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Quantitative of Mass Transfer in Liquid-Liquid Operations of Oil-Alcohol-Glycerin Systems

Benjamim H.L. Silva and Cesar A.M. Abreu

Abstract

The effects of mass transfer were quantified for the effective performance of mixtures between partially miscible phases, or for the promotion of their separations. To consolidate the analysis of heterogeneous liquid-liquid processes, variations in the composition of the liquid phases over the evolution of contact operations were considered, detailing the physical mechanisms involved in the mixtures of oil (soy, sunflower) and alcohol (methanol, ethanol), and in the separation between biodiesel and glycerin. Based on experimental evaluations, the average distribution coefficients for triglycerides (oil-alcohol) and glycerol (biodiesel-glycerin) were estimated at 1.31 and 1.46, and 3.42×10^{-2} and 4.06×10^{-2} , for soybean and sunflower, respectively, while their mass transfer coefficients, depending on their concentration ranges in the phase, varied in orders of magnitude from 10^{-2} s^{-1} to 10^{-4} s^{-1} . Including the values of the physical parameters, a heterogeneous model for the alkaline transesterification of soybean oil (methanol, ethanol, NaOH, 25°C, 40°C, 60°C, 600 rpm) was validated.

Keywords: Mass transfer, liquid-liquid, vegetable oil, biodiesel, glycerin

1. Introduction

The effects of mass transfer are highlighted in heterogeneous processes involving mixing, reaction and separation, affecting operations that seek to evaluate intimate contacts between two or more phases [1, 2].

In operations involving slightly miscible liquids, interactions occur between the phases through their contact interfaces, where the migration of components subjected to mass transfers with a predominance of diffusive effects occurs. The knowledge of these effects is associated with the dynamics of fluids in operations, highlighting actions for the purposes of mixing and separation.

In the last few decades, the search for independence from fossil fuels has led to significant developments in the field of renewable energies. Among them, biodiesel or green diesel has positioned itself prominently and its production is growing. In order to have this fuel more available, several processes converge to obtain it, among which the most widespread is the transesterification of vegetables oils.

From an operational point of view, this process has been improved and developed according to the needs of production and quality characteristics for energy

purposes. Thus, in-depth knowledge of the phenomena involved in its operations involves detailing the interactions between the different partially miscible or immiscible liquid phases present, including oil, alcohol, biodiesel and glycerin. The different approaches to assess liquid–liquid interactions in the production of biodiesel identified as a heterogeneous process have highlighted the contributions of mass transfer, although associated with reaction effects [3–6]. However, this type of approach in which the mass transfer is not considered independently as a relevant step, prevents accurate descriptions of the effects that directly influence the performance of the process. By highlighting in detail the effects of mass transfer, a description of the supply of reagents (triglycerides) and release of the main co-product (glycerol) in the separation of biodiesel is provided [7].

The heterogeneous system formed in the transesterification operation occurs with the contact between the partially miscible polar and nonpolar phases: alcohol and triglycerides, and in its evolution includes the formation of the glycerin phase.

In batch operations, the effects of the mixture involve the dispersion of alcohol in the oil in the form of droplets, whose interfaces allow the dissolution of the triglycerides that are transferred internally [8–10]. On the other hand, the separation of glycerol involving the transfer of oil to glycerin is a determining step for obtaining high-purity biodiesel [11–13].

A more accurate knowledge of all the effects on the global kinetics of biodiesel production involving reaction and mass transfer can provide a reduction in operating time, decreasing them by intensifying the initial interactions between the phases and with the reactions, and in the separation of the final stages, where less interaction should take place.

Different investigations on the effects related to mass transfers between liquid phases in alkaline transesterification processes have indicated orders of magnitude of parameters representing these phenomena, although always combined with reaction effects, and for a fixed composition of each phase [14–16]. During biodiesel production, variations in composition result from the reactive process in which concentrations continue to evolve [5, 17].

Reflecting these effects, orders of magnitude of mass transfer parameters can be quantified according to the compositions of the interacting oil and alcohol phases and relative to the separation of glycerol from the mixture of esters [18–20].

The present work aims to consolidate the analysis of heterogeneous liquid–liquid processes using a detailed approach to quantify the interactions involved in the contacts between partially miscible phases. In this context, changes in the composition of the liquid phases throughout the evolution of operations were considered. Detailed knowledge of the physical mechanisms of the oil-alcohol and biodiesel-glycerol interaction processes was applied to describe the evolution of experimental concentrations. The mass transfer coefficients and the distribution coefficients of triglycerides (oil-alcohol) and glycerol (biodiesel-glycerin) were estimated based on experimental evaluations. These quantifications associated with the transesterification rates, allowed the orientation towards the best operating conditions and product quality in the production of biodiesel.

2. Evaluation of mass transfer and equilibrium between phases

Experiments carried out under non-reactive conditions provided measurements of triglyceride content in alcohol and residual glycerol in biodiesel. The values obtained in time evolution provided results described by a heterogeneous model. The adjustment of the model equations led to the quantification of the mass transfer and distribution equilibrium parameters.

2.1 Experimental

In assessing the effects of mass transfer and dissolution between the partially miscible phases of vegetable oil (O) and alcohol (A), and biodiesel (B) and glycerol (G), the mixtures and phase separations were carried out in an isothermal manner (60° C, 600 rpm). The oil-alcohol mixture (molar ratio A:O/6:1) was maintained for 50 min, when samples were collected every 2 min. Mixtures of glycerol and biodiesel (volumetric ratios G:B/ 0.50:0.50 - /0.40: 0.30) were maintained for 30 minutes, after which they were transferred to graduated hoppers where the phase separations occurred, while the corresponding times were counted. The levels of triglycerides accumulated in alcohol and residual glycerol in biodiesel were quantified by the corresponding chromatographic analytical methodologies (analytical method Hartman and Lago [21]; HPLC). The interfacial areas of contact between the phases were estimated based on the scattered droplet sizes measured by photographic technique (Canon EOSD60 camera, 28-300 mm lens, ImageJ® software). The specific interfacial area a ($a_{OL/A} = 6\phi/d_{32}$) was calculated with 40–50 drops, diameter d_i , where d_{32} is the average Sauter diameter ($d_{32} = \sum d_i^2 (\sum d_i^3)^{-1}$; $i = 1, N$) and ϕ is the volume of the dispersed phase.

2.1.1 Analyzes

Samples of $5.0 \times 10^{-6} \text{ m}^{-3}$ were taken from the reactor at times 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 40 and 50 minutes, neutralized with $2.0 \times 10^{-6} \text{ m}^3$ aqueous hydrochloric acid (HCl, 15.0 mol m^{-3}), washed with $10.0 \times 10^{-6} \text{ m}^3$ of distilled water saturated with sodium chloride and left in decanting funnels until complete phase separation (biodiesel, glycerin). The samples from the biodiesel phase were diluted in hexane and analyzed by gas chromatography (CG Master-Peak Simple II, SRI Instruments; Carbowax 20 M megabore column, 30 m, $0.54 \times 10^{-3} \text{ m}$, FID detector), using methyl heptadecanoate (Sigma-Aldrich, purity $\geq 99.0\%$) as an internal standard. In the glycerin phase, glycerol analyzes were performed by high performance liquid chromatography (HPLC, Gilson chromatography, RI detector, Prevail Carbohydrate ES column, $0.25 \mu\text{m}$, $0.25 \text{ m} \times 0.42 \times 10^{-2} \text{ m}$) using an external standardization and the mobile phase acetonitrile / water (75:25 with flow of $1.0 \times 10^{-6} \text{ m}^3 / \text{min}$) at 25° C.

3. Results and discussion

3.1 Experimental results

The interactions between the liquid phases oil and alcohol, and biodiesel and glycerol were evaluated through measurements carried out in the respective phases (TG/alcohol, G/biodiesel) as a function of the time of operation. In relation to the two oils (soy, sunflower) used in the experiments, **Table 1** shows the composition (% by weight) in terms of its main triglycerides (TG).

For both oils, the unsaturated components (C18: 1, 18: 2) represented more than 80% of the composition, according to data already established [22].

Figure 1 shows the evolution of triglyceride concentrations (TG) in the alcohol phase (A) in each system (oil-alcohol) investigated, indicating the contents transferred over time.

It was observed that the transfer of triglycerides (TG) was faster in the soy / ethanol system, throughout the time domain, and that this also occurred in the sunflower/ethanol system, but only after 25 minutes of operation. The higher levels

Component	Soybean (% wt.)	Sunflower (% wt.)
C16:0	12.96	6.54
C18:0	4.23	3.23
C18:1	26.39	41.76
C18:2	50.41	48.09
C18:3	6.01	0.38

Table 1.
Composition of vegetable oils (% wt.).

Figure 1.
Evolution of triglyceride concentrations (% wt.). Conditions: A:O/6:1, 60°C, 600 rpm.

obtained with ethanol at the end of the operation indicated that the distribution of TG between the oil and the alcoholic phase was more favorable for this alcohol. In fact, the TG of the two vegetable oils is more soluble in ethanol, of less polarity (Dielectric ct. 24.5) than in methanol (Dielectric ct.32.7).

3.2 Mass transfer and miscibility

Considering the phenomena involved in the mixing and miscibility of the oil in the alcohol, alcohol droplets are formed and dispersed in the oil, establishing interfaces through which the triglycerides are transferred, so that the solubilization and its accumulation in the phase occurs. When the biodiesel and glycerol phases are separated, the glycerol is transferred and released, decreasing its content in biodiesel and providing its decantation. To quantify the effects of the observed, the mass balance equations Eqs. (1) and (2) were formulated and applied to the related processes.

$$\frac{dC_{TG/A}}{dt} = K_{TG}(C_{TG/AI} - C_{TG/A}) \quad (1)$$

$$\frac{dC_G}{dt} = K_G(C_{GB} - C_G) \quad (2)$$

where $C_{TG/A}$, $C_{TG/A0}$, C_G , C_{G0} are the concentrations of triglycerides and glycerol, respectively. In both cases, at the beginning of the contact between the phases,

$t = 0, C_{TG} = C_{TG/A0}, C_G = C_{G0}$. K_{TG} and K_G are the respective mass transfer coefficients.

The solutions in Eqs. (1) and (2) (Runge Kutta 4th order; *software* gPROMS ModelBuilder®) describe the evolutionary behavior of the concentrations of triglycerides and glycerol in the alcohol and biodiesel phases, respectively. To do so, they must include the values of the volumetric mass transfer coefficients K_{TG} and K_G .

3.3 Predictions versus experimental

The evolution of the concentrations of triglycerides (TG) measured in each oil phase served to adjust the solution of Eq. (1) allowing to quantify $K_{TG/A}$ and α_{TG} . The values of specific interfacial area ($a_{TG/A}$) measured are included in the mass transfer coefficient. **Figure 2** shows for TG concentrations the parity between the predicted and experimental values, with indication of weak linear concordances (correlation coefficients, $R^2 \sim [0.82-0.91]$).

Although the parameter values were obtained from weak numerical adjustments, they were considered as initial orders of magnitude for the elaboration of more precise adjustments. The initial values of the mass transfer coefficients ($k_{TG/A}$) and the distribution parameters between the phases (α_{TG}) and the specific interfacial areas measured are listed in **Table 2**.

Changes in the characteristics of the alcoholic phase (composition, density, viscosity) are considered during the supply of triglycerides via mixing. Thus, a

Figure 2.
Predicted versus experimental values of triglycerides mass fractions. Conditions: A:OL/6:1, $C_{NaOH} = 0.50\%$ wt., 600 rpm. a) Soybean/methanol, b) sunflower/methanol, c) soybean/ethanol, d) sunflower/ethanol.

Parameter	Soy/MeOH	Sunflower/MeOH	Soy/EthOH	Sunflower/EthOH
$k_{TG} \text{ (ms}^{-1}\text{)}$	3.60×10^{-7}	3.39×10^{-7}	5.22×10^{-7}	6.87×10^{-7}
α_{TG}	2.64	2.88	1.37	2.18
$a \text{ (mm}^{-1}\text{)}$	1.87	1.79	0.57	0.81

Table 2.
Mass transfer and equilibrium parameters of triglycerides. Oil/alcohol systems. Conditions: A:O = 6:1, 60°C, 600 rpm.

more realistic approach was applied to improve the predictions, admitting the effect of the concentration of triglycerides, focusing on the mass transfer coefficient expressed through the Darken equation (Eq. (3); [23, 24]).

$$K_{TG/A} = a_{OL/A} \lambda D_{TG/A} y_{TG/A} \tag{3}$$

where, $\lambda = \left(1 + y_{TG/A} d \ln \gamma_{TG} / dy_{TG/A}\right)$ is a non-ideality factor, and $D_{TG/ROH}$ is estimated by the Wilke-Chang correlation ([24], $D_{TG/A} = 7.4 \times 10^{-8} T [\psi M_A]^{1/2} (\mu_A^{-1} V_{TG}^{-6})$). The parameters and properties introduced in the formulations are listed in **Tables 3 and 4**.

The values of the volumetric coefficients of mass transfer of triglycerides in the alcohol phases, as a function of the different concentrations are in **Table 5**.

3.3.1 Mass transfer of glycerol

For glycerol, the effects of mass transfer were evaluated by mixing it with the biodiesel phase. Then, the evolution of the residual content in biodiesel was monitored (**Figure 3**). **Figure 4** shows the evolution of the experimental and calculated concentrations by the solution of Eq. (2). From the biodiesel-glycerol mixtures, decreasing evolutions of the glycerol concentration were observed as the phase separation occurred. At the end of the experiments, no residual glycerol was detected in the biodiesel phase (measured by HPLC, droplet images), indicating that the phase separation was effective. Observing the behavior of the biodiesel

Parameter	Sobeany/MeOH	Sunflower/MeOH	Soybean/EthOH	Sunflower/EthOH
$V_{Alcol} \text{ (cm}^3 \text{ mol}^{-1}\text{)}$	40.45	40.45	58.43	57.16
$M_B \text{ (g mol}^{-1}\text{)}$	871.1	877.6	871.1	877.6
$\mu_B \text{ (cP)}$	16.7	16.4	16.7	16.4
α_{TG}	2.64	2.88	1.37	2.18
$a \text{ (mm}^{-1}\text{)}$	1.87	1.79	0.57	0.81

Table 3.
Parameters and properties [24, 25].

Parameter	Sobeany/MeOH	Sunflower/MeOH	Soybean/EthOH	Sunflower/EthOH
$D^0_{A/TG} \text{ (m}^2 \text{ s}^{-1}\text{)}$	6.52×10^{-10}	6.67×10^{-10}	4.65×10^{-10}	5.35×10^{-10}
$\lambda \text{ (m)}^{-1}$	2.09×10^4	2.56×10^4	6.13×10^4	5.62×10^4

Table 4.
Estimated model parameters.

	Sobeany/MeOH	Sunflower/MeOH	Soybean/EthOH	Sunflower/EthOH
$C_{TG/A}$	$K_{TG/A}$	$K_{TG/A}$	$K_{TG/A}$	$K_{TG/A}$
(% wt.)	($\times 10^4 s^{-1}$)	($\times 10^4 s^{-1}$)	($\times 10^4 s^{-1}$)	($\times 10^4 s^{-1}$)
0.01	2.55	3.06	1.62	2.44
0.025	6.39	7.64	4.06	6.09
0.05	12.8	15.0	8.12	12.2
0.1	25.5	30.6	16.2	24.4
0.2	51.1	61.1	32.5	48.7
0.3	76.6	91.7	48.7	73.1
0.4	102	122	65.0	97.4
0.5	128	153	81.2	122
0.6	153	183	97.4	146
0.7	179	214	114	170

Table 5.
 Volumetric coefficients of mass transfer triglycerides-alcohol. Concentration effect. Conditions: A:O = 6:1, 60°C, 600 rpm.

Figure 3.
 Evolution of triglyceride mass fractions in the alcohol phase. Conditions: A:OL/6:1, C_{NaOH} = 0.50% wt., 600 rpm. a) Soybean/methanol, b) sunflower/methanol, c) soybean/ethanol, d) sunflower/ethanol.

Figure 4.

Evolution of glycerol concentrations in the biodiesel phase. Conditions: R a:OL/6:1, $C_{NaOH} = 0.50\%$ wt., 600 rpm. a) Soy/methanol; b) sunflower/methanol; c) soy/ethanol; e d) sunflower/ethanol.

(ethyl)-glycerol mixture, it was found that the phase separation occurred more slowly than in the case of biodiesel (methyl)-glycerol.

The mass transfer coefficients of glycerol from biodiesel to glycerine (K_G) denote the transfer and also the speed with which the separation of the two phases (glycerine-biodiesel) occurred, where mean K_G values were $1.49 \times 10^{-3} \text{ s}^{-1}$ (soy-bean/methanol), $1.20 \times 10^{-3} \text{ s}^{-1}$ (sunflower/methanol), and $6.75 \times 10^{-3} \text{ s}^{-1}$ (soy-bean/methanol), $7.42 \times 10^{-3} \text{ s}^{-1}$ (sunflower/methanol), respectively. The evolutions represented for triglycerides and glycerol according to the model showed good levels of compatibility ($R^2 = 0.9345\text{--}0.9806$ linear parity, experimental vs. calculated; analysis of variance ANOVA F (95%) = 5.14; Snedecorv F: 5%).

In the context of kinetic effects for triglycerides and glycerol, orders of magnitude of mass transfer parameters ($10^{-4} - 10^{-3} \text{ s}^{-1}$, [16, 18, 19]) were in the range of results obtained.

4. Application to the reactive process

From the point of view of using the quantified parameters via assessments of the effects of mass transfer in the mixture and in the separation of the phases involved in the biodiesel production processes, it is taken into account that its orders of magnitude are comparable to those obtained in previous studies [17, 26]. For purposes of application to the reactive process, the values of the mass transfer

parameters, obtained in the physical evaluations, were used to simulate the alkaline transesterification kinetics of soybean oil (methanol, ethanol, NaOH). Thus, a heterogeneous model was formulated in terms of the mass balance equation as follows:

$$\frac{dC_{TG}}{dt} = K_{TG}(C_{TG0} - C_{TG}) - r_B \tag{4}$$

$$\frac{dC_G}{dt} = -K_G(C_{G0} - C_G) + r_B \tag{5}$$

where the biodiesel production rate (r_B) was introduced according the formulation by Silva et al. [5]:

$$r_B = \frac{dC_B}{dt} = k[(C_{TG0} + C_{A0}) - (C_G + C_B)] \tag{6}$$

As initial condition, at the start of the reaction operation, $t = 0$, $C_{TG} = C_{TG0}$, $C_A = C_{A0}$, $C_{B0} = C_{G0} = 0$. Using the values of the reaction rate constants estimated from methanolysis and ethanolysis operations (**Table 6**), conducted under kinetic-chemical regime [5], simulations of kinetic behaviors were performed at temperatures of 25°C, 40°C and 60°C.

Figure 5 shows the evolution of the concentrations of soybean alkyl esters, constituting the production of methyl and ethyl biodiesels. Their behaviors, already reported in different evaluations [14], show increases from the beginning of each operation to the levels reached in about 35 to 40 minutes of operation.

Temperature (°C)	Methanolise $k_{MeOH} \times 10^3$ ($m^3 mol^{-1} min^{-1}$)	Ethanolise $k_{MeOH} \times 10^3$ ($m^3 mol^{-1} min^{-1}$)
25	2.08	2.31
40	2.28	3.79
60	3.33	4.74

Table 6.
Reaction rate for alkaline transesterification of soybean (k). Conditions: A:OL/6:1, $C_{NaOH} = 0.50\%$ wt., 600 rpm [5].

Figure 5.
Evolution of concentrations of biodiesel (alkyl esters) derived from soybean oil. Temperature effect. Conditions: A:OL/6:1, $C_{NaOH} = 0.50\%$ wt., 600 rpm. (a) Biodiesel (methyl esters) (b) biodiesel (ethyl esters).

5. Conclusions

An approach focused on the triglyceride mass transfer coefficients, based on their concentration in alcohol during the oil-alcohol mixing process, led to quantitative assessments, which are associated with those obtained for the glycerol mass transfer in biodiesel separation constituted the phenomenological base used in the predictions of behavior of the reactive processes of transesterification of vegetable oil.

A heterogeneous model was validated for the alkaline transesterification of soybean oil (methanol, ethanol, NaOH), including values of the physical parameters (distribution and mass transfer coefficients) determined experimentally, varying in the intervals $[1.01\text{--}1.62]$ and $[2.05\text{--}4.78] \times 10^{-2}$, respectively, while the mass transfer coefficients were in the order of magnitude in the range 10^{-2} to 10^{-4} s^{-1} for triglycerides and $[1.20\text{--}7.42] \times 10^{-3} \text{ s}^{-1}$ for glycerol. The kinetic behavior of biodiesel production was simulated using the specific reaction rates for each biodiesel produced by methanolysis and ethanolysis in the range of 25° C to 60° C .

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