

Preparation and Characterization of a Stable Test Fuel Comparable to Aged Biodiesel for Use in Accelerated Corrosion Studies

Annika Talus and Lisen Johansson
Swerea KIMAB AB

Francesco Regali and Ali Saramat
Scania CV AB

ABSTRACT

Biodiesel is chemically unstable and sensitive to oxidation. Aging of biodiesel results in the formation of degradation products, such as short chain fatty acids (SCFA) and water. These products may cause corrosion of metals in fuel systems. When performing corrosion tests, biodiesel continuously degrades during the test, resulting in an uncontrolled test system. In order to obtain a stable corrosion testing system, a test fuel was developed using a saturated FAME (methyl myristate), which was doped with RME degradation products at levels typically seen in field tests. The test fuel was compared to RME with regards to structure, SCFA and water content before and after aging tests.

In addition, an accelerated corrosion study of copper was performed in both the test fuel and in RME. The copper specimens were analyzed before and after test using light optical microscope and weight measurements. The Cu content in the test fuel and RME was also analyzed.

The results show that the proposed test fuel is chemically stable and satisfies the targeted acceptance criteria of solubility of degradation products and oxidation stability. The corrosion behavior of copper in the test fuel shows similarities regarding corrosion products and deposits formed compared to copper corrosion in RME.

The proposed test fuel enables laboratory tests where parameters affecting corrosion can be kept constant and studied separately. This allows for the development of methods for screening corrosion properties of components and materials in the fuel system.

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INTRODUCTION

As fossil fuel resources are decreasing, there is a growing need for alternative energy resources. Biodiesel is a renewable fuel resource which can be used in existing oil heating systems and diesel engines without significant alterations to the systems. Chemically, biodiesel consists of mono-alkyl esters of long chain fatty acids which are commonly derived from the reaction between renewable feedstock, such as vegetable oils and alcohol [1]. Despite having many advantages there are some disadvantages with biodiesel that make it problematic, especially when it comes to usage during longer periods. Biodiesel degrades with time due to oxidation of double bonds in the carbon chains, forming harmful degradation products which may cause corrosion of metals. The main degradation products are short chain fatty acids (SCFA) and water [2, 3, 4]. The degradation process involves several reaction steps, i.e.

initiation, propagation/radical formation and termination [5, 6]. Peroxidation processes are a part of the propagation step and besides SCFA, result in formation of sludge causing internal injector deposits (IID) and fuel filter blocking (FFB) and/or aldehydes [7, 8, 9, 3]. The test fuel in this work is aimed for studying the effect of water and SCFA on metal corrosion.

The degradation of biodiesel is a continuous process, accelerated by the presence of oxygen, water and catalyzed by metals. Therefore, the amounts of corrosive degradation products increase with aging time, making accurate corrosion tests at the laboratory scale impossible. Due to fuel degradation, acidity of biodiesel, water content and other parameters affecting metal corrosion change during exposure time. This results in an uncontrolled system in which the effect of single parameters is very difficult to study.

The aim of this work was to develop a stable test fuel simulating a degraded biodiesel with a specific amount of SCFA and water aimed for use in accelerated corrosion tests of metal materials in a closed system in the laboratory. A secondary objective was to study the corrosion of copper (Cu) by the use of the developed test fuel in an accelerated corrosion tests (closed system, autoclaves) and to compare the result with a corrosion test in biodiesel (RME) performed in an open system.

EXPERIMENTAL

This study includes the following steps:

1. *Development of a test fuel* for accelerated corrosion tests. Stability tests have been performed in autoclaves for RME and the proposed test fuel.
2. *Corrosion test of Cu in RME* in an open system for three degradation points (acidity levels).
3. *Accelerated corrosion test of Cu in the test fuel* in a closed system, simulating acidity levels achieved in (2) with proposed test fuel from (1).

In the open system with unlimited access to oxygen degradation of an unstable fuel like RME is expected and also corrosion of materials exposed in the fuel. In a closed system, the limited access to oxygen would mainly cause fuel degradation and is not believed to be sufficient for a simultaneous corrosion process. A closed system can however be considered a more controlled test system since no evaporation occurs during the test and the oxygen amount in the system is known. In combination with a stable test fuel, not sensitive to degradation, the closed test method would be a good alternative for accelerated corrosion tests since the oxygen is not consumed by fuel degradation.

Methods for analyzing the fuel samples during the study have been the following: ion chromatography (IC) for SCFA; gas chromatography with mass spectrometry (GC-MS) for fuel composition; inductively coupled plasma optical emission spectroscopy (ICP-OES) for metal ions; and Karl Fischer volumetric titration (KF) for water content analyses. For most fuel analyses only one sample from each test was evaluated and the standard deviations given in the data tables represent the accuracy in the test method and not the spread between samples. For the metal specimens in the study, weight measurement was used as the evaluation method, and two or three samples from each test were evaluated, with the standard deviation representing the spread between the samples.

Development of Test Fuel

In order to develop a test fuel not susceptible to degradation during testing, several saturated esters were considered. After evaluation of melting point, flash point and solubility, methyl myristate (C14:0) was chosen as the base fuel for this study. Methyl myristate consists of 14 carbon atoms with no double bonds (C14:0). Degradation products, (water and SCFA) were added based on typically observed levels from real-world field tests performed by Scania CV AB, [Table 1](#).

Table 1. Concentrations of degradation products in the test fuel (mg/kg).

Water	460
Formic acid	20
Acetic acid	10
Propionic acid	5

In the accelerated corrosion tests, the test fuel should be stable with respect to the amount of degradation products. In order to evaluate its stability, the fuel was aged at 80°C for 120 h in a closed system, which would prevent evaporation of added degradation products. In this closed system the fuel/air ratio was approximately 0.43 ml/ml in the autoclave at closure. For comparison, biodiesel (RME) was aged in the same way. The fuels were analyzed before and after aging with respect to composition and the antioxidant vitamin E using GC-MS, water content using KF and SCFA content using ion IC [2].

Corrosion of Cu in RME and Test Fuel

In order to verify that the corrosion observed in an accelerated corrosion test in a closed system using test fuel is comparable to that observed in an open test system using degraded biodiesel, a corrosion study of Cu specimens was performed using both methods.

Corrosion Test of Cu in RME

For the corrosion test with RME, an open system consisting of a three neck laboratory glass equipped with a cooler was used. This system was equipped with stirring and had unlimited access to air through a drying tube at the top of the condenser and Cu specimens were immersed in 250 ml RME, according to [Figure 1](#). The temperature for the test was set to 80°C and three exposure times were utilized, 24, 48 and 72 h, respectively. The water content and SCFA were measured in the RME before test and after 24, 48 and 72 h of Cu-exposure. Additionally, the levels of Cu ions in the fuel were analyzed before and after the test. The metal specimens were evaluated by weight change measurements (from duplicate samples) and surface appearance by the use of light optical microscope (LOM).



Figure 1. Exposure of Cu specimens to RME in an open system at 80°C during 24, 48 and 72 h.

Accelerated Corrosion Test of Cu in Test Fuel

Three test fuels (A, B and C) were prepared in order to simulate aged RME, based on the SCFA and water concentrations observed in the test with RME after 24 h (test fuel A), 48 h (test fuel B) and 72 h (test fuel C), Table 2. An accelerated corrosion test was performed for Cu in all three test fuels during 24 h at 80°C in a closed autoclave system, Figure 2. Each Cu specimen was exposed in 100 ml test fuel and the total volume of the autoclave was 1000 ml meaning an air head space of approximately 700 ml was present in the autoclave since three samples were exposed in each autoclave. The test fuels were evaluated with respect to water, SCFA and Cu ion content after exposure (one sample from each test fuel). The metal specimens were evaluated by weight change measurements (three samples) and surface appearance using LOM.



Figure 2. Exposure of Cu specimens to test fuel simulating three levels of degradation of RME (24, 48 and 72 h respectively).

Additionally, myristic acid was added to the test fuels in order to further simulate actual biodiesel. The presence of longer fatty acids in the fuel is not believed to affect corrosion of the Cu specimens to the same extent as the shorter acids. However, the solubility of corrosion products is one factor which might be affected by longer fatty acids. Myristic acid was chosen in order to use a similar carbon chain length for the acid as the base fuel (C14). The added levels of myristic acid

were calculated based on fuel analysis in previous studies [2] giving the ratio of SCFA and longer fatty acids in fresh RME. A simplification was made to keep the amounts of long chain fatty acid constant in the three test fuels, since the increase of long chain fatty acid and its additional effect on corrosion is lower compared to that of SCFA. The composition of the test fuels A, B and C is given in Table 2.

Table 2. Concentrations of degradation products in test fuel used in accelerated corrosion tests in closed system (mg/kg).

Compound	A	B	C
Water	350	750	1100
Formic acid	50	150	250
Acetic acid	15	30	50
Propionic acid	7	15	25
Myristic acid	400	400	400

RESULTS AND DISCUSSION

Stability of Test Fuel and RME

GC-MS analysis of the fuels showed that the only ester found in the test fuel before and after exposure was the saturated methyl myristate ester C14:0. The result confirms that no impurities of unsaturated esters are present which can lead to oxidation and change the composition. The RME fuel consisted of several unsaturated and saturated esters at levels given in Table 3, and no significant change could be measured with the technique used after aging. With this technique a change of approximately 2% would have been needed in order to draw any conclusions regarding compositional change. For the antioxidant E-vitamin a decrease from 115 mg/kg to 60 mg/kg was measured after exposure. In the test fuel no antioxidant was added.

Table 3. Composition of RME (wt-%).

	C16:1	C16:0	C18:2	C18:1	C18:0	Other
Before	0,3	4,3	17,7	74,4	1,3	1,9
After	0,3	4,4	17,4	74,7	1,3	1,8

The analysis of SCFA in the fuels shows that the added SCFA levels remain stable in the test fuel during exposure, Figure 3, while formic acid and acetic acid levels increase in the RME, Figure 4. The measured levels are still relatively low and for propionic acid the levels are below the detection limit both before and after exposure. This low increase of SCFA in RME indicates that the degradation in a closed system is suppressed comparing to that of an open system at similar exposure times [3].