

Transesterification of Heated Rapeseed Oil for Extending Diesel Fuel¹

M. Mittelbach* and H. Enzelsberger

Institute of Organic Chemistry, Karl-Franzens-Universität Graz, A-8010 Graz, Austria

ABSTRACT: Fatty acid methyl esters are well established as an alternative fuel called "biodiesel." For economic reasons, used frying oil is an interesting alternative feedstock for biodiesel production. The chemical changes that occur during heating of rapeseed oil, especially the formation of polymers, were investigated. Heated rapeseed oil samples were transesterified with methanol and analyzed by size-exclusion chromatography. During heating, the amount of polymers in the starting oil increased up to 15 wt%, but only up to 5 wt% in the transesterified samples. So during transesterification, dimeric and trimeric triglycerides in the starting oil were mainly converted into monomeric and dimeric fatty acid methyl esters. The amount of polymeric fatty acid methyl esters had a negative influence on fuel characteristics. After 6 h of heating, the amount of Conradson carbon residue and after 16 h the viscosity exceeded that of the existing specifications for biodiesel. Therefore, the amount of polymers in waste oil is a good indicator for the suitability for biodiesel production.

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During the last 15 yr, the production and use of fatty acid methyl esters (biodiesel) as alternative fuel have been established worldwide (1,2). Adapting the fuel to the engine is preferred to adapting the engine to the fuel. Transesterifying vegetable oils to form fatty acid methyl esters, which can be used directly in common diesel engines, has achieved more importance than using unmodified vegetable oils in specially designed diesel engines. The main advantage of biodiesel over neat vegetable oils is that biodiesel has similar fuel characteristics to diesel, so either blends or 100% alternative fuel can be used without major modifications of the engine.

Today, world production capacity of biodiesel is estimated at 1.3 million tons (3). The total production for 1997 was estimated at 660 thousand tons, mainly produced in Europe (3). Owing to the limited availability of crop land leading to competition with the food industry as well as the relatively high

price for vegetable oils at the present time, it is increasingly important to look for alternative feedstocks for biodiesel production, especially waste oils such as used frying oils.

As early as 1983 the first biodiesel production and engine tests were done in Austria with used frying oil. In 1985, emission tests with 100% used frying oil methyl esters were done in cooperation with AVL (Graz, Austria) (4). In 1994, the first plant for the production of methyl esters from used frying oil was put into operation in Mureck, Austria (5). Up to the end of 1998, 3,500 tons of used frying oil methyl esters have been produced and used successfully as a 100% fuel substitute in a series of different vehicles (6).

The fuel quality of biodiesel depends upon factors that arise during and following transesterification, such as completion of reaction and presence of trace levels of catalyst or alcohol. Therefore, in several countries specifications for biodiesel have been developed that establish limits for the most important parameters describing quality (7). Another important factor in deriving feedstocks from used frying oils is the presence of food and dust particles, which must be removed prior to transesterification. Biodiesel quality also depends on the quality of the used frying oil, especially on the duration and temperature of its heating. During heating of vegetable oils for frying purposes, thermal, oxidative, or hydrolytic reactions can cause chemical changes. Thermal reactions, initiated by free radicals, can lead to intra- or intermolecular cyclization and oligomerization (8,9); the Diels-Alder reaction may be a possible cyclization mechanism (8). Also, oxidation reactions are initiated by free radicals. The reaction with oxygen leads to peroxy radicals and hydroperoxides (10). Cleavage of hydroperoxides can lead to the formation of volatile aldehydes and acids. In the presence of excess oxygen, however, the alkoxy and peroxy radicals can be transformed into dimeric and oligomeric compounds (8). Finally, mono- and diglycerides, as well as free fatty acids, are formed by hydrolytic reactions.

The formation of oligomers may be crucial for the use of used frying oil as feedstock for biodiesel production. Higher contents of these products may influence viscosity, volatility, and other fuel parameters. The objective of this paper was to investigate how the oligomers, which are formed during heating of rapeseed oil, are transformed during transesterification and how the remaining products influence fuel characteristics.

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*To whom correspondence should be addressed at Institute of Organic Chemistry, Karl-Franzens-Universität Graz, Heinrichstrasse 28, A-8010 Graz, Austria. E-mail: mittelba@balu.kfunigraz.ac.at

MATERIALS AND METHODS

For the heating experiments, fully refined edible grade rapeseed oil (canola) was used as starting material. The chemicals used for the transesterification reaction were reagent grade; high-performance liquid chromatography (HPLC)-grade tetrahydrofuran for high-performance size exclusion chromatography (HPSEC) was purchased from Promochem (Wesel, Germany). A sample of dimeric fatty acid methyl ester was prepared from a commercially available dimeric fatty acid (Pripol 1014; Unichema, Emmerich, Germany) by methylation using a standard procedure (11).

Transesterification and sample preparation. Four liters of oil were heated to 180°C under constant stirring with a mechanical stirrer at 120 rpm in an open stainless-steel vessel. At 2-h intervals, 200-mL samples were taken until the final heating time of 20 h was reached. The samples were transesterified at room temperature using methanol and KOH as catalyst (4). The degree of transesterification was measured by gas chromatography (12); in all samples the sum of glycerides was less than 1.0 %.

The separation of the oil samples into polar and nonpolar fractions was done by column chromatography with silica gel according to IUPAC (13). The sample (5 g) was dissolved in a petroleum ether/diethylether mixture (87:13, vol/vol) and transferred to a chromatographic column packed with silica gel. The different fractions were eluted with solvent mixtures having different polarities. The separation was controlled by thin-layer chromatography; the fractions were evaporated and weighed.

Determination of polymers. A modified IUPAC method using HPSEC was used to determine the polymer content (13). The modification was the use of a second column in series to get better resolution. The reproducibility of the method was within the ranges evaluated in a collaborative study with the original method (14). Analyses were carried out with a Hewlett-Packard model 1100 HPLC (Palo Alto, CA), equipped with a quaternary pump, a vacuum degasser, an autosampler, a chem station and a Knauer (Berlin, Germany) differential refractometer detector. Two gel-permeation chromatography columns were connected in series (Phenomenex, Torrance, CA), the first column 300 × 7.8 mm, pore size 10 nm; the second column 300 × 7.8 mm, pore size 50 nm. The columns and detector were thermally controlled at 40°C. Tetrahydrofuran eluent at a flow rate of 1 mL/min was used. The samples were diluted in tetrahydrofuran (10 mg/mL) and filtered; 50 µg of sample solutions were injected. For each sample a mean value was calculated from two analysis runs.

High-temperature gas chromatography was carried out using a Hewlett-Packard 5890 gas chromatograph, Series II (Palo Alto, CA), equipped with an autosampler, an on-column inlet system, and a flame-ionization detector. A fused-silica column, 10 m × 0.25 mm, 0.25 µm DB-5 (J&W Scientific, Inc., Folsom, CA), was used. The column was connected with a 2 m × 0.53 mm uncoated precolumn. The temperature program was 50°C (1 min), 15°C/min to 180°C (0 min),

7°C/min to 230°C (0 min), and 30°C/min to 370°C (10 min). The detector temperature was 380°C; carrier gas hydrogen; and injection volume 1 µL.

RESULTS AND DISCUSSION

Oil analyses. The heated oil samples were separated into polar and nonpolar fractions by column chromatography. The polar fraction rose from 2.8% for the unheated oil up to 16.8% after 20 h of heating (Fig. 1). With HPSEC the compounds were separated according to their molecular masses. As Cuesta *et al.* (15) have shown, the response factors for free fatty acids, mono-, di-, and triglycerides, as well as polar and polymeric compounds, were similar. Quantification was done by normalizing the peak areas. The chromatograms of the heated oil samples (Fig. 2) had good separation between triglycerides and dimeric triglycerides, but traces of trimeric triglycerides were also detected. Because the main part of the polymers consisted of dimeric compounds, the dimers and trimers were summed. The amount of polymers rose from 1.2% in the untreated oil to 14.6% after 20 h of heating (Fig. 3). By comparing the HPSEC chromatograms of the polar and nonpolar fractions, one can assume that most of the dimeric and trimeric triglycerides were in the polar fraction.

Methyl ester analyses. A typical HPSEC chromatogram of a methyl ester sample is shown in Figure 4. In front of the methyl ester peak only one peak with higher molecular mass was detected. This peak was identified as dimeric fatty acid methyl esters by comparison with a standard. Because of possible interference with sterol esters, which have similar molecular mass as dimeric esters, the values were corrected by subtracting the average content of sterol esters in fatty acid methyl esters (approximately 0.7%) (16). The content of dimeric fatty acid esters in all methyl ester samples was far lower than the polymer content in the corresponding oil (Fig. 5). So during transesterification, dimeric and trimeric triglycerides were mainly converted into monomeric and dimeric fatty acid methyl esters; this comparison was made on a mass basis. The dimeric methyl esters were also found by high-temperature gas chromatography (12). However, owing to the broad signal, exact quantification was not possible (Fig. 6).

Content of polymers and fuel characteristics. Higher content of oligomeric compounds in fatty acid methyl esters may influence the fuel characteristics, such as viscosity and poorer burning characteristics, because lower volatility may result. The viscosities of the oils and their corresponding methyl esters at 40°C are shown vs. time of heating (Fig. 7). For the methyl esters, the viscosity limit of 5.0 cSt (16) in specifications for biodiesel was reached after 16 h of heating.

One of the most important parameters for characterizing biodiesel is Conradson Carbon Residue (CCR). Despite the fact that the procedure for determining CCR is an old method compared to modern analytical techniques, this parameter is an excellent quality indicator for biodiesel (7). It corresponds to the content of glycerides as well as free fatty acids, soaps, remaining catalyst, and other impurities. In most specifica-

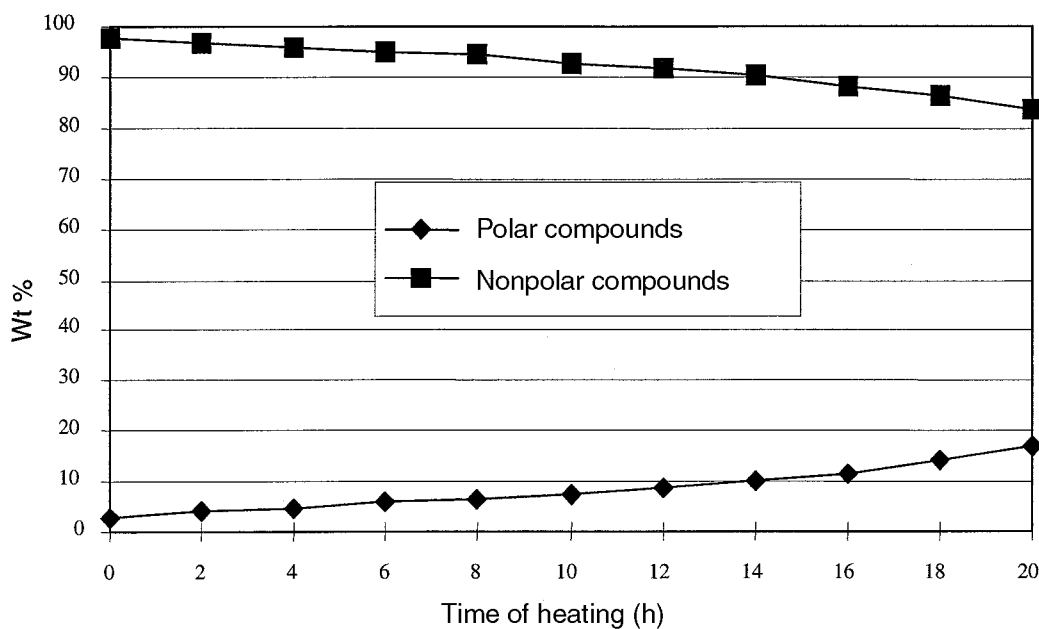


FIG. 1. Formation of polar compounds during heating of rapeseed oil.

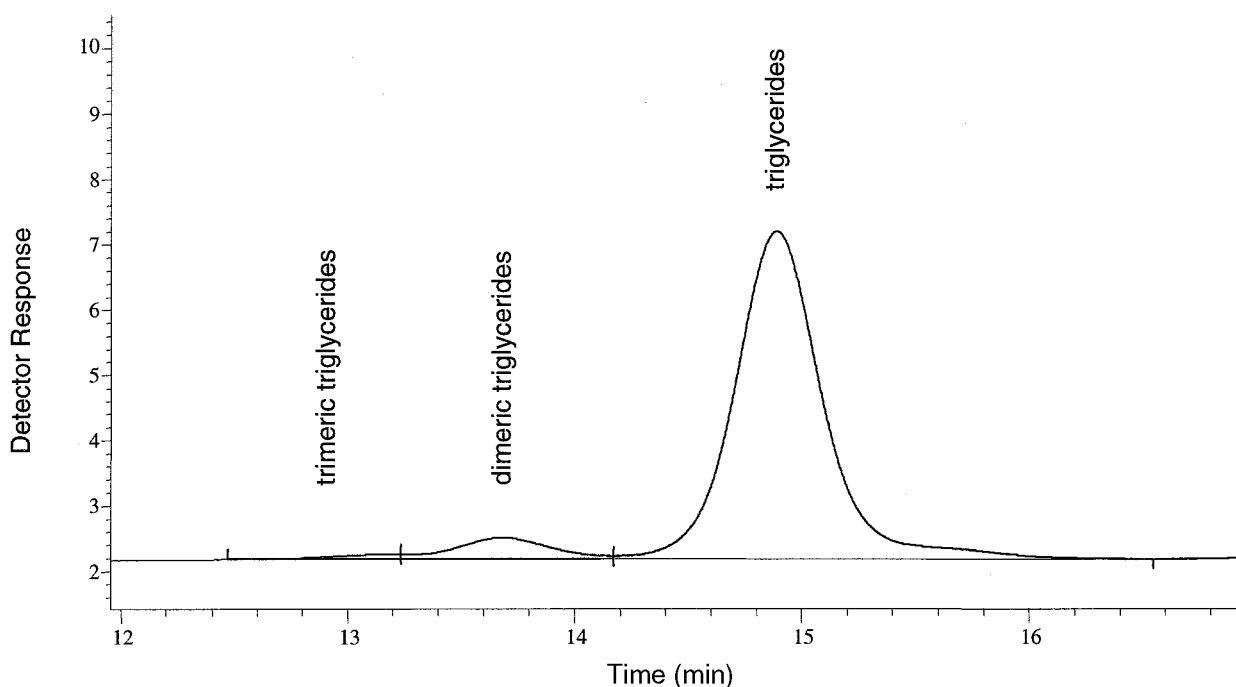


FIG. 2. High-performance size exclusion chromatogram of rapeseed oil after 14 h of heating.

tions it is limited to 0.05%. As one can see in Figure 8, the value increased with heating time and correlated with the amount of dimeric fatty acid methyl esters.

During heating of rapeseed oil, the amounts of polymers and polar compounds continuously increased. During transesterification with methanol the polymers were cleaved, leading mainly to monomeric and dimeric fatty acid methyl esters. Because of higher molecular mass and lower volatility, these esters influence fuel characteristics, mainly the viscosity and the Conradson carbon residue. No other effect could

be observed. Because of the absence of glycerol these dimeric methyl esters have no negative influence on engine performance in long-term performance tests. In the frame of an AL-TENER project (6) two city buses, equipped with catalytical converters, were tested over a period of 3 yr covering a distance of almost 200,000 km each, equivalent to a running time of almost 10,000 h each. In using 100% used frying oil methyl esters for fuel, no negative influences on performance and engine parts were observed. Therefore, it does not seem to be necessary to limit the content of dimeric methyl esters,

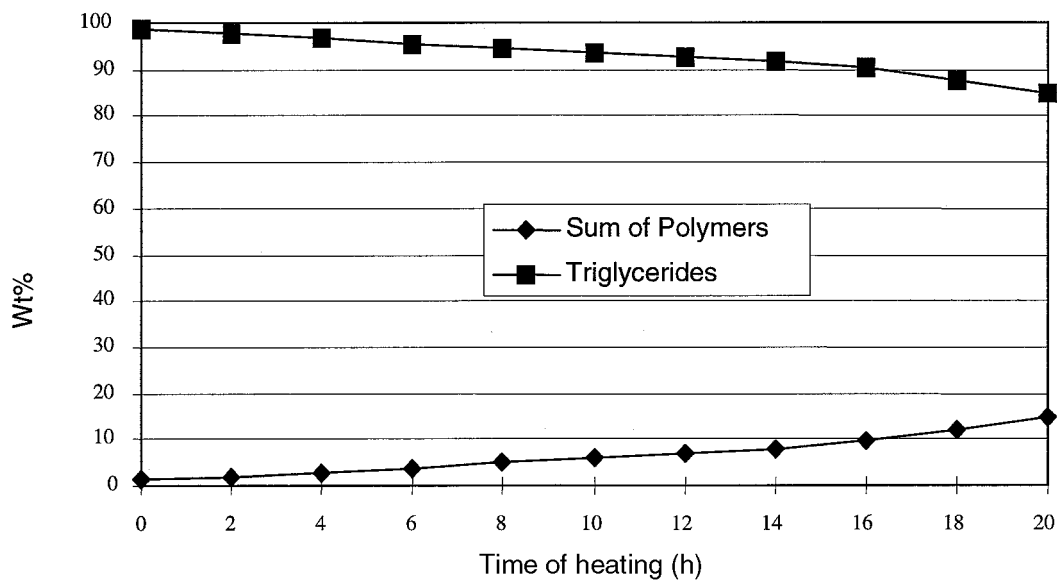


FIG. 3. Formation of polymers during heating of rapeseed oil.

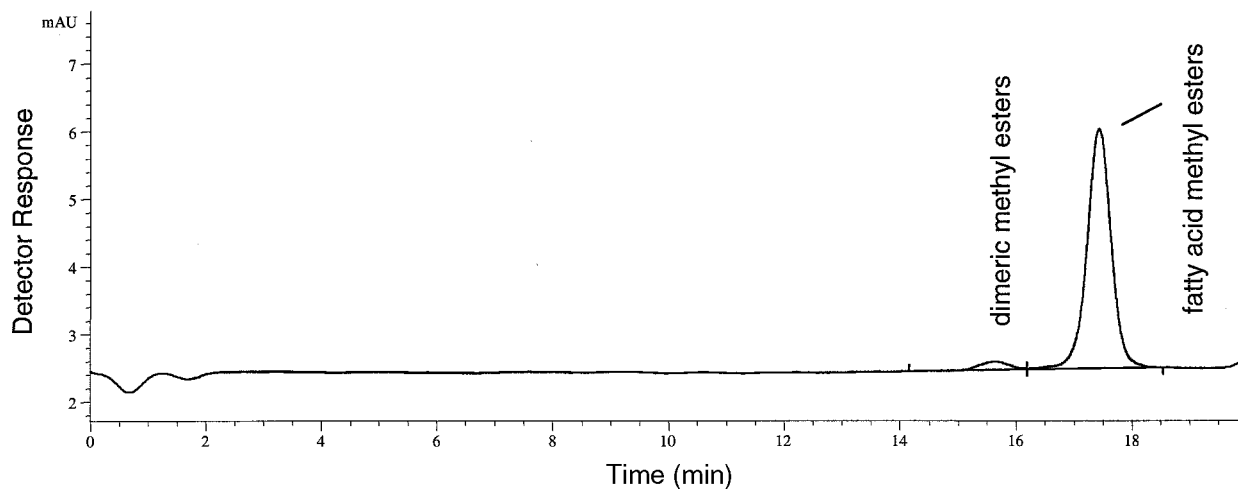


FIG. 4. High-performance size exclusion chromatogram of methyl esters prepared from rapeseed oil after 14 h of heating.

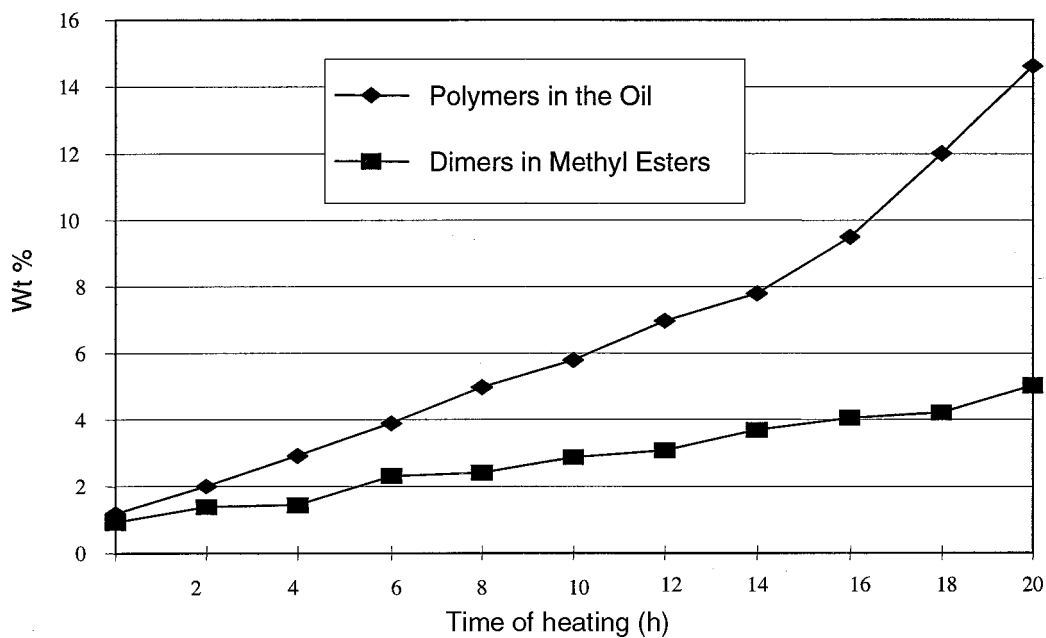


FIG. 5. Contents of polymers in the oils and dimeric fatty acid methyl esters after transesterification.

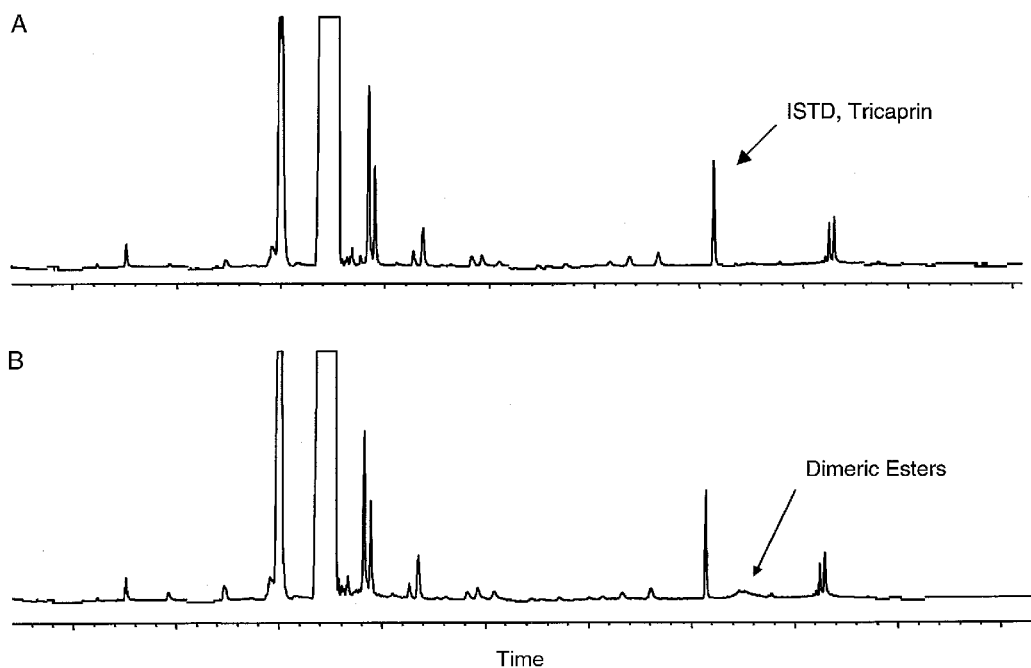


FIG. 6. Gas chromatograms of (A) rapeseed oil methyl esters and (B) methyl esters from used frying oil. ISTD, internal standard.

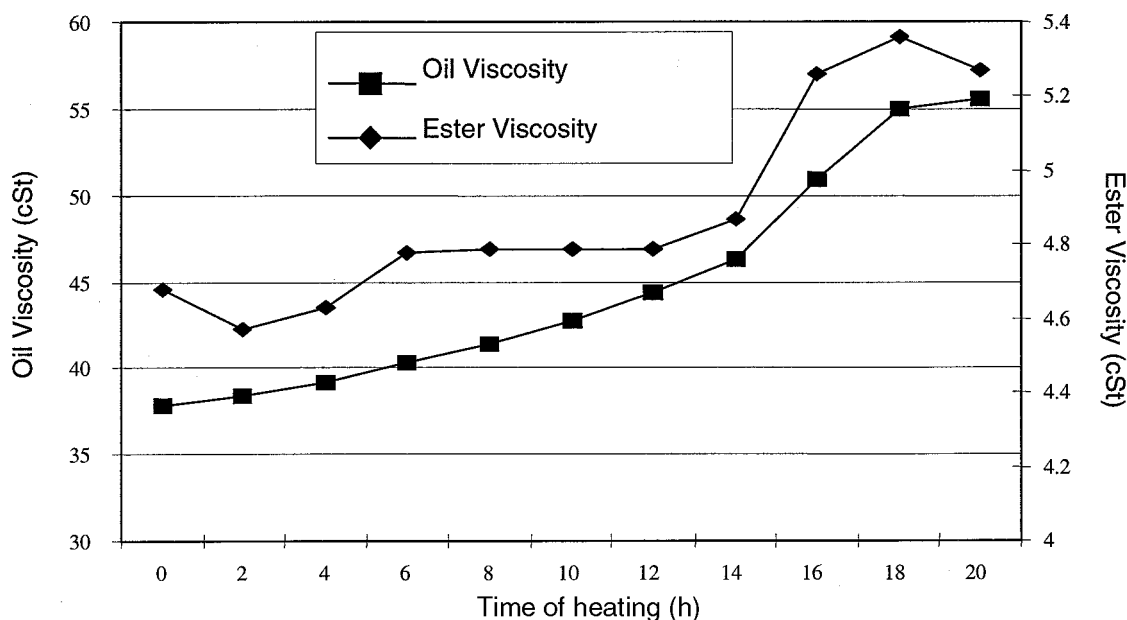


FIG. 7. Viscosity at 40°C of heated oil samples and transesterified methyl esters.

as an additional parameter in fuel specifications for biodiesel, because viscosity and carbon residue are good indicators for the existence of higher levels of dimers.

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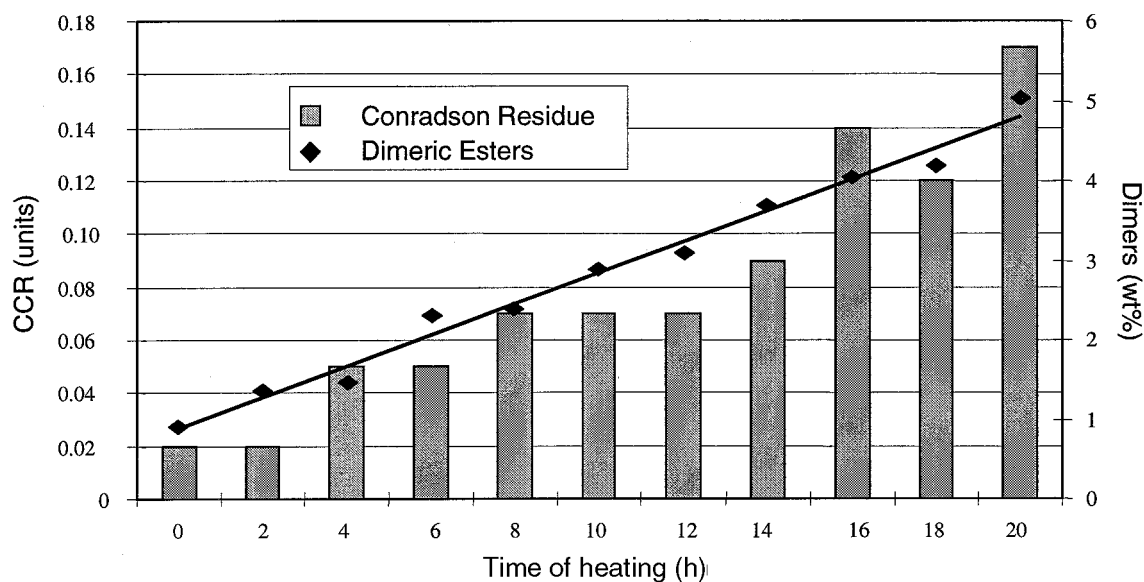


FIG. 8. Conradson carbon residue and percentage of dimers in transesterified methyl esters.

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