Stability of Biodiesel

Used as a Fuel for Diesel Engines and Heating Systems

Presentation of the BIOSTAB Project Results

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BIO STAB

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Content

Stability of Biodiesel – Introduction to the BIOSTAB project

Biodiesel has become a rapidly growing market of renewable biofuels in the European Union. Especially the substantial expansion of the production capacity in Germany requires special attention and special measures for the market adaptation. The European biofuel directive (2003/30/EC, published in May 2003) serves as another impetus to the development.

In order to ensure customers' acceptance, standardisation and quality assurance are key factors in the market introduction of biodiesel. In 1997 the European Commission gave a mandate to CEN to develop standards for biodiesel as a transport and heating fuel. Minimum requirements and test methods are included in the forthcoming standards, prEN 14214 (Biodiesel as automotive diesel fuel) and prEN 14213 (Biodiesel as heating fuel).

However, during the standardisation process major significance was attached to fuel stability. In 2001 the European project 'Stability of Biodiesel' (BIOSTAB) was started in order to obtain information on this very important topic.

The main objective of the project is to establish criteria and corresponding analytical methods to determine the stability of biodiesel. In detail the project aims at:

1. appropriate methods for the determination of stability under realistic conditions
2. understanding the influence of storage conditions on the quality of pure and blended biodiesel
3. definition of a minimum level of natural and/or synthetic antioxidants
4. determination of the effects of the fuel stability during utilisation of biodiesel as automotive diesel fuel and as fuel for heating.

Nine experienced partners from industry, science and research were involved in the project. 7 out of 9 partners were members of one or more CEN working groups during the Biodiesel standardisation process. All partners have specific and long-term biodiesel experience.

The working programme is divided into four work packages. For each work package (WP) a work package leader had to co-ordinate the tasks between the several partners. An overview of the content of the work packages is given below:

WP1 – Determination methods: The objective of this work package is to evaluate and to develop accurate methods for the determination of oxidation, storage and thermal stability. Concerning oxidation stability the Rancimat test (prEN 14112) has already been chosen in the Biodiesel standards. The relationship between the induction period provided by this test and other quality parameters has to be clarified. Due to a lack of knowledge no test method has been chosen for thermal stability and storage stability. One of the main goals is to select and develop a method for each item considering criteria such as reflection of real conditions, correlation with quality parameters of biodiesel, precision, cost.

WP2 – Storage tests: Previous research demonstrated that storage conditions (i.e. temperature, light, atmosphere, presence of pro-oxidant metals, etc.) have a strong impact on storage behaviour. The nature of feedstock might also influence the final result considerably. The main task is to carry out a systematic study of the changes in biodiesel samples, made of different feedstock and prepared by means of different production technologies, during a long term storage experiment under real conditions.

WP3 – Antioxidants: The content of natural antioxidants like tocopherol and carotenoids in vegetable oils prevents oxidation reactions. However, the content of natural antioxidants in biodiesel varies significantly depending on the feedstock as well as the process technology.

Thus, natural or synthetic antioxidants have to be found to improve the oxidation stability. Besides, the influence of natural and synthetic antioxidants on other quality parameters have to be studied in order to find appropriate additives to improve oxidation stability.

WP4 – Utilisation of biodiesel: Finally, bench tests and field tests were carried out in order to investigate effects of the stability during the use of biodiesel. Both applications, the use of biodiesel as transport fuel as well as the use as domestic heating fuel is included in the tests. Thus, work package 4 is divided into 2 parts:

WP4.1 – Biodiesel as automotive diesel fuel: Long term tests were carried out with 3 different modern injection systems on the test bench. 3 fuel qualities, rape seed oil methyl ester with a low, a standard and a high stability were used. Furthermore, two long term bench tests were carried out with modern passenger car engines equipped with a common rail injection system. Biodiesel with a low and a high stability was used in the tests.

Four cars were operated in a field test program, using biodiesel with a low stability. Chassis dynamometer measurements and inspections of the injection system accompanied the test programme.

Another field test with 3 vehicles aimed at fuel blends: fossil diesel fuel was incorporated with 5% FAME with a very low stability. The influence of fuel stability on the performance of the fuel delivery chain from the storage tank to the vehicle fuel system was investigated.

WP 4.2 – Biodiesel as heating fuel: Bench tests were carried out comprising emission tests and tests of functionality on several heating systems. 1000h intersectional tests with 4 fuels (containing 5% and 20% biodiesel) were carried out in 3 different small-scale combustion units with conventional technology. Interval checks, emission control measurements and product analysis accompany the programme.

Eight test facilities were installed and operated during 2 heating seasons in a field test programme. Rape seed oil methyl ester and used frying oil methyl ester were used in 5% blends to fossil heating fuel. 4 out of 8 systems were operated with fuel including an antioxidant additive.

The extremely comprehensive test programme could be carried out professionally and in due time thanks to the excellent co-operation of the project partners. The results should help to further improve the quality of biodiesel on the market. High quality is the basic prerequisite for a wide use of biodiesel. Thus, the project contributes to achieving the objectives of the European Commission as regards the use of bioenergy.

Heinrich Prankl
Project Co-ordinator

Work Package 1

Determination Methods

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1 OBJECTIVES

The objectives of the work package are to evaluate and/or develop accurate methods for determination of oxidation, storage and thermal stability. Three items referring to behaviour of biodiesel submitted to oxidative conditions have been defined by the CEN working group in charge of specifications in the execution of Mandate M/245, depending on the uses of biodiesel :

Oxidation stability (presence of oxygen): although ISO 6886 (Rancimat test) has been chosen in the execution of Mandate M/245 as the test method for thermal oxidation stability, it has to be to clarified the relationship between the induction period provided by this test and other quality parameters. Indeed, this test is unfavourable to distilled biodiesels compared to undistilled products without correlation of experience on the field.

Thermal stability (absence of oxygen) and storage stability: Due to a lack of knowledge no test method has been chosen for these two items in the execution of Mandate M/245. One of the main goals is to select a method for each item (already existing or new) considering criterions such as reflection of real conditions, correlation with quality parameters of biodiesel, precision, cost.

2 METHODOLOGY

task 1) Preparation of biodiesel samples of different feedstocks at pilot scale and characterisation by standardised methods (done by University Graz).

Oxidation stability :

task 2) Determination of quality parameters (e.g. tocopherol content, peroxide value,..) in aliquots sampled along the Rancimat test (done by ITERG).

Storage and thermal stability :

task 3) Drawing up a list of real conditions of uses and storage of biodiesel with producers and users : temperature, pressure, oxygen, light, metals (common work).

task 4) Selection/modification of existing methods according to their reflection of real conditions (common work).

task 5) Test of each selected method for a set of samples prepared according to 1). Determination of quality parameters on aliquots sampled before and after the accelerated ageing test (done by ITERG and SSOG).

task 6) Evaluation of precision for each method tested.

task 7) Selection for each item of the best method (common work).

task 8) "Mini"-interlaboratory trials on the two new methods developed (common work).

3 RESULTS

3.1 Samples

Eight biodiesel samples, representative of different feedstock, both undistilled and distilled, were supplied by European producers to Uni Graz in charge of checking the quality of these products according to CEN draft specification (prEN 14214, [1]). Table 1 gives a list of these biodiesel samples.

Nature of the product		Code	Production Country
Undistilled	Rapeseed FAME	RU	Austria
	Used frying oil FAME	UU	Austria
	Sunflower FAME	SU	Austria
	Tallow FAME	TU	Austria
Distilled	Sunflower FAME	SD	France
	Rapeseed FAME	RD	Austria
	Used frying oil FAME	UD	Austria
	Tallow FAME	TD	Austria

Table 1 : WP1 Biodiesel samples

3.2 Oxidation stability

The end of Rancimat induction period (prEN 14112 [2]), is determined by the formation of volatile acids measured by a sudden increase of conductivity during forced oxidation of an oil sample at 110 °C with an air flow passing through the sample (10 L/h). The aim of the work was to study the variation of different quality parameters during the Rancimat test and to compare their individual induction period to the one provided by the Rancimat apparatus.
Tests were carried out for seven samples (samples of table 1 except TD because the induction period was lower than half an hour). Thus, every each half an hour, air flow was switched off and the Rancimat tube was cooled down immediately using tap water during five minutes. Then, quality parameter analysis was carried out immediately (peroxide value NF T 60-220 [3], anisidine value EN ISO 6885 [4] and UV absorbency ISO 3656 [5]) or after freezing at -18 °C under nitrogen (acid value pr EN 14104 [6], ester and linolenic acid content pr EN 14103 [7], kinematic viscosity EN ISO 3104 [8], polymer content ISO 16931[9] and tocopherol content ISO 9936 [10]).

3.2.1 Evolution of quality parameters along Rancimat test

For each quality parameter studied, a ranking of samples was done based on their resistance towards oxidation (figure 1). This ranking was compared to the one provided by the Rancimat induction period. Conclusion was that peroxide value, anisidine value, acid value, kinematic viscosity at 40 °C, ester content, linolenic acid content, UV absorbency at 232 nm and polymer content give similar ranking of samples that the one given by conductivity measurement of the Rancimat test. On the other hand, evolution of absorbency at 270 nm does not present visible variation along the Rancimat test. Also, it is difficult to compare the evolution of total tocopherol content along the Rancimat test of the different samples as the initial concentration is very different according to feedstock or process. It seems that tocopherol content before ageing is not a good criteria to predict the duration of the IP.

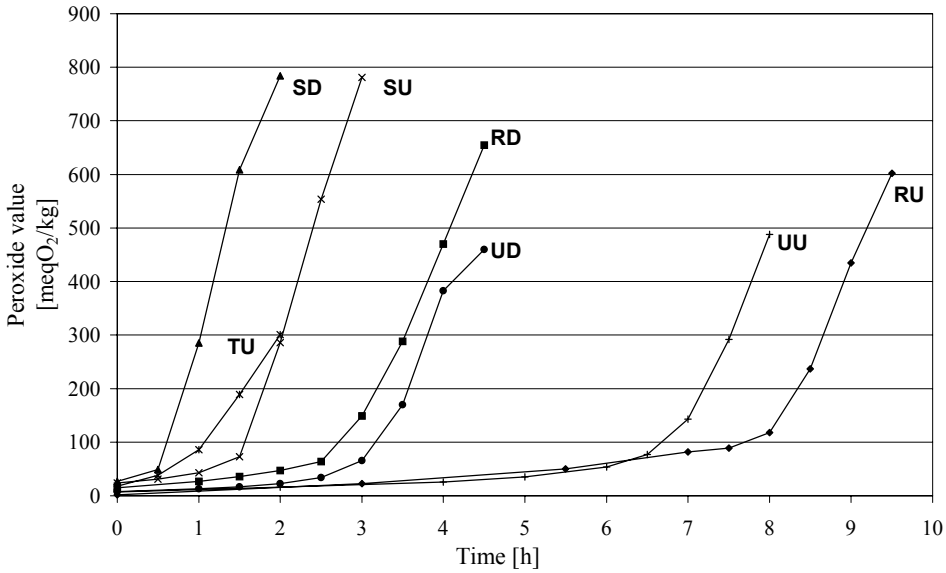

Figure 1 : Peroxide value determination along Rancimat test, according to NF T 60-220

3.2.2 Evaluation of samples at the end of Rancimat test

The quality of samples tested was checked at the end of the induction period of Rancimat test comparing to FAME or Oils and Fats specification limits (pr EN 14214 for ester content, acid value and kinematic viscosity at 40 °C - AOCS Cd 12-57 for peroxide value). Table 2 shows that for every sample at the end of Rancimat IP, one or two parameters have reached or exceeded the specification limit. So it is possible to confirm that at the end of the induction period of Rancimat, no sample meets the specifications of FAME or Oils and Fats.

Sample	Rancimat IP [h]	FAME or Oils and Fats specification limits			
		Ester 96,5 %	Acid Value 0,5 mg KOH/g	Kinematic viscosity 5 mm^2/s	Peroxide value 100 $meqO_2/kg$
SD	1,2	-	+	+	-
SU	2,0	-	-	+	-
RD	3,2	+	0	+	-
RU	8,6	-	-	-	-
UD	3,4	+	+	+	-
UU	7,1	0	-	-	-
TU	1,2	0	-	+	-

Table 2 : FAME or Oils and Fats specification limits reached (-) or not reached (+) by the samples at the Rancimat induction period time
(0 : specification limit already reached before ageing test)

3.2.3 Interpretation according to inflexion point of the evolution curve of quality parameters along Rancimat test

Considering the variation of each quality parameter along the Rancimat test, a value of the induction period (IP) was calculated by searching the intersection of the two tangents [11]. Then for each sample, a mean value (table 3) was calculated using all the induction periods given by the following quality parameters : tocopherol content, UV absorbency at 232 nm, peroxide value (PV), ester content, linolenic acid content, kinematic viscosity at 40 °C, polymer content, anisidine value and acid value. IP mean values were compared with the IP provided by the Rancimat.

First remark is that studied parameters give an induction period duration very homogenous. Second remark is that the mean value duration given by quality parameters is 10 % lower than the IP measured by the Rancimat test.

The three first parameters presenting the shortest IP are tocopherol content, UV 232 nm and peroxide value (natural antioxidant content or primary products of oxidation). Whereas parameters such as anisidine value which measure secondary products of oxidation are ranked in last.

SAMPLE	SD	SU	RD	RU	UD	UU	TU
Mean Value of calculated IP	0,7	1,6	2,9	7,8	3,0	6,4	0,8
Standard deviation	0,2	0,2	0,3	0,1	0,2	0,6	0,2
Rancimat IP	1,2	2,0	3,2	8,6	3,4	7,1	1,2

Table 3 : Induction period [h] calculated for quality parameters

The correlation between Rancimat IP and mean value of calculated IP for each sample is very good : R^2 = 0,99 (figure 2). We observe too a very good correlation between calculated IP for each parameter and Rancimat IP.

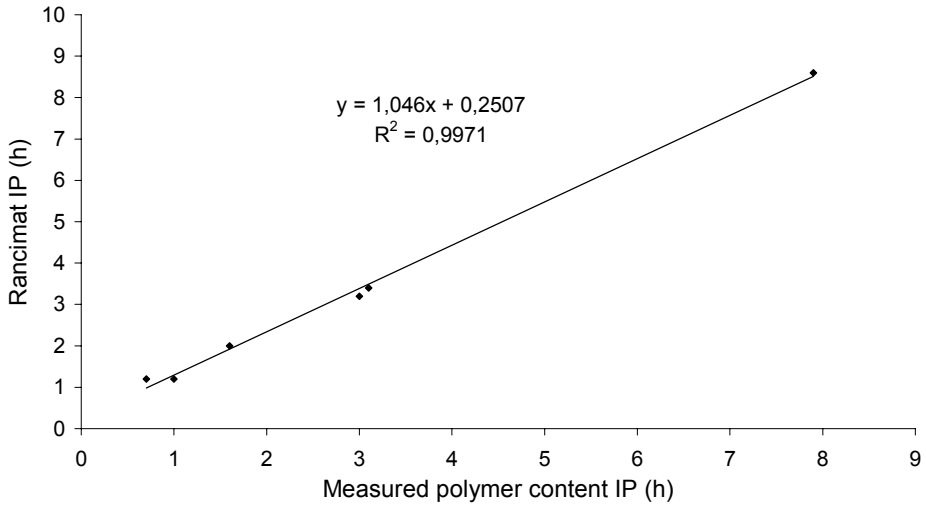

Figure 2 : Correlation between Rancimat IP and calculated polymer content IP for each sample

Main conclusion is that induction period determined by conductivity is well correlated to degradation of quality parameters along Rancimat test.

A paper was published in the European Journal of Lipid Science and Technology, 105 (2003) 149-155; the title is *"Quality parameters evolution during biodiesel oxidation using Rancimat test"* (Florence Lacoste and Lionel Lagardère).

3.3 Storage stability

At the beginning of the project it was decided to evaluate two test methods. The first one was the petroleum field reference method (ASTM D 4625 : storage at 43°C during 24 weeks), the second one corresponded to an accelerated IP48/IP306 like method at 90°C with an airflow

above the surface of the sample. For each test method, a list of seven quality parameters to be looked at, was defined : peroxide value [3], kinematic viscosity at 40 °C [8], acid value [6], ester and linolenic content [7], polymer content [9], oxidation stability [2] and turbidity measurement (internal procedure).

3.3.1 ASTM D 4625

A critical review of evaluation of storage stability with ASTM D4625 was carried out. All quality parameters of biodiesel are changing during time, according to the storage stability of different samples (figure 3).
Samples were also evaluated in terms of insoluble formation (filterable + adherent) according to ASTM D 2274 [15] but in any case no significant insoluble formation was observed. The conclusion was that polymer formed during storage of biodiesel in controlled conditions are soluble in oxidised biodiesel, thanks to its high polarity and become insoluble only when oxidised biodiesel is mixed with diesel fuel.

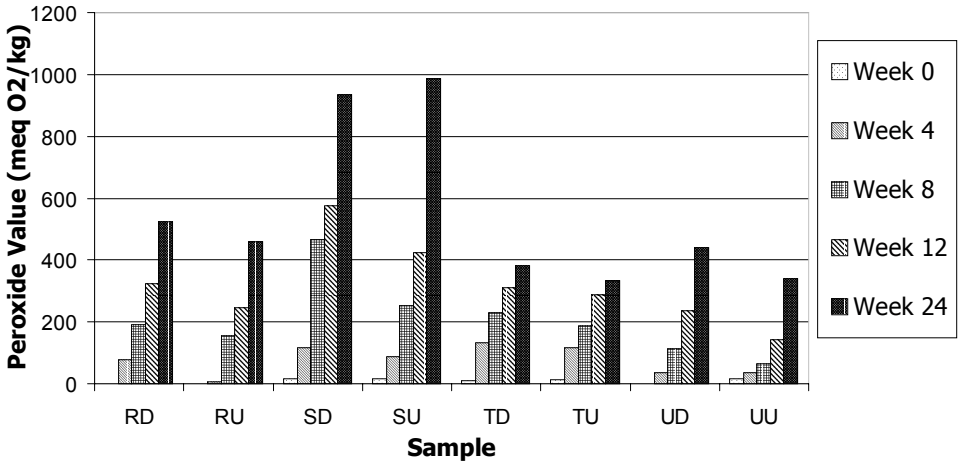

Figure 3 : Peroxide value changes during ageing with ASTM D 4625

ASTM D 4625 is considered to mimic storage of diesel fuel at ambient temperature. In the case of FAME, recorded changes of FAME quality parameters during real storage are very different to the ones recorded during accelerated storage at 43 °C (table 4). So ASTM D 4625 does not mimic correctly storage of FAME at ambient temperature.

Parameter	Real storage	43 °C Accelerated storage (ASTM D 4625)
Peroxide value	increases slowly	increases strongly
40 °C viscosity	increases slowly	increases
Acid value	nearly stable	increases strongly
Ester content	no change	decreases
Polymers	no change	increases
Free Glycerol	no change	no change
Total glycerol	no change	no change
Oxidation stability	decreases slowly	decreases strongly

Table 4 : Recorded changes during storage of FAME

A paper was published in the European Journal of Lipid Science and Technology, 104 (2002) 777-784; the title is *"Evaluation of biodiesel storage stability using reference methods"* (Paolo Bondioli, Ada Gasparoli, Laura Della Bella and Silvia Tagliabue).

3.3.2 Accelerated storage stability test

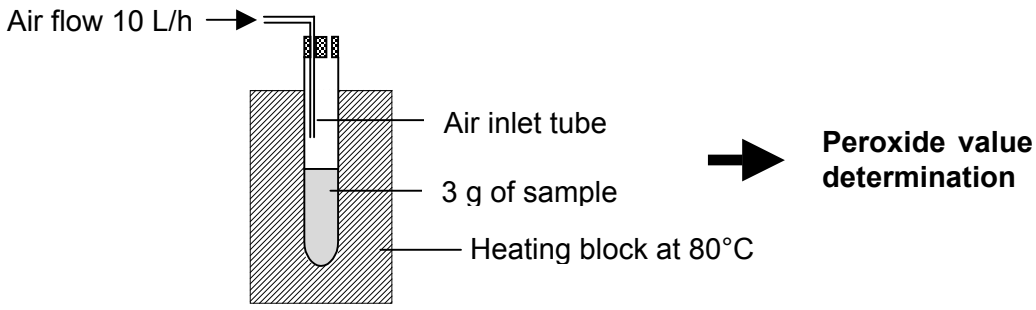

Figure 4 : Modified Rancimat apparatus for storage stability test

The selected experimental conditions based on IP48/IP306 were : 40 g of sample aged at 90 °C during 48 hours with air above the surface of the sample at 10 l/h. The main problem coming from these conditions applied to WP1 samples (see 3.1) was an evident lack of repeatability. So it was decided to use Rancimat apparatus, specially modified for quick storage stability evaluation. A stream of purified air (10 l/h) is passed above the surface of 3 grams of sample heated at 80 °C during 24 hours. Then peroxide value, ester content and polymer content are determined (figure 4).

The method was applied on all 8 samples in quadruplicate. The correlation with ASTM D 4625 is as follows (table 5) :

- good quality samples were deteriorated such as after 4 weeks in 43°C test
- low quality samples were deteriorated such as after 8-12 weeks in 43°C test

Sample (ASTM D 4625)	Increase of PV ($meqO_2/kg$)	Increase of ester content (% m/m)	Increase of polymer content (%)
RD (4W)	12	0,7	0,4
RU (4W)	33	0,0	0,3
UD (4W)	3	0,9	0,1
TD (8W)	202	0,1	1,0
TU (8W)	152	0,2	0,8
SD (12W)	678	10,4	3,4
SU (12W)	356	7,1	0,9
UU (12W)	143	0,9	0,2

Table 5 : Increase of peroxide value, ester content and polymer content after 24 hours at 80°C and correlation with ASTM D 4625 (number of weeks W)

In conclusion, the accelerated storage stability test does correlate with ASTM D 4625. It allows also to distinguish samples with a high and low stability.

The repeatability evaluation of the storage stability method was carried out for three parameters (polymer content, ester content and peroxide value) on the eight samples. The results showed a good repeatability for each parameter (see figure 5). The relative standard deviation is lower than 0,8 % for ester content, it is lower than 6,8 % for peroxide value and the maximum value is 22 % for polymer content.

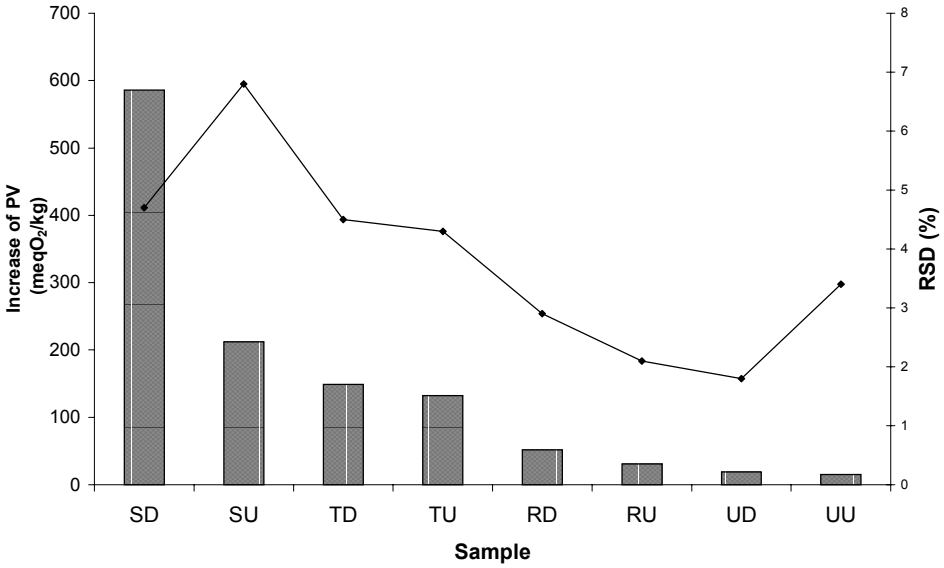

Figure 5 : Repeatability test - Increase of peroxide value and relative standard deviation for the increase of PV obtained for each sample

A mini ring test with 5 laboratories on five samples was organised to evaluate reproducibility of the storage stability test method (only peroxide value evaluation before and after ageing). Relative standard deviation (RSD) for reproducibility is between 20 and 30% for almost all samples tested (table 6).

Sample	**1**	**2**	**3**	**4**	**5**
Nature of the FAME	Rapeseed	UFO	Sunflower	Blend	Tallow
N° of participating laboratories	5	5	5	5	5
N° of participating laboratories after eliminating outliers	4	5	5	5	5
Mean value (*meqO₂/kg*)	**43,5**	**38,8**	**519,8**	**42,2**	**9,0**
Repeatability standard deviation (*meqO₂/kg*)	1,5	1,7	16,2	2,1	1,7
Coefficient of variation of repeatability (%)	3,4	4,5	3,1	5,0	18,7
Repeatability limit, *r* (*meqO₂/kg*)	4,2	4,9	45,2	5,9	4,7
Reproducibility standard deviation (*meqO₂/kg*)	12,8	11,8	160,9	8,5	8,7
Coefficient of variation of reproducibility (%)	29,5	30,5	31,0	20,1	96,5
Reproducibility limit *R* (*meqO₂/kg*)	**35,9**	**33,1**	**450,5**	**23,8**	**24,4**

Table 6 : Interlaboratory results for storage stability test (according to ISO 5725)

3.4 Thermal stability

The ageing conditions of ASTM D 6468 [16] were chosen for the accelerated test method for thermal stability : 150°C (oil heating bath) during 180 or 90 minutes in open air tube made of borosilicate glass. Before and after the end of the ageing test acid value [6], polymer content [9], oxidation stability [2], kinematic viscosity at 40°C [8], ester and linolenic contents [7], turbidity measurement (internal procedure) were determined. The variation of quality parameters such as acid value, Rancimat IP, ester content was too low to be measured correctly.

In order to get higher variation of viscosity and polymer content, different ageing conditions were tested such as increase of test duration, temperature increase or even stirring or arrival of air above the sample (table 7).

Source of heating	Temperature (°C)	Ageing time (h)	Relative viscosity increase (%)	Relative polymer content increase (%)
Oil bath	150	1,5	1,7	0,6
		3	3	0,9
		5	Not determined	1,6
	170	5	4,2	Not determined
	200	5	6	3,5

Table 7 : Effect of ageing conditions on maximum relative variation for viscosity and polymer content

These results demonstrate that samples tested in this study are really stable when heated at high temperature in absence of air flow.

A ring test with 4 laboratories was carried out using more drastic ageing conditions (5h at 200°C). The increase of kinematic viscosity at 40 °C and acid value variation was determined. Reproducibility relative standard deviation obtained for the viscosity variation parameter was about 45 % so the precision of the method was assessed as too low.

Consequently, it was decided to test different ageing conditions with the Rancimat apparatus, specially modified for thermal stability evaluation (absence of air flow, 15 g of sample). Using the Rancimat ageing device leads to a much higher variation of kinematic viscosity and acid value but the repeatability is still insufficiently (table 8).

Source of heating	Temperature (°C)	Ageing time (h)	Relative viscosity increase (%)	Relative standard deviation for viscosity
Rancimat	150	5	13	Up to 25 %
		16	42	Up to 68 %
	200	16	100	Not determined

Table 8 : Effect of ageing conditions on maximum relative variation for viscosity and repeatability of viscosity variation measurement

Results were not acceptable, so it was decided to perform ageing test at 200°C using a smaller amount of sample (8 g) in Rancimat tube (figure 6). A smaller test portion allows the sample convection within the tube and consequently improves repeatability. It was also decided to measure the polymer content at the end of the ageing test, as this parameter presents a greater increase than viscosity and acid value.

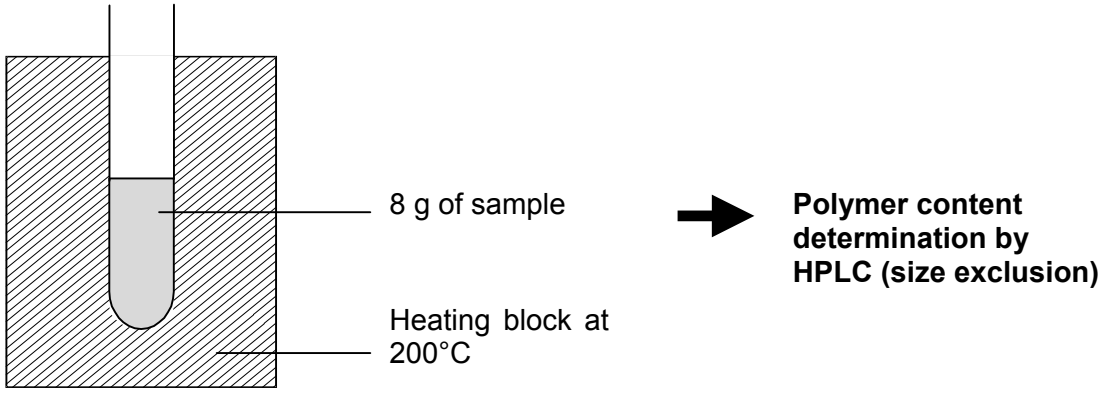

Figure 6 : Modified Rancimat apparatus for thermal stability test

Depending on the sample the increase of polymer content may vary from 5 % to 18 % (table 9), so the test is suitable for a discrimination of samples.

SAMPLE	Increase of polymer content (%)	RSD % (8 determinations)
TU	5,5	
UU	8,3	10,5
RU	8,8	12,7
RD	9,3	7,7
TD	11,8	
UD	12,5	
SD	16,9	
SU	18,2	

Table 9 : Increase of polymer content after 6 hours at 200°C with modified Rancimat apparatus

The modified Rancimat test seems to be suitable for use in terms of repeatability. Indeed, repeatability evaluation was carried out for three samples (RU, RD and UU) and the relative standard deviation is lower than 13 %.

In conclusion, thermal stability test can be performed using the Rancimat device and measuring the increase of polymer after 6 h at 200°C ageing period.

4 SUMMARY AND CONCLUSIONS

Oxidation stability: Rancimat test (pr EN 14112) was evaluated for seven biodiesel samples (Methyl ester from rape seed oil, sunflower oil, used frying oil and tallow). Determination of quality parameters was carried out on aliquot samples along every each ½ hour. All parameters present a visible variation along the Rancimat test except UV 270 nm. At the end of Rancimat induction period, the samples do not meet FAME or Oils and Fats specifications such as viscosity, acid value, ester content or peroxide value. Rancimat induction period is well correlated to induction period given by quality parameters, but Rancimat induction period is almost 10 % higher than induction period given by quality parameters. Main conclusion is that induction period determined by conductivity is well correlated to degradation of quality parameters along Rancimat test.

Storage stability: At the beginning of the project it was decided to evaluate two test methods. The first one is the petroleum field reference method (ASTM D4625 : storage at 43°C during 24 weeks), the second one corresponds to an accelerated IP48/IP306-like method at 90°C with an airflow above the surface of the sample. For each test method, a list of seven quality parameters was defined. Critical review of evaluation storage stability with ASTM D4625 was carried out. Because it was difficult to make a correlation between ASTM D 4625 and results of accelerated method initially proposed (accelerated IP48/IP306-like method at 90°C), it was decided to use Rancimat apparatus, specially modified for storage stability evaluation. A stream of purified air (10l/h) is passed above the surface of 3 grams of sample heated at 80°C during 24 hours. Then peroxide value, ester content and polymer content are measured. The modified Rancimat test is suitable for use in terms of repeatability, significance and it is easy to handle. Peroxide value determination shows the best correlation with ASTM D 4625 (storage at 43°C during 24 weeks). Using this method “bad stability” and “good stability” samples can be separated.

Thermal stability: At the beginning of the project it was decided to keep the ageing conditions of ASTM D 6468 (150°C, 180 or 90 minutes) as they were considered not too far from the real conditions. A list of seven quality parameters to be looked at before and after the ageing

test, was defined. But the variation of quality parameters (acid value, Rancimat, ester content) after the ageing test was too low to be measured correctly. Thermal stability tests at 200°C (oil bath) during 5 hours applied to all samples collected for WP1 demonstrate that samples coming from European productions are really stable when heated at high temperature in absence of air flow. Viscosity and acid value were chosen to evaluate the ageing effect . But repeatability results were not acceptable. So, it was decided to use Rancimat apparatus with a procedure specially modified for thermal stability evaluation. Eight grams of sample are aged for 6 hours at 200°C in open tubes with air exposure. After ageing and cooling, polymer content is determined by HPLC. The modified Rancimat test is suitable for use in terms of repeatability and it is easy to handle.

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Work Package 2

Storage Tests

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1 OBJECTIVES

The main objective of this work package was to carry out a systematic study of the changes occurring in biodiesel samples, prepared using different feedstock and different production technologies, during a long term storage experiment in real conditions. For each sample 15 parameters were monitored periodically. After the results became available of a questionnaire issued by WP1 regarding the common storage conditions of biodiesel in practice, storage tests in presence of direct light and at temperatures higher than ambient temperature were discarded. Major emphasis was devoted to the study of storage behaviour of additivated samples.
Another objective of this work package was the contemporary preparation of a relevant amount (> 100 litres) of biodiesel samples obtained from different feedstock and aged under normal conditions. These samples were supplied to WP 4, in order to study the fuel behaviour.
All tests were carried out only after assessment of biodiesel quality, according to the European biodiesel standards prEN 14213 and prEN 14214. Minor deviations from the specification limits were tolerated in order to have a wider spectra of different samples under ageing. Several non-additivated samples did not fulfil the requirement for oxidation stability, but this fact was expected because in most cases additivation could be a necessity.
Some previous studies about biodiesel storage were published in the past [1-3] and they represented the starting point for our activity. More recently a study about an accelerated storage test carried out at 43 °C in controlled conditions was published by our group [4].

2 METHODOLOGY

Several samples were collected in Europe from different manufacturers and different sources. The following steps were conducted in practice:

1. Selection of biodiesel samples: a selection of biodiesel samples already on the market, obtained from different feedstock and according to the different available technologies (mainly undistilled and distilled products) was prepared. The collected samples also included samples prepared from used frying oils as well as from animal fats, taking into account that these products may be used as raw material in the near future. After the kick off meeting it was decided to study the storage behaviour of an additivated sample

containing 400 mg/kg of tertbuthylhydroquinone (TBHQ). A parallel blank consisting of the same biodiesel without additive was stored under the same conditions. Two months after the beginning of the storage tests a second additivated sample, containing 250 mg/kg of pyrogallol (PYRO) was prepared and monitored along with the corresponding blank. The additivation of samples was carried out by means of the preparation of a concentrated solution (solvent was the sample itself in the case of TBHQ and methanol in case of PYRO) where the whole amount of antioxidant was dissolved. Then the solution was added to the sample in the drum which was shaken vigorously to ensure the complete mixing. The complete list of samples along with their main characteristics is reported in table 1.

Table 1 - Biodiesel samples used for long term studies

Sample	Source	Production Technology	Additivation (mg/kg)	Deviation from specification
TBHQ Blank	Rapeseed	Undistilled	None	
TBHQ Additivated	Rapeseed	Undistilled	TBHQ - 400	
Low Stability	Rapeseed	Undistilled	None	
Rape	Rapeseed	Undistilled	None	
Rape-distilled	Rapeseed	Distilled	None	Rancimat Induction Period = 4,2 hours
Sun-distilled	Sunflower	Distilled	None	Iodine Value = 131,1 Rancimat Induction Period = 1,3 hours
Rape/Sun	Rapeseed 67 % Sunflower 33 %	Undistilled	None	
Used Frying Oils	Used Frying Oils	Undistilled	None	Ester Content = 94,2 %
PYRO Blank	Rapeseed	Undistilled	None	
PYRO Additivated	Rapeseed	Undistilled	PYRO - 250	
Tallow	Tallow	Undistilled	None	Ester Content = 88,0 % Rancimat Induction Period = 0,7 hours

2. Set-up of storage tests: all collected samples (200 litres each) were stored in SSOG's facilities under controlled conditions. Nine samples were stored in an unheated shed without external heating, avoiding contact with direct sunlight at ambient temperature. The storage temperature profile, consisting of average temperatures recorded by Milano Duomo Meteo Station ranged, for the whole test period between –1.2 °C (minimum average temperature value recorded during winter) and + 30.1 °C (maximum average temperature value recorded during summer). One drum belonging to the same lot of TBHQ additivated/non additivated rapeseed oil methylester was stored outdoors, in direct contact with the external environment. This drum, containing the "Low Stability" sample, periodically underwent strong stirring and shaking in order to promote contact with external air. Finally the sample from beef tallow was stored in a 20 °C heated room inside the Institute, in order to avoid solidification of the sample because of the well known cold behaviour of tallow methyl ester.
3. Monitoring of stored biodiesel: all selected and collected samples according to 1., and stored under the conditions reported in 2. were sampled periodically and analysed using the following standard test methods: 40 °C Kinematic Viscosity – EN ISO 3104, Acid Value – EN 14104, Ester Content + Linolenic Acid Methylester – EN 14103, Iodine Value EN 14111, Free and Total Glycerol – EN 14105, Oxidation Stability EN 14112, Peroxide Value (PV) was determined according to NFT 60-220, Tocopherol content according to ISO 9936, Polymer content according to mod. IUPAC 2.508. For the evaluation of

synthetic antioxidants a HPLC method was set-up. In short the analysis was carried out using a RP8 column, UV detection at 254 and 280 nm, gradient elution [5]. All indicated tests were done in SSOG.

4. Samples for bench tests: a selection of one year aged samples was delivered to TUG to be used in bench tests.

3. RESULTS

During our one-year study we recorded the changes in composition of the above listed eleven samples of biodiesel stored in standard conditions. We must underline that several parameters did not show any significant change during the ageing process, such as acidity, ester content, linolenic acid methylester content, Iodine Value (IV), monoglyceride, diglyceride, triglyceride as well as free glycerol, polymer and tocopherol content. This statement is 100 % valid for the ten samples stored in a steady state, while in the sample kept in a drum with occasional shaking some changes were observed. This aspect will be discussed separately in this paper.

Peroxide Value

Looking at recorded changes in PV, as shown in table 2, we can see that PV increases in each sample up to the fifth month of ageing.

Table 2 - Changes in PV recorded during twelve months of storage
(according to NF T 60-220, results expressed as meq O_2/kg)

Ageing time, month	**0**	**1**	**2**	**3**	**5**	**7**	**9**	**12**
TBHQ Blank	7,3	8,9	8,7	8,8	9,5	9,2	13,5	11,4
TBHQ Additivated	2,3	3,4	3,6	3,9	5,3	3,9	4,3	5,4
Low Stability	10,2	14,9	20,7	25,4	28,6	33,6	37,5	20,5
Rape	3,4	5,1	5,2	6,7	9,9	9,2	9,2	13,3
Rape DISTILLED	18,9	19,3	20,1	21,2	21,9	15,6	15,4	17,7
Sun DISTILLED	79,0	78,8	80,6	83,6	87,1	66,6	65,4	68,5
Rape/sun	2,5	5,3	6,9	12,2	13,7	14,4	15,4	17,6
Used frying oils	9,3	10,6	11,5	12,4	14,4	12,8	11,9	16,9
Pyro Blank	5,8	7,9	6,5	7,3	8,8	7,4	9,4	9,4
Pyro Additivated	6,9	7,7	6,8	5,9	4,6	4,9	6,0	7,1
Tallow	n.d.	28,9	24,7	23,3	22,2	21,6	24,8	22,0

n.d. = not determined

After this time some samples show a clear degradation of hydroperoxide with probable formation of secondary oxidation products. We had already observed this fact [3] and at that time PV decrease was linked to the presence of iron. It is not the case in this study, as no significant metal presence was detected in samples stored. The starting PV does not represent a discriminating factor for the PV increase rate. Observing the behaviour of PV in the sample stored with occasional shaking (Low Stability sample) we can observe that changes are more evident and take place at very high rate.

Kinematic Viscosity

In table 3 the changes in 40 °C Kinematic Viscosity (KV) are reported. The KV shows a constant slight increase for each sample during time and does not seem a significant parameter to be used for the evaluation of storage behaviour. The range of starting values is very wide, depending on the nature of feedstock as well as on the production technology.

Distilled products show a lower value for KV, probably because of the nearly complete removal of non-methylester material (unsaponifiable, glycerides, etc.).

Table 3 - Changes in 40 °C KV recorded during twelve months of storage (according to EN ISO 3104, results expressed as mm^2/sec)

Ageing time, month	0	1	2	3	5	7	9	12
TBHQ Blank	4,37	4,52	4,40	4,42	4,43	4,37	4,47	4,49
TBHQ Additivated	4,41	4,45	4,46	4,46	4,57	4,45	4,56	4,50
Low Stability	4,36	4,56	4,41	4,44	4,46	4,46	4,49	4,52
Rape	4,41	4,37	4,39	4,47	4,53	4,45	4,54	4,53
Rape DISTILLED	4,04	4,07	4,10	4,13	4,14	4,12	4,09	4,12
Sun DISTILLED	4,07	4,10	4,12	4,17	4,07	4,15	4,22	4,22
Rape/sun	4,23	4,38	4,33	4,31	4,44	4,34	4,34	4,48
Used frying oils	4,67	4,72	4,80	4,87	4,92	4,87	4,96	4,94
Pyro Blank	4,60	4,61	4,56	4,40	4,54	4,49	4,50	4,49
Pyro Additivated	4,55	4,57	4,50	4,44	4,54	4,55	4,53	4,50
Tallow	4,73	4,94	4,90	4,89	5,06	4,98	5,00	5,04

In only one case does the maximum specification go over the limit (Tallow sample) and only after twelve months of ageing. Finally these slight changes in KV have not a noticeable effect on polymer concentration as underlined in other stronger degradation conditions [6].

Rancimat Induction Period

The strongest differences during long term storage appear in oxidation stability changes expressed as Rancimat Induction Period (RIP). In table 4 the complete set of data is collected.

Table 4 - Changes in RIP recorded during twelve months of storage (according to EN 14112, results expressed as hours)

Ageing time, month	0	1	2	3	5	7	9	12
TBHQ Blank	7,51	6,93	6,75	6,64	6,55	6,50	6,19	6,20
TBHQ Additivated	36,00	35,85	35,00	34,17	33,05	33,18	33,73	32,77
Low Stability	6,30	5,92	5,00	4,47	2,27	1,04	1,04	1,24
Rape	9,20	8,84	8,35	7,65	7,37	7,22	7,08	6,83
Rape DISTILLED	4,16	4,21	4,23	4,25	4,11	4,02	4,01	3,89
Sun DISTILLED	1,31	1,37	1,38	1,40	1,45	1,34	1,44	1,43
Rape/sun	7,24	6,77	6,45	6,00	5,65	5,49	5,28	5,22
Used frying oils	7,98	7,59	7,10	6,88	6,65	6,35	5,94	5,83
Pyro Blank	7,75	7,40	n.d.	7,21	7,15	7,09	6,98	7,00
Pyro Additivated	22,42	22,25	n.d.	22,25	22,33	21,82	21,54	20,85
Tallow	0,7	0,68	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

By looking at these data there are some observations to be made: RIP decreases for each sample during time, except for samples having a very low initial value, such as Sun distilled and Tallow. A proper additivation increases the RIP, but this value tends to decrease with time as well. The rate of RIP decrease during time is a function of intrinsic quality of the product. Claiming that two samples having comparable RIP immediately after production will have comparable RIP decay during storage might be a wrong statement. That is the reason why, within the BIOSTAB project, we tried to find a suitable method which could predict the

behaviour of a sample maintained in steady environmental conditions for a reasonable period of time. This will be the subject of our next paper [7].

Special attention must be paid to the RIP evolution for the sample occasionally stirred. In this case we can observe a dramatic decrease in RIP, suggesting that the decrease is mainly due to the contact with air absorbed during shaking. We must remember that this sample, even if labelled Low Stability, belongs to the same lot and has the same starting properties as samples TBHQ blank and TBHQ additivated. In other words the "Low Stability" is not an intrinsic property of sample, but it is induced by incorrect storage conditions. This is the confirmation of the strong impact of air contact on biodiesel stability, suggesting which kind of simple technological solutions must be used when storing biodiesel along the complete distribution chain. Therefore it would seem necessary to limit the contact with air (stirring). Temperature, when below 30 °C does not have a big influence on quality of FAME.

Tocopherols

As a complement of our monitoring process we also decided to analyse samples for tocopherol content. Because of the very low variation in tocopherol content during storage in all samples we only report the initial and final values obtained for these natural antioxidants in table 5. Tallow sample was not analysed because of the known absence of tocopherols in animal fats. Some doubts still remain on real tocopherol content of sample Used frying oils, in which peaks having the same Retention Time as reference tocopherols are detected using two different detectors (UV and Fluorescence). For this reason the results obtained on this sample are not shown.

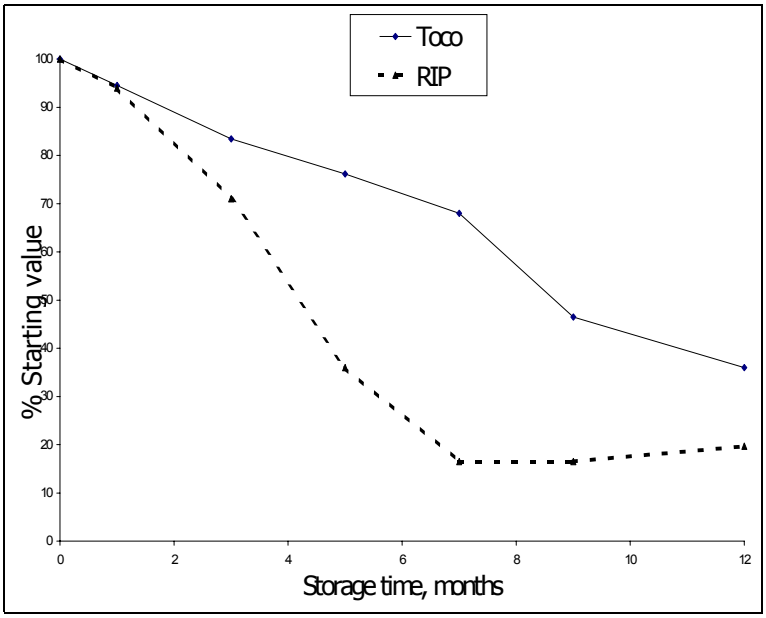
Table 5 - Changes in Tocopherols content recorded during twelve months of storage (according to ISO 9936, results expressed as mg/kg)

Ageing time, month	**0**	**12**
TBHQ Blank	597	559
TBHQ Additivated	586	577
Low Stability	559	201
Rape	476	486
Rape DISTILLED	152	142
Sun DISTILLED	95	56
Rape/sun	480	403
Used frying oils	---	---
Pyro Blank	574	564
Pyro Additivated	568	568

Once again the most dramatic decrease in tocopherol content was observed for Low Stability sample. Plotting the decrease of RIP for this sample in comparison with decrease of tocopherols content we come to the graph shown in Figure 1. Values are reported as a percent of initial value set in both cases at 100%. After a short initial period of parallel decrease we can observe that RIP decreases at a higher rate than tocopherols content does. This observation might mean that tocopherols are not the only compounds having significant impact on oxidation stability as determined according to EN 14112 and overall biodiesel stability is a function of other different parameters, storage conditions included. Another interesting result from the Low Stability sample concerns the individual tocopherol behaviour. Alpha-tocopherol degraded at very high rate, reaching the zero value after 9 months of

storage, while Gamma-tocopherol varied from 322 down to 159 mg/kg at the end of the monitoring period.

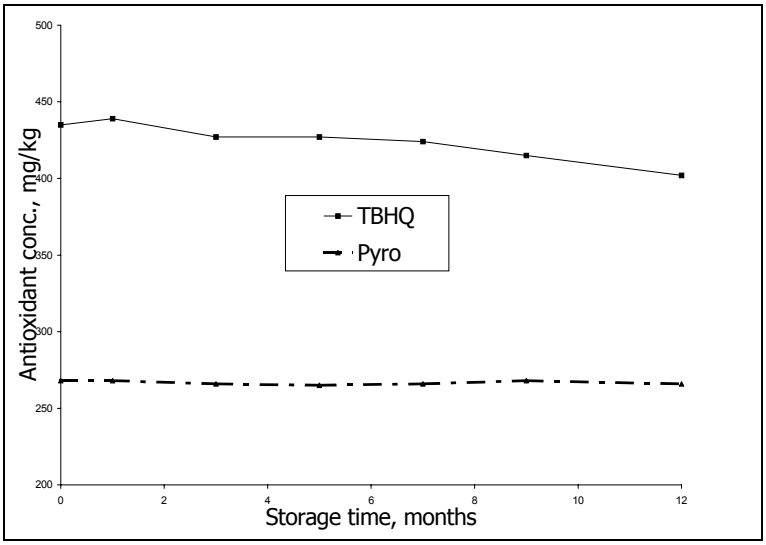
Figure 1 - Sample "Low Stability"- Percent decrease in RIP and Tocopherol concentration vs storage time



A final remark about the sample stored in very bad conditions concerns the parameters that did not change in the other samples. On the contrary to these other samples some changes were recorded in this sample for the following parameters (time 0 → time 12 months values and units under brackets): Acid Value (0,08 → 0,14 mg KOH/g) and Polymers (3,0 → 3,9 % m/m).

Finally we also investigated the fate of added synthetic antioxidants during storage. In figure 2 the values obtained following the concentration of both TBHQ and PYRO additives are shown.

Figure 2 - Changes in synthetic antioxidants concentration during storage (results expressed in mg/kg)



It is interesting to note the different behaviour of two synthetic antioxidants: while TBHQ decreases by approximately 8 % of its initial value, PYRO does not show any significant variation during the complete storage period. The impact of this behaviour on RIP is a reduction of 9 and 7 % of original value respectively. A wider discussion on the effects and of the impact of additivation was published by our BIOSTAB partners *Mittelbach and Schober* [8].

4 SUMMARY AND CONCLUSIONS

After the discussion on all experimental data we can come to some conclusions:

- After a one year storage study carried out on eleven different biodiesel samples, we can say that it was not possible to observe strong changes in 15 monitored characteristics. All samples met the specification limits even at the end of storage period, with the exception of RIP;
- PV changes are different depending on samples. For samples initially not too oxidised, PV increase is slow. For samples initially oxidised, PV first increases and then decreases due to the formation of secondary oxidation products. We must remember that PV is not included in the biodiesel specification table;
- the most important changes were recorded in oxidation stability, evaluated according to Rancimat test: this fact means that ageing takes place in biodiesel, independently from the monitored parameters and makes biodiesel less stable during time. This phenomenon can be monitored by means of Rancimat test EN 14112. The Rancimat takes a picture of the actual situation, but it is impossible with this test to predict the RIP value after a long term storage. There are ageing processes that can't be observed by analysing the parameters reported in prEN 14213 and prEN 14214 and we are trying to develop a method for storage stability prediction;
- RIP decreases with time: the rate of this decrease depends on the quality of the sample and on storage conditions as well;
- a proper additivation allows RIP to increase even greatly: studies could be carried out to identify quality and minimum quantity of antioxidant. The already mentioned paper from *Mittelbach and Schober* [8] provides several answers to this question;
- the right additivation must, in our opinion, allow the sample to fulfil specification for oxidation stability for at least six months; super-additivation procedures leading to a RIP higher than 20 hours have no meaning and might have a negative impact on other parameters (e.g. Conradson Carbon Residue);
- once again the necessity of correct storage and logistic solutions, to avoid the contact of biodiesel with air during its complete life cycle has been pointed out. The impact that a simple and occasional shaking of product in presence of air is really impressive and biodiesel actors must take account of it.

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Work Package 3

Antioxidants

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1 OBJECTIVES

Within the BIOSTAB project, the Institute of Chemistry is in charge of the co-ordination of work package 3 dealing with the evaluation of the effects of synthetic and natural antioxidants on the oxidation stability of biodiesel. Within the European specifications the value for the oxidative stability, expressed as the induction period using a Rancimat instrument, has to be higher than 6 h and should be guaranteed during the whole supply chain of the fuel. However, the stability of biodiesel varies significantly depending on the feedstock as well as the process technology. Biodiesel produced from rapeseed oil showed higher induction periods, whereas biodiesel produced from used frying oil, sunflower oil, soybean oil or animal fat had similar or significantly lower values for the induction period. A reason for this is the different fatty acid composition among the feedstocks and of course, the different content of natural antioxidants which prevent vegetable oils as well as the remaining esters from oxidative degradation. Also, distilled biodiesel, which has the highest purity from the chemical point of view, has a very low oxidative stability due to the lack of natural antioxidants, which had been removed during the distillation. Therefore, in the future most of the biodiesel produced will have to be additivated with appropriate antioxidants. Because of these facts different commercially available natural and synthetic antioxidants were tested in order to improve the oxidative stability of biodiesel. Furthermore the influence of the most effective antioxidants on specific parameters, existing in the international specifications for biodiesel was investigated in order to find appropriate additives to improve oxidation stability without deterioration of the other parameters. Finally a screening of the most promising antioxidants was performed to evaluate the optimum antioxidant amount.

2 METHODOLOGY

First of all a comprehensive literature search was performed in order to get an overview about existing knowledge on chemistry, mechanism, properties, availability and analysis of antioxidants. These literature studies were the basis for further selection of antioxidants. These antioxidants were checked for their ability to improve the oxidative stability of biodiesel prepared from different feedstocks. Furthermore the literature research pointed out that there were innumerable publications on the effect of natural and synthetic antioxidants on the stability of oils and fats used as food and feed, but very little is known on the effect of antioxidants on the behavior of fatty acid methyl esters used as biodiesel. Du Plessis et al. (1) carried out stability studies on methyl and ethyl fatty acid esters of sunflower oil, measuring different physical and chemical parameters during storage under different conditions. A two-year storage study was reported for rapeseed oil esters, measuring the increase of peroxide value, acid value, viscosity and density (2). For the measurement of oxidative stability of fats and oils as well as fatty acid methyl esters, the Rancimat method

was used very successfully (3,4). Bondioli et al. measured the induction period during storage of rapeseed oil methyl esters and found a rapid decrease after 30 days of storage (5). Mittelbach et al. studied the stability of undistilled and distilled samples of rapeseed oil and used frying oil methyl esters and found a similar decrease of induction period except for distilled samples, which had already shown low values at the beginning (6). Simkovsky and Ecker studied the effect of different antioxidants on the induction period of rapeseed oil methyl esters at different temperatures, but did not find significant improvements (7). Canakci et al. tested the influence of the antioxidant t-butylhydroquinone (TBHQ) on the peroxide value of soybean oil methyl esters during storage and found good improvement of stability (8). Dunn most recently described the effect of the antioxidants tert-butylhydroquinone and □-tocopherol on fuel properties of methyl soyate and found beneficial effects on retarding oxidative degradation of the sample (9).

The basis for the selection of the different types of biodiesel was the current situation on the biodiesel market. Therefore biodiesel prepared from rapeseed oil, sunflower oil, used frying oil and tallow were selected for the tests within the BIOSTAB project. Rapeseed oil methyl esters (RME) was purchased from NOVAOL/Austria, used frying oil methyl esters (UFOME) was purchased from SEEG/Austria. A batch of both was distilled under reduced pressure by OMV/Vienna to remove natural antioxidants. Sunflower oil methyl esters (SME) and tallow methyl esters (TME) were prepared following a standard procedure (10) by transesterification of refined sunflower oil and edible grade tallow at the institute. Additionally, a batch of TME was distilled in our laboratory. Distilled sunflower oil methyl ester was donated by COGNIS/France.

All the biodiesel samples mentioned were analysed according to the European draft specifications to check their quality. Furthermore the content of natural antioxidants of the biodiesel samples was determined.

After the selection and analysis of the biodiesel samples and prior to the screenings of the antioxidants for their ability to improve stability, the solubility of the selected 20 antioxidants in biodiesel and fossil diesel even at low temperature was checked

Subsequently to the selection and analysis of the biodiesel samples, the selected antioxidants were tested in a first screening on RME and UFOME in order to identify the products most effective in improving biodiesel stability. The most promising antioxidants were tested on the biodiesel samples and furthermore the dependence of antioxidant concentration on the oxidative stability of those biodiesel samples was evaluated. Finally the influence of the most effective antioxidants on other fuel parameters was determined.

3 RESULTS

Selection of Antioxidants:

Based on the literature search, 20 antioxidants, which were commercially available at a reasonable price, were selected and purchased. Characteristics of the antioxidants are given in figure 1 and table1.

Figure 1: Synthetic Antioxidants

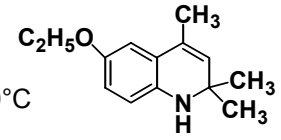
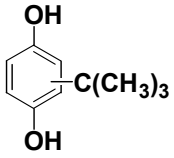
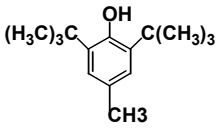
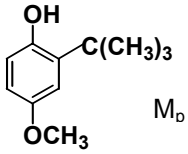
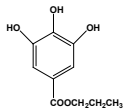
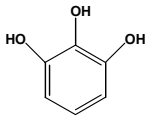
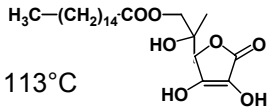
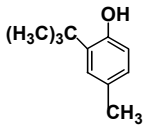
Ethoxyquin: 1,2-Dihydro-6-ethoxy-2,2,4-trimethylquinoline, 75% (GC) Sigma, Vienna  M_D < 0°C	**TBHQ:** tert-Butylhydroquinone, purum Sigma, Vienna  M_D 125°C
BHT: Butylhydroxytoluene; 2,6-Di-tert-butyl-4-methylphenol, purum Sigma, Vienna  M_D 69°C	**BHA:** 2-tert-Butyl-4-methoxyphenol, purum Sigma, Vienna  M_D 59°C
Propyl gallate: 3,4,5-Trihydroxybenzoic acid n-propyl ester, purum Sigma, Vienna  M_D 146°C	**Pyrogallol**: 1,2,3-Trihydroxybenzene purum Sigma, Vienna  M_D 132°C
L-Ascorbyl palmitate: Ascorbic acid 6-palmitate, purum Merck, Vienna  M_D 113°C	**2-tert-Butyl-4-methylphenol (t-BHT):** purum Sigma, Vienna  M_D 51°C
Tenox 20: 70% Propylene glycole, 20% TBHQ, 10 % citric acid Eastman Kodak, Germany	**RENDOX ACP:** Propylene glycol, BHA, propyl gallate, citric acid Kemin Ind. USA

Table 1 Composition of Tocopherol Type Antioxidants

Antioxidant	□-Tocopherol (%)	□-Tocopherol (%)	□-Tocopherol (%)	□-Tocopherol (%)	Carrier Oil (%)	Others (%)
Covi Ox T50	6.5	1	29	13.5	50	
Covi Ox T70	9.1	1.4	40.6	18.9	30	
Copherol F1300	87.2				12.8	
CONTROX VP	> 17					< 83[a]
DADEX TRC		33.6% mixed tocopherols				66.4[b]
BIOCAPS ER		12% mixed tocopherols			31	57[c]
BIOCAPS LT		31% mixed tocopherols			37	32[d]
BIOCAPS PA		28% mixed tocopherols			52	20[e]
BIOCAPS A70	6		47	15	31	
BIOCAPS GP			30% mixed tocopherols			70[f]

[a]20-40% lecithin,20-40% AP,5-10% citric acid esters of palm oil glycerides
[b]2% AP, distilled monoglycerides, propylene glycol, citric acid, Rosemary extract
[c]17% AP, 25% Rosemary extract, 15% lecithin
[d]17% AP, 15% lecithin
[e]AP
[f]5% AP, 5% lecithin, 30% PG, 30% excipient

Sample Analysis:

Not every biodiesel sample meets the specification limits in each case: e.g. SME has a higher iodine value, due to the higher amount of unsaturated fatty acid esters; the ester content of UFOME was too low due to the higher content of polymers, formed during the heating processes; also the limits for CFPP could not be reached by the samples prepared out of tallow because of their high content of saturated fatty acid esters. Detailed analysis data are listed in annex 1 and 2. Contents of natural antioxidants are given in table 2. Remarkable was the fact that natural antioxidants could not be removed completely during distillation. Furthermore, UFOME still had notable values of tocopherols, although the raw material used frying oil has been thermally stressed more often (natural antioxidants were discussed to be thermally not stable or even volatile).

Table 2: Content of Natural Antioxidants[a]

Sample	α-Tocopherol [mg/kg]	γ-Tocopherol [mg/kg]	Carotenoids [mg/kg][c]
RU	263	320	70
RD	98	142	n.d.
SU	264	12	n.d.
SD	84	nd.	n.d.
TU	n.d.	n.d.	n.d.
TD	n.d.	n.d.	n.d.
UU	80	77	n.d.
UD	trace[b]	32	n.d.

[a]Abbreviations: RU, RME undistilled; RD, RME distilled; SU, SME undistilled; SD, SME distilled; TU, TME undistilled; TD, TME distilled; UU, UFOME undistilled; UD, UFOME distilled; n.d., not detectable.
[b]Bellow 10mg/kg.
[c]Carotenoids were calculated by using carotene as reference.

Solubility:

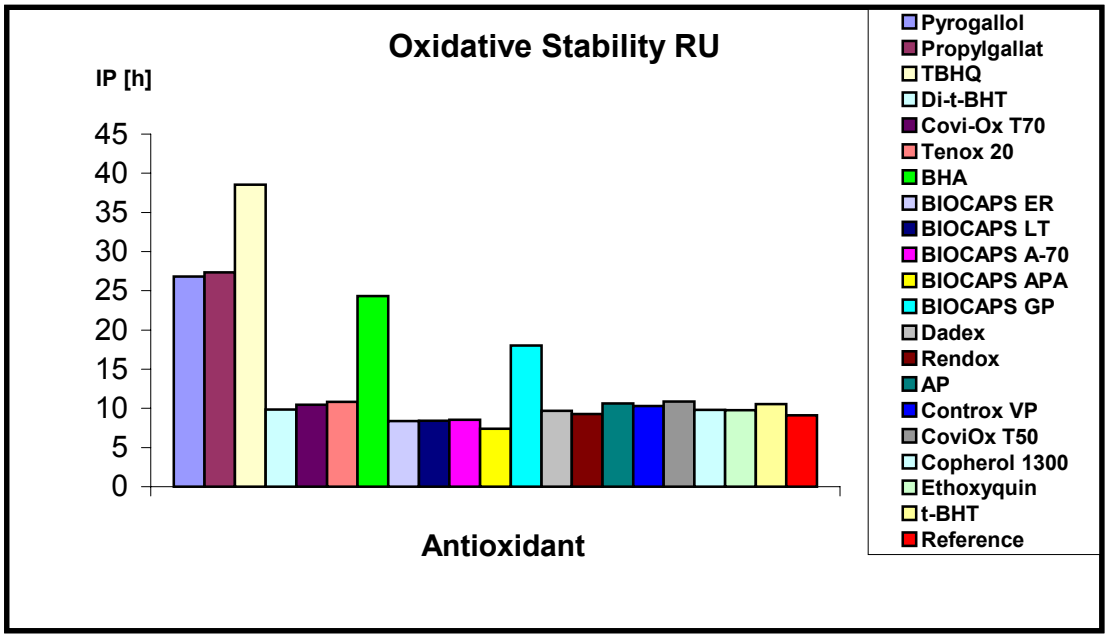
Results showed that those antioxidants containing either lecithin or ascorbic acid 6-palmitate were insoluble in biodiesel and therefore were not suitable as additives. Furthermore, most of the synthetic antioxidants were totally insoluble in fully additivated, winterised fossil diesel but no negative effects (e.g. formation of deposits) in blends with biodiesel could be observed, even at low temperature. Blends containing 2, 5, and 20 % (v/v) additivated biodiesel (RME

and UFOME, respectively) were prepared and stored at 0 °C and 20 °C for three months and currently controlled concerning the formation of any deposits.

Screening of Antioxidants

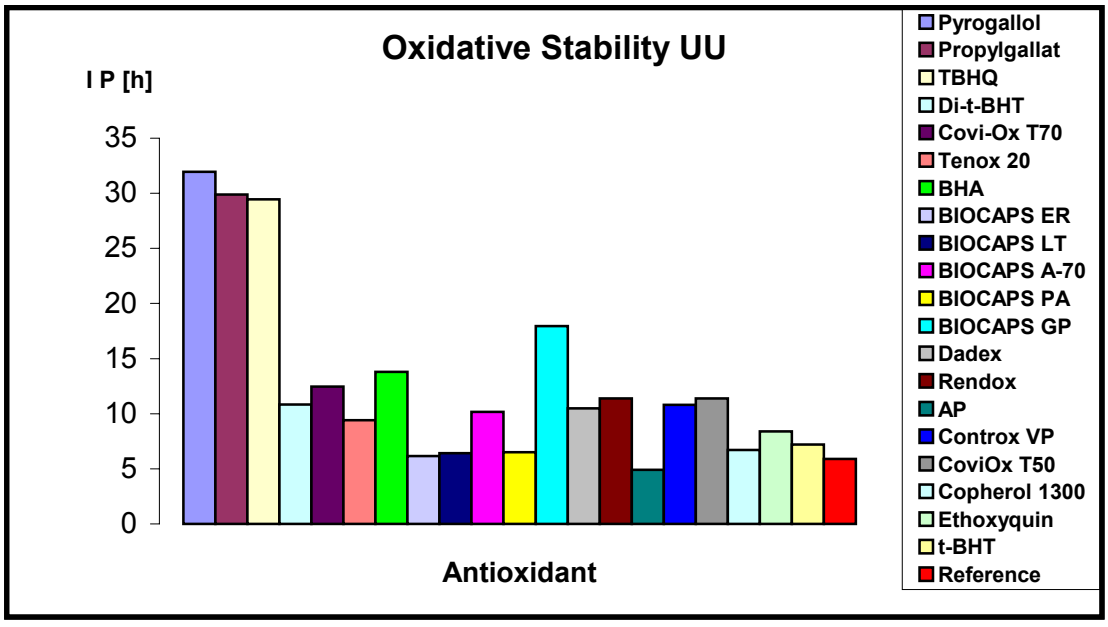
In a first screening all antioxidants were tested at a concentration of 1000 mg/kg with biodiesel from undistilled rapeseed oil (RU) and used frying oil (UU) in order to evaluate the most effective products (figure 2,3).

Figure 2: Oxidative Stability of Additivated Rapeseed Oil Methyl Esters[a]



[a]Reference: RU without Antioxidant

Figure 3: Oxidative Stability of Additivated Used Frying Oil Methyl Esters[a]



[a]Reference: UU without Antioxidant

In table 3 the values of the induction periods, as well as the calculated stabilization factors (F = IP_X/IP_0 where IP_X is the induction period in the presence of the antioxidant, and IP_0 is the induction period in the absence of the additive) according to their effectiveness, are listed. It

can be shown that in both biodiesel samples pyrogallol (PY), propylgallate (PG) and TBHQ were the most effective antioxidants leading to stabilization factors from 2.93 to 5.40, which means that the induction period was increased by these factors. In general, addition of synthetic antioxidants had a strong influence on the stability, whereas on the other hand, antioxidants on the basis of natural products, showed only small or even negative effects. Such negative effects can be explained by the fact that antioxidants under certain conditions (especially at high concentrations) could have prooxidative properties. Furthermore the volatility of antioxidants should be kept in mind. Among the natural antioxidants, Biocaps GP seems to be the most effective one, but it has to be considered, that the product contains also about 30 % PG.
As already mentioned above, antioxidants containing either lecithin or ascorbic acid 6-palmitate were not suitable additives because of their insolubility in biodiesel. These compounds often act as synergists in antioxidant mixtures and were therefore included in the first screenings (pre-dissolved in methanol). As shown in table 3 these antioxidants had only a small influence on the oxidation stability and therefore could be eliminated for further screenings.

Table 3 Influence of Antioxidants on the Oxidative Stability[a]

Antioxidant	Concentration [mg/kg]	RU Induction Period [h]	UU Induction Period [h]	F_{RU}	F_{UU}
Reference		9.15	5.92		
TBHQ	1000	38.53	29.44	4.21	4.97
Propylgallat	1000	27.36	29.90	2.99	5.05
Pyrogallol	1000	26.81	31.95	2.93	5.40
BHA	1000	24.30	13.80	2.66	2.33
BIOCAPS GP	1000	18.02	17.94	1.97	3.03
CoviOx T50	1000	10.88	11.48	1.19	1.94
Tenox 20	1000	10.83	9.42	1.18	1.59
AP	1000	10.61	4.91	1.16	0.83
Di-t-BHT	1000	10.54	7.23	1.15	1.22
Covi-Ox T70	1000	10.46	12.46	1.14	2.10
Controx VP	1000	10.32	10.81	1.13	1.83
t-BHT	1000	9.85	10.84	1.08	1.83
Copherol 1300	1000	9.82	6.77	1.07	1.14
Ethoxyquin	1000	9.78	8.49	1.07	1.43
Dadex	1000	9.69	10.52	1.06	1.78
Rendox	1000	9.28	11.46	1.01	1.94
BIOCAPS A-70	1000	8.54	10.16	0.93	1.72
BIOCAPS TL	1000	8.42	6.42	0.92	1.08
BIOCAPS ER	1000	8.38	6.17	0.92	1.04
BIOCAPS PA	1000	7.40	6.51	0.81	1.10

[a] $F = IP_X/IP_0$

Dependence of Concentration

For further study of the dependence of antioxidant concentration on the other biodiesel samples, the four most effective antioxidants were selected. Furthermore BHT was used because this antioxidant is easily available and well known in mineral and food oil industry. The antioxidants were added to the biodiesel samples in a concentration range between 100 and 1000 mg/kg, and the corresponding induction periods were measured with the Rancimat instrument. The goal of the measurements was to find the optimum antioxidant for each

feedstock and to determine the corresponding antioxidant concentration which leads to an induction period of at least 10 h, which is sufficient for meeting the specification for the oxidation stability for a one year storage time. In figure 4 the results of the measurements with the rapeseed oil samples are shown. With the undistilled sample, PG and PY showed the best results, doubling the induction period with an amount of 250 mg/kg, each. The distilled sample gave the best results with PY and BHA at lower concentrations, and very linear improvement with PG. There was almost no effect with BHT, whereas TBHQ showed good results only with the undistilled sample. The great difference between distilled and undistilled samples can be explained by the removal of natural antioxidants during distillation. This is in accordance with observations of Mittelbach et al., who observed very poor oxidation stability with distilled biodiesel samples (6).
Both used frying oil samples had low oxidation stability without antioxidants. Significant improvement could be achieved with the addition of PY and PG, but also TBHQ was quite efficient (figure 5). Even a concentration of 1000 mg/kg BHT did not lead to values over 10 h. BHA had a slightly better effect than BHT.
The undistilled sunflower oil sample (SU) showed good effects with PY and PG at a concentration of 1000 mg/kg, whereas the other products were not sufficiently effective (figure 6). The relatively poor improvement of oxidation stability with all antioxidants can be explained by the higher concentration of linoleic acid, which is less stable towards oxidation than oleic acid. These results are in accordance with findings by Niklova et al., who studied the effect of natural and synthetic antioxidants on oxidative stability of sunflower and rape seed oil (11). With the distilled sample (SD) even antioxidant concentrations of 1000 ppm did not lead to an induction period of 10 h in any case (figure 6).
Obviously because of low concentrations of natural antioxidants, both tallow methyl ester samples showed very poor oxidation stability (figures 7). With the undistilled sample (TU) PY showed the best improvement, leading to induction periods of over 20 h in a concentration over 500 mg/kg; the other antioxidants led to significantly lower induction periods, hardly reaching 10 h. Surprisingly PG showed a far better effect on the distilled sample (TD), leading to induction periods of over 50 h; BHA and BHT were not very effective.

Figure 4: Influence of Antioxidant Concentration on the Oxidative Stability of RU and RD

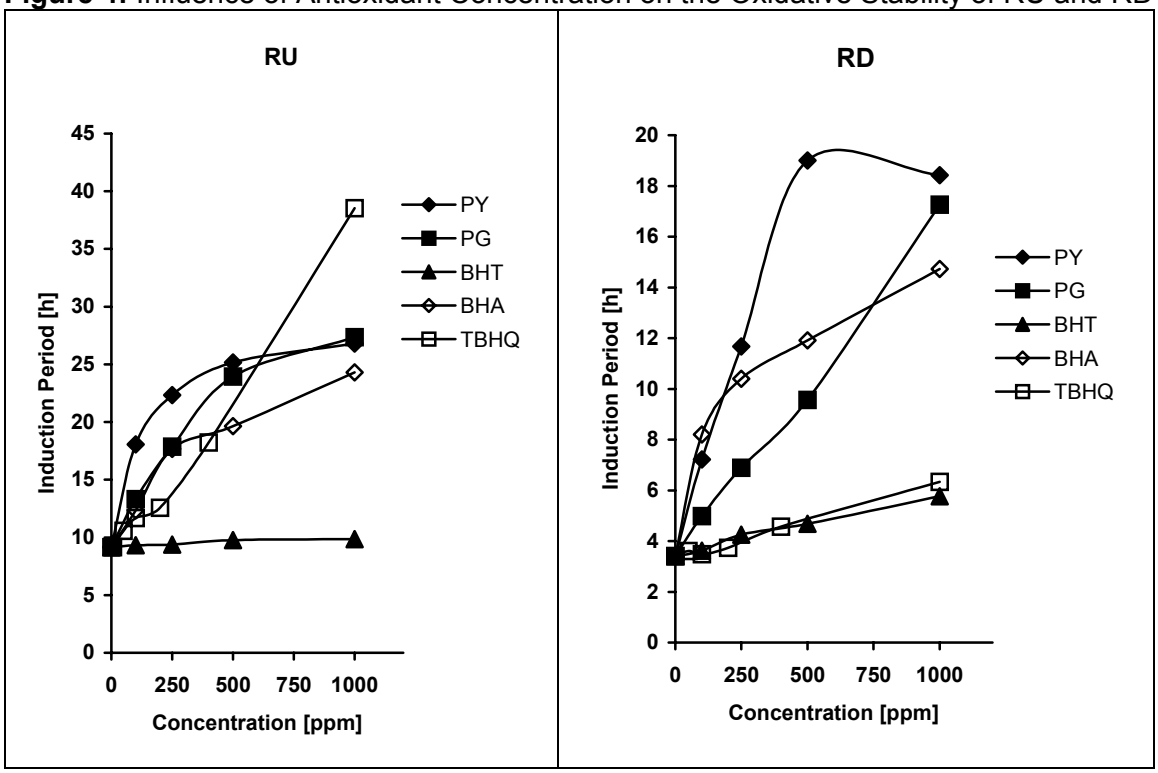


Figure 5: Influence of Antioxidant Concentration on the Oxidative Stability of UU and UD

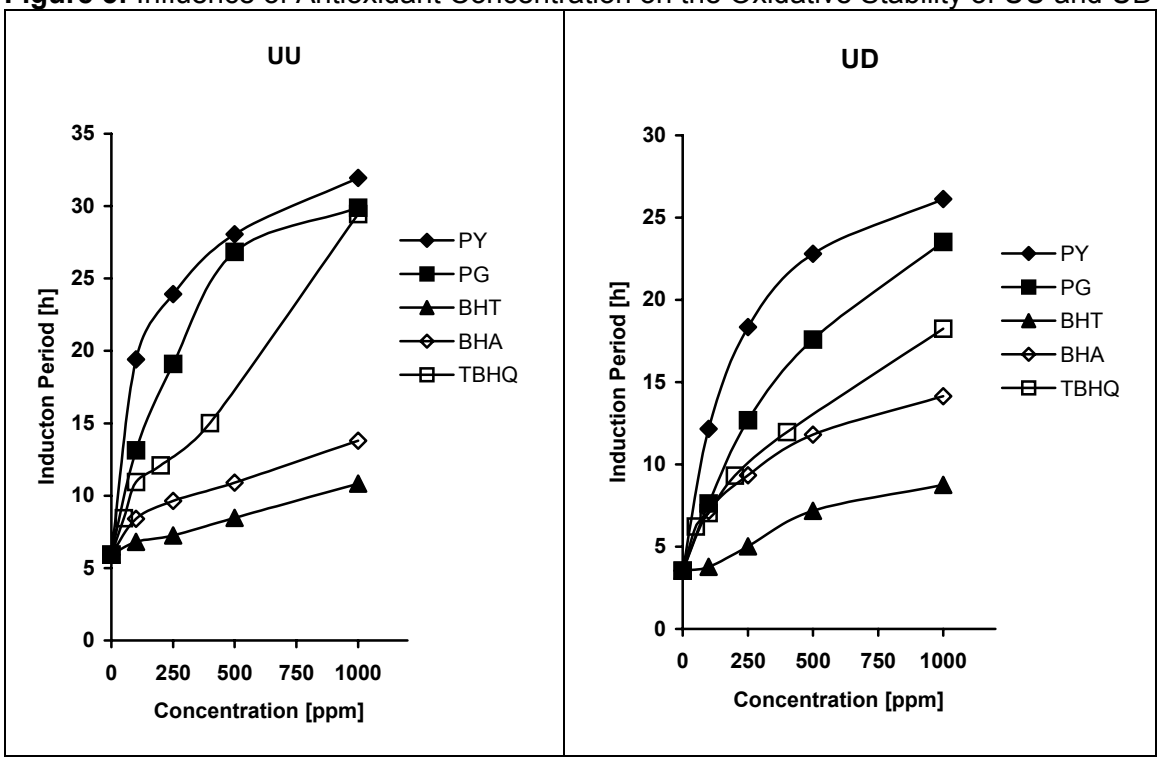


Figure 6: Influence of Antioxidant Concentration on the Oxidative Stability of SU and SD

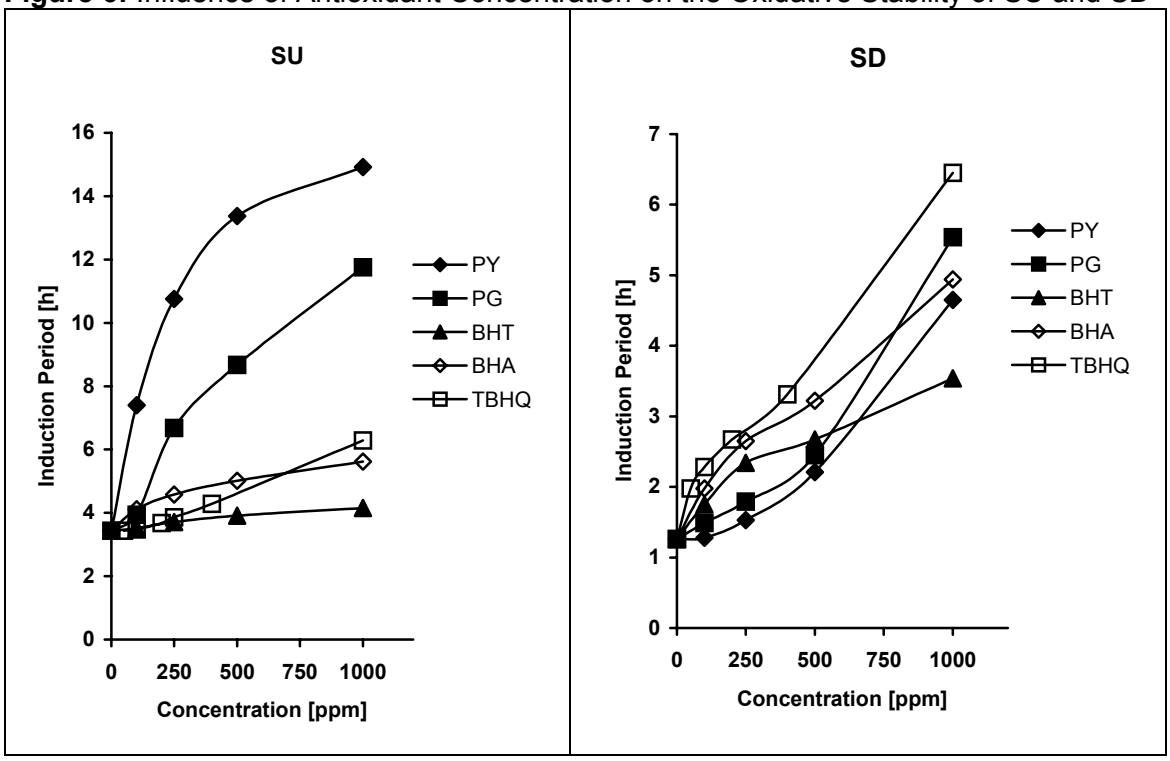
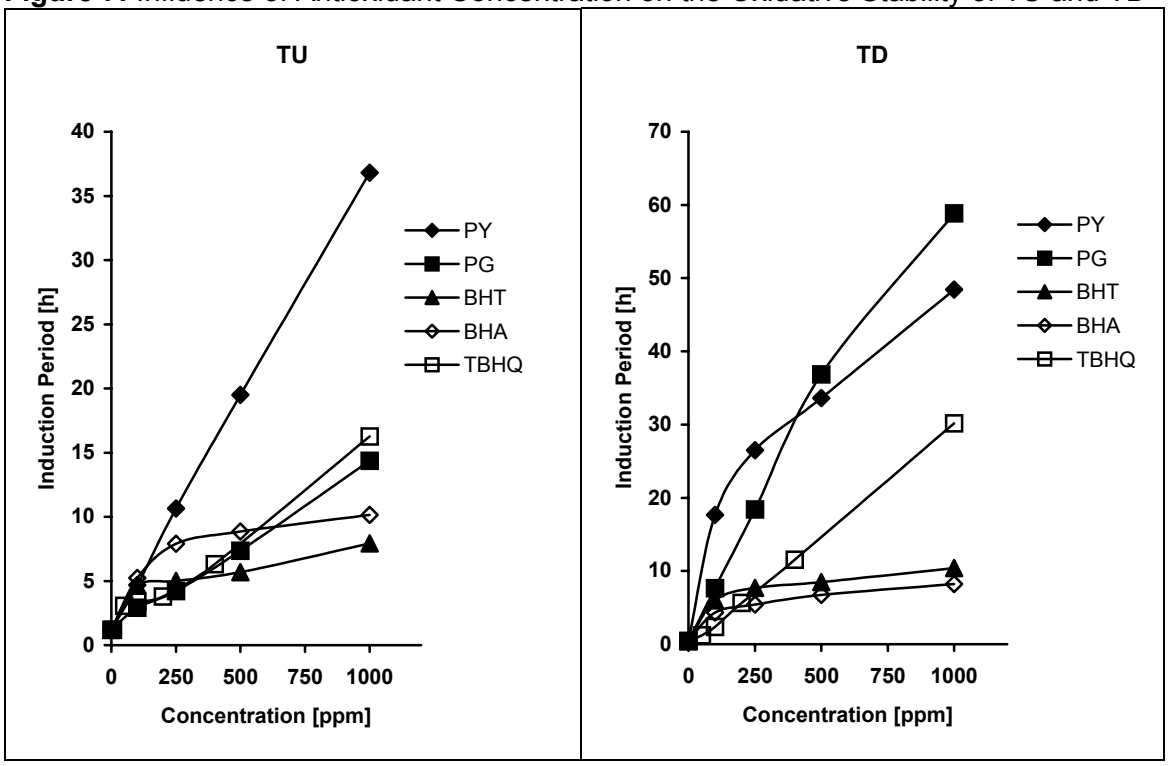


Figure 7: Influence of Antioxidant Concentration on the Oxidative Stability of TU and TD



Influence of antioxidants on biodiesel quality parameters

To ensure that the addition of antioxidants to biodiesel had no negative influence on fuel behavior, selected parameters of prEN 14214 were checked in order to determine possible changes. Results are listed in tables 4-9. Antioxidant concentration was set at 1000 ppm.

Table 4: Influence of Antioxidants on CCR of 100% Sample [%m/m]

Antioxidant	UD	UU	RD	RU	TD	TU	SD	SU
Reference[a]	<0.005	0.04	0.01	0.01	<0.005	0.01	0.01	0.02
Pyrogallol	0.01	0.03	0.03	0.02	0.01	0.01	0.01	0.02
Propylgallate	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.01
BHA	0.015	0.02	0.01	0.03	0.01	0.01	0.015	0.02
BHT	0.005	0.03	0.01	0.03	0.01	0.01	0.016	0.02
TBHQ	0.01	0.04	0.02	0.01	0.005	0.01	0.03	0.03

[a]Reference: Biodiesel without Antioxidant

On the whole, only a slight influence on CCR could be observed at some samples, but all values were within the specifications.

Table 5: Influence of Antioxidants on Viscosity at 40°C [mm^2/s]

Antioxidant	UD	UU	RD	RU	TD	TU	SD	SU
Reference[a]	4.27	4.63	4.22	4.24	4.45	4.57	3.88	3.93
Pyrogallol	4.29	4.64	4.20	4.27	4.48	4.59	3.89	3.96
Propylgallate	4.29	4.64	4.20	4.27	4.47	4.60	3.90	3.95
BHA	4.33	4.65	4.21	4.30	4.50	4.59	3.89	3.98
BHT	4.29	4.64	4.19	4.29	4.46	4.57	3.87	3.96
TBHQ	4.30	4.61	4.23	4.26	4.48	4.62	3.94	3.98

[a]Reference: Biodiesel without Antioxidant

Only a small variation of viscosity could be observed, but all samples met the specifications.

Table 6: Influence of Antioxidants on Density at 20°C [g/cm^3]

Antioxidant	UD	UU	RD	RU	TD	TU	SD	SU
Reference[a]	0.8802	0.8809	0.8819	0.8796	0.8723	0.8756	0.8829	0.8836
Pyrogallol	0.8808	0.8829	0.8824	0.8852	0.8736	0.8783	0.8844	0.8850
Propylgallate	0.8792	0.8835	0.8820	0.8832	0.8738	0.8723	0.8792	0.8837
BHA	0.8798	0.8796	0.8817	0.8815	0.8697	0.8748	0.8827	0.8844
BHT	0.8824	0.8843	0.8853	0.8841	0.8769	0.8725	0.8861	0.8877
TBHQ	0.8742	0.8808	0.8736	0.8829	0.8631	0.8779	0.8772	0.8861

[a]Reference: Biodiesel without Antioxidant

No negative influence of antioxidants on density could be observed.

Table 7: Influence of Antioxidants on Acid No. [mgKOH/g]

Antioxidant	UD	UU	RD	RU	TD	TU	SD	SU
Reference[a]	0.28	0.36	0.57	0.37	0.26	0.26	0.20	0.41
Pyrogallo	0.46	0.25	0.62	0.88	0.39	0.43	0.41	0.53
Propylgallate	0.51	0.49	0.68	0.84	0.59	0.75	0.58	0.62
BHA	0.32	0.29	0.38	0.38	0.30	0.36	0.15	0.33
BHT	0.28	0.26	0.48	0.33	0.28	0.35	0.14	0.31
TBHQ	0.38	0.28	0.58	0.48	0.36	0.42	0.17	0.38

[a]Reference: Biodiesel without Antioxidant

Pyrogallol and especially propyl-gallate showed negative effects on acid no. of some Biodiesel samples. Some values were significantly out of specifications. Therefore the Acid Numbers were checked again at lowest possible antioxidant concentration (250 ppm). Results are listed in table 7a.

Table 7a: Influence of Antioxidants (250 mg/kg) on Acid No. [mgKOH/g]

Antioxidant	UD	UU	RD	RU	TD	TU	SD	SU
Reference[a]	0.28	0.36	0.57	0.37	0.26	0.26	0.20	0.41
Pyrogallol	0.33	0.33	0.60	0.41	0.28	0.31	0.26	0.44
Propylgallate	0.30	0.41	0.62	0.46	0.34	0.38	0.26	0.43

[a]Reference: Biodiesel without Antioxidant

At lower antioxidant concentration only a slight increase of Acid Number could be observed. All samples were within the specification limit except RD, whereas already the reference sample was out of specifications.

Table 8: Influence of Antioxidants on CFPP [°C]

Antioxidant	UD	UU	RD	RU	TD	TU	SD	SU
Reference[a]	-1	0	-1	-10	15	11	0	0
Pyrogallol	-2	-1	1	-9	14	12	-1	0
Propylgallate	-2	-1	1	-10	14	12	-2	1
BHA	1	0	2	-10	16	12	-1	1
BHT	-1	0	1	-10	16	12	0	2
TBHQ	-1	1	0	-10	15	13	0	-2

[a]Reference: Biodiesel without Antioxidant

A slight increase/decrease of CFPP could be observed.

Table 9: Influence of Antioxidants on Sulphated Ash [%m/m]

Antioxidant	UD	UU	RD	RU	TD	TU	SD	SU
Reference[a]	0.001	0.002	0.001	0.006	0.005	0.006	0.002	0.002
Pyrogallol	0.001	0.001	0.003	0.002	0.008	0.002	0.001	0.002
Propylgallate	0.001	0.001	0.003	0.002	0.001	0.002	0.002	0.002
BHA	<0.001	<0.001	0.003	0.005	<0.001	0.002	0.006	0.002
BHT	0.001	0.001	0.003	0.003	0.001	0.001	0.001	0.001
TBHQ	0.001	0.001	0.002	0.002	0.001	0.001	0.002	0.001

[a]Reference: Biodiesel without Antioxidant

No significant influence of antioxidants on sulphated ash values was observed.

4 SUMMARY AND CONCLUSIONS

The influence of different antioxidants on the oxidative stability of biodiesel prepared from different feedstocks was investigated. The results can be interpreted as follows:

- Generally, the limit for the proposed oxidative stability could be reached by addition of antioxidants with all different types of biodiesel.
- Within the variety of antioxidants, synthetic antioxidants were more effective than natural.
- The efficiency and the necessary amount of the different antioxidants are strongly dependent on the feedstock and production technology used for biodiesel production.
- Under the given conditions, no significant negative influence of antioxidants on fuel behaviour could be observed. Influences of additives on engine performance have **not** been investigated within the project. However, to minimize possible negative effects it is recommended to use antioxidants at very low concentrations.

WARNING: The present paper does not include any recommendations for the use of specific antioxidants. Long term engine tests have to be carried out in order to study the influence of synthetic antioxidants on engine performance.

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6 ANNEXES

Annex 1: Fatty Acid Composition of Biodiesel Samples.

Fatty acid	RU (% m/m)	RD (% m/m)	SU (% m/m)	SD (% m/m)	UU (% m/m)	UD (% m/m)	TU (% m/m)	TD (% m/m)
C 14:0	0.09	n.d.	n.d.[a]	n.d.	0.41	0.27	2.20	2.84
C 16:0	5.95	2.05	5.98	7.22	14.38	11.55	21.88	25.61
C 16:1	n.d.	n.d.	n.d.	n.d.	0.39	0.34	1.57	2.11
C 18:0	2.07	2.61	4.66	4.20	4.26	4.43	17.03	21.95
C 18:1	60.34	62.20	23.95	27.40	57.17	58.04	45.12	37.61
C 18:2	20.87	21.05	63.74	61.18	17.08	19.18	8.05	4.71
C 18:3	8.15	7.90	n.d.	n.d.	2.08	2.25	1.09	0.58
C 20:0	0.61	1.02	0.29	n.d.	0.53	0.50	n.d.	n.d.
C 20:1	1.27	2.10	0.23	n.d.	0.88	0.92	n.d.	n.d.
C 22:0	0.34	0.55	0.77	n.d.	0.67	0.42	n.d.	n.d.
C 22:1	0.19	0.39	n.d.	n.d.	n.d.	0.21	n.d.	n.d.
Not identified	0.12	0.13	0.38	--	2.15	1.89	3.06	4.59

[a]n.d., Not detectable

Annex 2: Analysis Data of Biodiesel Samples

Parameter	Method[a]	Units	RU[b]	RD[b]	SU[b]	SD[b]	UU[b]	UD[b]	TU[b]	TD[b]	prEN 14214
Density at 15°C	EN ISO 3675	[kg/m^3]	879.9	881.9	883.6	882.9	880.9	880.2	875.6	872.3	860-900
Viscosity at 40°C	EN ISO 3104	[mm^2/s]	4.24	4.22	3.93	3.88	4.63	4.27	4.57	4.45	3.50-5.00
CFPP	EN 116	[°C]	-10	-1	0	0	0	-1	+15	+11	0/-20
Flash point	DIN EN 22719[c]	[°C]	164	165	145	146	166	169	167	168	≥ 120
Sulfur content	DIN EN ISO 14596	[mg/kg]	4	2	2	1	8	3	9	3	≤10
Carbon residue of 100%	DIN EN ISO 10370[c]	[%m/m]	0.01	0.01	0.02	0.01	0.04	<0.005	0.01	<0.005	≤ 0.3
Sulfated ash	ISO 3987	[%m/m]]	0.006	0.001	0.002	0.002	0.002	0.001	0.006	0.005	≤ 0.02
Water content	EN ISO 12937	[mg/kg]	300	200	200	100	400	100	200	200	≤ 500
Total contamination	EN 12662	[mg/kg]	6	6	8	3	7	15	11	2	≤ 24
Acid value	prEN 14104	[mgKOH/g]	0.37	0.57	0.41	0.2	0.36	0.28	0.26	0.26	≤ 0.50
Oxidation stability	prEN 14112	[h]	9,1	3,4	3,4	1,2	5,9	3,5	1,2	0,4	≥ 6
Methanol content	prEN 14110	[%m/m]	0.04	n.d.[d]	n.d	n.d.	0.03	n.d.	n.d.	n.d.	≤ 0.20
Ester content	prEN 14103	[%m/m]	98.2	99.0	99.6	99.9	95.4	98.7	93.5	94.2	≥ 96.5
Monoglycerides	prEN 14105	[%m/m]	n.d.	n.d.	0.02	0.006	0.165	n.d.	n.d.	n.d.	≤ 0.80
Diglycerides	prEN 14105	[%m/m]	n.d.	n.d.	0.038	n.d.	n.d.	n.d.	n.d.	n.d.	≤ 0.20
Triglycerides	prEN 14105	[%m/m]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	≤ 0.20
Free Glycerol	prEN 14105	[%m/m]	n.d.	0.0025	0.003	0.011	0.003	n.d.	n.d.	n.d.	≤ 0.02
Total Glycerol	prEN 14105	[%m/m]	n.d.	0.0025	0.014	0.013	0.046	n.d.	n.d.	n.d.	≤ 0.25
Iodine value	prEN 14111	[gI_2/100g]	112.9	112.5	124.4	125.7	88.7	90.2	55.8	44.1	≤ 120
Phosphorus content	pr EN 14107	[mg/kg]	1	<1	<1	<1	<1	<1	<1	<1	≤ 10
Alkaline metals (Na+K)	pr EN 14108 (Na) pr EN 14109 (K)	[mg/kg]	0.1 + 1.2	0.6 + 0.05	0.1 + 0.7	0.5 + 0.1	0.2 + 1.5	0.3 + 0.1	0.1 + 0.5	0.4 + 0.6	≤ 5

[a]Reference (12) unless otherwise modified
[b]Abbreviations: RU, rapeseed oil methyl ester; RD, distilled RU; SU, sunflower oil methyl ester; SD, distilled SU; UU, used frying oil methyl ester; UD, distilled UU; TU, beef tallow methyl ester; TD, distilled TU
[c]Reference (13)
[d]n.d., Not detectable

NATURAL ANTIOXIDANTS

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1 OBJECTIVES

To investigate the influence of natural antioxidants on the oxidation stability of fuel grade biodiesel.

2 METHODOLOGY

Tocopherols, α-, γ- and δ- and carotenoids, carotene retinoic acid and astaxanthin were obtained from Sigma-Aldrich (Ireland) Ltd.. SME (sunflower methyl ester) RME (rape methyl ester) WCOME (waste cooking oil methyl ester) and TME (tallow methyl ester) were prepared from commercial oils and tallow and CME (camelina methyl ester) from oil pressed at Oak Park, according to a reported method (Frohlich and Rice, 1995). Tocopherols in the methyl esters were deactivated by heating at 110°C with gentle stirring for about 20 minutes, and the loss of tocopherols was monitored by HPLC. After the deactivation of tocopherols the methyl esters were destabilised by stirring at 100-110°C, until peroxide levels increased to 30-35 mg/kg. When peroxide levels are above 30 mmole/kg. the viscosity of the methyl ester increases after one day at 65°C.

Required amounts of tocopherols and carotenoids were weighed directly into the destabilised methyl ester. Oxidation of the methyl ester was carried out according to the Schaal accelerated storage test (Jacobs,1958). Eight 25 g samples were stored for 8 days at 65°C in 250 ml beakers of identical geometry, covered with watch glasses. Samples were taken daily. Peroxide and free fatty acid levels and viscosities were determined by standard methods (AOAC 1984). Tocopherols were determined by HPLC. at 295 nm, with amino- reverse phase column (25 cm), and 80:20 hexane-ethyl acetate mobile phase (Simkovski, 1999). Coloured compounds in RME made from unrefined rape oil were separated with the same column, but the detector wavelength was 448 nm, and the mobile phase 50:50 hexane ethyl acetate. The efficiency of antioxidants was determined from the period of stability, defined as the time in days required to reach an increase of viscosity reached by destabilised methyl ester (0.5 cSt) after 1 day at 65°C.

3 RESULTS

Tocopherols:

Effect of tocopherols on the stability of SME

The effect of tocopherols on the oxidation rate of SME is shown in the tables 1-3. Considering that atmospheric oxidation of fatty acid methyl esters leads to the formation of oligomers and polymers, which increase viscosity, viscosity was used initially as the indicator of oxidation. Monitoring of viscosity during exposure to air at 65°C shows that all three tocopherols delay oxidation (tables 1-3). The period of stability, the period when viscosity is less than 0.5 cSt higher than the initial value, seems to depend on the type and amount of antioxidant added. At

natural antioxidant levels, 250-500 mg/kg of α-tocopherol in SME, the stability is about the same as before destabilisation, and viscosities start to increase after 1 day in accelerated storage. At higher tocopherol levels however, viscosities can remain stable (<0.5 cSt increase) for a much longer period.

Table 1: Accelerated storage of SME, α-tocopherol levels vs. increase of viscosity[a]

α-Tocopherol [mg/kg]									
	0	250		500		1000		2000	
Day	Viscosity [cSt]	Viscosity [cSt]	Tocoph. Level [mg/kg]	Viscosity [cSt]	Tocoph. Level [mg/kg]	Viscosity [cSt]	Tocoph. Level [mg/kg]	Viscosity [cSt]	Tocoph. Level [mg/kg]
1	0.48	**0.04**[b]	36	**0.06**	47	**0.02**	485	**0.05**	1074
2	0.90	1.12	11	**0.40**	11	**0.06**	383	**0.12**	869
3	1.29	1.83	n.d.[c]	1.50	n.d.	**0.12**	346	**0.22**	728
4	2.75	3.58	n.d.	1.62	n.d.	**0.22**	287	**0.32**	418
5	3.81	5.03	n.d.	3.33	n.d.	**0.24**	160	**0.40**	418
6	4.88	7.37	n.d.	4.67	n.d.	**0.26**	78	**0.46**	300
7	6.83	8.28	n.d.	5.90	n.d.	0.77	n.d.	**0.49**	261
8	8.41	13.77	n.d.	9.60	n.d.	1.75	n.d.	0.80	15

[a]Increase of viscosity = (viscosity day n) – (viscosity day 0)
[b] period of stability, increase of viscosity < 0.5 cSt, in bold
[c]abbreviations: n.d., not detected

Of the three antioxidants, γ tocopherol proved to be the most effective. A concentration of 250 mg/kg of γ-tocopherol stabilised SME for 6 days (table 3), whereas the same amounts of α- and δ- tocopherols had stabilising effects of only 1 (table 1) and 2 days (table 2) respectively. The stabilising effect also increased with the amount of antioxidant, but little additional stability was gained above 1000 mg/kg of α- and 500 mg/kg of δ-tocopherols. At all levels of α-tocopherol viscosity starts to increase very slowly after day 1, whereas with δ- and γ-tocopherols, particularly at higher levels, it remains stable for several days.

Table 2: Accelerated storage of SME, δ-tocopherol levels vs. increase of viscosity[a]

δ-Tocopherol [mg/kg]									
	0	250		500		1000		2000	
Day	Viscosity [cps]	Viscosity [cps]	Tocoph. level [mg/kg]	Viscosity [cps]	Tocoph. level [mg/kg]	Viscosity [cps]	Tocoph. level [mg/kg]	Viscosity [cps]	Tocoph. level [mg/kg]
1	0.48	**0.12**[b]	66	**0.01**	364	**0.04**	535	**0.06**	1268
2	0.90	**0.28**	47	**0.10**	229	**012**	446	**0.09**	1027
3	1.29	**0.34**	39	**0.11**	217	**0.08**	422	**0.09**	951
4	2.75	0.89	11	**0.21**	93	**0.12**	345	**0.13**	772
5	3.81	0.96	n.d.[c]	**0.22**	89	**0.21**	254	**0.19**	583
6	4.88	1.72	n.d.	**0.36**	52	**0.30**	149	**0.25**	562
7	6.83	2.39	n.d.	**0.43**	43	**0.37**	128	**0.29**	407
8	8.41	3.71	n.d.	0.77	23	**0.49**	68	**0.39**	140

[a]Increase of viscosity = (viscosity day n) – (viscosity day 0)
[b] period of stability, increase of viscosity < 0.5 cSt, in bold
[c]abbreviations: n.d., not detected

Table 3: Accelerated storage of SME, γ-tocopherol levels vs. increase of viscosity[a]

γ-Tocopherol [mg/kg]							
	0	250		500		1000	
Day	Viscosity [cps]	Viscosity [cps]	Tocoph. level [mg/kg]	Viscosity [cps]	Tocoph. level [mg/kg]	Viscosity [cps]	Tocoph. level [mg/kg]
1	0.48	**0.00**[b]	128	**0.00**	227	**0.05**	532
2	0.90	**0.00**	80	**0.04**	202	**0.06**	426
3	1.29	**0.01**	*57*[c]	**0.07**	120	**0.07**	323
4	2.75	**0.07**	*57*	**0.02**	*88*	**0.05**	226
5	3.81	**0.15**	*63*	**0.07**	*88*	**0.15**	178
6	4.88	**0.23**	*63*	**0.31**	*67*	**0.15**	*98*
7	6.83	0.50	*63*	**0.23**	*67*	**0.30**	*67*
8	8.41	1.00	*25*	**0.23**	*67*	**0.14**	143

[a]Increase of viscosity = (viscosity day n) – (viscosity day 0)
[b] period of stability, increase of viscosity < 0.5 cSt, in bold
[c]values in *italic:* tocopherol determinations not accurate because HPLC peaks changed shape

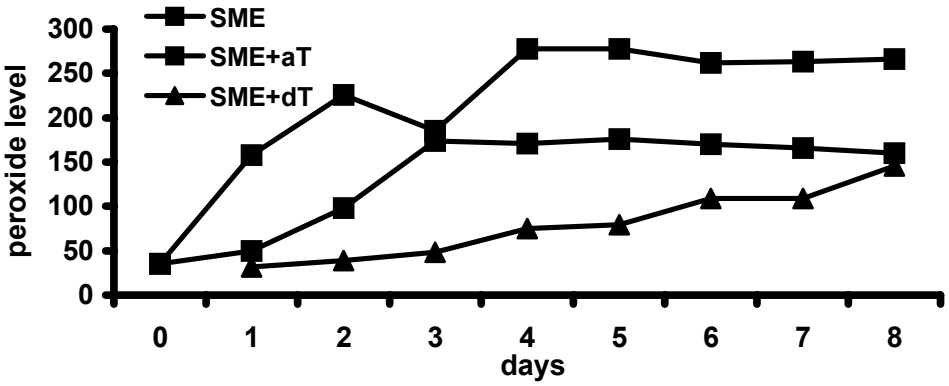
In all samples tocopherol levels decreased during accelerated storage, but not at a uniform rate (tables 1-3). Generally 50% of the antioxidant was lost after the first day, but losses were more gradual thereafter. According to the obtained data tocopherols did not entirely prevent viscosity increases, but the rate of increase is much slower (0.01-0.2cps/day) while they are present. This is particularly noticeable in the case of α-tocopherol, where the daily increase of viscosity is below 0.1cps while the antioxidant remains above 100 mg/kg (table 1). Once the tocopherols are exhausted viscosity increases at about the same rate as that of destabilised SME. The period of stability more or less corresponded to the time when effective amounts of antioxidants are present in the methyl ester.

Stabilisation of methyl esters with δ-tocopherol:
Stabilisation of methyl esters other than SME namely RME, WCOME and TME with tocopherol was also investigated. δ-Tocopherol was used, because it is more effective than α-tocopherol and concentrations could be determined more accurately than for γ-tocopherol. δ-Tocopherol, 1000 mg/kg, was added to the methyl esters and they were oxidised for 8 days as per SME. It was not possible to obtain exact stabilisation times as before because none of the methyl esters reached a viscosity increase of 0.5 cSt after 8 days of oxidation. However oxidation indicators such as peroxide levels and antioxidant losses after 8 days of oxidation could be used to estimate comparative stabilising effects.

The stabilising effect of δ-tocopherol, and possibly of other tocopherols, seemed to depend on the composition of the methyl ester. The antioxidant was considerably more effective in stabilising TME WCOME, and RME than SME. About 93% of the tocopherol of SME was lost and peroxide level increased to 115 mmole/kg after 8 days of oxidation, whereas 83% of the tocopherol remained in TME, and there was no increase in peroxide level during the same period. Peroxide increase and tocopherol losses in RME and WCOME were between the two extremes. Hence it can be concluded that the stabilising effect of δ-tocopherol in the four methyl esters is of the order of TME>WCOME>RME>SME.

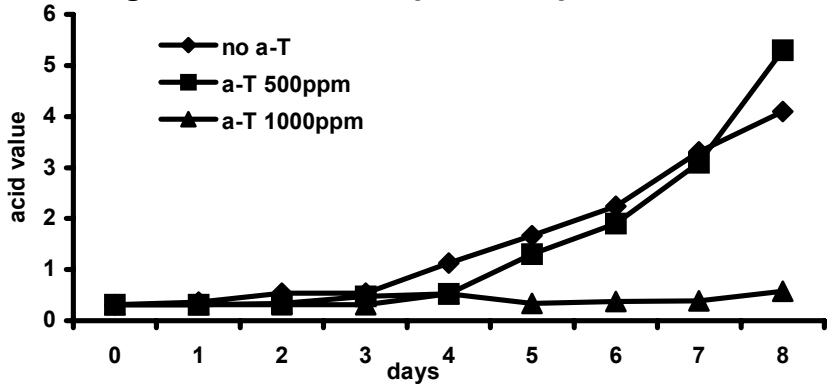
Effect of tocopherols on peroxide levels:
Monitoring of peroxide levels indicates that the effect of tocopherols on oxidation is to slow down the build up of peroxides, which in turn delays increase of viscosity. Seemingly, a certain "critical" peroxide level must be reached before there is a significant increase of viscosity, possibly over 100 mmole/kg in SME but lower in RME, WCOME and TME. Tocopherols extend the time needed to reach the "critical" peroxide level. In general over 100 mmole/kg is not reached while effective amounts of antioxidants remain in the methyl ester. The delaying effect depends on the type of tocopherol. Destabilised SME reaches a peroxide level of 150 mmole/kg after only 1 day of oxidation whereas with 500 mg/kg α-tocopherol takes 3 and the same amount of δ-tocopherol 8 days to reach the same level (figure 1).

figure 1: Effect of 500 ppm of alpha and delta Tocopherols on peroxide levels



Effect of tocopherols on FFA levels:
Along with peroxides FFAs (free fatty acids, expressed here as acid values) also increase (figure 2). FFAs are formed when peroxides are converted into secondary oxidation products, and their increase indicates that secondary oxidation is taking place. While tocopherols are present there is no significant increase of FFAs, and acid values remain below 0.5, the specified maximum. However once the tocopherols are lost FFAs begin to rise and continue to rise more rapidly as the oxidation progresses.

figure 2: Effect of alpha Tocopherol on FFA levels



Carotenoids

Effects of carotenoids on stability:
The antioxidant effect of β-carotene in combination with γ-tocopherol has been reported before (Henry, 1998). Similarly we have shown that RME is considerably more stable than CME during oxidation although their tocopherol composition, particularly γ-tocopherol level were almost identical (Frohlich, 1999). RME made from unrefined oil however showed a much higher absorbance at 448 nm than CME, and the absorbance decreased along with tocopherols during oxidation. Visible spectrum of RME showed three absorbtion maxima at 423, 448 and 475 nm, indicating the presence of a carotenoid, which could contribute to the stabilisation of the methyl ester.

Astaxanthin and retinoic acid:
Initially the effect of a strong carotenoid antioxidant, astaxanthin (Schroeder and Johnson, 1995), and a carotene derivative, retinoic acid were investigated. The carotenoids were added to destabilised SME at the rate of 500 and 100 mg/kg, and were oxidised for 8 days. Neither retinoic acid nor asthaxanthin had any effect on the stability of the methyl esters, both viscosities and peroxide levels increased at the same rate as in the SME before the addition of carotenoids.

β-Carotene:
The effect of β-carotene was also examined because it was reported to be present in rapeseed oil (Patterson, 1989), and we could also detect it in RME. Hence if carotene stabilises RME it should also stabilise CME which has similar tocopherol composition. Sufficient carotene was added to CME to give the same absorbance as RME at 448 nm and some α-tocopherol was also added to obtain the same tocopherol composition. In addition β-carotene was added to CME to give a carotene level higher and lower than found in RME. Oxidation of the samples with added β-carotene and the corresponding controls indicated that β-carotene did not improve the stability of CME, irrespective of the amounts added, or if tocopherol levels were increased. The CME samples with added β-carotene had approximately the same rate of increase of viscosity as destabilised CME (table 4).

Table 4: Effects of carotene on the stability of CME, viscosity during accelerated storage[a]

Day	CME natural	+α-Tocopherol	+α-Tocopherol +carotene	CME destabilised
2	0.14	0.03	0.26	0.32
4	0.34	0.27	0.62	0.76
6	0.85	0.64	0.86	1.45
8	1.15	1.82	1.50	2.66

Day	CME natural	+Carotene 10 mg/kg	+Carotene 100 mg/kg	CME destabilised
2	0.14	0.31	0.32	0.32
4	0.34	0.64	0.62	0.76
6	0.85	1.18	1.75	1.45
8	1.15	2.68		2.66

[a]viscosity difference [cSt]

Identification of other carotenoids:

Considering that carotene did not stabilise RME, attempts were made to identify similar antioxidants, by separating the orange coloured compounds in RME by HPLC. Conditions used for the separation of tocopherols at 448 nm showed only carotene, but with a more polar mobile phase, five orange compounds were separated. Carotene accounted for only about 10-15% of the peak area of the separated compounds, and about 70% were due to a single compound with much higher retention time than carotene. The other three compounds were present in smaller amounts.

The detected compound was present in RME from different sources at about the same level (relative to carotene) as tocopherols (table 5). Very small amount of the compound was present in CME, it was absent from TME and SME, and only 10% of the compound was left in RME after heating for 3 hrs at 110 °C. In addition, when RME with high absorbance at 448 nm (prepared from raw oil) was heated at 110°C 5 hrs were required to remove the tocopherols, whereas from RME with low absorbance (prepared from refined oil) tocopherols were removed within 20 minutes. The results seem to indicate that along with tocopherols the detected compound also stabilises RME. Consequently absence of tocopherols and low absorbance at 448nm (<0.05au) should indicate that the particular methyl ester is destabilised

Table 5: Compound detected at 448 nm and β-carotene in different methyl esters.

Methyl Ester	Absorbance 450 nm[a]	β-Carotene [mg/kg]	Detected compound[b]	Peak area of det. comp.(% of total)
RME G	0.57	47	247	67
RME W01	0.38	31	140	63
RME W98	0.53	83	316	70
SME G	0.01	n.d.[c]	n.d.	
CME OP	0.08	n.d.	17	100
TME G	0.01	n.d.	n.d.	
RME W01 (heated at 110°C)	0.11	n.d.	17	

[a]10% solution in hexane
[b]mg/kg β-carotene used as reference
[c]abbreviations: n.d., not detected

To test our hypothesis tocopherols were removed from RME made from refined rapeseed oil, which has a very low absorbance at 448 nm, by heating at 110°C with gentle stirring. Some of the tocopherol free RME was heated for another 3 hrs. Oxidation stability was tested by accelerated storage and viscosity was monitored. Contrary to expectations the RME was not destabilized and the viscosities remained constant 5 days (table 6). However the viscosity of RME heated for 3hrs after the removal of tocopherols increased after 1 day in accelerated storage, and it continued to increase during the 8 days period. Consequently tocopherols and the detected compound are probably not the only antioxidants in RME. The work on the stability of RME is being continued.

Table 6: Accelerated storage of destabilised RME, viscosity differences[a]

Day	RME, tocopherols and colour removed	RME, heated at 110°C for additional 3 hrs
1	0.00	0.70
2	0.07	1.13
3	0.06	1.51
4	0.16	2.13
5	0.30	2.72
6	0.59	3.38
7	1.39	3.96
8	1.52	4.84

[a]viscosity difference = (viscosity day n) – (viscosity day 0)

4 SUMMARY AND CONCLUSIONS

Tocopherols, α-, δ-, and γ- delay the oxidation of SME, RME, WCOME and TME, in some cases by more than a factor of 10 compared to methyl esters without tocopherols. γ-Tocopherol was found to be the most effective of the three, α-tocopherol the least, and their antioxidant effect increased with concentration up to an optimum level. Above the optimum level the increase in antioxidant effect with concentration is relatively small. The stabilising effect of tocopherols was also found to depend on the composition of the methyl ester, the order of effectiveness was found to be: TME>WCOME>RME>SME.

Oxidation of methyl esters begins with the build-up of peroxides; viscosity starts to increase only after the peroxides reach a certain level. Tocopherols stabilise the methyl esters by reducing the rate of peroxide formation, thereby extending the time needed to reach the peroxide level where viscosity starts to increase.

The carotenoids astaxanthin and retinoic acid had no detectable effect on the stability of SME. Similarly β-carotene added to CME along with some α-tocopherol, to give the same maximum absorbance at 448 nm as RME, had no stabilising effect on the methyl ester. However a carotenoid, at much higher level than β-carotene, was detected in RME, but it was not present in less stable methyl esters such as CME and SME. The effect of the detected carotenoid on the stability of RME is being investigated.

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Work Package 4.1

Biodiesel as Automotive Fuel

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BENCH TESTS

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1 OBJECTIVES

The aim of work package 4.1 is the investigation of the effects of the fuel stability on diesel engines and injection systems.

Several fuels with varying stability were used in bench and field tests. Tests were carried out on vehicles and vehicle injection systems. The results of the tests should help to find a relationship between laboratory test methods and effects of a low stability during the utilisation.

2 METHODOLOGY

Task 1: Bench tests: Altogether 3 different fuels were produced and delivered by NOVAOL in accordance with the results of WP1 and WP3 (**R**apeseed **M**ethyl **E**ster **RME** with a low, a standard and a high fuel stability). The fuels were tested in a long term test in 3 different modern injection systems by the TUG. Wear and sedimentation were analysed after the tests. Chemical analysis of the fuels accompanied the tests.

Injection system	Test no.	Test run	Duration [h]	Tested fuel	Induction period oft the fuel at start [h] Rancimat 110°C, prEN 14112
Heavy duty common rail, 6 cylinder	1a	Stationary test run	500	RME “low stability”	1.8
Heavy duty common rail, 6 cylinder	1b	Stationary test run	500	RME “high stability”	14.7
Passenger car distribution pump, 4 cylinder	2a	Dynamic test run	500	RME “standard stability”	6.6
Passenger car distribution pump, 4 cylinder	2b	Dynamic test run	500	RME “high stability”	18.37
Passenger car common rai, 4 cylinder	3a	Dynamic test run	500	RME “standard stability”	5.86
Passenger car common rail, 4 cylinder	3b	Dynamic test run	500	RME “high stability”	17.07
Passenger car common rail, 4 cylinder	3c	Dynamic test run	500	RME “low stability”	3.47

Table 1: injection system test runs

All systems were operated on the injection test bed of TUG. 75 litres of the test fuel were cycled through the injection system periodically.

The fuel quality fulfil the European biodiesel standard prEN 14214 besides two parameter. The fuel with a low stability exceeds the limit of oxidation stability (induction period < 6 h) and acid value (0.5 - 0.6 mg KOH/g). To reduce the stability the fuel was treated by temperature and air for a specific period of time. This special procedure was developed by BLT Wieselburg based on information from TEGASC in Ireland. To get a high fuel quality the fuel was additivated with an amount of 250 ppm Pyrogallol.
In test run 1a and 1b there was no fuel change planned during the complete test duration. So the conditions were much sharper than in practice. In all other test runs the fuel was changed every 50 hours (fuel volume: 75 lt.) to maintain constant fuel conditions over the complete test duration.

Engine tests: The fuels showing a low and high oxidation stability were also tested in two long term real world engine tests at a test bench. Direct injection diesel engine applied in a commercial passenger car and equipped with a modern common rail injection system were used.

Engine	**Test no.**	**Test run**	**Duration [h]**	**Tested fuel**	**Induction period oft the fuel at start [h]** Rancimat 110°C, prEN 14112
Di diesel engine, cr-injection system	1a	Dynamic test run	500 hours	RME "high stability"	20.00
Di diesel engine, cr-injection system	1b	Dynamic test run	500 hours	RME "low stability"	3.5

Table 2: engine long term test run

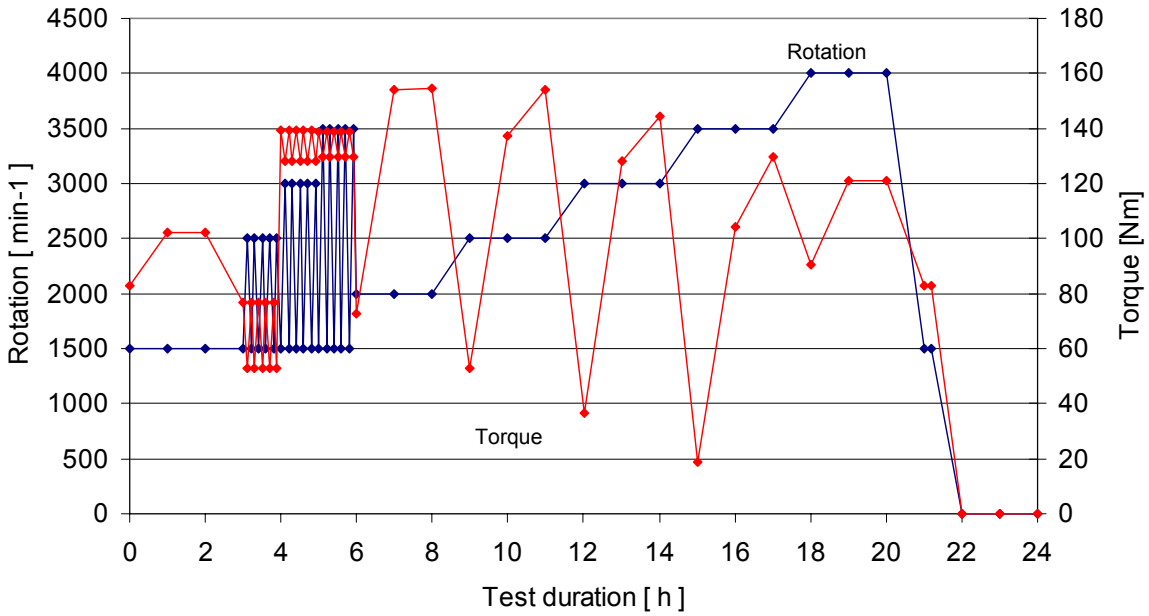


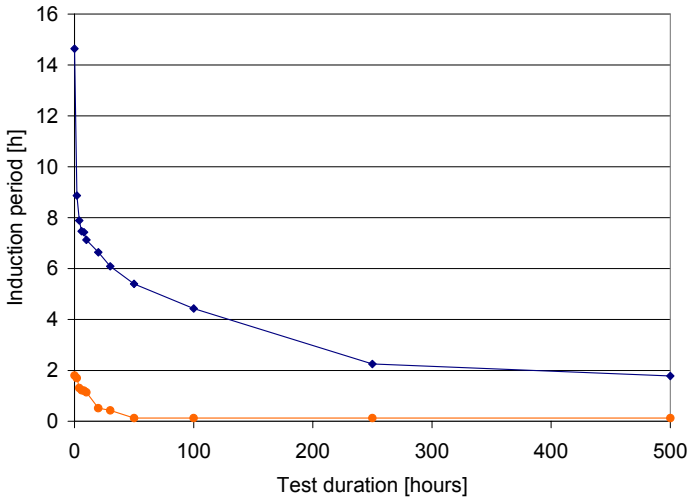
Figure 1: engine test bed; long term test run

3 RESULTS

3.1 Injection system bench tests

3.1.1 Heavy duty common rail system

The test duration at both test runs was 500 hours. At each test there was no fuel change planned during the complete test duration. Samples of the fuel were already analysed by the Institute of Chemistry of the University of Graz.

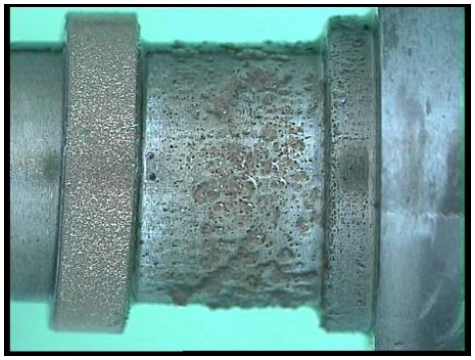


Parameter	RME low	RME high
Density [g/cm]	0,88	0,88
Viscosity [mm2/s]	4,26	4,26
CCR [%mass]	0,03	0,01
Polymer content [%]	3,4	2,7

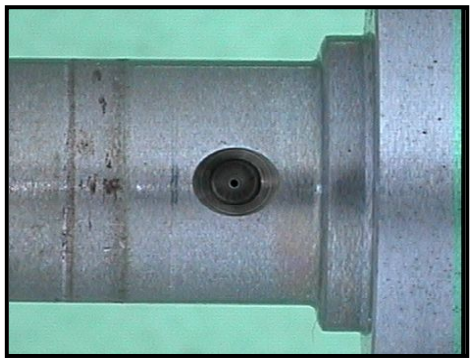
Figure 2: course of the fuel induction period (Rancimat 110°C, prEN 14112) over 500 hours test duration, fuel parameters at test run start

During the test run1a (fuel with low stability) two short term injectior failures occurred after 366 and 370 hours. In test run 1b (fuel with high stability) no problems arose over the complete test duration. Wear, sedimentation and function of all injectors were analysed by the manufacturer of the injection system. These investigations were done at 4 different check-points with standardised test oil on a standardised test bench to get results which can be reproduced. The objections (short term failures at test run 1) could not be reproduced because the injectors were flushed with test oil before running at the standardised test bench in order to prevent glueing by service lives. All injectors worked at that bench without any problems. The injection amount deviations proved to be normal for a 500 hour runtime, but they were clearly higher in the test run with low fuel quality than in that with a high fuel quality. The injector-needle residues were standard for a 500-hour runtime. In the test run with low fuel quality the needle residues were clearly higher. One injector operated with RME low quality sticked during the analyses. This was due to the fact that the injectors were dismantled and then stored till the analyses began. In that time remainders of RME firmly stuck the injector-needle.

All wearing parts show uncritical custom tracks. The fat-similar deposits at the injectors operated with low quality fuel are one feature which must be regarded critically. Such deposits can be the reason for the malfunction during the test run 1a (see picture 1 and 2).



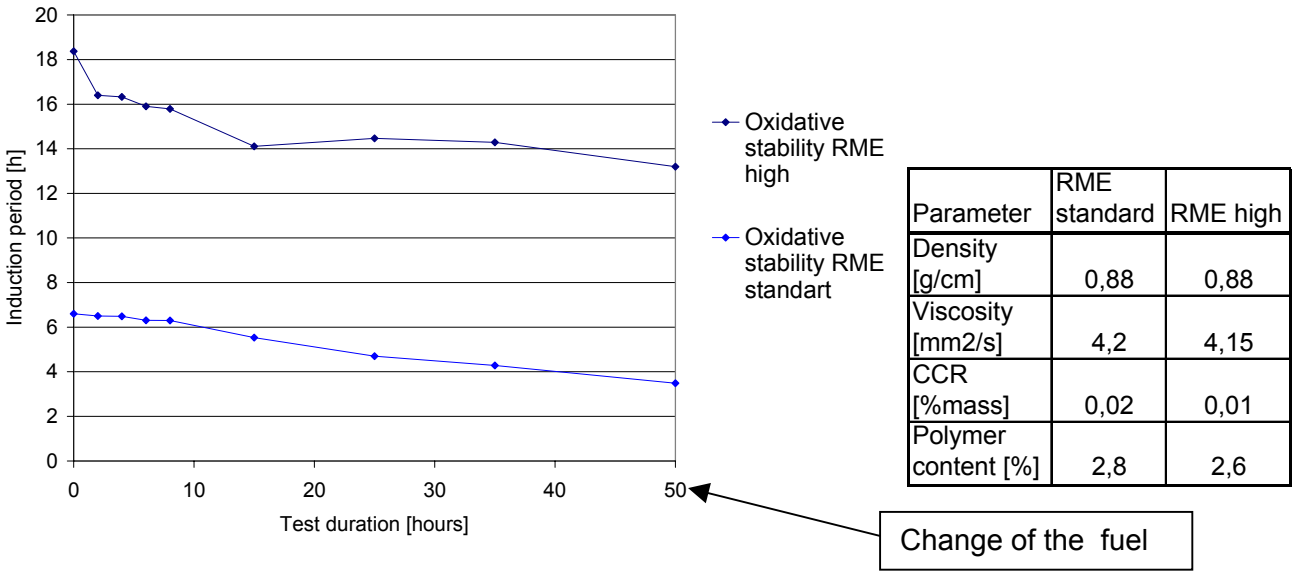
Picture 1: fat-similar deposits after test run 1a



Picture 2: deposit-free injector after test run 1b

3.1.2 Passenger car Distribution pump system

The passenger car injection systems were tested in dynamic long term test runs. The test duration was also 500 hours. To maintain constant fuel conditions over the complete test duration the fuel was changed every 50 hours.



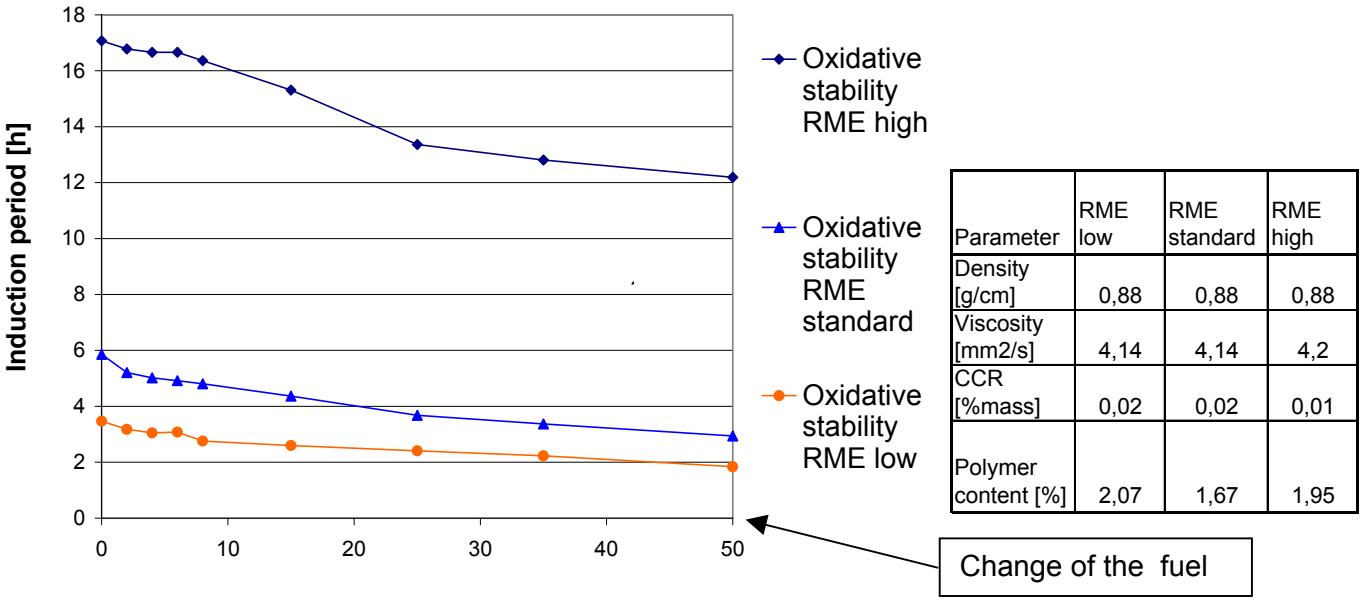
Parameter	RME standard	RME high
Density [g/cm]	0,88	0,88
Viscosity [mm2/s]	4,2	4,15
CCR [%mass]	0,02	0,01
Polymer content [%]	2,8	2,6

Figure 3: course of the fuel induction period (Rancimat 110°C, prEN 14112) over 50 hours test duration (=1 “fuel cycle”), fuel parameters at test run start

There were no system failures over the complete test duration. After 300 hours runtime it was necessary to change the fuel filter. After the test run the complete system was checked by the injection system manufacturer. All wearing parts showed uncritical custom tracks for a 500-hour runtime. Seals at the pressure control valve and the distribution cylinder poured easily. Particles into the fuel could be the reason of scratch marks. In both systems no sedimentations could be detected.
All enumerated effects were normal for the runtime but they were clearly more salient at those parts which were used in the test run with the fuel having the lower oxidation stability.

3.1.3 Passenger car common rail system

In these test runs the fuel was also changed every 50 hours. The fuel filter were changed after 300 hours at each test.



Parameter	RME low	RME standard	RME high
Density [g/cm]	0,88	0,88	0,88
Viscosity [mm2/s]	4,14	4,14	4,2
CCR [%mass]	0,02	0,02	0,01
Polymer content [%]	2,07	1,67	1,95

Figure 4: course of the fuel induction period (Rancimat 110°C, prEN 14112) over 50 hours test duration (=1 fuel cycle), fuel parameters at test run start

Every 50 hours the injection amount was measured at 4 check points and compared to each other. No significant differences in the injection amount could be detected over the complete test duration.

At all three tests no system failures happened. The injection system check at the end of test run no. 3a (RME standard oxidation stability) shows that the injection amount deviation was normal for a 500 hours runtime. The hydraulic operativeness of the injection pump was given. All wearing parts show uncritical custom tracks for a 500-hour runtime and no critical deposits could be detected. The injection system tested in test run 3b and 3c has not been accomplished yet.

3.2 Long term engine test runs

At the engine test bed two 1.4 direct injection diesel engines were tested in two long term test runs with RME with a high and with RME with a low oxidation stability. The test duration added up to 500 hours for each test.

Cylinder	4
Cubic capacity	1398 ccm
Rated power	50 kW / 4000 rpm
Rated torque	150 Nm /1750 rpm
Injection system	Common rail, Piezo injectors

Table 3: engine data

Test run	1a	1b
Parameter	RME high	RME low
Density [g/vm]	0.88	0.88
Viscosity [mm2/s]	4.15	4.14
CCR [%mass]	0.01	0.02
Polymer content [%]	2.6	2.07
Induction period [h], Rancimat 110°C, prEN 14112	20	3.47

Table 4: Long term engine test run 1a, 1b: fuel parameters

At the beginning of the long term test run a special test routine was started to measure the emissions, the fuel consumption and the power in 23 different operating points. These start up measurements were done with both fossil diesel and biodiesel. After 50 hours and after 250 hours the measuring programme was repeated with biodiesel. Representative for all measurements figure 5 and figure 6 show the comparison of the injection amount for the engines operated with RME with a “high” oxidative stability and with RME with a “low” oxidative stability.

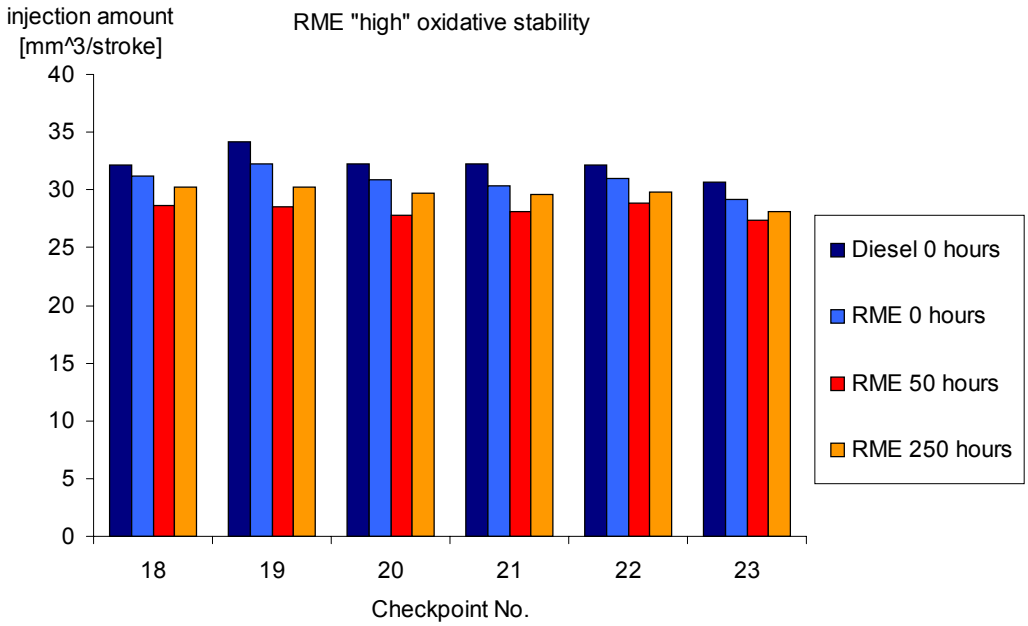


Figure 5: comparison injection amount in 6 checkpoint no 18 –23, RME high oxidative stability

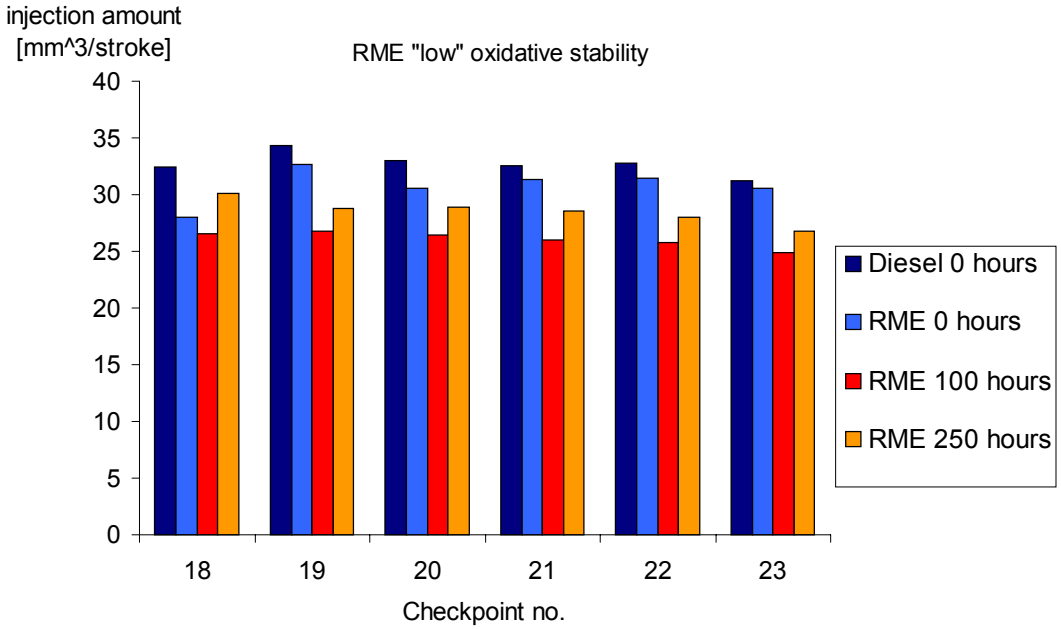


Figure 6: comparison injection amount in 6 checkpoint no 18 –23, RME high oxidative stability

The difference of the injection amount between the start up measurement and the measurement after 250 hours test duratio was in test run no 1b with RME “low” clearly higher than test run no 1a. The power loss of the tested engines between 0 and 250 hours test duration was also higher in the test runs with RME “low”. The measured differences in emissions and power between diesel- and RME-operation at the beginning of each test were normal for biodiesel use. Due to problems during the testing procedure, test run no. 1a (RME “high”) had to be stopped after 390 hours because an inadequately installed injection line between the rail and injector leaked. So the results of the check from the injection system parts after the test could not be compared to the results of test run no.1b (RME “low”). In test run no. 1b there were no problems during the complete test duration. No sedimentation could be detected. The feature which can be regarded critically is the abrasion at the injection nozzle seats. This wear was in the test run with RME with a low oxidation stability higher than usually common in test runs with excellent fuel quality.

4 SUMMARY

Long term tests were carried out with 3 different modern injection systems on the test bench. 3 fuel qualities, rape seed oil methyl ester with a low, a standard and a high stability were used.
3 different fuels were produced and delivered by NOVAOL in accordance with the results of WP1 and WP3.

Test fuels

- RME standard oxidation stability (6 hours induction time, Rancimat 110°C prEN 14112)
- RME high oxidation stability (14 – 18.37 hours induction time, Rancimat 110°C prEN 14112)
- RME low oxidation stability (1.8 - 3.47 hours induction time, Rancimat 110°C prEN 14112)

The fuels were tested in a long term test in 3 different modern injection systems. Wear and sedimentation were analysed after the tests. Chemical analysis of the fuels accompanied the tests.

At each injection system which was analysed wear and sedimentation were normal for the runtime.

All enumerated effects were more salient at those parts which were operated in test runs with fuel with the lower oxidative stability (for all parts analysed till now). Fat similar deposits could only be detected at system parts which were operated in the test run with very strong conditions (RME low oxidation stability, no change of the fuel during the complete test run at the injection system test bed). At all other systems no critical sedimentations could be detected. After the test runs, the functionality was given in each tested system.

Two long term real world engine tests were carried out on the test bench fuelled by biodiesel with a low and a high stability. The direct injection diesel engine were equipped with a modern common rail injection system. The test duration at each test was 500 hours.

Test fuels

- RME high oxidation stability (20 hours induction time, Rancimat 110°C prEN 14112)
- RME low oxidation stability (3.47 hours induction time, Rancimat 110°C prEN 14112)

The measured differences in emissions and power between diesel- and RME-operation at the begin of each test were normally for biodiesel use. The power loss and the different in the injection amount after a 250-hour runtime were higher than expected. The analyses of the test run engines show that the abrasion was normal for a 500-hour runtime and no significant difference to diesel operation was notified.

FIELD TEST PROGRAMME WITH SOLE BIODIESEL

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1 OBJECTIVES

Low stable Biodiesel containing ageing products may cause problems during use in sophisticated fuel injection systems. Thus, a fleet test was carried out with different vehicles and injection systems. The objective of the test was to determine possible effects of a low stable biodiesel used in vehicles.

2 METHODOLOGY

Four test vehicles were chosen for a 1.5 year field test. The cars were operated with rape seed oil methyl ester with a low oxidation stability. A special ageing process was applied to reduce the stability of the fresh fuel. The cars were prepared, fuelled and controlled by BLT. After the tests the injection systems of the cars were inspected by the manufacturer. Passenger car chassis dynamometer measurements were carried out by the University of Technology Graz (TUG) at the beginning and the end of the programme.

3 MATERIALS AND METHODS

3.1 Test fleet

Table 1: Test fleet description

Car	Passat Variant CL TDI	Almera – N15	Golf TDI	Audi A2
Engine	4-cylinder diesel engine with direct injection, supercharged	4-cylinder diesel engine with direct injection, supercharged	4-cylinder diesel engine with direct injection, supercharged	3-cylinder diesel engine with direct injection, supercharged
Capacity	1.9 l	2.2 l	1.9 l	1.2 l
Engine performance	66 kW at 4000 rev/min	81 kW at 4000 rev/min	85 kW at 4000 rev/min	45 kW at 4000 rev/min
Injection system	Bosch VP37 distributor pump	Bosch VP 44 distributor pump	Bosch Unit injector system	Bosch Unit injector system

Figure 1: Passat BLT1

Figure 2: Nissan Almera

Figure 3: VW Golf TDI

Figure 4: Audi A2

3.2 Test fuel

It was decided to use rape seed oil methyl ester for all vehicles. The fuel quality should fulfil the future European biodiesel standard with the exception of one parameter, the fuel stability. In order to examine the effects in the injection system it was necessary to reduce the fuel stability significantly. Thus, the fresh fuel received from the production facility had to be treated with special methods. The fuel had to be provided in sufficient amount for the whole test duration.

A special procedure was developed by BLT based on information from TEAGASC in Ireland. Experiments in the laboratory have shown that the induction period can be lowered without a dramatic change of other ageing parameters, like acid number or viscosity. The fuel had to be treated by temperature and air for a specific period of time.

The trends of the induction period, acid value and peroxide value during the ageing procedure are given in figure 5 – 7. It is demonstrated that the temperature has a clear impact if a stirrer is used. The test at 128°C without a stirrer shows nearly no changes in any parameter. Based on those results the optimal test conditions were determined in order to receive a stability < 2hours at 110°C in the Rancimat. The peroxide value can be used as an indicator for achieving the induction period of approx. 2 hours at 110°C (figure 8).

Analyses of the test fuels are given in table 2. The fresh fuel (RME fresh) was processed in several batches. Analyses of the aged fuel were made in 2001 and 2002.

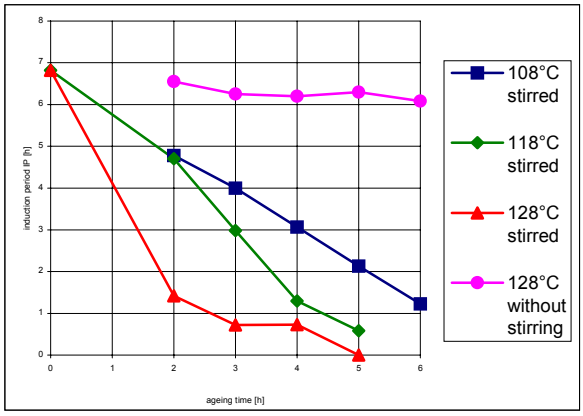


Fig. 5: Lab tests – induction period

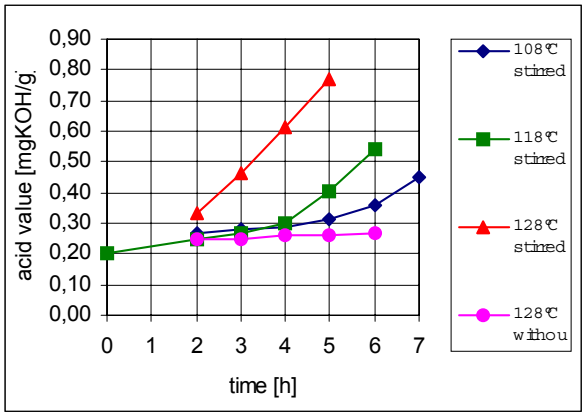


Fig. 6: Lab tests – acid value

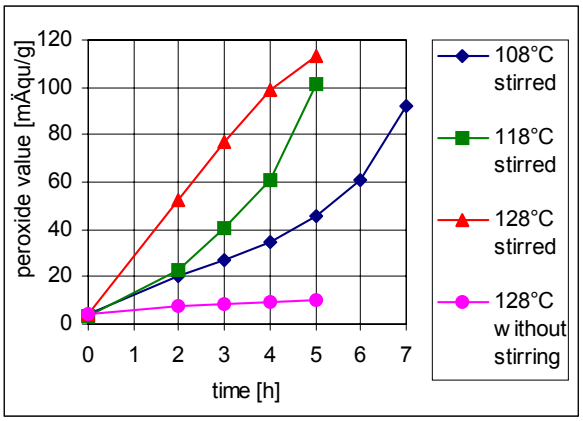


Fig. 7: Lab tests – peroxide value

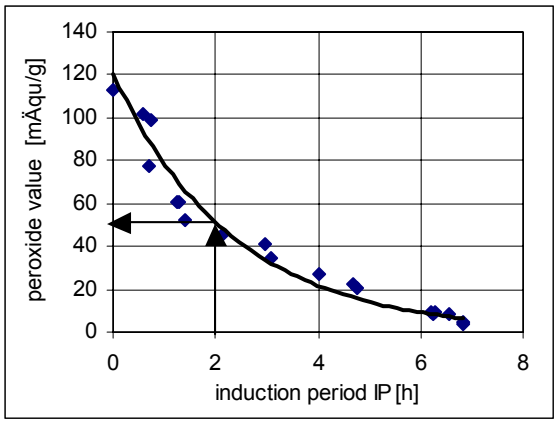


Fig. 8: Lab tests – peroxide value vs. induction period

Table 2: Test fuel analyses

	Sample	RME fresh	RME aged	RME aged
		01-198	01-199	02-067
Parameter	Year	2001	2001	2002
Flash point	°C	140	140	> 150
CFPP	°C	-15	-14	-16
Viscosity V40	mm²/s	4.57	4.5	4.55
Conradson carbon residue	%m	0.01	0.03	0.035
Cetane number		56.6	60.4	-
Acid number	mgKOH/g	0.26	0.43	0.41
Methanol content	%m	0.047	0.001	0.004
Total glycerol	%m	0.107	0.091	0.089
Free glycerol	%m	0.006	0.006	0.005
Monoglycerides	%m	0.235	0.222	0.253
Diglycerides	%m	0.109	0.104	0.1
Triglycerides	%m	0.23	0.12	0.029
Water content	ppm	320	397	500
Phosphorus content	mg/kg	0.8	0.5	0.4
Potassium content	mg/kg	n.d.	n.d.	0.7
Total contamination	mg/kg	1	2	7
Oxidation stability (Rancimat 110°C)	h	7.63	1.6	2.1

n.d. ….. not determinable

3.3 Investigations at the beginning and at the end of the field test

Each car was inspected at BLT before and after the field test. The following tasks were completed: engine oil drainage, change of fuel filter; for cars with a distribution pump: inspections of nozzle opening pressure, nozzle characteristic, pressure loss of the combustion chamber, compression of engine.

At the beginning and at the end of the field test a chassis dynamometer measurement of the passenger cars was carried out by TU Graz. The **N**ew **E**uropean **D**riving **C**ycle **NEDC** and the **Artemis** driving cycle were applied. The Artemis cycle is a real world driving cycle which is subdivided into three parts: Artemis urban, Artemis road and Artemis highway. Before starting the Artemis cycle each car was conditioned by driving the fist cycle part (Artemis urban). Afterwards the measurement started with the urban part. The ambient temperature was 25°C at each test. The NEDC was started as a cold-start cycle where the ambient temperature, the engine-oil and the engine-water temperature were 25°C. For each test the emissions CO_2, CO, HC, NO_x and particles were measured and compared to each other. The fuel consumption was calculated by means of the carbon balance and the results were compared.

The tested vehicles were VW Passat 1.9 TDI, VW Golf 1.9 TDI PD and Nissan Almera 2.4 TDI. Due to an engine damage of VW Passat only the results of the remaining two vehicles could be used. Each vehicle was measured at the test bench with both, fossil diesel fuel and biodiesel.

3.4 Data recording

The BIOSTAB fleet was equipped with a data logging system. Measurements of the engine oil temperature, filter temperature, ambient temperature, the time while engine ran and in two cars also the fuel tank temperature were taken every 2 minutes. These were the only data evaluated during operation of the engine. Besides, the drivers were asked to record each drive and all relevant observations in a log book.

3 RESULTS

The test lasted from June 2001 until November 2002. The cars were operated with the test fuel during the whole period, except for some very cold days in winter. When temperatures fell below –10°C a special winter biodiesel (CFPP < -20°C) provided by BLT was used. Fossil diesel fuel was never used during the test period. But diesel fuel was applied during the bench tests at TU Graz.

The cars could be operated with the test fuel without interruptions. Some problems occurred during the winter period. The driver of the VW Golf noticed a loss of engine performance. It was caused by a filter blocking. The fuel filter had to be changed several times in different cars. In winter the VW Passat had starting problems. Sometimes several start trials were necessary. The problem disappeared when ambient temperatures rose.

3.1 Data recording

The total mileage varied between 21000 km and 60000 km per car. The cars were operated mainly on the motorway (63%-72% of the total distance). The total fuel consumption ranged between 1400 and 4100 l per car, i.e. between 5.5 and 7.1 l/100km (figure 9, 10).

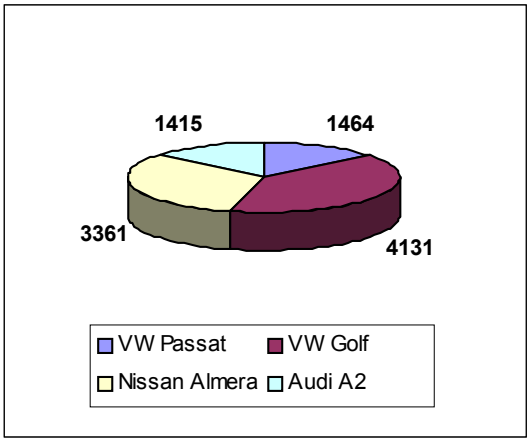
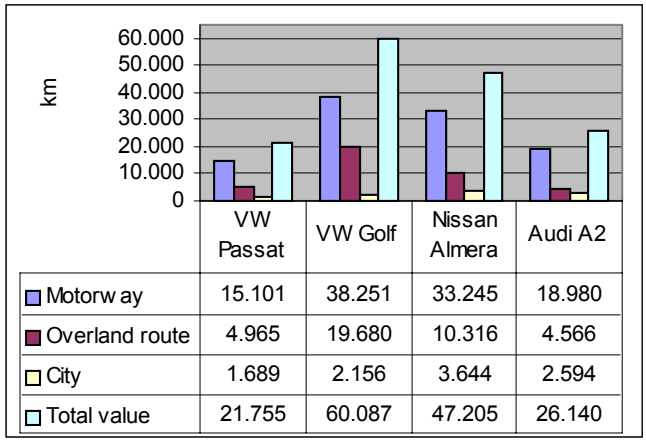


Fig. 9: Fuel consumption per car



	VW Passat	VW Golf	Nissan Almera	Audi A2
Motorway	15.101	38.251	33.245	18.980
Overland route	4.965	19.680	10.316	4.566
City	1.689	2.156	3.644	2.594
Total value	21.755	60.087	47.205	26.140

Fig. 10: Total mileage in the field test per car

In two cars (VW Passat, Nissan Almera) the fuel tank temperature was recorded. A distribution of the data (histogram) is given in fig. 11 and 12. Values ranged between 0 and 79°C, most values were recorded at 43 to 45 °C.

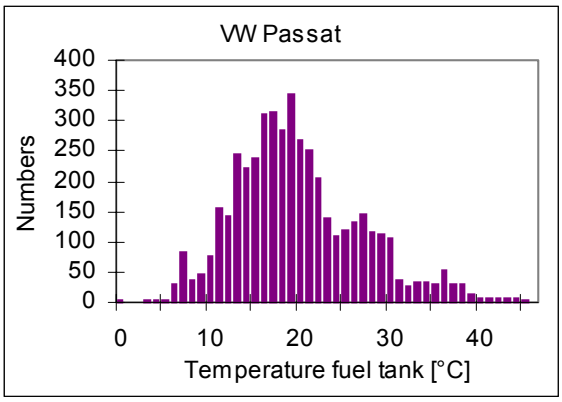


Fig. 11: Fuel tank temperature distribution of VW Passat

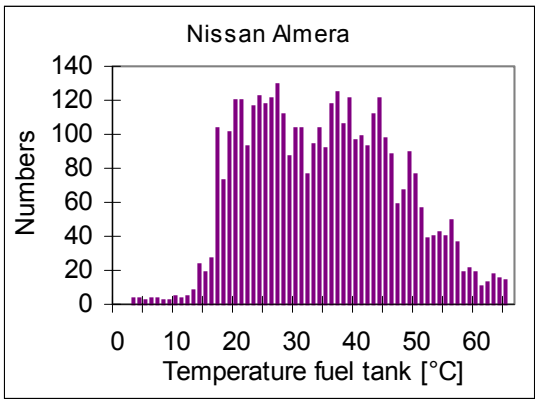


Fig. 12: Fuel tank temperature distribution of Nissan Almera

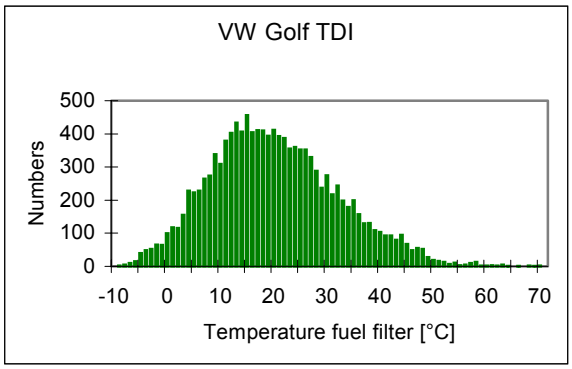


Fig. 13: Fuel filter temperature distribution of VW Golf

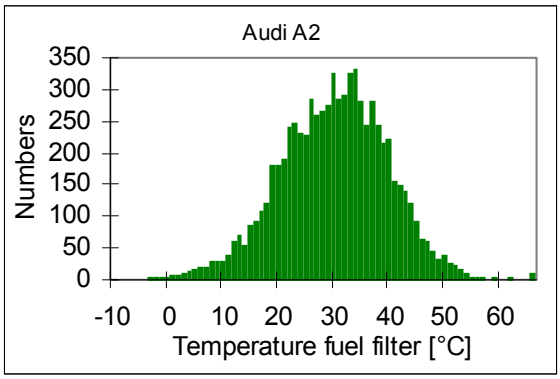


Fig. 14: Fuel filter temperature distribution of Audi A2

In figures 13 and 14 the distribution of fuel filter temperatures are shown (VW Golf, Audi A2). Values ranged between –10°C and 80°C. When comparing the data of all four cars, the majority amounted to 15, 34, 40 and 45 °C.

3.2 Chassis dynamometer tests

The differing values of biodiesel consumption measured in the start up phase and after terminating the field test could not be attributed to the biodiesel operation (figure 15). The diesel measurements at the end of the field test can only be used for assessment to a certain extent. The conditioning time was too short to neutralise all influences of the biodiesel operation. In general, CO emissions are not critical in diesel engines, especially in biodiesel operations because of the oxygen content in the fuel (figure 16).

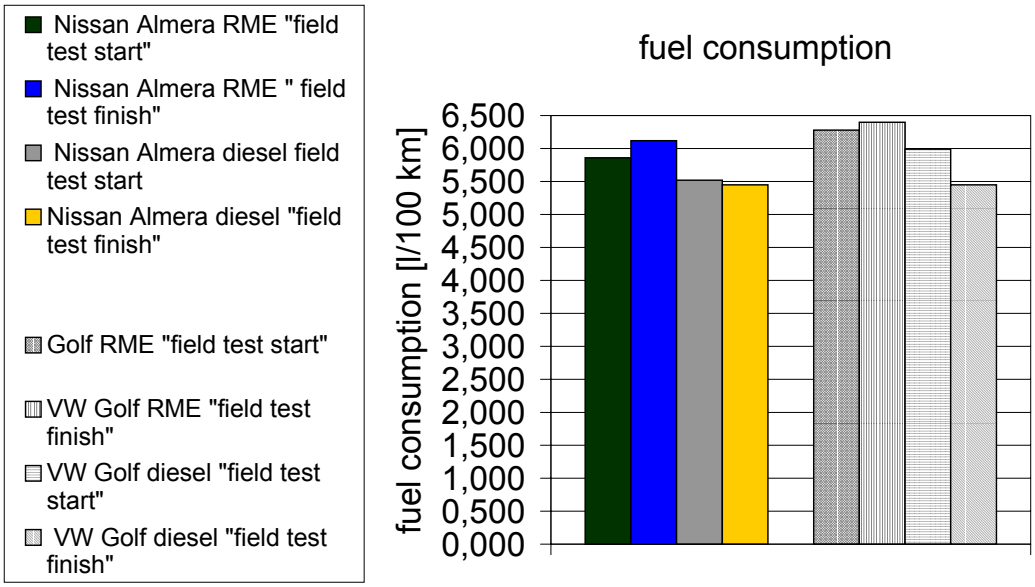


Fig: 15: Fuel consumption (RME beginning / RME end / diesel beginning / diesel end) of Nissan Almera and VW Golf (NEDC driving cycle)

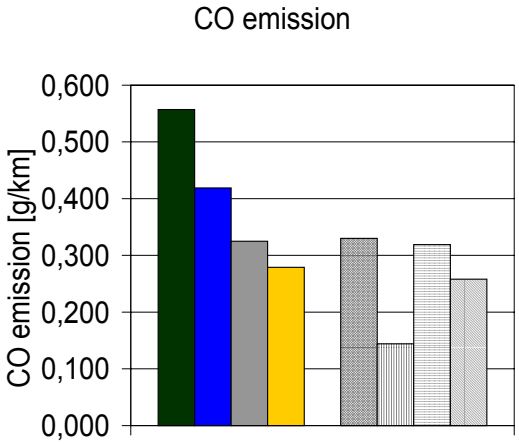


Fig. 16: CO emissions (RME beginning / RME end / diesel beginning / diesel end) of Nissan Almera and VW Golf (NEDC)

The limited summary of the NO_x and HC emission level in biodiesel test runs remains high during all driving cycles. Especially at driving cycles with a high engine load (Artemis road,

Artemis highway) the NO_x emissions were clearly higher in biodiesel operation (high temperature level and bound oxygen in the fuel) than in diesel operation (figure 17).

The particle level is obviously lower in biodiesel runs. The measurements after the field test show that the particle level in biodiesel operation was up to 30% higher than at the beginning (figure 18).

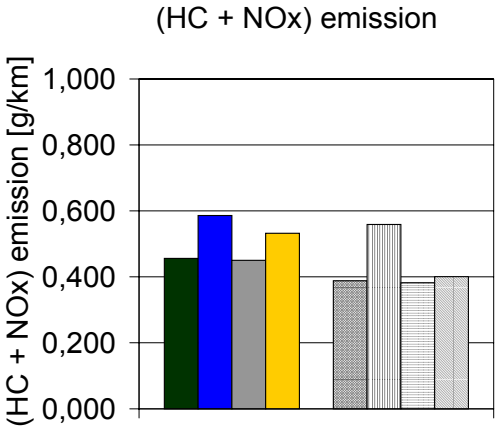


Fig. 17: (HC+NOx) emissions (RME beginning / RME end / diesel beginning / diesel end) of Nissan Almera and VW Golf (NEDC)

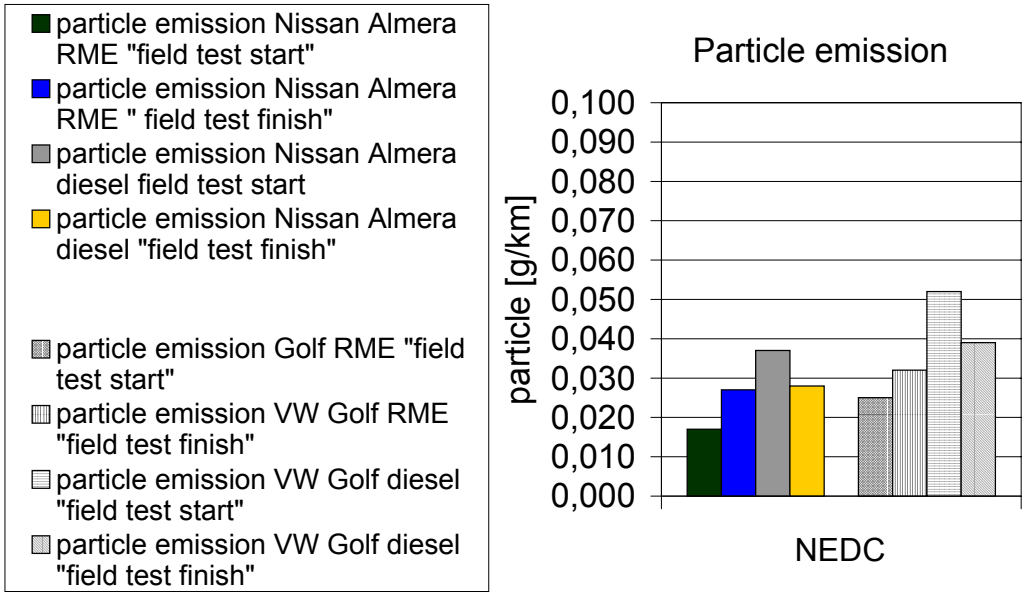


Fig. 18: Particle emissions (RME beginning / RME end / diesel beginning / diesel end) of Nissan Almera and VW Golf (NEDC)

Additionally, the power output was measured in one checkpoint. Between the start-up measurement and the measurement at the end of the field test no significant differences could be detected in both test cars. Table 3 shows the results for Nissan Almera.

Table 3: Power output in checkpoint 4000rpm/2nd gear, comparison RME – diesel operation (Nissan Almera)

measurement	Ratio [rpm]	Gear [-]	fuel	Power [kw]
Beginning of the field test	4000	2	RME (field test fuel)	61.7
	4000	2	Diesel D3 EN 590	63.4
End of the field test	4000	2	RME (field test fuel)	59.8
	4000	2	Diesel D3 EN 590	61.7

3.3 Final inspection of the injection system

All injection systems were presented to the fuel injection equipment manufacturer for a final inspection. The following results are summarised for both injection system groups, distribution pumps and pump injectors systems.

Distribution pumps: The distribution pumps were investigated on the test bench, afterwards dismantled and inspected. Wear and tear was listed as appropriate for the running time. Fuel deposits could be found on several parts in the VP37 distributor pump. Considerable coking residues were found on the tip of one injector. Seals were swelled in some cases. In one case, the fuel feed pump had to be changed.

Pump injector systems: Two injectors of the 4-cylinder engine and one injector of the 3-cylinder engine were subjected to a function test. The remaining injectors were dismantled and inspected immediately to avoid removal of residues. The functions of the injectors were found to be okay. Notable corrosion and traces of oxidation were found in some parts of the injector. No deposits were found inside the pumps.

4 SUMMARY

Four passenger cars were operated in a fleet test with a low stable biodiesel from July 2001 to November 2002. The test fuel was pre-aged by a special treatment with temperature and air. The oxidation stability determined by the induction period (Rancimat, 110°C) could be reduced from 7 hours to < 2 hours. Two cars were equipped with a fuel distribution pump, the other cars with a pump injector system.

The passenger cars were used in typical operation, mainly on the motorway. Distance and fuel consumption were recorded in a log book. Some temperatures (engine oil, fuel filter, fuel tank, ambient) were recorded automatically during the whole test period. The total driving distance ranged from 21000 to 60000 km per car.

Initial and final tests were carried out at the roller test bed at TUG - University of Technology in Graz. The tests comprised performance and exhaust emission analyses (CO, HC+NOx, particles). The differences in emissions and performance could not be assigned to the biodiesel operation (in combination with the results of the injection system check after the test run). The diesel measurement at the end of the biodiesel field test can only be assessed to a certain extent (short conditioning time). Before and after the field test all limited emissions were below the EURO 3 level (EURO 3 limit vehicle group 2, 1305 kg<RW<1760 kg).

After the tests the injection systems were inspected by the manufacturer. The functions of all systems were found to be okay. Swelling of elastomers was found in a distributor pump which can lead to leakage particularly when using diesel fuel. RME deposits could be found on several parts of a distributor pump. Traces of oxidation and notable corrosion were found on some parts of the pump injectors. The continued use of the UI-pumps could lead to fault. One fuel filter blocked and some fuel filters had to be changed in winter.

The results of the field test are obtained from four individual cars. A general conclusion about the performance with low stability biodiesel cannot be drawn. This would require an extensive car fleet and a total coverage of all field influences. It would have to include the employment of critical car applications as well as boundary operation conditions like full load and idle periods extending over several weeks.

VEHICLE FLEET TEST WITH A DIESEL FUEL/FAME BLEND

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ABSTRACT

In a 19 months fleet test run with 4 diesel vehicles (light duty LD; heavy duty HD) the performance of a diesel fuel (EN 590) blended with 5% UFOME (used frying oil methyl ester) was evaluated. Parameters controlled regularly during the test were:

- fuel quality
- cleanness of the fuel storage and supply system and its operability
- vehicle exhaust emissions
- engine lubricant performance
- driveability of the vehicles in warm and cold conditions
- cleanness and wear of the vehicles` fuel systems and fuel injection equipment.

Having successfully ended the test at a total distance of approximately 66,000 km driven in daily traffic no significant complaints about the operability of the vehicles were registered. No excessive wear or deposit build up occurred during this period compared to previous results gained in fleet tests with diesel fuel.
The engine lubricant showed a similar performance to the experience with pure diesel fuel and there was no need for a premature change of the lubricant.
A moderate increase in exhaust emissions was measured during the test interval.
The fuel storage and delivery system did not suffer from deterioration.
The quality of the fuel remained constant in terms of most specification parameters. Microbial contamination was not recorded, probably due to proper cleaning of the logistic system at the start of the test. The oxidation stability in the bottom layers of the storage vessels increased dramatically and exceeded the limit of EN 590 (25 g/m³; EN ISO 12205) by far.

1 OBJECTIVES

There is quite a lot of experience in the operation of diesel vehicles using FAME as a fuel. Most of this FAME was made from rape seed (colza), at least in Central Europe. But if FAME is to be used to a wider extent, which is the basic idea of the European Biofuels Directive, it seems necessary to deal with the properties of FAME in a wider scope than the mere vehicle performance. Taking into account FAME of diverse origin as a blending component of diesel fuel, which will be possible within EN 590 as of 2004, the performance of such a blend in the fuel production, storage and delivery system including the tank of the vehicle and the respective critical parameters have to be attributed close attention. Consequently, parameters influencing storage stability and their control are important in the long run.

In the future one very likely use of FAME will be as an up to 5% blending component for diesel fuel and therefore, the aim of the test programme was to produce such a blend according to current standards and in a sufficient amount for an endurance test. The fuel was stored in bulk and delivered in regular intervals to a specific filling station where the test vehicles could be refuelled. Thus the fuel quality, the influence on the storage and delivery

system (e.g. deposits) and the influence on vehicle performance in terms of emissions, operability and maintenance could be controlled.

2 TEST PROGRAMME SCHEDULE

To obtain the results aimed at, the following test schedule was defined and used:

- Clean and dry the fuel storage system consisting of a bulk tank, a delivery tank and its filling equipment. Replace all filters and elastomers by new ones.
- Blend the test fuel and store it in the bulk tank and document the fuel quality taking into account all important parameters especially concerning stability and microbial contamination.
- Prepare the test vehicles by cleaning the fuel system, by replacing filters and injection nozzles by new ones and by cleaning valves and combustion chambers from deposits. Change engine lubricant and oil filter. Document the wear status of the injection equipment and the emissions performance and fuel economy.
- Prepare an operability evaluation sheet for the collection of drivers' experiences.
- Start fleet test.
- Control and document emission performance every 6 month.
- Control and document engine lubricant performance every 5,000 km and change only if necessary due to deterioration.
- Document drivers` comments by collecting and analysing the report sheets regularly.
- Document maintenance effort during test period.
- Repeat all checks of the fuel system and the vehicles at the end of the test.

3 TEST EQUIPMENT

3.1 Test vehicles:

Due to limitations in the programme only 3 vehicles had been chosen originally. They should cover the engine range from passenger car to truck and represent volume models of the market. All vehicles were well maintained. They have always been operated under the control of scientists but mainly used in daily traffic. For these vehicles a significant amount of reference data from other fuel and lubricant test programmes was available to support the BIOSTAB test regarding e.g. emissions, wear and lubricant performance. To represent also modern injection technology a fourth vehicle with a common rail injection system was added to the test vehicle fleet midway through the fleet test.

	Vehicle type	Engine	km at start of test
Vehicle A	Passenger car	2.0 l; 60 kW; 4 cyl; TDI; rot. pump	135,260
Vehicle B	LD; Pick up	2.0 l; 85 kW; 4 cyl; TDI CR	1,532
Vehicle C	LD truck	2.5 l; 75 kW; 4 cyl; TDI; rot. pump	134,637
Vehicle D	MD truck	6.6 l; 105 kW; 6 cyl; TDI; rot. pump	50,562

3.2 Test fuel

Taking into account the EU Biofuels Directive and anticipating the amended version of EN 590 with the inclusion of up to 5% FAME content in the specification, a blend of 95% regular diesel fuel and 5% FAME was chosen as test fuel. As biodiesel made from Used Frying Oil (UFO) seems to become more important for environmental reasons and as there is less experience available than with biodiesel made from rape seed, UFOME was taken as blending component. To simulate a worst case scenario the fuel underwent a thermal ageing

process before blending (implemented by BLT Wieselburg) until the oxidation stability was far below the limit of prEN 14214. The diesel fuel had winter quality with a sulphur content of 340 mg/kg according to EN 590. For satisfactory cold operability during winter an additional flow improver was added to the blend to keep the CFPP below -20°C. Analysis of the finished blend product proved that the specification limits of EN 590 were not exceeded in any parameters measured.

3.3 Engine lubricant

Two different engine lubricants should be tested, whether there is a difference in oil performance depending on the fuel/lubricant combination. A quantity sufficient for the whole test was bought of one production batch to avoid differences in lubricant composition from different batches.
Vehicles A and B used a synthetic passenger car lubricant in the viscosity range SAE 5W-40 with fuel economy improvement properties (API CF/SL). Vehicles C and D were filled with a synthetic truck lubricant in the viscosity range SAE 10W-40 of the SHPD type (API CG-4/CF-4/SJ).

3.4 Fuel storage and delivery system

For the simulation of the supply logistics the following equipment was used: The fuel was stored in a cylindrical bulk storage tank made of steel with a maximum volume of 15,000 l. As the tank was mounted above ground it had to be isolated and electrically heated in winter to keep a minimum fuel temperature of +5°C similar to real market conditions.
A test filling station with a 5,000 l underground storage tank made of steel with the usual filling station equipment (e.g. pumps, piping, filters, nozzles) was used to fuel the test vehicles. No other vehicles used this filling station during the test time and the equipment was exclusively under control of the BIOSTAB operators during the entire test.
Transport of the test fuel from the bulk tank to the filling station was done by a tank truck dedicated to the transport of middle distillates to avoid detrimental contaminations from other fuel types.

4 TEST RESULTS

4.1 Fuel quality

The quality of the stored test fuel which decreased in the storage tank during the test from 15,000 to approximately 7,000 l stayed constant in most parameters. There was no change in viscosity due to ageing, the water content of 100 ppm immediately after blending decreased slightly to 80 ppm and the microbial contamination was also <1 at the end of the test. This positive effect is probably a result of intensive cleaning and drying of the tank vessel shortly before filling it with the test fuel.
The oxidation stability (EN ISO 12205) changed dramatically especially in samples taken at the bottom of the tank vessel. A value of 45.1 g/m³ was measured compared to 3 g/m³ measured at the beginning. In the top phase sample an increase from 3 to approximately 20 was found. Also the colour of the fuel samples changed from L 1.0 at the beginning to 1.5 at the end.
This change had no obvious influence on the operability of the filling station during the test period but the filling station will be observed closely until all the remaining test fuel is used.

4.2 Vehicle exhaust emissions

The exhaust emissions of CO, HC, NOx, particulates, transient smoke and CO2 were measured in the NEDC for the LD and under stationary load conditions for vehicle D on the chassis dynamometer. The test fuel was compared to a standardised reference diesel fuel to distinguish between general change in engine behaviour and influence of fuel deterioration. Generally, the emissions increased during the test between 2 and 30 % for both fuels. Only the new vehicle B showed a decrease in HC and CO as well as in transient smoke during the test period.
The CO2 emissions increased by about 2%, only vehicle D showed an increase of 10% at the end of the test. Again this increase was found for both fuels tested, which points to a change in engine performance rather than an effect of combustion quality of the test fuel.

4.3 Engine lubricant

Parameters used to evaluate lubricant performance were viscosity, soot content, FAME content, TBN and content of selected wear metals (Fe, Cu, Si). Oil did not have to be changed with any of the 2 engine lubricants chosen before reaching 15,000 km.
At that checkpoint a significant decrease in TBN, which had before been only slightly lowered, showed that an oil change was required.
In 3 vehicles the FAME content rose to a maximum of 0.2% while in vehicle C a maximum of 0.8% was reached. Vehicle B had a FAME content even below the detection limit of the method used.
The soot content reached between 0.3 and 0.4% at the time of oil change but did not lead to an increase in oil viscosity.
The increase in the content of wear metals in the engine oils was comparable to oil samples from engines operated with diesel fuel only.

4.4 Wear of injection equipment

Parts of the injection equipment which are known to be sensitive against wear were evaluated for wear optically and by weighing. The results were similar to those from vehicle tests with pure diesel fuel but were not really better than these, although the lubricity of the test fuel was quite good in terms of HFRR-values.

4.5 Vehicle maintenance

During the whole 19 months test period no extra maintenance work on the vehicles had to be done, which could be attributed to the fuel influence.

4.6 Vehicle operability

The vehicles were driven by a group of not specially skilled drivers in random order. For each travel drivers were asked to evaluate startability, acceleration, engine noise and smooth running of the engine on a 1 (good) to 5 (not acceptable) rating scale. They also had to record the distance driven, the mean ambient temperature and the traffic type (town; country road; motorway).
The operability ratings for all parameters mainly ranged between 1 and 2. Only during winter the ratings for cold start and noise of the HD vehicle were sometimes only 3 or 4. This was especially the case, when the drivers were not really used to driving a HD vehicle and compared it with their experience from diesel passenger cars.

4.7 Vehicle test mileage and fuel consumption

	Test mileage [km]	Fuel consumption [l/100 km]
Vehicle A	17,010	6.60
Vehicle B	15,900	9.52
Vehicle C	20,713	8.82
Vehicle D	12,734	19.85

5 SUMMARY OF TEST EXPERIENCE

- After approximately 66,000 km driven in daily traffic there were no significant complaints about the operability of the vehicles registered.
- No excessive wear or deposit build up occurred during this period compared to the operation with diesel fuel, which was known from previous fleet tests.
- The engine lubricant showed a similar performance to the experience with pure diesel fuel and there was no need for a premature change of the lubricant.
- A moderate increase in exhaust emissions was measured during the test interval.
- The fuel storage and delivery system did not suffer from deterioration.
- The quality of the fuel in terms of most specification parameters stayed principally constant.
- Microbial contamination did not occur, probably due to proper cleaning of the logistic system at the start of the test.
- The oxidation stability in the bottom layers of the storage vessels increased dramatically and exceeded the limit of EN 590 (25 g/m³; EN ISO 12205) by far.

Work Package 4.2

Biodiesel as Heating Fuel

Leader:	OMV AG	Austria
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UTILISATION OF BIODIESEL AS A FUEL FOR HEATING PURPOSES

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1 OBJECTIVES

The objective of the work package was to investigate the effects of the fuel stability while being used in heating systems. The effects of the fuel stability during the application and the operation parameters of the residential heating systems using blended fuels were studied. Therefore bench and field tests were carried out on different heating systems. The results of the tests help to find a relationship between laboratory test methods (WP1 and WP2) and effects during the utilisation for heating purpose.

2 METHODOLOGY

2.1 Test fuels

The test fuels were based on Light Heating Oil (LHO) blended with different types of biodiesel. FAME types were chosen due to their relevance in the market: rape seed methyl ester (=RME, produced by Novaol Austria) and used frying oil methyl ester (=UFOME, produced by SEEG Mureck):

- LHO + 5% RME
- LHO + 5% RME
- LHO + 20% RME
- LHO + 20% UFOME

The blends were produced on the calculation basis of mass per cent. In total 200 litres were mixed in a 200 litre metal drum. The drums were stored in a storage room, closed to air and no direct sun light. Temperature and humidity was recorded.

The FAME products were used in 3 different qualities with a varying stability:

- **Low Stability:** The quality of the fuel fulfils the specifications of prEN 14213 - except the oxidation stability. After a special treatment carried out by BLT the Rancimat induction time was reduced from 7 hours originally to < 2 hours.
- **Standard Stability**: FAME produced freshly and fulfilling specifications of prEN 14213. The stability ranges between 6 and 9 hours.
- **Excellent Stability:** FAME produced freshly and including an antioxidant (250 mg/kg Pyrogallol).

2.2 Bench tests

2.2.1 Short description

Emission tests and tests of functionality were carried out in the start up mode on 5 different heating systems at the test rig. The following fuels were used: LHO[1], LHO+5% RME[2] or UFOME[3] and blends with 20% RME or UFOME. Beside the start stop tests a long term test of 2000h with blends LHO+5% FAME and a 500h test with a blend LHO+20% FAME were done on 3 different small-scale combustion units with conventional technology. Interval checks of the operational parameter, visual checks, emission control measurements and product analysis accompanied the bench test programme.

2.2.3 Start up mode

Start and stop mode are non-stationary conditions during the combustion process in a heating system. At this mode the flue gas emissions are normally high and the efficiency of the system is low. However, the time between start and stop mode are considered as stationary conditions if operational parameters (temperatures, oil pressure …) of the heating unit are stable. The tests were carried out with **5 different conventional heating units** (Table 1 and 2) and with **4 fuels** (containing 5 and 20% FAME).

- Test fuels: LHO, LHO+5% FAME, LHO+20% FAME, 100% FAME.
- Fuel qualities: LHO (OMV AG, Austria), UFOME (SEEG Mureck, Austria) and RME (NOVAOL Austria).

Test procedure:

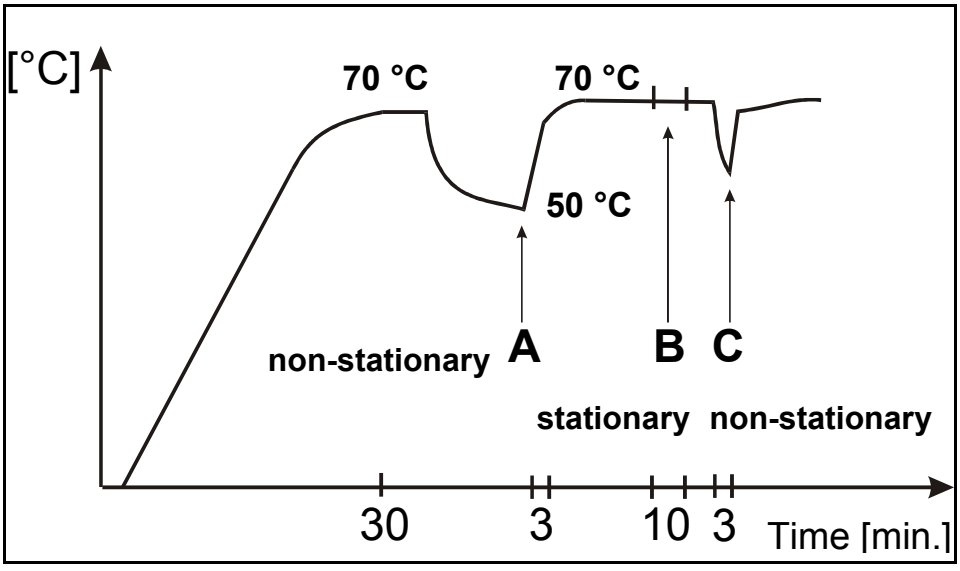

Figure 1: Test procedure for the heating unit showing the boiler flow temperature versus time. At the time A, B and C the measurement of the operating data and the emissions were carried out. A: non stationary conditions = medium warm start; B: stationary conditions, C: non stationary conditions = warm start. This running procedure was repeated once.

The heating unit was started and heated up to 70°C boiler flow temperature (approx. 30 min.). Then the unit was shut off. The boiler cooled down and when the boiler flow temperature achieved 50°C the unit was restarted. During this “medium warm start” at non stationary condition the flue gas emissions (O_2,CO, CO_2, NO_x, C_xH_y, soot) were measured (3

[1] LHO – Light Heating Oil (heating gasoil) a mineral oil product
[2] RME – Rape seed methyl ester
[3] UFOME – Used frying oil methyl ester, also named as RCO – Recycled cooking oil or AME – Altspeisefett Methyl Ester

minutes measurement time). Afterwards, the heating units ran in stationary conditions and the flue gas emissions were recorded (10 minutes measurement time). 3 minutes later a "warm start" at non stationary conditions was carried out with measurement of flue gas emissions (3 minutes measurement time). This running procedure was repeated once.

All 5 heating units contain a fuel preheating device, where the heating fuel receives a temperature of approx. 80°C. This can be a critical point in the heating system because of the unknown thermal stability of the blends.

Test conditions:

- Fuel storage before the test: in metal drums 200 litre, closed to air
- Production of the blends: Volume per cent
- Fuel storage during test: 10 litre plastic tank
- Fuel temperature at test: 15°C with a water thermostat
- Fuel delivery system: 2 ways system (fuel pass the burner and goes back to the tank)
- Combustion air: room temperature
- Testing conditions according to EN 303
- Measurements non stationary: start soot according LRV 92 (EMPA), combustion vessel pressure acc. EN 267, flue gas emissions NO_x, O_2, CO_2, C_xH_y
- Measurements stationary: soot according Bacharach, flue gas emissions and operational data as in non stationary mode
- Boiler inlet temp. /outlet temp. 50/70°C
- The unit was calibrated with LHO as the standard fuel with a flue gas CO_2 value of 13% volume. All tests were carried out with this parameter setting.

Table 1: Overview of the amount of measurements of the tests in start up mode

UNIT No.	No. of Test run	Total tests	Station. Emiss.	Non-station. Emissions	Soot	Combust. Vessel press.
1	1	33	11	22	33	22
2	2	33	11	22	33	22
3	3	33	11	22	33	22
4	4+5	33+18	11+6	22+12	33+18	22+12
5	6	35	11	24	35	24
Total		**185**	**61**	**124**	**185**	**124**

Table 2: Overview of the burners

UNIT No.	Type of burner	Fuel nozzle	max. Unit Power	Burner Orientation
1	Yellow flame	Fluidics 0.60/60° HF	29 kW	Normal
2	Blue flame	Steinen 0.40/60° H	19 kW	Normal
3	Yellow flame	Danfoss 0.45/60° LH	17 kW	Top down
4	Hybrid	Fluidics 0.60/60° HF	25 kW	Normal
5	Yellow flame	Fluidics 0.45/45° HF	19 kW	Top down

2.3 Long Term Tests

Long term tests of 2000h with blends of LHO+5% UFOME of different quality and a 500h test with blends of LHO+20% FAME of different quality, were carried out at 3 different small-scale combustion units with conventional technology (Table 3 and 4).

- Test fuels: LHO+5% UFOME standard stability, LHO+5% UFOME high stability, LHO+5% UFOME low stability.

- Fuel qualities: LHO (OMV AG) according to Austrian standards - normal market quality, UFOME (SEEG) normal market quality, UFOME high stability, UFOME low stability.

Test conditions:

- Fuel storage before the test: in metal drums 200 litre, closed to air
- Production of the blends: Volume per cent (50 litre FAME + 950 litre LHO)
- Fuel storage during test: 1000 litre plastic tank
- Fuel temperature at test: room temperature
- Fuel delivery system: 1 way system (fuel passes the burner and circle)
- Combustion air: room temperature

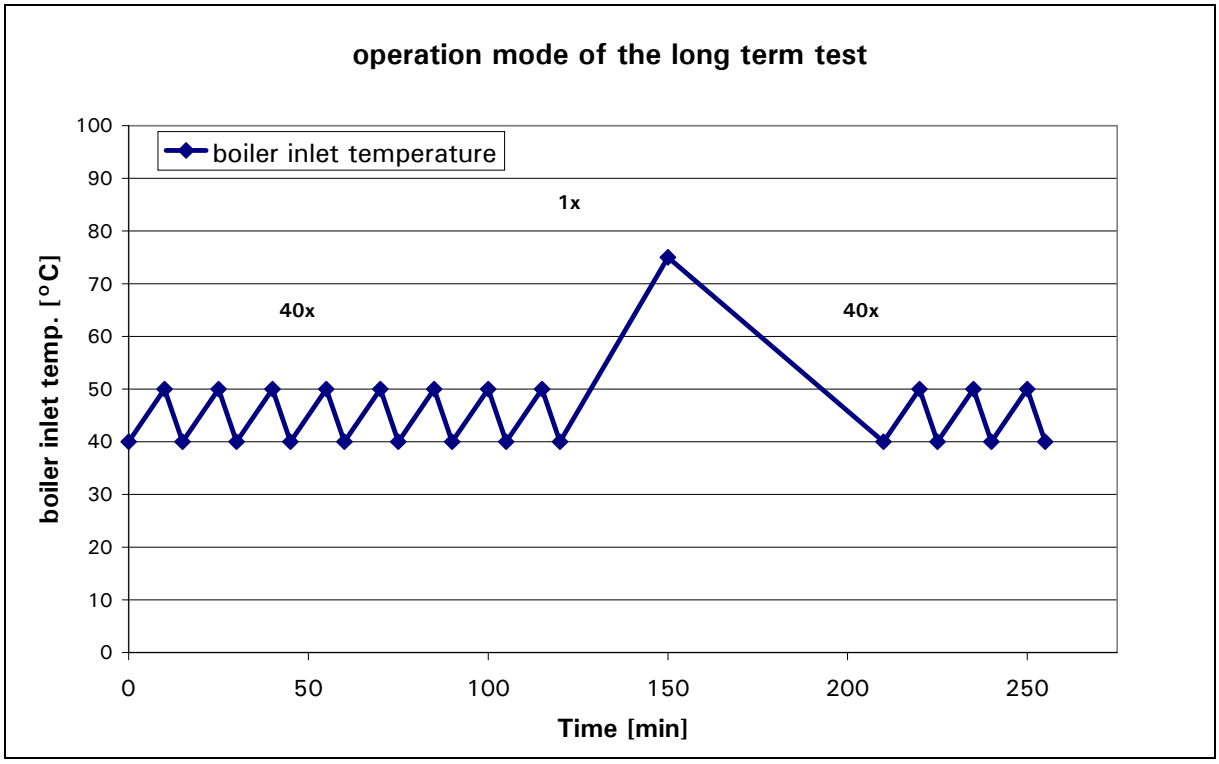

Figure 2: Daily test procedure of the long term runs.

Test procedure: Warm starts (40 times a day for 10 minutes, than 20 minutes simulating the generation of hot water – a typical event in households (shower, bath)). Daily check of the operation parameters of the heating unit.

Table 3: Overview of the fuels used in the long term test

UNIT No.	**0-500 h**	**500-1000 h**	**1000-1500 h**	**1500-2000 h**	**2000-2500 h**
1	5%UFOME	5%UFOME	5%UFOME	5%UFOME	20%UFOME stored UFOME
2	5%UFOME +Antiox.	5%UFOME +Antiox.	5%UFOME +Antiox.	5%UFOME +Antiox.	20%UFOME stored UFOME+Antiox.
3	5%UFOME artific aged	5%UFOME artific aged	5%UFOME stored fuel	5%UFOME stored fuel	20%RME distilled and stored fuel
Fuel	**1000 liter**	**1000**	**1000**	**1000**	**1000**

Table 4: Overview of the burners used for the long term test

UNIT No.	Type of burner	Fuel nozzle	Used Power	Flue gas temp.	Type	Burner Orientation
1	Yellow flame	Fluidics 0.45/45° HF	19 kW	51-79	Condensing	Top down
2	Yellow flame	Danfoss 0.45/60° LH	17 kW	120-154	Low temp.	Top down
3	Blue flame	Steinen 0.40/60° H	19 kW	118-145	Low temp.	Normal

2.4 Field Tests

The field tests were organised, administrated and controlled by OMV, Competence Centre Heating Fuels. 8 small-scale units in normal households were selected in Lower Austria. The units were operated with 4 different fuels (blends with RME, UFOME and antioxidant). The final decision about the fuel quality (5% blends of RME and UFOME) was based on the results of the bench tests – start up mode. 4 Fuels were used containing an appropriate antioxidant recommended by the WP3. The field test heating systems were operated for 2 heating seasons 2001/2002 and 2002/2003. Emission measurements and fuel analysis were carried out quarterly. The inspection period of the units were enlarged to every 2 or 3 month due to the unproblematic operation.

The 8 heating systems were selected in Lower Austria (maximum 150 km away from the OMV test rig at Schwechat) in co-operation with the burner and boiler producers and are operating in typical detached houses. A letter of acceptance was requested by OMV from the burner / boiler and tank manufacturers permitting the use of LHO+FAME blends in the field test. The heating system owner and OMV signed a contract to clarify responsibilities in case of difficulties with the fuel. The owner had to avoid any changes in the setting of operation conditions of the heating unit. OMV is responsible for the heating fuel quality and problems caused by the fuel and committed oneself to eliminate arising disturbances as fast as possible.

Checking the BIOSTAB field test plants

- 9 visits during test time, Schedule: Dec. 2001, Jan 2002, Feb 2002, April 2002, June 2002, Sep 2002, Oct 2002, Dec 2002, Feb 2003, April 2003.
- Flue gas emissions (Oxygen, CO_2, CO, NO_x, soot number), documentation with data list
- Visual check of boiler, burner, filter and tank, documentation with photos.
- Data recording: combustion air temperature, flue gas temperature, boiler temperature, oil pump pressure, oil flow counter, documentation with data list.
- Fuel sampling: 2 litres per sample, 2 samples per facility (tank bottom, tank liquid surface), transport in glass bottles.
- No tank cleaning is carried out before a refilling is done.

Table 5: List of 8 heating plants in Lower Austria with the corresponding burner / boiler / tank – data and the fuel which is used.

Location	N* [kW]	Burner	type of burner	boiler	type of boiler	Tank	5% FAME blend	amount [litre/a]
HAI Hainburg	28-32	Vaillant	VKOAT 32/4	Vaillant	VKO Unit 30/4	Werit 2xW2003	**UFOME**	3953
JSP Jeden speigen	15-22	Elco	SYSTRON 2-22 Öko Plus	Elco	EKO 1B 28L-NH	Rotex 4x1000	**UFOME**	3068
DRO Drösing	37	Weishaupt	Weishaupt WL5/2-A	Weishaupt	Weishaupt WTU 37-G	Werit 2xW2003	**RME**	6813
BOF Bockfliess	25	Hoval	R1-V-L-LN	Hoval	EUROLYT -3 25	Werit 2xW2003	**RME**	3793
MAN Mannersd.	40	Garvens	SPARK 36 NOx RED	Garvens	G40	Werit 4xW2003	**UFOME + antioxid**	5629
MOD Mödling	39	Garvens	SPARK 36 NOx RED	HOVAL	MINI - 3H	Werit 4xW2003	**RME + antioxid**	8833
STP St. Pölten	18	Viessmann	VB 2	Viesmann	VEK/VEM 1	Techno 2 x 1000	**UFOME + antioxid**	2582
PYR Pyhra	33	Viessmann	VITOLA 200	Viesmann	VEGV 1	Werit 3xW2003	**RME + antioxid**	7369

3 RESULTS

3.1 Fuel Quality

The fuels were selected and stored at OMV under defined conditions: clean metal drums 200 litre, closed to air, a storage room with recorded temperature and humidity, no direct sun light, no movement of the storage drums. During the year the temperature ranged between 10°C and 29°C and the humidity ranged between 25% and 90% in the storage room of OMV. A daily variation of the humidity of 30 % in maximum was recorded. Under those conditions no changes in product quality could be determined after 12 months, neither for the pure FAME fuel nor for the blends.

The stability of some fuels were tested with the Baader test (DIN 51 554 Part 1) which is a stability test for lubricants. The sample is aged for 48 hours at 95°C with periodically dipping of a copper coil. Increase of viscosity and density is determined. Both FAME qualities RME and UFOME showed 10% higher values after the treatment than pure LHO, indicating a lower stability of the FAME products. The presence of copper metal at least doubles the effect of ageing with the Baader treatment for all products.
The comparison between the FAME products shows that the pure FAME products RME and UFOME suffer in the same manner after treatment with the Baader method, whereas SME[4] shows a higher instability.
The distillation of the RME and UFOME caused lower long term storage stability in comparison with the original products (10-20% higher values after treatment).
No differences between RME and UFOME could be seen in the chemical parameters, combustion behaviour, emissions and operational data in the heating systems. Blends up to 20% FAME show no separation tendency even a after storage period of about 12 months. Blends with a higher percentage as 5% FAME exceed the standards for heating fuel (viscosity, density, water content …) in some European countries. Most of the boiler and

[4] SME: Sunflower Methyl Ester

burner producer (including manufactures of pumps and other spare parts) are giving no commitment for using pure FAME or FAME / heating fuel blends.

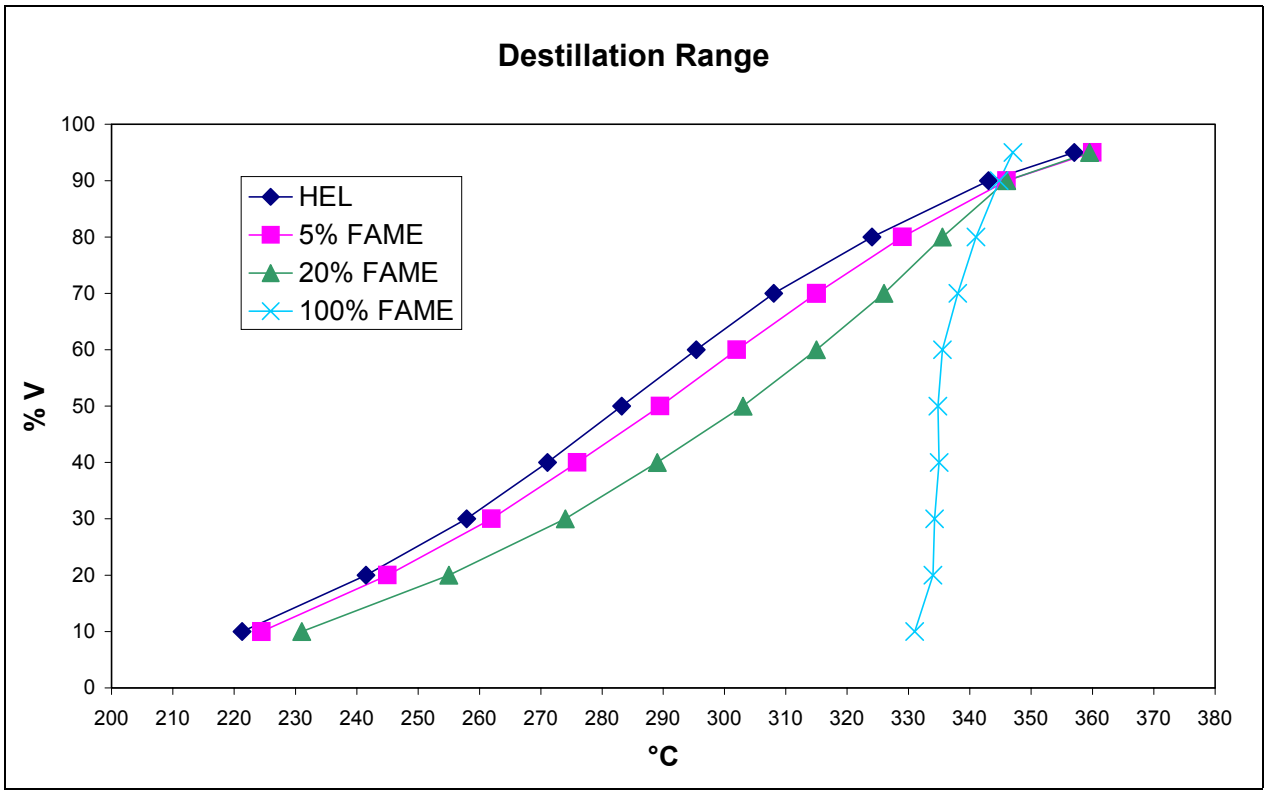

Figure 3: Distillation range of LHO (=HEL), blends and of pure FAME showing the narrow distillation range of FAME and the lack of fuel components with a low vapour pressure in FAME.

3.2 Bench tests: Start up mode

Fuels: The use of different fuel qualities has shown no differences between RME and UFOME as blending component to LHO used as a heating fuel on conventional heating systems. No differences between RME and UFOME could be seen in the start up mode with 5% and 20% blends.

Running the heating systems in the **stationary mode** no major differences could be observed during the emission tests with different fuels or blends. Despite different technologies and different fuels no remarkable deviation could be detected in the five different heating systems.

However in the **non stationary mode** the heating units act very different.
- Flue gas emissions depend strongly on the technology
- Big differences in start emissions
- Some units show worse CO and C_xH_y emissions with increasing FAME percentage in the blend
- Soot numbers for some units are higher than the Swiss limits (soot no. 3). Unit 1 gave the highest soot values of all heating units. Moreover the soot numbers for the FAME-blends were near or above the limit (No. 3) with unit 1.
- Higher start-soot numbers were detected for the semi-cold start than for the warm start (sometimes above the limit - unit 1)
- Start-soot for the cold start is in general a problem for FAME-blends

- Unstable situation during start phase at the combustion vessel pressure, especially unit 2 and 4.

3.3 Bench tests: Long term tests

Unit 1 and Unit 2 could be operated without any problems under the described conditions: proved good quality of LHO and FAME (5% and 20% blends), 2500 hours, 5000 litre, new installations, clean filter, good maintenance of the heating units.
Unit 1 (condensing boiler) seemed to produce a thicker covering in the inner side of the boiler in comparison with conventional fossil heating fuel.

However, some problems were found with unit 3 which was operated under the described conditions: critical quality of FAME (5% and 20% blends), 2500 hours, 5000 litre, new installations, clean filter, good maintenance of the heating units.
In unit 3 a blockage of the oil feed rate counter occurred 3 times. May be it was caused by using FAME with a low stability as blending component. UFOME aged artificially, stored during 1 year and RME distilled and stored during 1.5 years.

Beside the well organised storage and blending procedure one irregularity occurred. Water was added to the tank of unit 2. After 2 weeks unit 2 showed a little bit higher flue gas emission caused by a microbiological (bacterial, mouldy) growth in the storage tank. This problem was caused by a water content of 2300 ppm in the fuel and resulted in a total blockage of the filter. The water content had nothing to do with the product quality of LHO or FAME. As a conclusion: It is remarkable that after 2.5 weeks a fuel tank of 1000 litre with a 5% blend cause a filter blockage and a stop of the heating unit. The tank of unit 2 had to be cleaned completely.

3.4 Field tests

Table 6: The following blend parameters were recorded every 2-3 months.

Method	min	max	tolerance	remarks
Acid number [mg KOH/g]	0.08	0.15	0.023	Acid no. depends on the basic parameter of the heating fuel not on the storage time (longest storage time 10 months).
Iodine number [g/100g]	10	18	2.95	No clear trend can be observed.
Water content [mg/kg]	52	110	45	It seems that the water content rises very low with the storage time. No high differences between tank bottom and fuel surface could be observed.
Total contamination [mg/kg]	0	15	17,7% of the average	Lower values were obtained for new fuels. No high differences between tank bottom and fuel surface. No increase within the storage time.
Density 15°C [kg/m3]	841.5	847.4	0.295	The density depends on the basic parameter of the heating fuel. No differences between tank bottom and fuel surface.
Viscosity 40°C [mm2/s]	2.474	3.159	2.8% of the average	The viscosity depends on the basic parameter of the heating fuel. No differences between tank bottom and fuel surface.

Test conditions of the 8 units:

- proved good quality of the fuels, LHO and FAME
- 5% blends with UFOME or RME
- 4 of 8 units were operated with a fuel including an antioxidant
- fuel consumption: 4000 – 10.000 litre heating fuel
- test time: 14 months
- new installations, burner, boiler, plastic tanks, oil pipes
- one way fuel system
- new oil filter
- good maintenance of the heating unit
- fuel change (filling) minimum 4 months, maximum 10 months.

No differences between the blends with UFOME or RME or between the blends with antioxidants could be seen.

4 SUMMARY AND CONCLUSIONS

In general the bench tests in the **start up mode** showed two different results depending on the operation mode of the heating system: stationary or non stationary conditions. Under stationary conditions the emissions are as low as expected and all units fulfil the general standards for heating units. However during the starting procedure of the heating unit (medium warm start – non stationary condition) the concentration of the hydrocarbons and the carbonmonoxid in the flue gas were higher than some seconds after the start. These irregularities depend very much on the technology of the heating units. Additionally, these heating systems having high emissions during the starting process show worse CO and C_xH_y emissions with increased FAME percentage in the blend.

In the **long term test** of three different heating units with different fuels one fact can be seen clearly. The blends made from FAME products with a critical stability (aged artificially, stored for 1 year or distilled and stored for 1.5 years) caused problems in the oil feed rate counter.

Up to now in the **field test** no significant problems can be reported. But it has to be taken into account that the conditions for the test were as perfect as possible.

Open Questions

- Microbiological attack of the blends by bacteria or germ
  - because of the fast biological decomposition of FAME
- Storage stability of the blends
  - influenced by the materials of the tank, plastics, softening agents
- Reason for higher foaming behaviour during filling
  - problems with tank run-over
  - problems with a correct volume measurement at the filling procedure
- Decomposition of the EUROMARKER - or other additives
  - EUROMARKER (European tax marker)
- Swelling effect of the used plastic material
  - Sealing, Pipes, parts in flow counter, pumps, nozzles.