RECOVERY OF CARBOXYLIC ACIDS FROM FERMENTATION BROTH VIA

ACID SPRINGING

A Thesis

by

JIPENG DONG

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2008

Major Subject: Chemical Engineering

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Approved by:

Chair of Committee,	Mark T. Holtzapple
Committee Members,	Mahmoud M. El-Halwagi
	Sergio C. Capareda
Head of Department,	Michael Pishko

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ABSTRACT

Recovery of Carboxylic Acids from Fermentation Broth

via Acid Springing. (December 2008)

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Chair of Advisory Committee: Dr. Mark T. Holtzapple

A proprietary technology owned by Texas A&M University, named the MixAlco Process, can process biodegradable wastes (e.g., paper fines, municipal solid waste, sewage sludge, and industrial biosludge) to obtain carboxylic acids and mixed alcohol fuels as downstream products. The process uses a mixed culture of naturally occurring microorganisms, found in natural habitats such as the rumen of cattle and marine and terrestrial swamps, to convert biomass wastes into a mixture of carboxylic acids. As the microorganisms digest the biomass and convert it into a mixture of carboxylic acids, the pH must be controlled. This is done by adding a buffering agent (e.g., calcium carbonate), thus a mixture of carboxylate salts is produced.

Carboxylic acids can be recovered from the carboxylate salts directly through a process known as 'acid springing.' This process mixes carboxylate salts (e.g., $Ca(Ac)_2$) with carbon dioxide (CO_2) and a low-molecular-weight tertiary amine ($\mathscr{R}_3N$) to precipitate calcium carbonate ($CaCO_3$). The low-molecular-weight tertiary amine carboxylate ($\mathscr{R}_3NHAc$) remains in the liquid. Then, this liquid is mixed with tri-*n*-

octylamine (R_3N) and distilled. During distillation, tertiary amine carboxylate can be thermally decomposed into the amine itself, which is recycled, and carboxylic acids. Theoretically, no chemicals are consumed or wastes produced during this process.

Essentially, the 'acid springing' process consists of precipitation and thermal conversion. The research described in this thesis focuses on choosing a proper low-molecular-weight tertiary amine suitable for the process and determining the optimal temperature for thermal conversion. Because the fermentation broth mainly contains calcium acetate (more than 80% by weight), an aqueous solution of reagent-grade calcium acetate is used for research purposes instead of fermentation broth. Then, the actual fermentation broth is used to verify the conclusions.

A 0.3-L pressure vessel reactor was designed and made for precipitation and a distillation bench was prepared for thermal conversion. The recovery effectiveness was evaluated by gas chromatography (GC) and a pH test. The results indicated that tributylamine is the best choice among several kinds of low-molecular-weight tertiary amine. The optimal temperature for concentrating tributyl ammonium acetate is about 110 ^{o}C, and the optimal temperature for recovering acetic acid from tributyl ammonium acetate is about 170 ^{o}C. The corresponding optimal temperatures for the process dealing with fermentation broth are 110 and 190 ^{o}C.

DEDICATION

To my beloved wife, Suining

To my lovely daughter, Nancy

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CHAPTER I

INTRODUCTION

Although it has just 5% of the global population, the United States burns nearly 25% of the world's oil (Figure 1-1). In 2006, oil imports (670.9 million tonnes) were 71.4% of US oil consumption (938.8 million tonnes) (BP, 2007). Furthermore, the use of oil is projected to peak about 2007 and the supply is then projected to be extremely limited in 40 to 50 years (Pimentel et al., 2004), so the United States desperately needs a liquid fuel replacement for oil in the future to decrease its dependence on imports, thereby improving energy security.
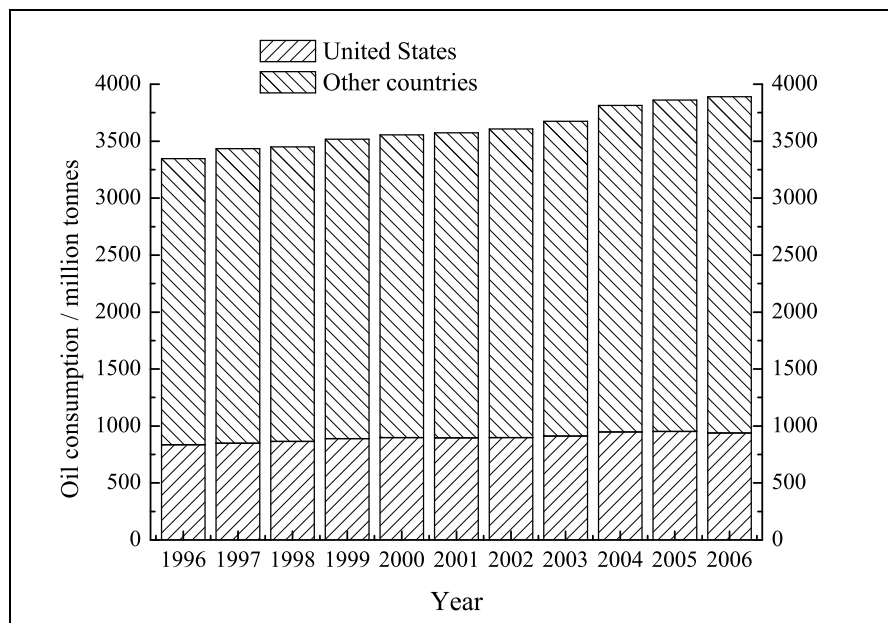
Figure 1-1. Oil consumption of the United States and other countries.

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This thesis follows the style of Biotechnology and Bioengineering.

In the face of these questions and concerns, ethanol fuel is steadily becoming a promising alternative to gasoline based on the following merits:

1) Ethanol can be made from food feedstocks such as corn and sugarcane. The conversion of corn and sugarcane into ethanol by fermentation is a well-known and established technology.

2) Ethanol is compatible with today's vehicles, and can be blended with traditional gasoline in grades from E10 (10% ethanol) to E85 (85% ethanol).

3) Ethanol is a renewable fuel and very safe for the environment because it is biodegradable.

4) Ethanol reduces pollution and greenhouse gas emissions. Because ethanol contains a higher percentage of oxygen than traditional petroleum-based gasoline, it burns more completely than petroleum-based fuels.

With government support, U.S. ethanol production increased about 25% from 3.9 billion gallons in 2005 (Form EIA-819, 2005) to 4.9 billion gallons in 2006 (Form EIA-819, 2006). Meanwhile, the Renewable Fuels Association reported that the number of ethanol plants operating in the United States increased from 95 in January of 2006 to 110 in January 2007, with 76 plants under construction or expansion (RFA website, 2008). In 2006, ethanol only accounted for about 4% of U.S. finished motor gasoline (EIA, 2007).

Unfortunately, corn grain, the current source of ethanol in the United States, requires large amounts of land. Besides, there is a large demand for corn as food. These all limit the total amount of ethanol that can be produced from corn. So corn is unlikely

to be a long-term source of ethanol, and scientists are turning to other alternative sources.

The amount of biomass waste produced in the United States is staggering. There is a huge amount of inexpensive, usable energy available in the form of paper fines, municipal solid waste, sewage sludge, and industrial biosludge. Table 1-1 summarizes the current annual production of biodegradable wastes in the United States. These resources are locally available nearly everywhere. Further, they are inexpensive and often free. How to make ethanol from them is a promising subject.

Table 1-1. Approximate annual production of U.S. biodegradable wastes

Waste	**Amount (million tonnes)**
Municipal Solid Waste	78
Sewage Sludge	10.9
Industrial Biosludge	3
Recycled Paper Fines	4.3
Agricultural Residues	400
Forestry Residues	330
Manure	220
Total	**1046**

(http://www.asee.org/conferences/edi/upload/2004-EDI-Holtzapple-PDF.pdf)

Over the past 30 years, converting biomass waste into useful products has aroused increasingly intense interest. Much great research has been done in this field. Methane production from anaerobic fermentation of sewage sludge has been studied by Ghosh (Ghosh et al., 1975). Producing methane via anaerobic fermentation of municipal solid wastes (Debaere et al., 1985) and agricultural residues (Sterzinger, 1995) has been discussed separately. Simultaneous saccharification and fermentation (SSF) has been developed for converting biomass into fuel ethanol efficiently and economically (Takagi et al., 1977; Wright et al., 1988).

A proprietary technology owned by Texas A&M University – which can process biodegradable wastes to obtain carboxylic acids $(C_2–C_7)$ and mixed alcohol fuels as downstream products – has been in development since 1991 (Holtzapple et al., 1997; 1999). Named the MixAlco Process, the flowchart is shown in Figure 1-2.

The process uses a mixed culture of naturally occurring microorganisms, found in natural habitats such as the rumen of cattle and marine and terrestrial swamps, to convert biomass into a mixture of carboxylic acids produced by anaerobic digestion (Agbogbo and Holtzapple, 2007). The pH must be controlled by adding a buffering agent, calcium carbonate, for the microorganisms to digest the biomass and convert it into a mixture of carboxylic acids. Thus, a mixture of carboxylate salts is produced. Methanogenesis, which is the natural final stage of anaerobic digestion, is inhibited by adding an inhibitor, iodoform. The resulting fermentation broth contains the produced calcium carboxylate that must be dewatered. Then the carboxylic acids can be recovered from the concentrated calcium carboxylate.
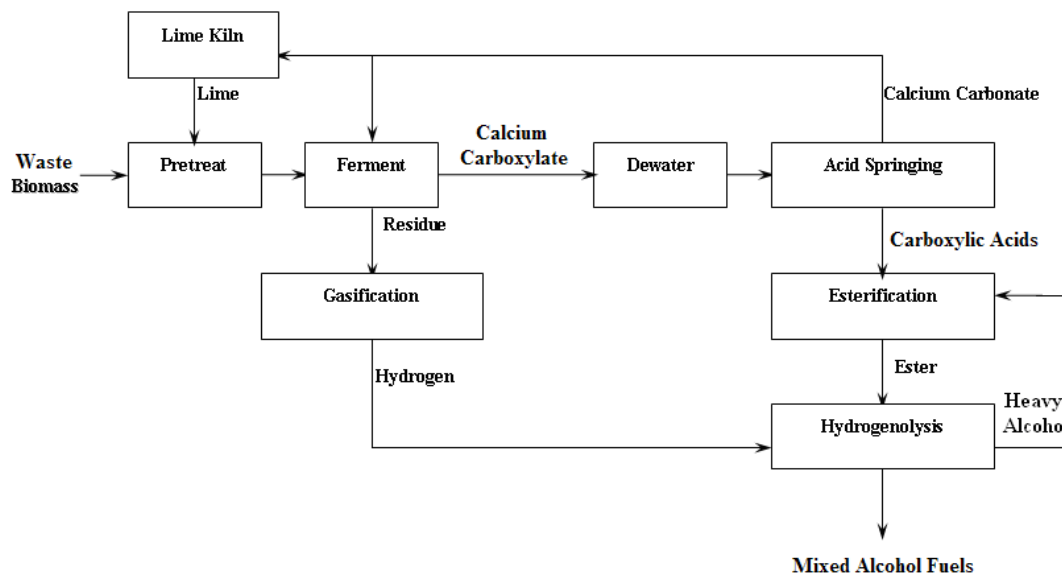
Figure 1-2. MixAlco process overview.

Recovering carboxylic acids with long-chain tertiary amines by reactive extraction has been the subject of many publications (Vanura and Kuca, 1976; Wennersten, 1983; Sato et al., 1985; Tamada et al., 1990; King, 1992; Bizek et al., 1993; Prochazka et al., 1994; Juang and Huang, 1994; Juang and Huang, 1997). Because the acids must be separated from the extraction solvent by distillation after reactive extraction, a simplified method has been developed to recover acids directly through reactive distillation using triethylamine and tri-*n*-octylamine (Williamson, 2000), which is known as the 'acid springing' process.

As shown in Figure 1-3, the 'acid springing' process mixes carboxylate salts (e.g., $Ca(Ac)_2$) with carbon dioxide (CO_2) and triethylamine ($\mathcal{R}_3N$) to precipitate

calcium carbonate ($CaCO_3$). Triethyl ammonium acetate ($\mathscr{R}_3NHAc$) remains in the liquid.

$$Ca(Ac)_2 + H_2O + 2\ \mathscr{R}_3N + CO_2 \longrightarrow CaCO_3 \downarrow\ +\ 2\ \mathscr{R}_3NHAc \qquad (1)$$
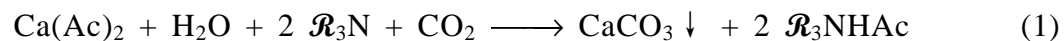
Then this liquid is mixed with tri-n-octylamine (R_3N) and distilled. In the distillation process, triethylamine ($\mathscr{R}_3N$) is recovered from the top of the distillation column whereas the remaining liquid contains tri-n-octyl ammonium acetate (R_3NHAc).

$$\mathscr{R}_3NHAc \xrightarrow{\Delta} \mathscr{R}_3N\ +\ HAc \qquad (2)$$

$$HAc\ +\ R_3N \longrightarrow R_3NHAc \qquad (3)$$

Tri-n-octyl ammonium acetate (R_3NHAc) is then distilled to recover acetic acid (HAc) from the top of the distillation column leaving tri-n-octylamine (R_3N) in the bottom of the column, which is recycled. Theoretically, no chemicals are consumed or wastes produced during this process.

$$R_3NHAc \xrightarrow{\Delta} R_3N\ +\ HAc \qquad (4)$$
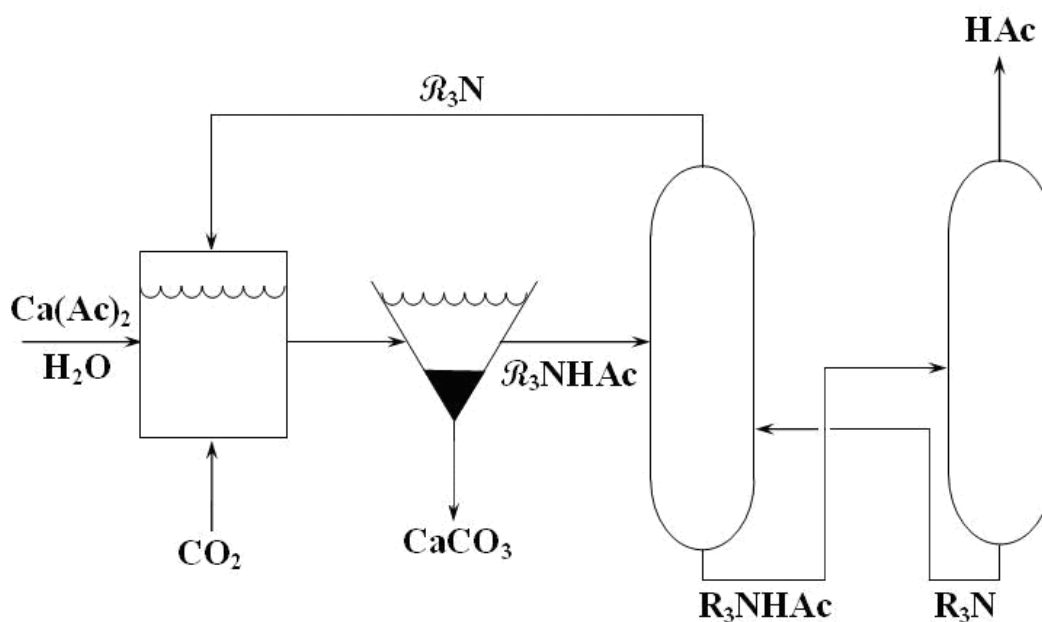
Figure 1-3. Acid springing process.

In Williamson's work, Reaction 3 mentioned above was not clearly proven to occur during the process. It is the key reaction for recovery of acetic acid through distillation. One of the challenges is that triethylamine and acetic acid form a maximum azeotrope (Table of Binary Organic Azeotropes, 2008). In this thesis, an intensive study has been performed to evaluate the feasibility of using triethylamine. As will be shown, the results indicate that the process using triethylamine cannot recover acetic acid effectively.

To address this problem, the objectives of this project are to choose the best low-molecular-weight tertiary amine and to redesign the 'acid springing' process accordingly. Because the process essentially consists of precipitation and thermal

conversion, the best low-molecular-weight tertiary amine should meet the following criteria:

1) The amine can precipitate calcium carbonate from the fermentation broth to form amine carboxylate.

2) The resulting amine carboxylate can decompose into amine itself and carboxylic acids.

3) Carboxylic acids are easy to recover from the liquid mixture via distillation.

According to these criteria, several low-molecular-weight tertiary amines will be screened in a precipitation study. Then, the best low-molecular-weight tertiary amine will be identified during the thermal conversion step. Finally, the optimal parameters will be determined for the 'acid springing' process involving the chosen tertiary amine.

Because the fermentation broth mainly contains calcium acetate (more than 80% by weight), an aqueous solution of reagent-grade calcium acetate is used at first for research purposes instead of fermentation broth, which simplifies the process and makes it easier to understand. Furthermore, the results derived from this simplified process are readily applied to the real process involving fermentation broth without too much deviation. Then, actual fermentation broth is used to verify the optimal parameters derived from the aqueous solution of reagent-grade calcium acetate.

CHAPTER II

EXPERIMENTAL METHODS

Precipitation of Calcium Carbonate

The primary purpose of the precipitation study is to find the appropriate tertiary amines that can precipitate calcium carbonate from fermentation broth and the optimum reaction pressure that produces higher product yields and shorter times to reach equilibrium.

The aqueous solution of reagent-grade calcium acetate is reacted with carbon dioxide and low-molecular-weight tertiary amine to form tertiary amine acetate and calcium carbonate. Because low-molecular-weight tertiary amine is volatile, it can escape the system. A 0.3-L stainless steel pressure vessel is used to perform the precipitation (Figure 2-1).
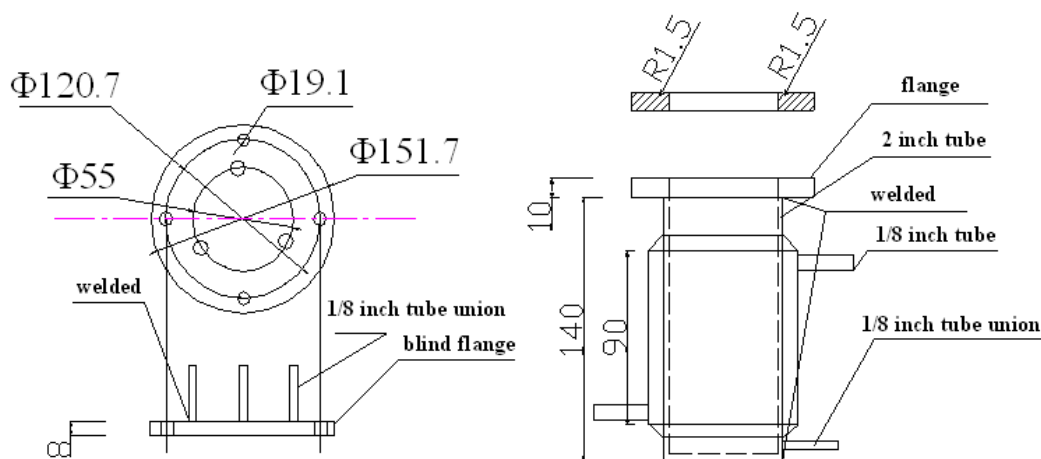
Figure 2-1. Projected dimensions of 0.3-L pressure vessel reactor.

A 2-inch tube, with a flange welded on one end and a 4-mm stainless steel sheet welded on the other end, is employed as the reactor. An O-ring seal is used to prevent loss of volatile components from the reactor top. A blind flange is secured to the reactor by bolting with four screw bolts and nuts. Three 1/8-inch tube unions are welded on the blind flange. Two of them are for use as CO_2 inlet and outlet whereas a 1/8-inch tube with a blind end is fixed on the other tube union through which a thermocouple is inserted into the reactor. Another 1/8-inch tube union is welded at the bottom of the reactor for sampling. The reactor is wrapped with the heat insulation (PVC/NBR rubber-plastic heat insulation materials) for thermal insulation. A schematic of the precipitation unit is shown in Figure 2-2.

An aqueous solution containing reagent-grade calcium acetate is put in the reactor with low-molecular-weight tertiary amine and mixed by a magnetic stirrer during the reaction. The reactor is then pressurized to 308 kPa (30 psig) with carbon dioxide which remains until the system comes to equilibrium. The time for this procedure to reach equilibrium is determined by monitoring the solution temperature in the reactor. The reaction is exothermic and the heat dissipated through the reactor wall is small because of the slight temperature difference between solution and environment. Further, the system is well insulated. Once the solution temperature stops increasing, equilibrium is assumed to be achieved. Then the solution is centrifuged for 25 minutes at 4000 rpm to separate the solids from the liquid.
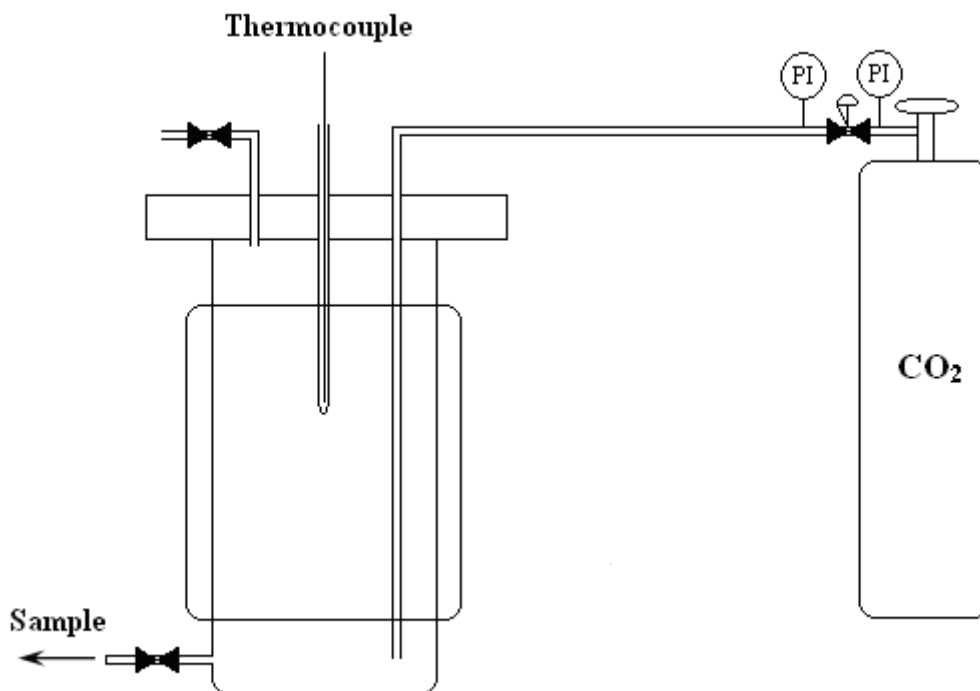
Figure 2-2. Schematic of precipitation unit.

As shown in Figure 2-3, the centrifuge makes a very nice separation and the liquid containing tertiary amine acetate is saved for the concentration and distillation study. The remaining solids are rinsed with water to remove excess amine. Then the solid is dried in the oven at 105℃ and weighed for product yield calculations.

Then the precipitation is repeated at 446 kPa (50 psig), 584 kPa (70 psig), and 722 kPa (90 psig) whereas the other conditions are unchanged. The time to reach equilibrium and product yield are recorded as a function of reaction pressure.
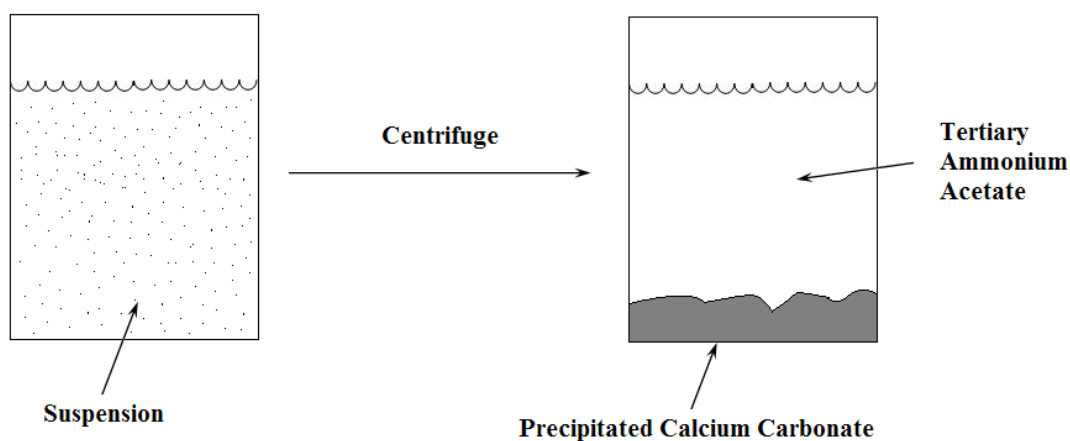
Figure 2-3. Centrifugal separation.

Simple Distillation

A variety of tertiary amines were chosen for the precipitation study. Several studies were performed via simple distillation to evaluate their performances in concentration and thermal conversion.

The original fermentation broth contains only 2.5–4% (by weight) calcium carboxylate and the remainder is water. Even after being dewatered by vapor compression, the fermentation broth still has more than 70% (by weight) water. This water must be removed before the thermal conversion step. Because the solubility of calcium carboxylate is limited to about 30% (by weight), concentrating the fermentation broth to 100% purity is not practical. The remaining water is removed after the precipitation step by concentration the aqueous solution of tertiary amine acetate. To determine if water and acetic acid can be recovered from the aqueous solution of tertiary

amine acetate separately, the apparatus shown in Figure 2-4 was used. The apparatus has been assembled inside a hood and is attached to a metal support using clamps.

A round-bottom flask sits in a heating mantle, which is controlled by a Variac. The temperature of the liquid in the flask is measured by a thermocouple, which is connected to a temperature display. Then, the vapors are sent to a water-cooled condenser. The distillate is collected into sample tubes according to the corresponding liquid temperature in the flask for gas chromatography analysis and pH test.
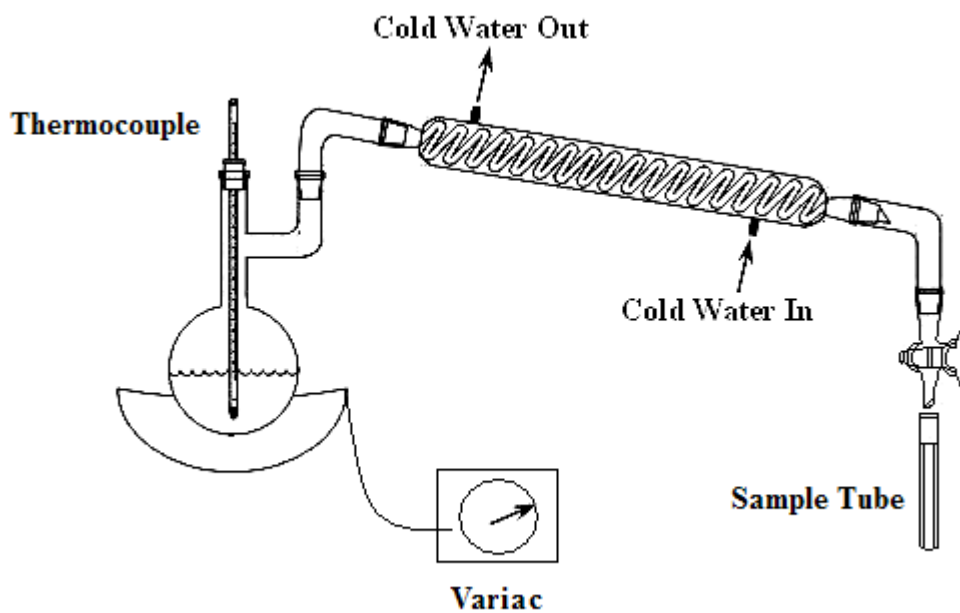
Figure 2-4. Schematic of simple distillation unit.

Batch Distillation

Once a tertiary amine is chosen as the most suitable option for the process according to the results of precipitation and simple distillation, optimization studies were performed through batch distillation to determine the optimal temperature that led to high-purity products for water recovery (concentration) and acid recovery (thermal conversion). As shown in Figure 2-5, a batch distillation unit is employed in the laboratory. The apparatus has been assembled inside a hood and is attached to a metal support using clamps.

A flat-bottom flask is used as the reactor, which is heated by a heating plate controlled by a temperature controller. The vapors were sent into the condenser through a column. The temperature of the vapors leaving the column was measured by a thermocouple. The distillate was collected into sample tubes according to its corresponding liquid temperature in the flask. The column was wrapped with the heat insulation (PVC/NBR rubber-plastic heat insulation materials) to prevent loss of heat. Because tri-*n*-octylamine is reactive with oxidizing agents at high temperature, a nitrogen stream is supplied at the bottom of column as a blanket when the distillation is ended.
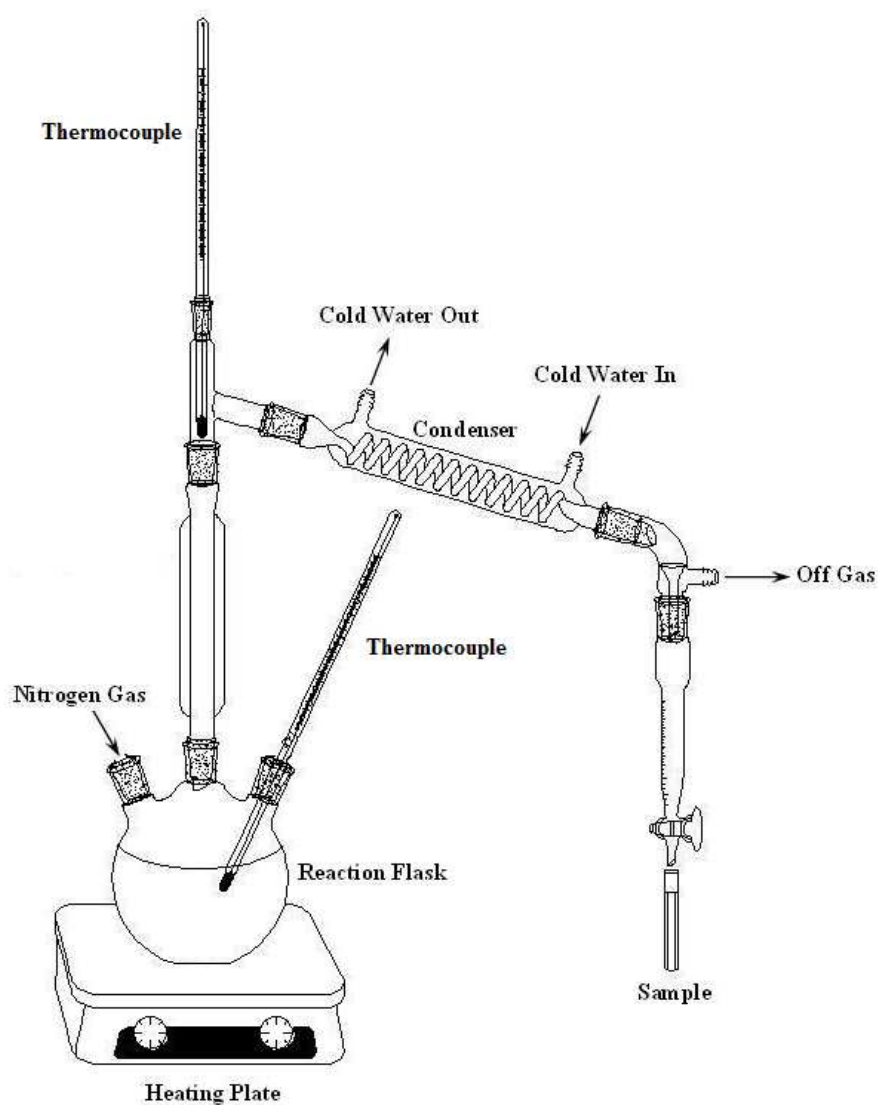
Figure 2-5. Schematic of batch distillation unit.

Gas Chromatography

Acetic acid is analyzed by a gas chromatograph (Agilent Model: 6890 No. G1530, USA) equipped with a flame ionization detector (FID). Collected liquid samples collected are diluted with distilled water and combined with the internal standard (4-

methyl-*n*-valeric acid) and acidified with 3-M phosphoric acid before injection into the gas chromatograph.

pH Test

Because the GC (gas chromatography) analysis cannot distinguish between acetic acid and tertiary amine acetate existing in the aqueous solution, a pH test is necessary to determine the composition of distillate samples. A pH meter is used for this purpose.

Balances

The densities of all the liquids studied are listed in Table 2-1, by which volumes can be translated into mass balances.

Table 2-1. Densities of liquids studied

Liquid	*Density*
Water	1 g/mL
Acetic acid	1.05 g/mL
Triethylamine	0.73 g/mL
Tripropylamine	0.76 g/mL
Tributylamine	0.78 g/mL
Tri-*n*-octylamine	0.81 g/mL

CHAPTER III

EXPERIMENTAL RESULTS

Precipitation of Calcium Carbonate

Trimethylamine is a gas at room temperature because of its low boiling point (2.9 ^{o}C), so it is not an option for the 'acid springing' process. Besides trimethylamine, there are still several kinds of low-molecular-weight tertiary amine as candidates including triethylamine, tripropylamine, tributylamine, triamylamine, and trihexylamine. Precipitation studies are performed to determine if a particular tertiary amine can make calcium carbonate precipitate from the aqueous solution of calcium acetate.

An aqueous solution (51 mL) containing calcium acetate (15% by weight) was mixed with 10% excess tertiary amine and put into the reactor which was then pressurized to 308 kPa (30 psig) by carbon dioxide. During the reaction, the solution temperature monitored by thermocouple was recorded as a function of time to determine if equilibrium was achieved. Then the solid product was dried and weighed for product yield calculation.

Unlike triethylamine, tripropylamine, and tributylamine, when triamylamine and trihexylamine were used, no reaction appeared to occur and no solids precipitated. So triamylamine and trihexylamine are not suitable for the process.

As shown in Figures 3-1, 3-2, and 3-3, triethylamine is the quickest to achieve equilibrium whereas tributylamine is the slowest. The results of product yield for these systems are listed in Table 3-1.
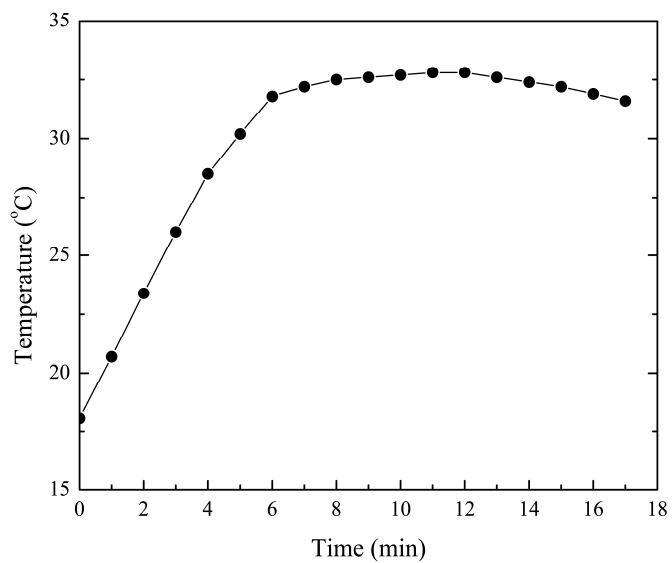
Figure 3-1. Temperature-time curve of system involving triethylamine.
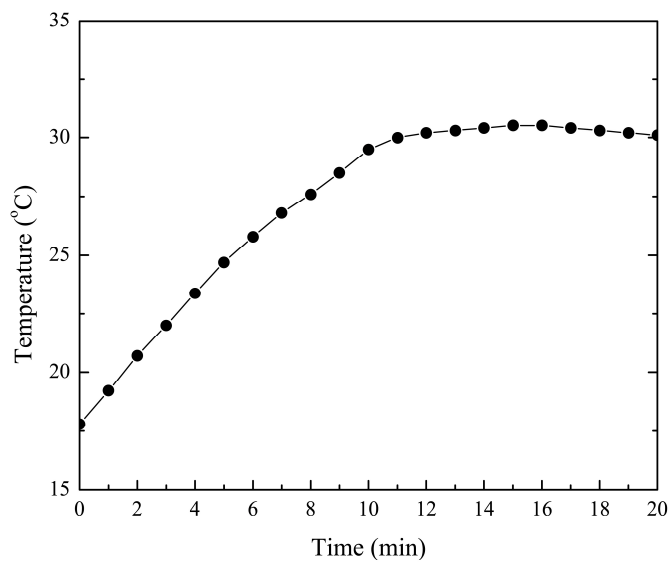
Figure 3-2. Temperature-time curve of system involving tripropylamine.
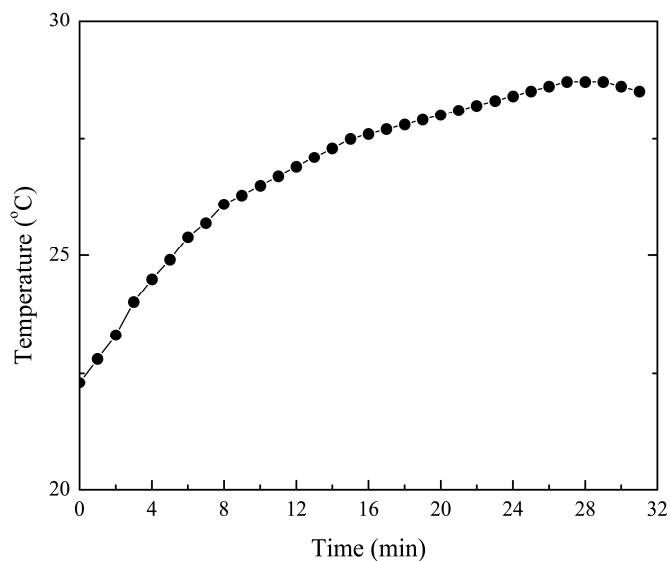
Figure 3-3. Temperature-time curve of system involving tributylamine.

Table 3-1. Results of product yield calculation

Tertiary Amine	Weight of Solid Product (g)	Product Yield (%)
Triethylamine	5.6	98.1
Tripropylamine	5.5	96.5
Tributylamine	5.5	96.5

Concentration of Tertiary Amine Acetate

Concentrating tertiary amine acetate can be done either before mixing it with tri-n-octylamine, or afterward. Three preliminary studies were performed to determine if

water could be separated from tertiary amine acetate via distillation and to determine the temperature range that tertiary amine acetate decomposes.

Concentration Study I involves triethyl ammonium acetate. First, the temperature needed to decompose triethyl ammonium acetate into triethylamine and acetic acid was determined. Reagent-grade triethyl ammonium acetate was put into the flask and heated. The top and bottom temperatures were recorded as a function of time and are shown in Figures 3-4 and 3-5. According to the temperature curves, the reaction occurs between 110 and 120 ^{o}C. So, the temperature should not exceed 110 ^{o}C to concentrate triethyl ammonium acetate.
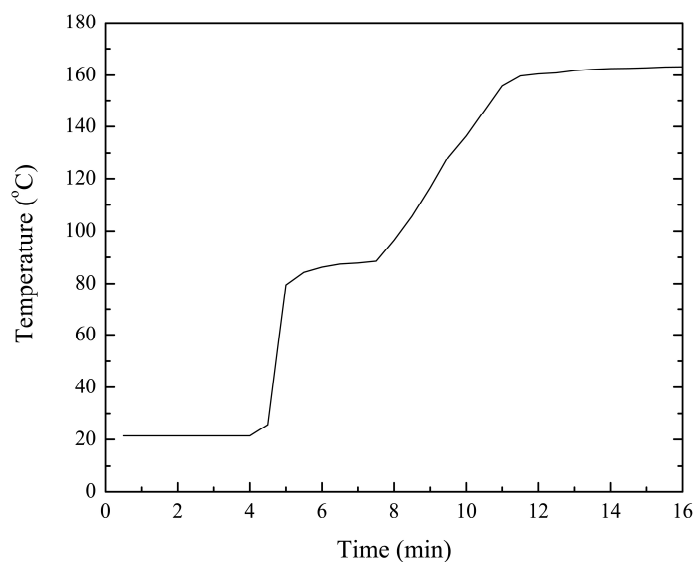
Figure 3-4. Time profile for top temperature of batch distillation of triethyl ammonium acetate.
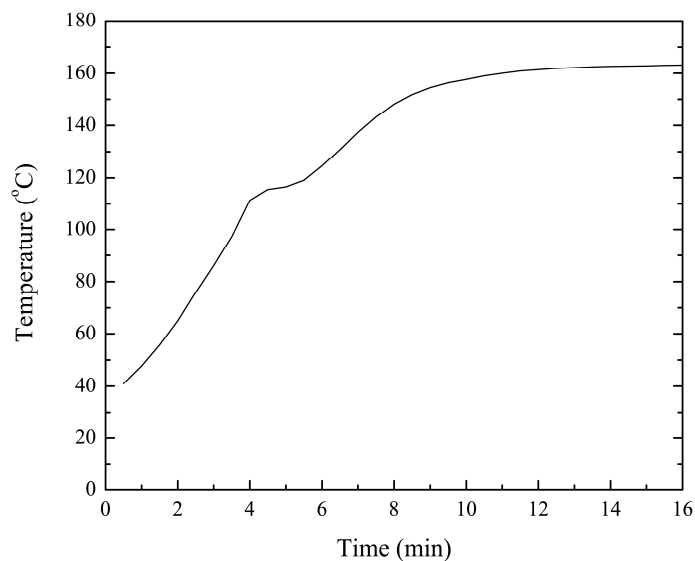
Figure 3-5. Time profile for bottom temperature of batch distillation of triethyl ammonium acetate.

Then, a 156-mL sample containing triethyl ammonium acetate (75 mL), excess triethylamine (11 mL), and water (70 mL) was put into the flask and distilled. The temperature curve is shown in Figure 3-6 and the collected distillate samples are summarized in Figure 3-7. Because excess triethylamine and water codistill at 76 $^{\circ}$C (vapor composition is 90% w/w triethylamine and 10% w/w water) (Anderson et al., 1992), there is a flat in the temperature curve around 76 $^{\circ}$C. The first distillate sample is collected at 76 $^{\circ}$C, which is far below the boiling point of each component of this system.
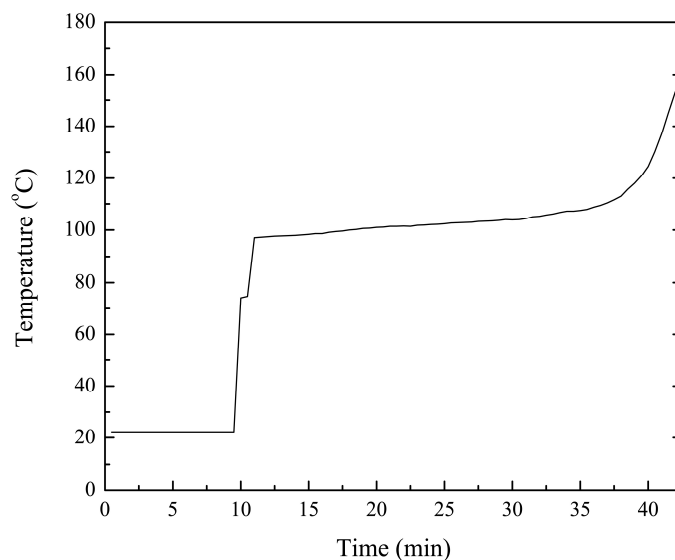
Figure 3-6. Time profile for bottom temperature of simple distillation of the system containing triethyl ammonium acetate, excess triethylamine, and water.
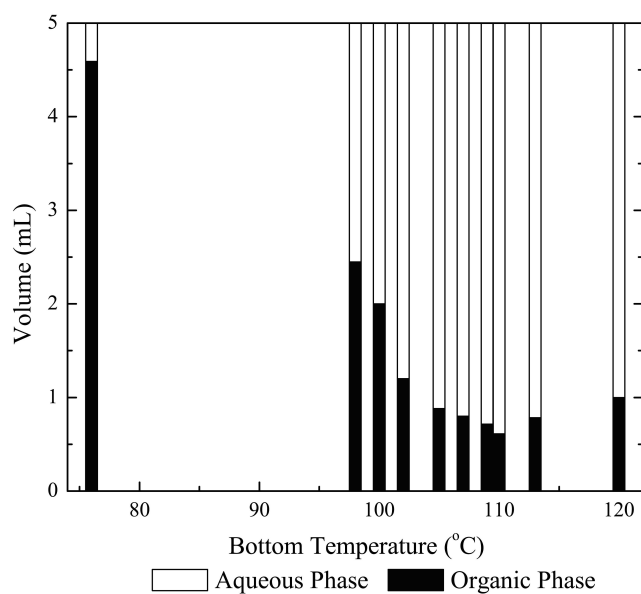
Figure 3-7. Distillate samples of triethyl ammonium acetate collected at different bottom temperatures.

Because triethylamine is not miscible with water whereas triethyl ammonium acetate is, the distillate sample will be a two-phase liquid mixture if there is triethylamine present. According to Figure 3-7, excess triethylamine leaves the system steeply within the temperature range from 76 ^{o}C to 100 ^{o}C. When the temperature exceeds 110 ^{o}C, triethyl ammonium acetate cracks and produces triethylamine, so the volume of the organic phase starts to increase. The acetic acid concentration of the distillate samples (Figure 3-8) demonstrates that some acetic acid exits the system when the temperature is above 100 ^{o}C. As shown in Figure 3-9, the pH of all samples is above 10 because of the presence of triethylamine. In other words, acetic acid exists in the distillate as triethyl ammonium acetate.
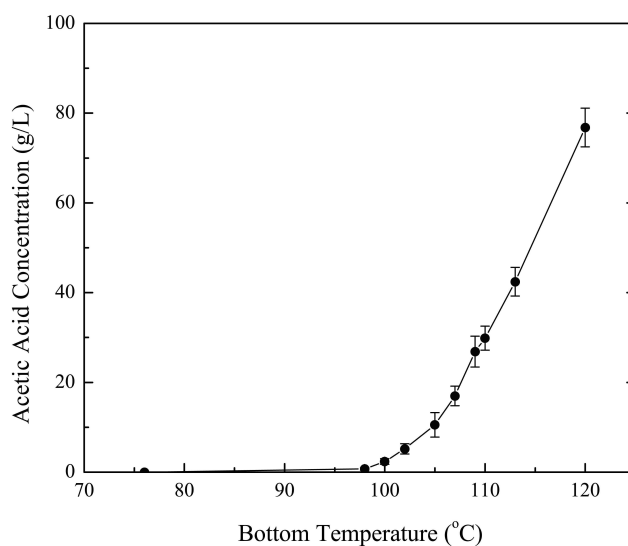
Figure 3-8. Acetic acid concentration of distillate samples collected from triethyl ammonium acetate at different bottom temperatures. (Error bars represent 95% confidence interval.)
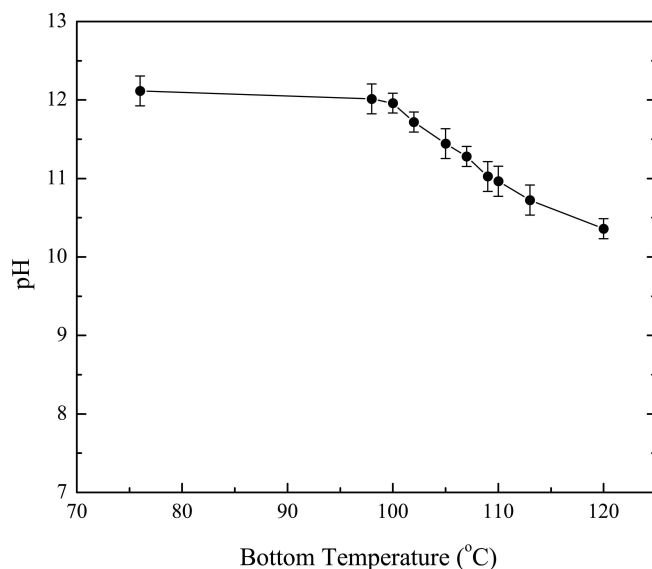
Figure 3-9. pH of distillate samples collected from triethyl ammonium acetate at different bottom temperatures. (Error bars represent 95% confidence interval.)

Then, the concentration of triethyl ammonium acetate is studied after it mixes with tri-*n*-octylamine. A 156-mL sample containing triethyl ammonium acetate (75 mL), excess triethylamine (11 mL), and water (70 mL) was mixed with 166 mL of tri-*n*-octylamine and distilled. The temperature curve is shown in Figure 3-10 and the collected distillate samples are summarized in Figure 3-11. Compared to the results of the system without tri-*n*-octylamine, the codistillation of triethylamine and water seems to be destroyed by adding tri-*n*-octylamine and the first distillate sample was collected at about 92 ^{o}C, which is near the boiling point of triethylamine.
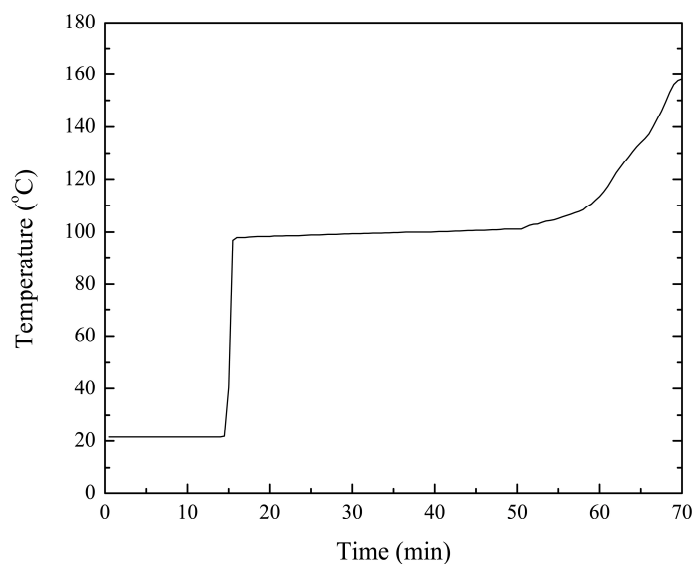
Figure 3-10. Time profile for bottom temperature of simple distillation of the system containing triethyl ammonium acetate, excess triethylamine, water, and tri-*n*-octylamine.

Figure 3-11. Distillate samples of triethyl ammonium acetate with tri-*n*-octylamine collected at different bottom temperatures.

According to Figure 3-11, excess triethylamine leaves the system steeply within the temperature range from 92 ^{o}C to 100 ^{o}C. When the temperature is above 113 ^{o}C, triethyl ammonium acetate is cracked and produces triethylamine, so the volume of the organic phase starts to increase.

The acetic acid concentration and pH results of distillate samples are shown in Figures 3-12 and 3-13. Comparing to the results of triethyl ammonium acetate, adding tri-*n*-octylamine does not make a notable difference. Some acetic acid will leave the system in the form of triethyl ammonium acetate when the temperature is above 100 ^{o}C.
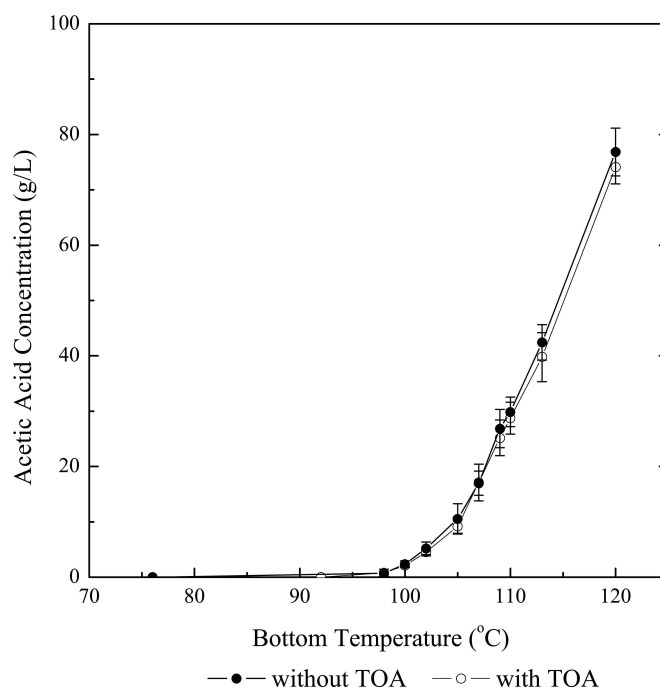
Figure 3-12. Acetic acid concentration of distillate samples collected from triethyl ammonium acetate with and without tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)
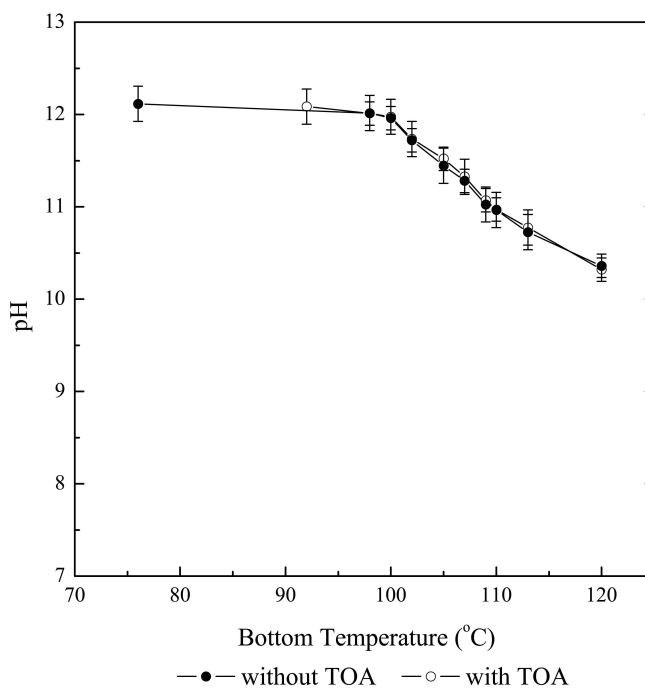
Figure 3-13. pH of distillate samples collected from triethyl ammonium acetate with and without tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)

Concentration Study II deals with tripropyl ammonium acetate. The temperature needed to decompose tripropyl ammonium acetate into tripropylamine and acetic acid is determined by the top (Figure 3-14) and bottom (Figure 3-15) temperature curves of the distillation of reagent-grade tripropyl ammonium acetate. According to the temperature curves, the reaction occurs between 145 and 150 ^{o}C. So, the temperature should not exceed 145 ^{o}C for concentrating tripropyl ammonium acetate.
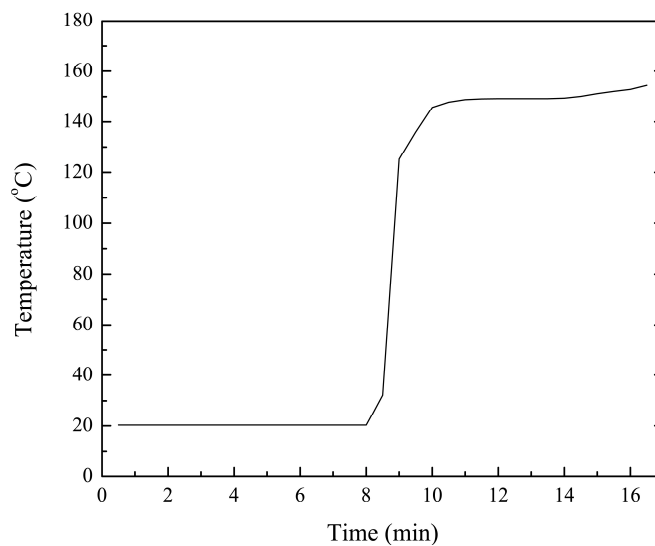
Figure 3-14. Time profile for top temperature of batch distillation of tripropyl ammonium acetate.
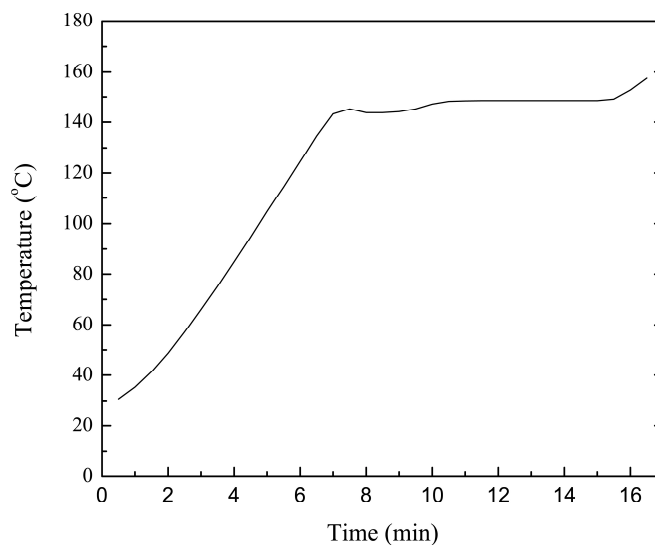
Figure 3-15. Time profile for bottom temperature of batch distillation of tripropyl ammonium acetate.

Then a 172-mL sample containing tripropyl ammonium acetate (94 mL), excess tripropylamine (8 mL), and water (70 mL) was put into the flask and distilled. The collected distillate samples are summarized in Figure 3-16. Because tripropylamine is not miscible with water and tripropyl ammonium acetate is, the distillate sample will be a two-phase liquid mixture if it contains tripropylamine. According to Figure 3-16, all the distillate samples are two-phase liquid mixtures, indicating that tripropylamine leaves the system with water between 98 and 122 $^{\circ}$C although the boiling point of tripropylamine is 155 $^{\circ}$C. A probable reason is that excess tripropylamine and water codistill at about 98 $^{\circ}$C.
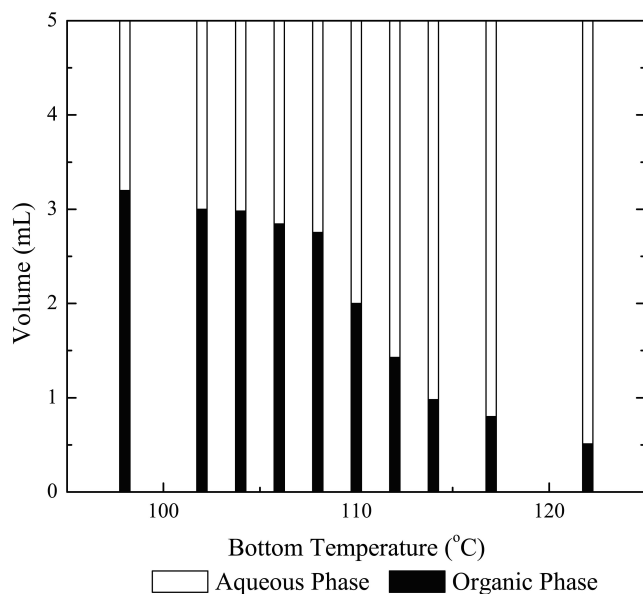
Figure 3-16. Distillate samples of tripropyl ammonium acetate collected at different bottom temperatures.

As shown in Figure 3-17, the acetic acid concentration of distillate samples demonstrates that acetic acid starts to exit the system steeply when the temperature is above 102 ^{o}C. The pH results of samples (Figure 3-18) are all above 7, indicating that acetic acid leaves in the form of tripropyl ammonium acetate.
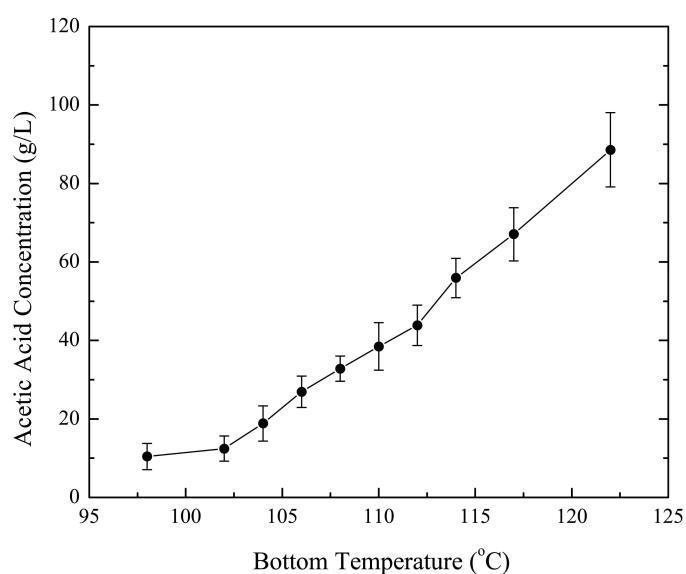
Figure 3-17. Acetic acid concentration of distillate samples collected from tripropyl ammonium acetate at different bottom temperatures. (Error bars represent 95% confidence interval.)
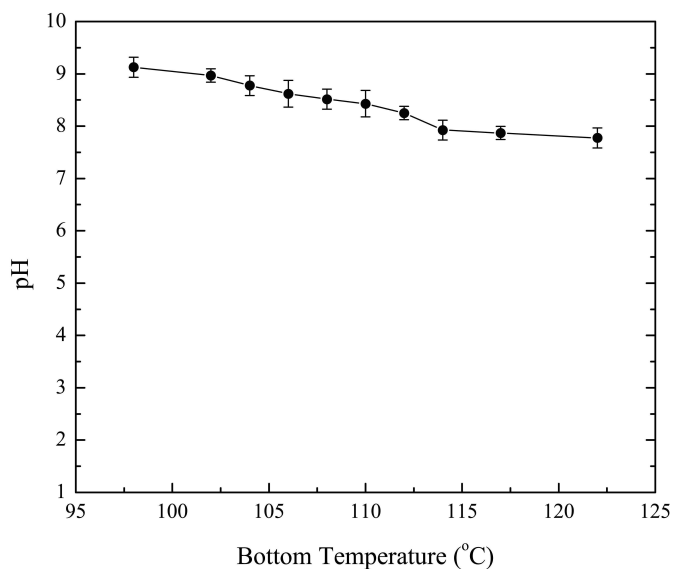
Figure 3-18. pH of distillate samples collected from tripropyl ammonium acetate at different bottom temperatures. (Error bars represent 95% confidence interval.)

The next study focuses on the concentration of tripropyl ammonium acetate after it was mixed with tri-*n*-octylamine. A 172-mL sample containing tripropyl ammonium acetate (94 mL), excess tripropylamine (8 mL), and water (70 mL) was mixed with 166 mL of tri-*n*-octylamine and distilled. The collected distillate samples are summarized in Figure 3-19. Compared to the results without tri-*n*-octylamine, adding tri-*n*-octylamine reduces the volume of organic-phase distillate samples. The first distillate sample was collected at 100 $^{\circ}$C.
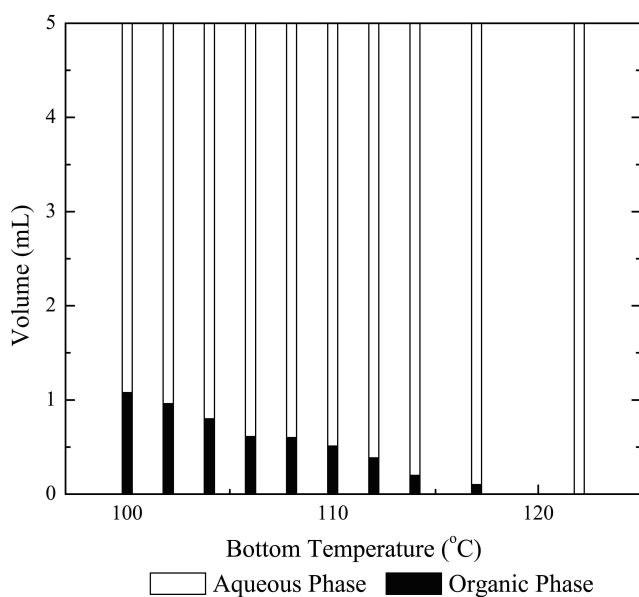
Figure 3-19. Distillate samples of tripropyl ammonium acetate with tri-*n*-octylamine collected at different bottom temperatures.

The acetic acid concentration in the distillate samples is shown in Figure 3-20. Because tripropyl ammonium acetate (R_3N**:**HAc) is a complex, there is decomposition equilibrium existing in the aqueous solution of tripropyl ammonium acetate as follows:

$$R_3N\textbf{:}HAc \leftrightarrow R_3N\textbf{:} + HAc \tag{5}$$

When tri-*n*-octylamine is added, tripropylamine is extracted into the organic phase because it is completely miscible with tri-*n*-octylamine. Thus, the acetic acid concentration of the aqueous phase increases. Accordingly, the acetic acid concentration of the distillate samples increases. As shown in Figure 3-21, the pH of the distillate samples decreases by adding tri-*n*-octylamine.
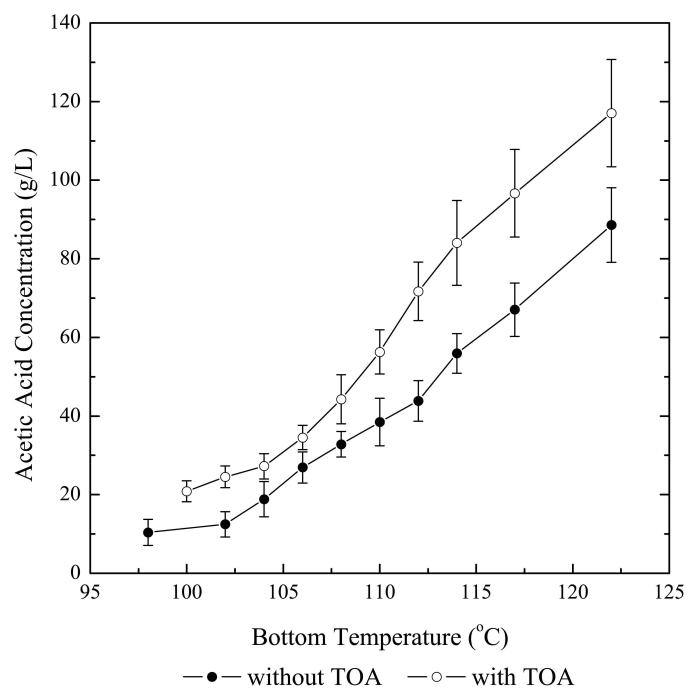
Figure 3-20. Acetic acid concentration of distillate samples collected from tripropyl ammonium acetate with and without tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)
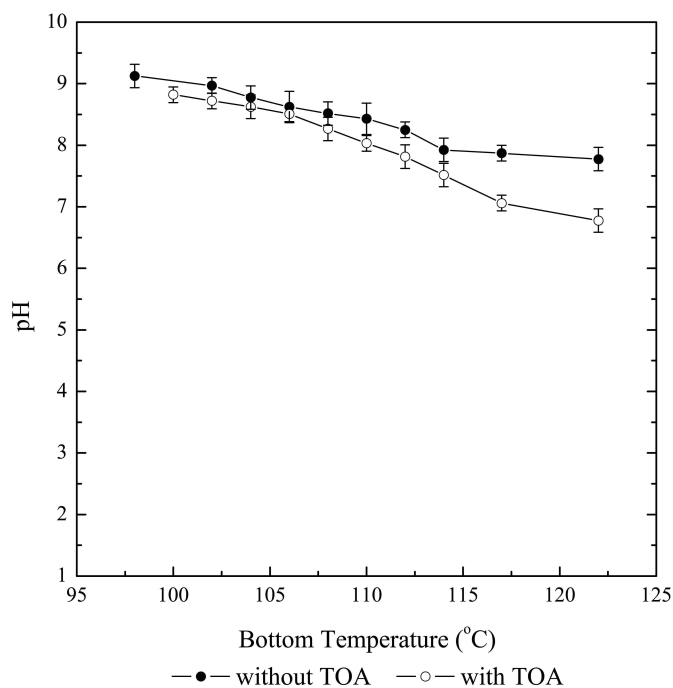
Figure 3-21. pH of distillate samples collected from tripropyl ammonium acetate with and without tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)

Concentration Study III involves tributyl ammonium acetate. First the temperature needed for decomposing tributyl ammonium acetate into tributylamine and acetic acid is determined by heating reagent-grade tributyl ammonium acetate. The top and bottom temperature were recorded as a function of time and are shown in Figures 3-22 and 3-23. According to the temperature curves, the reaction occurs between 160 and 170 ^{o}C. So, the temperature should not be above 160 ^{o}C when concentrating tributyl ammonium acetate.
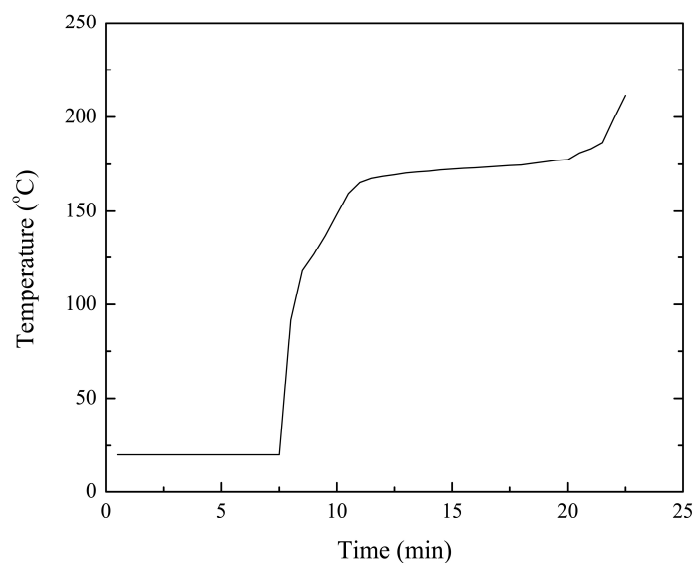
Figure 3-22. Time profile for top temperature of batch distillation of tributyl ammonium acetate.
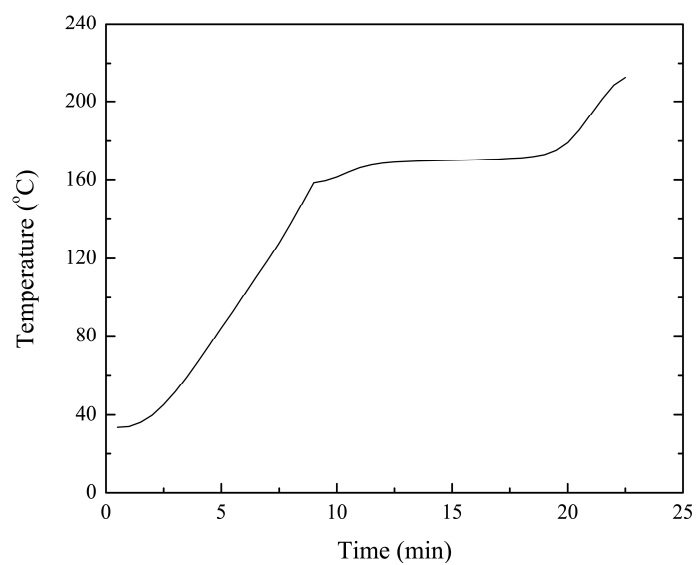
Figure 3-23. Time profile for bottom temperature of batch distillation of tributyl ammonium acetate.

Then a 192-mL sample containing tributyl ammonium acetate (112 mL), excess tributylamine (10 mL), and water (70 mL) was put into the flask and distilled. The collected distillate samples are summarized in Figure 3-24. Because tributylamine is not miscible with water, whereas tributyl ammonium acetate is, the distillate sample is a two-phase liquid mixture if there is tributylamine in it. According to Figure 3-24, the distillate samples collected between 100 and 117 $^{\circ}$C are two-phase liquid mixtures indicating that tributylamine leaves the system with water even though the boiling point of tributylamine is 216 $^{\circ}$C. This is caused by the codistillation of water and tributylamine.

The acetic acid concentration of distillate samples (Figure 3-25) demonstrates that acetic acid starts to leave the system steeply when the temperature is above 100 $^{\circ}$C. As shown in Figure 3-26, the pH results of distillate samples are between 6 and 8. So acetic acid exits in the form of tributyl ammonium acetate.
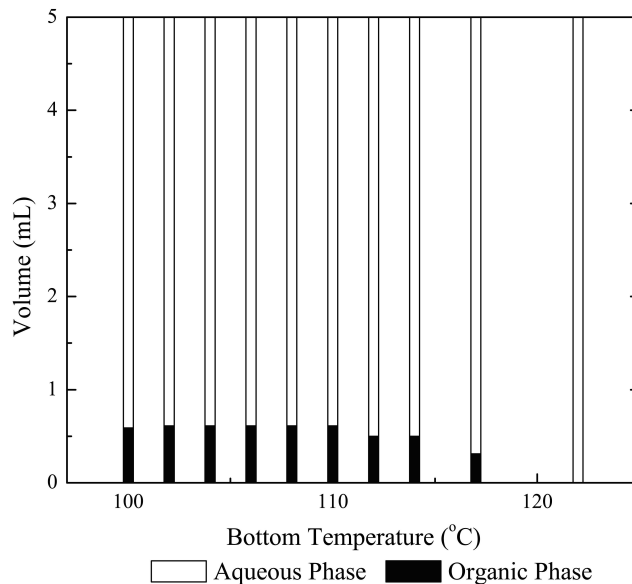
Figure 3-24. Distillate samples of tributyl ammonium acetate collected at different bottom temperatures.
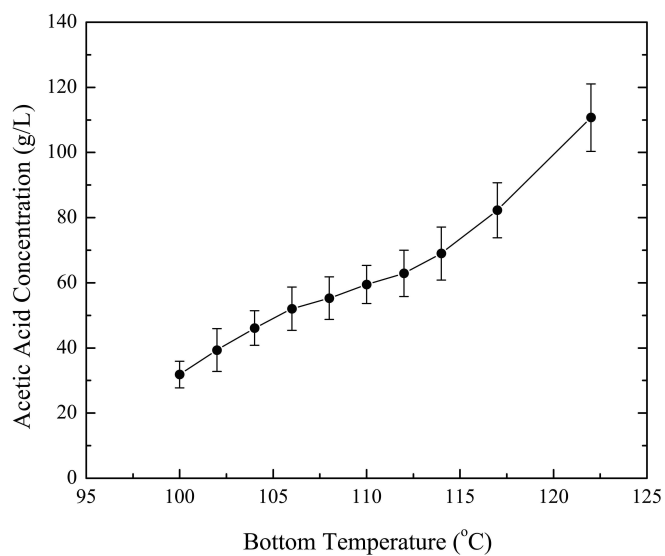
Figure 3-25. Acetic acid concentration of distillate samples collected from tributyl ammonium acetate at different bottom temperatures. (Error bars represent 95% confidence interval.)
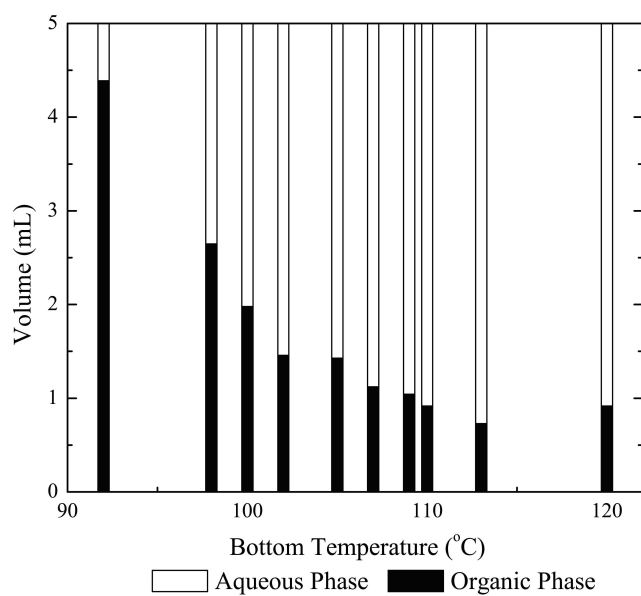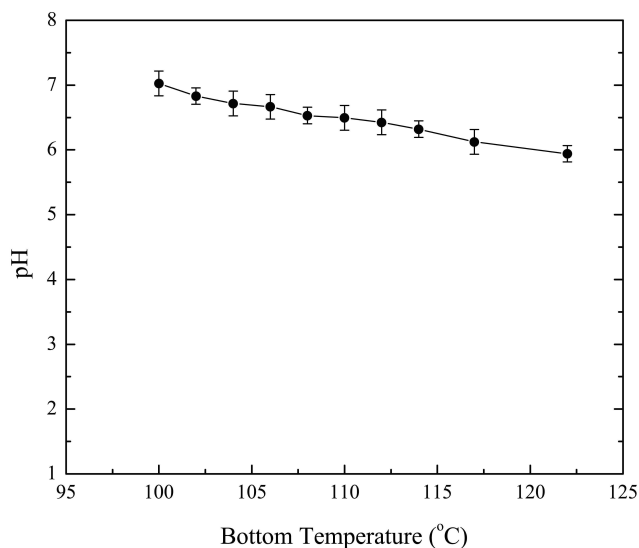
Figure 3-26. pH of distillate samples collected from tributyl ammonium acetate at different bottom temperatures. (Error bars represent 95% confidence interval.)

Concentration of tributyl ammonium acetate can also be done after it is mixed with tri-*n*-octylamine. A 192-mL sample containing tributyl ammonium acetate (112 mL), excess tributylamine (10 mL), and water (70 mL) was mixed with 166 mL of tri-*n*-octylamine and distilled. The collected distillate samples are summarized in Figure 3-27. Comparing to the results of the system without tri-*n*-octylamine, adding tri-*n*-octylamine eliminates the organic phase in all distillate samples.
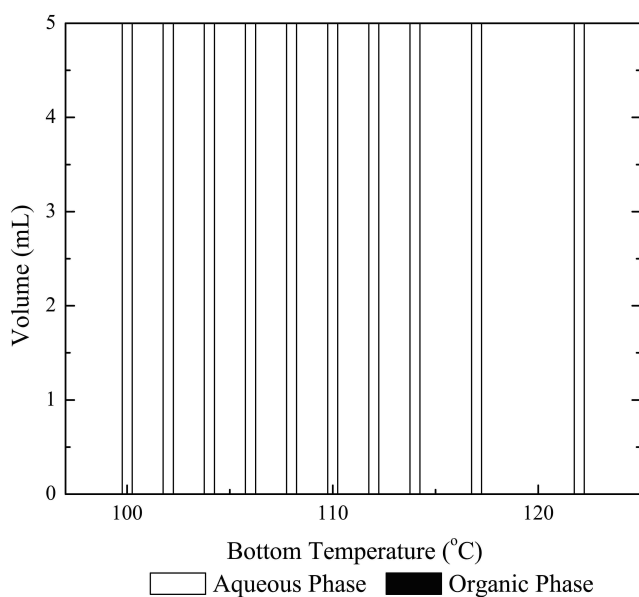
Figure 3-27. Distillate samples of tributyl ammonium acetate with tri-*n*-octylamine collected at different bottom temperatures.

The acetic acid concentration of distillate samples is shown in Figure 3-28. Because tributyl ammonium acetate ($R_3N{:}HAc$) is a complex, there is decomposition equilibrium existing in the aqueous solution of tributyl ammonium acetate as follows:

$$R_3N{:}HAc \leftrightarrow R_3N{:} + HAc \tag{6}$$

When tri-*n*-octylamine is added, tributylamine is extracted into the organic phase because it is completely miscible with tri-*n*-octylamine. Thus, the acetic acid concentration of the aqueous phase increases. Accordingly, the acetic acid concentration of the distillate samples increases. As shown in Figure 3-29, the pH of distillate samples decreases by adding tri-*n*-octylamine.
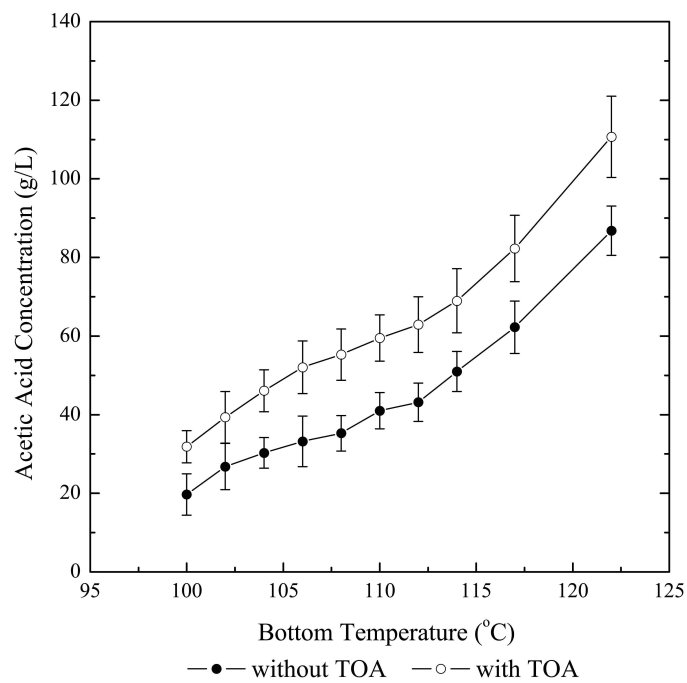
Figure 3-28. Acetic acid concentration of distillate samples collected from tributyl ammonium acetate with and without tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)
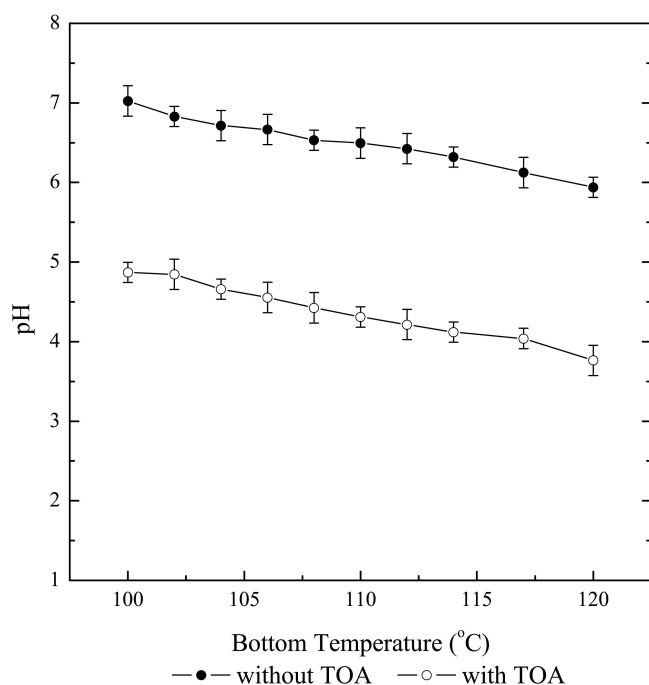
Figure 3-29. pH of distillate samples collected from tributyl ammonium acetate with and without tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)

Recovery of Acetic Acid from Tertiary Amine Acetate

Recovering acetic acid from tertiary amine acetate is the key element of the process. Three preliminary studies were performed to determine if acetic acid can be retrieved from the aqueous solution of tertiary amine acetate via distillation.

Recovery Study I deals with triethyl ammonium acetate. As mentioned before, triethyl ammonium acetate will be decomposed into triethylamine and acetic acid when the temperature is between 110 and 120 ^{o}C. So, triethyl ammonium acetate will be converted into a binary mixture of triethylamine and acetic acid when the temperature is

above 120 ^{o}C. Triethylamine and acetic acid form a maximum azeotrope (71% w/w acetic acid and 29% w/w triethylamine) in which the boiling point is about 163 ^{o}C (Table of Binary Organic Azeotropes, 2008).

Figure 3-30 shows the temperature curve of the distillation of a 156-mL sample containing triethyl ammonium acetate (75 mL), excess triethylamine (11 mL), and water (70 mL). There is a flat occurring around 160 ^{o}C which corresponds to the azeotrope. Because of this azeotrope, acetic acid cannot be recovered from triethyl ammonium acetate via distillation. To address this problem, tri-*n*-octylamine is introduced.
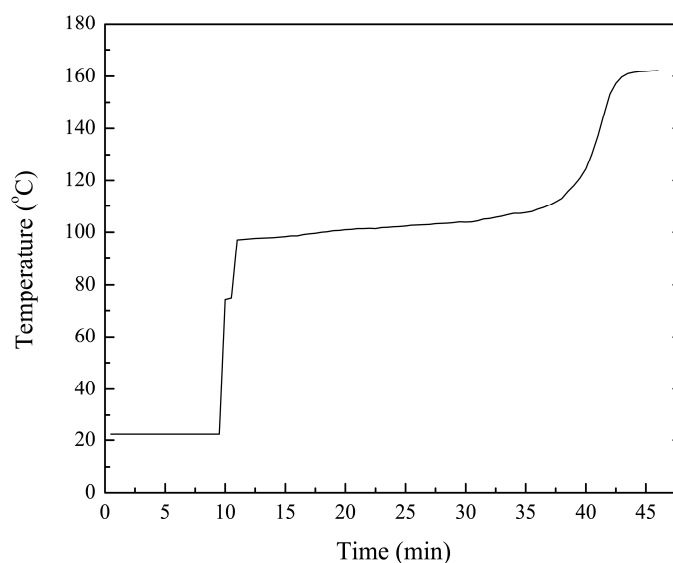
Figure 3-30. Time profile for bottom temperature of simple distillation of the system containing triethyl ammonium acetate, excess triethylamine, and water.

Tri-*n*-octylamine can react with acetic acid, and the product, tri-*n*-octyl ammonium acetate, will decompose into tri-*n*-octylamine and acetic acid between 155 and 160 $^{\circ}$C, as shown in Figures 3-31 and 3-32. Theoretically, tri-*n*-octylamine could keep acetic acid away from triethylamine when temperature is above 120 $^{\circ}$C and destroy the azeotrope.

$$HAc + R_3N \longrightarrow R_3NHAc \qquad (3)$$

$$R_3NHAc \xrightarrow{\Delta} R_3N + HAc \qquad (4)$$
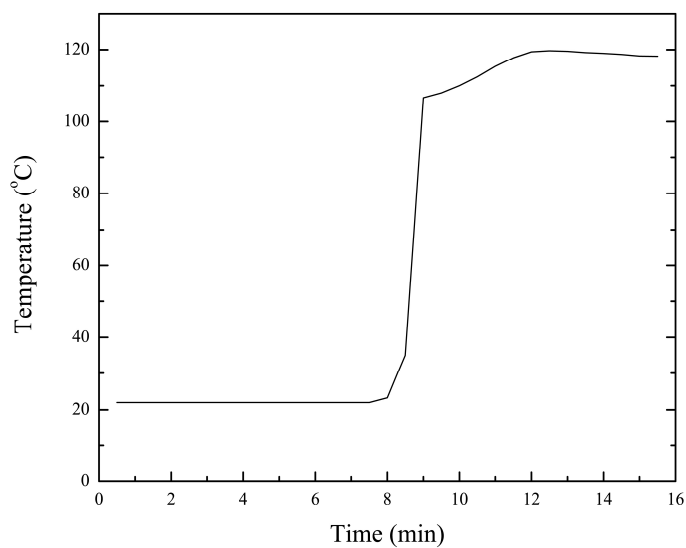
Figure 3-31. Time profile for top temperature of batch distillation of tri-*n*-octyl ammonium acetate.
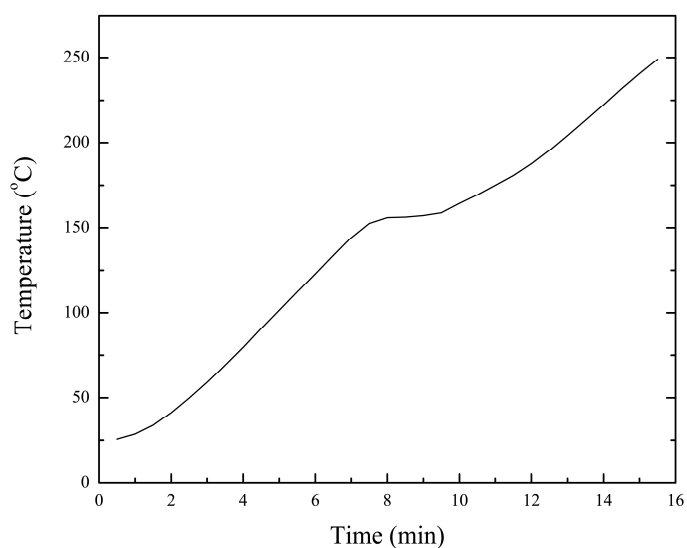
Figure 3-32. Time profile for bottom temperature of batch distillation of tri-*n*-octyl ammonium acetate.

To determine the effect of tri-*n*-octylamine, the temperature curve from the distillation of a 322-mL sample containing triethyl ammonium acetate (75 mL), excess triethylamine (11 mL), water (70 mL), and tri-*n*-octylamine (166 mL) is recorded. As shown in Figure 3-33, there still is a flat occurring around 160 $^{\circ}$C, which is close to the boiling point of the negative azeotrope formed by triethylamine and acetic acid.
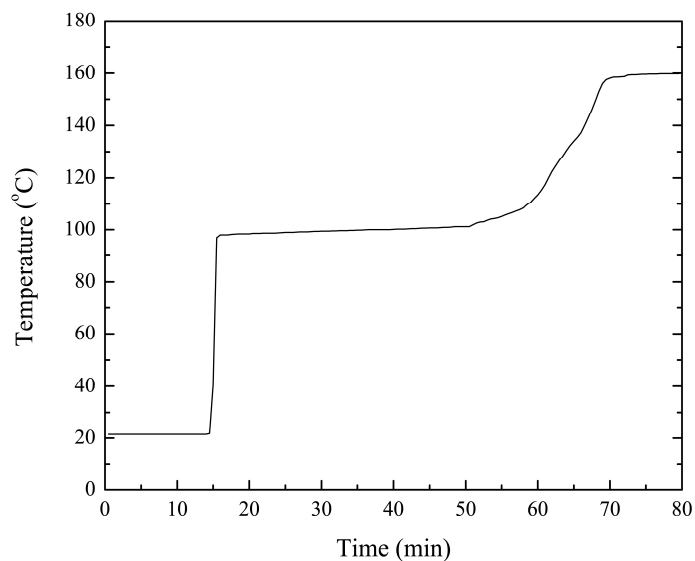
Figure 3-33. Time profile for bottom temperature of simple distillation of the system containing triethyl ammonium acetate, excess triethylamine, water, and tri-*n*-octylamine.

Figures 3-34 and 3-35 show the acetic acid concentration and pH results, respectively, of distillate samples collected from these two systems. Each figure shows the results with and without tri-*n*-octylamine. There is no notable difference between the samples collected from these two systems; therefore, tri-*n*-octylamine does not react with acetic acid and destroy the azeotrope as expected. Furthermore, pH results of all distillate samples are above 3.5, indicating that triethyl ammonium acetate exists in all distillate samples and acetic acid cannot be recovered because of an azeotrope.
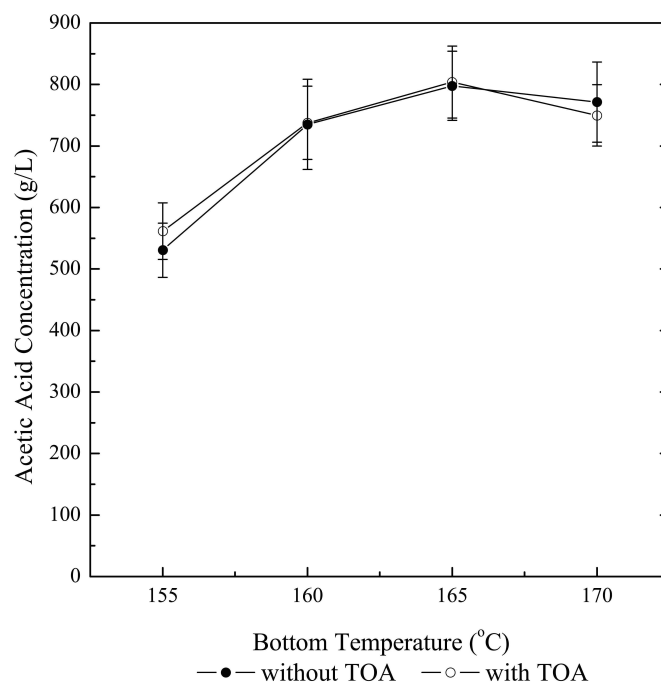
Figure 3-34. Acetic acid concentration of distillate samples collected from triethyl ammonium acetate with and without tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)
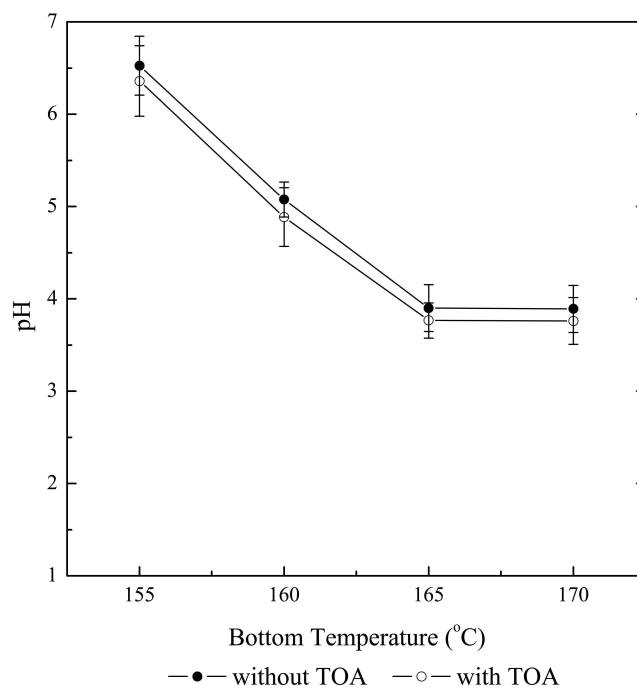
**Figure 3-35.** pH of distillate samples collected from triethyl ammonium acetate with and without tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)

Tri-*n*-octylamine is not miscible with the aqueous solution of triethyl ammonium acetate, so reaction (3) is heterogeneous. Moreover, tri-*n*-octylamine is viscous, which makes the reaction difficult to occur. To eliminate this obstacle, the viscosity of tri-*n*-octylamine is reduced by dilution. Table 3.2 summarizes some agents commonly used to dilute tri-*n*-octylamine. According to their boiling points, the only one that can be used in this process is octanol because it will not leave the system before the reaction occurs. The acetic acid concentration and pH results of the distillate samples collected from these two systems (with and without dilution by octanol) are compared.

Table 3-2. Dilution agents for tri-*n*-octylamine

Dilution Agent	*Boiling Point*
Chloroform	62 ^{o}C
Hexane	69 ^{o}C
Methyl Isobutyl Ketone	117 ^{o}C
Octanol	195 ^{o}C
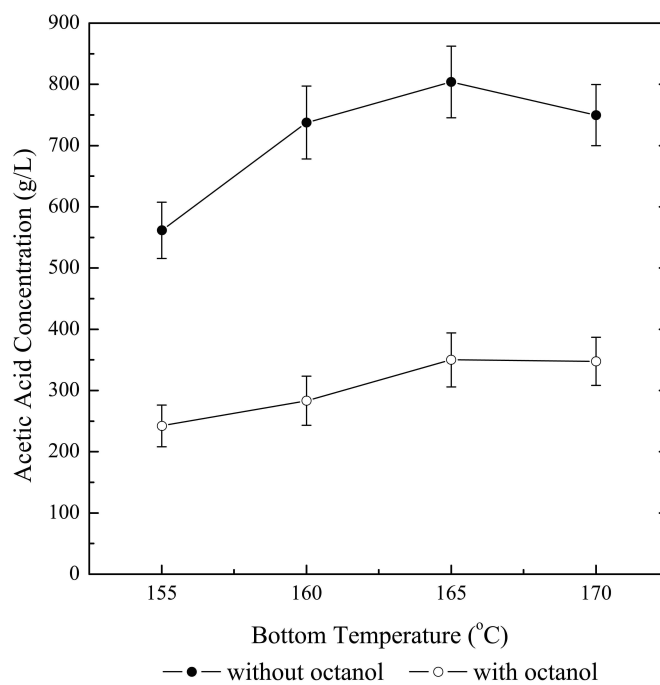
Figure 3-36. Acetic acid concentration of distillate samples collected from triethyl ammonium acetate with undiluted and diluted tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)
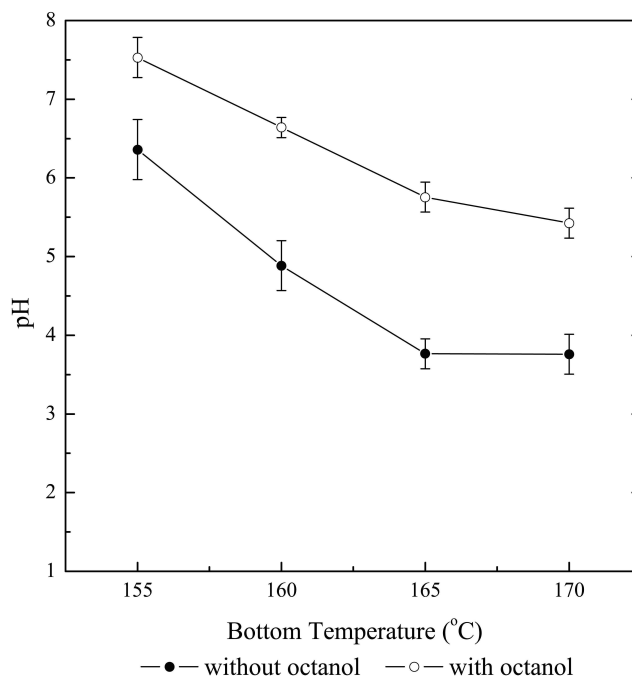
Figure 3-37. pH of distillate samples collected from triethyl ammonium acetate with undiluted and diluted tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)

As shown in Figures 3-36 and 3-37, the acetic acid concentration in the distillate samples is reduced by adding octanol as dilution agent, and accordingly the pH of distillate samples increases. The reason may be that acetic acid reacts with octanol to form an ester, which is left at the bottom. So, octanol is not a proper dilution agent for this process either.

Taken together, the results suggest that acetic acid cannot be recovered from the aqueous solution of triethyl ammonium acetate via distillation. Even though it performs well in the precipitation step, it is not a good choice for the 'acid springing' process.

Recovery Study II involves tripropyl ammonium acetate. As mentioned before, the temperature needed to decompose tripropyl ammonium acetate into tripropylamine and acetic acid occurs between 145 and 150 ^{o}C. The acetic acid concentration and pH results of distillate samples collected above 150 ^{o}C are shown in Figures 3-38 and 3-39, respectively. According to Figure 3-38, the maximum acetic acid concentration appears around 155 ^{o}C. Because the boiling point of tripropylamine is 156 ^{o}C, the acetic acid concentration decreases when the boiling evaporation of tripropylamine occurs above 156 ^{o}C.
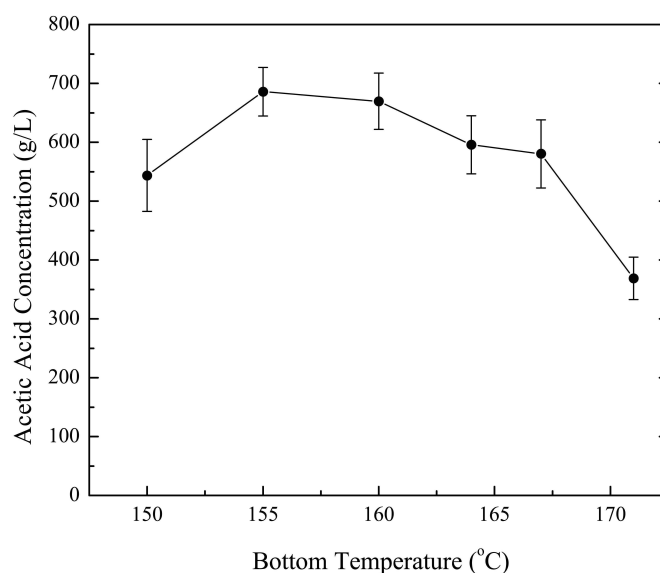
Figure 3-38. Acetic acid concentration of distillate samples collected from tripropyl ammonium acetate with tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)
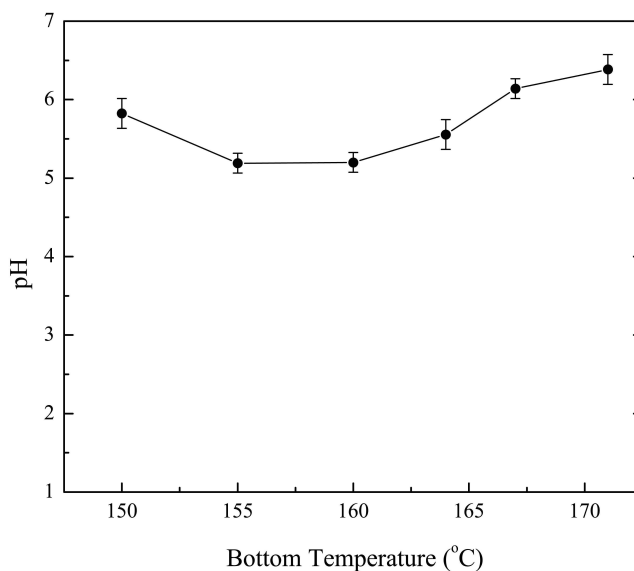
Figure 3-39. pH of distillate samples collected from tripropyl ammonium acetate with tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)

Correspondingly, the minimum pH appears at 155 ^{o}C, as shown in Figure 3-39. When the temperature is above 155 ^{o}C, the pH starts to increase. The minimum pH is still above 5.0 proving that tripropylamine exists in all distillate samples. Acetic acid is difficult to recover from tripropyl ammonium acetate through distillation because the boiling point of tripropylamine is close to the decomposition temperature of tripropyl ammonium acetate.

Recovery Study III explores tributyl ammonium acetate. Because tributyl ammonium acetate decomposes into tributylamine and acetic acid when the temperature is above 160 ^{o}C, acetic acid concentration (Figure 3-40) and pH results (Figure 3-41) of distillate samples collected above 160 ^{o}C are measured.
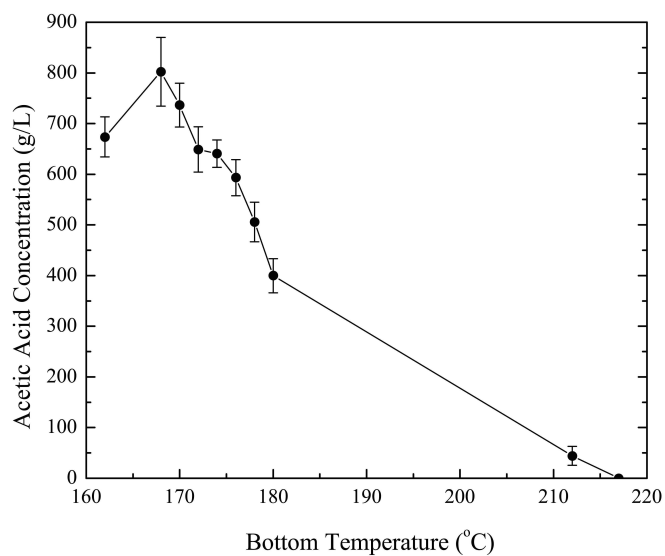
Figure 3-40. Acetic acid concentration of distillate samples collected from tributyl ammonium acetate at different bottom temperatures. (Error bars represent 95% confidence interval.)
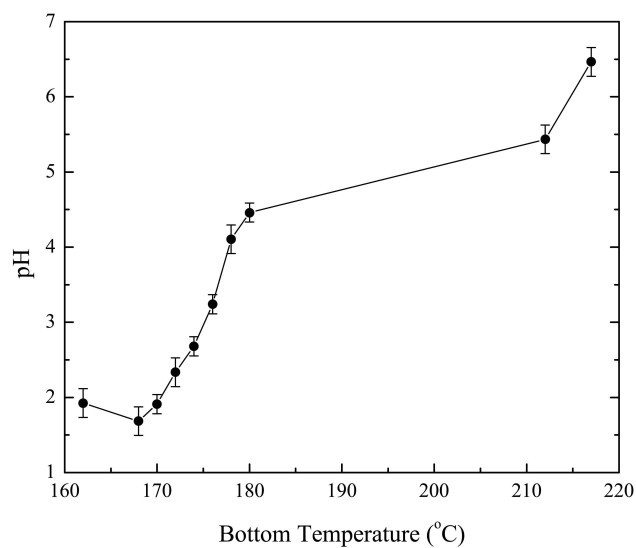
Figure 3-41. pH of distillate samples collected from tributyl ammonium acetate at different bottom temperatures. (Error bars represent 95% confidence interval.)

As shown in Figure 3-40, the maximum acetic acid concentration appears at 167 ^{o}C. When the temperature is above 167 ^{o}C, acetic acid concentration decreases along with increase of temperature. Accordingly, as shown in Figure 3-41, the minimum pH appears at 167 ^{o}C and then the pH of distillate samples increases.

The minimum pH is around 1.7, which means that the distillate sample collected at 167 ^{o}C does not contain too much tributylamine. Because the boiling point of tributylamine (216 ^{o}C) is much higher than the decomposition temperature of tributyl ammonium acetate, it is easy to retrieve acetic acid from tributyl ammonium acetate via distillation.

To determine the role of tri-*n*-octylamine in the distillation process, the acetic acid concentration (Figure 3-42) and pH results (Figure 3-43) of distillate samples collected from two systems (with and without tri-*n*-octylamine) are compared. The results show that the acetic concentration of distillate samples collected between 160 and 180 ^{o}C increases and pH decreases because of tri-*n*-octylamine addition. All of these results demonstrate that tributylamine has been trapped by tri-*n*-octylamine in the bottom until the temperature is close to its boiling point. So, adding tri-*n*-octylamine does enhance the separation of acetic acid and tributylamine during distillation.

Simply stated, acetic acid can be easily recovered from tributyl ammonium acetate; therefore, tributylamine is the best choice for the 'acid springing' process.
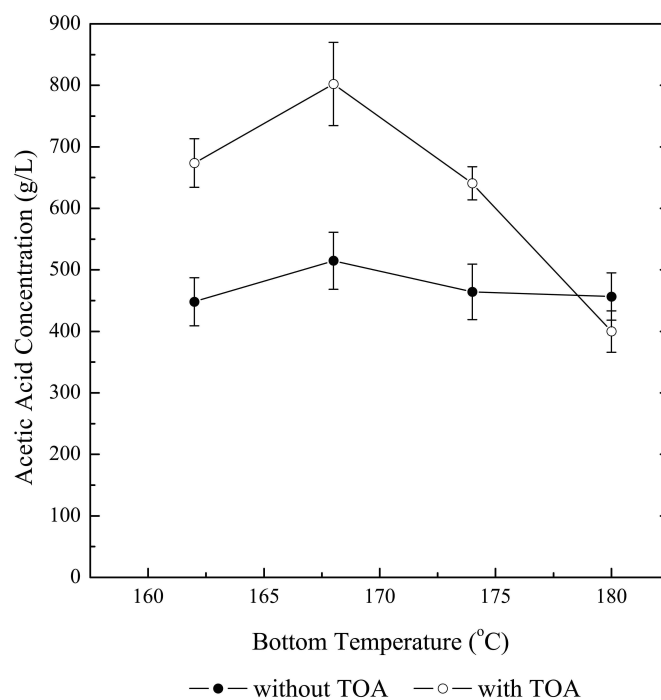
Figure 3-42. Acetic acid concentration of distillate samples collected from tributyl ammonium acetate with and without tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)
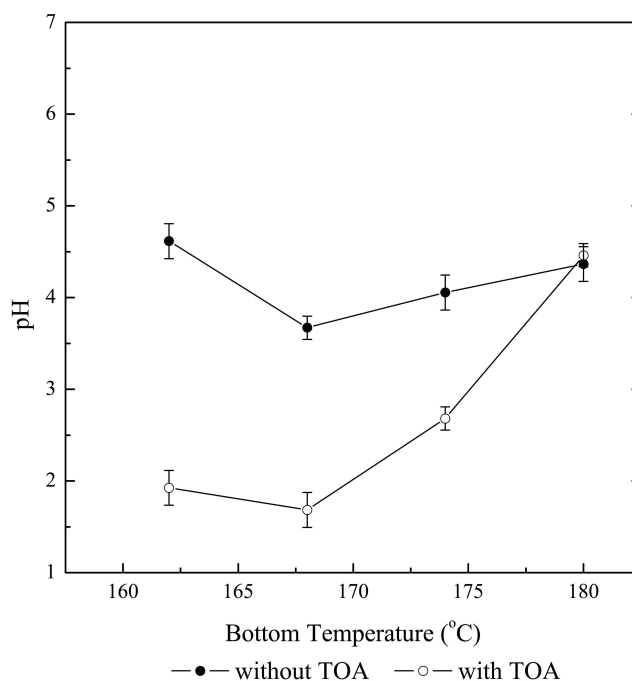
Figure 3-43. pH of distillate samples collected from tributyl ammonium acetate with and without tri-*n*-octylamine at different bottom temperatures. (Error bars represent 95% confidence interval.)

Optimization of the 'Acid Springing' Process

Because tributylamine is the best choice for the 'acid springing' process, optimal parameters should be determined.

Optimization Study I deals with the process using aqueous solutions of reagent-grade calcium acetate to simulate fermentation broth. A 51-mL aqueous solution containing calcium acetate (15% by weight) was mixed with 10% excess tributylamine and put into the reactor, which was then pressurized to 308 kPa (30 psig) by carbon dioxide. Then, the precipitation was repeated at 446 kPa (50 psig), 584 kPa (70 psig),

and 722 kPa (90 psig) while the other conditions remained the same. The time to reach

equilibrium and product yield were recorded as a function of reaction pressure, as shown

in Figures 3-44 and 3-45.

The results show that increasing the carbon dioxide pressure reduces the reaction

time, but it barely affects the product yield. Thereby higher reaction pressure is better,

without considering the capital cost of the pressure vessel.
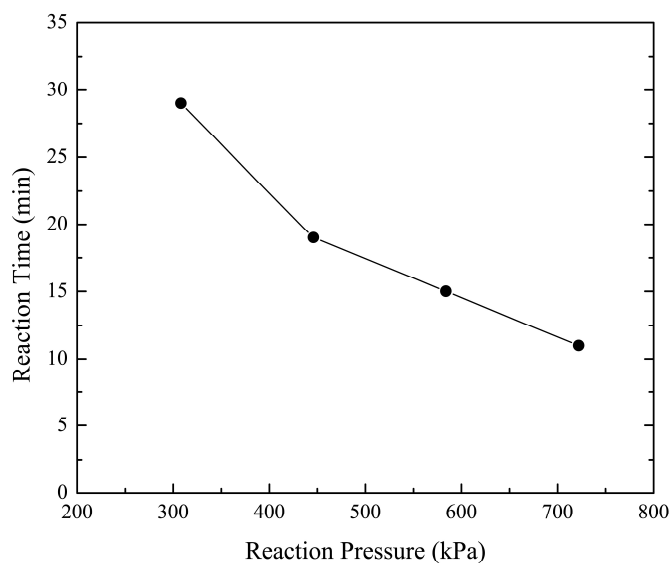
Figure 3-44. Reaction time of the precipitation with tributylamine under different
pressures.
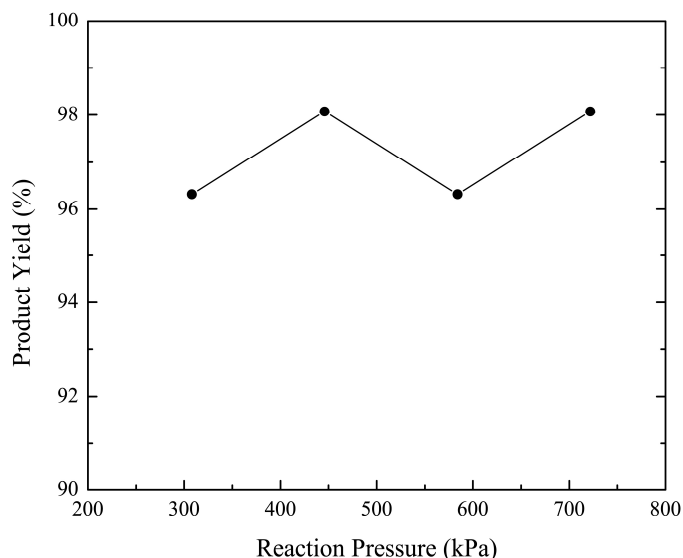
Figure 3-45. Product yield of the precipitation with tributylamine under different pressures.

Then a 192-mL sample containing tributyl ammonium acetate (112 mL), excess tributylamine (10 mL), and water (70 mL) was mixed with 166 mL of tri-*n*-octylamine and distilled at 90 $^{\circ}$C to concentrate tributyl ammonium acetate. Then, the concentration was repeated at 100, 110, and 120 $^{\circ}$C while the other conditions remained the same. The volume and acetic acid concentration of the distillate was recorded and the mass of acetic acid in the distillate was calculated. The results are summarized in Table 3-3.

The acetic acid concentrations of the solution remaining at the bottom are shown in Figure 3-46. When the temperature is above 110 $^{\circ}$C, raising the temperature cannot increase the concentration of the bottom solution significantly, so the optimal temperature is around 110 $^{\circ}$C.

Table 3-3. Results of concentrating tributyl ammonium acetate with tri-*n*-octylamine at different temperatures

Temperature (*°C*)	Volume of Distillate (*mL*)	Acetic Acid Concentration of Distillate (*g/L*)	Mass of Acetic Acid in Distillate (*g*)
90	0	0	0
100	60	42.64	2.56
110	80	49.68	3.97
120	82	50.65	4.15
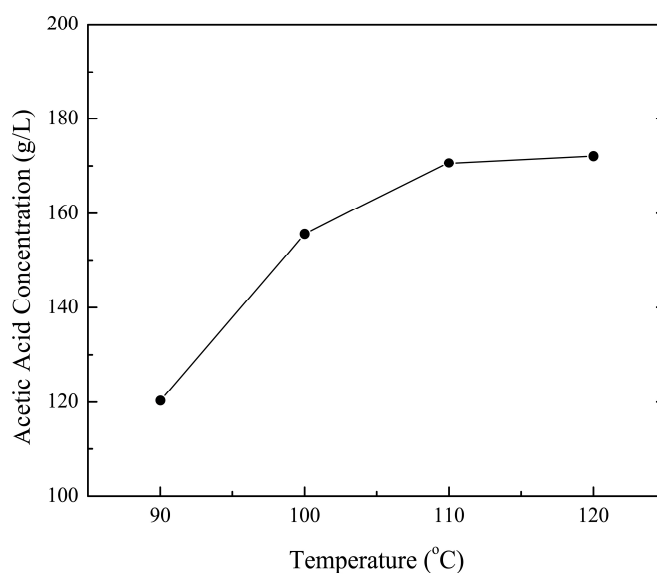
Figure 3-46. Acetic acid concentration of the bottom solution concentrated at different temperatures.

To recover acetic acid, a 278-mL concentrated sample, which was derived from the concentration of a 358-mL sample containing tributyl ammonium acetate (112 mL), excess tributylamine (10 mL), water (70 mL), and tri-*n*-octylamine (166 mL) at 110 ^{o}C, was distilled at 160 ^{o}C. When no more distillate came out, the temperature was raised to 170 ^{o}C to distill the residual liquid. Then, the temperature was raised to 180, 190, and 200 ^{o}C in the same manner. Acetic acid concentrations of distillates are recorded as a function of temperature. As shown in Figure 3-47, the biggest increase of concentration occurs at 170 ^{o}C. Once the temperature reaches 180 ^{o}C, acetic acid concentration begins to decrease. So, the optimal temperature for recovering acetic acid from the aqueous solution of reagent-grade calcium acetate is around 170 ^{o}C.
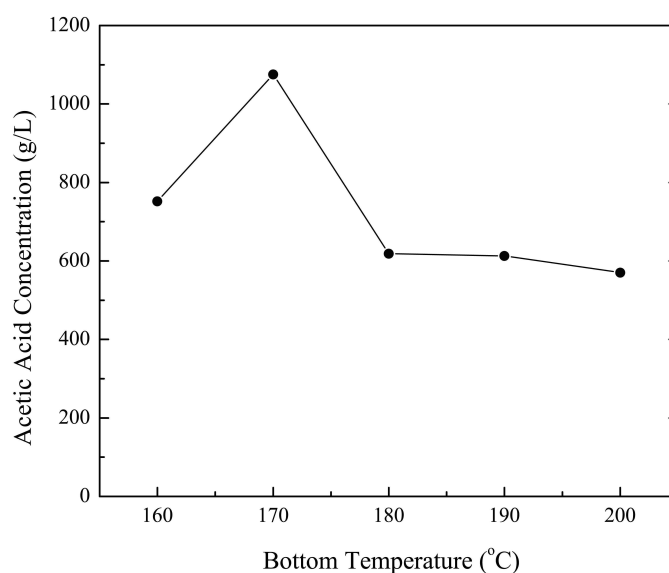
Figure 3-47. Overhead acetic acid concentration recovered from batch distillation of tributyl ammonium acetate at different bottom temperatures.

Optimization Study II optimizes the process involving actual fermentation broth. The fermentation broth was obtained from the pilot-plant scale fermentation of shredded office paper (80%) and chicken manure (20%). Figure 3-48 describes the initial acid concentrations of the fermentation broth.
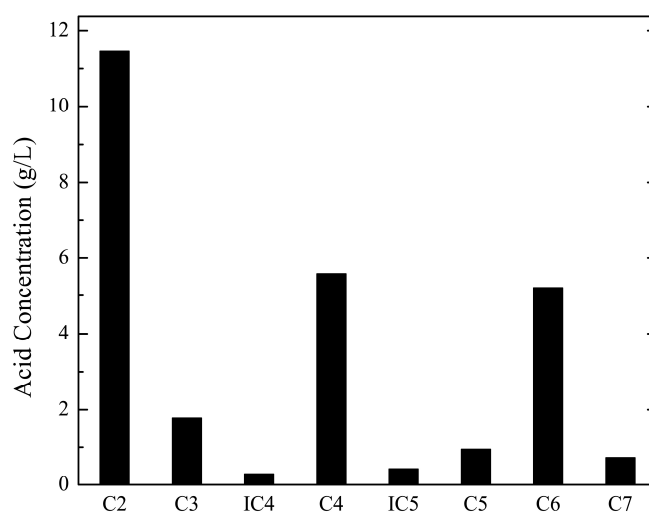
Figure 3-48. Acid concentrations of the fermentation broth.

The fermentation broth (300 mL) was mixed with tributylamine (50 mL) and carbon dioxide to precipitate calcium carbonate at atmospheric pressure. The liquid sample (318 mL) derived from the precipitation was mixed with 190 mL of tri-*n*-octylamine and distilled at 90 ^{o}C to concentrate tributylamine carboxylate. Then the concentration was repeated at 100, 110, and 120 ^{o}C while the other conditions remained

the same. The volume and acid concentration of distillate was recorded and the mass of

acid in the distillate was calculated. The results are summarized in Table 3-4.

Table 3-4. Results of concentrating tributylamine carboxylate with tri-*n*-octylamine at different temperatures

Temperature (^{o}C)	Volume of Distillate (mL)	Total Acid Concentration of Distillate (g/L)	Mass of Acid in Distillate (g)
90	0	0	0
100	214	8.29	1.77
110	268	9.53	2.55
120	282	11.03	3.11

Total acid concentration of the solution remaining at the bottom is shown in

Figure 3-49. Once the temperature is above 110 ^{o}C, raising temperature cannot increase

acid concentration significantly, so the optimal temperature should be around 110 ^{o}C.

Figures 3-50, 3-51, and 3-52 describe the acid concentrations in the overhead when

tributylamine carboxylate is concentrated at 100, 110, and 120 ^{o}C, respectively.
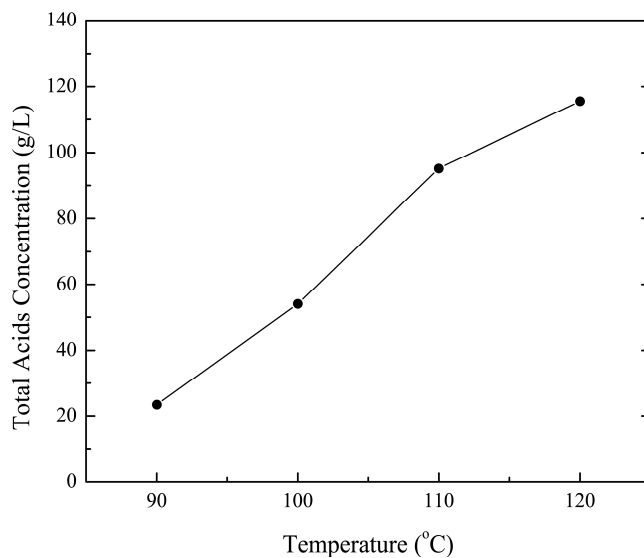
Figure 3-49. Total acid concentration of the bottom solution concentrated at different temperatures.
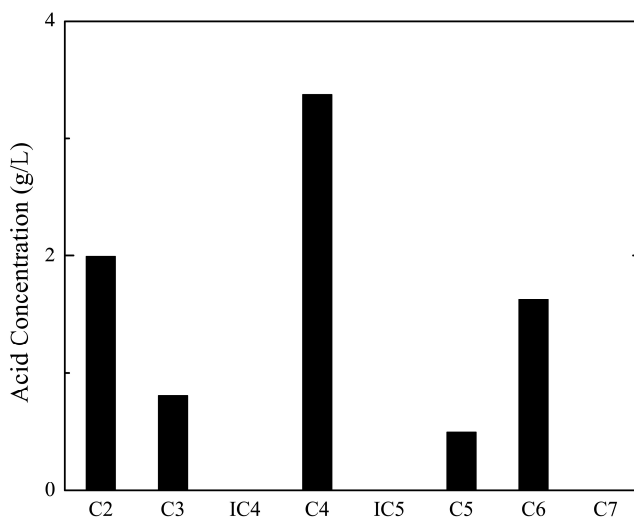
Figure 3-50. Overhead acid concentration collected from concentrating tributylamine carboxylate at 100 $^{\circ}$C.
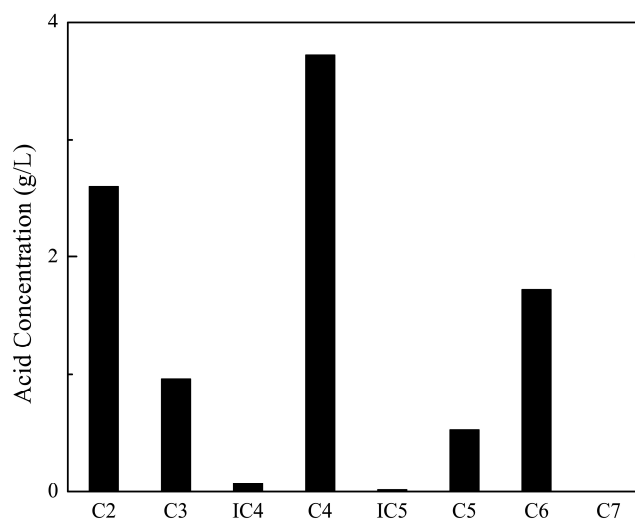
Figure 3-51. Overhead acid concentration collected from concentrating tributylamine carboxylate at 110 $^{\circ}$C.
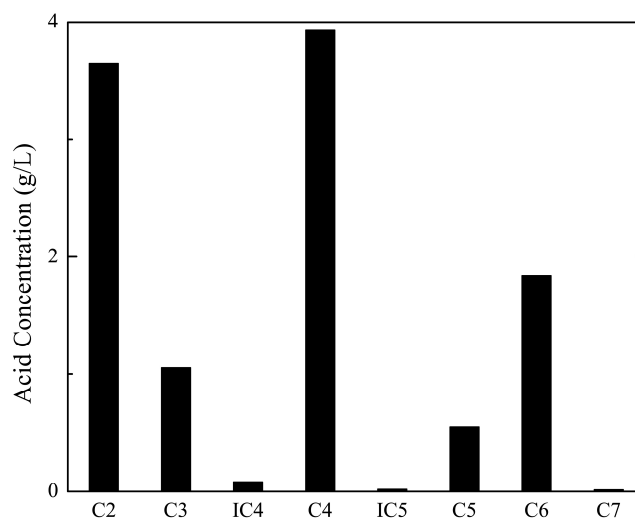
Figure 3-52. Overhead acid concentration collected from concentrating tributylamine carboxylate at 120 $^{\circ}$C.

To recover carboxylic acids, the concentrated sample (240 mL) derived from the concentration at 110 ^{o}C mentioned above was distilled at 160 ^{o}C. When no more distillate came out, the temperature was raised to 170 ^{o}C to distill the residual liquid. Then, the temperature was raised to 180, 190, 200, 210, and 220 ^{o}C in the same manner. Figure 3-53 shows the overhead acid concentrations at different bottom temperatures.
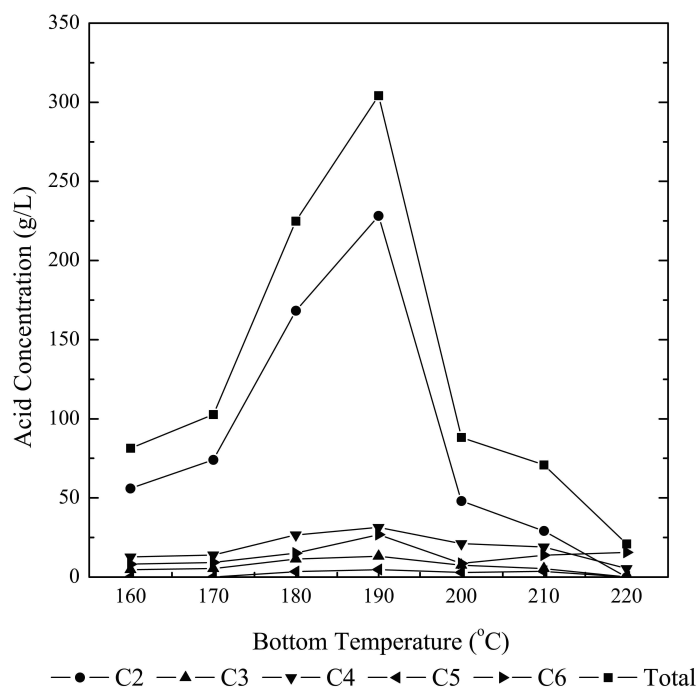
Figure 3-53. Overhead acid concentration recovered from distillation of tributylamine carboxylate at different bottom temperatures.

The maximum acid concentration appears at 190 ^{o}C. When the temperature reaches 200 ^{o}C, the acid concentration reduces. So, the optimal temperature for

recovering carboxylic acids from the fermentation broth is around 190 ^{o}C. Figures 3-54, 3-55, and 3-56 describe the acid concentrations in the overhead at 180, 190, and 200 ^{o}C, respectively.
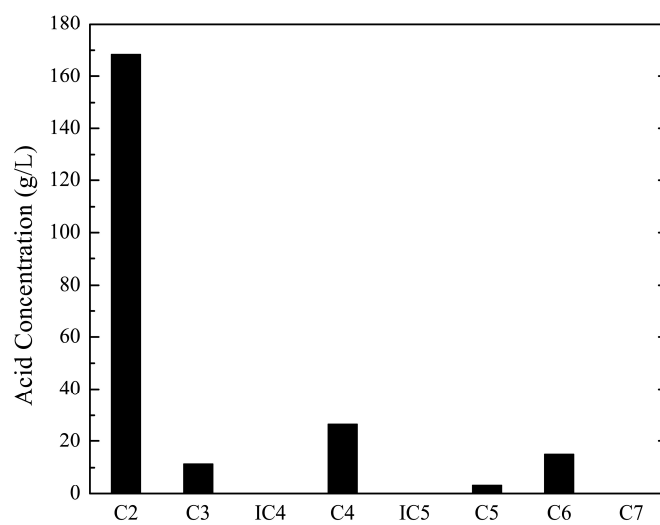
Figure 3-54. Overhead acid concentration collected from distillation of tributylamine carboxylate at 180 ^{o}C.
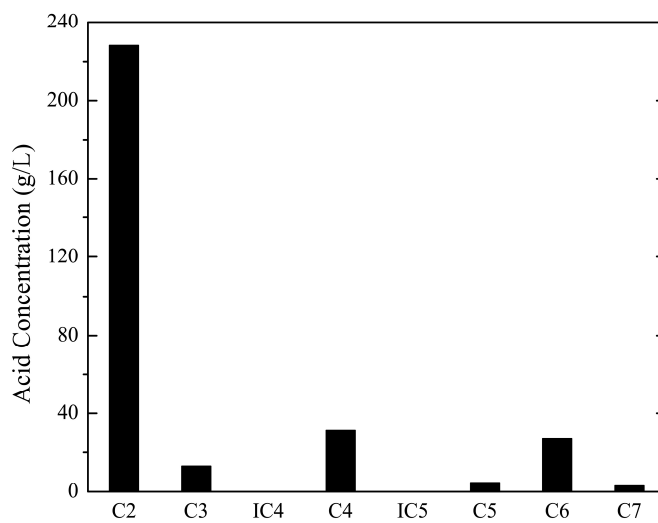
Figure 3-55. Overhead acid concentration collected from distillation of tributylamine carboxylate at 190 ^{o}C.
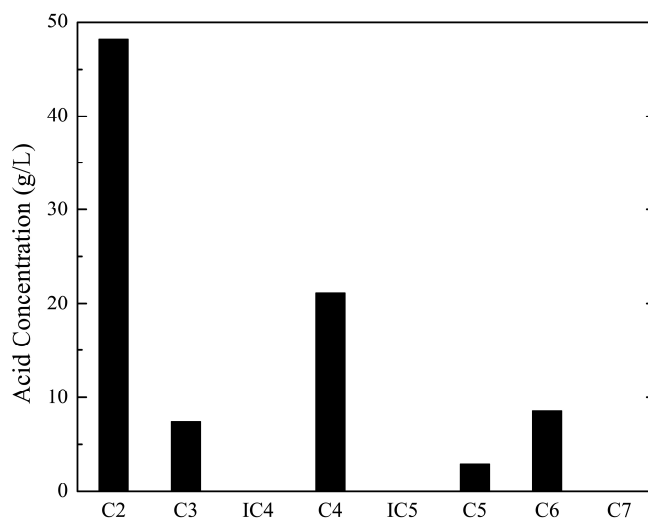
Figure 3-56. Overhead acid concentration collected from distillation of tributylamine carboxylate at 200 ^{o}C.

CHAPTER IV

CONCLUSIONS

Based on the results, a revised process diagram is shown in Figure 4-1.
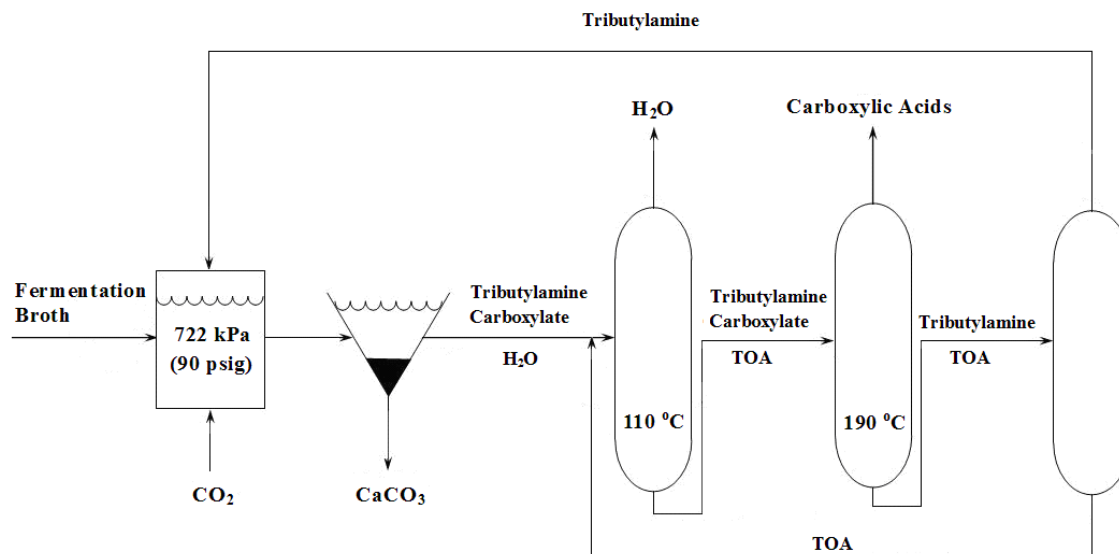
Figure 4-1. Revised 'acid springing' process flow diagram.

The following was learned from the precipitation studies:

1. Calcium carbonate precipitated from aqueous solution of calcium acetate with the presence of triethylamine, tripropylamine, or tributylamine.

2. Calcium carbonate did not precipitate from aqueous solutions of calcium acetate in the presence of triamylamine or trihexylamine.

3. Under the same conditions of temperature and pressure, the reaction time of precipitation with the presence of triethylamine was the shortest, while that

with the presence of tributylamine was the longest.

4. Increasing the pressure of carbon dioxide reduced the reaction time of precipitation with the presence of tributylamine, but it barely affected the product yield.

5. Calcium carbonate precipitated from fermentation broth with the presence of tributylamine.

The following was learned from the concentration studies:

1. Triethylamine, tripropylamine, and tributylamine codistilled with water. The codistillation was destroyed by adding tri-*n*-octylamine.

2. Triethyl ammonium acetate, tripropyl ammonium acetate, and tributyl ammonium acetate began to decompose when the temperature exceeded 110, 145, and 160 $^{\circ}$C, respectively.

The following was learned from the recovery studies:

1. Acetic acid could not be recovered from the aqueous solution of triethyl ammonium acetate via distillation because triethylamine formed a maximum azeotrope with acetic acid. The azeotrope could not be destroyed by adding tri-*n*-octylamine.

2. Acetic acid was difficult to recover from the aqueous solution of tripropyl ammonium acetate through distillation because the boiling point of tripropylamine was close to the decomposition temperature of tripropyl ammonium acetate.

3. Acetic acid was easy to recover from the aqueous solution of tributyl

ammonium acetate via distillation with the presence of tri-*n*-octylamine.

The following was learned from the optimization studies:

1. The optimal temperature for recovering water from the aqueous solution of tributyl ammonium acetate is around 110 $^{\circ}$C.

2. The optimal temperature for recovering acetic acid from the aqueous solution of tributyl ammonium acetate is around 170 $^{\circ}$C.

3. The optimal temperature for recovering water from the fermentation broth is about 110 $^{\circ}$C.

4. The optimal temperature for recovering carboxylic acids from the fermentation broth is around 190 $^{\circ}$C.

CHAPTER V

RECOMMENDATIONS FOR FUTURE WORK

The following are recommendations for future work:

1. Build a larger reactor to evaluate precipitation with the simultaneous presence of tributylamine and tri-*n*-octylamine.

2. Design a continuous multi-stage distillation system based on modeling of the preliminary work to determine the optimal size and operating parameters for concentration and thermal conversion.

3. Analyze the effect of the molar ration of tri-*n*-octylamine and tributylamine on the recovery performance.

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APPENDIX A

PRECIPITATION PROCEDURE

This procedure was used to find the appropriate tertiary amines that can precipitate calcium carbonate from fermentation broth and to determine the optimum reaction pressure.

1. Record the mass of the empty glass beaker.

2. Put tertiary amine and the aqueous solution of reagent-grade calcium acetate into the reactor and record both volume and mass.

3. Put a magnetic stirring bar into the reactor and place the reactor on a magnetic stirrer.

4. Secure the reactor head with bolts and wrap the reactor with the heat insulation.

5. Connect the inlet of reactor with a CO_2 cylinder and open the outlet valve of the reactor.

6. Open the cylinder. Then close the outlet valve of reactor and adjust the regulator of cylinder to pressurize the reactor to the desired pressure.

7. Turn on the magnetic stirrer and set the mixing speed to 90 rpm.

8. Record the temperature of the solution every minute until it starts to drop.

9. Close the cylinder and open the outlet valve of the reactor. Then remove the reactor head and decant the mixture into a centrifuge bottle.

10. Centrifuge the centrifuge bottle for 20 minutes at 4000 rpm.

11. Decant the liquid from the centrifuge bottle into a container.

12. Rinse the solid in the centrifuge bottle with distilled water and centrifuge twice.

13. After the final rinsing, place the solid in the pre-weighted glass beaker and then put the beaker in the oven at 105 $^{\circ}$C.

14. After complete drying, take the beaker out and record the mass.

APPENDIX B

PROCEDURE FOR SIMPLE DISTILLATION

This procedure was used to understand the reactive distillation and determine the required thermal decomposition temperature.

1. Put the liquid in a round-bottom flask and record the volume.

2. Place the round-bottom flask on a heating mantle and connect it to a cold water condenser. Insert a thermocouple probe into the flask and immerse its front into the liquid.

3. Secure the joints with leakproof seal.

4. Connect the heating mantle to a variac and set the variac at 80% power.

5. Turn on the Variac and cold water.

6. Record the temperature every 30 seconds.

7. Collect distillate at different temperature with sample tubes for GC analysis and pH test and record the corresponding temperature.

APPENDIX C

BATCH DISTILLATION PROCEDURE

This batch distillation procedure was used to determine the optimum temperature for concentration and acid recovery.

1. Put the liquid in a round-bottom flask fitted with a Vigreux column and record the volume.

2. Place the round-bottom flask on a heating mantle and connect the Vigreux column to a cold water condenser.

3. Insert a thermocouple probe into the flask and immerse its front into the liquid. Place another thermocouple probe at the top of the Vigreux column.

4. Secure the joints with leakproof seal.

5. Wrap the flask and column with the heat insulation.

6. Connect the heating mantle to a Variac controlled by temperature controller. And set the Variac at 80% power.

7. Turn on cold water and set the temperature controller.

8. Put a graduated cylinder on the exit side of the condenser so that the volume recovered can be recorded.

9. After the distillation is done, decant the distillate into a beaker with magnetic stirrer and mix for 5 minutes.

10. Pipette 3 mL distillate into a 15-mL conical bottom centrifuge tube and label it with the corresponding temperature.

11. Store the samples in refrigerator at $-15\ ^{\mathrm{o}}$C for GC analysis.

APPENDIX D

CARBOXYLIC ACIDS ANALYSIS

For carboxylic acids analysis, at least 3 mL of sample should be collected and placed in a 15-mL conical bottom centrifuge tube. If not used immediately, samples may be stored at -15 ^{o}C.

GC LIQUID SAMPLE PREPARATION

1. Centrifuge the liquid sample for 5 min at 3500 rpm if the sample has scum.

2. Pipette 1 mL of sample into a 15-mL round-bottom ultracentrifuge tube.

3. Add to the same tube, 1 mL of 10-mM of internal standard 4-methyl-valeric acid (1.162 g/L internal standard, ISTD).

4. Add to the same tube, 1 mL of 3-M phosphoric acid to acidify the sample and allow the carboxylic acids to be released in the GC injection port.

5. Cap the tube and vortex.

6. Pipette 1 mL of the mixture into a glass GC vial and cap.

GC OPERATION

1. Before starting the GC, check the gas supply cylinders (compressed hydrogen, zero-grade helium, and compressed zero-grade air) to insure the pressure in each is not less than 100 psig. If there is not enough gas, switch cylinders and place an order for new ones.

2. Establish gas flow by setting the regulators at 40 psig for hydrogen, 60 psig for helium, and 50 psig for air.

3. Check the solvent and waste bottles on the injection tower. Fill the solvent

bottles with methanol, and be sure the waste bottles are empty.

4. Make sure the column head pressure gauge on the GC indicates the proper pressure (15 psig). Low head pressure usually indicates a worn-out septum. Replace the septum before starting the GC.

5. Up to 100 samples can be loaded in the autosampler plate. Place the samples in the autosampler racks, not leaving empty spaces between samples. Place volatile acid standard mix (Matreya, Inc. # 1075) solution every 50 samples for calibration.

6. Check the setting conditions in the method:

   a. Oven temperature = 50°C

   b. Ramp = 20°C/min

   c. Inlet temperature = 230°C

   d. Detector temperature = 250°C

   e. H2 flow = 40 mL/min

   f. He flow = 180 mL/min

   g. Air flow = 400 mL/min

7. Start the GC on the computer with the setting conditions above mentioned. Set and load the sequence of samples to run. Once the conditions are reached, run the sequence. Details about operation, setting sequence and calibration are in Agilent 6890 instrument manual.

8. Periodically check to ensure that the equipment is working properly. Be sure to indicate the number of samples and any maintenance performed (changes of

septum, gas cylinders, liner, etc.) in the GC logbook.

9. When finish running the sequence, put the GC on standby and close air and hydrogen cylinder valves.

APPENDIX E

DATA AND PLOTS

Table E-1. Data of temperature-time curve for precipitation study

Triethylamine		Tripropylamine		Tributylamine	
Time (min)	Temperature (^{o}C)	Time (min)	Temperature (^{o}C)	Time (min)	Temperature (^{o}C)
0	18.1	0	17.8	0	22.3
1	20.7	1	19.2	1	22.8
2	23.4	2	20.7	2	23.3
3	26.0	3	22.0	3	24.0
4	28.5	4	23.4	4	24.5
5	30.2	5	24.7	5	24.9
6	31.8	6	25.8	6	25.4
7	32.2	7	26.8	7	25.7
8	32.5	8	27.6	8	26.1
9	32.6	9	28.5	9	26.3
10	32.7	10	29.5	10	26.5
11	32.8	11	30.0	11	26.7
12	32.8	12	30.2	12	26.9
13	32.6	13	30.3	13	27.1
14	32.4	14	30.4	14	27.3
15	32.2	15	30.5	15	27.5
16	31.9	16	30.5	16	27.6
17	31.6	17	30.4	17	27.7
		18	30.3	18	27.8
		19	30.2	19	27.9
		20	30.1	20	28.0
				21	28.1
				22	28.2
				23	28.3
				24	28.4
				25	28.5
				26	28.6
				27	28.7
				28	28.7
				29	28.7
				30	28.6
				31	28.5

Table E-2. Data of temperature curves of distillation of triethyl ammonium acetate

Time (min)	Top Temperature (^{o}C)	Bottom Temperature (^{o}C)
0.5	21.4	41.0
1	21.4	47.8
1.5	21.4	55.7
2	21.4	65.0
2.5	21.4	75.9
3	21.4	86.1
3.5	21.4	97.3
4	21.4	111.4
4.5	25.6	115.5
5	79.5	116.5
5.5	84.3	119.1
6	86.3	124.6
6.5	87.4	130.8
7	87.8	137.4
7.5	88.5	143.3
8	96.6	148.2
8.5	105.7	151.8
9	116.6	154.5
9.5	128.3	156.3
10	136.5	157.6
10.5	146.0	159.0
11	155.7	160.0
11.5	159.7	160.8
12	160.4	161.3
12.5	160.8	161.8
13	161.7	162.1
13.5	162.2	162.4
14	162.5	162.6
14.5	162.6	162.7
15	162.8	162.8
15.5	163.1	163.0
16	163.2	163.1
16.5	163.3	163.2
17	163.4	163.4

Table E-3. Data of temperature curve of simple distillation of the system containing triethyl ammonium acetate, excess triethylamine, and water

Time (min)	Temperature (^{o}C)	Time (min)	Temperature (^{o}C)	Time (min)	Temperature (^{o}C)
0.5	22.3	15	98.4	29.5	104.0
1	22.3	15.5	98.6	30	103.9
1.5	22.3	16	98.6	30.5	104.0
2	22.3	16.5	99.1	31	104.3
2.5	22.3	17	99.4	31.5	105.0
3	22.3	17.5	99.6	32	105.2
3.5	22.3	18	100.0	32.5	105.7
4	22.3	18.5	100.2	33	106.1
4.5	22.3	19	100.6	33.5	106.7
5	22.3	19.5	100.7	34	107.2
5.5	22.3	20	101.0	34.5	107.2
6	22.3	20.5	101.1	35	107.5
6.5	22.3	21	101.4	35.5	107.9
7	22.3	21.5	101.4	36	108.8
7.5	22.3	22	101.5	36.5	109.5
8	22.3	22.5	101.4	37	110.4
8.5	22.3	23	101.8	37.5	111.6
9	22.3	23.5	101.9	38	113.0
9.5	22.3	24	102.1	38.5	115.6
10	74.1	24.5	102.2	39	118.0
10.5	74.7	25	102.4	39.5	120.8
11	97.1	25.5	102.7	40	124.5
11.5	97.3	26	102.8	40.5	130.2
12	97.5	26.5	102.9	41	137.2
12.5	97.7	27	103.0	41.5	145.2
13	97.8	27.5	103.3	42	153.2
13.5	97.9	28	103.4	42.5	157.2
14	98.0	28.5	103.5		
14.5	98.2	29	103.7		

Table E-4. Data of temperature curve of simple distillation of the system containing triethyl ammonium acetate, tri-*n*-octylamine, excess triethylamine, and water

Time (min)	Temperature (^{o}C)	Time (min)	Temperature (^{o}C)	Time (min)	Temperature (^{o}C)	Time (min)	Temperature (^{o}C)
0.5	21.5	19.5	98.4	38.5	100.0	57.5	107.8
1	21.5	20	98.4	39	100.0	58	108.5
1.5	21.5	20.5	98.5	39.5	100.0	58.5	109.7
2	21.5	21	98.5	40	100.1	59	110.6
2.5	21.5	21.5	98.5	40.5	100.2	59.5	112.1
3	21.5	22	98.6	41	100.2	60	113.5
3.5	21.5	22.5	98.6	41.5	100.2	60.5	115.3
4	21.5	23	98.6	42	100.3	61	117.3
4.5	21.5	23.5	98.6	42.5	100.4	61.5	120.0
5	21.5	24	98.7	43	100.4	62	122.5
5.5	21.5	24.5	98.8	43.5	100.5	62.5	124.6
6	21.5	25	98.9	44	100.6	63	126.6
6.5	21.5	25.5	98.9	44.5	100.6	63.5	128.5
7	21.5	26	98.9	45	100.7	64	130.6
7.5	21.5	26.5	99.0	45.5	100.7	64.5	132.4
8	21.5	27	99.1	46	100.7	65	134.0
8.5	21.5	27.5	99.1	46.5	100.8	65.5	135.5
9	21.5	28	99.1	47	100.9	66	137.3
9.5	21.5	28.5	99.2	47.5	100.9	66.5	140.0
10	21.5	29	99.3	48	101.0	67	143.0
10.5	21.5	29.5	99.3	48.5	101.2	67.5	146.0
11	21.5	30	99.4	49	101.2	68	149.4
11.5	21.5	30.5	99.4	49.5	101.2	68.5	153.1
12	21.5	31	99.4	50	101.2	69	156.0
12.5	21.5	31.5	99.5	50.5	101.2	69.5	157.5
13	21.5	32	99.5	51	101.9	70	158.1
13.5	21.5	32.5	99.6	51.5	102.6		
14	21.5	33	99.6	52	103.0		
14.5	21.8	33.5	99.6	52.5	103.1		
15	40.4	34	99.7	53	103.7		
15.5	96.9	34.5	99.7	53.5	104.1		
16	98.0	35	99.8	54	104.3		
16.5	98.0	35.5	99.8	54.5	104.6		
17	98.0	36	99.9	55	105.1		
17.5	98.2	36.5	100.0	55.5	105.7		
18	98.3	37	100.0	56	106.2		
18.5	98.4	37.5	100.0	56.5	106.7		
19	98.4	38	100.0	57	107.3		

Table E-5. Acetic acid concentration and pH results of distillation samples collected from triethyl ammonium acetate

Temperature (°C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
76	0	0	12.13	12.10
98	0.68	0.73	12.00	12.03
100	2.41	2.32	11.97	11.95
102	5.30	5.12	11.71	11.73
105	10.3	10.8	11.46	11.43
107	16.8	17.2	11.29	11.27
109	27.1	26.6	11.04	11.01
110	30.1	29.7	10.95	10.98
113	42.2	42.7	10.74	10.71
120	77.2	76.5	10.37	10.35

Table E-6. Acetic acid concentration and pH results of distillation samples collected from triethyl ammonium acetate with tri-*n*-octylamine

Temperature (°C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
92	0	0	12.10	12.07
98	0.86	0.76	12.00	12.02
100	2.08	2.14	11.99	11.96
102	4.51	4.62	11.72	11.75
105	9.09	9.28	11.53	11.51
107	17.4	16.9	11.31	11.34
109	24.9	25.4	11.06	11.08
110	28.5	29.0	10.98	10.96
113	39.4	40.1	10.79	10.76
120	73.9	74.4	10.33	10.31

Table E-7. Data of temperature curves of distillation of tripropyl ammonium acetate

Time (min)	Top Temperature (°C)	Bottom Temperature (°C)
0.5	20.3	30.7
1	20.3	35.3
1.5	20.3	41.4
2	20.3	48.7
2.5	20.3	57.2
3	20.3	66.0
3.5	20.3	75.2
4	20.3	84.9
4.5	20.3	94.7
5	20.3	104.7
5.5	20.3	114.5
6	20.3	124.6
6.5	20.3	134.6
7	20.3	143.3
7.5	20.3	145.2
8	20.3	143.7
8.5	32.1	143.7
9	125.2	144.1
9.5	135.9	145.2
10	145.8	147.2
10.5	147.9	148.3
11	148.9	148.5
11.5	149.1	148.6
12	149.2	148.6
12.5	149.2	148.6
13	149.2	148.6
13.5	149.2	148.6
14	149.4	148.6
14.5	150.1	148.6
15	151.2	148.6
15.5	152.1	149.1
16	152.9	152.8
16.5	154.5	157.5

Table E-8. Acetic acid concentration and pH results of distillation samples collected from tripropyl ammonium acetate

Temperature (°C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
98	10.2	10.7	9.14	9.11
102	12.2	12.7	8.96	8.98
104	19.2	18.5	8.79	8.76
106	26.6	27.2	8.60	8.64
108	32.6	33.1	8.50	8.53
110	39.0	38.0	8.41	8.45
112	43.5	44.3	8.26	8.24
114	56.3	55.5	7.94	7.91
117	66.5	67.6	7.86	7.88
122	87.8	89.3	7.79	7.76

Table E-9. Acetic acid concentration and pH results of distillation samples collected from tripropyl ammonium acetate with tri-*n*-octylamine

Temperature (°C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
100	21.1	20.7	8.81	8.83
102	24.3	24.7	8.73	8.71
104	27.5	27.0	8.64	8.61
106	34.8	34.3	8.52	8.50
108	43.8	44.7	8.25	8.28
110	56.7	55.9	8.02	8.04
112	72.3	71.1	7.80	7.83
114	83.2	84.9	7.53	7.50
117	97.5	95.8	7.07	7.05
122	118	116	6.76	6.79

Table E-10. Data of temperature curves of distillation of tributyl ammonium acetate

Time (min)	Top Temperature (^{o}C)	Bottom Temperature (^{o}C)	Time (min)	Top Temperature (^{o}C)	Bottom Temperature (^{o}C)
0.5	20.0	33.7	12.5	169.3	169.0
1	20.0	34.0	13	170.3	169.3
1.5	20.0	36.1	13.5	170.8	169.5
2	20.0	39.7	14	171.3	169.7
2.5	20.0	45.1	14.5	171.9	169.8
3	20.0	51.5	15	172.3	169.9
3.5	20.0	59.0	15.5	172.7	170.0
4	20.0	67.1	16	173.0	170.2
4.5	20.0	75.5	16.5	173.5	170.4
5	20.0	84.2	17	173.9	170.6
5.5	20.0	92.6	17.5	174.3	170.9
6	20.0	101.6	18	174.6	171.2
6.5	20.0	110.6	18.5	175.4	171.9
7	20.0	119.0	19	176.2	172.9
7.5	20.0	127.8	19.5	177.0	175.1
8	91.9	137.7	20	177.4	179.1
8.5	118.1	148.1	20.5	181.0	185.5
9	126.6	158.5	21	183.1	193.3
9.5	136.7	159.5	21.5	186.4	201.3
10	148.2	161.4	22	199.3	208.4
10.5	159.4	163.9	22.5	211.4	212.4
11	165.2	166.1			
11.5	167.4	167.6			
12	168.5	168.5			

Table E-11. Acetic acid concentration and pH results of distillation samples collected from tributyl ammonium acetate

Temperature (°C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
100	19.3	20.1	7.04	7.01
102	26.3	27.3	6.84	6.82
104	30.6	30.0	6.70	6.73
106	33.7	32.7	6.65	6.68
108	34.9	35.6	6.54	6.52
110	41.4	40.7	6.48	6.51
112	43.5	42.8	6.41	6.44
114	50.6	51.4	6.33	6.31
117	61.7	62.8	6.14	6.11
122	87.3	86.3	5.93	5.95

Table E-12. Acetic acid concentration and pH results of distillation samples collected from tributyl ammonium acetate with tri-*n*-octylamine

Temperature (°C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
100	32.2	31.5	4.86	4.88
102	38.8	39.9	4.83	4.86
104	46.5	45.7	4.67	4.65
106	52.6	51.5	4.54	4.57
108	54.8	55.8	4.44	4.41
110	60.0	59.0	4.30	4.32
112	63.5	62.4	4.20	4.23
114	68.3	69.6	4.11	4.13
117	83.0	81.6	4.03	4.05
122	110	111	3.78	3.75

Table E-13. Data of temperature curves of distillation of tri-*n*-octyl ammonium acetate

Time (min)	Top Temperature (^{o}C)	Bottom Temperature (^{o}C)
0.5	22.0	25.7
1	22.0	28.7
1.5	22.0	33.8
2	22.0	41.1
2.5	22.0	49.8
3	22.0	59.2
3.5	22.0	69.3
4	22.0	79.6
4.5	22.0	90.5
5	22.0	101.4
5.5	22.0	112.3
6	22.0	123.0
6.5	22.0	133.6
7	22.0	144.0
7.5	22.0	152.5
8	23.3	155.9
8.5	35.0	156.2
9	106.6	157.1
9.5	107.9	158.8
10	110.0	164.4
10.5	112.5	169.5
11	115.4	175.1
11.5	117.8	180.8
12	119.4	187.5
12.5	119.7	195.3
13	119.6	204.2
13.5	119.2	213.2
14	119.0	222.5
14.5	118.7	231.7
15	118.3	240.5
15.5	118.2	248.9

Table E-14. Acetic acid concentration and pH results of distillation samples collected from triethyl ammonium acetate

Temperature (^{o}C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
155	534	527	6.50	6.55
160	729	741	5.09	5.06
165	802	793	3.88	3.92
170	776	766	3.87	3.91

Table E-15. Acetic acid concentration and pH results of distillation samples collected from triethyl ammonium acetate with tri-*n*-octylamine

Temperature (^{o}C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
155	565	558	6.33	6.39
160	733	742	4.91	4.86
165	808	799	3.75	3.78
170	746	754	3.78	3.74

Table E-16. Acetic acid concentration and pH results of distillation samples collected from triethyl ammonium acetate with tri-*n*-octylamine diluted by octanol

Temperature (^{o}C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
155	245	239	7.51	7.55
160	286	280	6.65	6.63
165	353	347	5.77	5.74
170	344	351	5.44	5.41

Table E-17. Acetic acid concentration and pH results of distillation samples collected from tripropyl ammonium acetate with tri-*n*-octylamine

Temperature (°C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
150	548	539	5.81	5.84
155	683	689	5.20	5.18
160	673	666	5.19	5.21
164	592	600	5.57	5.54
167	576	585	6.15	6.13
171	372	366	6.37	6.40

Table E-18. Acetic acid concentration and pH results of distillation samples collected from tributyl ammonium acetate with tri-*n*-octylamine

Temperature (°C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
162	677	671	1.91	1.94
168	797	808	1.70	1.67
170	733	740	1.92	1.90
172	652	645	2.32	2.35
174	639	643	2.69	2.67
176	596	591	3.25	3.23
178	509	503	4.09	4.12
180	402	397	4.47	4.45
212	45.7	42.8	5.45	5.42
217	0	0	6.45	6.48

Table E-19. Acetic acid concentration and pH results of distillation samples collected from tributyl ammonium acetate

Temperature (°C)	Acetic Acid Concentration (g/L)		pH	
	#1	#2	#1	#2
162	451	445	4.63	4.60
168	511	518	3.66	3.68
174	461	468	4.07	4.04
180	460	454	4.35	4.38

Table E-20. Acetic acid concentration and pH results of distillation samples collected from tributyl ammonium acetate

Time (min)	Temperature (°C)			
	30 psig	50 psig	70 psig	90 psig
0	22.3	22.1	21.0	21.7
1	22.8	23.2	22.1	23.0
2	23.3	24.4	23.0	24.3
3	24.0	25.4	24.0	25.4
4	24.5	25.9	24.9	26.4
5	24.9	26.4	25.4	27.0
6	25.4	26.6	25.9	27.4
7	25.7	26.9	26.3	27.6
8	26.1	27.2	26.6	27.8
9	26.3	27.4	26.8	27.9
10	26.5	27.6	27.0	28.0
11	26.7	27.7	27.2	28.0
12	26.9	27.8	27.3	27.9
13	27.1	28.0	27.4	27.8
14	27.3	28.1	27.5	27.7
15	27.5	28.2	27.5	
16	27.6	28.3	27.4	
17	27.7	28.4	27.3	
18	27.8	28.5	27.2	
19	27.9	28.5	27.1	
20	28.0	28.4		
21	28.1	28.3		
22	28.2	28.2		
23	28.3	28.1		
24	28.4			
25	28.5			
26	28.6			
27	28.7			
28	28.7			
29	28.7			
30	28.6			
31	28.5			

Table E-21. Acetic acid concentration of bottom solution at different temperature for concentrating tributyl ammonium acetate

Temperature (^{o}C)	Acetic Acid Concentration (g/L)
90	120
100	156
110	171
120	172

Table E-22. Overhead acetic acid concentration of batch distillation of tributyl ammonium acetate

Temperature (^{o}C)	Acetic Acid Concentration (g/L)
160	752
170	1076
180	618
190	613
200	571

Table E-23. Total acid concentration of bottom solution at different temperature for concentrating tributylamine carboxylate derived from fermentation broth

Temperature (^{o}C)	Total Acid Concentration (g/L)
90	23.4
100	54.1
110	95.2
120	116

Table E-24. Overhead acid concentrations collected from concentrating tributylamine carboxylate derived from fermentation broth at different temperature

Temperature (^{o}C)	Acid Concentration (g/L)								
	C2	C3	IC4	C4	IC5	C5	C6	C7	Total
100	1.99	0.80	0	3.38	0	0.50	1.63	0	8.30
110	5.02	1.59	0.34	5.09	0.07	0.65	2.12	0	14.9
120	23.8	2.83	0.39	7.92	0.10	1.02	4.03	0.30	40.4

Table E-25. Overhead acid concentrations of batch distillation of tributylamine carboxylate derived from fermentation broth

Temperature	Acid Concentration (g/L)								
(°C)	C2	C3	IC4	C4	IC5	C5	C6	C7	Total
160	56.1	4.63	0	12.6	0	0	8.06	0	81.4
170	74.1	5.44	0	14.0	0	0	9.24	0	103
180	168	11.4	0	26.6	0	3.42	15.1	0	225
190	228	13.1	0	31.4	0	4.78	26.8	2.96	307
200	48.2	7.44	0	21.2	0	2.94	8.56	0	88.3
210	29.1	5.32	0	19.0	0	3.56	13.8	0	70.8
220	0	0	0	5.37	0	0	15.6	0	21.0

VITA

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