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# 1 Phase equilibria of mixtures involving fatty acid ethyl esters and 2 fat alcohols between 4 and 27 kPa for bioproduct production

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5  
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11

## 12 **Abstract**

13 The aim of this paper is to bring valuable phase equilibria information for the design  
14 and operation of biolubricant and related biofuel product processes. As a result, Vapor-Liquid  
15 Equilibrium (VLE) measurements, at different temperatures, pressures and global  
16 compositions, for the ternary systems [Ethanol + 2-Ethyl-1-hexanol + 1-Dodecanol] and  
17 [Ethanol + 1-Octanol + 1-Dodecanol], as well as a multicomponent system containing these  
18 alcohols together with *Balanites aegyptiaca* fatty acid ethyl esters are reported for the first  
19 time (data pressure and temperature ranges: 4394-26790 Pa, 306-423 K). The Dortmund  
20 modified UNIFAC model showed very high accuracy in the prediction of these VLE, with  
21 overall average absolute deviations on the liquid and vapor molar compositions of 0.007 and  
22 0.0003 for the ternary systems, 0.003 and 0.006 for the multicomponent system.

23

24 **Keywords:** Vapor-liquid equilibria; Multicomponent systems; Ebulliometry; Dortmund  
25 modified UNIFAC; Biodiesel; Biolubricants

## 26 **1. Introduction**

27 Biomass harnessing in accordance with the biorefinery and green circular economy  
28 concepts to generate energy carriers and high value-added products from conversion  
29 technologies satisfying the eco-design, eco-energy and eco-materials criteria is an essential  
30 environmental, economic and social issue [1,2]. Production of biodiesel and biolubricants  
31 from non-edible oilseed plants by reactive distillation using transesterification as conversion  
32 route is such an illustration [2,3]. Indeed, first, this class of biomass does not bring about  
33 indirect land use change and even often contributes to soil improvement (erosion prevention  
34 or biofumigation). It also offers a wide range of applications beneficial for human and his  
35 environment by using all the biomass (pharmaceuticals, feed, biopesticides...) [1,2,4].  
36 Second, the other possible oil conversion routes into biolubricants (through estolide formation  
37 or epoxidation followed by acetylation) are economically less favorable than  
38 transesterification that can be used to produce both bioproducts successively (with biodiesel  
39 being a precursor of biolubricants) [3,5,6]. Third, thanks to its intensification, reactive  
40 distillation offers significant savings in terms of material and energy consumed and effluents  
41 produced [2,7]. Lastly, besides reducing dependence on fossil resources and environmental  
42 footprint thanks to their biodegradability, biodiesel and biolubricants also improve the  
43 economic and social development of a country through employment opportunities and the  
44 required education upstream [2,7,8].

45 Compared to the commonly commercialized methyl biodiesel, ethyl biodiesel has  
46 better biodegradability, higher flash point, improved cold-flow properties and oxidation  
47 stability, and lower emissions of NO<sub>x</sub>, CO, and ultrafine particles [9,10]; not to mention the  
48 possibility of integrating the ethanol fermentation industry into the production process of  
49 biodiesel and biolubricants (by using ethanol and fusel oil respectively) [3,8]. Moreover,  
50 biolubricants whose fatty acid group is esterified with long-chain alcohol such as 2-ethyl-1-

51 hexanol, 1-octanol, or even 1-dodecanol exhibit excellent lubricating characteristics,  
52 especially for metalworking applications [2,3,5]. Non-edible oils with high amounts of oleic  
53 and linoleic acids (30-40% each) and much lower level of linolenic acid, such as oils from  
54 *Balanites aegyptiaca* (BA), cottonseeds, or Indian mustard seeds, are considered optimal for  
55 producing biofuel and biolubricants exhibiting a good balance between thermal-oxidative  
56 stability, viscosity and cold-flow properties [2,6,11].

57 Robust process simulation of biolubricants production from biodiesel requires  
58 quantitative and reliable information about the vapor-liquid equilibria (VLE) of mixtures  
59 containing alcohols and fatty acid esters, as well as the liquid-liquid and vapor-liquid-liquid  
60 equilibria with the presence of glycerol, and eventually water, when dealing with the  
61 preliminary biodiesel production step [7,12,13]. Nevertheless, despite the recently published  
62 extensive work on phase equilibria involved in biodiesel production [7,13,14], VLE  
63 information for the biolubricant production operating under low pressure is still lacking. As  
64 an illustration, **Table 1** [12,15-20] gives an overview of the low-pressure VLE related to  
65 biodiesel components that were published over the past 10 years. No similar information was  
66 found for biolubricants.

67 Accordingly, this paper aims to provide complete experimental VLE data for mixtures  
68 of relevance for the biolubricant and related biofuel industries. Besides, the predictive  
69 capabilities of a thermodynamic model implemented in most commercial process simulators  
70 have been evaluated over the investigated ternary and multicomponent mixtures, containing  
71 BA oil ethyl esters (BAEEs) and/or fat alcohols, such as 2-ethyl-1-hexanol, 1-octanol, or 1-  
72 dodecanol. It is shown that the phase equilibria behavior of the reaction mixture at the start of  
73 the BAEE transesterification, leading to the BA oil biolubricant, can be accurately described.

74

75

## 76 **2. Material and Methods**

77

### 78 *2.1 Chemicals and BAEs production*

79 The description of the chemicals used in this study as internal standards, solvent, or  
80 ternary system formulation is given in **Table 2**. The BAEs were produced in a batch stirred  
81 tank reactor according to Nitièma-Yefanova et al. procedure ((i) two-stage transesterification  
82 with intermediary addition of glycerol after 30 min of reaction, the whole carried out for 50  
83 min at 35 °C and 1 atm, with 1.0 wt% potassium hydroxide as the catalyst and ethanol to oil  
84 molar ratio equal to 8; (ii) dry-purification using 4 wt% of rice husk ash as adsorbent under 35  
85 °C, for 20 min) [21,22]). Lastly, a vacuum distillation (180-200 °C; 10 mbar) was carried out  
86 to obtain a high-grade BAE mixture (composition and details of the analysis given in  
87 **Supplementary Material**, respectively **SM1** and **SM2** [23]).

88

### 89 *2.2 VLE experiments and procedure*

90 The VLE experiments were carried out in an all-glass ebulliometer, operating between  
91 1 and 100 kPa, with dynamic recirculation of the vapor and liquid phases helping to reach  
92 more quickly the equilibrium conditions in addition to the Cottrell pump (model EEA 3000,  
93 Pignat, France) [24]. Similar devices have proven to be performant for yielding VLE  
94 measurements of high level [25,26]. A detailed description of the ebulliometer of which a  
95 schematic diagram is provided in **Figure 1** is available in the paper by Muhammad et al. [12].  
96 The uncertainties on the measured temperature and pressure are, respectively,  $\pm 0.01$  K and  $\pm$   
97  $0.013$  kPa ( $\pm 0.1$  mmHg). These were determined, prior to any VLE experiment series, by  
98 checking the calibration of the ebulliometer sensors using an external reference thermometer  
99 and measuring the vapor pressure of ethanol, selected as a reference compound, over a wide  
100 temperature range. The composition of the vapor and liquid phases were determined by gas-  
101 chromatography coupled with a flame ionization detector (GC-FID 7820, Agilent

102 Technology, USA). Details of the equipment, operating conditions, and calibration are given  
103 in [Supplementary Material \(SM2\) \[23\]](#). All compositional analyzes were performed by  
104 using three internal standards (one specific for the BAEs, one different for short, and another  
105 for fat alcohols; [SM2](#)). Thus, for the GC-FID calibration, standard solutions of well-known  
106 composition were prepared by weighing the components of the studied system (with ethyl  
107 oleate as a surrogate of the BAEs), and the required IS(s). Performance of the GC-FID  
108 calibration was then checked by analyzing the composition of supplementary standard  
109 solutions and was used to estimate the mole fraction uncertainty:  $\pm 0.002$  for the ternary  
110 systems,  $\pm 0.004$  for the multicomponent system.

111       Regarding the procedure for generating the VLE measurements, the liquid mixture of  
112 well-known composition (prepared by weighing the required amounts of pure alcohols and/or  
113 BAEs) was loaded into the ebulliometer until complete filling the reboiler (total liquid  
114 volume poured: around 120 mL). After reaching the selected set-point pressure under  
115 vigorous mixing, the heating power was adjusted to observe a satisfactory boiling: 1 drop per  
116 second for the condensed vapor phase, a semi-continuous flowrate for the liquid phase. When  
117 the equilibrium state was reached (commonly after 1 to 1.5 h of recirculating for the ternary  
118 mixtures, 3 to 3.5 h for the multicomponent mixtures), the temperature and pressure were  
119 noted down, and samples were collected for quantification, starting first with the global  
120 mixture (via the mixing cell septum) and then dealing with simultaneously the liquid and  
121 condensed vapor phases (via the tubes placed in the sampling ports). The equilibrium state  
122 was identified when steady temperature and pressure were observed for the selected set-point  
123 pressure, leading then to assume that the composition of both the liquid and vapor phases  
124 were also constant. After withdrawing for GC-FID analysis the required amount of liquid  
125 from the collected samples, these were re-introduced into the ebulliometer (via the mixing cell  
126 septum) to keep approximatively the same mixture global composition. Subsequently, this

127 procedure was repeated for higher set-point pressures by adjusting both the heating power and  
128 the total amount of liquid inside the ebulliometer to maintain a satisfactory boiling. While the  
129 heating power required to be increased, a supplementary volume of liquid needed to be  
130 introduced in the ebulliometer (allowing thus operating at nearly constant volume during  
131 subsequent experiments). This additional liquid (introduced via the loading funnel) was: (i)  
132 for the ternary systems, the mixture initially loaded in the ebulliometer (or the C8-alcohol for  
133 the highest pressures); (ii) for the multicomponent system, the ternary mixture [Ethanol + 2-  
134 Ethyl-1-hexanol + 1-Dodecanol] of well-known composition (in order to induce a significant  
135 change in the global composition of the investigated system, without nonetheless perturbing  
136 the equilibrium state of the ebulliometer radically).

137

### 138 *2.3 VLE modeling*

139         Given the large number of components present in the reaction mixture during the  
140 transesterification of biodiesel into biolubricant (over 10 typically), the resulting lack of  
141 information regarding the VLE data for each of the binaries involved, the highly non-ideal  
142 thermodynamic behavior of these mixtures, and the operating conditions of the production  
143 process (low pressure), the excess Gibbs energy ( $G^E$ ) models based on the group contribution  
144 (GC) concept are the most appropriate. Indeed, cubic equations of state with GC-estimated  
145 binary interaction parameters were applied successfully to systems involving molecules similar  
146 to biodiesel or biolubricants, but under moderate to high-pressures with supercritical carbon  
147 dioxide [27-29]. Among the  $G^E$ -GC approaches, namely original UNIFAC [30] and its  
148 variants (Lyngby modified UNIFAC [31], Dortmund modified UNIFAC [32-34], linear  
149 UNIFAC [35]), the regularly updated Dortmund modified UNIFAC model [32-34] was  
150 selected as it has yielded excellent VLE predictions for complex mixtures involving ethyl

151 esters and alcohols [12,14,36]. Accordingly, the implicit  $\gamma$ - $\phi$  approach leads to express the  
 152 vapor-liquid equilibrium condition by:

$$153 \quad x_i \cdot \gamma_i(T, x) \cdot P_i^s(T) = P \cdot y_i \cdot \mathfrak{S}_i(T, P, y) \quad (1a)$$

$$154 \quad \text{with } \mathfrak{S}_i(T, P, y) = \frac{\phi_i^V(T, P, y)}{\phi_i^*(T, P_i^s)} \cdot \exp\left(\frac{1}{RT} \cdot \int_P^{P_i^s} v_{i,L}^*(T, P) dP\right). \quad (1b)$$

155 In this expression,  $x_i$  ( $y_i$ ) refers to the mole fraction of component  $i$  in the liquid (vapor)  
 156 phase;  $\gamma_i$  ( $\phi_i^V$ ) denotes the activity (fugacity) coefficient of component  $i$  in the liquid (vapor)  
 157 phase of composition  $x$  ( $y$ ), temperature  $T$  and pressure  $P$ ;  $P_i^s$ ,  $\phi_i^*$  and  $v_{i,L}^*$  are specific to the  
 158 pure component  $i$  and refer respectively to its vapor pressure, fugacity coefficient, and liquid  
 159 molar volume. Being concerned with low pressure VLEs of mixtures with no molecular  
 160 association in the vapor phase, the latter was assumed perfect (so  $\phi_i^*(T, P_i^s) = 1$  and  
 161  $\phi_i^V(T, P, y) = 1$ ), leading to set  $\mathfrak{S}_i(T, P, y) = 1$ . While the activity coefficients  $\gamma_i$  were  
 162 estimated by the Dortmund modified UNIFAC model (UNIFAC-Do), the vapor pressures  $P_i^s$   
 163 were evaluated according to the following equation:

$$164 \quad \ln(P_i^s / Pa) = A_i + \frac{B_i}{(T / K)} + C_i \cdot \ln(T / K) + D_i \cdot (T / K)^{E_i} \quad (2)$$

165 of which values of coefficients  $A_i$  to  $E_i$ , were taken from the DIPPR database [37] for all the  
 166 pure components investigated. Values of these coefficient together with the component  
 167 decomposition into UNIFAC structural groups are given in **Supplementary Material (SM3**  
 168 **and SM4**, respectively; [30,32-34,38,39]). Thus, it was possible to calculate the compositions  
 169 of the liquid and vapor phases at a given temperature, pressure, and global composition for  
 170 each investigated mixture.

171

172



### 173 3. Results and Discussion

174

175 The comparisons between the experimental and estimated values of the vapor and  
176 liquid phase compositions (at a given temperature, pressure, and global composition of the  
177 considered mixture) were performed in terms of various deviations described in **Table 3**.

178

#### 179 3.1 Ternary systems

180 For each of the two ternary systems investigated, five VLE data sets were measured  
181 for pressure and temperature ranging respectively: (i) from 13574 to 26790 Pa and 317 to 332  
182 K regarding system [Ethanol + 2-Ethyl-1-hexanol + 1-Dodecanol]; (ii) from 7051 to 23657 Pa  
183 and 306 to 332 K regarding system [Ethanol + 1-Octanol + 1-Dodecanol]. This information,  
184 as well as the relating predictions obtained with the UNIFAC-Do model, were gathered in  
185 **Tables 4 and 5**, and **Figure 2**, the last displaying additionally the deviations per component ( $AAD_i$ )  
186 and per data set ( $AAD_k$ ).

187 Not surprisingly, on the basis of the accuracy depicted by the UNIFAC-Do model for  
188 the binaries [Ethanol + 2-Ethyl-1-hexanol] and [Ethanol + 1-Octanol] (**Supplementary**  
189 **Material, SM4 [30,32-34,38,39]**), predictions obtained for both ternary systems are in very  
190 good agreement with the experimental data ( $AAD_k(x) \leq 0.012$ ; **Figure 2**); even excellent  
191 regarding the vapor phase for which the observed deviations are much lower than the  
192 experimental uncertainty (i.e., 0.001). **Figure 2** also shows that the deviations on the liquid  
193 phase composition are somewhat randomly distributed, although the poorest results are  
194 obtained for ethanol while remaining acceptable ( $AAD_i(x) \leq 0.015$ ). Globally, the deviations  
195 obtained for the two ternary systems are  $AAD_{overall}(x) = 0.007$  and  $AAD_{overall}(y) = 0.0003$ ,  
196 which is remarkable considering the structural specificities of these mixtures, both on the

197 entropic and enthalpic aspects (molecules different in shape and size, with additionally cross-  
198 associations).

199

### 200 3.2. Multicomponent systems

201 The investigated system contains 10 components, i.e., the BAEEs with ethanol, 2-  
202 ethyl-1-hexanol, 1-octanol, and 1-dodecanol. In total, 15 VLE data sets were measured for  
203 this system at various global compositions, for pressures and temperatures ranging from 4394  
204 to 10270 Pa and 360 to 423 K, respectively. These measurements, together with the  
205 corresponding predictions obtained with the UNIFAC-Do model, were gathered in **Table 6**,  
206 and **Figure 3** displays additionally the deviations per component ( $AAD_i$ ) and per data set ( $AAD_k$ ).  
207 More pronounced deviations are observed compared to the ternary systems,  
208 particularly for the vapor phase compositions, which are now predicted by the UNIFAC-Do  
209 model with much less accuracy than the liquid phase compositions. Nonetheless, the overall  
210 deviations remain very acceptable for both phases:  $AAD_{overall}(x) = 0.003$  and  
211  $AAD_{overall}(y) = 0.006$ . These results are likely due to the large amounts of alcohols in the  
212 vapor phase for these multicomponent mixtures, particularly ethanol, which was already the  
213 poorest represented among the substances studied in the ternary systems previously  
214 investigated (here for ethanol:  $AAD_i(y) = 0.05 \max$ ). Furthermore, in the liquid phase, the  
215 cross-association involved by the alcohols might be mitigated by the presence of the BAEEs,  
216 although the mixture studied here also contains a structural complexity on the entropic aspect  
217 with molecules differing in size and shape. These two aspects can be realized looking at the  
218 activity coefficients in the **SM5** section (**Supplementary Material**) [32-34]. Moreover, the  
219 deviations on the liquid and vapor phase compositions are rather randomly distributed,  
220 particularly at the lowest pressure (4394 Pa), for which the very good prediction results are  
221 worthy of being stressed ( $AAD_k(x) \leq 0.002$  and  $AAD_k(y) \leq 0.005$ , for all data sets measured at

222 4394 Pa). Lastly, let mention that, in that case, the assumption of the ideal liquid solution  
223 yields rougher predictions of the liquid and vapor phase compositions ( $AAD_k(x)$  and  
224  $AAD_k(y)$  up to 0.004 and 0.008, respectively), with a deviation on the vapor mole fraction  
225  $AAD_i(y)$  up to four times larger for ethanol (which agrees with the bad results obtained when  
226 assuming the ideal liquid solution for the investigated ternaries involving alcohols;  
227 [Supplementary Material, SM5](#)). At higher temperatures, the activity coefficients are closer  
228 to one, and consequently, for the system [Alcohols + BAEs], better predictions are found  
229 assuming ideality.

230

#### 231 **4. Conclusions**

232

233 VLE measurements, at different temperatures, pressures, and global compositions, for  
234 the ternary systems [Ethanol + 2-Ethyl-1-hexanol + 1-Dodecanol] and [Ethanol + 1-Octanol +  
235 1-Dodecanol], as well a multicomponent system containing these alcohols together with  
236 *Balanites aegyptiaca* fatty acid ethyl esters are reported for the first time. The Dortmund  
237 modified UNIFAC model showed very high accuracy in the prediction of these VLE, with  
238 overall average absolute deviations on the liquid and vapor molar compositions of 0.007 and  
239 0.0003, respectively, for the ternary systems, and 0.003 and 0.006 for the multicomponent  
240 systems. The VLE experiments and modelling carried out in this work bring valuable  
241 information for the design and operation of bioproduct production processes under low  
242 pressures.

243

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249

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390

## TABLES

391

392 **Table 1.** Overview of the low-pressure VLE information related to biodiesel components

393 published over the past 10 years (no similar information was found for biolubricants).

System	T/K range	P/MPa range	Experimental technique	Modeling information	Ref.
Ethanol + Ethyl stearate	313-419	0.017-0.098	Dynamic ebulliometry (recirculation	NRTL, UNIQUAC	[15]
Ethanol + Ethyl palmitate	309-422	0.0150-9.300	of only the vapor phase)	and UNIFAC-Do	
Ethyl palmitate + Ethyl stearate	502-520	0.0053	Differential scanning calorimetry	Wilson, NRTL	[16]
Ethyl palmitate + Ethyl oleate	502-537	0.0053; 0.0093		and UNIQUAC	
Ethyl palmitate + Ethyl linoleate	514-537	0.0093			
Ethyl myristate + Ethyl palmitate	420-443	0.0005;	Dynamic ebulliometry (recirculation	NRTL, original	[17]
	435-458	0.0010;	of both the vapor and liquid phases)	UNIFAC,	
	444-468	0.0015		UNIFAC-Do	
Methyl myristate + Methyl linoleate	467-511	0.00533;	Differential scanning calorimetry	NRTL, UNIQUAC	[18]
Methyl palmitate + Methyl linoleate	491-511	0.00533			
<i>Jatropha</i> ethyl esters <sup>a</sup> + Ethanol + Water	296-342	0.0067-0.0667;	Dynamic ebulliometry (recirculation	UNIQUAC	[19]
<i>Jatropha</i> ethyl esters <sup>a</sup> + Ethanol + Water	283-329	0.0067-0.0667;	of only the vapor phase)		
Soybean methyl esters <sup>a</sup> + Methanol	283-365	0.0067-0.0667;	Dynamic ebulliometry (recirculation	UNIQUAC	[20]
Soybean ethyl esters <sup>a</sup> + Ethanol	295-386	0.0067-0.0667;	of only the vapor phase)		
Soybean methyl esters <sup>a</sup> + Methanol + Glycerol	283-328	0.0067-0.0667;			
Soybean ethyl esters <sup>a</sup> + Ethanol + Glycerol	296-341	0.0067-0.0667			
1-Octanol + 1-Dodecanol + <i>Balanites</i>	448-471	0.0080-0.0120	Dynamic ebulliometry (recirculation	CPA, NRTL,	[12]
<i>aegyptiaca</i> ethyl esters (Ethyl- palmitate +			of both the vapor and liquid phases)	UNIFAC-Do	
Ethyl stearate + Ethyl oleate + Ethyl cis-					
vaccenate + Ethyl linoleate + Ethyl arachidate)					

394 <sup>a</sup> The mixture of fatty acid ethyl esters was considered as a pseudo-pure component, both for

395 the experimental study and modeling.

396

397 **Table 2.** Description of the chemicals used in this study (as internal standards, solvent or for  
 398 ternary systems synthesis).

Chemical name	CAS	Source	Purity/mass %
Ethanol	64-17-5	Sigma Aldrich	$\geq 99.8$
1-Butanol	71-36-3	Fluka	$\geq 99.5$
2-Ethyl-1-hexanol	104-76-7	Sigma Aldrich	$\geq 99.0$
1-Octanol	111-87-5	Sigma Aldrich	$\geq 99$
1-Decanol	112-30-1	Fluka	$\geq 99.5$
1-Dodecanol	112-53-8	Sigma Aldrich	$\geq 98$
Ethyl oleate	111-62-6	Sigma Aldrich	$\geq 98$
Methyl heptadecanoate	1731-92-6	Fluka	$\geq 99$
n-Heptane	142-82-5	Sigma Aldrich	$\geq 99$

399

400 **Table 3.** Expressions of the deviations used in this work.

Definition	Expression	
<ul style="list-style-type: none"> <li>• Deviation between the experimental and calculated liquid (vapor) mole fractions of component <math>i</math> for the data set <math>k</math></li> </ul>	$\Delta x_i = x_i^{k,exp} - x_i^{k,cal}$	1a
	$(\Delta y_i = y_i^{k,exp} - y_i^{k,cal})$	1b
<ul style="list-style-type: none"> <li>• Average absolute deviation between the experimental and calculated liquid (vapor) mole fractions for component <math>i</math> over all the <math>N_{sets}</math> data sets</li> </ul>	$AAD_i(x) = \sum_{k=1}^{N_{sets}}  \Delta x_i  / N_{sets}$	2a
	$(AAD_i(y) = \sum_{k=1}^{N_{sets}}  \Delta y_i  / N_{sets})$	2b
<ul style="list-style-type: none"> <li>• Average absolute deviation between the experimental and calculated liquid (vapor) mole fractions for the data set <math>k</math> over all the <math>N_C</math> components of the mixture</li> </ul>	$AAD_k(x) = \sum_{i=1}^{N_C}  \Delta x_i  / N_C$	3a
	$(AAD_k(y) = \sum_{i=1}^{N_C}  \Delta y_i  / N_C)$	3b
<ul style="list-style-type: none"> <li>• Overall average absolute deviation between the experimental and calculated liquid (vapor) mole fractions over all the mixture <math>N_C</math> components and all the <math>N_{sets}</math> data sets</li> </ul>	$AAD_{overall}(x) = \sum_{k=1}^{N_{sets}} \left( \sum_{i=1}^{N_C}  \Delta x_i  / N_C \right) / N_{sets}$	4a
	$(AAD_{overall}(y) = \sum_{k=1}^{N_{sets}} \left( \sum_{i=1}^{N_C}  \Delta y_i  / N_C \right) / N_{sets})$	4b

401



402 **Table 4.** Experimental VLE data and predictions by the UNIFAC-Do model for the ternary system [Ethanol (1) + 2-Ethyl-1-hexanol (2) +  
403 1-Dodecanol (3)] (are given at different pressures and temperatures: the molar compositions of the global mixture ( $z$ ) and of the liquid ( $x$ ) and  
404 vapor ( $y$ ) phases in equilibrium, as well as the deviations between the experimental and predicted mole fractions of each component in the liquid  
405 (vapor) phase  $\Delta x_i$  ( $\Delta y_i$ ) as defined in **Table 3**; the experimental uncertainties  $u$  are:  $u(T) = 0.01$  K,  $u(P) = 0.013$  kPa,  $u(x_i) = u(y_i) = 0.002$ ).

Component	Set 1 P (Pa) = 13574; T (K) = 317.48					Set 2 P (Pa) = 16878; T (K) = 321.98				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.5917	0.5579	0.9972	0.0088	-0.0003	0.5895	0.5627	0.9969	0.0147	-0.0002
2-Ethyl-1-hexanol	0.2727	0.2901	0.0028	-0.0109	0.0003	0.2749	0.2927	0.0031	-0.0099	0.0002
1-Dodecanol	0.1356	0.1520	0.0000	0.0022	0.0000	0.1356	0.1446	0.0000	-0.0048	0.0000
Component	Set 3 P (Pa) = 20182; T (K) = 325.67					Set 4 P (Pa) = 23486; T (K) = 328.97				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.5847	0.5450	0.9965	-0.0056	-0.0003	0.5843	0.5452	0.9962	-0.0050	-0.0002
2-Ethyl-1-hexanol	0.2783	0.3047	0.0035	0.0037	0.0003	0.2786	0.3046	0.0038	0.0033	0.0003
1-Dodecanol	0.1370	0.1503	0.0000	0.0019	0.0000	0.1371	0.1502	0.0000	0.0018	0.0000
Component	Set 5 P (Pa) = 26790; T (K) = 332.06									
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$					
Ethanol	0.5753	0.5415	0.9960	-0.0039	0.0000					
2-Ethyl-1-hexanol	0.2845	0.3070	0.0040	0.0026	0.0001					
1-Dodecanol	0.1401	0.1515	0.0000	0.0014	0.0000					

406

407

408 **Table 5.** Experimental VLE data and predictions by the UNIFAC-Do model for the ternary system [Ethanol (1) + 1-Octanol (2) +  
409 1-Dodecanol (3)] (are given at different pressures and temperatures: the molar compositions of the global mixture ( $z$ ) and of the liquid ( $x$ ) and  
410 vapor ( $y$ ) phases in equilibrium, as well as the deviations between the experimental and predicted mole fractions of each component in the liquid  
411 (vapor) phase  $\Delta x_i$  ( $\Delta y_i$ ) as defined in **Table 3**; the experimental uncertainties  $u$  are:  $u(T) = 0.01$  K,  $u(P) = 0.013$  kPa,  $u(x_i) = u(y_i) = 0.002$ ).

Component	Set 1 P (Pa) = 7051; T (K) = 306.44					Set 2 P (Pa) = 10372; T (K) = 313.74				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.5488	0.4881	0.9989	-0.0096	-0.0001	0.5478	0.5091	0.9988	0.0097	0.0002
1-Octanol	0.2777	0.3152	0.0011	0.0062	0.0001	0.2780	0.3006	0.0012	-0.0071	-0.0001
1-Dodecanol	0.1736	0.1967	0.0000	0.0034	0.0000	0.1742	0.1903	0.0000	-0.0026	0.0000
Component	Set 3 P (Pa) = 13693; T (K) = 319.34					Set 4 P (Pa) = 17014; T (K) = 323.64				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.5437	0.4797	0.9988	-0.0187	0.0004	0.5374	0.4889	0.9989	-0.0154	0.0008
1-Octanol	0.2804	0.3198	0.0012	0.0116	-0.0004	0.2843	0.3101	0.0011	0.0055	-0.0007
1-Dodecanol	0.1759	0.2005	0.0000	0.0071	0.0000	0.1783	0.2010	0.0000	0.0099	0.0000
Component	Set 5 P (Pa) = 23657; T (K) = 332.04									
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$					
Ethanol	0.5043	0.4552	0.9985	-0.0187	0.0012					
1-Octanol	0.3049	0.3350	0.0015	0.0115	-0.0012					
1-Dodecanol	0.1908	0.2098	0.0000	0.0072	0.0000					

412

413

414 **Table 6.** Experimental VLE data and predictions by the UNIFAC-Do model for the multicomponent systems [Alcohols + BAEs] (are given at  
415 different pressures and temperatures: the molar compositions of the global mixture ( $z$ ) and of the liquid ( $x$ ) and vapor ( $y$ ) phases in equilibrium,  
416 as well as the deviations between the experimental and predicted mole fractions of each component in the liquid (vapor) phase  $\Delta x_i$  ( $\Delta y_i$ ) as  
417 defined in **Table 3**; the experimental uncertainties  $u$  are:  $u(T) = 0.01$  K,  $u(P) = 0.013$  kPa,  $u(x_i) = u(y_i) = 0.004$ ).

Component	Set 1 P (Pa) = 10270; T (K) = 416.93					Set 2 P (Pa) = 10270; T (K) = 418.73				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.0178	0.0058	0.2164	0.0038	0.0414	0.0167	0.0000	0.1987	-0.0017	0.0463
2-Ethyl-1-hexanol	0.2624	0.2381	0.6174	0.0138	-0.0238	0.2570	0.2281	0.6324	0.0146	-0.0175
1-Octanol	0.0535	0.0505	0.0947	0.0014	-0.0026	0.0530	0.0492	0.0951	0.0015	-0.0060
1-Dodecanol	0.4211	0.4390	0.0710	-0.0159	-0.0132	0.4310	0.4475	0.0733	-0.0208	-0.0208
Ethyl Palmitate	0.0397	0.0419	0.0004	-0.0017	-0.0001	0.0409	0.0428	0.0005	-0.0025	-0.0002
Ethyl Stearate	0.0297	0.0313	0.0000	-0.0013	-0.0002	0.0305	0.0320	0.0000	-0.0018	-0.0002
Ethyl Oleate	0.0786	0.0834	0.0000	-0.0031	-0.0008	0.0802	0.0853	0.0000	-0.0037	-0.0009
Ethyl Cis-Vaccenate	0.0019	0.0020	0.0000	-0.0001	0.0000	0.0019	0.0020	0.0000	-0.0001	0.0000
Ethyl Linoleate	0.0946	0.1071	0.0000	0.0031	-0.0007	0.0880	0.1121	0.0000	0.0144	-0.0008
Ethyl Arachidate	0.0008	0.0008	0.0000	-0.0001	0.0000	0.0008	0.0008	0.0000	-0.0001	0.0000

Component	Set 3 P (Pa) = 10270; T (K) = 420.93					Set 4 P (Pa) = 10270; T (K) = 421.93				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.0167	0.0000	0.1601	-0.0014	0.0281	0.0149	0.0000	0.1586	-0.0013	0.0331
2-Ethyl-1-hexanol	0.2523	0.2156	0.6578	0.0168	0.0142	0.2424	0.2020	0.6419	0.0102	-0.0116
1-Octanol	0.0524	0.0473	0.0993	0.0018	-0.0054	0.0510	0.0453	0.1047	0.0010	-0.0011
1-Dodecanol	0.4368	0.4576	0.0823	-0.0232	-0.0245	0.4410	0.4655	0.0942	-0.0160	-0.0178
Ethyl Palmitate	0.0415	0.0441	0.0005	-0.0029	-0.0003	0.0420	0.0451	0.0006	-0.0020	-0.0002
Ethyl Stearate	0.0310	0.0330	0.0000	-0.0021	-0.0002	0.0314	0.0337	0.0000	-0.0015	-0.0003
Ethyl Oleate	0.0813	0.0877	0.0000	-0.0043	-0.0010	0.0826	0.0897	0.0000	-0.0029	-0.0011
Ethyl Cis-Vaccenate	0.0019	0.0021	0.0000	-0.0001	0.0000	0.0020	0.0021	0.0000	-0.0001	0.0000
Ethyl Linoleate	0.0851	0.1117	0.0000	0.0153	-0.0008	0.0919	0.1157	0.0000	0.0126	-0.0009
Ethyl Arachidate	0.0008	0.0009	0.0000	-0.0001	0.0000	0.0008	0.0009	0.0000	0.0000	0.0000

Component	Set 5 P (Pa) = 10270; T (K) = 423.02					Set 6 P (Pa) = 6966; T (K) = 360.02				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.0140	0.0000	0.1303	-0.0012	0.0151	0.0728	0.0524	0.9429	0.0191	0.0521
2-Ethyl-1-hexanol	0.2381	0.1944	0.6514	0.0092	-0.0035	0.2781	0.2830	0.0509	-0.0041	-0.0412
1-Octanol	0.0504	0.0441	0.1088	0.0009	0.0014	0.0544	0.0559	0.0054	-0.0006	-0.0064
1-Dodecanol	0.4458	0.4711	0.1087	-0.0161	-0.0103	0.3854	0.3986	0.0008	-0.0051	-0.0045
Ethyl Palmitate	0.0426	0.0459	0.0007	-0.0020	-0.0001	0.0360	0.0372	0.0000	-0.0005	0.0000
Ethyl Stearate	0.0318	0.0343	0.0000	-0.0015	-0.0003	0.0268	0.0278	0.0000	-0.0003	0.0000
Ethyl Oleate	0.0836	0.0912	0.0000	-0.0028	-0.0011	0.0703	0.0724	0.0000	-0.0013	0.0000
Ethyl Cis-Vaccenate	0.0020	0.0022	0.0000	-0.0001	0.0000	0.0017	0.0017	0.0000	-0.0001	0.0000
Ethyl Linoleate	0.0909	0.1159	0.0000	0.0136	-0.0010	0.0738	0.0702	0.0000	-0.0071	0.0000
Ethyl Arachidate	0.0008	0.0009	0.0000	0.0000	0.0000	0.0007	0.0007	0.0000	0.0000	0.0000

Component	Set 7 P (Pa) = 6966; T (K) = 377.29					Set 8 P (Pa) = 6966; T (K) = 404.65				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.0509	0.0223	0.7739	0.0068	0.0490	0.0158	0.0000	0.2244	-0.0019	0.0401
2-Ethyl-1-hexanol	0.2860	0.2890	0.2002	0.0001	-0.0302	0.2759	0.2463	0.6252	0.0014	-0.0260
1-Octanol	0.0560	0.0569	0.0206	-0.0005	-0.0087	0.0557	0.0518	0.0921	-0.0007	-0.0020
1-Dodecanol	0.3975	0.3989	0.0053	-0.0187	-0.0098	0.4220	0.4374	0.0579	-0.0138	-0.0108
Ethyl Palmitate	0.0371	0.0371	0.0000	-0.0020	-0.0001	0.0398	0.0415	0.0003	-0.0015	-0.0001
Ethyl Stearate	0.0277	0.0276	0.0000	-0.0015	0.0000	0.0300	0.0310	0.0000	-0.0014	-0.0001
Ethyl Oleate	0.0721	0.0735	0.0000	-0.0024	-0.0001	0.0777	0.0826	0.0000	-0.0015	-0.0006
Ethyl Cis-Vaccenate	0.0017	0.0018	0.0000	0.0000	0.0000	0.0018	0.0020	0.0000	0.0000	0.0000
Ethyl Linoleate	0.0703	0.0922	0.0000	0.0183	-0.0001	0.0805	0.1066	0.0000	0.0195	-0.0004
Ethyl Arachidate	0.0007	0.0007	0.0000	0.0000	0.0000	0.0008	0.0008	0.0000	-0.0001	0.0000

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Component	Set 9 P (Pa) = 6966; T (K) = 404.85					Set 10 P (Pa) = 6966; T (K) = 405.95				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.0160	0.0078	0.2191	0.0061	0.0421	0.0171	0.0000	0.1996	-0.0018	0.0216
2-Ethyl-1-hexanol	0.2787	0.2511	0.6321	0.0060	-0.0262	0.2683	0.2382	0.6404	0.0062	-0.0091
1-Octanol	0.0557	0.0523	0.0924	0.0001	-0.0022	0.0546	0.0508	0.0965	0.0002	0.0006
1-Dodecanol	0.4141	0.4308	0.0560	-0.0137	-0.0124	0.4274	0.4447	0.0631	-0.0161	-0.0117
Ethyl Palmitate	0.0390	0.0408	0.0003	-0.0016	-0.0001	0.0404	0.0424	0.0004	-0.0018	-0.0001
Ethyl Stearate	0.0296	0.0305	0.0000	-0.0017	-0.0001	0.0302	0.0317	0.0000	-0.0014	-0.0001
Ethyl Oleate	0.0768	0.0810	0.0000	-0.0025	-0.0006	0.0789	0.0841	0.0000	-0.0022	-0.0006
Ethyl Cis-Vaccenate	0.0018	0.0019	0.0000	0.0000	0.0000	0.0019	0.0020	0.0000	-0.0001	0.0000
Ethyl Linoleate	0.0876	0.1029	0.0000	0.0076	-0.0005	0.0806	0.1053	0.0000	0.0170	-0.0005
Ethyl Arachidate	0.0008	0.0008	0.0000	-0.0001	0.0000	0.0008	0.0008	0.0000	0.0000	0.0000

Component	Set 11 P (Pa) = 4394; T (K) = 400.12					Set 12 P (Pa) = 4394; T (K) = 402.92				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.0216	0.0050	0.1477	0.0039	-0.0137	0.0040	0.0000	0.0416	-0.0003	-0.0056
2-Ethyl-1-hexanol	0.2473	0.1767	0.6839	-0.0093	0.0182	0.2268	0.1880	0.7500	0.0050	0.0155
1-Octanol	0.0378	0.0309	0.0841	-0.0012	0.0074	0.0468	0.0419	0.1161	0.0006	0.0049
1-Dodecanol	0.4317	0.4876	0.0840	0.0064	-0.0101	0.4357	0.4624	0.0917	-0.0019	-0.0128
Ethyl Palmitate	0.0398	0.0457	0.0004	0.0001	-0.0001	0.0436	0.0467	0.0005	-0.0006	-0.0001
Ethyl Stearate	0.0298	0.0342	0.0000	0.0000	-0.0002	0.0326	0.0350	0.0000	-0.0004	-0.0002
Ethyl Oleate	0.0796	0.0913	0.0000	0.0002	-0.0007	0.0871	0.0936	0.0000	-0.0010	-0.0009
Ethyl Cis-Vaccenate	0.0019	0.0022	0.0000	0.0000	0.0000	0.0021	0.0022	0.0000	0.0000	0.0000
Ethyl Linoleate	0.1097	0.1256	0.0000	-0.0001	-0.0007	0.1203	0.1292	0.0000	-0.0014	-0.0009
Ethyl Arachidate	0.0008	0.0009	0.0000	0.0000	0.0000	0.0008	0.0009	0.0000	0.0000	0.0000

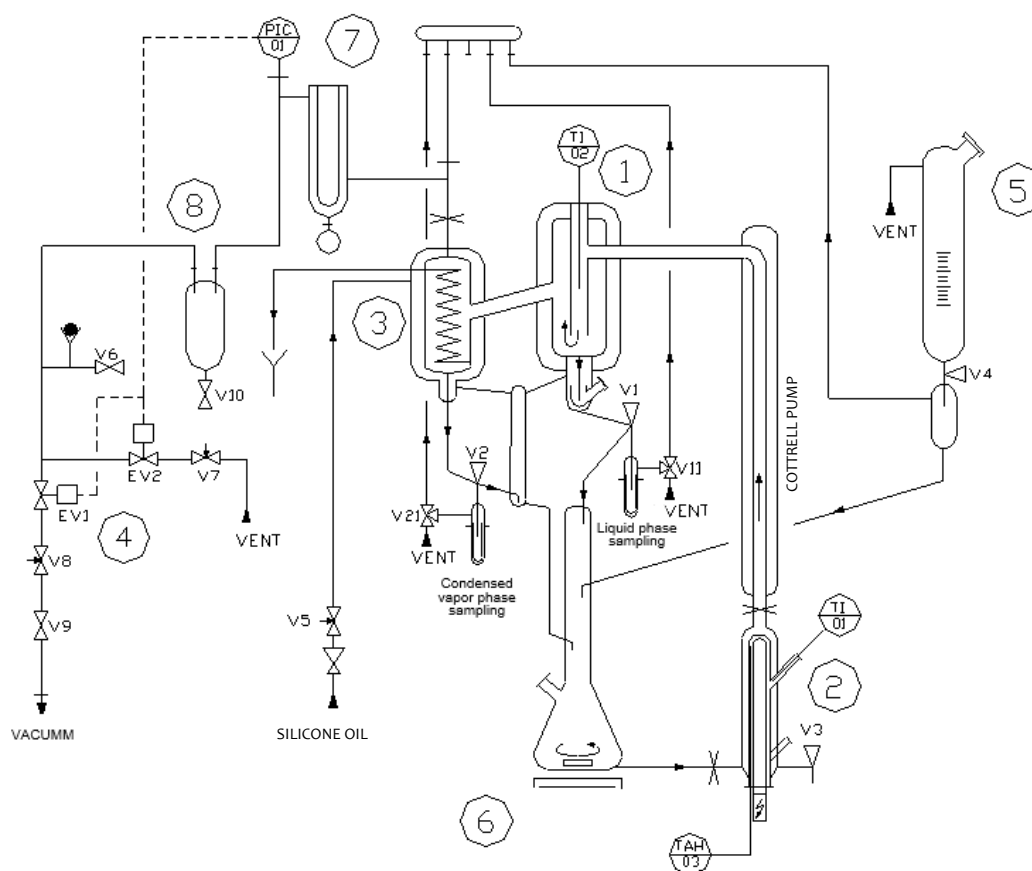
Component	Set 13 P (Pa) = 4394; T (K) = 403.12					Set 14 P (Pa) = 4394; T (K) = 403.12				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.0122	0.0000	0.1073	-0.0007	-0.0036	0.0234	0.0037	0.1293	0.0028	0.0013
2-Ethyl-1-hexanol	0.2217	0.1718	0.6930	0.0036	0.0120	0.2594	0.1665	0.6886	-0.0019	0.0082
1-Octanol	0.0417	0.0355	0.1009	0.0001	0.0047	0.0367	0.0278	0.0808	-0.0004	0.0044
1-Dodecanol	0.4415	0.4792	0.0982	-0.0010	-0.0110	0.4271	0.4989	0.1007	0.0038	-0.0118
Ethyl Palmitate	0.0430	0.0477	0.0006	-0.0003	-0.0001	0.0385	0.0461	0.0005	-0.0006	-0.0001
Ethyl Stearate	0.0322	0.0357	0.0000	-0.0002	-0.0002	0.0289	0.0346	0.0000	-0.0005	-0.0002
Ethyl Oleate	0.0861	0.0955	0.0000	-0.0005	-0.0009	0.0771	0.0923	0.0000	-0.0012	-0.0009
Ethyl Cis-Vaccenate	0.0021	0.0023	0.0000	0.0000	0.0000	0.0018	0.0022	0.0000	0.0000	0.0000
Ethyl Linoleate	0.1187	0.1314	0.0000	-0.0011	-0.0009	0.1063	0.1271	0.0000	-0.0020	-0.0009
Ethyl Arachidate	0.0008	0.0009	0.0000	0.0000	0.0000	0.0008	0.0009	0.0000	0.0000	0.0000

Component	Set 15 P (Pa) = 4394; T (K) = 404.52				
	$z_i$	$x_i$	$y_i$	$\Delta x_i$	$\Delta y_i$
Ethanol	0.0054	0.0000	0.0473	-0.0003	-0.0016
2-Ethyl-1-hexanol	0.2287	0.1764	0.7410	0.0065	0.0142
1-Octanol	0.0437	0.0369	0.1090	0.0005	0.0040
1-Dodecanol	0.4394	0.4749	0.1021	-0.0027	-0.0142
Ethyl Palmitate	0.0430	0.0474	0.0006	-0.0006	-0.0001
Ethyl Stearate	0.0322	0.0355	0.0000	-0.0004	-0.0002
Ethyl Oleate	0.0860	0.0949	0.0000	-0.0011	-0.0010
Ethyl Cis-Vaccenate	0.0020	0.0023	0.0000	0.0000	0.0000
Ethyl Linoleate	0.1186	0.1307	0.0000	-0.0018	-0.0010
Ethyl Arachidate	0.0008	0.0009	0.0000	0.0000	0.0000

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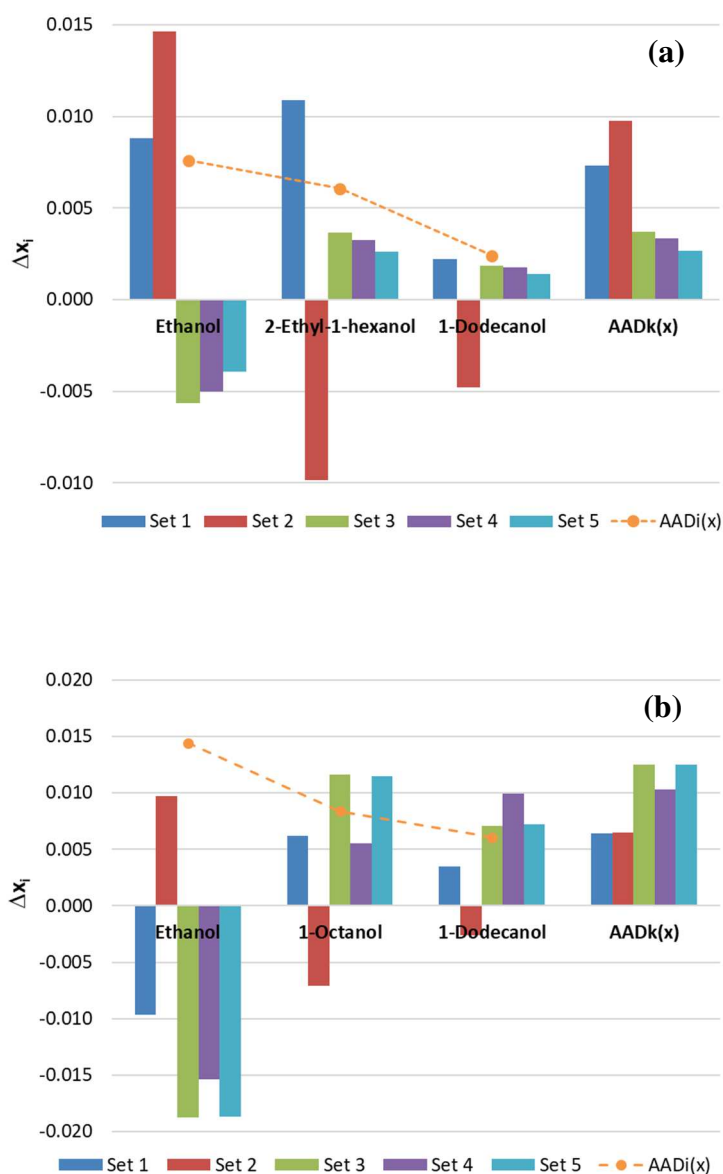


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Number	Description
1	Double envelope adiabatic equilibrium chamber - An optional plug for sampling a potential second liquid phase is also provided
2	Reboiler: electrical resistance placed in a quartz sleeve (maximum power 500 W)
3	Glass condenser (comprising a pipe coil arranged inside a double envelope cell with cooling by circulating silicone oil operating from $-40^{\circ}\text{C}$ up to $205^{\circ}\text{C}$ )
4	Vacuum circuit (comprising pump valves, vent valves, control solenoid valves)
5	Funnel for loading the liquid fluid to be studied (maximum volume $150\text{ cm}^3$ )
6	Mixing cell equipped with a magnetic stirrer - A plug with septum allows for potential sampling
7	Dry ice trap
8	Glass buffer reserve (capacity: 8 L) used for vacuum balancing in order to stabilize the pressure of the device after sampling
V1 (V2)	Valve for sampling the liquid (condensed vapor) phase
V11 (V21)	3-Way valve of vacuum setting the sampling tube of the liquid (condensed vapor) phase
V3; V10	Drain valves of the ebulliometer and of the vacuum buffer reserve 8
V4; V6	Valves of pouring and vent
V5; V7; V8	Condenser cooling oil flow control valve; vent flow control valve; vacuum flow control valve
EV1; EV2	Vacuum control solenoid valve; air inlet regulation solenoid valve

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430 **Figure 1.** Schematic diagram of the dynamic ebulliometer (Pignat Company, France, EEA  
 431 model 3000) [24].



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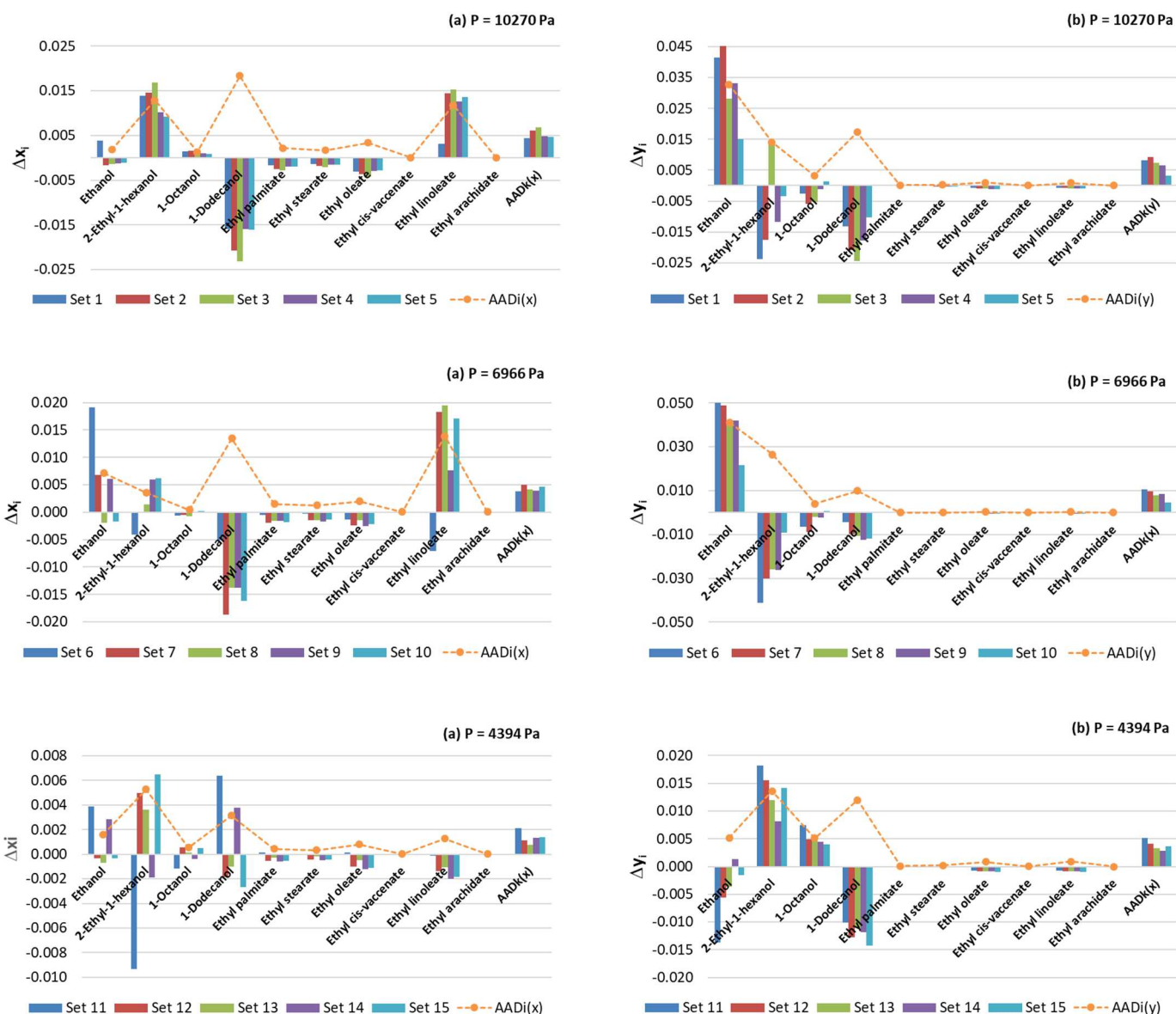
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434

435 **Figure 2.** Deviations between the experimental and predicted liquid mole fractions for the  
 436 ternary systems [Ethanol (1) + 2-Ethyl-1-hexanol (2) + 1-Dodecanol (3)] (a) and [Ethanol (1)  
 437 + 1-Octanol (2) + 1-Dodecanol (3)] (b) (the deviations observed for the vapor mole fractions  
 438 are all below the experimental uncertainty, i.e. 0.001; the predictions are obtained with the  
 439 UNIFAC-Do model [32-34]; the analytical expressions of the deviations are given in **Table**  
 440 **3**).

441





442 **Figure 3.** Deviations between the experimental and predicted mole fractions in the liquid (a)  
 443 or in the vapor (b) phase in equilibrium for the multicomponent system [Alcohols + BAEEs]  
 444 at different temperatures and pressures (predictions obtained with UNIFAC-Do model [32-  
 445 34]; see Table 3 for the analytical expressions of the deviations).

446

# Phase equilibria of mixtures involving fatty acid ethyl esters and fat alcohols between 4 and 27 kPa for bioproduct production

## Graphical abstract

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