# Storage Stability of Biodiesel

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**ABSTRACT:** Renewable vegetable fuels are spreading rapidly throughout Europe and North America. Because biodiesel fuel has now acquired an important market share, it is necessary to thoroughly examine aspects of its use not previously considered either at the research stage or when overhauling the production technology. One of these aspects is its medium-term storage. The object of the present work is to study the behavior of biodiesel under controlled storage conditions that simulate those found in reality. Samples of biodiesel were kept in the dark, at two different temperatures (20°C and 40°C), in both glass and iron containers. They were controlled by the parameters that indicate their state of oxidation. Another group of samples was stored in glass and kept under the conditions described above in the presence of increasing quantities of water to determine its influence on the formation of acidity.
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**KEY WORDS:** Biodiesel, fuel, oxidation, peroxide, stability, storage.

Diesel fuels derived from vegetable oils are finding favor in the markets of Europe and the United States. The main advantages of using this alternative fuel are its renewability, better-quality exhaust gas emissions, its biodegradability and, given that all the organic carbon present is photosynthetic in origin, it does not contribute to a rise in the level of carbon dioxide in the atmosphere and consequently to the greenhouse effect. Different technologies are currently available and used in the industrial production of biodiesel, which is sold under different trademarks. For example, there are the Italian processes Novamont (1) and Ballestra (2), the French IFP (3), and the German Henkel (4) and ATT (5).

While the available literature reveals a large amount of experimental work carried out on analysis, product characterization and performance of this product, the same cannot be said for its behavior during storage. Moreover, the same methods of control normally used for fuels cannot be adapted for a product of a nonhydrocarbon nature.

The only bibliographical reference currently available dates back to 1985 when Du Plessis, De Villiers, and Van der Walt (6) published a study on the oxidative stability of methyl and ethyl esters produced from sunflower oil. They observed storage behavior under various experimental conditions for a period of 90 days.

The problems encountered in the long-term storage of biodiesel are mainly due to hydrolytic and oxidative degradation. The first of these, consisting of hydrolysis of methyl esters when water is present in the reaction medium, can be influenced by the initial acid content of the product, which has a catalytic effect on the abovementioned reaction, the quantity of water actually present, and the temperature and form in which it is present (dissolved, emulsified, or separated on the bottom of the vessel). It is important to emphasize that the solubility and the emulsifiability in water of this fuel are heavily dependent on the quality of the product. In particular, a biodiesel with a high content of intermediate reaction products (mono- and diglycerides) will have the tendency to absorb water, with all the associated negative effects, to a higher degree than a biodiesel that is constituted mainly of methyl esters. Oxidative degradation, which develops from hydroperoxide toward secondary oxidation products, is influenced by the nature of the original fatty substance (in terms of number of double bonds), by its quality with particular reference to the presence of hydroperoxides and natural antioxidants, by the presence of pro-oxidizing agents (such as ultraviolet light and some metals), and by temperature and air.

In the course of this work, we have tried to simulate the storage conditions as realistically as possible, by using temperatures similar to those found in tanks, in the absence of light, with an air chamber above the level of the product with little air turnover. The material of which the containers were made was also taken into account by using dark glass to simulate tanks made of plastic or vitrified material, or otherwise adding iron to a sufficient degree to make the metallic surface exposed to the biodiesel equivalent to a hypothetical metal container of the same dimensions.

## EXPERIMENTAL PROCEDURES

*Materials.* The tests were carried out with a sample of DIESELBI™ produced by NOVAMONT SpA (Milan, Italy) and based on rapeseed oil. The product previously analyzed (Table 1) corresponded to the specifications supplied by the producer for use as diesel fuel.

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**TABLE 1**
**Analytical Characterization of Biodiesel Used in the Tests**

| | | |
|---|---|---|
| Methylesters | (% w/w) | 98.1 |
| Monoglycerides | (% w/w) | 0.7 |
| Diglycerides | (% w/w) | 0.1 |
| Triglycerides | (% w/w) | <0.1 |
| Acid value | (mg KOH/g) | 0.32 |
| Free glycerol | (% w/w) | 0.03 |
| Methanol | (% w/w) | 0.18 |
| Soaps | (ppm) | 15 |
| Moisture | (ppm) | 350 |

**TABLE 2**
**Storage Test in Presence of Different Quantities of Water**[a]

T = 20°C

| Moisture (% w/w) | Time (days) 0 | 15 | 32 | 48 | 60 | 90 | 180 |
|---|---|---|---|---|---|---|---|
| 0.1 | 0.32 | 0.33 | 0.32 | 0.34 | 0.33 | 0.34 | 0.33 |
| 0.3 | 0.32 | 0.33 | 0.33 | 0.34 | 0.33 | 0.34 | 0.33 |
| 0.7 | 0.32 | 0.34 | 0.33 | 0.34 | 0.34 | 0.33 | 0.34 |
| 1.0 | 0.32 | 0.33 | 0.33 | 0.33 | 0.32 | 0.32 | 0.33 |

T = 40°C

| Moisture (% w/w) | Time (days) 0 | 15 | 32 | 48 | 60 | 90 | 180 |
|---|---|---|---|---|---|---|---|
| 0.1 | 0.32 | 0.34 | 0.32 | 0.32 | 0.32 | 0.33 | 0.33 |
| 0.3 | 0.32 | 0.34 | 0.35 | 0.35 | 0.36 | 0.37 | 0.41 |
| 0.7 | 0.32 | 0.35 | 0.36 | 0.35 | 0.36 | 0.37 | 0.43 |
| 1.0 | 0.32 | 0.34 | 0.34 | 0.35 | 0.34 | 0.36 | 0.44 |

[a]Results expressed as acid value mg KOH/g.

*Working methods.* To study the hydrolytic phenomenon, samples of biodiesel were placed in 20-mL vials, and enough distilled water was added to bring the total moisture level to 0.1, 0.3, 0.7, and 1.0%, respectively. Results shown are the average values of two determinations. A sufficient number of containers were prepared to carry out the analysis in the time allotted. Some of them were kept in the dark in a room thermostated at 20°C (±1°C), and the rest in an oven maintained at 40°C (±1°C). In the same way, the samples intended for study of oxidative degradation were made up in 2.5-L dark glass containers, filled to 2/3 and secured with screw tops to simulate the presence of air above the mass of stored product. Strips of iron material were added to those containers intended to simulate metallic vessels. The maintenance conditions were identical to those reported above. The sample containers were opened at fixed times, and the samples were removed to guarantee an occasional turnover in the overhead air.

*Methods of analysis.* Method NGD C10-1976 was used for free fatty acid determination. Method NGD C35-1976 (7) was used for peroxide value determination. Total phosphorus was determined according to method DGF CIII-16a (8). Methyl esters and mono-, di-, and triglycerides were determined by the method suggested by Mariani *et al.* (9). For free glycerol and methanol determination, methods suggested by Bondioli *et al.* (10,11) were used. High-performance liquid chromatography (HPLC) analysis of oxidized products has been carried out by using the methodology suggested by Gasparoli and Fedeli (12). Induction times were measured with a Rancimat 679 (Metrohm, Herisan, Switzerland) in the following operative conditions: temperature 120°C, air flow rate 20 L/h, sample 3 g.

## RESULTS AND DISCUSSION

The acidity values at different times for each of the working conditions are reported in Table 2. Despite adding varying amounts of water, there was no significant change in acidity with storage at 20°C, even over a long period of time. The tests carried out at 40°C on samples with humidity over 0.1% showed an increase in free acidity in the sample analyzed after six months. However, these increases are low, and even after six months of storage, acidity values are within the limits of technical specifications.

The results obtained during six months of storage in dark glass and simulated iron regarding acidity evolution and primary oxidation, measured by peroxide value determination (PV), are reported in Table 3. The previous observations regarding acidity evolution are confirmed: With a limited amount of moisture (in this case 350 ppm), there is no observable change linked to storage time, temperature, or the presence of iron.

The phenomena linked to the determination of PV are particularly interesting. In this case, a varied behavior can be observed: PV evolution of samples stored in glass follows a regular growth line, seemingly faster at lower temperatures. On the contrary, the sample stored in the presence of iron at 20°C shows a weak tendency to increase PV, while the sample kept at 40°C, paradoxically, showed a reduction. This phenomenon is explained quite simply by analyzing the values ob-

**TABLE 3**
**Storage Test in Different Containers**[a]

T = 20°C

| Container | | Time (days) 0 | 17 | 32 | 47 | 60 | 90 | 120 | 150 | 180 |
|---|---|---|---|---|---|---|---|---|---|---|
| Iron | AV | 0.32 | 0.33 | 0.32 | 0.33 | 0.32 | 0.32 | 0.32 | 0.33 | 0.32 |
| | PV | 2.3 | 3.2 | 3.4 | 3.4 | 3.9 | 4.2 | 5.2 | 4.8 | 5.2 |
| Glass | AV | 0.32 | 0.33 | 0.31 | 0.31 | 0.32 | 0.31 | 0.33 | 0.34 | 0.34 |
| | PV | 2.3 | 4.7 | 9.7 | 7.1 | 11.9 | 13.7 | 15.6 | 16.9 | 18.6 |

T = 40°C

| Container | | Time (days) 0 | 17 | 32 | 47 | 60 | 90 | 120 | 150 | 180 |
|---|---|---|---|---|---|---|---|---|---|---|
| Iron | AV | 0.32 | 0.31 | 0.31 | 0.32 | 0.31 | 0.30 | 0.31 | 0.33 | 0.30 |
| | PV | 2.3 | 0.4 | 0.7 | 1.1 | 0.5 | 0.7 | 0.8 | 0.6 | 0.9 |
| Glass | AV | 0.32 | 0.32 | 0.32 | 0.33 | 0.32 | 0.33 | 0.33 | 0.33 | 0.32 |
| | PV | 2.3 | 5.4 | 7.2 | 9.9 | 8.4 | 9.2 | 10.1 | 10.5 | 11.6 |

[a]Results expressed as peroxide value (PV, meq $O_2$/kg) and acid value (AV, mg KOH/g).

tained from HPLC monitoring of oxidation products, reported in Table 4. This type of monitoring consists in HPLC separation of a fatty substance into three or more fractions. The first of these represents the unaltered product, the second hydroperoxides, while the last units represent detectable products of secondary oxidation. The results are normally expressed as ratios between the area under the peaks representing an oxidized fraction and the area under the peaks of the unaltered fatty substance. This technique has found numerous applications in the past to evaluate the shelf life of cooking oils (13) and in the study of the performance of fatty substances during deep frying (14). A representative chromatogram is shown in Figure 1. The data in Table 4 show how the evolution of secondary oxidation products is different for products in a presence of iron. In particular, primary oxidation products stay at low concentrations for the first class of samples, thus confirming the observations carried out by means of PV analysis, although this absolutely does not mean increased stability of the products. On the contrary, the concentration of secondary oxidation products increases rapidly in old samples with iron. It appears to be more important for the sample that has been kept at higher temperature. The influence of temperature is also evident from samples stored in glass jars because temperature seems to favor degradation of the hydroperoxide at a faster rate compared to a sample stored at room temperature.

From these tests we can conclude that the path of oxidation of biodiesel samples is strongly influenced by the characteristics of the storage container and, obviously, by temperature. The same observations have been confirmed by the Rancimat induction times (Fig. 2), which show that the samples stored in glass behave substantially differently from those stored in the presence of iron. The storage temperature factor does not seem to be determinant in relation to the Rancimat induction time.

**TABLE 4**
**Storage Test in Different Containers—Changes in HPLC Parameters as a Function of Time**[a]

T = 20°C

| | | Time (days) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Container | | 0 | 17 | 32 | 47 | 60 | 90 | 120 | 150 | 180 |
| Iron | I[b] | 95 | 93 | 82 | 79 | 131 | 135 | 228 | 169 | 133 |
| | II[c] | 6 | 32 | 49 | 59 | 83 | 106 | 138 | 138 | 149 |
| Glass | I[b] | 95 | 145 | 250 | 286 | 423 | 453 | 660 | 603 | 557 |
| | II[c] | 6 | 14 | 10 | 11 | 16 | 18 | 17 | 16 | 23 |

T = 40°C

| | | Time (days) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Container | | 0 | 17 | 32 | 47 | 60 | 90 | 120 | 150 | 180 |
| Iron | I[b] | 95 | 90 | 50 | 50 | 17 | 20 | 119 | 64 | 0 |
| | II[c] | 6 | 40 | 70 | 83 | 133 | 115 | 119 | 140 | 147 |
| Glass | I[b] | 95 | 157 | 182 | 246 | 273 | 379 | 427 | 388 | 366 |
| | II[c] | 6 | 13 | 13 | 13 | 14 | 36 | 31 | 38 | 54 |

[a] Results expressed as 1000 × area of significant peaks/peak area of unaltered products; HPLC, high-performance liquid chromatography.
[b] Primary oxidation products.
[c] Secondary oxidation products.

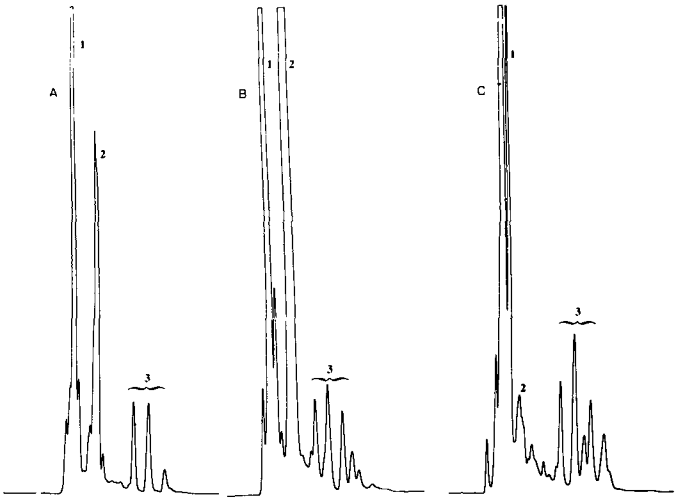

**FIG. 1.** High-performance liquid chromatography analysis of oxidation products. A, unaltered product; B, product stored in a glass container; C, product stored in presence of iron; 1, unaltered methylesters; 2, hydroperoxides; 3, secondary oxidation products.

The last issue to evaluate was the effect of aging on the performance of the product, which, we must not forget, is to be used as diesel fuel. For this purpose, the samples that had been aged at 40°C, stored in glass or iron tanks, were completely characterized as fuels. Table 5 provides the results given by the tests and the characteristics of the fresh samples. From the reported data, no major differences can be seen. The only difference consists of the presence of particulate matter, which can certainly be due to release from the container.

In conclusion, it can be stated that this study has allowed evaluation of the behavior of rapeseed oil methyl ester fuel during medium-term storage at conditions similar to those realistically expected. The possibility of influence of the oxidation kinetics by the containing material has also been demonstrated. However, it also has been highlighted that some products with a completely different pattern of oxidation do not perform differently.

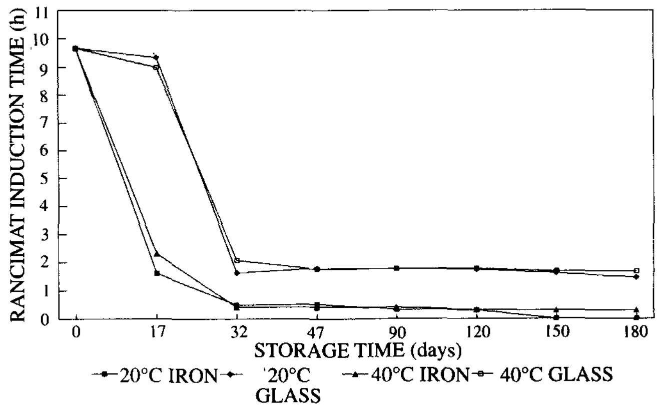

**FIG. 2.** Changes during storage of Rancimat induction time.

**TABLE 5**
**Comparison of Fuel Characteristics Between Unaltered and Oxidized Biodiesel**

| Parameter | ASTM method[a] | Units | Fresh product | Oxidized product |
|---|---|---|---|---|
| Density 15/4°C | D 1298 | kg/L | 0.883 | 0.883 |
| Distillation | D 86 | | | |
| Starting point | | °C | 324.0 | 315.0 |
| 5% distillate | | °C | 334.0 | 332.0 |
| 95% distillate | | °C | 359.0 | 355.0 |
| Final point | | °C | 361.0 | 356.0 |
| Recover | | % | 98.0 | 98.0 |
| Residue | | % | 1.0 | 1.0 |
| Losses | | % | 1.0 | 1.0 |
| Cetane number | D 613 | | 47.7 | 48.0 |
| Water and sediment | D 2709 | % | <0.005 | <0.005 |
| Flash point | D 93 | °C | 132 | 138 |
| Sulphur | D 1552 | % | <0.01 | <0.01 |
| Viscosity 37.8°C | D 445 | cSt | 4.88 | 4.90 |
| Viscosity 20.0°C | D 445 | cSt | 7.34 | 7.32 |
| Conradson residue | D 189 | % | 0.02 | 0.03 |
| Ash | D 482 | % | <0.001 | 0.004 |
| Cloud point | D 2500 | °C | −3 | −3 |
| Pour point | D 97 | °C | −12 | −12 |
| CFPP | IP 309 | °C | −14 | −15 |
| Copper corrosion | D 130 | | 1a | 1a |
| Heat of combustion | D 240 | kcal/kg | 9525 | 9510 |
| Total contamination | DIN51419 | mg/kg | 6 | 9 |

[a] If not otherwise specified. *ASTM Standards,* American Society for Testing and Materials, Philadelphia, 1995.

The issue of acidity is different because negative differences have been noticed only with respect to temperature, contact time, and elevated moisture content. Despite this, it also seems that, to obtain effects on the increase in acidity (which could be noxious to the product), it is necessary that the three negative issues mentioned above act contemporaneously. The presence of free organic acidity is one of the factors that promote the corrosion of materials, and it is therefore important to keep this parameter under control so that utilization of this diesel fuel substitute can be favorably considered. Clearly, these considerations are valid for samples produced with the appropriate technology which allows to minimize the presence of those molecules that could facilitate emulsification with water that may be present. Those materials include monoglycerides, diglycerides, free glycerol, phospholipids, and in the case of production processes that include alkaline catalysis, soaps.

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