

Correlation and Prediction of Biodiesel Density

Nieves M. C. Talavera-Prieto, Abel G. M. Ferreira, António T. G. Portugal, Rui J. Moreira, Jaime B. Santos

Abstract—The knowledge of biodiesel density over large ranges of temperature and pressure is important for predicting the behavior of fuel injection and combustion systems in diesel engines, and for the optimization of such systems. In this study, cottonseed oil was transesterified into biodiesel and its density was measured at temperatures between 288 K and 358 K and pressures between 0.1 MPa and 30 MPa, with expanded uncertainty estimated as $\pm 1.6 \text{ kg}\cdot\text{m}^{-3}$. Experimental pressure-volume-temperature (pVT) cottonseed data was used along with literature data relative to other 18 biodiesels, in order to build a database used to test the correlation of density with temperature and pressure using the Goharshadi–Morsali–Abbaspour equation of state (GMA EoS). To our knowledge, this is the first that density measurements are presented for cottonseed biodiesel under such high pressures, and the GMA EoS used to model biodiesel density. The new tested EoS allowed correlations within $0.2 \text{ kg}\cdot\text{m}^{-3}$ corresponding to average relative deviations within 0.02%. The built database was used to develop and test a new full predictive model derived from the observed linear relation between density and degree of unsaturation (DU), which depended from biodiesel FAMES profile. The average density deviation of this method was only about $3 \text{ kg}\cdot\text{m}^{-3}$ within the temperature and pressure limits of application. These results represent appreciable improvements in the context of density prediction at high pressure when compared with other equations of state.

Keywords—Biodiesel, Correlation, Density, Equation of state, Prediction.

I. INTRODUCTION

CHEMICALLY, biodiesel is a mixture of monoalkyl esters of long chain fatty acids obtained from vegetable oils, animal fats, or their mixtures. It is produced by transesterification of triglycerides with short chain alcohols, such as methanol or ethanol in the presence of a catalyst, leading to fatty acid methyl esters (FAMES) or fatty acid ethyl esters (FAEEs) and glycerol. The main components of biodiesel are palmitate, stearate, oleate, and linoleate esters [1], [2]. In diesel engines, the injection is one of the most important parameters for high performance. An appropriate quantity of fuel must be delivered into the engine cylinder and mixed with air to achieve proper combustion mixture. This operation is carried out under pressure, usually at $p \approx (15 \text{ to } 50) \text{ MPa}$ and moderate temperature $T \approx (300 \text{ to } 350) \text{ K}$, and is strongly affected by the fuel density [3]-[5]. With the common

rail injection technology the pressure can reach up 100 to 120 MPa [6], [7]. Therefore the simulation of biodiesel production, blending, and design of injection systems requires accurate knowledge of volumetric properties over wide ranges of pressure and temperature. Literature usually reports biodiesel density measurements made close to the ambient temperature (285 to 295) K and atmospheric pressure [8]-[14] and few measurements of this property have been reported in wider temperature ranges [15]-[20]. The inclusion of pressure has been made in the works by Pratas et al. [1], Tat and Van Gerpen [2], [21], [22], Nikolic et al. [23], Aparicio et al. [24], Dzida and Prusakiewicz [25], and recently by Chhetri and Watts [26] and Schedemann et al. [27]. Since density depends on the used raw material from which biodiesel was produced, FAMES profile is crucial for applying the correlation and prediction models to that property, which also has not been provided by authors [23]-[25].

To correlate pure FAME and biodiesel densities the Tait equation of state (EoS) [28] has been used [1], [24], [27]. Pratas et al. [1] used this EoS to correlate density of pure FAME (methyl laurate, myristate, and oleate), methyl biodiesels from palm (P), soybean (S), and rapeseed (R) oils, binary (RP, SP, SR) mixtures, and ternary mixture (SRP) for temperatures from 283 K to 333 K and pressures up to 45 MPa. Schedemann [27] used Tait equation to correlate data for methyl linoleate at temperatures between 278 K to 367 K and pressures between 0.4 MPa and 130 MPa. The relative deviations in density obtained from those correlations have been usually lower than 0.01%. Cubic equations of state such as the cubic-plus-association equation of state (CPA EoS) [29], [30], and the volume translated Peng-Robinson (PR) equation of state (VTPR EoS) [31] have been applied to density correlation and prediction. The CPA EoS combines a physical contribution from a cubic density EoS (Soave-Redlich Kwong EoS) with an association term accounting for intermolecular hydrogen bonding and solvation effects, which disappears for non-associating components, such as esters. The VTPR EoS uses the cubic Peng-Robinson EoS in which the predictive UNIFAC group contribution method developed by Dortmund [32] is employed for calculation of the needed parameters. Pratas et al. [1] applied the CPA EoS to correlate pure FAME density, and the calculated pure component parameters were applied to predict the density of methyl biodiesels with deviations ranging from 0.79% to 2.5%. Schedemann et al. [27] used the VTPR method to predict density data of methyl linoleate and biodiesel. For the biodiesel deviations $\approx 1\%$ were found at 396.8 K and pressures up to 55 MPa whereas at temperatures lower than 386.9 K and pressures up to 130 MPa deviations ranged from -1 to -7%. More complex EoS such as variants of SAFT EoS were also used. The SAFT EoS is based on a clear physical

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molecular model, assuming that a molecule is composed of chains of freely jointed spherical segments and several intermolecular forces are taken in consideration [33]. Recently Oliveira et al. [34] applied the soft-SAFT EoS to density prediction of FAMES and of biodiesels measured by Pratas et al. [1] and obtained mean deviations of 0.49%. Dong et al. [35] were the first to apply the PC-SAFT equation of state using group contribution methods for the calculation of parameters and prediction of FAMES and biodiesel densities. For FAMES at atmospheric pressure, deviations in density were less than 0.5%, and for biodiesels studied by Pratas et al. [1] predicted densities were all within 1% deviation. Pratas et al. [36] extended a group contribution method developed for the prediction of molar volume (GCVOL) under high pressure. The prediction of biodiesel density with this method was made with relative deviations between 0.2% and 0.7%. Recently Meng et al. [37] revised the modified Rackett equation proposed by Spencer and Danner [38] to predict biodiesel densities over wide temperature range (298 to 523) K at atmospheric pressure. The revised Rackett equation allowed the density prediction for three biodiesels with a maximum deviation of 0.42%. An attempt was made to use fundamental relations of thermodynamics in particular the Helmholtz free energy [16] to model thermodynamic properties of biodiesel. Using this approach, biodiesel density was predicted within 0.6% deviation for temperatures between 278 K and 333 K. A new interesting approach and never applied to biodiesel for the correlation of density is provided by the Goharshadi–Morsali–Abbaspour equation of state (GMA EoS), which was found valid for polar, non-polar, and H-bonded fluids [39]. The GMA EoS equation is based on the theory of the average potential energy and has shown linear behavior for various thermodynamic properties. The existence of such regularities is very important because they can be used for safe extrapolation in the density calculation for high pressures.

In this work, densities of cottonseed biodiesel produced by transesterification of oil (PCS) were measured at pressures between 0.1 and 30.0 MPa and temperatures from 288 K to 358 K using a vibrating tube densimeter, model DMA 512P from Anton Paar. This work is part of a broader project aiming the determination of temperature and pressure dependences of the biodiesel thermophysical properties, and their use in the monitoring and control of this biofuel production. Density data regarding cottonseed biodiesel is very scarce in the literature compared with other FAME diesels. Nogueira et al. [40] presented density data at temperatures between 293.15 and 373.15 K at atmospheric pressure, and Alptekin and Canakci [10] presented the value at 288.15 K. To the best of our knowledge, no high-pressure results were presented so far for this biodiesel. Cottonseed is a byproduct from cotton with high production level in many countries and it is envisaged as an alternative oleaginous species traditionally cultivated for biodiesel production [41], [42]. Moreover, cottonseed biodiesel can be considered a second generation biofuel, since it has not been used in the human food chain and results from

a cotton crop waste. Also the studies on production [43] and use of cottonseed biodiesel as fuel for engines are increasing [41], [44].

Aiming to gather a sufficiently large amount of data, and for the sake of statistical significance for biodiesel density correlation and prediction, the measured densities for cottonseed made in this study were combined with biodiesel data provided by Pratas et al. [1], Tat and Van Gerpen [2], [21], and Schedemann et al. [27].

The information regarding all biodiesels was included in the so constituted pVT database and used to establish correlations using the GMA EoS. A new model related with the degree of unsaturation of biodiesel was developed to predict density as function of temperature and pressure. The predictive GCVOL for high pressure used by Pratas et al. [36] was also applied to the fuels that constituted the built database. The relative deviations of the predicted densities against experimental data were calculated for accurate evaluation of the predictive methods.

II. EXPERIMENTAL

A. Materials

The detailed specifications of all materials are summarized in Table I, where the FAMES and N- heptane (used as eluent in gas chromatography) are presented. The terminology (Cm:n) was used for FAMES, where m is the number of carbon atoms and n the number of double bonds of the related fatty acid. Table I also reports the name, purity, supplier, and CAS number of each compound used in this study.

B. Cottonseed Biodiesel Preparation

The transesterification of cottonseed oil was carried out in a 50 ml three-necked double wall jacketed reactor. The reactor was equipped with a reflux condenser to avoid methanol losses, a magnetic stirrer, a digital thermometer (ERTCO-EUTECHNICS Model 4400 Digital thermometer) and one stopper to feed reagents. The reaction vessel was initially charged with a known amount of cottonseed oil (Acros Organics). Solutions of known amounts of sodium methoxide in methanol were prepared and fed to the reactor for transesterification of the previously heated cottonseed oil. After feeding, the reactor was air tight closed, and the temperature maintained constant by circulating hot water through the vessel jacket. The reaction mixture was held at a temperature just above the boiling point of the alcohol i.e. around 65°C. Excess alcohol was used to provide enough driving force for total conversion of the oil into methyl esters. After two hours of reaction the methyl ester formation process was completed, so the heating and stirring were stopped and the products were cooled and transferred to a sedimentation funnel. The ester layer containing mainly FAMES, and the glycerol layer containing mainly glycerol and methanol were separated. The biodiesel was washed and dried under vacuum to remove impurities and traces of moisture, respectively.

TABLE I
SAMPLE MATERIAL PURITIES

| Material | Supplier | Cas No | Sample purity (wt%) | properties |
|-------------------------------|----------------|-----------|---|---|
| Sodium metoxide | Fluka | 124-41-4 | ≥97 | |
| Methanol | Carlo Herba | 67-56-1 | ≥99.9 | |
| Methyl myristate (C14:0) | Fluka | 124-10-7 | ≥99 | |
| Methyl Pentadecanoate (C15:0) | Fluka | 7132-64-1 | ≈99 | |
| Methyl palmitate (C16:0) | Fluka | 112-39.0 | ≥99 | |
| Methyl stearate (C18:0) | Sigma | 112-61-8 | ≈99 | |
| Methyl oleate (C18:1) | Aldrich | 112-62-9 | ≈99 | |
| Methyl linoleate (C18:2) | Acros Organics | 112-63-0 | ≈99 | |
| Methyl linolenate (C18:3) | Fluka | 301-00-8 | ≥99 | |
| Methyl heptadecanoate (C17:0) | Fluka | 1731-92-6 | ≥99 | |
| N-Heptane | Sigma Aldrich | 142-82-9 | 99 | |
| Cottonseed oil | Acros Organics | 17711 | Fatty acid composition: MeC14:0 and lower: ca 1.5%; MeC16:0 ca 25%; MeC18:0 ca 3%; MeC18:1, 16 to 24%; MeC18:2, 50 to 55%; MeC18:3 and higher < 1.5%. | $AV \leq 0.5 \text{ mg KOH}\cdot\text{g}^{-1}$ $SV = 185 - 198 \text{ mg KOH}\cdot\text{g}^{-1}$ $IV = 95 \text{ to } 115 \text{ g I/100g}$ $UM < 1.5\%$ $n = 1.4720 \text{ to } 1.4730 (20^\circ\text{C}, 589 \text{ nm})$ |

AV =acid value; SV =Saponification value; IV =Iodine value; UM =unsaponifiable matter; n =refractive index.

C. Biodiesel Characterization

The so produced FAMES were analyzed by gas chromatography (GC) in a TRE METRICS 9001 gas chromatograph equipped with a flame ionization detector (FID). A fused silica capillary column DB-225 (J & W Scientific, Agilent) of 30 m length, 0.15 μm film, and 0.25 mm internal diameter were used. Samples (1 μL) were injected at temperature of 280°C without split. Helium was used as the carrier gas at a flow rate of 1 $\text{ml}\cdot\text{min}^{-1}$, and also used as auxiliary gas for the FID. The following temperature ramp was used: initial temperature of 70°C maintained for 1 min, followed by an increase of 10°C $\cdot\text{min}^{-1}$ up to 180°C, and then 3°C $\cdot\text{min}^{-1}$ up to 220°C maintained for 15 min. The biodiesel components were quantified using heptadecanoate methyl ester as internal standard. Calibration curves were developed using different concentrations of each methyl ester in n-heptane with addition of internal standard. The composition (w/w)% of the cottonseed biodiesel (PCS) was found from three injections: methyl myristate (0.93±0.28)%, methyl palmitate (26.76±1.56)%, methyl stearate (2.81±0.29)%, methyl oleate (17.89±1.71)%, and methyl linoleate (51.61±2.99)%.

D. Experimental Density Measurement

Cottonseed biodiesel densities were determined using an Anton Paar DMA 60 digital vibrating tube densimeter, with a DMA 512P measuring cell. The temperature in the vibrating tube cell was measured with a platinum resistance probe (PT100). A Julabo F12-ED thermostatic bath with ethylene glycol was used as circulating fluid in the thermostat circuit of the measuring cell and the temperature was held constant to ±0.01 K. The required pressure was generated and controlled using a Pressure Generator model 50-6-15, High Pressure Equipment Co., with acetone as hydraulic fluid. The diameter of the metallic tube was 1.59×10^{-3} m, and the buffer had more than 1 m length, which guaranteed the inexistence of hydraulic liquid diffusion in the liquid contained within the densimeter cell. Pressures were measured with a pressure transducer

(Wika Transmitter S-10, WIKA Alexander Wiegand GmbH & Co.). A PCI-6220 data acquisition board (DAQ) from National Instruments (NI) was used for real time collection of period, temperature, and pressure values. For this task a Labview application was developed. Modules of temperature (NI SCC-FT01) and pressure (NI SCC-CI20) were installed into a NI SC-2345 bus and connected to the DAQ board. The measuring setup and the calibration of the vibrating tube densimeter were described with detail in a previous paper [45]. The performance of the densimeter was checked against water (Milli-Q) at temperatures (298.15, 318.15, 328.15, 338.15, 358.15) K and for each temperature different pressures (0.1, 10, 20, 30) MPa were considered. At each (T, p) coordinate the density was measured five times in increasing pressure direction, and other five times in decreasing pressure one. The repeatability in density was better than 0.1 $\text{kg}\cdot\text{m}^{-3}$. The measured densities compared with the reference NIST data [46], showed relative deviations in the range (0.03 to 0.07)%, except for 358.15 K where deviations reached 0.15%. The influence of viscosity on density uncertainty (damping effects on the vibrating tube) for liquids with viscosities less than 100 mPa·s can be important. An approximate value of such uncertainty was obtained using the method proposed by Anton Parr [47] for the DMA 512P densimeter. From densities and viscosities presented by Nogueira et al. [40] for babassu, soybean and cottonseed biodiesels the obtained uncertainty was 0.03 $\text{kg}\cdot\text{m}^{-3}$ thus contributing with a negligible value to the combined standard uncertainty. The expanded uncertainties, U , were calculated with confidence level 95% (with coverage factor $k=2$) for temperature, pressure, and density. The expanded uncertainties in temperature and pressure were $U(T) = \pm 0.02 \text{ K}$ and $U(p) = \pm 0.02 \text{ MPa}$, respectively. The combined standard uncertainty of the density measurements, estimated taking into account the influence of uncertainties associated with calibration equation [45], temperature, pressure, period of oscillations (six-digit frequency counter), viscosity, and density data of calibrating fluids was estimated as $\pm 0.81 \text{ kg}\cdot\text{m}^{-3}$. Hence, the expanded

uncertainty in the measurement of density by this method was estimated to be $U(\rho) = \pm 1.6 \text{ kg}\cdot\text{m}^{-3}$.

III. DENSITY DATABASE FOR BIODIESELS

The information concerning biodiesel density under high pressures with detailed FAMES profile is available in literature as explained in the introduction section. The composition of biodiesel is a crucial issue for suitable application of the thermodynamic property models. Pratas et al. [36] have shown that discrepancies in density data reported by different authors are usually due to differences in the oil composition, and not caused by experimental errors during measurements. Thus, biodiesel detailed composition must be known for reliable prediction of their densities. The database used for the development of density models containing 19 biodiesels was built using measurements made by Pratas et al. [1], Tat and Van Gerpen [2], [21], and Schedemann et al. [27], and our measurements regarding cottonseed biodiesel. Tat et al. [22] presented density values at 294 K and up to 35 MPa for methyl soy biodiesel. However, access to the values is difficult and uncertain because they are presented in graphic form. Their biodiesel had practically the same composition of N21 biodiesel, which was also measured up to 35 MPa for temperatures between 293 K and 373 K. Dzida and Prusakiewicz [25] measured density from 263 K up to 373 K at atmospheric pressure and the values at pressures up to 100 MPa in the range (293 to 318) K were calculated following a numerical procedure proposed by Sun et al. [48]. However, the FAMES profile was not presented, neither by Nikolić et al. [23] who made density measurements for rapeseed biodiesel at 293 K and up to 160 MPa and presented density data in graphic form, which for our purpose was useless. Density as a function of temperature at atmospheric pressure for all fuels in the database is plotted in Fig. 1. Density decreases as temperature increases, as expected. Lower and upper density limits for the envelope density in the database correspond to N23 (methyl tallow) and N7 (methyl linolenate) fuels studied by Tat and Van Gerpen [2], [21], respectively. This was expected since density increases with increasing content in unsaturated FAMES and unsaturation level. According to the biodiesel composition, the degree of unsaturation (DU) can be calculated taking into account the amount of monounsaturated and polyunsaturated FAMES (wt.%) present in the biodiesel by the empirical expression [49]-[51],

$$DU = (\text{monosat Cn:1;wt.}\%) + 2(\text{polyunsat Cn:2,3;wt.}\%) \quad (1)$$

The degree of unsaturation of N23 and N7 biodiesels were 49 and 153, respectively, being the lowest and the highest values of DU in database. The biodiesels presented by Pratas et al. [1], the cottonseed biodiesel and the fuel measured by Schedemann et al. [27] showed intermediate behaviour in density as function of temperature compared with N7 and N23 biodiesels. All the fuels in the set presented lower contents in C18:3 than N7 biodiesel. The C18:3 content ranges from a minimum of 0.09% (P fuel, $DU=62.0$) to a maximum of 8.0% (SCHB fuel, $DU=117.4$). The cottonseed biodiesel showed a

density value well in the middle of the (temperature, density) plot, corresponding to an intermediate DU . The degree of unsaturation is strongly dependent on the C18:2 and C18:3 contents, which has great influence in the density, and therefore it is expected that this parameter might be important in density calculations. For this reason we have used this parameter to develop a predictive model of density.

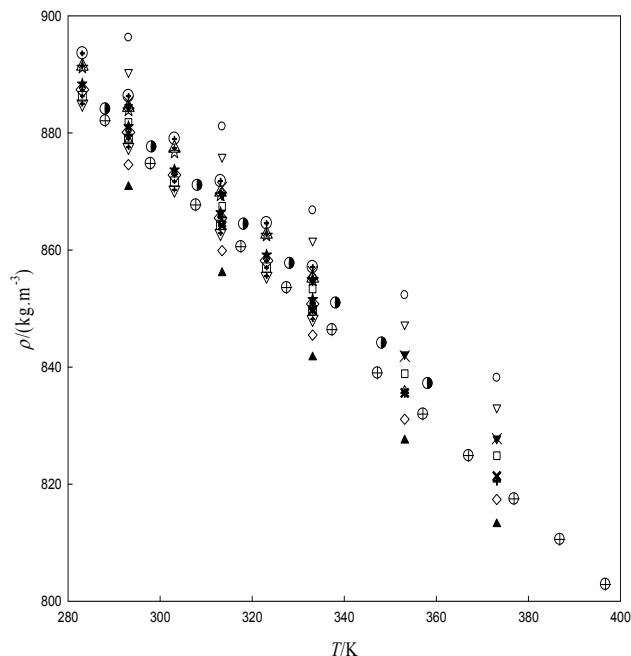


Fig. 1 Density as a function of temperature at 0.1 MPa for the biodiesels in database: Δ , N5; ∇ , N6; \circ , N7; \square , N21; \diamond , N19; $+$, N20; \blacktriangle , N23; \blacktriangledown , N17; \times , N8; \times , N9; \blacktriangleleft , R; \blacktriangledown , P; \oplus , S; \star , SR; \boxplus , RP; \diamond , SP; \star , SRP; \bullet , PCS; \oplus , SCHB

IV. RESULTS AND DISCUSSION

A. Density of Cottonseed Biodiesel

Cottonseed biodiesel pVT data measured during our experiments is plotted in Fig. 2 for temperatures between 288.15 K and 358.15 K and pressures between 0.1 MPa and 30.0 MPa. To our knowledge these are the first measurements for cottonseed biodiesel under pressure. The experimental data showed that biodiesel density behaved as expected, meaning that density decreases as temperature increases and pressure drops. The density at 288.15 K and atmospheric pressure is $884.1 \text{ kg}\cdot\text{m}^{-3}$ and, thus it is well within the limits between 860 to $900 \text{ kg}\cdot\text{m}^{-3}$ required by the EN 14214 standard [52].

Our density measurements were comparable with those presented by Nogueira et al. [40], whose measurements were made at (293.15, 313.15, 333.15, 353.15, and 373.15) K, and the ones presented by Alptekin and Canakci [10] at 288.15 K, all data at atmospheric pressure (vd. Fig. 3). Taking linear representations of density data on the temperature obtained for the present work and data presented by Nogueira et al. [40], calculated deviations were between 0.1% and 0.4%. No explanation was found for the differences between our values

and those presented by Nogueira et al., since the measurement techniques were similar, and the FAMEs profile of the samples were almost the same resulting in comparable molecular weights (PCS: $M=287.53$, Nogueira et al.: $M=288.33$) and degrees of unsaturation (PCS: $DU=121.1$, Nogueira et al.: $DU=129.7$).

B. Density Correlation

In the present work the GMA EoS was used to correlate density with temperature and pressure of cottonseed and all the other biodiesels in the database built for this work. The GMA EoS is conveniently given by [39],

$$(2z-1)V_m^3 = A(T) + B(T)\rho_m \quad (2)$$

where z , V_m , and ρ_m are the compressibility factor, molar volume, and molar density, respectively. The temperature dependent parameters $A(T)$ and $B(T)$ are given by the following equations [39]:

$$A(T) = A_0 - \frac{2A_1}{RT} + \frac{2A_2 \ln T}{R} \quad (3)$$

$$B(T) = B_0 - \frac{2B_1}{RT} + \frac{2B_2 \ln T}{R} \quad (4)$$

where A_0 - A_2 and B_0 - B_2 are the fitting parameters, and R is the gas constant.

Density at different temperatures and pressures was calculated from

$$B(T)\rho_m^5 + A(T)\rho_m^4 + \rho_m - 2p/RT = 0 \quad (5)$$

The coefficients A_0 - A_2 and B_0 - B_2 of the GMA EoS regressed by fitting (2) to (4) to the pVT data through least-squares method Lavenberg-Marquardt method with confidence limits of 95% are given in Table II. Standard deviation, σ , correlation coefficient r , number of data points N_p , are also indicated. The average relative deviation, ARD , and the standard deviation for density, σ_ρ , calculated respectively by

$$ARD\% = 100 \sum_{i=1}^{N_p} |1 - \rho_{calc} / \rho_{exp}|_i / N_p \quad (6)$$

and

$$\sigma_\rho = \left[\sum_{i=1}^{N_p} (\rho_{calc} - \rho_{exp})_i^2 / (N_p - k) \right]^{1/2} \quad (7)$$

are also presented in Table II. In (6) and (7), ρ_{calc} and ρ_{exp} are the densities calculated from (5) and those experimentally determined for the measurement i , respectively, and k (=6) is the number of adjusted parameters. The statistical indicators allowed to conclude that GMA EoS gives an excellent pVT data correlation for biodiesels, since the standard deviation in density is generally less than $0.2 \text{ kg}\cdot\text{m}^{-3}$ and the ARD is less than 0.02% .

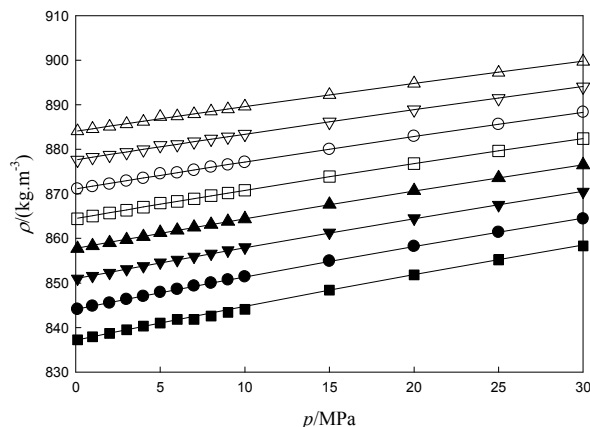


Fig. 2 Isotherms of density, ρ , for cottonseed biodiesel. The symbols refer to experimental data of this work: Δ , 288.15 K; ∇ , 298.15K; \circ , 308.15 K; \square , 318.15 K; \blacktriangle , 328.15 K; \blacktriangledown , 338.15 K; \bullet , 348.15 K; \blacksquare , 358.15 K. The lines represent the calculations from GMA EoS

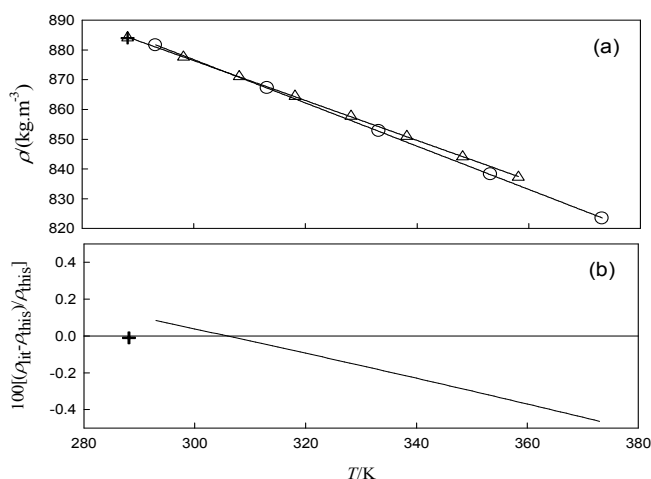


Fig. 3 Comparison between the densities of this work and values from the literature. (a) Δ , this work; \circ , Nogueira et al. [40]; $+$, Alptekin and Canakci [10]. (b) Deviations between the densities of this work (ρ_{this}) and values from the literature (ρ_{lit}). The line shows the deviations from density of Nogueira et al. [40]

Under isothermal conditions, the quantity $(2z-1)V_m^3$ showed a linear behavior with the molar density. The isotherms of $(2z-1)V_m^3$ versus molar density are presented in Fig. 4 for cottonseed and Schedemann [27] biodiesels selected from our database, having in consideration the differences in temperature and pressure ranges at which density measurements were made. The linearity held well for all isotherms and was slightly improved when shorter temperature and pressure ranges were considered like in the cottonseed case. Good results were also obtained for the other biodiesels from our database. The linearity seem to be very important for safe extrapolation of density at high temperatures and pressures.

TABLE II

FITTING PARAMETERS OF GMA EOS APPLIED TO THE CORRELATION OF EXPERIMENTAL *PVT* DATA OF BIODIESEL FUELS WITH 95% CONFIDENCE LIMITS. THE STANDARD DEVIATION (σ), CORRELATION COEFFICIENT (R), AND NUMBER OF DATA POINTS (N_p) ARE GIVEN. ALSO REFERRED ARE THE STANDARD DEVIATION IN DENSITY (σ_ρ), AND THE AVERAGE RELATIVE DEVIATION IN DENSITY (ARD)

| Parameter | R | P | S | SR | PR | SP | SRP |
|-----------------|----------------------------|-------------------------|--------------------------|--------------------------|---------------------------|-------------------------|--------------------------|
| A_0^a | 156.6408 | 155.02365 | -191.31330 | -203.12707 | -19.90696 | 88.19071 | -76.56096 |
| A_1^b | 57.4777 | 54.62277 | -9.48038 | -10.92667 | 21.34827 | 43.52531 | 12.35306 |
| A_2^c | -0.0916 | -0.090737 | 0.1232171 | 0.1308369 | 0.0167058 | -0.0490859 | 0.0525300 |
| B_0^d | -49.4897 | -44.08269 | 69.27326 | 74.10448 | 12.63065 | -22.26999 | 32.08480 |
| B_1^e | -17.4004 | -15.45037 | 5.47409 | 6.09774 | -4.71302 | -11.88194 | -1.60108 |
| B_2^f | 2.9599×10^{-2} | 2.6243×10^{-2} | -4.3751×10^{-2} | -4.6842×10^{-2} | -8.56398×10^{-3} | 1.2664×10^{-2} | -2.0847×10^{-2} |
| σ^g | 0.001653 | 0.000960 | 0.001426 | 0.001633 | 0.000928 | 0.000918 | 0.002572 |
| σ_ρ^h | 0.09 | 0.06 | 0.13 | 0.14 | 0.06 | 0.06 | 0.15 |
| r | 0.9993 | 1.0000 | 0.9999 | 0.9999 | 1.0000 | 1.0000 | 0.9997 |
| N_p | 84 | 84 | 84 | 84 | 84 | 84 | 84 |
| $ARD\%$ | 0.008 | 0.006 | 0.013 | 0.013 | 0.005 | 0.005 | 0.010 |
| Parameter | N5 | N6 | N7 | N8 | N9 | N17 | N19 |
| A_0 | -11.65220 | 130.32820 | -28.91800 | 117.74356 | 230.08141 | -365.23193 | 146.2366 |
| A_1 | 23.78009 | 51.95599 | 19.70029 | 49.70914 | 74.50985 | -45.43698 | 54.5771 |
| A_2 | 0.0121614 | -0.074832 | 0.0226279 | -0.0664370 | -0.1343981 | 0.2292324 | -0.0846 |
| B_0 | 10.02161 | -35.802429 | 18.70439 | -29.83708 | -65.78690 | 136.99403 | -39.8071 |
| B_1 | -5.56848 | -14.65893 | -3.54271 | -13.51784 | -21.47494 | 19.30164 | -15.2526 |
| B_2 | -7.164697×10^{-3} | 0.0209081 | -0.012448 | 0.017005 | 0.038765 | -0.085119 | 0.023366 |
| σ | 0.001888 | 0.001772 | 0.002621 | 0.002117 | 0.002045 | 0.005443 | 0.001481 |
| σ_ρ^h | 0.14 | 0.14 | 0.22 | 0.16 | 0.14 | 0.39 | 0.12 |
| r | 0.9999 | 0.9999 | 0.9995 | 0.9997 | 0.9998 | 0.9989 | 0.9999 |
| N_p | 30 | 30 | 30 | 24 | 30 | 30 | 30 |
| $ARD\%$ | 0.012 | 0.011 | 0.018 | 0.014 | 0.012 | 0.032 | 0.010 |
| Parameter | N20 | N21 | N23 | PCS | SCHB | | |
| A_0 | -12.2901 | 168.1241 | 112.1672 | 93.75307 | 31.96439 | | |
| A_1 | 25.0475 | 60.8676 | 47.5108 | 45.51811 | 34.23931 | | |
| A_2 | 0.0128 | -0.0974 | -0.0637 | -0.05195 | -0.014476 | | |
| B_0 | 10.7011 | -49.1615 | -28.5269 | -25.7089 | -4.14103 | | |
| B_1 | -5.9416 | -17.7889 | -12.9304 | -12.9335 | -8.94477 | | |
| B_2 | -7.6505×10^{-3} | 0.028891 | 0.016435 | 0.014473 | 0.0015429 | | |
| σ | 0.001989 | 0.001553 | 0.003008 | 0.001458 | 0.005861 | | |
| σ_ρ^h | 0.73 | 0.11 | 0.22 | 0.10 | 0.37 | | |
| r | 0.9999 | 0.9999 | 0.9997 | 0.9998 | 0.9998 | | |
| N_p | 30 | 30 | 30 | 120 | 324 | | |
| $ARD\%$ | 0.064 | 0.009 | 0.018 | 0.007 | 0.033 | | |

Proceeding with the evaluation of the GMA EoS capacity to correlate the density data for all temperatures and pressures, the relative deviations between experimental and calculated values with (2) were evaluated. In Fig. 5, the relative deviation as a function of temperature and pressure is shown for cottonseed and Schedemann biodiesels. Due to more restricted temperature and pressure ranges of the fitting for cottonseed biodiesel the relative deviations were very small, usually in the range $\pm 0.02\%$ (less than $\pm 0.2 \text{ kg.m}^{-3}$), while for the biofuel measured by Schedemann et al. [27] the deviations were usually less than $\pm 0.05\%$ (less than $\pm 0.5 \text{ kg.m}^{-3}$). For the other biodiesels in our database the deviations were in the same range as found for cottonseed biodiesel.

C. Density Prediction

1. The Group Contribution Methods (GCVOL)

A group contribution method (GCVOL) for the prediction of liquid densities as a function of temperature from the triple

point to the normal boiling point was presented by Elbro et al. [53]. In that method (original GCVOL) the molar volume was calculated by

$$V_m = \sum_i n_i \Delta v_i \quad (8)$$

where n_i is the number of group i in the substance and Δv_i is a temperature dependent group molar volume given by

$$\Delta v_i = A_i + B_i T + C_i T^2 \quad (9)$$

where the group volume parameters A_i , B_i , and C_i were obtained by Elbro et al. [53], whose original model presented 36 different group parameters for a large variety of chemical substances, including alkanes, alkenes, aromatic, alcohols, ketones, aldehydes, esters, ethers, chlorides, and siloxanes. The densities for strongly polar solvents were predicted by this

method with an average relative deviation of 1% approximately.

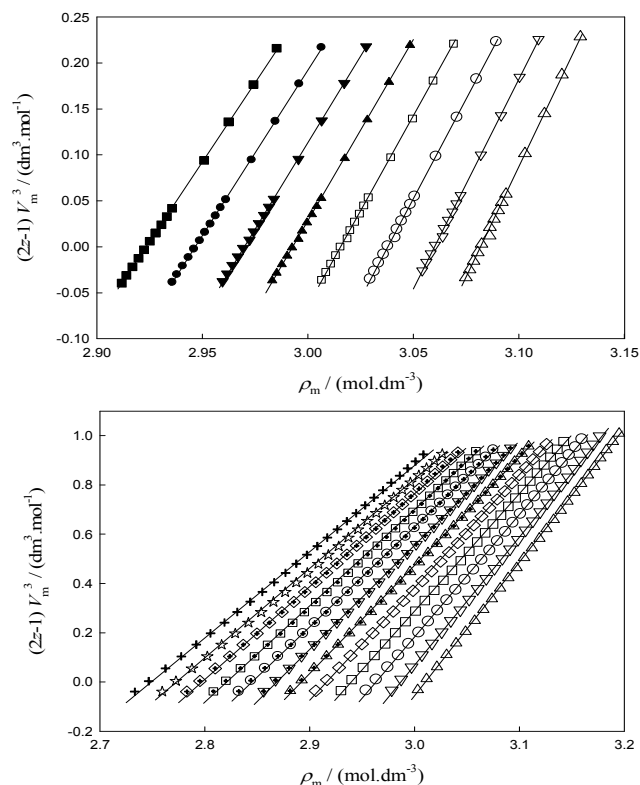


Fig. 4 Isotherms of $(2z-1)V_m^3$ versus the molar density (ρ_m) for cottonseed and Shedmann (SCHB) biodiesels calculated from GMA EoS. (a) Cottonseed (experimental data of this work): legend as in Fig. 2. (b) SCHB: Δ , 288.12 K; ∇ , 297.93 K; \circ , 307.8 K; \square , 317.6 K; \diamond , 327.49 K; \blacktriangle , 337.38 K; \blacktriangledown , 347.26 K; \oplus , 357.13 K; \boxplus , 367.03 K; \diamond , 376.91; \star , 386.84 K; $+$, 396.76 K. Full curves calculated from correlation with GMA EoS

In 2003, Ihmels and Gmehling [54] added 24 new groups to the 36 existing ones using the Dortmund Data Bank for Pure Component Properties (DDB-Pure). With this extension (extended GCVOL) densities of tertiary alcohols, alkynes, carboxylic acids, allenes, cycloalkanes, fluorides, bromides, iodides, thiols, sulfides, sulfates, amines, nitriles, and nitro compounds were calculated with an average mean deviation of 1.5% for a database of 1040 compounds. Pratas et al. [55], [56] applied the original CGVOL to density prediction of pure FAMES present in biodiesel in greater content, and those existing in minority. They concluded that for the majority FAMES the density can be predicted within an *ARD* of 0.5%, except for the methyl linoleate since the model describes poorly the effect of unsaturation on density. For the case of minority FAMES and FAEEs the density could be predicted within a deviation of 1.5%, except for the linolenate esters at high temperatures, again due to the poor description of the polyunsaturation effect on densities. Pratas et al. [36] also applied the original and the extended GCVOL models to 18 biodiesel samples of soy, rapeseed, palm, cottonseed, jatropha,

and mixtures thereof at temperatures between 273.15 and 373.15 K and densities from 815 to 898 $\text{kg}\cdot\text{m}^{-3}$, and obtained overall *ARDs* of 0.6% and 2.7% for the original and the extended GCVOL, respectively. To solve the precision lack for the polyunsaturation ester effect, Pratas et al. [36] found new parameter values A_i , B_i , and C_i relative to the double bond ($-\text{CH}=\text{}$) contribution, based on density data measured for FAMES [55], [56]. This revised variant of GCVOL was applied to the 18 biodiesels leading to a decrease in the overall *ARDs* to 0.25% in density, corresponding to $\approx 2 \text{ kg}\cdot\text{m}^{-3}$ [36]. Pratas et al. extended the revised GCVOL to high pressures using the equation [36]

$$\rho(T, p) = \frac{M}{V_m(T)(1 + Ap)} \quad (10)$$

where ρ is the density in $\text{g}\cdot\text{cm}^{-3}$, M is the molecular weight in $\text{g}\cdot\text{mol}^{-1}$, $V_m(T)$ is the molar volume in $\text{cm}^3\cdot\text{mol}^{-1}$ predicted by revised GCVOL, and p is the absolute pressure (MPa). For biodiesel the mean molecular mass is

$$M = \sum_i x_i M_i \quad (11)$$

where x_i and M_i are the molar fraction and the molecular weight of FAME i in the fuel, respectively. Pratas et al. obtained $A = -5.7 \times 10^{-4} \text{ MPa}^{-1}$ [36] by fitting (10) to high pressure densities for laurate, myristate, and oleate methyl esters, reported by Pratas et al. [55], [56]. The (10) correlated the high pressure densities of these methyl esters with an *ARD* of 0.3%, and the high pressure densities for 8 biodiesel fuels were predicted with *ARDs* from 0.23 to 0.74% [36]. We have recalculated the constant A in (10) by fitting densities of methyl palmitate [57], methyl oleate [1], [58], and methyl linoleate [27], [58], since they were the most abundant FAMES in the biodiesels. The fitting of (10) gave $A = (-5.46 \times 10^{-4} \pm 4.35 \times 10^{-6}) \text{ MPa}^{-1}$ with standard deviation of 5.0 $\text{kg}\cdot\text{m}^{-3}$ and *ARD* = 0.43%.

The *ARDs* resulting from application of (10) to the prediction of high-pressure densities for the nineteen biodiesels in the database are presented in Table III. Some of the biodiesels measured by Tat and Van Gerpen as N7, N8, N9, N17 showed *ARDs* higher than 1%. These biodiesels could be considered as outliers from the point of view of the dominant FAMES profiles since N7 had a very high C18:3 content, N8 and N9 showed high values of C18:0, and N17 presented a very high content of C18:1. The overall average deviation of 0.60% corresponding to about 5 $\text{kg}\cdot\text{m}^{-3}$, can be regarded as an indicator of a reasonable performance in predicting the density with (10). A huge advantage of this method is its simplicity and straightforward density estimation.

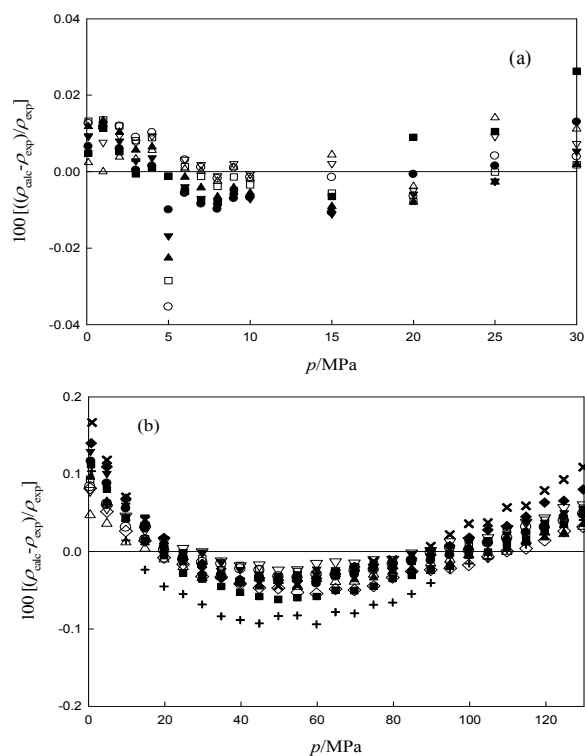


Fig. 5 Relative density deviations between the calculated values with GMA EoS (ρ_{cal}) and the experimental values (ρ_{exp}). (a) Cottonseed fuel: legend as in Fig. 2; (b) SCHB: legend as in Fig. 4 (b)

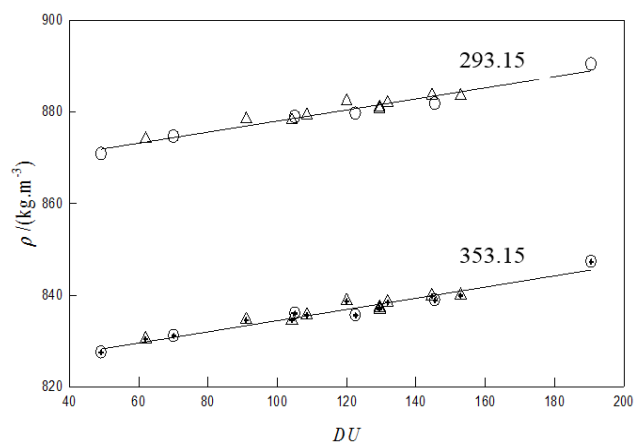


Fig. 6 Density as function of the degree of unsaturation for some biodiesels in the database. At 293K and 0.1 MPa: Δ , [1]; \circ , [2], [21]; at 353 K and 0.1 MPa: \triangle , [1], \odot , [2], [21]

2. Degree of Unsaturation

The density data for several biodiesels measured by Pratas et al. [1] and by Tat and Van Gerpen [2], [21] are represented in Fig. 6 as function of the degree of unsaturation for 293.15 K and 353.15 K, at atmospheric pressure.

Clearly, for each temperature the density was a linear function of the DU . For this reason and taking into account that density is a linear function of temperature with a slight curvature at high pressures [23], [27], the equation

$$\rho = (d_1 + d_2T + d_3p + d_4p^2) + (d_5 + d_6T + d_7p + d_8p^2)DU \quad (12)$$

is proposed to represent the biodiesel density within wide ranges of temperatures and pressures.

The biodiesels (S,R,P) reported by Pratas et al. [1] and (N6, N20, N23) studied by Tat and Van Gerpen [2], [21] were used as the training set for fitting with (12), and the other thirteen biodiesels were included in the validation set. The training set was selected to fulfil the following: (i) biodiesels having a linear density dependence on DU ; (ii) biodiesels covering a wide range of DU (the range of DU is between 49.2 (N23) to 190.6 (N6)); (iii) biodiesels from different authors should spread in wide density ranges. The parameters of (12) for 95% confidence limits were $d_1=(1088.017 \pm 3.359)$, $d_2=(-0.74348 \pm 0.01054)$, $d_3=(0.50665 \pm 0.06776)$, $d_4=(1.6074 \times 10^{-3} \pm 1.6572 \times 10^{-3})$, $d_5=(0.02599 \pm 0.02719)$, $d_6=(2.7723 \times 10^{-4} \pm 8.485 \times 10^{-5})$, $d_7=(8.8455 \times 10^{-4} \pm 5.6863 \times 10^{-4})$, $d_8=(-2.1255 \times 10^{-5} \pm 1.4024 \times 10^{-5})$ with correlation coefficient and standard deviation of 0.996 and 1.7 kg.m^{-3} , respectively. Equation (12) gave overall ARD s of 0.15% for the training set and 0.42% for the validation set. The minimum ($ARD=0.09\%$) and the maximum ($ARD=1.09\%$) deviations in the validation set were observed in SR and N7 biodiesels, respectively (see Table III). The overall average deviation of 0.42% corresponding to less than 4 kg.m^{-3} , can be regarded as a good indicator for the density prediction. Equation (12) gives better density predictions than more complex methods, including those based in SAFT or CPA equations of state. The $ARD = 0.42\%$ obtained for the validation set was close to the value 0.49% reported by Oliveira et al. [34] with soft-SAFT EoS applied to density prediction of FAMES and biodiesels measured by Pratas et al. [1].

3. Predictive Capacity of GMA EoS

Taking the advantage of the large ranges of temperature and pressure available for the density data of Schedemann fuel (SCHB), we have evaluated the possibility of predicting plausible values for the density at temperatures and pressures significantly higher than the (T,p) ranges used in the fitting of the GMA EoS. As the biodiesel density measurements have usually been made for temperatures lower than 373.15 K and pressures up to 50 MPa, the GMA EoS was tested under restrictive temperature and pressure ranges considering two approaches: (i) for $T=(288 \text{ to } 357)$ K and $p=(0.4 \text{ to } 5)$ MPa; (ii) $T=(288 \text{ to } 357)$ K and $p=(0.4 \text{ to } 50)$ MPa. This approach (i) was based on the fact that density measurements in some studies just were evaluated up to 5 MPa [26]. We have concluded that this approach (i) gave good predictions of density for pressures up to 40 MPa and temperatures up to 397 K. With procedure (ii) it should be possible to extend the good prediction of density to higher temperatures and pressures. The density deviations were only about 3 Kg.m^{-3} near the maximum temperature ($T=397$ K) and pressure ($p=130$ MPa) and the predictions were in excellent agreement with the experimental values up to 75 MPa even at 397 K (vd. Fig. 7).

These results are certainly important for density prediction in fuel injection and combustion simulations, especially in diesel engines operating at high pressure.

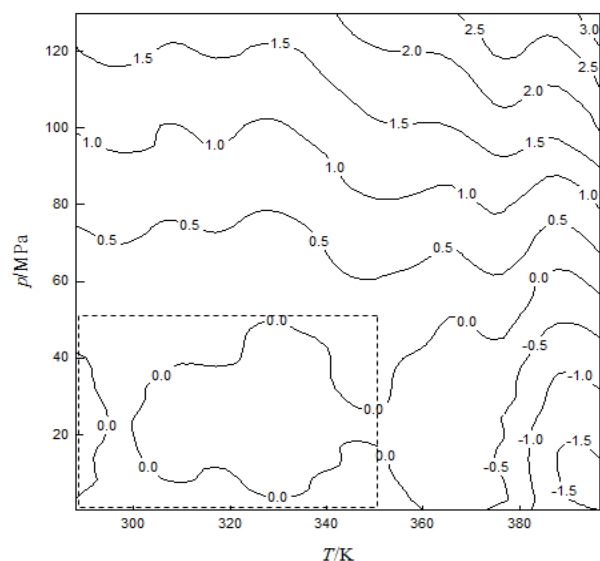


Fig. 7 Difference in density isosolines ($\text{kg}\cdot\text{m}^{-3}$) obtained from GMA EoS as function of the temperature and pressure for the SCHB biodiesel. The isolines were calculated from fitting GMA EoS to pVT data in the restricted ranges (288 to 357) K and (0.4 to 50) MPa (dotted square)

TABLE III
AVERAGE RELATIVE DEVIATION ON DENSITY FOR THE PREDICTIVE METHODS APPLIED TO THE BIODIESELS

| Biod. | Equation (10) | Equation (12) |
|--------------------------|---------------|---------------------|
| S | 0.55 | (0.06) ^a |
| R | 0.61 | (0.13) ^a |
| P | 0.49 | (0.13) ^a |
| SR | 0.44 | 0.09 |
| PR | 0.34 | 0.12 |
| SP | 0.32 | 0.16 |
| SRP | 0.37 | 0.12 |
| <i>ARD</i> ^b | 0.45 | 0.12 ^c |
| N5 | 0.39 | 0.21 |
| N7 | 1.15 | 1.09 |
| N8 | 1.30 | 1.05 |
| N9 | 1.07 | 0.84 |
| N17 | 1.15 | 0.56 |
| N19 | 0.38 | 0.25 |
| N20 | 0.29 | (0.36) ^a |
| N21 | 0.34 | 0.36 |
| N23 | 0.32 | (0.33) ^a |
| <i>ARD</i> ^c | 0.71 | 0.62 ^c |
| N6 | 0.80 | (0.12) ^a |
| PCS | 0.50 | 0.16 |
| SCHB | 0.67 | 0.50 |
| <i>ARD</i> ^d | 0.66 | 0.33 ^c |
| <i>OARD</i> ^f | 0.60 | 0.42 ^c |

^a Biodiesels in the training set; ^b Total *ARD* for the biodiesels from Pratas et al. [1]; ^c Total *ARD* for the biodiesels from Tat and Van Gerpen [21]; ^d Total *ARD* for the biodiesels N6 [2],[21], cottonseed, and SCHB [27]; ^e *ARD* for the subsets from the validation set; ^f $i_{OARD} = \sum_{i=1}^{i_{OARD}} ARD_i$ ($i=19$ for (10); $i=13$ for (12)).

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