What Information about High-Pressure Thermophysical Properties of Liquids Can Provide Low-Intensity Ultrasonic Waves

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Abstract—**In many technological processes liquids are subjected to high pressures (up to 800 MPa), e.g., in high pressure preservation of liquid foodstuffs. Similarly, in modern fuel injection systems for diesel engines, biofuels are subjected to pressures up to 300 MPa. In such severe conditions, thermophysical properties of liquid change considerably. Conventional methods for measuring thermophysical properties of liquids completely fail at high pressure conditions. Hence, these methods are of no use in real industrial conditions, during on-line monitoring of industrial processes. Thus, there exist a strong demand for industrial grade measurements methods, which can be used to monitor on-line the actual parameters of liquids. A very promising solution is offered by ultrasonic techniques which are particularly suitable for measurements of thermophysical properties of liquids at high pressures. In addition, the ultrasonic methods (that use low-intensity ultrasonic waves) are totally non-destructive and can be fully automated in real time.**

Keywords—ultrasonic methods, thermophysical properties, high pressure, acoustic impedance, thermal conductivity

I. INTRODUCTION

The increasingly common method applied for food preservation and processing is to treat food products with high hydrostatic pressure. For example, vegetable oils are processed using high hydrostatic pressure up to 700 MPa [1]. In order to optimize the efficiency of high-pressure technological processes and to design new systems and devices in the food industry, it is necessary to know the high-pressure physicochemical parameters of processed liquid foodstuffs. Unfortunately, there are no data on these parameters in the literature. This is due to the fact that traditional methods of measuring thermophysical parameters of liquids fail in the high pressure range. Moreover, these methods are of no use in real industrial conditions, especially in an on-line monitoring of technological parameters of liquids. A similar problem occurs in the case of biofuels subjected to high pressure (of the order of 300 MPa) in common rail fuel injection systems in diesel engines.

The solution to the presented above problem is the use of ultrasonic methods [2-6], i.e., measurements of the velocity and attenuation of bulk and surface ultrasonic waves. It is worth noting that the intensity of these waves is low ($< 1\,W/m^2$). These ultrasonic waves can propagate directly in an investigated liquid or in the surface wave waveguides loaded on their surface by the investigated liquid. Ultrasonic methods have been used so far almost exclusively at atmospheric pressure. There is a direct relationship between the speed of sound and the thermophysical parameters of the liquid. For that reason, from measuring the speed of sound in an investigated liquid subjected to high pressure and simultaneously measuring the density of liquid, one can evaluate the following thermophysical parameters of liquids:

1) adiabatic compressibility	β_a
2) isothermal compressibility	β_T
3) surface tension,	σ
4) thermal conductivity	k
5) thermal diffusivity	a
6) thermal effusivity	e
7) thermal expansion coefficient	α_p
8) thermal pressure coefficient	γ
9) internal pressure	P_{int}
10) intermolecular free length	L_f
11) specific heat capacity	c_p
12) specific heat ratio	κ
13) Van der Waals constant	b
14) effective Debye temperature	Θ_D
15) Grüneisen constant	Γ
16) nonlinear parameter	B/A
17) acoustic impedance	Z_a

Other high-pressure thermophysical parameters can be determined by measuring the liquid viscosity as a function of pressure and temperature. Classical methods for measuring liquid viscosity at high pressures (over 200 MPa), e.g., the Höppler method that uses falling ball, are also useless. The solution of this problem was given by the Authors. We have established a new method to measure the viscosity of liquids in the high-pressure range [7]. In this method , sensors using Love or Bleustein-Gulyaev surface waves are applied. Knowing the speed of sound measured in parallel with the density and viscosity of an investigated liquid one can determine, among others:

1) free volume V_f

2) relaxation time τ

3) absorption coefficient α

It is worth noticing that such physicochemical parameters of biofuels as: surface tension, adiabatic compressibility, viscosity and density are crucial in the process of biofuels atomization. These parameters determine the size of biofuel droplets and consequently the efficiency of diesel engine operation.

It should be stressed that the ultrasonic technology is at present the only technology which can provide on-line measurement in high-pressure conditions. Other advantages of the ultrasonic technology (that employ low-intensity waves) is, its non-intrusiveness and a possibility of full automation.

In present work, as an example of the possibility of using ultrasonic methods in the high pressure range, we present evaluated by the authors isotherms of the acoustic impedance, thermal conductivity and surface tension of Camelina sativa oil. This oil can be used for consumption purposes due to its health-promoting properties [8], as well as a raw material for the production of biofuels for diesel engines [9] and jet biofuels [10]. At last year's IUS conference, we presented the results of the study of high-pressure phase transitions in this oil, detected for the first time by the authors [11]. The results of the evaluation of high-pressure physicochemical parameters of Camelina sativa oil presented in this work are novel and have not been yet published in the world literature.

The Authors believe that the results of research, presented in this paper, have broadened our knowledge about the high-pressure parameters of liquid foodstuffs at various temperatures and can be useful in the actual engineering practice in the accurate design of new technological processes, systems and devices in the food and chemical industries.

II. MATERIAL AND METHODS

A. *Investigated liquid*

The cold-pressed Camelina sativa virgin oil, used in our investigation, was manufactured by the Polish company “Złoto Polskie” (Kalisz, Poland). This Camelina sativa oil was used as an exemplary liquid in the investigations performed in this work.

B. *Experimental Setup*

Measurements of high-pressure physicochemical parameters of liquids were performed in the computerized ultrasonic setup shown in Fig. 1.

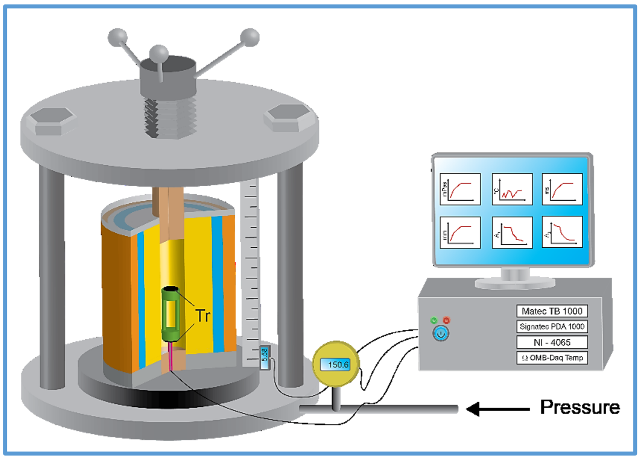

Fig.1. Basic diagram of the computerized ultrasonic setup used in measurements of the speed of sound c and density ρ of investigated liquids subjected to high pressures at various temperatures. The “Tr” symbol denotes ultrasonic transducers.

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 longitudinal waves used in measurements was 5 MHz. The speed of sound in the liquid was determined from the time of flight measured using the cross-correlation method.

The changes in the liquid density ρ, as a function of pressure for various temperatures, were parallel 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 [3, 4, 6].

III. EXPERIMENTAL RESULTS

Figure 2 displays the measured values (indicated by circles) of the speed of sound in Camelina sativa oil as a function of pressure and temperature.

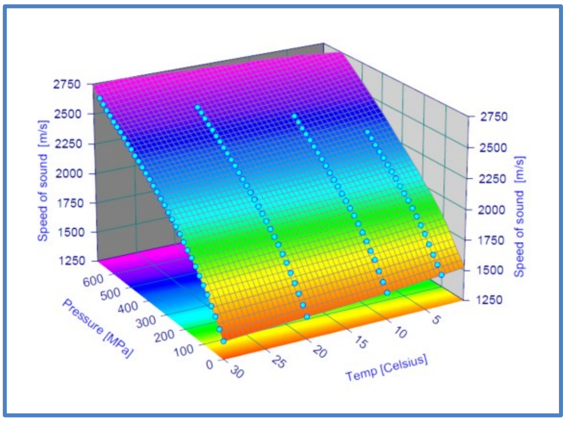

Fig. 2. Measured isotherms of the speed of sound c in the Camelina sativa oil, as a function of pressure p, (measured values are indicated by circles), f = 5 MHz.

The measured dependence of the speed of sound $c(p, T)$ on pressure p and temperature T was subsequently approximated by a polynomial of the 3rd order of two independent variables, i.e., the pressure p and temperature T, see Eq.1.

$$c(p,T) = a + bp + cT + dp^2 + eT^2 + fpT + gp^3 + \\ +hT^3 + ipT^2 + jp^2T \qquad (1)$$

where: the coefficients of the polynomial are as follows: 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 measured density ρ isotherms of the Camelina sativa oil are shown in Figure 3.

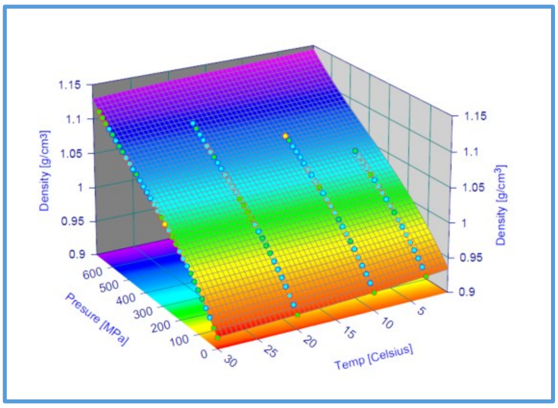

Fig. 3. Density ρ isotherms of the Camelina sativa oil measured as a function of pressure p (measured values are indicated by circles).

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:

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

where: the coefficients of the approximation polynomial were found to be:

A = 0.933876, B = 0.0004567, C = -0.0009742, D = -5.15941e-07, E = 2.36582e-05, F = 1.96998e-06, G = 4.17576e-10, H = -3.59353e-07, I = -1.44167e-08, J= -1.97983e-09.

The values of the speed of sound c and density ρ, determined from the polynomial approximation Eqs.1 and 2, will be used in the following calculations (see Section IV) involving the measured speed of sound c and density ρ of the Camelina sativa oil sample.

IV. HIGH-PRESSURE PHYSICOCHEMICAL PARAMETERS OF THE CAMELINA SATIVA OIL EVALUATED FROM THE MEASURED SPEED OF SOUND c AND DENSITY ρ

A. *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 [12].

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) [13].

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:

$$Z_a(p,T) = \rho(p,T) \cdot c(p,T) \qquad (kg/m^2 \cdot s) \qquad (3)$$

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.1, 2 and 3) is presented in Fig.4.

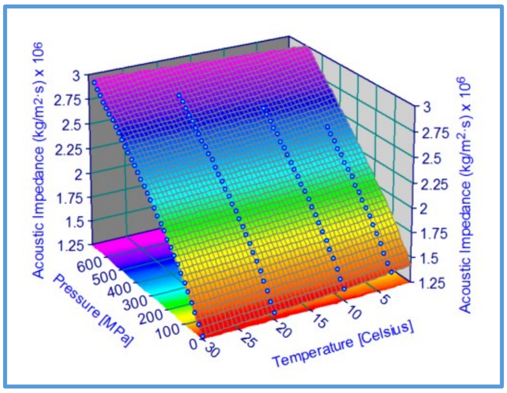

Fig. 4. Acoustic Impedance Z_a of the low-pressure phase of the Camelina sativa oil (evaluated values are indicated by circles), as a function of pressure p and temperature T.

B. *Surface Tension* σ

The surface tension σ is defined as the energy dW (Gibbs free energy) that must be supplied to increase the surface area of a liquid by one unit dA, namely:

$$\sigma(p,T) = \frac{dW}{dA} = 6.33 \cdot 10^{-10} \cdot \rho(p,T) \cdot c^{3/2}(p,T) \; [N/m] \qquad (4)$$

Figure 5 displays the dependence of the surface tension of Camelina sativa oil on pressure and temperature calculated from Eqs. (1), (2), and (4).

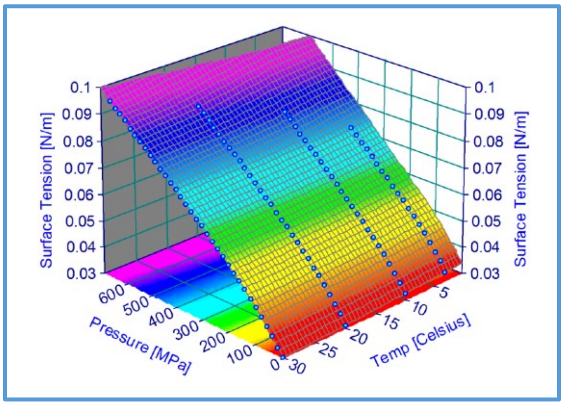

Fig.5. Surface tension σ of the low-pressure phase (evaluated values are indicated by circles) of the Camelina sativa oil, as a function of pressure p and temperature T.

C. *Thermal Conductivity k*

To evaluate the thermal conductivity k, we applied the modified Bridgman formula [14]. 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 of thermal phonons and anharmonic vibrations of the particles in the medium (quasi-lattice):

$$k(p,T) = 3 \cdot \delta \cdot \left(\frac{N}{M}\right)^{2/3} \cdot \rho^{2/3}(p,T) \cdot k_B \cdot c(p,T)\ (W/mK) \tag{5}$$

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

Fig. 6 shows the dependence of the thermal conductivity k of the low-pressure phase of the Camelina sativa oil, versus pressure and temperature, calculated from Eqs.1, 2 and 5.

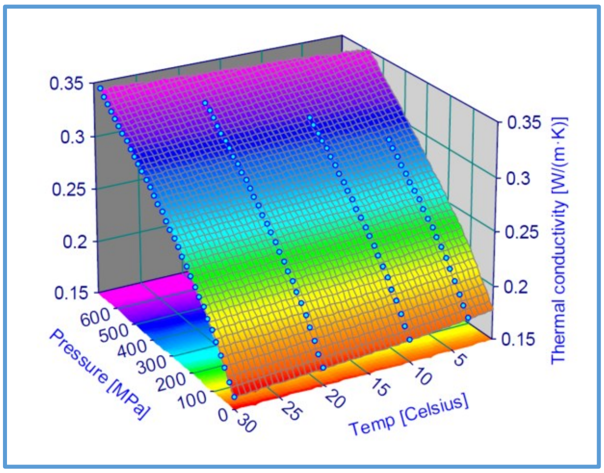

Fig.6. Thermal conductivity k of the low-pressure phase (evaluated values are indicated by circles) of the Camelina sativa oil, as a function of pressure p and temperature T.

V. DISCUSSION

Changes in pressure and temperature influence considerably physicochemical (thermophysical) properties of liquids (e.g., oils). Such quantities (that characterize physicochemical properties of liquids) as: speed of sound, thermal conductivity, acoustic impedance and surface tension may increase more than two times when the pressure rises from atmospheric pressure up to 600 MPa, see Figs. 2, 4-6.

Large variation of physicochemical parameters of the investigated liquids versus pressure demonstrates the need for knowledge of these parameters in the entire range of considered pressures. It should be noted that low-intensity ultrasonic waves are inherently suitable for measuring physicochemical parameters of liquids in the high pressure range.

VI. CONCLUSIONS

The applicability of low-intensity ultrasonic waves to investigate high-pressure physicochemical parameters of liquids has been confirmed experimentally by measuring the high-pressure isotherms of speed of sound and density of Camelina sativa oil that was chosen as an exemplary liquid. The results of our investigations show that:

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 low-intensity ultrasonic waves can be very convenient to characterize the high-pressure thermo-physical properties of biofuels and raw materials for the production of biofuels, without the necessity for complex and time consuming off-line experimental investigations.

3) Knowledge of high-pressure thermophysical parameters of liquid foodstuffs, such as the Camelina sativa oil, is of crucial importance in design and optimization of high-pressure technological processes, systems and devices in the food industry as well as in jet-biofuels technology.

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