Blending Rules for Formulating Biodiesel Fuel

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ABSTRACT

The utilization of a number of sources of triglycerides to produce biodiesel fuel requires an accurate, but easy means of predicting basic fuel properties such as density, viscosity, cetane number and cloud point *a priori*. Biodiesel is chemically simple, since no more than six or seven fatty acid esters make up the biodiesel mixture. The properties of the ester blend can be predicted from pure component values, given appropriate blending equations.

This work uses pure component data for methyl palmitate, methyl stearate, methyl oleate, and methyl linoleate to develop and test blending equations for the prediction of fuel density, viscosity, cetane number, cloud point, and heating value. The results from the blending relationships are compared with literature values for biodiesel from a number of triglyceride sources. Typical average errors are less than 2 percent, with the exception of viscosity, where the average error is 10 percent. The further development of these blending relations will allow biodiesel from a blend of sources to be "designed" to meet fuel specifications without significant additional testing.

Keywords. Biodiesel, Fuel properties, Density, Viscosity, Cetane, Cloud point, Heating value

INTRODUCTION

Biodiesel fuel is gaining acceptance in a number of markets as an enhanced performance fuel for compression ignition engines. The most significant hurdle for broader commercialization of biodiesel is its cost. Because the most important cost factor in biodiesel production is the raw material, there has been an increasing effort in the utilization of lower cost raw materials such as tallow, recovered cooking oils, and yellow grease for the production of the fuel quality esters.

At the same time there has been a significant effort in development of fuel specifications for biodiesel that will assure quality performance, but not tie the final fuel to any specific triglyceride source. The **Biodiesel Report** (March, 1996) gives a definition of biodiesel and property specifications for biodiesel. Many of the properties are directly measured by chemical analysis, or are calculable from the ester composition in the fuel. Specifically, the kinematic viscosity, cetane number, and cloud point of the fuel are ester composition dependent. The total glycerine and free glycerine values will also be determined by compositional analysis. It is possible that the acid number and copper strip corrosion values may also be correlated with the detailed compositional analysis, but they will not be addressed here.

The use of chemical composition and structure as the basis for estimating physical, thermodynamic and transport properties is not new. Reid, Prausnitz and Poling (1987) show how chemical structure can be used to compute properties for pure components. They also discuss mixing rules to estimate properties for mixtures. The petroleum industry has long employed rather simple experimental data to represent both the chemistry and behavior of very complex mixtures. Equipped with a boiling point curve, the specific gravity, two

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viscosity measurements, an empirical parameter (the Watson's K factor) and a copy of Nelson's **Petroleum Refinery Engineering** (1958), an engineer can estimate all of the properties needed to design a refinery that will make fuel and other products that will meet specifications as stringent as those for biodiesel.

In the formulation of biodiesel fuel, there is an advantage over petroleum in that the chemistry of the components is well defined. The fuel is an ester of fatty acids derived from natural sources. As a result the only fatty acids typically present in significant quantity are palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid and erucic acid. Relative compositions change by source, but the components do not. Similarly, the most common alcohol used for biodiesel is methanol, but ethanol, isopropanol and n-butanol also have been used. This chemical simplicity makes property prediction equally simple.

The results presented here focus only on methyl palmitate, methyl stearate, methyl oleate and methyl linoleate as components because they are the only pure components with significant data available. To extend the approach recommended here, it will be necessary to build a somewhat larger base of pure component data, but the basic approach will be the same.

BASIC PROPERTY DATA

The property data for the pure components were assembled from a number of literature sources and are summarized in Table 1. The approach for estimating the cloud point is based on the pure component melting point. It is new to this work and will be discussed in detail below.

Table 1. Pure Component Property Data for Fatty Acid Methyl Esters

Ester	Density, g/cc @ 15.5 C	Viscosity, cSt @ 40 C	Cetane	Heating value MJ/kg	Melting Point, C
Palmitate	0.867	4.37	74	39.4	30.6
Stearate	0.867	5.79	75	40.1	39.1
Oleate	0.878	4.47	55	39.9	- 19.8
Linoleate	0.890	3.68	33	39.7	- 35.
Source	Janarthanan, et al., 1996	Janarthanan, et al., 1996	Bagby & Freedman, 1989	Freedman and Bagby, 1989 1988	Teoh and Clements, nts,

The literature for biodiesel fuels does not always give the chemical analysis for the actual esters present, so it was necessary to use literature data for the fatty acid ester composition for the fuels used in testing the property equations. The oil/tallow compositions and sources for the data are given in Table 2.

Table 2. Fatty Acid Compositions Used for the Oils/Tallow

| Oil/Tallow | Fatty Acid Composition, percent | | | | | | | |
	14:0	16:0	16:1	18:0	18:1	18:2	18:3	Reference
Palm Oil	1	41	0	3	45	9	1	Zaizi, et al., 1996
Soybean Oil	0	12	0	3	23	55	6	Bagby, et al., 1987
Sunflower Oil	0	6	0	3	17	74	0	Bagby, et al., 1987
Tallow	3	24	4	21	45	3	0	Ali, et al., 1995

The data for actual biodiesel fuels used for testing the estimating equations were for methyl esters of palm oil, soybean oil, sunflower oil and beef tallow. The data and sources are summarized in Table 3.

Table 3. Property Data for Methyl Ester Biodiesel Fuels

Source Oil	Density, g/cc @ 15.5 C	Viscosity cSt @ 40 C	Cetane	Heating value MJ/kg	Cloud Point, C
Palm (Pischinger, et al., 1982)	0.880	5.7	62	37.8	+ 13
Soybean (Schwab, et al., 1987)	0.884	4.08	46.2	39.8	+ 2
Sunflower (Pischinger, et al., 1982)	0.880	4.6	49	38.1	+ 1
Tallow (Ali, et al., 1995)	0.877	4.1	58	39.9	+ 12

ESTIMATION TECHNIQUES FOR BIODIESEL PROPERTIES

Density

The density of hydrocarbons as a function of temperature is best estimated using an empirical equation, based upon corresponding states theory, called the modified Rackett equation (Reid, et al., 1987). This approach has been applied to fatty acids (Clements, et al., 1993) and to methyl esters of fatty acids (Janarthanan, et al., 1996) with good accuracy.

A simpler method for estimating the density of methyl esters of fatty acids, however, is to use the empirical relation developed by Janarthanan, et al. (1996)

$$\rho_i = a_i t + b_i \qquad (1)$$

where t is the temperature in C and the component dependent empirical constants are reported in Table 4. The density of a mixture of these components can be estimated using a simple linear mixing rule, as shown in Eq. 2.

$$\rho_{mix} = \sum x_i (a_i t + b_i) \qquad (2)$$

The compositions of the four biodiesel fuels summarized in Tables 2 and 3 were modified to fit the data available for the methyl esters by grouping C14:0 and C16:1 fractions as C16:0. Similarly, the C18:3 component was added to the C18:2 fraction for all of the comparisons made in this work. After making these adjustments, the estimated densities were calculated and compared with the reported values. As seen from Table 5, the accuracy of the estimates is reasonably good.

Table 4. Empirical Constants Used to Estimate Methyl Ester Density

Ester	Constant a	Constant b	Temperature Range, C
Palmitate	-7.4608E-4	0.879094	26.7 - 98.9
Stearate	-6.9247E-4	0.877325	48.9 - 110
Oleate	-6.8563E-4	0.888357	26.7 - 110
Linoleate	-7.2226E-4	0.900981	37.8 - 110

Table 5. Comparison of Estimated and Reported Densities for Biodiesel Fuels

Fuel	Density Reported	Density Estimated	Percent Error
Palm oil	0.880	0.874	0.7
Soybean oil	0.884	0.883	0.1
Sunflower oil	0.880	0.886	- 0.7
Beef tallow	0.877	0.873	0.5

Viscosity

Pure component data for viscosity, particularly over a range of temperatures, are scarce for many organic compounds and very scarce for methyl esters of fatty acids. Janarthanan, et al. (1996) have presented experimental data for a number of esters. Also, they have tested a number of empirical expressions for representing the temperature dependance of liquid viscosity. The liquid viscosity for methyl palmitate, stearate and oleate follow the expression

$$\ln \eta = A + \frac{B}{T} + \frac{C}{T^2} \qquad (3)$$

and the viscosity of methyl linoleate is represented best by the expression, where the empirical constants for Eq. 3 and 4 are given in Table 6.

$$\ln \eta = A + BT + \frac{C}{T} \qquad (4)$$

The estimation of the viscosity of mixtures is one of the most difficult problems in the entire domain of property estimation. Even with highly complicated, system specific expressions the errors are significant. A number of expressions have been suggested in the literature of the form

$$\ln \eta_{mix} = \sum x_i f(\eta) \qquad (5)$$

where $f(\eta)$ is chosen by trial and error. In this work the form used to estimate the viscosity of biodiesel is

$$\ln \eta_{mix} = \sum x_i \sqrt[3]{\ln \eta_i} \qquad (6)$$

As seen in the comparisons in Table 7, the errors are rather large. The errors may be due in part to the presence of small amounts of methanol and/or glycerides in the biodiesel samples, to the lack of data for all of the components, particularly the linolenic ester, or to the fact the no mixture estimator is very good. However, the estimates are sufficiently accurate for initial blending calculations.

Table 6. Empirical Constants for Estimating Methyl Ester Viscosity

Ester	Constant A	Constant B	Constant C	Temperature Range, C
Palmitate	-17.7087421	0.0194820	4095.98793	26.7 - 98.9
Stearate	-12.2620883	0.0109932	3310.50996	48.9 - 110
Oleate	- 9.6133497	0.0075371	2739.10625	26.7 - 110
Linoleate	- 0.5705778	-680.80715	396575.647	38.7 - 110

Table 7. Comparison of Estimated and Reported Viscosities for Biodiesel Fuels

Fuel	Viscosity Reported	Viscosity Estimated	Percent Error
Me Palmate	5.7	5.1	+ 10.5
Me Soyate	4.08	4.9	- 20.1
Me Sunate	4.6	4.8	- 4.3
Me Tallowate	4.1	5.3	- 29.3

Cetane Number

The cetane number of a diesel fuel is a measure of its ignition quality under compression ignition conditions. The cetane number is measured using a special single-cylinder compression engine following the ASTM D-613 protocol. The experimental cetane number is based on a comparison of the test fuel ignition properties with the properties of mixtures of hexadecane (CN = 100) and heptamethylnonane (CN = 15).

The cetane number for conventional petroleum derived diesel fuels has been shown to be affected by the molecular structure of the hydrocarbons present, with long chain, normal paraffins having higher cetane numbers and cycloparaffins and aromatics having lower cetane numbers. Branched paraffins (iso-paraffins) and olefins tend to have lower cetane numbers than their comparable carbon-number paraffins (Guilder, et al., 1985; Olson, et al., 1960). O'Connor, et al. (1992) found similar results for synthetically derived diesel fuel. Twenty-two estimating equations for the cetane number were tested with results from > 500 fuels to find the best equation form and correlating parameter (Ladommatos and Goacher, 1995). For the conventional petroleum-derived fuels, the analine point, a measure of relative amounts of paraffins, iso-paraffins and cyclo compounds, was shown to be the single best predictor of cetane number.

As stated before, the molecular chemistry of biodiesel is simple. It is a mixture of C_{14} to C_{22} alcohol esters that exhibit varying degrees of unsaturation, depending on source. Freedman and Bagby (1990) have examined the cetane number of the saturated methyl esters as a function of a number of physical properties. They found the the boiling point was the correlating property for the esters they tested. Earlier, Klopfenstein (1985) had suggested a correlation of cetane number as a function of chain length of the esters.

This work takes a different approach, since the goal is the estimation of fuel properties for blends of esters. The component cetane numbers given in Table 1 were assumed to be givens, with the problem to be the estimation of the blend cetane number. The result was somewhat surprising, with a simple Kay's rule mixing equation (shown in Eq. 7) providing satisfactory results. The comparison of reported and predicted biodiesel cetane numbers is given in Table 8. In this case the P_i used in Eq. 7 are the pure component cetane numbers given in Table 1.

$$P_{mix} = \sum x_i P_i \qquad (7)$$

The methyl tallowate result is questionable, possibly because the reported value may be low due to the presence of methanol. The low reported viscosity for the methyl tallowate supports this contention. The large error for methyl sunate is less easily explained, unless the low cetane number associated with methyl linoleate under predicts, or the reported value is too high.

Table 8. Comparison of Estimated and Reported Cetane Numbers for Biodiesel Fuels

Fuel	Cetane Reported	Cetane Estimated	Percent Error
Methyl Palmate	62	61	1.6
Methyl Soyate	46	45	2.0
Methyl Sunate	49	41	16.3
Methyl Tallowate	58	64	- 10.3

Heating Value

The fuel heating value is important as a measure of the potential power to be derived from combustion. The components in biodiesel have nearly identical heating values, as seen in Table 1. Typically enthalpic thermodynamic properties, such as heating value, follow Eq. 7 in mixtures. Table 9 shows that reported and measured heating values for the biodiesel fuels are well represented by this simple mixing rule, where the P_i are the heating values for the pure components.

Table 9. Comparison of Reported and Esimated Heating Values for Biodiesel Fuels

Fuel	Heating Value Reported	Heating Value Estimated	Percent Error
Methyl Palmate	37.8	39.7	- 5.0
Methyl Soyate	39.8	39.7	0.3
Methyl Sunate	38.1	39.7	- 4.2
Methyl Tallowate	39.9	39.8	0.3

Cloud Point

Diesel fuels are characterized, in part, by their relatively large carbon number. One result of the large carbon number is that the fuels are sensitive to low temperatures where some of the component compounds can begin to crystallize. The presence of solid crystals in the fuel affects the viscosity, volatility and the passage of the fuel through the fuel filter.

There are various measures applied to describe the crystallization tendency of a diesel fuel. The most common are pour point (ASTM D-97), cloud point (ASTM D-2500), cold filter plugging point (IP-309), and the low-temperature flow test (ASTM D-4539). All of these tests have the common goal of describing fuel plugging and/or crystallization at low temperatures.

The thermodynamics and kinetics of crystallization of even simple mixtures are highly complex. Some data exist for binary systems, less for ternaries, and essentially none for multicomponent systems of any kind. Thus, attempts to modify low temperature behavior for any diesel fuel have been mostly to use additives to modify crystallization temperatures or to modify the composition of the fuel to adjust for winter conditions, rather than to exploit known mixture properties.

Recent examples of the exploration of additives to improve low temperature properties of biodiesel include the work of Stournas, et al. (1995) and Lee, et al. (1995). Lee, et al. used branched chain esters as additives, while Stournas, et al. used other fatty acid derivatives.

An alternative approach to improving low temperature properties has been to winterize the biodiesel by deliberately crystallizing out a fraction of the biodiesel, leaving a liquid with better properties (Lee, et al., 1996). These results provided insight for the approach used in this work to use composition data for biodiesel as the basis for estimating the cloud point. The winterization of methyl soyate to increasingly lower temperatures results in a selective removal of the methyl palmitate and methyl stearate. These two materials have melting points some 50 C or more above the unsaturated esters.

While attempts to use a mixing rule based on melting points was unsuccessful in describing cloud points, the fraction of unsaturates was useful in developing a purely empirical expression that represents data for a number of biodiesels reasonably well. Cloud point data from Lee, et al. (1996), Bagby, et al. (1987), Ali, et al. (1995), and Pishinger, et al. (1982) were used to construct the plot shown in Fig. 1. The resulting empirical expression representing cloud point as a function of the fraction of unsaturates is

$$ \ln\,(t+10)=2.2-1.57\ln\,(\textstyle\sum x_{unsat})\qquad(8) $$

The estimated cloud points found using Eq. 8 are compared with the reported values in Table 10. The errors are sufficiently good to merit further comparisons.

Table 10. Comparison of Estimated and Reported Cloud Point for Biodiesel Fuels

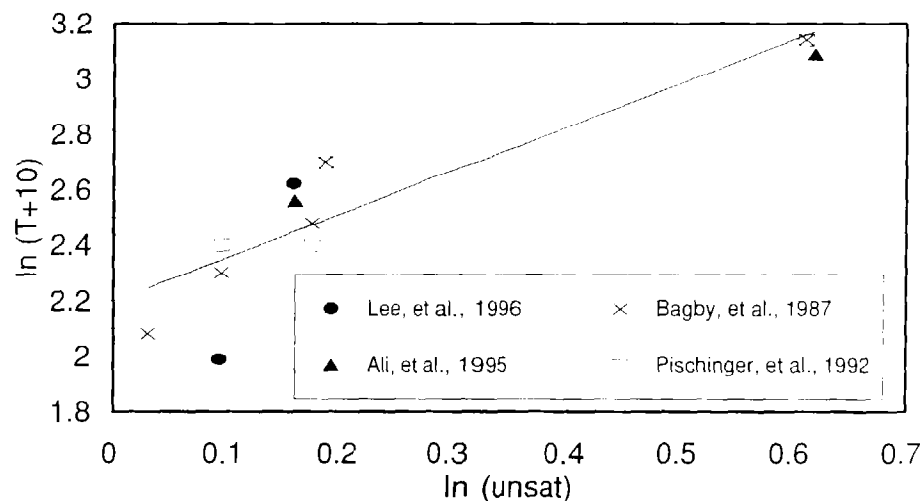| Fuel	Cloud Point Reported	Cloud Point Estimated	Percent Error
Methyl Palmate	23	22.1	3.9
Methyl Soyate	12	11.7	2.5
Methyl Sunate	11	10.4	5.5
Methyl Tallowate	22	24.	- 9.1

Figure 1. Cloud Point of Biodiesel Fuels as a Function of Mole Fraction Unsaturates

CONCLUSIONS

The results presented in this paper should not be presumed to be the final answer to the *a priori* estimation of biodiesel properties, but as the basis to justify the development of some additional data for pure component esters that occur in biodiesel. The results are good enough, however, to aid in the making and testing of biodiesel blends from various sources.

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