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Refractive Index and Effective Polarizability of Biodiesel

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ABSTRACT

This work presents original experimental results of refractive index and density of ten biodiesel, from different feedstock, measured at the same temperature (within 0.1°C), in the range between 20 and 50°C, every 5°C. The chromatographic analysis showed that the biodiesel samples were highly unsaturated and with a carbon chain length close to 18. The quality of biodiesel samples was verified according to international standards. The effective polarizability was calculated from the experimental data of both properties, by a generalization of the Lorentz – Lorenz formula. The value, 0.309cm^3/g (RMS uncertainty below 0.002cm^3/g), was the same for all the samples and practically independent of temperature. This is in very good agreement with the effective polarizability calculated from density and refractive index data (measured at the same temperature) available in the literature, for biodiesel from soybean, sunflower and lard. Remarkably, similar values were reported in the literature for a wide variety of liquid hydrocarbons and crude oils, in the range from 0.330 to 0.350cm^3/g.

This work is part of a research program on the correlations between molecular structure and macroscopic properties. The measurements, at the same temperature, of refractive index and density, together with the effective polarizability result, fill a gap in the literature on biodiesel.

Keywords: Effective Polarizability; Refractive Index; Density; Biodiesel

1. Introduction

Since its creation in 2003, the Renewable Energy Group (GER) of the Universidad de Buenos Aires carries out systematic studies of the properties of liquid fossil fuels, liquid biofuels, and their blends. Optical, electrical, and acoustical properties were exhaustively studied, and correlated with those indicated in international standards. Applications in the literature include liquid biofuels and feedstock characterization[1], contaminants and adulterants detection[2], and aging assessment. In industrial settings and field applications, alternative properties are attractive, including small – scale producers and end users.

Among the liquid biofuels studied at GER, biodiesel (BD) is one of the most interesting. It is a mixture of esters obtained from a transesterification reaction of renewable feedstock (vegetable oils or animal fats) with a short chain alcohol (methanol or ethanol).[3] The usual process uses a basic catalyst (sodium or potassium hydroxide), at constant temperature and under constant stirring. The reaction products (a mix of fatty acid esters – FAE – and glycerin) are separated (by decantation or centrifugation). To comply with the international quality standards, the FAE phase is post-treated (by washing, neutralization and drying). Since the feedstock used for production have different fatty acid content, the values of the BD properties will vary.[4] In consequence, international standards establish allowable ranges for BD properties.

BD in blends with diesel fossil fuel is used for automotive applications in many countries.[5] The worldwide increase in the use of BD in the last two decades, due to environmental concerns, highlights the need of alternative techniques for characterization and quality control. Clearly, strict controls of BD quality are critical for the users and the environment.

Optical properties have several advantages[6]: they are fast and accurate, do not require specialized personnel and may be applied in laboratory and field settings. Moreover, they adapt very well to applications in industrial plants, including "in-line" sensors. The ratio between the speed of light in vacuum (c = 299.792.458m/s) and in a substance is a non-dimensional parameter defined as the refractive index (RI). As remarked by Vargas and Chapman,[7] RI and density measurements may be correlated with physico-chemical properties, including phase behavior and transport properties of petroleum systems. Moreover, as shown in the literature, density and refractive index are strongly correlated.[8] The measurement of RI, [9] known as refractometry, is used extensively for quality control of petroleum products and in manufacturing operations, as pointed out by Bykov.[10] Measurements of RI have been used in regression models related to the molecular structure of BD,[11] to monitor the transesterification reaction in the BD production,[12] in models to estimate other properties[13] and the composition of BD blends with fossil Diesel fuel.[14] Other refractometry applications include combustion studies.[15]

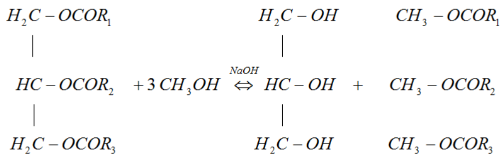
It must be remarked that, even though refractometry is a very interesting technique for BD technology, there are few references that report experimental data of refractive index and density, measured at the same temperature, for BD from different feedstock. To address this lack of data, this work presents original results from a systematic study of RI and density in BD, as a function of temperature. This is part of an ongoing research program at GER on the relation between molecular structure and polarizability.

The effective polarizability is a property, practically independent of temperature, that relates RI and density. It makes possible to estimate the RI from density measurements or vice-versa. In this work, the effective polarizability of the studied BD samples was calculated from our experimental data of IR and density and compared with the result for pure liquid hydrocarbons and crude oils reported by Bykov,[10] and Vargas and Chapman.[7]

2. Materials & Methods

The BD samples studied in this work were produced in the laboratory, through the usual basic transesterification reaction in a batch reactor, followed by a purification process.[9] The feedstock used were soybean, corn, peanut, sunflower, canola, olive, grape, linseed, chia, and almond.

The chemical reaction to convert a triglyceride (vegetable oil or animal fat) into a mixture of fatty acid methyl esters (FAME), using NaOH (sodium hydroxide) as catalyst may be described as follows:



$$\begin{array}{c} H_2C-OCOR_1 \\ | \\ HC-OCOR_2 \\ | \\ H_2C-OCOR_3 \end{array} + 3\,CH_3OH \overset{NaOH}{\Leftrightarrow} \begin{array}{c} H_2C-OH \\ | \\ HC-OH \\ | \\ H_2C-OH \end{array} + \begin{array}{c} CH_3-OCOR_1 \\ CH_3-OCOR_2 \\ CH_3-OCOR_3 \end{array}$$

The temperature was kept at 60°C under continuous stirring for 1 hour. After separation of both phases by decantation, the upper phase (FAME) was purified by three washing steps with water (the first one with acidified water to neutralize the remnants of NaOH) and then dried by heating above 100°C. This last step eliminates the traces of water and methanol in the FAME. This was checked by measurements of the FAME electrical properties (conductivity and permittivity) after the purification process. The electrical properties were measured with an automatic measuring system described in detail in a previous work.[16] To reduce the effects of electrode polarization, the measuring cell had platinized electrodes. A thermostat (Lauda) was used to control the temperature of the samples to ±0.1°C. Cyclo-hexane (pro analisi) was used as reference liquid for system calibration. The measurement uncertainty was below 1%.

Additionally, the properties indicated in the international standards such as kinematic viscosity at 40°C, density at 15°C, sulfated ash, cloud point, copper strip corrosion, acid number, iodine number, flash point, water content, free and total glycerin, were measured according to ASTM D 6751 standard[17] to assure that the mix of FAME can be considered as BD. The BD samples were analyzed by chromatography according to EN 14103[18], to determine the ester content, using a Perkin Elmer Clarus 500 chromatograph with injector split/splitless and a FID detector.

Refractive index measurements of the BD were made with an Abbe refractometer Warkzawa Model RL- 3, in the Sodium D line, according to ASTM D 1218 standard.[19] Density was measured with a densimeter, according to ASTM D 1298 standard.[20] The measurement uncertainty was 10^{-3}g/cm^3.

Refractive index and density measurements were made between 20 and 50°C, in 5°C steps, at a temperature controlled to within +/-0.1°C, using a Lauda thermostat.

3. Results & Discussion

The interaction of liquids with electromagnetic fields is described at the macroscopic level by the electric permittivity (), conductivity (σ), and magnetic permeability (μ). In the optical range, electronic polarization processes are the most important contribution to permittivity. In substances where the optical attenuation is small and the magnetic permeability is practically equal to its value in vacuum (μ_0), such as hydrocarbons and BD, at the visible wavelengths, the refractive index is given by:

$$n(\omega) = \sqrt{\varepsilon'(\omega)} \qquad (1)$$

where is the real part of the complex permittivity. Therefore, in pure substances, the refractive index and density are related to the molecular polarizability by the Lorentz – Lorenz equation by[21]:

$$\alpha = \left(\frac{n^2-1}{n^2+2}\right)\frac{MW}{\rho}\frac{1}{4\pi N_A} \qquad (2)$$

where α is the molecular polarizability of a pure substance (cm^3) as a function of its refractive index, density ρ (g/cm^3), and molar mass, (mol/g); is the Avogadro constant (mol^{-1}). It must be noted that equation (2) is the extension to the optical domain of the well-known Clausius-Mossotti formula for dielectrics.[22]

For mixtures of pure substances, equation (2) may be generalized as:

$$\bar{\alpha} = \left(\frac{n^2-1}{n^2+2}\right)\frac{1}{\rho} \qquad (3)$$

where $\bar{\alpha}$ is the effective polarizability (cm^3/g). This equation is applicable to crude oils and fossil fuels, i.e. mixture of hydrocarbons, and also to BD, a mixture of FAME. In these substances, the electronic polarizability and therefore $\bar{\alpha}$, it is practically independent of temperature but depends on the polarizability of the mixture components.

The chromatographic analysis shows that the length of the carbon chain of the esters is about 18, with a number of double bonds (unsaturation degree) between 1 and 3. Therefore, the molecular structure of all the BD samples studied in this work is similar.

Table I shows our original experimental data (previously unpublished) of density and RI for the D line of sodium, at temperatures between 20C and 50°C, together with the effective polarizability, . As it could be expected, for the BD samples studied in this work is the same for all the feedstock and changes very slightly with temperature. Therefore, within the experimental uncertainty, may be considered as constant within the studied range. From the table, the value of is (0.309±0.002) cm^3/g. This value of , for BD, from ten different feedstock, coincides with that reported in the pioneering work of Colman et al.,[6] (0.311±0.0002) cm^3/g, for soybean BD. Moreover, it also agrees with the value (0.310±0.002) cm^3/g of for BD from sunflower, lard and rapeseed calculated from the density and RI as a function of temperature reported in the literature.[23,24]

The value of for BD found in this work is close to the values reported by Bykov[10] for pure liquid hydrocarbons (0.33 to 0.35 cm^3/g). Additionally, Vargas and Chapman[7] found that this result was applicable to pure liquid hydrocarbons and crude oils. The later authors called their results “the one-third rule”.

The difference in the effective polarizability between BD, hydrocarbons, and crude oils is not surprising, due to the presence of the ester group in the FAME molecules.

Remarkably, for BD produced from coconut oil, that is highly saturated (unsaturation degree lower than 0.15) and with shorter chain length (12), is 0.300 cm^3/g. A possible explanation is that the influence of the ester group in a molecule with shorter chain length is more pronounced, thus increasing the difference from the value of of hydrocarbons and crude oils.

Table I: Refractive index, density, and effective polarizability of BD from different feedstock, at temperatures between 20 and 50°C.

BD feedstock	T (°C)	RI	Density (g/cm^3)	(cm^3/g)
Soybean	20	1.4555	0.881	0.308
	25	1.4537	0.879	0.308
	30	1.4519	0.876	0.308
	35	1.4500	0.872	0.308
	40	1.4482	0.868	0.309
	45	1.4463	0.864	0.309
	50	1.4446	0.861	0.309
Corn	20	1.456	0.881	0.309
	25	1.4545	0.878	0.309
	30	1.4531	0.875	0.309
	35	1.4514	0.871	0.309
	40	1.4498	0.868	0.309
	45	1.4485	0.865	0.310
	50	1.4463	0.862	0.310
Peanut	20	1.4516	0.872	0.309
	25	1.4499	0.868	0.310
	30	1.4486	0.865	0.310
	35	1.4466	0.862	0.310
	40	1.4453	0.859	0.310
	45	1.4434	0.857	0.310
	50	1.4420	0.854	0.310
Sunflower	20	1.4559	0.880	0.309
	25	1.4540	0.877	0.309
	30	1.4520	0.874	0.309
	35	1.4500	0.87	0.309
	40	1.4481	0.867	0.309
	45	1.4460	0.864	0.309
	50	1.4440	0.861	0.309
Canola	20	1.4551	0.879	0.309
	25	1.4530	0.875	0.309
	30	1.4510	0.872	0.309
	35	1.4491	0.869	0.309
	40	1.4472	0.865	0.309
	45	1.4456	0.862	0.309
	50	1.4433	0.858	0.309
Olive	20	1.4511	0.877	0.307
	25	1.4495	0.873	0.308
	30	1.4479	0.87	0.308
	35	1.4461	0.866	0.308
	40	1.4443	0.863	0.308
	45	1.4425	0.859	0.308
	50	1.4406	0.855	0.309
Grapeseed	20	1.4580	0.884	0.309
	25	1.4564	0.881	0.309
	30	1.4548	0.877	0.309
	35	1.4524	0.873	0.309
	40	1.4504	0.87	0.309
	45	1.4486	0.867	0.309
	50	1.4465	0.863	0.309
Linseed	20	1.4617	0.89	0.309
	25	1.4602	0.887	0.309
	30	1.4575	0.883	0.309
	35	1.4562	0.88	0.309
	40	1.4542	0.876	0.309
	45	1.4521	0.873	0.309
	50	1.4500	0.87	0.309
Chia	20	1.4648	0.895	0.309
	25	1.4630	0.892	0.309
	30	1.4618	0.888	0.309
	35	1.4601	0.885	0.310
	40	1.4580	0.882	0.309
	45	1.4559	0.879	0.309
	50	1.4540	0.876	0.309

Almond	20	1.4548	0.879	0.309
	25	1.4520	0.876	0.308
	30	1.4507	0.873	0.308
	35	1.4490	0.87	0.308
	40	1.4478	0.866	0.309
	45	1.4465	0.862	0.310
	50	1.4448	0.859	0.310

It is possible to obtain the RI of BD from the effective polarizability value found in this work and the measured value of density. Remarkably, RI may be correlated with other properties of BD and BD/diesel fossil fuel blends,[25] for instance to estimate the composition of the blends.

4. Conclusion

The biodiesel samples studied in this work were obtained by basic transesterification followed by a purification process. The feedstock were vegetable oils from soybean, corn, peanut, sunflower, canola, olive, grape, linseed, chia, and almond. As measured by chromatography, the length of the carbon chain of all the BD samples was about 18, with a concentration of unsaturated esters higher than 80%.

Measurements of electrical properties, and also those properties included in the international standards were made to assure the quality of BD samples.

The refractive index and density of the BD samples were measured between 20 and 50°C, in 5°C steps, using an Abbe refractometer and a densimeter, respectively.

Effective polarizability was calculated from the experimental data using a generalization of the Lorentz – Lorenz equation. The value, 0.309 cm^3/g with a relative dispersion of 0.65%, is the same for all BD studied in this work, independently of the feedstock. This value of effective polarizability agrees very well with those calculated in this work from density and refractive index, at the same temperature, reported in the literature for different BD samples (soybean, sunflower and lard BD).

It is worth mentioning that for BD from coconut oil (with shorter chain length and very high concentration of saturated esters compared to BD studied in this work), the effective polarizability value is very close (0.300 cm^3/g).

Since the effective polarizability of hydrocarbons is clearly different (0.33 – 0.35 cm^3/g) to that of BD, the presence of hydrocarbons in the biofuel (for instance, adulteration with kerosene) may be detected by the measurement of RI and density, at the same temperature.

In future articles, we will explore the correlations between molecular structure and macroscopic physico-chemical properties.

Based on the availability in the literature of density and refractive index data measured at the same temperature, further works could extend the results in this article to BD from other feedstock.

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6. Conflicts of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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8. Ethical Approval

The authors declare that, according to the guidelines to the Universidad de Buenos Aires, no ethical approval was necessary for this work.

9. References

1. Lapuerta M, Rodríguez-Fernández j, Patiño-Camino R, Cova-Bonillo A, Monedero E, Meziani YM. Determination of optical and dielectric properties of blends of alcohol with diesel and biodiesel fuels from terahertz spectroscopy. Fuel 2020;274:117877.
2. Prasanth A, Harini VK, Manivannan P, et al. Detection of biofuel adulterants using an optical fiber-based refractive index sensor. Optik 2023;291:171345.
3. Fukuda H, Kondo A, Noda H. Biodiesel fuel production by transesterification of oils. J Biosci Bioeng 2001;92(5):405–416.
4. Shelare SD, Belkhode PN, Nikam KC, et al. Biofuels for a sustainable future: Examining the role of nano-additives, economics, policy, internet of things, artificial intelligence, and machine learning technology in biodiesel production. Energy 2023;282:128874.
5. Renewable Energy Market Update 2021. International Energy Agency (IEA) 2021.
6. Colman M, Sorichetti PA, Romano SD. Refractive index of biodiesel-diesel blends from effective polarizability and density. Fuel 2018;211:130–139.
7. Vargas FM, Chapman WG. Application of the One-Third rule in hydrocarbon and crude oil systems. Fluid Phase Equilib 2010;290(1–2):103–108.
8. Krishnaswamy RK, Janzen J. Exploiting refractometry to estimate the density of polyethylene: The
9. Lorentz-Lorenz approach re-visited. Polymer Testing 2005;24(6):762-765.
10. Romano SD, Sorichetti PA. Introduction to Dielectric Spectroscopy. In: Romano SD, Sorichetti PA, editors. Dielectric Relaxation Spectroscopy in Biodiesel Production and Characterization 2011:59-70.
11. Bykov MI. Calculation of specific and molar refraction of hydrocarbons. Chem Technol Fuels Oils. 1984;20:310–312.
12. Alviso D, Romano SD. Prediction of the refractive index and speed of sound of biodiesel from its composition and molecular structure. Fuel 2021;304:120606.
13. Santos RC, Vieira RB, Valentini A. Monitoring the conversion of soybean oil to methyl or ethyl esters using the refractive index with correlation gas chromatography. Microchem J 2013;109:46-50.
14. Geacai S, Iulian O, Nita I. Measurement, correlation, and prediction of biodiesel blends viscosity. Fuel 2015;143:268-274.
15. Chuck CJ, Bannister CD, Hawley JG, Davidson MG. Spectroscopic sensor techniques applicable to real-time biodiesel determination. Fuel 2010;89(2):457–461.
16. Merchan-Merchan W, McCollam S, Pugliese JFC. Soot formation in diffusion oxygen-enhanced biodiesel flames. Fuel 2015;156:129-141.

17. Sorichetti PA, Matteo CL. Low-frequency dielectric measurement of complex fluids using high-frequency coaxial sample cells. Measurement 2007;40(4):437–49.
18. Standard specification for biodiesel fuel blend stock (B100) for middle distillate fuels. ASTM D 6751 - 2023.
19. Fat and oil derivatives. Fatty Acid Methyl Esters (FAME). Determination of ester and linolenic acid methyl ester contents. EN 14103 2020.
20. Standard test method for refractive index and refractive dispersion of hydrocarbon liquids, West Conshohocken, PA: ASTM International 2021.
21. ASTM D1298 - Standard test method for density, relative density, or API gravity of crude petroleum and liquid petroleum products by hydrometer method, West Conshohocken, PA: ASTM International 2023.
22. Talebian E, Talebian M. A general review on the derivation of Clausius-Mossotti Relation. Optik 2013;124:2324–2326.
23. Von Hippel AR. Dielectric materials and Applications. Editorial John Wiley and Sons 1954.
24. Ivaniš GR, Radović IR, Veljković VB, Kijevčanin MLj. Biodiesel density and derived thermodynamic properties at high pressures and moderate temperatures. Fuel 2016;165:244-251.
25. Nita I, Geacai S, Iulian O. Measurements and correlation of physico-chemical properties to composition of pseudo-binary mixtures with biodiesel. Renewable Energy 2011;36(12):3417–3423.
26. Alviso D, Emir S, Clevenot P, Romano SD. Flash point, kinematic viscosity, and refractive index: variations and correlations of biodiesel–diesel blends. J. Brazil. Soc. Mech. Sci. and Eng 2020; 42:347.