Long Storage Stability of Biodiesel Made from Rapeseed and Used Frying Oil

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ABSTRACT: The degree of physical and chemical deterioration of biodiesel produced from rapeseed and used frying oil was studied under different storage conditions. These produced drastic effects when the fuel was exposed to daylight and air. However, there were no significant differences between undistilled biodiesel made from fresh rapeseed oil and used frying oil. The viscosity and neutralization numbers rose during storage owing to the formation of dimers and polymers and to hydrolytic cleavage of methyl esters into fatty acids. However, even for samples studied under different storage conditions for over 150 d the specified limits for viscosity and neutralization numbers had not been reached. In European biodiesel specifications there will be a mandatory limit for oxidative stability, because it may be a crucial parameter for injection pump performance. The value for the induction period of the distilled product was very low. The induction period values for the undistilled samples decreased very rapidly during storage, especially with exposure to light and air.

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KEY WORDS: Biodiesel, fatty acid methyl esters, rapeseed oil, storage stability, thermal oxidative stability, used frying oil.

Biodiesel is defined as the monoalkyl esters of long-chain fatty acids derived from renewable lipid feedstocks, such as vegetable oils and animal fats. During the last 15 yr, the production and use of biodiesel as alternative fuel have been thoroughly investigated and established in many countries (1,2). The ease of replacing fossil diesel fuel with biodiesel and governmental actions such as the U.S. Energy Policy Act and the European Commission "White Paper for a Community Strategy and Action Plan" will promote biodiesel usage in the future. Furthermore, steep increases in the price of petroleum in the last months have accelerated activities involving biodiesel worldwide. Thus alternative feedstocks for biodiesel production, like waste oils and animal fat, will need to be processed to meet the increasing demand for biodiesel.

Due to the bovine spongiform encephalopathy (BSE) crisis the use of waste oils and fats for animal feed production will be restricted in Europe, so large quantities will be available for energy production. Up to the end of 2000, about 6,000 tons of used frying oil methyl esters (UFOME) had been produced in Austria and used successfully as a 100% fuel substitute in a series of different vehicles. The use of 100% biodiesel from used frying oil in 40 city buses in Graz, Austria, is the largest application of that type of fuel yet. The acceptance and successful use of biodiesel from waste material require a high-quality continuous source of the fuel that meets the existing international specifications (3). In the United States an American Society for Testing and Materials proposal has been developed. In Europe a mandate of the European commission was given to the European Committee for Standardization (CEN) to develop a European specification for biodiesel by the end of 2000, with the purpose of harmonizing the existing national specifications; this new specification will be mandatory for all countries of the European Union. The draft specifications for fatty acid methyl esters (FAME), used as diesel fuel, will be published in 2001. They will not take effect until the end of 2002.

One of the main criteria for the quality of a biofuel is its storage stability. Vegetable oil derivatives especially tend to deteriorate owing to hydrolytic and oxidative reactions. Their degree of unsaturation makes them susceptible to thermal and/or oxidative polymerization, which may lead to the formation of insoluble products that cause problems within the fuel system, especially in the injection pump. Naturally occurring antioxidants like tocopherols prevent the oxidation of vegetable oils. Depending on feedstock and process technology, the amount of natural antioxidants in biodiesel is quite variable. Most production plants for biodiesel are operated without distillation of the end product, so most of the natural antioxidants remain in the product. During distillation, however, most of the tocopherols remain behind in the distillation residue. During the use of vegetable oils in frying most of the antioxidants are consumed, so one can assume poor oxidative stability of biodiesel made from used frying oil. In this report the storage stability, especially the oxidative stability, of biodiesel made from used frying oil, either distilled or not, was investigated over a storage time of 6 mon under different storage conditions and compared with that of rapeseed oil methyl esters (RME).

Du Plessis *et al.* (4) performed the first storage tests with FAME, using sunflower oil methyl esters at different temperatures for 90 d. The effects of air temperature, presence of light, addition of the antioxidant *tert*-butyl hydroquinone, and contact with steel were evaluated by comparing the free fatty acids, peroxide and anisidine values, light viscosities, and in-

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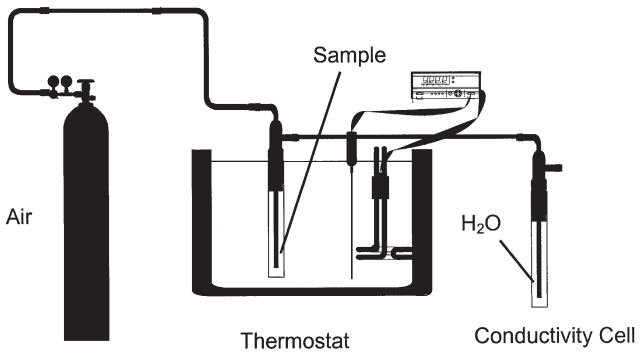
duction periods. Other work has been done with soybean oil and RME. Bondioli *et al.* (5) studied the deterioration of RME under different storage conditions, including changes in acidity, peroxide value, and oxidative induction period. Thompson *et al.* (6) investigated the extent of deterioration of rapeseed oil methyl and ethyl esters under different storage conditions (6). For both fuels they found that peroxide and acid values, density, and viscosity increased over time. Container type generally had no effect. Using a Rancimat instrument, Prankl *et al.* (7) tested the oxidative stability of 22 biodiesel samples, mainly from rapeseed oil, produced by seven European biodiesel producers. The induction period, which was measured at 110°C, varied between 1 and 10 h. The addition of various antioxidants to RME did not improve its oxidative stability significantly (8). In a previous paper in this series, the effect of oligomers formed during the heating of rapeseed oil on the fuel characteristics of methyl esters made from the heated oil was investigated (9). During transesterification the dimeric and trimeric triglycerides were transformed mainly into dimeric and trimeric methyl esters, which influence fuel parameters like viscosity and Conradson carbon residue.

Critical parameters for a high-quality biodiesel are storage and oxidative stability. During the development of unified European specifications, both parameters have been thoroughly discussed. As no method for measuring storage stability could be agreed upon, a thermal oxidative stability parameter was introduced into the specifications with a limit of the induction period at 110°C of 6 h. European engine and injection pump producers insisted on that limit for thermal oxidative stability, although the exact influence of thermal oxidative stability on engine and injection pump behavior is not clear. Because there is a limit value, studying the change in thermal oxidative stability of biodiesel during storage is important.

In this paper we investigated the thermal oxidative stability of undistilled and distilled FAME made from UFOME in comparison to that of RME. The focus of the study was on the influence of storage time and storage conditions on the fuel parameters of biodesel, such as oxidative stability, neutralization number, and viscosity.

MATERIALS AND METHODS

For the storage tests RME and UFOME were used. These samples came from production runs of the transesterification plant of SEEG (Südsteirische Energie- und Eiweissgenossenschaft) in Mureck, Austria. As starting material, unrefined rapeseed oil as well as used frying oil, which was collected from households and restaurants in the surrounding communities, was used. Furthermore, a batch of the UFOME was distilled under reduced pressure in the laboratory. The samples were analyzed according to the German specifications valid for FAME when used as biodiesel (DIN 51606) (10). The peroxide number was measured using the Deutsche Gesellschaft für Fettforschung method (11). Fatty acid composition was determined by gas–liquid chromatography by standard methods (12).



SCHEME 1

Determination of thermal oxidative stability. Thermal oxidative stability of the biodiesel samples was determined by using standard procedure IP 306 (13). The principle of the method is shown in Scheme 1: the biodiesel sample is heated to 110°C. Air is then passed through the sample, and then through a water solution; the conductivity of the water is then measured. After a given heating time, referred to as the induction period, the conductivity of the water trap increases rapidly as a result of the formation of volatile acidic organic compounds, following the total consumption of antioxidants in the heated oil.

Storage conditions and analysis. The biodiesel samples (1 L each) were stored for 170 to 200 d between 20 and 22°C at six different storage conditions: Samples i–iv were stored in polyethylene bottles that were open to the air (i, iii) or closed to the air (ii, iv) and exposed (i, ii) or not exposed (iii, iv) to daylight. Samples v and vi were stored in tin cans (i.e., exposed to metal) with (v) or without (vi) exposure to air. During storage, samples were withdrawn at specific times and analyzed using standard methods (Table 1).

RESULTS AND DISCUSSION

Biodiesel analyses. The results of the analyses of the biodiesel samples are listed in Table 1. All values of the different parameters met the DIN 51606 specification except the values for density and water of the two UFOME samples, which were slightly out of specification. Also, the methanol value for the RME sample was slightly above the limit of 0.3%. The values for the induction period, a measure of the oxidative stability, were similar for the two undistilled biodiesel samples, with the higher value being for the UFOME sample. It was expected that the value for the induction period for the UFOME would be lower than that of the RME from unused fresh rapeseed oil owing to the consumption of antioxidants during heating of the frying oil. However, the UFOME sample also had a low peroxide number, which indicated a low thermal degradation of the oil during usage. Apparently, sufficient antioxidants were available in the UFOME sample to limit oxidation. Alternatively, the lower content of PUFA in the UFOME sample may account for its oxidative stability (Table 2). Distilled UFOME had a shorter induction period

TABLE 1
Results of Analysis of Biodiesel Samples

Parameter	Unit	Method[a]	Rapeseed oil methyl esters	Used frying oil methyl esters	Distilled used frying oil methyl esters	DIN 51606 specification limit
Density at 15°C	g/cm^3	DIN EN ISO 3675	0.875	0.873	0.873	0.875–0.900
Viscosity at 40°C	mm^2/s	DIN EN ISO 3104	4.42	4.55	4.37	3.5–5.0
Water	%m/m	DIN 51777-1	0.03	0.04	0.08	≤0.03
Neutralization number	mg KOH/g	DIN 51556-1	0.32	0.35	0.46	≤0.5
Sulfated ash	%m/m	DIN 51575	<0.001	0.003	<0.001	≤0.03
Conradson carbon residue	%m/m	DIN EN ISO 10370	0.01	0.01	0.01	≤0.05
Total impurities	mg/kg	DIN 51419	14	19	2	≤20
Methanol	%m/m	E DIN 51608	0.34	0.10	<0.01	<0.3
Free glycerol	%m/m	E DIN 51609	0.006	0.019	0.015	0.02
Monoglycerides	%m/m	E DIN 51609	0.10	0.14	0.07	≤0.8
Diglycerides	%m/m	E DIN 51609	0.08	0.16	<0.05	≤0.4
Triglycerides	%m/m	E DIN 51609	0.10	0.12	<0.05	≤0.4
Total glycerol	%m/m	E DIN 51609	0.06	0.09	0.03	≤0.25
Peroxide number	mval O_2/kg	DGF C-VI 6a[b]	2.3	2.2	1.4	—
Oxidative stability, 110°C	h	IP 306 modified[c]	5.6	5.9	1.2	—

[a]Reference 10, unless otherwise modified.
[b]Reference 11.
[c]Reference 13.

than undistilled UFOME, which suggested a loss in antioxidants during distillation.

Thermal oxidative stability. Even at the beginning of the storage tests both undistilled biodiesel samples showed induction periods that were slightly lower than the proposed limit of 6 h. The change in oxidative stability during storage for RME is shown in Figure 1 and in Figure 2 for the two UFOME samples. It can be seen that the induction period decreases very rapidly, especially in open bottles stored under light. Under those conditions the induction period for both RME and undistilled UFOME reached zero after 150 d of storage. For the samples in closed containers, the induction period of both samples decreased significantly, reaching values between 1 and 2 h for RME and between 2 and 3 h for UFOME after a storage time of 200 d. The latter results are in agreement with the results of Bondioli *et al.* (5) who measured the induction period with the Rancimat instrument and found a very rapid decrease in induction period during the first 30 d of storage. The distilled sample prepared from used frying oil, which was stored in a closed bottle in the dark, showed poor oxidative stability even at the beginning. This observation might be explained by the removal of natural antioxidants during distillation. Surprisingly, the induction period for this product remained quite constant during storage.

In practical operation one may assume that commercial fuels may not meet the proposed limit for the induction period of 6 h at the fueling station as a result of the rapid change of thermal oxidative stability during storage. Further investi-

TABLE 2
Fatty Acid Composition of Biodiesel Samples

Fatty acid	Rapeseed oil methyl esters (% m/m)	Used frying oil methyl esters (% m/m)
Palmitic	4.8	14.4
Palmitoleic	Not detected	0.4
Stearic	1.8	4.8
Oleic	62.2	51.6
Linoleic	19.9	21.6
Linolenic	8.9	3.5
Arachidic	0.6	Not detected
Gadoleic	1.3	Not detected
Behenic	0.3	Not detected
Erucic	0.2	Not detected
Unidentified		3.7

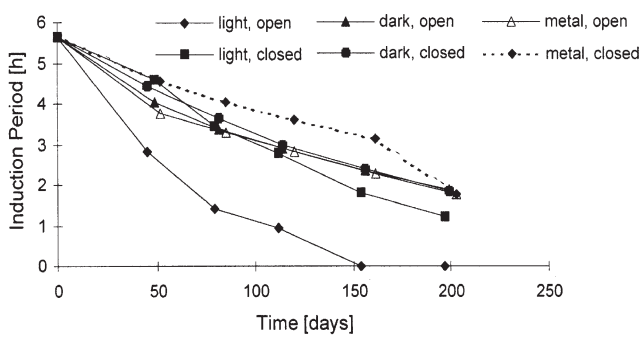


FIG. 1. Thermal oxidative stability of rapeseed oil methyl esters during storage.

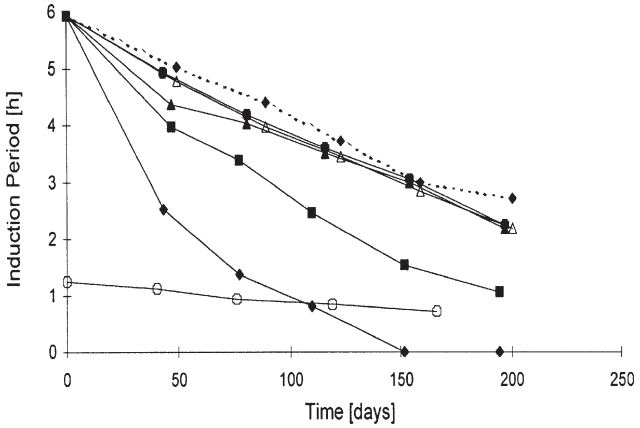


FIG. 2. Thermal oxidative stability of used frying oil methyl esters during storage. ○, distilled sample prepared from used frying oil; for other symbols see Figure 1.

gations have to be carried out to find appropriate natural or synthetic antioxidants to ensure high oxidative stability even under long storage conditions.

Peroxide number. In agreement with the results of the determination of the oxidative stability, the values for the peroxide number increased with storage time (Figs. 3, 4). This was especially noted for samples stored under light and exposure to air, where peroxide numbers of over 300 mVal O_2/kg were found after a storage time of over 200 d. Storage in the dark, however, lead to only a slight increase in peroxide numbers with the smallest increase being for the distilled UFOME sample.

In Figure 5 a strong correlation between the induction period and the peroxide number of the UFOME samples with storage time is shown. The undistilled samples exhibited higher peroxide numbers with increasing induction period. The distilled UFOME sample, however, showed very low peroxide numbers even at low induction periods.

Neutralization number. The neutralization number of both biodiesel samples also increased with increasing storage time,

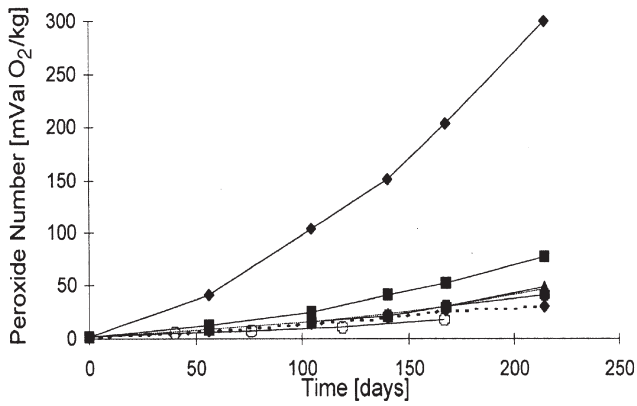


FIG. 4. Peroxide numbers of used frying oil methyl esters during storage. For symbols see Figures 1 and 2.

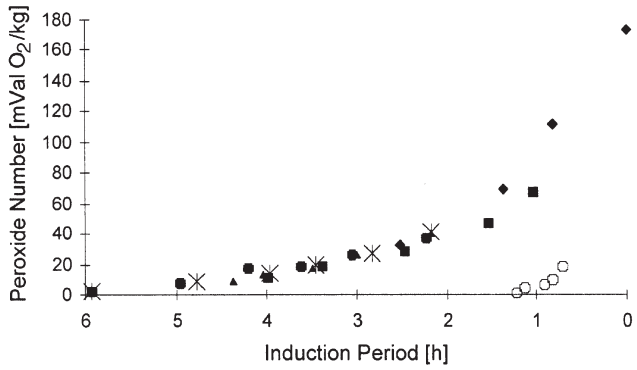


FIG. 5. Correlation between oxidative stability and peroxide numbers in used frying oil methyl esters during storage. ✕, Sample stored in open metal container. For other symbols see Figures 1 and 2.

a result of hydrolysis of FAME to fatty acids (Figs. 6, 7). A difference in neutralization number that is related to storage conditions also could be seen, but it was not so significant as with the oxidative stability and the peroxide numbers. The specification limit of 0.5 mg KOH/g is exceeded with the

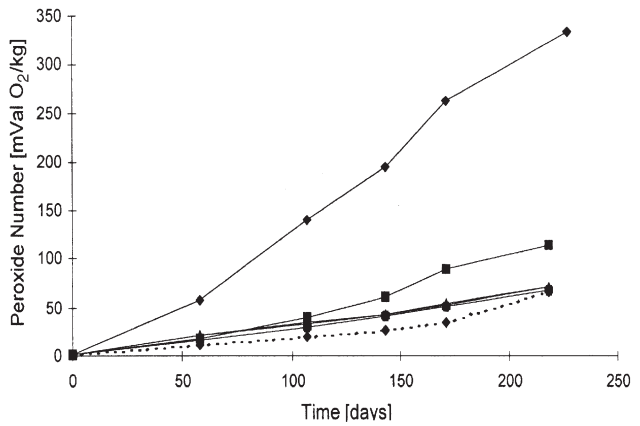


FIG. 3. Peroxide numbers of rapeseed oil methyl esters during storage. For symbols see Figure 1.

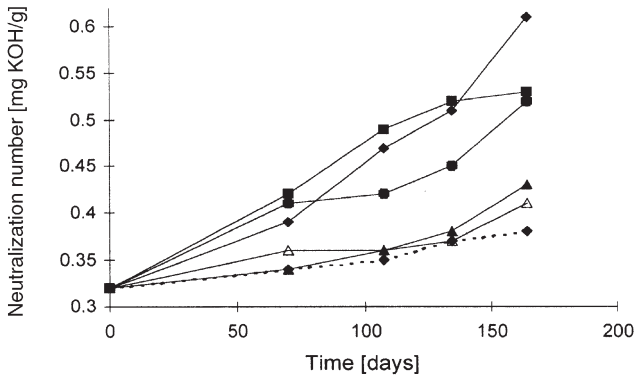


FIG. 6. Neutralization numbers of rapeseed oil methyl esters during storage.

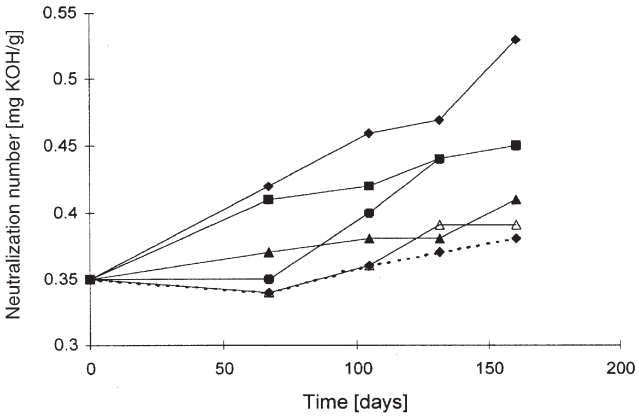


FIG. 7. Neutralization numbers of used frying oil methyl esters during storage.

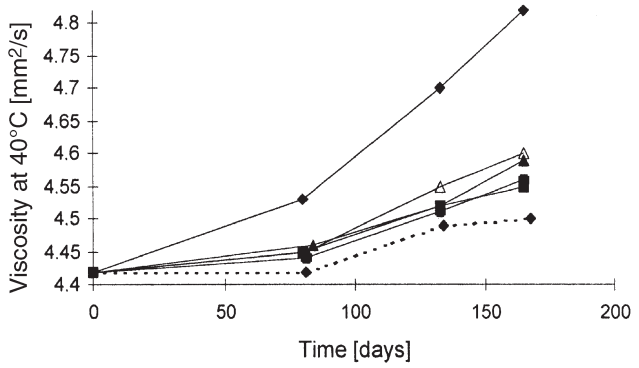


FIG. 8. Viscosity of rapeseed oil methyl esters during storage.

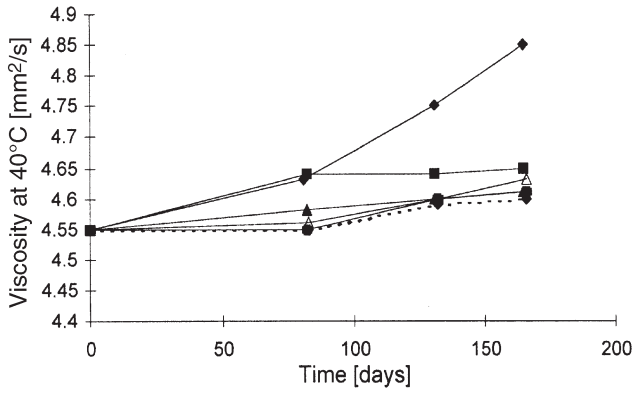


FIG 9. Viscosity of used frying oil methyl esters during storage. For symbols see Figure 1.

RME sample after storage with light exposure after 130 d, whereas with UFOME only open storage with light exposure over 150 d leads to a value exceeding 0.5 mg KOH/g.

Viscosity. During storage the viscosity of fats and oils increases owing to the formation of oxidized polymeric compounds. In the biodiesel samples only the samples stored under light and oxygen showed a significant increase in viscosity. However, the limit value of 5.0 mm^2/s at 40°C for the viscosity was not reached in any case (Figs. 8,9). All samples under other storage conditions only showed a slight increase in viscosity after a storage time of 170 d.

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