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Research Article

The Study of Sound Speed as a Function of Pressure at Different Temperatures in Biofuel Component Liquids

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Abstract

In the present study, an approximation is applied to study the sound speed in liquids as a function of pressure at different temperatures. The relation obtained is applied in the case of biofuel component liquids. The calculated results for each liquid were found to be in good agreement with the experimental results throughout the range of pressure and temperature. The maximum percentage error and average percentage error are not more than 5.2 and 1.9, respectively, in the entire range of pressure and temperature for all liquids. Furthermore, the internal pressure and nonlinear Bayer's parameters are also computed as a function of temperature at one atmosphere from sound speed for the first time in biofuel component liquids.

Keywords: *Sound speed; pressure; temperature; biofuel component liquids; internal pressure; nonlinear Bayer's parameter.*

1. Introduction

The exhaustive use of fossil fuels to sustain and develop the economy not only puts pressure on fossil fuel reservoirs but also abuses our environment due to the ejection of greenhouse gases (CO_2, NO_x, etc.). As a result, a large community of scientists and engineers are engaging themselves and coming up with alternatives to fossil fuels to reduce their dependency and minimize greenhouse gas emissions [1] – [2]. Different sources of renewable energy have been presented so far, such as biofuel, wind energy, solar photovoltaic solar thermal, and geothermal energy. Biofuels have attracted attention as an alternative, at least in the transport sector [3]. Transesterification reactions occur when biofuels are derived from vegetable oils or animal fats, where fats/oils are blended with alcohol (methanol or ethanol) to form fatty acid alkyl esters. Broadly, alcohol alongside biodiesel is the most suitable type of biofuel [4]. However, conventional diesel fuel can be blended in optimized proportions with biodiesel to decrease toxic gas emissions in existing diesel engines or be used without any adulteration as renewable energy for diesel engines. However, the major challenge with biofuels is that they are derived from various sources, and consequently, fatty acids have diff erent chain lengths and may differ in the degree of undersaturation. The chain lengths of fatty acids derived from different sources (palm, soybean, rapeseed, and sunflower) have a chain of 16 and 18 carbons, whereas chains of 20 and 22 carbon atoms may not be ruled out (rape species and animal fats). However, a chain of 10 to 14 carbons was also observed, particularly in the fatty acids derived from palm kernel and coconut oils [5] – [7]. The varying nature of chain length and degree of unsaturation affect the thermo-physical properties of biofuels obtained from different sources and, consequently, influence the engine's overall performance. In addition, optimization of the fraction of biodiesel and diesel fusion requires accurate familiarity of thermal-physical physiognomies in biodiesel based on pressure and temperature. The density, bulk modulus, thermal expansion coefficient, internal pressure, and nonlinear Bayer's parameters play an essential role in designing the engine and injection process [8] – [10].

The thermo-physical properties of biofuels can be estimated from the properties of biofuel components using mixing rules if these properties of the components are available. The study of thermos-physical properties as function pressure and temperature of liquids from sound speed measurement is comparatively more accurate as the measurement of sound speed as a function of pressure and temperature is more precise than the equation of state.

Therefore, this study aims to develop a model that can describe the sound speed as a function of pressure at different temperatures from which other thermophysical properties can be derived. To the best of our knowledge, the internal pressure [11] – [14] and nonlinear Bayer's parameter, which are strongly correlated with the structural properties of biofuels, are rarely studied in the case of biofuels. Generally, the value of (B/A) lies in the range of 5–13. A lower value was observed in water, while the highest value was observed for fluorocarbons [13] – [15]. Therefore, both parameters are also computed as function temperatures in biofuel component liquids, where the experimental data are available in a wide range of pressures and temperatures. Methyl caprate, ethyl caprate, methyl oleate, methyl linoleate, methyl myristate, ethyl myristate, and methyl palmitate were considered for this study. The experimental data for these liquids were obtained from [4], [7], [16].

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2. Methodology

The investigation of the sound speed u(p, T_R) as a function of pressure (p) at the reference temperature (T_R) in the biofuel component liquids, the ratio of the second pressure derivative of sound speed to the first pressure derivative of sound speed, is independent of pressure is used and given by Eq. (1)

$$\frac{\left(\partial^2 u/\partial p^2\right)_{T_R}}{\left(\partial u/\partial p\right)_{T_R}} = -z \tag{1}$$

This approximation was successfully applied to describe the sound speed as a function of pressure and temperature in liquid metals [17]. Moreover, this approximation also explains the anomalous behavior of sound speed in water [18]. Integrating the Eq. (1) successively in the pressure limit of p_0 to p yields the following equations [17]:

$$u'(p, T_R) = u'(p_0, T_R)\exp(-z(p - p_0)) \tag{2}$$

$$u(p, T_R) = u(p_0, T_R) + \left(u'(p_0, T_R)/z\right)[1 - \exp(-z(p - p_0))] \tag{3}$$

where, $u'(p_0, T_r)$ is the first pressure derivative of sound speed, $u(p, T_r)$ at pressure, p_0 and temperature, T_R.

Eq. (3) reveals that the sound speed increases as a function of pressure and converges to $u(p_0, T_R) + \left(u'(p_0, T_R)/z\right)$ as the pressure approaches infinity.

The following relation between $u'(p_0, T)$ and $u(p_0, T)$ is proposed to include the temperature effect.

$$u'(p_0, T) = a\exp\{-bu(p_0, T)\} \tag{4}$$

The pressure in the liquids is the sum of the external and internal pressures [13]. Since Eq. (4) is applied at a constant external pressure, and it may be written as

$$\left(\frac{du(p,T)}{dp_i}\right)_{p_0} = a\exp\{-bu(p_0, T)\} \tag{5}$$

The integration of Eq. (5) under the limit of temperature T_r to T gives

$$p_i(T) - p_i(T_R) = \frac{1}{ab}\left[e^{bu(p_0,T_R)} - e^{bu(p_0,T)}\right] \tag{6}$$

Eq. (6) suggests that

$$p_i(T) = \frac{e^{bu(p_0,T)}}{ab} \tag{7}$$

The thermal pressure coefficient, ξ given by Eq. (8) is computed by linear fitting between p_i and T, which is used to introduce the temperature effect into Eq. (3).

$$p_i = \xi T + C \tag{8}$$

To study the sound speed as a function of pressure at different temperatures, Eq. (2) and Eq. (3) can be written as [15]:

$$u'(p,T) = u'(p_0,T_R)exp[-z(p - p_0) + \xi(T - T_R)] \tag{9}$$

$$u(p, T) = u(p_0, T_R) + \left(u'(p_0, T_R)/z\right)[1 - \exp\{-z(p - p_0) + +\xi(T - T_R)\}] \tag{10}$$

The sound speed as a function of pressure at different temperatures can be computed using Eq. (10) indicates that $u(p_0, T_r)$, $u'(p_0, T_r)$, z, and ξ are known as the liquids of interest.

Moreover, the internal pressure as a function of temperature at atmospheric pressure can also be computed from its thermodynamic definition [11], as given by Eq. (11)

$$p_i(T) = \frac{\alpha}{k_T}T \tag{11}$$

where α and k_T are the isobaric thermal expansion coefficient and isothermal compressibility, respectively.

This study is further extended to determine nonlinear Bayer parameters as a function of pressure and temperature. The nonlinear Bayer parameter is well understood to understand the molecular dynamics of the liquid along with the distortion of a finite amplitude of the wave due to nonlinearity associated with the medium. Moreover, the estimation of the Bayer parameter may be considered as a corresponding parameter to understand biofuels.

The Bayer Parameter can be expressed as [15]

$$\frac{B}{A} = 2\rho u\left(\frac{\partial u}{\partial p}\right)_s = 2\rho u\left(\frac{\partial u}{\partial p}\right)_T + \frac{2uT\alpha}{C_p}\left(\frac{\partial u}{\partial p}\right)_p \tag{12}$$

$$\frac{B}{A} = \left(\frac{B}{A}\right)' + \left(\frac{B}{A}\right)''$$

The first pressure derivative of the sound speed as a function of the pressure and temperature is given by Eq. (9), while the first temperature derivative of the sound speed as a function of pressure and temperature can be determined by differentiating Eq. (10) for temperature and is given by Eq. (13).

$$\left(\partial u(P,T)/\partial T\right)_p = \xi u'(p_0, T_R)\exp[-z(p - p_0) + +\xi(T - T_R)] \tag{13}$$

3. Results

The proposed Eq. (3) was used to study the sound speed as a function of pressure at different temperatures for all liquids. As a first step, the adjustable parameters $u(p_0, T_R)$, $u'(p_0, T_R)$ and z in Eq. (3) were determined using a non-linear fitting toolbox in MATLAB. The values of these parameters are reported in Table-1, along with R^2 for all liquids. The value of R^2 indicate the applicability of Eq. (3) to describe the sound speed as a function of the pressure and temperature for all liquids of concerned.

In the second step, nonlinear fitting is used to determine the values of constants a and b in Eq. (4) at ambient pressure, p_0. The values of $u'(p_0, T)$ and $u(p_0, T)$ are listed in Table-1. The values of a and b obtained are reported in Table-2, along with R^2.

The values of R^2 give us the confidence to use it to calculate the internal pressure. However, fitting in all Biofuel components is relatively poor, particularly in ethyl myristate, but Eq. (7), we can calculate the internal pressure directly from the sound speed. The internal pressure calculated from Eq. (7) are plotted in Figure 1 at different temperatures for all Biofuel components.

In the third step, the value of the thermal pressure coefficient ξ in Eq. (8) is computed by a linear fitting between the internal pressure and temperature. Figure1 shows that there is an almost linear relationship between the internal pressure and temperature. The values of the adjustable parameters ξ and C are reported in Table-2 along with the values of R^2. It should be noted that the second-order polynomial gives a better fit between the internal pressure and temperature.

Table 1. The fitting parameters of Eq. (3) along with R^2 at different temperatures in all biofuel component liquids of study.

Liquid	T(K)	$u(p_0, T_R)$ ($m\ s^{-1}$))	$u'(p_0, T_R)$ ($m\ s^{-1}\ MPa^{-1}$)	$Z(x10^{-3})$ (MPa^{-1})	R^2	Pressure Range (MPa)	Reference
Methyl Caprate	283.15	1365	4.505	4.472	0.9999	0.1013-140	[7]
	303.15	1295	4.678	4.109	0.9998	0.1013-210	
	323.15	1222	4.980	4.396	0.9997		
	343.15	1152	5.330	4.723	0.9996		
	363.15	1093	5.462	4.711	0.9997		
	383.15	1030	5.826	5.029	0.9997		
	403.15	969	6.128	5.258	0.9996		
Ethyl Caprate	283.15	1357	4.403	3.769	0.9999	0.1013-210	
	303.15	1281	4.731	4.184	0.9998		
	323.15	1212	4.989	4.278	0.9997		
	343.15	1142	5.374	4.707	0.9996		
	363.15	1077	5.722	5.057	0.9995		
	383.15	1044	6.060	5.358	0.9994		
	403.15	953.45	6.447	5.737	0.9991		
Methyl Oleate	283.15	1447	4.089	3.478	0.9999	0.1013-200	[16]
	303.15	1375	4.406	3.869	0.9999		
	323.15	1307	4.684	4.135	0.9998		
	343.15	1242	4.951	4.372	0.9998		
	363.15	1178	5.270	4.716	0.9998		
	383.15	1119	4.473	4.784	0.9996		
	393.15	1090	5.623	4.936	0.9996		
Methyl Linoleate	283.15	1457	4.214	3.988	0.9999	0.1013-150	
	303.15	1388	4.323	3.701	0.9998	0.1013-210	
	323.15	1318	4.619	4.033	0.9998		
	343.15	1252	4.891	4.278	0.9997		
	363.15	1188	5.185	4.566	0.9997		
	383.15	1127	5.441	4.760	0.9997		
	393.15	1098	5.564	4.841	0.9997		
Ethyl Myristate	293.15	1360	5.034	7.805	1	0.1 – 50	[4]
	303.15	1322	5.072	6.191	1	0.1-100	
	323.15	1253	5.264	5.659	1		
	343.15	1186	5.658	6.193	0.9999		
	363.15	1123	6.010	6.565	0.9999		
	383.15	1059	6.495	7.339	0.9999		
	403.15	999.7	6.901	7.718	0.9998		
Methyl Myristate	303.15	1336	4.793	5.5556	1	0.1 – 70	
	323.15	1265	5.280	5.9440	1	0.1 – 80	
	343.15	1196	5.674	6.4670	1		
	363.15	1132	6.0660	7.1190	1		
	383.15	1068	6.559	7.8690	1		
	403.15	1038	6.767	8.141	0.9999		
Methyl Palmitate	313.15	1317	5.041	6.357	1	0.1 – 40	
	323.15	1284	5.202	6.201	1	0.1-50	
	343.15	1216	5.661	7.604	1		
	363.15	1151	6.022	7.768	0.9999		
	383.15	1088	6.400	6.942	0.9999		
	403.15	1057	6.608	7.390	0.9999		

Table 2. Fitted parameters of Eq. (4) and Eq. (8) along with values of R^2.

Liquid		Equation (4) coefficients			Equation (8) coefficients		
	T_R	A	b ($x\ 10^{-04}$)	R^2	ξ	C	R^2
Methyl Caprate	283.15	13.14	7.916	0.9944	-0.6325	459.3	0.9931
Ethyl Caprate	283.15	16.39	9.722	0.9934	-0.6134	404.4	0.9867
Methyl Oleate	283.15	14.66	8.762	0.9972	-0.6681	462.6	0.9939
Methyl Linoleate	283.15	13.68	8.196	0.9941	-0.6791	484.1	0.9951
Ethyl Myristate	293.15	17.32	9.317	0.9812	-0.5695	384.6	0.9941
Methyl Myristate	303.15	22.03	1.136	0.9985	-0.5782	355.7	0.9947
Methyl Palmitate	313.15	19.85	1.039	0.9981	-0.5640	366.2	0.9975

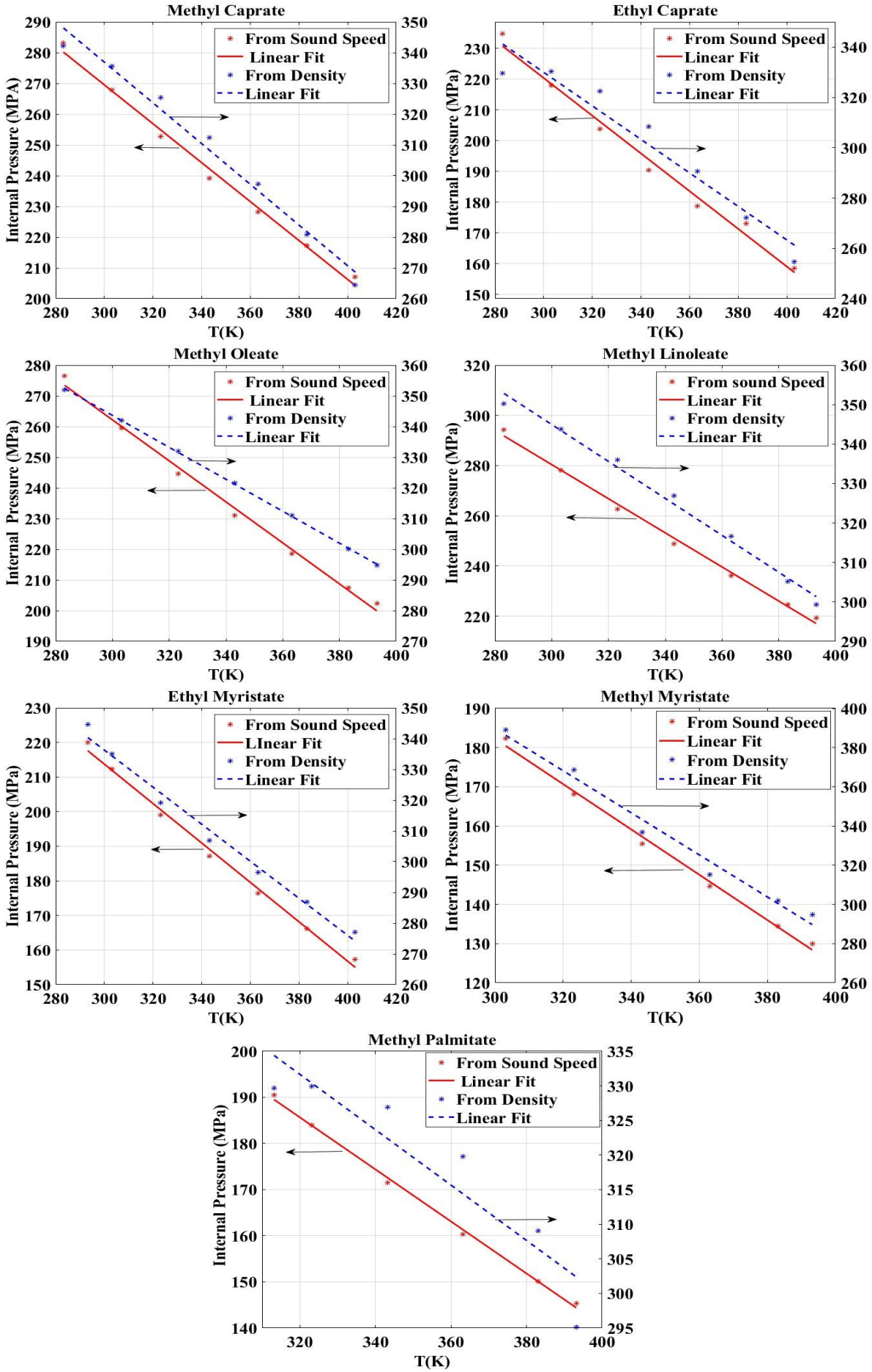

Figure 1. The variation of internal pressure as a function of temperature at atmospheric pressure as calculated from Eq, (7) and Eq. (11) for all biofuel component liquids of interest.

In the final step, Eq. (10) was applied successfully in all liquids to study the sound speed as a function of pressure at different temperatures. Moreover, the internal pressure is also calculated by calculating the thermal pressure coefficient, $\xi = \frac{\partial p_{th}}{\partial T} = \frac{\alpha}{k_T}$, from the density data given in reference papers and compared with the internal pressure calculated from the sound speed in Figure 1. Moreover, Eq. (12) is used to compute the nonlinear Bayer's parameter [20] as a function of temperature for all biofuel components. The computed values of the nonlinear Bayer's parameters are listed in Table-3. The variations in density ρ, α and C_p as a function of pressure-temperature were taken from the source papers [4], [7], [16].

4. Discussion

The computed speed as a function of pressure at different temperatures was compared with the experimental data for all liquids, and the maximum percentage error (MPE) is plotted in Figure 2.

Figure 2 shows that the MPE is not more than 5.2, over the entire range of pressure and temperature for all biofuel components of the study.

This error may be due to multiple reasons, such as the slight deviation of Eq. (8) from the linear fit as depicted in R^2 value in Table-2 or experimental error at high pressure and high-temperature regions or the approximation given by Eq. (1) may become temperature-dependent at high temperatures. However, the second-order polynomial fits the internal pressure vs. temperature curve more accurately, and the values of R^2 were found to be very close to unity in all cases. The thermal effect through a second-order polynomial is also included in Eq. (3) by adding $p_{th}= (T - T_A)[a(T + T_A)+b]$ in the pressure term. In that case, the MPE is not more than 4.9, in the entire pressure and temperature range. Moreover, the average errors in both approaches were found to be 1.9% and 1.0%, respectively. Because the error obtained from second-order polynomial fitting is not far better than linear fitting, a linear approximation was used for this study.

The internal pressure is also computed as a function of the temperature for each liquid from Eq. (7) and plotted in Figure 1, and the internal pressure computed from Eq. (11). The ratio of the isobaric thermal expansion coefficient and isothermal compressibility required in Eq. (11) are computed from the density measurements [4,7,16]. Figure 1 shows that the internal pressure decreases as the temperature increases and possesses a negative thermal pressure coefficient, which is consistent with the results reported for ethyl caprate [12] and methyl linoleate [18]. To the best of our knowledge, the study of internal pressure as a function of temperature in biofuels has hardly been investigated. However, the internal pressure, computed from Eq. (7) is smaller than that computed using Eq. (11), but the values of ξ are found to close from both equations, except in methyl myristate, where the difference is quite significant. However, the difference between the internal pressures calculated from Eq. (7) and Eq. (11) does not introduce much error on the inclusion of the temperature effect in Eq. (3) as the internal pressure from Eq. (7), is negatively biased.

At atmospheric pressure, internal pressure varies from 0.2 to 0.8 GPa for non-associated and associated liquids over the temperature range below their boiling points [14]. Based on the discussion given in [14], liquids are characterized into two classes based on the temperature dependence of the internal pressure. Liquids with a positive thermal pressure coefficient include n-alkanes, carbon tetrachloride, and benzene with comparatively weak intermolecular interactions. On the other hand, liquids with a negative coefficient of thermal expansion coefficient include the spatial networks of H-bonds such as water, ethylene glycol, 1,2-, and 1,3-propanediol. In the present study, the observed internal pressure was near the lower limit for the non-associated liquids.

Moreover, to the best of our knowledge, the calculations of nonlinear Bayer's parameters as a function of temperature for all biofuel component liquids. Table-3 shows the fragile dependence of $\left(\frac{B}{A}\right)$ on temperature. However, the values of $\left(\frac{B}{A}\right)''$ is negative but small compared to the $\left(\frac{B}{A}\right)'$ increase with an increase in temperature for all liquids of concern. The $\left(\frac{B}{A}\right)$ values obtained here are consistent with the results reported for various classes of molecular green liquids at room temperature and atmospheric pressure [19].

Table 3. Variation of Bayer's parameters as a function temperature in biofuel component liquids of study.

Liquids		283.15K	303.15K	323.15K	343.15K	363.15K	383.15K	403.15K
Methyl Carpet	$(B/A)'$	10.82	10.76	10.64	10.46	10.20	9.87	9.46
	$(B/A)''$	-1.01	-1.11	-1.20	-1.29	-1.36	-1.41	-1.44
	B/A	9.81	9.65	9.44	9.17	8.85	8.46	8.01
Ethyl Carpet	$(B/A)'$	10.41	10.27	10.09	9.85	9.56	9.22	8.83
	$(B/A)''$	-1.04	-1.18	-1.30	-1.39	-1.46	-1.50	-1.51
	B/A	9.37	9.10	8.79	8.46	8.10	7.72	7.32
Methyl Oleate	$(B/A)'$	10.42	10.33	10.19	10.01	9.78	9.50	9.34
	$(B/A)''$	-0.93	-0.99	-1.05	-1.11	-1.17	-1.22	-1.25
	B/A	9.49	9.34	9.14	8.90	8.62	8.28	8.09
Methyl Linoleate	$(B/A)'$	10.63	10.44	10.22	9.99	9.76	9.53	9.41
	$(B/A)''$	-1.01	-1.08	-1.15	-1.22	-1.30	-1.37	-1.41
	B/A	9.62	9.36	9.07	8.77	8.47	8.16	8.00
Ethyl Myristate	$(B/A)'$	11.61	11.95	12.23	12.42	12.49	12.41	12.15
	$(B/A)''$	-0.65	-0.70	-0.77	-0.85	-0.93	-1.03	-1.12
	B/A	10.97	11.25	11.46	11.57	11.55	11.38	11.03
Methyl Myristate	$(B/A)'$	10.97	11.01	11.02	10.99	10.89	10.70	10.40
	$(B/A)''$	-1.13	-1.09	-1.09	-1.12	-1.20	-1.33	-1.48
	B/A	9.83	9.92	9.94	9.86	9.68	9.37	8.92
Methyl Palmitate	$(B/A)'$	11.02	11.21	11.34	11.40	11.38	11.27	11.05
	$(B/A)''$	-0.70	-0.8057	-0.9052	-0.9981	-1.081	-1.1503	-1.2019
	B/A	10.32	10.4044	10.4363	10.4047	10.3019	10.1189	9.84501

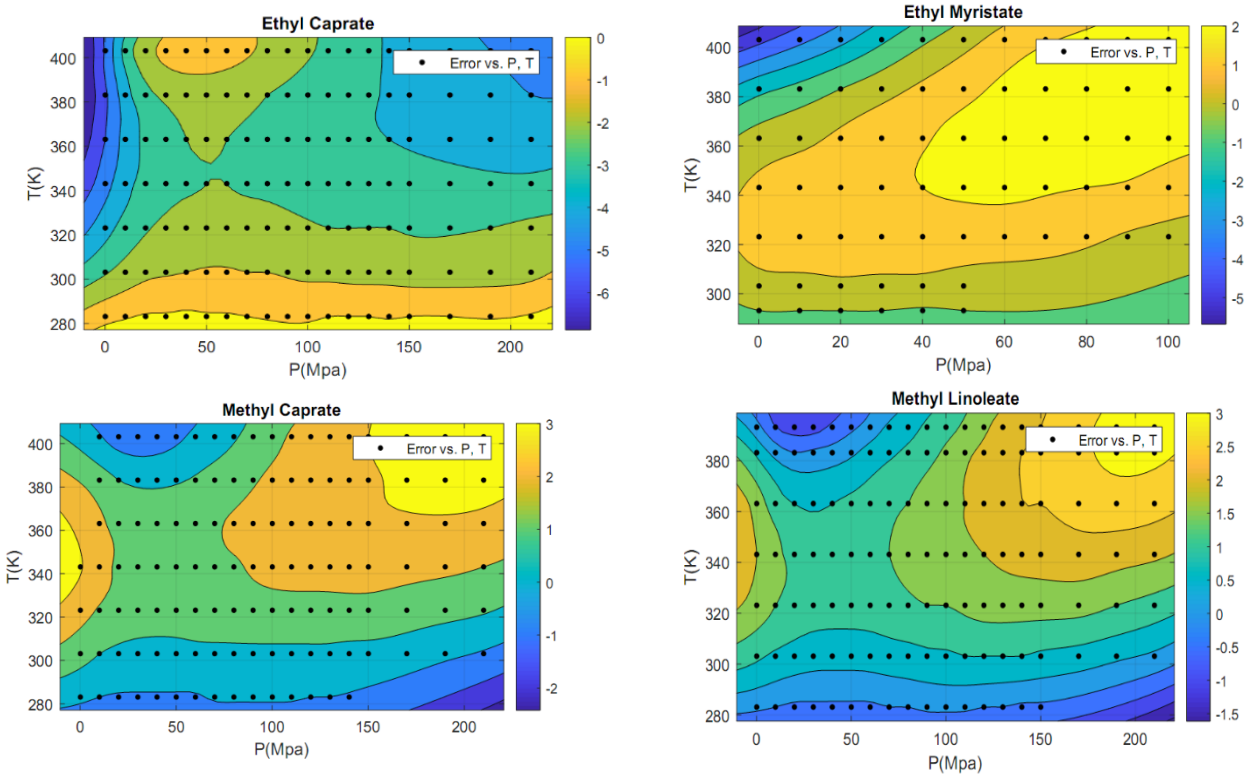

Figure 2. Error Vs pressure and temperature contours for all biofuel component liquids of study. Error color code bar for each liquid is included alongside of the figure.

5. Conclusion

In conclusion, we can say that Eq. (10) is successful in describing the sound speed as a function of pressure at different temperatures for biofuel component liquids. Moreover, for the first time, the internal pressure as a function of temperature was computed using two different approaches and used to make Eq. (3) temperature dependence. However, the calculations of internal pressure from sound speed measurement show lower values than the calculations from the thermodynamic definition of internal pressure in all liquids of interest, but the coefficient of thermal pressure is found to be close for both approaches. In addition, the nonlinear Bayer's parameter is also computed as a function of temperature in all liquids for the very first time, to the best of our knowledge. The calculated values of B/A were found to be in reasonable agreement with the values reported by other workers for other liquids.

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Nomenclature

u, Sound speed (m s^{-1})
p, Pressure (MPa)
p_0, Atmospheric pressure (MPa)
T, Temperature (K)
T_R, Reference Temperature (K)
u', First pressure derivative of sound speed (m s^{-1} MPa^{-1})
pi, Internal pressure (MPa)
p_{th}, Thermal pressure (MPa)
ξ, Thermal pressure coefficient (MPa K^{-1})
α, Isobaric thermal expension coefficient(K^{-1})
k_T, Isothermal compressibility (MPa^{-1})

Cp, Heat capacity at constant pressure (Joule mole^{-1} K^{-1})
B/A, Bayer's parameter
ρ, Density (kg m^{-3})

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