Distribution of Methanol and Catalysts between Biodiesel and Glycerin Phases

Chuang-Wei Chiu, Michael J. Goff, and Galen J. Suppes
Dept. of Chemical Engineering, W2028 Engineering Bldg. East, University of Missouri, Columbia, MO 65211

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When transesterifying alcohols with fats and oils to produce biodiesel, the phase behavior and respective distribution of catalyst and alcohol between liquid phases can significantly impact both reaction rates and product workup. To better understand this phase behavior, the distribution of methanol and catalysts, potassium hydroxide and sulfuric acid, between the biodiesel and alcohol phases was experimentally investigated and modeled. Experimental vapor-liquid equilibrium data were modeled by using the Wilson activity coefficient model and two temperature-independent model parameters are used to obtain good agreement between calculated and experimental data. The distribution coefficients of methanol between biodiesel and glycerin phases were accurately predicted by the VLE activity coefficients and Wilson model. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 1274-1278, 2005

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Introduction

Currently, fossil fuels are used in diesel engines and are essential in industrialized nations. However, petroleum-based diesel fuels increase environmental pollution. In order to solve this problem, use of fatty acid methyl esters (FAME) derived from vegetable oils and animal fats as diesel fuel extenders (biodiesel) has received considerable attention because of its many environmental benefits. Transesterification is used to convert triglycerides to FAME. The transesterification of vegetable oils with alcohols using basic or acid homogeneous catalysts has been studied extensively[1-4]. Many studies have identified the most important variables that influence the transesterification reaction including; the reaction temperature, the type and amount of catalyst, the reaction time, and so on.[5-9] However, partitioning phenomenon in the biodiesel production (namely, the distribution of methanol and catalysts among the transesterification products) has not been extensively studied.

The distribution of a solute among coexisting liquid phases is of both laboratorial and industrial importance in purification procedures and reaction engineering. The partitioning data of a solute between two immiscible liquid phases is usually reported in terms of a distribution coefficient *K*. The distribution coefficient is characteristic of the solute and the solvent pair, which is defined to be the ratio of the solute concentrations in the two phases. The distribution coefficient of the solute determined experimentally under ideal conditions is often used to simulate the practical distribution of the solute under real conditions.

From process simulation and design to process operation and control, modeling has become a routine activity at almost all levels of chemical engineering. In problems related to process simulation and design, thermodynamic models are used to calculate mixture properties. Walas[10] as well as Gani and O'Connell[11] have presented that models with different formulation, complexity and accuracy may be used to solve different process problems. The most commonly used mixture properties are those related to the prediction of the phase behavior using an appropriated model with the fitted parameters. Proper selection of thermodynamic models and reliable estimation of model parameters are absolutely necessary during process simulation, design

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Correspondence concerning this article should be addressed to G. J. Suppes at suppesg@missouri.edu.

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and optimization per the following well-known liquid-liquid equilibrium condition

$$\gamma_i^{BD} x_i^{BD} = \gamma_i^{Al} x_i^{Al} \tag{1}$$

where: γ is the activity coefficient of component *i*, *x* is mole fraction, *BD* is biodiesel, and *Al* is alcohol.

The following equations (modified Raoult's law) were used for VLE at the experimental pressures of less than 4 bars

$$y_i P = \gamma_i x_i P_i^{Sat} \tag{2}$$

$$P = \sum \gamma_i x_i P_i^{Sat} \tag{3}$$

where *P* is pressure, "*Sat*" indicates pure component vapor pressure at the temperature of interest, and the summation is over all components *i*.

Walas recommends the Wilson equation for VLE modeling of alcohol systems and the NRTL equation for LLE systems. The Wilson equation was used to model VLE, and the activity coefficients were applied at the LLE condition in this article.

A process for manufacturing methyl esters from fats and oils was proposed by Kreutzer et al.[12] High operating costs is one of the obstacles that limit the commercialization of biodiesel.[13-15] An efficient process design can optimize the process and lower the operating costs. Both the ability to accurately predict phase behavior and the determination of distribution of methanol and catalysts in the transesterification reactor are important when doing process design, simulation and optimization.

This work reports liquid-liquid distributions for methanol and catalysts in biodiesel/glycerin mixtures at 25 and 75°C, and activity coefficients based on VLE data and the modeling of that data by the Wilson equation. The distribution coefficients correlated with the predictive activity coefficient model according to the equilibrium relationship of Eq. 1.

Experimental procedures

Materials. Methanol HPLC grade, glycerin certified A.C.S., potassium hydroxide certified A.C.S. pellets and sulfuric acid certified A.C.S. were purchased from Fisher Scientific Co. (Fairlawn, NJ). SOYGOLD® Biodiesel Fuel (soybean oil methyl esters) was purchased from AG Environmental Products L.L.C. (Omaha, NE). The pure biodiesel, glycerin and methanol were used to simulate the system of transesterification products. The potassium hydroxide and sulfuric acid were used to simulate the basic and acid catalyst in the transesterification.

Distribution of Catalysts. The simulation of the distribution of basic and acid catalysts was carried out by loading varying amounts of methanol, biodiesel, and glycerin at given temperatures. Three different molar ratios of 0:1:3, 3:1:3 and 6:1:6 methanol/glycerin/biodiesel were used to examine the distribution of catalysts between the glycerin-rich and biodiesel-rich phases at 25 and 75°C.

For the 25°C measurement, the biodiesel, glycerin, methanol and catalyst (1 wt. % potassium hydroxide or 0.5 wt. % sulfuric acid) were individually added into a 50-mL separatory funnel and weighed. The funnel was stoppered and shaken to ensure complete mixing. It was allowed to settle for about 1 h. The two phases were separated, weighed, and sampled for subsequent analysis.

For the 75°C measurement, proper amounts of biodiesel, glycerin, methanol and catalyst were mixed in a 20-mL sealed vial. The quantities of the basic and acid catalysts were fixed at 1% and 0.5% in weight of mixture, respectively. The mixtures were strongly shaken, then settled in a 75°C oven for over 1 h. A 5-mL glass syringe was used to remove the bottom phase of mixture and transfer into a well sealed glass vial in order to prevent the loss of methanol in this high temperature. The two liquid phases were weighed, and sampled to quantitatively measure their compositions.

Distribution of Methanol. The measurements of the distribution of different molar ratios of methanol in the biodiesel/glycerin mixture were also conducted at 25 and 75°C. Two molar ratios of 3:1:3 and 6:1:3 methanol/glycerin/biodiesel were selected to test the distribution of methanol between the glycerin and biodiesel phases. The same sampling procedure was used as described in the section on distribution of catalysts.

Method of Analysis. The concentrations of potassium hydroxide and sulfuric acid were measured by a Metrohm 758 KFD Titrino (Herisau, Switzeland) with 0.01 mol/L hydrochloric acid solution and 0.01 mol/L sodium hydroxide solution, respectively. The samples were diluted with methanol before titration. The concentration of methanol was measured using a Hewlett-Packard 6890 GC (Wilmington, DC). Data collection and analysis were accomplished with Hewlett-Packard Chemstation software.

Activity Coefficient Procedure. Activity coefficients were determined by placing 2-mL samples into 2 mL brass capped tubes fitted with a Hamilton pressure gauge capable of reading pressure to the nearest 0.2 psi. The pressure gauge apparatus was placed into a pre-heated oven. Samples were left in the oven for 1 h to allow the temperature inside the pressure gauge apparatus to reach equilibrium. Each composition was prepared twice, and the average vapor pressure was used to calculate the activity coefficient. Pressure readings were taken at 100 and 120°C for each sample.

Results and discussion

Distribution of Catalysts. The distribution coefficient *K*, defined as the ratio of the mass fraction of the electrolyte (potassium hydroxide or sulfuric acid) in the glycerin phase to that in the biodiesel phase. Table 1 summarizes the distribution coefficients of potassium hydroxide and sulfuric acid among the glycerin/biodiesel mixture loaded with different amounts of methanol at 25 and 75°C.

The distribution coefficients of potassium hydroxide and sulfuric acid, respectively, decreased from 97.6 to 77.1 and 60.3 to 46.3 with the increase of the ratio of methanol. Higher methanol ratios also increase the amount of glycerin phase since methanol is only sparingly soluble in the biodiesel phase, and this results in lower concentrations of potassium hydroxide and sulfuric acid at higher temperatures in the glycerin phase. Distribution coefficients decreased with increasing temperatures in every methanol loading of both potassium hydroxide and sulfuric acid. The data indicate that as higher conversions of biodiesel are attained during transesterification and a glycerin phase is formed (at about

Table 1. Distribution of Basic and Acid Catalyst among Glycerin/Biodiesel Mixture Loaded with Different Amounts of Methanol at 25°C and 75°C

Temperature °C	Solute	Solvent*	Solute, wt.% Glycerin-rich Phase	Solute, wt.% Biodiesel-rich Phase	K**
25	1 wt.% KOH	0:1:3	8.60	0.088	97.6
		3:1:3	5.79	0.061	94.5
		6:1:3	4.29	0.056	77.1
75	1 wt.% KOH	0:1:3	8.11	0.172	47.2
		3:1:3	5.57	0.125	44.5
		6:1:3	4.13	0.119	34.7
25	0.5 wt.% H_2SO_4	0:1:3	4.52	0.075	60.3
		3:1:3	2.91	0.055	52.9
		6:1:3	2.27	0.049	46.3
75	0.5 wt.% H_2SO_4	0:1:3	3.39	0.108	31.4
		3:1:3	1.98	0.071	27.9
		6:1:3	1.60	0.066	24.2

*Solvent molar ratio: methanol:glycerin:biodiesel.

**K = [(wt.% solute in glycerin-rich phase)/(wt.% solute in biodiesel-rich phase)].

>80% conversion), the reaction rate should significantly reduce due to the reduction of catalyst in the biodiesel phase.

Distribution of Methanol. Typically, 1:4.5 to 1:9 molar ratio (2X to 3X stoichiometric) of oil/methanol is used in the transesterification of vegetable oil to biodiesel. After the reaction is finished, large amounts of the methanol is unreacted. The distribution of catalyst in the biodiesel product is significantly influenced by the unreacted methanol composition. The information on partitioning phenomenon of methanol and catalyst between glycerin and biodiesel phases is important both to optimize processes for attaining high conversions (>98%) and to identify subsequent separation process.

Table 2 shows the distribution of methanol between glycerin and biodiesel phases at 25 and 75°C stoichiometric molar ratios of 9:1:3 and 6:1:3 of methanol:glycerin: biodiesel. By the definition of distribution coefficient K, a K value much greater than 1.0 indicates that methanol preferentially distributes into glycerin, and only a relatively small amount dissolves in biodiesel. Since methanol and glycerin both have carbon-to-alcohol ratios of 1:1 (similar at molecular scale) with associated high degrees of hydrogen bonding, the methanol is expected to distribute predominantly in the glycerin phase. As the temperature increases, the distribution coefficients of methanol with a molar ratio of 3:1:3 and 3:1:6 decreased from 10.9 to 7.5 and 8.5 to 4.8, respectively. At higher temperatures, translational energies of the molecules lessen the impact of hydrogen bonding and create lower distribution coefficients.

Table 2. Distribution of Methanol between Biodiesel and Glycerin at 25°C and 75°C

Temperature °C	Molar Ratio*	Methanol, wt.% Glycerin	Methanol, wt.% Biodiesel	K
25	3:1:3	37.3	3.41	10.9
	6:1:3	54.2	6.38	8.5
75	3:1:3	35.9	4.79	7.5
	6:1:3	41.7	8.60	4.8

*Molar ratio: methanol:glycerin:biodiesel.

Prediction of Distribution Coefficient. The modified Raoult's Law and Eq. 3 are accurate for the moderate pressures of this study. In this study, the activity coefficient data were calculated from experimental VLE data by neglecting the biodiesel and glycerin partial pressures of Eq. 3. The experimental P-T-x data at 100 and 120°C are shown in Tables 3 and 4. The mole fractions reported in this work are accurate to within ±0.0025 and the measured pressures for each binary system are generally reproducible to within ± 0.01 bar.

The phase equilibrium data obtained were modeled with the Wilson activity coefficient model. The Wilson model for the excess Gibbs free energy of the system is based on the local composition concept for describing a solution. Variations in local composition are presumed to account for the short-range order and the nonrandom molecular orientations that result in differences of molecular size and intermolecular interaction forces. The two-component Wilson equations[16] are

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + x_2\Lambda_{12}) - x_2 \ln(x_2 + x_1\Lambda_{21}) \tag{4}$$

$$\ln \gamma_1 = -\ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \tag{5}$$

Table 3. Pressure-Composition Data for Methanol-Biodiesel Binary System at 100°C and 120°C

Mole Fraction Methanol	Pressure, bar 100°C	Pressure, bar 120°C
0.0430	0.28	0.54
0.1543	0.86	1.79
0.2714	1.40	3.12
0.4374	2.21	4.57
0.4983	2.52	4.93
0.6909	3.08	5.63
0.7930	3.21	5.72
0.8994	3.27	5.96
0.9543	3.31	6.14

Table 4. Pressure-Composition Data for Methanol-Glycerin Binary System at 100°C and 120°C

Mole Fraction Methanol	Pressure, bar	
	100°C	120°C
0.0554	0.09	0.18
0.1314	0.22	0.46
0.2421	0.43	0.89
0.4182	0.83	1.81
0.5520	1.21	2.45
0.7419	2.00	3.67

$$\ln \gamma_2 = -\ln(x_2 + x_1\Lambda_{21}) + x_1\left(\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_2 + x_1\Lambda_{21}}\right) \tag{6}$$

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L}\exp\left[-\frac{\lambda_{ij}}{RT}\right] \tag{7}$$

Here V_i^L and V_j^L are the molar volumes of each component. These λ_{ij} and λ_{ji} are the Wilson paired energy parameters which are considered temperature-independent and regressed to experimental data by ChemCAD Process Flowsheet Simulator 5.3[17]. The parameters λ_{ij} and λ_{ji} were determined at 100 and 120°C and found to give a good fit to data at both temperatures (Figure 1 and 2). The dashed line denotes the regressed line for the 120°C experimental data, and the solid line denotes the regressed line for 100°C experimental data.

The distribution coefficient can be related to the activity coefficients of the distributing components through the LLE condition of Eq. 1. The distribution coefficient for solute mole fractions is equal to the reciprocal of the ratio of the solute activity coefficients in the two phases. In terms of the equilibrium relation, the ratio of concentrations of a solute in two-liquid phases becomes

$$\frac{x_i^{Al}}{x_i^{BD}} = K = \frac{\gamma_i^{BD}(T, P, x_i^{BD})}{\gamma_i^{Al}(T, P, x_i^{Al})} \tag{8}$$

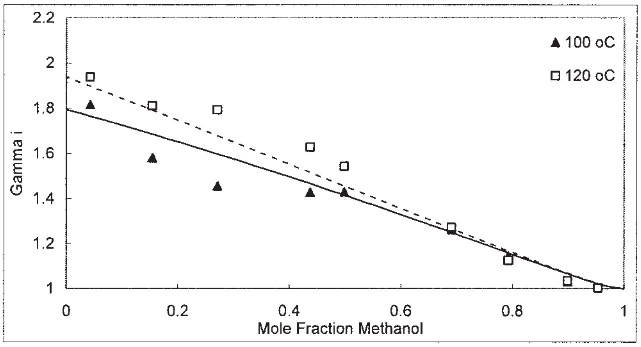

Figure 1. Experimental and calculated activity coefficients for the methanol-biodiesel binary system at 100 and 120°C.

The solid line and dashed line represent the Wilson model with regressed parameters of λ_{ij} = 1326.57 and λ_{ji} = 797.20.

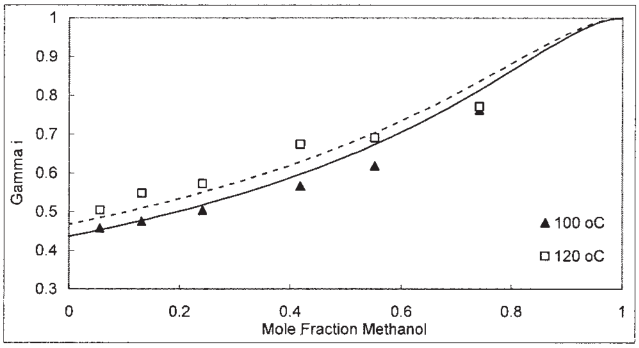

Figure 2. Experimental and calculated activity coefficients for the methanol-glycerin binary system at 100 and 120°C.

The solid line and dashed line represent the Wilson model with regressed parameters of λ_{ij} = -868.41 and λ_{ji} = 1106.17.

Equation 8 allows experimentally measured values of the distribution coefficient to be independently confirmed by VLE data from a solution model.

Using the Wilson activity coefficient model parameters of λ_{ij} = 1326.57 and λ_{ji} = 797.20 for methanol-biodiesel system, and λ_{ij} = -868.41 and λ_{ji} = 1106.17 for methanol-glycerin system the distribution coefficients for these systems were calculated. Table 5 compares experimental and predicted values of the distribution coefficients of methanol. Good agreement between experimental and predicted data was obtained.

Conclusions

In a molar ratio of 3:1 blend of biodiesel and glycerin system, the distribution coefficients of methanol and catalysts (potassium hydroxide and sulfuric acid) were measured. The distribution of methanol was observed to be in good agreement with values predicted by the Wilson equation and independent VLE data. Methanol, potassium hydroxide and sulfuric acid, each, selectively distributed into the glycerin phase. On a mass basis, the measured distribution coefficients varied from a high of 97 for potassium hydroxide at 25°C to a low of 4.8 for methanol at 75°C.

The presence of methanol in the biodiesel-glycerin system tends to increase the distribution of catalyst in the biodiesel phase. However, if the mass of all other components are held

Table 5. Comparison between Experimental (*Ke*) and Predicted (*Kp*) Distribution Coefficients, Obtained Using the Experimental Equilibrium Data and the ChemCAD Process Flowsheet Simulator 5.3

Temperature °C	Molar Ratio*	Experimental Value	Predicted Value		
		*Ke***	$\gamma^{Biodiesel}_{Methanol}$***	$\gamma^{Glycerin}_{Methanol}$***	*Kp***
25	3:1:3	2.5208	1.643	0.717	2.29
	6:1:3	2.0418	1.371	0.838	1.64
75	3:1:3	1.9881	1.510	0.794	1.90
	6:1:3	1.4379	1.316	0.891	1.48

*Molar ratio: methanol:glycerin:biodiesel.

***Ke*, *Kp* mole distribution coefficient.

***$\gamma^{Biodiesel}_{Methanol}$, $\gamma^{Glycerin}_{Methanol}$ activity coefficients of methanol in biodiesel and glycerin phase.

constant, methanol decreases the fraction of catalyst in the biodiesel phase by increasing the volume of the glycerin phase. A potential application of these fundamental solubility data and Wilson model parameters is in the modeling of the biodiesel reaction which tends to be quenched by the formation of a glycerin phase at conversions greater than about 80%.

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