Volumetric Properties of Sunflower Methyl Ester Oil at High Pressure

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Biodiesel is an alternative to diesel oil (DO), because it is a fuel obtained from renewable resources that has lower emissions than DO. Biomass production should promote agricultural activity to obtain fuels for the transport sector. The study of the behavior of biodiesel at varying pressure and temperature is very interesting because diesel engines are mechanical systems that work with fuels submitted to high pressure. The specific volume, isothermal compressibility, and cubic expansion coefficients of refined sunflower methyl ester oil (SMEO) and unrefined sunflower methyl ester oil (URSMEO) were obtained and compared with those of DO from 0.1 to 350 MPa and 288.15 to 328.15 K. This work shows that oil refinement did not significantly modify any of the properties studied of the final biodiesel. Compared with DO, both SMEOs were about 6% denser, whereas isothermal compressibility and cubic expansion coefficients were bigger or smaller for DO depending on pressure and temperature.

KEYWORDS: Cubic expansion; diesel oil; high pressure; isothermal compressibility; sunflower methyl ester oil; unrefined sunflower methyl ester oil

INTRODUCTION

Some products obtained from the chemical processing of seeds are currently being considered as an alternative to the long-chain petroleum hydrocarbons used in engines. In contrast with petroleum, these oils may represent excellent renewable resources and may play an important role for agricultural and oleochemical production. Sunflower oil is attractive to farmers as an alternative cash crop usually grown under contract. Vegetable oils cannot be used as a direct substitute of diesel oil (DO) in engines because their viscosity is approximately 10−20 times greater than that of diesel (*1*). By a transesterification reaction, vegetable oils with initial large branched molecules, high viscosity, and a high proportion of carbon become less viscous esters with small linear chain molecules, a lower percentage of carbon, and physical, chemical, and energy characteristics similar to those of diesel oil (*2*). Several of these esters are methyl ester oils or ethyl ester oils. A refinement may or not be performed during their production process. In this work, both the methyl ester from the refined sunflower oil (SMEO) and the methyl ester from the unrefined sunflower oil (URSMEO) were considered. They are currently being checked to be used for their application in biotechnology and as renewable energy in engines. The main advantage of biodiesels compared with DO is the reduction of carbon dioxide and, consequently, a better environment. They also have other advantages, such as extending the life time of engines due to their good lubricity.

To explore the possibilities of applying biodiesels, knowledge of their thermophysical properties as a function of both pressure and temperature is required (*3*). For example, the compressibility coefficient is a crucial parameter in the modeling of a fuel-injection system. Moreover, the cubic expansion coefficient, α, is necessary for calculating the temperature change of a fluid with pressure (e.g., heating during compression). This calculation involves other thermophysical properties. All properties are of interest not only for the present case, but also for all hydrostatic high-pressure processes, and especially food technology (*4−6*). The data here are of particular significance because there is hardly any data on the high-pressure properties of biodiesels in the bibliography. Comparing these new data with data on DO will provide the necessary information to adapt future engines.

In this work, the changes in volume, ΔV, of SMEO, URSMEO, or DO samples were studied at three temperatures, 288.15, 308.15, and 328.15 K, as a function of the pressure from 0.1 MPa up to 350 MPa. The objective was to describe the behavior of the specific volume, v, the density, ρ, the isothermal compressibility coefficient, k_T, and the cubic expansion coefficient, α, as a function of pressure and temperature in the interval studied.

MATERIALS AND METHODS

The SMEO and URSMEO were supplied by CIDAUT, Valladolid, Spain, and the DO by Repsol YPF. The SMEO and

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URSMEO samples presented a kinematics viscosity of 4.200×10^{-6} m^2 s^{-1} and the DO sample presented a kinematics viscosity of 2.075×10^{-6} m^2 s^{-1}. As expected, the biodiesels were more viscous than DO.

The setup for determining the thermophysical properties was designed to measure changes in sample volume with pressure or temperature (7). It contained a linear variable differential transformer (LVDT) (Peltron. Ldt. System) and a piston that could move in a cylindrical sample holder. The movement of the ferromagnetic extremity of the piston was detected by the LVDT when the sample volume varied. One of the characteristics of its construction was that the pressure transmitting fluid completely bathed the system, preventing any possible pressure gradient between the sample and outside. The working interval was 0.1−350 MPa for pressure and 288.15 − 328.15 K for temperature. The volume change cell (18 mL capacity) was introduced into a slightly larger high-pressure vessel, where it was surrounded by silicone oil (SilOil Typ M40.165.10) that acted as the pressure and temperature transmitting fluid. The vessel was connected to high-pressure equipment (U111, Institute of High-Pressure Physics, Warsaw, Poland) that pumped the silicon oil and varied and regulated the pressure. This magnitude was measured near the high-pressure vessel with an accuracy of 0.1 MPa for all pressures higher than atmospheric pressure. A cryostat (Haake K, Karlsruhe, Germany) fed a bath where the vessel and its connections were immersed at a controlled temperature. An internal thermocouple in contact with the sample container measured the temperature with an accuracy of 0.01 K. Data on the temperature, pressure, and position of the piston were monitored every 0.5 s using a data acquisition system (DC100 Data Collector Yokogawa, Tokyo, Japan) for their subsequent analysis.

The procedure for specific volume measurements was the following: the volume change cell was filled with about 17 mL of sample and weighed (m) after tare. It was placed in the vessel and immersed in the bath at the required temperature. When the temperature in the vessel was stable, pressure was slowly increased by 50 MPa steps, waiting for temperature equilibration between each pressure increase. So the specific volume at pressure p was

$$v(p) = \frac{V_0 + \Delta V(p)}{m} \tag{1}$$

where $V_0 = v_0 \cdot m$ was the sample volume at atmospheric pressure and $\Delta V(p) = S\Delta x(p)$ was its volume change due to an increase in pressure (S being the section of the cell and Δx the piston displacement deduced from LVDT measurements). The results were averages of the measurements (p, T, LVDT) done during 1 min after equilibration at each step. When 350 MPa was reached, pressure was released and the cell was weighed again to check that there was no leak from the sample and that the sample was not contaminated by the pressure-transmitting fluid. The complete procedure was repeated at least three times for each sample and temperature.

RESULTS AND DISCUSSION

Determination of the Specific Volume at Atmospheric Pressure, $v_0 = v(p_0, T)$. The density of the samples at atmospheric pressure was determined with pycnometers (7). The values obtained (**Table 1**) were close to those of Rodríguez-Antón (3) who gave a density of 881 kg m^{-3} for SMEO and 835 kg m^{-3} for DO at 293.15 K. The slight differences were within the limits of the sample specifi-

Table 1. Density Experimental Values of SMEO, URSMEO, and DO at 0.1 MPa

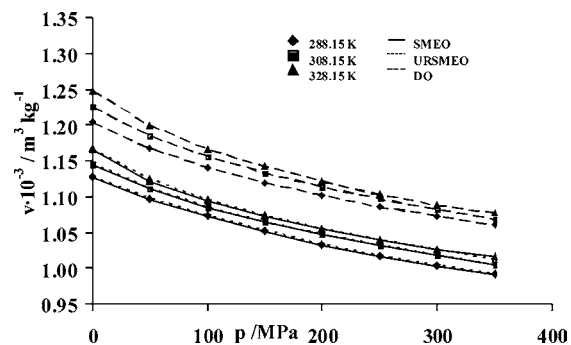| T (K)	density (kg m^{-3})		
	SMEO	URSMEO	DO
288.15	887.76	886.22	830.20
308.15	873.16	871.65	815.8
328.15	858.46	857.03	801.32

Figure 1. Specific volume of SMEO, URSMEO, and DO versus pressure at 288.15, 308.15, and 328.15 K.

cations and due to variability in raw materials. Next, the specific volume was calculated as the inverse of the measured densities.

Determination of the Specific Volume at High Pressure, $v(p, T)$. The experimental device was calibrated with water at the three temperatures, 288.15, 308.15, and 328.15 K, over the pressure interval from 0.1 to 350 MPa (7−9).

The sample assay results are represented in **Figure 1**, where the specific volume is shown as a function of pressure at different temperatures for the SMEO, URSMEO, and DO. The SMEO and URSMEO showed a great similarity between them. The specific volume increased as the temperature increased, and the DO values were always greater than both sunflower methyl ester oils. The specific volume of DO was approximately 6.4% greater than SMEO and 6.3% greater than URSMEO under the same pressure and temperature conditions.

Equation for the Specific Volume $v(p, T)$. Hayward (10, 11) completed an extensive study on several equations proposed throughout history to express the specific volume $v(p)$ and isothermal compressibility $k_T(p)$. The original equation was that proposed by Tait, currently known as "linear secant-modulus equation" (8)

$$\frac{v_0(p - p_0)}{v_0 - v} = B_0 + n(p - p_0) \tag{2}$$

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.

Then, from the definition of the bulk modulus B

$$B \equiv -v \frac{dp}{dv} \tag{3}$$

and considering that the specific volume depends not only on the pressure but also on the temperature (3, 11, 12), eq 2 can

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Table 2. Constants and Coefficient of Determination of the Modified Tait–Tammann Equation

fluid	C_1	C_2	C_3	C_4	C_5	r^2
SMEO	0.0987	150.08	0.0035	−0.8320	0.0034	0.9993
URSMEO	0.0980	145.26	0.0037	−0.8700	0.0032	0.9950
DO	0.0880	117.83	0.0062	−0.8900	0.0046	0.9993

be rearranged into a new one called the modified Tait–Tammann equation

$$v(p,T) = \frac{1 - C_1 \ln\left(\dfrac{C_2\, e^{-C_3(T - T_0)} + p}{C_2\, e^{-C_3(T - T_0)} + p_0}\right)}{\dfrac{1}{v_0} + C_4(T - T_0) + C_5(T - T_0)^2} \tag{4}$$

where T_0 is the reference temperature.

The modified Tait–Tammann equation was chosen from other fit equations because it had the highest coefficient of determination (7). Moreover, it included temperature as a variable, which was the advantage of letting us calculate the isothermal compressibility coefficient, k_T, and the cubic expansion coefficient, α. Both properties are partial derivatives of the specific volume as a function of pressure or temperature. Although the volume was theoretically measured under isothermal conditions, in fact it was not, and a slight change in the temperature can have a noticeable effect on the final results of the derived properties.

To fit the constants for eq 4 with the specific volume, pressure, and temperature experimental values, the TableCurve 3D, version 4.0, program (SYSTAC Software Inc., 501 Canal Boulevard, Suite F, Richmond, CA 94804-2028) was used. Fitted constants for eq 4 are shown in **Table 2**.

Determination of Thermophysical Properties Derived from $v(p, T)$. *Isothermal Compressibility.* By using the equation $k_T = -(1/v)(\partial v/\partial p)_T$, we obtained the isothermal compressibility coefficient according to eq 5

$$k_T = \frac{C_1}{(C_2\, e^{-C_3(T - T_0)} + p)\cdot\left[1 - C_1 \ln\left(\dfrac{C_2\, e^{-C_3(T - T_0)} + p}{C_2\, e^{-C_3(T - T_0)} + p_0}\right)\right]} \tag{5}$$

Results are illustrated in **Figure 2**. The standard deviation calculated for the isothermal compressibility coefficient was $\pm 0.0009 \times 10^{-4}$ MPa^{-1}. In **Figure 3A**, SMEO was compared with URSMEO at each temperature. Both show a similar behavior. The isothermal compressibility coefficient decreased when pressure increased and when temperature decreased, e.g., for SMEO at 0.1 MPa, it varied from 6.56×10^{-4} MPa^{-1} at 288.15 K to 7.55×10^{-4} MPa^{-1} at 328.15 K; at 100 MPa, it varied from 4.16×10^{-4} MPa^{-1} at 288.15 K to 4.5×10^{-4} MPa^{-1} at 328.15 K. The URSMEO values were slightly higher than the corresponding SMEO ones. The variation in the isothermal compressibility coefficient of SMEO and URSMEO was compared with DO in panels **B** and **C** in **Figure 2**, respectively. The isothermal compressibilities obtained for both SMEOs were lower than those obtained for DO up to a certain pressure, which was around 150–250 MPa (depending on the temperature). The DO isothermal compressibility coefficient varied more with pressure than the sunflower methyl ester oils coefficients: for DO at 328.15 K, it varied from 9.4×10^{-4} MPa^{-1} at 0.1 MPa to 2.5×10^{-4} MPa^{-1} at 350 MPa, whereas
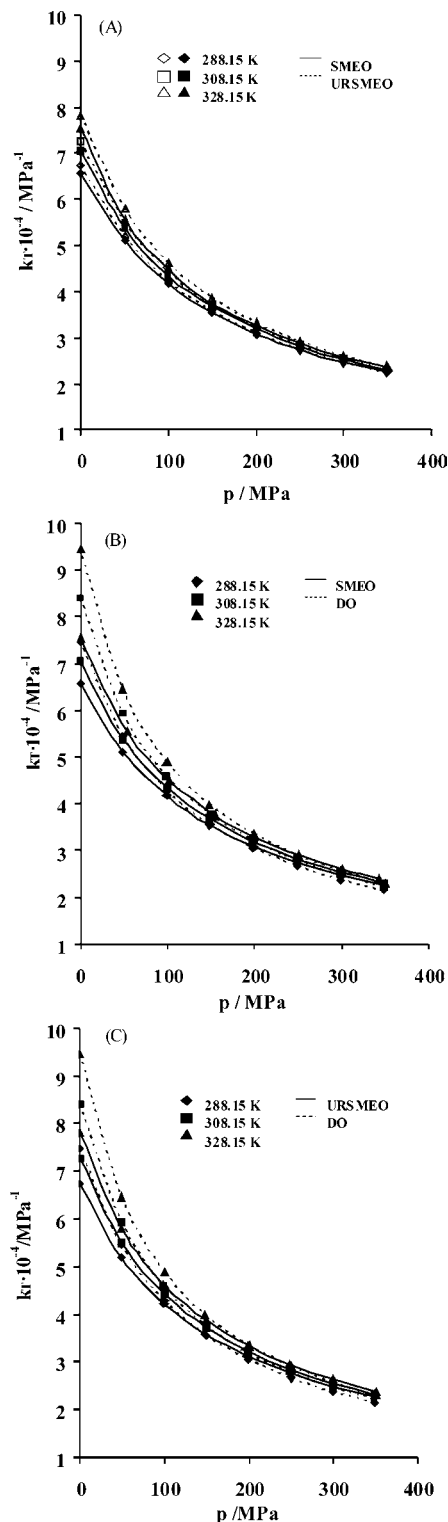

Figure 2. (**A**) Isothermal compressibility of SMEO and URSMEO versus pressure. (**B**) Isothermal compressibility of SMEO and DO. (**C**) Isothermal compressibility of URSMEO and DO.

for URSMEO at 328.15 K, it varied from 7.8×10^{-4} MPa^{-1} at 0.1 MPa to 2.4×10^{-4} MPa^{-1} at 350 MPa. Additionally, it was observed that the three isotherms of each fluid approached each other asymptotically and had a similar minimal value of isothermal compressibility at high pressure.

Rodríguez-Antón (3) determined the experimental changes in volume of an SMEO sample up to 40 MPa and extrapolated them to 140 MPa; his values were similar to the ones determined here. **Figure 3** shows a comparison of his data for isothermal
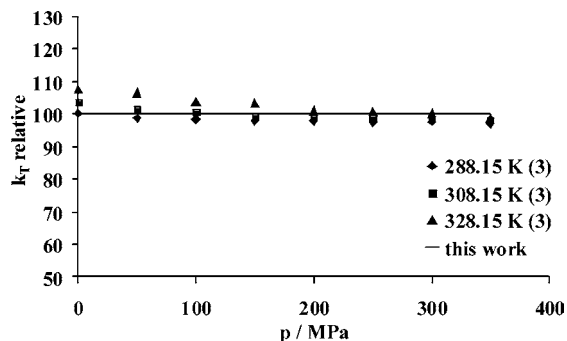
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Figure 3. Relative Isothermal compressibility SMEO experimental data (line) versus (*3*) data (symbols).

Figure 4. (**A**) Cubic expansion coefficient versus pressure for SMEO and DO. (**B**) Cubic expansion coefficient versus pressure for URSMEO and DO.

compressibility, extrapolated up to 350 MPa, with the values determined in this article. The same trend with pressure was observed in both instances.

Cubic Expansion Coefficient. From the specific volume, the cubic expansion coefficient $\alpha = (1/v)(\partial v/\partial T)_p$ as a function of pressure and temperature was calculated according to eq 6

$$\alpha = \frac{C_1 C_2 C_3\, e^{-C_3(T-T_0)}(p_0 - p)}{1 - C_1 \ln\left(\dfrac{C_2\, e^{-C_3(T-T_0)} + p}{C_2\, e^{-C_3(T-T_0)} + p_0}\right)(C_2\, e^{-C_3(T-T_0)} + p)(C_2\, e^{-C_3(T-T_0)} + p_0)} -$$

$$\frac{C_4 - 2C_5(T - T_0)}{\rho_0 + C_4(T - T_0) + C_5(T - T_0)^2} \quad (6)$$

The α values for SMEO and URSMEO are shown in **Table 3** for different pressures and three temperatures ($T = 288.15$, 308.15, and 328.15 K). It was possible to verify that URSMEO had a cubic expansion coefficient approximately 3% greater than SMEO under the same pressure and temperature conditions.

In panels **A** and **B** of **Figure 4**, the behaviors of SMEO and URSMEO were compared with those of DO. For SMEO, URSMEO, and DO, cubic expansion decreased with pressure and increased with temperature. DO had a greater cubic expansion coefficient than SMEO and URSMEO at 308.15 and 328.15 K; this difference increased with temperature by 16 and 18%, respectively. At 288.15 K, the DO cubic expansion coefficients were higher than those of the SMEO and URSMEO up to approximately 100 MPa. From this pressure, DO had a lower cubic expansion coefficient than both biodiesels. This means that DO at 288.15 K increased its volume more than the biodiesels for the same increase of temperature until 100 MPa. A larger cubic expansion coefficient causes a larger power loss in the engine as a result of the fuel heating.

In spite of the current potential application of biodiesels, there is insufficient knowledge on their thermophysical properties in the high-pressure domain. To determine the compressibility properties of biodiesels in the high-pressure interval, the
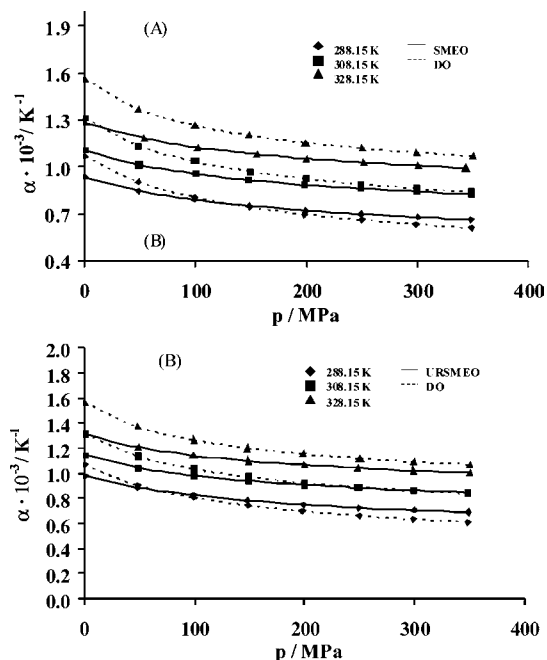
modified Tait−Tammann equation seems to be the most appropriate (*7*).

The remarked results of this work are that the volume-related data obtained for SMEO and URSMEO are very similar although they do have several differences from DO. Thus the refinement operation does not significantly modify the thermophysical properties. This is important because the price of refined oils such as sunflower is high compared with that of DO. This increases the overall production cost of biodiesel as well. Biodiesel production from refined oils would not be viable or economical for developing countries like India (*13*). Nevertheless, refinement is indeed advantageous because it affects biodiesel's chemical properties and improves its quality and behavior in the engine. The specific volume of both SMEOs is more than 6% greater than for diesel oil. When SMEOs are applied as substitute fuels for DO, filling up with a given volume implies a greater mass of fuel than with DO. The isothermal compressibility coefficient is greater the higher the temperature and the lower the pressure. It is greater for DO than for SMEO and URSMEO up to 150−250 MPa. From this pressure, biodiesel is as compressible or even more so than DO. It can thus be expected that from 250 MPa biodiesel and DO will behave the same for compressibility. The cubic expansion coefficient of DO is greater than that of SMEO and URSMEO over the whole pressure interval at 308.15 and 328.15 K. All

Table 3. Cubic Expansion Coefficient α (K^{-1}) of SMEO and URSMEO 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	
	SMEO	URSMEO	SMEO	URSME	SMEO	URSMEO
0.1	9.349×10^{-4}	9.795×10^{-4}	1.107×10^{-3}	1.146×10^{-3}	1.281×10^{-3}	1.314×10^{-3}
50	8.463×10^{-4}	8.842×10^{-4}	1.014×10^{-3}	1.044×10^{-3}	1.183×10^{-3}	1.207×10^{-3}
100	7.898×10^{-4}	8.240×10^{-4}	9.554×10^{-4}	9.821×10^{-4}	1.123×10^{-3}	1.142×10^{-3}
150	7.499×10^{-4}	7.819×10^{-4}	9.150×10^{-4}	9.392×10^{-4}	1.082×10^{-3}	1.099×10^{-3}
200	7.199×10^{-4}	7.504×10^{-4}	8.848×10^{-4}	9.074×10^{-4}	1.052×10^{-3}	1.067×10^{-3}
250	6.963×10^{-4}	7.256×10^{-4}	8.611×10^{-4}	8.825×10^{-4}	1.028×10^{-3}	1.042×10^{-3}
300	6.770×10^{-4}	7.05×10^{-4}	8.419×10^{-4}	8.624×10^{-4}	1.009×10^{-3}	1.022×10^{-3}
350	6.609×10^{-4}	6.886×10^{-4}	8.259×10^{-4}	8.456×10^{-4}	9.931×10^{-4}	1.005×10^{-3}

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these similarities and differences will have to be taken into account for the development of new generation enhanced motor engines. The use of suitable oil seeds will contribute to the development of both agricultural and oleochemical production.

ABBREVIATIONS USED

C_1, C_2, C_3, C_4, C_5, constants;
k_T (MPa^{-1}), isothermal compressibility;
$k_{Trelative}$, relative isothermal compressibility;
m (kg), sample mass;
n, constant;
p (MPa), pressure;
p_0 (MPa), atmospheric pressure;
T (K), temperature;
v ($m^3 kg^{-1}$), specific volume;
v_0 ($m^3 kg^{-1}$), specific volume at atmospheric pressure;
α (K^{-1}), cubic expansion coefficient;
ρ (kg m^{-3}), density.

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