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Optimal Separation of Glycerol and Methyl Oleate via Liquid−Liquid Extraction[†]

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To meet the ASTM D-6751-02 Standard for biodiesel, impurities, particularly glycerol, must be reduced to acceptable levels. Liquid−liquid extraction (i.e., solvent partitioning) is commonly used to achieve this standard. Evaluation of the technical feasibility of a single-stage mixer−settler liquid−liquid equilibrium process to separate glycerol and methyl oleate (as a model for biodiesel) was carried out based on the following criteria: (a) a volume ratio of the liquid phases close to 1:1, (b) a high recovery of biodiesel, (c) a short residence time of the liquid phases in the settler, and (d) achievement of the ASTM Standard for glycerol mass fraction of 0.0002 or less. Eight liquid−liquid extraction processes using different combinations of three potential solvents, hexane, methanol, and water, were studied. All data for the optimal compositions of each solvent system were obtained by calculations using the UNIFAC activity coefficient model, and no experimental measurements were done. Extraction using multisolvent systems containing hexane, methanol, and water were found to be technically feasible and gave the best results.

Introduction and Background

Biodiesel, a renewable, biodegradable, and relatively clean-burning source of energy, is considered to be an appropriate alternative for fossil fuels and is compatible with most diesel engines without engine modification.[1−7] Biodiesel (i.e., fatty acid alkyl esters) is produced by alkali- or acid-catalyzed transesterification of vegetable oils or animal fat, with an alcohol (usually methanol). Because of the significantly lower price of waste cooking oil compared to virgin vegetable oil, the use of the former oil as a biodiesel feedstock has been widely studied.[8−10] Glycerol is the main byproduct of transesterification, but its presence in biodiesel reduces the quality of the fuel.[11] According to the ASTM Standard for biodiesel (ASTM D-6751-02), glycerol must comprise less than 0.0002 mass fraction of the purified biodiesel.[12]

Few studies have specifically focused on large-scale purification of biodiesel. In contrast, bench-scale purification of biodiesel has been an essential part of studies that dealt primarily with the kinetics or the mechanism of transesterification.[13−16] Although these studies do not focus on the efficiency of the separations or the analysis of the separated products, they provide a source of potential methodologies for purification of biodiesel.

In many studies, removal of glycerol, excess alcohol, and catalyst was achieved by several consecutive stages of water-washing.[8,13−15] However, in alkali-catalyzed transesterification of waste cooking oil, the free fatty acids present are converted to soaps which cause emulsions in the water-washing step and lead to large losses of biodiesel.

In a bench-scale study, after alkali-catalyzed transesterification of waste frying oil, Nye et al.[16] employed hexane to separate biodiesel from impurities, including glycerol. They added hexane to the reaction mixture, which contained biodiesel, glycerol, residual methanol, and catalyst, to form a biodiesel + hexane phase and a glycerol + methanol + catalyst phase. This method was one of the first approaches used for hexane extraction of biodiesel.

Hexane is not a cheap solvent, and its flammability requires the use of special safety precautions in the plant, but it has been commonly used commercially as a solvent for lipids in oilseed extraction processes since the 1930s.[17−19] Biodiesel readily dissolves in hexane, which because of its relatively low normal boiling point (≈ 69 °C) can easily be distilled off in biodiesel purification processes. Hexane also reduces the density and viscosity of the biodiesel-rich stream, which enhances its separation from the glycerol + methanol + water phase. For the alkali-catalyzed transesterification of waste cooking oil, the presence of hexane was speculated to reduce or eliminate the formation of emulsions.[10]

Karaosmanoglu et al.[15] used two solvent extraction methods for separating impurities from biodiesel made by alkali-catalyzed transesterification of virgin rapeseed oil, after an initial separation of glycerol-rich and biodiesel-rich phases in a separatory funnel. In the first method, they washed the biodiesel-rich phase with hot distilled water and dried the biodiesel over Na_2SO_4. In the second method, the biodiesel-rich phase was dissolved in petroleum ether (low boiling petroleum), and the solution was washed three times with distilled water after adjusting its pH to 7 with acetic acid. The petroleum ether + biodiesel solution was dried over Na_2SO_4 and filtered, and the petroleum ether was distilled off in a vacuum rotary evaporator. The yield of refined biodiesel, calculated as a percentage of the mass of initial vegetable oil consumed in the transesterification, was (82 to 84) % for both methods of biodiesel purification.

In contrast to the alkali-catalyzed process, acid-catalyzed transesterification of low quality oils with methanol does not convert free fatty acids to soaps[10,20] but to methyl esters,[21,22]

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Table 1. Constituents of the Solvent Systems Investigated in the Present Study

solvent system	hexane	methanol residual	methanol added	water
1			√	
2		√		√
3			√	√
4	√	√		
5	√		√	
6	√			√
7	√	√		√
8	√		√	√

so that water can be used as an inexpensive solvent for separating glycerol from biodiesel without the formation of emulsions.

Zhang et al.[10,20] used HYSYS process simulation software to design and evaluate four possible biodiesel processing plants: an alkali-catalyzed process using virgin vegetable oil or waste cooking oil (Processes I and II, respectively), an acid-catalyzed process using waste cooking oil with a water-washing process (Process III), and an acid-catalyzed process using waste cooking oil with a hexane + methanol + water extraction process (Process IV). For the latter process, they found that partitioning of the biodiesel and glycerol components between hexane and methanol was improved by adding water to the methanol solvent without any emulsions being formed. The focus of the studies by Zhang et al.[10,20] was on the technical and economical evaluation of the overall biodiesel plant. Detailed technical assessment of a biodiesel extraction unit (e.g., a mixer−settler) was not carried out.

This task is the main objective of the current study. Some units of the plants designed by Zhang et al.,[10] such as transesterification reaction, methanol distillation, and catalyst removal units, were employed in the present study. These units are all located prior to the biodiesel purification unit and will not be further discussed here. In the present study, the performance of eight different combinations of three potential solvents, hexane, methanol, and water (Table 1), for separation of glycerol and methyl oleate (as a model for biodiesel) in a single-stage mixer−settler was investigated by developing a computer code with MatLab (version 7.1.0.246, R14 developed by MathWorks, Inc.).

Optimal compositions of each solvent were calculated using the UNIFAC activity coefficient model so as to achieve the ASTM Standard for biodiesel purity with respect to its glycerol mass fraction of 0.0002 in biodiesel, as well as a desirable phase volume ratio in the settler, a minimal liquid residence time in the settler, and minimal losses of biodiesel.

Process Description

Overall Process Design. When the biodiesel reaction mixture is diluted with solvent systems 1 through 8 (Table 1), two liquid phases are formed. When all of the three potential solvents are present (solvent systems 7 and 8), the upper phase contains hexane, most of the biodiesel, and a small amount of methanol, while the lower phase contains most of the glycerol, methanol, and water. The driving force for such a separation is the high solubilities of biodiesel in hexane, and glycerol in methanol or aqueous methanol, and the low solubility of biodiesel in methanol + water. On shaking the mixture, the continuous phase was experimentally found to be the biodiesel-rich phase, and the dispersed phase was the glycerol-rich phase. The time required for the separation of the two liquid phases in the settler is defined as the residence time. Following the previous experimental studies[21,22] and also the HYSYS process simulation results of Zhang et al.,[10,20] the performance of the extraction systems at a temperature of 20 °C and at atmospheric pressure were calculated using the UNIFAC activity coefficient model.

Properties of the Standard Feed Mixture. In the biodiesel plant (Process IV), the stream exiting the methanol recovery column after the acid-catalyzed transesterification reactor contains biodiesel, glycerol, small amounts of unreacted oil (triglycerides), acid catalyst (H_2SO_4), and the remaining methanol (Zhang et al.,[10] Figure 5, stream 203). This stream was used as the standard feed to the mixer−settler unit except that it was assumed to be free of acid catalyst after passing through the catalyst-removal unit.[10] In addition, the stream entering the extraction unit was assumed to be free of unreacted oil. This assumption was based on the results of experiments by Zheng et al.,[22] showing that high conversion of oil to biodiesel ($\approx$ 99.7 %) could be achieved by the acid-catalyzed reaction at 80 °C after 4 h.

Since biodiesel consists of a variety of fatty acid esters with different chain lengths and degrees of unsaturation, a single methyl ester, methyl oleate, was substituted as a model for biodiesel to simplify the calculations used here which cannot deal with systems having more than five components. This choice was made because methyl oleate is the major component [(40 to 60) %] in biodiesel made from the commonly used oils, canola, rapeseed, olive, rice bran, etc., and has the same solubility as biodiesel. The results of these calculations should thus be applicable to biodiesel prepared from a variety of vegetable oils.

On the basis of the above assumptions, the mole/mass fractions of methyl oleate, glycerol, and methanol in the standard feed entering the mixer were calculated to be 0.434/0.826, 0.146/0.087, and 0.420/0.087, respectively.

The ternary phase diagram of the system methyl oleate + glycerol + methanol, the standard feed mixture, is shown in Figure 1. The tie-line corresponding to the standard feed composition indicates the separation of the standard feed mixture into two liquid phases consisting of a bottom phase of mostly glycerol and methanol and an upper phase of mostly methyl oleate, some methanol, and traces of glycerol. Although there is a spontaneous partitioning between the two liquid phases, the mass fraction of glycerol remaining in the methyl oleate-rich phase is $\approx 0.0003 = 0.0008\ \mathrm{mol \cdot L^{-1}}$, which shows the ASTM Standard is not met and further purification must be carried out.

Methods

Phase Equilibria Calculations. The fugacity-matching method developed by Bunz et al.[23] and Nelson[24] was employed to determine the multicomponent, multiphase equilibria compositions at 20 °C and atmospheric pressure. As part of this method, a stability test was carried out to indicate the number and nature of the phases at equilibrium. The fugacity-matching method can handle up to three coexisting phases at equilibrium, one vapor and two liquid phases. The component and overall material balances, the $\gamma-\varphi$ equations given by Smith et al.,[25] along with the SRK equation of state for predicting the vapor-phase properties (Holderbaum and Gmehling[26] and Walas[27]) were employed for the phase equilibria calculations. To predict the properties of the liquid phases, the UNIFAC group contribution method of Magnussen et al.[28] was used. This choice was made because good predictions were obtained in a prior study (Tizvar et al.[29]) for the liquid−liquid phase equilibria of the quaternary system of methyl oleate, glycerol, hexane, and methanol. By

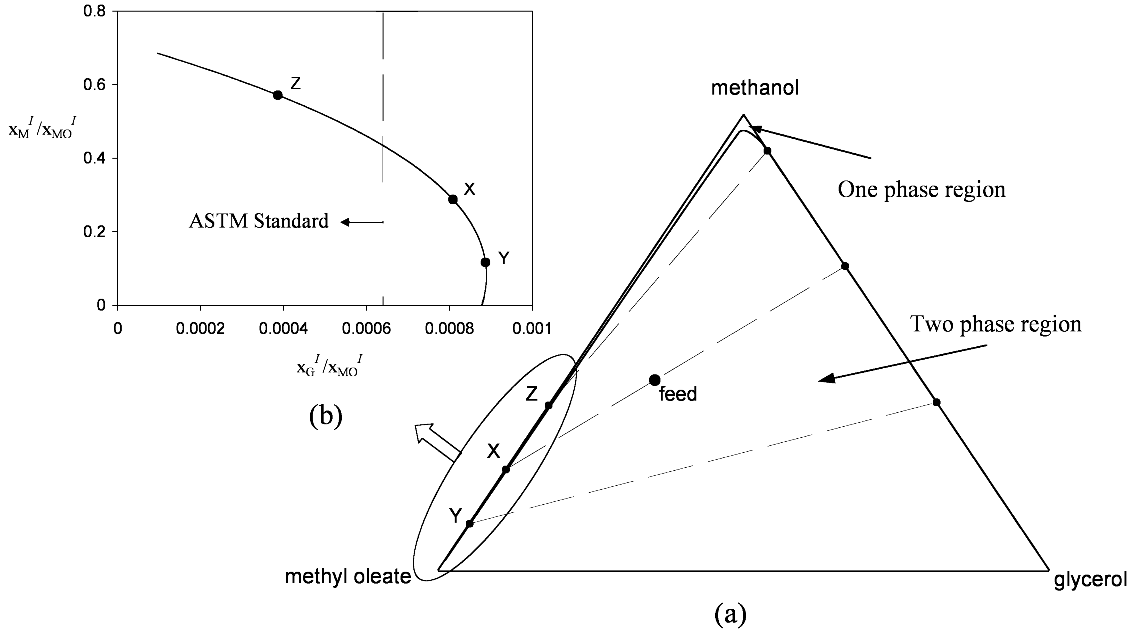

Figure 1. (a) Ternary phase diagram of methyl oleate + glycerol + methanol and the sample tie-lines (X, Y, Z) at 293.15 K and 1 bar (based on mole %). (b) x^I_M/x^I_{MO} vs x^I_G/x^I_{MO} in the methyl oleate-rich phase —; ASTM D-6751-02 — —; x^I_G, x^I_M, and x^I_{MO} are mole fractions of glycerol, methanol, and methyl oleate in the methyl oleate—rich phase, respectively.

developing the necessary computer codes in MATLAB[32] (version 7.1.0.246, R14 developed by MathWorks, Inc.) and employing an appropriate nonlinear optimization routine (fminsearch), the composition and physical properties of the coexisting phases at equilibrium were determined for every given overall composition. The quantity of components in the vapor phase was found to be negligible, at 20 °C and atmospheric pressure, over the entire composition range used for the extraction systems under investigation. Therefore, the system was assumed to contain essentially only two liquid phases at equilibrium. A detailed description of the multicomponent vapor—liquid—liquid equilibria calculations used in this work and some of the codes in MATLAB are presented by Tizvar.[30]

Design Criteria. The technical feasibility of various extraction processes was evaluated on the basis of the following criteria:

1. The ratio of the mass of glycerol to the mass of methyl oleate plus that of glycerol in the methyl oleate-rich phase must meet the corresponding ASTM Standard[12] such that

$$\frac{m_G^I}{m_G^I + m_{MO}^I} \leq 0.0002 \tag{1}$$

where m_G^I and m_{MO}^I are the masses of glycerol and methyl oleate in the methyl oleate-rich phase, respectively.

2. For effective operation of a mixer—settler system, the volume ratio of the two liquid phases should be close to 1:1. The more equivalent the phase volumes are, the better the contact of the molecules in the mixture, and accordingly, the more effective the mass transfer. In continuous discharge of both top and bottom liquid phases, equivalent phase volumes result in lessened sensitivity of the mixer—settler operation to changes in flow or composition of the inlets. The mathematical expression of this criterion is

$$\frac{V^I}{V^{II}} \approx 1 \tag{2}$$

where V^I and V^{II} are the volumes of phase I (methyl oleate-rich phase) and phase II (glycerol-rich phase), respectively. This criterion was implemented as a soft inequality constraint expressed as

$$\max\left\{\frac{V^I}{V^{II}}, \frac{V^{II}}{V^I}\right\} - n \leq 0 \tag{3}$$

where n represents an upper limit for the phase ratio. For instance, when n is equal to five, the phase volume ratio will be less than 5:1.

3. A highly effective extraction process is a system with a low loss of methyl oleate in the glycerol-rich phase, which can be expressed as

$$\min\left\{\frac{m_{MO}^{II}}{m_{MO}^{II} + m_{MO}^I}\right\} \tag{4}$$

where m_{MO}^I and m_{MO}^{II} denote the mass of methyl oleate in phases I and II, respectively. This quantity was used as one of the performance measures.

4. The size of the settler unit depends largely on the residence time of the phases in the settler. The shorter the residence time, the smaller the settler. The residence time can be calculated as

$$t = 0.1\left[\frac{\mu^I}{SG^{II} - SG^I}\right] \tag{5}$$

where t is the residence time in hours, μ^I is the viscosity of the continuous phase (methyl oleate-rich phase) in mPa·s, and SG^I and SG^{II} are the specific gravities of the top phase and bottom phase, respectively.[31] Any decrease in the viscosity of the methyl oleate-rich phase or increase in the difference between the densities of the two liquid

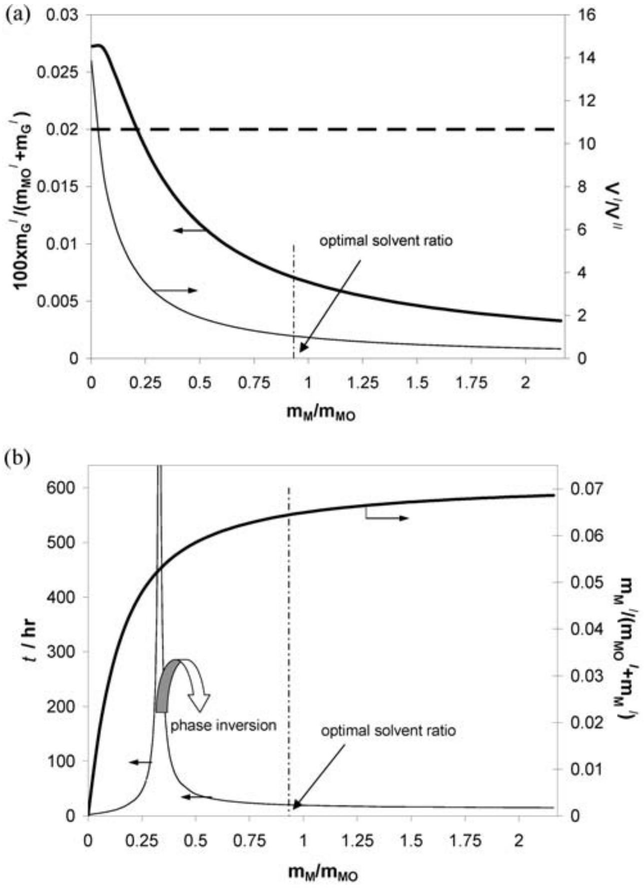

Figure 2. Solvent System 1: Methanol. Effects of addition of methanol to the standard feed mixture on: (a) $100 \cdot m_G^I/(m_G^I + m_{MO}^I)$ −; ASTM D-6751-02 − −; V^I/V^{II}, − and (b) $m_M^I/(m_M^I + m_{MO}^I)$ −; residence time in the settler, t/h −.

phases results in reduction of the residence time. Minimization of t was also an element of the performance measure.

5. Since water may be used as a solvent, some residual water may appear in the methyl oleate-rich phase. Consequently, it must be minimized to simplify the removal of water after the extraction unit and achieve the relevant ASTM Standard[12] for water content of biodiesel < 0.050 % by volume of water in biodiesel at normal temperature and pressure. This criterion is expressed as

$$\min\left\{\frac{m_W^I}{m_{MO}^I}\right\} \tag{6}$$

where m_W^I and m_{MO}^I are the masses of water and methyl oleate in the methyl oleate-rich phase, respectively.

Optimization Method. To determine the optimal values of the variables (i.e., relative masses of hexane, methanol, and water to methyl oleate in the mixer, m_H/m_{MO}, m_M/m_{MO}, and m_W/m_{MO}, respectively), the performance measures and constraints, discussed previously, were coded in MATLAB[32] and optimized by means of a nonlinear multiobjective solver (fgoalattain). In this implementation, eqs 4, 5, and 6 were introduced as objective functions, to be minimized, and subjected to a hard constraint (eq 1) and a soft constraint (eq 3).

Depending on which potential solvent system is being optimized, the vector of optimization variables had one, two, or three elements. The maximum and minimum values that these variables could attain were chosen to be $m_{solvent}/m_{MO} = 100$ and $m_{solvent}/m_{MO} = 0$, respectively. An exceptional minimum value of $m_M/m_{MO} = 0.104$ was used for methanol since the standard feed mixture entering the mixer was assumed to contain this quantity of methanol. m_M and m_{MO} are the mass of methanol and methyl oleate in the mixture, respectively.

Results and Discussion

Solvent System 1: Methanol. When methanol alone is employed as the extraction solvent, the ASTM Standard for glycerol content in biodiesel is met at a methanol to methyl oleate mass ratio of 0.24 (Figure 2a). Because of the high solubility of glycerol in methanol, which can be seen from the ternary phase diagram of methyl oleate + glycerol + methanol (Figures 1a and 1b), the more methanol added, the better the separation of glycerol and methyl oleate. This ternary system forms two liquid phases for a large range of overall compositions, with mostly methyl oleate in one phase and glycerol and methanol in the other phase. On adding more methanol to this ternary mixture, the quantity of glycerol in the methyl oleate-rich phase diminishes to significantly lower values than the required ASTM Standard glycerol mass fraction of 0.0002 (Figure 2a). However, when the concentration of methanol in the ternary mixture becomes very large, formation of a single liquid phase will occur (Figure 1a).

The phase volume ratio approaches 1 on adding more methanol to the reaction mixture since most of the methanol remains in the glycerol-rich phase.

Table 2. Phase Separation Properties for the Optimal Quantity of Methanol in Solvent System 1 (Methanol)[a]

components	m	m^I	m^{II}	V^I/V^{II}	ρ^I (g·cm^{-3})	ρ^{II} (g·cm^{-3})	μ^I (mPa·s)	μ^{II} (mPa·s)
methyl oleate	0.4909	0.9355	0.0102	1.04	0.842	0.811	6.32	0.82
glycerol	0.0511	0.0001	0.1070					
methanol	0.4580	0.0644	0.8827					

[a] m, m^I, and m^{II} are overall mass fractions of each component, mass fractions in phase I (methyl oleate-rich phase), and mass fractions in phase II (glycerol-rich phase), respectively.

Table 3. Phase Separation Properties for the Optimal Quantity of Water in Solvent System 2 (Water and Residual Methanol)

components	m	m^I	m^{II}	V^I/V^{II}	ρ^I (g·cm^{-3})	ρ^{II} (g·cm^{-3})	μ^I (mPa·s)	μ^{II} (mPa·s)
methyl oleate	0.4584	0.9955	0.0000	≈ 1	0.874	1.024	8.11	1.14
glycerol	0.0477	0.0000	0.0884					
methanol	0.0476	0.0034	0.0854					
water	0.4463	0.0011	0.8262					

Table 4. Phase Separation Properties for the Optimal Quantities of Methanol and Water in Solvent System 3 (Water and Added Methanol)

components	m	m^{I}	m^{II}	V^{I}/V^{II}	ρ^{I} ($g\cdot cm^{-3}$)	ρ^{II} ($g\cdot cm^{-3}$)	μ^{I} (mPa·s)	μ^{II} (mPa·s)
methyl oleate	0.4630	0.9881	0.0000	≈1	0.869	0.987	8.15	1.07
glycerol	0.0481	0.0000	0.0905					
methanol	0.1625	0.0107	0.2964					
water	0.3264	0.0012	0.6131					

Table 5. Phase Separation Properties for the Optimal Quantity of Methanol and Hexane in Solvent System 5 (Hexane and Added Methanol)

components	m	m^{I}	m^{II}	V^{I}/V^{II}	ρ^{I} ($g\cdot cm^{-3}$)	ρ^{II} ($g\cdot cm^{-3}$)	μ^{I} (mPa·s)	μ^{II} (mPa·s)
methyl oleate	0.2576	0.4926	0.0095	1.13	0.736	0.793	1.04	0.73
glycerol	0.0268	0.0001	0.0552					
hexane	0.2974	0.4250	0.1627					
methanol	0.4182	0.0823	0.7726					

Table 6. Phase Separation Properties for the Optimal Quantities of Water and Hexane in Solvent System 6 (Hexane and Water without Methanol)

components	m	m^{I}	m^{II}	V^{I}/V^{II}	ρ^{I} ($g\cdot cm^{-3}$)	ρ^{II} ($g\cdot cm^{-3}$)	μ^{I} (mPa·s)	μ^{II} (mPa·s)
methyl oleate	0.1608	0.2103	0.0000	4.98	0.677	1.035	0.42	1.14
glycerol	0.0166	0.0000	0.0709					
hexane	0.6039	0.7894	0.0003					
water	0.2187	0.0003	0.9288					

Table 7. Phase Separation Properties for the Optimal Quantities of Water and Hexane in Solvent System 7 (Hexane, Water and Residual Methanol)

components	m	m^{I}	m^{II}	V^{I}/V^{II}	ρ^{I} ($g\cdot cm^{-3}$)	ρ^{II} ($g\cdot cm^{-3}$)	μ^{I} (mPa·s)	μ^{II} (mPa·s)
methyl oleate	0.3711	0.5540	0.0000	2.87	0.721	1.021	0.93	1.19
glycerol	0.0387	0.0000	0.1175					
hexane	0.2956	0.4408	0.0009					
methanol	0.0385	0.0045	0.1075					
water	0.2561	0.0007	0.7741					

Table 8. Phase Separation Properties for Optimal Quantities of Methanol, Water and Hexane in Solvent System 8 (Hexane, Water and Added Methanol)

components	m	m^{I}	m^{II}	V^{I}/V^{II}	ρ^{I} ($g\cdot cm^{-3}$)	ρ^{II} ($g\cdot cm^{-3}$)	μ^{I} (mPa·s)	μ^{II} (mPa·s)
methyl oleate	0.2202	0.2997	0.0001	3.54	0.699	0.897	0.58	0.90
glycerol	0.0228	0.0000	0.0861					
hexane	0.4995	0.6654	0.0412					
methanol	0.1914	0.0340	0.6265					
water	0.0661	0.0009	0.2461					

In the present work, the recovery of methyl oleate is defined as the ratio of the mass of methyl oleate in the methyl oleate-rich phase to the initial mass of methyl oleate fed to the mixer. The recovery of methyl oleate was found to be relatively high; however, it decreases slightly to ≈ 96 % on adding methanol.

While methanol seems to be a good choice for glycerol extraction, at a methanol-to-methyl oleate mass ratio of ≈ 0.3, the difference between the densities of the top and bottom phases approaches zero, as a result of which the residence time in the settler increases to a very high value and phase separation becomes practically impossible without centrifugation (Figure 2b). On adding even more methanol, phase inversion occurs, and the residence time approaches ≈ 15 h. The inversion of phases occurs because the density of the glycerol-rich phase decreases on adding methanol to the mixture of glycerol, methyl oleate, and methanol. From a practical point of view, to have the extractor operate at steady state, the composition of the ternary system should be far from the phase inversion region (i.e., at a methanol to methyl oleate mass ratio of 0.2 to 0.5 as shown in Figure 2b).

The composition and phase separation properties for the optimal quantity of methanol as extractant (mass ratio of methyl oleate:methanol of 1:0.93) are given in Table 2. It should be noted that the derived properties in Tables 2 to 8 are all modeled properties. For this optimal amount of methanol, methyl oleate was almost completely recovered, but the residence time was calculated to be ≈ 20 h, which is too high to be practical.

Therefore, although methanol alone is capable of separating glycerol from methyl oleate, it is not a suitable solvent due to the lengthy residence time required for separation of the liquid phases in the settler. Furthermore, because of the phenomenon of phase inversion and the possible formation of a single liquid phase at high methanol concentrations, one should be cautious in choosing methanol as the only extraction solvent for the separation of glycerol from biodiesel.

Solvent System 2: Water and Residual Methanol. Figure 3a shows the changes in the mass fraction of glycerol in the methyl oleate-rich phase, $m_{G}^{I}/(m_{G}^{I} + m_{MO}^{I})$, and the phase volume ratio, V^{I}/V^{II}, on adding water to the standard feed stream. The glycerol content in the methyl oleate-rich phase decreases as the quantity of water is increased. Because glycerol has a much higher solubility in water than in methyl oleate, the required ASTM separation of glycerol and methyl oleate is achieved even with small amounts of water, such as with the methyl oleate:

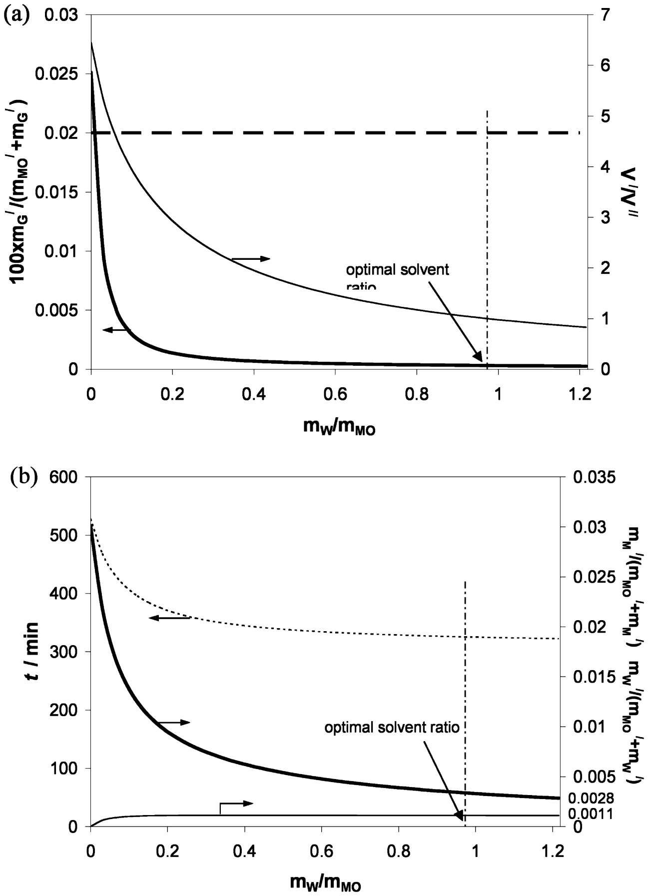

Figure 3. Solvent System 2: Water and residual methanol. Effects of addition of water to the standard feed mixture on: (a) $100 \cdot m_G^I/(m_G^I + m_{MO}^I)$ —; ASTM D-6751-02 – –; V^I/V^{II} — and (b) $m_M^I/(m_M^I + m_{MO}^I)$ —; $m_W^I/(m_W^I + m_{MO}^I)$ —; residence time in the settler, t/min.

methanol:water mass ratio of 1:0.104:0.007 (Figure 3a). Since water dissolves in the glycerol-rich phase, which initially has a smaller volume compared to the methyl oleate-rich phase, addition of water will equalize the volumes of the liquid phases. Complete recovery of biodiesel obtained by water washing the reaction mixture makes this extraction process a low loss system.

On further addition of water, the quantity of water in the methyl oleate-rich phase increases slightly to a constant value of $m_W^I/(m_W^I + m_{MO}^I) = 0.001$ (Figure 3b), where m_W^I is the mass of water in the methyl oleate-rich phase. Also, the methanol content in the methyl oleate-rich phase $m_M^I/(m_M^I + m_{MO}^I)$ decreases, on further addition of water, to a minimum of ≈ 0.003. The water and methanol remaining in the methyl oleate-rich phase can be easily removed by flash evaporation at reduced pressure. Since water dissolves in the glycerol-rich phase, which is usually the bottom phase, its addition results in an increase in the density of the bottom phase. Consequently, the residence time reduces to a minimum of ≈ 5.5 h (Figure 3b).

The composition and properties of the two phases separated at the optimal methyl oleate:methanol:water mass ratio of 1:0.104:0.973, which satisfies the design criteria, are shown in Table 3. For this optimal composition, the liquid residence time in the settler is ≈ 320 min, and methyl oleate is almost completely recovered.

From the above discussion, it can be seen that water mixed with residual methanol is a very good solvent for removal of glycerol. However, the relatively lengthy residence time in the settler indicates this mixed solvent might not be the best choice. Moreover, the possibility of formation of a single liquid phase and also the formation of emulsions in alkali-catalyzed transesterification of waste cooking oil become more problematic in the presence of water.

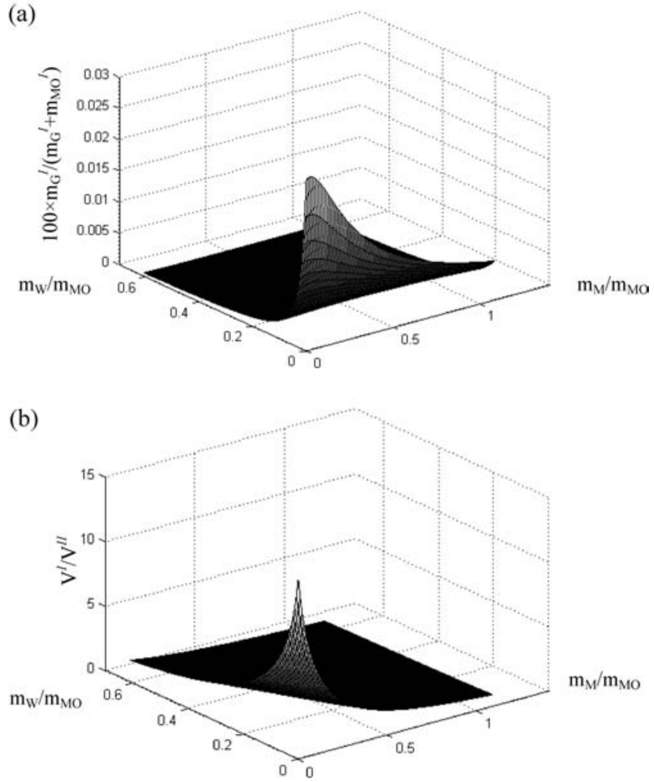

Figure 4. Solvent System 3: Water and added methanol. Effect of addition of methanol and water solvents to the standard feed mixture on: (a) $100 \cdot m_G^I/(m_G^I + m_{MO}^I)$; (b) V^I/V^{II}.

Solvent System 3: Water and Added Methanol. Figure 4a shows the change in the glycerol content of the methyl oleate-rich phase on adding both methanol and water to the system. As expected, the more methanol and water added, the better the separation of glycerol from methyl oleate. The phase volume ratio becomes closer to unity on adding both solvents since both methanol and water remain in the glycerol-rich phase (Figure 4b). For a $(m_G/m_{MO}) = 0.104$ in the standard feed mixture entering the extractor, Table 4 contains the optimal composition of Solvent System 3. An optimal mass ratio of methyl oleate:methanol:water of 1:0.351:0.705 results in a ≈ 420 min residence time in the settler and almost complete recovery of methyl oleate. Due to the higher quantity of methanol in this solvent system, the residence time in the settler was higher than that in Solvent System 2 (Figure 3b).

Solvent System 4: Hexane and Residual Methanol. On adding hexane as the extraction solvent to the standard feed mixture, not only is the ASTM Standard for biodiesel never met, but also the quantity of glycerol in the methyl oleate-rich phase increases (Figure 5a). This increase of the glycerol in the methyl oleate-rich phase is mainly due to partial miscibility of methanol in hexane and complete miscibility of glycerol in methanol. On increasing the quantity of hexane, more methanol and accordingly more glycerol enters the hexane-rich phase. This miscibility continues to the point where at very high concentrations of hexane, roughly starting at a methyl oleate:glycerol:hexane:methanol mass fraction of 0.0170:0.0053:0.9758:0.0018, a single liquid phase is formed.

Due to the high solubility of methyl oleate in hexane, the ratio of the phase volumes, V^I/V^{II}, is increased significantly by

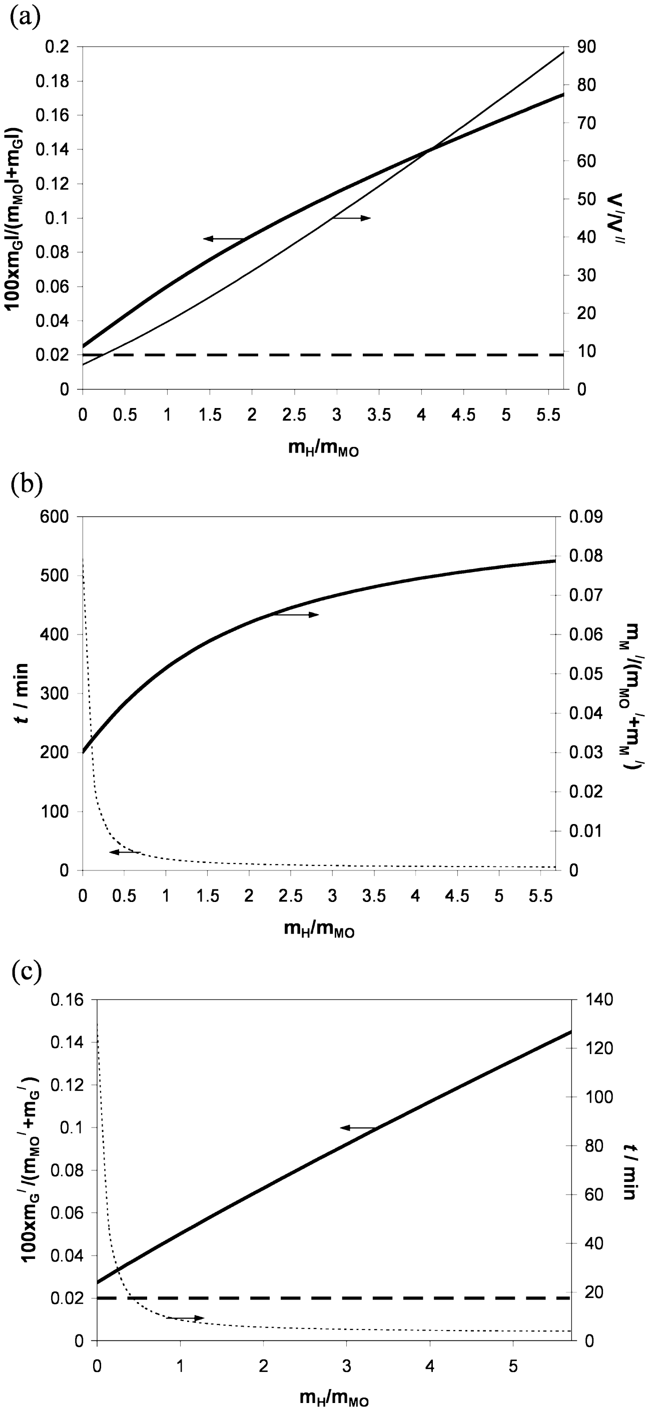

Figure 5. Solvent System 4 - Hexane and residual methanol. Effect of addition of hexane to the standard feed mixture on: (a) $100\cdot m_G^I/(m_G^I + m_{MO}^I)$ —; ASTM D-6751-02 — —; V^I/V^{II} —. (b) $m_M^I/(m_M^I + m_{MO}^I)$ —; residence time in the settler, *t*/min. (c) For ($m_M/m_{MO} = 0$), $100\cdot m_G^I/(m_G^I + m_{MO}^I)$ —; residence time in the settler, *t*/min.

adding hexane to the standard feed mixture. The recovery of methyl oleate remains roughly constant at ≈ 99 %, and the quantity of methanol in the methyl oleate-rich phase, $m_M^I/(m_M^I + m_{MO}^I)$, increases to ≈ 0.08 on adding hexane solvent (Figure 5b).

The major advantage of hexane as the extraction solvent in this system is the significant reduction in the settler residence time it causes. Hexane decreases the density and viscosity of the methyl oleate-rich phase significantly and results in an easier and faster separation of the two liquid phases in the settler. The density and viscosity of the methyl oleate-rich phase decrease, respectively, from 0.856 $g\cdot cm^{-3}$ and 8.03 mPa·s at $m_H/m_{MO} = 0$ (m_H is the total mass of hexane added to the mixture) to 0.675 $g\cdot cm^{-3}$ and 0.40 mPa·s at $m_H/m_{MO} = 5.8$. For such an increase in the quantity of hexane, the residence time decreases from ≈ (530 to 6) min (Figure 5b).

Figure 5c shows the effect of addition of hexane on the quantity of glycerol remaining in the methyl oleate-rich phase and on the residence time in the settler when methanol was completely distilled off prior to the extraction. Again, the ASTM Standard for glycerol content of biodiesel is not met. In the absence of methanol, the glycerol phase (bottom phase) becomes denser and more viscous, resulting in the liquid residence time in the settler decreasing to a lower value of ≈ 4 min, compared to the liquid residence time of 6 min shown in Figure 5b.

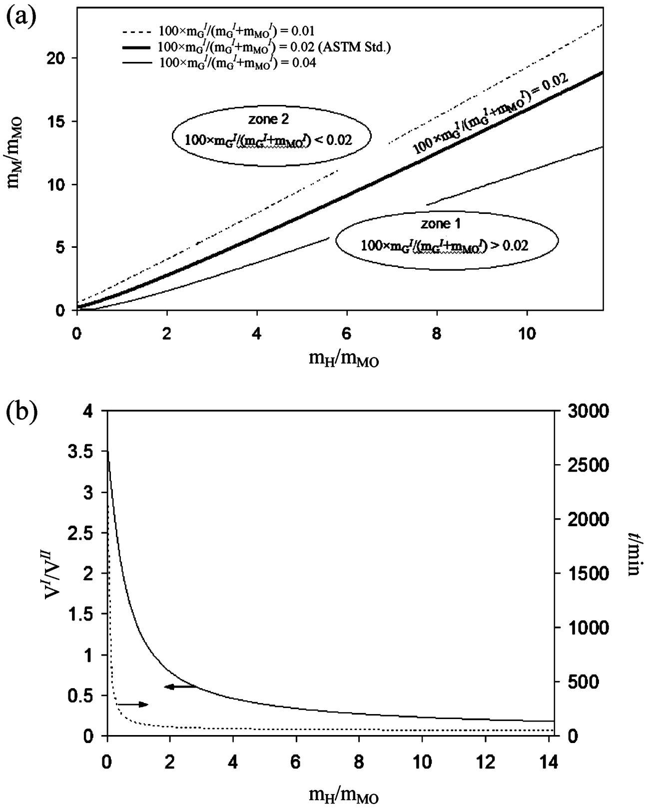

Figure 6. Solvent System 5: Hexane and added methanol. (a) The quantities of methanol required for given quantities of hexane to meet $100\cdot m_G^I/(m_G^I + m_{MO}^I) = 0.04$, 0.02, and 0.01 (zone 1: ASTM Std. not met; zone 2: ASTM Std. met). (b) The corresponding phase volume ratio and residence time in the settler, *t*/min, for $100\cdot m_G^I/(m_G^I + m_{MO}^I) = 0.02$ (ASTM Std.).

Solvent System 5: Hexane and Added Methanol. To show the effect of both hexane and methanol on the separation of glycerol and methyl oleate in such a system, the value of $100\cdot m_G^I/(m_G^I + m_{MO}^I)$ was set at 0.01, 0.02 (corresponding to the ASTM Standard), and 0.04. The quantities of methanol for the given quantities of hexane were plotted in Figure 6a. The ASTM Standard for the glycerol content of biodiesel is achieved only at low levels of hexane and high levels of methanol. The liquid phase volume ratios and the residence time of the liquid phases in the settler corresponding to $100\cdot m_G^I/(m_G^I + m_{MO}^I) = 0.02$ are shown in Figure 6b. The desired phase volume ratio of between one and five was achieved since for each unit mass of hexane added, ≈ 0.7 times more methanol was required to separate glycerol from methyl oleate. However, the effect of adding ≈ 0.7 times more methanol than hexane on the residence time is less apparent, and the residence time decreases to 49

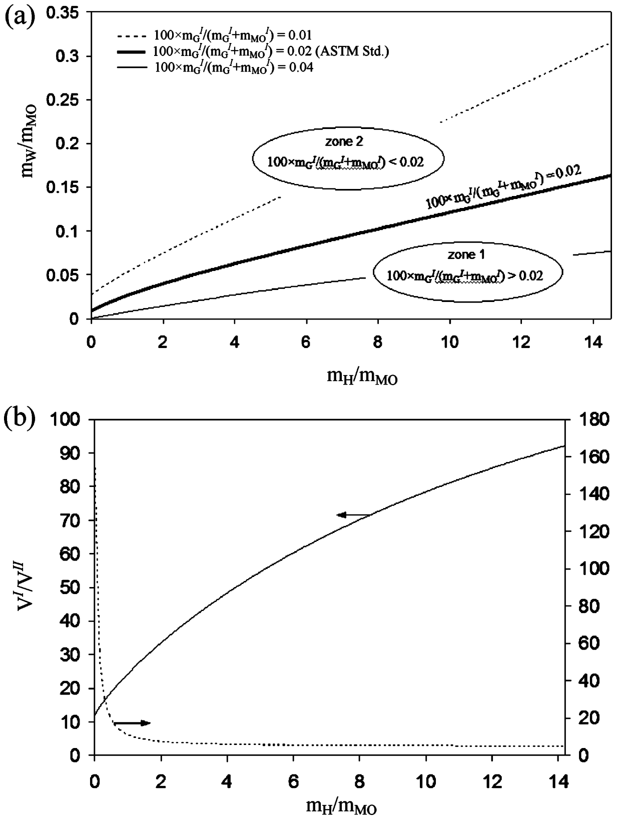

Figure 7. Solvent System 6: Hexane and water without methanol. For $(m_M/m_{MO}) = 0$ (a) the required quantities of water for given quantities of hexane to meet $100 \cdot m_G^I/(m_G^I + m_{MO}^I) = 0.04$, 0.02, and 0.01 (zone 1: ASTM Std. not met; zone 2: ASTM Std. met). (b) The corresponding phase volume ratio and residence time in the settler, *t*/min, for $100 \cdot m_G^I/(m_G^I + m_{MO}^I) = 0.02$ (ASTM Std.).

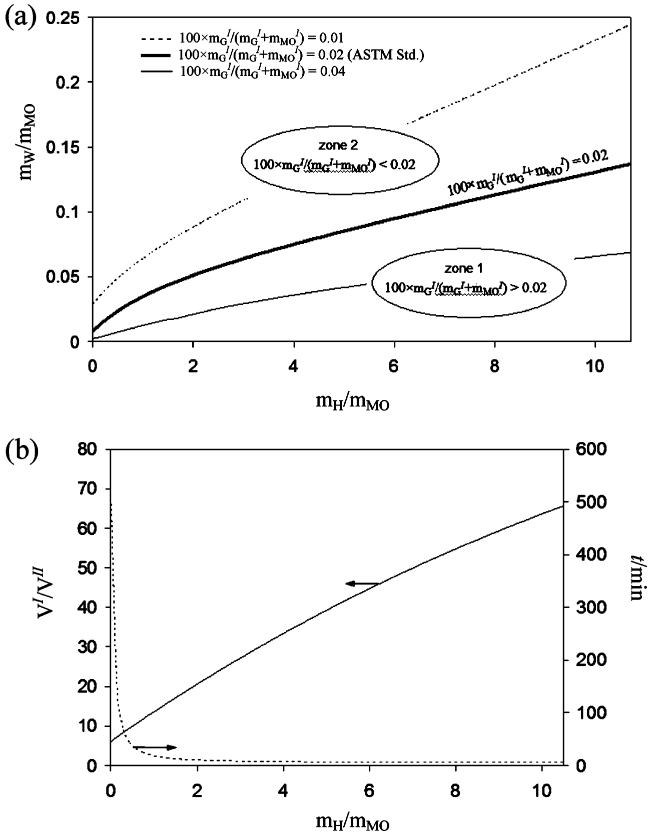

Figure 8. Solvent System 7: Hexane, water, and residual methanol. (a) The required quantities of water for given quantities of hexane to meet $100 \cdot m_G^I/(m_G^I + m_{MO}^I) = 0.04$, 0.02, and 0.01 (zone 1: ASTM Std. not met; zone 2: ASTM Std. met). (b) The corresponding phase volume ratio and residence time in the settler, *t*/min, for $100 \cdot m_G^I/(m_G^I + m_{MO}^I) = 0.02$ (ASTM Std.).

min when the value of $m_H/m_{MO} = 14.5$, requiring a value of $m_M/m_{MO} = 23.9$ to meet the ASTM Standard.

On the basis of the multicriteria optimization described in the Methods section, the optimal mass ratio of methyl oleate:hexane:methanol was found to be 1:1.15:1.62. The composition and some physical properties of the separated phases for this optimum ratio are shown in Table 5. The corresponding residence time of the liquid phases in the settler is rather high at 109 min, and the methyl oleate recovery is 98 %.

Solvent System 6: Hexane and Water without Methanol. To illustrate the effect of hexane and water on the separation of glycerol and methyl oleate, for different mass ratios of hexane to methyl oleate, the term $100 \cdot m_G^I/(m_G^I + m_{MO}^I)$ was set at 0.04, 0.02 (the ASTM Standard), and 0.01. The required quantities of water calculated to meet these glycerol levels are plotted in Figure 7a. Due to the high miscibility of glycerol in water, the separation of glycerol and methyl oleate is enhanced on adding water to the mixture.

The ratios of the phase volumes as well as the liquid residence time in the settler corresponding to the ASTM Standard level are shown in Figure 7b. In terms of the phase volume ratio, the more water and the less hexane are added, the more equal the phase volumes become. The residence time decreases on adding hexane and water to the standard feed mixture freed of methanol (Figure 7b), due to a significant reduction in the density and viscosity of the methyl oleate-rich phase on adding hexane (Table 6).

For Solvent System 6, the quantities of hexane and water were optimized to satisfy the extraction criteria. The optimized mass ratio of methyl oleate:hexane:water of 1:3.76:1.36 yields a residence time of ≈ 7 min and almost complete recovery of methyl oleate. Table 6 lists the properties and composition of the partitioned phases for the optimized quantity of hexane and water.

Solvent System 7: Hexane, Water, and Residual Methanol. On adding hexane and water to the standard feed mixture, for each mass ratio of hexane to that of methyl oleate, the quantities of water required to meet the specified glycerol levels, $100 \cdot m_G^I/(m_G^I + m_{MO}^I)$, of 0.01, 0.02, and 0.04 are shown in Figure 8a. Due to the limited capability of hexane alone to achieve the separation of glycerol and methyl oleate, as was discussed previously, the more hexane that is added, the more water is required to reduce the glycerol content of the methyl oleate-rich phase.

The phase volume ratio and the residence times in the settler, corresponding to the glycerol mass fraction of 0.0002 (ASTM Std.), are shown in Figure 8b. The more water and less hexane,

Table 9. Summary of the Optimal Compositions of the Solvent Systems (Values Are Given in Kilograms)

	methyl oleate	hexane	methanol	water
Solvent System 1	1	--	0.93	--
Solvent System 2	1	--	0.10	0.97
Solvent System 3	1	--	0.35	0.71
Solvent System 4	optimal composition could not be determined due to violation of the hard constraint on glycerol content			
Solvent System 5	1	1.15	1.62	--
Solvent System 6	1	3.76	--	1.36
Solvent System 7	1	0.79	0.10	0.69
Solvent System 8	1	2.27	0.87	0.30

Table 10. Values of the Performance Criteria for the Optimal Ratios of Each Solvent System Given in Table *9*

	Solvent System 1	Solvent System 2	Solvent System 3	Solvent System 5	Solvent System 6	Solvent System 7	Solvent System 8
$m^{\mathrm{I}}_{\mathrm{G}}/(m^{\mathrm{I}}_{\mathrm{G}} + m^{\mathrm{I}}_{\mathrm{MO}})$	0.0001	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000
$V^{\mathrm{I}}/V^{\mathrm{II}}$	1.04	≈ 1	≈ 1	1.13	4.98	2.87	3.54
$m^{\mathrm{I}}_{\mathrm{MO}}/(m^{\mathrm{I}}_{\mathrm{MO}} + m^{\mathrm{II}}_{\mathrm{MO}})$	0.99	≈ 1	≈ 1	0.98	≈ 1	≈ 1	≈ 1
t (min)	≈ 20 (h)	320	420	109	7	19	17
$m^{\mathrm{I}}_{\mathrm{W}}/(m^{\mathrm{I}}_{\mathrm{W}} + m^{\mathrm{I}}_{\mathrm{MO}})$	--	0.0011	0.0012	--	0.0014	0.0013	0.0030

the more equal the phase volumes become. Addition of hexane results in a reduction in the density and viscosity of the methyl oleate-rich phase. Moreover, in the presence of methanol, adding water results in an increased density of the glycerol-rich phase. Hence, the separation of the two liquid phases becomes faster, and the liquid residence time in the settler decreases to about 6 min (Figure 8b).

For the fixed amount of methanol in the standard feed mixture, the mass ratio of methyl oleate:hexane:water of 1:0.79:0.69 was found to provide optimal separation of glycerol from methyl oleate. Some physical properties of the two liquid phases for this optimal solvent ratio are given in Table 7. The corresponding residence time is ≈ 19 min, and recovery of methyl oleate is almost complete.

Solvent System 8: Hexane, Water, and Added Methanol. When additional methanol is fed to the extractor along with hexane and water as solvents, the methyl oleate:hexane:methanol:water mass ratio of 1:2.27:0.87:0.30 provided the optimal separation. The properties of the separated phases for the optimized values of each solvent are presented in Table 8. For the optimal solvent ratio the residence time in the settler was ≈ 17 min, and methyl oleate recovery was almost complete.

Conclusions

A summary of the optimal compositions of the solvent systems studied and the values of the design objectives are given in Tables 9 and 10, respectively. On the basis of the findings in Table 10, it may be concluded that when formation of emulsions is of no concern (e.g., in acid-catalyzed transesterification of waste cooking oil), mixtures of hexane, water, and methanol (Solvent Systems 7 and 8) were found to be the most suitable solvents with respect to achievement of the ASTM glycerol standard, residence times [(≈ 19 and ≈ 17) min, respectively], and recovery of methyl oleate. In these solvent systems, the presence of water and hexane together ensures the formation of a two-phase liquid system in the settler.

In biodiesel production systems that are insensitive to the water content, mixtures of methanol and water were also found to be very good solvents for glycerol separation (Solvent Systems 2 and 3). Although these solvents satisfy the ASTM Standard for the glycerol content of biodiesel, the liquid residence time in the settler is relatively high, and there is a potential for formation of a single liquid phase at high methanol or water concentrations. To reduce the residence time in the settler, the quantity of methanol entering the extractor must be minimized, and a mixture of only hexane and water should be employed as the extraction solvent. This is possible by distilling all of the methanol present in the reaction mixture prior to entering the extraction unit (Solvent System 6).

The ASTM Standard for glycerol content is achieved on adding methanol alone to the standard feed mixture, but methanol alone is not a suitable solvent due to the lengthy residence time needed for separating the two liquid phases in the settler. Furthermore, phase inversion and the possible formation of a single liquid phase at high methanol concentrations make methanol alone unsuitable as the extraction solvent for purification of biodiesel from glycerol.

When formation of emulsions due to the presence of water and free fatty acids in low quality feedstock is of concern, a dual solvent mixture consisting of hexane and methanol can satisfy the ASTM Standard (Solvent System 5). However, use of this solvent leads to a relatively high residence time of the liquid phase in the settler and to a relatively lower recovery of methyl oleate.

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