Rheology of Vegetable Oil Analogs and Triglycerides

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ABSTRACT: The rheological properties of two complex mixtures of short-chain triglycerides were experimentally determined. Dynamic or absolute viscosities of the mixtures were measured for shear rates of 0.32 to 64.69 s^{-1} at temperatures between 25 and 80°C. The compositions of the mixtures were based on the oil of the plant species *Cuphea viscosissima* VS-320, a natural source of short-chain triglycerides. The dynamic viscosities of these mixtures were compared to those of a traditional vegetable oil (peanut oil) and diesel fuel. The results of this comparison were used to make estimates of the performance of such triglyceride mixtures as diesel fuel substitutes, since viscosity can be a key indicator of fuel performance for possible substitute diesel fuels. The crystallization temperatures of these two mixtures were also determined experimentally, and the effects of crystallization on fuel performance were projected. Additionally, the dynamic viscosities of pure triglycerides from C6:0 to C18:0 at 75°C were plotted vs. chain length. These viscosities were measured at high shear rates (>6 s^{-1}) where dynamic viscosity is shear-independent. An obvious trend in the relationship between triglyceride chain length and viscosity was observed. A second-order regression was used to obtain an equation for this relationship. This equation was used as a model for composition dependence of viscosity. This model was applied to the viscosities of the triglyceride mixtures examined here. There was good agreement between the model and the actual, measured viscosity values determined in this study.

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The physical properties, including viscosity, of pure, short-chain triglycerides such as tricaproin (C6:0), tricaprylin (C8:0), and tricaprin (C10:0) have been evaluated in previous studies (1–3). These studies sought to develop models for the use of oils containing such compounds as diesel fuel substitutes, i.e., biodiesel. The results obtained suggest that vegetable oils containing high concentrations of short-chain saturated triglycerides may provide effective diesel fuel substitutes without the additional processing costs incurred when converting commercial vegetable oils into effective alternative fuels. Studies on the properties of binary mixtures of triglycerides have also been published (1,4,5). These investigations have been useful in understanding how such compounds interact with each other and how triglyceride chain length affects the physical properties of vegetable oils. This information has been useful in the design and evaluation of equipment used for the chemical processing of oils containing low-molecular-weight saturated triglycerides for cosmetic and pharmaceutical applications. Such information is also important for the development of triglyceride-based diesel fuel substitutes derived from vegetable oils.

Studies concerning the behavior and properties of short-chain triglycerides in the pure state and in simple mixtures can be very useful in the development of biologically derived fuels and other valuable products. However, natural vegetable oils are not composed of pure triglycerides or simple binary mixtures of triglycerides. They are complex mixtures of several triglycerides with varying chain lengths. In order to develop useful products from oils containing low-molecular weight-oils, it is necessary to study triglyceride mixtures similar to those produced naturally. Recently, the physical properties of a natural source of short-chain triglycerides, *Cuphea viscosissima* VS-320 oil, were examined (6). The oils synthesis of this plant species was altered by induced mutations resulting in an increase of medium- and short-chain fatty acids (7). Natural sources of these triglycerides are rare and usually only contain a small percentage of short-chain triglycerides. *Cuphea viscosissima* is unique because it provides a renewable source of these rare triglycerides. Further research is under way to make *Cuphea* a more efficient producer of these valuable compounds and to improve its adaptability to mechanized growth and harvesting (7).

Two triglyceride mixtures were examined in this study. The compositions of these oils were based on that of *Cuphea* VS-320 oil and of a projected "ideal" vegetable oil for diesel fuel purposes. An analog of *Cuphea* VS-320 oil was prepared by mixing pure reagent triglycerides to simulate the composition of the natural oil. Also, a commercial preparation of triglycerides, Captex 355, was selected as an "ideal" vegetable oil analog for use as a diesel fuel substitute based on previous studies concerning the behavior and properties of short-chain triglycerides (2,3). Captex 355 is a preparation of mixed triglycerides with a high concentration of caprylic (C8:0) and capric (C10:0) carbon chains. Such triglyceride blends are predicted to perform well as diesel fuel substitutes, assuming ideal solution behavior of mixtures of short- and medium-chain triglycerides (1).

A model for viscosity dependence on fatty acid chain length would be very useful in estimating the relative viscosi-

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ties of mixtures of straight-chain saturated homogeneous triglycerides. Such a viscosity-based model would be a valuable tool for preliminary, rapid screening of vegetable oils for use as diesel fuel substitutes. Viscosity data of pure homogeneous triglycerides with saturated fatty acid chains 12 to 18 carbon atoms in length previously have been published (8). This study adds data for triglycerides with 6 to 10 carbon atoms for the development of a model for compositional dependence of viscosity.

The objective of this study was to expand on the studies of *Cuphea* by providing measurements of viscosity, a key engineering parameter, for *Cuphea* oil analogs. Specifically, measurements of the temperature and shear rate dependence of dynamic viscosity were examined. The effects of short- and medium-chain triglycerides on viscosity were examined in depth to illustrate the promise of *Cuphea* as a source of alternative diesel fuel. The viscosities of diesel fuel and a commercial vegetable oil (peanut oil) were used as comparisons for this illustration.

MATERIALS AND METHODS

Captex 355 and Cuphea *VS-320 oil composition*. The triglyceride composition of *Cuphea* VS-320 oil was determined by gas chromatography according to the method of Knapp *et al.* (9). Captex 355 was purchased from Karlshamns (Janesville, WI). The compositional information was provided by the vendor and was determined by gas–liquid chromatographic (GLC) analysis. Compositional data for these oils are shown in Table 1.

Simulated VS-320 oil. Owing to the present difficulty in harvesting *Cuphea* VS-320 seeds, a sufficient volume of oil was not available for viscosity analysis. Therefore, a mixture of chemical reagent triglycerides and Captex 355 was prepared to simulate VS-320 oil properties and to supply the volume of oil needed for viscosity tests. Genetic modifications of *Cuphea* are currently underway to improve its agronomic properties, which will facilitate the collection of large quantities of oil in the near future (7).

The composition of the simulated VS-320 oil was based on GLC analysis of *Cuphea* VS-320 oil as illustrated in Table 1. The mixture was brought into solution by heating to 80°C with stirring. The oil was characterized by thermogravimetric analysis of boiling point and vapor pressure before conducting viscosity analysis. Tricaproin, tricaprylin, trimyristin, tripalmitin, and triolein were obtained from Sigma Chemical Co. (St. Louis, MO). Tricaprin and trilaurin were purchased from TCI (Portland, OR). Triolein was purchased from ICN Biomedicals (Costa Mesa, CA).

TABLE 1
Composition of VS-320 Seed Oil vs. Simulated Seed Oil and Captex 355

Triglyceride	VS-320 (%)	Simulated VS-320 (%)	Captex 355 (%)
C6:0	4.19	4.20	0.4
C8:0	40.24	40.20	58.5
C10:0	36.90	36.90	40.2
C12:0	4.81	4.80	—[a]
C14:0	6.84	6.80	—[a]
C16:0	3.33	3.33	—[a]
C18:0	0.15	0.00	—[a]
C18:1	1.37	1.37	—[a]
C18:2	2.05	2.05	—[a]
C18:3	0.13	0.00	—[a]

[a]C12:0 to C18:3 constitutes 0.9% of total Captex 355 composition.

Viscosity determination. Viscosities were determined with a Brookfield Synchro-Lectric LVT rotating cylinder-type viscometer with UL adapter (Stoughton, MA). The viscometer operates at eight fixed shear rates from 0.32 to 64.7 s^{-1}. The Brookfield manual states that viscosity may be measured to ±0.02 mPa·s in the interval of 0–10 s^{-1}. Measurements were taken according to the method of Eiteman and Goodrum (2). A circulating water bath was used to maintain constant experimental temperatures from 25 to 80°C with an accuracy of ±0.1°C. Replicate viscosity tests showed an average precision of ±3.64% for the four temperatures evaluated.

Crystallization temperature determination. Crystallization temperatures were determined using differential scanning calorimetry (DSC). A PerkinElmer (Norwalk, CT) model DSC-2 provided crystallization point data at 1 atm pressure. Nitrogen purge flow through the cell was maintained by 1.36 atm (20 psi) pressure applied to the DSC module. Approximately 5.0- mg samples (±1.0 mg) were placed in 20 µL pans (PerkinElmer Corp., part no. 219-0662). Samples were heated and/or cooled at a rate of 10°C/min. Samples were subjected to three heating and cooling cycles to verify results. Several peaks were observed for simulated VS-320 oil and two peaks were observed for Captex 355. The onset temperature for crystallization was taken as the highest observed melting onset temperature.

RESULTS AND DISCUSSION

The dynamic viscosities of Captex 355 were measured as a function of shear rate for four discrete temperatures—25, 40, 60, and 80°C. The results of these experiments are shown in Figure 1. A previous study on the physical properties of *Cuphea* oil provided similar data for simulated VS-320 oil (6). The dynamic viscosities of the triglyceride mixtures at the highest measured shear rate (12.94, 32.34, and 64.69 s^{-1}) were 5.9 to 27.2 mPa·s for simulated VS-320 oil and 4.96 to 24.6 mPa·s for Captex 355. These viscosity analyses show several characteristics of the rheological behavior. Viscosity becomes shear-dependent (non-Newtonian flow or pseudoplastic behavior) below shear rates of 7 s^{-1}. At shear rates higher than these, the oils begin to behave as Newtonian fluids. In the temperature interval studied, the viscosity decreased by at least 25% for each 20°C temperature increase for shear rates above the point of shear independence. It should be noted that at around 25°C, simulated *Cuphea* oil began to crystallize, resulting in inaccurate viscosity readings at high shear rates. This might have resulted from the presence of saturated long-chain triglycerides in the oil, because

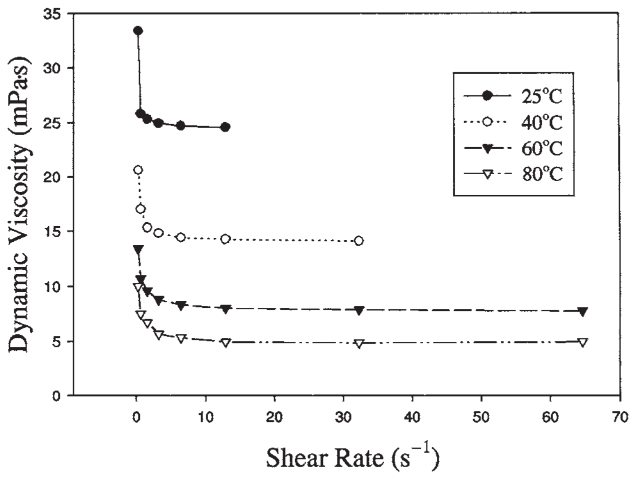

FIG. 1. Dynamic viscosity vs. shear rate for Captex 355 at various temperatures.

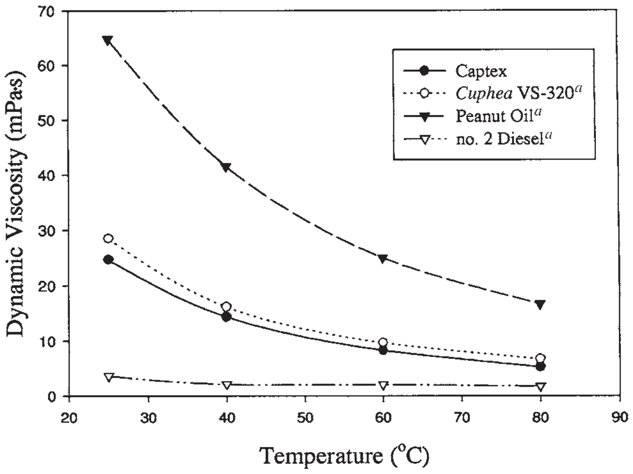

FIG. 2. Dynamic viscosity vs. temperature for various diesel fuels. ^{a}Data from Reference 4.

these triglycerides are solid at room temperature. Crystallization analysis of the oils using DSC resulted in an initial crystallization temperature of approximately 33°C for *Cuphea* VS-320 oil and about −5.5°C for Captex 355. Both oils produced several peaks as different triglycerides melted and crystallized during the heating and cooling cycles. High crystallization temperatures, such as those found in VS-320 oil, are undesirable for fuel purposes. Reduction of this temperature to near that of Captex 355 may result in a more effective diesel fuel substitute.

Figure 2 compares the viscosities of both Captex 355 and simulated VS-320 oil with diesel fuel and commercial vegetable oil (peanut oil). This figure shows the dynamic viscosities of Captex 355, VS-320 oil, diesel fuel, and peanut oil as a function of temperature. Dynamic viscosity was determined to be lower for the lower-molecular-weight Captex 355 mixture than for VS-320 oil. This is consistent with previous studies that showed a decrease in viscosity for triglycerides with decreasing average molecular weights (2). Figure 2 shows that the viscosity for both of the oils studied here falls between those of diesel fuel and peanut oil, a vegetable oil with a predominantly long-chain triglyceride composition. Although these oils may not have viscosities as low as diesel fuel, their viscosity values are approximately one-third that of commercial vegetable oils. Methyl esters of commercial vegetable oils (i.e., biodiesel) have viscosities near this interval; they are reportedly effective technical alternatives for diesel fuel (2).

The dynamic viscosities of pure, saturated triglycerides from C6:0 to C18:0 at 75°C are shown in Figure 3. A second-order regression of this data is also shown. The equation resulting from this regression is as follows:

$$n = 0.0576C^2 - 0.2339C + 3.8424 \qquad [1]$$

where n is the dynamic viscosity in mPa·s and C is the number of carbon atoms per fatty acid residue for each triglyceride. The regression produced an R^2 value of 0.9974. This relatively good fit to the model suggested that the regression equation may be used to predict the viscosity of mixtures of triglycerides within this size interval.

To test this possibility, the regression equation was used to predict the viscosity of the triglyceride mixtures studied by assigning an effective carbon number (ECN) for each oil. This method assumes these mixtures behave as ideal solutions. For mixtures of triglycerides, ECN replaces C in Equation 1. The ECN was determined by multiplying the number of carbon atoms in the fatty acid chain of each component triglyceride by its percent composition in each mixture. The influence of double bonds was approximated by subtracting 1 for each double bond from the actual number of carbon atoms in the triglyceride fatty acid chains to compensate for the reduction in viscosity seen in unsaturated compounds (10). The resulting equation for determining ECN is as follows:

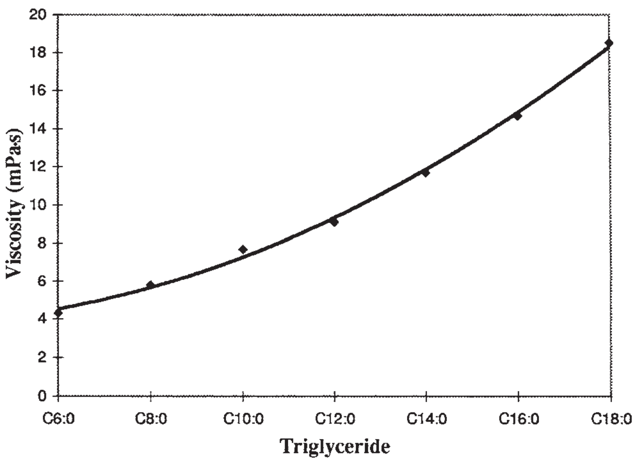

FIG. 3. Dynamic viscosity of pure triglycerides vs. number of carbon atoms in fatty acid chains.

TABLE 2
Viscosity Model Agreement with Experimental Data

Mixture	Effective carbon number (ECN)	Viscosity (mPa·s) Model	Viscosity (mPa·s) Actual	Error (%)
Cuphea VS-320	9.78	7.06	7.45	5.18
Captex 355	8.87	6.30	6.04	4.30

$$\mathrm{ECN} = \Sigma\, P_i\, (C_i - \mathrm{db}_i) \quad [2]$$

where P is the percent composition of each triglyceride, C is the number of carbon atoms in the fatty acid chains of each triglyceride, and db is the number of double bonds in each fatty acid chain. The ECN for each oil are included in Table 2 along with their predicted viscosities determined by substituting the ECN for C in Equation 1. The model values are compared to the actual viscosities from Figure 2 that were determined experimentally. This model provided a simple but accurate method of predicting the viscosities of the triglyceride mixtures. This method allowed estimation of the viscosity of Captex 355 and VS-320 oil with reasonable accuracy (~5% error).

The viscosity of the higher average molecular weight *Cuphea* VS-320 oil was greater than that of Captex 355 under all conditions studied. Both triglyceride mixtures exhibited slightly pseudoplastic behavior that decreased with increasing temperatures. In addition, viscosities exhibited a clear transition from non-Newtonian to Newtonian behavior at shear rates greater than 7 s^{-1}.

On the other hand the triglycerides studied here show a consistent trend in viscosity based on fatty acid composition. The structure-based viscosity model presented here provides good estimates of viscosity based on oil composition. Such a model may serve as a quick and easy screening tool for triglyceride-based alternative fuels.

The high crystallization temperature of *Cuphea* VS-320 oil is a complicating factor in its use as a diesel fuel substitute. Captex 355 exhibited both a lower crystallization temperature and decreased viscosity under the conditions studied. Both of these properties suggest better fuel performance for Captex 355 as compared to VS-320. For this reason, the triglyceride composition of Captex 355 may serve as a target for the future genetic manipulation of vegetable oils for the production of diesel fuel substitutes.

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