

DIESEL BIOFUEL VISCOSITY AND HEAT OF COMBUSTION

**Yu. V. Maksimuk, Z. A. Antonova, V. V. Fes'ko,
and V. N. Kursevich**

Measurements have been made on the kinematic viscosity at 20-80°C and on the upper heat of combustion of methyl esters of fatty acids from rapeseed, mustard, and colza oils and the oil of oily radish, as well as the ethyl esters of rapeseed oil. A method is proposed for calculating the viscosity of a mixture of esters from the fatty-acid composition. Matched data have been obtained on the specific heat of combustion of plant oils and their esters.

EN 14214:2003 lays down the specifications for biofuel or the methyl esters (ME) of fatty acids, which is used as diesel fuel either in pure form (Germany and Austria) and in the form of 5% additive to oil-based diesel fuel (EN 590:2004). In many countries, the second is common in accordance with the modified analogs adopted there to the European standard EN 590; for example, in Russia we have GOST R 52368-2005, in Belarus STB 1658-2006, and in the Ukraine DSTU 4840-2007. It is possible to use ME also as boiler fuel (EN 14213). No corresponding standard has yet been developed for the ethyl esters (EE) of fatty acids.

The feedstocks for making ME and EE are provided by plant oils, animal and fish oils, tallow, and others (including wastes, in which the main component is an oil. The composition of these fats corresponds to the fatty-acid composition of the synthesized esters, which directly govern the physicochemical characteristics such as the viscosity, heat of combustion, iodine number, density, and so on.

There are several papers [1-4] dealing with the dependence of the ester characteristics on the composition. In particular, various correlations have been established for the viscosity [5-12], the solid point [8, 13], the density [9, 10], the surface tension [10, 14], the heat of combustion [15], the boiling point [16] and the cetane number [17], and so on. The large number of papers on the viscosity is due to the considerable practical significance of this and the variation that is wide for different specimens. For example, the viscosities of plant oils are about ten times larger than those of the corresponding ME at 20°C [18], while those of ME mixtures may differ by as much as a factor 2 [2, 7] because of differences in viscosity of the individual esters, for example, the viscosity of methyl linolenate (S18:3) is 3.14 mm²/sec, while that of methyl erucate (S22:1) is 7.33 mm²/sec [5].

Ester mixtures should be examined as fuels in order to forecast their characteristics from the fatty acid composition of the feedstock. This is particularly important in connection with the rapid development of methods

Laboratory for Fuel, Oil, and Fodder, Physicochemical Research Institute. Belorussian State University.
Translated from *Khimiya i Tekhnologiya Topliv i Masel*, No.5, pp. 27 – 30, September – October, 2009.

Table 1

Indexes	EN 14214 specification	RO EE	ME			
			RO	OR	MO	CO
Ester content according to EN 14103:2003*, wt. %	Not less than 96.5	98.0	99.5	98.9	98.5	99.2
C16:0		6.6	6.4	6.1	4.3	3.1
C16:1		0.4	0.3	0.2	0.2	0.2
C18:0		2.8	2.7	3.6	2.6	2.8
C18:1 <i>cis</i>		51.1	50.1	30.4	31.8	14.5
C18:1 <i>trans</i>		1.6	1.9	0.9	1.7	1.0
C18:2		23.2	24.0	19.8	12.0	17.3
C18:3	Not more than 12	11.7	12.0	18.1	14.6	12.7
C20:0		0.5	0.5	0.9	0.8	0.9
C20:1		1.4	1.6	6.9	9.6	8.9
C22:0		0.1	0.1	0.3	0.3	0.6
C22:1		0.5	0.9	14.0	23.3	39.5
Water content according to ISO 12937:2001**, %	Not more than 0.05	0.059	0.025	0.015	0.043	0.015
Iodine number (EN 1411:2003***), mg I ₂ /100 g	Not more than 120	–	120	123	114	114
Flash point (according to ISO 2719:2002 [†]), °C	Not below 120	179	176	181	183	186
Density at 15°C (ISO 3675), kg/m ³	860–900	877	882	882	880	880
Viscosity at 40°C, mm ² /sec						
experimental from ISO 3104 (GOST 33)	3.5–5	4.49	4.16	4.49	4.89	5.21
calculated from equation (2)		–	4.18	4.45	4.83	5.19
Difference between experimental and calculated viscosities, %;		–	–0.48	+0.89	1.22	+0.38
Notes. * Gas-liquid chromatography with S17:0 standard and Tsvet-800 chromatograph (Tsvet Company), fitted with a Supelco Wax column 10 (60 m r 0.53 mm r 0.5 mm) and Unichrom system (NAS Company)						
** Karl Fischer method with Mettler coulometric titrator type Toledo DL 39.						
*** Viis method						
[†] Martens-Penskii method in a closed crucible for the use of a Flash-A instrument (BMTs Company).						

for gene engineering, which enables one artificially to adjust the fatty acid composition of the oil even for a single oily crop, and thus optimize the properties of ME and EE mixtures [19].

Here we examine the characteristics of ME made from rapeseed oil (RO), mustard oil (MO), and colza oil (CO), as well as oil from the oil radish (OR), in addition to EE from RO synthesized by esterification of the corresponding unrefined oil by methanol (or ethanol in the case of EE) in the presence of calcium hydroxide followed by distillation of the neutralized and washed ester layer at a temperature of 145–185°C and a pressure not more than 0.3 kPa.

Chromatography shows that the mixtures consist to about 90% of unsaturated esters, which on the one hand provide setting temperatures lower than those of saturated esters (below -14°C), and consequently maintain the liquid state, while on the other hand there is low oxidation stability and correspondingly rapid biodegradation and lower load on the environment.

Ester analyses (Table 1) indicate a slight effect from the fatty-acid composition of the ME on the density

Table 2

Coefficients in (1)	RO EE	ME			
		RO	OR	MO	CO
$a \cdot 10^5$	-1.51	-1.35	-1.67	-1.72	-2.28
$b \cdot 10^3$	3.41	3.05	3.63	3.90	4.86
$c \cdot 10$	-2.949	-2.643	-3.033	-3.361	-3.928
d	11.789	10.733	11.898	13.188	14.569

(variation over a range of 0.2-0.3%) and flash point (1-5.5%). On the other hand, the maximum difference between the viscosities of these esters attains 25%.

We examined the dependence of the kinematic viscosity ν on temperature t over the range 20-80°C for all these esters. The ν measurements were performed with calibrated viscometers based on the State standard specimen with various diameters for the capillaries and two overlapping temperature ranges. The set measurement temperatures were maintained with an error of 0.01°C by means of an A2 thermostat (BMTs Company), which had built-in electronic timer with a division of 0.01 sec. The errors in the experimental values did not exceed ± 0.01 mm/sec². Data processing showed that the experimental points fitted an equation of third degree with a correlation coefficient not less than 0.9998:

$$\nu = at^3 + bt^2 + ct + d \quad (1)$$

from which one can calculate the viscosity with an error of not more than 0.2% on the entire working temperature range. Table 2 gives the values of the coefficients in (1).

The substantial differences in ν (Table 1) indicate that this parameter can be estimated by additive methods. There are various methods of calculating the viscosities for liquids [20] on the basis of the molar, volume, or mass fractions of the components. They are used as a rule as estimates.

An equation proposed [7] for the dynamic viscosity η of ME is

$$\ln \eta = \sum_{i=1}^n y_i \ln \eta_i \quad (2)$$

where η is the predicted viscosity in mPa.sec, n the number of esters in the mixture, y_i the mass fraction of ester i , and η_i the viscosity of ester i in mPa.sec.

This equation is a modified form of the Grunberg-Nissan equation [21] intended for forecasting η on the basis of molecular interaction. This interaction can be neglected because ME are unassociated liquids constituting mixtures of compounds with similar structures (linear hydrocarbon chains). Also, ME above 5°C [22] or 40°C [7] are newtonian liquids.

The densities of ME mixtures are similar, so we used (2) in calculations for these specimens at 40°C on the basis of the ν for the individual esters [5] and with allowance for the weight fractions in the mixtures as determined by chromatography. The values of ν for methyl eicosanate (S20:0) and methyl decanate (S22:0) were estimated with the values of ν for methyl palmitate (S16:0) and methyl stearate (S18:0) correspondingly as $\nu_{S20:0} = \nu_{S18:0} + (\nu_{S18:0} - \nu_{S16:0})$ and $\nu_{S22:0} = \nu_{S18:0} + 2(\nu_{S18:0} - \nu_{S16:0})$.

Table 1 gives the calculated values of ν for the ME mixtures and the divergence from the experimental

Table 3

Feedstock	High heat value, MJ/kg					Reference
	Oil (O)	ME	ME – O	EE	EE – ME	
Radish	39.72±0.02	40.04±0.07	+0.32	–	–	This study
Mustard	40.07±0.06	40.25±0.04	+0.18	–	–	same
Colza	40.09±0.06	40.28±0.02	+0.19	–	–	same
Rape	39.59±0.04	39.87±0.05	+0.28	40.12±0.07	+0.25	same
	39.78	40.07	+0.29	40.41	+0.34	[3]
	39.80±0.01	40.21±0.04	+0.41	–	–	[23]
	40.27	40.43	+0.16	40.97	+0.54	[3]
	40.33±0.04	40.35 ±0.06	+0.02	–	–	[23]
Sunflower	39.46	39.71	+0.25	39.80	+0.09	[3]
Flax	39.51	40.00	+0.49	39.65	–0.35	[3]

data. The absolute deviations (0.1-0.6 mm²/sec) and the relative ones (0.3-1.3%) of the calculated values from the experimental ones are less than those obtained in [6, 7] and are close to the requirements of reproducibility in viscosity measurement laid down by ISO 3104. The method allows one to forecast the viscosity ν of synthesized ME on the basis of the fatty-acid compositions of the plant oils with satisfactory accuracy.

Quite detailed data have been published on the heats of combustion of plant oils and their esters [2, 3, 11, 23]. However, the discrepancies between the individual values make it difficult to classify them, because the values of the upper heats of combustion of such substances lie in a narrow range: 39-41 MJ/kg. The values of 21-26 MJ/kg from [2] are to be considered as erroneous, possibly because the calculations lack corrections for the joint combustion of benzoic acid.

To obtain consistent data, we determined the heats of combustion for the esters and for the plant oils from which they were obtained. The measurements were made in a bomb isoperibolic calorimeter type V-08MA with isothermal water jacket [24]. The effective thermal capacity of the instrument was determined from the data in calibration experiments with certified benzoic acid grade K-3 (Mendeleev All-Russia Metrology Research Institute) in accordance with the recommendations of MI 2096. The determination error was calculated from the mean deviation for the confidence interval of 95% and did not exceed 0.1%. Specimens of mass 0.4-0.6 g were placed in terylene ampules, whose masses varied in the range 0.03-0.06 g and were hermetically sealed. The heat of combustion for terylene as determined in a separate series was 22879.7 ± 11.1 J/g.

The specimens were burned in platinum crucibles. The ignition was provided by a platinum wire of diameter 0.05 mm. To the bomb we added 1 ml of distilled water and filled it with pure oxygen to a pressure of 3 MPa after preliminary flushing.

The heat of combustion was calculated from the mass of the specimen converted to the mass in vacuum and with correction for the combustion of the terylene and the formation of nitric acid, as referred to standard conditions (0.1 MPa). The values of the latter two corrections did not exceed 0.05% of the final value.

As the plant oils and their esters contained small amounts of sulfur and nitrogen, there are differences in the methods of calculating the upper heat of combustion of the liquid fuels in accordance with DIN 51900, ASTM 240, and GOST 21261 associated with the different approaches to determination of the thermochemical corrections, but these did not have an appreciable effect on the final result. We did not use the analogous foreign standards (ASTM 4809, ASTM 240, and DIN 51900) in GOST 21261 for reduction to standard

conditions and conversion of the specimen mass to the mass in vacuum. In [23], the first correction for biofuel has been equated to zero.

Table 3 gives the experimental values of the upper specific heat of combustion as converted to the dry material together with the published data. The differences in heat of combustion between rapeseed oil and its esters are associated mainly with the differing ratios of the oleic acid (S18:1) and the erucic acid (S22:1) in the specimens. The higher heat of combustion for the latter is due to the longer hydrocarbon chain in the molecule.

Table 3 shows that there are differences ranging from +0.02 to +0.49 MJ/kg between the heats of combustion for the oils and the corresponding ME. The increases in discrepancy are related to the higher percentage content of hydrogen in the ME relative to the oils. One molecule for example of the oleic triglyceride $C_{57}H_{105}O_6$, which is the main component of the RO, on reesterification forms three molecules of methyl oleate $3C_{19}H_{36}O = C_{57}H_{108}O_6$, which is the main component of the mixture of RO ME, so the amount of hydrogen in the ME by comparison with that in the oil is increased by 0.4%, while in methyl erucate it is 0.33%. In accordance with Mendeleev's formula, this should increase the higher heat of combustion by 0.5 MJ/kg for methyl oleate and by 0.42 MJ/kg for methyl erucate.

The differences of 0.18-0.32 MJ/kg for the oils and ME used here are less than the theoretically predicted ones, which is due probably to losses of certain amounts of heavy but higher-energy components in the vacuum distillation of the synthesized esters. This is confirmed by the smaller differences between the oils and ME with the higher contents of heavy esters: for mustard and colza, correspondingly 0.18 and 0.19 MJ/kg, while for rapeseed and oil radish one correspondingly has 0.28 and 32 MJ/kg.

The higher energy capacities of EE by comparison with ME are due to their molecules containing an additional CH_2 group each. This difference on using Mendeleev's formula for methyl oleate constitutes 0.25 MJ/kg, while the calorimetric data for methyl stearate and ethyl stearate give 0.24 MJ/kg, which agrees well with our data for RO ME and EE.

When a plant oil is to be selected for making esters, one should examine its fatty-acid composition, which allows one to forecast quite accurately the characteristics of the resulting fuel.

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