Table 1 – Adjusted parameters for pure alkyl esters (related to biodiesel systems).

Compound	*FA**	MW [g.mol^{-1}]	m [-]	σ [A]	ε/k [K]	μ [D]	x_P	AAD%		T range [K]		Reference	
								P^{Sat}	ρ^L	P^{Sat}	ρ^L	P^{Sat}	ρ
Methyl laurate	C12:0	214.35	6.5942	3.7242	249.25			0.51	0.0420	336.32-485.15	283.15-353.15	[36, 37]	[38]
			6.4641	3.7527	250.77	1.9	0.0928	0.67	0.0411				
Methyl myristate	C14:0	242.40	7.2167	3.7782	252.17			0.64	0.0257	412.03-510.95	298.15-353.15	[36, 39]	[38]
			7.1664	3.7889	252.32	1.9	0.0837	0.64	0.0284				
Methyl palmitate	C16:0	270.75	7.7791	3.8338	255.40			3.51	0.0106	408.30-511.25	308.15-363.15	[36, 40]	[38]
			8.7281	3.8437	255.65	1.9	0.0776	3.50	0.0106				
Methyl stearate	C18:0	298.51	8.4790	3.8575	256.38			2.15	0.0269	427.50-535.50	313.15-363.15	[36, 40]	[38]
			8.3952	3.8718	256.94	1.9	0.0715	2.15	0.0180				
Methyl oleate	C18:1	296.49	8.6676	3.8015	251.78			1.62	0.1045	401.21-485.22	283.15-353.15	[37, 41]	[38]
			8.5950	3.8138	252.32	1.9	0.0698	1.63	0.1051				
Methyl linoleate	C18:2	294.47	8.2695	3.8400	257.55			0.24	0.1105	392.05-458.61	278.15-363.15	[37]	[38]
			8.2148	3.8499	257.89	1.9	0.0731	0.24	0.1132				
Methyl linolenate	C18:3	292.46	8.8656	3.7178	249.72			2.23	0.1356	398.14-458.85	278.15-338.15	[37]	[42]
			8.4544	3.7847	255.13	1.9	0.0710	1.70	0.1191				
Ethyl laurate	C12:0	228.37	6.8101	3.7785	250.72			4.27	0.0274	386.95-464.35	283.15-353.15	[43, 44]	[38]
			7.0147	3.7390	246.69	1.7	0.0855	3.56	0.0405				
Ethyl myristate	C16:0	256.42	7.5140	3.8093	251.26			5.58	0.0434	392.17-492.47	283.15-353.15	[43, 45]	[38]
			7.4562	3.8206	251.78	1.7	0.0805	5.54	0.0443				
Ethyl palmitate	C16:0	284.48	8.2179	3.8355	252.43			2.35	0.0236	412.63-514.98	303.15-363.15	[43, 45]	[38]
			8.1284	3.8513	253.48	1.7	0.0738	2.34	0.0229				
Ethyl stearate	C18:0	312.50	10.5588	3.6279	234.77			10.18**	0.0682	323.15-533.97	313.15-363.15	[43, 44, 46]	[38]
			10.4479	3.6421	235.72	1.7	0.0574	10.33	0.0664				
Ethyl oleate	C18:1	310.51	9.8000	3.7016	240.79			5.91**	0.1307	354.05-536.83	278.15-363.15	[43, 47]	[38]
			9.7644	3.7068	240.91	1.7	0.0615	5.90	0.1324				
Ethyl linoleate	C18:2	308.50	9.8376	3.6726	241.40			9.29**	0.1531	486.64-537.39	278.15-363.15	[43]	[48]
			10.1502	3.6320	237.96	1.7	0.0591	9.08	0.1706				
Hexyl acetate	C6:0	144.22	4.8883	3.5739	240.39			0.64	0.5526	304.29-595.59	304.29-595.59	[49]	[49]
			4.7874	3.6049	240.61	1.9	0.1253	0.84	0.6001				
Ethyl Acetate	C2:0	88.11	3.5421	3.2936	230.90			1.30	0.81	189.6-505.7	189.6-505.7	[49]	[49]
Set 1			2.8367	3.5911	231.79	1.78	0.5288	1.21	1.33	224.7-505.7	224.7-505.7		
Set 2			3.4476	3.3292	231.61	1.78	0.1146	0.70	0.91				
Set 3			3.3213	3.3769	233.23	1.78	0.1809	0.68	1.02				

** Symbol FA is refereeing to the fatty acid that forms the alkyl ester with the respective alcohol.*

*** Units used in this work: P^{sat} [bar] and ρ [mol.cm^{-3}].*

Table 2 – Adjusted parameters for pure alcohols (related to biodiesel systems).

Compound	MW [g.mol^{-1}]	m [-]	σ [A]	ε/k [K]	κ^{HB}	ε^{HB}/k [K]	μ [D]	x_P	AAD%		T range [K]		Reference	
									P^{Sat}	ρ^L	P^{Sat}	ρ^L	P^{Sat}	ρ
Methanol	32.04	1.5337	3.2289	188.53	0.03525	2899.47			2.20	0.54	175.5-494.8	175.5-489.9	[50]	[50]
(2 sites)		1.8628	3.0603	170.36	0.07529	2479.37	1.7	0.3184	0.46	0.67				
Ethanol	46.07	2.2924	3.2472	221.30	0.02233	2511.24			1.43	1.14	159.1-495.3	159.1-495.3	[49]	[49]
(2 sites)		2.2983	3.2376	190.16	0.035584	2544.28	1.7	0.2976	0.76	0.37				

Table 3 - Enthalpy of fusion and normal melting temperature of pure alkyl esters used in this work [56].

Compound	$\Delta_{fus}h$ (kJ.mol^{-1})	T_{fus} (K)
Ethyl laurate	38.07	272.59
Ethyl palmitate	53.75	298.30
Ethyl oleate	25.39	255.12
Ethyl linoleate	24.39	217.94

Table 4 – Cross-association parameters of ethyl ethanoate (ethyl acetate) and different alcohols.

Alcohol(1) + ethyl etanoate(2)	ε^{B_2} [K^{-1}]	κ^{B_2}	NOBS		*AD*	*rmsd*
			T (K)	P (bar)		
Fitting with both components as polar						
Methanol(1)	1167.85	0.017426	27 [312.91; 313.15 K]	19 [1.013 bar]	4.64×10^{-3} bar	5.45×10^{-3} bar
					0.24 K	0.33 K
Ethanol(1)	1017.19	0.015130	37 [313.15; 333.15 K]	---	8.82×10^{-3} bar	1.01×10^{-2} bar
2-Propanol(1)	808.36	0.016281	34 [313.15; 333.15 K]	---	1.01×10^{-2} bar	1.25×10^{-2} bar
1-Butanol(1)	414.43	0.013581	---	34 [0.9733; 1.013 bar]	0.78 K	0.94 K
Fitting with both components as non polar						
Methanol(1)	964.26	0.02111	27 [312.91; 313.15 K]	19 [1.013 bar]	9.15×10^{-3} bar	1.09×10^{-2} bar
					0.55 K	0.65 K
Ethanol(1)	837.97	0.012437	37 [313.15; 333.15 K]	---	9.36×10^{-3} bar	1.11×10^{-2} bar
2-Propanol(1)	659.91	0.014916	34 [313.15; 333.15 K]	---	6.61×10^{-3} bar	8.10×10^{-3} bar
1-Butanol(1)	501.91	0.004291	---	34 [0.9733; 1.013 bar]	0.67 K	0.83 K

Experimental data form [57].
Polar components 1-butanol and 2-propanol from [18].
Ester was considered containing two positives sites.

Table 5 – Predicted VLE results for alcohol + ester systems by the PC-SAFT and polar PC-SAFT using transferable cross-association parameters.

System	PC-SAFT		Polar PC-SAFT		Ref.
Txy type systems	*AD, T (K)*	*AD, y* x 10^2	*AD, T (K)*	*AD, y* x 10^2	
Ethanol(1) + hexyl acetate(2)	1.59 (*4.55*)	1.22 (*2.94*)	1.76 (*7.02*)	1.14 (*5.89*)	[58]
Methanol(1) + hexyl acetate(2)	3.40 (*14.2*)	2.59 (*9.52*)	3.45 *(16.2)*	2.26 (*10.6*)	[58]
Ethanol(1) + butyl acetate(2)	2.49 *(7.37)*	3.26 *(7.29)*	2.45 *(8.89)*	3.09 (*9.40*)	[59]
Ethanol(1) + ethyl palmitate(2)	2.89 (*5.86*)	---	2.02 (*6.62*)	---	[7]
Ethanol(1) + ethyl stearate(2)	1.89 *(3.25)*	---	3.67 *(7.92)*	---	[7]
Methanol(1) + methyl laurate(2)	3.87 (*6.81*)	---	3.12 (*9.71*)	---	[2]
Methanol(1) + methyl myristate(2)	4.85 (*6.57*)	---	3.78 (*9.74*)	---	[2]
Methanol(1) + methyl oleate(2)	4.19 (6.79)	---	2.99 (*11.20*)	---	[2]
Ethanol(1) + methyl laurate(2)	4.45 (*2.42*)	---	3.05 (*5.69*)	---	[2]
Ethanol(1) + methyl myristate(2)	4.62 (*2.93*)	---	2.87 (*7.07*)	---	[2]
Ethanol(1) + methyl oleate(2)	4.08 *(3.59)*	---	3.51 *(8.26)*	---	[2]
Pxy type systems	*AD, P (MPa)*	*AD, y* x 10^2	*AD, P (MPa)*	*AD, y* x 10^2	
Ethanol(1) + ethyl laurate(2)					[60]
493 K	0.13 (*0.20*)	0.45 (*0.52*)	0.25 (*0.35*)	0.56 (*0.67*)	
523 K	0.19 (*0.29*)	1.16 (*1.28*)	0.42 (0.57)	1.34 (*1.54*)	
543 K	0.23 (*0.35*)	2.06 (*2.19*)	0.56 (*0.74*)	2.21 (*2.43*)	
Ethanol(1) + ethyl myrisate(2)					[60]
493 K	0.04 (*0.11*)	0.24 (*0.27*)	0.19 (*0.31*)	0.28 (*0.34*)	
523 K	0.08 (*0.18*)	0.77 (*0.84*)	0.35 (*0.52*)	0.85 (*0.96*)	
543 K	0.10 (*0.22*)	1.33 (*1.40*)	0.45 (*0.67*)	1.37 (*1.55*)	
Methanol(1) + methyl laurate(2)					[61]
493 K	0.08 (*0.21*)	0.81 (*0.91*)	0.13 (*0.26*)	0.85 (*0.96*)	
523 K	0.08 (*0.26*)	1.64 (*1.86*)	0.14 (*0.32*)	1.70 (*1.95*)	
543 K	0.08 (*0.27*)	2.40 (*2.75*)	0.16 (*0.37*)	2.45 (*2.85*)	
Methanol(1) + methyl myrisate(2)					[61]
493 K	0.13 (*0.14*)	0.35 (*0.40*)	0.13 (*0.25*)	0.36 (*0.32*)	
523 K	0.18 (*0.20*)	0.94 (*1.30*)	0.21 (*0.33*)	0.96 (*1.10*)	
543 K	0.18 (*0.30*)	1.34 (*1.53*)	0.26 (*0.31*)	1.38 (*1.60*)	

AD: absolute deviation

(Calculations performed without cross-association)