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Liquid–Liquid Extraction of Acetic Acid with 2-Methyltetrahydrofuran: Experiments, Process Modeling, and Economics

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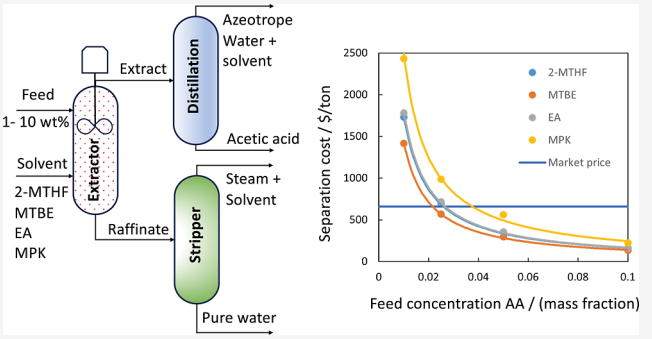
ABSTRACT: Acetic acid production from renewable processes such as biomass hydrolysis and electrochemical reduction of CO_2 exhibits low concentrations, which make downstream separation challenging. We measured the vapor–liquid equilibria of the binary systems acetic acid + 2-methyltetrahydrofuran (2-MTHF), methyl-*t*-butyl ether (MTBE) + acetic acid, and the ternary liquid–liquid equilibria of the system 2-MTHF + AA + water, fitted the data to the UNIQUAC-HOC and NRTL models, designed a hybrid extraction-distillation process for acetic acid separation with 2-MTHF, and evaluated its economics and compared with that of three other commonly used solvents (i.e., ethyl acetate, MTBE, and methyl propyl ketone). The lowest and highest costs of separation were observed for MTBE and MPK, while 2-MTHF and EA showed similar performance. The cost of separation increased exponentially as the feed concentration decreased, and renewable processes should aim for at least 5 wt % acetic acid in the feed to allow economically feasible separation.



INTRODUCTION

Acetic acid (AA) is an important base chemical that is mainly used for the production of vinyl acetate (33%), acetic anhydride (18%), acetate esters (17%), terephthalic acid (17%), and monochloroacetic acid + others (15%).[1] Currently, AA is predominantly produced from the carbonylation of methanol (Cativa process). However, AA can also be produced by enzymatic fermentation, biomass hydrolysis, and electrochemical CO_2 or CO conversion. For example, CO_2 can be converted in an electrochemical cell to AA according to the half–cell reaction

$$2CO_2 + 8H^+ + 8e^- \rightarrow CH_3COOH + 2H_2O \quad (1)$$

A key characteristic of biochemical and electrochemical conversion processes is that a dilute AA mixture is obtained.[2,3] It is also important to note that the vapor–liquid equilibria (VLE) of the AA/water mixture shows a tangent pinch point near the pure water end; see Figure 1. For this reason, it is difficult and costly to obtain pure acetic acid with conventional distillation. In practice, liquid–liquid extraction and azeotropic distillation is used to concentrate dilute (<30 wt %) AA mixtures.[4] Different types of chemical and physical solvents have been proposed for AA extraction. Typically, chemical solvents, such as amines, phosphonates, and phosphine oxides, have a higher extraction coefficient compared to physical solvents, such as ethyl acetate (EA) and methyl-*tert*-butylether (MTBE). However, as shown by Shah et al.,[5] solvent selection should be based not only on the partition ratio but also on other factors such as thermal stability, ease of regeneration, separation factor, and cost. In general, the raffinate treatment and recovery of chemical solvents are more difficult than those for physical solvents. A low boiling solvent is often preferred over a high boiling solvent because the raffinate treatment of the latter is more complicated. Steam stripping can be used to purify water for solvents that form a low boiling azeotrope with water, while high boiling solvents require a costly back extraction step.[6] The dehydration of AA has been studied by Chilev et al.[7] and Li et al.,[8] while liquid–liquid extraction and azeotropic distillation have been reported in several studies.[9−12] Most of these studies considered AA extraction from relatively concentrated streams (>20 wt %), but the processes of our interest (electro- or biochemical) typically produce dilute streams (<10 wt %). Separation cost estimates for high-

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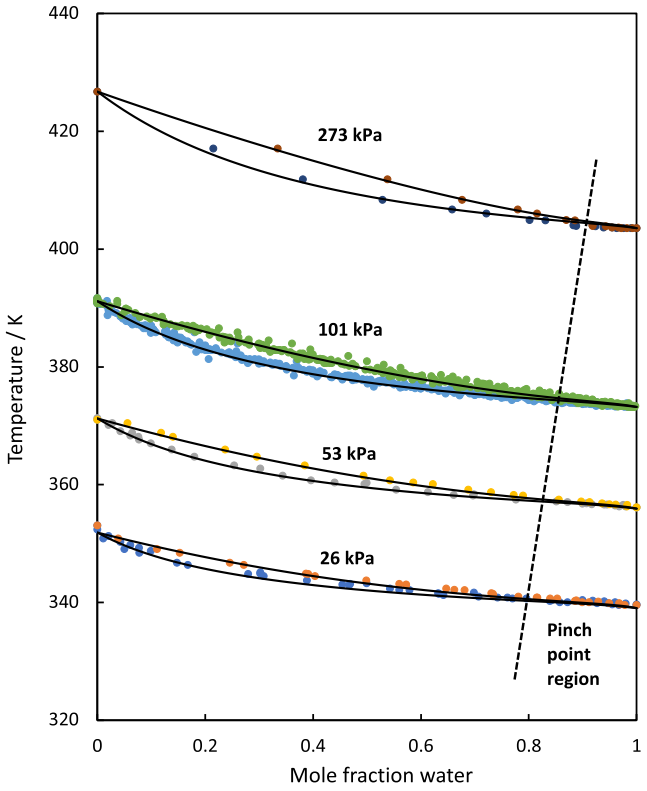

Figure 1. VLE of acetic acid and water for different pressures. Dashed line is a guide to the eye that shows the region of the tangent pinch point. Solid lines are UNIQUAC-HOC modeling results. Experimental data taken from Gmehling.[31]

concentration feeds cannot be extrapolated to low concentrations, since the cost scales inversely with the feed concentration and shows a nonlinear behavior (Sherwood plot).[13]

In our previous study, we have shown that 2-methyltetrahydrofuran (2-MTHF) is an interesting biosolvent for the extraction of formic acid from dilute streams.[14] Here, we extend the study to acetic acid extraction from dilute streams using 2-MTHF, EA, MTBE, and methyl propyl ketone (MPK). Due to the lack of experimental data in the literature, we measured the vapor−liquid equilibria (VLE) of the binary systems acetic acid +2-MTHF and MTBE + acetic acid, and the ternary liquid−liquid equilibria (LLE) of 2-MTHF + water + acetic acid. The VLE and LLE data were correlated with the NRTL and UNIQUAC models, which were used in Aspen Plus to design a hybrid extraction-distillation (HED) process for the separation of acetic acid from water. The HED process is optimized for four different concentrations of acetic acid (1, 2.5, 5, and 10 wt %) in the feed. The economics of the optimized process based on 2-MTHF are evaluated and compared with the other three commonly used solvents (i.e., MTBE, EA, and MPK).

Our economic analysis shows that MTBE is the best solvent for AA extraction due to its favorable properties, but 2-MTHF and EA are good alternatives considering that MTBE has some environmental concerns.

EXPERIMENTAL SECTION

VLE Measurements

The VLE of the MTBE-AA system was measured in two laboratories (Aalto University (AU) and V.V.P. Engineering College (VVP)) to cross-check the data because the system showed an azeotropic behavior in the presence of trace amounts of water, while no azeotropes are observed when MTBE and AA are free of water. The measurement procedure and results from both laboratories will be presented.

Materials. Methyl-*tert*-butyl-ether (CAS 1634-04-4) was dried overnight in an Erlenmeyer with molecular sieve 3Å prior to measurements to remove the traces of moisture. The glacial acetic acid (CAS 64-19-7) was dried with a 3Å molecular sieve for 2 days in an Erlenmeyer. Then, 400 mL of acetic acid was poured into the reboiler of a batch distillation column and 75 mL of distillate was taken. Distillation was performed at an atmospheric pressure. The traces of water accumulated in the distillate, and dry acetic acid that remained in the reboiler was used for the VLE measurements.

The VLE of the binary mixture of MTBE and AA was measured under isobaric atmospheric pressure conditions. At AU, the measurement technique was the Yerazunis-type recirculation still, where samples were taken from the liquid and condensed vapor phase and analyzed with gas chromatography (GC) equipped with both a flame ionization detector (FID) and thermal conductivity detector (TCD). Before the measurements, the temperature meter was calibrated with a VTT/MIKES instrument (calibration certificate M-21T034). The correction for the reading was −0.016 K. The pressure meter of the VLE apparatus was calibrated on site, but the Beamex MC-2 field calibrator was calibrated at the Beamex company (certificate K026-21P734). The correction of the reading of the calibrator was at the highest value of 20 Pa. In practice, the reading of the calibrator was used as such. The pressure correction of the VLE apparatus was +20 Pa and was taken into account. The details of the apparatus are presented in Uusi-Kyyny et al.[15] In this case, the measurement was run at a constant atmospheric pressure of 101.5 kPa. The experiments started with measuring the pure MTBE vapor pressure curve. Subsequently, successive additions of acetic acid were performed, and samples of the liquid phase and the condensed vapor phase were taken and analyzed until an equimolar liquid composition was reached. Afterward, the apparatus was carefully cleaned. Next, the vapor pressure curve of acetic acid was measured. Then, successive additions of MTBE were performed, and samples were taken and analyzed until the liquid composition overlapped with the first part of the isobar. The standard uncertainties in temperature, pressure, and composition are 0.2 K, 0.1 kPa, and 0.005 in the mole fractions.

At VVP, an ebulliometer was used to measure the VLE of the systems MTBE-AA and 2-MTHF-AA at isobaric conditions. The VLE of system MTBE-AA was measured at atmospheric pressure (101.1 kPa), while the VLE of system 2-MTHF-AA was measured at five different pressures ranging from 60.0 to 101.2 kPa. A detailed description of the setup can be found in Parsana et al.[16,17] Here, only a brief description of the setup is provided. Before the experiments, the setup was thoroughly cleaned with acetone to remove impurities and traces of chemicals from the ebulliometer and condenser. A sample of approximately 60 mL was loaded in the ebulliometer and heated with a belt heater. The heating rate was adjusted carefully to avoid bumping and superheating the inside of the equilibrium cell. The system was considered to be in equilibrium once the temperature and drop rate were constant. A vacuum pump was used to maintain the pressure at the desired level. The pressure and temperature were measured with a mercury-filled U-tube and a Pt-100 temperature sensor with a precision of 0.133 kPa and 0.1 K, respectively. $P - T - x$ diagrams can be generated by repeating the experiments for different pressures and compositions. The composition of the liquid samples at the end of the experiment was analyzed with a five-digit automatic digital refractometer (RFM-950 by LABMAN). The measurement range and accuracy of the refractometer are between 1.30000 and 1.70000 and ±0.00002, respectively. The calibration curve was prepared by plotting the refractive index values of different

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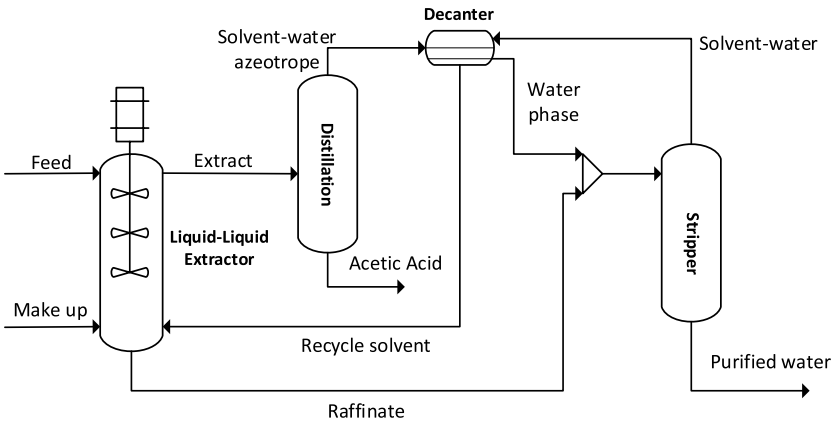

Figure 2. Process flow diagram of the hybrid extraction-distillation system. The feed containing the acetic acid is introduced at the top of extractor, while the extraction solvent is fed at the bottom. The extract is fed to the azeotropic distillation column, where a solvent−water azeotrope is obtained as tops, while glacial acetic acid is obtained as bottoms. The solvent−water azeotrope is condensed in a decanter yielding a water-rich phase which is combined with the raffinate and sent to the stripper, while the solvent-rich phase is recycled to the extractor. In the stripper, steam is used to purify water. Any loss of solvent is added as make up to the extractor.

samples of known composition with R^2 = 0.998. A calibration curve for the refractometer is shown in Figure S1 of the Supporting Information. The expanded uncertainties in the reported temperature, pressure, and composition are 0.2 K, 0.2 kPa, and 0.001 in the mole fraction. The details of the uncertainty analysis can be found in the Supporting Information.

LLE Measurements

Materials. Methyltetrahydrofuran (2-Methyltetrahydrofuran, anhydrous >99%, inhibitor free) and acetic acid (Reag Ph Eur >98%) were purchased from Sigma-Aldrich, and used without further purifications. Sodium hydroxide solution (Reag Ph Eur, 0.1 M) was obtained from Fluka Analytical.

LLE experiments were carried out to determine the composition of acetic acid, water, and 2-MTHF in the extract and raffinate phases at temperatures of 298.2, 313.2, and 328.2 K and atmospheric pressure. Aqueous solutions, initially containing 0.5−28 wt % acetic acid, were first prepared by dissolving appropriate amounts of acid in ion-exchanged water. Equal masses (50 g) of the aqueous phase and 2-MTHF solvent phase were poured into a glass cell (150 mL) equipped with an external heating jacket to maintain the constant temperature during measurement and sampling. The temperature was measured by a calibrated probe (VWR digital thermometer ±0.1 °C) placed inside the glass cell. After the stabilization of the temperature, the mechanical stirrer (Heidolph RZR 2102 control) was turned on and the mixture stirred vigorously (350 rpm) for 1 h. The stirrer was then turned off, and the formation of two clear phases was noticed to take place within a few minutes. Two settling times (30 and 90 min) were initially tested and 30 min was proved to be a long enough time to reach equilibrium. The bottom valve of the glass cell was very carefully opened, and the phases were separated, collected, and weighed. The mass balance deviation of the amount of loaded and analyzed acetic acid was typically within 3%. The mass balance deviation values for water computed in a similar way were typically within 1.5%. It was assumed that no chemical reactions took place during the experiments and that the third component in the mixture is the solvent (2-MTHF). The deviation in the mass balance arises from the uncertainties in separation of both phases, weighing, and analysis. The reproducibility of the LLE data was tested by carrying out three repetition trials, and the results were almost identical. The uncertainty in the temperature is 0.1 K, while the uncertainty in the phase mass fractions is 5%.

Analytical Methods. The concentration of acetic acid in the extract and raffinate phases was analyzed by titration (799 GPT Titrino Metrohm) with 0.1 M sodium hydroxide, and the amount of water in each sample was analyzed by a Karl Fischer titrator (Mettler-Toledo). In Karl Fischer titration, the weighed samples were injected to the titration solvent (ASTM D 203 Chloroform/methanol 1:3). The titration reagent contained 2-metoxyethanol, sulfur dioxide, iodine, and pyridine to keep the pH at the optimal range (Karl Fischer reagent 5).

Process Design and Modeling

In Figure 2, an overview of the hybrid extraction−distillation (HED) process to extract and concentrate AA is shown. The dilute feed stream is sent to the extraction column (EC), which is operated in a counter-current mode to extract AA using a physical solvent. The self-entrained extract mixture containing AA is sent to the azeotropic distillation column (ADC), while the raffinate is sent to the stripper. Note that the selected extractants function as an entrainer in the ADC, because they form a heterogeneous azeotrope with water. For this reason, the AA/water/solvent mixture is called a self-entrained azeotropic distillation system. In the ADC, an azeotropic mixture of water and solvent is obtained as a distillate, while glacial acetic acid is produced as the bottom product. The heterogeneous water−solvent azeotrope is condensed in a decanter into a solvent-rich phase and a water-rich phase. The solvent-rich phase is recycled to the EC, while the water-rich phase is combined with the raffinate stream and sent to the steam stripper. A small amount of solvent that is lost through the purified water stream is added as make up to the extractor.

The modeling of extractors is more challenging than distillation columns since pilot plant data is typically required for a scale-up. The EC was modeled in Aspen Plus at a high-level with the EXTRACT unit block. The extractor was operated at 25 °C and 1 bar. The solvent flow rate and number of stages were optimized to have an AA recovery of 99.5% in the extractor. For designing extraction columns, the extraction factor (E) is typically set between 1.5 and 2.0, where E is defined as[18]

$$E = K_B \frac{S}{F} \tag{2}$$

where K_B is the partition coefficient in Bancroft coordinates and S/F is the solvent to feed ratio on a mass basis. The recovery (R) is defined as

$$R\ (\%) = \frac{m_{FA}^{Ext.}}{m_{FA}^{F}} \times 100 \tag{3}$$

where $m_{FA}^{Ext.}$ and m_{FA}^{F} are the mass flows of FA in the extract and feed, respectively. The extraction column can then be optimized by calculating the extraction factor and the recovery for different solvent flows and number of theoretical stages. In the modeling, we selected the solvent flow that satisfied the constraints for the extraction factor and the recovery.

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The ADC and stripper were modeled with the rigorous RADFRAC unit block in Aspen Plus. Two design specifications were used to optimize the ADC; the bottom stream should have a purity of at least 99.9 wt % (glacial AA) and the mass recovery of AA should be at least 99.9%. The reflux ratio and the bottom rate were varied to meet the design specifications. The Model Analysis Tool in Aspen Plus was used to optimize the number of stages and the feed stage by minimizing the reboiler duty. The stripper was optimized by varying the reboiler duty for different numbers of stages to produce nearly pure water (99.98%) as bottoms. The tray efficiency of the ADC and the stripper was set to 100%.

One of the most important steps in performing the simulations in Aspen Plus is the selection of the thermodynamic model for the property calculations. For a meaningful process design, it is important that the LLE and VLE of the systems are represented well by the selected model. It was difficult to simultaneously describe the (binary and ternary) LLE and the VLE by a single model with one set of parameters. Aspen Plus does not allow multiple parameter sets to be used for the same model, but different models can be used for different simulation blocks. Therefore, we used the NRTL model to describe the LLE in the extractor and the decanter, while the UNIQUAC-HOC model was used for the VLE calculations in the ADC and stripper. The HOC model is recommended by the Aspen Plus manual to describe the dimerization of AA in the gas phase. The HOC model is thus important for the correct representation of the VLE, but it is not strictly needed to describe the LLE. The NRTL and UNIQUAC parameters were optimized by fitting to binary VLE and LLE data. The fitted parameters for all studied systems can be found in the Supporting Information (Tables S1 to S12). Note that the ternary LLE is predicted from the fitted binary parameters (i.e., no ternary parameters were included in the fitting).

Selection of Physical Solvents

We performed a detailed screening to select solvents for the HED process. Initially, ten promising solvents reported in the literature for the extraction of acetic acid were selected (see Table 1). Next, an elimination procedure, as shortly described below and detailed in our previous work,[19] was used to select the most promising candidates. Typically, the distribution coefficient is used to judge the extraction efficiency of a solvent, but the recovery of the solvent should also be considered in screening studies. For this reason, all solvents with the following properties were eliminated:

- Low distribution coefficient (K). A low K will require an excessive solvent flow, which will increase the solvent recovery costs.
- Azeotrope with acetic acid. Solvents that form an azeotrope with acetic acid require a complicated solvent recovery step and should be avoided.
- Close boilers with acetic acid will require a large number of stages and a high reflux ratio, increasing the capital and operating costs.
- Difficult raffinate treatment. If the boiling point of the solvent−water azeotrope is too close to that of water, and when the water content of the azeotrope is too high (e.g., hexanol), then steam stripping is not efficient for solvent recovery.

By applying this elimination procedure, the solvents 2-MTHF, MPK, MTBE, and EA were selected for process modeling. Kürüm et al.[20] used a similar procedure to screen 34 solvents for acetic acid separation. These authors selected DIPE, MTBE, and EA as the best solvents, but 2-MTHF and MPK were not part of their screening study. Here, we did not select DIPE, because the distribution coefficient is relatively low (K = 0.4 kg/kg at 25 °C, see Table 1). Note that all selected solvents are low boiling and form an azeotrope with water below 100 °C, such that steam stripping can be used for raffinate treatment. Steam stripping cannot be applied for high boiling solvents, which require a more complicated back-extraction step for the raffinate treatment. The reader is referred to Ramdin et al.[19] for a detailed discussion on solvent selection for carboxylic acid extraction.

Table 1. Selection of Solvents for Liquid−Liquid Extraction of Acetic Acid Based on the Distribution Coefficient (K), Density of the Solvent (ρ_s), Boiling Point of the Solvent (T_b), Boiling Point of the Water/Solvent Azeotrope ($T^{w/s}_{b,az.}$), and the Weight Fraction of Water in the Water/Solvent Azeotrope ($w^w_{az.}$)

component	K[a] (kg/kg)	ρ_s (kg/m^3)	T_b (°C)	$T^{w/s}_{b,az.}$ (°C)	$w^w_{az.}$ (w %)	reason[b]
2-MTHF	1.6	854	80.2	71.0	10.6	
MPK	1.0	809	101.0	83.3	19.5	
DIPE	0.4	725	69.0	61.4	3.6	A
MTBE	1.0	740	55.2	52.6	2.2	
ethyl acetate	1.0	902	77.1	70.4	8.2	
n-butanol	1.4	810	117.7	92.5	43.0	B
butyl acetate	0.5	882	126.1	90.2	26.7	C
CPME	0.7	863	106.0	83.0	16.3	A
hexanol	0.9	814	157.0	97.8	70.1	D, E
isoamyl alcohol	1.1	810	132.0	95.2	49.6	D, E

[a]Distribution coefficient based on roughly 10 wt % acetic acid in the extract. [b]Elimination reason: A, low K; B, forms azeotrope with acetic acid; C, close boiling with acetic acid; D, high water content in azeotrope; and E, close boiling with water. Distribution coefficient data taken from refs 23−30.

Economic Evaluation

After the optimization of the HED process, the capital cost (CAPEX) and operating cost (OPEX) were directly taken from the Aspen Economic Analyzer. The OPEX is mainly determined by the requirement of utilities for heating and cooling. The cost of cooling water ($1.0/GJ), low pressure steam ($6.0/GJ), and medium pressure steam ($8.0/GJ) were taken from our previous work.[21]

The CAPEX and OPEX are used to calculate the total annual cost (TAC) of the process

$$\mathrm{TAC} = \mathrm{TIC}*\mathrm{CRF} + \mathrm{OPEX} \tag{4}$$

where TIC is the total investment cost and CRF is the capital recovery factor

$$\mathrm{CRF} = \frac{i(1+i)^n}{(1+i)^n - 1} \tag{5}$$

with i is the interest rate and n is the lifetime of the process. For the economic analysis, the TIC is taken as the total CAPEX of all units, and the interest rate and lifetime are assumed to be 5% and 20 years, respectively.

The cost of acetic acid production is then calculated from

$$C_{AA} = \frac{\mathrm{TAC}}{P_{AA}} \tag{6}$$

where C_{AA} is the cost of acetic acid in $/ton and P_{AA} is the annual production of acetic acid in tons/year. It is important to note that we present a Class 4 estimate of the economics, which has an accuracy of ±30%.

RESULTS AND DISCUSSION

The raw VLE data of the binary systems MTBE-AA and 2-MTHF-AA can be found in the Supporting Information (Tables S13 to S15). The results of the thermodynamic consistency test for the system MTBE-AA can be found in the Supporting Information. In Figure 3, the VLE data of the system MTBE-AA measured by both groups (AU and VVP) are compared to the UNIQUAC-HOC modeling results. The experimental data of both groups are in good agreement with each other and the modeling results. The system MTBE-AA

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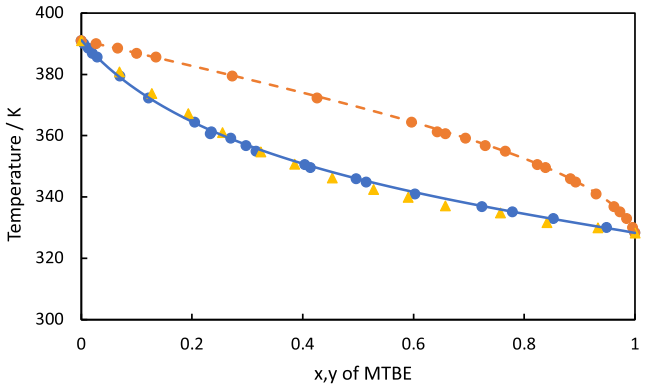

Figure 3. Isobaric VLE of acetic acid and MTBE. Data measured in this work by AU at 101.5 kPa (circles), and VVP at 101.1 kPa (triangles). Lines are UNIQUAC-HOC modeling results for the liquid phase (x, solid line) and vapor phase (y, dashed line), respectively.

shows a simple phase behavior with no azeotrope formation. The VLE of binary system 2-MTHF-AA at different pressures is shown in Figure 4. The UNIQUAC-HOC modeling results

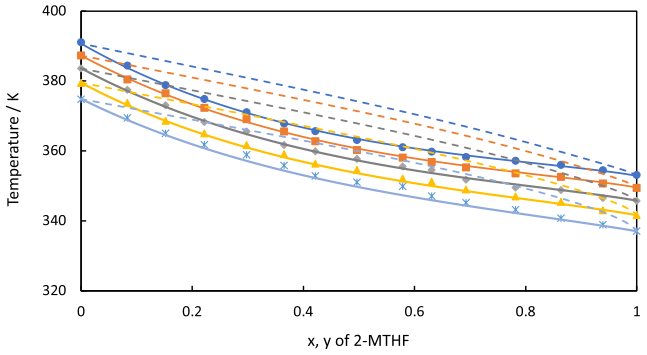

Figure 4. Isobaric VLE of acetic acid and 2-MTHF at different pressures; 101.2 kPa (circles), 90.0 kPa (squares), 80.0 kPa (diamonds), 70.0 kPa (triangles), and 60.0 kPa (crosses). Lines are UNIQUAC-HOC modeling results for the liquid phase (x, solid lines) and gas phase (y, dashed lines), respectively.

are in good agreement with the measured PTx data. Note that the vapor phase composition was not measured because this is not possible in an ebulliometer. The system 2-MTHF-AA also shows a simple phase behavior without the presence of any azeotropes.

The raw LLE data of the ternary system 2-MTHF-AA-water can be found in the Supporting Information (Table S16). In Figure S2 of the Supporting Information, we provide a Hand plot to check and confirm the reliability of the data. In Figure S3 of the Supporting Information, a plot of the distribution coefficients and selectivities as a function of the AA content in the extract for different temperatures is shown. The distribution coefficient and selectivity of AA decrease as the concentration of AA increases in the extract. The distribution coefficient decreases as the temperature increases, while the selectivity is almost independent of the temperature. The reason for this is the coextracted amount of water, which increases as a function of the AA concentration in the extract, but the effect of temperature on water coextraction is small (see the Supporting Information). Note that the distribution coefficient of AA in 2-MTHF is the highest among the solvents screened, as shown in Table 1. A comparison of the experimental data and the model predictions for the ternary systems water-AA-solvent is provided in Figure 5. Clearly, the NRTL model can accurately represent the ternary LLE data of all of the studied systems.

In Figure 6, the performance of the extractor is provided for the water-AA-2-MTHF system that contains 10 wt % AA in the feed. Similar plots for the other solvents can be found in Figure S4 of the Supporting Information. The combination of the solvent flow and the number of stages that satisfied the constraints for the recovery (99.5%) and the extraction factor (between 1.5 and 2.0) was selected for the process design. We have run continuous counter-current extraction experiments in a Kuhni ECR60/50G (Sulzer Chemtech) column to confirm that such high recoveries are possible; see the Supporting Information for more details. For all systems, we selected 15 stages for the extractor. In Table 2, the optimized parameters for the extractor, ADC, and stripper can be found for all the systems. The differences between the systems are mainly in the reflux ratio and the reboiler duty. The reflux ratio is determined by the mass balance considering the composition of the feed (water-to-solvent ratio in the extract) and the azeotropic composition of the water-solvent mixture. The reboiler duty generally increases with an increasing fraction of water in the azeotrope, which is confirmed in Table 2. MTBE has a significantly lower reboiler duty compared to the other solvents due to its excellent properties like low water content and boiling temperature of the azeotrope (low vaporization enthalpy), a reasonably high distribution coefficient (low solvent flow), and a low coextraction of water (low reflux ratio to meet mass balance).

Subsequently, we computed the TAC and the separation cost of AA using different extraction solvents. In Table 3, the results are presented for a feed concentration of 10 wt % AA. The lowest and highest TAC and cost are observed for MTBE and MPK, while 2-MTHF and EA show a similar cost of merit. In Figure 7, we present the separation cost as a function of the AA concentration in the feed. Clearly, the separation cost increases exponentially as the concentration is decreased, which has been seen for other processes as well.[13] The separation cost in the studied range shows the following order MTBE < 2-MTHF ~ EA < MPK. The similar performance of 2-MTHF and EA can be explained by their comparable properties (water content in the azeotrope and the boiling temperature of the azeotrope, see Table 1). Similarly, the poor performance of MPK is related to the high water content and boiling temperature of the azeotrope. Although MTBE has superior properties for AA extraction, it has some environmental concerns and has been banned or phased-out in the United States as a gasoline additive. Taking this into account, 2-MTHF and EA are good alternatives to AA extraction. In Figure 7, we also plotted the European market price of acetic acid ($660/ton), which essentially shows that the lowest concentration allowing for an economical recovery of AA with the HED process is roughly 5 wt %, assuming that the separation cost contributes half to the production cost. Therefore, electrochemical and biochemical processes for AA production should aim for a product concentration of at least 5 wt %. This is an important target for (electro)chemists who aim to optimize the conversion process of CO_2 to acetic acid. State-of-the-art CO_2 electrolyzers currently produce acetic acid with concentrations less than 2 wt %,[22] but the concentration

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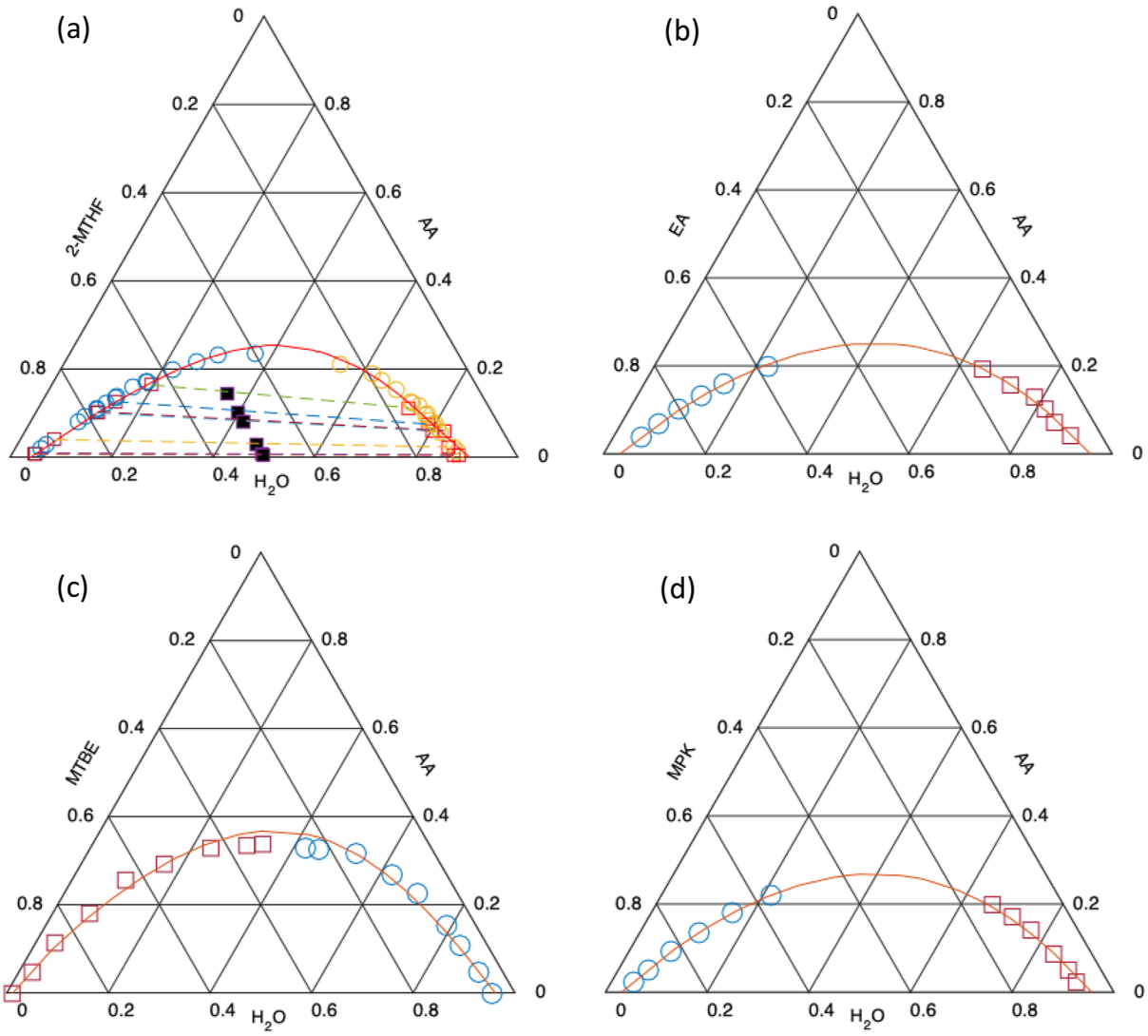

Figure 5. Ternary LLE of the systems water + AA + solvent at 298.15 K. (a) 2-MTHF data measured in this study (squares) and Männistö et al.[32] (circles), dashed lines are tie-lines and solid squares are overall compositions from this work, (b) EA data from Colombo et al.,[26] (c) MTBE data from Miao et al.,[25] and (d) MPK data from Bianco et al.[23] Solid lines are calculated with the NRTL model. Mass fractions are plotted on the axes.

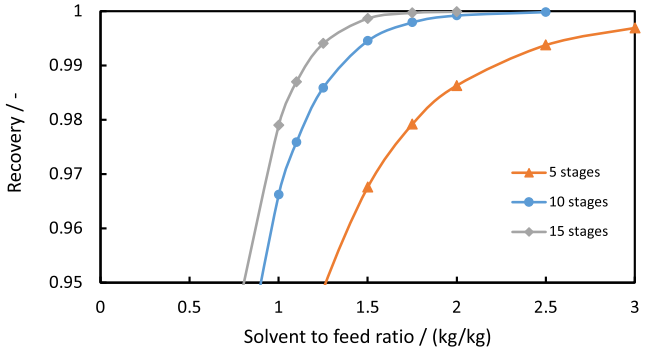

Figure 6. Optimization of the number of stages in the extractor for the system water-AA-2-MTHF with a feed of 10 wt % AA. The recovery is calculated as a function of the solvent to feed ratio for different theoretical stages.

can be and should be increased to the desired target with a proper reactor design to have an economically viable process.

CONCLUSIONS

Acetic acid (AA) is an important chemical that is mainly produced from the carbonylation of methanol, which is an energy-intensive process. Recently, enzymatic fermentation, biomass hydrolysis, and electrochemical reduction of CO_2 or CO have been used to produce acetic acid. Unfortunately, these processes produce a dilute AA stream that requires purification to comply with market specifications. Conventional distillation for separation of AA from water is not possible due to the presence of a pinch point at the pure end of water. Here, we have used a liquid–liquid extraction followed by azeotropic distillation to concentrate dilute AA streams (1, 2.5, 5, and 10 wt %) up to glacial AA. The solvents 2-MTHF, MPK, MTBE, and EA were selected for the process modeling. Due to lack of data, we measured the VLE of the binary systems acetic acid + 2-MTHF, and MTBE + acetic acid, and the ternary liquid–liquid equilibria (LLE) of 2-MTHF + water + acetic acid. The experimental data was used to fit the NRTL and UNIQUAC models, which were used in Aspen Plus to design and model the hybrid extraction and azeotropic distillation (HED) process. After optimization for different

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Table 2. Optimized Extraction and Azeotropic Distillation System for the Separation of 10 wt % of Acetic Acid from Water with Different Solvents

solvent	2-MTHF	MTBE	MPK	EA
		Extractor		
feed flow (kg/h)	10,000	10,000	10,000	10,000
AA concentration (wt %)	10	10	10	10
solvent flow (kg/h)	13,000	13,000	11,500	12,500
number of stages	15	15	15	15
		ADC		
number of stages	40	30	50	40
feed stage	25	20	20	23
reflux ratio (kg/kg)	0.09	0.05	0.9	0.02
reboiler duty (MW)	2.578	1.639	3.924	2.299
AA purity (wt %)	99.9	99.9	99.9	99.9
		Stripper		
number of stages	10	10	10	10
feed stage	1	1	1	1
reboiler duty (kW)	875	780	826	795

Table 3. Total Annual Cost and Cost for the Separation of 10 wt % of Acetic Acid from Water with Different Solvents

solvent	2-MTHF	MTBE	MPK	EA
TAC (M$/y)	1.25	1.06	1.77	1.26
C_{AA} ($/ton)	158	134	225	161

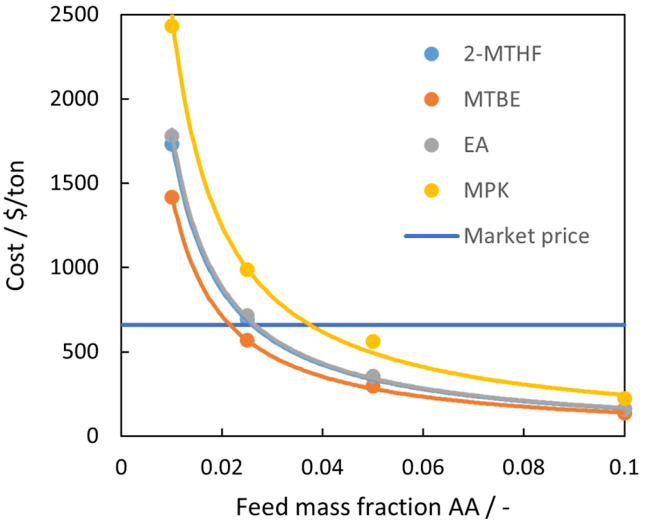

Figure 7. Separation cost of acetic acid as a function of feed concentration for different extraction solvents. Lines are power fits to modeling data to guide the eye. European market price of acetic acid taken from ref 33.

feed concentrations, the economics of the HED process was evaluated for all solvents. For 10 wt % of AA in the feed, our analysis shows that the lowest and highest separation cost is obtained for MTBE (~$135/ton) and MPK (~$225/ton), while 2-MTHF and EA show similar performance (~$160/ton). The superior performance of MTBE is related to its properties such as low water content and boiling temperature of the solvent−water azeotrope, relatively high distribution coefficient, and low coextraction of water. We show that the separation cost increases exponentially with decreasing feed concentrations. From this analysis, we derived minimum concentration requirements (~5 wt %) beyond which it is possible to have an economically feasible separation of AA. Renewable processes for AA production, such as electrochemical conversion of CO_2 or CO, should aim for at least this concentration target. Future research should focus on developing processes to efficiently extract acetic acid from dilute streams.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.5c03913.

Raw data of the VLE and LLE measurements, optimized binary interaction parameters, toxicity data of the solvents, uncertainty analysis, thermodynamic consistency tests, counter-current extraction results, plots of distribution coefficient and selectivity, Hand plot, and plots for optimization of solvent flow as a function of recovery in the extractor (PDF)

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Notes

The authors declare no competing financial interest.

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