

Evaluation of Group-Contribution Methods to Estimate Vegetable Oils and Biodiesel Properties

E. G. Lima Neto, G. P. Silva, G. F. Silva

Department of Chemical Engineering, Federal University of Sergipe – UFS,
CEP 49400-00, São Cristóvão, Brazil

ABSTRACT

Knowing the phase equilibrium has fundamental importance on mixture separation; and physical and thermodynamic properties of the compounds underlie that equilibrium. Estimation methods are supposed to be a powerful skill for predicting physical and thermodynamic properties of the involved compounds, not only because the large number of properties that can be predicted (vapor pressure, boiling point, melting point, critical properties, etc) but also due to the low deviation to experimental measure. This work focuses the prediction of some properties of organic substances present in vegetable oils and in the biodiesel of these oils through group-contribution methods and empiric relations. Estimations were compared to data available on literature and experimental data. This comparison shows satisfactory deviation for application on engineering problems.

Keywords: Estimation, group-contribution, properties, biodiesel

1. INTRODUCTION

Biodiesel is a mixture of methyl or ethyl monoesters obtained from vegetable oils or animal fats. Biodiesel production can be performed by two technological routes: esterification and transesterification reactions of those oils and fats. On these reactions, raw-material (oil or fat) reacts with a low-chain alcohol (methyl or ethyl alcohol) and a catalyst (homogeneous or heterogeneous) producing a monoester (biodiesel) and glycerol (glycerin).

Because of its environmental benefits, resulting from a decrease in CO₂ emissions, its origin from renewable resources, and the increase in crude oil costs, biodiesel is become increasingly attractive. However, the high cost is still the main limitation to widespread commercialization because the final price of biodiesel depends upon 60–70% of the cost of the fats and oils used on their production. (Coutinho *et al.*, 2008).

When reaction ends, the phases (biodiesel, alcohol and glycerin) should be separated. For that, glycerin is commonly separated by decantation and the alcohol is eliminated by distillation. During the design of equipments that will be used on those operations, it is necessary knowing phase equilibrium. For this equilibrium prediction, physical and thermodynamic properties of its compounds might be known. Some of these properties are hard to be measured experimentally or impossible due to degradation of the substance.

Estimation of those properties can be performed, satisfactorily, by group-contribution methods. These

methods fragment the compound into several chemical groups and sum the contribution of each group (that is presented on the method) to get the final property of the substance. Besides their accurate estimations, some of those methods have easy implementation in widely known computational skills.

The main objective of this work is the estimation of physical and thermodynamic properties through empiric relations and group-contribution. Besides that, it focuses the comparison of those estimations to experimental data available on literature.

2. METHODOLOGY

Table 1 lists estimated properties in this work and their respective estimation methods. All methods were implemented on Microsoft Excel 2007 spreadsheets.

Table 1. Estimated properties and estimation methods.

Property	Methods
Melting point	Constantinou and Gani (1994) and Joback and Reid (1987)
Boiling point	Willman and Teja (1985) modified by Silva and Cabral (1998), Tsibanogiannis <i>et. al.</i> (1995) and Constantinou and Gani (1994)
Critical properties	Constantinou and Gani (1994) and Somayajulu (1989)
Vapor pressure	Reidel (1954) and Willman and Teja (1985) modified by Silva and Cabral (1998)
Acentric factor	Constantinou <i>et. al.</i> (1995) and Han

and Peng (1993)

First, properties of fatty acid / methyl esters present in oil / biodiesel of some vegetables were estimated. From the property of those compounds, it was carried out a weighed average to obtain the oil / biodiesel property. Percentages that were used in the weighed average are listed in Table 2 as well as the vegetable that were

studied. It was considered, to easy the calculations, that fatty acid composition in the oil is equal to its respective methyl ester in biodiesel. Reidel (1954) needs the temperature on which the vapor pressure will be calculated; in this work, this temperature was equal to 303,15 K. In this work, just C10-C18 acids (and its derivatives) were taken in account. The other acids are present in irrelevant amount.

Table 2. Fatty acid percentage in vegetable oils.

Fatty acid	MW*	Castor	Sunflower	Soy	Moringa	Corn	Coconut	Jartropha	Cotton	Canola	Palm
C10:0	200,32						6,0				0,1
C12:0	228,38						46,7				0,9
C14:0	256,43		0,1	0,1			18,3		0,8	0,1	1,3
C16:0	254,42	2,3	6,0	10,3	6,5	9,9	9,2	16,4	22,9	3,9	43,9
C18:0	284,49	3,0	5,9	4,7	6,0	3,1	2,9	5,4	3,1	3,1	4,9
C18:1	250,47	9,0	16,1	22,5	72,2	29,1	6,9	40,3	18,5	60,2	39,0
C18:1_{10H}	294,43	80,3									
C18:2	280,45	4,5	71,4	54,1	1,0	56,8	1,7	37,0	54,2	21,1	9,5
C18:3	278,45		0,6	8,3		1,1			0,5	11,1	0,3
Ref.		[2]	[1]	[1]	[3]	[1]	[1]	[2]	[1]	[1]	[1]

* Molecular weight ($\text{g}\cdot\text{mol}^{-1}$)

[1] – Pegg *et al.*, 1999; [2] – Peres e Lucena, 2007; [3] – Knothe *et al.*, 2008

3. RESULTS AND DISCUSSION

3.1 Melting point

Figures 1 and 2 show estimation of fatty acid / methyl esters melting point, according to their molecular weight. Experimental values were taken from Lide (2000).

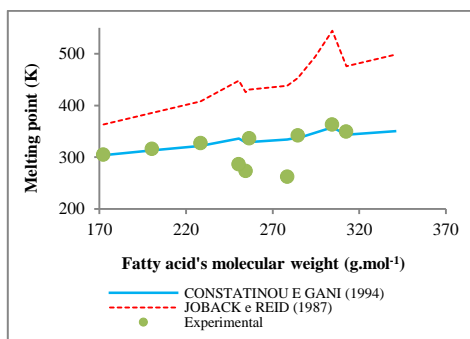


Fig. 1. Melting point x molecular weight for fatty acids

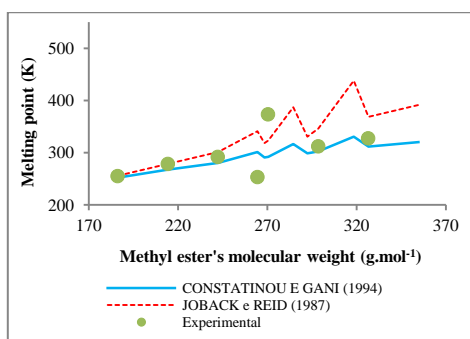


Fig. 2. Melting point x molecular weight for methyl esters

Estimations show that Constantinou and Gani (1994) and Joback and Reid (1987) are very concordant between them because they have similar behavior according to variation on fatty acid's and methyl ester's molecular weight.

Between both methods, Constantinou and Gani (1994) was the one that showed, in general, more accurate predictions for melting points (not only for fatty acids but also for methyl esters). Best values of estimation were found in low-chain fatty acids and methyl esters (10 to 16 carbons). Joback e Reid (1987), in general, overestimates the property.

3.2 Boiling point

Experimental values in the figures below were taken from Lide (2000). These figures show boiling point predictions for fatty acid and methyl esters.

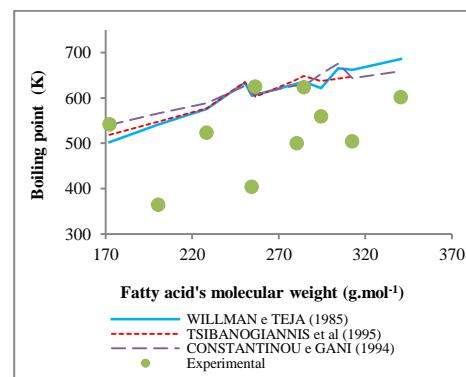


Fig. 3. Boiling point x molecular weight for fatty acids

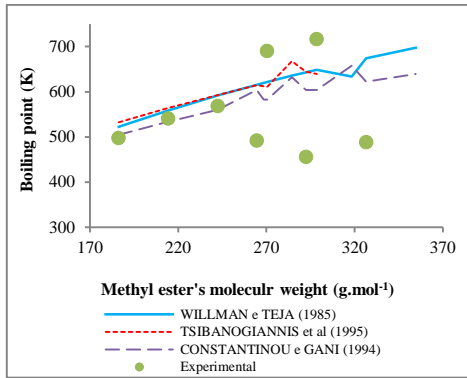


Fig. 4. Boiling point x molecular weight for methyl esters

From Figures 3 and 4, it is notorious that Willman and Teja (1985) modified by Silva e Cabral (1998), Tsibanogiannis *et. al.* (1995) and Constantinou and Gani (1994) have concordance on their estimations. But, they generally overestimate fatty acid's boiling temperature and have a middle behavior in relation to methyl esters.

3.3 Critical properties

Boiling point values on which Somayajulu (1989) depends were taken from Willman and Teja (1985) modified by Silva and Cabral (1998)'s estimation. Predictions of critical properties are presented below.

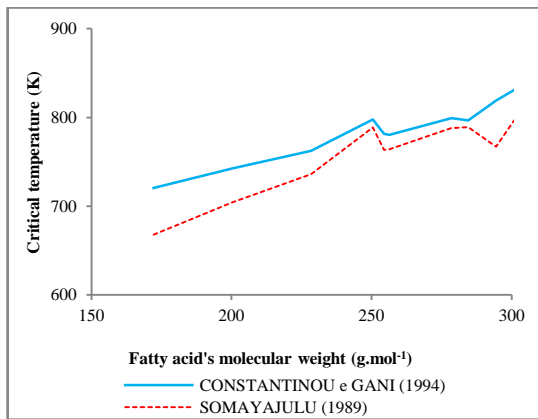


Fig. 5. Critical temperature x molecular weight for fatty acids

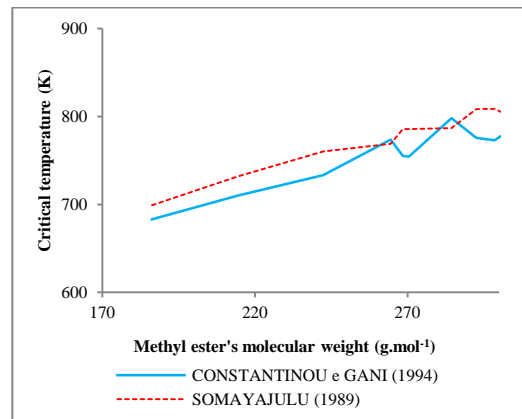


Fig. 6. Critical temperature x molecular weight for methyl esters

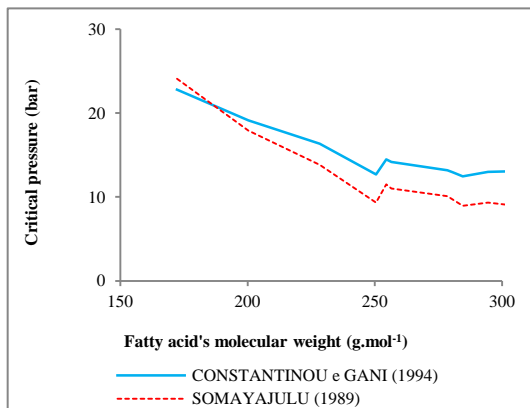


Fig. 7. Critical pressure x molecular weight for fatty acids

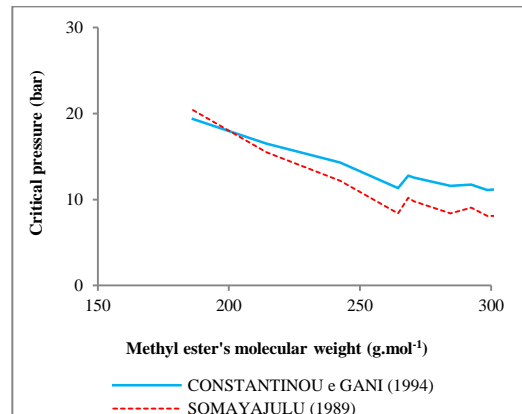


Fig. 8. Critical pressure x molecular weight for methyl esters

Constantinou and Gani (1994) and Somayajulu (1989) have similar behaviors in relation to the estimated properties. Because experimental / others estimations values were not found for critical properties, it is not possible say anything about these methods' coherence in relation to reality.

Probably, Somayajulu (1989) has higher deviations to experimental values because, besides own method's deviation, it will have an additional deviation due to Willman and Teja (1985) modified by Silva and Cabral (1998)'s estimation (deviation propagation).

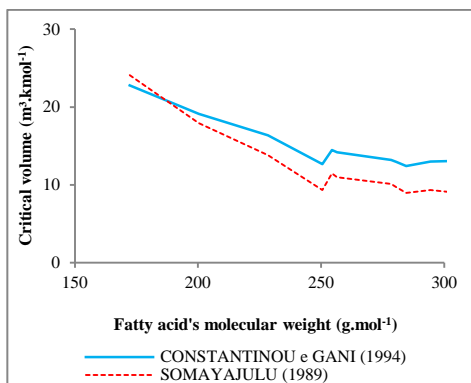


Fig. 9. Critical volume x molecular weight for fatty acids.

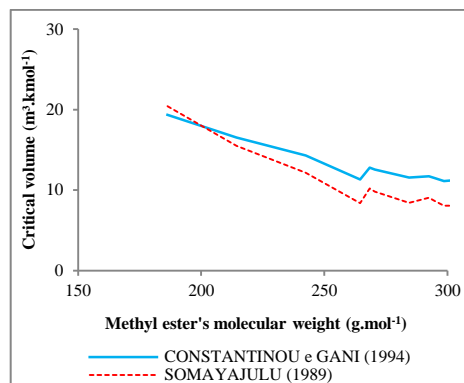


Fig. 10. Critical volume x molecular weight for methyl esters.

3.4 Vapor Pressure

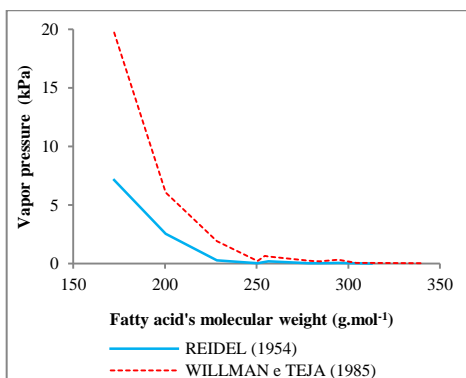


Fig. 11. Vapor pressure x molecular weight for fatty acids.

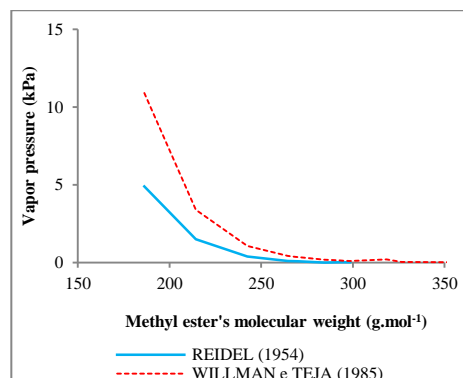


Fig. 12. Vapor pressure x molecular weight for methyl esters.

It is notorious, by analyzing the curves above, that Willman and Teja (1985) modified by Silva and Cabral (1998) and Reidel (1954) have similar behaviors in relation to acid / ester molecular weight. However, estimations show that the difference between the values of those two methods is considerable. Experimental values are needed to confirm the methods' accuracy.

3.5 Acentric Factor

Acentric factor of a molecule is a theoretic property which represents its deviation in relation to perfect sphericity. Molecules with perfect spherical shape have acentric factor equal to zero and more imperfect the molecule is higher its acentric factor will be.

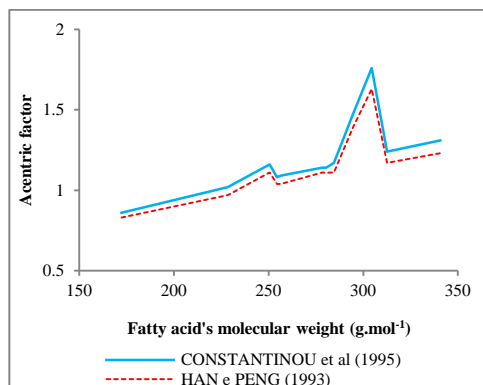


Fig. 13. Acentric factor x molecular weight for fatty acids.

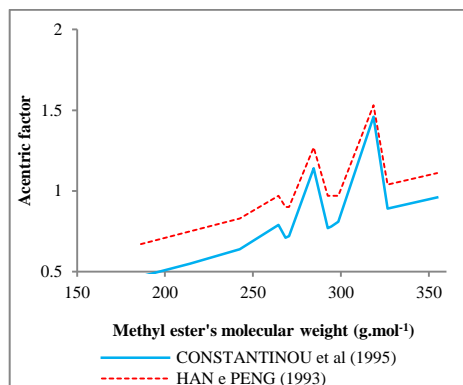


Fig. 14. Acentric factor x molecular weight for methyl esters.

Constantinou *et. al.* (1995) and Han and Peng (1993) have higher concordance when estimate fatty acids' acentric factors, but when they estimate methyl esters' acentric factor, they have good concordance too.

3.6 Final Properties of Vegetable Oils and Biodiesel

The methods that were chosen for oils' and biodiesel's properties were: Constantinou and Gani (1994) to melting point, boiling point and critical properties; Willman and Teja (1985) modified by Silva and Cabral (1998) to vapor pressure and Constantinou *et. al.* (1995) to acentric factor.

The upcited methods were chosen because they have lower deviations in relation to experimental data and because they have estimation values for all fatty acids / methyl esters. Table 3 shows the results.

3.7 Comparison with Another Works

Few experimental measures / estimations of fatty acid / biodiesel properties (those performed here) were found on literature. Table 4 shows the comparison between data found on literature and those estimated in this work.

Table 4. Comparison between this work estimation and literature data.

Boiling point				
	This work	Literature	Deviation	Reference
Canola biodiesel	602,8 K	611,28 K	1,39%	(Goodrum, 2002)
Soybean biodiesel	601,3 K	620,8 K	3,14%	(Goodrum, 2002)
Critical properties				
	This work	Literature	Deviation	Reference
Soybean biodiesel – Tc	797,2 K	785,7 K	1,44 %	(Zhang <i>et. al.</i> , 2003)
Soybean biodiesel – Pc	11,60 bar	12,08 bar	0,97%	(Zhang <i>et. al.</i> , 2003)
Soybean biodeisel – Vc	1,086 m ³ /kmol	1,082 m ³ /kmol	0,37%	(Zhang <i>et. al.</i> , 2003)

By analyzing the table above, it can be clearly noticed that the deviations are minimum in relation to experimental measurement and others estimations.

4. CONCLUSION

Some properties of organic compounds can be satisfactorily predicted by group-contribution methods

and others estimation methods. Selecting these methods is an important factor on accuracy of the final estimation result. Minimum deviations showed between experimental measurement and estimation carried out here confirm the applicability on using estimation method on engineering problems.

Tabela 3. Estimated properties for vegetable oils and biodiesel

	Oil plant	Melting point (K)	Boiling point (K)	Critical temperature (K)	Critical pressure (bar)	Critical volume (m ³ .kmol ⁻¹)	Vapor pressure (kPa)	Acentric factor
Oil	Castor	346,0	650,1	720,40	12,99	1,061	0,331	1,437
	Sunflower	335,4	626,1	742,68	12,87	1,037	0,233	1,149
	Soy	334,8	624,7	762,51	13,02	1,027	0,266	1,142
	Moringa	336,4	627,1	780,38	12,64	1,055	0,232	1,160
	Corn	334,8	624,7	781,32	13,00	1,029	0,265	1,143
	Coconut	290,0	528,0	796,65	15,98	0,733	4,459	0,902
	Jartropha	334,7	623,6	837,45	13,02	1,027	0,284	1,142
	Cotton	333,9	621,8	797,50	13,02	1,014	0,334	1,134
	Canola	335,5	626,1	818,95	12,85	1,038	0,232	1,150
	Palm	331,7	614,7	798,36	13,71	0,984	0,522	1,113
Biodiesel	Castor	315,0	629,6	787,8	11,57	1,120	0,198	1,107
	Sunflower	300,4	602,9	791,2	11,47	1,096	0,265	0,786

Soy	299,5	601,3	797,2	11,60	1,086	0,221	0,779
Moringa	301,7	604,0	778,3	11,28	1,114	0,378	0,799
Corn	299,6	601,3	795,5	11,58	1,088	0,234	0,780
Coconut	250,8	501,0	680,1	13,88	0,787	2,508	0,556
Jatropha	299,3	600,1	788,8	11,60	1,086	0,288	0,778
Cotton	298,2	598,1	795,7	11,60	1,073	0,243	0,769
Canola	300,5	602,8	783,3	11,45	1,097	0,328	0,787
Palm	295,1	590,0	790,2	12,17	1,043	0,321	0,746

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