Acetic Acid Extraction from Fermentation Broth

Experimental and modelling studies

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This paper intends to emphasize the importance of adopting an effective recovery method for the solvent, in order to improve acetic acid extraction from the fermentation broth. Thus, liquid-liquid extraction was coupled with solvent recovery by stripping and by simple pseudo-continuous distillation and its recycling, in two different laboratory setups. Experimental procedures were performed with ethyl acetate, diethyl ether, and diethyl ether – hexane mixture, under different flow rate levels of the solvent. The effect of physicochemical properties of contacting phases, operating conditions (temperature, organic flow), and contacting hydrodynamics (number, dimension and ascending time of solvent drops) were investigated. Mathematical modelling of the processes is based on transport phenomena equations and describes the dynamic operation of the plants.

Keywords: acetic acid, liquid – liquid extraction, solvent recycling, mathematical modelling

Acetic acid is an important chemical species with multiple applications in chemical and food industries. In many industrial processes, it is used as solvent (in the pharmaceutical industry) or as raw material for other valuable products such as acetic esters.

Acetic acid can be obtained by synthetic route or by fermentation. In the last years, orientation to an environmentally friendly industry, determined an increased interest for acetic acid production via fermentation [1-6]. However, in the biosynthesis process, important quantities of aqueous solutions are produced, from which acetic acid should be economically recovered [7-10]. The separation of carboxylic acids (acetic acid in particular) from aqueous solutions by simple distillation or azeotropic distillation is difficult, requiring a column with many stages, a high reflux ratio or a great amount of azeotropic agent, which leads to a very expensive process [11].

Other processes can be used for separation, depending on the acetic acid concentration in the solution. For acid concentrations between 50 and 70% w/w, extractive distillation was studied [12]. In the extractive distillation, a convenient selection of the solvent is fundamental to ensure an effective and economical process [13]. For example, for acid concentrations lower than 40% w/w, liquid-liquid extraction can be an appropriate process [14-16].

Recent studies concerned to the efficient and economical separation of acetic acid refer to the use of the esterification agents, based on difference of acetic acid and acetic ester solubility in water [17-20]. Tertiary amines are considered highly efficient as extractants, especially used in capsulated systems in order to avoid emulsion formation and toxicity effect towards microorganisms [21-24]. The problem of toxicity of solvent can be partly solved by using membrane processes: ultrafiltration [25] electrodialysis [26], pervaporation [27-29], reverse osmosis [30-31], or pertraction [32].

Present paper focuses, in experimental and modelling way, on the acetic acid separation from fermentation broth, when the liquid-liquid extraction coupled with continuous solvent recycling is the working procedure. As solvents, ethyl acetate, diethyl ether, and diethyl ether- hexane mixtures were tested, because of some common characteristics: low boiling point and low acquisition price (in order to minimize energy costs, especially in the distillation stage) and compatibility with food industry.

Experimental part

Fermentation broths that contain acetic acid were obtained in a laboratory experimental setup whose construction was described elsewhere [33]. The initial acetic acid concentration in the used fermentation broths was 20 $g{\cdot}L^{-1}$ and 50 $g{\cdot}L^{-1}$. The organic (solvent) phase was diethyl ether, ethyl acetate and mixture of diethyl ether and hexane. Acetic acid concentration was determined by titration with NaOH 0.1N. The experiments were conducted in two different laboratory experimental setups. Both contain an extraction column, charged with the fermentation broth up to 90 % of the full capacity, to allow organic phase accumulation at the top. Reextraction column is also charged up to 90 % of the full capacity with the sodium hydroxide solution (stripping agent). In figure 1, process flow sheets are presented.

In the first procedure, a piston pump maintains solvent circulation (as dispersed drops) at G_y fixed flow rate, through the continuous phase, charged in the extraction column (of volume V_{a1}). The drops are accumulating at the top of the extraction column as organic phase of volume V_{o1}. From this first storage zone, solvent streams through the stripping column, and accumulates at the top of the column as organic phase of volume V_{o2}. From the second storage zone, the solvent flows in the recycling vessel of volume V_{o3}, and from here, its circulation is restarted. Acetic acid, extracted from the fermentation broth, in the organic phase, is reextracted in the stripping column as sodium acetate. The reaction between acetic acid and sodium hydroxide takes places at the organic drops surface, and is considered instantaneous and irreversible.

In the second experimental setup, a simple distillation unit replaces reextraction column (fig.1b). From the first storage zone, the solvent, containing extracted acetic acid, is pumped in the distillation reboiler, which has the working volume V_{o2}. The vapours produced by the reboiler, are condensed, and collected in the distillation plant collector,

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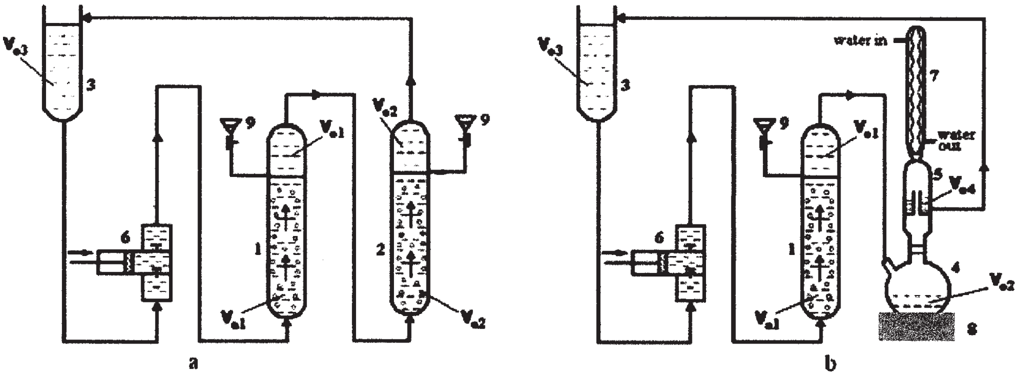


Fig. 1. Process flow sheet
a) liquid-liquid extraction coupled with solvent recovery and recycling by stripping, b) liquid-liquid extraction coupled with solvent recovery and recycling by simple distillation, 1 – extraction column; 2 – stripping column, 3 – solvent recycling vessel; 4 – distillation reboiler; 5 – solvent collector; 6 – piston pump; 7 – condenser; 8 – heat source; 9 – solutions feed; V_{o1}, V_{o2}, V_{o3}, V_{o4} – volume of solvent storage zones; V_{a1} – volume of the fermentation broth; V_{a2} – volume of the stripping solution

which has the constant volume V_{o4}. Because of the big difference between boiling points of solvent and acetic acid, the vapours can be considered free of acid (pure solvent). Before recycling, the solvent is collected in a storage vessel of V_{o3} volume.

Mathematical modelling

<u>Modelling liquid-liquid extraction coupled with solvent recovery and recycling by stripping</u>

In the development of mathematical model, the following assumptions have been made:

-all volumes (V_{a1},V_{o1},V_{o2},V_{o3}) are constant and perfectly mixed;

-contact time between the two phases in the two columns is equal with drops ascending time;

-drops size is considered uniformly distributed between R_{min} and R_{max};

-acetic acid transfer between liquid and drops in the extraction column is a pure diffusive process with type III boundary conditions at drop surface;

-in the stripping column, diffusive transport is accompanied by an interfacial, instantaneous, irreversible chemical reaction at the drop surface;

According to the assumption given above, the model equations are as follows:

-flow rate of dispersed phase (disperse phase is recycled with a piston pump):

$$G_v = \begin{cases} G_{VM} \cdot \sin(2\pi n\tau) \ \text{for} \ \sin(2\pi n\tau) > 0 \\ 0 \ \text{for} \ \sin(2\pi n\tau) < 0 \end{cases} \tag{1}$$

-acetic acid differential balance equation for the continuous phase in the extraction column, and associated boundary conditions:

$$-V_{a1}\frac{dC_{a1}}{d\tau} = G_V\left(C_{o3} - \overline{C}_{o1}\right) \tag{2}$$

$$\tau = 0, \quad C_{a1} = C_{a1,0} \quad C_{o3} = 0 \quad \overline{C}_{o1} = 0, \quad C_{o2} = 0, \quad C_{o3} = 0 \tag{3}$$

-acetic acid concentration field, boundary and initial conditions for a rising drop in the extraction column:

$$\frac{\partial C_{d1}}{\partial \tau} = D_{o1}\left(\frac{\partial^2 C_{d1}}{\partial r^2} + \frac{2}{r}\cdot\frac{\partial C_{d1}}{\partial r}\right) \tag{4}$$

$$\tau = 0; \quad 0 < r < R_1; \quad C_{d1} = C_{o3} \tag{5}$$

$$0 < \tau < \tau_{as,1}; \quad r = 0; \quad \frac{\partial C_{d1}}{\partial r} = 0 \tag{6}$$

$$0 < \tau < \tau_{as,1}; \quad r = R_1; \quad D_{o1}\frac{dC_{d1}}{dr} = K_1\left(C_{a1} - \frac{C_{d1}}{K_{d1}}\right) \tag{7}$$

-solute distribution between the two contacting phases from the extraction column:

$$C^*_{d1} = K_{d1}C_{a1} \tag{8}$$

-average concentration of acetic acid in the drops at its entrance in the first organic phase storage zone [34]:

$$\overline{C}_{o1} = \frac{1}{R_{max} - R_{min}} \cdot \int_{R_{min}}^{R_{Max}} \left(\frac{1}{R_1}\int_0^{R_1} C_{d1}(r,\tau_{as,1})\,dr\right) dz \tag{9}$$

-balance equation for the extracted species in the first storage zone:

$$V_{o1}\frac{dC_{o1}}{d\tau} = G_V\left(\overline{C}_{o1} - C_{o1}\right) \tag{10}$$

$$\tau = 0, \qquad C_{o1} = 0 \tag{11}$$

For the stripping section (stripping column), model equations can be written by accepting the following supplementary assumptions:

-active component from the drops (A) reacts at the interface with the reextraction agent (B) by a three stages sequence:

$$A_{org} \rightarrow A_{org\,/interface}$$

$$A_{org\,/interface} + bB_{1\,/interface} \rightarrow C_{1\,/interface}$$

$$C_{1\,/\,interface} \rightarrow C_1$$

-chemical reaction, occurs at a reaction front which has the position determined by the values of reactant B concentration in the stripping liquid. The component A (acetic acid) flux from drops to the interface is equal, as shown in the relation (12), with the flux from interface to continuous phase. This consideration shows that relation (14) gives the component B critical concentration. Concentration decreases in time, because the component B (sodium hydroxide) is consumed in the chemical reaction.

$$N_{A_T} = K_{d2} \cdot (\overline{C}_{o2} - C_{Ai}) = K_2 \cdot \left(C_{Ai} + \frac{1}{b} \cdot \frac{D_B}{D_{o2}} \cdot C_{B1} \right) \quad (12)$$

$$C_{Ai} \cdot (K_{d2} + K_2) = K_{d2} \cdot \overline{C}_{o2} - K_2 \cdot \frac{1}{b} \cdot \frac{D_B}{D_{o2}} \cdot C_{B1} \quad (13)$$

Because reaction takes place at the interface, $C_{Ai} = 0$:

$$C_{Bcr} = b \frac{K_{d2}}{K_2} \frac{D_o}{D_B} \overline{C}_{o2} \quad (14)$$

-when the concentration of the reactant B, in the stripping liquid, is higher than its critical value ($C_B > C_{Bcr}$) the phenomenological model shows that the stripping process is controlled, as shown in relations (15-18), by the diffusion of active component A in the organic drops:

$$\frac{\partial C_{d,2}}{\partial \tau} = D_{o2} \cdot \left(\frac{\partial^2 C_{d,2}}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C_{d,2}}{\partial r} \right) , \quad (15)$$

$$\tau = 0 ; \; 0 \prec r \prec R_2 ; \; C_{d,2} = C_{0,1} ; \quad (16)$$

$$0 \prec \tau \prec \tau_{as,2} ; \; r = 0 ; \; \frac{\partial C_{d,2}}{\partial r} = 0 ; \quad (17)$$

$$0 \prec \tau \prec \tau_{as,2} ; \; r = R_2 ; \; C_{d,2} = C_{A,i} ; \quad (18)$$

-average concentration of the active component (acetic acid) in the drop, at the exit of the stripping column:

$$\overline{C}_{o2} = \frac{1}{R_{max} - R_{min}} \cdot \int_{R_{min}}^{R_{Max}} \left(\frac{1}{R_2} \int_0^{R_2} C_{d2}(r,\tau) dr \right) dz \quad (19)$$

The process mathematical model is completed by the following equations:

-balance equations for acetic acid in the second storage zone and in the storage vessel:

$$V_{o2} \frac{dC_{o2}}{d\tau} = G_V \left(\overline{C}_{o2} - C_{o2} \right) \quad (20)$$

$$V_{o3} \frac{dC_{o3}}{d\tau} = G_V \left(\overline{C}_{o3} - C_{o3} \right) \quad (21)$$

- initial conditions associated with the last differential relations:

$$\tau = 0; \; C_{o2} = C_{o3} = 0 \quad (22)$$

Modelling liquid – liquid extraction coupled with solvent recovery and recycling by simple, pseudo-continuous distillation

Model assumptions include those afore-mentioned, for the liquid-liquid extraction column, and the following assumptions, for the simple distillation unit:

-perfect mixing of contacting phases in the distillation reboiler;

-inlet flow and outlet flow are equal;

-the feed of the distillation unit is a binary mixture of solute (acetic acid) and solvent;

-operation at constant pressure, and the liquid-vapors equilibrium accepts an ideal description (constant relative volatility of solvent with respect to the solvent/acetic acid mixture);

Models equations contain the group of (1) to (11) equations and the following (23-31), which give the model for distillation unit-recycling vessel assembly:

-solvent balance equation with respect to distillation unit, with initial condition:

$$\frac{dx}{d\tau} = \frac{G_v}{V_{o2}} (x_0 - y) \quad (23)$$

$$\tau = 0, \; x = x_0 = 0.99 \quad (24)$$

-relation for vapours-liquid equilibrium in the bottom of the simple distillation unit:

$$y = \frac{\alpha x}{1 + (\alpha - 1)x} \quad (25)$$

-boiling temperature of the bottom mixture:

$$p_f = x * 10^{\left(A_s - \frac{B_s}{t_f + C_s} \right)} + (1 - x) * 10^{\left(A_a - \frac{B_a}{t_f + C_a} \right)} \quad (26)$$

-relative volatility between solvent and acetic acid:

$$\alpha = \frac{10^{\left(A_s - \frac{B_s}{t_f + C_s} \right)}}{10^{\left(A_a - \frac{B_a}{t_f + C_a} \right)}} \quad (27)$$

-acetic acid balance equation for the condenser of distillation unit, and the initial conditions:

$$V_{o4} \frac{dc_{o4}}{d\tau} = \frac{G_v \rho_{ls}}{M_s} y - G_V c_{o4} \quad (28)$$

$$\tau = 0, \; V_{o4} = V_{o40}, \; c_{o4} = c_{o40} = 0 \quad (29)$$

-the acetic acid balance equation for the storage vessel and its associated initial condition:

$$V_{o3} \frac{dc_{o3}}{d\tau} = G_V (c_{o4} - c_{o3}) \quad (30)$$

$$\tau = 0, \; c_{o3} = 0, \; V_{o3} = V_{O30} \quad (31)$$

Results and discussions

In case of coupled liquid-liquid extraction of acetic acid with solvent recovery and recycling by stripping, initial acetic acid concentrations were $C_{a10}=20$ g·L^{-1}, $C_{o1}=C_{o2}=C_{o3}=C_{a2}=0$ g/L (table 1). The experiments were conducted with three different types of solvents: pure ethyl acetate, pure diethyl ether, and diethyl ether - hexane mixture (mixture – 2:1 v/v).

Figures 2 and 3 present the dynamics of acetic acid concentration in the extraction column and show the experimental uptakes in different experimental conditions and a comparison between experiment (points) and theory (lines).

In case of coupled liquid-liquid extraction of acetic acid with solvent recovery and recycling by simple distillation, initial acetic acid concentration was increased at $C_{a10}=50$ g·L^{-1} (table 2). The same three different types of solvents were used.

In figures 4 and 5 are presented the experimental uptakes and the comparison between experimental data (points) and model predictions (lines).

Although in these experiments acetic acid concentration was increased, and solvent flow rate was decreased, extraction process was intensified. With 250 mL solvent, in two hours for example, at 3.3·10^{-7} m^{3}s^{-1} ethyl acetate

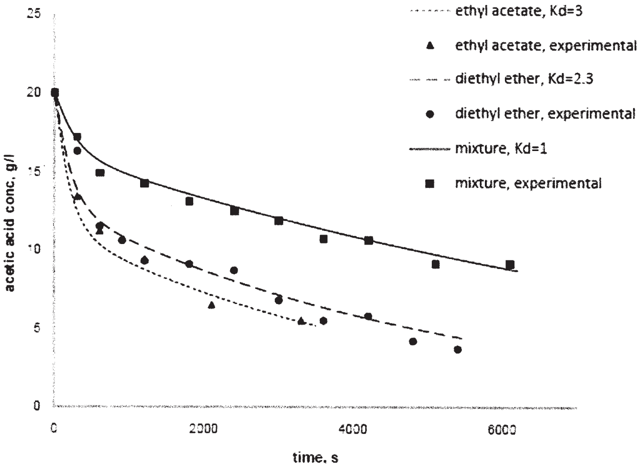


Fig. 2. Experimental and calculated acetic acid concentration vs. time (solvent flow rate $G_v=6.7\cdot10^{-7}$ m^3s^{-1})

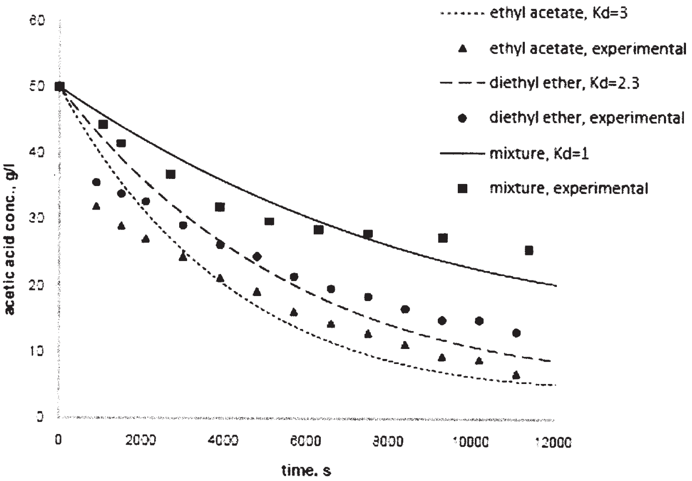


Fig. 4. Experimental and calculated acetic acid concentration vs. time (solvent flow rate $G_v=1.7\cdot10^{-7}$ m^3s^{-1})

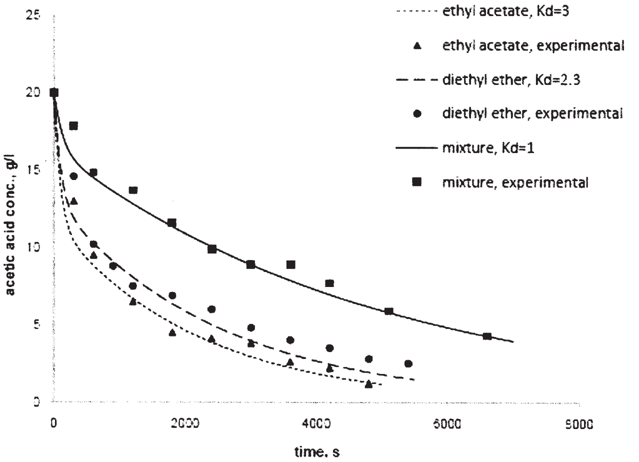


Fig. 3. Experimental and calculated acetic acid concentration vs. time (solvent flow rate $G_v=1.3\cdot10^{-6}$ m^3s^{-1})

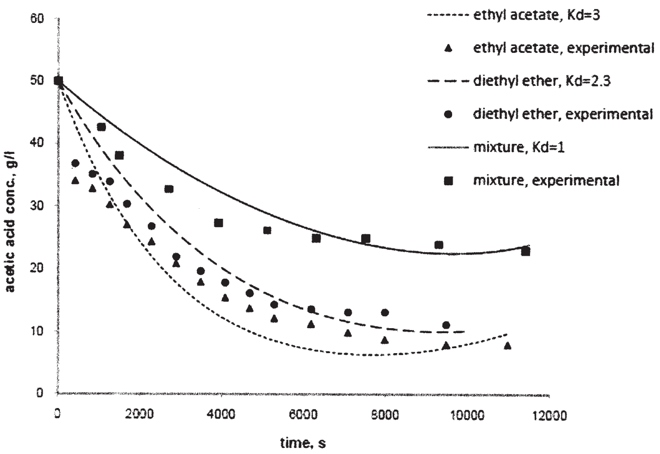
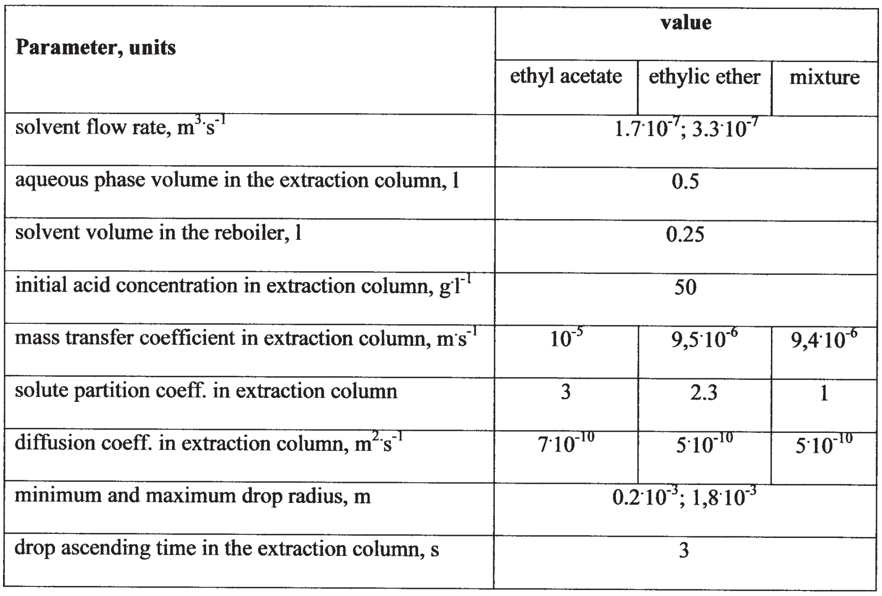


Fig. 5. Experimental and calculated acetic acid concentration vs. time (solvent flow rate $G_v=3.3\cdot10^{-7}$ m^3s^{-1})

Table 1
PROCESS AND MASS TRANSFER PARAMETERS IN THE CASE OF COUPLED LIQUID-LIQUID EXTRACTION OF ACETIC ACID WITH SOLVENT RECOVERY AND RECYCLING BY STRIPPING

Parameter, units	**value**		
	ethyl acetate	ethyl acetate	mixture
solvent flow rate, $m^3\cdot s^{-1}$	$6.7\cdot10^{-7}$; $1.3\cdot10^{-6}$		
aqueous phase volume in the extraction column, l	0,5		
aqueous phase volume in reextraction column, l	2		
initial concentration of the stripping agent, $g\cdot l^{-1}$	20		
initial acid concentration in extraction column, $g\cdot l^{-1}$	20		
mass transfer coefficient in extraction column, $m\cdot s^{-1}$	$2.1\cdot10^{-6}$	$2\cdot10^{-6}$	10^{-6}
mass transfer coeff. in reextraction column, $m\cdot s^{-1}$	10^{-5}	10^{-5}	$2\cdot10^{-6}$
solute partition coeff. in extraction column	3	2.3	1
solute partition coeff. in reextraction column	1.5	1.1	0.8
diffusion coeff. in extraction column, $m^2\cdot s^{-1}$	$7\cdot10^{-10}$	$7\cdot10^{-10}$	$5\cdot10^{-10}$
diffusion coeff. in reextraction column, $m^2\cdot s^{-1}$	$8\cdot10^{-10}$	$8\cdot10^{-10}$	$6\cdot10^{-10}$
minimum and maximum drop radius, m	$0.5\cdot10^{-3}$; $2\cdot10^{-3}$		
drop ascending time in the extraction column, s	3		
drop ascending time in the reextraction column, s	4		



Parameter, units	value		
	ethyl acetate	ethylic ether	mixture
solvent flow rate, $m^3 \cdot s^{-1}$	$1.7 \cdot 10^{-7}$; $3.3 \cdot 10^{-7}$		
aqueous phase volume in the extraction column, l	0.5		
solvent volume in the reboiler, l	0.25		
initial acid concentration in extraction column, $g \cdot l^{-1}$	50		
mass transfer coefficient in extraction column, $m \cdot s^{-1}$	10^{-5}	$9{,}5 \cdot 10^{-6}$	$9{,}4 \cdot 10^{-6}$
solute partition coeff. in extraction column	3	2.3	1
diffusion coeff. in extraction column, $m^2 \cdot s^{-1}$	$7 \cdot 10^{-10}$	$5 \cdot 10^{-10}$	$5 \cdot 10^{-10}$
minimum and maximum drop radius, m	$0.2 \cdot 10^{-3}$; $1{,}8 \cdot 10^{-3}$		
drop ascending time in the extraction column, s	3		

Table 2
PROCESS AND MASS TRANSFER PARAMETERS IN THE CASE OF LIQUID – LIQUID EXTRACTION COUPLED WITH SOLVENT RECOVERY AND RECYCLING BY SIMPLE, PSEUDO-CONTINUOUS DISTILLATION

extracted about 88 % and diethyl ether about 83 % of the initial quantity of acetic acid introduced in the extraction column.

In order to apply the model to experimental data, some model parameters were estimated and computed using adequate relationships (case of diffusion coefficients, relative volatility, etc) or have been experimentally measured (R_{max}, R_{min}, τ_{as}) (table 1 and 2).

Conclusions

Two pilot plants for liquid-liquid extraction coupled with solvent recovery have been realized. Experimental setups were used to study acetic acid separation from fermentation broth. Experimental data shows that coupling acid extraction with solvent recovery and recycling by continuous, steady-state fractional distillation, intensifies the process, and allows obtaining highly concentrate acetic acid solutions, with convenient energy consumption (relative to the classical water-acetic acid distillation process). For diluted acetic acid fermentation broths, coupled liquid-liquid extraction with solvent recovery and recycling by simple distillation or stripping can also be applied.

Extraction with ethyl acetate as pure solvent is faster and apparently more efficient than extraction with diethyl ether or mixtures, but, two major drawbacks, high water solubility and alkaline hydrolysis in hydroxide medium, lead to an increased solvent demand. Diethyl ether also has proved to be a good extraction agent, but because of its inflammability, diethyl ether- hexane mixture was tested, even if, for this mixture, lower distribution coefficient was measured. Regardless the type of solvent, and the experimental setup, increasing solvent flow rate has a positive effect on the extraction process.

The mathematical model that describes coupling of liquid-liquid extraction with solvent recovery was developed. Comparison between model prediction and experimental data shows a good agreement between theoretical and experimental curves.

Symbols

A,B,C - Antoine coefficients
b - stoichiometric coefficient of B component (sodium hydroxide) in the chemical reaction
C_{al} - acetic acid concentration in the extraction column (aqueous phase) ($g\ l^{-1}$)
C_{Ai} - acetic acid concentration at the interface ($mol\ L^{-1}$)
C_{al0} - initial acetic acid concentration in the extraction column ($g\ L^{-1}$)
C_B - component B (sodium hydroxide) concentration ($mol\ L^{-1}$)
C_{Bcr} - critical component B(sodium hydroxide)concentration ($mol.L^{-1}$)
C_{oi} - acetic acid concentration in organic phase, in storage zone "i" ($g\ L^{-1}$)
$\overline{C}_{oi}$ - average acid molar concentration in organic phase, in storage zone i ($mol\ L^{-1}$)
C_d - acid molar concentration in the disperse phase ($mol\ L^{-1}$)
C^*_d - acid molar concentration in the disperse phase in equilibrium with continuous phase ($mol\ L^{-1}$)
d_p - drop diameter (m)
D_o - acetic acid diffusion coefficient in drops ($m^2\ s^{-1}$)
D_B - component B (sodium hydroxide) diffusion coefficient in drops ($m^2\ s^{-1}$)
g - acceleration of gravity ($m\ s^{-2}$)
G_V - solvent volumetric flow rate ($m^3\ s^{-1}$)
G_{VM} - momentary solvent volumetric flow rate ($m^3\ s^{-1}$)
K - overall mass transfer coefficient ($m\ s^{-1}$)
K_d - partition coefficient
M - molecular weight ($g\ mol^{-1}$)
N_{Ar} - acetic acid flux
p_f - vapor pressure (torr)
R - average drop radius (m)
Re - Reynolds number
R_{max} - maximum drop radius (m)
R_{min} - minimum drop radius (m)
r - current radius (m)
Sh - Sherwood number
t_f - boiling point (°C)
V_{al} - volume of the extraction column (acetic acid solution volume) (m^3)
V_{oi} - volume of storage zone "i" (organic phase volume) (m^3)
x - acetic acid mole fraction in the liquid phase
y - acetic acid mole fraction in the vapor phase
z - flow direction

Greek symbol

α - volatility coefficient (Fenske equation)
β_n - dimensionless parameter for analytic solution (depending on the radius)

ρ_{ls} - solvent mean density (kg m^{-3})
τ - current time (s)
τ_{as} - drop ascending time (s)

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