

# Model-Based Simultaneous Solvent Screening and Column Design Based on a Holistic Consideration of Extraction and Solvent Recovery

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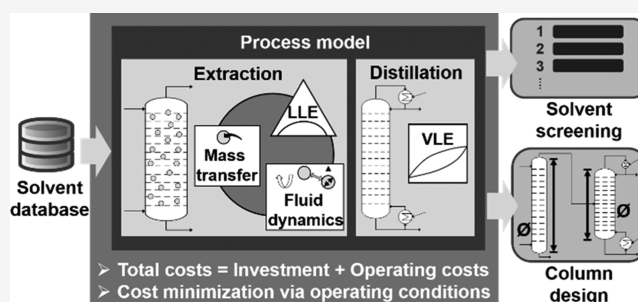


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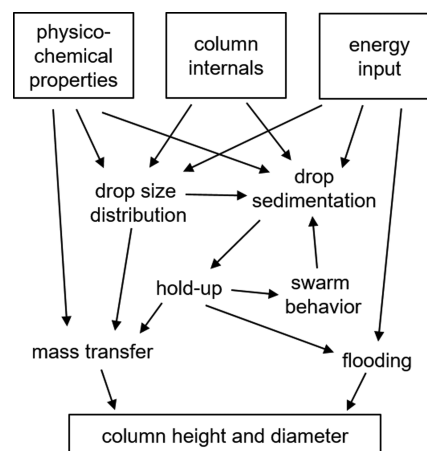
Supporting Information

**ABSTRACT:** A methodology for a model-based simultaneous solvent screening and dimensioning of extraction columns is presented. Therefore, a rate-based extraction model is combined with a distillation model for solvent recovery and product purification to consider the whole extraction process. The optimal operating point and the required column dimensions are determined for each solvent candidate specifically to minimize total costs, which are used as a basis for solvent ranking. The methodology is applied to the extraction of levulinic acid from an aqueous feed with a special focus on the influence of mutual solubility between the solvent candidates and water. It is shown that using mixture properties for both phases in accordance with the mutual solubility significantly impacts the calculation of fluid dynamics, mass transfer, and thereby on the required extraction column height. Furthermore, additional costs due to solvents solubilized in the aqueous raffinate strongly affect the economic evaluation of the solvents.



## 1. INTRODUCTION

Liquid–liquid extraction (LLE) is applied in chemical engineering, for example, to separate components with similar boiling points, azeotropic mixtures, or temperature-sensitive substances. The solvent selection as well as the determination of operating conditions and apparatus design are crucial to ensure optimal performance of the extraction process. Typically, simple performance indicators, such as the distribution coefficient, are used to choose a suitable solvent. Subsequently, the extraction column is designed based on pilot-plant experiments and relatively simple models, e.g., based on equilibrium stages.<sup>1</sup> However, this stepwise procedure does not necessarily result in the optimal combination of solvent and apparatus design. Recently, system engineering approaches have been developed to enable solvent selection based on the overall process performance. Therefore, process costs are determined using pinch-based or equilibrium stage models. These models take not only the extraction column but also solvent regeneration in a distillation column into account.<sup>2,3</sup> Pinch-based models are based on the idea of columns of infinite height. In contrast, equilibrium stage models like the HTU-NTU method<sup>4</sup> can be used to describe finite columns but with a fixed height equivalent of a theoretical equilibrium stage (HETS). However, neither of these model approaches are capable of depicting the complex interactions of fluid dynamics and mass transfer in an extraction column as shown in Figure 1. Depending on the operating point as well as on the physicochemical properties of



**Figure 1.** Interactions of main phenomena in an extraction column.

the selected solvent system, the HETS can vary by a factor of 6 in extraction columns.<sup>5</sup> On this account, fluid dynamics and

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mass transfer phenomena need to be taken into account for an accurate design estimate.

To determine the operation domain of an extraction column, e.g., in terms of flooding behavior and extraction efficiency, models based on population balance equations (PBEs) have been developed during the last few decades.<sup>6–8</sup> In PBE models, drop breakage and coalescence are explicitly calculated based on experimental parameters retrieved from laboratory experiments. Furthermore, the computational effort for this type of model is very high compared to equilibrium stage models. Thus, PBE models are not suitable for the screening of a large number of solvents.

To overcome this drawback, Kampwerth et al.<sup>9</sup> developed a novel design framework that considers the fluid dynamics in an extraction column solely based on substance property data to screen possible solvents for a given separation task. Simultaneously, the optimal operating point in terms of the solvent to feed volume flow ratio as well as the required column dimensions is determined for each solvent candidate individually. The resulting solvent evaluation is based on the minimum total costs consisting of operating and investment costs for the extraction column as well as a distillation column for solvent regeneration and product purification. It has been shown that fluid dynamics have a significant effect on the HETS and thereby on the required extraction column dimensions. Due to the consequential influence on the investment costs, a change in the solvent ranking was observed. Accordingly, accounting for physicochemical properties affecting the fluid dynamics in an extraction column is advisable for a coupled solvent screening and column design. However, Kampwerth et al.<sup>9</sup> performed their screening based on pure component parameters in their methodology. Mutual solubilities were neglected by assuming that the carrier component of the feed stream (e.g., water) was not soluble in the selected solvent and vice versa. Since mutual solubilities are depending on the solvent system, a considerable influence not only on the estimated operating point and column design but also on the solvent selection is to be expected. Consideration of mutual solubilities leads to different properties of both phases influencing the extraction performance. Furthermore, the calculated compositions of the extract and raffinate stream leaving the extraction column change. Thus, the distillation column for solvent recovery is affected and, most likely, solvent solubilized in the raffinate stream causes additional costs.

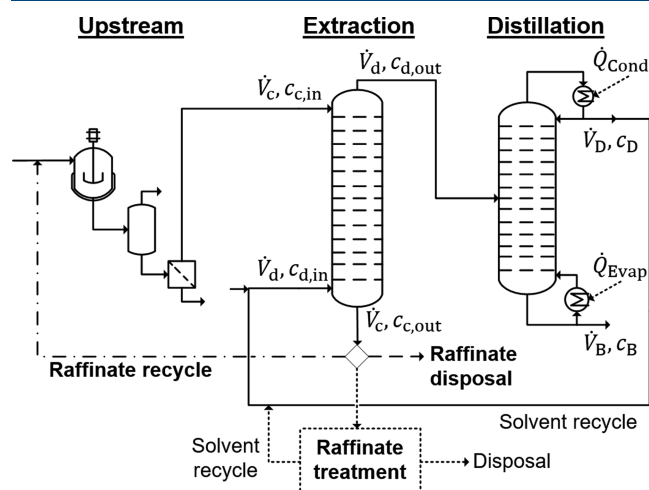
Assuming that the solvent in the raffinate is lost, Kruber et al.<sup>3</sup> proposed to calculate the costs for adding fresh solvent using a fixed price, e.g., of the benchmark solvent. However, this approach does not take into account that the price of different solvent candidates can vary tremendously. Furthermore, in general, it is not permissible to dispose the raffinate stream contaminated with a solvent. Therefore, most likely, a raffinate treatment is required for ecological reasons, which is not considered when applying this approach. Also, from an economic point of view, a raffinate treatment enabling solvent recovery may be favorable compared to adding fresh solvent.

In this manuscript, the framework described by Kampwerth et al.<sup>9</sup> is enhanced by the consideration of mutual solubilities. First, an overview of the current model is presented in Section 2. In Sections 2.1 and 2.2, the extensions made for this work are explained in detail. The special focus is on the development of a suitable approach to take costs due to solvents solubilized in the raffinate into account. A case study is described in

Section 2.3 to analyze the influence of mutual solubilities on the extraction column in particular (Section 3.1) as well as on the overall methodology (Section 3.2). Finally, a conclusion is given in Section 4.

## 2. METHODS

For the methodology described by Kampwerth et al.,<sup>9</sup> solely physicochemical and thermodynamic properties are required as input. The developed extraction process model consists of a pulsed sieve plate extraction column followed by a tray distillation column for solvent recovery as depicted in Figure 2.



**Figure 2.** Process flowsheet with an exemplary upstream followed by a combination of an extraction and a distillation column as considered in the developed model. Three alternatives to consider the raffinate stream are proposed: recycle (••), disposal (---), and treatment (•••).

The feed stream provided from the upstream enters the extraction column as a continuous phase with a fixed volume flow  $\dot{V}_c$  and concentration  $c_{c,in}$  of the product P. In most cases, this is an aqueous stream with water being the carrier component, which will be denoted by W in the following. The pure solvent S is dispersed at the bottom of the extraction column if the density of S is lower than the density of W. The drops rise counter current to the continuous phase while extracting the product. The enriched dispersed phase leaves the extraction column at the top as an extract stream and is fed to the distillation column for solvent recovery and product purification. The nearly product-free solvent stream can be recycled to the extraction column. Depending on the boiling temperatures of the solvent and product, this is either the distillate stream  $\dot{V}_D$  or the bottom stream  $\dot{V}_B$ . Since no mutual solubilities are considered in the current model, the continuous phase leaving the extraction column as a raffinate stream at the bottom consists mainly of W with small amounts of P depending on the desired extraction rate. The raffinate stream can be recycled to the upstream of the process. In exceptional cases, the raffinate stream might also be disposed.

For the extraction column model, suitable submodels describing the relevant fluid dynamics phenomena, such as flooding, drop size, rising velocity, and hold-up, are incorporated in a rate-based model to determine the separation performance. For modeling the distillation column, the shortcut method of Fenske,<sup>10</sup> Underwood,<sup>11</sup> and Gilliland<sup>12</sup> (FUG) as well as an energy balance is applied. For each solvent, the required energy demand and the dimensions of

both the extraction and distillation column are calculated in dependence on the dispersed phase flow rate  $\dot{V}_d$ . This flow rate can be expressed by the dimensionless solvent to feed volume flow ratio  $\dot{V}_d/\dot{V}_c$  (S/F ratio). The minimum S/F ratio is determined by the minimum solvent flow rate, which is necessary to reach the desired extraction rate and correlates with the distribution coefficient  $K = c_{d,P}/c_{c,P}$  of the applied solvent system. Theoretically, there is no upper limit for the S/F ratio, but, in reality, it is typically not higher than 10:1.<sup>4</sup> Kampwerth et al.<sup>9</sup> estimate the investment and operating costs for a wide range of S/F ratios for each solvent candidate individually. Thus, the total costs can be minimized by determining the optimal combination of solvents, operating conditions, and apparatus design.

For a more detailed description of the extraction and distillation model as well as the cost calculation, we refer to Kampwerth et al.<sup>9</sup> In the following sections, the enhancement of this model required for the consideration of mutual solubilities is described in detail.

**2.1. Calculation of Liquid–Liquid Equilibrium and Mixture Properties.** To take mutual solubilities into account, the liquid–liquid equilibrium (LLE) defined by

$$x_{d,j}\gamma_{d,j} = x_{c,j}\gamma_{c,j} \quad \text{with } j = P, W, S \quad (2.1)$$

needs to be calculated first.  $x_{d,j}$  and  $x_{c,j}$  are the molar fractions of component  $j$  in the disperse and continuous phase. The activity coefficients  $\gamma_{d,j}$  and  $\gamma_{c,j}$  can be calculated using nonrandom two-liquid (NRTL) parameters  $\tau_{jk,1-6}$  and  $\alpha_{jk,1-2}$  in dependency of the temperature  $T$  and the compositions of both phases  $i$  by

$$\gamma_{i,j} = \exp \left( \frac{\sum_k \tau_{kj} G_{kj} x_{i,k}}{\sum_l G_{lj} x_{i,l}} + \sum_k \left( \frac{G_{jk} x_{i,j}}{\sum_l G_{lk} x_{i,l}} \right) \left( \tau_{jk} - \frac{\sum_m \tau_{mk} G_{mk} x_{i,m}}{\sum_l G_{lk} x_{i,l}} \right) \right) \quad (2.2)$$

$$G_{jk} = \exp(-\alpha_{jk} \tau_{jk}) \quad (2.3)$$

$$\tau_{jk} = \tau_{jk,1} + \frac{\tau_{jk,2}}{T} + \frac{\tau_{jk,3}}{T^2} + \tau_{jk,4} \ln(T) + \tau_{jk,5} T^{\tau_{jk,6}} \quad (2.4)$$

$$\alpha_{jk} = \alpha_{jk,1} + \alpha_{jk,2} T \quad (2.5)$$

where  $i = c, d$  and  $j, k, l, m = P, W, S$ .<sup>13</sup>

Since the activity coefficients are required to determine the composition of both phases, an iterative calculation is required. Due to mass transfer, the compositions change with the column height. Thus, the LLE needs to be calculated for every discrete height element. Furthermore, the physicochemical properties change with the composition, resulting in an additional iteration for coupling of fluid dynamics and mass transfer. This is avoided in this work to reduce the computing time by the following assumptions.

The influence of the product concentration on the mutual solubility between components W and S as well as on the properties of the phases is neglected. The concentrations of W and S in both phases are calculated based on the binary LLE and are constant throughout the extraction column, meaning that no mass transfer needs to be calculated for these components.

Based on this assumption, the binary LLE for the components W and S is calculated using NRTL parameters and eqs 2.1–2.5 with  $x_{d,P} = x_{c,P} = 0$ . Subsequently, the physicochemical properties of the continuous and dispersed phase are determined via ideal mixing rules based on pure component data<sup>14</sup>

$$\eta_i = \exp \left( \sum_j x_{i,j} \ln(\eta_j) \right) \quad \text{with } i = c, d \text{ and } j = W, S \quad (2.6)$$

$$M_i = \sum_j x_{i,j} M_j \quad \text{with } i = c, d \text{ and } j = W, S \quad (2.7)$$

$$\rho_i = \frac{M_i}{\sum_j x_{i,j} \frac{M_j}{\rho_j}} \quad \text{with } i = c, d \text{ and } j = W, S \quad (2.8)$$

These mixture properties are used instead of pure component properties to calculate the relevant fluid dynamics phenomena and subsequently the mass transfer of component P over the column height as described by Kampwerth et al.<sup>9</sup>

**2.2. Costs Due to Solvents Solubilized in the Raffinate.** Due to mutual solubilities, a specific amount of solvent is dissolved in the continuous phase and leaves the extraction column with the raffinate stream. Therefore, the amount of solvent which is recovered in the distillation column and recycled to the extraction is reduced. In this work, three options to consider the solvent solubilized in the raffinate stream are proposed as depicted in Figure 2.

The first option is a direct recycle of the raffinate stream to the upstream without additional treatment (Figure 2: ●). In this case, the solvent in the raffinate is probably recycled via the upstream to the extraction column within the feed stream of the continuous phase. In this case, the costs due to the solvent solubilized in the raffinate can be set to zero. Thus, the use of a raffinate recycle is the best choice from an economic point of view. However, some conditions need to be fulfilled, and a holistic consideration of the overall process is required for this option. First, the adjustment of the feed stream to the upstream must be possible to prevent an accumulation of W in the process. This means that the feed of W to the upstream needs to be reduced in accordance to the amount of recycled W, such that the stream  $\dot{V}_c$  going into the extraction column, remains constant. Additionally, the resulting concentration of the solvent must not have a negative effect on the unit operations in the upstream. Especially, the influence on reaction yields, selectivity, and kinetics needs to be investigated carefully. Furthermore, a possible solvent loss in the upstream needs to be evaluated. This could be caused, for example, due to conversion of the solvent or side streams leaving the process.

If recycling of the raffinate to the upstream is for some reason not possible, solvent dissolved in the raffinate causes additional costs. Assuming a raffinate disposal (Figure 2: --) and thereby a loss of the solubilized solvent, Kruber et al.<sup>3</sup> proposed to calculate the costs for adding fresh solvent. However, this second option is most likely not the best solution in a technical process.

The third option which is developed in this work is an additional raffinate treatment to recover the solvent (Figure 2: ●●). Therefore, the solvent loss is below a certain maximum, which needs to be defined beforehand. This option also enables the disposal of purified W. To recover the solvent from

the raffinate stream, an additional distillation column is modeled using the FUG shortcut method combined with an energy balance analogously to the treatment of the extract. However, the components W and S form an azeotropic mixture in most cases (see Table 1). Several publications are

**Table 1. Azeotropic Data of Each Solvent with Water**

azeotrope	water content/wt %	boiling point/K	source
butanol–water	42.5	365.85	a <sup>28</sup>
hexanol–water	75.0	370.95	a <sup>28</sup>
octanol–water	90.0	372.55	a <sup>28</sup>
cyclohexanone–water	61.6	368.15	b <sup>29</sup>
EHA–water	96.4	373.05	b <sup>29</sup>
MIBK–water	24.3	361.05	a <sup>28</sup>
MTHF–water	10.6	344.15	c <sup>30</sup>

available dealing with a model-based design of potential processes for the separation of azeotropic mixtures.<sup>15,16</sup> Since the focus of this work is not on the separation of azeotropic mixtures, a simplified calculation is applied. According to Vogelpohl,<sup>15</sup> the FUG shortcut method can also be applied to azeotropic mixtures by treating the azeotrope as a pseudo-component. This has been applied to binary and multi-component systems forming homogeneous as well as heterogeneous azeotropes.<sup>17–19</sup> Therefore, it is also used in this work. First, the vapor–liquid equilibrium (VLE) of the components W and S is calculated via

$$y_j = \frac{\gamma_j^0 p_j^0 x_j}{p} \quad \text{with } j = W, S \quad (2.9)$$

with the liquid and vapor phase molar fractions  $x_j$  and  $y_j$ , the activity coefficient  $\gamma_j$  (calculated as described in Section 2.1), the system pressure  $p$ , and the saturated vapor pressure  $p_j^0$ , which is derived from the Antoine equation (see the Supporting Information). The VLE of the real system is then transformed to a subsystem consisting of the component W and the pseudocomponent Az. Therefore, the molar fraction  $x_W$  of the real system needs to be converted to the molar fraction  $x_{W,trans}$  of the transformed system via

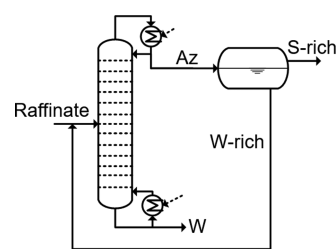
$$x_{w,trans} = \frac{x_W - x_{Az,W}}{1 - x_{Az,W}} \quad (2.10)$$

where  $x_{Az,W}$  is the molar fraction of W in the azeotropic mixture. Equation 2.11 can also be used to transfer the vapor phase composition  $y_W$  into the transformed composition  $y_{W,trans}$ . The relative volatility of the transformed system is then defined by

$$\alpha_{trans} = \frac{y_{W,trans} - (1 - x_{Az,W})}{x_{Az,W} - (1 - y_{W,trans})} \quad (2.11)$$

Thus, the FUG shortcut method can be applied to the transformed system, enabling the calculation of a distillation separating an azeotropic system.

In this work, solvents forming a homogeneous azeotrope with the component W are disclosed from the evaluation since a pressure-swing distillation or an additional entrainer would be required to reach the desired maximum solvent loss. In case of a heterogeneous azeotrope, the azeotropic mixture Az leaving the distillation is sent to a decanter and splits into a S-rich phase and a W-rich phase, as shown in Figure 3, for a low-



**Figure 3.** Flowsheet of the raffinate treatment in case of a low-boiling heterogeneous azeotrope Az between the components S and W.

boiling azeotrope. The S-rich phase can be recycled to the extraction column since the composition is equal to the dispersed phase inlet. The W-rich phase is recycled to the distillation column. Thus, the desired maximum solvent loss determines the amount of S in the stream W, which is recycled to the upstream or leaves the process. Based on the model results, investment and operating costs for the raffinate distillation are calculated analogously to the extract distillation as described by Kampwerth et al.<sup>9</sup>

The different options are applied and compared using the case study, which is described in the following section.

### 2.3. Case Study: Extraction of Levulinic Acid (LA)

Levulinic acid (LA) can be derived from lignocellulosic biomass and is identified by Werpy and Petersen<sup>20</sup> as one of the most promising platform chemicals to substitute petrochemical products. In a typical process,<sup>21,22</sup> lignocellulosic biomass is hydrolyzed to LA at an elevated temperature and pressure using an acid catalyst like sulfuric acid. After the reaction, flash evaporation enables to concentrate the aqueous product mixture by partially removing water and other light boiling components. Solid biomass residues are removed by filtration. To recover LA from the resulting liquid product mixture, liquid–liquid extraction is considered as a promising process. While LA is extracted into the organic solvent, the acid catalyst remains in the aqueous raffinate phase to be recycled to the reactor. The extract phase is fed to a distillation column for LA purification and solvent recovery. Several possible solvents for the extraction of LA have been proposed and evaluated in literature.<sup>21–26</sup> However, to the best of our knowledge, solvent screening that includes the influence of the fluid dynamics on the extraction efficiency has never been performed.

Using the methodology described in this work, a simultaneous solvent evaluation and column design for the extraction of LA from an aqueous feed is conducted while taking the influence of fluid dynamics as well as mutual solubilities into account. Therefore, an annual production capacity of 50 kt LA and an aqueous feed to the extraction column containing 10 wt % LA are assumed. To ensure a product loss close to zero, the extraction rate is set to 0.999, and the LA recovery in the distillation column is specified with 99.9%. The desired LA purity after the distillation is >99% and corresponds to an almost total solvent recovery from the extract phase. If the costs for solvent loss in the raffinate are calculated by adding fresh solvent, the solvent prize is set to 1.5 €/kg corresponding to the prize for methylisobutylketone (MIBK).<sup>27</sup> If a treatment of the raffinate via distillation is considered, the maximum solvent loss is set to 0.01 kg<sub>S</sub>/kg<sub>LA</sub>. The extraction temperature is set to 293.15 K and the system pressure is 1 bar. Seven solvents are considered, which are mentioned in literature, as possible candidates for the LA



extraction. All solvent candidates form a heterogeneous azeotrope with water. The compositions as well as the boiling points of the azeotropes are listed in Table 1. The NRTL parameters for all solvent systems are taken from literature or calculated as described by Scheffczyk et al.<sup>2</sup> (see the Supporting Information). Required physicochemical and thermodynamic data of all components are taken from literature (see the Supporting Information).

### 3. RESULTS AND DISCUSSION

To investigate the influence of mutual solubilities on the extraction process, binary LLEs are calculated for the eight water-solvent-systems based on the NRTL parameters using eqs 2.1–2.5. The resulting concentrations of water in the dispersed phase and solvent in the continuous phase are listed in Table 2. For hexanol, octanol, ethylhexanoic acid (EHA),

**Table 2. Concentrations of Water in the Solvent-Rich Disperse Phase and of Solvent in the Water-Rich Continuous Phase Calculated Based on the NRTL Parameters**

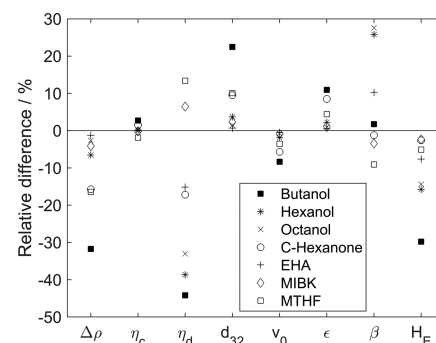
solvent	mass fraction of water in disperse phase $w_{d,W}/wt\%$	mass fraction of solvent in continuous phase $w_{c,S}/wt\%$
butanol	23.45	9.82
hexanol	6.93	0.64
octanol	3.07	0.05
C-hexanone	5.51	9.98
EHA	1.20	0.13
MIBK	2.17	1.92
MTHF	4.19	11.17

and MIBK, the calculated concentrations of water in the disperse phase and of solvent in the continuous phase are quite low. In contrast, the concentrations for the systems with butanol, cyclohexanone (C-hexanone), and 2-methyltetrahydrofuran (MTHF) are relatively high.

In the following section, the influence of using mixture properties instead of pure component data for the calculation of fluid dynamics and mass transfer phenomena on the dimensioning of the extraction column is investigated.

**3.1. Influence on Dimensioning of the Extraction Column.** Depending on the mutual solubility, mixture properties can be calculated for the continuous as well as the dispersed phase instead of using pure component data. If mixture densities are calculated for both phases via eqs 2.7 and 2.8, the density difference  $\Delta\rho$  is lowered by 1–32% compared to pure component data (see Figure 4). Using eq 2.6, the viscosity of the continuous phase  $\eta_c$  increases for the mixture if the viscosity of the solvent  $\eta_s$  is higher than the viscosity of water  $\eta_w$  and decreases for the opposed case. However, the changes are quite small with a range of –2 to +3%. Contrarily, the viscosity of the dispersed phase is significantly reduced for the mixture if  $\eta_s > \eta_w$  and vice versa (–44 to +13%). High mutual solubilities tend to have a more significant effect on the phase properties. However, depending on the difference between the pure component properties, low mutual solubilities can cause major changes as well. For example, the viscosity of octanol is reduced by 33% and only by 17% for C-hexanone even so the solubility of water is higher in C-hexanone.

The flooding correlation of Berger and Walter,<sup>33</sup> which is applied to determine the required column diameter  $D_E$ , is



**Figure 4.** Influence of using mixture properties instead of pure component data in the extraction model for all solvent candidates at their specific optimal S/F ratio: Relative differences of the calculated phase properties, fluid dynamics phenomena, mass transfer coefficient, and required column height.

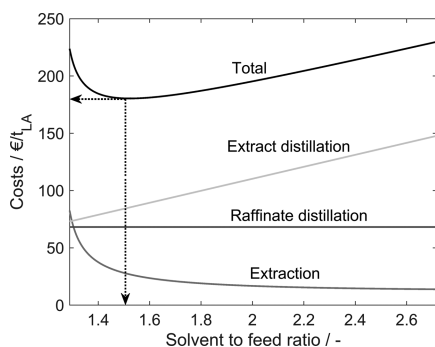
independent of the phase densities and viscosities. Thus, no influence of the consideration of mutual solubilities on the calculated  $D_E$  can be observed. However, some other important fluid dynamic parameters are affected using mixture properties instead of pure component data in the extraction model. The resulting relative differences are shown in Figure 4. The Sauter mean diameter  $d_{32}$  is up to 22% higher if mixture properties are used. The correlation of Kumar and Hartland,<sup>31</sup> which is applied for the calculation of  $d_{32}$ , is based on the theory of isotropic turbulence.<sup>32</sup> For the development of this equation, it is assumed that the disruptive energy caused by continuous phase turbulence is dependent on the density difference between both phases  $\Delta\rho$ . For lower density differences, the disruptive energy is smaller resulting in larger drops. Thus, the relative difference of the Sauter mean diameter correlates antiproportional with the density difference as can also be seen in Figure 4. In general, the rising velocity of a drop  $v_0$  increases with its diameter but decreases for smaller  $\Delta\rho$ . In this case, the latter effect is dominant, leading to a slight reduction of  $v_0$  by up to 8% if mutual solubilities are considered. Due to the smaller rising velocity, the disperse phase hold-up  $\epsilon$  is calculated to be up to 11% higher. Not only fluid dynamics phenomena but also the mass transfer coefficient  $\beta$  is dependent on the phase properties. For some solvents, it is calculated to be up to 28% higher based on mixture properties. However, a contrary effect is observed as well, leading to a reduction of  $\beta$  by up to 9%.

Fluid dynamics phenomena and mass transfer influence the extraction column height  $H_E$  required to match the desired product recovery. Larger drops as calculated under consideration of mutual solubilities implicate a lower volume-specific surface area corresponding to a decreased mass transfer. A higher hold-up increases the surface area and thereby the mass transfer. Furthermore, a high mass transfer coefficient favors the mass transfer. In this case study, using mixture properties in the model instead of pure component data resulted in a reduction of the calculated column height for all solvent candidates. For C-hexanone, MIBK, and MTHF, the increased hold-up more than compensated the decreased mass transfer coefficient, thus highlighting the importance to consider fluid dynamics phenomena for the dimensioning of extraction columns. This can also be shown by comparing butanol and octanol. The mass transfer coefficient of octanol is increased by 27% using mixture properties, whereas the fluid dynamics phenomena are only slightly affected. Contrarily, for butanol,

the most significant changes of all solvents for the calculation of fluid dynamics can be observed but the mass transfer coefficient is nearly unchanged. The resulting relative reduction of the column height is twice as high for butanol (−30%) than for octanol (−14%). This shows not only the impact of fluid dynamics phenomena but also the importance of considering mutual solubilities for an adequate dimensioning of extraction columns. Furthermore, the influence on the calculated column height varies in a broad range from −2 to −30% for the different solvent candidates. Thus, also an impact on the solvent evaluation is possible, which will be analyzed in the following section.

### 3.2. Influence on Total Costs and Solvent Selection.

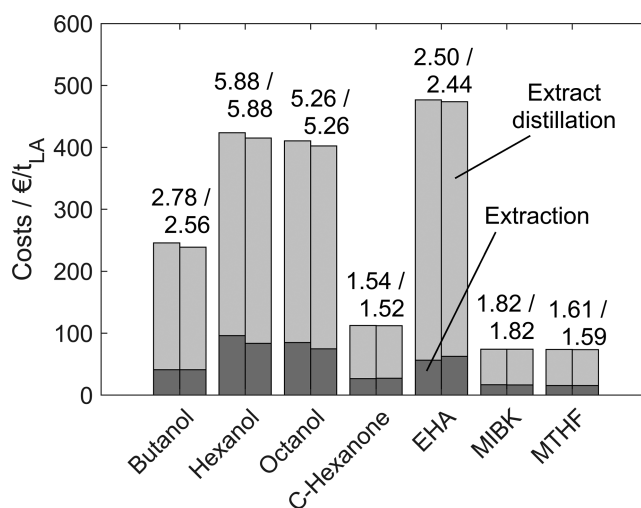
In Figure 5, the cost structure of the extraction process using



**Figure 5.** Dependency of the cost structure on the S/F ratio using C-hexanone as a solvent for the extraction of LA. Minimum total costs of 180 €/t<sub>LA</sub> are achieved with an optimal S/F ratio of 1.52.

C-hexanone as a solvent is shown in dependence on the S/F ratio. A low S/F ratio is equivalent to a low solvent flow rate and a high LA concentration in the extract. Thus, a high and thereby expensive extraction column is required. With increasing S/F ratio, the costs for the extraction decrease. Contrarily, the costs for the distillation increase with the S/F ratio not only due to a higher energy demand but also because of larger column and heat exchanger dimensions. The feed flow rate is fixed, and also, the solubility of C-hexanone in water is constant. On this account, the flow rate as well as the composition of the raffinate stream and thus the raffinate distillation costs are independent on the S/F ratio. The same applies if costs for solvent loss are calculated based on a constant solvent prize instead of the raffinate distillation. The sum of extraction and both distillation costs results in the total costs. The curve of the total costs in Figure 5 has a minimum of 180 €/kg<sub>LA</sub> at an S/F ratio of 1.52. In this way, the optimal S/F ratio and the resulting minimum total costs can be determined for each solvent candidate specifically. Based on this, the solvents can be compared based on the overall process performance.

In Figure 6, the cost structures for the seven solvent candidates are shown at their specific optimum. The left bar for each solvent represents the costs if mutual solubilities are neglected as described by Kampwerth et al.<sup>9</sup> The right bar shows the costs if mutual solubilities are considered according to this work. Ideally, a raffinate recycle is possible and no costs arise due to the solvent solubilized in the raffinate. This is assumed for the cost structures in Figure 6. In this way, it is also possible to exclude the raffinate treatment from the investigation of the influence of mutual solubilities on the original process configuration proposed by Kampwerth et al.<sup>9</sup>



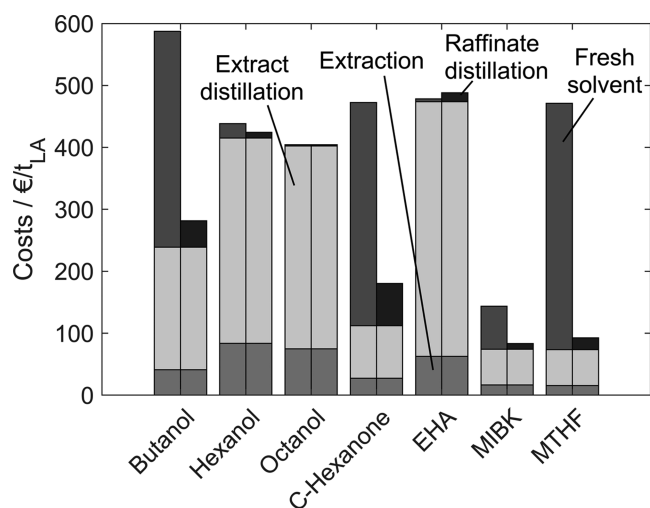
**Figure 6.** Comparison of the cost structure without consideration of mutual solubilities (left bar) and with consideration of mutual solubilities and a raffinate recycle (right bar). The corresponding optimal S/F ratio is shown on top of the bars.

As explained in Section 3.1, using mixture properties results in a smaller extraction column for a specific S/F ratio, which leads to a reduction of the extraction costs. In Figure 6, this can be seen clearly for hexanol and octanol. Since the minimum total costs are a trade-off between the costs for extraction and extract distillation (see Figure 5), a lower optimal S/F ratio was determined for some solvent candidates. In this case, the extract distillation costs are reduced due to a lower solvent flow rate. For EHA, this is accompanied by an increase in the extraction costs. In summary, the minimum total costs of all solvent candidates change only marginally. Therefore, neglecting the influence of mutual solubilities has no effect on the solvent evaluation in this case study as long as a raffinate recycle is possible (compare columns 1 and 2 in Table 3). Under these conditions, MTHF is in first place closely followed by MIBK.

**Table 3. Solvent Rankings Based on the Developed Method without Consideration of Mutual Solubilities and with Consideration of Mutual Solubilities and Different Options to Consider Costs for Solvents Solubilized in the Raffinate**

	without consideration of mutual solubilities	with consideration of mutual solubilities		
		raffinate recycle	raffinate disposal	raffinate distillation
1	MTHF	MTHF	MIBK	MIBK
2	MIBK	MIBK	octanol	MTHF
3	C-hexanone	C-hexanone	hexanol	C-hexanone
4	butanol	butanol	MTHF	butanol
5	octanol	octanol	C-hexanone	octanol
6	hexanol	hexanol	EHA	hexanol
7	EHA	EHA	butanol	EHA

If a direct recycle of the raffinate stream is not possible, a possibility to account for that during the solvent evaluation is required. Two options will be compared in the following: First, the approach from literature assuming a solvent loss via raffinate disposal and second, a raffinate treatment by distillation to recover the solvent. The resulting cost structures for both options are shown in Figure 7, in which the seven



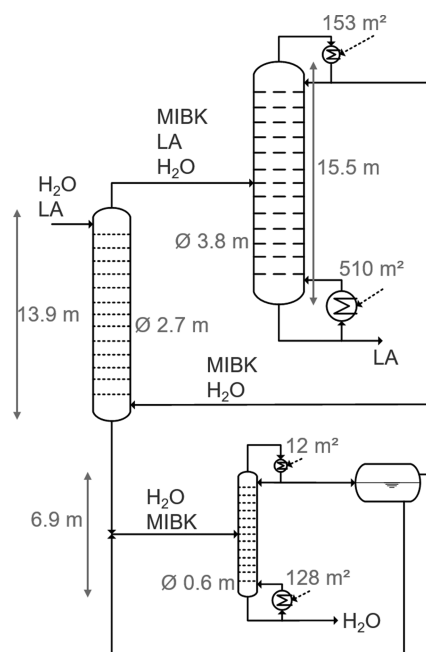
**Figure 7.** Comparison of the cost structure for different options to calculate the costs due to the solvent solubilized in the raffinate: solvent loss compensated by adding fresh solvent with a fixed price (left bar), raffinate distillation for solvent recovery (right bar).

solvent candidates are shown at their specific optimum. The left bar for each solvent represents the costs if the costs for fresh solvent compensating the solvent loss are calculated. Huge differences can be observed for the different solvent candidates. For solvents with good solubility in water (see Table 2), these costs are very high and dominate the total costs. The costs for extraction and extract distillation of butanol, C-hexanone, and MTHF are considerably lower than those of hexanol, octanol, and EHA. However, due to the high solubility of these 3 solvents in water, the costs for solvent loss are extremely high. Because of that, butanol and C-hexanone are on the last and second to last place of the ranking in Table 3. Furthermore, this ranking indicates that hexanol and octanol seem to be a better choice than MTHF, which has been in the second place in the ranking without costs for solvents solubilized in the raffinate.

Calculating the costs for a raffinate distillation to recover most of the solvents results in the right bar for each solvent in Figure 7. For all solvents except of octanol and EHA, this option leads to lower total costs compared to the left bar with adding fresh solvent to compensate for the solvent loss. For octanol, both bars are identical because the amount of octanol solubilized in the raffinate is below the specified maximum solvent loss. For EHA, the raffinate treatment is challenging and it is more expensive than buying a fresh solvent to compensate for the solvent loss. In all other cases, solvent recovery via a raffinate distillation is advantageous and results in lower total costs than buying the fresh solvent. For the raffinate distillation, a low-boiling heterogeneous azeotrope with a high content of S and low content of W is advantageous. In this case, the S-rich phase coming from the decanter is larger than the W-rich phase, which needs to be recycled to the distillation column (see Figure 3). In this regard, especially, the properties of the butanol–water and MTHF–water azeotrope are favorable as listed in Table 1. Indeed, the costs for butanol and MTHF are reduced tremendously, resulting in an improvement from the 4th to 2nd and from 7th to 4th place, respectively (compare columns 3 and 4 in Table 3). Also, for MIBK and C-hexanone, solvent recovery leads to a great reduction of the cost. In contrast, the EHA–water

azeotrope has a high water content and a boiling point, which is much closer to the boiling point of water (see Table 1). Thus, raffinate distillation is more challenging and expensive. Therefore, assuming a solvent loss and calculating the costs for fresh solvent seems to be cheaper for EHA. However, additional costs are to be expected for the disposal of solvent-contaminated raffinate. Furthermore, the solvent price which is assumed to be 1.5 €/kg for the method has a significant influence on the costs.

The option to consider costs for solvents solubilized in the raffinate via a raffinate distillation for solvent recovery is not only more realistic but also advantageous from an economic point of view. For the LA extraction process, MIBK is in the first place with 83 €/kg<sub>LA</sub> at an optimal S/F ratio of 1.81. The corresponding flowsheet and apparatus dimensions are depicted in Figure 8. The second and third place are MTHF



**Figure 8.** Setup for a LA extraction and purification process using MIBK with an optimal S/F ratio of 1.81.

(92 €/kg<sub>LA</sub> at S/F ratio 1.57) and C-hexanone (180 €/kg<sub>LA</sub> at S/F ratio 1.52), in which both would have been rated very bad without solvent recovery. Consequently, the design of a raffinate treatment for solvent recovery is not only relevant at a later stage of process development to minimize the costs but should also be taken into account at an early stage for solvent selection.

#### 4. SUMMARY AND CONCLUSIONS

The methodology of Kampwerth et al.<sup>9</sup> for a model-based simultaneous solvent selection and column design is enhanced by the consideration of mutual solubilities between the main components W and S of the continuous and dispersed phase, respectively. Based on the calculation of the binary LLE, mixture properties are used for both phases instead of pure component properties. Furthermore, different options to deal with solvents solubilized in the raffinate are implemented. To evaluate the influence of the extensions on the model results, the extraction of LA from an aqueous phase is used as a case study.

In the extraction model, accounting for mutual solubilities during the calculation of fluid dynamics phenomena and mass transfer has a significant effect on the resulting extraction performance and thereby on the required column dimensions. The impact on the calculated column height is highly diverse depending on the solvent. Therefore, consideration of mutual solubilities is recommended for a model-based column design and solvent selection even so a minor influence on the cost structure is observed in this case study.

With regard to costs and the resulting solvent ranking, the handling of the raffinate stream, which contains a specific amount of solvent plays a much more important role. Preferably, the raffinate stream is directly recycled to the upstream and thereby enables a solvent recycle to the extraction column. However, the feasibility of this option demands for experimental investigation, which cannot be covered with the methodology presented in this work. In case direct recycling is not possible, the methodology is enhanced by a suitable raffinate distillation model to recover the solubilized solvent. This option is compared to a more simple approach by calculating the costs for adding fresh solvent to compensate for a loss due to raffinate disposal. Raffinate distillation is not only the more ecological way to go for but also by far the more economical option. It is shown that promising solvent candidates could be excluded if solely the costs for solvent loss are considered even though a relatively effective solvent recovery is possible.

In the developed methodology, the whole extraction process including the extraction column as well as distillation columns for the make-up of the extract and raffinate phases are considered. The optimal S/F ratio, the required apparatus dimensions, and energy demand are determined for each solvent candidate individually. Based on the resulting minimum costs, a ranking for the solvents is obtained. Accordingly, MIBK and MTHF are identified to be the most promising solvents for the extraction of LA.

If LA is produced from lignocellulosic biomass, the aqueous feed to the extraction column will contain further components like an acid catalyst and side products. This can have a significant effect on the extraction performance, which is not considered in this work. Thus, the experimental investigation is still essential for a reliable column design. Moreover, the selectivity of the solvent could be an additional evaluation parameter. Therefore, the methodology will be further developed in future work to account for multicomponent mass transfer.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.1c03312>.

Device specifications properties and parameters for property calculations NRTL parameter (PDF)

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## Notes

The authors declare no competing financial interest.

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## ■ SYMBOLS

$c$	concentration, [mol m <sup>-3</sup> ]
$d_{32}$	Sauter mean diameter, [m]
$D_E$	extraction column diameter, [m]
$G$	Gibbs free energy, [J]
$H_E$	extraction column height, [m]
$K$	distribution coefficient
$M$	molar mass, [kg mol <sup>-1</sup> ]
$\dot{Q}$	heat flow rate, [J s <sup>-1</sup> ]
$T$	temperature, [K]
$\dot{V}$	volume flow rate, [m <sup>3</sup> s <sup>-1</sup> ]
$v_0$	rising velocity, [m s <sup>-1</sup> ]
$w$	weight fraction of product
$x$	molar fraction of product
$\alpha$	NRTL parameter
$\beta$	mass transfer coefficient, [m s <sup>-1</sup> ]
$\gamma$	activity coefficient
$\Delta\rho$	density difference, [kg m <sup>-3</sup> ]
$\epsilon$	hold-up
$\eta$	viscosity, [Pa s]
$\rho$	density, [kg m <sup>-3</sup> ]
$\sigma$	surface tension, [N m <sup>-1</sup> ]
$\tau$	NRTL parameter

## ■ SUB- AND SUPERScript

$c$	continuous phase
Cond	condenser
$d$	disperse phase
Evap	evaporator
in	inlet
out	outlet
P	product
S	solvent
W	water

## ■ ABBREVIATIONS

C-hexanone	cyclohexanone
EHA	ethylhexanoic acid
FUG	Fenske, Underwood, Gilliland
HETS	height equivalent to a theoretical stage



MIBK	methylisobutylketone
MTHF	2-methyltetrahydrofuran
NRTL	nonrandom two-liquid
PBE	population balance equations
S/F	ratio solvent to feed volume flow ratio $\dot{V}_d/\dot{V}_c$

## REFERENCES

- (1) Kopriwa, N.; Buchbender, F.; Ayesterán, J.; Kalem, M.; Pfennig, A. A Critical Review of the Application of Drop-Population Balances for the Design of Solvent Extraction Columns: I. Concept of Solving Drop-Population Balances and Modelling Breakage and Coalescence. *Solvent Extr. Ion Exch.* **2012**, *30*, 683–723.
- (2) Scheffczyk, J. D. Integrated Computer-Aided Design of Molecules and Processes Using COSMO-RS. Dissertation, RWTH Aachen: Aachen, 2018.
- (3) Kruber, K. F.; Scheffczyk, J.; Leonhard, K.; Bardow, A.; Skiborowski, M. In *A Hierarchical Approach for Solvent Selection Based on Successive Model Refinement*, 28th European Symposium on Computer Aided Process Engineering; Computer Aided Chemical Engineering; Elsevier, 2018; pp 325–330.
- (4) Goedecke, R. *Fluidverfahrenstechnik*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2006.
- (5) Sattler, K. *Thermische Trennverfahren*, 3rd ed.; John Wiley & Sons: Weinheim, Germany, 2012.
- (6) Henschke, M. *Auslegung pulsierter Siebboden-Extraktionskolonnen*; Berichte aus der Verfahrenstechnik: Shaker, 2004.
- (7) Attarakih, M.; Al-Zyod, S.; Abu-Khader, M.; Bart, H. J. PPBLAB: A New Multivariate Population Balance Environment for Particulate System Modelling and Simulation. *Procedia Eng.* **2012**, *42*, 1445–1462.
- (8) Weber, B.; Meyer, C.; Jupke, A. Performance Map for the Design of Liquid-Liquid Extraction Columns. *Chem. Ing. Tech.* **2019**, *54*, 1674–1680.
- (9) Kampwerth, J.; Weber, B.; Rußkamp, J.; Kaminski, S.; Jupke, A. Towards a holistic solvent screening: On the importance of fluid dynamics in a rate-based extraction model. *Chem. Eng. Sci.* **2020**, *227*, No. 115905.
- (10) Fenske, M. R. Fractionation of Straight-Run Pennsylvania Gasoline. *Ind. Eng. Chem.* **1932**, *24*, 482–485.
- (11) Underwood, A. J. V. Fractional Distillation of Multicomponent Mixtures. *Ind. Eng. Chem.* **1949**, *41*, 2844–2847.
- (12) Gilliland, E. R. Multicomponent Rectification Estimation of the Number of Theoretical Plates as a Function of the Reflux Ratio. *Ind. Eng. Chem.* **1940**, *32*, 1220–1223.
- (13) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1968**, *14*, 135–144.
- (14) *Albright's Chemical Engineering Handbook*; Albright, L. F., Ed.; CRC Press: Boca Raton, 2009.
- (15) Skiborowski, M.; Harwardt, A.; Marquardt, W. Efficient optimization-based design for the separation of heterogeneous azeotropic mixtures. *Comput. Chem. Eng.* **2015**, *72*, 34–51.
- (16) Kruber, K. F.; Grueters, T.; Skiborowski, M. In *Efficient Design of Intensified Extractive Distillation Processes Based on a Hybrid Optimization Approach*, 29th European Symposium on Computer Aided Process Engineering; Computer Aided Chemical Engineering; Elsevier, 2019; pp 859–864.
- (17) Liu, G. Synthesis of Multicomponent Azeotropic Distillation Sequences. Doctoral Thesis, University of Manchester: Manchester, 2003.
- (18) Liu, G.; Jobson, M.; Smith, R.; Wahnschafft, O. M. Shortcut Design Method for Columns Separating Azeotropic Mixtures. *Ind. Eng. Chem. Res.* **2004**, *43*, 3908–3923.
- (19) Yang, X.; Dong, H.-G.; Grossmann, I. E. A framework for synthesizing the optimal separation process of azeotropic mixtures. *AIChE J.* **2012**, *58*, 1487–1502.
- (20) Werpy, T.; Petersen, G. *Top Value Added Chemicals from Biomass: Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; No. DOE/GO-102004-1992; National Renewable Energy Lab: Golden, CO, 2004.
- (21) Seibert, F. A Method of Recovering Levulinic Acid. WO Patent WO2010/030617A12010.
- (22) Isoni, V.; Kumbang, D.; Sharratt, P. N.; Khoo, H. H. Biomass to levulinic acid: A techno-economic analysis and sustainability of biorefinery processes in Southeast Asia. *J. Environ. Manage.* **2018**, *214*, 267–275.
- (23) Nhien, L. C.; Long, N. V. D.; Lee, M. In *Production of Levulinic Acid from Lignocellulosic Biomass: A Solvent Case Study*, International conference on Chemical and Biochemical Engineering, 2015.
- (24) Laitinen, A. T.; Penttilä, K. J. T.; Kaunisto, J. M. Physical solvent extraction of levulinic acid from dilute aqueous solution with 2-methyltetrahydrofuran. *Sep. Purif. Technol.* **2016**, *51*, 465–473.
- (25) Brouwer, T.; Blahusiak, M.; Babic, K.; Schuur, B. Reactive extraction and recovery of levulinic acid, formic acid and furfural from aqueous solutions containing sulphuric acid. *Sep. Purif. Technol.* **2017**, *185*, 186–195.
- (26) Leal Silva, J. F.; Maciel Filho, R.; Wolf Maciel, M. R. Process Design and Technoeconomic Assessment of the Extraction of Levulinic Acid from Biomass Hydrolysate Using n-Butyl Acetate, Hexane, and 2-Methyltetrahydrofuran. *Ind. Eng. Chem. Res.* **2020**, *59*, 11031–11041.
- (27) Palagacheva, Y. OUTLOOK '19: Europe IPA, MEK, MIBK Likely to be Less Volatile in 2019. 2019, <https://www.icis.com/explore/resources/news/2018/12/28/10300225/outlook-19-europe-ipa-mek-mibk-likely-to-be-less-volatile-in-2019/> (accessed Aug 8, 2020).
- (28) Tamplin, W. S.; Horsley, L. H. *Azeotropic Data I*; Advances in Chemistry Series, 6, 35, 116; American Chemical Society, 1952–1973.
- (29) Tamplin, W. S.; Horsley, L. H. *Azeotropic Data II*; Advances in Chemistry Series, 6, 35, 116; American Chemical Society, 1952–1973.
- (30) Aycock, D. F. Solvent Applications of 2-Methyltetrahydrofuran in Organometallic and Biphasic Reactions. *Org. Process Res. Dev.* **2007**, *11*, 156–159.
- (31) Kumar, A.; Hartland, S. Unified Correlations for the Prediction of Drop Size in Liquid–Liquid Extraction Columns. *Ind. Eng. Chem. Res.* **1996**, *35*, 2682–2695.
- (32) Kolmogorov, A. N. The local structure of turbulence in incompressible viscous fluid for very large Reynolds numbers. *C. R. Acad. Sci. URSS* **1941**, *30*, 301–305.
- (33) Berger, R.; Walter, K. Flooding in pulsed sieve plate extractors. *Chem. Eng. Sci.* **1985**, *40* (12), 2175–2184.