Investigation of regular and anomalous behavior of liquid media under high pressure using ultrasonic methods

Piotr Kielczynski, Marek Szalewski, Andrzej Balcerzak, Krzysztof Wieja
Institute of Fundamental Technological Research
Polish Academy of Sciences
Pawinskiego 5B, 02-106 Warsaw, Poland
pkielczy@ippt.pan.pl

Stanislaw Ptasznik
Department of Fat and Meat Technology
Institute of Agricultural and Food Biotechnology
Jubilerska 4, 04-190 Warsaw, Poland

Aleksander J Rostocki
Department of Physics
Warsaw University of Technology
Koszykowa 75, 00-662 Warsaw, Poland

***Abstract*—In many industrial technological processes, liquids are subjected to high pressures, e.g., in the high pressure food preservation. Similarly, in modern fuel injection systems for diesel engines, biofuel is subjected to a pressure up to 300 MPa. In such conditions, in liquids, high-pressure phase transitions (solidification) can occur that substantially increase the density and liquid viscosity. This solidification can result in significant problems with engine failure under cold-start conditions. This is an evident recipe for disaster, since the engine and its accessories would be very likely quickly destroyed. Thus, it is important to determine at what pressures and temperatures phase transitions occur. Conventional mechanical methods for measuring physicochemical properties of liquids at these extreme conditions do not operate. By contrast, ultrasonic techniques are very suitable for measurements of physicochemical properties of liquids at high pressure, since they are non-destructive, can be fully automated and are characterized by the absence of moving parts. The aim of this work is to study the high-pressure physicochemical properties of liquids (exemplified by a Camelina sativa - false flax oil) using novel ultrasonic methods.**

Keywords—high pressure; ultrasonic methods; phase transitions; Camelina sativa

I. INTRODUCTION

In many industrial technological processes, liquids are subjected to high pressures, e.g., during the high pressure food preservation. Similarly, in modern fuel injection systems (common rail) in diesel engines, biofuels are subjected, in a prolonged time interval, to pressures as high as 300 MPa. In such extreme conditions, liquids may undergo phase transitions that usually are characterized by a substantial increase of the density and liquid viscosity. This phenomenon can be very detrimental for the engine operating parameters as well as for exploitation and maintenance of the technological equipment. The liquids with high molar volumes, like oils, undergo phase transitions (solidification) at pressures in the range of several hundred MPa. As result of the high-pressure phase transition, a polymorphous solid-like phase, arises [1]. At the same time thermophysical properties of oils change significantly. These effects are transient in character and after depressurization the liquid returns almost exactly to its original state (properties).

Lipids (e.g. oils) are pressure-sensitive, since their assemblies are governed by hydrophobic interactions. In fact, high pressure significantly alters the interatomic distance between molecules thus influences physical or chemical reactions involving volumetric changes including phase transition from liquid to solid-like phase [2].

There is still scarce information concerning high-pressure phase transitions in oils. Similarly, there is a lack of information about high-pressure thermophysical properties of oils. Such an information is indispensable for optimal design, modeling and exploitation of high-pressure devices and technological systems. Unfortunately, conventional methods for measuring physicochemical properties of liquids cannot be extended to these extreme conditions of operation. Hence, these methods are useless in industrial conditions, especially in monitoring on-line technological parameters of liquids. As a result, there exist a strong demand for industrial grade measurements methods, which can be used to monitor on-line actual parameters of liquids. One possible alternative is offered by ultrasonic techniques [3-7], which are particularly suitable for measurements of physicochemical properties of liquids at high pressures. In addition, the ultrasonic methods are non-intrusive, non-destructive and can be fully automated.

The aim of this work is to study high-pressure phase transitions and the corresponding changes in physicochemical properties of liquids (exemplified by Camelina sativa - false flax oil), using ultrasonic methods. The measurements have been performed for the speed of sound and density in Camelina sativa oil under high pressure conditions at various temperatures. Camelina sativa oil has been chosen because of its numerous potential applications. Camelina sativa oil is a promising raw material to produce biofuels for aviation. Camelina-based jet fuels are successfully tested by US Air Forces and Navy as well

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as by commercial airlines such as: Japan Airlines and KLM. Camelina sativa (false flax) has also several favorable agronomic characteristics.

The discovery of high-pressure phase transitions in Camelina sativa oil and the investigation of their kinetics, by means of ultrasonic methods, is in our opinion an original contribution of the Authors into the state-of-the-art.

II. MATERIALS AND METHODS

A. Investigated Liquid

Table I. Determination of fatty acid composition

Type of FA	**Content, %**
Tetradecanoic 14:0	0,1 ± 0,05
Heksadecanoic 16:0	5,5 ± 0,3
(Z)-9-hexsadecaenoic 16:1	0,1 ± 0,05
Heptadecanoic 17:0	0,1 ± 0,05
Octadecanoic 18:0 *(stearic)*	2,8 ± 0,2
(Z)-9-octadecaenoic 18:1cis9 *(oleic)*	15,8 ± 0,9
(Z)-11-octadecaenoic 18:1cis11 *(oleic)*	0,7 ± 0,1
(Z,Z)-9,12-octadecadienoic 18:2 *(linoleic)*	17,0 ± 0,6
(Z,Z,Z)-9,12,15-octadecatrienoic 18:3 *(liniolenic)*	34,2 ± 2,0
Eicosanoic 20:0	1,4 ± 0,1
(Z)-11-icosaenoic 20:1	14,7 ± 0,8
Dokozanoic 20:2	2,0±0,05
(Z,Z,Z)-8,11,14-icosatrienoic 20:3 *(dihomo-γ-linolenic)*	1,4 ± 0,1
Docosanoic 22:0	0,3 ± 0,05
(Z)-13-dokozaenowy 22:1 *(Erucic)*	2,7±0,2
(Z,Z,Z,Z)-9,12,15,18-eicosatetraenoic 22:4 *(arachidonic)*	0,4±0,1
Tetracosanoic 24:0	0,2 ± 0,05
(Z,Z,Z,Z,Z)- 7,10,13,16,19-docosapentaenoic 22:5	0,6±0,1
FA saturated	10,4
FA monounsaturated	34,0
FA polyunsaturated	55,6
FA omega 3	36,6

In this work, as an example liquid, Camelina sativa (false flax) oil was chosen for investigation. Camelina sativa (false flax) is an ancient oil and a food crop that has gained recently a renewed interest due to its high poly-unsaturated fatty acids and n-3 fatty acid content and for its potential for biodiesel production. Benefits for health of Camelina oil was also confirmed. Possible industrial applications of Camelina include, among others, environmentally safe paintings, coatings, cosmetics, animal feeds and low emission biodiesel fuels [8,9]. Synthetic isoparaffin-rich fuels produced by hydroprocessing camelina oil showed great promise as an alternative to petroleum jet and diesel fuel [10]. Camelina is adapted to various climatic conditions, has low nutrient requirements and good resistance to diseases and pests. A number of papers on the physicochemical and thermodynamic properties of camelina oil have been published [11,12], but there is a lack of studies on the properties of this oil in the high pressure range. The fatty acid composition of the investigated Camelina sativa oil has been evaluated by means of the gas chromatography method using Hewlett-Packard HP 6890 device working in conjunction with a Flame Ionization Detector and a high-polar column BPX70. The analysis was conducted following the AOCS Cd 11b-91 method and was carried out according to the standard ISO 5508. The composition of the investigated Camelina sativa oil is presented in Table I.

B. Experimental setup

Ultrasonic measuring setup is presented in Fig.1.

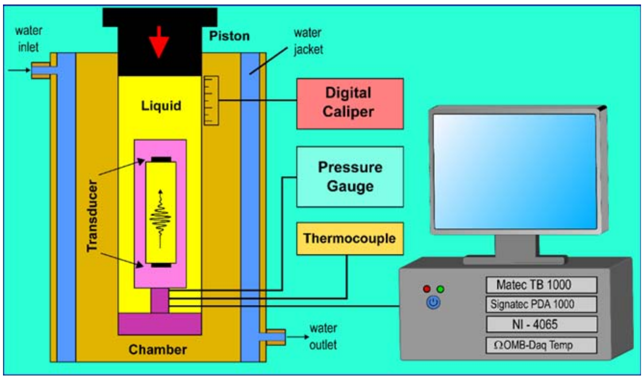

Fig. 1 Ultrasonic computerized experimental setup for measuring the speed of sound c and density ρ of liquids under high pressures conditions and various temperatures.

The computerized ultrasonic measuring setup is presented in Fig.1. In this study, phase transitions and physicochemical properties of the investigated liquid (Camelina sativa oil) were evaluated in the high-pressure range, using bulk longitudinal ultrasonic waves (f = 5 MHz). The speed of sound in the liquid was determined from the time of flight measured with the cross-correlation method. At the same time, changes in liquid density, as a function of pressure for various temperatures, were specified from the changes in the volume of the investigated oil sample in a high-pressure chamber.

Measuring methods and the experimental setup were thoroughly described in previous papers of the authors [13-16]. The sound velocity and density of Camelina sativa oil isotherms have been evaluated. The measurements were performed in the pressure range from 0.1 MPa up to 650 MPa and for temperatures from 3 °C to 30 °C (f = 5 MHz).

II. RESULTS

The results of measurements reported in this work (speed of sound and density of Camelina sativa oil), were performed over the entire pressure range, i.e., commencing from an atmospheric pressure up to the pressure at which the phase transition begins, next during the phase transition, and finally during the compression of the newly obtained high-pressure phase. The measurements were carried out at a pressure range from 0.1 to 650 MPa, and at temperatures ranging from 3 to 30 ℃.

Figure 2 shows the measured values of the speed of sound in the Camelina sativa oil as a function of pressure at four different temperatures ($3, 10, 20$ *and* 30 ℃).

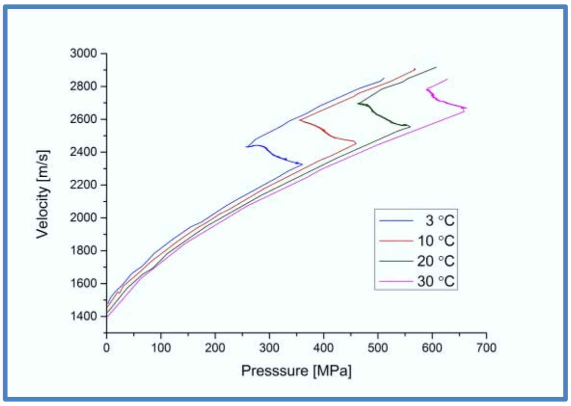

Fig.2. Isotherms of the speed of sound in Camelina sativa oil as a function of pressure (f = 5 MHz).

The dependence of the Camelina sativa oil density on pressure and temperature is shown in Figure 3.

The kinetics of high-pressure phase transitions in Camelina sativa oil at various temperatures is presented in Fig.4.

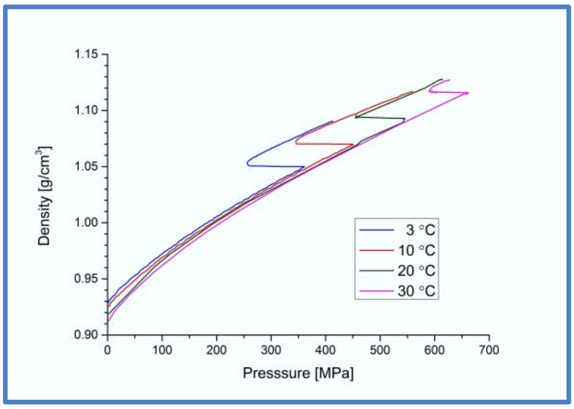

Fig.3. Camelina sativa oil density isotherms as a function of pressure.

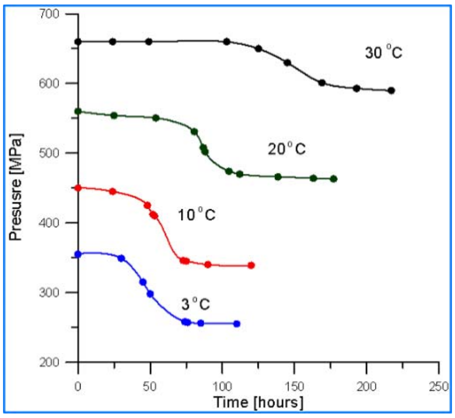

Fig.4. Kinetics of high-pressure phase transitions in Camelina sativa oil for various temperatures.

III. DISCUSSION

As it is seen in Figs.2 and 3, the regions of high pressure phase transitions are clearly visible. In fact, in the region of high pressure phase transition, the measured thermophysical parameters of the oil, i.e., the speed of sound and density of Camelina sativa oil exhibit abrupt discontinuities. A spontaneous pressure drop during the phase transition is of the order of 100 MPa. The change of the speed of sound during the high-pressure phase transition is very high and can reach 200 m/s (~ 10%). High-pressure phase transition region separates the regions of low-pressure phase and high-pressure phase respectively.

The Camelina sativa oil has a high fatty acid content with three unsaturated bonds and complex hydrocarbon chains. Fatty chains due to their complex shape enter reluctantly into compound complexes during pressure rise. This Camelina sativa oil property can explain a very long incubation time of the high pressure phase transition, as well as a long duration of the high-pressure phase transition, see Fig.4. For example, at a temperature $t = 30$ ℃ the incubation time equals, approximately, 120 hours and the subsequent phase transition lasts approximately 80 hours.

IV. CONCLUSIONS

The assumption on anomalous behavior of the Camelina sativa oil at high pressure range was confirmed experimentally using ultrasonic methods, such as measurement of speed of sound and density.

In particular the results of our research show that:

1) In Camelina sativa oil the high pressure phase transitions do occur. Isotherms of the sound velocity and density as a function of pressure exhibit sharp discontinuities in the region of high-pressure phase transitions.

2) The incubation time (the time between piston stopping and the beginning of the phase transition) of the phase transition in Camelina sativa oil is large and depends on the temperature (e.g., for t = 3 °C this time is 24 hours, for t = 30 °C amounts to 120 hours).

3) The duration time of the high-pressure phase transition is also relatively long (e.g., for t = 3 °C this time interval equals 24 hours, and for t = 30 °C the duration of the phase transition is equal to 80 hours).

4) The ultrasonic technique, i.e., the measurement of the speed of sound in liquids, is at present a unique technology that allows for an on-line detection and investigation of high-pressure phase transitions occurring in liquids.

The results of this study allow for better understanding of the physicochemical properties and the nature of molecular interactions in the liquids. They can also be useful for developing models of thermophysical phenomena occurring in liquids at high pressures.

The results of research conducted in this study can also be useful in the fuel industry, due to the fact that the Camelina sativa oil is an attractive raw material in production of biofuels for aviation applications [17,18].

The discovery and investigation (using ultrasonic methods) of high-pressure phase transitions in Camelina sativa oil is an original contribution of the authors to the state-of-the-art.

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