# REMOVAL Of MIXED ACIDS FROM AQUEOUS SOLUTION

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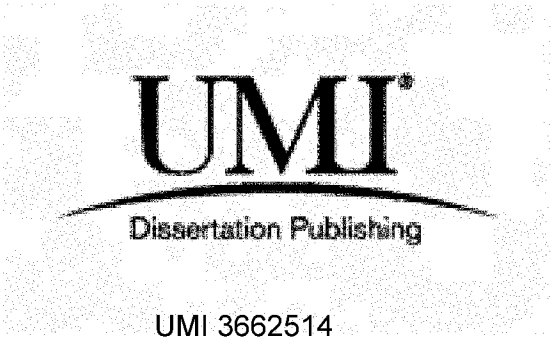





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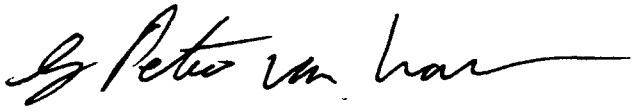

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# REMOVAL OF MIXED ACIDS FROM AQUEOUS SOLUTION

By Aymn Abdulrahman

Thesis Advisor: Dr. G. Peter van Walsum

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
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Carboxylic acids are commonly generated in biorefinery operations such as fermentation or aqueous extraction of hemicellulose feedstocks. In most cases, organic acids are generated as dilute components in aqueous streams. If they can be recovered from solution inexpensively they may find value as pure chemical products or as starting materials for a wide variety of organic products, including biofuels.

Liquid-liquid extraction is a separation method applied to recover mixed carboxylic acids from a fermented wood extract. These acids included: acetic, propionic, butyric, valeric, caproic and heptanoic acids. An organic solution, such as trialkylphosphine oxide (CYANEX 923, a mixture of four trialkylphosphine oxides), was mixed with fermented wood extract to extract these acids. Although the extraction was highly effective, however it was shown that distillation was not able to recover these acids from the extraction solvent.

In this study, after liquid-liquid extraction of the acids from the aqueous phase, the mixed acids are recovered from the organic phase by a back extraction with sodium hydroxide. The mixture is agitated and centrifuged to separate the organic and aqueous phases. Results present the extraction and recovery efficiencies of this method of recovery organic acids.

## ACKNOWLEDGEMENTS

I would like to express my thanks to my advisors, Dr. G. Peter van Walsum for his guidance, time and insight in this research. In addition, many thanks go to the members of my committee, Dr. Adriaan R.P van Heiningen, Dr. M. Clayton Wheeler, Dr. Joseph M. Genco and Dr. Barbara J. W. Cole. I would like to thank Dr. Yang Yu for his help and input in the wood fermentation process. I would also like to thank Diane Smith, the analytical specialist, for the analytical support she provided and Nick Hill, Scientific Technician, for his technical support. In addition, many thanks go to my group researchers, friends and staff members in the Chemical and Biological Engineering Department, and in the Forest Bio-products Research Initiative. Finally, I would like to thank my parents and family, wife and kids, for their emotional support.

## NOMENCLATURE

| Item | Description |
|---|---|
| TOPO | Trioctyl phosphine oxide |
| TOA | Trioctyl amine |
| CYANEX 923 | Four trialkylphosphine oxides |
| C11 | Undecane |
| LLE | Liquid-liquid extraction |
| HAc | Acetic acid |
| Prop. | Propionic acid |
| But. | Butyric acid |
| Val. | Valeric acid |
| Hex. | Hexanoic acid |
| Hept. | Heptanoic Acid |
| $D_C$ | Distribution coefficient |
| $P_C$ | Partition coefficient |
| K | Equilibrium constant |
| HPLC | High Performance Liquid Chromatography |
| GC | Gas Chromatography |
| KFT | Karl Fischer Titration |

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# CHAPTER ONE

# INTRODUCTION

## *1.1 General Introduction*

Fossil fuels, generated from crude oil, coal and natural gas, have been reported to be one of main causes to the global warming, greenhouse gas emissions and associated environmental problems. Moreover, increasing crude oil prices and petrochemical fuel demands, rising foreign oil imports and decreasing domestic fuel supplies lead researchers to search for renewable, reliable and alternative energy sources. The United States of America is one of many countries trying to utilize and apply biomass technology to produce renewable fuels and energy to displace or reduce dependency on crude oil [1-4].

## *1.2 Motivation*

As a renewable, widespread, cheap and sustainable fuel, biomass-derived fuels such as ethanol are attractive because of their potentially plentiful supply and relatively low cost. Biomass conversion can also be applied to produce and recover valuable and important by-product chemicals such as acetic acid [1-4].

In addition, removing carboxylic acids such as acetic acid can enhance biofuels production. For example, at moderate concentrations, acetic acid can be a harmful compound to some organisms used in the fermentation process applied to produce ethanol or other biofuels from biomass. While harmful to fermenting organisms, separated acetic acid could also generate value as a product for the commodity chemical

market. Therefore, it is recommended to remove and recover acetic acid from biomass streams prior to fermenting their sugars to biofuels.

This thesis focuses on an important project at the University of Maine that includes extracting mixed organic acids (from 2 carbon to 7 carbon) from aqueous solutions, such as wood extract or pretreated and fermented wood. This introduction gives a general background on biomass conversion, wood composition, pulping and hydrolysis processes, fermentation of monosaccharides and extraction of organic acids.

### *1.3 Literature Review*

#### *1.3.1 Biomass Conversion*

Biomass has been used as a primary energy source for a long time, all over the world. Approximately 12% of the world's energy supply is derived from biomass. In many developing countries the percentages of energy derived from biomass are reaching up to 40% and 50% [5]. Biomass has been used or converted to produce renewable fuels and energy sources in solid, liquid and gas phases.

Manufacture of bioproducts through biomass conversion is not a new concept. Biomass conversion has been used since the 1800's to produce some products like paint, glue and cloths. However, since the petrochemical revolution began in 1930 to 1940, biomass fuels and bioproducts have been rapidly decreasing in prominence while demands for petrochemicals have increased. Biomass resources can be categorized as sugar feedstock like sugarcane, starchy feedstock like grains, and cellulosic feedstock like fibrous plant material [5].

The United States is one of many countries trying to use biomass conversion processes to produce bio-fuels and energy in an effort to reduce fossil energy

consumption. As an example, it has been proposed by the U.S. Department of Energy [6] that about 512 million dry tons of biomass residues in the United States could be converted to liquid fuels and 10% to 50% of transportation fuels could be replaced by biomass fuels between 2010 and 2050.

In the United States, about 13.1 billion gallons of ethanol were produced in 2012 [49 and 50]. Ethanol from biomass conversion is a renewable bio-based fuel and it can be used as an oxygenate additive to gasoline to decrease tailpipe emissions [5].

### *1.3.2 Lignocellulose Composition*

Wood lignocellulose consists mainly of a mixture of polymerized carbohydrates (cellulose and hemicelluloses), lignin, extractive components and ash. Wood can be generally categorized as hardwood or softwood and the physical and chemical properties between them vary. Hardwood has a higher amount of cellulose and hemicelluloses than softwood, while softwood is higher in lignin content (Table 1.1 [5,7]). Hardwood has about 45% cellulose, 22% lignin, and 35% hemicelluloses, while softwood has about 42% cellulose, 29% lignin, and 28% hemicelluloses [5,7]. Usually extractives range from 1 to as high as 35 % depending on the species.

Table 1.1 Wood compositions of softwood and hardwood [5,7]

| Component | Softwood | Hardwood |
|---|---|---|
| Cellulose | 41-42 % | 45 % |
| Hemicelluloses | 25-30 % | 28-35 % |
| Lignin | 25-30 % | 18-22 % |

Note: This is based on extractive-free wood

Cellulose is a linear polymer of glucose that has β-1,4-glycosidic bonds. Cellulose in wood has a degree of polymerization on the order of 500 to 10000. The majority of cellulose is located in plant cell walls and its chemical properties are determined by the glucosidic linkage and hydroxyl groups. Cellulose forms a skeleton that is surrounded by hemicelluloses and lignin that work as a matrix and encrusting materials. Cellulose has parallel and ordered regions, called crystalline regions, and less ordered regions, called amorphous regions. Hydrolysis proceeds faster in amorphous regions compared with crystalline regions [3].

Hemicelluloses are linear and Y branched polymers that are shorter than cellulose with a degree of polymerization of 50-200 units. They consist of three hexoses (D-glucose, D-galactose, and D-mannose) and two pentoses (D-xylose and L-arabinose). Hemicelluloses work as a linkage between cellulose and lignin [3].

There are two common types of hemicelluloses in wood: xylans and galactoglucomannans, (Figures 1.1 and 1.2). These two vary in terms of compositions and properties from one species to another, (Table 1.2 [7]).

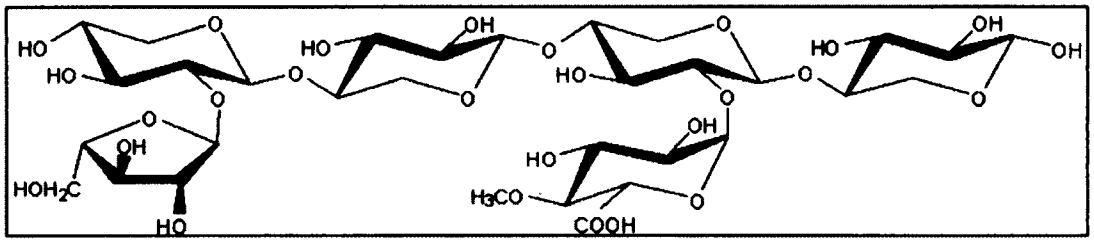



Figure 1.1 Structural representation of softwood xylan. Constituents: β-D-xylopyranose (backbone), α-L-arabinofuranose (bottom left), 4-O-methyl-α-D glucopyranosyluronic acid (bottom right) [7]

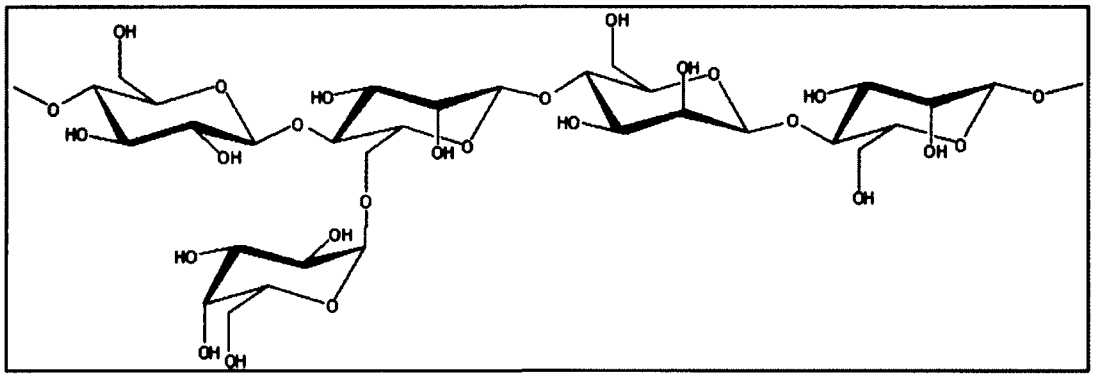


Figure 1.2 Structural representation of softwood galactoglucomannans. Constituents: β-D glucopyranose (left), β-D-mannopyranose (right three), α-D-galactopyranose (branch) [7]

Table 1.2 Wood hemicelluloses [7]

| **Hemicelluloses** | **Hardwood** % | **Softwood** % |
|---|---|---|
| Xylan | 20-30 | 10-15 |
| Glucomannan | 2-5 | 15-18 |
| Galactoglucomannan | ------- | 5-10 |

A homopolymeric backbone consisting of 1,4-linked β-D-xylopyranose units and side-chains of glucuronic acid or its 4-O-methylether are found in hardwood hemicellulose. Hardwood xylans are highly substituted with acetyl groups (Figure 1.3), containing about 7 per 10 xylose units. On the other hand, a heterogeneous backbone of 1,4-linked β-D-glucopyranose and β-D-mannopyranose is found in hardwood glucomannans [8]. Furthermore, pretreatment under alkaline conditions is useful to get oligomeric forms of xylans, while the peeling reaction will degrade both xylans and glucomannans to mono-sugars [9].

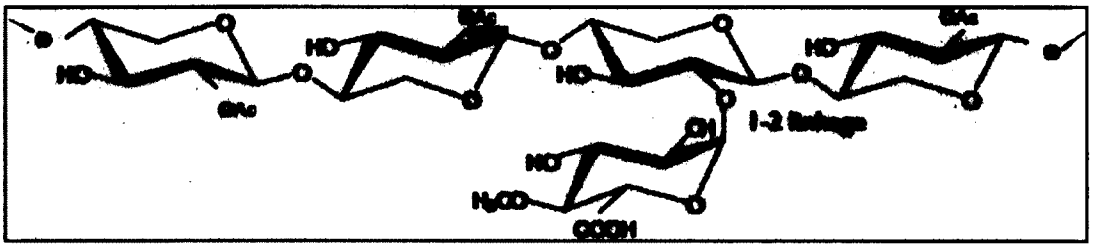


Figure 1.3 Acetyl group attached to hemicellulose xylan [7]

Lignin is a three dimensional macromolecule polymer made up of phenyl-propane joined to each other by ether and carbon-carbon bonds. It has a high molecular weight, about 5000, [3].

### *1.3.3 Kraft Pulping Process*

As an important process for pulp and paper technology, the Kraft pulping process is used widely all over the world and especially in the state of Maine. For more than 100 years, it has been the most economical chemical pulping process. In the Kraft process approximately 50% of the wood weight is dissolved into pulping liquor and is not included in the final fiber product. This solution is primarily composed of hemicelluloses and lignin [9-10].

About half of wood hemicelluloses can be removed in the Kraft pulping process. This is because hemicelluloses have a lower degree of polymerization (50-200) that can be more easily dissolved into the alkaline solution than other lignocellulosic components [9]. Hemicelluloses are usually burned to produce energy during the chemical recovery process [9], but because they have a heating value of about 13.6MJ/kg, which is only about half the heating value of lignin [7], they may find a more optimal use as a feedstock for chemical conversion.

Green liquor, which results from the kraft chemical recovery process is an alkaline aqueous solution that contains $Na_2S$, $Na_2CO_3$, $Na_2SO_4$ and smaller quantities of other alkali metal salts [9]. In a kraft pulping mill, green liquor can be used to extract some of the lignin and hemicellulose prior to pulping the chips. This extraction will preserve the quantity and quality of wood pulp while providing an extract that can then be converted to fuels and chemicals, enabling the development of a kraft-based biorefinery.

### *1.3.4 Hydrolysis*

In the pre-pulping extraction biorefinery process, an initial hydrolysis process is used to break down the complex hemicelluloses in wood chips to soluble short chain oligomers and mono sugars (Figure 1.4 [2, 10-12]). The hydrolysis step is carried out in the extraction vessel (digester), which uses water or dilute green liquor as the solvent (Figure 1.5).

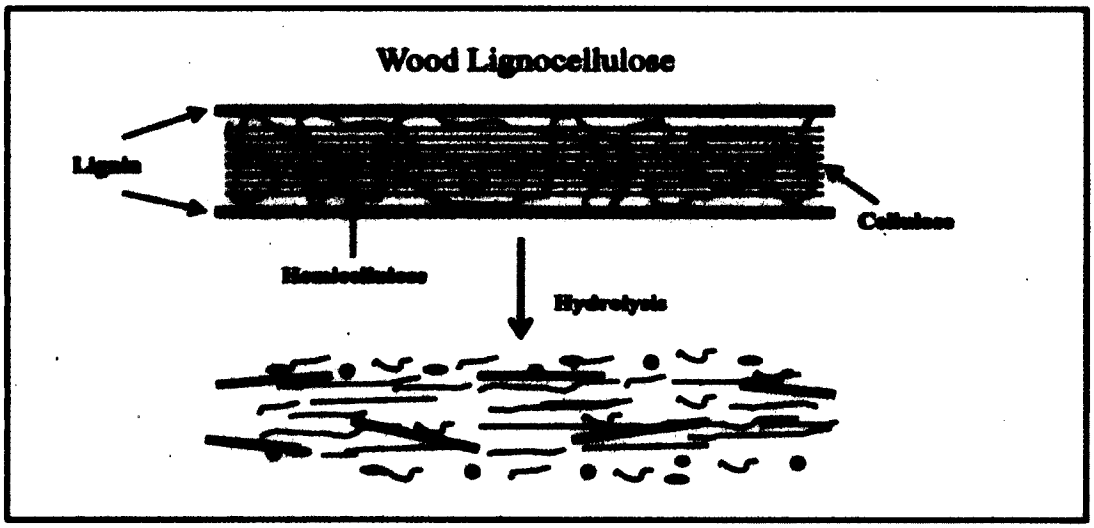
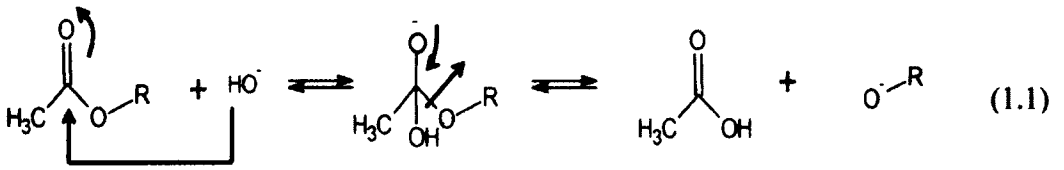



Figure 1.4 Hydrolysis processes of wood compositions to break down the sugar complex to mono sugars

The hydrolysis is carried out by mixing hot water or green liquor, resulting from the Kraft chemical recovery process, with wood chips in the digester (Figure 1.5). Portions of the hemicellulose and lignin are separated from the wood chips by dissolving in the digester liquor, while most of the cellulose and the remainder of the hemicellulose and lignin stay in the wood chips that are transferred for the completion of the Kraft pulping process.

Figure 1.5 University of Maine digester to extract wood components and break down the sugar complex

The chemical reaction that releases the acetyl groups from the sugar during green liquor extraction is called saponification; and functions under alkaline condition as shown below [7].



(1.1)

When the hydroxyl group attaches to the acetyl group, the double bond of the carboxylic acid (between the oxygen and the carbon) will break and form a negative charge on the oxygen. Then when the ion of oxygen connects again with carbon to remake a double bond, the bond between the acetyl group and the sugar will break and release the acetyl group.

A second hydrolysis, or acid hydrolysis, completes the release of mono sugars by using sulfuric acid. The second hydrolysis is carried out on the wood liquor (hemicelluloses extract) using sulfuric acid to lower pH and release more mono sugar. In addition, the remaining acetyl groups still attached to the sugar backbones are also released by the second hydrolysis.

### *1.3.5 Fermentation of Wood Extracts*

#### *1.3.5.1 Fermentation of Monosaccharides*

Certain organisms are used to ferment lignocellulosic biomass to useful chemicals such as carboxylic acids and ethanol. Lignocellulosic sugars including glucose, mannose, galactose, xylose and arabinose can be fermented by specific organisms such as *Pichia stipitis*, *Pachysolen tannophilus*, and *Candida shehatae*. Furthermore, brewer's yeast, or *Saccharomyces cerevisiae* can be used to ferment only glucose and fructose while *Escherichia coli* can be used in a variety of sugars [9].

To improve the fermentation and increase the production of useful chemicals, genetic engineering is used to co-ferment five and six carbon sugars and block metabolic

pathways resulting in more desired products. Bacteria are preferred over yeast for genetic manipulation because of their less complex genome. For ethanol production by fermentation, bacteria such as Escherichia coli, Klebsiella oxytoca and Zymomonas mobilis have been chosen due to their capability for fermenting a variety of sugars. Optimum organisms must be able to ferment all major lignocellulosic sugars and produce only low levels of undesired products [10-12].

### *1.3.5.2 Fermentation Affected by Acetic Acid*

Acetic acid, $CH_3COOH$, is an important biomass product which has a higher selling price than ethanol (approximately double the ethanol price) [8]. It is released when the acetyl groups of hemicellulose, especially hardwood xylans, are saponified (neutral and high pH) or hydrolyzed (secondary hydrolysis by using sulfuric acid). Acetic acid can be used in many industrial applications such as: chemicals, light industry, textiles, pharmaceuticals, printing/dyeing, rubber, pesticides, photographic chemicals, electronics, and food processing (as vinegar) [1,12-16].

Acetic acid is a typical weak acid and is partially ionized in aqueous solution according the following reaction.

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^- \qquad (1.2)$$

The thermodynamic equilibrium constant, $K_a$ can be defined by:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \qquad (1.3)$$

Acetic acid is one of the components that could inhibit fermentation organisms, which affects ethanol production efficiency [14]. Under low pH conditions, acetic acid can penetrate the bacteria cell walls and acidify the cytoplasm. As a result of this, the proton gradient across the cell membrane is disrupted [8]. Therefore, it is recommended to extract and recover acetic acid before reaching the fermentation stage. Liquid- liquid extraction and distillation form a common process to extract acetic acid from aqueous solutions.

### *1.3.6 Conversion of Wood Extracts*

#### *1.3.6.1 Acetic Acid Extraction from Hemicellulose Extract*

The primary processes to produce ethanol from extracted hemicellulose are shown in Figure 1.6. These processes include: hemicellulose extraction, hydrolysis to release sugars using sulfuric acid, filtration to extract lignin, liquid-liquid extraction to recover acetic acid and furfural, gypsum separation and fermentation of C5-C6 sugars to produce ethanol [8].

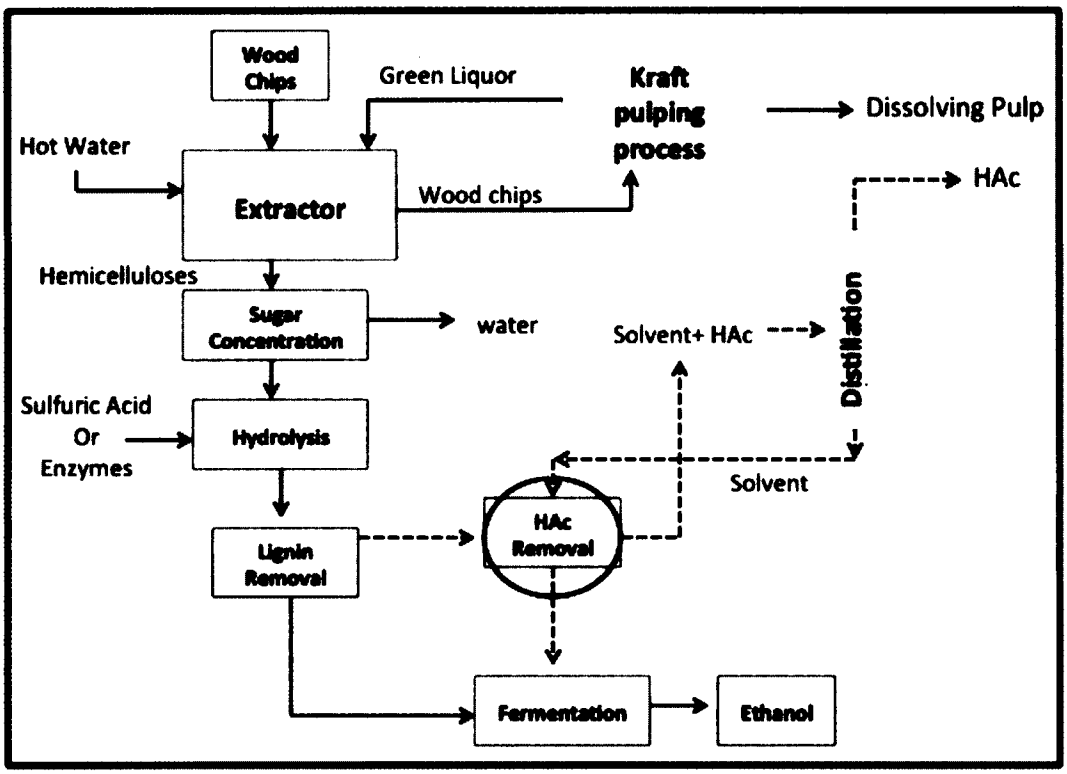



Figure 1.6 Overall pre-pulping extraction and fermentation processes to produce ethanol

Note: ——— is a real process pathway

▪▪▪▪▪ is a proposal process pathway to extract mixed acids

There are three common steps to convert lignocellulose to ethanol: pretreatment; hydrolysis, either by acid or by enzymes; and fermentation. The hydrolysis process is used to break the crystalline structure of the lignocellulosic material (cellulose and hemicelluloses) and release monomer sugars such as glucose and xylose in order to make them more digestible in the fermentation process. Hydrolysis can be accomplished using acids, such as sulfuric acid, or cellulolytic enzymes. These sugars are then fermented using microbes such as *baker's* yeast to produce ethanol [3]. Degradation products from the hydrolysis process, such as furfural, hydroxymethyl furfural (HMF) and acetic acid could be harmful for some fermentation organisms. Xylose is converted to furfural while glucose is converted to HMF, (Figure 1.7 [9]).

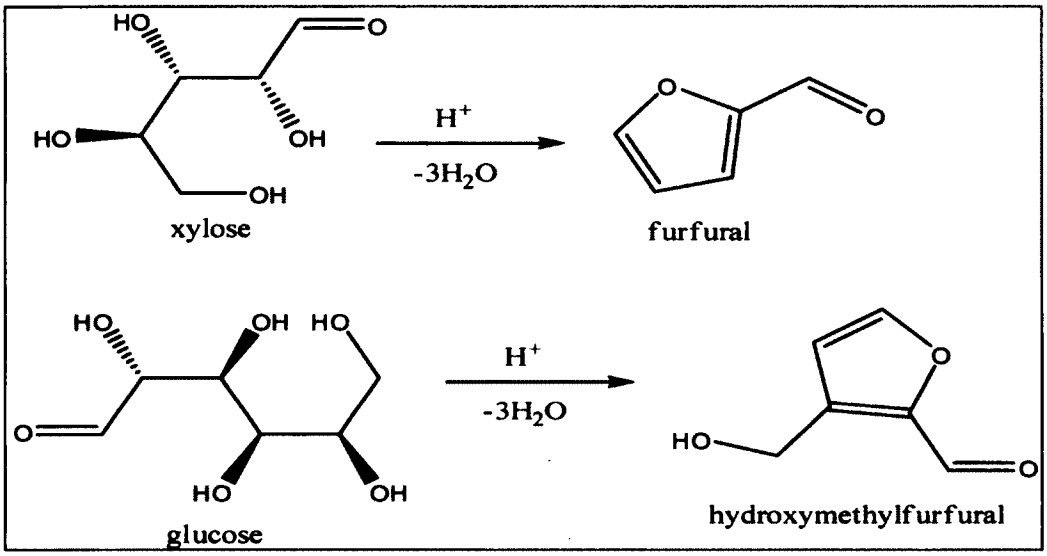



Figure 1.7 Formation of degradation products furfural and hydroxymethyl furfural [7]

### *1.3.6.2 MixAlco Process*

The MixAlco process is a process to produce liquid fuels from biomass with low cost and high efficiency considerations. In development since 1991, the MixAlco process has been shown to effectively convert biomass of many different types to valuable chemicals and fuels such as ethanol [1]. The MixAlco process is started by lime pretreatment to improve the digestibility and then fermentation to produce carboxylic acids. Next calcium carbonate is added to maintain pH at neutral and to make acid salts such as calcium acetate. The acid salts are dried by using an evaporator and converted to mixed alcohols by thermal decomposition to ketones followed by hydrogenation to alcohols.

Some advantages of using the MixAlco process compared to ethanol production from pretreated biomass include [17]:

- Applicable to diverse types of feed stocks.

- Inexpensive materials of construction can be used for equipment.
- No expensive enzymes required.
- The mixed culture gives stable fermentation performance.
- No contamination risks for cells and no need to recycle microorganisms.

### *1.3.6.3 Mixed Carboxylic Acids Extraction from Fermentation Broth*

The primary processes to extract mixed acids after acidogenic fermentation are shown in Figure 1.8, 1.9 and 1.10. Figure 1.8 shows a process flow diagram of mixed acids extraction from a MixAlco process for producing chemicals and fuels. The hemicellulose extract from a Kraft pulping process is taken and used for the MixAlco process to produce chemicals and fuels. The processes include: wood extraction from Kraft pulping process, hydrolysis and fermentation combined in one consolidated process step, lowering pH by using sulfuric or phosphoric acids to improve acid extraction and lignin removal, filtration to remove solid lignin and liquid-liquid extraction to recover mixed acids. Next solvent distillation and making acid salts processes are used to recover the carboxylic acids from the solvent after extraction step. Extraction of the acids enables the production of organic acids as a product, or as an intermediate for biofuel production.

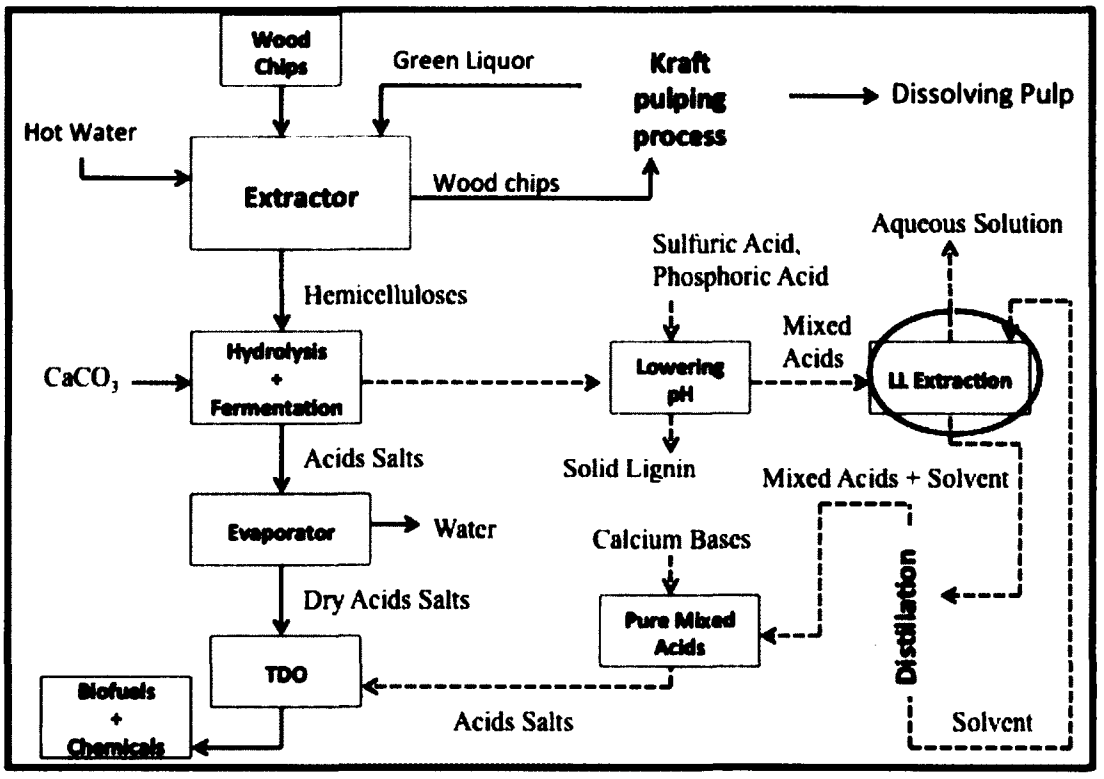



Figure 1.8 Overall pre-pulping extraction and liquid-liquid extraction of mixed acids after fermentation from the MixAlco process

Note: ——— is a real process pathway
▪▪▪▪▪ is a proposal process pathway to extract mixed acids

Figure 1.9 shows process flow diagram of mixed acids production from Whole Wood Chips process. This process utilizes the whole wood chip components (celluloses and hemicelluloses). Different types of pretreatments such as hot lime, wet oxidation or simple soaking, are used to accelerate hydrolysis and fermentation and increase mixed acids production and concentration in the fermentation broth. The processes includes: whole wood pretreatment, hydrolysis and fermentation consolidated in one process step, lowering pH by using sulfuric or phosphoric acids to improve acid extraction and lignin removal, filtration to remove solid lignin and liquid-liquid extraction to recover mixed

acids. Next, distillation and making acid salts processes are used to recover the carboxylic acids from the solvent after the extraction step.

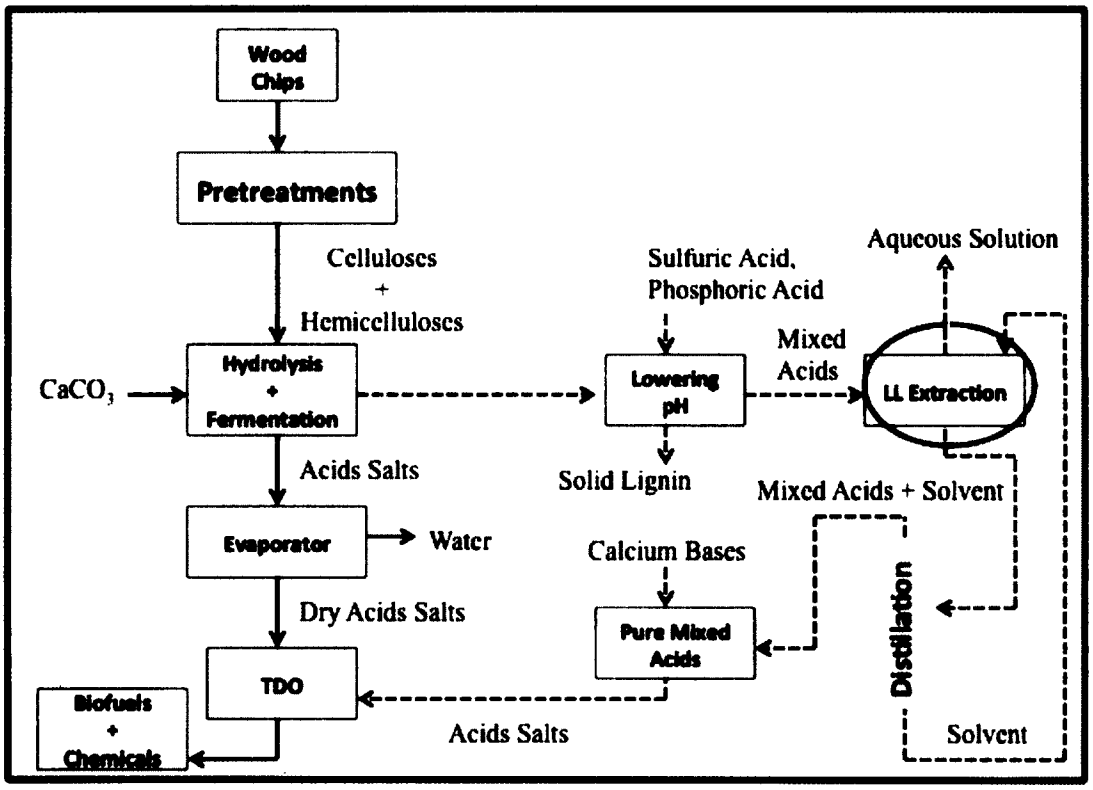



Figure 1.9 Flow diagram of whole wood process and liquid-liquid extraction of mixed acids after fermentation broth

Note: ——— is a real process pathway
▪▪▪▪ is a proposal process pathway to extract mixed acids

Figure 1.10 shows process a flow diagram of mixed acids extraction from the Whole Wood Chips process. This process utilizes the whole wood chip components (celluloses and hemicelluloses). The processes includes: whole wood pretreatment, hydrolysis and fermentation consolidated in one process step, lowering pH by using sulfuric or phosphoric acids to improve acid extraction and lignin removal, filtration to

remove solid lignin and liquid-liquid extraction to recover mixed acids. Next a back extraction process by using a dilute aqueous NaOH is used as another separation process to recover carboxylic acids from the solvent after the extraction step.

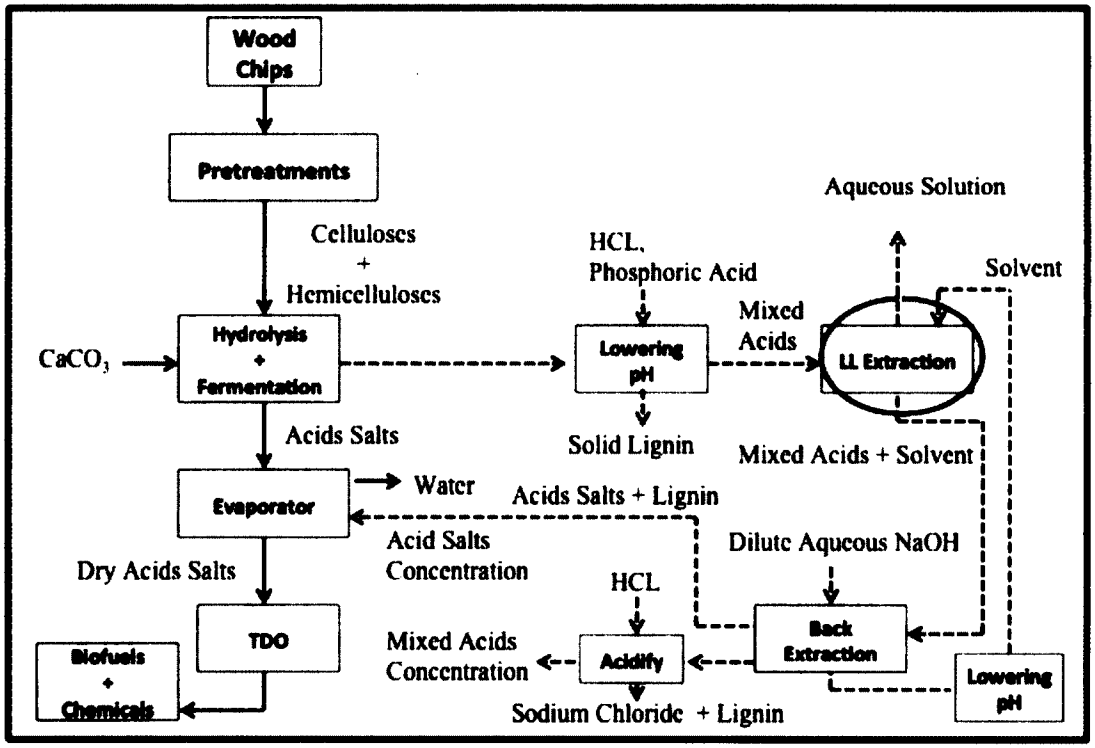



Figure 1.10 Flow diagram of whole wood process, liquid-liquid extraction of mixed acids after fermentation broth and back extraction with a dilute aqueous NaOH

Note: ——— is a real process pathway
▪▪▪▪▪ is a proposal process pathway to extract mixed acids

### *1.3.7 Recovery Process*

#### *1.3.7.1 Liquid-Liquid Extraction*

Liquid-liquid extraction, or solvent extraction, is a method to transfer substances from one liquid phase to another liquid phase by mass-transfer operations. The mass-transfer operations happen when two immiscible liquid phases are mixed, starting in a

non equilibrium distribution of the target substance and then moving towards equilibrium [4, 18-21]. The equilibrium distribution of the substances depends on their solubility in the respective liquid phases. In other words, the substance from one liquid phase will move to the other phase which has higher solubility for the transferred substance. For example, acetic acid is partially extracted from an aqueous solution by mass transfer equilibration between the aqueous and a second, immiscible phase [4, 22-24].

Liquid-liquid extraction has been used in the laboratory for many years. In 1883 a patented method was found for extracting acetic acid from a dilute aqueous solution by countercurrent extraction. Also in 1908 the first industrial scale extraction was established. It was used to extract the smoke-forming aromatic constituents from Rumanian illuminating oil by using liquid $SO_2$ as a solvent. Also, the same solvent was used later in Rouen, France in 1911 for the refining of lubricating oil. In addition, liquid-liquid extraction was used in nuclear energy programs during and after World War II to produce nuclear grade uranium and reprocess the spent fuel. Currently, liquid-liquid extraction is being widely used in many university departments, industrial and atomic energy establishments to selectively separate a substance from a mixture, or to remove unwanted impurities from a solution [25-27]. At the University of Maine Chemical and Biological Engineering Department, acetic acid is seen as one valuable component found in hemicelluloses extracts that can be extracted and recovered as a final product by using the liquid-liquid extraction method.

There are several advantages of using liquid-liquid extraction as the technique to separate recover the components from the aqueous phase:

1- Liquid-Liquid extraction is a less expensive separation process than other separation processes such as distillation. For instance, liquid-liquid extraction could be more recommended than distillation for separation of two components that have close boiling points. For example, a separation of butadiene (bp,-4.75 °C) from butylenes (bp, -5 to -6 °C) benefits from liquid-liquid extraction.

2- Similarly, separation where boiling points are overlapping can be done by liquid-liquid extraction, and it is cheaper and easier than other methods. An example of this situation is the separation of benzene, toluene and xylene from paraffin hydrocarbons.

3- Some mixtures, such as azoetropic mixtures which are hard to separate by direct distillation, will be better suited for this separation. As an example, using liquid-liquid extraction to separate methyl ethyl ketone from water is a better choice compared to distillation.

4- Liquid-liquid extraction is a good choice for separation of a liquid that has poor relative volatility compared to its solvent, such as acetic acid dissolved in water. For a dilute acid solution, distillation would require a very large amount of water to evaporate prior to recovering the acetic acid. [25,28].

For an effective liquid extraction, it is important to choose a suitable extraction solvent. Usually, the extraction happens between water or water-based (aqueous) solutions and an organic solvent which is immiscible with water [29].

### *1.3.7.2 Solvent Selection*

Choosing suitable solvents is necessary for getting the best liquid-liquid extraction performance. Distribution coefficient, $D_C$ (the ratio of the concentration of a solute in the organic phase divided by its concentration in the aqueous phase), density, viscosity, interfacial tension, polarity, volatility, boiling point and flammability are some criteria of solvent selection. In addition, an optimum solvent with high efficiency extraction has some other desirable characteristics, such as: low cost, easily recycled, high distribution coefficient, totally immiscible with aqueous phase, low viscosity, environmental friendly and nontoxic [30-32].

Solvent toxicity can be influenced by the solvent solubility in aqueous phase. Low solvent solubility in the aqueous phase implies low toxicity to microorganisms in the aqueous phase and low waste treatment and recovery costs, as well [31].

Solvent viscosity affects extraction performance by affecting the mass transfer coefficient. Mass transfer coefficient increases with decreasing solvent viscosity. Low viscosity solvents are more easily handled at Lab scale and consume less power and energy for mixing and pumping [33].

Interfacial tension affects on phase separation between organic and aqueous phases. High interfacial tension affects mass transfer and increases energy requirements to maintain sufficient contact area, while low interfacial tension can lead to stable emulsions of phases and makes them difficult to separate [34].

Selecting solvents for their suitable extraction products with a high efficiency performance can be determined systematically from computer databases. From different solvent and aqueous systems, liquid-liquid equilibria data can be calculated by using

programs such as UNIQUAC Functional-group Activity Coefficients, or the UNIFAC. A prediction of non electrolyte activity in non ideal mixtures is used systemically in UNIFAC program. The program is used to calculate the activity coefficients of the liquid mixture by using the functional groups present on the molecules of the mixture. Furthermore, distribution coefficient and solubility of solvents and aqueous solution can be calculated by UNIFAC program for liquid-liquid equilibria data system and determining suitable solvents for that system [35-38].

For extraction of products using mixed solvents such as CYANEX 923 (a mixture of four trialkylphosphine oxides), the extraction depends on the functional groups in solvent molecules. The extraction and separation of the products become difficult to predict because the interaction between product and solvent become complex. On other hand, extraction by pure solvents is easily predictable [31].

### *1.3.7.3 Distribution Coefficient ($D_C$)*

The distribution coefficient, $D_C$ is the ratio of the concentration of a solute in the organic phase divided by its concentration in the aqueous phase. The distribution coefficient is a metric that indicates how well the extraction of a component is going to work. When two immiscible liquids are mixed, the components of one liquid will move to the other liquid and distribute themselves between the two liquids [38].

$$\mathbf{D_C = \frac{concentration\ of\ a\ solute\ in\ the\ organic\ phase}{concentration\ of\ a\ solute\ in\ the\ aqueous\ phase}} \qquad (1.4)$$

Some extraction parameters, such as temperature and concentration of solvent, might affect the distribution coefficient, thereby affecting the distribution of the components between two liquids and then ultimately affect the extraction efficiency. Most organic compounds are more soluble in organic solvents than in water.

There are two parameters that are used to determine the distribution coefficient for solvent and solute system. These are the number of electron donor to acceptor, or Lewis basicity to acidity, and solubility parameters, or polar to non polar character. All these numbers and parameters are reported in solvents handbook [56] and can be used to select list of solvents suitable for the extraction system [39].

The polarity of solvents affects the coefficient as a higher number of polar groups in the solvent molecule will increase the distribution coefficient and result in better extraction. For example, extraction of ethanol from aqueous solution by organic phosphate is more effective than by ether because organic phosphate has more polar groups than ether [39-40].

As a comparison between carboxylic acids and ketones for extracting ethanol from water, carboxylic acids have better ethanol extraction than ketones due to their higher electron donor number than the ketones.

For extraction with polar solvents, carboxylic acids with longer chain length have lower distribution coefficients and lower extraction than shorter chain length acids [40]. This is because a long chain length on a carboxylic acid decreases the solute polarity and it becomes less soluble in water. Therefore, polar solvents would have less acid extraction distribution than non polar solvents. For example, kerosene, which is a non polar hydrocarbon solvent, is more recommended to extract caproic acid (C6), in aqueous

solution than organic phosphate, which is a polar solvent [41-43]. The distribution coefficients of extracting long chain length carboxylic acids such as caproic acid by kerosene are about 3.1 compared to 0.01 to 0.03 $D_C$ for short chain carboxylic acids such as acetic acid [44].

Similarly, the distribution coefficient is decreasing by using saturated and unsaturated hydrocarbon because of their non polarity concerns [45]. For extraction of acetic acid from aqueous solution, solvents of organophosphates such as di-2 ethylhexylphosphoric acid or trioctylphosphine oxide have distribution coefficients of 10 or more and better acids extraction compared to aliphatic hydrocarbons (about 0.003 $D_C$) and aliphatic acids or ketones (about 2 to 3 $D_C$) [46].

#### *1.3.7.4 Acid Recovery from Solvent*

##### *1.3.7.4.1 Distillation Process*

During the liquid-liquid extraction process step, the mixed carboxylic acids are transferred from the aqueous phase to the organic phase by the solubility differential. Then the two immiscible phases are separated by decanting or centrifuge. The mixed acids in solvent are recovered from the organic solution by distillation [4,48]. For analysis, High Performance Liquid Chromatography, HPLC, and Gas Chromatography, GC, are used to quantify mixed acids in the aqueous and organic phases (Figure 1.11). The recovered acids from distillation might include some volatile organics, so a centrifuge was used for final separation of the acids in the condensate.

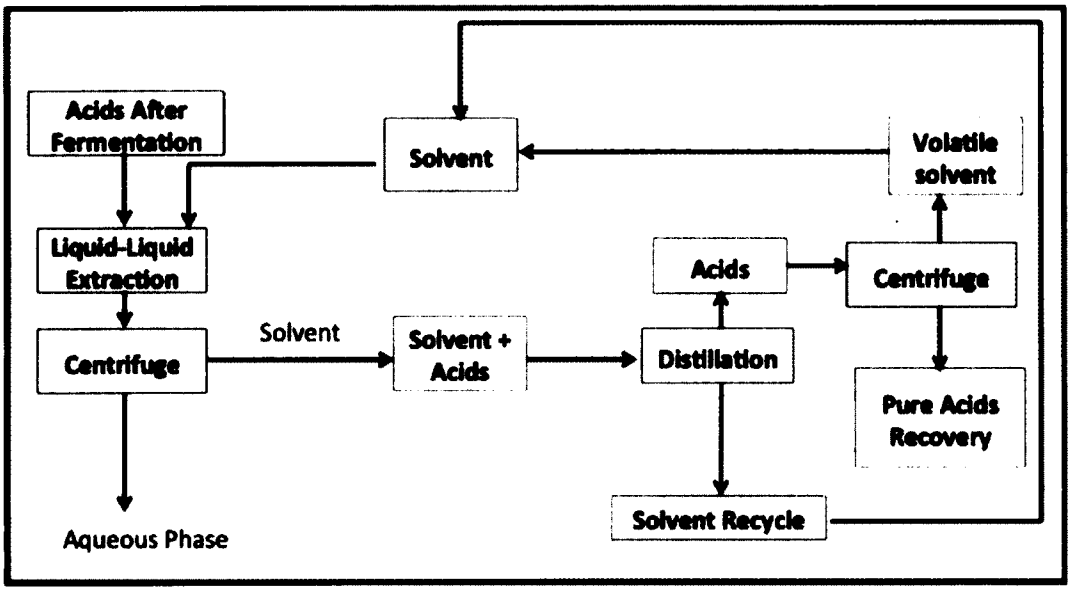



Figure 1.11 Mixed acids extraction and recovery by distillation flow diagram

### *1.3.7.4.2 Acid Salts Precipitation*

Figure 1.12 shows the liquid-liquid extraction process step to extract carboxylic acids from the aqueous phase to the organic phase by the solubility differential. Then the two immiscible phases are separated by decanting or centrifuge. The mixed acids in solvent are recovered from the organic solution by adding calcium bases to form calcium carboxylic acid salts. Then the acid salts are recovered from the solvent by precipitation techniques. Next the acid salts are dried by oven to be used in Thermal Deoxygenation process later.

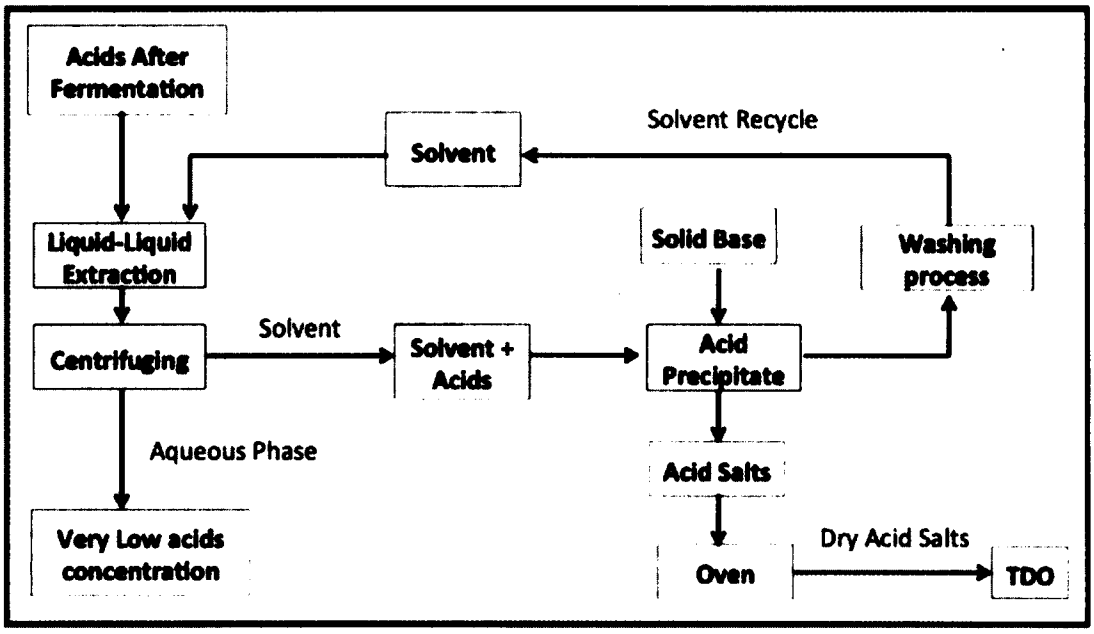



Figure 1.12 Mixed acids extraction and recovery by acid salts precipitation

### *1.3.7.4.3 Back Extraction with Caustic Solution*

Back extraction with a strong caustic solution, NaOH, is another method to recover carboxylic acids from solvent after liquid-liquid extraction. Adding an aqueous solution of concentrated NaOH to the organic solution has the carboxylic acids returning to aqueous solution, this time at higher concentration than they were originally, in the form of sodium carboxylic salts as shown in equation 1.5 below. As a result, the sodium carboxylic salts become more soluble in aqueous phase than organic phase due to carboxylic salts ionic attribute. Therefore, the salts will transfer from organic phase to aqueous phase, which it is called a back extraction method. Next by acidifying the aqueous solution using HCL the carboxylic salts will be retuned back to original carboxylic acids [47-48].

$$RCO_2H + NaOH \longrightarrow RCO_2^- \; Na^+ \xrightarrow{HCL} RCO_2H + NaCl \qquad (1.5)$$

Figure 1.13 shows the liquid-liquid extraction process step to extract carboxylic acids from the aqueous phase to the organic phase by the solubility differential. Then the two immiscible phases are separated by decanting or centrifuge. The mixed acids in solvent are recovered from the organic solution by back extraction with a concentrated aqueous sodium hydroxide solution. The sodium hydroxide in aqueous solution will react with carboxylic acids in organic solution to form sodium carboxylic acid salts. Next the salts are transferred back to aqueous solution due to utilizing of solubility properties different and pH different between carboxylic acids ion and sodium hydroxide ion showing in above equation 1.5. In addition, the transferring acid salts are concentrated in aqueous solution because carboxylic acids as sodium salt ionic form are more soluble and polar in aqueous solution than original carboxylic acids. Further more, the sodium carboxylic acid salts could be acidified to release the acids from the salts and get pure carboxylic acids.

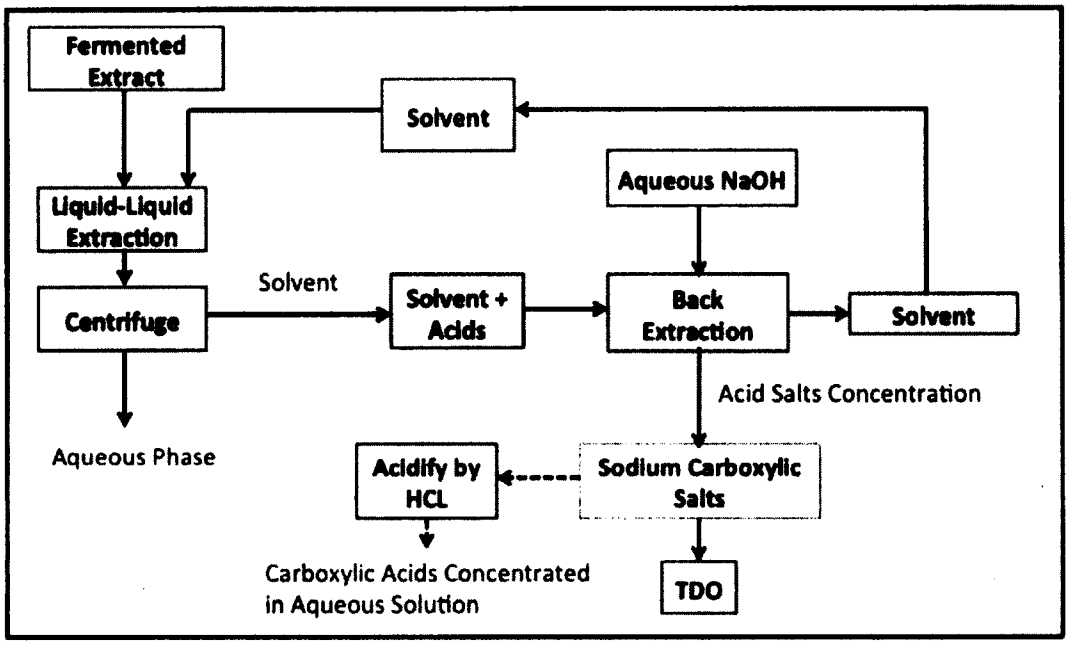



Figure 1.13 Mixed acids extraction and recovery by back extraction with a dilute aqueous NaOH

Note: ——— is a real process pathway
••••• is a future process pathway to extract mixed acids

### *1.4 Extraction and Solvent Recovery Experiments*

Extraction variables that have been investigated and are reported in this thesis include:

- Effect of concentrations of solvent in the organic solution.
- Effect of ratios of organic to aqueous phase.
- Effect of pH.
- Effect of temperature.
- Effect of agitation on extraction % (using CYANEX 923).
- Effect of centrifuging on extraction % (using CYANEX 923).

Solvent recovery experiments reported in this thesis include:

- Distillation of acetic acid from TOPO/undecane and TOA/octanol.
- Distillation of mixed acids from CYANEX 923 and CYANEX 923/tridecane.
- Back extraction (washing) of distilled TOPO/undecane and TOA/octanol.
- Calcium precipitation of mixed acids from CYANEX 923.
- Back extraction of mixed acids in CYANEX 923 to NaOH solution.

# CHAPTER TWO

# MATERIALS AND METHODS

## *2.1 Materials*

### *2.1.1 Solvent Phase*

An extraction solvent is used to extract a specific component such as acetic acid from the aqueous phase. This thesis compares different solvents to determine which has better extraction efficiency. These solvents are: trioctylphosphine oxide (TOPO), diluted in undecane; trioctylamine (TOA), diluted in octanol; CYANEX 923 (a mixture of four trialkyl phosphine oxides) diluted in tridecane, and ethyl acetate (EA).

#### *2.1.1.1 Trioctylphosphine oxide (TOPO)*

In this research, a pure trioctylphosphine oxide, TOPO, ($[CH_3(CH_2)_7]_3PO$, Mol W. 386.64, Reagent Plus, 99 % pure, Fisher) was purchased. TOPO is a strong and stable extraction agent. It is a stable white solid at room temperature and has strong hydrogen bonding acceptor properties that enhance the carboxylic acid transfer from the aqueous phase to the organic phase [18]. TOPO is proven to have excellent chemical stability, high boiling point and low solubility in water (Figure 2.1 [20]). It has a melting point of 50-55 °C and a boiling point of 201-202 °C at 2 mm Hg or 411 °C at atmospheric pressure.

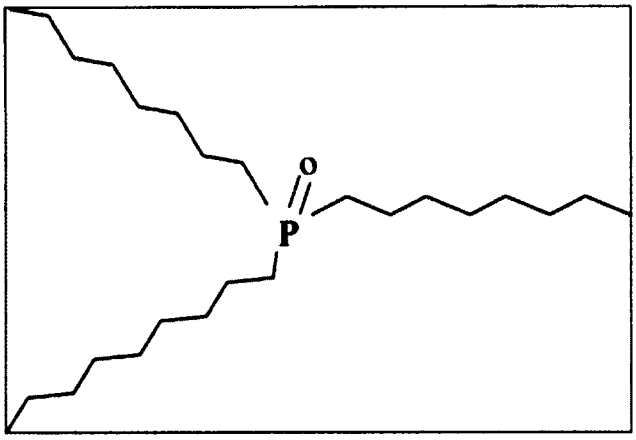
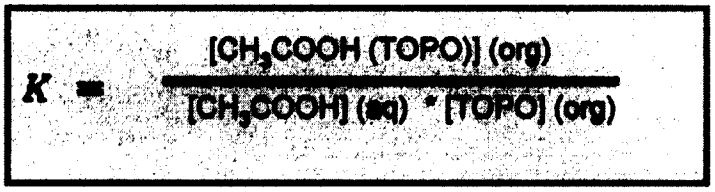



Figure 2.1 Trioctylphosphine oxide, TOPO, structure

The equilibrium chemical reaction of TOPO to extract acetic acid is shown as the following:

(2.1)

Where the equilibrium constant, K, is:




(2.2)

TOPO is an expensive extraction solvent compared to other solvents such as TOA [19]. Its cost at laboratory scale is $200 per 100 g of TOPO, which is three times the cost of TOA. Therefore, it is important to recycle TOPO to reduce its cost. In addition, TOPO is often diluted in an alkane hydrocarbón liquid such as undecane, $CH_3(CH_2)_9CH_3$, to reduce the consumption of TOPO, lower its melting point, and to reduce its cost.

### *2.1.1.2 Trioclylamine (TOA)*

Pure trioctylamine, TOA, ($[CH_3(CH_2)_7]_3N$, density 0.809 g/mL at 25 °C, Mol W. 353.67, 98% purity, Sigma-Aldrich) was used. It has a melting point of -40 °C, a boiling point of 365 – 367 °C and is insoluble in water (Figure 2.2).

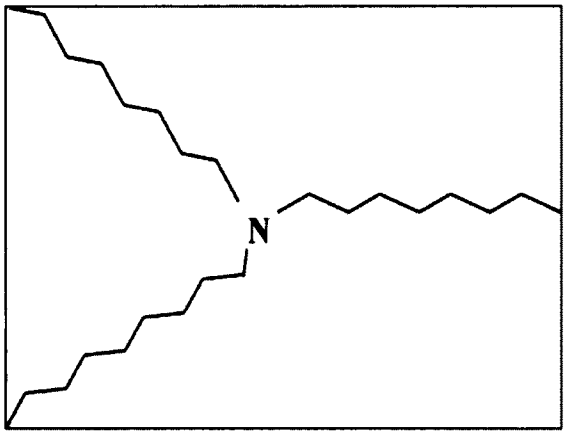



Figure 2.2 Trioctylamine, TOA, structure

### *2.1.1.3 CYANEX 923*

CYANEX 923 is a strong solvent extractant that can be used to extract both organic and inorganic solutes from aqueous solutions, such as extraction of carboxylic acids. It is a mixture of four components including: trihexyl phosphine oxide, dihexylmonooctyl phosphine oxide, dioctylmonohexyl phosphine oxide and trioctyl phosphine oxide (Figure 2.3). It has strong hydrogen bonding acceptor properties than the carboxylic acid to transfer from aqueous phase to organic phase. CYANEX 923 is proven to have excellent chemical stability, high boiling point and low solubility in water. An advantage of CYANEX 923 compared with other similar solvents is that it is completely miscible with all common hydrocarbon diluents, even at low ambient temperatures. It can

be used at room temperature without dilution with other chemicals due to its lower melting point. A sample of pure CYANEX 923, (Mol W. 348, Reagent Plus, 93 % pure, CYTEC) was purchased. It has a freezing point of -5 to 0 °C and a boiling point of 310 °C at 50 mm Hg.

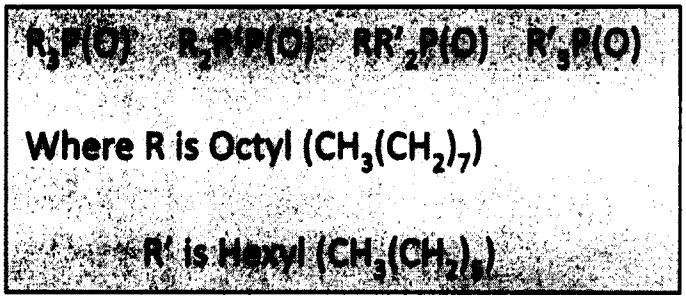



Figure 2.3 CYANEX 923 structure

### *2.1.1.4 Ethyl Acetate*

Ethyl acetate, $C_4H_8O_2$, (density 0.897 g/cm³, Mol W. 88.11, 98% purity, Sigma-Aldrich) was used. It has a melting point of −83.6 °C, a boiling point of 77.1 °C and its solubility in water is 8.3 g/100 mL at 20 °C.

### *2.1.1.5 Other Chemicals*

Undecane ($C_{11}H_{24}$, density is 0.74 g/mL, Mol. W. 156.3, 99+%, Fisher) is an organic component used as diluent for TOPO. It has a melting point of -26 °C and a boiling point of 196 °C. It is insoluble in water.

Octanol ($CH_3(CH_2)_7OH$, density is 0.827 g/mL at 25 °C, Mol W. 130.23, 99% purity, Sigma-Aldrich) ) is an organic component used as diluent for TOA. It has a melting point of −15 °C and a boiling point of 196 °C. It is insoluble in water.

Tridecane ($C_{13}H_{28}$, density is 0.76 g/mL, Mol. W. 184.37, 99%, Sigma-Aldrich) is an organic component used as diluent for CYANEX 923. It has a melting point of -4 °C and a boiling point of 236 °C. It is insoluble in water.

Dichloromethane ($CH_2Cl_2$, density is 1.325 g/mL at 25 °C, Mol W. 84.93, 99.8% purity, ACROS) is an organic component used as a diluent for analysis of organic solvents such as Cyanex 923. It has a melting point of -96.7 °C and a boiling point of 39.6 □C. It has solubility in water of 13 g/L at 20 °C.

### *2.1.2 Aqueous Phase*

Two systems were tested: a clean or pure system (pure acid dissolved in DI-water) usually with 10-20 g/L initial acids, and a real extract system such as hemicellulose extract derived from hardwood or softwood.

#### *2.1.2.1 Clean System*

Pure carboxylic acids (C2 to C7) including acetic, propionic, butyric, valeric, caproic and heptanoic acids and ethanol were dissolved in deionized water at varying concentrations to perform liquid-liquid extractions (Table 2.1).

Table 2.1 Carboxylic acids and ethanol used for generating "clean system" samples

| # | Name | Chemical formula | Purity % | Density g/mL | Mw g/mole | Boiling point °C | pKa | Solubility in water g/100 mL |
|---|---|---|---|---|---|---|---|---|
| 1 | Acetic acid | $CH_3COOH$ | 99 | 1.049 | 60 | 118.1 | 4.76 | Miscible |
| 2 | Propionic acid | $CH_3CH_2COOH$ | 98 | 0.99 | 74 | 141 | 4.86 | Miscible |
| 3 | Butyric acid | $CH_3(CH_2)2COOH$ | 99 | 0.96 | 88 | 163.5 | 4.82 | Miscible |
| 4 | Valeric acid | $CH_3(CH_2)3COOH$ | 98 | 0.94 | 102 | 186 | 4.82 | 5 |
| 5 | Caproic acid | $CH_3(CH_2)4COOH$ | 98 | 0.93 | 116 | 205 | 4.85 | 1.1 |
| 6 | Heptanoic acid | $CH_3(CH_2)5COOH$ | 99 | 0.92 | 130 | 223 | 4.89 | 0.24 |
| 7 | Ethanol | $C_2H_6O$ | 99 | 0.789 | 46 | 78 | 15.9 | Miscible |

### *2.1.2.2 Real Extract System*

For hemicellulose extraction, hemicellulose extracts such as green liquor or hot water extract were prepared in the University of Maine Chemical Engineering pilot plant from mixed Northeast hardwood chips. The mixed hardwoods consisted largely of maple with the balance being mostly birch and aspen.

Green liquor is an intermediate pulping liquor that is obtained after dissolution in water of the liquid smelt obtained from the bottom of the Kraft pulping recovery boiler. It consists of an aqueous solution of $Na_2CO_3$, $Na_2S$, $Na_2SO_4$ and smaller quantities of other alkali metal salts (Table 2.2). The amount of green liquor added to the extraction process was quantified as % of total titratable alkali (TTA, quantified as $Na_2O$ equivalents) based on wood. About 1-3 % TTA of green liquor is used for the extraction process. By mixing

the green liquor with wood chips in the extraction process, the polymer sugars, or complex sugars, are broken down into oligomer and mono sugars. Similarly, the wood chips can be mixed with hot water in a partial hydrolysis process to obtain a hot water extract. During extraction and any subsequent hydrolysis, the acetyl groups in the hemicellulose are released as acetic acid and can then be recovered through liquid-liquid extraction.

Table 2.2 Chemical composition of green liquor used in extraction process [49]

| Chemicals | Value |
|---|---|
| Total titrated alkali (TTA) | 3% on wood as $Na_2O$ [a] |
| Sodium hydroxide (NaOH) | 9.0 g/L as $Na_2O$ |
| Sodium sulfide ($Na_2S$) | 29.1 g/L as $Na_2O$ |
| Sodium carbonate ($Na_2CO_3$) | 70.0 g/L as $Na_2O$ |
| Sodium sulfate ($Na_2SO_4$) | 0.8 g/L as $Na_2O$ |
| TTA | 108.9 g/L as $Na_2O$ |

[a] The dissolved solution in the green liquor had a mass equal to 3 % of the wood mass fraction

### *2.1.3 Distillation*

Consumable materials used for the distillation included:

1- High vacuum grease (Dow Corning, high vacuum silicone grease, colorless, weight 5.3 oz tube, Sigma-Aldrich) is used for sealing the distillation apparatus. It is a mixture of poly dimethyl siloxane, silica and amorphous dimethyl siloxane.

2- Boiling chips (Chemware Ultra-Pure Polytetrafluoroethylene (PTFE), 16 oz. (450g) plastic bottle, Fisher Scientific) are used for distillation to promote gentle, efficient boiling and minimize bumping and violent boiling.

3- PTFE thread seal tape (520" x 1/2" threaded roll of PTFE Tape, Fisher Scientific) is used for sealing of distillation apparatus to help prevent water, gas and air from leaking.

### *2.1.4 Solid Bases*

Calcium hydroxide ($Ca(OH)_2$, density 2.211 g/cm$^3$ solid, Mol W. 74.093, basicity ($pK_b$) 2.4, 95% purity and other such as fluoride, magnesium and alkali salts, ACROS) is used to precipitate acids from organic phase. It has a melting point is 580 °C and solubility in water is 0.173 g/100 mL at 20 °C.

Calcium carbonate ($CaCO_3$, density 2.71 g/cm$^3$ solid, Mol W. 100.0869, basicity ($pK_b$) 3.7, 99% purity, Sigma-Aldrich) is used to precipitate acids from organic phase. It has a melting point is 825 °C and solubility in water is 0.0013 g/100 mL at 25 °C.

Calcium oxide (CaO, density 3.34 g/cm$^3$ solid, Mol W. 56.0774, basicity ($pK_b$) 2.4, 95% purity and other such as fluoride, magnesium and alkali salts, ACROS) is used to precipitate acids from organic phase. It has a melting point is 2850 °C and solubility in water is 1.19 g/100 mL at 25 °C.

Calcium acetate ($Ca(C_2H_3O_2)_2$, density 1.509 g/cm$^3$, Mol W. 158.17, 99% purity, ACROS) is used for precipitating acid experiments. It has a melting point is 160 °C and solubility in water is 34.7 g/100 mL at 20 °C.

### *2.1.5 Dilute Aqueous Sodium Hydroxide Solution*

An aqueous sodium hydroxide solution (12.5 M NaOH in DI water, density 1.515 g/mL at 25 °C, Mol W. 39.99, boiling point 1388 °C, basicity ($pK_b$) 0.2, 50% w/w purity, Sigma-Aldrich) used to recover carboxylic acids from solvent by back extraction method.

### *2.1.6 Filtration*

A filter paper (Whatman, Grade 934-AH, 1.5 μm pore size) is used to separate the solid materials such as lignin and solid bases from the solution.

### *2.1.7 pH Control*

Sodium hydroxide pellets (NaOH, density 2.13 g/cm$^3$, Mol W. 39.99, boiling point 1388 °C, solubility in water 111 g/100 mL at 20 °C, basicity ($pK_b$) 0.2, 98% purity, Fisher Scientific), sulfuric acid ($H_2SO_4$, density 1.84 g/cm$^3$, Mol W. 98.079, boiling point 337 °C, miscible in water, acidity ($pK_a$) −10, 96% purity, ACROS), phosphoric acid ($H_3PO_4$, density 1.885 g/cm$^3$, Mol W. 97.995, boiling point 158 °C, solubility in water 5.48 g/mL, acidity ($pK_a$) 2.148, 98% purity, ACROS) and hydrochloric acid (10N HCL in water, density 1.3 g/mL, Mol W. 36.5, boiling point 83 °C, soluble in water, acidity ($pK_a$) -7, Fisher Scientific) are used for pH control.

### *2.1.8 Analysis*

L-Fucose ($C_6H_{12}O_5$, Mol W. 164.16, 97% purity, ACROS) is a hexose deoxy sugar used as an internal standard for the HPLC calibration curve method for aqueous analysis.

Isocaproic acid ($C_6H_{12}O_2$ , density 1.004 g/mL, Mol W. 116.16, 99.8% purity, ACROS) is an organic component used as internal standard for the GC calibration curve method for aqueous analysis. It has a boiling point of 200 °C and less soluble in water.

Volatile acids mixture (formic acid 0.46 g/L, acetic acid 0.601 g/L, propionic acid 0.741 g/L, isobutyric acid 0.881 g/L, butyric acid 0.881 g/L, isovaleric acid 1.021 g/L, valeric acid 1.021 g/L, isocaproic acid 1.162 g/L, caproic acid 1.162 g/L and heptanoic acid 1.302 g/L) (by Matreya) in 100 mL water is an aqueous mixture used as reference solution for GC calibration method for aqueous analysis.

### *2.2 Methods*

#### *2.2.1 Feed Stock*

In this research, two materials had been used as biomass-derived feedstock for extraction acids. These were Hemicellulose Extract and Fermented Mixed Wood chips.

##### *2.2.1.1 Hemicellulose Extracts*

The hemicellulose extracts (green liquor and hot water extract) were prepared by a sequential hydrolysis processes, the first hydrolysis by using a rotating digester for extracting the hemicellulose out of wood chips, and the second hydrolysis using added sulfuric acid to hydrolyze the polymers and oligomers to smaller sugar molecules.

###### *2.2.1.1.1 First Hydrolysis Using Rotating Digester*

Northeast hardwood chips were immersed and cooked in green liquor or hot water to obtain a green liquor or hot water extract that could be used for liquid-liquid extraction. The hemicellulose extract was prepared by using a 60 L rotating digester at the University of Maine Pilot Plant. The digester was loaded with 7 kg (oven dry weight) of fresh chips sized between 16 and 22.6 mm and mixed with green liquor and water (including wood moisture) at an overall liquor to wood ratio of 4:1 L/kg. For the extracts studied in this work, the green liquor charges used were from 1.44 to 3%, expressed as grams of $Na_2O$ per 100 gram of dry wood. In the case of extraction with pure water, the

same liquor to wood ratio was used without any green liquor charge. This system was agitated (2 rpm) at 160 °C for 110 minutes yielding an H-factor 800 hrs. The reactor was then cooled below 100 °C. The free-draining liquor was collected and used for the acetic acid extraction experiments.

#### *2.2.1.1.2 Acid Hydrolysis Using Sulfuric Acid*

The liquor from the first hydrolysis process, which was hemicellulose extract, was used for second hydrolysis (acid hydrolysis). Sulfuric acid was added to the hemicellulose extract to give a final concentration of 40 g/L of sulfuric acid in the solution, which reduced the pH to approximately 1. Then the solution was autoclaved for 1 hour and at 121 °C.

#### *2.2.1.1.3 Lignin Removal*

Lignin is a complex and high molecular weight component that causes many problems with processing and analyzing wood extract liquids. Reducing the effectiveness of liquid-liquid extraction of organic acids and blocking of GC syringes and injection ports during compositional analysis are some examples of problems associated with lignin. Therefore, it is a highly recommended that lignin be removed prior to the liquid-liquid extraction process. Lignin can take the form of an insoluble solid or soluble content. The procedure for lignin removal is as follows:

1. Filter the solution by passing it through a filter paper (Whatman, Grade 934-AH, 1.5 μm pore size) under vacuum to remove solid lignin. Probably 52-71 % of solid lignin can be removed by filtration.
2. Conduct secondary hydrolysis with sulfuric acid, or for unhydrolyzed samples, add phosphoric or sulfuric acid to the solution to lower pH from

7 to less than 3. When the pH is lowered, the soluble lignin will be released and precipitates down from solution.

3. Agitate the solution by using a shaker machine for 30 min and 230 rpm speed to release more of the lignin.
4. Centrifuge the solution for 30 min at12000 rpm. All lignin content will precipitate down to the bottom of bottle.
5. Separate the solution from solid lignin by pipetter.

About 29 to 48 % of the lignin can be removed this way. After these steps the hemicellulose extract becomes ready for liquid-liquid extraction (Table 2.3).

Table 2.3 Composition of 3 % green liquor (GL) and hot water (HW) extract derived from northern hardwood [49]

| Composition of Extract | GL Extract[3] [g/L] Extraction only | GL Extract[2] [g/L] Extraction and Hydrolysis | HW Extract[3] [g/L] Extraction only | HW Extract[2] [g/L] Extraction and Hydrolysis |
|---|---|---|---|---|
| Glucose | 0.09 | 0.36 | 0.09 | 1.01 |
| XMG[1] | 0.11 | 1.62 | 0.65 | 9.06 |
| Arabinose | 0.02 | 0.24 | 1.07 | 1.37 |
| Acetic Acid | 8.32 | 9.40 | 1.27 | 3.47 |
| Total Sugars | 0.22 | 2.22 | 1.81 | 11.44 |

Note: [1] xylose, mannose, and galactose, [2] secondary hydrolyzed with 4 % sulfuric acid, [3]analyzed without secondary hydrolysis

#### *2.2.1.2 Fermented Mixed Wood Chips*

A mixture of northern hardwood chips was used as raw material for fermentation to mixed acids. Different types of wood chips were mixed with a ratio of 1:1 and then ground to 0.5 mm. Next the mixture was hydrolyzed using 2-step hydrolysis (72% $H_2SO_4$

at 40°C followed by 4% $H_2SO_4$at 121°C) to break down polymer-sugars to mono-sugars. The composition was analyzed by HLPLC (Table 2.4 [50]).

Table 2.4 Sugar compositions

| | %[1] | %[2] |
|---|---|---|
| **Glucose** | 35.87±1.73 | 38.07±0.66 |
| **XMG/xylose** | 17.24±0.20 | 16.68±0.19 |
| **Acetic Acid** | 9.59±0.67 | 5.68±0.28 |
| **Furfural** | 2.07±0.15 | 0 |
| **Formic Acid** | 0.84±0.00 | 0 |
| **Glycolic Acid** | 0.41±0.09 | 0 |
| **Arabinose** | in XMG | 0.49±0.01 |
| **Mannose** | in XMG | 1.72±0.05 |
| **Galactose** | in XMG | 1.06±0.02 |
| **Acid Dissolved Lignin** | 3.66±0.33 | 7 |
| **Klason Lignin** | 68±0.05 | 20.84±0.05 |
| **Ash** | *** | 0.22±0.01 |
| **4-OMGA** | 0 | 6.23±0.4 |

[1] Done by Dr. Yang Yu, [2] Done by Dr. Sefik Tunc, *** not measured

#### *2.2.1.2.1 Pretreatments Prior to Fermentation*

To improve access of organisms to the wood sugars in the mixed hardwood, and thus accelerate fermentation, a pretreatment process such as lime pretreatment is needed. Three lime pretreatments were used. These were: boiling, hot and wet oxidation pretreatments, applied to either whole or ground wood chips (Table 2.5 [18-20]). Soaking the chips in water for an equivalent period of time was carried out as a negative control. Unbleached brownstock was also included in the experimental design.

Table 2.5 Types of pretreatments

| | Liquor/wood ratio | Catalyst % | T °C | Time hours | Particle size | Oxygen |
|---|---|---|---|---|---|---|
| **Soaking** | 9:1 | None | ~ 20 | 6 | Chips | None |
| **Boiling lime** | 9:1 | $Ca(OH)_2$, 10% | 100 | 6 | Chips or ground | None |
| **Hot lime** | 9:1 | $Ca(OH)_2$, 10% | 150 | 6 | Chips or ground | None |
| **Pressurized $O_2$ hot lime** | 9:1 | $Ca(OH)_2$, 10% | 150 | 6 | Chips or ground | 60 psig at 20 °C |
| **Brownstock** | 4:1 | 0 | Typical Kraft pulping conditions | | | |

Done by Dr. Yang Yu

#### *2.2.1.2.2 Fermentation*

Mixed cultures of microorganisms under anaerobic fermentation condition are used to ferment wood carbohydrate to mixed acids. These organisms are added to pretreated wood biomass in a rotary container (digester) to perform the fermentation under anaerobic conditions. Chicken manure (as a nutrient source for fermentation) was mixed with wood biomass at a ratio of 20:80 manure to wood. Then this mixture was mixed with water at an overall 1:9 solid to liquid ratio to produce wood slurry. Next 500 mL of the wood slurry were added to a 1 L bottle and the pH was neutralized to 7 before fermentation by adding lime (for soaked wood chips) or by bubbling $CO_2$ (for other pretreatment conditions). Then iodoform was added to suppress methanogenesis and the mixed culture was added to inoculate. Finally the fermentation was run for 4 weeks at 37 °C and 1 rpm. Results from the fermentation are shown below in figure 2.4 and table 2.6.

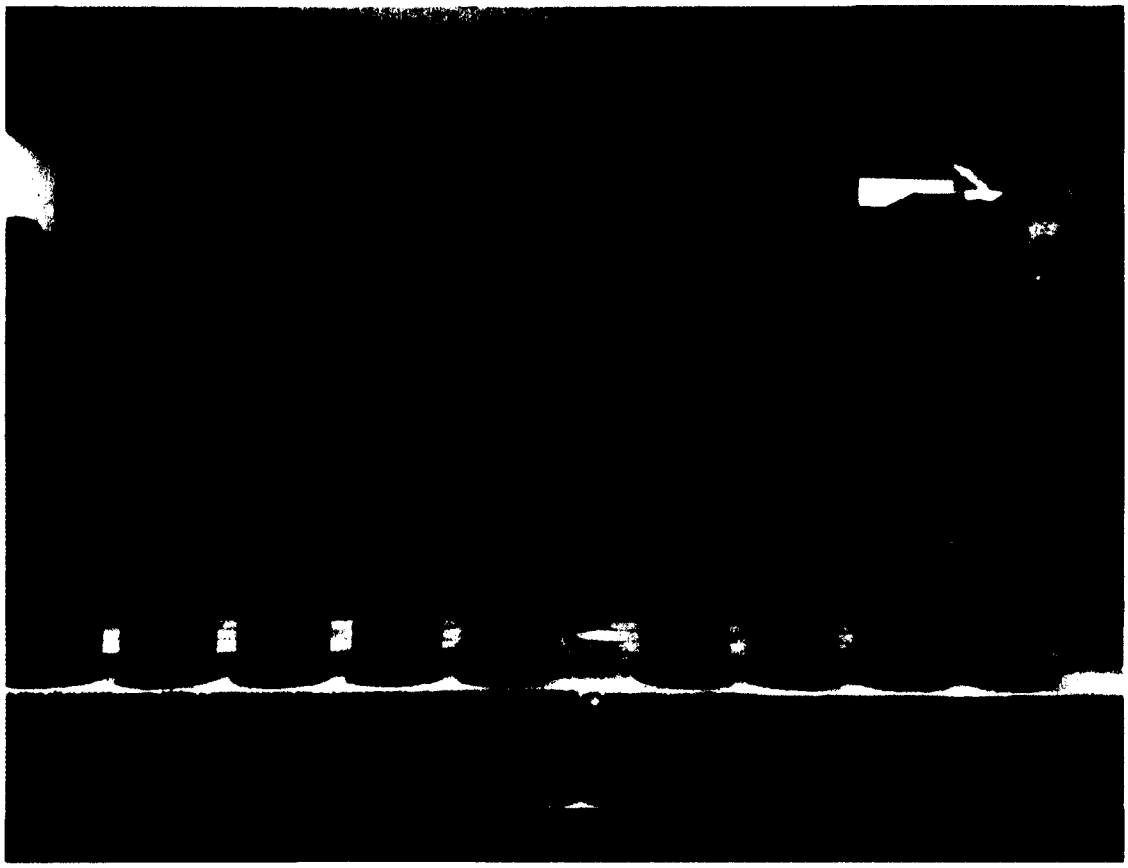


Figure 2.4 Mixed acids in aqueous solution after different types of pretreatments and fermentation

Note: #1 mixed wood chips after soaking pretreatment and fermentation, #2 mixed wood chips after boiling pretreatment and fermentation, #3 and #4 ground mixed wood chips after boiling pretreatment and fermentation, #5 mixed wood chips after hot lime pretreatment and fermentation, #7 mixed ground wood chips after hot lime pretreatment and fermentation, #9 mixed wood chips after oxygen pressurized pretreatment and fermentation, #10 and #11 tubes are mixed ground wood chips after oxygen pressurized pretreatment and fermentation.

Table 2.6 Acids concentration after pretreatment and mixed culture fermentation

| | S | B | GWB | WHL | GWHL | Pressurized | GW Pressurized | BS |
|---|---|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** |
| **HAc** | 2.6 | 3.8 | 5.1 | 5.0 | 3.7 | 5.1 | 5.6 | 5.1 | 3.2 | 5.5 | 5.2 | 2.9 |
| **Prop.** | 0.9 | 1.2 | 2.3 | 2.1 | 1.3 | 1.6 | 1.6 | 1.5 | 0.9 | 2.3 | 2.4 | 1.6 |
| **Buty.** | 2.1 | 3.5 | 4.1 | 4.2 | 5.6 | 5.5 | 6.6 | 6.2 | 3.4 | 4.6 | 3.9 | 2.6 |
| **Val.** | 1.3 | 1.0 | 1.5 | 1.6 | 1.1 | 1.3 | 1.1 | 1.2 | 0.8 | 1.3 | 1.1 | 3.0 |
| **Hex.** | 8.2 | 7.4 | 7.4 | 7.3 | 11.2 | 10.1 | 10.6 | 10.3 | 7.2 | 7.6 | 7.3 | 6.9 |
| **Hept.** | 1.0 | 0.3 | 0.2 | 0.2 | 0.1 | 0.4 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.5 |
| **Total Acids** | **13.5** | **13.4** | **15.5** | **15.4** | **19.3** | **18.9** | **20** | **19.3** | **12.4** | **15.9** | **14.8** | **14.6** |

Note: S is Soaking pretreatment, B is boiling pretreatment, GWB boiling pretreatment for ground wood, WHL is hot lime pretreatment for wood chips, GWHL is hot lime pretreatment for ground wood, GW is ground wood and BS is brownstock wood

### *2.2.2 Liquid-Liquid Extraction*

The liquid-liquid extraction technique is used to extract carboxylic acid from the aqueous phase by using an immiscible organic solution (Figure 2.5). The extraction was tested for two systems: the clean system (using pure acids dissolved in DI- water) and real extract (such as hemicelluloses) extract system. The laboratory procedure was used at small scale (10-20 mL) and large scale (1 L).

For small scale extraction, 50 ml centrifuge tubes (50 mL, plug seal closure, Fisher) were used to contain 10 mL and 10 mL, or 20 mL and 20 mL, of aqueous and organic solutions, respectively. While for large scale extraction, a 3 L mixing tank with a stirrer was used to mix 1L of aqueous and 1 L of organic solutions. The extraction temperature was measured by an electronic thermometer (Omega, No. HH23). In addition, a water bath was used (as needed) to heat and control the temperature for the

small scale experiments, while a hot plate was used for the larger scale. Samples varying from 0.1- 5 mL were collected from the centrifuge tubes with pipettes.

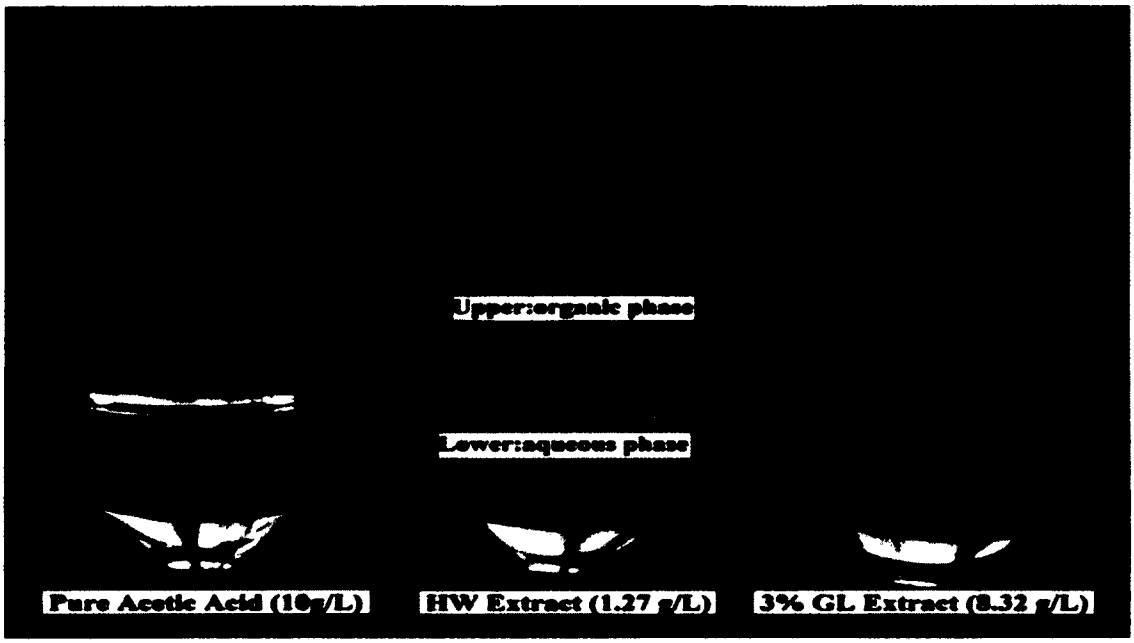



Figure 2.5 Liquid-liquid extraction of acetic acid by using TOPO at 1 pH and 70 °C [43]

For small scale, 10 or 20 mL of aqueous solution (pure acids in water or real extract) were taken into a 50 mL centrifuge tube and mixed with an organic solution such as TOPO in undecane at a specific volume ratio (v/v) of organic to aqueous phases. Then the mixture was vigorously shaken for 30 minutes and heated (as needed) at 70 °C by using a heating mantle [19]. Next the mixture was centrifuged at 9000 rpm for 30 min. The aqueous and organic phases were separated from each other by carefully using a pipette (Figure 2.6). Then the aqueous phase was taken for analysis by high performance liquid chromatography (HPLC) or gas chromatography (GC) while organic phase was taken for analysis by gas chromatography (GC) only. Finally, the acids were recovered from the organic phase by further separation techniques such as distillation.

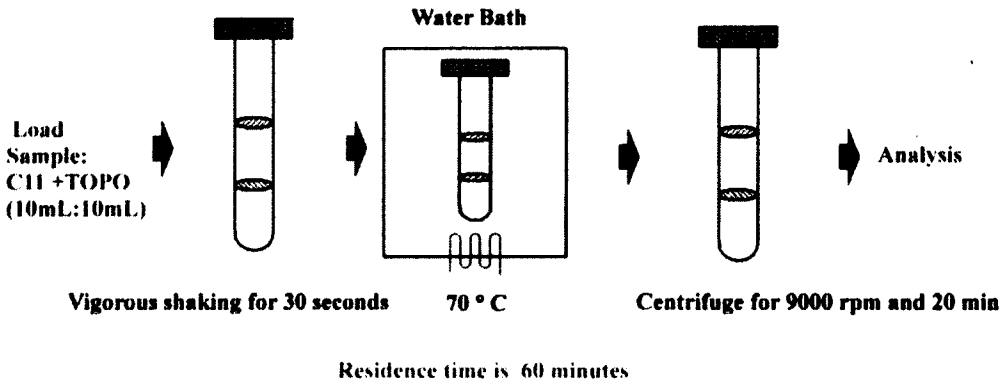



Figure 2.6 Diagram for small scale procedure of liquid-liquid extraction

For large scale, 1 L of aqueous solution was mixed with 1 L of organic solution in a 3 L mixing tank with stirrer. Then the mixture was agitated and heated for 1 hour by using a hot plate. Next the mixture was dispensed in to 1L centrifuge tubes and centrifuged at 9000 rpm for 1 hour. The aqueous and organic phases were separated carefully from each other by using a vacuum system (Figure 2.7). Then the aqueous phase was taken for analysis by HPLC or GC while the organic phase was taken for analysis by GC only. Finally, the acids were recovered from the organic phase by further separation techniques such as distillation.

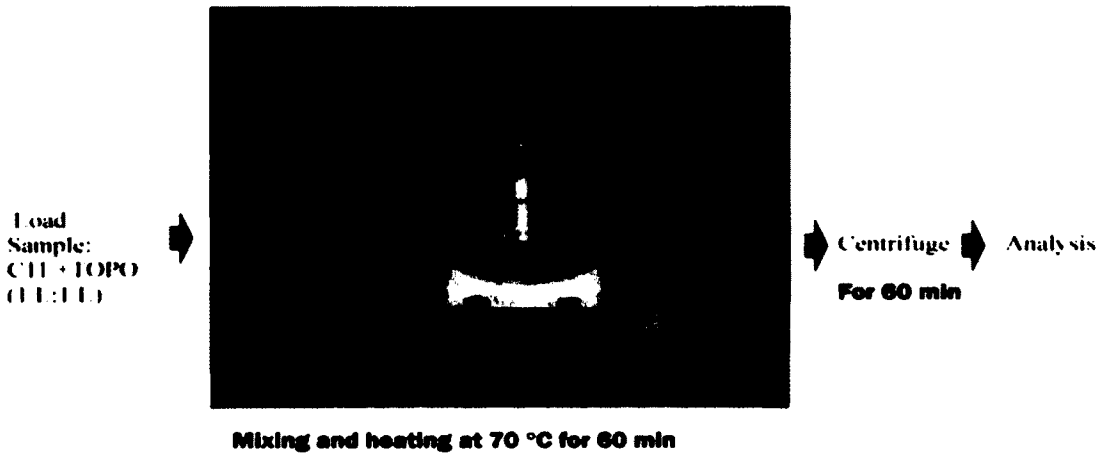



Figure 2.7 Photograph of 3L liquid-liquid extraction system

### *2.2.3 Agitation*

Vigorous agitation was recommended to perform a liquid- liquid extraction. Different mixing techniques were tested to find the optimum method of mixing aqueous solution with organic solvent and with a high extraction performance. These included shaking by hand, machinery shaker and mixing by using magnetic stirrer. In addition, testing with no agitation was also tried.

10 or 20 mL of aqueous solution was taken into a 50 mL centrifuge tube and mixed with an organic solvent such as TOPO in undecane at a specific volume ratio (v/v) of organic to aqueous phases. Four more tubes of above mixture were prepared to be used for the agitation test. One tube was taken to be shaken by hand for 30 seconds and heated (as needed) at 70 °C for 5 min by using a heating mantle [15]. This step was repeated six times. Two tubes were put into the shaker (I 24 Incubator Shaker series, New Brunswick Scientific) in either a horizontal or vertical position (Figure 2.8). Then the shaker was run for 30 minutes at room temperature. A magnetic stirrer was put in one mixture tube and the mixture was agitated for 30 minutes on a stirring plate (Thermo Scientific Cimarec

stirring hot plate) and at room temperature. The fifth tube was kept without agitation for 30, 60, 90, 120 minute. Next all the five mixture tubes were centrifuged at 9000 rpm for 30 min. The aqueous and organic phases were separated carefully from each other by using a pipette.

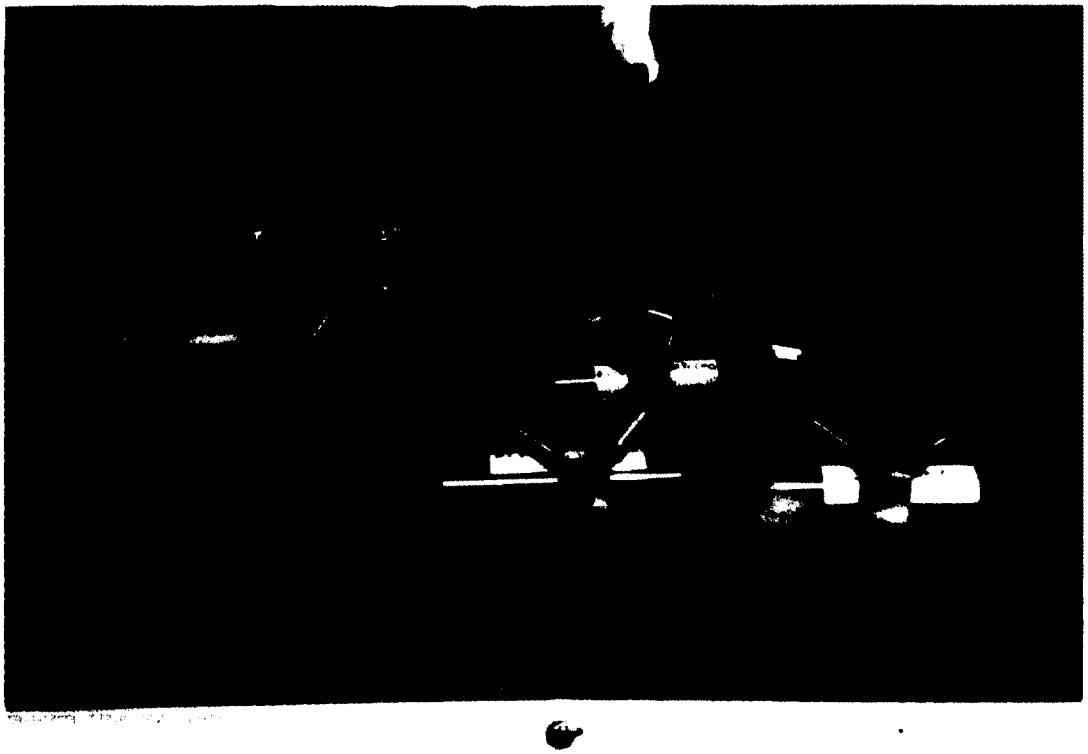


Figure 2.8 Mixture of aqueous and organic solution in 50 mL centrifuge tube was put horizontally in I 24 Incubator Shaker series

### *2.2.4 Centrifuge*

A centrifuge was used to enhance the separation of the two phases. For the small scale experiments, the 50 mL centrifuge tubes were mounted in a Sorvall RC-6 Plus super speed centrifuge from Thermo Electron Corporation with F13-S14x50 rotor spinning at 9000 rpm for 30 minutes. For the large scale experiments, the same centrifuge

with F9-SLC-4000 rotor and 1000 mL centrifuge bottles (Fisher Scientific model Sorvall) was used at 8000 rpm for 60 minutes. The effect of using centrifuge on separation of aqueous and organic phases was tested. Two 50 mL centrifuge tubes of 20 mL of aqueous solution mixed with an organic solvent at a specific volume ratio (v/v) of organic to aqueous phases were prepared. The tubes were shaken by hand for 30 minutes to perform liquid-liquid extraction. One tube was spun at 9000 rpm for 30 minutes by using Sorvall RC-6 Plus super speed centrifuge. The second tube was kept still for a week, for which the separation between the phases happened only by gravity force. From the results shown in chapter three, using the centrifuge improved and accelerated the separation between aqueous and solvent phases. As a result, the extraction percentage increased.

### *2.2.5 Acids Recovery*

Separation processes are applied to recover mixed acids from the organic phase while the organic solvent was recycled back to extraction process. Results present the extraction and recovery efficiencies. Three separation techniques were studied in this research to recover acids from the organic phase. These were the distillation system, acids precipitation using solid bases and back extraction with an aqueous sodium hydroxide solution.

#### *2.2.5.1 Distillation Apparatus*

Distillation apparatus was used to recover mixed acids from the organic solution and recycle the organic solution to be reused in liquid-liquid extraction. Distillations were conducted using different scale equipment. The systems consisted of a boiling flask (50-3000 mL capacity), a heating mantle to heat the solution, a short neck and distillation column, condenser and a distillate, or receiving flask (Figure 2.9).

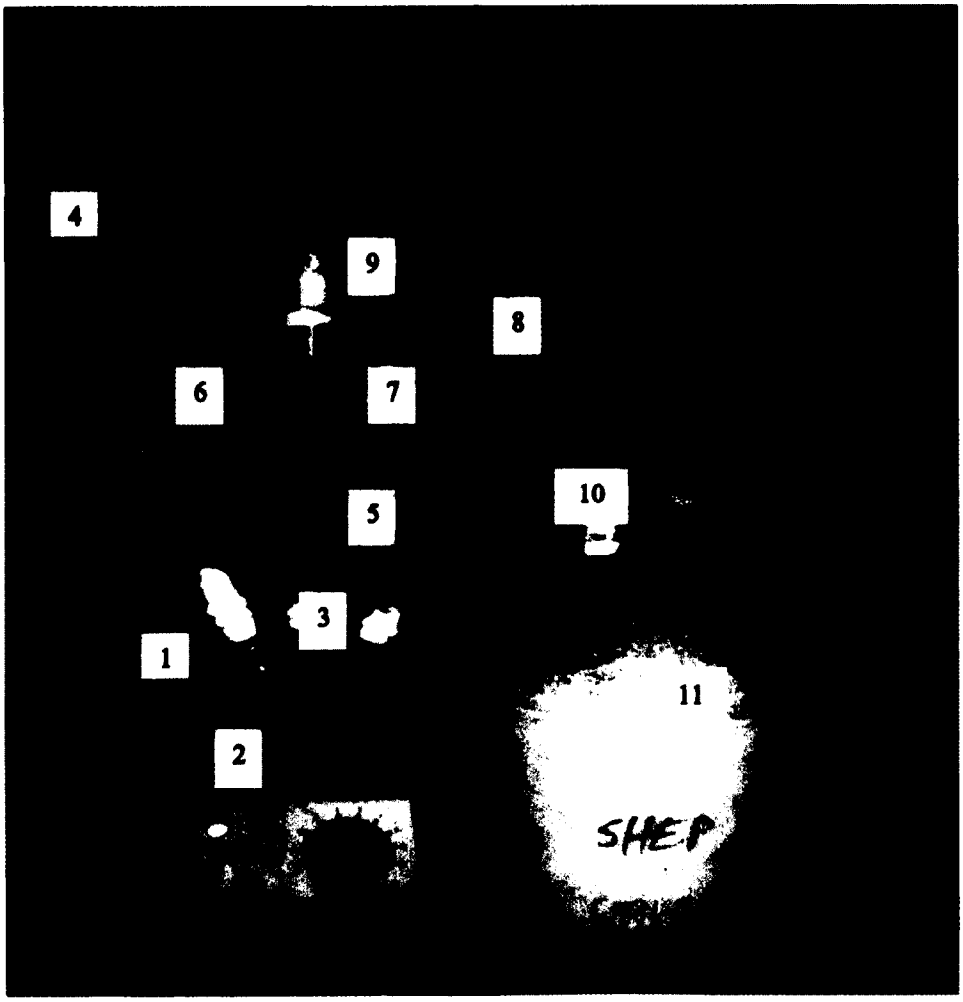



Figure 2.9 Photograph of distillation system: **1:** A heating mantle **2:** Heat control 3: Boiling flask **4:** Thermometer 5: Sampling outlet 6: Distillation column **7:** Condenser **8:** Cooling water in **9:** Cooling water out **10:** Distillate/receiving flask **11:** Ice pocket

The distillation ran as follows:

1. The organic solution after liquid-liquid extraction was transferred to a round-bottom boiling flask.
2. 2-3 boiling chips were added to avoid violent boiling.
3. The boiling flask was connected to a distillation column and heated gradually by using a heating mantle.

4. Cooling water (18 °C) was applied to the condenser tube.
5. The receiving flask was cooled by using crushed ice in a jacket around the flask.
6. The organic acids separated from organic solution were collected in the receiving flask after approximately 1-2 hours running time.

The recovered acids from distillation might include some organics such as undecane, so a centrifuge was applied for final separation of the acids in the condensate. Some modifications have been used to improve distillation performance. Results of these modifications are shown and discussed in the results and discussion chapters. Six scenarios implemented to improve distillation performance are shown in table 2.7. However the results showed that distillation was not able to recover the longer carbon chain acids from the extraction solvent. Therefore, another separation technique, which was acid salts precipitation, is discussed next section.

Table 2.7 Modification of distillation system to improve acid recovery from solvent

| Scenario # | Distillation Rate (Heating) | Boiling Flask | Distillation Column | Distillation Condenser | Retention Time (min) | Solvent to Undecane |
|---|---|---|---|---|---|---|
| 1 | Slow | None | None | None | 240 | Pure |
| 2 | Fast | Boiling chips 1/3 headspace | None | None | 15 | Pure |
| 3 | Moderate | Boiling chips 1/3 headspace | Heating lamps | None | 120 | Pure |
| 4 | Moderate | Boiling chips 1/3 headspace | Insulated | None | 120 | Pure |
| 5 | Moderate | Boiling chips 1/3 headspace | Insulated | Cooling by ice pack | 120 | Pure |
| 6 | Moderate | Boiling chips 1/3 headspace | Insulated | Cooling by ice pack | 120 | 1:1 |

*2.2.5.2 Acid Salts Precipitation*

An organic solution, such as Trialkylphosphine oxide, or CYANEX 923, is mixed with fermented wood extract to extract mixed carboxylic acids. The extraction was highly effective, however it was shown that distillation was not able to recover the longer carbon chain acids from the extraction solvent. Therefore, in these experiments, the mixed acids are recovered from the organic phase in the form of acid salts, such as calcium acetate [51-52]. Different types of calcium base, including calcium hydroxide, calcium carbonate and calcium oxide, were used to precipitate and separate the mixed acids from the organic solution. The mixture is agitated, centrifuged and filtered to separate the solid and liquid phases (Figure 2.10).

Small scale10 or 20 mL of organic solution after liquid liquid extraction (which includes the extracted mixed acids) was taken into a 50 mL centrifuge tube. A certain mass of solid such as calcium hydroxide (ex. 1:1 molar ratio, moles of solid bases to total moles of acids) was added to the organic solution and the mixture was agitated by shaker in a horizontal position for 30 minutes. Then, the resulting solids, containing residual solid bases and precipitated organic salts, were separated from the liquid by filtration under vacuum. Next, the filtrated solids were placed in an oven at 120 °C and dried for a week (Figure 2.11). Meanwhile, the organic solution after filtration was centrifuged at 9000 rpm for 30 min to precipitate additional solids. The above filtration procedure was repeated to separate the solid from the liquid. Finally, the organic solution was taken for analysis by GC while the dry solids were dissolved in DI water and the resulting aqueous solution taken for analysis by HPLC or GC. DI water was used as needed to wash the organic solution after this experiment to remove more solid particles and make the

organic more suitable for recycling. Different types of solid bases were tested for this research and results were shown and discussed in the results chapter.

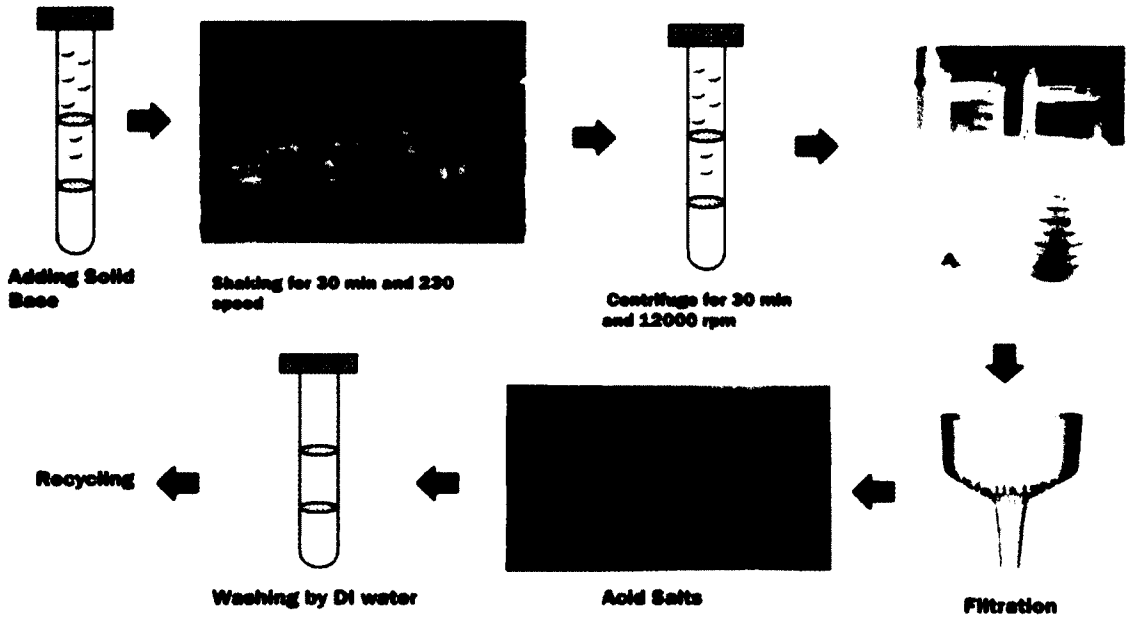



Figure 2.10 Flow diagram of acid salts formation

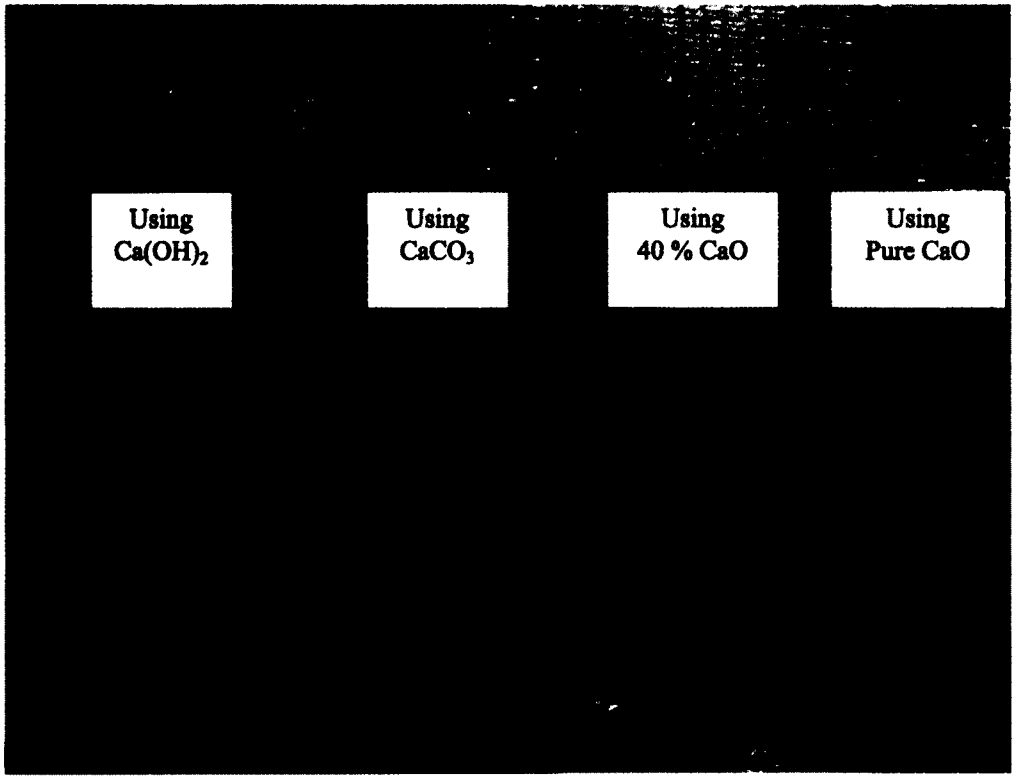



Figure 2.11 Different types of dried solid bases after acids precipitation and filtration

Note: Pure of calcium hydroxide ($Ca(OH)_2$) , calcium carbonate ($CaCO_3$) and calcium oxide (CaO) are used as well as 40 % CaO in 60 % of mixture bases such as Magnesium, Magnesium oxide, calcium hydroxide and calcium carbonate , 1 g of each bases adding initially.

Similar to distillation technique, the results showed that separating acids from solvent by acid salts precipitation technique was also not able to recover the longer carbon chain acids from the extraction solvent. Therefore, another separation technique, which is back extraction with a dilute aqueous sodium hydroxide solution, is discussed in the section.

### *2.2.6 Back Extraction with a Dilute Aqueous Sodium Hydroxide (NaOH) Solution*

An organic solution, such as trialkylphosphine oxide, or CYANEX 923, was mixed with fermented wood extract to extract mixed carboxylic acids. The extraction was

highly effective, however it was shown that distillation and acid precipitation were not able to recover the longer carbon chain acids from the extraction solvent. Therefore, in these experiments, the mixed acids are recovered from the organic phase in the form of sodium acid salts, such as sodium acetate salts, dissolved in water. The mixture is agitated and centrifuged to separate the organic and sodium aqueous phases. Next a dilute hydrochloric acid solution, HCL, was added to both organic and sodium aqueous solutions to release the carboxylic acids from the salts before analysis with GC.

Small scale10 or 20 mL of organic solution after liquid liquid extraction (which includes the extracted mixed acids) was taken into a 50 mL centrifuge tube. A certain molar concentration (0.9 moles NaOH in aqueous solution, or 3 molarity ratio of $OH^-$ to $H^+$ ratio) of sodium hydroxide solution was mixed to the organic solution to preform back extraction. The volume ratio (v/v) of organic to sodium aqueous solutions was 1:0.5 to concentrate the carboxylic acids in aqueous phase. Next the mixture was agitated by shaker in a horizontal position for 30 minutes and centrifuged at 9000 rpm for 30 min. The organic and aqueous phases were separated from each other by carefully using a pipette (Figure 2.12). Then a dilute hydrochloric acid solution was added to both organic and sodium aqueous solutions to lower the pH and release the carboxylic acids from the salts before analysis with GC. For organic phase, a certain amount of HCL was added to lower pH before analysis by GC and to remove the excess sodium hydroxide in solvent. As result, sodium chloride salts were formed and participated out from the solvent. Next, the mixture was centrifuged at 9000 rpm for 30 min and organic phase was separated from solid salts by using a pipette to be recycled again. Similarity, 10 N of hydrochloric acid (HCl) was added to sodium aqueous solution after back extraction to lower pH and

release the carboxylic acids from sodium salts. Because the long chain acids are less soluble in aqueous solution, a certain amount of pure CYANEX was added to the aqueous solution to quantify all released acids from sodium salts in aqueous solution. Then, the liquid liquid extraction product was accomplished and both organic and aqueous phases were analysis by GC. The results are shown and discussed in the results chapter.

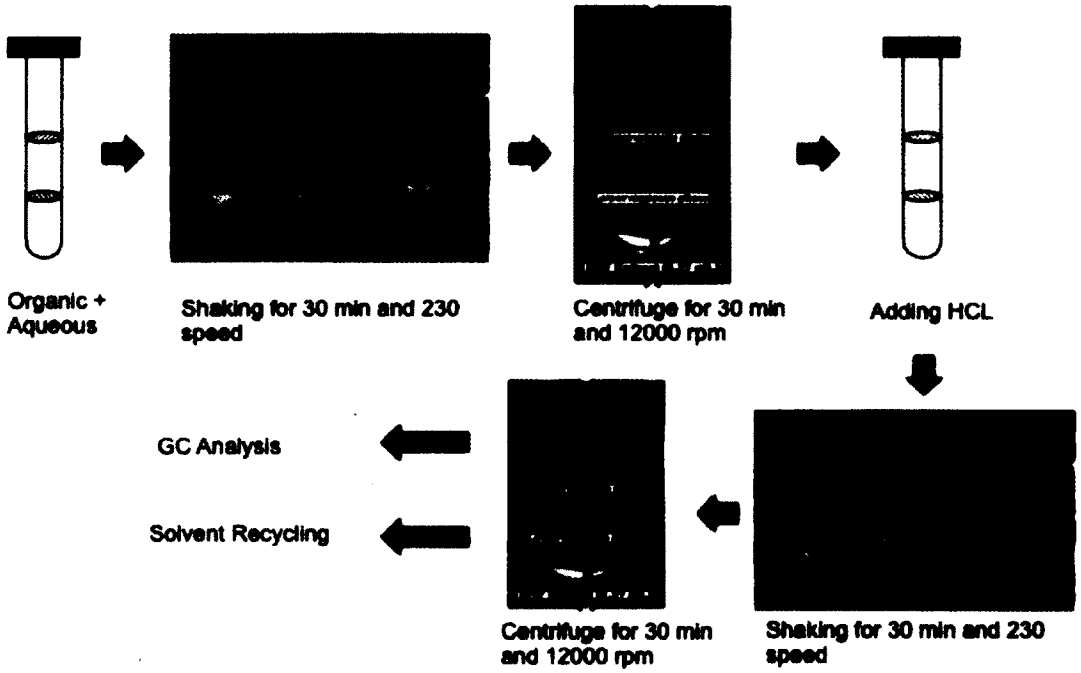



Figure 2.12 Diagram for small scale procedure of back extraction with a dilute aqueous sodium hydroxide solution

### *2.2.7 Washing with Sodium Hydroxide (NaOH)*

In the case of extracting mixed acids from real wood extract, some amount of lignin could be transferred with these acids into the organic solution. Therefore, when recycling the solvent, washing with 1 M of NaOH is a beneficial step to remove the soluble lignin from the organic solution (Figure 2.13). The washing procedure at large

scale was started by mixing 1 L of the organic solution after the distillation with 1 L of 1 M of NaOH in a 3 L mixing tank with stirrer. Then the mixture was agitated and heated for 1 hour at 70 °C by using a hot plate. Next the mixture was centrifuged at 9000 rpm speed for 1 hour. Finally, the two phases were separated carefully from each other by using a vacuum aspiration system.

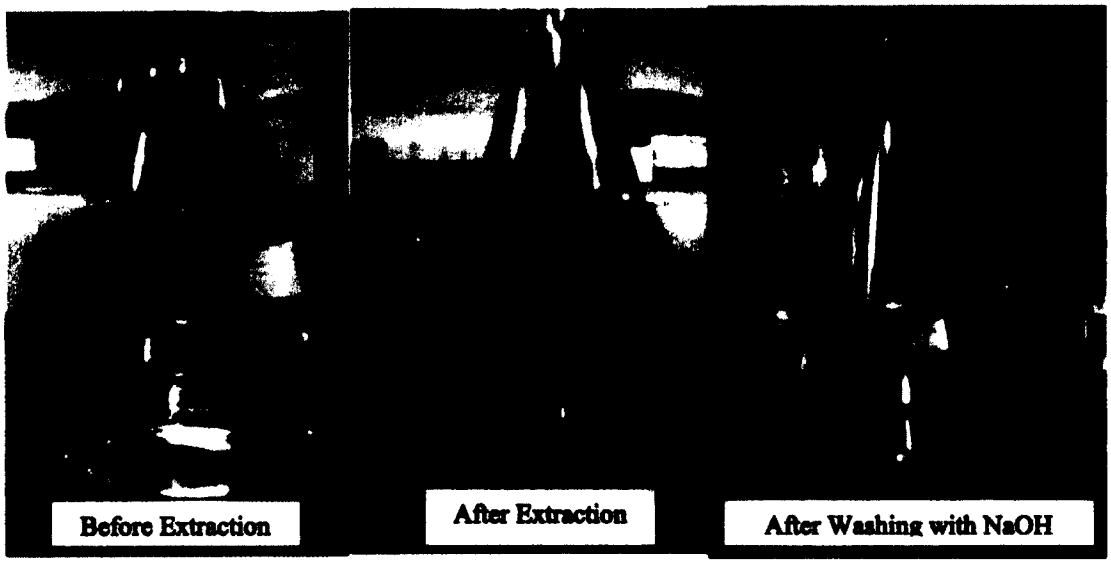



Figure 2.13 TOPO solvent before and after washing with 1 M NaOH

### *2.2.8 Aqueous and Organic Analysis*

After liquid-liquid extraction, the aqueous phase was analyzed for mixed carboxylic acids by HPLC and GC, while organic and sodium aqueous phases were analyzed by only GC. Lignin in the hemicellulose extract was analyzed by using ultraviolent light at 280 nm. The water content in the organic solution was measured by Karl Fischer Titration.

### *2.2.8.1 High Performance Liquid Chromatography (HPLC)*

High performance liquid chromatography, or high pressure liquid chromatography, HPLC, is a device used to identify and quantify compounds. It has been used frequently in many important application areas such as biochemistry and analytical chemistry as an analytical device. HPLC consists of a column (stationary phase) that holds chromatography packing material, a pump that moves the mobile phases through the column and a detector to identify the compounds and show the retention times of the separated molecules (Figure 2.14 [53]).

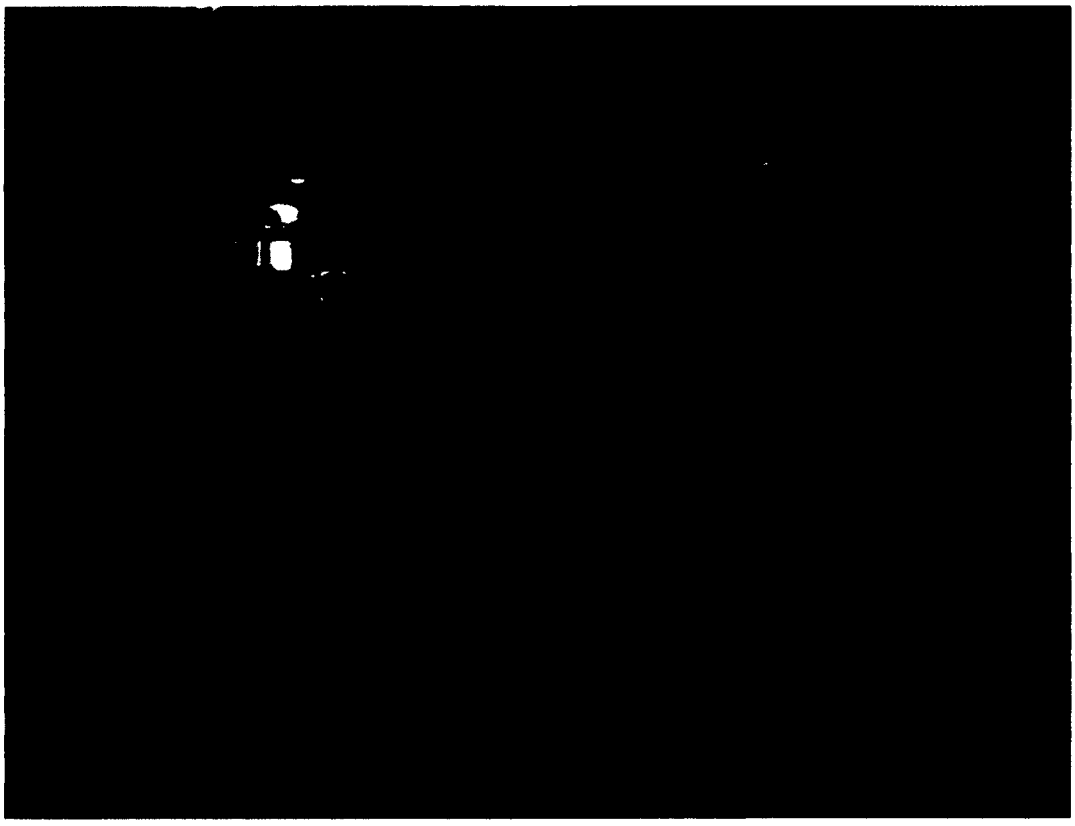


Figure 2.14 High Performance Liquid Chromatography, HPLC

About 60 % of the worldwide separation science market is served by HPLC while about 35% by gas chromatography, GC [53]. The refractive index, RI, is the ratio of

speed in vacuum of an electromagnetic wave, when it passes from one medium to another, to the speed in given medium. RI is a universal property of light transmitting materials and can be used to detect any compound. The change in RI of the mobile phase is due to the presence of dissolved analyte.

HPLC retention times are 5- 30 min depending on the analytical compound which is faster than classical column chromatography, where the column is gravity fed and taken hours or even days for separation.

As one example, the aqueous phase of hemicellulose extract, which has sugars and some amount of acetic acid, was quantitatively analyzed by HPLC with RI detector. A Shimadzu model LC-10AT HPLC was equipped with a Bio-Rad Aminex HPX-87H column kept at 60 °C and 5 mM $H_2SO_4$ eluent at a flow rate of 0.6 mL/min.. The concentrations of the analytes were quantified using an internal standard and a calibration curve prepared with known concentrations.

Standard samples were prepared by taking different known concentrations (0.3-5 g/L) of the desired analyte, in this case acetic acid, dissolved in DI-water as described in the following (Table 2.8):

1. 10 g/L concentration of acetic acid in water was prepared and used as stock solution.
2. Different volume samples (0.3-5 mL) from the stock were taken.
3. Pure water was added to each sample to make equal volume (10 mL total volume).
4. 1 mL of each sample was mixed with 1 mL of diluted fucose (internal standard).

Table 2.8 Standard sample preparation for HPLC analysis

| HAc g/L | Stock mL | Water mL | Total mL |
|---|---|---|---|
| 0.3 | 0.3 | 9.7 | 10 |
| 1 | 1 | 9 | 10 |
| 3 | 3 | 7 | 10 |
| 5 | 5 | 5 | 10 |

Then the samples were injected into the HPLC. The analysis is shown in table 2.9. The HPLC chromatogram shows the peak of acetic acid and the internal standard. By taking the area under the acetic acid peak divided by the area of the internal standard peak, the area ratio was determined. Then the calibration curve was obtained by plotting the standard sample concentration of acetic acid verses the area ratio of acetic acid to internal standard (Figure 2.15).

Table 2.9 HPLC analysis

| HAc g/L | HAc area | Fucose area | Area Ratio |
|---|---|---|---|
| 0.3 | 3862 | 2476626 | 0.0016 |
| 1 | 45795 | 2466059 | 0.0186 |
| 3 | 139557 | 2485103 | 0.0562 |
| 5 | 233046 | 2485803 | 0.0938 |

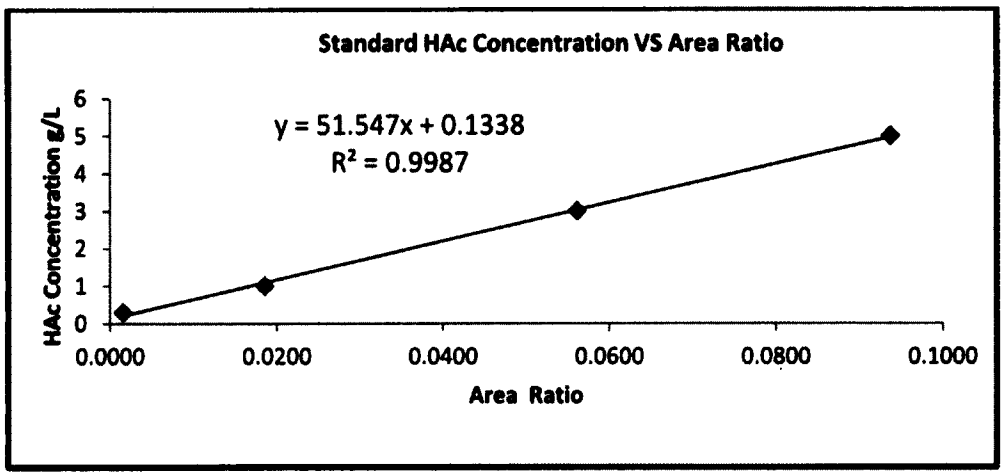



Figure 2.15 Calibration graph of acetic acid analysis by HPLC

Unknown samples were taken for HPLC analysis to find out organic acid concentrations. 1 mL was taken from the unknown sample and diluted 10 times by adding water. 1 mL of the sample was mixed with 1 mL of internal standard and then the solution was injected into HLPC for analysis. The area ratios of sample peaks to the internal standard were determined from the HPLC chromatogram. Finally, by using the calibration equation for each compound, the concentrations in the unknown sample were determined. The dilution factor should be considered to get the correct concentration of acetic acid in the sample.

***2.2.8.2 Gas Chromatography (GC)***

Headspace gas chromatography, from Shimadzu Scientific Instrument, with auto injector AOC-5000 and FID detector was used to analyze both aqueous and organic solutions. Polar and non-polar columns used were Stabilwax-DA (30m, 0.25mm ID, 0.25μm film-thickness) and RTX5 (30m, 0.32mm ID, 0.1 μm film-thickness), respectively. The polar column was used to separate the components according to polarity of interaction between injection samples and GC column and boiling point of

samples, while the non-polar column works according to boiling point only [55]. The carrier gas was helium.1 μL of sample was injected at specific temperature depends on injection component and detector temperature was reaching up to 360 °C (Figure 2.16).

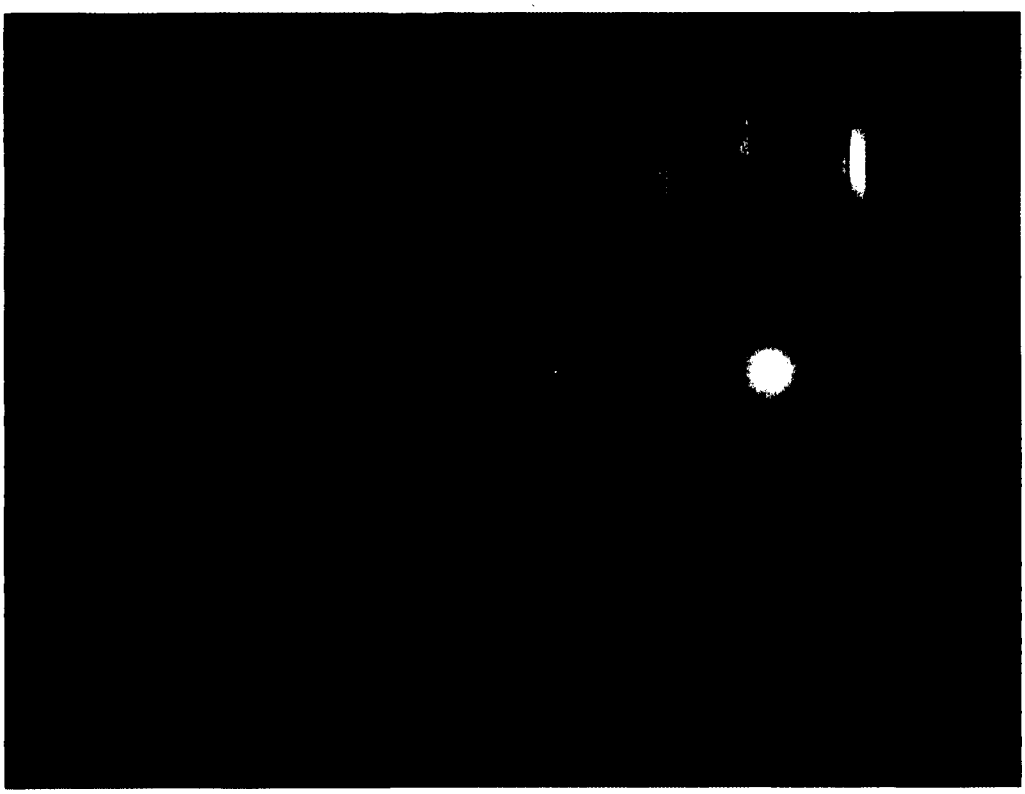


Figure 2.16 Gas Chromatograph with a headspace sampler

Gas Chromatography was used to analyze aqueous and organic solutions before and after the liquid liquid extraction and distillation steps to determine the amount of carboxylic acids extracted in both phases [54]. Two GC analytical methods were used to analysis carboxylic acids. These were analytical method for aqueous and for organic solutions.

#### *2.2.8.2.1 Analytical Method for Aqueous Solution*

GC analytical method for aqueous solution is a method used to determine the amount of carboxylic acids in aqueous solution before and after liquid-liquid extraction. A polar GC column (Stabilwax-DA) is used. A calibration curve and an internal standard reference solution are used for calculating carboxylic acids in aqueous solution.

The calibration curve made use of five standard sample levels that were prepared by taking different known concentrations (0.01-5 g/L) of six carboxylic acids (acetic, propionic, butyric, valeric, carpoic and heptanoic acids) and dissolving in DI water (Table 2.10), prepared as following:

1. 10 g/L concentration of each six acids in 100 mL DI water was prepared and used as stock solution.
2. Different volume samples (0.001-1 mL) from the stock were taken and diluted with 1 ml DI water to make five standard levels concentration (0.01-5 g/L).
3. Duplicate samples from each standard level were injected directly to GC.
4. The calibration graph was made by plotting standard concentrations on the Y axis versus the GC areas on the X axis.

Table 2.10 Standard sample preparation for GC analysis of aqueous solution

| | | **From Stock** | **Total** |
|---|---|---|---|
| | **g/L** | **mL** | **mL** |
| 1 | 0.01 | 0.001 | 1.001 |
| 2 | 0.1 | 0.01 | 1.01 |
| 3 | 1 | 0.11 | 1.11 |
| 4 | 3 | 0.43 | 1.43 |
| 5 | 5 | 1 | 2 |

For the unknown sample, 0.01 mL was taken and diluted with 1 mL DI water in a GC vial. Then the vial was injected into the GC to be analyzed. Finally, by using the calibration equation, the concentration of the unknown sample was determined.

Another way to determine the amount of carboxylic acids is using an internal standard reference solution. The method is used by comparing unknown samples with a known reference solution to determine unknown concentration. A volatile acids mixture solution (by Matreya) is used as internal standard reference solution (Table 2.11). 1.162 g/L of Isocaproic acid was prepared and used as internal standard solution for calculation of unknown samples. The procedure is done as following:

1. Samples of internal standard reference solution were injected directly to GC and peak areas of each acid were determined.
2. Table 2.13 and above areas were applied with equation 2.3 (below) to calculate response factor (RF).
3. For unknown sample, 0.01 mL was taken and mixed with 1 mL internal standard solution (1.162 g/L of isocaproic acid) in a 1.5 mL GC vial.
4. The vial was injected to GC to be analyzed and areas of each acid were determined.
5. Apply RF and above areas for unknown samples in equation 2.3 to calculate unknown samples concentrations.

Table 2.11 Acids concentrations in internal standard reference solution

| Acids | g/L |
|---|---|
| Formic acid | 0.46 |
| Acetic acid | 0.601 |
| Propionic acid | 0.741 |
| Isobutyric acid | 0.881 |
| Butyric acid | 0.881 |
| Isovaleric acid | 1.021 |
| Valeric acid | 1.021 |
| Isocaproic acid | 1.162 |
| Caproic acid | 1.162 |
| Heptanoic acid | 1.302 |

$$\mathbf{RF} = \frac{A_{IS} * C_{acid}}{A_{acid} * C_{IS}} \qquad (2.3)$$

Where RF is response factor, $A_{IS}$ is area of internal standard (1.162 g/L of isocaproic acid), $A_{acid}$ is area of carboxylic acids, $C_{IS}$ is concentration of internal standard and $A_{acid}$ is area of carboxylic acids.

***2.2.8.2.2 Analytical Method for Organic Solution***

GC analytical method for organic solution is used to determine the amount of carboxylic acids in organic solution before and after liquid-liquid extraction and distillation system. A polar GC column (Stabilwax-DA) and non-polar column (RTX5)

were used for this analysis. The carrier gas was helium, He, 1.7 mL/min constant flow and the split ratio was 1:100. 1 μL of sample was injected at 340 °C at injection port. Then the sample was heated with a temperature profile of 2-5 °C/min at column oven and up to 250 °C. Finally, the sample was detected by a FID detector at temperature of 340 °C (Figure 2.17).

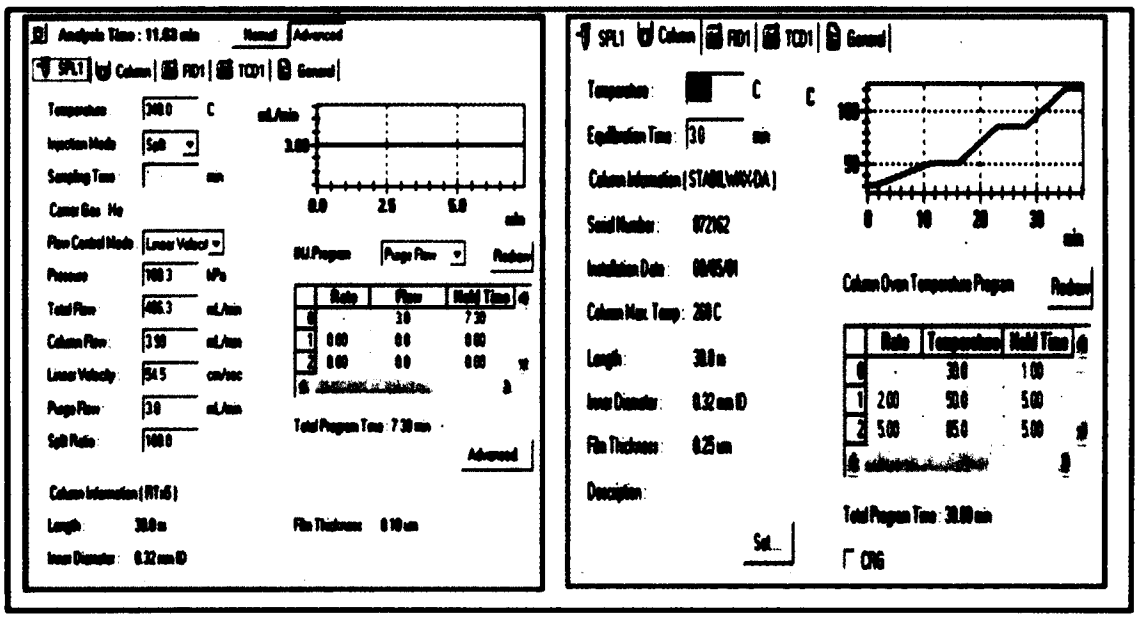


Figure 2.17 Screen monitor of GC specification for injection (on right) and column (on left) sections from GC soft ware using non polar column (RTX5)

The calibration graph is used for both columns to calculate carboxylic acids in organic solution. The polar GC column has shown better separation and detection of acids than the non polar column due to the acids separation in the polar column depending on the polarity of interaction between injection samples and the column, and the boiling point of samples, while for the non polar column, only the boiling point distinguishes the acids (Table 2.12 and Figure 2.18).

Table 2.12 Retention time and boiling points of carboxylic acids, Undecane and CYANEX 923 using polar column (Stabilwax-DA)

| # | | Components | Retention Time min | Boiling Point °C |
|---|---|---|---|---|
| 1 | | Acetic Acid | 1.207 | 118 |
| 2 | | Propionic Acid | 1.609 | 141 |
| 3 | | Butyric Acid | 2.531 | 163.5 |
| 4 | | Valeric Acid | 4.464 | 186 |
| 5 | | Hexanoic Acid | 5.178 | 204 |
| 6 | | Heptanoic Acid | 5.579 | 223 |
| 7 | | Undecane | 5.447 | 196 |
| 8 | CYANEX 923 | Trihexylphosphine oxide | 8.18 | 310 |
| 9 | | Dihexylmonooctylphosphine oxide | 8.758 | 310 |
| 10 | | Dioctylmonohexylphosphine oxide | 9.579 | 310 |
| 11 | | Trioctylphosphine oxide | 10.831 | 310 |

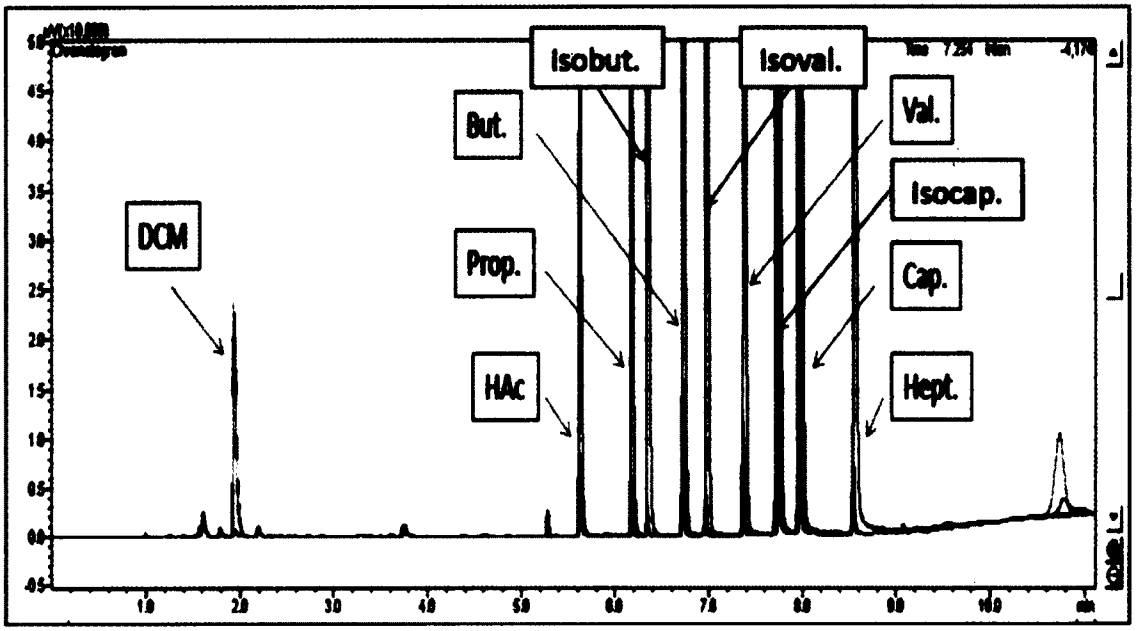



Figure 2.18 Peaks and retention time of carboxylic acids from GC screen monitor using a polar column (Stabilwax-DA)

Note: DCM is dichloromethane

Different concentrations (0.001-100 g/L) of mixed acids (acetic, propionic, butyric, valeric, caproic and heptanoic acids) in pure CYANEX 923 were prepared to test GC column (Tables 2.13).

Table 2.13 Different concentrations of mixed carboxylic acids analyzed by using polar column (Stabilwax-DA)

| # | g/L in DI Water | g in 1 uL injected to GC | Comments |
|---|---|---|---|
| 1 | 100 | 1.1E-06 | Very big peaks cause overlapping |
| 2 | 50 | 5.5E-07 | Very big peaks cause overlapping |
| 3 | 10 | 1.1E-07 | Showing peaks |
| 4 | 5 | 5.5E-08 | Showing peaks |
| 5 | 1 | 1.1E-08 | Showing peaks |
| 6 | 0.5 | 5.5E-09 | Showing peaks |
| 7 | 0.1 | 1.1E-09 | Showing peaks |
| 8 | 0.01 | 1.1E-10 | Very small peaks |
| 9 | 0.001 | 1.1E-11 | No peaks showing |

For a calibration graph method, five standard sample levels were prepared by taking different known concentrations (0.01-10 g/L) of six carboxylic acids (acetic, propionic, butyric, valeric, carpoic and heptanoic acids) and dissolving in dichloromethane (DCM) (Table 2.14), prepared as follows:

1. 2 g from each of the six acids were totally mixed with 2 g of pure CYANEX 923 at total mass and volumes of 16 g and 17.5 mL, respectively, and used as stock solution. About 115 g/L of each acid is concentrated in the total solution.
2. Different volume samples (0.1-100 uL) from the stock were taken and diluted with 1 mL DCM to make five standard levels concentration (0.01-10 g/L).
3. Duplicate samples from each standard levels were injected directly to GC.

The calibration graph was made by plotting the standard level concentrations on the Y axis versus GC areas on the X axis (Appendix E).

Table 2.14 Standard sample preparation for GC analysis of organic solution

| | g/L | From Stock uL | Total mL |
|---|---|---|---|
| 1 | 0.01 | 0.1 | 1.0001 |
| 2 | 0.1 | 1 | 1.001 |
| 3 | 1 | 10 | 1.01 |
| 4 | 5 | 45 | 1.045 |
| 5 | 10 | 100 | 1.1 |

For unknown sample, 0.01 mL was taken and diluted with 1 mL DCM in a GC vial. Then the vial was injected to GC to be analyzed. Finally, by using the calibration equation, the concentration of the unknown sample was determined.

***2.2.8.3 Ultraviolet (UV) for Lignin Analysis***

The Nicolet Evolution 100 UV-Vis spectrophotometer, from Thermo Electron Corporation, was used for lignin analysis. Absorbance at 280 nm was used to quantify the lignin with a standard calibration curve (Figure 2.19).

Figure 2.19 Ultraviolent (UV) device

A certain amount of aqueous or organic solution (about 2 mL) was dispensed into a quartz macro cell (Cuvette, 10mm, from Agilent Technologies). Next, the cell was put inside the UV device and the analysis was run. The amount of lignin absorption by UV light was determined at wavelength 280 nm. Then the concentration of lignin in the solution was calculated by using the equation below.

$$C = \frac{A}{e \times L} \qquad (2.4)$$

Where A is lignin absorption by UV

e is specific absorption (g/L.cm) =20 for hardwood and 24 for softwood

C is lignin concentration (g/L)

L is light path length (cm) (absorption tub width) = 1 cm

### *2.2.8.4 Karl Fischer Titration*

Karl Fischer Titration, KFT, is a method used to analyze the water content in organic solutions. A Brinkmann Metrohm coulometric Karl Fischer Titrator, available from Fisher, was used to determine trace quantities of water in the organic phase. It includes platinum generator electrode, double platinum indicator electrode, titration vessel, and magnetic stirrer (Figure 2.20).

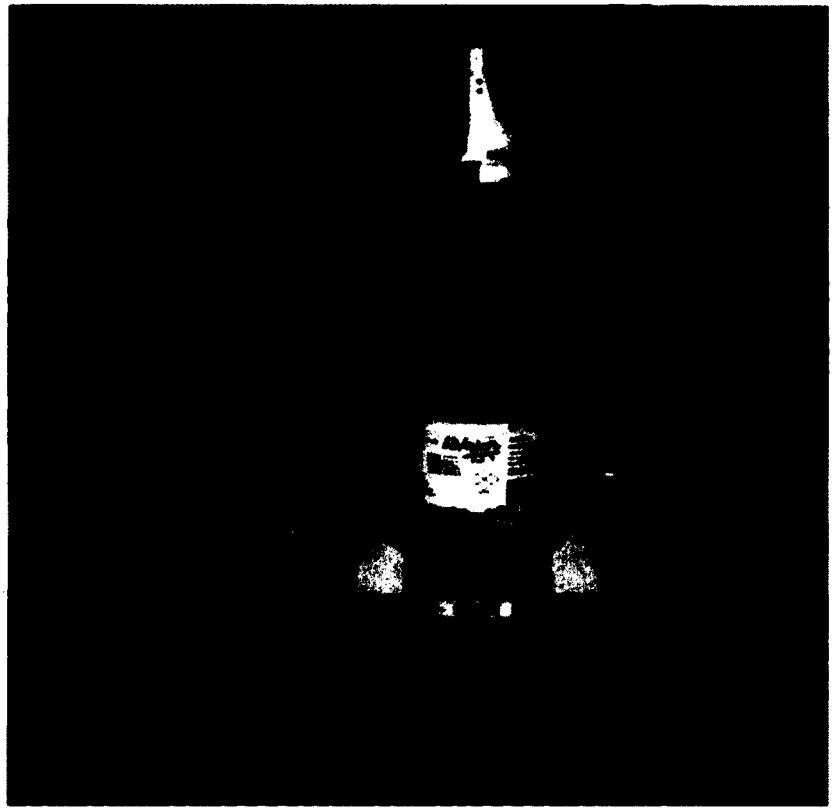


Figure 2.20 Karl Fischer Titration device

KFT is a classic titration method in analytical chemistry that was found by the German chemist Karl Fischer in 1935. The anode solution in the titration cell consists of an alcohol (such as methanol or diethylene glycol monomethyl ether), a base (such as

imidazole), $SO_2$ and $I_2$. When current is run through the electric circuit, $I_2$ is generated. Then, $I_2$ reacts with $SO_2$ as shown below and that will consume the water in the sample. Finally, the amount of water is calculated by the amount of current needed to generate $I_2$ in order to reach the end point [55].

$$B{\bullet}I_2 + B{\bullet}SO_2 + B + H_2O \rightarrow 2BH^{+}I^{-} + BSO_3 \qquad (2.5)$$

$$BSO_3 + ROH \rightarrow BH^{+}ROSO_3^{-} \qquad (2.6)$$

Where: B is base and ROH is alcohol

### *2.3 Constraints*

The mixed carboxylic acids recovery efficiency from solvent may be constrained by recovering CYANEX 923 through a distillation system. It appears that the CYANEX and the higher molecular weight acids develop boiling point changing behavior in the distillation process. As a result of this, acid recovery from solvent becomes more difficult.

Similarly mixed acids recovery from solvent can be also constrained when adding different types of bases to make acid salts and precipitate them from the solvent. Adding bases will react with acids in organic phase and appear to make acid-base-solvent complexes which are not totally separated and precipitated from the organic phase as acid salt. In addition, small amounts of acid-base salts are precipitating from solvent while the

majority the salts appear to be staying in the solvent as complex compounds. Therefore, the mass balance of making acid salts becomes difficult to achieve.

At small scale and using less than 10 g/L of mixed carboxylic acids as initial concentration, the distillation performance is constrained because a very small amount of acids will be separated (such as 0.06 g for acetic acid) and it is difficult to quantify this small amount. In addition, some acids are volatile such as acetic acid and preventing loss to evaporation is difficult. Therefore, very small amounts of extracted acids make them very hard to keep good track of all mass flows.

Analyzing the organic solution by GC can be constrained by some components such as DCM and sulfuric acid. For example, DCM is a very volatile component, and this makes it difficult to be used for analytical method. Therefore, it needs special tools to handle it such as pipetters with piston for more accurate volume dispensing and tubes with well sealing caps. Similarly, using sulfuric acid to lower pH for acids extraction effects the GC analysis because its boiling point is higher than the maximum temperature of GC. As a result of that GC column will be ruined.

Distillation parameters such as using boiling chips, boiling temperature and distillation column height can cause bad separation if they are not well matched to each other.

### *2.4 Experimental Design*

Some extraction experiments have been done to find the best extraction conditions using TOPO, TOA and CYANEX 923. These were:

- Effect of concentrations of solvent in the organic solution
- Effect of ratio of organic to aqueous phase

- Effect of pH
- Effect of temperature
- Effect of agitation on extraction % (using CYANEX 923)
- Effect of centrifuging on extraction % (using CYANEX 923)

***2.5 Extraction Conditions***

Different initial concentrations of mixed carboxylic acid (5- 20 g/L) dissolved in DI water were prepared to study extraction conditions.

From pervious works (Master research), the concentration of solvent in the organic solution, such as concentration of TOPO in undecane, has been studied to find the effect of solvent concentration on extraction efficiency. The extraction was carried out for the clean system (acetic acid in DI-water). Therefore, extraction by using TOPO, different organic samples with different concentrations (50- 550 g/L) of TOPO in undecane were prepared and mixed with fresh 10 g/L concentration of acetic acid in water. The extraction conditions were pH 1, 70 °C extraction temperature and 1:1 volume ratio of organic to aqueous phases. In addition, extraction by TOA, with different organic samples at different concentrations (100- 500 g/L) of TOA in octanol were prepared and mixed with fresh 10 g/L concentration of acetic acid in water. The extraction conditions were 2.9 pH, 70 °C extraction temperature and 1:1 volume ratio of organic to aqueous.

Similarly, the volume ratio of organic to aqueous phases was studied from Master research by testing different ratios for the clean system. [0.25:1], [0.5:1], [0.67:1], [1:1], [1.5:1] and [2:1] samples were prepared and mixed with 10 g/L initial concentration of acetic acid in water. The extraction conditions using TOPO were 370 g/L of TOPO in undecane, pH 1 and at 70°C, while by using TOA were 200 g/L of TOA in octanol, pH

2.9 and at 70 °C. Varied pH (1- 7 pH) in the aqueous phase and varied extraction temperature (30- 90 °C) were done to study their effects on extraction efficiency. The extraction was done on the clean system (mixed acids in DI-water). Therefore, for extraction by using TOPO, 1-5 pH in 10 g/L concentration of acetic acid in aqueous solution were prepared by using sodium hydroxide and sulfuric acid and mixed 370 g/L of TOPO in undecane and 1:1 volume ratio of organic to aqueous. For extraction by TOA, 1-5 pH in 10 g/L concentration of acetic acid in aqueous solution were prepared by using sodium hydroxide and sulfuric acid and a mixture of 200 g/L TOA in octanol and 1:1 volume ratio of organic to aqueous. For extraction by using pure CYANEX 923, 1-7 pH in 10 g/L concentration of mixed carboxylic acids in aqueous solution were prepared by using sodium hydroxide and sulfuric acid and 1:1 volume ratio of organic to aqueous. The extraction temperature was varied from 30 to 90 °C and studied for using TOPO, TOA and CYANEX 923.

# CHAPTER THREE

# RESULTS & DISCUSSION

In this chapter, results are presented from experiments investigating two extraction systems: previous work on extraction of acetic acid using trioctylphosphineoxide (TOPO) and trioctylamine (TOA) as solvents, and a more recent study on extraction of mixed carboxylic acids using a mixture of four trialkyl phosphine oxides (CYANEX 923). The former study was part of my Master's research program.

The effects of different extraction conditions on the efficiency of carboxylic acid extraction are shown. I compare the current solvent used for my PhD work with solvents used previously in my Master study in order to determine which solvent is most suitable for use in a forest biorefinery. Experiments were carried out on two model systems: a "clean solution," which consists of water and mixed carboxylic acids, and a wood-derived aqueous solution from fermentation broth. Methods for recovering acids from solvents, such as distillation, acid precipitation and back extraction methods, are also included in this chapter.

The extraction conditions that were tested to determine optimal conditions using different solvents include:

- Effect of concentrations of solvent in the organic solution
- Effect of ratio of organic to aqueous phase
- Effect of pH
- Effect of temperature
- Effect of agitation on extraction % (using CYANEX 923)
- Effect of centrifuging on extraction % (using CYANEX 923)

In addition, different solvents, including: Dichloromethane (DCM), Ethyl Acetate (EA), TOA, TOPO and CYANEX 923, were compared in terms of extraction % of acetic acid and for different aqueous solutions: the clean system, hemicellulose extract and wood fermentation mixed acids solutions. Mass balances of liquid-liquid extraction, distillation and back extraction were also calculated. Furthermore, results for molar ratio effects on back extraction, and solvent recyclability of acids and solvents were included in this chapter. In addition, analyses for determining lignin and water contents in organic solution were implemented on samples from previous work using UV for lignin analysis and Karl Fischer Titration, KFT, for water analysis. Finally, a result from using a McCabe-Thiele method to determine the theoretical stages of extraction needed to achieve 94 % extraction of acids was also shown.

### *3.1 Effect of Concentrations of Solvent in Organic Solution*

Tables 3.1 to 3.3, figure 3.1 and figure 3.2 present the effects of varied concentration of extractant in the organic solution for the clean system. It shows extraction % of acetic acid affected by changing the concentration of extractant (TOPO, TOA and CYANEX) in organic solution. It is observed from the figure that when the concentration of extractant increases it results in improved acetic acid extraction. However, there is no significant extraction benefit when the concentration of extractant rises above a certain level. For example, raising TOPO concentration in undecane under constant extraction conditions (1 pH, at 70 °C and [1:1] volume ratio) will increase the extraction %, but increasing the concentration to more than 370 g/L shows little significant further improvement. Similarly, CYANEX in tridecane at constant extraction

conditions (1 pH, at room temperature and [1:1] volume ratio) shows no significant improvement as levels increase above a concentration of 400 g/L in tridecane. In addition, TOA in octanol at constant extraction conditions (2.9 pH, 70 °C and [1:1] volume ratio) shows no significant improvement as levels increase above a concentration of 200 g/L in octanol.

Table 3.1 Effects of varied concentration of TOPO in undecane

| Extractant Concentration g/L | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|
| 50 | 4.18 | 5.82 | 0.7 | 42 |
| 90 | 5.37 | 4.63 | 1.2 | 54 |
| 180 | 6.49 | 3.51 | 1.8 | 65 |
| 280 | 7.02 | 2.98 | 2.4 | 70 |
| 370 | 7.47 | 2.53 | 3.0 | 75 |
| 460 | 7.54 | 2.46 | 3.1 | 75 |
| 550 | 7.59 | 2.41 | 3.1 | 76 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, at 70 °C, pH 1, solvent : aqueous ratio [1:1]

Table 3.2 Effects of varied concentration of TOA in octanol

| Extractant Concentration g/L | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|
| 100 | 8.5 | 1.8 | 4.7 | 82 |
| 200 | 6.4 | 0.9 | 7.1 | 91 |
| 300 | 7 | 1 | 7.0 | 90 |
| 400 | 8.2 | 1.2 | 6.8 | 88 |
| 500 | 5.9 | 1.2 | 4.9 | 88 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, at 70 °C, pH 1, solvent : aqueous ratio [1:1]

Table 3.3 Effects of varied concentration of CYANEX in tridecane

| Extractant Concentration g/L | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|
| 50 | 0.81 | 9.2 | 0.1 | 8.1 |
| 100 | 2.4 | 7.6 | 0.3 | 24 |
| 200 | 5.33 | 4.7 | 1.1 | 53.3 |
| 300 | 6.68 | 3.3 | 2.0 | 66.8 |
| 400 | 7.5 | 2.5 | 3.0 | 75.2 |
| 550 | 8 | 2.0 | 4.0 | 80 |
| 600 | 8.8 | 1.2 | 7.3 | 88 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, at 22 °C, pH 1, solvent : aqueous ratio [1:1]

Figure 3.1 and 3.2 show that when the concentration of solvent in the organic extraction solution increases the extraction % will increase up to a point, after which no more significant increase of extraction is observed. Thus the active component of the extraction solution, the TOPO, TOA or CYANEX 923 can eventually attain a level of excess, after which the equilibrium is no longer affected by an increase in the quantity of the extracting solvent.

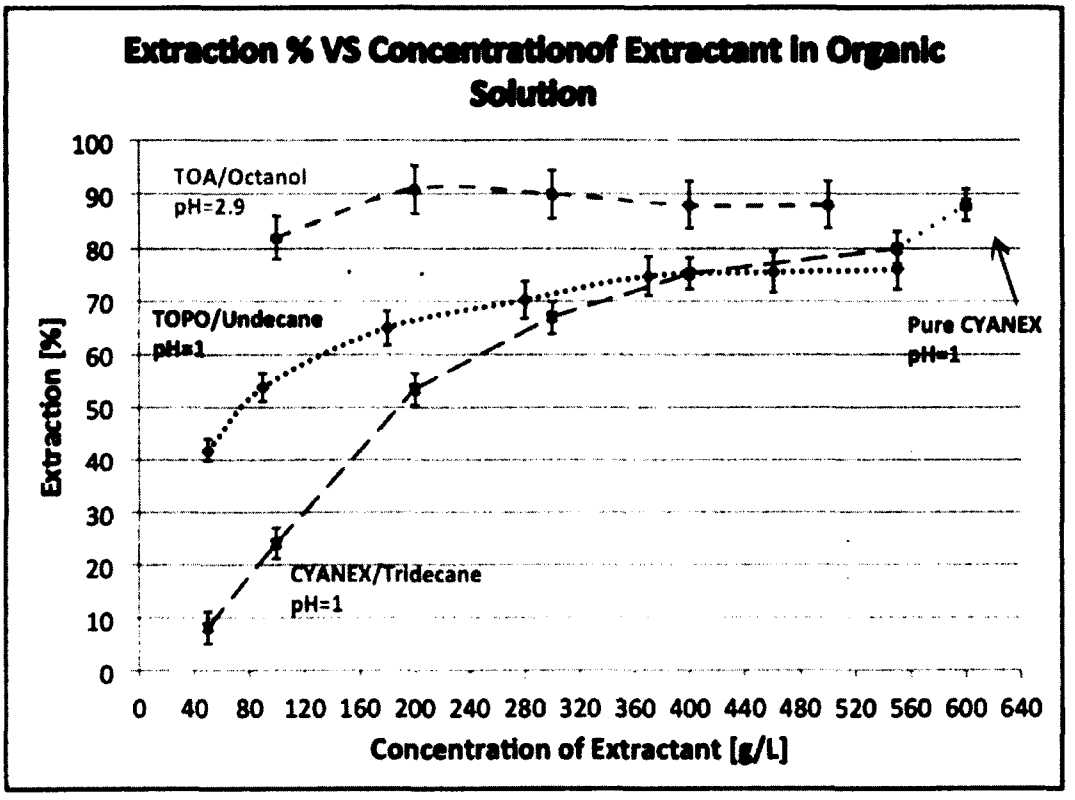



Figure 3.1 Extraction % versus concentration of extractant in organic solution

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, solvent : aqueous ratio [1:1]

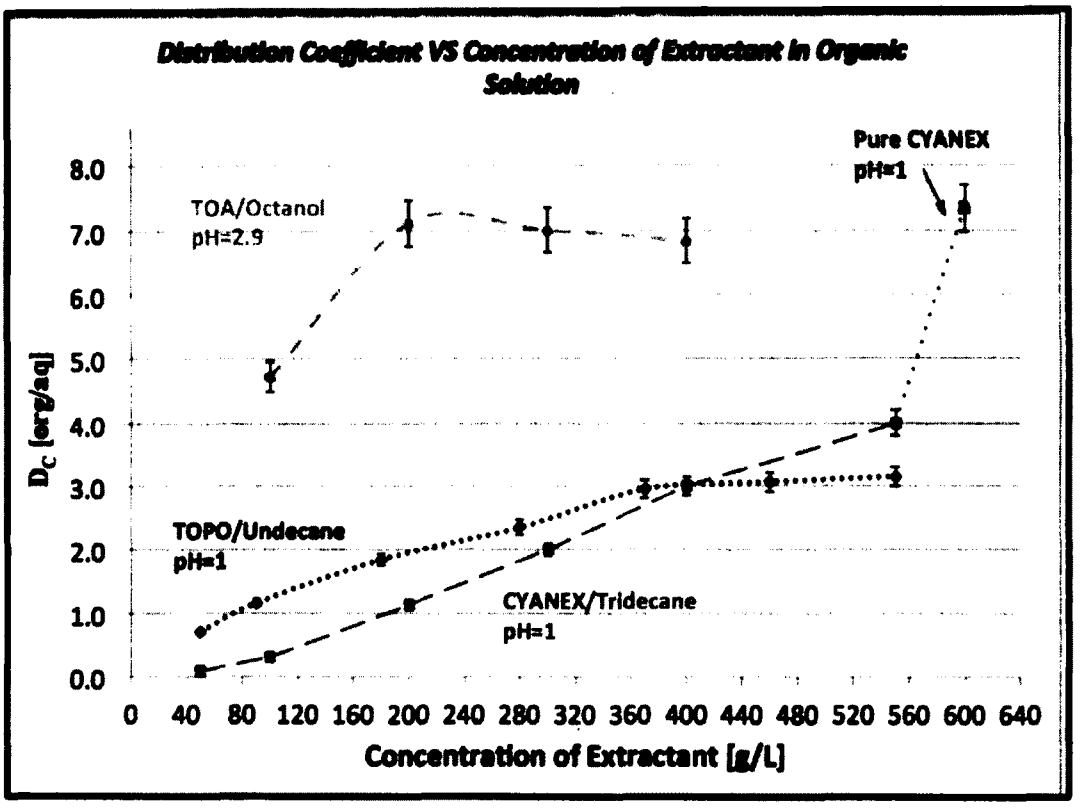



Figure 3.2 Distribution coefficients versus concentration of extractant in organic solution

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, solvent : aqueous ratio [1:1]

### *3.2 Effect of Ratio of Organic to Aqueous Phase*

Tables 3.4 to 3.6, figure 3.3 and figure 3.4 illustrate the effect of varied volume ratios of organic to aqueous solutions for the clean system (pure acetic acid dissolved in water). Figure 3.3 shows extraction % of acetic acid affected by changing volume ratios of organic to aqueous solutions, while figure 3.4 shows the distribution coefficient of acetic acid in organic solution to aqueous solution affected by changing volume ratios. It shows extraction % of acetic acid affected by changing the volume ratio and using all solvents (TOPO, TOA and CYANEX). It is observed from the figures that when the volume ratio increases it improves acetic acid extraction. However, there is no significant

extraction benefit when increasing above a certain level. For example, from figure 3.3 it can be seen that extraction with 370 g/L of TOPO in undecane at constant extraction conditions (1 pH and 70 °C), results in significant extraction % increases from around 37% to 75% when the volume ratio is increased from 0.25 to 1. In addition, extraction with 400 g/L of CYANEX in tridecane at constant extraction conditions (1 pH and 22 °C), results in significant extraction % increases from around 40% to 76% when the volume ratio is increased from 0.25 to 1 and there is no significant affect on extraction % when the volume ratio is increased to more than 1. Similarly, for extraction with 200 g/L of TOA in octanol at constant extraction conditions (2.9 pH and 70 °C), the extraction % increases from 41% to a maximum of 91% when the volume ratio is increased from 0.25 to 1.5 and then no significant improvement to extraction % is observed at higher levels.

Table 3.4 to 3.6 present the extraction % and partition coefficient of acetic acid extracted by TOPO/undecane solution, TOA/octanol solution and CYANEX 923/tridecane solution, all for a clean system acetic acid dissolved in DI water. From the tables, it is suggested that using a low solvent ratio, which enables the dewatering action of the back extraction, is feasible. Furthermore, repeated extractions would result in better overall extraction than using a high ratio with one extraction. From the entries in table 3.6 one can see that a single stage extraction with a 2:1 organic to aqueous ratio would give 88% extraction, while two sequential 1:1 volume ratio extractions would give 75 and 95% extractions after the first and second stages, respectively.

Table 3.4 Effects of volume ratio of organic to aqueous by using TOPO in undecane

| Ratio of Organic to Aqueous | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|
| 0.25 | 14.8 | 6.3 | 2.3 | 37 |
| 0.5 | 10.6 | 4.71 | 2.2 | 53 |
| 0.67 | 9.1 | 3.88 | 2.4 | 61 |
| 1 | 7.5 | 2.54 | 2.9 | 75 |
| 1.5 | 5.5 | 1.85 | 3.0 | 82 |
| 2 | 4.4 | 1.35 | 3.3 | 87 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, at 70 °C, 1 pH, 370 g/L solvent concentration

Table 3.5 Effects of volume ratio of organic to aqueous by using TOA in octanol

| Ratio of Organic to Aqueous | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|
| 0.25 | 16.4 | 5.9 | 2.8 | 41 |
| 0.5 | 13.2 | 3.4 | 3.9 | 66 |
| 0.67 | 11.2 | 2.5 | 4.5 | 75 |
| 1 | 8.4 | 1.6 | 5.3 | 84 |
| 1.5 | 6.1 | 0.9 | 6.7 | 91 |
| 2 | 4.6 | 0.8 | 5.8 | 92 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, at 70 °C, 2.9 pH, 200 g/L solvent concentration

Table 3.6 Effects of volume ratio of organic to aqueous by using CYANEX in tridecane

| Ratio of Organic to Aqueous | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|
| 0.25 | 16 | 6.0 | 2.7 | 40 |
| 0.5 | 11.2 | 4.4 | 2.5 | 56 |
| 0.67 | 10.1 | 3.2 | 3.2 | 68 |
| 1 | 7.8 | 2.2 | 3.5 | 76 |
| 1.5 | 5.6 | 1.6 | 3.5 | 85 |
| 2 | 4.25 | 1.5 | 2.9 | 88 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, at 22 °C, 1 pH, 400 g/L solvent concentration

From figure 3.3, it is noticed that when the volume ratio of organic to aqueous increases, the extent of acetic acid extraction will increase until reaching at a point after which no more significant increase of extraction of acetic acid occurs. This is because the aqueous phase has become so depleted of acetic acid that it can no longer reach equilibrium with the organic phase. The distribution coefficient, or acetic acid distribution in both organic and aqueous phases, shows a relatively constant value through the changes of relative volume, and reaches its maximum towards the ratio of 1:1 between the phases.

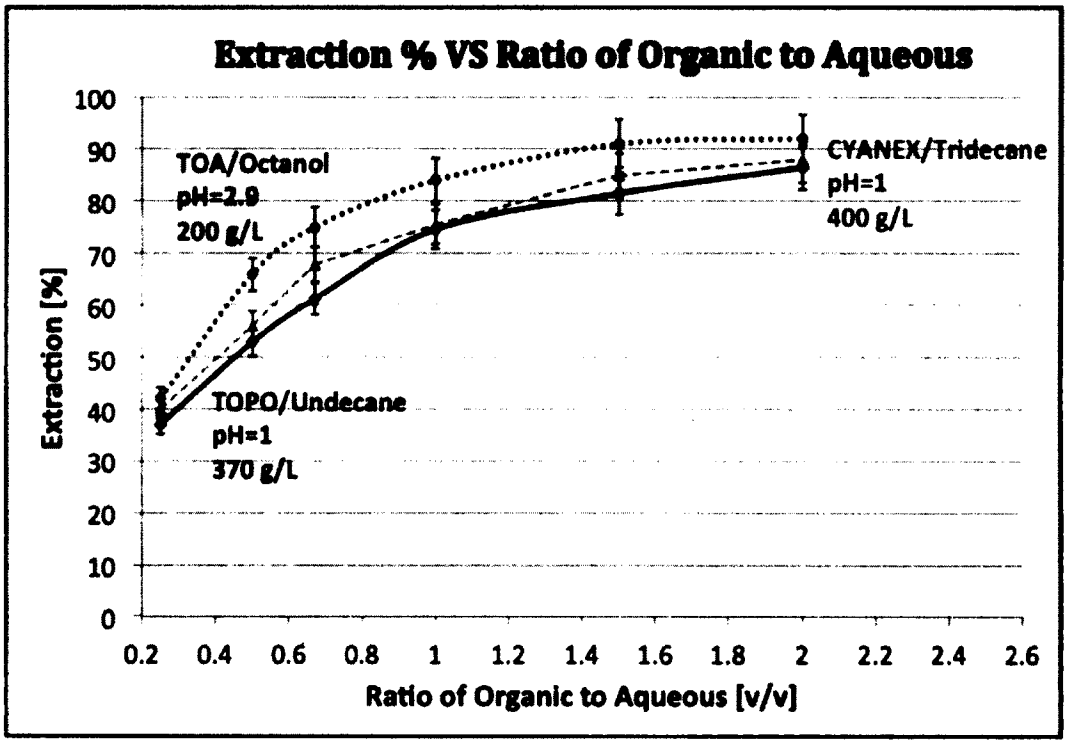



Figure 3.3 Extraction % versus volume ratio of organic to aqueous

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L

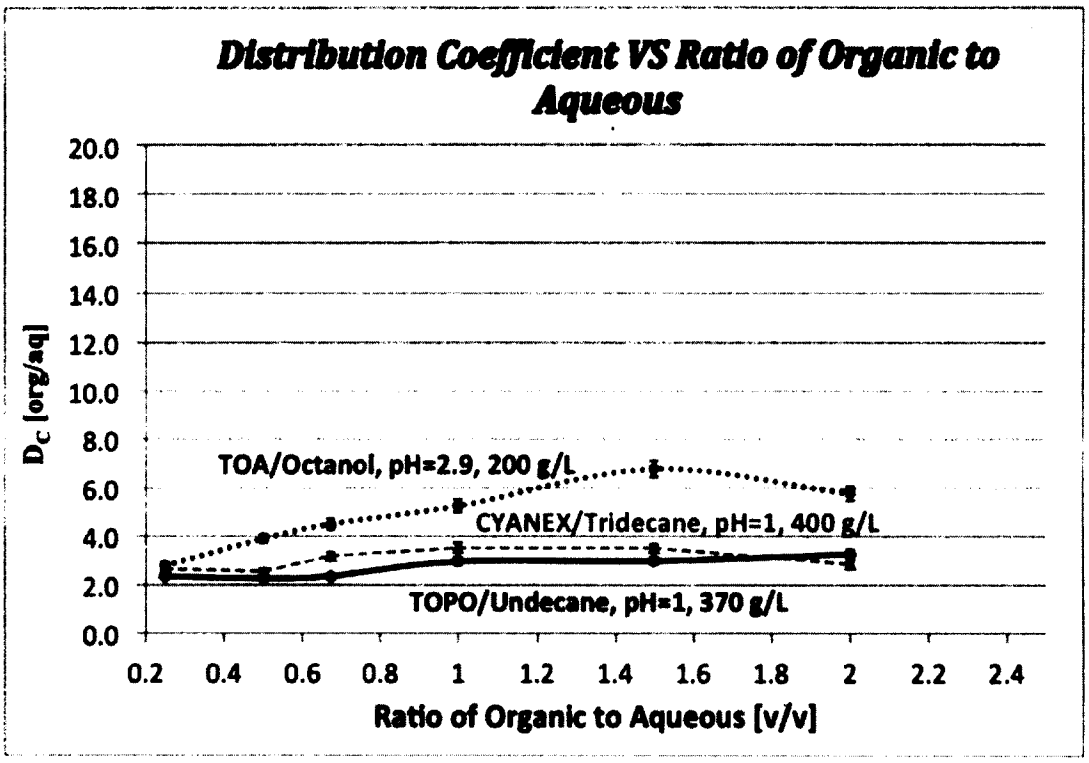



Figure 3.4 Distribution coefficients versus volume ratio of organic to aqueous

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L

### *3.3 Effect of pH*

Tables 3.7 to 3.9 show the effects of changing pH on acetic acid extraction using TOPO in undecane, TOA in octanol and CYANEX 923 in tridecane, respectively.

Table 3.7 Effect of changing pH on extraction of acetic acid using TOPO solvent

| pH | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|
| 1 | 7.47 | 2.53 | 3.0 | 75 |
| 2 | 7.41 | 2.59 | 2.9 | 74 |
| 3 | 7.29 | 2.71 | 2.7 | 73 |
| 4 | 5.41 | 4.59 | 1.2 | 54 |
| 5 | 1.82 | 8.18 | 0.2 | 18 |

Note: Extraction for clean system, initial concentration of pure acetic acid Solution is 10 g/L, 370 g/L TOPO, at 70 °C, solvent : aqueous ratio [1:1]

Table 3.8 Effect of changing pH on extraction of acetic acid using TOA solvent

| pH | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|
| 1 | 4.6 | 5.4 | 0.9 | 46 |
| 2 | 7.1 | 2.9 | 2.4 | 71 |
| 3 | 7.5 | 2.5 | 3.0 | 75 |
| 4 | 7.7 | 2.3 | 3.3 | 77 |
| 5 | 4.4 | 5.6 | 0.8 | 44 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, 200 g/L TOA, at 70 °C, solvent : aqueous ratio [1:1]

Table 3.9 Effect of changing pH on extraction of acetic acid using CYANEX solvent

| pH | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|
| 1 | 36.5 | 8.9 | 4.1 | 81 |
| 2 | 36 | 9 | 4.0 | 80 |
| 3 | 33.8 | 11.3 | 3.0 | 75 |
| 5 | 9 | 36 | 0.3 | 20 |
| 7 | 2 | 43 | 0.05 | 4 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 45 g/L, pure CYANEX, at 22 °C, solvent : aqueous ratio [1:1]

Figures 3.5 and 3.6 illustrate the effects of varied pH on acetic acid extraction for the clean system. Figure 3.5 shows extraction % of acetic acid affected by changing pH, while figure 3.6 shows the distribution coefficient of acetic acid in organic solution to aqueous solution affected by changing pH. The figures show that in general low pH favors good acetic acid extraction. For extraction using TOPO in undecane (370 g/L TOPO, 70 °C) and CYANEX 923 in tridecane (400 g/L CYANEX, 22 °C) at a specific extraction condition ([1:1] volume ratio), a maximum extraction is shown when the pH is at or below 3. In a somewhat different pH response, TOA in octanol at specific extraction conditions (200 g/L TOA, 70 °C and [1:1] volume ratio), shows a maximum extraction response to an intermediate pH level, with extraction performing best between pH 2 and 4, and tapering off at both higher and lower pH. In terms of distribution coefficient, the TOA shows a defined maximum at pH 4 while TOPO and CYANEX show a continuously increasing trend with lower pH.

The figures show that acetic acid extraction is enhanced at low pH. For example, the best extraction of acetic acid using TOPO and CYANEX 923 occur when the pH is 3 or lower, while extraction by using TOA is show the best extraction of acetic acid at pH 2-4. The acid hydrolysis process, used to convert oligomers to monomer sugars, and also to release additional acetic acid, requires that the pH of hemicelluloses extract be dropped to about pH 1. This puts the hydrolyzed extract in a suitable condition for applying liquid-liquid extraction with TOPO or CYANEX 923. At low pH, acetic acid in aqueous solution will be in its protonated form, which is more likely to transfer to the organic phase because the protonated groups are less polar and thus more soluble in organic solution than when they are deprotonated. The distribution coefficient ($D_C$) for such

compounds, which is the ratio of concentration in the organic phase to the concentration in the aqueous phase, can become greater than 4. At high pH, acetic acid in the aqueous phase will ionize to acetate ions, $CH_3COO^-$, and the hydrogen proton, $H^+$. The acetate ions become more likely to dissolve in the aqueous solution than transfer to the organic solution. This results in poor extraction at high pH compared with low pH. In addition, the solvent has a strong hydrogen acceptor to enhance the acetic acid to transfer to organic phase.

Extraction by TOA/octanol at pH 1 is shown in the figures 3.5 and 3.6. Under these conditions, TOA demonstrates a lower extraction than at higher pH, reaching only 41 %, compared to 91 % at pH 2.9. TOA is a basic compound (pKa is 10.78) and is ionized at low pH and forms a salt that is soluble in aqueous solution. As a result of this, at low pH the organic solution loses some of its extraction features, and acetic acid becomes again more attracted to the aqueous phase. This explains the drop off in TOA extraction efficiency at lower pH. As an example of this effect, when an amine reacts with hydrochloric acid, HCl, it will ionize and become more soluble in water than in an organic solution, as shown below.

$$R_3N: \xrightarrow{H^+\ Cl^-} R_3\overset{+}{N}-H + Cl^- \qquad (3.1)$$

| Amine | Amine ion |
|---|---|
| Soluble in organic<br>Not soluble in water | Not soluble in organic<br>Soluble in water |

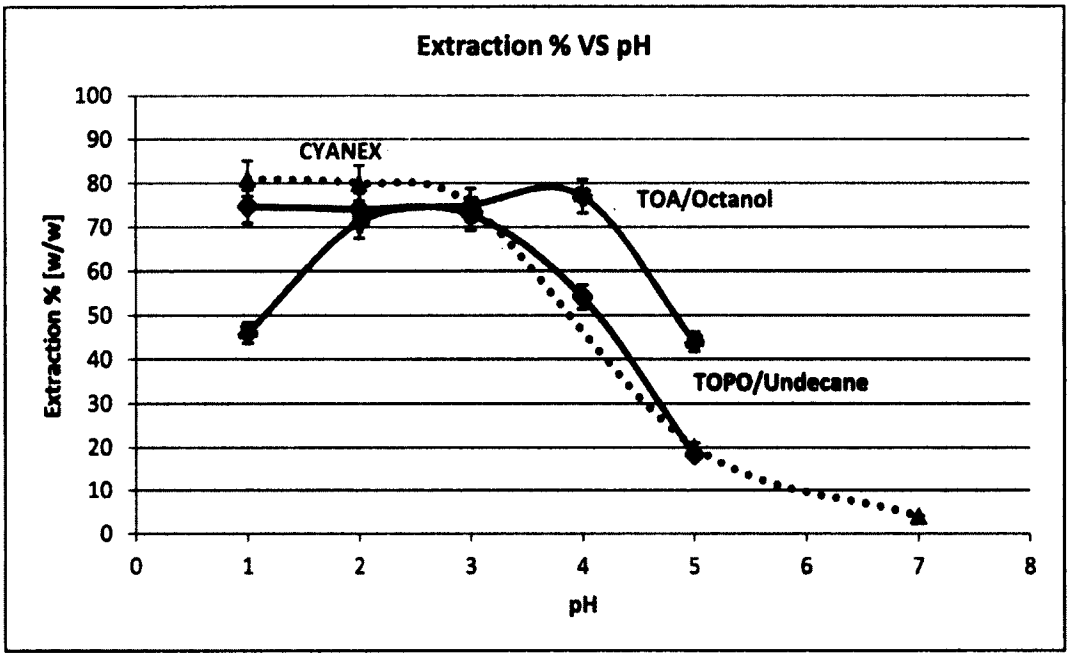



Figure 3.5 Extraction % versus pH

Note: Extraction for clean system, volume ration of organic: aqueous phases [1:1], 370 g/L of TOPO/undecane, 200 g/L of TOA/octanol, 400 g/L of CYANEX/tridecane

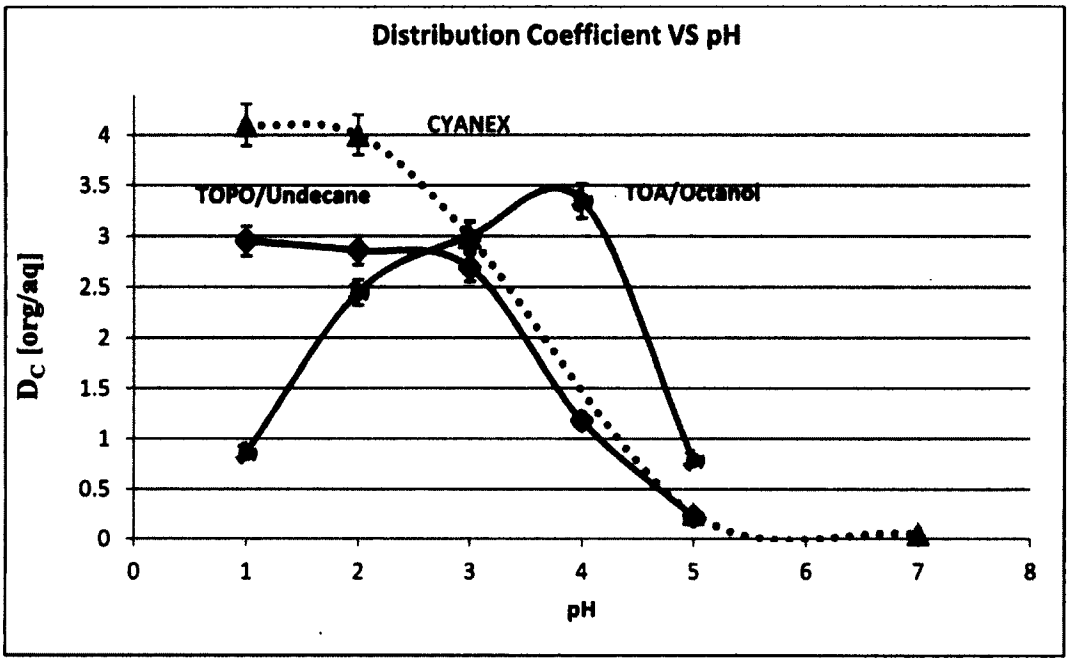



Figure 3.6 Distribution coefficient versus pH

Note: Extraction for clean system, volume ratio of organic: aqueous phases [1:1]

Figure 3.7 illustrates the effects of pH on mixed carboxylic acids, including acetic acid, for extraction from fermented wood broth. The figure shows CYANEX 923 extractions of samples prepared using different wood pretreatments and fermentation to generate the acids in solution at neutral pH. From the figure, it is observed that long chain length carboxylic acids have higher extraction percentages than short chain lengths. For example, heptanoic acid shows higher extraction % (more than 90 %) than acetic acid (less than 3 %).

At neutral pH, the extraction of short chain acids is lower than extraction of long chain length acids. The reason for low extraction of short chain length acids at high pH is explained above. Increasing the number of carbons in carboxylic acids leads to decreasing polarity of the carboxylic acids and they become less soluble in aqueous solution. As result, the longer carbon chain acids become more likely to dissolve in the solvent than the aqueous solution and they show high extraction percentages at neutral pH.

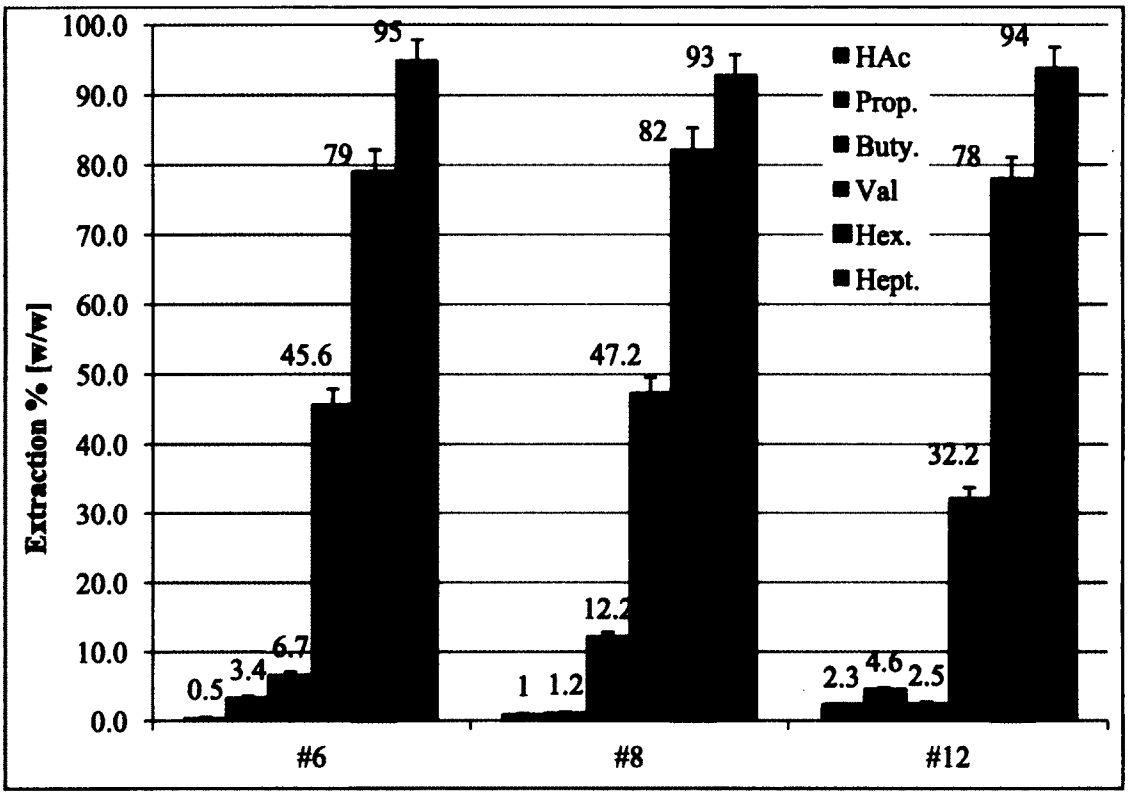



Figure 3.7 Extraction % of mixed carboxylic acids at pH 7 for samples of fermented wood that were pretreated at different conditions

Note: #6 is hot lime pretreatment, #8 is Pressurized $O_2$ and hot lime pretreatment, #12 is Brownstock pretreatment. Solvent extraction at room temperature and volume ratio of organic: aqueous phases [1:1]

Figures 3.8 shows the effects of using sulfuric, phosphoric and hydrochloric acid for lowering pH on acetic acid extraction using CYANEX 923 as solvent. Sulfuric, phosphoric and hydrochloric acids were used to lower pH to 1 and then the extraction was established by using CYANEX 923 with ratio of 1:1 organic to aqueous. The figure shows no significant affect on extraction percentage in response to using sulfuric, phosphoric and hydrochloric acid to lower pH to 1.

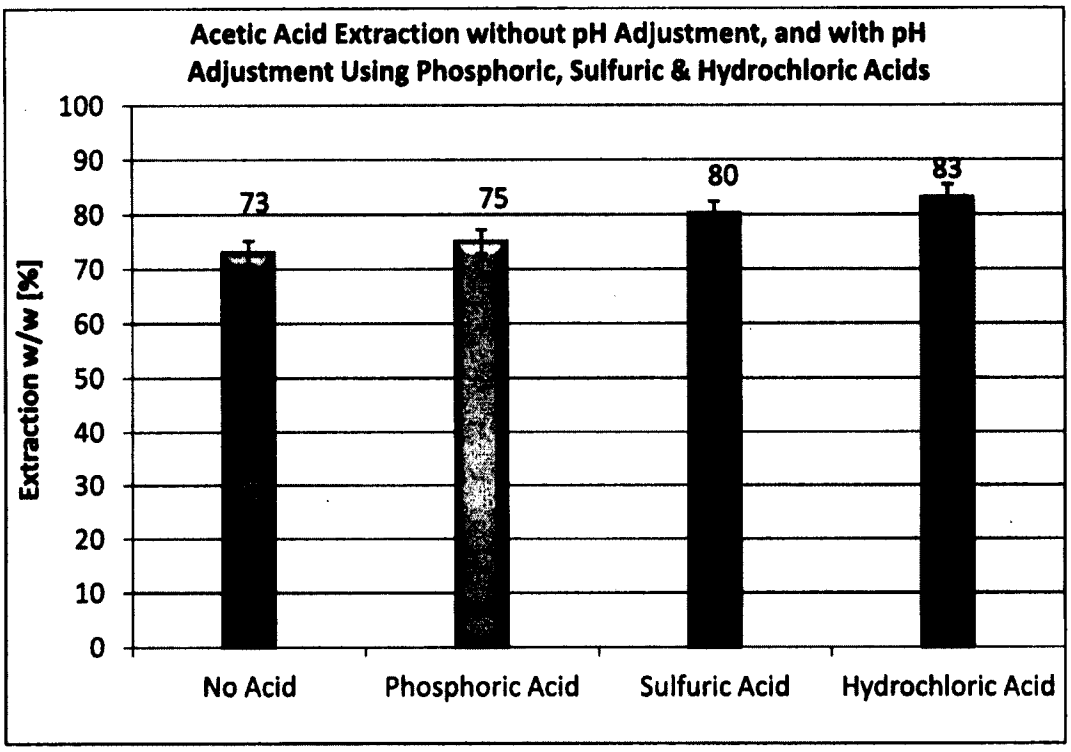



Figure 3.8 Effects of using phosphoric, sulfuric and hydrochloric acids for lowering pH down to 1 on acetic acid extraction

Note: Extraction is for clean system, using CYANEX 923, at initial pH 2.6, at room temperature and volume ratio of organic: aqueous phases [1:1]

### *3.4 Effect of Temperature*

Tables 3.10 to 3.12 show the effect on acetic acid extraction of changing extraction temperature.

Table 3.10 Effect of temperature changes on extraction of acetic acid by using TOPO solvent

| pH | Temperature °C | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|---|
| | 30 | 7.39 | 2.61 | 2.8 | 74 |
| | 50 | 7.41 | 2.59 | 2.9 | 74 |
| | 70 | 7.42 | 2.58 | 2.9 | 74 |
| | 90 | 7.4 | 2.6 | 2.8 | 74 |
| 1 | 110 | 7.2 | 2.8 | 2.6 | 72 |
| | 30 | 1.8 | 8.2 | 0.22 | 18 |
| | 50 | 1.87 | 8.13 | 0.23 | 19 |
| | 70 | 1.96 | 8.04 | 0.24 | 20 |
| | 90 | 1.73 | 8.27 | 0.21 | 17 |
| 5 | 110 | 1.69 | 8.31 | 0.20 | 17 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution 10 g/L, 370 g/L TOPO, solvent : aqueous ratio [1:1]

Table 3.11 Effect of temperature changes on extraction of acetic acid by using TOA solvent

| pH | Temperature °C | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|---|
| | 30 | 4.2 | 5.8 | 0.7 | 42 |
| | 50 | 4.3 | 5.7 | 0.8 | 43 |
| | 70 | 4.5 | 5.5 | 0.8 | 45 |
| 1 | 90 | 4.6 | 5.4 | 0.9 | 46 |
| | 30 | 3.9 | 6.1 | 0.6 | 39 |
| | 50 | 4.4 | 5.6 | 0.8 | 44 |
| | 70 | 4.4 | 5.6 | 0.8 | 44 |
| 5 | 90 | 4.4 | 5.6 | 0.8 | 44 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution 10 g/L, 200 g/L TOA, solvent : aqueous ratio [1:1]

Table 3.12 Effect of temperature changes on extraction of acetic acid by using pure CYANEX 923 solvent

| pH | Temperature °C | Organic g/L | Aqueous g/L | $D_C$ | Extraction % [w/w] |
|---|---|---|---|---|---|
| 1 | 22 | 37.2 | 8.8 | 4.2 | 83 |
| | 50 | 36.4 | 8.9 | 4.1 | 82 |
| | 70 | 36.5 | 8.9 | 4.1 | 81 |
| | 90 | 36.3 | 9.2 | 4 | 81 |

Note: Extraction for clean system, initial concentration of pure acetic acid solution 45 g/L, CYANEX 923, solvent : aqueous ratio [1:1]

Figures 3.9 and 3.10 present the effect of varied extraction temperature on acetic acid extraction for the clean system. Figure 3.9 shows extraction % of acetic acid affected by changing temperature, while figure 3.10 shows the distribution coefficient of acetic acid in organic solution to aqueous solution affected by changing temperature. It is observed that there is no significant affect on extraction in response to increasing or decreasing temperature. For example, from figure 3.9, extraction using TOPO in undecane and at specific extraction conditions (370 g/L TOPO, 1 pH and [1:1] volume ratio), the extraction % of acetic acid stays approximately constant (around 74 %) in response to an increase in temperature from 30 to 110 °C.

Most of the extractions were done at 70 °C; in particular extractions using TOPO/undecane, because the melting point of TOPO is in the range of 50 to 55 °C. Therefore, it is difficult to handle TOPO at room temperature since it solidifies. TOA and CYANEX 923 do not need any heating prior to extraction because their melting points are – 40 °C and -5 °C, respectively. Therefore, TOA and CYANEX 923 are easier to deal with than TOPO at room temperature.

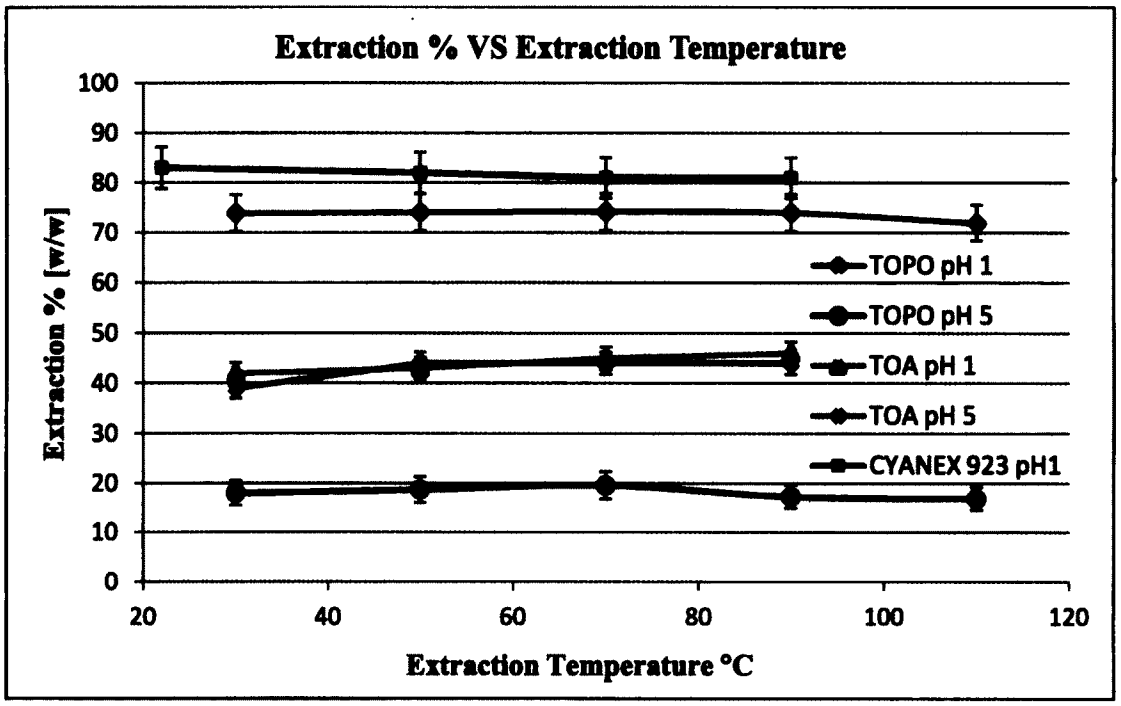



Figure 3.9 Extraction % versus extraction temperature

Note: Extraction for clean system, using sulfuric acid to lower pH, 370 g/L for TOPO, 200 g/L for TOA, pure CYANEX 923 and volume ratio of organic to aqueous phases [1:1]

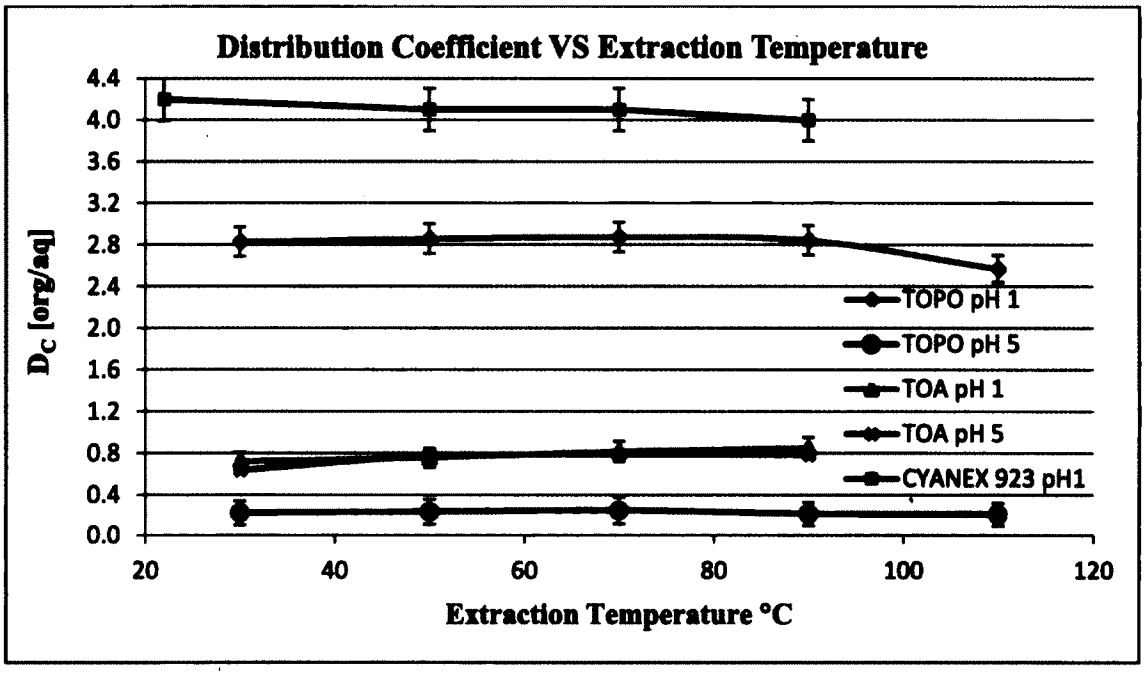



Figure 3.10 Distribution coefficients versus extraction temperature

Note: Extraction for clean system, using sulfuric acid to lower pH, 370 g/L for TOPO, 200 g/L for TOA, pure CYANEX 923 and volume ratio of organic : aqueous phases[1:1]

### *3.5 Effect of Agitation*

Testing of agitation methods was undertaken to develop a higher throughput method for conducting experiments. Initially, the agitation method consisted of intermittent manual shaking, which was time consuming and limited the number of samples that could be tested at once. Table 3.13 shows the effect on acetic acid extraction of using different methods of agitation of aqueous and solvent mixture. The results are for different agitation methods including: using the shaker by placing the sample tubes in vertical or horizontal positions, mixing by using a magnetic stirrer, shaking by hand, and no agitation of the mixture.

Table 3.13 Effect of agitation on extraction of acetic acid using CYANEX solvent

| Agitation | Organic g/L | Aqueous g/L | $D_C$ | Extraction [w/w] % |
|---|---|---|---|---|
| **V Shaker** | 7.1 | 43.6 | 0.16 | 14 |
| **H Shaker** | 44 | 6.5 | 6.7 | 88 |

Note: Without: no agitation, V Shaker: sample tubes placed in vertical position in the shaker, H Shaker: sample tubes placed in horizontal position in the shaker, Stirred mixing: agitation by using magnetic stirrer, By Hand: shaking by hand

Figure 3.11 illustrates the effects of agitation on acetic acid extraction. From the figure, agitation of aqueous and solvent mixture by using shaker and placing sample tubes in a horizontal position, mixing by using magnetic stirrer, and shaking by hand show high acetic acid extraction percentages (more than 80 %). On the other hand, agitation by using the shaker with vertical placement shows low extraction percentages (less than 15 %) as does the unagitated sample. Thus, subsequent experiments made use of the horizontal orientation shaking method.

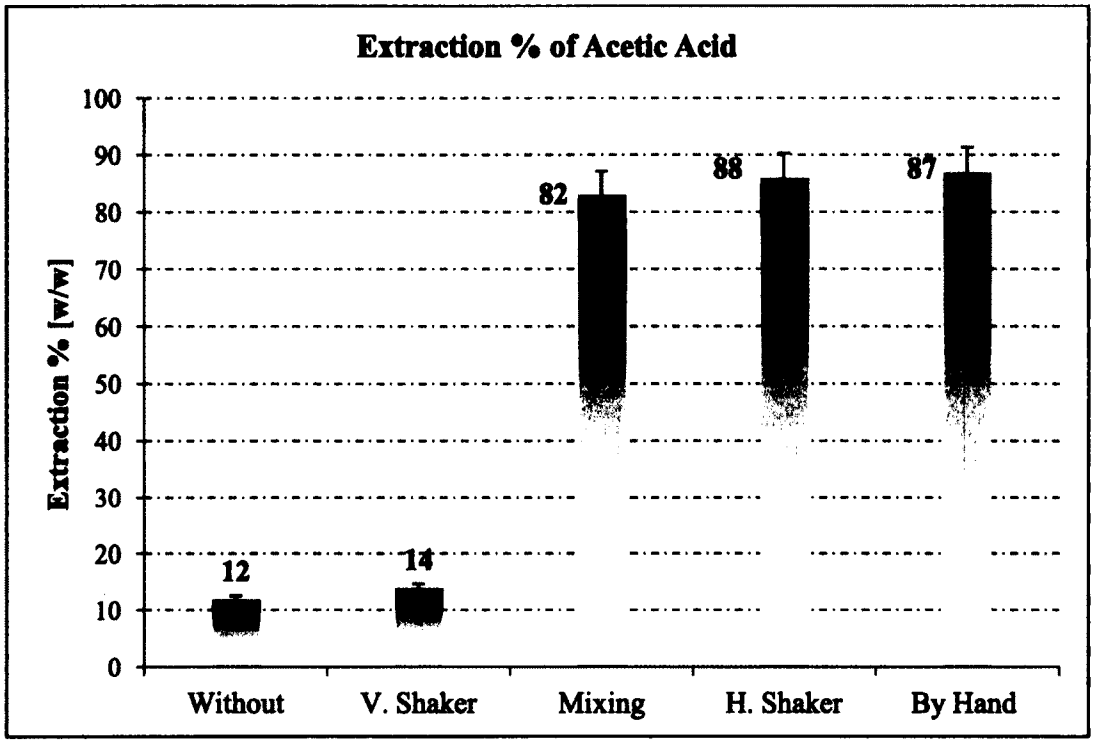



Figure 3.11 Effects of agitation on acetic acid extraction

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 50 g/L, pure CYANEX, extraction at room temperature, solvent : aqueous ratio [1:1], Without: no agitation, V Shaker: sample tubes placed in a vertical position in the shaker, H Shaker: sample tubes placed in a horizontal position in the shaker, Mixing: agitation by using magnetic stirrer, By Hand: shaking tubes by hand

### *3.6 Effect of Centrifuging*

Table 3.14 shows the effect on acetic acid extraction of using centrifuge or gravity separation for different periods of time.

Table 3.14 Effect of centrifuging phase separation on extraction of acetic acid using CYANEX solvent

| | Organic g/L | Aqueous g/L | $D_C$ | Extraction [w/w] % |
|---|---|---|---|---|
| 2 days gravity | 35.8 | 16 | 2.2 | 64 |
| 30 min. centrifuging | 44 | 7.1 | 6.2 | 87 |

Figure 3.12 illustrates the effects of centrifuging on acetic acid extraction. From the figure, it is observed that using the centrifuge machine is increasing acetic acid extraction percentage by helping and accelerate the separation between aqueous and solvent phases. While without centrifuging, the extraction needs a week to do an effective separation between aqueous and solvent phases. This suggests that there was relatively poor phase separation in the gravity methods. The lengthy time required for gravity to achieve similar separation to centrifugation indicates that phase separation will be an important design issue for application of this solvent.

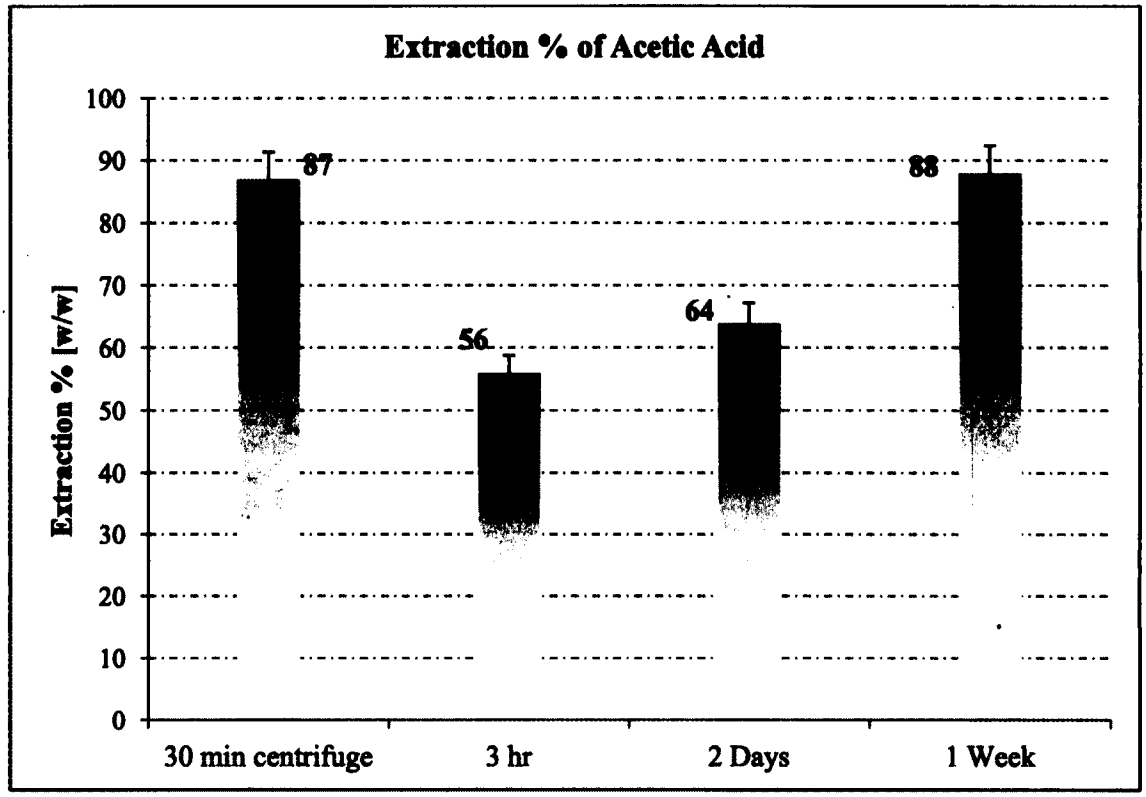



Figure 3.12 Effects of centrifuging and gravity settling time on acetic acid extraction

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 51 g/L, pure CYANEX, extraction at room temperature, solvent : aqueous ratio [1:1]

### *3.7 Comparing between Different Solvents Extraction % for Two Systems*

Figure 3.13 shows a comparison between different solvents, including: Dichloromethane (DCM), Ethyl Acetate (EA), TOA, TOPO and CYANEX 923, in terms of extraction % of acetic acid and for different aqueous solutions: the clean, hemicellulose extract and mixed acids fermented aqueous solutions. The figure shows that CYANEX 923 has highest extraction % while DCM has lowest extraction %. Furthermore, there is no significant difference in extraction % between three aqueous solutions extracted by TOPO, TOA and CYANEX 923. For example, extraction by CYANEX 923 shows 88 % and 87 % for clean and fermented aqueous solutions. TOPO

shows extraction % (78 and 62 %), while TOA shows moderated extraction % (46 and 41 %) because the extraction was done at pH 1, which is not optimal for TOA.

Figures 3.13 show that one stage extraction of the clean system by CYANEX 923 had the best acetic acid removal compared to dichloromethane (DCM), ethyl acetate (EA), TOA and TOPO. Extraction by TOA shows low extraction of acetic acid for the acid hydrolyzed green liquor, possibly because of the very low pH of this liquor. TOA is less costly than TOPO or CYANEX 923, and has optimal extraction at a higher pH than they do, so in the absence of acid hydrolysis of the aqueous phase, this could reduce the process cost since reducing pH for the phosphine oxide solvents requires the expense of a strong mineral acid.

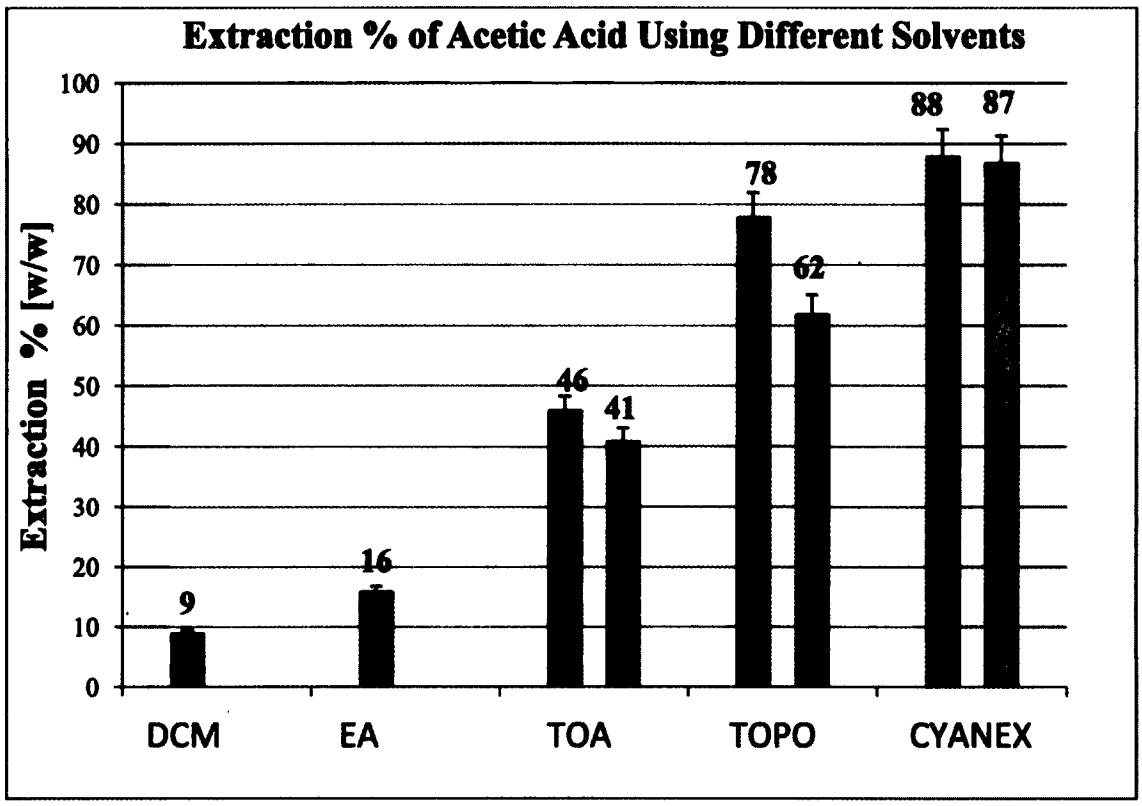



Figure 3.13 Comparing extraction by different solvents in term of acetic acid extraction %

Note: The solvent concentration for TOPO was 370 g/L TOPO/undecane, for TOA was 200 g/L TOA/octanol and a pure CYANEX 923, solvent : aqueous ratio [1:1] and pH 1

Figure 3.14 and table 3.15 show extraction % of mixed carboxylic acids from fermented wood broth, produced after different pretreatments of the wood samples. Figure 3.14 shows extraction % of mixed carboxylic acids after the hot lime pretreatment and fermentation. Its results show the comparison between extraction % at pH 2 and 7. Table 3.15 shows extraction % of mixed carboxylic acids after different pretreatments.

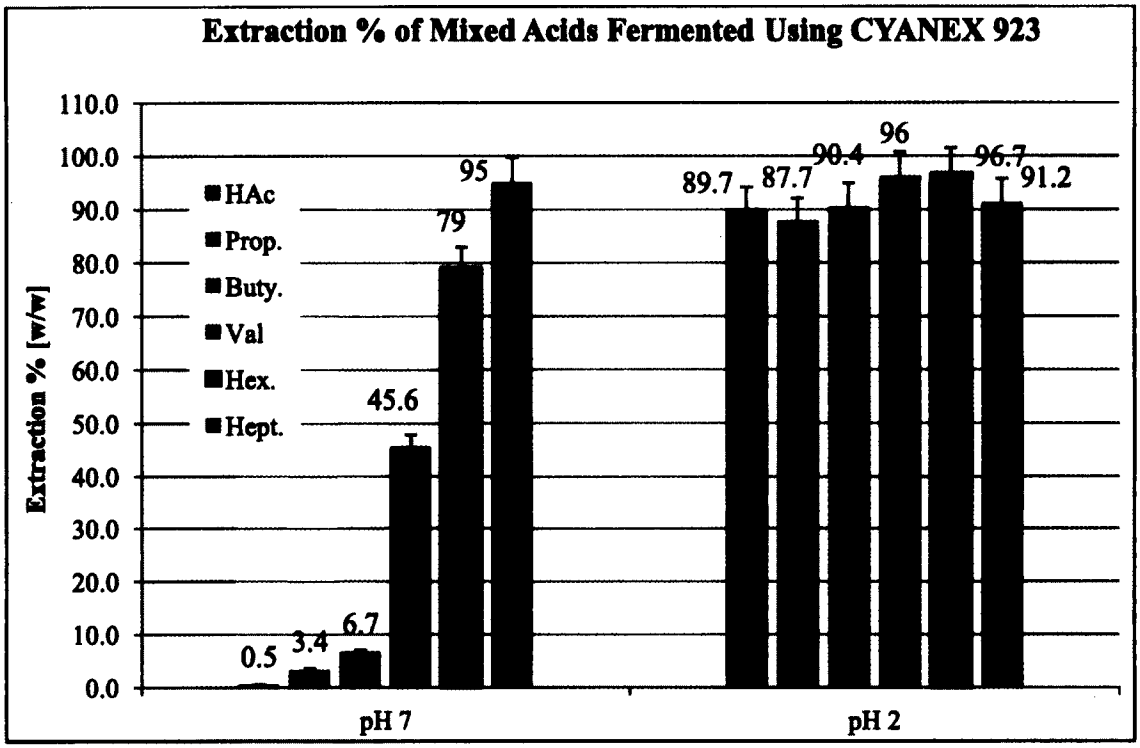



Figure 3.14 Extraction % of mixed carboxylic acids from fermented broth after pretreatment by hot lime

Note: Using pure CYANEX 923, solvent : aqueous ratio [1:1], initial concentration of acids as following: 5.6 g/L of acetic acid, 1.6 g/L of propionic acid, 6.6 g/L of butyric acid, 1.1 g/L of valeric acid, 10.6 g/L of hexanoic acid and 0.1 g/L of heptanoic acid

Table 3.15 Extraction % of mixed carboxylic acids from fermented broth produced from different pretreatments

| Pretreatment applied | Extraction % [w/w] after acid organic fermentation | | | | | |
|---|---|---|---|---|---|---|
| | HAc | Prop. | Buty. | Val. | Cap. | Hept. |
| **Soaked** | 90.3 | 94.4 | 97.2 | 98.6 | 98.8 | 93.4 |
| **WC Boiling Lime** | 89.9 | 95.7 | 97.4 | 98.7 | 98.3 | 92.9 |
| **GW Boiling Lime** | 89.1 | 94.4 | 98.7 | 98.1 | 98.8 | 95.1 |
| **WC Hot Lime** | 87.1 | 95.3 | 97.8 | 97.7 | 97.9 | 95.8 |
| **GW Hot Lime** | 88.0 | 95.1 | 98.6 | 98.8 | 98.9 | 94.9 |
| **WC Pressurized** | 89.8 | 96.7 | 97.6 | 98.4 | 98.8 | 93.4 |
| **GW Pressurized** | 89.8 | 97.1 | 98.7 | 98.0 | 98.3 | 92.5 |
| **Brown Stock** | 90.1 | 96 | 98.3 | 98.4 | 98.6 | 95.9 |

Note: Using pure CYANEX 923, solvent : aqueous ratio [1:1], pH 2, WC is wood chips, GW is ground wood chips

### *3.8 Distillation System*

Table 3.16 shows the percentages of acetic acid recovery by distillation using TOPO/undecane , TOA/octanol and CYANEX 923 and for hemicellulose extract and mixed acids fermented aqueous solutions. It is observed that about 89 % of acetic acid is recovered from TOPO solution and 84 % from CYANEX 923 while zero amount is recovered from TOA.

Table 3.16 Acetic acid recovered by distillation

| Solvent | HAc before Distillation g/L | HAc after Distillation g/L | HAc Recovery [w/w] % |
|---|---|---|---|
| TOA | 3.6 | 3.6 | 0 |
| TOPO | 5.6 | 0.2 | 89 |
| CYANEX 923 | 5.1 | 0.3 | 84 |

Note: Green liquor extracts are used for TOA and TOPO, fermented broth is used for CYANEX 923, volume ratio was 1, pH is 2, 370 g/L TOPO/undecane, 200 g/L TOA/octanol and pure CYANEX 923

Figure 3.15 show recovery % of mixed carboxylic acids for clean system from CYANEX 923 with several modifications used to improve distillation recovery %. Separation of long chain length acids from CYANEX 923 is more difficult than short chain length acids. The reason for this is the apparent increase of the boiling point of the mixture, which became higher than the boiling points of its individual components. As a result, the separation of acids by distillation becomes difficult. For example, the boiling point of pure heptanoic acid is 223 °C while the boiling point of heptanoic acid in CYANEX 923 mixture was above 250 °C. At elevated temperature, thermal degradation of the solvent was observed.

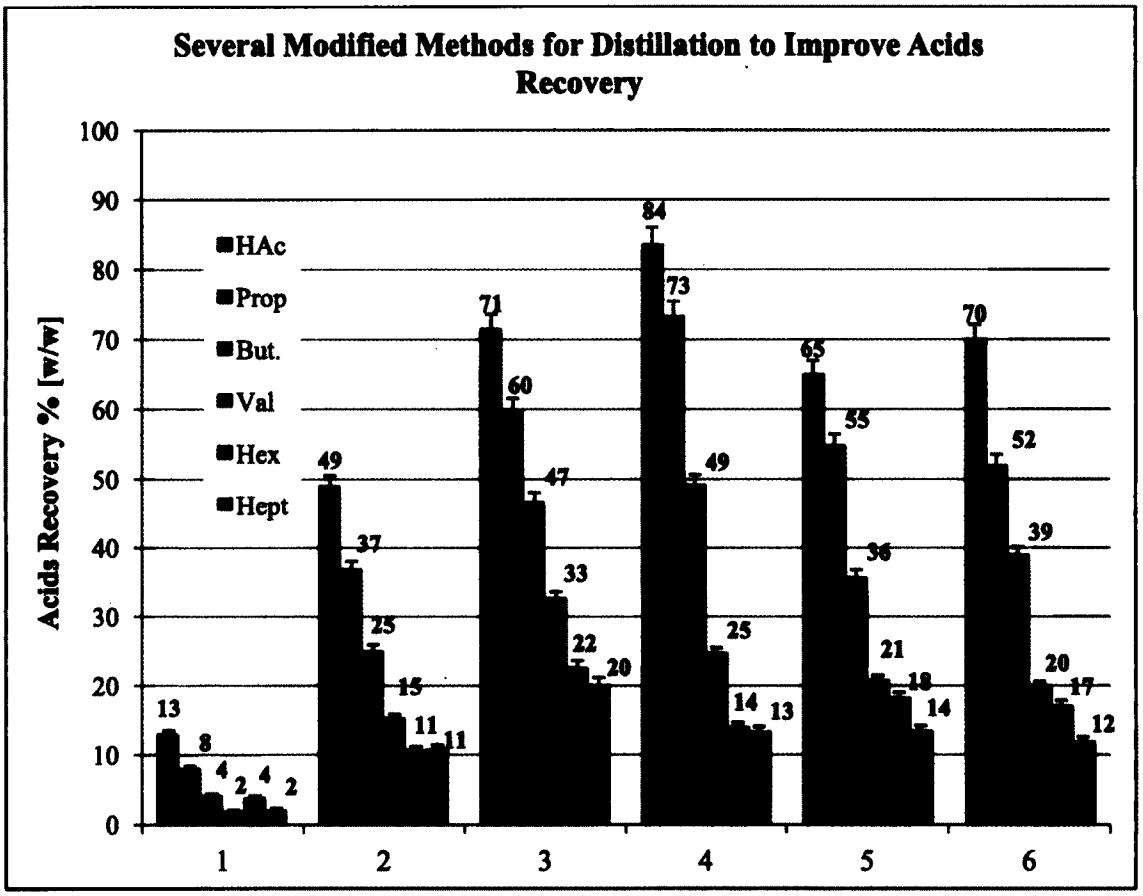



Figure 3.15 Recovery % of mixed carboxylic acids from CYANEX 923 by distillation system

Note: 1: slowly increasing heat and slow separation (Retention time 4 hr), no headspace in boiling flask, with vacuum, 2: fast increasing heat and fast separation (Retention time 15 min), with headspace (1/3 of boiling flask is empty) with vacuum, 3: Moderate rate of separation, using lamp-heated column, with vacuum, 4: Moderate rate of separation, insulated column, with vacuum 5: Moderate separation rate, insulated column, ice-cooled condenser with vacuum and 6: Organic mixture diluted with undecane before distillation

Figure 3.16 shows that high boiling temperature during the distillation process will cause solvent degradation as evidenced by the color change from colorless to black. It was observed that the solvent's color becomes darker when temperature increases from

22 °C to more than 260 °C. As a result, degradation through high temperature distillation will affect its efficiency and recyclability.

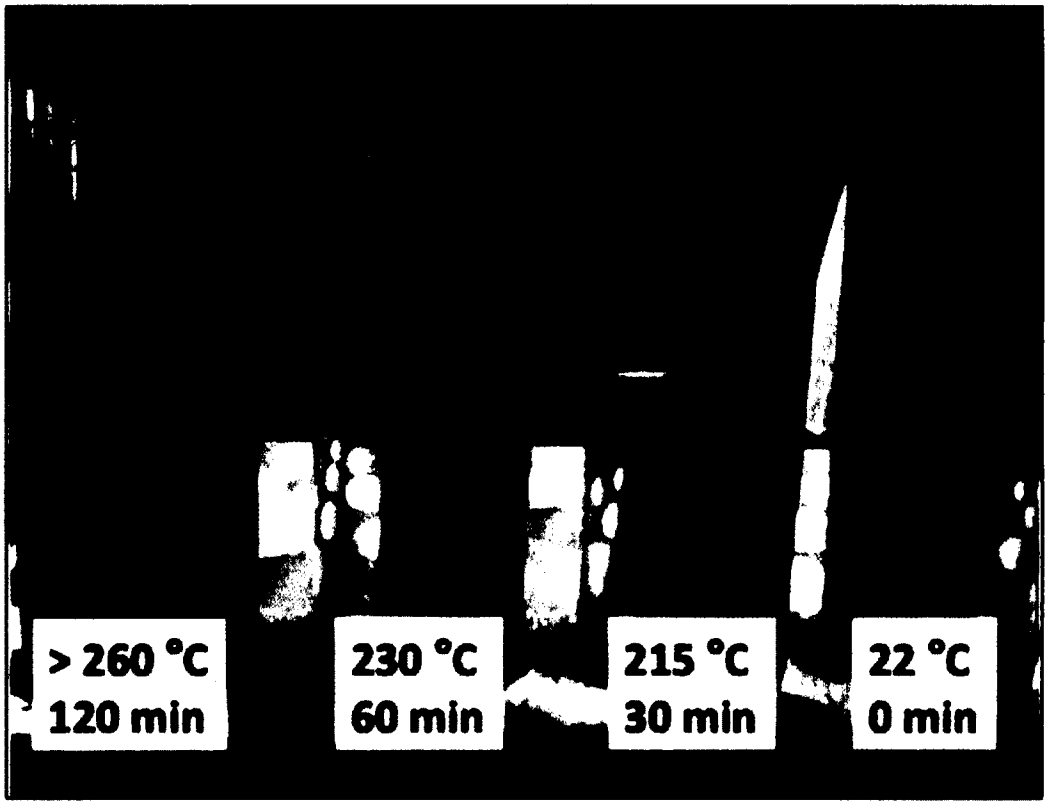



Figure 3.16 Effect of high boiling temperature on solvent's color
Note: Boiling temperature is the temperature at the bottom of the distillation column

Figure 3.17 and 3.18 show results for different boiling flask temperatures in the distillation system recovery of mixed carboxylic acids from CYANEX 923 extractant from a clean system. The results shown in figure 3.16 were without using a vacuum system while figure 3.17 shows results from using a vacuum system. From the figures, it is observed short chain acids are more recoverable from CYANEX 923 than long chain acids. For example, figure 3.16 shows 99.5% and 99.2% recovery of acetic acid and propionic acids respectively, while 1.7% and 1.2% for hexanoic acid and heptanoic acid

when the temperature of bottom distillation was more than 250 °C. In addition, using the vacuum system through distillation processes will improve the acid recovery.

From the figures, it is observed that mixed acids recovery % increases when using a vacuum system due to lowing of the vapor pressure in the distillation system that causes lowering of boiling points of the mixture.

The vapor mixture is reduced to - 0.08 atm by applying the vacuum system, the boiling point of the mixture will be lower than its boiling point at atmospheric pressure. As a result, the recovery of acids can be accomplished at lower temperature and there by reduce solvent degradation. However, figure 3.17 shows improvement of recovery for the short chain acids at lower temperature, but unfortunately little effect was observed for of recovering long chain acids, such as hexonoic and heptanoic acids, when applying the vacuum system.

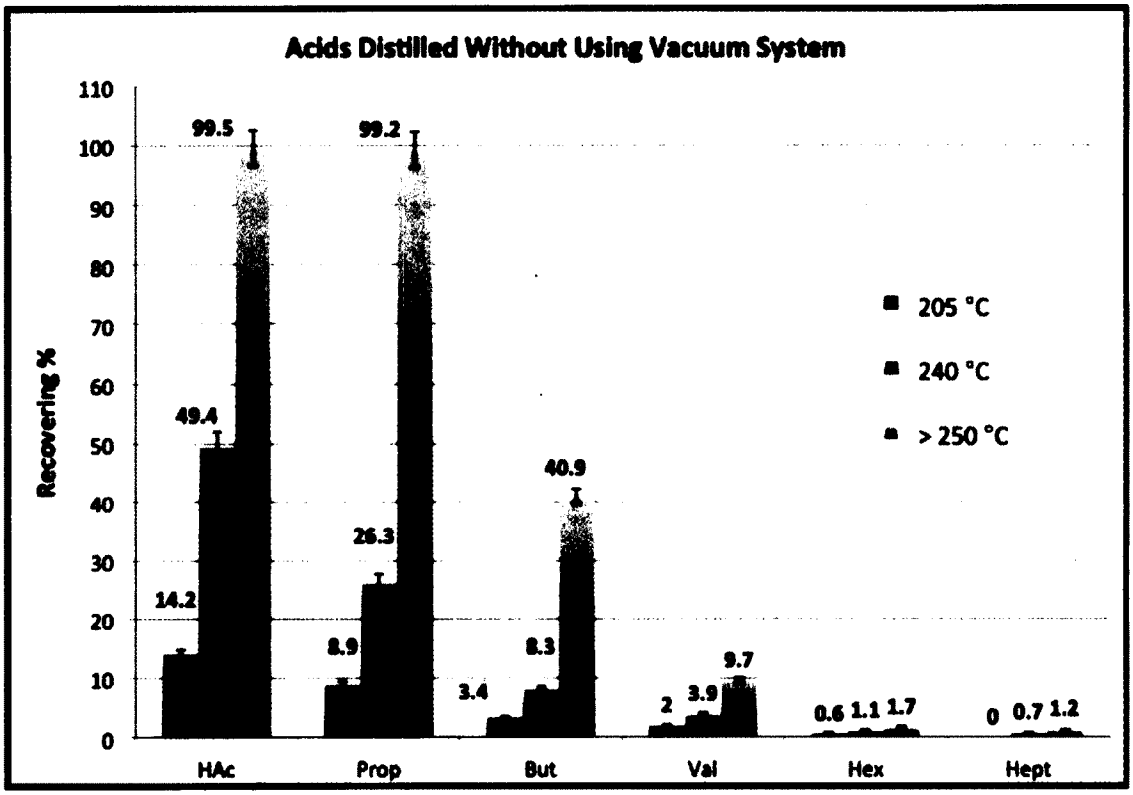



Figure 3.17 Recovery % of mixed carboxylic acids from CYANEX 923 distillation without employing vacuum

Note: Using 400 g/L CYANEX 923 in tridecane, initial concentration of acids as follows: 9 g/L of acetic acid, 9 g/L of propionic acid, 5 g/L of butyric acid, 2.5 g/L of valeric acid, 2.5 g/L of hexanoic acid and 2.5 g/L of heptanoic acid

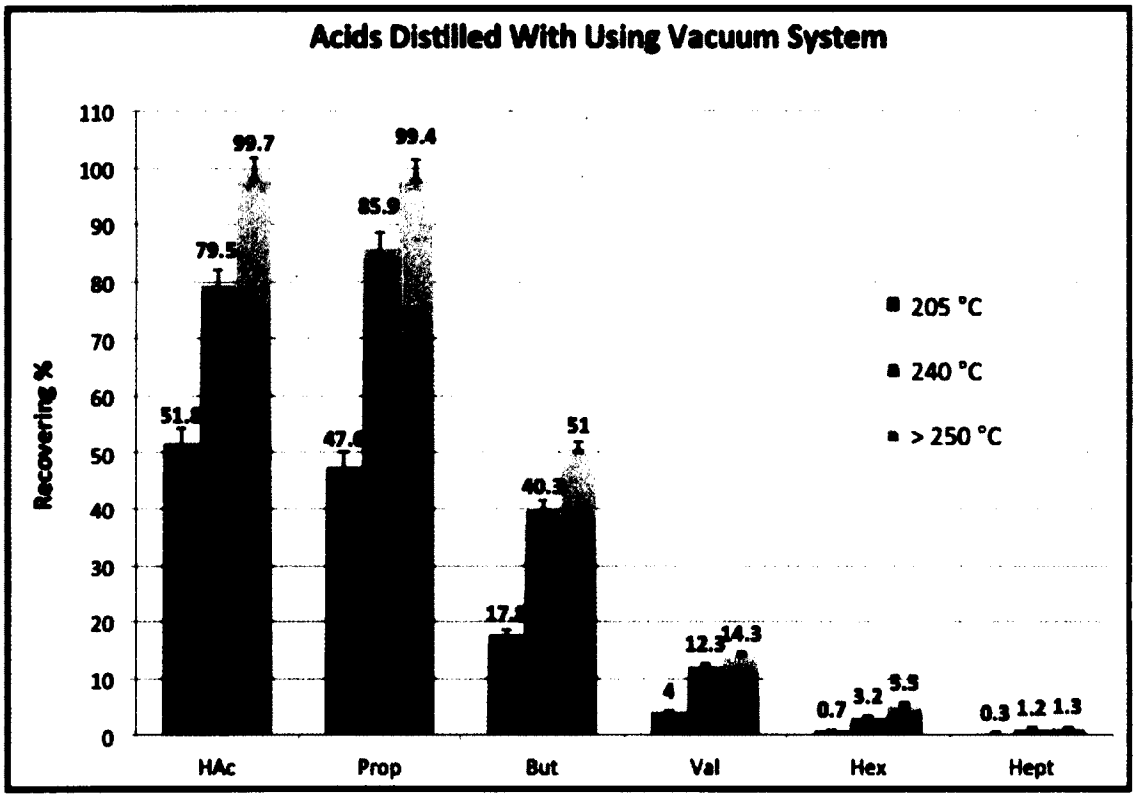



Figure 3.18 Recovery % of mixed carboxylic acids from CYANEX 923 distillation with -0.08 atm vacuum

Note: Using 400 g/L CYANEX 923/tridecane, initial concentration of acids as following: 9 g/L of acetic acid, 9 g/L of propionic acid, 5 g/L of butyric acid, 2.5 g/L of valeric acid, 2.5 g/L of hexanoic acid and 2.5 g/L of heptanoic acid

### *3.9 Acid-Base Precipitation*

As an alternative to distillation, precipitation from the organic phase was tested as a means for recovering carboxylic acids as their calcium salts, which could then be used as feed for ketonization in the MixAlco process. Figures 3.19 to 3.21 show moles undetected of mixed acids in pure CYANEX 923 versus moles of $OH^-$ supplied by the different solid bases added to the organic phase. The bases tested were: calcium hydroxide, calcium oxide and calcium carbonate. From figures 3.19 and 3.20, it is obvious that there are acid-base chemical reactions between acids and solid bases that

prevent detection of the acids in the organic phase and these reactions increase with increasing base addition. For example, they show that acetic acid reacts more (from 0.001 to 0.01 moles of acids eliminated from the solution) when adding more calcium hydroxide (from 0.007 to 0.03 moles of $OH^-$ supplied by bases) and calcium oxide (from 0.009 to 0.04), and then no significant improvement to acid-base reaction at higher levels. On other hand, there is no affect on acid-base chemical reaction by adding calcium carbonate showing in Figure 3.21 This is because calcium hydroxide and calcium oxide are strong bases for which about all moles of bases will react with all moles of acids. While calcium carbonate is a weak base and not all moles of bases reacted with moles of acids. In addition, calcium carbonate may stay unreacted in organic phase and affects on GC analysis results because it is a week base.

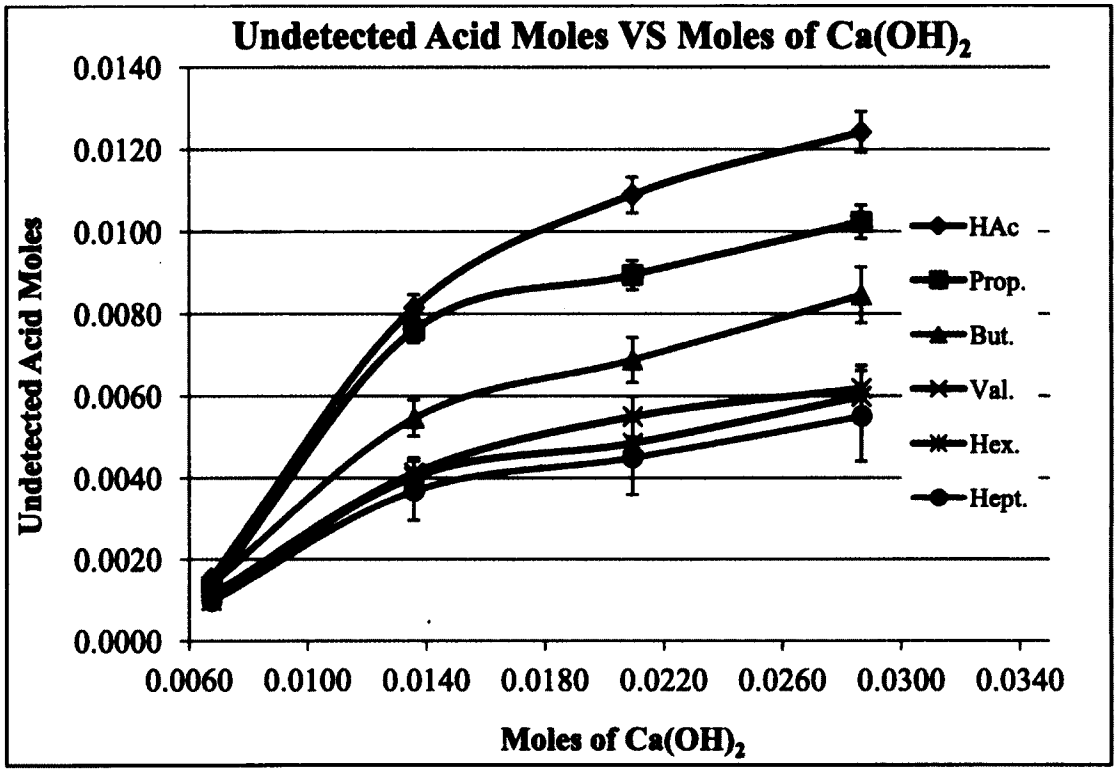



Figure 3.19 Acid-base reaction of mixed carboxylic acids and calcium hydroxide in CYANEX 923

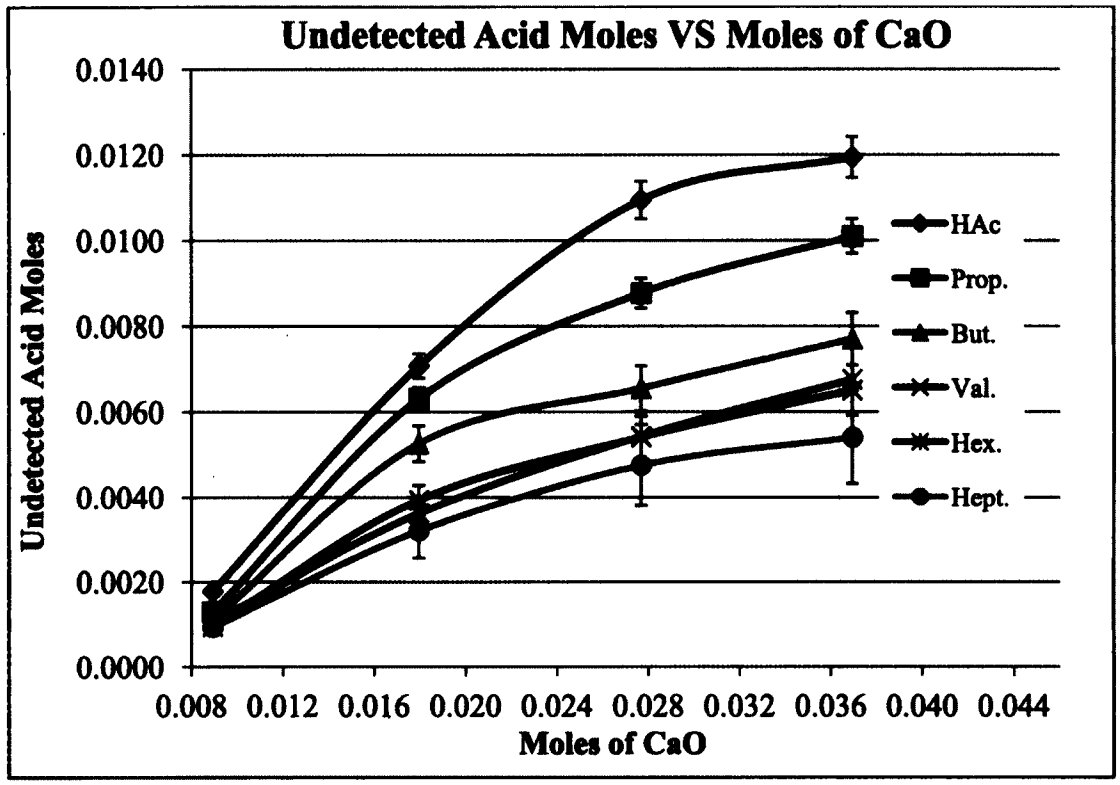



Figure 3.20 Acid-base reaction of mixed carboxylic acids and calcium oxide in CYANEX 923

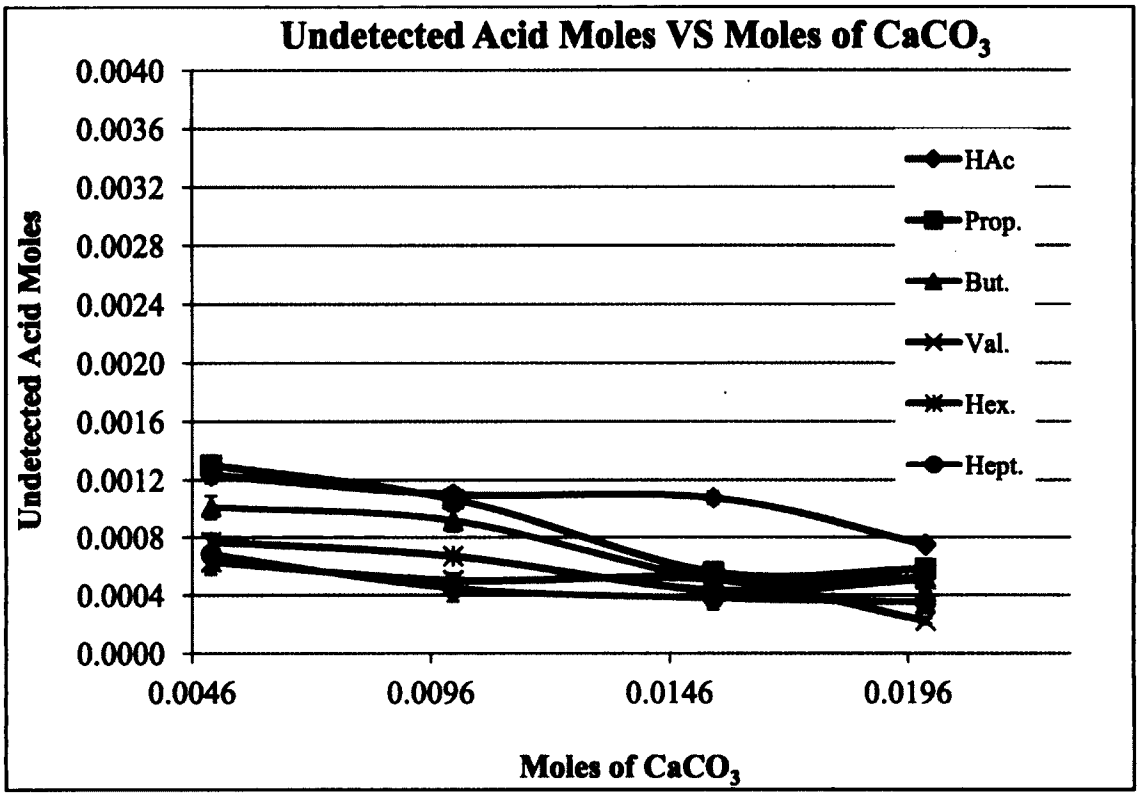



Figure 3.21 Acid-base reaction of mixed carboxylic acids and calcium carbonate in CYANEX 923

The calcium bases react with carboxylic acids in CYANEX 923 and form a calcium-acid complex in the organic phase. For example, calcium carbonate reacts with acetic acid and form calcium acetate salt, water and carbon dioxide according to the following chemical reaction:

$$CaCO_3 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + H_2O + CO_2 \qquad (3.2)$$

The acid-base reaction study aimed to recover the mixed acids from the solvent by adding different types of bases, including calcium hydroxide, calcium oxide and calcium carbonate, to make acid salts and precipitate them from the solvent. The figures show that adding bases will react with acids in the organic phase and make acid-base

complexes that are not detected by GC. These complexes are increased when adding more base, due to increasing of acid-base reaction. However, re-dissolution of the precipitates into acidic water did not indicate recovery of the acids as had been expected. Apparently the acid-base complexes are not necessarily precipitated from the organic phase as their carboxylate salt, and appear to remain in the organic phase in a form undetectable by GC.

Figure 3.22 shows the effect of adding moles of different solid bases (calcium hydroxide, calcium oxide and calcium carbonate) to total acids moles in CYANEX 923. From the figure, it is obvious that acid-base reaction of total acids in CYANEX 923 increases when adding more moles of calcium hydroxide and oxide while showing no affect or decreasing when adding more mole of calcium carbonate.

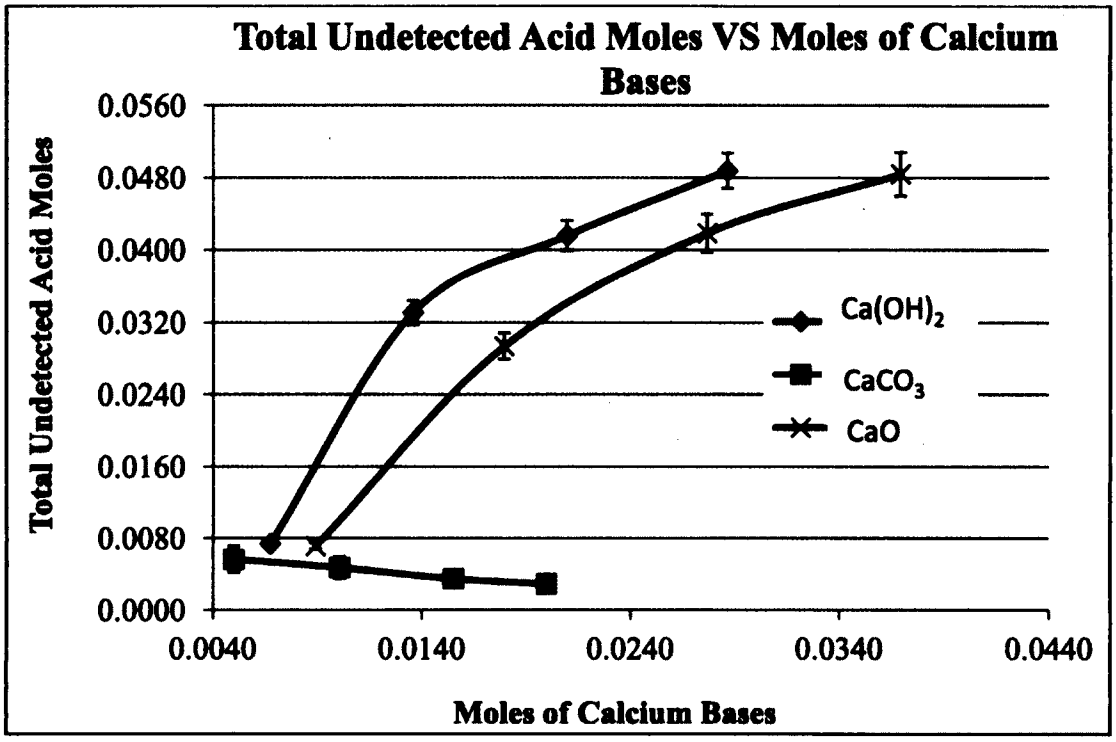



Figure 3.22 Acid-base reaction of total acids moles in CYANEX 923 and moles of different solid bases added to the organic phase

Figure 3.23 shows effect on pH of CYANEX 923 containing mixed carboxylic acids after adding different amounts of different calcium bases. An amount of 0 to 2 g of calcium hydroxide, calcium oxide, calcium carbonate or a mixture of 40 % of calcium oxide and 60 % of mixture bases including calcium carbonate, calcium hydroxide, magnesium carbonate and magnesium oxide were added to acid-containing post-extraction CYANEX 923.

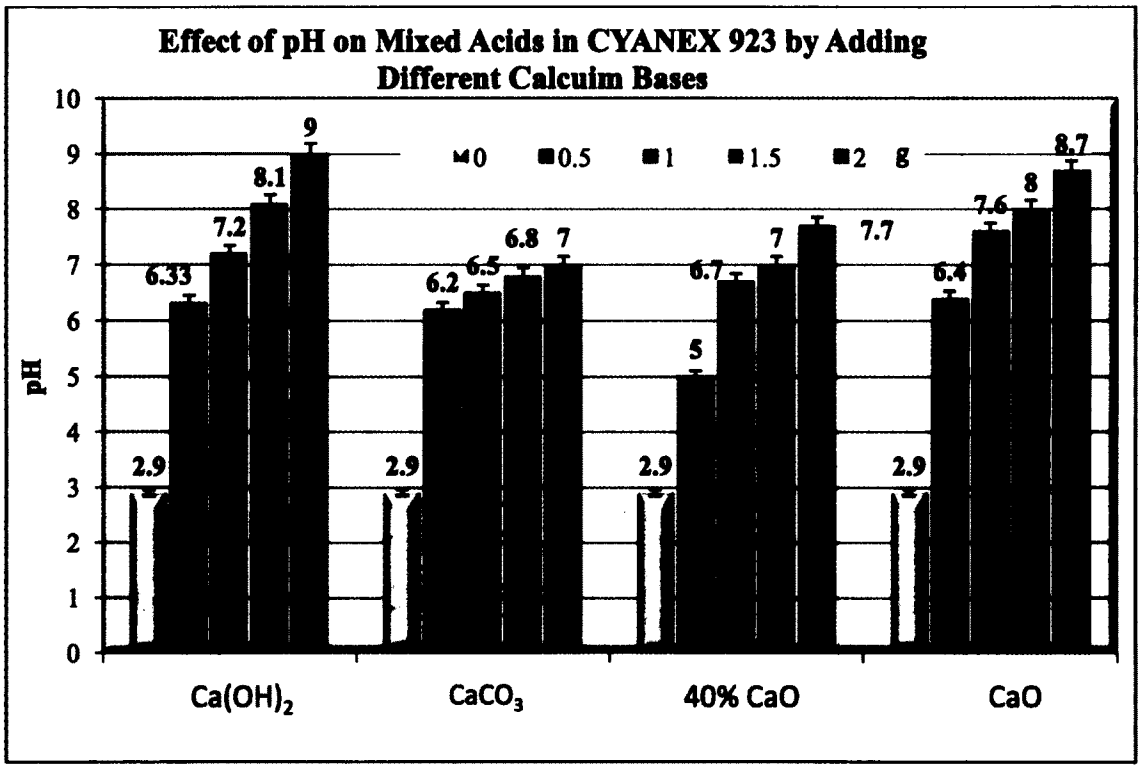



Figure 3.23 Effect on pH of CYANEX 923 containing carbon 2 to carbon 7 carboxylic acids salts after adding different calcium bases

Note: Different amounts as grams (0 to 2 g) of different calcium bases are used in this figure

Figure 3.24 studies the effect on pH of washing CYANEX 923 with DI water after adding calcium bases. The results of pH of CYANEX 923 after liquid-liquid

extraction, adding different calcium bases and 10 mL of DI water washing was showed in the figure.

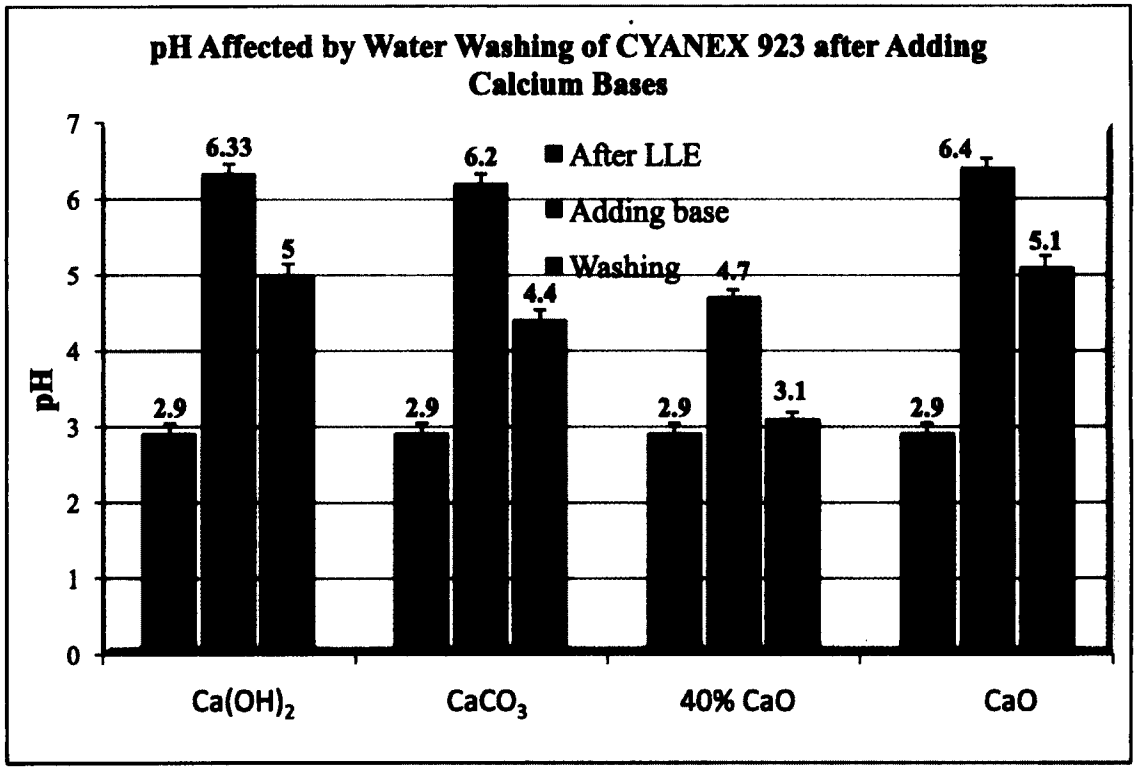



Figure 3.24 Effect on pH of CYANEX 923 having mixed carboxylic acids after adding different calcium bases and washing by DI water

Note: 0.5 g of different calcium bases adding to CYANEX 923, pH of CYANEX 923 after liquid-liquid extraction, after adding different calcium bases and after washing with pure DI water were measured

From table 3.17, it is observed that no calcium acetate salts precipitated from CYANEX. Therefore, the calcium acetate dissolved in CYANEX and made acid-base complex, which remained in organic phase. In addition, GC did not detect the acid-base complex at pH 6, while it detected acetic acid at pH 1.

Table 3.17 Dissolve calcium acetate in CYANEX

| | Initial mass of CaAc added to organic solution | Area | | | [Ac] concentration in organic | [Ac] mass dissolved in 20 mL organic solution | Initial mass of [Ac] added to organic solution |
|---|---|---|---|---|---|---|---|
| | g | 1 | 2 | Average | g/L | g | g |
| pH 6.33 | 0.1 | 4721.6 | 6293.5 | 5507.6 | 0.1 | 0.0030 | 0.07 |
| pH 1, no centrifuging | 0.1 | 42085.5 | 36391.4 | 39238.5 | 1.1 | 0.021 | 0.07 |
| pH 1, 30 min. centrifuging | 0.1 | 109291.8 | 149157.6 | 129224.7 | 3.5 | 0.0698 | 0.07 |

Note: CaAc is calcium acetate, [Ac] is acetate, 0.1 g of calcium acetate adding to 20 mL of pure CYANEX 923 (3.5 g/L of acetate in solvent), using 10 N of HCL to lower pH

Table 3.18 to 3.21 show mass tracking of acetic acid, calcium hydroxide and calcium carbonate through extraction and acid salt precipitation. The mass of acetic acid was determined after liquid-liquid extraction by using pure CYANEX, before and after adding calcium bases, and after acid salt precipitation. The mass of calcium bases was determined before and after the precipitation as well.

The solid particles after precipitation process was dissolved in DI water and then HCL was added to lower pH to be 1 before analyzing by GC. From table 3.18, it is observed that no mass of acetic acid was found in solid particles after precipitation at pH 1. Therefore, carboxylic acids did not recovered from CYANEX by precipitation process.

Table 3.18 Mass tracking of extraction of acetic acid by pure CYNANEX

| | | | |
|---|---|---|---|
| 0.42 | 0.37 | 0.04 | 88 |

Note: [1] is mass calculated from GC analysis, [2] is mass calculated by the different between mass before LLE in aqueous and after in organic

Table 3.19 Mass tracking of washing process of organic solution after precipitation

| Solid bases | [Ac] mass before AP in 20 mL (org) g | [1][Ac] mass after washing in 20 mL (aq) g | [Ac] mass after washing in 20 mL (org) g | Recovery [w/w] % |
|---|---|---|---|---|
| $Ca(OH)_2$ | 0.37 | 0.15 | 0.22 | 41 |
| $CaCO_3$ | 0.37 | 0.06 | 0.31 | 17 |

Note: Organic solution after AP was not analyzed as well as after filtration, [1] HCL was added to the aqueous solution after washing process to lower pH, mass calculated from GC analysis

Table 3.20 Mass tracking of solid particles separated from the organic solution after precipitation

| Solid bases | [Ac] mass before AP in 20 mL (org) g | [1][Ac] mass after AP in 20 mL (aq) g | Recovery [w/w] % |
|---|---|---|---|
| $Ca(OH)_2$ | 0.37 | 0 | 0 |
| $CaCO_3$ | 0.37 | 0 | 0 |

Note: [1] solid particles after precipitation were dissolved in DI water and then HCL was added to lower pH, mass calculated from GC analysis

Table 3.21 Mass tracking of solid bases added to organic solution after extraction acetic acid

| | | |
|---|---|---|
| $Ca(OH)_2$ | 0.3 | [2]0.34 |
| $CaCO_3$ | 0.34 | [2]0.36 |

Note: Mass of solid bases were measured by lab scale before and after adding solid bases, AP is acid precipitation method, [1] is mass measured after precipitation and filtration steps, [2] is mass of wet solid bases (hard to dry it due to high boiling point of CYANEX)

### *3.10 Acid Recovery by Back Extraction*

Because acid precipitation with calcium bases failed to recover the carboxylates in the precipitate, back extraction was attempted, with the intent of recovering the acids in a reduced volume of aqueous solution, compared to their original source. Since the long chain acids are the most hydrophobic, they were considered the most challenging for back extraction.

Figure 3.25 shows a comparison between different bases, including: solid calcium hydroxide, an aqueous calcium hydroxide (a slurry of water with calcium hydroxide suspended in it), solid calcium carbonate and an aqueous sodium hydroxide solution in term of removal % of acetic acid from CYANEX 923. The figure shows adding solid calcium hydroxide and calcium carbonate as same as the earlier precipitation experiments and then back extraction with pure DI water. It is observed that by using a back extraction of sodium hydroxide has the highest removal of acetic acid, around 99%, while by adding calcium hydroxide and calcium carbonate and back extraction with DI water have 40% and 17%, respectively. These recovery percentages were measured from the

acetate salts remained in organic phase and then back extraction by washed with DI water follow by adding HCL solution to lower pH and analyzed by GC to obtain these recovery percentages.

In addition, figure 3.25 shows that not all the acid-base reaction complex (only about 40% by calcium hydroxide) recover as acid salts, implying that about 60% of the reaction complex either stayed in solvent (was not reacted) or stayed in the acid salts (not totally dissolved in acidified DI water). Therefore, the mass balance of making acid salts becomes difficult to achieve.

The figure shows acids removal % by adding calcium hydroxide or back extraction with sodium hydroxide shows higher effectiveness than by adding calcium carbonate. Although both calcium hydroxide and sodium hydroxide are strong bases, the back extraction using NaOH is considerably more effective. While calcium carbonate is a weak base and does not totally react with acids in organic phase. Thus, it appears that allowing extra time for acid-base reactions to occur is not practically effective at improving the extent of these reactions.

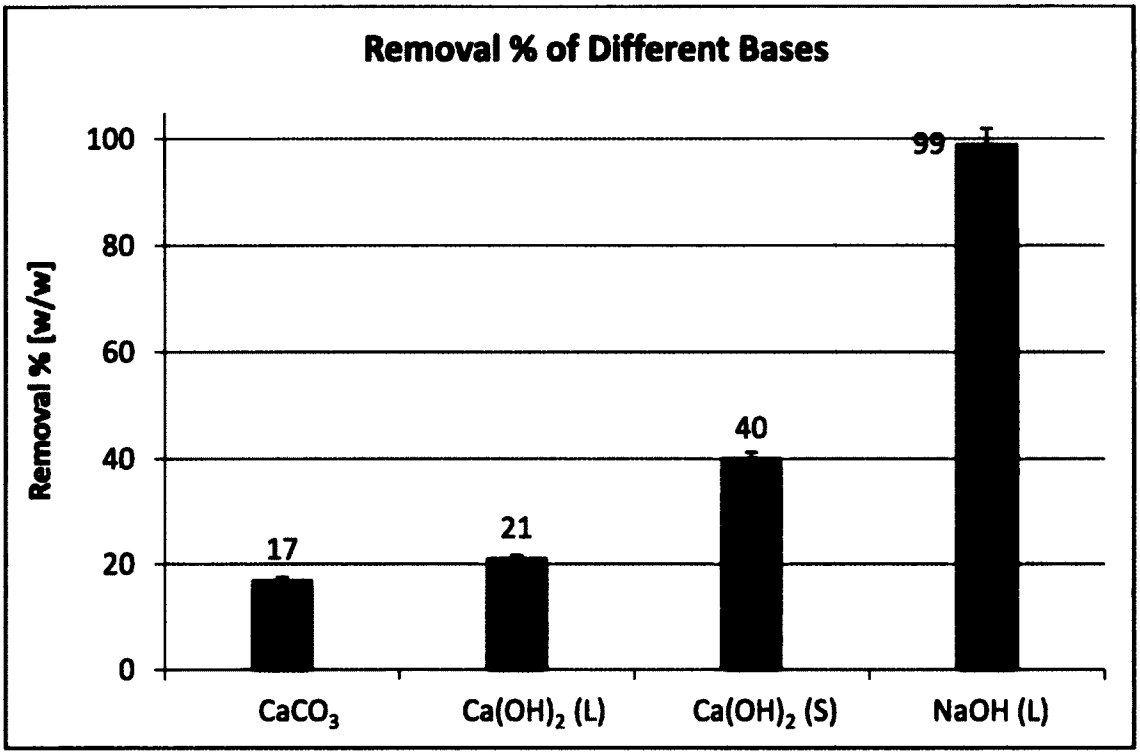



Figure 3.25 Comparison between different bases, including: calcium hydroxide as solid and an aqueous calcium hydroxide solution, calcium carbonate as solid phase and an aqueous sodium hydroxide solution (0.9 moles of NaOH), in term of removal % of acetic acid from CYANEX

Note: S is solid base, L is bases dissolved in DI water, initial concentration of acetic acid in pure CYANEX 923 is 21.1 g/L (0.0035 moles of acetic acid), adding 0.003 moles of calcium hydroxide and calcium carbonate, 0.9 moles of NaOH in aqueous solution (3 molar ratio of NaOH in aqueous to acetic acid in organic), at room temperature

Table 3.22 and figure 3.26 present the effect of varied reaction time of acid-base reaction on mixed acids removal in an organic solution for the clean system. Because calcium bases have low solubility, it was hypothesized that longer reaction times would compensate for this limitation. It is observed that there is no significant effect on removal % in response to long or short reaction time. For example, the removal % of acetic acid

by using a back extraction of $Ca(OH)_2$ solution stays approximately constant (around 40 %) in response to an increase in reaction time from 30 minute to 240 minute.

Table 3.22 Effect of varied reaction time of acid-base reaction on mixed acids removal

| | | | | | |
|---|---|---|---|---|---|
| | 30 | 20.3 | 4.1 | 0.2 | 17 |
| | 60 | 20.0 | 4 | 0.2 | 18 |
| | 90 | 19.8 | 4.6 | 0.2 | 19 |
| | 120 | 19.8 | 4.6 | 0.2 | 19 |
| | 240 | 19.8 | 4.6 | 0.2 | 19 |
| | 30 | 14.6 | 9.8 | 0.7 | 40 |
| | 60 | 14.4 | 10 | 0.7 | 41 |
| | 90 | 14.2 | 10.2 | 0.7 | 42 |
| | 120 | 14.2 | 10.2 | 0.7 | 42 |
| | 240 | 13.9 | 10.5 | 0.8 | 43 |
| | 30 | 0.2 | 24.2 | 99 | 99 |
| | 60 | 0.2 | 24 | 99 | 99 |
| | 90 | 0.2 | 24.2 | 124 | 99.2 |
| | 120 | 0.2 | 24.2 | 142 | 99.3 |
| | 240 | 0.2 | 24.2 | 142 | 99.3 |

Note: S is solid base, L is bases dissolved in DI water, initial concentration of acetic acid in pure CYANEX 923 is 21.1 g/L (0.0035 moles of acetic acid), adding 0.003 moles of calcium hydroxide and calcium carbonate, 0.9 moles of NaOH in aqueous solution (3 molar ratio of NaOH in aqueous to acetic acid in organic), at room temperature

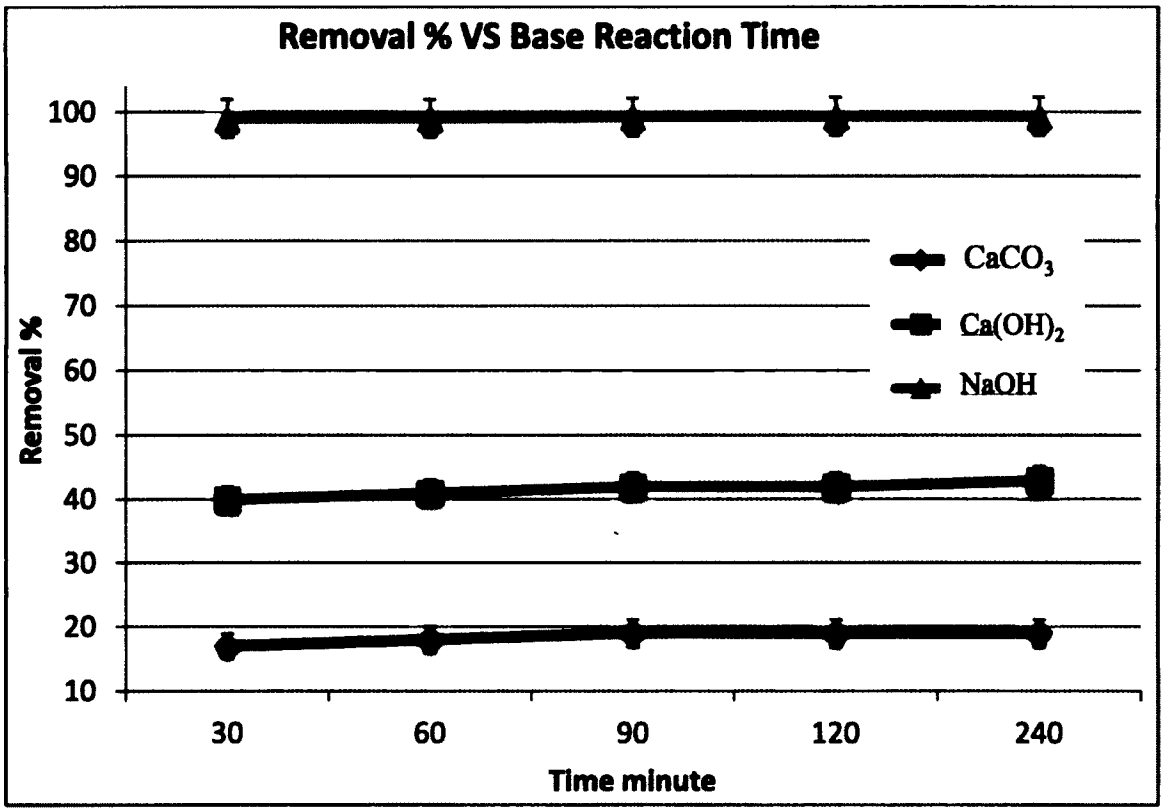



Figure 3.26 Effect of varied reaction time of acid-base reaction on acetic acid removal in an organic solution by using back extraction of NaOH solution, adding solid bases of calcium hydroxide and calcium carbonate

Note: Extraction for clean system, initial total molarity of acetic acid in pure CYANEX 923 is 21.1 g/L (0.0035 moles of acetic acid), 0.9 moles of NaOH in aqueous solution (3 molar ratio of NaOH in aqueous to acetic acid in organic), adding 0.003 moles of calcium hydroxide and calcium carbonate, at room temperature

Figure 3.27 studies the effect on removal of mixed hexanoic and heptanoic acids from CYANEX 923 after liquid-liquid extraction by a back extraction using a caustic solution (sodium hydroxide, NaOH). The figure shows moles of hexanoic and heptanoic acids in a pure CYANEX 923 versus moles of NaOH in aqueous solution. It is observed raising the moles of NaOH in the aqueous solution from 0.04 to 0.12 will increase moles removal of hexanoic and heptanoic acids from 0.002 to 0.02 and from 0.0002 to 0.02,

respectively. However, it shows no significant improvement as levels increase above 0.12 moles of NaOH in aqueous solution.

From the figure, when NaOH moles increase the acids are deprotonated and revert to the aqueous solution. As a result the carboxylate ions are separated from the solvent and transferred to the caustic solution.

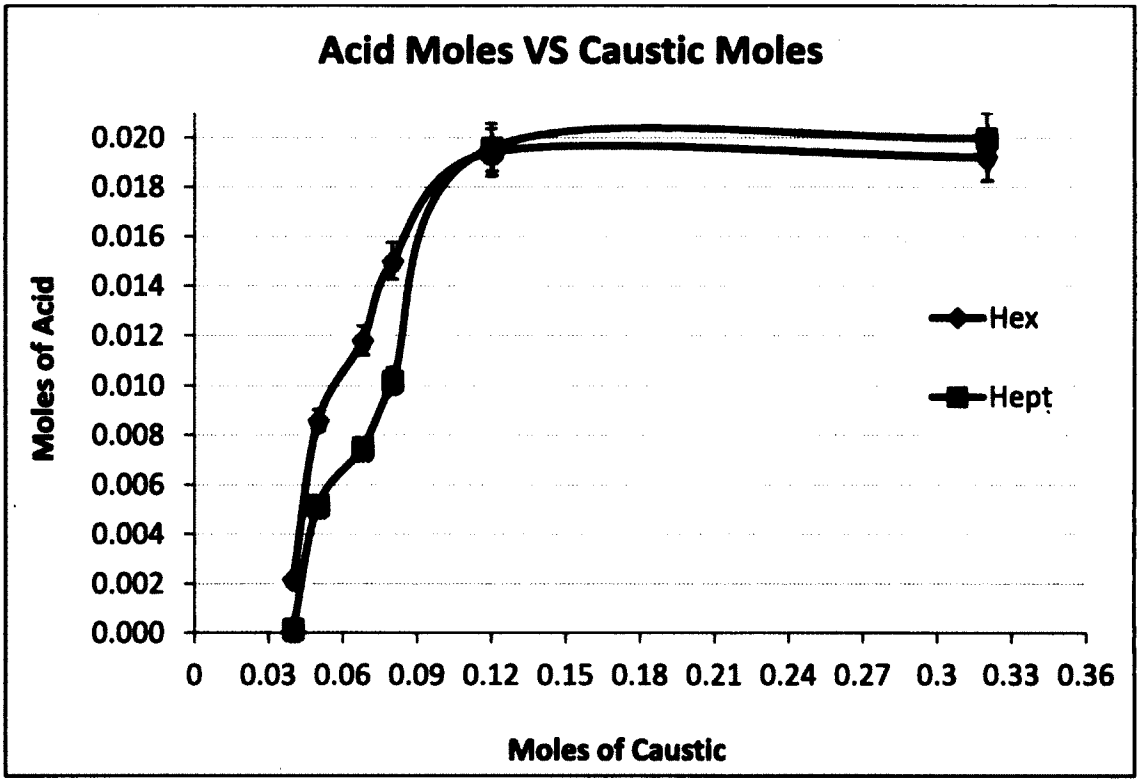



Figure 3.27 Effect on hexanoic and heptanoic acids removal from CYANEX 923 after a back extraction using a caustic solution

Note: Total moles of hexanoic and heptanoic acids in pure CYANEX 923 is 0.04, NaOH is diluted in DI-water

Figure 3.28 studies the minimal moles of NaOH in aqueous solution required for acids removal from organic solution. It shows the effect on removal % of hexanoic and heptanoic acids in CYANEX 923 by the molar ratio of NaOH in the aqueous to mixed

acids in the organic phases. It is observed from the figure that when the molar ratio increases it improves acids removal. However, there is no significant removal % benefit when increasing above a certain level. This level was found to be approximately 3:1 molar ratio NaOH to acids. In other words, an excess 3 times stoichiometric of NaOH in aqueous solution was needed to achieve high recovery of the long chain acids from solvent by the back extraction technique.

The figure shows removal % of hexanoic and heptanoic acids increase from 1% to 98% and from 2% to 98%, respectively when the molar ratio increases from 1 to 3. However, there is no significant affect on removal % when the molar ratio is increased to more than 3.

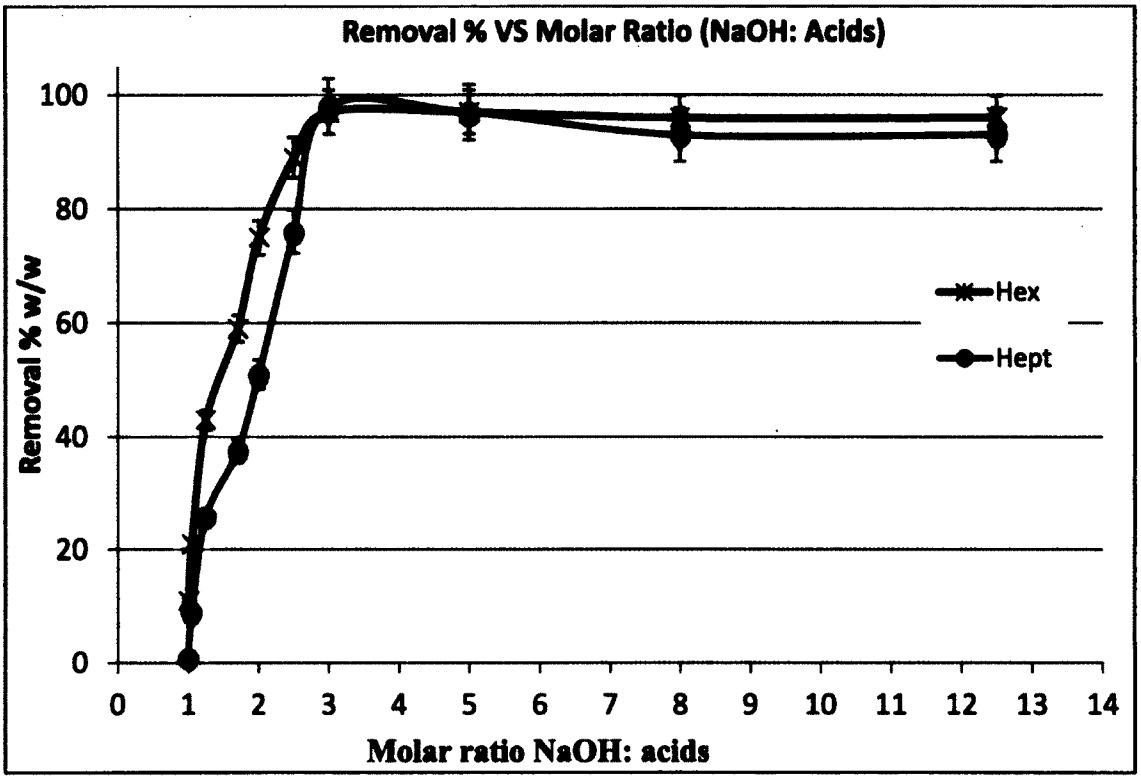



Figure 3.28 Effect on removal % of hexanoic and heptanoic acids from CYANEX 923 with respect to molar ratio of NaOH in the aqueous to mixed acids in the organic phases

Note: Extraction for clean system, initial total moles of hexanoic and heptanoic acids in pure CYANEX 923 is 0.04, NaOH is diluted in DI-water; solvent: NaOH aqueous solution volume ratio [1:1], at room temperature

The carboxylic acids in aqueous solution are either protonated when adding $H^+$ (at low pH), forming conjugate acid or deprotonated when adding $OH^-$ (at high pH), forming conjugate base. For example, acetic acid is a week acid, which is forming both anion [$A^-$] and protonated acetic acid [HA] in aqueous solution. At low pH (below 7 pH), there is high proton [$H^+$] in aqueous solution and that forms more [HA] and less [$A^-$] in the solution (Equation 3.3). On other hand, at neutral pH or high pH (pH 7 and more), there

is high hydroxide [$OH^-$] in aqueous solution and that forms more [$A^-$] and less [HA] in the solution (Equation 3.4).

$$CH_3COO^- + H_3O^+ \rightleftharpoons CH_3COOH + H_2O \qquad (3.3)$$

Acetate ions — Hydronium ion — Acetic acid — Water

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O \qquad (3.4)$$

Acetic acid — Hydroxide ion — Acetate ions — Water

For liquid-liquid extraction of acetic acid by using CYANEX 923 at pH 2, the acetate ions are protonated to form acetic acid compound in aqueous solution, which becomes less polar in the aqueous phase and transfers to the organic phase. For back extraction of acetic acid by using NaOH solution, the acetic acid compounds in organic solution are ionized to form acetate ion, which becomes more polar in the organic phase and transfers back to the aqueous phase. The acetate ions react with sodium ion, $Na^+$ to form sodium acetate salts, which transfer to aqueous phase (Equation 3.5).

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O \qquad (3.5)$$

Acetic acid — Sodium Hydroxide — Sodium acetate salt — Water

Because acetic acid is a week acid, the organic solution needs more number of hydroxide ions to increase the pH and ionize the acetic acid compound and form acetate ions. Therefore, high NaOH concentration is needed to release more hydroxide ion in

organic solution. Table 3.23 shows the effect of NaOH concentration on recovery of hexanoic and heptanoic acids from CYANEX by using caustic solution. From the table, it is observed that the pH of organic solution increases with increase of NaOH concentration in aqueous solution and results in a better acid recovery percentage.

In addition, at 3 to 1 molar ratio of moles of NaOH in aqueous solution to moles of acids in organic solution, or 0.12 molarity of NaoH, shows optimum recovery percentage for both hexanoic and heptanoic acids. This is because of more hydroxide ions were added to organic solution and resulting high pH of the organic (pH 9.4). In addition, more acetic acid ions were formed in organic solution and high acids recover percentage was achieved. However at 1 to 1 molar ratio, or 0.04 molarity of NaOH, less hydroxide ions were added to organic solution and resulting low pH of organic (pH 6). In addition, less acetic acid ions were formed in organic solution and low acids recover percentage was achieved. The excess of NaOH required to transfer the organic acids to the aqueous phase appears to be due either to a buffering action of the solvent itself (present at approximately 2.47 mol/L) or a very low solubility of NaOH in the organic phase.

Table 3.23 Recovery of hexanoic and heptanoic acids by using back extraction with different caustic concentrations

| | NaOH M (aq) | pH (org) | Acid in caustic (aq) g/L | Acid in organic g/L | $D_C$ | Recovery [w/w] % |
|---|---|---|---|---|---|---|
| | 0.04 | 6 | 0.22 | 1.6 | 0.14 | 11 |
| | 0.04 | 6.3 | 0.42 | 1.4 | 0.30 | 21 |
| | 0.05 | 6.6 | 0.82 | 1 | 0.82 | 43 |
| | 0.07 | 6.8 | 1.18 | 0.8 | 1.47 | 59 |
| Hex. | 0.08 | 7.2 | 1.48 | 0.5 | 2.96 | 75 |
| | 0.10 | 7.8 | 1.78 | 0.2 | 8.89 | 89 |
| | **0.12** | **9.4** | **1.88** | **0.1** | **18.78** | **97** |
| | 0.20 | 10 | 1.88 | 0.1 | 18.78 | 97 |
| | 0.32 | 10.9 | 1.88 | 0.1 | 18.78 | 96 |
| | | | | | | |
| | 0.04 | 6 | 0.036 | 2.2 | 0.02 | 0.9 |
| | 0.04 | 6.3 | 0.24 | 2 | 0.12 | 9 |
| | 0.05 | 6.6 | 0.54 | 1.7 | 0.32 | 26 |
| | 0.07 | 6.8 | 0.91 | 1.5 | 0.61 | 38 |
| Hept. | 0.08 | 7.2 | 1.21 | 1.2 | 1.01 | 51 |
| | 0.10 | 7.8 | 1.81 | 0.6 | 3.02 | 76 |
| | **0.12** | **9.4** | **2.30** | **0.11** | **20.92** | **98** |
| | 0.20 | 10 | 2.31 | 0.1 | 23.11 | 97 |
| | 0.32 | 10.9 | 2.31 | 0.1 | 23.11 | 93 |

Note: Initial concentration of hexanoic and heptanoic acids in CYANEX were 2.5 g/L each (0.0002 moles each in 10 mL), use pure CYANEX, vol. ratio [1:1]

Table 3.24 and figure 3.29 illustrate the effect of varied volume ratio of aqueous NaOH to organic (constant 3 moles of NaOH to 1 mole of mixed acids in solvent) for the clean system (pure acetic acid dissolved in water). It shows removal % of mixed acids in CYANEX 923 affected by changing the volume ratio of aqueous NaOH to organic. It is observed from the figure that when the volume ratio increases it improves acids removal. However, there is no significant extraction benefit when increasing above a certain level. This is because the acid-base reaction will keep going until no more acid moles left over in organic solution. For example, from figure 3.29 it can be seen that the removal % of

heptanoic acid from CYANEX 923 at constant extraction conditions (3 molar ratio of NaOH in aqueous to mixed acids in organic and at room temperature), results in significant removal % increases from less than 1% to 93% when the volume ratio is increased from 0.05 to 1 and there is no significant affect on removal % when the volume ratio is increased to more than 1.

Table 3.24 Effect of varied volume ratio of organic to NaOH in aqueous solution (constant 0.9 moles NaOH)

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 99.7 | 99.7 | 99 | 98 | 96 | 93 |
| 0.75 | 99.5 | 99.5 | 99 | 96 | 90 | 80 |
| 0.5 | 99 | 99 | 98 | 92 | 82 | 71 |
| 0.25 | 98 | 96 | 89 | 65 | 58 | 47 |
| 0.1 | 93 | 75 | 40 | 11 | 10 | 3 |
| 0.05 | 83 | 41 | 8 | 5 | 1 | 0.7 |

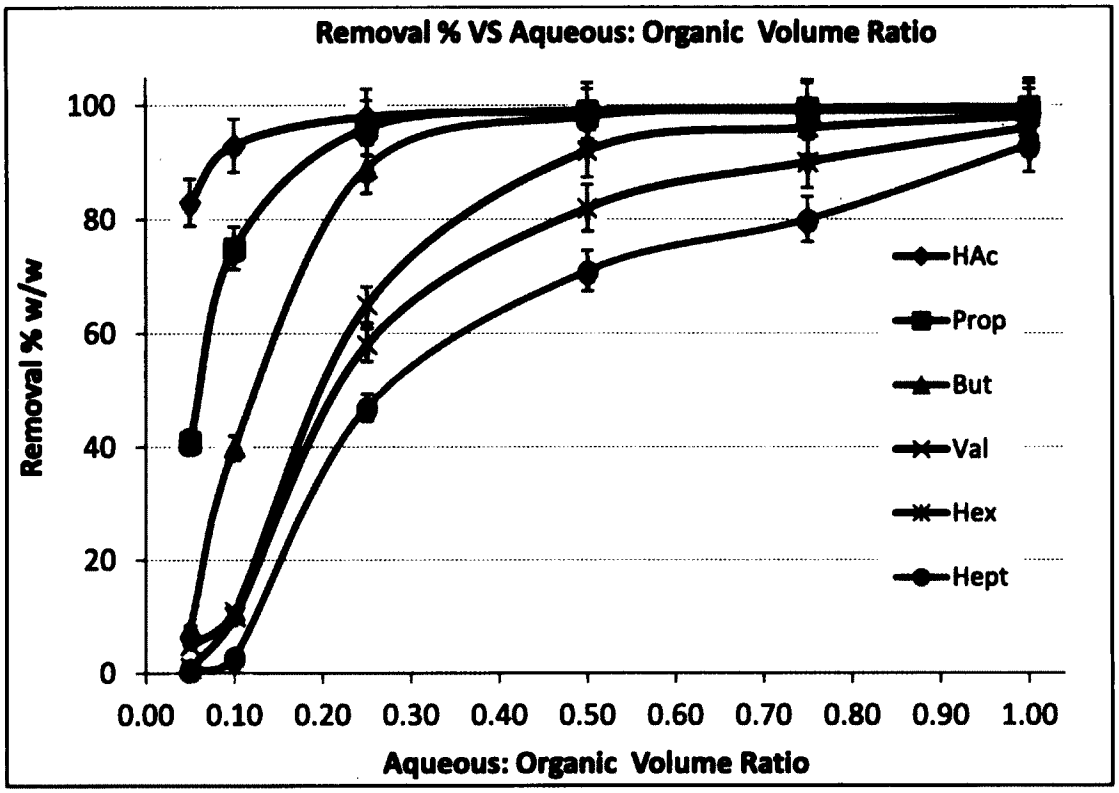



Figure 3.29 Effect of varied volume ratio of organic to NaOH in aqueous solution

Note: Extraction for clean system, initial total moles of mixed acids in pure CYANEX 923 is 0.3, NaOH is diluted in DI-water, 3 molar ratio of NaOH in aqueous to mixed acids in organic, at room temperature

### *3.11 Lignin Removal*

This former study was from my Master's research program on extraction of acetic acid using trioctylphosphineoxide (TOPO) and trioctylamine (TOA) as solvents. When operating with hemicellulose extraction samples, recycling the solvent after extraction and solvent distillation resulted in accumulation of lignin in the solvent phase. Two methods were tested to diminish this accumulation of lignin. First, hydrolyzing the hemicellulose solution at low pH and removing the precipitated lignin sent less lignin on to the liquid-liquid extraction step. Second, attempts were made to back extract, or "wash" the solvent after distillation with water or caustic.

In the case of back extracting the hemicellulose system, table 3.25 shows the effects of washing the organic solution after back extraction with deionized water in an attempt to remove the content of dissolved lignin. Table 3.26 shows results from washing the solvent with 1 molar NaOH.

Table 3.25 Organic solution after distillation and back-extraction by deionized water

| UV Analysis for Lignin | Lignin g/L |
|---|---|
| Org before Washing | 10.5 |
| Org after Washing | 9.9 |
| Water after Washing | 0.6 |

Table 3.26 Organic solution after distillation and back extraction by 1 M NaOH solution

| UV Analysis for Lignin | Lignin g/L |
|---|---|
| Org before Washing | 4.5 |
| Org after Washing | 1.2 |
| NaOH solution after Washing | 3.3 |

Lignin contents have been observed to affect the extraction (Figure 3.30 and 3.31). Therefore, it is recommended to remove lignin, as much as possible, prior to liquid-liquid extraction. Lignin is present in wood extracts as acid insoluble (Klason lignin) and acid soluble components. The acid insoluble lignin can be easily separated from the liquid phase by filtration at low pH, while the acid soluble lignin is separated from the organic phase during a back extraction technique. The soluble lignin in wood extracts transfers with the mixed acids to the organic phase when liquid-liquid extraction

is performed. As result, the recyclability of the organic phase is reduced because of lignin content accumulation. Therefore, back extraction by using a strong inorganic base, such as sodium hydroxide (NaOH), will remove the majority of soluble lignin (73 %) from the organic solution and increase the recyclability of solvent.

Figure 3.30 is comparison of results on the washing of the TOPO solution after back-extraction by deionized water and 1 M NaOH solution. From the figure is clear that washing with water alone has no significant affect on removing lignin from the organic solution, which shows only 0.2 g/L of lignin removed out of 4.5 g/L initial concentration of lignin. On the other hand, washing with 1 M NaOH solution removed the majority of the lignin, about 3.3 g/L out of 4.5 g/L (73 %) (Figure 3.26 shows a significant effect on lignin removal).

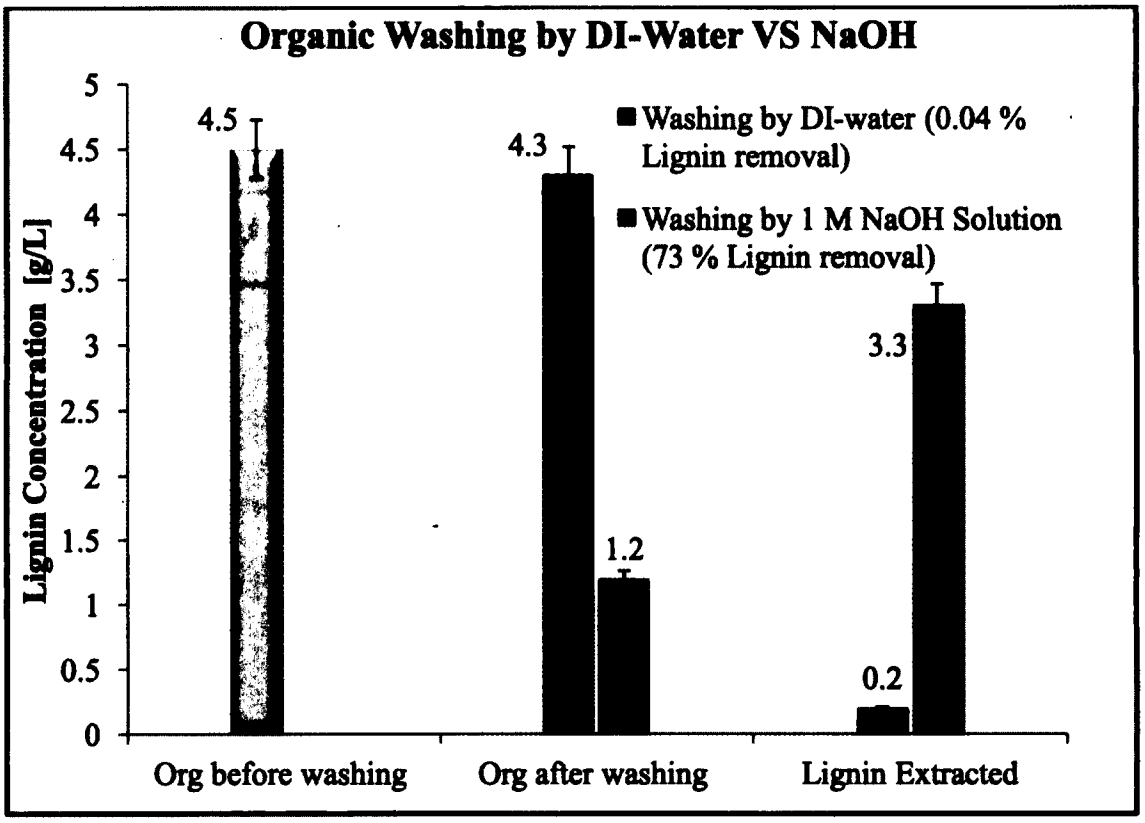



Figure 3.30 Comparing between washing the organic solution by DI-water and NaOH to remove lignin contents

Note: Volume ration of water to organic is 1:1

Figure 3.31 shows the lignin concentration before and after hydrolysis, liquid-liquid extraction and washing with NaOH. As seen in the figure, the initial concentration of lignin in green liquor extract was 20 g/L. It was reduced to 7.2 g/L after doing acid hydrolysis and filtration of acid-precipitated lignin. Then about 65% (4.7 g/L) of the lignin in the aqueous phase transferred to the organic phase through the one stage of liquid-liquid extraction. Finally, about 73% (3.5 g/L) of lignin was removed from the organic solution by washing with 1 M NaOH solution.

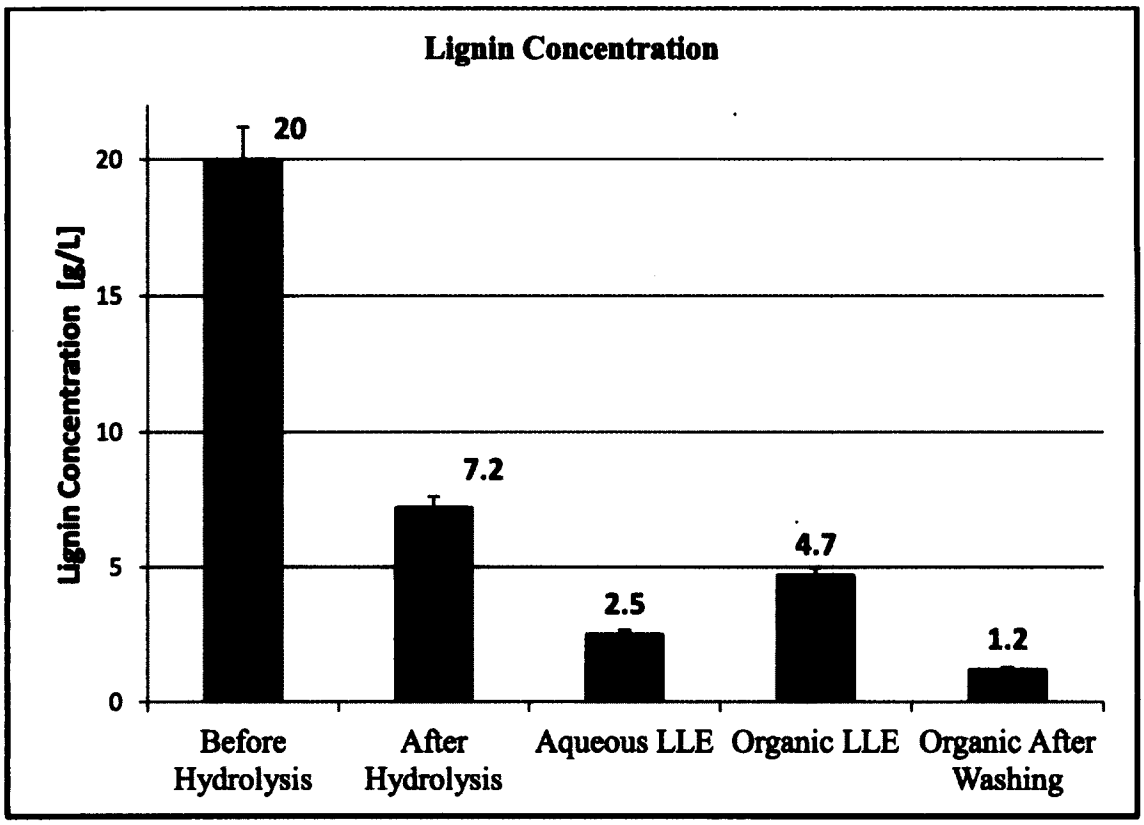



Figure 3.31 Lignin concentration before and after hydrolysis, liquid-liquid extraction and washing with NaOH

### *3.12 Solvent Recyclability*

It is important to recover the solvent so that it can be reused in liquid-liquid extraction. For example, TOPO and CYANEX 923 are costly solvents. Commercial grade TOPO is available for $40/kg and $60/kg for CYANEX 923. For this study, laboratory grade TOPO and CYANEX 923 was purchased for the very high prices of $2/g and $3.5/g, which were on the order of 5 times more costly than laboratory grade TOA at $0.7 per g. Therefore, it is essential to recover the solvent after liquid-liquid extraction. It was suggested that this could be done by distilling the acids off the solvent, thus recovering the acids and recycling the solvent. However, previous distillation results show that distillation is not able to recover long chain acids from the solvent due to

elevated boiling point effects and thermal degradation of the solvent. Therefore, a back extraction with a strong caustic aqueous solution such as NaOH was used to recover the acids and recycle the solvent.

### *3.12.1 Recyclability of Solvents through Liquid-Liquid Extraction, Distillation and Back Extraction of Acetic Acid (Previous works)*

Figure 3.32 shows a comparison of results for recycling solvent before and after doing hydrolysis and without or with back extraction using 1 M NaOH.. The results are for green liquor extract system and TOPO in undecane. From the figure, the extraction % of acetic acid through each recycling round tends to be constant (around 62%) in the case of using hydrolyzed hemicellulose extract and washing with NaOH as integral steps. On the other hand, the extraction % diminishes through each recycle round in the case where there is no acid hydrolysis of the hemicellulose and no washing procedure.

Recycle of TOPO on unhydrolyzed extract and without the back extraction showed poor recyclability. Presumably the improved performance was due to removal of Klason lignin after acid hydrolysis and then further removal of the acid soluble lignin through the caustic washing step.

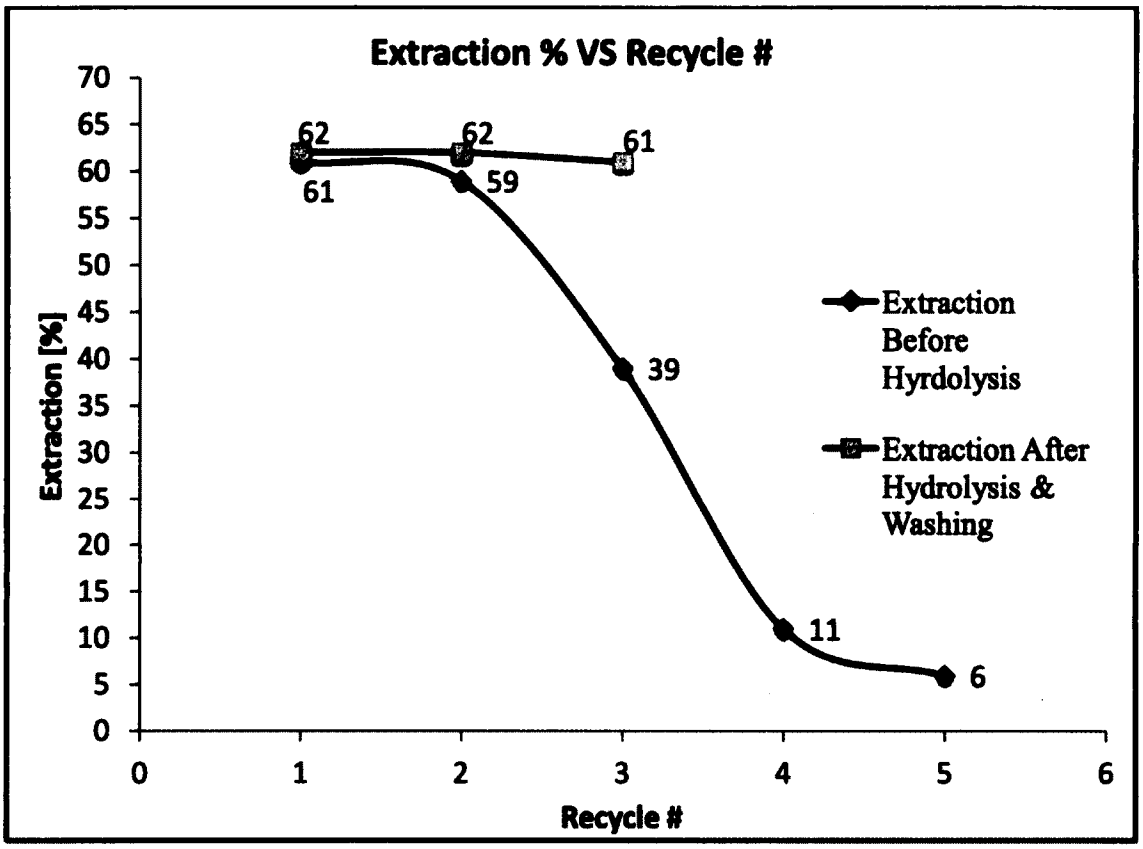


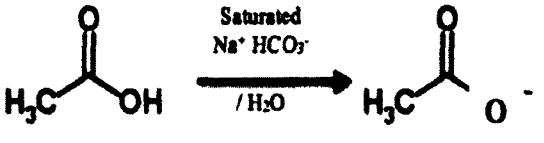

Figure 3.32 Comparing results of distillation-recycled liquid-liquid extract of hydrolyzed and non-hydrolyzed hemicellulose extract, with and without washing (respectively) with 1 M NaOH solvent at 70 °C

Note: This is for green liquor extract system with 8.7 g/L initial acetic acid concentration, using 370 g/L of TOPO/undecane, pH 1, volume ratio 1:1 organic : aqueous

Figure 3.33 illustrates the extraction performance through distillation-recycles of different extraction systems. This demonstrates that on both the clean system and the green liquor extract system, the TOPO in undecane solution appears to be more recyclable and recoverable than TOA in octanol. This may be because more acetic acid was recovered from the TOPO/undecane solution by distillation during each recycling round. Distillation results shown above indicated that distillation did not effectively recover acetic acid from the TOA solvent and apparently acetic acid accumulated in the

organic solution through recycling rounds. Back extraction results appear to support this observation, as well. It can be seen that TOA extraction diminished quickly through unwashed recycles, even with the clean system that contained no lignin. However, back extraction the TOA solvent, applied to the hemicellulose system, did appear to enhance solvent recyclability to some extent. Together, these TOA results suggest that the distillation step is not removing the acetic acid from the TOA, and that the back extraction system lends credence to the observation that no acetic acid was detected in the distillate from the TOA distillations.

Separation of acetic acid from TOA solution by distillation was done at low pH (pH was 1). This may have played a role for making difficult the separation of acetic acid from the amine. It has been suggested that increasing the pH of the organic may aid in the separation of acetic acid by distillation. Alternatively, as was demonstrated in the washing of the TOA solvent, separating acetic acid from TOA could be done simply by back extraction with inorganic bases such as 5% sodium hydroxide solution or saturated sodium bicarbonate, into a second aqueous solution. This would ionize the acetic acid into acetate ions and then enable its transfer back to the aqueous phase as shown below [38].




$$+ Na^+ + H_2O + CO_2 \quad (3.6)$$

Soluble in organic solution
Not soluble in water

Not soluble in organic solution
Soluble in water

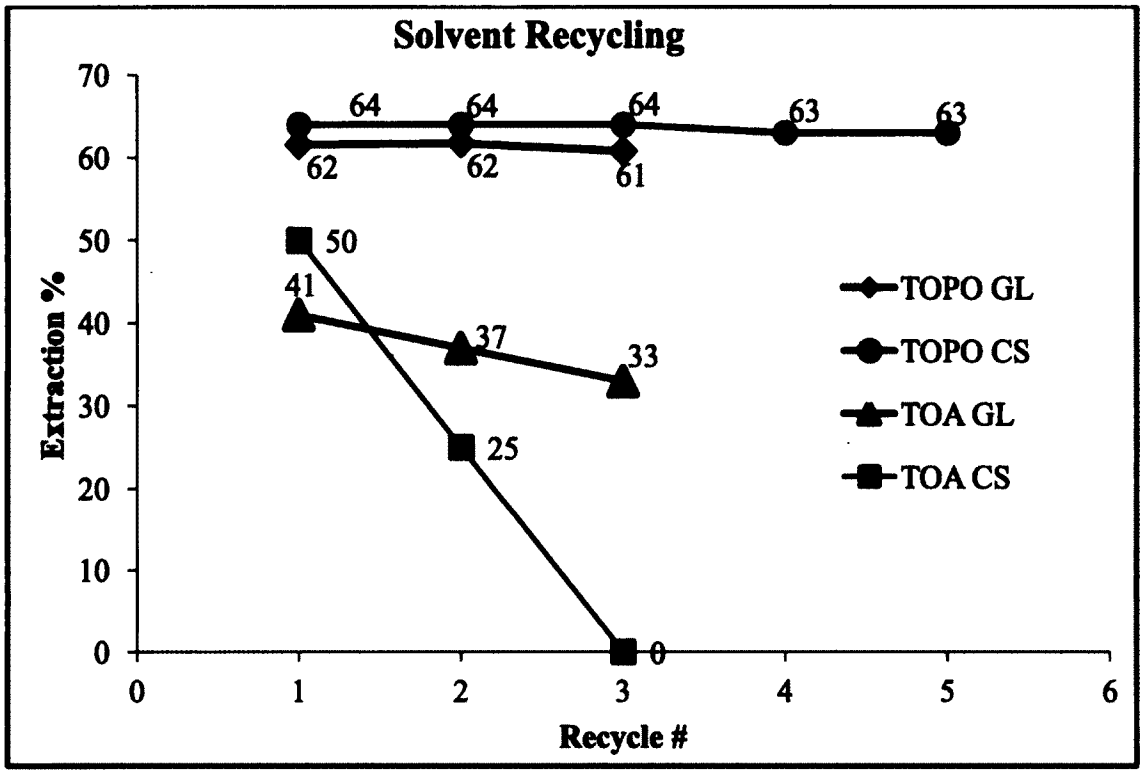



Figure 3.33 Recycle efficiency of solvent

Notes: CS: clean system (water and acetic acid)

GL: green liquor extract system

The initial aqueous acetic acid concentration is 10 g/L for the clean system and 8.7 g/L for the green liquor

The extraction conditions were pH 1, organic to aqueous ratio 1:1, 70 °C

Using 370 g/L TOPO/undecane, 200 g/L TOA/octanol

### *3.12.2 Recyclability Solvent through Extraction and Distillation of Mixed Acids*

Figure 3.33 and 3.34 illustrate the results of work on the extraction performance through distillation-recycle systems. These results report on the recyclability of 400 g/L CYANEX in tridecane after liquid-liquid extraction of mixed acids from clean system. Both aqueous and organic phases were analyzed through the distillation-recycle systems. Figure 3.34 presents results based on aqueous solution analysis, while figure 3.35 results are based on the organic solution. From figure 3.33, it is observed that the extraction of

short chain acids, such as acetic acid, decrease from 70% to 42% through three recycles of the solvent, while the recovery of long chain acids, such as heptanoic acid, remain constant at 98%. This is because of the failure to recover long chain acids by distillation due boiling point rise and as a result, acids will remain in solvent and then accumulate through each recycle of the solvent. Therefore that will reduce recovery of short chain acids. Figure 3.35 shows accumulation of long chain acids in solvent each time recycling due to above the reason.

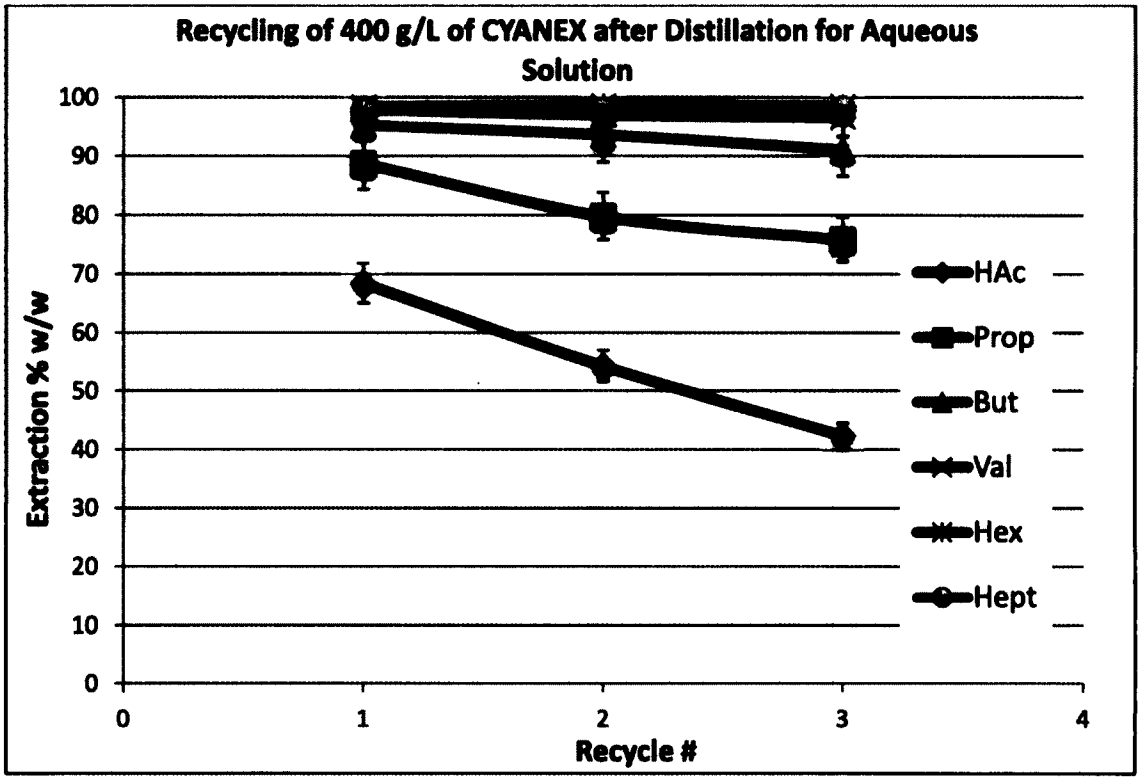



Figure 3.34 Recycle efficiency of solvent based on aqueous solution GC analysis

Note: Initial total acids concentration is 31 g/L in aqueous solution for clean system, the extraction conditions were 1 pH, 1 ratio and at room temperature, using 400 g/L CYANEX/tridecane as solvent

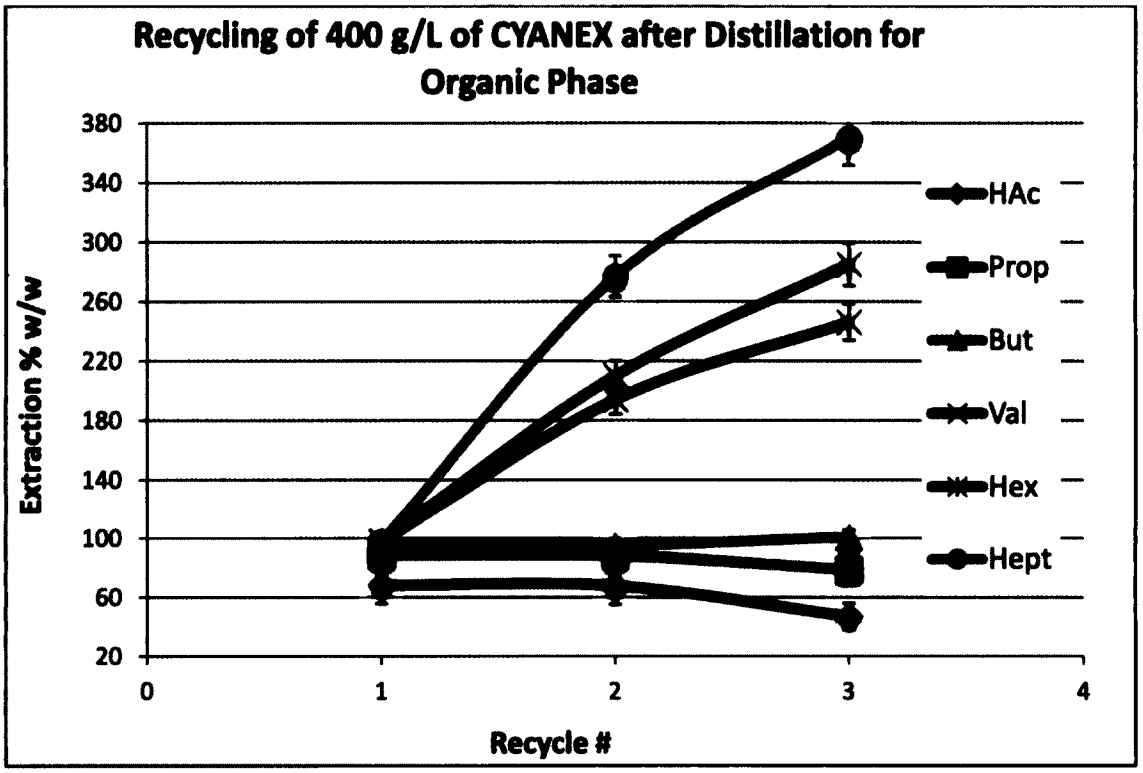



Figure 3.35 Recycle efficiency of solvent based on organic solution GC analysis

Note: Initial total acids concentration is 31 g/L in aqueous solution for clean system, the extraction conditions were pH 1, volume ratio 1 and at room temperature, using 400 g/L CYANEX/tridecane as solvent

### *3.12.3 Back Extraction Using Sodium Hydroxide*

Tables 3.27 to 3.29 and figures 3.36 to 3.38 illustrate recyclability performance of CYANEX 923 through back extraction-recycles system. This demonstrates that for both the clean system and fermented acids system, the pure and tridecane diluted CYANEX 923 solutions appear to be recyclable and recoverable, as was found with TOPO extracting acetic acid. From the figures, it is observed that mixed acids become more recoverable from CYANEX 923 by using back extraction with 3 molarity ratio of sodium hydroxide. As a result of this, the solvent becomes more recyclable after back-extraction than other separation process such as distillation.

Table 3.27 Recyclability of pure CYANEX 923 after liquid-liquid extraction and back extraction with 3 molar ratio of NaOH and for a clean system

| | | | | | | |
|---|---|---|---|---|---|---|
| | 83.1 | 95.2 | 98.6 | 99.5 | 96.6 | 99.1 |
| | 83.3 | 95.4 | 98.7 | 99.6 | 99.5 | 99.2 |
| | 83 | 95.1 | 98.5 | 99.5 | 99.4 | 99.1 |
| | 83.3 | 95.2 | 98.6 | 99.4 | 99.5 | 99.1 |
| | 83.1 | 95.1 | 98.4 | 99.5 | 99.3 | 99 |
| | 83.2 | 95.4 | 98.5 | 99.5 | 99.5 | 99.1 |

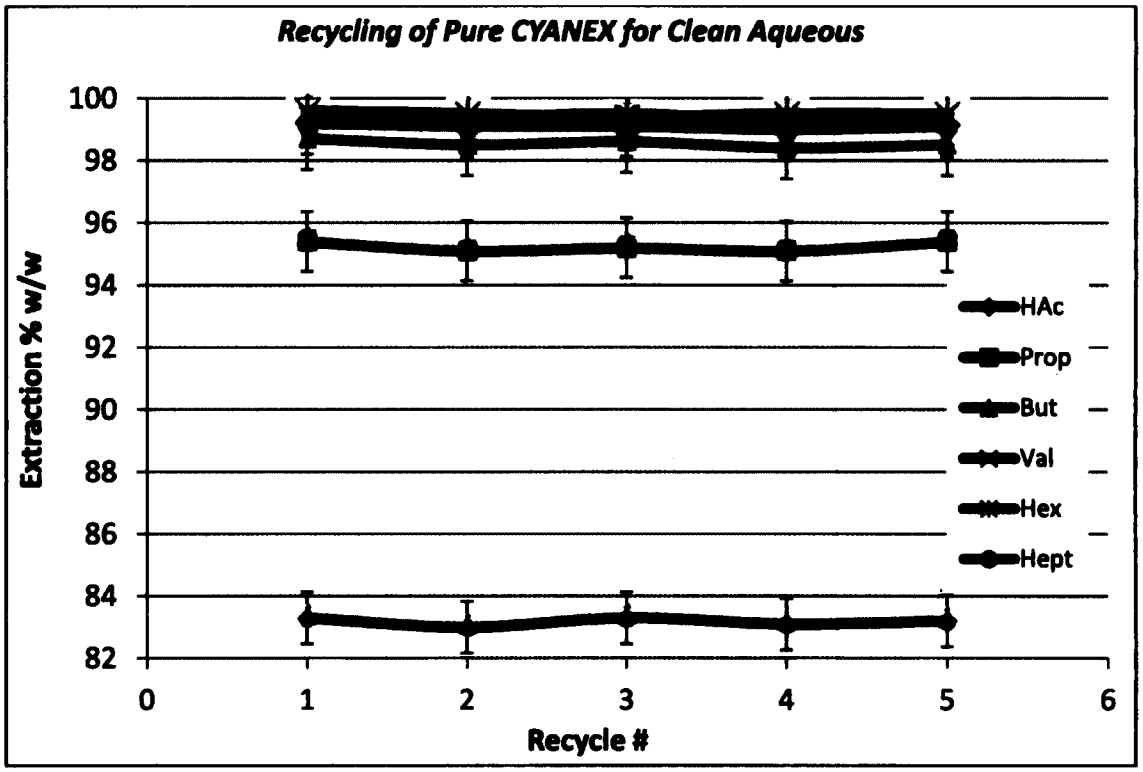



Figure 3.36 Recycle efficiency of pure CYANEX 923 through liquid-liquid extraction and NaOH back extraction system

Note: Initial total acids concentration is 31 g/L in aqueous solution for clean system, the extraction conditions were pH 1, volume ratio 1:1 and at room temperature. The back extraction conditions were a 3 to 1 molar ratio of NaOH to acids and at room temperature

Table 3.28 Recyclability of 400 g/L CYANEX 923/tridecane after liquid-liquid extraction and back extraction with 3 molar ratio of NaOH for a clean system

| | | | | | | |
|---|---|---|---|---|---|---|
| [redacted] | | | | | | |
| [redacted] | 74.5 | 92.7 | 97.5 | 99.1 | 99.1 | 98.8 |
| [redacted] | 74.6 | 92.5 | 97.7 | 99.4 | 99.4 | 99 |
| [redacted] | 74.1 | 92.6 | 97.9 | 99.4 | 99.5 | 99.2 |
| [redacted] | 74.3 | 92.7 | 97.6 | 99.3 | 99.4 | 99 |
| [redacted] | 74.6 | 92.5 | 97.7 | 99.2 | 99.5 | 99.1 |
| [redacted] | 74.3 | 92.5 | 97.8 | 99.3 | 99.4 | 99.1 |

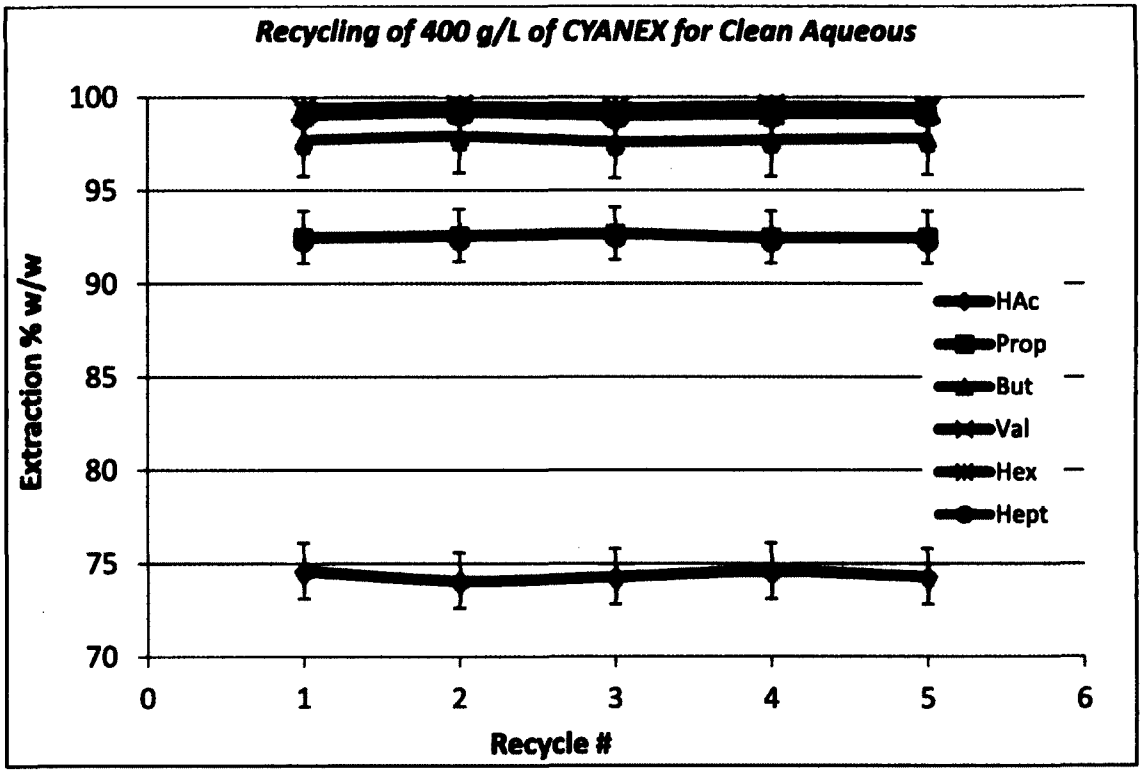



Figure 3.37 Recycle efficiency of 400 g/L CYANEX 923/tridecane through liquid liquid extraction and back extraction system

Note: Initial total acids concentration is 31 g/L in aqueous solution for clean system, the extraction conditions were pH 1, volume ratio 1:1 and at room temperature. T The back extraction conditions were a 3 to 1 molar ratio of NaOH to acids and at room temperature

Table 3.29 Recyclability of 400 g/L CYANEX 923/tridecane after liquid-liquid extraction and back extraction with 3 molar ratio of NaOH to acids for fermentation-derived mixed acids

| | | | | | | |
|---|---|---|---|---|---|---|
| 0 | 80.8 | 94.1 | 98.9 | 99.7 | 99.1 | 98.9 |
| 1 | 80.5 | 93.5 | 98.5 | 99.6 | 98.9 | 98.7 |
| 2 | 81 | 94 | 98.6 | 99.5 | 98.9 | 98.8 |
| 3 | 80.6 | 93.8 | 98.5 | 99.6 | 98.8 | 98.8 |
| 4 | 80.9 | 93.9 | 98.8 | 99.6 | 98.9 | 98.6 |
| 5 | 80.8 | 94 | 98.6 | 99.8 | 98.8 | 98.7 |

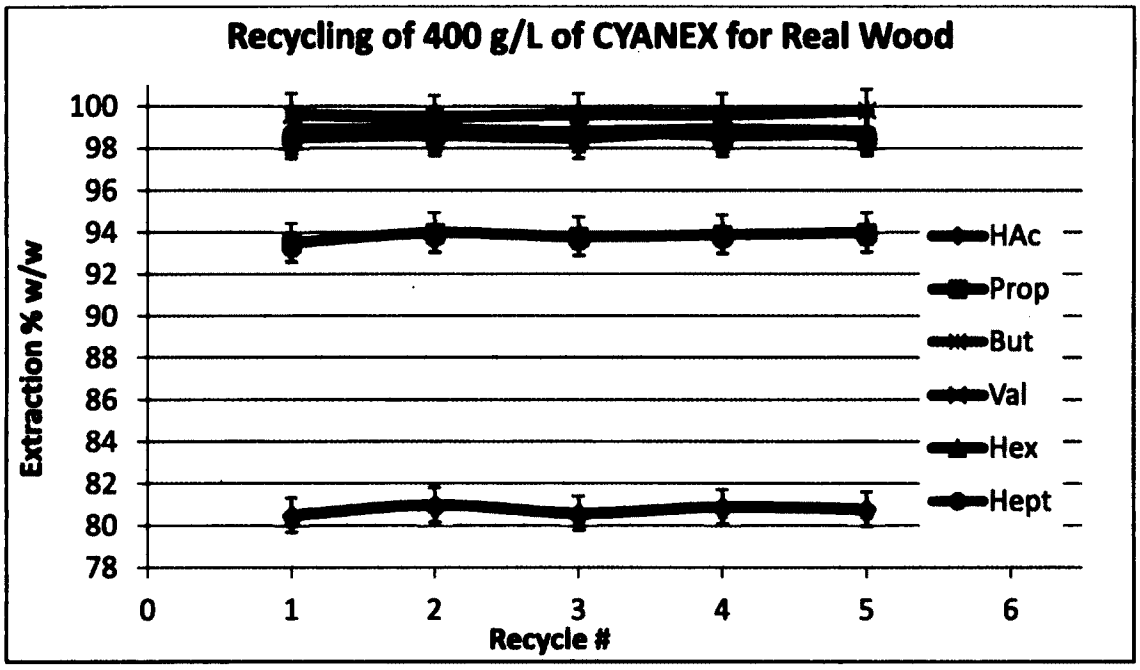



Figure 3.38 Recycle efficiency of 400 g/L CYANEX 923/tridecane for fermentation-derived mixed acids solution and through liquid liquid extraction and back extraction

Note: Initial total acids concentration is 33 g/L in aqueous solution, the extraction conditions were pH 1, volume ratio of 1:1 and room temperature. The back extraction conditions were a 3 to 1 molar ratio of NaOH to acids and at room temperature

### *3.13 Mass Balance*

Table 3.30 to 3.32 show a mass balance of liquid-liquid extraction of mixed acids, distillation process and back extraction with sodium hydroxide for a clean system by using CYANEX 923 as extractant. The mass was measured before, during and after each processes and percentages of error are measured to evaluate each processes' performances. From the tables, it is observed that error % of liquid-liquid extraction and back extraction processes are less than the distillation process. Because some carboxylic acids are volatile and easy to lose, some mass losses are expected to occur during distillation due incomplete condensation while liquid-liquid extraction and back extraction are done at room temperature. Also, some degradation of the acids is apparently occurring at the high temperatures of the distillation.

Table 3.30 shows a mass balance of liquid-liquid extraction of mixed acids from aqueous solution for a clean system by using CYANEX 923. The mass was measured before and after extraction and for both aqueous and organic phases. From the table it is observed that the extraction % increases from 75% to 99% as the carbon numbers in carboxylic acids increase from carbon 2 to 7, while the error percentage decreases from 7% to 3%.

Table 3.30 Mass balance of liquid-liquid extraction

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 6.1 | 2.2 | 0.35 | 0.24 | 0.09 | 3 | 75.2 | 7 |
| | 8.1 | 0.6 | 0.37 | 0.33 | 0.03 | 13 | 93.2 | 6 |
| | 4.2 | 0.1 | 0.18 | 0.17 | 0.003 | 51 | 98.2 | 6 |
| | 2.3 | 0.01 | 0.10 | 0.09 | 0.0005 | 191 | 99.5 | 4 |
| | 2.1 | 0.01 | 0.09 | 0.08 | 0.0004 | 193 | 99.5 | 3 |
| | 1.8 | 0.02 | 0.08 | 0.07 | 0.001 | 107 | 99.1 | 3 |

Table 3.31 shows a mass balance of distillation after liquid-liquid extraction of mixed acids from aqueous solution for a clean system using CYANEX 923. The mass was measured before and after distillation, the latter in both the organic phase and condensate phase. From the table 3.31, it is observed that the recovery % decreases from 99% to 16% as the carbon numbers in carboxylic acids increase from carbon 2 to 7, while the error percentage increases from 13% to 15%.

Table 3.31 Mass balance of distillation

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 6.1 | 0.1 | 104.8 | 0.24 | 0.002 | 0.21 | 99 | 13 |
| | 8.1 | 0.1 | 142.0 | 0.33 | 0.003 | 0.28 | 99 | 12 |
| | 4.2 | 1.9 | 41.1 | 0.17 | 0.08 | 0.08 | 55 | 12 |
| | 2.3 | 1.5 | 13.6 | 0.09 | 0.06 | 0.03 | 35 | 15 |
| | 2.1 | 1.7 | 8.0 | 0.08 | 0.07 | 0.02 | 22 | 14 |
| | 1.8 | 1.5 | 5.0 | 0.07 | 0.06 | 0.01 | 16 | 15 |

Table 3.32 shows a mass balance of a back extraction using a 3 molar ratio of sodium hydroxide to acid to recover mixed acids from CYANEX 923. The mass was

measured before and after back extraction for the organic phase and the NaOH aqueous phase. From the table is observed that the extraction % decreases from 99% to 71% as the carbon numbers in carboxylic acids increase from carbon 2 to 7, while the error percentage increases from 5% to 9%.

In addition, table 3.30 shows decreasing error % in extraction as carbon carbon chain length increases. This could be because the longer carbon chain molecules are less volatile. In contrast, table 3.31 and 3.32 show increasing of error % as carbon carbon chain length increases in distillation and back extraction due to other factors, such as high temperature of distillation and less solubility of long chain acids in aqueous solution. High temperature of distillation process plays a role for losing some acid masses during the process and increases the error %. Similarity, long chain acids are less soluble in aqueous solution and when they are recovered from the organic phase by back extraction with NaOH, they will not totally dissolve again in aqueous phase. This reduces the accuracy of the analysis of this mixture.

Table 3.32 Mass balance of a back extraction by using sodium hydroxide

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 6.1 | 0.1 | 11 | 0.24 | 0.002 | 0.23 | 99 | 5 |
| | 8.1 | 0.1 | 15 | 0.33 | 0.003 | 0.31 | 99 | 4 |
| | 4.2 | 0.1 | 8 | 0.17 | 0.003 | 0.16 | 98 | 4 |
| | 2.3 | 0.2 | 4 | 0.09 | 0.007 | 0.08 | 92 | 6 |
| | 2.1 | 0.4 | 3 | 0.08 | 0.015 | 0.06 | 82 | 7 |
| | 1.8 | 0.5 | 2 | 0.07 | 0.021 | 0.05 | 71 | 9 |

### *3.14 Theoretical Stages for Extraction Column*

Making use of the experimental lab results of liquid-liquid extraction, the McCabe-Thiele method was used to determine the theoretical stages of extraction column needed to achieve 94 % extraction of acetic acid from a solution of 10 g/L initial acetic acid in DI-water [25]. Figure 3.39 to 3.41 show theoretical stages of acetic acid extraction by using TOPO, TOA and CYANEX 923, respectively. The figures show that four stages are needed to extract 94% of acetic acid by TOPO solution, about one stage by TOA solution and three stages by CYANEX 923 solution. While figure 3.42 shows theoretical stages of back extraction by sodium hydroxide for recovering acetic acid from CYANEX 923. The figure shows three stages need to recover 94% of acetic acid from CYANEX 923 solution.

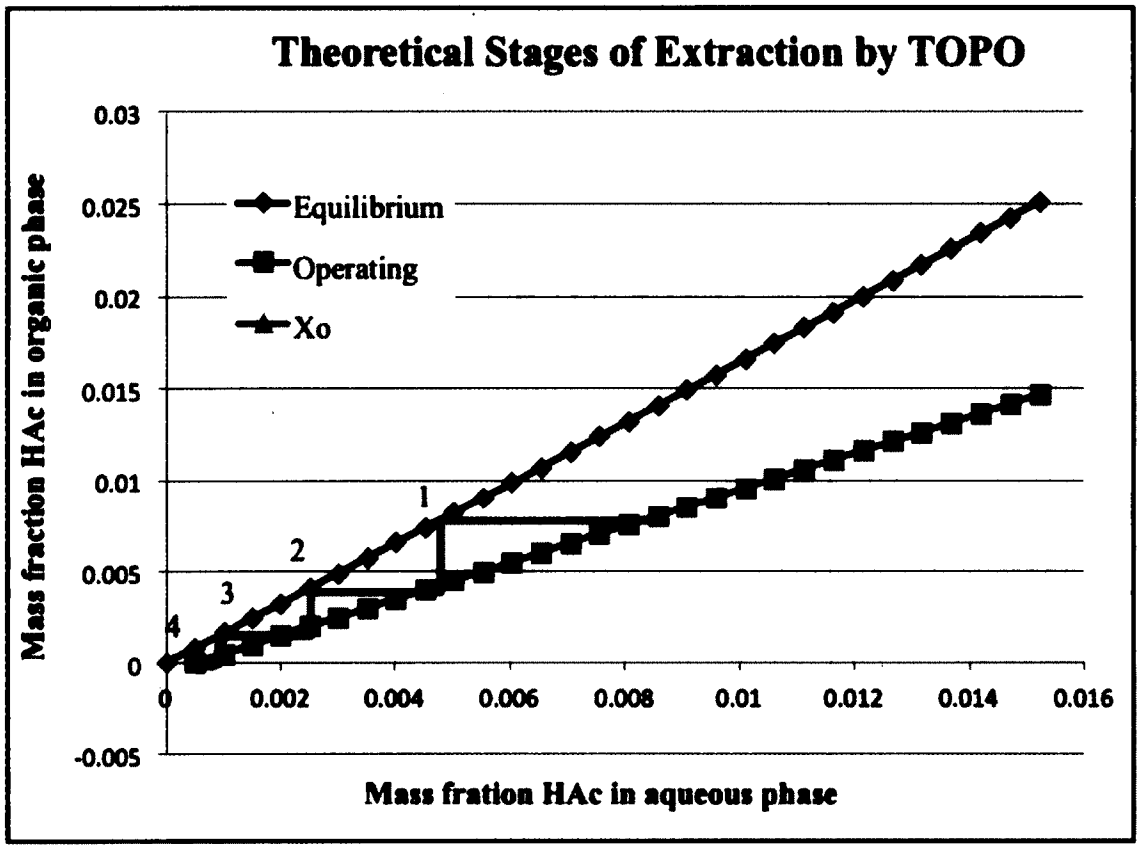



Figure 3.39 Theoretical stages of acetic acid extraction by TOPO

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, 370 g/L TOPO, pH 1, at 70 °C, volume ratio of organic: aqueous phases [1:1]

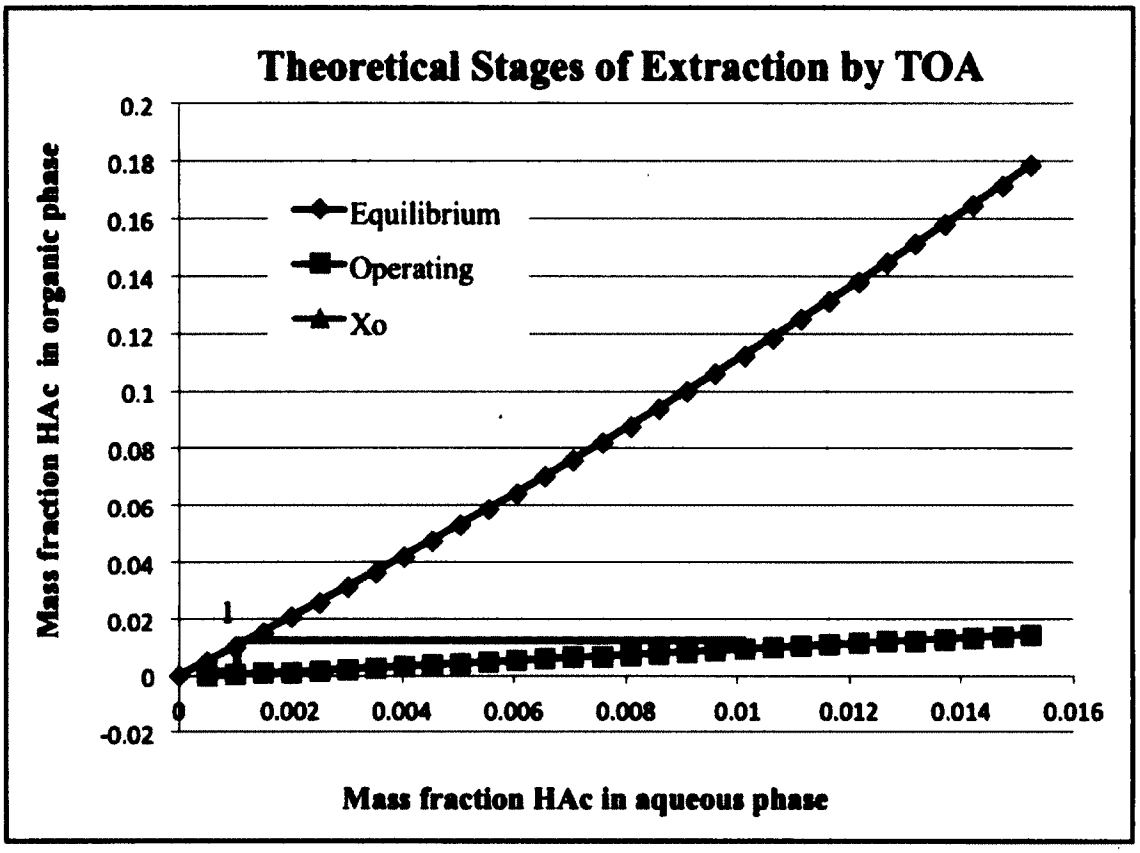



Figure 3.40 Theoretical stages of acetic acid extraction by TOA

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, 200 g/L TOA, 2.9 pH, at 70 °C, volume ratio of organic: aqueous phases [1:1]

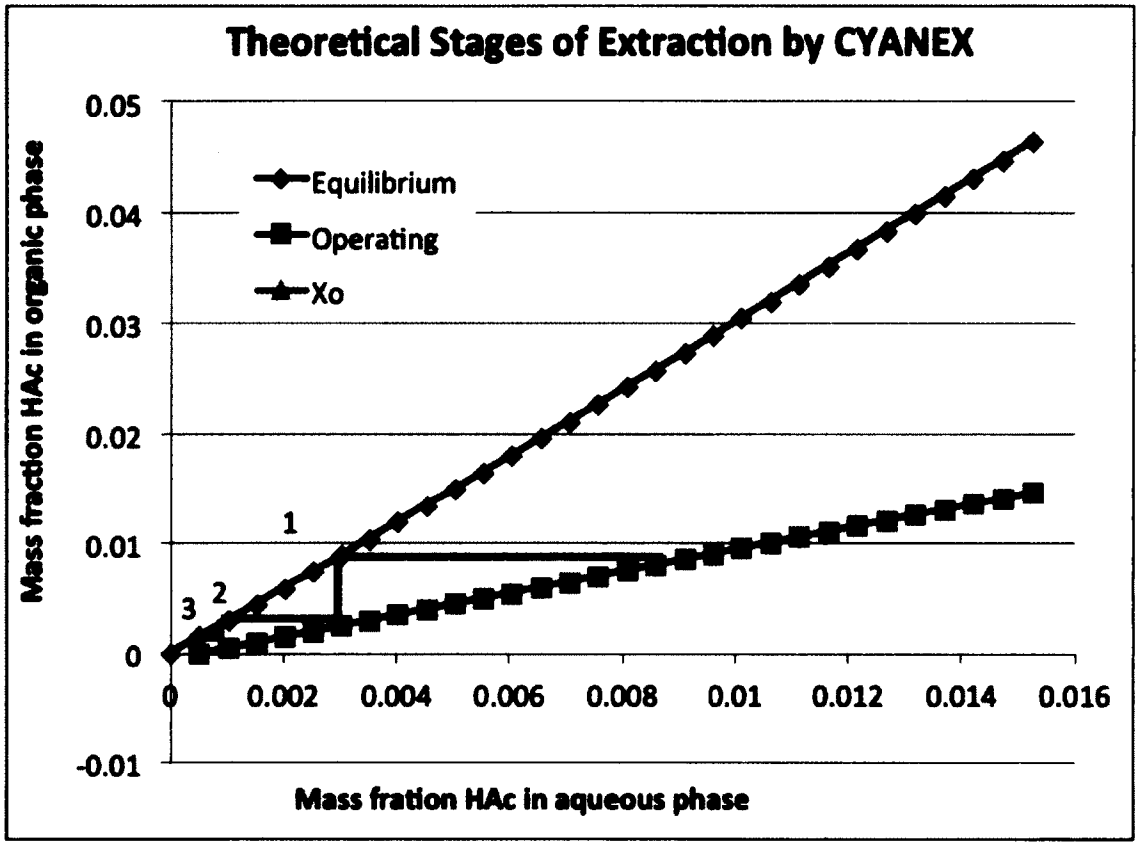



Figure 3.41 Theoretical stages of acetic acid extraction by CYANEX 923

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, 400 g/L CYANEX 923/tridecane, pH 1, at 22 °C, volume ratio of organic: aqueous phases [1:1]

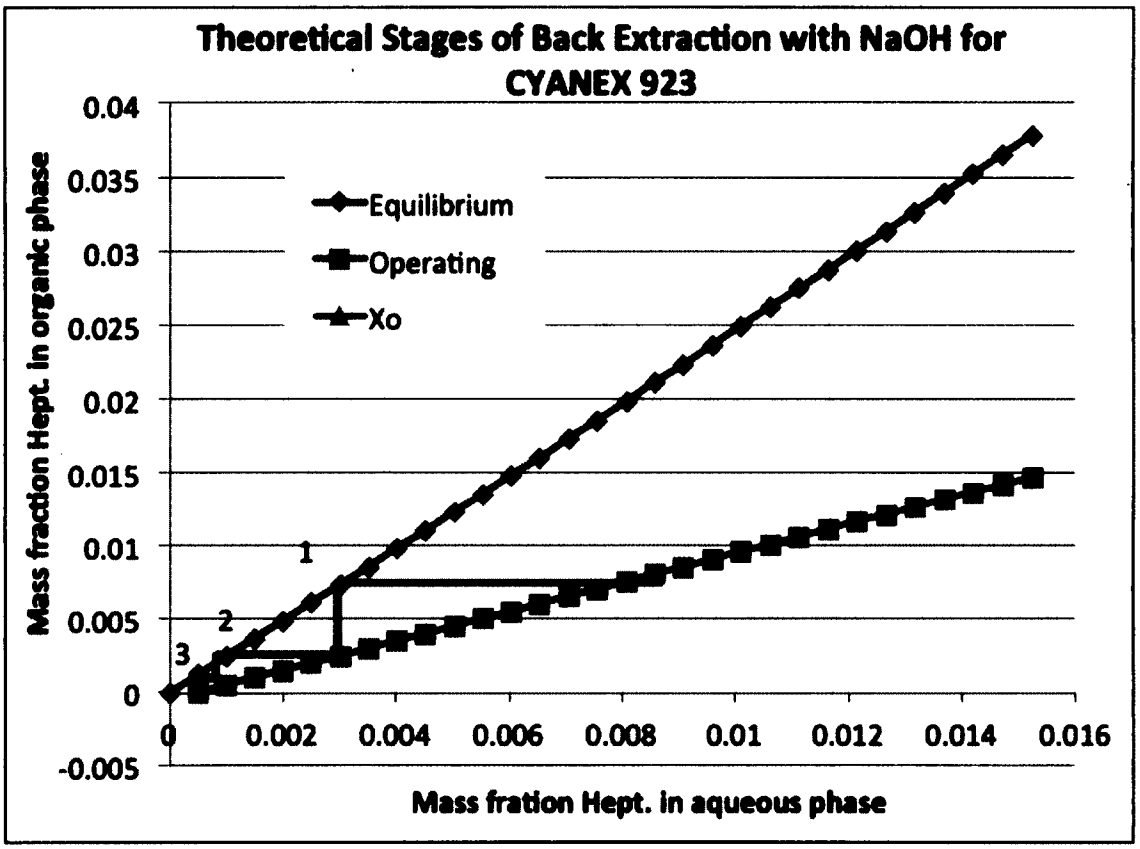



Figure 3.42 Theoretical stages of acetic acid back extraction by NaOH for CYANEX 923

Note: Extraction for clean system, initial concentration of pure acetic acid solution is 10 g/L, 400 g/L CYANEX 923/tridecane, at 22 °C, 3 molarity ratio NaOH, volume ratio of organic: NaOH aqueous phases [1:1]

### *3.15 Solvents Comparison*

Table 3.33 shows that one stage extraction of the clean system by TOA and CYANEX 923 have better acetic acid removal than by TOPO (without recycling of solvent). However, extraction by TOA shows low extraction of acetic acid for a more realistic aqueous extract system, possibly because of very low pH, while extraction by CYANEX 923 and TOPO show to be more stable and constant for both systems. TOA gives a better extraction at lower concentration in the organic phase (200 g/L) than TOPO (370 g/L) and CYANEX 923 (400g/L). In addition TOA is less costly than TOPO and

CYANEX 923 and has optimal extraction at a higher pH than them, which could reduce the process cost since reducing pH requires the expense of adding acids such as sulfuric acid. On the other hand, TOPO and CYANEX 923 are more stable than TOA in terms of its recyclability.

Table 3.33 Comparisons between TOPO, TOA and CYANEX 923 for extraction of acetic acid

| | TOPO | TOA | CYANEX 923 |
|---|---|---|---|
| **Solvent concentration in organic** | 370 g/L | 200 g/L | 400 g/L |
| **pH** | 3 or lower | 2-4 | 3 or lower |
| **Volume ratio of org. to aq.** | 1:1 | 1.5:1 | 1:1 |
| **Extraction for clean system** | 78% | 91% | 88% |
| **Extraction for real Aqueous** | 62% | 41% | 87% |
| **Distillation efficiency** | 89% of C2 | 0% of C2 | 50%-99% C2-C4<br>1%-14% C5-C7 |
| **Acid Precipitation** | ---- | ---- | 17%-40% of C2 |
| **Back extraction with NaOH** | ---- | ---- | 99% of C2-C7 |
| **Handling at room Temperature** | Hard | Easy | Easy |
| **Cost** | Expensive | Less expensive | Expensive |
| **Recyclability** | Stable | Deteriorates | Stable |

Note: ---- is not analyzed

# CHAPTER FOUR

# CONCLUSIONS AND FUTURE WORKS

## *4.1 Conclusions*

Extraction of single acid (acetic acid) and multiple acids using different solvents were tested. The extraction was done first for a clean system (mixed acids in water) and then for wood extract or pretreated (green liquor extract) and mixed acids fermented broth after fermentation. Several separation processes were tested to recover carboxylic acids from the solvent including: distillation, acid salts precipitation and back extraction with dilute aqueous sodium hydroxide. Next the recycling of solvent had been used to reduce the cost of the solvent. In addition, lignin content might be transferred with acids to solvent and affect the solvent recyclability. Therefore, a washing by 1 M of sodium hydroxide, NaOH, had been used to remove lignin content from the solvent.

A comparison of results of extraction by several extractant agents including trioctylphosphine oxide (TOPO), diluted in undecane; trioctylamine (TOA), diluted in octanol and CYANEX 923 (a mixture of four trialkyl phosphine oxides) dilute in tridecane were shown. TOPO showed 64% extraction of a single acid (acetic acid) for clean system and 62% for green liquor extract system. Similarity, TOA showed 90% extraction of acetic acid for clean system and 41 % for green liquor extract system. While CYANEX showed the best extractions for multi acids individually (carbon-2 to carbon-7) (more than 90% extraction) and for both clean and wood extract systems. The optimum extraction conditions were shown as follows:

- The concentration of TOPO in organic solution was 370 g/L, 200 g/L for TOA and 400 g/L for CYANEX.

- The pH was 3 or lower for TOPO and CYANEX, while 2-4 for TOA.
- The volume ratio of organic to aqueous was 1:1 for TOPO and CYANEX, while 1.5:1 for TOA.
- Extraction temperature was 70 °C for TOPO and TOA, while at room temperature for CYANEX.
- Agitation of aqueous and solvent mixture showed 88% extraction of acetic acid by using shaker and placing sample tubes in a horizontal position, 87% by shaking using hand and 82% by mixing using magnetic stirrer. While it showed low extraction percentage by agitation using the shaker with vertical placement (less than 15 %) as does the unagitated sample.
- Centrifuging of aqueous and solvent mixture using centrifuge machine was increasing acetic acid extraction percentage by helping and accelerate the separation.

Separation of long chain length acids from CYANEX 923 by distillation was more difficult than short chain length acids due to a boiling point rise phenomenon which the boiling points of the mixture became higher than the boiling points of its individual components.

Similarly, separation of carboxylic acids from CYANEX 923 by making acid salts and precipitating out of the solvent showed some difficulties in term of quantitative mass recovery from solvent. In addition, re-dissolution of the precipitates of acid-base complexes into acidic water did not indicate recovery of the acids as had been expected. Apparently the acid-base complexes are not separated and precipitated from the organic

phase as their acid salt, and appear to remain in the organic phase in a form undetectable by GC.

On the other hand, separation of carboxylic acids from CYANEX 923 by back extraction using a dilute aqueous sodium hydroxide showed high removal percentage (99% removal). In addition, mixed carboxylic acids could be concentrated back in aqueous solution up to 50% for long chain acids by using back extraction with NaOH.

Extraction by using TOPO and CYANEX showed to be more stable than TOA in term of recyclability. Finally, washing the solvent with 1 M NaOH showed a significant affect for lignin removal from the solvent (about 73% of lignin removal).

### *4.2 Recommendations of Future Works*

Recovering % of long chain length carboxylic acids from CYANEX 923 by distillation was more difficult than short length acids due to a boiling point rise phenomenon of mixture with two or more components. Therefore, well known studies will proceed to understand the behavior of separation of acids from solvent by distillation.

In addition, recovering acids from solvent by adding calcium bases showed to be more difficult. The reasons behind this are not clearly know at this time. Therefore, more investigation and study will proceed to well know the behavior of making acid salts and choose different solvent such as Ethyl acetate, EA.

All the data and results have been generated at laboratory, so the results should be utilized and used to scale up for a pilot plant scale. An extraction pilot plant will be established to extract mixed acids from wood extracts and to be a continuous extraction rather than a batch extraction.

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## APPENDIX A

## LIGNIN CONTENT

Table A.1 Lignin content

| Lignin content | Recycle # | Raw GL. | GL after hydrolysis | Aq. before LLE | Aq. after LLE | Org. before LLE | Org. after LLE | Org. before distill. | Org. after distill. | Org. before washing | Org. after washing | Washing solu. before washing step | Washing solu. after washing step |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | | | | 2.5 | | 4.9 | 4.9 | 4.5 | 4.5 | 1.2 | | 3.3 |
| | 2 | | | | 2.5 | | 5.2 | 5.2 | 4.8 | 4.8 | 1.3 | | 3.5 |
| g/L | 3 | 20 | 7.2 | 7.2 | 2.6 | 0 | 5.2 | 5.2 | 4.7 | 4.7 | 1.3 | 0 | 3.4 |
| | 1 | | | | 2.4 | | 4.9 | 4.9 | 4.4 | 4.4 | 1.2 | | 3.2 |
| | 2 | | | | 2.4 | | 5.2 | 5.2 | 4.5 | 4.5 | 1.2 | | 3.3 |
| g | 3 | 73.8 | 21.7 | 21.7 | 2.6 | 0 | 5.2 | 5.2 | 4.5 | 4.5 | 1.1 | 0 | 3.3 |

# APPENDIX B

## MATERIAL BALANCE

Table B.1 Overall material balance of large scale acetic acid extraction from hemicellulose extract by using TOPO

| | | Recycle # | Raw GL | Hydrolyzed GL before filtration | Hydrolyzed GL after filtration | Aq. Before LLE | Aq. After LLE | Org. before LLE | Org. after LLE | Org. before distillation | Org. after distillation | Conds. | Org. before washing | Org. after washing | 1 M NaoH solu. before washing | 1 M NaoH solu. after washing |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | | | | 1030 | 990.3 | 750 | 753.2 | 749.2 | 733 | 8.2 | 729 | 707 | 1029.3 | 1025.6 |
| | | 2 | | | | 1030 | 990.4 | 750 | 752 | 747 | 703.8 | 27.6 | 699.8 | 660.7 | 1029.3 | 1022.8 |
| | Mass g | 3 | 3800 | 3625 | [1]3100 | 1030 | 1001 | 750 | 752.5 | 748.5 | 719.4 | 8.95 | 715.4 | 676 | 1031.4 | 1029.2 |
| | | 1 | | | | 1000 | 961.5 | 1000 | 1004.3 | 998.9 | 977.3 | 7.8 | 972.0 | 942.7 | 999.3 | 995.7 |
| | Volume | 2 | | | | 1000 | 961.6 | 1000 | 1002.7 | 996.0 | 938.4 | 8 | 933.1 | 880.9 | 999.3 | 993.0 |
| Material | mL | 3 | 3689.3 | 3519.4 | 3009.7 | 1000 | 971.8 | 1000 | 1003.3 | 998.0 | 959.2 | 8.5 | 953.9 | 901.3 | 1001.4 | 999.2 |
| | | 1 | | | | | 3.38 | 0 | 5.6 | 5.6 | 0.22 | 600 | 0.22 | 0.22 | | |
| | | 2 | | | | | 3.36 | 0 | 5.6 | 5.6 | 0.22 | 558 | 0.22 | 0.22 | | |
| | g/L | 3 | | | 8.7 | 8.7 | 3.45 | 0 | 5.7 | 5.7 | 0.25 | 556 | 0.25 | 0.22 | | |
| | | 1 | | | | | 3.25 | 0 | 5.5 | 5.59 | 0.22 | 4.68 | 0.21 | 0.21 | | |
| | | 2 | | | | | 3.23 | 0 | 5.5 | 5.58 | 0.21 | 4.46 | 0.21 | 0.19 | | |
| [2]HAc | g | 3 | | | 8.7 | 8.7 | 3.35 | 0 | 5.3 | 5.69 | 0.24 | 4.73 | 0.24 | 0.20 | | |
| | | 1 | | | | | | 370 | 337 | 337 | 353 | 0 | 340 | 326 | | |
| | | 2 | | | | | | 370 | 327 | 327 | 357 | 0 | 348 | 324 | | |
| | g/L | 3 | | | | | | 370 | 316 | 316 | 349 | 0 | 335 | 316 | | |
| | | 1 | | | | | | 370 | 338 | 338 | 345 | 0 | 331 | 307 | | |
| | | 2 | | | | | | 370 | 327 | 325 | 335 | 0 | 325 | 285 | | |
| [3]TOPO | g | 3 | | | | | | 370 | 317 | 315 | 335 | 0 | 320 | 285 | | |
| | | 1 | | | | | 2.5 | | 4.9 | 4.9 | 4.5 | | 4.5 | 1.2 | 0 | 3.3 |
| | | 2 | | | | | 2.5 | | 5.2 | 5.2 | 4.8 | | 4.8 | 1.3 | 0 | 3.5 |
| | g/L | 3 | | | 7.2 | 7.2 | 2.6 | | 5.2 | 5.2 | 4.7 | | 4.7 | 1.3 | 0 | 3.4 |
| | | 1 | | | | | 2.4 | | 4.9 | 4.9 | 4.4 | | 4.4 | 1.2 | 0 | 3.2 |
| | | 2 | | | | | 2.4 | | 5.2 | 5.2 | 4.5 | | 4.5 | 1.2 | 0 | 3.3 |
| [4]Lignin | g | 3 | | | 21.7 | 21.7 | 2.6 | | 5.2 | 5.1 | 4.5 | | 4.5 | 1.1 | 0 | 3.3 |
| | | 1 | | | | | | | 1.4 | 1.4 | 1.6 | 1.88 | 1.6 | 2.4 | | 11.87 |
| | | 2 | | | | | | | 1.45 | 1.45 | 1.64 | 2.88 | 1.64 | 2.8 | | 11.9 |
| | pH | 3 | 4.3-4.5 | 1 | 1 | 1 | 1 | | 1.43 | 1.43 | 1.7 | 2.8 | 1.7 | 2.9 | 1.2 | 11.86 |

Note: [1] about of 500 g of hydrolyzed hemicellulose extract was lost due to experimental mistake

[2] analysis by HPLC, [3] analysis by GC, [4] analysis by UV

Table B.2 Mass balance of acetic acid and TOPO

| | HAc g | | TOPO |
|---|---|---|---|
| | Aq. | Org. | Weight g |
| Before LLE | 8.7 | 0 | 370 |
| After LLE | 3.3 | 5.4 | 337 |
| Before Distillation | 0 | 5.4 | 337 |
| After Distillation | 0 | 0.2 | 353 |
| Before Washing | 0 | 0 | 340 |
| After Washing | 0 | 0 | 326 |
| Final | 3.3 | 4.7 | 326 |
| Total Lost | 0.48 | | 44 |
| Total Lost % | 6 | | 6 |

## APPENDIX C

## MOLAR RATIO

Table C.1 Molar ratio of varied solvent concentration

| Solvent | Solvent g/L | Acid in organic g/L | Acid in aqueous g/L | Solvent M | Acid in organic M | Molar ratio of solvent to acid | $D_c$ | $D_c$ (solvent/aqueous) |
|---|---|---|---|---|---|---|---|---|
| | 100 | 8.2 | 1.8 | 0.283 | 0.137 | 2.069 | 4.56 | 45.56 |
| TOA | 200 | 8.9 | 1.1 | 0.565 | 0.148 | 3.812 | 8.09 | 40.45 |
| Mw | 300 | 8.7 | 1.3 | 0.848 | 0.145 | 5.850 | 6.69 | 22.31 |
| 353.67 | 400 | 8.6 | 1.4 | 1.131 | 0.143 | 7.891 | 6.14 | 15.36 |
| | 500 | 8.6 | 1.4 | 1.414 | 0.143 | 9.863 | 6.14 | 12.29 |
| | 50 | 4.18 | 5.82 | 0.129 | 0.070 | 1.856 | 0.72 | 14.36 |
| | 90 | 5.37 | 4.63 | 0.233 | 0.090 | 2.601 | 1.16 | 12.89 |
| TOPO | 180 | 6.49 | 3.51 | 0.466 | 0.108 | 4.304 | 1.85 | 10.27 |
| Mw | 280 | 7.02 | 2.98 | 0.724 | 0.117 | 6.190 | 2.36 | 8.41 |
| 386.64 | 370 | 7.47 | 2.53 | 0.957 | 0.125 | 7.686 | 2.95 | 7.98 |
| | 460 | 7.54 | 2.46 | 1.190 | 0.126 | 9.467 | 3.07 | 6.66 |
| | 550 | 7.59 | 2.41 | 1.423 | 0.127 | 11.245 | 3.15 | 5.73 |
| | 50 | 0.81 | 9.2 | 0.144 | 0.014 | 10.643 | 0.09 | 1.76 |
| | 100 | 2.4 | 7.6 | 0.287 | 0.040 | 7.184 | 0.32 | 3.16 |
| CYANEX 923 | 200 | 5.33 | 4.7 | 0.575 | 0.089 | 6.470 | 1.13 | 5.67 |
| Mw | 300 | 6.68 | 3.3 | 0.862 | 0.111 | 7.743 | 2.02 | 6.75 |
| 348 | 400 | 7.5 | 2.5 | 1.149 | 0.125 | 9.195 | 3.00 | 7.50 |
| | 550 | 8 | 2 | 1.580 | 0.133 | 11.853 | 4.00 | 7.27 |
| | 600 | 8.8 | 1.2 | 1.724 | 0.147 | 11.755 | 7.33 | 12.22 |

Note: Initial HAc is 0.1 g (0.0017 moles), pH 1 for TOPO and CYANEX and pH 2.9 for TOA, Vol. ratio [1:1], 70 °C for TOA and TOPO, 22 °C for CYANEX, yellow color marking is an optimum condition

Table C.2 Molar ratio of varied solvent to aqueous solution

| Solvent | Volume ratio (org/aq) | Acid in organic g/L | Acid in aqueous g/L | Solvent M | Acid in organic M | Molar ratio of solvent to acid | $D_c$ | $D_c$ (solvent/aqueous) |
|---|---|---|---|---|---|---|---|---|
| TOA Mw 353.67 | 0.25 | 16.4 | 5.9 | 0.565 | 0.273 | 2.069 | 2.78 | 13.90 |
| | 0.5 | 13.2 | 3.4 | 0.565 | 0.220 | 2.570 | 3.88 | 19.41 |
| | 0.67 | 11.2 | 2.5 | 0.565 | 0.187 | 3.029 | 4.48 | 22.40 |
| | 1 | 8.4 | 1.6 | 0.565 | 0.140 | 4.039 | 5.25 | 26.25 |
| | 1.5 | 6.1 | 0.9 | 0.565 | 0.102 | 5.562 | 6.78 | 33.89 |
| | 2 | 4.6 | 0.8 | 0.565 | 0.077 | 7.376 | 5.75 | 28.75 |
| TOPO Mw 386.64 | 0.25 | 14.8 | 6.3 | 0.957 | 0.247 | 3.880 | 2.35 | 6.35 |
| | 0.5 | 10.6 | 4.71 | 0.957 | 0.177 | 5.417 | 2.25 | 6.08 |
| | 0.67 | 9.1 | 3.88 | 0.957 | 0.152 | 6.310 | 2.35 | 6.34 |
| | 1 | 7.5 | 2.54 | 0.957 | 0.125 | 7.656 | 2.95 | 7.98 |
| | 1.5 | 5.5 | 1.85 | 0.957 | 0.092 | 10.440 | 2.97 | 8.04 |
| | 2 | 4.4 | 1.35 | 0.957 | 0.073 | 13.049 | 3.26 | 8.81 |
| CYANEX 923 Mw 348 | 0.25 | 16 | 6 | 1.149 | 0.267 | 4.310 | 2.67 | 6.67 |
| | 0.5 | 11.2 | 4.4 | 1.149 | 0.187 | 6.158 | 2.55 | 6.36 |
| | 0.67 | 10.1 | 3.2 | 1.149 | 0.168 | 6.828 | 3.16 | 7.89 |
| | 1 | 7.8 | 2.2 | 1.149 | 0.130 | 8.842 | 3.55 | 8.86 |
| | 1.5 | 5.6 | 1.6 | 1.149 | 0.093 | 12.315 | 3.50 | 8.75 |
| | 2 | 4.25 | 1.5 | 1.149 | 0.071 | 16.227 | 2.83 | 7.08 |

Note: Initial HAc is 0.1 g (0.0017 moles), pH 1 for TOPO and CYANEX and pH 2.9 for TOA, 200 g/L of TOA/octanol, 370 g/L of TOPO/undecan, 400g/L of CYANEX/tridecane, 70 °C for TOA and TOPO, 22 °C for CYANEX, yellow color marking is an optimum condition

Table C.3 Molar ratio of varied pH on extraction of acetic acid by different solvents

| Solvent | pH | Acid in organic g/L | Acid in aqueous g/L | Solvent M | Acid in organic M | Molar ratio of solvent to acid | $D_c$ | $D_c$ (solvent/aqueous) |
|---|---|---|---|---|---|---|---|---|
| | 1 | 4.6 | 5.4 | 0.565 | 0.077 | 7.376 | 0.85 | 4.26 |
| TOA | 2 | 7.1 | 2.9 | 0.565 | 0.118 | 4.779 | 2.45 | 12.24 |
| Mw | 3 | 7.5 | 2.5 | 0.565 | 0.125 | 4.524 | 3.00 | 15.00 |
| 353.67 | 4 | 7.7 | 2.3 | 0.565 | 0.128 | 4.406 | 3.35 | 16.74 |
| | 5 | 4.4 | 5.6 | 0.565 | 0.073 | 7.711 | 0.79 | 3.93 |
| | 1 | 7.47 | 2.53 | 0.957 | 0.125 | 7.686 | 2.95 | 7.98 |
| TOPO | 2 | 7.41 | 2.59 | 0.957 | 0.124 | 7.749 | 2.86 | 7.73 |
| Mw | 3 | 7.29 | 2.71 | 0.957 | 0.122 | 7.876 | 2.69 | 7.27 |
| 386.64 | 4 | 5.41 | 4.59 | 0.957 | 0.090 | 10.613 | 1.18 | 3.19 |
| | 5 | 1.82 | 8.18 | 0.957 | 0.030 | 31.548 | 0.22 | 0.60 |
| | 1 | 36.5 | 8.9 | 1.149 | 0.688 | 1.889 | 4.10 | 10.25 |
| CYANEX 923 | 2 | 36 | 9 | 1.149 | 0.800 | 1.916 | 4.00 | 10.00 |
| Mw | 3 | 33.8 | 11.3 | 1.149 | 0.563 | 2.040 | 2.99 | 7.48 |
| 348 | 4 | 9 | 36 | 1.149 | 0.150 | 7.663 | 0.25 | 0.63 |
| | 5 | 2 | 43 | 1.149 | 0.033 | 34.483 | 0.05 | 0.12 |

Note: Initial HAc is 0.1 g (0.0017 moles), vol. ratio [1:1], 200 g/L of TOA/octanol, 370 g/L of TOPO/undecan, 400g/L of CYANEX/tridecane, 70 °C for TOA and TOPO, 22 °C for CYANEX, yellow color marking is an optimum condition

Table C.4 Molar ratio for affect of agitation on extraction acetic acid

| Agitation | Acid in organic g/L | Acid in aqueous g/L | Solvent M | Acid in organic M | Molar ratio of solvent to acid | $D_c$ | $D_c$ (solvent/aqueous) |
|---|---|---|---|---|---|---|---|
| Without | 6.1 | 44.5 | 1.149 | 0.102 | 11.306 | 0.14 | 0.34 |
| V Shaker | 7.1 | 43.6 | 1.149 | 0.118 | 9.713 | 0.16 | 0.41 |
| Stirred Mixing | 41.5 | 9.2 | 1.149 | 0.692 | 1.662 | 4.51 | 11.28 |
| H Shaker | 44 | 6.5 | 1.149 | 0.733 | 1.567 | 6.77 | 16.92 |
| By Hand | 43.6 | 7.1 | 1.149 | 0.727 | 1.582 | 6.14 | 15.35 |

Note: Initial HAc is 0.1 g (0.0017 moles), vol. ratio [1:1], pure CYANEX/tridecane, 22 °C, yellow color marking is an optimum condition



Table C.5 Molar ratio for affect of centrifuging on extraction acetic acid

| Centrifuge | Acid in organic g/L | Acid in aqueous g/L | Solvent M | Acid in organic M | Molar ratio of solvent to acid | $D_c$ | $D_c$ (solvent/aqueous) |
|---|---|---|---|---|---|---|---|
| 3 hours gravity | 27.2 | 23.8 | 1.149 | 0.453 | 2.535 | 1.14 | 2.86 |
| 2 days gravity | 35.8 | 16 | 1.149 | 0.597 | 1.926 | 2.24 | 5.59 |
| One week gravity | 44.7 | 6.3 | 1.149 | 0.745 | 1.543 | 7.10 | 17.74 |
| 30 min. centrifuging | 44 | 7.1 | 1.149 | 0.733 | 1.567 | 6.20 | 15.49 |

Note: Initial HAc is 0.1 g (0.0017 moles), vol. ratio [1:1], pure CYANEX/tridecane, 22 °C, yellow color marking is an optimum condition

# APPENDIX D

## $D_C$ AND $P_C$ CALCULATIONS

Table D.1 $D_C$ and $P_C$ calculations for affect of pH on extraction acetic acid

Yellow = experimental data: g/L acid (org), g/L acid (aq), pH

[redacted]

System: Acetic acid in 200 g/L TOA, pH variable, vol 1:1, T = 70 °C

| | pH | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|
| pKa | 1 | 4.6 | 5.4 | 0.077 | 0.090 | 0.85 | 0.077 | 0.0900 | 0.852 |
| Ka | 2 | 7.1 | 2.9 | 0.118 | 0.048 | 2.45 | 0.118 | 0.0482 | 2.453 |
| Mw acid | 3 | 7.5 | 2.5 | 0.125 | 0.042 | 3.00 | 0.125 | 0.0409 | 3.053 |
| | 4 | 7.7 | 2.3 | 0.128 | 0.038 | 3.35 | 0.128 | 0.0325 | 3.943 |
| | 5 | 4.4 | 5.6 | 0.073 | 0.093 | 0.79 | 0.073 | 0.0336 | 2.183 |

System: Acetic acid in 370 g/L TOPO, pH variable, vol 1:1, T = 70 °C

| | pH | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | Pc |
|---|---|---|---|---|---|---|---|---|---|
| pKa | 1 | 7.47 | 2.53 | 0.125 | 0.042 | 2.95 | 0.125 | 0.0422 | 2.953 |
| Ka | 2 | 7.41 | 2.59 | 0.124 | 0.043 | 2.86 | 0.124 | 0.0431 | 2.866 |
| Mw acid | 3 | 7.29 | 2.71 | 0.122 | 0.045 | 2.69 | 0.122 | 0.0444 | 2.738 |
| | 4 | 5.41 | 4.59 | 0.090 | 0.077 | 1.18 | 0.090 | 0.0650 | 1.388 |
| | 5 | 1.82 | 8.18 | 0.030 | 0.136 | 0.22 | 0.030 | 0.0491 | 0.618 |

System: Acetic acid in 400 g/L CYANEX, pH variable, vol 1:1, T = 22 °C

| | pH | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | Pc |
|---|---|---|---|---|---|---|---|---|---|
| pKa | 1 | 36.5 | 8.9 | 0.608 | 0.148 | 4.10 | 0.608 | 0.1483 | 4.102 |
| Ka | 2 | 36 | 9 | 0.600 | 0.150 | 4.00 | 0.600 | 0.1497 | 4.007 |
| Mw acid | 3 | 33.8 | 11.3 | 0.563 | 0.188 | 2.99 | 0.563 | 0.1850 | 3.044 |
| | 4 | 9 | 36 | 0.150 | 0.600 | 0.25 | 0.150 | 0.5094 | 0.294 |
| | 5 | 2 | 43 | 0.033 | 0.717 | 0.05 | 0.033 | 0.2580 | 0.129 |

Table D.2 $D_C$ and $P_C$ calculations for affect of solvent concentration on extraction acetic acid

**System:** **g/L TOA variable, pH 1, vol 1:1, T = 70 °C**

| | pH | Extractant g/L | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|---|
| pKa | 1 | 100 | 8.5 | 1.8 | 0.142 | 0.030 | 4.72 | 0.142 | 0.0300 | 4.723 |
| Ka | 1 | 200 | 6.4 | 0.9 | 0.107 | 0.015 | 7.11 | 0.107 | 0.0150 | 7.112 |
| Mw acid | 1 | 300 | 7 | 1 | 0.117 | 0.017 | 7.00 | 0.117 | 0.0167 | 7.001 |
| | 1 | 400 | 8.2 | 1.2 | 0.137 | 0.020 | 6.83 | 0.137 | 0.0200 | 6.835 |
| | 1 | 500 | 5.9 | 1.2 | 0.098 | 0.020 | 4.92 | 0.098 | 0.0200 | 4.918 |

**System:** **g/L TOPO variable, pH 1, vol 1:1, T = 70 °C**

| | pH | Extractant g/L | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|---|
| pKa | 1 | 50 | 4.18 | 5.82 | 0.070 | 0.097 | 0.72 | 0.070 | 0.0970 | 0.718 |
| Ka | 1 | 90 | 5.37 | 4.63 | 0.090 | 0.077 | 1.16 | 0.090 | 0.0772 | 1.160 |
| Mw acid | 1 | 180 | 6.49 | 3.51 | 0.108 | 0.059 | 1.85 | 0.108 | 0.0585 | 1.849 |
| | 1 | 280 | 7.02 | 2.98 | 0.117 | 0.050 | 2.36 | 0.117 | 0.0497 | 2.356 |
| | 1 | 370 | 7.47 | 2.53 | 0.125 | 0.042 | 2.95 | 0.125 | 0.0422 | 2.953 |
| | 1 | 460 | 7.54 | 2.46 | 0.126 | 0.041 | 3.07 | 0.126 | 0.0410 | 3.066 |
| | 1 | 550 | 7.59 | 2.41 | 0.127 | 0.040 | 3.15 | 0.127 | 0.0402 | 3.150 |

**System:** **g/L CYANEX variable, pH 1, vol 1:1, T = 22 °C**

| | pH | Extractant g/L | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|---|
| pKa | 1 | 50 | 0.81 | 9.2 | 0.014 | 0.153 | 0.09 | 0.014 | 0.1533 | 0.088 |
| Ka | 1 | 100 | 2.4 | 7.6 | 0.040 | 0.127 | 0.32 | 0.040 | 0.1266 | 0.316 |
| Mw acid | 1 | 200 | 5.33 | 4.7 | 0.089 | 0.078 | 1.13 | 0.089 | 0.0783 | 1.134 |
| | 1 | 300 | 6.68 | 3.3 | 0.111 | 0.055 | 2.02 | 0.111 | 0.0550 | 2.025 |
| | 1 | 400 | 7.5 | 2.5 | 0.125 | 0.042 | 3.00 | 0.125 | 0.0417 | 3.001 |
| | 1 | 550 | 8 | 2 | 0.133 | 0.033 | 4.00 | 0.133 | 0.0333 | 4.001 |
| | 1 | 600 | 8.8 | 1.2 | 0.147 | 0.020 | 7.33 | 0.147 | 0.0200 | 7.335 |

Table D.3 $D_C$ and $P_C$ calculations for affect of volume ration of organic to aqueous on extraction acetic acid

**System:** **vol. ratio variable, pH 2.9, 200 g/L TOA, T = 70 °C**

| | | pH | vol. ratio | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pKa |  | 2.9 | 0.25 | 16.4 | 5.9 | 0.273 | 0.098 | 2.78 | 0.273 | 0.0970 | 2.819 |
| Ka | | 2.9 | 0.5 | 13.2 | 3.4 | 0.220 | 0.057 | 3.88 | 0.220 | 0.0559 | 3.937 |
| Mw acid | | 2.9 | 0.67 | 11.2 | 2.5 | 0.187 | 0.042 | 4.48 | 0.187 | 0.0411 | 4.543 |
| | | 2.9 | 1 | 8.4 | 1.6 | 0.140 | 0.027 | 5.25 | 0.140 | 0.0263 | 5.324 |
| | | 2.9 | 1.5 | 6.1 | 0.9 | 0.102 | 0.015 | 6.78 | 0.102 | 0.0148 | 6.874 |
| | | 2.9 | 2 | 4.6 | 0.8 | 0.077 | 0.013 | 5.75 | 0.077 | 0.0131 | 5.831 |

**System:** **vol. ratio variable, pH 1, 370 g/L TOPO, T = 70 °C**

| | | pH | vol. ratio | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pKa |  | 1 | 0.25 | 14.8 | 6.3 | 0.247 | 0.105 | 2.35 | 0.247 | 0.1050 | 2.350 |
| Ka | | 1 | 0.5 | 10.6 | 4.71 | 0.177 | 0.079 | 2.25 | 0.177 | 0.0785 | 2.251 |
| Mw acid | | 1 | 0.67 | 9.1 | 3.88 | 0.152 | 0.065 | 2.35 | 0.152 | 0.0647 | 2.346 |
| | | 1 | 1 | 7.5 | 2.54 | 0.125 | 0.042 | 2.95 | 0.125 | 0.0423 | 2.953 |
| | | 1 | 1.5 | 5.5 | 1.85 | 0.092 | 0.031 | 2.97 | 0.092 | 0.0308 | 2.974 |
| | | 1 | 2 | 4.4 | 1.35 | 0.073 | 0.023 | 3.26 | 0.073 | 0.0225 | 3.260 |

**System:** **vol. ratio variable, pH 1, 400 g/L CYANEX, T = 22 °C**

| | | pH | vol. ratio | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pKa |  | 1 | 0.25 | 16 | 6 | 0.267 | 0.100 | 2.67 | 0.267 | 0.1000 | 2.667 |
| Ka | | 1 | 0.5 | 11.2 | 4.4 | 0.187 | 0.073 | 2.55 | 0.187 | 0.0733 | 2.546 |
| Mw acid | | 1 | 0.67 | 10.1 | 3.2 | 0.168 | 0.053 | 3.16 | 0.168 | 0.0533 | 3.157 |
| | | 1 | 1 | 7.8 | 2.2 | 0.130 | 0.037 | 3.55 | 0.130 | 0.0367 | 3.546 |

Table D.4 $D_C$ and $P_C$ calculations for affect of agitation on extraction acetic acid

System: vol 1:1, pH 1, pure CYANEX, T = 22 °C

pKa
Ka
Mw acid

| pH | vol. ratio | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Without | 6.1 | 44.5 | 0.102 | 0.742 | 0.14 | 0.102 | 0.7415 | 0.137 |
| 1 | V Shaker | 7.1 | 43.6 | 0.118 | 0.727 | 0.16 | 0.118 | 0.7265 | 0.163 |
| 1 | Stirred Mixing | 41.5 | 9.2 | 0.692 | 0.153 | 4.51 | 0.692 | 0.1533 | 4.512 |
| 1 | H Shaker | 44 | 6.5 | 0.733 | 0.108 | 6.77 | 0.733 | 0.1083 | 6.770 |
| 1 | By Hand | 43.6 | 7.1 | 0.727 | 0.118 | 6.14 | 0.727 | 0.1183 | 6.142 |

Table D.5 $D_C$ and $P_C$ calculations for affect of centrifuging on extraction acetic acid

System: vol 1:1, pH 1, pure CYANEX, T = 22 °C

pKa
Ka
Mw acid

| pH | vol. ratio | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3 hours gravity | 27.2 | 23.8 | 0.453 | 0.397 | 1.14 | 0.453 | 0.3966 | 1.143 |
| 1 | 2 days gravity | 35.8 | 16 | 0.597 | 0.267 | 2.24 | 0.597 | 0.2666 | 2.238 |
| 1 | One week gravity | 44.7 | 6.3 | 0.745 | 0.105 | 7.10 | 0.745 | 0.1050 | 7.096 |
| 1 | 30 min. centrifuging | 44 | 7.1 | 0.733 | 0.118 | 6.20 | 0.733 | 0.1183 | 6.198 |

D.6 $D_C$ and $P_C$ calculation for extractions mixed acids by pure CYANEX and for a clean system

System: Pure CYANEX, pH 2.5, vol 1:1, T = 22 °C

| | pKa | Ka | Mw | pH | g/L acid(org) | g/L acid(aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hac | | | | 2 | 36 | 9 | 0.600 | 0.150 | 4.00 | 0.600 | 0.1497 | 4.007 |
| Prop. | | | | 2.5 | 7.3 | 1 | 0.099 | 0.013 | 7.30 | 0.099 | 0.0134 | 7.330 |
| But. | | | | 2.5 | 4.6 | 0.5 | 0.052 | 0.006 | 9.20 | 0.052 | 0.0056 | 9.244 |
| Val. | | | | 2.5 | 2.5 | 0.1 | 0.024 | 0.001 | 25.00 | 0.024 | 0.0010 | 25.120 |
| Hex. | | | | 2.5 | 2.1 | 0.1 | 0.018 | 0.001 | 21.00 | 0.018 | 0.0009 | 21.088 |
| Hept. | | | | 2.5 | 1.6 | 0.16 | 0.012 | 0.001 | 10.00 | 0.012 | 0.0012 | 10.041 |

## D.7 $D_C$ and $P_C$ calculations for extraction mixed fermentation acids by pure CYANEX at pH 7 and 2

**System:** **Mixed fermentation acids, Pure CYANEX, pH 7, vol 1:1, T = 22 °C** note: data analyzed using % extraction values

| | pKa | Ka | Mw | pH | % extraction acid(org) | % extraction (aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hac | | | | 7 | 0.03 | 5.30 | 0.0005 | 0.088 | 0.005 | 0.0005 | 0.0005 | 0.914 |
| Prop. | | | | 7 | 0.06 | 1.60 | 0.001 | 0.022 | 0.035 | 0.001 | 0.0002 | 4.651 |
| But. | | | | 7 | 0.38 | 5.33 | 0.004 | 0.060 | 0.072 | 0.004 | 0.0004 | 10.972 |
| Val. | | | | 7 | 0.60 | 0.71 | 0.006 | 0.007 | 0.837 | 0.006 | 0.0000 | 127.593 |
| Hex. | | | | 7 | 8.10 | 2.32 | 0.070 | 0.020 | 3.490 | 0.070 | 0.0002 | 463.594 |
| Hept. | | | | 7 | 0.45 | 0.02 | 0.003 | 0.000 | 24.075 | 0.003 | 0.0000 | 3125.522 |

**System:** **Mixed fermentation acids, Pure CYANEX, pH 2, vol 1:1, T = 22 °C** note: data analyzed using % extraction values

| | pKa | Ka | Mw | pH | % extraction acid(org) | % extraction (aq) | [A](org) | [A](aq) | $D_c$ | [HA] (org) | [HA](aq) | $P_c$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hac | | | | 2 | 4.8 | 0.55 | 0.080 | 0.009 | 8.71 | 0.080 | 0.0091 | 8.724 |
| Prop. | | | | 2 | 1.5 | 0.20 | 0.020 | 0.003 | 7.13 | 0.020 | 0.0027 | 7.139 |
| But. | | | | 2 | 5.2 | 0.55 | 0.059 | 0.006 | 9.42 | 0.059 | 0.0062 | 9.431 |
| Val. | | | | 2 | 1.3 | 0.05 | 0.012 | 0.001 | 24.00 | 0.012 | 0.0005 | 24.036 |
| Hex. | | | | 2 | 10.1 | 0.34 | 0.087 | 0.003 | 29.30 | 0.087 | 0.0030 | 29.342 |
| Hept. | | | | 2 | 0.4 | 0.04 | 0.003 | 0.000 | 10.36 | 0.003 | 0.0003 | 10.377 |

## APPENDIX E

## ANALYTICAL METHOD FOR ORGANIC SOLUTION BY USING GC

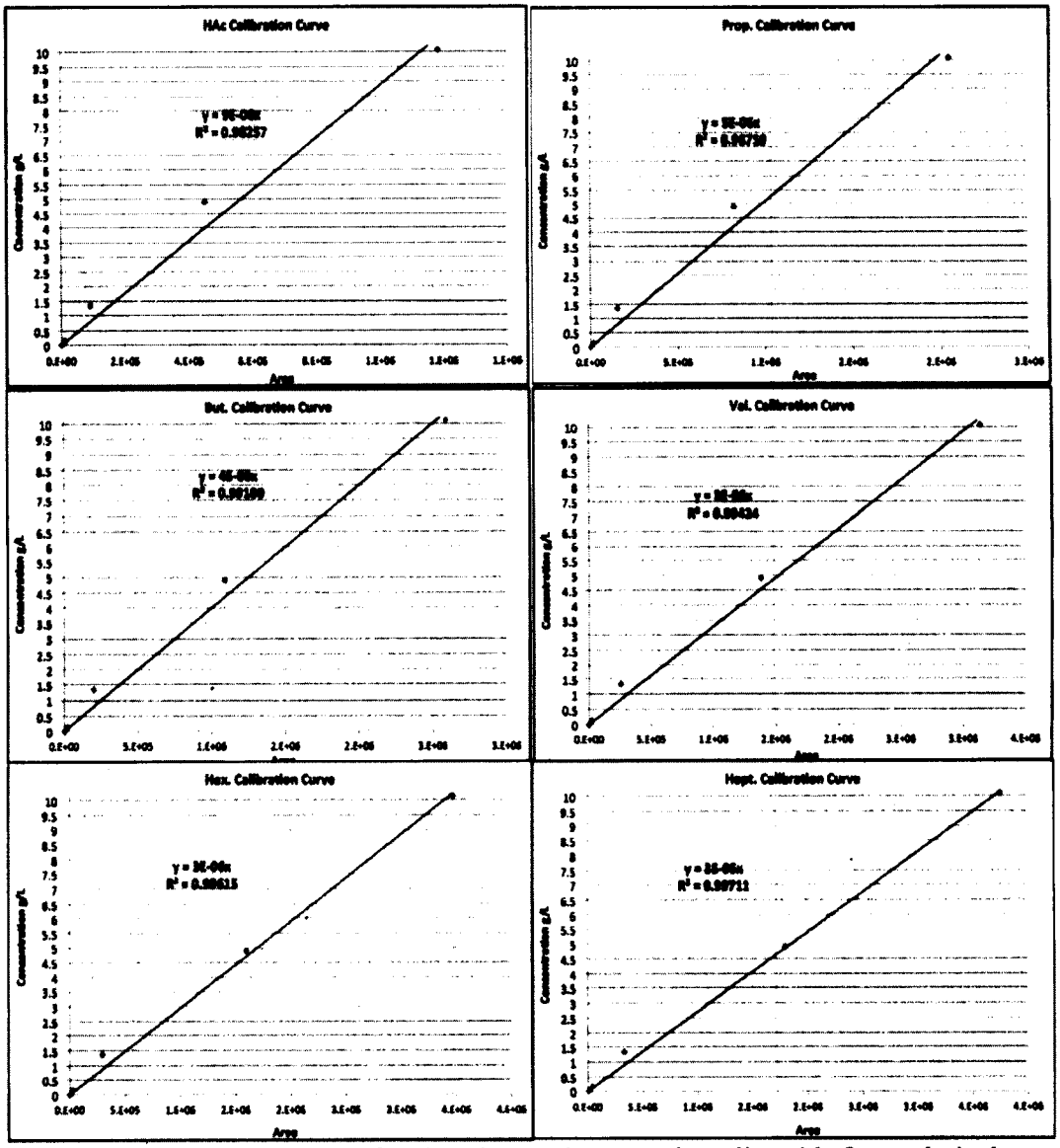



Figure E.1 Calibration curves of carbon 2 to carbon 7 carboxylic acids for analytical method for organic solution using GC

Table E.1 and E.2 show some stander reference solutions (STD) used as a validation for analytic method for organic solution using GC. Different known concentrations of stander reference solution of mixed acids in CYANEX diluted in DCM, were prepared to be used to test the validation of the calibration cure and get accurate analyzing results. Table E.1 and E.2 show known STD 2 (0.018 g/L of mixed acids in CYANEX) and STD 5 (3.36 g/L), respectively.

Table E.1 Known stander reference solutions (STD 2)

| STD 2 | | From Calibration Curve | |
|---|---|---|---|
| | | Area | Calculating Concentration g/L |
| 1 | HAc | 2067.3 | 0.019 |
| 2 | Prop. | 3972.1 | 0.020 |
| 3 | But. | 4593.1 | 0.018 |
| 4 | Val. | 6304.5 | 0.019 |
| 5 | Hex. | 6503.6 | 0.020 |
| 6 | Hept. | 6493.8 | 0.019 |

Table E.2 Known stander reference solutions (STD 5)

| STD 5 | | From Calibration Curve | |
|---|---|---|---|
| | | Area | Calculating Concentration g/L |
| 1 | HAc | 380706.1 | 3.43 |
| 2 | Prop. | 700714.4 | 3.50 |
| 3 | But. | 898628.7 | 3.59 |
| 4 | Val. | 1126361.4 | 3.38 |
| 5 | Hex. | 1200112.9 | 3.60 |
| 6 | Hept. | 1150053.6 | 3.45 |

## APPENDIX F

## THEORETICAL STAGES OF EXTRACTION ACETIC ACID

The McCabe-Thiele method is applied for liquid-liquid extraction to calculate the theoretical extraction stages needed to recover acetic acid from aqueous solution [21]. The initial concentration of acetic acid in hemicellulose extract was 8.7 g/L, while 10 g/L of acetic acid in water solution. Three solvents have been used (370 g/L of TOPO, 200 g/L of TOA and 400 g/L of CYANEX) to extract acetic acid. Best extraction conditions have been used. The goal is to calculate the theoretical stages needed to extract 94% of acetic acid from aqueous solution. Table F.1 and F.2 are the experimental data of extraction acetic acid by using TOPO, TOA and CYANEX.

Table F.1 Experimental data of acetic acid extraction by TOPO, TOA and CYANEX

| Solvent | Initial HAc g/L | HAc in Aq. g/L after LLE | HAc in Org. g/L after LLE | $D_C$ | Extraction % |
|---|---|---|---|---|---|
| TOPO | 8.7 | 3.3 | 5.4 | 1.6 | 62 |
| TOA | 10 | 0.9 | 9.1 | 10 | 91 |
| CYANEX | 10 | 2.5 | 7.5 | 3.0 | 75.2 |

Note: LLE: Liquid-liquid extraction.

Extraction conditions for TOPO was (370 g/L TOPO/undecane, 1 volume ratio and pH 1), for TOA (200 g/L TOA/octanol, 1 volume ratio and pH 2.9) and for CYANEX (400 g/L CYANEX/tridecane, 1 volume ratio and pH 1)

The mass ratio is defined as:

$$X = x/(1-x) \quad \text{and} \quad Y = y/(1-y)$$

Where: x: Mass fraction of HAc in aqueous solution

X : Mass ratio of HAc in aqueous solution

y: Mass fraction of HAc in organic solution

Y : Mass ratio of HAc in organic solution

Table F.2 Experimental data of acetic acid extraction in terms of mass fraction and ratio of acetic acid in both aqueous and organic solution

| Solvent | Mass fraction of HAc in aq. | Mass fraction of HAc in org. | Mass ratio of HAc in aq. | Mass ratio of HAc in org. | $D_C$ | Extraction % |
|---|---|---|---|---|---|---|
| TOPO | 0.0033 | 0.0054 | 0.003 | 0.0054 | 1.6 | 62 |
| TOA | 0.0009 | 0.0091 | 0.0009 | 0.0092 | 10 | 91 |
| CYANEX | 0.0025 | 0.0075 | 0.0025 | 0.0075 | 3.0 | 75.2 |

The operating equation is showing below is used to generate an operating line that can be derived from a mass balance.

$$Yn+1 = (Fd/Fs)Xn + (Y1-(Fd/Fs)Xo) \qquad \text{(AF.1)}$$

Where: Fd: mass flow rate of aq.

Fs: mass flow rate of Org.

n: stage number

Assuming a counter- current extraction column with n stages is used to extract acetic acid as showing below. The system is isothermal, isobaric and the heat of mixing is negligible, so that will give straight operation line. 94% of acetic acid extraction is desirable.

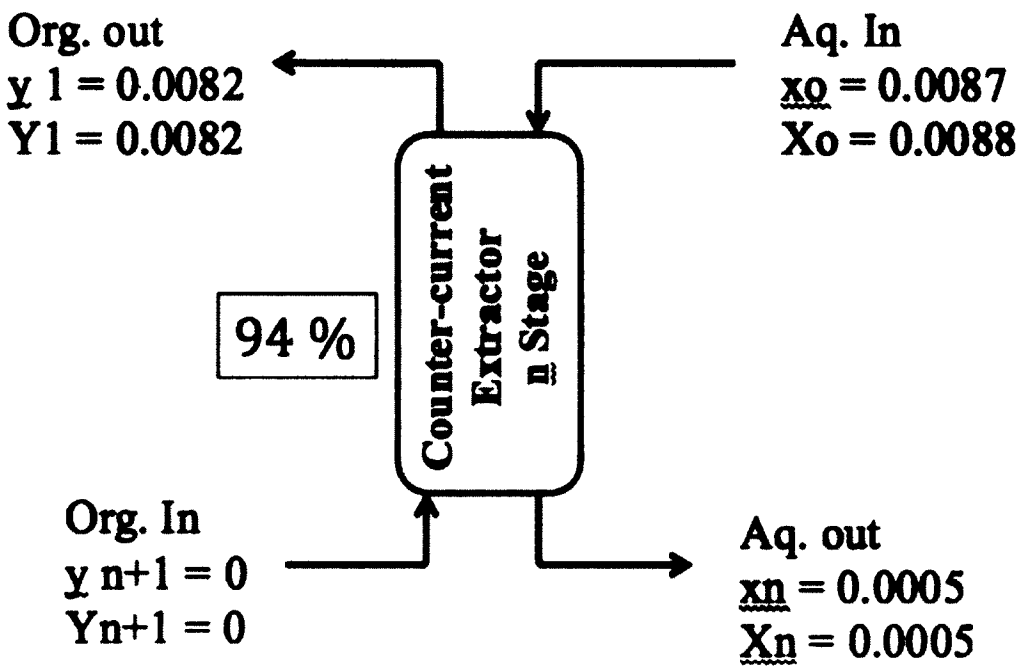



Figure F.1 Diagram of counter-current extractor to extract 94% of acetic acid, where:

- xo: Initial mass fraction of HAc in Aq.
- Xo : Initial mass ratio of HAc in Aq., Xo = xo/(1-xo)
- xn: Final mass fraction of HAc in Aq.
- Xn : Final mass ratio of HAc in Aq., Xn = xn/(1-xn)
- y n+1: Initial mass fraction of HAc in org.
- Y n+1 : Initial mass ratio of HAc in Org.
- Yo = yo/(1-yo)
- yn: Final mass fraction of HA c in Org.
- Yn : Final mass ratio of HAc in Org.
- Yn = yn/(1-yn)

Table F.3 to F.5 show the equilibrium data for 94% of acetic acid extraction by using TOPO, TOA and CYANEX solvents needed to generate the theoretical stages (Figures 3.39 to 3.41). In addition, the operating equation (AF.1) was used to generate the operating data.

Table F.3 Equilibrium and operating data for acetic acid extraction by using TOPO

| x | X<br>x/(1-x) | y<br>x $P_C$ | Y<br>y/(1-y) | $Y_o$ |
|---|---|---|---|---|
| 0.0005 | 0.00050 | 0.00082 | 0.00082 | 0.00001 |
| 0.001 | 0.00100 | 0.00164 | 0.00164 | 0.00049 |
| 0.0015 | 0.00150 | 0.00245 | 0.00246 | 0.00099 |
| 0.002 | 0.00200 | 0.00327 | 0.00328 | 0.00150 |
| 0.0025 | 0.00251 | 0.00409 | 0.00411 | 0.00200 |
| 0.003 | 0.00301 | 0.00491 | 0.00493 | 0.00250 |
| 0.0035 | 0.00351 | 0.00573 | 0.00576 | 0.00300 |
| 0.004 | 0.00402 | 0.00655 | 0.00659 | 0.00351 |
| 0.0045 | 0.00452 | 0.00736 | 0.00742 | 0.00401 |
| 0.005 | 0.00503 | 0.00818 | 0.00825 | 0.00452 |
| 0.0055 | 0.00553 | 0.00900 | 0.00908 | 0.00502 |
| 0.006 | 0.00604 | 0.00982 | 0.00992 | 0.00553 |
| 0.0065 | 0.00654 | 0.01064 | 0.01075 | 0.00603 |
| 0.007 | 0.00705 | 0.01145 | 0.01159 | 0.00654 |
| 0.0075 | 0.00756 | 0.01227 | 0.01243 | 0.00705 |
| 0.008 | 0.00806 | 0.01309 | 0.01326 | 0.00756 |
| 0.0085 | 0.00857 | 0.01391 | 0.01411 | 0.00806 |
| 0.009 | 0.00908 | 0.01473 | 0.01495 | 0.00857 |
| 0.0095 | 0.00959 | 0.01555 | 0.01579 | 0.00908 |
| 0.01 | 0.01010 | 0.01636 | 0.01664 | 0.00959 |

Table F.3 Continued

| x | X<br>x/(1-x) | y<br>x *$P_C$ | Y<br>y/(1-y) | $Y_o$ |
|---|---|---|---|---|
| 0.0105 | 0.01061 | 0.01718 | 0.01748 | 0.01010 |
| 0.011 | 0.01112 | 0.01800 | 0.01833 | 0.01061 |
| 0.0115 | 0.01163 | 0.01882 | 0.01918 | 0.01113 |
| 0.012 | 0.01215 | 0.01964 | 0.02003 | 0.01164 |
| 0.0125 | 0.01266 | 0.02045 | 0.02088 | 0.01215 |
| 0.013 | 0.01317 | 0.02127 | 0.02174 | 0.01266 |
| 0.0135 | 0.01368 | 0.02209 | 0.02259 | 0.01318 |
| 0.014 | 0.01420 | 0.02291 | 0.02345 | 0.01369 |
| 0.0145 | 0.01471 | 0.02373 | 0.02430 | 0.01420 |
| 0.015 | 0.01523 | 0.02455 | 0.02516 | 0.01472 |

Note: $D_C$: Distribution coefficient of acetic acid in organic to aqueous is 1.6

$Y_o$: mass ratio of acetic acid in organic calculated from operating equation (AF.1)

Table F.4 Equilibrium and operating data for acetic acid extraction by using TOA

| x | X<br>x/(1-x) | y<br>x *$P_C$ | Y<br>y/(1-y) | $Y_o$ |
|---|---|---|---|---|
| 0.0005 | 0.00050 | 0.00506 | 0.00508 | 0.00001 |
| 0.001 | 0.00100 | 0.01011 | 0.01021 | 0.00049 |
| 0.0015 | 0.00150 | 0.01517 | 0.01540 | 0.00099 |
| 0.002 | 0.00200 | 0.02022 | 0.02064 | 0.00149 |
| 0.0025 | 0.00251 | 0.02528 | 0.02593 | 0.00200 |
| 0.003 | 0.00301 | 0.03033 | 0.03128 | 0.00250 |
| 0.0035 | 0.00351 | 0.03539 | 0.03669 | 0.00300 |
| 0.004 | 0.00402 | 0.04044 | 0.04215 | 0.00351 |
| 0.0045 | 0.00452 | 0.04550 | 0.04767 | 0.00401 |
| 0.005 | 0.00503 | 0.05056 | 0.05325 | 0.00452 |
| 0.0055 | 0.00553 | 0.05561 | 0.05889 | 0.00502 |

Table F.4 Continued

| x | X<br>x/(1-x) | y<br>x *$P_C$ | Y<br>y/(1-y) | $Y_o$ |
|---|---|---|---|---|
| 0.006 | 0.00604 | 0.06067 | 0.06458 | 0.00553 |
| 0.0065 | 0.00654 | 0.06572 | 0.07035 | 0.00603 |
| 0.007 | 0.00705 | 0.07078 | 0.07617 | 0.00654 |
| 0.008 | 0.00806 | 0.08089 | 0.08801 | 0.00755 |
| 0.0085 | 0.00857 | 0.08594 | 0.09403 | 0.00806 |
| 0.009 | 0.00908 | 0.09100 | 0.10011 | 0.00857 |
| 0.0095 | 0.00959 | 0.09606 | 0.10626 | 0.00908 |
| 0.01 | 0.01010 | 0.10111 | 0.11248 | 0.00959 |
| 0.0105 | 0.01061 | 0.10617 | 0.11878 | 0.01010 |
| 0.011 | 0.01112 | 0.11122 | 0.12514 | 0.01061 |
| 0.0115 | 0.01163 | 0.11628 | 0.13158 | 0.01112 |
| 0.012 | 0.01215 | 0.12133 | 0.13809 | 0.01164 |
| 0.0125 | 0.01266 | 0.12639 | 0.14467 | 0.01215 |
| 0.013 | 0.01317 | 0.13144 | 0.15134 | 0.01266 |
| 0.0135 | 0.01368 | 0.13650 | 0.15808 | 0.01317 |
| 0.014 | 0.01420 | 0.14156 | 0.16490 | 0.01369 |
| 0.0145 | 0.01471 | 0.14661 | 0.17180 | 0.01420 |
| 0.015 | 0.01523 | 0.15167 | 0.17878 | 0.01472 |

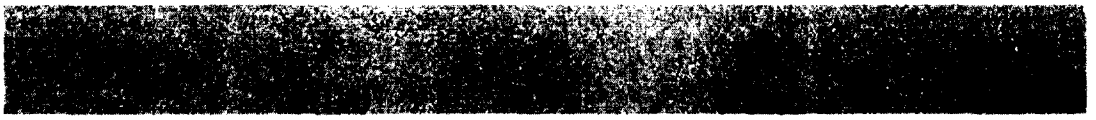
Note: $D_C$: Distribution coefficient of acetic acid in organic to aqueous is 10

$Y_o$: mass ratio of acetic acid in organic calculated from operating equation (AF.1)

Table F.5 Equilibrium and operating data for acetic acid extraction by using CYANEX

| | | | | |
|---|---|---|---|---|
| 0.0005 | 0.00050 | 0.00148 | 0.00148 | 0.00001 |
| 0.001 | 0.00100 | 0.00295 | 0.00296 | 0.00049 |
| 0.0015 | 0.00150 | 0.00443 | 0.00445 | 0.00099 |
| 0.002 | 0.00200 | 0.00591 | 0.00594 | 0.00150 |
| 0.0025 | 0.00251 | 0.00739 | 0.00744 | 0.00200 |
| 0.0035 | 0.00351 | 0.01034 | 0.01045 | 0.00300 |
| 0.004 | 0.00402 | 0.01182 | 0.01196 | 0.00351 |
| 0.0045 | 0.00452 | 0.01330 | 0.01347 | 0.00401 |
| 0.005 | 0.00503 | 0.01477 | 0.01499 | 0.00452 |
| 0.0055 | 0.00553 | 0.01625 | 0.01652 | 0.00502 |
| 0.006 | 0.00604 | 0.01773 | 0.01805 | 0.00553 |
| 0.0065 | 0.00654 | 0.01920 | 0.01958 | 0.00603 |
| 0.007 | 0.00705 | 0.02068 | 0.02112 | 0.00654 |
| 0.0075 | 0.00756 | 0.02216 | 0.02266 | 0.00705 |
| 0.008 | 0.00806 | 0.02364 | 0.02421 | 0.00756 |
| 0.0085 | 0.00857 | 0.02511 | 0.02576 | 0.00806 |
| 0.009 | 0.00908 | 0.02659 | 0.02732 | 0.00857 |
| 0.0095 | 0.00959 | 0.02807 | 0.02888 | 0.00908 |
| 0.01 | 0.01010 | 0.02955 | 0.03044 | 0.00959 |
| 0.0105 | 0.01061 | 0.03102 | 0.03202 | 0.01010 |
| 0.011 | 0.01112 | 0.03250 | 0.03359 | 0.01061 |
| 0.0115 | 0.01163 | 0.03398 | 0.03517 | 0.01113 |
| 0.012 | 0.01215 | 0.03545 | 0.03676 | 0.01164 |
| 0.0125 | 0.01266 | 0.03693 | 0.03835 | 0.01215 |
| 0.013 | 0.01317 | 0.03841 | 0.03994 | 0.01266 |
| 0.0135 | 0.01368 | 0.03989 | 0.04154 | 0.01318 |
| 0.014 | 0.01420 | 0.04136 | 0.04315 | 0.01369 |

Table F.5 Continued



| | | | | |
|---|---|---|---|---|
| 0.0145 | 0.01471 | 0.04284 | 0.04476 | 0.01420 |
| 0.015 | 0.01523 | 0.04432 | 0.04637 | 0.01472 |

Note: $D_C$: Distribution coefficient of acetic acid in organic to aqueous is 3

$Y_o$: mass ratio of acetic acid in organic calculated from operating equation (AF.1)

## BIOGRAPHY OF THE AUTHOR

Aymn Abdulrahman was born in Makkah, Saudi Arabia on March 10th, 1979. He graduated from High School in 1997. In 2003, He received a Bachelor of Science in Chemical Engineering from King Fahd University of Petroleum and Mineral in Saudi Arabia. In 2010, He received a Master degree of Science in Chemical Engineering from University of Maine in USA.

Aymn worked for 9 months in Arabian Petroleum Supply (APSCO) in Saudi Arabia and then about two years in sugar refinery as shift manager trainee. Aymn is a candidate for the Doctor of Philosophy degree in Chemical Engineering from the University of Maine in December 2014.