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Application of Ultrasonic Methods for Evaluation of High-Pressure Physicochemical Parameters of Liquids

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An emerging ultrasonic technology aims to control high-pressure industrial processes that use liquids at pressures up to 800 MPa. To control these processes it is necessary to know precisely physicochemical properties of the processed liquid (e.g., Camelina sativa oil) in the high-pressure range. In recent years, Camelina sativa oil gained a significant interest in food and biofuel industries. Unfortunately, only a very few data characterizing the high-pressure behavior of Camelina sativa oil is available. The aim of this paper is to investigate high pressure physicochemical properties of liquids on the example of Camelina sativa oil, using efficient ultrasonic techniques, i.e., speed of sound measurements supported by parallel measurements of density. It is worth noting that conventional low-pressure methods of measuring physicochemical properties of liquids fail at high pressures. The time of flight (TOF) between the two selected ultrasonic impulses was evaluated with a cross-correlation method. TOF measurements enabled for determination of the speed of sound with very high precision (of the order of picoseconds). Ultrasonic velocity and density measurements were performed for pressures 0.1–660 MPa, and temperatures 3–30°C. Isotherms of acoustic impedance Z_a, surface tension σ and thermal conductivity k were subsequently evaluated. These physicochemical parameters of Camelina sativa oil are mainly influenced by changes in the pressure p, i.e., they increase about two times when the pressure increases from atmospheric pressure (0.1 MPa) to 660 MPa at 30°C. The results obtained in this study are novel and can be applied in food, and chemical industries.

Keywords: ultrasonic methods; speed of sound; acoustic impedance; surface tension; thermal conductivity; physicochemical properties.

1. Introduction

Ultrasonic techniques are at present well established technologies in typical industrial applications such as high temperature ultrasonic flow measurements, ultrasonic temperature measurements, etc. On the other hand, in various industrial technological processes, liquids are subjected to high pressures (up to 800 MPa), e.g., during high pressure food preservation and processing. Classical measuring methods do not apply to the assessment of physicochemical properties of liquids subjected to high pressures. Knowledge of high-pressure physicochemical parameters of processed liquids is indispensable for the design and control of high-pressure industrial technological processes. In this study, the authors extend the applicability of modern

ultrasonic methods into the high-pressure range to determine the physicochemical properties of liquids.

This paper presents an innovative application of ultrasonic methods for determining physicochemical parameters of liquids under high pressure. The determination of physicochemical parameters of liquids using classical (mechanical) methods is practically impossible in the high-pressure range (>200 MPa). This fact motivated the authors to take up this challenge.

Recently, we witness a "renaissance" of the ultrasonic technology in industrial applications due to developments in modern digital electronics (computerized instrumentation), implementation of sophisticated signal processing algorithms and progress in high pressure (high temperature) ultrasonic transducers. Indeed, the results of the research, presented in this paper, would be impossible without the application of modern state-of-the-art ultrasonic measurement techniques.

It should be stressed that the ultrasonic technology is at present the only technology which can provide online measurement in high-pressure conditions. Other advantages of the ultrasonic technology are, its nonintrusiveness and a possibility of full automation.

To attain the goal of our research, the authors applied innovative ultrasonic methods (i.e., measurement of the speed of sound and parallel density measurements under high pressure) that are particularly convenient for determining physicochemical parameters of liquids at high pressure range. Investigations of high-pressure physicochemical parameters of liquids have been carried out in this work (on the example of Camelina sativa oil).

Camelina sativa oil is successfully used in both edible and industrial products. Camelina sativa has recently gained new interest due to high content of omega-3 fatty acids (polyunsaturated fatty acids) and vitamin E.

Potential Camelina's industrial applications include: environmentally safe paints, cosmetics, biopolymers and low-emission biodiesel fuels (Rokka *et al.*, 2002; Ciubota-Rosie *et al.*, 2013; Waraich *et al.*, 2013; Popa *et al.*, 2017). Moreover, biofuel based on Camelina sativa oil (as a raw material) has recently been used in the aviation (Shonnard *et al.*, 2010; Kamin, Rudy, 2011).

A number of papers on the physicochemical and thermodynamic properties of the Camelina oil (at atmospheric pressure) have been published (Abramovič, Abram, 2005; Petcu *et al.*, 2016), but there is a general lack of studies on the properties of this oil in the high pressure range. Such an information is however indispensable in optimal design, modeling and performance of high-pressure processes and technological systems. Modeling the thermodynamic behavior of foods during high-pressure processing is difficult due to the lack of quantitative data describing their thermophysical properties under high pressure conditions (Kondakci, Zhou, 2017).

The knowledge of thermophysical properties of liquids is of vital relevance in design process in a number of industrial applications. Thermophysical properties play also an important role in prediction of heat transfer during the handling, processing, canning, storing, and distribution of foods at an ambient pressure (Ardia *et al.*, 2004).

Thermal conductivity k is one of the most important physical properties of food and agricultural materials, and is a critical parameter in the design and modeling of many thermal processes in food engineering (Zhu *et al.*, 2008; Zúñiga, Le-Bail, 2009). For this reason, the authors use an original (at high-pressure range) ultrasonic method (i.e., speed of sound measurements), evaluated in this paper isotherms of the thermal conductivity k of Camelina sativa oil in the high pressure range.

Hydrostatic pressures used in high pressure industrial technologies may range from 100 to 800 MPa. In order to reflect the reality of the existing industrial procedures, our experiments were performed in the pressure range from 0.1 to 660 MPa.

Conventional (mechanical) methods for measuring physicochemical properties of liquids cannot be extended to high pressure conditions. As a result, these methods are of no use in real industrial conditions, especially in an on-line monitoring of technological parameters of liquids. As a consequence, there exist a strong demand for new industrial grade measurement methods, which can be used to monitor the actual online parameters of liquids.

Ultrasonic techniques are a very promising solution to this problem (Rostocki *et al.*, 2013; Kiełczyński, Szalewski, 2011; Kiełczyński *et al.*, 2012; 2014a; 2014b; 2015; 2017a; 2017b; Povey, 2017; Dzida, 2010) which are particularly suitable for measuring physicochemical properties of liquids at high pressures.

The main objective of the research, presented in this paper, was quantitative determination of the impact of high pressure on physicochemical parameters of liquids on the example of the Camelina sativa oil.

To this end, the authors employed innovative (at high-pressure range) measurement techniques, such as ultrasonic measurement of the speed of sound c supported by parallel measurements of density ρ.

The measurements of the speed of sound c and the density ρ, in the Camelina sativa oil, with known composition, were performed under high pressure conditions (from an atmospheric pressure up to 660 MPa), at various temperatures (from 3 to 30°C).

The measured values of the speed of sound c and the density ρ (as a function of pressure p and temperature T), were basis for further evaluation of isotherms of the acoustic impedance Z_a and thermal conductivity k of the investigated Camelina sativa oil.

To the best authors' knowledge, quantitative evaluation of the speed of sound c, the density ρ of the Camelina sativa oil and its related physicochemical parameters, i.e., acoustic impedance Z_a, surface tension σ, and thermal conductivity k, in the high pressure range, was not yet published in the scientific literature.

The authors hope that the results of research, presented in this paper, enriched our knowledge about the application of modern ultrasonic measuring methods to evaluate high-pressure parameters of liquid foodstuffs at various temperatures and can be of crucial importance in the engineering practice in the precise design of new technological processes, systems and devices in the food and chemical industries.

2. Experimental setup

High pressure measurements were performed in the computerized ultrasonic setup shown in Fig. 1.

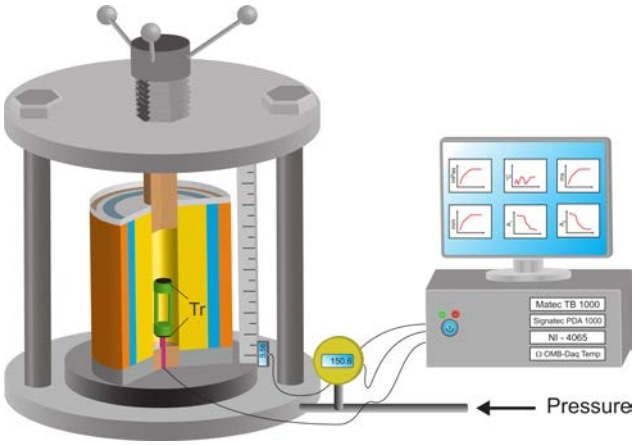

Fig. 1. Basic diagram of the computerized ultrasonic setup used in measurements of the speed of sound c and density ρ of investigated liquids subjected to high pressures at various temperatures. The "Tr" symbol stands for ultrasonic transducers.

The investigated liquid was pressurized in a custom-designed high pressure chamber, which was essentially a cylinder with the following dimensions: length = 23 cm, inner diameter = 1.7 cm, working volume = 52 cm^3. The chamber was equipped with a vertically moving piston and sealed with a Bridgman sealing system of the second type. The temperature inside the chamber was stabilized with a precision of ±0.1°C and measured with a type K thermocouple. The pressure was measured with a Manganin resistive sensor.

Two ultrasonic transducers placed in the high pressure chamber (see Fig. 1), were immersed in the measured liquid. The longitudinal ultrasonic wave propagates in the investigated liquid between these two transducers. The frequency of ultrasonic waves used in measurements was 5 MHz.

The changes in the liquid density ρ, as a function of pressure for various temperatures, were inferred from changes in the volume of the investigated oil sample in the high-pressure chamber.

More details about the measurement methods and the experimental setup were given in previous papers of the authors (Rostocki *et al.*, 2013; Kiełczyński *et al.*, 2014a; 2014b; 2017a; 2017b).

The isotherms of the speed of sound c and the density ρ of the Camelina sativa oil were evaluated in the pressure range from 0.1 MPa up to 660 MPa and for temperatures changing from 3°C to 30°C, namely at 3, 10, 20 and 30°C.

3. Signal processing procedures

In this paper, the speed of sound c of the ultrasonic waves propagating in the investigated liquid was determined from measurements of the time-of-flight (TOF) τ_d between two selected ultrasonic impulses (see Fig. 2) and the distance between the transducers.

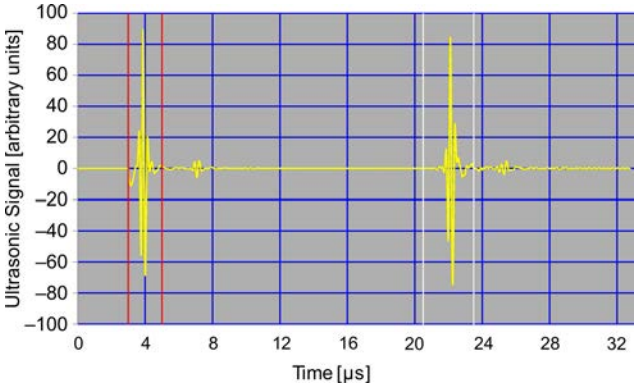

Fig. 2. An example of two ultrasonic impulses of RF frequency ~5 MHz received in the measurement setup at ~4 μs and ~22 μs. Approximate time difference (TOF) between impulses ~18 μs. The ultrasonic signal was digitized with a sampling rate 62.5 MHz (every 16 ns). Total number of points in the ultrasonic signal equals 2048.

Many different signal processing techniques have been proposed in the past to determine the time delay (TOF), such as those using Hilbert transform, Kalman filtering, cepstrum analysis, cross-spectrum, adaptive tracking, etc. However, the classical cross-correlation method of TOF determination (Sugasawa, 2002; Viola, Walker, 2003), still holds its many unique features, such as robustness, computational efficiency, fast execution time, ability to work with very noisy ultrasonic signals, etc.

In this paper, the measurements of the TOF were performed digitally within an industrial PC computer using an advanced cross-correlation method (Sugasawa, 2002; Viola, Walker, 2003).

In the theory of signal processing, the cross-correlation function $h(t)$, between two continuous

functions (impulses) of time t, $f(t)$, and $g(t)$, is defined as:

$$h(t) = \int_{-\infty}^{+\infty} f(\tau) g(t+\tau)\, \mathrm{d}\tau. \tag{1}$$

If the second impulse (echo) $g(t)$ is a scaled and time shifted version of the first echo $f(t)$, see Fig. 2, then the maximum of the cross-correlation function $h(t)$ occurs exactly at the time $t = \tau_d$, which equals the time-of-flight τ_d = TOF, between the two selected ultrasonic impulses. In fact, the second echo $g(t)$ is proportional to the shifted in time first echo $f(t-\tau_d)$, i.e., $g(t) = A \cdot f(t-\tau_d)$. So that, for square integrable functions the Schwartz inequality (Arfken, Weber, 2005) resulting from Eq. (1) can be written as:

$$\begin{aligned} h(t) &= A \cdot \int_{-\infty}^{+\infty} f(\tau) \cdot f\,(t-\tau_d+\tau)\, \mathrm{d}\tau \\ &\leq A \cdot \left(\int_{-\infty}^{+\infty} |f\,(\tau)|^2\, \mathrm{d}\tau \right)^{1/2} \\ &\quad \cdot \left(\int_{-\infty}^{+\infty} |f\,(t-\tau_d+\tau)|^2\, \mathrm{d}\tau \right)^{1/2}. \end{aligned} \tag{2}$$

The inequality "≤" sign in relation (2) can be substituted by the equality "=" sign if and only if $f(\tau) = f(t-\tau_d+\tau)$, i.e., when the following condition $t - \tau_d = 0$ holds, see Subsec. 4.2 in (Haykin, 2001). Consequently, for $t = \tau_d$ relation (2) can be written as:

$$h(\tau_d) = A \cdot \int_{-\infty}^{+\infty} |f(\tau)|^2\, \mathrm{d}\tau = A \cdot \int_{-\infty}^{+\infty} |F(f)|^2\, \mathrm{d}f, \tag{3}$$

where the second equality on the right-hand-side of Eq. (3) results from the Parseval's theorem and $F(f)$ stands for the Fourier transform of function $f(t)$.

Equation (3) shows clearly that, at the time instance $t = \tau_d$, equal to the time delay (TOF) between the two echoes, the cross-correlation function $h(t)$ given by Eq. (1) reaches maximum. For discrete signals this property of the cross-correlation function was proven in Subsec. 2.6.2 in (Proakis, Manolakis, 1966). It is worth noticing that the value of the cross-correlation function $h(\tau_d)$ at the instant of time $t = \tau_d$ is proportional to the energy of the first echo signal $f(t)$, in the ultrasonic signal, see Eq. (3).

The cross-correlation function, for two ultrasonic impulses delimited in Fig. 2 by red and white vertical cursors, is shown in Fig. 3. The cross-correlation method used in determination of the TOF has many advantages. Firstly, it can be calculated very fast in real time using Fourier Transformation (FT) in conjunction with its fast digital implementation FFT, see Chap. 6 in (Proakis, Manolakis, 1966), i.e.,

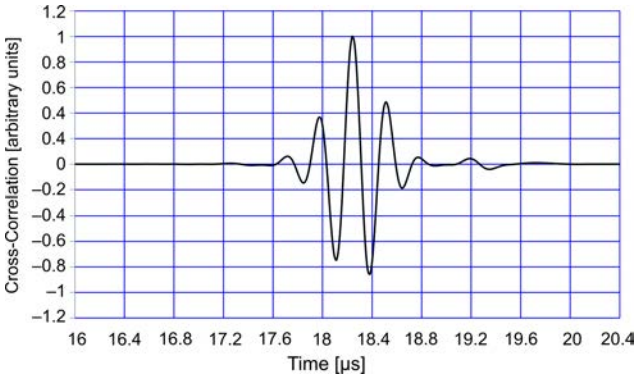

Fig. 3. Cross-correlation function $h(t)$ (for two ultrasonic impulses delimited in Fig. 2 by red and white vertical cursors) calculated digitally, employing three times FFT algorithm in Eq. (4). The maximum of the cross-correlation function determines the TOF = 18.288 μs between the ultrasonic impulses.

$$h(t) = \mathrm{FT}^{-1}\left\{\mathrm{FT}^{*}\left[f(t)\right] \cdot \mathrm{FT}\left[g(t)\right]\right\}, \tag{4}$$

where an asterisk "$*$" stands for complex conjugation.

In general, for a discrete ultrasonic signal with N points the number of multiplications resulting from employment of Eq. (1) is of the order of $\sim N^2$ and that following Eq. (4) is only $\sim 3N \log_2 N + N$. Thus, if $N = 2048$ then $N^2 \approx 6 \cdot 10^6$ and $3N \log_2 N + N \approx 8 \cdot 10^4$ (i.e., 75 times less). Secondly, the cross-correlation method can be used efficiently even for very noisy ultrasonic signals, due to its matched-filtering (noise-reduction) properties, see Chap. 5.6 in (Haykin, 2001).

Further reduction of noise can be achieved with signal averaging. In fact, ultrasonic signals were averaged 1024 times during our measurements what reduced random noise by a factor of $\sqrt{1024} \approx 32$.

3.1. Uncertainty in measurements of the speed of sound c

The speed of sound c in liquids was calculated from an elementary formula $c = L/\tau_d$, where L is the length of the ultrasonic path and τ_d the time-of-flight (TOF) for the selected ultrasonic impulses.

According to the ISO Guide, the expanded $(2\,\sigma)$ relative uncertainty $(U_c/c)_{2\sigma}$ of the speed of sound c, can be expressed as:

$$\left(\frac{U_c}{c}\right)_{2\sigma} = 2\sqrt{\left(\frac{U_L}{L}\right)^2 + \left(\frac{U_{\tau_d}}{\tau_d}\right)^2}, \tag{5}$$

where U_L/L is the relative standard $(1\,\sigma)$ uncertainty of the ultrasonic path L and U_{τ_d}/τ_d is the relative standard $(1\,\sigma)$ uncertainty of the TOF delay τ_d.

The TOF delay τ_d was measured digitally with a picosecond (repeatability) resolution. However, due to extra sources of systematic errors, such as the diffraction of ultrasonic waves, imperfections of phase characteristics of ultrasonic transducers., etc., the resulting relative standard ($1\,\sigma$) uncertainty U_{τ_d}/τ_d for the TOF delay τ_d was estimated as: $U_{\tau_d}/\tau_d = \pm 0.1\%$. Similarly, the relative standard ($1\,\sigma$) uncertainty of the ultrasonic path L (resulting from direct physical measurements and auxiliary calibration measurements in water) was estimated as: $U_L/L = \pm 0.1\%$.

Consequently, the final expanded relative uncertainty $(U_c/c)_{2\sigma}$, for the speed of sound c in liquids, equals ±0.3%. The expanded relative uncertainty corresponds in this case to the 95% confidence level.

3.2. Uncertainty in measurements of the density ρ

The density ρ of the Camelina sativa oil was measured initially at an atmospheric pressure (at various temperatures), using a MG-2 U-shaped tube densitometer, provided by UniLab, Poland. The density of the Camelina sativa oil at high-pressure conditions (up to 660 MPa) was evaluated by measuring changes in the volume occupied by a sample of the Camelina sativa oil, i.e., applying the following standard formula: $\rho(p, T) = m/V(p, T)$, where m is the mass and $V(p, T)$ is the actual volume of the sample of the Camelina sativa oil in the chamber at a pressure p and temperature T. The initial volume of the investigated Camelina sativa oil in the chamber at an atmospheric pressure was 22 cm^3. Changes in volume of the pressure chamber were determined from observations of the displacement of the piston mounted on the chamber's top. The mechanical displacement of the piston has been measured by a digital caliper, see Fig. 1. Corrections resulting from expansion of the chamber diameter, were calculated from Lamé equations and taken onto account during the final calculations of the actual chamber volume. The main source of error in evaluation of the actual volume of the pressure chamber was consequently the error in measurements of the piston displacement, that has been measured by a digital caliper with a standard uncertainty σ of 0.02%. Hence, the standard uncertainty σ in determination of the chamber volume was estimated to be 0.06%.

4. Experimental results

4.1. Speed of sound c

The measurements of the speed of sound c and density ρ of the Camelina sativa oil were performed at a pressure range from 0.1 to 660 MPa, and at temperatures ranging from 3 to 30°.

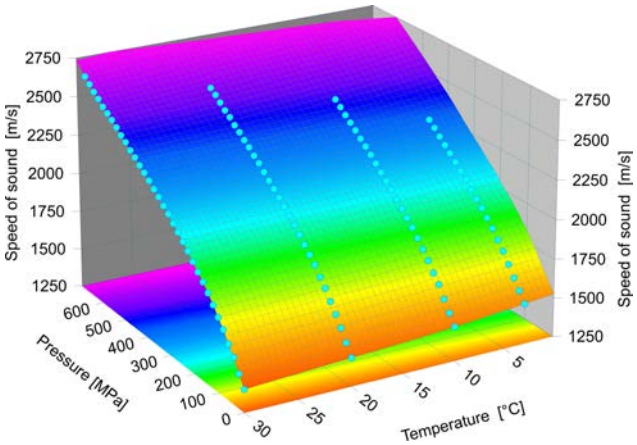

Fig. 4. Measured isotherms of the speed of sound c in the Camelina sativa oil, as a function of pressure.

Figure 4 shows the measured values of the speed of sound c in the Camelina sativa oil as a function of pressure at four different temperatures (3, 10, 20 and 30°).

The discrete set of values of the speed of sound $c(p, T)$, measured for a finite number of the selected pressures p and temperatures T, was subsequently approximated by a continuous polynomial of the order of 3 of two independent variables, i.e., the pressure p and temperature T, see Eq. (6),

$$c(p,T) = a + bp + cT + dp^2 + eT^2 + fpT + gp^3 + hT^3 + ipT^2 + jp^2T, \tag{6}$$

where the coefficients of the approximation polynomial were found to be: a = 1529.0798, b = 3.27583, c = −6.68048, d = −0.004012, e = 0.14375, f = 0.01014, g = 3.2794e–06, h = −0.00207, i = 1.8118e–05, j = −2.2857e–05.

The coefficients a, b, c, d, e, f, g, h, i, and j in Eq. (8) were fit to the experimental data applying the commercial software package Table Curve 3D (Systat, USA).

The above continuous formula (Eq. (6)) for p and T will be very convenient in further calculations of selected physico-chemical parameters, such as: adiabatic compressibility β_a, surface tension σ, and thermal conductivity k.

To estimate the quality of the continuous polynomial approximation with Eq. (6), the authors compared the values of the speed of sound c measured in the sample of the Camelina sativa oil with the numerical values provided by the polynomial approximation itself. To quantify the difference between the measured and approximated values of the speed of sound c, the authors calculated a number of the corresponding statistical parameters, such as the absolute average deviation (AAD), the maximum deviation (MD), the average deviation (Bias) and the standard deviation σ that

are defined, respectively, as follows (Comunas *et al.*, 2009)

$$\text{AAD} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{c_i^{\text{exp}} - c_i^{\text{cal}}}{c_i^{\text{exp}}}\right|, \tag{7}$$

$$\text{MD} = \max\left(100\left|\frac{c_i^{\text{exp}} - c_i^{\text{cal}}}{c_i^{\text{exp}}}\right|\right), \tag{8}$$

$$\text{Bias} = \frac{100}{N}\sum_{i=1}^{N}\frac{c_i^{\text{exp}} - c_i^{\text{cal}}}{c_i^{\text{exp}}}, \tag{9}$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N}\left(c_i^{\text{exp}} - c_i^{\text{cal}}\right)^2}{N-m}}, \quad i = 1, ..., N, \tag{10}$$

where c_i^{exp} is the experimentally measured speed of sound, c_i^{cal} represents the speed of sound calculated from the polynomial formula (Eq. (6)), N is the number of the experimental data ($N = 106$), and m is the number of adjustable parameters in the polynomial formula (in our case $m = 10$).

Statistical parameters of the polynomial approximation for the measured speed of sound c in the Camelina sativa oil are given in Table 1.

Table 1. Statistical parameters of the continuous polynomial approximation (Eq. (6)) for the measured speed of sound c in the Camelina sativa oil sample, r^2 is the coefficient of determination.

Statistical parameter	AAD [%]	MD [%]	Bias [%]	σ [m/s]	r^2
Numerical value	0.188	0.53	–0.00131	4.46	0.99982

4.2. Density ρ

The density ρ of the Camelina sativa oil sample, measured as a function of pressure and temperature, is shown in Fig. 5.

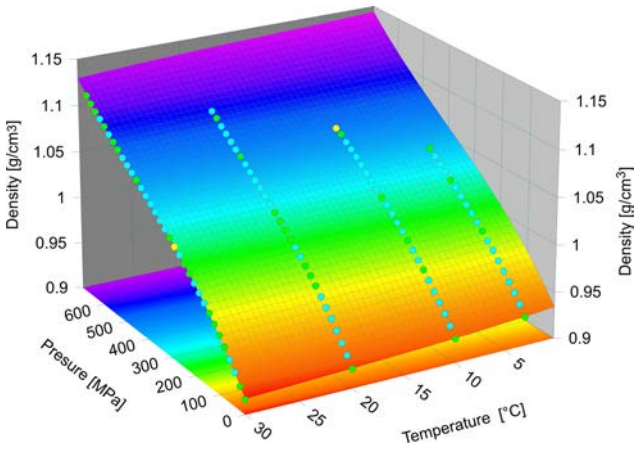

Fig. 5. Density ρ isotherms of the Camelina sativa oil measured as a function of pressure.

Figure 5 shows that the density ρ isotherms as a function of pressure have the same character as the corresponding isotherms of the speed of sound c in Fig. 4.

Similarly to the speed of sound c, the discrete set of the measured density ρ of the Camelina sativa oil was approximated by a continuous third order polynomial of two independent variables, p and T, as follows:

$$\rho(p,T) = A + Bp + CT + Dp^2 + ET^2 + FpT + Gp^3 + HT^3 + IpT^2 + Jp^2T, \tag{11}$$

where the coefficients of the approximation polynomial were found to be: $A = 0.933876$, $B = 0.0004567$, $C = -0.0009742$, $D = -5.15941\text{e}{-07}$, $E = 2.36582\text{e}{-05}$, $F = 1.96998\text{e}{-06}$, $G = 4.17576\text{e}{-10}$, $H = -3.59353\text{e}{-07}$, $I = -1.44167\text{e}{-08}$, $J = -1.97983\text{e}{-09}$.

The coefficients A, B, C, D, E, F, G, H, I, and J in Eq. (11) were fit to the experimental data employing a commercial software package Table Curve 3D (Systat, USA).

To evaluate the quality of the approximation with Eq. (11), the statistical parameters given by Eqs (7)–(10) were calculated and presented in Table 2.

Table 2. Statistical parameters of the continuous polynomial approximation (Eq. (11)) for the measured density ρ of the Camelina sativa oil, r^2 is the coefficient of determination.

Statistical parameter	AAD [%]	MD [%]	Bias [%]	σ [m/s]	r^2
Numerical value	0.0344	0.10	$-2.42 \cdot 10^{-5}$	$4.45 \cdot 10^{-4}$	0.99993

The calculated statistical parameters (AAD, MD, Bias and Standard Deviation) are lower than the experimental uncertainties of the measured speed of sound c and density ρ. This justifies the use of the values of the speed of sound c and density ρ, determined from the continuous polynomial approximations (Eqs (6) and (11)), in the following calculations (see Sec. 5) involving the measured speed of sound c and density ρ of the Camelina sativa oil.

5. High-pressure physicochemical parameters of the Camelina sativa oil evaluated from the measured speed of sound c and density ρ

All physicochemical parameters of the Camelina sativa oil sample, presented in Sec. 5, such as the acoustic impedance Z_a, surface tension σ and thermal conductivity k, were calculated in the low-pressure liquid phase region, i.e., for pressures not exceeding 660 MPa.

5.1. Acoustic impedance Z_a

The acoustic impedance Z_a is a fundamental physical parameter of liquids. It is directly correlated with the structure and composition of the liquid. The acoustic impedance Z_a is of vital importance in the ultrasonic investigation of liquids and liquid mixtures because it can provide a valuable information about the properties of liquid foodstuffs (McClements, 1995).

Acoustic impedance is also a very helpful quantity in Non-Destructive Testing of Materials. The knowledge of changes of acoustic impedance can be used to estimate the quality and composition of liquid foodstuffs (e.g. edible oils) (Ali, Ali, 2014).

Acoustic impedance Z_a which, by definitions, equals to the ratio of acoustic pressure to particle velocity of the acoustic wave, can be evaluated on the basis of the speed of sound c and density ρ as follows:

$$Z_a(p,T) = \rho(p,T) \cdot c(p,T) \quad [\mathrm{kg}/(\mathrm{m}^2 \cdot \mathrm{s})]. \tag{12}$$

The dependence of the acoustic impedance Z_a of the low-pressure phase of the Camelina sativa oil on pressure p and temperature T (evaluated from Eqs (6), (11), and (12)) is presented in Fig. 6.

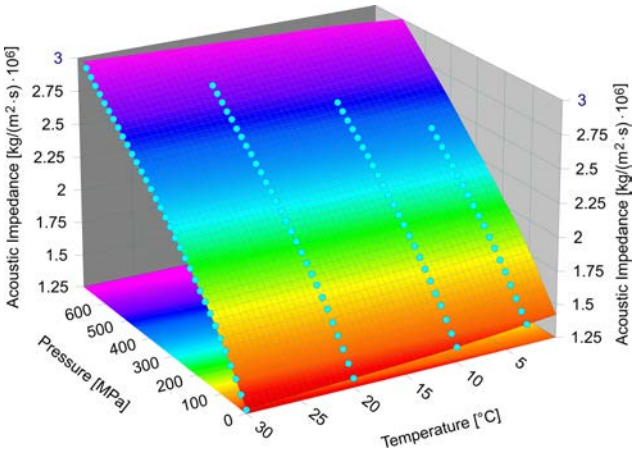

Fig. 6. Acoustic impedance Z_a of the low-pressure phase of the Camelina sativa oil, as a function of pressure p and temperature T.

5.2. Surface tension σ

Surface tension is one of the key physicochemical parameters of liquid foodstuffs necessary in the optimization of high-pressure food processing. Precise control of surface tension is crucial in high-pressure food processing.

The surface tension σ is defined as the energy $\mathrm{d}W$ (Gibbs free energy) that must be supplied to increase the surface area of a liquid by one unit $\mathrm{d}A$, namely (Auerbach, 1948):

$$\sigma(p,T) = \frac{\mathrm{d}W}{\mathrm{d}A} = 6.33 \cdot 10^{-10} \cdot \rho(p,T) \cdot c^{3/2}(p,T) \quad [\mathrm{N/m}], \tag{13}$$

where c and ρ are speed of sound and density, respectively.

Figure 7 displays the dependence of the surface tension σ in the Camelina sativa oil sample versus pressure p and temperature T (computed from Eqs (6), (11), and (13)).

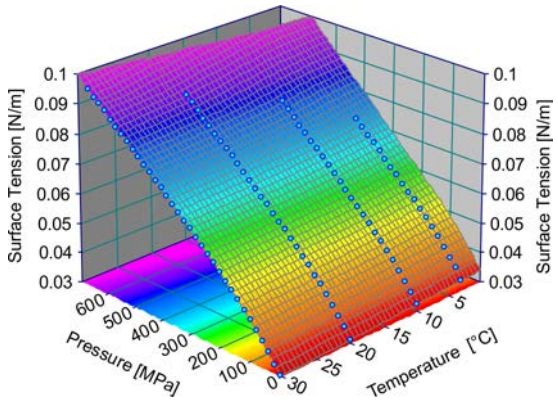

Fig. 7. Surface tension σ (evaluated values are indicated by circles) of the Camelina sativa oil, as a function of pressure p and temperature T.

5.3. Thermal conductivity k

Thermal conductivity k reflects the rate at which heat is conducted in a medium. Thermal conductivity k of materials is a relevant thermophysical parameter for heat transfer modeling and evaluating thermal profiles in high-pressure technological processes. In quantitative terms, the thermal conductivity specifies the quantity of heat that will be transferred in a unit of time across a unit thickness of the material if a unit temperature gradient occurs through this thickness (Singh, Heldman, 2009).

To evaluate the thermal conductivity k, we applied the modified Bridgman formula (Bird *et al.*, 1976). This formula follows the theory of heat conduction in liquids based on the Debye's concept, in which the phenomenon of heat conduction is described in terms

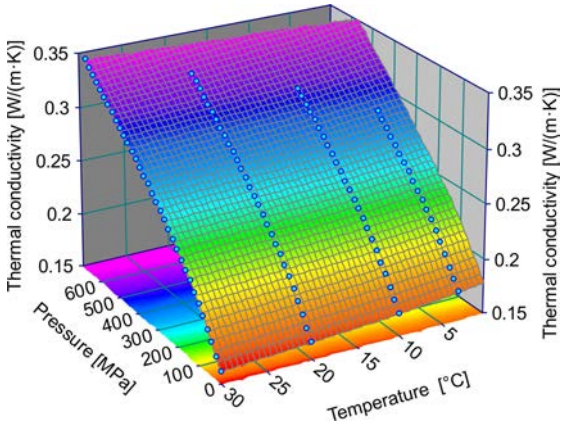

Fig. 8. Thermal conductivity k of the Camelina sativa oil, as a function of pressure p and temperature T.

of thermal phonons and anharmonic vibrations of the particles in the medium (quasi-lattice):

$$k(p,T) = 3 \cdot \delta \cdot \left(\frac{N}{M}\right)^{2/3} \cdot \rho^{2/3}(p,T) \cdot k_B \cdot c(p,T) \quad [\mathrm{W/(m \cdot K)}], \tag{14}$$

where δ is the correction factor, $\delta = 3.844$ for Camelina sativa oil, $N = 6.02214 \cdot 10^{23}$ mol^{-1} is the Avogadro number, M is the molar mass ($M = 0.8989$ kg/mol for Camelina sativa oil), $k_B = 1.38065 \cdot 10^{-23}$ J/K is the Boltzmann's constant.

Figure 8 shows the dependence of the thermal conductivity k of the Camelina sativa oil, versus pressure and temperature, calculated from Eqs (6), (11), and (14).

6. Discussion

The objective of the research, presented in this paper, was to investigate an impact of high pressure on the physicochemical parameters of liquids (on the example of Camelina sativa oil), by using a novel (in the high-pressure range) ultrasonic methods. Subsequently, on the basis of measured isotherms of the speed of sound and density, high-pressure isotherms of various physicochemical parameters of the Camelina sativa oil, such as the acoustic impedance Z_a, surface tension σ and thermal conductivity k were evaluated.

The physicochemical parameters of the Camelina sativa oil change significantly with increasing temperatures and pressures. For example, the acoustic impedance Z_a is affected mostly by the changes of pressure p, i.e., it increases about two and half times when the pressure increases from the atmospheric pressure (0.1 MPa) to 660 MPa at a temperature of 30°C, see Fig. 6. Similarly, the thermal conductivity k depends mainly on the pressure, i.e., it increases approximately two times when the pressure rises from 0.1 to 660 MPa at a temperature of 30°C, see Fig. 8.

According to the Bridgman formula, the thermal conductivity is inversely proportional to the distance between the adjacent particles in the medium (quasi-lattice). This distance diminishes with the increase in pressure and increases with temperature augmentation. Therefore, the thermal conductivity of the Camelina sativa oil grows with increasing pressure and diminishes (slightly) with the rise of temperature, see Fig. 8.

7. Conclusions

Main implications following from the results of research presented in this paper can be summarized as follows:

1) At present, only the ultrasonic methods can be efficiently used in an on-line monitoring of high-pressure physicochemical parameters of liquids (e.g., Camelina sativa oil). By contrast, the conventional mechanical methods cannot be extended to the high pressure region.
2) Application of efficient signal processing procedures enhances markedly the accuracy of high-pressure ultrasonic measurements in liquids.
3) Knowledge of quantitative and qualitative characteristics of high-pressure thermophysical parameters of liquid foodstuffs, such as the Camelina sativa oil, is of crucial importance in modeling and optimization of high-pressure technological processes of preservation and conservation of liquid foodstuffs as well as in jet-biofuels technology.

The determination of Camelina sativa oil selected physicochemical parameters, such as the acoustic impedance Z_a, surface tension σ and thermal conductivity k, is an original authors' contribution to the state-of-the art.

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