 and 5 mg/kg for S1 and S2 respectively. The difference can be explained by the formation of salt with copper as the copper and acid levels were high and could therefore drive the reaction to form more salts according to Le Châtelier’s principle. This gives support to the theory of formation of salts which should decrease the acid concentration.

The water content in B100 when adding formic acid can be seen in Figure 40.

The graph in Figure 40 shows identical content for the two acid additions S1 (225 mg/kg) and S2 (450 mg/kg). This suggests that the B100 fuel was degraded similarly in both the acid additions. However, comparing to when not adding formic acid (Figure 30) the levels for when adding formic acid were higher at 18 h but lower at 100 h. This shows that from the water content, the age of the fuel and the corrosiveness cannot be predicted between different conditions.
Samples of the exposed copper coupons at the three aging times can be seen in Figure 41.

Figure 41. Exposed copper coupons to B100 with addition of 225 mg/kg (S1) and 450 mg/kg (S2) formic acid at 18 h, 48 h and 100 h aging time.

The copper coupons in Figure 41 show a different kind of corrosion with both local corrosion attacks as seen before (Figure 31) but also a general corrosion over the whole surface. The whole surface is covered by dark products which could be corrosion products and/or formed salts with copper.

5.6 Free waters influence on copper corrosion

The effect of free water addition on corrosion was studied; see method and analysis details in section 4.8.

Copper concentration in the water phase respective the B100 phase can be seen in Figure 42.

Figure 42. Copper concentrations in water respective biodiesel phase.

Most of the copper was in the water phase in all sets (Figure 42); copper has higher affinity to the water phase. Slightly more copper relatively in the B100 phase for the W48 and W72 sample, this can
be because of more water solved in the B100 increase copper solubility in B100 as seen previously (Figure 30). Important to note that the concentrations of each phase were in 220 ml biodiesel and 220 ml water respectively.

The total copper content over time can be seen in Figure 43.

![Cu content total](image)

**Figure 43.** Total copper concentration, adjusted for 220 ml B100, over time when adding free water to B100.

The graph in Figure 43 shows a linear increase from 6 to 48 hours with no stable period. This suggests that no protective layer was formed when free water was present in B100. The copper concentrations were also much higher when adding free water (compare Figure 27) which points at higher corrosion with free water. This was probably because acids from B100 were dissolved into the water and thus creating a very acidic aquatic environment.

Acid concentrations over time can be seen in Figure 44.

![Acid concentration in B100, free water](image)

**Figure 44.** Acid concentrations in B100 plotted vs. aging time when adding free water to B100.

Formic acid showed a linear increase with time and similar levels at the beginning 6-24 hours as when not adding free water (Figure 29) and lower levels at 48 to 72 hours. The lower levels of formic
acid can be explained by the high levels of copper in total which can form salts with formic acid or that carboxylic acids have transferred to the water phase present.

Samples of the copper coupons exposed to B100 with free water addition can be seen in Figure 45.

![Figure 45](image)

**Figure 45.** Copper coupons aged with B100 and 10 ml free water. W6, W16, W24, and W48 are aged 6 h, 16 h, 24 h, and 48 h respectively.

Some local corrosion attacks could be seen on all samples. However, there was also a uniform corrosion which suggests that no protective layer was formed. Both in W24 and W48 a gray layer was formed on the surface and at W48 the layer has at some point exfoliated. The layer seen cannot be considered protective at first since the copper levels were increasing (Figure 43). However, this layer could explain why the increase in copper concentration slowed down at 48 to 72 hours (Figure 43).
5.7 Visual corrosion damage over time

The visual corrosion damage during aging was studied from 8-164 h; see section 4.9 for further details.

The four sides of the two copper coupons exposed to B100 can be seen in Figure 46 and Figure 47. For placement and designation of the copper coupons’ sides see section 4.9 and Figure 22.

Figure 46. The left column is the coupon side inside outwards and the right is inside inwards. The aging time from above: 0 h, 68 h, 92 h, 116 h, 140 h, 164 h.
Figure 47. The left column is the coupon side outside outwards and the right is outside inwards. The aging time from above: 0 h, 68 h, 92 h, 116 h, 140 h, 164 h.

From Figure 46 and Figure 47 it is clear that corrosion of copper increased with time and the aging of B100. At 68 h some smaller corrosion damage could be seen as dark spots and the damage increased drastically thereafter. Most damage was on the edges and the edges seem as most vulnerable in this setup.

On the copper coupon inside inwards at 140 h and 164 h (Figure 46) an interesting pattern could be seen. Corrosion products have formed at the surface of the copper to the right of the hole and this could be due to the flow pattern, see 4.2 and Figure 20. Either the products have adhered to the surface in the turbulence after the rod holding the coupons in place, or the protective layer have eroded because of the turbulence first and facilitated local corrosion, which gave corrosion products. In Figure 46 the liquid flow in the distillation flask was approximately left to right.

From 116 h to 164 h the surfaces in Figure 46 and Figure 47 showed a change in the pattern of the surface. A grayer surface on new locations on whole general areas and not only spots and also
patterns that appeared like flow patterns. From 140 h to 160 h it is clear that the grayer surface also replaced darker corrosion products at their locations. It seems the corrosion attacked wider areas, etching of the surface and old corrosion products dissolved into the B100. This can be explained by the much higher acid concentration than previously seen (Figure 29) which could break through a possible protective layer easier.

5.8 Changes of parameters after stable period (ASP)
To study parameters after stable period changes was done to the system at 72 h, see section 4.10.

The copper concentrations can be seen in Figure 48 and Figure 49.

![Cu concentration, ASP](image1)

**Figure 48.** Copper concentrations at 72 h and 140 h after changing conditions.

![Cu concentration, ASP, free water](image2)

**Figure 49.** Copper concentrations at 72 h and 140 h after adding free water.

The copper levels were the same in all parallel set-ups at 72 h (around 4 mg/kg). At 140 h the reference curve had a copper concentration of 16.4 mg/kg. Adding of 225 (S1) and 450 (S2) mg/kg formic acid at 72 h gave significantly higher copper concentration with 24.1 and 25.7 mg/kg respectively. This in line with previous results (section 5.5); addition of formic acid increased corrosion. However, the copper levels were much lower. This suggests, that when the protective layer had formed on the surface of copper it gives a resistance to the corrosion caused by formic acid. Lowering the temperature (T60) seems to prolong the stable period. This can be either because
aging of the biofuel was slower at lower temperatures and acids are not formed as quickly or that the protective layer was more stable at lower temperatures. The reaction kinetics could also be so low at the lower temperature (60 °C) it would seem like the corrosion was stable. Having moist air appeared to decrease the copper content but the difference was too small to draw any definite conclusions as only one set was done. Adding free water (W1 in Figure 49) gave significantly higher copper concentration and as previous results have shown free water increased copper corrosion drastically.

The copper concentrations change over time are shown in Figure 50.

Figure 50. Copper concentration over time when changing conditions.

From Figure 50 it is clear that the 225 mg/L difference in added amount of formic acid between S1 and S2 did not amount in difference in copper concentration.

Acids concentration at 72 hours before any changes and after 140 hours can be seen in Figure 51.

Figure 51. Acid concentrations at 72 h before any changes and at 140 h.
The concentrations at 72 hours were in levels with previous sets (Figure 29), with formic acid around 250-270 mg/kg. All sets at 140 hours showed similar levels except W1 ASP and this was probably because the acids can have gone to the water phase.

The added formic acid in S1 (225 mg/kg) and S2 (450 mg/kg) gave the same behaviour as in section 5.5; acids caused higher copper corrosion but this in turn decreased the acid concentration, probably because of salt formation between copper and acids, reactions (23-24). T60 showed no lower acid concentration as one could expect at the lower temperature. The lower temperature was expected to cause a decrease in degradation of the B100 fuel and less formation of acids but the same concentrations were seen. This can be because the considerable lower copper concentration gave less formation of salts and therefore less acid was consumed; the same acid concentration was thereby attained.

Water contents can be seen in Figure 52.

![Water content, ASP](image)

**Figure 52.** Water content at 72 h and 140 h

The water contents in all samples (Figure 52) were similar (1200-1300 ppm) before any changes at 72 hours. Water content at 140 hours was too similar to draw any certain deductions for most sets; the levels were around 2300-2700 ppm. However the similar levels suggest that the fuel has degraded equally.

In Figure 53 images of the copper coupons can be seen.
Added formic acid 225 (S1) respective 450 mg/kg (S2) at 72 h showed higher corrosion than the reference (Ref). S2 showed more products on the surface than S1 which can be due to higher formation of salts because of more added formic acid. Added free water (W1) showed much higher corrosion as expected from the copper corrosion and the whole surface was covered in products. Moist air (Moist) showed no significant difference in damage from the reference (Ref). Lowering the temperature to 60 °C (T60) showed less corrosion but some products have accumulated on the surface.
5.9 FTIR analyses on selected copper coupons and B100

Selected copper coupons and fuel, see section 4.11, was analyzed with FTIR. FTIR was used to study the surface of the copper.

The spectra for unaged B100 and aged B100 without copper for 72 h can be seen in Figure 54.

![Figure 54. FTIR spectra of new B100 fuel (green) and aged B100 fuel without Cu for 72h (blue). Note X over artifact due to analysis error on both spectra.](image)

Fresh B100 and aged B100 (Figure 54) showed very similar spectra without any notable difference. The by-products from degradation of the fuel did not occur in detectable amounts. However the fuels showed expected spectra with peaks at 1735 cm\(^{-1}\) and 1100-1300 cm\(^{-1}\) which could be C-O and C=O in esters, respectively. 1260, 1380 and 2870-3000 cm\(^{-1}\) could be methyl groups. The main component in the B100 fuel was therefore seen: methyl esters.

In Figure 55 below a comparison between the spectra of aged B100 with copper for 100 h and copper aged in B100 for 100 h can be seen.

![Figure 55. FTIR spectra. Comparison between aged fuel with Cu for 100h (blue) and copper aged for 100h (red). Note X over artifact due to analysis error on both spectra.](image)
The peak at 3300 cm\(^{-1}\) may indicate that an alcohol has adsorbed on the copper surface and the peak at 1047 cm\(^{-1}\) indicates a primary alcohol. This alcohol probably originated from when the copper was washed with ethanol after aging to get a clean surface. However the peak 3300 could also be water but the peak 1047 cm\(^{-1}\) still shows that there is a primary alcohol on the surface. Esters also seem to be absorbed on the surface even after washing with peaks still at 1735 cm\(^{-1}\) which could be C=O and 1100-1300 cm\(^{-1}\) which could be C-O in esters. Otherwise interesting were the peaks around 1579-1660 cm\(^{-1}\) which could be carboxylate salts in different forms on the surface. This could confirm that salts were formed from carboxylic acids and copper.

Comparison between copper aged with B100 100 h (B100h), aged with addition of 10 ml free water for 72 h (W72h) and aged with addition of 450 mg/kg formic acid for 100 h (S2 100h) can be seen in Figure 56 below.

Figure 56. FTIR spectra. Comparison between copper aged with addition of 450 mg/kg formic acid for 100h (green), copper aged with addition of 10 ml water for 72h (blue) and copper aged 100h (red). Intensities are comparable between all three spectra.

B100h, W72h, and S2 100h (Figure 56) showed a broad peak at around 3300 which was either water or an alcohol. They also had a peak at 1047 cm\(^{-1}\) which correlates to a primary alcohol, probably ethanol from the cleaning of the samples. From the comparable frequencies it showed that a lot more of the fuel is stuck on the surface on the W72 copper coupon. More salts seemed to be adhered at the surface S2 100 h than B100h, looking at 1579-1660 cm\(^{-1}\), which was in coherence with previous analysis: more acid and more copper gave more salts. W72’s peak at 1596 cm\(^{-1}\) point that the high levels of copper have driven the salt formation longer compared to S2 100h and B100h, and that one salt has deposited on the surface much more than any other.
5.10 Aging B100 with brass

The alloy brass was aged with B100 to investigate if it has similar behaviour as copper, see method in section 4.12.

The oxidation stability can be seen in Figure 57 for the 3 shortest aging times; 8, 18 and 48 hours.

![Figure 57. Oxidation stability curves for B100 aged with brass at 8, 18 and 48 hours with the Rancimat method. Unaged B100 (pink) has the induction point at 6.5 hours.](image)

The reference sample of unaged B100 (Figure 57) showed an induction time of about 6.5 hours. 8 hours showed about 4.9 hours induction time and 18 hours had about 3.1 hours induction time. The results showed that brass degraded B100 to a lesser extent than copper; where no oxidation stability was left in even the shortest time (8h), compare Figure 28. At 48 hours of aging with brass there was no oxidation stability left compared with B100 aged without metal contact (Figure 24) which had about 1.5 hours induction time. This showed that the brass had accelerated the aging of B100; the acceleration was however less with brass than with copper.

The concentrations for copper and zinc can be seen in Figure 58.

![Metal concentrations, B100 with brass](image)

Figure 58. Copper and zinc concentrations over time in B100 with brass at 80 °C.
Zinc (Figure 58) went from a concentration of about 1 mg/kg for unaged B100 (0 hours) down linearly to about 0.5 mg/kg at 140 hours. The already present zinc could mask if there was zinc leaching from the brass due to corrosion. Therefore any definite conclusions cannot be made.

Copper levels (Figure 58) were below the detection limit 0.10 mg/kg at 8 and 18 hours. At 48 hours the copper concentration was 0.15 and was stable until 140 hours where it goes up to 0.27 mg/kg. Brass released less copper in aging B100 even considering the tested brass only had about 58 % copper. From 48 to 100 hours there seemed to be a stable period which ended at 140 hours. However more data points at longer aging times are needed to confirm this stable period.

The acid concentrations for copper and zinc can be seen in Figure 59.

**Acid concentrations in B100 with brass**

*Figure 59. Acid concentrations over time in B100 aging with brass at 80 °C.*

Looking at the acid concentrations in Figure 59 it is also clear that the brass accelerated the degradation of the B100 fuel less than pure copper. With levels about 70-90 mg/kg formic acid at 48-56 hours which were considerably less than with copper (Figure 29). This could explain to a degree the lower metal concentrations, Figure 58.

Water content over time when aging B100 with brass can be seen in Figure 60.
The graph in Figure 60 shows a linear increase with aging time. The water content levels were lower than when aging with copper but higher than when aging without metal which again suggest that brass accelerated aging of B100 but to less extent than copper.

In Figure 61 the exposed brass coupons can be seen.

No corrosion products could be seen from 8 to 56 hours. On brass exposed to B100 for 100 hours and 140 hours local corrosion attacks could be seen on the surface together with corrosion products. This clearly showed that brass was less prone to corrosion in B100 compared to pure copper. One reason was that brass does not accelerate aging as fast as copper as discussed before and therefore B100 contained less amounts of aggressive degradation products during the aging.
5.11 Aging B100 with aluminum

The aluminum with a content of 3.2 weight % copper was aged with B100 to investigate if it has similar behaviour as copper, see method in section 4.13.

The oxidation stability can be seen in Figure 62 for the B100 aged with aluminum.

![Oxidation stability curves for B100 aged with brass at 8, 18, 48, 56, 124 and 140 hours with the Rancimat method.](image)

8 hours showed about 5.9 hours induction time which was much greater than with pure copper where no oxidation stability was left in even the shortest time (8h) (Figure 28). At 48 hours of aging with aluminum there was 1.6 hours induction time compared with B100 aged without metal contact (Figure 24) which has about 1.5 hours induction time. This shows that the aluminum had not accelerated the aging of B100.

The concentrations of copper and aluminum in B100 can be seen in Table 1.

<table>
<thead>
<tr>
<th>ID</th>
<th>Alu 8h</th>
<th>Alu 18h</th>
<th>Alu 48h</th>
<th>Alu 56h</th>
<th>Alu 124h</th>
<th>Alu 140h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time [h]</td>
<td>8</td>
<td>18</td>
<td>48</td>
<td>56</td>
<td>124</td>
<td>140</td>
</tr>
<tr>
<td>Cu [mg/kg]</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Al [mg/kg]</td>
<td>&lt;0.50</td>
<td>&lt;0.50</td>
<td>&lt;0.50</td>
<td>&lt;0.50</td>
<td>&lt;0.50</td>
<td>&lt;0.50</td>
</tr>
</tbody>
</table>

Table 1 shows that all samples were below the detection limit; 0.10 mg/kg for Cu and 0.50 mg/kg for Al. This indicates that the corrosion was much lower in aluminum and one reason was probably the protective oxide layer on aluminum.

The acid concentrations can be seen in Figure 63.
Acid concentrations in B100 with aluminium

![Acid concentrations in B100 with aluminium](image)

Figure 63. Acid concentrations over time in B100 aging with aluminium at 80 °C.

Acid concentrations in B100 aged in contact with aluminium (Figure 63) showed lower concentrations as expected from a less degraded fuel as seen in Figure 62. Less degradation and therefore lower acid concentrations could also explain the less corrosion seen from the metal concentrations.

Water content is shown in Figure 64.

Water content in B100 with aluminium

![Water content in B100 with aluminium](image)

Figure 64. Water content over time in B100 aging with aluminium at 80 °C.

Water content (Figure 64) showed lower levels than when aging B100 fuel with copper (Figure 30). This was expected since the fuel was less degraded.

Figure 65 shows images of the aluminum coupons aged with B100.
Figure 65. Aluminum coupons exposed to B100 with aging times from 8 to 140 hours. Red circles highlight products stuck on the surface. Note that the black holes are already present in the material from the manufacturing.

The black dots (8-140 h in Figure 65) were defects from the production of the aluminum. These voids could possibly be weak spots for corrosion; products could easily adhere inside them. In most images darker areas over the surface are seen: this was B100 fuel not washed away from the coupon. This since the fuel was left in the voids when washing and the B100 then spreads over the surface. No corrosion damage was however seen on any of the coupons. Only some products could be seen on the coupons at 124 and 140 hours. There was no evidence that aluminum could accelerate the degradation of B100 under these conditions.
6 Conclusions

Summarizing the conclusions on the corrosion behaviour and chemistry of RME fuel:

- Maintaining B100 fuel at 80 °C in presence of air (oxygen) caused it to degrade; after between 48-72 hours it had no more oxidative stability left. At the same time as the B100 fuel passed the induction point, acid concentrations dramatically rose together with water content. Acid and water were byproducts of the degradation of the fuel and hygroscopy could also increase with the degradation.

- The stable period of copper corrosion has been confirmed and occurs around 18-56 h of aging B100 fuel at 80 °C with copper. The stable period was not directly connected to the oxidative stability as previously believed, however it followed acid concentration and possibly water content. This stable period could also be seen on visual analysis of the copper plates; corrosion was not visible until 48 h.

- The stable period was conformed to be due to the properties of the material and not the fuel. Likely it was caused by a protective layer consisting of corrosion products formed on the copper surface.

- Solved water in unaged B100 quickly evaporated which confirmed that the hygroscopy increases with the aging and possibly that water was produced in the degradation. Added formic acid went into equilibrium with either adsorption on the distillation glass surface or something in the B100 fuel leaving two thirds of the original formic acid.

- Added formic acid increase corrosion and prevented any protective layer to form. The decrease in copper levels from 48 to 100 hours pointed to formation of salts. The lower formic acid levels when having copper comparing when not having copper also pointed to formation of salts between copper and formic acid.

- Adding free water increased corrosion drastically and the reason was probably because acids went into the water phase creating a very acidic aquatic phase.

- Visually evaluating the corrosion on copper over time made it clear that the corrosion damage increased exponentially with time. The high acidic levels probably etched the surfaces at 140-164 hours and dissolved the corrosion products.

- Looking at what happens at the end of the stable period (72 hours): moist air did not affect corrosion, added formic acid gave higher corrosion while higher added levels did not affect (at 250-450 mg/kg) and free water gave much higher corrosion.

- FTIR analysis confirmed salt formation on the copper surface and higher copper and acids levels seemed to increase the salt formation.

- Brass accelerated the aging of B100 fuel but to a less extent than pure copper. This also gave lower acid levels which could give less corrosion on the brass. A stable period similar to copper was observed but at lower copper levels (4-8 times) and this needs to be confirmed with longer aging times. The corrosion resistance on brass in B100 fuel also seemed higher because of the low copper levels even considering the brass only had a copper level of 58 % and less acids in the fuel.
- Aluminum did not accelerate the aging of B100 fuel in this experiment. The acid levels were therefore lower compared to when aging with copper. This together with the fact that aluminum has a stable oxide layer which protects the aluminum is probably why no corrosion was detected. Aluminum has low electrode potential and is prone to oxidizing. However, the oxide layer on aluminum was already oxidized. It was therefore stable and protected the aluminum metal.

The proposed evaluation methods from the results:

- Corrosion of copper can be evaluated by measuring the copper concentration in an aging system with B100. The corrosion can be deemed stable if the stable period has not been passed and this is connected with copper concentration in the B100 fuel. Copper concentration over a certain level will indicate that the corrosion has passed the stable period. In this bench scale experiment with 250 ml B100 and 40 cm$^2$ area copper this level was above 5 mg Cu/kg B100.

- The knowledge that there is a stable corrosion period can be used to evaluate other copper alloys. Similarly, reference curves for copper corrosion can be obtained for each copper alloy according to the method in 4.2. If they exhibit a stable period when aging B100 with them, the level of copper can be used as indicator.

- The knowledge that there is a stable period can be used in field tests (engines) to understand the behaviour of corrosion of copper and to design a stable window, where the stable period is and there is no further corrosion. Important to remember is that copper corrosion behaviour can be drastically different in field tests (engines) compared to the lab scale experiments performed in this Master’s thesis. This because of different temperature, flow patterns, additional factors, etc.
7 Future work and recommendations

Suggested future work and recommendations:

- Aging B100 with brass over longer times needs to be done to confirm that there is a stable period as with pure copper.

- Look at how acid and water additions affect brass corrosion in B100. This is to confirm that the behaviour is similar as for pure copper.

- Aging B100 with aluminum over longer times needs to be done to confirm that aluminum doesn’t show corrosion on longer aging times.

- Look at the brass’s microstructure after aging to confirm that the corrosion follows copper concentration and if zinc leaches from the brass.

- Look at how acid and water additions affect aluminum corrosion in B100. This is to confirm that the behaviour is similar as for pure copper.

- Other metallic materials than copper, brass, and aluminum can be aged in B100 to see if they also show a stable period in their corrosion.

- In field test (engines) it would be possible to design stable windows for other metallic materials by the same method if they also exhibit a stable period in their corrosion. Important to note is that the corrosion behaviour can be drastically different in field tests (engines) compared to the lab scale experiments performed in this Master's thesis. This because of different temperature, flow patterns, additional factors, etc.
8 References


