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A Universal Procedure for Crude Glycerol Purification from Different Feedstocks in Biodiesel Production: Experimental and Simulation Study

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ABSTRACT: It is important to utilize crude glycerol, the main byproduct of biodiesel production, to manufacture high value-added chemicals. Since crude glycerol typically contains less than 65 wt % glycerol, purification is the first step for its utilization. Owing to the wide variety of triglycerides, alcohols, catalysts, and separation processes used in biodiesel production, crude glycerol composition varies widely, leading to different crude glycerol purifications. In the present work, we develop a universal procedure for crude glycerol purification, including as key steps initial microfiltration of the crude glycerol, saponification, acidification, phase separation, and biphasic extraction of upper- and lower-layer products. The procedure was utilized to purify crude glycerol samples from two biodiesel production companies, experimentally upgrading both samples to >94 wt % purity. On an Aspen Plus software platform, the purification procedure was simulated using a process model based on two submodels to obtain a good match with the experiments. The developed procedure is suitable for the purification of crude glycerol obtained from different biodiesel production technologies.

1. INTRODUCTION

Biodiesel, an important renewable energy source, has attracted the attention of both researchers and practitioners all over the world because it shows bright prospects of economics, environmentally benign features, and sustainability. In general, biodiesel is produced mainly by esterification and/or transesterification of vegetable oil, animal fat, or waste cooking oil with lower alcohols (methanol, ethanol, etc.), catalyzed by alkaline, acidic, or enzymatic catalysts.^{1–4} Although numerous works have focused on heterogeneous catalyst development to produce biodiesel more simply, economically, and efficiently, homogeneous catalysts such as sodium hydroxide and sulfuric acid are still the primary ones in industrial-scale biodiesel production.⁵ In all cases, glycerol with some impurities is produced as the main byproduct of biodiesel production and is usually called crude glycerol or raw glycerol.⁶

Typically, biodiesel production generates about 10% (w/w) glycerol as the main byproduct. Thus, approximately one pound of glycerol is generated when every gallon of biodiesel is produced. Therefore, in recent years, the development of the biodiesel industry has resulted in a large surplus of glycerol with a low price.⁷ In order to increase the economics of biodiesel production, crude glycerol should be utilized in some high value-added manner including animal feedstock, cosmetics, drugs, and especially catalytic conversion products.⁸ For example, hydrogen or syngas, acrolein, monoglycerides, and (2,2-dimethyl-1,3-dioxolan-4-yl) methyl acetate can be produced starting from crude glycerol.⁹ In our previous work, we developed an optimal catalyst converting glycerol to dihydroxyacetone, a valuable chemical.¹⁰ Note that in most cases, crude glycerol cannot be used directly in catalytic conversion processes due to possible catalyst deactivation caused by the impurities in the crude glycerol.¹¹ Thus, purification of crude

glycerol is often necessary before the value-added catalytic conversion of glycerol.

Because of variations in biodiesel production methods, the composition of crude glycerol also varies widely. All crude glycerol, however, contains glycerol, soap, light solvents (water, methanol, and/or ethanol), fatty acid methyl esters (FAMES), glycerides (referring to monoglycerides, diglycerides, and triglycerides), several types of free fatty acids (FFAs), and ash, although in different proportions. Table 1 shows three typical compositions of crude glycerol: CG1, CG2, and CG3,¹² which demonstrates that compositions of different crude glycerol vary significantly.

Table 1. Three Typical Compositions of Crude Glycerol (CG) Samples (wt %)¹²

component	CG1	CG2	CG3
glycerol	63.0	22.9	57.1
methanol	6.2	10.9	11.3
water	28.7	18.2	1.0
soap	BDL ^a	26.2	31.4
FAMES	BDL	21.3	0.5
glycerides	BDL	1.2	0.4
FFAs	BDL	1.0	BDL
ash	2.7	3.0	5.7
total ^b	99.4	102.9	103.6

^aBelow detectable level. ^bInorganic salts were double-counted in soap and ash content.

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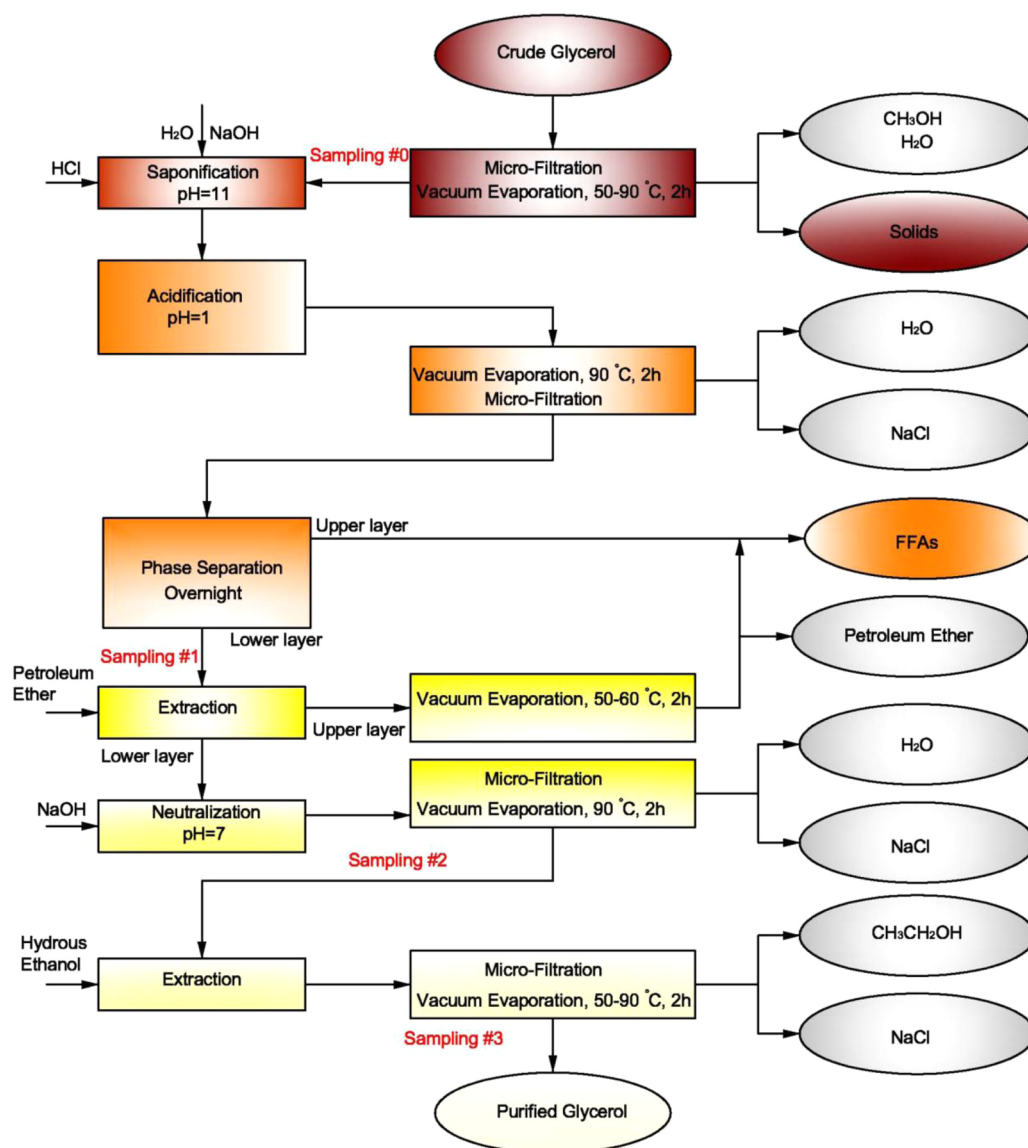


Figure 1. A universal procedure for crude glycerol purification.

Owing to the different compositions of various crude glycerol feedstocks, glycerol purification processes are also necessarily different. Ismail et al.¹³ developed a method to purify crude glycerol to a technical grade by employing a three-step procedure: a neutralization step, followed by microfiltration and ion-exchange resin adsorption steps. Ooi et al.¹⁴ recovered glycerol from crude glycerol at an average of 51.4 wt % purity by the sequence of acidification, filtration, neutralization, solvent extraction, and vacuum distillation steps. Hajek and Skopal,¹⁵ by exploiting treatments including saponification, neutralization, filtration evaporation, and phase separation, achieved 86 wt % glycerol purity without distillation. Kongjao et al.¹⁶ carried out laboratory-scale crude glycerol purification by using the combination of chemical and physical treatments based on repeating cycles of acidification, phase separation, neutralization, and ethanol extraction, obtaining 93.3 wt % glycerol purity. Manosak et al.¹⁷ performed crude glycerol purification by acidification, polar solvent extraction, and activated carbon adsorption. Under optimal conditions, 95.7 wt % glycerol purity was obtained. For some conditions, to obtain ultrahigh purity glycerol, adsorption by ion-exchange

resin is added to remove trace salts, as for example by Carmona et al.¹⁸ Generally, in most research and industrial practices, vacuum distillation at high temperatures (150–200 °C) must be employed as the final step to obtain refined-grade (>99.5 wt %) glycerol. This step, however, introduces large capital and operating costs, making the process less economical and more challenging.^{19,20}

In addition to the experimental method, process modeling is a powerful tool to evaluate chemical reaction and/or separation processes, providing information such as material and energy balances, equipment size, and economic evaluation that is useful for process design, rating, and scale-up. Aspen Plus, a widely used process-simulation software, has a variety of data for pure components, interaction parameters, thermodynamic models, unit operation models, and model analysis tools, which can simulate various chemical processes. In particular, there are pure component data including glycerol, methanol, ethanol, methyl oleate, oleic acid, monoolein, diolein, and triolein in the Aspen Plus database, which can be used to represent FAMES, FFAs, monoglycerides, diglycerides, and triglycerides in crude glycerol process simulations.^{21,22}

In the present work, our goal is to develop a universal procedure with low energy consumption to upgrade crude glycerol into purified grade (≈ 95 wt %). This purity level, which may be called technical grade, is more suitable than unrefined raw glycerol for a number of high value-added applications, such as catalytic conversions and production of fuel additives, hydrogen, methanol, and ethanol.²³ Moreover, the universality of the purification procedure is demonstrated by a model developed based on Aspen Plus software with two revised submodels.

2. EXPERIMENTAL SECTION

2.1. Materials. Two crude glycerol samples (CG4 and CG5) were obtained from Community Fuels (Encinitas, CA) and Indiana Biodiesel (Converse, IN), respectively. Hydrochloric acid solution (37 wt %) and sodium hydroxide pellets, both ACS grade, were from Mallinckrodt Chemicals. Petroleum ether (35–65 °C) and anhydrous ethanol were purchased from Mallinckrodt and Municipal Supplies, respectively, while the following chemicals were purchased from Sigma-Aldrich: reagent grade pyridine, reagent grade *n*-heptane, MSTFA derivatization grade reagent (*N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide), glycerin stock standard, monoolein stock standard, diolein stock standard, triolein, butanetriol internal standard #1, and tricaprins internal standard #2. Ultrahigh purity grade gases (99.999% helium and 99.999% hydrogen) and air were from Indiana Oxygen.

2.2. Crude Glycerol Analysis. Quantitative analysis of glycerol, FAME, and glycerides (mono-, di-, and tri-) in samples was conducted using a gas chromatograph (Agilent GC 5890) equipped with a flame ionization detector (FID) and a Select Biodiesel for glycerides ultraMetal Column (15m, 0.32 mm, 0.10 μ m) with a retention gap. Helium was used as the carrier gas with a constant flow rate of 3.0 mL/min and a split ratio of 100. The temperatures of the injector and the detector were 300 and 380 °C, respectively. The GC oven employed a temperature program as follows: 50 °C (maintaining for 1 min), to 180 °C at 15 °C/min (maintaining for 0 min), to 230 °C at 7 °C/min (maintaining for 0 min), and to 380 °C at 30 °C/min (maintaining for 10 min). Other details can be found in the work of Hu, Luo, Wan, and Li¹² and also in ASTM international documents (ASTM D 6584-10). Soap and FFAs contents in samples were determined by a titration method according to references (AOCS Recommended Practice Cc 17-95, ASTM D4662-08 and AOCS Official Method Ca 5a-40).

2.3. Crude Glycerol Purification Procedure. The purification procedure and sampling steps are shown in Figure 1. First, 100 g of each crude glycerol sample (CG4 and CG5) was microfiltered (0.45 μ m pore size) to remove all solid materials. Among the impurities in crude glycerol samples, methanol and water can be easily removed by vacuum evaporation. For this, both crude glycerol samples were treated under vacuum conditions using a rotary evaporator at 50–90 °C for more than 2 h. After the samples were cooled, 100 g of deionized water as solvent was added to each sample. Then 12.5 M NaOH was added to the samples until the pH was 11, and then the samples were kept stirred for 30 min at 50 °C to implement saponification. HCl was used to acidify the alkaline samples until the pH was 1, and then the samples were kept stirred for another 30 min at 25 °C. The acidified solutions were vacuum evaporated at 90 °C for more than 2 h and microfiltered. The samples were then placed in a separation funnel for phase split overnight. The next day, the upper layer

was decanted out slowly as FFAs product, while the lower layer was extracted by 100 g of petroleum ether to remove residual FFAs. Subsequently, the lower layer was neutralized with 12.5 M NaOH until the pH was 7 and microfiltered to eliminate salt, followed by vacuum evaporation of solvent at 90 °C for more than 2 h. The neutral solutions were extracted by 100 g of anhydrous ethanol in order to reduce residual salt. Finally, after microfiltration, all the light solvents were evaporated out at 50–90 °C for more than 2 h, and the purified glycerol was obtained. In addition, petroleum ether and ethanol were recycled by vacuum evaporation. Four samples (samples #0–3) at specific steps in the procedure were quantitatively analyzed by the methods described in section 2.2.

3. MODEL DEVELOPMENT

On an Aspen Plus software platform, we used methyl oleate ($C_{19}H_{36}O_2$) to represent FAMES (biodiesel), oleic acid ($C_{18}H_{34}O_2$) to represent FFAs, and monoolein ($C_{21}H_{40}O_4$), diolein ($C_{39}H_{72}O_5$), and triolein ($C_{57}H_{104}O_6$) to represent monoglycerides, diglycerides, and triglycerides, respectively. The electrolyte nonrandom two-liquid (ELECNRTL) activity coefficient model was selected owing to the existence of electrolytes.

Further, to simulate the crude glycerol purification process with Aspen Plus software accurately, the following two submodels were added in the process simulation software: a submodel of phase equilibrium behavior and a submodel of NaCl solubility in ethanol–glycerol mixtures. In the first submodel, the NRTL binary interaction parameters of glycerides–FFAs, FAMES–glycerol, and glycerol–FFAs were regressed using phase equilibrium data from the literature.^{24–26} Then the regressed NRTL binary interaction parameters were used to calculate the phase equilibrium behavior in the phase separation step shown in Figure 1. In the second submodel, a mathematical model based on the salts' thermodynamic properties and activity coefficients, proposed by Pinho and Macedo,²⁷ was used to predict NaCl solubility in ethanol–glycerol mixtures, with the only modification that the NRTL model was used instead of the universal quasichemical (UNIQUAC) model to calculate the activity coefficients. In the solubility submodel, generally, the salt equilibrium constant and solubility can be calculated by solving the following two simultaneous equations:

$$K_{\text{salt}} = \exp\left(\frac{\mu_{\text{salt}}^0(s) - \mu_{\text{salt}}^0(l)}{RT}\right) = \frac{\gamma_+ \gamma_- x_{\text{salt}}^2}{4} \quad (1)$$

$$K_{\text{salt}} = \exp\left(\frac{\Delta H_m}{R}\left(\frac{1}{T_m} - \frac{1}{T}\right) + \frac{\Delta C_{pm}}{R}\left(\frac{T_m}{T} - 1 + \ln \frac{T}{T_m}\right)\right) \quad (2)$$

where the symbols are defined in the Nomenclature. The values of salt thermodynamic properties in eq 2 were obtained from joint Army, Navy, and Air Force (JANAF) thermochemical tables.²⁸

With Aspen Plus including the aforementioned two submodels, the saponification, acidification, and neutralization steps were simulated in the RGibbs model. The phase separation and solvent extraction steps were simulated in the Decanter model, while the vacuum evaporation step was simulated in the Flash2 model. With this described procedure, the purification processes for four different crude glycerol samples (CG2–5) were simulated.

4. RESULTS AND DISCUSSION

Five crude glycerol samples (CG1–5) were investigated in this work. As noted previously, information regarding samples CG1–3 was taken from the literature,¹² while samples CG4 and CG5 were obtained from two different biodiesel companies and studied in our lab. Our specific work with each sample is described in this section.

4.1. Composition of the Crude Glycerol Samples.

Because methanol, water, and ash in crude glycerol samples are easily removed, these impurities were excluded from CG1, CG2, and CG3 as shown in Table 1 to facilitate the comparison of these glycerol samples with samples CG4 and CG5, as shown in Table 2. Thus, for the CG1 sample, essentially pure

Table 2. Composition of Crude Glycerol (CG) Samples (wt %)

component	CG1	CG2	CG3	CG4	CG5
glycerol	100.0	31.5	63.9	74.5	53.2
soap	0.0	36.1	35.1	19.8	32.4
FAMEs	0.0	29.3	0.6	4.6	4.9
glycerides	0.0	1.7	0.4	0.5	4.3
FFAs	0.0	1.4	0.0	0.0	3.6
total ^a	100.0	100.0	100.0	99.4	98.4

^aThe compositions of CG1–3 were normalized to 100 wt % excluding residual solvents and ash. The compositions of CG4 and CG5 did not include salt and ash.

glycerol was obtained. In Table 2, for the other samples (CG2–5), glycerol content varied widely from 31.5 to 74.5 wt %. Soap, as a main impurity, accounted for 19.8–36.1 wt % content. In CG3–5, FAMEs remained at a low level below 5 wt %. However, in CG2, the FAMEs content was 29.3 wt %, which may result in different phase equilibrium behavior in FFAs–glycerol phase separation because FAMEs are a cosolvent in this system.²⁹ The glycerides and FFAs contents were all below 5 wt %, probably because both of these are nonpolar substances while glycerol is polar. Since CG4 and CG5 were physical samples, they were purified experimentally, while simulations were conducted for samples CG2–5.

4.2. Experimental Results of the Crude Glycerol Purification. The CG4 and CG5 samples were purified by the procedure described in Figure 1 to give the purified glycerol samples PG4 and PG5, respectively, with the compositions shown in Table 3. The glycerol contents in purified glycerols PG4 and PG5 were 95.6 and 94.4 wt %, respectively. These purity levels are somewhat higher than those obtained by Hajek and Skopal¹⁵ (86.0 wt %) and Kongjao, Damronglerd, and Hunsom¹⁶ (93.3 wt %). By our universal purification procedure, as compared with that of Hajek and Skopal,¹⁵

Table 3. Composition of Purified Glycerol (PG) Samples (wt %)

component	PG4	PG5
glycerol	95.6	94.4
soap	BDL	BDL
FAMEs	0.3	1.8
glycerides	0.1	0.1
FFAs	0.1	0.2
total ^a	96.1	96.5

^aSalt and ash contents were not included.

ethanol extraction of the glycerol layer was employed to eliminate salt that was soluble in glycerol because salt has a lower solubility in ethanol than in glycerol. When compared with the process used by Kongjao, Damronglerd, and Hunsom,¹⁶ the saponification step was conducted before the acidification step. This ensured that FAMEs and glycerides converted into soap in the saponification step and then into FFAs in the acidification step, which may explain a higher glycerol purity than that reported in the work of Kongjao, Damronglerd, and Hunsom.¹⁶

4.3. Modeling of Phase Equilibrium Behavior in the Crude Glycerol Purification System. The phase equilibrium behavior is the most important principle in the purification of the crude glycerol system. In the phase separation step in Figure 1, there may be glycerides, FFAs, FAMEs, and glycerol in the acidified solution. The NRTL binary interaction parameters of glycerides–FFAs, FAMEs–glycerol, and glycerol–FFAs were regressed in Aspen Plus software using phase equilibrium data in the literature, and the regressed parameters are listed in Table 4.

Table 4. NRTL Binary Interaction Parameters in Crude Glycerol Purification System

component i	glycerides	FAMEs	glycerol
component j	FFAs	glycerol	FFAs
b_{ij} (/K)	2176	1694	1231
b_{ji} (/K)	1946	2432	1789
c (–)	0.3	0.3	0.2

As proposed in AspenTech,³⁰ the value of parameter c in Table 4 was 0.2 for glycerol–FFAs because of the immiscibility of these moieties, while it was 0.3 for the other binary systems. The parameters for the FAMEs–glycerol system were also consistent with the work of Bell et al.³¹ Using these binary parameters, ternary phase diagrams could be predicted, for example, as shown in Figure 2 for the FAMEs–glycerol–FFAs system.

From Figure 2, we conclude that, in the absence of FAMEs, FFAs and glycerol were nearly immiscible. In the presence of FAMEs, however, as a cosolvent of both FFAs and glycerol, some regions of the phase diagram became single phase which results in failure of phase separation. A similar conclusion was also obtained by Liu, Piao, Wang, and Zhu.²⁹ As compared with other procedures, the present work includes a saponification step, which can convert glycerides and FAMEs into soap first and then into FFAs after acidification. Saponification ensured that almost no FAMEs and glycerides existed in the acidified solution, provided the largest possibility of glycerol and FFAs separation, and thus yielded the highest purity of glycerol phase. In addition, any solvent such as water, methanol, and ethanol shows a similar but lower effect when compared to FAMEs. Therefore, we suggest that before phase separation of FFAs and glycerol, it is better to remove all light solvents at the initial vacuum evaporation step, as shown in Figure 1.

4.4. Modeling of NaCl Solubility in the Crude Glycerol Purification System. In general, between 298.15 K and 323.15 K, NaCl has a solubility of 35–37 g per 100 g of pure water, 7–8 g per 100 g of pure glycerol, 0.1–0.2 g per 100 g of pure methanol, and 0.06–0.07 g per 100 g of pure ethanol.³² Further, lower alcohols and glycerol are completely miscible. For this reason, it is good to employ alcohols such as methanol and ethanol to extract glycerol from NaCl. Another interesting

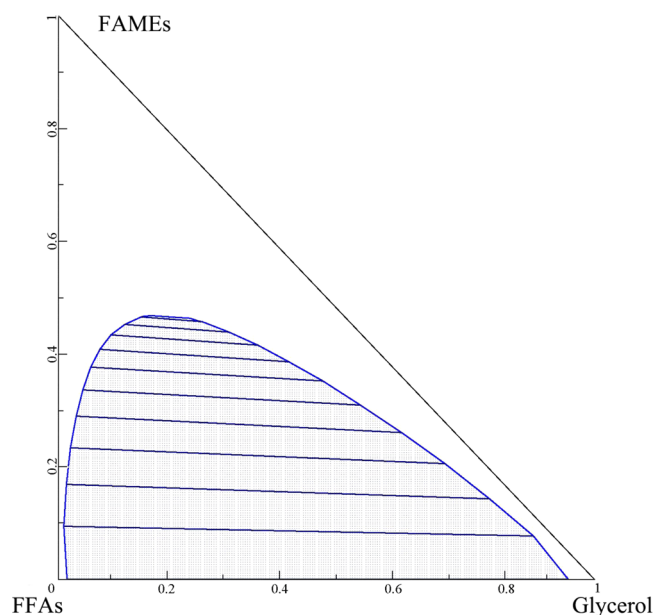


Figure 2. Ternary phase diagram of the FAMES–glycerol–FFAs system using the NRTL activity coefficients model at 298 K and 1 atm.

aspect is that NaCl solubility in ethanol–glycerol mixtures is lower than it is in either pure solvent. Thus, although NaCl solubility in ethanol is very small, it is even smaller in a mixture of ethanol and glycerol. For this reason, addition of ethanol to salt containing glycerol can cause the salt to precipitate out. This feature is similar to the fact that two substances with close boiling points can form a low-boiling azeotrope. Thus, the activity coefficient model can be used to describe these two phenomena in vapor–liquid phase equilibrium or liquid–solid phase equilibrium fields. It was assumed that NaCl in solution was in the molecular form,²⁷ and the NRTL model was used instead of the UNIQUAC model to calculate activity coefficients, because the NRTL model was also used to calculate activity coefficients in both submodels of phase equilibrium behavior and in the entire separation process simulation (see section 3). Figure 3 shows the predicted values and the literature-experimental data of NaCl solubility³³ in glycerol solution. In Figure 3, observe that, in general, the model-predicted values and the literature-experimental data match well, especially when the mass fraction of glycerol in the

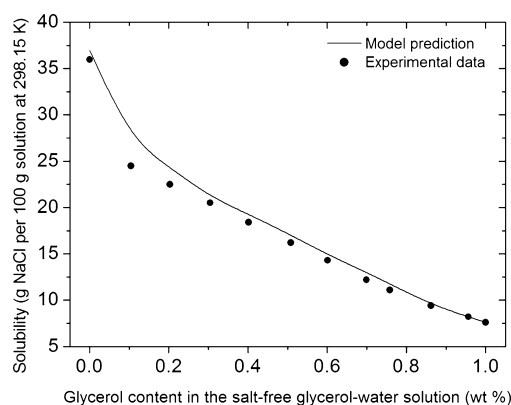


Figure 3. Comparison of NaCl solubility in glycerol solution: experimental data³³ and predicted values using the model²⁷ at 298 K and 1 atm.

salt-free solution is larger than 30 wt %, which demonstrates that the model successfully predicts NaCl solubility in glycerol solution. Further, as a part of the entire process model, this solubility submodel contributed to simulation of the crude glycerol purification process.

4.5. Comparison of Process Simulation and Experimental Results. The FFAs and NaCl are two main impurities in the crude glycerol after the saponification and acidification steps. On the basis of the two submodels described previously, the entire process of crude glycerol purification could be simulated. A comparison of simulation results with experimental data for CG4 and CG5 can be made using Table 5, where the simulation results for CG2 and CG3 are also listed.

Table 5. Simulation Results for CG2–5 and Experimental Results for CG4 and CG5.

	CG2-simu (%)	CG3-simu (%)	CG4-simu (%)	CG4-exp (%)	CG5-simu (%)	CG5-exp (%)
sample #0 ^a	31.5	63.9	74.5	74.5	53.2	53.2
sample #1	89.9	88.7	90.7	89.2	90.4	88.4
sample #2	91.3	92.1	92.9	92.4	91.2	90.7
sample #3	93.3	93.9	94.3	95.6	93.0	94.4

^aSamples described in terms of wt % of glycerol purity.

In Table 5, observe that the experimental and simulation results match well for both CG4 and CG5 samples, which implies that the process model based on the submodels of phase equilibrium behavior and NaCl solubility is accurate and reliable. Notice in Table 5 that for different compositions of crude glycerol in CG2–5, purified-grade glycerol with about 94 wt % purity was obtained, which suggests that the procedure described in Figure 1 is a successful universal crude glycerol purification method.

5. CONCLUSIONS

In this work, a universal procedure to purify crude glycerol from different biodiesel production processes is described. Using this procedure, two crude glycerol samples were upgraded experimentally to >94 wt % purity. A process model based on submodels of phase equilibrium behavior and NaCl solubility in ethanol–glycerol mixtures was developed to simulate the entire crude glycerol purification procedure. The simulation results agreed well with the experimental results, demonstrating that the universal procedure is suitable to purify a variety of crude glycerol samples.

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

ΔC_{pm} = salt heat capacity change at melting point [$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$]

ΔH_m = salt fusion heat at melting point [$\text{J}\cdot\text{mol}^{-1}$]

K_{salt} = salt equilibrium constant [–]

R = gas constant [$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$]

T = temperature [K]

T_m = salt melting point [K]

x_{salt} = salt mole fraction [–]

Greek Letters

$\mu_{\text{salt}}^0(\text{s})$ = standard chemical potential of the salt in the solid state [$\text{J}\cdot\text{mol}^{-1}$]

$\mu_{\text{salt}}^0(\text{l})$ = standard chemical potential of the salt in the liquid state [$\text{J}\cdot\text{mol}^{-1}$]

γ_+ = cation activity coefficient [–]

γ_- = anion activity coefficient [–]

REFERENCES

- (1) Vyas, A. P.; Verma, J. L.; Subrahmanyam, N. A Review on FAME Production Processes. *Fuel* **2010**, *89*, 1–9.
- (2) Pinzi, S.; Garcia, I. L.; Lopez-Gimenez, F. J.; de Castro, M. D. L.; Dorado, G.; Dorado, M. P. The Ideal Vegetable Oil-Based Biodiesel Composition: A Review of Social, Economical and Technical Implications. *Energy Fuels* **2009**, *23*, 2325–2341.
- (3) Kulkarni, M. G.; Dalai, A. K. Waste Cooking Oil—an Economical Source for Biodiesel: A Review. *Ind. Eng. Chem. Res.* **2006**, *45*, 2901–2913.
- (4) Talukder, M. M. R.; Wu, J. C.; Chua, L. P. L. Conversion of Waste Cooking Oil to Biodiesel via Enzymatic Hydrolysis Followed by Chemical Esterification. *Energy Fuels* **2010**, *24*, 2016–2019.
- (5) Di Serio, M.; Tesser, R.; Pengmei, L.; Santacesaria, E. Heterogeneous Catalysts for Biodiesel Production. *Energy Fuels* **2008**, *22*, 207–217.
- (6) Ayoub, M.; Abdullah, A. Z. Critical Review on the Current Scenario and Significance of Crude Glycerol Resulting from Biodiesel Industry Towards More Sustainable Renewable Energy Industry. *Renewable Sustainable Energy Rev.* **2012**, *16*, 2671–2686.
- (7) McCoy, M. Making Chemicals from the Biodiesel by-Product Proves Challenging. *Chem. Eng. News* **2009**, *87*, 16–17.
- (8) Johnson, D. T.; Taconi, K. A. The Glycerin Glut: Options for the Value-Added Conversion of Crude Glycerol Resulting from Biodiesel Production. *Environ. Prog.* **2007**, *26*, 338–348.
- (9) Yang, F. X.; Hanna, M. A.; Sun, R. C. Value-Added Uses for Crude Glycerol—a Byproduct of Biodiesel Production. *Biotechnol. Biofuels* **2012**, *5*, 13–22.
- (10) Hu, W. B.; Knight, D.; Lowry, B.; Varma, A. Selective Oxidation of Glycerol to Dihydroxyacetone over Pt-Bi/C Catalyst: Optimization of Catalyst and Reaction Conditions. *Ind. Eng. Chem. Res.* **2010**, *49*, 10876–10882.
- (11) Chatzifragkou, A.; Papanikolaou, S. Effect of Impurities in Biodiesel-Derived Waste Glycerol on the Performance and Feasibility of Biotechnological Processes. *Appl. Microbiol. Biotechnol.* **2012**, *95*, 13–27.
- (12) Hu, S. J.; Luo, X. L.; Wan, C. X.; Li, Y. B. Characterization of Crude Glycerol from Biodiesel Plants. *J. Agric. Food Chem.* **2012**, *60*, 5915–5921.
- (13) Ismail; Yarmo; Jahim; Salimon. Purification of Crude Glycerol from Transesterification RBD Palm Oil over Homogeneous and Heterogeneous Catalysts for Biolubricant Preparation. *J. App. Sci.* **2010**, *10*, 2590–259.
- (14) Ooi, T. L.; Yong, K. C.; Dzulkefly, K.; Wan Yunus, W. M. Z.; Hazimah, A. H. Crude Glycerine Recovery from Glycerol Residue Waste from a Palm Kernel Oil Methyl Ester Plant. *J. Oil Palm Res.* **2001**, *13*, 16–22.
- (15) Hajek, M.; Skopal, F. Treatment of Glycerol Phase Formed by Biodiesel Production. *Bioresour. Technol.* **2010**, *101*, 3242–3245.
- (16) Kongjao, S.; Damronglerd, S.; Hunsom, M. Purification of Crude Glycerol Derived from Waste Used-Oil Methyl Ester Plant. *Korean J. Chem. Eng.* **2010**, *27*, 944–949.
- (17) Manosak, R.; Limpattayanate, S.; Hunsom, M. Sequential-Refining of Crude Glycerol Derived from Waste Used-Oil Methyl Ester Plant via a Combined Process of Chemical and Adsorption. *Fuel Process. Technol.* **2011**, *92*, 92–99.
- (18) Carmona, M.; Lech, A.; de Lucas, A.; Perez, A.; Rodriguez, J. F. Purification of Glycerol/Water Solutions from Biodiesel Synthesis by Ion Exchange: Sodium and Chloride Removal. Part II. *J. Chem. Technol. Biotechnol.* **2009**, *84*, 1130–1135.
- (19) Yong, K. C.; Ooi, T. L.; Dzulkefly, K.; Wan Yunus, W. M. Z.; Hazimah, A. H. Refining of crude glycerine recovered from glycerol residue by simple vacuum distillation. *J. Oil Palm Res.* **2001**, *13*, 39–44.
- (20) Hazimah, A. H.; Ooi, T. L.; Salmiah, A. Recovery of Glycerol and Diglycerol from Glycerol Pitch. *J. Oil Palm Res.* **2003**, *15*, 1–5.
- (21) Chang, A. F.; Liu, Y. A. Integrated Process Modeling and Product Design of Biodiesel Manufacturing. *Ind. Eng. Chem. Res.* **2010**, *49*, 1197–1213.
- (22) Zhang, Y.; Dube, M. A.; McLean, D. D.; Kates, M. Biodiesel Production from Waste Cooking Oil: 1. Process Design and Technological Assessment. *Bioresour. Technol.* **2003**, *89*, 1–16.
- (23) Leoneti, A. B.; Araújo-Leoneti, V.; Oliveira, S. V. W. B. d. Glycerol as a by-Product of Biodiesel Production in Brazil: Alternatives for the Use of Unrefined Glycerol. *Renewable Energy* **2012**, *45*, 138–145.
- (24) Batista, E.; Monnerat, S.; Kato, K.; Stragevitch, L.; Meirelles, A. J. A. Liquid–Liquid Equilibrium for Systems of Canola Oil, Oleic Acid, And Short-Chain Alcohols. *J. Chem. Eng. Data* **1999**, *44*, 1360–1364.
- (25) Andreatta, A. E.; Casas, L. M.; Hegel, P.; Bottini, S. B.; Brignole, E. A. Phase Equilibria in Ternary Mixtures of Methyl Oleate, Glycerol, And Methanol. *Ind. Eng. Chem. Res.* **2008**, *47*, 5157–5164.
- (26) Marrone, L.; Pasco, L.; Moscatelli, D.; Gelosa, S. Liquid–Liquid Phase Equilibrium in Glycerol–Methanol–Fatty Acids Systems. *Chem. Eng. Trans.* **2007**, *11*, 629–634.
- (27) Pinho, S. P.; Macedo, E. A. Representation of Salt Solubility in Mixed Solvents: A Comparison of Thermodynamic Models. *Fluid Phase Equilib.* **1996**, *116*, 209–216.
- (28) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. JANAF Thermochemical Tables, 3rd ed. *J. Phys. Chem. Ref. Data, Suppl.* **1985**, *14*.
- (29) Liu, X. J.; Piao, X. L.; Wang, Y. J.; Zhu, S. L. Model Study on Transesterification of Soybean Oil to Biodiesel with Methanol Using Solid Base Catalyst. *J. Phys. Chem. A* **2010**, *114*, 3750–3755.
- (30) *Aspen Physical Property System 11.1*; Aspen Technology: Cambridge, MA, 2001.
- (31) Bell, J. C.; Messerly, R. A.; Gee, R.; Harrison, A.; Rowley, R. L.; Wilding, W. V. Ternary Liquid–Liquid Equilibrium of Biodiesel Compounds for Systems Consisting of a Methyl Ester + Glycerin + Water. *J. Chem. Eng. Data* **2013**, *58*, 1001–1004.
- (32) Pinho, S. P.; Macedo, E. A. Solubility of NaCl, NaBr, and KCl in Water, Methanol, Ethanol, And Their Mixed Solvents. *J. Chem. Eng. Data* **2005**, *50*, 29–32.
- (33) Carr, A. R.; Townsend, R. E.; Badger, W. L. Vapor Pressures of Glycerol–Water and Glycerol–Water–Sodium Chloride Systems. *Ind. Eng. Chem.* **1925**, *17*, 643–646.