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Simulation of an Industrial-Scale Reactive Liquid-Liquid Extraction Tower using Polar PC-SAFT for Improving the Hydrolysis of Triglycerides

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Abstract

A comprehensive model for simulation and optimization of industrial-scale splitting towers, able to predict yield for the hydrolysis of bio-based triglyceride feedstocks, is presented in this work. This model includes a variable glycerol equilibrium ratio in function of composition and temperature, calculated by the polar version of PC-SAFT, the autocatalytic effect of fatty acids in hydrolysis, and isomerization of poly-unsaturated fatty acids. Model validation is performed using process data from three real-life splitting towers covering four feedstock types, i.e., tallow, rapeseed oil, palm oil and palm fatty acid distillate. Due to composition gradients of the organic phase throughout the tower, it is crucial to properly account for changes in the glycerol equilibrium ratio. The importance of feedstock flow rate, water/oil ratio and temperature profile throughout the tower is analyzed and confirmed by sensitivity analysis. Our results show that modifying the

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temperature profile may shift the reaction equilibrium towards the fatty acid product. This knowledge is crucial for improving the energy and resource efficiency of fatty acid production, thereby improving its economic and environmental sustainability.

Keywords

Hydrolysis, Process Simulation, Phase-behavior, Lipids, Fatty Acids, Sensitivity Analysis, Biorefinery

Introduction

Changes in the world of oleochemicals are putting a strain on European oleochemical companies.[1] To begin, palm oil became the main source of fatty acids globally, due to a rapid development of the oleochemical industry in Southeast-Asia.[2] Secondly, animal fats are increasingly used for biofuels, causing a lower supply of this feedstock for oleochemistry. This competition urges oleochemical companies to diversify their feedstocks, ranging from low-quality animal fat to high-quality rapeseed oil. Fatty acid composition and quality vary greatly among these feedstocks. Operating a continuous installation with a variable feed composition poses significant challenges for process control to ensure high yields and excellent product quality.[3] The 12th goal of the United Nations Sustainable Development Goals aims to achieve an efficient use of natural resources by using renewable feedstocks for the production of chemicals.[4] From both an economic and environmental sustainability perspective, it is more interesting to use lower quality feedstocks for the production of fatty acids. Triglyceride hydrolysis is the first step in fatty acids production. In the past, related process optimization was typically performed via ad-hoc experiments, neglecting possible adjustments for other feedstocks.[5] This lack of accounting for feedstock variability highly limits an oleochemical plant's flexibility to switch between feedstocks. In other fields, process modelling has been used for optimization of processes with a variable feedstock, for example, in the biodiesel industry.[6] However, modelling research on fatty acid production is scarce.[7] This motivates developing a process model of triglyceride hydrolysis to investigate optimal processing parameters for different renewable feedstock types. A process model of triglyceride hydrolysis could be used to investigate if high quality fatty acids can be produced from lower quality feedstocks, and determine the optimal process parameters to do so.[8]

In hydrolysis, triglycerides (TG) in the oil react with water to form fatty acids (FA) and glycerol (Gly). Batch experiments have shown TG conversion into FA is initially slow at a high temperature (225-260 °C) and pressure (max 50 bar) range. After the induction period the conversion increases rapidly until it flattens and reaches a maximum.[9] Several kinetic models have been proposed for TG hydrolysis.[9-12] Sturzenegger and Sturm (1951) reported a kinetic approximation assuming a first order, irreversible, single step reaction[10]:

$$TG + 3W \xrightarrow{k_{irr}} 3FA + Gly \quad (1)$$

Patil et al. (1988) proposed a 3-step reversible reaction based on the results of Mills and McClain (1949), who reported that the oil phase contained mono- (MG), di- (DG) and triglycerides.[9, 13] Recent studies have pointed out the importance of the autocatalytic effect of FA in TG hydrolysis.[11, 12] FAs dissociate, eliminating a proton, causing protonation of a TG and allowing an easier nucleophilic attack by water. The same effect enhances DG and MG hydrolysis.[9, 11]

On an industrial scale, fat/oil hydrolysis is performed in splitting towers, in which counter-current reactive liquid-liquid extraction occurs.[14] The oil feed is introduced at the bottom of the tower and forms the continuous organic phase, while water is introduced at the top and forms the disperse aqueous phase. The formed glycerol is extracted via the aqueous phase. After hydrolysis, the glycerol is purified and can be used as a platform chemical for the production of commodity chemicals such as propylene glycol.[15] Different models have been presented for simulating splitting towers. Jeffreys et al. (1961) developed an analytical model, assuming a first order and irreversible hydrolysis reaction.[16] El-Rifai et al. (1977) extended this model by including a varying water solubility for changing composition over column height, and assuming a reversible second-order reaction.[17] More recently, Jones et al. (2020) developed a finite volume model and assessed the sensitivity of the glycerol content in the aqueous product for liquid density of the organic phase, overall mass-transfer coefficient for glycerol, reaction rate coefficient and glycerol equilibrium ratio.[7] Jones et al. (2020) used a single-step simplified hydrolysis reaction and assumed a constant glycerol equilibrium ratio, irrespective of varying composition of the organic phase over tower height.[7] However, taking into account a variable glycerol equilibrium ratio is deemed to be important for properly predicting the conversion, as Jones et al. (2020) showed

glycerol distribution ratio has the highest effect on the glycerol fraction in the aqueous product.[7] The presented models also do not take into account the autocatalytic effect of FA. Another key consideration for industrial oil hydrolysis is limiting thermal degradation.[9] At the conditions used for oil hydrolysis, isomerization of poly-unsaturated FA occurs.[18] However, in previous modelling studies of splitting towers, thermal isomerization has not been included.[7, 19]

In recent studies, Perturbed Chain Statistical Association Fluid Theory Equation of State (PC-SAFT) has been used to model phase behavior of biodiesel related systems.[20] Silva et al. (2016) found PC-SAFT gave the best agreement with liquid–liquid phase equilibria (LLE) data for a simplified biodiesel system compared to property methods SAFT-γ-Mie and RK-ASPEN.[21] Rodriguez and Beckman (2019) proposed using the polar version of PC-SAFT (PPC-SAFT), developed by Nguyen-Huynh et al.(2008), which includes a segment localized polar contribution.[22, 23] To extend the methodology to systems for which data is scarce, Rodriguez and Beckman (2020) used a group-contribution method (GC-PPC-SAFT) to model phase equilibria amongst mixtures containing MG, DG and TG.[20] However, to the authors' best knowledge, PC-SAFT has not been used to model LLE during oil hydrolysis or in modelling a splitting tower.

In this work, a model is developed capable of simulating the processing of different industrially relevant triglyceride feedstocks in industrial splitting towers. This model extends the state of the art by including a variable glycerol equilibrium ratio, calculated by GC-PPC-SAFT; the autocatalytic effect of FA and the thermal isomerization of poly-unsaturated FA. The model is validated using data from three industrial splitting towers and for four feedstock types. Suggestions for optimization are given taking into account a high splitting degree, a high glycerol fraction in the aqueous phase and minimal isomerization.[9]

Materials and Methods

Modelling Approach

A general approach for modelling a counter-current reactive liquid-liquid extraction is by representing the 'splitting tower' as a series of continuous stirred reactors (CSTR) and liquid-liquid separators, see Figure 1.[24] In every reactor, reaction rates are determined by the applied reaction mechanism, temperature and density of the mixture. In every separator, temperature, composition and thermodynamic component properties determine the LLE. This compartmental modelling

Slettet: Figure 1

approach results in a variable equilibrium ratio for varying composition of the organic phase over tower height. Through backmixing and holdup, column hydrodynamics influence axial dispersion in the tower, and thereby primarily determine the number of stages needed to represent the total tower.[25] Assuming a series of reactors and separators allows modelling the system in commercial process simulators such as Aspen Plus® or ProSim®.[24]

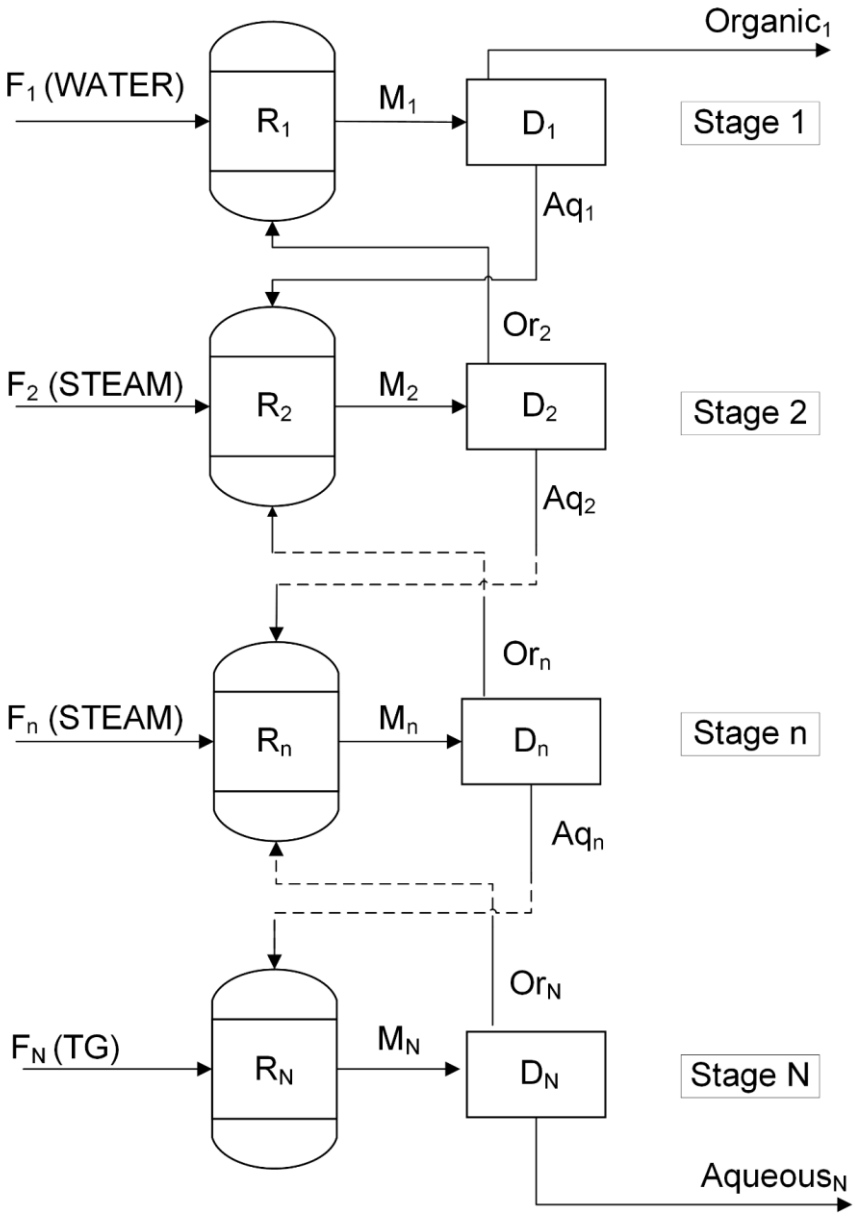

Figure 1. Schematic representation of a model for counter-current reactive liquid-liquid extraction by a series of continuous stirred reactors (R) and liquid-liquid separators (D). The

organic (Or) stream flows upwards while the aqueous (Aq) stream flows downwards inside the tower. Possible feeds (F) to the reactors are triglycerides (TG) at the bottom stage, water at the top stage and steam may be applied to the middle stages at several locations in the tower.

Reaction Kinetics: Hydrolysis

The reaction mechanism as suggested by Milliren et al. (2013) is used to simulate hydrolysis.[11] Because of the acid character of selected components in the organic phase, TG, DG and MG will get protonated, which allows an easier nucleophilic attack by water.[9, 11] Three reversible reactions with autocatalytic effect (5-7) are included to account for the acidity of fatty acids. In addition, three reversible reactions without autocatalytic effect (2-4) are included to account for the potential acidity of all other components:

$$TG + H_2O \underset{k_{-rev}}{\overset{k_{rev}}{\rightleftarrows}} DG + FA \tag{2}$$

$$DG + H_2O \underset{k_{-rev}}{\overset{k_{rev}}{\rightleftarrows}} MG + FA \tag{3}$$

$$MG + H_2O \underset{k_{-rev}}{\overset{k_{rev}}{\rightleftarrows}} Gly + FA \tag{4}$$

$$TG + H_2O + FA \underset{k_{-ac}}{\overset{k_{ac}}{\rightleftarrows}} DG + 2FA \tag{5}$$

$$DG + H_2O + FA \underset{k_{-ac}}{\overset{k_{ac}}{\rightleftarrows}} MG + 2FA \tag{6}$$

$$MG + H_2O + FA \underset{k_{-ac}}{\overset{k_{ac}}{\rightleftarrows}} Gly + 2FA \tag{7}$$

Milliren et al. (2013) assume the kinetic coefficients are the same for TG, DG and MG and are independent of carbon chain length or degree of unsaturation of fatty acid groups.[11] The reaction rate (k_i) follows an Arrhenius dependency upon temperature, with pre-exponential factor (10^{a_i}) and reaction energy (E_i):

$$k_i = 10^{a_i} \exp\left(\frac{-E_i}{RT}\right) \tag{8}$$

A scaling factor amounting to 1.60 was applied to the pre-exponential factors reported by Milliren et al. (2013) to account for different modelling assumptions, e.g., in calculation of liquid density.[11]

Reaction Kinetics: Thermal Breakdown

Apart from the main hydrolysis reactions, also side reactions can occur. Both geometrical isomerization and oxidative degradation reactions of poly-unsaturated FA are possible.[18] However, as only traces of oxygen are present in the splitting tower, only the former reaction is considered. In the investigated feedstocks, poly-unsaturated FA are represented by C18:2 and C18:3. The observed geometrical isomerization of cis,cis-C18:2 during industrial hydrolysis is limited to 1-3 wt%, while for cis,cis,cis-C18:3 up to 60 wt% isomerization to trans-C18:3, in which at least one of the unsaturated bounds has a trans configuration, is observed. Therefore, only isomerization of C18:3 is included. Geometrical isomerization of C18:3 acid follows a first-order reaction with $E_{a,C18:3}$ = 77.9 kJ/mol.[18] A scaling factor of 3.80 was applied to the pre-exponential factor, to match observed isomerization in the industrial data, amounting to $k_{C18:3} = 2.23 * 10^7$ h^{-1}.[18]

Partition Coefficient by polar PC-SAFT

A version of PC-SAFT accounting for polarity (PPC-SAFT) is used to model phase equilibria amongst mixtures containing water, glycerol, FA, MG, DG and TG.[23] The equations-of-state are used to calculate fugacity coefficients (ϕ). We refer to Gross and Sadowski (2001) for a summary of equations for calculating ϕ using the PC-SAFT model.[26] The LLE estimated by PPC-SAFT is compared to more traditional property methods: UNIFAC_DMD, UNIQUAC and SRK, which are frequently used for such systems in literature.[27-29] Furthermore, the estimated glycerol distribution coefficient and wt% water in the organic phase are compared to values fitted by Patil *et al (1988)* for their splitting tower model.[9]

For PC-SAFT, pure component properties such as segment number m_i (-),segment diameter σ_i (-), and molecule dispersive potential ε_i (K), had to be determined. Preferably, vapor pressure and liquid density data are used to regress pure component parameters. For water and glycerol, the properties determined by regression by Silva et al. (2016) are used.[21] Dipole or quadrupole moment μ (-) and fraction of the molecule considered polar/quadrupolar X_p (-) are taken from

Rodriguez and Beckman (2019) for glycerol and from Nguyen-Huynh et al. (2011) for water.[22, 30] The parameters of water and glycerol are listed in Table S1 of the supporting information. For the lipid components under study, insufficient experimental data could be found in literature or from commercial databases (such as the NIST database) to perform parameter regression. Especially for MG, DG and TG, vapor pressure and liquid density data are rarely reported. In order to be consistent, the group-contribution method for PPC-SAFT (GC-PPC-SAFT) is used for all FA, MG, DG and TG.[20] The calculated parameters are given in Table 1. Polar PC-SAFT takes into account the dipole–dipole interactions in polar systems by a contribution Z^{dipol} for the compressibility factor Z. Therefore, polar PC-SAFT does not need binary interaction parameters like non-polar PC-SAFT. However, binary interaction parameters may still be determined by regression to further improve the LLE predictions. Currently, insufficient LLE data is available in literature or commercial databases to allow regressing binary interaction parameters between all lipid components, glycerol and water. Previous studies have shown that when insufficient LLE data is available, proper predictions may already be acquired without such interaction parameters.[32] For future research, the LLE predictions may be further improved by collecting LLE data and regressing binary interaction parameters."

Slettet: Table 1

Table 1. Pure-component parameters used in the Perturbed-Chain SAFT equation of state for triglycerides, diglycerides, monoglycerides and fatty acids, calculated using the group-contribution method GC-PPC-SAFT.[23]

Parameter	Units	TG C16:0	DG C16:0	MG C16:0	FA C16:0	TG C18:0	DG C18:0	MG C18:0	FA C18:0	TG C18:1	DG C18:1
m_i	-	21.55	15.52	8.25	6.95	23.84	17.05	9.78	7.71	22.72	16.30
ε_i	K	263.48	265.60	271.88	259.21	263.22	265.15	269.97	259.42	265.90	267.71
σ_i	-	3.89	3.87	3.81	3.88	3.89	3.88	3.83	3.89	3.89	3.87
Parameter	**Units**	**MG C18:1**	**FA C18:1**	**TG C18:2**	**DG C18:2**	**MG C18:2**	**FA C18:2**	**TG C18:3**	**DG C18:3**	**MG C18:3**	**FA C18:3**
m_i	-	9.41	7.34	21.60	15.56	9.03	6.97	20.48	14.81	8.66	6.59
ε_i	K	272.24	262.20	268.60	270.29	274.52	265.01	271.33	272.90	276.82	267.85
σ_i	-	3.83	3.88	3.88	3.86	3.82	3.87	3.87	3.86	3.81	3.87

Absolute (Sa) and relative (Sr) sensitivity measures are calculated by model simulations with a small perturbation, Δx, of model inputs around their nominal values, x^0, to investigate sensitivity of model output, y, to a change in these parameters using a forward perturbation:

$$Sa = \frac{\partial y}{\partial x} = \frac{f(x^\circ + \Delta x) - f(x^\circ)}{\Delta x} \quad (9)$$

$$Sr = \frac{\partial y}{\partial x}\frac{x^\circ}{y^\circ} = Sa\frac{x^\circ}{f(x^\circ)} \quad (10)$$

$$\Delta x = \varepsilon * x \quad (11)$$

A perturbation factor ε = 0.01 is used.[33]

Liquid Density by Modified Rackett Equation

Most methodologies for estimating density of lipids are based on the Rackett equation. Spencer and Danner (1972) broadened its applicability by considering compressibility factor as an empirical parameter, Z_{RA}, whose value can be optimized for each compound.[34] This modified Rackett equation gives the best predictions of liquid density of lipids over a range of temperatures and was therefore used.[35] Not all critical properties and Z_{RA} of all components could be found in databases, such as NIST, or literature. Therefore, missing properties were estimated by interpolation. The estimated critical properties and Z_{RA} are given in Table S2-S4 of the supporting information.

Column Hydrodynamics

The effect of axial dispersion can be quantified by the number of CSTR's representing the splitting tower.[25] Van Egmond and Goossens (1982) quantify that an empty splitting tower is equivalent to 7 CSTR's and a splitting tower with Sulzer packing to 63 CSTR's. Perfect plug flow can be assumed above 50 CSTR's.[25] In the splitting towers considered in this study, bubble-cap trays and other internals such as sieve trays are used to increase exchange between the continuous and disperse phase. The effect of increasing the number of CSTR's on the splitting degree is shown in Figure S1 of the supporting information. When using only 5 base units (N =5), the model underestimates conversion by over 5%. At N = 25, the model underestimates conversion by only 1% and at N = 50, the estimated splitting degree nearly equals the measured conversion. This justifies using 50 base units to simulate the splitting towers.[25]

Industrial Oil Hydrolysis: Process Flowsheet

A simplified flowsheet of the industrial process is given in Figure 2. In this work, three splitting towers of the company Oleon NV, located in Belgium, are addressed. Two of these towers (T1, T2) have a height H_C of 30m, while T3 has a height of 50m. The oil feed inlet H_F is close to the bottom and the water inlet H_W is close to the top. The fatty acid H_{FA} and glycerol H_{GLY} outlets are respectively at the top and bottom of the tower. High-pressure steam (P_S = 60-64 bar) is injected on three different locations (H_{S1}, H_{S2}, H_{S3}). Above the aqueous/organic interface, fat/oil is the continuous phase and water is the disperse phase, while below the interface this is reversed. In the upper section, above the highest steam inlet, bubble-cap trays are used. In the other sections, sieve trays are used. Temperatures of outlet streams (T_{GLY}, T_{FA}) and on several locations in the column (T_{C1}, T_{C2}, T_{C3}) give a temperature profile, with an average around 260-270°C for T1 and T2 and 250-260°C for T3, to prevent the formation of VLE and VLLE inside the tower. Finally, the column pressure P_C is kept constant over the whole column at 60-62 bar for T1 and T2 and 50-52 bar for T3. Both the organic and aqueous product are flashed to almost atmospheric pressure.

Slettet: Figure 2

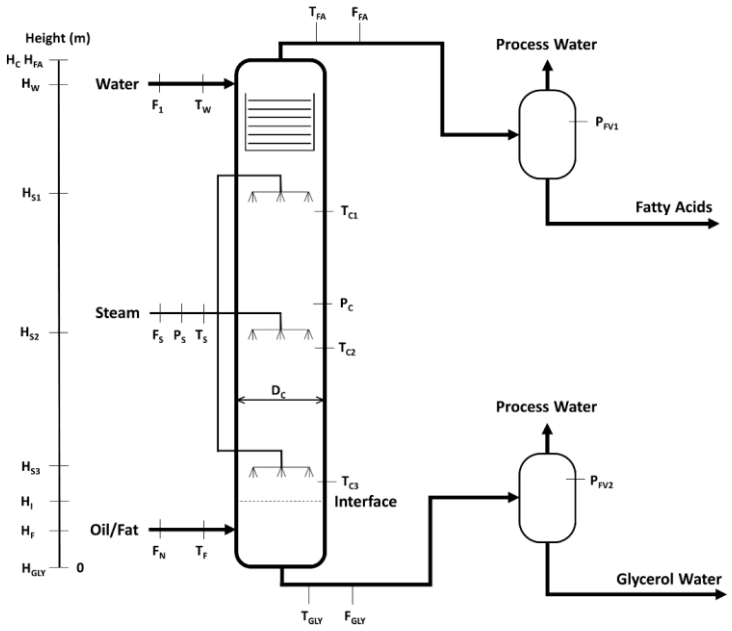

Figure 2: Simplified flowsheet of an industrial splitting tower with the location of important height (H), diameter (D), flow (F), temperature (T) and pressure (P) measurements.

Data Collection

In total, samples from 105 campaigns of oil hydrolysis were acquired and analyzed. 20 for rapeseed oil on T1, 13 for palm oil on T3, 9 for PFAD on T2, 20 for tallow on T2 and 21 for tallow on T3. Average compositions and process parameters were used for construction and validation of the splitting tower models. Samples were taken after 8h, when the process reached steady state. A detailed fatty acid composition of the feedstock and organic product was determined by GC-FID analysis on an AGILENT G3-00 chromatograph with CP-Sil 88 stationary phase. Hydrogen was used as carrier gas with split injection. MG, DG and TG in the organic product were determined by an in-house chromatographic method. %Glycerol is measured via a refractometer. Splitting degree is the ratio of the acid value on the saponification value of the crude fatty acids, multiplied by 100 (ISO 660 and ISO 3657).

Feedstock Composition

The feedstocks used in hydrolysis are complex mixtures of glycerides, free fatty acids (FFA) and minor components. A simplified composition is used in which components are lumped and represented by a set of key components.[8] A detailed composition of the feedstocks is given in Table S5 of the supporting information. Table 2 lists the simplified composition used in the model. C16:0 stands for a fatty acid chain with 16 carbon atoms and 0 unsaturated bonds. For simplicity, only DG and TG having the same fatty acid chain groups are assumed. Therefore, TG_C16:0 stands for a triglyceride containing three C16:0 fatty acid chain groups. Only triglycerides with weight percentages (wt%) above 2% for one of the feedstocks are considered. Triglycerides below 2% were lumped with the triglyceride having the most representative physical properties, e.g., density. The weight percentage of DG and MG in the feedstock is calculated based on %FFA.[36]

Slettet: Table 2

Table 2. Average simplified composition of the feedstocks used (wt%).

	TG C16:0	**TG C18:0**	**TG C18:1**	**TG C18:2**	**TG C18:3**	**DG C16:0**	**DG C18:0**	**DG C18:1**	**DG C18:2**	**DG C18:3**
Rapeseed	5.5	2.8	62.5	19.1	8.2	0.0	0.0	0.5	0.2	0.1
Palm	42.2	5.3	38.0	9.0	0.3	1.0	0.1	0.9	0.2	0.0
PFAD	16.3	1.8	12.8	3.0	0.1	1.4	0.2	1.1	0.3	0.0
Tallow	32.5	17.6	37.6	4.7	0.6	1.0	0.6	1.2	0.2	0.0
	MG C16:0	**MG C18:0**	**MG C18:1**	**MG C18:2**	**MG C18:3**	**FFA C16:0**	**FFA C18:0**	**FFA C18:1**	**FFA C18:2**	**FFA C18:3**
Rapeseed	0.0	0.0	0.2	0.1	0.0	0.0	0.0	0.5	0.2	0.1
Palm	0.3	0.0	0.3	0.1	0.0	1.0	0.1	0.9	0.2	0.0
PFAD	0.5	0.1	0.4	0.1	0.0	29.8	3.2	23.3	5.5	0.2
Tallow	0.3	0.2	0.4	0.1	0.0	1.0	0.6	1.2	0.1	0.0

Optimization of Key Process Parameters

For oil hydrolysis, important considerations are achieving a high splitting degree, a high glycerol fraction in the aqueous product (%glycerol) and minimal isomerization (%trans-C18:3). For every

feedstock, sensitivity of splitting degree, %glycerol and %trans-C18:3, for changes in key process parameters is investigated using a central difference method[33]:

$$Sa = \frac{f(x^{\circ} + \Delta x) - f(x^{\circ} - \Delta x)}{2 * \Delta x} \quad (12)$$

With a perturbation factor ε = 0.025. The process parameters included in this investigation, feed flow, water flow and the column temperatures at the top, middle and bottom of the tower, are selected based on our previous work, in which multivariate data analysis was used to find the key process parameters affecting product properties.[5]

Results and Discussion

Liquid-Liquid Equilibrium

For water, Patil et al. (1988) found a mass fraction of water in the fat phase (tallow) at 240°C between 0.01 and 0.05 depending on %FA.[9] The estimated mass fraction of water in the organic phase (x_w) by different property methods is given in Table 3. SRK, UNIFAC_DMD, UNIQUAC and PC-SAFT all correctly estimate a higher x_w when %FA increases in the organic phase. However, SRK and UNIFAC_DMD estimate a too high x_w, while UNIQUAC and PC-SAFT properly estimate x_w. SRK and UNIQUAC likely overestimate the mass-based glycerol distribution coefficient m ($=y_{GLY}/x_{GLY}$), while UNIFAC_DMD results in an underestimation. Based on these results, PC-SAFT most properly predicts both x_w and m, and is therefore further employed within the splitting tower model. The large difference for m between pure oil (m = 9.2) and pure FA (m = 6.5) show the importance of taking into account a variable glycerol equilibrium ratio throughout the tower.

Slettet: Table 3

Table 3. Mass fraction of water in the organic phase at 240°C and mass-based distribution coefficient of glycerol between the aqueous and organic phase at 250°C determined by different property methods for tallow.

	WATER **Mass fraction (x_w)**		**GLYCEROL** **Distribution Coefficient** **($m = y_{GLY}/x_{GLY}$)**	
	100% TG	100% FA	100% TG	100% FA
SRK	0.03	0.08	208.1	16.3
UNIFAC_DMD	0.03	0.11	2.1	0.1
UNIQUAC	0.01	0.04	262.7	23.0
PC-SAFT	0.01	0.03	9.4	6.5
Patil et al.[9]	0.02	0.04	12	n.d.

n.d. = not determined

x_w and m were also calculated for different feedstocks. The results show similar x_w and m values for tallow (x_w = 0.013; m = 9.20) and palm (x_w = 0.013; m = 9.31), as both feedstocks have high TG_C16:0 and TG_C18:1 fractions. For rapeseed, x_w is slightly lower (x_w = 0.012) while m is slightly higher (m = 9.58), likely due to a lower amount of shorter-chain TG_C16:0 and a higher amount of TG_C18:2 and TG_C18:3 present in rapeseed oil. The difference is most pronounced for PFAD, with a much higher x_w (x_w = 0.022) and lower m (m = 7.36), explained by the large amount of FFA. As Jones et al. (2020) showed that small differences in these parameters may have a big effect on the process outcome, these results indicate the importance of investigating adjustments in process parameters for different feedstocks.[7]

Table 4 lists the sensitivity measures Sa and Sr, which indicate the sensitivity of m to a change in the PC-SAFT parameters. The relative sensitivity measure, Sr, is used to evaluate and compare importance of parameters relative to each other. Accordingly, m is most sensitive for changes in segment diameter (σ_i) of water and glycerol, energy potential for bonding sites (ε_{ABi}) of glycerol and molecule dispersive potential ε_i of water and glycerol. In PC-SAFT, σ_i and ε_i are used to calculate the effective collision diameter of chain segments and in determining interaction

between chains.[26] m is less sensitive for changes in parameters for triglycerides, volumetric overlap of association sites (κ_{ABi}), fraction of the molecule considered polar/quadrupolar (χ_{pi}) and dipole or quadrupole moment (μ_i) of glycerol and water. The lower sensitivity for TG parameters is advantageous, as the parameter uncertainty for those parameters can be considered higher as they were determined by GC-PPC-SAFT instead of by regression.

Table 4. Absolute (Sa) and Relative (Sr) sensitivity measures, indicating the sensitivity of the glycerol distribution coefficient (m) to a change in the PC-SAFT parameters, sorted in declining order for Sr.

	Sa	**Sr**
σ_Glyc	15.45	0.07
εAB_Glyc	0.01	0.04
ε_Glyc	0.06	0.03
μ_Glyc	2.66	0.01
εAB _water	0.00	0.01
κAB Glyc	2122.28	0.01
Xp_Glyc	10.07	0.00
μ_water	1.69	0.00
σ_TG	0.73	0.00
Xp_water	5.26	0.00
κAB_water	93.60	0.00
m_water	-4.93	0.00
m_TG	-0.10	0.00
ε_TG	-0.02	-0.01
m_Glyc	-5.19	-0.01
ε_water	-0.12	-0.02

σ_water	-15.79	-0.09

Model Evaluation

Predicted and measured values for splitting degree, %glycerol and wt% trans-C18:3 for different feedstocks are given in Table 5. The model properly simulates a lower conversion (<97.7%) for rapeseed on T1 and tallow on T2, a high conversion (>99.5) for tallow and palm on T3 and an intermediate conversion (±99%) for PFAD on T2. This motivates an investigation on how higher conversions can be achieved in T1 and T2. For %glycerol, both predicted and measured values are low (<5 wt%) for PFAD on T2 due to the large amount of FFA in the feedstock. The model properly predicts a higher %glycerol for Tallow on T3 and Palm on T2 and a lower %glycerol for Rapeseed on T1 and Tallow on T2. However, the model underestimates %glycerol for those feedstocks by ±2 wt%. For PFAD, the model overestimates %glycerol, which is correctly estimated to be lower compared to other feedstocks. The larger %error for %glycerol is likely due to an inadequate prediction of the vapour-liquid equilibrium in the flash vessels. This could not be validated directly, as there is no flow measurement of the flashed process water, which will be considered for future measurement campaigns.

Slettet: Table 5

The model properly estimates isomerization of cis,cis,cis-C18:3 inside the splitting towers for rapeseed oil on T1 and Tallow on T2, with a %error equal to or lower than 1%. This parameter is most important for rapeseed oil hydrolysis, as it has the highest initial wt% cis,cis,cis-C18:3 in the feedstock (±8.3 wt%). For palm and PFAD, the initial wt% cis,cis,cis-C18:3 in the feed is low (±0.3 wt%), resulting in a wt% trans-C18:3 in the FA product below 0.2%. Therefore, the isomerization of C18:3 can be considered less important for those feedstocks.

Table 5. Predicted and measured values for splitting degree and %glycerol for oil hydrolysis in three industrial splitting towers (T1, T2, T3) for different feedstocks.

	Predicted Splitting Degree (%)	Measured Splitting Degree (%)	Percentage error (%)	Predicted %Glycerol (wt%)	Measured %Glycerol (wt%)	Percentage error (%)	Predicted wt% trans-C18:3 in product	Measured wt% trans-C18:3 in product	Percentage error
Rapeseed on T1	96.9	97.6 ± 0.9	-0.7	10.4	12.1 ± 0.7	-14.1	4.1	4.1 ± 1.1	-0.8

Tallow on T2	97.6	97.7 ± 1.1	-0.1	10.3	12.8 ± 1.1	-19.5	0.5	0.5 ± 0.1	+1.0
Tallow on T3	99.7	99.6 ± 0.9	+0.1	14.1	16.4 ± 0.9	-14.0	0.4	0.4 ± 0.0	-13.9%
Palm on T3	99.6	99.5 ± 1.4	+0.1	14.0	16.1 ± 1.9	-13.0	0.2	0.2 ± 0.1	-10.3%
PFAD on T2	99.2	98.9 ± 0.7	+0.3	5.3	4.5 ± 1.4	+17.8	0.2	0.1 ± 0.1	-59.6%

Concentration Profile

The combination of extraction and reaction results in distinct concentration profiles over the continuous and disperse phase throughout the tower. The modelled concentration profile (wt%) for tallow hydrolysis on T2 is shown in Figure 3. The profile shows that the formation of FA at the bottom of the tower is slow. At the bottom, as fresh oil is introduced, the concentration of water in the organic phase is low due to a low temperature and a limited amount of FA. Higher in the tower, the solubility of water in the oil phase will have increased sufficiently. The reaction rate also further increases due to the autocatalytic effect. The rate at which FA are formed reaches a maximum in the middle of the tower, between 10-20m, after which the conversion rate slows down. Above 20m the concentration of FFA is high, and the reaction slows down because of the approach to equilibrium. At 25m, a more rapid increase of wt% FA is observed. Above 25m the temperature drops, shifting the reaction equilibrium towards the FA product. The wt% of glycerol in the aqueous phase is highest around 5m, just above the lowest steam inlet.

Slettet: Figure 3

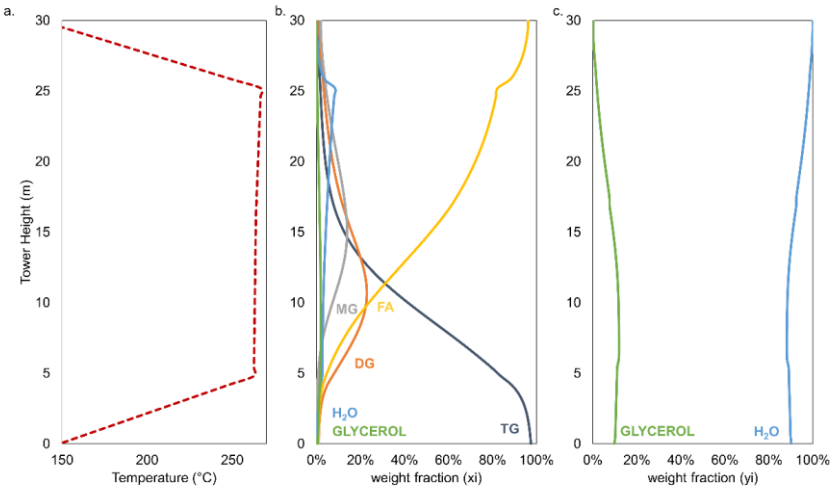

Figure 3. Temperature (a) and concentration profile over the organic phase (b) and aqueous phase (c) throughout the tower for the hydrolysis of tallow on T2

Sensitivity analysis

Relative (Sr) sensitivity measures, indicating sensitivity of splitting degree, %glycerol and %trans-C18:3 to a change in process parameters for rapeseed oil hydrolysed on T1, are given in Table 6. A decrease of feed flow, top and middle temperature results in an increase of the splitting degree. This was expected for feed flow, as a decrease in flow results in a higher water/oil ratio and a longer residence time. However, the effect of top and middle temperature was not expected, as higher temperatures are needed to achieve a high reaction rate. Reducing the temperature at the bottom indeed reduces the splitting degree, explained by a kinetics-controlled reaction between the bottom and the middle of the tower. However, between the middle and the top, the reaction is controlled by reaching the reaction equilibrium, explaining the positive effect of a lower middle/top temperature by shifting the equilibrium for the reactions towards the FA product.

An increased feed flow or reduced water flow results in a higher %glycerol, as both result in a higher maximum %glycerol at full conversion. A reduction in tower temperatures results in the most prominent decrease of wt% trans-C18:3. An increase of feed or water flow results in a lower isomerization, as higher flows correspond to a lower residence time, thereby reducing the

exposure of the fatty acids to the high temperatures of the tower. In a previous multivariate analysis study, feed flow was also found to be a key source of variability with a clear negative contribution to the prediction of wt% trans-C18:3, while tower temperatures had a positive contribution.[5] The developed model thus properly captures the same trend observed in the data.

Table 6. Relative (Sr) sensitivity measures, indicating the sensitivity of the splitting degree, %glycerol and %trans-C18:3 to a change in the key process parameters for rapeseed oil hydrolysed on T1.

	Sr		
	Splitting Degree	**%Glycerol**	**Trans-C18:3**
Flow Feed	-0.20	0.46	-0.59
Flow Water	0.07	-0.70	-0.26
Temp Top	-0.12	-0.24	1.28
Temp Middle	-0.17	-0.37	2.22
Temp Bottom	0.15	0.88	1.45

Suggestions for optimization

A decrease of feed flow has a positive effect on splitting degree and %glycerol, but increases C18:3 isomerization and reduces tower capacity. Increasing the water to oil ratio might slightly increase the splitting degree but lowers the %glycerol. Most interesting would be to adjust the temperature profile. For all investigated feedstocks, the splitting degree might be improved by lowering the top temperature, resulting in a more efficient use of the renewable feedstocks for the production of fatty acids. For rapeseed on T1, a reduction of the top temperature by 25° to 240°C and middle temperature by 15° to 250°C is recommended to reach a splitting degree exceeding 98.5%. This change in temperatures also results in a reduction of the isomerization, from 4.1 to 2.9 wt% trans-C18:3, and a slight increase of the %glycerol (+0.1%). In addition, the lower temperature settings result in a reduced steam consumption (-8%), saving water and energy.

Conclusions and perspectives

The suggested compartmental model allows representing reactive liquid-liquid extraction towers for the hydrolysis of various triglyceride feedstocks. The model has a comprehensive

character, as it can be used for simulating different splitting towers and includes important side reactions. The property method polar PC-SAFT was used to predict LLE of water, glycerol, tri-, di- and monoglycerides, and fatty acids. Thermodynamic properties can be calculated by GC-PPC-SAFT. However, when experimental LLE data is available, estimations of parameters may be further improved by regression and by including interaction parameters.

The splitting tower model properly estimated splitting degree for tallow, palm, PFAD and rapeseed oil hydrolysis and the %trans-C18:3 for PFAD and tallow hydrolysis. Concentration profiles over the tower showed that the reaction is slow at the bottom of the tower due to a low amount of FA in the organic phase. The reaction rate increases towards the middle, due to a better solubility of water in the organic phase and the autocatalytic effect. At the top, the reaction approaches equilibrium and thus slows down. The process may be improved by lowering the top temperature, and thereby shifting the reaction equilibrium for the reactions towards the FA product.

Mechanistic modeling clearly results in a better understanding of the different phenomena affecting yield, and cost-efficiency, of splitting towers. This knowledge is crucial to increase an oleochemical plant's flexibility to switch to other and lower quality feedstocks and contribute to improving energy and resource efficiencythereby improving its economic and environmental sustainability.

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Supporting Information

A. PC-SAFT, pure component properties
B. Critical properties and Z_{RA}
C. Feedstock Composition
D. Effect of number of CSTR's
E. Sensitivity analysis
F. Kinetic Coefficients

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Synopsis

A comprehensive model is developed, simulating reactive liquid-liquid extraction towers, for improving the economic and environmental performance of triglyceride hydrolysis

Graphic for manuscript

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