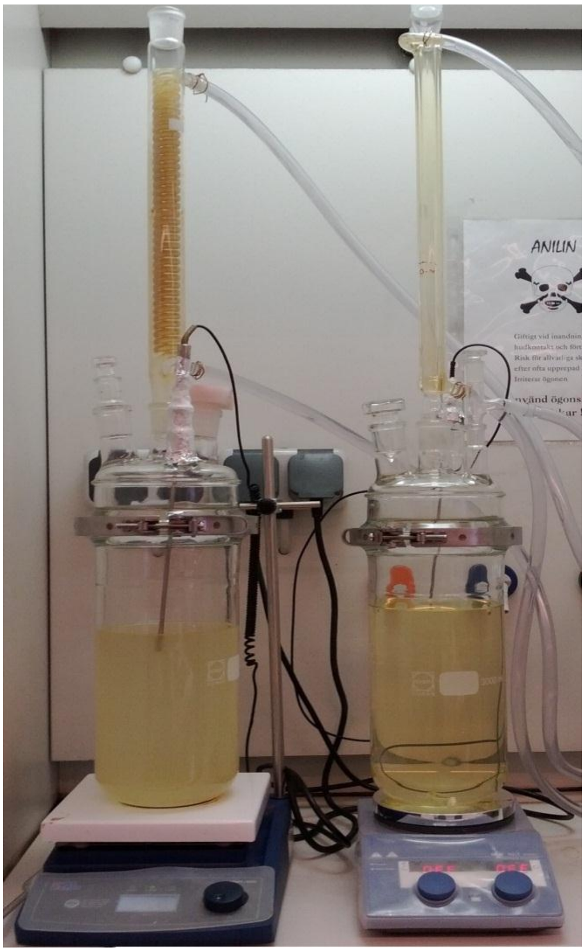

Characterisation of chemical decomposition of biodiesel

With a focus on B10, B30 and B100 blends

Bachelor of Science Thesis

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Gothenburg, Sweden, 2012

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Cover: [The reaction vessels used for the ageing of biodiesel blends. For more information, see section 3.1 Ageing of biodiesel]

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Abstract

For many years, fossil fuels have dominated the diesel market. As the availability of fossil fuels decrease and as their environmental impact becomes clearer, more renewable and more environmentally friendly fuels have been developed. Because biodiesel fulfils both of these requirements, it is one of the candidates for replacing the fossil fuels. In Europe, rapeseed methyl ester is the most used biodiesel.

Before biodiesel can become fully accepted as a replacement for the fossil diesel, there are some problems that must be addressed. These problems include biodiesel breaking down plastics, corroding metals and clogging filters and pumps. Almost all of these problems stem from one source; its oxidation products. If the oxidation of the diesel can be limited, these problems can be almost entirely avoided.

This project has been carried out as collaboration between Chalmers University of Technology and Volvo Car Corporation. The project aimed to characterise the oxidation products formed during the ageing of biodiesel, and show how they develop in different blends under different conditions.

During the project, biodiesel blends have been aged for 100 hours at 85°C in an open system or in a nitrogen atmosphere. Two different kinds of rapeseed methyl ester have been used, one with added antioxidants and one without. Samples were taken continuously and analysed to see trends in the development of acids, peroxides and water content.

The results show that out of the blends tested, the B30 blend was most readily oxidised. It is also clear that either an oxygen-free atmosphere or addition of antioxidants are very effective for reducing oxidation of the biodiesel.

This report is written in english.

Keywords: biodiesel, RME, rapeseed methyl ester, oxidation, decomposition, ageing

Sammanfattning

I många år har fossila bränslen dominerat världsmarknaden för diesel. Allt medan tillgängligheten av fossila bränslen minskar och deras miljöpåverkan blir allt mer uppenbar utvecklas mer förnyelsebara och mer miljövänliga bränslen. Eftersom biodiesel uppfyller båda dessa krav har den blivit en kandidat till att ersätta den fossila dieseln. I Europa är rapsmetylester den mest använda typen av biodiesel.

Innan biodiesel kan bli fullt accepterad som ersättare för den fossila dieseln finns det vissa problem vars skadeverkningar måste minimeras. Dessa problem innefattar biodieselns nedbrytning av plaster, dess korrodering av metaller och dess tendens att polymerisa vilket sätter igen bränslefilter och pumpar. Nästan alla dessa problem härstammar från samma källa; biodieselns oxidationsprodukter. Om denna oxidation kan minimeras, kan även en stor del av dessa problem undvikas.

Projektet har genomförts som ett samarbete mellan Chalmers Tekniska Högskola och Volvo Car Corporation. Detta projekt har syftat till att karaktärisera oxidationsprodukterna som bildas under åldringen av biodiesel, samt visa hur de utvecklas i olika blandningar under olika förhållanden.

Under projektet har biodieselblandningar åldrats i 100 timmar vid 85°C i antingen ett öppet system eller i kvävgasatmosfär. Två olika sorters rapsmetylester har åldrats, en med tillsats av antioxidanter och en utan. Prover har tagits regelbundet och dessa har sedan analyserats för att visa trender med avseende på syra-, peroxid- och vattenhalt.

Resultaten visar att av de testade blandningarna är B30 den mest lättoxiderade. Det är även tydligt att en syrefri atmosfär eller tillsats av antioxidanter är mycket effektiva sätt att minska oxidationen av biodiesel.

Denna rapport är skriven på engelska.

Nyckelord: biodiesel, RME, rapsmetylester, oxidation, nedbrytning, åldring

Contents

1 Introduction **1**
- 1.1 Purpose . . . 1
- 1.2 Scope . . . 1

2 Background **2**
- 2.1 Origins of biodiesel . . . 2
  - 2.1.1 Biodiesel from rapeseed oil . . . 2
  - 2.1.2 Biodiesel from alternative feedstocks . . . 2
- 2.2 MK1-diesel . . . 3

3 Theory **4**
- 3.1 Transesterification reaction . . . 4
- 3.2 Composition of diesel . . . 5
- 3.3 Composition of RME . . . 5
- 3.4 Oxidation products and mechanisms . . . 6
- 3.5 Antioxidants as stabilisers . . . 7
- 3.6 Analysis methods . . . 8
  - 3.6.1 Acid number determination . . . 8
  - 3.6.2 Peroxide number determination . . . 8
  - 3.6.3 Water content analysis with Karl-Fischer titration . . . 9

4 Method **11**
- 4.1 Ageing of biodiesel . . . 11
- 4.2 Acid number determination . . . 11
- 4.3 Peroxide number determination . . . 12
- 4.4 Water Content . . . 13

5 Results and discussion **14**
- 5.1 B10 blends . . . 14
- 5.2 B30 blends . . . 14
- 5.3 B100 blends . . . 15
- 5.4 Visual observations . . . 16
  - 5.4.1 Colour change . . . 16
  - 5.4.2 Polymerisation . . . 17

6 Conclusion **18**

7 References **19**

A Acid number graphs **21**

B Peroxide number graphs **25**

C Water content graphs **29**

D Terminology **32**

E Reaction vessels **33**

F Specifications **35**

F.1 9h stable RME, IBC 120320 FAME 35

F.2 1.6h stable RME 37

F.3 MK1 diesel 39

F.4 Environmental classifications, fossil diesel 41

1 Introduction

Rapeseed methyl ester (RME) is a fatty acid methyl ester (FAME) made from rapeseed oil, a renewable energy source [1]. It is used to decrease the environmental impact of diesel fuels by replacing a percentage of the fossil diesel with biodiesel. This greatly reduces the emissions of carbon dioxide and eliminates the need for synthetic lubricant oils in the diesel [1].

Currently in Sweden, all diesel sold at gas stations must contain between 5 and 7 % biodiesel during the summer, but starting in May 2014 these levels will increase to minimum 7 % and maximum 10 % [2]. This makes it important to study the reactivity and characteristics of such blends.

A problem with biodiesel is that it tends to wear down parts of the car engines quicker than regular diesel, and under certain conditions it polymerises which may lead to clogging of the fuel injectors and the diesel filters [3].

1.1 Purpose

The goal of this report is to study the decomposition products of biodiesel. The main areas of interest are the concentrations of each respective type of product, when the decomposition occurs and to a lesser degree, how and why it occurs.

This report does not aim to produce absolute numbers for the quantities and concentrations of oxidation products, but to show which blends are susceptible to oxidative reactions under which conditions, and to present which kind of decomposition trends can be expected from certain configurations.

1.2 Scope

This study was limited to the decomposition of the biodiesel without simulating a car-like environment, to reduce the required time and the complexity of the project. This means that the biodiesel was aged without the presence of metals and polymers. The reduced complexity of the ageing-environment allowed the project to clearly characterise oxidation products of each specific blend under each set of conditions.

Having the results from this kind of tests is a necessary precursor for other ageings in more complex settings, where consideration must be taken to possibilities such as catalytic oxidation due to presence of metal ions and varying temperatures over time.

2 Background

Biodiesel is a fuel with great potential. It comes from renewable energy sources, it is easy to produce and has a high effect [3]. Because of its reactive oxidation products and its subsequent tendency to polymerise, efforts must be made to inhibit the oxidation if biodiesel is to prevail on the fuel market.

2.1 Origins of biodiesel

The majority of this report will concern the use of biodiesel from rapeseed oil, rapeseed methyl ester (RME). RME is produced by a transesterification reaction where rapeseed oil is reacted with an alcohol and a strong acid or base to produce rapeseed methyl esters (see section 3.1).

The two types of RME used for the experimental parts of this project are produced by Perstorp Bioproducts and sold by Preem. A specification for the composition of the 9h stable RME is available in appendix F.1, for the 1.6h stable RME see appendix F.2.

2.1.1 Biodiesel from rapeseed oil

In northern Europe, most of the biodiesel produced is made from rapeseed oil [3]. It is well suited for use in northern climates since it can be used until it reaches its cold filter plugging point at -22°C (appendix F.1). This can be lowered further with additives. For even lower temperatures it is best to use a blend containing more fossil diesel to ensure that the combustion can be initiated without pre-heating of the fuel. Even though rapeseed oil is not the cheapest oil available in the European Union, it is the one that has the best low-temperature characteristics as stated above. This is the main reason to why it is able to compete with cheaper imported vegetable oils such as soybean oil [4].

2.1.2 Biodiesel from alternative feedstocks

The main reason that there is such a discrepancy between the choices of biodiesel feedstocks is the local availability [3]. This can be attributed both to the more reliable supply and to the generally lower cost of locally produced raw materials. Because of this predisposition towards certain types of precursors, it is possible to generalise a bit about the biodiesel types originating from specific parts of the world. In the European Union, most biodiesel is based on rapeseed- and sunflower oil while in the Unites States the predominant type is made from soybean oil and animal fats [3].

There is a lot of on-going research into alternative feedstocks for biodiesel. For example, SP Technical Research Institute of Sweden is currently investigating microalgae as the next generation of raw material for fuel production [5]. These have the advantage of a short growth cycle and low demands on their habitat which means that they can be grown on inhospitable land without competing with food production while still producing quality fuel [5].

The choice of biodiesel feedstocks can be heavily influenced by a number of economic factors, arguably the most important of which is government intervention. This can manifest itself in ways such as a subsidisation favouring one of several competing raw materials. An example of this can be seen on the Brazilian market where the government is working to shift the biodiesel production from using soybeans, which can be used for many other things, to castor oil which can be grown in regions of the country that is inhospitable to soy beans [3].

In Sweden, the government has introduced a 100 % tax cut for biodiesel on the energy and carbon monoxide taxes that burden fossil fuels [6]. This is done to facilitate the transition from a fossil-fuel dependant energy sector into the use of renewable energy sources. This greatly improves the outlook for emerging biofuels such as biodiesel.

2.2 MK1-diesel

In Sweden, fossil diesel is classified into one of three groups. There are Miljöklass 1 (MK1), Miljöklass 2 (MK2) and Miljöklass 3 (MK3) which mean Environmental Class 1/2/3. This classification system has been used since 1991 and its purpose is to facilitate the reduction of environmental impact of fossil fuels [7].

The system does not impose an exact composition, but sets maximum allowed concentrations of compounds (see appendix F.4 for a comparison of various classification levels). The lower the number in the classification, the more aliphatic carbon chains, thereby the more environmentally friendly. In Sweden, only MK1 is available for sale. The major difference between MK1 and diesel from other parts of the European Union is the allowed polyaromatic content which is often considerably lower in MK1 as opposed to foreign diesel [25].

As is often the case, the ”cleaner” a product is the more it costs. This is something the Swedish government has decided to compensate by cutting taxes for MK1 diesel in order to encourage consumers to choose the more environmentally friendly alternative [7].

The MK1 diesel used for the practical experiments in this project was free from the usual 5 % addition of biodiesel mentioned in section 1.0. For a composition of the MK1 diesel used in this project, see appendix F.3.

3 Theory

This section will outline the basic theoretical background required for understanding the results section of the report.

3.1 Transesterification reaction

The basic theory behind a transesterification reaction is to change the functional group of an organic molecule from an alcohol to an ester. This is accomplished with an exchange reaction where an alcohol and an ester exchange their organic groups with each other. This reaction is often catalysed with a strong base [8].

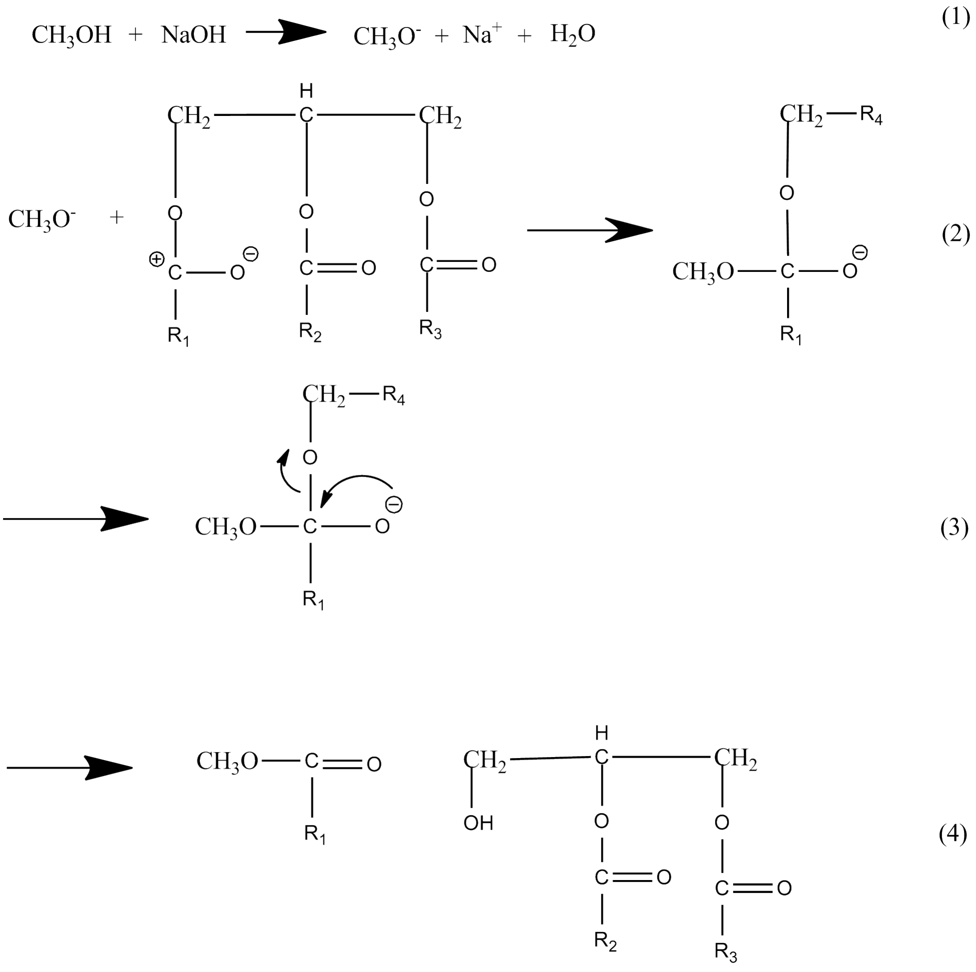


Figure 1: Transesterification reaction

In the case of biodiesel production from rapeseed oil, the reaction is carried out in a few steps explained below. First, a strong base such as NaOH, KOH et. c., is used to deprotonate the alcohol (step 1, figure 1). The resulting negatively charged carbonyl oxygen then forms a tetrahedral intermediate when it binds to the slightly positive carbon in the ester bond of the triglyceride (step 2, figure 1). The pair of free electrons pushed onto the formerly double bonded ester oxygen will then return to a more stable conformation which will in turn break the oxygen bridge and cause the resulting diacylglycerol to detach (step 3, figure 1). This process will result in a fatty acid methyl ester and a diacylglycerol, eventually ending with three fatty acid methyl esters and one glycerol per triglyceride reacted [9].

When this reaction is carried out in mass production, it is important to add alcohol in excess quantities to prevent the reverse transesterification from occurring. The stoichiometric relation imply that a 3:1 ratio of alcohol:triglyceride should be sufficient, but to minimize the risk of reverse reaction a 6:1 ratio is often preferred [10]. It is possible to catalyze this reaction using acids or enzymes instead of strong bases, however using a strong base greatly improves the kinetics at which this reaction occur. The choice of alcohol is arbitrary, and as such is mainly governed by economic factors such as price and availability. This often favors methanol, since it is often the cheapest and most abundant alcohol except for in areas such as Brazil where a very well developed ethanol production industry makes ethanol a cheaper choice [3].

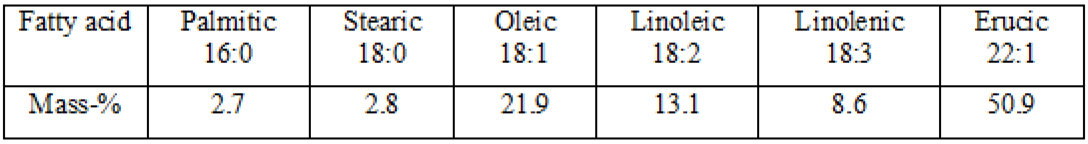
3.2 Composition of diesel

Fossil diesel is a transparent liquid and is the middle distillate from crude oil distillation with a bubble point interval at 180-320°C [11]. Diesel is mostly made up by saturated carbon chains ranging from 10 to 22 carbon atoms per molecule but it also contains some aromatics, unsaturated carbon chains and sulphur [12].

The sulphur and aromatics content in diesel sold at Swedish gas stations, MK1 diesel, has been reduced to be more environmentally friendly. The exact composition of MK1 is shown in appendix F.4.

3.3 Composition of RME

Because of the use of rapeseed oil as a raw material for RME, the biodiesel contains various types of FAME. A composition of rapeseed oil is shown in figure 2, the concentrations shown in the table are not absolute for all rapeseed oils as the composition changes somewhat depending on where the rapeseed has grown [13].



Fatty acid	Palmitic 16:0	Stearic 18:0	Oleic 18:1	Linoleic 18:2	Linolenic 18:3	Erucic 22:1
Mass-%	2.7	2.8	21.9	13.1	8.6	50.9

Figure 2: Composition of rapeseed oil

The colour of RME varies from green to yellow depending on the manufacturing process. RME of green colour originates from solid-phase catalysed production such as the methods used at Perstorp Biofuels while yellow-coloured RME is generated during production with liquid-phase catalysts [26]. The green colour disappears readily when the biodiesel is oxidised and the diesel turns yellow. The amount of oxidation that is needed to change colour is so small that it is not detectable [24]. Due to the large quantities of oxygen and unsaturations in the RME it is very susceptible to oxidation which will break down the FAME molecules producing decomposition products such as peroxides and acids. These reactions are also promoted by metal traces and high temperatures [14]. As peroxides and fatty acids corrode metals and break down plastics it is very important to keep these concentrations of these compounds as low as possible in the diesel fuel.

The breakdown of the FAME does not only promote corrosion it also alters the properties of the RME, its combustion energy and viscosity gets lower and density increases. This increases the fuel consumption but it also makes the combustion more complete which results in lower CO and soot emissions [16]. The NO_x emissions are generally lower from biodiesel compared to fossil diesel but increases as the FAME oxidises [17]. Compared to fossil diesel the FAME has higher density, viscosity and a slightly higher cetane number [17].

3.4 Oxidation products and mechanisms

Lipid oxidation reactions, such as in biodiesel, is generally initiated by the formation of peroxides. A prerequisite for this reaction is the availability of free radicals. These free radicals are often formed from molecular oxygen present in the atmosphere. The first step of this peroxide formation is the attack of a free radical on an unsaturation of the lipid [18]. This leads to the formation of a lipid radical which can then react with an oxygen molecule to form a lipid-peroxide radical. This process is self-propagating with the lipid-peroxide radicals capable of creating new lipid radicals when they react with another unsaturated lipid [18]. This process is shown in figure 3.

The termination of such a reaction occurs when two lipid-peroxide radicals react with each other to form a dimer and initiate a polymerization. The lipid-peroxides can also react further to produce a wide variety of products such as epoxides, aldehydes, free water, ketones and alcohols. Many of these products are not in themselves stable and can continue to react to form a number of tertiary oxidation products such as formic acid and other low-molecular carboxylic acids [19].

As can be seen from the reaction pathways in figure 3, the most critical step in lipid oxidation is the initiation, which is to say the availability of oxygen and oxygen

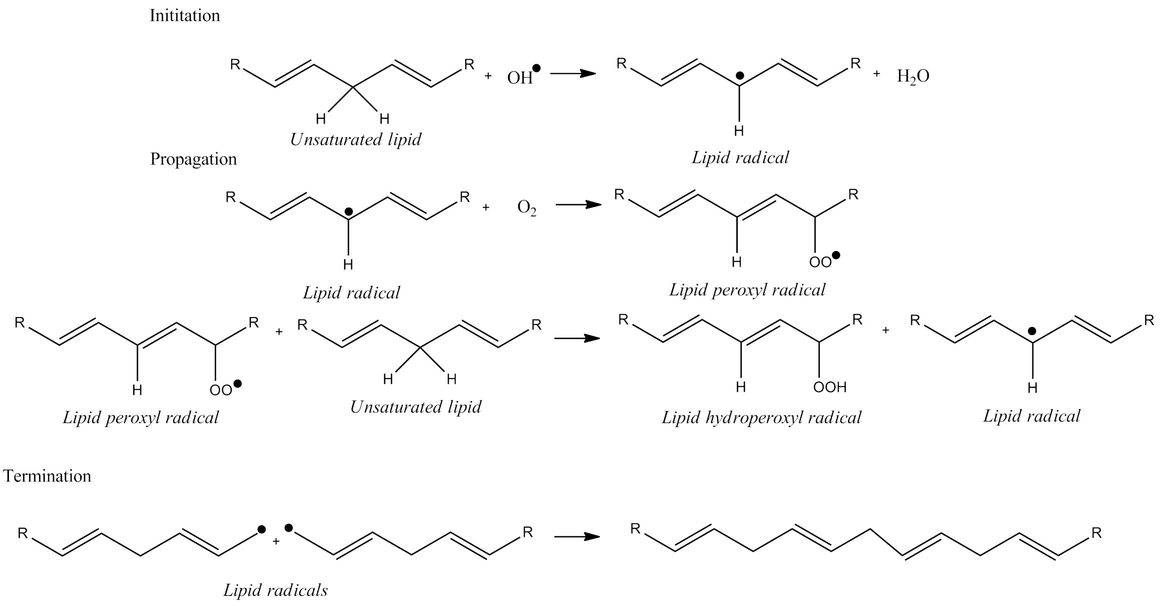


Figure 3: Peroxidation reaction

radicals. In order to inhibit the oxidation of the biodiesel, the most effective way is to limit its exposure to oxygen. This is often hard to achieve during normal use of diesel. An alternative to oxygen limitation is to add antioxidants to the FAME which can dispose of the formed oxygen radicals [15].

3.5 Antioxidants as stabilisers

There exists a number of commonly used antioxidants for stabilising biodiesel. A selection of such compounds can be seen in figure 4. These chemicals function by donating a hydrogen to the hydroxyl radicals or to the lipid radical if such have been formed, thereby neutralising them. This leads to a quinone-like structure of the antioxidants which is significantly more stable than the radicals [22].

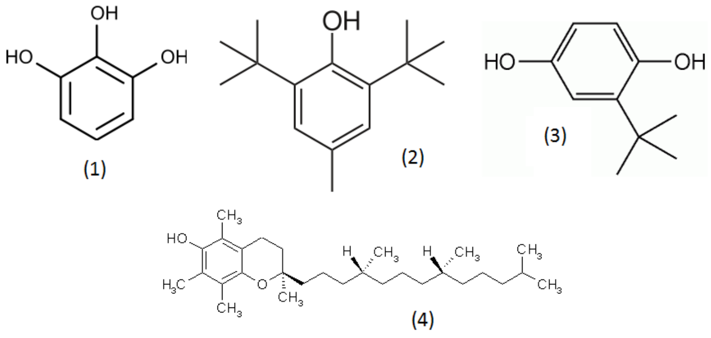


Figure 4: A few common antioxidants. (1) Pyrogallol, (2) Butylated hydroxytoluene (BHT), (3) tert-Butylhydroquinone (THBQ), (4) α-tokopherol

While pyrogallol, TBHQ and BHT are synthetically produced, α-tokopherol (commonly known as vitamin E) is naturally occurring. The antioxidation capacity is significantly lower for α-tokopherol than the other three [15, 20].

Another important property of chemicals used as stabilisers is their solubility in the fuel. For diesel it is very important that the antioxidant is fat soluble, something that vastly reduces the number of potential compounds available.

Antioxidants are added in concentrations ranging from 100-2000 ppm. The 9h oxidative stable RME used in this project had an added 300 ppm of BHT. No change in combustion characteristics can be shown after the addition of antioxidants to the biodiesel at these levels [20].

3.6 Analysis methods

Three different practical analyses have been used for the determination of acid-, peroxide and water levels in aged samples of diesel.

3.6.1 Acid number determination

Acid-base titration is used to determine the concentration of an acid or base in a solution. This is done by adding a strong acid or base with known concentration to the solution until a predetermined pH is reached. The volume added is then used to calculate the concentration of the unknown sample. This is reported as an acid number which is given as milligrams KOH required to neutralise one gram of sample. To visualise when a desired pH is reached, an indicator is often used which changes colour at different pHs. In this case α-naphtholbenzein was used as indicator which changes colour from yellow/orange to green/blue at pH 8.2-10 [21].

3.6.2 Peroxide number determination

Peroxide number is the concentration of peroxides present in the solution in mg/kg. To measure the peroxide number the solution is titrated with sodium thiosulphate ($Na_2S_2O_4$) with excess iodide and acetic acid present in the solution. The excess iodine is added to make sure all peroxides react and the excess acetic acid to neutralise any alkali formed in the reactions. Water is added to the solution to extract all peroxides from the diesel phase enabling titration with the water based thiosulfate solution. The redox reactions which occur when $Na_2S_2O_4$ is added are shown in reactions 1 and 2. Starch solution is used as an indicator as it turns dark blue/black in the presence of iodine and the colour disappears when all the iodine is consumed.

$$ROOR' + 2I^- + 2H^+ \Rightarrow 2ROH + I_2 \tag{1}$$

$$I_2 + 2S_2O_3^{2-} \Rightarrow 2I^- + S_4O_6^{2-} \tag{2}$$

3.6.3 Water content analysis with Karl-Fischer titration

For the water content analysis in this project, an automated Karl Fischer 774 Metrohm Oven Sample Processor combined with a 756 Metrohm KF-Coulometer was used. This machine works by applying a predetermined amount of heat to a sample which evaporates the water without entraining any of the other components in the sample. The water vapour is then transported away using a dry carrier gas, dried air or N_2, and a hollow needle inserted through the septum in the top of the glass vials that the samples are stored in. The evaporated water is then carried into a titration cell where it is bubbled through and absorbed in a titration solution while the carrier gas simply passes through the liquid without being absorbed. [23] This procedure is illustrated in figure 5.

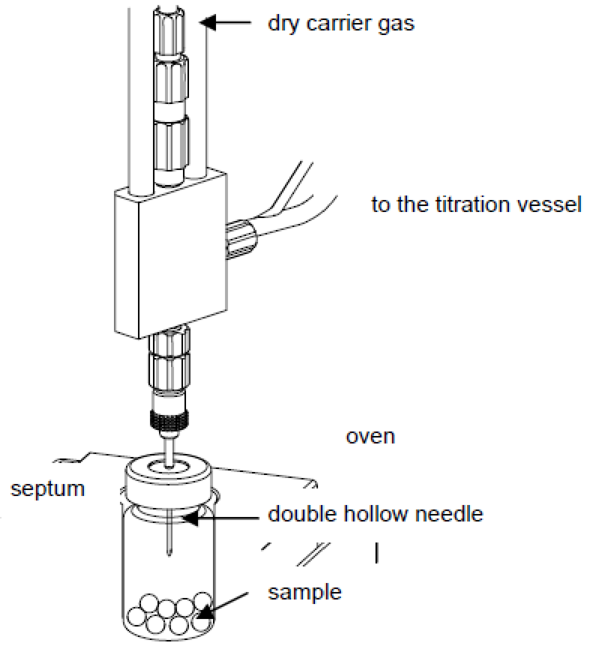


Figure 5: Karl Fischer analysis equipment, water transfer

The titration solution contained in the titration cell is composed of an alcohol, a base, iodine and sulphur dioxide. There is also another cell containing the same solution, these two cells are separated by a semi-permeable (ion-permeable) membrane. Immersed in both cells are the anode and the cathode of a platinum electrode. During the analysis a constant current is maintained through the electrode circuit and the end-point of the analysis is reached when the voltage over the circuit suddenly drops. This voltage drop is due to the formation of excess I_2 when all water has been consumed. The type of apparatus used during this project is pictured in figure 6 [23].

Figure 6: Karl Fischer analysis equpiment, Metrohm 774 Sample Processor

4 Method

With the exception of the water content analysis, all weighing were done on the same analytical scale with a margin of error of ± 0.0005 g. The weighing for the water content analysis was done at the Volvo laboratories' scale which had a margin of error of ± 0.005 mg.

In some of the ageings, visual observations revealed that polymerisation and/or colour change had occurred. These results were documented using a camera.

4.1 Ageing of biodiesel

The ageing is carried out in a glass reactor with four necks, placed on a hot plate with a magnetic stirrer. The necks are used for a thermometer, a pipe for vapour cooling, one is plugged with a glass stopper and one is either used for nitrogen gas injection or is also shut with a glass stopper. Pictures of the reaction vessels can be seen in appendix E. The reactors were covered with aluminium foil to avoid photocatalysed oxidation and to keep the temperature stable.

All blends were aged for 100 hours and the samples are withdrawn by removing a glass stopper and using a volumetric pipette. The samples are stored in glass vials covered with aluminium foil and put in a fridge at 7°C until analysed.

The first two ageings carried out were B0 and B30 of 1.6h stable RME. These were done in 1 l reactors. Following these first ageings, further tests were carried out using 3 l reactor vessels to minimise the change in biodiesel volume during the ageing. The blends aged were B0, B10, B30 and B100 using both 1.6h stable RME and 9h stable RME, aged both in open system and under nitrogen atmosphere.

4.2 Acid number determination

This analysis is carried out according to ASTM D 974-08 *Standard Test Method for Acid and base Number by Color-Indicator Titration.*

100 mL titration solvent and the diesel sample was added to a 250 mL Erlenmeyer flask. After addition of 0.5 mL p-Naphtholbenzein the solution was titrated with potassium hydroxide solution until the colour changed from orange-yellow to green.

A blank sample was also titrated to colour change to determine the internal acid number of the titration solution.

The acid number is calculated using the formula:

$$Acid\,number(mgKOH/g) = ((V_{KOH} - V_{Blank}) * C_{KOH} * MW_{KOH})/m_{Sample} \qquad (3)$$

where V is the volume of KOH-solution required for the titration, C is the concentration of the KOH-solution, MW is the molecular weight of KOH and m is the mass of the sample analysed.

Titration Solvent

Toluene (reagent grade), distilled water and anhydrous isopropyl alcohol (reagent grade) are mixed in an Erlenmeyerflask in the proportions 100 : 1 : 99.

p-Naphtholbenzein Indicator

A solution is made from p-Naphtholbenzein (pH 8.2-10) and titration solvent with the concentration 10.0 g/L p-Naphtholbenzein.

Hydrochloric acid solution

1 mL Hydrochloric acid (sp gr 1.19, 37%) is diluted to 100 mL with water.

Potassium Hydroxide Solution

1000 mL anhydrous isopropyl alcohol is measured and transferred to a 2000 mL Erlenmeyer flask where 6.00 g of solid KOH is added. The solution is boiled for 10 minutes with constant stirring before 2.26 g of solid $Ba(OH)_2$ is added. The solution is then boiled for another 10 minutes. The solution is then left to cool over night at room temperature and then the supernatant is vacuum-filtered into a chemically resistant HDPE-container.

The solution was titrated with the hydrochloric acid solution to determine the concentration.

4.3 Peroxide number determination

This analysis is carried out according to ASTM D 3703-07, *Standard Test method for Hydroperoxide Number of Aviation Turbine Fuels, Gasoline and Diesel Fuels.*

25 mL of trimethylpentane is added to an Erlenmeyer flask flushed with nitrogen, into which the sample is introduced. To this mixture, 20 mL of acetic acid solution is added while a vigorous flow of nitrogen gas is passed through the solution. The flow of nitrogen is then reduced to approximately one bubble per second and 2 mL of potassium iodide solution is added. The solution is thoroughly mixed and let to rest for 5 minutes.

After 5 minutes have passed, 100 mL of distilled water and 5 mL of starch solution is added. This solution is then titrated with sodium thiosulphate solution to colour change.

The peroxide number is calculated from the formula:

$$Peroxide\,number(mg/kg) = ((V_{Na_2S_2O_3} - V_{Blank}) * C_{Na_2S_2O_3} * 1000 * mEq)/m_{Sample} \quad (4)$$

where V is the volumes of sodium thiosulphate required for the sample and the blank titrations, C is the concentration of the thiosulphate solution, mEq is the milliequivalent which in this case is 8 and m is the mass of the sample.

Sodium Thiosulphate Solutions

The first solution is made of 12.58 g of $Na_2S_2O_3*5H_2O$ mixed in 500 mL of distilled water and 0.1 g of Na_2CO_3. The concentration is then determined with $K_2Cr_2O_7$ by titration.

The second solution is then made by diluting a sample from the first one 20 times with distilled water.

The choice of sodium thiosulphate solution used for the titrations depends on the expected peroxide number of the solution.

Potassium Dichromate Solutions

A solution is made from 2.46 g of $K_2Cr_2O_7$ diluted to 500 mL with distilled water. The second solution is made from 100 mL of the first diluted to 1000 mL with distilled water.

Starch Solution

A paste is made from 6.60 g Arrowroot and cold water; this is then added to 1000 mL of boiling water. 20.26 g of KOH is added to the solution which is then left to rest for 2 h. 6 mL of glacial acetic acid is then added and the pH of the solution is adjusted with hydrochloric acid (sp gr 1.19) to pH 4.0.

Potassium Iodide Solution

120.94 g of KI is solved in 100 mL of distilled water. The solution is covered with nitrogen gas.

Acetid acid solution 4 mL concentrated hydrochloric acid (sp. gr. 1.19) is diluted to 1000 mL with glacial acetic acid.

4.4 Water Content

This analysis is carried out using an automated Karl-Fischer titration apparatus. It contains a 756 KF Metrohm Coulometer and a 774 Oven Sampler Processor. The oven operates at 150°C or 110°C depending on the sample set. The flow of carrier gas is 90 mL/min nitrogen. The titration time for each sample is set to at least 900 seconds at 150°C or at least 1800 seconds at 110°C. The samples are weighed in with a margin of error of ± 0.005 mg.

5 Results and discussion

For B0 (pure MK1) all results were very close to the blank analysis values, they can therefore be considered zero.

5.1 B10 blends

In the ageings of B10 blends, the only setup which generates a significant amount of decomposition products is the 1.6h RME in an open system. As shown in figure 7, the stabilised fuels do not form enough acids to show any change during the ageing. The same trend can also be seen in the peroxide number and water content graphs (see appendix B and C).

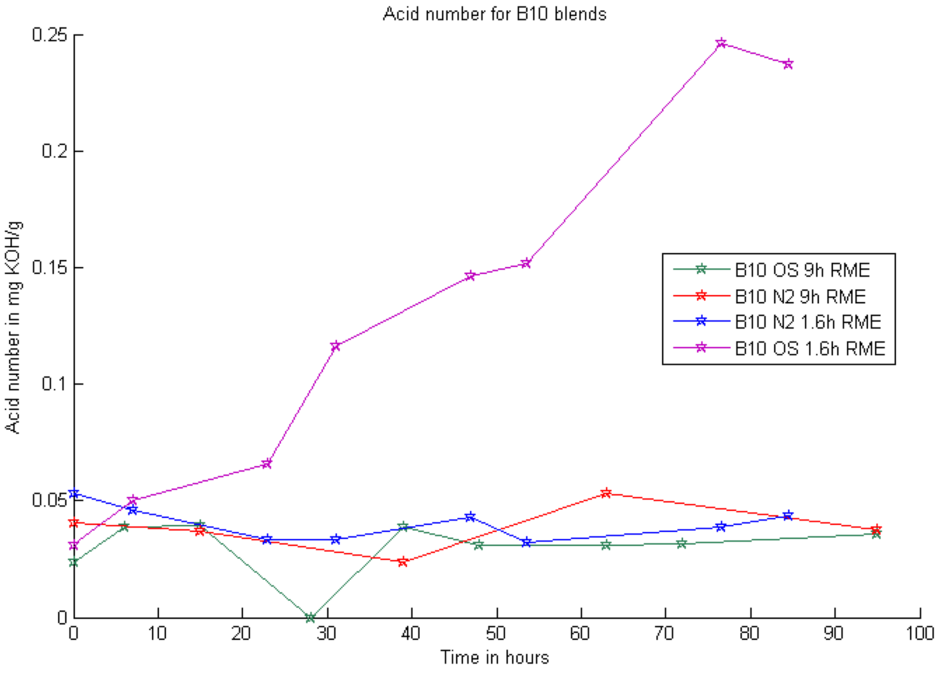


Figure 7: Acid number over time for B10 blends

These results show the importance of stabilisation of the biodiesel fuels. This stabilisation can be achieved either through the addition of antioxidants as in the 9h RME or by the removal of oxygen from the atmosphere as in the N_2 ageings. Without any of these preventive measures, oxidation will occur soon after the initiation of the ageing.

5.2 B30 blends

From figure 8 it is clear that the unstabilised B30 blend is much more readily oxidised than its stabilised counterpart. The peroxide number for the 1.6h RME increases from

200 to 1700 mg/kg while the 9h RME varies between 100 and 200 mg/kg. Similar behaviour is displayed in the acid number and water content figures (see appendix A and C).

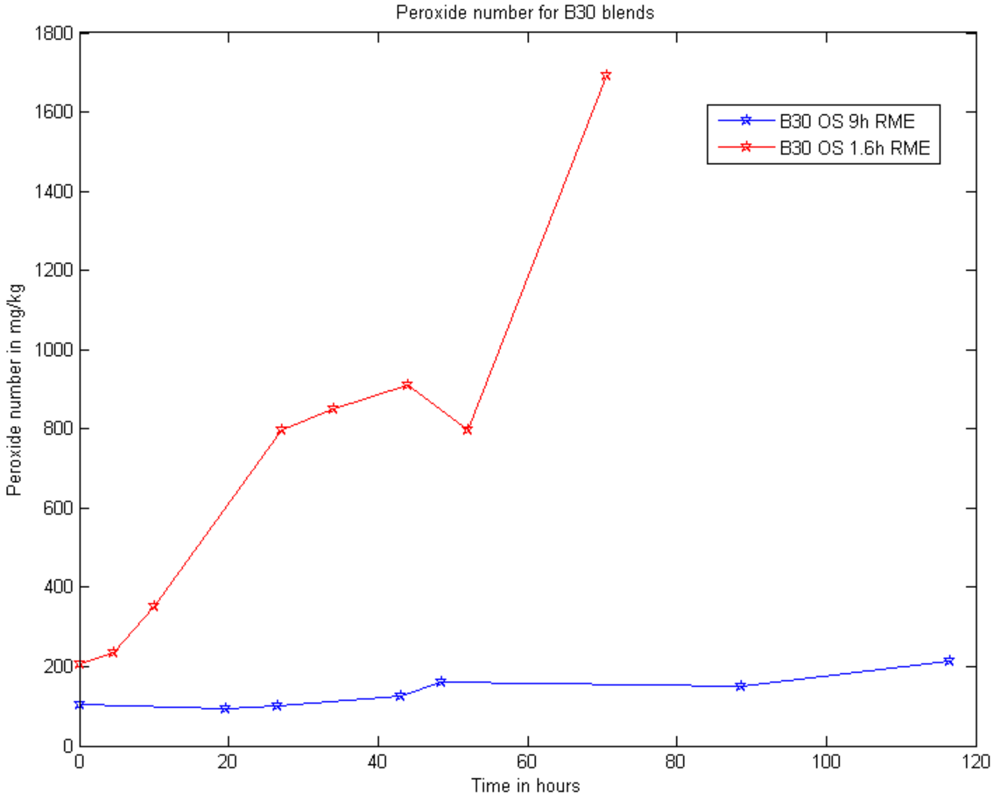


Figure 8: Peroxide number over time for B30 blends

The increase in decomposition products for B30 blends compared to B10 blends is much larger than the expected threefold increase from the concentration difference. This shows that an increase in biodiesel concentration does not always entail a proportional increase in decomposition products, i.e. the reactivity varies non-linearly with biodiesel proportions. This is important to consider when choosing biodiesel as fuel. When increasing biodiesel concentrations, it might sometimes be better to avoid the most reactive concentrations by making a larger increase.

5.3 B100 blends

In the same way as for B10 and B30 blends, biodiesel that either has an addition of antioxidants or is aged in nitrogen atmosphere is stable.

However, the 1.6h RME B100 blend in open system does not behave as could be expected from the earlier decomposition patterns. It has a constantly high peroxide

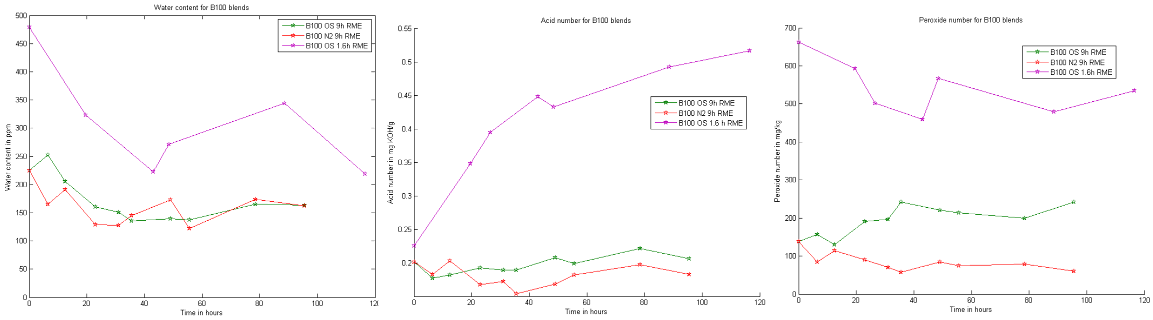


Figure 9: Water, Acid and Peroxide content for B100 blends

number, decreasing water content and a increasing acid number as can be seen in figure 9. There is no obvious explanation for this data, but during the project a theory has been developed.

This theory is based on the oxidation mechanism detailed in section 3.4. From the mechanism in figure 3 it is clear that water is only formed in the initiation step, together with a lipid radical. Since no new peroxides are formed, neither is any new water released. The slight decrease in water content can be due to evaporation from the diesel into the atmosphere caused by the elevated temperature. The acid content on the other hand can still increase due to the high peroxide concentration which catalyses the formation of acids.

5.4 Visual observations

During the ageing, several effects have been visually observable that are not measured. These will be displayed in this section.

5.4.1 Colour change

When ageing the biodiesel with the higher oxidative stability (9h) the green colour readily disappears from the ageing done in an open system as shown in figure 10. As explained earlier this colour change does not produce detectable amounts of decomposition products. As the change from an open system to nitrogen atmosphere stops this colour change, that shows how extremely effective limiting oxygen availability is for preventing oxidation.

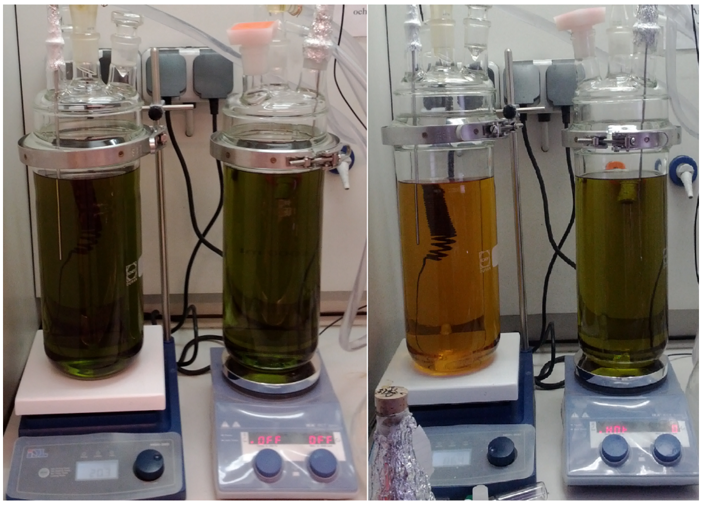


Figure 10: Colour change in 9 h B100 before and after 100 hours. From left to right: fresh B100 OS, fresh B100 N2, aged B100 OS, aged B100 N2.

5.4.2 Polymerisation

According to figure 3, the termination of the propagation step is formation of polymers. In the ageings of B10 and B30 blends in open systems with 1.6h RME polymers were formed as can be seen in figure 11. The picture was taken after brief washing and drying. The stains on the inside of the glass vessel are polymers coating the walls of the reaction vessel. The brown sludge at the bottom of the vessel is also polymerised biodiesel.

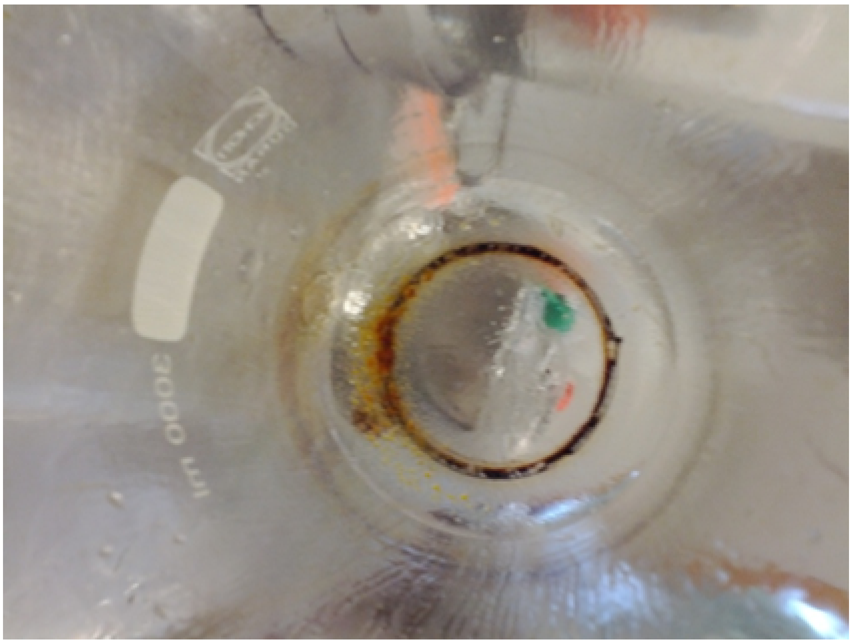


Figure 11: Polymerisation in ageing of B10 in open system with 1.6h RME

6 Conclusion

From the results it is clear that stabilising biodiesel is very important. This can be done both by reduction of the availability of atmospheric oxygen or addition of antioxidants to the biodiesel. Stabilising the diesel prevents peroxide formation which prevents any further oxidation and formation of polymers.

Some blends of biodiesel are more easily oxidised than a linear relationship between reactivity and biodiesel concentration would predict. The B10 and B30 blends showed the greatest percentage increase in decomposition products and were also the only blends to polymerise. The aged B10 did produce enough decomposition products to rival the starting levels of the B100 blend after the full 100 hours of ageing. This occurs even though the B100 has a tenfold concentration of biodiesel content compared to the B10 blend. This indicates that when an increase in biodiesel content in fuel is desired, it is preferred to make a larger increase in concentration to avoid using the most reactive blends, such as B30. To determine which blends are most reactive and at what concentration the reactivity decreases, more studies on the subject are needed.

Polymerisation only occurred in the B10 and B30 blends, this is presumed to be caused by some kind of influence or interaction with the fossil diesel. This polymerisation may lead to clogging of filters and injectors. As polymerisation is such a strongly undesirable characteristic, polymerisation must be avoided when using biodiesel as a fuel.

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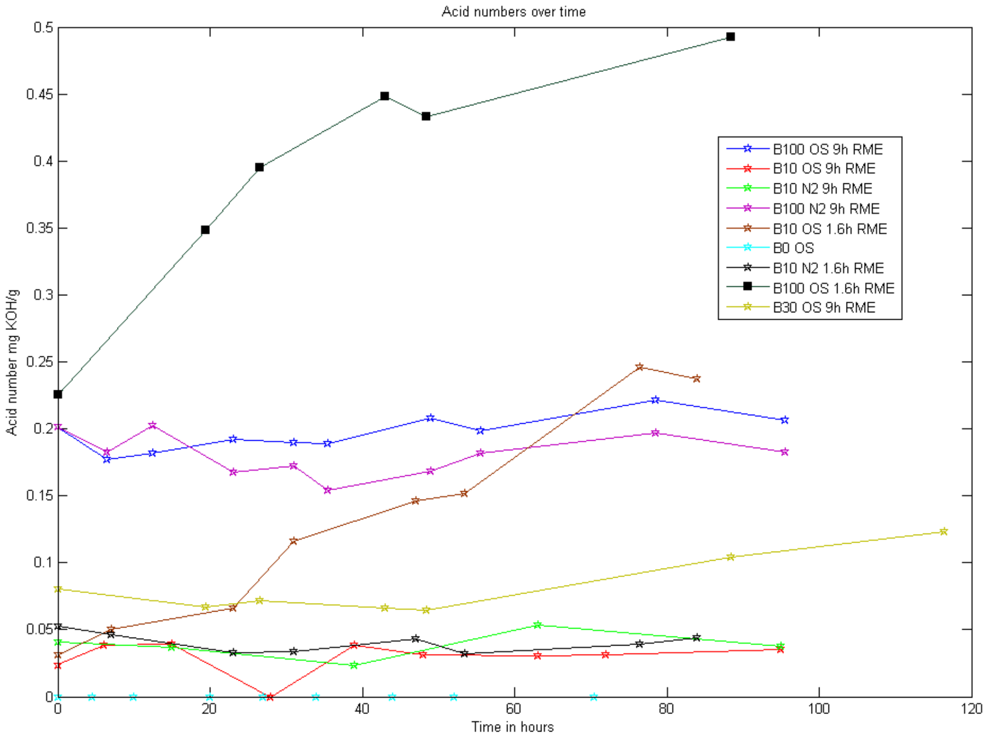
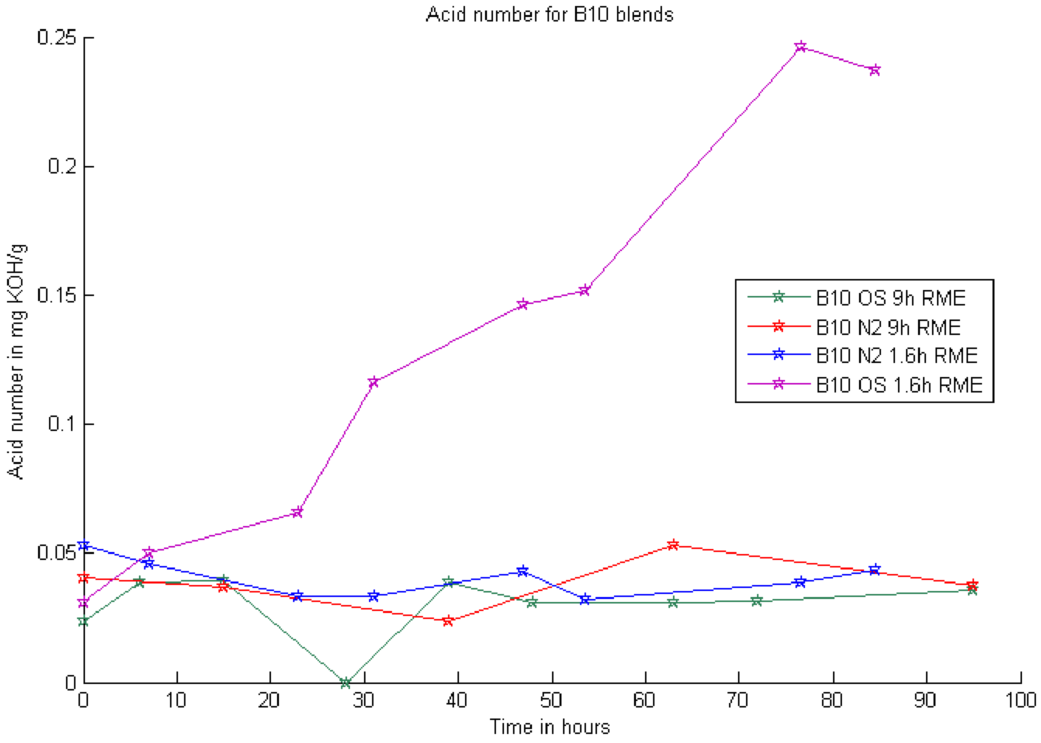
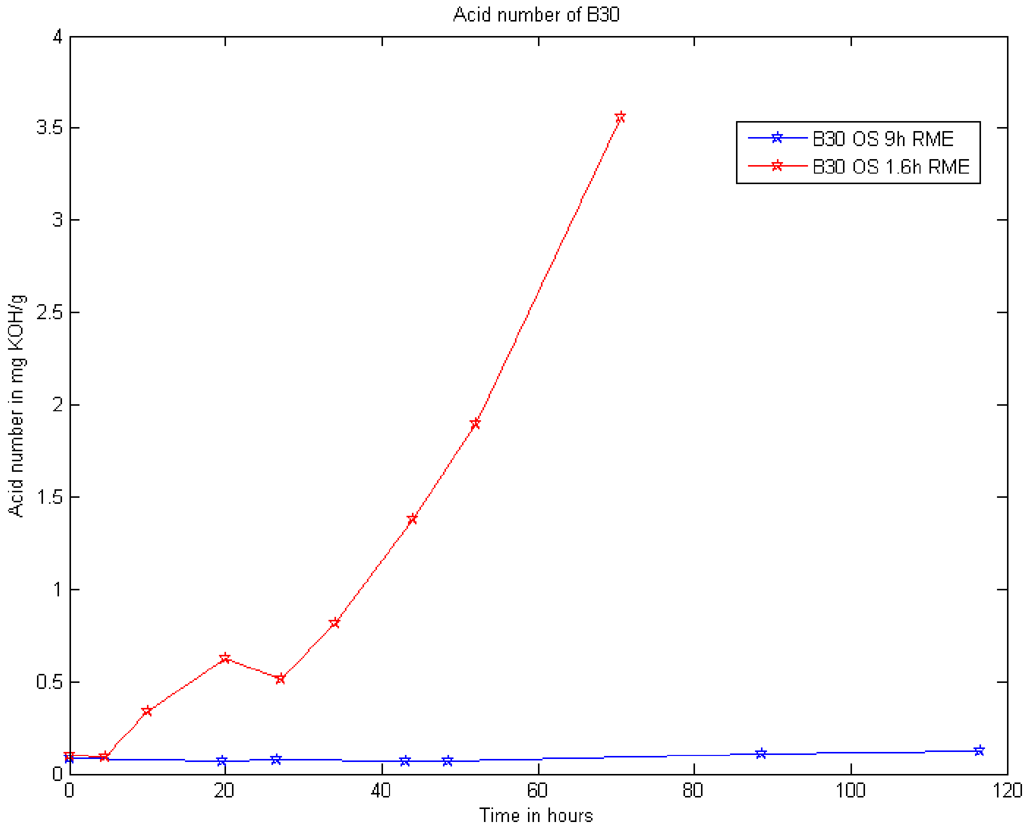
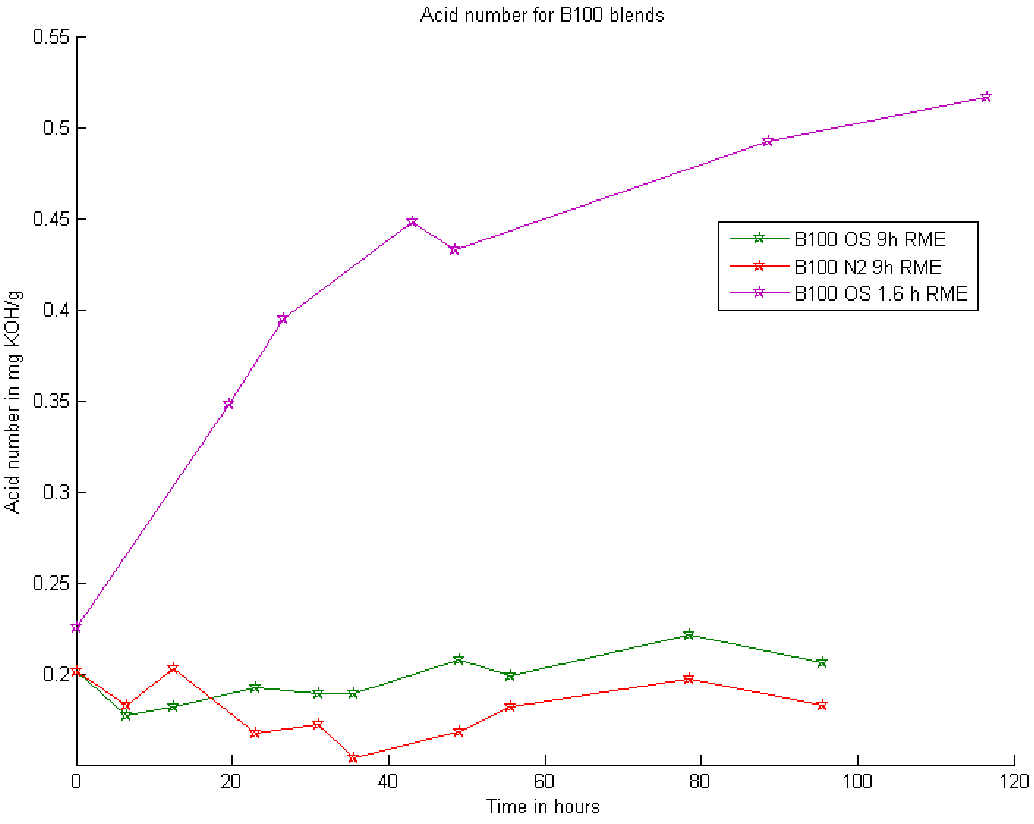
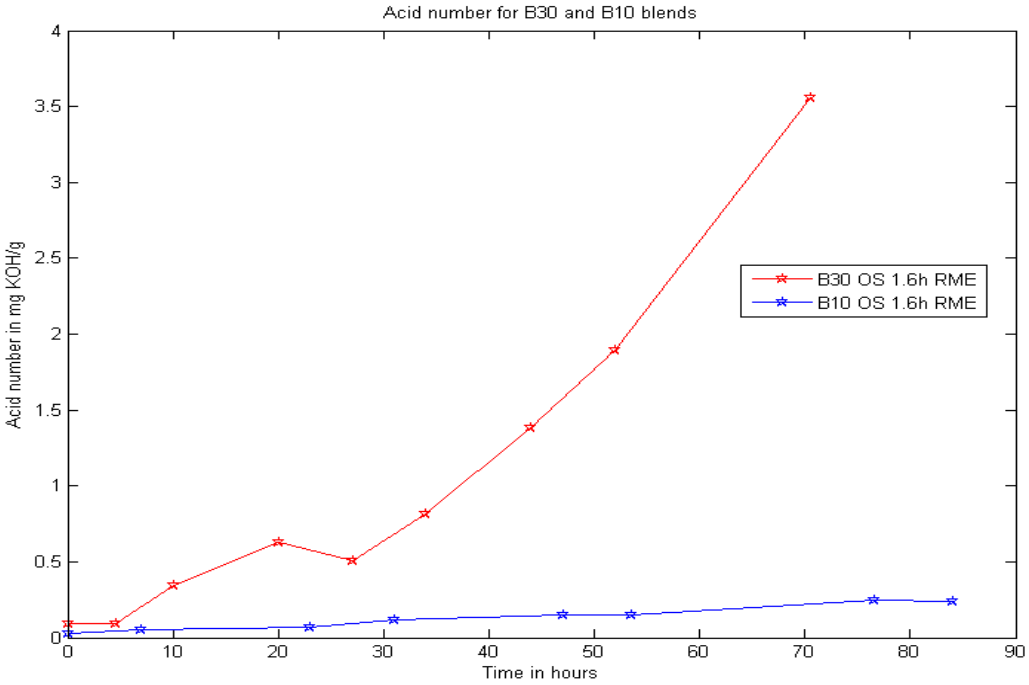
A Acid number graphs


Acid numbers over time
Acid number mg KOH/g
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0
20
40
60
80
100
120
Time in hours
B100 OS 9h RME
B10 OS 9h RME
B10 N2 9h RME
B100 N2 9h RME
B10 OS 1.6h RME
B0 OS
B10 N2 1.6h RME
B100 OS 1.6h RME
B30 OS 9h RME

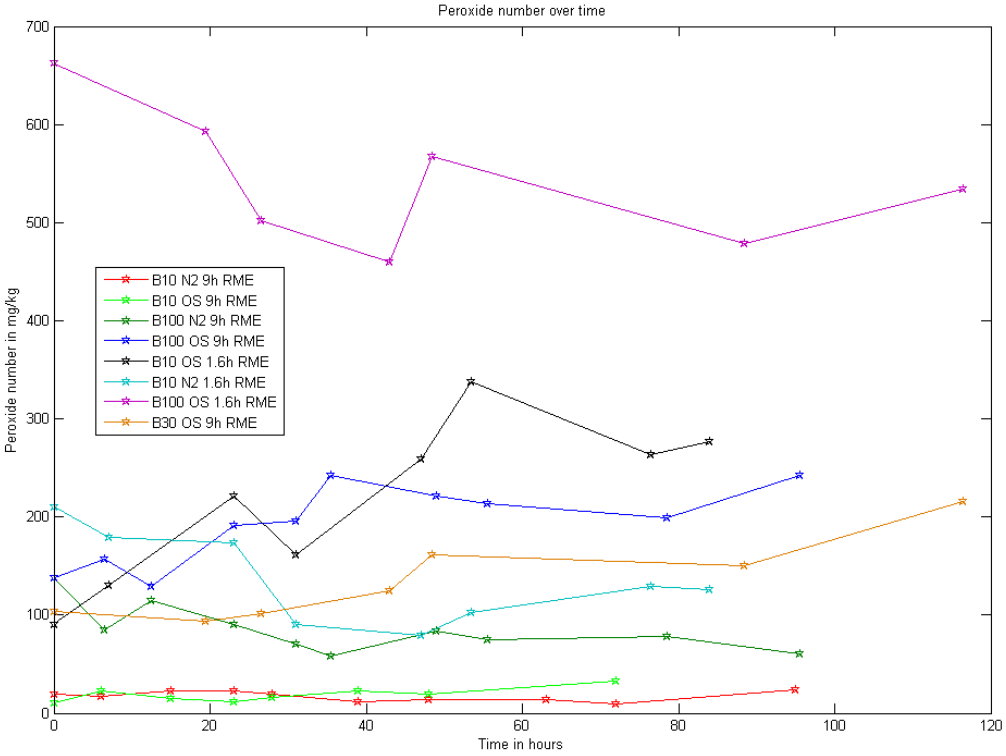

Acid number for B10 blends
Acid number in mg KOH/g
0
0.05
0.1
0.15
0.2
0.25
0
10
20
30
40
50
60
70
80
90
100
Time in hours
B10 OS 9h RME
B10 N2 9h RME
B10 N2 1.6h RME
B10 OS 1.6h RME

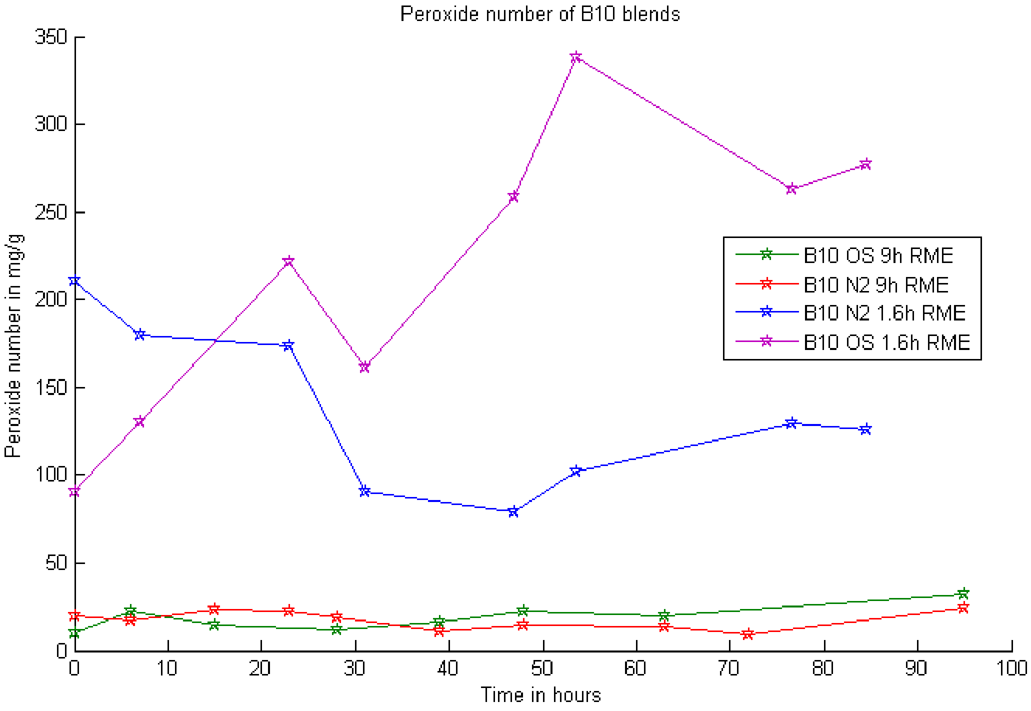

Acid number of B30
Acid number in mg KOH/g
Time in hours
B30 OS 9h RME
B30 OS 1.6h RME
0
0.5
1
1.5
2
2.5
3
3.5
4
0
20
40
60
80
100
120


Acid number for B100 blends
Acid number in mg KOH/g
Time in hours
B100 OS 9h RME
B100 N2 9h RME
B100 OS 1.6 h RME
0.2
0.25
0.3
0.35
0.4
0.45
0.5
0.55
0
20
40
60
80
100
120


Acid number for B30 and B10 blends
Acid number in mg KOH/g
Time in hours
B30 OS 1.6h RME
B10 OS 1.6h RME
0
0.5
1
1.5
2
2.5
3
3.5
4
0
10
20
30
40
50
60
70
80
90

B Peroxide number graphs


Peroxide number over time
Peroxide number in mg/kg
Time in hours
700
600
500
400
300
200
100
0
0
20
40
60
80
100
120
B10 N2 9h RME
B10 OS 9h RME
B100 N2 9h RME
B100 OS 9h RME
B10 OS 1.6h RME
B10 N2 1.6h RME
B100 OS 1.6h RME
B30 OS 9h RME


Peroxide number of B10 blends
Peroxide number in mg/g
Time in hours
350
300
250
200
150
100
50
0
0
10
20
30
40
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60
70
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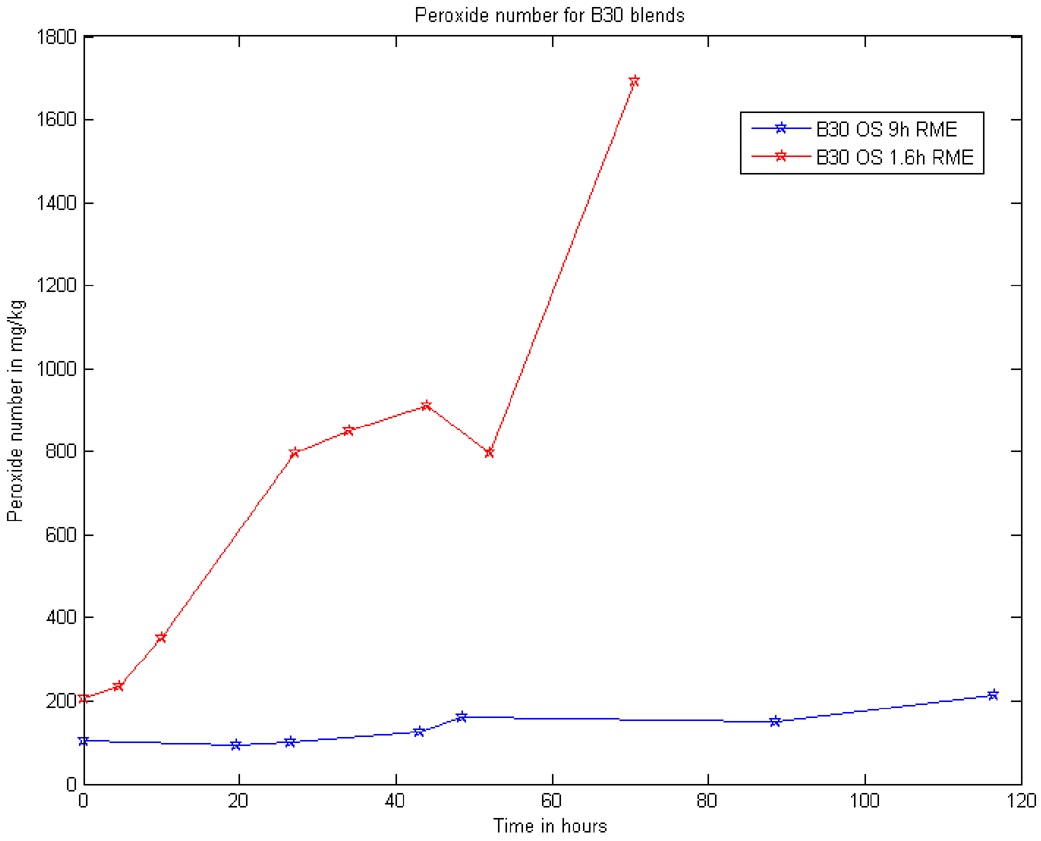
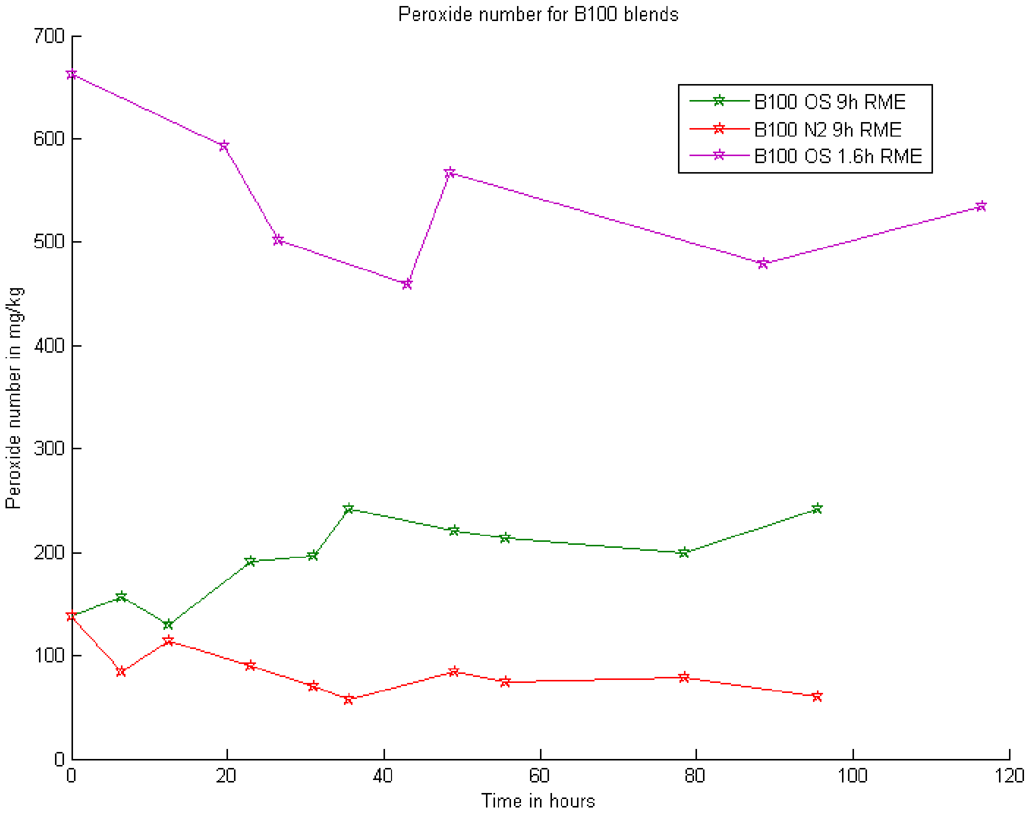
90
100
B10 OS 9h RME
B10 N2 9h RME
B10 N2 1.6h RME
B10 OS 1.6h RME


Peroxide number for B30 blends
Peroxide number in mg/kg
Time in hours
B30 OS 9h RME
B30 OS 1.6h RME
0
200
400
600
800
1000
1200
1400
1600
1800
0
20
40
60
80
100
120


Peroxide number for B100 blends
Peroxide number in mg/kg
Time in hours
B100 OS 9h RME
B100 N2 9h RME
B100 OS 1.6h RME
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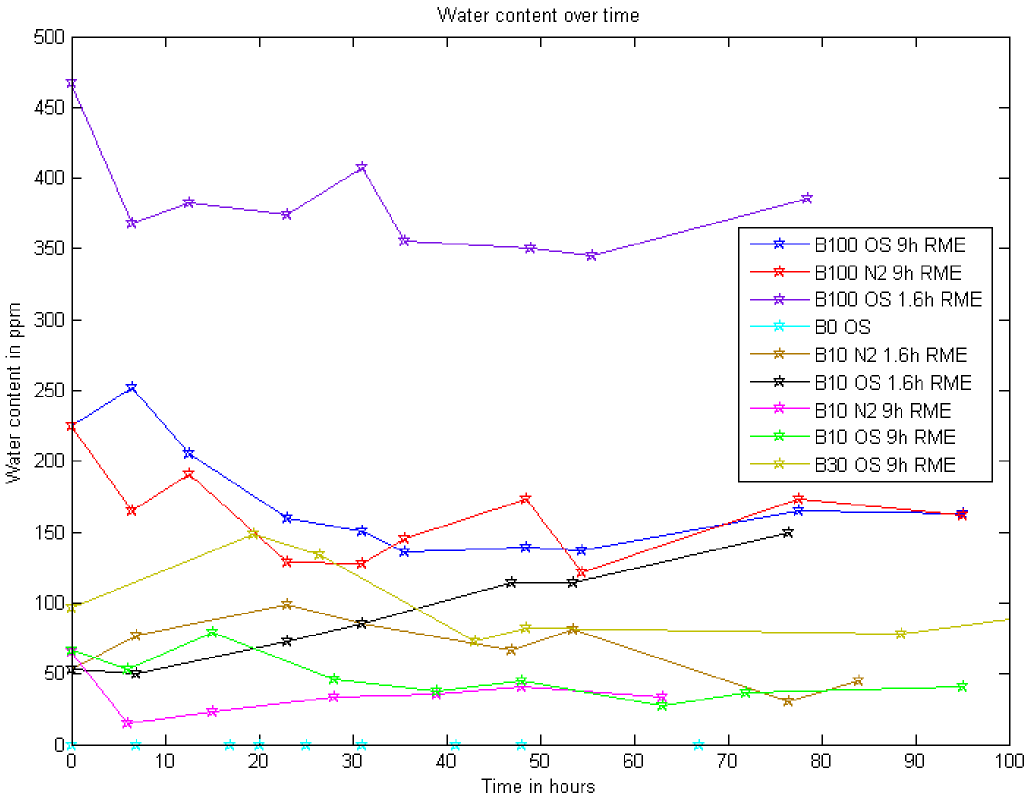
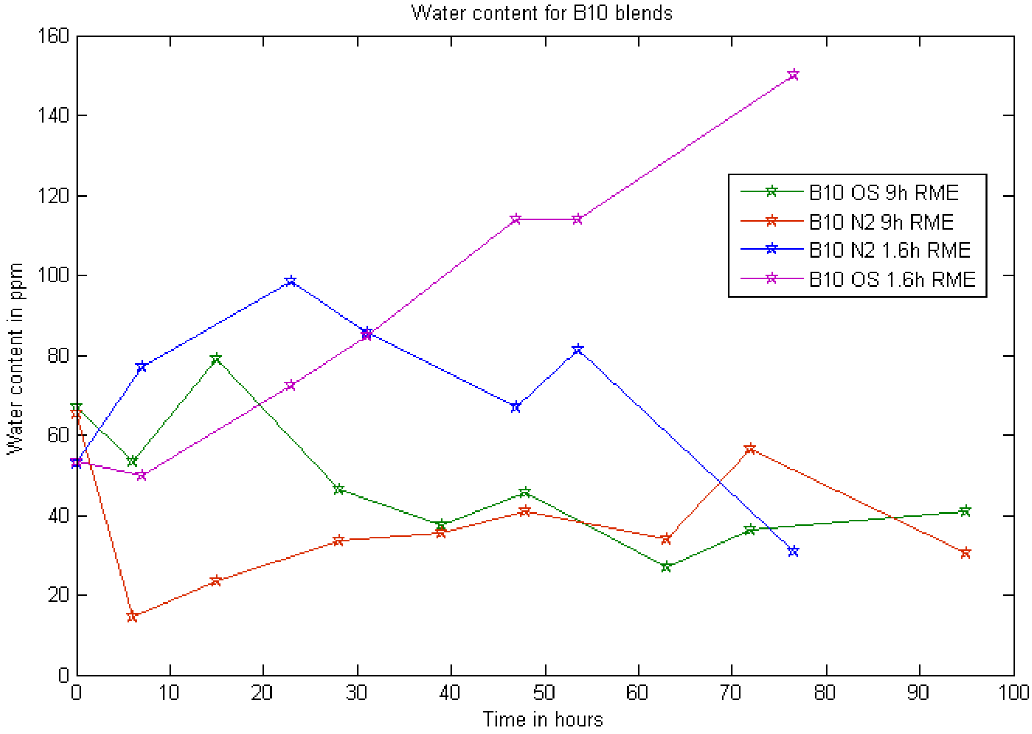
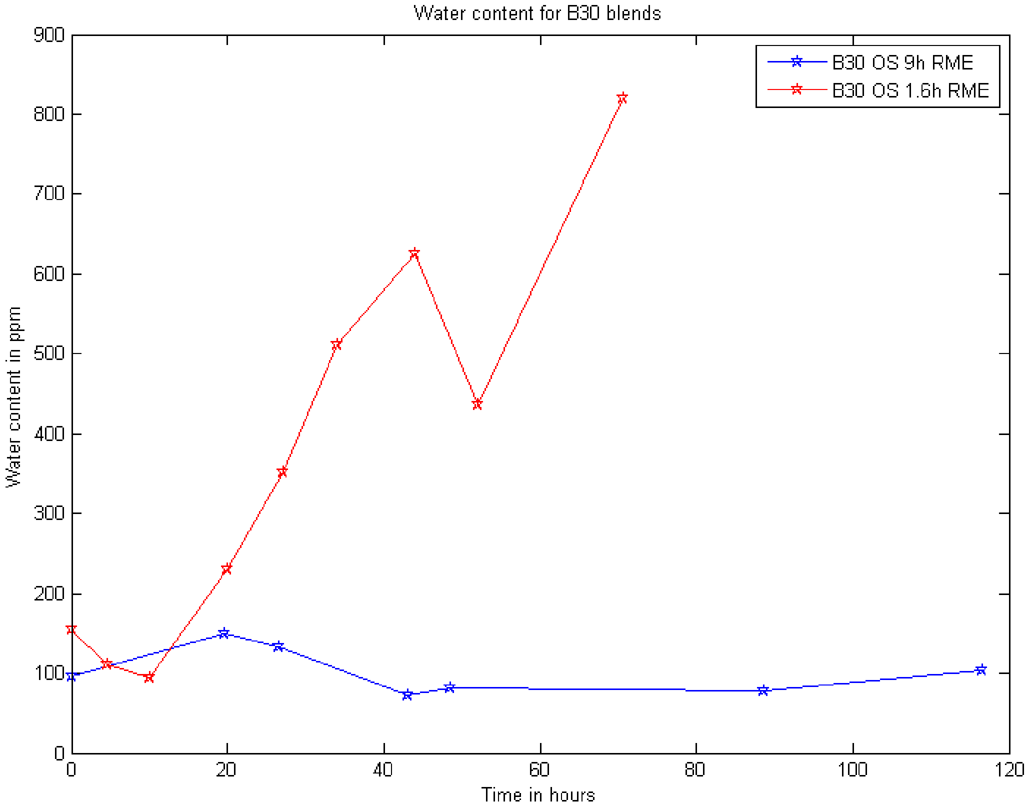
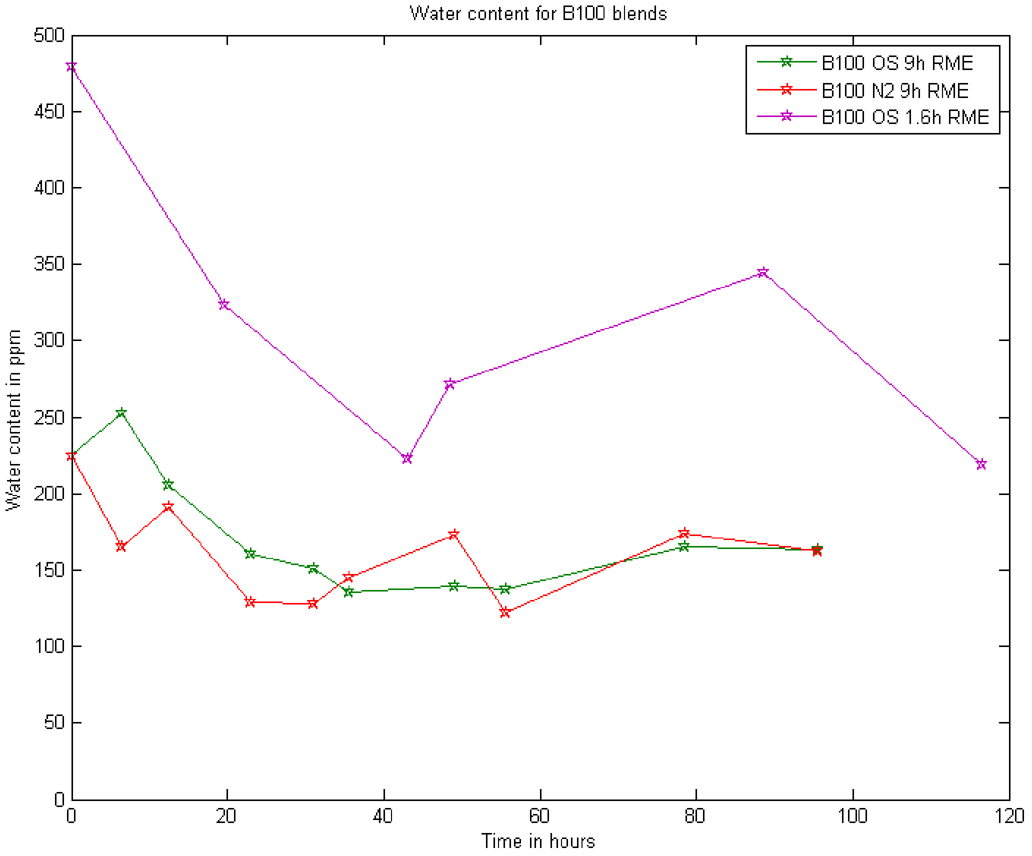
100
200
300
400
500
600
700
0
20
40
60
80
100
120

C Water content graphs


Water content over time
Water content in ppm
Time in hours
0
50
100
150
200
250
300
350
400
450
500
0
10
20
30
40
50
60
70
80
90
100
B100 OS 9h RME
B100 N2 9h RME
B100 OS 1.6h RME
B0 OS
B10 N2 1.6h RME
B10 OS 1.6h RME
B10 N2 9h RME
B10 OS 9h RME
B30 OS 9h RME


Water content for B10 blends
Water content in ppm
Time in hours
0
20
40
60
80
100
120
140
160
0
10
20
30
40
50
60
70
80
90
100
B10 OS 9h RME
B10 N2 9h RME
B10 N2 1.6h RME
B10 OS 1.6h RME


Water content for B30 blends
B30 OS 9h RME
B30 OS 1.6h RME
Water content in ppm
0
100
200
300
400
500
600
700
800
900
Time in hours
0
20
40
60
80
100
120


Water content for B100 blends
B100 OS 9h RME
B100 N2 9h RME
B100 OS 1.6h RME
Water content in ppm
0
50
100
150
200
250
300
350
400
450
500
Time in hours
0
20
40
60
80
100
120

D Terminology

B0 B10 B30 et c - Blends of biodiesel containing 0% 10% 30% biodiesel mixed with fossil diesel

BHT - Butylated hydroxytoluene, an antioxidant

MK1 - ”Miljöklass 1” Swedish standard for fossil diesel

RME - Rapeseed methyl ester, a type of biodiesel

Stabilised diesel - Biodiesel that does not oxidise due to added antioxidants or nitrogen atmosphere

TBHQ - Tert-butylhydroquinone, an antioxidant

E Reaction vessels

Figure 12: 3 l reactor vessel

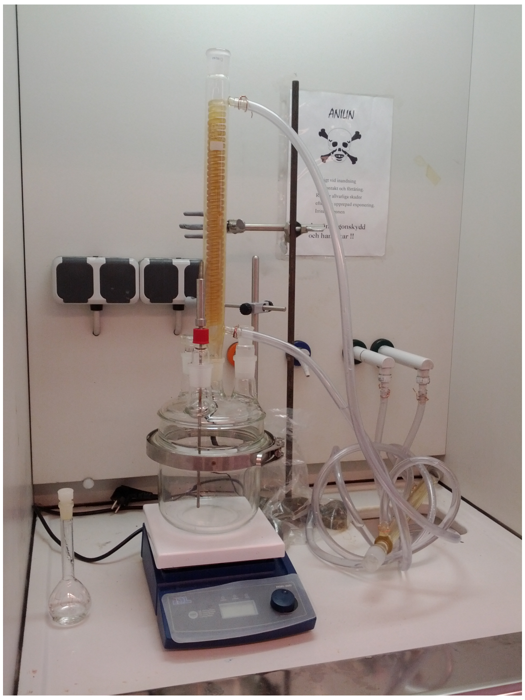


Figure 13: 1 l reactor vessel

F Specifications

F.1 9h stable RME, IBC 120320 FAME

PREEM AB
Certificate of Quality

Product Code:	**FAME-SE**	Vessel:	
Nomination number:	**IBC.120320.FAME**	Destination:	
Lineblend:		Account:	
Tank:	**IBC**	Delivery Date:	**2012-03-20**
Revised Issue:		Sample Number:	**2012008082**

FATTY ACID METHYL ESTERS (FAME)

Properties	Results	Units	Ref. Test Methods
Acid value	0,14	mg KOH/g	EN 14104:2004
Carbon residue (on 10% dist res)	< 0,10	% m/m	EN ISO 10370:1995
Cetane number	52,3		EN ISO 5165:1998
Cloud point	-7	°C	EN 23015:1994
Cold Filter Plugging Point	-22	°C	EN 116:1997/AC:1999
Cu strip corrosion (3h at 50°C)	1A		EN ISO 2160:1998
Density at 15°C	882,0	kg/m3	EN ISO 12185:96/C1:01
Diglyceride content	< 0,01	% m/m	EN 14105:2003
Ester content	99,6	% m/m	EN 14103:2004
Flash point	> 120,0	°C	EN ISO 3679:2004
Free glycerol	0,01	% m/m	EN 14105:2003
Group 1 metals (Na + K)	< 2,0	mg/kg	EN 14538:2006
Group 2 metals (Ca + Mg)	< 2,0	mg/kg	EN 14538:2006
Iodine value	111	g I/100g	EN 14111:2003
Linolenic acid methyl ester	9	% m/m	EN 14103:2004
Methanol content	0,11	% m/m	EN 14110:2004
Monoglyceride content	0,30	% m/m	EN 14105:2003
Oxidation stability at 110°C	9,0	hours	EN 15751:2009
Phosphorus content	< 1,0	mg/kg	EN 14107:2007
Polyunsaturated methyl esters	< 1,00	% m/m	--
Sulfated ash content	< 0,020	% m/m	ISO 3987:2004
Sulphur content	4	mg/kg	EN ISO 20884:2004
Total contamination	3	mg/kg	EN 12662:2008
Total glycerol	0,08	% m/m	EN 14105:2003
Triglyceride content	< 0,01	% m/m	EN 14105:2003
Use of CFPP additive - treat rate	2000	µl/l	Calculated
Water content	75	mg/kg	EN ISO 12937:2000
Viscosity at 40°C	4,421	mm2/s	EN ISO 3104:96/AC:99

Results according to ISO 4259

This product meets the quality requirements according to customer's nomination.

Work by: Dolores Martinez
Chemist in Charge:

Telephone: +46 (0)10 450 41 85
Fax: +46 (0)10 450 41 86

For Preemraff Göteborg: Dolores Martinez

F.2 1.6h stable RME

IIS
Independent Inspection Services

The exclusive agent in Sweden for Intertek Caleb Brett

Client: **SEPV, Volvo Car Corporation**

ANALYTICAL REPORT

Report No: **96652**
Order No: 310845
Sample Identity: B100 RME-oxstab
Sample Received Date: 2012.03.07 from Client
Sample Volume: 1 x 1 litre
Sample Container: Brown Glass Bottle

Test	**Unit**	**Test Method**	**Result**
Oxidation Stability 110°C	hours	EN 15751	1,6

Independent Inspection Services AB
Gothenburg, 2012.03.19

Andreas Öien

F.3 MK1 diesel

PREEM AB
Certificate of Quality

Product Code: **DMK1UA-SE**
Nomination number: **IBC.120224.DMK1UA**

Tank: **IBC**

Delivery Date: **120227**
Sample Number: **2012005598**

DMK1UA-SE

Properties	Results	Units	Ref. Test Methods
Appearance at 20°C	1	rating	ASTM D 4176-04
Appearance at 20°C	BRIGHT AND CLEAR		Visual inspection
Aromatic content	4,8	% V/V	SS 15 51 16:1993
Ash content	< 0,010	% m/m	SS-EN ISO 6245:2003
Carbon residue (on 10% dist res)	< 0,20	% m/m	SS-EN ISO 10370:1996
Cetane index	54,6	-	SS-EN ISO 4264:2007
Cetane number	56,0		SS-EN ISO 5165:1998
Cloud point	< -22	°C	SS-EN 23015:1994
Cold Filter Plugging Point	-35	°C	SS-EN 116:1999
Colour (ASTM scale)	< 0,5		SS-ISO 2049:1997
Conductivity	615	pS/m	SS-ISO 6297:1998
Cu strip corrosion (3h at 50°C)	1A		SS-EN ISO 2160:1998
Density at 15°C	808,6	kg/m3	SS-EN ISO 12185 T1:99
Dist: IBP	183,2	°C	SS-EN ISO 3405:2000
Dist: Temp. at 65% V/V evap.	241,3	°C	SS-EN ISO 3405:2000
Dist: Temp. at 95% V/V rec.	278,7	°C	SS-EN ISO 3405:2000
FAME content	NOT ADDED		SS-EN 14078:2009
Flash point	71,0	°C	SS-EN ISO 2719:2003
Lubricity additive	NOT ADDED		--
Oxidation stability	< 25	g/m3	SS-EN ISO 12205:1996
PAH content	< 0,02	% V/V	SS 15 55 16:1993
Sulphur content	< 1	mg/kg	SS-EN ISO 20884:2004
Total contamination	< 24	mg/kg	SS-EN 12662:2008
Water content	< 30	mg/kg	SS-EN ISO 12937:2001
Viscosity at 40°C	2,000	mm2/s	SS-EN ISO 3104/AC:99

Results according to ISO 4259

This product meets the quality requirements according to customer's nomination.

Work by: Carina Zell
Chemist in Charge:

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For Preemraff Göteborg: ………………………………….

F.4 Environmental classifications, fossil diesel

Miljöklasser för dieselbränsle från 1.5.2011

Egenskaper	Enhet	Utdrag ur Lagkrav enligt §§ 8-9, drivmedelslag, SFS 2011:319		
		Miljöklass 1	Miljöklass 2	Miljöklass 3
Cetanindex, min		50	47	-
Cetantal, min		51,0[a]	51,0[a]	51,0
Densitet vid 15°C, min	kg/m^3	800,0	800,0	-
Densitet vid 15°C, max	kg/m^3	830,0	830,0	845,0
Destillation				
- begynnelsekokpunkt, min	°C	180	180	-
- vid 95% destillat, max	°C	340,0	340,0	360,0
Aromatiska kolväten, max	vol-%	5	20	-
Polycykliska aromatiska kolväten, max	vol-%	Inte mätbar[b]	0,1[b]	-
Polycykliska aromatiska kolväten, max	vikt-%	-	-	8,0[c]
Svavel, max	mg/kg	10,0	10,0	10,0
Fettsyrametylestrar[d] max	vol-%	7,0	7,0	7,0
Ytterligare krav finns enligt Svensk Standard		SS 15 54 35 under uppdatering	SS 15 54 35 under uppdatering	SS-EN 590:2009 Utgåva 5

[a] Gäller dieselbrännoljor som omfattas av nr 2710 19 41 o Kombinerade nomenklaturen (KN-nr) enligt förordningen (EEG) 2658/87

[b] Enligt Svensk Standard SS 155116, utgåva 1 eller motsvarande, före inblandning av fettsyrametylestrar.

[c] Enligt SS-EN 12916, utgåva 2

[d] Fettsyrametylestrarna skall uppfylla kraven i Svensk Standard SS-EN 14214, utgåva 2 eller motsvarande