DIRECT CONVERSION OF CARBOXYLATE SALTS TO CARBOXYLIC ACIDS VIA REACTIVE EXTRACTION

A Thesis

by

XIN XU

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

August 2008

Major Subject: Chemical Engineering

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Approved by:

Chair of Committee,	Mark T. Holtzapple
Committee Members,	Cady R. Engler
	Charles J. Glover
Head of Department,	Michael V. Pishko

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ABSTRACT

Direct Conversion of Carboxylate Salts to Carboxylic Acids

via Reactive Extraction. (August 2008)

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Chair of Advisory Committee: Dr. Mark T. Holtzapple

The MixAlco process, a proprietary technology owned by Texas A&M University, converts biomass (e.g., municipal solid waste, sewage sludge, paper, agricultural residues, and energy crops) into usable chemicals (e.g., acetic acid) and fuels (e.g., ethanol). Historically, calcium carbonate has been used as the buffer. Recently, it was found that using ammonium bicarbonate as the buffering agent enhances the fermentation conversion. In this case, fermentation broth contains ammonium salts (e.g., ammonium acetate, propionate, butyrate, pentanoate). Therefore, the downstream processing steps (including extraction, purification, esterification, and product separation) must be compatible with the ammonium carboxylate salts formed in the fermentation.

This research focuses on converting fermentation broth carboxylate salts into their corresponding acids via “acid springing.” Reactive extraction and thermal conversion (distillation) are crucial parts of the acid springing process.

Because the components of the fermentation broth are over 80% ammonium acetate and 20% other ammonium carboxylate salts (ammonium propionate, butyrate, pentanoate, etc.), all the initial experiments in this study were performed using reagent-grade ammonium acetate to simplify the reaction. Later, actual fermentation broth was employed.

The primary objective of this study was to provide the optimal operating conditions to make the downstream processing steps of the MixAlco process compatible with ammonium carboxylate salts formed in the fermentation. The optimal initial concentration for reactive extraction should be 150–200 g/L and the volume ratio of aqueous phase and extractant should be 1:1. The distribution coefficient reaches the maximum value when the concentration of TOA is 20% (vol %) in *n*-octanol. The batch distillation study shows that there are two reaction stages: (1) water leaves the system at 100−106 °C and (2) the acid-amine complex decomposes at 160−180 °C.

DEDICATION

Not what we give,
But what we share,
For the gift
without the giver
Is bare.

— James Russell Lowell (1819-1891)

To my loving husband, Xi Ouyang.

To my lovely daughter, Emily, the little angel came to this amazing world on May 20, 2008.

To my family and friends for their endeavor, encouragement and enlightening.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor, Dr. Mark T. Holtzapple, for his continuous academic guidance and professional training. I wouldn't be who I am today without his invaluable help. I would like to thank the other members of the committee, Dr. Charles J. Glover and Dr. Cady R. Engler, for their guidance and support throughout the course of this research.

I would like to thank my colleagues and friends: Dr. Cesar Granda, for his tremendous guidance for my research project and thesis; Dr. Li Zhu, for her kind help and guidance of my research; Ms. Andrea Forrest and Hema Rughoonundun, for training me the operation of GC analysis and providing the fermentation broth for my experiment; and Ms. Rocio Sierra and Mr. Jipeng Dong for their generous help during setting up the laboratory equipment. Thanks also go to Towanna Hubacek and Missy Newton for their moral help.

I am also grateful to the Chemical Engineering Department and the Graduate School at Texas A&M University for their support through my graduation study.

Finally, my special gratitude goes to my husband, Dr. Xi Ouyang, for his continuous love and encouragement throughout my thesis work. Indebtedness also goes to my parents and my family for their love and support through this educational endeavor.

TABLE OF CONTENTS

Page

ABSTRACT iii

DEDICATION v

ACKNOWLEDGEMENTS vi

TABLE OF CONTENTS vii

LIST OF FIGURES ix

LIST OF TABLES xii

CHAPTER

I INTRODUCTION 1

Biomass Conversion to Alcohol 2
Traditional Process 4
MixAlco Process 4
Reactive Extraction 8
Objective 10

II EXPERIMENTAL METHODS 12

Pretreatment and Fermentation 12
Concentration Study 12
Reactive Extraction Study 14
Batch Distillation Study 16
Determination of Ammonia Loss 17
Gas Chromatography 18
Volume and Mass Balance 18

III EXPERIMENTAL RESULTS 19

Concentration Study 19
Reactive Extraction Study 37
Batch Distillation Study 52

CHAPTER Page

IV CONCLUSIONS 65

V RECOMMENDATIONS FOR FUTURE WORK 67

REFERENCES 68

APPENDIX A 71

APPENDIX B 73

APPENDIX C 74

APPENDIX D 75

APPENDIX E 77

APPENDIX F 80

VITA 89

LIST OF FIGURES

FIGURE Page

1-1 Schematics of biomass conversion to alcohols: (A) traditional process; (B) MixAlco process 3

1-2 Process overview 6

2-1 Apparatus for determine boiling point elevation and ammonium acetate loss 13

2-2 Apparatus for extraction of carboxylic acid from their salts. 15

2-3 Apparatus for batch distillation 16

3-1 Comparison of boiling point for the boiling artificial ammonium acetate and calcium acetate solution. 22

3-2 pH of the condensed fractions for the artificial ammonium acetate solution 23

3-3 The relation between the concentration of the condensed fraction and the concentration of the bottom solution for the artificial ammonium acetate solution 24

3-4 The overhead fraction recovery for the artificial ammonium acetate solution 24

3-5 Total acetate loss for the boiling artificial ammonium acetate solution ... 26

3-6 The concentration of the boiling artificial ammonium acetate solution as a function of time 27

3-7 The concentration of fractions as a function of time for the artificial ammonium acetate solution 27

3-8 Closure study for the artificial ammonium acetate solution 28

3-9 Boiling point of the boiling fermentation broth 29

3-10 pH of condensed overhead fraction of the boiling fermentation broth 30

FIGURE Page

3-11 The relation between concentration of overhead condensed fractions and time for fermentation broth 31

3-12 The relation between concentration of boiling solution and time for fermentation broth 31

3-13 Total acid loss and concentration of boiling solution for fermentation broth 32

3-14 The concentration of NH_3 in the overhead fraction for fermentation broth 33

3-15 The overhead NH_3 to acid ratio for fermentation broth 33

3-16 The overhead water recovery for fermentation broth..... 34

3-17 The overhead NH_3 recovery for fermentation broth 35

3-18 Closure study of fermentation broth..... 36

3-19 Distribution coefficient as a function of initial acid concentration at various mole ratios (M_{AQ}:M_{OR}= mole solute/mole extractant) 41

3-20 The relation between distribution coefficient D_i and various mole ratios 41

3-21 Various volume ratios and distribution coefficient D_i 42

3-22 The relation between pH and various mole ratios 44

3-23 The relation between distribution coefficient and pH 45

3-24 TOA concentration in various polar diluents and distribution coefficients 46

3-25 The relation between pH and TOA concentration in various polar diluents 47

3-26 TOA concentration in various non-polar diluents and distribution coefficients 48

FIGURE Page

3-27 The relation between pH and TOA concentration in various non-polar diluents 49

3-28 The distribution coefficient at volume ratios for extraction of acetic acid from ammonium acetate by TOA 51

3-29 Temperature of boiling solution and time for the artificial ammonium acetate solution using pure TOA as extractant (Method II) 56

3-30 Closure study of the artificial ammonium acetate solution using pure TOA as extractant (Method II)..... 57

3-31 The relation between time and temperature of boiling solution for the artificial ammonium acetate solution using TOA/*n*-octanol (20%/80% by volume) as extractant (Method II)..... 59

3-32 Closure study of the artificial ammonium acetate solution using TOA/*n*-octanol (20%/80% by volume) as extractant (Method II) 60

3-33 The relation between time and temperature of boiling solution for the fermentation broth using pure TOA as extractant (Method II)..... 61

3-34 Closure study of the fermentation broth using TOA as extractant (Method II) 63

LIST OF TABLES

TABLE Page

3-1 pH study at equilibrium 43

3-2 Survey of polar diluents experimental investigations 45

3-3 Survey of the non-polar diluents experimental investigations 47

3-4 Batch distillation study (Method I) on the artificial solution (pure TOA) 53

3-5 Batch distillation study (Method I) on fermentation broth (pure TOA) 54

3-6 Batch distillation study (Method II) on the artificial ammonium acetate solution (pure TOA) 57

3-7 Batch distillation study (Method II) for the artificial ammonium acetate solution (TOA/octanol, 20%/80% by volume) 59

3-8 Batch distillation study (Method II) for the fermentation broth (pure TOA) 62

CHAPTER I

INTRODUCTION

Increasing oil prices and decreasing oil reserves are causing researchers to explore alternative energy sources that can substitute for fossil fuels. Furthermore, people believe that fossil fuel greenhouse gas emissions are causing global warming. In the United States and elsewhere, governments initiated major programs to develop alternative renewable energy sources in response to deficiencies of fossil energy (coal, petroleum, and natural gas) and environmental problems associated with their use. Lignocellulose as a sustainable source of fuels (e.g., ethanol) and chemicals is attractive because it is plentiful and low-cost.

Since the 1970s, Brazil has taken the lead position in the modern ethanol fuel industry. In recent years, this industry has also grown dramatically in the United States. In 2006, the total amount of ethanol production reached almost 5 billion gallons in the United States, about 1 billion gallons more than that in 2005. Further expansion is continuing with production expected to exceed 10 billion gallons by 2009 (Westcott 2007). In the United States, most ethanol is produced from sugar and starch feedstocks, which competes with food. To meet increased demand for fuel, it is important to consider the effects of drastically increasing agricultural production, which necessitates more land usage, more pesticides and fertilizer application, all of which bring a host of

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This thesis follows the style of Biotechnology and Bioengineering.

environmental concerns. The use of lignocellulose for fuels not only brings the benefits of a sustainable energy source, but solves disposal problems and reduces greenhouse gases (Kheshgi et al. 2000). Converting lignocellulose to biofuel can dramatically improve our environment and economy; therefore, it has the potential to become prevalent and significant.

Biomass Conversion to Alcohol

The three major components of lignocellulose are cellulose, hemicellulose, and lignin, which are sometimes called ligocellulosic materials. Cellulose is a linear polymer consisting of D-anhydroglucopyranose joined together by β-1,4-glycosidic bonds. Cellulose forms a skeleton that is surrounded by hemicellulose and lignin functioning as matrix and encrusting materials, respectively. Hemicellulose polymers are shorter than cellulose polymers with degree of polymerization of 50–200. The role of hemicellulose is to provide a linkage between cellulose and lignin. Lignin is a three dimensional phenyl-propane polymer with phenylpropane units held together by ether and carbon-carbon bonds (Fan et al. 1987). It has a high molecular weight 5000 (DP about 25) and is amorphous in nature. Lignin gives structural rigidity and its hydrophobic nature prevents water loss from plant vascular systems.

There are three basic methods used to produce ethanol from lignocellulose (EFC): acid hydrolysis, thermochemical processes, and enzymatic hydrolysis. Compared to the other two methods, enzymatic hydrolysis has advantages such as mild process conditions, low energy costs, and reduced by-products. However, enzyme costs are high,

which is being addressed by research (Badger 2002).

Generally, there are two biological processes that convert lignocellulosic biomass to alcohols (Zhu 2005), as shown in Figure 1-1.

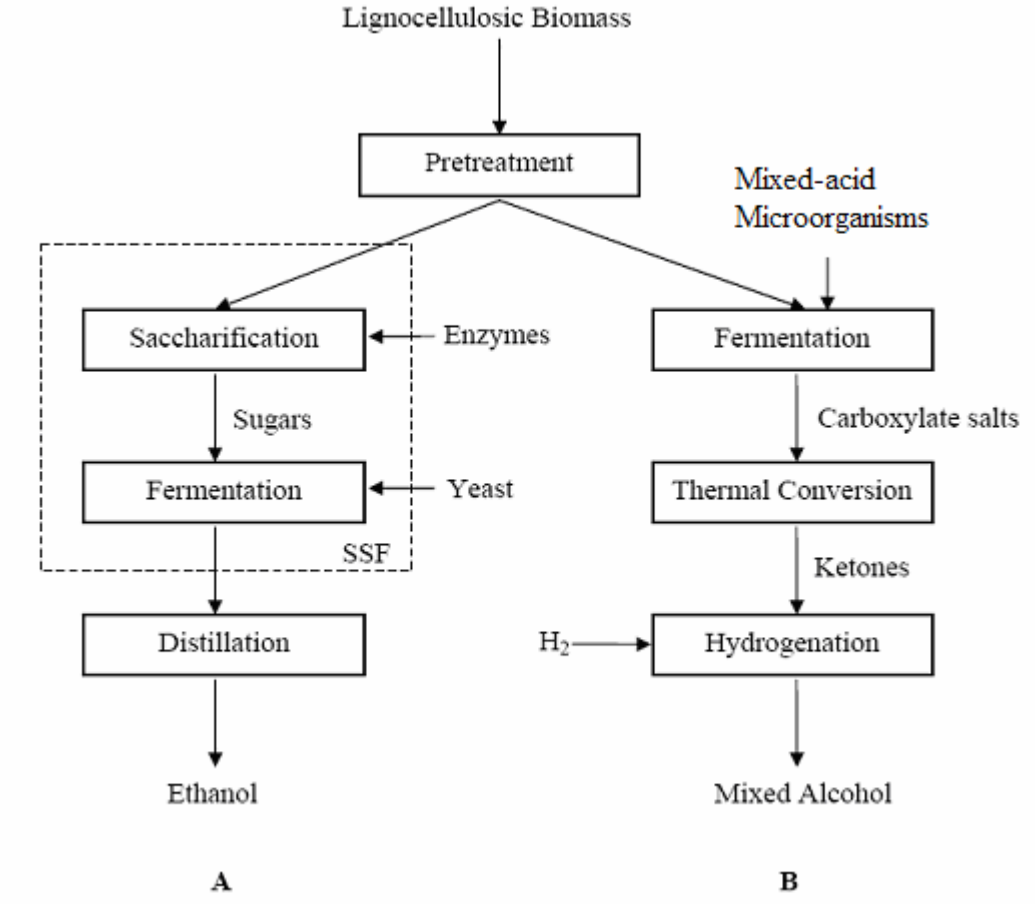


Figure 1-1. Schematics of biomass conversion to alcohols: (A) traditional process; (B) MixAlco process.

Traditional Process

The traditional method for converting lignocellulose to ethanol contains four steps: (1) pretreatment to change structural features to make cellulose accessible to enzymes, (2) formation of fermentable sugars, called saccharification, (3) fermentation of these sugars to ethanol, and (4) separation and purification of the ethanol. Separate hydrolysis and fermentation (SHF) allows each step to operate at its optimal temperature. Combining saccharification and fermentation into a single step is called simultaneous saccharification fermentation (SSF). The primary advantage of SSF is that the immediate consumption of sugars by microorganisms reduces the glucose and cellobiose concentrations in the fermentor, which significantly reduces enzyme inhibition to improve the kinetics and economics of biomass conversion (Takagi et al. 1997; Wright et al. 1988).

MixAlco Process

During the past few decades, scientists have been searching for a cost-effective way to produce liquid fuels from biomass. Since 1991, a new method has come onto the stage. The MixAlco process has evolved into several versions since it was first developed. The first version is shown in Figure 1-1 (Method B). The MixAlco process converts biomass (e.g., municipal solid waste, sewage sludge, paper, agricultural residues, and energy crops) into usable chemicals and fuels, such as acetic acid and ethanol. It is a continuous process and has reached the pilot plant level.

In the MixAlco process, biomass is first pretreated with lime to enhance digestibility and then is fermented to produce carboxylic acids, such as acetic, propionic, and butyric acids. To prevent the pH from decreasing as the acids are formed, a neutralizing agent ($CaCO_3$) is added to the fermentor; thus carboxylate salts such as calcium acetate, propionate, and butyrate will exit the fermentor. After concentration and thermal conversion steps, the salts are converted into ketones, and finally hydrogenated to mixed alcohols.

Compared to the traditional approach mentioned previously, the MixAlco process offers the following advantages (Holtzapple et al. 1999):

- It is adaptable to a wide variety of feedstocks.
- Aseptic process conditions are not required.
- Inexpensive tanks can be employed.
- Expensive extracellular enzymes are not required.
- The fermentation organisms regenerate themselves and are stable.
- Cells and microorganisms can be recycled without contamination risk.

Recently it was found that using ammonium bicarbonate as the buffering agent can enhance the fermentation (Agbogbo 2005). In this case, the fermentation broth contains ammonium carboxylate (e.g., ammonium acetate, propionate, butyrate, pentanoate) instead of calcium carboxylate; therefore, redesign and modification of the downstream steps (including extraction, purification, esterification, and products separation) is needed. Figure 1-2 shows the new version using ammonium bicarbonate as the buffering agent.

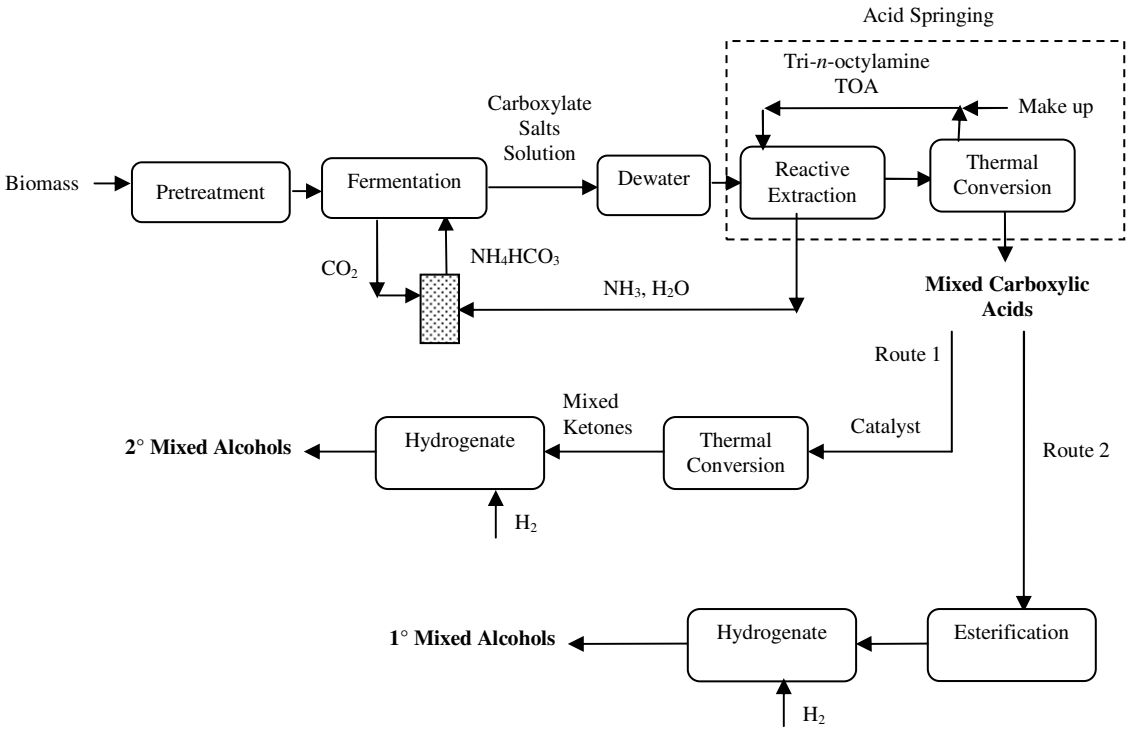


Figure 1-2. Process overview.

As an important intermediate product of the MixAlco process, carboxylic acids (C_2–C_7) have a high market value and can be recovered and sold. To recover these useful industrial chemicals (e.g., acetic acid) and primary alcohols (e.g., ethanol), the concept of "acid springing" is introduced into the MixAlco process, as shown in Figure 1-2. Historically, the fermentation broth containing calcium carboxylate can be converted into carboxylic acids using acid springing (Williamson 2000). The calcium carboxylate salts were concentrated and reacted with a low-molecular-weight tertiary amine and carbon dioxide to precipitate calcium carbonate. In a distillation column, the

low-molecular-weight amine carboxylate reacted with a high-molecular-weight tertiary amine allowing the low-molecular-weight amine to be recovered from the top of the column. The resulting amine carboxylate can then be thermally decomposed into the amine itself for recycling, and also the corresponding carboxylic acids. The new process version uses ammonium bicarbonate as the buffering agent, so the acid springing procedures are different from the previous version. First, the ammonium carboxylate salts react with high-molecular-weight tertiary amine (tri-*n*-octylamine) while supplying heat. Because ammonium carboxylate salts are not thermally stable, the released ammonia is reused in the fermentation step as a buffer. At the same time, the tri-*n*-octylamine extracts acetate from the aqueous phase and forms acid-amine complex. Then after thermal conversion, the complex decomposes into amine and acetic acid. The new version has no precipitate and low-molecular-weight tertiary amine involved; it is more efficient, and is relative simple. Theoretically, in this way, there are no chemicals consumed or wastes produced during this step. The mixed carboxylic acids can be converted to ketones or mixed alcohols.

Acetic acid is an important chemical product. About 75% of synthetic acetic acid is produced from methanol carbonylation. Its derivatives have reached several hundred varieties that are extensively used in many industries, such as chemicals, light industry, textiles, pharmaceuticals, printing/dyeing, rubber, pesticides, photographic chemicals, electronics, and food processing. Because acetic acid is under severe pressure from the high cost of methanol and producers are seeking price increases, recovered acetic acid represents an additional major supply and can make considerable profits.

Reactive Extraction

The extraction of organic acids with ternary amines (e.g., tri-*n*-octylamine) has been widely studied for fermentation broths and wastewater streams (Kertes and King 1986; Tamada et al. 1990; Wasewar and Pangarkar 2006). A thermodynamic model was developed based on experimental data for the partitioning of single carboxylic acids (Kirsch and Maurer 1996). Later, the model was extended to the competitive extraction of two carboxylic acids. The effect of sodium chloride, hydrochloric acid, and sodium acetate on the partitioning between the aqueous solution and tri-*n*-octylamine has been studied at 298 K (Roos and Bart 2001). Liquid-liquid equilibria of aqueous solutions of acetic, propionic, butyric, and valeric acids with tri-*n*-octylamine in various diluents were determined at 298 K (Li et al. 2002). The selective extraction of acetic acid from the fermentation broth was performed using tri-*n*-octylamine as the extractant (Huh et al. 2004).

Extensive equilibrium studies with acid/amine systems were performed by King and his co-workers (Kertes and King 1986; Tamada and King 1990). They have presented evidence that the variety of the strength of acid/amine complexation is depend on the solvation efficiency of diluents (e.g., *n*-hexane, benzene, chloroform), and is sensitive to polarity and hydrogen bonding ability. Recently, liquid–liquid equilibrium data for the distribution of C_1–C_4 monocarboxylic acids into conventional diluents have been reported (Malmary et al. 1997; Reinsel et al. 1994). The experimental studies (Yang et al. 1991) revealed that Alamine 336 (a water insoluble, tri-octyl/decyl amine that forms oil-soluble salts of anionic species at low pH) bound the non-dissociated part

of the acid in the organic phase through reversible complexation. The extraction power of Alamine 336 has been found to decrease in the following order: butyric acid > propionic acid > lactic acid > acetic acid.

The effect of diluents mainly focuses on their ability to solvate polar ion-pair organic species through dipole-dipole interaction or hydrogen bonding, favoring the formation of one or simultaneously at least two acid-amine complexes. Data covering different classes of diluents (protic, non-protic, and inert) were interpreted (Tamada et al. 1990). Senol A. (Senol 2000; 2002; 2004) elucidated that the stoichiometry of acid-amine complexes is intimately connected to the strength of the complex solvation by the diluent, which increases in the following order: aliphatic hydrocarbon < alkyl aromatic < halogenated aromatic < ketone < protondonating halogenated hydrocarbon < nitrobenzene < alcohols. Attempts were also made to estimate the properties of an acid/amine system of hydrogen-bond formation through theoretical models of the mass action law, including physical interaction terms (Juang and Huang 1994; Kirsch and Maurer 1996).

There are very few research reports on the recovery of carboxylate salts by reactive extraction. A process was developed to recover organic acid and ammonia from their salts obtained from microbial fermentation (Mani and Hadden 1996). The fermentation broth is passed through nanofiltration, a chelating resin ion-exchange bed, or both to reduce divalent or multivalent metal contaminants. Then, the filtered material is processed in a multi-compartment electrodialysis unit containing bipolar and anion membranes.

Objective

The research described in this thesis focuses on converting fermentation broth ammonium carboxylate salts into their corresponding acids via "acid springing" (see Figure 1-2). Reactive extraction and thermal conversion (distillation) are crucial parts of the acid springing process. The process involves mixing fermentation broth – which contains mainly ammonium carboxylate salts (ammonium acetate, propionate, butyrate, pentanoate) – with a high-molecular-weight tertiary amine (tri-*n*-octylamine). The ammonium carboxylate salts decompose into ammonia and corresponding carboxylic acids at high temperatures. Because the ammonia is volatile, it can leave the system with the condensed fraction or be captured by a tail gas trap through a conduit. Then the solution becomes carboxylic acids. The component change makes it possible to extract carboxylic acids from the aqueous phase into high-molecular-weight tertiary amine (tri-*n*-octylamine). Through the physical solubility of the solute in the extractant phase, the carboxylic acids form acid-amine complexes with high-molecular-weight tertiary amine.

After reactive distillation, the carboxylic acids are recovered from the top of the distillation column and the high-molecular-weight tertiary amine is recovered from the bottom of the column, which can be reused as the extractant. The released ammonia can be reused in the fermentation step as a buffer.

The reaction stoichiometry can be represented by the following equations:

$$NH_4Ac + H_2O \underset{\Delta}{\longleftrightarrow} HAc + NH_3 \bullet H_2O \qquad (1\text{-}1)$$

$$R_3N + HAc \leftrightarrow R_3NHAc \qquad (1\text{-}2)$$

$$R_3NHAc \underset{\Delta}{\longrightarrow} HAc + R_3N \qquad (1\text{-}3)$$

Because the acid in the fermentation broth is over 80% ammonium acetate and 20% other ammonia carboxylate salts (ammonium propionate, butyrate, pentanoate, etc.), the preliminary experiments in this study were performed using reagent-grade ammonium acetate to simplify the reaction. After getting the preliminary data, then fermentation broth was employed.

The primary objective of this study was to identify appropriate optimal parameters for the downstream parts of the MixAlco process to respond to the switch from calcium to ammonium carboxylate salts formed in the fermentation. The initial carboxylate concentration, extract efficiency with various diluents, and temperature range of distillation was determined in this study.

This study is original because it is the first look at acid springing using ammonium carboxylate salts in the MixAlco process.

CHAPTER II

EXPERIMENTAL METHODS

Pretreatment and Fermentation

Bagasse was treated with lime at 50 °C for 2 months at a lime loading of 0.1 g $Ca(OH)_2$/g biomass in air. Non-pretreated mixed sludge from wastewater treatment plants (40%) and pretreated bagasse (60%) were used for continuous countercurrent fermentation. Ammonium bicarbonate was added to the fermentation to maintain the pH near 7.0; therefore, ammonium carboxylate salts exited the fermentor. The fermentation broth containing ammonium carboxylate was about 2.5 to 4% by weight. The addition of methane inhibitor (iodoform) blocked methane generation and ensured that ammonium carboxylate was the main product. Without inhibitors, about 1 to 8% of the carbon digested was lost to methane, depending upon the feedstock. The consequence of adding methane inhibitors is that the reducing power that previously went into methane caused higher molecular weight ammonium carboxylate to form. Group member Hema Rughoonundun performed the pretreatment and fermentation processes.

Concentration Study

The fermentation broth from the fermentor had a carboxylic acid concentration of 25–40 g acid/L, and the remainder was water and "scum," which was removed using the centrifuge. The broth was collected for the consequent procedures and the scum was

discarded. Prior to the acid springing process, the fermentation broth was concentrated via evaporation at about 100 °C. See Appendix A for the detailed procedures.

The purpose of the concentration study was to determine the loss of ammonia and acids and the boiling point elevation during concentration. A round-bottom flask, heating mantle, thermometer, water condenser, tail gas trap, and graduated cylinder were used to perform the experiment (Figure 2-1).

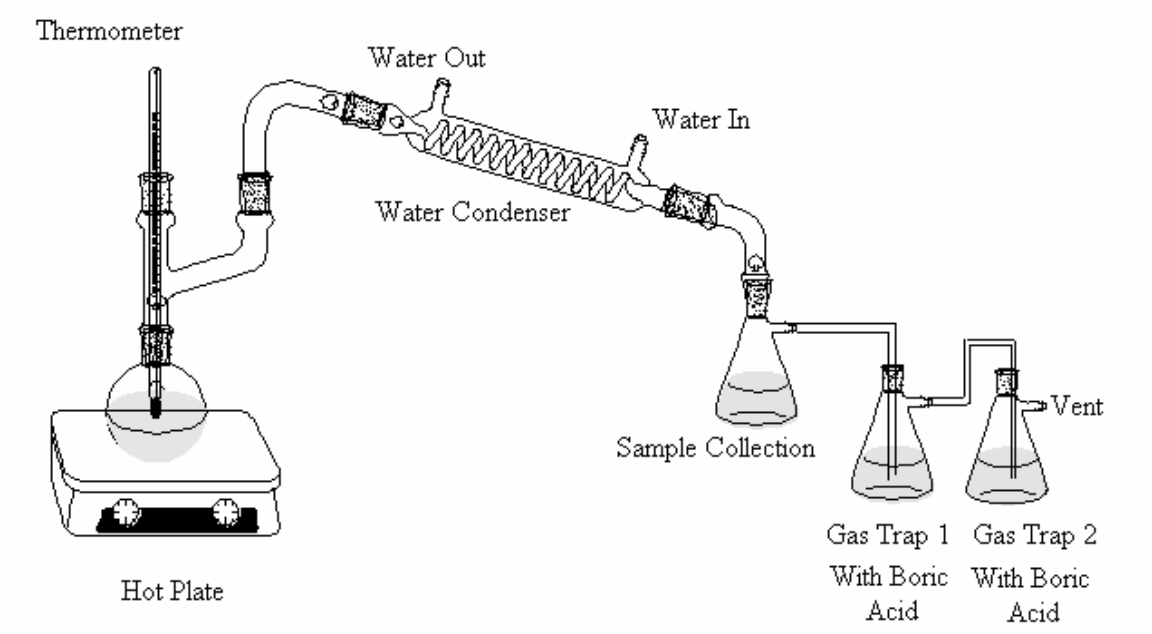


Figure 2-1. Apparatus for determine boiling point elevation and ammonium acetate loss.

The solution was boiled using a heating mantle controlled by a Variac. Temperature was monitored at all times to determine the boiling point change with solution concentration. The resulting vapor was condensed using a water condenser.

Samples of condensed vapor and liquid from the round-bottom flask were collected for GC analysis. Also, ammonia vapors were trapped by boric acid with methyl red as an indicator in the tail gas trap. The amount of captured ammonia was determined by titration. The samples were analyzed with the GC to find the actual acid concentration, and the amount of acids lost during evaporation. From mass balances, the amount of acid and ammonia present in the boiling side and condensed side at any given temperature was determined.

Reactive Extraction Study

Reactive extraction, which exploits reversible chemical complexation in the extractant phase, provides an effective separation, especially for relatively dilute solutions, such as the aqueous solution of carboxylic acids in a fermentation broth. Solutions of long-chain tertiary amines in diluents (e.g., alkanes, alcohols, and chloroform) are very effective extractants for carboxylic acids.

This study focused on the extraction equilibrium of monocarboxylic acids and carboxylate salts from aqueous solutions with tri-*n*-octylamine in various diluents at selected ratios. The diluents employed in this study were polar diluents (*n*-butanol, *n*-heptanol, and *n*-octanol) and non-polar diluents (pentane, hexane, and heptane). Also, the effect of initial concentration and pH on the extraction was studied.

All extraction experiments were conducted using 100-mL flasks at ambient temperature (25 ± 0.5 °C). Extractant and the aqueous solution with the initial concentration of solute were added to each flask at desired ratios. The flask containing

the mixture was stirred at 500 rpm for about 2 hours. Phase separation was ensured by transferring the mixture to a separatory funnel and leaving it quiescent for 30 minutes. Consequently, the upper layer (organic phase) was removed, and samples of the aqueous phase were taken from the bottom layer for pH and concentration analysis. The carboxylic acid concentration in the aqueous phase was determined by GC analysis, whereas the carboxylic acid concentration in the organic phase was calculated through mass balances. See Appendix B for detailed procedures.

The extraction of carboxylic acid from their salts was performed by heating the system to drive out the ammonia. The released ammonia was collected by boric acid solution with methyl red indicator (Figure 2-2). All extraction experiments were conducted using 100-mL flasks. Extractant and the aqueous solution with the initial concentration of ammonium carboxylate salts were added to each flask at desired ratios. The flask containing the mixture was stirred at 500 rpm for about 2 hours by heating to the desired temperature. The released gas rose through conduit and was collected in the boric acid solution. Other procedures were the same as mentioned above.

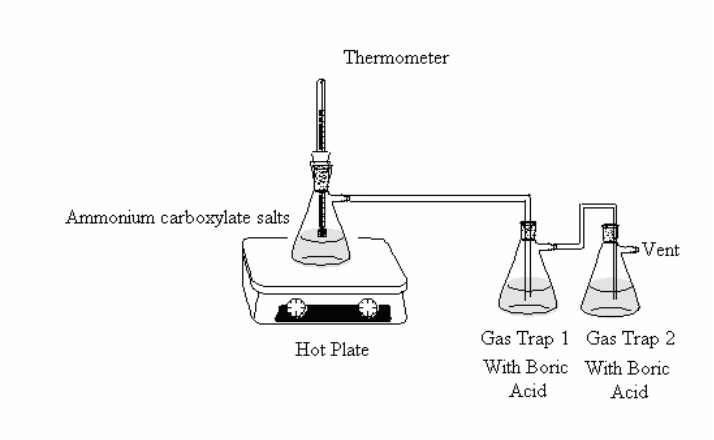


Figure 2-2. Apparatus for extraction of carboxylic acid from their salts.

Batch Distillation Study

This batch distillation study was performed to determine the temperature range over which the acid-amine complex thermally decomposes to carboxylic acid and tri-*n*-octylamine. Also the amount of ammonium loss in this process was determined. Figure 2-3 shows a schematic of the apparatus used to perform the batch distillation. Extractant and ammonium acetate solution (or fermentation broth) in desired ratios were added into a three-mouth round-bottom flask. Nitrogen was employed to prevent amine oxidation. The temperatures of the bottom solution and overhead fractions were monitored at all times. Overhead fractions were collected in Erlenmeyer flasks. Boric acid with methyl red indicator solution was applied to capture the ammonia released during distillation.

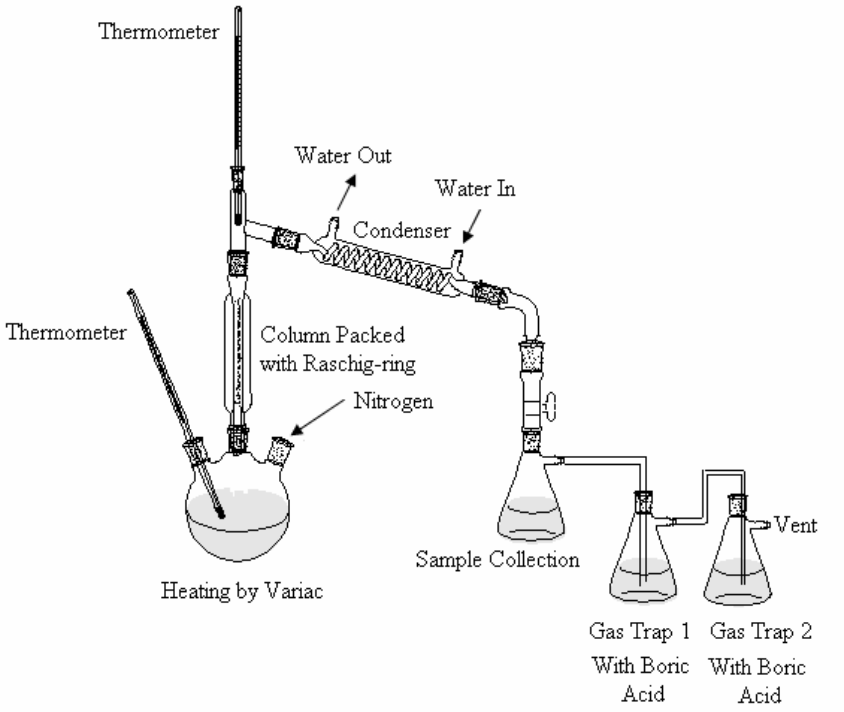


Figure 2-3. Apparatus for batch distillation.

The primary purpose of the batch distillation was to understand the reaction and provide the necessary data to design a continuously operating acid springing process. See Appendix C for detailed procedures.

Determination of Ammonia Loss

To determine the amount of ammonia loss in the concentration and distillation steps, boric acid was used as the receiving solution to capture ammonia released. The chemical reaction follows:

$$NH_3 + H_3BO_3 \rightarrow NH_4H_2BO_3 \qquad (2\text{-}1)$$

The boric acid captured the ammonia gas and formed an ammonium-borate complex. Methyl red was added to the boric acid solution as an indicator, so the color of the receiving solution changed from pink to yellow as ammonia was collected. The titrimetric addition of sulfuric acid exactly neutralized the ammonium borate complex, and a reverse color change was produced (see Equation 2-2).

$$2NH_4H_2BO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H_3BO_3 \qquad (2\text{-}2)$$

To determine the amount of ammonia dissolved in the collected fraction, the fraction was heated and a caustic solution (e.g., NaOH) was added to cause ammonia release. The ammonia exited the flask through a conduit and was received in an

Erlenmeyer flask containing a 4% boric acid solution with methyl red indicator. Then, the boric acid with ammonia was titrated with sulfuric acid in the same way as explained previously. See Appendix D for detailed procedures.

Gas Chromatography

Carboxylic acids and salts were analyzed with a Hewlett Packard 5890A gas chromatograph equipped with a flame ionization detector. The samples were combined with an internal standard (4-methyl-*n*-valeric acid) and acidified with 3-M phosphoric acid before injection into the gas chromatograph. See Appendix E for detailed procedures. To get accurate results, samples were diluted with deionized water when the estimated concentration was over 50 g/L.

Volume and Mass Balances

To determine material flows in the acid springing process, volume and mass balances were conducted in all studies. In addition, mole balances were calculated for some studies.

CHAPTER III

EXPERIMENTAL RESULTS

Concentration Study

The fermentation broth had a carboxylic acid concentration of 25–40 g acid/L. The concentration step reduces the amount of solution in the thermal conversion step, which reduces energy consumption. The recovered water can be reused in the fermentation steps. Because ammonium carboxylate salts are not thermally stable (Olszak-Humienik 2001), ammonia will evolve in the concentration procedure. Released ammonia is reused in the fermentation step as a buffer to adjust the pH and provide an optimal living environment for bacteria.

In this concentration study, the ammonia and acid loss, as well as boiling point elevation, were determined. Although other carboxylate salts were present in the fermentation broth, ammonium acetate was the primary focus. For this reason, the preliminary study used an artificial solution of reagent-grade ammonium acetate as the model salt. Then, the fermentation broth was evaluated.

The solution was boiled using a heating mantle controlled by a Variac. The power setting depended on the boiling solution. The fermentation broth produced more foam than the artificial ammonium acetate solution during concentration; therefore, the artificial ammonium acetate solution used a higher power input (70%), and fermentation broth used a lower power input (50–60%). Temperature of the boiling side was monitored at all times. The resulting vapor was condensed using a cold water condenser,

and fractions of this condensed vapor were collected for GC analysis. From mass balances, the amount of acid present in the boiling solution at any given temperature was determined. At a given temperature T_i, the accumulated acetate loss (A_{loss}), expressed as weight of NH_4Ac in volume of total liquid evaporated (g/L), was determined by GC analysis of each fraction collected. The equation for the calculation follows:

$$A_{loss} = \frac{\sum_{i=1}^{n} C_i^f V_i^f}{\sum_{i=1}^{n} V_i^f} \tag{3-1}$$

where,

A_{loss} = Loss of acetate per total volume evaporated (g/L)

C_i^f = Concentration in collected fraction i (g/L)

V_i^f = Volume of collected fraction i (L)

In the same way, at a given temperature T_i and assuming that n fractions were collected, the concentration of ammonium acetate in the boiling solution was determined as follows:

$$C_i = \frac{C_0 V_0 - \sum_{i=1}^{n} C_i^f V_i^f}{V_0 - \sum_{i=1}^{n} V_i^f} \qquad (3\text{-}2)$$

where,

C_i = Concentration in boiling solution after collecting fraction i (g/L)

C_0 = Starting concentration of boiling solution as prepared and determined by GC (g/L)

V_0 = Starting volume of boiling solution as prepared (L)

These calculations were applied to each component in fermentation broth study as well.

The boiling point is the temperature where the vapor pressure of the liquid equals the external pressure. As shown in Figure 3-1, the artificial calcium acetate solution had a boiling point elevation of about 1.6 °C when the solution became saturated. In the contrast, for the artificial ammonium acetate solution, the boiling point increased as the concentration in the boiling solution increased. When the concentration of the boiling solution reached 1065.5 g acetate/L, the boiling point elevation was about 50 °C. This obeys Raoult's Law, which states that increasing the solute in a solution depresses the vapor pressure and raises the boiling point.

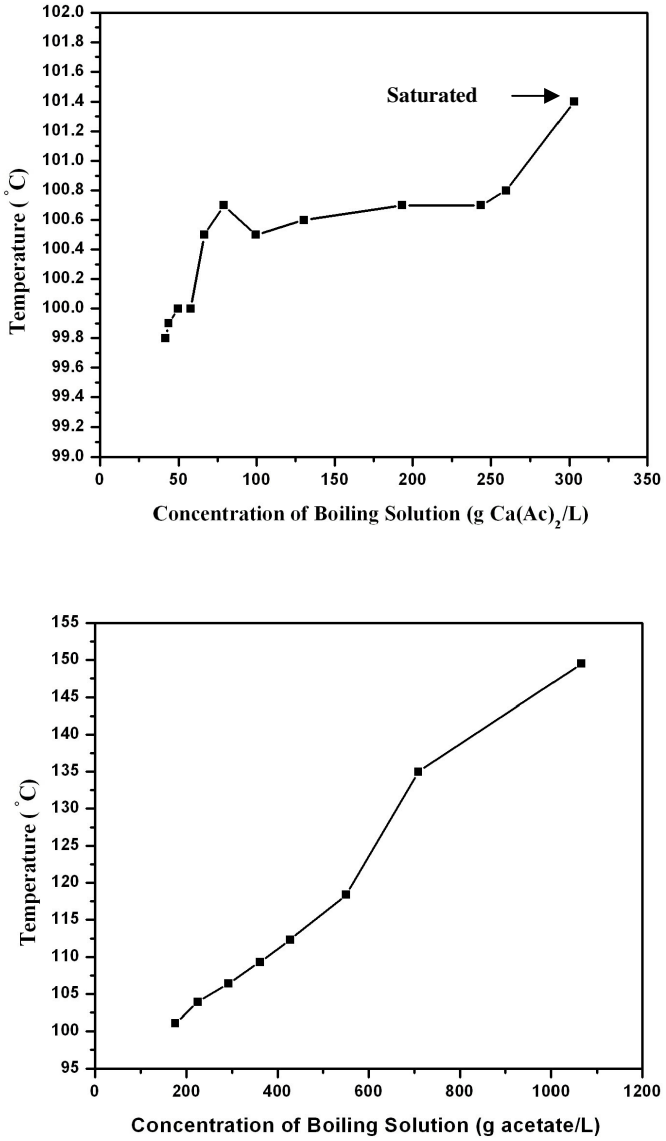


Figure 3-1. Comparison of boiling point for the boiling artificial ammonium acetate and calcium acetate solution.

The pH variation of condensed fractions for the artificial ammonium acetate solution is shown in Figure 3-2. The pH of all condensed fractions was greater than 7.0, which means the condensed fractions were enriched in ammonia rather than acetic acid.

The pH of the first overhead fraction was 10.68, and the pH of the second overhead fraction was 9.88. The pH may have dropped because the main component in the boiling solution was acetate, some of which might have evaporated.

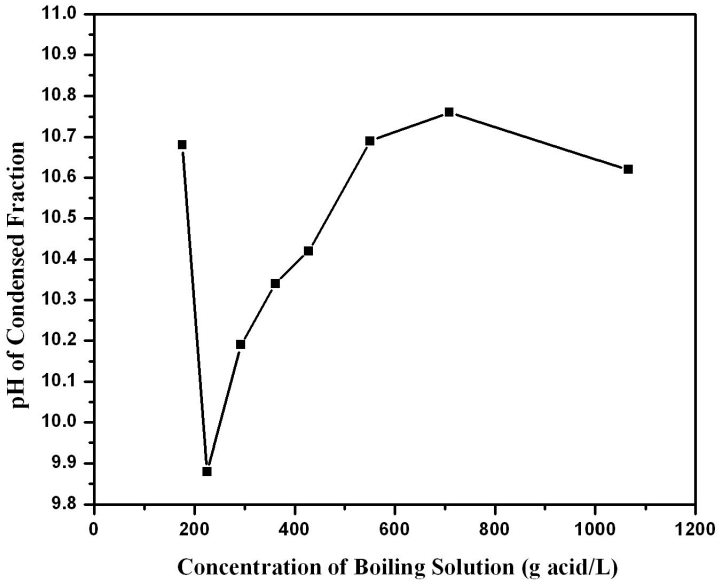


Figure 3-2. pH of the condensed fractions for the artificial ammonium acetate solution.

Figure 3-3 shows the relation between the concentration of the condensed fraction and the concentration of the bottom solution. The concentration of the condensed fraction increased with increasing concentration of the bottom solution.

Figure 3-4 shows the overhead water recovery (%) as a function of the concentration of the bottom solution for the artificial ammonium acetate solution. When the concentration of bottom solution reached 1065.6 g/L, 96.6% water was recovered in the overhead.

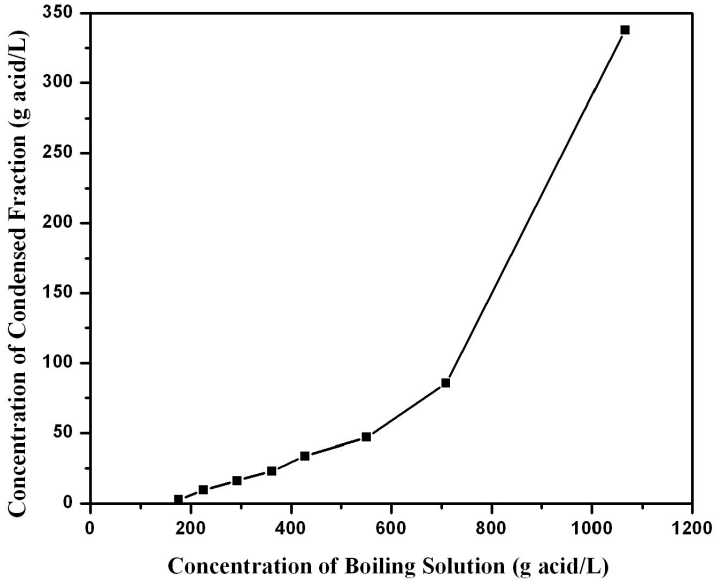


Figure 3-3. The relation between the concentration of the condensed fraction and the concentration of the bottom solution for the artificial ammonium acetate solution.

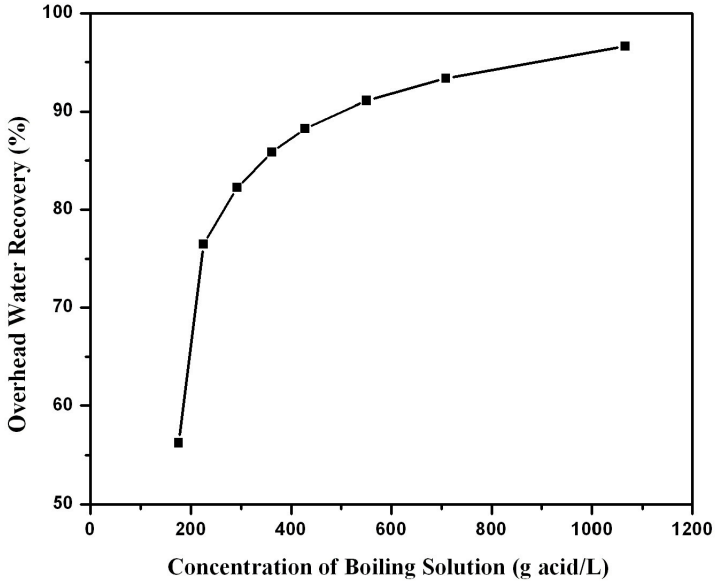


Figure 3-4. The overhead fraction recovery for the artificial ammonium acetate solution.

Figure 3-5 shows the total acetate loss as a function of concentration in the boiling artificial ammonium acetate solution. When the boiling concentration reached 1065.6 g/L, the total acetate loss was around 36%, as calculated with Equation 3-3.

$$\text{Total Acetate Loss (\%)} = \frac{A_{loss} \times \sum_{i=1}^{n} V_i^f}{C_0 \times V_0} \qquad (3\text{-}3)$$

where,

A_{loss} = Loss of acetate per total volume evaporated (g/L)

V_i^f = Volume of collected fraction i (L)

C_0 = Starting concentration of boiling solution as prepared and checked by GC (g/L)

V_0 = Starting volume of boiling solution as prepared (L)

Figures 3-1 and 3-5 indicate that when the concentration of the artificial ammonium acetate solution increases from 60 to 200 g acetate/L, the total acetate loss is about 5%, and the boiling point elevation is 3 °C.

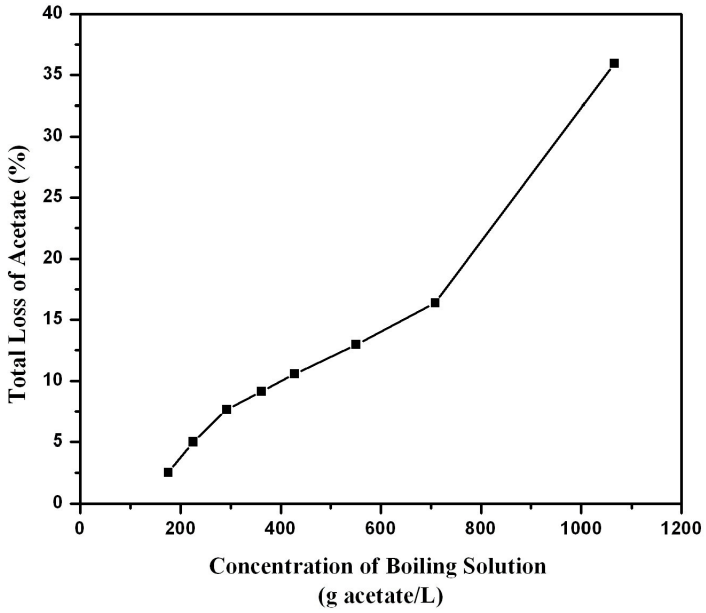


Figure 3-5. Total acetate loss for the boiling artificial ammonium acetate solution.

Figure 3-6 shows the relation between the concentration of the boiling artificial ammonium acetate solution and time, and Figure 3-7 shows the relation between concentration of condensed fractions and time. The concentration of boiling solution dramatically increased after 3 hours, and the concentration of overhead condensed fractions increased too. The total acetate loss was less than 5%, when the total batch operation time was less than 3 hours for the batch concentration unit.

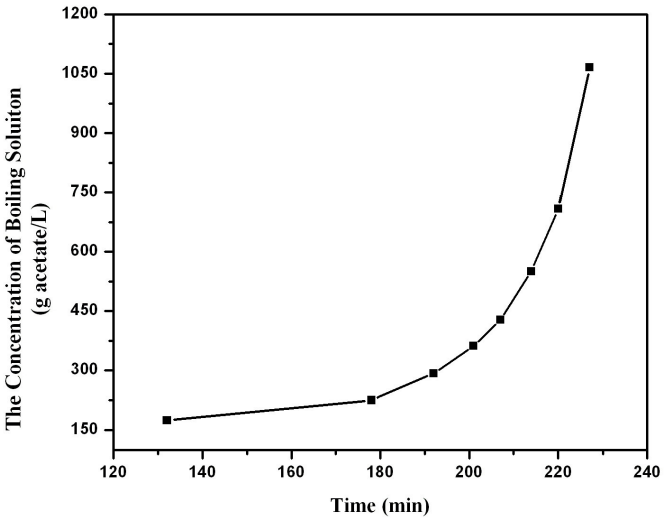


Figure 3-6. The concentration of the boiling artificial ammonium acetate solution as a function of time.

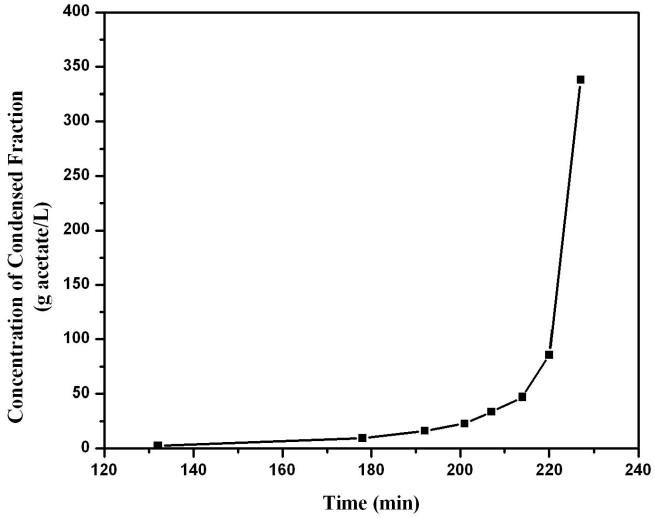


Figure 3-7. The concentration of fractions as a function of time for the artificial ammonium acetate solution.

Figure 3-8 shows the volume closure for the artificial ammonium acetate solution is 99.4%. The loss was due to sampling and manipulation. There was a 2.78% difference in the ending concentration between GC analysis result and theoretical calculation. The

pH values of all condensed fractions were greater than 7, which means that on a molar basis, more decomposed ammonia was released from the boiling solution than acetic acid. Trace amounts of ammonia captured in the tail gas traps were ignored. After titrating the condensed fractions, when the concentration of the boiling artificial ammonium acetate solution was 1065.6 g acetate/L, about 85% of the ammonia was released from the boiling side and dissolved in the overhead condensed fractions. See Appendix F for detailed GC data and closure calculations.

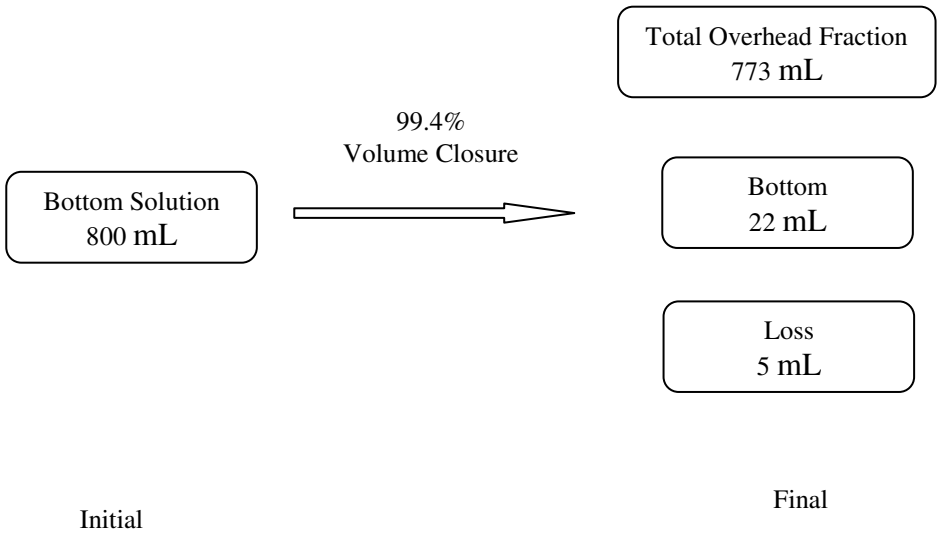


Figure 3-8. Closure study for the artificial ammonium acetate solution.

Fermentation broth was obtained from other research group members who were conducting fermentations. Based on the results of the artificial ammonium acetate solution study, fermentation broth was concentrated from an initial concentration of

about 30 g acetate/L to a final concentration of 150 g acetate/L to keep the total acetate loss within 5%.

Because the fermentation broth produced more foam than the artificial solution, the power input was set about 30% less than the artificial solution; therefore, the total time for condensing the same volume of fermentation broth to the same concentration was longer than that of the artificial ammonium acetate solution. The color of the bottom solution changed from yellow to dark yellow, which might have been caused by scum in the broth. For the fermentation broth, Figure 3-9 shows the boiling point elevation as a function of the concentration of boiling fermentation broth.

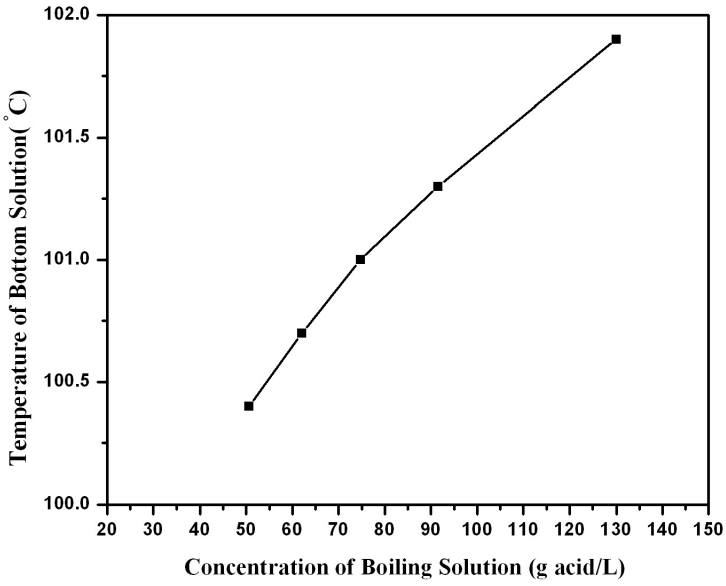


Figure 3-9. Boiling point of the boiling fermentation broth.

Figure 3-10 shows the pH variation with the increase of the concentration of bottom solution. The pH of all overhead condensed fractions was around 10. Figure 3-11 shows the relation between the concentrations of each overhead condensed fraction and

time. The concentrations of C_2–IC_5 acids of overhead fractions increased with time. During the overall concentrating process, the changes of acetate concentration for each overhead fraction were not significant.

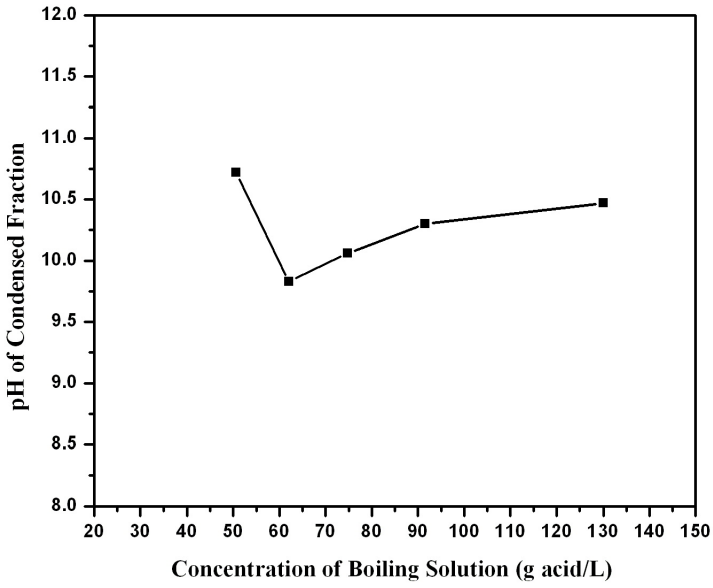


Figure 3-10. pH of condensed overhead fraction of the boiling fermentation broth.

Figure 3-12 shows the relation between concentration of boiling solution and time for the fermentation broth. In the bottom flask, the concentrations of C_2–IC_5 acids increased with time. The C_2 acid was the dominate component of the fermentation broth.

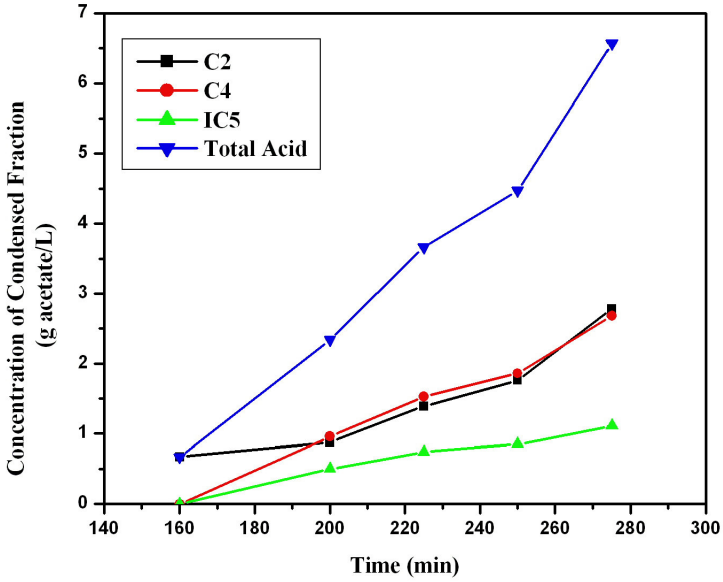


Figure 3-11. The relation between concentration of overhead condensed fractions and time for fermentation broth.

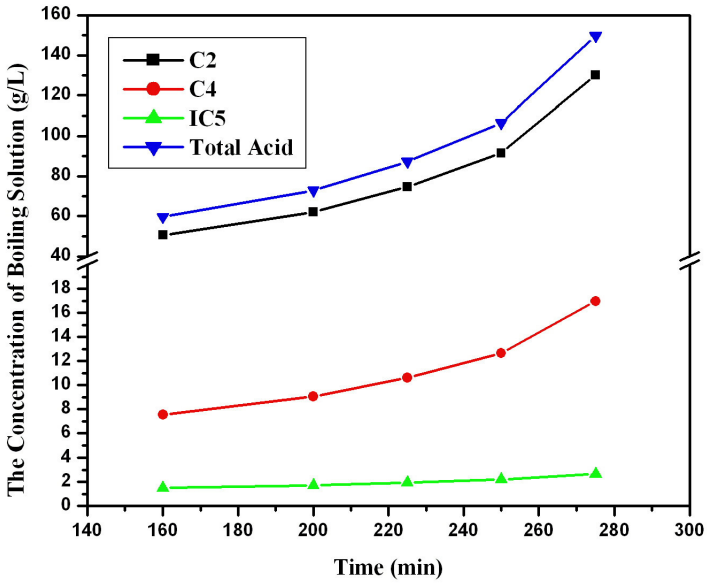


Figure 3-12. The relation between concentration of boiling solution and time for fermentation broth.

Figure 3-13 shows the relation between total acid loss and the concentration of boiling solution for the fermentation broth. When the boiling solution was concentrated to 150 g acid/L, the total acid loss reached 5.37%, which is similar to the artificial ammonium acetate solution.

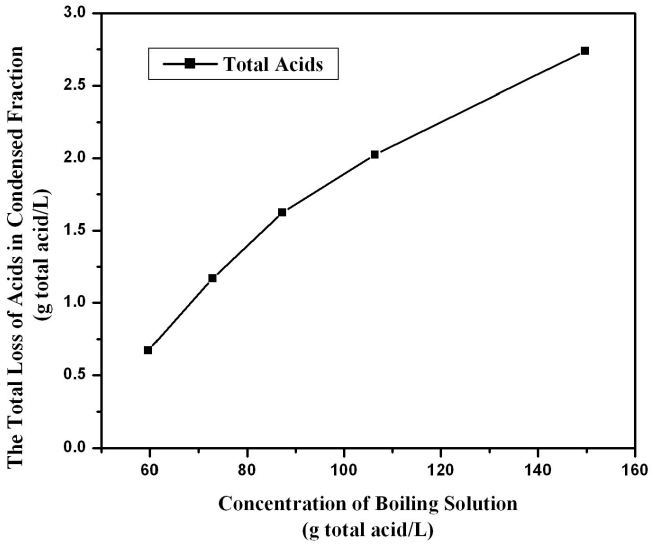


Figure 3-13. Total acid loss and concentration of boiling solution for fermentation broth.

Figure 3-14 shows the concentration of NH_3 in the overhead fraction for the fermentation broth. The trend of the curve is similar to the pH variation (Figure 3-10). Figure 3-15 shows the overhead NH_3 to acid ratio as a function of the concentration of bottom solution for the fermentation broth. The ratio of NH_3 to acid in the overhead fraction decreased with increase of concentration of bottom solution.

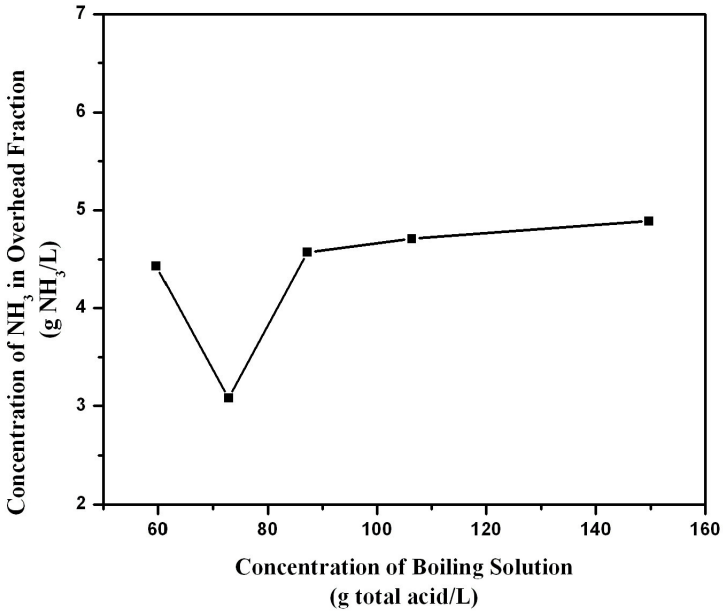


Figure 3-14. The concentration of NH_3 in the overhead fraction for fermentation broth.

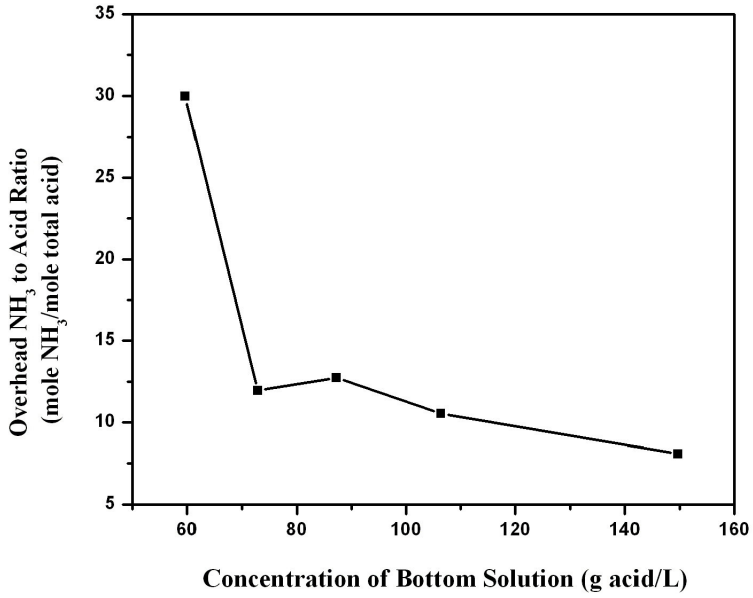


Figure 3-15. The overhead NH_3 to acid ratio for fermentation broth.

Figure 3-16 shows the overhead water recovery for the fermentation broth. The water recovery increased with the increase of concentration of bottom solution. When the bottom solution was around 150 g/L, about 70% water was recovered from the bottom. Figure 3-17 shows the overhead NH_3 recovery for the fermentation broth. The recovery of NH_3 in the overhead fraction was increased with the increase of the concentration of bottom solution. When the bottom solution was around 150 g/L, about 60% ammonia was lost from the bottom.

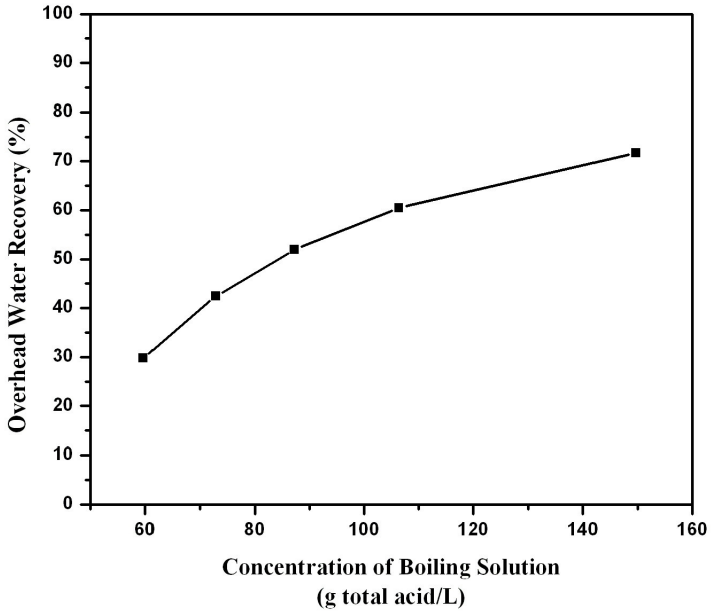


Figure 3-16. The overhead water recovery for fermentation broth.

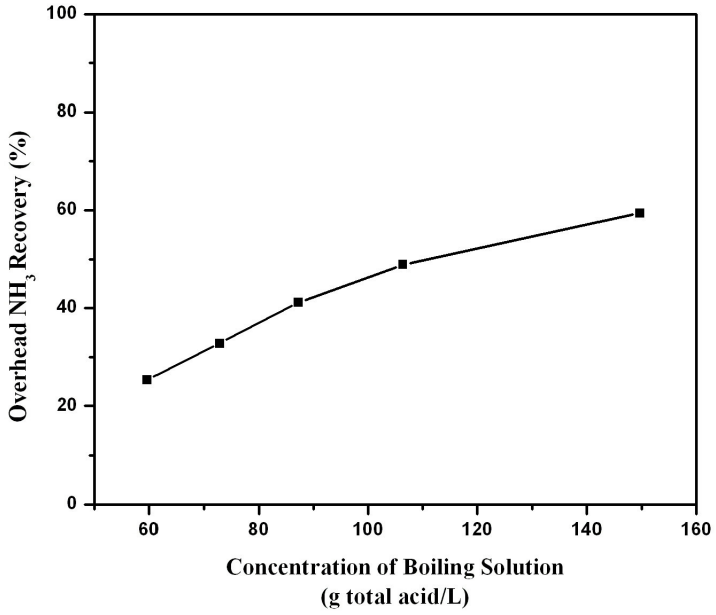


Figure 3-17. The overhead NH_3 recovery for fermentation broth.

Figure 3-18 shows a volume balance study of the fermentation broth experiment. The volume closure for the fermentation broth was 98.4%. The final concentration had a 7.97% difference between the GC analysis result and the calculated result, which all are acceptable. Figure 3-10 shows that the pH of all overhead condensed fractions was around 10 due to the release of ammonia from the boiling solution. At the end of the experiment, by titrating the condensed fractions, around 60% ammonia was lost from the bottom. See Appendix F for closure calculation and GC data of the fermentation broth.

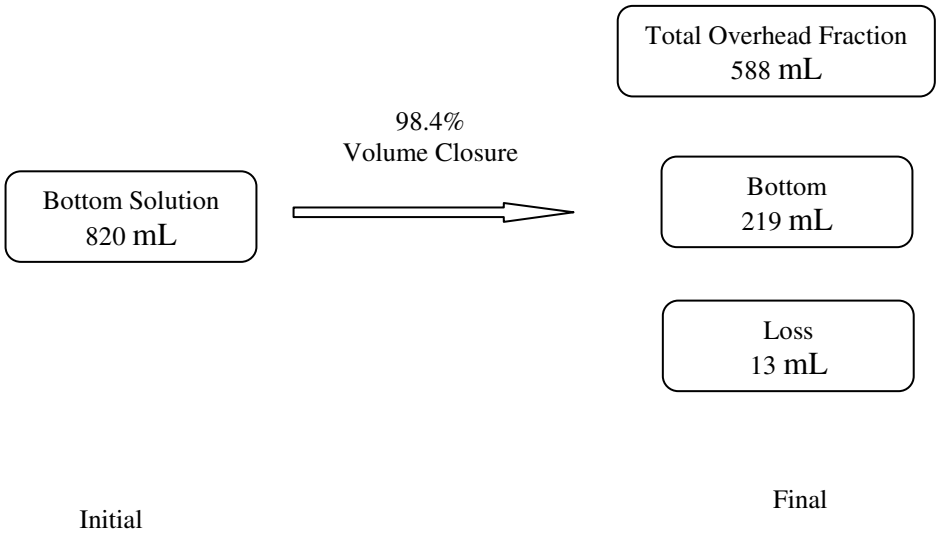


Figure 3-18. Closure study of fermentation broth.

Compared to the artificial ammonium acetate solution, the fermentation broth is more sensitive to the power input rate. The Variac power input should be controlled lower than 60% to avoid violent foaming. To control the total acetate loss to be less than 6%, the fermentation broth can be condensed to 30% of its original volume. There was 3 °C boiling point elevation while the solution was condensed to 30% of its original volume, and around 60% ammonia was released from the boiling side. The volume and mass balance were satisfied because all the experiments were performed in a close system. All the overhead condensed fractions were alkaline and the boiling solution was acidic.

Reactive Extraction Study

Recently, many researchers have studied solvent extraction to recover carboxylic acids from dilute aqueous solutions, notably with hydrophobic tertiary amines dissolved in various organic diluents (Fahim 1992; Hartl and Marr 1993; Wasewar and Pangarkar 2006). The specific affinity of long-chain tertiary amines for carboxylic acids gives high selectivity for this type of solute with respect to water and non-acidic species in the mixture (Poole and King 1991). The formation of acid-amine complexes depends on the nature of diluents, which affects the basicity of the amine and the stability of the ion-pair association in the extractant phase. These diluents may hydrogen bond with oxygens on the carboxylic acids. Because the hydroxyl and carboxyl groups increase the solubility of acids in water, strong interactions of solvent with solutes are necessary to extract carboxylic acids from dilute aqueous phase.

This study presents the extraction equilibrium of carboxylic acids and carboxylate salts in the aqueous solution with a long-chain tertiary amine (tri-*n*-octylamine) in various diluents at selected ratios. Equilibrium data were analyzed for the system of carboxylic acids or carboxylate salts with tri-*n*-octylamine in alkanes (hexane, pentane, and heptane) and alcohols (*n*-butanol, *n*-heptanol, and *n*-octanol).

The initial thought of extracting carboxylic acids from their salts is to mix the fermentation broth, which contains mainly ammonium carboxylate salts (ammonium acetate, propionate, butyrate, pentanoate) with high-molecular-weight tertiary amine (tri-*n*-octylamine). At high temperature, the ammonium carboxylate salts will decompose to ammonia and carboxylic acids. The ammonia will leave the solution with condensed

fractions and make the solution acidic. The carboxylic acids will form acid-amine complexes with high-molecular-weight tertiary amine and ammonia will release from the system. By this means, the ammonium carboxylate can be treated as potential acid.

Two crucial factors should be considered when studying the extraction of carboxylic acids from their salts. One is the extractant tri-*n*-octylamine (TOA) capacity for acid; another is the effect of releasing ammonia during the extraction. Because there are no peer studies on the extraction of carboxylic acid from their ammonium salts, this study started with the extraction of free acid to determine the optimal parameters. Then the parameters can be applied as reference to perform the extraction from ammonium acetate to understand the effect of ammonia release on extraction.

Based on the mass action law, an expression for the extraction equilibrium of carboxylic acid with tri-*n*-octylamine as extractant can be obtained assuming the carboxylic acid dissociates in water, is extracted into the extractant phase through its physical solubility, and forms acid-amine complexes. The process steps are as follows:

(1) Carboxylic acid transfers from the aqueous phase to the organic phase:

$$HAc \Leftrightarrow \overline{HAc} \tag{3-4}$$

(2) The (1:1) acid-amine complex forms:

$$\overline{R_3N} + \overline{HAc} \Leftrightarrow \overline{R_3NHAc} \tag{3-5}$$

(3) The (2:1), (3:1) complex forms:

$$(p-1)\overline{HAc} + \overline{R_3NHAc} \Leftrightarrow \overline{R_3N(HAc)_p} \qquad p = 1, 2, 3 \tag{3-6}$$

where, the superscript "‾" denotes organic phase.

To quantify the effect of extraction, the distribution coefficient (D_i) is introduced and defined in Equation 3-7. The distribution coefficient characterizes the solubility of Component *i* in the organic relative to that in the aqueous phase. A large D_i means a higher solubility in the organic phase.

$$D_i = \frac{C_i^{org}}{C_i^{aq}} \tag{3-7}$$

where,

D_i = Distribution coefficient

C_i^{org} = Equilibrium concentration of Component *i* in the organic phase g/L

C_i^{aq} = Equilibrium concentration of Component *i* in the aqueous phase g/L

The equilibrium concentrations of Component *i* in the aqueous phase were determined by GC analysis. The equilibrium concentrations of Component *i* in the organic phase were calculated based on the following mass balance equation:

$$C_i^{org} = \frac{(C_{i0}^{aq} - C_i^{aq}) \times V^{aq}}{V^{org}} \tag{3-8}$$

where,

C_{i0}^{aq} = Initial concentration of Component *i* in the aqueous phase

V^{aq} = Volume of the aqueous phase

V^{org} = Volume of the organic phase

The effect of initial concentration on extraction was first studied. Five different initial acid concentrations (about 30, 60, 100, 150, and 200 g/L) were used at selected mole ratios with extractant, as shown in Figures 3-19 and 3-20. The extractant was pure tri-*n*-octylamine (TOA). Figure 3-19 shows that at certain mole ratios of solute and extractant, the distribution coefficients increased with increasing initial acid concentration. When the mole ratio of solute and extractant was 2:1, the distribution coefficients were higher than other ratios at all initial concentrations; however, there was an inflexion on the curve, which means there is an optimal initial concentration. As shown in Figure 3-20, when the initial concentration was low (30 g/L), the mole ratio had little effect on the extraction; and when the concentration increased, the effect of mole ratio became significant. Thus the optimal mole ratio of solute in aqueous phase and extractant was 2:1, and the optimal initial concentration in the aqueous phase should be 150–200 g/L.

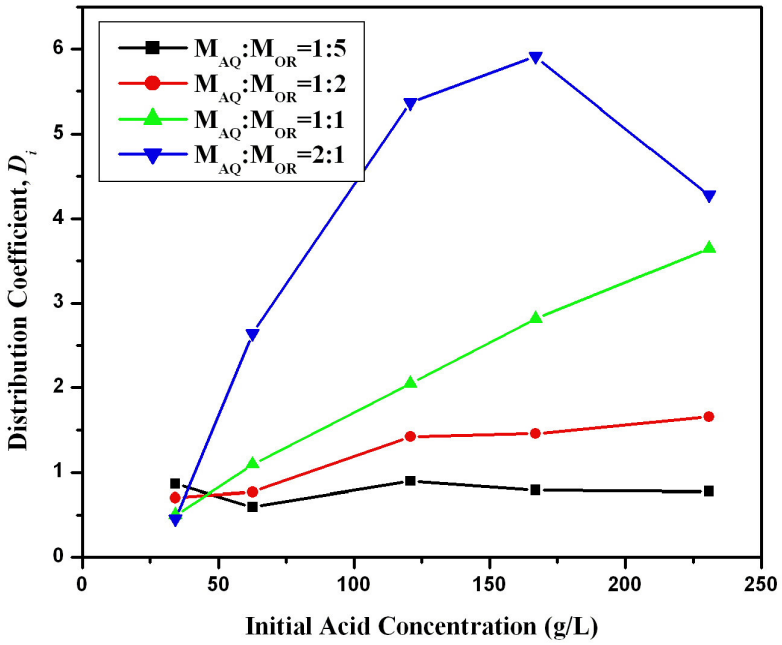


Figure 3-19. Distribution coefficient as a function of initial acid concentration at various mole ratios (M_{AQ}:M_{OR}= mole solute/mole extractant).

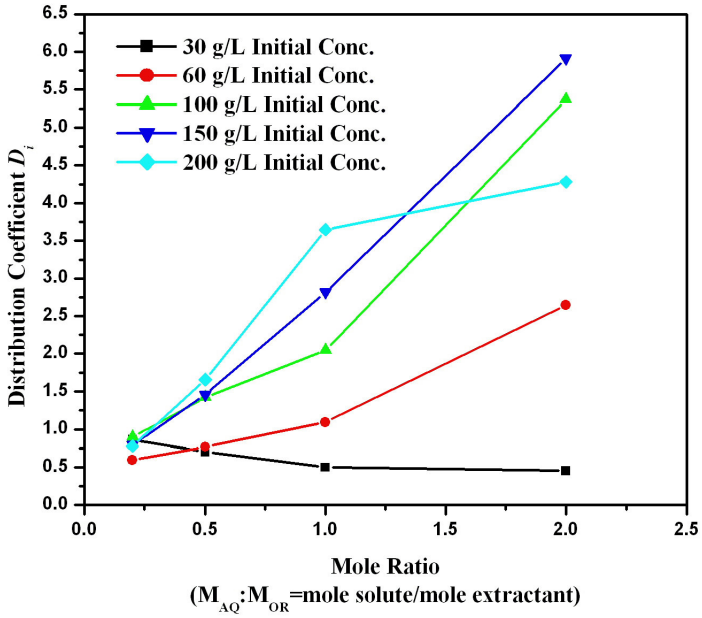


Figure 3-20. The relation between distribution coefficient D_i and various mole ratios.

Figure 3-21 shows the effect of volume ratio in the aqueous and organic phases on extraction. At certain concentrations, the distribution coefficients increased by increasing the volume ratios, which means at higher volume ratios, better extraction results can be achieved. Higher aqueous-phase volumes ensured the acid-amine complex forms. The slope of 200 g/L initial concentration is the largest compared to the other initial concentrations, which means the volume ratio has greater effect on the distribution coefficient at higher initial concentration.

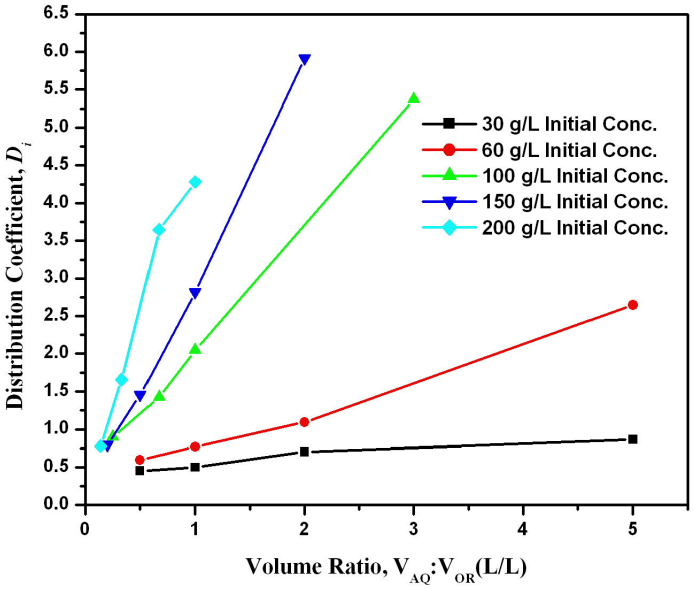


Figure 3-21. Various volume ratios and distribution coefficient D_i

Table 3-1 shows the equilibrium pH in the aqueous phase, which is different from the initial value because acids are removed from the aqueous phase. The solution pH had a tendency to increase in this study; however, the pH difference was less than 1.

Table 3-1. pH study at equilibrium

Initial Acid Solution	Initial pH	Mole Ratio M_{AQ}:M_{OR} (Mole solute /Mole extractant)	Equil. pH in Aqueous Phase	Distribution Coefficient D_i
30 g/L acetic acid (0.05 mol/L)	3.38	1:5	3.45	0.865
		1:2	3.49	0.702
		1:1	3.68	0.497
		2:1	3.88	0.453
60 g/L acetic acid (0.1 mol/L)	3.29	1:5	3.71	0.595
		1:2	3.60	0.769
		1:1	3.55	1.094
		2:1	3.50	2.644
100 g/L acetic acid (0.17 mol/L)	3.22	1:5	3.63	0.896
		1:2	3.54	1.421
		1:1	3.51	2.047
		2:1	3.44	5.370
150 g/L acetic acid (0.25 mol/L)	3.15	1:5	3.68	0.793
		1:2	3.52	1.456
		1:1	3.48	2.816
		2:1	3.53	5.910
200 g/L acetic acid (0.33 mol/L)	3.06	1:5	3.80	0.778
		1:2	3.64	1.656
		1:1	3.58	3.645
		2:1	3.54	4.280

Figure 3-22 shows that when the initial concentration was low (30 g/L), the pH tends to increase with increasing mole ratio ($M_{solute\ in\ AQ}$:M_{OR}). In contrast, for higher initial concentrations, the pH decreases with an increase of mole ratio ($M_{solute\ in\ AQ}$:M_{OR}).

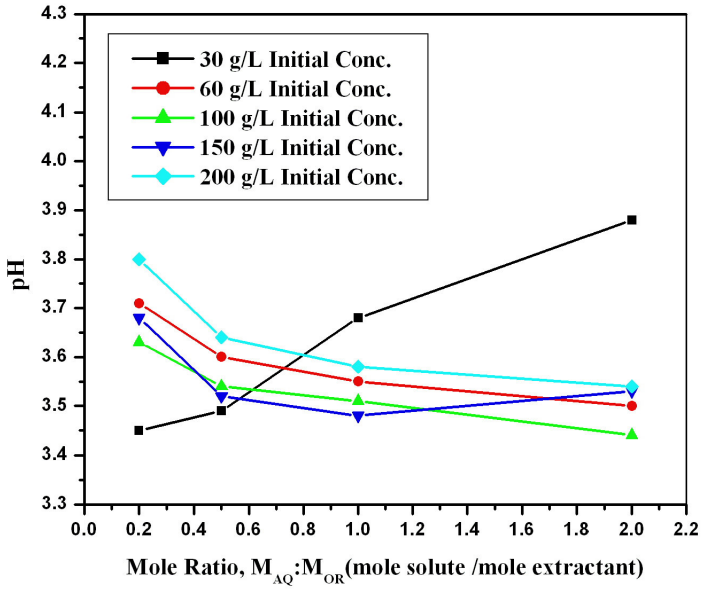


Figure 3-22. The relation between pH and various mole ratios.

Figure 3-23 shows the relation between distribution coefficient and pH. The pH tends to increase with increased distribution coefficient when the initial concentration is low (30 g/L). When the initial concentration increases, the pH has a reverse trend and decreases with increased mole ratio ($M_{solute\ in\ AQ}$:M_{OR}). The variation makes it difficult to determine the pH effect on the extraction; therefore, pH dependence is not significant.

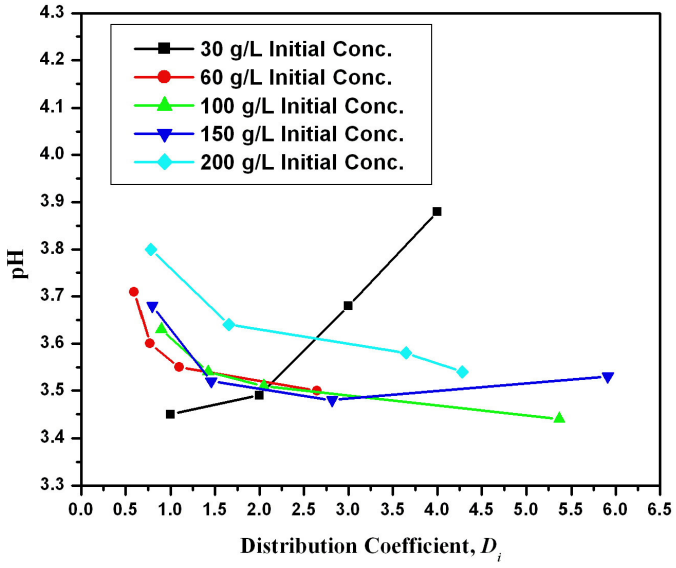


Figure 3-23. The relation between distribution coefficient and pH.

Polar diluents (*n*-butanol, *n*-heptanol, and *n*-octanol) were employed in this study to evaluate their effect on extraction efficiency. Various volume ratios of tri-*n*-octylamine and diluents were studied. Based on the previous initial concentration study, the initial concentration employed in this part was 200 g/L. The mole ratio of solute in the aqueous phase and extractant in the organic phase was M_{AQ}:M_{OR} = 2:1. Table 3-2 summarizes the experimental investigations. Detailed data are shown in Appendix F.

Table 3-2. Survey of polar diluents experimental investigations

Diluent	TOA Concentration in Diluent (vol %)
n-butanol	20, 30, 50, 60, 80
n-heptanol	20, 30, 50, 60, 80
n-octanol	20, 30, 50, 60, 80

Figure 3-24 shows the relation between the concentration of tri-*n*-octylamine (TOA) in the organic phase and the distribution coefficient. There was no obvious trend, but when the concentration reached 200 g/L, the distribution coefficient had the maximum value. Figure 3-25 shows the effect of equilibrium tri-*n*-octylamine (TOA) concentration in the organic phase on the pH in the aqueous phase.

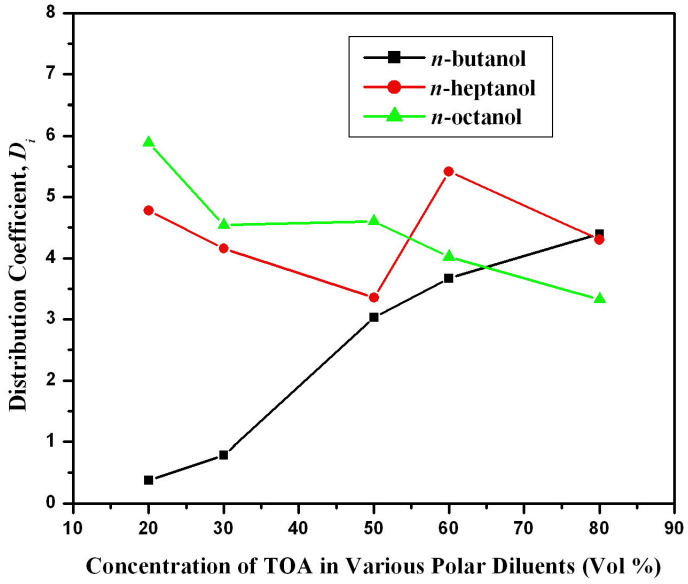


Figure 3-24. TOA concentration in various polar diluents and distribution coefficients.

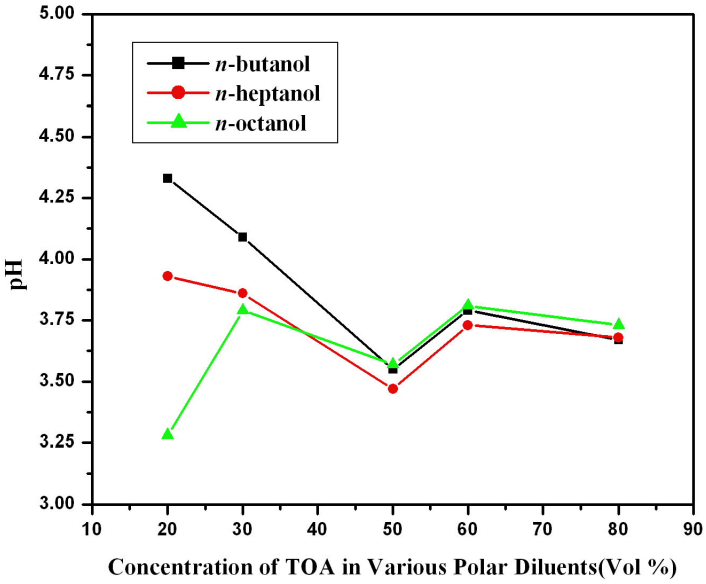


Figure 3-25. The relation between pH and TOA concentration in various polar diluents.

Non-polar diluents (pentane, hexane, and heptane) were employed in this study to evaluate the effect of polar diluent on the extraction efficiency. Various volume ratios of tri-*n*-octylamine and diluents were studied here. The initial concentration employed in this part was 200 g/L, and the mole ratio of solute in the aqueous phase and extractant in the organic phase was about M_{AQ}:M_{OR} = 2:1. Table 3-3 summarizes the experimental investigations. Appendix F shows the detailed data.

Table 3-3. Survey of the non-polar diluents experimental investigations

Diluent	TOA Concentration in Diluent (vol %)
Pentane	20, 30, 50, 60, 80
Hexane	20, 30, 50, 60, 80
Heptane	20, 30, 50, 60, 80

Figure 3-26 shows the relation between the concentration of tri-*n*-octylamine (TOA) in the organic phase and the distribution coefficient. The distribution coefficients were increased with the concentration of tri-*n*-octylamine (TOA) in the organic phase, but the difference was not significant among various diluents. Figure 3-27 shows the effect of equilibrium tri-*n*-octylamine (TOA) concentration in the organic phase on the pH in the aqueous phase.

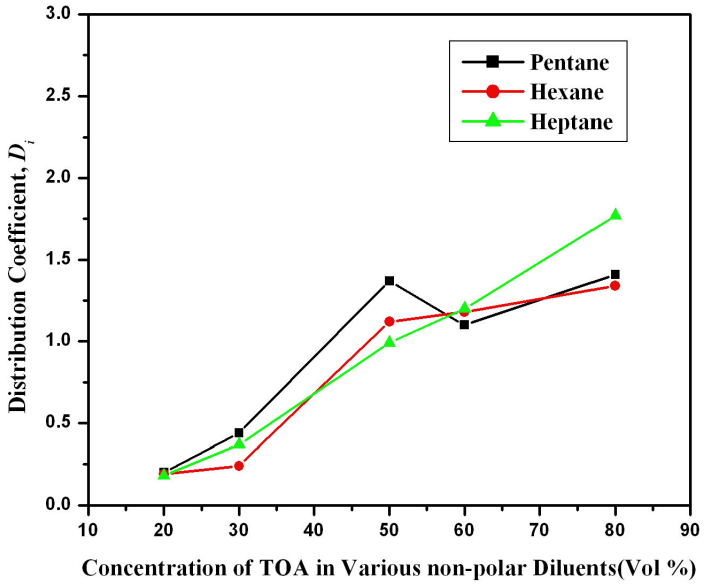


Figure 3-26. TOA concentration in various non-polar diluents and distribution coefficients.

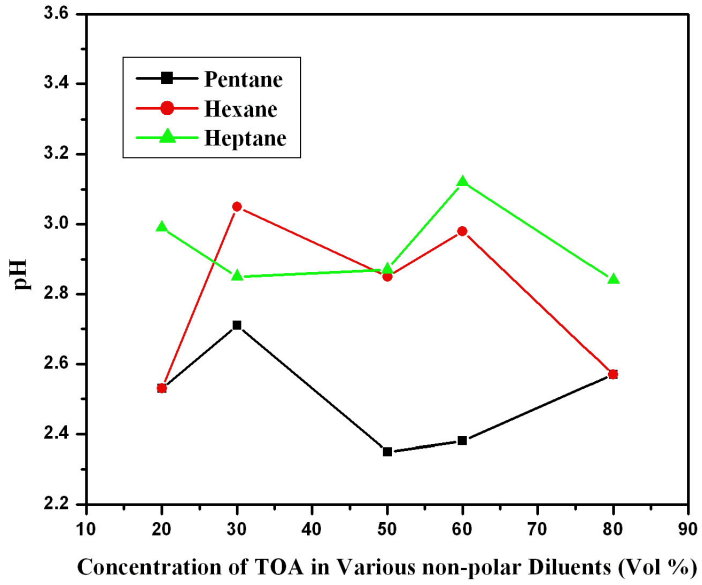


Figure 3-27. The relation between pH and TOA concentration in various non-polar diluents.

The degree of extraction depends on the type of diluent used and the resulting extractant concentration in the solvent phase (Ricker et al. 1980). A polar diluent increases the extracting ability of relatively low-polarity amines by providing additional solvating power that allows higher concentrations of polar-amine complexes to stay in the extractant phase. On the other hand, a non-polar diluent does not affect the extraction process with low-polarity amines (Wen et al. 1998).

The above study indicates that the range of distribution coefficient was 0–6 ($g/L_{organic\ phase}/g/L_{aqueous\ phase}$) in polar diluents whereas it was 0–2 ($g/L_{organic\ phase}/g/L_{aqueous\ phase}$) in non-polar diluents. Thus, polar diluents increase the extraction ability of TOA in the aqueous phase. The extraction ability of TOA varied in different

polar diluents, but the effect of non-polar diluents on the extraction ability was not significant.

Through the study of initial concentration effect on the extraction, the optimal extraction conditions can be summarized as follows:

- The initial concentration should be 150 to 200 g/L.
- The volume ratio should be V_{AQ}: V_{OR} = 1:1.

The study of diluents on the extraction demonstrates that polar diluents help increase the extraction ability of tri-*n*-octylamine (TOA). The distribution coefficient reached the maximum value when the concentration of TOA was 20 vol % in *n*-octanol.

Based on the optimal conditions obtained from the extraction of carboxylic acids, the extraction of carboxylic acids from ammonium carboxylate was performed subsequently to determine the effect of ammonia release on extraction.

About 200 g/L ammonium acetate solution was made for the extraction of the carboxylic acid from its salt. The extractant employed was pure tri-*n*-octylamine (TOA). The volume ratios employed were V_{AQ}:V_{OR}=1:1, 1:2, 2:1, 1:4, and 4:1. The mixture of ammonium acetate solution and tri-*n*-octylamine at each desired volume ratio was heated to 60 °C for about 2 hours to release ammonia from the mixture. Boric acid with methyl red indicator was used for the tail gas trap. The color of the tail gas trap solution changed only a little, which can be ignored. Figure 3-28 shows the extraction results for extracting acetic acid from ammonium acetate. The distribution coefficients were small, which means only slight amounts of acetic acid

go the organic phase. Also the volume ratio had little effect on the distribution coefficients.

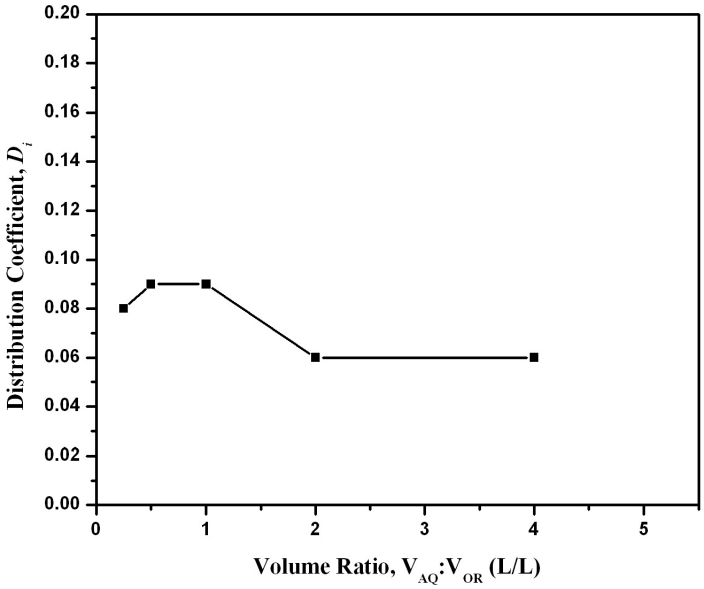


Figure 3-28. The distribution coefficient at volume ratios for extraction of acetic acid from ammonium acetate by TOA.

The study of this part showed that the ammonia was still in solution at 60 °C, which interfered with the extraction of acetic acid from ammonium acetate. The previous concentration study shows that ammonia selectively releases from the solution by dissolving in the condensed fraction. So, the next study (batch distillation) was designed to heat the solution over 100 °C to enhance ammonia release with the condensed fraction. Appendix F shows the detailed data.

Batch Distillation Study

Batch distillation was used to get the preliminary data for further process design. The relation between time and temperature, the closure of materials, and the efficiency of acid recovery were determined in this study. In the same manner as the previous concentration study, the batch distillation study included two parts: a) artificial ammonium acetate solution and b) fermentation broth. Two distillation methods (Methods I and II) were applied to each part.

Method I for the artificial ammonium acetate solution had three steps as follows:

- The first step was to concentrate ammonium acetate aqueous solution from 30–40 g/L to 150–200 g/L. The condensed fraction was collected in the overhead for balance study.
- The second step was to mix the bottom solution together with an equal volume of tri-*n*-octylamine and heat to drive out the ammonia and some water. Heating was stopped when the mixture became milky, which indicated the acid-amine complex formed. The condensed fraction was collected in the overhead for balance study. The bottom solution (the mixture of aqueous solution and tri-*n*-octylamine) was transferred to a quiescent separatory funnel for at least 30 minutes to separate the aqueous and organic phases.
- The third step was to distill the organic phase to decompose the acid-amine complex. The condensed fraction was collected in the overhead for balance study. Samples of the condensed fraction and bottom solution in each step were collected for GC analysis.

Table 3-4 lists the concentration of each sample for the artificial ammonium acetate solution using Method I. The concentration of the condensed fraction in the third step for the artificial ammonium acetate was 514.6 g/L.

Table 3-4. Batch distillation study (Method I) on the artificial ammonium acetate solution (pure TOA)

Sample	Volume (mL)	pH	Concentration of Sample (g/L)
Original Solution	1000	7.41	44.9
Condensed Fraction in 1st step	742	9.84	1.83
Bottom Solution in 1st step	253	5.96	158.5
Condensed Fraction in 2st step	97	10.16	28.4
Bottom solution in 2st step	148	6.3	243.14
Condensed Fraction in 3rd step	2	3.5	514.6

Similar to the artificial ammonium acetate solution, Method I for the fermentation broth had three steps as follows:

- The first step was to concentrate fermentation broth from 30–40 g/L to 150–200 g/L. The condensed fraction was collected in the overhead for balance study.
- The second step was to mix the bottom solution together with an equal volume of tri-*n*-octylamine and heat to drive out the ammonia and some water. Heating was stopped when the mixture became milky, which indicated the acid-amine complex formed. The condensed fraction was collected in the overhead for balance study. The bottom solution (the mixture of aqueous solution and tri-*n*-octylamine) was transferred to a quiescent separatory funnel for at least 30 minutes to separate of aqueous and organic phases.

- The third step was to distill the organic phase to decompose the acid-amine complex. The condensed fraction was collected in the overhead for balance study. Samples of the condensed fraction and bottom solution in each step were collected for GC analysis.

Table 3-5 lists the concentration of each sample for the fermentation broth using Method I. The concentrations of the condensed fraction in the third step for fermentation broth is 484.6 g/L. Using Method I, the concentrations of the condensed fraction in the third step for both the artificial ammonium acetate solution and fermentation broth are about 500 g/L, which is 48% pure acetic acid concentration (1048 g/L). This shows that using Method I for batch distillation cannot get high-purity acid.

Table 3-5. Batch distillation study (Method I) on fermentation broth (pure TOA)

Sample	Volume (mL)	pH	Total Acid Concentration (g/L)
Fermentation Broth	1400	6.67	54.3
Condensed Fraction in the 1st step	920	9.82	3.4
Bottom Solution in the 1st step	473	5.89	147.1
Condensed Fraction in the 2st step	120	10.12	4.6
Bottom solution in the 2st step	337	6.28	181.8
Condensed Fraction in the 3rd step	3	2.1	484.6

Method II for the artificial ammonium acetate solution was to mix the aqueous solution about 200 g/L ammonium acetate and tri-*n*-octylamine in molar ratio (M_{AQ}:M_{OR} = 2:1) and distill in a batch distillation column. Small bubbles started to release in the boiling side and a cloudy condensed fraction began to form when the system reached

100 °C. The bottom solution was transparent and clear. The system was maintained at a relatively stable stage for about 2 hours. Then the temperature of the bottom solution increased slowly to 110 °C (about 0.03 °C/min). The cloudy condensed fraction kept coming out and the bottom solution became milky. Then, the boiling side became violent with large bubbles. The system temperature increased at a rate of 1°C/min at this stage. After the system temperature reached 130 °C, the bottom solution turned to a clear pale yellow color. When the temperature of the bottom solution reached 160 °C, the overhead fraction became clear and the temperature increased at a rate of 0.3 °C/min to 180 °C. After that, a slight amount of condensed fraction was formed and the temperature increased quickly. Heating was then stopped.

Figure 3-29 shows there are two flat regions: the first temperature range is around 100−106 °C indicating that water exited the system together with ammonia, as well as the acid-amine complex was formed. Later, most water left the boiling side, and the system temperature increased at a relative high rate to the second flat region; the second temperature range is about 160−180 °C. At this stage the acid-amine complex decomposed to acid and amine, which kept the system temperature relatively stable. The acid was collected in the overhead. The boiling point of tri-*n*-octylamine is 365−367 °C; therefore, it stays at the boiling flask.

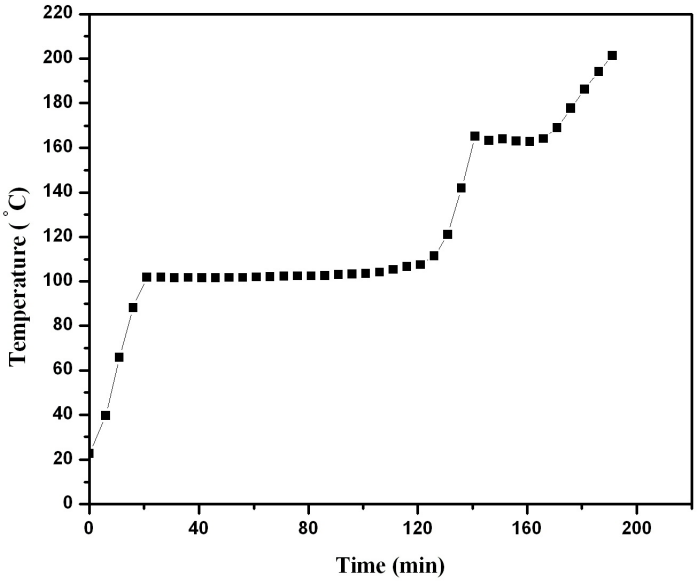
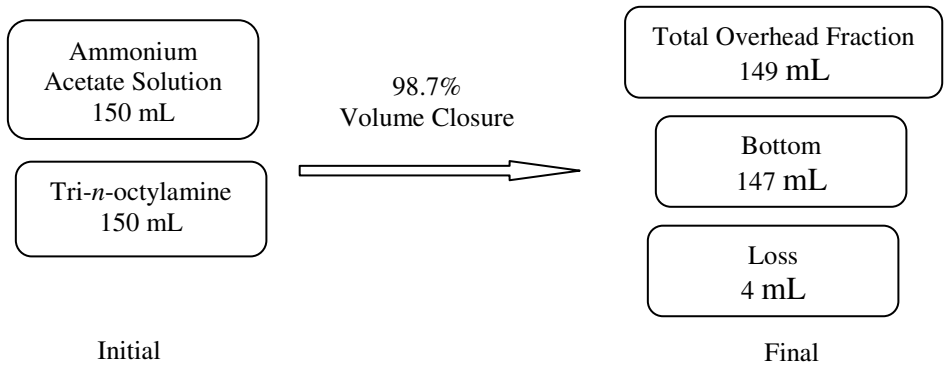


Figure 3-29. Temperature of boiling solution and time for the artificial ammonium acetate solution using pure TOA as extractant (Method II).

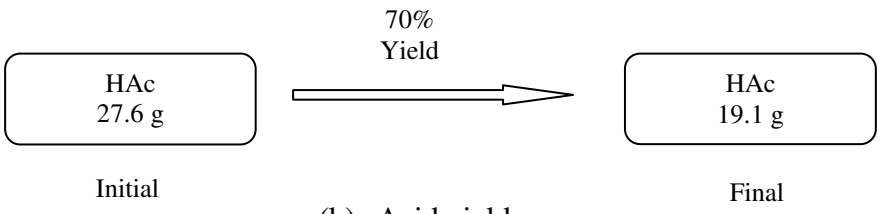
Table 3-6 lists the concentration of overhead fractions for the artificial ammonium acetate solution using Method II. As shown at this table, the last fraction stopped at 167 °C. Its acid concentration was 818.9 g/L. Figure 3-30 shows the closure study of the artificial ammonium acetate solution with pure TOA as extractant. The volume closure was 98.7% and the acid yield was 70%. The volume closure was satisfied but the acid yield was not. The reason for the low acid yield might be the (2:1) and (3:1) acid-amine complexes did not decompose thoroughly. The acid stayed in the organic phase and made the acid yield discrepancy.

Table 3-6. Batch distillation study (Method II) on the artificial ammonium acetate solution (pure TOA)

Temperature (°C)	Volume of Condensed Fraction (mL)	Acetic acid Concentration in the Condensed Fraction (g/L)
129.6	112	16.0
141	17	54.97
167	20	818.9



(a) Volume closure.



(b) Acid yield.

Figure 3-30. Closure study of the artificial ammonium acetate solution using pure TOA as extractant (Method II).

The extraction study demonstrated that the extraction ability of TOA increased using *n*-octanol as diluent. When the TOA concentration in octanol was 20% (vol %), the distribution coefficient reached the maximum value. Therefore, an aqueous solution of about 200 g/L ammonium acetate and tri-*n*-octylamine/octanol was distilled in a batch distillation column. The TOA concentration in octanol used was 20% (vol %). The phenomena were similar to the procedure with pure TOA as extractant.

Figure 3-31 shows the temperature with time. There are two flat regions. The temperature ranges were identical to the procedure with pure TOA as extractant. One was around 100−106 °C and the other was 160−180 °C. Although the boiling point of octanol is 195 °C, the organic phase was observed in the overhead condensed fractions (see Table 3-7).

Table 3-7 illustrates the concentration of overhead fractions. The last fraction stopped at 174 °C when the acetic acid concentration in aqueous phase reached 843.8 g/L. There was 7–10 % (vol %) organic phase found in each overhead fraction.

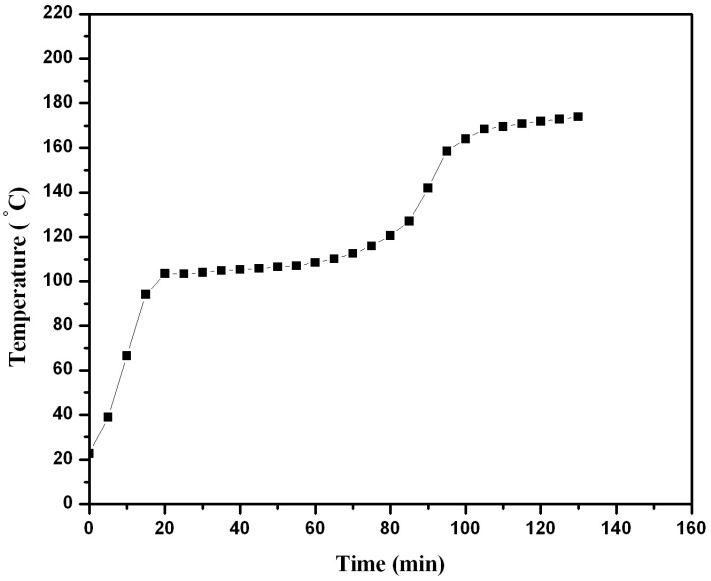


Figure 3-31. The relation between time and temperature of boiling solution for the artificial ammonium acetate solution using TOA/*n*-octanol (20%/80% by volume) as extractant (Method II).

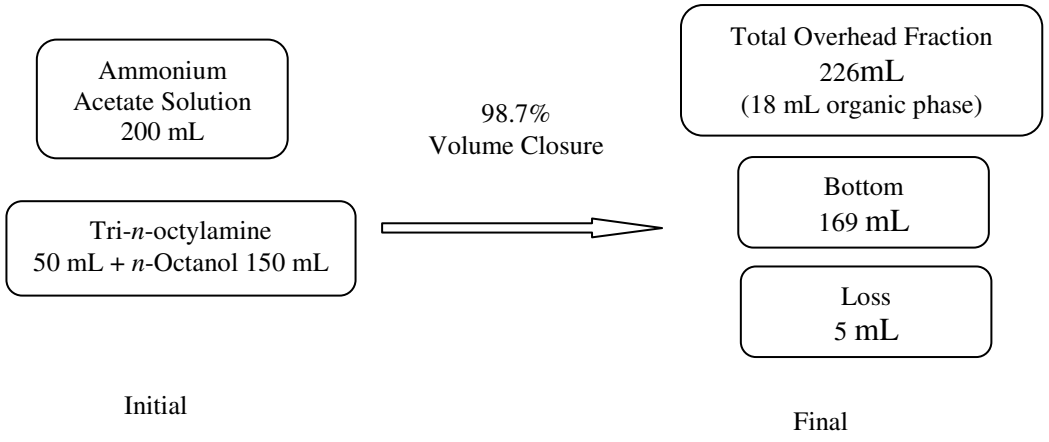
Table 3-7. Batch distillation study (Method II) for the artificial ammonium acetate solution (TOA/octanol, 20%/80% by volume)

Temperature (°C)	Volume of Condensed Fraction (mL)	Acetic acid Concentration in the Condensed Fraction (g/L)
141	208 (16 mL organic phase)	20.37
174	18 (2 mL organic phase)	843.8

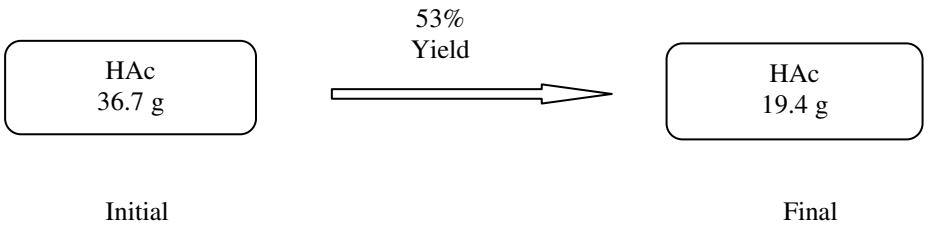
Figure 3-32 shows the closure of artificial ammonium acetate solution with TOA/octanol as extractant. The volume closure was 98.7% and the acid yield was 53%.

Compared to the procedure using pure TOA as the extractant, the procedure using octanol as the diluent got the same concentration of the final fraction. The

concentration of final fraction for both procedures was about 800 g/L, which is lower than pure acetic acid (1048 g/L, 99.5% pure). To get the same final concentration, using octanol as diluent reduced the amount of TOA by four times. However, *n*-octanol comes out with the overhead condensed fractions and makes an additional separation necessary.



(a) Volume closure



(b) Acid yield

Figure 3-32. Closure study of the artificial ammonium acetate solution using TOA/*n*-octanol (20%/80% by volume) as extractant (Method II).

In the same manner as the previous artificial ammonium acetate solution study (Method II), the fermentation broth and tri-*n*-octylamine in molar ratio (M_{AQ}: M_{OR}= 2:1) was distilled in a batch distillation column. The phenomena were similar to the artificial

ammonium acetate solution using pure TOA as extractant. Extra attention was paid to the power input. Because the fermentation broth made more foam than artificial solution, the power input was controlled 30% lower than the artificial solution.

Figure 3-33 shows the temperature with time for fermentation broth. The figure has two flat regions. The temperature ranges were same as the artificial ammonium acetate solution : one was around 100−106 °C and the other was about 160−180 °C.

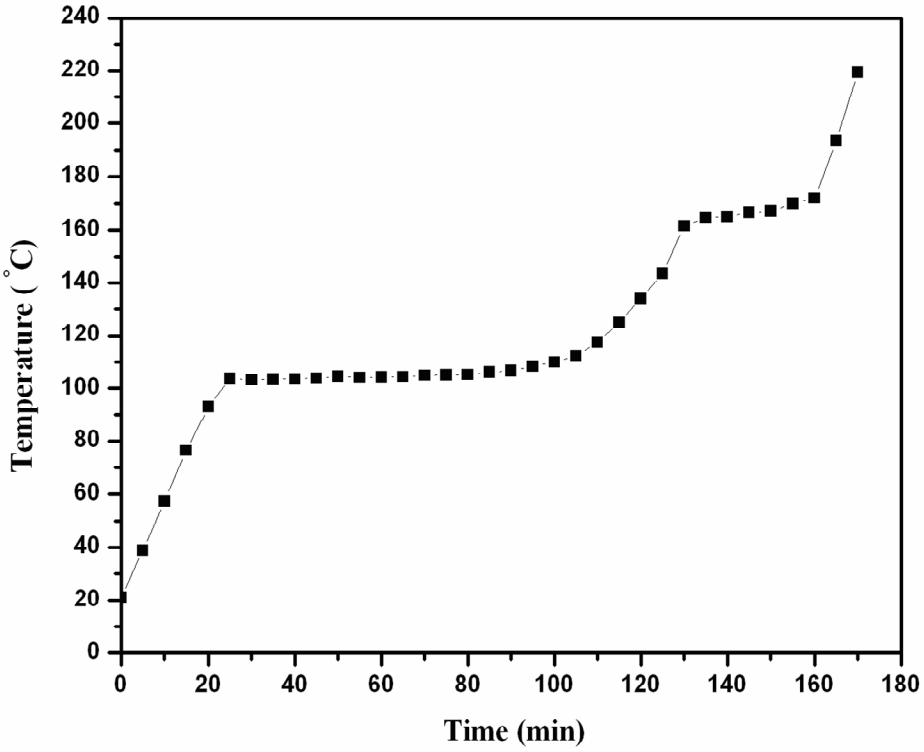


Figure 3-33. The relation between time and temperature of boiling solution for the fermentation broth using pure TOA as extractant (Method II).

Table 3-8 lists the concentration of the overhead fractions. As shown in the table, the last condensed fraction stopped at 219.4 °C and its acid concentration was 795.1 g/L.

Figure 3-34 shows the closure of the fermentation broth with TOA as extractant. The volume closure was 97 % and the acid yield was 89 %.

Table 3-8. Batch distillation study (Method II) for fermentation broth using pure TOA as extractant

Temperature (°C)	Volume of Overhead Fraction (mL)	Total Acid Concentration of Overhead Fraction (g/L)
143.6	92	9.94
219.4	26	795.1

The batch distillation study is very helpful to understand the reaction and get primary data for further process design. This study shows that there are two reaction stages: (1) water leaves the system at 100−106 °C and (2) the acid-amine complex decomposes at 160−180 °C.

The concentration of the final condensed fraction using Method II is around 800 g/L, which is 78% pure acetic acid (1048 g/L). This proves that using batch distillation cannot get high-purity acid; therefore, it is necessary to develop a continuous multi-stage reactive distillation system to get high-purity acid.

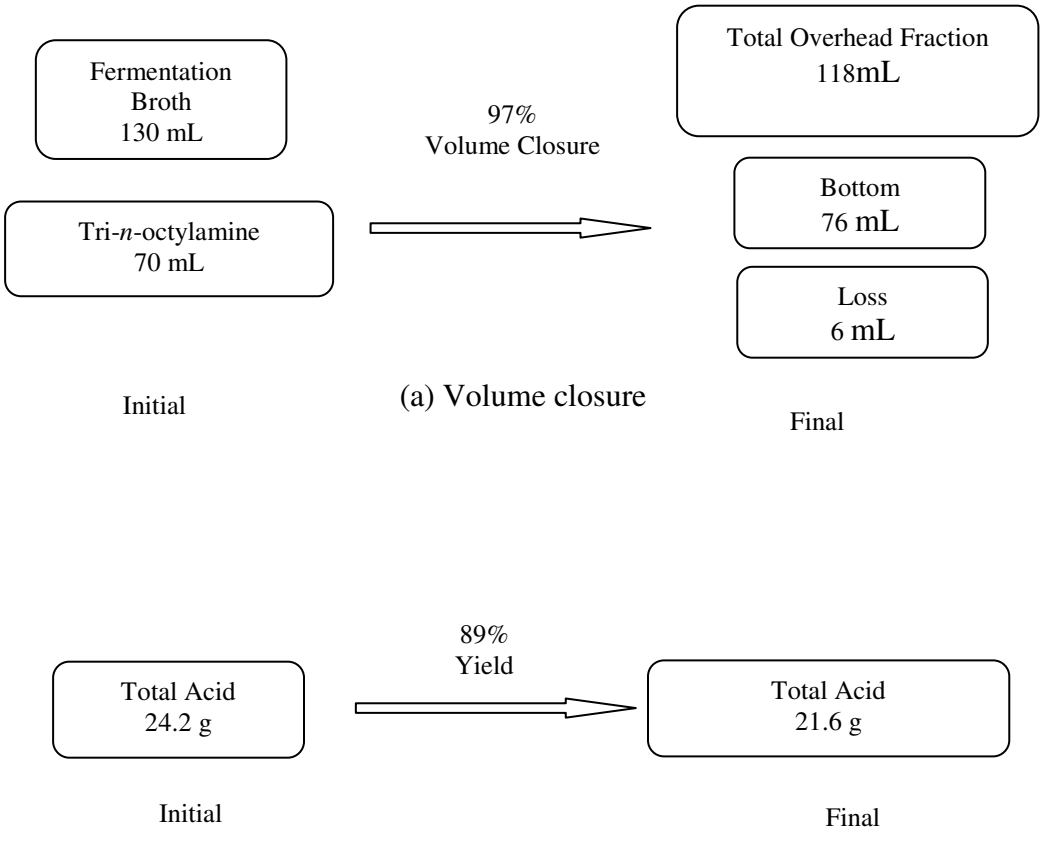


Figure 3-34. Closure study of fermentation broth with TOA as extractant (Method II).

The acid yield for the fermentation broth using Method II is 89%, and the acid yield for the artificial ammonium acetate solution is 70% using pure TOA as extractant. This discrepancy is because the acid yield of fermentation broth is the total acid amount including other carboxylic acid such as propionic, butyric, etc. The longer chain carboxylic acids are more hydrophobic and can be extracted with tri-*n*-octylamine. The

reason for relative low acid yield might be the (2:1) and (3:1) acid-amine complex cannot decompose thoroughly at the batch distillation condition. So the acid stays in the organic phase. By employing a continuous multi-stage distillation method, the efficiency of extraction will be enforced by the continuous countercurrent flow of aqueous and organic phases. And the reflux of condensed fractions will reduce the loss of acid and improve the acid yield.

CHAPTER IV

CONCLUSIONS

Compared to the artificial ammonium acetate solution, the fermentation broth is more sensitive to the power input rate. The Variac power input should be controlled lower than 60% to avoid violent foaming produced. To control the total acetate loss to less than 6%, the fermentation broth can be condensed from 30–40 g/L to 150–200 g/L (about 70% of its original volume can be removed). There is 3 °C boiling point elevation while the solution is condensed from 30–40 g/L to 150–200 g/L, as well as around 60% ammonia is released from the boiling side. The volume and mass balances are satisfied. Meanwhile, all the overhead fractions are shown alkaline.

Through the study of initial concentration effect on the extraction of carboxylic acids from aqueous solution, the recommended extraction conditions can be summarized as follows:

- The initial concentration: 150–200 g/L.
- The volume ratio: V_{AQ}:V_{OR} = 1:1.

The study of diluents on the extraction indicates that polar diluents help increase the extraction ability of tri-*n*-octylamine (TOA). The distribution coefficient reaches the maximum value when the concentration of TOA is 20% (vol %) in *n*-octanol.

Batch distillation study is a useful tool to understand the reaction mechanism and get preliminary data for further process design. The batch distillation study shows that

there are two reaction stages: (1) water leaves the system at 100−106 °C and (2) the acid-amine complex decomposes at 160−180 °C.

The concentration of acid collected in the overhead from the decomposition of the acid-amine complex was about 800 g/L, which is 78% pure acetic acid (1048 g/L). Using pure TOA as extractant, the acid yield closure for fermentation broth and the artificial ammonium acetate solution are 89% and 70% respectively. The reason for the high closure with fermentation broth is that it contains high-molecular-weight acids (e.g., propionic, butyric) that are hydrophobic and extract better into the tri-*n*-octylamine phase.

The reason for the relative low acid yield for both fermentation broth and artificial ammonium acetate solution might be the (2:1) and (3:1) acid-amine complex cannot decompose thoroughly at the batch distillation condition, so the acid stays in the organic phase.

CHAPTER V

RECOMMENDATIONS FOR FUTURE WORK

The recommendations for future work are as follows:

1. To better evaluate the process, build a continuous multi-stage distillation system based on the primary data from batch distillation. Attention should be paid to the distillation column and the reflux ratio.
2. Use *n*-octanol as diluent in the continuous distillation because *n*-octanol increases the extraction ability and reduce the amount of TOA by four times. A decanter can be used to separate it from the overhead fraction.
3. Because the fermentation broth has multiple acid components, conduct research on the competition of carboxylic acids during the extraction.
4. The laboratory study presented here is only a primary step for developing a process. In the future, energy efficiency should be improved for industry by using heat pump technology.

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APPENDIX A

PROCEDURE FOR CONCENTRATION OF FERMENTATION BROTH

First, this procedure was performed using ammonium acetate as the model salt. Later, fermentation broth was used instead.

1. Prepare the ammonium acetate solution by adding reagent-grade ammonium acetate into deionized water in a volumetric flask. The concentration is determined by GC analysis.
2. Centrifuge the fermentation broth for about 20 minutes at 4,000 rpm.
3. Decant the top centrifuge liquid and save for GC analysis. The solids at the bottom of the centrifuge bottle were thrown away.
4. Boil the solution in Step 1 or 3 by setting the Variac at 100. Monitor the temperature at all times. Change the Variac to 70 after the solution boiled. Condense the resulting vapor and collect the fractions of this condensed vapor. Take the volume and a sample of each fraction.
5. The time consumed in the concentration step varies depending on the total amount of the solution to be concentrated. On average it will take about 4−6 hours for 1 liter solution.
6. Record the volume of each fraction and bottom solution for volume balance and mass balance.

7. Perform GC analysis on the samples to find the acid concentration and calculate the amount of acids lost during evaporation.
8. From mass balance, determine the amount of acid present in the boiling side at any given temperature.

APPENDIX B

PROCEDURES FOR REACTIVE EXTRACTION

1. Make the monocarboxylic acids (C_2–C_5) solution by adding reagent-grade monocarboxylic acids into deionized water at various concentration in a volumetric flask. Analyze the sample of each solution through GC.
2. Make the extractants by adding tri-*n*-octylamine (purity > 99 mass%, TCI) into various diluents at certain volume ratios.
3. Mix the extractant and acid solution in a 100–mL flask at desired temperatures.
4. Stir the flask containing the mixture at 500 rpm about 2 hours.
5. Ensure the phase separation by transferring to a quiescent separatory funnel and leave for 30 min.
6. Remove the upper layer (extractant phase), and take samples of the aqueous phase from the bottom layer for pH and GC analysis.

APPENDIX C

BATCH DISTILLATION PROCEDURES

This batch procedure was applied to determine the basic temperatures reached in the distillation column. This procedure was to understand the reactive distillation and determine the required thermal decomposition temperature.

1. Mix the ammonium acetate solution or fermentation broth with extractant (tri-*n*-octylamine with or without diluents) at desired ratios in a round-bottom flask.
2. Place the round-bottom flask with a stir bar on a 1200-W heating mantle and directly connect to a column packed with Rasching ring, then a cold water condenser. Monitor the temperature of the bottom solution at all times and protect the system with nitrogen.
3. Connect the heating mantle to a Variac set at a desired power input rate.
4. Record the volume of condensed fractions from the condenser and take samples for GC analysis.

APPENDIX D

DETERMINATION OF AMMONIA LOSS

a. Determination of Ammonia in Boric Acid Solution

To determine the ammonia collected in the tail gas trapped with boric acid solution, a titration is performed. The procedures follow:

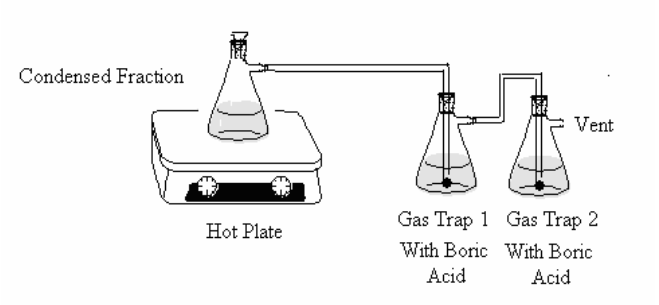
1. Take the Erlenmeyer flask with boric acid solution and add methyl red indicator, 2 mL for each liter of solution (Wagner 1940).
2. Make a reference solution, which will help identify the color end points.
3. Pour a standard H_2SO_4 solution into a burette. Ensure that there is no air-space at the tip of the burette. This can be seen as a bubble in between the tap and the end tip of the burette. To remedy this, open the tap and allow a fast jet of solution to flow through, shake the burette vigorously if necessary.
4. Read and record the starting volume of liquid in the burette.
5. Begin the titration. Slowly open the burette valve.
6. The indicator should change color as the H_2SO_4 is added, then quickly return to its original color. Shake the receiving flask as H_2SO_4 is added.
7. As the end-point is approached, the indicator takes longer to turn back to its starting color. Add H_2SO_4 slowly at this point (one drop at a time), making sure that the receiving flask is shaken well.

8. When the indicator remains permanently at its end color, the reaction has reached its end point. Record the volume of H_2SO_4 remaining, as shown on the scale of the burette.

b. Determination of Ammonia Dissolved in Water

To determine the ammonia dissolved in the fractions (H_2O mainly). The following procedures were performed:

1. Transfer the collected water fraction into an Erlenmeyer flask quickly and close immediately with a stopper equipped with a septum and a hose, which is connected to a diffuser stone to allow the ammonia to be collected by boric acid solution in the second and third Erlenmeyer flasks as the following sketch.



2. Make the boric acid solution where the ammonia will be collected.
3. Add caustic solution (NaOH) to the Erlenmeyer flask that contains the water with ammonia by injecting it through the septum in the stopper.
4. Heat slowly on a heating plate until the temperature reaches about 40 to 50 ºC.
5. Ammonia vapors will begin to rise through the conduit and be collected in the boric acid solution.
6. Titrate with sulfuric acid in the same way as explained in Part a.

APPENDIX E

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 °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. The sample in the vial is ready to be analyzed. If the sample will not be analyzed immediately, it can be stored in the freezer. If frozen, care should be taken to thaw and vortex the sample before the GC analysis.

GC OPERATION

1. Before starting the GC, check the gas supply cylinders (compressed hydrogen, zero-grade helium, and compressed zero-grade air from Praxair, Bryan, TX) to insure at

least 100 psig pressure in each. If there is not enough gas, switch cylinders and place an order for new ones.

2. Establish gas flow by setting the regulators in 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 = 50ºC

   b. Ramp = 20ºC/min

   c. Inlet temperature = 230ºC

   d. Detector temperature = 250ºC

   e. H_2 flow = 40 mL/min

   f. He flow = 180 mL/min

   g. Air flow = 400 mL/min
7. Start the GC on the computer by selecting the method with the setting conditions above mentioned. Set and load the sequence of samples to run. Once the conditions

are reached and the green start signal is on the screen, start the run sequence. Details about operation, setting sequence and calibration are in Agilent 6890 instrument manual.

8. Periodically check back 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, turn the GC on standby and close air and hydrogen cylinder valves.

APPENDIX F

DATA AND PLOTS

Table F-1. Concentration Study of Artificial Ammonium Acetate Solution

No. of Fraction	Temp. (°C)	Time (min)	C_i^f(g/L)	V_i^f(L)	pH	A_{loss}(g/L)	C_i(g/L)
1	101.1	132	2.55	0.45	10.68	2.55	175.10
2	103.9	178	9.56	0.162	9.88	3.68	224.61
3	106.4	192	16.24	0.046	10.19	5.23	292.10
4	109.3	201	22.84	0.029	10.34	5.97	361.21
5	112.3	207	33.70	0.019	10.42	6.72	427.40
6	118.4	214	46.95	0.023	10.69	7.99	550.65
7	135.0	220	85.61	0.018	10.76	9.86	708.59
8	149.5	227	337.89	0.026	10.62	20.89	1065.6

A_{loss} = Loss of acetate per total volume evaporated (g/L)

C_i^f = Concentration in collected fraction *i* (g/L)

V_i^f = Volume of collected fraction *i* (L)

C_i = Concentration in boiling solution after collecting fraction *i* (g/L)

Balance Study of Artificial Solution:

Starting volume of boiling solution as prepared:

$$V_0 = 0.8 \text{ L}$$

Ending volume of boiling solution:

$$V_{end} = 0.022 \text{ L}$$

Starting concentration of boiling solution by GC:

$$C_0 = 56.15 \text{ g/L}$$

Ending concentration of boiling solution by GC:

$$C_{end}^{GC} = 1096.0 \text{ g/L}$$

Ending concentration of boiling solution by calculation:

$$C_{end}^{cal} = 1065.6 \text{ g/L}$$

$$\text{Total fraction volume } = \sum_{i=1}^{8} V_i^f = 0.773 \text{ L}$$

$$\text{Volume closure} = \frac{\sum_{i=1}^{8} V_i^f + V_{end}}{V_0} = \frac{0.773 \text{ L} + 0.022 \text{ L}}{0.8 \text{ L}} = 99.4\%$$

$$\text{Total ammonium acetate loss (\%)} = \frac{A_{loss} \times \sum_{i=1}^{8} V_i^f}{C_0 \times V_0} = \frac{20.892 \text{ g/L} \times 0.773 \text{ L}}{56.15 \text{ g/L} \times 0.8 \text{ L}} \approx 36\%$$

Table F-2. Concentration Study of Fermentation Broth

No. of Fraction	Temp. (°C)	Time (min)	C_i^f(g/L)	V_i^f(L)	pH	A_{loss}(g/L)	C_i(g/L)
C2							
1	100.4	160	0.67	0.244	10.72	0.67	50.62
2	100.7	200	0.88	0.104	9.83	0.73	62.07
3	101.0	225	1.39	0.078	10.06	0.85	74.72
4	101.3	250	1.76	0.07	10.3	0.98	91.52
5	101.9	275	2.78	0.092	10.47	1.26	130.04
C4							
1	100.4	160	0	0.244	10.72	0	7.54
2	100.7	200	0.96	0.104	9.83	0.29	9.05
3	101.0	225	1.53	0.078	10.06	0.52	10.62
4	101.3	250	1.86	0.07	10.3	0.70	12.63
5	101.9	275	2.68	0.092	10.47	1.01	16.95
IC5							
1	100.4	160	0	0.244	10.72	0	1.50
2	100.7	200	0.50	0.104	9.83	0.15	1.74
3	101.0	225	0.74	0.078	10.06	0.26	1.94
4	101.3	250	0.85	0.07	10.3	0.34	2.20
5	101.9	275	1.11	0.092	10.47	0.46	2.67

A_{loss} = Loss of acetate per total volume evaporated (g/L)

C_i^f = Concentration in collected fraction *i* (g/L)

V_i^f = Volume of collected fraction *i* (L)

C_i = Concentration in boiling solution after collecting fraction *i* (g/L)

Balance Study of Fermentation Broth (Total Acid):

Starting volume of boiling solution as prepared:

$$V_0 = 0.82 \text{ L}$$

Ending volume of boiling solution:

$$V_{end} = 0.219 \text{ L}$$

Starting concentration of boiling solution by GC:

$$C_0 = 36.59 \text{ g/L}$$

Ending concentration of boiling solution by GC:

$$C_{end}^{GC} = 137.7 \text{ g/L}$$

Ending concentration of boiling solution by calculation:

$$C_{end}^{cal} = 149.7 \text{ g/L}$$

$$\text{Total fraction volume (L)} = \sum_{i=1}^{5} V_i^f = 0.588 \text{ L}$$

$$\text{Volume closure (\%)} = \frac{\sum_{i=1}^{5} V_i^f + V_{end}}{V_0} = \frac{0.588 \text{ L} + 0.219 \text{ L}}{0.82 \text{ L}} = 98.4\%$$

$$\text{Total ammonium acetate loss (\%)} = \frac{A_{loss} \times \sum_{i=1}^{5} V_i^f}{C_0 \times V_0} = \frac{2.738 \text{ g/L} \times 0.588 \text{ L}}{36.59 \text{ g/L} \times 0.82 \text{ L}} \approx 5.37\%$$

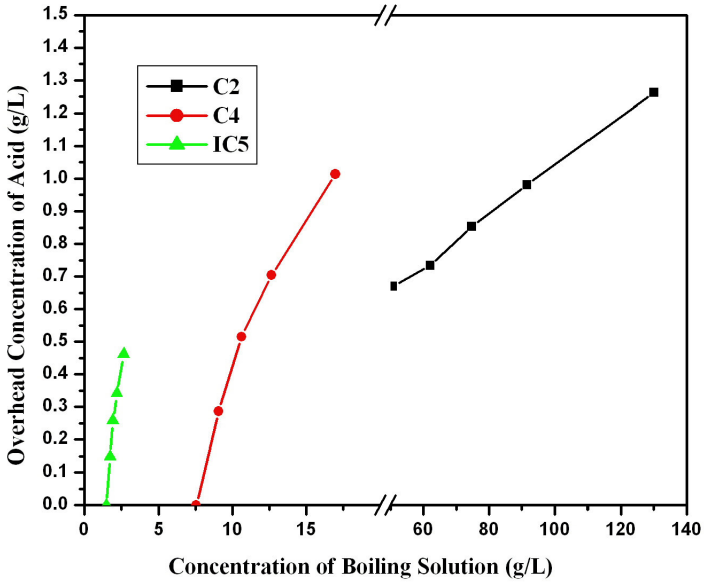


Figure F-1. Overhead concentration of acid and concentration of boiling solution.

Table F-3. The Effect of Initiation Concentration on Extraction

Solution	Extractant	Volume Ratio AQ:OR	Mole ratio AQ:OR	Actual Amount AQ:OR	Equil. pH in AQ. Phase	Total conc. of acid (g/L)		D_i
						AQ. conc.	OR conc.	
Acetic acid (0.05 mol/L) pH= 3.38 C_0=34.03 g/L	Pure TOA	5:1	1:5	50 mL+ 10 mL	3.45	29.01	25.1	0.865
		2:1	1:2	20 mL+10 mL	3.49	25.19	17.68	0.702
		1:1	1:1	10 mL+10 mL	3.68	22.73	11.3	0.497
		1:2	2:1	10 mL+20 mL	3.88	17.85	08.09	0.453
Acetic acid (0.1 mol/L) pH=3.29 C_0=62.54 g/L	Pure TOA	1:2	1:5	10 mL+ 20 mL	3.71	28.55	17.0	0.595
		1:1	1:2	10 mL+10 mL	3.60	35.36	27.18	0.769
		2:1	1:1	20 mL+10 mL	3.55	40.43	44.22	1.094
		5:1	2:1	50 mL+10 mL	3.50	40.91	108.15	2.644
Acetic acid (0.17 mol/L) pH=3.22 C_0=120.83 g/L	Pure TOA	1:4	1:5	10 mL+ 40 mL	3.63	26.35	23.62	0.896
		1:1.5	1:2	10 mL+15 mL	3.54	38.58	54.83	1.421
		1:1	1:1	10 mL+10 mL	3.51	39.66	81.17	2.047
		3:1	2:1	30 mL+10 mL	3.44	43.31	232.56	5.370
Acetic acid (0.25 mol/L) pH=3.15 C_0=166.95 g/L	Pure TOA	1:5	1:5	10 mL+ 50 mL	3.68	33.64	26.66	0.793
		1:2	1:2	20 mL+20 mL	3.52	42.67	62.14	1.456
		1:1	1:1	10 mL+10 mL	3.48	43.75	123.2	2.816
		2:1	2:1	20 mL+10 mL	3.53	42.21	249.48	5.910
Acetic acid (0.33 mol/L) pH=3.06 C_0=230.69 g/L	Pure TOA	1:7	1:5	10 mL+ 70 mL	3.80	35.78	27.84	0.778
		1:3	1:2	10 mL+30 mL	3.64	38.65	64.01	1.656
		1:1.5	1:1	10 mL+15 mL	3.58	35.67	130.01	3.645
		1:1	2:1	10 mL+10 mL	3.54	43.69	187.	4.280

2 hours extraction at room temperature, 25°C, 30 minutes quiescent set in separatory funnel

Table F-4. The Effect of Polar Diluents on Extraction

Extractant (TOA/diluent, vol ratio)	AQ:TOA Mole ratio	AQ:OR Actual Volume Amount	Equil. pH in AQ. Phase	Total conc. of acid (g/L)		D_i
				AQ. conc.	OR conc.	
Diluent: *n*-Butanol						
4:1 (40 mL:10 mL)	2:1	10 mL + 20 mL	3.67	23.55	207.14	4.398
2:1 (20 mL:10 mL)		10 mL + 23 mL	3.79	24.43	216.26	3.671
1:1 (20 mL:20 mL)		10 mL + 15 mL	3.55	41.60	189.09	3.030
1:2 (20 mL:40 mL)		10 mL + 45 mL	4.09	50.72	179.97	0.789
1:4 (20 mL:80 mL)		10 mL + 75 mL	4.33	60.47	150.22	0.375
Diluent: *n*-Heptanol						
4:1 (40 mL:10 mL)	2:1	10 mL + 20 mL	3.68	24.02	206.67	4.302
2:1 (20 mL:10 mL)		10 mL + 23 mL	3.73	17.14	213.55	5.417
1:1 (20 mL:20 mL)		10 mL + 15 mL	3.47	38.20	192.49	3.359
1:2 (20 mL:40 mL)		10 mL + 45 mL	3.86	11.70	218.99	4.159
1:4 (20 mL:80 mL)		10 mL + 75 mL	3.93	6.26	224.43	4.780
Diluent: *n*-Octanol						
4:1 (40 mL:10 mL)	2:1	10 mL + 20 mL	3.73	30.14	200.55	3.327
2:1 (20 mL:10 mL)		10 mL + 23 mL	3.81	22.51	208.18	4.021
1:1 (20 mL:20 mL)		10 mL + 15 mL	3.57	29.20	201.49	4.600
1:2 (20 mL:40 mL)		10 mL + 45 mL	3.79	10.76	219.93	4.542
1:4 (20 mL:80 mL)		10 mL + 75 mL	3.28	5.11	225.58	5.886

2 hours extraction at room temperature, 25°C, 30 minutes quiescent set in separatory funnel

Table F-5. The Effect of Polar Diluents on Extraction

Extractant (TOA/diluent, vol ratio)	AQ:TOA Mole ratio	AQ:OR Actual Volume Amount	Equil. pH in AQ. Phase	Total conc. of acid (g/L)		D_i
				AQ. conc.	OR conc.	
Diluent: Pentane						
4:1 (40 mL:10 mL)	2:1	10 mL + 20 mL	2.57	52.27	73.87	1.41
2:1 (20 mL:10 mL)		10 mL + 23 mL	2.38	56.81	62.26	1.10
1:1 (20 mL:20 mL)		10 mL + 15 mL	2.35	65.60	89.6	1.37
1:2 (20 mL:40 mL)		10 mL + 45 mL	2.71	67.37	29.47	0.44
1:4 (20 mL:80 mL)		10 mL + 75 mL	2.53	79.33	16.09	0.20
Diluent: Hexane						
4:1 (40 mL:10 mL)	2:1	10 mL + 20 mL	2.57	54.35	72.83	1.34
2:1 (20 mL:10 mL)		10 mL + 23 mL	2.98	54.01	63.47	1.18
1:1 (20 mL:20 mL)		10 mL + 15 mL	2.85	74.81	83.46	1.12
1:2 (20 mL:40 mL)		10 mL + 45 mL	3.05	95.13	23.30	0.24
1:4 (20 mL:80 mL)		10 mL + 75 mL	2.53	83.16	15.58	0.19
Diluent: Heptane						
4:1 (40 mL:10 mL)	2:1	10 mL + 20 mL	2.84	44.09	77.96	1.77
2:1 (20 mL:10 mL)		10 mL + 23 mL	3.12	53.33	63.77	1.20
1:1 (20 mL:20 mL)		10 mL + 15 mL	2.87	80.70	79.53	0.99
1:2 (20 mL:40 mL)		10 mL + 45 mL	2.85	74.54	27.88	0.37
1:4 (20 mL:80 mL)		10 mL + 75 mL	2.99	84.81	15.36	0.18

2 hours extraction at room temperature, 25°C, 30 minutes quiescent set in separatory funnel

TableF-6 The effect of volume ratio on extraction of acetic acid from ammonium acetate (60 °C)

Solution	Volume Ratio AQ:OR	Total conc. of acid (g/L)		D_i
		AQ. conc.	OR conc.	
acetic acid C_0= 170.3 g/L	1:1	157.5	12.8	0.08
	2:1	156.7	13.6	0.09
	1:2	156.4	13.9	0.09
	4:1	160.6	9.7	0.06
	1:4	161.0	9.3	0.06

2 hours extraction at 60 °C, 30 min set in quiescent separatory funnel

VITA

Xin Xu was born and raised in Beijing, China. In 1997, she graduated from Jiangsu Polytechnic University in China with a B.S. in material science and engineering. In 1997 she began working as a chemical process engineer for Research Institute of Petroleum and Petrochemical (RIPP), which is a subsidiary institute for China Petrochemical Corporation. While working at RIPP, she got her M.S. degree in chemistry technology from RIPP. In 2006 she began her graduate study in the Department of Chemical Engineering at Texas A&M University. Her contact address after graduation will be Department of Chemical Engineering, 3122 TAMU, College Station, TX 77843-3122.