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Laboratory Oxidation Stability Study on B10 Biodiesel Blends

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Laboratory Oxidation Stability Study on B10 Biodiesel Blends

This study was conducted jointly by CONCAWE and DGMK[1]:

CONCAWE:
B. Engelen (Chair)
L. Baldini
T. Cipriano
C. Diaz Garcia
N. Elliott
G. Fiolet
G. Giammarco
A. Jackson
M. Krár
T. Kweekel
S. Mikkonen
W. Mirabella
K. Murphy
A. Nieto Riaguas
C. Olivares Molina
A. Orfaniotis
S. Sasloglou
R. Terschek
J. Woldendorp

K.D. Rose (Science Executive)

DGMK:
M. Schmidt
I. Stopper
J. Baumgarten
U. Nowak
U. Mayer

Brussels
November 2013

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[1] Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V. (German Society for Petroleum, Gas and Coal Science and Technology)

ABSTRACT

A laboratory oxidation stability study has been completed jointly by CONCAWE and DGMK on three biodiesel blends containing 10% v/v (B10) Fatty Acid Methyl Ester (FAME). The results of the study are compared to measurements from an in-vehicle storage stability study on similar B10 diesel fuels that had been conducted previously in a Joint Industry Study[2].

This laboratory study monitored the oxidation stability of the three B10 blends during six weeks of laboratory storage under ambient (25°C) and elevated temperature (43°C) conditions. Various test methods were used to monitor oxidation stability changes in the B10 diesel fuel blends including electrical conductivity, viscosity, Rancimat oxidation stability (EN 15751), PetroOxy oxidation stability (EN 16091), acid number (EN 14104), Delta Total Acid Number (Delta TAN), and peroxide number (ISO 3960). Elemental analyses by ICP were also completed on the FAME and B10 blends at the start and end of the laboratory study. The concentrations of dissolved metals were very low in all cases except for silicon which was found to be between about 600-700ppb in the B10 blends. A limited study was also conducted on one neat FAME sample (B100) to investigate the effect of air/oxygen exposure on the rate of decrease in oxidation stability.

KEYWORDS

FAME, biodiesel, oxidation stability, Rancimat, PetroOxy, peroxide number, acid number, delta TAN

INTERNET

This report is available as an Adobe pdf file on the CONCAWE website (www.concawe.org).

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[2] "Effect of in vehicle storage on B10 diesel quality, a Joint Industry Study sponsored by the petroleum industry, automotive, and fuel injection system industries" [7]

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SUMMARY

A laboratory oxidation stability study has been completed jointly by CONCAWE and DGMK on three biodiesel blends containing 10% v/v (B10) Fatty Acid Methyl Ester (FAME). The study monitored the oxidation stability of these blends during six weeks of laboratory storage under ambient (25ºC) and elevated temperature (43ºC) conditions. Various test methods were used to monitor oxidation stability changes in the B10 diesel fuel blends including electrical conductivity, viscosity, Rancimat oxidation stability (EN 15751), the PetroOxy oxidation stability (EN 16091), acid number (EN 14104), Delta Total Acid Number (Delta TAN), and peroxide number (ISO 3960). An additional study was conducted to investigate the impact of air/oxygen exposure on the rate of oxidation stability decrease for one neat FAME (B100) sample.

The objective of this laboratory study was to explore unresolved questions from a previous Joint Industry Study [7] that investigated biodiesel aging in parked vehicles. In this previous study, three B10 blends having different initial Rancimat oxidation stability values were stored under summer temperature conditions in six test vehicles, three passenger cars and three vans, over an elapsed period of 6 months.

In order to relate the results of this laboratory study to the previous vehicle aging study, three B10 fuels were re-blended having similar initial oxidation stabilities to the B10 fuels used in the previous vehicle study. FAME blends of Rapeseed Methyl Ester (RME) and Soya Methyl Ester (SME) and the addition of different quantities of antioxidant were used to achieve this variation in initial oxidation stability.

Compared to the rapid initial drop in oxidation stability observed for the B10 diesel blends in vehicle tanks, very little aging was observed for similar B10 diesel blends under laboratory conditions at both 25°C and 43°C storage temperatures. These differences between studies may have been due to the following factors:

- Different storage conditions for the fuels in vehicle tanks compared to uncapped glass bottles in the laboratory resulting in different air/oxygen availability in the fuels under the given storage conditions and time.
- During the vehicle aging study, the diesel fuels were periodically agitated and mixed in the vehicle tank. This was done by operating the vehicles for six hours at the start of the 6-month aging period and by idling the engine for 15 minutes two times per week after the start of testing.
- In addition to aerating the fuel, this procedure ensured that a small amount of fuel was exposed to higher temperatures in the fuel injectors and returned to the vehicle's fuel tank, potentially increasing the contribution from thermal oxidative aging.
- In both studies, there was the possibility that trace amounts of dissolved metals could have catalysed oxidative aging to some extent. However, direct measurements of dissolved metals in the diesel blends, both initially and at the end of the studies, suggested that catalytic metals were very low in concentration and not an important contributor to oxidative aging in both of these studies.

Based on the combined results of the vehicle and laboratory studies, it is concluded that an important contributor to the rapid drop in oxidative stability of the B10 fuels was the oxygen availability. The periodic idling of the engine in the vehicle study ensured that the oxygen concentration was sufficient to encourage oxidation.

The results of this laboratory oxidation storage study on B10 biodiesel fuels are expected to provide valuable information to fuel blenders both for today's B7 market fuels allowed according to the EN 590 [4] specification and as input to future discussions regarding diesel blends having FAME concentrations higher than B7.

1. BACKGROUND

The European Renewable Energy Directive [1] (RED, 2009/28/EC) mandates the use of 10% renewable energy in transportation by 2020. Transport fuels are defined in this context as gasoline, diesel, and biofuels for road and rail transport as well as electricity for battery electric vehicles. This mandate for transport fuels relates not only to the use of biofuels, such as Fatty Acid Methyl Ester (FAME) and bioethanol, but also to renewable electricity and hydrogen from renewable sources. A parallel legislation, the European Fuel Quality Directive [2] (FQD, 2009/30/EC), requires a 6% reduction in the greenhouse gas (GHG) intensity of transportation fuels by 2020, compared to a 2010 baseline, which may largely be achieved by blending sustainably-produced liquid biofuels having favourable GHG footprints. Both targets must be met.

Increasing the allowed biofuel blending in market gasoline and diesel is an important way to achieve the RED and FQD targets as long as vehicles are fully compatible with market blends. While gasoline containing up to 2.7 wt% oxygen using ethanol or ether is widely available, some gasoline containing up to 3.7 wt% oxygen is already in use in some countries. These gasoline blends are commonly called ‘E5’ (up to 2.7 wt% oxygen) or ‘E10’ (up to 3.7 wt% oxygen). European gasoline vehicles are not yet warranted for oxygen levels higher than 3.7 wt% except for those that are marketed as flexi-fuel (E85) vehicles.

For diesel fuels, up to 7% v/v FAME (B7) in diesel fuel is currently allowed by the EN 590 standard. Although FAME blends at 10% v/v FAME (B10) or higher might enable fuel suppliers to approach the RED and FQD targets, most passenger cars are not warranted to operate at FAME levels higher than B7 due to concerns with regulated emissions, lubricant degradation, and performance durability. In addition, Indirect Land Use Change (ILUC) effects, associated with vegetable oils used to manufacture FAME, limit the GHG reduction value of these products.

Concerns have also been expressed about the sensitivity of FAME and FAME blends to oxidation instability. Oxidation stability quality requirements have been included in the EN 14214 [3] standard for neat FAME (B100) and in the EN 590 [4] standard for diesel fuel containing more than 2% v/v and less than 7% v/v FAME. These standards and other references [8] recommend the addition of oxidation stability enhancing additives to the FAME product as soon as possible in the manufacturing process in order to protect the FAME from oxidation and degradation before and after blending.

Because of these fuel stability concerns, a Joint Industry Study was conducted in 2008, and reported in 2010 [7]. In this study, six vehicles that had been partially filled with different B10 diesel fuel blends were parked for long periods of time at high ambient (summertime) temperatures. These conditions simulated a worst case scenario for fuel aging such as for a vehicle parked unattended in hot summertime temperatures at an airport parking lot or on a dealer’s forecourt.

The hypothesis for this vehicle study was that B10 fuels in vehicle tanks could degrade quickly under some conditions and cause performance problems for fuel filters, injectors, or other engine parts. The objective then was to investigate the change in properties of B10 fuels under extreme but potentially ‘real world’ vehicle conditions, as described in the next section. Other studies have also investigated the oxidation stability of FAME and low-level biodiesel blends and its impact on vehicle performance [9,10,11,12].

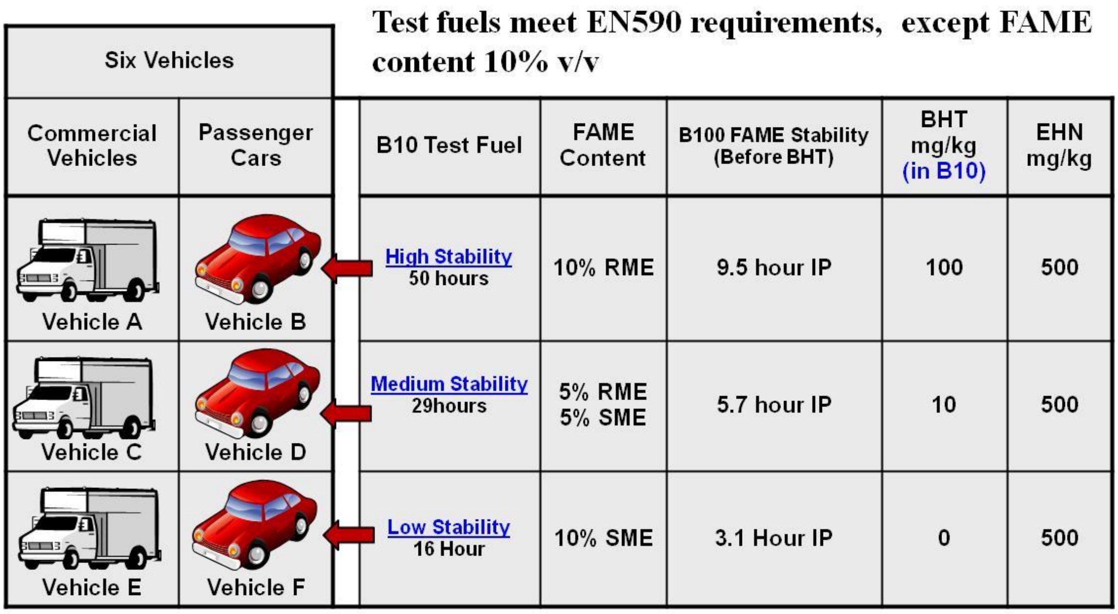
2. JOINT INDUSTRY STUDY ON FUEL AGING IN VEHICLES

To achieve the objectives of this vehicle study, six different vehicles (three light-duty vans and three passenger cars) were parked for 27 weeks (six months) at a test facility in southern France. The vehicles were parked outdoors from the late spring until the early autumn during which time they experienced a range of warm to hot temperature conditions. Details on this vehicle aging study can be found in [7].

Three B10 fuels having different initial oxidation stabilities were blended by CONCAWE for the vehicle study from two types of FAME (RME and SME) and the blended diesel fuels were put into the vehicle tanks to ½ to ¾ of the total tank volume at the start of the aging test.

Figure 1 shows the six vehicles and the B10 fuels that were stored in each vehicle. In order to achieve a range of initial oxidation stability values for the three B10 fuels, FAME mixtures having different oxidation stability were blended into one diesel base fuel. Two of the B10 fuels were blended with different amounts of the antioxidant BHT (butylated hydroxy-toluene) to improve their initial stability. The third B10 fuel, which had the lowest initial oxidation stability, had no antioxidant treatment. Each fuel blend also received 500 ppm of Ethyl-Hexyl Nitrate (EHN) combustion improver which could contribute to fuel instability at elevated temperatures.

Figure 1 B10 fuel matrix for the Joint Industry Study on vehicle aging [7]



Test fuels meet EN590 requirements, except FAME content 10% v/v

Six Vehicles						
Commercial Vehicles	Passenger Cars	B10 Test Fuel	FAME Content	B100 FAME Stability (Before BHT)	BHT mg/kg (in B10)	EHN mg/kg
Vehicle A	Vehicle B	High Stability 50 hours	10% RME	9.5 hour IP	100	500
Vehicle C	Vehicle D	Medium Stability 29hours	5% RME 5% SME	5.7 hour IP	10	500
Vehicle E	Vehicle F	Low Stability 16 Hour	10% SME	3.1 Hour IP	0	500

In order to simulate occasional vehicle use and long-time parking, each test vehicle was operated at the start of the 6-month test for 6 hours. In each following week, the vehicles were idled for 15 minutes twice per week. Fuel samples were withdrawn from the vehicle tanks each week and several different oxidation stability analyses were completed:

- modified Rancimat (EN 15751) [6];
- PetroOxy (EN 16091) [5];

- Delta TAN, or the change in Total Acid Number; and
- EN 12205 (insolubles) [11].

This test procedure meant that the volume of diesel fuel in the vehicle tank continuously dropped from its initial ½ to ¾ of the total tank volume over the course of the study.

In addition to the samples withdrawn from the vehicle tanks, the same three B10 fuel blends were also stored in sealed drums under different conditions (best case: in epoxy-lined steel drums inside the laboratory at room temperature; worst case: in polyethylene drums stored outside the laboratory in a shaded enclosure) in order to compare the change in oxidation stability with the samples from vehicle tank storage. All fuel sampling from the vehicle tanks and drums and the laboratory analysis of the fuels were conducted by the testing facility.

The oxidation stability test results, based on the modified Rancimat test, are shown in **Figures 2, 3** and **4** for the high, medium and low initial stability B10 fuels. A similar trend in the oxidation stability change was found with the PetroOxy method.

Figure 2 Change in modified Rancimat (EN 15751) oxidation stability for the B10 diesel fuel having the highest initial stability (50 hours)

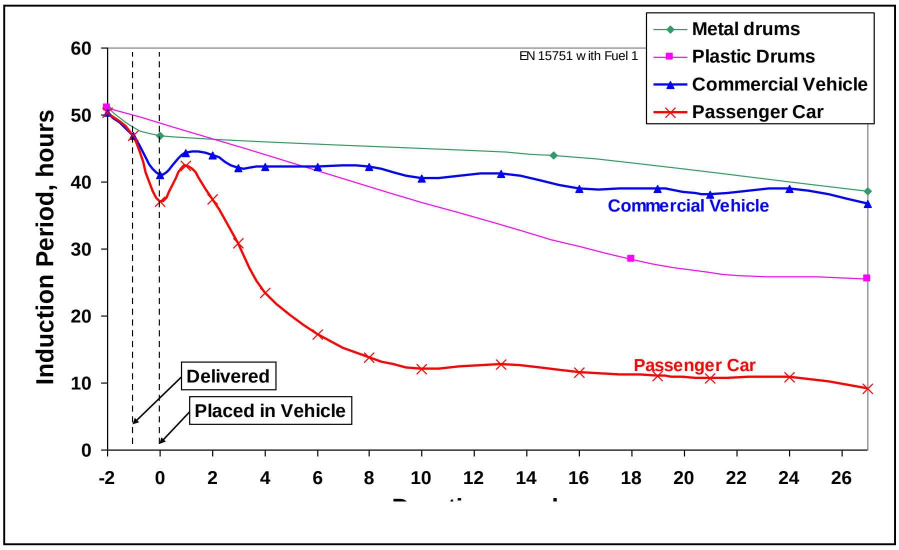


Figure 3 Change in modified Rancimat (EN 15751) oxidation stability for the B10 diesel fuel having an intermediate initial stability (29 hours)

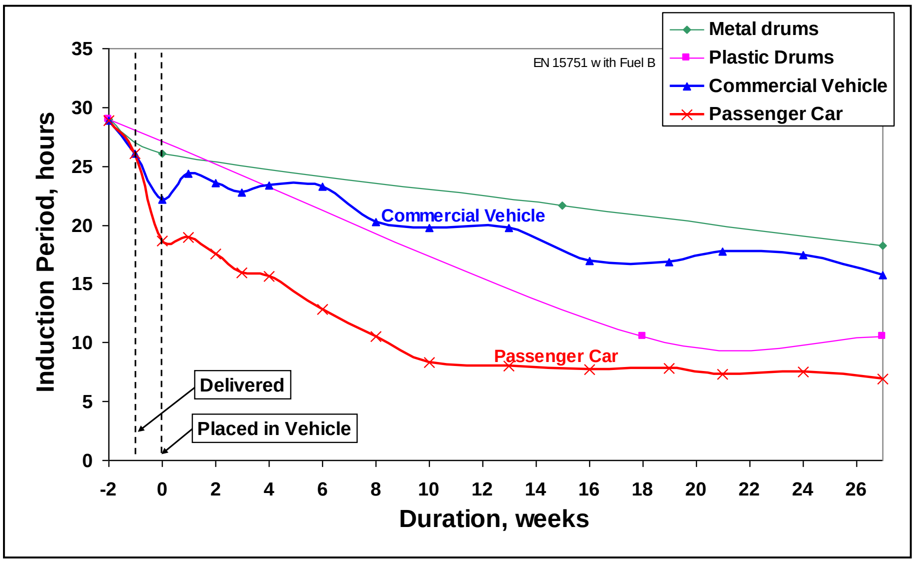
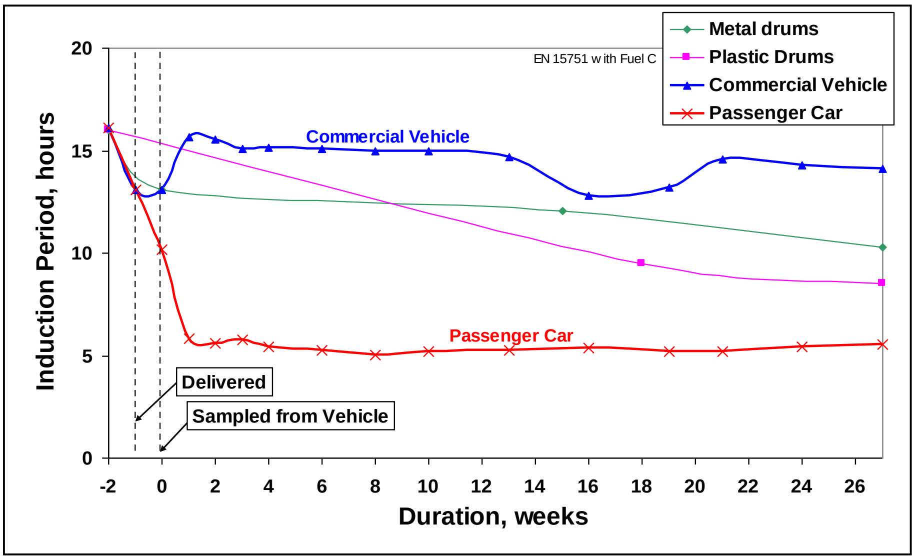


Figure 4 Change in modified Rancimat (EN 15751) oxidation stability for the B10 diesel fuel having the lowest initial stability (16 hours)



These figures show that the fuel's oxidation stability decreased slightly for all three B10 blends between the initial blending and filling into the vehicle tanks, an elapsed time of approximately two weeks. Similar trends were observed between the Rancimat and PetroOxy test results. This decrease in oxidation stability could be due to reproducibility differences between the two different measurement laboratories (that is, the blending laboratory and the test facility where the aging study was completed). Alternatively, they could indicate a real decrease in oxidation stability due to several decanting processes before the fuels were placed in the vehicle tanks.

After the fuels had been placed in the vehicle tanks and the aging test procedure was started, the following trends in oxidation stability were observed for each of the three B10 fuels.

- A relatively slower decrease in oxidation stability was observed for the B10 diesel fuels withdrawn from the commercial vehicles compared to those withdrawn from the passenger cars. The rate of aging in the commercial vehicles was generally lower than for the fuels stored in the sealed polyethylene drums and in some instances was similar to that observed for fuels stored in the epoxy-lined steel drums.
- Compared to the commercial vehicles, more rapid fuel aging was observed in all three passenger cars. Here the Rancimat stability values decreased quite quickly by about 75% over the first 8 to 10 weeks of storage for the high- and medium-stability B10 blends. For the low-stability B10 blend, the largest decrease occurred within the first 2 weeks of storage in the passenger car. After these initial decreases, the Rancimat oxidation stability values levelled off for each B10 blend.
- Considering the differences that were observed between the commercial vehicles and passenger cars, it is possible that the fuel tanks' size, shape, and material of construction, as well as the fuel system materials, might be different and result in different oxygen concentrations in the fuel and different thermal exposure of the fuel in the vehicle tanks. Unfortunately, there was not enough information provided on the vehicle tanks and fuel system materials to fully understand these differences.
- The commercial vehicles had larger volume tanks than the passenger cars and this could have resulted in a lower ratio of fuel surface area to fuel volume and a lower concentration of dissolved oxygen in the fuel. This could be a reason for the smaller aging differences observed in the commercial vehicles compared to the passenger cars. However, there might also be other factors, such as the fuel line size and composition, injection system differences, and the exposure time of fuel to higher temperatures in the injectors and these effects could have contributed to the different aging patterns between vehicle types.
- Elemental analyses of the fuels at the end compared to the start of the storage period did not show appreciably higher levels of dissolved metals in the fuels, apparently ruling out the possibility of oxidation promotion by traces of dissolved metals.
- Comparatively slow rates of aging were observed for fuel samples taken from the sealed epoxy-lined steel drums stored inside the laboratory, possibly due to the lack of oxygen availability. A slightly larger drop in oxidation stability occurred for the fuels stored outside in polyethylene drums possibly due to the outside storage of these drums at higher ambient temperatures. This observation was unexpected, however, because oxygen availability was expected to have the largest effect in controlling the rate of change in oxidation stability.

An important observation from the study was that all six vehicles were able to start easily and drive at the end of the 6-month test period, even though the final oxidation stabilities of the B10 fuels in the vehicle tanks had stabilised at about 8 to 5 hours oxidation stability in the modified Rancimat test[3]. Photographs taken of the test fuels at the end of the storage period showed no evidence of fuel darkening or sediments (see **Figures A-2** and **A-3** in [7]).

The following questions were not resolved from the vehicle aging study:

- Why did the oxidation stability of all three B10 blends drop relatively quickly in the first weeks following blending? This occurred even for the B10 diesel that was stabilized with 100ppm BHT and had the highest initial Rancimat oxidation stability?
- Why did the three commercial vehicles show slower decreases in oxidation stability compared to the three passenger cars?
- Why did the storage in the plastic drums show different rates of oxidation stability decrease compared to the same fuels stored in vehicles?
- Would similar oxidation stability decreases also be seen in larger volume storage of B10 diesel fuel blends?

In order to evaluate these questions under more controlled conditions than were possible in the vehicle study, a laboratory oxidation stability study was completed which is the subject of this report.

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[3] In comparison, for diesel fuels dispensed at service stations that contain more than 2% and less than 7% v/v FAME, the minimum Rancimat oxidation stability limit in the EN 590 standard is 20 hours.

3. LABORATORY OXIDATION STABILITY STUDY ON B10 BLENDS

To evaluate these questions further, a laboratory oxidation stability study was conducted jointly by CONCAWE and DGMK. The objective of this laboratory study was to measure the change in oxidation stability under two different laboratory storage conditions using similar B10 diesel fuels to those used in the Joint Industry Study. A previous CONCAWE report [8] provided operational guidelines related to handling and blending FAME for diesel fuel use.

As was the case in the vehicle study, the fuel samples were analysed with different oxidation stability methods that are already included in the EN 590 specification or are being considered for future addition. It was expected that the results from this laboratory study could be used to relate the oxidation stability changes to those measured in the vehicle storage study. For this reason, the results of the lab study were intended to guide future B10 specifications for oxidation stability and test method developments.

Furthermore, the results were expected to provide valuable information to fuel blenders on biodiesel properties that are important to achieve good storage stability as well as providing an approach for comparing the performance of different antioxidant types and concentrations. The results of the lab study could also be used to relate the kinetics of oxidation under different storage conditions to fundamental properties of the FAME and diesel fuel blends.

3.1. FUELS FOR THE LABORATORY STUDY

In order to relate the results of this laboratory study to the vehicle aging study, the B10 fuels were intended to have similar initial oxidation stability values and compositions. The following fuels were blended for testing in this laboratory study:

- **B0:** diesel base fuel
- **B10 (RME):** blended from B0 and a high stability FAME (RME) + 100ppm BHT antioxidant in the B10 blend. The target value for this blend was an initial Rancimat (EN 15751) value greater than 48 hours.
- **B10 (RME/SME):** blended from B0 and a medium stability FAME mix (RME/SME) + 20ppm BHT antioxidant in the B10 blend. The target value for this blend was an initial Rancimat value between 20 and 30 hours.
- **B10 (SME):** blended from B0 and a low stability FAME (SME) without the addition of BHT antioxidant. The target value for this blend was an initial Rancimat value between 10 and 20 hours.

The Rancimat oxidation stability results after blending were:

EN 15751	**B0**[4]	**B10 (RME)**	**B10 (RME/SME)**	**B10 (SME)**
h	(20.8)	49.0	29.8	21.2

Detailed analytical results on the FAME samples can be found in **Appendix 1** and the results on the blended B10 fuels at the start of the laboratory study can be found in

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[4] This B0 fuel is out of scope for the Rancimat oxidation test method.

Appendix 2. The results obtained on the blended fuels are consistent with the above targets.

Other relevant fuel specifications included:

- The B0 diesel base fuel complied with the EN 590 standard;
- All FAME samples complied with EN 14214;
- 500 ppm of EHN combustion improver was added to all test fuels. This EHN concentration is typical of diesel fuels in the European market.

3.2. STORAGE CONDITIONS IN THE LABORATORY

The blended fuels were stored under two different conditions:

- Lab storage in inert borosilicate bottles at a constant temperature of 25^{o}C. The tops of the bottles were plugged with cotton wool to allow exposure to air.
- Accelerated laboratory storage at 43^{o}C following the principles of ASTM D4625 [14]. Glass fibre filters (0.8 micron) were substituted for the nitrocellulose filters specified in the test procedure in order to avoid potential problems with FAME-containing fuels. The accelerated storage at 43°C corresponds to about 4 times the storage time at 21°C based on the Arrhenius principle**.**

The same B10 blends at 25°C and at 43°C were stored for 45 days (about 6 weeks) in closed rooms without light. According to the ASTM D4625 procedure, 45 days storage at 43°C would relate to about 26 weeks storage at 21°C which was approximately the time that the B10 fuels had remained in the vehicle tanks from the Joint Industry Study. All B10 fuel samples were stored in 1-litre inert borosilicate glass bottles. For analysis a certain amount of fuel was taken from the bottle and filtered through a new glass fibre filter before analysis.

Photos of the sample bottles throughout the laboratory test are shown in **Appendix 3**. As can be seen, the colours of the B0 and B10 blends are somewhat different because of the properties of the FAME but the samples did not darken appreciably throughout the test. Slight sediments were reported in some sample bottles but the amount of sediment did not change appreciably throughout the storage period suggesting that the sediments were associated with trace insolubles in the initial B10 blends.

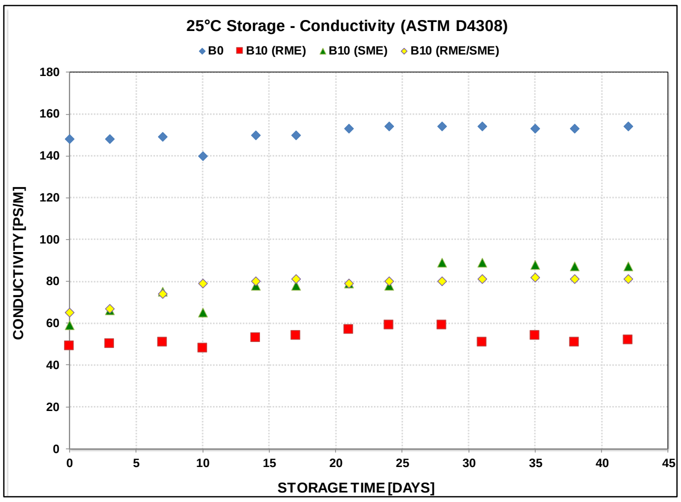
4. RESULTS FROM THE LABORATORY STORAGE STUDY

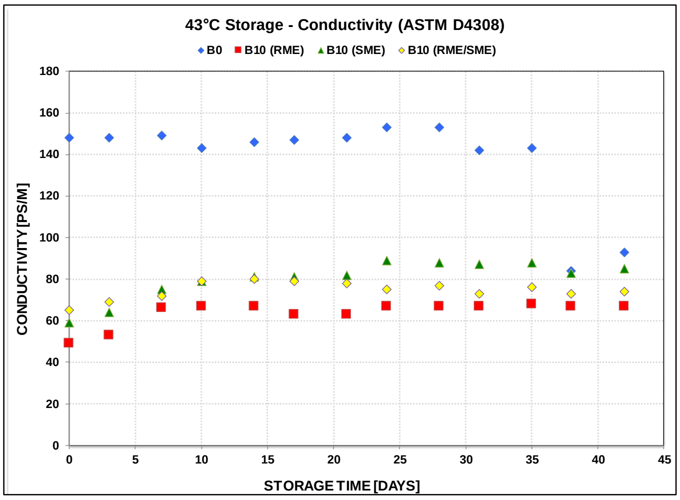
The initial analysis data of the 4 test fuels B0, B10 (RME), B10 (RME/SME) and B10 (SME) are shown in **Appendix 1**. The graphs for the selected fuels property changes over the storage time are shown in the next sections.

4.1. CONDUCTIVITY AND VISCOSITY

The conductivity of each sample was measured using ASTM D4308 [15]. As would be expected, **Figure 5** shows clear differences in the measured conductivity between the B0 and the B10 fuels. According to CONCAWE Report 9/09 [8], reductions in electrical conductivity have been observed upon blending FAME into diesel fuels that already contain conductivity improver additive. As FAME-containing fuels age, it is possible that oxidation products such as peroxides and acids could increase the conductivity. However, at the 25°C and 43°C storage conditions, no notable changes in electrical conductivity were observed for the B10 blends. The reason for the drop in electrical conductivity for the B0 fuel at the end of the 43°C storage period is not known and was not investigated further.

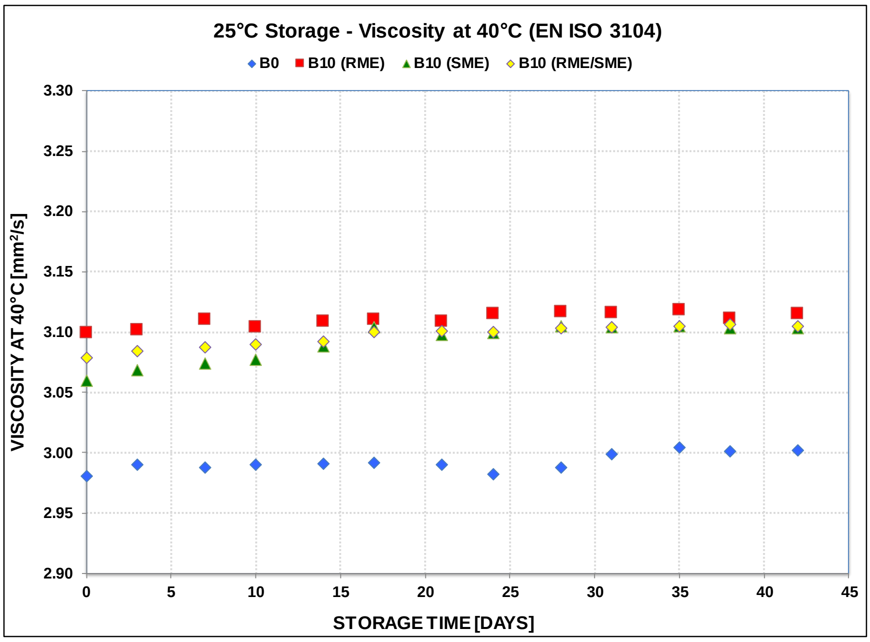
Figure 5 Conductivity changes at 25°C and 43°C

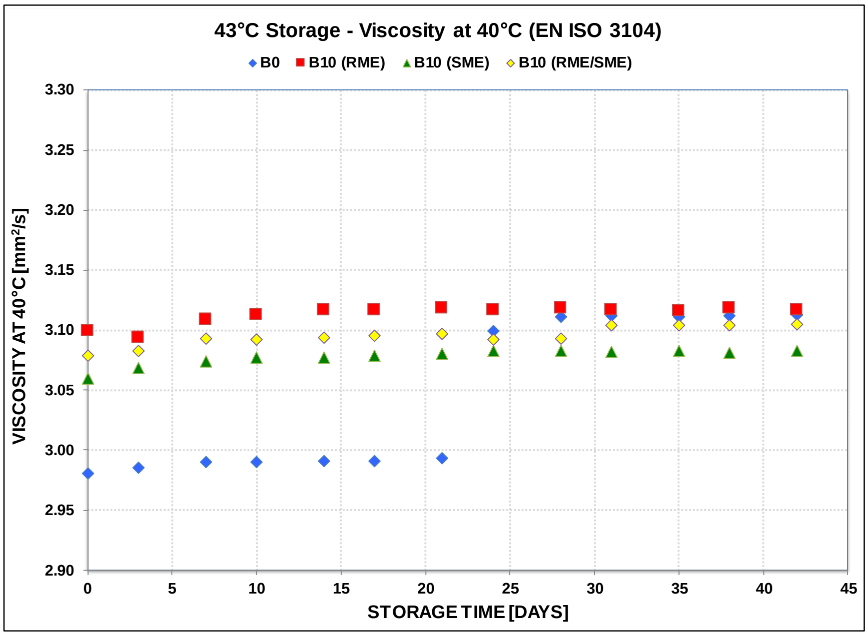




Aging of diesel/FAME blends might also lead to insoluble polymers and hence higher viscosity for the aged fuels. **Figure 6** shows that no notable viscosity increases were observed for the B10 blends at both storage temperatures. This is consistent with the visual appearance reported previously at the start of Section 5.

Figure 6 Viscosity changes at 25°C and 43°C





The viscosity increase for the B0 fuel at about 24 days storage time was unexpected but was not investigated further because the viscosity remained stable for the remainder of the storage time.

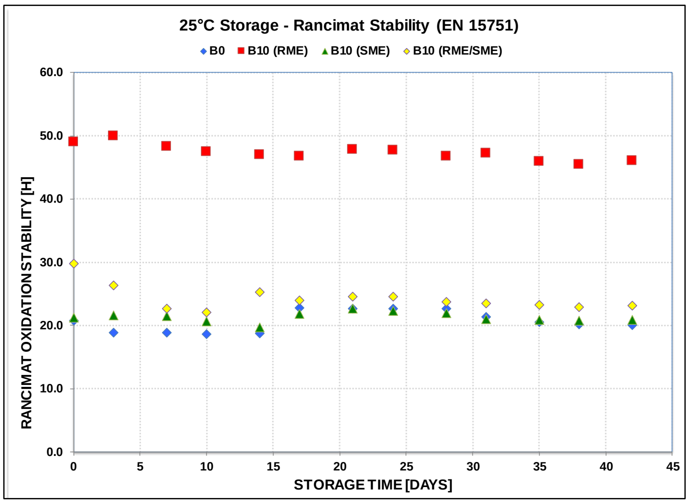
4.2. OXIDATION STABILITY

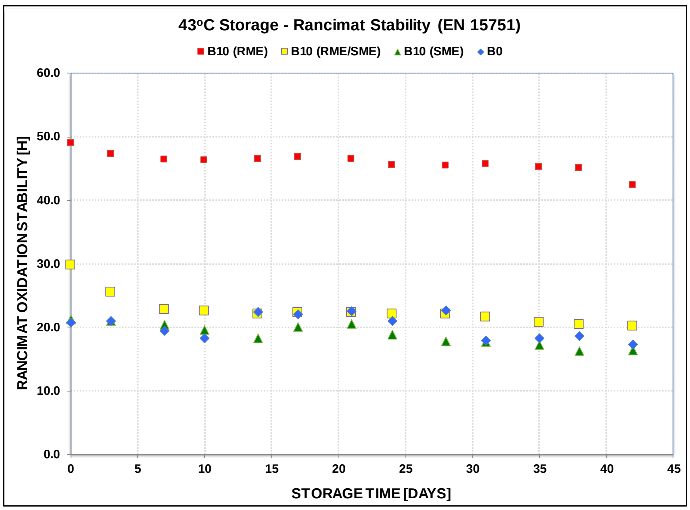
The modified Rancimat (EN 15751) and PetroOxy (EN 16091) test methods are key analysis methods here, with EN 15751 having been defined as a mandatory analysis for oxidation stability in the European diesel fuel specification EN 590. This method primarily monitors FAME oxidation and applies to diesel fuel blends that contain at least 2% v/v FAME.

4.2.1. Rancimat Oxidation Stability (EN 15751)

The Rancimat oxidation results at the 25°C storage condition show no notable degradation for the B0 and the three B10 fuels. For the B10 (RME/SME) blend, that had a medium initial Rancimat stability, a slight decrease was observed within the first 10 days but results stabilized after this time. The small oxidation stability change for the B10 (RME) having the highest initial Rancimat stability stayed within the normal variation of the Rancimat method over the entire storage period. The same trend was observed for the B10 (SME) having the lowest initial stability. The Rancimat results are shown for the B0 fuel even though this fuel is out of scope for this test method.

Figure 7 Rancimat results over storage time at 25°C and 43^{o}C





As shown in **Figure 7**, the higher storage temperature of 43°C, compared to 25°C, had very little impact on the Rancimat oxidation stability for all test fuels.

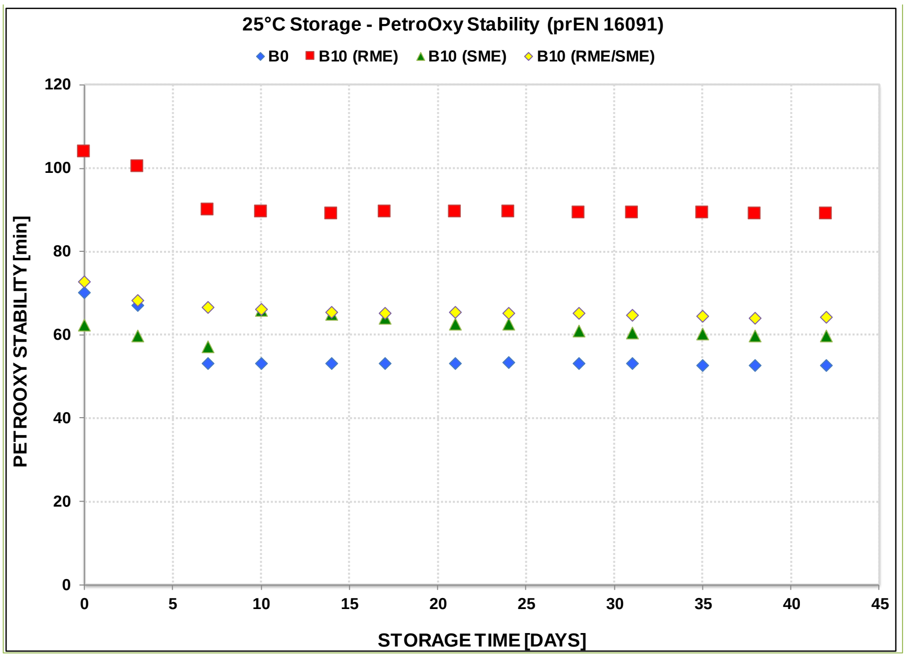
Overall, the trends in Rancimat oxidation stability for the B0 and three B10 diesel blends showed no notable aging at both storage temperatures. This result is quite different compared to the Rancimat trends observed for the fuels in the vehicle tanks of the Joint Industry Study that were shown in **Figures 2** to **4**. Even the storage of the B10 fuels in metal drums from the previous study showed larger decreases in Rancimat stability compared to the current laboratory study.

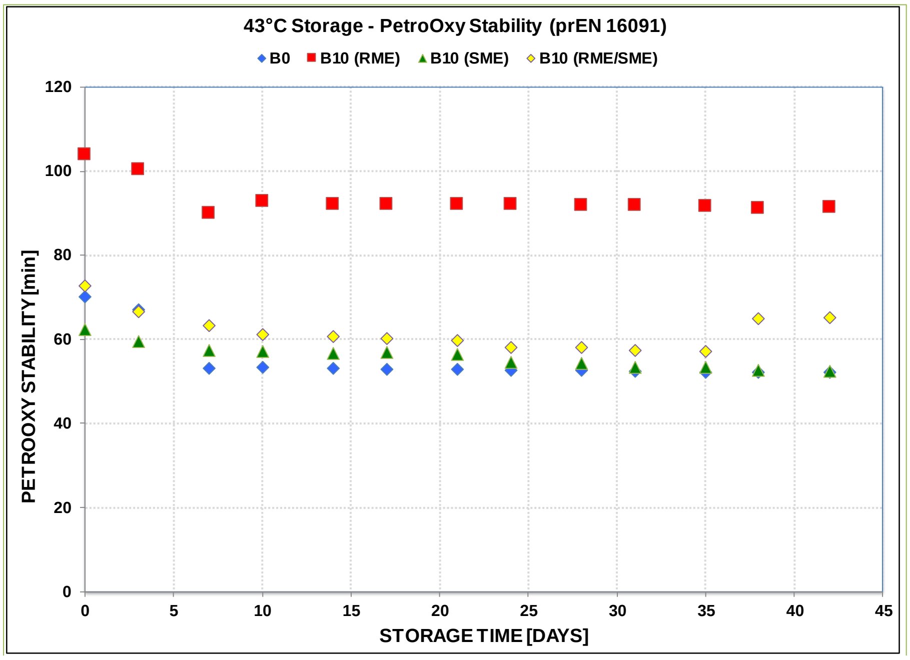
4.2.2. PetroOxy Oxidation Stability (EN 16091)

The trends in PetroOxy oxidation stability are similar to those for the Rancimat results both at the 25°C and 43°C storage conditions (**Figure 8**). The similarity in trends indicates the relatively good relationship between these two oxidation stability methods for FAME-containing diesel fuels.

The PetroOxy data show a moderate decrease in oxidation stability for the B10 (RME) and B10 (RME/SME) blends during the first few days in storage followed by a stabilization in the PetroOxy values. Even the B0 fuel showed a slight reduction in PetroOxy values during the first days of storage with a subsequent stabilization. It could be questioned whether this tendency of the B0 fuel during the first days of storage might also be the reason for the reduction in the B10 PetroOxy values at the same storage time. No notable changes were observed for the B10 (SME) blend.

Figure 8 PetroOxy results over storage time at 25°C and 43°C

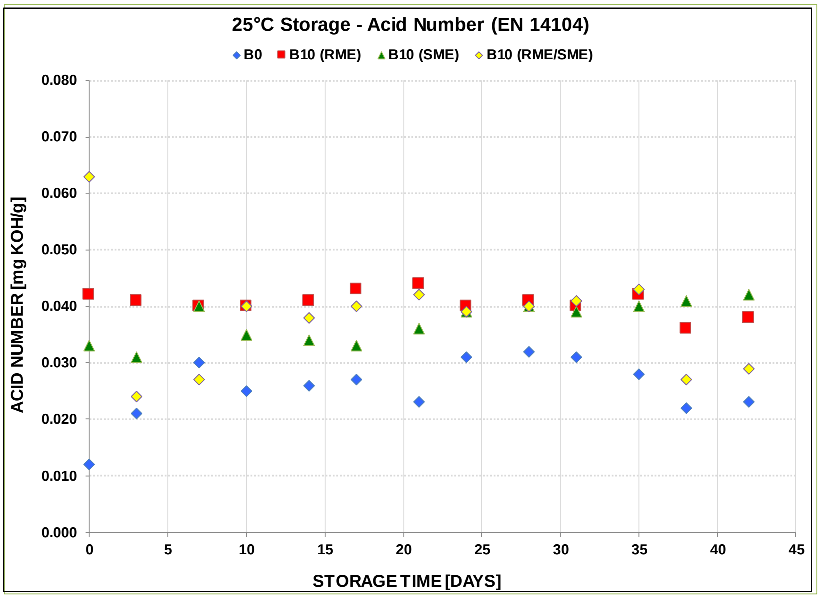


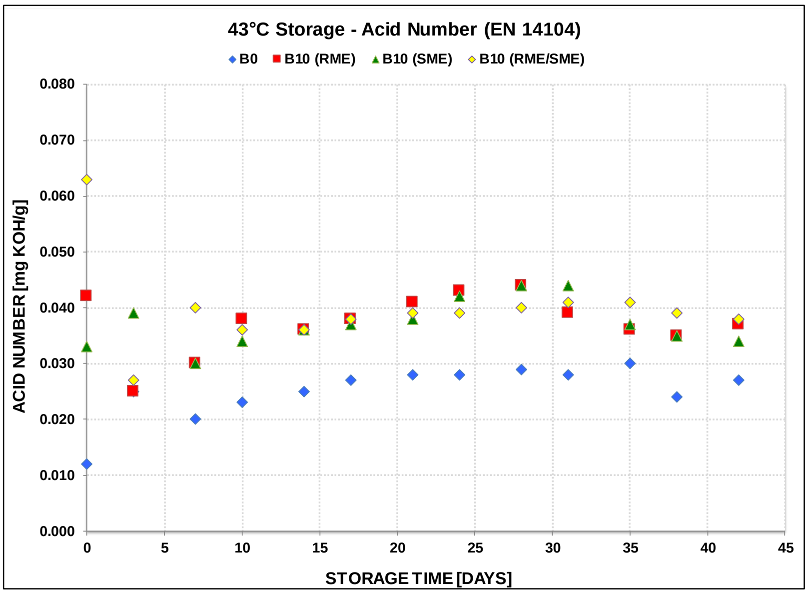


4.2.3. Acid Number (EN 14104)

The acid number data shown in **Figure 9** are all very low for all test fuels, between the repeatability (0.02mg KOH/g) and reproducibility (0.06mg KOH/g) of the EN 14104 method. No notable conclusions could be drawn from these results.

Figure 9 Acid number results over storage time at 25°C and 43°C

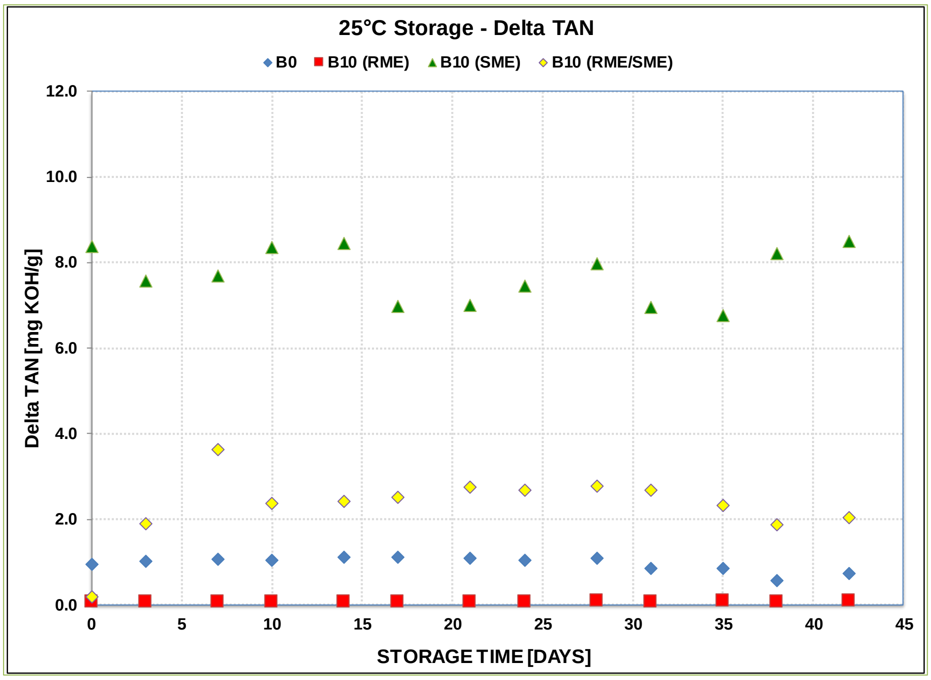


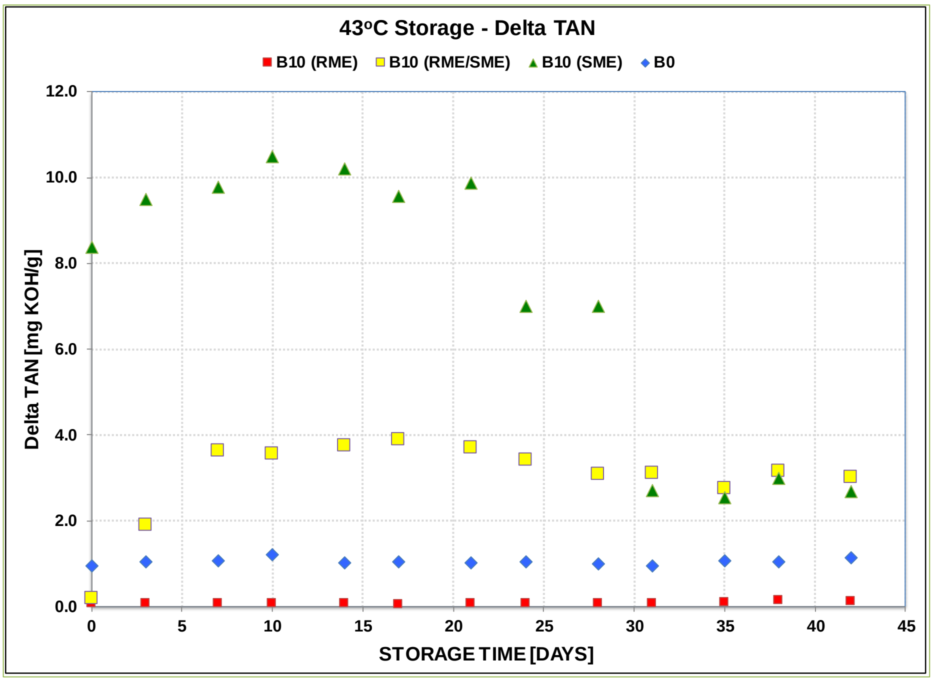


4.2.4. Delta TAN

The Delta TAN (Total Acid Number) method has been proposed in Japan and France as an alternative oxidation stability method for diesel fuels with proposed national limits of 0.13 and 0.30mg KOH/g respectively. Due to the precision of this method, the French procedure was modified to a draft AN method but it has not been incorporated into the EN 590 diesel standard. The results in **Figure 10** show no notable changes in Delta TAN for the test fuels versus storage time, except for the B10(SME) blend at the 43°C storage condition which shows a decrease in Delta TAN after 25-30 days. No explanation can be proposed and this result was not investigated further.

Figure 10 Delta TAN results over storage time at 25°C and 43°C

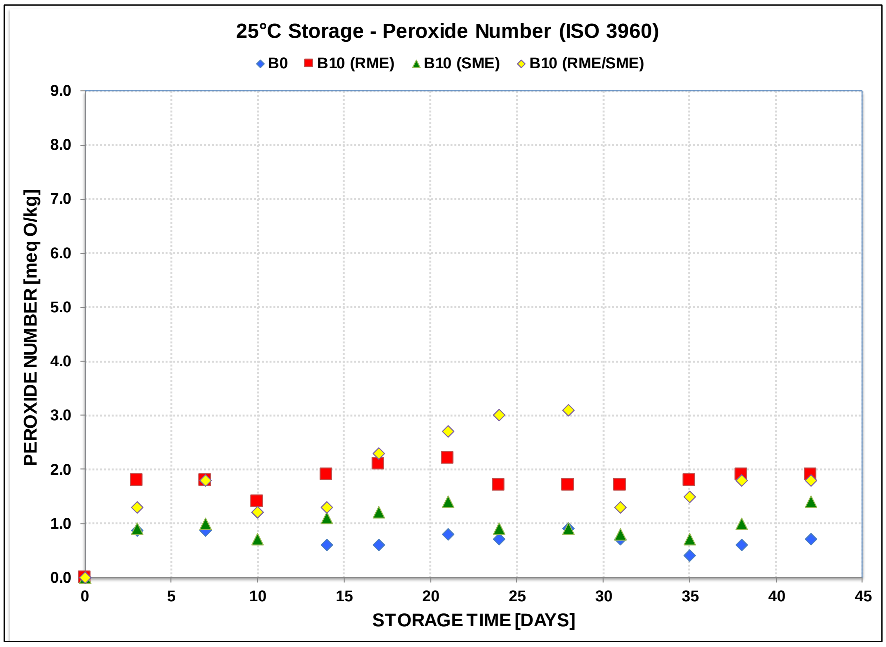


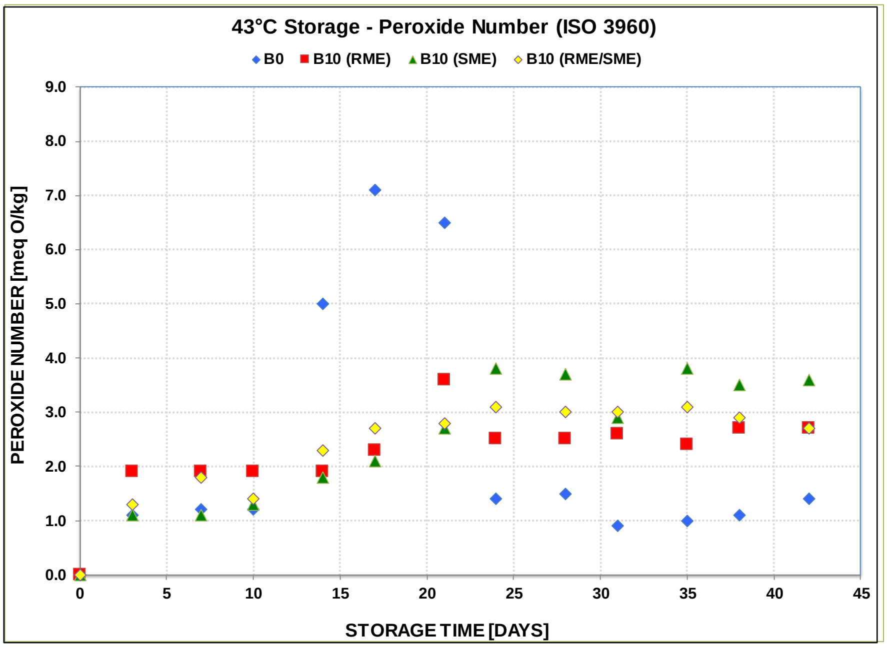


4.2.5. Peroxide Number (ISO 3960)

The peroxide number values in **Figure 11** show no obvious trends in results, compared to the results from the other oxidation stability methods discussed in previous sections. Because peroxides are comparatively reactive species, they may have changed in concentration between the end of the storage time and the start of the measurements.

Figure 11 Peroxide number results over storage time at 25°C and 43°C





4.3. ELEMENTAL ANALYSIS

Elemental analysis of dissolved metals in the test fuels were measured by Inductively Coupled Plasma (ICP) at the start and end of the storage time and the results are shown in **Appendix 4**. In general, the concentrations of dissolved metals in the fuels were very low, in the ppb range. Because the B10 test fuels had been stored in borosilicate glass bottles, there were minor increases in the boron and sodium contents in the fuels.

4.4. IMPACT OF FUEL SURFACE/VOLUME ON OXIDATION STABILITY

In the Joint Industry Study on vehicles, the fuel tank shape and size and hence the surface to volume ratio for the fuel in the tanks could have had an impact on the rate of oxidation stability change. In this laboratory study, however, most of the measurements did not show important trends, at either of the two storage conditions. For this reason, one additional experiment was completed as part of the laboratory study in order to test whether the oxygen availability or dissolved oxygen content might have been a factor in the laboratory study.

One FAME sample (B100) having an initial Rancimat value of 7.5h was stored at 43°C in 5 glass bottles such that there were different surface to volume ratios in each bottle, as shown in **Figure 12**. Laboratory air was provided to the air space above the FAME and the bottles were equilibrated with the outside conditions by means of a glass tube containing cotton wool. For comparison, the typical fuel volume used in the laboratory storage study is shown in **Figure 13**.

Figure 12 5 bottles containing FAME (B100) during surface/volume experiment

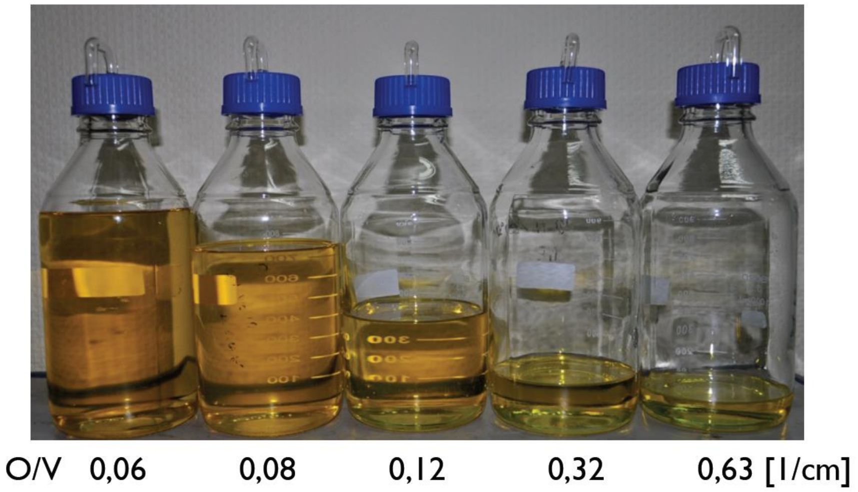


Figure 13 Example sample bottle from the 43°C storage stability test

Figure 14 Change of Rancimat oxidation stability for FAME (B100) stored in bottles with different surface to volume ratios

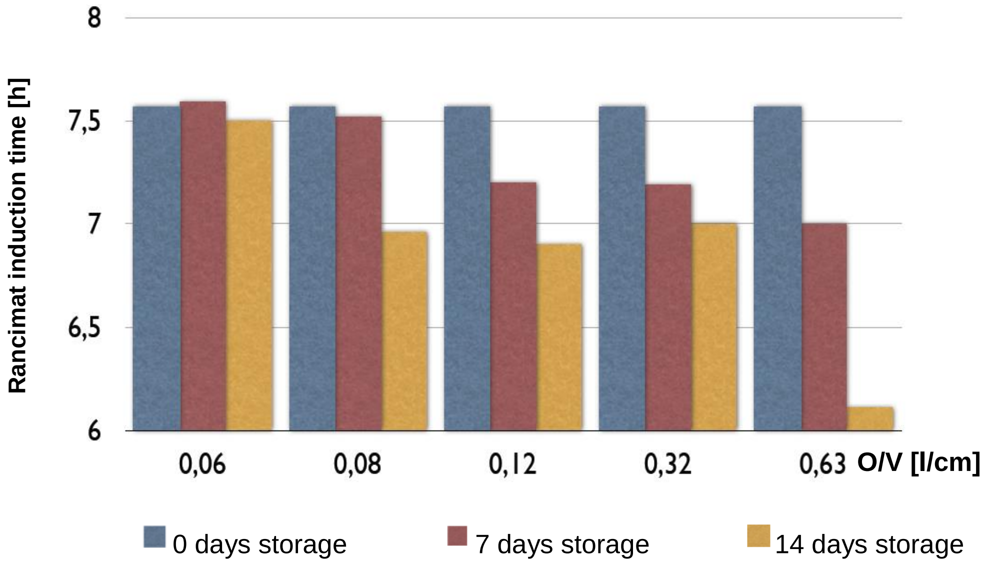


Figure 14 shows that there are greater decreases in oxidation stability as the surface to volume ratio increases. The results of this experiment suggest that the dissolved oxygen concentration was limited in the laboratory study and seems likely to be the primary reason for the difference in oxidation stability change between the vehicle study and the laboratory study.

Although few details were provided at the time, the six vehicles in the Joint Industry Study on vehicles had different tank volumes and tank shapes. The tanks were filled to about ½ to ¾ volume at the start of the vehicle aging study which might be comparable to a mid-range ratio or even a high surface to volume ratio for the stored fuel. The fuel surface to volume in the vehicle tanks did increase during the 6-month study as samples were withdrawn from the tanks. Furthermore, the vehicles were idled twice per week for 15 minutes ensuring that there was sufficient dissolved oxygen. On the other hand, in the current laboratory study, the surface to volume ratio of the fuels in the test glass bottles was relatively low (**Figure 13**) and there was no active means to ensure that the dissolved oxygen contents were sufficient.

5. CONCLUSIONS FROM THE LABORATORY STORAGE STUDY

- Compared to the change in oxidation stability of the three B10 fuels in vehicle tanks under severe test conditions (Joint Industry study), very small changes were observed for three comparable B10 blends in the current laboratory storage study at both aging temperatures of 25°C and 43°C. A range of test methods that are sensitive to oxidation stability changes in biodiesel blends all showed similar trends. An additional experiment in which the surface to volume ratio in the laboratory study was intentionally changed suggested that the availability of air/oxygen is a critical parameter in these laboratory aging studies.
- Possible reasons for this difference in oxidation stability trends between both studies may be:
  - During the laboratory aging study, the B10 diesel fuels were stored in glass bottles which were open to air via a glass tube but no active air intake into the samples was included (e.g. by shaking or bubbling), consistent with the test procedure. Furthermore, the relatively high initial filling volume of the fuel samples in the bottles resulted in a relatively low surface to volume ratio which reduced air intake into the samples and hence reduced oxidative degradation.
  - In the vehicle study, the test procedure resulted in regular intake of additional air/oxygen into the fuels due to operation of the vehicles at the start of the test (6h operation) and during the 15 minute idling period that occurred twice per week. It should be noted that this regular period of short idling is unlike what would be encountered by a car that is parked unattended at an airport or at a dealer's forecourt. For this reason, it is feasible that this regular idling in the vehicle study test procedure may have increased the severity relative to the 'real world' scenarios described above.
  - In the vehicle study, fuel temperature changes were largely determined by the outside ambient temperatures but the impact of brief exposures to presumably higher temperatures at the fuel injectors with backflow to the vehicle tank could not be assessed.
  - Because of the mounting of the fuel tanks in the vehicles, the fuel surface to volume ratio might be more favourable for air intake compared to the storage of fuels in glass bottles during the current laboratory study.

A main objective of this laboratory aging study was to compare the results of different measures of oxidation stability on fuels similar to those that had been used in the previous Joint Industry Study on six test vehicles. The results of this laboratory aging study showed that the decreases in oxidation stability were not notable at either the 25°C or 43°C storage condition. The results did not unequivocally show a preferred aging condition or a preferred measure of oxidation stability because the differences were too small to interpret.

The results did show, however, that the test methods selected for the EN 14214 and EN 590 standards give a good indication of the initial oxidation stability for the FAME/diesel fuel blends and are sensitive to such fundamental properties as the FAME type and antioxidant content. Because all of the fuels contained the same amount of EHN combustion improver, it could not be determined whether this additive contributed to the oxidation measurements.

A second objective of the study was to propose answers to the four unresolved questions from the vehicle aging study (Section 2).

- *Why did the oxidation stability of all three B10 blends drop relatively quickly in the first weeks following blending? This initial decrease occurred even for the B10 diesel having the highest initial Rancimat oxidation stability of 50hrs and was stabilized with 100ppm BHT.*
    - Assuming that the availability of dissolved oxygen is an important factor in controlling oxidation stability, it can be inferred that the fuel blending and decanting process increased the dissolved oxygen content in the fuel. This, in turn, resulted in a measureable drop in the initial oxidation stability of the B10 fuel blends.
- *Why did the three commercial vehicles show slower decreases in oxidation stability compared to the three passenger cars?*
    - The results suggest that the dissolved oxygen content in the fuel is an important parameter. The change in stability results in the commercial vehicles suggest that the dissolved oxygen contents may be lower in these vehicles compared to the passenger cars due to the shape and volume of the fuel tanks.
- *Why did the storage in metal and plastic drums show different rates of oxidation stability decrease compared to the same fuels stored in vehicles?*
    - Although the differences in oxidation stability decrease were not large between the two types of drums, the fuels stored in the epoxy-lined metal drums were kept in the dark and in a cool laboratory environment resulting in a smaller decrease in oxidation stability with time.
    - Although the vehicles and polyethylene drums were both kept outside over the same time period, the drums were not routinely opened to the air, limiting the replenishment of dissolved oxygen, at least compared to the vehicles.
    - Thus, the differences observed between the two types of drum and the two types of vehicle seem likely to be a consequence of dissolved oxygen availability and storage temperature.
    - Additional studies could be done using dissolved oxygen sensors to quantitatively monitor fuels under different storage conditions, both in vehicle tanks and in drums or bottles. It is expected that these measurements would help clarify the relative importance of oxygen availability, thermal conditions, and other factors, including dissolved metals.
- *Would similar effects of oxidation stability degradation also be seen in larger volume storage of B10 diesel fuel blends?*
    - The results suggest that similarly rapid degradation would not be observed in larger volume storage, such as in refinery tanks or in trucks. First, the addition of oxidation stability enhancing additives to the FAME product has been strongly recommended in order to protect the product from oxidation and degradation before and after storage. Second, the normal operation of large volume storage facilities generally limit the exposure of fuels to air, which also limits oxygen availability. Finally, fuels stored in large volumes often encounter lower ambient temperatures compared to smaller volumes of fuels in vehicles that can experience hotter environments for a longer period of time.

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7. ABBREVIATIONS

B7 / B10	Diesel fuel containing up to 7% v/v / 10% v/v FAME
BHT	Butylated hydroxy-toluene (antioxidant)
CEN	European Committee for Standardisation
CONCAWE	The oil companies' European association for environment, health and safety in refining and distribution
DGMK	Deutsche Wissenschaftliche Gesellschaft fuer Erdoel, Erdgas und Kohle e.V.
E5 / E10	Gasoline containing up to 2.7 wt% oxygen / 3.7 wt% oxygen
EHN	Ethyl Hexyl Nitrate
FAME	Fatty Acid Methyl Ester
FQD	Fuel Quality Directive
GHG	Greenhouse Gas
ILUC	Indirect Land Use Change
RED	Renewable Energy Directive
RME	Rapeseed Methyl Ester
SME	Soya Methyl Ester
TAN	Total Acid Number

8. ACKNOWLEDGMENTS

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- Mr. Theo Kweekel and colleagues at KPI for blending the FAME and FAME/diesel fuels and for analysing the blended samples.
- ASG Analytik for completing the laboratory oxidation procedure and analysing the FAME/diesel fuel blends throughout the study.

Before this study report could be published, Mr. Theo Kweekel, from KPI, most regrettably passed away after a short illness. Theo was a capable scientist, a kind person, and a good friend who will be sorely missed by all of his CONCAWE colleagues.

APPENDIX 1 FAME (B100) BLENDS: ANALYTICAL RESULTS

EN14214 Parameter	Method	Unit	B100 (SME)	B100 (RME)	B100 (RME/SME)
Ester content	DIN EN 14103	% (m/m)	>99	>99	>99
Density (15°C)	DIN EN ISO 12185	kg/m3	884.9	882.7	883.8
Kin. viscosity (40°C)	DIN EN ISO 3104	mm2/s	4.084	4.492	4.280
Flash point	DIN EN ISO 3679	°C	180.5	146.5	180
CFPP	DIN EN 116	°C	-6	-17	-9
Sulfur content	DIN EN ISO 20884	mg/kg	1.4	11.1	6.7
Carbon residue (10% Dist.)	DIN EN ISO 10370	% (m/m)	0.07	0.17	0.13
Cetane number (DCN)	DIN EN 15195	-	49.4	55.2	51.9
Sulfated ash	ISO 3987	% (m/m)	<0.01	<0.01	<0.01
Water content	DIN EN ISO 12937	mg/kg	185	164	179
Copper strip corrosion	DIN EN ISO 2160	Korr.Grad	1	1	1
Oxidation stability 110°C	DIN EN 14112	h	6.8	13.1	8.3
Acid value	DIN EN 14104	mg KOH/g	0.162	0.182	0.176
Iodine value	DIN EN 14111	g Iod/100g	132	109	120
Linolenic acid content	DIN EN 14103	% (m/m)	7.3	7.6	7.5
Polyunsaturated FAME	DIN EN 15779	% (m/m)	0.1	0.2	0.2
Methanol content	DIN EN 14110	% (m/m)	0.02	0.06	0.04
Free glycerol content	DIN EN 14105	% (m/m)	<0.01	0.01	0.01
Monoglyceride content	DIN EN 14105	% (m/m)	0.34	0.54	0.45
Diglyceride content	DIN EN 14105	% (m/m)	0.07	0.15	0.12
Triglyceride content	DIN EN 14105	% (m/m)	<0.01	<0.01	<0.01
Total glycerol content	DIN EN 14105	% (m/m)	0.1	0.17	0.14
Alkali content (Na+K)	DIN EN 14108/109	mg/kg	0.5	1.1	0.9
Earth alkali content (Ca+Mg)	DIN EN 14538	mg/kg	<0.5	<0.5	<0.5
Phosphorous content	DIN EN 14107	mg/kg	<0.5	<0.5	<0.5
Elemental Analysis					
Si	ICP-OES	mg/kg	<0.5	<0.5	<0.5
Na	ICP-OES	mg/kg	0.3	0.8	0.7
Ag	ICP-MS	µg/kg	<5	<5	<5
Al	ICP-MS	µg/kg	<20	<20	<20
B	ICP-MS	µg/kg	<5	124	132
Ba	ICP-MS	µg/kg	<5	<5	<5
Ca	ICP-MS	µg/kg	<20	<20	<20
Ce	ICP-MS	µg/kg	<5	<5	<5
Cr	ICP-MS	µg/kg	<5	<5	<5
Cu	ICP-MS	µg/kg	<5	6	<5
Co	ICP-MS	µg/kg	<5	<5	<5
Fe	ICP-MS	µg/kg	<5	5	5
K	ICP-MS	µg/kg	5	8	7
Mg	ICP-MS	µg/kg	<20	<20	<20
Mn	ICP-MS	µg/kg	<5	<5	<5
Mo	ICP-MS	µg/kg	<5	<5	<5
Ni	ICP-MS	µg/kg	<5	<5	<5
Pb	ICP-MS	µg/kg	<5	<5	<5
Sn	ICP-MS	µg/kg	<5	<5	<5
Ti	ICP-MS	µg/kg	<5	<5	<5
Zn	ICP-MS	µg/kg	18	13	20

APPENDIX 2 B10 DIESEL FUELS AT THE START OF THE LABORATORY AGING STUDY: ANALYTICAL RESULTS

EN590 Parameter	Method	Unit	B0 Diesel Fuel	B10 (SME) without BHT	B10 (RME/SME) + 20 mg/kg BHT	B10 (RME) + 100 mg/kg BHT
Cetane index	DIN EN ISO 4264	-	60	59.6	59.2	59.3
Density (15°C)	DIN EN ISO 12185	kg/m^3	825.5	831.1	831	831
PAH content	DIN EN 12916	% (m/m)	1.5	1.2	1.2	1.2
Sulfur content	DIN EN ISO 20884	mg/kg	9.1	8.7	8.5	8.2
Flash point	DIN EN ISO 2719	°C	67.5	67.5	70.5	69.5
Carbon residue (10% Dist.)	DIN EN ISO 10370	% (m/m)	0.03	0.05	0.1	0.08
Ash content	DIN EN ISO 6245	% (m/m)	<0.005	<0.005	<0.005	<0.005
Water content	DIN EN ISO 12937	mg/kg	<30	32	32	<30
Copper strip corrosion	DIN EN ISO 2160	Corr.Grad	1	1	1	1
FAME Content	DIN EN 14078	% (V/V)	< 0.1	10.2	9.9	10
Oxidation stability	DIN EN ISO 12205	g/m^3	15	3	5	6
Oxidation stability mod.	DIN EN 15751	h	20.8 (Note 1)	21.2	29.8	49
HFRR (Lubricity) 60°C	DIN EN ISO 12156-1	µm	291	206	188	167
Kinematic Viscosity (40°C)	DIN EN ISO 3104	mm^2/s	2.9807	3.06	3.079	3.099
% (V/V) recovery at 250°C	DIN EN ISO 3405	% (V/V)	26.5	22.8	23.3	23.2
% (V/V) recovery at 350°C	DIN EN ISO 3405	% (V/V)	93.9	94.1	94.1	93.9
95% (V/V) recovery	DIN EN ISO 3405	°C	353.6	352.2	352.2	353
CFPP	DIN EN 116	°C	-10	-11	-11	-12
Elemental Analysis						
Si	ICP-OES	mg/kg	0.7	0.6	0.7	0.6
Ag	ICP-MS	µg/kg	<5	<5	<5	<5
Al	ICP-MS	µg/kg	<20	<20	<20	<20
B	ICP-MS	µg/kg	<5	<5	<5	<5
Ba	ICP-MS	µg/kg	<5	<5	<5	<5
Ca	ICP-MS	µg/kg	40	30	40	48
Ce	ICP-MS	µg/kg	<5	<5	<5	<5
Cr	ICP-MS	µg/kg	<5	<5	<5	<5
Cu	ICP-MS	µg/kg	<5	<5	<5	<5
Co	ICP-MS	µg/kg	<5	<5	<5	<5
Fe	ICP-MS	µg/kg	18	16	17	17
K	ICP-MS	µg/kg	<5	<5	<5	<5
Mg	ICP-MS	µg/kg	<20	<20	<20	<20
Mn	ICP-MS	µg/kg	<5	<5	<5	<5
Mo	ICP-MS	µg/kg	<5	<5	<5	<5
Na	ICP-MS	µg/kg	<20	30	91	130
Ni	ICP-MS	µg/kg	<5	<5	<5	<5
Pb	ICP-MS	µg/kg	<5	<5	<5	<5
Sn	ICP-MS	µg/kg	12	10	21	24
Ti	ICP-MS	µg/kg	<5	<5	<5	<5
Zn	ICP-MS	µg/kg	<5	<5	<5	<5
Note 1:	This sample is out of scope for this test.					

APPENDIX 3 PHOTOS OF B10 DIESEL FUELS THROUGHOUT THE LABORATORY AGING STUDY

APPENDIX 4 ANALYSIS OF DISSOLVED METALS IN B10 DIESEL FUELS AT THE START AND END OF THE LABORATORY AGING STUDY

Elemental Analysis	Method	Unit	B0 Diesel Fuel	B10 (SME) without BHT	B10 (RME/SME) + 20 mg/kg BHT	B10 (RME) + 100 mg/kg BHT
			Week 0 (start of test)			
Si	ICP-OES	mg/kg	0.7	0.6	0.7	0.6
Ag	ICP-MS	µg/kg	<5	<5	<5	<5
Al	ICP-MS	µg/kg	<20	<20	<20	<20
B	ICP-MS	µg/kg	<5	<5	<5	<5
Ba	ICP-MS	µg/kg	<5	<5	<5	<5
Ca	ICP-MS	µg/kg	40	30	40	48
Ce	ICP-MS	µg/kg	<5	<5	<5	<5
Cr	ICP-MS	µg/kg	<5	<5	<5	<5
Cu	ICP-MS	µg/kg	<5	<5	<5	<5
Co	ICP-MS	µg/kg	<5	<5	<5	<5
Fe	ICP-MS	µg/kg	18	16	17	17
K	ICP-MS	µg/kg	<5	<5	<5	<5
Mg	ICP-MS	µg/kg	<20	<20	<20	<20
Mn	ICP-MS	µg/kg	<5	<5	<5	<5
Mo	ICP-MS	µg/kg	<5	<5	<5	<5
Na	ICP-MS	µg/kg	<20	30	91	130
Ni	ICP-MS	µg/kg	<5	<5	<5	<5
Pb	ICP-MS	µg/kg	<5	<5	<5	<5
Sn	ICP-MS	µg/kg	12	10	21	24
Ti	ICP-MS	µg/kg	<5	<5	<5	<5
Zn	ICP-MS	µg/kg	<5	<5	<5	<5

Elemental Analysis	Method	Unit		B10 (SME) without BHT	B10 (RME/SME) + 20 mg/kg BHT	B10 (RME) + 100 mg/kg BHT	B10 (SME) without BHT	B10 (RME/SME) + 20 mg/kg BHT	B10 (RME) + 100 mg/kg BHT
				Storage Temperature 25°C			Storage Temperature 43°C		
				Week 6 (end of test)			Week 6 (end of test)		
Si	ICP-OES	mg/kg		0.6	0.7	0.63	0.66	0.65	0.64
Ag	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Al	ICP-MS	µg/kg		<20	<20	<20	<20	<20	<20
B	ICP-MS	µg/kg		14	18	14	13	16	11
Ba	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Ca	ICP-MS	µg/kg		37	37	42	48	39	49
Ce	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Cr	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Cu	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Co	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Fe	ICP-MS	µg/kg		12	11	14	14	10	13
K	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Mg	ICP-MS	µg/kg		<20	<20	<20	<20	<20	<20
Mn	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Mo	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Na	ICP-MS	µg/kg		35	50	97	36	49	97
Ni	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Pb	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Sn	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Ti	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5
Zn	ICP-MS	µg/kg		<5	<5	<5	<5	<5	<5

CONCAWE
Boulevard du Souverain 165
B-1160 Brussels
Belgium

Tel: +32-2-566 91 60
Fax: +32-2-566 91 81
e-mail: info@concawe.org
website: http://www.concawe.org

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