

ENHANCED SEPARATION OF AZEOTROPIC MIXTURES BY ULTRASOUND-
ASSISTED DISTILLATION PROCESS

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A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

JANUARY 2015

DEDICATION

*To almighty Allah (SWT), for the favours granted me throughout the course
of my studies.*

*And to my parents, for their blessings and siblings for the unwavering love,
sacrifices, encouragement and best wishes.*

ACKNOWLEDGEMENT

First of all I would like to appreciate the effort of my supervisors, Prof. Dr. Mohamed Mahmud Nasef, Prof. Dr. Arshad Ahmad and Assoc. Prof. Adnan Ripin, for their guidance and assistance *and all their intellectual support and constructive advices* during the course my PhD research and all the staff of Chemical Engineering Faculty and members of Institute of Hydrogen Economy (IHE).

I am also thankful to *Middle Refineries Company and Ministry of Oil, Iraq for providing the facilities, time and budget money needed to complete this study. I would like to thank the Najaf refinery.*

I wish to express my deep appreciation to my parents for their encouragement, advices, helps, and prayers. Special thanks to my dearest wife, Zahraa, for her patience and endurance for staying with me from the beginning to the end of my study. My heartiest thanks to my darling children. Not forgotten, my appreciation goes to my brothers and sisters for their co-operations during my study. Last but not least, thanks to all my friends and fellow PhD colleagues for their kindness and moral support during my study.

ABSTRACT

The main objective of this study is to develop an ultrasound-assisted distillation process that can break minimum boiling azeotropes under various operating conditions for enhancing the effectiveness of distillation processes in providing solution to high purity separation requirement. As a case study, ethanol/ethyl acetate (ETOH/ETAC) separation process was considered. The effect of both intensity and frequency of the ultrasonic waves on the vapor–liquid equilibrium (VLE) of this system was experimentally studied. The sonication was found to affect the VLE significantly in a way which led to an alteration in the relative volatility and a complete elimination of the azeotropic point, with the preference towards a combination of low frequency and high intensity operation. A mathematical model describing the system was developed based on conservation principles, VLE of the system and sonication effects. The model, which took into account a single-stage VLE system enhanced with ultrasonic waves, was coded using the Aspen Custom Modeler. The effects of ultrasonic waves on the relative volatility and azeotropic point were examined and the experimental data were successfully used in validating the model with a reasonable accuracy. The mathematical model was exported to the Aspen Plus to form a model that represents the sonication equilibrium stages, which were connected serially to configure an ultrasound-assisted distillation (UAD) process for separation of ETOH/ETAC mixture. The simulation results revealed that ETAC can be recovered from the azeotropic mixture with a purity of 99 mol% using 27 sonication stages. To validate the suitability of UAD process for separation of other minimum boiling azeotropes, separation of other mixtures were tested such as ethanol/water, methanol/methyl acetate and n-butanol/water. The developed model was found to have some limitations with respect to separation of maximum boiling azeotropes.

ABSTRAK

Objektif utama kajian ini adalah untuk membangunkan proses penyulingan berbantuan ultrabunyi bagi memecahkan azeotrop yang mempunyai takat didih minimum dalam pelbagai keadaan operasi untuk mempertingkatkan keberkesanan proses penyulingan bagi menyediakan penyelesaian untuk keperluan pemisahan berketulenan tinggi. Sebagai kes kajian, proses pemisahan campuran etanol-etil asetat (ETOH/ETAC) telah dipilih. Kesan keamatan dan frekuensi gelombang ultrasonik ke atas keseimbangan wap-cecair (VLE) telah diselidik. Pensonikan didapati memberikan kesan yang ketara kepada VLE dengan perubahan kepada kemeruapan relatif dan penghapusan sepenuhnya titik azeotrop, dengan kecenderungan kepada gabungan frekuensi rendah dan keamatan tinggi. Satu model matematik yang menggambarkan sistem itu dibangunkan berdasarkan prinsip keabadian, VLE sistem tersebut dan kesan pensonikan. Model itu mengambilkira sistem VLE satu peringkat dan diperkayakan dengan gelombang ultrasonik yang dikodkan menggunakan perisian "Aspen Custom Modeler". Kesan gelombang ultrasonik ke atas kemeruapan relatif dan titik azeotrop telah diteliti dan data ujikaji telah digunakan bagi tujuan validasi dan telah menunjukkan ketepatan yang berpatutan. Model matematik tersebut dieksport ke perisian "Aspen Plus" bagi membentuk model yang mewakili proses keseimbangan satu peringkat ultrabunyi. Modul-modul ini dihubungkan secara siri bagi menggambarkan proses penyulingan berbantuan ultrabunyi (UAD) untuk pemisahan campuran ETOH/ ETAC. Keputusan penyelakuan menunjukkan bahawa perolehan ETAC dengan ketulenan 99 % mol dari titik campuran azeotropik telah dicapai dengan menggunakan 27 peringkat pensonikan. Untuk membuktikan keupayaan proses UAD bagi pemisahan campuran azeotrop titik didih minimum, pemisahan beberapa campuran seperti etanol/air, metanol/metil asetat dan n-butanol/air telah diuji. Model yang dibangunkan didapati mempunyai beberapa batasan terhadap pemisahan azeotrop pendidihan maksimum.

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LIST OF ABBREVIATIONS

VLE	-	Vapor liquid equilibria
VLLE	-	Vapor liquid liquid equilibria
CAMD	-	Computer aided molecular design
ACM	-	Aspen Custom Modeler
PSD	-	Pressure swing distillation
THF	-	Tetra hydrofuran
HP	-	High pressure
LP	-	Low pressure
PV	-	Pervaporation
MTBE	-	<i>Methyl tertiary-butyl ether</i>
ETBE	-	<i>Ethyl tertiary-butyl ether</i>
ETAC	-	<i>Ethyl acetate</i>
ETOH	-	<i>Ethanol</i>
ILs	-	<i>Ionic liquids</i>
DWC	-	Dividing wall column
GC	-	Gas Chromatography
FricDiff	-	Frictional diffusion
AD	-	Azeotropic distillation
ED	-	Extractive distillation
AAD	-	Average absolute deviation
UAD	-	Ultrasound-assisted distillation
USF	-	Ultrasonic flash distillation
GA	-	Genetic algorithm

LIST OF SYMBOLS

A	-	Light component
B	-	Heavy component
C_i	-	Concentration of component (i)
C	-	Velocity of sound through the liquid
D	-	Diffusivity
F	-	Feed flow
f	-	Ultrasound frequency
F_B	-	Bjerknes force
I	-	Ultrasound intensity
J	-	Diffusion flux
J_p	-	Permeate flux
J_o	-	Pre-exponential factor
R	-	Radius of the bubble
R_{max}	-	Maximum radius of the bubble
m_g	-	Mass of air
M_g	-	Molecular weight of air
N_{col}	-	Number of columns
N_p	-	Number of pure component
N_B	-	Number of boundaries crossed
n_i	-	Number of moles of component (i)
P_i^o	-	Vapor pressure of component (i)

P_o	-	Bulk solution pressure
P_A	-	Acoustic pressure amplitude
$P(R)$	-	Pressure in the liquid at the bubble boundary
R	-	Radius of the bubble
S	-	Solvent (entrainer)
$V(t)$	-	Instantaneous bubble volume
y_i	-	<i>Mole fraction of component (i) in vapor phase</i>
x_i	-	<i>Mole fraction of component (i) in liquid phase</i>
x_i^I	-	<i>Concentration component (i) in the upper liquid phase</i>
x_i^{II}	-	<i>Concentration component (i) in the lower liquid phase</i>
t	-	Time
T_{max}	-	Maximum temperature within the bubble
T_o	-	Bulk solution temperature

Greek Letters

θ	-	Correction factors for high pressure
γ_i	-	Activity coefficients of component (i)
γ	-	Polytropic ratio= c_p/c_v
Γ	-	Activity coefficients in the lower liquid phase
α_{ij}	-	Relative volatility of components (i) and (j)
α	-	<i>Overall selectivity of membrane</i>
α_s	-	<i>Sorption selectivity</i>

σ	-	Surface tension of the liquid
μ	-	Viscosity of the liquid
ω	-	Angular frequency
\mathcal{R}	-	Universal gas constant

Subscripts

A	-	Component (A)
B	-	Component (B)
i	-	Component (i)
j	-	Component (j)
g	-	Gas
v	-	Vapor
l	-	Liquid
o	-	Initial condition
max	-	Maximum condition

CHAPTER 1

INTRODUCTION

1.1 Research Background

The separation of liquid mixtures is an important task in the process industry, and much research has been carried out to meet the requirements of the industry. Of all available liquid separation techniques, distillation stands as the most widely applied technique, which is at the heart of the separation processes in many chemical and petroleum plants. Despite its widespread use in the chemical process industries, distillation is known to consume large amounts of energy. The advantages of distillation process include: the presence of many products throughput with high purity, flexibility to design requirement with heights ranging from 6 to 60 meters and diameters that range between 0.65 and 6 meters, and the ability to operate with any feed concentration (Richardson *et al.*, 2002). The separation of liquid mixtures by distillation process depends on the differences in the volatility between the components (Poling *et al.*, 2008). The component having a great relative volatility is easier for separation and condensation to form product. Since distillation offers many processing advantages and is well-understood, it remains the preferred process whenever possible.

However, distillation has limitation in use when the mixtures to be separated exhibit complex phenomena. Such complexity is clearly exhibited when the liquid

mixtures involved form azeotropes or possess very low relative volatility. This situation led to the development of various distillation techniques, either by pressure variation such as pressure swing distillation process (Luyben, 2013), or the addition of third component as a separating agent such as azeotropic distillation (Skiborowski *et al.*, 2014) and extraction distillation processes (Gerbaud and Rodriguez-Donis, 2014), that may change the phase equilibrium of the mixture. This makes distillation a good candidate for application of process intensification offering strong potential for the enhancement the separation of azeotropic mixtures.

Azeotropes are defined as the mixtures of liquids, which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as in the vapor phase (Richardson, *et al.*, 2002). Azeotropes are formed due to differences in intermolecular forces of attraction among the mixture components (hydrogen bonding and others). The particular deviation from ideality is determined by the physiochemical forces between identical and different components (Henley *et al.*, 2011). There are two types of azeotropes depending on the boiling point of the mixture: maximum and minimum boiling azeotrope. A solution that shows large negative deviation from Raoult's law forms a maximum boiling azeotrope at a specific composition. The boiling point of this azeotrope is higher than the boiling points of its components. A solution that shows a greater positive deviation from Raoult's law forms a minimum boiling azeotrope at a specific composition and the boiling point of this mixture is lower than its components (Lei *et al.*, 2005).

In last decades, many efforts have been studied to find new and more efficient processes that improve the azeotropic separation techniques in practice. This includes membrane distillation, ionic liquids extraction, hyperbranched polymers, friction diffusion. These processes are especially attractive for separation azeotropic mixtures because they have a reduction in the process costs by decreasing the total energy consumption and simple alternative for many azeotropic separation processes (Baker, 2012). In the recent years, several studies have focused on understanding of the intensification technology to enhance the separation of azeotropic mixtures and improve the performance of the distillation process such as dividing wall column which is alternative process for azeotropic distillation and extractive distillation

(Yildirim *et al.*, 2011). For example, if the dividing wall column is used as alternative process for extractive distillation, it yields the lightest component at the top of the column and the heaviest component (solvent) at the bottom. The middle component (second component of an azeotropic mixture) is withdrawn at a selected stage of the main fractionator where its concentration is at a maximum.

1.2 Case Study: Ethanol (ETOH)-Ethyl Acetate (ETAC) Mixture

ETAC is an important environmental friendly solvent and it is one of the most popular solvents in chemical industry. Particularly, it is used in a wide range of applications such as adhesives, varnishes, cleaning, thinners, inks, coated papers, silk, explosives, artificial leather and photographic films. It also finds extensive use in the preparation of synthetic fruit essences, flavors and perfumes (Deb, 2006). Furthermore, ETAC is an important component in extractants for the concentration and purification of antibiotics. It is also used as an intermediate in the manufacture of various drugs (SOPO *et al.*, 2007).

The production of ETAC in industries is using several routes such as dehydrogenation of ETOH, oxidation of ETOH, and addition of acetic acid to ethylene in the presence of sulfuric acid as catalyst (Deb, 2006). In fact, ETAC is usually produced on the large scale from the esterification of ETOH with acetic acid (Colley *et al.*, 2009). In all cases the reactant components are not totally converted to the ester in about 65% yield at 333.15 °K and 1 bar. Unfortunately, a mixture of ETAC and ETOH is known to form azeotrope at 55 mole % of ETAC at minimum boiling point of 71.8 °C. Therefore, separation of this mixture introduces a significant difficulty which can only be separate under a complex processes (Hassan *et al.*, 2009).

The production of ETAC from ETOH was an obvious candidate for a commercial process and the initial concept was quickly demonstrated. The

consumption of ETAC as an industrial solvent has increased in recent years, due to it is economic, environmentally compatible and reliable process routes (Gaspar *et al.*, 2009). During 2004- 2011, the global production of ETAC grew by over 80% and exceeded 3 million tonnes in 2011, because strong demand for surface coatings and as a replacement for restricted solvents (Oil and Gas, 2000). In 2012, the overall ETAC supply registered a 4% increase and touched the 3.12 million - tonne mark. In the same year, Southeast Asia and China - Pacific captured the biggest share of the global production volume– over 2.44 million tonnes. It is also the largest global producer and consumer of ETAC in the world, due to the Southeast Asian paints and coatings market was grown rapidly (ICIS, 2007). Figure 1.1 shows China is an unrivalled leader of the world ETAC market, accounting for over half of the global ETAC production in 2013. It is followed by India, the UK, Japan and Brazil. It is forecast that in near future China will maintain its leading position in ETAC market, while Europe and North American countries are not expected to show significant growth.

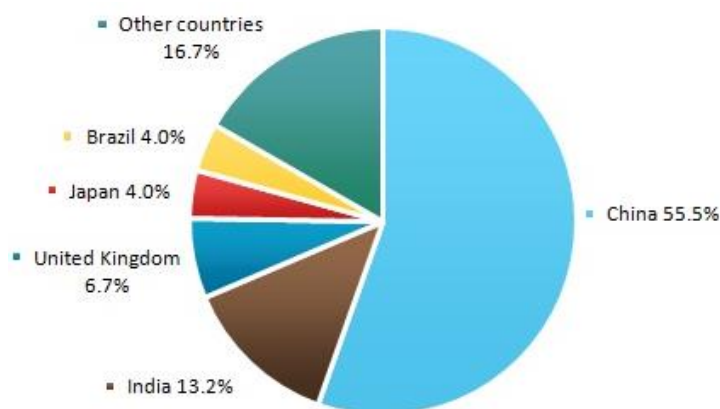


Figure 1.1 Global ETAC production in 2013

1.3 Problem statement

A traditional method of producing ethyl acetate is by esterification of ethanol with acetic acid as described by the following stoichiometry (Santacesaria *et al.*, 2012):



ETOH unconverted and ETAC product is among the most important mixture and difficult separation processes in petrochemical industry. The boiling points of ETAC and ETOH mixture are 78.65 and 77.35°C, respectively. The separation of this mixture by conventional fractional distillation process is impossible due to their close boiling points and form azeotrope.

Several potential processes for separation ETOH/ETAC mixture have been investigated such as azeotropic distillation (Skiborowski, *et al.*, 2014), extractive distillation (Nieuwoudt and Van Dyk, 2002), pressure swing distillation (Colley, *et al.*, 2009) and membrane separation (pervaporation) (Sato *et al.*, 2008). Azeotropic distillation and extractive distillation are the main technologies presently available for separation of this mixture. However, these processes have some disadvantages that can be noted. They include the selectivity of entrainer, complexity of the process and a secondary distillation needed for recovery the entrainer. Moreover, the use of entrainer leads to environmental pollution due to it is volatile organic compounds.

Over the few decades, membrane separation processes such as pervaporation has received grown interest. Pervaporation process is a suitable alternative candidate to separate ETOH/ETAC mixture because it has interesting features such as relatively low energy consumption, no requirements for adding chemicals as separating agents and no limitation by vapor liquid equilibrium (Uragami *et al.*, 2014). However, major efforts conducted in universities and research institutes show membrane processes are not suitable for separation of this mixture in chemical and petrochemical industries (Nagy, 2012). Because it needs a large surface area to

process embraces a large amount of the fluxes. Furthermore, membrane modules when equipped with ceramic membranes are very expensive. Polymeric membranes are also difficult to control because they have a low chemical and thermal stability. For all these reasons, the industries have always been eager to look for alternative processes for the separation of ETOH/ETAC mixture. Hence, any new separation technology that can lead to important improvements in terms of sustainable development criteria has an incentive to be researched. Therefore, this work is good candidate and potential alternative to traditional separation processes to separate this system, because it has the features that are looking for researchers.

1.4 Objectives of the Study

The main objective of this study is to develop an ultrasound-assisted distillation system that can break minimum boiling azeotropes under various operating conditions for enhancing the effectiveness of distillation separation processes in providing solution to high purity separation requirement. This shall be accomplished by implementing the following detailed objectives:

- i. To study the vapor-liquid equilibrium of the ETOH/ETAC mixture experimentally under ultrasonically intensified environment with respect to intensity and frequency.
- ii. To develop a mathematical model to describe the system based on conservation principles, vapor-liquid equilibrium with presence of ultrasound waves.
- iii. To simulate the design of ultrasound-assisted distillation process in order to break the azeotrope of a mixture and obtain higher purity product.

1.5 Scope of Study

To achieve all of the objectives, several stages have been outlined, which are:

- i. Using experimental work to estimate the vapor liquid equilibrium (VLE) of the ETOH/ETAC mixture with and without the presence of ultrasonic equipment.
- ii. Examining the effect of different ultrasonic intensity and frequency values on VLE of the ETOH/ETAC mixture.
- iii. Developing a mathematical model to describe a single stage VLE system with presence of ultrasound waves using Aspen Custom Modeler simulator version 8.0, university package, Universiti Teknologi Malaysia.
- iv. Examining the effect of ultrasonic waves on the relative volatility and azeotropic point of the mixture and validating this model with the experimental data
- v. Exporting this model to Aspen Plus flowsheeting environment to form a module (block) represent an intensified equilibrium stages in a distillation column. The model block can be linked via streams with all the other blocks.
- vi. Using Aspen Plus (version 8.0, university package, Universiti Teknologi Malaysia) to connect the number of sonication stages serially in order to design the ultrasound-assisted distillation (UAD) process, for separating an azeotropic mixture.
- vii. Determining the performance of the propose design for separation other azeotropic mixtures.

1.6 Significance of Research and Contributions of the Present Study

Ultrasound-assisted distillation process not likes other processes, which are partly carried out by adding a third component to the mixtures. Removal of the third component from distillate or residue adds to the complexity of the process. For this reason, this technology may offer great benefits in terms of environmental friendly. It

also has ability to operate with any feed concentration and different capacity, and also it is not affected by chemical components and feed temperature. Moreover, since ultrasonic technology is intensification of the distillation process, this process may offer a reduction in the equipment size as it reduces the separation requirement by altering the VLE.

The contribution to be made in this study involves:

1. Introduce experimental results of a VLE study on ETOH/ETAC mixture under ultrasonically intensified environment.
2. A mathematical model representing the VLE of the system under sonication has been developed. This model is very important to facilitate simulation works for design of the ultrasound-assisted distillation process to separate an azeotropic mixture.
3. An approach in implementing ultrasound-assisted process in separating azeotropic mixture is proposed, and supported by results from simulation studies.
4. The proposed mathematical model and distillation design provided the basis for the development of a pilot plant for proof of concept on ultrasonic distillation process.

1.7 Thesis Outline

The present thesis is divided into six chapters. Chapter 1 describes a background of the study and motivation for the research is being explained to give a basic overview of the problem statement. Significance, contribution, research objectives and scope also have been identified in this chapter to explain the objective of the whole research. Chapter 2 reviews the conventional and challenge alternative separation technologies, used to solve azeotropic problem and provided the advantages and disadvantages of these technologies. The examples of azeotropic

mixtures found in industries are included in this chapter. Chapter 3 shows the effects of ultrasonic waves on VLE of ETOH/ETAC mixture which will be carried out in the experimental work. Then develop a mathematical model of a single stage VLE system with present of ultrasonic waves and comparison this model with experimental data will be described in chapter 4. In chapter 5, the proposed design of ultrasound-assisted distillation process for separation minimum boiling azeotropes is presented. This is followed by the conclusions and recommendations for future works in chapter 6.

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