Biodiesel, Analytical Aspects

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Biodiesel, which is composed of fatty acid methyl esters (FAME), has been produced in Europe since 1992 and its utilisation is nowadays widely spread for different applications. It is used mainly as an automotive fuel or as heating oil, pure or as a blending component in diesel.

In 2004, the European Union production of biodiesel was nearly 2 millions tons, with an increase of about 25 % per year.

- **European specifications**

In 1997, the European Commission gave a Mandate to the CEN (European Committee for Standardization) in order to provide a standard that would specify FAME applicable as fuel and blending component in diesel for automotive and heating appliances. In 2003, several standards were issued:

- 2 specification standards: EN 14214 for automotive purposes and EN 14213 for heating oils purposes

- 11 test methods for biodiesel quality control

- 2 test methods for FAME quantification and identification in blends.

EN 14214 contains 10 parameters covering the automotive uses such as density, viscosity, flash point, sulphur content, carbon residue, total contamination, copper strip corrosion. These parameters are common for all diesel fuels even if the limits fixed are adapted to biodiesel (table 1).

Table 1 - European Specification EN 14214: 2003 - Automotive Uses

Property	Unit	CEN Limits	Test method
Density at 15 °C	kg/m^3	860 min	EN ISO 3675
		900 max	EN ISO 12185
Viscosity at 40 °C	mm^2/s	3,50 min	EN ISO 3104

		5,00 max	
Flash point	°C	120 min	pr EN ISO 3679
Sulfur content	mg/kg	10,0 max	pr EN ISO 20846
			pr EN ISO 20884
Carbon residue	% (m/m)	0,30 max	EN ISO 10370
(on 10 % distillation residue)			
Cetane number		51,0 min	EN ISO 5165
Sulfated ash content	% (m/m)	0,02 max	ISO 3987
Water content	mg/kg	500 max	EN ISO 12937
Total contamination	mg/kg	24 max	EN 12662
Copper strip corrosion (3 h at 50 °C)	rating	class 1	EN ISO 2160

- **Standardization of test methods for FAME quality**

EN 14214 has also 15 parameters covering the quality of the FAME (table 2). Most of the criteria are necessary to verify the purity of the biodiesel: ester content, acid value, methanol content, mono-,di- and triglyceride content, free and total glycerol, sodium, potassium, magnesium and calcium content, phosphorus content. These components are part of the feedstock, products or by-products of the transesterification reaction used to produce biodiesel.

Some criteria are necessary to provide biodiesel with good oxidation stability. These parameters are iodine value, linolenic acid methyl ester, polyunsaturated methyl esters with more than 3 double bounds and oxidation stability assessment. Only one parameter, polyunsaturated methyl esters with more than 3 double bounds, has no test method for the time being due to the lack of an existing method. Among these test methods standardised for quality control of FAME, some of them need to be improved due to their poor reproducibility. It is the case of the methods dedicated to the determination of: ester content, diglyceride and triglyceride content, glycerol content; sodium and potassium content.

Table 2 - European Specification EN 14214 : 2003 - Quality of the FAME

Property	Unit	CEN Limits	Test method
Ester content	% (*m/m*)	96,5 min	EN 14103
Oxidation stability, 110 °C	hours	6,0	EN 14112
Acid value	mg KOH/g	0,50 max	EN 14104
Iodine value	g iodine/ 100 g	120 max	EN 14111
Linolenic acid methyl ester	% (m/m)	12,0 max	EN 14103
Polyunsaturated methyl esters (≥ 4)	% (m/m)	1 max	-
Methanol content	% (m/m	0,20 max	EN 14110

Monoglyceride content	% (m/m)	0,80 max	EN 14105
Diglyceride content	% (m/m)	0,20 max	EN 14105
Triglyceride content	% (m/m)	0,20 max	EN 14105
Free glycerol	% (m/m)	0,02 max	EN 14105 & EN 14106
Total glycerol	% (m/m)	0,25 max	EN 14105
Na+K	mg/kg	5,0 max	EN 14108 & EN 14109
Ca + Mg		5,0 max	pr EN 14538
Phosphorus content	mg/kg	10,0 max	EN 14107

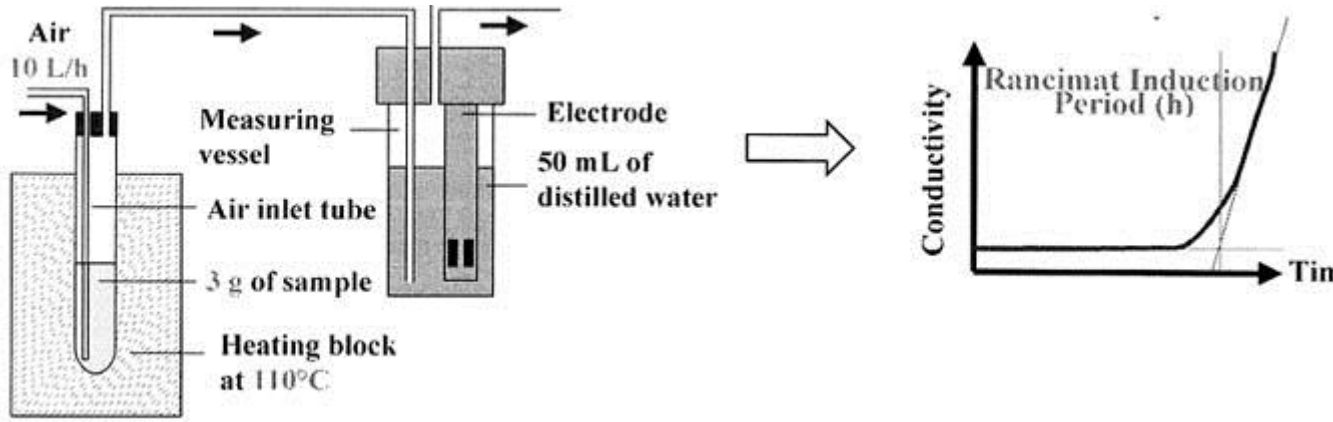
During the CEN work on specifications, several demands have been brought to the working groups in order to develop test methods to evaluate the stability of biodiesel according to different conditions:

Parameter	To measure	Requirement for
Oxidation stability	influence of oxygen and ambient air	both automotive diesel and heating oil applications
Thermal stability	influence of temperature in absence of oxygen	both automotive diesel and heating oil applications
Storage stability	influence of time and storage conditions	heating oil application

Oxidation stability is measured in the petroleum field using the EN ISO 12205 which is based on the determination of total insoluble content generated after an accelerated ageing test. This method is also suitable for biodiesel blends with diesel fuel but it is not suitable for pure biodiesel, as it was proved by Bondioli and coworkers in 2002, mainly because polymers formed are soluble in pure biodiesel.

In the biodiesel field, EN 14112 is used. It is based on the Rancimat test which measures the conductivity of a cell of water where is dissolved an exhaust air coming from a heated and oxygenated sample of biodiesel (figure 1). The induction period is determined when a sudden increase of the conductivity which is due to the formation of carboxylic acids as formic and acetic acids. Limits have been fixed at 6 hours for biofuel used as automotive fuel and 4 hours for heating oil uses.

Figure 1 - Oxidation stability of biodiesel - Principle of Rancimat test (EN 14112)



- **Main results of European Project BIOSTAB (http://www.biostab.info)**

At the end of the CEN work, no test method was available to measure thermal stability and storage stability. An European project was designed to answer this question.

BIOSTAB project (March 2001 - August 2003) aims were:

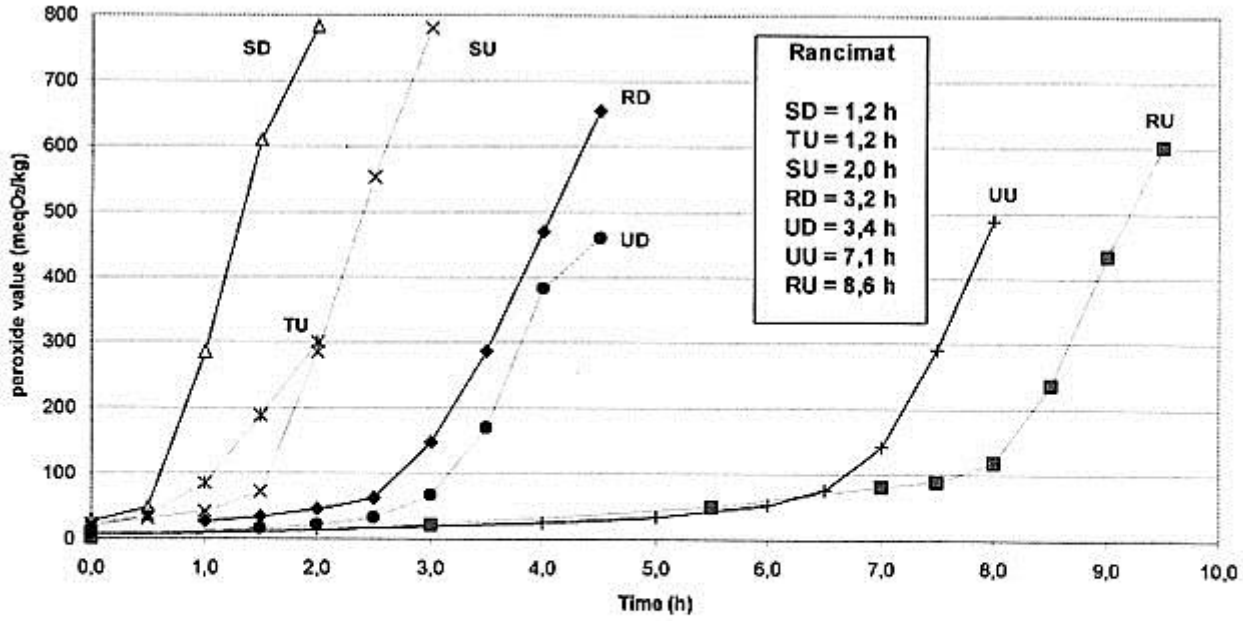
- to find appropriate methods for the determination of stability under realistic conditions
- to understand the influence of storage conditions on the quality of biodiesel
- to define a minimum level of natural and/or synthetic antioxidants
- to determine the effects of the fuel stability during the utilisation of biodiesel as an automotive diesel fuel and heating fuel

Results dealing with stability test methods are reported here.

Oxidation stability

The experimental procedure was built to clarify the relationship between the induction period measured with conductivity compared to the evolution of other quality control parameters along the Rancimat test. Several samples of biodiesel, distilled or undistilled, coming from different feedstock (sunflower, rapeseed, tallow, used frying oil) were submitted to Rancimat test following EN 14112. Every 30 minutes, test portions were analysed looking at different parameters such as peroxide value, ester content, tocopherol content and polymer content…

Figure 2 presents the curves obtained following the peroxide value of the different samples along Rancimat test. Induction periods determined using the peroxide value are in good accordance with the ones given with the conductivity determination of the Rancimat test.



SD : sunflower distilled FAME
SU : sunflower undistilled FAME
RD : rapeseed distilled FAME
RU : rapeseed undistilled FAME
TD : tallow distilled FAME
TU : tallow undistilled FAME
UD: used frying oil distilled FAME
UU : used frying oil undistilled FAME

Figure 2 - Oxidation stability of biodiesel - Evolution of peroxide Value along Rancimat test

Conclusions of this study were published by Lacoste and Lagardère in 2003:
- visible variation of each parameter along Rancimat test was observed,
- induction period determined with conductivity is well correlated with the degradation of quality parameters in the ageing test conditions of Rancimat test.

Storage stability

A method for the evaluation of FAME storage stability was developed and published by Bondioli and coworkers (2004), from the Stazione Sperimentale per le Industrie degli Oli e dei Grassi (SSOG) in Milano (Italy).

This method uses a modified Rancimat equipment for the ageing test of the sample (24 h at 80°C) and the evaluation of the stability of the sample is determined with

the peroxide value change induced by the ageing test.

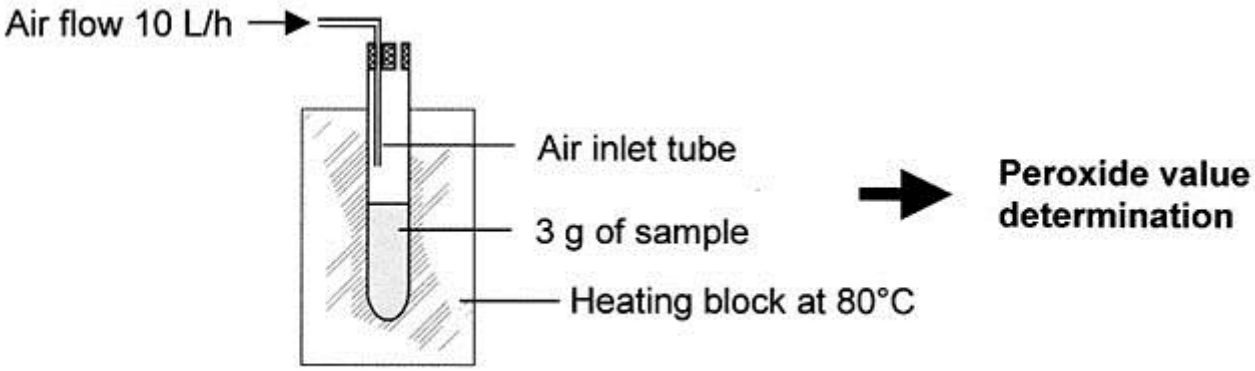


Figure 3 - Storage stability of biodiesel - Principle of the developed method by SSOG

Several samples of biodiesel, distilled or undistilled, coming from different feedstock (sunflower, rapeseed, tallow, used frying oil) were submitted to this new test method and the increase of peroxide value recorded varied from 20 to 600 meq O_2/kg of biodiesel, depending on the sample nature. Repeatabilty was acceptable.

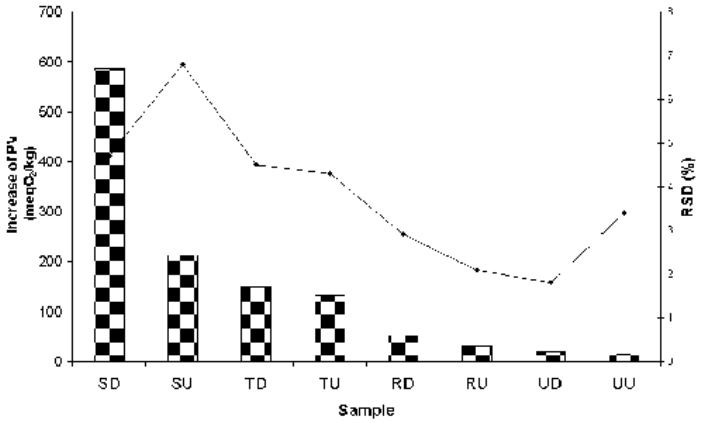


Figure 4 - Storage Stability - Increase of peroxide value after the ageing test for different samples -
Repeatability evaluation (RSD in %)

Thermal stability

A method was developed by ITERG (France) for the evaluation of FAME thermal stability.
The ageing test described in ASTM D 6468 was first used (1.5 h at 150 °C).
Various test methods were performed to evaluate the degradation of the sample at the end of the ageing test: acid value, Rancimat test, polymer content, ester content, viscosity and turbidity.

Variations of these parameters were too low so it was decided to modify the ageing conditions by increasing the temperature.

Working at 200 °C allowed observing a good correlation between viscosity variation and polymer content increase (figure 5).

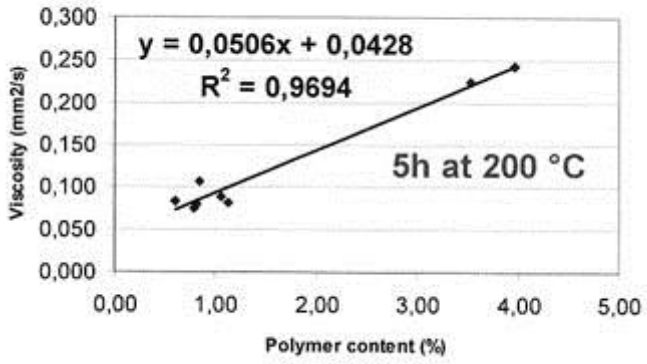
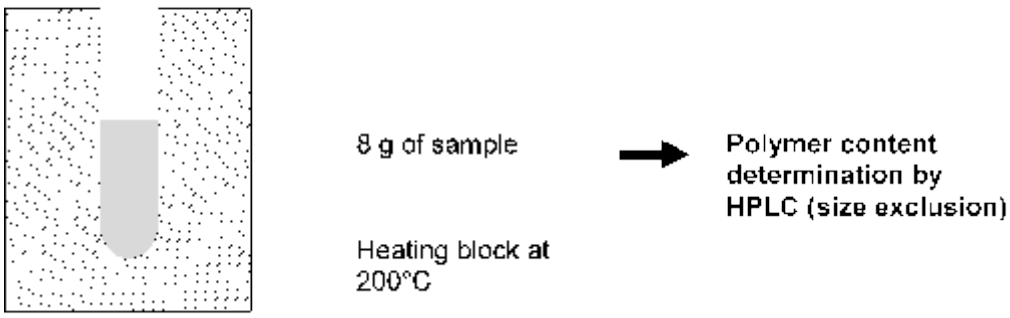


Figure 5 - Thermal stability of biodiesel - Correlation between Viscosity and Polymer Content

So a new test was designed to assess thermal stability, using Rancimat equipment for the ageing step (6 h at 200 °C) and the determination of the polymer content increase (figure 6).

Figure 6 - Thermal stability of biodiesel - Principle of the developed method by ITERG



Depending on the sample the increase of polymer content may vary from 5 % to 18 % (figure 7), so the test is suitable for a discrimination of samples.

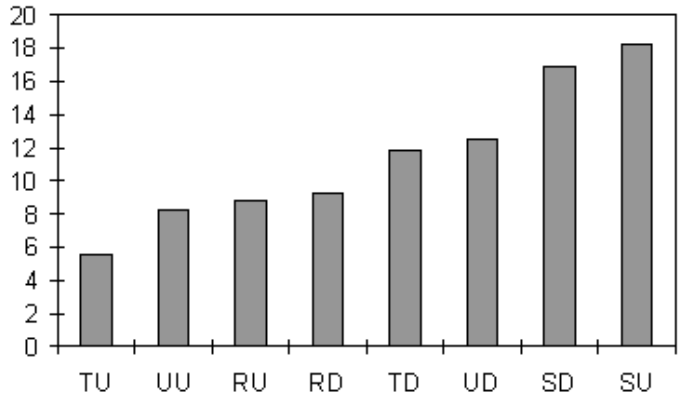


Figure 7 - Thermal stability of biodiesel - Increase of polymer content after 6 hours at 200°C

Also, the modified Rancimat test seems to be suitable for use in terms of repeatability. Indeed, repeatability evaluation (8 g of sample aged at 200 °C during 6 hours) was carried out for three samples (RU, RD and UU) and the relative standard deviation is lower than 13 %.

- **Work in progress about test methods for FAME quality**

At the end of the Mandate given to CEN, it had been stated that some methods dealing with the analysis of the composition of FAME, did not meet the required precision level for the limit stated (the 2R requirement of EN-ISO 4259). As the EC needed the FAME standards, there was no time left to re-investigate these methods: the standards needed to be published. It has been agreed that improvement of the methods (and the standards) would be done at a latter stage. TC19/WG24/TF has started its work with TC307/WG1 members in July 2004 for this purpose.

The methods to be improved are the determinations of: ester content, triglyceride content, free glycerol content, sodium content and potassium content.

Evaluation of the test methods for thermal stability and storage stability developed within BIOSTAB is also needed.

The development of a test method for polyunsaturated methyl ester with more than 3 double bounds is required.

And last, a revision of the specification standard EN 14214 is also awaited by the European Commission in order to cover different feedstocks and not only rapeseed FAME.

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