COMPARATIVE STUDIES ON THE PURIFICATION PROCESS OF BIO-ETHANOL FROM RICE HUSKS

SITI AISHAH MUSTAFA

A thesis submitted in fulfillment of the requirements for the award of the degree of Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
University College of Engineering & Technology Malaysia

NOVEMBER 2006

I declare that this thesis entitled *"Comparative Studies on the Purification Process of Bio-ethanol from Rice Husks"* is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....

Name of Candidate : Siti Aishah Mustafa

Date : 27 November 2006

DEDICATION

Special dedication to my mum and family members that always inspire, love and stand besides me, my supervisor and previous supervisors, all FKKSA personnels, my beloved friends, my fellow colleagues, and all faculty members

For all your love, care, support, and believe in me.Thank you so much.

ACKNOWLEDGEMENT

Throughout two semesters, I met numbers of lecturers and professionals who have assisted me in many ways towards completing my research. Firstly, I would like to express my sincere appreciation to my supervisor, Miss Farhan Mohd Said, who generously shared her insights and suggestions. Not forgotten, my previous supervisors, Tuan Haji Kamal Yusoh for his critics, trust, encouragement, and attention and also Mr. Rozaimi Abu Samah who guides me a lot in improving my research methodology.

I also would like to express my gratitude to the personnels of Faculty of Chemical and Natural Resources Engineering (FKKSA), especially Mr. Mior Ahmad Khushairi, Mr Mohd Shaiful Zaidi, Mr Ashaari, Miss Wan Salwanis, Miss Nina Suhaity, Mr. Mazrul Nizam and Mr. Arman as my panels and also Mr Mohamad Rizza as my external examiner. Special thanks to FKKSA Laboratory officers especially Miss Idayu, Madam Norlia, Mr Mohd Hafiz, Mr Zainal, Mr. Hairul Nizam, Mr Mohd Anuar and Mr Mohd Masri.for their kindness in helping me to manage my experimental work. Not forgotten, Madam Ku Syahidah and Madam Chua for your guidance and support.

I am also obliged to express my appreciation towards my beloved mother and family members for their enduring patience, moral and financial supports. Lastly, I would like to thank to my friends especially Jess, Hani, Marcel, Mimi, Yih Tin, Linda, Ida, and Naz for their friendship, support and care on me. I will miss all of you. Also to Fiza, Hisyam, Hajar, and Atan who involved in the same research area for sharing their opinions in this project. Thank you to all. Thank you for everything. May God bless all of you.

ABSTRACT

The objective of this research is to study the purification process of bio-ethanol production by different distillation methods. In this research, continuous study is done which the same production method is repeated, scaled up and improved. After production process, the process is continued with the comparative studies on the purification process.In the previous thesis, rice husks is selected as the raw material for the production of bio-ethanol from biomass waste. The production method comes into 3 main processes which are the pre-treatment of rice husks using NaOH at ambient condition, followed by enzymatic hydrolysis , and end up with anaerobic fermentation After bio-ethanol is produced, simple distillation is done first for the on the purification followed by the extractive distillation which used ethylene glycol as solvent. Then, the effect of adding salt in ethylene glycol is determined by performing extractive distillation with salt. The distillation processes are compared. It is proven that by scaling up the anaerobic fermentation process yields higher amount of bio-ethanol which is 8.3 vol% and 6.3 wt% in weight composition than in the previous thesis. The extractive distillation with salt performed the highest result in concentrating the bio-ethanol to 22 vol% and 17 wt% in weight composition. As a conclusion, purification process by the extractive distillation with salt yields the highest performance in removing water from bio-ethanol and better than other distillation process.

ABSTRAK

Objektif kajian ini adalah untuk mempelajari proses penyulingan terhadap bio-ethanol yang telah dihasilkan melalui pelbagai jenis proses penyulingan. Pada penyelidikan ini, kajian berterusan dijalankan di mana cara penghasilan yang sama di dalam kajian lepas diulang, diperbaiki dan dipertingkatkan skala. Selepas proses penghasilan dijalankan, ia diikuti dengan kajian berbentuk perbandingan dijalankan terhadap proses penyulingan. Pada kajian lepas, sekam padi telah dipilih sebagai bahan mentah bagi penghasilan bio-ethanol daripada sisa buangan biojisim. Proses penghasilan terbahagi kepada 3 peringkat iaitu pra-rawatan bagi sekam padi menggunakan NaOH pada suhu bilik, diikuti dengan hidrolisis enzim, dan diakhiri dengan penapaian secara anaerobik. Selepas bio-ethanol terhasil, penyulingan mudah dijalankan diikuti dengan penyulingan ekstraktif menggunakan ethylene glycol sebagai pelarut. Kesan penambahan garam ke dalam ethylene glycol telah ditentukan dengan menjalankan penyulingan ekstraktif dengan garam. Kesemua proses penyulingan diperbandingkan. Ia terbukti dengan mempertingkatkan skala terhadap proses penapaian secara anaerobik menghasilkan jumlah komposisi bio-ethanol yang lebih tinggi daripada kajian lepas sebanyak 8.3 vol % dan 6.3 wt% dlm komposisi jisim . Penyulingan ekstraktif dengan garam memberikan keputusan terbaik dalam memekatkan komposisi bio-ethanol sebanyak 22 vol% dan 17 wt% dalam komposisi jisim. Kesimpulannya, penyulingan ekstraktif dengan garam memberikan pencapaian terbaik dalam menyingkirkan air daripada bio-ethanol dan lebih baik dari proses penyulingan yang lain.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

g - gram
mL - mililitre
L - litre
Tg - tonne gram
Mm^2 - megameter square
$\mathrm{Mg\ ha}^{-1}$ - megagram per hectar
GL - gigalitre
kg - kilogram
°C - degree Celcius
% - percent
µg/mL - microgram per mililitre
mm - milimeter
rpm - rotation per minute
L/h - litre per hour
g/mL - gram per mililitre
vol% - volume percent
wt % - weight percent

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.0 Introduction

Alternative fuels appeared as a popular phrase during the latter years of the twentieth century which referred to fuels that were not totally based on petroleum and held potential as clean-burning, low polluting, commercially viable fuel sources. Reasons for considering alternative fuels are because of two motivating factors which the needs to ensure an adequate supply of low cost-fuel, and the desire to use fuel that burns completely and cleanly without undesirable exhaust emissions. Alternative fuels have been considered good energy sources to power engines since the early years of engine development. The original engine developed by Rudolf Diesel, for example, was designed to be fueled by powdered coal (Peyton, 2002). Transport fuel production from biomass is technically feasible and liquid and gaseous bio-fuels can be derived from range of biomass sources. For example bio-methanol, bio-ethanol, di-methyl esters, pyrolytic oil, and bio-diesel can be produced from a variety of energy crops. Bio-ethanol and bio-diesel are already commercially available, albeit with government support, as when produced from energy crops they cannot easily compete with cheap petroleum-based products (Sims and Bassam, 2003).Henry Ford considered ethanol to be good fuel source because it was renewable besides its benefit towards culture (Peyton, 2002).

Ethanol can be readily produced chemically by industrial processes such as the sulfonation-hydrolysis process and the direct catalytic process which used ethylene as the feedstock. Biomass fermentation, however, yields the greatest supply of fuel grade ethanol (Peyton, 2002). In the previous study, production of bio-ethanol is done biologically through biomass fermentation. Bio-ethanol can be produced using raw materials from agricultural crops like rice husks, bagasse, maize cobs, coconut husks (copra), groundnut, other nut shells, sawdust, and cereal straw. In this study, rice husks are selected as the raw materials for production of bio-ethanol from biomass fermentation. Rice husks, the lignocelluloses material must be pre-treated, then continued by hydrolyzed into glucose and fermented into bio-ethanol. Production of bio-ethanol from rice husks in the previous study is obtained by using 3 major processes which are: a) alkali pre-treatment of rice husk with NaOH at ambient condition, b) enzymatic hydrolysis of pre-treated rice husks and finally c) anaerobic fermentation. These 3 main processes produced 0.24 vol % concentration of bio-ethanol at this condition (Noranisah Hisa, 2005). In this study, the same production method is repeated, improved and followed by scaled up.

Through alcoholic fermentation process, large quantity of polluted water is generated (Varma and Behera, 2003). Purification of bio-ethanol from fermentation is necessary to recover ethanol from final fermented product in order to get anhydrous ethanol or dry ethanol. Later, it can be used as fuel ethanol for the vehicle engines without the needs of any modification on the engines. If the remaining water is not removed, water contamination can damaged the vehicles engine. So, the objective of this study is to purify the bio-ethanol from anaerobic fermentation using various distillation methods in order to get concentrate bio-ethanol.

For instance, the common methods of purification are solvent extraction and distribution, distillation, recrytallization, sublimation, and chromatography. It is note that more than one method of purification may need to be implemented in order to obtain the highest purity (Armarego and Chai, 2003). In the purification of bio-ethanol from anaerobic fermentation, the common technologies that have been used were distillation and pervaporation which used membrane. During this study, simple distillation is done followed the extractive distillation which used ethylene glycol as solvent. The performance of both processes is then compared. Ethanol-water system cannot be completely separated with simple distillation because this system performed azeotropic condition. Extractive distillation is commonly used for the dehydration process because traditional distillation leaves approximately 3 to 5 percent of water in the finished ethanol (Kohl, 2004). Finally, the extractive distillation with salt is done to determine the effect of adding salt in solvent that can influenced the performance of the extractive distillation. Salt that have been selected is calcium chloride since it is easy to get.

Extractive distillation was the basic operation used in order to separate compounds with close boiling points or mixtures that form azeotrope, by means of the utilization of an additional compound and was named as entrainer or agent that alters the relative volatility of the compounds of the mixture**.** The use of ethylene glycol with salt as an extractive agent in the production of anhydrous ethanol has proven to be an effective alternative in replacing highly toxic separation liquids agents, such as benzene and more ecologically process can be done.

1.1 Problem Statement

As an automotive fuel, ethanol has been utilized throughout the world. Brazil, Scandinavia, France, the United States, Germany, Japan, New Zealand, and other countries have found that ethanol to be an effective alternative fuel for transportation vehicles (Peyton, 2002).

In Malaysia, the increment of price for petrol and diesel in the year 2006 has raised attention in producing alternative fuels from biomass wastes. This issue has created the needs to produce alternative fuels that are environmental friendly. Ikegami *et al*. (2001) described that it is very important to efficiently produce bio-ethanol as an energy source by yeast fermentation employing renewable biomass resources. This processes of not only getting ready for exhaustion of fossil energy resources in future, but also decreasing greenhouse gas emission, CO_2, which causes global warming today.

Biomass fermentation however yields the greatest supply of fuel grade ethanol. As a transportation vehicle fuel, ethanol can be used directly, blended with conventional fuel, or used as an oxygenate in reformulated fuels. Since ethanol is single, highly polar organic molecule, it can provide different performance from traditional non-polar hydrocarbon fuels that contain numerous organic molecules. As a result, handling, storage, use, and performance of ethanol and ethanol blended fuels can differ from conventional fuels (Peyton, 2002).

Since water is completely soluble in ethanol, water contamination can cause ethanol to separate from gasohol blends. If brought onto the fuel, these deposits can create problems with filter plugging or fuel discoloration. Less than 1% water contamination can increase the specific gravity of a gasohol-ethanol-water solution causing it to separate as a heavier, distinct phase from the lower-specific gravity gasoline. This problem is more pronounced in cold temperatures. Although the freezing point of ethanol is lower than conventional fuels, when ethanol contaminated with water, the freezing point of ethanol may rises (Peyton, 2002). This is where the comparative studies of purification method are needed where simple distillation, extractive distillation, and extractive distillation with salt are studied and the separation ability of the solvents in the extractive distillation is determined.

1.2 Objective

The aim of this study is:

i. To study the effect of using different distillation methods in purifying bio-ethanol from rice husks by performing simple distillation, extractive distillation and extractive distillation with salt.

1.3 Scope of Study

To achieve the objective, there are five scopes that have been identified:

i. To produce bio-ethanol from rice husks using pre-treatment of rice husks with NaOH at ambient condition, enzymatic hydrolysis of pre-treated rice husks and anaerobic fermentation.
ii. To determine whether higher concentration of bio-ethanol could be achieved by scaling up the anaerobic fermentation by working volume.
iii. To compare the performance of purification of bio-ethanol through extractive distillation and simple distillation.
iv. To study the effect of adding salt in ethylene glycol as the solvent in the extractive distillation.
v. To analyze the composition of bio-ethanol after production and purification processes using analytical equipment.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to the Purification Process

Purity is a matter of degree. From Merriam-Webster Online Dictionary, purification can be defined as the act or an instance of purifying or of being purified. From Pharmaceutical Technology, purification is the process of removing impurities by sterilization or filtering or any other methods. The important question, then, is not whether a substance is pure but whether a given sample is sufficiently pure for some intended purpose. That is, are the contaminants likely to interfere in the process or measurement that is to be studied. By suitable manipulation it is often possible to reduce levels of impurities to acceptable limit, but absolute purify is an ideal which, no matter how closely approached, can never be attained (Armarego and Chai, 2003).

2.1.1 Assessing Criteria for Purification Process

Solvents and substances that are specified as pure for a particular purpose may, in fact, be quite impure for other uses. Irrespective of the grade of material to be purified, it is essential that some criteria exist for assessing the purity of the final product (Armarego and Chai, 2003). The more common of these include:

i. Examination of physical properties such as:
   a. Melting point, freezing point, boiling point, and the freezing curve.
   b. Density.
   c. Refractive index at a specified temperature and wavelength.
   d. Specific conductivity.
   e. Optical rotation, optical rotatory dispersion and circular dichroism.

ii. Empirical analysis, for C, H, N, ash, etc.

iii. Chemical tests for particular types of impurities.

iv. Physical tests for particular types of impurities**:**
   a. Emission and atomic absorption spectroscopy for detecting organic impurities and determining metal ions.
   b. Chromatography, including paper, thin layer, liquid (high, medium and normal pressure) and vapor phase.
   c. Electrons spin resonance for detecting free radicals.
   d. X-ray spectroscopy.
   e. Mass spectroscopy.
   f. Fluorimetry.

v. Examination of spectroscopic properties
   a. Nuclear Magnetic Resonance.
   b. Infrared Spectroscopy (IR).
   c. Ultraviolet Spectroscopy (UV).
   d. Mass spectroscopy.

vi. Electrochemical methods.

vii. Nuclear methods which include a variety of radioactive elements as in organic reagents, complexes or salt.

A substance is usually taken to be of an acceptable purity when the measured property is unchanged by further treatment (especially if it agrees with a recorded value). In general, at least two different methods, such as recrystallisation and distillation, should be used in order to ensure maximum purity (Armarego and Chai, 2003).

The common methods of purification comprised distillation (including fractional distillation, distillation under reduced pressure, sublimation and steam distillation), crystallization, and extraction, chromatographic and other methods. In some cases, volatile and other impurities can be removed simply by heating. Impurities can also sometimes be eliminated by the formation of derivatives from which the purified material is regenerated (Armarego and Chai, 2003).

2.2 Overview of Bio-ethanol from Biomass Waste

The meaning of the word “biomass” varies considerably, even among those individuals most concerned with its production and utilization. From the Webster’s New Collegiate Dictionary, biomass can be defined as the amount of living matter or residues of living matter present in a unit area or volume of habitat. By this definition, it focused on the available municipal refuse, wood, and agricultural residues, feedlot wastes and sewage sludge as a source of fuel (Robinson, 1980).

Biomass energy is derived from renewable resources (Dale and Kim, 2004). Ethanol derived from biomass, one of the modern forms of biomass energy, has the potential to be sustainable transportation fuel, as well as a fuel oxygenate that can replace gasoline (Wang, 2000; Dale and Kim, 2004). Ethanol can be produced from any sugar or starch crops. Another potential resource for ethanol is lignocelluloses biomass, which includes materials such as agricultural residues, herbaceous crops, forestry wastes, wastepaper, and other wastes (Wyman, 1996; Dale and Kim, 2004). These crops include corn, barley, oat, rice, wheat, sorghum, and sugar cane. To avoid conflicts between food used and industrial used of crops, only wasted crops are assumed to be available for producing ethanol (Dale and Kim, 2004).

2.2.1 Rice Husks

In global situation, the annual global production of dry rice is about 526 Tg. Asia is the primary production region with over 90% of global production and the largest harvested area for rice, 1.4 Mm^2 .The rice yield in Asia is 3.5 dry Mg ha^{-1}, which is equal to the global average rice yield. The highest yield occurs in Australia with 7.8 Mg of dry rice per hectare.

Most rice (about 88% of global production) is used for human food. About 2.6% of global production is used for animal feed, but there is no rice used for animal feed in North America. About 4.8% of world rice production is lost as waste. About 22 Tg of dry rice in Asia is wasted, a quantity larger than the rice production of any other region. The highest fraction of wasted rice occurs in North America (Dale and Kim, 2004). The uses of rice are illustrated in Table 2.1.

Table 2.1: Uses of Rice Grain

	Feed (%)	Seed (%)	Waste (%)	Food manufacture (%)	Food (%)	Other uses (%)
Africa	1.41	2.32	7.17	0.48	86.67	1.94
Asia	2.71	3.05	4.55	0.68	88.85	0.16
Europe	6.53	2.36	0.82	0.34	87.40	2.55
North America	0.00	3.18	12.15	12.31	66.78	5.57
Central America	0.73	1.23	4.11	3.89	89.66	0.38
Oceania	0.05	2.31	2.06	1.73	92.71	1.14
South America	2.05	2.75	8.35	3.00	83.18	0.66
World	2.62	2.99	4.82	0.88	88.35	0.33

If wasted rice could fully utilize to produce bio-ethanol, then 12.3 GL of bio-ethanol could be produced, replacing 8.9 GL of gasoline. Rice dry milling could produce 0.8 dry kg of DDGS per kg of ethanol as a co-product, replacing rice grain used for animal feed. About 9.3 Tg of rice would be available due to the utilization of DDGS and could produce 4.5 GL of bio-ethanol (Dale and Kim, 2004).

No rice straw must be left on the field to prevent erosion. Thus, rice straw could be fully utilized, resulting in 731 Tg of rice straw from which 205 GL of bio-ethanol could be produced. Furthermore, lignin-rich fermentation residue could generate 123 TWh of electricity and 708 PJ of steam (Dale and Kim, 2004).

Globally, wasted rice grain and rice straw could produce 221 GL of bio-ethanol, replacing 159 GL of gasoline (about 14.3% of global gasoline consumption). Asia has the greatest potential, 200 GL of ethanol from wasted rice grain and rice straw (Dale and Kim, 2004). The regional potential bio-ethanol production is shown in Table 2.2.

Table 2.2: Regional Potential Bio-ethanol Production (GL) from Wasted Rice Grain and Rice Straw

	From wasted grain	From grain replaced by DDGS	From rice straw	Total bio-ethanol (GL)	Gasoline Equivalent (GL) from wasted grain
Africa	0.52	0.19	5.86	6.57	4.72
Asia	10.5	3.87	186.8	201.2	144.5
Europe	0.01	0.004	1.10	1.11	0.80
North America	0.46	0.17	3.06	3.69	2.65
Central America	0.04	0.01	0.77	0.83	0.59
Oceania	0.01	0.004	0.47	0.49	0.35
South America	0.68	0.25	6.58	7.51	5.39
World	12.3	4.5	204.6	221.4	159

2.3 Overview of Bio-ethanol Production

The primary reason for the current great interest in ethanol is its potential used as a transportation fuel either alone or blended with gasoline (Robinson, 1980). Noranisah Hisa (2005) stated that ethanol production from biomass waste which is rice husk can be obtained by 3 major processes:

a) Pre-treatment of rice husks
b) Enzymatic hydrolysis
c) Anaerobic fermentation

2.3.1 Pre-treatment of Rice Husks

Pre-treatment is an important tool for practical cellulose conversion processes. Pre-treatment is required to alter the structure of celluloses biomass to make cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars. The goal is to break the lignin seal and disrupt the crystalline structure of cellulose (Noranisah Hisa, 2005).

Pre-treatment refers to the solubilization and separation of one or more of the major components of biomass-hemicellulose, cellulose, lignin, and extractives to make the remaining solid biomass more accessible to further chemical or biological treatment. There are numerous pre-treatment methods or combinations of pre-treatment methods available. Physical pre-treatment breaks down the feedstock size by milling or aqueous or steam processing. For celluloses materials, it required more intense physical pre-treatments such as steam explosion. The most common chemical pre-treatment methods used for celluloses feedstock's are dilute acid, alkaline, organic solvent, ammonia, sulfur dioxide, carbon dioxide, or other chemicals to make the biomass more digestible by the enzymes (Noranisah Hisa, 2005).

There are several pre-treatment method options available for enzymatic hydrolysis such as pre-treatment with dilute-acid hydrolysis, steam explosion, ozone, water or alkali. However, alkali pre-treatment had been used in the previous studies (Noranisah Hisa, 2005). Alkali pre-treatment processes utilized lower temperatures and pressures compared to other pretreatment technologies. Alkali pre-treatment may be carried out at ambient conditions, but pre-treatment time is measured in terms of hours or days rather than minutes or seconds. Unlike acid-catalyzed pre-treatments, a limitation occurs because some of the alkali is converted to irrecoverable salts or incorporated as salts into the biomass by the pre-treatment reactions. Lime has been used to pre-treat wheat straw, poplar wood, switch grass and corn stover. Pre-treating sugarcane bagasse with lime at ambient conditions for up to 192 hours improved the enzyme digestibility of the cellulose from 20% to 72% after pre-treatment (Playne, 1984).

Higher temperatures and shorter reactions times were also shown to effectively pre-treat lignocellulose with lime (Chang *et al.*, 1998), obtained similar digestibility results by pre-treating bagasse with lime at 120 °C for 1 hour. Other alkali pre-treatments use sodium, potassium, calcium, and ammonium hydroxide as reactants. Sodium hydroxide has received the most attention (Sharmas *et al*, 2002). Lime (calcium hydroxide) has the additional benefits of low reagent cost and safety (Chang *et al.*, 1997) and be recoverable from water as insoluble calcium carbonate by reaction with carbon dioxide. Oxidative lime pre-treatment of poplar (Chang *et al.*, 2001) at 150 °C for 6 hours removed 77.5% of the lignin from the wood chips and improved the yield of glucose from enzymatic hydrolysis from 7% (untreated) to 77% (treated) compared to untreated and pre-treated poplar wood.

2.3.2 Enzymatic Hydrolysis

There are three basic types of EFC (ethanol-from-cellulose) processes which are acid hydrolysis, enzymatic hydrolysis and thermo-chemical. The most common is acid hydrolysis. However, enzymatic hydrolysis will be discussed since in the previous study, this process had been selected for the experimental work (Noranisah Hisa, 2005).

Cellulases are enzymes that hydrolyze the β-(1→4) linkages in cellulose. Cellulases are produced as a multicomponent enzyme system comprised usually of three enzymes that act synergistically in the hydrolysis of cellulose: endoglucanase (EC 3.2.1.4), cellobiohydrolase (EC 3.2.2.91), and cellobiase (β- glucosidase, EC 3.2.1.21). The first two enzymes acted directly on cellulose is then hydrolyzed into glucose by cellobiase. Endoglucanases and cellobiohydrolases degrade soluble cellodextrins and amorphous cellulose. On the other hand, it is the cellobiohydrolases that degrade crystalline cellulose most efficiently (Bhat and Bhat, 1997). Cellulose is the most abundant and renewable bio-polymer on earth. The enzymatic modification of cellulose is a challenge in all applications using cellulose based fibers due to the potential benefits.

Currently, the most widely exploited cellulose applications are in the textile industry, for example the stone washing of jeans and finishing of cotton fabrics (Kumar *et al*., 1997). In the pulp and paper industry, cellulases are used together with hemicellulases to improve the drainage and running of paper machines and to enhance the deinking of recycled fibers (Noe' *et al*, 1986). To date, many studies on the action of cellulases or purified cellulases on cellulose have revealed the mechanism by which the enzymes degrade cellulose (Bhat, 2000). The substrate concentration and effect of endoglucanase and cellobiohydrolase on the properties of cellulose need further study. The aim of the present study is to investigate the treatment of dissolving pulp with different cellulases and determine whether such treatment improves the properties (Cao and Tan, 2002).

2.3.3 Anaerobic Fermentation

Fermentation is the anaerobic decomposition process of organic compounds, basically carbohydrate into alcohols by the action of bacterial enzymes. Ethanol is the desired product of carbohydrate fermentation, but other alcohols, acids, ketones, and aldehydes can form as by-products (Peyton, 2002). Production of ethanol via fermentation is based on the conversion of sugars to ethanol by yeast under anaerobic conditions (Robinson, 1980). To ensure that the anaerobic bacteria thrived, careful control over substrate concentration, pH, temperature, nutrients, and toxins must be maintained (Peyton, 2002).

In the previous study, batch fermentation had been selected for the experimental work where substrate and yeast culture are charged into the bioreactor together with nutrients (Noranisah binti Hisa, 2005). Most of the ethanol produced today is done by the batch operation since the investment costs are low, do not require much control and can be accomplished with unskilled labor (Caylak and Sukan, 1998). Complete sterilization and management of feedstock are easier than in the other processes. The other advantage of batch operation is the greater flexibility that can be achieved by using a bioreactor for various product specifications.

2.4 Purification of Bio-ethanol

Many methods exist for the purification of reagents and solvents. A number of these methods are routinely used in synthetic as well as analytical chemistry and biochemistry. It is important to note that more than one method of purification may need to be implemented in order to obtain the highest purity compound. Common methods of purification are solvent extraction and distribution, distillation, recrystallisation, sublimation and chromatography (Armarego and Chai, 2003).

For substances contaminated with water or solvents, drying with appropriate absorbents and desiccants may be sufficient (Armarego and Chai, 2003). As fermentation is completed, the next stage of ethanol production is purification. Purification separated the ethanol from the other components of fermentation; since water is the largest to remove. This step is necessary because fuel purposes required very pure ethanol to proper blend with gasoline. The current separation technology used in the ethanol industry is comprised of two steps: 1) distillation followed by 2) dehydration (Kohl, 2004).

2.4.1 Introduction to Distillation Process

Distillation is a technique which has been utilized by humans for hundreds, even thousands of years for the purification of ethanol. Distillation operates under the principles that different materials boil at different temperatures. Using this principle, a two-component mixture of ideal liquids can be heated in a “pot” under controlled conditions, with the boiling point material completely vaporized and collected at the top of the pot. The material with the higher boiling point remains a liquid and is found at the bottom of the pot as stillage (Kohl, 2004).

2.4.1.1 Fractional Distillation

One of the most widely applicable and most commonly used methods of purification of liquids or low melting solids (especially of organic chemicals) is fractional distillation at atmospheric, or some lower, pressure. Without exception, this method can be assumed to be suitable for all organic liquids and most of the low-melting organic solids. For this reason it has been possible to omit many procedures for purification of organic chemicals when only a simple fractional distillation is involved. The suitability of such a procedure is implied from the boiling point (Armarego and Chai, 2003).

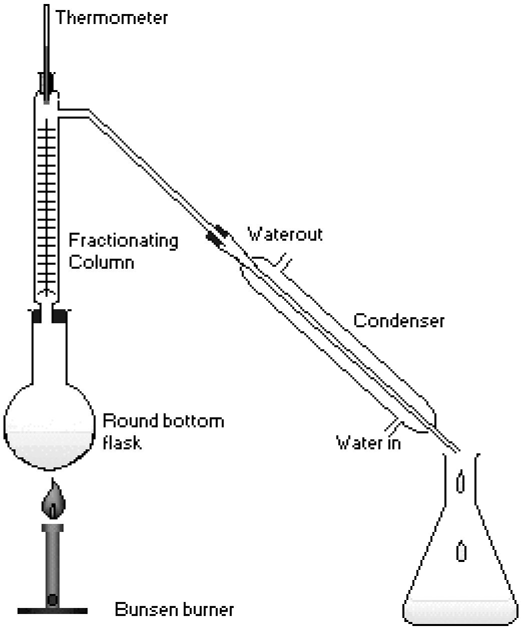

Figure 2.1 Fractional Distillation Diagram

For instance, consider the distillation of a mixture of water and ethanol. Ethanol boils at 79°C whilst water boils at 100°C. So by gently heating the mixture, the most volatile component will boil off first. Some mixtures form azeotropes, where the mixture boils at a lower temperature than either component. In this example, a mixture of 95% ethanol and 5% water boils at 78°C, which is being more volatile than pure ethanol. For this reason, ethanol cannot be completely purified by direct fractional distillation of ethanol-water mixtures. The apparatus is assembled as in the Figure 2.1. The mixture is put into the round bottom flask along with a few anti bumping granules, and the fractionating column is fitted into the top. As the mixture boils, vapor rises up to the column. The vapor condenses on the glass platforms known as trays, inside the column and runs back down into the liquid below then refluxing distillate. The column is heated from the bottom. The hottest tray is at the bottom while the coolest is at the top. At steady state conditions, the vapor and liquid on each tray is at equilibrium. Only the most volatile of the vapors stays in gaseous form all the way to the top. The vapor at the top of the column then passes into the condenser, which cools it down until it liquefies. The separation is more pure with the addition of more trays (to a practical limitation of heat, flow, etc.) The condensate that was initially very close to the azeotrope composition becomes gradually richer in water. The process continues until all the ethanol boils out of the mixture. This point can be recognized by the sharp rise in temperature shown on the thermometer.

2.4.2 Introduction to Dehydration Process

After fermentation and distillation are completed, the next stage of ethanol purification is dehydration. Dehydration is necessary because traditional distillation leaves approximately 3 to 5 percents water in the finished ethanol. The ethanol will be blended with gasoline, and the presence of water significantly enhances the natural molecular polarity of ethanol. Stated more simply, if the ethanol has significant amounts of water (5 percent is a significant amount), it will act more like water than ethanol when mixed with hydrocarbon solutions, such as gasoline. When “wet” ethanol is mixed with gasoline, the ethanol separates out with all the ethanol settling to the bottom of the container and the gasoline to the top. This separation is much like what happens when water is mixed with oil. The oil separates and floats on top of the water. It is because of at this phase separation problem that the time and expense are taken to use dehydration systems in the production of fuel ethanol (Kohl, 2004).

There are three main dehydration techniques in the industry, azeotropic distillation, extractive distillation, and molecular sieve dehydration. As these systems are both quite energy intensive, research is ongoing looking for other dehydration systems. Some systems which look promising are pervaporation and flow-through zeolite tubes. As with any new technology, these systems will need to be extensively tested and proven to provide reliable performance along with lower operating cost before they will be able to replace the current techniques (Kohl, 2004)

In cases where the components of mixtures are difficult or impossible to separate by fractional distillation either low relatively volatility or the existence of an azeotrope, it maybe possible to carry out the separation by azeotropic or extractive distillation. (Galindez, and Fredenslund, 1988)

Azeotropic and extractive are old processes which have become widely used since 1930. In 1908 Emile Guillaume patented an extractive distillation process for the removal of fusel oil from fermentation alcohol. The name “extractive distillation” is said to have been introduced by Dunn et al. Azeotropic and extractive distillation are the names given to processes in which advantage is taken of the nonideal behavior exhibited by certain mixtures in the presence of selected solvents.

Because of the tendency toward non-ideal behavior of mixtures, it is generally possible to find some component which when added to a given mixture will increase the difference between the volatilities of the light and heavy key components to be separated. The component or material added to the mixture is withdrawn from the column, usually in the distillate, as an azeotrope with one or both of the key components. The separation process called azeotropic distillation. When the solvent added to the mixture is withdrawn almost exclusively in the bottom product without forming an azeotrope, the process is called extractive distillation. (Holland, 1981)

Molecular sieves are zeolites (synthetic and highly ordered aluminosilicate) which have very precise pore sizes and are processed into small beads or pellets. The pores openings are very small (generally measured in Angstroms or nanometers) but lead to an internal structure which is much larger (similar to doorway leading to a much larger room). The molecular sieves used in ethanol dehydration have pore sizes generally around 3 Angstroms in diameter. This opening is too small for ethanol molecules to enter as ethanol is 4.4 Angstroms in diameter. Water molecules are 2.8 Angstroms in diameter and can fit into the sieve pores. This size-sorting property of the zeolite responsible for the “sieve” term in the descriptive name molecular sieve. While the molecular sieve system is much superior to the azeotropic distillation method, it is still has some areas of concern. The process is very energy intensive, though energy recovery systems can greatly minimize net energy cost. The high pressure ethanol vapors are highly flammable and catastrophic tank rupture or even minor leaks are legitimate safety concerns (Kohl, 2004).

2.4.2.1 Azeotropic Distillation

An early application of azeotropic distillation was proposed by Guinot and Clark for the separation of ethanol and water by the use of benzene as the solvent. This process is based on the fact that benzene forms a ternary azeotrope with ethanol and water which has a higher ratio of water to ethanol than does the ethanol-water azeotrope (Holland, 1981).

Azeotropic distillation has been used for decades by chemists for the purification of azeotropic mixtures. Azeotropic distillation involves adding a third chemical (entrainer) into the system during the distillation process. This third chemical interacts with both of the other chemicals in the system making a ternary azeotrope (three component azeotrope) which is stronger than the original binary azeotrope. When separation of ethanol from water is performed by azeotropic distillation, benzene or cyclohexane is commonly used as the entrainer chemical. When benzene is fed as the entrainer, three distinct regions are present with different composition in the distillation column. The bottom of the column contains the first fraction which is composed of almost pure water. The middle of the column contains a near-ternary azeotrope mixture of water, benzene, and alcohol. And the top of the column contains anhydrous ethanol. The trace quantity of water in the ethanol is controlled by the energy input into the column, product removal rate and specific column design. Downfalls of the azeotropic system are the high energy input required, the complex system of columns required regenerating the entrainer, and the propensity for ethanol contamination with the entrainer when plant upsets occur. In addition to these issues there are significant logistical and safety concerns with the storage of highly flammable and often carcinogenic (e.g. benzene) chemicals on site. Due to the problems associated with entrainer distillation, an alternate system was developed which used extractive distillation for the dehydration step (Kohl, 2004)

2.4.2.2 Extractive Distillation

Extractive distillation is commonly applied in industry and becoming important separation method in petrochemical engineering. It is generally used in two areas (Ellis and Jonah, 1962; Lei *et al*., 2002), separating hydrocarbons with close boiling point such as C4 mixtures which can represent as non-polar system and the other is the separation of mixtures with azeotropic points found with many aqueous ethanol systems which can represent as polar system (Lei *et al*., 2002).

Extractive distillation is defined as distillation in the presence of a miscible, high boiling, relatively non-volatile component and the solvent that forms no azeotrope with the other components in the mixture. Mixtures having a low relative volatility can not be separated by simple distillation because the volatility of both the components in the mixture is nearly the same may cause them to evaporate at nearly same temperature to a similar extent, whereby reducing the chances of separating either by condensation.

The method of extractive distillation used a solvent, which is generally non-volatile, has a high boiling point and is miscible with the mixture but doesn't form an azeotropic mixture. The solvent interacts differently with the components of the mixture whereby causing their relative volatilities to change. This causes the mixture to be separated through distillation. The component with the greater volatility separates out as the top product. The bottom product consists of a mixture of the solvent and the other component, which can be separated easily because the solvent doesn't form an azeotrope with it. The two can be separated by any of the methods available.

Extractive distillation with a combination of salt and solvent as the separation agent is a new process for producing high-purity products. This process integrates traditional extractive distillation with the principle of the salt effect. In the application of the extractive distillation process, there is an apparent advantage of the combination of salt and solvent over salt. In industrial operation, when salt is used, dissolution, reused and transport of salt is quite a problem. The concurrent tub-jam and erosion limits the industrial value of extractive distillation with salt only. However, the mixture of solvent and salt can avoid the defects and realize continual production in industry (Lei *et al.*, 2002).

It is reported that polar and non-polar systems can be separated by extractive distillation. Anhydrous ethanol is used not only as a fuel ethanol, chemical reagent and organic solvent, but also as the raw material of many important chemical products and intermediates. Because anhydrous ethanol is very important in chemical engineering, aqueous ethanol separation by extractive distillation process is worth studying (Lei *et al.*, 2002).

2.4.3 Solvent Effects in Extractive Distillation

In the distillation of ideal or non-azeotropic mixtures, the component with the lowest pure component boiling point is always recovered primarily in the distillate, while the highest boiler is recovered in the bottoms. The situation is not straightforward for an extractive-distillation operation. With some solvents, the component with the lower pure-component boiling point will be recovered in the distillate as in ordinary distillation. For where as, another solvent, the expected order is reversed, and the component with the higher pure-component boiling point will be recovered in the distillate. The possibility that the expected relative volatility may be reversed by the addition of solvent is entirely a function of the way the solvent interact with and modifies the activity coefficients and, thus the volatility of the components in the mixture (Perry *et. al,* 1998).

Examples of application of industrial uses of extractive distillation grouped by distillation region diagram type are in given in Table 2.3.

Table 2.3: Examples of Extractive Distillation, Salt Extractive Distillation

System	Type	Solvents	Remark
Ethanol-water	Minimum boiling azeotrope	Ethylene glycol, acetate salts for salt process	Alternative to azeotropic distillation, pressure swing distillation
Benzene-cyclohexane	Minimum boiling azeotrope	Aniline	
Ethyl acetate-ethanol	Minimum boiling azeotrope	Higher esters or alcohols, aromatics	Process similar for other alcohol-ester systems
THF-water	Minimum boiling azeotrope	Propylene glycol	Alternative to pressure swing distillation
Acetone-methanol	Minimum boiling azeotrope	Water, aniline, ethylene glycol	
Isoprene-pentane	Minimum boiling azeotrope	Furfural, DMF, acetonitrile	
Pyridine-water	Minimum boiling azeotrope	Bisphenol	
Methyl acetate-methanol	Minimum boiling azeotrope	Ethylene glycol, monomethyl ether	Element of recovery system for alternative to production of methyl acetate by reactive distillation alternative to azeotropic, pressure swing distillation

2.4.4 Solvent Screening and Selection for Extractive Distillation

Choosing an effective solvent can have the most profound effect on the economics of an extractive distillation process. The approach most often adopted is to first generate a short list of potential solvents using simple qualitative screening and selection methods. Experimental verification is the undertaken only after a list of promising candidate solvents has been generated and some chance at economic viability has been demonstrated via preliminary process modeling (Perry *et. al,* 1998).

Solvent selection and screening approaches can be divided into two levels of analysis. The first level focused on identification of functional group or chemical families that are likely favorable solvent-key component molecular interactions and the second level of analysis identified and compared individual-candidate solvents (Perry *et. al,* 1998).

One of the most important steps in developing a successful (economical) extractive distillation sequence is selecting a good solvent. In general, selection criteria include the following:

i. Should enhance significantly the natural relative volatility of the key component. Should not require an excessive ratio of solvent to nonsolvent (because of cost of handling in the column and auxiliary equipment.
ii. Should remain soluble in the feed components and should not lead to the formation of two phases.
iii. Should be easily separable from the bottom product.
iv. Should be inexpensive and readily available.
v. Should be stable at the temperature of the distillation and solvent separation. Should be nonreactive with the components in the feed mixture. Should have a low latent heat.
vi. Should be noncorrosive and nontoxic.