

# **BINARIES AND TERNARIES PHASE DIAGRAMS FOR MIXTURES OF OIL, ALCOHOL AND CO<sub>2</sub>**

Arvelos, S., Watanabe, E. O., Hori, C. E., Romanielo\*, L. L.  
Av. João Naves de Ávila, 2121, Bloco 1K, Faculdade de Engenharia Química, Universidade Federal de  
Uberlândia, CEP38408-144 Uberlândia, MG, Brazil; lucienne@ufu.br Fax +55 34 3239 4249

## **ABSTRACT**

The production of biodiesel by supercritical route has the advantages of promoting a better contact between the reagents leading to good conversions in short time when comparing with the traditional transesterification route. In addition, the supercritical route has the ability of accepting lower quality oils. However, one of the problems with of supercritical route is the high pressure and temperature involved to allow the presence of a single phase, along the reaction. The addition of carbon dioxide is an efficient method for producing a single phase in lower critical points than those obtained for the pseudo binary mixtures oil/alcohol. In this work, pseudo binary (oil/alcohol mixtures) and pseudo ternary (oil/alcohol/CO<sub>2</sub> mixtures) phase diagrams have been calculated for ten different oils, such as sunflower, palm, and soybean. The most used alcohols: methanol and ethanol; were evaluated. The Peng-Robinson cubic equation in addition with group contribution methods were used. The calculations were performed in a wide range of temperature, pressure and oil/alcohol/carbon dioxide molar ratios. The results showed that only the correct choice of parameters to represent the oils can promote the representation of critical points of these mixtures. It was observed that the addition of CO<sub>2</sub> can promote a reduction up to 4% of the critical temperature of pseudo-binary mixture, when using a molar rate of CO<sub>2</sub>/alcohol equal to 0.4, however it increases the pressure up to 43%.

## **INTRODUCTION**

Biodiesel is a mixture of alkyl esters yield from long chain fatty acids, derived from vegetable oils or animal fats. These feedstock are composed predominantly of molecules called triglycerides (TG). A large number of studies have shown that this fuel may be used in conventional diesel engines [1-2].

Transesterification is a general term used to describe the class of organic reactions by which an ester is transformed into another through exchange of the alkoxy groups. The synthesis of biodiesel by transesterification consists in the transformation of the triglycerides present in vegetables oils and animal fats into fatty acid methyl/ethyl esters (FAME/FAEE) [3-5]. An excess of alcohol is always used to shift the equilibrium of the reaction towards the products and a catalyst is commonly used. [6-8].

In recent years, a non-catalytic biodiesel production route with supercritical alcohol has been developed. Furthermore, according to the literature, transesterification with pressurized solvents provides an increase in solubility between heterogeneous phases, decreasing transport limitations between them, providing higher rates of reaction. Supercritical route provides the elimination of the pre-treatment of oils and fats because there is no sensitivity to water and other contaminants. There is also a simplification of the process of separation of the

products because there is no presence of catalysts [9-10]. Added to all these advantages the fact that conversions around 95-99 % are obtained in very short reaction times [11-12].

Many raw materials such as canola, coconut, corn, cottonseed, jatropha, palm, rice bran, soybean, sunflower and tallow oils have been used to produce biodiesel. These oils are mixtures which are based on seven fatty acids. The references used to determine the free fatty acid content of each oil are reported in Table 1.

Table 1- Reference of free fat acid content used

Reference	oil									
	Canola	Coconut	Corn	Cotton	Jatropha	Palm	Rice	Soybean	Sunflower	Tallow
[13]	[15]	[15]	[15]	[14]	[13]	[16]	[14]	[14]	[15]	[15]
[18]	[22]	[21]	[25]	[23]	[15]	[17]	[15]	[15]	[15]	[25]
[24]	[25]	[24]			[20]		[19]	[18]		

In transesterification reactions of oils under conditions of temperature and pressure above the critical point of the alcohol, the reaction mixture may be in the form of vapor-liquid equilibrium (VLE), the liquid phase being rich in oil and the vapor phase (dense) being rich in alcohol. The presence of 2 phases can limit the mass transfer between them. The solubility of the oil in the supercritical alcohol phase is a keystone for rapid and complete transesterification reactions. [10, 12 ,26-28]. Therefore, it is necessary to investigate the conditions of temperature, pressure and excess reagent required to provide a single supercritical phase, from the beginning to the end of the reaction.

Carbon dioxide has been used as co-solvent aiming to reduce the operational temperature. Sawangkeaw et al. [29] reports that small amounts of CO<sub>2</sub> (0.10 mol) per mol of methanol can result in high conversion at relatively low operating parameters because the co-solvents increase the homogeneity of the system and do not affect the reaction mechanism.

The general goal of this study was to calculate the critical point of the mixtures present in biodiesel production. The evaluation of using pseudo components for the triglycerides mixtures of each feedstock (FS) were made. The critical point of pseudobinary reagent mixture (FS/alcohol) and pseudoternary reagent mixture (FS/alcohol/CO<sub>2</sub>). In this work the methanol (MeOH) and ethanol (EtOH) were tested.

## MATERIALS AND METHODS

To calculate the properties for the different feedstocks tested, it was considered the fatty acid average composition calculated from the references presented in Table 1. In this paper, the properties such as acentric factor, critical temperature, pressure and volume of each triglycerides, were estimated by the best combination gotten in our earlier work that tested various combinations of parameters to represent this molecules in VLE at high pressure with alcohol and CO<sub>2</sub> [30].

All the feedstock tested are a mixture of several triglycerides (Table 2). Despite of that, in this work they were considered a pseudo pure component. Then, their properties were calculated using Lorentz-Berthelot's mixing rules [31].

The Peng-Robinson equation of state with classical mixing rule of Van der Waals were used to evaluate the critical point of the pseudo binaries (FS/MeOH, FS/EtOH)) and ternaries (FS/MeOH/CO<sub>2</sub>, FS/EtOH/CO<sub>2</sub>).

## RESULTS

Table 2 presents the content of fatty acids in the feedstock (FS), evaluated by the average of values presented in the references.

**Table 2.** Average content of fatty acids in vegetable oils (wt.%)

Oil	Free fatty acids							Saturated	Unsaturated
	12:0	14:0	16:0	18:0	18:1	18:2	18:3		
<b>Formula</b>	C <sub>39</sub> H <sub>74</sub> O <sub>6</sub>	C <sub>45</sub> H <sub>86</sub> O <sub>6</sub>	C <sub>51</sub> H <sub>98</sub> O <sub>6</sub>	C <sub>57</sub> H <sub>110</sub> O <sub>6</sub>	C <sub>57</sub> H <sub>104</sub> O <sub>6</sub>	C <sub>57</sub> H <sub>98</sub> O <sub>6</sub>	C <sub>57</sub> H <sub>92</sub> O <sub>6</sub>	-	-
<b>MM</b>	639,01	723,16	807,34	891,48	885,43	879,38	873,34	-	-
Canola	0,00	0,03	5,23	2,27	61,09	20,59	10,78	7,54	92,46
Coconut	53,63	21,81	10,61	4,02	8,26	1,67	0,00	90,06	9,94
Corn	0,00	0,00	13,23	2,34	30,98	52,41	1,04	15,58	84,42
Cotton	0,03	0,50	23,90	2,21	17,08	55,92	0,37	26,64	73,36
Jatropha	0,00	0,05	16,47	4,69	47,20	31,49	0,10	21,21	78,79
Palm	0,20	1,11	43,98	4,46	39,92	10,13	0,20	49,75	50,25
Rice	0,00	0,56	15,28	2,18	44,59	35,93	1,47	18,02	81,98
Soybean	0,00	0,03	11,01	3,84	23,24	54,43	7,44	14,88	85,12
Sunflower	0,00	0,03	6,21	3,38	16,68	73,69	0,00	9,63	90,37
Tallow	0,10	3,18	25,30	20,14	47,63	2,92	0,73	48,72	51,28

Table 3 presents the pure components parameters of triglycerides used in this work, calculated using a combination of methods proposed by[30]: T<sub>c</sub> by Constantinou and Gani method, P<sub>c</sub> and V<sub>c</sub> by Marrero and Gani method and ω by Pitzer rule. It can be noted that the properties for all triglycerides are close, which allows the use of mixing rules for evaluation mixtures of them. The alcohol and CO<sub>2</sub> properties used are presented in Table 4.

**Table 3.** Properties of triglycerides (TG)

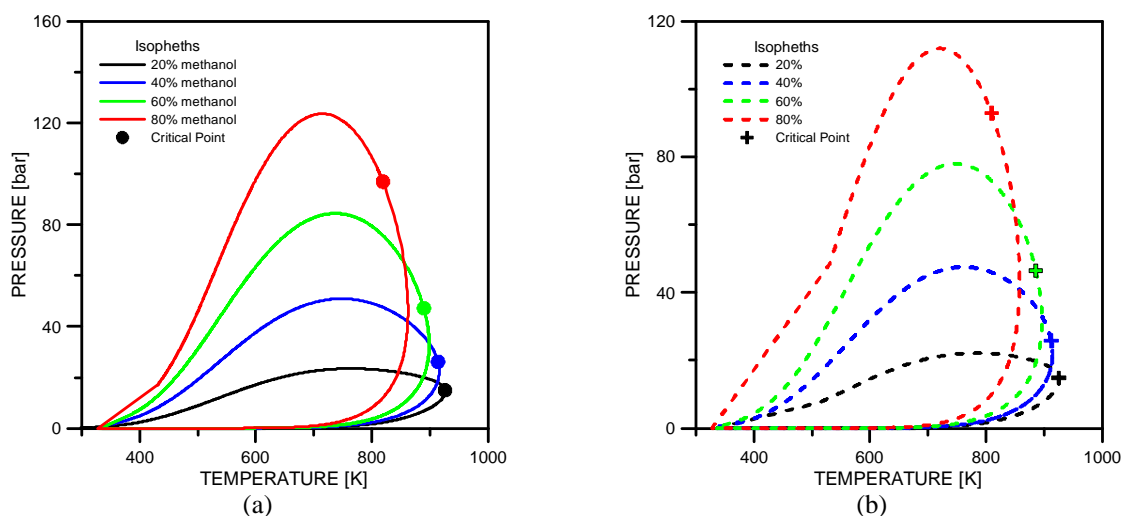
TG	V <sub>c</sub> [cm <sup>3</sup> /mol]	T <sub>c</sub> [K]	P <sub>c</sub> [bar]	ω [-]
Trilaurin	2294,97	915,99	8,39	1,24
Trimyristin	2632,65	938,66	7,88	1,35
Trialmitin	2970,33	958,80	7,52	1,45
Tristearnc	3308,01	976,93	7,25	1,56
Trioleinc	3265,62	977,88	7,28	1,59
Trilinolein	3223,23	978,82	7,32	1,63
Trilinolenin	3180,84	979,76	7,36	1,66

The Figure 1 presents the complete isopheths for the binaries coconut oil/alcohols. The parameters estimated were used in PR-EOS with the van der Waals mixing rule without any adjustable binary parameter.

**Table 4.** Properties of alcohols and CO<sub>2</sub> [32]

Substance	T <sub>c</sub> [K]	P <sub>c</sub> [ bar]	ω [-]	M <sub>w</sub> [kg/kmol]
CO <sub>2</sub>	304,12	73,74	0,225	44,01
Methanol	512,64	80,97	0,565	32,04
Ethanol	513,92	61,48	0,649	46,07

Since the mainly focus of this work is the biodiesel production for the others feedstock it was calculated just the critical locus curves with different molar ratio alcohol/oil (RAO). Figure 3 presents the results.



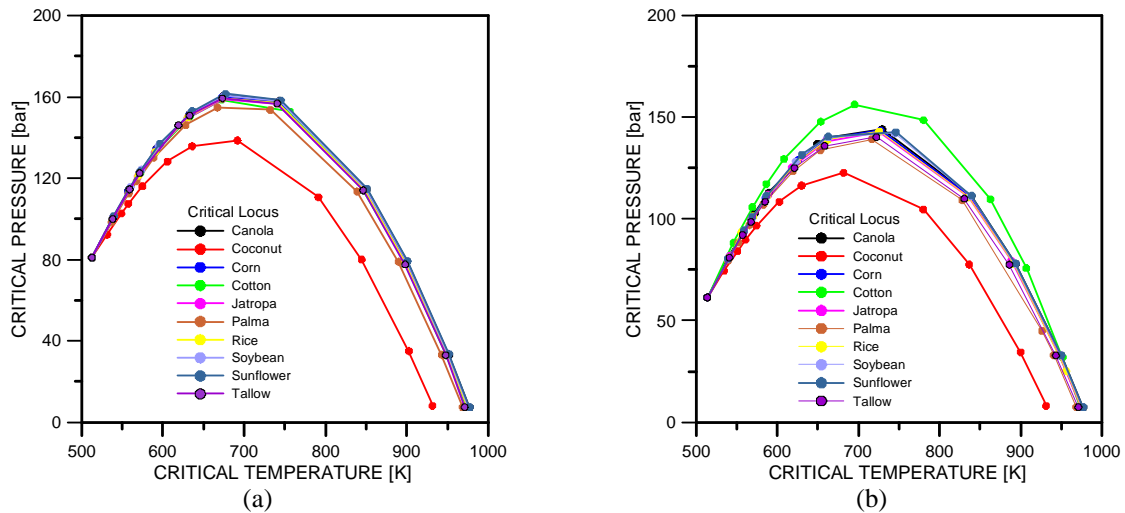
**Figure 1.** Isopheths for: (a)- Coconut oil/Methanol and (b)- Coconut oil/Ethanol.

**Table 5.** Parameters calculated for the feedstock tested

	Feedstock									
	Canola	Coconut	Corn	Cotton	Jatropha	Palm	Rice	Soybean	Sunflower	Tallow
<b>Tc[K]</b>	977,19	932,76	975,73	973,42	974,83	968,71	974,94	976,28	977,28	971,31
<b>Pc[bar]</b>	7,31	8,08	7,34	7,37	7,34	7,40	7,34	7,34	7,33	7,36
<b><math>\omega</math></b>	1,6002	1,3234	1,5926	1,5752	1,5789	1,5272	1,5819	1,6002	1,6092	1,5413

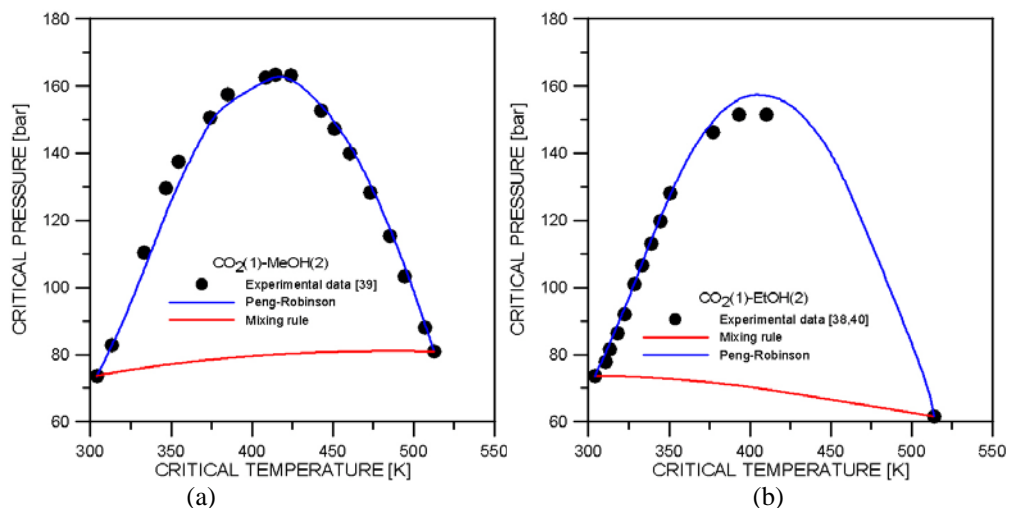
It can be notice that the critical locus for the binary oil-alcohol is quite similar except to for the coconut oil in both alchools. It is probably associated with the percentage of unsaturated triglycerides in the oil. The coconut oil presents the smallest percentage: less then 10%, with the smallest critical temperature among the feedstock tested. The results for the canola, soybean, corn and sunflower oils are virtually identical. All of them have high percentage of unsaturated triglycerides (>84%).

When comparing the results obtained for methyl route, in this work, with those reported by Anikeev et al. [33] it was observed that the choose of the group contribution methods can lead to significative differences in the mixture critical point. For instance these authors reported to the mixture of methanol/corn oil, at molar ratio of 15:1, presents critical point at 728.58 K and 127bar. In this study the critical point found was: 673.01 K and 159.9 bar. It is important to say that the group contribution methods used in this work were those who presented the better performance when used to predict the VLE of triglycerides and alcohols at high pressures.



**Figure 2.** Critical locus for the pseudo binary oil-methanol (a) and oil- ethanol (b). Molar ratios alcohol/oil (RAO): 0, 1, 3, 5, 10, 15, 20, 30, 40, 50, 90 and 100.

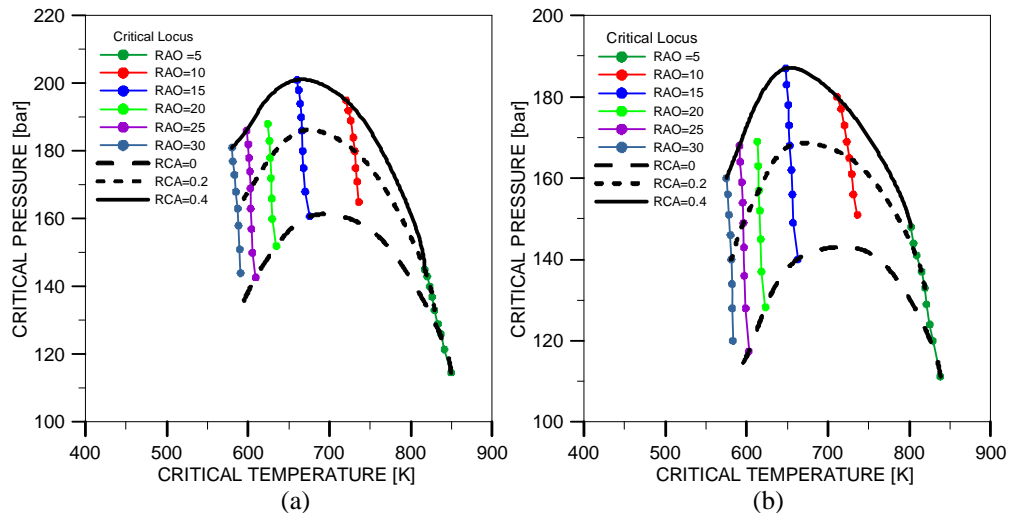
The calculus of critical locus curves of oil/alcohol/ $\text{CO}_2$  can be very hard, since the mixture presents a highly non ideal behavior. To simplify the problem, some author [36, 37] proposed a strategy of considering a binary system, by treating the mixture alcohol/ $\text{CO}_2$  as one component. To verify what will be the impact of using this strategy the evaluation of alcohol/ $\text{CO}_2$  critical locus curve was made in both ways. The first one using the PR-EOS with van der Waals's mixing rule to evaluate the mixture EOS parameters. The second one using the Lorentz-Berthelot's mixing rules [31] to calculate directly the critical properties, as made for the feedstock. The results, presented in Figure 3, were compared with experimental data ([38], [39] and [40]). It can be notice that the use of this approach cannot predict the non ideal behavior presented by this binary. The relative mean deviation found for methanol/ $\text{CO}_2$  were 1.47% and 5% for  $T_c$  and  $P_c$  respectively and 8.30% and 14.87% for ethanol/ $\text{CO}_2$



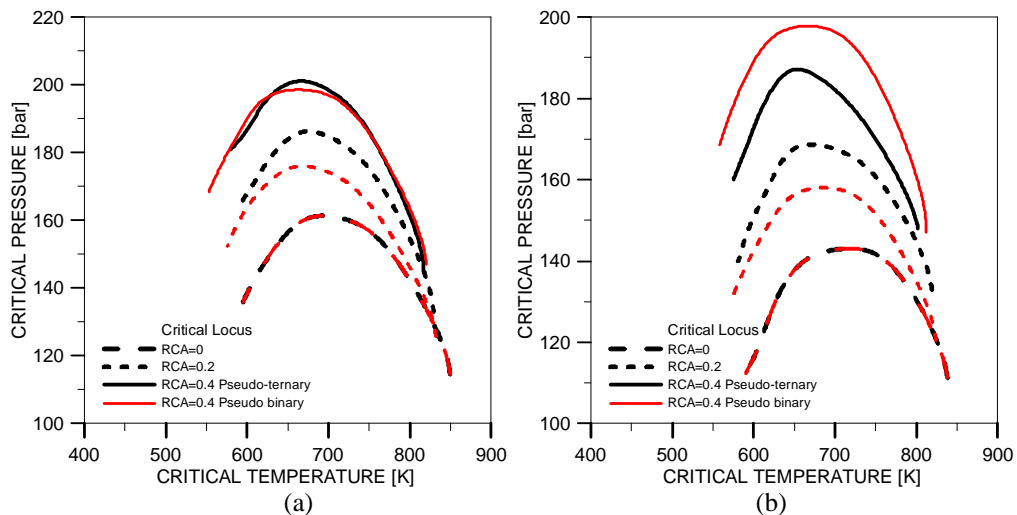
**Figure 3 -** Critical locus for binary  $\text{CO}_2$ -methanol (a) and  $\text{CO}_2$ - ethanol (b).

Since, the critical locus curves of some feedstock are very similar, as showed in the Figure 2, just few feedstock were selected to evaluate the pseudo ternary. The selected feedstock were: (1) soybean oil to represent feedstock with high levels of unsaturated fatty acids (>84%) as the oils of sunflower, canola and corn; (2) coconut oil to represent low level of unsaturated

fatty acids (<10%)); (3) palm oil to represent intermediate unsaturated fatty acids (>10% and <84%) as the tallow. The Figure 4 presents the results obtained for the pseudo ternary mixtures (FS/alcohol/CO<sub>2</sub>), using the PR-EOS with the van der Waals mixing rule to evaluate de EOS parameters and the Figure 5 presents a comparison with the results obtained when considering the CO<sub>2</sub>+alcohol a pseudo component, as proposed by [36, 37]. It can be notice that for the highest molar ratio CO<sub>2</sub>/alcohol (RCA) were observed the major differences in temperature and pressure.

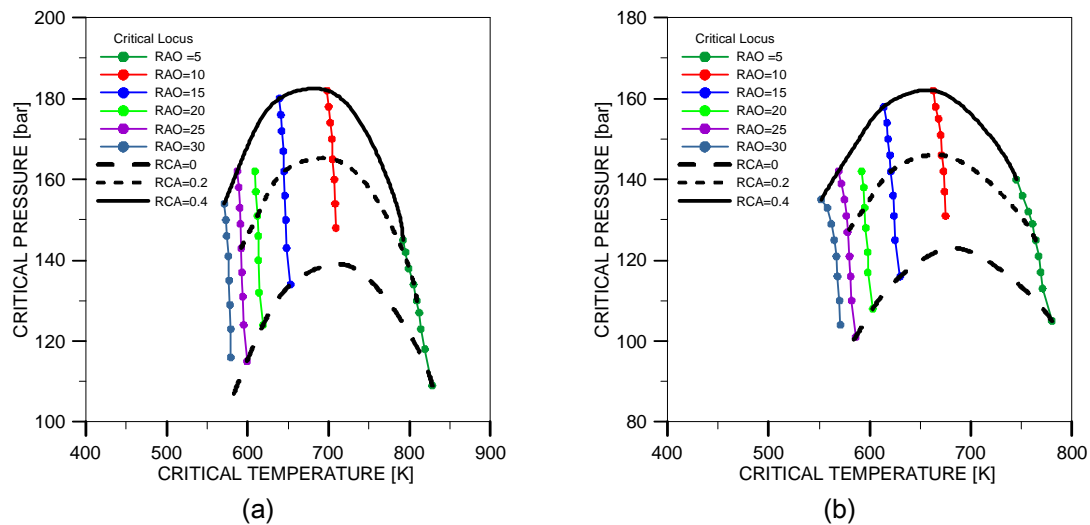


**Figure 4.** Critical locus for (a) soybean oil/methanol/CO<sub>2</sub> and (b) soybean oil/ethanol/CO<sub>2</sub> Molar ratios: alcohol/oil (RAO)= 5, 10, 15, 20, 25, 30 and CO<sub>2</sub>/alcohol (RCA):0, 0.05, 0.1,0.15, 0.2, 0.25, 0.3, 0.35 and 0.4.



**Figure 5.** Critical locus for the pseudo ternary (a) soyben oil/methanol/CO<sub>2</sub> and b) soybean oil/ethanol/CO<sub>2</sub> using the pseudo ternary strategy and pseudo binary strategy. Molar ratios: alcohol/oil (RAO)= 5, 10, 15, 20, 25, 30 and CO<sub>2</sub>/alcohol (RCA):0, 0.2, 0.3, and 0.4.

The Figure 6 presents the critical locus curves for the pseudo ternaries palm oil/ethanol/CO<sub>2</sub> and coconut oil/ ethanol/CO<sub>2</sub>. It can be observed that the addition of CO<sub>2</sub> promotes a higher effect in the critical pressure over the higher unsaturated feedstock.



**Figure 6.** Critical locus for the pseudo ternary mixture FS/EtOH/CO<sub>2</sub>: (a)-FS=palm oil, (b) FS=coconut oil. Molar ratios alcohol/oil (RAO): 5 10, 15, 20, 25, 30 and Molar ratios CO<sub>2</sub>/alcohol (RCA):0, 0.05, 0.1,0.15, 0.2, 0.25, 0.3, 0.35 and 0.4.

## CONCLUSION

Based on the results found we can conclude that the use of classical Peng-Robison EOS can be a valuable tool in order to estimate the critical point of oil/alcohol/CO<sub>2</sub> mixtures. The strategy proposed by [36, 37] to consider the mixture alcohol+CO<sub>2</sub> a pseudo pure component yield a poor estimation to the critical point of oil/alcohol/CO<sub>2</sub> mixtures. The addition of CO<sub>2</sub>, despite of promote a reducing in critical temperature it leads an increase of critical pressure.

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