Determination of the oxidative stability of biodiesel (fatty acid methyl esters, FAME)

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Metrohm
Ion analysis

Stability

Summary

Biodiesel (fatty acid methyl esters, FAME) has become an important renewable fuel source for diesel-powered vehicles. Like edible oils, biodiesel is oxidized by ambient air. A high oxidation stability guarantees that the biodiesel can be used reliably under conditions of normal use.

The described instrumental setup allows the convenient and reliable determination of the oxidation stability. The increased temperature accelerates the oxidation of the biodiesel, in which low-molecular organic acids are formed. These are transferred by the air stream to a second vessel containing distilled water. The conductivity in this vessel is recorded continuously to detect the organic acids.

The time that elapses until these secondary reaction products appear is called oxidation stability, induction time or induction period and characterizes the resistance of biodiesel against oxidation. The test is standardized in the European Standard EN 14112 «Fat and oil derivatives – Fatty acid methyl esters (FAME) – Determination of oxidation stability (accelerated oxidation test)».

The influence of method parameters on the determination of the induction time was investigated. Sample size and gas flow have no observable influence provided their effect on the temperature is compensated. The key parameter is the temperature. It shows a significant impact on the measured induction time and therefore has to be adjusted and controlled precisely.

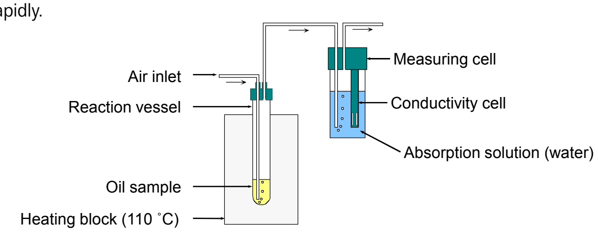
Introduction

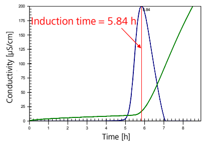
The use of alternative fuels obtained from renewable vegetable sources has become increasingly widespread in recent years, as the life cycle of biogenic fuels is neutral with respect to CO_2 release. The carbon dioxide released has already been assimilated from the atmosphere during plant growth. In contrast to fossil fuels, biogenic fuels neither contribute to the accumulation of CO_2 in the atmosphere nor to global warming. In addition, most alternative fuels are readily biodegradable and thus less environmentally harmful. In addition to other alternative fuels such as ethanol, methanol or biogas (methane), fatty acid methyl esters are increasingly being found on the market; these are also known as biodiesel or FAME (fatty acid methyl esters). Fatty acid methyl esters are usually obtained from oil seeds and are mainly used in their pure form or mixed with conventional diesel fuel in the transport sector.

During the manufacture of fatty acid methyl esters the vegetable oil is transesterified with methanol in the presence of a catalyst. This produces the methyl esters of long-chain fatty acids present in the oil together with glycerol as a valuable byproduct. Biodiesel is relatively unstable on storage, as like all natural oils and fats it is slowly oxidized by atmospheric oxygen. The primary oxidation products being formed during oxidation are peroxides. After some time the esters are completely destroyed; the secondary oxidation products formed include low-molecular organic acids, other volatile organic compounds and substances of a polymeric nature, often referred to as sludge. The latter can cause motor damage. The resistance of fatty acid methyl esters against oxidation, the so-called oxidation stability, is therefore an important quality criterion for biodiesel and thus is regularly determined during the production process and during storage.

Rancimat method

In the Rancimat method, a stream of purified air passes through a biodiesel sample, which is held at a specified temperature in a thermostated aluminum block. The effluent air from the oil or fat sample is then bubbled through a vessel containing deionized water. The conductivity of the water is continually monitored and stored by the software on the attached PC. The end of the induction period corresponds to the appearance of the secondary oxidation products – volatile organic acids, predominantly formic acid – which are blown out of the biodiesel sample and absorbed in the water. At that time the conductivity begins to increase rapidly.

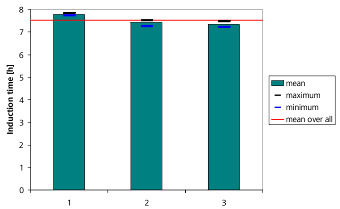




The PC software derives the induction time automatically from the maximum of the **second derivative** of the **conductivity** versus time plot.

Statistical method characteristics

To provide a statistical basis for the following experiment a biodiesel sample was analyzed by three operators using different instruments. The graph shows the mean of 12 determinations as well as the highest and lowest induction time determined in each experiment.



	Repeatability r	Reproducibility R
Number of participating laboratories	3	3
Total number of results	36	36
Mean value oxidation stability	**7.52 h**	**7.52 h**
Standard deviation	**0.07 h***	**0.24 h****
Relative standard deviation	0.9%	3.2%
Repeatability limit r according to EN 14112	0.84 h	-
Reproducibility limit R according to EN 14112	-	2.18 h

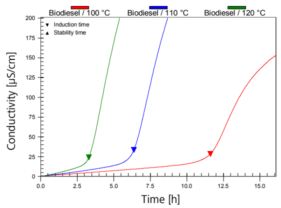
* under repeatability conditions
** under reproducibility conditions

Method parameters

In the following the influence of the most important method parameters such as temperature (1), sample quantity (2) and gas flow (3) on the induction time was investigated.

(1) Temperature

According to the Arrhenius equation the reaction rate of a given chemical reaction is increasing with the temperature T. In order to determine the temperature dependance of the induction time a biodiesel sample was analyzed at 100, 110 and 120 °C.



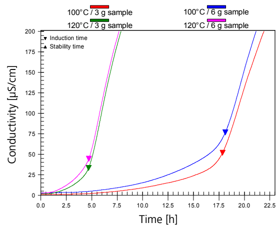
Temperature [°C]	Induction time[1] [h]
120	3.3
110	6.3
100	11.6

[1]mean of two determinations

Lowering the analysis temperature by 10 °C results in an approximate doubling of the induction time. This means that strict temperature control is an absolute requirement.

(2) Sample quantity

The oxidation stability of a biodiesel sample was determined with different sample quantities in the reaction vessel at 100 and 120 °C.



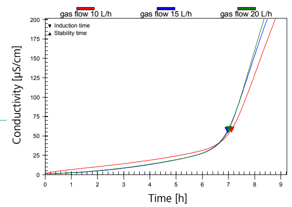
Sample weight [g]	Induction time[2] [h] 100 °C	120 °C
3	17.94 ± 0.57	4.72 ± 0.15
6	18.12 ± 0.58	4.74 ± 0.15

[2]mean of two determinations

Sample amounts of 3 and 6 g yielded constant induction times within reproducibility limits.

(3) Gas flow

The oxidation stability of a biodiesel sample was determined with different gas flow rates. The cooling effect of the gas flow was compensated by a temperature adjustment ΔT.



Gas flow [L/h]	ΔT [°C]	Induction time[3] [h]
10	0.9	7.12 ± 0.22
15	1.2	6.97 ± 0.22
20	1.5	7.03 ± 0.22

[3]mean of four determinations

Compensating the cooling effect, different gas flow rates (10 L/h, 15 L/h and 20 L/h) yielded the same induction time within reproducibility limits.

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