Temperature and pressure dependence of density of a shale oil and derived thermodynamic properties

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Abstract

The temperature and pressure dependence of density was measured experimentally from 293 to 473 K and 0.1 to 12 MPa for a shale oil produced from Kukersite oil shale in Estonia. The shale oil sample was a fuel oil fraction of a whole oil produced in a commercial plant that uses solid heat carrier retorting technology. The fraction had a boiling range of approximately 460 to 780 K and contained significant quantities of polar phenolic compounds (hydroxyl group content of 5.3 wt%). The effect of these compounds on the properties of the oil was investigated by removing most of the phenolic compounds via extraction to create the second sample (dephenolated sample with hydroxyl group content of 1.1 wt%). The dephenolation resulted in a shale oil with a composition being more similar to that of other shale oils from well explored deposits. Based on a review of the literature, this is the first experimental data on the pressure dependence of density for this shale oil, and shale oils generally. Thermal expansion coefficients, isothermal compressibilities and speeds of sound were calculated from the experimental data. Empirical relationships describing the temperature dependence of the heat capacities between 288 and 423 K at atmospheric pressure are also presented here.

Keywords: density, thermal expansion coefficient, isothermal compressibility, speed of sound, shale oil, Kukersite oil shale, heat capacity

1. Introduction

Information about thermodynamic properties is important for designing and modeling chemical processes. Because materials can be subject to a range of temperatures and pressures, it is important to know how the properties of a substance change with temperature and pressure. Data for thermodynamic properties, including density, heat capacity or the speed of sound, can provide this information, and this data can then be used for determining parameters for equations of state.^{1,2}

Although data on the pressure dependence of density gives valuable information for developing processes to upgrade shale oil to motor fuels, to our knowledge no data exists in the public literature for the density of Kukersite shale oil, or shale oils generally, at high temperatures and pressures.³ For petroleum fuels densities and other properties can often be estimated by using equations of state and empirical correlations, but prediction methods based on conventional fuels may not perform accurately for shale oils because of their different composition.^{3–7} For this reason, prior experimental verification is necessary.

Oil shale is a source of energy and liquid fuel that attracts attention from time to time due to the large reserves available around the world. However, oil shale has never been a significant global source of energy due to the relatively high cost of obtaining energy from it and its large environmental footprint.⁸ Nevertheless, it has been estimated that $4.7 \cdot 10^{12}$ barrels of oil could be produced from the known reserves,⁹ and oil shale has been an important local resource in several countries.¹⁰ For example, shale oil has been produced

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in Estonia for about a century,¹¹ and shale oil is produced on an industrial scale in other countries as well (e.g. Brazil and China).⁹

In contrast to conventional petroleum production, shale oil is produced from solid oil shale via pyrolysis (the industrial process is called retorting).^{10,12} The composition of shale oil can vary depending on the composition of the raw oil shale and the retorting method (i.e. pyrolysis method) used for producing the oil.^{13,14} Shale oils often contain large quantities of alkyl aromatic and heteroatomic compounds, making them different from conventional petroleum.^{10,15} Their composition also makes them an interesting option for developing and testing thermodynamic correlations for liquid fuels. For example, shale oil produced from Kukersite oil shale (Estonia) contains a large number of oxygenated compounds, the majority of which have an alkylphenolic nature.^{5,6,16} This high oxygen content gives Kukersite shale oil a composition that is somewhere between conventional petroleum and biofuels, and studying it can help bridge the gap between different fuels to create a unified thermodynamic model. Because the differences in composition affect the properties of the oil, it has been found that conventional prediction methods used for petroleum fuels can give erroneous predictions for Kukersite shale oil.^{17–19} This makes experimental data all the more important for these types of fuels. This article presents, to our knowledge, the first experimental data that examines the pressure dependence of density for Kukersite shale oil.

2. Experimental

2.1. Sample preparation

The shale oil sample was obtained from Eesti Energia's Narva Oil Plant (Auvere, Estonia). This plant uses solid heat carrier retorting technology (also known as the Galoter process),^{20–22} and uses Kukersite oil shale (from the Baltic oil shale basin in Estonia) as the raw material. The plant separates the crude shale oil into three wide fractions (gasoline, fuel oil and heavy oil fractions), and a sample of fuel oil was used for these measurements. Kukersite shale oil contains significant amounts of polar phenolic compounds, often amounting to about half of the whole shale oil.¹⁶ To investigate the effect these polar compounds have, extraction was used to remove the phenolic compounds from a portion of the shale fuel oil to create a second sample. By removing the phenolic compounds the composition of the fuel also becomes more similar to that of other shale oils that do not contain as much oxygen.¹⁵ The procedure involves extraction with 10% NaOH, washing with distilled water and drying the oil.^{5,16,23} The hydrogen solubilities of these same samples were also measured as part of a separate set of experiments.²³

2.2. Sample characteristics

Characteristic properties of the fuel oil and its dephenolated subfraction are given in Table 1. Due to the removal of phenolic compounds using 10% NaOH, the dephenolated oil sample had a somewhat lower specific gravity and refractive index, but a higher number average molecular weight than the initial oil. The specific gravity values correspond to API gravities of 7.2 and 14.2 for the fuel oil and dephenolated fuel oil, respectively.

Table 1. Properties of the shale oil samples used in this study and their expanded uncertainties at the 95% level.

Characteristic	Fuel oil	Dephenolated oil
Specific gravity (20°C/4°C)	1.0170 ± 0.0003	0.9682 ± 0.0003
Refractive index at 293 K	1.557 ± 0.0021	1.541 ± 0.0021
Molecular weight (g mol ⁻¹)	240 ± 14	250 ± 14

Hydrogen content (wt%)	9.4 ± 0.28	10.7 ± 0.28
Carbon content (wt%)	80.9 ± 1.3	82.5 ± 1.3
H/C ratio	1.38 ± 0.033	1.55 ± 0.033
Hydroxyl group content (wt%)	5.3 ± 0.72	1.1 ± 0.72

The infrared spectra of the samples, which gives information about the functional groups they contain, can be found at <https://osf.io/dhkew/>. Based on these spectra the hydroxyl group, hydrogen and carbon contents were calculated via support vector regression models developed in our laboratory²⁴ and these values are also given in Table 1. These values indicate that the dephenolated fuel oil had a higher atomic H/C carbon ratio and a significantly lower hydroxyl group content than the initial fuel oil. In this study, only the carbon and hydrogen contents were determined. The remaining 9.8% and 6.8% for the fuel oil and dephenolated fuel oil, respectively, was mostly oxygen with some sulfur and nitrogen.^{15,16} The sulfur and nitrogen contents are known to be relatively small, less than 1.5%.¹⁵

The vaporization curves of the oil samples, which approximate the boiling point distributions of the samples, were evaluated using a thermogravimetric analyzer.²⁵ These curves indicated that the boiling range of both samples was approximately 460 to 770 K. For both samples the majority boils above 473 K at atmospheric pressure, which is the highest temperature at which densities were measured at elevated pressures. Therefore, the measured ranges do not extend down to where saturated liquid densities occur.

2.3. Experimental methods

2.3.1. Density at atmospheric pressure

Densities were measured at atmospheric pressure from 293 to 353 K using a DMA 5000M density meter (Anton Paar GmbH, Graz, Austria). This was done because the high pressure density meter had difficulty reaching atmospheric pressure and required the sample to be degassed. The standard uncertainty of the measured data was 0.15 kg m⁻³ (expanded uncertainty of 0.3 kg m⁻³ at the 95% level). This is a relative expanded uncertainty of about 0.03%. The manufacturer states the repeatability of the temperature data as being 0.001 K.

2.3.2. Density at high pressure

Density measurements at high pressure were performed using a DMA HPM density measurement cell (Anton Paar GmbH, Graz, Austria) in the range of 293 to 473 K and 0.15 to 12 MPa. The density meter was calibrated with nitrogen and pure water. Reference data for nitrogen and pure water were taken from reference equations of state,^{26,27} which are implemented in CoolProp's²⁸ Excel add-in. The accuracy of CoolProp's implementation was checked by manually comparing the densities at multiple temperatures and pressures with the NIST thermophysical properties calculator,²⁹ which also implements the same equations of state. All values checked were the same. Based on the calibration the standard uncertainty of the device was estimated to be 0.047 kg m⁻³ (expanded uncertainty of 0.091 kg m⁻³ at the 95% level). The pressure sensor used for measuring the density in the density measurement cell was calibrated against a Beamex MC2-PE calibrator with an EXT600 external pressure module, which had been calibrated by Beamex Oy Ab. Based on this calibration the standard uncertainty of the pressure data is 0.0031 MPa (expanded uncertainty of 0.0063 MPa at the 95% level). For the measured temperature the manufacturer only states that its accuracy is better than 0.1 K.

The samples were degassed before being fed into the density meter. For the shale fuel oil the weight was measured before and after degassing, and 0.6 g was lost during degassing (or 1.1% of the sample by mass). The effect of this loss can be estimated by comparing

the density values at 293 K measured at atmospheric pressure (without degassing) and in the DMA HPM. Using Equation 6, the density at 0.1 MPa and 293.2 K was calculated to be 1018.0 kg m⁻³ (experimental data at 0.152 MPa gives the same value). Thus, the difference due to degassing can be estimated to be an increase of 1 kg m⁻³.

The viscosity of a sample can also affect the density measurements made using the oscillating tube method,³⁰ so a viscosity correction was applied to the measured data. Although the viscosity correction is small (no more than 0.07% of the density value), it was still taken into account to achieve a better accuracy. For the purposes of this study, the viscosity correction factor was defined as the relative deviation of the actual density from that measured by the density meter (see Equation 1).

$$f = \frac{(\rho - \rho_{non})}{\rho_{non}} \quad (1)$$

In Equation 1 f is the viscosity correction factor, ρ is the “true” density with the viscosity correction applied and ρ_{non} is the non-corrected density given by the density meter.

The viscosity correction was calculated based on information from Stabinger³⁰ and 232 experimental data points for other oil shale fractions that had been measured at atmospheric pressure with a density meter that included an automatic viscosity correction (DMA 5000M, Anton Paar GmbH, Graz, Austria). First, the viscosity correction factor was calculated for the experimental data points. This was then combined with experimental viscosity data for these other oil shale fractions to determine how the viscosity correction factor varied with sample viscosity. Based on this information it was found that when the viscosity is greater than 500 mPa·s then a constant correction factor of -0.0007 can be used. For lower viscosities a simple power equation was used (Equation 2), which was fit to the experimental data.

$$f = -2.4979 \cdot 10^{-5} v^{0.61241} \quad (2)$$

In Equation 2 v is the viscosity of the sample (mPa·s) at the given temperature and pressure. The viscosities of the samples were estimated based on earlier measurements made for other shale fuel oil and dephenolated fuel oil samples. Viscosity correction factors were then calculated and used to adjust the experimental density data measured in this study.

The process of correcting for the viscosity of the sample introduces a small amount of uncertainty to the density data. The largest viscosity correction was 0.72 kg m⁻³ (the smallest was 0.018 kg m⁻³). Given that the viscosity correction factor reaches a constant upper value at high viscosities, the added uncertainty is certainly less than 0.72 kg m⁻³. A more reasonable estimate, based on the form of the viscosity correction equation and the expected uncertainty of the estimated viscosity values, is ± 0.4 kg m⁻³. That is, it can be expected that most of the density values are within ± 0.4 kg m⁻³ of the “true” density value, and this can be taken as the expanded uncertainty of the density data presented here.

2.3.3. Heat capacity measurements

Heat capacity temperature dependences were determined between 288 and 423 K using a micro reaction calorimeter (Thermal Hazard Technology, Bletchley, UK). The instrument was calibrated using heptane (purity >99%) and Al₂O₃ (Mettler-Toledo thermal analysis standard). The accuracy of the measurements was assessed by measuring naphthalene (purity >99%). Reference data for all three of these compounds were taken from Sabbah et al.³¹. Based on the measurements with naphthalene, the standard uncertainty was estimated to be 0.015 J g⁻¹ K⁻¹ (expanded uncertainty of 0.032 J g⁻¹ K⁻¹ at the 95% level). This is a relative expanded uncertainty of about 2%.

2.3.4. Measurement of characteristic properties

An Abbemat HT refractometer (Anton Paar GmbH, Graz, Austria) was used to measure the refractive indexes of the samples at 293 K, and these measurements had a standard uncertainty of 0.0011 (expanded uncertainty of 0.0021 at the 95% level). This equates to a relative expanded uncertainty of about 0.1%.

Vapor pressure osmometry (Knauer K-7000, Wissenschaftliche Gerätebau Dr. Ing. Herbert KNAUER GmbH, Germany) was used to measure the number average molecular weights of the samples. The standard uncertainty was 7 g mol⁻¹ (expanded uncertainty of 14 g mol⁻¹ at the 95% level), which is a relative expanded uncertainty of about 6%.

An Interspec 301-X portable mid-infrared spectrometer (Interspectrum OÜ, Tõravere, Estonia) was used to measure the infrared spectra of the samples. Based on these spectra the hydroxyl group, hydrogen and carbon content were calculated via models that had been created earlier (creation of the models was described in our earlier publications^{5,24,32}). These models were created using support vector regression. The uncertainties of these predicted values were estimated based on the residuals of the models. The standard uncertainties were 0.35, 0.13 and 0.57 wt% for hydroxyl group, hydrogen and carbon content, respectively. The expanded uncertainties at the 95% level were 0.72, 0.28 and 1.3 wt% (relative expanded uncertainties of 12, 3 and 2%). The atomic hydrogen-carbon ratio was also calculated from this data (standard uncertainty of 0.016, expanded uncertainty of 0.033 at the 95% level).

2.4. Calculation of thermodynamic properties

The isothermal expansion coefficient, bulk modulus of compressibility and speed of sound can all be calculated from density data at different temperatures and pressures using basic thermodynamic definitions and relationships. It is important to have data that allows these derived properties to be reliably estimated because they indicate that equations of state, or other models, based on the data can be used for extrapolation.

The thermal expansion coefficient shows how a material expands with changes in temperature, and is defined as shown in Equation 3³³

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \quad (3)$$

where α is the volumetric thermal expansion coefficient, ρ is density, V is volume, T is temperature and P is pressure. Changes in volume that occur with changes in pressure are often characterized using the isothermal compressibility (κ), which is defined by Equation 4.³⁴

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T \quad (4)$$

The speed of sound (a) can then be calculated from these properties and the constant pressure heat capacity (C_P) via Equation 5.^{35,36}

$$a = \left(\frac{\partial P}{\partial \rho} \right)_S = \sqrt{\frac{C_P}{\rho \kappa C_P - \alpha^2 T}} \quad (5)$$

Here S signifies entropy, and C_P , ρ , α and κ are at the same temperature and pressure for which the speed of sound is being calculated. Equation 5 and the relationships used in deriving it have been presented in many textbooks.^{35–39} These equations have also been used before by other researchers for calculating the speed of sound or the bulk modulus from density data and vice versa.⁴⁰

The experimental density data were fit with a polynomial equation (Equation 6) to describe both the temperature and pressure dependence of the density, and then this equation was used to calculate the necessary partial derivatives. To calculate the heat capacity at the temperatures at which the density data had been measured a linear equation was fit to the experimental heat capacity data (Equations 7 and 8).

2.5. Uncertainty analysis

The uncertainty values for the calculated thermodynamic properties were estimated using a Monte Carlo method (see ISO/IEC Guide 98-3⁴¹). Two variables were varied when determining the uncertainties: density and heat capacity. To describe the uncertainty of the density measurements a Gaussian distribution was used and the standard deviation was specified to be 0.2 kg m^{-3} , based on the estimated uncertainty of the measurements and the viscosity correction (see Section 2.3.2). For the uncertainty of the heat capacity a Gaussian distribution was also assumed, and the standard deviation was set to be $0.057 \text{ J g}^{-1} \text{ K}^{-1}$. This value is slightly higher than the standard measurement uncertainty (see Section 2.3.3), and was chosen to account for the fact that the heat capacity data was extrapolated to higher temperatures (up to 473 K) and that the pressure dependence of the heat capacity was not taken into account. The magnitude of this additional uncertainty was based on values for pure compounds obtained from reference equations of state using CoolProp's Excel add-in.²⁸ For all of the 9 compounds checked the difference between the heat capacities at 0.1 and 12 MPa was less than $0.035 \text{ J g}^{-1} \text{ K}^{-1}$. The pressure dependence of heat capacity is also related to the second derivative of volume with respect to temperature,⁴² and the change in C_p with pressure was also estimated from the density data using this relationship. This calculation gave a value that was at least an order of magnitude smaller than the measurement uncertainty. The conservative estimate of $0.035 \text{ J g}^{-1} \text{ K}^{-1}$ was used in further uncertainty calculations. To check the effect of extrapolation to higher temperatures the heat capacity at a higher temperature was calculated using a linear fit to values that were at least 50 K lower. This was done with o-xylene, n-undecane and methyl oleate and the difference was always less than $0.042 \text{ J g}^{-1} \text{ K}^{-1}$. These two uncertainties were then combined with the measurement uncertainty ($0.015 \text{ J g}^{-1} \text{ K}^{-1}$), which gave the value of $0.057 \text{ J g}^{-1} \text{ K}^{-1}$ used in the uncertainty calculations.

These distributions were then sampled (sample size of 2000) and each sample set was used to calculate thermal expansion coefficients, isothermal compressibilities and speeds of sound. With each sample set a separate regression was performed to find the constants to use with Equation 6. This was done to ensure that uncertainty associated with the regression was also taken into account. Using this Monte Carlo method a distribution was obtained for each property at each temperature and pressure. The standard deviation of each distribution was taken to be the standard uncertainty, and the lower and upper confidence limits at the 95% level were calculated as 2.5 and 97.5% of the cumulative distribution, respectively.

3. Results and Discussion

3.1. Temperature and pressure dependence of density

The experimental density data is presented in Table 2 and Table 3, and has also been graphically presented in Figure 1. The densities measured at atmospheric pressure are also included in these tables, but it should be noted that there is a small difference in the values (about 1 kg m^{-3}) due to the degassing performed before high pressure measurements.

Figure 1. The experimental density data for the shale oil samples.

Table 2. Densities (ρ), volumetric thermal expansion coefficients (α), isothermal compressibilities (κ), and speeds of sound (a) of the shale fuel oil sample along with expanded uncertainties at the 95% level (u).^a

T	P	ρ	$\rho_{\text{calc}} - \rho$	α	$u(\alpha)$	κ	$u(\kappa)$	a	$u(a)$
K	MPa	kg m ⁻³	kg m ⁻³	K ⁻¹	K ⁻¹	MPa ⁻¹	MPa ⁻¹	m s ⁻¹	m s ⁻¹
293.15	0.1	1017.0							
293.15	0.152	1017.9	0.0	$7.36 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-6}$	$5.1 \cdot 10^{-4}$	$\pm 8.1 \cdot 10^{-5}$	1520	± 79
293.15	1.020	1018.3	0.1	$7.33 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-6}$	$5.1 \cdot 10^{-4}$	$\pm 6.9 \cdot 10^{-5}$	1520	± 130
293.15	1.984	1018.9	0.0	$7.29 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-6}$	$5.0 \cdot 10^{-4}$	$\pm 5.7 \cdot 10^{-5}$	1530	± 70
293.15	3.989	1019.9	0.0	$7.23 \cdot 10^{-4}$	$\pm 3.6 \cdot 10^{-6}$	$4.9 \cdot 10^{-4}$	$\pm 3.6 \cdot 10^{-5}$	1550	± 160
293.16	3.990	1019.9	0.1	$7.23 \cdot 10^{-4}$	$\pm 3.6 \cdot 10^{-6}$	$4.9 \cdot 10^{-4}$	$\pm 3.6 \cdot 10^{-5}$	1550	± 150
293.15	3.992	1019.9	0.0	$7.23 \cdot 10^{-4}$	$\pm 3.6 \cdot 10^{-6}$	$4.9 \cdot 10^{-4}$	$\pm 3.6 \cdot 10^{-5}$	1550	± 100
293.15	6.984	1021.4	0.0	$7.13 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-6}$	$4.7 \cdot 10^{-4}$	$\pm 3.8 \cdot 10^{-5}$	1570	± 69
293.15	9.929	1022.9	0.0	$7.03 \cdot 10^{-4}$	$\pm 4.0 \cdot 10^{-6}$	$4.6 \cdot 10^{-4}$	$\pm 7.4 \cdot 10^{-5}$	1600	± 68
298.15	1.022	1014.7	0.0	$7.34 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-6}$	$5.2 \cdot 10^{-4}$	$\pm 6.9 \cdot 10^{-5}$	1500	± 54
298.15	2.051	1015.2	0.1	$7.31 \cdot 10^{-4}$	$\pm 3.4 \cdot 10^{-6}$	$5.2 \cdot 10^{-4}$	$\pm 5.6 \cdot 10^{-5}$	1510	± 97
298.15	5.019	1016.8	-0.1	$7.21 \cdot 10^{-4}$	$\pm 3.4 \cdot 10^{-6}$	$5.0 \cdot 10^{-4}$	$\pm 3.0 \cdot 10^{-5}$	1530	± 150
298.15	7.452	1018.1	0.0	$7.13 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-6}$	$4.9 \cdot 10^{-4}$	$\pm 4.3 \cdot 10^{-5}$	1550	± 120
298.15	9.962	1019.3	-0.1	$7.05 \cdot 10^{-4}$	$\pm 3.8 \cdot 10^{-6}$	$4.7 \cdot 10^{-4}$	$\pm 7.4 \cdot 10^{-5}$	1570	± 83
313.15	0.1	1002.6							
333.15	0.1	988.0							
333.15	1.996	989.5	-0.1	$7.44 \cdot 10^{-4}$	$\pm 2.3 \cdot 10^{-6}$	$6.4 \cdot 10^{-4}$	$\pm 5.4 \cdot 10^{-5}$	1360	± 70
333.15	3.970	990.7	-0.1	$7.37 \cdot 10^{-4}$	$\pm 2.2 \cdot 10^{-6}$	$6.3 \cdot 10^{-4}$	$\pm 3.1 \cdot 10^{-5}$	1370	± 40
333.15	5.992	991.9	0.0	$7.30 \cdot 10^{-4}$	$\pm 2.2 \cdot 10^{-6}$	$6.2 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-5}$	1390	± 110
333.15	7.965	993.1	0.0	$7.23 \cdot 10^{-4}$	$\pm 2.4 \cdot 10^{-6}$	$6.0 \cdot 10^{-4}$	$\pm 4.6 \cdot 10^{-5}$	1400	± 64
333.15	9.931	994.2	-0.1	$7.16 \cdot 10^{-4}$	$\pm 2.7 \cdot 10^{-6}$	$5.9 \cdot 10^{-4}$	$\pm 7.2 \cdot 10^{-5}$	1410	± 35
353.15	0.1	973.3							
393.15	0.516	944.4	-0.1	$7.72 \cdot 10^{-4}$	$\pm 1.9 \cdot 10^{-6}$	$8.7 \cdot 10^{-4}$	$\pm 7.8 \cdot 10^{-5}$	1180	± 46
393.15	1.993	945.6	0.1	$7.67 \cdot 10^{-4}$	$\pm 1.6 \cdot 10^{-6}$	$8.6 \cdot 10^{-4}$	$\pm 5.5 \cdot 10^{-5}$	1190	± 41

393.15	4.006	947.2	0.0	$7.59 \cdot 10^{-4}$	$\pm 1.3 \cdot 10^{-6}$	$8.5 \cdot 10^{-4}$	$\pm 2.9 \cdot 10^{-5}$	1200	± 25
393.15	5.958	948.7	-0.1	$7.51 \cdot 10^{-4}$	$\pm 1.3 \cdot 10^{-6}$	$8.4 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-5}$	1200	± 62
393.15	7.956	950.2	0.0	$7.44 \cdot 10^{-4}$	$\pm 1.6 \cdot 10^{-6}$	$8.2 \cdot 10^{-4}$	$\pm 4.6 \cdot 10^{-5}$	1210	± 21
393.16	9.929	951.7	0.2	$7.36 \cdot 10^{-4}$	$\pm 2.1 \cdot 10^{-6}$	$8.1 \cdot 10^{-4}$	$\pm 7.4 \cdot 10^{-5}$	1220	± 68
433.15	0.419	915.7	0.3	$7.89 \cdot 10^{-4}$	$\pm 3.3 \cdot 10^{-6}$	$1.03 \cdot 10^{-3}$	$\pm 8.3 \cdot 10^{-5}$	1100	± 54
433.16	1.995	916.4	0.1	$7.83 \cdot 10^{-4}$	$\pm 3.1 \cdot 10^{-6}$	$1.02 \cdot 10^{-3}$	$\pm 6.0 \cdot 10^{-5}$	1100	± 23
433.15	4.001	918.4	-0.4	$7.74 \cdot 10^{-4}$	$\pm 2.9 \cdot 10^{-6}$	$1.01 \cdot 10^{-3}$	$\pm 3.6 \cdot 10^{-5}$	1110	± 21
433.15	5.965	920.8	-0.4	$7.66 \cdot 10^{-4}$	$\pm 2.9 \cdot 10^{-6}$	$9.9 \cdot 10^{-4}$	$\pm 3.1 \cdot 10^{-5}$	1120	± 52
433.15	7.943	921.9	0.3	$7.58 \cdot 10^{-4}$	$\pm 2.9 \cdot 10^{-6}$	$9.8 \cdot 10^{-4}$	$\pm 5.1 \cdot 10^{-5}$	1120	± 36
433.15	9.924	923.7	0.3	$7.50 \cdot 10^{-4}$	$\pm 3.3 \cdot 10^{-6}$	$9.7 \cdot 10^{-4}$	$\pm 7.8 \cdot 10^{-5}$	1130	± 38
473.15	0.515	886.4	0.2	$8.06 \cdot 10^{-4}$	$\pm 5.3 \cdot 10^{-6}$	$1.20 \cdot 10^{-3}$	$\pm 8.8 \cdot 10^{-5}$	1030	± 34
473.15	2.010	888.0	0.2	$8.00 \cdot 10^{-4}$	$\pm 5.1 \cdot 10^{-6}$	$1.19 \cdot 10^{-3}$	$\pm 6.6 \cdot 10^{-5}$	1040	± 44
473.16	3.979	890.1	-0.1	$7.91 \cdot 10^{-4}$	$\pm 4.9 \cdot 10^{-6}$	$1.18 \cdot 10^{-3}$	$\pm 4.7 \cdot 10^{-5}$	1040	± 22
473.15	5.985	892.4	-0.3	$7.82 \cdot 10^{-4}$	$\pm 5.0 \cdot 10^{-6}$	$1.16 \cdot 10^{-3}$	$\pm 4.3 \cdot 10^{-5}$	1050	± 47
473.15	7.951	894.5	-0.2	$7.74 \cdot 10^{-4}$	$\pm 5.0 \cdot 10^{-6}$	$1.15 \cdot 10^{-3}$	$\pm 6.0 \cdot 10^{-5}$	1050	± 32
473.15	9.925	896.7	0.1	$7.65 \cdot 10^{-4}$	$\pm 5.1 \cdot 10^{-6}$	$1.13 \cdot 10^{-3}$	$\pm 8.5 \cdot 10^{-5}$	1050	± 23

^a Standard uncertainty {and expanded uncertainty at 95% level}: pressure = ± 0.0031 {0.0063} MPa, density = ± 0.2 {0.4} kg m⁻³, density at atmospheric pressure = ± 0.15 {0.3} kg m⁻³.

^b Deviation between density calculated using Equation 6 and the experimentally determined density.

Table 3. Densities (ρ), volumetric thermal expansion coefficients (α), isothermal compressibilities (κ), and speeds of sound (a) of the dephenolated shale fuel oil sample along with expanded uncertainties at the 95% level (u).^a

T	P	ρ	$\rho_{\text{calc}} - \rho$	α	$u(\alpha)$	κ	$u(\kappa)$	a	$u(a)$
K	MPa	kg m ⁻³	kg m ⁻³	K ⁻¹	K ⁻¹	MPa ⁻¹	MPa ⁻¹	m s ⁻¹	m s ⁻¹
293.15	0.1	968.2							
293.15	0.518	969.5	0.2	$7.53 \cdot 10^{-4}$	$\pm 2.7 \cdot 10^{-6}$	$5.8 \cdot 10^{-4}$	$\pm 4.6 \cdot 10^{-5}$	1460	± 68
293.16	1.007	969.8	0.1	$7.51 \cdot 10^{-4}$	$\pm 2.6 \cdot 10^{-6}$	$5.8 \cdot 10^{-4}$	$\pm 4.2 \cdot 10^{-5}$	1460	± 55
293.15	1.025	969.8	0.1	$7.50 \cdot 10^{-4}$	$\pm 2.7 \cdot 10^{-6}$	$5.8 \cdot 10^{-4}$	$\pm 4.2 \cdot 10^{-5}$	1460	± 39
293.15	1.995	970.3	0.0	$7.46 \cdot 10^{-4}$	$\pm 2.6 \cdot 10^{-6}$	$5.6 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-5}$	1480	± 33
293.15	3.982	971.4	0.0	$7.38 \cdot 10^{-4}$	$\pm 2.6 \cdot 10^{-6}$	$5.4 \cdot 10^{-4}$	$\pm 2.4 \cdot 10^{-5}$	1510	± 48
293.15	5.970	972.5	-0.1	$7.29 \cdot 10^{-4}$	$\pm 2.6 \cdot 10^{-6}$	$5.2 \cdot 10^{-4}$	$\pm 1.9 \cdot 10^{-5}$	1540	± 79
293.15	7.957	973.6	-0.2	$7.21 \cdot 10^{-4}$	$\pm 2.6 \cdot 10^{-6}$	$5.0 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-5}$	1570	± 120
293.15	9.941	974.6	0.2	$7.13 \cdot 10^{-4}$	$\pm 2.8 \cdot 10^{-6}$	$4.8 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-5}$	1610	± 64
293.15	11.922	975.6	0.2	$7.05 \cdot 10^{-4}$	$\pm 2.9 \cdot 10^{-6}$	$4.6 \cdot 10^{-4}$	$\pm 5.1 \cdot 10^{-5}$	1650	± 66
298.15	0.510	965.9	0.2	$7.56 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-6}$	$6.0 \cdot 10^{-4}$	$\pm 4.7 \cdot 10^{-5}$	1430	± 63
298.15	0.511	965.9	0.1	$7.56 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-6}$	$6.0 \cdot 10^{-4}$	$\pm 4.6 \cdot 10^{-5}$	1430	± 60
298.15	0.528	965.9	0.1	$7.56 \cdot 10^{-4}$	$\pm 2.6 \cdot 10^{-6}$	$6.0 \cdot 10^{-4}$	$\pm 4.6 \cdot 10^{-5}$	1430	± 60
298.15	1.005	966.1	0.1	$7.54 \cdot 10^{-4}$	$\pm 2.6 \cdot 10^{-6}$	$6.0 \cdot 10^{-4}$	$\pm 4.2 \cdot 10^{-5}$	1440	± 65
298.15	1.024	966.2	0.1	$7.54 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-6}$	$6.0 \cdot 10^{-4}$	$\pm 4.2 \cdot 10^{-5}$	1440	± 64
298.15	1.990	966.8	0.1	$7.50 \cdot 10^{-4}$	$\pm 2.4 \cdot 10^{-6}$	$5.9 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-5}$	1450	± 52
298.15	3.980	967.9	0.1	$7.41 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-6}$	$5.6 \cdot 10^{-4}$	$\pm 2.4 \cdot 10^{-5}$	1480	± 36
298.15	5.969	969.0	0.0	$7.33 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-6}$	$5.4 \cdot 10^{-4}$	$\pm 1.8 \cdot 10^{-5}$	1510	± 30
298.15	7.956	970.1	0.0	$7.24 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-6}$	$5.2 \cdot 10^{-4}$	$\pm 2.4 \cdot 10^{-5}$	1540	± 45
298.15	9.939	971.1	-0.1	$7.16 \cdot 10^{-4}$	$\pm 2.7 \cdot 10^{-6}$	$5.0 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-5}$	1580	± 72
298.15	11.919	972.2	-0.2	$7.08 \cdot 10^{-4}$	$\pm 2.8 \cdot 10^{-6}$	$4.8 \cdot 10^{-4}$	$\pm 5.2 \cdot 10^{-5}$	1610	± 110
313.15	0.1	954.2							
323.16	0.524	947.8	-0.1	$7.72 \cdot 10^{-4}$	$\pm 2.0 \cdot 10^{-6}$	$7.1 \cdot 10^{-4}$	$\pm 4.6 \cdot 10^{-5}$	1320	± 26
323.16	1.019	948.2	-0.1	$7.70 \cdot 10^{-4}$	$\pm 2.0 \cdot 10^{-6}$	$7.1 \cdot 10^{-4}$	$\pm 4.3 \cdot 10^{-5}$	1330	± 46

323.15	1.024	948.2	0.0	$7.70 \cdot 10^{-4}$	$\pm 1.9 \cdot 10^{-6}$	$7.1 \cdot 10^{-4}$	$\pm 4.3 \cdot 10^{-5}$	1330	± 20
323.15	1.995	948.8	0.0	$7.66 \cdot 10^{-4}$	$\pm 1.9 \cdot 10^{-6}$	$7.0 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-5}$	1340	± 31
323.15	3.980	950.1	0.0	$7.57 \cdot 10^{-4}$	$\pm 1.9 \cdot 10^{-6}$	$6.7 \cdot 10^{-4}$	$\pm 2.1 \cdot 10^{-5}$	1360	± 52
323.15	5.968	951.3	0.0	$7.48 \cdot 10^{-4}$	$\pm 1.9 \cdot 10^{-6}$	$6.5 \cdot 10^{-4}$	$\pm 1.5 \cdot 10^{-5}$	1380	± 76
323.15	7.956	952.5	-0.1	$7.40 \cdot 10^{-4}$	$\pm 1.9 \cdot 10^{-6}$	$6.3 \cdot 10^{-4}$	$\pm 2.2 \cdot 10^{-5}$	1410	± 39
323.15	9.941	953.7	-0.1	$7.31 \cdot 10^{-4}$	$\pm 2.1 \cdot 10^{-6}$	$6.1 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-5}$	1430	± 46
323.15	11.920	954.8	-0.1	$7.22 \cdot 10^{-4}$	$\pm 2.3 \cdot 10^{-6}$	$5.8 \cdot 10^{-4}$	$\pm 5.2 \cdot 10^{-5}$	1460	± 51
333.15	0.1	939.9							
353.15	0.1	925.4							
353.16	0.527	926.1	-0.3	$7.93 \cdot 10^{-4}$	$\pm 1.4 \cdot 10^{-6}$	$8.5 \cdot 10^{-4}$	$\pm 4.7 \cdot 10^{-5}$	1220	± 36
353.15	1.023	926.4	0.0	$7.91 \cdot 10^{-4}$	$\pm 1.4 \cdot 10^{-6}$	$8.4 \cdot 10^{-4}$	$\pm 4.3 \cdot 10^{-5}$	1220	± 56
353.16	1.024	926.4	-0.2	$7.91 \cdot 10^{-4}$	$\pm 1.3 \cdot 10^{-6}$	$8.4 \cdot 10^{-4}$	$\pm 4.3 \cdot 10^{-5}$	1220	± 13
353.15	1.994	927.2	-0.1	$7.86 \cdot 10^{-4}$	$\pm 1.3 \cdot 10^{-6}$	$8.3 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-5}$	1230	± 22
353.15	3.981	928.6	0.0	$7.77 \cdot 10^{-4}$	$\pm 1.2 \cdot 10^{-6}$	$8.1 \cdot 10^{-4}$	$\pm 2.1 \cdot 10^{-5}$	1250	± 38
353.15	5.968	930.0	-0.2	$7.68 \cdot 10^{-4}$	$\pm 1.2 \cdot 10^{-6}$	$7.9 \cdot 10^{-4}$	$\pm 1.3 \cdot 10^{-5}$	1260	± 19
353.15	7.953	931.4	-0.3	$7.59 \cdot 10^{-4}$	$\pm 1.3 \cdot 10^{-6}$	$7.6 \cdot 10^{-4}$	$\pm 2.1 \cdot 10^{-5}$	1280	± 29
353.15	9.938	932.7	-0.4	$7.50 \cdot 10^{-4}$	$\pm 1.5 \cdot 10^{-6}$	$7.4 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-5}$	1300	± 39
353.15	11.918	934.0	-0.3	$7.41 \cdot 10^{-4}$	$\pm 1.8 \cdot 10^{-6}$	$7.2 \cdot 10^{-4}$	$\pm 5.3 \cdot 10^{-5}$	1320	± 36
383.15	0.525	903.8	-0.2	$8.15 \cdot 10^{-4}$	$\pm 1.2 \cdot 10^{-6}$	$9.9 \cdot 10^{-4}$	$\pm 4.7 \cdot 10^{-5}$	1140	± 32
383.15	1.023	904.2	-0.1	$8.13 \cdot 10^{-4}$	$\pm 1.1 \cdot 10^{-6}$	$9.9 \cdot 10^{-4}$	$\pm 4.4 \cdot 10^{-5}$	1140	± 24
383.16	1.024	904.3	0.0	$8.13 \cdot 10^{-4}$	$\pm 1.1 \cdot 10^{-6}$	$9.9 \cdot 10^{-4}$	$\pm 4.3 \cdot 10^{-5}$	1140	± 15
383.15	1.994	905.1	0.1	$8.08 \cdot 10^{-4}$	$\pm 1.0 \cdot 10^{-6}$	$9.8 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-5}$	1140	± 10
383.15	3.978	906.7	0.1	$7.98 \cdot 10^{-4}$	$\pm 8.7 \cdot 10^{-7}$	$9.5 \cdot 10^{-4}$	$\pm 2.1 \cdot 10^{-5}$	1160	± 18
383.15	5.967	908.3	-0.1	$7.89 \cdot 10^{-4}$	$\pm 9.1 \cdot 10^{-7}$	$9.3 \cdot 10^{-4}$	$\pm 1.3 \cdot 10^{-5}$	1170	± 29
383.15	7.955	909.9	0.2	$7.79 \cdot 10^{-4}$	$\pm 1.1 \cdot 10^{-6}$	$9.0 \cdot 10^{-4}$	$\pm 2.2 \cdot 10^{-5}$	1190	± 29
383.15	9.938	911.5	0.3	$7.70 \cdot 10^{-4}$	$\pm 1.4 \cdot 10^{-6}$	$8.8 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-5}$	1200	± 44
383.15	11.918	912.9	-0.2	$7.60 \cdot 10^{-4}$	$\pm 1.6 \cdot 10^{-6}$	$8.6 \cdot 10^{-4}$	$\pm 5.4 \cdot 10^{-5}$	1220	± 29
413.16	0.527	881.6	0.2	$8.38 \cdot 10^{-4}$	$\pm 1.7 \cdot 10^{-6}$	$1.15 \cdot 10^{-3}$	$\pm 4.9 \cdot 10^{-5}$	1070	± 11
413.15	1.022	882.0	0.2	$8.36 \cdot 10^{-4}$	$\pm 1.6 \cdot 10^{-6}$	$1.14 \cdot 10^{-3}$	$\pm 4.5 \cdot 10^{-5}$	1070	± 16
413.16	1.022	882.1	0.3	$8.36 \cdot 10^{-4}$	$\pm 1.6 \cdot 10^{-6}$	$1.14 \cdot 10^{-3}$	$\pm 4.5 \cdot 10^{-5}$	1070	± 24
413.15	2.004	883.0	0.4	$8.31 \cdot 10^{-4}$	$\pm 1.5 \cdot 10^{-6}$	$1.13 \cdot 10^{-3}$	$\pm 3.7 \cdot 10^{-5}$	1080	± 35
413.14	3.980	884.9	0.1	$8.20 \cdot 10^{-4}$	$\pm 1.4 \cdot 10^{-6}$	$1.10 \cdot 10^{-3}$	$\pm 2.2 \cdot 10^{-5}$	1090	± 14
413.14	5.966	886.7	0.0	$8.10 \cdot 10^{-4}$	$\pm 1.4 \cdot 10^{-6}$	$1.08 \cdot 10^{-3}$	$\pm 1.5 \cdot 10^{-5}$	1100	± 25
413.14	7.952	888.5	0.0	$8.00 \cdot 10^{-4}$	$\pm 1.6 \cdot 10^{-6}$	$1.05 \cdot 10^{-3}$	$\pm 2.4 \cdot 10^{-5}$	1110	± 21
413.14	9.937	890.3	-0.1	$7.90 \cdot 10^{-4}$	$\pm 1.8 \cdot 10^{-6}$	$1.03 \cdot 10^{-3}$	$\pm 4.0 \cdot 10^{-5}$	1120	± 27
413.14	11.917	892.0	-0.1	$7.81 \cdot 10^{-4}$	$\pm 2.0 \cdot 10^{-6}$	$1.00 \cdot 10^{-3}$	$\pm 5.6 \cdot 10^{-5}$	1130	± 25
443.16	0.525	859.2	0.2	$8.63 \cdot 10^{-4}$	$\pm 2.6 \cdot 10^{-6}$	$1.31 \cdot 10^{-3}$	$\pm 5.2 \cdot 10^{-5}$	1010	± 22
443.15	1.013	859.7	0.1	$8.60 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-6}$	$1.30 \cdot 10^{-3}$	$\pm 4.8 \cdot 10^{-5}$	1010	± 22
443.15	1.020	859.8	0.2	$8.60 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-6}$	$1.30 \cdot 10^{-3}$	$\pm 4.7 \cdot 10^{-5}$	1010	± 30
443.16	1.994	860.9	0.2	$8.55 \cdot 10^{-4}$	$\pm 2.5 \cdot 10^{-6}$	$1.29 \cdot 10^{-3}$	$\pm 3.9 \cdot 10^{-5}$	1020	± 14
443.15	3.979	863.0	0.2	$8.44 \cdot 10^{-4}$	$\pm 2.4 \cdot 10^{-6}$	$1.26 \cdot 10^{-3}$	$\pm 2.6 \cdot 10^{-5}$	1030	± 22
443.15	5.966	865.1	0.1	$8.33 \cdot 10^{-4}$	$\pm 2.4 \cdot 10^{-6}$	$1.23 \cdot 10^{-3}$	$\pm 2.0 \cdot 10^{-5}$	1040	± 13
443.15	7.953	867.2	0.2	$8.23 \cdot 10^{-4}$	$\pm 2.4 \cdot 10^{-6}$	$1.21 \cdot 10^{-3}$	$\pm 2.8 \cdot 10^{-5}$	1050	± 11
443.15	9.937	869.3	0.1	$8.12 \cdot 10^{-4}$	$\pm 2.6 \cdot 10^{-6}$	$1.18 \cdot 10^{-3}$	$\pm 4.2 \cdot 10^{-5}$	1060	± 19
443.15	11.915	871.2	0.1	$8.02 \cdot 10^{-4}$	$\pm 2.7 \cdot 10^{-6}$	$1.15 \cdot 10^{-3}$	$\pm 5.8 \cdot 10^{-5}$	1070	± 24
473.16	0.529	836.9	-0.4	$8.88 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-6}$	$1.47 \cdot 10^{-3}$	$\pm 5.5 \cdot 10^{-5}$	970	± 14
473.15	1.026	837.7	-0.2	$8.85 \cdot 10^{-4}$	$\pm 3.6 \cdot 10^{-6}$	$1.47 \cdot 10^{-3}$	$\pm 5.1 \cdot 10^{-5}$	970	± 11
473.15	1.030	837.3	0.0	$8.85 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-6}$	$1.47 \cdot 10^{-3}$	$\pm 5.1 \cdot 10^{-5}$	970	± 20

473.15	1.997	838.9	0.4	$8.80 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-6}$	$1.45 \cdot 10^{-3}$	$\pm 4.4 \cdot 10^{-5}$	970	± 20
473.15	3.980	841.4	-0.1	$8.69 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-6}$	$1.42 \cdot 10^{-3}$	$\pm 3.2 \cdot 10^{-5}$	980	± 13
473.14	5.969	843.9	-0.5	$8.57 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-6}$	$1.40 \cdot 10^{-3}$	$\pm 2.6 \cdot 10^{-5}$	990	± 19
473.14	7.955	846.3	-0.5	$8.46 \cdot 10^{-4}$	$\pm 3.5 \cdot 10^{-6}$	$1.37 \cdot 10^{-3}$	$\pm 3.2 \cdot 10^{-5}$	990	± 26
473.15	9.938	848.7	0.0	$8.35 \cdot 10^{-4}$	$\pm 3.6 \cdot 10^{-6}$	$1.34 \cdot 10^{-3}$	$\pm 4.6 \cdot 10^{-5}$	1000	± 18
473.15	11.918	851.0	0.1	$8.24 \cdot 10^{-4}$	$\pm 3.7 \cdot 10^{-6}$	$1.31 \cdot 10^{-3}$	$\pm 6.2 \cdot 10^{-5}$	1010	± 22

^a Standard uncertainty {and expanded uncertainty at 95% level}: pressure = ± 0.0031 {0.0063} MPa, density = ± 0.2 {0.4} kg m⁻³, density at atmospheric pressure = ± 0.15 {0.3} kg m⁻³.

^b Deviation between density calculated using Equation 6 and the experimentally determined density.

As seen by comparison of the two surfaces, the density noticeably decreases when phenolic compounds are removed. At a constant pressure, the change in the density with temperature was essentially linear to within the measurement accuracy of the data. Linear equations fit to the constant pressure data had R^2 values greater than 0.999. The same was true of the pressure dependence at a constant temperature.

To be able to fit the data as a function of both temperature and pressure a polynomial equation (Equation 6) was used.

$$\rho = A + B \cdot T + C \cdot P + D \cdot P^2 + E \cdot T \cdot P + F \cdot T^2 \quad (6)$$

In Equation 6, ρ is the density (kg m⁻³), T is the temperature (K), P is the pressure (bar) and A through F are empirical constants. The constants used for each sample are shown in Table 4. This equation is valid for temperatures from 293.15 to 473.15 K and pressures from 0.1 to 10 MPa (0.1 to 12 MPa for the dephenolated sample). These constants were found by minimizing the root mean squared error (RMSE) of Equation 6 using the differential evolution solver⁴³ implemented in the SciPy package⁴⁴ for Python. The data at atmospheric pressure were not included when fitting Equation 6 because there was a slight difference between the datasets due to degassing. When using Equation 6 the RMSE for the fuel oil was 0.17 kg m⁻³ and 0.18 kg m⁻³ for the dephenolated fuel oil. The residual for each data point are given in the fourth column of Table 2 and Table 3. A polynomial equation was used because it is simple, but still provided an accurate fit of the data. This form of the polynomial equation was used because simpler polynomials gave somewhat poorer fits. A more complicated polynomial with more terms was also tested, but the uncertainty of the partial derivatives calculated using this equation were higher. Additionally, it was worried that the higher order polynomial overfit the data. Partial derivatives of Equation 6 were later used for calculating additional thermodynamic properties.

Table 4. Constants used with Equation 6 for estimating the density as a function of temperature and pressure.

	Shale fuel oil	Dephenolated fuel oil
A	$1.24548 \cdot 10^3$	$1.18055 \cdot 10^3$
B	$-8.03226 \cdot 10^{-1}$	$-7.09138 \cdot 10^{-1}$
C	$-3.72502 \cdot 10^{-2}$	$-5.23979 \cdot 10^{-2}$
D	$-2.63639 \cdot 10^{-5}$	$-5.10395 \cdot 10^{-5}$
E	$3.04502 \cdot 10^{-4}$	$3.72620 \cdot 10^{-4}$
F	$9.19393 \cdot 10^{-5}$	$-3.84895 \cdot 10^{-5}$

3.2. Expansion coefficients, compressibilities and speeds of sound

Thermal expansion coefficients (Equation 3) and isothermal compressibilities (Equation 4) were calculated by taking the appropriate partial derivatives of Equation 6, and these partial derivatives are given as Equations 7 and 8.

$$\left(\frac{\partial \rho}{\partial T}\right)_P = B + E \cdot P + 2F \cdot T \quad (7)$$

$$\left(\frac{\partial \rho}{\partial P}\right)_T = C + 2D \cdot P + E \cdot T \quad (8)$$

In these equations all the variables and coefficients have the same values as in Equation 6. The calculated expansion coefficients and isothermal compressibilities were then used with Equation 5 to calculate the speed of sound at the experimental conditions. The constant pressure heat capacity required for the Equation 5 was obtained from Equation 9 (for the shale fuel oil) and Equation 10 (for the dephenolated shale fuel oil).

$$C_p = 0.002911 T + 1.009 \quad (9)$$

$$C_p = 0.002833 T + 0.9918 \quad (10)$$

These linear equations were fit to experimental data (14 data points) measured in this work in the temperature range between 288.2 and 423.2 K. In these equations T is temperature (K) and C_p is the constant pressure heat capacity ($\text{J g}^{-1} \text{K}^{-1}$). The R^2 coefficients for these linear fits are 0.996 and 0.997 for Equations 9 and 10, respectively. Although the heat capacity also depends somewhat on pressure, this was not taken into account here. The effect of the pressure dependence on the speed of sound calculation is minor, as shown in Section 2.5.

The calculated expansion coefficients, isothermal compressibilities and speeds of sound along with expanded uncertainties at the 95% level are presented in Table 2 and Table 3 for fuel oil and dephenolated fuel oil, respectively.

The dephenolated sample had higher expansion coefficients and compressibilities, but lower speeds of sound. The relative difference between the fuel oil and dephenolated samples can be seen from Figure 2, Figure 3 and Figure 4. In these figures the relative difference was calculated using the fuel oil sample as the reference. These differences are larger than the expanded uncertainty of the data for almost all of the points, and taken as a whole there is a consistent positive or negative trend. Therefore, the phenolic compounds have a significant impact on the thermodynamic properties of the oil, as expected. As shown, the difference between the two samples increased with temperature and decreased with pressure.

Figure 2. The relative deviation between the thermal expansion coefficients of the fuel oil and dephenolated samples. Relative deviation = $(\text{Dephenolated} - \text{Fuel oil}) / \text{Fuel oil} * 100$.

Figure 3. The relative deviation between the isothermal compressibilities of the fuel oil and dephenolated samples. Relative deviation = $(\text{Dephenolated} - \text{Fuel oil}) / \text{Fuel oil} * 100$.

Figure 4. The relative deviation between the speeds of sound of the fuel oil and dephenolated samples. Relative deviation = $(\text{Dephenolated} - \text{Fuel oil}) / \text{Fuel oil} * 100$.

For comparison we selected several different fuels and pure compounds. This comparison is given in Figure 5 and Figure 6, and shows that the shale oil samples have relatively low compressibilities. The petroleum fraction was a narrow distillation cut with an average boiling point of about 523 K.⁴⁵ The bio-derived jet fuels consisted mostly of linear and branched paraffins (BIO-SPK and Cs-HRJ samples in ⁴⁶). The curves shown in the figures were calculated by fitting polynomials to the experimental data given in the references and then using those polynomials to calculate the compressibility. This was done because the data for different compounds had been measured at different temperatures and pressures. Figure 5 presents a comparison in terms of pressure at 303 K. The petroleum fraction and jet fuel samples had significantly higher compressibilities than the shale oil samples, as expected because these samples have lower boiling points and contain, on average, smaller molecules. However, even tridecylbenzene and pentadecylbenzene, which are larger compounds with molecular weights comparable to the shale oil samples, had compressibilities that were higher. Therefore, the polar and alkylaromatic character of Kukersite shale oil gives it compressibilities that are lower than fuels and pure hydrocarbons that have more of an aliphatic nature. Figure 6 shows a comparison in terms of temperature at a constant pressure of 2 MPa. In both figures the shale oil samples matched best with 1-methylnaphthalene and quinoline, which are aromatic molecules with two rings.

Figure 5. Comparison of the compressibilities at 303 K for the shale oil samples with literature data for a petroleum fraction,⁴⁵ jet fuel,⁴⁷ bioderived jet fuels,⁴⁶ tridecylbenzene,⁴⁸ pentadecylbenzene,⁴⁸ 1-methylnaphthalene⁴⁹ and quinoline⁴⁹.

Figure 6. Comparison of the isothermal compressibilities at 2 MPa for the shale oil samples with literature data for a petroleum fraction,⁴⁵ jet fuel,⁴⁷ bioderived jet fuels,⁴⁶ tridecylbenzene,⁴⁸ pentadecylbenzene,⁴⁸ n-hexadecane,⁵⁰ 1-methylnaphthalene⁴⁹ and quinoline⁴⁹.

The speeds of sound determined for these shale oil samples are compared to literature values for common materials in Table 5. Liquids in general have speeds of sound that are much higher than in air, but even among liquids the shale oil samples have high speeds of sound. Small molecules like tetrachloromethane and nonpolar alkanes like heptane and octane have much lower speeds of sound. Common fuels such as jet fuel and gasoline also have lower speeds of sound, likely because they often contain large amounts of alkanes and have lower molecular weights than the shale oil. The shale fuel oil sample has a speed of sound that is most similar to water and cresols. The similarity to cresol was expected because a main component of Kukersite shale oil is alkylphenols. The higher speed of sound is related to lower compressibilities.

Table 5. The speed of sound in various materials at ambient conditions (about 293 K and 1 bar).

Material	Speed of sound (m s ⁻¹)	Reference
Air, dry	343	51
Tetrachloromethane	930	51
Hexane	1078	51
Heptane	1149	51
Octane	1166	51
1-propanol	1223	51
1-butanol	1262	51
Jet fuel (from camelina)	1262	46
1-undecene	1275	51
Kerosene	1280	52
Oil (SAE 30)	1280	52
Jet fuel (from castor seed oil)	1284	46
Jet fuel (from waste fat and grease)	1288	46
Jet fuel (from plant isoprenoid)	1297	46
Cyclohexane	1299	51
Benzene	1302	51
Chlorobenzene	1311	51
Jet fuel	1317	47
Gasoline	1380	52
Dephenolated shale fuel oil	1450	this work
Mercury	1450	52
Water (distilled)	1483	52
m-Cresol	1497	53,54
Eugenol	1497	53
p-Cresol	1503	53,54
Shale fuel oil	1520	this work
o-Cresol	1522	53,54
Water (sea, S = 3.5%)	1534	51
Glycerine	1895	52

4. Conclusions

The densities of two Kukersite shale oil samples were measured, and thermal expansion coefficients, isothermal compressibilities and speeds of sound were calculated from this data. The heat capacities of the samples were also measured, and empirical equations based on this data were presented. The experimental density data confirmed that removing polar phenolic compounds from the oil causes a noticeable decrease in the

density, as would be expected. Removing phenolic compounds from the oil also caused changes in other thermodynamic properties of the shale fuel oil: the expansion coefficient and compressibility increased, the speed of sound decreased.

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