

Recovery of Acetic Acid from An Ethanol Fermentation Broth by Liquid-Liquid Extraction (LLE) Using Various Solvents

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Abstract – Liquid-liquid extraction (LLE) using various solvents was studied for recovery of acetic acid from a synthetic ethanol fermentation broth. The microbial fermentation of sugars presented in hydrolyzate gives rise to acetic acid as a byproduct. In order to obtain pure ethanol for use as a biofuel, fermentation broth should be subjected to acetic acid removal step and the recovered acetic acid can be put to industrial use. Herein, batch LLE experiments were carried out at 25°C using a synthetic fermentation broth comprising 20.0 g l⁻¹ acetic acid and 5.0 g l⁻¹ ethanol. Ethyl acetate (EtOAc), tri-*n*-octylphosphine oxide (TOPO), tri-*n*-octylamine (TOA), and tri-*n*-alkylphosphine oxide (TAPO) were utilized as solvents, and the extraction potential of each solvent was evaluated by varying the organic phase-to-aqueous phase ratios as 0.2, 0.5, 1.0, 2.0, and 4.0. The highest acetic acid extraction yield was achieved with TAPO; however, the lowest ethanol-to-acetic acid extraction ratio was obtained using TOPO. In a single-stage batch extraction, 97.0 % and 92.4 % of acetic acid could be extracted using TAPO and TOPO when the ratio of organic-to-aqueous phases is 4:1 respectively. A higher solvent-to-feed ratio resulted in an increase in the ethanol-to-acetic acid ratio, which decreased both acetic acid purity and acetic acid extraction yield.

Key words: Acetic Acid, Ethanol, Fermentation, Liquid-liquid Extraction, Partition Coefficient

1. Introduction

With the increasing global demand for energy and declining resources of fossil fuels, renewable energy resources continue to gain importance for energy production. In particular, bioethanol production from various renewable sources, including agricultural residues, woods, and cellulosic residues from pulp and paper production facilities, through fermentation has great potential to replace the conventional transportation fuel [1].

Acetic acid is a normal end-product of alcoholic fermentation in the biorefinery process, and can also be formed by *Saccharomyces cerevisiae*; additional amounts may be produced after alcoholic fermentation by lactic acid bacteria [2-5] and/or acetic acid bacteria [6]. The concentration of acetic acid produced during alcoholic fermentation may vary with the species of strains [7,8], the composition of hydrolysates [9], and other physical factors [10,11]. Acetic acid is projected to be recovered as a valuable coproduct using liquid-liquid extraction followed by stripping and distillation. Acetic acid is an important platform chemical in the synthesis of many valuable chemicals, such as cellulose acetate, vinyl acetate, acetic acid esters, terephthalic acid, and so on. The demand for acetic acid has accelerated

in recent years [12] owing to increased demand for derivatives such as the vinyl acetate monomer (VAM). Currently, acetic acid is produced primarily from non-renewable feedstock, for example, by methanol carbonylation [12,13]. Market prices of acetic acid (\$1.2 kg⁻¹, 2010 level) are considerably higher than the price predictions for ethanol (\$0.05~0.15 kg⁻¹, 2011 level). Therefore, if such a recovery process could be integrated into the biorefinery process for biofuel production, extraction and utilization of acetic acid from the fermentation broth could significantly boost the economic attractiveness of whole biorefinery process, in addition to improving the purity of main product, ethanol.

The extraction of acetic acid from an ethanol fermentation broth needs to be cost effective to compete with synthetic processes. Current methods of extracting acetic acid from ethanol fermentation broths are time consuming and costly. Various techniques for the separation of organic acids from complex mixtures have been reported, examples of which include (catalytic) distillation [14], adsorption using ion-exchange resins [15], and micro-emulsion liquid membrane separation [16]. Successful extraction of acetic acid from aqueous solution into an organic phase using the liquid-liquid extraction (LLE) process has been achieved with various solvents in our laboratory [17]. Organophosphorus compounds and alkylamines with high molecular weight, dissolved in various diluents, have been explored for liquid-liquid extraction (LLE) of acetic acid from dilute aqueous solution. The partition coefficients for these systems vary between 3 and 5 [17,18-21]. A molar loading of greater than one was deduced by Senol [19] for

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the removal of carboxylic acids from water using alamine 336 in halogenated hydrocarbon diluents. The use of trioctylphosphine oxide (TOPO) as an extractant for the removal of fatty acids from aqueous solutions is discussed in several papers [18,22-29]. Due to its high hydrogen bonding acceptor basicity, TOPO undergoes strong complexation with carboxylic acids in the organic phase, thereby enhancing the transfer of the carboxylic acid into the extract phase. In addition, TOPO is characterized by excellent stability, a high boiling point, and low solubility in water. Al-Mudhaf *et al.* [28] reported the separation of acetic acid from aqueous NaCl solutions into cyclohexane containing various concentrations of TOPO (as an extractant) at 30 °C. They concluded that optimized TOPO use is required for economic organic acid recovery and that the sensitivity towards salts increases with increasing distribution ratio based on the evident effect that free TOPO is able to complex with a larger number of acetic acid molecules when acetic acid salted out from the aqueous phase. The current study utilizes a distillation process that facilitates recovery and reuse of the solvents being studied from the organic phase containing acetic acid.

The primary objective of this study is to evaluate the separation process of acetic acid from a synthetic ethanol fermentation broth by using various solvents in a batch LLE. The effectiveness of the solvents for separation and the optimal solvent-to-feed ratio are determined herein. Based on the objective to obtain pure acetic acid in the extracted organic phase, the extraction yield of ethanol is also determined.

2. Materials and Methods

2-1. Fermentation broth preparation

A synthetic fermentation broth was prepared in the laboratory; a solution of 2.0% (w/v) acetic acid (Cat No. 320099, >99.7% purity, Sigma-Aldrich, St. Luis, MO, USA) and 0.5% (w/v) ethanol (Cat No. 459844, >99.5% purity, Sigma-Aldrich, St. Luis, MO, USA) was used as a model fermentation broth. The pH of the solution was measured to be 2.59. The concentration of each component corresponded to the average values reported in the literature representing a typical ethanol fermentation broth [30].

2-2. Extractant preparation

Tri-*n*-octylphosphine oxide solution (TOPO) (CYTEC Inc., 93.0% purity, Woodland Park, NJ, USA) was diluted with alkane (Sigma-Aldrich, >99.0% purity, St. Luis, MO, USA), i.e. diluent ratio of 37.0% (w/w), that was heated to 60 °C in order to dissolve the TOPO. Trioctylamine (TOA) (Cat. No. T81000 >98.0% purity, Sigma-Aldrich, St. Luis, MO, USA) was prepared by diluting the extractant in 1-octanol (Alfa Aesar, 99.0% purity, Ward Hill, MA, USA), i.e. diluent ratio of 20.0% (w/w). Ethyl acetate (EtOAc) (Cat. No. 270989, >99.5% purity, Sigma-Aldrich, St. Luis, MO, USA) and tri-*n*-alkylphosphine oxide (TAPO) (CYTEC Inc., 93.0% purity, Woodland Park, NJ, USA) were used as received. Table 1 summarizes the sol-

vent/diluent percentages optimized in our previous work [17].

2-3. Experimental and analytical procedures

The liquid-liquid extraction (LLE) of acetic acid was run using EtOAc, TOPO, TOA, and TAPO solvents at five different solvent-to-feed ratios of 0.2, 0.5, 1.0, 2.0, and 4.0. The typical extraction procedure for each experiment was initiated by the addition of the organic phase and aqueous solution into a 250 ml separatory funnel. Extraction was conducted in batch mode with vigorous shaking for 6 seconds, and subsequent intermittent shaking a six minute intervals at 25 °C. The sample was then allowed to settle at 25 °C for 20 minutes for separation of the two phases. Samples of both phases were analyzed immediately after the phase separation. The concentration of acetic acid in the aqueous phase was determined using HPLC. The Shimadzu model (LC-20AT Liquid Chromatogram, Shimadzu Corp., Kyoto, Japan) HPLC used for carbohydrate measurement had a Bio-Rad Aminex HPX-87H column (300 mm × 7.8 mm) and Cation H micro-guard cartridge (30 mm × 4.6 mm), (Bio-Rad Laboratories Inc., Hercules, CA), the HPLC column operation conditions were as follows: column temperature: 65°C, flow rate: 0.6 ml min⁻¹, mobile phase: 0.005 M sulfuric acid. The concentration of acetic acid in the organic phase was determined by means of GC (gas chromatography) (Shimadzu model GC-2010, Shimadzu Corp., Kyoto, Japan), equipped with a FID (flame ionization detector) and using a Rtx 5 column (Restek Corp., Bellefonte, PA, USA). The GC injector and detector temperatures were set at 280 °C and 340 °C, respectively. Helium was used as a carrier gas at 30 ml min⁻¹.

2-4. Partition coefficient (P_c) and extraction yield

The equilibrium partitioning of acetic acid between the two phases was evaluated based on the partition coefficient (P_c) under the various evaluated conditions, where P_c is defined as:

$$P_c = \frac{[\text{HAc}]_{org}}{[\text{HAc}]_{aq}} \quad (1)$$

where [HAc] is the acetic acid concentration; the subscript “org” denotes the concentration of acid extracted from the aqueous phase into the organic phase; and the subscript “aq” denotes the concentration of acid remaining in the aqueous phase. An alternate means of expressing the extraction efficiency is as percentage extraction. The percentage extraction is defined as the fraction of acetic acid removed from the aqueous phase into the organic phase in one extraction step, as defined below:

$$\% \text{ Extraction} = \left(1 - \frac{[\text{HAc}]_{remaining\ aq}}{[\text{HAc}]_{initial\ aq}} \right) \times 100 \quad (2)$$

2-5. ASPEN HYSYS simulation

HYSYS software (Version 7.1) was used to simulate the liquid-liquid extraction of acetic acid from a model fermentation broth using ethyl acetate as a solvent. TOPO, TOA, and TAPO extractions were not simulated because the chemical properties of these species

are not programmed into HYSYS. The effectiveness of ethyl acetate as an extraction solvent was determined from the simulation parameters in terms of the counter-current liquid-liquid extraction simulation and the recyclability of the solvent in the simulated distillation process. The thermodynamic fluid package, UNIQUAC (universal quasi-chemical), with the Soave-Redlich-Kwong (SRK) function was used based on the use of organic compounds used in the simulation. The LLE column was designed with zero pressure-drop and defaulted to 10 trays, starting and ending at 121.6 kPa. The distillation column was set at 10 trays with no pressure drop. The reboiler and condenser pressure was set at 200 kPa. The condenser was set to collect the distillate after condensation back to the liquid phase at the bottom of the condensate tank. The counter-current liquid-liquid extraction simulation with solvent distillation was simulated to observe both the effectiveness of EtOAc as a solvent in a counter current liquid-liquid extraction procedure and the recyclability of EtOAc. The fermentation broth feed stream was kept at a constant mass flow rate of 50 kg h^{-1} , with a fresh feed stream connected after each recycle. The EtOAc solvent stream was initially set at a mass flow rate of 206 kg h^{-1} and contained 100.0% EtOAc. Both streams were set at $25 \text{ }^\circ\text{C}$ and at 101.3 kPa. The fermentation broth consisted of 20 g l^{-1} acetic acid and 5 g l^{-1} ethanol. The initial fermentation broth feed stream and solvent feed stream were connected to a counter-current liquid-liquid extraction reactor. The extractant stream was then connected to a distillation column to recycle the solvent. The distillate solvent stream was then connected to a new counter-current liquid-liquid extraction reactor with a new fermentation broth stream set at the initial conditions. This process was repeated 24 times. The extractant solvent stream and raffinate stream were both analyzed to determine the recyclability of the solvent as well as the effectiveness of the recycled solvent. Figure 1 shows a process flow diagram of the procedure used herein for acetic acid extraction using ASPEN HYSYS.

3. Results and Discussion

3-1. Extraction of acetic acid and ethanol

Table 2 shows the experimental yields and partition data for extraction of acetic acid and ethanol from aqueous synthetic fermentation broth at $25 \text{ }^\circ\text{C}$ upon the solvent-to-feed ratio of EtOAc, TOPO, TOA, and TAPO.

3-1-1. EtOAc

With EtOAc extraction, the concentration of acetic acid that was extracted into the organic phase increased from 17.1 g l^{-1} , corresponding to 17.1% extraction yield, at a ratio of 0.2 to a concentration of 4.43 g l^{-1} , i.e. 88.6% extraction yield, at a ratio of 4.0. The extent of extraction of ethanol from the fermentation broth as a function of the EtOAc solvent-to-feed ratio is also presented in Table 2. The concentration of ethanol that was extracted to the organic phase increased from 3.41 g l^{-1} (13.7% extraction yield) at a ratio of 0.2 to a concentration of 1.03 g l^{-1} (82.4% extraction yield) at a ratio of 4.0. The extraction yield of acetic acid increased roughly linearly over the evaluated EtOAc-to-feed ratio, whereas that of ethanol increased slightly at lower EtOAc-to-feed ratios (0.2-2.0), and then increased rapidly at a feed ratio above 2.0.

3-1-2. TOPO

In case of extraction test using 37.0% (w/v) of TOPO (Table 2), the

Table 1. Solvent/diluent percentages used for the experiments

Solvent	Abbreviation	Diluent	Concentration (w/w)
Tri- <i>n</i> -octylphosphine oxide	TOPO	Alkane	37
Tri-octylamine	TOA	1-octanol	20
Tri- <i>n</i> -alkylphosphine	TAPO	ND ^a	100
Ethyl ethanoate	EtOAc	ND	100

^aND: No dilution.

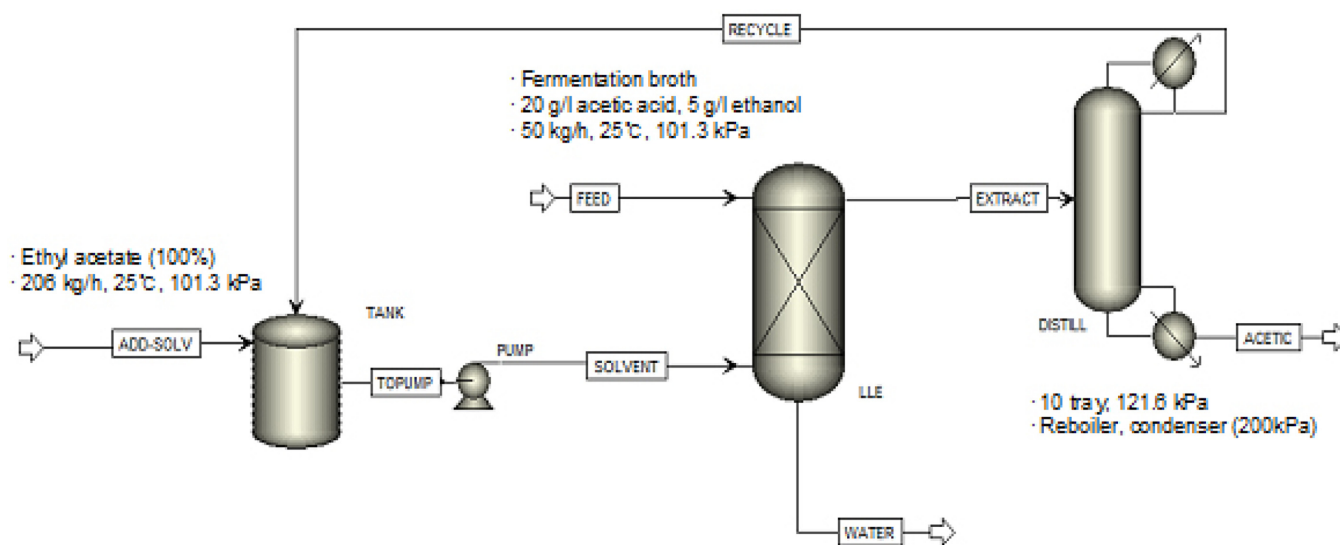


Fig. 1. Process flow diagram (simplified PFD by ASPEN) of acetic acid extraction process using ethyl acetate.

Table 2. Extraction of acetic acid (AA) and ethanol (EtOH) from fermentation broth upon various ratio of EtOAc, TOPO, TOA and TAPO to feed

Feed ratios [ml:ml]	Concentration [g l ⁻¹]				Extraction yield [%]	
	AA		EtOH		AA	EtOH
	aq ^a	org ^b	aq ^a	org ^b		
EtOAc						
0.2 [2:10]	16.6	17.1	4.32	3.41	17.1	13.7
0.5 [5:10]	12.3	15.4	3.48	3.03	38.5	30.3
1 [10:10]	8.06	11.9	2.58	2.42	59.7	48.4
2 [20:10]	4.38	7.81	1.61	1.69	78.1	67.7
4 [40:10]	2.27	4.43	0.88	1.03	88.6	82.4
TOPO						
0.2 [2:10]	15.7	21.3	4.27	3.67	21.3	14.7
0.5 [5:10]	11.0	18.1	3.42	3.15	45.2	31.5
1 [10:10]	6.67	13.3	2.53	2.47	66.7	49.5
2 [20:10]	3.39	8.31	1.57	1.71	83.1	68.6
4 [40:10]	1.53	4.62	0.84	1.04	92.4	83.2
TOA						
0.2 [2:10]	13.5	32.6	4.06	4.71	32.6	18.8
0.5 [5:10]	6.89	26.2	3.03	3.94	65.5	39.4
1 [10:10]	3.28	16.7	2.03	2.97	83.6	59.3
2 [20:10]	1.52	9.24	1.15	1.92	92.4	77.0
4 [40:10]	0.73	4.82	0.56	1.11	96.3	88.8
TAPO						
0.2 [2:10]	11.6	42.2	4.03	4.86	42.2	19.5
0.5 [5:10]	5.80	28.4	2.87	4.27	71.0	42.7
1 [10:10]	2.88	17.1	1.79	3.21	85.6	64.3
2 [20:10]	1.32	9.34	0.91	2.05	93.4	81.8
4 [40:10]	0.60	4.85	0.39	1.15	97.0	92.1

-EtOAc extraction: acetic acid (AA) and ethanol (EtOH) determined by calculation^a and GC^b

-TOPO, TOA, and TAPO extractions: acetic acid (AA) and ethanol (EtOH) determined by HPLC^a and calculation^b

concentration of acetic acid that was extracted to the organic phase increased from 21.3 g l⁻¹ (21.3% extraction yield) at a ratio of 0.2 to a concentration of 4.62 g l⁻¹ (92.4% extraction yield) at a ratio of 4. The extent of extraction of ethanol as a function of the TOPO-to-feed ratio is also presented in Table 3. The concentration of ethanol extracted to the organic phase increased from 3.67 g l⁻¹ (14.7% extraction yield) at a ratio of 0.2 to 1.04 g l⁻¹ (83.2% extraction yield) at a ratio of 4.0. A similar trend was observed for the extraction yield of acetic acid when the LLE was performed using EtOAc. Increasing the TOPO-to-feed ratio from 2.0 to 4.0 improved not only the acetic acid extraction yield from 83.1% to 92.4%, but also the ethanol yield from 68.6% to 83.2%. Based on these results, it was speculated that the liquid extraction is significantly influenced by the concentration of undissociated acid in the aqueous phase.

3-1-3. TOA

Aliphatic amines in TOA solvent extract carboxylic acids from an aqueous phase by forming an acid-amine complex (acid-TOA complex) with the undissociated acid. The fraction of remaining acetic acid is defined as the ratio of the acetic acid concentration after extraction

Table 3. Simulated counter-current LLE data for the extraction of acetic acid (AA) and ethanol (EtOH) from fermentation broth feed as a function of different EtOAc-to-feed ratios

Feed ratios [ml:ml]	Concentration [g l ⁻¹]				Extraction yield [%]	
	AA		EtOH		AA	EtOH
	aq ^a	org ^b	aq ^a	org ^b		
0.6	14.7	8.9	3.8	2.1	26.6	24.8
0.7	14.0	8.6	3.6	2.0	30.2	28.0
0.9	12.7	8.1	3.3	1.9	36.5	34.0
1.0	12.1	7.9	3.2	1.8	39.5	36.6
1.1	11.6	7.7	3.0	1.8	42.1	39.2
1.3	10.6	7.3	2.8	1.7	47.2	43.8
1.4	10.1	7.1	2.7	1.6	49.5	46.0
1.5	9.7	6.9	2.6	1.6	51.6	48.0
1.7	8.9	6.5	2.4	1.5	55.7	51.8
1.8	8.5	6.4	2.3	1.5	57.5	53.6
2.0	7.8	6.1	2.2	1.4	60.8	56.8
2.2	7.2	5.8	2.0	1.4	63.8	59.6
2.3	7.0	5.7	2.0	1.3	65.2	61.0
2.5	6.5	5.4	1.8	1.3	67.6	63.4
2.7	6.1	5.2	1.7	1.2	69.7	65.6
2.8	5.9	5.1	1.7	1.2	70.7	66.6
3.0	5.5	4.8	1.6	1.1	72.6	68.6
3.2	5.1	4.6	1.5	1.1	74.4	70.4
3.3	5.0	4.5	1.4	1.1	75.1	71.2
3.5	4.7	4.4	1.4	1.0	76.6	72.8
3.6	4.5	4.3	1.3	1.0	77.4	73.6
3.8	4.1	4.2	1.2	1.0	79.8	75.8
3.9	3.2	4.3	1.1	1.0	84.3	78.2
4.0	2.2	4.5	0.8	1.0	89.1	83.4

to the initial acetic acid concentration in the aqueous phase. In our previous study, it was found that the extraction of acetic acid is critically influenced by the pH of the aqueous phase [17]. With the extraction experiments using TOA, the initial concentration of acetic acid in the aqueous phase was 20 g l⁻¹ (pH = 2.59 and the TOA concentration in the organic phase was 20.0% (w/v) (Table 1). The concentration of acetic acid that was extracted to the organic phase increased from 32.6 g l⁻¹ (32.6% extraction yield) at a ratio of 0.2 to a concentration of 4.82 g l⁻¹ (96.3% extraction yield) at a ratio of 4.0. In case of ethanol extraction using TOA, the concentration of ethanol extracted to the organic phase increased from 4.71 g l⁻¹ (extraction yield of 18.8%) at a ratio of 0.2 to a concentration of 1.11 g l⁻¹ (extraction yield of 88.8%) at a ratio of 4.0. It was also observed that the extraction yield of acetic acid increased almost linearly over the range of evaluated TOA-to-feed ratios, whereas that of ethanol increased slightly at lower ratios of TOA-to-feed (0.2-2.0). Increasing the TOA-to-feed ratio beyond 2.0 did not result in substantial increase in terms of acetic acid recovery, whereas it improved the ethanol yield from 77.0% to 88.8%.

3-1-4. TAPO

A trend found in this test was similar to the other three tests using EtOAc, TOPO, TOA, TAPO; i.e. a significant amount of acetic acid was extracted into the organic phase in response to an increasing vol-

ume fraction of extractant. The concentration of acetic acid that was extracted into the organic phase increased from 42.2 g l^{-1} (42.2% extraction yield) at a ratio of 0.2 to a concentration of 4.85 g l^{-1} (97.0% extraction yield) at a ratio of 4.0. The concentration of ethanol extracted to the organic phase was 4.86 g l^{-1} , corresponding to an extraction yield of 19.5%, at a ratio of 0.2 and moved to a concentration of 1.15 g l^{-1} (extraction yield of 92.1%) at a ratio of 4.

The LLE test results shown in Table 2 indicated that TAPO seems to be more effective than other solvents. Acetic acid extraction was largely completed at a low TAPO-to-feed ratio; that is, 71.0%, 85.6%, and 93.4% of acetic acid was extracted at TAPO-to-feed ratios of 0.5, 1.0, and 2.0, respectively, which are significantly lower ratios than required for with LLE using other solvents. The remaining acetic acid in the aqueous phase was the minimum (0.60 g/L) when the ratio of organic to aqueous phase exceeded 4:1.

3-2. Overall effects of various solvents on LLE of acetic acid

The choice of a suitable extraction solvent for LLE process depends primarily on the solvent's extractive capacity and the equilibrium characteristics as well as its stability, favorable density, viscosity, and interfacial tension properties and a sufficient difference in the boiling point of the solute and the solvent [16]. Figure 2 shows the data acquired for the equilibrium between the concentration of acetic acid in the organic phase and that in the aqueous phase during extraction using different solvents for 36 minutes at $25 \text{ }^\circ\text{C}$ and $\text{pH} = 2.59$. In the acetic acid extraction tests using EtOAc, TOPO, TOA, and TAPO, as the solvent-to-feed ratio increased from 0.2 to 4.0, P_c of acetic acid increased from 1.03 to 1.95, from 1.35 to 3.02, from 2.42 to 6.56, and from 3.65 to 8.12, respectively. The parameters affecting the partitioning were evaluated by plotting all of the obtained P_c values for acetic acid extraction at various solvent-to-feed ratios (Fig. 2a). The P_c of acetic acid in EtOAc, TOPO, TOA, and TAPO increased linearly as the solvent-to-feed ratio was increased to 4.0. The P_c of acetic acid in TAPO increased logarithmically as the solvent-to-feed ratio was increased to 4.0 (Fig. 2a). The extraction effect became more pronounced as the ratio increased. In view of the high association constant of acetic acid in these solvents, a very low concentration of the free solvents is present in the organic phase at low [solvent]/[acetic] aqueous ratios, thereby significantly altering the partition equilibrium due to the limited capacity of the solvent to accept the transfer of more acetic acid molecules from the aqueous phase. On the other hand, an appreciable amount of free solvent is available at higher ratios, and these free solvent molecules are able to complex with additional acid molecules extracted from the aqueous phase, giving rise to a high partition coefficient.

The P_c of ethanol in each of the solvents increased linearly as the solvent-to-feed ratio was increased to 4.0 (Fig. 2b). In the ethanol extraction tests using EtOAc, TOPO, TOA, and TAPO, as the solvent-to-feed ratio increased from 0.2 to 4.0, P_c of acetic acid increased from 0.79 to 1.17, from 0.86 to 1.24, from 1.16 to 1.99, and from 1.21 to 2.92, respectively. Of the solvents evaluated, the highest acetic acid

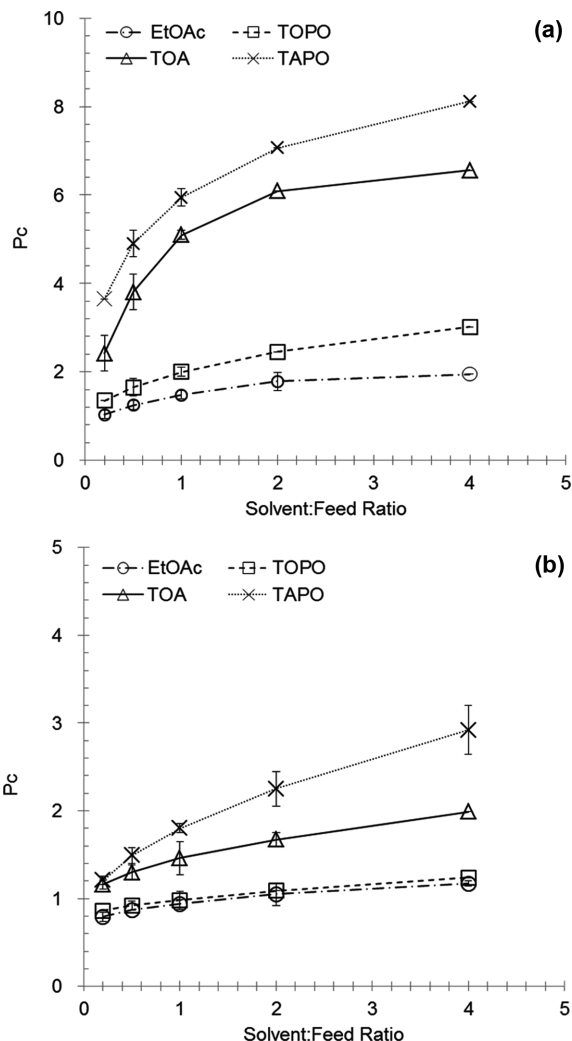


Fig. 2. Partition coefficients (P_c) results in LLE tests for (a) acetic acid and (b) ethanol using various solvents (as organic/aqueous solution ratio).

extraction P_c was achieved with TAPO; however, the data also revealed that the lowest ethanol-to-acetic acid extraction ratio was achieved with TOPO, giving rise to higher purity of the acetic acid extract. The acetic acid extraction P_c was similar for TAPO and TOPO; however, the highest ethanol-to-acetic acid extraction ratio was achieved with TAPO among the evaluated solvents.

3-3. ASPEN HYSYS simulation

To assess the commercial feasibilities of the proposed processes, complete process simulations were carried out. The UNIQUAC (universal quasi-chemical) with the Soave-Redlich-Kwong (SRK) program of the HYSYS simulation software were used to estimate the partition coefficient (P_c) for the feed concentration ($=20.0 \text{ g l}^{-1}$ acetic acid and 5.0 g l^{-1} ethanol) and mixed solvent (EtOAc) in a counter-current LLE. The calculated P_c values were compared with batch experimental results (Fig. 3). The HYSYS simulation of a counter-current LLE using EtOAc as a solvent revealed a steady linear increase in the acetic acid P_c until the solvent-to-feed ratio reached 3.9 with a P_c

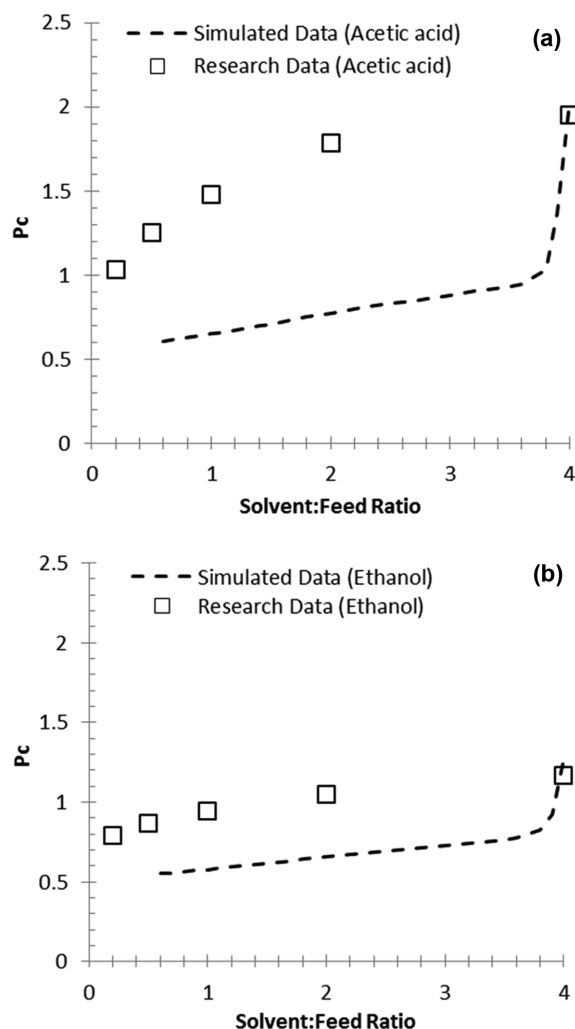


Fig. 3. Partition coefficient (P_c) profiles determined from the batch experiment (symbol) and from ASPEN HYSYS simulation (dashed line: continuous mode): (a) acetic acid and (b) ethanol.

of 1.37; the P_c increased sharply to 2.03 at a solvent-to-feed ratio of 4.0. In the batch extraction of acetic acid using EtOAc, however, the maximum P_c was only 1.95 at a solvent-to-feed ratio of 4.0 for the batch mode extraction. Additionally, with the extraction of ethanol, P_c of ethanol increased from 0.55 to 1.26 as the ratio increased from 0.6 to 4.0. The simulation results indicated the P_c of 1.26 at a solvent-to-feed ratio of 4.0, compared with the maximum P_c of only 1.17 at a ratio of 4.0 for the batch experimental data.

This large discrepancy between the P_c of the continuous counter-current and batch LLE processes shown in Fig. 3 was due to different extraction conditions and solvent uses. The fresh solvent was used in batch LLE tests, while recycled solvent was used for the simulation study. The result indicated that a trade-off between the batch and continuous extraction process associated costs of an acetic acid separation mechanism, which is related to the efficiency. However, our future research should thoroughly evaluate the feasibility of LLE in an industrial setting given that the counter-current extraction is currently believed to be the most apposite method for separation. In

addition, future studies should also focus on the effect of contact time between the solvents and fermentation broth to maximize the effectiveness of acetic acid extraction in the counter-current LLE using relevant solvents.

Table 3 presents the simulation data for the extent of acetic acid extraction upon various EtOAc solvent-to-feed ratio in a continuous counter-current LLE. The concentration of acetic acid that was extracted into the organic phase increased from 8.9 g l^{-1} (26.6% extraction yield) at a ratio of 0.6 to a concentration of 4.45 g l^{-1} (89.1% extraction yield) at a ratio of 4.0. Table 3 also presents the simulation data for the extent of ethanol extraction upon various EtOAc solvent-to-feed ratios in a counter-current LLE. The concentration of ethanol extracted into the organic phase increased from 2.1 g l^{-1} , a 24.8% extraction yield, at a ratio of 0.6 to a concentration of 1.0 g l^{-1} , an 83.4% extraction yield, at a ratio of 4.0.

In addition, the recyclability of the solvent is the one of most important factors in determining the optimal solvent for industrial use. Tables 4 summarize the EtOAc recyclability evaluation with proposed use over 24.0 cycles. The HYSYS program was set to obtain a final acetic acid purity of 94.0% for the 20.0 g l^{-1} acetic acid feed concentration (data not shown). The simulation was programmed with the addition of heat until an acetic acid purity of 94.0% was reached. Given that the minimum solvent-to-feed mass flow ratio was around 1:1, the recycling was discontinued after 24.0 runs when the ratio finally reached a value of 0.6. The data also revealed an approximately

Table 4. Simulation input data for EtOAc recycling as a function of number of recycle events

Number of recycling	Concentration of EtOAc [%]	EtOAc:Feed ratio
0	100.0	4.1
1	98.4	4.0
2	95.5	3.9
3	92.2	3.8
4	88.4	3.6
5	84.5	3.5
6	80.6	3.3
7	76.6	3.2
8	72.6	3.0
9	68.6	2.8
10	64.5	2.7
11	60.5	2.5
12	56.5	2.3
13	52.6	2.2
14	48.6	2.0
15	44.8	1.8
16	41.1	1.7
17	37.4	1.5
18	33.8	1.4
19	30.4	1.3
20	27.1	1.1
21	23.8	1.0
22	20.7	0.9
23	17.6	0.7
24	14.7	0.6

3-4% linear reduction of the original EtOAc solvent stream with each run as it was recycled by distillation, with a consequent reduction of the solvent-to-fermentation broth ratio from 4.1 to 0.6 during the 24.0 recycling runs. Overall, the acetic acid did not significantly affect the solvent recovery based on the low level of contamination.

4. Conclusion

The solvent extraction equilibria of acetic acid and ethanol were evaluated using various solvents. The highest percentage acetic acid extraction was achieved with TAPO; however, the lowest ethanol-to-acetic acid extraction ratio was achieved with TOPO among the solvents studied. The optimal solvent-to-feed ratio for both TAPO and TOPO was determined to be 2.0, with respective extraction yields of 93.4% and 83.1% for acetic acid. For initial concentrations on the order of 20.0 g l⁻¹ acetic acid, the extraction percent is little improved when the ratio of solvent-to-feed phase rises above 2:1. Accordingly, a higher solvent-to-feed ratio resulted in an increase in the ethanol -to-acetic acid ratio, which decreased the acetic acid purity.

Considering the composition of alcohol fermentation broths derived from bacterial fermentation, selective removal of other acids such as formic acid and lactic acid, recovery of ethanol from the organic phase, and recyclability test of the solvents need to be further studied. However, this study should furnish fundamental data and provide an insight into the complex and conflicting parameters governing the batch and continuous LLE processes.

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References

- van Heiningen, A., "Converting a Kraft Pulp Mill Into an Integrated Forest Biorefinery," *Pulp Paper Canada*, **107**(6), 38-43 (2006).
- Cogan, T. M., "Co-metabolism of Citrate and Glucose by *Leuconostoc spp.*: Effects on Growth, Substrate, and Products," *J. Appl. Bacteriol.*, **63**, 551-558(1987).
- Oliva-Neto, P. and Yokoya, F., "Effect of 3,4,4'-trichlorocarbonyl on Growth of Lactic Acid Bacteria Contaminants in Alcoholic Fermentation," *Biores Technol.*, **63**, 17-21(1998).
- Rodríguez-López, J., Romani, A., González-Muñoz, M. J., Garrote, G. and Parajó, J. C., "Extracting Value-added Products Before Pulping: Hemicellulosic Ethanol from Eucalyptus Globulus Wood," *Holzforchung*, **66**, 591-599(2012).
- Um, B. H. and Hanley, T. R., "A CFD Model for Predicting the Flow Patterns of Viscous Fluids in a Bioreactor Under Various Operating Conditions," *Korean J. Chem. Eng.*, **25**(5), 1094-1102(2008).
- Drysdale, G. S. and Fleet, G. H., "Acetic Acid Bacteria in Wine-making: A Review," *Am. J. Enol. Vitic.*, **39**(2), 143-153(1988).
- Shimazu, Y. and Watanabe, M., "Effects of Yeast Strains and Environmental Conditions on Formation of Organic Acid in Must During Fermentation," *J. Ferment. Technol.*, **59**(1), 27-32(1981).
- Galanakis, C. M., Kordulis, C., Kanellaki, M., Athanasios, A. K., Bekatorou, A. and Lycoirghiotis, A., "Effect of Pressure and Temperature on Alcoholic Fermentation by *Saccharomyces Cerevisiae* Immobilized on γ -alumina Pellets," *Biores Technol.*, **114**, 492-498 (2012).
- Delfini, C. and Costa, A., "Effects of the Grape Must Lees and Insoluble Materials on the Alcoholic Fermentation Rate and on the Production of Acetic Acid, Pyruvic Acid, and Acetaldehyde," *Am. J. Enol. Vitic.*, **44**(1), 86-92(1993).
- Radler, F., Yeast-metabolism of organic acids, in: Fleet, G. H. (Eds.), *Wine microbiology and biotechnology*, Harwood Academic Publishers, Philadelphia, USA(1983).
- Klosowski, G., Mikulski, D., Grajewski, J. and Blajet-Kosicka, A., "The influence of Raw Material Contamination with Mycotoxins on Alcoholic Fermentation Indicators," *Biores Technol.*, **101**, 3147-3152(2010).
- Pawelzik, P., Carus, M., Hotchkiss, J., Narayan, R., Selke, S., Wellisch, M., Weiss, M., Wicke, B. and Parel, M. K., "Critical Aspects in the Life Cycle Assessment (LCA) of Bio-based Materials - Reviewing Methodologies and Deriving Recommendations," *Resour. Conserv. Recycl.*, **73**, 211-228(2013).
- Um, B. H., "A Comparative Study on Green Liquor Pre-pulping Extraction of Mixed Hardwood Chips," *Korean Chem. Eng. Res.*, **51**(5), 561-567(2013).
- Xu, Z. P., Afacan, A. and Chuang, D. T., "Removal of Acetic Acid from Water by Catalytic Distillation. Part 1. Experimental Studies," *Canadian. J. Chem. Eng.*, **77**, 676-681(1999).
- Anasthas, H. M. and Gaikar, V. G., "Removal of Acetic Acid Impurities from Ethyl Acetate by Adsorption on ion Exchange Resins," *Sep. Sci. Technol.*, **36**, 2623-2646(2001).
- Wiencek, J. M. and Qutubuddin, S., "Microemulsion Liquid Membranes. 1 Application to Acetic Acid Removal from Water," *Sep. Sci. Technol.*, **27**, 1211-1228(1992).
- Um, B. H., Friedman, B. and van Walsum, G.P., "Conditioning Hardwood-derived Pre-pulping Extracts for Use in Fermentation Through Removal and Recovery of Acetic Acid Using Trioctylphosphine Oxide (TOPO)," *Holzforchung*, **65**, 51-58(2011).
- Ricker, N. L., Michaels, J. N. and King, C. J., "Solvent Properties of Organic Bases for Extraction of Acetic Acid from Water," *J. Sep. Proc. Technol.*, **1**, 36-41(1979).
- King, C. J., "Amine-based System for Carboxylic Acid Recovery," *Chem. Tech.*, **5**, 285-291(1992).
- Senol, A., "Extraction Equilibria of Formic, Levulinic, and Acetic Acids Using (alamine 336/diluent) and Conventional Solvent Systems: Modeling Consideration," *J. Chem. Eng. Jpn.*, **32**, 717-731(1999).
- Sabolova, E., Schlosser, S. and Martak, J., "Liquid-liquid Equilibria of Butyric Acid in Water+solvent Systems with Trioctylamine as Extractant," *J. Chem. Eng. Data*, **46**, 735-745(2001).
- Helsel, R. W., "Removing Carboxylic Acids from Aqueous Wastes," *Chem. Eng. Prog.*, **73**(5), 55-59(1977).
- Niitsu, M. and Sekine, T., "Solvent Extraction Equilibria of acids.

- VI. The extraction of Several Mono-and Dicarboxylic Acids with Trioctylphosphine Oxide in Hexane”, *Bull. Chem. Soc. Jpn.*, **51**, 705-709(1978).
24. Wardell, J. M. and King, C. J., “Solvent Equilibriums for Extraction of Carboxylic Acids from Water,” *J. Chem. Eng. Data.*, **23**, 144-148(1978).
25. Hano, T., Matsumoto, M., Ohtake, T., Sasaki, K. and Kawano, Y., “Extraction Equilibria of Organic Acids with tri-*n*-octylphosphineoxide,” *J. Chem. Eng. Jpn.*, **23**, 260-264(1990).
26. Reisinger, H. and King, C. J., “Extraction and Sorption of Acetic Acid at pH Above pK_a to form Calcium Magnesium Acetate,” *Ind. Eng. Chem. Res.*, **34**, 845-852(1995).
27. Juang, R. S. and Wu, R. T., “Extraction of Acetate from Simulated Waste Solutions in Chloromycetin Production,” *Sep. Purif. Technol.*, **17**, 225-233(1999).
28. Al-Mudhaf, H. F., Hegazi, M. F. and Abu-Shady, A. I., “Partition Data of Acetic Acid Between Aqueous NaCl Solutions and Trioctylphosphine Oxide in Cyclohexane Diluents,” *Sep. Purif. Technol.*, **27**, 41-50(2002).
29. Wisniewski, M. and Pierzchalska, M., “Recovery of Carboxylic Acids C_1 - C_3 with Organophosphine Oxide Solvating Extractant,” *J. Chem. Technol. Biotechnol.*, **80**, 1425-1430(2005).
30. Walton, S., van Heiningen, A. and van Walsum, P., “Inhibition Effects on Fermentation of Hardwood Extracted Hemicelluloses by Acetic Acid and Sodium,” *Biores. Technol.*, **101**, 1935-1940 (2010).