

Predicting the phase behavior of fatty acid methyl esters and their mixtures using the GC-SAFT-VR approach



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ARTICLE INFO

Article history:

Received 30 June 2015

Received in revised form

11 November 2015

Accepted 11 November 2015

Available online 22 November 2015

Keywords:

Biodiesel fuel

Molecular modeling

Phase equilibria

Heteronuclear

Group contribution

Binary mixtures

Carbon dioxide

Vapor liquid equilibrium

SAFT

ABSTRACT

Biodiesel fuels, which consist of a blend of long chain fatty acid methyl esters, have attracted increased interest in recent years as possible alternates to fuels derived from petroleum. An understanding of the thermophysical properties and phase behavior of these molecules are therefore important to the investigation and design of biodiesel processes; however, such data is limited, making the development of molecular based modeling approaches that can accurately and reliably determine the thermophysical properties of fatty acid methyl esters an important research area. Here we apply the group contribution based statistical associating fluid theory for potential of variable range (GC-SAFT-VR) equation of state to the study of long chain fatty acid methyl esters that comprise biodiesel fuels. With minimal reliance on experimental data, the GC-SAFT-VR equation of state offers a predictive approach that allows for the description of hetero-segmented chains that can correlate and predict the phase behavior of pure associating and non-associating fluids and their mixtures. Model parameters for the C=O, CH₃, CH₂, CH=CH₂, OCH₂, and OCH₃ functional groups and their cross interactions were taken from earlier work and used here in a transferable fashion to predict the thermophysical properties and phase behavior of pure fatty acid methyl esters and their mixtures with other fatty acid methyl esters, alcohols, and carbon dioxide. It is shown that the GC-SAFT-VR approach can be used as a purely predictive tool without fitting any new model parameters) to accurately predict the phase behavior of the fatty acid methyl ester fluids and their mixtures studied.

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1. Introduction

Due to the depletion of non-renewable resources, the search for alternatives to petroleum-derived fuels is an active area of research. One proposed alternative, biodiesel, is a renewable and biodegradable energy source made up of mixtures of esters of long chain fatty acids [1–3]. The most common compounds utilized in biodiesel are fatty acid methyl esters (FAME) with molecular formula CH₃(CH₂)_nCOOCH₃ (Table 1).

Although the molecular size of the components of biodiesel and petroleum diesel are similar, they differ in chemical composition and structure [4], which results in several notable variations in the physical properties of the two fuels [4]. Specifically, biodiesel has

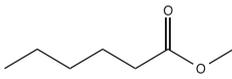
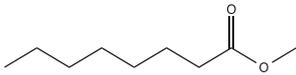
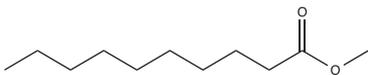
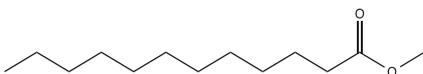
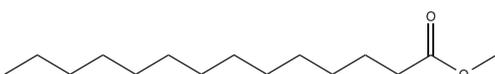
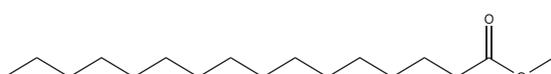
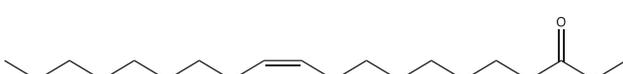
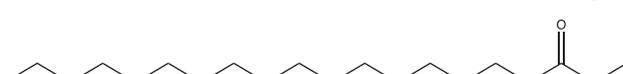
superior characteristics in terms of flash point, aromatic content, lubricity, sulfur and oxygen content, and toxicity [2,4]. In addition, the use of biofuels for transportation could result in an average greenhouse gas emission reduction of about 57% as compared to the emissions that would occur from the production and use of equivalent quantities of petroleum fuels [5].

Presently, the cost of biodiesel is twice that of petroleum derived diesel fuel [6], presenting significant economic challenges to its implementation on a larger scale. Understanding the thermodynamics and phase behavior of these fluids and their mixtures can provide insight into how to optimize the molecular composition in order to provide more ideal fuel conditions and properties, as well as to reduce costs. For example, the vapor pressure, which is an important thermodynamic property as it controls the volatility, safety, and stability of the fuel [7], can be adjusted by changing the fuel composition. A higher value of vapor pressure can favor evaporative emissions while a lower value can lead to delayed ignition, poor atomization, and problematic combustion [7]. It is

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Table 1
Chemical structure of fatty acid methyl esters considered in this work.

Compound	Formula	Chemical Structure
Methyl Caproate	C ₇ H ₁₄ O ₂	
Methyl Caprylate	C ₉ H ₁₈ O ₂	
Methyl Caprate	C ₁₁ H ₂₂ O ₂	
Methyl Laurate	C ₁₃ H ₂₆ O ₂	
Methyl Myristate	C ₁₅ H ₃₀ O ₂	
Methyl Palmitate	C ₁₇ H ₃₄ O ₂	
Methyl Oleate	C ₁₉ H ₃₆ O ₂	
Methyl Stearate	C ₁₉ H ₃₈ O ₂	

however impractical to experimentally determine the vapor pressure at every necessary condition the decomposition of feed oils usually takes place at high temperatures.

The limited available experimental data for the vapor pressure and other thermodynamic properties of FAME molecules hinders process development and as such reinforces the need for accurate and predictive models for the determination of such data. While modeling tools that utilize correlations derived from a limited number of data points are readily implemented, the development of accurate models, that are not heavily reliant on experimental data, to predict the properties of biodiesel fuels and their blends is more difficult [8]. However, more recently, statistical mechanics based equations of state, such as the statistical associating fluid theory (SAFT) [9–14] have been applied to study biodiesel systems. Based on Wertheim's theory of association [11–14], the SAFT equation of state describes molecules as chains of tangentially bonded homonuclear segments that interact through dispersion and association interactions. Being rooted in statistical mechanics and based on a molecular-level model, SAFT typically lends itself well to the development of a predictive modeling approach. For a detailed discussion of the various versions of SAFT and its applications, the reader is directed to the review of M^cCabe and Galindo [15].

To date several versions of SAFT have been used to examine the thermodynamic properties and phase behavior of FAME molecules [3,16–24], with some investigating the phase behavior of light FAME molecules [21,22] only. In this work, we focus on heavy FAME systems, which constitute the major components of biodiesel fuels and for which limited studies of the vapour liquid equilibria (VLE) have been performed. In the first study, Perdomo et al. [16] examined three common biodiesel compounds (methyl palmitate, methyl linoleate, and methyl oleate) with the SAFT-VR [25] equation of state, which describes chain molecules formed from hard-

core segments that interact via square well (SW) potentials of variable range (VR). The molecules of interest were modeled as associating chains and model parameters were determined by fitting to saturated liquid density and vapor pressure data, with deviations found to be less than 1%. Improvements to the VLE predictions were observed when a discretized version of a modified Lennard–Jones potential, instead of the usual SW interaction, was used to describe the segment–segment interactions [16]. Extending the study to mixtures, Perdomo et al. [17] used the SW SAFT-VR approach, to describe model biodiesel blends containing FAME molecules methyl palmitate, methyl linoleate, and methyl oleate. Parameters for the pure fluids were taken from earlier work [16] and cross binary–interaction parameters were obtained by fitting to liquid densities and speed of sound data for each mixture studied. Isochoric heat capacities, speed of sound, and phase diagrams for binary and ternary mixtures were then predicted at conditions not considered in the fitting procedure. Although, exact deviations were not reported, in general good agreement was found between the experimental results and predicted isochoric heat capacities; however, the speed of sound predictions showed fairly significant deviations at low temperatures. In a subsequent study, Perdomo et al. [18] utilized the group contribution based SAFT- γ approach to study several FAME molecules and esters that contain hydroxyl groups. In the SAFT- γ [26] approach molecules are broken down into segments of different types that represent the chemical functional groups within the molecule and are then combined to describe a homonuclear model chain. To describe the phase coexistence properties of the molecules of interest, ester (COOCH₃) and hydroxyl ester (CHOH) functional groups were defined and characterized by fitting to experimental vapor pressure and saturated liquid density data for secondary alcohols and methyl alkanoates, respectively whilst the remaining model parameters were taken from earlier work [26]. The absolute average deviation

in vapor pressure (AADP%) was found to be 3.62% for the ester series (methyl ethanoate to methyl heptanoate) and 2.42% for the secondary alkanols series (2-propanol to 4-decanol). Deviations were not provided for the saturated liquid density predictions, however, from graphical representations comparing saturated liquid densities with experimental results they appear to be greater than for the vapor pressure. Using these parameters, the thermophysical properties of long chain pure biodiesel components and the specific gravity and flash point of commercial biodiesel blends were then predicted; however, significant deviations from experimental data for the specific gravity was observed, especially for blends containing high fractions of unsaturated FAME molecules.

In another study, Oliveira et al. [19] used the density gradient theory approach coupled with the soft-SAFT equation to describe the interfacial properties of several fatty acid esters. The esters were modeled as non-associating homonuclear chain fluids with the model parameters fitted to vapor pressure and liquid density data. Deviations from experimental data were found to be 0.047% for the liquid density and of 5.8% for the vapor pressure. Density, surface tension, viscosity, and speed of sound data were then predicted for fatty acid methyl and ethyl esters with deviations of less than 5%. In a subsequent study, Oliveira [3] et al., extended their work to study binary mixtures of FAMES with alcohols. Parameters for the FAME molecules were combined with those for alcohols from the literature [27] and an adjustable cross interaction parameter fitted to experimental data for mixtures of ethyl butanoate + methanol and hexyl acetate + methanol was used. This fitted energy parameter was then transferred to the study of other FAME + methanol mixtures; however, it was not transferable to other alcohols and so mixtures with ethanol required a new fitted interaction, thus reducing the predictability of the approach. Additionally, when pressures above atmospheric were studied (2–16 MPa) significant deviations were observed and a new fitted cross interaction for the FAME + methanol systems was proposed by fitting to methanol + methyl laurate at 523 K. More recently, also utilizing the soft-SAFT equation, Llovel et al. [20] investigated the solubility of supercritical CO₂ in fatty acid methyl esters. The parameters for the ester family was taken from the work of Oliveira et al. [19] and used to predict the VLE of mixtures of methyl myristate, methyl palmitate, methyl stearate, and methyl oleate and CO₂. Two fitted binary interaction parameters, to account for the differences in molecular size and dispersive energy between the CO₂ and the ester mixtures, were required. The dispersive energy parameters were adjusted for each mixture studied, as slight chain length dependence was observed, while the molecular size interaction parameter, which adjusts the molecular diameter was held constant for all mixtures studied. Although, exact deviations were not reported, good agreement was generally found between the theoretical results and experimental data using this approach.

The polar group contribution statistical associating fluid theory (GC-SAFT) [28] has also been used to investigate the phase equilibrium and thermodynamic properties of FAME molecules in three separate SAFT studies using three different versions of SAFT (SAFT [9], SAFT-VR [25], and PC-SAFT [29,30]), all modified to include a polar term. In the GC-SAFT approach, parameters for the chemical groups are obtained by fitting to vapor pressure and saturated liquid density experimental data for molecules containing the chemical group of interest and then averaged using established relations to predict pure and mixture properties, as a result the theory reduces to the original SAFT equation (i.e., it describes a homonuclear chain at both the segment (monomer) and chain levels). In the first study, Nguyen Thi et al. [24] determined parameters for the groups not previously studied with the polar GC-SAFT approach (i.e., the COO and HCOO groups) by simultaneous regression of all the available vapor pressure and saturated liquid

density data. The dipole moment was also determined during the fitting process for the COO group. The thermodynamic properties of esters, formates, and acetates were then investigated, with similar results obtained from the three different versions of SAFT. The vapor pressure of pure long chain esters not included in the fitting process were also studied and deviations from experimental data of 15.82%, 15.25%, and 36.24% for methyl palmitate, methyl stearate, and methyl tetracosanoate, respectively were obtained. Subsequently Nguyen Huynh et al. [22] extended the work of Nguyen Thi et al. to mixtures; however, the pure ester parameters were reinvestigated using a multipolar segment approach, where multipole moments are assumed to be localized on certain segments in the chain. The value of this approach is however unclear given that the group parameters are averaged in the GC-SAFT approach and so the model reverts to that of a homonuclear fluid; it is perhaps therefore not surprising that comparable results were found using both the multipolar segment and polar molecule approach. Again the results from three different versions of SAFT were compared and deviations were observed to increase with chain length, resulting in average deviations in vapor pressure of greater than 10% for all three approaches. As for mixtures, only light ester molecules such as methyl acetate and methyl octanoate were considered.

Although several SAFT approaches [3,16,17,19] have been shown to provide an accurate description of the thermodynamic properties of FAME molecules [16,17], as discussed above these theories require parameters for every molecule studied to be fitted to experimental data and additional fitted binary interaction parameters are needed when considering mixtures. To overcome these issues, group contribution approaches provide an attractive alternative as new molecules can in principal be studied by combining the groups of interest without fitting to experimental data. However, although GC approaches have been applied to the study of FAME systems [18,22,24], additional functional groups (and in the case of polar GC-SAFT additional parameters) fitted to experimental data for FAME molecules needed to be defined. In contrast the group-contribution SAFT-VR (GC-SAFT-VR) approach used in this work does not require the definition of any new groups to study FAME molecules and therefore represents a truly predictive approach. We also note that GC-SAFT-VR considers the chemical makeup of the molecules being studied more explicitly through the definition of a hetero-nuclear model chain i.e., molecules are described as chains of tangentially bonded segments of different size and/or energy parameters. The GC-SAFT-VR approach thus combines the SAFT-VR equation, where chain molecules are formed from hard-core segments interacting through attractive potentials of variable range [25,31] with a group contribution [21] approach. The different functional groups within the molecule are explicitly represented in the model chain, allowing for a description of the effects of molecular structure on the thermodynamic properties of the fluid. As in other GC approaches, group parameters can be obtained by fitting to pure component experimental vapor pressure and saturated liquid density data for molecules containing the groups of interest. The parameters can then be used in a transferrable manner to determine the phase behavior of other fluids not included in the fitting process and mixtures. Another advantage to utilizing a GC approach is that when groups of interest are contained in the same molecule, binary interactions parameters between the groups can be obtained from pure component experimental data alone, i.e., without fitting to binary experimental data. Thus a truly predictive approach can be developed, which offers an improved physical chemistry interpretation of the molecules of interest as compared to other simpler versions of SAFT. In previous work, the GC-SAFT-VR approach has been successfully applied to study the thermodynamics and phase behavior of a wide range of fluids including hydrocarbons [21], ketones [21], alcohols

[32], polymers [33], and aromatics [34]. In this work, the predictive character of the GC-SAFT-VR equation of state is further evaluated through the description of the thermophysical properties and phase behavior of several long chain FAME molecules as well as mixtures with CO₂, alcohols, and other FAME molecules. By utilizing groups already developed, a predictive approach is realized that allows the phase behavior of FAME systems to be accurately predicted.

The remainder of the paper is organized as follows: the molecular model and theory are presented in Section 2, the functional group parameter estimation and results for both pure components and mixtures studied are discussed in Section 3, and conclusions drawn in Section 4.

2. Molecular model and theory

The GC-SAFT-VR approach allows for the predictive study of the thermodynamic properties of fluids and their mixtures. Molecules are described by tangentially bonded segments in which each type of segment represents a functional group present in the molecule [21,35]. The segments representing each functional group interact via a square well potential, which can be described by,

$$u_{ki,lj}(r) = \begin{cases} +\infty & \text{if } r < \sigma_{ki,lj} \\ -\varepsilon & \text{if } \sigma_{ki,lj} \leq r \leq \lambda_{ki,lj}\sigma_{ki,lj} \\ 0 & \text{if } r \leq \lambda_{ki,lj}\sigma_{ki,lj} \end{cases} \quad (1)$$

where $u_{ki,lj}$ represents the interaction between a functional group of type i present in molecule k with a functional group of type j in molecule l , σ is the segment diameter, ε is the depth of the square well, λ is the potential range, and r is the distance between the two groups. The unlike size and energy interactions can be obtained from the Lorentz-Berthelot combining rules expressed by,

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (2)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (3)$$

and the unlike potential range is given by,

$$\lambda_{ij} = \frac{\lambda_{ii}\sigma_{ii} + \lambda_{jj}\sigma_{jj}}{\sigma_{ii} + \sigma_{jj}} \quad (4)$$

For non-ideal interactions, deviations from the Lorentz-Berthelot combining rules are expected. To account for these non-idealities, as discussed above, the unlike interactions between functional groups can be fitted to pure component experimental data for molecules containing both functional groups.

The GC-SAFT-VR equation of state is written in terms of the total Helmholtz free energy, expressed as a sum of four separate contributions:

$$\frac{A}{Nk_B T} = \frac{A^{ideal}}{Nk_B T} + \frac{A^{mono}}{Nk_B T} + \frac{A^{chain}}{Nk_B T} + \frac{A^{assoc}}{Nk_B T} \quad (5)$$

where N is the total number of molecules in the system, T is the temperature, and k_B is the Boltzmann constant. In equation (5), A^{ideal} is the ideal free energy, A^{mono} is the contribution to the free energy due to the monomer segments, A^{chain} is the contribution due to the formation of bonds between monomer segments, and A^{assoc} is the contribution due to association. Since the theory has been presented previously [21,36] only a brief overview of the main expressions are provided below.

The ideal Helmholtz free energy, A^{ideal} , is given by,

$$\frac{A^{ideal}}{Nk_B T} = \sum_{i=1}^{n_{components}} x_i \ln(\rho_i \Lambda_i^3) - 1 \quad (6)$$

where $n_{components}$ represents the number of pure components, $\rho_i = N_i/V$ (the molecular number density of chains of component i), x_i is the mole fractions of component i in the mixture, and Λ_i is the thermal de Broglie wavelength, N is the total number of molecules in the system, T is the temperature, and k_B is the Boltzmann constant.

The monomer free energy, A^{mono} , is given by a second order high temperature expansion using Barker and Henderson perturbation theory for mixtures [37]

$$\frac{A^{mono}}{Nk_B T} = \sum_{i=1}^{n_{components}} \sum_{k=1}^{n'_k} m_{ki} x_i \left(a^{HS} + \frac{a_1}{k_B T} + \frac{a_2}{(k_B T)^2} \right) \quad (7)$$

where the first sum is over the components in the system, the second sum is over all n'_k types of functional groups within each component and m_{ki} is the number of segments of type k in chains of component i .

The chain term, A^{chain} , for a mixture of heterosegmented chain molecules is given by,

$$\frac{A^{chain}}{Nk_B T} = - \sum_{i=1}^n x_i \sum_{kj} \ln y_{ik,ij}^{SW}(\sigma_{ik,ij}) \quad (8)$$

where the first sum is over all components in the mixture and the second sum considers the chain formation and connectivity of the segments within a given chain. The background correlation function is given by,

$$y_{ik,ij}^{SW}(\sigma_{ik,ij}) = \exp\left(\frac{-\varepsilon_{ik,ij}}{k_B T}\right) g_{ik,ij}^{SW}(\sigma_{ik,ij}) \quad (9)$$

where $g_{ki,kj}^{SW}(\sigma_{ki,kj})$ is the radial distribution function for the square well monomers at the contact distance $\sigma_{ki,kj}$ and is approximated by a first-order high-temperature perturbation expansion.

Finally, the contribution due to association [25] interactions, (A^{assoc}), between sites on different functional groups that form the molecules of interest is expressed as:

$$\frac{A^{assoc}}{Nk_B T} = \sum_{k=1}^n x_k \sum_{i=1}^{n'_k} v_{ki} \sum_{a=1}^{n'_i} n_{ia} \left(\ln X_{kia} + \frac{1 - X_{kia}}{2} \right) \quad (10)$$

where the first sum is over the number of components n , the second over all types of functional groups in the molecule k (n'_k), and the third sum is over the total number of site types in a functional group i (n'_i). The fraction of molecules of type i not bonded at site a , $X_{a,i}$, is obtained from the solution of the mass balance equations and is given in terms of the total number density for the system, shown as [9,10]:

$$X_{a,i} = \frac{1}{1 + \rho \sum_{l=1}^n x_l \sum_{j=1}^{n'_l} v_{lj} \sum_{b=1}^{n'_j} n_{jb} x_{ijb} \Delta_{kia,lib}} \quad (11)$$

$\Delta_{kia,lib}$ is the parameter that characterizes the association between site a in molecule i and site b in molecule j in the mixture and is given by:

$$\Delta_{kia,ljb} = K_{kia,ljb}^{HB} f_{kia,ljb} g_{ki,lj}^{SW} (\sigma_{ki,lj}) \quad (12)$$

where $K_{kia,ljb}^{HB}$ is the volume available for bonding, $f_{kia,ljb}$ the Mayer f -function, and $g_{ki,lj}^{SW}$ the radial distribution function for the square well monomers. At this point, it is important to note that in the usual homonuclear SAFT equations (i.e. SAFT-HR [29], soft-SAFT [38], SAFT-VR [25], etc.) the location of association sites on a molecule is arbitrary and are averaged over the whole molecule. However, in the GC-SAFT-VR equation, because of the hetero-segmented chain model used, the location of the association sites can be specified on a given functional group and hence their position within the model chain defined [25].

With the Helmholtz free energy defined, thermodynamic properties such as pressure, temperature, and chemical potential, can then be obtained using standard thermodynamic relationships.

3. Results and discussion

3.1. Pure fluids

Taking advantage of the transferability of the GC-SAFT-VR approach, as stated above previously reported parameters [21] were utilized for the functional groups (i.e., the CH₃, CH₂, CH=CH₂, C=O, OCH₃, and OCH₂) that comprise the FAME molecules of interest. These group parameters were determined in the work of Peng et al. [21] by fitting to experimental vapor pressure and saturated liquid density data for molecules containing the group of interest (i.e., alkanes, alkenes, ketones, alkyl acetates, and esters). We note that for the OCH₂ and OCH₃ functional groups data for select alkyl acetates and methyl esters, not considered in this work, were used to determine the group parameters. The molecular parameters (m , σ , λ , and ϵ) used to describe the FAME molecules studied (i.e., methyl laurate, methyl myristate, methyl caprate, methyl caprylate, methyl palmitate, methyl oleate, and methyl stearate) are reported in Tables 2–4. Also reported in Tables 2–4 are the parameters for carbon dioxide that were taken from the work of Blas and Galindo [39,40] and the cross interaction between the CH₂ group and the CO₂ molecule that was fitted to the hexane and CO₂ binary mixture at 313.15 K.

Utilizing the model described above, the vapor pressure and saturated liquid density for pure FAME fluids were first predicted. Fig. 1 shows the comparison between theoretical results and experimental data for the vapor pressure for the molecules: methyl laurate, methyl myristate, methyl caprate, methyl caprylate, methyl palmitate, methyl oleate, and methyl stearate. Similarly, Fig. 2 shows a comparison between the theoretical results and experimental data for the saturated liquid density, for the FAME molecules methyl laurate, methyl myristate, methyl caprate, and methyl caprylate, which were chosen as a representative sample. Table A1 in the Appendix summarizes the absolute average deviation in pressure (AADP) and saturated liquid density (AADL), respectively.

Table 2
GC-SAFT-VR parameters for the segment size and segment number of each functional group studied.

Groups	σ (Å)	m_i
CH ₃	3.737	0.667
CH ₂	4.041	0.333
CH=CH ₂	3.574	1.052
C=O	3.496	0.58
OCH ₂ (esters)	2.9499	1.0
OCH ₃ (esters)	3.0783	1.33
CO ₂	2.7864	2.0

We note that good agreement between the theoretical predictions and experimental data (AADP = 5.37% and AADL = 2.48%) are observed over a wide temperature range. However, a slight increase in deviation for the unsaturated methyl oleate molecule is observed. As discussed previously, these long chain FAME molecules were also studied by Nguyen Thi et al. [24] using the polar GC-SAFT equation [28] and four different chemical groups (CH₃, CH₂, COO and HCOO) with deviations in vapor pressure for methyl palmitate, methyl stearate, and methyl tetracosanoate of 10.31%, 15.30%, and 51.77%, respectively. Using a simpler approach (i.e., no dipole term and the associated additional fitted parameter), we find significantly lower deviations using the GC-SAFT-VR equation. We also note that although Oliveira et al. [19] for the same molecules obtained comparable, and in some cases lower average deviations from experimental data, the model parameters were fitted to experimental FAME data, while the GC-SAFT-VR approach provides similar results using a truly predictive approach.

3.2. Binary mixtures

To model the binary mixtures of interest, model parameters taken from previous work in a transferable manner are again used to determine the properties of the mixtures of interest. The results shown are therefore pure predictions as no model parameters have been adjusted to experimental binary mixture data.

First we consider the VLE of binary mixtures of FAME molecules. We focus on mixtures of long chain FAME molecules, for which to our knowledge, no other SAFT studies have been performed. In Fig. 3a and b the isobaric VLE of the binary mixture of methyl caprylate (C₉H₁₈O₂) + methyl caprate (C₁₁H₂₂O₂) and methyl caprylate + methyl caproate (C₇H₁₄O₂), respectively are presented. From the figures we can see that good agreement between the theoretical predictions and experimental data is obtained and that the theory is able to capture the change in phase behavior as the number of CH₂ groups present is increased. Next we investigate in Fig. 3c the methyl laurate (C₁₃H₂₆O₂) + methyl caprate (C₁₁H₂₂O₂), binary mixture at 0.0053 MPa, 0.0066 MPa, and 0.0133 MPa. Good agreement is again found as compared to experimental results. Further increasing the length of the carbon backbone of the FAME molecules, we show in Fig. 3d that the theory accurately predicts the phase behavior of mixtures of methyl myristate (C₁₅H₃₀O₂) + methyl laurate (C₁₃H₂₆O₂), again without fitting to experimental results. Finally, the isobaric VLE curves of the binary mixture of methyl myristate (C₁₅H₃₀O₂) + methyl palmitate (C₁₇H₃₄O₂) are predicted in Fig. 3e. In all cases as the chemical structures of the ester molecules changes the theory is able to predict and capture the changes in phase behavior without fitting to the experimental data. Finally, we consider a binary mixture of the longest saturated FAME molecules studied. The T_{xy} phase behavior of methyl palmitate (C₁₇H₃₄O₂) + methyl stearate (C₁₉H₃₈O₂) is investigated in Fig. 3f at constant pressures of 0.010 MPa, 0.001 MPa, 0.005 MPa, and 0.0001 MPa. From the figure we can see that good agreement is obtained between the theoretical predictions and experimental data even for the long chain molecules considered and over a range of pressures. Following the classifications scheme for binary mixtures given by Scott and van Konynenburg [41,42], the theory suggests Type 1 phase diagrams for binary mixtures of saturated FAME molecules that have a difference in carbon chain length of up to 12, which is the difference between the shortest and longest FAME molecule of interest in this study.

Turning to unsaturated FAME molecules, in Fig. 4 we present experimental results and GC-SAFT-VR predictions for the methyl oleate (C₁₉H₃₆O₂) + methyl stearate (C₁₉H₃₈O₂) binary mixture at 473.15 K. The theoretical predictions for the xy distribution are seen

Table 3
GC-SAFT-VR segment–segment dispersion energy well depth parameters $\epsilon_{ki,lj}/k_B(K)$.

Type	CH ₃	CH ₂	CH=CH ₂	C=O	OCH ₂ (ester)	OCH ₃ (ester)	CO ₂
CH ₃	234.250	235.735	226.675	307.2232	157.702	191.144	204.951
CH ₂	235.735	237.230	228.112	309.1712	158.702	192.355	206.251
CH=CH ₂	226.675	228.112	219.344	297.288	152.602	184.962	198.323
C=O	307.223	309.171	297.288	402.929	206.829	250.689	268.797
OCH ₂ (ester)	157.702	158.702	152.602	206.8288	106.168	128.682	137.977
OCH ₃ (ester)	191.144	192.356	184.962	250.6887	128.682	155.970	167.237
CO ₂	204.951	206.251	198.323	268.7973	137.977	167.237	179.317

Table 4
GC-SAFT-VR segment–segment dispersion energy range parameters $\lambda_{ki,lj}$.

Type	CH ₃	CH ₂	CH=CH ₂	C=O	OCH ₂ (ester)	OCH ₃ (ester)	CO ₂
CH ₃	1.492	1.583	1.529	1.685	1.546	1.566	1.506
CH ₂	1.583	1.667	1.621	1.586	1.645	1.662	1.609
CH=CH ₂	1.529	1.621	1.568	1.728	1.764	1.608	1.550
C=O	1.685	1.586	1.728	1.891	1.764	1.558	1.729
OCH ₂ (ester)	1.546	1.645	1.764	1.764	1.614	1.635	1.571
OCH ₃ (ester)	1.566	1.662	1.558	1.635	1.635	1.655	1.594
CO ₂	1.506	1.609	1.550	1.729	1.571	1.594	1.526

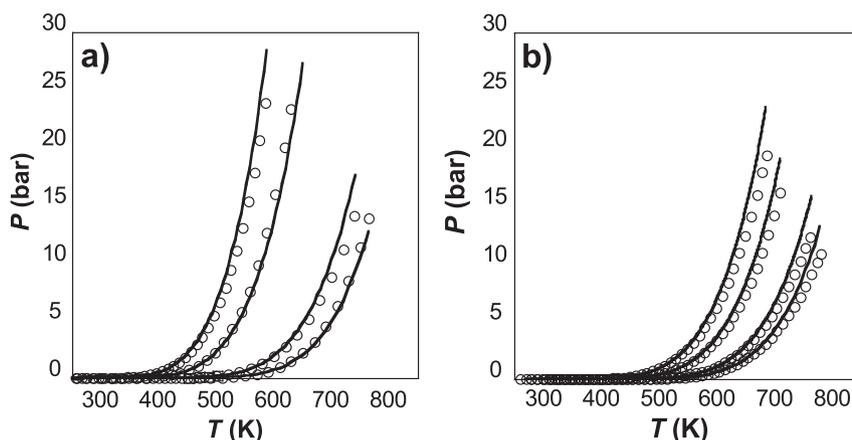


Fig. 1. Comparison between theoretical predictions from the GC-SAFT-VR equation and experimental data for the vapor pressure of a) methyl caproate, methyl caprylate, methyl myristate, and methyl oleate (left to right) and b) methyl caprate, methyl laurate, methyl palmitate, and methyl stearate (left to right). Symbols correspond to the experimental data and the solid lines to the theoretical results.

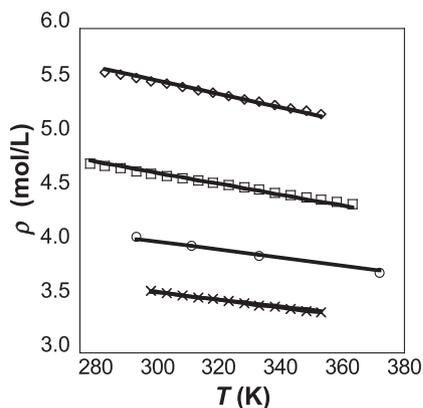


Fig. 2. Comparison between theoretical predictions from the GC-SAFT-VR equation and experimental data for the saturated liquid density of methyl caprylate (diamonds), methyl caprate (squares), methyl laurate (circles), and methyl myristate (crosses) (top to bottom). Symbols represent the experimental data and solid lines the theoretical results.

to be in good agreement with the experimental data however, experimental results are not available for comparison with the corresponding Pxy behavior (Fig. 4a), for which the theory predicts azeotropic behavior implying separation would present difficulties.

We next consider binary mixtures of FAMES with the light alcohols methanol and ethanol. Experimentally it has been shown that in mixtures of alcohols and esters hydrogen bonding occurs between the hydrogen atom in the OH group of the alcohol and the oxygen atom in the ester [46–49]. In previous work [32], this was accounted for through the addition of an association site on the carbonyl group (C=O) that enabled cross association between the alcohol and ester. To describe the alcohol molecules we have utilized GC-SAFT-VR parameters from the literature [32], which describe methanol and ethanol as a combination of the CH₃ and CH₂ groups with a 3 site linear alcohol hydroxyl group ($\sigma = 5.299$ (Å) $\lambda = 1.495$ $\epsilon/k_B = 534.805$ (K), $m = 0.176$). We note that the energy and range parameters (ϵ^{HB} and K^{HB}) for the cross association were of the same strength and value as the self-association between alcohol groups ($\epsilon^{HB} = 2797$ K and $K^{HB} = 0.16014$ Å³ [32]) and so were not fitted parameters. Using this same approach, in Fig. 5a we consider the VLE at atmospheric pressure for methyl

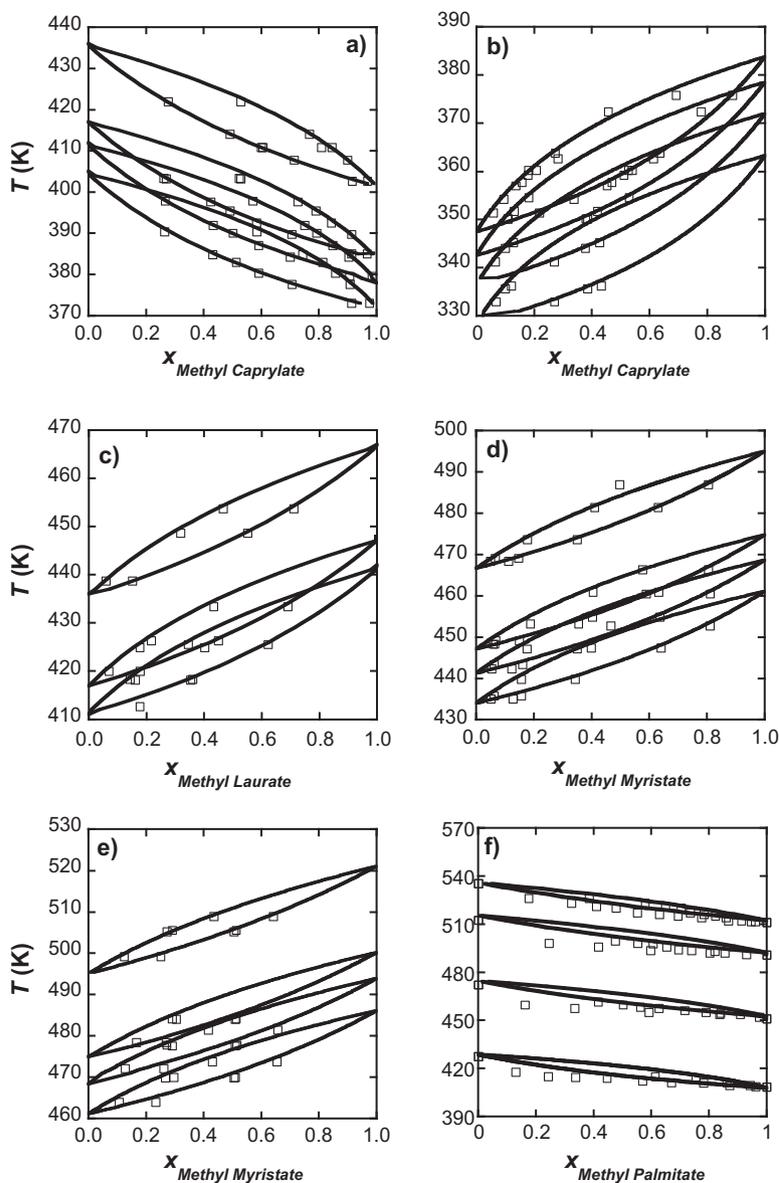


Fig. 3. Constant pressure Txy slices of the (a) methyl caprylate + methyl caprylate phase diagram at 0.0133 MPa, 0.0066 MPa, 0.0053 MPa, and 0.0039 MPa (from top to bottom), (b) methyl caprylate + methyl caproate phase diagram at 0.0066 MPa, 0.0053 MPa, 0.0039 MPa, and 0.0027 MPa (from top to bottom), (c) methyl laurate + methyl caprylate phase diagram at 0.0133 MPa, 0.0066 MPa, and 0.0053 MPa (from top to bottom), (d) methyl myristate + methyl laurate phase diagram at 0.0133 MPa, 0.0066 MPa, 0.0053 MPa, and 0.0039 MPa (from top to bottom), (e) methyl myristate + methyl palmitate phase diagram at 0.0133 MPa, 0.0066 MPa, 0.0053 MPa, and 0.0039 MPa (from top to bottom), (f) methyl palmitate + methyl stearate phase diagram at 0.010 MPa, 0.001 MPa, 0.005 MPa, and 0.0001 MPa (from top to bottom) The solid lines correspond to the theoretical predictions and the symbols represent the experimental data [43,44].

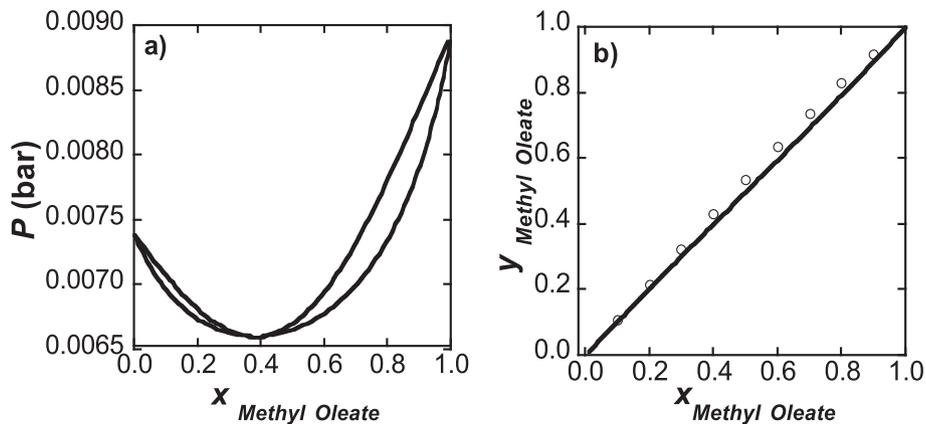


Fig. 4. Pxy (a) and xy (b) diagram for the methyl oleate + methyl stearate binary mixture at 473.15 K. The solid lines represent the theoretical predictions and the symbols represent the experimental [45] data.

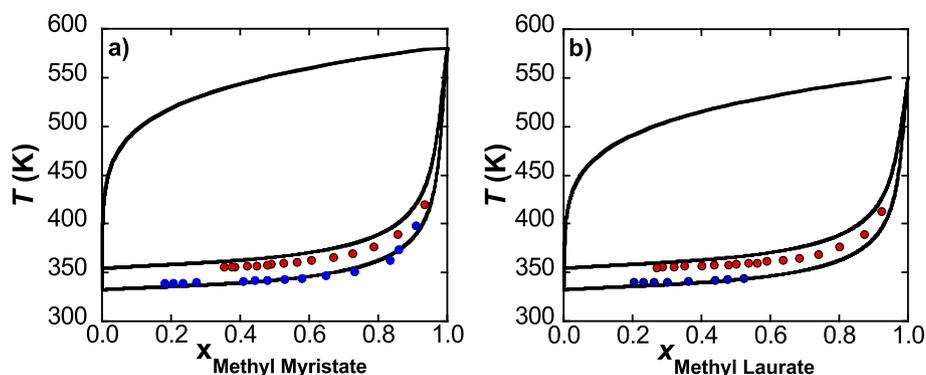


Fig. 5. VLE at atmospheric pressure for the a.) methanol + methyl myristate and ethanol + methyl myristate and b.) methanol + methyl laurate and ethanol + methyl laurate binary mixtures. The solid lines represent predictions from the GC-SAFT-VR equation and the symbols the experimental data [3].

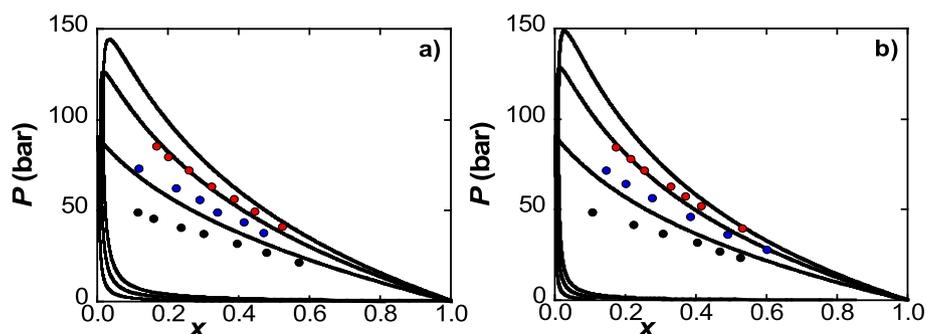


Fig. 6. VLE of a.) methanol + methyl laurate at 493 K, 523 K, 543 K (bottom to top) and b.) methanol + methyl myristate at 493 K, 523 K, 543 K (bottom to top). The solid lines represent predictions from the GC-SAFT-VR equation and the symbols the experimental data [3].

laurate + methanol and ethanol and for methyl myristate + methanol and ethanol in Fig. 5b. As can be seen from the figure, good agreement with the experimental data is found in all cases, without fitting to the experimental mixture data. As previously discussed, in the work of Oliveira et al., adjustable cross interaction parameters fitted to experimental data for the ester + alcohol mixtures studied were required to obtain good agreement with the experimental data, thus limiting the predictability of the approach. In our work, no cross interactions fitted to ester + alcohol binary mixtures are needed, thus the theory is fully predictive.

Next we consider high pressure VLE data for binary mixtures of methanol with methyl laurate and methyl myristate at 493 K, 523 K, and 543 K [3,50]. As can be seen from Fig. 6 (a) and 6 (b), good agreement with experimental data [3] is obtained, although deviations due to the over-prediction of the vapor pressure of pure methanol and ethanol fluids are observed. We note, however, that these results are pure predictions; while Oliveira et al. [3] observed smaller deviations from the experimental data fitted cross interaction parameters were used that were pressure dependent.

Finally, results are presented using the GC-SAFT-VR approach to predict the phase behavior of FAME + CO₂ mixtures. FAME + CO₂ mixtures display large deviations from ideal behavior due to electron donor–acceptor complexes formed between CO₂ and the carbonyl group being more energetically favorable when compared to the CO₂–CO₂ interactions and the carbonyl–carbonyl interactions established between the ester molecules [51]. Due to the non-ideal nature of the FAME + CO₂ mixtures, Lorentz Berthelot combining rules (shown in Fig. 7 for the methyl palmitate + CO₂ at 343.15 K) fail to accurately predict the phase behavior of the system. However, if the cross interaction between CO₂ and the CH₂ group

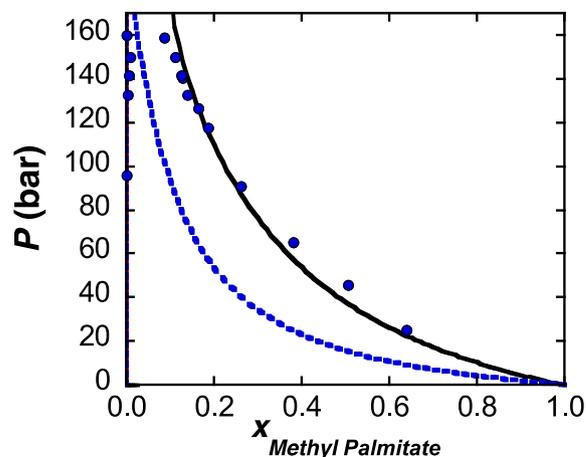


Fig. 7. Constant temperature P_{xy} slice at 343.15 K of the methyl palmitate + CO₂ binary mixture. The solid lines represent predictions from the GC-SAFT-VR equation with a fitted cross interaction between the CO₂ molecule and the CH₂ group, while the dotted lines are predictions using Lorentz Berthelot combining rules, and the symbols experimental data [53].

determined in previous work [40], by fitting to the phase behavior of CO₂ + alkane mixtures is used, excellent agreement is obtained. Using this approach, in Fig. 8 the phase behavior of the binary mixtures of methyl myristate, methyl oleate, methyl stearate, and methyl palmitate with CO₂ are predicted over a range of temperatures and good agreement with the experimental data points obtained; however, we observe an over prediction in the critical region which is typical of all equations of state that are analytical in

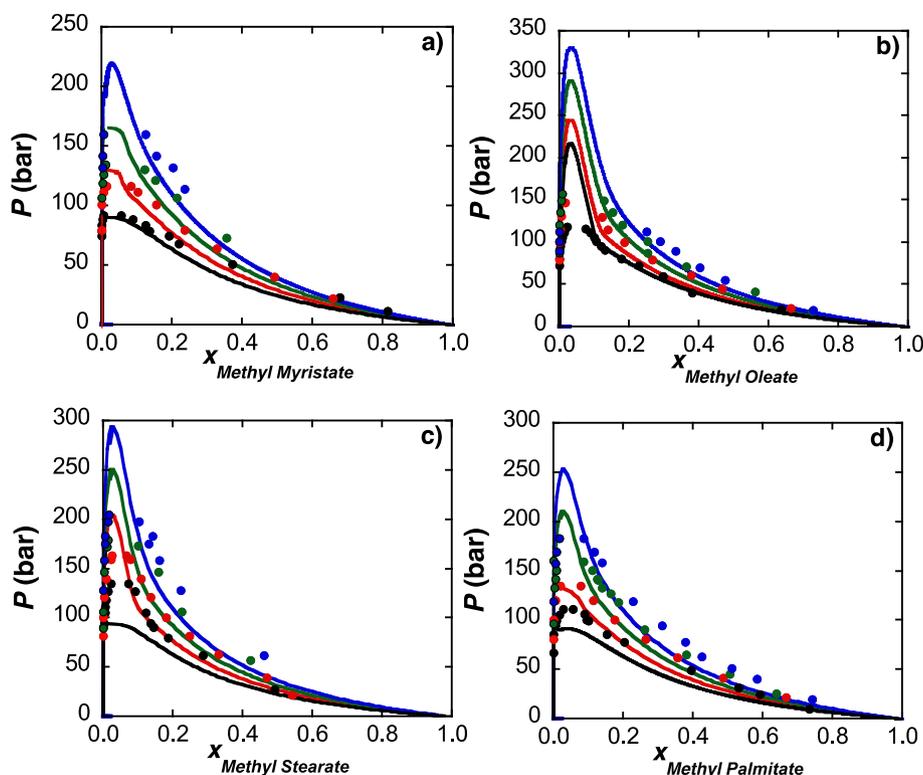


Fig. 8. Constant temperature Pxy slices of the (a) methyl myristate, (b) methyl oleate, (c) methyl stearate, and (d) methyl palmitate + CO_2 phase diagrams at 313.15 K, 323.15 K, 333.15 K, 343.15 K (bottom to top). The solid lines represent the predictions from the GC-SAFT-VR equation and the symbols the experimental data [53].

the free energy [52]. We note that in order to obtain a similar level of agreement in the work of Lovell et al. [20], two fitted binary interaction parameters were introduced, with the dispersive energy parameters adjusted for each mixture studied.

4. Conclusions

In this work, the GC-SAFT-VR approach has been used to predict the phase behavior of fatty acid methyl ester (FAME) molecules and their binary mixtures. The parameters for the groups that comprise the FAME molecules were determined in previous work and used in a transferable fashion to describe the FAME molecules of interest. The phase behavior of binary mixtures of FAME molecules with alcohols, CO_2 and other FAME molecules were then predicted without fitting any cross interactions to experimental data for the binary mixtures being studied. Accordingly, we can conclude that the GC-SAFT-VR approach can be used successfully in a predictive fashion to describe the phase behavior of FAME pure fluids and mixtures without reliance on experimental data. The theory has also been used to predict the global phase behavior for binary mixtures of FAME molecules in the classification scheme of Scott and van Konynenburg.

Acknowledgments

The authors gratefully acknowledge financial support from the National Science Foundation under Grant CBET-1067642 and the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Geoscience Research Program, through Grant No. ERKCC72 of Oak Ridge National Laboratory, which is managed for DOE by UT Battelle, LLC under Contract No. DE-AC05-00OR22725. JH also acknowledges support from the U.S. Department of Education for a Graduate Assistance in Areas of National Need (GAANN) Fellowship

under grant number P200A090323.

Appendix

The agreement between the experimental and GC-SAFT-VR predictions was quantified by calculating the percentage of absolute average deviation of the vapor pressure (%AADP) and saturated liquid density (%AAD ρ_{liq}) for the predicted phase equilibrium. The results are provided in Table A1 in the Appendix.

$$AAD P(\%) = \frac{1}{N_{pt}} \sum_{i=1}^{N_{pt}} \left| \frac{p_i^{theo} - p_i^{exp}}{p_i^{exp}} \right| \times 100\% \quad (\text{A.1})$$

$$AAD \rho_{liq}(\%) = \frac{1}{N_{pt}} \sum_{i=1}^{N_{pt}} \left| \frac{\rho_i^{theo} - \rho_i^{exp}}{\rho_i^{exp}} \right| \times 100\% \quad (\text{A.2})$$

Table A.1

Absolute deviations in vapor pressure and saturated liquid density for FAME chemical family.

Molecule	Formula	% AADP	% AADL
Methyl Caproate	$\text{C}_7\text{H}_{14}\text{O}_2$	1.70	1.69
Methyl Caprylate	$\text{C}_9\text{H}_{18}\text{O}_2$	1.32	1.23
Methyl Caprate	$\text{C}_{11}\text{H}_{22}\text{O}_2$	4.22	0.33
Methyl Laurate	$\text{C}_{13}\text{H}_{26}\text{O}_2$	4.36	0.34
Methyl Myristate	$\text{C}_{15}\text{H}_{30}\text{O}_2$	3.32	0.26
Methyl Palmitate	$\text{C}_{17}\text{H}_{34}\text{O}_2$	10.94	3.46
Methyl Oleate	$\text{C}_{19}\text{H}_{36}\text{O}_2$	8.33	8.52
Methyl Stearate	$\text{C}_{19}\text{H}_{38}\text{O}_2$	8.82	1.96
Average		5.37	2.22

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