Chromatogr.
237 (1993).
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Transesterification Processes for Vegetable Oils: A Simple Control Method of Methyl Ester Content

P. De Filippis[a], C. Giavarini[a,*], M. Scarsella[a] and M. Sorrentino[b]

[a]Dipartimento Ingegneria Chimica, Università La Sapienza, 00184 Rome, Italy and [b]Dipartimento Dogane, Direzione Centrale Analisi Merceologica e Laboratorio, Rome, Italy

ABSTRACT: One of the main problems in the study or industrial application of transesterification processes for vegetable oils is how to measure the methyl ester content. In this work, a quick analytical method was developed for assessing the methyl ester content of purified "fuel grade" transesterification products by applying a simple correlation with viscosity. The correlation was tested on a wide range of samples with various methyl ester contents; the results were in agreement with the values measured by gas-chromatographic analysis. In a defined range of weight fractions the correlation allows for the determination of the methyl ester content of purified transesterification products by a single viscosity measurement. This method is especially suitable for process control purposes as it determines the methyl ester content quickly and simply.
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KEY WORDS: Density measurement, diesel oil substitute, esterification, methyl ester density, methyl ester determination, methyl ester viscosity, vegetable oils, viscosity measurement.

The use of vegetable oils as potential substitutes for current petroleum-derived diesel fuel has been extensively investigated in the past years (1–4), especially due to the ever-growing interest for the impact on the environment by the use of various fuels. In comparison with diesel fuels, vegetable oils have good heating power and provide exhaust gas with almost no sulphur compounds and the reduction of carbon dioxide and aromatic polycyclics. Their use in modern diesel engines is limited, however, due to their high viscosity, which is nearly ten times that of gas oil (5,6).

The reduction of vegetable oil viscosity has been studied by both physical and chemical methods (7), including dilution (8,9), microemulsification (10,11), cracking, and hydrocracking (12–14). Transesterification, producing fatty acids methyl esters (FAME) by alkali-catalyzed reaction, is the most applied process (4,15–17).

The use of FAME in unmodified diesel engines is possible on the condition that high purity standards are applied (18). These concern, above all, the maximum content of those compounds which produce deposits when burned; for example, glycerine and glycerine esters can produce acrolein which polymerizes to disacryl, a solid plastic material. Standards have been developed for fuel-grade esters (also called "biodiesel") by a number of countries, including Italy (19).

Analytical methods for the evaluation of the FAME content in transesterification products are based on gas–liquid chromatography (GLC), thin-layer chromatography/flame-ionization detector (TLC/FID), or high-performance liquid chromatography (HPLC)/gel permeation chromatography (GPC) systems (20–24).

They are usually very sensitive and measure, besides FAME, by-products such as mono- and diglycerides, as well as unreacted triglycerides. However, they have some drawbacks—high accuracy is required during sample preparation; moreover, chemical modification of the sample is often necessary for analysis, and the time required for the analysis is usually long, so that "on-line" application in a transesterification plant is very difficult.

The purpose of this work was to develop a quick analytical method for the evaluation of FAME in transesterification products, to be utilized as a process control. The proposed method is based on viscosity measurements—fatty acids, mono-, di-, and triglycerides, and methyl esters show different viscosity values. Reflecting higher molecular weight, polarity, steric hindrance, and intermolecular forces, the glycerides of fatty acids usually show higher viscosity than the corresponding methyl esters. This viscosity difference is sufficient to give an indication of the FAME content in a transesterification product.

EXPERIMENTAL PROCEDURES

In order to have samples with various degrees of purity, a number of transesterification reactions were carried out in the laboratory. The soybean oils used for transesterification reactions were refined, edible-grade oils. Methanol, HPLC-grade (Aldrich, Steinheim, Germany), was used without further purification. These oils exhibited an average saponification number of 192, iodine number of 133, and an acid number of 0.06. Karl Fischer titration before use gave values <0.15% water. Reagent-grade sodium hydroxide was used as a catalyst.

In order to determine the FAME and glyceride content of the transesterification products, sample preparation and GLC

*To whom correspondence should be addressed.

analyses were carried out according to the most frequently used analytical procedures (22). An HP 5890/II (Waldbronn, Karlsruhe, Germany) gas chromatograph was used, fitted with an FID detector and a 15 m × 0.53 mm i.d. column with a 1-m retention gap (Supelco SPB TM-1; Supelco, Bellefonte, PA). The film thickness was 0.1 μm. The main parameters were: helium as carrier gas with a flow of 8.5 mL/min; injection temperature, 75°C; detector temperature, 350°C; temperature program, 75°C for the first minute, 75–140°C at 24°C/min, 140–330°C at 8°C/min, 330°C for 2 min, 330–345°C at 12°C/min, and 345°C for 12 min.

Viscosities were determined using an Hoeppler microviscometer (Haake, Berlin, Germany). Densities were measured with the use of pycnometer and analytical balance. Fourier transform infrared (FTIR) analysis was performed using a Matteson 5000 FTIR spectrophotometer (Madison, WI). Atomic absorption spectroscopy was carried out using a Philips PU 9200 atomic absorption spectrophotometer (Cambridge, England).

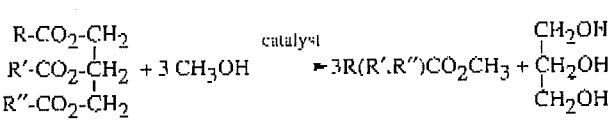
Transesterification reactions were carried out in a 500-mL reaction vessel equipped with mechanical stirrer, thermometer, and reflux condenser. The solid catalyst, sodium hydroxide, was dissolved in methanol, and soybean oil was added by stirring. The catalyst/methanol/soybean oil ratios varied in order to obtain a large range of methyl ester yields.

The mixture was heated up to 65°C and then kept at this temperature for a time ranging from ten minutes to two hours. The time of reaction varied according to the catalyst/methanol/soybean oil molar ratios. Heating and stirring were then stopped, and the reaction mixture was let stand to separate glycerol.

After elimination of the glycerol layer, crude methyl esters were treated with a few drops of sulfuric acid (30% by weight) to disactivate the catalyst residues. Excess methanol was then distilled off under reduced pressure, and the methyl ester was finally centrifuged to separate the last glycerol traces. All reactions were conducted in N_2 atmosphere to minimize oxidative degradation and hydrolysis. The ash content of the purified products was less than 0.01%. The sodium content, determined by atomic absorption spectroscopy, was less than 0.01 ppm. The methanol concentration was about 100 ppm. The transesterification product, a mixture of methyl esters, unreacted oil, and mono- and diglycerides, was analyzed by gas chromatography. Viscosity and density also were measured.

RESULTS AND DISCUSSION

The simple stoichiometry of the applied transesterification reaction can be written as in Scheme 1. However, transesterification consists of a number of consecutive, reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and of monoglycerides to glycerol, yielding one methyl ester molecule from each glyceride molecule at each step. The methanol/triglyceride molar ratio required by the stoichiometry should be 3:1, but it needs to be higher than 3 to have a maximum methyl ester yield. A molar ratio of 6:1 normally is used in industrial processes to obtain methyl ester yields higher than 98% by weight. In this work, molar ratios varying from 1.3 to 12 were used to obtain a large range of methyl ester yields, including samples with low methyl ester and high mono- and diglyceride content.



SCHEME 1

Such samples do not fulfill the standards for fuel-grade oils; however, they were useful for checking the proposed control method in a wider range of concentrations. Table 1 lists the conditions for the transesterification reactions. The aim of the transesterification reactions carried out in this work was to obtain a large range of samples containing different percentages of methyl ester in order to study a correlation with viscosity.

Table 1 also shows the results of the gas-chromatographic analysis of the obtained purified products. A typical gas chromatogram of silylated transesterification product is shown in Figure 1.

Viscosity and density were measured at 20.0 and 37.8°C in order to have a complete range of viscosity data. In fact, low methyl ester samples (batches 18–25) developed a gelati-

TABLE 1
Reaction Conditions and Composition of the Products

Batch	Molar ratios (oil/MeOH/NaOH)	Reaction time (min)	Composition[a] (GC/FID, wt %) ME	MG	DG	TG
1	1:12:0.21	120	98.63	0.37	<0.01	<0.01
2	1:12:0.21	60	98.51	0.49	<0.01	<0.01
3	1:12:0.06	120	98.35	0.65	<0.01	<0.01
4	1:8.6:0.08	60	98.27	0.73	<0.01	<0.01
5	1:6.0:0.08	35	98.10	0.78	0.10	<0.01
6	1:6.5:0.07	45	98.03	0.88	0.11	<0.01
7	1:6.0:0.08	90	97.34	1.11	0.53	0.01
8	1:6.0:0.07	15	97.04	0.93	0.74	0.27
9	1:8.0:0.05	25	96.91	0.84	0.61	0.64
10	1:8.0:0.06	20	95.54	1.04	1.03	1.39
11	1:7.1:0.05	15	93.90	0.93	1.77	2.39
12	1:7.0:0.05	20	93.32	1.29	1.87	2.52
13	1:6.4:0.05	15	92.10	1.15	2.45	3.31
14	1:6.0:0.05	10	90.83	1.29	2.93	3.95
15	1:5.3:0.05	20	90.58	1.59	2.90	3.92
16	1:5.0:0.05	10	87.87	1.65	4.04	5.45
17	1:5.0:0.05	15	85.48	2.17	4.83	6.52
18	1:3.4:0.05	60	79.59	4.12	9.86	5.07
19	1:3.4:0.05	50	78.87	2.85	7.43	9.84
20	1:3.4:0.04	50	73.27	3.58	9.59	5.14
21	1:2.6:0.04	30	67.37	4.23	11.79	15.61
22	1:2.6:0.04	30	67.25	4.25	11.83	15.67
23	1:2.6:0.04	15	62.94	4.72	13.43	17.91
24	1:2.1:0.03	90	52.66	5.87	17.26	23.21
25	1:1.3:0.03	60	47.57	6.44	19.16	25.86

[a]ME, methyl esters; MG, DG, TG, mono-, di-, and triglycerides. GC/FID, gas chromatography/flame-ionization detector.

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TABLE 2
Viscosity

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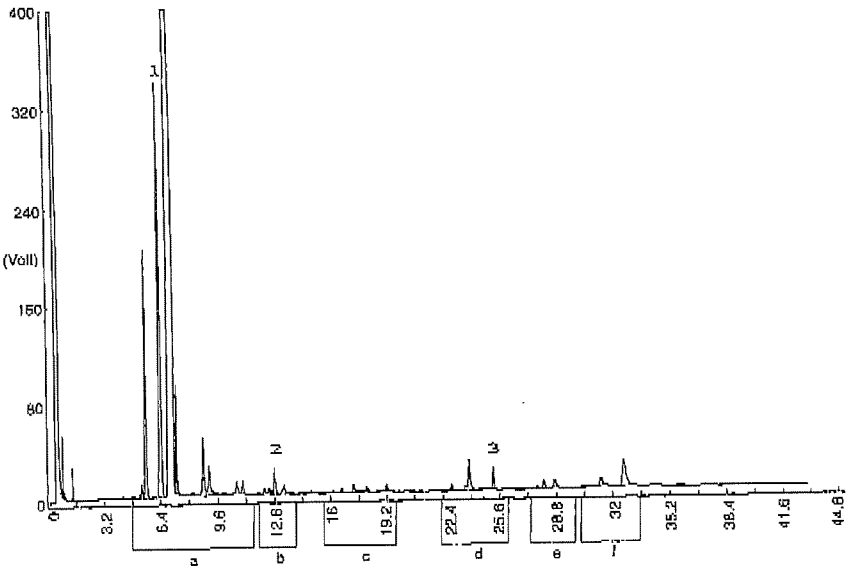

FIG. 1. Chromatogram of silylated soybean oil methyl esters with methyleptadecanoate (1), monoheptadecanoate (2), and dinonadecanoate (3), as internal standards; a, fatty acid methyl esters; b, monoglycerides; c, free sterols; d, diglycerides; e, steryl esters; and f, triglycerides.

nous precipitate at low temperatures, essentially formed by mono- and diglycerides (as shown by the FTIR analysis of the precipitate). This precipitate, not present in high methyl ester samples (batches 1–17), did not allow accurate viscosity measurements at temperatures below 30°C.

Table 2 reports viscosity values measured at 37.8°C for all samples, and the values at 20°C for the high conversion samples. Densities measured at both temperatures are listed in the same table.

TABLE 2
Viscosity (η) and Density (ρ) of the Purified Products

Batch	$\rho_{20°C}$ (g/cm³)	$\eta_{20°C}$ (mPa • s)	$\rho_{37.8°C}$ (g/cm³)	$\eta_{37.8°C}$ (mPa • s)	Methyl ester (wt%)
1	0.88640	5.828	0.87465	3.658	98.63
2	0.88644	5.851	0.87469	3.690	98.51
3	0.88635	5.895	0.87493	3.733	98.35
4	0.88689	5.853	0.87474	3.713	98.27
5	0.88701	5.874	0.87498	3.722	98.10
6	0.88681	5.845	0.87479	3.721	98.03
7	0.88710	6.014	0.87503	3.720	97.34
8	0.88733	6.155	0.87530	3.877	97.04
9	0.88726	6.064	0.87520	3.821	96.91
10	0.88866	6.265	0.87648	3.953	95.54
11	0.88949	6.543	0.87765	4.119	93.90
12	0.89012	6.648	0.87790	4.162	93.32
13	0.89067	6.873	0.87889	4.270	92.10
14	0.89150	7.141	0.87961	4.403	90.83
15	0.89188	7.142	0.87960	4.424	90.56
16	0.89343	7.698	0.88149	4.708	87.87
17	0.89519	8.192	0.88290	5.044	85.48
18	0.90121	—	0.89027	6.221	79.95
19	0.89922	—	0.88720	6.008	78.87
20	0.90432	—	0.89043	6.883	73.27
21	0.90676	—	0.89438	8.029	67.37
22	0.90684	—	0.89466	8.109	67.25
23	0.90742	—	0.89740	9.023	62.94
24	0.91645	—	0.90384	11.947	52.66
25	0.91980	—	0.90711	13.827	47.57

To correlate methyl ester content and viscosity of transesterification products, it is necessary to assume that eventual methyl ester–glycerides associations are neglected in the range of the weight fractions considered. With this assumption, it is possible to use the Irving equation, normally introduced to correlate viscosities of nonpolar liquid mixtures with weight fractions (25,26):

$$\ln \eta_{mix} = \Sigma w_j \ln \eta_j \qquad [1]$$

where η_{mix} = viscosity of the mixture; η_j = viscosity of component j; and w_j = weight fraction of component j.

Assuming that the purified samples are considered as a binary system of two groups of components, methyl esters and glycerides, that differ tenfold in viscosity, the Irving equation may be written, as a function of the viscosity measured:

$$w = a \ln \eta + b \qquad [2]$$

where w = FAME weight fraction; η = measured viscosity; and a, b = equation constants, depending on the seed oil used, and on the temperature.

Figure 2 shows the graphics obtained applying the Irving equation, related to viscosity data at 20 and 37.8°C. In the defined range of weight fractions, this correlation allows for the determination of the FAME content of purified fuel grade samples by making a single viscosity measurement.

In Tables 3 and 4, calculated methyl ester content is compared with methyl ester content measured by gas-chromatographic analysis, relative to viscosity data at 20 and 37.8°C. The correlation gives results which are in good agreement with the gas-chromatographic methyl ester content.

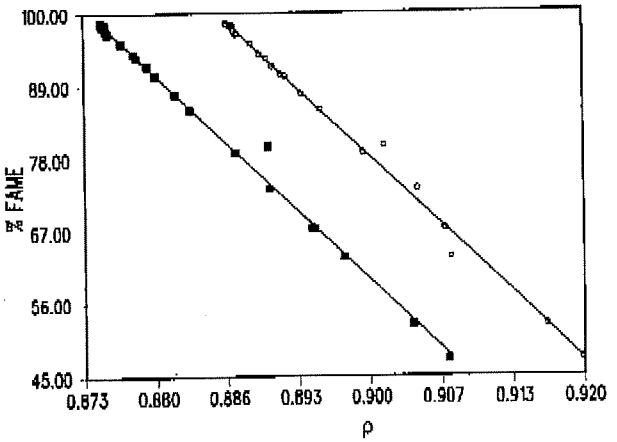

FIG. 2. Plots of fatty acid methyl ester (FAME) weight fraction vs. measured viscosity (ln); ○, 20°C; ■, 37.8°C.

By using the same assumptions as before, it is possible to correlate the density data with the methyl ester content by applying the linear equation:

$$w = c\,\rho + d \qquad [3]$$

where w = FAME weight fraction; ρ = measured density; and c, d = equation constants, depending on the seed oil used, for each temperature. The resulting graphs are reported in Figure 3 for densities at 20 and 37.8°C.

Tables 5 and 6 show the comparison between methyl ester content calculated from gas chromatography and the methyl ester content calculated from density data at 20 and 37.8°C. The correlation density–weight fraction gives satisfactory results. However, the average absolute deviation from the gas-chromatographic data is higher than that obtained by applying the correlation viscosity–weight fraction. Such a correlation appears more reliable than that based on density and,

TABLE 3
Comparison Between Methyl Ester Contents Measured by Gas Chromatography (GC) and Calculated from Viscosity Data at 20°C ($\eta_{20°C}$)[a]

$\eta_{20°C}$ (mPa • s)	Metyl ester (wt%) by GC	Metyl ester (wt%) from $\eta_{20°C}$	Error (%)
5.828	98.63	98.52	−0.11
5.851	98.51	98.37	−0.14
5.895	98.35	98.08	−0.27
5.853	98.27	98.36	0.09
5.874	98.10	98.22	0.12
5.845	98.03	98.41	0.39
6.014	97.34	97.31	−0.03
6.155	97.04	96.42	−0.64
6.064	96.91	96.99	0.08
6.265	95.54	95.74	0.21
6.543	93.90	94.07	0.18
6.648	93.32	93.46	0.14
6.873	92.10	92.18	0.09
7.141	90.83	90.71	−0.13
7.142	90.58	90.70	0.13
7.698	87.87	87.82	−0.07
8.192	85.48	85.42	−0.07
Average absolute deviation			0.17

[a]Slope a = −38.46645; intercept b = 166.32644; 95% confidence interval, for the true slope: ±0.1308; for the true intercept, ±0.2289. Correlation coefficient: −0.9985.

TABLE 4
Comparison Between Methyl Ester Contents Measured by GC and Calculated from Viscosity Data at 37.8°C ($\eta_{37.8°C}$)[a]

$\eta_{37.8°C}$ (mPa • s)	Metyl ester (wt%) by GC	Metyl ester (wt%) from $\eta_{37.8°C}$	Error (%)
3.658	98.63	98.24	−0.39
3.690	98.51	98.19	−0.32
3.733	98.35	97.74	−0.61
3.713	98.27	97.95	−0.32
3.722	98.10	97.85	−0.25
3.721	98.03	97.86	−0.17
3.720	97.34	97.87	0.54
3.877	97.04	96.27	−0.79
3.821	96.91	96.83	−0.08
3.953	95.54	95.51	−0.03
4.119	93.90	93.91	0.01
4.162	93.32	93.52	0.21
4.270	92.10	92.52	0.46
4.403	90.83	91.32	0.54
4.424	90.58	91.14	0.62
4.708	87.87	88.72	0.97
5.044	85.48	86.04	0.65
6.221	79.95	77.89	−2.57
6.008	78.87	79.25	0.48
6.883	73.27	73.95	0.93
8.029	67.37	67.98	0.90
8.109	67.25	67.59	0.50
9.023	62.94	63.44	0.79
11.947	52.66	52.54	−0.22
13.827	47.57	46.86	−1.48
Average absolute deviation			0.59

[a]Slope a = −38.74190; intercept b = 148.92468; 95% confidence interval: for the true slope: ±0.6887; for the true intercept: ±1.5252. Correlation coefficient: −0.9992. Abbreviation as in Table 3.

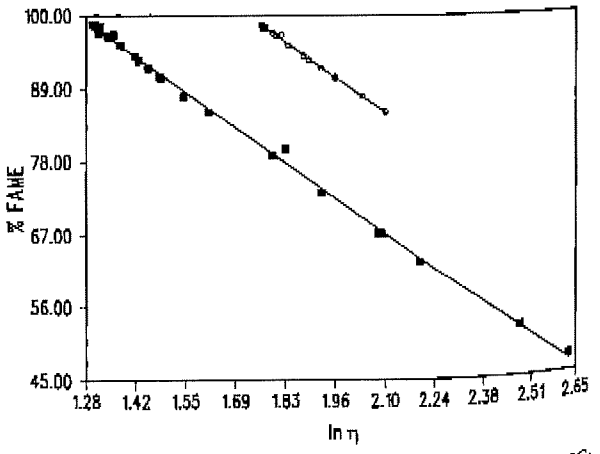

FIG. 3. Plots of FAME weight fraction vs. measured density; ○, 20°C; ■, 37.8°C. Abbrevation as in Figure 2.

TABLE 5
Comparison Between … and Calculated from D

$\rho_{20°C}$ (g/cm³)
0.88640
0.88644
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[a]Slope c = −1531.647… val: for the true slope: …tion coefficient: −0.99

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TABLE 5
Comparison Between Methyl Ester Contents Measured by GC and Calculated from Density Data at 20°C ($\rho_{20°C}$)[a]

$\rho_{20°C}$ (g/cm³)	Metyl ester (wt%) by GC	Metyl ester (wt%) from $\rho_{20°C}$	Error (%)
0.88640	98.63	98.78	0.15
0.88644	98.51	98.72	0.21
0.88635	98.35	98.86	0.52
0.88689	98.27	98.03	0.24
0.88701	98.10	97.85	−0.25
0.88681	98.03	98.15	0.12
0.88710	97.34	97.71	0.35
0.88733	97.04	97.36	0.33
0.88726	96.91	97.46	0.57
0.88866	95.54	95.32	−0.23
0.88949	93.90	94.04	0.15
0.89012	93.32	93.08	−0.26
0.89067	92.10	92.24	0.15
0.89150	90.83	90.97	0.15
0.89188	90.58	90.38	−0.22
0.89343	87.87	88.01	0.16
0.89519	85.48	85.31	−0.20
0.90121	79.95	76.09	−4.83
0.89922	78.87	79.14	0.34
0.90432	73.27	71.32	−0.27
0.90676	67.37	67.58	0.31
0.90684	67.25	67.46	0.31
0.90742	62.94	66.57	5.77
0.91645	52.66	52.73	0.13
0.91960	47.57	47.60	0.06
Average absolute deviation			0.67

[a]Slope c = −1531.64744; intercept b = 1456.42409; 95% confidence interval: for the true slope: ±50.9822; for the true intercept: ±54.8513. Correlation coefficient: −0.9970. Abbreviation as in Table 3.

TABLE 6
Comparison Between Methyl Ester Contents Measured by GC and Calculated from Density Data at 37.8°C ($\rho_{37.8°C}$)[a]

$\rho_{37.8°C}$ (g/cm³)	Metyl ester (wt%) by GC	Metyl ester (wt%) from $\rho_{37.8°C}$	Error (%)
0.87465	98.63	98.49	−0.14
0.87469	98.51	98.43	−0.08
0.87493	98.35	98.06	−0.29
0.87474	98.27	98.41	0.14
0.87498	98.10	97.97	−0.13
0.87479	98.03	98.27	0.24
0.87503	97.34	97.90	0.58
0.87530	97.04	97.48	0.45
0.87520	96.91	97.64	0.75
0.87648	95.54	95.66	0.13
0.87765	93.90	93.85	−0.05
0.87790	93.32	93.46	0.15
0.87889	92.10	91.93	−0.18
0.87961	90.83	90.82	−0.01
0.87960	90.58	90.83	0.28
0.88149	87.87	87.91	0.05
0.88290	85.48	85.73	0.29
0.89027	79.95	74.33	−7.02
0.88720	78.87	79.08	0.27
0.89043	73.27	74.08	1.10
0.89438	67.37	67.97	0.89
0.89466	67.25	67.54	0.43
0.89740	62.94	63.30	0.57
0.90384	52.66	53.33	1.27
0.90711	47.57	48.28	1.49
Average absolute deviation			0.68

[a]Slope c = −1546.87374; intercept b = 1451.46164; 95% confidence interval: for the true slope: ±51.4981; for the true intercept: ±47.3720. Correlation coefficient: −0.9969. Abbreviation as in Table 3.

therefore, is suggested as an analytical control method for the transesterification process. The density–weight fraction correlation could be utilized in the evaluation of the FAME content in cases where a high degree of accuracy is not required.

The suggested viscosity–weight fraction correlation can be utilized only in a defined weight fraction range and it is not possible to extrapolate it for FAME contents less than 45%. Below this value, the polar associations between glycerides and methyl esters are not negligible.

The proposed analytical method was developed using soybean oils. In order to extend it to other seed oils, it is necessary to prepare a specific calibration curve for each seed oil. Once the equation constants are determined for the utilized seed oil, the FAME content in transesterification products could be evaluated directly by a single viscosity measurement.

The aim of transesterification industrial processes is to obtain fuels with a higher than 98% FAME content (19). Viscosity measurements at 20°C correlate best with 85–100% FAME content. Therefore, the 20°C measure seems especially suitable for application in process control.

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ABSTRACT: A com
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KEY WORDS: Enz

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[1]Current address: Johns
School of Hygiene and
21205.
*To whom correspondei
partment of Chemistry a
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