

Vapor pressure and normal boiling point predictions for pure methyl esters and biodiesel fuels

W. Yuan*, A.C. Hansen, Q. Zhang

*Department of Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign,
360 AESB 1304 W. Pennsylvania Avenue, Urbana, IL 61801, USA*

Received 17 February 2004; received in revised form 14 September 2004; accepted 10 January 2005
Available online 19 January 2005

Abstract

Temperature dependent vapor pressures of the methyl esters of fourteen fatty acids that are commonly present in biodiesel fuels were predicted by the Antoine equation and a group contribution method. The predicted boiling points of these esters up to a pressure of 100 mmHg were within $\pm 1.0\%$ of reported data for these two methods. Normal boiling points were determined from both the predicted vapor pressure and a correlation equation and the prediction errors were less than 5 K comparing to available published data. The vapor pressure and normal boiling points of 19 real-world biodiesel fuels were predicted and compared with reported data where available. The prediction errors of normal boiling points were less than 1.0%, and the predicted vapor pressures were also observed to closely match the reported data among the methyl esters of soybean oil, rapeseed oil and tallow. The predicted results showed that, except for coconut and butterfat, most of the methyl esters of the vegetable oils and animal fats had a normal boiling point in the range of 620–630 K. A sensitivity analysis indicated that the variation of fatty acid composition and the uncertainty of the normal boiling point of C18:2 were the main factors that affected the predicted normal boiling points of the biodiesel fuels.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Biodiesel; Methyl ester; Normal boiling point; Vapor pressure

1. Introduction

Animal fat or vegetable oil ester biodiesel fuels have been shown to be a very promising alternative to crude-oil derived diesel fuels because they are renewable, they reduce particulate matter emissions and the net production of CO₂ from combustion sources, and they relieve US dependence on foreign crude oil. Because of these advantages, biodiesel has gained considerable attention and support in the past few years, as demonstrated by its commercial availability in many parts of the US and the provision of state tax incentives to encourage its use. The provision of standards and quality control in the manufacture and distribution of biodiesel is necessary to insure that the quality and properties of this fuel are reliable and consistent when

supplied to users. Boiling point, T_b , is a key fuel property for biodiesel as is the case for quality control in petroleum based diesel fuel industry.

Besides its importance for quality control, boiling point, especially at atmospheric pressure, called normal boiling point T_{nb} , is also the basis for the prediction of the critical properties, and temperature-dependent properties such as vapor pressure, density, latent heat of vaporization, viscosity, and surface tension of biodiesel. These properties are required for biodiesel combustion modeling [1], but the wide range of temperature required for these properties makes it difficult to experimentally measure them. Therefore, the accurate boiling points of the pure fatty acid esters and their biodiesel mixtures will be useful for predicting fuel properties and consequently will be important for combustion modeling.

Several equations were reviewed by Reid et al. [2] to estimate or correlate the temperature dependent vapor pressure of pure liquids, of which the following three

* Corresponding author. Tel.: +1 217 333 8595; fax: +1 217 244 0323.
E-mail address: w yuan@uiuc.edu (W. Yuan).

equations are widely used in the oil industry:

$$\log P_v = A - \frac{B}{T} \quad (1)$$

$$\ln(P_{vr}) = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{T_r} \quad (2)$$

$$\log(P_v) = A - \frac{B}{T + C} \quad (3)$$

Eqs. (1–3) are called the Clapeyron equation, Wagner equation, and Antoine equation respectively, where P_v denotes the vapor pressure (Pa) at temperature T (K), P_{vr} and T_r represent reduced vapor pressure and reduced temperature respectively, and $\tau = 1 - T_r$. The other unknown parameters are correlation constants. Because of its simplicity and the accuracy, the Antoine equation has been more widely used than the other two equations in the oil industry. However, the application of the Antoine equation on fatty acid esters has been limited.

Although the normal boiling points of some fatty acid esters have been published [3–8], those of real world biodiesel fuels are scarce. Goodrum [9] measured the normal boiling points of some biodiesel fuels using the Thermo Gravimetric Analysis (TGA) method. However, considering that there are dozens of biodiesel source materials, and each type of material may have thousands of combinations of compositions, it is impractical to experimentally measure the normal boiling point for each combination. Moreover, the expensive high-quality equipment and the decomposition of some compounds at high temperature are some obstacles to these measurements. Therefore, the importance of this work is that if it is possible to predict the vapor pressure and normal boiling point of any given biodiesel fuel based on its fatty acid composition, there may be less need for expensive measurement of the properties of the ester mixtures, which will be valuable for biodiesel fuel quality control and meet the requirements of combustion modeling.

The objectives of this study were (1) to predict the normal boiling points of fourteen fatty acid methyl esters (FAMES) that are commonly present in biodiesel fuels, and (2) to predict the normal boiling point of nineteen real world biodiesel fuels. This was accomplished by (3) predicting the temperature dependent vapor pressure of pure fatty acid methyl esters and their biodiesel fuel mixtures.

2. Method

The Antoine equation, Eq. (3), was used to predict the vapor pressure of saturated FAMES from C8 to C18 with the aid of published vapor pressure data as detailed in Section 2.1. The normal boiling points of these esters were also

determined from the predicted vapor pressure. In Section 2.2, the vapor pressure of the methyl esters of unsaturated C18 and longer fatty acids chains were predicted using a group contribution method. The normal boiling points were calculated from the predicted vapor pressure and a correlation method in Section 2.3. The temperature dependent vapor pressures and normal boiling points of the biodiesel mixtures of FAMES were calculated by the method presented in Section 2.4.

2.1. Vapor pressure of saturated C8–C18 methyl esters

The Antoine equation was employed to fit vapor pressure with temperature based on the experimental data reported by Scott et al. [10] and Rose and Supina [11] using the Method of Least Squares (MLS). When implementing the MLS, three points that yielded the least squares were first found from the data set, and the initial values of the adjustable parameters A, B, and C were calculated based on these three points. Then A, B, and C were varied from -1.0 to 1.0 , -100.0 to 100.0 and -10.0 to 10.0 , respectively, relative to the initial values using computational steps of 0.01, 1.0, 0.1, respectively. These variance ranges and computational steps were determined from computational results.

It must be noted that when applying the Antoine equation to extrapolate the vapor pressure, at least three data points that are in the 1–200 kPa range must be available. The more data points that can be used, the more accurate the extrapolation will be. Therefore, the data reported by Scott et al. [10] and Rose and Supina [11] were combined for C8:0–C18:0 fatty acid methyl esters. The pressure range covers 27 Pa up to 20 kPa for most of these esters. Methyl stearate only had data available up to 4.8 kPa, but was still sufficient for applying the Antoine equation. Once the vapor pressure was predicted, the normal boiling points were determined by finding the temperature where the vapor pressure equaled 1 atm.

2.2. Vapor pressure of unsaturated C18–C24 methyl esters

For unsaturated fatty acid methyl esters, such as methyl oleate (C18:1), methyl linoleate (C18:2) and methyl linolenate (C18:3), the data from Scott et al. [10] were available only from 13 to 600 Pa, which was too narrow a range for the Antoine equation. Very limited vapor pressure data were available for methyl esters of fatty acids with more than 18 carbons. Therefore, in order to apply the Antoine equation to these FAMES, additional vapor pressure data points are required. A group contribution method reported by Ceriani and Meirelles [12] was applied to predict the vapor pressure of these methyl esters from 100 to 210 °C, which was the applicable temperature range for this method. The method relies on the following

Table 1
Published normal boiling points for common pure methyl esters

Compositions	T_{nb} (K) and reference
C8:0	466 [3], 466 [4], 466 [5]
C10:0	497 [3], 496 [4], 497 [5], 497 [6]
C12:0	535 [3], 535 [4], 535 [7],
C14:0	568 [3], 569 [8],
C16:0	611 [3]
C18:0	625 [3]
C18:1	622 [3]
C18:2	639 [3]
C18:3	No published data available
C20–C24	No published data available

equations:

$$\ln P_{i,vp} = \sum_k N_k \left(A_{1k} + \frac{B_{1k}}{T^{1.5}} - C_{1k} \ln T - D_{1k} T \right) + \left[M_i \sum_k N_k \left(A_{2k} + \frac{B_{2k}}{T^{1.5}} - C_{2k} \ln T - D_{2k} T \right) \right] + Q \quad (4)$$

$$Q = \xi_1 q + \xi_2 \quad (5)$$

$$q = \alpha + \frac{\beta}{T^{1.5}} - \gamma \ln T - \delta T \quad (6)$$

$$\xi_1 = f_0 + N_c f_1 \quad (7)$$

$$\xi_2 = s_0 + N_{cs} s_1 \quad (8)$$

where N_k is the number of groups k in the molecule; M_i the component molecular weight; N_c the number of carbons;

N_{cs} the number of carbons from the alcohol; k represents the groups of component i ; $P_{i,vp}$ and T vapor pressure (Pa) and temperature (K), respectively; The other unknown parameters are constants given by Ceriani and Meirelles [12].

The Ceriani and Meirelles method was applicable to all the FAMEs from C8 to C24 in biodiesel fuels. The predicted vapor pressures of ME of saturated C8–C18 were compared to reported data to justify the accuracy of this method. The predicted vapor pressures of unsaturated C18 and longer chains were employed to compute Antoine equation constants. Normal boiling points that are predicted in the next section were used to constrain the vapor pressure-temperature curve.

2.3. Normal boiling points of pure FAMEs

Normal boiling points can be used to justify the vapor pressure predicted from Antoine equation, or to constrain the vapor pressure-temperature curve when experimental data are insufficient. The normal boiling points of some of the pure methyl esters commonly present in biodiesel fuels were reported by some researchers [3–8] as listed in Table 1. Most of the reported data focused on short chain saturated FAMEs (C8–C14), while the data for C16 and C18 are either limited or are not available, especially for the methyl esters of fatty acids with 20 carbon atoms or more.

An analysis of the T_{nb} of aliphatic hydrocarbons in the petroleum based diesel industry showed that the normal boiling points of unbranched alkanes were logarithmically correlated to the carbon number as shown in Fig. 1. Considering the similarity of the structure between the hydrogen-carbon chain of fatty acid methyl esters and the unbranched alkanes, it is feasible to evaluate and correlate the limited data of fatty acid methyl esters based on the trends from unbranched alkanes. This concept of relating

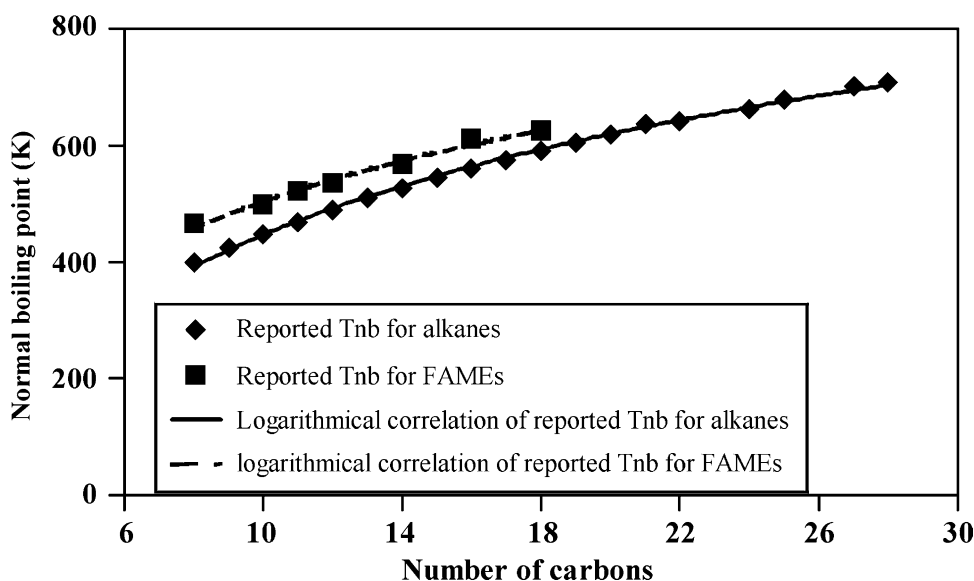


Fig. 1. Correlation of T_{nb} with carbon number for alkanes and FAMEs.

esters of saturated fatty acids to normal paraffins was first applied by Rose and Supina [11]. Fig. 1 shows the T_{nb} reported by Owczarek and Blazej [13] for unbranched alkanes to which the logarithmic correlation of T_{nb} with carbon number has been fitted. The R^2 of the correlation is almost 1.0. The normal boiling points of pure FAMES were also logarithmically correlated to the carbon number in fatty acids based on the data from Graboski and McCormick [3]. The R^2 of the logarithmic correlation is 0.986 for FAMES from C8 to C18.

The correlation equation,

$$T_{nb} = 206.9 \ln(\text{CN}) + 27.0 \quad (9)$$

where CN is the number of carbons in the FAMES was applied to correlate the T_{nb} of the pure fully-saturated FAMES with carbon number from 8 up to 24. In the absence of published data, this equation is able to provide a prediction of the normal boiling point of pure FAMES that are commonly present in biodiesel fuels.

For the unsaturated FAMES, Graboski and McCormick [3] reported that the T_{nb} of methyl oleate (C18:1) was 349 °C, which is 3 °C lower than methyl stearate. This was in agreement with the relationship of the normal boiling points for alkanes and alkenes, in which the T_{nb} of alkenes were usually slightly lower than those for alkanes with the same carbon number [13]. Therefore, this 3 °C difference between fully saturated and one-double bond FAMES was applied to C20/C20:1, C22/C22:1 in addition to C18/C18:1. The T_{nb} for FAMES or alkenes with more than one double bond appear to be absent from the literature. Therefore, the reported value of

639.2 K was accepted for C18:2 [3], and was assigned to C18:3 based on the conclusion from Graboski and McCormick [3] that the normal boiling points were nearly independent of the degree of unsaturation of the fatty acid.

2.4. The vapor pressure and normal boiling point of mixtures of FAMES

The biodiesel mixtures of FAMES can be regarded as near-ideal solutions [4,14]. Therefore, once the vapor pressure of each individual FAME was known, the total vapor pressure of the mixtures could be calculated from Raoult's law by the following equation:

$$P_{\text{vmix}} = \sum_i P_{vi} x_i \quad (10)$$

where P_{vi} and P_{vmix} are the vapor pressures of the i th pure FAME and the mixture respectively, and x_i is the molar fraction of that composition.

The normal boiling point of the mixture of FAMES was determined from the mixture vapor pressure by finding the temperature where the mixture vapor pressure equaled 1 atm. All the calculations above were processed in a computer program developed for this study.

3. Results and discussion

Using the equations presented above, the T_{nb} and P_v of the pure FAMES that were commonly present in biodiesel

Table 2
Reported and predicted boiling points of selected FAMES at various pressures

Esters		Pressure, kPa (mmHg)									
		0.27(2)	0.53 (4)	0.8(6)	1.07(8)	1.33(10)	2.67(20)	5.33(40)	8.0(60)	10.67(80)	13.33(100)
		Temperature (K)									
C8:0	Reported ^a	324.7	335.7	342.1	347.0	351.0	364.1	378.4	387.3	392.3	398.8
	Predicted ^b	321.3	332.5	339.5	344.8	348.9	362.8	378.1	387.9	395.2	401.1
	Predicted ^c	322.4	333.7	340.7	345.9	350.0	363.7	378.7	388.2	395.4	401.2
C10:0	Reported ^a	351.9	364.0	371.3	376.5	381.2	395.5	411.0	420.4	428.0	433.8
	Predicted ^b	350.3	362.5	370.0	375.7	380.2	395.0	411.2	421.4	429.0	435.2
	Predicted ^c	351.4	363.1	370.4	375.8	380.1	394.5	410.5	420.7	428.5	434.8
C12:0	Reported ^a	376.0	389.2	397.6	403.6	408.2	424.2	441.0	452.0	459.6	465.2
	Predicted ^b	376.7	389.2	397.1	403.0	407.7	423.2	440.5	451.4	459.6	466.2
	Predicted ^c	377.0	389.2	396.9	402.6	407.2	422.6	439.7	450.9	459.4	466.3
C14:0	Reported ^a	400.3	414.5	423.5	429.8	435.0	451.8	470.0	481.4	***	***
	Predicted ^b	400.3	413.6	421.9	428.1	433.0	449.4	467.5	478.9	487.5	494.4
	Predicted ^c	400.3	413.3	421.5	427.6	432.5	448.9	467.6	479.8	***	***
C16:0	Reported ^a	421.7	436.4	445.8	452.4	458.0	475.4	***	***	***	***
	Predicted ^b	423.1	436.8	445.4	451.8	456.9	473.9	492.6	504.4	513.3	520.4
	Predicted ^c	422.2	436.0	444.7	451.3	456.5	474.3	***	***	***	***
C18:0	Reported ^a	442.6	457.8	466.8	472.0	479.8	***	***	***	***	***
	Predicted ^b	444.2	458.3	467.2	473.8	479.1	496.8	516.2	528.6	537.9	545.4
	Predicted ^c	443.2	457.9	467.2	474.2	479.9	***	***	***	***	***

***Indicates no data reported or predicted due to the limitation of the method.

^a Reported by Bonhorst et al. [15].

^b Predicted from Antoine equation. The Antoine equation constants are given in Table 3.

^c Predicted by Ceriani and Meirelles method.

Table 3
 T_{nb} and Antoine equation constants of pure FAMES

	T_{nb}^a	T_{nb}^b	T_{nb}^c	T_{nb}^d	A	B	C
C8:0	466.2	457.9	466.2	***	9.4660	1765.00	−70.61
C10:0	497.2	504.0	501.6	496.2	10.0582	2261.99	−53.91
C12:0	535.2	541.6	539.8	536.0	9.4297	1958.77	−96.99
C14:0	568.2	573.4	570.5	569.7	9.6258	2194.36	−95.50
C16:0	611.2	601.0	599.4	598.8	9.5714	2229.94	−111.01
C18:0	625.2	625.3	628.9	624.6	9.3746	2174.39	−131.23
C18:1	622.2	622.2	***	622.2	9.9155	2583.52	−96.15
C18:2	639.2	639.2	***	639.2	8.2175	1450.62	−188.03
C18:3	***	639.2	***	639.2	8.1397	1387.93	−196.16
C20:0	***	647.0	***	647.6	10.3112	2987.15	−84.56
C20:1	***	644.0	***	644.6	10.3525	3009.62	−81.66
C22:0	***	666.7	***	668.4	10.6867	3380.86	−73.20
C22:1	***	663.7	***	665.4	10.7518	3423.99	−69.43
C24:0	***	684.6	***	687.4	11.0539	3776.89	−62.90

***Indicates no data reported or predicted due to the limitation of the method.

^a From Ref. [3].

^b Predicted by Eq. (9).

^c Predicted by Eq. (3) using the constants listed in this table.

^d Predicted by Eq. (11).

fuels were computed. Prediction of T_{nb} and P_v for nineteen real-world biodiesel fuels were also carried out. In addition, the effect of the variance of fatty acid composition and uncertainty of T_{nb} for C18:2 and C18:3 on the T_{nb} of biodiesel was also investigated.

3.1. The normal boiling point and vapor pressure of pure FAMES

The vapor pressure of all the FAMES that are commonly present in biodiesel fuels were calculated by both the Antoine equation and the Ceriani and Meirelles method. The boiling points of the methyl esters of C8–C18 at various pressures were predicted from both the Antoine equation and Ceriani Method and were compared to a set of data reported by Bonhorst et al. [15] and are presented in Table 2. The Antoine equation constants are given in Table 3.

From Table 2, it can be found that the maximum prediction error of the boiling points at various pressures from Antoine equation is 3.3 K, and that from Ceriani and Meirelles method is about 3.1 K. Both of these methods achieved relative errors below 1%. This proves that both the Antoine equation and the Ceriani method give accurate estimations of vapor pressure for the methyl esters of C8–C18 up to 13.3 kPa (100 mmHg). For higher pressures up to 100 kPa (760 mmHg), the normal boiling point can be used to justify the accuracy of the estimation. The reported normal boiling point, T_{nb}^1 , correlated normal boiling point from Eq. (9), T_{nb}^2 and predicted normal boiling point from Antoine equation, T_{nb}^3 of the FAMES are listed in Table 3.

As can be seen from Table 3, the predicted normal boiling points from the Antoine equation are in close agreement with the reported data except for C16:0. The prediction error for C16:0 is 11.8 K, otherwise

the maximum error is 4.6 K. The same result occurred with the correlation method. C16:0 yielded the maximum prediction error of 10.2 K, but the results from the correlation method and Antoine equation are very close. Therefore, the reported normal boiling point of the ME of C16:0 was replaced for correlation purposes by the predicted result from Antoine equation. Further investigation of the correlations showed that C8:0 gave a relatively high prediction error. This suggested that the FAME with short carbon-hydrogen chains should be excluded from the correlation. The new correlation equation was then formulated as the following:

$$T_{nb} = 218.49 \ln(CN) - 6.933 \quad (11)$$

where CN is the number of carbons in the fatty acids. The new correlation equation was obtained from the data of C10–C18 and was applied up to C24. The new correlation had a R^2 of 0.9996, and the maximum prediction error was less than 1.5 K. The predicted normal boiling points are shown as T_{nb}^4 in Table 3.

The Antoine equation was not used to predict the normal boiling point for MEs of unsaturated C18 and longer fatty acids since there were insufficient data. Normal boiling points predicted from the correlation equation were used to constrain the vapor pressure-temperature curve. Some published boiling points for these FAMES are listed in

Table 4
 Reported and predicted boiling points of selected FAMES

	Pressure (Pa)	Predicted T_b (K)	Reported T_b (K)	Ref.
C18:1	2000	486.7	487	[5]
C18:3	400	446.8	455	[5]
C20:0	300	465.9	461	[5]
C24:0	500	514.9	505	[16]

Table 5
Fatty acid compositions of nineteen fats and oils provided by Allen et al. [17] and Goering et al. [18]

Oil or fat type	C8:0	C10:0	C12:0	C14:0	C16:0	C18:0	C20:0	C22:0	C24:0	C18:1	C22:1	C18:2	C18:3
Soybean	0	0	0	0.1	10.3	4.7	0	0	0	22.5	0	54.1	8.3
Rapeseed	0	0	0	0	2.7	2.8	0	0	0	21.9	50.9	13.1	8.6
Beef tallow	0	0.1	0.1	3.3	25.2	19.2	0	0	0	48.9	0	2.7	0.5
Peanut	0	0	0	0	10.4	8.9	0	0	0	47.1	0.2	32.9	0.5
Canola	0	0	0	0.1	3.9	3.1	0	0	0	60.2	0.5	21.1	11.1
Olive	0	0	0	0	11	3.6	0	0	0	75.3	0	9.5	0.6
Coconut	8.3	6	46.7	18.3	9.2	2.9	0	0	0	6.9	0	1.7	0
Corn	0	0	0	0	9.9	3.1	0	0	0	29.1	0	56.8	1.1
Palm	0.1	0.1	0.9	1.3	43.9	4.9	0	0	0	39	0	9.5	0.3
Safflower	0	0	0	0.1	6.6	3.3	0	0	0	14.4	0	75.5	0.1
Sunflower	0	0	0	0.1	6	5.9	0	0	0	16	0	71.4	0.6
Sunola	0	0	0	0	3	4.4	0	0	0	88.2	0	4.3	0.1
Butterfat	5.5	3	3.6	11.6	33.4	11.4	0	0	0	27.8	0	3.1	0.6
Lard	0	0.1	0.1	1.4	25.5	15.8	0	0	0	47.1	0	8.9	1.1
Cottonseed	0	0	0	0.8	22.9	3.1	0	0	0	18.5	0	54.2	0.5
Crambe	0	0	0	0	2.07	0.7	2.09	0.8	1.12	18.86	58.51	9	6.85
Linseed	0	0	0	0	4.92	2.41	0	0	0	19.7	0	18.03	54.94
H.O. safflower	0	0	0	0.34	5.46	1.75	0.23	0	0	79.36	0	12.86	0
Sesame	0	0	0	0	13.1	3.92	0	0	0	52.84	0	30.14	0

Table 4. It can be seen that the prediction errors are about 1.9% for C18:3 and C24:0. For C18:1 and C20:0, the errors are less than 5 K (1%). These errors are higher than those for C8–C18 due to the lack of data points, but are still acceptable.

3.2. Properties of real world biodiesel fuels

The normal boiling points of nineteen real world biodiesel fuels were predicted. The fatty acid compositions of these fuels are listed in Table 5. The fatty acid compositions of the first fifteen fuels were from Allen et al. [17] and others were from Goering et al. [18].

The predicted normal boiling point and vapor pressure of the methyl ester of soybean oil (SME), rapeseed oil (RME) and tallow (TME) were compared to the data reported by Goodrum [9]. Table 6 gives the comparison of boiling points and Fig. 2 shows the vapor pressure.

It can be seen from Table 6 that the predicted normal boiling points of the three biodiesel fuels are in good agreement with the reported data. The highest error of 1.0% occurred with SME, while the other two biodiesel fuels had errors less than 0.2%. The prediction error for SME could have contributed to the uncertainty of the normal boiling points of highly unsaturated pure methyl esters (C18:2 and C18:3) as described in Section 2.1 since SME has a high percentage of C18:2 and C18:3 (62.4% in total mass) as

Table 6
Comparison of predicted and measured normal boiling point [9] of RME, SME and TME

	Predicted T_{nb} (K)	Measured T_{nb} (K)	Absolute error (K)	Relative error (%)
RME	642.5	642.1	0.4	0.06
SME	627.0	620.8	6.2	1.0
TME	612.4	611.3	1.1	0.18

seen from Table 5. Another possible reason is the variance of fatty acid composition among the same types of fuels but from different sources. The fatty acid composition of the SME used by Goodrum [9] could be different than that listed

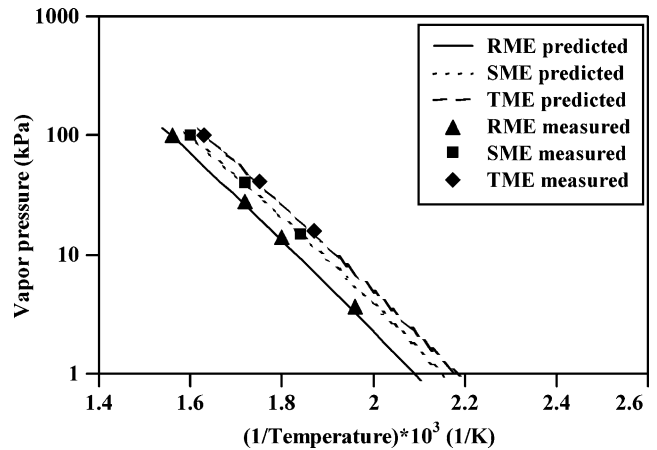


Fig. 2. Predicted and measured vapor pressure of RME, SME and TME.

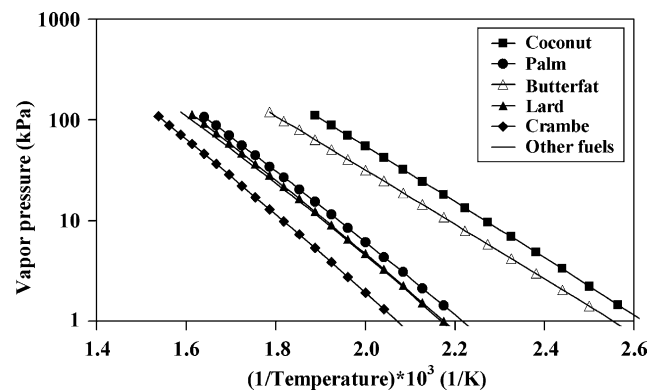


Fig. 3. Predicted vapor pressure of biodiesel fuels.

Table 7

The range of the weight percent of fatty acid compositions for soybean, rapeseed, and beef tallow methyl esters reported by Graboski and McCormick [3]

Fuel	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C22:1
Soybean	0.1	7–11	3–6	22–34	50–60	2–10	0
Rapeseed	0	2–5	1–3 (2)	10–22.5 (15)	10–20	5–10	50–60
Beef tallow ^a	3.3	25–30	19.2 (21)–26	39–48.9 (42)	2.7	0.5	0

^a C10:0 (0.1), C12:0 (0.1).

in Table 3 since the range of the fatty acid composition is quite wide [3]. The error analysis was discussed in detail in Section 3.3.

Fig. 2 presents the plot of $\log P$ vs. $1/T$. It can be seen that predicted results are in close agreement with the data reported by Goodrum [9]. Also, the predicted vapor pressure of the biodiesel fuels followed the Clausius–Clapeyron regression but was slightly curved, which means that the simple Clausius–Clapeyron relation, $\log P = A - B/T$ does not adequately describe the vapor pressure-temperature characteristic. These results support the result from Goodrum et al. [14] that the vapor pressure of these ester mixtures might be an average value influenced by all of the component esters.

The $\log P$ vs. $1/T$ of the other sixteen fuels are shown in Fig. 3. Crambe has the highest normal boiling point of 646.5 K because it has the most C22:1 and C24:0 in its composition. On the other hand, coconut has the lowest predicted normal boiling point of 525.8 K since it has the most short-chain fatty acids in its composition. Except for butterfat, palm and lard biodiesel who has a normal boiling point of 551.6, 606.7, and 614.4 K, respectively, other oils have a normal boiling point in or around the range of 620–630 K, such as 620.4 K of olive, 621 K of cottonseed, 621.9 K of H.O. safflower, 622 K of sesame, 622.1 K of sunola, 623.6 K of peanut, 625.2 K of canola, 626.9 K of corn, 631 K of sunflower, and 631.2 K of safflower and linseed.

3.3. Sensitivity analysis

The prediction of the boiling point and vapor pressure of biodiesel fuels is sensitive to two main factors. One is the composition of the FAMES in the fuel, and the other is the boiling point of the pure FAMES. This section focuses mainly on how the uncertainties of these two factors affect the predicted normal boiling point of RME, SME and TME since the experimental data of these fuels are available.

3.3.1. Variation in biodiesel fatty acid composition

The fatty acid composition of biodiesel fuel derived from the same type of material may also vary as shown in Table 7 for soybean, rapeseed and tallow. All the values except those followed by a parenthesis were reported by Graboski and McCormick [3]. The limits in the parentheses were replaced by new values to expand the ranges to

include the compositions listed in Table 5. A computational step of 0.5% of weight percent for each fatty acid was applied.

The computed maximum and minimum normal boiling points of SME, RME and TME due to variations in composition are shown in Table 8. The difference between minimum and maximum values is the expected variance of normal boiling point due to changes in composition. Considering that the reported T_{nb} could fall into the lower or upper end of the T_{nb} range, the expected range of the T_{nb} was calculated from the reported value \pm (Max–Min), which represents the full range of possible predicted normal boiling points for the variations of compositions in Table 7. The predicted value of SME (627.0 K) is a little beyond its expected range. This suggested that there could be other factors, besides the variance of fatty acid compositions in the source materials, that affected the predicted normal boiling point of the biodiesel fuels.

3.3.2. Normal boiling points of C18:2 and C18:3 methyl esters

As described in Section 2.2, the published data for the normal boiling point of highly-unsaturated FAMES, such as C18:2 and C18:3 are limited. For the fatty acid chains with more than one double bond, the normal boiling point depends on both the number and the position of these double bonds, similar to the unbranched alkenes. In order to study the effect of the uncertainty of the normal boiling point of C18:2 and C18:3 on the predicted normal boiling point of biodiesel fuels, combinations of normal boiling point for C18:2 and C18:3 were applied within the range of 620–650 K at a computational step of 2 K. The boiling point of other pure FAMES were fixed in accordance with the values in Table 1. The lowest and highest predicted fuel normal boiling points versus the normal boiling point of C18:2 of SME, RME and TME are shown in Fig. 4.

Table 8

Minimum and maximum limits and expected range of T_{nb} caused by composition variation in fatty acid composition

	Min (K)	Max (K)	Expected range (K)
RME	640.5	650.0	637.6–646.6
SME	625.8	630.3	616.3–625.3
TME	611.1	612.7	609.7–612.9

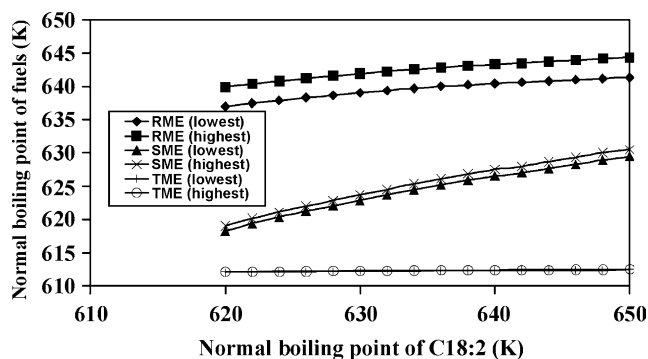


Fig. 4. The effect of T_{nb} of C18:2 and C18:3 on predicted T_{nb} of the fuels.

Given the expected range of normal boiling point in Table 7 and the curves in Fig. 4, it was observed that the normal boiling point of C18:2 should be in the range of 622–632 K, while C18:3 did not affect the result significantly due to its low weight percent. Therefore, the reported normal boiling point of 639 K for C18:2 was considered to be too high.

4. Conclusions

1. The Antoine equation and a group contribution method were used to predict the temperature dependent vapor pressures of fourteen pure fatty acid methyl esters that are commonly present in biodiesel fuels. Antoine equation constants were calculated for each of these esters. The predicted boiling points of these esters up to 100 mmHg were within $\pm 1.0\%$ of reported data for these two methods with the exception of C18:3 and C24:0 which had a prediction error of about 1.9%.
2. A correlation equation was provided to estimate the normal boiling points of fourteen pure fatty acid methyl esters within a 1.5 K prediction error. The normal boiling points were also determined by the predicted vapor pressure from the Antoine equation and the prediction errors were less than 5 K compared to published data.
3. The vapor pressures of nineteen biodiesel fuels were predicted by weighting the vapor pressure of each component in the mixture with the percent composition of each component in the ester blends. The predicted temperature dependent vapor pressures were found to closely match the reported data.
4. The normal boiling points of the nineteen biodiesel fuels were calculated from the predicted vapor pressure. The maximum prediction error was 1.0%. Except for coconut and butterfat, most of the methyl esters of the vegetable oils and animal fats had a normal boiling point in the range of 620–630 K.

5. The variance of the fatty acid composition and the uncertainty of the normal boiling point of C18:2 were the main factors that affected the predicted normal boiling points of the biodiesel fuels. The expected normal boiling point of C18:2 was within 622–632 K instead of 639 K.

Acknowledgements

This material is based upon work supported by the cooperative State Research, Education and Extension Services, US Department of Agriculture, under Project no. Hatch 10–311 AE. Financial support was also provided by the University of Illinois Campus Research Board.

References

- [1] Yuan W, Hansen AC, Zhang Q. Combustion optimization of biodiesel for diesel engines with the aid of KIVA-3 code. ASAE Paper 026082, St Joseph, Mich.: ASAE 2002.
- [2] Reid RC, Prausnitz JM, Sherwood TK. The properties of gases and liquids. 4th ed. New York: McGraw-Hill Inc.; 1987.
- [3] Graboski MS, McCormick RL. Combustion of fat and vegetable oil derived fuels in diesel engines. Prog Energy Combust Sci 1998;24(2): 125–64.
- [4] Swern D. 4th ed Bailey's industrial oil and fat products. vol. 1. New York: Wiley; 1979.
- [5] Weast RC, Grasselli JG, editors. CRC handbook of data on organic compounds. 2nd ed.. Boca Raton, FL: CRC Press, Inc.; 1989. p. 1.
- [6] Stage H. Separation of natural and synthetic fatty acid mixtures by distillation. Fette, Seifen, Anstrichm 1953;55:217–24.
- [7] Weast RC, editor. Handbook of chemistry and physics. 62nd ed. Boca Raton, FL: CRC Press, Inc.; 1981. p. C-359.
- [8] Windholtz M, Green DW, editors. Perry's chemical engineering handbook. 6th ed. New York, NY: McGraw-Hill Inc.; 1984. p. 3–58.
- [9] Goodrum JW. Volatility and boiling points of biodiesel from vegetable oils and tallow. Biomass Bioenergy 2002;22:205–11.
- [10] Scott TA, Macmillan D, Melvin EH. Vapor pressure and distillation of methyl esters of some fatty acids. Ind Eng Chem 1952;44(1):172–5.
- [11] Rose A, Supina WR. Vapor pressure and vapor-liquid equilibrium data for methyl esters of the common saturated normal fatty acids. J Chem Eng Data 1961;6(2):173–9.
- [12] Ceriani R, Meirelles AJA. Predicting vapor-liquid equilibria of fatty systems. Fluid Phase Equilib 2004;215(2):227–36.
- [13] Owczarek I, Blazej K. Recommended critical temperature. Part I. aliphatic hydrocarbons. J Phys Chem Ref. Data 2003;32(4):1435–46.
- [14] Goodrum JW, Geller DP, Lee SA. Rapid measurement of boiling points and vapor pressure of binary mixtures of short-chain triglycerides by TGA method. Thermochim Acta 1998;311:71–9.
- [15] Bonhorst CW, Althouse PM, Triebold HO. Esters of naturally occurring fatty acids. Ind Eng Chem 1948;40(12):2379–84.
- [16] Aldrich Chemical Company Inc. Catalog handbook of fine chemicals. Milwaukee, WI: Aldrich Chemical Company Inc; 1990. p. 1.
- [17] Allen CAW, Watts KC, Ackman RG, Pegg MJ. Predicting the viscosity of biodiesel fuels from their fatty acid ester composition. Fuel 1999;78:1319–26.
- [18] Goering CE, Schwab AW, Daugherty MJ, Pryde EH, Heakin AJ. Fuel properties of eleven vegetable oils. Trans ASAE 1982;25(6):1472–7 and 1483.