Markus Hochegger, BSc

Influence of Diesel Additives on Oxidation Stability of Biodiesel and B7 Blends

MASTER'S THESIS

to achieve the university degree of

Diplom-Ingenieur

Master's degree programme: Technical Chemistry

submitted to

Graz University of Technology

Supervisors:

Ao. Univ.-Prof. Dr.phil. Martin Mittelbach

Dr.rer.nat. Sigurd Schober

Renewable Resources Group

Institute of Chemistry, University of Graz

Graz, November 2016

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BASF SE, Germany

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Abstract

Biodiesel is produced via transesterification of lipid matrices such as vegetable oils or animal fats using methanol in the presence of a catalyst, resulting in a fatty acid methyl ester (FAME). In comparison to petrodiesel, biodiesel is much more susceptible to oxidative degradation, thus requires antioxidants to ensure long-term stability. Due to ever-increasing demands on fuel quality, diesel fuel also requires a multitude of different additives. However, only little information is available in literature about possible interactions between diesel additives, antioxidants and the FAME matrix or their influence on oxidation stability.

The aim of this master thesis was to assess the influence of two diesel performance packages and three different deposit control additives on the oxidation stability of different biodiesel matrixes and their respective B7 blends using the Rancimat technique. The main tests were performed in soybean oil methyl ester and tallow methyl ester, where four of the five tested diesel additives did show a clear negative impact on oxidation stability. Furthermore, none of a total of four different antioxidants was able to fully compensate the negative effects of both tested diesel performance packages on the induction period. Interestingly, a distinct synergistic effect between BHT and one deposit control additive, DCA#1, was observed in B7 blends of soybean oil methyl ester. Furthermore, DCA#1 was also able to compensate almost completely the negative impact of both other deposit control additives. Additionally, neither diesel performance packages nor deposit control additives had a distinct impact on long term storage stability of B7 blends of SME as well as TME.

The influence of all five diesel additive was evaluated in two further biodiesel matrices, both with high market relevance for Europe; a stabilised rapeseed oil methyl ester (RME) and a stabilised FAME blend. Interestingly, the oxidation stability of RME was not affected negatively by any of the five diesel additives, in contrast to all previously made results.

Kurzfassung

Biodiesel wird durch Umesterung von fetthaltigen Rohstoffen wie Pflanzenöl oder tierischem Fett unter Anwesenheit eines Katalysators gewonnen. Der so entstandene Fettsäuremethylester ist im Vergleich zu Petrodiesel deutlich oxidationsempfindlicher und muss mit Antioxidantien versetzt werden, um die Stabilität des Treibstoffes über einen längeren Zeitraum gewährleisten zu können. Jedoch wird Petrodiesel ebenfalls mit einer Vielzahl von unterschiedlichen Additiven versetzt, da die Anforderungen an die Treibstoffqualität immer weiter ansteigen. Es gibt nur wenig Literatur bezüglich des Zusammenspiels von Antioxidantien, Diesel Additiven und der Biodieselmatrix sowie deren Auswirkung auf die Oxidationsstabilität.

Das Ziel dieser Masterarbeit war es, den Einfluss von zwei Diesel Performancepaketen (DPP) und drei unterschiedlichen Deposit Control Additiven (DCA) auf die Oxidationsstabilität verschiedener Biodieselarten und deren B7 Blends zu evaluieren; zu diesem Zweck wurde ein Rancimat verwendet. Haupttests wurden in einem Sojamethylester und einem Tierfettmethylester durchgeführt. Dabei führten vier der fünf getesteten Performance Additive in beiden Proben zu einer deutlichen Reduktion der Oxidationsstabilität. Mit insgesamt vier unterschiedlichen Antioxidantien wurde versucht den negativen Effekten der beiden Performancepakete auszugleichen, jedoch konnte mit keinem die Reduktion der Oxidationsstabilität vollständig kompensiert werden. Des Weiteren wurde ein synergistischer Effekt zwischen BHT und DCA#1 im B7 des Sojamethylesters beobachtet. Mit DCA#1 war es außerdem möglich, den negativen Einfluss der beiden anderen Deposit Control Additiven auf die Oxidationsstabilität beinahe vollständig auszugleichen. Andererseits konnte festgestellt werden, dass keines der fünf getesteten Diesel Additive die Langzeit-Lagerstabilität der B7 Blends von SME und TME signifikant negativ beeinflusst.

Des Weiteren wurde der Einfluss der fünf Diesel Additiven in zwei, für den europäischen Markt relevanten, stabilisierten Biodiesel Proben getestet. Dabei wurde ein Rapsmethylester (RME) und ein FAME Blend verwendet. Im Gegensatz zu den anderen drei getesteten Biodieselproben wurde die Oxidationsstabilität des RME nicht von den Diesel Additiven beeinflusst.

Chapter 1: Introduction

The steady advances in diesel engine technology and ever-increasing regulations concerning motor vehicle emissions require a diesel fuel of exceptional quality. To meet these sophisticated requirements numerous additives are in use. According to the European Union directive 2009/30/EC [1] diesel is allowed to contain up to 7 % (v/v) of fatty acid methyl esters, which is known to be prone to degradation and less stable compared to petrodiesel. Therefore, diesel additive producers are interested to investigate, if and to what extend their products influence the oxidation stability of biofuels and, even more important, their respective B7 blends.

The focus of this master thesis was to assess the impact of various diesel additives and antioxidants on the induction period of different biodiesel samples and their respective B7 blends. The Rancimat measurement technique was used to determine the influence of the different additives on the oxidation stability.

First, the efficiency of four antioxidants was evaluated in two different biodiesel matrixes, a soybean oil methyl ester and a tallow methyl ester, and their respective B7 blends. These particular samples were chosen due to their great difference in fatty acid composition and content of natural antioxidants on the one hand and industrial relevance on the other.

Additionally, the influence of two diesel performance packages on the oxidation stability was determined. Afterwards, these additives were added to stabilised biofuel samples to assess the most suitable antioxidant to counter their negative impact on the oxidation stability. Furthermore, the influence of three different deposit control additives was evaluated in B100 as well as B7 samples of both biodiesel matrices. Additionally, binary additive mixtures were prepared to determine, if this represents a viable option to reduce the negative impact of the individual products on oxidation stability.

Furthermore, the influence of both diesel performance packages and all three deposit control additives was assessed in two real life biodiesel samples that were highly relevant for the European market, a fatty acid methyl ester blend and a rapeseed oil methyl ester.

Chapter 2: Theoretical Background

2.1 Biodiesel

Biodiesel is a fuel made from renewable resources, using feedstocks containing mainly triacylglycerols, such as oils and fats. Triacylglycerols are fatty acid triesters of 1, 2, 3 - propanetriol, better known as glycerine. The fatty acids attached to the glycerol backbone differ for each raw material, resulting in a unique and characteristic profile. This composition is the main influence on the properties of the raw material as well as the resulting biofuel.[2]

The predominant method to produce biodiesel is a chemical reaction known as transesterification. Thereby a lipid containing feedstock is reacted with an alcohol to the respective alkyl esters in the presence of a catalyst. This reaction proceeds in three consecutive reversible reactions, requires three moles of alcohol for each mole of triacylglycerol and produces one mole of glycerol and three moles of the respective alkyl ester.

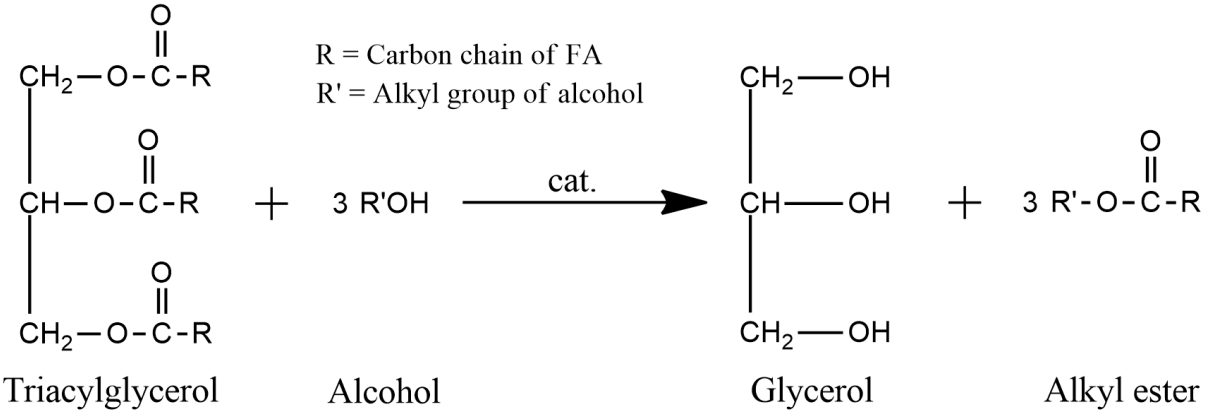


Figure 1: Reaction scheme of the transesterification

Feedstocks

The feedstocks usable for biodiesel production are plentiful. They range from refined vegetable oil and high quality animal fats to crude and unrefined vegetable oils, tallow, used frying oil as well as trap grease and other waste products. Raw materials of high quality can be converted to biodiesel with high yields and require little to no pre-treatment. However, the price of the resulting biofuel is quite high compared to that of petrodiesel. Waste fats, however, are rich in saturated fatty acids, which, compared to vegetable oil derived biodiesel, results in biofuels with higher cetane numbers but also poor low temperature behaviour.[3,4]

One major drawback of animal based raw materials is that they can contain up to 30% free fatty acids. These compounds heavily interfere with the classical biodiesel production process because of soap formation. Therefore, esterification as an additional pre-treatment step has to be carried out. Low quality feedstocks, such as trap grease, would be an excellent choice for biodiesel production, because they are waste materials. However, they can constitute up to 100% of free fatty acids and have an extremely bad odour.[2]

Table 1: Fatty acid profile of typical biodiesel feedstocks in % (m/m) [5]

Fatty acid	Sunflower oil	Soybean oil	Rapeseed oil	Palm oil	Beef Tallow
C6:0	< 0.05	< 0.05	< 0.05	< 0.05	
C8:0	< 0.05	< 0.05	< 0.05	< 0.05	Σ C6 – C12
C10:0	< 0.05	< 0.05	< 0.05	< 0.05	< 0.5 %
C12:0	≤ 0.1	≤ 0.1	< 0.05	≤ 0.5	
C14:0	≤ 0.2	≤ 0.2	≤ 0.2	0.5 - 2.0	2.0 - 6.3
C16:0	5.0 – 7.6	**8.0 - 13.5**	2.5 - 7.0	**39.9 - 47.5**	**20.0 - 30.0**
C16:1	≤ 0.3	≤ 0.2	≤ 0.6	≤ 0.6	1.0 - 2.5
C17:0	≤ 0.2	≤ 0.1	≤ 0.3	≤ 0.2	< 1.5
C17:1	≤ 0.1	≤ 0.1	≤ 0.3	< 0.05	< 1.0
C18:0	2.7 - 6.5	2.0 - 5.4	0.3 - 3.0	3.0 - 6.0	**15.0 - 30.0**
C18:1	**14.0 - 39.4**	**17.0 - 30.0**	**51.0 - 70.0**	**36.0 - 44.0**	**30.0 - 45.0**
C18:2	**48.3 - 74.0**	**48.0 - 59.0**	**15.0 - 30.0**	**9.0 - 12.0**	1.0 - 6.0
C18:3	≤ 0.3	**4.5 – 11.0**	**5.0 - 14.0**	≤ 0.5	< 1.5
C20:0	0.1 - 0.5	0,1 - 0,6	0.2 - 1.2	≤ 1.0	< 0.5
C20:1	≤ 0.3	≤ 0.5	0.1 - 4.3	≤ 0.4	< 0.1
C20:2	< 0.05	≤ 0.1	≤ 0.1	< 0.05	< 0.5
C22:0	0.3 - 1.5	≤ 0.7	≤ 0.6	≤ 0.2	< 0.1
C22:1	≤ 0.3	≤ 0.3	≤ 5	< 0.05	< 0.05
C22:2	≤ 0.3	< 0.05	≤ 0.1	< 0.05	< 0.05
C24:0	≤ 0.5	≤ 0.5	≤ 0.3	< 0.05	< 0.05
C24:1	< 0.05	< 0.05	≤ 0.4	< 0.05	< 0.05

Catalysts

The transesterification reaction can be catalysed using acids, bases or even enzymes.

Brønsted acids such as hydrochloric acid, phosphoric acid, sulfonic acids as well as sulfuric acid can be used. However only with H_2SO_4 complete conversion can be achieved.[6] One major advantage of acid catalysis is that the reaction can proceed at high free fatty acid concentration of up to 100%. [7,8]

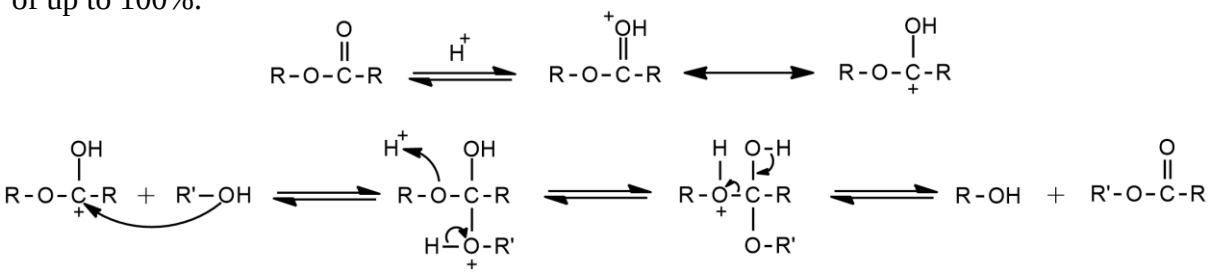


Figure 2: Mechanism for the acid catalysed transesterification

Usually strong bases are used as alkaline catalysts, such as sodium and potassium hydroxide, -methoxide or -carbonate. Their advantages over the acidic catalysts include a highly reduced reaction time, decreased reaction temperature as well as a lower need for alcohol to reach complete conversion.[7]

Additionally, the usage of potassium based catalysts leads to fertilizer production during the neutralisation step of glycerine as well as biodiesel phase (see *Figure 4*). When phosphoric acid is used as neutraliser, potassium phosphate is produced as a valuable side product.[2] One major drawback of the use of alkaline catalysts is that presence of water leads to saponification rather than transesterification of triacylglycerols, making anhydrous alcohol and feedstocks mandatory. In contrast to acid catalysis, the highest tolerable FFA content is as low as 5%; the glycerine phase does not readily separate from the methyl ester phase at higher concentrations. Additionally, soaps are also responsible for the formation of a stable emulsion during the water washing step, which is used to remove residual alcohol and catalyst from biodiesel.[8,9]

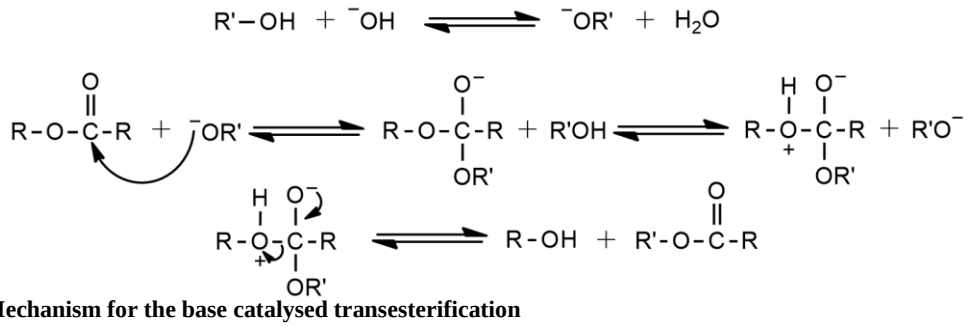


Figure 3: Mechanism for the base catalysed transesterification

Enzymes such as lipases can also be used as catalysts. Their major advantage is that a one-step esterification of both triacylglycerols and free fatty acids is possible. Furthermore, no catalyst recovery is needed and no inorganic materials are involved. However, the long reaction time as well as the high costs and possible deactivation due to contaminations in the feedstock or short chain alcohols are major disadvantages hindering their use on an industrial scale. [10–12]

Alcohols

The predominantly used alcohol for transesterification is methanol, as it is cheaper as well as able to reach full conversion even at lower temperatures compared to its two main competitors, ethanol and butanol.[7] Longer-chain alcohols, especially branched ones such as iso-propanol and iso-butanol, result in esters with significantly lower freezing points, but aren't considered economically viable alternatives due to their high costs.[13] Ethanol may be less toxic compared to methanol and cheaper in countries like Brazil, but it promotes the formation of stable emulsions between the glycerine- and ester phase, which is a major disadvantage.[14]

Furthermore, the regeneration of ethanol is more difficult, as it forms an azeotrope with water. Since transesterification is a reversible reaction, a large excess of alcohol is required to reach full conversion. A 6:1 ratio for methanol has proven to result in the best results for the alkali catalysed reaction. Higher ratios lead to an increased solubility of glycerol in the ester phase, which lowers the yield significantly. The acid catalysed reaction on the other hand requires a 30:1 excess of methanol to yield in a full conversion.[15]

Industrial production processes

On an industrial scale, feedstock, methanol and KOH are brought into a continuous stirred or plug flow reactor and are thoroughly mixed for approximately an hour at 60°C.[16] The next step is to remove glycerol from the ester phase using either a simple settler or a centrifuge. Glycerine at this point has a purity of roughly 50%, which can be further purified in a two-step process, generating a valuable side-product. First phosphoric acid is added to split the soaps into free fatty acids, making them readily separable, which are reused as part of the feed stream.[17] After that, methanol is removed using an evaporator, resulting in glycerol with 85 % purity. Further measures can be taken to increase the purity of glycerol to about 99.5 %. Glycerol has a broad field of applications including drugs, medicinal applications, oral care products, cosmetics, explosives, tobacco processing, urethane foams, food, packaging and wrapping materials, lubricants and detergents.[9,18]

The methyl ester stream is treated similarly; acid and water are added to remove traces of catalyst, soaps, methanol and glycerine. After that the wash water is removed via vacuum flash process, yielding in purified biodiesel. The collected methanol can be reused in the transesterification process after water has been removed via distillation.[9]

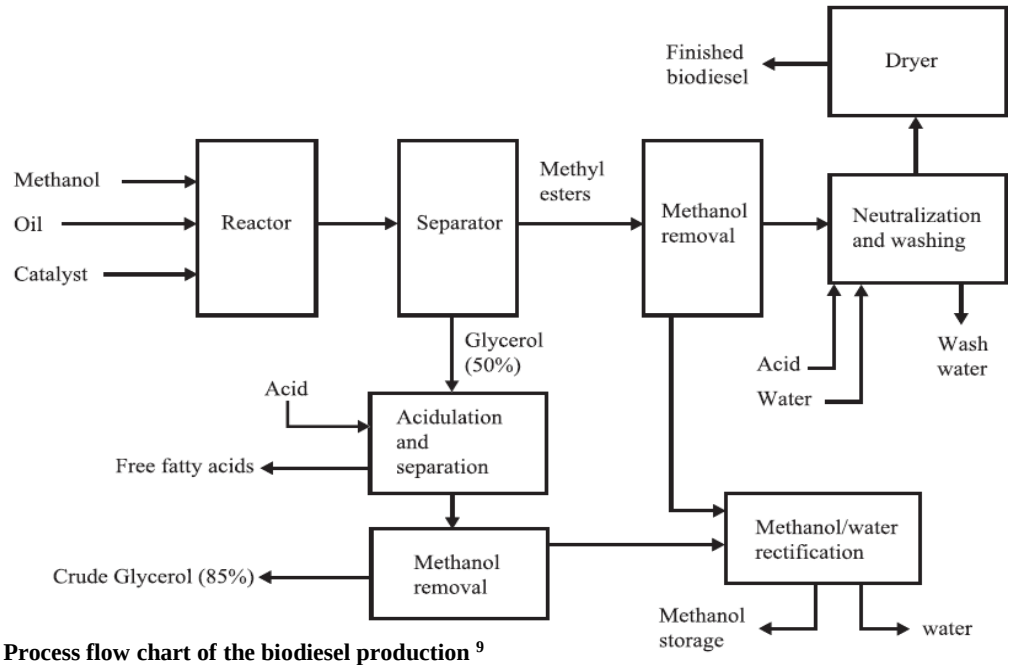


Figure 4: Process flow chart of the biodiesel production [9]

Advantages and disadvantages of biodiesel

First and foremost, biodiesel is made from renewable resources, thus has a closed carbon cycle and does not contribute towards global warming. Additionally, waste and excess products, such as trap grease and tallow, can be used as feedstock. Furthermore, biodiesel is biodegradable and acts as an excellent lubricant when added to petrodiesel, making lubrication additives for blends obsolete. Fatty acid methyl esters have reduced hydrocarbon, carbon monoxide and particulate matter emissions as well as higher flash points compared to conventional diesel fuel. Additionally, biofuels can help to reduce a nation's dependence of fossil fuel imports. [2,9]

However, biodiesel does not come without its flaws. It is a lot less stable in presence of oxygen, more corrosive and has poorer cold flow properties compared to petrodiesel. Additionally, biodiesel is currently significantly more expensive and leads to slightly higher NO_x emissions. Furthermore, microbial contamination poses a threat to biofuel and its blends, leading to fouling of various parts of the fuel delivery system as well as tank corrosion.[19] Another serious flaw of biodiesel is that the use of edible feedstocks, such as sunflower oil and palm oil, are part of the so-called food vs. fuel dilemma. Using palm oil as feedstock as especially problematic, as its production causes serious tropical deforestation in Southeast Asia. [2,19]

2.2 Aging of biodiesel

The textbook "Lipid Oxidation" by E. Frankel [20] is used as primary source for this section, due to its extensive information on the aging mechanisms of oils and fats.

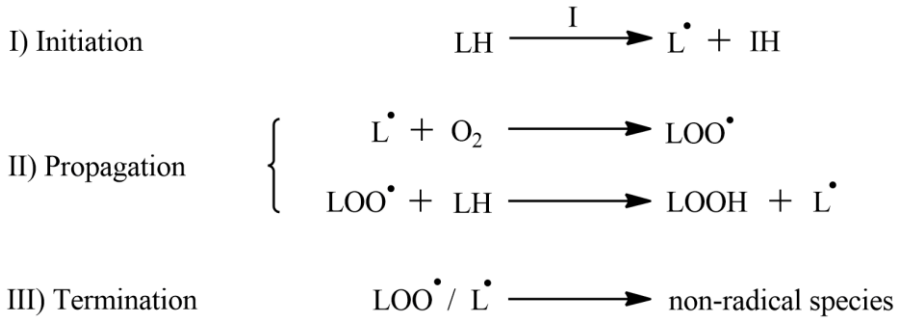


Figure 5: Scheme of the autoxidation process of lipids [20]

The main mechanism responsible for the aging of lipid containing matrices, such as biodiesel, is the so called radical autoxidation. It comprises of a reaction of molecular oxygen with unsaturated fatty acids and proceeds according to a free radical chain mechanism, consisting of an initiation, propagation and termination step.

The direct reaction of ground state oxygen with lipid species (L/LH) is spin forbidden, as the former has a triplet and the latter a singlet spin multiplicity. Therefore, some kind of initiator (I) is required to produce radicals via an alternative route. The most prominent type of initiators among redox metals, such as copper and cobalt. These metals are able to catalyse the dissociation of hydroperoxides, which are present in traces even in fresh, high quality biofuel samples. This leads to the formation of lipid oxide- ($LO^{\bullet}$) as well as highly reactive hydroxide radicals ($^{\bullet}OH$); both of them are able to abstract hydrogen from unsaturated fatty acid to initiate the chain reaction. Furthermore, thermal decomposition of hydroperoxides and UV-light can act as radical generators, but they only play a minor role, because the complete removal of metals from biofuel is rather challenging.

Molecular oxygen is now able to rapidly react with the lipid radical moieties to form peroxyl radicals, which is regarded as first part of radical chain propagation. The follow-up formation of hydroperoxyl radicals proceeds at a much slower rate, making it the rate determining step of the autoxidation process. This leads to a selective abstraction of the weakest bound hydrogen atoms, which are located on the carbon atoms adjacent to double bounds, in the so called allylic positions. Hydrogen atoms bound to a carbon situated between two double bonds, such as C11 in linoleic acid, are in the so-called bisallylic position. These are even more susceptible to abstraction compared to the ones on an allylic position.

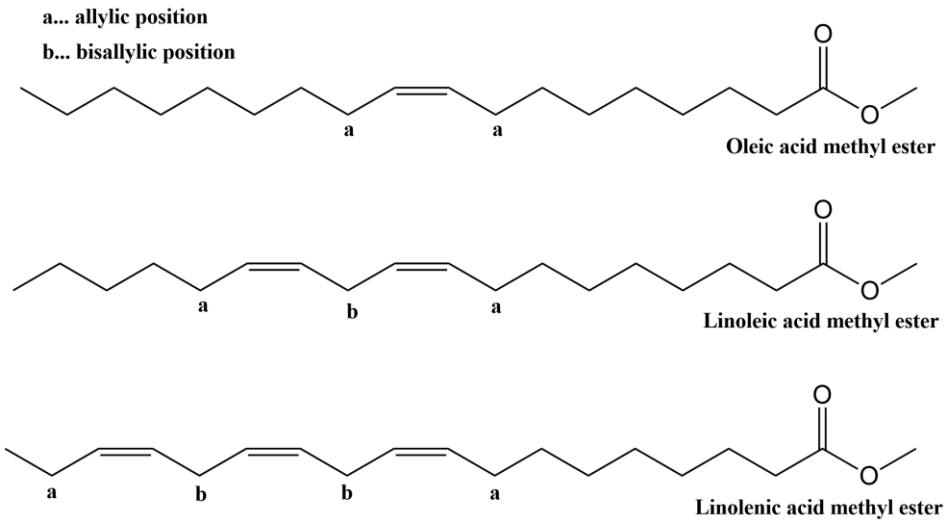


Figure 6: Common C18 unsaturated methyl esters

Table 2: Tendency of unsaturated fatty acid towards autoxidation

Fatty acid		Bisallylic -CH_2-	Relative reactivity at 37°C [21]
Oleic acid	C18:1	0	1
Linoleic acid	C18:2	1	41
Linolenic acid	C18:3	2	98 (2.4x C18:2)
Arachidonic acid	C20:4	3	195 (2x C18:3)

The tendency of an unsaturated fatty acid towards autoxidation therefore directly correlates with the number of bisallylic sites present, as seen in *Table 2*. The relative reactivities listed there were determined via oxygen absorption measurements using a Warburg respirometer.[21]

The abstraction of a hydrogen atom from one of the two allylic positions of monounsaturated fatty acids and their respective methyl esters leads to the formation of a hybrid radical. It is delocalisation between three carbon atoms, with partial free radicals at both ends.

The reaction of oxygen with the lipid radical yields four different hydroperoxides with similar abundance. The resulting double bonds can show *cis*- as well as *trans*-configuration, yielding in a total of eight different compounds. For the autoxidation of oleic acid under ambient conditions these are *8*-hydroperox*y*-*cis*-9-octadecenoate, 9-hydroperoxy-*trans*-10-octadecadienoate, *trans*-8-OOH, *cis*-10-OOH, *trans*-10-OOH each around 13 %. *trans*-9-OOH and *trans*-11-OOH occur at around 22 % each. The two other configurations *cis*-9-OOH and *cis*-11- OOH are only found at concentrations of around one percent.[22]

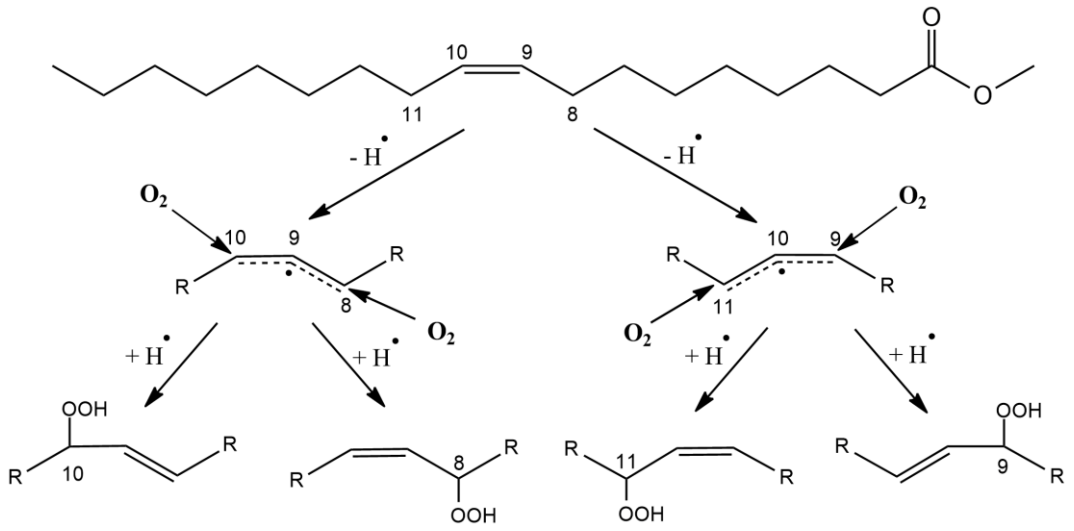


Figure 7: Autoxidation mechanism for oleic acid

The autoxidation mechanism of di-unsaturated fatty acids, such as linoleic acid, is similar to that of monounsaturated FA. One of the key differences is that hydrogen is abstracted from a bisallylic position instead of one of the two allylic ones. This results in the formation of a hybrid pentadienyl radical. Oxygen attacks one of the two partial free radicals, forming either 9- or 13-hydroperoxides. At room temperatures, 13-hydroperoxy-*trans*-9, *trans*-11-octadecadienoate and 9-hydroperoxy-*trans*-10, *cis*-12-octadecadienoate are the two dominant species for primary linoleic acid oxidation. The other two moieties 9-hydroperoxy-*trans*-10, *trans*-12-octadecadienoate and 13-hydroperoxy-*cis*-9, *trans*-11-octadecadienoate are only observed in significant concentrations at elevated temperatures (50 °C - 65 °C) and advanced oxidation of the fatty acid.[23]

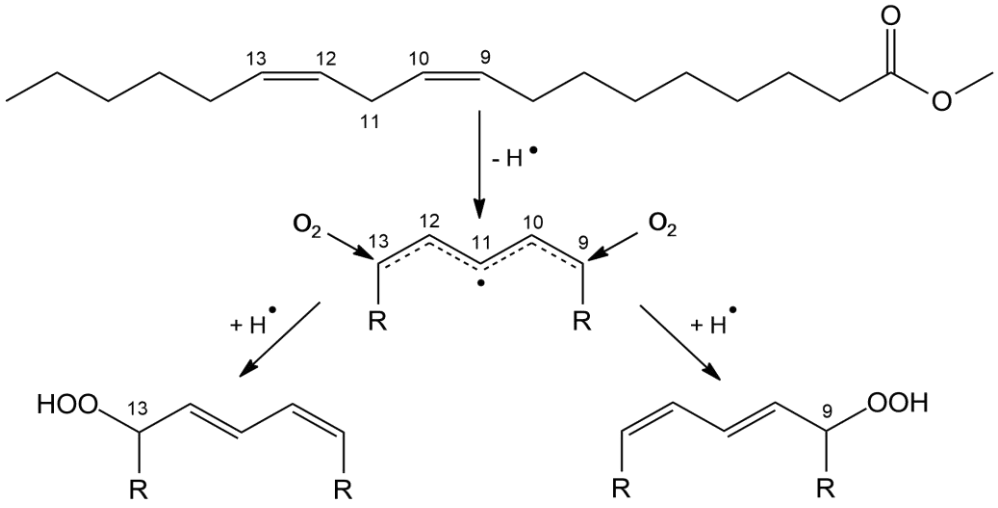


Figure 8: Autoxidation mechanism for linoleic acid

The autoxidation of both tri- and polyunsaturated fatty acids strongly resemble the mechanisms described above, also yielding in mixtures of different hydroperoxides, with *cis*- and *trans*-configuration. They will not be covered in detail in this section due to their lower abundance in biodiesel compared to mono- and di-unsaturated fatty acid methyl esters.

The resulting hydroperoxides are prone to further decomposition as they are rather instable products. A multitude of follow-up reactions are known that can occur simultaneously and lead to a huge variety of aging products. *β*-Scission is one most abundant secondary reactions. This type of fragmentation leads to the formation of aldehydes, that can be further oxidized to acids, and either alkyl or olefinic radicals. The former can react to hydrocarbons, primary alcohols or a primary hydroperoxides, which undergo further degradation to shorter chain aldehydes. Olefinic radicals on the other hand either form olefins, 1-enols or aldehydes.

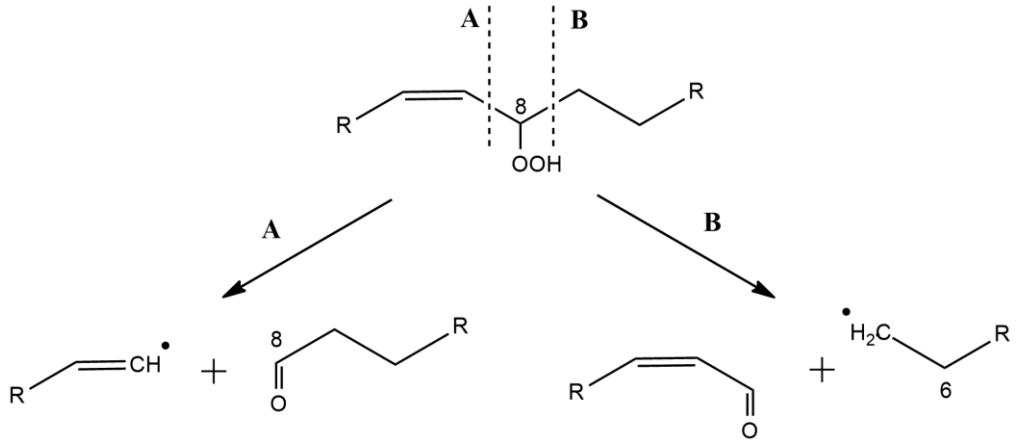


Figure 9: β-Scission of *8*-hydroperoxy-*cis*-9-octadecenoate

Other prominent hydroperoxide decomposition mechanisms include epoxidation, intramolecular cyclisation as well as di- and oligomerisation. The formation of dimers and higher oligomers is achieved either through carbon- carbon bond formation or oxidative or peroxidative linkage between the methyl ester moieties.

The aging of biodiesel results in the formation of ketones, aldehydes and organic acids that lead to a significant increase in acidity and consequently corrosiveness, potentially harming fuel storage and delivery system. Furthermore, oxidative degradation of biofuel results in the formation of polymeric species and insoluble gums that can cause serious injector problems, such as faulty fuel spray characteristics. On the other hand, aged biodiesel has a beneficial emission profile compared to petrodiesel and fresh biodiesel, due to the presence of oxygenated species.[24–26]

Flitsch et al.[27] quantified several of these oxidation products in non-stabilised rapeseed oil methyl ester. They found that significant amounts of formic (~400 mg/kg) and acetic acid (~290 mg/kg) were formed after eight hours of accelerated aging using the Rancimat measurement technique; the chosen duration approximately corresponded to the induction period of the biodiesel sample (see chapter *2.6 Oxidation stability*). Additionally, several short chain fatty acids ranging from C5 to C9 were identified, originating solely from fragmentation reactions. Among those, nonanoic acid was present at the highest concentrations (up to 4000 mg/kg). Furthermore, Flitsch et al. were able to quantify several epoxides during the accelerated aging process. Trans-9,10-epoxy stearic acid methyl ester and cis-9,10-epoxy stearic methyl esters were pinpointed as major aging products; they were detectable after the RME sample surpassed its induction period.

2.3 Antioxidants

The textbook "Lipid Oxidation" by E. Frankel [20] was used as the primary source for this section, due to its extensive information on antioxidants for fats and oils.

As mentioned before, most types of biodiesel contain a significant amount of unsaturated fatty acid methyl esters that are labile to autoxidation, leading to degradation in fuel quality affecting viscosity, acid number as well as peroxide value. This effect is especially severe if the biofuel additionally lacks natural antioxidants, contains high amounts of oxidation promoters, such as metal ions, free fatty acids and hydroperoxides, or high concentration of unsaturated fatty acids. The most efficient method to increase the stability is the addition of various antioxidants that are able to inhibit or at least retard the degradation of the instable compounds.

The easiest method to characterise antioxidants is to look at their respective mechanism to inhibit the radical autoxidation process. The most abundant class among them are chain-breaking antioxidants, also called primary antioxidants. They are able to inhibit the lipid oxidation through hydrogen-atom transfer reactions and thus interfere either with the radical initiation or chain propagation reaction (see *Figure 11*). They are secondary aromatic amines, such as N, N'-diphenyl-*p*-phenylenediamine (DPPD), or phenolic compounds, like 2,6-*tert*-butyl-*p*-hydroxytoluene (BHT), with the latter type being the most prominent among them.[20,28]

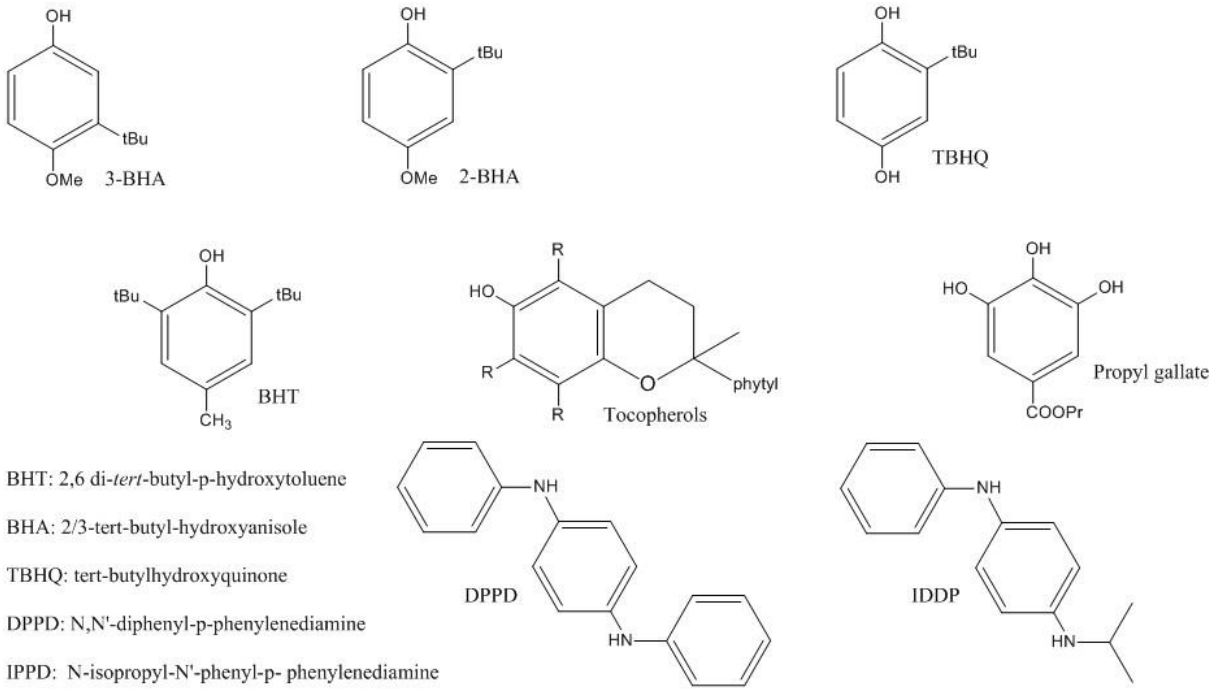


Figure 10: Chemical structures of prominent chain-breaking antioxidants

Phenolic antioxidants have at least a single free hydroxyl group at the phenyl ring that readily donates a hydrogen atom to peroxyl radicals. This leads to a highly resonance stabilized phenoxyl radical, due to electron delocalization around the aromatic ring. The activity of phenolic antioxidants is directly linked to the hindrance of the aforementioned OH group. A hindered radical centre leads to less reactive and thus more stable radicals. The highest antioxidative effect can be achieved when the *para* and both *ortho* positions are substituted and at least one of the two *ortho* substituents is a bulky branched group, like a *tert*-butyl group. Additionally, a sterically less demanding group, such as methyl or *n*-butyl, is required at the para position for maximum activity, making 2,6-*tert*-butyl-*p*-hydroxytolouene (BHT) a highly potent antioxidant. [20,29]

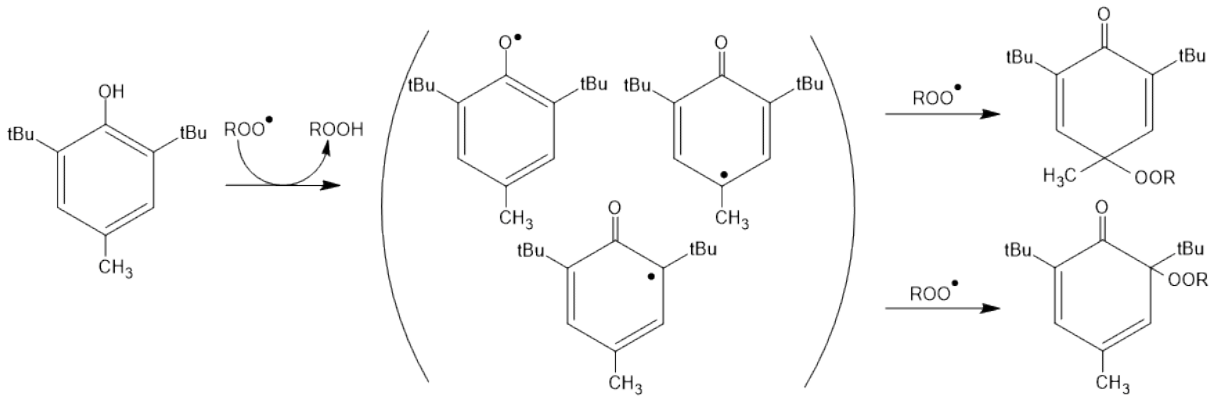


Figure 11: The radical autoxidation inhibition mechanism of BHT (modified from E. Frankel [20])

Secondary aromatic amines on the other hand generally show a higher efficiency in inhibiting the radical initiations and chain propagation reactions, due to lower sterical hindrance of the hydrogen donating group. However, they can lead to severe discolouring especially under presence of UV light, which is regarded as a major disadvantage particularly in the food sector. Additionally, the use of secondary amines as stabilizers for lipid based biofuel is quite limited, due to the low price of phenolic antioxidants and the increased NO_x emissions.[30]

Furthermore, both types of chain-breaking antioxidants are partially able to inhibit the decomposition of hydroperoxide radicals into secondary oxidation products by forming stable species, such as alcohols.

One major drawback of this class of antioxidants is that they show pro-oxidative activity at high additive concentration, elevated temperatures and the presence of oxidation promotors such as metal catalysts, free fatty acids or hydroperoxides. This deteriorating effect is especially severe in less-substituted phenols such as propyl gallate (PG) or *tert*-butylhydroquinone (TBHQ).[20]

Antioxidants, which inactivate free radical chains, can be categorized as secondary antioxidants. They only play a minor role in the stabilisation of biofuel and its blends compared to the chain-breaking antioxidants.[31,32] One sub-class of secondary antioxidants are hydroperoxide destroyers. These compounds inhibit the oxidation of aforementioned groups to secondary oxidation products. They form either stable alcohols or inactive products via non-radical reactions such as reduction or hydrogen donation. Reducing agents like ascorbic acid, organic sulfides, phosphites and phosphines, like triphenylphospine (TPP) are potent hydroperoxide destroyers. [20,33,34]

Another class of secondary antioxidants are initiator inhibitors or preventative antioxidants; the most important representatives are metal chelators. These compounds are able to complex free metal ions that are otherwise capable of catalysing the initiation and decomposition of hydroperoxide species. Copper has the most deleterious effect followed by cobalt, manganese, nickel and iron.[35,36] Examples for initiator inhibitors are citric acid, phosphoric acid, ethylenediamine tetraacetic acid (EDTA) or N, N'-disalicylidene-1,2-propanediamine. [20,32,34,37]

The third class of secondary antioxidants are the so-called ultraviolet light deactivators. These compounds are able to absorb harmful electromagnetic radiation without forming radical species. Thus, they hinder the degradation of UV-labile compounds such as hydroperoxides and thus retard the radical autoxidation process. These additives are usually not used for biodiesel and its blends due to the fact, that fuels are normally stored in closed, non-transparent tanks.[20,38]

In addition to the classes and mechanisms described above, there is the special group of synergists. One speaks of a synergistic effect if a sample containing a mixture of an antioxidant and another additive, not necessarily a second antioxidant, achieves an induction period greater than the sum of the IPs for the individual admixtures. The highest synergism can be achieved if both initiation as well as propagation of the radical autoxidation process are inhibited. Frankel et al. [37] reported a strong synergistic effect between tocopherols (chain-breaking antioxidants) and citric acid (initiator inhibitor) in soybean oil, stating that the metal chelating capabilities of the latter compound are responsible for the increase of oxidative stability. Another example is a mixture of a primary antioxidant and a reducing agent, such as ascorbic acid, where the increase in induction period is attributed to radical exchange reactions between both compounds. [20,29,37]

2.4 Overview on diesel additives

The steady advances in diesel engine technology and ever-increasing regulations concerning motor vehicle emissions among others require the use of an exceptional diesel fuel. To meet these sophisticated requirements numerous additives have been developed and improved over the years. Below follows a list of relevant fuel additives for B7 blends based on a publication by the *Technical Committee of Petroleum Additive Manufactures in Europe* [32], sorted according to date of implementation starting with the oldest one.

Cetane number (CN) improvers

The cetane number is defined as the tendency of a fuel to self- ignite. A higher number corresponds to a shorter ignition delay after the fuel is injected into the combustion chamber, which is filled with compressed air. A low cetane quality leads to high fuel consumption, increased emissions and bad cold start properties. In biodiesel blends, significant amounts of highly unsaturated fatty acid methyl esters, like methyl linoleate (C18:2) and methyl linolenate (18:3), lead to a decrease in CN.[39,40] However, in general biodiesel has higher cetane numbers than fossil fuels.[2,8]

Ignition improvers are able to easily form radicals under increased temperatures and pressures, leading to increased degradation rates of the fuel and consequently to a higher cetane quality. The most widely used cetane number improver is 2- ethylhexyl nitrate (2-EHN), other organic nitrates, azo compounds as well as alkyl peroxides are also available.[39–42]

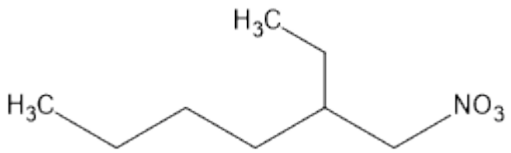


Figure 12: 2-Ethylhexyl nitrate

Corrosion inhibitors

Water, either incorporated in the fuel or entering the system elsewhere, can corrode metallic surfaces, leading to rust formation in the diesel storage and delivery system. This can potentially block filters and fuel lines as well as harm precision equipment. Corrosion inhibitors are able to form thin films on the metal surfaces of the fuel system and thus hinder the deleterious effect of water. They are amphiphilic compounds, which allow adhesion to metallic surfaces as well as guarantee a complete solubility of the additives in the fuel. Carboxylic acids, amines and amine salts of carboxylic acids are effective corrosion inhibitors, with one specific example being dodecenyl succinic acid.[43,44]

Cold flow improvers

High amounts of n-paraffinic compounds in diesel on the one hand lead to a high cetane number, which is highly favourable, but on the other have a tremendously negative impact on cold flow properties. They tend to precipitate as rather large crystals at low temperatures, leading to clogged filters and fuel transport systems. Blending of biodiesel with petrodiesel also leads to a deterioration of the low temperature behaviour, mainly due to high freezing points of saturated methyl esters, especially that of stearic (33.7 °C) and palmitic acid (24.4 °C), as well as the presence of glycerides. [45–48]

Cold flow improvers are predominantly polymeric compounds that have a precipitation temperature close to the cloud point of biodiesel. These additives lead to the formation of large amounts of small nuclei at low temperatures that form rather small paraffinic crystals, which do not harm the fuel supply line. Additionally, so called wax dispersants are applied, which reduce the size of paraffinic crystal even further and lead to a better dispersion of the nuclei. The most widely used cold flow improver are based on poly (ethylene-co-vinylacetate), furthermore polyacrylates and -methacrylates are available on the market.[49]

Demulsifiers / emulsion preventatives

Like mentioned earlier, water can pose a significant threat to the fuel storage and delivery system, leading to corrosion and rust formation. Additionally, especially in biodiesel blended fuels, the presence of water is an important factor for bacterial growth, due to its increased solubility in biodiesel compared to petrodiesel. Thus, the need for demulsifiers arises that are able to break the emulsion of diesel and water, allowing an easy removal of H_2O. Emulsion preventatives on the other hand are used to hinder the formation of a stable mixture between diesel and water in the first place. Due to their amphiphilic nature, they are able to change the interfacial rheological properties of the emulsion, specifically interfacial tension viscosity, which leads to a destabilisation and consequently separation of the two phase system.[43,50]

Demulsifiers and emulsion preventatives are mostly intricate mixtures of polymeric compounds, reacted with ethylene- or propylene oxide, following alkoxylation synthesis routes. One specific compound group of this type of additive are phenolic resin alkoxylates.[32]

Deposit control additives

Deposit formation does play a significant role in modern diesel engines, especially in the fuel injection system. The injector nozzle is a critical component of the fuel delivery system, that is responsible for transferring a predefined amount of diesel, at an exact timing, as a fine spray, into the combustion chamber. At optimum conditions this leads to maximised power output and minimised emission. Deposit formation around the nozzle, so called injector fouling, has a tremendously deleterious impact on engine performance, lowering power output as well as increasing fuel consumption and in the worst case even causes engine failure.[51]

Deposit control additives are high molecular amphiphilic compounds, like corrosive inhibitors. They are able to form thin films on the metallic surfaces of the fuel delivery system, which prevents the adherence of solid compounds. In a much lesser extent, these types of additives are also able to hinder the agglomeration of deposit precursors. These additives are mostly polymeric substances based on succinimide chemistry, with the group of polyisobutylene succinimides (PISBIs) being one of the most prominent among them.[52]

Antifoam additives

The tendency of diesel and diesel blends to form foams during refuelling is a major inconvenience for the consumer. It leads to only partly filled tanks as well possible spilling of fuel, which poses a major safety and environmental threat. Antifoam additives are applied to break foams by reducing the surface tension of the air – diesel interface, thus leading to a rapid collapse of bubbles. The highest activity can be achieved if the compound is insoluble in diesel, has a high tendency to accumulate at the aforementioned face boundary and does not form large particles. The most commonly used antifoam additives are silicones, such as polydimethylsiloxane. Acrylate copolymers and quaternary ammonium salts containing hydroxyl-ethylated fragments are also in use, although in a much lesser extent.[41,53]

Fuel borne catalysts

Fuel borne catalysts are mostly organometallic compounds, containing transition metals such as iron, manganese, cerium and palladium or combinations.[48] Metal based additives have two different uses in diesel fuel. On the one hand they reduce emissions of soot, hydrocarbons and polyaromatic hydrocarbons (PAH), acting as catalysts to enhance the oxidation of carbonaceous matter. More importantly, they also ease the oxidation of soot after initial combustion, reducing the diesel particulate filter recycling temperature, from 600 °C to roughly 400 °C, leading to a significantly decreased diesel consumption.[54,55]

Through combustion of fuel borne catalyst, fine metal oxides are formed that act as nuclei for soot, leading to smaller, finely distributed particles in the ceramic-based wall-flow monolith, the most common type of particle trap.[56] The oxidation of this carbonaceous matter can be achieved at an increased exhaust gas temperature, leading to an overall drastic reduction of soot emission. Ferrocene, to name a specific example for a fuel borne catalyst, reacts to iron oxides during combustion and is known to drastically decrease PAH emission.[54,57]

2.5 Short literature review on FAME stabilisation using additives

Mittelbach and Schober [31,58] assessed a total of ten synthetic and ten natural tocopherol based antioxidants on their efficiency of stabilising eight different biodiesel samples within the so-called BIOSTAB project. The additives were chosen based on their ability to stabilise lipid matrices as well as their price. For selecting the biodiesel samples, the current market situation was decisive, thus rapeseed oil methyl ester, used frying oil methyl ester, sunflower oil methyl ester and tallow methyl ester were used. Each of them was analyses in distilled as well as unstilled form, to be able to properly assess the effect of the natural antioxidants contained in the samples. They found that synthetic antioxidants such as pyrogallol, propylgallate and TBHQ have a major positive impact on the oxidation stability, significantly outperforming all tested additives solely based on tocopherols. Mittelbach and Schober also determined, that biofuels with a high concentration of unsaturated fatty acids, such as RME and sunflower oil methyl ester are rather difficult to stabilise in comparison to tallow methyl ester and used frying oil methyl ester. Furthermore, they also found that addition the aforementioned antioxidants has no drastically negative effect on other fuel quality parameters regulated by the European specification prEN 14214 [59].

Bondioli et al.[38] found during the same project that stabilised biodiesel can be stored a full year at normal conditions without major changes in fuel quality parameters. Additionally, they published that both TBHQ and pyrogallol are able to additionally significantly increase the long-term storage stability of pure biodiesel.

Within the aforementioned BIOSTAB project, Fröhlich [60] and Fröhlich and Schober [61] investigated the stabilisation effects of naturally occurring α-, δ-, and γ-tocopherols as well as commercially available tocopherol mixtures. They determined that these class of compounds are indeed suitable for stabilising different biofuel samples, including SME and TME. Furthermore, they found that the stabilisation efficiency of the tocopherols heavily depends on the biodiesel matrix and that α-tocopherol is the least potent antioxidant among them.

Schober and Mittelbach [62] additionally investigated the influence of eleven different synthetic antioxidants on the oxidation stability of various biofuel samples. They found that not only the efficiency of an antioxidants is heavily depending on the biodiesel matrix but also that non-distilled biofuels are significantly harder to stabilise in comparison to their distilled counterparts. They also recommended that the smallest treat rate possible should be used for all antioxidants, to reduce their negative influence on other fuel quality parameters.

Dunn [63] reported that BHA or TBHQ are most suitable for stabilising soybean oil methyl ester and noted that α-tocopherol was a lot less efficient than the synthetic antioxidants tested. He also analysed the compatibility of the aforementioned additives in SME blends with petrodiesel. Dunn found that propylgallate is unsuitable for use in blends as it tends to form solids at petrodiesel contents as low as 10 % (v/v) at a treat rate of 3000 mg/kg. He also reported that both TBHQ and BHT also tend to form solids at 5000 and 3000 mg/kg. respectively at a blend ratio as low as 10 % (v/v). Additionally, α-tocopherol as well as BHA were compatible with blend ratios of up to 50% (v/v) at treat rates of 2500 and 5000 mg/kg, respectively.

Linag et al. [64] investigated the influence of TBHQ, BHT and α-tocopherol on the oxidation stability of crude as well as distilled palm oil methyl ester. As stated earlier, they also reported that synthetic antioxidants are more active in comparison to α-tocopherol and that TBHQ was the most efficient in stabilising palm oil derived biodiesel.

2.6 Oxidation stability

Induction period (IP)

The induction period in chemical kinetics represents the initial stage of an oxidation, at which reactions do proceed at a relatively slow rate, mainly involving radical species. When surpassing the IP, the reaction accelerates significantly.[65] In case of biodiesel and its petrodiesel blends, Christensen and McCormick [66] stated that it represents the time needed to deplete the oxidative reserve of biodiesel and represents a proportionality between factors preventing and promoting oxidation:

$$oxidative\ reserve\ \propto \frac{antioxidants\ concentration}{oxygen\ conc. + conc.\ of\ bissallylic\ sites + \ radical\ iniitators\ conc.}$$

This is also called lag phase and is regarded as the first phase of oxidation of unsaturated fatty acids as well as their respective esters. During this phase, oxygen consumption is rather low, antioxidant concentration, if present at all, is decreasing but the composition of the fuel stays nearly unchanged.[66]

In the second phase, also called exponential phase, the peroxide concentration and oxygen consumption both increase rapidly, due to a total depletion of antioxidants in the fuel. In the third and final phase, peroxide degradation surpasses peroxide formation reactions in terms of their respective reaction rates, leading to a rapid increase of secondary oxidation products like aldehydes, ketones and organic acids.[67] These reaction pathways and their products have a tremendously negative impact on the quality of biofuel, as described before in chapter *2.2*. [66]

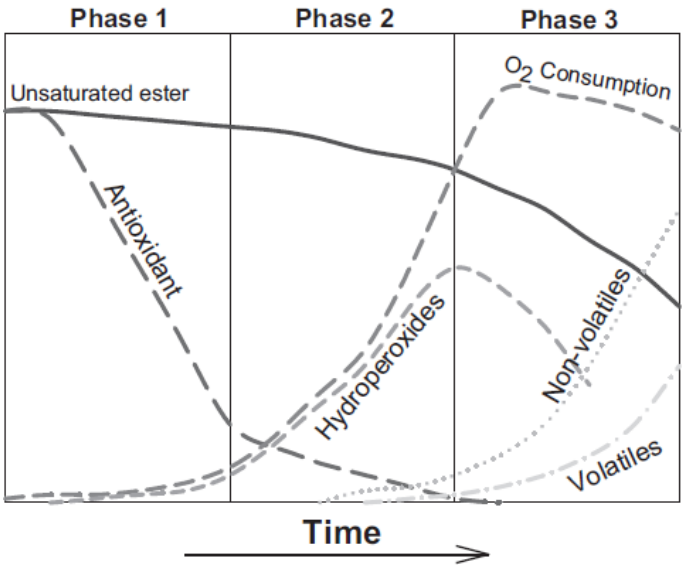


Figure 13: The three phases of (poly)-unsaturated fatty acid oxidation [66]

Regulations

There exist two major standardisation institutes that published regulations concerning diesel, biodiesel and blends, ASTM International and the European Committee for Standardization, which follow a different approach. The American standard for diesel fuel oils ASTM D975 [68] does not explicitly cover oxidation stability. Instead the standard for biodiesel ASTM D6751 [69] is also in use for the respective petrodiesel blends. In contrast to that, the oxidation stability of pure petrodiesel and biodiesel blends of up to B7 is covered by the European specification EN 590 [70], whereas pure biofuel is regulated by EN 14214 [71]. All national regulations concerning oxidation stability are more or less based on the aforementioned standards.

Table 3: Major regulations concerning the oxidation stability of biodiesel and biodiesel blends

Standard	Limit	Test Method
ASTM D975 [68]	Not covered	Not covered
ASTM D6751 [69]	min. 3 h	EN 14112
EN 590 [70]	max. 25 g/m³	ASTM D2274 / EN ISO 12205
	min. 20 h *	EN 15751
EN 14214 [71]	min. 8 h	EN 14112

* *Additional diesel fuel quality requirement for a FAME content exceeding 2% (v/v)*

As can be seen in *Table 3*, the oxidation stability requirements set by the European standards for pure biodiesel are rather severe in comparison to their American counterparts, with a minimum required induction period of eight instead of just three hours.

2.6.1 Rancimat

The Rancimat method represents the standard measurement technique to determine the induction period of lipid matrices, such as biodiesel, fats and oils, as it is able to accurately monitor the ageing reserve by means of accelerated oxidation. The determination method for the oxidative stability of pure biodiesel is regulated in the European specification DIN EN 14112 [72]. For petrodiesel-blends with a fatty acid methyl ester content of at least 2 % (v/v) DIN EN 15751 [73] has to be considered. According to European specification DIN EN 14214 [71] the induction period of pure biodiesel has to be at least 8 hours. Blends from 2 to 7 % (v/v) FAME need an oxidative stability of 20 hours to meet the requirement set by EN 590 [70]. This specification defines which parameters a diesel fuel has to fulfil to be suitable for use in diesel engines, especially in the automotive sector. The induction period of pure petrodiesel on the other hand seems of no particular interest, as it is not included in any standards concerning fuel quality. One disadvantage of the Rancimat method is, that it only able to detect highly volatile secondary oxidation products (see chapter *2.2 Aging of biodiesel*), thus providing only an incomplete evaluation of the oxidative stability. Additionally, quantification as well as characterisation of neither polymers nor insolubles are covered by this measurement technique.[74]

Principle of the Rancimat measurement

Determining the induction period using a Metrohm® Rancimat device is based on a simple distillation followed by a conductivity measurement. A predefined amount of sample is heated in a reaction vessel and a constant stream of dry air is bubbled through at 10 L/h.

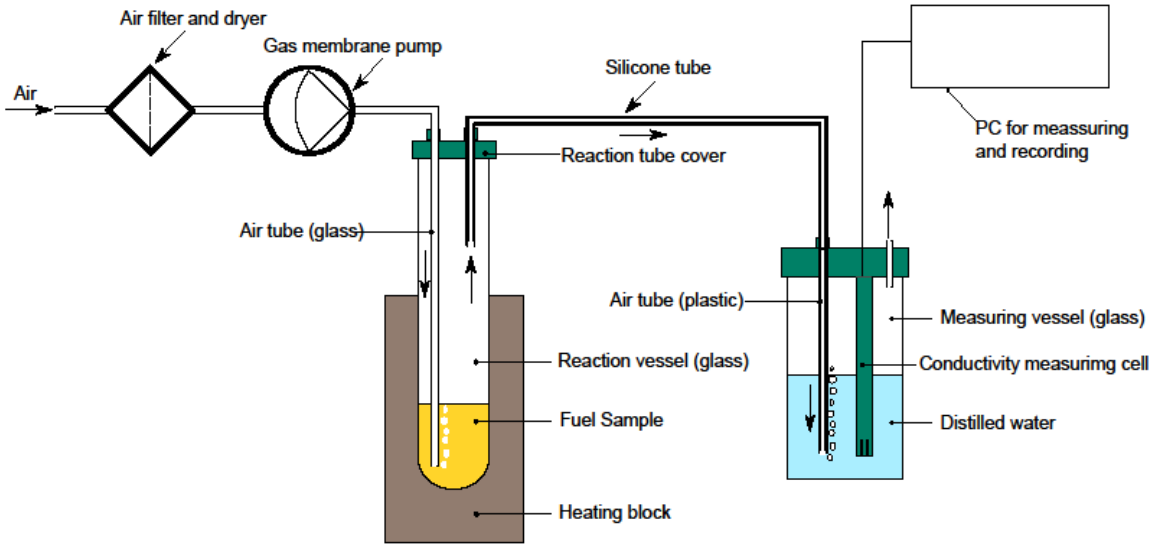


Figure 14: Scheme of a Metrohm® Rancimat device (modified from Flitsch et al.[75])

This oxidative stress leads to autoxidation of the sample and subsequent evolution of volatile compounds like acids, aldehydes and ketones. These secondary oxidation products are transferred via a silicon tube into the measuring cell that contains distilled water, leading to a rise in conductivity. This increase is rather small until the oxidation reserve of the fuel is depleted, indicated by an almost exponential rise of conductivity. The Metrohm® software calculates the induction period at the point of greatest inflection of the measuring curve, which corresponds to a maximum of the second derivative. A manual determination of the IP is also possible, using the so called tangential intersection point. [76]

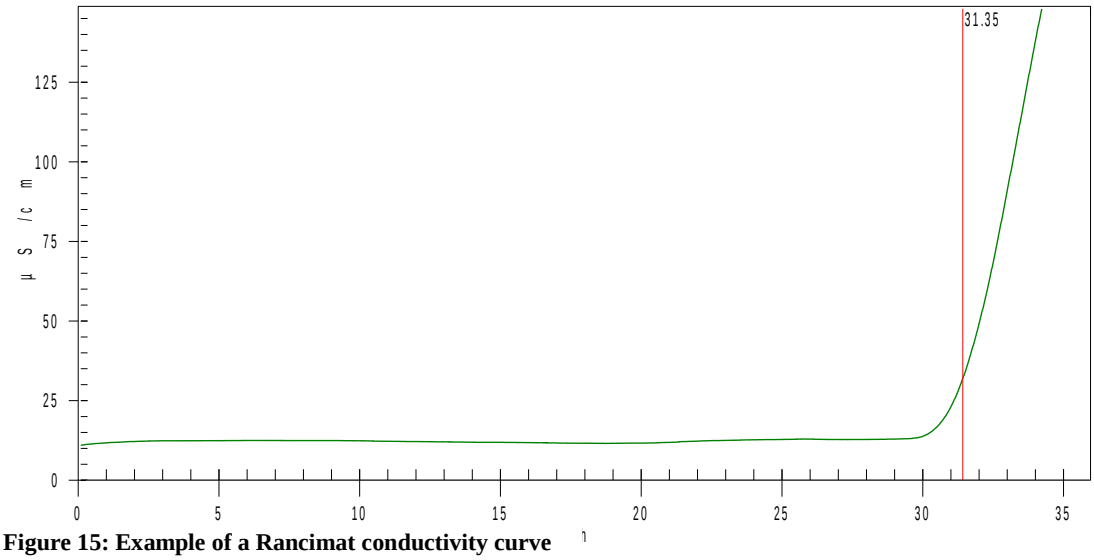


Figure 15: Example of a Rancimat conductivity curve

2.6.2 PetroOxy

An alternative technique to determine the oxidation stability of biofuel and its petrodiesel blends is the so-called PetroOxy method, which is regulated in the European specification DIN EN 16091 [77]. It is an accelerated oxidation test, where 5 mL of sample is placed in a pressure bomb and partially oxidised at 140 °C with a pure oxygen pressure of 7 bar. Pressure is monitored during the whole measurement, which is initially increasing due to the heating up phase from room temperature to 140°C. At this step the oxidation reserve is starting to deplete. After surpassing a maximum in pressure, it declines slightly; the complete depletion of the oxidation reserve is indicated by a sharp decrease of the pressure. When the pressure drop reaches a deviation of ten percent from the observed maximum, the measurement is stopped and the time elapsed corresponds to the induction period. Note that this IP is different from the one determined via Rancimat, as it not only represents the oxidation reserve but also some partial fuel aging.[76]

The advantages of this method include a significantly shorter testing time compared to the Rancimat method and less amount of sample required for analysing biodiesel blends. However, in contrast to the aforementioned method only one sample at a time can be analysed. Additionally, as for the Rancimat technique, quantification as well as characterisation of neither polymers nor insolubles are covered by this measurement technique. [76]

2.6.3 TOST

The so-called turbine oil oxidation stability test (TOST) represents a third method to determine the oxidation stability of pure biofuel and blends, which is regulated in the American specification ASTM D 7462 [78] . Additionally, the oxidation stability of pure petrodiesel is also determined via TOST, regulated by ASTM D 2274 [79] as well as DIN EN ISO 12205 [80]. In contrast to the methods described above, TOST is used to measure the total insoluble sludge formed and not some sort of induction period; a lower amount of insolubles corresponds to a higher fuel quality. A total of 350 mL of sample are aged for 16 hours at 95 °C with a constant stream of oxygen passing through the sample at 3 L/h. After that, the aged fuel is filtered and the reaction vessel thoroughly cleaned to be able to collect all the formed sludge for weighing. TOST is significantly less precise compared to PetroOxy and Rancimat, due to minimal amounts of insolubles formed it is only able to distinguish between fuels of terrible and good quality. Additionally, it is a lot more time consuming and prone to error compared to the PetroOxy method. [74]

Chapter 3: Experimental Section

3.1 Materials

3.1.1 Instruments

Cloud point: Herzog; HCP 852

Cold filter plugging point: Herzog; HCP 842

Flash point tester: Herzog; Pensky Martens Closed Cup HFP 339

GC-FID: Agilent; 7890A GC system, CTC Analytics autosampler, DB-HP-Wax column (30 m, 0.25 mm, 0.15 µm)

GC-FID-HT: Agilent; 7890B GC System, DB-5HT column (5 m, 0.53 mm, 0.15 µm**)**

ICP-OES: Spectro Genesis; FES + ASX-520 autosampler

Muffle furnace: Heraeus

Rancimat: Metrohm; 743 Rancimat device

Sulfur and Nitrogen Analyser: Mitsubishi; TS-100SD-100 sulfur detector, ND-100 nitrogen detector, ABC-100 automatic boat controller

Viscometer™: Anton Paar; Stabinger Viscometer SVM 300

Water content: Metrohm; 808 Titrando + 801 Stirrer

3.1.2 Standards

1,3-Diolein solution 97.3%, Supelco (Steinheim, Germany)

Triolein solution 99.9%, Supelco (Steinheim, Germany)

Nonadecanoic acid methyl ester ≥ 99%, NU-CHECK PREP, Inc. (Elysian, USA)

Monononadecanoin 99%, Larodan (Malmö Sweden)

1,3-Dinonadecanoin 99%, Larodan (Malmö Sweden)

Trinonadecanoin 99%**,** Larodan (Malmö Sweden)

1-Monopalmitoleoyl-rac-glycerol ≥ 99%, Sigma-Aldrich (Steinheim, Germany)

3.1.3 Fuel samples

A total of four different biodiesel samples and a single petrodiesel were used in this thesis.

Soybean oil methyl ester (SME)

One of the biodiesel samples was an Argentinian pure soybean oil methyl ester, the predominant biodiesel in USA and South America. It was directly taken from a biodiesel production site in Rosario, the heart of Argentina's soybean and biodiesel production and was sent by Dr. Guillermo Labadie, University of Rosario. It contains neither antioxidants nor other additives and has an orange-reddish colour and a smell characteristic for an unrefined and non-distilled SME.

Tallow methyl ester (TME)

The second biodiesel sample was a distilled tallow methyl ester. It was obtained from Biodiesel Kärnten GmbH from their production site at Arnoldstein, Carinthia. The main resource was beef tallow, no fresh vegetable oils were used as feedstocks. Furthermore, it also did not contain a single additive and both the yellowish colour as well as distinct odour are characteristic for a distilled TME.

Fatty acid methyl ester blend (MBD)

The third biodiesel was a fatty acid methyl ester blend produced by MÜNZER Bioindustrie GmbH in Ölhafen Lobau, Vienna. It was stabilised at the production site to meet the oxidation stability requirement set by DIN EN 14214 [71] as it is used at OMV, Austria, to produce B7 blends. The raw materials used for this biodiesel were mainly rapeseed oil, used frying oil, and other vegetable oils. The sample had a yellowish-brown colour, which is associated with used frying oil methyl esters.

Rapeseed oil methyl ester (ASG)

The fourth biofuel sample was a pure rapeseed oil methyl ester, the predominant biodiesel in Europe. It was obtained from the Analytik Service GmbH, situated in Neusäss, Germany. The sample had been stabilised to meet the requirements of the European specifiation for biodiesel DIN EN 14214 [71]. Its yellow colour is characteristic for an RME.

Haltermann reference diesel RF-06-03

A petrodiesel was required for the dilution of biodiesel samples to their respective B7 blends. Therefore, a reference diesel from Haltermann Solutions™ was obtained via BASF SE, Germany, which contained neither fatty acid methyl esters nor fuel additives.

3.1.4 Fuel additives

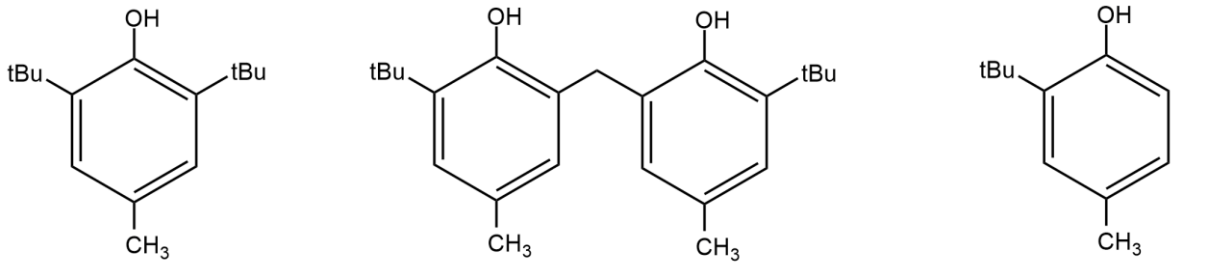
In this thesis four different antioxidants, two diesel performance packages and four deposit control additives were tested on their influence on the oxidation stability of pure biodiesel and B7 blends. All products but Vulkanox® BHT were provided by BASF SE, Germany.

Vulkanox® BHT

The main antioxidant used in this thesis was Vulkanox® BHT, which is produced by LANXESS. As the name already hints, it constitutes solely of 2,6-di-*tert*-butyl-4-methylphenol (see *Figure 16*), better known as BHT, and has a purity greater than 99%. It's a colourless and odourless crystalline compound that belongs to the class of hindered phenolic antioxidants. As mentioned earlier, BHT is by far the most predominantly used antioxidant in the fuel and biodiesel sector (see chapter *2.3 Antioxidants* for further details).

Baynox® Plus

The second antioxidant tested was Baynox® Plus, which is also produced by LANXESS. It is a yellow, odourless finely grained powder. This product consists 97 - 98 % of 2,2'-methylene-*bis*-(4-methyl-6-*tert*-butylphenol) and 0.2 - 0.3 % of 2-*tert*-butyl-4-methylphenol. Both compounds belong to the group of hindered phenolic antioxidants and strongly resemble the chemical structure of BHT. The former is a dimer of BHT and the latter only lacks a *tert*-butyl group on one of the *ortho* positions compared to it (see *Figure 16*). LANXESS claims that it is a highly potent antioxidant, especially suited for stabilising highly unsaturated fatty acid methyl esters. Additionally, the company states that the antioxidative efficiency of Baynox® Plus, in contrast to the majority of antioxidants, is independent of concentration.[81]



2,6-di-*tert*-butyl-4-methylphenol | 2,2'-Methylene-bis-(4-methyl-6-*tert*-butylphenol) | 2-*tert*-Butyl-4-methylphenol

Figure 16: Chemical compounds of Vulkanox® BHT (left) and Baynox® Plus (center and right)

AO#3 and AO#4

Two further antioxidants were tested, AO#3 and AO#4. Both of them are liquid products, the former contains a mixture of several different phenolic antioxidants, all of them strongly resemble the chemical structure of BHT. AO#4 contains a secondary aromatic amine as active component (see *2.3 Antioxidants* for further details).

Diesel performance packages (DPP)

Two different liquid diesel performance packages, DPP#1 and DPP#2, were tested on their influence on the oxidation stability of biodiesel and B7 blends. Both packages contain the same active component. DPP#1 additionally contains significant amounts of 2-ethylhexylnitrate, a common cetane number improver (see chapter *2.4 Overview on diesel additives*)

Deposit control additives (DCA)

A total of three different deposit control additives were used in this master thesis (see chapter *2.4 Overview on diesel additives*). One of them, DCA#3, contains the same active component as both diesel performance packages, but differs in solvent composition. The other two additives, DCA#1 and DCA#2, are based on alternative active components. DCA#1 is additionally labelled to contain 40% active antioxidant.

3.2 Methods

3.2.1 Rancimat method

The required amount of sample (3.0 or 7.5 g) was weighed into the respective borosilicate glass reaction tube (*see Table 4*). A nitrile rubber O-ring and a glass air tube were fitted to the plastic reaction vessel cover that were fixed with a thread adapter. An airtight cover was required to prevent leakage of volatile compounds. As a next step, the measuring cell was prepared. The glass measuring vessel was filled with 60 mL of distilled water and closed with the plastic measuring vessel cover that contains a conductometric measuring cell. After that, a silicon tube was attached to the tubing adapter on top of the measuring cell. When the heating block of the Rancimat measuring device had reached a stable temperature of 110 °C (+1,4 °C temperature correction) the closed reaction vessel was placed in one of eight measuring positions. Next, the silicone tubing of the measuring cell was attached to the thread adapter of the reaction vessel and measurement was started. A constant stream of 10 L/h of dry air was bubbled through the sample throughout the whole measurement. The Rancimat automatically stopped after the induction period was reached. [72,76]

Table 4: Parameters for the Rancimat analysis

Parameter	DIN EN 14112 (B100) [72]	DIN EN 15751 (Blends) [73]
Amount of sample	3.0 g	7.5 g
Reaction vessel	Short (15 cm)	Long (25 cm)
Glass air tube	Short (15 cm)	Long (25 cm)
Air stream	10 L/h	10 L/h
Temperature correction*	+ 1.4 °C	+ 1.4 °C
Amount of distilled water	60 mL	60 mL
Measuring temperature	110 °C	110 °C

**** Pre-set in the METROHM software***

3.2.2 Rancimat cleaning procedure

To be able to reuse the glass reaction vessels and air tubes, an intensive cleaning procedure had to be applied. First the glassware was rinsed with acetone, followed by hot water. After that the alkaline high performance cleaning agent Mucasol® was used at around 5% (v/v) with water to thoroughly clean the vessels and tubes using a cleaning brush. The last step was to flush them with hot water, acetone and distilled water and to put them in a drying oven at 110 °C for at least 30 minutes.

The measuring vessel and its cover were thoroughly cleaned using hot water and acetone as well as distilled water. Additionally, the two metallic rods of the conductometric measuring cell were carefully cleaned using small pipe cleaners.

3.2.3 Biodiesel analysis according to DIN EN 14214

Several standardised methods were used to determine the quality parameters of the used biofuel samples according to EN 14214 [71]. The following section is dedicated to briefly describe these procedures.

Acid value

The acid value was determined according to EN 14104 [82].

Cloud point

The cloud point was determined using a Herzog HCP 852 measuring device, following EN 23015 [83].

Cold filter plugging point

The cold filter plugging point (CFPP) was determined according to the normative EN 116 [84] using a Herzog HCP 842 measuring device.

Density

The density of the samples was determined using a Stabinger Viscometer ™ from Anton Paar at 15°C as reported in EN ISO 16896 [85].

Flash point

The flash point was determined according to EN ISO 3679 [86], using a Pensky Martens closed cup HFP 339 measuring device.

Content of mono-, di-, triglycerides, free- and total glycerine

The concentration of monoglycerides, diglycerides, triglycerides, free glycerine and total glycerine was determined using a GC-FID measurement as reported in EN 14105 [87] (see chapter *3.1.1*).

Content of group I (Na, K) and group II (Mg, Ca) metals

An ICP-OES measurement according to the normative EN 14538 [88] was used to determine the amount of sodium, potassium, magnesium as well as calcium present in the samples.

Methanol content

The methanol content was analysed using a headspace GC-FID as reported in EN 14110 [89] (see chapter *3.1.1*).

Methyl ester and linolenic acid methyl ester content and Iodine Value

Methyl ester as well as linolenic ester content were determined according to EN 14103 [90] via a GC-FID. The iodine value was calculated from chromatographic data following the normative EN 16300 [91] (see chapter *3.1.1*).

Oxidation stability

The oxidation stability was determined according to EN 14112 [72] for B100 and EN 15751 [73] for B7 blends at 110°C using a Metrohm Rancimat measuring device as described in section *3.2.1 Rancimat method.*

Phosphorus content

The phosphorus content was determined according to EN 14107 [92] using ICP-OES.

Sulfated ash content

The sulphated ash content was determined gravimetrically according to ISO 3987 [93], where the sample is burned, treated with concentrated as well as 40 % sulfuric acid and distilled water. Additionally, it includes several heating steps in a muffle furnace.

Sulfur content

The content of sulfur was determined according to ISO 20846 [94] using a sulfur and nitrogen analyser.

Total contamination

The total contamination was determined using the normative EN 12662 [95]. This standardised procedure involves a heating step, followed by a filtration of the sample through a glass microfiber filter and weighing of the filter to determine the amount of insolubles.

Viscosity

The viscosity was determined using a Stabinger Viscometer ™ from Anton Paar at 40°C as reported in EN ISO 16896 [85].

Water content

An 808 Titrando from Metrohm was used to determine the water content of the samples as reported in EN ISO 12937 [96].

Table 5: Parameters of EN 14214 [71]

Parameter	*Method*	*Unit*	*Lower limit*	*Upper limit*
Acid value	EN 14104	mg KOH/g	-	0.5
Cloud point	EN 23015	°C	-	16 to -3*
Cold filter plugging point	EN 116	°C, max.	-	13 to -10*
Density	EN ISO 16896	kg/m³	860	900
Flash point	EN ISO 3679	°C	101	-
Monoglyceride content	EN 14105	mg/kg	-	0.7
Diglyceride content	EN 14105	mg/kg	-	0.2
Triglyceride content	EN 14105	mg/kg	-	0.2
Free glycerine content	EN 14105	mg/kg	-	0.02
Total glycerine content	EN 14105	mg/kg	-	0.25
Group I metals (Na, K)	EN 14538	mg/kg	-	5
Group II metals (Ca, Mg)	EN 14538	mg/kg	-	5
Iodine value	EN 16300	-	-	120
Linolenic acid methyl ester	EN 14103	% (m/m)	-	12
Methanol content	EN 14110	% (m/m)	-	0.2
Methyl ester content	EN 14103	% (m/m)	96.5	-
Oxidation stability	EN 14112	hours	8	-
Phosphorus content	EN 14107	mg/kg	-	4
Sulfated ash content	ISO 3987	% (m/m)	-	0.02
Sulfur content	ISO 20846	mg/kg	-	10
Total contamination	EN 12662	mg/kg	-	24
Viscosity	EN ISO 3104	mm²/s	3.5	5
Water content	EN ISO 12937	mg/kg	-	500

**** Depended on national regulations***

3.3 Stabilisation of SME and TME with BHT

A) In pure biodiesel

Soybean oil methyl ester and tallow methyl ester were both stabilised using Vulkanox® BHT in a wide concentration range. Therefore, two stock solution were prepared for SME, one containing 2 g/kg (2000 ppm) and the other 1 g/kg (1000 ppm). In case of TME, a single stock solution with 1 g/kg or 1000 ppm BHT was sufficient.

Table 6: Preparation of the stock solutions

Stock Solution	*Biodiesel [g]*	*BHT [mg]*	*BHT conc. [mg/kg]*
TME, 1000 mg/kg BHT	100.0113	99.9	998
SME, 1000 mg/kg BHT	100.0210	100.9	1008
SME, 2000 mg/kg BHT	100.0000	201.3	2013

The stock solutions were stirred at 40 °C for 10 minutes, to guarantee complete antioxidant dissolution in the biodiesel matrix.

The desired concentrations were prepared via dilution of the stock solutions directly in the Rancimat reaction vessels, where each level of BHT was tested in duplicate.

Table 7: BHT concentration series in TME

TME	*Stock Solution [g]*	*Biodiesel [mg]*	*BHT conc. [mg/kg]*
1000 mg/kg BHT	2.9991	-	998
	3.0262	-	998
500 mg/kg BHT	1.5042	1.5002	500
	1.5421	1.5439	499
200 mg/kg BHT	0.6039	2.4053	200
	0.6014	2.4018	200
100 mg/kg BHT	0.3027	2.7039	100
	0.3026	2.7015	101

Table 8: BHT concentration series in SME I

SME	*Stock Solution 2 [g]*	*Biodiesel [mg]*	*BHT conc. [mg/kg]*
2000 mg/kg BHT	2.9998	-	2013
	2.9940	-	2013
1500 mg/kg BHT	2.2721	0.7757	1501
	2.2509	0.7502	1510

Table 9: BHT concentration series in SME II

SME	*Stock Solution 1 [g]*	*Biodiesel [mg]*	*BHT conc. [mg/kg]*
1000 mg/kg BHT	3.0149	-	1009
	3.0260	-	1009
500 mg/kg BHT	1.5012	1.5004	505
	1.5003	1.5046	504
200 mg/kg BHT	0.6032	2.4072	202
	0.6007	2.4014	202
100 mg/kg BHT	0.3054	2.7020	102
	0.3013	2.7055	101

B) In B7 blends

The stock solutions were used to prepare 4 g of each desired BHT concentration, based on results from the stabilisation experiments of B100 samples. After that, 1.4 mL of each sample was diluted with 18.6 mL Haltermann reference diesel, yielding in a 20 mL B7 blend with a biodiesel content of 7 % (v/v). Like before, a double determination was performed for each level of BHT tested. Additionally, the induction period of non-stabilised B7 blends of SME and TME were determined as references.

Table 10: TME samples for B7 blending

TME	*Stock solution [g]*	*Biodiesel [g]*	*BHT conc. [mg/kg]*
200 mg/kg BHT	0.8054	3.2000	201
150 mg/kg BHT	0.6121	3.3881	153
100 mg/kg BHT	0.4472	3.6461	109

Table 11: SME samples for B7 blending

SME	*Stock solution [g]*	*Biodiesel [mg]*	*BHT conc. [mg/kg]*
1000 mg/kg BHT	4	-	1009
500 mg/kg BHT	2.0065	1.9974	506
250 mg/kg BHT	1.0005	2.9988	252

3.4 Comparison of BHT with 3 other antioxidants in TME and SME

In case of SME, stock solutions of all three antioxidants, namely Baynox® Plus, AO#3 and AO#4, were prepared, each at a treat rate of 1 g/kg (1000 ppm). For TME a second step was conducted to dilute the initial solutions to an active component concentration of 200 mg/kg (200 ppm). The samples listed in *Table 13* and *Table 14* were analysed in B100 as well as in B7, each of them was tested in duplicate.

Table 12: Preparation of the stock solutions, TME

TME, Stock solution	*Biodiesel [g]*	*Antioxidant [mg]*	*AO conc. [mg/kg]*
1000 mg/kg Baynox® Plus	100.0083	99.9	999
1000 mg/kg AO#3	53,4000	53,4	1000
1000 mg/kg AO#4	58,3007	58,3	1000

Table 13: Dilution of the stock solutions, TME

TME	*Stock solution [g]*	*Biodiesel [g]*	*AO conc. [mg/kg]*
200 mg/kg Baynox® Plus	20,0092	80,0064	200
200 mg/kg AO#3	9,9982	40,0030	200
200 mg/kg AO#4	9,9992	40,0020	200

Table 14: Preparation of the stock solutions, SME

SME, Stock solution	*Biodiesel [g]*	*Antioxidant [mg]*	*AO conc. [mg/kg]*
1000 mg/kg Baynox® Plus	100.0004	99.9	999
1000 mg/kg AO#3	53,00038	53,0	1000
1000 mg/kg AO#4	58,3007	58,3	1000

The following six sample analysed as B100 and B7:

- SME, 1000 ppm Baynox® Plus
- SME, 1000 ppm AO#3
- SME, 1000 ppm AO#4
- TME, 200 ppm Baynox® Plus
- TME, 200 ppm AO#3
- TME, 200 ppm AO#4

3.5 Influence of DPPs on the oxidation stability of TME and SME

A) In non-stabilised biodiesel and B7 blends

7 mL of the stabilised biofuel samples were first diluted using 93 mL of Haltermann reference diesel and then the required amount of diesel performance package was added using a 1 µL micro syringe, the exact treat rate was determined gravimetrically on a precision balance. The samples were shaken vigorously thereafter to ensure homogeneity.

The following four samples were prepared and analysed in duplicate:

- B7 SME, DPP#1
- B7 SME, DPP#2
- B7 TME, DPP#1
- B7 TME, DPP#2

As a reference, the B100 and B7 of both SME as well as TME containing none of the above mentioned additives were measured as references.

B) In stabilised B7 blends

The already prepared stock solutions of soybean oil methyl ester and tallow methyl ester were used, containing an antioxidant concentration of 1000 mg/kg for the SME and 200 mg/kg for TME, respectively. 8.3 mL from each stock solution was diluted with 110 mL of Haltermann reference diesel for both diesel performance packages. This procedure results in a total of sixteen different samples of stabilized B7 blends (two biodiesel samples times four antioxidants times two DPP), each with a weight of approximately 100 g. After that, DPP#1 was added to one half of the blends and DPP#2 to the other, where the exact treat rates were determined gravimetrically, using a precision balance.

The following 16 samples were prepared and tested in duplicate:

- B7 SME, Vulkanox® BHT, DPP#1
- B7 SME, Vulkanox® BHT, DPP#2
- B7 SME, Baynox® Plus, DPP#1
- B7 SME, Baynox® Plus, DPP#2
- B7 SME, AO#3, DPP#1
- B7 SME, AO#3, DPP#2
- B7 SME, AO#4, DPP#1
- B7 SME, AO#4, DPP#2
- B7 TME, Vulkanox® BHT, DPP#1
- B7 TME, Vulkanox® BHT, DPP#2
- B7 TME, Baynox® Plus, DPP#1
- B7 TME, Baynox® Plus, DPP#2
- B7 TME, AO#3, DPP#1
- B7 TME, AO#3, DPP#2
- B7 TME, AO#4, DPP#1
- B7 TME, AO#4, DPP#2

3.6 Influence of DCAs on the oxidation stability of TME and SME

A) In non-stabilised B7 blends

Due to the fact that the additive treat-rates were rather low, B7 stock solutions containing the tenfold concentration were required. The respective additive was therefore directly added to 100 mL of B7, where the exact treat rate was determined gravimetrically. Then the blend was diluted to the desired level of active component using non-additivated B7. Additionally, the influence of diesel performance packages on the oxidation stability was retested to be able to directly compare the results (see chapter *3.5*).

The following ten samples were prepared and tested in duplicate:

- B7 SME, DCA#1
- B7 SME, DCA#2
- B7 SME, DCA#3
- B7 SME, DPP#1
- B7 SME, DPP#2
- B7 TME, DCA#1
- B7 TME, DCA#2
- B7 TME, DCA#3
- B7 TME, DPP#1
- B7 TME, DPP#2

B) In stabilised B7 blends

A new stock solution for each of the two biodiesel samples was required, with 1000 mg/kg BHT for SME and 200 mg/kg in case of TME. At next, 7 mL of each stock solution was mixed with 93 mL of Haltermann reference diesel for each of the three DCAs, yielding in a total of six stabilised B7 blends. Next, the tenfold treat-rate of the deposit control additive was added and they were diluted using stabilised B7 samples to the required treat-rates. Again, the influence of both diesel performance packages on the oxidation stability of stabilised B7 blends was retested to be able to directly compare the results (see chapter *3.5*).

The following ten samples were prepared and tested in duplicate:

- B7 SME, Vulkanox® BHT, DCA#1
- B7 SME, Vulkanox® BHT, DCA#2
- B7 SME, Vulkanox® BHT, DCA#3
- B7 SME, Vulkanox® BHT, DPP#1
- B7 SME, Vulkanox® BHT, DPP#2
- B7 TME, Vulkanox® BHT, DCA#1
- B7 TME, Vulkanox® BHT, DCA#2
- B7 TME, Vulkanox® BHT, DCA#3
- B7 TME, Vulkanox® BHT, DPP#1
- B7 TME, Vulkanox® BHT, DPP#2

3.7 Combination of different DCAs in TME and SME

A) In non-stabilised B7 blends

At first, new B7 stock solutions were prepared for all three diesel additives, each containing the twofold treat-rate of one DCA. The respective additive was directly added to 100 mL of B7, where the exact treat rate was determined gravimetrically. Then, the two stock solutions were mixed in a 1:1 ratio, resulting in a B7 blend containing both additives, each at the desired treat rate.

The following four samples were prepared and tested in duplicate:

- B7 SME, DCA#1 + DCA#2
- B7 SME, DCA#1 + DCA#3
- B7 TME, DCA#1 + DCA#2
- B7 TME, DCA#1 + DCA#3

B) In stabilised B7 blends

The sample preparation for the stabilised B7 blends was performed as described above.

The following four samples were prepared and tested in duplicate:

- B7 SME, BHT, DCA#1 +DCA#2
- B7 SME, BHT, DCA#1 + DCA#3
- B7 TME, BHT, DCA#1 + DCA#2
- B7 TME, BHT, DCA#1 + DCA#3

3.8 Evaluation of the possible synergistic effect of DCA#1 in SME

Two B7 blends containing half of the treat rate of DCA#1 were prepared, one of them stabilised with the aforementioned hindered phenolic antioxidant. Both B7 blends from chapter *3.6* containing DCA#1 were used to prepare the required samples. These were diluted at a 1:1 ratio using either non stabilised B7 SME or Vulkanox® BHT additivated B7 SME respectively.

The following four samples were prepared and tested in duplicate:

- B7 SME, DCA#1
- B7 SME, ½ DCA#1
- B7 SME, Vulkanox® BHT, DCA#1
- B7 SME, Vulkanox® BHT, ½ DCA#1

3.9 Long-term storage of SME and TME

After their initial preparation, the samples were transferred into 100 mL Duran® bottles, which were sealed and stored for one or two month at 17 - 21 °C in absence of light. During this storage period, the samples were neither moved nor shaken. They were shaken vigorously to ensure homogeneity, only immediately before analysis on the Rancimat measuring device.

The following ten samples were stored for one month:

- B7 SME, Vulkanox® BHT, DPP#1
- B7 SME, Vulkanox® BHT, DPP#2
- B7 SME, Vulkanox® BHT, DCA#1
- B7 SME, Vulkanox® BHT, DCA#2
- B7 SME, Vulkanox® BHT, DCA#3
- B7 TME, Vulkanox® BHT, DPP#1
- B7 TME, Vulkanox® BHT, DPP#2
- B7 TME, Vulkanox® BHT, DCA#1
- B7 TME, Vulkanox® BHT, DCA#2
- B7 TME, Vulkanox® BHT, DCA#3

The following four samples were stored for two months:

- B7 SME, DPP#1
- B7 SME, DPP#2
- B7 SME, Vulkanox® BHT
- B7 SME, Vulkanox® BHT, DPP#1
- B7 SME, Vulkanox® BHT, DPP#2
- B7 TME, DPP#1
- B7 TME, DPP#2
- B7 TME, Vulkanox® BHT
- B7 TME, Vulkanox® BHT, DPP#1
- B7 TME, Vulkanox® BHT, DPP#2

3.10 Influence of diesel additives on the stability of MBD and ASG

The samples were prepared as described in chapter *3.5* and *3.6*, respectively.

The following ten samples were prepared and tested in duplicate:

- B7 ASG, DPP#1
- B7 ASG, DPP#2
- B7 ASG, DCA#1
- B7 ASG, DCA#2
- B7 ASG, DCA#3
- B7, MBD, DPP#1
- B7, MBD, DPP#2
- B7, MBD, DCA#1
- B7, MBD, DCA#2
- B7, MBD, DCA#3

3.11 Combination of different DCAs in MBD and ASG

The additivated B7 blends were prepared exactly as described in chapter *3.7*.

The following four samples were prepared and tested in duplicate:

- B7 ASG, DCA#1 +DCA#2
- B7 ASG, DCA#1 + DCA#3
- B7, MBD, DCA#1 + DCA#2
- B7, MBD, DCA#1 + DCA#3

Chapter 4: Results and Discussion

4.1 Analysis of biodiesel as by DIN EN 14214

As first step of this master thesis all biodiesel sample were analysed according to the European biodiesel specification DIN EN 14214.[71] This set of analyses was conducted to guarantee that the chosen samples are suitable representatives for the different types of biodiesel available on the market.

4.1.1 Soybean oil methyl ester

Table 15: DIN EN 14214 analysis of soybean oil methyl ester

Parameter	*Method*	*Unit*	*Result*
Acid value	EN 14104	mg KOH/g	0.39
Cloud point	EN 23015	°C	1
Cold filter plugging point	EN 116	°C, max.	-3
Density	EN ISO 16896	kg/m³	886
Flash point	EN ISO 3679	°C	160
Monoglyceride content	EN 14105	mg/kg	0.52
Diglyceride content	EN 14105	mg/kg	0.13
Triglyceride content	EN 14105	mg/kg	0.25
Free glycerine content	EN 14105	mg/kg	0.002
Total glycerine content	EN 14105	mg/kg	0.18
Group I metals (Na, K)	EN 14538	mg/kg	0.5
Group II metals (Ca, Mg)	EN 14538	mg/kg	<< 5
Iodine value	EN 16300	g I_2/100g	102
Linolenic acid methyl ester	EN 14103	% (m/m)	6.3
Methanol content	EN 14110	% (m/m)	< 0.01
Methyl ester content	EN 14103	% (m/m)	95.6
Oxidation stability	EN 14112	hours	5.7
Phosphorus content	EN 14107	mg/kg	5.7
Sulfated ash content	ISO 3987	% (m/m)	0.003
Sulfur content	EN ISO 20846	mg/kg	< 1
Total contamination	EN 12662	mg/kg	19
Viscosity	EN ISO 3104	mm²/s	4.1
Water content	EN ISO 12937	mg/kg	670

The Argentinian soybean oil methyl ester sample is not able to meet all requirements set by EN 14214 [71]. The content of monoglycerides, triglycerides and phosphorus exceed the limit, whereas oxidation stability as well as methyl ester content are too low. Nevertheless, the biodiesel sample is of high market relevance in USA and South America, where a different specification concerning fuel quality is used, namely ASTM D 6751.[69]

In this specification, the maximum allowable phosphorus content is set to 10 mg/kg and the oxidation stability requirement is as low as 3 hours. Furthermore, determination of methyl ester content as well as mono- and triglyceride content is not part of ASTM D 6751.[69] Additionally, it is not surprising that soybean oil methyl ester had an induction period below eight hours. On the one hand, it contained high amounts of polyunsaturated fatty acid methyl esters, like C18:2 and C18:3. On the other, no antioxidants were added to the biodiesel sample to increase its stability. Soybean oil does contain small amount of *β*-carotene naturally, which is the reason for its colour and relatively high initial stability, despite being a highly unsaturated vegetable oil.

Table 16: Fatty acid profile of SME in % (m/m)

Fatty acid		***SME***	***Soybean oil reference*** [5]
Myristic acid	**C14:0**	0.3	≤ 0.2
Palmitic acid	**C16:0**	12.3	8.0 - 13.5
Palmitoleic acid	**C16:1**	0.3	≤ 0.2
Heptadecanoic acid	**C17:0**	0.1	≤ 0.1
Heptadecenoic acid	**C17:1**	-	≤ 0.1
Stearic acid	**C18:0**	5.5	2.0 - 5.4
Oleic acid	**C18:1**	23.7	17.0 - 30.0
Linoleic acid	**C18:2**	48.1	48.0 - 59.0
Linolenic acid	**C18:3**	6.61	4.5 – 11.0
Icosanoic acid	**C20:0**	0.4	0.1 – 0.6
Icosenoic acid	**C20:1**	0.2	0,1 - 0,6
Icosadienoic acid	**C20:2**	0.1	≤ 0.5
Docosanoic acid	**C22:0**	0.4	≤ 0.1
Docosenoic acid	**C22:1**	-	≤ 0.3
Docosadienoic acid	**C22:2**	-	< 0.05
Tetracosanoic acid	**C24:0**	-	≤ 0.5
Tetracosenoic acid	**C24:1**	-	< 0.05

Regarding the fatty acid profile, there is no doubt that the only feedstock used for this biodiesel was indeed soybean oil. Additionally, the content of unsaturated fatty acid methyl esters, especially of C18:3, indicates that it is a relatively fresh sample.

4.1.2 Tallow methyl ester

Table 17: DIN EN 14214 analysis of tallow methyl ester

Parameter	*Method*	*Unit*	*Result*
Acid value	EN 14104	mg KOH/g	0.26
Cloud point	EN 23015	°C	13
Cold filter plugging point	EN 116	°C, max.	10
Density	EN ISO 16896	kg/m³	875
Flash point	EN ISO 3679	°C	172
Monoglyceride content	EN 14105	mg/kg	0.05
Diglyceride content	EN 14105	mg/kg	< 0.01
Triglyceride content	EN 14105	mg/kg	< 0.01
Free glycerine content	EN 14105	mg/kg	0.002
Total glycerine content	EN 14105	mg/kg	0.01
Group I metals (Na, K)	EN 14538	mg/kg	0.4
Group II metals (Ca, Mg)	EN 14538	mg/kg	<< 5
Iodine value	EN 16300	g I_2/100g	67
Linolenic acid methly ester	EN 14103	% (m/m)	0.9
Methanol content	EN 14110	% (m/m)	< 0.01
Methyl ester content	EN 14103	% (m/m)	98.9
Oxidation stability	EN 14112	hours	5.5
Phosphorus content	EN 14107	mg/kg	4.5
Sulfated ash content	ISO 3987	% (m/m)	0.003
Sulfur content	EN ISO 20846	mg/kg	9
Total contamination	EN 12662	mg/kg	29
Viscosity	EN ISO 3104	mm²/s	4.1
Water content	EN ISO 12937	mg/kg	42

The tallow methyl esters sample did also not meet all the requirements set of EN 14214 [71]. For this particular biodiesel, total contamination as well as phosphorus content are above the limit and again oxidation stability was too low. Unsurprisingly, both cloud point and cold filter plugging point are well above 0 °C, due to high concentrations of saturated fatty acids in animal based feedstocks., such as C16:0 and C18:0. Nevertheless, it was a biofuel of high quality, as the low oxidation stability originated from a complete absence of natural as well as synthetic antioxidants in the sample. The clear colour, high methyl ester and low sulfur content, despite being a beef tallow based biodiesel, are all typical for a distilled FAME.

Furthermore, the raw material might be responsible for the high content of insoluble contaminations, as it could stem from various plastics originating from packaging materials or from other insoluble contaminants.

Table 18: Fatty acid profile of TME in % (m/m)

Fatty acid		***TME***	***Beef tallow reference [5]***
Myristic acid	**C14:0**	2.1	2.0 - 6.3
Myristoleic acid	**C14:1**	0.1	not listed
Pentadecanoic acid	**C15:0**	0.4	not listed
Palmitic acid	**C16:0**	24.8	20.0 - 30.0
Palmitoleic acid	**C16:1**	3.2	1.0 - 2.5
Heptadecanoic acid	**C17:0**	0.7	< 1.5
Heptadecenoic acid	**C17:1**	0.4	< 1.0
Stearic acid	**C18:0**	15.9	15.0 - 30.0
Oleic acid	**C18:1**	39.6	30.0 - 45.0
Linoleic acid	**C18:2**	9.2	1.0 - 6.0
Linolenic acid	**C18:3**	0.9	< 1.5
Icosanoic acid	**C20:0**	0.2	< 0.5
Icosenoic acid	**C20:1**	0.45	< 0.1
Icosadienoic acid	**C20:2**	0.2	< 0.5
Icosatrienoic acid	**C20:3**	0.2	not listed

The fatty acid profile of TME was almost identical to that of beef tallow, only palmitoleic and linoleic acid are beyond the excepted concentrations. Additionally, small amount of C14:1, C15:0 and C20:3 can be detected, which are not covered by the reference. However, due to only minimal deviations from the fatty acid profile of beef tallow, it cannot be determined if another raw material was used for the production of this biodiesel sample.

4.1.3 Fatty acid methyl ester blend

Table 19: DIN EN 14214 analysis of the fatty acid methyl ester blend

Parameter	*Method*	*Unit*	*Result*
Acid value	EN 14104	mg KOH/g	0.26
Cloud point	EN 23015	°C	-*
Cold filter plugging point	EN 116	°C, max.	-9
Density	EN ISO 16896	kg/m³	878
Flash point	EN ISO 3679	°C	101
Monoglyceride content	EN 14105	mg/kg	0.47
Diglyceride content	EN 14105	mg/kg	0.15
Triglyceride content	EN 14105	mg/kg	0.10
Free glycerine content	EN 14105	mg/kg	0.018
Total glycerine content	EN 14105	mg/kg	0.155
Group I metals (Na, K)	EN 14538	mg/kg	0.8
Group II metals (Ca, Mg)	EN 14538	mg/kg	1.0
Iodine value	EN 16300	g I_2/100g	102
Linolenic acid methyl ester	EN 14103	% (m/m)	5.3
Methanol content	EN 14110	% (m/m)	0.065
Methyl ester content	EN 14103	% (m/m)	97.0
Oxidation stability	EN 14112	hours	9.1
Phosphorus content	EN 14107	mg/kg	1.9
Sulfated ash content	ISO 3987	% (m/m)	< 0.001
Sulfur content	EN ISO 20846	mg/kg	< 1
Total contamination	EN 12662	mg/kg	8
Viscosity	EN ISO 3104	mm²/s	4.4
Water content	EN ISO 12937	mg/kg	175

*** Malfunction of the measuring device**

The fatty acid methyl ester blend, produced by MÜNZER Bioindustrie GmbH, fulfils all requirements set by the European specification EN 14214 [71]. This result was expected, as this kind of biodiesel is sold to OMV, Austria, to produce B7 blends for the European market.

A relatively low methyl ester content is typical for biodiesel made from significant amounts of used frying oil, due to polymer formation during thermal stress.[62] A low acid value hints that at least some of the raw materials used to produce the biodiesel were fresh neat vegetable oils. A high oxidation stability, despite its elevated iodine value of 102, was a clear indication for a stabilisation of the sample with antioxidants.

Table 20: Fatty acid profile of the FAME blend in % (m/m)

Fatty acid		*MBD*	*Rapeseed oil reference* [5]
Caproic acid	**C6:0**	0.3	< 0.05
Caprylic acid	**C8:0**	0.2	< 0.05
Perlagonic acid	**C9:0**	0.2	not listed
Capric acid	**C10:0**	0.2	< 0.05
Lauric acid	**C12:0**	0.2	< 0.05
Myristic acid	**C14:0**	0.3	≤ 0.2
Palmitic acid	**C16:0**	9.9	2.5 - 7.0
Stearic acid	**C18:0**	2.8	0.3 - 3.0
Oleic acid	**C18:1**	54.1	51.0 - 70.0
Linoleic acid	**C18:2**	22.94	15.0 - 30.0
Linolenic acid	**C18:3**	5.5	5.0 - 14.0
Icosanoic acid	**C20:0**	0.5	0.2 - 1.2
Icosenoic acid	**C20:1**	0.8	0.1 - 4.3

Regarding the fatty acid profile, there was no doubt that the main feedstock used for this biodiesel was rapeseed oil. However, presence of significant amounts of short chain fatty acids methyl esters indicated that there were also other raw materials involved. These FAMEs also explain the relatively low flash point of 101 °C, due to the fact that they are able to form ignitable mixtures in air at lower temperatures, as the chain length is directly proportional to the flash point. [97]

Possible other raw materials include palm oil (see *Table 1*), coconut oil, as well as clarified butter. The latter two contain significant amounts of short chain fatty acids and all three of them are used for frying or cooking.

Table 21: Fatty acid profile of coconut oil and clarified butter in % (m/m) [5]

Fatty acid		*Coconut oil*	*Butter fat*
Caproic acid	**C6:0**	≥ 0.7	2.9 - 3.0
Caprylic acid	**C8:0**	4.6 - 10.0	1.0- 1.7
Capric acid	**C10:0**	5.0 - 8.0	1.9 - 4.1
Lauric acid	**C12:0**	45.1 - 53.2	2.3 - 4.6
Myristic acid	**C14:0**	16.8 - 21.0	8.6 - 14.6
Palmitic acid	**C16:0**	7.5 - 10.0	22.2 - 36.7
Stearic acid	**C18:0**	2.0 - 4.0	6.1 - 12.7
Oleic acid	**C18:1**	5.0 - 10.0	17.2 - 29.7
Linoleic acid	**C18:2**	1.0 - 2.5	1.0 - 3.1
Linolenic acid	**C18:3**	≥ 0.7	0.7 - 3.0

4.1.4 Rapeseed oil methyl ester

Table 22: DIN EN 14214 analysis of rapeseed oil methyl ester

Parameter	*Method*	*Unit*	*Result*
Acid value	EN 14104	mg KOH/g	0.24
Cetane number	EN 15195	-	51.3
Cloud point	EN 23015	°C	-4
Cold filter plugging point	EN 116	°C, max.	-19
Copper band corrosion	EN ISO 2160	rating	1
Density	EN ISO 16896	kg/m³	883
Flash point	EN ISO 3679	°C	180
Monoglyceride content	EN 14105	mg/kg	0.45
Diglyceride content	EN 14105	mg/kg	0.09
Triglyceride content	EN 14105	mg/kg	0.03
Free glycerine content	EN 14105	mg/kg	0.002
Total glycerine content	EN 14105	mg/kg	0.133
Group I metals (Na, K)	EN 14538	mg/kg	< 1
Group II metals (Ca, Mg)	EN 14538	mg/kg	< 1
Iodine value	EN 16300	g I_2/100g	111
Linolenic acid methyl ester	EN 14103	% (m/m)	8.8
Methanol content	EN 14110	% (m/m)	0.02
Methyl ester content	EN 14103	% (m/m)	98.8
Oxidation stability	EN 14112	hours	16.1
Phosphorus content	EN 14107	mg/kg	< 0.5
PUFA	EN 15779/A1	% (m/m)	< 0.6
Sulfated ash content	ISO 3987	% (m/m)	< 0.001
Sulfur content	EN ISO 20846	mg/kg	3.4
Total contamination	EN 12662	mg/kg	3
Viscosity	EN ISO 3104	mm²/s	4.4
Water content	EN ISO 12937	mg/kg	57

Table 23: Fatty acid profile of RME in % (m/m)

Fatty acid		*RME*	*Rapeseed oil reference* [5]
Palmitic acid	**C16:0**	4.7	2.5 - 7.0
Palmitoleic acid	**C16:1**	0.2	≤ 0.6
Stearic acid	**C18:0**	1.6	0.3 - 3.0
Oleic acid	**C18:1**	62.6	51.0 - 70.0
Linoleic acid	**C18:2**	18.9	15.0 - 30.0
Linolenic acid	**C18:3**	8.7	5.0 - 14.0
Icosanoic acid	**C20:0**	0.5	0.2 - 1.2
Icosenoic acid	**C20:1**	1.3	0.1 - 4.3
Icosatrienoic acid	**C20:3**	0.2	not listed
Docosanoic acid	**C22:0**	0.2	≤ 0.6
Docosenoic acid	**C22:1**	0.3	≤ 5

As mentioned earlier, DIN EN 14214 [71] analysis for that particular sample was performed by the Analytik Service GmbH and the test report was sent with the RME sample, which was able to fulfil all requirements. Oxidation stability and methyl ester as content were retested, yielding the exact same results.

There was no doubt that this biodiesel sample had been stabilised, due to an exceptionally high oxidation stability of 16.1 hours, despite its high iodine value of 111 g I_2/100g and low CFPP of -19 °C. Both parameters indicate that unsaturated fatty acid methyl esters constitute a major part of the sample.

Regarding the fatty acid profile, it can be assumed that only rapeseed oil was used as feedstock for this biodiesel sample.

4.2 Stabilisation of SME and TME with BHT in B100

Soybean oil methyl ester and tallow methyl ester were both stabilised using Vulkanox® BHT in a wide concentration range to evaluate the efficiency of the aforementioned antioxidant in different biodiesel matrices.

4.2.1 Soybean oil methyl ester

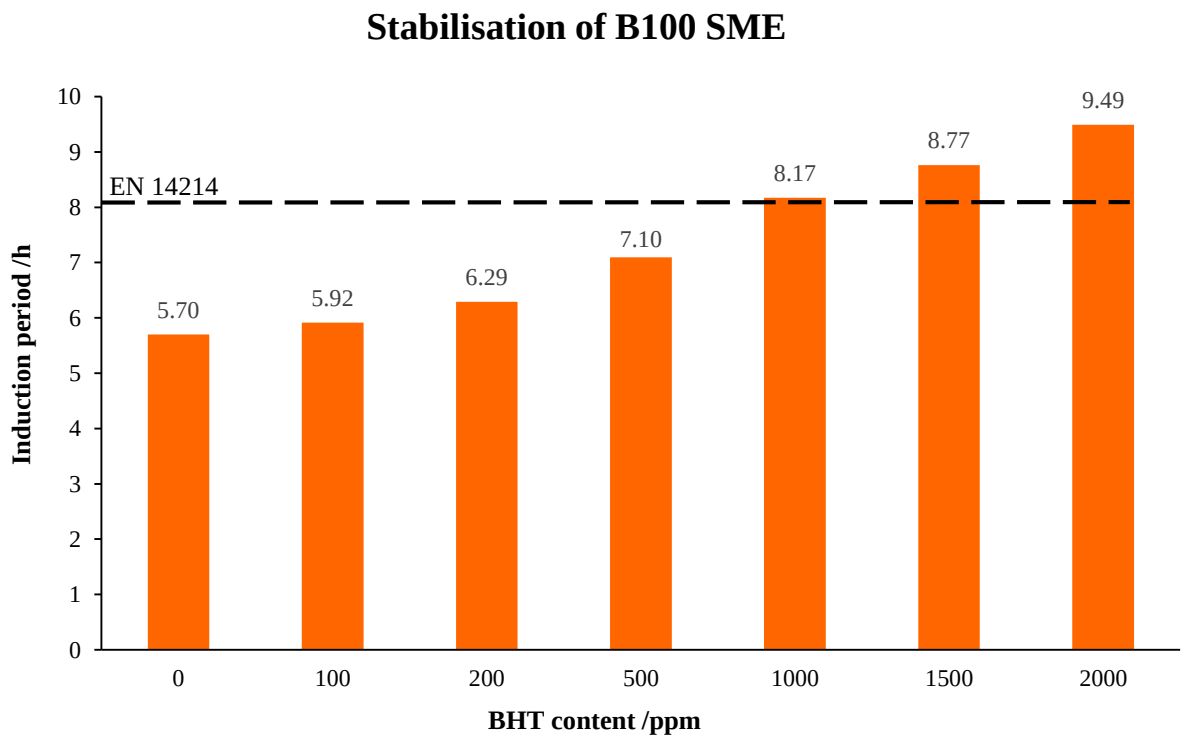


Figure 17: Results from B100 SME stabilisation experiments using BHT

Table 24: Results from B100 SME stabilisation experiments using BHT

SME	*Induction period [h]*	*Average IP [h]*
2000 mg/kg BHT	9.42	9.49
	9.56	
1500 mg/kg BHT	8.85	8.77
	8.68	
1000 mg/kg BHT	8.00	8.17
	8.34	
500 mg/kg BHT	7.19	7.10
	7.00	
200 mg/kg BHT	6.21	6.29
	6.37	
100 mg/kg BHT	6.02	5.92
	5.81	
0 mg/kg BHT	5.70	-

As can be seen in the table and figure above, pure soybean oil methyl ester sample was rather difficult to stabilise with BHT. 200 mg/kg of the antioxidant increase the oxidation stability only slightly above an hour. High doses of the antioxidant were required (1000 ppm) to reach an oxidation stability above eight hours, the minimum requirement set by DIN EN 14214 [71]. As much as 2000 mg/kg BHT were required to increase the induction period of the fresh SME sample by four hours, which corresponds to a rise of 66%.

Possible explanations for this behaviour include high content of unsaturated fatty acids as well as presence of significant amounts of natural antioxidants. Frankel et al. [37] found that the natural content of tocopherols in soybean oil is too high to sustain a high oxidation stability, even showing pro-oxidative effects. However, they also stated that the common antioxidants BHT, BHA and propylgallate did fail to significantly increase the oxidation stability in tocopherol-free soybean oil. Thus they concluded, that the main reason for the difficulty of stabilising soybean oil is its fatty acid profile. Dunn [98] on the other hand reported that BHT was highly suitable for stabilising soybean oil methyl ester, especially in low treat rates. However, he also noted that the efficiency of all tested antioxidants was significantly diminished at higher treat rates.

4.2.2 Tallow methyl ester

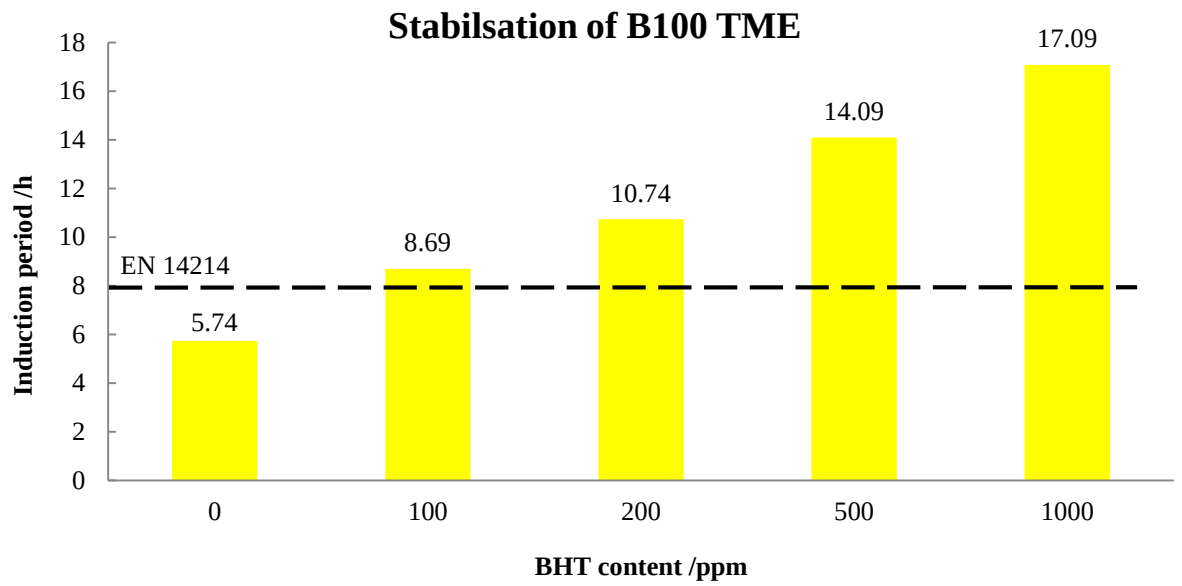


Figure 18: Results from B100 TME stabilisation experiments using BHT

Table 25: Results from B100 TME stabilisation experiments using BHT

TME	*Induction period [h]*	*Average IP [h]*
1000 mg/kg BHT	16.65	17.09
	17.52	
500 mg/kg BHT	13.88	14.09
	14.29	
200 mg/kg BHT	10.88	10.74
	10.59	
100 mg/kg BHT	8.64	8.69
	8.74	
0 mg/kg BHT	5.74	-

For the tallow methyl ester sample as little as 100 mg/kg of BHT were enough to reach an oxidation stability above 8 hours. Additionally, the antioxidant was also more active at higher concentrations, as there was almost a linear correlation between BHT content and induction period, which can be seen in *Figure 18.* This phenomenon can be explained through the lack of natural antioxidants as well as low content of polyunsaturated fatty acid methyl esters of beef tallow, the main feedstock used for this biodiesel (see *Table 18*).

When comparing the effect of BHT on both biofuels, TME was easier to stabilise, as a treat rate of 1000 mg/kg BHT more than tripled the initial induction period. In contrast to that, the same amount of antioxidant only led to a 66% increase in oxidation stability (see *Figure 19*).

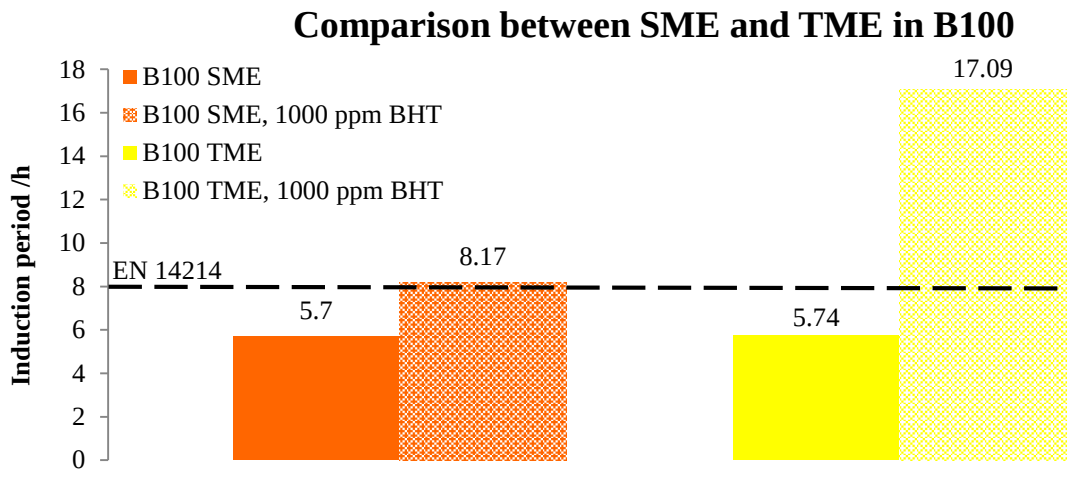


Figure 19: Comparison between SME and TME in B100

4.3 Stabilisation of SME and TME with BHT in B7

Both Soybean oil methyl ester and tallow methyl ester were also stabilised with Vulkanox® BHT in a wide concentration range in their respective B7 blends. This was performed to compare the efficiency of the aforementioned antioxidant in B7 blends to that in pure biodiesel.

4.3.1 Soybean oil methyl ester

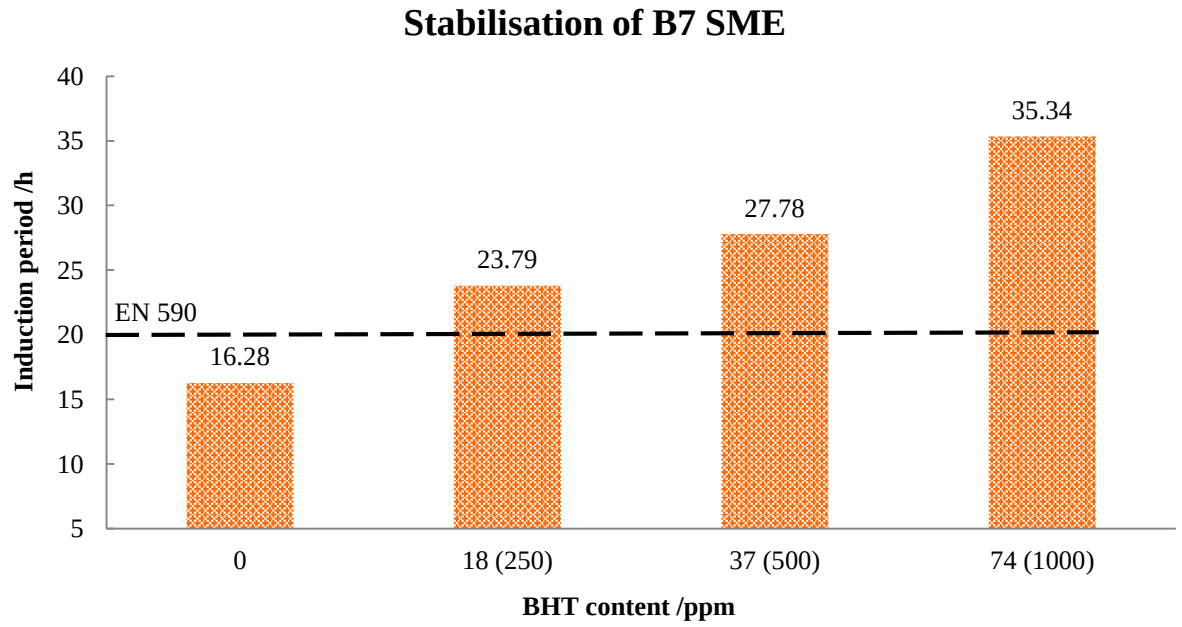


Figure 20: Results from B7 SME stabilisation experiments using BHT

The numbers in parentheses in *Figure 20* correspond to the BHT concentration of the respective stock solution that was diluted to B7 level.

Table 26: Results from B7 SME stabilisation experiments using BHT

B7 blends	*Stock solutions*	*Induction period (averaged)*
0 mg/kg BHT	0 mg/kg BHT	16.28 h (16.60, 15,95)
18 mg/kg BHT	250 mg/kg BHT	23.79 h (24.03, 23.55)
37 mg/kg BHT	500 mg/kg BHT	27.78 h (28.34, 27.22)
74 mg/kg BHT	1000 mg/kg BHT	35.34 h (36.05, 34.63)

The BHT concentration in B7 blends was calculated as followed:

$$c_{BHT}\ [B7] = \frac{m\ [Biodiesel]}{m\ [Petrodiesel] + m\ [Biodiesel]} * c_{BHT}\ [Stock\ solution]$$

The fresh non-stabilised SME B7 blend was not able to reach the required induction period of 20 h set by EN 590 [70]. However, only 18 mg/kg BHT were sufficient to increase the oxidation stability of fresh B7 SME blends to approximately 24 h. The antioxidant was much more effective at stabilising B7 blends compared to pure biodiesel. This phenomenon is called *polar paradox* [99], as the polar BHT has an enhanced performance in nonpolar petrodiesel compared to the significantly more polar biodiesel. This is attributed to the tendency of polar antioxidants to accumulate at the water-biodiesel interface rather than evenly distribute across the whole blend. [100]

4.3.2 Tallow methyl ester

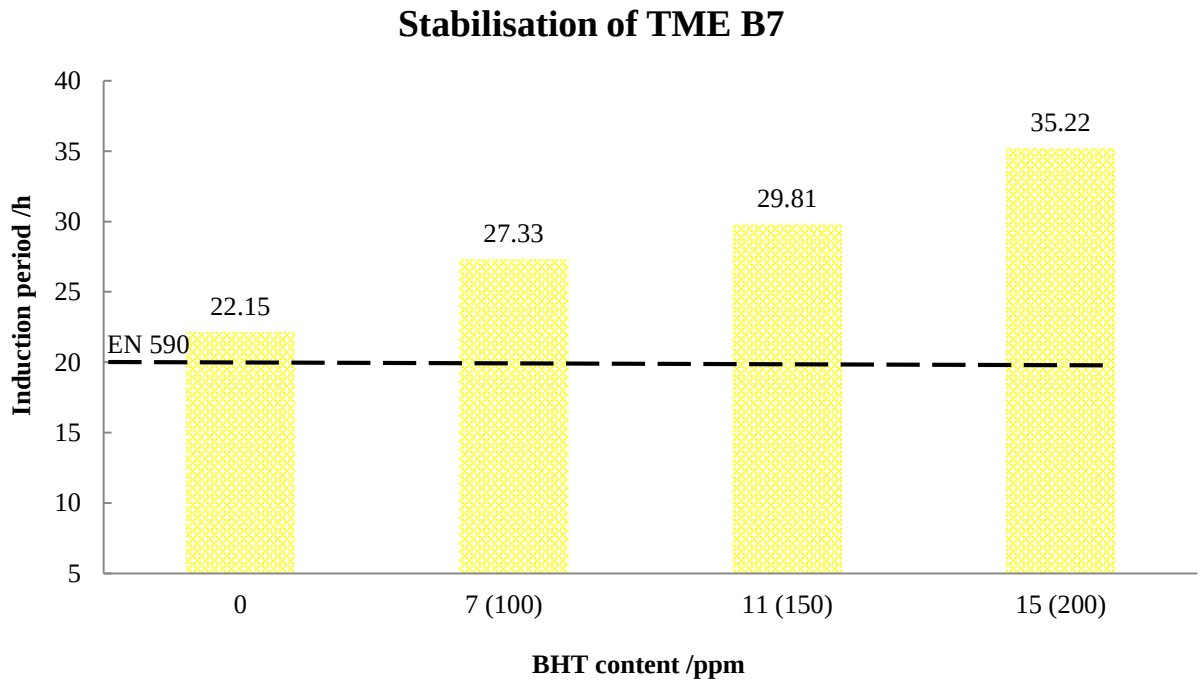


Figure 21: Results from B7 TME stabilisation experiments using BHT

Table 27: Results from B7 TME stabilisation experiments using BHT

B7 blends	*Stock solutions*	*Induction period (averaged)*
0 mg/kg BHT	0 mg/kg BHT	22.15 h (22.26, 22.04)
7 mg/kg BHT	100 mg/kg BHT	27.33 h (27.60, 27.06)
11 mg/kg BHT	150 mg/kg BHT	29.81 h (29.21, 30.41)
15 mg/kg BHT	200 mg/kg BHT	35.22 h (35.92, 34.51)

Although the neat B7 TME has a rather high oxidation stability, there was still a sharp increase with a BHT concentration of just 7 mg/kg BHT with a plus of more than 20 percent. Additionally, these blends were easier to stabilise compared to soybean oil methyl ester. An induction period of 35 h was achieved with just 15 mg/kg of BHT for B7 TME, almost the fivefold antioxidant concentration (74 mg/kg) was required for SME (see *Figure 21*). There was no BHT required to reach the minimum oxidation stability set by EN 590 [70], as pure B7 TME had an induction point of over 22 h. In contrast to SME however, the antioxidant performed better in pure biodiesel. B100 TME stock solution containing 100 mg/kg BHT had roughly a 50% higher induction period (2h) compared to the non-stabilised sample, whereas in B7 it was only 23% (5h).

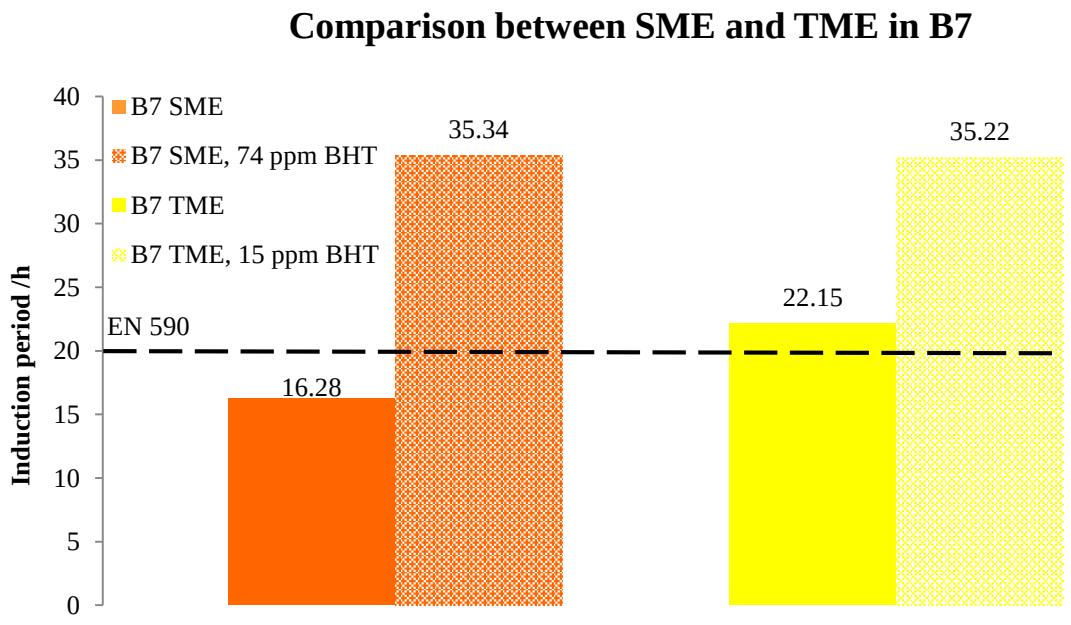


Figure 22: Comparison between SME and TME in B7

4.4 Comparison of BHT to 3 other antioxidants in SME and TME

The next step of this theses was to compare the antioxidative efficiency of BHT in soybean oil methyl ester and tallow methyl ester to three other antioxidants, namely Baynox® Plus, AO#3 and AO#4. SME was tested at an additive treat rate of 1000 mg/kg, whereas TME at 200 mg/kg, the concentrations were based on the results of BHT in B100 samples. The decreased antioxidant concentration was chosen for the TME, as it was enough to exceed the minimum requirement for the oxidation stability set by EN 14214 [71].

4.4.1 Soybean oil methyl ester

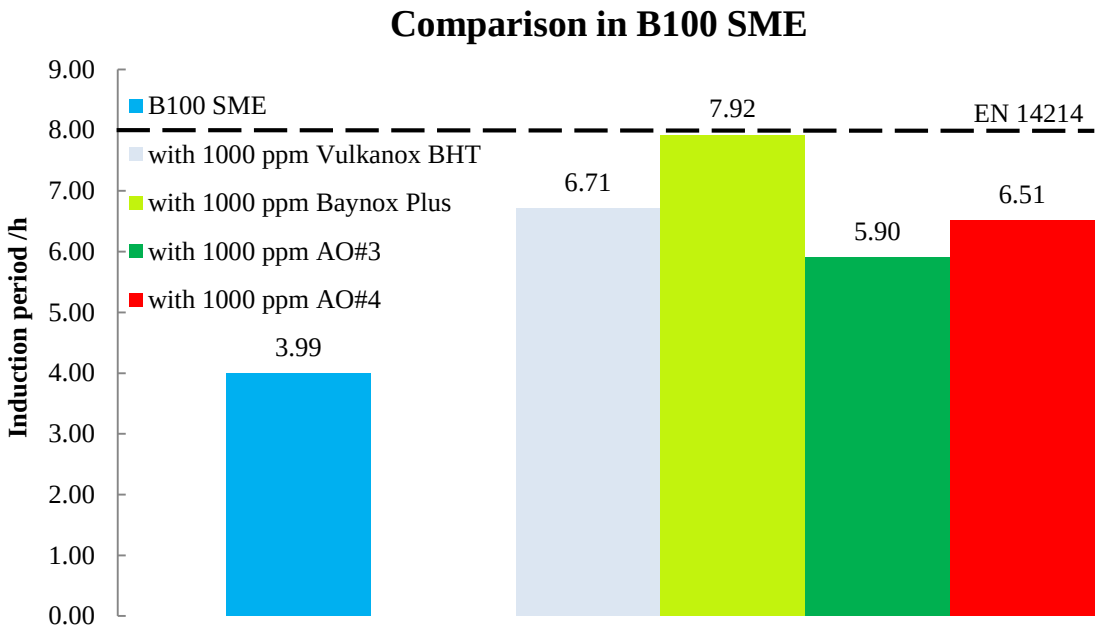


Figure 23: Comparison of Vulkanox® BHT, Baynox® Plus, AO#3 and AO#4 in B100 SME

Table 28: Results from B100 SME stabilisation experiments

B100 samples	*AO content*	*Induction period (averaged)*
SME	-	3.99 h (3.99, 3.99)
SME, Vulkanox® BHT	1000 mg/kg	6.71 h (6.70, 6.72)
SME, Baynox® Plus	1000 mg/kg	7.92 h (7.91, 7.93)
SME, AO#3	1000 mg/kg	5.90 h (5.99, 5.81)
SME, AO#4	1000 mg/kg	6.51 h (6.61, 6.42)

The soybean oil methyl ester sample had significantly aged compared to the initial stabilisation experiments, which were performed almost three months prior. Pure SME was now only able to reach an induction period of only four hours, compared to the former 5.7 h.

Furthermore, in contrast to the initial experiments, 1000 ppm of Vulkanox® BHT were not sufficient to reach the minimum required oxidation stability of 8 h set be EN 14214.[71] This significant deterioration of oxidation stability was a result of storing the non-stabilised biodiesel at room temperature without a proper inert gas atmosphere in a metallic storage container.

From this set of experiments onwards, both non stabilised biodiesel samples were stored in a refrigerator under nitrogen atmosphere.

Of the four tested antioxidants Baynox® Plus was the most active. It was able to increase the oxidation stability of B100 SME to almost 8 hours, nearly doubling the induction period (+98 %). Vulkanox® BHT and AO#4 were equally effective at stabilising pure SME, both achieved induction periods of above six hours. AO#3 was the least active antioxidant, as it achieved an oxidation stability of less than six hours.

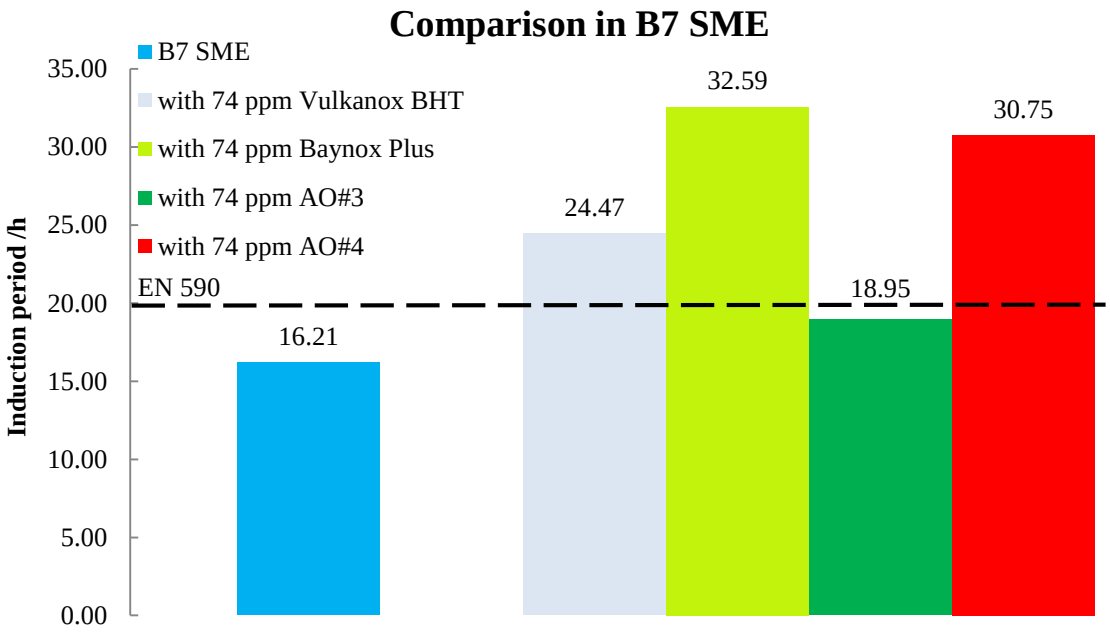


Figure 24: Comparison of Vulkanox® BHT, Baynox® Plus, AO#3 and AO#4 in B7 SME

Table 29: Results from the B7 SME stabilisation experiments

B7 samples	*AO content*	*Induction period (averaged)*
SME	-	16.21 h (16.29, 16.13)
SME, Vulkanox® BHT	74 mg/kg	24.47 h (24.84, 24.10)
SME, Baynox® Plus	74 mg/kg	32.59 h (33.24, 31.94)
SME, AO#3	74 mg/kg	18.95 h (18.76, 19.14)
SME, AO#4	74 mg/kg	30.75 h (30.81, 30.69)

Interestingly enough, the induction period of the non-stabilised B7 blend stayed unchanged in contrast to B100 SME. However, 74 mg/kg of Vulkanox® BHT only led to oxidation stability of 24 h, whereas 35 h were achieved in fresh B7 SME with the same additive concentration. Similar to pure SME, Baynox® Plus was able to achieve the highest induction period with over 32 hours. AO#4 was only slightly less effective at stabilising B7 SME, reaching almost 31 hours. The least effective antioxidant was again AO#3, the only additive not able to increase the oxidation stability to the minimum requirement of 20 hours set by EN 590.[70]

4.4.2 Tallow methyl ester

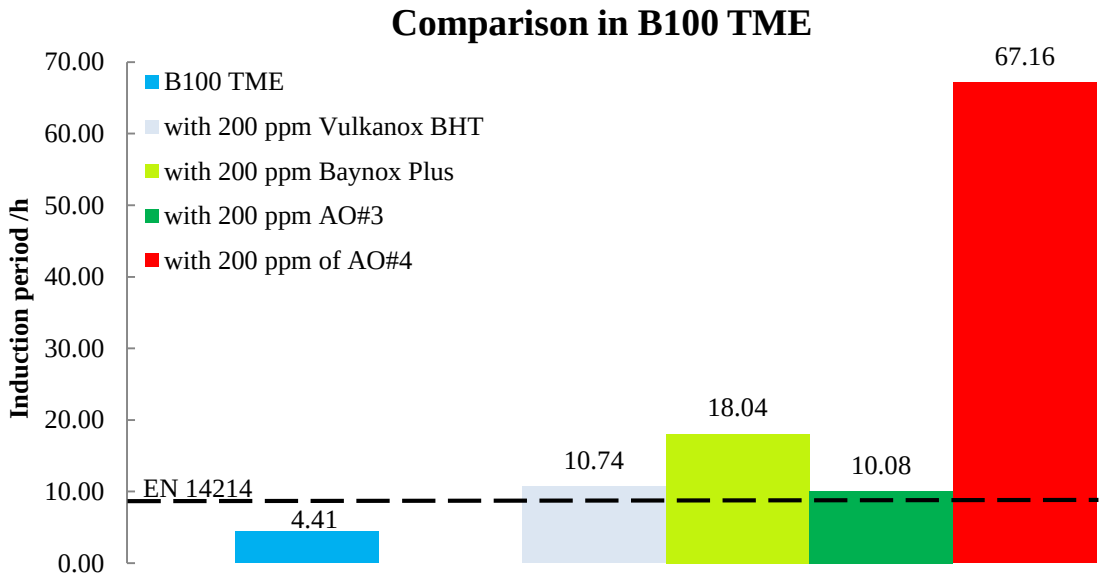


Figure 25: Comparison of Vulkanox® BHT, Baynox® Plus, AO#3 and AO#4 in B100 TME

Table 30: Results from B100 TME stabilisation experiments

B100 samples	*AO content*	*Induction period (averaged)*
TME	-	4.41 h (4.40, 4.42)
TME, Vulkanox® BHT	200 mg/kg	10.74 h (10.69, 10.79)
TME, Baynox® Plus	200 mg/kg	18.04 h (18.31, 17.77)
TME, AO#3	200 mg/kg	10.08 h (10.07, 10.08)
TME, AO#4	200 mg/kg	67.16 h (65.47, 68.85)

The oxidation stability of pure tallow methyl ester did also significantly decrease while storing at room temperature without an inert gas atmosphere, from 5.7 to 4.4 hours, which is less as drastic compared to SME. However, stabilising the sample with 200 mg/kg BHT led to the same induction period as in the previous measurement.

Of the four antioxidants tested in B100 TME, AO#4 did stand out quite impressively. It resulted in a massive induction period of 67 hours at a treat-rate of 200 mg/kg, easily surpassing even the minimum oxidation stability set by EN 590 [70] for petrodiesel blends. However, this exceptional result could potentially be an artefact originating from the Rancimat measurement technic, as it is so far off from the results of the other three antioxidants.

Baynox® Plus performed also exceptionally well, resulting in an induction period of 18 hours, corresponding to an increase of 14 hours compared to the non additivated B100 TME. AO#3 was as effective as BHT at stabilising TME, both led to an induction period of 10 h, meaning that all four antioxidants were able to surpass the minimum requirement for the oxidation stability set by EN 141214.[71]

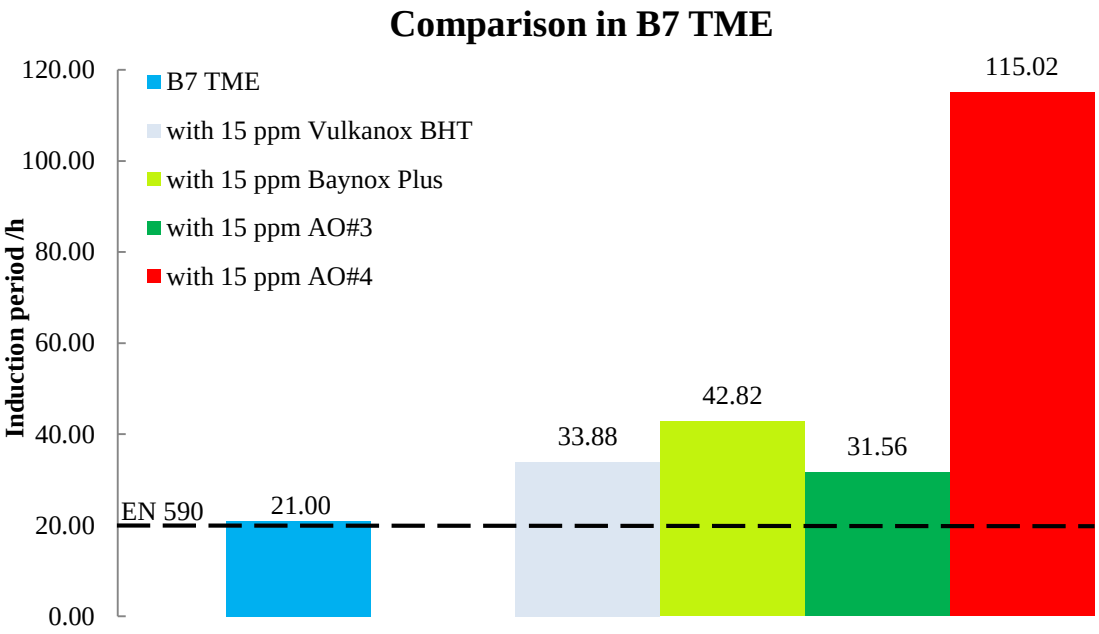


Figure 26: Comparison of Vulkanox® BHT, Baynox® Plus, AO#3 and AO#4 in B7 TME

Table 31: Results from B7 TME stabilisation experiments

B7 samples	*AO content*	*Induction period (averaged)*
TME	-	21.00 h (20.83, 21.17)
TME, Vulkanox® BHT	15 mg/kg	33.88 h (34.22, 33.54)
TME, Baynox® Plus	15 mg/kg	42.82 h (42.28, 43.36)
TME, AO#3	15 mg/kg	31.56 h (31.72, 31.40)
TME, AO#4	15 mg/kg	115.02 h*

* No double determination possible

Compared to the initial measurements almost two months earlier, the oxidation stability of non-additivated B7 TME decreased from 22 to 21 hours and the sample stabilised with 200 mg/kg Vulkanox® BHT also had a by one hour reduced induction period (34 vs. 35 hours).

AO#4 did also stand out in B7 TME, achieving a very high oxidation stability of 115 hours, quintupling the initial induction period of the non-stabilised sample (21 h). Again, this could be an artefact by the Rancimat method and further investigations with varying concentrations and other test methods, such as PetroOxy, would be required to pinpoint the reason for this massive increase in oxidation stability.

The usage of 200 mg/kg of Baynox® Plus led to an induction period of almost 43 hours, doubling the stability of the initial sample. Vulkanox® BHT did slightly outperform AO#3 in B7 TME but both antioxidants were clearly able to stabilises the blend beyond the minimum requirement set by EN 590.[70]

4.5 Influence of DPPs on the oxidation stability of TME and SME

The influence of two acquired diesel performance packages (DPP) was evaluated in B7 blends of SME and TME. The treat rates for both DPP#1 and DPP#2 were chosen that the additivated samples contain the same amount of active components. This step was taken to be able to properly asses and compare their impact on the oxidation stability. Due to the fact that the exact composition of both diesel performance packages is unknown, the evaluation can only be performed on a phenomenological level.

4.5.1 Soybean oil methyl ester

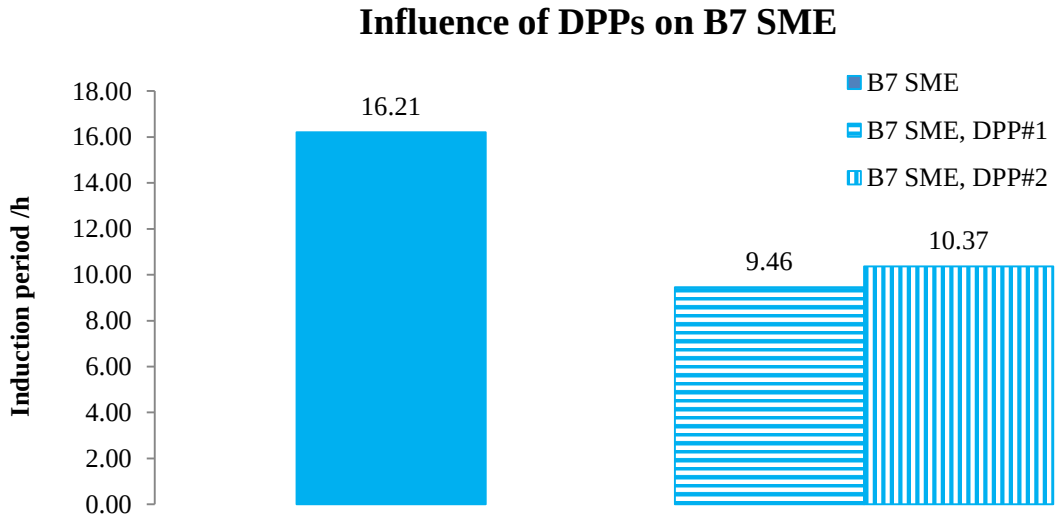


Figure 27: Influence of DPPs on non-stabilised B7 SME

Table 32: Influence of DPPs on non-stabilised B7 SME

B7 samples	*Induction period (averaged)*
SME	16.21 h
SME, DPP#1	9.46 h (9.51, 9.41)
SME, DPP#2	10.37 h (10.43, 10.33)

The oxidation stability of non-stabilised B7 SME blends significantly decreased at the presence of either diesel performance package. DPP#1 led to a decrease in the induction period of more than 40 % (5,75 h), reaching only 9.46 hours. DPP#2 resulted in a slightly better oxidation stability of 10.37 h, corresponding to a drop of roughly 36 %.

Both diesel performance packages, as stated by BASF Germany, contain the same polymeric active component, therefore the worse behaviour of DDP#1 had to originate from one of its other constituents, most likely 2-ethylhexyl nitrate (2-EHN). As mentioned earlier this compound belongs to the group of cetane number improvers, reducing the ignition temperature of diesel fuel, as it possesses a high tendency towards radical formation (see chapter *2.4 Overview on* diesel additives). Theses radicals could also be formed during the Rancimat measurement as samples are held at 110 °C, which could explain the difference in oxidation stability of both diesel performance packages.

The next step of the thesis was to evaluate the influence of both diesel performance packages on the oxidation stability of B7 SME in the presence of different antioxidants, namely Vulkanox® BHT, Baynox® Plus, AO#3 and AO#4.

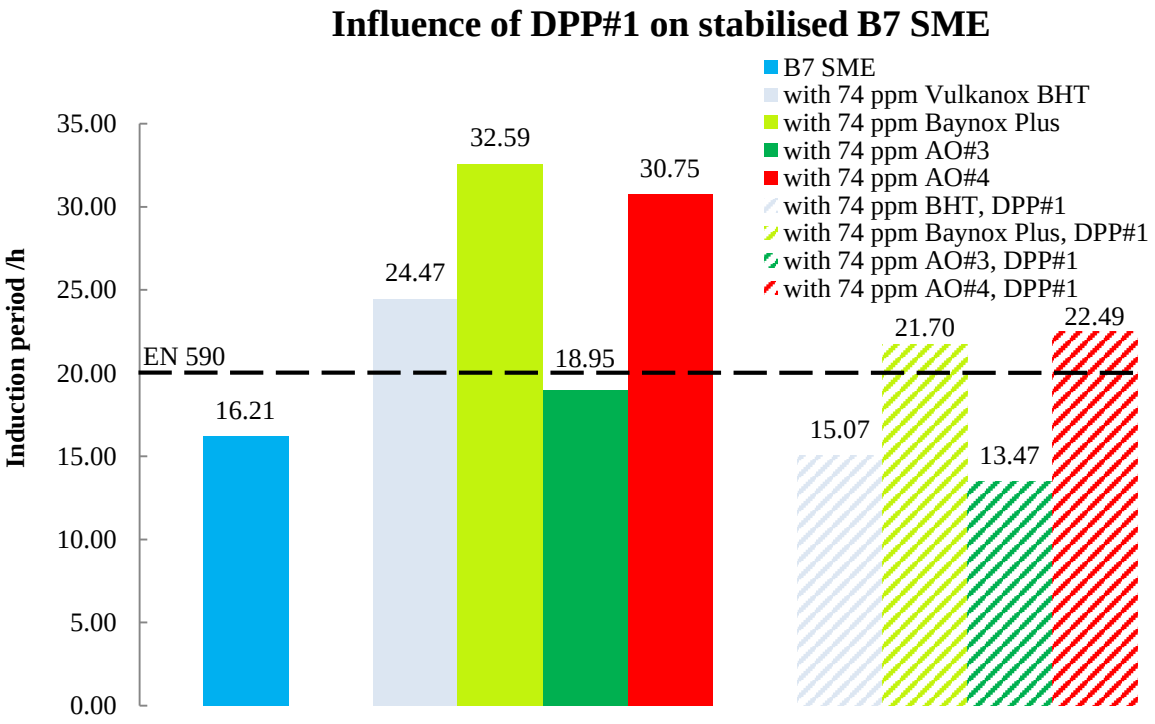


Figure 28: Influence of DPP#1 on stabilised B7 SME

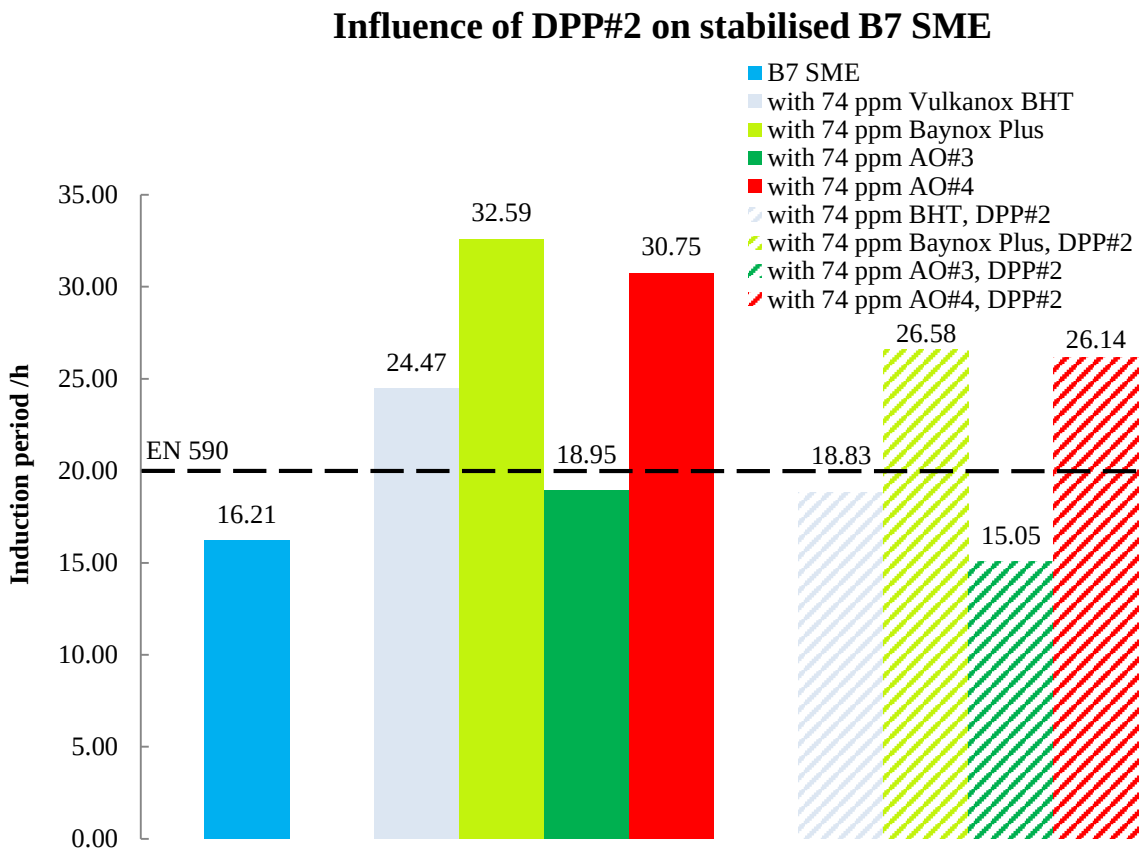


Figure 29: Influence of DPP#2 on stabilised B7 SME

Table 33: Influence of both DPPs on the oxidation stability of B7 SME

B7 samples	*AO content*	*Induction period (averaged)*
SME	-	16.21 h
SME, Vulkanox® BHT	74 mg/kg	24.47 h
with DPP#1	74 mg/kg	15.07 h (15.90, 14.24)
with DPP#2	74 mg/kg	18.83 h (18.63, 19.03)
SME, Baynox® Plus	74 mg/kg	32.59 h
with DPP#1	74 mg/kg	21.70 h (21.72, 21.67)
with DPP#2	74 mg/kg	26.58 h (26.76, 26.40)
SME, AO#3	74 mg/kg	18.95 h
with DPP#1	74 mg/kg	13.47 h (13.47, 13.47)
with DPP#2	74 mg/kg	15.05 h (15.02, 15.07)
SME, AO#4	74 mg/kg	30.75 h
with DPP#1	74 mg/kg	22.49 h (23.39, 21.58)
with DPP#2	74 mg/kg	26.14 h (25.40, 26.88)

None of the four antioxidants was able to fully compensate the negative impact of neither DPP#1 nor DPP#2 on the oxidation stability of B7 SME, as can be seen in *Figure 28* and *Figure 29*. Adding either one of diesel performance packages to B7 SME, stabilised with 74 mg/kg Vulkanox® BHT, resulted in both cases in induction periods falling short of 20 hours. DPP#1 led to a decrease of almost nine hours in oxidation stability (-38 %), whereas DPP2# resulted in a reduction of 5.6 hours (-23%).

SME B7 blends containing Baynox® Plus or AO#4 were able to retain induction periods above 20 hours when diesel performance packages were added, in contrast to both other antioxidants. Nevertheless, the oxidation stability of the aforementioned blends did decrease significantly. AO#4 performed slightly better, as the relative decrease in oxidation stability was six percent lower for DPP#1 (-27% vs -33%) and three percent less for DPP#2 (-15% vs -18%). Again, as in pure SME and blends, AO#3 was the least effective antioxidant, resulting in the lowest induction periods, 13.74 h (-29 %) for DPP#1 and 15.05 h (-21 %) for DPP#2.

Comparing these results to non-stabilised B7 blends of SME it was quite obvious that the negative impact of DPP#2 on the oxidation stability was more effectively countered by antioxidants compared to DPP#1.

4.5.2 Tallow methyl ester

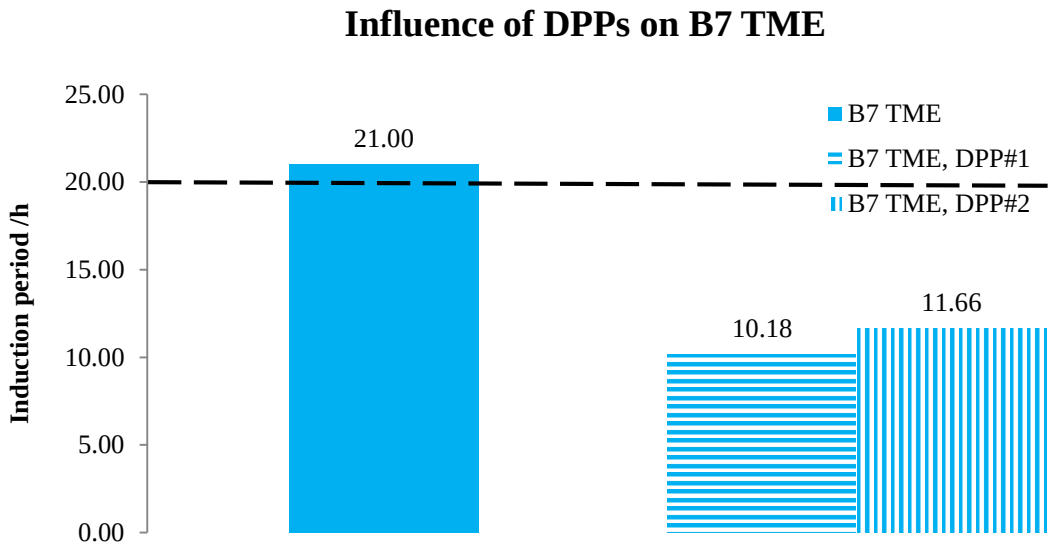


Figure 30: Influence of DPPs on non-stabilised B7 TME

Table 34: Influence of DPPs on non-stabilised B7 TME

B7 samples	*Induction period (averaged)*
TME	21.00 h
TME, DPP#1	10.18 h (10.12, 10.23)
TME, DPP#2	11.66 h (11.23, 11.19)

The oxidation stability of non-stabilised B7 TME blends also decreased significantly at the presence of either diesel performance package. DPP#1 led to a decrease in induction period of 52 % (10,82 h), reaching only 10.18 hours. DPP#2 resulted in a slightly better oxidation stability of 11.66 h, corresponding to a drop of roughly 44 %.

Comparing these results to SME, non-stabilised TME was significantly more affected by the negative impact of DPPs. Although the achievable oxidation stability was higher for TME with both diesel performance packages, the induction periods decreased around 10 % compared to SME.

One possible explanation is that B7 TME was more susceptible towards oxidative stress due to the lack of natural antioxidants, such as *β*-carotene. These are also efficient radical scavengers as they are able to form stable radical species, suppressing radical initiation and chain growth reactions (see *2.3 Antioxidants*).

The next step of the thesis was to evaluate the influence of both diesel performance packages on the oxidation stability of B7 TME in the presence of different antioxidants, namely Vulkanox® BHT, Baynox® Plus, AO#3 and AO#4.

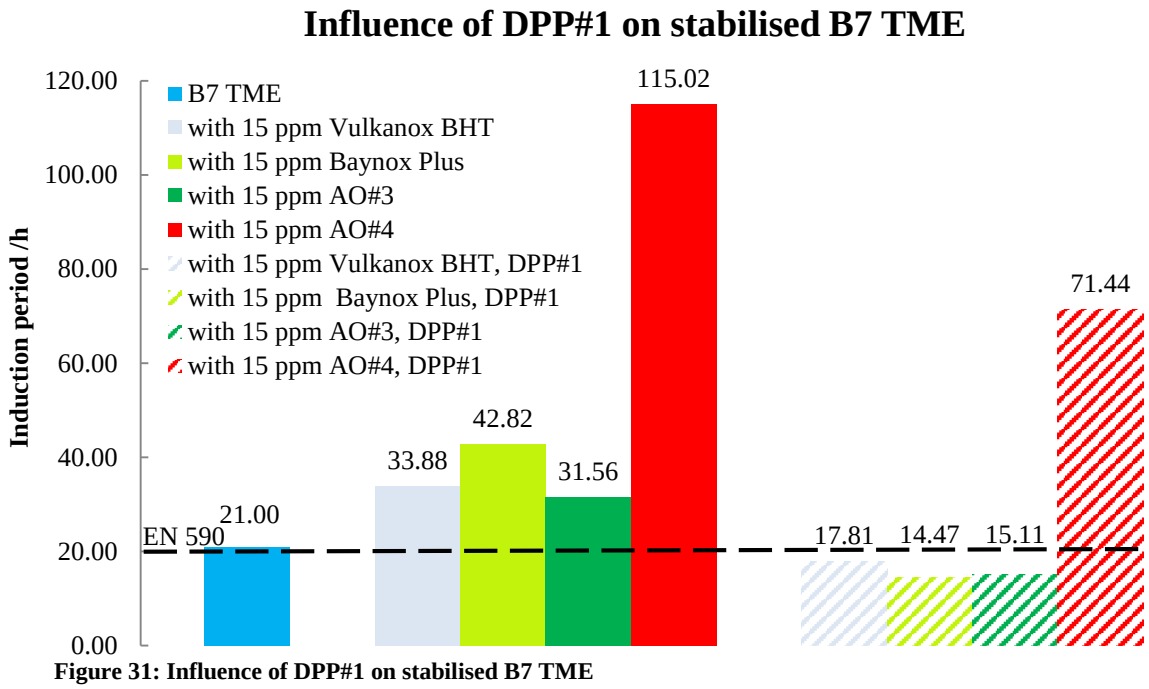


Figure 31: Influence of DPP#1 on stabilised B7 TME

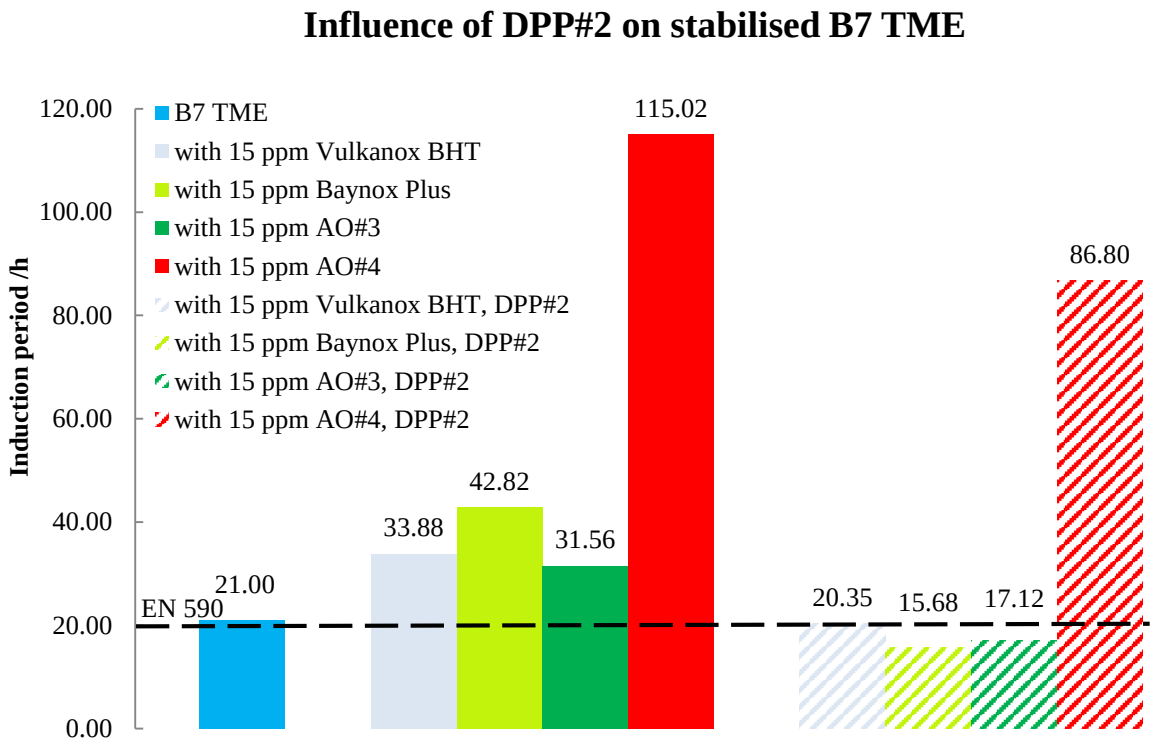


Figure 32: Influence of DPP#2 on stabilised B7 TME

Table 35: Influence of both DPPs on the oxidation stability of B7 TME

B7 samples	*AO content*	*Induction period (averaged)*
TME	-	21.00 h
TME, Vulkanox® BHT	15 mg/kg	33.88 h
with DPP#1	15 mg/kg	17.81 h (17.31, 18.31)
with DPP#2	15 mg/kg	20.35 h (19.81, 20.88)
TME, Baynox® Plus	15 mg/kg	42.82 h
with DPP#1	15 mg/kg	14.47 h (14.63, 14.31)
with DPP#2	15 mg/kg	15.68h (15.31, 16.04)
TME, AO#3	15 mg/kg	31.56 h
with DPP#1	15 mg/kg	15.11 h (14.95, 15.26)
with DPP#2	15 mg/kg	17.12h (17.57, 16.67)
TME, AO#4	15 mg/kg	115.02 h
with DPP#1	15 mg/kg	71.44 h (71.41, 71.47)
with DPP#2	15 mg/kg	86.80 h (87.68, 85.93)

Again as in B7 SME, none of the four antioxidants was able to fully compensate the negative impact of neither DPP#1 nor DPP#2 on the oxidation stability of B7 TME, as can be seen in *Figure 31* and *Figure 32*. Adding DPP#1 to B7 TME containing 15 mg/kg Vulkanox® BHT resulted in an induction period of roughly 18 hours, corresponding to a decrease of sixteen hours (47%). DPP2# reduced the oxidation stability by thirteen hours (23%) to 20.35 h, hardly reaching the minimum requirement set by EN 590.[70] TME B7 blends containing neither Baynox® Plus nor AO#3 were able to retain induction periods above 20 hours when diesel performance packages were added. Oxidation stabilities of TME blends containing the former antioxidant did decrease by far the most. For DPP#1, the induction period decreased by 66 %, reaching only 14.5 hours. DPP#2 resulted in a loss of 63 %, leading to an oxidation stability of 15.7 hours. Therefore, although being second best at stabilising non-additivated blends, Baynox® Plus was not suitable to counter the negative impact of both DPPs in B7 TME.

Unsurprisingly, AO#4 performed best, as oxidation stability was extremely high prior to adding either DPP#1 or DPP#2. Nevertheless, both induction periods decreased significantly, 25 % for DPP#1 and 38 % for DPP#2 respectively.

Interestingly, except for AO#4, none of the stabilised blends containing a diesel performance package was able to reach the induction period of non-stabilised B7 TME (21 h). This clearly proofed, as mentioned earlier, that biofuels containing no natural antioxidants, such as TME, possess an increased susceptibility to the negative impact of DPPs on the oxidation stability.

4.6 Influence of DCAs on the oxidation stability of TME and SME

The influence of three different deposit control additives, namely DCA#1, DCA#2 and DCA#3, on the oxidation stability of B7 blends was evaluated. First, they were tested in blends of both tallow methyl ester and soybean oil methyl ester without the presence of antioxidants, to get a better insight on their impact on the induction period. The treat-rates of the individual DCAs were chosen so that the additivated B7 blends contain equal amounts of active component compared to the formerly tested diesel performance packages.

4.6.1 Soybean oil methyl ester

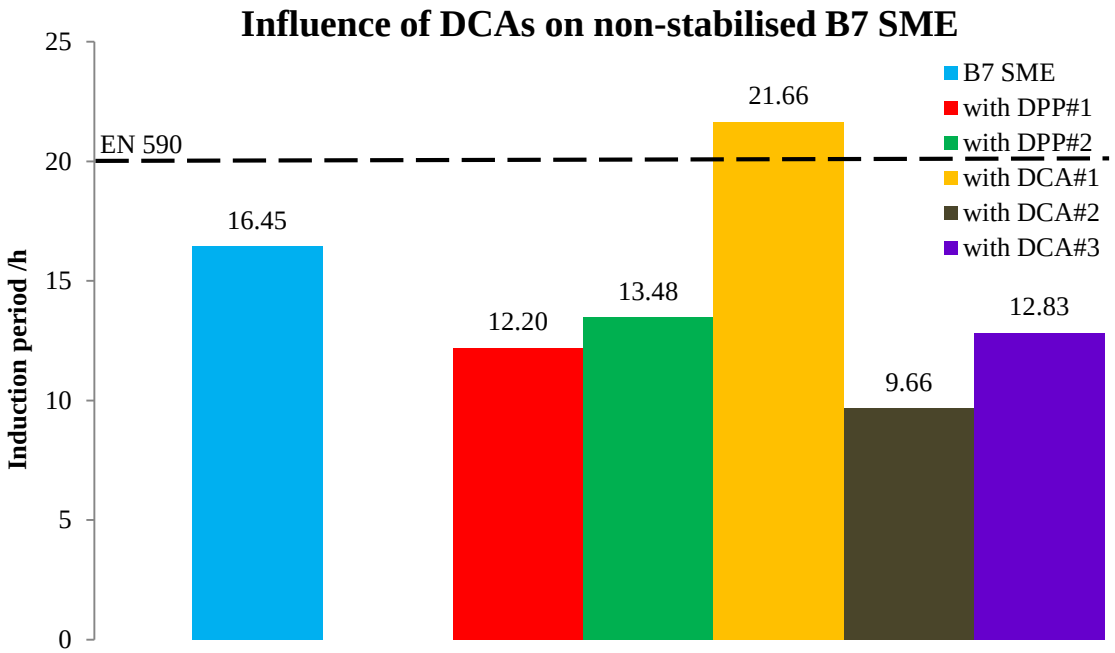


Figure 33: Influence of DCAs on non-stabilised B7 SME

Table 36: Influence of DCAs on non-stabilised B7 SME

B7 samples	*Induction period (averaged)*
SME	16.45 h
with DPP#1	12.20 h (11.94, 12.44)
with DPP#2	13.48 h (13.41, 13.55)
with DCA#1	21.66 h (21.69, 21.62)
with DCA#2	9.66 h (9.24, 10.07)
with DCA#3	12.83 h (12.46, 13.19)

Non-stabilised B7 SME and samples containing DPP#1 as well as DPP#2 had an increased induction period compared to the initial measurement, from 9.5 to 12.2 hours and 10.4 to 13.5 hours, respectively.

However, this was kind of expected, as the portion of SME used in this set of experiments was stored in a refrigerator rather than at room temperature, thus being able to retain a fresher, less oxidised, state for a longer time. DCA#3 resulted in a similar oxidation stability compared to DPP#1 and DPP#2, which was unsurprising, as all three diesel additives to contain the same active components, thus only minimal deviations were excepted. DCA#2 led to the lowest induction period of less than 10 hours, corresponding to a decrease of 41 % compared to the pure blend. B7 SME containing DCA#1 was able reach an induction period of almost 22 hours, increasing the oxidation stability by 32 %. This could be expected as the deposit control additive is labelled to contain 40% active antioxidant.

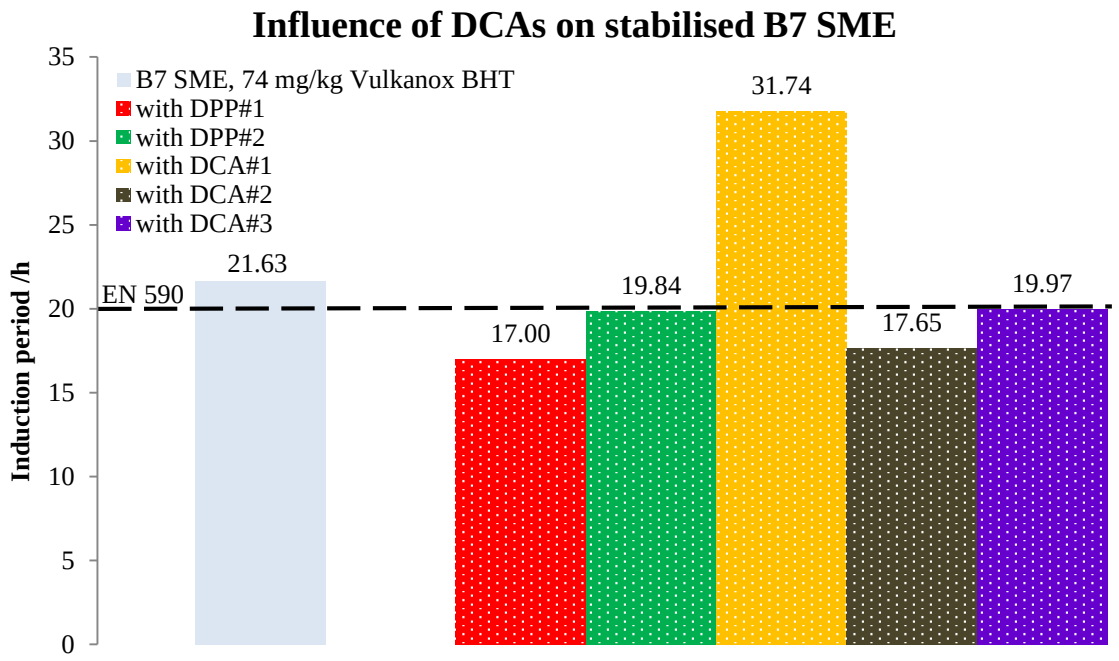


Figure 34: Influence of DCAs on stabilised B7 SME

Table 37: Influence of DCAs on stabilised B7 SME

B7 samples	*BHT content*	*Induction period (averaged)*
SME	-	16.45 h
SME, Vulkanox® BHT	74 mg/kg	21.63 h
with DPP#1	74 mg/kg	17.00 h (17.33, 16.66)
with DPP#2	74 mg/kg	19.84 h (18.88, 20.80)
with DCA#1	74 mg/kg	31.74 h (31.35, 32.13)
with DCA#2	74 mg/kg	17.65 h (17.88, 17.42)
with DCA#3	74 mg/kg	19.97 h (19.39, 20.54)

Again, DCA#3 behaved similar to DPP#2 in presence of 74 mg/kg Vulkanox® BHT, where for both additives oxidation stabilities close to 20 hours were achieved. However, DPP#1 performed significantly worse (17.00 h), which further confirms the theory of 2-EHN being indeed responsible for the drop in oxidation stability.

DCA#2 resulted in an induction period of 17.7 hours, slightly better compared to DPP#1 but still significantly below the minimum requirement set by EN 590. [70]

Adding DCA#1 to stabilised B7 SME resulted in an oxidation stability of 31 hours, exceeding the non-additivated sample by ten hours. This was quite surprising, as an increase of about five hours was excepted, similar to the non-stabilised sample. The additional increase of five hours therefore has to be attributed to so-called synergistic effects, which were evaluated later in this thesis in chapter *4.8*.

4.6.2 Tallow methyl ester

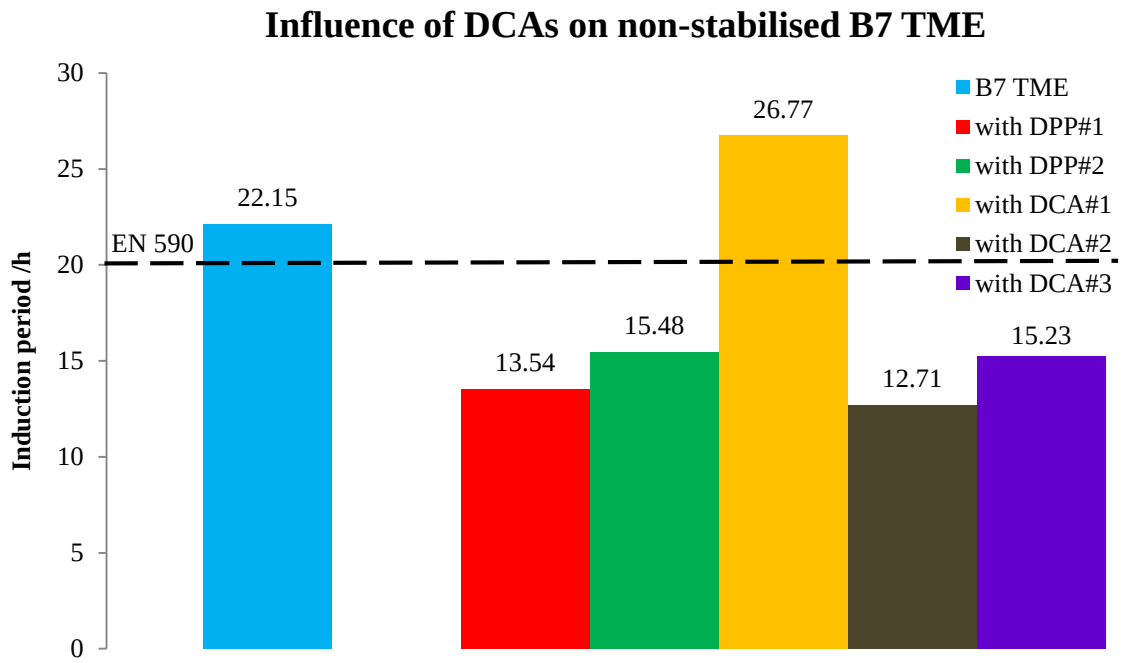


Figure 35: Influence of DCAs on non-stabilised B7 TME

Table 38: Influence of DCAs on non-stabilised B7 TME

B7 samples	***Induction period (averaged)***
TME	22.15 h
with DPP#1	13.54 h (13.69, 13.39)
with DPP#2	15.48 h (16.01, 14.94)
with DCA#1	26.77 h (26.40, 27.14)
with DCA#2	12.71 h (12.88, 12.53)
with DCA#3	15.23 h (14.98, 15.48)

Again, as for SME, the portion of TME used for this set of experiments was kept in a refrigerator, explaining the higher oxidation stability of B7 TME and blends containing DPP#1 and DPP#2 compared to the previous measurement.

DCA#2 resulted in the lowest oxidation stability with just 12.74 hours, corresponding to a decrease of 43 %, similar to the results made in non-stabilised SME. DCA#3 decreased the oxidation stability to 15.2 hours analogous to DPP#2 but performed significantly better than DPP#1.

As for SME, DCA#1 did enhance the oxidation stability of B7 TME from 22.2 to 26.7 hours, corresponding to an increase of roughly 20 %. However, this rise was significantly smaller compared to the results achieved in SME, which could stem either from the absence of natural antioxidants or sheer differences of biodiesel matrix.

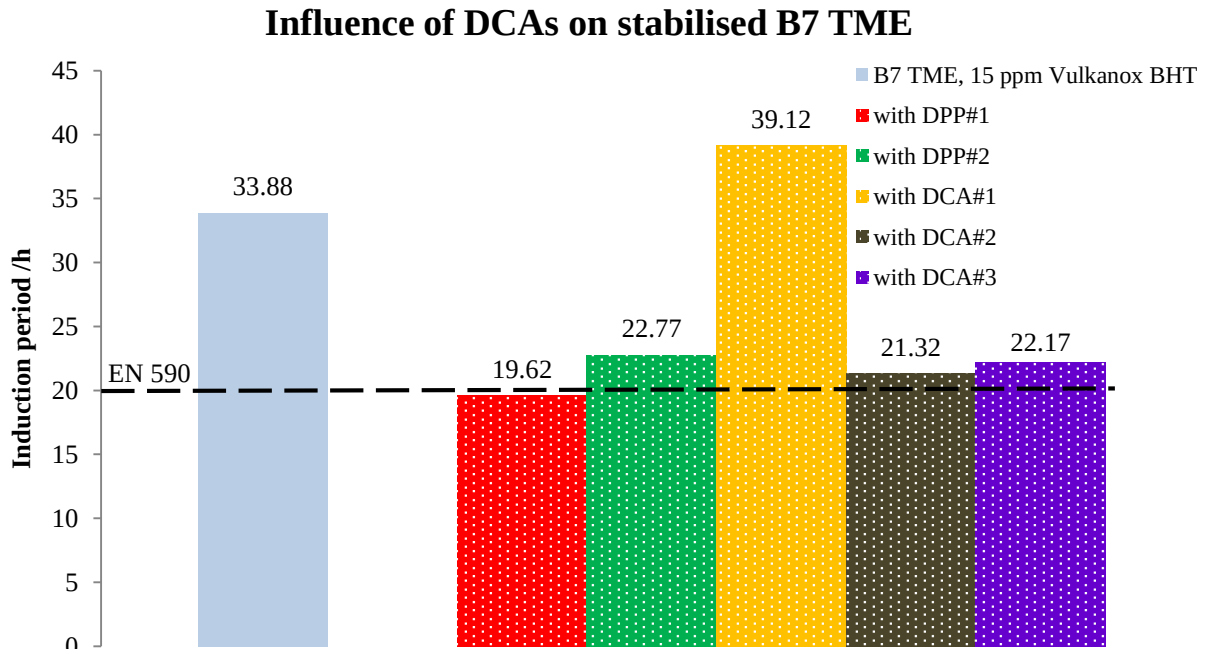


Figure 36: Influence of DCAs on stabilised B7 TME

Table 39: Influence of DCAs on stabilised B7 TME

B7 samples	*BHT content*	*Induction period (averaged)*
TME	-	22.15 h
TME, Vulkanox® BHT	15 mg/kg	33.88 h
with DPP#1	15 mg/kg	19.62 h (19.52, 19.72)
with DPP#2	15 mg/kg	22.77 h (23.45, 22.08)
with DCA#1	15 mg/kg	39.12 h (39.12, 39.12)
with DCA#2	15 mg/kg	21.32 h (21.27, 21,37)
with DCA#3	15 mg/kg	22.17 h (22.02, 22.31)

Again, as in the non-stabilised samples, the additive DCA#3 behaved similar to DPP#2, where for both additives oxidation stabilities around 22 hours were achieved. However, DPP#1 performed significantly worse (19.62 h), most probably due to its content of 2-EHN, making it the only diesel additives that did fail to meet the requirement set by EN 590.[70]

DCA#2 resulted in an induction period of 21.32 hours, significantly better compared to DPP#1, which is contrary to the previously made results.

Adding DCA#1 to a stabilised B7 of TME resulted in an oxidation stability of 39 hours, exceeding the non-additivated sample by approximately four hours. In contrast to B7 SME, the increase in induction period is equally high for both the non-stabilised as well as stabilised B7 TME. This means that DCA#1 did not show any synergistic effect in tallow methyl ester. This can possibly be attributed to the absence of natural antioxidants.

4.7 Combination of different DCAs in TME and SME

The next step of the master thesis was to combine DCA#1 with either DCA#2 or DCA#3. This experiment was conducted to determine, if DCA#1, labelled as containing 40% active antioxidant, is capable of compensating the negative impacts of both other deposit control additives on the oxidation stability.

4.7.1 Soybean oil methyl ester

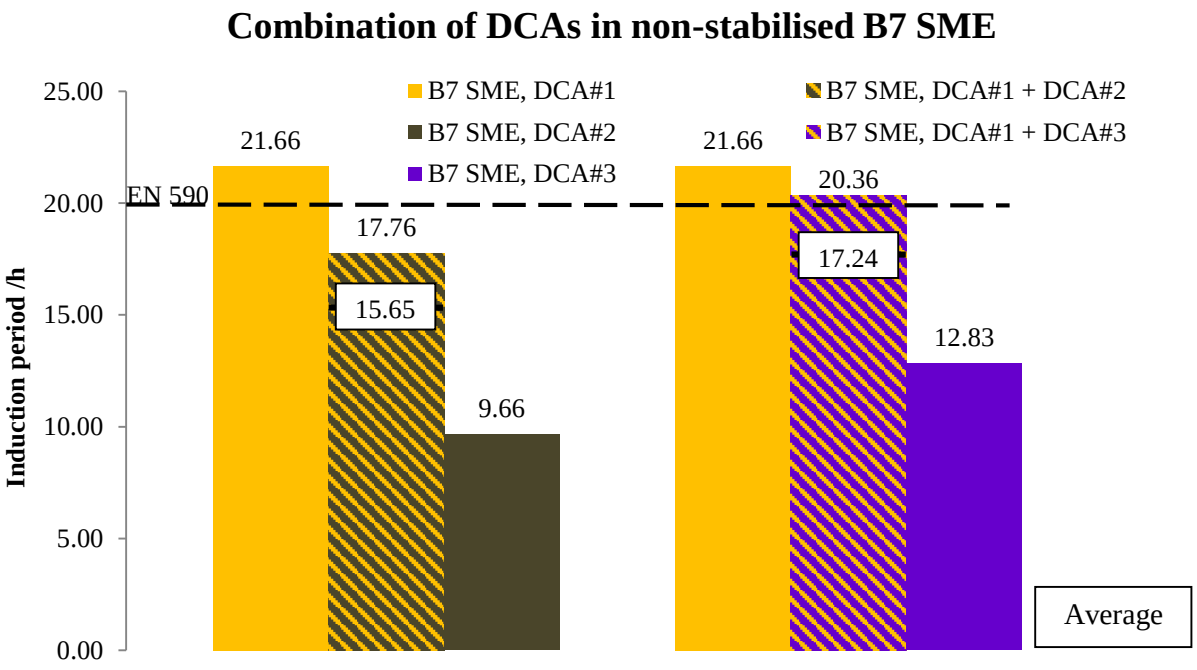


Figure 37: Combination of DCAs in non-stabilised B7 SME

Table 40: Combination of DCAs in non-stabilised B7 SME

B7 samples	*Induction period (averaged)*
B7 SME, DCA#1	21.66 h (21.69, 21.62)
B7 SME, DCA#2	9.66 h (10.07, 9.24)
B7 SME, DCA#1 + DCA#2	17.76 h (17.84, 17.68)
B7 SME, DCA#3	12.83 h (11.96, 13.69)
B7 SME, DCA#1 + DCA#3	20.36 h (20.45, 20.26)

Adding DCA#1 to B7 SME containing DCA#2 or DCA#3 did result in a significant increase of oxidation stability for both additives. This beneficial effect was higher for the latter deposit control additive, as there is only a minor difference (~1 h) in induction periods between the sample containing only DCA#1 and the binary mixture with DCA#3. With an oxidation stability of 20.4 hours, this particular mixture was able to meet the requirement set by EN 590.[70]

For DCA#2 the induction period nearly doubled, from previously 9.6 to 17.8 hours. Interestingly, the achievable induction periods for all mixtures were significantly above the calculated average value, which could possibly originate from the antioxidative properties of DCA#1.

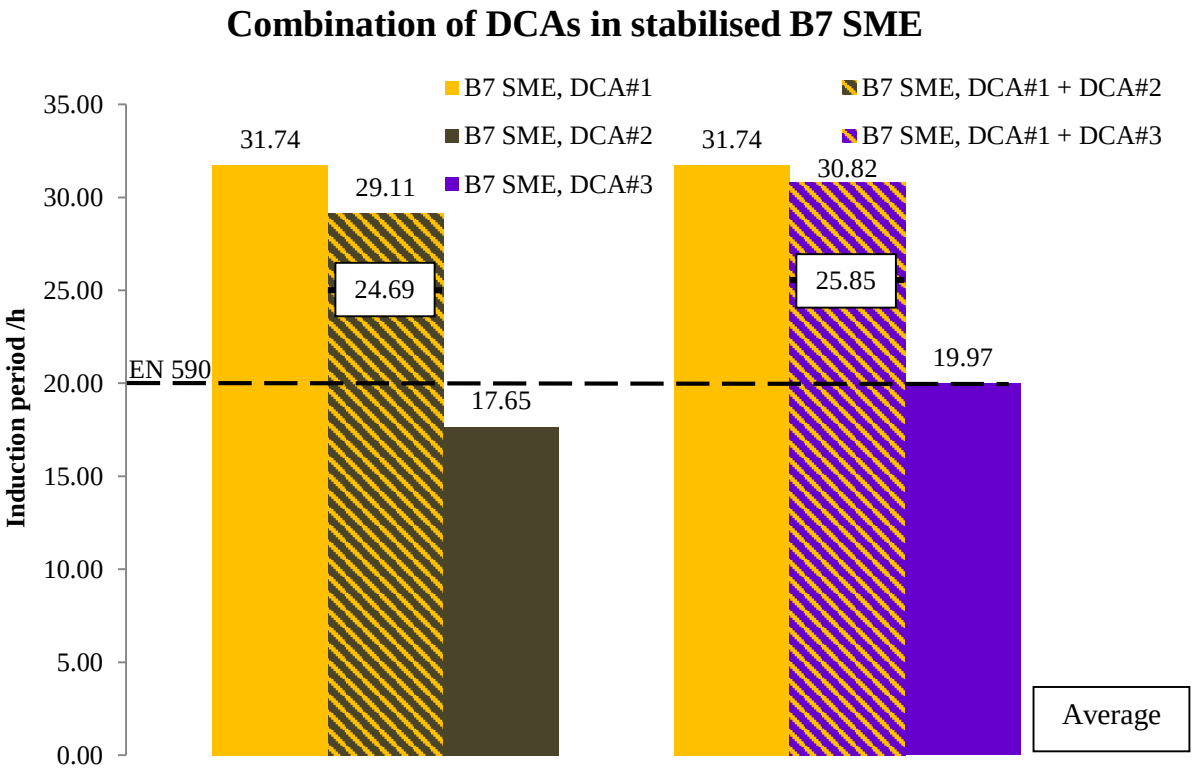


Figure 38: Combination of DCAs in stabilised B7 SME

Table 41: Combination of DCAs in stabilised B7 SME

B7 samples	*BHT content*	*Induction period (averaged)*
B7 SME, DCA#1	74 mg/kg	31.74 h (31.35, 32.13)
B7 SME, DCA#2	74 mg/kg	17.65 h (17.88, 17.42)
B7 SME, DCA#1 + DCA#2	74 mg/kg	29.11 h (28.42, 29.80)
B7 SME, DCA#3	74 mg/kg	19.97 h (19.39, 20,54)
B7 SME, DCA#1 + DCA#3	74 mg/kg	30.82 h (30.91, 30.72)

Combining DCA#1 with either DCA#2 or DCA#3 was also very beneficial for the oxidation stability of B7 SME blends stabilised with 74 mg/kg Vulkanox® BHT. The induction period of stabilised B7 SME containing DCA#2 was increased by 65 % (12 h), reaching 29 hours, clearly surpassing the minimum requirement set by EN 590.[70] Again, as for non-stabilised B7 SME samples, there was only a minor difference (~1 h) in induction periods between the sample containing only DCA#1 and the binary mixture with DCA#3. Additionally, the oxidation stabilities of all deposit control additive mixtures were again significantly above the calculated average.

To summarise, DCA#1 is definitely a suitable additive to reduce the negative impact of DCA#2 as well as DCA#3 on the oxidation stability of B7 SME.

4.7.2 Tallow methyl ester

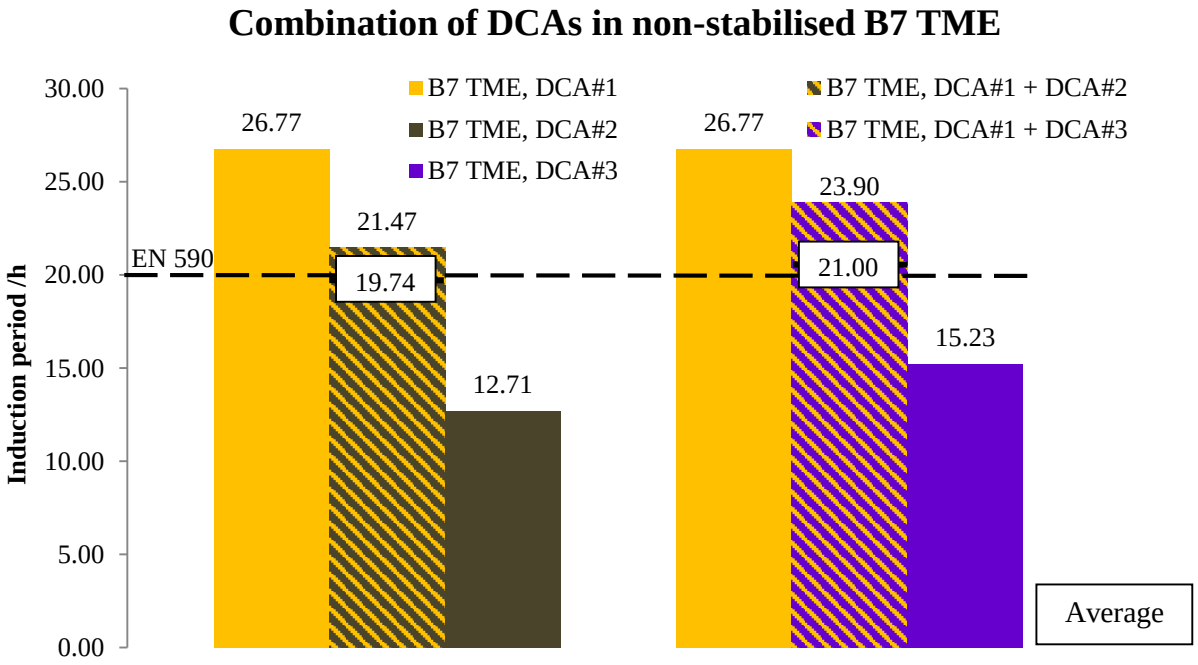


Figure 39: Combination of DCAs in non-stabilised B7 TME

Table 42: Combination of DCAs in non-stabilised B7 TME

B7 samples	*Induction period (averaged)*
B7 TME, DCA#1	26.77 h (26.40, 27.14)
B7 TME, DCA#2	12.71 h (12.88, 12,53)
B7 TME, DCA#1 + DCA#2	21.47 h (21.21, 21.72)
B7 TME, DCA#3	15.23 h (14.98, 15.48)
B7 TME, DCA#1 + DCA#3	23.90 h (23.95, 23.86)

Similar to the results achieved in SME, adding DCA#1 to B7 TME containing either DCA#2 or DCA#3 resulted in a significant increase of oxidation stability. However, the beneficial effect of DCA#1 was lower compared to SME, when comparing relative increases.

Combining DCA#3 with DCA#1 resulted in an oxidation stability of 21.5 hours, increasing the induction period by almost nine hours (+68 %). The addition of DCA#1 to B7 TME containing DCA#3 also led to a significant rise in oxidation stability, again clearly exceeding the minimum requirement set by EN 590.[70]

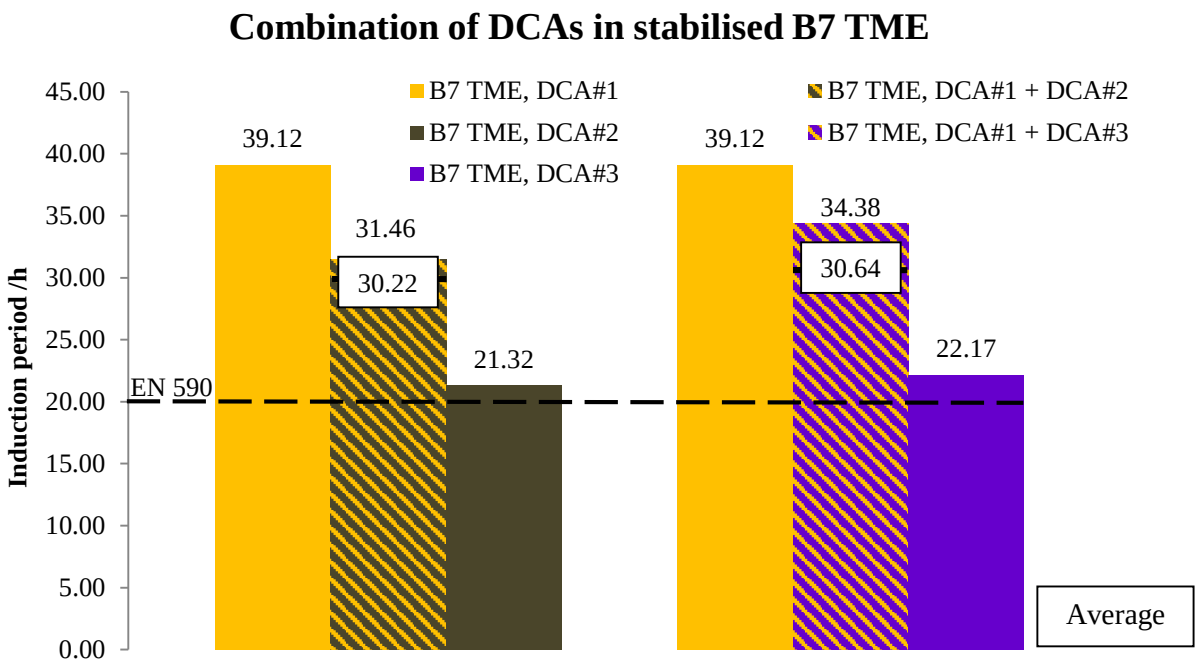


Figure 40: Combination of DCAs in stabilised B7 TME

Table 43: Combination of DCAs in stabilised B7 TME

B7 samples	*BHT content*	*Induction period (averaged)*
B7 TME, DCA#1	15 mg/kg	39.12 h (39.12, 39.12)
B7 TME, DCA#2	15 mg/kg	21.32 h (21.27, 21.37)
B7 TME, DCA#1 + DCA#2	15 mg/kg	31.46 h (31.97, 30.96)
B7 TME, DCA#3	15 mg/kg	22.17 h (22.02, 22,31)
B7 TME, DCA#1 + DCA#3	15 mg/kg	34.38 h (35.90, 32.85)

Combining DCA#1 with either DCA#2 or DCA#3 was also very beneficial for the oxidation stability of stabilised B7 TME blends. The induction period of stabilised B7 TME containing DCA#2 was increased by 48 % (10 h), reaching 31 hours, clearly surpassing the minimum requirement set by EN 590. [70]

Again, as for the non-stabilised samples, a higher oxidation stability was reached for the combination of DCA#1 and DCA#3. Additionally, in contrast to previous results, the relative increase of induction period was higher compared to the other combination (55 % vs. 48%).

Interestingly, the oxidation stabilities of both deposit control additive combinations in B7 TME were significantly closer to the calculated average values compared to SME.

4.8 Evaluation of the possible synergistic effect of DCA#1 in SME

The occurrence of unexpected results for DCA#1 in presence of Vulkanox® BHT in soybean oil methyl ester needed further investigations. The achievable induction periods were far above expectations.

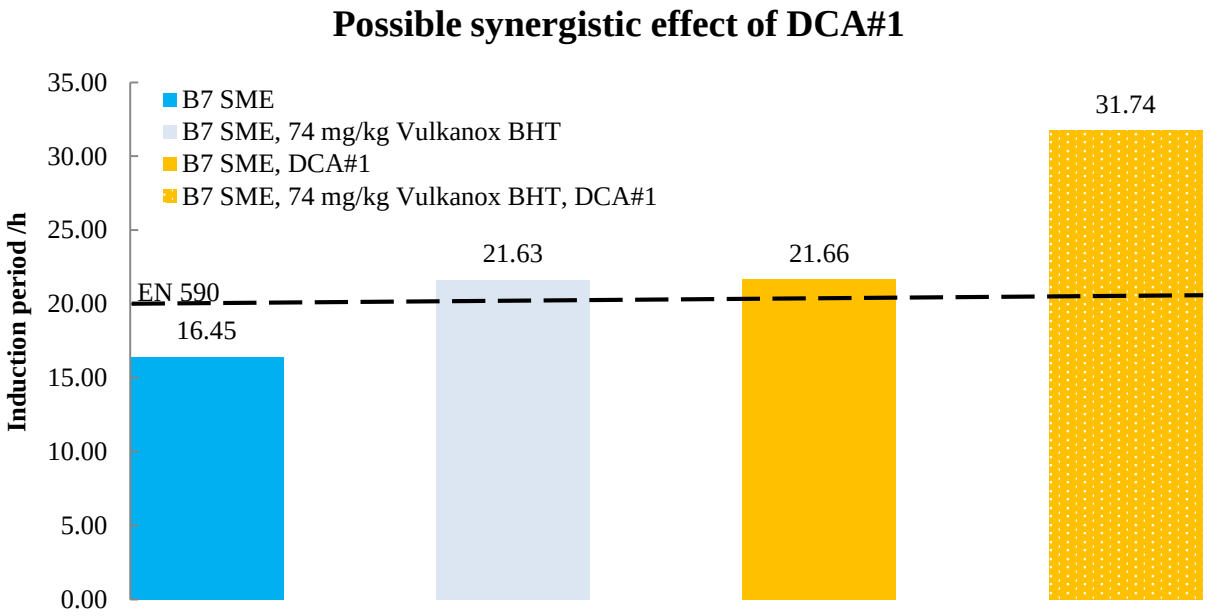


Figure 41: Evaluation of the synergistic effect of DCA#1 in SME I

Table 44: Evaluation of the synergistic effect of DCA#1 in SME I

Samples	*BHT content*	*Induction period (averaged)*	*Increase compared to B7 SME*
B7 SME	-	16.45 h (16.47, 16.43)	-
B7 SME, BHT	74 mg/kg	21.63 h (22.06, 21.20)	5.18 h (31 %)
B7 SME, DCA#1	-	21.66 h (21.69, 21.62)	5.21 h (32 %)
B7 SME, BHT, DCA#1	74 mg/kg	31.74 h (31.35, 21.13)	15.29 h (93 %)

DCA#1 was as potent as 74 mg/kg BHT in stabilising B7 SME at the previously chosen treat-rate. Both additives increased oxidation stability by around five hours. This was quite impressive, as DCA#1 is used as a deposit control additive, which normally do not possess any antioxidative properties. Furthermore, as can be seen in *Figure 41* and *Table 44*, combining DCA#1 with BHT resulted in an oxidation stability that was much higher than excepted. Theoretically, the combination of DCA#1 and BHT should have resulted in an increase of 63% or 10.4 hours.

However, the resulting induction period was 31.74 hours, which was 30 % or five hours above the theoretical calculation. This over performance clearly indicated a strong synergism between Vulkanox® BHT and DCA#1 in soybean oil methyl ester.

To get a better insight, two B7 blends containing half of the treat rate of DCA#1 were prepared additionally, one of them was stabilised with the aforementioned hindered phenolic antioxidant. The samples from chapter *4.7.1* were used to prepare the required solutions seen in *Table 45*. Additionally, the original solutions they were retested, to allow a proper comparison.

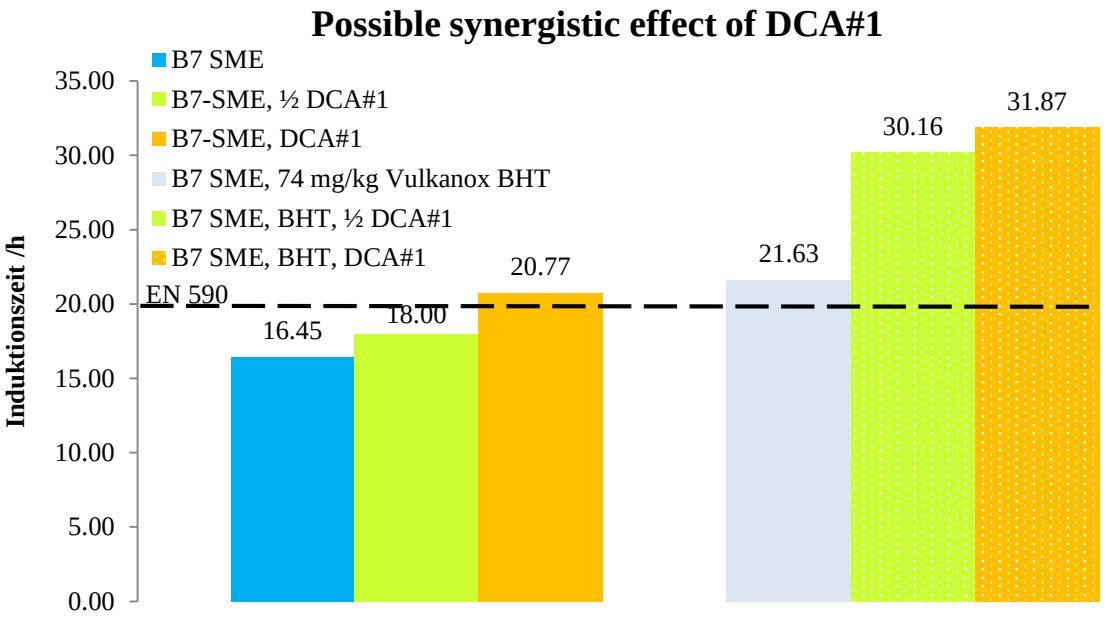


Figure 42: Evaluation of the synergistic effect of DCA#1 in SME II

Table 45: Evaluation of the synergistic effect of DCA#1 in SME II

Samples	***BHT content***	***Induction period (averaged)***	***Increase compared to B7 SME***
B7 SME	-	16.45 h (16.47, 16.43)	-
B7 SME, ½ treat rate of DCA#1	-	18.00 h (18.05, 17.95)	1.55 h (9 %)
B7 SME, BHT ½ treat rate of DCA#1	74 mg/kg	30.16 h (31.19, 29.12)	13.71 h (83 %)
B7 SME, BHT	74 mg/kg	21.63 h (22.06, 21.20)	5.18 h (31 %)
B7 SME, DCA#1	-	20.77 h (20.90, 20.64)	4.32 h (26 %)
B7 SME, BHT, DCA#1	74 mg/kg	31.87 h (30.73, 33.00)	15.66 h (94 %)

A significant synergistic effect was also observed with only half of DCA#1's original treat rate. This can be seen in *Figure 42*, where the big step between fourth and fifth column indicates this unexpected beneficial effect. Interestingly, the synergistic effect was even more pronounced at half the initial treat rate of DCA#1, reaching as high as 43% or almost seven hours. Note that the difference in achievable induction period between the full and half treat rate of DCA#1 was less than two hours (30.16 h versus 31.87 h).

4.9 Long-term storage for SME and TME

As the next step, a simple storage test was performed, to get an insight if the tested diesel additives have a significant negative impact on the long term storage stability of B7 blends. Therefore, some of the already prepared samples were stored for either one or two months at room temperature in darkness (see chapter *3.9*).

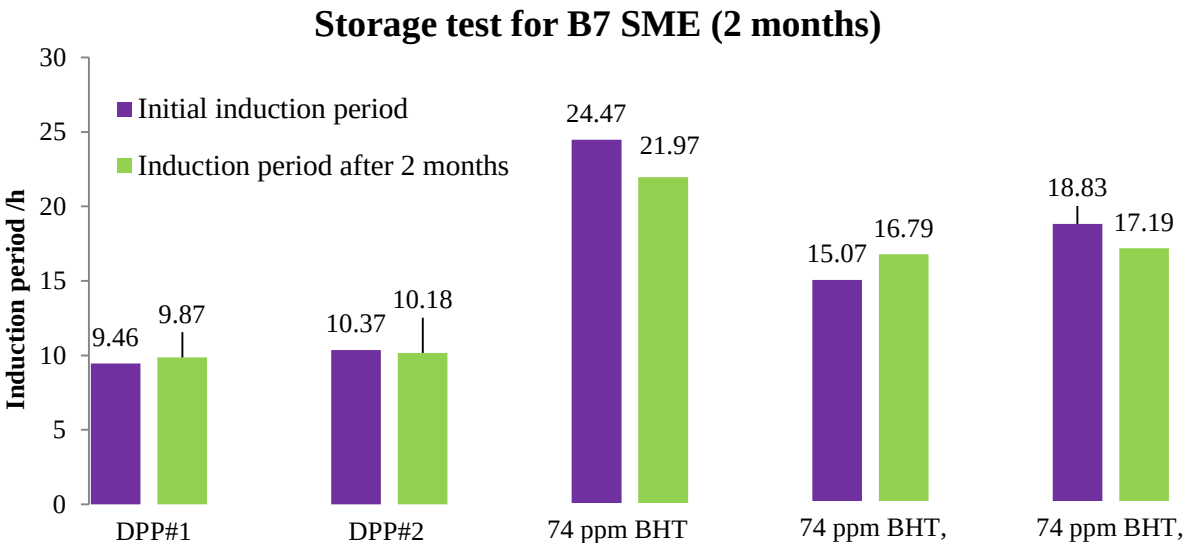


Figure 43: Storage test for B7 SME for two months

Table 46: Storage test for B7 SME for two months

Samples	*Initial IP*	*IP after 2 months (averaged)*	*Relative change [%]*
B7 SME, DPP#1	9.46 h	9.87 h (9.52, 10.21)	+ 4.11
B7 SME, DPP#2	10.37 h	10.18 h (10.20, 10.15)	- 1.92
B7 SME, 74 ppm BHT	24.47 h	21.97 h (22.12, 21.82)	- 11.38
B7 SME, BHT, DPP#1	15.07 h	16.79 h (16.80, 16.77)	+ 10.22
B7 SME, BHT, DPP#2	18.83 h	17.19 h (17.39, 16.98)	- 9.57

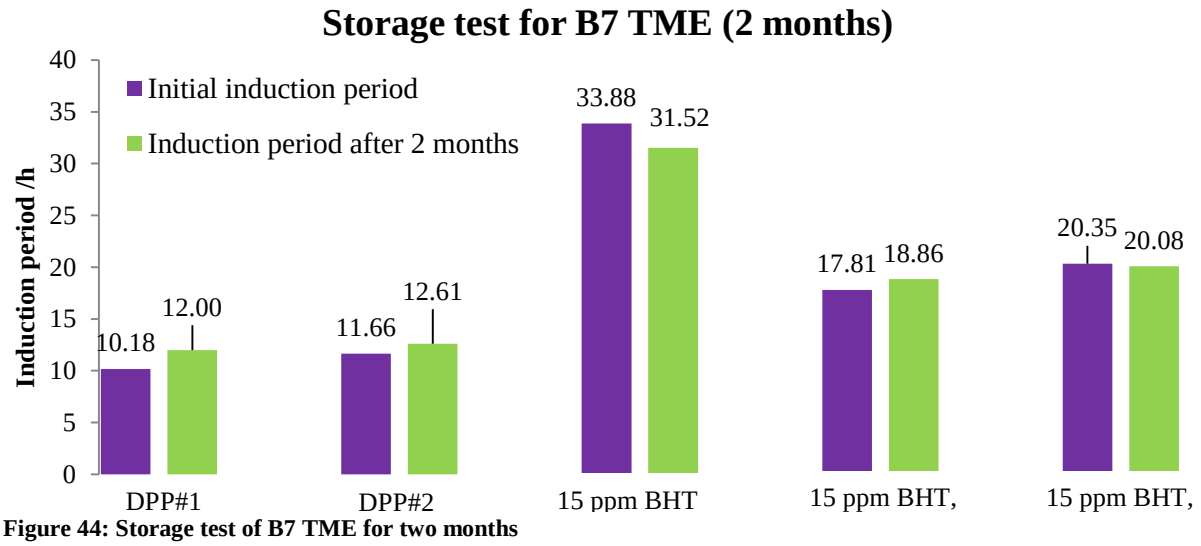


Figure 44: Storage test of B7 TME for two months

Table 47: Storage test for B7 TME for two months

Samples	*Initial IP*	*IP after 2 months (averaged)*	*Relative change [%]*
B7 TME, DPP#1	10.18 h	12.00 h (11.71, 12.28)	+ 13.13
B7 TME, DPP#2	11.66 h	12.61 h (12.72, 12.49)	+ 7.50
B7 TME, 74 ppm BHT	33.88 h	31.52 h (32.63, 30.40)	- 7.50
B7 TME, BHT, DPP#1	17.81 h	18.86 h (18.67, 19.04)	+ 5.57
B7 TME, BHT, DPP#2	20.35 h	20.08 h (20.01, 20.15)	- 1.34

This set of experiments was only able to provide some basic information on the influence of diesel performance packages on long-term storage stability of B7 blends, due to simplicity of the test setup. To be able to get a detailed insight several other factors would have to be taken additionally into consideration, such as water and rust in storage tanks, cyclisation as well as strong temperature fluctuations of diesel fuel in modern common rail engines and possible tank breathing. It has to be stated that the experiments were not performed under strictly controlled conditions. The only solid finding for this set of experiments was that diesel performance packages did not result in a drastic decrease in oxidation stability, neither in non- nor stabilised B7 blends of SME and TME.

One other interesting observation was that for both SME and TME, the steepest decreases of oxidation stability samples were observed for the samples stab only containing BHT and no diesel additives. For example, the B7 blend of TME with 74 ppm of BHT decreased by 7.5 % during storage. In contrast to that, the oxidation stability of stabilised B7 TME samples additionally containing DPP#1 increased by 5.6 % and for DPP#2 decreased by only 1.3%, respectively. This effect is also pronounced in the B7 blends of SME with a decrease in induction period of 11.4 % for B7 SME with 74 mg/kg BHT that was stored for two months. Compared to that, the oxidation stability of stabilised B7 SME containing DPP#1 increased by 10.2 %. This phenomenon could have potentially originated from the high antioxidant content, as hindered phenolic antioxidants, such as BHT, show pro-oxidative effects at high concentrations (see chapter *2.3*). However, further experiments are required to proof this hypothesis.

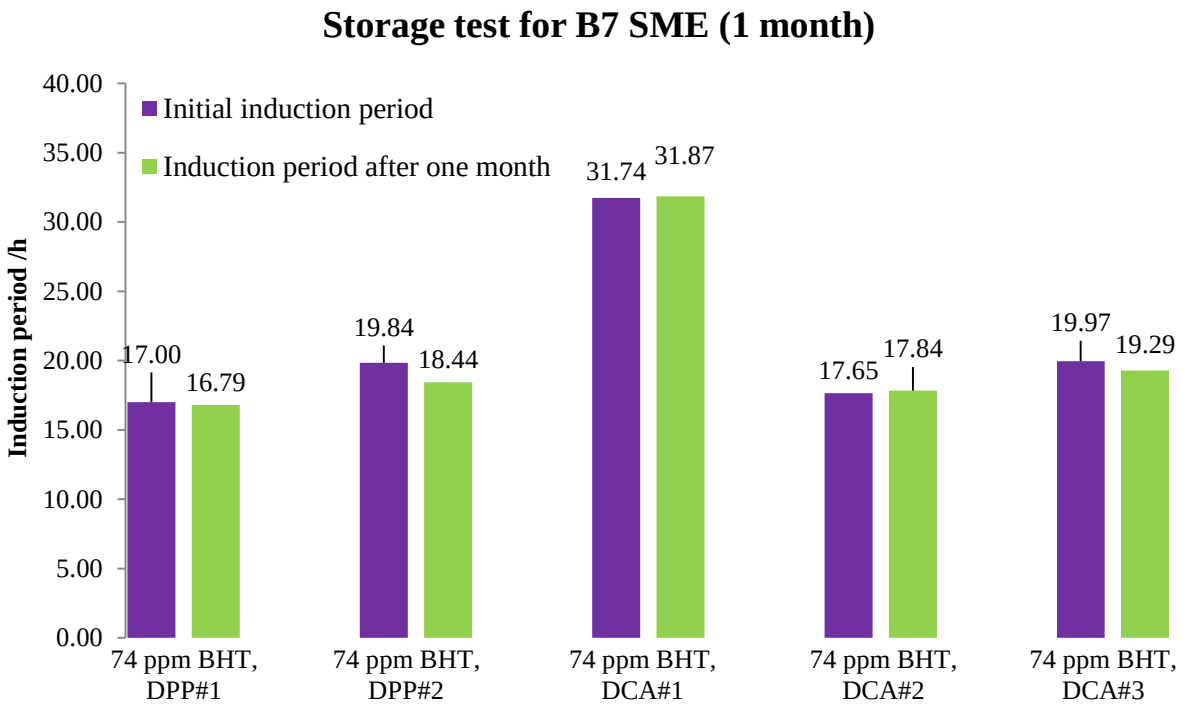


Figure 45: Storage test for B7 SME for one month

Table 48: Storage test for B7 SME for one month

Samples	*Initial IP*	*IP after 1 month (averaged)*	*Relative change [%]*
B7 SME, DPP#1	17.00 h	16.79 h (16.80, 16.77)	- 1.28
B7 SME, DPP#2	19.84 h	18.44 h (18.33, 18.54)	- 7.62
B7 SME, DCA#1	31.74 h	31.87 h (30.73, 33.00)	+ 0.39
B7 SME, DCA#2	17.65 h	17.84 h (17.62, 18.06)	+ 1.07
B7 SME, DCA#3	19.97 h	19.29 h (20.06, 18.52)	- 3.53

Most of the analysed samples did retain their initial induction periods after one month of storage, only DPP#2 seemed to slightly decrease in oxidation stability. However, this reduction was still below two hours, from initially 19.84 to 18.44 hours.

Again, the only solid finding of this set of experiments was that storing stabilised B7 SME containing either diesel performance packages or deposit control additives did not lead to a drastic decrease in oxidation stability.

4.10 Influence of diesel additives on the stability of MBD and ASG

The next step of this thesis was to determine if the results made in soybean oil methyl ester and tallow methyl esters can be reproduced in biodiesel matrices relevant to the European market. Therefore, the influence of five diesel additives was evaluated in stabilised rapeseed oil methyl ester (ASG) and in a stabilised fatty acid methyl ester blend (MBD).

4.10.1 Fatty acid methyl ester blend (MBD)

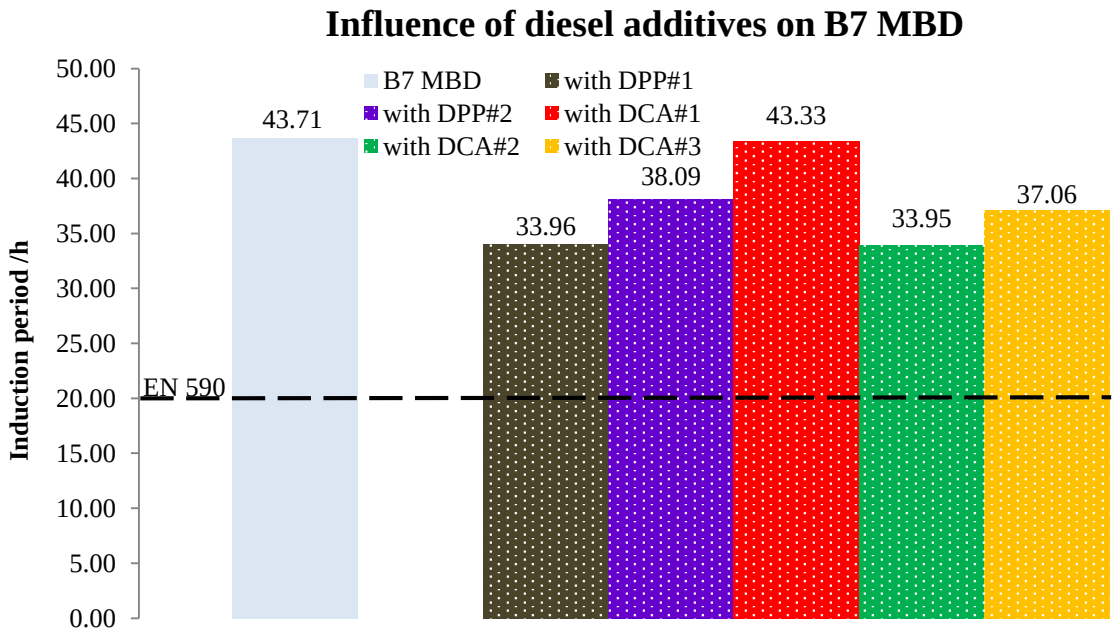


Figure 46: Influence of diesel additives on B7 MBD

Table 49: Influence of diesel additives on B7 MBD

Samples	*Induction period (averaged)*
MBD	9.11 h (9.30, 8.93)
B7 MBD	43.71 h (43.03, 44.37)
with DPP#1	33.96 h (34.05, 33.87)
with DPP#2	38.09 h (39.15, 37.02)
with DCA#1	43.33 h (42.66, 43.99)
with DCA#2	33.95 h (33.77, 34.12)
with DCA#3	37.06 h (37.29, 36.83)

In contrast to results made in SME as well as TME, adding DCA#1 to B7 MDB did not result in an increase of oxidation stability, instead it stayed unchanged. However, because only little is known about DCA#1 or its antioxidative properties, it can only be speculated that either the biodiesel matrix, antioxidant used for stabilisation or a combination of both did suppress the beneficial properties of the diesel additive.

The other four diesel additives all had a negative impact on the induction period of B7 MBD, although in a much lower extent compared to SME and TME. This might be due to the high initial oxidation stability of the pure fatty acid methyl ester blend (MBD) as well as its B7 mixture with petrodiesel. DPP#1 and DCA#2 had the most deleterious effect on the induction period, which could also be observed in the other biodiesel samples. Nevertheless, all mixtures were able to easily surpass the minimum induction period requirement of 20 hours, set by EN 590.[70]

4.10.2 Rapeseed oil methyl ester (ASG)

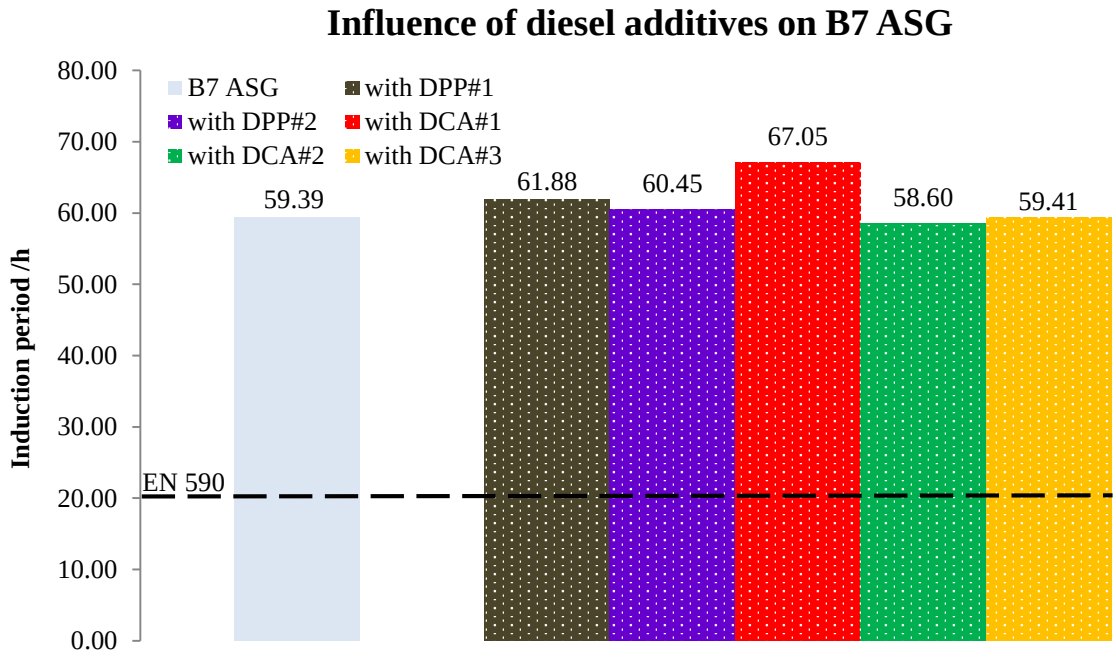


Figure 47: Influence of diesel additives on B7 ASG

Table 50: Influence of diesel additives on B7 ASG

Samples	*Induction period (averaged)*
ASG	16.10 h (16.26, 15.94)
B7 ASG	59.39 h (60.58, 58.20)
with DPP#1	61.88 h (61.88, 61.88)
with DPP#2	60.45 h (61.30, 56.60)
with DCA#1	67.05 h (66.13, 67.96)
with DCA#2	58.60 h (59.26, 57.93)
with DCA#3	59.41 h (58.55, 60.26)

The high oxidation stability of the stabilised B100 rapeseed oil methyl ester as well as its B7 blend, which was reaching an induction period of almost 60 hours, was striking. It was even more remarkable that adding DCA#1 to the B7 blend resulted in an eight hours increase in oxidation stability of, corresponding to a plus of 13%.

Interestingly, also none of the other four diesel additives led to a change in the induction period, as all of them are in the range of ± 5%, which corresponds roughly to the uncertainty of the Rancimat method.[72]

One possible explanation could be that high amounts of antioxidants in this particular biodiesel matrix were able to fully counter the negative impact of the diesel performance additives on oxidation stability.

4.11 Combination of different DCAs in MBD and ASG

As the last step of this master thesis, the consequences of the combination of DCA#1 with the two other deposit control additives DCA#2 and DCA#3 on the oxidation stability of ASG and MBD were evaluated. This was performed so see, if DCA#1, is also capable of compensating the negative impacts of both other deposit control additives on the oxidation stability of highly stable B7 blends.

4.11.1 Fatty acid methyl ester blend (MBD)

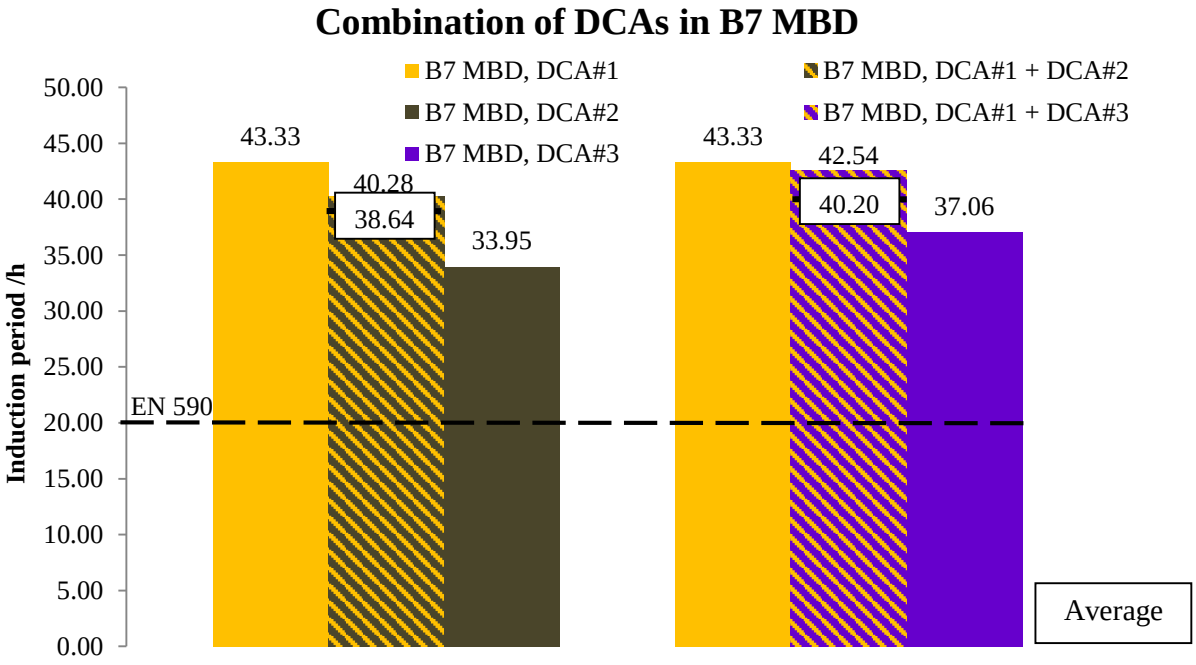


Figure 48: Combination of DCAs in B7 MBD

Table 51: Combination of DCAs in B7 MBD

B7 samples	*Induction period (averaged)*
B7 MBD, DCA#1	43.33 h (42.66, 43.99)
B7 MBD, DCA#2	33.95 h (33.77, 34.12)
B7 MBD, DCA#1 + DCA#2	40.28 h (42.09, 42.99)
B7 MBD, DCA#3	37.06 h (37.29, 36.83)
B7 MBD, DCA#1 + DCA#3	42.54 h (40.79, 39.77)

Again, as for SME as well as TME, combining DCA#1 with either DCA#2 or DCA#3 was very beneficial for the oxidation stability of B7 MBD blends. The induction period of both additive mixtures were significantly above the ones containing only DCA#2 or DCA#3 respectively. This beneficial effect was more pronounced for the latter deposit control additive, as there is only a minor difference (~1 h) in induction periods between the sample containing only DCA#1 and the binary mixture with DCA#3. Interestingly, the oxidation stabilities of both deposit control additive combinations in B7 MBD were again, as for SME and TME, above calculated average value, but only for about two hours in each case.

4.11.2 Rapeseed oil methyl ester (ASG)

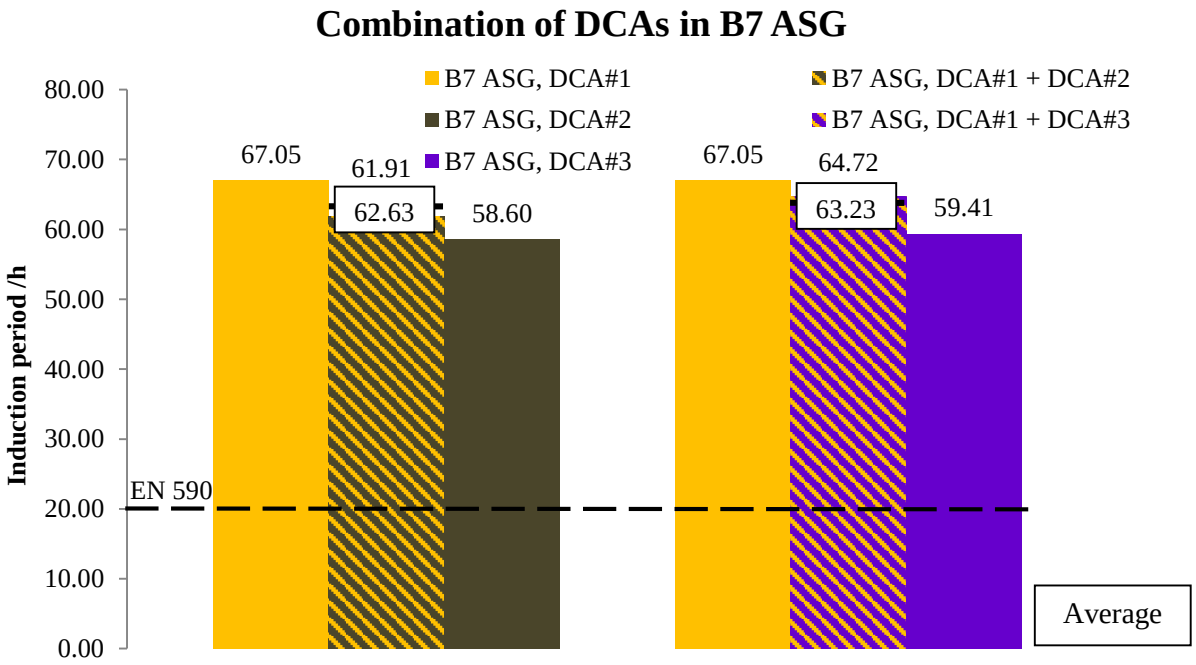


Figure 49: Combination of DCAs in B7 ASG

Table 52: Combination of DCAs in B7 ASG

B7 samples	*Induction period (averaged)*
B7 ASG, DCA#1	67.05 h (66.13, 67.96)
B7 ASG, DCA#2	58.60 h (59.26, 57.93)
B7 ASG, DCA#1 + DCA#2	61.91 h (61.91, 61.91)
B7 ASG, DCA#3	59.41 h (58.55, 60.26)
B7 ASG, DCA#1 + DCA#3	64.72 h (66.93, 62.50)

Interestingly, adding DCA#1 to B7 ASG containing either DCA#2 or DCA#3 resulted in a significant increase of oxidation stability, although having exceptionally high initial induction periods. In contrast to the other biodiesel matrixes tested, the oxidation stability of both deposit control additive combinations in B7 ASG were at exactly or even slightly below the calculated average value. An explanation for this could be the aforementioned extremely high oxidation stability of the individual samples.

Chapter 5: Conclusions and Outlook

The main focus of this thesis was to assess the impact of various diesel additives and antioxidants on the oxidation stability of biodiesel and petrodiesel blends. Therefore, the influence of four antioxidants, two diesel performance packages and four deposit control additives were tested in soybean methyl ester, tallow methyl ester, fatty acid methyl ester blend and rapeseed oil methyl ester, as well as their respective B7 blends, using the Rancimat measurement technique. It was determined, that all diesel performance packages and two of the three deposit control additives had a distinct negative impact on the oxidation stability of all biofuels tested, except for the rapeseed oil methyl ester. Furthermore, none of the antioxidants tested was able to fully cope the negative influence of any of the diesel additives tested.

This thesis could provide a solid basis for further investigations, as there is currently no literature available on the influence of diesel additives on the oxidation stability of biodiesel and petrodiesel blends.

Of the four antioxidants tested, Baynox® Plus was the most suitable antioxidant for stabilising SME in B100 as well as B7, in terms of reachable induction period. In TME, AO#4 did significantly outperform the three competitors at B100 as well as B7 level.

Both diesel performance packages had a drastic impact on the oxidation stability of soybean oil methyl ester as well as tallow methyl ester. None of the four antioxidants was able to fully cope with the negative influence of neither DPP#1 nor DPP#2. Additionally, it was determined that 2-ethylhexyl nitrate (2-EHN) was responsible for the bad performance of DPP#1.

Two of the three tested deposit control additives, DCA#2 and DCA#3, had a deleterious effect on the oxidation stability of both SME and TME, which could not be fully countered using BHT as stabiliser. Contrary to that, DCA#1 was able to increase the oxidation stability of both biodiesel samples. Additionally, combining DCA#1 with DCA#3 did almost fully compensate its negative influence on the induction period regardless of BHT presence. With DCA#2, a significant difference to the non-additivated sample could still be observed. The positive effect of DCA#1 was more pronounced in SME, where a distinct synergistic effect between biodiesel matrix, BHT and deposit control additive was found. Furthermore, neither diesel performance packages nor deposit control additives had a major impact on long term storage stability of B7 blends of SME as well as TME. However, for a detailed elucidation of long term storage stability, tests under strictly controlled conditions and continuous sampling are required.

The oxidation stability of B7 samples from a stabilised fatty acid methyl ester blend were affected by both diesel performance packages. However, they did not impact the induction period of B7 blends from stabilised rapeseed oil methyl ester. Likewise, DCA#2 as well as DCA#3 did decrease the induction period of the FAME blend but did not have a negative effect on the stability of RME. Interestingly, DCA#1 did not increase the induction period of the fatty acid methyl ester blend B7 sample. However, the aforementioned additive indeed had a positive impact on the exceptionally stable rapeseed oil methyl ester, significantly increasing oxidation stability of the respective B7 blend.

Unfortunately, there is the possibility that the antioxidative effect of DCA#1 is just an artefact of the Rancimat measuring technique. Therefore, alternative stability determinations, such as PetroOxy or TOST & TOO, are required to properly asses this phenomenon. Additionally, it would be of high importance to assess the individual diesel additive components on their influence on the oxidation stability of biodiesel and B7 blends. Especially, the high potency of DCA#1 needs further investigation, as the chemical structure of its active component is not that of a classical antioxidant. Furthermore, the influence of all tested diesel additives on the long term storage stability needs to be assessed in strictly controlled conditions, to rule out any negative impact on the induction period and to get a better insight on long term stability of fully additivated diesel fuels.

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