Speed of Sound and Isentropic Bulk Modulus of Alkyl Monoesters at Elevated Temperatures and Pressures

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ABSTRACT: Biodiesel is a biodegradable, sulfur-free, oxygenated, and renewable alternative diesel fuel consisting of the alkyl monoesters of FA from vegetable oils and animal fats. Biodiesel can be used in existing diesel engines without significant modifications. However, differences in physical properties between biodiesel and petroleum-based diesel fuel may change the engine's fuel injection timing and combustion characteristics. These altered physical and chemical properties also may cause the exhaust emissions and performance to differ from the optimized settings chosen by the engine manufacturer. In particular, the density, speed of sound, and isentropic bulk modulus have a significant effect on the fuel injection system and combustion. The objective of this study was to measure these three properties for biodiesel (and the pure esters that are the constituents of biodiesel) at temperatures from 20 to 100°C and at pressures from atmospheric to 32.5 MPa. Ten different biodiesel fuels, 16 different pure FA esters, three hydrocarbons, and one diesel fuel were tested. The measured values of density, speed of sound, and isentropic bulk modulus are presented. Correlations between pressure and temperature are demonstrated. Speed of sound and isentropic bulk modulus tend to increase as the degree of unsaturation increases and as the chain length increases. However, density increased with shorter chain length and decreased with saturation.

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KEY WORDS: Alkyl esters, biodiesel, bulk modulus, compressibility, density, diesel engine, diesel fuel, fuel injection, physical properties, speed of sound.

Biodiesel, an alternative diesel fuel consisting of the alkyl monoesters of FA from vegetable oils and animal fats, can be used in existing diesel engines without modifications. However, differences in physical properties between biodiesel and petroleum-based diesel fuel may change the engine's injection timing and combustion delay, thus altering the combustion timing and combustion rate. The combustion timing changes can cause exhaust emissions and performance different from the optimized settings chosen by the engine manufacturer. The properties that will have the greatest effect on the fuel injection timing are the speed of sound, the isentropic bulk modulus, and the viscosity. Monyem *et al.* (1) showed that for fixed injection-pump timing, the injection pressure pulse for biodiesel was 1.5–2.0° advanced from the diesel fuel baseline. The injection timing advance was at least partially due to differences in the fuel properties, such as the bulk modulus and speed of sound. Additional work on the same engine showed that changes in the pump static timing associated with the injection of the greater fuel volume needed to compensate for biodiesel's lower energy content are also responsible for the injection timing advance. The higher viscosity, higher cetane number, and lower volatility of the biodiesel combine with the earlier injection timing to effect the start of combustion. Since emissions of nitrogen oxides (NO_x) generally increase with advanced timing, this effect may be partly responsible for the increase in NO_x observed with biodiesel (2–6).

The objective of the current project was to measure the density, speed of sound, and isentropic bulk modulus of biodiesel at temperatures from 20 to 100°C and at pressures from atmospheric to 32.5 MPa. These ranges should cover most of the commonly encountered start-of-injection conditions since most engines have nozzle opening pressures below 32.5 MPa. We measured the properties of biodiesel made from soybean oil and other feedstocks as well as the properties of pure ester constituents of biodiesel.

This paper presents the results of measurements of these properties for the 26 pure esters and ester blends and the four hydrocarbons listed in Table 1.

EQUIPMENT AND PROCEDURES

Samples of some of the compounds shown in Table 1 were provided by the Colorado Institute for Fuels and High-Altitude Engine Research at the Colorado School of Mines. In this research, speed of sound and density were measured in the 30 fuel samples listed in Table 1 from atmospheric pressure to 32.5 MPa and at temperatures of 20, 40, 60, 80, and 100°C. The isentropic bulk modulus was calculated at each pressure and temperature level using Equation 1 (7,8),

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

where β is the isentropic bulk modulus in Pa, c is the speed of sound in the sample in m/s, and ρ is the density in kg/m^3.

As shown in Table 1, the 30 fuel samples included 16 FA alkyl esters or simple mixtures of esters, 10 biodiesel fuels produced from vegetable oils or animal fats, three pure hydrocarbons, and a sample of emissions certification grade No. 2 diesel fuel. Information about the physical and chemical properties of the samples is given in Tables 1 and 2.

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TABLE 1
FA Composition (%) of Fuels Tested[a]

Ester	Lauric 12:0	Myristic 14:0	Palmitic 16:0	Palmitoleic 16:1	Margaric 17:0	Stearic 18:0	Oleic 18:1	Linoleic 18:2	Linolenic 18:3	Total glycerin (%)
Alkyl monoesters of FA										
1. Methyl butyrate (99+%)										
2. Methyl laurate	99.2	0	0	0	0	0	0.6	0.2	0	0.003
3. Methyl palmitate			99+							
4. Methyl stearate					99+					
5. Methyl oleate	0	3.0	6.5	4.1	1.5	1.9	64.5	9.1	9	0.022
6. Methyl linoleate	0	0	1.4	0	0	0.7	5.2	86.5	6.2	0.126
7. Methyl linolenate	0	0	7.4	0	0	3.7	24.8	2.9	61.2	0.089
8. 2:1 Methyl stearate/methyl linseed	0	0	38.6	0	0	44.1	4.8	2.4	10.1	0.024
9. 1:2 Methyl stearate/methyl linseed	0	0	20.8	0	0	28	15.2	7.6	27.8	0.062
10. Ethyl butyrate (99+%)										
11. Ethyl caprylate (99+%)										
12. Ethyl stearate	0	2.2	43.6	0	2.4	49.8	0.2	0.1	0	0.025
13. Ethyl linoleate	0	0	2.7	0	0	2.4	6.4	88.5	0	0.089
14. Ethyl linseed	0	2.5	7.6	0	3.3	2.8	22.3	11.2	50.3	0.041
15. Isopropyl palmitate			99+							
16. Isopropyl stearate						99+				
Alkyl esters of vegetable oils and animal fats (biodiesel)										
17. Oxidized methyl soy	0	0	15.2	0	0	5.3	57	22.5	0	0.012
18. Methyl hydrogenated soy	0	0	11.3	0	0	88.7	0	0	0	0.099
19. Methyl lard[b]	0.1	1.5	24.8	3.1	0.5	12.3	45.1	9.9	0.1	2.6
20. Methyl canola[b]	—[c]	—	3.9	0.2	—	1.9	64.1	18.7	9.2	
21. Methyl soy ester[b]	—	0.1	11.0	0.1	—	4.0	23.4	53.2	7.8	0.4
22. Methyl yellow grease										
23. Methyl tallow	0.1	3.3	25.5	3.4	1.5	21.6	38.7	2.2	0.6	3.1
24. Oxidized ethyl soy[b]	—	0.1	11.0	0.1	—	4.0	23.4	53.2	7.8	0.4
25. Ethyl hydrogenated soy	0	0	11.9	0	0	88.1	0	0	0	0.097
26. Ethyl soy	0	0	14	0	0	9	52.7	24.3	0	0.031
Hydrocarbons and diesel fuel										
27. *n*-Octadecane (99+% pure)										
28. *n* Hexadecane (99+% pure)										
29. *n*-Dodecane (99+% pure)										
30. Certified D2 diesel fuel (99+% pure)										

[a] Samples 1, 3, 4, 10, 11, 15, 16, 27–29 from Aldrich Chemical (Milwaukee, WI). Others from the Colorado Institue for Fuels and High-Altitude Engine Research (Colorado School of Mines, Golden, CO).

[b] Amounts reported for individual FA combine methyl and ethyl esters when both were present during measurement.

[c] Not found.

The pulse echo technique was used (8,10–15) to measure the speed of sound in the fuel samples. In this technique, an ultrasonic pulse is directed through the wall of a pressure vessel containing the sample. The first echo is reflected from the transition of the pressure vessel wall to the sample, and the second echo is produced from the sample interface on the other side of the sample chamber. The time difference between the first and second echoes is divided by two times the sample length to give the speed of sound in the sample.

A Panametrics Model 5072 PR general-purpose ultrasonic

TABLE 2
Distillation Results of Some Samples

Description[a]	Methyl soy ester	Methyl lard	Methyl canola	Methyl tallow
Distillation points (°C)				
IBP	323	304	316	324
10%	340	322	324	279
20%	343	324	331	336
50%	346	329	336	341
90%	354	337	341	352
EP%	356	354	355	361
Recovery (mL)	98.2	98.5	99	98.2
Residue (mL)	1.1	0.5	0.5	1.8
Loss (mL)	0.7	1.0	0.5	0.0

[a] ASTM D 86 (Ref. 9), which measures distillation recovery as a function of distillation, was used. Abbreviations: IBP, initial boiling point; EP, end point.

TABLE 3
Atmospheric Pressure Density Measurement Comparisons for Some of the Samples

Samples	Measured value (g/cm^3)	Literature value (g/cm^3)	Temperature (°C)	Reference
Water	0.9730	0.9716–0.9718	80	26,27
Dodecane	0.7482	0.7487–0.7491	20	28,29
Methyl laurate	0.8094	0.8073	100	29
Methyl palmitate	0.8075	0.8065	100	29
Methyl stearate	0.8213	0.8210	80	29
Methyl butyrate	0.8970	0.8980	20	29
Ethyl butyrate	0.8156	0.8147	80	29
Ethyl caprylate	0.8658	0.8672	20	29

TABLE 4
Maximum Error[a] in Water and Dodecane Measurement Comparisons at Higher Temperatures and Pressures

	Water		Dodecane	
Properties	% Error	Error point[b]	% Error	Error point
Density	–0.19	60°C, 34.4 MPa	0.24	60°C, 34.4 MPa
Speed of sound	0.19	80°C, 34.4 MPa	0.68	100°C, 0.1 MPa
Isentropic bulk modulus	0.19	80°C, 34.4 MPa	1.41	100°C, 0.1 MPa

[a] Calculated as percentage error = [(measurement result – literature value)/literature value]·100.
[b] Error point: pressure and temperature conditions at which maximum differences are found.

pulser/receiver and a Panametrics 10-MHz videoscan immersion transducer (Waltham, MA) were used. A pressure vessel with a piston and cylinder assembly for raising the pressure was fabricated, and the ultrasonic transducer was located at the bottom of the vessel. The pressure vessel and equipment have been described elsewhere (16–18). The ultrasonic transducer housing was connected to the pressure vessel, and both the housing the vessel were submerged in an oil bath. The temperature of the fuel sample in the vessel was not measured. However, the temperature of the oil bath was controlled by using an Omega CN 9000A (Chicago, IL) temperature controller and Fisher Scientific Isotemp Immersion Circulator Model 70 (Stamford, CT). Temperature was measured with a thermometer with ±0.5°C accuracy, and before each measurement 40 min was allowed for temperature equilibrium. This time was adequate to provide a stable measurement. The ultrasonic echo signals were captured with a Hewlett-Packard Model 54601A 100 MHz, four-channel digital oscilloscope (Colorado Springs, CO). The system pressure was measured using a Sensotec Model 2 Z/1108-04Z9 pressure transducer (Columbus, OH). To obtain elevated temperatures, the entire pressure vessel was submerged in a temperature-controlled bath.

Density measurements were made at atmospheric pressure and at elevated pressures. Densities at atmospheric pressure and at temperatures from 20 to 100°C were measured in 20°C temperature increments by using a specific gravity balance (Troemner Company, Philadelphia, PA). The specific gravity balance was modified so that a small constant-temperature bath could be used to control the sample temperature; for details see Reference 13. At each temperature, four consecutive measurements were taken, and then the entire temperature sequence was repeated. Therefore, at atmospheric pressure, eight measurements were obtained. The balance was calibrated with distilled water to 1.0000 at 15.5°C before each set of measurements.

At elevated pressures, density measurements were taken simultaneously with the speed of sound measurements by using a vernier to show the piston location in the cylinder to calculate the relative fuel volume under pressure. As the sample pressure was raised using the piston and cylinder, the piston position was used to calculate the volume change. Since the sample mass was constant, the volume change was used to determine the density change. This density change was added to the density measured during the first step to get the density at the elevated pressure. A correction was calculated for the expansion of the vessel at high pressure and high temperature, although this correction was no more than 0.06% of the cell volume for the range of temperatures and pressures in this study.

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. Thus, the pressure vessel was filled with the sample fluid two times, and each time two 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. Thus, a total of four data points were collected for each pressure and temperature level. Subsequent analysis showed no statistically significant difference between the measurements associated with different filling operations or with

TABLE 5
Correlation Constants from Equation 3[a] for Sample Densities[b] (g/cm^3)

Samples	$C_1 \times 10^7$	$C_2 \times 10^6$	$C_3 \times 10^4$	$C_4 \times 10^4$	$C_5 \times 10$	$SE_y \times 10^4$
Methyl esters of FA						
Methyl butyrate	−1.0711	6.4758	−11.068	6.3563	9.2018	8.0
Methyl laurate	7.0375	3.5311	−8.3264	5.1716	8.8633	6.7
Methyl palmitate	11.137	3.1087	−8.6821	4.8997	8.8374	6.4
Methyl stearate	0.24181	2.8652	−7.0651	4.9171	8.7813	5.4
Methyl oleate	−1.7442	2.8121	−6.7480	4.9471	8.9084	4.6
Methyl linoleate	−2.4107	2.7030	−6.6629	5.0739	9.0533	4.7
Methyl linolenate	0.91722	2.7982	−7.3107	4.8250	9.0582	4.3
2:1 Me stearate/Me linseed	5.7612	3.1389	−7.7178	4.7513	8.9267	4.5
2:1 Me linseed/Me stearate	5.5003	3.1407	−7.7590	4.6986	9.0297	5.3
Ethyl esters of FA						
Ethyl butyrate	−2.3582	6.3538	−10.349	6.3947	9.0030	7.3
Ethyl caprylate	−0.62125	4.0758	−8.3744	5.8994	8.8324	5.6
Ethyl stearate	6.0752	3.6002	−7.7954	4.8898	8.7641	6.7
Ethyl linoleate	0.49900	2.7530	−7.0449	5.1564	8.9772	6.8
Ethyl linseed	−1.1161	2.5849	−6.9431	5.0375	9.0685	5.1
Isopropyl esters of FA						
Isopropyl palmitate	−4.3583	3.1613	−6.2884	5.1645	8.6459	10.1
Isopropyl stearate	−1.5717	3.0535	−6.7468	5.1279	8.6642	4.9
Methyl biodiesel fuels						
Methyl soy ester	5.8985	2.9275	−7.7598	4.8517	8.9623	5.3
Methyl canola	2.8659	2.8153	−7.5505	4.9403	8.9576	4.9
Methyl tallow	6.8397	2.9019	−7.8136	5.0136	8.8721	4.7
Methyl lard	−1.4499	2.6850	−6.9914	4.9947	8.8888	4.3
Methyl yellow grease	0.49788	2.9201	−7.0235	4.9010	8.8837	4.6
Methyl oxidized soy	2.0264	2.8895	−7.3502	4.8075	9.0026	4.0
Methyl hydrogenated soy	−1.7182	2.4881	−6.6732	5.0880	8.7854	5.8
Ethyl biodiesel fuels						
Ethyl soy ester	−1.6990	2.9578	−6.9131	5.2530	8.8959	5.3
Ethyl oxidized soy	−1.9132	2.8622	−6.9397	4.9693	8.9555	4.5
Ethyl hydrogenated soy	−1.6629	2.9515	−6.6892	4.7997	8.7428	4.8
Hydrocarbons and diesel fuel						
n-Octadecane	2.2552	3.1164	−6.9982	4.8032	7.9525	4.5
n-Hexadecane	6.4165	2.7235	−7.5272	5.2803	7.9004	6.5
n-Dodecane	−3.4395	3.9310	−6.8834	5.3510	7.6278	5.6
Certified D-2	−2.6272	2.9186	−6.5999	5.3916	8.5422	6.2

[a]Density (g/cm^3) = $C_1T^2 + C_2TP + C_3T + C_4P + C_5$, where T is °C and P is MPa.
[b]SE_y, the standard error for the y estimate.

measurements taken while increasing or decreasing the pressure. Therefore, all four measurements were averaged and included in the confidence limit calculations. All measurements were taken from 20 to 100°C except for methyl palmitate, methyl stearate, the 2:1 mixture of methyl stearate and methyl linseed, methyl hydrogenated soy, ethyl hydrogenated soy, ethyl stearate, and *n*-octadecane, which were solid at 20°C. The lowest temperature at which measurements were taken for these esters was 40°C.

Validation of the measurement technique. The extensive amounts of very accurate data are available for the speed of sound in distilled water (19–26). These data were used as a reference to validate the speed of sound measurement technique. In this study, comparisons also were made with dodecane because it is much more compressible than distilled water. This means that the speed of sound and density show greater variability and sensitivity to temperature and pressure changes in dodecane than in water.

Reagent water was purchased from Aldrich (Milwaukee, WI) and was boiled and cooled before the density and speed of sound measurements. Dodecane with a purity of 99+ also was purchased from Aldrich.

The density measurements at atmospheric pressure were compared with literature values; representative values are provided in Table 3. The speed of sound and density measurements at higher temperatures and pressures were compared with the reference; maximal deviations are listed in Table 4. In the tables, the percentage error was calculated using Equation 2,

$$\text{percentage error} = \left(\frac{\text{measurement result} - \text{literature value}}{\text{literature value}}\right) \cdot 100 \quad [2]$$

In Table 4, a maximal error of 0.2% was observed for the density of both water at 80°C and dodecane at 100°C. The measured values for the speed of sound and isentropic bulk modulus are in very good agreement for water, but the deviations with dodecane are larger. This is due to the greater property changes with hydrocarbons and perhaps to the lower reliability of the published data for this compound.

TABLE 6
Correlation Constants from Equation 3[a] for Speed of Sound[b] (m/s)

Samples	$C_1 \times 10^3$	$C_2 \times 10^2$	C_3	C_4	$C_5 \times 10^{-3}$	SE_y
Methyl esters of FA						
Methyl butyrate	7.1090	2.6780	–4.7542	4.0046	1.3037	5.8
Methyl laurate	4.1639	1.6973	–3.9702	3.9322	1.4412	3.2
Methyl palmitate	5.1325	1.5287	–4.0771	3.9214	1.4790	3.3
Methyl stearate	4.0687	1.4657	–3.8059	3.8604	1.4806	2.8
Methyl oleate	4.2764	1.4364	–3.8749	3.8429	1.4916	2.8
Methyl linoleate	4.6079	1.4445	–3.8959	3.7565	1.4989	2.5
Methyl linolenate	4.0790	1.4554	–3.8576	3.6984	1.5021	2.5
2:1 Me stearate/Me linseed	6.1113	1.5489	–4.0767	3.7318	1.4946	3.4
2:1 Me linseed/Me stearate	4.5796	1.5551	–3.9340	3.6368	1.4998	2.5
Ethyl esters of FA						
Ethyl butyrate	4.2618	2.6945	–4.3512	4.1040	1.2858	4.0
Ethyl caprylate	4.1106	1.8532	–4.0327	4.2110	1.3645	3.5
Ethyl stearate	7.1445	1.4823	–4.1614	3.9704	1.4758	3.7
Ethyl linoleate	3.8879	1.4545	–3.8099	3.7642	1.4888	2.6
Ethyl linseed	3.7469	1.3822	–3.7770	3.7771	1.4939	2.8
Isopropyl esters of FA						
Isopropyl palmitate	3.6438	1.5213	–3.7285	4.0840	1.4377	3.1
Isopropyl stearate	4.9160	1.5096	–3.8565	4.0376	1.4541	4.3
Methyl biodiesel fuels						
Methyl soy ester	3.7242	1.5141	–3.8329	3.7500	1.4945	2.9
Methyl canola	3.8388	1.4662	–3.8009	3.7877	1.4934	2.5
Methyl tallow	7.7473	1.5551	–4.3789	3.8101	1.5000	3.7
Methyl lard	4.3140	1.4075	–3.8634	3.8487	1.4862	2.6
Methyl yellow grease	4.6346	1.4528	–3.8750	3.8458	1.4889	2.6
Methyl oxidized soy	4.1917	1.5081	–3.8504	3.7072	1.4961	2.8
Methyl hydrogenated soy	4.0553	0.95901	–3.8224	4.1518	1.4852	4.1
Ethyl biodiesel fuels						
Ethyl soy ester	4.7384	1.5190	–3.8445	4.0151	1.4811	3.0
Ethyl oxidized soy	3.8501	1.4751	–3.7798	3.8172	1.4855	2.6
Ethyl hydrogenated soy	4.7127	1.5836	–3.9429	3.8237	1.4811	3.0
Hydrocarbons and diesel fuel						
n-Octadecane	5.5890	1.6046	–4.0992	4.2365	1.4655	3.8
n-Hexadecane	2.9168	1.5219	–3.6847	4.4486	1.4310	3.6
n-Dodecane	3.9613	2.1205	–4.0218	4.5267	1.3817	3.6
Certified D2	4.7612	1.6718	–4.0413	4.2395	1.4580	3.2

[a] Speed of sound (m/s) = $C_1T^2 + C_2TP + C_3T + C_4P + C_5$, where T is °C and P is MPa.
[b] SE_y, the SE for the y estimate.

RESULTS AND DISCUSSION

The variations in density, speed of sound, and isentropic bulk modulus of the fuel samples were approximately linear with pressure and temperature. However, a polynomial that was second order in temperature and first order in pressure, as shown in Equation 3, provided the best fit to the data:

$$y = C_1T^2 + C_2TP + C_3T + C_4P + C_5 \qquad [3]$$

where y is the density, speed of sound, or isentropic bulk modulus of the sample, T is the temperature in °C, P is the gauge pressure in MPa, and C_i, where i = 1–5 are the correlation constants given in Tables 5–7. The SE for y calculated by an Excel spreadsheet is also shown in the tables. Higher-order polynomials were also tested, but the accuracy obtained with more coefficients did not justify the added complexity.

The following discussion focuses on identifying common trends for the esters with different levels of saturation, chain length, or alcohol type. In the figures, the points represent the measured values, and the lines represent predicted values from Equation 3.

Figure 1A shows the effect of temperature at atmospheric pressure on the isentropic bulk modulus for four fuels with different levels of saturation: methyl stearate, methyl oleate, methyl linoleate, and methyl linolenate. The isentropic bulk modulus tends to increase as the degree of unsaturation increases. Methyl linolenate, because its purity was not high and it included substantial amounts of more saturated compounds (see Table 1), showed values very similar to those of methyl linoleate. All of the compounds appear to have approximately the same property variation with temperature as indicated by similar slopes of the lines on these figures. Figure 1B shows the variations in the isentropic bulk modulus as the pressure increases for the four levels of saturation; the temperature was held at 40°C. A complete comparison could not be made at 20°C because methyl stearate is a solid at this temperature. Again, the slope of the isentropic bulk modulus as the pressure increased was about the same for

TABLE 7
Correlation Constants from Equation 3[a] for Isentropic Bulk Modulus[b] (MPa)

Samples	$C_1 \times 10^2$	$C_2 \times 10^3$	$C_3 \times 10^{-1}$	$C_4 \times 10^{-1}$	$C_5 \times 10^{-3}$	SE_y
Methyl esters of FA						
Methyl butyrate	3.1720	1.1600	−1.2074	1.2130	1.5382	9.9
Methyl laurate	2.4982	1.4211	−1.1278	1.1999	1.8282	5.8
Methyl palmitate	2.6737	−1.8906	−1.1644	1.2190	1.9109	6.2
Methyl stearate	2.1157	0.41592	−1.0713	1.1880	1.9057	5.3
Methyl oleate	2.3539	−0.67354	−1.1303	1.2123	1.9709	4.9
Methyl linoleate	2.4433	0.53428	−1.1557	1.2119	2.0231	4.5
Methyl linolenate	2.4167	1.0464	−1.1630	1.1928	2.0328	5.5
2:1 Me stearate/Me linseed	2.7359	2.1624	−1.1670	1.1839	1.9716	6.2
2:1 Me linseed/Me stearate	2.5911	3.7365	−1.1792	1.1679	2.0185	4.9
Ethyl esters of FA						
Ethyl butyrate	2.4760	1.2607	−1.0865	1.2073	1.4666	5.5
Ethyl caprylate	2.3636	−1.6746	−1.0709	1.2283	1.6314	4.9
Ethyl stearate	2.8333	0.24623	−1.1432	1.2113	1.8845	6.5
Ethyl linoleate	2.2948	0.25081	−1.1245	1.2008	1.9786	4.9
Ethyl linseed	2.3020	−1.2131	−1.1359	1.2158	2.0143	6.3
Isopropyl esters of FA						
Isopropyl palmitate	1.9149	−2.0898	−0.99983	1.2219	1.7707	5.0
Isopropyl stearate	2.2380	−1.2664	−1.0467	1.2175	1.8141	8.1
Methyl biodiesel fuels						
Methyl soy ester	2.4172	1.3673	−1.1493	1.1936	1.9909	5.6
Methyl canola	2.3572	0.19670	−1.1350	1.2048	1.9865	4.4
Methyl tallow	3.3752	1.1433	−1.2644	1.1983	1.9826	8.0
Methyl lard	2.3895	−1.7181	−1.1285	1.2073	1.9532	5.0
Methyl yellow grease	2.4528	0.11858	−1.1296	1.2060	1.9582	4.7
Methyl oxidized soy	2.4307	2.1386	−1.1498	1.1850	2.0039	5.3
Methyl hydrogenated soy	2.2256	−13.593	−1.0906	1.2784	1.9237	8.0
Ethyl biodiesel fuels						
Ethyl soy ester	2.4131	0.4.0191	−1.1150	1.2590	1.9404	5.4
Ethyl oxidized soy	2.2477	0.48846	−1.1126	1.2082	1.9656	4.5
Ethyl hydrogenated soy	2.2947	0.98222	−1.0975	1.1866	1.8995	5.0
Hydrocarbons and diesel fuel						
n-Octadecane	2.3332	−2.1502	−1.0272	1.1857	1.6875	5.8
n-Hexadecane	1.9595	−4.5985	−0.95101	1.2088	1.6091	4.8
n-Dodecane	1.9104	0.093166	−0.92151	1.1737	1.4414	4.1
Certified D-2	2.3791	−1.0217	−1.0944	1.2626	1.8043	4.8

[a] Isentropic bulk modulus (MPa) = $C_1T^2 + C_2TP + C_3T + C_4P + C_5$, where T is °C and P is MPa.
[b] SE_y, the standard error for the y estimate.

the esters with different saturation levels. Figures 1A and 1B indicate that the increase in isentropic bulk modulus is fairly uniform with the addition of each double bond. The change in isentropic bulk modulus from stearate to oleate is about the same as from oleate to linoleate.

The property data for methyl butyrate, methyl laurate, methyl palmitate, and methyl stearate in Figures 2–4 show the effect of FA chain length. These data demonstrate that the speed of sound and isentropic bulk modulus increase as the chain length increases, which supports the observation made for hydrocarbons in Reference 9. However, density showed characteristics that were different from the speed of sound and the isentropic bulk modulus. The density increased with shorter chain length, and the slope with temperature changed with chain length. Figure 4 shows the effect of pressure for different chain-length esters at 40°C. Clearly, properties make an approximately linear change with pressure.

Soy methyl ester, soy ethyl ester, emissions certification grade No. 2 diesel fuel (Cert D2), and dodecane are compared with each other in Figure 5. The soy methyl ester is approximately 0.5% more dense than ethyl soy ester and 5% more dense than the Cert D2. The speed of sound in the soy methyl ester is about 0.7% faster than in the soy ethyl ester and 2.8% faster than in the Cert D2. The calculated isentropic bulk modulus of the methyl soy ester was 1% higher than that of the ethyl soy ester and 10% higher than the Cert D2. The higher bulk modulus means that biodiesel will experience a more rapid pressure rise than petroleum-based diesel fuel as the injection pump displaces a fixed volume. This will result in earlier injection for biodiesel and may be the cause of the higher NO_x emission with biodiesel.

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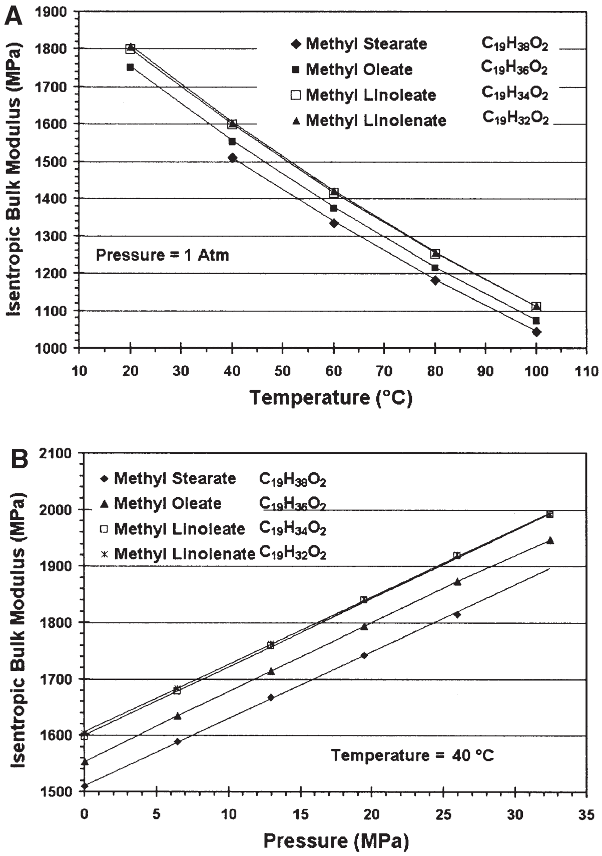

FIG. 1. Effect of degree of saturation on isentropic bulk modulus (A) at 20–100°C and atmospheric pressure and (B) at 40°C and 0–32 MPa.

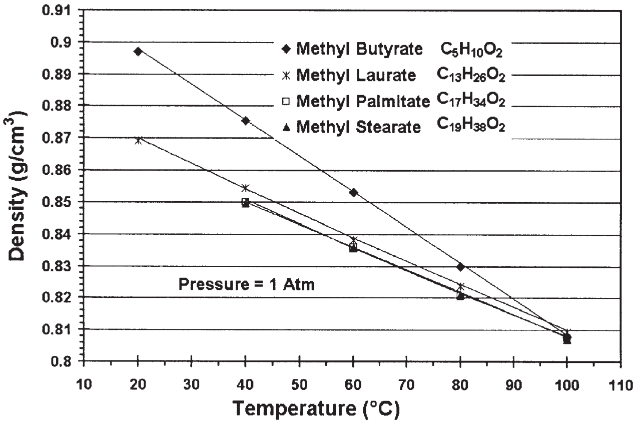

FIG. 2. Effect of chain length and temperature on density at atmospheric pressure.

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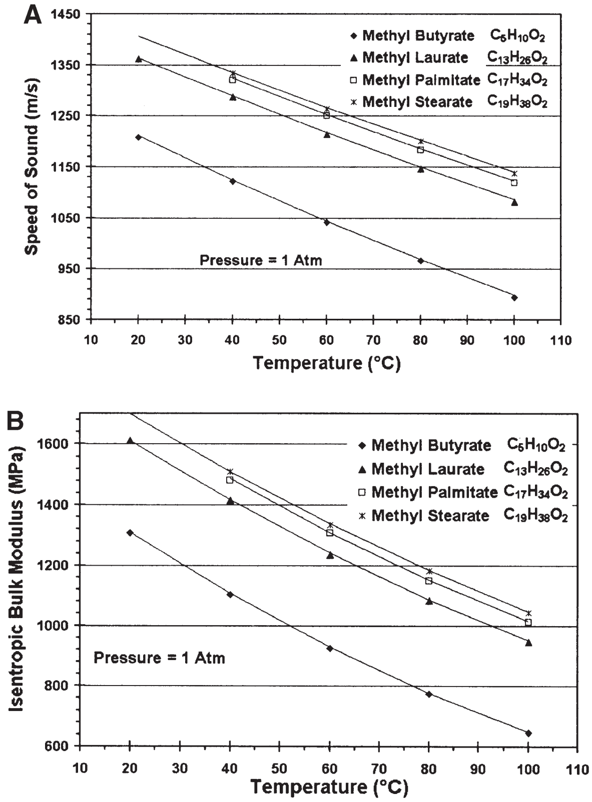

FIG. 3. Temperature-dependent chain-length effect at atmospheric pressure on (A) speed of sound and (B) isentropic bulk modulus.

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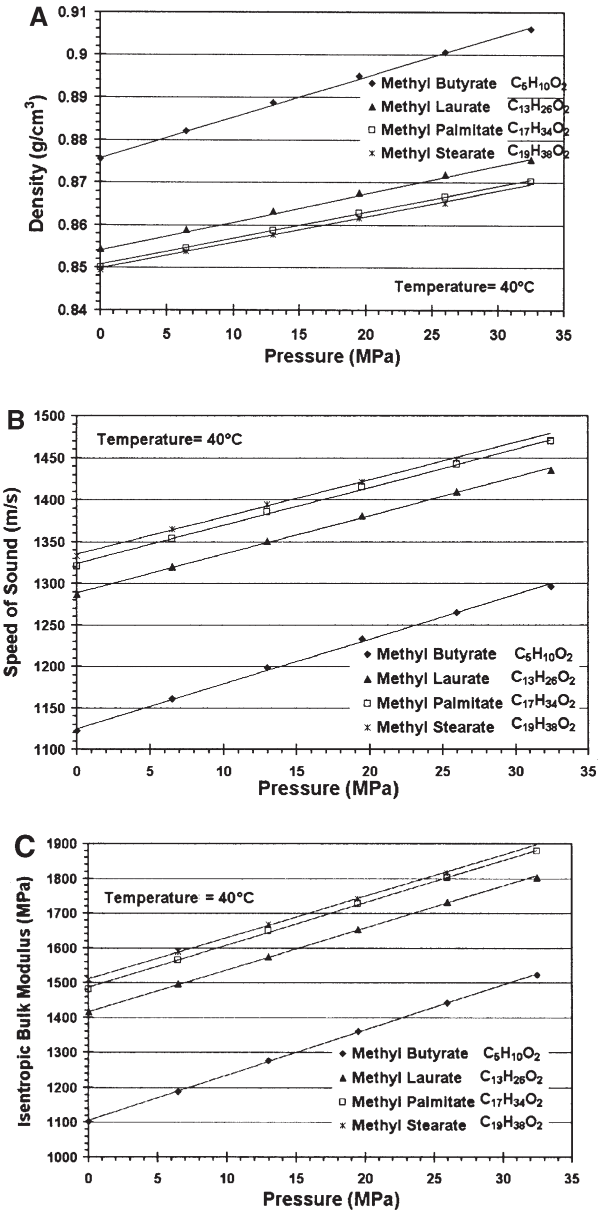

FIG. 4. Chain-length effect at elevated pressures and 40°C on (A) density, (B) speed of sound, and (C) isentropic bulk modulus.

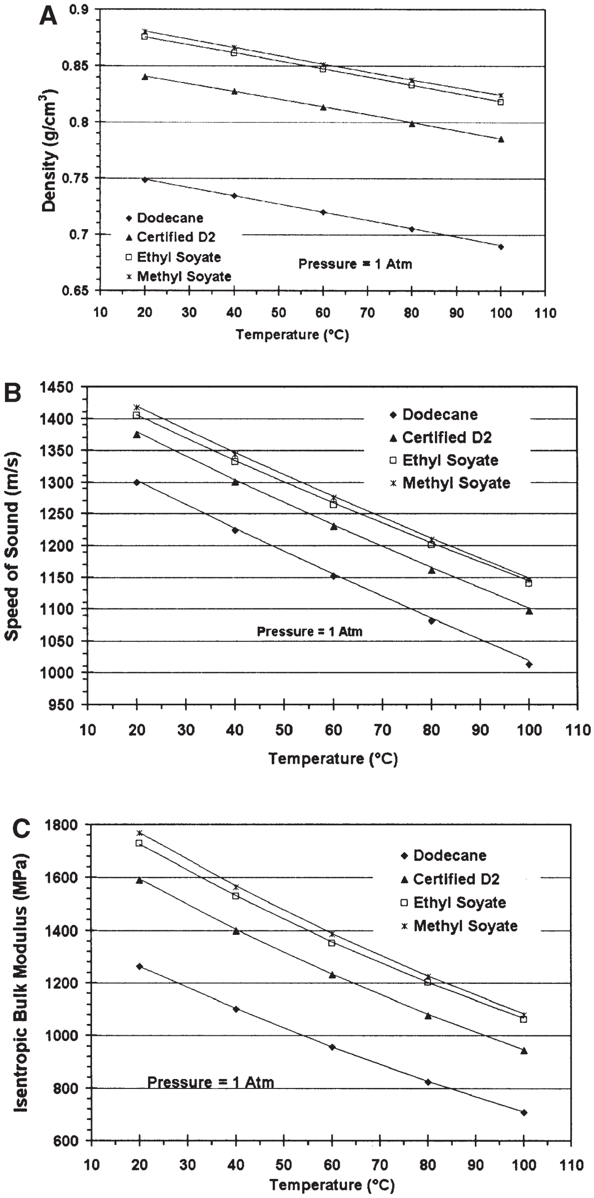

FIG. 5. Comparison of methyl, ethyl, certified D2 diesel fuel, and dodecane at atmospheric pressure with respect to (A) density, (B) speed of sound, and (C) isentropic bulk modulus.

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