

1 Introduction

The environmental pollution that arises in connection with increasing mobility must be reduced.^[1] In order to achieve set climate targets, a holistic approach must be pursued that includes not only electromobility but also renewable fuels.^[2] As so-called drop-in fuels, regenerative fuels can be used with the existing infrastructure, and cars that are already on the market can thus be operated in a more environmentally friendly way.^[3] However, increasing the regenerative share of fuel is only part of the reduction in emissions.^[4] Since the design of the internal combustion engine is always a compromise between stable operation, low emissions and high efficiency, the importance of the three parameters must be determined during development (Figure 1). For example, high operational reliability and high efficiency play a decisive role in aircraft engines. This is where the fuel plays a crucial role, as the influence of the fuel on the combustion can minimise emissions.^[5] Sensors for recognising the fuel composition in automobiles are useful in order to reduce emissions in the best possible way.^[6]

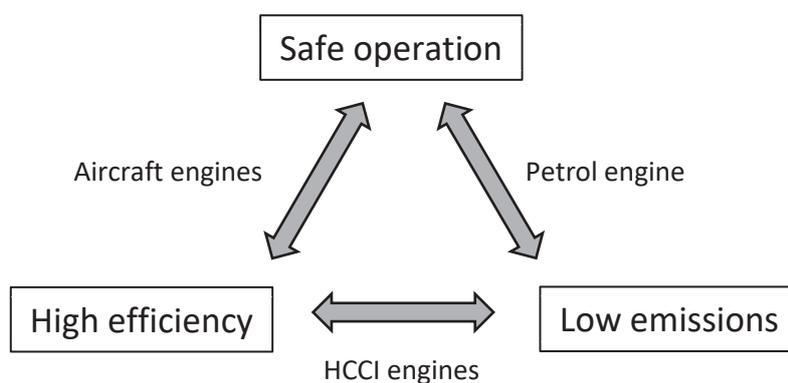


Figure 1: Compromise in engine combustion design.

By recognising the fuel composition and the degree of ageing or oxidation, the engine control device can be set specifically to the fuel present. A sensory fuel detection can also be used to detect regenerative fuels. Because the emissions of the combustion engine are mainly caused by the operation of the automobile (only a small part of the emissions are generated by production), a contribution can be made through regenerative fuel.^[7] In combination with tax relief for regenerative fuels, an effective control mechanism can be implemented in the car that documents the use of regenerative fuels. In order to replace fossil fuels in the future, different raw material sources can be used to produce synthetic fuels.^[8] This results in fuels that can differ greatly in their chemical composition.^{[9][33][10]} For optimal combustion, the fuel components or the fuel composition must be recognised in the future so that the engine management can be optimally adjusted. Subsidised electromobility is also increasingly influencing electrification in the form of plug-in hybrids. In plug-in hybrids, the advantages of both technologies (electric drive and combustion engine) are combined: This means that local emission-free driving and a long range can be guaranteed.^[11] The short driving cycles in everyday life make it possible to charge the accumulator in a stationary manner from the mains. The short driving cycles mean that the fuel in plug-in hybrid vehicles is exposed to far more critical conditions than before. The fuel remains in the tank for longer, which can lead to changes in the physical and chemical properties of the fuel. Accordingly, the detection of the degree of ageing is an important property for a fuel sensor system.

The first part of the research project presented here discusses a detailed investigation of the ageing of rapeseed oil methyl ester (RME). For the increased use of biodiesel in the future, also in connection with new regenerative fuels, understanding ageing is an important aspect in order to be able to ensure stable fuel formulations. As a result, the ageing of biodiesel in its pure form must be understood and



since fuel ageing is not the same for all fuels, the ageing in biodiesel blends must also be examined. For RME ageing, the investigations presented below aim to answer the following questions:

- What products are produced by fuel ageing?
- What is the mechanism behind the creation of the products?
- What is the development of the individual products over time like?
- Influence of the fuel matrix on ageing behaviour?

The answer to these questions is based on the investigation of fuel ageing with high-resolution mass spectrometry, which describes the different stages of oxidation that increases over the ageing process. By identifying the structures of ageing products, new insights into the ageing behaviour are presented in the area of the oligomerisation of RME. The second part presents the developed sensor system for recognising the fuel composition and the degree of ageing. In the following, the theoretical basics, the fuels used, the measuring methods and the procedure for evaluating high-resolution mass spectra for the structure identification of the ageing products are presented initially. After that, the results obtained in the course of this research project will then be discussed.

2 Theory – State of Research

The fuel ageing of RME or fatty acid methyl esters in general has already been discussed many times in literature. ^[12,13,14,15] The following section summarises the most important principles of autoxidation. Three mechanisms from literature are used for the discussion of the results, which are presented below in their original interpretation.

2.1 Autoxidation

Autoxidation is the process of a chemical compound being slowly oxidised by oxygen from the air. This process takes place autocatalytically and, among other things, leads to the formation of hydroperoxides. Some examples of autoxidation reactions are the formation of acetic acid from alcohols, the fading of colours, fats turning rancid and in everyday life the browning of cut apples. ^[16]

The process of autoxidation can be divided into three phases. The first phase is called the start reaction, in which homolytic bond splitting is initiated. If radicals have formed in the initial reaction, chain propagation describes the further reaction with renewed formation of a radical. Chain termination occurs when two radicals form stable products with one another. ^[17] In autoxidation, hydroperoxides (ROOH) are of particular importance. Hydroperoxides are formed during chain propagation (equations 4 and 5) and are also starting compounds for the start reaction (equation 2). The great influence of the hydroperoxides results from the branching of the reaction process, since two radicals are formed from one hydroperoxide (equation 2). This process is known as chain branching. ^[18]

Start reaction:



Chain propagation:



Chain termination:



2.2 Thermal oxidative ageing

The autoxidation depends on the temperature.^[19] The ageing of substances is thus an interplay of radical stability and temperature. According to the Arrhenius equations, the logarithm of the reaction rate constant (k) is subject to a linear dependence on the reciprocal absolute temperature.

$$\ln k = \ln A - \frac{E_a}{RT} \quad (9)$$

In the equation, R represents the universal gas constant, E_a the activation energy, T the temperature in Kelvin and A an empirical constant that includes various probability parameters and oscillation constants of molecules.^[20] Fuel ageing occurs faster as the temperature increases, which is why the investigations on fuel ageing must always be considered in relation to the selected ageing temperature.^[19]

2.3 Radical stability

The formation of the ageing products depends largely on the stabilisation of the radicals involved. The more stable a radical is, the more easily it is formed and the easier the oxidation of the compounds that can form these radicals.^[21] The stability is determined by mesomerism (delocalisation), substituent effects (hyperconjugation), steric effects and the reactivity of the radical centre affects and results in a lower bond dissociation energy. In addition, the solvent has an influence on the stabilisation of the educts formed as well as products (dimers) or can itself react with the radical. Figure 2 shows the increasing stability of selected organic radicals. The stability increases from primary to secondary to tertiary alkyl radicals. The cause is the hyperconjugation of the binding electrons of the C–H bond into the half-occupied p-orbital on the sp^2 hybridised carbon (Figure 2) due to the methyl group. Aryl and benzyl radicals have a significantly higher stability due to mesomerism (Figure 3).^[22]

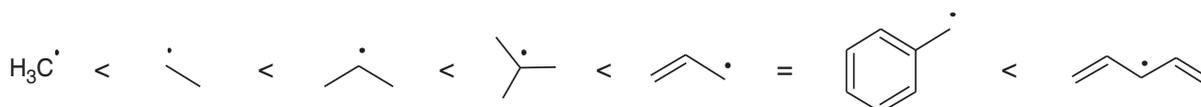


Figure 2: Radical stability. ^{[23][24][25]}

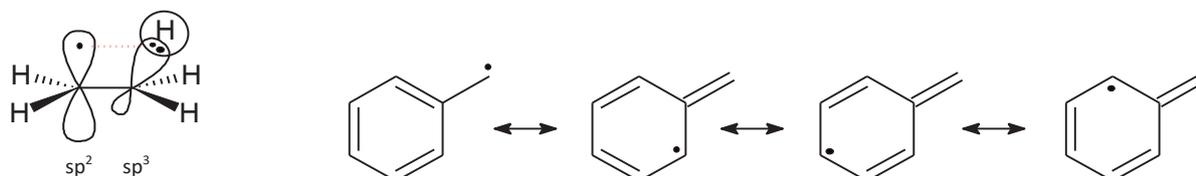


Figure 3: Hyperconjugation and resonance stabilisation. ^{[26][27]}



2.4 Reaction mechanisms used for explanation from the literature

The aspects described in Sections 2.1 to 2.3 represent the generally accepted general mechanism of the autoxidation of fatty acid methyl esters.^[29] The autoxidation is based on the spontaneous formation of radicals (initiation) and a subsequent reaction with molecular oxygen in which up to two radicals are formed from one radical (chain branching). However, these generally formulated reactions can be further differentiated and discussed. The general influences of autoxidation and radical stabilities must be extended to the structure of the fuel molecules for a detailed consideration of fuel ageing, since the structure influences the mesomeric stabilisation of radicals and these in turn influence the oxidation and the formation of ageing products. The core aspect of autoxidation is represented by the peroxides formed by the reaction of radicals and molecular oxygen.^[29] Starting from these peroxides, a number of different functional groups can be observed that are formed in secondary reactions. In addition, the greater the number of double bonds, the greater the diversity of the compounds that are formed. However, this does not affect the variety of functional groups that form. The investigation of FAME ageing is such a complex project that there are currently no studies that consider ageing in its entirety. Research on the mechanisms is often based on a selective consideration of individual steps, such as the formation of different peroxides and the reaction mechanisms derived from them.^[29] Thus, through targeted synthesis of individual products, the evaluation leads to an interpretation limited to this reaction. However, if the ageing is examined as a whole, a further interpretation of the subsequent reactions must be carried out using the selective interpretation. Products such as hydroperoxides do not represent completely stable products with the low dissociation energy of the oxygen-oxygen bond.^[28] Although they can be detected, the thermodynamically more stable products are of greater importance for the investigation of overall ageing or for ageing after defined time intervals. For the interpretation of these thermodynamically more stable products, however, the studies of intermediates and their reaction mechanisms are an indispensable contribution to understanding the products observed. Three reactions that are important for a deeper understanding of ageing and that are used below for the discussion of results are described in more detail below.

The first reaction mechanism relevant to the results section of this report relates to the mechanism of the radical reaction with molecular oxygen and the various subsequent reactions that follow the initial reaction with molecular oxygen (Figure 4). Figure 4 shows the hydrogen abstraction in the α -position of the double bond of C18:1 ME, as described in literature.^[29] The allyl radical formed in the first step reacts with molecular oxygen to form a peroxide radical in the second step. The reaction with RH with the release of a radical leads to hydroperoxides. Hydroperoxides, in turn, can break down into hydroxyl radicals and alkoxy radicals. Several reactions are possible starting from alkoxy radicals. By reacting RH with renewed release of a radical, alcohols can be formed, which can be further oxidised to ketones under the oxidative conditions. Alternatively, an epoxide can be formed by reaction of the alkoxy radical with an electron in the adjacent double bond (blue arrow). The alkoxy radical can, however, also react with cleavage of C-C bonds to form short-chain degradation products (red and green arrows). The initially formed radical in FAME is caused by several positions at which hydrogen abstraction can occur. As a result of the mesomeric stabilization the hydroperoxides can be located in different places in the molecule. The subsequent reactions that also occur there are then correspondingly in different positions. This results in a large number of ageing products that can be formed from a few starting materials (C18:1 ME, C18: 2 ME, ...). For further discussion see section 6.2.^[29]

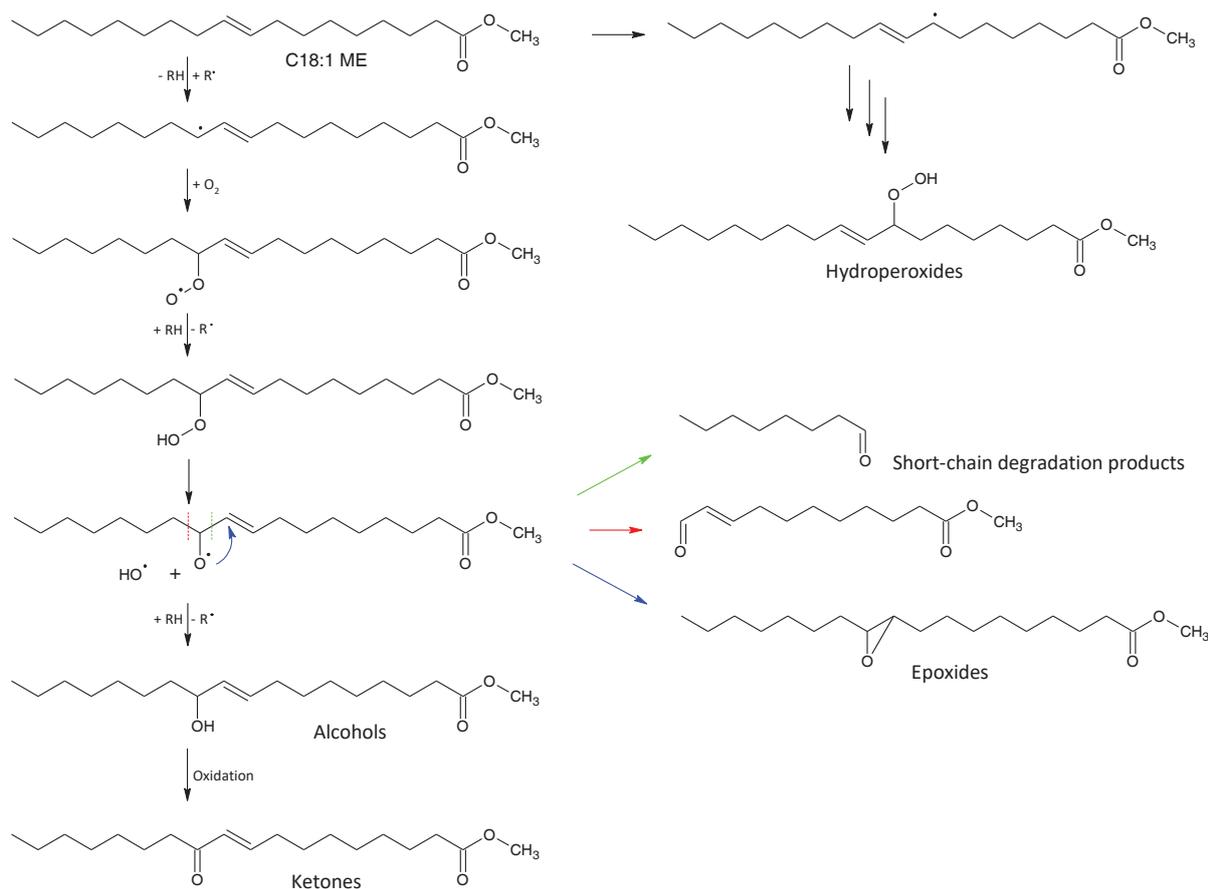


Figure 4: Mechanism of hydroperoxide formation and the possible subsequent reactions.^[29]

The second basic-relevant reaction for the discussion in the results section is directly related to the product distribution of the epoxides in monounsaturated fatty acid methyl ethers and other reactions in which the products formed cannot be explained by the mechanism shown in Figure 4. The second mechanism for epoxide formation found in connection with retinoic acid as a cooxidant is described.^[30] The oxidation products of retinoic acid found by Samokyszyn et al exclude the sole reaction mechanism from Figure 4. As here the epoxide is found at the position of the double bond and is necessary for a further explanation of identified products. For this reason, direct epoxidation through a peroxide radical with the double bond is suggested. The significance of this reaction in the ageing of fatty acid methyl esters is discussed in detail in Section 6.2 using the identified product ratio.

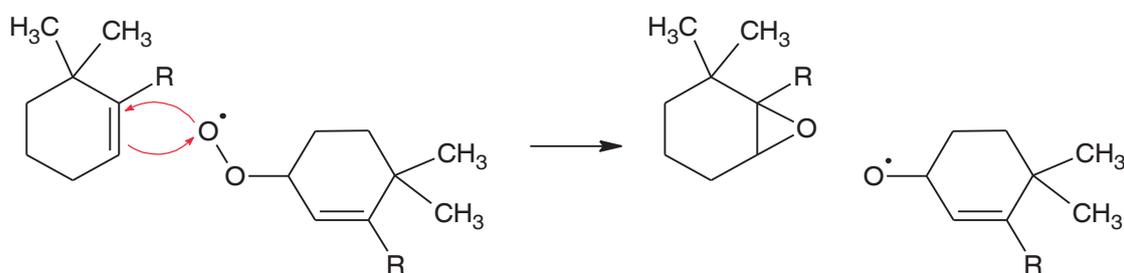


Figure 5: Epoxide formation through reaction of the double bond with a peroxide radical.^[30]

The third reaction is a secondary reaction that can occur with epoxides. The formation of ketones from epoxides as a result of a rearrangement reaction depending on various substituents is part of Winstein and Henderson's studies (Figure 6).

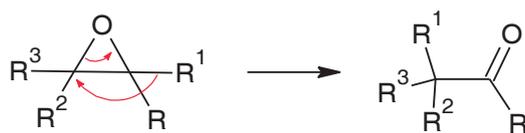


Figure 6: Ring opening reaction of monosubstituted epoxides.^[31]

By opening the C-O bond and rearranging R1, epoxides are converted into ketones. With a symmetrical arrangement of the radicals (R1 = R3 and R = R2) the two possible ketones are formed in equal parts, whereby either one or the other C-O bond can break. Both ketones are then available with a theoretical ratio of 1:1.

3 Utilised fuels

3.1 Biodiesel

Biodiesel is a fuel name that is used either as a pure fuel or as a blend component in fossil diesel fuel. Biodiesel is made from different oils and fats (triglycerides).^[32] Triglycerides consist of three fatty acids that are triple esterified with glycerine. In the biodiesel manufacturing process, the triglycerides are transesterified with methanol. Biodiesel therefore consists of fatty acid methyl esters (FAME), which differ in their fatty acid composition depending on the oil used.^[33]

Table 1: Fatty acid composition for different oils and fats.^[33]

Oil	Fatty acid composition [%]								
	C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C22:1
Rapeseed oil			0–1.5	1-6	0.5-3.5	8-60	9.5-23	1-13	5-64

The fatty acid composition of various oils used for biodiesel production is given in Table 1. The fatty acids are named according to their number of carbons (number before the colon) and the number of double bonds in the fatty acid (number after the colon). Based on the fatty acid composition, biodiesel consists of a mixture of unsaturated fatty acid methyl esters (compounds with a double bond) and saturated fatty acid methyl esters (compounds without a double bond). The composition of biodiesel affects the low temperature properties of the fuel. FAME with double bonds have a lower melting point than saturated FAME.^[34] For this reason, the biodiesel component in diesel fuel used in winter mainly comes from rapeseed oil, which contains a high proportion of unsaturated FAME. In summer, the biodiesel content can have a higher proportion of saturated FAME, which means that biodiesel based on palm oil can be used.^[35] In the context of this report, only biodiesel made from rapeseed oil is used. The biodiesel made from rapeseed oil is called rapeseed oil methyl ester (RME). The most frequently occurring FAMEs in RME are shown in Figure 7 with their structural formulas. For identification and differentiation from the fatty acids, the FAMEs have an addition of methyl ester (ME) in their designation. With the distinction between summer and winter diesel based on the fatty acid composition of the FAME, an important aspect is taken into account when using biodiesel, which plays an important role in the ageing investigation of RME.^[35] For this purpose, the molecular structures are examined more closely in Figure 7. The presence of a double bond in the molecule changes the geometry of the molecules. If two molecules come together, the contact areas of the molecules are reduced in comparison to saturated FAMEs if double bonds are present. There are fewer intermolecular interactions. The result is lower melting points, as less energy has to be expended to

separate the molecules from one another in the solid state.^[22] The aspect of the size of the intermolecular interactions affects not only the melting point, but also the miscibility of the fuels (see Section 6.4) and the chromatographic separation (see Section 5.2).

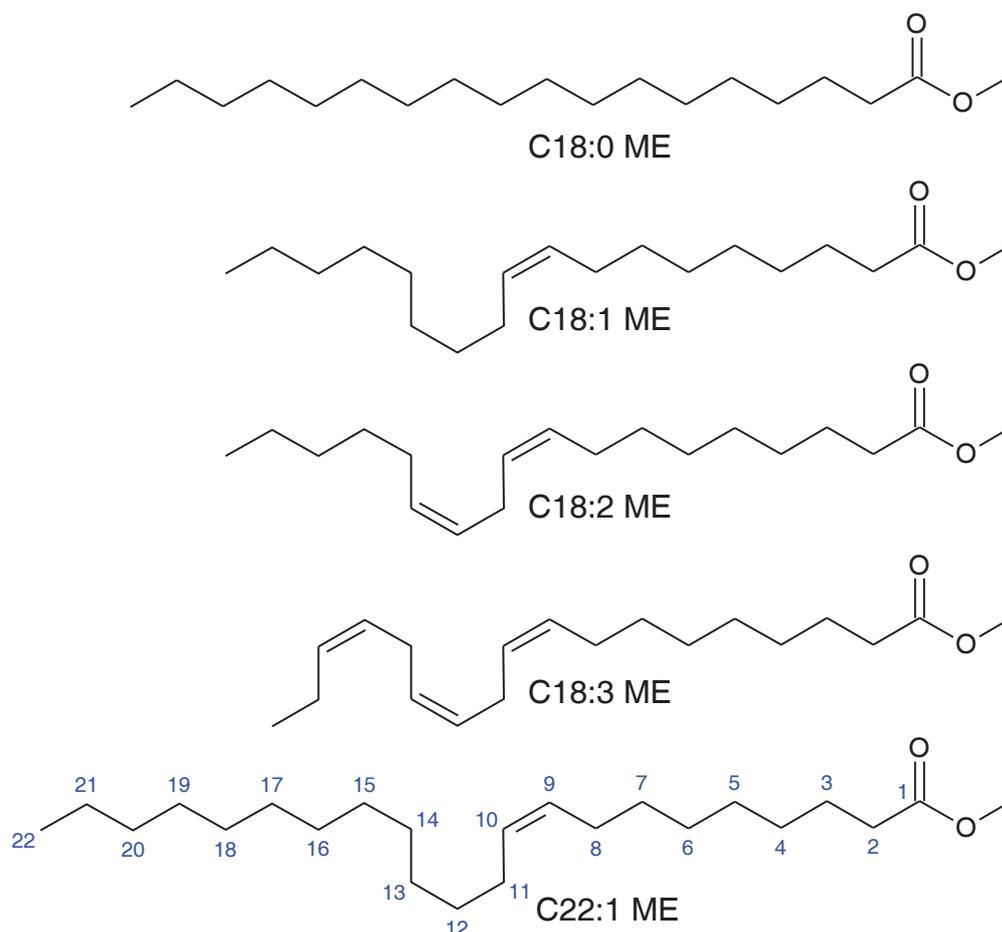


Figure 7: Structural formulas of C18:0 ME, C18:1 ME, C18:2 ME, C18:3 ME and C22:1 ME. For C22:1 ME the numbering of the carbons is shown, with which the position in the molecule is defined.

3.2 Hydrogenated vegetable oil (HVO)

Hydrogenated vegetable oil (HVO) is obtained from triglycerides in the same way as biodiesel. In contrast to biodiesel, HVO does not use transesterification, but rather the triglyceride is catalytically hydrogenated. The hydrogenation converts the triglycerides into alkanes, water and CO₂. Any unsaturated fatty acids present are converted into saturated hydrocarbons by hydrogenation. In addition, the hydrogenation causes an isomerisation of the hydrocarbons, whereby at the end the HVO is composed of n- and iso-alkanes.^[9]

3.3 Polyoxymethylene dimethyl ether (OME)

Polyoxymethylene dimethyl ether (OME) is a polyether with different chain lengths. The general structural formula is shown in Figure 8, with the chain length of the batch used being between $n = 3$ and $n = 6$. The large proportion of oxygen atoms in the OME leads to a higher polarity compared to HVO and RME. This creates a field of tension between HVO and OME, which affects the miscibility.^[36]

Due to the miscibility gap in HVO and OME, the influence of miscibility on fuel ageing can be examined in Section 6.4.

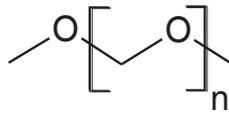


Figure 8: Structural formula of polyoxymethylene dimethyl ether.

4 Measurement and evaluation methods used and sensor details

4.1 Accelerated artificial ageing

To investigate the oxidation stability of fuels in the laboratory, a method must be used that allows the fuel to age within a short period of time. There are two methods according to DIN EN 590 which subject the fuel to accelerated thermo-oxidative ageing with a temperature increase and excess oxygen.

4.1.1 Rancimat method

The so-called Rancimat test determines the time from when the fuel begins to oxidise. The time it takes for oxidation to occur is known as the induction time. To determine the induction time, the fuel is heated to 110 °C in a defined reaction vessel (Figure 9). Through a glass tube, air is passed through the fuel with a volume flow of 10L / hour. If, for example, volatile acids are formed due to oxidation, these lead to an increase in conductivity in a separate conductivity measuring cell. The induction time can thus be determined by evaluating the conductivity over time. The induction time results from naturally occurring antioxidants, for example in rapeseed oil methyl ester, or from artificially added antioxidants that trap free radicals and thus suppress oxidation. The length of the induction time depends on the type and composition of the antioxidant and the interaction with the susceptibility of the fuel to oxidation. When the fuel is stored, the induction time of the fuel decreases continuously over time, depending on external influencing factors such as temperature, since the antioxidants are consumed over time.^[37]

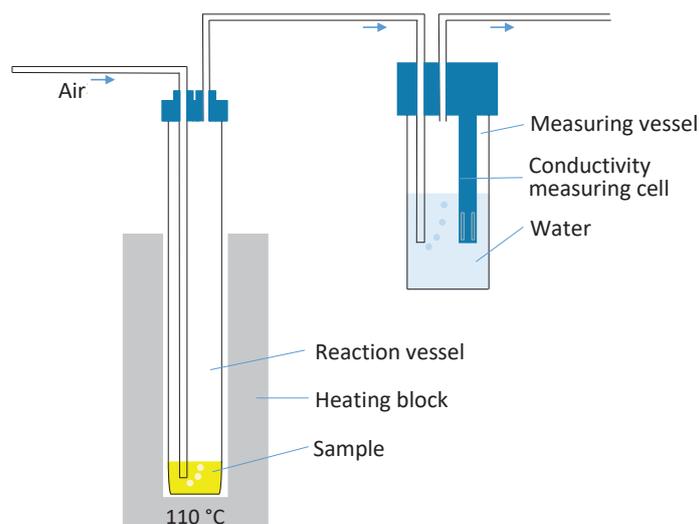


Figure 9: Schematic sketch of the ageing device Rancimat 873 Biodiesel for thermoxidative ageing of fuels.



4.1.2 Petrooxy method

The second test method is the so-called petrooxy test. In the petrooxy test, the fuel is tempered in a closed system together with pure molecular oxygen. The test cell is set to a pressure of 700 kPa by the molecular oxygen. When the oxidation occurs, the molecular oxygen is incorporated into the fuel molecules, which reduces the pressure in the test cell. According to the standard, the induction time is reached when the pressure drop is 10%. According to the standard, the test parameters are set at a temperature of 140 °C. The high pressure applied and the higher temperature compared to the Rancimat test result in a shorter measuring time. Another advantage is that the closed system enables even volatile fuels to be examined for oxidation stability. The respective induction time from Rancimat and Petrooxy refers exclusively to the measuring method. A direct general comparison of the induction times of both measurement methods is not possible due to the different test procedures.^[38]

4.2 Fourier transform infrared spectrometry (FTIR)

The analysis of functional groups through the wavelength-dependent absorption in the mid-infrared range is measured with a Nicolet 6700 FTIR spectrometer from Thermo Scientific. The measurement is carried out using the ATR measuring principle (*attenuated total reflection*) in the wave number range from 4000 cm⁻¹ to 650 cm⁻¹. The measurements are carried out at room temperature and evaluated with the Omnic software from Thermo Scientific.

4.3 Near infrared spectroscopy with laboratory measuring device

The near-infrared spectra are carried out with a NIRS XDS Rapid Liquid Analyser from Methrom. An Xds Monochromator Type XM – 1000 is used as the light source. The samples are taken with 8 mm cuvettes in a measuring range from 400 nm to 2400 nm at 35 °C. The evaluation was carried out with the VISION 4.0.3.0 software. Near-infrared spectroscopy is based on overtone or combination oscillations of the fundamental molecular oscillation, which leads to broad absorption bands and superimpositions. For this reason, the near-infrared data are further interpreted for detailed evaluations using multivariate methods.

4.4 Partial least squares Regression (PLS)

Partial least squares regression (PLS) is a multivariate method can be used in chemistry, for example, to determine properties from spectra. The PLS is based on the principal component analysis of independent variables X and the dependent variables Y. The matrices X and Y are each divided into two matrices T (score matrix) and P' (loading matrix) or U and Q plus a respective error matrix E and F.

$$X = T \cdot P' + E$$

$$Y = U \cdot Q' + F$$

The basic idea is that the main components of the matrices X and Y are calculated independently and that a regression model is created between the score matrices T and U. The target data Y are therefore included in the principal component analysis for the X data in the PLS. The aim of the PLS is to minimise the norm of the error matrix F while maintaining a correlation between X and Y. This is done using the relationship $U = B \cdot T$. Thus, the PLS can determine the target variable Y for unknown samples based on the measured values X.^[39]