Estimation of Physical Properties of Vegetable Oils and Biodiesel using Group Contribution Methods

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Most fatty acids, vegetable oils and fatty esters, especially those with long carbon chains, do not have all pure component physical properties described in the literature, relevant for design and analysis of chemical processes. One way to obtain these properties is to use estimation methods such as group contribution methods which need only the structural information of the molecule. In this study, eight pure component physical properties (boiling temperature, critical temperature, critical pressure, critical volume, Gibbs energy of formation, enthalpy of formation, acentric factor and liquid heat capacity) of twenty-two fatty acids (C-4 to C-20) and their corresponding methyl and ethyl esters, and eight vegetable oils and their respective biodiesels are considered. The performances of ten different methods are compared with respect to the eight pure component physical properties. Comparison among methods is made within available experimental data, indicating more reliable methods for estimating pure component physical properties and mixtures involving chemicals found in vegetable oils and biodiesel.

1. Introduction

Biofuels have emerged as a growing source of primary energy due mainly to the increase of global demands of fuels and of environmental impact concerns. More than 95% of world production of biodiesel uses edible vegetable oils and the ones that have been widely utilized for this purpose are obtained from cotton, coconut, sunflower seed, palm, soybean, peanut, canola and corn (Gui et al., 2008). Oils and fats are formed mainly by triacylglycerols (TAG), diacylglycerols (DAG), monoacylglycerols (MAG) and free fatty acids (FFA). In addition to these molecules, vegetable oils have around 5% (w/w) of other minor compounds (O´Brien, 1998). In recent years, there is a growing demand for thermophysical properties for oils/fats and biodiesel for process modelling and product design. And this demand comprises properties of individual compounds (Su et al., 2011) and also of the multicomponent mixtures (Silva et al., 2011). There is a lack of experimental data for individual fatty compounds and an effort to describe them by predictive methods (Su et al., 2011). In this work, a comparison of the performances of the most commonly used predictive methods for primary physical properties is done for fatty acids, methyl and ethyl esters. Predictions are also performed for twenty two fatty acids with pair carbon chain lengths from C-4 to C-20, and eight types of vegetable oils and their respective methyl and ethyl biodiesels.

2. Group Contribution Methods

Primary properties of pure components can be estimated based on the structure of their molecules. There are many methods that use the group contribution concept to estimate pure component primary properties (Reid et al., 1987). There are also methods like Cedeño et al. (2000) and Rowlinson-Bondi equation reported by Poling et al. (2004) that are based on primary properties for estimating other properties. As an example of the use of these methods, Díaz-Tovar et al.(2011) had calculated normal melting point temperature, normal heats of formation and critical properties using Marrero and Gani (2001) and Gani et al. (2005) methods for 65 triacylglycerols, 29 fatty acids and 58 esters (29 methyl and 29 ethyl). In this work, we selected a variety of methods for testing their predictive capacity based on experimental data for primary properties of fatty compounds, namely boiling point (T_b), critical temperature (T_c), critical pressure

(P_c), critical volume (V_c), acentric factor (ω), ideal heat capacity (cp^0), gibbs of formation ($\Delta_f G^0$) and enthalpy of formation ($\Delta_f H^0$), that we found in the open literature: Joback and Reid (1987) and Marrero and Gani (2001) for T_b , P_c , V_c , $\Delta_f G^0$ and $\Delta_f H^0$, Fedors (1982), Tu (1995) and Marrero and Gani (2001) for T_c , Constantinou et al. (1994) and Han and Peng (1993) for ω , and Rihani and Doraiswamy (1965), Cedeño et al.(2000), Rowlinson Bondi (Poling et al., 2004), and Joback and Reid (1987) for cp^0 . Both Rowlinson-Bondi equation and Cedeño et al.(2000) equations require as input the liquid heat capacity of the pure compound, which was estimated using the group contribution method of Ceriani et al. (2009). The performances of the models have been evaluated with respect to available data (experimentally measured) using the relative deviations (RD), calculated as:

$$\%RD = 100 \cdot |P_{lit} - P_{est}| / P_{lit} \tag{1}$$

where P_{lit} refers to the value of the physical property found in the literature and P_{est} refers to the value estimated in this study.

3. Results and discussion

Experimental data found in open literature for the selected pure component physical properties are given in Table 1. As one can see, few experimental values are available for fatty compounds. Most of them are critical properties. No value was found for ideal gas heat capacities and critical volumes. Acentric factor is, in general, determined from experimental data on vapor pressure and critical parameters.

Table 1: Experimental data for Fatty Acids (FA), Methyl Esters (ME) and Ethyl Esters (EE)

	C c:d[n]	T_b (K)	T_c (K)	P_c (10^6 Pa)	$\Delta_f G^0$ (J.mol^{-1}K^{-1})	$\Delta_f H^0$ (J.mol^{-1}K^{-1})
FA[l]	C 4:0	436.42[a]	615.20[a]	4.064[a]	-377300[b]	-
	C 6:0	478.38[c]	663.00[c]	3.377[a]	-338000[b]	-
	C 8:0	512.01[c]	694.26[a]	2.779[a]	-325000[b]	-
	C 10:0	541.92[c]	726.00[c]	2.250[a]	-305000[b]	-
	C 12:0	571.40[d]	743.43[e]	1.867[e]	-	-
	C 14:0	599.00[d]	765.19[e]	1.644[e]	-	-
	C 16:0	622.30[d]	785.22[e]	1.468[e]	-	-
	C 18:0	648.10[d]	805.09[e]	1.327[e]	-	-
ME	C 4:0	351.65[l]	554.50[f]	3.470[f]	-	-
	C 6:0	-	-	-	-	-494000[g]
	C 8:0	466.10[h]	-	-	-	-
	C 10:0	497.20[h]	-	-	-	-
	C 12:0	535.20[h]	712.00[i]	-	-	-
	C 14:0	596.20[j]	-	-	-	-674070[k]
	C 16:0	-	-	-	-	-728500[k]
	C 18:0	-	-	-	-	-778326[k]
	C 20:0	-	-	-	-	-815588[k]
EE	C 6:0	393.2[j]	-	-	-	-
	C 8:0	440.06[m]	-	-	-	-
	C 10:0	480.2[j]	-	-	-	-
	C 12:0	518.2[j]	-	-	-	-

[a]Andereya et al. (1990); [b]Pedley et al. (1986); [c]Ambrose and Ghiassee (1987); [d]Ashour and Wennersten (1989); [e]D'Souza and Teja (1987); [f]Young and Thomas (1983); [g]Adriaanse et al. (1965); [h]Weast and Grasselli (1987); [i]Kudchardker et al. (1968); [j]Aldrich Chemical Company Inc. (1990); [k]Freedman et al. (1984); [l] Susial et al. (1989); [m] Serijan et al. (1951); [n] c number of carbons and d = number of double bounds.

The relative deviations between experimental data and estimated values calculated using Equation 1 are listed in Table 2. For fatty acids, a lower average relative deviation (average value of RD) was found in the prediction of T_b for the method of Marrero and Gani (2001). Besides, there is a clear tendency of increase of relative deviations with carbon chain length (0.002% for C4:0 and 16.4% for C18:0) for the method of Joback and Reid (1987). Such tendency is not found for methyl and ethyl esters and both methods give comparable values of ARD. It should be mentioned that the value of T_b calculated for triolein (C57:3) with

the methods of Joback and Reid (1987) and Marrero and Gani (2001) are, respectively, 690.06 K and 609.56 K, and for tripalmitin (C51:0) are, respectively, 646.58 K and 586.77 K, while the experimental values reported by Santander et al. (2012) are, respectively, 692.25 K and 690.02 K. Based on these results, it is not possible to affirm which method is more suitable in the prediction of T_b of vegetable oils and fats, which are composed mainly by triacylglycerols.

Table 2: Comparison of predictive methods based on average relative deviations (ARD%)

	Method	T_b (K)	T_c (K)	P_c (10^6 Pa)	$\Delta_f G^0$ (J.mol^{-1}K^{-1})	$\Delta_f H^0$ (J.mol^{-1}K^{-1})
FA	Joback and Reid (1987)	7.53	8.24	7.65	2.18	-
	Marrero and Gani (2001)	1.25	6.09	3.51	2.04	-
	Fedors (1982)	-	1.59	-	-	-
	Tu (1995)	-	1.60	-	-	-
ME	Joback and Reid (1987)	2.65	1.39	17.81	-	2.22
	Marrero and Gani (2001)	2.86	0.62	0.13	-	1.81
	Fedors (1982)	-	1.97	-	-	-
	Tu (1995)	-	1.38	-	-	-
EE	Joback and Reid (1987)	11.24	-	-	-	-
	Marrero and Gani (2001)	9.73	-	-	-	-

The comparison of predictive methods based on average relative deviations (*RD*) is calculated as:

$$\%ARD = \sum_n RD / N \tag{2}$$

For T_c, four methods were evaluated according to Table 1. For fatty acids, the methods of Tu (1995) and Fedors (1982) provided very good predicted values in comparison with the experimental values reported in Table 2. There is a clear tendency of the methods of Joback and Reid (1987) and Marrero and Gani (2001) of decrease of relative deviations with carbon chain length (15.5 % for C4:0 and 3.46 % for C18:0, and 10.7 % for C4:0 and 4.22 % for C18:0, respectively). For methyl esters, the method of Marrero and Gani (2001) gave the lowest *ARD*. For P_c, the method of Marrero and Gani (2001) gave very good *ARD* for class of fatty acids and for methyl propionate (C4:0), which was the only experimental value of critical pressure of fatty methyl esters found in the open literature. There is also a clear tendency of the method of Joback and Reid (1987) of decrease of relative deviations with carbon chain length (47.7 % for C4:0 and 12.8% for C18:0). For $\Delta_f G^0$ and $\Delta_f H^0$, the methods of Marrero and Gani (2001) and Joback and Reid (1987) are comparable in terms of *ARD*, and both provided good predictions.

For the other physical properties considered in this work, acentric factor and ideal gas heat capacity, the open literature provides no experimental value. It is only possible to perform an analysis among selected methods related to the tendencies of their predicted values. Figures 1 and 2 show the estimated values for the acentric factors and ideal gas heat capacities (ω and cp^0, respectively) for fatty acids, methyl and ethyl esters as a function of their carbons chain length (horizontally positioned) and unsaturation (vertically positioned). For fatty acids and methyl esters, the estimated values of acentric factor and ideal gas heat capacity show the same tendency with chain length, i.e, to increase as CH$_2$ groups are added in the molecule. A lower contribution is assigned for the unsaturation.

As one can see in Figure 1, for the three classes of fatty compounds, the methods of Han and Peng (1993) and Constatinou et al. (1995) calculate similar values for acentric factor. As unsaturation increases, the values calculated for all three methods become closer. Figure 2 reveals that different curves are followed by the method of Cedeño et al. (2000) and Rowlinson-Bondi equation (Poling et al., 2004), and by the methods of Benson (Reid et al.,1987) and Rihani and Doraiswamy (1965). It is possible to note that as unsaturation increases, these differences become smaller. In fact, the method of Cedeño et al. (2000) differs from the Rowlinson-Bondi equation only by the values of parameters, and both use the same correlation for liquid heat capacity.

To finalize this work, the methods of Marrero and Gani (2001) for T_b, P_c, $\Delta_f G^0$ and $\Delta_f H^0$, and the methods of Tu (1995) and Fedors (1982) for T_c were used in the prediction of these properties for eight vegetable oils and their methyl and ethyl biodiesels. For vegetable oils, the fatty acid composition was used for estimating the probable triacylglycerol composition according to Ceriani (2005); for biodiesels, the composition in methyl and ethyl esters followed the fatty acid composition reported by Ceriani (2005).

Properties of these mixtures were considered as simple molar averages of the individual properties of each component. Results are reported in Table 3.
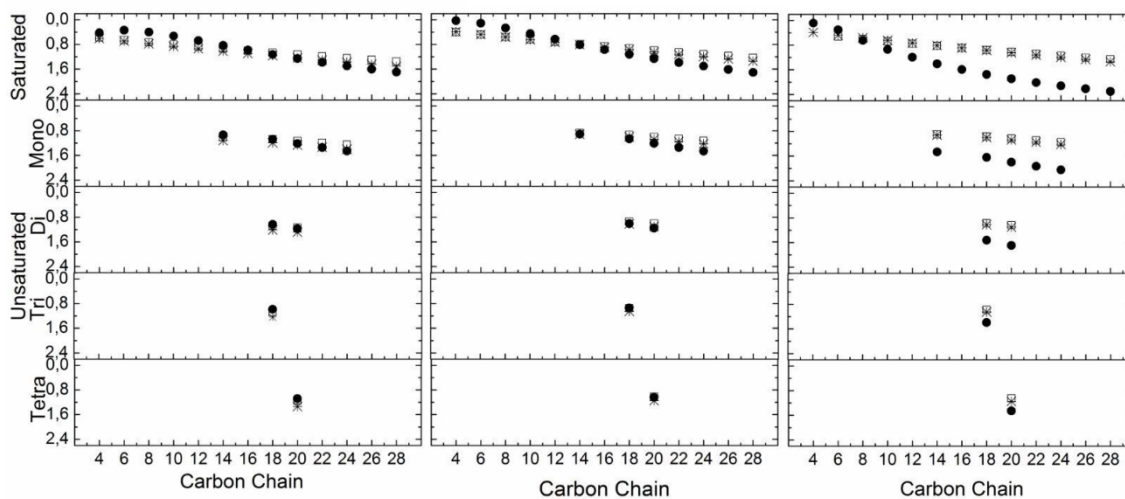

Figure 1: Acentric Factor physical property calculated with different methods of estimation of groups: ✶ Constatinou et al. (1995); □ Han and Peng (1993); ● Benson (Reid et al,(1987), for FA (a), ME (b), EE (c).
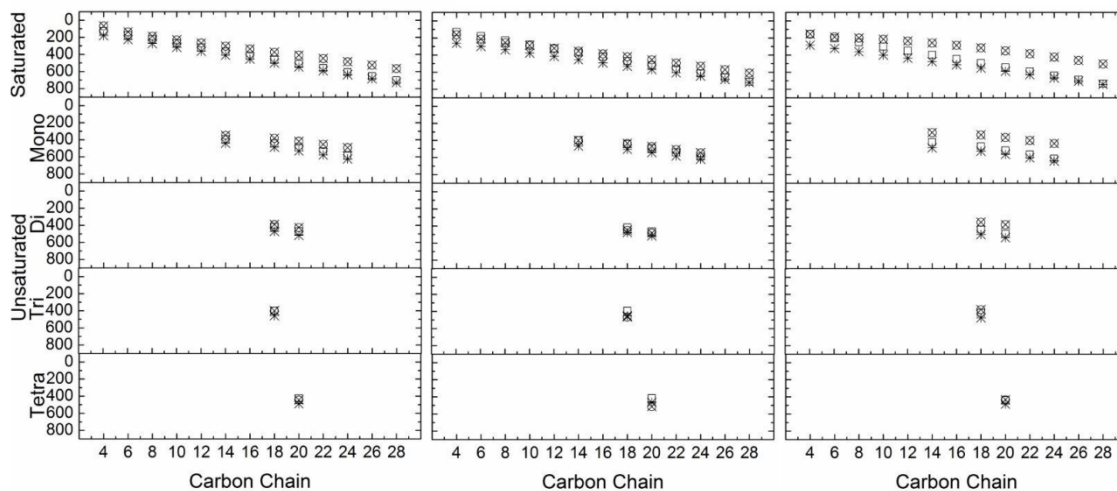

Figure 2: Ideal Gas Heat Capacity physical property at 298.15 K (J.mol^{-1}. K^{-1}) calculated with different methods of estimation of groups: ✶ Reid et al (1987), □ Rihani and Doraiswamy (1965), ○ Cedeño et al. (2000) and ✕ Rowlinson-Bondi (Poling et al,.(2004), for FA (a), ME (b), EE (c).

Calculated values for coconut oil (highly saturated oil with lauric acid, C12:0 as main fatty acid) and, in a less extension, for palm oil (palmitic acid and oleic acid, C16:0 and C18:1, as the main fatty acids) properties are dissimilar. The other oils are highly unsaturated, with oleic and/or linoleic acids as the main fatty acids, and their calculated properties are similar. The selected methods are capable of assigning these features. These calculated values are inputs in the design and analysis of vegetable oil and biodiesel processes.

Table 3. Physical Properties of Vegetable Oils (VO), Methyl Biodiesel (MB) and Ethyl Biodiesel (EB)

		Mixture	Coconut	Palm	Cotton	Corn	Soybean	Sunflower	Canola	Peanut
Fedors (1987)	T_c (K)	V. O.	975.70	1030.79	1042.19	1042.11	1042.80	1036.54	1030.87	1042.00
		M. B.	728.15	781.57	792.72	792.65	793.32	787.22	780.93	792.41
		E. B.	741.38	792.11	802.77	802.70	803.35	797.50	790.99	802.38
Tu (1995)		V. O.	960.89	1341.77	1335.30	1333.14	1331.81	1332.35	1318.76	1340.00
		M. B.	723.80	767.84	761.43	759.24	757.85	758.36	745.27	766.16
		E. B.	737.18	778.81	772.71	770.64	769.32	769.80	756.83	777.11
Marrero and Gani (2001)	T_b (K)	V. O.	779.97	835.98	841.95	838.72	847.60	848.32	847.66	847.83
		M. B.	542.79	597.11	602.98	597.28	608.50	609.20	608.56	608.29
		E. B.	555.49	607.11	612.71	606.79	617.99	618.65	618.05	617.72
	P_c (10^6 Pa)	V. O.	0.831	0.742	0.738	0.746	0.732	0.731	0.731	0.730
		M. B.	1.707	1.374	1.355	1.397	1.330	1.328	1.328	1.325
		E. B.	1.613	1.319	1.302	1.342	1.279	1.278	1.278	1.275
	$\Delta_f G^0$ (kJ. mol^{-1} .K^{-1})	V. O.	-652.4	-459.1	-297.1	-242.9	-240.7	-219.6	-264.1	-309.2
		M. B.	-244.9	-180.5	-126.5	-96.3	-107.7	-100.7	-115.5	-127.4
		E. B.	-236.9	-172.4	-118.5	-88.5	-99.6	-92.6	-107.4	-119.4
	$\Delta_f H^0$ (kJ.mol^{-1}.K^{-1})	V. O.	-1834.0	-1953.8	-1751.0	-1638.6	-1707.7	-1678.6	-1740.0	-1817.3
		M. B.	-633.4	-673.3	-605.7	-552.7	-591.2	-581.5	-602.0	-623.8
		E. B.	-654.2	-694.1	-626.5	-572.7	-612.1	-602.4	-622.8	-644.4

4. Conclusion

Very few experimental data are available in the literature for fatty acids and esters for primary properties as $T_b, T_c, P_c, V_c, \Delta_f G^0, \Delta_f H^0, cp^0$ and ω. Based on experimental data found in the open literature, we concluded that for fatty compounds, the method of Marrero and Gani (2001) is more suitable for predicting T_b and P_c, and has comparable predictive capacity in comparison with the method of Joback and Reid (1987) for $\Delta_f G^0$ and $\Delta_f H^0$. Both methods of Tu (1995) and Fedors (1982) are indicated in the prediction of T_c. Group contribution methods are very suitable for fatty compounds, considering that few function groups are able to describe acids, esters and acylglycerols, which correspond to the main fraction of vegetable oils and fats, and also biodiesels.

5. Acknowledgments

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