Phase Equilibria Modeling for Biofuels Production

Mariana Belo Oliveira

Orientador: João A. P. Coutinho

Co-orientador: António José Queimada

Outline

1. Motivation and Objectives

1.1 Biodiesel production and purification processes.

1.2 How commonly used thermodynamic models perform in describing phase equilibria of relevance for the biodiesel industry?

2. Introduction to the Cubic-Plus-Association Equation of State (CPA EoS)

3. CPA EoS results

For the VLE, LLE and SLE of systems containing fatty acid esters, fatty acids, water, glycerol and alcohols, in a broad range of pressures and temperatures.

4. CPA EoS vs. cubic EoS, EoS – g^E and g^E models

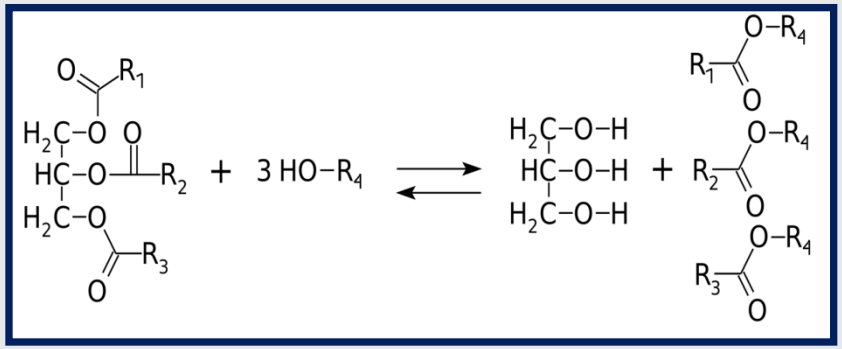
5. Conclusions

6. Future Work

7. Acknowledgments

Methods to produce biodiesel:

- Microemulsification
- Pyrolysis
- Transesterification:

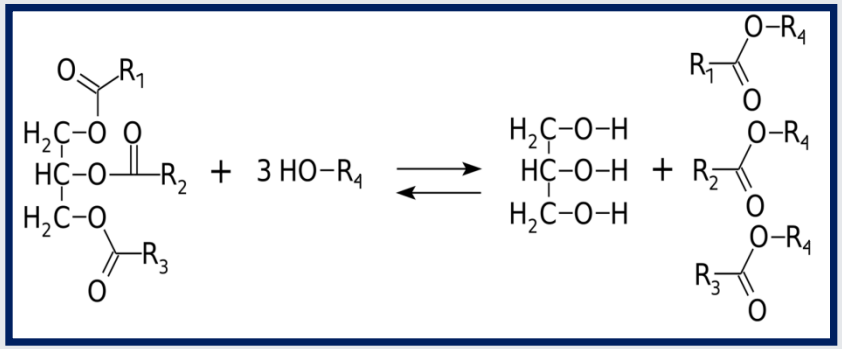


Raw materials: Vegetable oils
Tallow
Waste cooking oils
…

F.R. Ma, M.A. Hanna, Bioresource Technology, 1999. ***70****(1): p. 1-15.*

Methods to produce biodiesel:

- Microemulsification
- Pyrolysis
- **Transesterification:**



Raw materials: Vegetable oils
Tallow
Waste cooking oils
…

F.R. Ma, M.A. Hanna, Bioresource Technology, 1999. ***70****(1): p. 1-15.*

Methods to produce biodiesel:

Transesterification unit

Biodiesel purification section

Glycerol recovery section

1. Motivation and Objectives

1.1 Biodiesel production and purification processes

DIN EN 14214:2003 requirements and test methods for biodiesels

Property	Unit	Limits Max	Limits Test method
Density @ 15° C	kg/m^3	900	EN ISO 3675 EN ISO 12185
Viscosity @ 40° C	mm^2/s	5.00	EN ISO 3104
Sulfur content	mg/kg	10.0	prEN ISSO 20846 prEN ISSO 20884
Carbon residue (on 10% distillation residue)	% (m/m)	0.30	EN ISO 10370
Water content	mg/kg	500	EN ISO 12937
Total contamination	mg/kg	24	EN 12662
Acid value	mg KOH/g	0.50	EN 14104

Property	Unit	Limits Max	Limits Test method
Iodine value	giodine/100g	120	EN 14111
Linolenic acid methyl ester	% (m/m)	12.0	EN 14103
Polyunsaturated (>= 4 double bonds) methyl esters	% (m/m)	1	
Methanol content	% (m/m)	0.20	EN 14110
Monoglyceride content	% (m/m)	0.80	EN 14105
Diglyceride content	% (m/m)	0.20	EN 14105
Triglyceride content	% (m/m)	0.20	EN 14105
Free glycerol	% (m/m)	0.02	EN 14105 EN 14106
Total glycerol	% (m/m)	0.25	EN 14105

EN 14214, 2003. Automotive fuels – Fatty acid methyl esters (FAME) for diesel engine – Requirements and test methods, CEN, Brussels, Belgium. Available from: http://www.din.de

1. Motivation and Objectives

1.1 Biodiesel production and purification processes

DIN EN 14214:2003 requirements and test methods for biodiesels

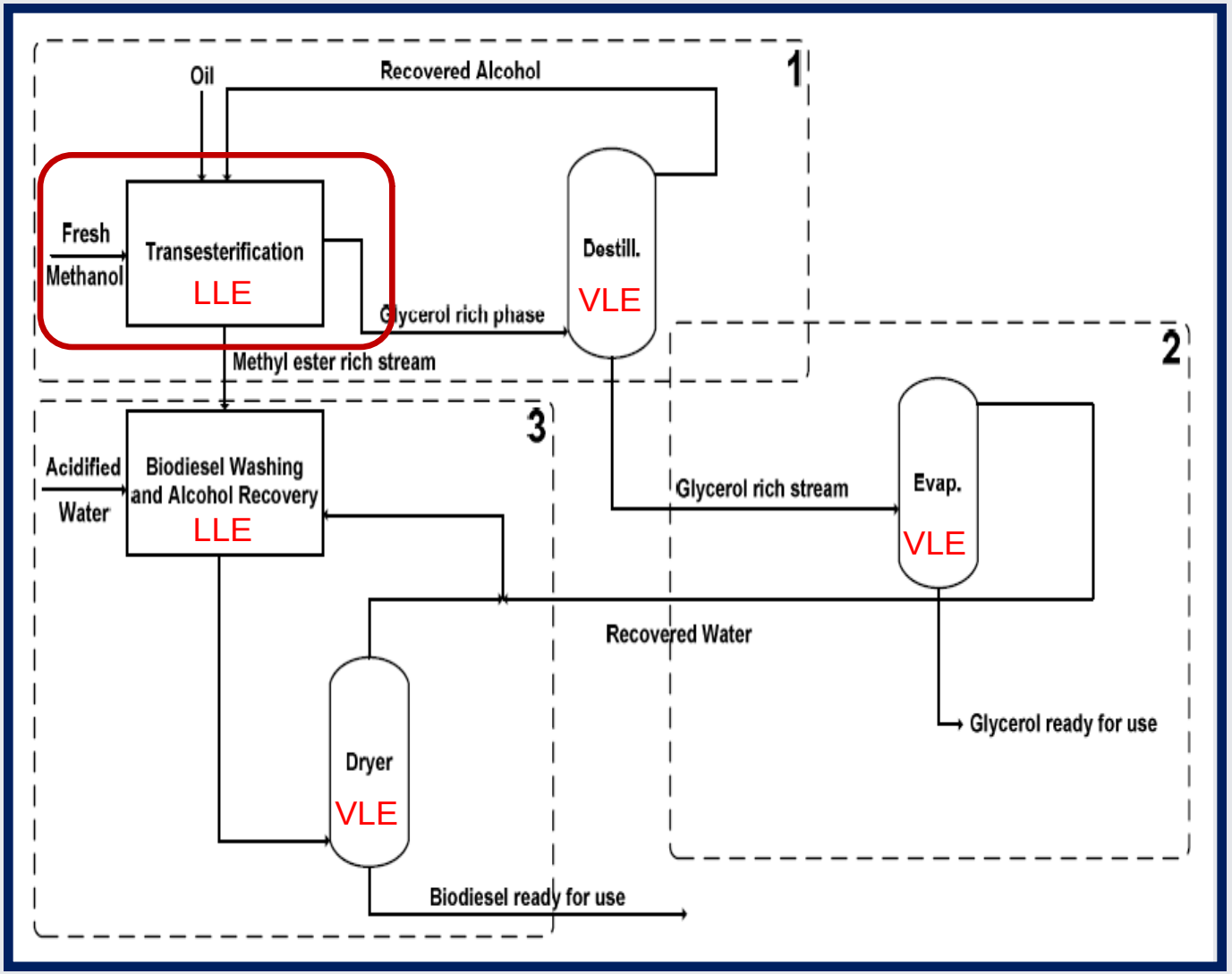
Property	Unit	Limits Max	Limits Test method
Density @ 15° C	kg/m^3	900	EN ISO 3675 EN ISO 12185
Viscosity @ 40° C	mm^2/s	5.00	EN ISO 3104
Sulfur content	mg/kg	10.0	prEN ISSO 20846 prEN ISSO 20884
Carbon residue (on 10% distillation residue)	% (m/m)	0.30	EN ISO 10370
Water content	mg/kg	500	EN ISO 12937
Total contamination	mg/kg	24	EN 12662
Acid value	mg KOH/g	0.50	EN 14104

Property	Unit	Limits Max	Limits Test method
Iodine value	giodine/100g	120	EN 14111
Linolenic acid methyl ester	% (m/m)	12.0	EN 14103
Polyunsaturated (>= 4 double bonds) methyl esters	% (m/m)	1	
Methanol content	% (m/m)	0.20	EN 14110
Monoglyceride content	% (m/m)	0.80	EN 14105
Diglyceride content	% (m/m)	0.20	EN 14105
Triglyceride content	% (m/m)	0.20	EN 14105
Free glycerol	% (m/m)	0.02	EN 14105 EN 14106
Total glycerol	% (m/m)	0.25	EN 14105

EN 14214, 2003. Automotive fuels – Fatty acid methyl esters (FAME) for diesel engine – Requirements and test methods, CEN, Brussels, Belgium. Available from: http://www.din.de

1. Motivation and Objectives

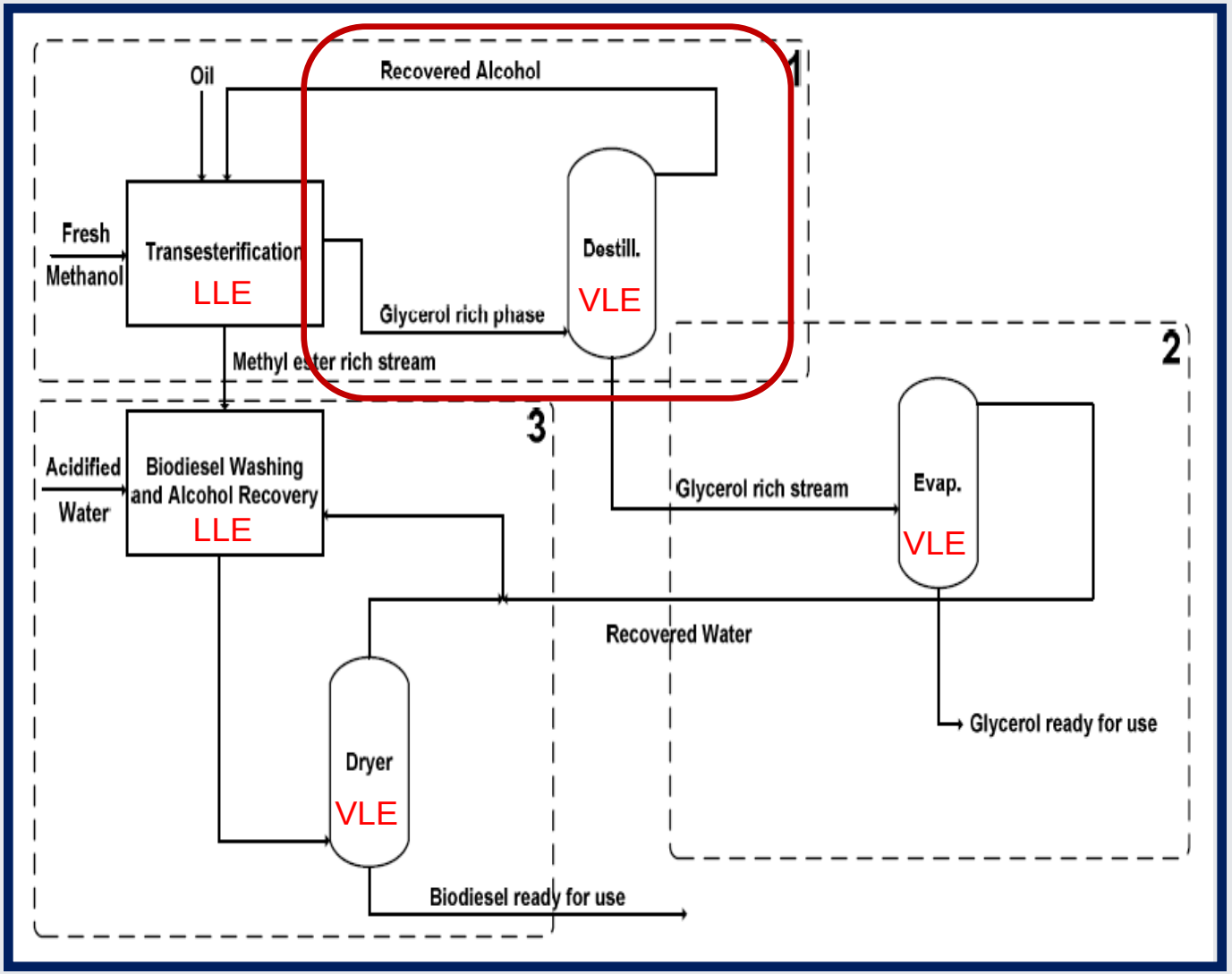
1.1 Biodiesel production and purification processes



*M.J. Haas, A.J. McAloon, W.C. Yee, T.A. Foglia, Bioresource Technology, 2006. **97**(4): p. 671-678.*

1. Motivation and Objectives

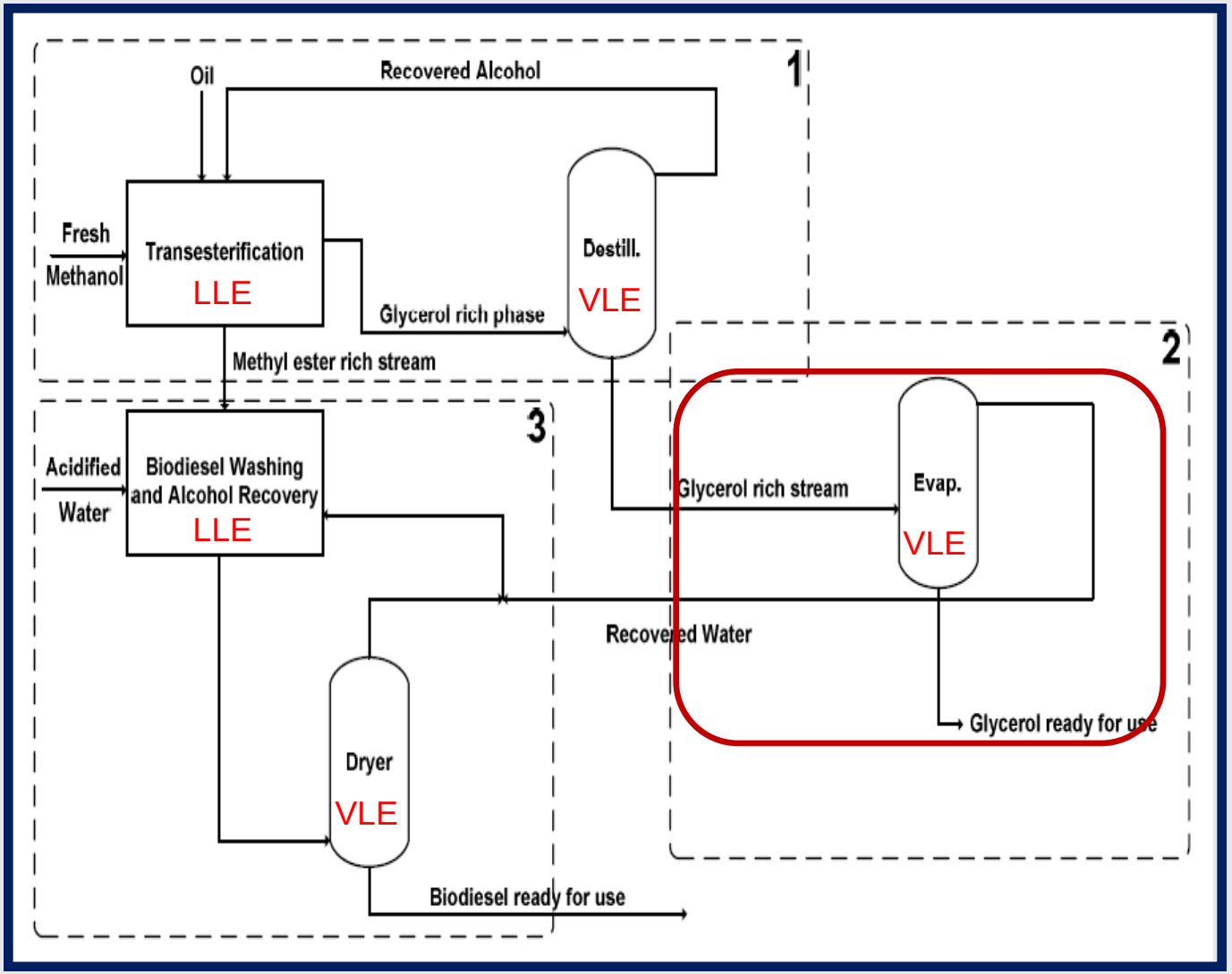
1.1 Biodiesel production and purification processes



M.J. Haas, A.J. McAloon, W.C. Yee, T.A. Foglia, Bioresource Technology, 2006. ***97****(4): p. 671-678.*

1. Motivation and Objectives

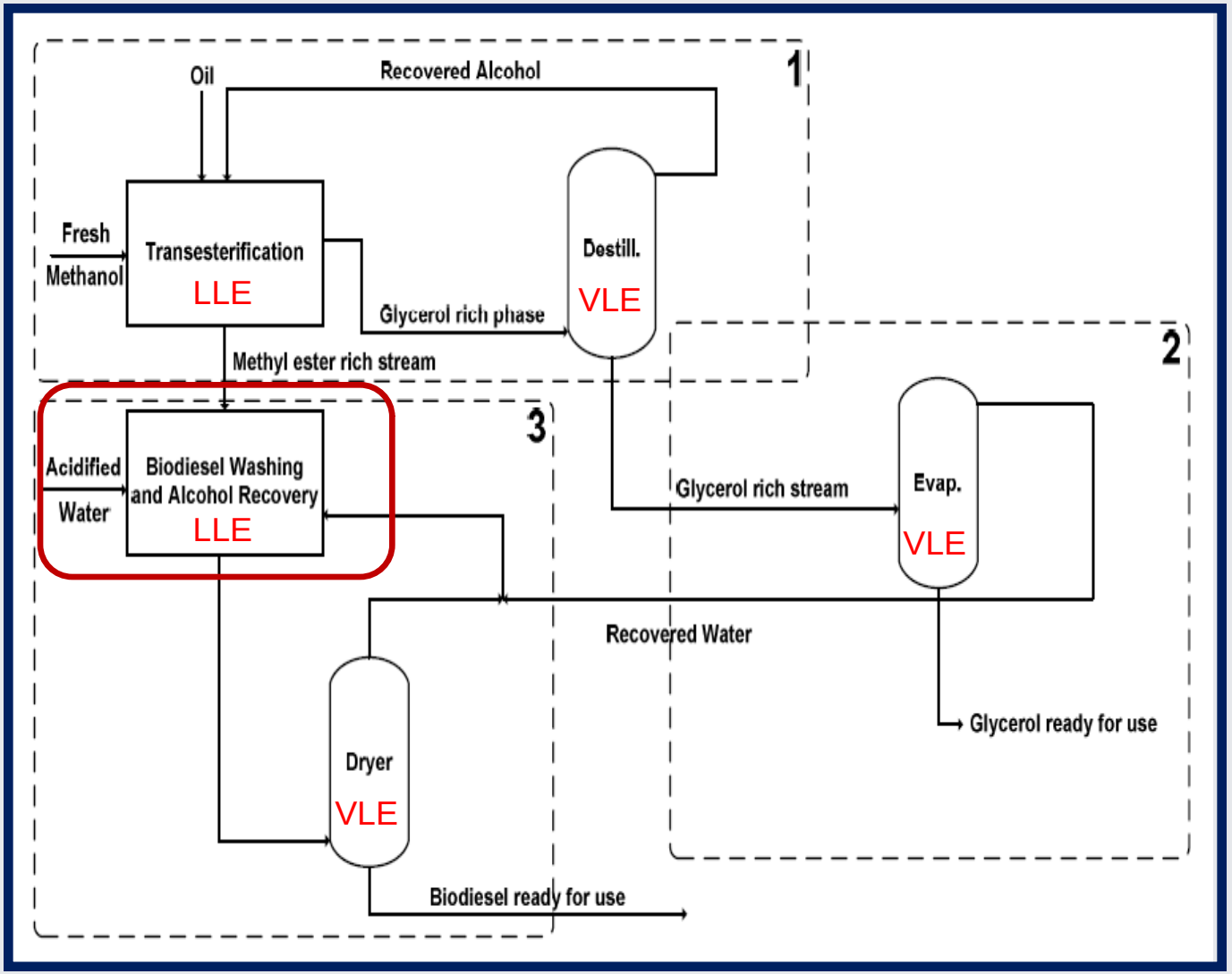
1.1 Biodiesel production and purification processes



*M.J. Haas, A.J. McAloon, W.C. Yee, T.A. Foglia, Bioresource Technology, 2006. **97**(4): p. 671-678.*

1. Motivation and Objectives

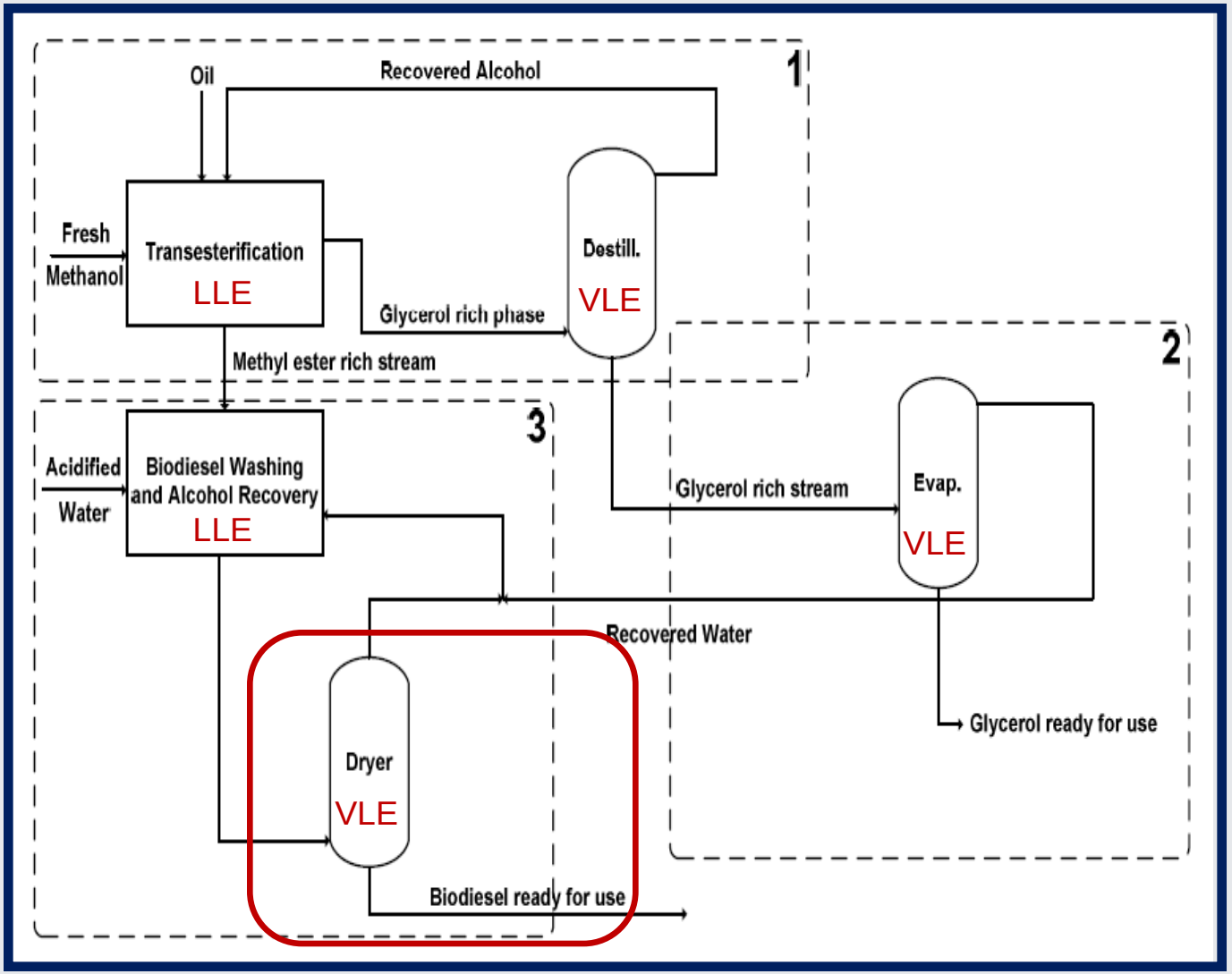
1.1 Biodiesel production and purification processes



M.J. Haas, A.J. McAloon, W.C. Yee, T.A. Foglia. Bioresource Technology, 2006. ***97****(4): p. 671-678.*

1. Motivation and Objectives

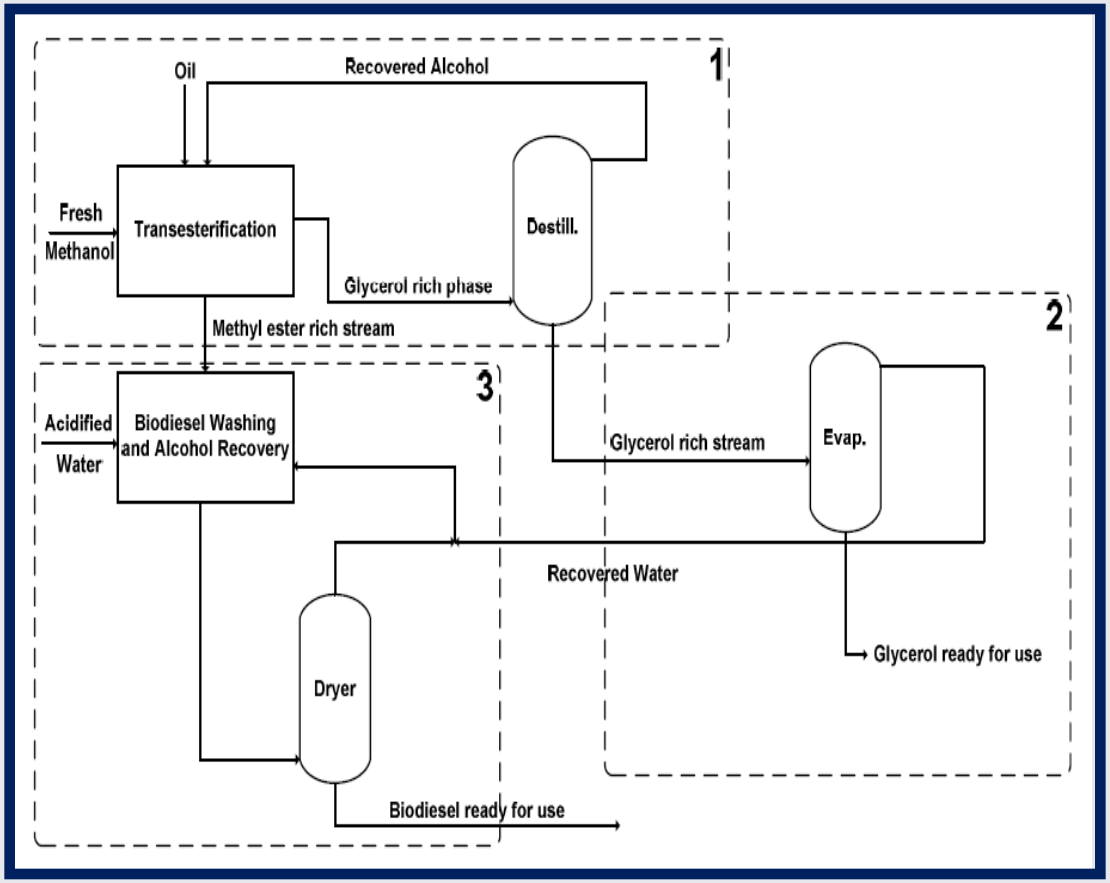
1.1 Biodiesel production and purification processes



*M.J. Haas, A.J. McAloon, W.C. Yee, T.A. Foglia, Bioresource Technology, 2006. **97**(4): p. 671-678.*

1. Motivation and Objectives

1.1 Biodiesel production and purification processes



Accurate knowledge of LLE:

- Vegetable oils / fatty acid esters / glycerol / water / alcohol (reactor).
- Water/fatty acid (washing).
- Water/fatty acid ester (washing).

Accurate knowledge of VLE:

- Glycerol/alcohol (alcohol recovery).
- Ester/alcohol (alcohol recovery).
- Glycerol/water (glycerol purification).

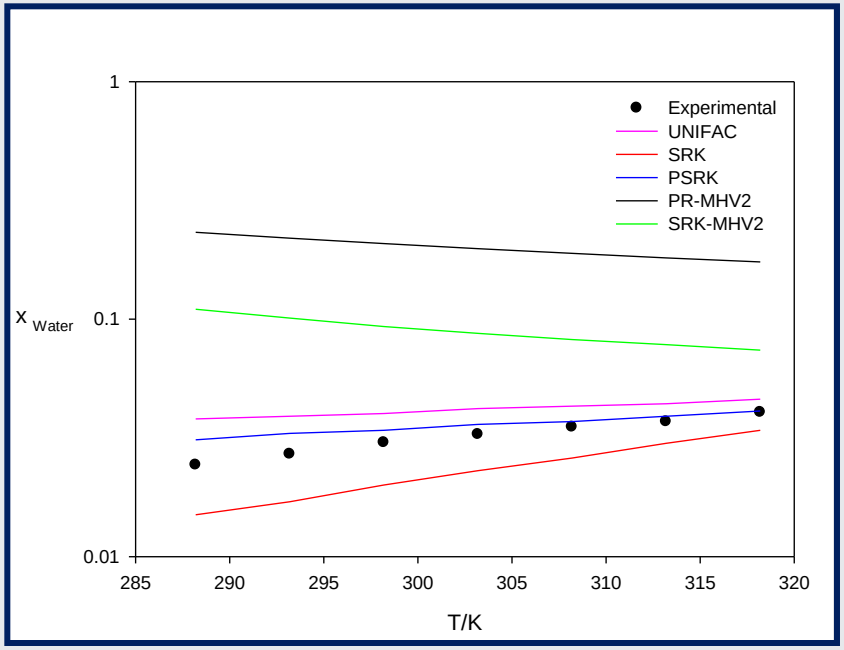
Essential for the design of the separation and purification processes!

1. Motivation and Objectives

1. 2 How commonly used models perform in describing phase equilibria of relevance for the biodiesel industry?

http://path.web.ua.pt

	UNIFAC	SRK	PSRK	PR-MHV2	SRK-MHV2
			Δx %		
ethyl butanoate	19.5	54.3	43.9	145.6	24.7
propyl butanoate	22.3	49.0	43.8	160.1	29.3
methyl hexanoate	25.1	42.8	44.5	167.5	34.3
methyl heptanoate	17.6	31.3	29.2	172.6	47.6
methyl octanoate	30.6	29.0	36.1	240.2	63.5
ethyl decanoate	31.1	28.5	12.2	546.0	190.0
methyl dodecanoate	28.3	19.5	9.1	536.4	184.7
methyl tetradecanoate	28.7	9.7	7.8	673.1	290.6
methyl hexadecanoate	15.8	31.4	11.3	613.4	224.9
methyl octadecanoate	8.3	25.2	22.7	738.8	322.2
methyl oleate	86.9	13.5	23.8	972.9	766.5
Global AAD %	**28.6**	**30.4**	**25.9**	**451.5**	**198.0**

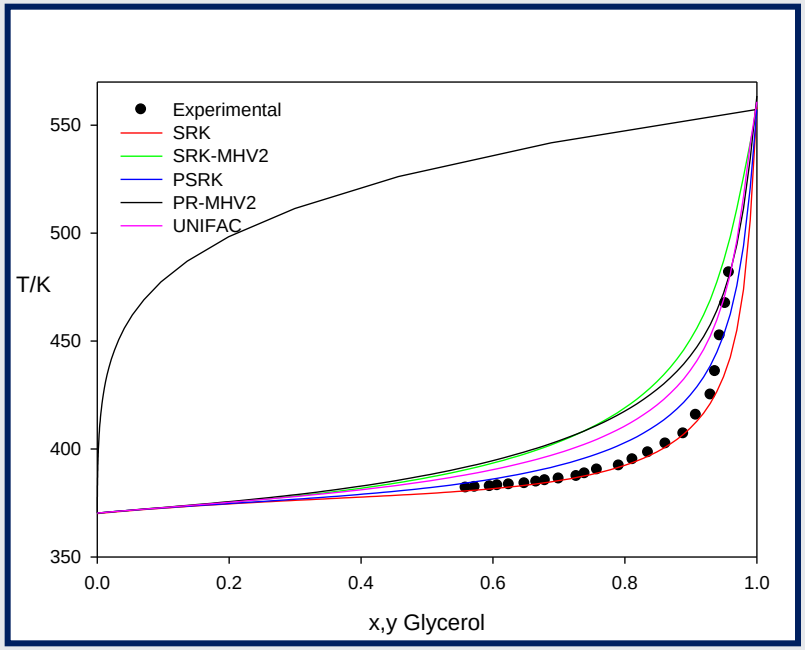


Water solubility in ethyl decanoate

1. Motivation and Objectives

1. 2 How commonly used models perform in describing phase equilibria of relevance for the biodiesel industry?

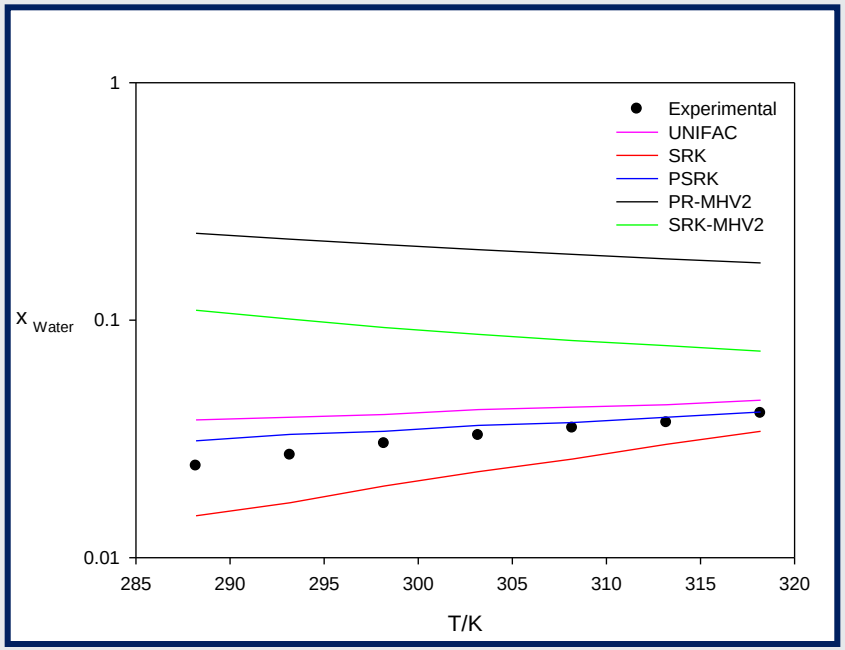
		UNIFAC	SRK	PSRK	PR-MHV2	SRK-MHV2
				ΔT_b %		
ester + methanol	methyl laurate + methanol	0.57	1.71	2.02	1.20	1.06
	methyl myristate + methanol	0.69	1.82	2.74	1.55	0.94
	methyl oleate + methanol	0.74	1.44	2.78	2.48	0.89
	Global AAD %	**0.67**	**1.66**	**2.51**	**1.74**	**0.96**
ester + ethanol	methyl laurate + ethanol	0.65	1.94	1.10	0.76	0.72
	methyl myristate + ethanol	0.97	1.43	1.90	0.52	1.28
	methyl oleate + ethanol	1.47	1.03	2.74	1.14	0.91
	Global AAD %	**1.03**	**1.47**	**1.91**	**0.81**	**0.97**
	glycerol + water	**2.49**	**3.67**	**2.84**	**1.84**	**2.12**

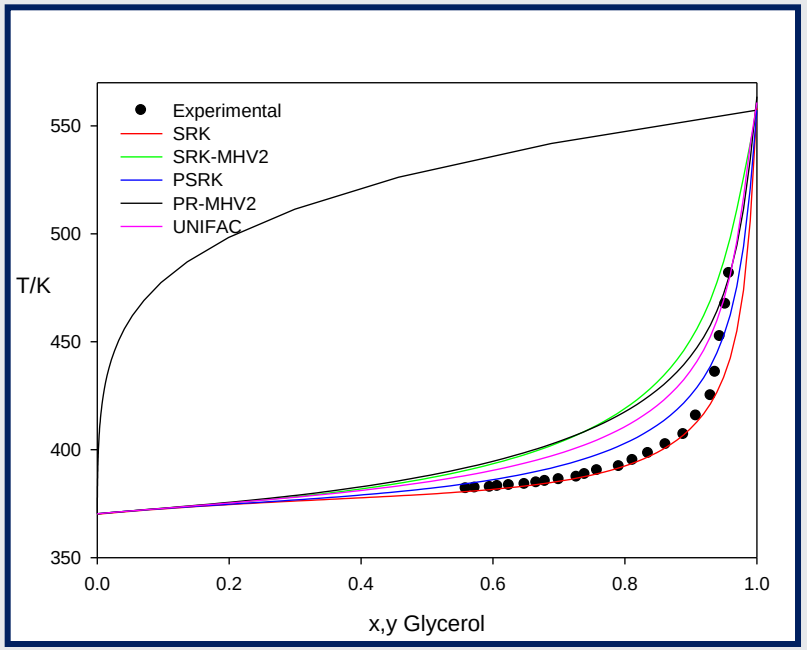


VLE for the glycerol + 1-propanol system

1. Motivation and Objectives

1. 2 How commonly used models perform in describing phase equilibria of relevance for the biodiesel industry?





- None of the models studied so far is able to accurately estimate the different phase equilibria equally well!
- CPA EoS (Cubic-Plus-Association equation of state) is extended to systems of interest for the biodiesel production.

2. Cubic-Plus-Association EoS

$$Z = Z^{phys} + Z^{assoc}$$

$$Z^{phys} = Z^{SRK} = \frac{v}{v-b} - \frac{a}{RT(v+b)}$$

$$Z^{assoc} = -\frac{1}{2}\left(1+\rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}\left(1-X_{A_i}\right)$$

Successfully applied to:

- Water + Hydrocarbons[a]
- Water + Alcohols[b]
- Water + Aromatic hydrocarbons[a,c]
- Glycols + Water[d]
- PFCs + Water[e]

a) M.B. Oliveira, J.A.P. Coutinho, A.J. Queimada, Fluid Phase Equilibria, 2007. **258**(1): p. 58-66.
b) G.K. Folas, J. Gabrielsen, M.L. Michelsen, E.H. Stenby, G.M. Kontogeorgis, Industrial & Engineering Chemistry Research, 2005. **44**(10): p. 3823-3833.
c) M.B. Oliveira, V.L. Oliveira, J.A.P. Coutinho, A.J. Queimada, Industrial & Engineering Chemistry Research, 2009. **48**(11): p. 5530-5536.
d) G.K. Folas, S.O. Derawi, M.L. Michelsen, E.H. Stenby, G.M. Kontogeorgis, Fluid Phase Equilibria, 2005. **228**: p. 121-126.
e) M.B. Oliveira, M.G. Freire, I.M. Marrucho, G.M. Kontogeorgis, A.J. Queimada, J.A.P. Coutinho, Industrial & Engineering Chemistry Research, 2007. **46**(4): p. 1415-1420.

2. Cubic-Plus-Association EoS

$$Z = Z^{phys} + Z^{assoc}$$

$$Z^{phys} = Z^{SRK} = \frac{v}{v-b} - \frac{a}{RT(v+b)}$$

$$Z^{assoc} = -\frac{1}{2}\left(1+\rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}\left(1-X_{A_i}\right)$$

$$X_{Ai} = \frac{1}{1+\rho\sum_j x_j \sum_{B_j} X_{Bj}\Delta^{A_iB_j}}$$

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right)-1\right]b_{ij}\beta^{A_iB_j}$$

$$a = a_0\left[1+c_1\times\left(1-\sqrt{T_r}\right)\right]^2$$

$$g(\rho) = \frac{1}{1-1.9\eta}$$

$$\eta = \frac{1}{4}b\rho$$

2. Cubic-Plus-Association EoS

$$Z = Z^{phys} + Z^{assoc}$$

$$Z^{phys} = Z^{SRK} = \frac{v}{v-b} - \frac{a}{RT(v+b)}$$

$$Z^{assoc} = -\frac{1}{2}\left(1+\rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}\left(1-X_{A_i}\right)$$

$$X_{Ai} = \frac{1}{1+\rho\sum_j x_j \sum_{B_j} X_{Bj}\Delta^{A_iB_j}}$$

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right)-1\right]b_{ij}\beta^{A_iB_j}$$

$$a = a_0\left[1+c_1\times\left(1-\sqrt{T_r}\right)\right]^2$$

$$g(\rho) = \frac{1}{1-1.9\eta} \qquad \eta = \frac{1}{4}b\rho$$

Non self - associating compounds : a_0, c_1 , b

Simultaneous regression of vapor pressure and liquid density data

2. Cubic-Plus-Association EoS

$$Z = Z^{phys} + Z^{assoc}$$

$$Z^{phys} = Z^{SRK} = \frac{v}{v-b} - \frac{a}{RT(v+b)}$$

$$Z^{assoc} = -\frac{1}{2}\left(1+\rho\frac{\partial \ln g}{\partial \rho}\right)\sum_i x_i \sum_{A_i}\left(1-X_{A_i}\right)$$

$$X_{Ai} = \frac{1}{1+\rho\sum_j x_j \sum_{B_j} X_{Bj}\Delta^{A_iB_j}}$$

$$\Delta^{A_iB_j} = g(\rho)\left[\exp\left(\frac{\varepsilon^{A_iB_j}}{RT}\right)-1\right]b_{ij}\beta^{A_iB_j}$$

$$a = a_0\left[1+c_1\times\left(1-\sqrt{T_r}\right)\right]^2$$

$$g(\rho) = \frac{1}{1-1.9\eta} \qquad \eta = \frac{1}{4}b\rho$$

Non self - associating compounds : a_0, c_1 , b

Self - associating compounds : a_0, c_1 , b, ε, β

Simultaneous regression of vapor pressure and liquid density data

2. Cubic-Plus-Association EoS Mixtures

Physical Term

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right)$$

$$b = \sum_i x_i b_i$$

Association Term

Combining rules are only needed in cross associating systems:

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}}$$ (CR-4 or Elliot Rule) [a]

$$\varepsilon^{A_i Bj} = \frac{\varepsilon^{A_i} + \varepsilon^{Bj}}{2}, \quad \beta^{A_i B_j} = \sqrt{\beta^{A_i} \beta^{B_j}}$$ (CR-2) [a]

a) G.K. Folas, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, Industrial & Engineering Chemistry Research, 2006. **45**(4): p. 1527-1538..

2. Cubic-Plus-Association EoS Mixtures

Physical Term

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right)$$

fitted

$$b = \sum_i x_i b_i$$

Association Term

Combining rules are only needed in cross associating systems:

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}}$$ (CR-4 or Elliot Rule) [a]

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i} + \varepsilon^{B_j}}{2}, \quad \beta^{A_i B_j} = \sqrt{\beta^{A_i} \beta^{B_j}}$$ (CR-2) [a]

a) G.K. Folas, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, Industrial & Engineering Chemistry Research, 2006. **45**(4): p. 1527-1538..

2. Cubic-Plus-Association EoS Mixtures

Self-associating compound and a non associating compound that can cross-associate with the associating compound

- A solvation scheme was considered:

$$\varepsilon^{A_{ester}B_{H_2O}} = \frac{\varepsilon^{A_{H_2O}B_{H_2O}}}{2} \qquad \beta^{A_{ester}B_{H_2O}} = fitted$$

*a) G.K. Folas, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, Industrial & Engineering Chemistry Research, 2006. **45**(4): p. 1527-1538..*

2. Cubic-Plus-Association EoS Mixtures

Self-associating compound and a non associating compound that can cross-associate with the associating compound

- A solvation scheme was considered:

$$\varepsilon^{A_{ester}B_{H_2O}} = \frac{\varepsilon^{A_{H_2O}B_{H_2O}}}{2}$$

$$\beta^{A_{ester}B_{H_2O}} = fitted$$

*a) G.K. Folas, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, Industrial & Engineering Chemistry Research, 2006. **45**(4): p. 1527-1538..*

2. Cubic-Plus-Association EoS

Association term depends on the number and type of association sites:

Water 4C

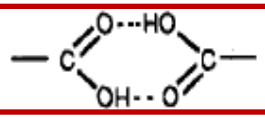
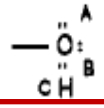
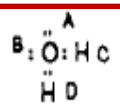
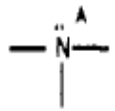
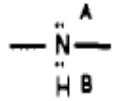
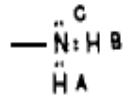
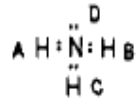
Alcohols 2B

Glycerol
- 4C
- New one: 6 associating sites 3×2B

Acids 1A

Esters A single association site is considered

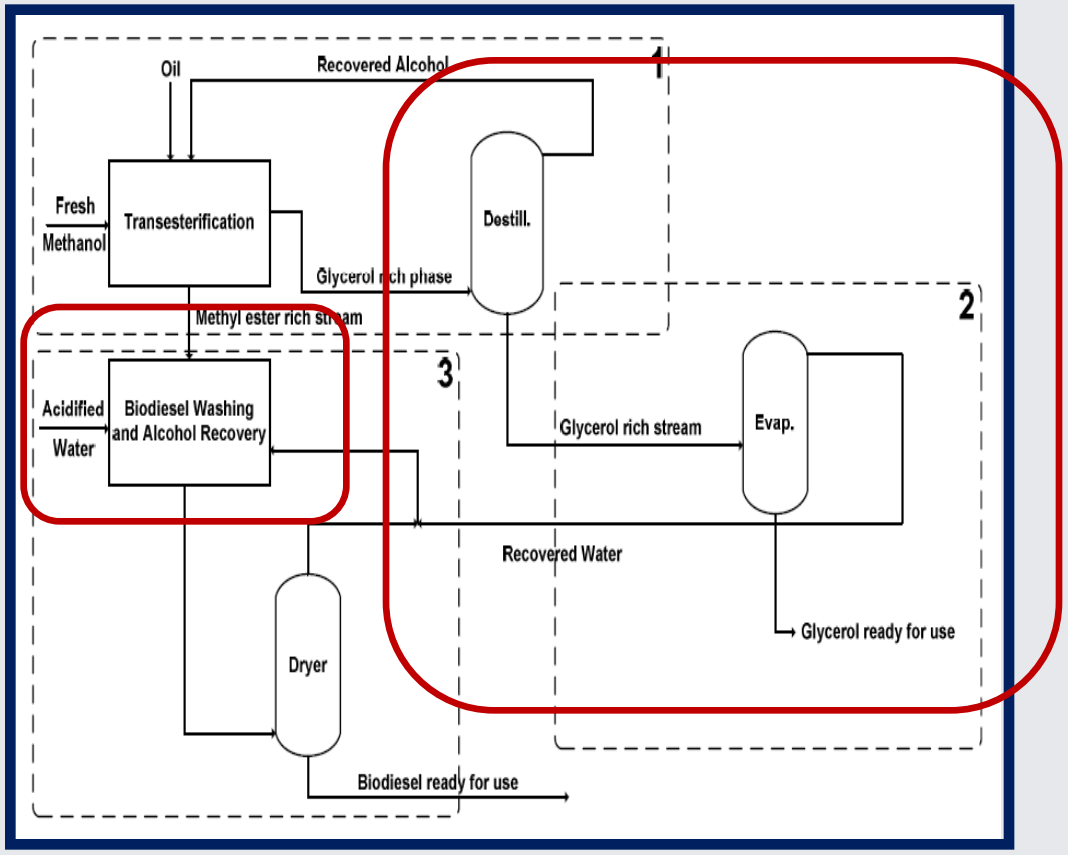
Table VIII. Types of Bonding in Real Associating Fluids[a]

species	formula	rigorous type	assigned type
acid		1	1
alkanol		3B	2B
water		4C	3B
amines			
tertiary		1	non-self-associating
secondary		2B	2B
primary		3B	3B
ammonia		4B	3B

S.H. Huang, M. Radosz, Industrial & Engineering Chemistry Research, 1990. ***29****(11): p. 2284-2294.*

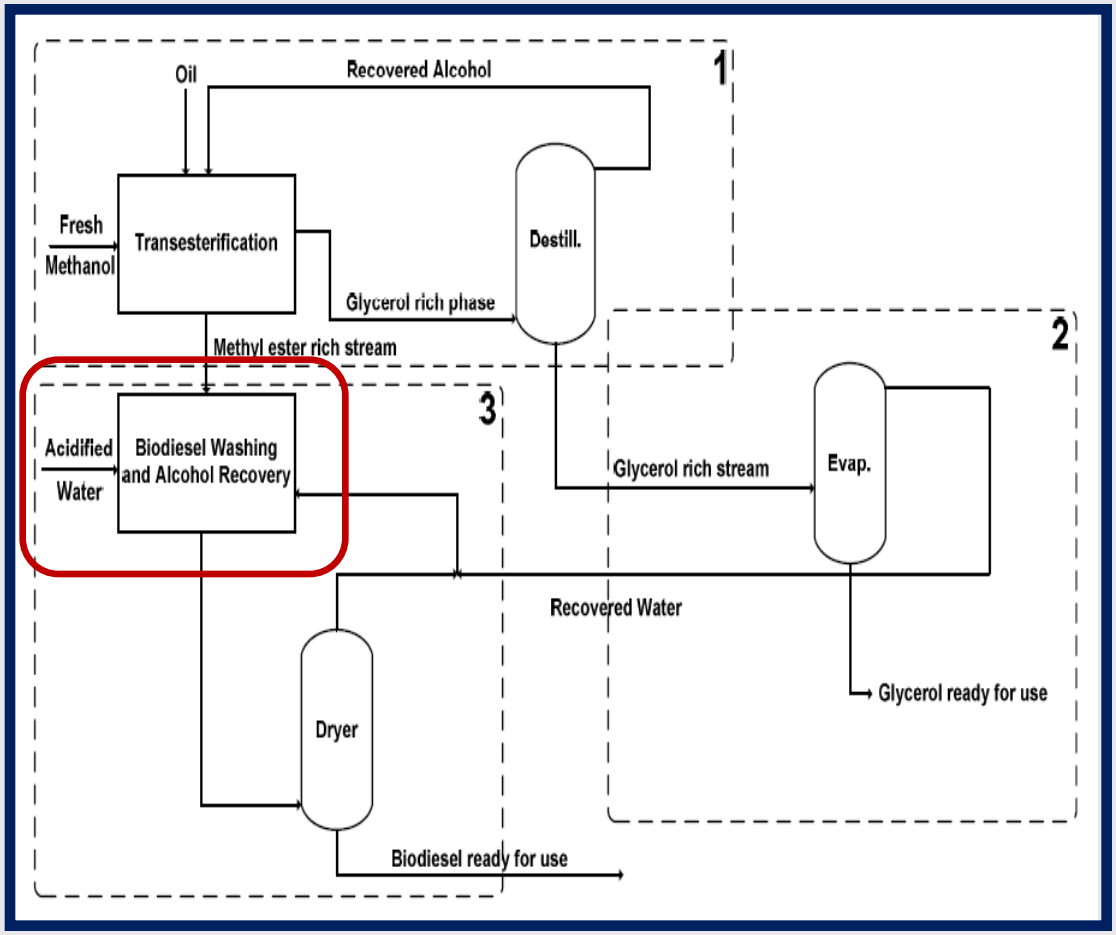
3. Results and Discussion
3.1. Binary systems

The CPA EoS was first applied to the modeling of the VLE and LLE of the simpler binary systems representative of the systems found at the biodiesel washing, alcohol recovery and glycerol purification units:



3. Results and Discussion
3.1. Binary systems

Water/Fatty acid ester systems



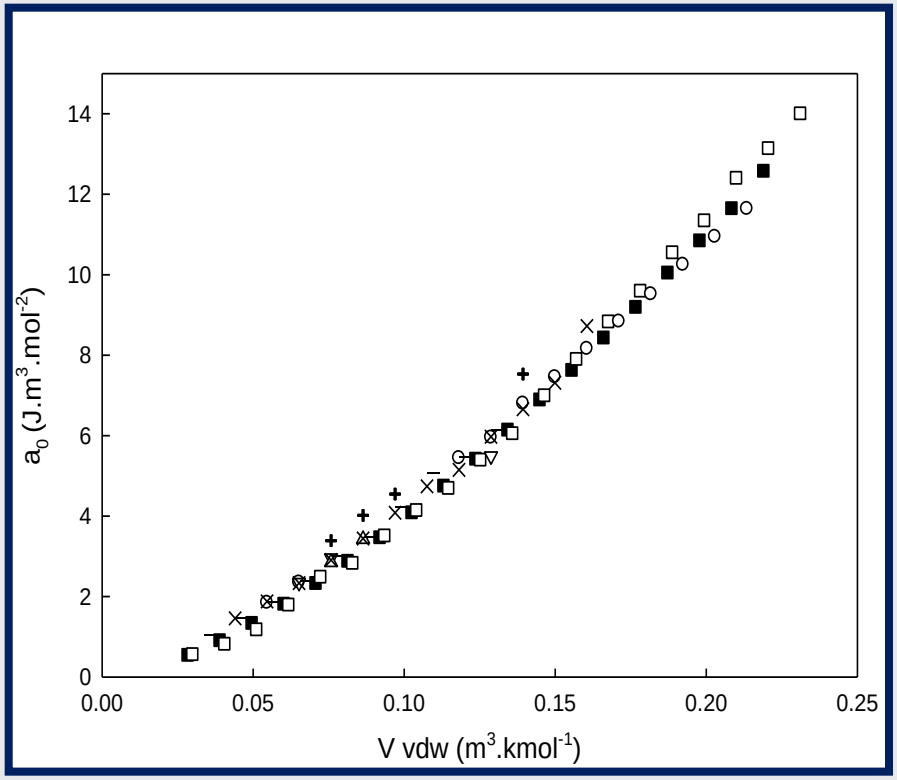
- The capacity to describe the water solubility in fatty acid ester systems and biodiesels is important to insure the fuel quality during production, seeing that the DIN EN 14214:2003 limits the water content to the maximum value of 0.05% (w/w).

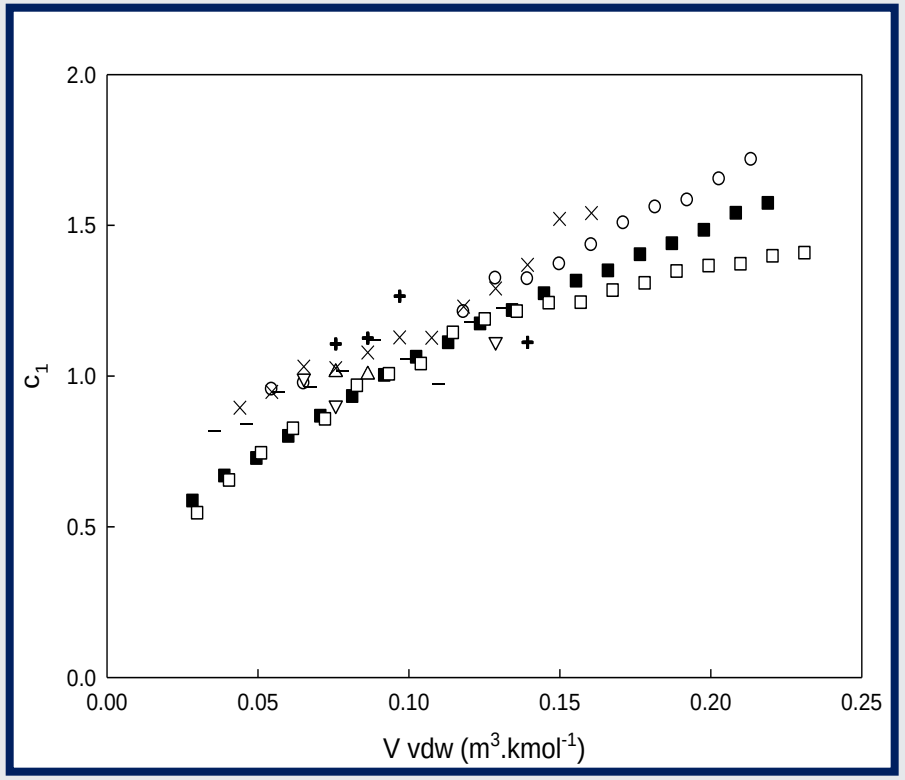
- Water affects biodiesel calorific value, shelf life and composition and can cause engine problems.

3. Results and Discussion
3.1. Binary systems

Water/Fatty acid ester systems

Correlation of the CPA pure compound parameters for esters



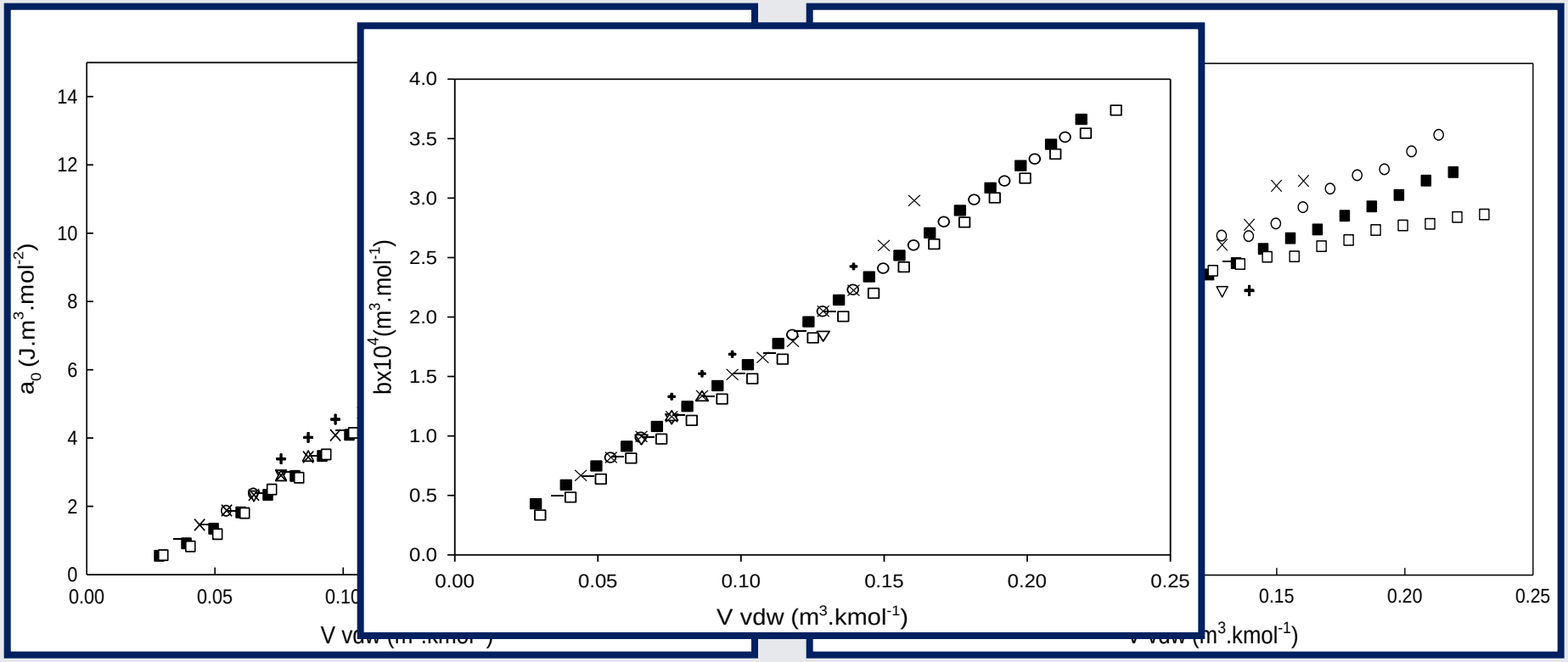


■, n-alkanes; □, n-alcohols; o, methyl esters; ∇, ethyl esters; Δ, propyl esters; +, butyl esters; ×, acetates; -, formates

3. Results and Discussion
3.1. Binary systems

Water/Fatty acid ester systems

Correlation of the CPA pure compound parameters for esters



■, n-alkanes; □, n-alcohols; o, methyl esters; ∇, ethyl esters; Δ, propyl esters; +, butyl esters; ×, acetates; -, formates

3. Results and Discussion
3.1. Binary systems

Water/Fatty acid ester systems

Physical Term

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right)$$

fitted

$$b = \sum_i x_i b_i$$

Association Term

Solvation scheme

$$\varepsilon^{A_{ester}B_{H_2O}} = \frac{\varepsilon^{A_{H_2O}B_{H_2O}}}{2}$$

$$\beta^{A_{ester}B_{H_2O}} = fitted$$

a) E.C. Voutsas, I.V. Yakoumis, D.P. Tassios, Fluid Phase Equilibria, 1999. ***160****: p. 151-163.*

3. Results and Discussion
3.1. Binary systems

Water/fatty acid esters systems

Deviations in the mole fraction water solubility from CPA and respective binary interaction parameters:

Compound	k_{ij}	AAD x $_{H2O}$ %
ethyl butanoate	-0.254	7.4
propyl butanoate	-0.238	7.0
methyl hexanoate	-0.234	7.4
methyl heptanoate	-0.226	6.3
methyl octanoate	-0.210	8.9
ethyl decanoate	-0.166	6.0
methyl dodecanoate	-0.150	7.4
methyl tetradecanoate	-0.125	7.0
methyl hexadecanoate	-0.107	9.4
methyl octadecanoate	-0.075	3.1
methyl oleate	-0.100	4.3
Global AAD %		**6.6**

- A single value for β_{ij} (0.201) was used for all the binary mixtures selected

$$k_{ij} = 0.0136 \text{ x } C_n - 0.3322$$

M.B. Oliveira, F.R. Varanda, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, Industrial & Engineering Chemistry Research, 2008. **47**(12): p. 4278-4285.

3. Results and Discussion
3.1. Binary systems

Biodiesels

The binary interaction parameter correlation and the constant cross association volume proposed (β_{ij} = 0.201) were used.

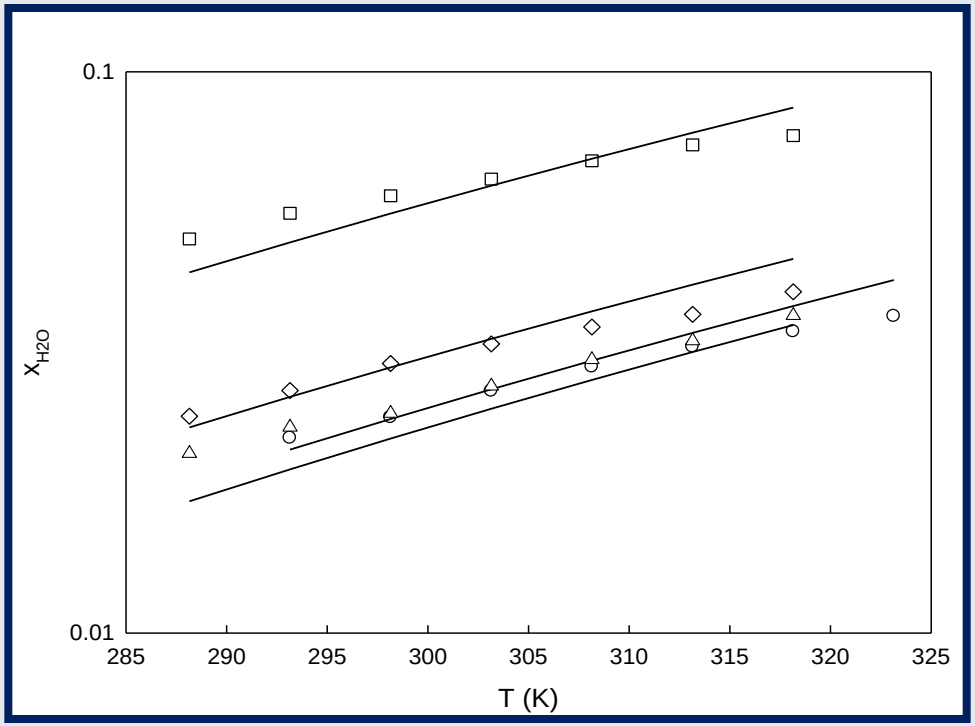
Compositions of the studied biodiesels and x_{H2O} solubility deviations from CPA:

	Biodiesel						Global AAD %
Compound	A %	B %	C %	D %	E %	F %	
methyl hexadecanoate	1.90	10.9		9.80	6.37	6.07	
methyl linoleate	60.3	32.6	13.8	2.20	30.9	22.5	
methyl oleate	37.8	56.2	86.2	87.4	60.7	63.8	
methyl octadecanoate		0.30		0.10	2.03	7.30	
AAD x_{H2O} %	18.6	15.8	18.4	13.3	16.9	9.8	**15.5**

*M.B. Oliveira, F.R. Varanda, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, Industrial & Engineering Chemistry Research, 2008. **47**(12): p. 4278-4285.*

3. Results and Discussion
3.1. Binary systems

Water/fatty acid esters systems

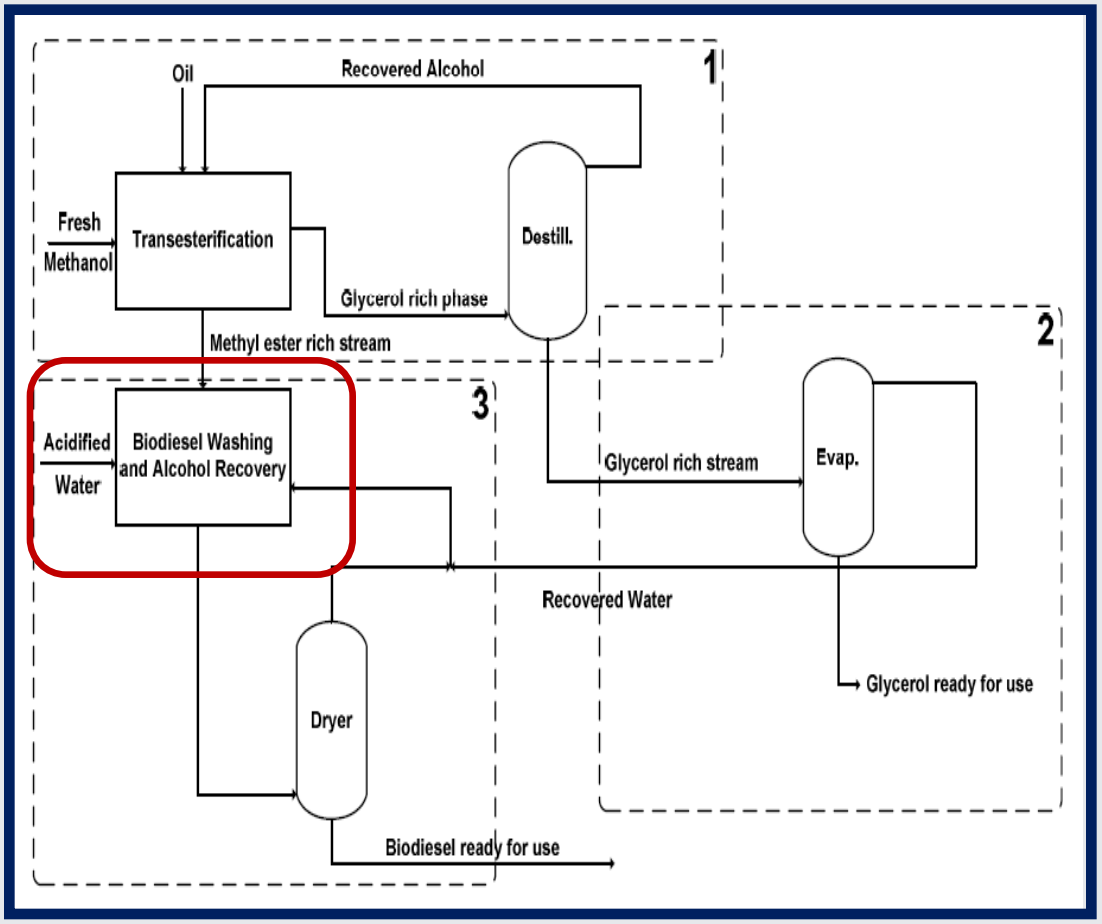


Water solubility in ethyl butanoate (□), ethyl decanoate (◇), methyl tetradecanoate (○) and in Biodiesel F (△). (-) CPA results

M.B. Oliveira, F.R. Varanda, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, Industrial & Engineering Chemistry Research, 2008. ***47****(12): p. 4278-4285.*

3. Results and Discussion
3.1. Binary systems

Water/Fatty acid systems



❑The design and optimization of the biodiesel purification section requires a model that can describe the phase equilibria of water + fatty acid systems that are formed during the fatty esters rich current washing in a liquid-liquid extractor with acidified water, were soaps are converted to free fatty acids.

3. Results and Discussion
3.1. Binary systems

Water/fatty acid systems

Correlation of the CPA pure compound parameters for carboxylic acids

							AAD %	
n.º Carbons	**T_c (K)**	**a_0 ($J.m^3.mol^{-2}$)**	**c_1**	**$bx10^5$ ($m^3.mol^{-1}$)**	**ε ($J.mol^{-1}$)**	**β**	**P^σ**	**ρ**
1	605.9	0.67	0.55	3.24	20725	$3.06x10^{-1}$	0.47	0.97
2	594.0	0.83	0.71	4.69	33710	$3.96x10^{-2}$	2.06	1.17
3	606.9	1.46	0.79	6.33	30122	$6.38x10^{-3}$	0.76	0.47
4	625.0	2.31	0.86	8.50	31665	$6.44x10^{-4}$	1.05	1.60
5	645.8	2.86	0.92	9.77	30739	5.58x10-4	2.77	4.66
6	660.4	3.41	1.00	11.50	37909	$1.31\ x10^{-4}$	2.56	3.02
7	677.9	4.07	1.03	13.40	39225	$1.21x10^{-4}$	3.52	3.00
8	693.5	4.82	1.09	15.30	41221	$4.23x10^{-5}$	1.42	1.68
9	708.6	5.55	1.14	17.30	38553	$7.71x10^{-5}$	1.51	2.47
10	721.7	5.95	1.19	18.80	40685	$1.34x10^{-4}$	1.06	1.38
11	734.9	6.87	1.24	20.70	39467	$6.97x10^{-5}$	2.30	2.85
12	746.0	7.49	1.29	22.40	44385	$3.77x10^{-5}$	2.75	1.87
13	761.0	8.14	1.34	24.10	44431	$3.77x10^{-5}$	3.77	2.22
14	763.7	9.10	1.38	26.00	43772	$3.14x10^{-5}$	2.57	1.95
15	778.3	9.80	1.44	27.80	45888	$1.54x10^{-5}$	3.78	2.29
16	788.3	10.93	1.47	30.70	44730	$2.54x10^{-5}$	1.98	2.04
17	801.5	11.42	1.51	31.50	44944	$1.60x10^{-5}$	1.30	2.70
18	808.3	12.34	1.56	33.70	44507	$1.99x10^{-5}$	2.88	2.16
18:01	781.0	11.74	1.23	32.90	55646	$4.71x10^{-5}$	1.84	3.05
19	817.7	13.26	1.59	35.90	43927	$2.54x10^{-5}$	3.81	2.83
20	830.0	14.15	1.63	38.20	41738	$4.51x10^{-5}$	3.54	2.93
Global AAD %							**2.27**	**2.25**

3. Results and Discussion
3.1. Binary systems

Water/fatty acid systems

Correlation of the CPA pure compound parameters for carboxylic acids

							AAD %	
n.º Carbons	**T_c (K)**	**a_0 ($J.m^3.mol^{-2}$)**	**c_1**	**$bx10^5$ ($m^3.mol^{-1}$)**	**ε ($J.mol^{-1}$)**	**β**	**P^σ**	**ρ**
1	605.9	0.67	0.55	3.24	20725	$3.06x10^{-1}$	0.47	0.97
2	594.0	0.83	0.71	4.69	33710	$3.96x10^{-2}$	2.06	1.17
3	606.9	1.46	0.79	6.33	30122	$6.38x10^{-3}$	0.76	0.47
4	625.0	2.31	0.86	8.50	31665	$6.44x10^{-4}$	1.05	1.60
5	645.8	2.86	0.92	9.77	30739	5.58x10-4	2.77	4.66
6	660.4	3.41	1.00	11.50	37909	$1.31\ x10^{-4}$	2.56	3.02
7	677.9	4.07	1.03	13.40	39225	$1.21x10^{-4}$	3.52	3.00
8	693.5	4.82	1.09	15.30	41221	$4.23x10^{-5}$	1.42	1.68
9	708.6	5.55	1.14	17.30	38553	$7.71x10^{-5}$	1.51	2.47
10	721.7	5.95	1.19	18.80	40685	$1.34x10^{-4}$	1.06	1.38
11	734.9	6.87	1.24	20.70	39467	$6.97x10^{-5}$	2.30	2.85
12	746.0	7.49	1.29	22.40	44385	$3.77x10^{-5}$	2.75	1.87
13	761.0	8.14	1.34	24.10	44431	$3.77x10^{-5}$	3.77	2.22
14	763.7	9.10	1.38	26.00	43772	$3.14x10^{-5}$	2.57	1.95
15	778.3	9.80	1.44	27.80	45888	$1.54x10^{-5}$	3.78	2.29
16	788.3	10.93	1.47	30.70	44730	$2.54x10^{-5}$	1.98	2.04
17	801.5	11.42	1.51	31.50	44944	$1.60x10^{-5}$	1.30	2.70
18	808.3	12.34	1.56	33.70	44507	$1.99x10^{-5}$	2.88	2.16
18:01	781.0	11.74	1.23	32.90	55646	$4.71x10^{-5}$	1.84	3.05
19	817.7	13.26	1.59	35.90	43927	$2.54x10^{-5}$	3.81	2.83
20	830.0	14.15	1.63	38.20	41738	$4.51x10^{-5}$	3.54	2.93
Global AAD %							**2.27**	**2.25**

3. Results and Discussion
3.1. Binary systems

Water/fatty acid systems

Physical Term

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right)$$

fitted

$$b = \sum_i x_i b_i$$

Association Term

Combining rules are only needed in cross associating systems:

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}}$$ (CR-4 or Elliot Rule) [a]

$$\varepsilon^{A_i Bj} = \frac{\varepsilon^{A_i} + \varepsilon^{Bj}}{2}, \quad \beta^{A_i B_j} = \sqrt{\beta^{A_i} \beta^{B_j}}$$ (CR-2) [a]

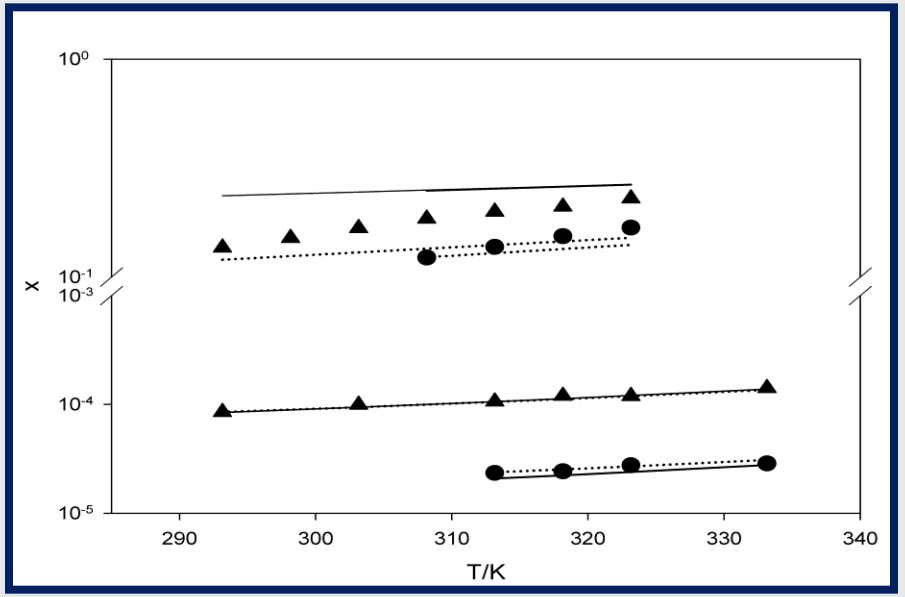
a) E.C. Voutsas, I.V. Yakoumis, D.P. Tassios, Fluid Phase Equilibria, 1999. **160**: p. 151-163.

3. Results and Discussion
3.1. Binary systems

Water/fatty acid systems

		CR-2	
		AAD %	
n. Carbons	k_{ij}	water in acid rich phase	acid in water rich phase
5	-0.0903	39.0	10.4
6	-0.0833	11.9	4.24
7	-0.0918	21.1	2.70
8	-0.0967	40.5	2.38
9	-0.1151	84.4	6.93
10	-0.1333	78.5	8.83
AAD Global %		**45.9**	**5.92**

		CR-4	
		AAD %	
n. Carbons	k_{ij}	water in acid rich phase	acid in water rich phase
5	-0.0951	56.2	9.19
6	-0.0894	42.4	4.67
7	-0.0987	29.5	2.08
8	-0.1033	24.8	2.63
9	-0.1217	11.1	8.11
10	-0.1430	9.05	3.88
AAD Global %		**28.8**	**5.09**



Mutual solubilities for two water + acid systems. Experimental [a,b] (▲, water + octanoic acid; ●, water + decanoic acid) and CPA results (—, CR-2; ····, CR-4)

$$k_{ij} = -0.0140 \times C_n + 0.0070 \quad \text{CR-2}$$

$$k_{ij} = -0.0142 \times C_n + 0.0020 \quad \text{CR-4}$$

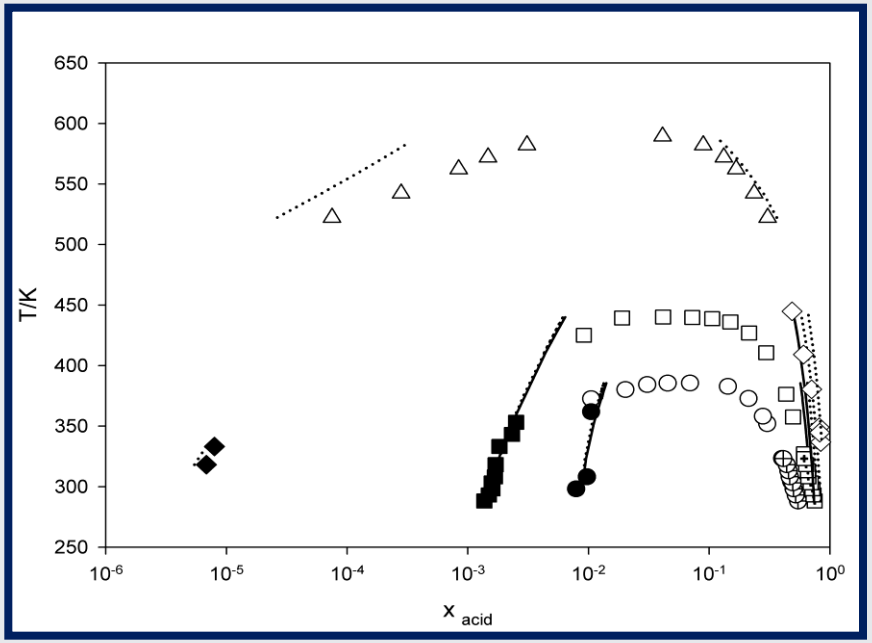
a) M.B. Oliveira, M.J. Pratas, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, AIChE Journal, 2009. **55**(6): p. 1604-1613.
b) S.H. Yalkowsky, H. Yan, Handbook of Aqueous Solubility Data, CRC Press: Boca Raton, 2003.

3. Results and Discussion
3.1. Binary systems

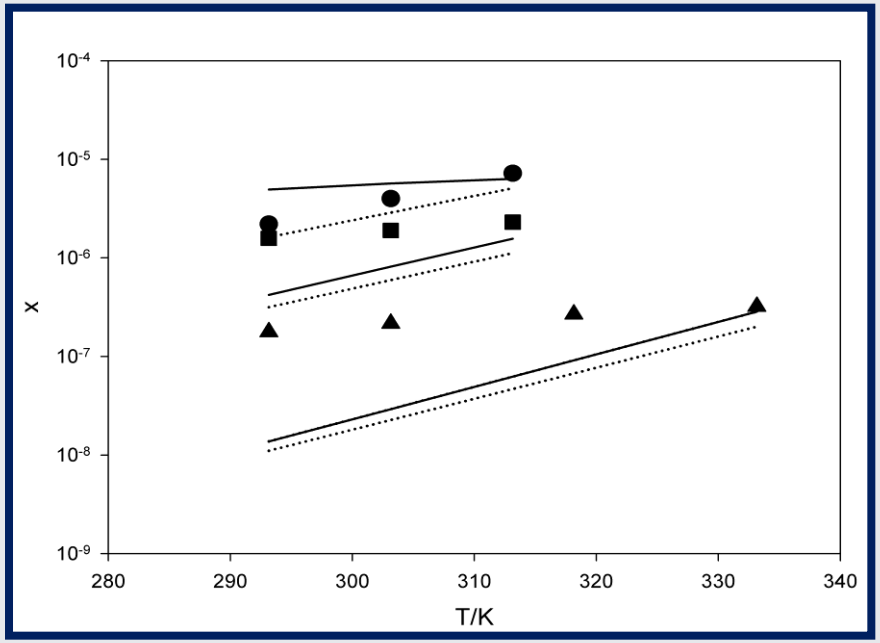
http://path.web.ua.pt

Water/fatty acid systems

The linear correlations for the k_{ij}'s were used for predicting heavy acids:



Water + acids LLE. Experimental values [a,b] for pentanoic acid (●), hexanoic acid (■), dodecanoic acid (◆) and oleic acid (Δ), and CPA results (—, CR-2; ····, CR-4)

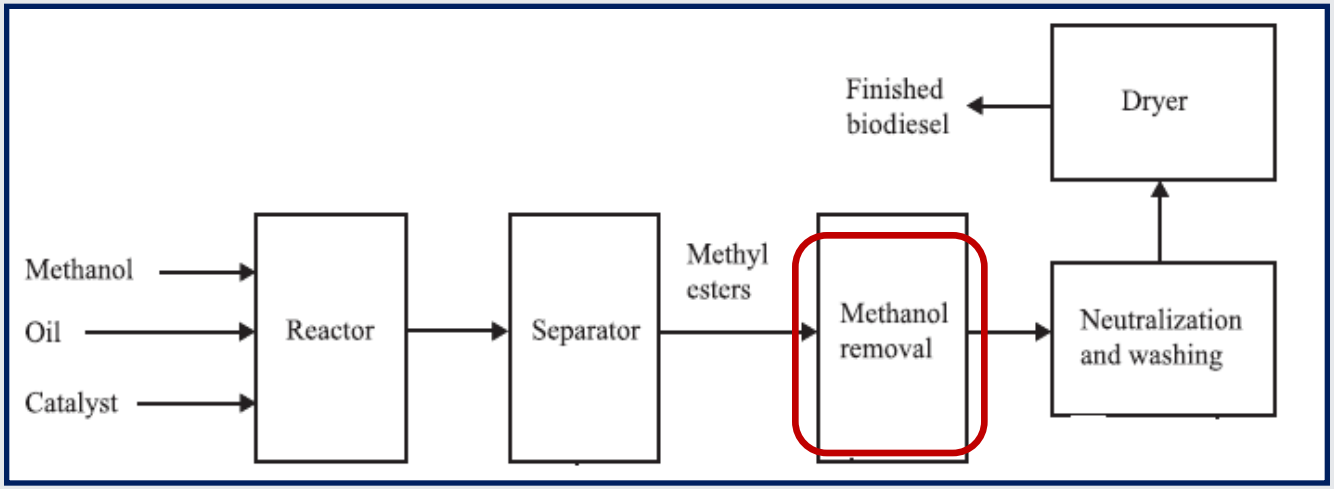


Water + acids SLE. Experimental values [a]: dodecanoic acid (●), tetradecanoic acid (■), octadecanoic acid (▲), and CPA results (—, CR-2; ····, CR-4)

a) M.B. Oliveira, M.J. Pratas, I.M. Marrucho, A.J. Queimada, J.A.P. Coutinho, AIChE Journal, 2009. **55**(6): p. 1604-1613.
b) S.H. Yalkowsky, H. Yan, Handbook of Aqueous Solubility Data, CRC Press: Boca Raton, 2003.

3. Results and Discussion
3.1. Binary systems

Ester/alcohol systems



- Alcohol removal from the fatty acid ester stream leaving the transesterification reactor can be performed by flash evaporation or distillation.
- Distillation is the most used method and the recovered alcohol is re-used in the transesterification process.
- The knowledge about the vapor-liquid equilibrium conditions of these systems is essential for a correct sizing of the operation units involved in alcohol recovery.

3. Results and Discussion
3.1. Binary systems

Ester/alcohol systems

Physical Term

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right)$$

fitted

$$b = \sum_i x_i b_i$$

Association Term

Solvation scheme

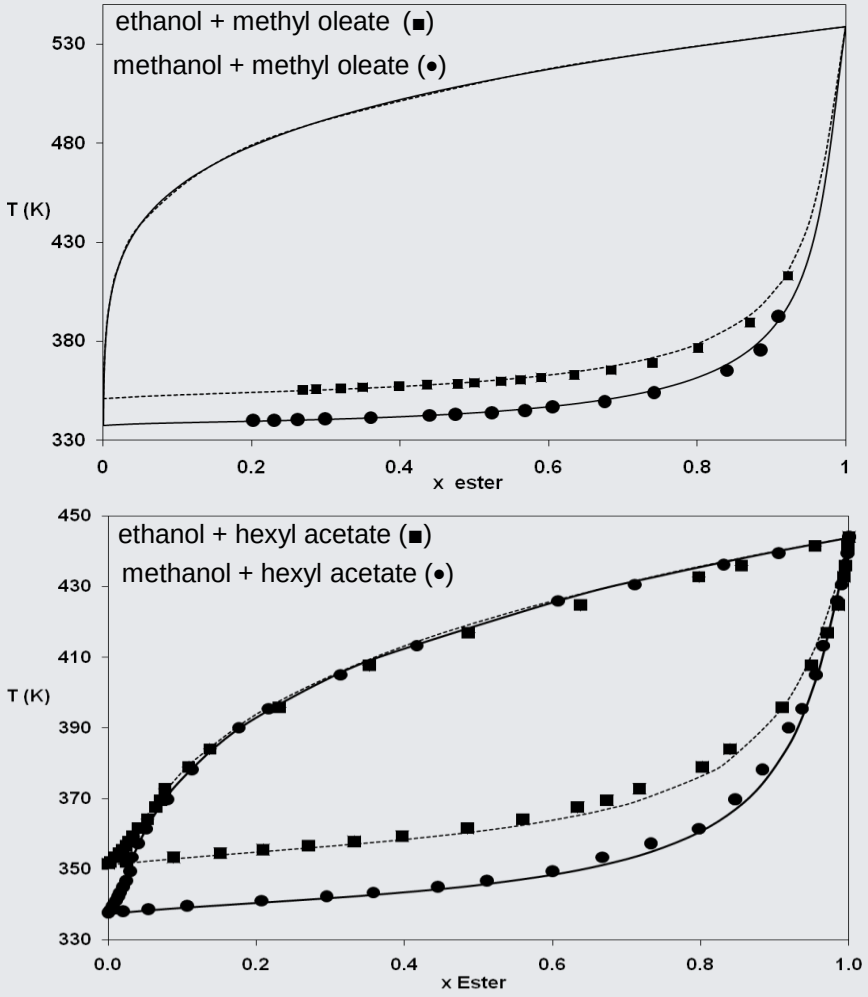
$$\varepsilon^{A_{ester}B_{alcohol}} = \frac{\varepsilon^{A_{alcohol}B_{alcohol}}}{2}$$

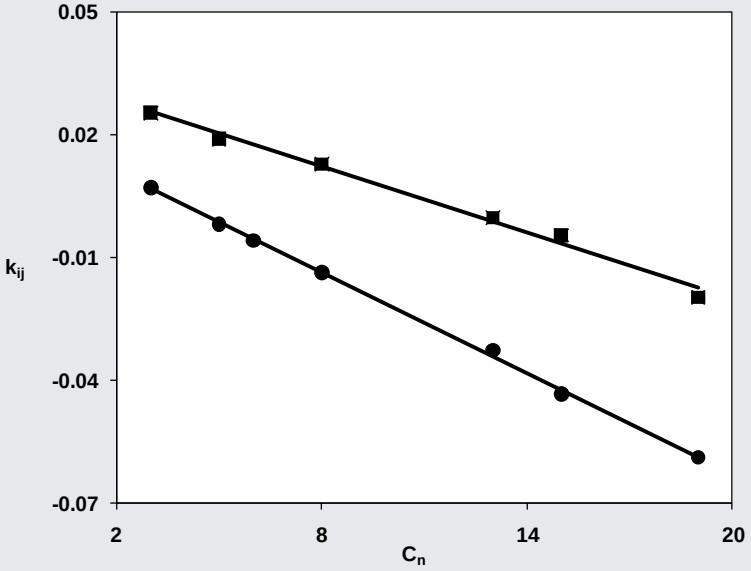
$$\beta^{A_{ester}B_{alcohol}} = fitted$$

E.C. Voutsas, I.V. Yakoumis, D.P. Tassios, Fluid Phase Equilibria, 1999. ***160****: p. 151-163.*

3. Results and Discussion
3.1. Binary systems

Ester/alcohol systems





k_{ij} trend with the ester carbon number for methanol systems (●) and for ethanol systems (■)

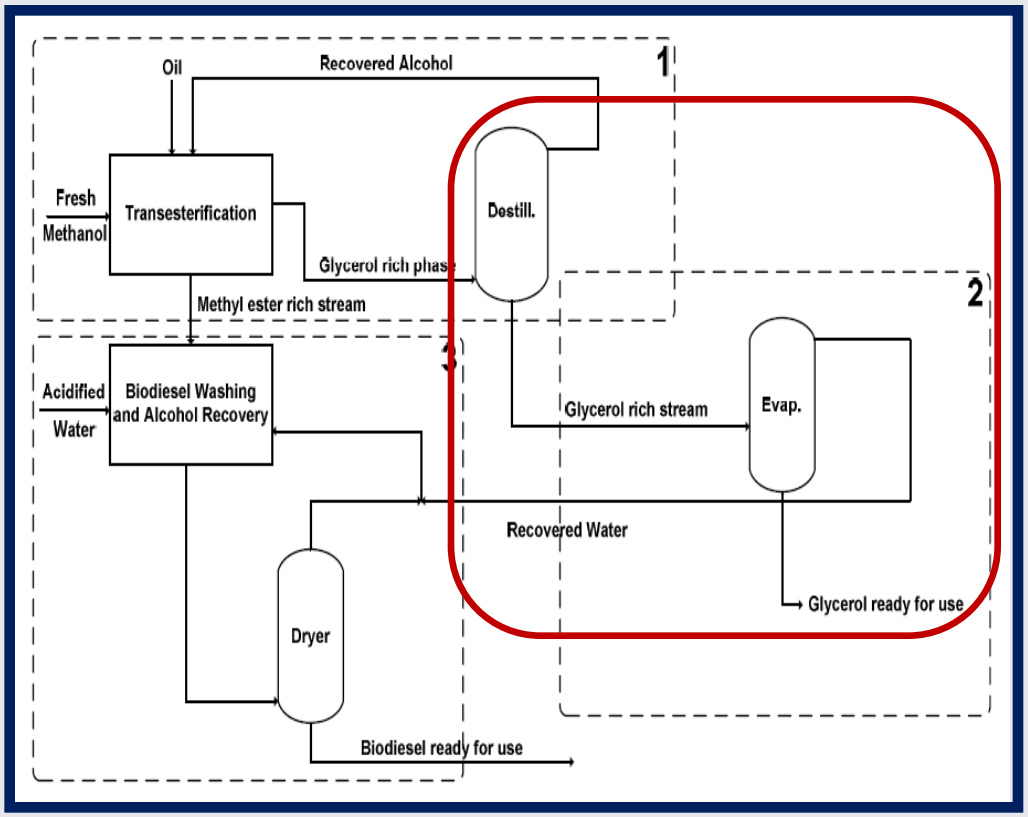
β(methanol + ester) = 0.13

β(ethanol + ester) = 0.10

*M.B. Oliveira, S.I. Miguel, A.J. Queimada, J.A.P. Coutinho, Industrial & Engineering Chemistry Research, 2010. **49**(7): p. 3452-3458.*

3. Results and Discussion
3.1. Binary systems

Glycerol/Water or Alcohol Systems



- The glycerol recovery section is incorporated in order to remove as much glycerol as possible from biodiesel, since the maximum free glycerol value admissible according to the European Standard EN 14214 is 0.02 wt %.

- Glycerol impacts negatively on the fuel properties and profits from selling it into the commercial glycerol market reduces biodiesel production costs in 22-36 %, improving the economic viability of biodiesel.

- The accurate knowledge of the vapor-liquid equilibria of glycerol + alcohol and glycerol + water systems is thus essential for the design of the separation and purification processes of the glycerol recovery section.

3. Results and Discussion
3.1. Binary systems

Glycerol/Water or Alcohol Systems

For glycerol, two different association schemes (4C and 3×2B) were investigated:

Compound			a_0 ($J.m^3.mol^{-2}$)	c_1	$b \times 10^5$ ($m^3.mol^{-1}$)	ε ($J.mol^{-1}$)	β	AAD % P^σ	AAD % ρ
Glycerol	4C		2.28	1.18	7.06	14036	0.025	1.42	1.07
	3×2B	Set-01	2.63	1.29	7.05	4794	0.007	0.53	0.56
		Set-02	1.21	1.06	6.96	19622	0.009	0.77	1.49

The best set of parameters for glycerol will be selected based on their suitability for modeling the VLE of binary mixtures of glycerol with alcohols and water

3. Results and Discussion
3.1. Binary systems

Glycerol/Water or Alcohol Systems

Physical Term

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right)$$

fitted

$$b = \sum_i x_i b_i$$

Association Term

Combining rules are only needed in cross associating systems:

$$\Delta^{A_i B_j} = \sqrt{\Delta^{A_i B_i} \Delta^{A_j B_j}}$$ (CR-4 or Elliot Rule) [a]

$$\varepsilon^{A_i Bj} = \frac{\varepsilon^{A_i} + \varepsilon^{Bj}}{2}, \quad \beta^{A_i B_j} = \sqrt{\beta^{A_i} \beta^{B_j}}$$ (CR-2) [a]

a) E.C. Voutsas, I.V. Yakoumis, D.P. Tassios, Fluid Phase Equilibria, 1999. **160**: p. 151-163.

3. Results and Discussion
3.1. Binary systems

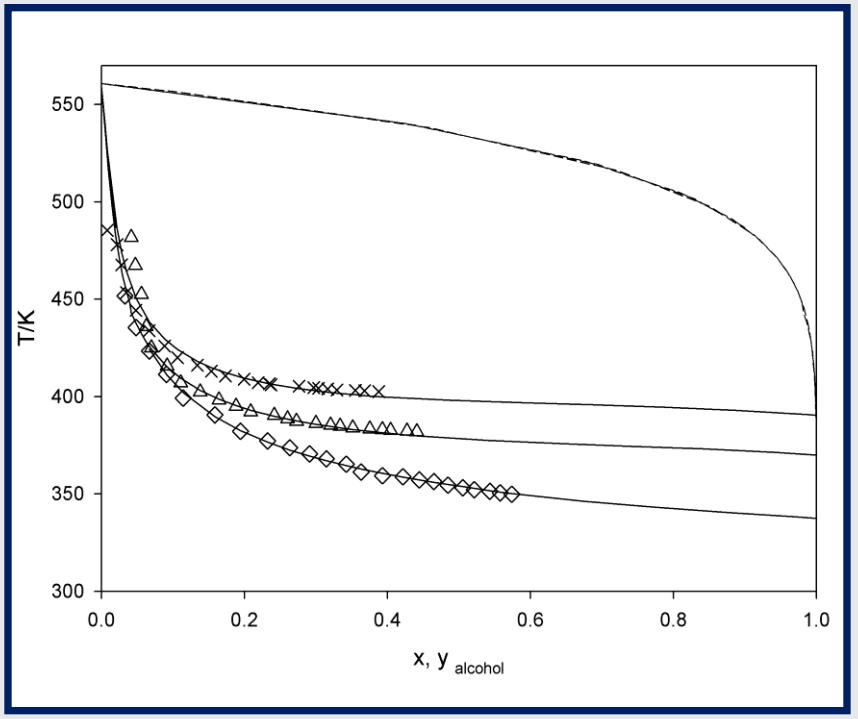
Glycerol/Water or Alcohol Systems

VLE results for glycerol + alcohol (or water) systems and binary interactions parameters using the CR-4 combining rule.

	k_{ij}			AAD %		
	4C	3×2B set 1	3×2B set 2	4C	3×2B set 1	3×2B set 2
water	-0.280	-0.395	-0.229	1.16	2.13	0.72
methanol	-0.041	-0.117	0.014	0.32	0.60	0.27
ethanol	-0.025	-0.106	0.060	1.97	1.52	1.55
1-propanol	-0.007	-0.031	0.002	1.00	0.92	1.06
2-propanol	-0.048	-0.118	0.049	1.90	1.76	1.36
1-butanol	-0.019	-0.049	0.015	0.93	1.08	0.60
Global AAD %				**1.21**	**1.33**	**0.93**

3×2B scheme second set:

- Positive and small k_{ij}.
- The right interactions between unlike molecules are being considered.
- Description of the bubble point curves with global average deviations inferior to 1 %.



VLE of alcohol + glycerol systems [a] (methanol, (◊), 1-propanol (Δ), 1-butanol (×)). CPA results with 3×2B (set 2) for glycerol. (liquid phase (—), vapor phase (----))

a) M.B. Oliveira, A.R.R. Teles, A.J. Queimada, J.A.P. Coutinho, Fluid Phase Equilibria, 2009. **280**(1-2): p. 22-29.

3. Results and Discussion
3.1. Binary systems

Glycerol/Water or Alcohol Systems

VLE results for glycerol + alcohol (or water) systems and binary interactions parameters using the CR-4 combining rule.

	k_{ij}			AAD %		
	4C	3×2B set 1	3×2B set 2	4C	3×2B set 1	3×2B set 2
water	-0.280	-0.395	-0.229	1.16	2.13	0.72
methanol	-0.041	-0.117	0.014	0.32	0.60	0.27
ethanol	-0.025	-0.106	0.060	1.97	1.52	1.55
1-propanol	-0.007	-0.031	0.002	1.00	0.92	1.06
2-propanol	-0.048	-0.118	0.049	1.90	1.76	1.36
1-butanol	-0.019	-0.049	0.015	0.93	1.08	0.60
Global AAD %				**1.21**	**1.33**	**0.93**

4C scheme:

- k_{ij} higher and negative
- Cross–association between glycerol and alcohols is being underestimated
- Higher global average deviations.

M.B. Oliveira, A.R.R. Teles, A.J. Queimada, J.A.P. Coutinho, Fluid Phase Equilibria, 2009. **280**(1-2): p. 22-29.

3. Results and Discussion
3.1. Binary systems

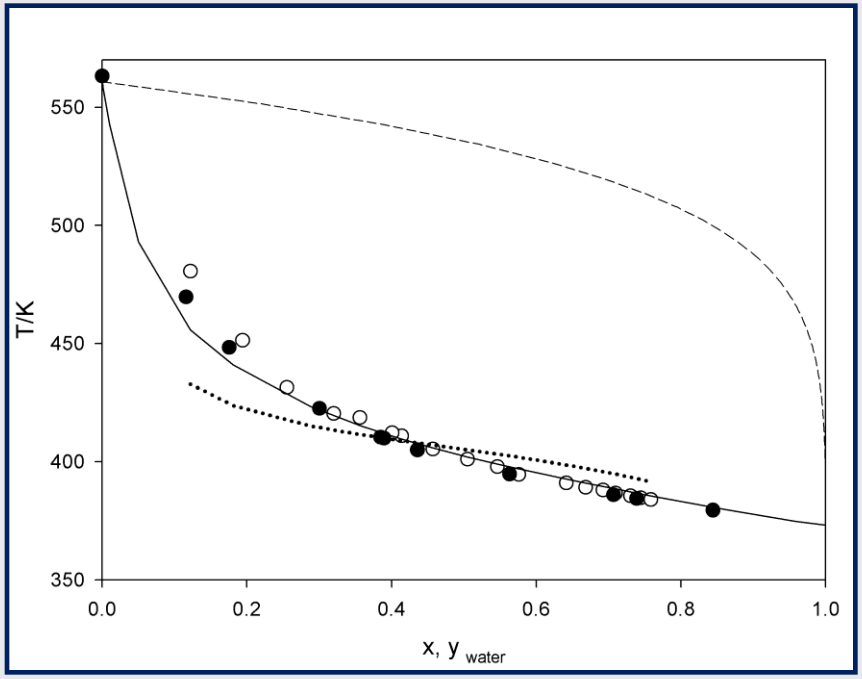
Glycerol/Water or Alcohol Systems

VLE results for glycerol + alcohol (or water) systems and binary interactions parameters using the CR-4 combining rule.

	k_{ij}			AAD %		
	4C	3×2B set 1	3×2B set 2	4C	3×2B set 1	3×2B set 2
water	-0.280	-0.395	-0.229	1.16	2.13	0.72
methanol	-0.041	-0.117	0.014	0.32	0.60	0.27
ethanol	-0.025	-0.106	0.060	1.97	1.52	1.55
1-propanol	-0.007	-0.031	0.002	1.00	0.92	1.06
2-propanol	-0.048	-0.118	0.049	1.90	1.76	1.36
1-butanol	-0.019	-0.049	0.015	0.93	1.08	0.60
Global AAD %				**1.21**	**1.33**	**0.93**

3×2B scheme first set :

- k_{ij} larger and negative.
- Higher global average deviations.

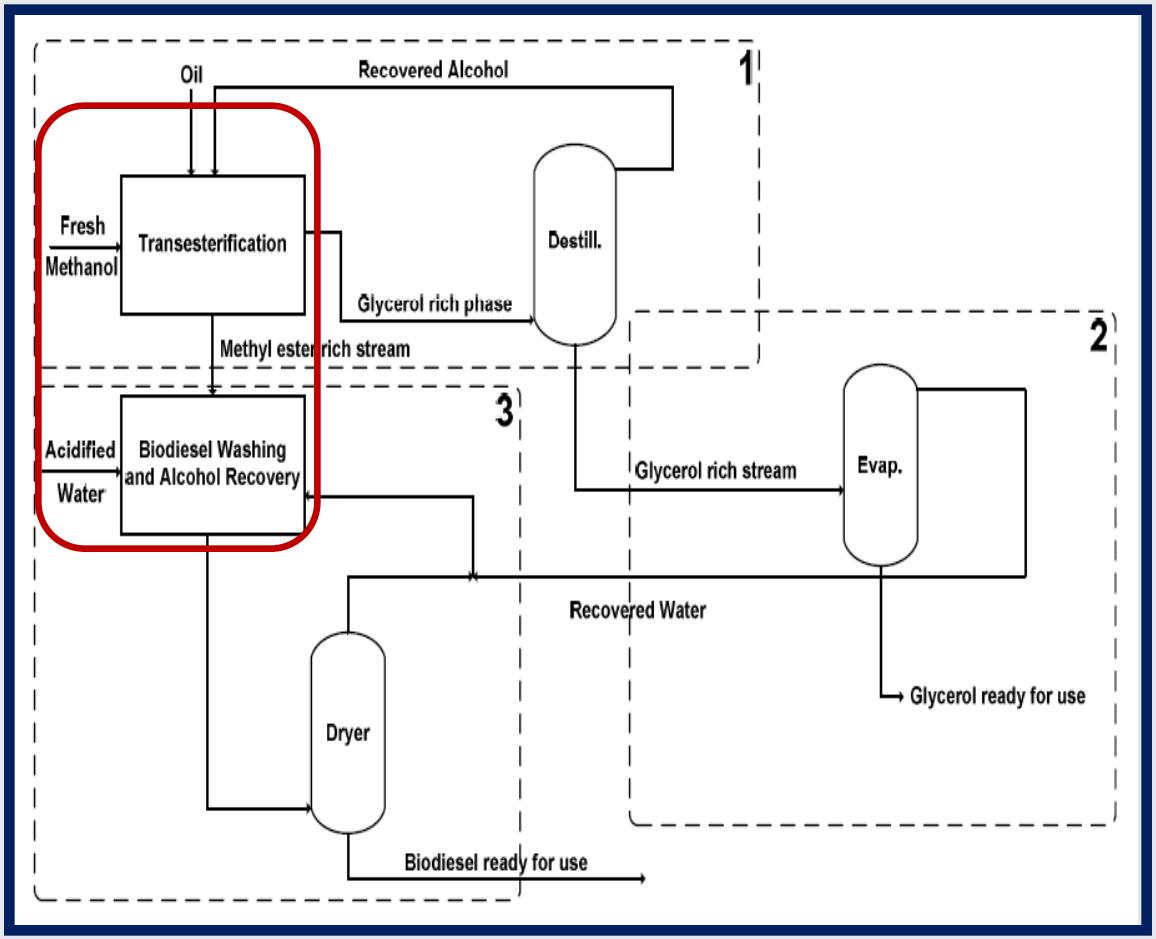


VLE of water + glycerol using the 3×2B scheme. set 1 (·····) and set 2 of parameters (—). Vapor phase (----). Experimental data from Oliveira *et al.* [a] (○) and Chen *et al.* [b](●)

a) M.B. Oliveira, A.R.R. Teles, A.J. Queimada, J.A.P. Coutinho, Fluid Phase Equilibria, 2009. **280**(1-2): p. 22-29.
b) D.H.T. Chen, A.R. Thompson,. Journal of Chemical and Engineering Data, 1970. **15**(4): p. 471-474.

3. Results and Discussion
3.1. Binary systems

After describing binary systems it was possible to describe multicomponent systems of relevance for the biodiesel industry.

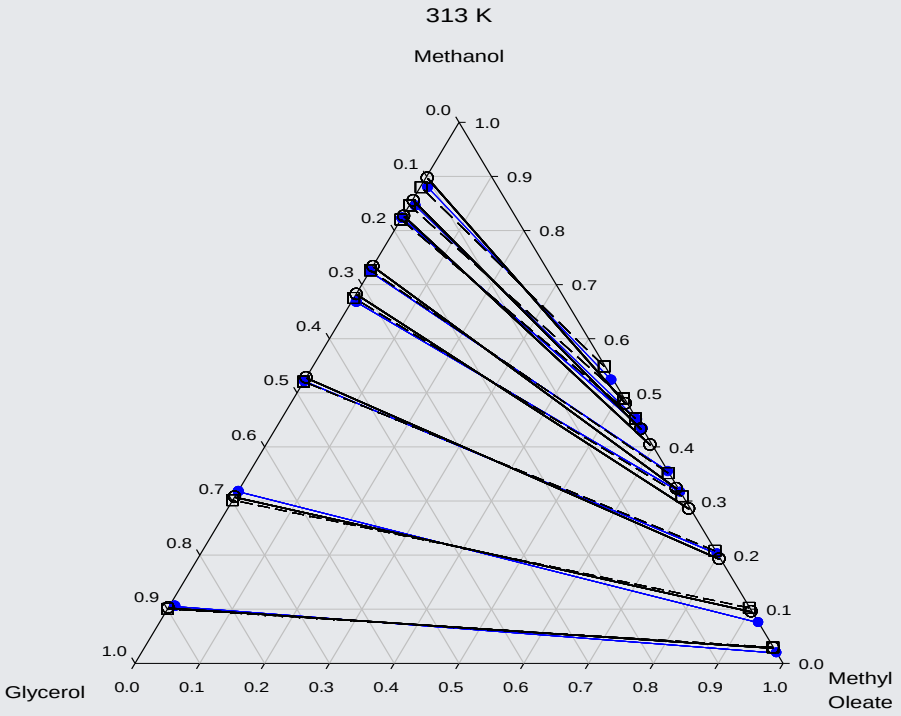


❑ As there is still a considerable lack of data for many of the binary subsystems and even more ternary and multicomponent systems of interest, different approaches had to be considered for estimating the binary interaction parameters needed:

- Binary interaction parameters from binary data.
- Binary interaction parameters from multicomponent data.

3. Results and Discussion
3.2. Multicomponent systems

Methyl Oleate/Methanol/Glycerol



CPA results for the methyl oleate + methanol + glycerol system (***k*ij* and/or *βij* from binary data (○, —); *kij* and/or *βij* from this ternary data (□, ---)).** Experimental data [a] (●, —)

k_{ij}'s and β_{ij}'s values obtained from LLE data of methyl oleate + methanol + glycerol system

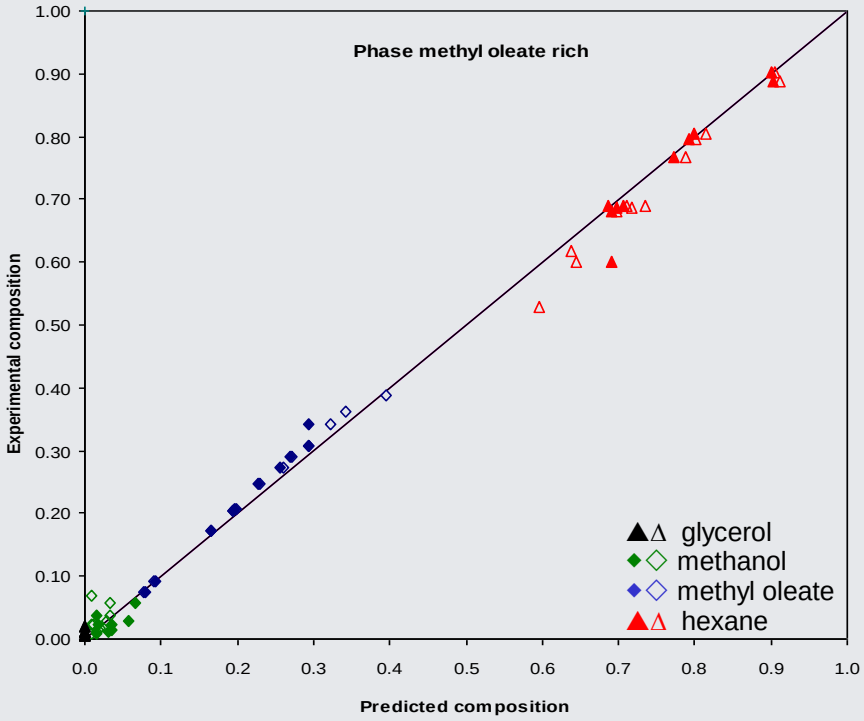
	k_{ij}	β_{ij}
Methyl Oleate + Glycerol	-0.0982	0.0110
Gycerol + Methanol	-0.0368	
Methyl Oleate + Methanol	-0.0217	0.2451

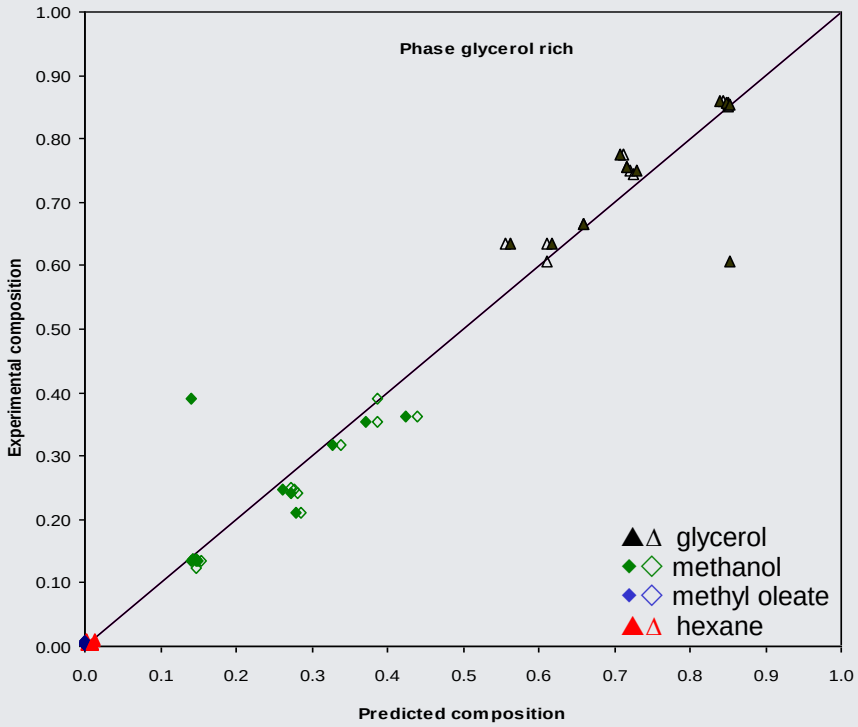
Improved the description of the glycerol rich phase in particular the methyl oleate composition

*a) A.E. Andreatta, L.M. Casas, P. Hegel, S.B. Bottini, E.A. Brignole, Industrial & Engineering Chemistry Research, 2008. **47**(15): p. 5157-5164.*

3. Results and Discussion
3.2. Multicomponent systems

Methyl Oleate/Methanol/Glycerol/Hexane





Experimental versus estimated compositions for the quaternary system methyl oleate + glycerol+ methanol + hexane (**full symbols represent results using binary interaction parameters from binary data and empty symbols represent results using binary interaction parameters correlated from methyl oleate + methanol + glycerol system**) [a]

*a) R. Tizvar, D.D. McLean, M. Kates, M.A. Dube, Industrial & Engineering Chemistry Research, 2008. **47**(2): p. 443-450.*

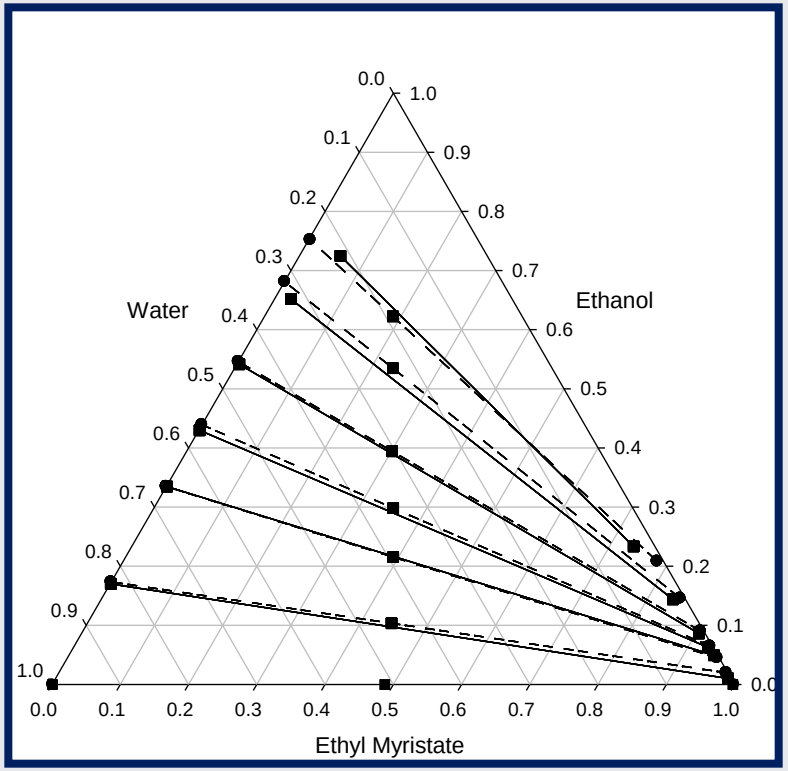
3. Results and Discussion
3.2. Multicomponent systems

Ethyl Ester/Ethanol/Water

Binary interaction and cross–association parameters used to model ethyl ester + ethanol + water systems:

	k_{ij}	β_{ij}
Ethyl Laurate + Ethanol	0.083	0.100
Ethyl Laurate + Water	0.172	0.201
Ethyl Myristate + Ethanol	0.094	0.100
Ethyl Myristate + Water	0.155	0.201

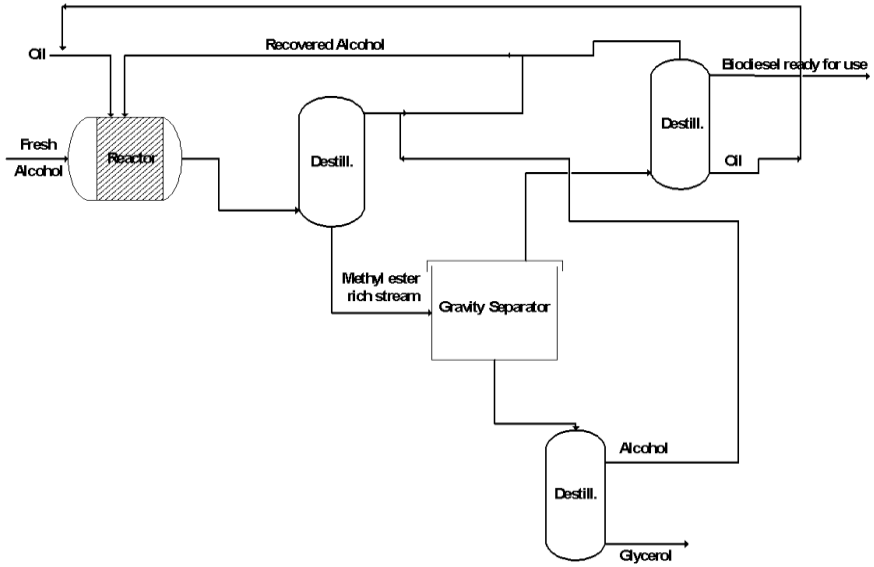
The estimated β_{ij}'s while modeling the LLE of water + fatty acid ester systems and the VLE of ethanol + fatty acid ester systems were applied.



Liquid–liquid equilibrium for the system containing ethyl myristate + ethanol + water at 298.15 K: experimental (■, —) and CPA results (●, --)

3. Results and Discussion

Near/supercritical synthesis of biodiesel

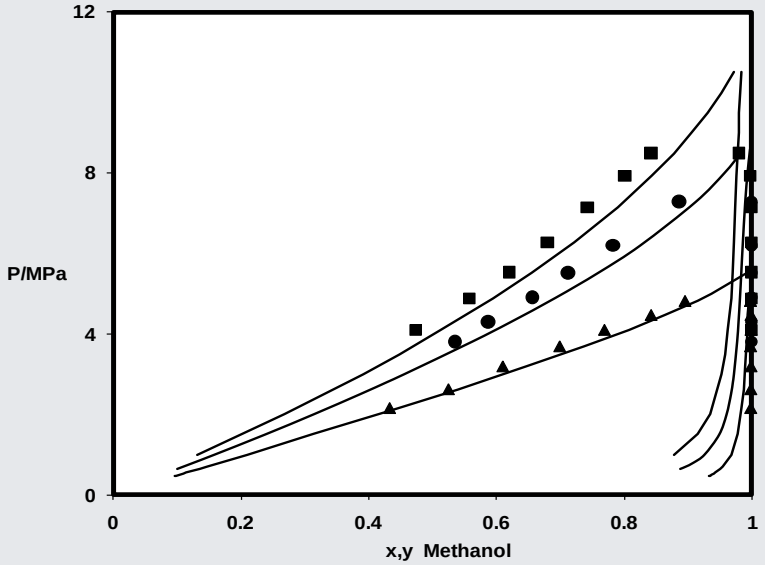


- Successfully overcome a number of the problems of conventional processes.
- The conversion is high.
- The reaction duration is significantly shorter, only minutes, even with low-quality raw materials.
- Requires a smaller reactor size to achieve the same production output of the conventional biodiesel production process.

Single and temperature independent binary interaction parameters, fitted to experimental VLE data at atmospheric pressure, were used to predict the experimental data.

Fatty Acid Ester/Alcohol Systems

For methanol systems, a degradation of the predictions with temperature was observed :



VLE for the methanol + methyl laurate system [a] at 493 K (▲), at 523 K (●) and at 543 K (■). CPA results (—)

CPA pure compound parameters and modeling results for methanol in the T_r range of 0.85-1:

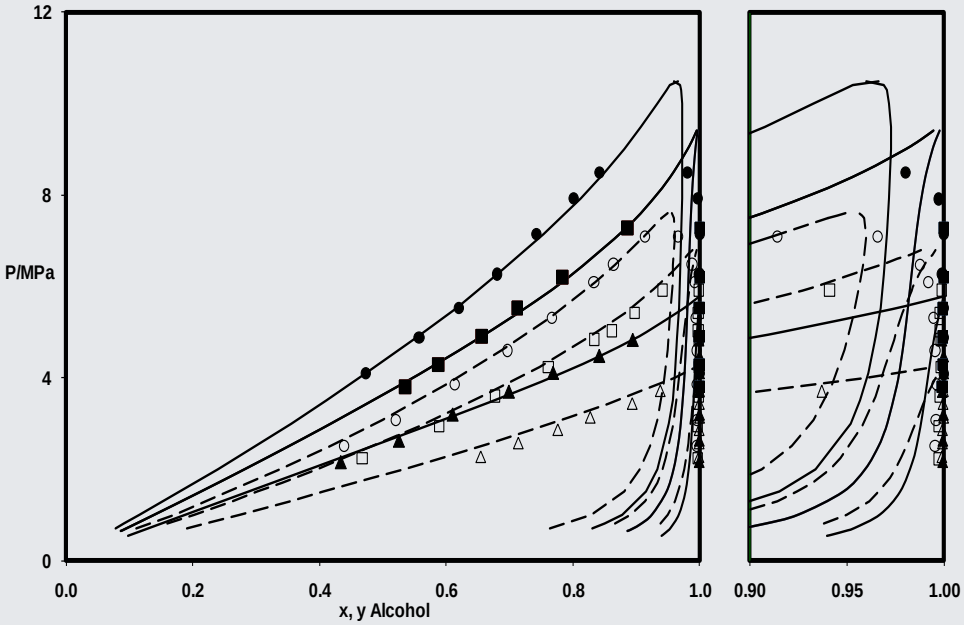
							AAD %	
Compound	**T_c (K)**	**a_0 (J.m^3.mol^{-2})**	**c_1**	**b×10^5 (m^3.mol^{-1})**	**ε (J.mol^{-1})**	**β**	**P^σ**	**ρ**
methanol- set 2	**512.7**	**0.41**	**1.18**	**3.25**	**19945**	**0.047**	**1.6**	**3.8**

*a) Y. Shimoyama, Y. Iwai, B.S. Jin, T. Hirayama, Y. Arai, Fluid Phase Equilibria, 2007. **257**(2): p. 217-222.*

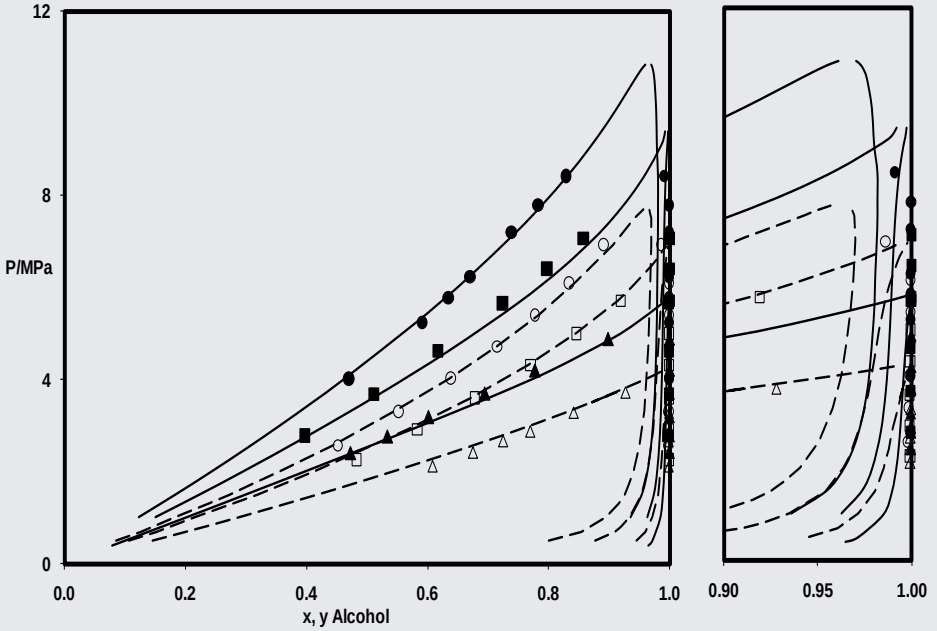
3. Results and Discussion

3.3. Prediction of near and supercritical fatty acid ester + alcohol systems

Fatty Acid Ester/Alcohol Systems



VLE for methanol + methyl laurate [a] (full symbols) and ethanol + ethyl laurate [b] (empty symbols) systems (▲, 493 K; ■, 523 K; ●, 543 K). CPA results (—, methanol systems; ----, ethanol systems)



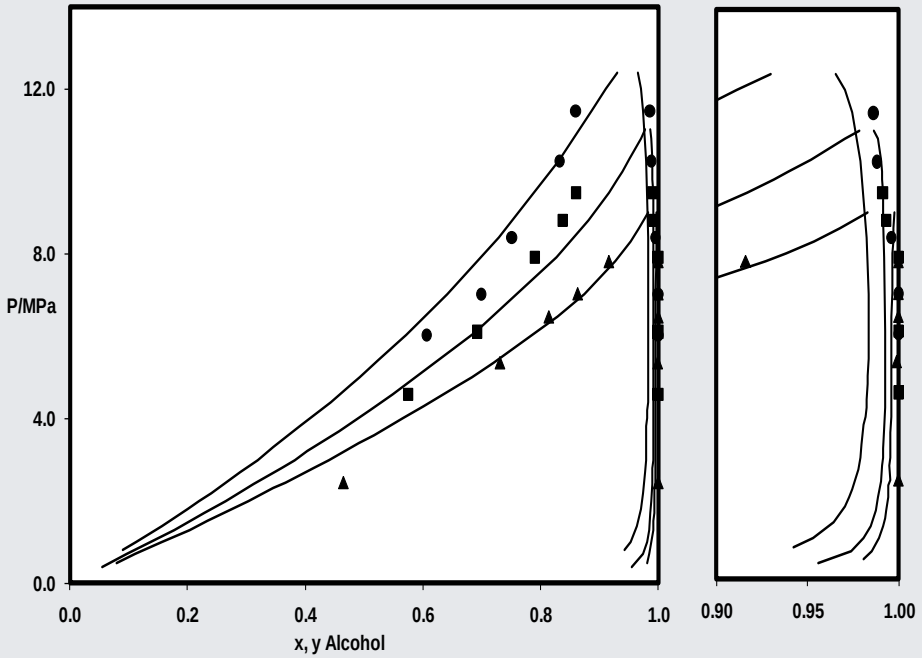
VLE for methanol + methyl myristate [a] (full symbols) and ethanol + ethyl myristate [b] (empty symbols) systems (▲, 493 K; ■, 523 K; ●, 543 K). CPA results (—, methanol systems; ----, ethanol systems)

a) Y. Shimoyama, Y. Iwai, B.S. Jin, T. Hirayama, Y. Arai, Fluid Phase Equilibria, 2007. ***257****(2): p. 217-222.*
b) Y. Shimoyama, Y. Iwai, T. Abeta, Y. Arai, Fluid Phase Equilibria, 2008. ***264****(1-2): p. 228-234.*

3. Results and Discussion

3.3. Prediction of near and supercritical fatty acid ester + alcohol systems

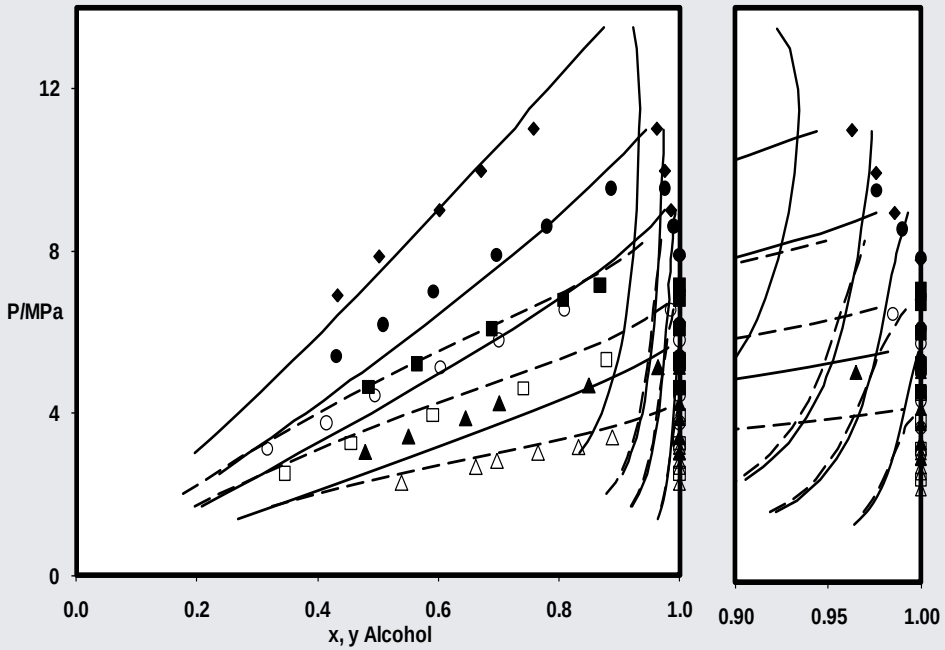
Fatty Acid Ester/Alcohol Systems



Experimental VLE for the system methanol + FAMEs (▲ , 523 K; ■, 548 K; ●, 573 K) [a]. CPA results (—)

FAMEs: 85 wt % of C_{18} methyl esters (mainly methyl oleate) and the rest C_{16} and C_{14} methyl esters.

Glycerol/Alcohol Systems



VLE for methanol + glycerol (full symbols) and ethanol + glycerol (empty symbols) systems (▲, 493 K; ■, 523 K; ●, 543 K; ◆, 573 K) [b]. CPA results (—, methanol systems; ---, ethanol systems)

a) T. Fang, Y. Shimoyama, T. Abeta, Y. Iwai, M. Sasaki, M. Goto, Journal of Supercritical Fluids, 2008. 47(2): p. 140-146.
b) Y. Shimoyama, T. Abeta, L. Zhao, Y. Iwai, Fluid Phase Equilibria, 2009. 284(1): p. 64-69.

4. CPA EoS vs. Traditional models

Modeling results for the VLE of fatty acid ester + methanol/ethanol and glycerol + alcohol/water systems

		UNIFAC	SRK	PSRK	PR-MHV2	SRK-MHV2	CPA
		ΔT_b %					
ester + methanol	methyl laurate + methanol	0.57	1.71	2.02	1.20	1.06	**0.28**
	methyl myristate + methanol	0.69	1.82	2.74	1.55	0.94	**0.40**
	methyl oleate + methanol	0.74	1.44	2.78	2.48	0.89	**0.42**
	Global AAD %	**0.67**	**1.66**	**2.51**	**1.74**	**0.96**	**0.37**
ester + ethanol	methyl laurate + ethanol	0.65	1.94	1.10	0.76	0.72	**0.36**
	methyl myristate + ethanol	0.97	1.43	1.90	0.52	1.28	**0.16**
	methyl oleate + ethanol	1.47	1.03	2.74	1.14	0.91	**0.35**
	Global AAD %	**1.03**	**1.47**	**1.91**	**0.81**	**0.97**	**0.29**
	glycerol + water	**2.49**	**3.67**	**2.84**	**1.84**	**2.12**	**0.72**
glycerol + alcohol	glycerol + methanol	3.89	0.86	1.33	4.89	3.37	**0.62**
	glycerol + ethanol	7.33	1.47	4.03	7.60	7.66	**3.52**
	glycerol + propanol	3.41	1.24	1.97	4.69	5.51	**1.07**
	glycerol + 2-propanol	7.52	2.36	4.02	8.64	9.37	**2.70**
	glycerol + 1-butanol	4.83	0.76	2.98	5.91	9.03	**1.03**
	Global AAD %	**5.40**	**1.34**	**2.87**	**6.35**	**6.99**	**1.79**

4. CPA EoS vs. Traditional models

Modeling results for the water solubility in fatty acid esters

	UNIFAC	SRK	PSRK	PR-MHV2	SRK-MHV2	CPA
				Δx %		
ethyl butanoate	19.5	54.3	43.9	145.6	24.7	**7.9**
propyl butanoate	22.3	49.0	43.8	160.1	29.3	**8.1**
methyl hexanoate	25.1	42.8	44.5	167.5	34.3	**7.7**
methyl heptanoate	17.6	31.3	29.2	172.6	47.6	**6.3**
methyl octanoate	30.6	29.0	36.1	240.2	63.5	**7.9**
ethyl decanoate	31.1	28.5	12.2	546.0	190.0	**6.6**
methyl dodecanoate	28.3	19.5	9.1	536.4	184.7	**8.0**
methyl tetradecanoate	28.7	9.7	7.8	673.1	290.6	**7.3**
methyl hexadecanoate	15.8	31.4	11.3	613.4	224.9	**8.2**
methyl octadecanoate	8.3	25.2	22.7	738.8	322.2	**3.9**
methyl oleate	86.9	13.5	23.8	972.9	766.5	**11.4**
Global AAD %	**28.6**	**30.4**	**25.9**	**451.5**	**198.0**	**7.6**

4. CPA EoS vs. Traditional models

Modeling results for the mutual solubilities of water + acid systems

	AAD %											
	UNIFAC		SRK		PSRK		PR-MHV2		SRK-MHV2		CPA	
	water in acid rich phase	acid in water rich phase	water in acid rich phase	acid in water rich phase	water in acid rich phase	acid in water rich phase	water in acid rich phase	acid in water rich phase	water in acid rich phase	acid in water rich phase	**water in acid rich phase**	**acid in water rich phase**
Pentanoic acid	8.2	73.0	84.7	168.4	4.6	53.3	49.0	79.5	19.7	56.8	**54.0**	**51.8**
Hexanoic acid	26.4	120.1	76.2	150.3	26.8	78.5	107.0	83.9	57.1	77.5	**13.0**	**18.8**
Heptanoic acid	58.1	282.1	69.7	100.0	50.8	414.2	180.0	1841.6	106.0	677.0	**22.0**	**2.8**
Octanoic acid	102.0	422.0	63.0	100.0	79.6	583.7	317.0	3271.3	187.0	939.4	**25.1**	**34.7**
Nonanoic acid	65.9	383.0	64.8	100.0	52.1	546.6	217.0	4106.9	124.0	1029.3	**11.1**	**8.1**
Decanoic acid	64.6	219.9	61.6	100.0	39.0	366.0	271.0	3371.0	150.0	374.5	**9.9**	**9.7**
Global AAD %	**54.2**	**250.0**	**70.0**	**119.8**	**42.2**	**340.4**	**190.2**	**2125.7**	**107.3**	**525.7**	**22.5**	**21.0**

5. Conclusions

❑ It was intended to describe phase equilibria of relevance for the biodiesel production and purification processes.

❑ Binary and multicomponent systems containing fatty acids, fatty acid esters, alcohols, water and glycerol were considered.

❑ The CPA EoS proves to be a valuable alternative to the demanding EoS/g^E models to evaluate the design, operation and optimization of biodiesel production and purification.

❑ The addition of an associating term proves to be a significant improvement, making possible to accurately describe all the association phenomena between associating molecules and the solvation between non-self-associating and associating compounds.

6. Future Work

❑ The regression and correlation of the pure component equation of state parameters for triglycerides, with the final aim of modeling equilibrium data for binary and multicomponent systems composed by vegetable oils.

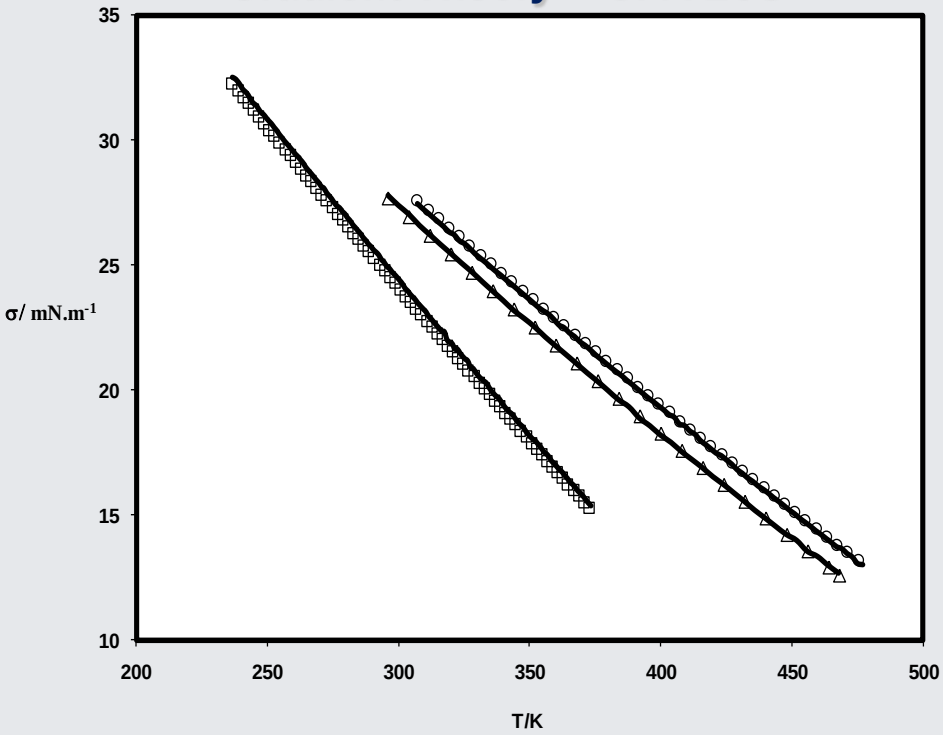
❑Surface and interfacial tensions and high pressure densities of biodiesels are expected to be modeled as soon as new experimental data appear in literature.

6. Future Work

❑ The regression and correlation of the pure component equation of state parameters for triglycerides, with the final aim of modeling equilibrium data for binary and multicomponent systems composed by vegetable oils.

❑ Surface and interfacial tensions and high pressure densities of biodiesels are expected to be modeled as soon as new experimental data appear in literature.

Gradient Theory + CPA EoS

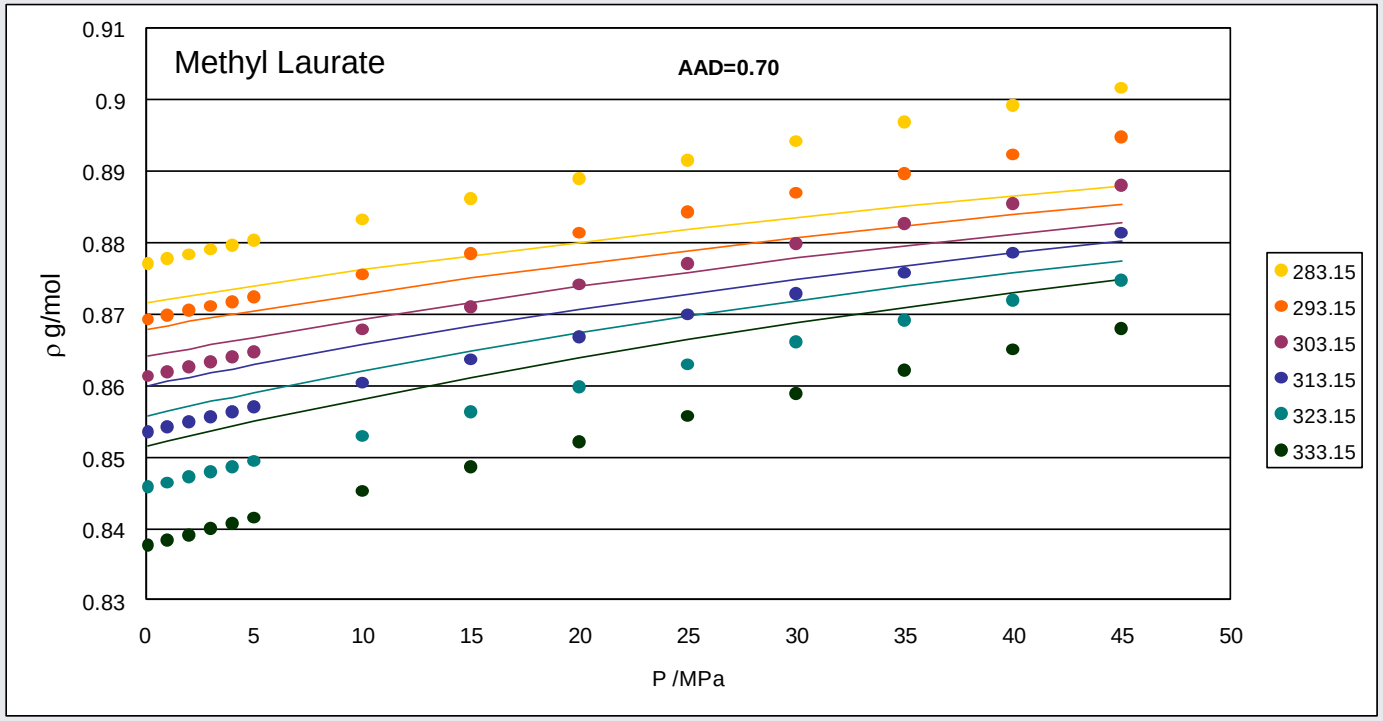


Esters surface tension. Experimental (□, methyl propanoate; Δ, nonyl formate; ○, methyl decanoate) and gradient theory results (–)

6. Future Work

❑ The regression and correlation of the pure component equation of state parameters for triglycerides, with the final aim of modeling equilibrium data for binary and multicomponent systems composed by vegetable oils.

❑Surface and interfacial tensions and high pressure densities of biodiesels are expected to be modeled as soon as new experimental data appear in literature.



6. Future Work

❑ The regression and correlation of the pure component equation of state parameters for triglycerides, with the final aim of modeling equilibrium data for binary and multicomponent systems composed by vegetable oils.

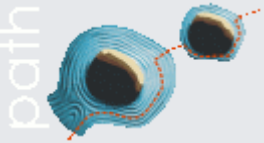
❑Surface and interfacial tensions and high pressure densities of biodiesels are expected to be modeled as soon as new experimental data appear in literature.

❑ CPA can still be combined with a Debye-Huckel term, able to deal with the presence of electrolytes, allowing to correctly model the thermodynamics of systems containing the alkaline catalysis.

7. Acknowledgements

Dr. João Coutinho e Dr. António José Queimada

Dr. Georgios Kontogeorgis



FCT Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR

Thank you all for your attention