

COMPARATIVE ANALYSIS OF THE ATOMIZATION CHARACTERISTICS OF FIFTEEN BIODIESEL FUEL TYPES

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ABSTRACT. Engine results using biofuels have varied considerably in the reported literature. This article addresses two potential sources of this variation, atomization differences and impurities due to lack of quality control during production. Atomization is the first process encountered during the combustion of fuels in a compression ignition engine and is largely determined by the fuel's viscosity and surface tension. Previous work using five experimentally produced methyl ester biodiesel fuels showed that the viscosity and surface tension could be predicted from their fatty acid ester composition, and the atomization characteristics in turn could be predicted from their viscosity and surface tension. This article utilizes the results of that work to give a quantitative comparison of the atomization characteristics of fifteen biodiesel fuel types using the fuel's viscosity and surface tension, predicted directly from the fatty acid composition of the fuels. Except for coconut and rapeseed biodiesel fuels, all of the rest of the 15 biodiesel fuels had similar atomization characteristics. Since the most likely contaminant in the fuel from the processing was residual glycerides, their effect on viscosity and surface tension was studied experimentally and their effect on the atomization characteristics was computed.

Keywords. Atomization, Biodiesel fuels, Methyl esters, Viscosity, Surface tension, SMD.

Biodiesel fuels generally take the form of methyl esters (ME) of plant and animal oils produced by means of the transesterification process. (Some other esters, such as ethyl, have occasionally been used.) Graboski and McCormick (1998), and Bhattacharyya and Reddy (1994) reviewed the results of various tests that have been carried out by many authors. The parameters that have been measured include density, viscosity, efficiency, power changes, emissions, injector coking, oil dilution, pour point, flash point, and cetane number, but seldom atomization because of the difficulty in measuring particle sizes. Ryan et al. (1982) measured 'atomization' using high speed photography in terms of spray angle and penetration into a cell. Vander Griend et al. (1988) sprayed one stroke of an injector into a pressurized jar and captured the droplets into a plate having another liquid on it 500 mm away. The droplets were analyzed optically and the results were used in the KIVA model (Vander Griend et al., 1990).

The general conclusion from the literature is that, in terms of power, wear, efficiency and emissions, biodiesel fuels are a viable alternative. The results of studies on the various performance parameters have, however, varied from one researcher to another depending on the type of fuel used and even with similar fuel types. Since the atomization process is the initial stage of combustion of a fuel in a diesel engine, it was postulated that the reported

variations between fuel types could be caused by differences in their atomization characteristics. It was also postulated that variations between the same fuel types may be caused by the presence of glycerides resulting from different degrees of completion of the transesterification process.

OBJECTIVES

The objectives of this work were to:

1. Quantitatively compare the atomization characteristics of 15 types of biodiesel fuels and diesel no. 2 fuel predicted from their viscosity and surface tension.
2. Experimentally investigate the effect of various levels of triglycerides on the viscosity and surface tension of biodiesel fuels on one potential fuel, canola methyl ester, and to compute the effect of triglycerides on atomization using the regression equations.

METHODS

EXPERIMENTAL METHOD FOR DERIVATION OF DATA FOR REGRESSION MODELS

Methyl ester biodiesel fuels from canola, coconut, palm, peanut, and soya oils were produced in a batch transesterification unit previously described by Allen and Watts (1996). The purity of the biodiesel fuels produced by the transesterification process was verified using thin-layer chromatography on Chromarods-SIII (silica gel) with flame ionization of the components (TLC-FID) by scanning in an Iatroscan Mark III (Ackman et al., 1990). The purity of the canola, peanut and soya was over 99.8%. The palm and coconut oil purities were 98.2 and 95% respectively, but with no triglycerides present. The impurities include mono- and diglycerides and stearols. A Malvern 2600 Particle Sizer was used for droplet analysis

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(Allen et al., 1998). The Sauter Mean Diameter (SMD) and Rosin-Rammler distribution were used to quantify the atomization characteristics of fuels. The SMD represents a droplet with the same volume to surface-area ratio as the spray. An injector and pump from a Kobota single cylinder direct injection engine was powered by an electric motor and run at a constant speed. The fuel was maintained at a constant temperature, 40°C, by a water bath. An optical encoder gave the cam angle, and the Malvern was triggered to take data only at one specific cam angle and at a fixed distance from the nozzle tip, so that consistent droplet sizes were obtained. A total of 30 runs was carried out for each of the five fuel types, each run consisting of 400 “snap shots” of the fuel spray. The atomization data acquired was then used to develop a regression model that correlated the atomization characteristics with the fuel’s surface tension and viscosity.

To determine the effect of glycerides on the surface tension and viscosity of biodiesel fuels, 1%, 2%, 4% and 6% by weight of canola oil (triglyceride) were added to separate samples of canola methyl ester biodiesel fuel. The viscosities and surface tension of these samples were then compared with the unadulterated samples. The SMD regression equations were used to determine the effect of the residual glycerides on the atomization.

REGRESSION MODELS

Models to predict the viscosity and surface tension of biodiesel fuels based on their fatty acid composition were developed by Allen et al. (1999a,b) using controlled mixtures of fatty acid methyl and ethyl ester gas chromatography (GC) standards and biodiesel fuels produced by the transesterification process. Equation 1 outlines the model for viscosity, and equations 2 and 3 outline the surface tension model.

$$\ln \mu_m = \sum_{i=1}^n y_i \ln \mu_i \tag{1}$$

$$\sigma_m = \sum_{i=1}^n w_i \sigma_i \tag{2}$$

$$w_i = m \sigma_i + c \tag{3}$$

where

- μ_m = mean dynamic viscosity of mixture (Pa·s)
- μ_i = dynamic viscosity of pure ith component (Pa·s)
- y_i = mass fraction of the ith component (-)
- n = number of components (-)
- σ_m = mean surface tension of the mixture (N/m)
- σ_i = surface tension of the ith component (N/m)
- w_i = surface tension weight factor for the ith component
- m = slope of the surface tension linear, weight-function line
- c = constant of the surface tension linear, weight-function line

The Rosin-Rammler distribution is given by equation 4. The ‘X’ parameter of the Rosin-Rammler distribution gives a measure of the mean droplet size while the ‘N’ parameter

is a measure of the spread of the distribution. The SMD can be calculated from the Rosin-Rammler distribution parameters using equation 5 (Allen et al., 1998):

$$1 - Q = R_{over} = \exp - \left(\frac{d}{X} \right)^N \tag{4}$$

$$SMD = \frac{X}{\Gamma \left(\frac{N-1}{N} \right)} \tag{5}$$

where

- Q = fraction of total volume contained in droplets of diameter less than d
- R_{over} = normalized fraction of droplets over diameter d
- X = Rosin-Rammler mean diameter parameter (m)
- N = Rosin-Rammler distribution spread parameter ($N = \infty$ implies a mono size distribution)
- d = droplet diameter (m)
- SMD = Sauter Mean Diameter (m)
- Γ = Euler Gamma function

Equations 6 to 8 gives the regression model developed for the experimental data acquired using the Malvern Particle Sizer and the five biodiesel fuels produced by the transesterification process.

$$SMD_2 = 0.002103 \mu + 0.000330 \sigma \tag{6}$$

$$X = 2.0993E -3 \mu + 7.8852E -4 \sigma \tag{7}$$

$$N = - 67.32 \mu + 67.63 \sigma \tag{8}$$

where

- μ = dynamic viscosity (Pa·s)
- σ = surface tension (N/m)

Equations 1 to 4 and 6 to 8 were used to predict the atomization characteristics of 15 types of biodiesel fuels based on their fatty acid compositions taken from the literature (Ackman, 1996).

Table 1. Fatty acid composition of 15 fats and oils (Ackman, 1996)

Oil Type	Fatty Acid Composition										
	Caprylic 0:3333	Capric 10:0	Lauric 12:0	Myristic 14:0	Palmitic 16:0	Stearic 18:0	Oleic 18:1	Lino- leic 18:2	Lino- lenic 18:3	Erucic 22:1	
Peanut	0.0	0.0	0.0	0.0	10.4	8.9	47.1	32.9	0.5	0.2	
Rapeseed	0.0	0.0	0.0	0.0	2.7	2.8	21.9	13.1	8.6	50.9	
Canola	0.0	0.0	0.0	0.1	3.9	3.1	60.2	21.1	11.1	0.5	
Olive	0.0	0.0	0.0	0.0	11.0	3.6	75.3	9.5	0.6	0.0	
Coconut	8.3	6.0	46.7	18.3	9.2	2.9	6.9	1.7	0.0	0.0	
Corn	0.0	0.0	0.0	0.0	9.9	3.1	29.1	56.8	1.1	0.0	
Palm	0.1	0.1	0.9	1.3	43.9	4.9	39.0	9.5	0.3	0.0	
Safflower	0.0	0.0	0.0	0.1	6.6	3.3	14.4	75.5	0.1	0.0	
Sunflower	0.0	0.0	0.0	0.1	6.0	5.9	16.0	71.4	0.6	0.0	
Soybean	0.0	0.0	0.0	0.1	10.3	4.7	22.5	54.1	8.3	0.0	
Sunola	0.0	0.0	0.0	0.0	3.0	4.4	88.2	4.3	0.1	0.0	
Cottonseed	0.0	0.0	0.0	0.8	22.9	3.1	18.5	54.2	0.5	0.0	
Beef tallow	0.0	0.1	0.1	3.3	25.2	19.2	48.9	2.7	0.5	0.0	
Butterfat	5.5	3.0	3.6	11.6	33.4	11.4	27.8	3.1	0.6	0.0	
Lard	0.0	0.1	0.1	1.4	25.5	15.8	47.1	8.9	1.1	0	

RESULTS AND DISCUSSION

Table 1 gives a listing of the oils/fats and the fatty acid composition of the 15 oils used in the analysis. (The oils are presented in order of increasing molecular weight in figs. 1-4. For clarity, the order is different for fig. 5.) Equation 1 was applied to predict the viscosity of the methyl esters (ME) of the 15 oils at 40°C. These results are summarized in figure 1 along with the upper prediction limit based on the average error of the model. Rapeseed oil ME had the highest predicted viscosity (4.72 mPa·s) while coconut oil ME had the lowest (2.25 mPa·s). By examining table 1, it can be seen that coconut oil is high in fatty acids with low carbon chain lengths, whereas rapeseed oil is very high in eruric (22:1) acid, a high carbon chain length. Thus the variation of viscosity is to be expected. Most of the other oils had similar viscosities ranging from 3.31 to 3.94 mPa·s. The r^2 correlation of viscosity with molecular weight is 0.75.

Equations 2 and 3 were applied to predict the surface tension of the 15 methyl ester biodiesel fuels at 40°C. The

predicted values, along with the upper prediction limits, are given in figure 2. Rapeseed ME had the highest surface tension (29.24 mN/m) while coconut ME had the lowest (26.82 mN/m). The others ranged from 27.69 to 28.98 mN/m. Again, it is observed that the carbon chain length affects the surface tension but not as dramatically as for viscosity. Vander Griend et al. (1988) obtained a surface tension value for rapeseed ME of 30.4 mN/m at 40°C, slightly higher than the value here, even though using the same type of equipment. Our surface tension meter was initially calibrated using iso-butanol and benzene, and repeatedly checked with a myristic acid methyl ester GC standard. The r^2 correlation of surface tension with molecular weight is 0.80.

Using the predicted viscosity and surface tension for the 15 fuel types, the Sauter Mean Diameter was predicted using equation 6. The SMD error bands were computed including the errors in the viscosities, surface tension and the SMD regression model. Figure 3 shows this data graphically and figure 4 shows the SMDs compared with diesel fuel. As expected from the viscosity and surface

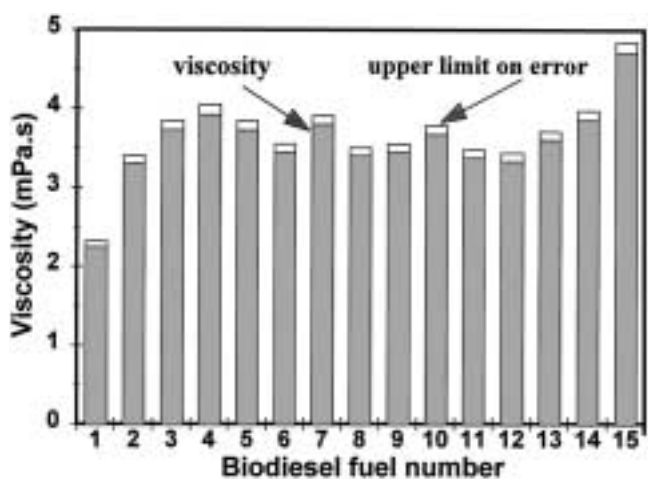


Figure 1—Predicted viscosities at 40°C for 15 methyl ester biodiesel fuels. In order of increasing molecular weight: 1, coconut; 2, butterfat; 3, palm; 4, beef tallow; 5, lard; 6, cottonseed; 7, olive; 8, soybean; 9, corn; 10, peanut; 11, safflower; 12, sunflower; 13, canola; 14, sunola; 15, rapeseed.

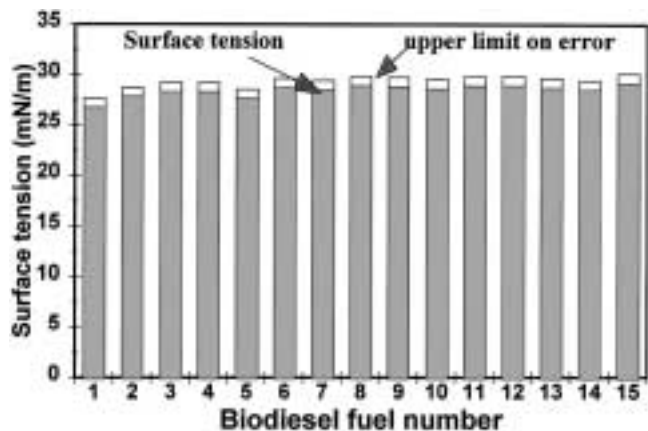


Figure 2—Predicted surface tensions at 40°C for 15 methyl ester biodiesel fuels. In order of increasing molecular weight: 1, coconut; 2, butterfat; 3, palm; 4, beef tallow; 5, lard; 6, cottonseed; 7, olive; 8, soybean; 9, corn; 10, peanut; 11, safflower; 12, sunflower; 13, canola; 14, sunola; 15, rapeseed.

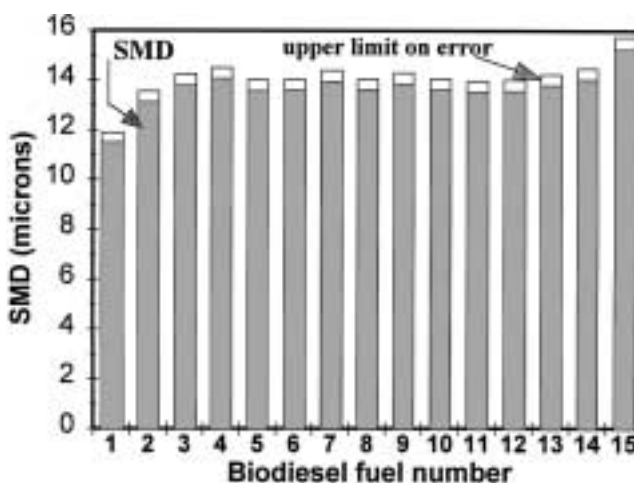


Figure 3—Predicted SMDs for 15 methyl ester biodiesel fuels. In order of increasing molecular weight: 1, coconut; 2, butterfat; 3, palm; 4, beef tallow; 5, lard; 6, cottonseed; 7, olive; 8, soybean; 9, corn; 10, peanut; 11, safflower; 12, sunflower; 13, canola; 14, sunola; 15, rapeseed.

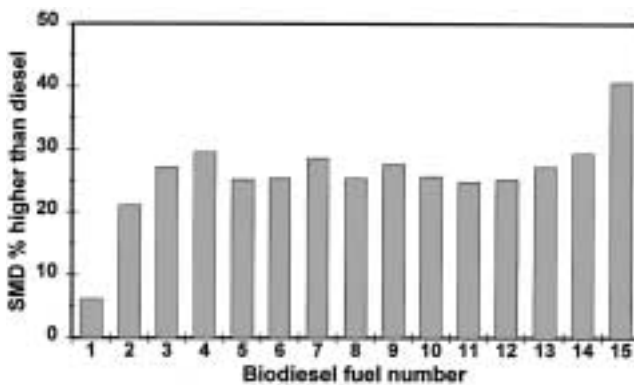


Figure 4—Predicted SMDs for 15 biodiesel types compared with diesel fuel. In order of increasing molecular weight: 1, coconut; 2, butterfat; 3, palm; 4, beef tallow; 5, lard; 6, cottonseed; 7, olive; 8, soybean; 9, corn; 10, peanut; 11, safflower; 12, sunflower; 13, canola; 14, sunola; 15, rapeseed.

tension results, the rapeseed oil ME had the highest SMD (15.31 μ m) while coconut oil ME had the lowest (11.55 μ m). The others were in the range of 13.17 to 14.10 μ m. Compared with diesel, most of the oils had SMDs that were 20 to 30% higher than diesel, while coconut oil ME was approximately 6% higher than diesel and rapeseed oil ME 40% higher. The r^2 correlation of SMD with molecular weight is 0.88.

The droplet distributions, including the two parameters of the distribution, X and N, for the 15 fuels were also predicted using the Rosin-Rammler distribution, equations 6 through 8. Figure 5 shows the distributions graphically where it can be seen that all of the fuel types had similar droplet distribution patterns.

Since the SMD and distribution of coconut biodiesel fuel was close to that of diesel fuel, a statistical test was carried out to ascertain if there was any statistical difference. The Duncan Mean Range Test (DMRT) was used at a 5% level of significance and it was found that no statistically significant difference existed between the two fuel types. The value of the SMD for rapeseed ME differs by almost an order of magnitude from the data of Vander Griend et al. (1988). Our SMD of about 14 μ m compared to Vander Griend's SMR (Sauter Mean Radius) of 59 μ m. Their measurement technique (droplet capture) is undoubtedly biased to larger droplets, with fine droplets not penetrating the capture liquid.

From figures 2 and 3, it can be seen that 13 of the 15 biodiesel fuels have similar atomization characteristics with SMDs being 25 to 29% higher than diesel fuel. This implies that, in terms of atomization, most of the biodiesel fuel tests reported in the literature should have had similar results. Since this was not the case, atomization characteristics may not be the primary cause for the different results reported in the literature.

One cause for the variation of the performance test results reported in the literature may be due to impurities in the fuels. Most of the reports do not present data on the extent of the transesterification reaction and therefore the fuel's purity could not be verified. However, for the tests carried out in this study where canola oil (triglycerides—TG) in mass fraction of 1%, 2%, 4%, and 6% was added to canola oil ME biodiesel fuel, it was found that 1% TG in the ME resulted in a 1.5% increase in viscosity; 2% gave a 3.8% increase; 4% gave a 7.8% increase; and 6% resulted

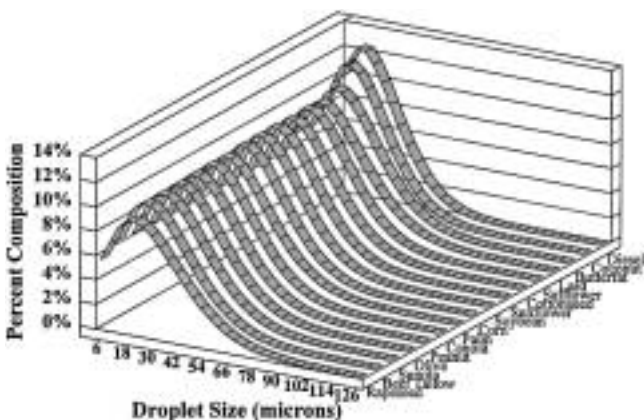


Figure 5—Predicted droplet distribution for 15 methyl ester biodiesel fuels.

in an 11.8% increase in the viscosity of the mixture. Surface tension was unaffected at all TG levels. The computed corresponding increases in SMD are 0.67%, 1.7%, 3.5%, and 5.2%. These changes are significant for viscosity, and to a lesser extent for droplet distribution.

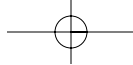
CONCLUSIONS

1. The viscosities of methyl ester biodiesel fuels may vary as much as 100% and may be a contributing factor to the difference in performance among some biodiesel fuels.
2. The variation of surface tension for methyl ester biodiesel fuels is 5% on average, and thus has little influence on the atomization characteristics.
3. The difference in the Sauter Mean Diameter between some biodiesel fuels is as high as 32%. However, it is similar for oils containing mainly C18 unsaturated fatty acids. Oils with mainly low carbon numbers (\leq C14 saturates) fatty acids have lower SMDs; those with high carbon numbers (\geq C16 saturates) fatty acids have higher SMDs; and those with mainly C18 unsaturates have moderate SMDs.
4. The SMDs of methyl ester biodiesel fuels vary from 5 to 40% higher than diesel fuel. The atomization characteristics of coconut oil ME biodiesel fuel was not significantly different from diesel no. 2 at a 95% confidence level.
5. Low levels of glyceride impurities in the ME biodiesel fuels do produce significant changes in the viscosity, and may contribute to the differences in performance reported in the literature.

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