Modeling and Simulation of Separation of an Ethanol-water Mixture using Pervaporation Membrane Method

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B.Sc. in Chemical Engineering Technology, University of Gezira(2011)

A Dissertation
Submitted to the University of Gezira in Partial Fulfillment of the Requirements for the Award of the Degree of Master of Science

in
Chemical Engineering

Department of Applied Chemistry and Chemical Technology
Faculty of Engineering and Technology

January 2014
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Dedication

Dedicated to my beloved parents, brothers, sister, family and friends for their everlasting love, guidance and support in the whole journey of my life.
Acknowledgement

First I would like to express my grateful, praise and thanks are due to Allah who had given me the power and patience to complete this study.

I would like My sincere thanks to my main thesis supervisor Assoc. Prof. Babiker Karama Abdalla for his encouragement, guidance, advices and motivation. He was one of most considerable and kind hearted person along his day guiding me.

Many special thanks go to my Co-supervisor Dr. Abdelbagi Osman Elsiddig for his continuous assistance, invaluable advice and useful suggestions through this study.

Also Many special thanks go to my friends and my teacher Dr. Mustafa Ohaj for their advice and support during this study.

I acknowledge my sincere indebtedness and gratitude to my parents, AHMED MOHAMED ALHAG and NAGAT AWAD ABDALLA for their love, dream and sacrifice throughout my life. They were always stood by me and help me to motivate myself to overcome any obstacles. Lastly, I would like to thank my siblings for their continuous supports and trusts. Thank you all.
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Abstract
The growing demand for energy and expected oil depletion have dramatically increased the fuel prices all over the world. Consequently, research and development are motivated to look-up other alternatives and discoveries to recover the shortage and maintain the fuel prices at lower rates. Ethanol is considered to be one of the fossil fuel alternatives which can be produced from renewable resources (Biomass) such as molasses (by-product of cane sugar industry). Molasses can be fermented then separated from water using the pervaporation membrane technology. The aim of this study is to model and simulate the permeable evaporation (pervaporation) membrane unit for the separation ethanol-water mixture at different operating conditions. The investigation of the permeable evaporation (pervaporation) model has been conducted by altering the mixture inlet temperature and concentration step wise. Due to the model complexity, simulation of the process has been conducted on a computer program that built using visual studio 2010 software. Different kinds of results were obtained including membrane selectivity, inlet and outlet partial pressure of water, inlet and outlet partial pressure of ethanol, separation factor of permeable evaporation (pervaporation), separation factor of membrane, separation factor of evaporation and flux of feed. Most of these parameters have steadily affected while changing the inlet temperature and concentration of the mixture. It has been noticed that for 5% water content and 70°C of the mixture inlet, the percentage of water output was 99.9%, selectivity 2550, βpervap 8168, partial pressure water out 31.0750 (Kpa), and Feed flux 1.36947 (kg.m⁻²h⁻¹) indicating a high efficiency of permeable evaporation (pervaporation) membrane at such condition. It is recommended to develop the proposed visual studio software to manage the overall ethanol production. suggest the results development the process to producing high purity ethanol in all sugar factories in Sudan and especially ethanol plant in Kenana. Also it is recommended that research in ethanol production should be encouraged.
النمذجة والمحاكاة لفصل خليط الإيثانول والماء باستخدام طريقة التبخير والنفاذيه عبر الأغشية

مهند أحمد محمد الحاج

ملخص الدراسة

إن الطلبات المتزايدة على الطاقة ونقص النفط المتوقع قد زاد بشكل كبير أسعار الوقود في جميع أنحاء العالم، وبالتالي لا بد من البحث والتطوير لاستكشاف البديل الممكنة والحفاظ على أسعار الوقود في أقل معدل ممكن. يعتبر الإيثانول واحداً من البديلات النفطية (النفط) التي يمكن أن تكون من مصادر الطاقة المتجددة مثل المولاس (ناتج ثانوي لصناعة السكر). يتم تخمير المولاس وفصل المياه باستخدام طريقة التبخير والتفاذيه خلال الأغشية. ولهذا من هذه الدراسة هو نمذجة ومحاكاة وحدة التبخير والتفاذيه خلال الأغشية لفصل خليط الإيثانول والماء في حالات تشغيلية مختلفة. قد تم إجراء التحقق من نموذج الوحدة المستخدمة عن طريق تغيير درجة الحرارة والتركيز تدريجيا. ونظراً لتعقيد معادلات النموذج أجريت محاكاة العملية على برنامج الكمبيوتر الذي تم إنشاؤه باستخدام برنامج (visual studio 2010) وقد تم الحصول على نتائج مختلفة مثل انتقالات الغشاء، الضغط الجزئي الداخل والخارج للماء، الضغط الجزئي الداخل والخارج للإيثانول، معدل الفصل الكلي للعملية، معدل الفصل للتبتخير، معدل الفصل للغشاء وتدفق التغذية. معظم هذه العوامل قد أظهرت تغيراً واضحاً عند تغيير درجة الحرارة والتركيز. وقد لوحظ أنه عندما تكون نسبة الماء في الخليط 5% ودرجة حرارته 70 درجة مئوية تكون نسبة الماء الخارج من الغشاء:99.99%،الانقاثية 5.25، معدل الفصل للعملية 8168، الضغط الجزيئي للمادة الخارج من الوحدة 31.2750.3، معدل تدفق التغذية 0.376947 (kg m^-2 h^-1). مما يدل على كفاءة عالية للغشاء في مثل هذه الظروف. فمن المستحسن تطوير البرنامج المستخدم في عملية المحاكاة لهذه الوحدة لإنتاج الإيثانول بشكل عام. وتشير النتائج والتوصلات إلى تطوير عملية إنتاج الإيثانول عالية النقاوة في جميع مصانع السكر في السودان وخاصة مصنع إنتاج الإيثانول في كينانة. أيضاً أوصت هذه الدراسة بتشييد الأبحاث التي تهم مجال إنتاج الإيثانول.
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**Nomenclature**

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<tr>
<td>$G_L$</td>
<td>giga liter</td>
</tr>
<tr>
<td>OPEC</td>
<td>The Organization of the Petroleum Exporting Countries</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>MTBE</td>
<td>methyl tertiary butyl ether</td>
</tr>
<tr>
<td>E10</td>
<td>mix of 10% ethanol and 90% gasoline.</td>
</tr>
<tr>
<td>E85</td>
<td>mix of 85% ethanol and 15% gasoline.</td>
</tr>
<tr>
<td>VHG</td>
<td>very high gravity</td>
</tr>
<tr>
<td>CEPM</td>
<td>continuous electrophoresis with porous membranes</td>
</tr>
<tr>
<td>OSW</td>
<td>Office of Saline Water</td>
</tr>
<tr>
<td>MMM</td>
<td>mixed matrix membranes</td>
</tr>
<tr>
<td>TMP</td>
<td>trans-membrane pressure</td>
</tr>
<tr>
<td>PV</td>
<td>Pervaporation</td>
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<tr>
<td>NF</td>
<td>Nanofiltration</td>
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<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>RO</td>
<td>reverse osmosis</td>
</tr>
<tr>
<td>VOC&lt;sub&gt;S&lt;/sub&gt;</td>
<td>volatile organic compounds</td>
</tr>
<tr>
<td>MTR</td>
<td>Membrane Technology and Research</td>
</tr>
<tr>
<td>DDG&lt;sub&gt;S&lt;/sub&gt;</td>
<td>distillers dry grains</td>
</tr>
<tr>
<td>MWCO</td>
<td>a molecular weight cut-off</td>
</tr>
<tr>
<td>$\beta_{\text{Pervap}}$</td>
<td>Separation factor of pervaporation</td>
</tr>
<tr>
<td>$\beta_{\text{Mem}}$</td>
<td>Separation factor of Membrane</td>
</tr>
<tr>
<td>$\beta_{\text{evap}}$</td>
<td>Separation factor of evaporation</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Selectivity of membrane</td>
</tr>
<tr>
<td>Temp</td>
<td>Temperature °C</td>
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<tr>
<td>$P$</td>
<td>Vapor Pressure(Kpa)</td>
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Chapter one

Introduction

1.1 Theoretical Background

Renewable, sustainable, and clean energy sources to replace fossil fuels are becoming increasingly important due to a rising concern surrounding issues such as fossil fuel dependence, global warming, and the depletion of fossil fuels. Many countries do not possess oil resources and are looking into alternative fuels for fuel security reasons [1].

Biomass is an alternative energy source from which Biofuels such as biogas, biodiesel, and ethanol can be produced. More environmentally orientated countries are considering biomass fuels to replace fossil fuels as it is generally believed that less carbon dioxide or general pollution is emitted when these fuels are burned, especially if compared to fossil fuels. Different biomass feedstock's can be used which make it possible for any country to grow Biofuels feedstock's and if managed correctly these fuels would be a renewable and sustainable energy source. Biomass can be directly burnt to produce heat (known as Bioenergy) or it can be converted to liquid fuels through chemical means. The major biomass based liquid fuels are biodiesel and ethanol and are mainly aimed at the transportation market [1].

Ethanol ($\text{C}_2\text{H}_5\text{OH}$) is a clear, colorless, flammable chemical. It has been produced and used as an alcoholic beverage for several thousand years. Ethanol also has several industrial applications (e.g., in detergents, toiletries, coatings, and pharmaceuticals) and has been used as transportation fuel for more than a century. Nicholas Otto used ethanol in the internal combustion engine invented in 1897. However, ethanol did not have a major impact in the fuel market until the 1970s, when two oil crises occurred in 1973 and 1979. Since the 1980s, ethanol has been a major actor in the fuel market as an alternative fuel as well as an oxygenated compound for gasoline. Ethanol can be produced synthetically from oil and natural gas, or biologically from sugar, starch, and lignocelulosic materials. The Application of ethanol as fuel has no or very limited net emission of carbon dioxide and is able to fulfill the decrease net emission of carbon monoxide. Biologically produced ethanol is sometimes called fermentative ethanol or ethanol [2].
Ethanol derived from the fermentation process (e.g., from corn or sugar) is widely used as a blend to improve the air quality and to decrease the demand for gasoline. During the production process, ethanol dehydration is usually carried out by azeotropic distillation, which consumes about twice amount of energy than the “pervaporation” method. The purpose of this study is to demonstrate an energy efficient nanofibrous composite pervaporation membrane system for production of dehydrated ethanol. The nanofibrous membrane system consists of a cross linked polyvinyl alcohol hydrophilic barrier layer, an buffer layer based on ultra fine cellulose nanofibers (diameter about 5 nm), and an electrospun nanofibrous scaffold layer with high porosity (e.g., 80%) and fully interconnected pore structures. The performance between the conventional pervaporation membranes and nanofibrous composite membranes was compared under the same pervaporation conditions. Bioethanol is the most commonly used Biofuels today. It is routinely added to gasoline because the blending can raise the octane number and improve the combustibility of gasoline, and thus the air quality. For the above reasons, ethanol consumption has grown rapidly in recent years. An innovation in recent years has been aroused to develop processes with reduced overall environmental impact and towards greater economics. The development of catalytic membrane reactor has sparked the revolution of technology, which create a synergistic combination involving chemical reaction sequence with a membrane based chemical separation.

1.2 Statement of the Research Problem

Increase in oil demand directly lead to depletion in fossil fuel. Demand for oil is outstripping the supply of oil and oil depletion is expected to cause crude oil prices to go up over the next 50 years. The accumulation of fossil fuels is a process that took hundreds of millions of years, yet in just the last few hundred years we have depleted a large percentage of the total amount formed. The future trends of fossil fuels are difficult to predict because of the many different factors that affect the production and consumption of each fossil fuel. To present accurate predictions about coal, oil, natural gas, and other energy sources like uranium, factors such as human population growth, the energy requirements in developing countries versus. developed countries. Use of comparable fossil and renewable fuels, and environmental concerns and responses must be considered. Currently, the fossil fuel industry has a strong interest in developing new fossil fuel production facilities. More and more, these are in remote areas and have relatively high greenhouse gas emissions. The question is
to what greenhouse gas emissions these new developments will lead and what the implications of these developments will be for climate change.

Also, Massive Production of Molasses(by Product of Sugar Industry)in Sudan,(Sudan entering the age of green fuel production by inauguration of Kenana Ethanol Factory. It is the first of its kind in Africa, thus putting the country at an advanced level in this strategic industry). Developing the technology to produce and use Biofuels will create transportation fuel options that can positively impact these issues and establish safe, clean, sustainable alternatives petroleum. The world is heading towards alternative sources of energy that are environmentally friendly and which reduce greenhouse gas emission hazards.

Figure 1.1: The End of Oil.
(source: Hirsch, 2005)
1.3 Objectives

1. To develop a method of increasing the purity of ethanol product (Absolute Alcohol) using *pervaporation* membrane technology.

2. To modeling and simulation of *pervaporation* membrane in order to find the optimum operating condition and design configuration.
Chapter Two

Literature Review

2.1 Renewable Energy

Renewable energy is an energy source provided by renewable natural resources such as biomass, hydroelectric and wind. Renewable energy is known to have reduced environmental impacts compared to conventional sources of energy such as coal, oil and natural gas. These systems are also referred to as sustainable energy systems because they generate energy from a renewable resource, unlike conventional energy sources, which rely on finite resources for energy.

2.1.1 Biomass as a Renewable Energy Source

The importance of biomass as a renewable energy source may increase again in future energy systems. Efficient biomass utilization contributes to the preservation of natural resources and reduces the need for long distance transport of energy.

2.1.2 Biomass Fuels

Solid Biofuels such as wood or dried dung have been used since man learned to control fire. On the other hand, liquid Biofuels for industrial applications was used since the early days of the car industry. Nicolas August Otto, the inventor of the combustion engine, conceived his invention to run on ethanol while Rudolf Diesel, the inventor of the diesel engine, conceived it to run on peanut oil. Henry Ford originally had designed the Ford Model. a car produced between 1903 and 1926, to run completely on ethanol. Ford’s desires to mass produce electric cars did not come to fruition. However, when crude oil began being cheaply extracted from deeper in the soil, cars began using fuels from oil. Nevertheless, before World War II, Biofuels were seen as providing an alternative to imported oil in countries such as Germany, which sold a blend of gasoline with alcohol fermented from potatoes under the name Reich Kraft sprit. under the name Discol and marketed through Esso’s affiliate Cleveland. after the war, cheap Middle Eastern oil lessened interest in Biofuels. Then, with the oil shocks of 1973 and 1979, there was an increase in interests from governments and academics in Biofuels. However, interest decreased with the counter shock of 1986 that made oil prices cheaper again. But since about 2000 with rising oil prices, concerns over the future.
2.2 Ethanol Fuels

Ethanol (C\textsubscript{2}H\textsubscript{5}OH) is a clear, colorless, flammable chemical. It has been produced and used as an alcoholic beverage for several thousand years. Ethanol also has several industrial applications (e.g., in detergents, toiletries, coatings, and pharmaceuticals) and has been used as transportation fuel for more than a century. Nicholas Otto used ethanol in the internal combustion engine invented in 1897. However, ethanol did not have a major impact in the fuel market until the 1970s, when two oil crises occurred in 1973 and 1979. Since the 1980s, ethanol has been a major actor in the fuel market as an alternative fuel as well as an oxygenated compound for gasoline. Ethanol can be produced synthetically from oil and natural gas, or biologically from sugar, starch, and lignocellulosic materials. The Application of Bioethanol as fuel has no or very limited net emission of carbon monoxide (CO) and is able to decrease the net emission of carbon dioxide (CO\textsubscript{2}).

Biologically produced ethanol is sometimes called fermentative ethanol or Bioethanol [2]. Ethanol is produced from a variety of feedstock. Fermentative ethanol is produced from grains, molasses, sugarcane juice, fruits, surplus wine, whey, and some other similar sources, which contain simple sugars and their polymers[2]. On the other hand, synthetic ethanol is produced from oil, e.g., through hydration of ethylene:

\[
\text{Oil} \rightarrow \text{CH}_2 = \text{CH}_2 (\text{ethylene}) \rightarrow \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} (\text{ethanol}) \text{..........................(2.1)}
\]

Furthermore, increasing oil price or declining ethanol price can harm the economic competition of synthetic ethanol production, compared to the fermentative one.Ethylene prices in 2005 rose to US $1000 per ton, while ethanol values were around US $500 per ton. If we consider the theoretical yield of ethanol from ethylene based on Eq. (2.1) as 1.64 kg/kg, the price of raw materials was higher than that of the product. In this case, it is economically feasible to produce bio based plastics

\[
\text{Biomass/crops} \rightarrow \text{Fermentation} \rightarrow \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{H}_2\text{O} \rightarrow \text{CH}_2 = \text{CH}_2 \rightarrow \text{Plastics} \text{..............(2.2)}
\]

The global demand for ethylene is around 120 megatons. It can be considered a new market for ethanol in the future. The total world ethanol production in 2006 was 49.8 GL (gigaliter) (39 megatons), where 77% of this production was used as fuel, 8% as beverage, and 15% in industrial applications [4]. Since 1975, potable ethanol production has not experienced a major growth, while industrial ethanol production has experienced growth by about 75%. However, fuel ethanol production has
increased aggressively from less than 1 GL in 1975 to more than 38 GL in 2006 (see Fig. 2.1) [2].

![Graph showing world ethanol production since 1976.](image)

**Figure 2.1: world ethanol production since 1976.**

*(source: Ahindra Nag, 2008)*

There is competition between Brazil and the United States to be the dominant ethanol producer in the world. So far, Brazil has been the largest ethanol producer, but the statistics from 2006 imply that the United States is the largest ethanol producer with 19.1 GL, followed by Brazil with 16.7 GL. Both countries produced almost identical amounts of ethanol in 2005 (16.2 and 16.0 GL, respectively). The American continents produced 72% of the world ethanol production (see Fig. 2.2), followed by Asia, Europe, Oceania, and the African continents. There is tough competition between sugar crops (particularly sugar cane juice and molasses) and starch crops (particularly maize) as feedstock for fuel ethanol production. While sugar crops were the feedstock for more than 60% of fuel ethanol production at the beginning of the 2000s, its share decreased to 47% in 2006 and starch crops were used for 53% of fuel ethanol production in the same year. The world fuel ethanol production is predicted to keep the latest trend, at least until 2015. In comparison to 2006, ethanol production by Brazil and the United States is expected to increase by 102% and 93%, respectively. However, total production of the rest of the world is expected to increase by 585%. Therefore, the world fuel ethanol production is expected to increase to around 100 GL [2].
2.2.1 The main reasons for this sharp increase in ethanol production and demand in the future might be:

1. Possible increase in oil prices.
2. Higher demand for liquid fuels in the future.
3. Decline of the crude oil supply in the future.
4. Environmental legislation in different countries to encourage using Biofuels.
5. Production of Bioplastic materials from ethanol [2].

![Figure 2.2: World ethanol production in 2006 divided by contents. (source: Ahindra Nag, 2008)](image)

2.2.2 Ethanol Production

In 2000, 29.9 billion liters of ethanol were produced worldwide. The majority of the production comes from Brazil and the United States. In 2003, 2.8 billion gallons of ethanol were produced in the United States alone. Production in 2005 is expected to be approximately 4.0 billion gallons of ethanol. The top four producers of ethanol are Iowa (575 million gallons per year), Illinois (523 million gallons per year), Minnesota (486 million gallons per year), and Nebraska (454 million gallons per year). These four states produce approximately 72% of the total ethanol for the United States. The demand for ethanol is approximately divided into 68% fuel, 21% industry, and 11% food and beverages. Over 95% of the fuel ethanol produced in the United States was used to make E10, however, a small portion is used for the ever increasing E85 market. In comparison, 120 billion gallons of gasoline are sold in the United States each year while only 2.8 billion gallons of ethanol are produced, so the United States does not produce enough ethanol for all gasoline sold to be E10.
(maximum ethanol concentrations allowed by the U.S. Environmental Protection Agency). Currently, E10 represents 8% to 10% of the total gasoline sales in the United States. This ethanol production shortage is likely to be a major problem as MTBE is phased out and there is more demand for ethanol as an oxygenate. This increase in demand will likely result in a dramatic increase in production of ethanol in the United States [3].

Similar energy efficiency data has been shown by several other researchers. Cost of production of ethanol is a function of plant location, feedstock, production scale, and end use. The choice of feedstock depends on the country. Brazil has used sugar cane as their primary feedstock. France has attempted to use Jerusalem artichokes, but later found that sugar beets and wheat were better for ethanol production. Sweden uses its surplus of wheat to produce the ethanol for their 6% ethanol-blended gasoline. However, in the United States, corn has been determined to be one of the best feedstock [3].

Ethanol production is a growing industry in the United States, where corn is the feedstock used to produce approximately 90% of fuel ethanol. Approximately 1.26 billion bushels of corn, equal to 11% of the total U.S. corn crop, were processed to ethanol in 2004 according to the Renewable Fuels Association. Globally, the only crop used to produce more ethanol is sugar cane. Approximately 61% of world ethanol production is from sugar crops, with the remainder being made primarily from corn. The success of corn as a feedstock for ethanol production can be directly tied to the huge and sustained improvements in yields in the United States; corn yields per acre quadrupled in the fifty years from 1954 to 2004 [3].

According to the U.S. Department of Agriculture-National Agricultural Statistics Service, the average U.S. corn grain yield in 2004 was 160.4 bushels per acre and the average price was $1.95 per bushel. Use of corn to make fuel ethanol dates back to the earliest days of automobiles [3].

2.3 Future Trends

It can be foreseen that Bioethanol production is expected increase continuously in Brazil, due to the growing investments in this field. New distilleries are being built, resulting in almost 400 operating plants all over the country. They will be producing near 30 billion liters of ethanol in the next season. Although Bioethanol production in Brazil is considered a mature process, there is plenty room for
improvements. The current broad interest for the use of very high gravity (VHG) fermentations in the industrial scenario is mainly focused in reducing production costs. It is also expected that this technology will bring benefits to the overall environmental sustainability of the process by decreasing water and energy consumption. Thus, it continues being possible to increase the efficiency of first generation fuel ethanol process by embracing this technology [4].

Fermentations resulting in high ethanol titers would not only benefit the energy balance, but would also result in a significant reduction of vinasse volume. There will be a great economical and environmental impact due to reduction costs of vinasse transportation and application as fertilizer in sugar cane plantations. Besides that, higher ethanol levels would repress bacterial growth during fermentation and for that reason, decrease antibiotics usage for controlling such contaminations. Despite all these advantages, the implementation of VHG technology in the Brazilian industrial scenario is limited by the availability of very high ethanol tolerant strains. It is expected that for VHG fermentations, substrates will be formulated with more molasses, where sugars are in a concentrated form [4].

2.4 Bioreactors vs. Chemical reactors

By definition, a bioreactor is a system in which a biological conversion is affected. Although this definition can apply to any conversion involving enzymes, microorganisms, and animal or plant cells, for the purposes of this article, we will limit the definition. The bioreactors referred to here include only mechanical vessels in which organisms are cultivated in a controlled manner and/or materials are converted or transformed via specific reactions. Quite similar to conventional chemical reactors, bioreactors differ in that they are specifically designed to influence metabolic pathways. Traditional chemical reactor models and designs that may be used for bioreactor as well include: continuous stirred-tank reactors, continuous flow stirred-tank reactors, and plug-flow reactors, singularly or in series; ebullizedbed (i.e., “bubbling and boiling”) reactors; and fluidized bed reactors. The term “bioreactor” is often used synonymously with “fermenter;” however, in the strictest definition, a fermenter is a system that provides an anaerobic process for producing alcohol from sugar. Bioreactors differ from conventional chemical reactors in that they support and control biological entities. As such, bioreactor systems must be designed to provide a higher degree of control over process upsets and contaminations, since the organisms are more sensitive and less stable than
chemicals. Biological organisms, by their nature, will mutate, which may alter the biochemistry of the bioreactor or the physical properties of the organism. Analogous to heterogeneous catalysis, deactivation or mortality occur and promoters or coenzymes influence the kinetics of the Bioreaction. Although the majority of fundamental bioreactor engineering and design issues are similar, maintaining the desired biological activity and eliminating or minimizing undesired activities often presents a greater challenge than traditional chemical reactors typically require. Organisms, influenced by their morphology and the bioreactor medium, are shear-sensitive to varying degrees. A number of bacteria, yeast and fungi cultures that can be relatively tolerant of high-shear environments exhibit a robustness in high-energy mixing vessels. Animal, fish, insect and plant cells are delicate and usually require low-shear environments for viability. The viscosities of Bioreaction masses may change during growth and production phases, and, often, the medium becomes non-Newtonian as a cycle progressed. Mixing within the bioreactor is integral to efficient heat and mass transfer during the production phases, which places additional constraints on the suitable agitation mechanism and theology of the bioreactor medium. Other key differences between chemical reactors and bioreactors are selectivity and rate. In bioreactors, higher selectivity that is, the measure of the system’s capability for producing the preferred product (over other outcomes) is of primary importance. In fact, selectivity is especially important in the production of relatively complex molecules such as antibiotics, steroids, vitamins, proteins and certain sugars and organic acids. Frequently, the activity and desired selectivity occur in a substantially smaller range of conditions than are present in conventional chemical reactors. Further, deactivation of the biomass often poses more severe consequences than a chemical upset. Rate is of secondary importance. For many biological systems, an incubation period is needed to prepare a culture used to inoculate the bioreactor with the producing microbes or their precursors. Although a bioreaction can be brief, in systems where organism or biomass growth is necessary, the bioreaction can take 10–20 d for completion of the batch. Further, the bioreactor should not be regarded as an isolated unit, but as part of an integrated unit operation with both upstream (preparation) and downstream (recovery) unit operations[13].
Figure (2.3): Installation of a batch, 765-bbl beer fermenter made of stainless steel.

(source: John A. Williams, 2002)

2.5 Membrane Technology

Membranes can be defined as semi permeable barriers that separate two phases and restrict the transport of various substances in a specific way. The primordial function of a membrane is to act as a selective barrier, allowing the passage of certain components and the retention of others from a determined mixture, implying the concentration of one or more components both in the permeate and in the retentate. Its selectivity is related to the dimensions of the molecule or particle of interest for separation and the pore size, as also the solute diffusivity in the matrix and the associated electric charges. The separation performance of a membrane is influenced by its chemical composition, temperature, pressure, feed flow and interactions between components in the feed flow and the membrane surface [5].

A combination of conventional electro dialysis and membranes with different pore sizes, used in processes such as: microfiltration, ultrafiltration and nanofiltration. This continuous electrophoresis with porous membranes (CEPM) can be defined as an electrochemical process for the separation of charged organic molecules. The separation driving force of this process is based on the direct application of an electric field. Under the effect of an electric current, the ions are transported from one solution to another through one or more semi permeable porous membranes [5].
2.6 Type of Membranes

2.6.1 Polymeric Membranes

Polymers provide a range of characteristics desirable for membrane separations, including ease of process ability, low cost, and good mechanical stability, making polymeric membranes one of the most common types of membranes. The mechanism of permeation in polymeric films can be described by the sorption diffusion model, in which a penetrant is sorbed into the dense film from a higher activity upstream, diffuses through the film driven by a chemical potential gradient, and is then desorbed on the lower activity downstream [7].

2.6.2 Inorganic Membranes

Inorganic membranes, such as those composed purely of molecular sieving zeolites, alumina, carbon, or silica (among many others), typically have higher thermal and chemical stabilities, making them useful under conditions which polymeric membranes will fall short. Additionally, inorganic membranes can greatly outperform polymeric membranes due to the separation mechanism being dominated by molecular sieving. Although this allows for very high selectivity's and permeability's, inorganic membranes tend to have poor process ability and are just now finding applications in some gas phase separations [7].

2.6.3 Concept of Mixed Matrix Membranes

In attempts to overcome the limits imposed by polymeric and inorganic membranes, new types of membranes, mixed matrix membranes, have recently been introduced. These so called mixed matrix membranes (MMM) are comprised of a continuous polymer phase, either glassy or rubbery, with uniformly distributed fillers that will ideally improve membrane performance beyond the trade-off curve. The presence of the selective filler creates a highly impaired path for the unfavored molecule, decreasing the flux of that component [7].

The permeability of the desired component is usually enhanced, or at least unimpaired, by the presence of the fillers, and thus the membrane’s overall selectivity is generally improved. Material selection for both polymer and filler is a key aspect in the development of successful mixed matrix membranes. While there are three main types of MMMs, solid polymer, liquid polymer, and solid liquid polymer, the first of the three will henceforth be the topic of primary focus [7].
2.7 Membrane Material

Normally, membrane material is manufactured from a synthetic polymer, although other forms, including ceramic and metallic “membranes,” may be available. Almost all membranes manufactured for drinking water are made of polymeric material, since they are significantly less expensive than membranes constructed of other materials. Membranes constructed of polymers that react with oxidants used in drinking water treatment should not be used with chlorinated feed water. Mechanical strength is another consideration, since a membrane with greater strength can withstand larger trans-membrane pressure (TMP) levels, allowing for greater operational flexibility and the use of higher pressures. Membranes with bidirectional strength may allow cleaning operations or integrity testing to be performed from either feed or filtrate side of the membrane. Membranes with a particular surface charge may remove particulate or microbial contaminants of the opposite charge due to electrostatic attraction. Membranes can also be hydrophilic (water attracting) or hydrophobic (water repelling). These terms describe how easily membranes can be wetted, as well as its ability to resist fouling to some degree [8].

2.8 Membrane Filtration and Application

A membrane is a thin layer of semi-permeable material that separates substances when a driving force is applied across the membrane. Membrane processes are increasingly used for removal of bacteria, microorganisms, particulates, and natural organic material, which can impart color, tastes, and odors to water and react with disinfectants to form disinfection by products. As advancements are made in membrane production and module design, capital and operating costs continue to decline. The membrane processes discussed here are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and pervaporation (PV) [8].

2.9 Microfiltration Membrane

Microfiltration refers to filtration processes that use porous membranes to separate suspended particles with diameters between 0.1 and 10µm. Thus, microfiltration membranes fall between ultrafiltration membranes and conventional filters. Like ultrafiltration, microfiltration has its modern origins in the development of collodion (nitrocellulose) membranes in the 1920s and 1930s. In 1926 Membrane filter was founded and began to produce collodion microfiltration membranes commercially.
The market was very small, but by the 1940s other companies, including Sartorius and Schleicher and Schuell, were producing similar membrane filters. The first large-scale application of microfiltration membranes was to culture microorganisms in drinking water; this remains a significant application. The test was developed in Germany during World War II, as a rapid method to monitor the water supply for contamination. The existing test required water samples to be cultured for at least 96 h. Mueller and others at Hamburg University devised a method in which a liter of water was filtered through a Sartorius microfiltration membrane. Any bacteria in the water were captured by the filter, and the membrane was then placed on a pad of gelled nutrient solution for 24 h. The nutrients diffused to the trapped bacteria on the membrane surface, allowing them to grow into colonies large enough to be easily counted under a microscope. After the war there was no US supplier of these membranes, so in 1947 the US Army sponsored a program by Goetz at Caltech to duplicate the Sartorius technology. The membranes developed there were made from a blend of cellulose acetate and nitrocellulose, and were formed by controlled precipitation with water from the vapor phase. This technology was passed to the Lowell Chemical Company, which in 1954 became the Millipore Corporation, producing the Goetz membranes on a commercial scale. Over the next 40 years Millipore became the largest microfiltration company. Membranes made from a number of non cellulosic materials, including poly(vinylidene fluoride), polyamides, poly olefins, and poly(tetra fluoro ethylene), have been developed over the last 40 years by Millipore and others. Nonetheless, the cellulose acetate/cellulose nitrate blend membrane remains a widely used micro filter. Until the mid-1960s, the use of microfiltration membranes was confined to laboratory or to very small scale industrial applications. The introduction of pleated membrane cartridges by Gelman in the 1970s was an important step forward and made possible the use of microfiltration membranes in large scale industrial applications. In the 1960s and 1970s, microfiltration became important in biological and pharmaceutical manufacturing, as did microfiltration of air and water in the production of microelectronics in the 1980s. The production of low cost, single use, disposable cartridges for pharmaceutical and electronics processes now represents a major part of the microfiltration industry. In most applications of microfiltration in these industries, trace amounts of particles are removed from already very clean solutions. The most widely used process design, is dead-end or in line filtration, in which the entire fluid flow is forced through the membrane under pressure. As particles accumulate on the membrane surface or in its interior, the pressure required to
maintain the required flow increases, until at some point the membrane must be replaced. In the 1970s, an alternative process design known as cross flow filtration, began to be used. In cross-flow systems, the feed solution is circulated across the surface of the filter, producing two streams: a clean particle free permeate and a concentrated retentate containing the particles. The equipment required for cross-flow filtration is more complex, but the membrane lifetime is longer than with in-line filtration. The commercial availability of ceramic tubular cross-flow filters from Membralox (now a division of US Filter), starting in the mid-1980s, has increased the application of cross-flow filtration, particularly for solutions with high particle concentrations. Streams containing less than 0.1% solids are almost always treated with in-line filters; streams containing 0.5% solids are almost always treated with cross-flow filters. Between these two limits, both in-line and cross-flow systems can be used, depending on the particular characteristics of the application. In the last few years, a third type of microfiltration operating system called semi-dead-end filtration has emerged. In these systems, the membrane unit is operated as a dead-end filter until the pressure required to maintain a useful flow across the filter reaches its maximum level. At this point, the filter is operated in cross-flow mode, while concurrently back flushing with air or permeate solution. After a short period of backflushing in cross flow mode to remove material deposited on the membrane, the system is switched back to dead-end operation. This procedure is particularly applicable in microfiltration units used as final bacterial and virus filters for municipal water treatment plants. The feed water has a very low loading of material to be removed, so in-line operation can be used for a prolonged time before back flushing and cross-flow to remove the deposited solids is needed. Beginning in 1990–1993, the first microfiltration/ultrafiltration systems began to be installed to treat municipal drinking water obtained from surface water [6].

Some of the important milestones in the development of microfiltration are charted in Figure (2.4).
2.9.1 Applications of Microfiltration Membrane

Bioengineering, food industry, wastewater treatment. Examples:

2. Juice, wine or beer clarification.
3. Fermentation product separation.
5. Recovering of precipitated metals [9].

2.10 Ultrafiltration Membrane

Ultrafiltration uses a finely porous membrane to separate water and micro solutes from macromolecules and colloids. The average pore diameter of the membrane is in the 10–1000 Å range. The first synthetic ultrafiltration membranes were prepared by Bechhold from collodion (nitro cellulose). Bechhold was probably the first to measure membrane bubble points, and he also coined the term ‘ultrafilter’. Other important early workers were Zsigmondy and Bachmann, Ferry and Elford. By the mid 1920s, collodion ultrafiltration and microfiltration membranes were
commercially available for laboratory use. Although collodion membranes were widely used in laboratory studies, no industrial applications existed until the 1960s. The crucial breakthrough was the development of the anisotropic cellulose acetate membrane by Loeb and Sourirajan in 1963. Their goal was to produce high flux reverse osmosis membranes, but others, particularly Michaels at Amicon, realized the general applicability of the technique. Michaels and his coworkers produced ultrafiltration membranes from cellulose acetate and many other polymers including polyacrylonitrile copolymers, aromatic polyamides, polysulfone and poly(vinylidene fluoride). These materials are still widely used to fabricate ultrafiltration membranes. In 1969, Abcor (now a division of Koch Industries) installed the first commercially successful industrial ultrafiltration system equipped with tubular membrane modules to recover electrocoat paint from automobile paint shop rinse water. The economics were compelling, and within a few years many similar systems were installed. Shortly thereafter (1970), the first cheese whey ultrafiltration system was installed. Within a decade, 100 similar systems had been sold worldwide. These early systems used tubular or plate and frame modules, which were relatively expensive, but lower cost designs were gradually introduced. Hollow fiber (capillary) modules were first sold by Romicon in 1973, and spiral wound modules, adapted to ultrafiltration applications by Abcor, became a commercial item by 1979–1980. Over the last 20 years, the ultrafiltration industry has grown steadily. The principal problem inhibiting wider application of the technology is membrane fouling. The problem is controlled, but not eliminated, by module and system design and by regular membrane cleaning protocols. Development of membranes with surface properties designed to minimize fouling has also helped. Recently, several companies have developed ceramic-based ultrafiltration membranes. Although much more expensive than their polymeric equivalents, these have found a place in applications that require resistance to high temperatures or require regular cleaning with harsh solutions to control membrane fouling. Some of the milestones in the development of ultrafiltration membranes are charted in Figure (2.5) [6].
2.10.1 Applications of Ultrafiltration Membrane

1. Food industry, wastewater treatment.
2. Also potentially useful paper pulping or textile industry.
4. Treatment of cutting-oil emulsion.
5. Treatment of black-liquor from paper pulping.
6. Protein recovery from blood plasma.
7. Egg white concentration.
8. Serum recovery from milk [9].

2.11 Nanofiltration Membrane

Nanofiltration membranes have a nominal pore size of approximately 0.001 microns. Pushing water through these smaller membrane pores requires a higher operation pressure than either MF or UF. Operating pressures are usually near 600 kPa (90psi) and can be as high as 1,000 kPa (150psi). These systems can remove virtually all cysts, bacteria, viruses, and humic materials. Because NF membranes also remove alkalinity, the product water can be corrosive, and measures, such as blending raw water and product water or adding alkalinity, may be needed to reduce corrosivity. NF also removes hardness from water, which accounts for NF membranes sometimes being called “softening membranes.” Hard water treated by NF will need
pretreatment to avoid precipitation of hardness ions on the membrane. However, more energy is required for NF than MF or UF [8].

2.12 Reverse Osmosis Membrane

Reverse osmosis is a process for desalting water using membranes that are permeable to water but essentially impermeable to salt. Pressurized water containing dissolved salts contacts the feed side of the membrane; water depleted of salt is withdrawn as a low pressure permeate. The ability of membranes to separate small solutes from water has been known for a very long time. Pfeffer, Traube and others studied osmotic phenomena with ceramic membranes as early as the 1850s. In 1931 the process was patented as a method of desalting water, and the term reverse osmosis was coined. Modern interest dates from the work of Reid and Breton, who in 1959 showed that cellulose acetate films could perform this type of separation. Their films were 5–20 µm thick so fluxes were very low but, by pressurizing the feed salt solution to 1000 psi, they obtained salt removals of better than 98% in the permeate water. The breakthrough discovery that made reverse osmosis a practical process was the development of the Loeb Sourirajan anisotropic cellulose acetate membrane. This membrane had 10 times the flux of the best membrane of Reid and Breton and equivalent rejections. With these membranes, water desalination by reverse osmosis became a potentially practical process, and within a few years small demonstration plants were installed. The first membrane modules were tubular or plate and frame systems, but West more land, Bray, and others at the San Diego Laboratories of Gulf General Atomics soon developed practical spiral wound modules. Later, Du Pont, building on the earlier work of Dow, introduced polyaramide hollow fine fiber reverse osmosis modules under the name Permasep Anisotropic cellulose acetate membranes were the industry standard through the 1960s to the mid-1970s, until Cadotte, then at North Star Research, developed the interfacial polymerization method of producing composite membranes. Interfacial composite membranes had extremely high salt rejections, combined with good water fluxes. Fluid Systems introduced the first commercial interfacial composite membrane in 1975. The construction of a large seawater desalination plant at Jiddah, Saudi Arabia using these membranes was a milestone in reverse osmosis development. Later, at Film Tec, Cadotte developed a fully aromatic interfacial composite membrane based on the reaction of phenylene diamine and trimesoyl chloride. This membrane has become the new industry standard. The most recent development, beginning in the
mid-1980s, was the introduction of low-pressure nanofiltration membranes by all of the major reverse osmosis companies. These membranes are used to separate trace amounts of salts and other dissolved solutes from already good-quality water to produce ultra-pure water for the electronics industry. An important recent advance by Grace Davison working with Mobil Oil, now ExxonMobil, is the development of a reverse osmosis (hyper filtration) process to separate a solution of methyl ethyl ketone and lube oil. A plant installed at a Beaumont, Texas, refinery in 1998 was the first large-scale use of pressure-driven membranes to separate organic solvent mixtures. Currently, approximately one billion gal/day of water are desalted by reverse osmosis. Half of this capacity is installed in the United States, Europe, and Japan, principally to produce ultrapure industrial water. The remainder is installed in the Middle East and other desert regions to produce municipal drinking water from brackish groundwater or seawater [6].

**Figure (2.6) : Milestones in the development of reverse osmosis.**

2.12.1 Applications of Reverse Osmosis Membrane

1. Organic Solvent Separation.
2. Seawater Desalination.
5. Wastewater Treatment [6].

2.13 Pervaporation Membrane(PV)

Pervaporation is a membrane separation technique in which the phase state on one side of the membrane is different from the other side. The feed is in liquid phase and vaporization occurs as the permeating species passes through the membrane. The basic concept of pervaporation is shown in Figure 2.7 [1].

![Basic Concept of Pervaporation](source: M. M. Meintjes,2011)

Figure (2.7): Basic Concept of Pervaporation

2.13.1 Pervaporation in History

The liquid feed at a higher pressure comes into contact with one side of the membrane and the permeate product is removed as a low pressure vapor from the other side. The driving force that facilitates pervaporation is the chemical potential (difference of partial pressure or activity) between the feed and the permeate side and separation is achieved by different mass transfer rates of the components through the membrane [6].

The pervaporation process to separate liquid mixtures is shown schematically in Figure (2.8). A feed liquid mixture contacts one side of a membrane; the permeate is
removed as a vapor from the other side. Transport through the membrane is induced by the vapor pressure difference between the feed solution and the permeate vapor. This vapor pressure difference can be maintained in several ways. In the laboratory, a vacuum pump is usually used to draw a vacuum on the permeate side of the system. Industrially, the permeate vacuum is most economically generated by cooling the permeate vapor, causing it to condense; condensation spontaneously creates a partial vacuum. The origins of pervaporation can be traced to the nineteenth century, but the word itself was coined by Kober in 1917. The process was first studied in a systematic fashion by Binning and coworkers at American Oil in the 1950s. Binning was interested in applying the process to the separation of organic mixtures. Although this work was pursued at the laboratory and bench scales for a number of years and several patents were obtained, the process was not commercialized. Membrane technology at that time could not produce the high performance membranes and modules required for a commercially competitive process. The process was picked up in the 1970s at Monsanto by Eli Perry and others. More than a dozen patents assigned to Monsanto issued from 1973 to 1980 cover a wide variety of pervaporation applications, but none of this work led to a commercial process. Academic research on pervaporation was also carried out by Aptel, Neel and others at the University of Toulouse. By the 1980s, advances in membrane technology made it possible to prepare economically viable pervaporation systems. Pervaporation systems are now commercially available for two applications. The first and most important is the removal of water from concentrated alcohol solutions. GFT, now owned by Sulzer, the leader in this field, installed the first pilot plant in 1982. The ethanol feed to the membrane contains about 10% water. The pervaporation process removes the water as the permeate, producing a residue of pure ethanol containing less than 1% water. All the problems of azeotropic distillation are avoided. More than 100 plants have since been installed by Sulzer (GFT) and its licensees for this application [6].

The current largest plant was installed at Bethenville, France in 1988; this unit contains 2400 m² of membranes and processes 5000 kg/h of ethanol. The second commercial application of pervaporation is the removal of small amounts of volatile organic compounds (VOCs) from contaminated water. This technology was developed by Membrane Technology and Research; the first commercial plant was sold in 1996. Both of the current commercial pervaporation processes concentrate on the separation of VOCs from contaminated water. This separation is relatively easy,
because organic solvents and water have very different polarities and exhibit distinct membrane permeation properties. No commercial pervaporation systems have yet been developed for the separation of organic/organic mixtures. However, current membrane technology makes pervaporation for these applications possible, and the process is being actively developed by a number of companies. The first pilot-plant results for an organic–organic application, the separation of methanol from methyl tert butyl ether/isobutene mixtures, was reported by Separex in 1988. This is a particularly favorable application because available cellulose acetate membranes achieve a good separation. More recently, Exxon, now ExxonMobil, started a pervaporation pilot plant for the separation of aromatic/aliphatic mixtures, a separation problem in refineries; poly-imide/polyurethane block copolymer membranes were used. A time line illustrating some of the key milestones in the development of pervaporation is shown in Figure 2.8 [6].

Figure (2.8) : Milestones in the development of pervaporation.

2.13.2 Membrane Modules

Pervaporation applications often involve hot feed solutions containing organic solvents. Such solutions can degrade the seals and plastic components of membrane modules. As a result, the first generation commercial pervaporation modules used a stainless steel plate and frame design. Recently attempts have been made to switch to lower cost module designs. Texaco, Membrane Technology and Research (MTR) have all used spiral wound modules for pervaporation, and Zenon developed hollow fiber modules. One particular issue affecting pervaporation module design is that the permeate side of the membrane often operates at a vacuum of less than 100 torr. The pressure drop required to draw the permeate vapor to the permeate condenser may then be a significant fraction of the permeate pressure. Efficient pervaporation modules must have short, porous permeate channels to minimize this permeate pressure drop[6].

2.14 Characteristics of Pervaporation Membrane

2.14.1 Swelling of The Membrane

One characteristic of pervaporation using polymeric membranes is that the membranes tend to swell. The feed liquid in contact with the membrane dissolves into it, which causes the membrane swelling. This swelling alters the membrane properties and leads to reduce permeability and lower selectivity. The swelling ratio of a membrane is used to describe the swelling of a membrane. It can be measured by bringing a membrane to equilibrium with a liquid by immersing the membrane in the liquid. The swelling ratio can be defined as the amount of solution absorbed by the membrane when equilibrium is reached ($W_\infty - W_0$) compared to the dry mass of the membrane ($W_0$). The degree of swelling (swelling ratio) can be calculated using Equation (2.3) [1].

$$\text{Swelling ratio}(M_\infty) = \frac{W_\infty - W_0}{W_0} \quad \text{..............(2.3)}$$

2.14.2 Coupling Effect

The partial flux of a component in a binary system can change due to the coupling of fluxes. This means that the transport of each permeate is not independent from each other and a change in flux of the component may be observed due to its own
movement and the movement of other components through the membrane. This phenomenon is difficult to measure but indirect information can be obtained through flux and sorption measurements [1].

2.14.3 Fouling of Membrane

Membrane fouling is caused by undesired interactions between components with the membrane material, which result in the coating or blocking of the membrane surface. The consequence of fouling is a reduction in membrane flux due to an additional barrier layer that forms or a decrease in the overall selectivity due to the formation of a second non-selective resistance on the membrane [1].

2.14.4 Concentration Polarization

Concentration polarization refers to a difference between the membrane boundary layer composition and the bulk feed composition. Membrane separation leads to an accumulation of the retained species and a depletion of the permeating species in the membrane boundary layer. This leads to a decrease in the overall efficiency of separation because of a decrease in the driving force of the preferential permeating species across the membrane and an increase in the driving force of the less permeable species. Concentration polarization can be minimized by maximizing mixing at the membrane surface. The effect of concentration polarization is often assumed insignificant for pervaporation processes, as the permeating fluxes are usually very small [1].

2.14.5 Mass transport through a Membrane

There are two extreme approaches to describe mass transport in pervaporation, namely the pore-flow model, and the solution diffusion model. According to Wijmans and Baker, the pore flow model describes separation due to pressure-driven convection flow through tiny pores. Separation is achieved because one of the components in the feed is excluded from some of the pores in the membrane through which other components move. In the second model, the solution-diffusion model, the feed components dissolve into the membrane material and then diffuse through the membrane down a concentration gradient. Separation is achieved due to the different amounts of each permeate that dissolve into the membrane and the difference in the rate at which these diffuse through the membrane. Currently the
solution-diffusion model is accepted by most researchers to describe pervaporation [1].

**2.15 Design and Modeling Used in Pervaporation Membrane:**

The flux of a component through a pervaporation membrane can be expressed in terms of the partial vapor pressures on either side of the membrane, $p_{i_o}$ and $p_{i_l}$, by the equation

$$J_i = \frac{P_i^G}{L} (P_{i_o} - P_{i_l}) \ldots \ldots \ldots (2.4)$$

Where $J_i$ is the flux, $L$ is the membrane thickness and $P_i^G$ is the gas separation permeability coefficient. A similar equation can be written for component $j$. The separation achieved by a pervaporation membrane is proportional to the fluxes $J_i$ and $J_j$ through the membrane [6].

Equation (2.4) is the preferred method of describing membrane performance because it separates the two contributions to the membrane flux: the membrane contribution, $P_i^G/L$ and the driving force contribution, $(p_{i_o} - p_{i_l})$. Normalizing membrane performance to a membrane permeability allows results obtained under different operating conditions to be compared with the effect of the operating condition removed. To calculate the membrane permeability’s using Equation (2.4), it is necessary to know the partial vapor pressure of the components on both sides of the membrane. The partial pressures on the permeate side of the membrane, $p_{i_o}$ and $p_{j_l}$, are easily obtained from the total permeate pressure and the permeate composition. However, the partial vapor pressures of components $i$ and $j$ in the feed liquid are less accessible. In the past, such data for common, simple mixtures would have to be found in published tables or calculated from an appropriate equation of state. Now, commercial computer process simulation programs calculate partial pressures automatically for even complex mixtures with reasonable reliability. This makes determination of the feed liquid partial pressures a trivial exercise. Having said this, the bulk of the pervaporation literature continues to report membrane performance in terms of the total flux through the membrane and a separation factor, $\beta_{pervap}$, defined for a two-component fluid as the ratio of the two components on the permeate side of the membrane divided by the ratio of the two components on the feed side of the membrane. The term $\beta_{pervap}$ can be written in several ways [6].
\[ \beta_{\text{pervap}} = \frac{c_i/c_j}{c_{i0}/c_{j0}} = \frac{n_i/n_j}{n_{i0}/n_{j0}} = \frac{p_i/p_j}{p_{i0}/p_{j0}} \quad \text{(2.5)} \]

Where \( c_i \) and \( c_j \) are the concentrations, \( n_i \) and \( n_j \) are the mole fractions, and \( p_i \) and \( p_j \) are the vapor pressures of the two components \( i \) and \( j \). The separation factor, \( \beta_{\text{pervap}} \), contains contributions from the intrinsic permeation properties of the membrane, the composition and temperature of the feed liquid, and the permeate pressure of the membrane. The contributions of these factors are best understood if the pervaporation process is divided into two steps, as shown in Figure (2.9). The first step is evaporation of the feed liquid to form a saturated vapor in contact with the membrane; the second step is diffusion of this vapor through the membrane to the low-pressure permeate side. This two-step description is only a conceptual representation; in pervaporation no vapor phase actually contacts the membrane surface. Nonetheless, the representation of the process shown in Figure (2.9) is thermodynamically completely equivalent to the actual pervaporation process. In the process illustrated in Figure(2.9), the first step is evaporation from the feed liquid to form a saturated vapor phase in equilibrium with the liquid. This evaporation step produces a separation because of the different volatilities of the components of the feed liquid. The separation can be defined as \( \beta_{\text{evap}} \), the ratio of the component concentrations in the feed vapor to their concentrations in the feed liquid[6]:

\[ \beta_{\text{evap}} = \frac{p_{i0}/p_{j0}}{n_{i0}/n_{j0}} \quad \text{(2.6)} \]

The second step in the process is permeation of components \( i \) and \( j \) through the membrane; this step is equivalent to conventional gas separation. The driving force for permeation is the difference in the vapor pressures of the components in the feed and permeate vapors. The separation achieved in this step, \( \beta_{\text{mem}} \), can be defined as the ratio of the components in the permeate vapor to the ratio of the components in the feed vapor

\[ \beta_{\text{mem}} = \frac{p_i/p_j}{p_{i0}/p_{j0}} \quad \text{(2.7)} \]

Equation (2.7) shows that the separation achieved in pervaporation is equal to the product of the separation achieved by evaporation of the liquid and the separation achieved by selective permeation through the membrane.

\[ \beta_{\text{pervap}} = \beta_{\text{evap}} \cdot \beta_{\text{mem}} \quad \text{(2.8)} \]
The first application of pervaporation was the removal of water from an azeotropic mixture of water and ethanol. By definition, the evaporative separation term $\beta_{evap}$ for an azeotropic mixture is 1 because, at the azeotropic concentration, the vapor and the liquid phases have the same composition. Thus, the 200- to 500-fold separation achieved by pervaporation membranes in ethanol dehydration is due entirely to the selectivity of the membrane, which is much more permeable to water than to ethanol.

This ability to achieve a large separation where distillation fails is why pervaporation is also being considered for the separation of aromatic/aliphatic mixtures in oil refinery applications. The evaporation separation term in these closely boiling mixtures is again close to 1, but a substantial separation is achieved due to the greater permeability of the membrane to the aromatic components. The $\beta_{pervap}$ term in Equation (2.5) and Equation (2.8) can be derived in terms of $\beta_{evap}$, membrane permeabilities, and membrane operating conditions using the standard solution-diffusion model. The membrane fluxes can be written as[6]:

$$J_i = \frac{P_i^G(P_i - P_i^o)}{l} \quad \ldots \ldots \quad (2.9)$$

$$J_j = \frac{P_j^G(P_j - P_j^o)}{l} \quad \ldots \ldots \quad (2.10)$$

Where $J$ is the permeation flux through the membrane, $P^G$ is the permeability coefficient of the vapors $i$ and $j$, and $L$ is the thickness of the separating layer of the membrane. Dividing Equation (2.9) by Equation (2.10) gives

$$\frac{J_i}{J_j} = \frac{P_i^G(P_i^o - P_i)}{P_j^G(P_j^o - P_j)} \quad \ldots \ldots \quad (2.11)$$

The fluxes $J_i$ and $J_j$ in Equation (2.11) are weight fluxes (g/cm²·s); similarly the permeabilities $P_i^G$ and $P_j^G$ are weight-based (g·cm²·s·cmHg). Equation (2.11) is more conveniently written in molar terms as

$$\frac{j_i}{j_j} = \frac{P_i^G(P_i^o - P_i)}{P_j^G(P_j^o - P_j)} \quad \ldots \ldots \quad (2.12)$$

Where $j_i$ and $j_j$ are molar fluxes with unit mols/cm²·s·STP/cm²·s and $P_i$ and $P_j$ are molar permeabilities with units mol·cm/cm²·s·unit pressure or more conventionally cm³(STP)·cm/cm²·s·cmHg. The ratio of the molar membrane
permeability coefficients $P_i^G/P_j^G$ is the conventional gas membrane selectivity, $\alpha_{\text{mem}}$. The ratio of the molar fluxes is also the same as the ratio of the permeate partial pressures[6]

$$\frac{j_i}{j_j} = \frac{P_i}{P_j} \ldots \ldots(2.13)$$

Combining Equations (2.7), (2.8), (2.12) and (2.13) yields

$$\beta_{\text{pervap}} = \frac{\beta_{\text{evap}}\alpha_{\text{mem}}(P_i - P_o)}{(P_j - P_j)(P_i/P_j)} \ldots \ldots(2.14)$$

Equation (2.14) identifies the three factors that determine the performance of a pervaporation system. The first factor, $\beta_{\text{evap}}$, is the vapor–liquid equilibrium, determined mainly by the feed liquid composition and temperature; the second is the membrane selectivity, $\alpha_{\text{mem}}$, an intrinsic permeability property of the membrane material; and the third includes the feed and permeate vapor pressures, reflecting the effect of operating parameters on membrane performance. As in gas separation, the separation achieved by pervaporation is determined both by the membrane selectivity and by the membrane pressure ratio. The interaction of these two factors is expressed in Equation (2.14). Also, as in gas separation, there are two limiting cases in which one of the two factors dominates the separation achieved. The first limiting case is when the membrane selectivity is very large compared to the vapor pressure ratio between the feed liquid and the permeate vapor[6]:

$$\alpha_{\text{mem}} \gg \frac{P_o}{P_i} \ldots \ldots(2.15)$$

This means that for a membrane with infinite selectivity for component $i$, the permeate vapor pressure of component $i$ will equal the feed partial vapor pressure of $i$. That is,

$$P_i = P_i \ldots \ldots(2.16)$$

Equation (2.16) combined with Equation (2.7) gives

$$\beta_{\text{mem}} = \frac{P_j}{P_j} \ldots \ldots(2.17)$$

which, combined with Equation (2.8), leads to the limiting case
\[ \beta_{pervap} = \beta_{evap} \cdot \frac{P_{jo}}{P_{jl}} \quad \text{When } \alpha_{mem} \gg \frac{P_o}{P_l} \quad \text{(2.18)} \]

Similarly, in the case of a very large membrane selectivity in favor of component j

\[ \beta_{pervap} = \beta_{evap} \frac{P_{i_o}}{P_{i_l}} \quad \text{........(2.19)} \]

For the special case in which component i is the minor component in the feed liquid, \( p_{jo} \) approaches \( p_o \), \( p_{jl} \) approaches \( p \), and Equation (2.18) reverts to

\[ \beta_{pervap} = \beta_{evap} \frac{P_o}{P_l} \quad \text{........(2.20)} \]

Where \( p_o/p_l \) is the feed-to-permeate ratio of the total vapor pressures. The second limiting case occurs when the vapor pressure ratio is very large compared to the membrane selectivity. This means that the permeate partial pressure is smaller than the feed partial vapor pressures, and \( p_i \) and \( p_j \rightarrow 0 \). Equation (2.14) then becomes[6]:

\[ \beta_{pervap} = \beta_{evap} \alpha_{mem} \quad \text{When } \alpha_{mem} \ll \frac{P_o}{P_l} \quad \text{........(2.21)} \]

Figure (2.9): The Pervaporation Process.

2.16 Simulation of the Pervaporation System:

Engineers are constantly being called upon to predict the behavior of systems. Chemical engineers in particular must be able to predict the actions of chemical species, a very difficult task. As chemical engineering students, when confronted with a large chemical system, you might ask, "Where do I even begin? Mass balances? Energy balances? Thermodynamic properties? Reaction Kinetics?" Over the past few years as a student you've learned about each of these crucial topics separately, however, "real world" situations will require an engineer to incorporate all of these areas. This is where the idea of a process model is helpful. A process model can be defined as an engineering system's "blue print." The process model is a complete layout of the engineering system including the following:

2.16.1 Flow Sheet

The process model flow sheet maps out the entire system. The flow sheet shows one or more inlet streams entering into the system's first unit operation (i.e., heat exchanger, compressor, pervaporation membrane, etc.) and continues through the process, illustrating all intermediate unit operations and the interconnecting streams. The flow sheet also indicates all product streams. Each stream and unit operation is labeled and identified.

2.16.2 Chemical Components

The process model specifies all chemical components of the system from the necessary reactants and products, to steam and cooling water.

2.16.3 Operating Conditions

All unit operations in the process model are kept under particular operating conditions (i.e., temperature, pressure, size). These are usually at the discretion of the engineer, for it is the operating conditions of the process that effect the outcome of the system.

2.17 Effect of Process Conditions on Pervaporation

It is important to understand the key aspects of a pervaporation process when designing or operating a pervaporation system. Factors that influence the
performance of a membrane during pervaporation, apart from the mass transfer through the membrane, are the pervaporation operating parameters. These include the composition of the feed, the temperature of the feed, and the permeate pressure. Understanding the effect of these factors on the membrane will ensure proper operating conditions during the separation process. The influence of the operating parameters on the flux and selectivity of the membrane is discussed in this section[1].

2.17.1 Feed Composition

The feed composition affects the sorption of liquid into the membrane, membrane swelling, and diffusion of components through the membrane and therefore the flux and selectivity of the membrane. Permeation takes place when the permeating species is absorbed into and diffused through the membrane. As the feed concentration of the permeating species increases, the quantity of this component absorbed by the membrane also increases (as the affinity by the membrane for a certain component is more than for the other components) and the membrane takes on a swollen state. It was found by various researchers that due to the membrane swelling the total flux as well as the specific flux of each component increases with an increase in feed concentration of the preferential permeating component. The selectivity, however, decreases as the specific flux of the other species in the mixture increases more than the permeating species. The reduction in selectivity can be ascribed to enhanced diffusivity of the other components through the membrane as the swollen membrane increases membrane free volume [1].

2.17.2 Feed Temperature

Temperature influences the transport in a membrane in two ways, i.e. firstly by modifying the sorption-diffusion step inside the membrane and secondly by changing the activity driving force across the membrane. Flux is strongly dependent on the feed temperature and the flux usually increases with an increase in temperature. This is due to an increase in mobility of the permeating molecules and the effect on permeate fluxes because of the strong influence on the vapor pressures of the feed. The permeation through a membrane is controlled by the amount of sorption into the membrane as well as the diffusion through the membrane. The amount of a component absorbed into a membrane decreases if the temperature increases, but the diffusion rate increases. This means that the flux may increase or decrease if the
temperature is increased, depending on the importance of the absorption or diffusion as rate controlling process. The preferential species usually has a higher affinity for the membrane material than the other components and if the temperature is increased, the permeability of this species will not increase as much because the decrease in absorption will have a larger influence than with the less permeable components. The diffusity of all the components will increase, however, thereby increasing the flux of the preferential permeating species as well as the non-preferential permeating species. The net effect of an increase in feed temperature will thus most likely be a decrease in membrane selectivity. Pervaporation involves a phase change from liquid to vapor, as previously discussed. This vaporization of a portion of the liquid feed requires heat of vaporization, which is withdrawn from the liquid feed stream. The result is a temperature loss between the feed entering the membrane module and the retentate leaving the process. If the flux of the membrane is very large, the temperature drop due to the heat loss by vaporization can be significant[1].

2.17.3 Permeate Pressure

The difference between the vapor pressure of the permeating species in the feed and the vapor pressure of the permeate stream is the driving force of the pervaporation process as it is a measure of the chemical potential or activity on the permeate side of the membrane. If the permeate pressure is decreased the driving force of the separation process will increase and thus the permeation rate (total flux) It was observed by Jiraratanaanon. The selectivity also increased if the permeate pressure is decreased. It is not economical to decrease the permeate pressure indefinitely as the energy cost rises sharply with a decrease in pressure. An optimum permeate pressure would be a pressure that maximises the driving force of pervaporation, thereby maximising the flux and selectivity of the membrane, while still being economically viable[1].

2.18 Applications For Pervaporation Membrane

Pervaporation is used in a variety of applications, which include the concentrating, or drying of solvents, purification of solutions, and the separation of mixtures. There are three major commercial applications for pervaporation; removal organics from water, and the separation of anhydrous organic mixtures. Dehydration of organic solvents (hydrophilic pervaporation) is especially useful to produce pure products from feed
streams that contain zoetrope’s, such as ethanol and water or isopropanol and water. Water is the targeted component and permeates through the membrane. Specific applications include breaking of zoetrope’s of binary mixtures and dehydration of multi-component mixtures. The removal of organics from water, also known as hydrophobic pervaporation, can be used to purify water contaminated with organic solvents. The organic compound is the target compound, which preferentially permeates through the membrane. Specific industrial examples include wastewater treatment, the removal of organic traces from ground and drinking water, removal of alcohol from beer and wine, the recovery of aromatics in food technology and separation of compounds from fermentation broths in biotechnology. The separation of organic mixtures is the least developed of the three categories as problems associated with membrane stability is experienced. One of the organic compounds is the target compound and permeates through the membrane. Examples are the separation of ethanol from ethyl-tetra-butyl-ether and the separation of benzene and cyclohexane [1].

2.19 Basic Functions of Membranes

1. Separation e.g. water and ethanol purifications.
2. Discrimination e.g. pH meter, blood glucose meters.
3. Selective Transport e.g. contact lenses.
4. Delivery e.g. control drug delivery [11].

2.20 Driving Forces in Membrane

1. Pressure and Concentration.
2. Partial Pressure.
4. Electric Field.
5. Magnetic Field.
2.21 The Separation Ability of a Synthetic Material Depends on its Physical, Chemical Properties:

1. Pore size and structure.
2. Design.
3. Chemical characteristics.

2.22 Factors Affecting Membrane Performance

1. Nature of the feed.
2. Gas-liquid mixture.
3. Liquid mixture.
4. Solid and liquid mixture.
5. Fouling feed, viscosity, density, etc.
6. Flow Rate.
7. Concentration.
8. Temperature.
9. Driving Force e.g. pressure, concentration, etc.
10. Type of Membrane Process and Material.

2.23 Problems Facing Membrane Performance

1. Concentration Polarization.
2. Fouling.
3. Swelling.
Chapter Three

Material and Method

3.1 Theoretical Background

General materials uses in ethanol production such as:

**Molasses:** Molasses is the liquid residue left after condensing the sap of sugar cane or sugar beets until sugar crystals precipitate. When all the crystals that can be formed have been centrifuged off, the syrup can be as high as 85% dry matter and 90°Brix. It is too viscous to be handled by ordinary mill equipment and is referred to as high Brix molasses. The molasses is shipped in the concentrated high Brix form to reduce freight costs. Upon arrival at a terminal distribution point, it will be diluted down to (in the U.S.) a standard of 79.5°Brix, which is still quite thick, but which is possible to handle in many mills[12].

**Fermentation Medium:** The fermentation medium used was a modification of that described and composed at (g L⁻¹): mud-free, H₂SO₄-Treated Molasses, Urea 1.08, MgSO₄·7H₂O 0.3, H₃PO₄ 0.3, PH5.

**Yeast:** Yeast is an organism belonging to the vegetable family. The yeast itself does not take a direct part in the fermentation process, but it secretes a complex of enzymes that act upon the sugar and convert it to alcohol and carbon dioxide gas. The yeast used in alcoholic fermentation is a special strain bred to be tolerant to variations in pH and resistant to alcohol. In the past, distilleries bred and propagated their own yeast strains. The yeast was kept alive in cultures and grown in batches of ever-increasing size to be used in the fermenters. Keeping yeast alive and growing cultures is a tricky business that requires precise control of temperature, nutrients, and the like. Fortunately, special active dry yeast is available. To use it, you merely add warm water to reactivate it and then add it to the mash in the fermenter. Two pounds is sufficient for 1000 gallons of mash. In a pinch, it is possible to use ordinary baker's yeast from your grocer's shelf. However, this yeast is not bred for alcohol tolerance, and you will probably not get the yields associated with the distiller's yeast. Such as(Saccharomyces cerevisiae).
Bioreactors vs. Chemical Reactors: By definition, a bioreactor is a system in which a biological conversion is affected. Although this definition can apply to any conversion involving enzymes, microorganisms, and animal or plant cells, for the purposes of this article, we will limit the definition. The bioreactors referred to here include only mechanical vessels in which organisms are cultivated in a controlled manner and/or materials are converted or transformed via specific reactions.

3.2 Material Used in This Study:

3.2.1 Visual Studio2010 Software:

Microsoft Visual Studio is an integrated development environment (IDE) from Microsoft. It is used to develop console and graphical user interface applications along with Windows Forms or WPF applications, web sites, web applications, and web services in both native code together with managed code for all platforms supported by Microsoft Windows, Windows Mobile, Windows CE, .NET Framework, .NET Compact Framework and Microsoft Silver light. Visual Studio includes a code editor supporting IntelliSense as well as code refactoring. The integrated debugger works both as a source-level debugger and a machine-level debugger. Other built-in tools include a forms designer for building GUI applications, web designer, class designer, and database schema designer. It accepts plug-ins that enhance the functionality at almost every level—including adding support for source-control systems (like Subversion and Visual SourceSafe) and adding new toolsets like editors and visual designers for domain-specific languages or toolsets for other aspects of the software development lifecycle (like the Team Foundation Server client: Team Explorer). Visual Studio supports different programming languages by means of language services, which allow the code editor and debugger to support (to varying degrees) nearly any programming language, provided a language-specific service exists. Built-in languages include C/C++[5] (via Visual C++), VB.NET (via Visual Basic .NET), C# (via Visual C#), and F# (as of Visual Studio 2010[6]). Support for other languages such as M, Python, and Ruby among others is available via language services installed separately. It also supports XML/XSLT, HTML/XHTML, JavaScript and CSS. Individual language-specific versions of Visual Studio also exist which provide more limited language services to the user: Microsoft Visual Basic, Visual J#, Visual C#, and Visual C++. Microsoft provides "Express" editions of its Visual Studio at no cost. Commercial versions of Visual Studio along with select past versions are available for free to students via Microsoft's Dream Spark program. You can run load
tests locally by using Microsoft Visual Studio 2010 Ultimate and simulate up to 250 users for your load test. If you want to test your application using more than 250 virtual users, you must purchase Visual Studio Load Test Virtual User Pack 2010 licenses. Additionally, if you want to distribute you load tests over multiple machines, you must install test controllers and test agents.

3.2.2 Microfiltration Membrane Used

Microfiltration is loosely defined as a membrane separation process using membranes with a pore size of approximately 0.03 to 10 microns (1 micron = 0.0001 millimeter), a molecular weight cut-off (MWCO) of greater than 1000,000 Daltons and a relatively low feed water operating pressure of approximately 100 to 400 kPa (15 to 60psi) Materials removed by MF include sand, silt, clays, Giardia lamblia and Cryptosporidium cysts, algae, and some bacterial species. MF is not an absolute barrier to viruses. However, when used in combination with disinfection, MF appears to control these microorganisms in water. There is a growing emphasis on limiting the concentrations and number of chemicals that are applied during water treatment. By physically removing the pathogens, membrane filtration can significantly reduce chemical addition, such as chlorination. Another application for the technology is for removal of natural synthetic organic matter to fouling potential. In its normal operation, MF removes little or no organic matter; however, when pretreatment is applied, increased removal of organic material can occur. MF can be used as a pretreatment to RO or NF to reduce fouling potential. Both RO and NF have been traditionally employed to desalt or remove hardness from groundwater [10].

3.2.3 Pervaporation Membrane

Pervaporation is a new membrane technique which is used to separate a liquid mixture by partly vaporizing it through a nonporous permselective membrane. The "feed" mixture is allowed to flow along one side of the membrane and a fraction of it (the "permeate") is evolved in the vapor state from the opposite side, which is kept under vacuum by continuous pumping or is purged with a stream of carrier gas. The permeate is finally collected in the liquid state after condensation on a cooled wall. It is thus enriched in the more rapidly permeating ("faster") component of the feed mixture whereas the retentate is depleted in this component; the "retentate" is the fraction of the feed that does not permeate through the membrane[1].
3.2.4 Dephlegmator (Fractional Condenser):

A dephlegmator is a device arranged for the partial condensation of a multicomponent vapor stream. The vapor stream flows vertically upwards and the condensate (condensed vapor) runs back down under the influence of gravity. The vapor stream and condensate thus move counter currently and are in direct contact with each other. In addition to heat transfer between the vapor stream and cooling medium, mass is transferred between the rising vapor and falling condensate. Vapor leaving the device has become concentrated in the more volatile components, while the condensate is richer in the less volatile components. In the industrial rather than laboratory contexts, many writers use the word 'dephlegmator,' only if the device being described is a main unit in the process plant. If an overhead condenser is used in continuous countercurrent distillation in an industrial setting, it is often designed to receive a multicomponent vapor which flows vertically upwards and is condensed only partially. The condensate forms a reflux of liquid to the distillation column and the remaining vapor has become enriched in the more volatile components. However, the overhead condenser is not a key process unit, but is merely part of a distillation column. Many writers do not, therefore, consider the rather uncommon word 'dephlegmator' appropriate to this subordinate and commonly-encountered device. In its stead, they use 'backward-return condenser' or less informatively, 'partial condenser' or 'reflux condenser.'
3.3 Research Methodology

3.3.1 Molasses Preparations

1. Dilution of Molasses

Molasses was firstly diluted to a 40% dry matter content.

2. Heating of Molasses

Diluted molasses was heated for sterilization and to serve the process of sedimentation of undisclosed dry matter. Temperature of 85°C is achieved.
3. Chemical Treatment

Molasses was treated with H2SO4 to convert the dissolved salts to their sulfates by double decomposition. And the sulfate are precipitated

4. Filtration

The prepared liquor is supposed to be filtered, but actually the clear juice taken off by decantation. The clear juice is stored as a buffer solution in an isolated tank to keep temperature as high as possible. Juice taken to the process (fermentation) is cooled through a heat exchanger, where its temperature drops to 30°C [12].

3.3.2 Fermentation process

All that is necessary to begin fermentation is to mix the activated yeast and the cooled, pH-adjusted mash in the fermentation tank. Aside from the considerations of pH, the most important thing during the fermentation is temperature control. When the fermentation begins, carbon dioxide gas will be given off. At the height of fermentation, the mash will literally "boil" from the carbon dioxide produced. The reaction also produces some heat. The optimum temperature for the fermentation process is between 70-85 deg F., and it is desirable not to let the temperature go much above 90-95 deg F. Cooling is readily done with the use of ice bags, or by the use of a cooling coil. A less desirable method of controlling temperature is to dilute the mash.

The actual time required to ferment a mash varies with the material being fermented, the pH, temperature, and several other factors. You will know that the fermentation is complete when the mash ceases bubbling and the yeast cake, which forms on top, sinks to the bottom. At this point, the fermented liquor is known as "beer" and it is ready to be distilled. Otherwise, the carbon dioxide (CO2) gas can carry with it a considerable amount of alcohol. Note that the small, glass fermentation locks available from wine making supply houses are suitable, at most for a 5-gallon container. Larger containers must have proportionately larger fermentation locks or a dangerous amount of pressure will build and the vessel could explode.

It is permissible to open the fermenter to check progress and take samples for pH analysis, etc. as long as care is taken not to introduce bacteria that could contaminate the mash. In fermentation processes the fermentation medium used was a modification of that described and composed (mash, H2SO4-Treated Molasses, Urea 1.08, MgSO4.7H2O 0.3, H3PO4 0.3, PH5, antibaiotic and yeast). After this "Beer" interfering
to the microfiltration membrane (solid-liquid separation) in this step solid separating from the liquid and liquid entering to pervaporation membrane to separated ethanol. solid separated from micromembrane recycled to bio reactor fermentation to enriched the ethanol.

3.3.3 Methodology of Pervaporation Membrane Separation Used

The feed to the membrane module is a liquid mixture, usually at ambient pressure but higher pressures may be necessary to maintain a liquid phase on the feed side. The membrane is in contact with the liquid feed. Liquid components are absorbed into the membrane, diffuse through the membrane, and is desorbed at the other side. A lower pressure than the dew point of the permeating species is maintained on the other side of the membrane by using a vacuum pump. A sweep gas can also be used instead of a vacuum pump to maintain a low permeate vapor pressure. The permeating species is recovered by condensing the vapor using a condenser. The retentate can be recycled back to the membrane module depending on the purpose of separation.

As mentioned above, there are different operational modes of pervaporation, vacuum-pervaporation, and sweeping-gas pervaporation. Both of these methods achieve rapid desorption of the permeating species at the downstream surface of the membrane. Sweeping-gas pervaporation uses a non-permeating gas directed past the downstream membrane surface to reduce the permeate concentration. The sweeping-gas mode of operation is more complex than vacuum pervaporation and the downstream surface of the membrane is usually not completely dried[1].

Vacuum pervaporation is most often used but sweeping-gas pervaporation can be used if the permeate can be released without first condensing it. The product stream of the pervaporation process can be the permeate or retentate stream. The membrane choice and composition of the feed mixture will influence this decision[1].
3.3.4 Method of Simulation to Pervaporation Membrane

The process model flow sheet maps out the entire system. The flow sheet shows one or more inlet streams entering into the system's first unit operation (i.e., heat exchanger, compressor, pervaporation membrane, etc.) and continues through the process, illustrating all intermediate unit operations and the interconnecting streams. The flow sheet also indicates all product streams. Each stream and unit operation is labeled and identified.
In this study, use software (visual studio 2010) to simulate the process unit (Pervaporation Membrane) and was used this program to develop a new system simulation. The program includes (Data Base) and showed all stages of the simulation and caused in the Appendix. The feed entering to the pervaporation membrane unit at concentration 80% ,25°C and was calculated more result by the soft ware. Then the temperature was changed at (25,30,35,40,45,50,55,60,65,70) °C . After that concentration and temperature was changed to( 85,90,95)% at different temperature. From this simulation it was obtained on all result in order to find optimum operating condition, such as mol fraction of water inlet and outlet, mole fraction of ethanol inlet and outlet, feed flux, separation factor of membrane, separation factor of evaporation, separation factor of pervaporation, selectivity of membrane ,vapor pressure of water inlet and outlet, and vapor pressure of ethanol inlet and outlet. And was choosing from thesis data to plotting in order to explains this result .
Chapter Four

Results and Discussions

4.1 Theoretical Background

Tables contain the results of the Temperature, partial pressure of Ethanol inlet and outlet, partial pressure of Water inlet and outlet, Selectivity of membrane, Separation factor of pervaporation, Separation factor of evaporation, Separation factor of membrane, Feed Flux, Mole fraction of Ethanol in and out of membrane And Mole fraction of Water in and out of membrane. And will be presented to all the supplements, but in this chapter will display tables containing the results of the Temperature, partial pressure of Ethanol in and out of membrane, partial pressure of Water in and out of membrane And Separation factor of pervaporation membrane, And also will be presented results in graphics. Will be presented and discussed as a result of any singular, and changed the concentrations for Ethanol and Water inlet to the pervaporation system so was choose the most appropriate focus through simulations.

Table(4.1): Partial pressure of EtoH and H2O inlet and outlet and (β) of pervaporation membrane at 20% H2O in, 80% EtoH in and 95% H2O out, 5% EtoH out.

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>P.EtOH.out(Kpa)</th>
<th>P.EtOH.in(Kpa)</th>
<th>P.H2O.out(Kpa)</th>
<th>P.H2O.in(Kpa)</th>
<th>β ·Pervap</th>
</tr>
</thead>
<tbody>
<tr>
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**Fig(4.1):** Partial pressure profile with different inlet temperature at 80% EtoH inlet, 20% H2O inlet and 95% H2O out and 5% EtoH out, for the mixture inlet and outlet.

From fig(4.1), the overall profile is clearly illustrated for the mixture in terms of partial pressure while altering the inlet temperature at affixed concentration. The effect of increasing the temperature has noticeably enhanced the separation process of the mixture. The partial pressure of the inlet ethanol has exponentially increased with temperature and it incomparable with the outlet ethanol profile. The obvious profile of inlet ethanol is due to its high concentration from the beginning. Meanwhile, the partial pressure profile for the water is clear from the figure but not the same as for ethanol. It must also be mentioned that the water concentration is very low in the mixture compared to ethanol.
Table(4.2): Partial pressure of EtoH and H2O inlet and outlet and (β) of pervaporation membrane at 15% H2O in, 85% EtoH in and 97% H2O out, 3% EtoH out.

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>P.EtoH. out(Kpa)</th>
<th>P.EtoH.in(Kpa)</th>
<th>P.H2O.out(Kpa)</th>
<th>P.H2O.in(Kpa)</th>
<th>β .Pervap</th>
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Fig(4.2): Partial pressure profile with different inlet temperature at 85% EtoH inlet, 15% H2O inlet and 97 H2O out and 3% EtoH out, for the mixture inlet and outlet.

From fig(4.2), the overall profile is clearly illustrated for the mixture in terms of partial pressure while altering the inlet temperature at affixed concentration. The effect of increasing the temperature has noticeably enhanced the separation process of the mixture. The partial pressure of the inlet ethanol has exponentially increased...
with temperature and it incomparable with the outlet ethanol profile. The obvious profile of inlet ethanol is due to its high concentration from the beginning. Meanwhile, the partial pressure profile for the water is clear from the figure but not the same as for ethanol. It must also be mentioned that the water concentration is very low in the mixture compared to ethanol.

**Table(4.3):** Partial pressure of EtoH and H2O inlet and outlet and (β)of pervaporation membrane at 10% H2O in, 90% EtoH in and 98% H2O out, 2% EtoH out.

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>P.EtOH. out(Kpa)</th>
<th>P.EtOH.in(Kpa)</th>
<th>P.H2O.out(Kpa)</th>
<th>P.H2O.in(Kpa)</th>
<th>β .Pervap</th>
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**Fig (4.3) :** Pervaporation separation factor profile with different inlet temperature at 10% H2O inlet 90% EtoH inlet and 98% H2O outlet, 2% EtoH outlet.

\[
y = 0.2716x + 171.13 \\
R^2 = 0.9997
\]
From fig(4.3) above, it is shown that the pervaporation separation factor ($\beta$) has been steadily increased with the inlet temperature of the mixture (water and ethanol). It must be mentioned that this profile was recorded only for constant concentration of the mixture which is **10% water inlet, 90% ethanol inlet and 98% water outlet, 2% ethanol outlet**.

![Temperature With Vapor Pressure](image)

**Fig (4.4):** Partial pressure profile with different inlet temperature at 90% Ethanol inlet, 10% H2O inlet and 98% H2O out, 2% Ethanol out, for the mixture inlet and outlet.

From fig(4.4), the overall profile is clearly illustrated for the mixture in terms of partial pressure while altering the inlet temperature at affixed concentration. The effect of increasing the temperature has noticeably enhanced the separation process of the mixture. The partial pressure of the inlet ethanol has exponentially increased with temperature and it incomparable with the outlet ethanol profile. The obvious profile of inlet ethanol is due to its high concentration from the beginning. Meanwhile, the partial pressure profile for the water is clear from the figure but not the same as for ethanol. It must also be mentioned that the water concentration is very low in the mixture compared to ethanol.
Table (4.4): Partial pressure of EtoH and H2O inlet and outlet and ($\beta$) of pervaporation membrane at 10% H2O in, 90% EtoH in and 98% H2O out, 2% EtoH out.

<table>
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<tr>
<th>Temp °C</th>
<th>P.EtOH.out(Kpa)</th>
<th>P.EtOH.in(Kpa)</th>
<th>P.H2O.out(Kpa)</th>
<th>P.H2O.in(Kpa)</th>
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Fig (4.5) : Pervaporation separation factor profile with different inlet temperature at 5% H2O and 95% EtoH.

From fig (4.5) above, it is shown that the pervaporation separation factor ($\beta$) has been steadily increased with the inlet temperature of the mixture (water and ethanol). It must be mentioned that this profile was recorded only for constant concentration of the mixture which is 5% water and 95% ethanol.
Fig(4.6): partial pressure profile with different inlet temperature at 95% EtoH inlet, 5% H2O inlet and 99.9 H2O out and 0.1% EtoH out, for the mixture inlet and outlet.

From fig(4.6), the overall profile is clearly illustrated for the mixture in terms of partial pressure while altering the inlet temperature at affixed concentration. The effect of increasing the temperature has noticeably enhanced the separation process of the mixture. The partial pressure of the inlet ethanol has exponentially increased with temperature and it incomparable with the outlet ethanol profile. The obvious profile of inlet ethanol is due to its high concentration from the beginning. Meanwhile, the partial pressure profile for the water is clear from the figure but not the same as for ethanol. It must also be mentioned that the water concentration is very low in the mixture compared to ethanol.
Chapter Five

Conclusions and Recommendation

5.1 Conclusions:

Modeling and simulation of pervaporation processes related to fuel ethanol production is a powerful tool for the design of ethanol dehydration plants since it allows saving time and resources in pilot plant tests. Additionally, these process engineering tools make possible to compare different technological options from energy point of view. Chemical process simulation software visual studio 2010 made easy the simulation of the different separation configurations, reaffirming its importance as a commercial simulator for the design, evaluation and optimization production processes.

And was find the pervaporation membrane was used in two phases because low selective in the case of high concentrations water and thus increase the selectivity in the second phase was been noticed selectivity is not much affected by the temperature at high concentrations of water on the reverse in low concentrations and therefore are producing high purity of ethanol. membranes was been made from polymer (poly vinyl alcohol) and very small of pore size less than 0.5 microns was shown these membranes high selectivity for mixtures of ethanol and water. was shown simulations pervaporation membrane to separate a mixture of ethanol and water results of design and was find all the parameters required such as (Temperature, vapor pressure of ethanol in and out, vapor pressure of water in and out, mole fraction of ethanol in and out, mole fraction of water in and out, flux of feed, separation factor of membrane, separation factor of evaporation, separation factor of pervaporation, and selectivity) and was developed a new program to simulated pervaporation membrane and review the results and is painted in the form of illustrations and the right program for data base and depends on the program originally a visual studio 2010 and was obtained the results and were discussed.
5.2 Recommendations:

- suggest the results development the process to producing high purity ethanol in all sugar factories in Sudan and especially ethanol plant in Kenana.
- It is recommended to develop the proposed visual studio software to manage the overall bioethanol production.
- Also it is recommended that research in ethanol production should be encouraged.
References:

4. Dr. Marco Aurelio Dos Santos Bernard’s" Biofuels Production-Recent Developments and Prospects" PP 96, 2011.