The Speed of Sound and Isentropic Bulk Modulus of Biodiesel at 21°C from Atmospheric Pressure to 35 MPa

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ABSTRACT: Biodiesel, an alternative diesel fuel consisting of the alkyl monoesters of fatty acids from vegetable oils and animal fats, can be used in existing diesel engines without modification. However, property changes associated with the differences in chemical structure between biodiesel and petroleum-based diesel fuel may change the engine's injection timing. These injection timing changes can change the exhaust emissions and performance from the optimized settings chosen by the engine manufacturer. This study presents the results of measurements of the speed of sound and the isentropic bulk modulus for methyl and ethyl esters of fatty acids from soybean oil and compares them with No. 1 and No. 2 diesel fuel. Data are presented at 21 ± 1°C and for pressures from atmospheric to 34.74 MPa. The results indicate that the speed of sound and bulk modulus of the monoesters of soybean oil are higher than those for diesel fuel and these can cause changes in the fuel injection timing of diesel engines. Linear equations were used to fit the data as a function of pressure, and the correlation constants are given.

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KEY WORDS: Biodiesel, bulk modulus, compressibility, diesel fuel, ethyl soyate, methyl soyate.

Biodiesel has come to be defined as the alkyl monoesters of fatty acids from vegetable oils or animal fats. It can be used as an alternative fuel for diesel engines. Many researchers have reported that oxides of nitrogen (NOx) increase, and particulate matter, carbon monoxide, and unburned hydrocarbons decrease when biodiesel is used in heavy-duty diesel engines (1,2). The reason for the higher NOx emissions is not currently understood but could be due to changes in the chemical composition and the physical properties of the fuel. A major difference between petroleum-based diesel fuel and biodiesel is the 10–11% oxygen content of the biodiesel. The oxygen could change the stoichiometry of the combustion process in a way that produces more NOx. Biodiesel also generally has a higher cetane number than petroleum-based diesel fuel. The cetane number is a diesel fuel property that quantifies the fuel's readiness to autoignite. Higher cetane number corresponds to a shorter ignition delay after the fuel is injected into the cylinder. This results in earlier combustion timing, which tends to increase NOx, and less of the fuel participating in the rapid combustion of the fuel that has premixed during the ignition delay period, which will reduce NOx. These two effects partially offset each other, but higher cetane number in petroleum-based diesel fuels is generally observed to reduce NOx (3). The contribution of biodiesel's higher cetane number to NOx production is still not understood. Changes in physical properties such as viscosity, speed of sound, and bulk modulus also may contribute to higher NOx levels. Injection system anomalies, such as longer injection duration, higher injection pressure, and early injection have been reported by other researchers (4–6).

Diesel engines operate by compressing fuel to a high pressure and injecting it into the cylinder where the fuel spontaneously ignites. The fuel is compressed with a piston and cylinder pump and, in many engines, this pressurized fuel is delivered to the fuel injector through a long length of heavy-wall tubing. Injection begins when the pressure at the injector exceeds a critical pressure, known as the nozzle opening pressure. If the fuel is less compressible and the speed of sound is greater, the fuel injection pressure will develop faster and the fuel will be injected sooner. When the start of injection is advanced in most engines, the exhaust NOx emissions increase. The unit injector systems currently used on large truck engines do not use long lines and control the start of injection electronically, but are still sensitive to the compressibility of the fuel.

Figure 1 shows a comparison of the fuel injection line pressures for a diesel engine fueled with a 20% blend of biodiesel in 80% No. 2 diesel fuel, and No. 2 diesel fuel (7). It is clear that the fuel injection timing is advanced by almost 2° for the biodiesel and about 1/2° for the 20% blend. These data support the hypothesis that fuel property changes can significantly affect fuel injection timing. The first step toward understanding the effect of the fuel properties on injection timing is to measure the relevant physical properties such as the speed of sound and bulk modulus at temperatures and pressures corresponding to those encountered in diesel fuel injection systems. This paper presents these data.

MATERIALS AND METHODS

The ultrasonic pulse echo technique was used to measure the speed of sound in methyl and ethyl esters of fatty acids from

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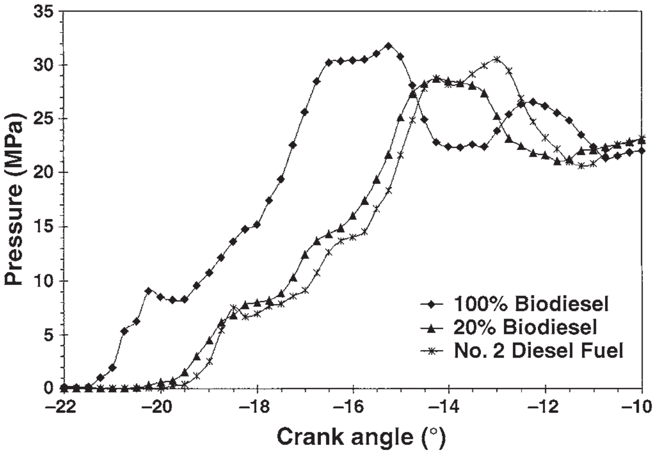

FIG. 1. Injection line pressures for 100% biodiesel, 20% biodiesel blend, and No. 2 diesel fuel at full load and standard injection timing (Ref. 7).

soybean oil and in No. 1 and No. 2 diesel fuels (8–10). A pressure vessel with a piston and cylinder assembly for raising the pressure was fabricated and an ultrasonic transducer was located at the bottom of the vessel. A section view of the vessel is shown in Figure 2. A Panametrics (Waltham, MA) model 5072 PR general-purpose ultrasonic pulser/receiver and a Panametrics 5 MHz videoscan immersion transducer were used. Signals were captured with a Hewlett-Packard model 54601A, 100 MHz, four-channel digital oscilloscope (Colorado Springs, CO). System pressure was measured using a Sensotec (Columbus, OH) Model 2 Z/1108-04Z9 pressure transducer.

The speed of sound was determined by measuring the time difference between the ultrasound echos reflected back to the transducer from the interface where the signal passed from the pressure vessel into the sample fluid and from the reflection when the signal left the sample and reentered the vessel wall. The time measurement was divided into two times the sample thickness, a measured quantity, to give the speed of sound in the fluid.

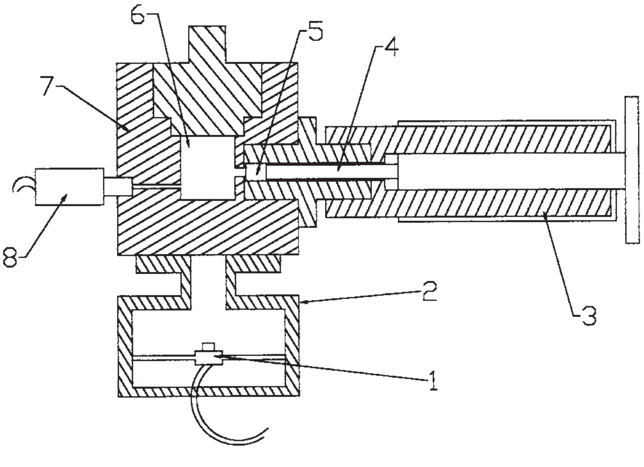

FIG. 2. Cross section of the pressure vessel. 1 = 5 MHz ultrasonic transducer, 2 = cooled chamber for transducer, 3 = pressure screw, 4 = plunger, 5 = piston, 6 = sample chamber, 7 = pressure vessel, 8 = pressure transducer.

Density measurements were taken simultaneously with the speed of sound measurements. To determine the density of the sample at elevated pressures, the sample density was initially measured at atmospheric pressure using a specific gravity balance. As the sample pressure was raised using the piston and cylinder, the piston position was measured using a vernier scale on the pressure screw. Since the sample mass was constant, the volume change was used to determine the density change. The density change could be combined with the initial density measurement to give the density at the elevated pressure. A correction was calculated for the expansion of the vessel at high pressure, although this was small for all of the data presented here.

The isentropic bulk modulus was calculated from the measured density and speed of sound using the following equation (11):

$$\beta = c^2 \times \rho \qquad [1]$$

where β is the isentropic bulk modulus, c is the speed of sound in the sample, and ρ is the density.

The two primary concerns with the use of the pressure vessel technique for density measurement were ensuring that air bubbles were eliminated from inside the vessel and that no fluid leaked from the vessel during the test. If air bubbles were present, their presence was expected to cause variations in measurements as the pressure vessel was filled, emptied, and refilled again. Thus, the pressure vessel was filled with the sample fluid three times and each time six sets of data were collected as the pressure was varied. Half of the measurements were collected while increasing the pressure and half while decreasing the pressure. This was to identify leakage from the chamber or any other hysteresis effects. A total of 18 data points was collected for each pressure level. Subsequent analysis showed no statistically significant difference between the measurements associated with different filling operations or with measurements taken while increasing or decreasing the pressure. Therefore, all 18 measurements were averaged and included in the confidence limit calculations. All measurements were taken at room temperature which was 21 ± 1°C.

The methyl and ethyl esters were prepared by mixing a 6:1 molar ratio of methyl or ethyl alcohol to soybean oil using 1% (based on the weight of oil) potassium hydroxide as a catalyst. The soybean oil was refined, bleached, and deodorized oil purchased from a local food store. The reactants were stirred at room temperature for 8 h and then allowed to settle so the glycerol could be removed. The resulting ester was washed four times with an approximately equal volume of distilled water to remove residual alcohol, catalyst, and soaps. Then the ester was washed with pure glycerol which has been found to be effective at reducing unreacted mono- and diglycerides. The No. 1 and No. 2 diesel fuels were commercial-grade fuels and were purchased from a local supplier. The chemical composition of the esters and the physical and chemical properties of the diesel fuels are given in Tables 1 and 2. All of the measured properties of the biodiesel fuels are within the provisional ASTM specification (12) for biodiesel with the exception of the free glycerol level of the methyl ester and the total glycerol level of the ethyl ester. The measured free glycerol level was 0.037% and the specification limit is 0.02%. This extra free glycerol is probably due to the final glycerol wash and was not believed to affect the measurements reported in this study. The total glycerol level of the ethyl esters was 0.29% and the specification limit is 0.24%. Even after several attempts with additional alcohol and catalyst, it was not possible to reduce the total glycerol below this level. As with the free glycerol in the methyl esters, the total glycerol was not believed to affect the measurements.

TABLE 1
Chemical Composition of the Esters Used

Properties (%)	Methyl ester	Ethyl ester[a]
Free glycerol	0.037	NA
Triglycerides	0.031	NA
Diglycerides	0.078	NA
Monoglycerides	0.315	NA
Total glycerol	0.133	0.290
Fatty acids		
Palmitic	10.26	10.44
Stearic	4.26	4.50
Oleic	21.50	24.46
Linoleic	53.67	51.50
Linolenic	8.17	7.19

[a] NA, not available.

TABLE 2
Physical and Chemical Properties of the Diesel Fuels Used

Properties[a]	No. 1 diesel	No. 2 diesel
Carbon (%)	85.96	86.64
Hydrogen (%)	13.6	12.84
Sulfur (%)	0.038	0.034
Heat of combustion (kJ/kg)		
Gross	45836	45529
Net	42949	42805
Aromatics (%)	19.0	34.2
Paraffin (%)	49.4	62.3
Olefin (%)	1.6	3.5
Olefin (%)	1.6	3.5
Distillation		
IBP	175	186
5%	188	205
10%	193	215
20%	201	231
40%	213	256
60%	225	280
80%	241	304
90%	253	320
95%	263	334
EP	283	349

[a] IBP, initial boiling point, EP, end point.

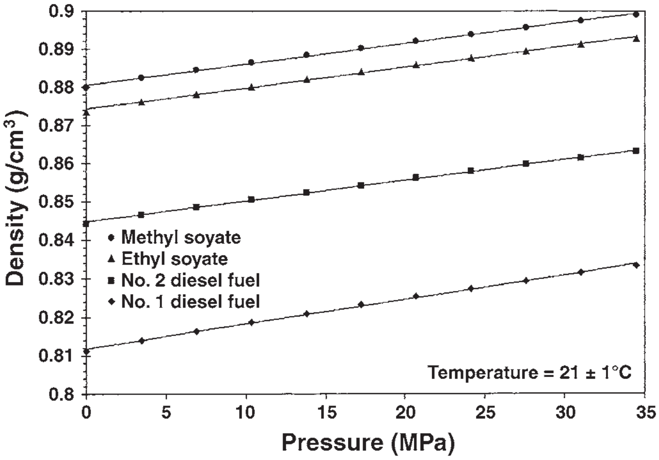

FIG. 3. Density of methyl soyate, ethyl soyate, and No. 1 and No. 2 diesel fuels.

RESULTS

To validate the measurement technique, the speed of sound, density, and isentropic bulk modulus of distilled water were measured and compared with published data at 21.6°C (13,14). The maximal differences obtained between the published data and the measured values were less than 0.2% for density, 0.13% for speed of sound, and 0.42% for the calculated isentropic bulk modulus at 34.47 MPa. The source of these errors is still being investigated, but the magnitudes were considered to be small and no corrections were made to the measurements reported here.

Figure 3 shows the measured density for the four fuels. The points represent the average of 18 measurements. Error bars are not shown on this plot because they are so small that they obscure the data symbols. The 90% confidence limits for the measured densities were typically about ±0.1% of the mean density values. The lines through the points are from linear regression and the coefficients are given in Table 3. The lines correlate the data well with the lowest r^2 value being 0.9978. The methyl esters were more dense than the ethyl esters and both were more dense than the diesel fuels.

Published data for the speed of sound of *n*-paraffins indicates that longer-chain paraffins have higher speeds of sound than shorter-chain paraffins (11). Therefore, biodiesel, with carbon chain lengths of 17–19 would be expected to have a higher speed of sound than No. 2 diesel fuel with chain lengths of 13–16 (15). No. 1 diesel fuel contains even shorter chain lengths. Figure 4 shows the measured speeds of sound for the four fuels. As expected, the methyl and ethyl esters have higher speeds of sound than No. 2 diesel fuel which is also higher than the No. 1 diesel fuel. The slopes of the lines for methyl and ethyl soyates are less steep than those for No. 1 and No. 2 diesel fuel, indicating less effect of pressure on the speed of sound. The error bars shown on the data define the 90% confidence limits. The coefficients for the linear regression are provided in Table 3. Straight lines correlate the data with r^2 values greater than 0.9979.

TABLE 3
Correlation Constants and Equations (21 ± 1°C)

Fuels[a]	Methyl soyate	Ethyl soyate	No. 2 diesel	No. 1 diesel	Distilled water
Density (g/cm^3) = $A_1 \times [P\ (\text{MPa})] + B_1$					
A_1	5.4784E-04	5.5140E-04	5.4045E-04	6.4350E-04	4.8965E-04
B_1	0.88056	0.87423	0.84480	0.81182	0.99722
r^2	0.9978	0.9978	0.9985	0.9981	0.9995
Speed of sound (m/s) = $A_2 \times [P\ (\text{MPa})] + B_2$					
A_2	3.8555	3.8950	4.5129	4.7493	1.7034
B_2	1410	1403.1	1375.8	1327.8	1489.5
r^2	0.9988	0.9983	0.9979	0.9990	0.9997
Isentropic bulk modulus (MPa) = $A_3 \times [P\ (\text{MPa})] + B_3$					
A_3	11.316	11.299	12.329	12.430	6.3324
B_3	1747.5	1717.8	1595.1	1423.1	2211.5
r^2	0.9996	0.9994	0.9993	0.9994	0.9998

[a] *P*, pressure.

The values of the isentropic bulk modulus calculated from the density and speed of sound data are shown in Figure 5. The methyl esters have a higher isentropic bulk modulus than the ethyl esters and are about as far above No. 2 diesel fuel as the No. 2 diesel fuel is above No. 1 diesel fuel. The slopes of the lines appear to be approximately the same, but inspection of the linear regression coefficients in Table 3 indicates that the diesel fuels have larger slopes which indicates a greater effect of pressure.

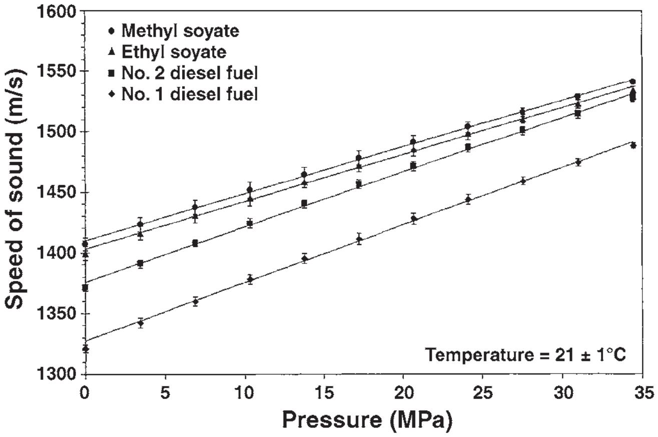

FIG. 4. Speed of sound of methyl soyate, ethyl soyate, and No. 1 and No. 2 diesel fuels.

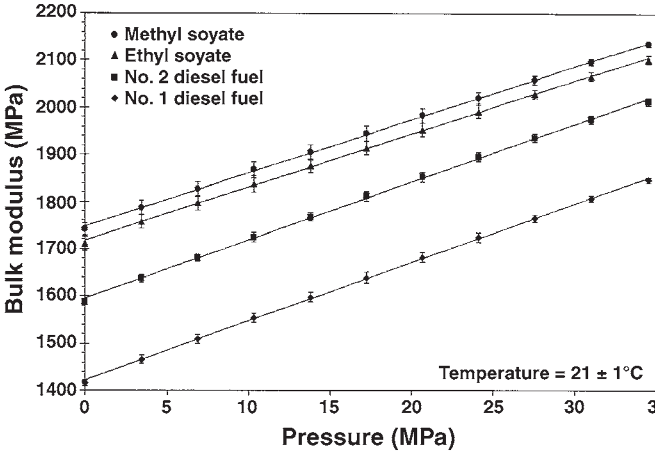

FIG. 5. Isentropic bulk modulus for methyl soyate, ethyl soyate, and No. 1 and No. 2 diesel fuels.

The isentropic bulk modulus of the methyl esters of soybean oil can be estimated at atmospheric pressure using density and speed of sound data published by Gouw and Vlugter (16,17). Their data indicate that the isentropic bulk modulus for methyl oleate is 1,732 MPa and 1,784 MPa for methyl linoleate. These two species compose about 80% of the methyl esters from soybean oil. These values are correspond well with the y-intercept value, 1747.5 MPa, given in Table 3 for the methyl esters.

Previous research has indicated that larger hydrocarbon molecules are less compressible than smaller molecules (14). Less compressible fuels can cause early injection timing, and this can produce higher combustion pressures and temperatures which in turn produce higher NOx emissions. The data presented here indicate that the isentropic bulk modulus and speed of sound for methyl and ethyl esters of fatty acids from soybean oil are higher than for diesel fuel. These changes are probably the reasons for the injection timing advance noted in Figure 1, and are at least partially responsible for the increase in exhaust NOx observed by many researchers.

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