Investigation of high-pressure phase transitions in biofuels by means of ultrasonic methods

Piotr Kielczyński, Marek Szalewski, Andrzej Balcerzak, Krzysztof Wieja
Institute of Fundamental Technological Research
Polish Academy of Sciences
Warsaw, Poland
pkielezy@ippt.pan.pl

Aleksander J. Rostocki
Institute of Physics
Warsaw University of Technology
Warsaw, Poland

Stanisław Ptasznik
Meat and Fat Technology Department
Institute of Agricultural and Food Biotechnology
Warsaw, Poland

Abstract— The fundamental goal of this work is to verify the hypothesis of the existence of high-pressure phase transitions in biofuel components on the example of rapeseed fatty acid methyl esters (RME), by using ultrasonic methods, in a wide range of pressures (from atmospheric pressure to 300 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 of 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 of high-pressure phase transitions in methyl esters were evaluated.

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

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.

Biofuels used in diesel engines, consist mainly of methyl and ethyl esters of fatty acids. This fact was the basis for selecting of liquids (i.e., rapeseed methyl esters) which are investigated in this paper. One of the major drawbacks of biofuels is the possibility of the occurrence of high-pressure phase transitions. Since in modern fuel injection systems (common rail) for diesel engines, larger values of pressure (above 200 MPa) are required, the occurrence of high-phase transitions at this range of pressures (> 200 MPa), and hence formation of high-pressure phases of high viscosity and increased density would result in damage or destruction of the engine and its equipment. The existence of these high-pressure phase transitions in biofuels has not yet been meticulously investigated and documented. The fundamental goal of this work is to verify the hypothesis of the existence of high-pressure phase transitions in biofuel components on the example of rapeseed fatty acid methyl esters (RME), by using ultrasonic methods.

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. 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.

Basing on the sound velocity and density measurements, the following important physicochemical parameters of RME were evaluated: a) bulk modulus and b) surface tension. These parameters determine the quality of atomization of the RME used as biofuels in diesel engines.

II. MATERIALS AND METHODS

The samples of fatty acid methyl ester (FAME) obtained by transesterification 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.
The TBigitized the input 𝛼𝜔(solete) and experimentally by the 𝑍𝑗𝛽𝐾0(draulic) was placed inside the high-pressure chamber.

A computer program that controlled the chamber with a simple piston and Bridgman II sealing system. High pressure was generated in a thick-walled cylinder chamber with a simple piston and Bridgman II sealing system.

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.

Sound speed, density and viscosity (of RME) isotherms versus pressure, have been measured. Direct measurements of physicochemical parameters of liquids using conventional methods are extremely difficult to carry out accurately at high pressures range. To overcome these disadvantages, the Authors apply the original ultrasonic methods. These methods, e.g., the measurement of viscosity of liquids under high pressure using the Love and Bleustein-Gulyaev (B-G) surface acoustic waves, have been established theoretically and experimentally by the Authors at the Institute of Fundamental Technological Research in Warsaw [2,4].

Measurements were performed in the pressure range from 0.1 MPa up to 300 MPa and for temperatures from 5 °C to 20 °C, (Γ = 2 MHz).

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 14:0</td>
<td>0.1</td>
</tr>
<tr>
<td>C 16:0</td>
<td>4.5</td>
</tr>
<tr>
<td>C 16:1</td>
<td>0.3</td>
</tr>
<tr>
<td>C 17:0</td>
<td>0.1</td>
</tr>
<tr>
<td>C 17:1</td>
<td>0.1</td>
</tr>
<tr>
<td>C 18:0</td>
<td>1.8</td>
</tr>
<tr>
<td>C 18:1cis9</td>
<td>58.1</td>
</tr>
<tr>
<td>C 18:1cis11</td>
<td>2.6</td>
</tr>
<tr>
<td>C 18:2cc</td>
<td>19.9</td>
</tr>
<tr>
<td>C 18:3ccc</td>
<td>9.1</td>
</tr>
<tr>
<td>C 20:0</td>
<td>0.6</td>
</tr>
<tr>
<td>C 20:1</td>
<td>1.5</td>
</tr>
<tr>
<td>C 20:2</td>
<td>0.1</td>
</tr>
<tr>
<td>C 22:0</td>
<td>0.3</td>
</tr>
<tr>
<td>C 22:1</td>
<td>0.5</td>
</tr>
<tr>
<td>C 24:0</td>
<td>0.2</td>
</tr>
<tr>
<td>C 24:1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

The piston displacement was controlled by a digital caliper. For pressure measurements a typical 75 Ω 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 μs. 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.

IV. 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 [14], one can prove that the change in the complex propagation constant γ of the B-G wave produced by viscoelastic liquid loading is as follows [15]:

\[
\Delta\gamma = -j \left( \frac{\nu_3^2}{4P} \right) Z_L = -j \cdot K \cdot Z_L
\]

where: \( j = (-1)^{1/2} \), \( \gamma = \alpha + j\beta \), \( \alpha \) is an attenuation coefficient, \( \beta = \omega/v_3 \), \( v_3 \) 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, \( v_3 \) 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:

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

(2)

where: $\eta$ is the viscosity.

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

$$\eta = \frac{2R_L^2}{\rho L \omega} = \frac{2X_L^2}{\rho L \omega}$$

(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 [15].

V. METHYL ESTERS VISCOSITY ISOTHERMS

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

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.

VI. PHASE TRANSITIONS IN METHYL ESTERS

The high-pressure phase transitions in RME were investigated during viscosity measurements, see Fig.2. Pressure changes, occurring during phase transition, were registered with the piston locked in a fixed position.

Phase transition regions are clearly visible in Fig.2, see phase transition parts marked in black. When the phase transition started (e.g., at 190 MPa for a temperature of 10 °C), we stopped the compression, and the piston in the high-pressure chamber was fixed to enable the phase transition to occur undisturbed. During the phase transition, the viscosity shows spontaneous rise despite the pressure drop. At the termination of the phase transition process we increased the pressure again (see high-pressure phase parts of curves marked in red in Fig.2).

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

VII. PHYSICOCHEMICAL PARAMETERS OF RME

The bulk modulus $B$ and surface tension $\sigma$ are crucial parameters that characterize the behavior of fuels in the injection systems in diesel engines [7]. The bulk modulus and surface tension of Rapeseed Methyl Esters were determined from the expressions (4) and (5):

$$B(p, T) = \frac{1}{\beta_s(p, T)} = \rho(p, T) \cdot v^2(p, T)$$

(4)

$$\sigma(p, T) = 6.33 \cdot 10^{-10} \cdot \rho(p, T) \cdot v(p, T) \cdot 3/2$$

(5)

where: $\beta_s$ is the adiabatic compressibility, $\rho$ is the density of RME sample and $v$ is the sound velocity in RME sample that were measured previously by the Authors.

The dependences of the bulk modulus $B$ and surface tension $\sigma$ on pressure and temperature are presented in Figs.3 and 4 respectively.

Fig.2. Viscosity of biofuel (methyl ester) versus pressure along various isotherms ($T = 5 \ ^\circ C, 10 \ ^\circ C, 15 \ ^\circ C, and \ 20 \ ^\circ C$).

Fig.3. Plot of bulk modulus $B$ of RME sample as a function of pressure and temperature.

Fig.4. Variation of surface tension $\sigma$ of RME sample on pressure and temperature.
VIII. 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 [16-20]. The quality of atomization of biofuels for diesel engines depends on the viscosity of the biofuel [21]. A priori knowledge of the high-pressure behavior of biofuels viscosity is of paramount importance for the optimization of engine performance and emission quality [22].

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 [23-25].

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 10 °C viscosity changes from 56 mPa s to 102 mPa s. Determination of the viscosity of biofuels (methyl esters) in the high-pressure condition and investigation of high-pressure phase transitions is a novelty.

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

REFERENCES