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DETERMINATION OF RAPESEED METHYL ESTER OIL VOLUMETRIC PROPERTIES IN HIGH PRESSURE (0.1 TO 350 MPa)

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The isothermal compressibility coefficient, the bulk modulus, the cubic expansion coefficient, the density and the propagation speed of the pressure waves of rapeseed methyl ester oil (RMEO) are the thermophysical properties derived from the specific volume determined in this work and compared with the properties of diesel oil (DO). The temperature measurement interval ranges from 288.15 to 328.15 K and the pressure measurement interval from atmospheric pressure to 350 MPa.

The experimental method used consisted of a volume change cell characterised by a linear variable differential transformer (LVDT) magnetic induction system adapted to a high-pressure vessel. To calculate the properties the modified Tait–Tammann equation was used and a high correlation coefficient was obtained with a 95% confidence level. The specific volume and compressibility coefficient were greater for DO than for RMEO; also, cubic expansion was greater for DO than for RMEO. These results pave the way for further practical application.

Keywords: *bulk modulus, cubic expansion coefficient, density, diesel oil, high pressure, isothermal compressibility, rapeseed methyl ester oil, specific volume, speed of pressure waves*

Introduction

Knowledge of the thermophysical properties of fuels as a function of pressure and temperature is especially important for their application in the engine industry and renewable energy research. It is of particular significance for biofuels, where there is hardly any data on their properties in the high-pressure interval.

The heat of combustion $\Delta_c Q$ of vegetable oil (~40000 kJ kg^{-1}) and diesel oil (~43000 kJ kg^{-1}) is very similar, but the viscosity of vegetable oils is approximately 10–20 times greater than that of diesel [1] and when they are used in diesel engines instead of diesel oil (DO) there are serious problems that prevent their direct use. Because of this, biofuels are used, which are transesterificated vegetable oils, where the initial large, ramified, high-viscosity molecules with a high proportion of carbon become small, chain molecules, with less viscosity, a lower percentage of carbon, and with physical, chemical and energy characteristics similar to the diesel ones [2].

The main advantage of biofuels compared with diesel is the reduction of carbon dioxide, and consequently, a better environment. They also have other advantages, like extending the useful life of engines thanks to their good lubricity.

The specific volume of any of the fluids used in injection engines and their derived properties are highly dependent on pressure and temperature. In this work a study is presented of these physical magnitudes from atmospheric pressure up to 350 MPa and at three temperatures: 288.15, 308.15 and 328.15 K. The thermophysical properties of rapeseed methyl ester oil (RMEO) are compared with those of DO and the advantages of biofuel with regard to diesel are discussed. The changes in volume, ΔV, of a sample were determined as a function of both pressure and temperature. In order to fit the specific volume, pressure and temperature to the experimental values, the modified Tait–Tamman equation is used. From this equation the density ρ, the isothermal compressibility coefficient κ_T, the bulk modulus B, the cubic expansion coefficient α and the speed of the pressure waves c_T are derived.

The thermophysical properties of biofuels, specifically RMEO, as functions of pressure and temperature, are of particular interest for the construction of a simulation model of diesel-injection equipment [3]. If the effects of biofuels in the injection process are known, the design of injection systems can be adapted to use them. In particular, the compressibility coefficient is one of the most important parameters and it is crucial in the modelling of a fuel-injection system. According to the first and the second laws of thermodynamics and by rearrangement of the Maxwell equations, the temperature change (i.e. heating during compression) can be described as a function of the cubic expansion coefficient, α, among others thermophysical properties

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Table 1 Sample specifications

	RMEO	DO
Ester content/% min^{-1}	98.9	–
Density at 15°C/kg m^{-3}	884 (860–900)*	830.2 (810–832)*
Viscosity at 40°C/m^2 s^{-1}	4.42	2.075
Ignition point/°C	162	67
Sulphur content/mg kg^{-1}	5	8
Water/mg kg^{-1}	382	24
Insoluble impurities/mg kg^{-1}	<0.1	–
Acidity/mg KOH g^{-1}	0.40	–
Iodine index/g I_2/100 g	111	–
H_c/kJ kg^{-1}	37090	43200

*Maximum and minimum limits

of the fluid. [4, 5]. This is closely related to the injection and pulverisation processes in the combustion chamber.

Experimental

Materials

The RMEO and DO samples were supplied by CIDAUT of Valladolid (Spain) and Repsol YPF®. The sample specifications are shown in Table 1.

Methods

The experimental device used for determining the thermophysical properties of RMEO and DO have already been described [6, 7]. Figure 1 is a diagram of the setup. The volume change cell, immersed in the high-pressure vessel, is equipped with a LVDT, Peltron Ldt. system that detects the change in volume of the sample as a result of the movement of the piston caused by a change in pressure or temperature. One of the characteristics of its construction is that the pressure fluid completely bathes all the system, preventing any possible pressure gradient between the sample and outside (grey colour around the cell in Fig. 1).

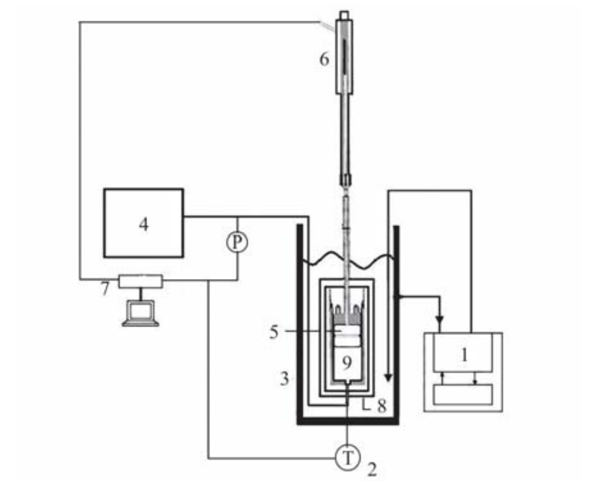

Fig. 1 Experimental device; 1 – cryostat, water bath; 2 – sample thermocouple; 3 – bath; 4 – high pressure pump; 5 – floating piston; 6 – linear variable differential transformer (LVDT); 7 – data acquisition system; 8 – high-pressure vessel; 9 – sample

The cell measures changes in volume from 0.1 to 350 MPa and covers the pressure range at which the nowadays injection systems work (up to 250 MPa for the most modern systems).

The volume change cell (18 mL capacity) is introduced into a slightly larger high-pressure vessel, where it is surrounded by silicone oil SilOil Typ M40.165.10, a pressure and temperature transmitting fluid. The vessel is connected to a high-pressure equipment High Pressure Pump 700 MPa type U111 that pumps the silicon oil, varying and regulating the pressure, measured at a point of the circuit close to the vessel with an accuracy of 0.1 MPa.

Temperature is controlled by a thermal bath where the vessel and its connections are immersed, fed by a Haake model K cryostat. An internal thermocouple in contact with the sample container monitors the temperature with an accuracy of 0.01 K. Data on the temperature, pressure and position of the piston are measured every 0.5 s using a data acquisition system DC100 Data Collector Yokogawa for their subsequent analysis.

Determination of the specific volume at atmospheric pressure, $v(p_0,T)$

The LVDT system detects changes in volume. To obtain the absolute specific volume it is necessary to know its initial value v_0, i.e., at atmospheric pressure. The density at atmospheric pressure $\rho_0=(1/v_0)$ was determined with pycnometers, which had been previously calibrated with water. A thermostatic bath, four pycnometers (narrow capillary volumetric flask) and a balance with a resolution of 0.0001 g were used. To determine the mass of the corresponding samples (Eq. (1)) they were weighed empty and full up to the reference mark and the difference in these masses was corrected with that of the air contained in the empty pycnometer (last term in Eq. (1)).

$$m = m_{\mathrm{full}} - m_{\mathrm{empty}} + \frac{(m_{\mathrm{full}} - m_{\mathrm{empty}})}{\rho_{\mathrm{s}|T=20°C}} \rho_{\mathrm{a}|T=20°C} \qquad (1)$$

where ρ_a is the air density Eq. (2):

$$\rho_{\mathrm{a}} = \frac{pM_{\mathrm{a}}}{RT} \qquad (2)$$

With this calculated mass and knowing the volume of the pycnometer from calibration with water, the

Table 2 Density and specific volume experimental values of RMEO and DO at 0.1 MPa

Temperature/K	Density/kg m^{-3}		Specific volume/m^3 kg^{-1}	
	RMEO	DO	RMEO	DO
288.15	884.52	830.2	$1.130\cdot10^{-3}$	$1.204\cdot10^{-3}$
308.15	869.92	815.8	$1.149\cdot10^{-3}$	$1.226\cdot10^{-3}$
328.15	855.27	801.32	$1.169\cdot10^{-3}$	$1.248\cdot10^{-3}$

density ρ_0 and the specific volume v_0 of RMEO and DO at atmospheric pressure were determined (Table 2).

Unfortunately, the densities obtained could not be compared with much data, Rodríguez-Antón [1] determined the experimental data in the biofuel RMEO and in DO, obtaining at atmospheric pressure and 293.15 K a density of 883 kg m^{-3} for RMEO and 835 kg m^{-3} for DO. These values are slightly greater than the experimental measurements determined in this work, which were 881.1 and 827 kg m^{-3} for RMEO and DO, respectively. The reason why the density is different is because the samples are not from the same sources and they are not pure compounds. The values obtained were within the limits of the sample specifications (Table 2).

After the initial specific volume of the fluids at atmospheric pressure had been obtained, the relevant experiments were done to determine the specific volume and its derived thermophysical properties for the other pressures p and temperatures T.

Determination of the specific volume at high pressure, v(p,T)

The experimental device was calibrated with water [7] at three temperatures 288.15, 308.15 and 328.15 K over the pressure interval from 0.1 to 350 MPa.

The sample assay results are represented in Fig. 2, where the specific volume is shown as a function of pressure for RMEO and DO. At each temperature under investigation DO had approximately 6% greater specific volume than RMEO under the same pressure conditions. This is important as regards the application of biofuels as a substitute fuel of DO, because during the filling up of a given volume, a greater mass is loaded with the biofuel, which to a great extent will offset its lower heat of combustion compared with DO. To understand this, the energy relative density ρ_{er} Eq. (3) depending on the pressure and temperature of RMEO and DO is represented in Fig. 3.

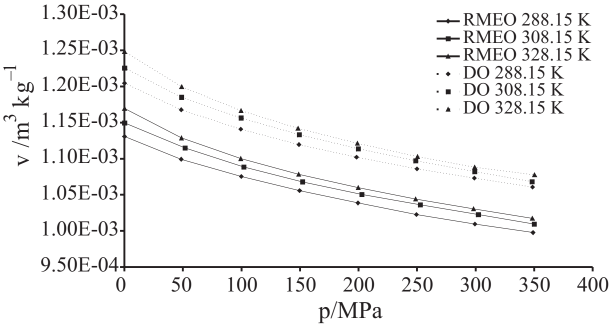

Fig. 2 Specific volume *vs*. pressure for RMEO and DO (experimental values)

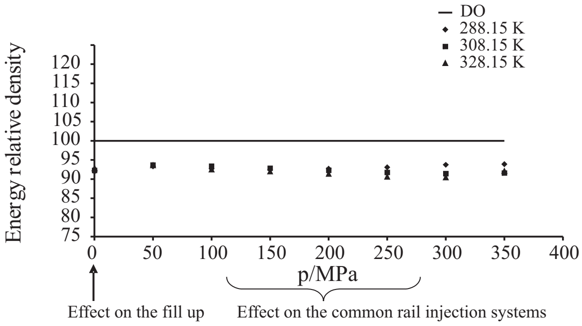

Fig. 3 Energy relative density of RMEO (symbols) compared with DO

$$\rho_{er} = \frac{\Delta_C Q_{RMEO}\rho_{RMEO}}{\Delta_C Q_{DO}\rho_{DO}}\cdot 100 \tag{3}$$

Choice of fit equation for the specific volume *v*(*p*,*T*)

Hayward [8, 9] does an extensive study on several equations proposed throughout history to express $v(p)$ and $\kappa_T(p)$. The original equation is that proposed by Tait, currently known as 'linear secant-modulus equation' [8]:

$$\frac{v_0(p-p_0)}{v_0-v} = B_0 + n(p-p_0) \tag{4}$$

where B_0 is a constant corresponding to the compressibility modulus at atmospheric pressure and n is a constant corresponding to the slope of the compressibility modulus curve to pressure.

Equation (4) is obtained from the definition of the bulk modulus B:

$$B \equiv -v\frac{dp}{dv} \tag{5}$$

Rearranging Eq. (4), one obtains Eq (6) :

$$v(p)=v_0\frac{B_0+(n-1)(p-p_0)}{B_0+n(p-p_0)} \tag{6}$$

Tammann made a correction to this equation, which resulted in the most known and used expression called Tait–Tammann equation Eq. (7).

$$v(p)=v_0\left[1-C_1\ln\left(\frac{C_2+p}{C_2+p_0}\right)\right] \tag{7}$$

There is also a third option [3, 10], where the variable on which the specific volume depends is not only pressure but also temperature. This equation is the modified Tait–Tammann equation Eq. (8).

$$v(p,T)=\frac{1-C_3\ln\left(\dfrac{C_4e^{-C_5(T-T_0)}+p}{C_4e^{-C_5(T-T_0)}+p_0}\right)}{1/v_0+C_6(T-T_0)+C_7(T-T_0)^2} \tag{8}$$

where T_0 is the reference temperature, in this instance 288.42 K.

To fit the constants n, B_0 of Eq. (6) and C_1, C_2 of Eq. (7) with the specific volume and pressure experimental values, the TableCurve2D version5 program (AISN Software Inc. P.O. Box 449, Mapleton, OR 97453) was used. To fit the constants C_3, C_4, C_5, C_6 and C_7 of Eq. (8), the TableCurve 3D version 4.0 program (SYSTAC Software Inc., 501 Canal Boulevard, Suite F, Richmond, CA 94804-2028) was used.

Of the three equations described above (Eqs (6)–(8)), Eq. (8) is used to adjust the values measured and determine the properties derived in this work. This choice is due to the fact that when fitting with the experimental values for each of the three equations above, a coefficient of greater correlation is obtained with the modified Tait–Tammann equation (Table 3). The fact of including temperature as a variable is important in high pressure, because although theoretically, the process under study is isothermal, in fact it is not, and a slight change in the temperature can have a noticeable effect on the final results of the derived properties.

Table 3 Coefficient of determination for each equation, r^2

Fluid	Tait equation	Tait–Tammann equation	3D modified Tait–Tammann equation
RMEO	0.9981	0.9982	0.9995
DO	0.9989	0.9993	0.9993

Fitted constants for Eq. (8) are shown in Table 4. These are necessary for determining the other thermophysical properties.

Determination of thermophysical properties derived from *v*(*p*,*T*)

Isothermal compressibility and bulk modulus coefficients

The isothermal compressibility coefficient was derived with the use of Eq. (9)

$$k_{\mathrm{T}}=\frac{C_3}{[C_4e^{-C_5(T-T_0)}+p]\left[1-C_3\ln\left(\dfrac{C_4e^{-C_5(T-T_0)}+p}{C_4e^{-C_5(T-T_0)}+p_0}\right)\right]} \tag{9}$$

Figure 4 shows how compressibility decreases when pressure increases, e.g. for DO at 328.15 K it varies from $9.4\cdot10^{-4}$ MPa^{-1} at 0.1 MPa, to $2.5\cdot10^{-4}$ MPa^{-1} at 350 MPa. On the other hand, κ_{T} increases with temperature, e.g. for RMEO at 0.1 MPa it varies from $6.5\cdot10^{-4}$ MPa^{-1} at 288.15 K, to $7.8\cdot10^{-4}$ MPa^{-1} at 328.15 K. The standard deviation calculated for the coefficient of isothermal compressibility was $\pm0.0009\cdot10^{-4}$ MPa^{-1}. The three isotherms of each fluid approach each other asymptotically. The isothermal compressibilities obtained for biofuels are lower than those obtained for diesel up to a certain pressure, which is around 250–300 MPa, but it depends on the temperature (Fig. 5). This fact affects injection systems with a

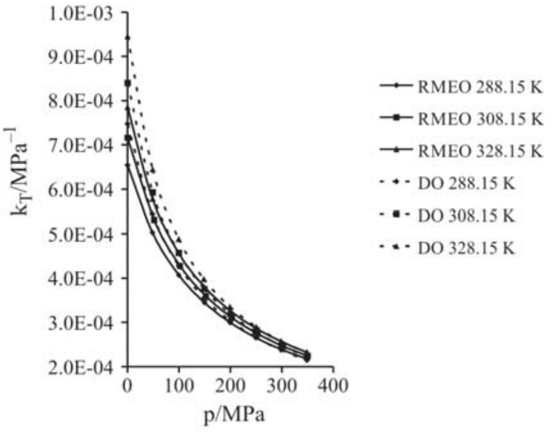

Fig. 4 Isothermal compressibility *vs.* pressure for RMEO and DO

Table 4 Constants of the modified Tammann–Tait equation

Fluid	C_3	C_4	C_5	C_6	C_7	r^2
RMEO	0.095	145.460	0.00467	–0.832	0.00308	0.9995
DO	0.088	117.829	0.00617	–0.890	0.00460	0.9993

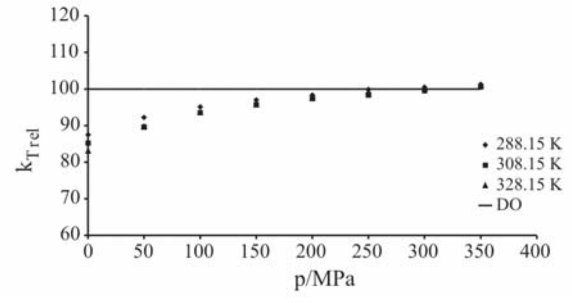

Fig. 5 Relative isothermal compressibility of RMEO (symbols) compared with DO

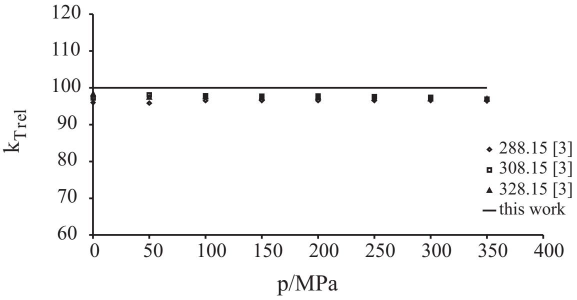

Fig. 6 Relative isothermal compressibility of RMEO experimental data (line) *vs.* Rodríguez-Antón [3] data (symbols)

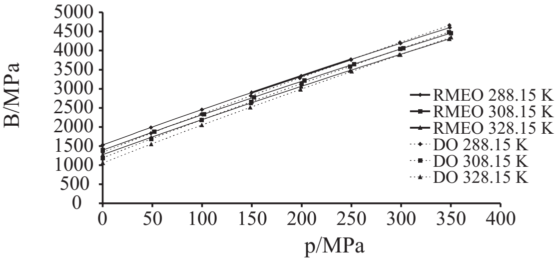

Fig. 7 Bulk modulus *vs.* pressure for RMEO and DO

rotary pump or in-line pump how the pressure is raised by the pump.

Rodríguez-Antón [3] determined the experimental changes in volume of a RMEO sample up to 40 MPa and extrapolated them to 140 MPa, these values are similar to those determined here. Figure 6 shows a comparison of his data for isothermal compressibility, extrapolated up to 350 MPa, with the values determined in this article for isothermal compressibility. The same trend with pressure was observed in both instances.

The bulk modulus *B* is the inverse of the isothermal compressibility coefficient (Eq. (5)). It represents the resistance of the sample to a reduction in its volume when pressure is increased at a given temperature. This is seen in Fig. 7 where the bulk modulus increases linearly with pressure from 1000–1500 MPa at atmospheric pressure to 4000–4500 MPa at the maximal studied pressure value. The standard deviation of the isothermal compressibility modulus obtained was ±0.6 MPa.

Cubic expansion coefficient

The cubic expansion coefficient was calculated from the specific volume determined as function of pressure and temperature (Eq. 10)). The α values for both fluids for each pressure and temperature are given in Table 5.

$$\alpha = \frac{C_3 C_4 C_5 e^{-C_5(T-T_0)}(p_0 - p)}{1 - C_3 \ln\left(\dfrac{C_4 e^{-C_5(T-T_0)} + p}{C_4 e^{-C_5(T-T_0)} + p_0}\right)(C_4 e^{-C_5(T-T_0)} + p)} - \frac{C_6 - 2C_7(T - T_0)}{\rho_0 + C_6(T - T_0 + C_7(T - T_0)^2} \tag{10}$$

It can be seen in Fig. 8 that DO has a greater cubic expansion coefficient than RMEO. This difference increases with temperature; 7% at 288.15 K, 16% at 308.15 K and 22% at 328.15 K. For both liquids, the cubic expansion coefficient decreases with pressure and increases with temperature.

Speed of pressure waves

One of the physical properties of the biofuel fluid is the propagation speed of the pressure waves. This

Table 5 The cubic expansion coefficient α (K^{-1}) from 0.1 to 350 MPa at 288.15, 308.15 and 328.15 K

Pressure/MPa	*T*=288.15 K		*T*=308.15 K		*T*=328.15 K	
	RMEO	DO	RMEO	DO	RMEO	DO
0.1	9.385E-04	1.069E-03	1.097E-03	1.316E-03	1.257E-03	1.565E-03
50	8.222E-04	9.030E-04	9.720E-04	1.135E-03	1.124E-03	1.368E-03
100	7.488E-04	8.069E-04	8.958E-04	1.035E-03	1.045E-03	1.265E-03
150	6.975E-04	7.429E-04	8.436E-04	9.702E-04	9.917E-04	1.200E-03
200	6.592E-04	6.966E-04	8.050E-04	9.239E-04	9.530E-04	1.154E-03
250	6.291E-04	6.610E-04	7.750E-04	8.887E-04	9.231E-04	1.120E-03
300	6.047E-04	6.325E-04	7.508E-04	8.608E-04	8.990E-04	1.092E-03
350	5.843E-04	6.090E-04	7.306E-04	8.378E-04	8.791E-04	1.070E-03

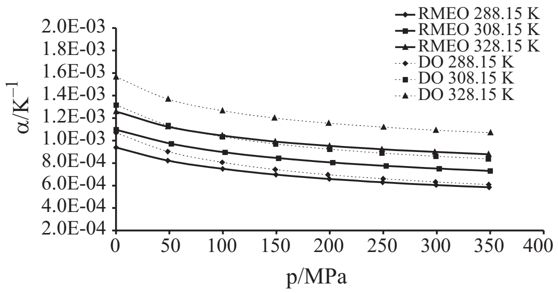

Fig. 8 Cubic expansion coefficient *vs*. pressure for RMEO and DO

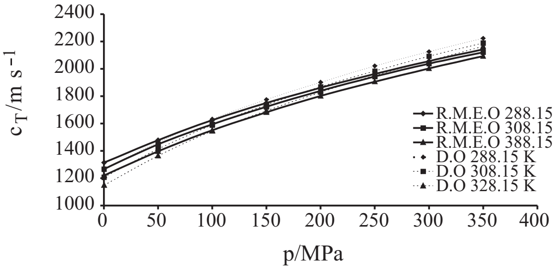

Fig. 9 Speed of pressure waves *vs*. pressure for RMEO and DO

property does not only depend on the substance, pressure and temperature but also on the kind of the process involved. Its magnitude in the injection tube is virtually the same as that obtained from an isothermal process [11]. To determine this speed it is necessary to know the density and the isothermal compressibility modulus at each pressure and at each temperature and to apply Eq. (11)

$$c_T = \sqrt{\frac{B}{\rho}} \tag{11}$$

When the fuel is compressed by the pump a series of pressure waves are generated that travel to the injector via the injection tube. The time that it takes the pressure wave generated by the pump to arrive depends on the length of the injection tube, and on the density and compressibility of the fuel. Figure 9 represents the speed of the pressure waves depending on the pressure. It varies between 1150–1300 m s^{-1} at 0.1 MPa to about 2000–2200 m s^{-1} at 350 MPa.

It can be seen that for the pressure interval from 0.1 to 100 MPa the speed of the pressure waves for RMEO is greater than for DO, the opposite occurs when this pressure is greater and this time the speed of the pressure waves is greater for DO. When the propagation speed of the pressure waves in RMEO is greater than for DO, these waves will take less time to reach the injector. The injection pump process for raising pressure should begin later so that the fuel is introduced at the right moment. When the propagation speed of the pressure waves is less than for DO, these waves will take longer and this time must be therefore considered when designing the functioning of the engine.

Conclusions

- The literature is very poor on the thermophysical data of biofuels in high pressure. There is nothing at pressures higher than 60 MPa.
- Of all the equations studied to determine the compressibility properties of biofuels in the high-pressure interval, the most appropriate is the modified Tait–Tammann equation.
- The density of biofuels is approximately 6% greater than for diesel. This is important as regards their application as substitute fuels of diesel: by filling up a given volume, a greater mass is acquired with the biofuel, which to a great extent offsets its lower calorific power compared with diesel.
- The isothermal compressibility coefficient of DO is greater than that of RMEO up to 250 MPa. From this pressure, the biofuel is so much or less compressible than the diesel. Compressibility is greater the higher the temperature and the lower the pressure. The bulk modulus increases linearly with pressure.
- The cubic expansion coefficient of DO is greater than that of RMEO over the whole the pressure interval up to 22% at 328.15 K and 7% at 288.15 K.
- The propagation speeds of the pressure waves of RMEO are greater than for DO up to a certain pressure which depends on the temperature. Consequently, for diesel injection systems, a greater propagation speed of the pressure waves produces less delay in the injection due to the compressibility of the fuel and vice versa. Up to a pressure of 100 MPa the speed of RMEO is greater than that of DO.

Nomenclature

B/Mpa	bulk modulus
B_0/MPa	bulk modulus at atmospheric pressure
c_T/m s^{-1}	speed of waves
C_1, C_2, C_3,	constants
C_4, C_5, C_6,	constants
C_7	constant
$\Delta_c Q$/kJ kg^{-1}	heat of combustion
k_T/MPa^{-1}	isothermal compressibility
$k_{T\ \mathrm{relative}}$	relative isothermal compressibility
m/kg	sample mass
m_{empty}/kg	mass of the empty pycnometer
m_{full}/kg	mass of the full pycnometer
M_a/kg	molecular mass of air
n	constant
p/MPa	pressure
p_0/MPa	atmospheric pressure

R/J mol^{-1} K^{-1}	universal gas constant
T/K	temperature
T_0/K	reference temperature
$v(p,T)$/m^3 kg^{-1}	specific volume
v_0/m^3 kg^{-1}	specific volume at atmospheric pressure
ΔV/m^3 kg^{-1}	change in the specific volume
α/K^{-1}	cubic expansion coefficient
ρ/kg m^{-3}	density
ρ_a/kg m^{-3}	air density
ρ_{er}	energy relative density
ρ_s/kg m^{-3}	sample density
ρ_0/kg m^{-3}	density at atmospheric pressure

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