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Thermophysical properties of biodiesel and related systems: Low-pressure vapour–liquid equilibrium of methyl/ethyl *Jatropha curcas* biodiesel

Josamaique G. Veneral [a], Dirceu L.R. Junior [a], Marcio A. Mazutti [b], Fernando A.P. Voll [c], Lúcio Cardozo-Filho [c], Marcos L. Corazza [d], J. Vladimir Oliveira [a,e,*]

[a] *Department of Food Engineering, URI – Campus de Erechim, Erechim, RS 99700-000, Brazil*
[b] *Department of Chemical Engineering, UFSM, Santa Maria, RS 97105-900, Brazil*
[c] *Department of Chemical Engineering, UEM, Maringá, PR 87020 900, Brazil*
[d] *Department of Chemical Engineering, UFPR, Curitiba, PR 81531-990, Brazil*
[e] *Department of Chemical and Food Engineering, UFSC, Florianópolis, SC 88040-900, Brazil*

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ABSTRACT

Biodiesel production from non-edible oils has been considered in recent years due to their economic, politics and environmental aspects. Vapour–liquid equilibrium data for the pseudo-binary and pseudo-ternary systems involving fatty acid methyl/ethyl esters from *Jatropha curcas* oil were determined over the pressure range from (6.7 to 66.7) kPa in an Othmer-type ebulliometer. All systems presented non-ideal behaviour and positive deviations from Raoult's law. It was observed that the addition of up to 10 wt.% of alcohol (methanol or ethanol) promoted a significant decrease in the boiling point temperatures for the evaluated systems. The UNIQUAC model was used to correlate the experimental values, with good agreement between experiment and model results.

1. Introduction

The major part of energy consumed worldwide comes from fossil sources (petroleum, coal and natural gas). However, these resources are limited, and will be exhausted near future [1]. Besides, the petrochemical industry is associated with numerous environmental damage as crude oil occasionally spills, leaving waste and toxic effluents in addition to the contamination of groundwater by gasoline and its additives. Then, the vision of an alternative source of energy like biodiesel is of vital importance.

Biodiesel, as an alternative fuel, has many promises attractive and merits. It is derived from a renewable, domestic resource, besides relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favourable combustion emission profile, such as low carbon monoxide emissions, particulate matter and unburned hydrocarbons. Carbon dioxide produced from biodiesel combustion can be recycled by photosynthesis, thereby minimizing the impacts on the greenhouse effect [2,3].

However, the low volatility of the biodiesel is responsible for ignition delay, poorer atomization and combustion problems in diesel engines [4,5]. Thus, vapour pressure and boiling point data are considered as key parameters to establish properties for biodiesel fuel because they are intrinsically related to the volatility of a component and have played a vital role in quality control of petroleum based diesel fuel (D2) industry. In this sense, Guo *et al.* [6,7] obtained vapour pressure data for binary mixtures of (sunflower ethyl biodiesel + ethanol) and (sunflower methyl biodiesel + ethanol), respectively.

Nevertheless, the production of biodiesel from edible oils is less attractive due to economics, politics and environmental aspects. In this sense, *Jatropha curcas* stands out for being a multipurpose species with many attributes and considerable potential [8].

In this context, the present work is focused on the boiling temperature measurements for the pseudo-binary systems (methanol/ethanol + fatty acid methyl/ethyl esters) (FAME/FAEE) from *Jatropha curcas* oil. Also, pseudo-ternary systems of (FAME/FAEE + methanol/ethanol + glycerol) and (FAME/FAEE + methanol/ethanol + water) were measured using an Othmer-type ebulliometer [9,10]. The experimental results were correlated using the UNIQUAC model.

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* Corresponding author at: Department of Food Engineering, URI - Campus de Erechim, Erechim, RS 99700-000, Brazil. Tel.: +55 48 37212508; fax: +55 48 37219687.

E-mail address: vladimir@enq.ufsc.br (J.V. Oliveira).

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2. Experimental

2.1. Materials

Jatropha curcas pulp oil, kindly donated by Biotins Energia Company (Brazil-TO), and deionised water were used as reagents without previous treatment, while other components used in this work are described in table 1.

2.2. Transesterification method and apparatus

Transesterification reactions were carried out following the procedure described in the work of Mazutti *et al.* [11]. Before trans-esterifications reaction, acid esterification reactions were carried out to reduce the fatty acid content so as not to affect negatively the alkali-catalysed trans-esterification of the oil, providing a final acid value always smaller than 0.5 mg · KOH/g. Then, trans-esterifications were accomplished with the final content of *Jatropha curcas* FAME and FAEE employed in the experiments of (99.2 and 98.8) wt.%, respectively, and fatty acid chemical profile presented in the work of Silva *et al.* [12].

2.3. Ebulliometric Method

Determination of VLE data was performed according to the dynamic method of vapour phase circulation using an Othmer-type ebulliometer. The boiling points were obtained at several pressures ranging from (6.7 to 66.7) kPa, with an uncertainty of ±0.05 kPa. Details regarding the experimental procedure, apparatus, amount of each component used for VLE measurements, steady-state conditions and reliability of the present methodology are given in reference [9]. Boiling point data for the systems (methanol + glycerol) and (ethanol + glycerol) were taken from Veneral *et al.* [9] while those for (methanol + water) and (ethanol + water) were taken from Soujanya *et al.* [13] and Gmegling and Onken [14], respectively.

3. Thermodynamic modelling

Experimental VLE data obtained in this work were correlated using the UNIQUAC model [15]. As before, to estimate the interaction parameters of the activity coefficient model, FAME and FAEE from *Jatropha curcas* oil were considered as a pseudo-pure (one) component [11,12]. Considering the major fatty acids present in *Jatropha curcas* oil [12], the average molar mass resulted in (291.3 and 305.4) g · mol^{-1}, for FAME and FAEE, respectively. The values of r and q of the UNIQUAC model are reported in [9,12], which were calculated using the parameters R_k and Q_k reported by Magnussen *et al.* [16].

The Antoine equation was used in this work for the estimation of vapour pressure for methanol, ethanol, glycerol and water, with constants taken from Veneral *et al.* [9]. Due to the working temperature limit of the ebulliometer used in the present work, boiling data of pure biodiesel could not be obtained. However the biodiesel (mixture de FAME or FAEE) could be regarded as a near-ideal solution [17] and therefore the vapour pressure of biodiesel could be estimated according to Yuan *et al.* [5] through the following equation:

$$P_i^{Sat} = \sum_{es}^{NC} P_{es}^{Sat} \cdot x_m^i, \tag{1}$$

where P_i^{Sat} is the saturation pressure of biodiesel i, P_{es}^{Sat} is the saturation pressure of FAME or FAEE (ester) present in biodiesel i, and x_m^i is the mole fraction of molecule m in the pseudo-component i. The value of P_{es}^{Sat} was calculated through the Antoine equation using the constants A, B and C reported by Yuan *et al.* [5] and Silva *et al.* [18] for FAME and FAEE, respectively.

$$\lg P_{es}^{Sat} = A - \frac{B}{T/K + C}, \tag{2}$$

where T is the temperature of system and A, B and C are adjustable parameters to each component i.

The binary interaction parameters of UNIQUAC model were fitted based on the minimization of the following objective function:

$$OF(T) = \sum_{i}^{NP} (T_i^{\text{calc}} - T_i^{\text{exp}})^2 \tag{3}$$

TABLE 1
Provenance and purity of the compounds employed in this work.

Component	Manufacturer	Minimum mole fraction purity
Methanol	Merck	0.999
Ethanol	Merck	0.999
Glycerol	Nuclear	0.995
Sodium hydroxide	Quimex	0.970

TABLE 2
Boiling point temperature data for the {FAME (1) + methanol (2)} binary system.[a]

p = 6.7 kPa		p = 13.3 kPa		p = 20.0 kPa		p = 26.7 kPa	
w_2[b]	T/K[c]	w_2	T/K	w_2	T/K	w_2	T/K
0.025	297.95	0.025	313.55	0.025	324.25	0.025	333.35
0.050	288.65	0.050	302.25	0.050	311.05	0.050	318.05
0.075	286.25	0.075	298.65	0.075	307.25	0.075	313.95
0.100	285.05	0.100	296.85	0.100	305.05	0.100	311.25
0.200	283.15	0.200	294.75	0.200	302.75	0.200	308.75
0.300	283.05	0.300	294.45	0.300	302.35	0.300	308.25
0.400	282.95	0.400	294.35	0.400	302.15	0.400	307.95
0.500	282.85	0.500	294.25	0.500	302.15	0.500	307.95
0.600	282.85	0.600	294.15	0.600	302.05	0.600	307.85
0.700	282.75	0.700	294.05	0.700	301.95	0.700	307.75
0.800	282.65	0.800	293.95	0.800	301.75	0.800	307.65
0.900	282.65	0.900	293.85	0.900	301.65	0.900	307.55
1.000	282.55	1.000	293.75	1.000	301.45	1.000	307.35
p = 33.3 kPa		p = 40.0 kPa		p = 46.7 kPa		p = 53.3 kPa	
w_2	T/K	w_2	T/K	w_2	T/K	w_2	T/K
0.025	339.45	0.025	344.65	0.025	348.95	0.025	354.45
0.050	323.75	0.050	327.75	0.050	331.85	0.050	335.55
0.075	319.25	0.075	323.85	0.075	327.85	0.075	331.45
0.100	316.25	0.100	320.25	0.100	323.95	0.100	327.15
0.200	313.55	0.200	317.55	0.200	321.05	0.200	324.05
0.300	312.95	0.300	316.85	0.300	320.25	0.300	323.25
0.400	312.75	0.400	316.65	0.400	320.05	0.400	323.05
0.500	312.65	0.500	316.55	0.500	319.85	0.500	322.85
0.600	312.45	0.600	316.35	0.600	319.65	0.600	322.65
0.700	312.35	0.700	316.25	0.700	319.55	0.700	322.55
0.800	312.15	0.800	316.05	0.800	319.35	0.800	322.35
0.900	312.05	0.900	315.95	0.900	319.25	0.900	322.25
1.000	311.85	1.000	315.75	1.000	319.05	1.000	322.05
p = 60.0 kPa		p = 66.7 kPa					
w_2	T/K	w_2	T/K				
0.025	357.95	0.025	360.75				
0.050	338.35	0.050	342.55				
0.075	334.75	0.075	337.55				
0.100	330.25	0.100	332.95				
0.200	327.05	0.200	329.65				
0.300	326.15	0.300	328.75				
0.400	325.75	0.400	328.35				
0.500	325.55	0.500	328.15				
0.600	325.35	0.600	327.95				
0.700	325.15	0.700	327.75				
0.800	324.95	0.800	327.55				
0.900	324.85	0.900	327.35				
1.000	324.65	1.000	327.25				

[a] Estimated standard error of 1.2%.
[b] w_2 denotes the mass fraction of component 2 in the liquid phase.
[c] T, system temperature.