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Revised Manuscript

For the Chemical Engineering Research and Design

Axial Dispersion and CFD Models for the Extraction of Levulinic Acid from Dilute Aqueous Solution in a Kühni Column with 2-Methyltetrahydrofuran Solvent

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Graphical abstract

Highlights

- Models (1D, 3D CFD) were prepared for the extraction of levulinic acid.
- The models fit the experimental extraction column data with an excellent accuracy.
- The models proved to be a very valuable tool for scale-up and design purposes.

Abstract

1D axial dispersion and 3D CFD models for the extraction of levulinic acid from dilute aqueous solution by applying 2-methyltetrahydrofuran as a solvent are presented. The models are validated by comparison with the measured levulinic acid concentration profile data obtained in a bench-scale Kühni column. The 1D model contains NRTL parameters for the system levulinic acid-water-2MTHF. Correlations for drop size and hold-up for Kühni columns were taken from literature. The values for overall mass transfer coefficient ranged from $1.4\text{E-}5$ to $2.2\text{E-}5 \text{ ms}^{-1}$, and increased as a function of the rotor speed. The fitting of the column performance resulted in a very good prediction of the solute concentration profiles in the extraction column, and the average absolute value of relative error for the 1D model was 23%. CFD model visualized the column performance at the column height of 150.5 - 160 cm giving valuable information on back mixing, phase velocities, dispersed phase volume fraction, and mass transfer. Dispersed phase volume fraction and mass transfer contours revealed, that the mass transfer rate (app. $0.25 \text{ gL}^{-1}\text{s}^{-1}$) is at its highest just below the rotor, and that there are blind spots in the compartments close to the extractor and just above each down comer. Values for the dispersed phase volume fraction are highest in the same area where the mass transfer reaches the highest values. The highest slip velocity values (app. 0.03 m^{-1}) are located in the tip of each compartment partition plates.

General correlations, such as hold-up and drop size correlations, can successfully be applied in levulinic acid - water - 2MTHF system reported in this work. The 1D axial dispersion model proved to be valuable tool for scale-up purposes, and CFD model, despite the long time needed for each simulation, gave useful information for the design purposes.

KEYWORDS: Modeling, CFD, Back-mixing model, Kühni-column, Levulinic acid, 2-methyltetrahydrofuran

Nomenclature

a	specific interfacial area (m^2)
A_d	droplet interfacial area (m^2)
A_r	cross sectional area of the column (m^2)
C_i	mass concentration of specie (kg m^{-3})
$C1, C2$	empirical parameters ()
D	diameter (m)
D_e	effective diffusivity ($\text{m}^2 \text{s}^{-1}$)
d	drop diameter (m)
d_{32}	Sauter diameter (m)
E_i	axial dispersion coefficient of phase i ($\text{m}^2 \text{s}^{-1}$)
g	gravity (m s^{-2})
h	compartment height (m)
k_i	overall mass transfer coefficient of specie i (m s^{-1})
K	partition coefficient ()
m	mass flow rate (kg h^{-1})
N	rotor speed (1/s)
U	superficial velocity (m s^{-1})
Z	agitated height of the column (m)
Q	volume flow rate ($\text{m}^3 \text{s}^{-1}$)
x_f	fractional free column cross sectional area ()
Re_c	continuous phase Reynolds number = $U_{\text{slip}} \rho_c d_d / \mu_c$ ()
Sc_c	continuous phase Schmidt number = $\mu_c / \rho_c D_e$ ()
Sh_c	continuous phase Sherwood number = $k_c d_d / D_e$ ()

Greek symbols

ϕ	hold-up
γ	interfacial tension (N m^{-1})
ρ	mass density (kg m^{-3})
μ	viscosity (Pa s)
η	molar mass transfer rate ($\text{mol s}^{-1} \text{m}^{-2}$)
κ	viscosity ratio = μ_d / μ_c
ψ	mechanical power dissipation per unit mass (W kg^{-1})

Superscript

*	equilibrium value
j	node index

Subscripts

c continuous phase
d dispersed phase
i specie

ACCEPTED MANUSCRIPT

1. Introduction

Liquid-liquid extraction is one of the most important separation techniques in chemical engineering practise, and it is widely applied in hydrometallurgy, pharmaceuticals, petrochemical industry, environmental protection, and nuclear industry. It has grown in importance in recent years due to several reasons. There is a growing need for heat-sensitive products especially in pharma industry, and availability of selective low cost solvents and chelating agents has improved. Interest in renewable feedstock for the production of platform chemicals from lignocellulosic materials and sugars has increased. Several potential processes exist for the treatment of biomass including pyrolysis, aqueous phase reforming, and acid hydrolysis. The products typically have to be separated from dilute aqueous solutions, and liquid-liquid extraction is often the best choice.

Despite the fact that liquid-liquid extraction is relatively mature separation technology, the design procedure is still today largely based on pilot plant data and design experience, which is mostly due to the complex phenomena of simultaneous mass transfer, dispersed phase drop breakage and coalescence taking place in the extraction column. Several modeling approaches have been proposed during the recent years, and mathematical models describing liquid-liquid extraction can be categorised into empirical, differential, and stage wise models (Pratt, 1983; Zhang et al., 1985; Dongaonkar et al., 1991; Korschinsky and Bastani, 1993; Weinstein et al., 1997; Chouai et al., 2000; Attarakih et al., 2006; Morales et al., 2007; Gameino et al., 2010; Ferreira et al., 2010; Safari et al., 2012; Neto and Mansur, 2013; Hemmati et al., 2014). A modern approach is the population balance method (Haunold et al., 1990; Bohro, 2002; Bart, 2005; Schmidt et al., 2006; Attarakih et al., 2006, 2009), which requires that several parameters, including Sauter mean drop size distribution, mass transfer and axial dispersion coefficients, breakage and coalescence parameters

among others need to be measured or correlated accurately. Even though population balance approach is promising from the academic point of view, it is not widely used in the design process due to the rigorous models, abundance of parameters, and scale-up difficulties (Grinbaum, 2006). Computational fluid dynamics (CFD) modelling of liquid-liquid extraction columns takes into consideration the hydrodynamics and mass-transfer simultaneously (Mate et al., 2000; Nabli et al., 1997; Bardin-Monnier et al., 2003; Kolb, 2004; Yadav and Patwardhan, 2009; Xiaojin and Guangsheng, 2011; Attarakih, 2015). It involves the solution of the conservation equations of mass, momentum and volume fractions for different fractions, and is regarded as a powerful tool in chemical engineering. Recently, modelling approach combining droplet population balance models (DPBM) and CFD has gained attention (Hlawitschka, 2016).

Work related to the design and scale-up of Kühni extraction columns is scarce, even though this type of column is widely used in industry. Further, many of the existing studies focus on the toluene-acetone-water (high interfacial tension) or n-butylacetate-acetone-water (medium interfacial tension) systems as recommended for the official tests systems by the European Federation of Chemical Engineering (EFCE). In this study, both 1D stage wise axial mixing and 3D CFD models are developed for the extraction of levulinic acid from dilute aqueous solution with 2-methyltetrahydrofuran (2MTHF) in a mechanically agitated Kühni column. In case of CFD modeling, ANSYS Fluent simulation program is applied to solve the momentum and mass transfer equations between the phases. The results were compared with the experimental column extraction data.

Levulinic acid (LA), or 4-oxopentanoic acid, is a carboxylic acid containing a ketone functional group, and it can be produced from a variety of inexpensive lignocellulosic biomass. The controlled degradation of C6-sugars by strong mineral acids, such as sulfuric acid, is the most

tested approach to prepare LA (Girisuta, 2007). LA has been employed as a potential precursor for the synthesis of pyrrolidones, diphenolic acid, delta-aminolevulinic acid, butanone, methyl vinyl ketone, methyltetrahydrofuran, levulinate esters, and gamma-valerolactone. The conceivable industrial applications of this platform chemical include synthetic fibres, pharmaceuticals, pesticides, perfumery, food additives, solder flux, stabilizers, printing inks, and fuels.

2. Experimental

2.1 Materials

2MTHF (2-Methyltetrahydrofuran, anhydrous $\geq 99\%$, inhibitor free) and LA (4-oxopentanoic acid, 98%) were purchased from Sigma-Aldrich, and used without further purifications. Sodium hydroxide solution (Reag Ph Eur, 0.1 M) for the analyses was obtained from Fluka Analytical. Ion-exchanged water was applied in the experiments.

2.2 Measurements

Liquid-liquid equilibrium for the system levulinic acid-water-2MTHF at temperatures 298.2 K, 313.2 K, and 328.2 K is presented elsewhere (Laitinen et al., 2015). Extraction experiments were carried out to determine the composition of levulinic acid in the extract and raffinate phases as well as the column concentration profile at temperature of 298 K. Further, column hold-up and average particle size were measured in order to evaluate the validity of the calculated values, which were used in models. Aqueous phase was the continuous phase and 2MTHF was the dispersed in the solution. Kühni ECR60/50G (Sulzer Chemtech) extraction column equipped with a heating jacket was applied for the counter-current extraction studies. The column contains 50 agitated compartments, and the active column height is 1860 mm. The inside diameter of the column is 60 mm. Each experiment lasted 2-4 hours depending on the feed rates. 3-4 raffinate and extract

samples were taken during each run to make sure that the column reached equilibrium. More detailed description of the experimental procedure can be found elsewhere (Laitinen et al., 2015). Concentration deviations in the consecutive extract and raffinate samples were within 4%, and the relative deviation of the mass balance around the column was always within 1.5%, whereas the average relative deviation of levulinic acid balance was 2.8%. The dispersed phase hold-up was obtained after each run by shutting the feed pumps off at steady-state conditions, and measuring the increase in the solvent phase level in the upper settler. Concentration of levulinic acid in the extract and raffinate phases was analyzed by titration (799 GPT Titrino Metrohm) with 0.1 M sodium hydroxide. In order to evaluate the accuracy of the calculated values of drop size, digital photos of the column contents using Olympus E-M1 digital camera focused on the middle section of the column were taken at solvent to feed (S/F) ratio 8.4/9.2. Particle dimensions were compared with known size of the column internal as a reference. Between 50 and 100 drops were analyzed in each photo to guarantee the statistical significance of the measured Sauter mean drop diameter. The symmetry correlated equivalent diameter was not calculated.

The interfacial tension between water and 2MTHF was measured via the drop shape analysis of an aqueous drop hanging from a capillary in 2MTHF. The measurements were carried out at room temperature (295 ± 0.5 K) with KSV CAM200 apparatus (KSV Instruments, Helsinki, Finland) that also includes the image analysis software. Immediately after forming the drop at the tip of the capillary (radius 2.1 mm), ten frames of the drop were captured for the shape analysis. In the analysis, the density of 0.86 g/mL was used for 2MTHF and 0.998 g/mL for water. The interfacial tension was found as 3.50 ± 0.01 mN/m and the drop volume as 9.91 ± 0.06 μ L.

3. Parameter estimation

Kumar and Hartland (1995) analyzed experimental results measured for eight different types of extraction column. The unified correlation developed contains ten parameters, and the authors fitted different values for different types of columns. The data with or without mass transfer reveals that the hold-up for the Kühni column can be expressed in terms of mechanical power dissipation, phase flow rates, physical properties, and column geometry as given in equations 1 and 2

$$\phi = \left(2.67 \cdot 10^{-2} + \left(\frac{\psi \theta}{g} \right)^{0.77} \right) (U_d \theta)^{0.64} \exp(20.7 U_c \theta) 0.9 \left(\frac{\rho_c - \rho_d}{\rho_c} \right)^{-0.34} 2.27 x_f^{-0.77} \quad (1)$$

where

$$\theta = \left(\frac{\rho_c}{g \gamma} \right)^{0.25} \quad (2)$$

where ϕ , ψ , g , U_d , U_c , ρ_c , ρ_d , x_f , and γ are hold-up, mechanical power dissipation, gravity, superficial velocity of the dispersed phase, superficial velocity of the continuous phase, density of the continuous phase, density of the dispersed phase, fractional free column cross sectional area, and interfacial tension, respectively. The average absolute value for the relative deviation for the prediction on the Kühni column data given by the authors for 75 mm diameter column was 13% and for all data the value was 21%. The measured values in this work for the levulinic acid-water-2MTHF system and the calculated values based on the unified equations (1) and (2) are compared in the Fig. 1. The value of the relative deviation in case of the levulinic acid-water-2MTHF system is 11.2%, which is close to the value given by Kumar and Hartland (1995). Equation (1) predicts the dispersed phase hold-up reasonably well at 100 and 125 rpm especially at the lower S/F ratio (8.4/9.2) tested, whereas a larger deviation of the measured and calculated values is seen at 150 rpm. Unified correlation for the prediction of drop size in liquid-liquid extraction columns was presented by Kumar and Hartland (1996). The correlation for mechanically agitated columns consists of a two-term additive model involving the ratio of interfacial tension to buoyancy forces at low agitation and the theory of isotropic turbulence at high agitation. The authors fitted 702 data

points and obtained equation (3) with Kühni specific parameters. The value of the average relative deviation was 22%.

$$\frac{d_{32}}{h} = \frac{e^{0.45}}{\frac{1}{1.6 \left(\frac{\gamma}{(\rho_c - \rho_d) g H^2} \right)^{1/2} + \frac{1}{0.034 \left(\left(\frac{\Psi}{g} \right) \left(\frac{\rho_c}{g \gamma} \right)^{1/4} \right)^{-0.63} \left(h \left(\frac{\rho_c g}{\gamma} \right)^{0.38} \right)^{-1}}} \quad (3)$$

The average drop size for the levulinic acid-water-2MTHF system was measured for the S/F ratio 8.4/9.2. According to the results, the drop size at the middle of the column was relatively small decreasing from 0.65 mm to 0.51 mm as the rotor speed was increased from 100 rpm to 150 rpm. The experimental values were compared with the calculated values in the Fig. 2 showing a significant deviance of the results. The experimental set-up failed to quantify the coalescence, breakup, and drop movement especially below the plates separating the compartments, and therefore the estimated relative error of the measurements is large, which can explain the deviance. The hold-up and drop size values obtained from equations (1) and (3) were applied in the 1D column modeling.

4. Mathematical models

4.1 One Dimensional (1D) axial dispersion model

In the liquid-liquid extraction column, the continuous heavier aqueous phase flows downwards and dispersed, lighter organic phase flows upwards. Mathematical model of the extraction column can be described with a set of differential conservation equations for the components in continuous and dispersed phases.

$$\frac{\partial}{\partial z} \left(U_c C_{c,i} - E_c \frac{\partial C_{c,i}}{\partial z} \right) - k_i a (K_d C_{c,i} - C_{d,i}) \quad (4)$$

$$\frac{\partial}{\partial z} \left(U_d C_{d,i} - E_d \frac{\partial C_{d,i}}{\partial z} \right) + k_i a (K_d C_{c,i} - C_{d,i}) \quad (5)$$

where a , $C_{x,i}$, k_{oi} , E_x , and U_x are the specific interfacial area, concentration of component i in phase x , the overall mass transfer coefficient of the component i in phase x , the dispersion coefficient of the phase x , and the superficial velocity of the phase x .

In the simplest case, the velocities of the both phases are assumed constant, meaning that the only variables would be the concentrations of the components in both phases. In this model column and each impeller compartment were divided into number of calculation nodes (with cell height dZ), and mass balance equations were written for each cell. Variables are the mass flow rates of the components in continuous and dispersed phases in each calculation node. Temperature is assumed constant in the column and it is given as input to the model. In this work, mass flow rates of components are used as variables instead of superficial velocity and concentrations and equations 4 and 5 can be given as

$$\frac{\partial}{\partial z} \left(\frac{m_{c,i}}{A_r} - E_c \frac{\partial(m_{c,i}/Q_c)}{\partial z} \right) - k_i a \left(\frac{K_d m_{c,i}}{Q_c} - \frac{m_{d,i}}{Q_d} \right) = 0 \quad (6)$$

$$\frac{\partial}{\partial z} \left(\frac{m_{d,i}}{A_r} - E_d \frac{\partial(m_{d,i}/Q_d)}{\partial z} \right) + k_i a \left(\frac{K_d m_{c,i}}{Q_c} - \frac{m_{d,i}}{Q_d} \right) = 0 \quad (7)$$

where $m_{x,i}$ and Q_x are the mass flow rate of component i and volume flow rate of phase x and A_r is the cross sectional area of the column. Volume flow rate of phase x is given as

$$Q_x = \sum_i^{n_c} \frac{m_{x,i}}{\rho_x} = \left(\sum_i^{n_c} m_{x,i} \right)^2 / \sum_i^{n_c} m_{x,i} \rho_{x,i} \quad (8)$$

where $\rho_{x,i}$ is the mass density of component i in phase x . The specific interfacial area between the continuous and the dispersed phases is given as

$$a = \frac{6\phi}{d_{32}} \quad (9)$$

where ϕ is the holdup or the volume fraction of the dispersed phase and d is the Sauter mean diameter of the dispersed phase particles. The overall mass transfer coefficient k_i is given as

$$k_i = \frac{k_c k_d}{k_c K_d + k_c} \quad (10)$$

And the partition coefficient K_d as

$$K_{d,i} = \frac{C_{d,i}^*}{C_{c,i}^*} \quad (11)$$

Continuous and dispersed phase mass transfer coefficients are given by Kumar and Hartland (1999).

$$\frac{\frac{Sh_c}{(1-\phi)} - Sh_{c,rigid}}{Sh_{c,\infty} - \frac{Sh_c}{(1-\phi)}} = 5.26 \cdot 10^{-2} Re^{\frac{1}{3}} + 6.59 \cdot 10^{-2} Re^{\frac{1}{4}} Sc_c^{1/3} \left(\frac{U_{slip} \mu_c}{\gamma} \right)^{\frac{1}{3}} \frac{1}{1+\kappa^{1.1}} \left(1 + C_1 \left(\frac{\psi}{g} \left(\frac{\rho_c}{g\gamma} \right)^{1/4} \right)^{1/3} \right) \quad (12)$$

where

$$Sh_{c,rigid} = 2.43 + 0.775 Re^{1/2} Sc_c^{1/3} + 0.0103 Re Sc_c^{1/3} \quad (13)$$

and

$$Sh_{c,\infty} = 50 + \frac{2}{\sqrt{\pi}} (Re Sc_c)^{1/2} \quad (14)$$

Equation (13) is valid for the Re number values of $10 < Re < 1200$. Our calculated Re number values are $6 < Re < 21$, which are in the lower part of the range. Equation (14) is valid for $0.1 < Re < 1400$, $180 < Sc_c < 571\ 600$, and $15 < Sh_c < 1919$. Our calculated values for Sc_c , and Sh_c are $Sc_c = 900$, and $65 < Sh_c < 66$, which are in the range. For dispersed phase mass transfer coefficient

$$Sh_d = 17.7 + \frac{3.19 \cdot 10^{-3} (Re Sc_d^{1/3})^{1.7}}{1 + 1.43 \cdot 10^{-2} (Re Sc_d^{1/3})^{0.7}} \left(\frac{\rho_d}{\rho_c} \right)^{2/3} \frac{1}{1+\kappa^{2.3}} \left(1 + C_2 \left(\frac{\psi}{g} \left(\frac{\rho_c}{g\gamma} \right)^{1/4} \right)^{1/3} \right) \quad (15)$$

Mass balances are linearized and written as linear system of equations where variables are the mass flow rates of components in the continuous and the dispersed phases.

$$m_{c,i}^{j+1} - m_{c,i}^j - \frac{A_r}{\Delta z} \left(E_c^{j+1} \left(\frac{m_{c,i}^{j+1}}{Q_c^{j+1}} - \frac{m_{c,i}^j}{Q_c^j} \right) - E_c^j \left(\frac{m_{c,i}^j}{Q_c^j} - \frac{m_{c,i}^{j-1}}{Q_c^{j-1}} \right) \right) - (A_r \Delta z) k_i a \left(K_d \frac{m_{c,i}^j}{Q_c^j} - \frac{m_{d,i}^j}{Q_d^j} \right) = -m_{c,f,i}^j \quad (16)$$

$$m_{d,i}^{j-1} - m_{d,i}^j - \frac{A_r}{\Delta z} \left(E_d^{j-1} \left(\frac{m_{d,i}^{j-1}}{Q_d^{j-1}} - \frac{m_{d,i}^j}{Q_d^j} \right) - E_d^j \left(\frac{m_{d,i}^j}{Q_d^j} - \frac{m_{d,i}^{j+1}}{Q_d^{j+1}} \right) \right) - (A_r \Delta z) k_i a \left(K_d \frac{m_{c,i}^j}{Q_c^j} - \frac{m_{d,i}^j}{Q_d^j} \right) = -m_{d,f,i}^j \quad (17)$$

where $m_{x,f,i}^j$ is the feed of component i to phase x in node j . The continuous phase dispersion coefficient E_c^{j+1} is zero for the topmost node and the dispersed phase dispersion coefficient E_d^{j-1} is zero for the bottommost node. Each compartment in the column can contain one or more calculation nodes. If there is more than one node in a compartment then the dispersion coefficient inside the compartment is higher than the dispersion coefficient between the compartments. All nonlinear terms are considered constant. Several iterations are needed to solve the final mass balances (typically 5 to 10). For example, mass fractions of components are calculated by dividing the mass flow rates of components with the total flow rate of continuous and the dispersed phases. In this case, the total flow rate is taken from previous iteration and it is thus constant. The simulation algorithm first initializes the column dispersed and continuous phase flow rates, extraction temperature, after which the nonlinear properties are calculated. The phase equilibria is calculated by non-random two-liquid (NRTL) model. The linearized conservation equations are written in matrix form and solved. New values for the mass flow rates are obtained, and the iteration is continued as long as the difference of initial and calculated value is less than $10E-7$.

4.2 CFD model

Modelling Approach. Eulerian two-phase model is used in the simulations with the aqueous primary phase and the secondary phase consisting of the 2MTHF droplets. Momentum and continuity equations are solved for each phase, with a single pressure shared by both phases. The extraction process involves mass transfer of levulinic acid from the water phase to the solvent droplets. In addition, a small amount of 2MTHF is dissolved from the droplets to water phase and water to the droplets. Therefore, each phase contains three material components, consisting of LA, 2MTHF, and water species. It would be beneficial to use population balance modeling with break up and coalescence predicting the droplet size distribution. This type of extraction column modeling has been done in 2D by Drumm et al. (2009) and Attarakih et al. (2015) using a one-scalar model for the population balance. Generally, the population balance models are not predicting reliably the size distribution without adapting the model to the process to be modeled. This would require experimentally determined droplet size distribution, which is not available for our case. In our 3D model, we have therefore settled on using constant average diameter (d_{32}) for the droplets. The values used for d_{32} are based on correlations for Kühni column reactor by Kumar and Hartland (1996), i.e. 1.09 mm for run 1 at 150 rpm, and 0.70 mm for runs 3 and 6 at 100 rpm. The droplets are reasonably spherical so that the standard Schiller-Nauman drag correlation was used on modeling the momentum exchange between the phases. Turbulent dispersion of the droplet phase is included in the model. Turbulence is modelled with mixture k - ϵ model, which is an extension of the standard model for multiphase processes. The model employs mixture velocities and properties in the equations for k and ϵ . The two layer zonal model of Fluent is applied for the near wall treatment. Wolfstein model is used near the wall, and blended with the k - ϵ model used in the fully turbulent region.

Model geometry. The purpose of the CFD modeling was to provide accurate flow field and information about local mass transfer inside the column compartments, not to model the whole length of the reactor. Therefore, a short section of the column, consisting of six compartments at 150.5-160 cm column height, was included in the model. Each compartment contains a four bladed disc turbine impeller attached to a common shaft. Between compartments, three vertical rods support circular down comer plates. Impeller blades, impeller discs and down comer plates are described as infinitely thin surfaces in the mesh, otherwise the geometry description is accurate. The computational grid consists of 1.04 million cells. The sliding mesh model is used in the simulations, with the rotating part of the grid moving physically relative to the stationary part along the grid interface in discrete steps in time dependent calculation. The rotating part contains the impeller and part of the shaft, and the stationary part the rest of the modelled geometry in the present simulation.

Mass transfer model in CFD simulations. Mass transfer modeling in CFD simulations is simplified by considering mass transfer of only LA species between continuous and dispersed phases. The molar mass transfer rate on the phase interface is described by equation

$$n_{LA} = k_c A_d (c_{cLA} - c_{cLA}^*) = k_d A_d (c_{dLA}^* - c_{dLA}) \quad (18)$$

Or using the overall mass transfer coefficient

$$n_{LA} = k A_d (K_{dLA} c_{cLA} - c_{dLA}) \quad (19)$$

The overall mass transfer coefficient were defined as seen in equations (10) and (11). Droplet interfacial area in computational cell equals $A_d = 6\phi_d V_{cell}/d_d$.

Mass transfer in continuous phase is described by

$$k_c = Sh_c D_e / d_d \quad (20)$$

And in dispersed phase by

$$k_d = Sh_d D_e / d_d. \quad (21)$$

Sherwood numbers Sh_c and Sh_d are obtained from equations for single drop following work of Kumar and Hartland (1999):

$$\frac{Sh_c - Sh_{c,rigid}}{Sh_{c,\infty} - Sh_c} = 0.0526 Re_d^{1/3 + 0.0659 Re_d^{1/4}} Sc_c^{1/3} \left(\frac{U_{slip} \mu_c}{\gamma} \right)^{1/3} \frac{1}{1 + \kappa^{1.1}} \quad (22)$$

Where $Sh_{c,rigid}$ and $Sh_{c,\infty}$ are defined as in equations (13) and (14), and

$$Sh_d = 17.7 + \frac{0.00319 (Re_d Sc_d^{1/3})^{1.7}}{1 + 0.0143 (Re_d Sc_d^{1/3})^{0.7}} \left(\frac{\rho_d}{\rho_c} \right)^{2/3} \frac{1}{1 + \kappa^{2/3}} \quad (23)$$

In the simulations the value for the LA diffusion coefficient in the continuous phase was $D_e = 1.0 \cdot 10^{-9}$. Mass transfer between continuous and dispersed phases, and appropriate species components, takes place by means of source and sink terms. Values for distribution coefficient in each run were based on equilibrium measurements for the levulinic acid-water-2MTHF system carried out in the earlier work.

Numerical Solution. The CFD simulations are carried out with ANSYS Fluent software version 16.0.0 with Linux cluster using 20-100 cores. Second order space discretization is used in the solution of the convective terms in the momentum, turbulence, dispersed phase volume fraction and species transport equations of the simulations. The pressure -velocity coupling is solved with phase coupled SIMPLE algorithm, and a first-order time discretization scheme is used. The time step size is chosen to correspond to a grid movement of 2.5° in the final stage of the calculation.

This leads to relatively minor steps and rather long computing times. The time step size ensures that the maximum Courant number in the computational domain is less than unity. In addition to monitoring residuals, integrals of phase and species fractions in compartments, as well as phase and species flow rates between compartments are tracked. The solution is considered converged to semi-steady state when these values remain constant. Extraction runs 1, 3 and 6 were simulated. The corresponding rotation speeds are 100 rpm, 150 rpm and 150 rpm, implying tip velocities 0.10 m/s and 0.16 m/s. Respective Reynolds numbers are 3200 – 4800, making the flow moderately turbulent.

5. Results and discussion

5.1 Experimental results

The experimental data including the LA concentration profiles in the extraction column at equilibrium, and hold-up is presented in Table 1. Two mass flow rates and three different rotor speeds were selected to measure the column overall performance, which can be expressed in terms of overall mass transfer coefficient k_a . Selected parameters including extraction column dimensions are introduced in Table 2. Further, values for interfacial tension, density, viscosity, and diffusion coefficient, applied in the models are given.

5.2 1D modeling results

The effect of agitation speed on column performance is seen in Fig. 3. A higher rotor speed results in smaller value of particle size as given in Table 3, and increased hold-up. The interfacial area available for mass transfer increases with both effects, and the column performance is enhanced. The numerical values for the mass transfer coefficient k_a ranges from 4.1E-3 to 14.7E-3 at the smaller mass flow rate (exp 4-6) and 8.0E-3 to 19.9E-3 at the higher rate (exp 1-3). Similar values,

i.e. from $5\text{E-}3$ to $13\text{E-}3$, for the overall mass transfer coefficient, have been measured for n-butylacetate-acetone-water and toluene-acetone-water systems in a 117 mm diameter Kühni column by Hemmati et al. (2014). The data measured by Dongaonkar et al. (1991) for the extraction system methyl isobutyl ketone (MIBK)-water-acetic acid in a 72.45 mm diameter Kühni column show k values in the range of $10\text{E-}5$, which are larger than calculated in this work, i.e. $1.4\text{E-}5$ to $2.2\text{E-}5$. Increasing the agitation rate to 180-200 rpm range in this work decreased further the particle size, and entrainment of the small particles increased eventually resulting in a second phase boundary at the bottom of the column. The dispersed phase hold-up increases with the dispersed phase velocity due to the accretion of the amount of dispersed phase droplets simultaneously increasing the interfacial area. The increase of turbulence was visually observed. With an increase of dispersed phase velocity, the drag forces arising from the relative velocity between a drop and continuous cause internal circulation and turbulence in drops, and the overall mass transfer coefficient will increase improving the column performance. Thus, higher values for the mass transfer coefficient were measured when the higher mass flow rate values (exp 1-3) were applied.

The experimental levulinic acid concentration points in the continuous phase along the column height were compared with the modeled points obtained from the 1D model at different solvent-to-feed ratios and rotor speeds as seen in Fig. 4. The results show, that the 1D fitting of the column performance resulted in a very good prediction of the solute concentration profiles in the extraction column, and the average absolute value of relative error was 23%. The 1D model is obviously more accurate at the lower section of the column, in which the dispersed solvent phase was introduced, and the change of levulinic acid concentration along the column is not large. However, there is clear deviation in the upper part of the extraction column, especially at the highest rotor speed selected (150 rpm). This is the part of the column, where the continuous phase feed is pumped in, and the mass transfer gradient is at its highest. According to Dongaonkar et al. (1991),

back mixing of the continuous phase is appreciable in a Kühni column with a diameter of 72.45 mm, while that of the dispersed phase is negligible. Their measured Kühni column profiles showed a typical “jump” at the continuous phase inlet due to the back mixing, and the absence of a jump at the dispersed phase inlet was observed. Similar kind of phenomena was noticed by Attarakih et al. (2015) while modeling the upper part of the RDC-column with a 1D detailed population balance model. Thus, the fast mass transfer rate and the back mixing phenomena taking place at the continuous phase inlet may be the reasons why fitting of the upper part of the column was more challenging. On the other hand, the absence of the back mixing and the slower mass transfer rate at the dispersed phase inlet resulted in a flatter concentration profile along the column, and a much better fit of the 1D model.

5.3 CFD modeling results

Levulinic acid concentration points at the column height 150.5-160 cm obtained from the CFD calculations can be seen in Fig. 4 for the experimental runs 1, 3, and 6. They seem to fit excellently with the experimental points. The CFD model gave hold-up values 8.9% (Run 1), 18.2% (Run 3), and 9.4% (Runs 6), whereas the experimental values for the same runs were 6.8%, 13.7%, and 9.4%. Fig. 5 shows the continuous phase velocity in the Kühni column compartments in experimental run 1 at 150 rpm, and the component axial velocity at the downcomer. It can be concluded, that compartments are well mixed with high velocities compared to the net flow through the reactor, and there is dramatic effect of the impeller blades. Based on the axial velocity simulation, it can be estimated that back mixing rate of water phase is 20-30 % of the downward net flow on the interface of two compartments. Coalesced layers below each plate do not disappear completely under selected conditions, which can be seen in Fig. 6. However, increasing the rotor speed results in smaller dispersed phase droplets and higher dispersed phase entrainment, which

eventually leads to phase inversion. Thus, the CFD model serves to identify the feasible operating conditions in the column. Fig. 7 shows the dispersed phase volume fraction and slip velocity contours, respectively. According to the CFD calculations, the volume fraction of the dispersed phase reaches the highest value close to the shaft just below the impeller disc. There are blind spots near the extraction column wall and above the down comer plates. The slip velocity value is obviously highest where the column diameter is smallest at the tip of the down comer plates. The LA mass transfer rate contour modeled in Fig. 8 is very similar to dispersed phase volume fraction. It makes sense to conclude that the mass transfer rate is highest just below the propeller due to the reason that the dispersed phase volume fraction is highest in the same location. Large volume of vigorously mixed solvent particles leads to high mass transfer rate. It is also worth noticing, that most of the mass transfer takes place in the middle section of the column, and large parts of each section, especially near the wall and above the down comer plates, are not efficient areas for mass transfer. In Fig. 9 levulinic acid mass fraction in droplets (left side) and water phase (right) can be seen. Both axial and vertical gradients can be detected. With the help of 3D two-phase CFD simulations, the flow fields inside the extraction column can easily be visualized in order to provide valuable information of the drop behavior, coalescence layers, and mass transfer in the Kühni column.

5.4 Comparison of 1D and 3D models

Compared to the CFD model, the 1D axial dispersion model is much faster to apply for scale-up purposes, and it can be used to predict the column performance, when the column parameters, such as feed flow rates and rotor speed etc. are changed. The 1D column model includes NRTL model for the system levulinic acid-water-2MTHF for the temperature range from 292.2 K to 328.2 K, which allows us to change the feed concentration, extraction temperature, and flow rates. CFD

model proved to be an excellent design tool, because it provided valuable information related to coalescence and mass transfer, and it revealed the existence of the blind spot in the column compartments. However, one CFD simulation run took weeks of running time, and therefore the efficient utilization of the CFD model in cases when quick answers are preferable is not yet possible.

6. Conclusions

Both 1D axial dispersion and 3D CFD models have been developed for the extraction of levulinic acid from dilute aqueous solutions by applying 2-methyltetrahydrofuran as a solvent to understand the complex hydrodynamic phenomena in mechanically agitated Kühni column. Models have been validated by comparison with the experimental extraction column levulinic acid concentration profile data. The models fit the experimental curve points with excellent accuracy especially at the lower section of the column, and successfully predicted the column concentration profile in a mechanically agitated Kühni column. 1D axial dispersion model contains NRTL phase equilibria model for the system levulinic acid-water-2MTHF, which is valid in the temperature range from 292.2 K to 328.2 K. Values for hold-up and dispersed phase drop size were taken from the correlations presented in literature. Mass flow rates of the phases, extraction temperature, rotor speed and concentration among others can be changed before each simulation, and axial dispersion model can be used for scale-up purposes. The numerical values for the mass transfer coefficient k_{da} ranges from 4.1E-3 to 14.7E-3 at the smaller mass flow rate (exp 4-6) and 8.0E-3 to 19.9E-3 at the higher rate (exp 1-3). The values increase as a function of rotor speed due to the reduced dispersed phase drop size. The average absolute value of the relative error in the predicted and measured column levulinic acid profiles is 23%. The results prove, that general correlations, such as hold-up and drop size correlations, can be successfully applied in modeling extraction systems,

such as levulinic acid - water - 2MTHF system reported in this work. CFD model visualized the column performance at the column height of 150.5 - 160 cm giving valuable information on back mixing, phase velocities, dispersed phase volume fraction, and mass transfer. Dispersed phase volume fraction and mass transfer contours revealed that the mass transfer rate is at its highest (app. $0.25 \text{ gL}^{-1}\text{s}^{-1}$) just below the rotor, and there are blind spots in the compartments close to the extractor and just above each down comer. Values for the dispersed phase volume fraction are the highest in the area where the mass transfer reaches the highest values. The highest slip velocity values (app. 0.03 m^{-1}) are located in the tip of the each compartment partition plates. Despite of the long time needed for each simulation, CFD proved to be a very valuable tool for design purposes.

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FIGURE CAPTIONS

Fig 1

Fig 1 - Comparison of measured and calculated hold-up values in a Kühni column for the system levulinic acid-water-2MTHF at different solvent-to-feed ratios.

Fig 2.

Fig 2 - Comparison of measured and calculated drop size values in a Kühni column for the system levulinic acid-water-2MTHF at different solvent-to-feed ratios.

Fig 3

Fig 3 - Overall mass transfer co-efficient k_a as function of Kühni column rotor speed.

Fig 4

Fig 4 - Comparison of experimental points with those obtained from model (1D) and CFD calculations.

Fig 5 (colour)

Fig 5 - Continuous phase velocity (ms^{-1})

Fig 6 (colour)

Fig 6 - Continuous phase axial velocity (ms^{-1}).

Fig 7 (colour)

Fig 7 - Dispersed phase volume fraction (left) and slip velocity magnitude (right as ms^{-1}).

Fig 8 (colour)

Fig 8 - Levulinic acid mass transfer rate ($\text{g L}^{-1}\text{s}^{-1}$).

Fig 9 (colour)

Fig 9 - LA mass fraction in dispersed droplet (left) and continuous water (right) phases.

TABLES

Table 1. Extraction of levulinic acid from dilute aqueous solution with 2MTHF in a Kühni ECR60/50G column.

No.	S/F ($\text{kg h}^{-1}/\text{kg h}^{-1}$)	N (rpm)	$\varnothing$ (%)	$x_{\text{LA, raf}}$ (wt%) 0 cm	x_{LA} (wt%) 23 cm	x_{LA} (wt%) 58 cm	x_{LA} (wt%) 93 cm	x_{LA} (wt%) 128 cm	x_{LA} (wt%) 163 cm	$x_{\text{LA, feed}}$ (wt%) 186 cm	$y_{\text{LA, ext}}$ (wt%)
1	12.5/13.9	100	7.92	0.08	0.17	0.39	0.75	1.39	2.70	4.32	4.78
2	12.2/14.0	125	11.11	0.02	0.11	0.14	0.40	0.95	2.36	4.35	5.02
3	12.0/14.3	150	16.04	0.01	0.04	0.11	0.27	0.66	2.19	3.91	5.19
4	8.3/9.4	100	3.98	0.06	0.13	0.32	0.67	1.30	2.66	4.11	4.78
5	8.4/9.2	125	6.94	0.02	0.05	0.10	0.28	0.72	2.10	4.10	4.58
6	8.4/9.0	150	10.86	0.01	0.03	0.07	0.19	0.53	1.97	4.11	4.74

Table 2. Selected parameter values used in models

Physical parameters of the equipment		
Active height of the column	1.86	m
Column's diameter	60	mm
Height of Column's compartment	30	mm
Rotor's diameter	48	mm
Number of agitated compartments	50	-
Free opening area of partition plates	30	%
Physical properties of the system		
Density of the continuous phase	997	kg m ⁻³
Density of the dispersed phase	854	kg m ⁻³
Viscosity of the continuous phase	0.790	mPa s
Viscosity of the dispersed phase	0.890	mPa s
Interfacial tension	3.50	N m ⁻¹
LA diffusion coefficient in the continuous phase	9.34×10^{-9}	m ² s ⁻¹
LA diffusion coefficient in the dispersed phase	2.4×10^{-9}	m ² s ⁻¹

Table 3. 1D modeling results

No.	d (mm)	a (m ² /m ³)	k _d (m/s)	k _e (m/s)	k (m/s)	ø (%)	E _e (m ² /s)			
1	1.08	379	4.47E-5	6.38E-5	2.16E-5	6.83	7.02E-5			
2	0.86	678	3.49E-5	3.67E-5	1.42E-5	9.75	8.54E-5			
3	0.70	1180	5.05E-5	3.83E-5	1.68E-5	13.68	1.01E-4			
4	1.11	258	3.43E-5	4.92E-5	1.66E-5	4.63	6.71E-5			
5	0.86	468	3.54E-5	3.91E-5	1.48E-5	6.71	8.21E-5			
6	0.68	807	5.12E-5	4.29E-5	1.81E-5	9.37	9.701E-5			