

Boiling Properties and Thermal Decomposition of Vegetable Oil Methyl Esters with Regard to Their Fuel Suitability

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Numerous vegetable oil methyl esters covering the entire range of fatty acid patterns of vegetable oils were investigated with a standard distillation apparatus. The course of the boiling curves and the suspected relationship between the drop in boiling temperatures and the start of decomposition are discussed. The suitability of the methyl esters for diesel engines was evaluated with regard to combustion conditions and specifications defined in fuel standards. The differences from regular diesel fuel are outlined.

Keywords: *Boiling diagram; combustion of vegetable oil methyl esters as fuel; decomposition of vegetable oil esters*

INTRODUCTION

The use of engine fuels from renewable resources has gained in importance in recent years. The necessity for reducing the impact of unhealthy emissions into the environment as well as the effect on the climate of carbon dioxide emissions is forcing science to find alternative fuels. Vegetable oils as well as their conversion products have the advantage that the environment will be protected by a nearly closed CO₂ cycle and reasonably low emission values. In addition, the cultivation of renewable natural resources in EU's set aside areas offers an interesting alternative to agriculture. For more than 20 years, specially designed engines and fuel from vegetable oils have been investigated for optimal use of vegetable oils and reduced emissions. Vegetable oils have a high calorific value compared to other liquid fuels recovered from biomass and are very similar to diesel fuel (Batel et al., 1980). The main restrictions on the use of vegetable oils in direct injection diesel engines are viscosity under ambient temperature conditions and residues in the engine cylinder (Peterson, 1986; Wenzel and Schulze Lammers, 1995). Therefore, vegetable oil should preferably be transesterized by using methanol. Other approaches aimed at reducing the viscosity of vegetable oils have been undertaken on blends and microemulsions of pure vegetable oil with short-chained alcohols (Vinyard et al., 1982; Johannson and Nordström, 1982; Goering et al., 1982). Refined crude vegetable oils have been taken into consideration as well as ordinary filtered vegetable oil for use in prechamber injection engines. Long-term tests, however, led to severe engine problems, e.g., deposits on pistons and valves (Peterson, 1986).

Additionally, vegetable oils were taken into consideration as a basis for value-added chemicals for petrol fuels (Glasser et al., 1992), and it is already in use as a lubricant oil as well as hydraulic liquid.

In Europe, rapeseed oil methyl ester (RME) is the most commonly produced vegetable oil fuel, and most of the European combustion engine manufacturers have already released their diesel engines for RME. In the United States, investigations on vegetable oil started

as long ago as 1978. Engelmann et al. (1978) compared waste soybean diesel oil blends with standard diesel fuel in short-term engines tests. In the United States, which is one of the major cultivators of soybeans, research has focused on soybean oil methyl ester (SME) (Einfalt and Goering, 1981; Borgelt and Harris, 1982). Great efforts have been made to reduce any storage problem of vegetable oil fuels and to achieve efficient and low-energy expression of vegetable oil from the seeds (Peterson et al., 1983; Wörgetter, 1991; Widmann, 1994).

Numerous investigations have been conducted to determine the emission behavior of combustion engines using RME and SME (Einfalt and Goering, 1981; Heinrich and Schäfer, 1990; Konen, 1992; Richter et al., 1991). The results of these investigations are inconsistent. Contradictory assessment of emission behavior may be due to nonadapted engines and different test conditions (e.g., different load cycles). Adapting a combustion engine to use vegetable oil esters as fuel presupposes the knowledge of basic properties of the oils. The boiling properties are vital for the combustion of liquid fuels and even for lubricants on the basis of vegetable oils, which have become important due to their biodegradability (Korber, 1991). A fundamental knowledge of this property is required for the optimization of the combustion process in internal combustion engines and for reducing harmful emissions in exhaust gases.

In the following investigation, the boiling properties of 10 different vegetable oil esters were studied. The results as well as conclusions to be drawn about their use in internal combustion are discussed.

CHOICE AND COMPOSITION OF THE VEGETABLE OIL METHYL ESTERS

The most important criterion in the choice of the vegetable oils was to obtain a broad spectrum of different fatty acid composition patterns. The vegetable oils used and their fatty acid compositions are shown in Table 1. The spectrum ranged from a high proportion of saturated fatty acids (palmgerm, 82.5%) to a high proportion of double unsaturated fatty acids (safflower oil, 79.7%). Oils with a high proportion of triple unsaturated fatty acids (linolenic acids, 18:3) were not considered because this type of vegetable oil is not

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Table 1. Fatty Acid Pattern for Vegetable Oils (%)

vegetable oil	shorthand notation for fatty acid					proportion of saturated fatty acids	proportion of multiple unsaturated fatty acids
	16:0	18:0	18:1	18:2	18:3		
palmgerm	7.5	2.2	15.4	2.2		8:0, 4.1; 10:0 3.8; 12:0 49.7; 14:0: 15.1	2.2
palm	42.7	7.9	36.1	10.6	0.2	14:0: 1.1	10.8
hazelnut	5.5	0.8	77.0	16.7			16.7
rapeseed e ⁺ ^a	3.8	0.4	16.2	18.1	11.5	22:1: 50.1	29.6
rapeseed e ⁻ ^a	4.1	0.5	63.9	21.1	10.4		31.5
ricegerm	16.2		41.5	37.9	1.9		39.8
sesame	9.7	5.4	40.7	42.6			42.6
cottonseed	19.9		20.1	53.3	1.2		54.5
sunflower	6.2	3.6	16.8	72.0	0.1	22:0: 1.1	72.1
safflower	6.7	1.5	12.0	79.7			79.7

^a e⁺ = high erucic acid; e⁻ = low erucic acid. ^b Remaining acids with less than 1% of the total amount are ignored in the table.

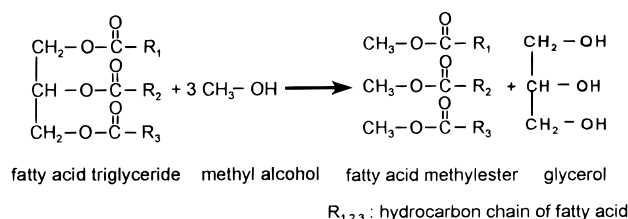


Figure 1. Equation for transesterification of fatty acid triglyceride to fatty acid methyl ester.

suitable for use as fuel due to its high polymerization tendency. Moreover, oils that can be isolated as byproducts of industrial plants (cottonseed oil, ricegerm oil) were considered.

The compositions of the vegetable oils were determined by gas chromatography analysis and checked according to supplier specifications. The proportion of multiple unsaturated fatty acids increased from a minimum in palmgerm oil (2.2%) to a maximum in safflower oil (79.9%). Rapeseed oil contained additional erucic acid (22:1 is the shorthand notation for chain length 22 with 1 double bond), which is an acid that rarely occurs in vegetable oils.

Transesterification. Potassium hydroxide (7.5 g, 0.13 mol) was diluted in 55 g (1.7 mol) of methanol. Vegetable oil (300 g, ca. 0.34 mol) was added to the solution, and the mixture was heated for 2 h at a temperature between 80 and 90 °C in a water bath. After cooling to room temperature, the glycerol was eliminated in a separating funnel and the upper phase was washed with water (50 mL). The vegetable oil methyl esters were stored at room temperature (Figure 1).

Distillation Process. Distillation was carried out in a standard distilling apparatus (see Figure 2). The transesterified oil was heated by a high-temperature electric mantle heater (3). For extension of the distillation path, a tubing adapter (5) was placed between the standard flask (4) and the distillation bridge. During distillation, a magnetic stirrer was in continuous operation. Methyl ester (50 mL) was distilled at a time with 3 repetitions. For temperature control of the mantle heater, a thermometer was installed (11). The boiling temperature was measured at the top of the tubing adapter just in front of the condenser inlet by a standard ground joint Hg thermometer (12). The Liebig condenser (6) was cooled by tap water, and condensates were collected in calibrated test tubes.

The heating mantle was heated for 15–20 min to temperatures of 500–550 °C. Nearly all distillations started at temperatures higher than 300 °C. During the first half of the distillation process, i.e., before half of the amount was distilled, distillation took place at a

- 1 Lifting Platform
- 2 Magnetic Stirrer
- 3 Pilz Heating Mantle
- 4 Standard Flask
- 5 Tubing Adapter
- 6 Liebig Condenser
- 7 Water exit
- 8 Water inlet
- 9 Delivery Adapter
- 10 Calibrated Test Tube
- 11 Contact Thermometer
- 12 Standard Ground Joint Hg-Thermometer

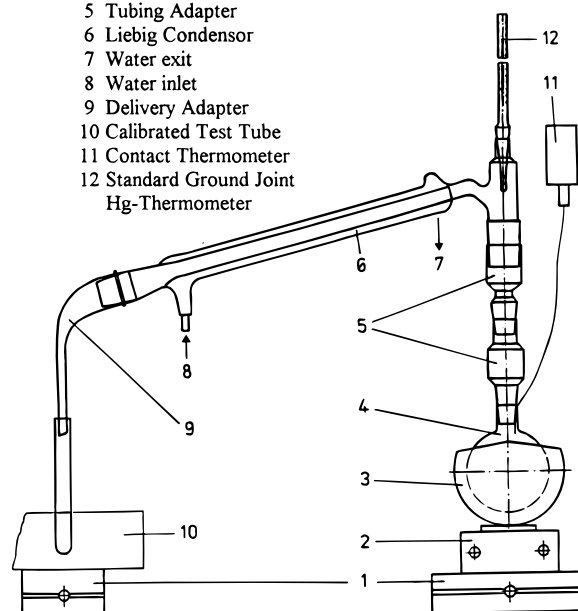


Figure 2. Distilling apparatus.

rate of ca. 2 min per 5 mL. The amount obtained was colorless. At the end of the experiment, the distillation became slower and the boiling temperature dropped. In this phase, the substrate turned yellow, which then intensified to dark yellow. The experiments were terminated when 90% of the input had evaporated. The nondistillable residue remained as a liquid and as black polymer residue in the flask. Losses of noncondensed mass, which were obtained by a mass balance of input oil mass, output of distilled amount, and residue in the flask, were on average lower than 5%.

RESULTS

Course of the Boiling Curves. The boiling diagram for the vegetable oil methyl esters being investigated is illustrated in Figure 3. These esters with very similar boiling graphs (hazelnut, rapeseed low erucic acid, ricegerm, sesame, cottonseed, sunflower, safflower methyl ester) are contained in a band consisting of an upper and a lower line. The boiling curves exceeding this sector (palmgerm and rapeseed oil methyl ester, high erucic acid) are outlined separately.

The starting point of boiling for most of the vegetable oil esters was found to be at a temperature exceeding 300 °C. Only palmgerm oil, which has as its main acid a short-chain acid (C12), started at 245 °C.

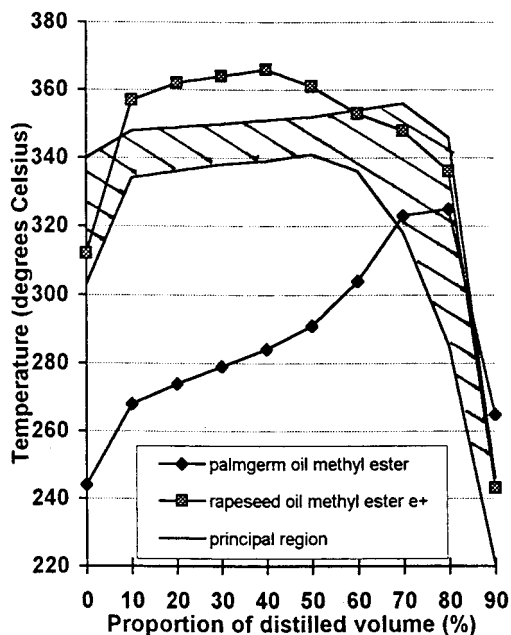


Figure 3. Main boiling sector for vegetable oil methyl esters.

In the initial phase (up to 10% of the evaporated volume) for all esters, the boiling temperature rose between 8 and 10 °C on average. The distillation continued at an almost steady temperature (temperature rise per 10% evaporated volume, ca. 1–2 °C). As a consequence, the courses of the boiling curves in this section are virtually horizontal. The rapid rise in temperatures at the beginning can be explained by impure oil esters containing low molecular compounds such as methanol and water, which decrease the total boiling temperature of the liquid solution. At the end of the distillation procedure, the temperatures decreased. The point at which the temperature starts to fall varies according to vegetable oil esters investigated. For 8 of the 10 esters, the temperatures start decreasing after evaporation of 60% of the volume. The phenomenon of decreasing boiling temperatures in the course of distillation is at variance with the boiling diagrams given in the literature. Authors of relevant publications (Wörgetter, 1991; Weidmann, 1994) report on an increasing course of the boiling temperatures at the end of the distillation but do not comment on this fact. Measurements made during this investigation did not confirm this. To show the differences in boiling curves in Figures 4 and 5, single graphs for rapeseed oil methyl ester, low erucic acid, and safflower oil methyl ester are provided. While for RME the boiling temperature followed an almost constant curve and dropped at 70% evaporated volume, the boiling temperature for safflower already starts decreasing at ca. 40% of the evaporated volume. The temperature drop can be explained by initiation of decomposition of the esters. The pyrolysis of fatty acid molecules produces short-chain compounds by breaking long-chain compounds. The short ones decrease the boiling temperature of the total liquid due to the low temperature level of the short-chain carbon compounds. The decomposition starts gradually because in the first phase of evaporation only a few chains are broken and their mass proportion is too small to contribute to a reduction in the boiling temperature. In the course of time, the evaporation continues, and additional molecules are pyrolyzed. Therefore, the proportion of short-chain components is steadily enlarged. It is assumed that in a secondary

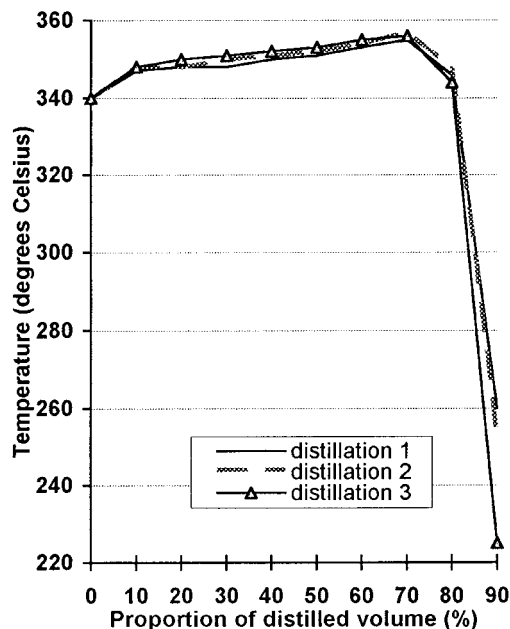


Figure 4. Boiling diagram of rapeseed oil methyl ester (low erucic acid).

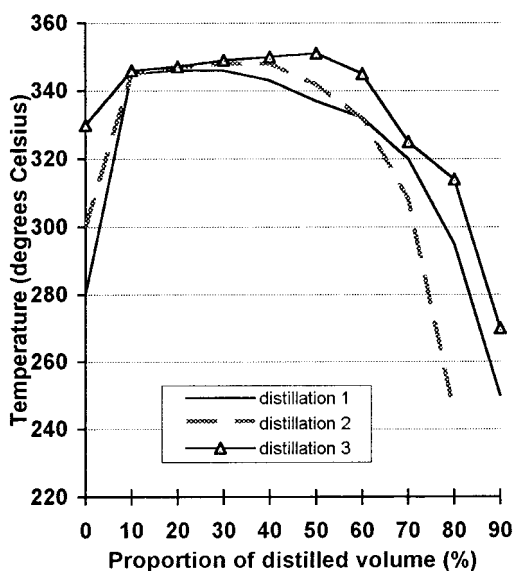


Figure 5. Boiling diagram of safflower oil methyl ester.

reaction, components with short carbon chains are generated and, accordingly, the boiling point of the total liquid drops in the course of the distillation. One characteristic of this effect is that the boiling temperature at 90% of the evaporated volume is slightly above 200 °C and is lower than at the beginning of the evaporation. The explanation of decreasing boiling temperatures at the end of the distillation was confirmed by chromatography analysis of the single fractions. Chromatograms showed the increase in the number of compounds in the condensate when a decrease in boiling temperatures begins; simultaneously, the bands for the different methyl esters disappeared.

In our investigations, no relationship between the number of double compounds in the ester and start of decomposition (and the rate of decomposition) could be detected. These esters, which are solid under room-temperature conditions (palmgerm oil and palm oil), begin decomposition later than the other oils starting at 75% of the evaporated volume.

Table 2. Maximum Difference in Boiling Temperatures^a (°C) in the Related Distilled Amounts (Fractions) for 10 Vegetable Oil Methyl Esters

methyl ester of	fractions									mean value ^c	av decreasing pt, ^d %
	10%	20%	30%	40%	50%	60%	70%	80%	90%		
palmgerm oil	3	3	2	3	4	7	13	13	55	11.4	77
palm oil	3	2	1	2	1	1	8	43	45	11.7	76
hazelnut oil	4	3	2	3	1	7	18	24	30	10.2	66
rapeseed oil e ⁺ b	5	6	7	10	17	23	26	34	60	20.9	43
rapeseed oil e ⁻ b	1	2	3	2	2	2	2	4	35	5.9	72
ricegerm oil	1	1	1	0	1	2	7	6	50	7.7	66
sesame oil	1	1	1	1	2	2	7	19	20	6.0	65
cottonseed oil	1	2	2	2	1	3	5	52	10	8.7	64
sunflower oil	3	1	1	1	1	1	11	22	41	9.1	66
safflower oil	1	1	3	7	14	13	17	69	100	25	39
mean value ^e	2.3	2.2	2.3	3.1	4.4	6.1	11.4	28.6	44.6		

^a Values are calculated for each vegetable oil methyl ester as a difference between the lowest and highest temperature within three experiments in the related fractions. ^b See Table 1, footnote a. ^c Mean value of maximum temperature-differences of the oils. ^d Percentage of distilled amount, when boiling temperature starts decreasing. ^e Mean value of maximum temperature differences of fractions.

Repeatability and Scatterband of Vegetable Oil Ester Distillation.

In Figures 4 and 5, the scattering of the boiling curves and the boiling diagrams for rapeseed oil methyl ester low erucic acid and safflower oil methyl ester are given. To point out the differences in temperatures for the single fractions, Table 2 contains the numeric values as temperature differences for all oil esters. The boiling diagrams demonstrate two tendencies concerning the repeatability of the temperature values. In the beginning, high repeatability is observed up to 40% of the evaporated volume. The difference between the maximum and the minimum boiling temperature in a fraction is limited to 2–3 °C for all vegetable oil methyl esters (see Table 2: mean values, last line). Only the temperatures at the onset of boiling vary depending on the rate of double bonds in the esters. While heating the ester, single, unstable molecules decompose. The pyrolysis reactions take place randomly, and as a consequence, the type and amount of products which occur are different in each distillation experiment and cause variations in the starting temperatures.

For the higher fractions of the amounts distilled, the average temperature difference increases continuously. The boiling curve has in this section a nonuniform shape which is typical of pyrolytic reactions. With increasing amounts of pyrolysis products, the differences between the distillation temperatures are steadily enlarged. For the last fraction (90% of the amount distilled), the temperature difference is, on average, 45 °C.

There was no relation between the compositions of the vegetable oils and the repeatability of the boiling diagrams with regard to the mean values of the temperature differences of the individual vegetable oil esters.

DISCUSSION OF RESULTS AND CONCLUSIONS

The boiling diagrams of the esters have a characteristic shape, which differs markedly from the boiling diagram of diesel fuel (see Figure 6). While the boiling curve of diesel steadily increases in a range located between 200 and 300 °C, the average boiling curve for the vegetable oil esters has a more or less horizontal course within a range of 320–350 °C and a drop in the last third of the distilled amount. This phenomenon is due to the beginning of the decomposition of the esters in the last part of the distillation.

The occurrence of decomposition products in the last phase of the internal combustion can help improve the combustion process in the engine. At the end of every

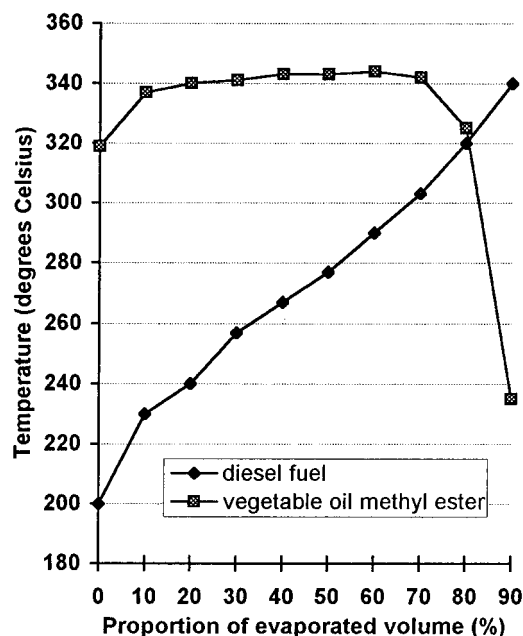


Figure 6. Comparison of average boiling curve for vegetable oil methyl esters with diesel fuel.

combustion procedure, the combustion temperature in the engine cylinder decreases. The decomposition products of the esters remain due to their low boiling temperatures in the gaseous phase, and as a consequence, combustion continues. Undecomposed esters, however, change in the course of decreasing temperatures and at the end of the combustion to the liquid phase, which is not suitable for combustion.

Investigations of the exhaust gases of engines using RME and diesel demonstrate that in both cases, uncombusted carbon is emitted in similar amounts (Weidmann, 1994). RME engines, however, have increased emissions of fuel when idling. Due to the low temperature under this load condition in the engine cylinder, the percentage of decomposed ester is low and the ester itself remains in the liquid phase in the cold zone of the combustion space. Both conditions explain the occurrence of RME in the exhaust gases.

Another fact noticed when using RME as the fuel for internal combustion engines is the lower emission of hydrocarbons, in particular of simple polycyclic aromatic hydrocarbons (Konen, 1992; May and Dietrich, 1994; Weidmann, 1994; Wörgetter, 1991) in the exhaust gases, compared with diesel engines. This may be due to the late decomposition of RME and a better combustion of

the decomposed products due to a longer period in the gaseous phase.

Vegetable oil esters are evaporated at the beginning of the combustion without decomposing. The properties of the ester itself and not of the decomposition products are responsible for ignition suitability. This is in contrast to chemically unchanged vegetable oils, which decompose while evaporating (Wenzel and Schulze Lammers, 1995). As a consequence, the decomposition products are significant for ignition of the fuel in the cylinder.

The specifications fixed in the standards for diesel fuel (DIN 51 601) defining the boiling range are fulfilled by vegetable oils esters. With some exceptions, 80% of the input amount of vegetable oil ester is evaporated in the range of 300–350 °C. Only rapeseed oil, high erucic acid, does not meet the specification of minimum evaporated amount of 85% of the volume at 350 °C, which is due to the high content of long-chain erucic acid (C22).

Palmgerm oil methyl ester with its high portion of short-chain fatty acids (C8, C12) is most similar to the boiling curve of diesel fuel. Its boiling curve increases continuously like the one for diesel up to 70% of the distilled amount (240–325 °C). Subsequently, decomposition starts, accompanied by a drop in the boiling temperatures.

The description and publication of boiling diagrams in the literature is not uniform. The values given by different authors for boiling temperatures differ in the same fractions by as much as 40 °C (Mittelbach, 1984; Sims, 1982; Weidmann, 1994; Wörgetter, 1991). Drops in temperature at the end of distillation have not been observed.

Our investigations demonstrate new approaches for explaining the emission characteristics of engines using vegetable oil esters. Advanced knowledge of the physical and chemical properties of fuel on the basis of vegetable oils contributes to the adaptation of internal combustion engines, supports the efforts at reducing harmful compounds in the exhaust gases, and contributes to energy efficiency.

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