

# Ultrasonic studies of physicochemical parameters of biofuels in a broad range of pressures and temperatures

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**Abstract**—The aim of the study was to investigate the phase transitions in biofuel components by using ultrasonic methods on the example of methyl esters of fatty acids, in a wide range of pressures (from atmospheric pressure to 400 MPa) and for various temperatures from 5 to 20 °C. Investigation of phase transitions in biofuels at high pressures is of great importance in the design of injection systems in modern diesel engines (common rail). Direct examination of phase transitions in liquids under high pressure, using classical methods, is very difficult. To overcome this disadvantage, the authors applied ultrasonic methods (viscosity measurement), which in contrast to the classical methods allow in a relatively simple way the investigation high-pressure properties of liquids. Viscosity was measured by the original method that uses ultrasonic surface waves of the Bleustein-Gulyaev type, developed by the authors at the Institute of Fundamental Technological Research in Warsaw. From the measured viscosity isotherms, the occurrence and kinetics of high-pressure phase transitions in methyl esters were evaluated.

**Keywords**—ultrasonic Bleustein-Gulyaev waves, viscosity measurements, biofuels, high-pressure phase transitions

## I. INTRODUCTION

Due to climate change on Earth (global warming), interest in the use of motor fuels of vegetable origin (biofuels) increases[1]. The physicochemical properties of biofuels over a wide range of pressures and temperatures are still not fully understood and investigated.

Investigation of physicochemical properties of biofuels and liquids in the range of high pressures is extremely difficult by using conventional methods. That is why, recently to determine the physicochemical parameters of liquids under high pressure ultrasonic methods have been applied [2-8]. These methods (measurement of the speed of sound in the liquid and the viscosity of the liquid) allow

in a relatively simple way determination of the physicochemical parameters of liquids under high pressure [9-13].

Viscosity of biofuels at high pressure is a key physicochemical parameter determining their quality as a fuel used in Diesel engines.

Measurement of the viscosity of biofuels by conventional methods (e.g., falling ball type) is not practically possible in the high pressure range (over 200 MPa).

In this work, in order to overcome this drawback, the authors applied an original method employing surface ultrasonic waves of the Bleustein-Gulyaev (BG) type. This method, developed by the authors, allows in a relatively simple way measurement of the viscosity of the liquid in the pressure range up to 1 GPa [2, 14, 15]. These waves (BG) propagate in the piezoceramic waveguide placed in the high-pressure chamber. The liquid acts on the surface of the waveguide. As the pressure increases liquid viscosity increases and therefore the amplitude of the surface BG wave decreases. From changes in BG wave attenuation we determine the viscosity of the liquid.

Viscosity measurement was used by the authors to detect and investigate high-pressure phase transitions in biofuels and study their kinetics.

This method is non-destructive method, that can be computerized. Measurements of high-pressure phase transition kinetics and viscosity of biofuels (methyl esters) at high pressure conditions and various temperatures (isotherms) is a novelty.

## II. EXPERIMENTAL SETUP

The samples of fatty acid methyl ester (FAME) obtained by esterification of rapeseed oil were investigated. The main compounds of a sample were: 60.7% methyl esters of oleic acid (C18:1), 19.9% methyl esters of linoleic acid (C18:2), and 9.1% of linolenic acid (C18:3), with a vestigial content of other unsaturated and saturated free fatty acids. Its chemical composition was evaluated by means of the gas chromatography method using Hewlett-Packard HP 6890 device with Flame Ionization Detector and high-polar column BPX70. The analysis was conducted following the AOCS Cd 11b-91 method and was performed according to the ISO 5508 and ISO 5509 norms. Composition of the investigated olive oil is presented in Table I.

Table I

Fatty acids content in the FAME sample according to ISO-5508.

Fatty acid	Amount (%)
C 14:0	0.1
C 16:0	4.5
C 16:1	0.3
C 17:0	0.1
C 17:1	0.1
C 18:0	1.8
C 18:1 cis9	58.1
C 18:1 cis11	2.6
C 18:2 cc	19.9
C 18:3 ccc	9.1
C 20:0	0.6
C 20:1	1.5
C 20:2	0.1
C 22:0	0.3
C 22:1	0.5
C 24:0	0.2
C 24:1	0.2

The experimental setup for measuring the viscosity of liquids under high pressure at various temperatures is presented in Fig. 1. High pressure was generated in a thick-walled cylinder chamber with a simple piston and Bridgman II sealing system. The piston displacement was controlled by a digital caliper. For pressure measurements a typical 75  $\Omega$  manganin transducer was used. Its resistance was measured by the National Instruments multimeter computer card. The temperature in the chamber was measured using T-type thermocouple (Cu-

constantan). A thermostatic bath was circulating in a thermostatic jacket around the chamber. The viscosity sensor (B-G waveguide) was placed inside the high-pressure chamber.

The sending-receiving piezoelectric transducer, attached to the B-G wave waveguide, was driven by the TB-1000 pulser-receiver computer card (Matec, USA). The TB-1000 pulser generated the rf (radio frequency) tone bursts with a frequency  $f = 2$  MHz and length equal to 0.5  $\mu$ s. The B-G wave impulse generated by the transducer was reflected in multiple ways between two opposite edges of the B-G wave waveguide. The signals received by the transducer were amplified by the TB-1000 receiver and sent into the PDA-1000 digitizer card (Signatec, USA). This card sampled and digitized the input analog signals. A computer program that controlled the operation of the computer cards and data acquisition was written in C++ language.

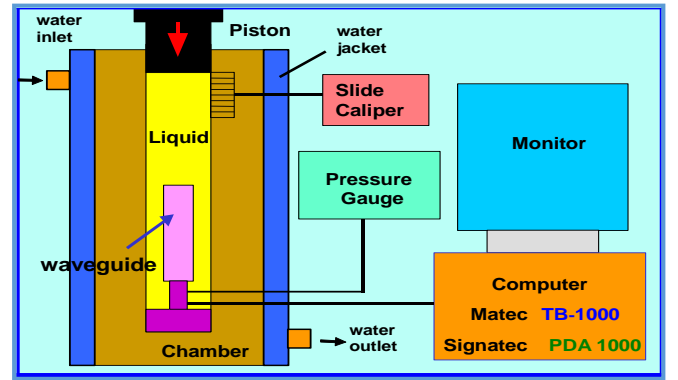


Fig.1. Ultrasonic setup for measuring the viscosity of biofuels under high pressure.

## III. MEASURING METHOD OF BIOFUELS VISCOSITY

The liquid covering the waveguide surface loads it mechanically. The value of this load is proportional to the value of the mechanical impedance  $Z$  of the liquid.

By applying the perturbation method [16], one can prove that the change in the complex propagation constant  $\gamma$  of the B-G wave produced by viscoelastic liquid loading is as follows [17]:

$$\Delta\gamma = -j \left( \frac{|u_3|_{x_2=0}^2}{4 \cdot P} \right) \cdot Z_L = -j \cdot K \cdot Z_L \quad (1)$$

where:  $j = (-1)^{1/2}$ ,  $\gamma = \alpha + j\beta$ ,  $\alpha$  is an attenuation coefficient,  $\beta = \omega/v_0$ ,  $v_0$  is the phase velocity of the non-perturbed B-G wave on the free surface,  $\omega$  is the angular frequency of the B-G wave,  $u_3$  is the B-G wave amplitude on the waveguide surface ( $x_2 = 0$ ),  $P$  is the mean power on the unit width of the B-G wave. The coefficient  $K$  is the

characteristic quantity for each B-G wave waveguide and depends solely on the material parameters of the waveguide and frequency.

In this paper, the liquids investigated under high pressure are treated as the Newtonian liquids. For the case of a Newtonian (viscous) liquid, the shear mechanical impedance (defined as a ratio of the shear stress to the shear vibrational velocity) can be expressed as follows:

$$Z_L = R_L + jX_L = \left(\frac{\rho_L \omega \eta}{2}\right)^{1/2} (1 + j) \quad (2)$$

where:  $\eta$  is the viscosity.

Considering the fact that the analyzed liquid is Newtonian ( $R_L = X_L$ ), from Eq.2 we obtain [2]:

$$\eta = \frac{2R_L^2}{\omega \rho_L} = \frac{2X_L^2}{\omega \rho_L} \quad (3)$$

where:  $R_L$  and  $X_L$  are the real and imaginary parts of the mechanical shear impedance of a liquid.

The shear mechanical impedance of a liquid  $Z_L = R_L + jX_L$  can be determined from the measurement of the change in attenuation and time of flight of wave trains that propagate in the waveguide loaded by a liquid [17].

#### IV. METHYL ESTERS VISCOSITY ISOTHERMS

The viscosity of methyl ester was measured in function of pressure and temperature at 5 °C intervals from 10 °C to 20 °C, and from atmospheric pressure to 350 MPa, see Fig.2.

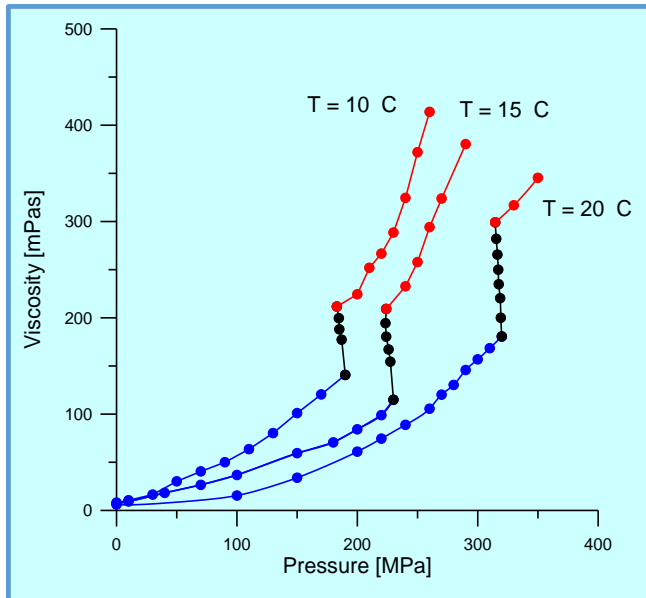


Fig.2. Viscosity of biofuel (methyl ester) versus pressure along various isotherms ( $T = 10\text{ }^\circ\text{C}$ ,  $15\text{ }^\circ\text{C}$ , and  $20\text{ }^\circ\text{C}$ ).

In the graph we can see 3 phases of methyl ester, namely, low-pressure phase (blue color), phase transition (black color), and high-pressure phase (red color). As the temperature rises, the pressure at which the phase transition begins augments.

#### V. PHASE TRANSITIONS IN METHYL ESTERS

The kinetics of the phase transition was investigated during viscosity measurements, see Fig.3. Pressure changes, occurring during phase transition, were registered with the piston locked in a fixed position.

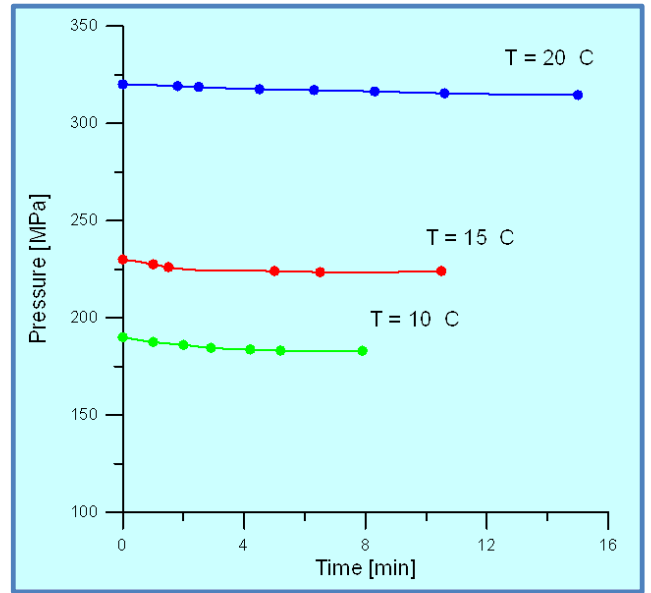


Fig.3. Kinetics of high-pressure phase transitions in methyl ester at various temperatures ( $T = 10\text{ }^\circ\text{C}$ ,  $15\text{ }^\circ\text{C}$ , and  $20\text{ }^\circ\text{C}$ ).

With the decrease of temperature, phase transitions run faster (e.g., phase transition at 10 °C runs about 6 minutes).

#### VI. CONCLUSIONS

Viscosity is a very important physicochemical parameter which determines the usefulness of the liquid (methyl esters) used as a biofuel for diesel engines. The viscosity value cannot be too large or too small [18-22]. The quality of atomization of biofuels for diesel engines depends on the viscosity of the biofuel [23]. A priori knowledge of the high-pressure behavior of biofuels viscosity is of paramount importance for the optimization of engine performance and emission quality [24].

It is shown that the use of ultrasonic methods enables efficient investigating of high-pressure phase transitions in methyl esters. The occurrence of these phase transitions (crystallization) can have a negative impact on the performance of modern injection systems of the common rail type, where the pressures above 200 MPa can occur [25, 26].

From the experimental investigations of the authors, it is apparent that the change in viscosity of biofuels is a better signature of the presence of high-pressure phase transitions than a change of the speed of sound. During the phase transition in methyl esters, the speed of sound changes slightly (approx. 0.1%).

On the other hand, the viscosity of the methyl ester during high-pressure phase transition varies by more than 50% (from 50% to 100%), e.g., at 20 °C viscosity changes from 180 mPas to 296 mPas. Determination of the viscosity of biofuels (methyl esters) in the high-pressure condition and investigation of high-pressure phase transition kinetics is a novelty.

Detailed knowledge of the physicochemical properties of the methyl esters under high pressure requires further systematic studies.

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