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Phase Equilibria (LLE and VLE) of Refining Operations for Enzymatic Biodiesel Production via Quantum Mechanical COSMO-RS Method

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DOI 10.1002/aic.13731

Phase equilibria, both liquid–liquid equilibria (LLE) and vapor-liquid equilibria (VLE), are equally important in the refining operations of biodiesel production. Equilibrium distributions of components at the down-processing of enzymatic ethanolysis reaction were investigated through quantum mechanical COnductor-like Screening MOdel-Real Solvent method with implemented vapor pressure equations. Due to the composite nature of fatty acid ethyl ester (FAEE) components as the biodiesel fuel, multicomponent predictive phase equilibria approach was applied for a model reaction system of refined soybean oil with 30% molar excess amount of ethanol. Simulation results for the LLE at 303 K were in significant agreement with reported experimental data. Minimum boiling azeotropes were found for FAEE-glycerol binaries at isothermal (at 423 and 473K) and isobaric (at reduced pressures) VLE simulations. Similar results were also found at the VLE of glycerol purification operations for multicomponent real case simulations. The feasibilities of simple and rigorous unit operations were also pointed up in this study. © 2012 American Institute of Chemical Engineers *AIChE J,* 58: 3504–3516, 2012

Keywords: LLE, VLE, biodiesel refining, phase equilibria, enzymatic ethanolysis

Introduction

Biodiesel is a renewable alternative diesel fuel, defined as the fatty acid alkyl esters (FAAE) of vegetable oils or animal fats. The alkyl esters produced depend on the alcohol used where methanol and ethanol are the most common with transesterification and esterification as the foremost reactions exerted for producing biodiesel. Since oils/fats mainly consist of triacylglycerides (TAG), the central reaction is transesterification, also called alcoholysis; whereas esterification is only necessary for feedstocks with higher content of free fatty acids (FFA). Transesterification is the exchange of alkoxy group of an ester compound (TAG) with an aliphatic alcohol (the acyl acceptor) in the presence of a catalyst. The reaction stoichiometry requires 3 mols of alcohol per 1 mol of oil to synthesize 3 mols of FAAE and 1 mol of glycerol by-product.

Currently, biodiesel is primarily produced from methanolysis of rapeseed, palm, and soybean oil, although numerous other edible/inedible vegetable oils, low-grade by-products of the oil refining industry, as well as waste cooking oils are also suitable feedstocks. In practice, due to the reversible nature of involved reactions, an excess amount of alcohol is required to shift the reaction equilibria towards the products side.[1] The catalysts involved could be conventional basic (alkali) or acidic type (sulfuric or phosphoric acids) ''homogeneous'' catalysts; heterogeneous (solid) metal oxides or immobilized lipase enzymes that catalyze both the hydrolytic cleavage and the synthesis of ester bonds in TAG.

Biodiesel produced from soybean or rapeseed oil feedstocks are mainly comprised of five different FAAE, which have conventional names of palmitic, stearic, oleic, linoleic, and linolenic acid alkyl esters. The compositions of biodiesel fuels can be considered essentially identical to the fatty acid (FA) composition of the corresponding TAG or FFA sources.[2,3] In other words, the produced biodiesel can be considered as the sum of individual FAAE components weighted with their corresponding FA compositions in the oil substrate. This implies that the various FA chains of the TAG molecules have essentially identical reactivity toward alcohols.[3] Indeed, it is expected that the catalyst used does not possess any substrate- or regio-specificity towards TAG components, particularly in case of enzymatic catalysis.

As an advantage of enzymatic biodiesel production, glycerol and biodiesel formed split into two equilibrated and rather limpid liquid phases of which the upper layer is rich in FAAE and lower one rich in glycerol. Generally, quick phase separations occur due to the low solubility of glycerol in the biodiesel and to the lack of liquid catalyst mingling or soap formation. In practice, the split-up of phases can be accomplished either with a settling tank or through centrifugation.[3] Next step is the recovery of excess alcohol from both phases succeeding with further purification of the biodiesel and glycerol phases. The excess and unreacted alcohol distributes between these two liquid phases with relatively high concentration in glycerol phase.[4] A representative

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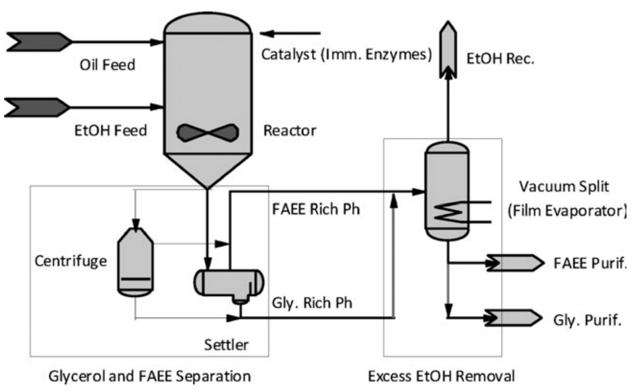

Figure 1. Representative process flowsheet diagram for down-stream operations (gray lines represent the EtOH recovery from glycerol rich phase).

flow-sheet diagram of the process concerning the unit operations was shown in Figure 1.

There are standardized specifications with the aim of controlling the quality of the biodiesel supplied to the market: EN-14214 in European countries and a few of its variants in some other countries, such as Brazil, and S. Africa; and ASTM-D6751 in USA, Canada, and Australia. According to both standards, the free glycerol content must be less than 0.02% (w/w). It is reported that high total glycerol content can cause injector fouling, and thus, pressure drop.[5] On the other hand, glycerol is a versatile product that can be used as either a final product like a pharmaceutical ingredient or as a substrate in cosmetic industry for more value added product synthesis. Therefore, instead of using "raw" glycerol as a feedstock like in fermentation operations for hydrogen production,[6] further purification is generally preferred which also encourage the biodiesel production processes becoming more profitable[7] and more widespread.

It is essential to specify the fluid phase compositions in equilibrium for detailed process analysis and/or design of unit operations, such as in simple or rigorous distillations. Besides, phase equilibria studies of such systems are essential for the elaboration of the optimum process conditions, their influence on reaction kinetics, and the selectivity of the desired product. In biodiesel production, both the vapor-liquid (VLE) and liquid–liquid equilibria (LLE) are equally important. Liu et al. reported an experimental study on the LLE of soybean oil ethyl ester-EtOH-glycerol ternary system at several temperatures.[8] Oliveira et al.[9] measured ternary LLE of MeLa/MeMy/MeSt/-EtOH-glycerol systems. They reported the ternary LLE of systems using the cubic plus association (CPA) EoS model. Recently, the same research group has also reported ternary LLE of canola oil ethyl ester-EtOH-glycerol system at 303–333 K range. Finally, Jachmanian et al.[10] measured sunflower oil ethyl ester-alcohol-glycerol ternary systems at 323 K. However, to the best of our knowledge, there is no published study on the VLE of glycerol-biodiesel (FAME or FAEE) systems, yet.

Phase equilibria of highly nonideal mixtures containing polar-associating and nonpolar components can be evaluated through methods based on quantum mechanical (chemical) (QM) calculations.[11] One of the most extensively used QM based method is the COnductor-like Screening MOdel (COSMO) which belongs to the class of quantum mechanical dielectric continuum solvation (or polarizable) models.[12,13] COSMO has become popular in computational chemistry since its first publication and following implementation in MOPAC (Molecular Orbital PACkage).[13] In QM-COSMO approach the solute molecules are considered in a virtual conductor environment where each solute molecule induces a screening (polarization) charge density, σ, on the interface between the molecule and the molecular surface (conductor).[14] The screening charge density distribution on the surface of each molecule i is converted into a probability distribution function known as σ-profile ($p_i(\sigma)$) which gives the relative amount of surface with polarity σ on the surface of the molecule.[14]

There are two thermodynamic model theories based on the implementation of the descriptors from the QM-COSMO method: COSMO-RS[15] and COSMO-SAC.[16] The COSMO-RS method where RS pertains to "Real Solvents" or "Realistic Solvation" has the basis of statistical thermodynamics approach combined with QM-COSMO calculations. It is based on the theory of interacting molecular surface charges which combines statistical thermodynamics methods with an electrostatic theory of locally interacting molecular surface descriptors derived from the dielectric continuum model COSMO.[14] COSMO-RS can be defined as the statistical thermodynamics treatment of molecular interactions. In this thermodynamic model theory a compound's polarization charge density, which is described by its σ-profile, is used for the quantification of the interaction energy of pairwise interacting surface segments, resulting in the compound's chemical potential (its partial Gibbs free energy).[15,17]

The activity coefficient of component i in the system S, γ_i^S then can be calculated through

$$\ln(\gamma_i^S) = \frac{\mu_i^S - \mu_i^0}{RT} \tag{1}$$

where μ_i^S is the chemical potential in the solvent (or solvent system) S, and μ_i^0 is the chemical potential of the pure component i.

COSMO-RS method was applied to describe the fluid phase equilibria of systems, such as the LLE of water-hydrocarbon mixtures,[18] VLE of mixtures containing polar chemicals,[19,20] VLE of butane + alcohols,[21] and VLE of binary mixtures of 1-propoxy-2-propanol with alcohols and water at reduced pressures.[22]

The evaluation of multicomponent phase equilibria required for down-processing operations of enzymatic biodiesel production accompanied by the elementary feasibility inspections of simple unit operations were the major objectives of this study. Multinary (multicomponent) reaction system for LLE simulation was the FAEE-EtOH-Glycerol "ternary", whereas for the VLE the "binary" system of FAEE-Glycerol was simulated for both the isothermal and isobaric operations. Phase simulations were performed through quantum chemical calculations using COSMO-RS method (via COSMO*therm* software v.C21-0111). The components with BP-TZVP parameterization (Becke-Perdew (BP) functional for density functional theory calculations with a triple valence plus polarization function (TZVP) basis set[14]) were used. The necessary parameterization file does always correspond to one functional and basis set. Study was focused on the enzymatic biodiesel production (using immobilized heterogeneous lipase enzymes) involving ethanolysis of refined vegetable oils, like soybean oil containing significantly low levels of FFA, as the feedstocks.

Table 1. Calculated and Experimental Saturation Temperatures of Individual FAEE Components at Reduced Pressures

	Ethyl Palmitate		Ethyl Stearate		Ethyl Oleate		Ethyl Linoleate		Ethyl Linolenate	
	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T(K)	P (kPa)	T (K)	P (kPa)	T (K)
Exp.	*6.90E−05*	323.15[a]	*7.00E−06*	323.15[a]						
Calc.		312.85		307.73						
Exp.	*2.06E−04*	333.15[a]	*2.33E−05*	333.15[a]						
Calc.		323.45		318.14						
Exp.	*6.16E−04*	343.15[a]	*9.12E−05*	343.15[a]			*3.33E−01*	448.15[b]	*3.33E−01*	447.15[b]
Calc.		335.05		331.03				447.57		451.47
Exp.	*1.333*	464.32[b],[c]	*0.267*	454.25[d]	*1.330*	486.64[c]	*1.330*	486.64[c]	*2.000*	491.15[e]
Calc.		458.58		442.57		478.39		479.02		493.18
Exp.	*2.670*	481.9[c]	*0.667*	468.75[d]	*1.733*	480.15[e]	*1.600*	485.15[e]		
Calc.		476.02		461.84		484.77		483.52		
Exp.	*4.000*	495.23[c]	*1.330*	490.97[c]	*2.000*	489.15[e]	*2.670*	501.94[c]		
Calc.		487.00		477.98		488.53		496.92		
Exp.	*5.330*	502.27[c]	*2.670*	505.55[c]	*2.670*	500.98[c]	*4.000*	510.65[c]		
Calc.		495.23		496.09		496.25		508.24		
Exp.	*6.670*	508.1[c]	*4.000*	512.98[c]	*4.000*	508.03[c]	*5.330*	515.7[c]		
Calc.		501.91		507.04		507.53		516.63		
Exp.	*8.000*	512.23[c]	*5.330*	520.56[c]	*5.330*	514.61[c]	*6.670*	520.91[c]		
Calc.		507.62		515.78		516.10		523.55		
Exp.	*9.330*	515.13[c]	*6.670*	524.45[c]	*6.670*	523.69[c]	*8.000*	527.47[c]		
Calc.		512.36		522.65		517.85		529.21		
Exp.	*101.325*	576.15[b]	*8.000*	525.78[c]	*8.000*	528.56[c]	*9.330*	537.69[c]		
Calc.		607.71		528.27		528.63		534.24		
Exp.			*9.330*	533.97[c]	*9.330*	536.83[c]	*23.998*	545.15[e]		
Calc.				533.27		533.51		567.89		
% MAD	*2.017*		*2.100*		*0.651*		*0.933*		*0.689*	
$T_{\min}$ (K)	273.15		273.15		273.15		273.15		273.15	
$T_{\max}$ (K)	767.65		785.93		788.16		791.07		800.79	
R^2	0.9997		0.9996		0.9996		0.9996		0.9996	

[a] Ref. 24.
[b] Ref. 3.
[c] Ref. 25.
[d] Ref. 26.
[e] Ref. 27.

Methods

Vapor pressures of FAEEs

Even though COSMO-RS method allows for the estimation of pure compound vapor pressures,[19] it is preferable to use available experimental data or correlations obtained using such data. As a matter of fact, reliable vapor pressure calculations of FAEE components are essential to obtain the high quality of estimations in VLE simulations. Consequently, the extended versions of Antoine equations (DIPPR 101 type equation[23]) were established and implemented into COSMO*therm* software for EtOH, glycerol, and the major FAEE components from soybean (or rapeseed oil) feedstock.

The vapor pressure versus temperature data of individual FAEE components for the temperature ranges given in Table 1 were taken from PRO/II v.9.0 chemical process simulation software[28] database and fitted to the extended type Antoine equations using the Levenberg-Marquardt nonlinear least squares method.[29] Some data points were modified with the available experimental ones before the regression. It is noteworthy that although they were measured at the same reduced pressures, reported experimental data from different sources also shows considerable inconsistencies for the same components. The extended type Antoine equation can be given as follows

$$\ln(p_i^0) = A + \frac{B}{T} + C\ln(T) + DT^2 \tag{2}$$

where p_i^0 is the vapor pressure of pure component i; T is temperature; and A, B, C, and D are the equation coefficients.

Experimental and calculated saturation temperatures at several respective pressures are presented in Table 1 accompanied by the correlation coefficients for the fitted equations. As reported by Goodwin and Newsham,[30] the fatty acid methyl esters (FAME) usually require use of vacuum distillation due to the thermal instability. Similarly, the majority of experimental values for FAEE saturation temperatures were also reported at reduced pressures.

It was found that the saturation temperatures of saturated FAEE have the highest mean absolute deviation (MAD) for ethyl stearate (EtSt) with 2.10% followed by 2.02% for ethyl palmitate (EtPa). A MAD of 0.69% was calculated for the polyunsaturated ethyl linolenate (EtLn) species where there was only two available experimental data points. The best performance with lowest MAD value was obtained for the monounsaturated ethyl oleate (EtOl) species (see Table 1). In overall, there is a significant agreement between experimental and calculated saturation temperatures (boiling points). Vapor pressure data values of glycerol and EtOH molecules changing with temperature were taken from CHEMCAD v.6.4 chemical process simulation software[31] and re-regressed to extended type Antoine equation to get the consistent coefficient values. The temperature ranges for glycerol and EtOH were taken between 291.33 to 850 K and 159.05 to 513.92 K, respectively.

LLE of FAEE-EtOH-glycerol ternary systems

In essence, ideal solutions or solutions exhibiting negative deviation from ideal behavior cannot form two liquid phases.[32] Instead, for two or more liquid phases to exist

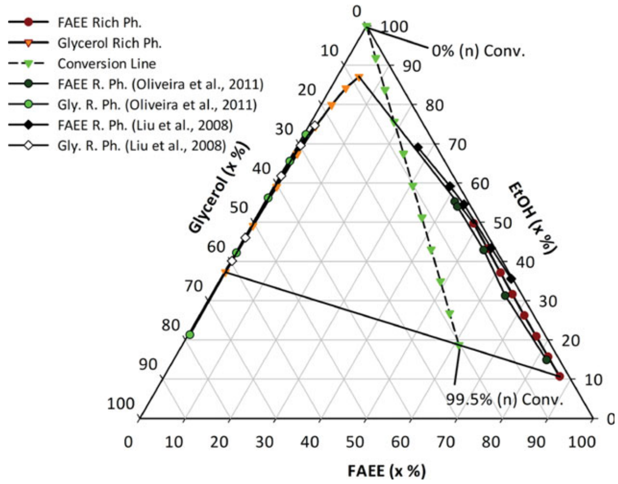

Figure 2. LLE of glycerol-EtOH–FAEE ternary system at 303 K (data reported by Liu et al.[8] were measured at 300 K). FAEE: Fatty acid ethyl ester, EtOH: Ethanol.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

together (i.e., for phase separation) significant positive deviation from ideal behavior is required. As mentioned above, the FAEE and glycerol are practically immiscible and, thus, imply significant positive deviation resulting equilibrated two phases when brought into contact. In other words, glycerol as a liquid capable of forming three-dimensional (3-D) networks of strong hydrogen bonds; whereas biodiesel (FAEE) composed of molecules containing donor atoms, but no active hydrogen atoms cannot form homogeneous solutions when mixed in equal amounts. The LLE condition (also called iso-activity condition) in which the same standard state is assumed for all components in two phases can be defined as follows

$$[\gamma_i^S x_i]^{\text{PhaseI}}(T, P, \{x\}^{\text{PhaseI}}) = [\gamma_i^S x_i]^{\text{Phase II}}(T, P, \{x\}^{\text{Phase II}}) \qquad i = 1, 2, \ldots, n \quad (3)$$

where Phase I and Phase II refer to the two equilibrated liquid phases.

The products of transesterification reaction with near complete conversion will eventually separate into two phases where each phase will comprise particular amounts of FAEE, glycerol, and unreacted (excess) EtOH in dissolved forms. The FAEE compositions of two phases were calculated as the sum of individual FAEE components distributed between the phases

$$x_{\text{FAEE}}^{I \text{ or } II} = \sum_{i=1}^{M} x_i^{I \text{ or } II} \quad (4)$$

For the sake of a realistic simulation, the LLE was estimated for an enzymatic transesterification reaction achieving a conversion of up to 99.5%. The substrate EtOH with 30% of molar excess amount and stoichiometric amounts of synthesized FAEE and glycerol were used in the global composition. In the beginning of reaction, the oil phase was supposed to be a medium completely miscible with EtOH and changing into a "fatty" phase (oil + FAEE) and an alcohol phase (EtOH+ glycerol) with the reaction progress. Since FAEE is miscible with EtOH at 303 K, the homogeneous media assumption for oil-EtOH binary mixture is valid above ca. 15% of conversion (Güzel et al., submitted). Hence, initially the EtOH mole fraction was taken as 1.0 which diminishes to 0.187 with the reaction course (conversion up to 99.5%). At that conversion level, mole fractions of FAEE and glycerol were calculated 0.610 and 0.203, respectively. The variation of global composition from 0 to 99.5% FAEE, so-called "conversion line," is represented in Figure 2.

It is worth noting that enzymatic transesterification reactions generally accomplished at moderate temperatures between 308 and 323 K and ambient pressure condition.[33] Consequently, the LLE of FAEE-EtOH-Glycerol ternary system was simulated at a lower-temperature of 303 K at which the collection of the reacted mixture was considered for refining operations. The estimations were illustrated together with the experimental data points[8,34] in Figure 2. To provide the data points consistency on the ternary phase diagram, values reported as weight fractions by Liu et al.[8] and by Oliveira et al.[34] were transformed into mole fractions through the assumption of the same FA compositions for oils and their corresponding ester derivatives. In this regard, the molecular weights of FAEE were calculated 305.75 g/mol for soybean oil FAEE[8] and 308.50 g/mol for canola oil FAEE.[34]

It is well-known that the rotational symmetry of a carbon–carbon single bond allows the atoms or groups of atoms connected by that bond to rotate about it. Due to this kind of rotation, many molecules assume several different 3-D forms. They are called as conformations where some conformations of a particular molecule are more stable than others are. Consequently, due to composite nature of biodiesel (FAEE), all the simulations were performed using three conformers for saturated FAEE species (EtPa and EtSt); though only one conformer for each unsaturated FAEE species (EtOl, EtLi, and EtLn) was used. Besides, EtOH is simulated using two conformers and the by-product glycerol with 10 conformers. The sigma profiles of FAEE, EtOH and glycerol conformations were given in the Appendix. In LLE and VLE simulations, all the conformers were weighted according to their Boltzmann distributions in the system.[14]

It was evidenced that using three different conformations for each saturated FAEE component do not affect the LLE and VLE estimations, as expected. Since, it is reported that in saturated hydrocarbons such bond-rotational conformations have minor influence on the phase equilibria and chemical potential estimations.[14] However, conformers of glycerol showed faintly different results, especially for the binary VLE calculation of unsaturated FAEE and glycerol.

VLE of FAEE-glycerol binary systems

Analogous to LLE, it was required that at equilibrium the partial molar Gibbs free energy (i.e., chemical potential) of each component must be the same in liquid and vapor phases present in the system. The total pressure used in the computation of VLE phase diagrams is calculated through Eq. 5 where x_i is the mole fraction of component i in the liquid phase.

$$P = \sum_{i=1}^{n} p_i^0 x_i \gamma_i^S \quad i = 1, \; 2, \ldots, n \quad (5)$$

The vapor phase mole fraction, y_i is defined as the ratio of partial vapor pressure, p_i to the total pressure, P with the assumption of ideal behavior for the gas phase[19] is given by Eq. 6.

$$y_i = \frac{p_i}{P} = \frac{p_i^0 x_i \gamma_i^S}{P} \tag{6}$$

VLE calculations can be performed both isothermally and isobarically. To simulate vacuum evaporation/distillation, isobaric VLE calculations were computed at reduced pressures of up to 10 and 50 kPa for both individual FAEE components and biodiesel fuel; whereas reduced pressure of 1 and 10 kPa were applied for the VLE simulation in glycerol purification step. It is reported that purified biodiesel fuel (FAME) and glycerol are susceptible to thermal decomposition above 523 K[35] and 423 K,[36] respectively. As a result, temperature values of 413 (for glycerol purification), 423, and 473 K (for biodiesel purification), were chosen for the isothermal VLE computations with the purpose of preventing separated biodiesel and glycerol phases from decomposition.

As mentioned above biodiesel is naturally a mixture of ethyl (methyl) esters of long-chain fatty acids and the simulation of real processes requires using such mixtures rather than using the major constituent as a pure single component. However, the calculation of thermodynamic properties, such as vapor pressure, generally requires such single component approximation. To provide a realistic simulation, the mixture of FAEE species was considered as a near-ideal solution which was pointed out for the mixture of FAME species by Goodrum et al.[37] Thus, the total vapor pressure of the FAEE mixture in the system was calculated from the vapor pressure of individual FAEE components using the Eq. 7 given below.[38]

$$p_{\text{FAEE}} = \sum_{i=1}^{N} p_i z_i \tag{7}$$

where z_i is the mole fraction of the FA composition of vegetable oil feedstocks applied as a weighing factor. Ultimately, instead of the single component approximation, both the LLE and VLE simulations where each FAEE is weighted with the corresponding FA composition of oil source were performed for multinary systems: 5 FAEE + EtOH + Glycerol for EtOH recovery and 5 FAEE + glycerol for the VLE of purification operations. Soybean oil was chosen as the biodiesel feedstock with the molar composition[39] of 10.82% C16:0; 4.89% C18:0; 25.21% C18:1; 51.51% C18:2; and 7.47% C18:3. The total biodiesel (FAEE) mole fraction at vapor phase was calculated as the sum of individual mole fractions of ethyl esters, analogous to Eq. 4

$$y_{\text{FAEE}} = \sum_{i=1}^{M} y_i \tag{8}$$

Results and Discussion

LLE of FAEE-EtOH-glycerol ternary system

The ternary LLE diagram shown in Figure 2 indicates that FAEE is virtually immiscible with glycerol, whereas the opposite is not correct. This can be evidenced through the left-shift of the binodal curve from the corresponding edge of the triangle on the FAEE rich phase. The diagram shows that the experimental data points of Oliveira et al.[34] and Liu et al.[8] are in significant agreement with the COSMO*therm* predictions. This is particularly valid for the glycerol rich phase, where FAEE is practically immiscible. On the other hand, there is a *pseudo*-homogeneous medium for the conversions up to 30% where both the diminishing EtOH and accumulating glycerol is completely soluble within the fatty (oil+partial glycerides+FAEE) medium (Güzel et al., submitted). This was accounted for the fact that high concentration of EtOH helps mutual solubility of FAEE and glycerol formed. In addition to completely miscible media assumption given above, it should be pointed out that the miscibility of glycerol with vegetable oil phase was lower than with FAEE, and can be considered practically insignificant (data was not presented).

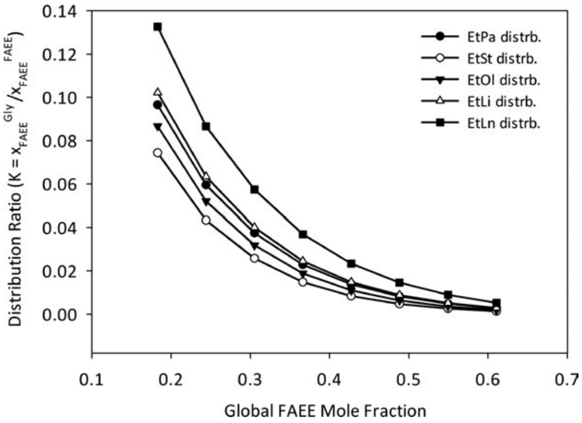

Figure 3. **Change of distribution ratios of individual FAEE components at 303 K through conversion (EtPa: Ethyl palmitate; EtSt: Ethyl stearate; EtOl: Ethyl oleate; EtLi: Ethyl linoleate; EtLn: Ethyl linolenate).**

Although the data reported by Liu et al. was measured at 300 K, it agrees significantly with the other two particularly in the glycerol rich phase. In contrast, the results reported by them show a significant solubility of glycerol in FAEE phase at higher concentrations of EtOH, which cannot be evidenced considering this predictive study and Oliveira and coworkers' study. Furthermore, the correspondence between experimental data of Oliveira et al. and predicted ones is highly reasonable with the exception of flimsily high solubility in experimental data at FAEE rich phase that can be attributed to polar impurities in FAEE substrate and analytical errors. In consequence, the approach of using biodiesel as the mixture of FAEE components weighted with corresponding FA composition values and using multinary LLE estimations was confirmed as merely reliable.

The distribution ratios of individual FAEE components in the mixture were illustrated in Figure 3 so as to reveal their affinity for the glycerol rich phase. As seen from the figure, in the beginning of the reaction the highest affinity for glycerol was revealed by polyunsaturated EtLn component followed by ethyl linoleate (EtLi) and then saturated EtPa component. This affinity can be analogously accounted for to the fact that degree of unsaturation and decrease in molecular weight of saturated components positively affect the solubility of FA in EtOH.[40] It is noticeable that with the reaction course the distribution ratio of each component approaches to the same minimum level in the glycerol phase. It is also worth noting that due to the higher affinity of polyunsaturated FAEE to glycerol, simultaneous removal of glycerol

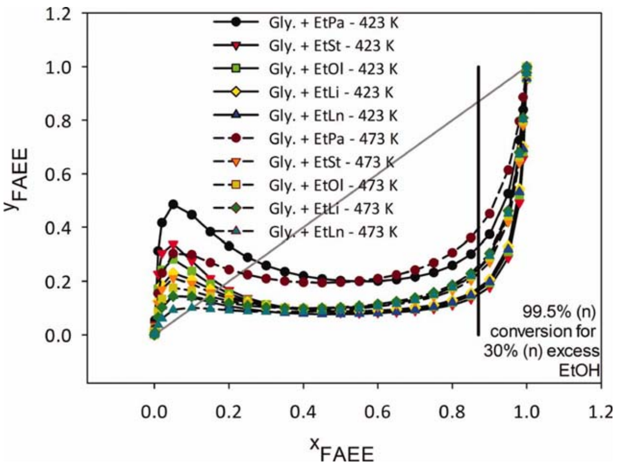

Figure 4. Isothermal VLE of individual FAEE–Glycerol binaries at 423 and 473 K.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formed may improve the cetane number and the oxidation stability of the final biodiesel product.[3]

Data represented in Figure 2 indicates that for the conversion levels above 30% glycerol formed will practically separate from the fatty phase and may remain as suspended droplets in the mixture depending on the physical conditions applied during the reaction. It is worth to recall that since the unreacted (excess) amount of EtOH acts as a cosolvent increasing the mutual solubility of glycerol and FAEE; some minor amounts of glycerol can be dissolved in the final biodiesel phase. However, as it is obviously shown in the ternary diagram (Figure 2), this small amount of dissolved glycerol exceeds the specified limit of 0.02% (w/w) (which corresponds to 0.066% (m/m)). Here, the molecular weight of FAEE was calculated as 306.46 g/mol according to the soybean oil composition given above. Stating briefly, with the aim of producing biodiesel in the specification limits further separation and purifications are evidently required.

VLE of FAEE-glycerol binary systems

In this section, the formation of minimum azeotropes will be discussed. However, it is noteworthy that due to significant immiscibility of FAEE and glycerol with each other such minimum boiling azeotropes cannot be practically observed in enzymatic biodiesel production processes, if the system temperature is lower than 333 K and also if the conversion is higher than 44%. The mole fraction(s) where such azeotrope points occur depends on the FAEE component (and on the biodiesel composition). Hence, the FA composition of substrate, in particular polyunsaturated FA composition, should be considered as a characteristic measure. These points will be further evaluated in the succeeding subsections, in particular for real case simulations of glycerol purification step.

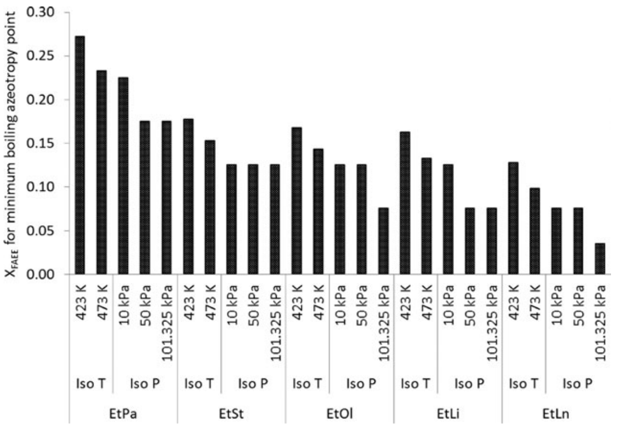

Figure 6. Minimum boiling azeotrope points for individual FAEE components.

Individual FAEE-glycerol binaries: isothermal case

Figures 4 and 5 illustrate the isothermal VLE of pure FAEE-glycerol binaries. As seen from the figures for each binary system azeotrope points were found. The corresponding temperature values were below the boiling points of pure components forming the binaries. Such mixtures are called as minimum boiling azeotrope mixtures. The azeotrope points were illustrated in Figure 6 where azeotrope mole fraction values of FAEE decrease with temperature; with the degree of unsaturation; and with the increase in carbon number for saturated FAEE. The lowest azeotrope mole fraction was calculated for EtLn-glycerol whereas the highest was observed for EtPa-glycerol binary system. The highest saturation pressure was calculated for EtPa-glycerol binary system which is not exceeding 9 kPa at 473 K (see Figure 5). Similar azeotrope point observations were reported for smaller methyl ester-alcohol binaries by Constantinescu and Wichterle[41] for the isothermal VLE of methyl propionate / methyl butanoate-EtOH mixtures.

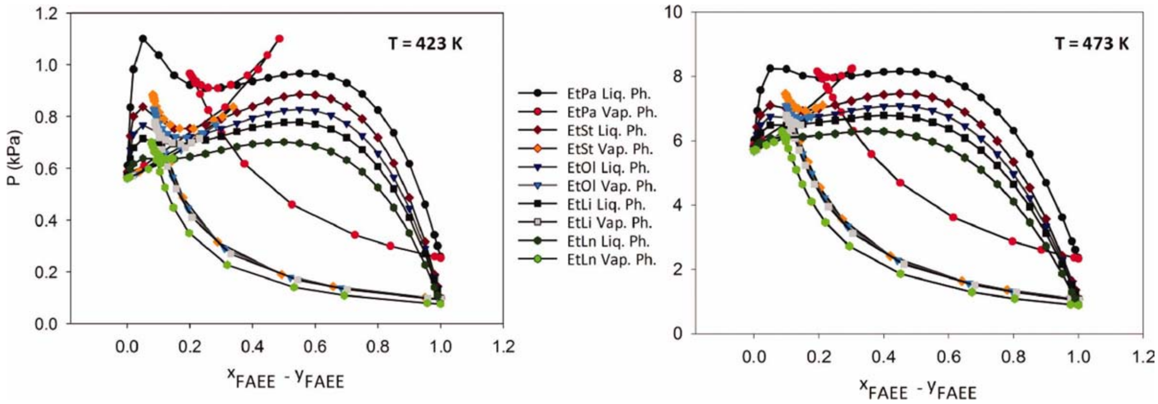

Figure 5. Isothermal *Pxy* diagram of individual FAEE–Glycerol binaries at 423 and 473 K.

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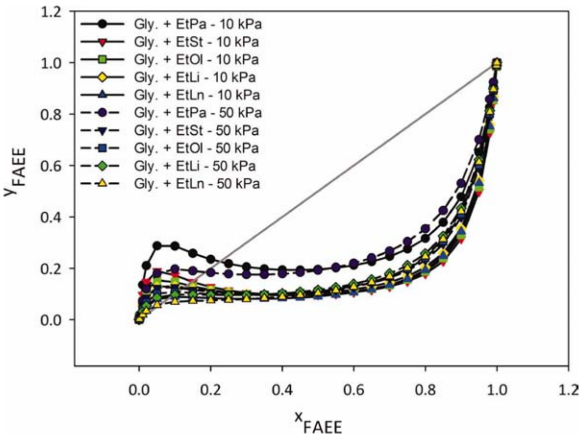

Figure 7. Isobaric VLE of individual FAEE–glycerol binaries at 10 and 50 kPa.

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Individual FAEE-glycerol binaries: isobaric case

Isobaric VLE of pure FAEE-glycerol were depicted in Figures 7 and 8 for reduced pressure values of 10 and 50 kPa. Analogous to isothermal case, each FAEE shows minimum boiling azeotrope points, while in that case the points are virtually the same at 10 and 50 kPa for binary systems containing EtSt, EtOl, and EtLn. However, it changes with the decrease in vacuum from 10 to 50 kPa for EtPa and EtLi cases. Interestingly, EtSt shows the same azeotropic points for three pressure values as illustrated in Figure 6. The azeotropic temperatures were ca. 480 K and ca. 530 K at 10 and 50 kPa, respectively (see Figure 8). It was reported that isobaric VLE measurements of small methyl,[42,43] ethyl,[44,45] propyl,[46] and butyl[47,48] ester-alcohol(s) binaries show similar azeotrope points at atmospheric pressure (101.325 kPa). In addition, Ortega and Susial[49] were reported minimum boiling azeotropes for methyl propanoate-EtOH mixture at higher pressures of 114.66 and 127.99 kPa.

VLE of refining operations: isothermal and isobaric real case simulations

VLE of Ethanol Recovery. As stated above, to shift the equilibrium reaction towards the products side it is always necessary to use acyl acceptors (alcohols) in excess amount. According to Knothe et al.[3] the excess amount of alcohol should not be removed before the separation of glycerol and ester phases due to the risk of reverse transesterification reaction, in particular while enzyme residues possibly remain within the phases. EtOH remained in both phases following this initial phase separation can be recovered using a flash distillation (evaporation), a vacuum stripping process,[3] or a falling film evaporator unit (see Figure 1).

The partition of EtOH between ester and glycerol phases was plotted in Figure 9. It can be perceived from these curves that the *K*-value is always higher than 1.0 and increases with the conversion, especially in case of COSMO-RS predictions. This means that on account of relatively higher solubility of alcohols, such as MeOH and EtOH, in the polar glycerol phase, EtOH will distribute in higher amounts into the glycerol phase. Therefore, most of the EtOH will remain in the glycerol phase after the initial phase separation. It should be noted that since the global composition of FAEE-EtOH-Glycerol ternary system is not mentioned in Oliveira et al.[34] these values were calculated as the average value of each tie-line data. Similar to the predicted results, EtOH distribution ratio measured by Oliveira et al. also increases with the decrease in global EtOH mole fraction (with conversion). Accordingly, although the rate of increase was not quantitatively comparable, Figure 9 shows that EtOH concentration in glycerol will always be higher than in ester phase.

The simulated VLE results of the EtOH recovery from biodiesel phase were presented in Table 2 for 85.2 and 99.5% conversion levels. As a measure of evaporation tendency, the *K*-values ($K_i = \frac{y_i}{x_i}$) for EtOH both in isothermal and in isobaric operations were significantly higher than the values of glycerol and FAEE in biodiesel rich phase. It was found that isothermal and isobaric VLE simulations have virtually the same *K*-values for EtOH component, but not for glycerol and FAEE mixture. This can be considered as an opportunity of finding the most feasible operation in terms of EtOH recovery and its purity. The applied temperature in isothermal operations may not be safe for the biodiesel components with carbon numbers of C12.0 and C14.0 where the decomposition and, thus, loss of such FAEE species might be relatively higher. The isobaric operation at a vacuum of 10 kPa was considered as the most feasible option with regard to the *K*-values.

On the other hand, the relative volatility ($\alpha_{ij} = \frac{K_i}{K_j}$) of components were also calculated as a measure of the ease of separation. Considering the purity of recovered EtOH

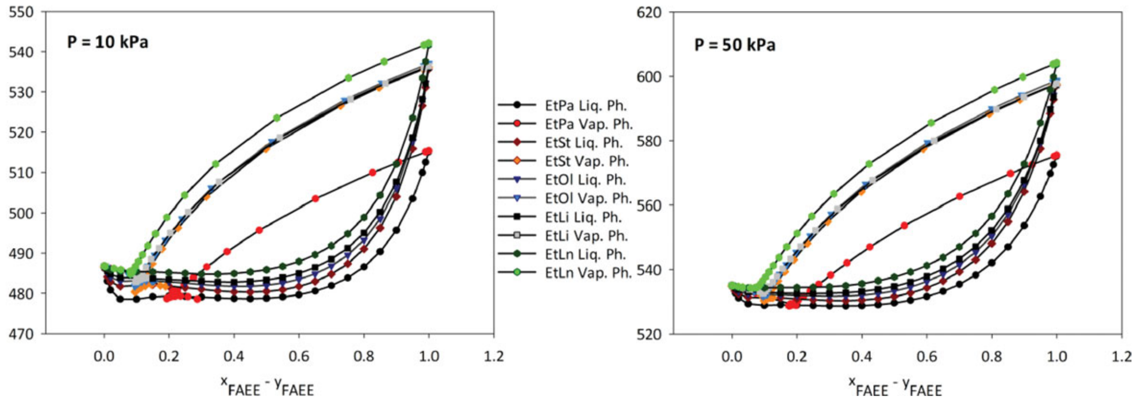

Figure 8. Isobaric *Txy* diagram of individual FAEE–Glycerol binaries at 10 and 50 kPa.

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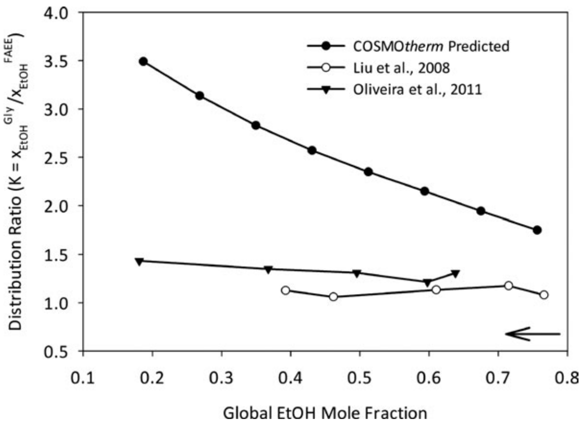

Figure 9. Change of distribution ratio of EtOH at 303 K through conversion (data reported by Liu et al.[8] were measured at 300 K).

($\alpha_{Gly,FAEE} = 61.87$ and $\alpha_{EtOH,Gly} = 1639.92$), isobaric operation under 50 kPa of vacuum was chosen as the most suitable option to strip excess EtOH from biodiesel phase. Yet, vacuum stripping is the generally preferred operation[3] which can also help to the further purification of FAEE at ambient pressure, such as the removal of glycerol impurities by mixing water with the hot mixture resulting from the EtOH recovery. For instance, if this unit operation were achieved isobarically at 50 kPa, the corresponding temperature of biodiesel phase would be ca. 365 K. Blending the succeeding biodiesel "mixture" with water at ambient temperature (such as, 1:1 (v:v)) will result with significantly high mixture temperature value. It is notable that for conversions above 50%, dissolved glycerol in biodiesel phase (and vice versa) was estimated to remain miscible with the respective system at ca. 365 K. Nonetheless, from the engineering viewpoint, process economics should also be considered in an attempt to make a feasible choice.

It is reported that isobaric VLE of methyl butanoate-EtOH at 101.325 kPa[42]; methyl propanoate-EtOH at 114.66 and 127.99 kPa[49]; and isothermal VLE of the same two binaries at 326.30 and 346.30 K[41] show minimum boiling azeotropes. In contrast to such minimum azeotrope points reported for lower alkyl esters-EtOH mixtures, analogous results were not observed for mixtures of EtOH and long-chain fatty acid ethyl esters of vegetable oils. To conclude this section, simulation results showed that the recovery of EtOH from glycerol rich phase is relatively easier than from the biodiesel rich phase (data was not shown). Simple distillation systems depicted in Figure 1 were considered rather adequate for the EtOH recovery.

VLE of Biodiesel Purification. The VLE simulation results for further purification of biodiesel phase were presented in Table 3 and illustrated for isobaric cases in Figure 10. As seen from the table, it is very achievable removing the dissolved glycerol through isothermal simple unit operations, such as flash distillation or evaporation for conversions above 89 to 99.5% (points indicated with black circles in Figure 10). In addition to glycerol tendency to decompose above 423 K,[36] operating at 473 K might be risky due to decomposition of shorter FAEE components. As a result, it was found better to operate at lower temperatures. On the other hand, since the temperature exceeds the critical

Table 2. VLE Simulation Results for FAEE-EtOH-Glycerol System at Isobaric and Isothermal Conditions for Biodiesel Rich Phase

Cond.	T (K) or *P* (kPa)	Species	*K*-value	Relative Volatility		Sat. *P* (kPa) or Sat. T (K)
85.2 % conversion						
Iso T	423 K	EtOH	6.046	$\alpha_{EtOH,FAEE}$	**1.314E + 04**	*243.273*
		Glycerol	1.384E-02	$\alpha_{Gly,FAEE}$	30.073	
		FAEE	4.601E-04	$\alpha_{EtOH,Gly}$	436.891	
	473 K	EtOH	6.035	$\alpha_{EtOH,FAEE}$	**3.109E + 03**	*609.856*
		Glycerol	3.783E-02	$\alpha_{Gly,FAEE}$	19.492	
		FAEE	1.941E-03	$\alpha_{EtOH,Gly}$	159.527	
Iso P	10 kPa	EtOH	6.0500	$\alpha_{EtOH,FAEE}$	**2.054E + 06**	**316.431**
		Glycerol	3.600E-04	$\alpha_{Gly,FAEE}$	122.215	
		FAEE	2.945E-06	$\alpha_{EtOH,Gly}$	1.681E + 04	
	50 kPa	EtOH	6.049	$\alpha_{EtOH,FAEE}$	**1.723E + 05**	**360.200**
		Glycerol	2.252E-03	$\alpha_{Gly,FAEE}$	64.174	
		FAEE	3.510E-05	$\alpha_{EtOH,Gly}$	2685.583	
	101.325 kPa	EtOH	6.048	$\alpha_{EtOH,FAEE}$	**5.483E + 04**	**385.256**
		Glycerol	5.090E-03	$\alpha_{Gly,FAEE}$	46.139	
		FAEE	1.103E-04	$\alpha_{EtOH,Gly}$	1188.317	
99.5 % Conversion						
Iso T	423 K	EtOH	9.361	$\alpha_{EtOH,FAEE}$	**1.361E + 04**	*161.702*
		Glycerol	2.232E-02	$\alpha_{Gly,FAEE}$	32.452	
		FAEE	6.879E-04	$\alpha_{EtOH,Gly}$	419.308	
	473 K	EtOH	9.335	$\alpha_{EtOH,FAEE}$	**3.153E + 03**	*398.756*
		Glycerol	6.028E-02	$\alpha_{Gly,FAEE}$	20.359	
		FAEE	2.961E-03	$\alpha_{EtOH,Gly}$	154.855	
Iso P	10 kPa	EtOH	9.371	$\alpha_{EtOH,FAEE}$	**1.468E + 06**	**323.997**
		Glycerol	8.749E-04	$\alpha_{Gly,FAEE}$	137.060	
		FAEE	6.384E-06	$\alpha_{EtOH,Gly}$	1.071E + 04	
	50 kPa	EtOH	9.369	$\alpha_{EtOH,FAEE}$	**1.015E + 05**	**372.967**
		Glycerol	5.713E-03	$\alpha_{Gly,FAEE}$	61.872	
		FAEE	9.234E-05	$\alpha_{EtOH,Gly}$	1639.922	
	101.325 kPa	EtOH	9.366	$\alpha_{EtOH,FAEE}$	**3.011E + 04**	**401.381**
		Glycerol	1.305E-02	$\alpha_{Gly,FAEE}$	41.949	
		FAEE	3.111E-04	$\alpha_{EtOH,Gly}$	717.758	

Italic values given in the last column correspond to saturation pressures, while ones in bold form correspond to saturation temperatures.

Table 3. VLE Simulation Results for Biodiesel and Glycerol Purifications at Isobaric and Isothermal Conditions

Conditon	T (K) or *P* (kPa)	Components	89% Conv.[a] (*K*-Value = y_i/x_i)	Sat. *P* (kPa) or T (K)	99.5% Conv. (*K*-Value = y_i/x_i)	Sat. *P* (kPa) or T (K)
FAEE Purification						
Iso T	**423**	FAEE	0.525	*0.211*	0.546	*0.203*
		Glycerol	19.249		20.109	
		$\alpha_{Gly,FAEE}$	**36.660**		**36.833**	
	473	FAEE	0.655	*1.800*	0.674	*1.748*
		Glycerol	14.254		14.712	
		$\alpha_{Gly,FAEE}$	21.758		21.822	
Iso P	*10*	FAEE	0.737	**523.817**	0.754	**524.681**
		Glycerol	11.110		11.342	
		$\alpha_{Gly,FAEE}$	**15.076**		**15.038**	
	50	FAEE	0.797	**585.379**	0.812	**586.260**
		Glycerol	8.790		8.930	
		$\alpha_{Gly,FAEE}$	**11.026**		**11.004**	
	101.325	FAEE	0.820	**618.642**	0.833	**619.544**
		Glycerol	7.918		8.029	
		$\alpha_{Gly,FAEE}$	**9.657**		**9.639**	
Iso T	**413**	FAEE	11.984	*0.448*	23.075	*0.364*
		Glycerol	0.752		0.917	
		$\alpha_{Gly,FAEE}$	**0.063**		**0.040**	
Iso P	*1*	FAEE	9.793	**429.250**	16.724	**432.071**
		Glycerol	0.801		0.941	
		$\alpha_{Gly,FAEE}$	**0.082**		**0.056**	
	10	FAEE	5.075	**484.013**	7.582	**486.071**
		Glycerol	0.908		0.975	
		$\alpha_{Gly,FAEE}$	**0.179**		**0.129**	

Italic values given in the second, the fifth, and the last columns correspond to saturation pressures, while ones in bold form correspond to saturation temperatures.

[a] 74.4% conversion in case of glycerol purification; *K*-values and relative volatilities were emphasized in bold form.

temperature limit (523 K) reported for FAME decomposition,[35] isobaric operations seems to be completely unsafe. Besides, neither 10 nor 50 kPa of vacuum levels perform better than isothermal cases for such simple unit operations (see Table 3). In brief, glycerol removal needs to be performed by means of isothermal simple distillation, film evaporation or more conveniently by means of hot water-washing operations, as stated earlier.

VLE of Glycerol Purification. VLE simulations of glycerol purification were shown for isobaric cases on Figure 11 and were tabulated in Table 3. In that case isothermal operation at 413 K showed yet again relatively better results than

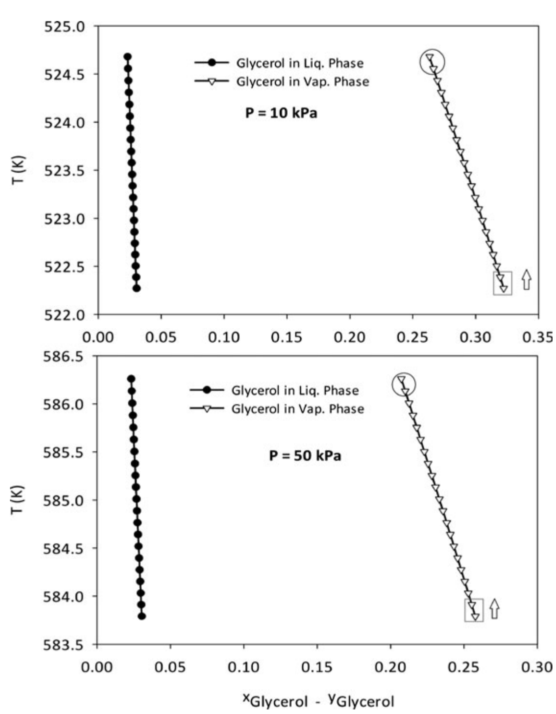

Figure 10. Isobaric *Txy* diagram of FAEE–Glycerol binary system at 10 and 50 kPa for biodiesel purification.

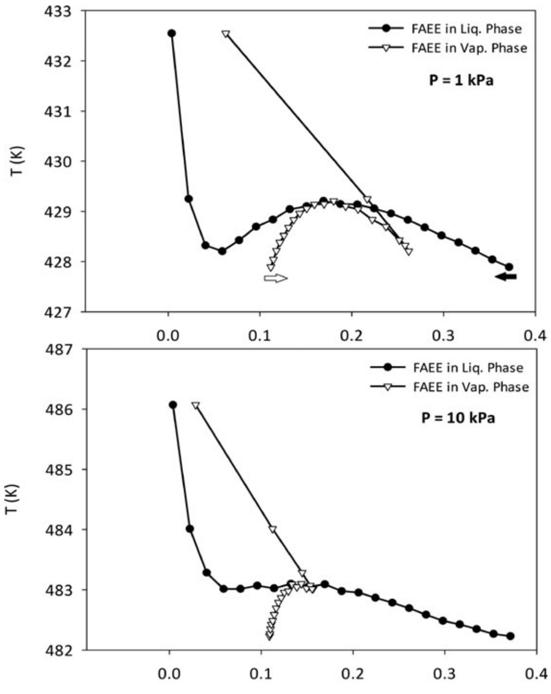

Figure 11. Isobaric *Txy* diagram of FAEE–Glycerol binary system at 1 and 10 kPa for glycerol purification.

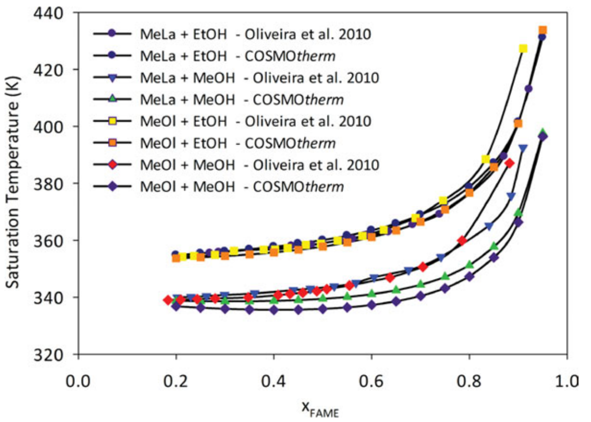

Figure 12. Isobaric predictive and experimental[51] saturation temperature data of FAME + Alcohol binary systems at 101.325 kPa. Predictions were simulated using COSMO-RS method.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

isobaric simple operations, even at 1 kPa of vacuum. Besides, at such a significantly low vacuum, the temperature still exceeds (ca. 430 K) the critical limit (see Figure 11). In contrary to the 423 *K* value mentioned by Zhang et al.[36] for decomposition of glycerol, Briggs[50] pointed out that glycerol is not decomposed even at a temperature of 473 K under vacuum. Despite the fact that glycerol has lower boiling points than FAEE mixture, in general, the *K*-values of FAEE was rather higher than of glycerol. Therefore, relative volatility of glycerol to FAEE ($\alpha_{\mathrm{Gly,FAEE}}$) which is defined as the ratio of *K*-value of more volatile to the less volatile component by convention, was lower than unity. Since the *K*-values of glycerol are very close to unity, glycerol will split equally between the vapor and liquid phases. This concluded that is not possible to purify glycerol phase by means of simple unit operations.

Nonetheless, it is worth noting that as an advantage of enzymatic biodiesel production, glycerol after the stripping of EtOH should theoretically have a purity of 98.3 to 98.8 wt % for the conversion levels of 74.4% and 99.5%, respectively. Moreover, since the solubility tends to decrease with the reduction in temperature, further purification might be practically achieved by settling at ambient temperature and removing the upper layer (fatty phase) after reaching to the equilibrium. Though, this condition depends on the level of impurities within the glycerol phase, the type of feedstocks used, and also the level of conversion. In overall, further purification of glycerol requires using vacuum distillation or rectification operations.

Figure 11 shows that for the low levels of conversion, there observed several ‘‘near’’ azeotrope point(s) formation (small arrows indicate the conversion direction). Since the major constituent of FAEE mixture is EtLi (51.51%) which shows minimum boiling azeotrope, for instance, at a mole fraction of 0.125 at 10 kPa (T_{az} = ca. 483 K) for the EtLi-Glycerol mixture and the others do not have enough concentration for the azeotropy formation (see Figure 6), the observed azeotrope points are not exact azeotrope points. Instead, due to composite nature of biodiesel, they should be called pseudo-azeotrope points ranging from 39 to 44% of conversion for isothermal and isobaric VLE simulations. Nonetheless, with the increase in conversion and subsequent phase splitting of glycerol and fatty phases, it is unlikely to observe such azeotrope points in enzymatic biodiesel production processes. On the other hand, in conventional biodiesel production the FAEE solubility is expected to be higher in the glycerol rich phase due to homogeneous catalysis, FFA content, soap formation, and some other impurities in the feedstocks, such azeotropes can be easily observed even at higher conversion levels.

VLE of FAME + Alcohol Binary Systems. To assess the prediction quality of COSMO-RS method (COSMO*therm*) experimental isobaric VLE data measured for MeLa/MeOl+MeOH/EtOH binary systems at atmospheric pressure (101.325 kPa)[51] was compared with COSMO*therm* predictions. The results were illustrated in Figure 12 where the best quantitative performance was obtained with MeLa-EtOH system which is followed by MeOl+EtOH system. However, significant deviation was observed for MeOl mole fractions higher than 0.6. This is expected to stem from the fact that the MeOl used in experimental measurements has 71.1 wt % of purity. The increase in ester concentration and, thus, in impurity significantly affects the saturation temperature. In contrast, relatively poorer performances were obtained with MeOH containing systems. It was evidenced that experimental data points of MeOl+MeOH system representing the highest deviation from the corresponding predictions almost overlaps with experimental data of MeLa+MeOH system. As seen from Figure 12 for lower FAME concentrations up to 0.4, COSMO*therm* predictions for binary systems containing MeOH still have reasonable agreements. In overall, due to 29 wt % of impurity in commercial MeOl species, MeOl+alcohol binary systems showed relatively higher deviations in terms of saturation temperatures. To bring this section to an end, the prediction quality of COSMO-RS method on VLE simulations of FAME+alcohol binaries, particularly FAME+EtOH system, showed reasonable correlations, which elucidate the suitability of using COSMO-RS method for phase equilibria simulation of biodiesel fuel refining operations.

The minimum boiling azeotrope points were also evaluated using the experimentally available data for shorter alkyl alkanoate-alkanol mixtures forming azeotrope points. For instance, experimental azeotrope point was reported at $x_{az,\text{ethyl propanoate}} = 0.628$, $T_{az} = 369.3$ K coordinates for the binary system of ethyl propanoate + butan-2-ol.[44] Hernandez and Ortega[44] have also reported an additional reference data for the same system as $x_{az,\text{ethyl propanoate}} = 0.450$ and $T_{az} = 368.9$ K which differs considerably from the value they measured. COSMO*therm* simulation of the same binary system produced azeotrope point at $x_{az,\text{ethyl propanoate}} = 0.575$ with the azeotrope temperature value of $T_{az} = 370.73$ K which is in significant agreement with the experimental values. To bring this study to an end, it was evidenced that COSMO-RS method predicts the VLE and azeotrope formation rather significantly either with the implemented vapor pressure equations or with default equations in the database of the software.

Conclusions

Phase equilibria (LLE and VLE) involved in refining operations of enzymatic ethanolysis reaction for biodiesel production were simulated using quantum chemical COSMO-RS method. The required vapor pressure vs. temperature data values of FAAE components were taken from PRO/II v.9.0 chemical process simulation software[28] database and fitted to the extended type Antoine equations after modifying some with experimental data points using nonlinear least squares method. The regressed equations were implemented into COSMO*therm* software. The comparisons with experimentally available data points showed a maximum of 2.10% MAD for EtPa.

Multinary phase equilibria simulation through near-ideal mixture approximation for biodiesel was performed to realistically simulate the system of FAEE mixture, EtOH, and glycerol instead of using ternary system including the major constituent of FAEE mixture as the biodiesel component plus EtOH, and glycerol. Isothermal and isobaric (at vacuum conditions) VLE involved in unit operations were estimated, analogously. It was observed that both multinary LLE and VLE approaches produce merely reliable results. The comparisons of available experimental data with LLE and VLE simulations were in significant agreement. Moreover, binary VLE of individual FAEE components and glycerol showed minimum boiling azeotropes where the highest azeotrope mole fraction of 0.2725 was observed for EtPa at 423 K. Similar *pseudo*-azeotrope points were also observed with FAEE-Glycerol binaries. At low conversions (ca. 39–44%) EtLi -as the major constituent of soybean oil derived FAEE-had sufficient concentration for the formation of azeotropy.

Finally, it was shown that simple unit operations such as flash distillation or evaporation are not feasible for further purification of glycerol phase, except for the unit operation of excess and unreacted EtOH recovery. Water washing was considered as adequate for further purification of biodiesel. Further purification of glycerol may well require rigorous distillation units consisting of rectification and stripping parts.

Acknowledgments

The authors thank the Advanced Technology Foundation (HTF) and the Novozymes A/S for the financial support (Sustainable Biodiesel Project).

Notation

p_i = partial vapor pressure, kPa
$p_i\ (\sigma)$ = probability distribution function (σ-profile)
$\{x\}$ = set of liquid phase mole fractions $x_1, x_2,..., x_n$
p_i^0 = the vapor pressure of pure component i, kPa
COSMO = COnductor-like Screening MOdel
COSMO-RS = COnductor-like Screening Model-Real Solvents
CPA = cubic plus association equation of state
EtLi = ethyl linoleate (linoleic acid ethyl ester)
EtLn = ethyl linolenate (linolenic acid ethyl ester)
EtOH = ethanol (ethyl alcohol)
EtOl = ethyl oleate (oleic acid ethyl ester)
EtPa = ethyl palmitate (palmitic acid ethyl ester)
EtSt = ethyl stearate (stearic acid ethyl ester)
FA = fatty acid
FFA = free fatty acid
FAAE = fatty acid alkyl ester
FAEE = fatty acid ethyl ester
FAME = fatty acid methyl ester
FFA = free fatty acid
K_i = tendency of evaporation or distribution value for component i
LLE = liquid–liquid equilibria
M = number of FAEE components in the separated phases
MAD% = mean absolute deviation percentage
MeLa = methyl laurate (lauric acid methyl ester)
MeMy = methyl myristate (myristic acid methyl ester)
MeOH = methanol (methyl alcohol)
MeOl = methyl oleate (oleic acid methyl ester)
MeSt = methyl stearate (stearic acid methyl ester)
m/m = mole per mole based
P = total pressure, kPa
QM = quantum mechanical
T = absolute temperature, K
TAG = triacylglyceride
VLE = vapor-liquid equilibria
w/w = weight per weight based
x_i = liquid phase mole fraction of component i
y_i = vapor phase mole fraction of component i
z_i = the mole fractions of FA composition of vegetable oil feedstocks

Greek letters

γ_i^S = activity coefficient of component i in the system (solvent system) S
μ_i^S = chemical potential of component i in the system (solvent system) S
μ_i^0 = chemical potential of pure component i
α_{ij} = relative volatility
σ = screening (polarization) charge density

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Manuscript received Oct. 5, 2011, and revision received Dec. 15, 2011.

Appendix

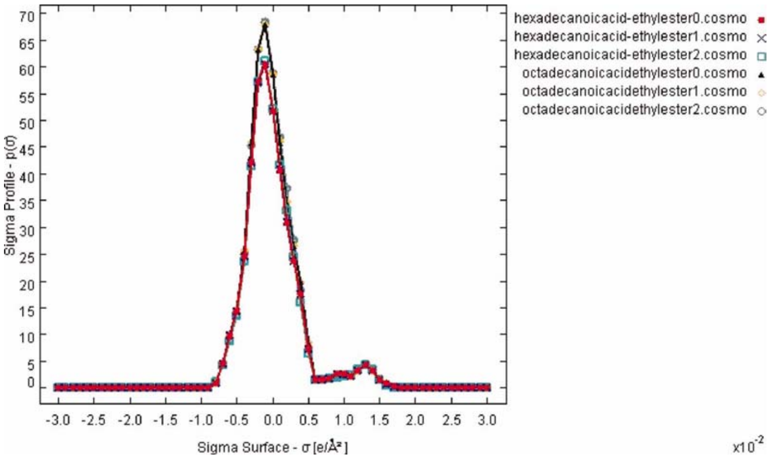

Figure A1. Sigma profiles of saturated FAEE components with conformations.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

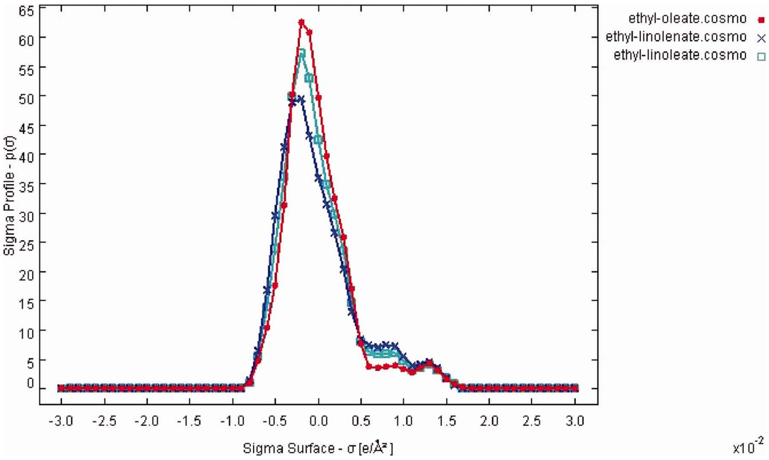

Figure A2. Sigma profiles of unsaturated FAEE components.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

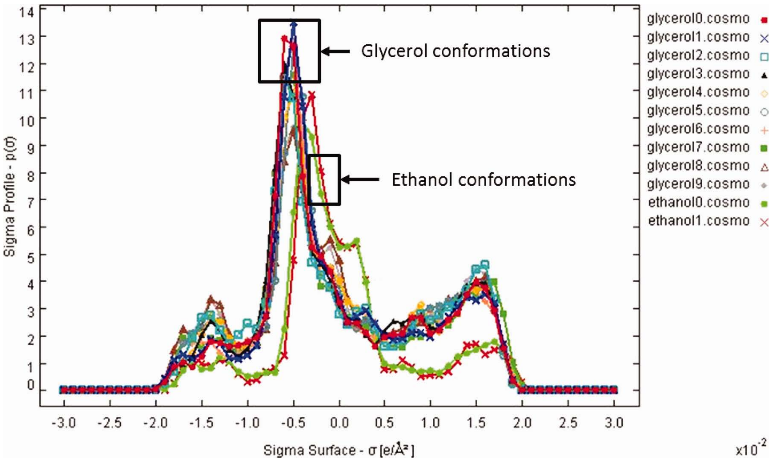

Figure A3. Sigma profiles of glycerol and ethanol components with respective conformations.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]