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A Comprehensive Evaluation of the Density of Neat Fatty Acids and Esters

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Abstract Density is one of the most important physical properties of a chemical compound, affecting numerous applications. An application in the case of fatty acid esters (biodiesel) is that density is specified in some biodiesel standards. In the present work, the density of fatty acid methyl, ethyl, propyl, and butyl esters as well as triacylglycerols in the C_8–C_{24} range was determined in the range of 15–40 °C with a densitometer utilizing the oscillating U-tube technique. Literature data on density are compiled and compared, showing that data for these compounds are incomplete with discrepancies existing in some cases. Besides known effects such as density decreasing with increasing chain length and increasing saturation, it is shown that *trans* fatty compounds exhibit lower density than *cis* fatty compounds. Density data for several saturated odd-numbered, C_{18}, as well as C_{20} and C_{22} polyunsaturated fatty esters are reported for the first time. The density contribution of compounds with high melting points is predicted. An equation is given for the calculation of the density of mixtures.

Keywords Biodiesel · Density · Fatty acid ethyl esters · Fatty acid methyl esters · Triacyglycerols

Introduction

The density of a substance is one of its most important physical properties. It is applied in chemical engineering in the oleochemical field for reactor splitting of fatty acids or conversion to derivatives, distillation for fatty acid separation, and designing storage tanks [1], as well as material characterization [2] to establish identity, purity and structure [3] and in combustion modeling [4] as it affects jet penetration as well as fuel mixing, vaporization, and atomization. Density is of significance for viscosity studies because it is the factor relating dynamic and kinematic viscosity ($\nu = \mu/\rho$; ν = kinematic viscosity, μ = dynamic viscosity, ρ = density). Biodiesel [5, 6], defined as the mono-alkyl esters of vegetable oils or animal fats or other triacylglycerol-containing materials, is produced via a transesterification reaction which has been monitored by measurements of density [7]. Density has been included as a specification (in the range of 860–900 kg/m^3) in the European biodiesel standard EN 14214 [8] but not the American standard ASTM (American Society for Testing and Materials) D6751 [9]. Furthermore, viscosity is often reported as dynamic viscosity despite kinematic viscosity being prescribed in biodiesel standards, requiring recalculation with density as the factor. Density is also of significance for practical weight-sensitive applications as, in many cases, lighter-weight material is preferred.

Besides the literature [1–4, 7] mentioned above, the density of fatty acid alkyl esters and biodiesel from various feedstocks as well as its prediction has been the subject of numerous reports in the literature [10–45]. Density data for neat fatty acids and their methyl, ethyl, propyl, and butyl esters as well as the corresponding triacylglycerols compiled from both primary and reference literature [1, 2, 10, 14, 17, 18, 26, 29, 34, 38, 41] are given in Table 1 for saturated fatty

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Table 1 Literature data for the density (g/cm^3) of saturated straight-chain fatty acids and esters

Fatty acid	Acid	Methyl ester	Ethyl ester	Propyl ester	Butyl ester	Triacylglycerol
8:0	0.9105^{20} [12], 0.9106^{20} [2]	0.8815^{15} [18], 0.8815^{15} [34]	0.8714^{15} [17]	0.8659^{20} [26]		
	0.9061^{25} [2], 0.9073^{25} [26]	0.8784^{20}[12], 0.8769^{20} [14], 0.8771^{20} [18], 0.8775^{20} [26], 0.8771^{20} [34]	0.866^{18} [26]			
	0.9033^{30} [2]	0.8592^{40} [14], 0.8594^{40} [18], 0.8596^{40} [34]	0.8693^{20} [12], 0.8668^{20} [17]			
	0.8998^{35} [2]		0.8494^{40} [17]			
	0.8962^{40} [2]					
9:0	0.9052^{20} [12, 26]	0.8799^{15} [12, 26]	0.8661^{20} [12], 0.8657^{20} [26]			
	$0.9018^{23.9}$ [1]	0.8743^{20} [14]				
	$0.8913^{37.8}$ [1]	0.8573^{40} [14]				
10:0	$0.8863^{37.8}$ [1]	0.8800^{10} [41]	0.8714^{10} [41]			
	0.8858^{40} [12, 26]	0.8763^{15} [18], 0.8764^{15} [34]	0.8681^{15} [17]			
		0.8733^{20} [12], 0.8724^{20} [14, 18], 0.8730^{20} [26], 0.8723^{20}[34], 0.8719^{20} [41]	0.8648^{20} [12], 0.8639^{20} [17], 0.8637^{20} [41]			
		0.8639^{30} [41]	0.8558^{30} [41]			
		0.8558^{40} [14, 18], 0.8560^{40} [34], 0.8557^{40} [41]	0.8474^{40} [17], 0.8478^{40} [41]			
		0.8475^{50} [41], 0.8392^{60} [41], 0.8309^{70} [41]	0.8396^{50} [41], 0.8313^{60} [41], 0.8229^{70} [41], 0.8145^{80} [41], 0.8061^{90} [41], 0.7976^{100} [41]			
11:0	0.8907^{20} [26]	0.8708^{20} [14]	0.8633^{20} [26]			
	0.8505^{80} [12]	0.8545^{40} [14]				
12:0	0.8679^{50} [26]	0.8732^{15} [18], 0.8737^{15} [34]	0.8651^{15} [17]			0.8986^{55} [26]
	0.8477^{80} [12]	0.8702^{20} [12, 26], 0.8694^{20} [14], 0.8691^{20} [18], 0.8698^{20} [34]	0.8618^{20} [12, 26], 0.8616^{20} [17]			
		0.8533^{40} [14, 18], 0.8539^{40} [34]	0.8464^{40} [17]			
13:0	0.8458^{80} [12, 26]	0.8681^{20} [14]				
		0.8524^{40} [14]				
14:0	0.8622^{54} [26]	0.8671^{20} [14] 0.8637^{25} [34]	0.8641^{15} [17]			0.8848^{60} [26]
	0.8439^{80} [12]	0.8598^{30} [41]	0.8607^{20} [17], 0.8616^{20} [12], 0.8610^{20} [41]			
		0.8517^{40} [14, 17], 0.8522^{40} [34], 0.8522^{40} [41]	0.8573^{25} [26]			
		0.8446^{50} [41], 0.8370^{60} [41], 0.8293^{70} [41], 0.8217^{80} [41], 0.8141^{90} [41], 0.8064^{100} [41]	0.8533^{30} [41]			
			0.8458^{40} [17], 0.8458^{40} [41]			
			0.8382^{50} [41], 0.8308^{60} [41], 0.8232^{70} [41], 0.8156^{80} [41], 0.8080^{90} [41], 0.8003^{100} [41]			
15:0	0.8423^{80} [12, 26]	0.8663^{20} [14], 0.8618^{25} [12]				
		0.8511^{40} [14]				

Table 1 continued

Fatty acid	Acid	Methyl ester	Ethyl ester	Propyl ester	Butyl ester	Triacylglycerol
16:0	0.8527^{62} [26]	856.1^{35} [29]	0.8568^{25} [12], 0.8577^{25} [26]			0.8752^{70} [26]
	0.8414^{80} [12]	0.8505^{40} [14], 0.8508^{40} [34], 852.4^{40} [29], 0.8507^{40} [41]				
		0.8487^{45} [29], 0.845^{50} [29], 0.8433^{50} [41], 0.8414^{55} [29], 0.8379^{60} [29], 0.8359^{60} [41], 0.834^{65} [29], 0.8285^{70} [41], 0.8247^{75} [26], 0.8210^{80} [41], 0.8316^{90} [41], 0.8061^{100} [41]				
17:0	0.8532^{60} [26]	0.8499^{40} [14]	0.8157^{30} [12]			
	$0.8355^{90.6}$ [12]					
18:0	0.9408^{20} [26]	0.8496^{40} [14], 0.8501^{40}[17], 0.8498^{40} [26, 34]	1.057^{20} [26]		0.854^{25} [26]	0.8559^{90} [26]
	0.8390^{80} [12]	0.8462^{45} [29], 0.8426^{50} [29], 0.8390^{55} [29], 0.8354^{60} [29], 0.8318^{65} [29]	$0.8481^{36.3}$ [12]			
19:0	0.8468^{70} [26]	0.8493^{40} [14]				
20:0	0.8240^{100} [12, 26]	0.8488^{40} [14]	0.8412^{45} [38]			
		0.8423^{45}, 0.8314^{65} [38]				
22:0	0.8223^{90} [12, 26]	0.8345^{60}, 0.8310^{65} [38]				
24:0	0.8207^{100} [26]	0.8305^{65} [38]				

Values in [29, 41] given in kg/m^3 and recalculated to g/cm^3. Density values in [29] determined at about 83 kPa

Superscripts indicate the temperature at which the density is reported

Table 2 Literature data for the density of unsaturated fatty acids and esters

Fatty acid	Acid	Methyl ester	Ethyl ester	Butyl ester	Triacylglycerol
C11:1 Δ10	0.9120^{24} [12]	0.889^{15} [26], 0.8861^{20}[12]	0.8827^{15} [26]		
	0.9072^{24} [26]		0.8788^{20} [12]		
C14:1 Δ9*c*	0.9018^{20}[12]				
C16:1 Δ9*c*	0.9003^{15} [12]	0.8728^{15} [38]			
		0.8690^{20} [38]			
		0.8538^{40} [38]			
C18:1 Δ6*c*	0.8700^{40} [12]	0.8767^{20} [12]			
C18:1 Δ9*c*	0.8901^{20} [2]	0.8808^{10} [41]	0.8720^{20} [26]	0.8704^{15} [26]	0.915^{15} [26]
	0.8905^{20} [12]	0.8777^{15} [34]	0.8687^{20} [12]		
	0.8935^{20} [26]	0.8739^{20} [12, 26], 0.8740^{20} [14], 0.8741^{20} [34], 0.8737^{20} [41]			
	0.8866^{25} [2]	0.8666^{30} [41]			
	0.8839^{30} [2]	0.8596^{40} [14], 0.8595^{40} [34], 0.8594^{40} [41]			
	0.8807^{35} [2]	0.8522^{50} [41], 0.8450^{60} [41], 0.8378^{70} [41], 0.8305^{80} [41], 0.8232^{90} [41], 0.8158^{100} [41]			
	0.8770^{40} [2]	0.8848^{5} [29], 0.8776^{15} [29], 0.8703^{25} [29], 0.8630^{35} [29], 0.8558^{45} [29], 0.8485^{55} [29], 0.8413^{65} [29]			
C18:1 Δ9*t*	0.8734^{45} [26]	0.8702^{20} [12]	0.8556^{25} [12]		
	0.8505$^{79.4}$ [12]				
C18:1 Δ11*t*	0.8560^{70} [12]				
C18:2 Δ9*c*,12*c*	0.9050^{15} [12]	0.8886^{10} [26], 0.8921^{10} [41]	0.8863^{15} [38]		
	0.9022^{20} [26]	0.8899^{15} [34], 0.8886^{18} [12]	0.8826^{20} [38]		
		0.8866^{20} [14], 0.8862^{20} [34], 0.8851^{20} [41]	0.8776^{25} [12]		
		0.8780^{30} [41]	0.8678^{40} [38]		
		0.8720^{40} [14], 0.8715^{40} [34], 08708^{40} [41]			
		0.8636^{50} [41], 0.8564^{60} [41], 0.8491^{70} [41],			
		0.8967^{5} [29], 0.8893^{15} [29], 0.8819^{25} [29], 0.8750^{35} [29], 0.8675^{45} [29], 0.8602^{55} [29], 0.8530^{65} [29]			
C18:3 Δ9*c*,12*c*,15*c*	0.9164^{20} [12, 26]	0.9057^{15} [38]	0.8970^{15} [38]		
		0.892^{20} [12], 0.8979^{20} [14]	0.8933^{20} [38]		
		0.9019^{20} [38]	0.8890^{25} [12]		
		0.895^{25} [26]	0.8783^{40} [38]		
		0.8834^{40} [14]^{a}, 0.8870^{40} [38]			
		0.9107^{5} [29], 0.9033^{15} [29], 08958^{25} [29], 0.8884^{35} [29], 0.8810^{45} [29], 0.8735^{55} [29], 0.8661^{65} [29]			

Table 2 continued

Fatty acid	Acid	Methyl ester	Ethyl ester	Butyl ester	Triacylglycerol
C20:1 Δ9*c*	0.8882^{25} [26]				
C20:1 Δ11*c*	0.8826^{25} [26][b]	0.8775^{15} [38]			
		0.8738^{20} [38]			
		0.8595^{40} [38]			
C22:1 Δ13*c*	0.860^{55} [26]	0.8743^{15} [38]			
	$0.860^{55.4}$ [12]	0.870^{20} [12], 0.8706^{20} [14], 0.8707^{20} [38]			
		0.8565^{40} [14]			
		0.8565^{40} [38]			
C22:1 Δ13*t*	0.8585^{57} [26]				
	$0.8585^{57.1}$ [12]				
Hydroxy					
C18:1 Δ9*c*, 12-OH	0.9450^{21} [26]	0.9236^{22} [12]	$0.9182^{20/20}$ [12]		
	$0.940^{27.4}$ [12]				

Values in [29, 41] given in kg/m^3 and recalculated to g/cm^3. Density values in [29] determined at about 83 kPa. No literature values available for propyl esters

Superscripts indicate the temperature at which the density is reported

[a] 27.5 % *trans* double bonds

[b] no double bond configuration indicated but is likely *cis*

compounds and Table 2 for unsaturated fatty compounds. Otherwise, a comprehensive collection of density data for neat fatty compounds taking different structural features into account does not appear to be available in the literature. Density data for individual compounds may be contained in other publications but are not compiled here.

Inspection of the data in Tables 1 and 2 reveals that some discrepancies exist, an observation made previously by Fisher with an approach to distinguish accurate and inaccurate data by homology [21], or that the data were obtained under varying conditions, especially varying temperature. Furthermore, density data for some common fatty compounds also do not appear to be readily available; for example, fatty esters with an odd number of carbons in the chain, polyunsaturated C_{20} and C_{22} esters, or a comparison of *cis vs. trans* double bonds and dependence of density on double bond position or fatty acid *vs* alcohol moiety. For these reasons, density data of a variety of fatty acid alkyl esters to include the aforementioned structural features were determined.

Density data in reference works was usually determined at 15 or 20 °C. The temperature prescribed in the European biodiesel standard EN 14214 for density determination is 15 °C while kinematic viscosity is determined at 40 °C in the American biodiesel standard ASTM D6751 and EN 14214. Tables 1 and 2 present a collection of density data from the literature at, mostly, 15, 20 or 40 °C, but also other temperatures, including temperatures above 40 °C. Therefore, in the present work, density data of fatty acid alkyl esters but also of some fatty acids and triacylglycerols were determined in the range of 15–40 °C in 5 °C increments besides investigating the structural features mentioned above.

Experimental

Straight-chain fatty acids and esters were obtained from Nu-Chek Prep (Elysian, MN, USA). Branched fatty acids and esters were obtained from Sigma–Aldrich (Milwaukee, WI, USA) or Matreya LLC (Pleasant Gap, PA, USA). To ensure purity and nature of the samples, some samples were randomly checked by GC–MS and NMR (solvent $CDCl_3$; 500 MHz for ^1H NMR, 125 MHz for ^{13}C NMR). All samples were found to be of advertised purities or higher (>98–99 %).

Densities were determined with an Anton Paar DMA 4,500 M density meter (Anton Paar USA, Ashland, VA, USA) utilizing the oscillating U-tube technology and requiring 1 mL of sample. Other methods for density determination exist such as the ASTM standard D1298 using a hydrometer [46]. All density data are given here in g/cm^3 in order to be consistent with the vast majority of previous literature although kg/m^3 is often used. It may be noted that, for example, the density specification in the biodiesel standard EN 14214 prescribes kg/m^3 as unit but, of course, conversion can be achieved by multiplying g/cm^3 data with the factor 1,000.

Results and Discussion

The density of fatty compounds in the range of 15–40 °C in increments of 5 °C was determined in the course of this

Table 3 Densities (g/cm^3) of saturated fatty acids and esters as determined in the course of the present work

Fatty acid/ ester	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
8:0						
Acid	0.9142	0.9101	0.9061	0.9020	0.8980	0.8940
Methyl	0.8802	0.8758	0.8715	0.8671	0.8628	0.8584
Ethyl	0.8708	0.8666	0.8623	0.8580	0.8537	0.8494
Propyl	0.8688	0.8648	0.8606	0.8564	0.8523	0.8481
Butyl	0.8670	0.8630	0.8589	0.8549	0.8508	0.8468
9:0						
Acid	0.9087	0.9047	0.9008	0.8969	0.8929	0.8890
Methyl	0.8784	0.8742	0.8700	0.8658	0.8616	0.8574
Ethyl	0.8682	0.8640	0.8599	0.8557	0.8515	0.8473
Propyl	0.8668	0.8627	0.8587	0.8546	0.8505	0.8465
Butyl	0.8644	0.8605	0.8566	0.8526	0.8486	0.8447
10:0						
Acid	–	–	–	–	0.8881	0.8843
Methyl	0.8764	0.8723	0.8682	0.8640	0.8600	0.8559
Ethyl	0.8678	0.8638	0.8598	0.8557	0.8516	0.8476
Propyl	0.8654	0.8615	0.8575	0.8535	0.8496	0.8456
Butyl	0.8646	0.8608	0.8569	0.8530	0.8491	0.8452
11:0						
Methyl	0.8747	0.8707	0.8667	0.8627	0.8587	0.8546
Ethyl	0.8653	0.8613	0.8574	0.8534	0.8494	0.8454
12:0						
Methyl	0.8730	0.8691	0.8652	0.8613	0.8573	0.8534
Ethyl	0.8659	0.8621	0.8582	0.8543	0.8504	0.8465
13:0						
Methyl	0.8720	0.8682	0.8643	0.8605	0.8566	0.8527
Ethyl	0.8656	0.8618	0.8579	0.8541	0.8502	0.8464
14:0						
Methyl	–	0.8670	0.8632	0.8594	0.8556	0.8518
Ethyl	0.8646	0.8608	0.8570	0.8532	0.8494	0.8456
15:0						
Methyl	–	0.8660	0.8622	0.8585	0.8547	0.8510
Ethyl	0.8631	0.8593	0.8556	0.8518	0.8481	0.8444
16:0						
Methyl	–	–	–	–	0.8535	0.8498

Table 4 Densities (g/cm^3) of unsaturated fatty acids and esters as determined in the course of the present work

Fatty acid/ester	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
14:1 Δ9*c*						
Acid	0.9042	0.9006	0.8970	0.8934	0.8898	0.8863
Methyl ester	0.8862	0.8824	0.8786	0.8747	0.8709	0.8671
16:1 Δ9*c*						
Acid	0.8983	0.8948	0.8913	0.8878	0.8842	0.8807
Methyl ester	0.8810	0.8774	0.8736	0.8700	0.8662	0.8625
16:1 Δ9*t*						
Methyl ester	0.8774	0.8737	0.8700	0.8662	0.8625	0.8588
18:1 Δ6*c*						
Methyl ester	0.8771	0.8735	0.8699	0.8662	0.8626	0.8590
Ethyl ester	0.8718	0.8682	0.8655	0.8600	0.8574	0.8538
18:1 Δ6*t*						
Methyl ester	–	–	0.8653	0.8616	0.8580	0.8543
18:1 Δ9*c*						
Acid	0.8941	0.8907	0.8872	0.8838	0.8803	0.8769
Methyl ester	0.8775	0.8738	0.8702	0.8666	0.8630	0.8594
Ethyl ester	0.8724	0.8688	0.8651	0.8615	0.8579	0.8543
18:1 Δ9*t*						
Methyl ester	0.8748	0.8712	0.8676	0.8640	0.8603	0.8567
Ethyl ester	0.8689	0.8653	0.8616	0.8580	0.8544	0.8507
18:1 Δ11*c*						
Acid	0.8931	0.8896	0.8862	0.8827	0.8792	0.8758
Methyl ester	0.8788	0.8752	0.8716	0.8679	0.8643	0.8607
18:1 Δ11*t*						
Methyl ester	0.8747	0.8711	0.8674	0.8638	0.8602	0.8565
18:1 Δ9*c*, 12-OH						
Methyl ester	0.9295	0.9259	0.9223	0.9187	0.9150	0.9114
18:2 Δ9*c*, Δ12*c*						
Acid	0.9063	0.9028	0.8993	0.8924	0.8889	0.8959
Methyl ester	0.8902	0.8865	0.8829	0.8792	0.8756	0.8720
Ethyl ester	0.8868	0.8832	0.8795	0.8759	0.8722	0.8686
18:2 Δ9*t*, Δ12*t*						
Methyl ester	0.8839	0.8803	0.8766	0.8729	0.8692	0.8656
18:3 Δ9*c*, Δ12*c*, Δ15*c*						
Methyl ester	0.9017	0.8980	0.8943	0.8906	0.8869	0.8832
Ethyl ester	0.8999	0.8962	0.8925	0.8887	0.8851	0.8814
18:3 Δ6*c*, Δ9*c*, Δ12*c*						
Methyl ester	0.9005	0.8968	0.8932	0.8894	0.8858	0.8821
19:1 Δ10*c*						
Methyl ester	0.8768	0.8732	0.8696	0.8660	0.8624	0.8589
20:1 Δ5*c*						
Methyl ester	0.8746	0.8710	0.8675	0.8639	0.8604	0.8568
20:1 Δ8*c*						
Methyl ester	0.8751	0.8715	0.8680	0.8644	0.8609	0.8573
20:1 Δ11*c*						
Methyl ester	0.8766	0.8730	0.8695	0.8660	0.8624	0.8589
Ethyl ester	0.8672	0.8637	0.8601	0.8566	0.8523	0.8494
20:2 Δ11,14						
Methyl ester	0.8848	0.8812	0.8776	0.8740	0.8705	0.8669

Table 4 continued

Fatty acid/ester	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
20:3 Δ11,14,17						
Methyl ester	0.8955	0.8919	0.8883	0.8846	0.8810	0.8774
20:4 Δ5,8,11,14						
Methyl ester	0.9064	0.9027	0.8991	0.8954	0.8918	0.8881
22:1 Δ13*c*						
Methyl ester	0.8744	0.8709	0.8674	0.8639	0.8604	0.8569
22:6 Δ4,7,10,13,16,19						
Methyl ester	0.9236	0.9199	0.9162	0.9125	0.90883	0.9052
24:1 Δ15*c*						
Methyl ester	0.8712	0.8677	0.8643	0.8608	0.8574	0.8539
Ethyl ester	0.8588	0.8553	0.8517	0.8482	0.8446	0.8411

work. As some compounds studied here have melting points in this range, the datapoint directly above the melting point was used for the onset of data collection in these cases. As mentioned above, Tables 1 and 2 present literature data on the density of fatty compounds for the sake of comparison. Table 3 contains density data for saturated fatty compounds determined in the course of this work. Table 4 lists density data for unsaturated fatty compounds investigated here. Table 5 give density data at 15 °C of some fatty acid methyl esters (FAME) with melting points >15 °C determined as discussed below. Density data of some triacylglycerols are given in Table 6. Figures 1, 2, and 3 are visualizations of data for saturated FAME, monounsaturated FAME and various fatty acid ethyl esters. In all tables, the fatty acid chains are given by their numerical acronyms (e.g., C18:1 Δ9*c* denoting the number of carbons, number of double bonds, double bond position and double bond configuration in oleic acid).

Density measurements may be affected by ambient atmospheric pressure which may also be the cause of some data discrepancies as data likely have been obtained in locations with different atmospheric pressure and meteorological conditions. A study has presented data on the density of methyl linoleate and various biodiesel fuels depending on pressure [43], while other density data for five FAME were obtained in a location with high elevation and a low atmospheric pressure of approximately 83 kPa [29], while atmospheric pressure at sea level is 101.3 kPa. As the location of the present measurements is approximately 200 m above sea level, an average atmospheric pressure of about 99 kPa can be assumed, which is a very minor deviation from “standard” conditions at sea level.

Effect of Chain Length

Density decreases with increasing number of CH_2 groups as the relative proportion of oxygen as the heaviest atom decreases. The data in Tables 3 and 4 also show that density decreases more when adding CH_2 groups to the alcohol moiety than to the fatty acid chain, not only for the first CH_2 group (methyl ester *vs* acid) but also for the second CH_2 group (ethyl ester *vs* methyl ester). This effect is chain-length dependent, however, as the decreases in density become less when adding even more CH_2 moieties to the alcohol moieties as shown for the propyl and butyl esters of some saturated fatty acids (Table 3). For example, the density difference (at 15 °C) between octanoic acid and methyl octanoate is about 0.34 g/cm^3, that between methyl octanoate and ethyl octanoate is 0.0093 g/cm^3, and that between methyl octanoate and methyl nonanoate is approximately 0.0017 g/cm^3. When extending the alcohol moiety beyond ethyl esters, however, the density differences between propyl and ethyl esters and between butyl and propyl esters are comparable to the density differences discussed for the fatty acid chains as was shown for the

Table 5 Calculated density contribution at 15 °C of saturated fatty acid methyl esters with melting points >15 °C

Fatty acid methyl ester	Calculated density (g/cm^3)
14:0	0.8699
15:0	0.8682
16:0	0.8666
17:0	0.8649
18:0	0.8632
19:0	0.8616
20:0	0.8599
21:0	0.8582
22:0	0.8566
23:0	0.8549
24:0	0.8533

Table 6 Density values of some triacylglycerols as determined in the course of the present work

Triacylglycerol	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C
Saturated						
8:0	0.9556	0.9518	0.9480	0.9441	0.9403	0.9365
9:0	0.9420	0.9382	0.9344	0.9306	0.9268	0.9231
10:0	–	–	–	–	0.9236	0.9199
11:0	–	–	–	0.9204	0.9168	0.9132
Unsaturated						
16:1 Δ9*c*	0.9181	0.9147	0.9112	0.9078	0.9043	0.9009
18:1 Δ9*c*	0.9152	0.9118	0.9084	0.9050	0.9016	0.8981
18:2 Δ9*c*, Δ12*c*	0.9286	0.9252	0.921	0.9183	0.91450	0.9116
20:1 Δ11*c*		0.9027	0.8993	0.8959	0.8926	0.8892

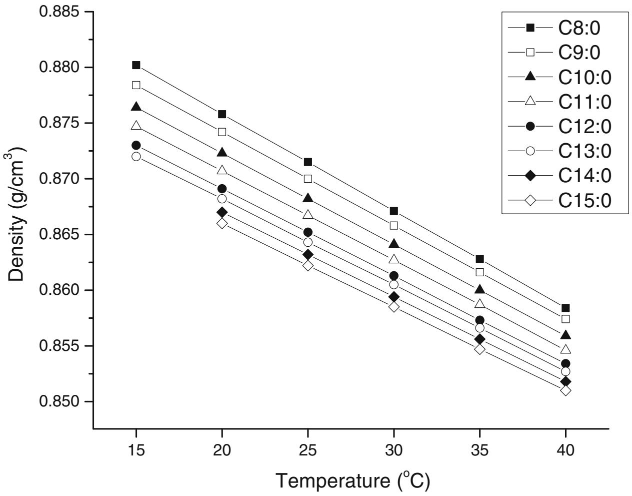

Fig. 1 Plot of the density of saturated fatty acid methyl esters (FAME) at 15–40 °C

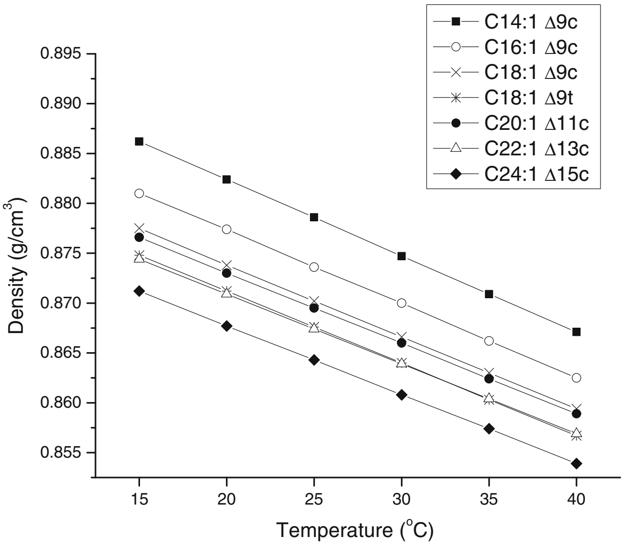

Fig. 2 Plot of the density of monounsaturated fatty acid methyl esters at 15–40 °C

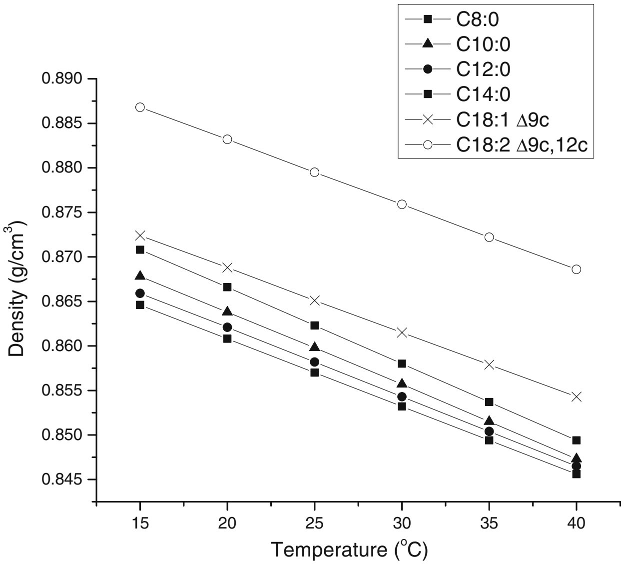

Fig. 3 Plot of the density of fatty acid ethyl esters at 15–40 °C

propyl and butyl esters of octanoic, nonanoic and decanoic acids (Table 3).

Effect of Double Bonds and Their Configuration

As expected, the introduction of a double bond in a fatty acid chain increases density due to the reduction of lighter-weight hydrogen. Accordingly, with increasing chain length but constant level of unsaturation, the density of an unsaturated fatty compound decreases, similar to saturated compounds. In this connection, prior data on the density of C16:1, C20:1 and C22:1 [38] appear contradictory because higher density is reported for C20:1 than for both C16:1 and C22:1. Clearly, the sequence must be C16:1 > C20:1 > C22:1.

Fatty compounds with *trans* unsaturation, however, exhibit lower density than those with *cis* unsaturation; see, for example, methyl oleate *vs.*methyl elaidate and methyl asclepate (C18:1 Δ11c) *vs* methyl vaccenate (C18:1 Δ11*t*) (Table 4). The difference at 15 °C is approximately 0.003

and 0.0027 g/cm^3 at 40 °C. This finding corresponds with the general observation that the physical properties of *trans* compounds more closely resemble those of the saturated species with the same number of carbon atoms. Other examples of physical properties of fatty compounds for which this observation holds are melting point [47] and viscosity [48]. It is also confirmed by data for straight chain alkenes such as hexenes and octenes [26].

Density increases slightly with increasing distance of the double bond from C1 of the FAME as was shown for the three *cis*-monounsaturated C18:1 and C20:1 methyl esters (Table 4). The effect is minor and additional confirmation by acquiring data for more compounds would be desirable, although such materials are not necessarily easily available in the necessary quantities.

Prediction

As discussed above, the density of biodiesel at 15 °C is prescribed as a specification in some biodiesel standards. Some components of biodiesel, however, typically the esters of palmitic and stearic or other saturated acids, are solids at this temperature. On the other hand, these components contribute to the overall density. Therefore, it is of interest to determine a calculated density at 15 °C for these compounds. This can be straightforwardly achieved by linear regression of the density values at 15 °C of saturated esters that are liquids at this temperature. Thus, linear regression of the density values at 15 °C of the methyl esters of C8:0–C13:0 (Table 5) gives $y = 0.89311 - 0.00166x$ ($r^2 = 0.99$) which can be used to calculate the density contribution density of the C14:0–C24:0 esters in mixtures that are liquid at 15 °C (Table 5). This procedure can, of course, beyond the example given here, be applied to determining the density at other temperatures or can be used for other classes of compounds if there are solids of interest in these classes of compounds. This procedure is similar to that used for calculating the cetane number [50] and kinematic viscosity [51] of compounds that are solids at 40 °C, the temperature prescribed in biodiesel standards for determining this property.

In the above connection it may be noted that the European biodiesel standard [8] presents a factor of 0.000723 g/(cm^3 °C) for correlating densities determined in the range of 20–60 °C to density at 15 °C but this value cannot be correlated to the present results because several biodiesel samples were used for which no information regarding their composition is provided.

Density of Mixtures

With density data for all major components of biodiesel available, including the calculated data for some saturated FAME, it is possible to calculate the density of mixtures of FAME (biodiesel) itself using the equation.

$$\rho_{\text{mix}} = \sum A_c \times \rho_c \quad (1)$$

in which ρ_{mix} is the density of the biodiesel sample (mixture of fatty acid alkyl esters), ρ_c is the density of an individual compound in the mixture and A_c is the amount (wt%) of an individual compound in the mixture. Three examples may underscore the utility of this approach. A sample of commercial soy methyl esters was found to have a density of 0.8851 g/cm^3 at 15 °C with the calculated density according to Eq. 1 being 0.8842 g/cm^3. For castor methyl esters, which contain a significant amount of methyl ricinoleate (methyl 12-hydroxy-9(*Z*)-octadecenoate), an experimental value of 0.9277 g/cm^3 (15 °C) was observed [51] with the calculated value according to Eq. 1 being 0.9227 g/cm^3 which includes some assumptions on the density of the minor components (approximately 2.5 % of the total fatty acid profile; for example, the density of methyl lesquerolate (14-hydroxy-11(*Z*)-eicosenoate) was assumed to be close to that of ricinoleic acid) of castor methyl esters. For olive oil methyl esters [52] the values are 0.8788 g/cm^3 (value determined during the course of this work) experimental and 0.8775 g/cm^3 calculated. This approach is again similar to that for determining the cetane number [49] and kinematic viscosity [50] of mixtures such as FAME. Furthermore, this approach to the determination of the density of mixtures can be applied to mixtures of fatty compounds other than biodiesel.

Application to Biodiesel

The major application of density in relation to biodiesel is that this property is contained in the European biodiesel standard EN 14214, prescribing that the density of biodiesel at 15 °C be in the range of 860–900 kg/m^3 (=0.86–0.90 g/cm^3). Most FAME meet this requirement with the exception of the highly polyunsaturated FAME C20:4 and C22:6 and hydroxylated FAME such as methyl ricinoleate.

Triacylglycerols

For the sake of completeness of study, triacylglycerols were also studied and experimental data are given in Table 6. The structural effects on density observed for triacylglycerols are similar to those discussed above for fatty acids and fatty acid alkyl esters.

Summary and Conclusions

The density values of a comprehensive collection of fatty compounds were determined. Effects of compound structure on density, prediction of density contribution of compounds that are solids at the temperature and prediction of the density of mixtures of fatty compounds was carried out. The prediction of density of fatty compounds and their mixtures resembles the prediction of cetane number and kinematic viscosity.

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