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Comparison of Methods for Estimating Critical Properties of Alkyl Esters and Its Mixtures

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ABSTRACT: Biodiesel is a renewable fuel which can be described chemically as a mixture of different alkyl esters. To predict its different thermophysical properties, critical properties (P_c, T_c, V_c) must be known or estimated. In this work, the use of group contribution and group interaction methods is compared regarding its goodness in the prediction of a widely measured property such as biodiesel density, as there is a lack of data of normal boiling point or densities of pure alkyl esters. The results show that a group interaction method, with the available data of 20 different biodiesels published, can predict better biodiesel density when methanol was used for the transesterification reaction. Data available for biodiesel produced with ethanol are scarcer; only six sets of biodiesel composition and density could be found, and in this case, both group interaction and group contribution methods predict density with a similar error, although more data are needed.

1. INTRODUCTION

Biodiesel is an alternative renewable fuel which has several advantages such as biodegradability and lower ecotoxicity in comparison with petroleum-based diesel[1] and the possibility of producing it at low scales from multiple raw materials.

From the chemical point of view, biodiesel is a mixture of monoalkyl esters of long chain fatty acids. Departing from vegetal oils (fresh or reused) as well as some kinds of animal tallows, they are forced to react with a short-chain alcohol, the most used being methanol and ethanol. The products obtained are fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs), respectively, for those two alcohols. Biodiesel obtained from ethanol is composed entirely of biobased materials, making the process more sustainable, but due to its lower price compared to that of ethanol, methanol is the most commonly used alcohol in biodiesel production.[2] For its commercialization, biodiesel must be further processed to fulfill cleaning conditions established by relevant standards, such as EN 14214:2008+A1:2009 (European Norm) or ASTM 6751-07 (American Society of Testing and Materials).

Depending on the composition of the used raw materials, biodiesel properties can show a low-quality performance in some aspects. For example, the presence of high amounts of unsaturated esters decreases the oxidation and storage stability[3] which makes necessary the use of additives. Cold flow properties such as cold filter plugging point (CFPP) and cloud point (CP) are also affected by the chemical composition of raw materials[4] causing, in some cases, problems in the fuel injection system.[5,6] Other important thermophysical properties of biodiesel such as density, viscosity, flash point, cetane number, and higher heating value also depend on the fatty ester profile, and its determination or estimation is a key parameter in spray and combustion modeling. To face a biodiesel process simulation, the behavior of these properties has to be known, and other useful properties such as vapor pressure, specific heat, thermal conductivity, and latent heat of vaporization are also necessary.

Predicting the final properties of biodiesel attending its chemical composition is nowadays an interesting issue, due to

the importance of having accurate property models to perform realistic simulations. Many papers dealing with biodiesel property modeling can be found in available literature. Composition-based models, theoretical and empirical, have been reported for density and viscosity.[7−10] The cetane number[11] and iodine value[12] can also be estimated by using empirical correlations, as well as CFPP or CP.[4,13] Recently, Su et al.[14] have presented a comprehensive study of prediction methods for thermophysical properties of oils and biodiesel.

When theoretical models are used, the critical properties (pressure, P_c; temperature, T_c; specific volume, V_c), acentric factor (ω), and normal boiling point (T_{nb}) are needed as input. The experimental determination of these parameters for pure alkyl esters or their mixtures is not a trivial issue, and when no experimental data are available or its determination is too expensive and time-consuming, they must be estimated theoretically. Some methods for estimating P_c, T_c, T_{nb}, V_c, and ω have been published in specialized literature,[15,16] but given the lack of experimental data, the selection of the proper model is a difficult task. In a very recent paper, Anand et al.[17] performed a comparison of different methods for estimating critical properties and normal boiling point of pure methyl esters. The estimated values were used as input in the calculation of vapor pressure, specific heat capacity, thermal conductivity, and latent heat of vaporization comparing the resulting values with available experimental data.

The selection of a correct model's package is a key step to ensure minimum error in the subsequent calculations. In this paper a comparison of different methods to estimate thermophysical properties of pure methyl and ethyl esters and its mixtures (biodiesel) has been performed. To compare these models, as no experimental data of critical properties and just a few normal boiling points and densities of pure biodiesel

Table 1. Description of the Estimation Methods Used for Each Property in the Packages

property	package 1	package 2	package 3
T_{nb}	CG	MP	Y/CG
T_c	CG	MP	A
P_c	WJ	WJ	A
V_c	CG	MP	J
ω	LK	LK	LK

compounds are published, an easily measurable property, density, has been used as a final testing variable.

2. METHODOLOGY

Being able to estimate macroscopic properties of biodiesel, such as density, implies, as well, being able to estimate thermophysical properties related to microscopic factors. Those are critical temperature, critical pressure, critical volume, acentric factor, and normal boiling point of its individual components and of the resulting mixture. These properties must be estimated as accurately as possible to generate the minimum error. For that purpose, different theoretical approaches with a microscopic focus such as the group contribution method and the groups interactions method have been selected based on available literature. Those methods are Constantinou and Gani (CG), Marrero and Pardillo (MP), Wilson and Jasperson (WJ), Ambrose (A), and Joback (J). Lee−Kesler equations (LK) were used in all cases to compute the acentric factor. A detailed description of these methods can be found in Poling et al.[15] and Reid et al.[16]

Departing from these models, three different estimation packages have been created and analyzed in this paper. Those packages are listed in Table 1. A part of this work is to evaluate the accuracy of two estimation methodologies, the group contribution method and the group interaction methods, which is the main reason for the creation of packages 1 and 2. In case of package 3 the selected methodologies to estimate the critical properties are based on the group contribution theory, but while CG method is a second-order contribution method, the A and J methods take into account only first-order contributions. Additionally, the Yuan correlation (Y),[18] an empirical correlation specifically designed for FAMEs, was used to compute T_{nb} in package 3 for FAMEs. These three packages constitute three different and representative paths to obtain the critical properties. A detailed explanation of each package can be found in the following section.

The followed procedure is shown in Figure 1: the critical properties, acentric factor, and normal boiling point are computed by using each package for each pure component. After that, two paths have been taken into account to compare the goodness of the proposed packages:

(i) Densities of pure methyl and ethyl esters at 15 °C (288.15 K) have been computed using the Spencer and Danner[19] modified Rackett equation (eq 1) in combination with the Soave[20] equation (eq 2) and compared with experimental pure densities.

(ii) Densities of alkyl ester mixtures (biodiesel) have been computed using the pseudocomponent concept, as explained below, and compared with experimental biodiesel densities.

The density computations are as follows:

$$\rho = \frac{MW_m}{\frac{RT_{cm}}{P_{cm}}Z_{Ra}^{[1 + (1 - T_r)^{2/7}]}} \tag{1}$$

$$Z_{Ra} = 0.02908 - 0.099\omega + 0.04\omega^2 \tag{2}$$

The acentric factor was computed using the following equations (LK);

$$\omega_i = \alpha/\beta \tag{3}$$

$$\alpha = -\ln P_{ci} - 5.92714 + 6.09648\theta^{-1} + 1.28862 \ln \theta - 0.160347\theta^6 \tag{4}$$

$$\beta = 15.2518 - 15.6875\theta^{-1} - 13.4721 \ln \theta + 0.435577\theta^6 \tag{5}$$

$$\theta = T_{nbi}/T_{ci} \tag{6}$$

Table 2 shows the 20 different alkyl esters that have been taken into account for the calculations for the methanol-based biodiesel, but just few of them were used to describe the biodiesel composition in the case of biodiesel obtained with ethanol due to the lack of more accurate compositions published. To compute the thermophysical properties of the mixture, also called the pseudocomponent, the LK mixing rules (LK_{mr}) were applied. Once thermophysical properties of the mixture were estimated, the Rackett−Soave (RS) equation was used to estimate the density values at 15 °C. The estimated data have been compared to the measured data reported by Sanford et al.[21] in the case of FAME and other references[22,23] in the case of FAEE.

2.1. Critical Properties and Estimation Packages. *2.1.1. Package 1 (Constantinou and Gani, CG, and Wilson−Jasperson, WJ).* Poling et al.[15] recommended the use of CG method to estimate the T_{nb} and T_c and the WJ method to estimate the P_c. Due to the inexistence of a recommendation to estimate the V_c, the CG method was used as well. The LK equations (eqs 3 to 6) were used to obtain ω. Both models are based on group contribution theory. What makes CG special, as a group contribution method, is the fact that it considers two orders of group contributions. Tables 3 and 4 show the calculated values of T_{nb}, T_c, P_c, and ω for each methyl and ethyl ester, respectively.

2.1.2. Package 2 (Marrero and Pardillo, MP, and Wilson−Jasperson, WJ). In this case, T_{nb}, T_c, and V_c were calculated with the MP model. Poling et al.[15] remark that the MP model is a good one for pure component critical properties estimation without any experimental data, although its range of application is still limited. It has been applied due to the fact that the calculations made were within its range of application. The P_c was calculated using the WJ model. This package was selected because its basis of calculation is the group interactions method or what is effectively a bond interactions method. The main difference between group interactions and group contributions is that the first considers the influence of a particular combination of atoms on the rest of elements that form the molecule, whereas the second builds the molecule group by group, assigning values to them and not to their influence in the rest of the elements that constitute the molecule. The estimated properties values are shown in Tables 5 and 6.
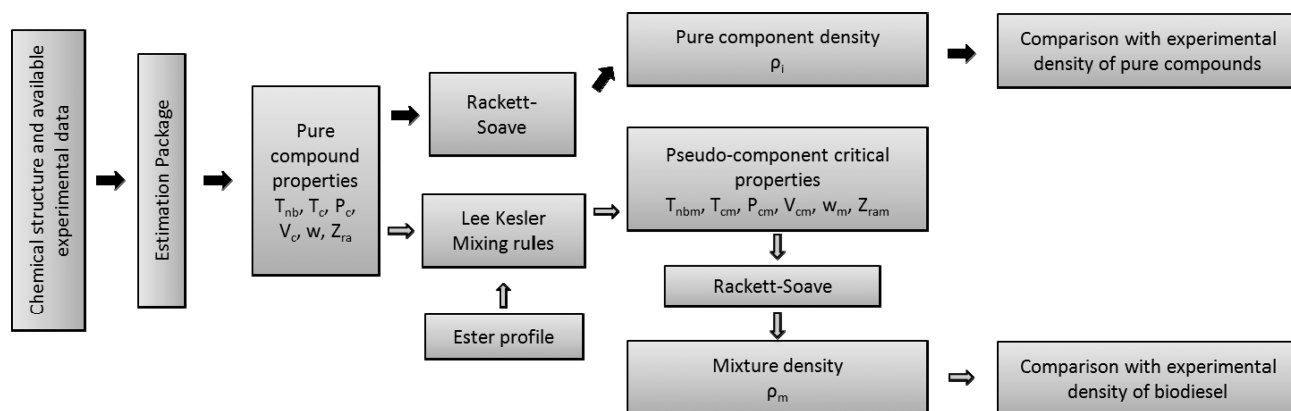
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Figure 1. Paths followed to perform the calculations.

Table 2. Fatty Acid Profile of Biodiesel from Different Oil Sources (% Mass Fractions). Data Adapted from References 21, 34, **and** 35

ester	C8:0	C10:0	C12:0	C14:0	C15:0	C16:0	C17:0	C18:0	C20:0	C22:0	C24:0	C16:1	C17:1	C18:1	C20:1	C22:1	C24:1	C18:2	C18:3	C18:1 (OH)	total
algae				0.6		6.9		3.0	0.4	0.1		0.2		75.2				12.4	1.2		100
babassu	0.5	3.8	48.8	17.2		9.7		4.0						14.2				1.8			100
beef tallow			0.2	2.9	0.6	24.3	1.2	22.8	0.2		2.1	0.4		40.2	0.6			3.3	0.7		99.5
borage						9.3		3.8	0.2					17.1	2.5	1.5		38.7	26.1		99.2
camelina oil						5.0		2.2	1.4	0.4	0.3			17.7	9.8	4.5	0.2	18.0	37.9		97.4
canola oil						3.8		1.9	0.6	0.4	0.2	0.3		63.9			0.2	19.0	9.7		100
castor						0.9		1.1						3.1				4	0.6	90.3	100
choice white grase				1.3		21.6	0.2	9.0	0.2		2.8	0.3		50.4	0.5	0.3		12.2	1.0		99.8
coconut 1	6.3	6.0	49.2	18.5		9.1		2.7						6.5				1.7			100
coconut 2	3.7	3.5	35.7	20.1		14.3		3.9						14.1				4.7			100
coconut 3	4.1	3.6	35.3	19.8		13.8		3.9						14.3				4.7			99.7
coffee						11.0		3.4	0.6	0.2	0.1	0.5		70.0	0.1			12.7	0.8		99.4
corn						12.1		1.8	0.4	0.2		0.1	0.1	27.2				56.2	1.3		99.4
evening primrose						6.0		1.8						6.6				76.3	9.0		99.7
hemp						5.2		2.4	0.7	0.5	0.3			13.1				57.1	20.0		99.3
hepar high IV			0.2	1		20.7	0.3	8.9	0.2	0.2		2.7	0.3	46.7	0.8	0.4	0.1	15.6	0.5		98.6
hepar low IV		0.1	0.1	1.5		28.0	0.3	20.2	0.2		1.9	0.2		36.1	0.7	0.3		9.7	0.3		99.6
Jatropha						12.7		5.5	0.2			0.7		39.1				41.6	0.2		100
linseed						4.4		3.8	0.2	0.3	0.1			20.7				15.9	54.6		100
Moringa oleifera						5.5		5.8	3.1	4.2	0.4	1.2		76.3	2.0			0.7			99.2
neem						14.9		20.6	1.6	0.3	0.3	0.1		43.9				17.9	0.4		100
palm			0.2	0.5		43.4		4.6	0.3	0.1		0.1		41.9				8.6	0.3		100
poultry fat			0.1	1.0		19.6	0.3	7.5	0.1	0.3		3.2	0.2	36.8		0.4		28.4	2.0		99.9
rice bran				0.3		12.5		2.1	0.6	0.3	0.2			47.5				35.4	1.1		100
soybean						9.4		4.1	0.3					22.0				55.3	8.9		100
sunflower						4.2		3.3	0.7	0.4				63.6				27.6	0.2		100
used cooking oil			0.1	0.1		11.8	0.1	4.4	0.3	0.4	0.1	0.4	0.1	25.3		0.3		49.5	7.1		100
yellow grease			0.1	0.5		14.3	0.3	8	0.3	0.3	1.1	0.2		35.6		0.2	0.1	35.0	4.0		100

2.1.3. Package 3 (Ambrose and Joback). The last package used is the combination of the Joback modification of Lydersen's method for V_c and Ambrose's method for T_c and P_c. The acentric factor was computed using LK equations, and T_{nb} was calculated according to the correlation reported by Yuan et al.[18] (eq 7) in the case of methyl esters, which is an empirical correlation specifically designed for FAMEs with a maximum prediction error of 1.0 %. The CG method was used in the case of ethyl esters due to the inexistence of an experimental correlation. The Ambrose and Joback methods have been reported as proper methods for critical properties estimation and biodiesel density;[22,24,25] their combination with Yuan's correlation is a good way to check the accuracy of pure theoretical packages. These two methods are also group contribution methods, but the main difference between package 1 and package 3 is that the Ambrose and Joback methods just consider first-order group contributions.

Table 3. Methyl Ester Critical Properties Calculated with Package 1: CG and WJ

methyl ester		T_{nb}	T_c	P_c	V_c	ω
		K	K	kPa	$cm^3 \cdot mol^{-1}$	
methyl octanoate	C8:0	501.80	669.80	2528	553.40	0.85
methyl decanoate	C10:0	531.84	698.81	2099	665.00	0.87
methyl dodecanoate	C12:0	558.02	723.82	1776	776.60	0.87
methyl tetradecanoate	C14:0	581.23	745.79	1523	888.20	0.87
methyl pentadecanoate	C15:0	591.92	755.85	1416	944.00	0.86
methyl hexadecanoate	C16:0	602.07	765.38	1320	999.80	0.85
methyl heptadecanoate	C17:0	611.74	774.43	1233	1055.60	0.84
methyl octadecanoate	C18:0	620.98	783.06	1154	1111.40	0.83
methyl icosanoate	C20:0	638.28	799.17	1016	1223.00	0.79
methyl docosanoate	C22:0	654.24	813.96	899	1334.60	0.76
methyl tetracosanoate	C24:0	669.04	827.63	800	1446.20	0.71
methyl hexadec-9-enoate	C16:1	600.53	765.01	1348	986.41	0.85
methyl cis-10-heptadecenoate	C17:1	610.28	774.08	1258	1042.21	0.84
methyl (Z)-octadec-9-enoate	C18:1	619.58	782.73	1177	1098.01	0.82
methyl (Z)-12-hydroxyoctadec-9-enoate	C18:1 OH	641.91	799.93	1161	1104.94	0.95
methyl cis-11-eicosenoate	C20:1	637.00	798.86	1035	1209.61	0.79
methyl (Z)-13-docosenoate	C22:1	653.05	813.68	915	1321.21	0.76
methyl cis-15-tetracosenoate	C24:1	667.93	827.37	814	1432.81	0.71
methyl (Z,Z)-octadeca-9,12-dienoate	C18:2	618.17	782.39	1200	1084.62	0.82
methyl (Z,Z,Z)-octadeca-9,12,15-trienoate	C18:3	616.75	782.06	1224	1071.23	0.82

Tables 7 and 8 show the calculated values of thermophysical properties for each methyl and ethyl ester.

$$T_{nb} = 218.49 \ln(CN) - 6.933 \qquad (7)$$

2.2. Density Calculation. A significant number of papers dealing with the estimation or correlation of biodiesel density can be found in available literature. Yuan et al.[26] reported the use of the modified Rackett equation using the data obtained by Tat and Van Gerpen[27] to determine Z_{Ra} in a temperature range from (0 to 100) °C. The authors predicted the density of soybean oil based biodiesel taking into account five methyl esters; linoleic acid methyl ester (C18:2), oleic acid methyl ester (C18:1), palmitic acid methyl ester (C16:0), linolenic acid methyl ester (C18:3), and stearic acid methyl ester (C18:0). The critical properties of these esters were calculated using Ambrose's method for T_c and P_c and Lydersen's method for V_c. These authors used the LK equations to compute the acentric factor, and LK mixing rules were used to compute the critical properties of the mixture. Using the same equations, Blangino et al.[28] reported a density prediction for soybean-made biodiesel. Baroutian et al.[25] used the Rackett modified equation to predict the density of palm oil-based biodiesel. Following the same procedure, other authors reported density predictions for *Jatropha* oil-based methyl esters[24] and palm, soybean, corn, canola, and ricebran oil-based ethyl esters.[22] Anand et al.[29] reported a unified correlation based on the modified Rackett equation. In this case, the Rackett constant was calculated with the Vetere[30] equation, and the required normal boiling point was calculated by the CG method, a simple mixing rule, called Kay's mixing rule, was used to obtain the final density values. Clements[31] reported the use of a correlation to estimate the biodiesel density as a function of temperature. The empirical model proposed by Clements uses the composition (four FAMEs

were taken into account) as input and correlates the constants of a temperature-dependent linear equation.

As stated before, the aim of this work is to compare three different models/packages to estimate critical properties of biodiesel by using density as a macroscopic measurable property to compare their suitability. To perform this comparison, 20 alkyl esters have been taken into account to represent the composition of biodiesel.

The Rackett—Soave equation, which is one of the most commonly employed methods to estimate the saturated liquid density, has been applied to the data obtained with the three proposed packages. The Rackett compressibility factor (Z_{Ra}) is also needed, and it is usually computed using experimental density values. If no experimental data are available, the estimation of Z_{Ra} must be performed using one of the correlations proposed by Soave,[20] Yamada and Gunn,[32] or Vetere.[30] In this work, the Soave equation (eq 2) has been used.

3. RESULTS AND DISCUSSION

3.1. Comparison of Experimental and Calculated Normal Boiling Temperature of Alkyl Esters. The lack of experimental data makes it difficult to compare the estimated values of critical properties and boiling point of pure components with experimental ones. To the best of these authors' knowledge, just a few experimental data dealing with normal boiling point of FAMEs[7] or FAAEs[33] are available in open literature.

Figure 2 shows experimental T_{nb} data of some methyl and ethyl esters with the values calculated with the two cited methods (CG and MP). The average relative deviation (ARD %), calculated according to eq 8, is also shown in Figure 2.

$$ARD(\%) = \frac{\sum_{i}^{N} (|x_{exp,i} - x_{est,i}| / x_{exp,i})}{N} \cdot 100 \qquad (8)$$

Table 4. Ethyl Ester Critical Properties Calculated with Package 1: CG and WJ

ethyl ester		T_{nb} K	T_c K	P_c kPa	V_c cm$^3\cdot$mol^{-1}	ω
ethyl octanoate	C8:0	506.32	675.46	2248	613.80	0.79
ethyl decanoate	C10:0	535.75	703.65	1893	725.40	0.81
ethyl dodecanoate	C12:0	561.47	728.04	1617	837.00	0.81
ethyl tetradecanoate	C14:0	584.31	749.53	1398	948.60	0.81
ethyl pentadecanoate	C15:0	594.84	759.39	1304	1004.40	0.80
ethyl hexadecanoate	C16:0	604.85	768.74	1219	1060.20	0.79
ethyl heptadecanoate	C17:0	614.39	777.63	1142	1116.00	0.78
ethyl octadecanoate	C18:0	623.51	786.11	1071	1171.80	0.77
ethyl icosanoate	C20:0	640.61	801.96	947	1283.40	0.74
ethyl docosanoate	C22:0	656.39	816.54	841	1395.00	0.70
ethyl tetracosanoate	C24:0	671.04	830.03	750	1506.60	0.66
ethyl hexadec-9-enoate	C16:1	599.21	768.38	1244	1046.81	0.73
ethyl *cis*-10-heptadecenoate	C17:1	609.02	777.29	1157	1102.61	0.72
ethyl (*Z*)-octadec-9-enoate	C18:1	618.38	785.78	1091	1158.41	0.71
ethyl (*Z*)-12-hydroxyoctadec-9-enoate	C18:1 OH	640.83	802.71	1072	1102.61	0.83
ethyl *cis*-11-eicosenoate	C20:1	635.89	801.66	964	1270.01	0.69
ethyl (*Z*)-13-docosenoate	C22:1	652.03	816.26	851	1381.61	0.65
ethyl *cis*-15-tetracosenoate	C24:1	666.98	829.77	759	1493.21	0.62
ethyl (*Z,Z*)-octadeca-9,12-dienoate	C18:2	613.11	785.46	1112	1145.02	0.66
ethyl (*Z,Z,Z*)-octadeca-9,12,15-trienoate	C18:3	607.70	785.13	1134	1131.63	0.61

Table 5. Methyl Ester Critical Properties Calculated with Package 2: MP and WJ

methyl ester		T_{nb} K	T_c K	P_c kPa	V_c cm$^3\cdot$mol^{-1}	ω
methyl octanoate	C8:0	419.14	574.23	2111	569.10	0.57
methyl decanoate	C10:0	472.47	629.84	1865	682.30	0.68
methyl dodecanoate	C12:0	525.79	685.55	1539	795.50	0.74
methyl tetradecanoate	C14:0	579.11	742.08	1517	908.70	0.88
methyl pentadecanoate	C15:0	595.67	758.01	1425	965.30	0.90
methyl hexadecanoate	C16:0	611.82	774.04	1341	1021.90	0.91
methyl heptadecanoate	C17:0	627.60	790.25	1265	1078.50	0.91
methyl octadecanoate	C18:0	643.03	806.74	1195	1135.10	0.90
methyl icosanoate	C20:0	672.96	840.86	1071	1248.30	0.86
methyl docosanoate	C22:0	701.76	877.01	965	1361.50	0.77
methyl tetracosanoate	C24:0	845.73	1061.64	1012	1474.70	0.77
methyl hexadec-9-enoate	C16:1	613.57	781.37	1377	1001.30	0.86
methyl *cis*-10-heptadecenoate	C17:1	639.16	809.12	1318	1057.90	0.89
methyl (*Z*)-octadec-9-enoate	C18:1	644.72	812.21	1224	1114.50	0.88
methyl (*Z*)-12-hydroxyoctadec-9-enoate	C18:1 OH	728.04	1014.13	1317	1200.30	0.24
methyl *cis*-11-eicosenoate	C20:1	674.59	844.37	1096	1227.70	0.86
methyl (*Z*)-13-docosenoate	C22:1	721.99	901.72	1012	1340.90	0.81
methyl *cis*-15-tetracosenoate	C24:1	793.08	995.17	966	1510.70	0.73
methyl (*Z,Z*)-octadeca-9,12-dienoate	C18:2	646.42	818.84	1255	1093.90	0.85
methyl (*Z,Z,Z*)-octadeca-9,12,15-trienoate	C18:3	648.14	826.68	1287	1073.30	0.80

where N is the number of data points, x_{exp} is the experimental value, and x_{est} is the estimated one.

In the case of FAME, a slight ARD difference can be observed between both methods, but ARD values are within an acceptable range. The error of the methods increases slightly in the case of low molecular weight methyl esters (C8:0 and C10:0), which can mean that more accurate experimental data for low weighted esters are necessary to check the suitability of used estimation methods. Since no experimental data for critical properties are available, a comparison of estimated values cannot be performed

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Table 6. Ethyl Ester Critical Properties Calculated with Package 2: MP and WJ

ethyl ester		T_{nb}	T_c	P_c	V_c	ω
		K	K	kPa	cm$^3\cdot$mol^{-1}	
ethyl octanoate	C8:0	440.29	593.80	1955	657.70	0.63
ethyl decanoate	C10:0	493.62	649.64	1744	770.90	0.74
ethyl dodecanoate	C12:0	546.94	705.92	1576	884.10	0.84
ethyl tetradecanoate	C14:0	600.26	763.36	1441	997.30	0.91
ethyl pentadecanoate	C15:0	616.35	779.34	1356	1053.90	0.92
ethyl hexadecanoate	C16:0	632.06	795.53	1278	1110.50	0.92
ethyl heptadecanoate	C17:0	647.43	812.00	1207	1167.10	0.91
ethyl octadecanoate	C18:0	662.48	828.84	1141	1223.70	0.89
ethyl icosanoate	C20:0	691.71	863.92	1025	1336.90	0.82
ethyl docosanoate	C22:0	719.90	901.40	925	1450.10	0.72
ethyl tetracosanoate	C24:0	866.88	1092.86	969	1563.30	0.69
ethyl hexadec-9-enoate	C16:1	633.87	801.98	1194	1089.90	0.82
ethyl *cis*-10-heptadecenoate	C17:1	659.45	830.41	1252	1146.50	0.90
ethyl (*Z*)-octadec-9-enoate	C18:1	664.22	833.36	1073	1203.10	0.82
ethyl (*Z*)-12-hydroxyoctadec-9-enoate	C18:1 OH	747.46	1060.19	1251	1272.50	0.14
ethyl *cis*-11-eicosenoate	C20:1	693.39	866.40	969	1316.30	0.78
ethyl (*Z*)-13-docosenoate	C22:1	787.38	983.99	1028	1429.50	0.82
ethyl *cis*-15-tetracosenoate	C24:1	838.55	1052.57	955	1542.70	0.72
ethyl (*Z,Z*)-octadeca-9,12-dienoate	C18:2	665.97	839.04	1099	1182.50	0.80
ethyl (*Z,Z,Z*)-octadeca-9,12,15-trienoate	C18:3	667.75	845.92	1126	1161.90	0.76

Table 7. Methyl Ester Critical Properties Calculated with Package 3: A and J

methyl ester		T_{nb}	T_c	P_c	V_c	ω
		K	K	kPa	cm$^3\cdot$mol^{-1}	
methyl octanoate	C8:0	457.24	619.72	1958	565.50	0.60
methyl decanoate	C10:0	503.40	666.32	1716	677.50	0.69
methyl dodecanoate	C12:0	541.13	701.89	1527	789.50	0.77
methyl tetradecanoate	C14:0	573.02	730.36	1375	901.50	0.86
methyl pentadecanoate	C15:0	587.30	742.66	1310	957.50	0.90
methyl hexadecanoate	C16:0	611.00	766.95	1250	1013.50	0.93
methyl heptadecanoate	C17:0	613.19	764.37	1196	1069.50	0.97
methyl octadecanoate	C18:0	625.02	774.04	1146	1125.50	1.01
methyl icosanoate	C20:0	646.82	791.52	1058	1237.50	1.08
methyl docosanoate	C22:0	666.54	806.98	983	1349.50	1.15
methyl tetracosanoate	C24:0	684.54	820.85	917	1461.50	1.21
methyl hexadec-9-enoate	C16:1	608.00	765.19	1274	993.50	0.92
methyl *cis*-10-heptadecenoate	C17:1	610.19	762.51	1220	1049.50	0.96
methyl (*Z*)-octadec-9-enoate	C18:1	622.20	772.34	1168	1105.50	1.00
methyl (*Z*)-12-hydroxyoctadec-9-enoate	C18:1 OH	686.15	859.29	1234	1118.50	0.95
methyl *cis*-11-eicosenoate	C20:1	643.82	789.48	1075	1217.50	1.07
methyl (*Z*)-13-docosenoate	C22:1	663.54	804.83	997	1329.50	1.14
methyl *cis*-15-tetracosenoate	C24:1	681.54	818.61	931	1441.50	1.20
methyl (*Z,Z*)-octadeca-9,12-dienoate	C18:2	639.20	795.33	1191	1085.50	0.99
methyl (*Z,Z,Z*)-octadeca-9,12,15-trienoate	C18:3	639.20	795.33	1183	1065.50	0.98

neither for FAME nor for FAEE. Because of this reason an easily measurable property such as density has been selected to test the proposed calculation packages.

As can be observed in Figure 2, both CG and MP methods overestimate the boiling temperature for FAEE, but the prediction of T_{nb} can be performed using package 1 with an ARD of 2.52 %; this package has a better accuracy in this case.

3.2. Density of Methyl Esters and Methanol-Based Biodiesel. A comparison of some experimental pure methyl ester density values[7] with those calculated with the proposed packages

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Table 8. Ethyl Ester Critical Properties Calculated with Package 3: A and J

| ethyl ester		T_{nb}	T_c	P_c	V_c	ω
		K	K	kPa	cm³·mol⁻¹	
ethyl octanoate	C8:0	506.32	677.84	1829	630.50	0.64
ethyl decanoate	C10:0	535.75	701.72	1616	742.50	0.73
ethyl dodecanoate	C12:0	561.47	721.70	1447	854.50	0.82
ethyl tetradecanoate	C14:0	584.31	738.89	1310	966.50	0.90
ethyl pentadecanoate	C15:0	594.84	746.66	1250	1022.50	0.93
ethyl hexadecanoate	C16:0	604.85	753.97	1196	1078.50	0.97
ethyl heptadecanoate	C17:0	614.39	760.89	1146	1134.50	1.01
ethyl octadecanoate	C18:0	623.51	767.45	1101	1190.50	1.04
ethyl icosanoate	C20:0	640.61	779.64	1019	1302.50	1.11
ethyl docosanoate	C22:0	656.39	790.79	949	1414.50	1.18
ethyl tetracosanoate	C24:0	671.04	801.09	888	1526.50	1.24
ethyl hexadec-9-enoate	C16:1	599.21	748.79	1220	1058.50	0.96
ethyl *cis*-10-heptadecenoate	C17:1	609.02	755.98	1168	1114.50	1.00
ethyl (*Z*)-octadec-9-enoate	C18:1	618.38	762.79	1121	1170.50	1.03
ethyl (*Z*)-12-hydroxyoctadec-9-enoate	C18:1 OH	640.83	797.09	1232	1183.50	1.02
ethyl *cis*-11-eicosenoate	C20:1	635.89	775.41	1036	1282.50	1.10
ethyl (*Z*)-13-docosenoate	C22:1	652.03	786.91	964	1394.50	1.17
ethyl *cis*-15-tetracosenoate	C24:1	666.98	797.51	901	1506.50	1.23
ethyl (*Z*,*Z*)-octadeca-9,12-dienoate	C18:2	613.11	757.98	1141	1150.50	1.02
ethyl (*Z*,*Z*,*Z*)-octadeca-9,12,15-trienoate	C18:3	607.70	751.29	1134	1130.50	1.02
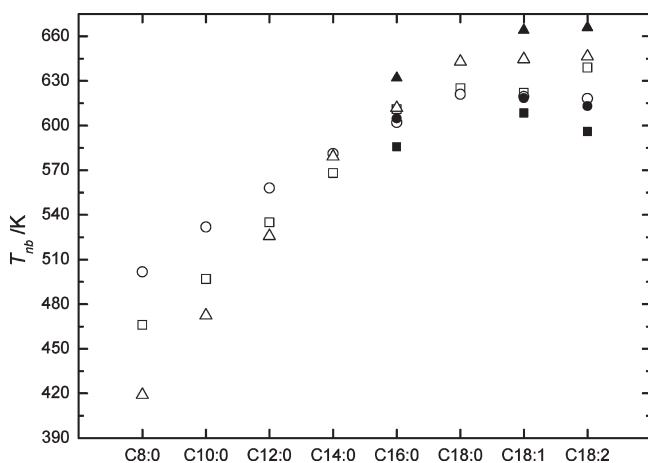
Figure 2. Experimental[7,33] and estimated values of T_{nb}/K for pure methyl and ethyl esters using CG and MP methods. □, exp. MeOH; ○, CG; △, MP; ■, exp. EtOH; ●, CG; ▲, MP. CG MeOH ARD = 3.25 %, MP MeOH ARD = 3.47 %, CG EtOH ARD = 2.52 %, MP EtOH ARD = 8.75 %.

Figure 3. Comparison of pure FAME densities calculated with packages 1 to 3 and experimental values in Lapuerta et al.[7] □, package 1; ○, package 2; △, package 3; ▽, experimental. ARD (%): package 1 = 8.72, package 2 = 5.42, package 3 = 6.61.

is shown in Figure 3. ARD values are also reported. It can be observed that package 3 underestimates the densities and shows an ARD of 6.61 %. Package 2 shows a slightly better ARD, but it underestimates the density of high weighted methyl esters such as C20:0 and C21:1. On the other hand, package 1 has the highest ARD, 8.72 %, and overestimates the density of saturated low weighted methyl esters (C8:0 to C15:0). As shown in Table 2, the presence of these esters in biodiesel composition is not usual, and its influence on final biodiesel density is, in most cases, very low. Nevertheless, the results reported are not in
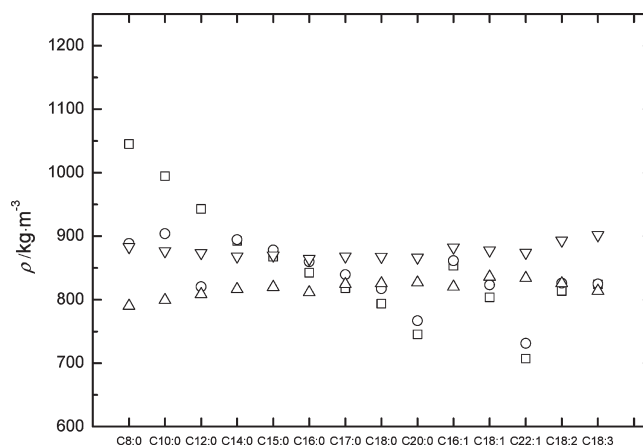
good agreement with the experimental ones in case of low and high chain length esters, while densities of intermediate chain length esters are accurately estimated; this fact may indicate that an improvement is necessary to make the model work in the whole range of chain length.

As commented before, to estimate biodiesel density, following the scheme shown in Figure 1, the critical properties of a pseudocomponent, which represents the biodiesel composition, were calculated by using the LK mixing rules, and the RS equation to estimate density was applied.

Table 9 shows the experimental values of biodiesel density reported by Sanford et al.,[21] for different raw materials and the

Table 9. Experimental Methanol-Based Biodiesel Density Values[21,34,35] and Estimated Densities

	exp. ρ	package 1		package 2		package 3	
	kg·m^{-3}	ρ/kg·m^{-3}	error (%)	ρ/kg·m^{-3}	error (%)	ρ/kg·m^{-3}	error (%)
algae 1	878.0	892.7	1.67	879.5	0.17	857.9	2.34
babassu	876.0	892.1	1.84	875.0	0.12	877.3	0.15
beef tallow	874.0	893.7	2.25	875.3	0.15	860.6	1.56
borage	886.5	902.5	1.80	898.8	1.38	875.0	1.32
camelina oil	888.0	915.7	3.12	914.7	3.00	887.2	0.10
canola oil	882.0	894.1	1.37	884.5	0.28	860.8	2.46
castor	899.0	917.0	2.00	873.0	2.89	915.6	1.82
choice white grease	877.0	893.0	1.83	877.7	0.08	860.8	1.89
coconut 1	807.3	893.1	10.63	874.5	8.33	880.4	8.30
coconut 2	874.8	893.0	2.08	875.9	0.13	877.4	0.30
coconut 3	874.7	895.2	2.34	877.9	0.37	879.5	0.55
coffee	881.5	896.6	1.72	883.3	0.20	862.7	2.17
corn	885.0	898.9	1.57	890.8	0.65	870.9	1.62
evening primrose	888.5	896.8	0.93	893.2	0.53	871.3	1.98
hemp	888.5	901.9	1.51	899.3	1.22	876.3	1.40
hepar. high IV	875.5	901.7	2.99	887.2	1.34	870.5	0.58
hepar. low IV	875.5	893.4	2.04	875.8	0.03	860.9	1.70
Jatropha	879.5	893.6	1.61	882.8	0.38	863.0	1.91
linseed	892.5	898.4	0.66	899.0	0.73	873.3	2.19
Moringa oleifera	877.0	897.6	2.35	883.7	0.76	858.7	2.13
neem	884.5	891.6	0.80	876.5	0.91	856.7	3.25
palm	876.0	890.4	1.65	872.3	0.42	860.0	1.86
perilla seed	899.0	899.1	0.01	901.3	0.25	875.7	2.66
poultry fat	880.5	893.5	1.47	880.7	0.02	863.1	2.02
rice bran	885.5	893.6	0.92	882.7	0.31	862.2	2.70
soybean	884.0	895.5	1.30	888.9	0.55	867.6	1.89
sunflower	880.0	893.5	1.53	882.4	0.28	859.5	2.39
used cooking oil	855.5	894.9	4.60	887.0	3.68	866.2	1.23
yellow grease	882.5	893.5	1.25	882.5	0.00	862.9	2.27

estimated values using each package. Additionally, the error (%) for each biodiesel density estimation is also shown. Only two experimental density values are out of the EN 14214 range; coconut 1 and used cooking oil based biodiesel. The low density value in case of coconut 1 biodiesel can be explained due to its high content in low weighted esters (C8:0, C10:0, C12:0, and C14:0) which mean around 80 wt % of that biodiesel. The estimations in this case show high errors, around 10 % for package 1 and 8 % for packages 2 and 3.

To compare with other coconut-based biodiesels, two additional experimental profiles have been taken into account. Coconut 2[34] and 3[35] show a similar ester profile (see Table 2) to those of coconut 1, but their densities are slightly higher, and they do accomplish the EN 14214 requirements. For coconut 2 and 3 the low weight esters are around 60 wt %, the more plausible explanation being the density differences and the low errors found for the density estimations.

Based on the composition of used cooking oil, which is similar to other reported profiles, the reason of such a density value is not explicable. Used cooking oils usually contain high amounts of impurities which can cause such a behavior if the cleaning step is not carried out properly. In any case, the reported errors are below 5 % for all packages, package 3 being the most accurate with an error of 1.23 %.

Figure 4 shows the error (%) for each biodiesel. With the exception of coconut and UCO biodiesels, both explained before, the error is below 4 % for all packages. Package 2 shows the lowest errors, usually under 1 %, while errors in Packages 1 and 3 are around 2 %. This tendency can also be observed in Figure 5 which shows the experimental versus estimated values for each package. The average relative deviation is also reported. Package 2 shows the lowest ARD of the proposed packages, while packages 1 and 3 over- and underestimate the density values, respectively. As a result, they consider out of the standard range (EN 14214) some biodiesels which do accomplish this specification. In the case of package 2, just a few biodiesels have an error over 1 %; camelina oil, borage, hemp, hepar high IV, castor, coconut 1, and UCO. For the first four biodiesels the explanation of the found deviation could be the high presence of methyl linolenate (C18:3), indicating that more accurate experimental data (normal boiling point and experimental density values) are needed to simulate the critical properties of methyl linolenate. Castor oil based biodiesel shows a similar issue, as the amount of methyl ricinoleate, around 90 wt %, has a strong influence in the final biodiesel properties. The presence of a hydroxyl group in the ricinoleate molecule makes this ester special, so to predict its properties accurately, proper experimental data are needed.
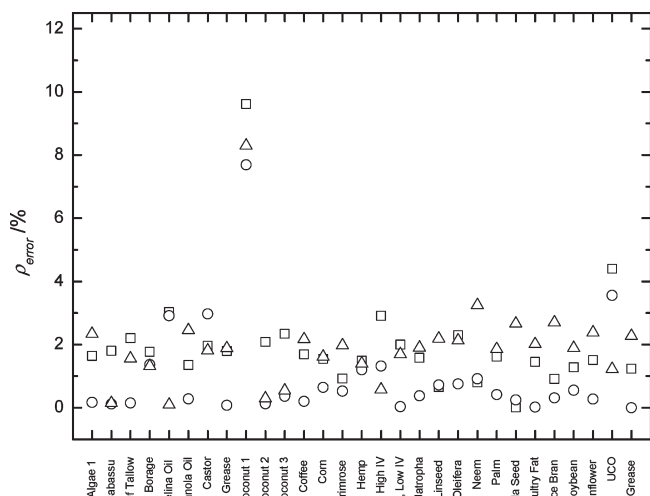
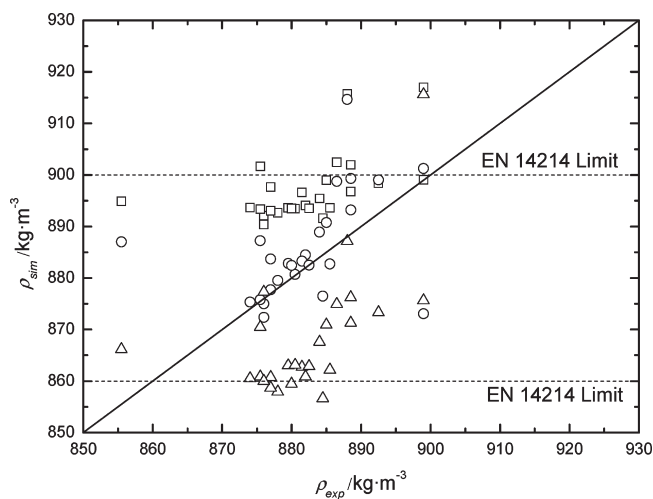**Figure 4.** Calculated density errors (%) for each package and biodiesel. □, package 1; ○, package 2; △, package 3.

Figure 6. Comparison of pure FAEE densities calculated with packages and reported experimental values in Lapuerta et al.[7] □, package 1; ○, package 2; △, package 3; ▽, experimental. ARD (%): package 1 = 10.09, package 2 = 8.34, package 3 = 5.81.

Figure 5. Experimental vs simulated density (kg·m^{-3}) data for different biodiesels.[21] □, package 1; ○, package 2; △, package 3. ARD (%): package 1 = 2.05, package 2 = 1.07, package 3 = 2.15.

Figure 7. Calculated density errors for each ethyl-based biodiesel. □, package 1; ○, package 2; △, package 3.

3.3. Density of Ethyl Esters and Ethanol-Based Biodiesel.

As it has been said before, it is not easy to find pure ethyl ester data. However a few density values can be found in Lapuerta et al.[7] In Figure 6 the experimental and calculated density values with the three packages and RS equation described above these lines are shown, as well as the calculation of the ARD for each package. The ARD values are higher than those in the FAME density calculation, and unlike the result that has been observed for FAME, package 3 seems to be the best one. On the contrary, package 1 seems to be the worst one to estimate density of pure ethyl esters, almost doubling the ARD from package 3.

While packages 1 and 3 respectively over and underestimate the density of low weighted ethyl esters, package 2 shows a better accuracy. Unfortunately, package 2 underestimates the densities in the case of unsaturated ethyl esters. In this case, the results show that a combination of package 2 and package 3 could be the best option, but once again, the need of new
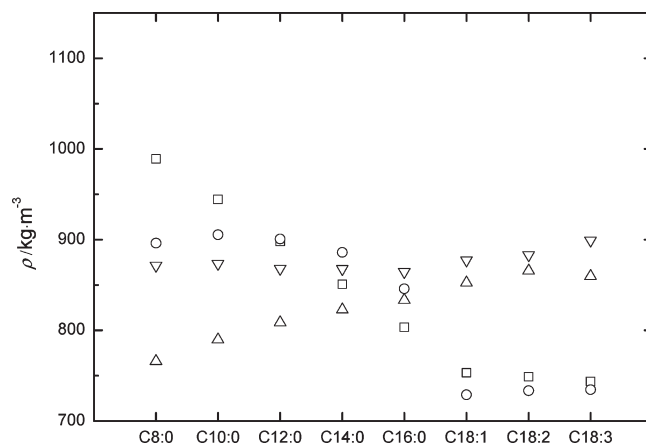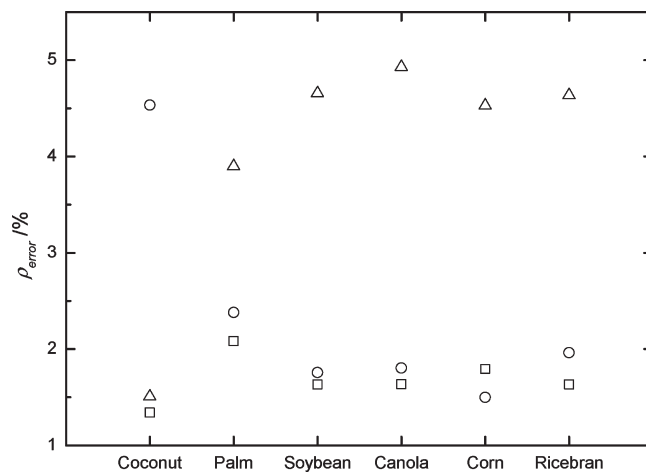
experimental density and boiling point data for ethyl esters is clearly a major issue.

Although many papers dealing with ethanolysis of oils and tallows can be found in available literature, just a few of them report an ester profile and density data at 15 °C. Figure 7 shows a comparison of some experimental[22,23] density values and the estimated ones. It is important to note that just four ethyl esters have been used to describe the composition of the biodiesel due to the lack of a more accurate ester profile description.

Regarding the errors, packages 1 and 2 incur on less error than package 3 compared to the experimental data except for the coconut that, in this case too, shows an awkward behavior; package 1 shows its biggest error for coconut oil, while packages 2 and 3 seem to be relatively accurate. Except for coconut, the error for package 3 is around 4 %, while the error for packages 1 and 2 is most times under 2 %.

Based on the obtained results, it is possible to say that packages 1 and 2 are the best option in the case of ethanol-based biodiesel. In any case, more experimental density data for

ethanol based biodiesel are needed to check the suitability of these models and methods.

4. CONCLUSIONS

In this work three different packages to estimate the critical properties of biodiesel have been compared, using density as a final testing variable. In case of methanol-based biodiesel 20 methyl esters were taken into account, and their critical properties and densities were calculated and compared with available experimental data. Package 2, with an ARD of 5.42 %, showed the highest accuracy when comparing predicted and experimental densities of 14 pure methyl esters. The normal boiling points of some methyl and ethyl esters were also compared with experimental data showing that some improvements are needed, especially for the low weighted methyl esters. The LK mixing rules were used to compute the pseudocomponent critical properties of different methyl ester mixtures, and the results so obtained were compared with experimental ones. The ARD was in all cases lower than 2.1 % and especially for package 2 was 1.0 %. A similar study was performed in the case of ethanol-based biodiesel, but due to the lack of experimental data, just eight ethyl esters were used in the calculations for pure compounds, and four were used in case of ethanol-based biodiesel. Six experimental density values were compared. The results show that packages 1 and 2 are good options to estimate the critical properties of biodiesel mixtures, although more data are needed.

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■ NOMENCLATURE

T/K	temperature
P/bar	pressure
$V/cm^3 \cdot mol^{-1}$	volume
ω	acentric factor
R	universal gas constant
Z	compressibility factor
MW	mass weight
CN	number of carbons in the fatty acid

Subscripts

nb	normal boiling
atm	atmospheric
c	critical
r	reduced
m	relative to mixture
i	component i
Ra	Rackett compressibility factor

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