

# EXPERIMENTAL DENSITY DATA AND EXCESS MOLAR VOLUMES OF COCONUT BIODIESEL + N-HEXADECANE AND COCONUT BIODIESEL + DIESEL AT DIFFERENT TEMPERATURES

F. M. R. Mesquita, F. X. Feitosa, R. S. de Santiago-Aguiar and H. B. de Sant'Ana\*

Grupo de Pesquisa em Termofluidodinâmica Aplicada, Departamento de Engenharia Química,  
Centro de Tecnologia. Phone: + (55) (85) 3366-9611, Universidade Federal do Ceará, Campus do Pici,  
Bloco 709, CEP: 60455-760, Fortaleza - CE, Brazil.  
E-mail: fmmr03@gmail.com; filipexfeitosa@hotmail.com; rilvia@ufc.br  
\*E-mail: hbs@ufc.br

(Submitted: March 13, 2013 ; Revised: August 8, 2013 ; Accepted: August 8, 2013)

**Abstract** - The density of the pure component (n-hexadecane), pure pseudo-components (coconut biodiesel and diesel) and pseudo-binary mixtures of coconut biodiesel with n-hexadecane (or + diesel) were measured at temperatures 293.15, 313.15, 333.15, 353.15 and 373.15 K and atmospheric pressure, over the entire composition range (mole fractions from 0.1 to 0.9, with a step de 0.1). Densities were determined using an Anton Paar SVM 3000 viscodensimeter. Experimental density values decreased with the increase of the temperature. The excess molar volumes of the pseudo-binary mixtures were calculated by using the experimental values of density. Excess molar volumes were correlated with the Redlich-Kister polynomial expansions. Excess molar volumes show positive and negative values in the two systems studied. Excess partial volumes at infinite dilution were calculated for coconut biodiesel, n-hexadecane and diesel in the mixtures studied.

**Keywords:** Density; Excess volume; Coconut biodiesel; Diesel; n-hexadecane.

## INTRODUCTION

In the last decade biodiesel has become an important alternative fuel due to concerns about environmental issues and the depletion of nonrenewable energy resources. It is constituted of a mixture of alkyl esters of long-chain carboxylic acids produced from vegetable oils, animal fat and residual fats. Generally, it is produced by homogeneous catalysis through a transesterification reaction (Knothe and Van Gerpen, 2009).

Although biodiesel-diesel blends are an important product distributed and commercialized in the diesel fuel marketplace, there is still a challenge of the

comprehension of the intermolecular interactions between the different molecules of biodiesel and diesel and how they affect their thermodynamic properties. For this reason, a set of new experimental data on transport, density and derived properties has been collected on biodiesel-diesel and biodiesel-biodiesel blends in our research group (Mesquita *et al.*, 2012; Nogueira *et al.*, 2012; Mesquita *et al.*, 2011; Parente *et al.*, 2011; Feitosa *et al.*, 2010; Nogueira *et al.*, 2010). It should be stressed that experimental data for the density and derived properties are important in many important chemical, industrial, and biological processes, especially for mixed systems, e.g., optimization of the combustion processes and serving

\*To whom correspondence should be addressed

as input for process simulation (Alptekin and Canakci, 2008; Ceriani *et al.*, 2008; Baroutian *et al.*, 2008; Baroutian *et al.*, 2008).

Additionally, the study of derivative functions such as excess molar volume, partial molar volume and excess partial molar volumes of binary liquid mixtures is useful in understanding the nature and strength of intermolecular interactions between the component molecules (Ali *et al.*, 2004; Besbes *et al.*, 2009; Nain *et al.*, 2008).

This work is therefore aimed at measuring the density of the pseudo-binary mixtures of coconut biodiesel + n-hexadecane and coconut biodiesel + diesel in the temperature range from  $T = (293.15, 313.15, 333.15, 353.15 \text{ and } 373.15) \text{ K}$  at atmospheric pressure, as a function of composition. The excess molar volumes,  $V^E$ , of binary mixtures were calculated from the density data. These data have been correlated using Redlich–Kister type functions in terms of mole fraction. It is very important to remember that n-hexadecane was used as a molecule representative of diesel fuel, usually used in the lumping procedure. Mesquita *et al.* (2011) and Mesquita *et al.* (2012) have already started a systematic analysis of the choice of n-hexadecane as a substitute for diesel in the determination of thermodynamics properties.

It is important to emphasize that biodiesel and diesel have a complex composition. Nevertheless, it has been assumed that systems formed by these components produce pseudo-binary mixtures.

## MATERIALS AND METHODS

### Materials and Experimental Methodology

Coconut oil was supplied by Petrobras S/A. The coconut biodiesel sample was obtained by a coconut oil transesterification reaction in a laboratory scale apparatus by an alkaline-catalyzed reaction (potassium methoxide,  $w = 0.008$ ), using methanol (supplied

from J. T. Baker) as the transesterification alcohol, without any pretreatment of the feed stocks due to their lower acidity number. Methanol in excess, about volume fraction ( $\varphi$ ) = 100%, was used in those reactions. Transesterification reactions were carried out homogeneously in the liquid phase. Oil and alcohol were added to the reactor, followed by the catalyst loading under mechanical agitation (1250 rpm), at 298 K during 1 h. After the transesterification, the resulting glycerin was removed by settling after 12 h and the resulting ester phase was washed in three steps. The first step was accomplished by a two-fold washing procedure with pure water ( $\varphi = 10\%$ ) to remove catalyst, soap, and excess glycerol. After that, it was washed once with hydrochloric acid (0.1 M), ( $\varphi$ ) = 10%, to neutralize the medium. It should be noted that, after each washing procedure, the dense phase was separated by settling. The coconut biodiesel sample was characterized following laboratory procedures and standards indicated by the Standard Resolution No. 7 (Brazilian Regulatory Agency/ANP, 2013).

Methyl ester composition analysis was performed by gas chromatography (GC), using a Varian CP-3800 gas chromatograph system equipped with a flame ionization detector (FID;  $T_{detector} = 523.15 \text{ K}$ ) and automated split injector ( $T_{injection} = 473.15 \text{ K}$ ). The column was a CP WAX 52CB 30 m  $\times$  0.25 mm  $\times$  0.05  $\mu\text{m}$  DB ( $T_{column} = 483.15 \text{ K}$ ). In Table 1, the chemical composition of the coconut biodiesel is summarized.

Diesel fuel was kindly furnished by Lubrificantes e Derivados de Petróleo do Nordeste – LUBNOR, Petrobras S/A. Physicochemical characterization of the diesel was performed by using four parameters, i.e., analysis of density, flash point, viscosity and distillation temperatures. Distillation analysis followed the procedure established by ASTM D86-05 (2005). Physicochemical properties of the coconut biodiesel and diesel fuel are presented in Table 2.

N-Hexadecane was supplied by Merck with 99% purity, confirmed by chromatographic analysis. This reagent was used as received from Merck.

**Table 1: Fatty acids methyl esters (FAME) profile of coconut biodiesel.**

Methyl ester	Mass fraction (%)
methyl caproate (C06:0)	0.28
methyl caprilate (C08:0)	4.08
methyl caprate (C10:0)	3.65
methyl laurate (C12:0)	35.35
methyl myristate (C14:0)	19.84
methyl palmitate (C16:0)	13.83
methyl stearate (C18:0)	3.94
methyl oleate (C18:1)	14.30
methyl linoleate (C18:2)	4.73

**Table 2: Physicochemical properties of pure coconut biodiesel and diesel.**

Physical property	Coconut biodiesel	Method	Diesel	Method
Flash point/K	386.15	ASTM D93	341.15	ASTM D975
Ester content/w	98.2	EN 14103	-	-
Free glycerin content/w	0.013	ASTM 6584	-	-
Total glycerin content/w	0.072	ASTM 6584	-	-
Acidity number/mg KOH/g	0.0320	ASTM 664	-	-
Kinematic viscosity at 313.15 K/mm <sup>2</sup> /s	2.450	ASTM D445	3.161	ASTM D445
Density/kg/m <sup>3</sup>	871.90	ASTM D7042	845.00	ASTM D7042
Distillation/%	-	-	-	ASTM D2887
10	-	-	488.75	
50	-	-	548.05	
90	-	-	612.25	
MW/g/mol	242.58	chromatography	184.43	osmometry

### Apparatus and Procedure

Pseudo-binary mixtures (coconut biodiesel + n-hexadecane and coconut biodiesel + diesel) for the measurements of densities were prepared by mass, using an electronic balance (Shimadzu, model AY220) to an accuracy of  $\pm 0.0001$  g, over the entire composition range  $w = (0.10 - 0.90)$ . Before analysis, these mixtures were agitated in a vortex for 3 min in order to ensure an adequate homogenization.

Densities of the pure components, pure pseudo-components and mixtures were measured using an oscillating U-tube digital viscodensimeter (SVM 3000, Anton Paar). A sample of approximately 5 mL is required to perform the analysis. For a single injection, analysis is performed in duplicate. The uncertainty of the experimental density and excess molar volume data is estimated to be  $\pm 0.0002$  g·cm<sup>-3</sup> and  $\pm 0.0007$  cm<sup>3</sup>·mol<sup>-1</sup>. The possible error in mole fraction is calculated to be less than  $\pm 1.8 \cdot 10^{-3}$ . The temperature in the cell was regulated to  $\pm 0.01$  K. Further details of the experimental procedure have been described elsewhere (Feitosa *et al.*, 2010; Nogueira *et al.*, 2010). It is important to mention that all density values reported in this paper are an average of at least three concurrent measurements.

### Thermodynamics Correlation

The experimental values of density ( $\rho$ ) for all pseudo-binary mixtures were fitted by a polynomial equation of first order (Eq. (1)):

$$\rho = B_0 + B_1T \quad (1)$$

where  $B_0$  and  $B_1$  are constants specific for a temperature ( $T$ ).

The excess molar volumes ( $V^E$ ) for the mixtures

were calculated using the following equation:

$$V^E = \sum_{i=1}^n x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (2)$$

where  $x_i$ ,  $M_i$ , and  $\rho_i$  are the mole fraction, molar mass, and density of component  $i$ ,  $\rho$  is the density on mixing.

The excess molar volume was correlated by Redlich and Kister (1948) as shown in Eq. (3):

$$V^E = x_1(1-x_1) \sum_{j=0}^k A_j(1-2x_1)^j \quad (3)$$

where  $V^E$  is the excess volume,  $x_1$  is the mole fraction and  $k$  is the degree of the polynomial expansion. The adjustment of the parameter of the Redlich-Kister equation,  $A_j$ , and the corresponding standard deviations,  $\sigma(V^E)$ , were calculated by using the equation:

$$\sigma(V^E) = \sqrt{\frac{\sum (V_{\text{exp}}^E - V_{\text{adj}}^E)^2}{(n-p)}} \quad (4)$$

where  $adj$  is adjusted data,  $n$  and  $p$  are the numbers of experimental points and numbers of parameters, respectively.

## RESULTS AND DISCUSSION

The fatty acid methyl esters (FAME) profile of coconut biodiesel is reported in Table 1. It could be observed that coconut biodiesel presents, as the major component, methyl laurate (C12:0) with a

mass percent of 35.35%.

Table 2 summarizes the characterization analysis for coconut biodiesel (flash point, ester content, free glycerin, total glycerin content, acidity number, viscosity and density). It can be noted that the viscosity and flash point data are outside the limits established by the National Petroleum, Biofuels and Gas Agency /ANP – BRAZIL. This unconformity can be attributed to the coconut biodiesel composition, which shows a large presence of saturated-short chain-lower molecular weight components. For this reason, its physicochemical properties are slightly outside the limits set by regulatory agencies.

The experimental values of density for the pure component (n-hexadecane) and for the pure pseudo-components (coconut biodiesel and diesel) at various

temperatures and atmospheric pressure are provided in Table 3. It could be observed that there is a systematic difference around 7-9% when comparing the diesel to n-hexadecane density.

The experimental measurements of density for pseudo-binary mixtures of coconut biodiesel + n-hexadecane and coconut biodiesel + diesel at different temperatures  $T = (293.15, 313.15, 333.15, 353.15$  and  $373.15)$  K and atmospheric pressure are summarized in Table 4. From this table it could also be stated that there is a gap between blends with diesel when compared to n-hexadecane blends. Although there is not an exact value of mole fraction between the blends produced using diesel and n-hexadecane, it is possible to inform that there is a difference of about 5%.

**Table 3: Experimental densities ( $\rho$ ) for the pure components at the temperatures  $T = (293.15\text{--}373.15)$  K and atmospheric pressure.**

T/K	Coconut biodiesel	Diesel	n-hexadecane
	$\rho/\text{g}\cdot\text{cm}^{-3}$		
293.15	0.8709	0.8459	0.7743
313.15	0.8555	0.8317	0.7605
333.15	0.8402	0.8177	0.7466
353.15	0.8246	0.8034	0.7327
373.15	0.8093	0.7893	0.7186

**Table 4: Experimental densities ( $\rho$ ) for the binary mixture ( $x_1$  coconut biodiesel + n-hexadecane ( $1 - x_1$ ) and  $x_1$  coconut biodiesel + diesel ( $1 - x_1$ )) at the temperatures  $T = (293.15 - 373.15)$  K and atmospheric pressure.**

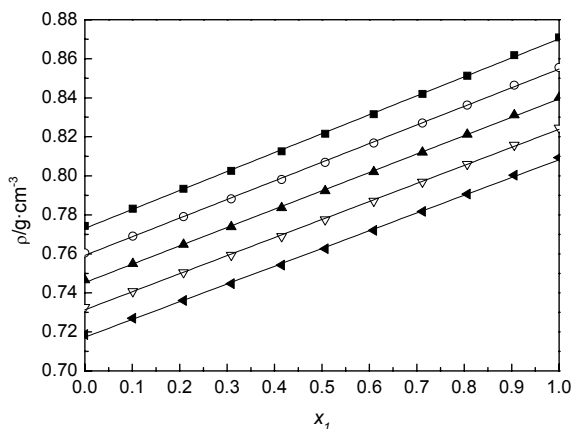
$x_1$	$\rho/\text{g}\cdot\text{cm}^{-3}$				
	T/K				
	293.15	313.15	333.15	353.15	373.15
<b><math>x_1</math> Coconut biodiesel + n-hexadecane (<math>1 - x_1</math>)</b>					
0.1013	0.7831	0.7691	0.7550	0.7408	0.7270
0.2079	0.7933	0.7791	0.7648	0.7505	0.7361
0.3087	0.8025	0.7882	0.7738	0.7594	0.7447
0.4148	0.8126	0.7981	0.7836	0.7690	0.7542
0.5070	0.8215	0.8069	0.7923	0.7776	0.7626
0.6094	0.8316	0.8168	0.8020	0.7871	0.7720
0.7122	0.8420	0.8270	0.8120	0.7969	0.7817
0.8066	0.8513	0.8362	0.8212	0.8060	0.7906
0.9054	0.8618	0.8464	0.8312	0.8158	0.8003
<b><math>x_1</math> Coconut biodiesel + diesel (<math>1 - x_1</math>)</b>					
0.0817	0.8484	0.8344	0.8203	0.8059	0.7917
0.1635	0.8509	0.8367	0.8226	0.8083	0.7935
0.2424	0.8535	0.8391	0.8247	0.8102	0.7956
0.3359	0.8558	0.8412	0.8267	0.8120	0.7972
0.4379	0.8586	0.8439	0.8292	0.8143	0.7993
0.5298	0.8607	0.8459	0.8310	0.8161	0.8010
0.6442	0.8636	0.8486	0.8336	0.8185	0.8032
0.7608	0.8664	0.8512	0.8361	0.8209	0.8055
0.8762	0.8692	0.8539	0.8386	0.8232	0.8077

The values of density for binary mixtures at different temperatures  $T = (293.15, 313.15, 333.15, 353.15 \text{ and } 373.15) \text{ K}$  are plotted against mole fraction in Figs. 1 and 2.

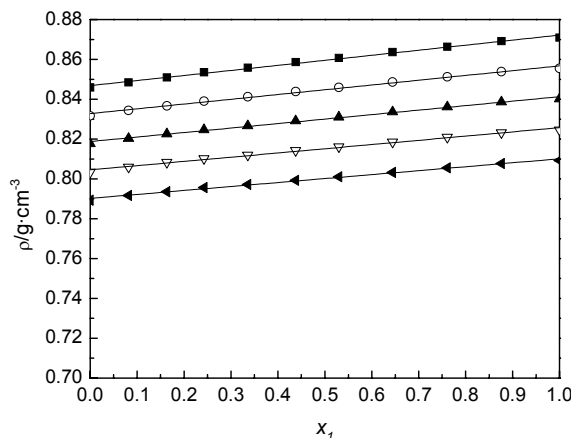
The data in Table 5 include the specific constants obtained for a temperature ( $B_0$  and  $B_1$ ) obtained through linear regression (Eq. (1)) for the mixture and the regression coefficient ( $R^2$ ). Good agreement can be observed,

with a regression coefficient ( $R^2$ ) better than 0.9.

The calculated excess molar volumes,  $V^E$ , for coconut biodiesel + n-hexadecane and coconut biodiesel + diesel mixtures as a function of composition are shown in Table 6. The adjustable parameters,  $A_j$ , for the mixtures obtained by Eq. (3), along with standard deviations ( $\sigma$ ) calculated through Eq. (4) at all investigated temperatures, are listed in Table 7.



**Figure 1:** Density of the binary mixture ( $x_1$  coconut biodiesel + n-hexadecane ( $1 - x_1$ )) at the temperatures  $T = (293.15\text{--}373.15) \text{ K}$  and atmospheric pressure. ■: 293.15 K ○: 313.15 K ▲: 333.15 K ▽: 353.15 K ◀: 373.15 K. Symbols represent the experimental points. Solid curves were calculated by linear fit.



**Figure 2:** Density of the binary mixture ( $x_1$  coconut biodiesel + diesel fuel ( $1 - x_1$ )) at the temperatures  $T = (293.15\text{--}373.15) \text{ K}$  and atmospheric pressure. ■: 293.15 K ○: 313.15 K ▲: 333.15 K ▽: 353.15 K ◀: 373.15 K. Symbols represent the experimental points. Solid curves were calculated by linear fit.

**Table 5:** Estimated parameters for density ( $\rho$ ) of the binary mixtures ( $x_1$  coconut biodiesel + n-hexadecane ( $1 - x_1$ ) and  $x_1$  coconut biodiesel + diesel ( $1 - x_1$ )), at different temperatures, along with regression coefficient ( $R^2$ ).

T/K	$B_0/\text{g}\cdot\text{cm}^{-3}$	$B_1/\text{g}\cdot\text{cm}^{-3}\text{K}^{-1}$	$R^2$
<b>Coconut biodiesel + n-hexadecane</b>			
293.15	0.7731	0.0971	0.99
313.15	0.7592	0.0955	0.99
333.15	0.7453	0.0941	0.99
353.15	0.7314	0.0925	0.99
373.15	0.7173	0.0910	0.99
<b>Coconut biodiesel + diesel</b>			
293.15	0.8468	0.0254	0.99
313.15	0.8328	0.0239	0.99
333.15	0.8188	0.0225	0.99
353.15	0.8045	0.0212	0.99
373.15	0.7902	0.0199	0.99

**Table 6: Excess molar volumes ( $V^E$ ) for the binary mixture ( $x_1$  coconut biodiesel + n-hexadecane ( $1 - x_1$ )) and  $x_1$  coconut biodiesel + diesel ( $1 - x_1$ )) at the temperatures  $T = (293.15-373.15)$  K and atmospheric pressure.**

$x_1$	$V^E/\text{cm}^3\cdot\text{mol}^{-1}$				
	T/K				
	293.15	313.15	333.15	353.15	373.15
<b><math>x_1</math> Coconut biodiesel + n-hexadecane (<math>1 - x_1</math>)</b>					
0.1013	0.2087	0.2333	0.2664	0.3327	0.1637
0.2079	0.1176	0.1514	0.2018	0.2338	0.2641
0.3087	0.2252	0.2408	0.2785	0.2859	0.3925
0.4148	0.2229	0.2500	0.2695	0.2854	0.3789
0.5070	0.2086	0.2179	0.2253	0.2175	0.3431
0.6094	0.1489	0.1687	0.1949	0.1959	0.3095
0.7122	0.0415	0.0687	0.1106	0.1170	0.2166
0.8066	0.0565	0.0653	0.0590	0.0396	0.1680
0.9054	-0.1472	-0.0997	-0.0911	-0.1062	0.0075
<b><math>x_1</math> Coconut biodiesel + diesel (<math>1 - x_1</math>)</b>					
0.0817	0.0138	-0.0729	-0.0840	-0.0960	-0.1058
0.1635	-0.0013	-0.0668	-0.1139	-0.1942	-0.0588
0.2424	-0.0943	-0.1381	-0.1350	-0.1922	-0.1506
0.3359	-0.0241	-0.0440	-0.0470	-0.0813	-0.0095
0.4379	-0.0654	-0.0951	-0.0811	-0.0978	-0.0010
0.5298	-0.0140	-0.0454	-0.0039	-0.0565	0.0407
0.6442	-0.0729	-0.0858	-0.0579	-0.0942	0.0279
0.7608	-0.1332	-0.1252	-0.1100	-0.1617	-0.0481
0.8762	-0.2462	-0.2482	-0.2132	-0.2452	-0.1387

**Table 7: Estimated parameters for excess molar volume ( $V^E$ ) of the binary mixtures ( $x_1$  coconut biodiesel + n-hexadecane ( $1 - x_1$ )) and  $x_1$  coconut biodiesel + diesel ( $1 - x_1$ )), at different temperatures, along with standard deviation ( $\sigma$ ).**

T/K	$A_0/\text{cm}^3\cdot\text{mol}^{-1}$	$A_1/\text{cm}^3\cdot\text{mol}^{-1}$	$A_2/\text{cm}^3\cdot\text{mol}^{-1}$	$A_3/\text{cm}^3\cdot\text{mol}^{-1}$	$A_4/\text{cm}^3\cdot\text{mol}^{-1}$	$\sigma/\text{cm}^3\cdot\text{mol}^{-1}$
<b>Coconut biodiesel + n-hexadecane</b>						
293.15	0.8321	0.1447	-1.0967	2.6200	0.6602	0.2461
313.15	0.9097	0.2208	-1.1555	2.4090	1.4716	0.7926
333.15	0.9738	0.2181	-0.4965	2.8345	0.7353	0.2985
353.15	0.9882	0.1442	-0.5573	3.8068	1.4260	0.3173
373.15	1.4154	0.6834	0.5545	0.1700	-1.9622	0.1637
<b>Coconut biodiesel + diesel</b>						
293.15	-0.1261	-0.3299	-1.4544	3.1509	-0.4792	0.2105
313.15	-0.2510	-0.3442	-0.7634	2.3003	-2.5195	0.1403
333.15	-0.1246	-0.4383	-1.4887	1.8486	-1.5292	0.0930
353.15	-0.2296	-0.3768	-2.5982	1.5423	-0.3104	0.0798
373.15	0.1340	-0.6068	-1.6805	1.4339	-0.9238	0.0792

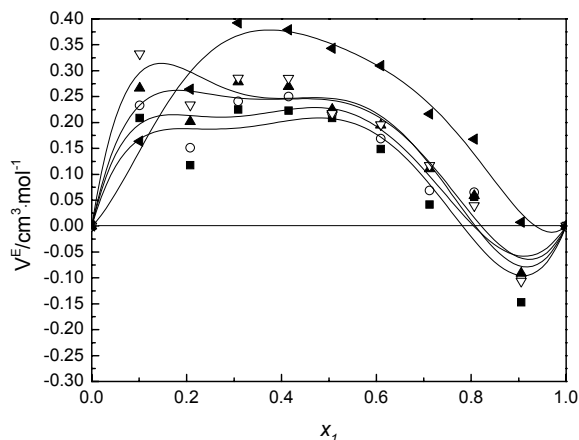
Figures 3 and 4 depict the experimental data and fitted curves obtained by using Redlich-Kister polynomial fits for the excess molar volume at  $T = (293.15, 313.15, 333.15, 353.15$  and  $373.15)$  K.

By definition, an excess property is the difference between the value of a property of solution thermodynamics and the value of this property for an ideal solution under the same PTx (pressure, temperature, and composition) conditions. This difference represents the positive or negative excess, as a function of

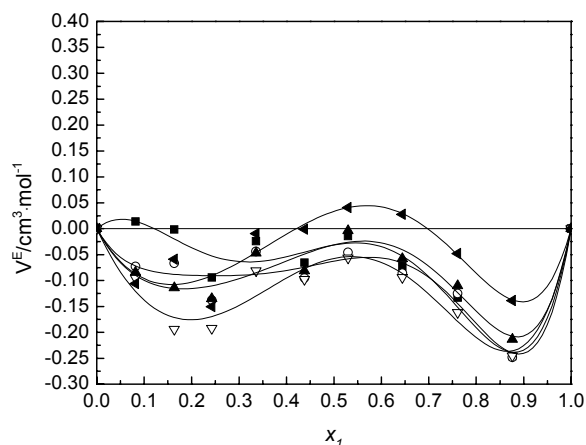
the solution thermodynamics, relative to the ideal solution as reference. The negative excess molar volume can be attributed to strong interactions between different molecules, while a positive excess results from strong interactions between similar molecules.

Figure 3 also indicates that coconut biodiesel + n-hexadecane mixtures present positive  $V^E$  values up to about  $x_1 = 0.80$ . At higher compositions,  $V^E$  values are negative. This behavior indicates the

presence of two distinct regions (an expansion area as well as a region of contraction). Temperature promotes the increased expansive tendencies. On the other hand, the contraction region decreases with an increase in temperature.



**Figure 3:** Excess molar volume for the binary mixture ( $x_1$  coconut biodiesel + n-hexadecane ( $1 - x_1$ )) at the temperatures  $T = (293.15\text{--}373.15)$  K and atmospheric pressure. ■: 293.15 K ○: 313.15 K ▲: 333.15 K ▽: 353.15 K ◀: 373.15 K. Symbols represent the experimental points. Solid curves were calculated by Redlich-Kister polynomial fit.



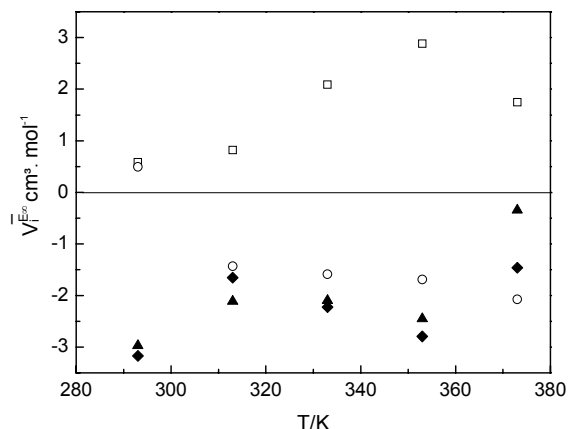
**Figure 4:** Excess molar volume for the binary mixture ( $x_1$  coconut biodiesel + diesel fuel ( $1 - x_1$ )) at the temperatures  $T = (293.15\text{--}373.15)$  K and atmospheric pressure. ■: 293.15 K ○: 313.15 K ▲: 333.15 K ▽: 353.15 K ◀: 373.15 K. Symbols represent the experimental points. Solid curves were calculated by Redlich-Kister polynomial fit.

Figure 4 shows the excess molar volume behavior for coconut biodiesel + diesel mixtures, with a negative trend for most of the composition range, except for  $x_1 = 0.1$  at  $T = 293.15$  K and  $x_1 = 0.5 - 0.7$  at

$T = 373.15$  K, with a tendency to expansion.

It can be seen from the results obtained in this study that the effect of temperature on  $V^E$  for systems containing coconut biodiesel + (n-hexadecane/diesel) presented a diversified behavior. This phenomenon can be attributed to the multicomponent composition of the coconut biodiesel and diesel.

The excess partial volume at infinite dilution ( $V_i^{E\infty}$ ) was calculated by the partial derivative of the excess partial volume of the mixture at  $x_i$  equal to zero. The effect of temperature on the partial excess volume at infinite dilution is shown in Figure 5. As can be seen, the excess partial molar volumes at infinite dilution for n-hexadecane in the coconut biodiesel + n-hexadecane mixtures and diesel in the coconut biodiesel + diesel mixtures are negative for all temperatures analyzed. For coconut biodiesel in the coconut biodiesel + n-hexadecane mixtures, the  $V_i^{E\infty}$  values are positive for all temperatures studied. For coconut biodiesel in the coconut biodiesel + diesel mixtures, the  $V_i^{E\infty}$  values are negative for temperatures above  $T = 313.15$  K.



**Figure 5:** Influence of temperature on the partial excess molar volume at infinite dilution for each compound in binary mixtures. □, coconut biodiesel in the coconut biodiesel + n-hexadecane mixtures; ○, coconut biodiesel in the coconut biodiesel + diesel mixtures; ◆, diesel in the coconut biodiesel + diesel mixtures; ▲, n-hexadecane in the coconut biodiesel + n-hexadecane mixtures.

From the results obtained, it can be seen that n-hexadecane was not able to satisfactorily represent conventional diesel in the study of excess molar volume of the mixture with coconut biodiesel because n-hexadecane had behavior different from mixtures containing diesel.

## CONCLUSIONS

This work reports experimental density ( $\rho$ ) data for the pseudo-binary systems coconut biodiesel + n-hexadecane and coconut biodiesel + diesel at  $T = (293.15, 313.15, 333.15, 353.15 \text{ and } 373.15) \text{ K}$  and atmospheric pressure. Increasing the temperature from  $T = (293.15 \text{ to } 373.15) \text{ K}$  decreases the values of density ( $\rho$ ) for mixtures. From these data excess molar volumes ( $V^E$ ) were calculated. The pseudo-binary mixtures studied presented positive and negative values of  $V^E$ . The  $V^E$  data were correlated satisfactorily using the Redlich–Kister equation. From these data it could be stated that there are systematic differences between the use of diesel when compared to n-hexadecane, with a deviation of 7-9% for pure compounds and about 5% for mixtures. In fact, readers should be warned that the use of n-hexadecane as a representative molecule for diesel could represent important errors, especially if these density and derived properties are intended to be used in project design. Mesquita *et al.* (2012) previously described a similar behavior for a transport property (viscosity).

## ACKNOWLEDGMENTS

The authors are grateful to the CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brazil), CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brazil) and FUNCAP (Fundação Cearense de Apoio ao Desenvolvimento Científico e Tecnológico).

## NOMENCLATURE

$A_j$	adjustment parameter in the Redlich-Kister equation
$B_0, B_1$	constants specific for a temperature
$k$	degree of the polynomial expansion
$M_i$	molar mass of component $i$
$n$	number of experimental points
$p$	number of parameters
$T$	temperature
$V_{adj}^E$	excess molar volume based on adjusted data
$V_{exp}^E$	excess molar volume based on experimental data
$V^E$	excess molar volume

$w$	mass fraction
$x_i$	mole fraction of component $i$

## Greek Letters

$\rho$	density
$\sigma$	standard deviation
$\varphi$	volume fraction

## REFERENCES

- Ali, A., Nain, A. K., Lal, B., Chand, D., Densities, viscosities, and refractive indices of binary mixtures of benzene with isomeric butanols at 30 °C. *Int. J. Thermophys.*, 25, 1835-1847 (2004).
- Alptekin, E. and Canakci, M., Determination of the density and the viscosities of biodiesel– diesel fuel blends. *Renewable Energy*, 33, 2623- 2630 (2008).
- ASTM D86-05, Standard test method for distillation of petroleum products at atmospheric pressure. Philadelphia (2005).
- Baroutian, S., Aroua, M. K., Raman, A. A. A., Sulaiman, N. M. N., Density of palm oil-based methyl ester. *J. Chem. Eng. Data*, 53, 877-880 (2008).
- Baroutian, S., Aroua, M. K., Raman, A. A. A., Sulaiman, N. M. N., Densities of ethyl esters produced from different vegetable oils. *J. Chem. Eng. Data*, 53, 2222-2225 (2008).
- Besbes, R., Ouerfelli, N., Latrous, H., Density, dynamic viscosity, and derived properties of binary mixtures of 1,4 dioxane with water at  $T = 298.15 \text{ K}$ . *J. Mol. Liq.*, 145, 1-4 (2009).
- Brazilian Regulatory Agency (Standard Resolution No. 7, de 19.3.2008), <[http://www.anp.gov.br/petro/legis\\_biodieselp](http://www.anp.gov.br/petro/legis_biodieselp)>. (In Portuguese). (Accessed: February 15, 2013).
- Ceriani, R., Paiva, F. R., Gonçalves, C. B., Batista, E. A. C., Meirelles, A. J. A., Densities and viscosities of vegetable oils of nutritional value. *J. Chem. Eng. Data*, 53, 1846-1853 (2008).
- Feitosa, F. X., Rodrigues, M. L., Veloso, C. B., Cavalcante, C. L., Albuquerque, M. C. G., de Sant'Ana, H. B., Viscosities and densities of binary mixtures of coconut + colza and coconut + soybean biodiesel at various temperatures. *J. Chem. Eng. Data*, 55, 3909-3914 (2010).
- Knothe, G. and Van Gerpen, J. H., *The Biodiesel Handbook*. 2nd Ed., AOCS Publishing, Urbana (2009).
- Mesquita, F. M. R., Feitosa, F. X., Santiago, R. S., de Sant'Ana, H. B., Density, excess volumes and



- partial volumes of binary mixtures of soybean biodiesel + diesel and soybean biodiesel + n-hexadecane at different temperatures and atmospheric pressure. *J. Chem. Eng. Data*, 56, 153-157 (2011).
- Mesquita, F. M. R., Feitosa, F. X., do Carmo, F. R., Santiago, R. S., de Sant'Ana, H. B., Viscosities and viscosity deviations of binary mixtures of biodiesel + petrodiesel (or n-hexadecane) at different temperatures. *Braz. J. Chem. Eng.*, 29(3), 653-664 (2012).
- Nain, A. K., Chandra, P., Pandey, J., Gopal, S., Densities, refractive indices, and excess properties of binary mixtures of 1,4-dioxane with benzene, toluene, o-xylene, m-xylene, p-xylene, and mesitylene at temperatures from (288.15 to 318.15) K. *J. Chem. Eng. Data*, 53, 2654-2665 (2008).
- Nogueira, Jr. C. A., Carmo, F. R., Santiago, D. F., Nogueira, V. M., Fernandes, F. A. N., Santiago, R. S. A., de Sant'Ana, H. B., Viscosities and densities of ternary blends of diesel + soybean biodiesel + soybean oil. *J. Chem. Eng. Data*, 57, 3233-3241 (2012).
- Nogueira, Jr. C. A., Feitosa, F. X., Fernandes, F. A. N., Santiago, R. S. A., de Sant'Ana, H. B., Densities and viscosities of binary mixtures of babassu biodiesel + cotton seed or soybean biodiesel at different temperatures. *J. Chem. Eng. Data*, 55, 5305-5310 (2010).
- Parente, R. C., Nogueira, Jr. C. A., do Carmo, F. R., Lima, L. P., Fernandes, F. A. N., Santiago, R. S. A., de Sant'Ana, H. B., Excess Volumes and deviations of viscosities of binary blends of sunflower biodiesel + diesel and fish oil biodiesel + diesel at various temperatures. *J. Chem. Eng. Data*, 56, 3061-3067 (2011).
- Redlich, O. and Kister, A. T., Algebraic representation of thermodynamics properties and the classification of solutions. *Ind. Eng. Chem.*, 40, 345-348 (1948).