# **Predicting the Surface Tension of Biodiesel Fuels from Their Fatty Acid Composition**

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**ABSTRACT:** The emergence of biodiesel fuels as diesel fuel substitutes has led to several studies on their properties. Surface tension, which plays a role in atomization, has lacked attention compared to other properties. This paper presents a method to predict the surface tension of biodiesel fuels based on the fatty acid composition. Several binary, ternary, and quaternary mixtures of fatty acid ethyl ester gas chromatographic (GC) standards were prepared, and we found that a mass-average equation predicted the surface tension of these mixtures within  $\pm$ 3.5% of their measured values. Six complex mixtures of fatty acid methyl ester GC standards that simulated typical oils used as biodiesel fuels were also prepared. For these complex mixtures the predicted surface tensions of the mixtures, calculated from a mass-average equation, were 2–6% higher than the measured values. A mass-average equation was developed in which we used a weighted surface tension for the individual components, and we found that this method predicted the surface tension of the simulated oils within ±4.5% of their measured values. Five natural vegetable oils were used to produce biodiesel fuels by the transesterification process. The predicted surface tensions of these fuels were all within ±3.5% of their measured values. The surface tensions of 15 biodiesel types were then predicted, based on their fatty acid composition as published in the literature. These results show that the differences in surface tension between biodiesel types are not the main cause of the reported differences in engine tests.

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Biodiesel fuels, which are generally made up of methyl or other esters of animal and vegetable oils, have received much attention since the apparent fuel crisis in the 1970s. There are several researchers actively involved in testing various properties and performance parameters of biodiesel fuels, but surface tension has received little attention (1).

Surface tension of a liquid is considered to be one of the fundamental properties that affects its atomization characteristics (2). The atomization process is the initial stage of the combustion of a fuel in a diesel engine, and thus the surface tension of a fuel has a role in the fuel's combustion. The re-

sults of studies on the various performance parameters of biodiesel fuels (e.g., power and specific fuel consumption) have varied from one researcher to another  $(1,3)$ , and some of these variations may be a result of the variation of the fuel's surface tension due to differences in atomization. This paper presents a procedure for predicting the surface tension of biodiesel fuels comprised of fatty acid ester mixtures, based on their fatty acid composition.

The reader may question at the outset whether results of tests carried out at temperatures and pressures not identical to engine conditions are relevant. In an operating engine, the injectors are cooled by the fuel passing through them, and hence the injectors do not operate at an excessively high temperature; otherwise, vapor lock could form in the injectors. Also, surface tension is not extensively affected by pressure (4). Thus, tests carried out at atmospheric pressure and the highest temperature allowable for the laboratory instruments available give results that demonstrate the comparative differences in surface tension among different biofuels, and these comparative differences will be evident at engine temperatures and pressures.

## **MATERIALS AND METHODS**

*Sample preparation*. Both fatty acid methyl and ethyl ester gas chromatography (GC) standards were acquired from Sigma-Aldrich Canada. Ethyl esters (EE) were used for binary, ternary, and quaternary mixtures because it was more economical to use these standards for validating the concept and Equation 2. The following samples were prepared for the different tests described later.

Twenty EE samples were produced by mixing, on a mass basis, varying proportions of 8:0, 10:0, 12:0, and 18:1 fatty acid ethyl esters.

Methyl esters (ME) were mixed on a mass basis in appropriate proportions to simulate the ME of fatty acids of canola, coconut, palm, peanut, rapeseed, and soybean oils.

Biodiesel fuels were produced from natural canola, coconut, palm, peanut, and soybean oils in a batch transesterification unit described earlier (5). These ME fuels were then heated to 100°C under nitrogen and filtered though a "Reeve Angel" grade 202 coarse paper filter to remove any sediments in the oil that were carried over from the oil extraction process.

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At 100°C, all fatty acid ester mixtures were fluid, making it easy for them to pass through the coarse filter.

The purity of the biodiesel fuels produced by the transesterification process was verified by thin-layer chromatography on Chromarods S-III with flame-ionization detection on an Iatroscan Mark III (6). The fatty acid composition of the biodiesel fuels was measured on a Perkin-Elmer gas chromatograph, model 8420, by a method described before (7).

*Surface tension measurement*. A "Kruss" model K8600E Interfacial Tensiometer with a Du Nouy ring was used to measure the surface tension of the samples. This tensiometer was equipped with a water bath to control the temperature of the samples at the test temperatures. A temperature of 25°C was used for the EE mixtures, while 40°C was used for all others. This higher temperature was needed to accommodate 16:0 and 18:0 fatty acid esters that were solid at 25°C. Isobutanol and benzene were initially used to calibrate the apparatus, and myristic acid ME GC standard (14:0 ME) was selected to check the repeatability of the apparatus on a regular basis. The ring was cleaned before testing each fuel by heating it in the oxidizing part of a propane flame until it was white hot. Only one replicate for each sample was required because the instrument provided consistently repeatable results.

*Error analysis*. The maximum allowable error for predicted results was derived through a sensitivity analysis of a generalized atomization model taken from the literature. This model (8) computes an atomization characteristic, Ka, which gives an overall view of the atomization quality. It includes the surface tension, viscosity, and density of the fuel. Equations 1 to 3 summarize this model, and further details can be found elsewhere (8):

$$
\mathbf{Ka} = \left[\frac{\rho_f \mathbf{W} \mathbf{e}_f}{\rho_g \mathbf{R} \mathbf{e}_f}\right]^{1/3} \tag{1}
$$

where Ka is the atomization characteristic; We<sub>f</sub> is the Weber number for the fuel;  $\text{Re}_f$  is the Reynolds number for the fuel; and ρ is the density for fuel (*f*) and gas atmosphere (*g*)  $\left(\frac{kg}{m^3}\right)$ .

The Reynolds and Weber numbers are given by:

$$
\text{Re}_f = \frac{V_0 d_0}{v_f} \tag{2}
$$

$$
We_f = \frac{\rho_f V_0^2 d_0}{\sigma_f}
$$
 [3]

where  $\sigma_f$  is the surface tension of the fuel (N/m);  $v_f$  is the kinematic viscosity of the fuel  $(m^2/s)$ ; and  $V_0$  is the velocity of the fuel jet (m/s).

Using the conventional 95% confidence, we decided to vary the surface tension to a maximum of  $\pm 5\%$  from its mean value to determine if there were any significant changes in the atomization characteristics. The mean values of all properties (10) are given in Table 1.

## **RESULTS AND DISCUSSION**

*Theoretical considerations: surface tension of pure components*. The Sugden expression gives good correlations with experimental data when predicting the surface tension of pure components. The Sugden expression is given below, and Table 2 gives the parachors (10):

$$
\sigma^{1/4} = \frac{[P]\rho}{M} \tag{4}
$$

where  $\sigma$  is the surface tension of the pure component (mN/m); [*P*] is a temperature-independent parameter, called the "parachor" of pure component;  $ρ$  is the density of the liquid phase in g/mL; and *M* is the molecular weight in g/mol. Further details on the computation of the parachor of an individual component are given in Reference 11.

*Surface tension of mixtures*. Reid *et al.* (10) stated that "the surface tension of a liquid mixture is not a simple function of the surface tension of the pure components because in a mixture the composition of the surface is not (necessarily) the same as the bulk." In a review of the literature, no research findings were found on the surface tension of ester mixtures. In fact, few data were found on surface tensions of nonaqueous mixtures. One relatively straightforward method for estimating the surface tension of a mixture is to use a Dalton-type mass-average equation:

$$
\sigma_m = \sum_{i=1}^n \sigma_i y_i \tag{5}
$$

where  $\sigma_m$  is the mean surface tension of the mixture (N/m);  $\sigma_i$  is the surface tension of component *i* (N/m); and  $y_i$  is the mass fraction of component *i*.

Because the composition of the surface of a liquid mixture is not necessarily that of the bulk, Equation 5 may not be adequate. Another method for predicting the surface tension of complex ester mixtures was therefore sought.

We found that the surface tensions predicted from an uncorrected mass-average equation consistently overpredicted the surface tension. We hypothesized that components with lower surface tensions would produce less than their 100% effect in a mixture, compared to their pure value, thus leading

**TABLE 1 Surface Tension of Saturated Methyl Esters at 40°C**



*a* From Reference 11.

**TABLE 2 Structural Contributions for the Computation of the Parachor***<sup>a</sup>*

Component	Parachor [P]	
C (not in -CH <sub>2</sub> -)	4.8	
$H$ (attached to $O$ )	11.3	
$H$ (attached to $C$ )	17.1	
$-CH2$	39	
Double (ethylenic) bond	23.2	
Semipolar	$-21.6$	
Triple bond	46.6	
O in ester or -COO-	60	

*a* From Reference 9.

to a higher predicted surface tension. The exact cause of this reduced surface tension is unknown; however, a mechanism for this effect is proposed herein. We assumed that components with higher intermolecular attraction in their pure state, i.e., higher surface tension, would likely have a higher intensity of attraction to each other in a mixture, thus tending to force the components with lower surface tensions away from the surface. Assuming that this is true, the lower-surfacetension components of a mixture will have less influence at the surface, compared with the higher-surface-tension components.

Based on this hypothesis, we assumed that a linear weightfunction could be utilized to obtain an effective surface tension for the individual components of a mixture. This "weight-function" was derived as a function of the numerical value of the surface tension. To obtain the weight-function, the maximal and minimal surface tension of the pure components in the particular mixture were used. A weight factor of 1 was applied to the maximal surface tension and a factor of 0.93 was applied to the minimal surface tension. The latter factor was derived by successive iterations to give the minimal error of predicted vs. measured surface tension of GC standards. From these extreme values for surface tension and weight factors, a linear equation was derived to compute a weight factor for each component as a function of its surface tension. An effective or weighted surface tension was thus computed. The weighted surface tension was then used to compute the mean surface tension of the mixture from

$$
\sigma_m = \sum_{i=1}^n w_i \sigma_i y_i
$$
 [6]

where  $w_i$  is the weight factor for component *i*.

The weight factor  $w_i$  is given by

$$
w_i = m\sigma_i + c \tag{7}
$$

where *m* is the slope of the linear weight-function line and *c* is the constant of the linear weight-function line.

Equation 7 implies that the weight factor of any given component is not a constant, but will be a function of its relative position in the mixture, with respect to the magnitude of its surface tension.

*Allowable error.* Figure 1 shows a graphical representation of the results of the sensitivity analysis. A  $\pm$ 5% variation in the surface tension resulted in a  $\pm 1.4\%$  variation in Ka from its mean value. This 2.8% variation in Ka over the entire 10% variation of surface tensions used can be considered negligible. Therefore, the maximum allowable error for the equation to predict the surface tension of the ester mixtures was set at ±5%.

*Measurements of individual GC standard esters*. Figure 2 shows the measured surface tension of individual fatty acid ME and EE from GC standards. When the surface tension of palmitic acid EE GC standard (16:0 EE) was measured at 40°C, a sharp deviation from the typical trend for the saturated esters was observed. This, however, did not occur with 16:0 ME. When this irregularity was first observed, a new batch of 16:0 EE GC standard with a different lot number was acquired from the supplier, but the same result was obtained when its surface tension was measured. GC and thin-layer chromatography–flame-ionization detection analyses were carried out to verify the purity of the samples, but all results showed only one sharp peak for 16:0 EE. A 15-mL sample was then heated at 200°C under nitrogen for 15 min to remove any volatile impurities that may have missed the GC output. The surface tension was retested, and the same low value was observed. All verification procedures for verifying the purity of the sample were exhausted, but there was no answer to this problem.

Apart from 16:0 EE, the surface tension of saturated fatty acid esters increased with increase in carbon number. For ME, this trend was curvilinear (Fig. 2). The data for EE had more random variation, and the trend was more or less linear, excluding the effect of 16:0 EE. The surface tension of saturated ME compared well with literature data (9), as shown in Table 1. No surface tension data for EE were found in the literature for the two test temperatures. Given the fact that the measured surface tensions for ME followed a trend line closely and compared well with data in the literature, it is believed that the EE GC standards used in these experiments had some peculiarity that caused a relatively high variation and, for 16:0, an anomalous result.



**FIG. 1.** Variation of normalized atomization characteristic (Ka*<sup>i</sup>* /Kamax) with 5% variation of surface tension for constant density and viscosity.



**FIG. 2.** Surface tension trend lines for saturated methyl and ethyl ester gas chromatographic standards at 40°C. Note the coincidence of the

When the GC standard unsaturated esters were tested, a pronounced deviation from the viscosity trend for saturated esters was observed when the unsaturated 18:1 was compared with the saturated 18:0 (Fig. 2). As the degree of unsaturation progressed to 18:2 and 18:3 the surface tension increased (Fig. 2), rather than continuing to decrease. For ME, the surface tension of 18:3 was higher than the saturated 18:0. There was also a significant difference between the measured surface tension for erucic acid (22:1) ME, compared with the

22:1 EE. No data were found in the literature to confirm the seemingly high value for 18:3 ME, the large drop in surface tension from 18:0 to 18:1, or the large difference between 22:1 ME and EE.

Despite these anomalies, because the individual GC standard ester components showed only one peak on the GC, we decided to use these components in control mixtures because their individual surface tensions could be measured. These measured surface tensions were used in the mixture equations for the mixtures of GC standard esters.

*Measurement of mixtures of GC standards.* The binary, ternary, and quaternary mixtures of 18:1, 12:0, 10:0, and 8:0 EE GC standards were used to test the concept of using a Dalton-type mass average (Eq. 5) for predicting the surface tension of mixtures of esters. Table 3 summarizes these results, and it shows that all errors in predicting the surface tension of these mixtures at 25°C were less than 4%. This error is within the maximum allowable limit previously defined. Thus, we decided to extend the analysis to more complicated mixtures by using the simulated vegetable oils previously described.

Table 4 shows the results of predicting the surface tensions of the simulated rapeseed, palm, canola, peanut, soybean, and coconut oil ME at 40°C. The prediction errors were all negative and ranged from  $-0.36$  to  $-1.41$  mN/m or  $-1.6$  to  $-5.9\%$ . Due to the fact that all errors were negative, an alternative model was derived based on the weighted mass-average method previously described (Eqs. 6,7). Errors for this method were reduced to 0.04 to 1.01 mN/m or 0.7 to 4.3%,

**TABLE 3**

Surface Tension of Binary, Ternary, and Quaternary Mixtures of Fatty Acid Ethyl Ester	
Gas Chromatographic Standards at 25°C	







and became more random. It is clear from these results that the weighted mass-average method gave better predicted surface tensions for the above-mentioned mixtures.

use an independent method for predicting the surface tension of the individual components of the biodiesel fuels.

*Measurements for five biodiesel types.* Biodiesel fuels made from the ME of coconut, peanut, soybean, palm, and canola oils were used in this phase. One should recall that the surface tension of 18:1 ME GC standard decreased by a significant amount compared with the saturated 18:0, and that there were other anomalies. We consider it unlikely that the addition of just one double bond to the 18:0 chain would cause such a drastic change to that component's surface tension. Because no values were found in the literature for the surface tension for 18:1, 18:2, 18:3, and 22:1, we decided to

The Sugden's parachor method previously described has been used by many authors (10,11) with some degree of success to predict the surface tension of pure components. Table 5 compares the calculated surface tension from the Sugden's parachor method with the measured values. The 8:0 to 18:0 data compared well with both the calculated and measured values, giving a maximal error of only 0.16 mN/m or 0.6%. Linolenic (18:3) and erucic (22:1) acid esters also compared well, with errors of 0.41 mN/m (1.4%) and 0.24 mN/m  $(0.8\%)$ , respectively. Oleic  $(18:1)$  and linoleic  $(18:2)$  acid esters, however, had errors of 5.88 mN/m (20%) and 5.57

#### **TABLE 5 Surface Tension of Pure Methyl Esters Calculated from Sugden's Parachor**









*a* ME, methyl ester.

mN/m (19%), respectively. These results show clearly that there were peculiarities with respect to the 18:1 and 18:2 ME GC standards. We thus decided to use the surface tensions calculated by the parachor method for all components as an independent data set for the mixture equation. This independent data set was used to compute the surface tensions of the ME of the naturally occurring vegetable oils.

Table 6 summarizes results of predicted surface tensions of vegetable oil ME biodiesel fuels by using component viscosities calculated with the parachor method. By way of comparison, the errors obtained from the mixture equation and the weighted surface tension parameter ranged from 0.04 to 0.87 mN/m or 0.2 to 3.3%.

## **TABLE 7 Predicted Surface Tension for 15 Biodiesel Fuel Types (40°C)**



Based on the maximum allowable error previously defined, it is clear from the results of the various surface tension tests that Sudgen's parachor and the weighted surface tension methods provide an acceptable procedure for predicting the surface tensions of biodiesel fuels based on their fatty acid compositions.

*Estimations for 15 biodiesel types*. Because Equations 6 and 7 were shown to give acceptable results for predicting the surface tensions of biodiesel fuels, they were used to estimate the surface tensions of the 15 ME biodiesel fuels with the objective of determining if there were significant variations in the surface tensions of typical types of biodiesel fuel. The predicted values, along with the upper and lower prediction limits, are given in Table 7. Rapeseed ME had the highest surface tension (29.24 mN/m), while coconut ME had the lowest (26.82 mN/m), representing a 9% difference. The others ranged from 27.69 to 28.98 mN/m, representing a 5% difference. For a ±5% variation of surface tension, the results of the error analysis showed that there will be negligible differences in the atomization characteristics. Thus, one could expect that the surface tensions of the different biodiesel types would play a negligible role in the reported differences in engine test results.

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