

IMPROVING THE ENERGY EFFICIENCY OF ETHANOL SEPARATION THROUGH PROCESS SYNTHESIS AND SIMULATION

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ABSTRACT

Worldwide demand for energy is increasing rapidly, partly driven by dramatic economic growth in developing countries. This growth has sparked concerns over the finite availability of fossil fuels and the impact of their combustion on climate change. Consequently, many recent research efforts have been devoted to the development of renewable fuels and sustainable energy systems. Interest in liquid biofuels, such as ethanol, has been particularly high because these fuels fit into the conventional infrastructure for the transportation sector.

Ethanol is a renewable fuel produced through the anaerobic fermentation of sugars obtained from biomass. However, the relatively high energy demand of its production process is a major factor limiting the usefulness of ethanol as a fuel. Due to the dilute nature of the fermentation product stream and the presence of the ethanol-water azeotrope, the separation processes currently used to recover anhydrous ethanol are particularly inefficient. In fact, the ethanol separation processes account for a large fraction of the total process energy demand.

In the conventional ethanol separation process, ethanol is recovered using several distillation steps combined with a dehydration process. In this dissertation, a new hybrid pervaporation-distillation system, named Membrane Dephlegmation, was proposed and investigated for use in ethanol recovery. In this process, countercurrent vapour-liquid contacting is carried out on the surface of a pervaporation membrane, leading to a combination of distillation and pervaporation effects. It was intended that this new process would lead to improved economics and energy efficiency for the entire ethanol production process.

The Membrane Dephlegmation process was investigated using both numerical and experimental techniques. Multiphase Computational Fluid Dynamics (CFD) was used to study vapour-liquid contacting behaviour in narrow channels and to estimate heat and mass transfer rates. Results from the CFD studies were incorporated into a simplified design model and the Membrane Dephlegmation process was studied numerically. The results indicated that the Membrane Dephlegmation process was more efficient than simple distillation and that the ethanol-water azeotrope could be broken. Subsequently, a pilot-scale experimental system was constructed using commercially available, hydrophilic NaA zeolite membranes. Results obtained from the experimental system confirmed the accuracy of the simulations.

RÉSUMÉ

La demande mondiale en énergie augmente rapidement, principalement causée par la forte croissance économique des pays émergents. Cette croissance suscite un questionnement sur la disponibilité future des combustibles fossiles et sur l'impact de leur utilisation sur les changements climatiques. En conséquence, un intérêt accru s'est manifesté pour le développement de carburants renouvelables et de systèmes énergétiques soutenable. L'intérêt pour les combustibles organiques liquides, tels que l'éthanol, a été particulièrement important parce que ces carburants peuvent s'insérer directement dans l'infrastructure conventionnelle pour le secteur du transport.

L'éthanol est un carburant renouvelable produit par la fermentation anaérobie des sucres obtenus à partir de la biomasse. Cependant, la demande d'énergie relativement haute de son procédé de fabrication limite son utilité comme carburant. En raison de sa faible teneur dans le bouillon de fermentation et de la présence de l'azéotrope eau-éthanol, les procédés de séparation actuellement utilisés pour récupérer l'éthanol sont particulièrement inefficaces. En fait, l'énergie nécessaire pour le procédé de séparation de l'éthanol représente une grande partie de la demande énergétique du procédé.

Dans le procédé conventionnel de séparation, l'éthanol est récupéré en utilisant plusieurs étapes de distillation combinées avec un procédé de déshydratation. Dans cette thèse, un nouveau système hybride de pervaporation-distillation, appelé Déflegmation par Membrane, a été proposé et étudié pour la récupération de l'éthanol. Dans ce procédé, un contact vapeur-liquide à contre-courant est effectué sur la surface d'une membrane de pervaporation, menant ainsi à un effet combiné de distillation et de pervaporation. La conception de ce système avait comme idée maîtresse de mener à des économies et à une plus grande efficacité énergétique du procédé de fabrication de l'éthanol.

Le procédé de Déflegmation par Membrane a été étudié utilisant à la fois des techniques numériques et expérimentales. La mécanique des fluides numériques multi-phases (CFD) a été employée pour étudier le contact vapeur-liquide dans des conduites étroites et pour estimer les taux de transfert de chaleur et de matière. Les résultats des études de CFD ont été incorporés à un modèle simplifié de conception et le procédé de Déflegmation par Membrane a été étudié numériquement. Les résultats ont indiqué que le procédé de Déflegmation par Membrane était

plus efficace que la simple distillation et que l'azéotrope eau-éthanol pourrait être franchi. Un système expérimental à l'échelle pilote a été construit utilisant des membranes commerciales hydrophiles de zéolite NaA. Les résultats obtenus à partir du système expérimental ont confirmé l'exactitude des simulations.

DEDICATION

Dedicated to my family and friends

STATEMENT OF CONTRIBUTIONS OF COLLABORATORS

I hereby declare that I am the sole author of this thesis. I have performed the computer simulations, experiments and data analysis and I have written all of the chapters contained in this thesis.

My supervisors, Dr. Jules Thibault and Dr. André Y. Tremblay, provided me with continual support and guidance throughout this work. They also contributed with many helpful editorial comments and corrections.

The experiments related to the paper presented in Chapter 7, were performed with the help of Xian Meng Huang during the summer and fall of 2010. He is a coauthor to the paper presented in this chapter.

I had many fruitful discussions with Dr. Seyed Gh. Etemad in the early stages of the CFD simulations related to the papers presented in Chapters 9 and 10. He is a coauthor to the papers presented in these chapters.

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INTRODUCTION

The availability of safe, secure and sustainable energy is crucial for social and economic development. The World Energy Council proposed three criteria, dubbed the three A's, which must be met for sustainable energy management. The energy supply should be available, accessible and acceptable. That is, energy must be available both geographically and well into the future. It must be accessible in terms of affordability, infrastructure and sustainability. Finally, it must be acceptable in terms of health, safety, public attitude and environmental policies. It is clear that in the long term such lofty goals can only be met by employing a variety of sustainable energy sources.

Table 1.1 shows the primary energy demand globally and in Canada in 2005. The energy consumed by the transportation sector is also shown. As shown in the table, the fraction of the primary energy supply consumed for transportation purposes is approximately 19 % globally and 22 % in Canada. This represents a considerable quantity of energy. Furthermore, gasoline and diesel are by far the most commonly used transportation fuels and thus transportation accounted for approximately 60.3 % of the global oil consumption in 2005 [1]. The most commonly used alternative transportation fuels include liquefied petroleum gas (LPG), ethanol, compressed natural gas (CNG) and fatty acid methyl ester (FAME or commonly referred to as biodiesel) [2].

Table 1.1. Primary and Transportation Energy Use in 2005

	World	Canada
Primary Energy Supply (EJ)	478.72	10.94
Transportation Energy (EJ)	91.39	2.38
Percent of Primary (%)	19.09	21.77
Reference	[1]	[3]

The term biofuel is commonly used to refer to any fuel derived from renewable resources. This can lead to some confusion since many fuels can be derived from either renewable or non-renewable resources. For example, hydrogen can be produced through the electrolysis of water but the electricity may or may not be obtained from a renewable resource.

In general, the production of biofuels can be accomplished through biochemical or chemical processes. For example, ethanol, butanol, biogas (containing methane) and even hydrogen can be produced by certain micro-organisms. Conversely, biomass gasification leads to a syngas which can be separated to produce hydrogen or converted to synthetic fuels through Fischer-Tropsch synthesis. The decision on which fuel(s) should be used is therefore quite complex because it must account for availability of resources, processing efficiency and finally, fuel consumption (end-use) efficiency. This dissertation is concerned with the biochemical production of ethanol. In particular, the focus is on improving the energy efficiency of the ethanol separation process, since this is one of the most energy intensive steps in the production process.

Ethanol can be produced through the fermentation of various sugars. These sugars can be derived from several different types of biomass. Traditionally, the sugar source has been saccharine biomass (sugar cane, sugar beets etc.) or starchy biomass (corn, wheat, rice etc.). However, these conventional substrates are also food sources. Thus, the conversion of these substrates into fuel has provoked some criticism due to concerns over their limited availability and the potential for food price increases which could result. These concerns have sparked an increased interest in non-conventional, cellulosic substrates. The two main groups of cellulosic substrates that have been investigated are waste residues and dedicated crops. Some of the waste residues that have been investigated include municipal waste, forestry residues (from logging or milling) and agricultural residues (corn stover, wheat straw etc.). Dedicated crops could include perennial herbaceous crops such as switchgrass or woody crops such as poplar or spruce [4,5].

The utility of ethanol as a biofuel for the transportation sector is two-fold. First, ethanol can be mixed with gasoline in mixtures up to 10 % and used in conventional gasoline engines. Flex-fuel vehicles, which are able to use gasoline mixtures with up to 85 % ethanol, have also been produced by several prominent automobile manufacturers [6]. Secondly, ethanol has the potential to be used in specially designed internal combustion engines, either in its azeotropic (95 % by weight) or anhydrous (>99 % by weight) form. In either case, ethanol could help alleviate the world's dependence on fossil fuel sources and potentially help mitigate climate change caused by carbon dioxide emissions. Since ethanol is an energy carrier that transmits the sun's energy, the ethanol production process must be as efficient as possible. That is, the use of non-renewable fuels and potential emissions in its production should be minimized. Further, it is

desirable to minimize energy losses so that the largest possible quantity of the solar energy absorbed by the biomass is delivered to the end user in the form of ethanol.

Currently, the USA and Brazil are the largest ethanol producers. Table 1.2 shows the ethanol production rates for the top five ethanol producing countries as well as the world total for 2005. Canada's ethanol production rate is also shown in Table 1.2. From this table, it should be noted that the USA and Brazil account for over 80 % of the World's ethanol production. Furthermore, it is important to note that most of the ethanol produced in the USA is derived from corn. Conversely, Brazil obtains almost all of its ethanol from sugar cane. In terms of resource availability, Canada has an abundant supply of biomass. However, much of this biomass is in the form of cellulosic materials. For example, Canada's forests, which are estimated to contain more than 21 billion m³ of merchantable softwood, represent a particularly large potential source of lignocellulosic materials [7]. The availability of this source, combined with a forestry industry that has recently seen declines in its profits, has led to increased interest in converting wood sources to ethanol [8,9]. Furthermore, the pine beetle problem in western Canada has sparked interest into using killed trees for ethanol production [10].

Table 1.2. Ethanol Production Capacity by Country in 2009 [11]

Country	Ethanol Production (Millions of Litres)
USA	40121
Brazil	24897
EU	3935
China	2050
Canada	1100
Total	73940

The recovery of ethanol following fermentation is one of the most energy intensive steps in the production of ethanol [12]. There are two main aspects making the ethanol recovery process difficult. First, in the conventional fermentation process, the final ethanol concentration is limited to approximately 10 % by mass due to the inhibitive effect of ethanol on the micro-organisms. Conversely, the genetically modified microbes employed to ferment five carbon sugars are even more susceptible to ethanol, usually limiting the final ethanol concentration to approximately 5 % by mass. The recovery of ethanol from such a dilute stream using conventional distillation is very energy intensive. Secondly, ethanol and water form an azeotrope

at approximately 95.6 % by mass at atmospheric pressure. The presence of this azeotrope prohibits the use of simple distillation to recover anhydrous ethanol. Thus, vacuum or extractive distillation, pressure swing adsorption (PSA) of water onto molecular sieves, pervaporation or vapour permeation must be used to break the azeotrope.

1.1. Objectives

Since ethanol recovery is the most energy intensive step in the ethanol production process, it is one of the primary factors limiting the economic viability of ethanol production for use as a transportation fuel. Further, if ethanol is to be used to mitigate carbon dioxide emissions the need for external energy inputs must be minimized. Thus, its production must be as energy efficient as possible. Consequently, the primary objectives of this dissertation are to improve the energy efficiency and economics of the ethanol production process by improving the efficiency of the recovery processes. It is proposed that an internally coupled hybrid distillation-pervaporation process, which has been named Membrane Dephlegmation, can improve the efficiency and economics of the ethanol separation process. The remainder of this dissertation is devoted to the testing of this general hypothesis. The following section provides an overview of the organization of this dissertation

1.2. Thesis Structure

Several studies have been carried out to directly or indirectly investigate the Membrane Dephlegmation process. To organize these studies, this dissertation has been divided into three sections and twelve chapters. The first chapter in each section introduces important theoretical considerations and reviews relevant literature. Chapter 12 presents a summary of major conclusions and contributions resulting from this research project. The other chapters are written in journal article format.

1.2.1. Section I. Introduction to Ethanol Production

The first section, which includes Chapters 2 and 3, introduces the current state of the ethanol production process. Chapter 2 provides a general overview of the production process and highlights key limitations and opportunities for improvement. The conventional ethanol separation process is also introduced and the primary factors limiting its efficiency are discussed. Chapter 3 compares the energy efficiency and economics of several conventional, energy saving, distillation-based separation processes for ethanol recovery. This chapter serves to provide

baseline economic and energy efficiency estimates, to which competing processes could be compared.

1.2.2. Section II. Membrane Dephlegmation: A Novel Hybrid Separation System

The second section, which includes Chapters 4, 5, 6 and 7, provides an in-depth analysis of the proposed hybrid separation process. Chapter 4 introduces the Membrane Dephlegmation process and important features of related separation processes. Chapter 5 provides a detailed overview of the Membrane Dephlegmation process. A simple design model is derived to facilitate the discussion and explain the fundamental phenomena occurring in the system. A model of the wetted-wall distillation process is derived simultaneously and important similarities and differences are discussed. The models are then used to carry out preliminary studies to investigate system performance. Specifically, differences in composition, temperature and velocity profiles are analyzed for various operating conditions and for wetted-wall distillation. In Chapter 6, the design model is used to carry out a detailed investigation into the efficiency of Membrane Dephlegmation for a wide range of operating conditions. The impact of critical operating parameters including flow rate, feed concentration, permeate pressure and reflux ratio is investigated. Additionally, an analysis using McCabe-Thiele plots is presented to compare Membrane Dephlegmation to conventional distillation. The system's effect on the energy efficiency of the overall ethanol recovery process is also qualitatively discussed. Chapter 7 presents experimental results from a pilot-scale experimental system. The experimental data from this system are used to validate the design model and determine important model parameters. The validated model and experimental results are used to explore the effects of pertinent operating conditions on performance. Finally, important physical limitations, including long-term membrane stability and flooding, are discussed.

1.2.3. Section III. Supporting Computational Investigations

The third section, which includes Chapters 8, 9, 10 and 11, presents several computational studies. These studies were carried out to support the simulations and experimental work presented in Section II. Chapter 8 provides an overview of the computational studies and explains the research methodology behind their implementation. Chapter 9 presents an investigation intended to study counter-current vapour-liquid flow in a narrow channel. It was important to study this type of flow, since the hydrodynamics are essentially the same as those

found in the Membrane Dephlegmation system. Chapter 10 proposes a new computational methodology for the Direct Numerical Simulation (DNS) of coupled multicomponent interphase heat and mass transfer. The proposed method uses the Volume-Of-Fluid (VOF) method to track the evolution of the vapour-liquid interface and solves the fully coupled species and energy equations to directly estimate heat and mass transfer rates. The method was used to estimate interphase heat and mass transfer coefficients, which were then incorporated into the design model presented in Section II. Finally, the study presented in Chapter 11 employs neural network models to correlate data for important transport properties for the ethanol-water system. These highly accurate correlations were incorporated into the simulations presented in Section II and Chapters 9 and 10.

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SECTION I. INTRODUCTION TO ETHANOL PRODUCTION

ETHANOL PRODUCTION OVERVIEW

Ethanol can be produced through chemical or biochemical pathways. However, for biofuel production, ethanol is typically produced through the anaerobic fermentation of sugars. Since the goal of this study is ethanol production for biofuel purposes, only the biochemical ethanol production process is reviewed in this chapter.

2.1. Biochemical Ethanol Production

The sugars, which act as the primary substrate for the fermentation process, can be derived from several different types of biomass. Some of the operations in the ethanol production process vary depending on the specific feedstock. Regardless, the overall production process can be divided into a series of general steps. The main steps of the ethanol production process are shown schematically in Figure 2.1 [1-4]. The complexity of each step depends on the specific type of biomass employed. Any of the steps involved in the overall process may require some supplementary inputs. In the pretreatment step, the biomass is mechanically prepared for the chemical and biochemical processes that follow. Following pretreatment, chemical and biochemical processes are used to extract sugars from the biomass and convert these sugars into ethanol. The separation step involves the separation of residual biomass materials, microbial cells and the purification of the ethanol stream. Some of the residues remaining after the separation step may be used in an integrated energy recovery scheme, while others may be recycled to improve process efficiency or treated as waste. Some valuable by-products may also be produced. For example, the production of ethanol from sugar cane produces bagasse, which is often burned to provide process energy. Conversely, ethanol production from corn produces dry distiller's grains with solubles (DDGS), which are sold as animal feed. Lignocellulosic ethanol production leaves a large amount of lignin and other biomass residuals, which can be combusted to provide heat and electrical energy to the process.

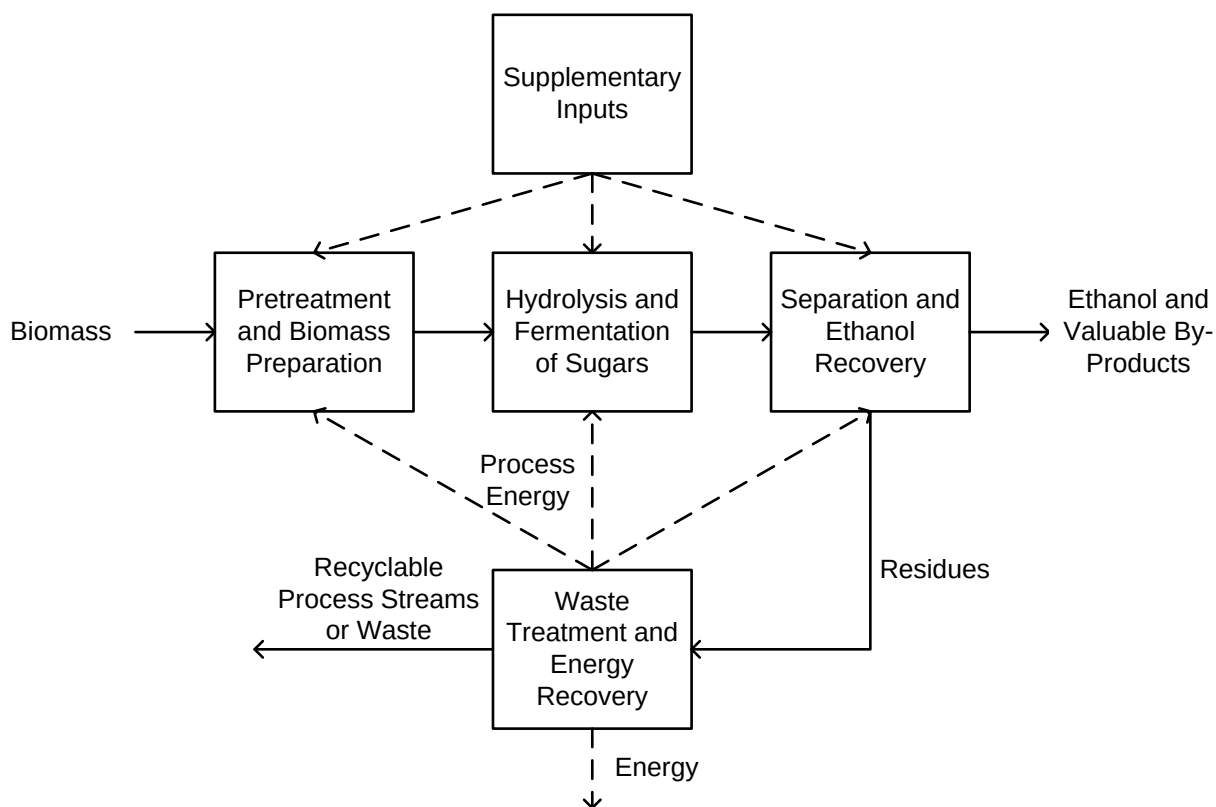


Figure 2.1. Schematic representation of the primary steps involved in the biochemical ethanol production process.

It is widely believed that cellulosic materials represent the best biomass source for ethanol production since these are the most abundant types of biomass and because they are not used as a human food source. Thus, the cellulosic ethanol production process is the main focus of this section.

2.1.1. Cellulosic Biomass

Conventional sugar sources for ethanol production include saccharine (ex. sugar cane) and starchy (ex. corn) biomass. Since the sugars in the saccharine biomass are already present in their utilizable form, their extraction is relatively straightforward. On the other hand, the starch found in the starchy biomass consists of long chains of sugar molecules. Thus, it is necessary to break down (hydrolyze or saccharify) these chains such that the micro-organisms used in the fermentation process can gain access to the sugar molecules. However, since starch is a relatively weak polymer, it is usually easy to break down the starchy biomass into usable sugars. Conversely, cellulosic materials are composed of very stable sugar polymers and are therefore difficult to break down into their sugar sub-units [1].

Even though cellulosic materials are more difficult to break down into usable sugars, they are much more abundant and therefore provide a greater potential biomass source for fuel ethanol production [3]. Cellulosic biomass contains cellulose, hemicellulose and lignin fractions. The proportion of the individual components present in the biomass depends on the type of material. For instance, typical agricultural residues have lower lignin fractions than hardwoods, which again have lower fractions than softwoods [5]. As an example, for wood, typical dry mass fractions of these components are 40-50 % cellulose, 20-25 % hemicellulose, 20-25 % lignin and 5 % other compounds [6]. Cellulose is a highly crystalline polymer composed entirely of glucose molecules, joined by beta-linkages. Conversely, hemicellulose is made up of several different sugars and its exact composition again depends on the type of biomass being considered. Lignin is composed of phenylpropylene subunits that are joined together by ether or carbon-carbon linkages [5].

2.1.2. Pretreatment

The main purposes of pretreatment are to reduce cellulose crystallinity, increase particle surface area, partially remove the lignin fraction of the biomass and partially or totally hydrolyze the hemicellulose fraction [2]. The pretreatment step should also limit the production of inhibitory substances, preserve the fermentable sugars and minimize capital and operating costs [7]. The extent to which each of these objectives is accomplished depends on the type of pretreatment used. Often, an acid catalyzed steam pretreatment method is employed. In this process, commonly referred to as steam explosion, the biomass is first exposed to steam at a very high pressure (~1300 kPa) in an acidic environment. The pressure is then rapidly released, resulting in an explosion and thereby breaking down the biomass. The pretreatment step yields both soluble and insoluble fractions. The soluble fraction, resulting mainly from the hydrolysis of hemicellulose, contains a large fraction of the pentose sugars. It also contains most of the toxic by-products and may therefore need to be detoxified prior to fermentation. Conversely, the insoluble fraction contains the lignin and most of the cellulose from the original biomass. The pretreatment step also transforms this cellulose fraction into a mainly amorphous material that is susceptible to hydrolysis.

2.1.3. Hydrolysis and Fermentation

The main goals of the hydrolysis and fermentation steps are to break down the remaining cellulose into glucose and then to convert all the sugars into ethanol. The soluble and insoluble fractions present very different processing challenges. That is, the soluble fraction presents a challenge since the fermentation of pentose sugars is not straightforward. Conversely, the insoluble fraction contains non-fermentable lignin as well as cellulose, which must be hydrolyzed prior to fermentation.

The hydrolysis (saccharification) of cellulose can be carried out using enzymes and is therefore often referred to as enzymatic hydrolysis (EH). This requires the use of three different types of enzymes, namely, endoglucanases, cellobiohydrolases and β -glucosidase. The endoglucanases and cellobiohydrolases act together to cut the cellulose chains into glucose dimers (cellobiose). The cellobiose is then converted into fermentable glucose molecules by β -glucosidase [1].

Once the cellulose fraction has been hydrolyzed to form glucose, the glucose can be fermented to produce ethanol. The fermentation of glucose is analogous to ethanol production using conventional substrates. That is, the micro-organisms used in the conventional ethanol fermentation processes are also applicable in this case. Baker's yeast (*Saccharomyces cerevisiae*) is one of the most commonly employed micro-organisms in conventional ethanol fermentations. *S. cerevisiae* produces ethanol under anaerobic conditions. However, a very small amount of oxygen must be supplied to the fermentation to keep the cells viable. Since the hydrolysis and fermentation steps can operate under similar conditions, these steps can be combined or carried out separately. If they are carried out separately the process is referred to as Separate Hydrolysis and Fermentation (SHF). Conversely, the combined process is called Simultaneous Saccharification and Fermentation (SSF). Of course, both options have certain advantages and disadvantages. For example, the SSF process results in capital cost savings while the SHF process allows both steps to operate under optimal conditions [1]. It has been shown that the SSF process is economically preferable to the SHF process [8]. Since the lignin fraction is commonly removed by filtration, the location of the filtration step also depends on the configuration of the hydrolysis and fermentation steps [8].

The fermentation of the pentose sugars, resulting from the hydrolysis of the hemicellulose fraction, presents another processing challenge. This challenge results from the

fact that most ethanol producing microbes are not able to metabolize pentose sugars. The pentose sugars can, however, be utilized by certain genetically modified micro-organisms. One caveat in using these genetically modified micro-organisms is that they are generally more susceptible to ethanol inhibition. Ethanol inhibition is experienced by all ethanol producing microbes. However, the conventional micro-organisms are usually limited to final ethanol concentrations of less than approximately 10 % (by mass). On the other hand, most recombinant micro-organisms are limited to considerably lower final concentrations of around 5 %. This lower final ethanol concentration reduces the separation efficiency. Since the recombinant micro-organisms are capable of using both hexose and pentose sugars, two other processing options become apparent (in addition to SHF and SSF). That is, enzymatic hydrolysis can be carried out separately and the two fermentation steps can be combined (Co-Fermentation or CF) or enzymatic hydrolysis can be combined with both fermentation steps (Simultaneous Saccharification and Co-Fermentation or SSCF) [2]. The decision concerning which process to use depends on economic considerations and the nature of the biomass source. Figure 2.2 provides a schematic representation of all the available processing options.

Regardless of the scheme employed for hydrolysis and fermentation, a crude product stream containing ethanol, water and residual solids is produced. To produce anhydrous ethanol, the water and residual solids must be removed from this stream. The following section highlights the pertinent issues surrounding the recovery of ethanol.

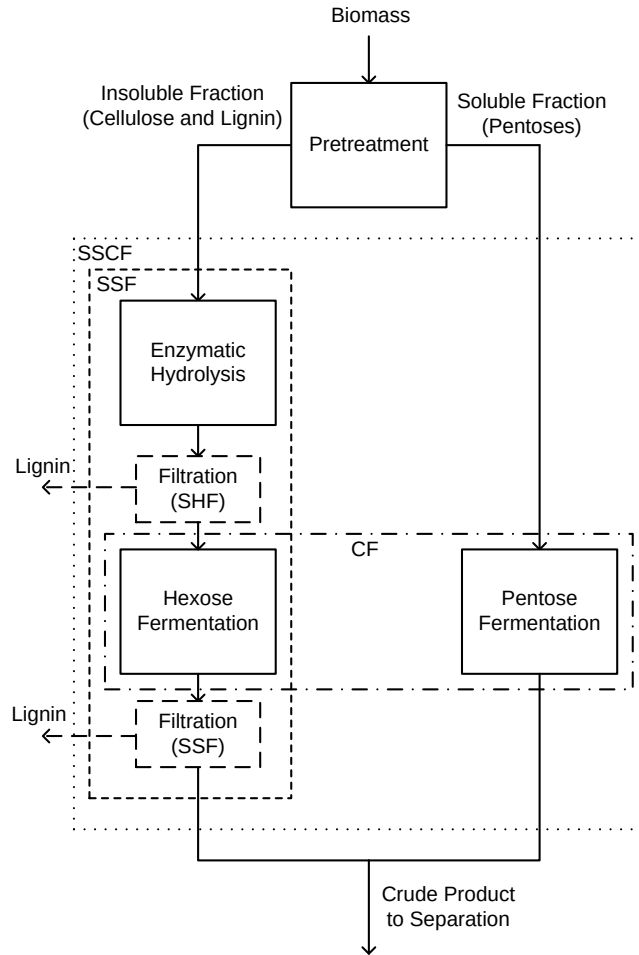


Figure 2.2. Simplified flowsheet for the hydrolysis and fermentation steps (SHF, Separate Hydrolysis and Fermentation; SSF, Simultaneous Saccharification and Fermentation; CF, Co-Fermentation; SSCF, Simultaneous Saccharification and Co-Fermentation).

2.1.4. Ethanol Recovery

There are two main problems encountered in the recovery of ethanol from the fermentation product stream. First, as indicated earlier, the ethanol concentration in this stream is quite low. Thus, conventional distillation is very energy intensive. Secondly, as shown in Figure 2.3, ethanol and water form an azeotrope at approximately 95.6 % ethanol (by mass) at atmospheric pressure.

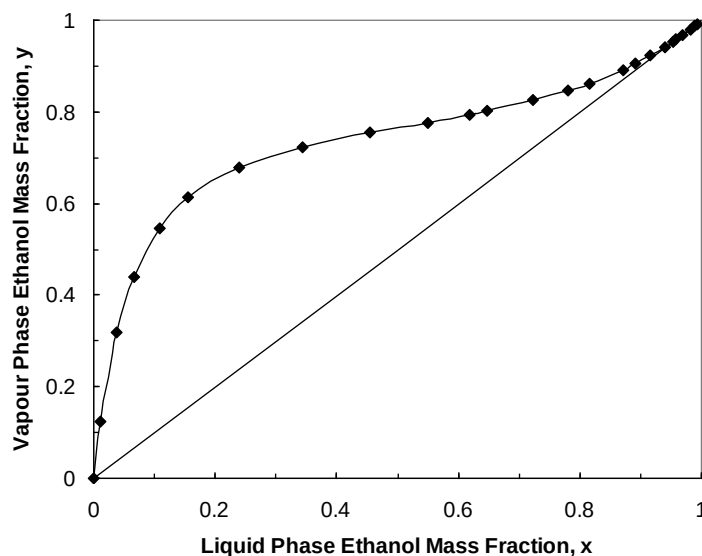


Figure 2.3. Vapour-liquid equilibrium curve for ethanol-water at 363.15 K (data from [9]).

Figure 2.4 shows the conventional ethanol separation scheme. Pretreatment and waste treatment processes are omitted from this simplified flowsheet. The concentration of ethanol leaving the fermentation system varies depending on the substrate and micro-organisms utilized and can be anywhere from 2 % to 10 % ethanol by mass. This stream is usually sent to a beer column (steam stripping column), which produces a relatively clean ethanol-water vapour stream having an ethanol concentration of approximately 30 % to 60 % by mass. The bottoms stream leaving this column is mainly water, with some residual dissolved solids. Conventionally, the distillate leaving the beer column is sent to enriching column, which brings the concentration to near the ethanol-water azeotrope (~90 %). The azeotrope can be broken through vacuum or extractive distillation, pressure swing adsorption using molecular sieves, pervaporation and vapour permeation. Extractive distillation has been commonly used in the past but PSA is now often the preferred method due to its much lower energy requirement. Pervaporation and vapour permeation are competitive with adsorption in many instances and are becoming increasingly popular. The bottoms stream leaving the enriching column can be returned to the beer column or reboiled in a side stripping column.

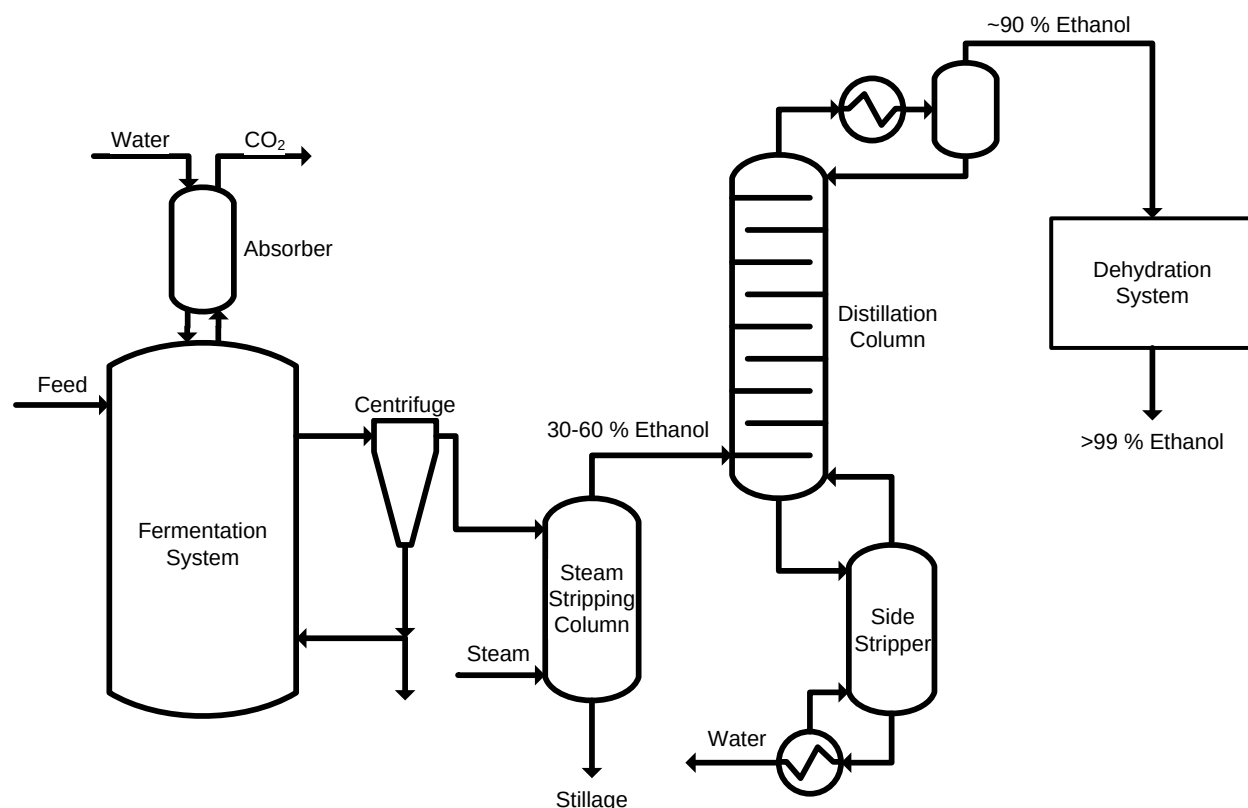


Figure 2.4. Simplified flowsheet for the conventional process for the production of anhydrous ethanol through fermentation (pre-treatment and waste treatment are not shown).

Although the separation scheme shown in Figure 2.4 is the most commonly employed approach, many other options have been proposed for improving process efficiency. Haelssig et al. [10] investigated six alternative, distillation based options for ethanol recovery (see Chapter 3). Many non-distillation methods have also been proposed for the recovery of ethanol from the dilute fermentation stream. Some of these methods include fermentation under vacuum, fermentation with an external flash tank, extractive fermentation using liquid or supercritical solvents, membrane-aided liquid extraction, stripping by an inert gas, reverse osmosis, pervaporation, membrane distillation, adsorption, phase inversion extraction and reactive extraction [11-16]. It has been claimed that some of these processes are advantageous in comparison to distillation, either economically or in terms of energy consumption. However, a comprehensive comparison of all these options on the same basis is not available.

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TECHNICAL AND ECONOMIC CONSIDERATIONS FOR VARIOUS RECOVERY SCHEMES IN ETHANOL PRODUCTION BY FERMENTATION

Jan B. Haelssig, André Y. Tremblay and Jules Thibault

Abstract

Six alternative ethanol recovery processes were investigated from an economic and technical perspective. The processes were evaluated using the commercial simulation software Aspen HYSYS 2004.2 with an integrated fermentation model. The six alternatives included two variations of the flash fermentation process as well as various distillation configurations. Certain weaknesses and potential processing improvements were highlighted and economic and technical targets were set for future comparisons. Distillation with two columns operating at different pressures and distillation with a vapour recompression system for heat recovery were found to be the best alternatives overall. However, from an energy standpoint, the modified flash fermentation process yielded the highest efficiency.

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3.1. Introduction

Bio-ethanol is a two-carbon alcohol that can be produced through the fermentation of sugars obtained from saccharine biomass such as sugar cane, starchy biomass (corn) or cellulosic biomass (agricultural or forest wastes). Bio-ethanol can be used advantageously as a

transportation fuel and has therefore been cited as a possible alternative to fossil fuels that could help alleviate environmental and energy dependency problems. Currently most of the world's bio-ethanol is produced through the fermentation by yeast or bacteria of sugars extracted from sugar cane and corn. Bio-ethanol production from lignocellulosic biomass is, however, gaining interest because wastes can be used and competition between food and fuel production as in the case of sugar cane and corn is eliminated. The traditional yeast fermentation process is limited to final ethanol concentrations of approximately 10 % (by mass) due to product inhibition. The inhibition problem is further exacerbated when genetically-modified microorganisms are used to ferment the pentose sugars resulting from the hydrolysis of lignocellulosic biomass. This product inhibition impacts both the efficiency of the fermentation system, since larger fermenters are required, and the efficiency of downstream separation, since a relatively dilute stream must be processed.

Various options have been proposed for the efficient recovery of ethanol from fermentation broth [1]. Generally, it is possible to divide these into two subcategories, namely, downstream and in situ recovery. As is implied by the term, downstream separation focuses on the recovery of ethanol after the broth has left the fermentation system and it is therefore somewhat decoupled from the fermentation process. Traditionally, downstream separation has been accomplished through various distillation schemes. Conversely, in situ recovery encompasses systems that are an integral part of the fermentation system. The fundamental aim of in situ recovery is to improve the efficiency of the fermentation process by maintaining a lower ethanol concentration while also improving the efficiency of downstream separation by producing a more concentrated stream.

Various in situ recovery processes have been proposed and experimentally investigated by a vast number of researchers. Some of these processes include separation by fermentation under vacuum, fermentation with an external vacuum flash tank, liquid extraction, supercritical fluid extraction, membrane aided liquid extraction, inert gas stripping, pervaporation, membrane distillation, reverse osmosis, adsorption, phase separation by salt addition, and reactive extraction. A number of reviews including some or all of the above processes have been published on in situ recovery of ethanol [2-7]. However, a direct comparison of all these processes on a technical and economic basis is not available.

The purpose of this paper is to evaluate some of the more traditional ethanol recovery schemes on a technical and economic basis and to lay the groundwork for further comparisons. Specifically, identical plant design bases are used to compare the various processing alternatives. Capital equipment costs and operating costs are evaluated and an overall production cost is calculated. Furthermore, since bio-ethanol as a renewable fuel can mitigate environmental problems associated with fossil fuel combustion, the energy consumption of the various alternatives is calculated and compared. These comparisons are meant to identify weaknesses and strengths in the different schemes and to find potential processing improvements. Additionally, this work will help set minimum energy and economic targets for future novel systems. Of course, since simplified flowsheets are used in the comparisons, the economic and energy targets calculated are only valid for the scope of the flowsheets presented and should not be taken to be representative of the entire ethanol production process.

3.2. Process Evaluations

3.2.1. Processing Alternatives

The six processing alternatives presented schematically in Figure 3.1 were compared based on their economic feasibility and energy efficiency. The fermentation process, including product inhibition by ethanol, was an integral part of the modeling and is described in the next section. Whenever possible, the bottoms stream leaving the distillation columns was used to preheat the distillation column feed stream (not shown on diagrams). Brief descriptions of the six alternatives are provided below.

The number of trays in the distillation column, used in schemes III to VI, was optimized using an inlet feed concentration of 5 % (by mass) ethanol. The production cost using this single column was determined as a function of the number of trays needed to obtain 90 % (by mass) ethanol distillate at a recovery of 99 %. Little improvement in cost was observed beyond 30 trays and this number was used for simulations in schemes III to VI. The reflux ratio and diameter of the column were allowed to vary in order to meet the distillation constraints of 90 % (by mass) ethanol concentration in the product stream and 99 % recovery.

3.2.2. Alternative I: Steam Stripping and Distillation

The first alternative represents a basic process in which a simple steam stripping column is used to remove dissolved CO₂ and produce a concentrated ethanol stream that is then fed to

the final distillation column. In this case, the steam stripping column was designed to have 12 ideal stages with a vapour phase draw from the second stage from the top of the column. This draw stream had a composition of approximately 45 % (by mass) ethanol and was subsequently sent to the distillation column which operated with 20 ideal stages.

3.2.3. Alternative II: Flash Fermentation

The flash fermentation process has been proposed as a potential efficient in situ ethanol recovery technique [8]. In this scheme, a series of vacuum flash tanks are used to recover ethanol. Further purification is then carried out via distillation. In this study, two alternatives to the basic process shown in Figure 3.1 were considered. The first case, denoted as IIa throughout this document, does not include a steam stripping column. Instead, one simple distillation column with 20 ideal stages is simply used for further purification. In the second case, denoted as IIb, 80 % of the total ethanol product flow rate is recovered as vapour from the flash system while the remainder is recovered as in alternative I.

3.2.4. Alternative III: Single Column Distillation

Alternative III represents the simplest case where the centrifuged fermentation broth is fed directly to a distillation column. In this case, the distillation column was designed to have 30 ideal stages.

3.2.5. Alternative IV: Two-Column Distillation

In the fourth process, two distillation columns operating at different pressures are used to recover the ethanol. The column pressures must be set such that the condenser of the first column may be used as the reboiler for the second column [9]. In this case, both columns were designed having 30 ideal stages. The case considered in this study was when the first column operates at atmospheric pressure and the second column operates at 25 kPa.

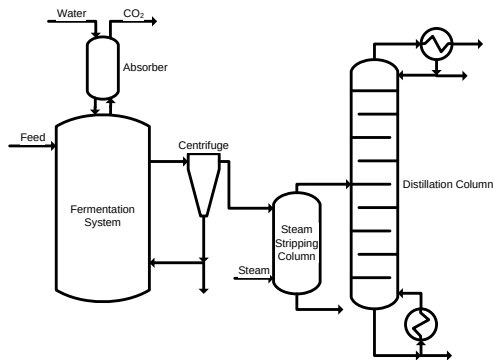
3.2.6. Alternative V: Distillation with Heat Pump

Distillation with a vapour recompression system to recover heat from the condenser has been cited as another feasible ethanol recovery option [10]. In this case, water was considered as the heat transfer fluid in the vapour recompression loop and the atmospheric distillation column was designed having 30 ideal stages.

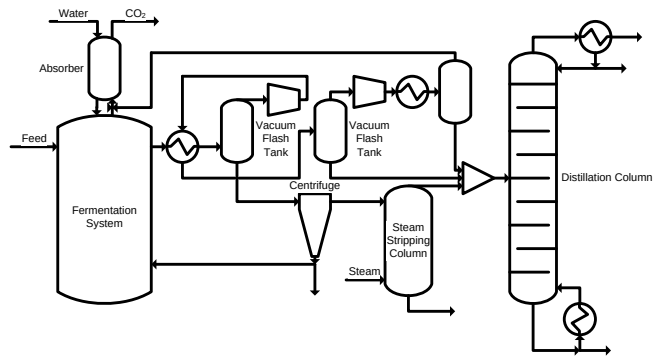
3.2.7. Alternative VI: Modified Flash Fermentation

Scheme VI presents a potential improvement on the flash fermentation process. In this case, only one flash stage is used and distillation is carried out under vacuum with an integrated vapour recompression system. Again, the distillation column was designed with 30 ideal stages. Since 99 % of the ethanol produced during fermentation is recovered in the flash system, the centrifuge serves only to concentrate the cells in the recycle stream and the clarified solution can be treated as wastewater.

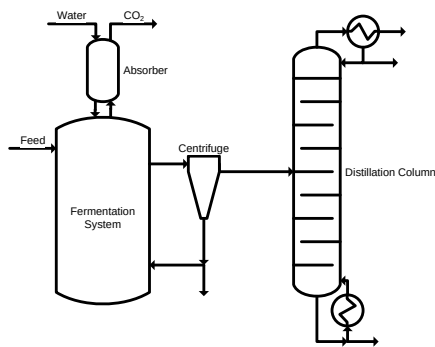
I. Basic Steam Stripping – Distillation:



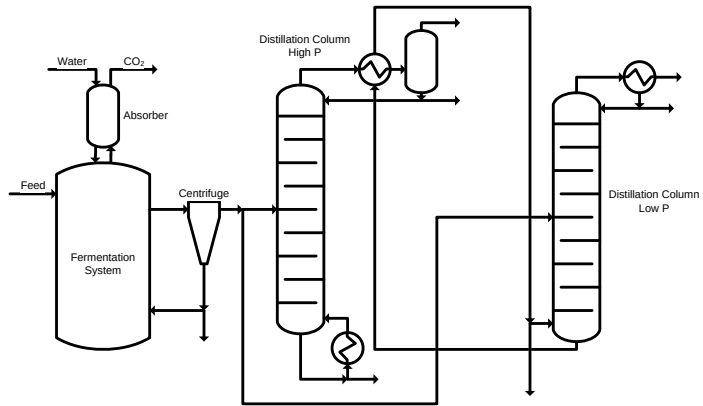
II. Flash Fermentation – Distillation:



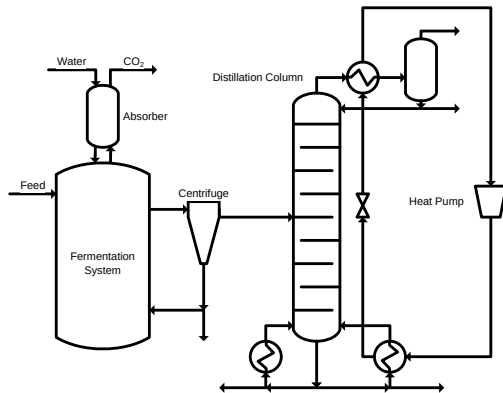
III. Single Column Distillation:



IV. Two-Column Distillation:



V. Distillation with Heat Pump:



VI. Flash – Vacuum Distillation:

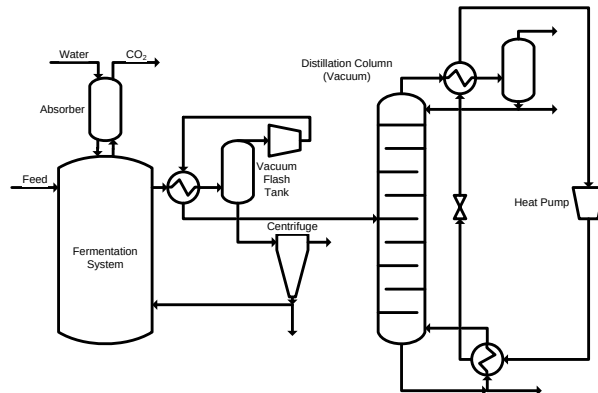


Figure 3.1. Six alternative schemes for ethanol recovery.

3.2.8. Fermentation Modelling

Ethanol fermentation from glucose approximately follows the Gay-Lussac equation.



As mentioned earlier, ethanol fermentation is product inhibited implying that the production rate decreases with increasing ethanol concentration. The limiting ethanol concentration as well as the decrease in production rate depends on the sugar source and microorganisms employed [11]. However, in general the specific ethanol production rate can be adequately represented by the following equation.

$$r_E = r_{E,max} \left(\frac{S}{S + C_m} \right) \left(1 - \frac{E}{E_{max}} \right)^n \quad (2)$$

Where r_E is the ethanol production rate, $r_{E,max}$ is the maximum ethanol production rate, S is the substrate concentration, C_m is a Monod constant, E is the ethanol concentration and E_{max} is the maximum ethanol concentration. Furthermore, the cell production rate (r_X) and the substrate consumption rate ($-r_S$) can be calculated using proportionality constants representing the efficiency of cell production (E_X) and the specific ethanol yield (Y).

$$r_S = -\frac{r_E}{Y} \quad (3)$$

$$r_X = E_X r_E \quad (4)$$

Finally, the rate of carbon dioxide production is assumed to follow the stoichiometry of Equation 1. In this investigation, the coefficients given by Maiorella et al. [12], based on the data of Bazua and Wilke [11] for *Saccharomyces cerevisiae* ATCC No. 4126, were used in the fermentation model. This model has previously been employed in economic evaluations and the coefficients are given in Table 3.1 [12,13].

Table 3.1. Fermentation Model Parameters

$r_{E,max}$ (L/h)	1.85
C_m (g/L)	0.315
E_{max} (g/L)	87.5
n	0.36
Y	0.434
E_X	0.249

3.2.9. Process Simulation

Process simulation was carried out using the commercial steady-state process simulation software Aspen HYSYS 2004.2. This software includes models for commonly used unit operations as well as comprehensive component, thermodynamic and property libraries. The fermenter was modeled as a simple continuously stirred reactor and the fermentation model was integrated into the simulation as a user-defined unit operation written in the Microsoft Visual Basic programming language. The yeast cells were modelled as $\text{CH}_{1.64}\text{O}_{0.52}\text{N}_{0.16}$ having a molecular weight of approximately 25.5 g/mol and a dry cell density of approximately 388 kg/m³ for simulation purposes [14,15].

For all simulations, the residual glucose concentration leaving the fermenter was set at 2.8 g/L, the cell concentration was set at 100 g/L and the ethanol production rate was set at 100 million L/y. The ethanol concentration inside the fermenter, which also corresponds to the ethanol concentration in the stream leaving the fermenter (perfect mixing), was varied for different simulations. It follows from the fermenter model that the feed flow rate, feed substrate concentration and fermenter volume are calculated variables.

3.2.10. Plant Design Basis

The processing alternatives were evaluated taking into account the energy consumption and operating and capital costs for major equipment. Specifically, the fermentation system, including the centrifuge, and ethanol recovery equipment were taken into account. Solids recovery equipment was neglected since it was assumed that this would be similar for all the cases considered. The ethanol production rate was set at 100 million L/y with a final ethanol concentration of 90 % (by mass). Ethanol dehydration above 90 % (by mass) was not considered as it would be identical for all schemes. This latter step is often performed by pressure-swing adsorption.

Cost analysis was carried out using standard chemical engineering principles and the equations and figures given by Turton et al. [16] and Seider et al. [17]. The capital investment was calculated by the method given by Turton et al. [16]. To compare the alternatives on an economic basis, the production cost without raw materials was calculated. In this case, the production cost was calculated to be the sum of direct manufacturing costs (DMC), fixed manufacturing costs (FMC) and general expenses (GE).

$$\text{Production Cost} = \text{DMC} + \text{FMC} + \text{GE} \quad (5)$$

Table 3.2 summarizes the calculation method for the production cost. Further pertinent assumptions made in the design of the plant are listed in Table 3.3.

Table 3.2. Production Cost Calculation [16]

Direct Manufacturing Cost	
Utilities	C_{UT}
Operating Labour	C_{OL}
Supervisory and Clerical	$0.18C_{OL}$
Maintenance and Repairs	$0.06FCI$
Operating Supplies	$0.009FCI$
Laboratory Charges	$0.15C_{OL}$
Fixed Manufacturing Cost	
Depreciation	10 year Straight Line
Taxes and Insurance	$0.032FCI$
Overhead	$0.708C_{OL} + 0.036FCI$
General Expenses	
Administration	$0.177C_{OL} + 0.009FCI$
Distribution and Selling	$0.11COM$
Research and Development	$0.05COM$

Table 3.3. Plant Design Assumptions

Plant Operation (d/y)	330
Operating Labour (people/shift)	6
Wages (\$/person.h)	25
Process Water (\$/1000kg)	0.067
Cooling Water (\$/1000m³)	14.8
Steam (LP) (\$/1000kg)	12.68
Electricity (\$/kWh)	0.06
Salvage Value (\$)	0
Plant Life (y)	10

3.3. Results and Discussion

3.3.1. Technical Considerations

It is important to realize that certain assumptions must always be made when evaluating and comparing various competing plant designs. As such, only the fermentation and recovery systems are included in the designs, as shown in the diagrams in Figure 3.1. All costs associated with pre-treatment and waste water treatment required are linked to plant capacity and feedstock. These were not included in calculations as they would be approximately the same for all schemes presented.

Furthermore, the comparisons are meant to be somewhat all inclusive in that they are independent of the glucose source. That is, a specific glucose feed concentration is not assumed. Rather a residual glucose concentration of 2.8 g/L is assumed and the ethanol production rate is set at the required 100 million L/y. This implies that, as the ethanol concentration in the fermenter is varied, the required glucose concentration in the feed also varies. Figure 3.2 shows how the glucose concentration in the feed varies with the ethanol concentration in the fermenter from 20 g/L to the maximum possible concentration beyond which microorganism growth and ethanol synthesis is impossible as indicated by a dashed line in Figure 3.2. The cell concentration in the fermenter was set at 100 g/L for all trials. Clearly the variation of the required glucose concentration with the ethanol concentration presents a complication since dilute sugar sources would need to be concentrated and concentrated sugar sources would require dilution. However, this complication is not considered in this study.

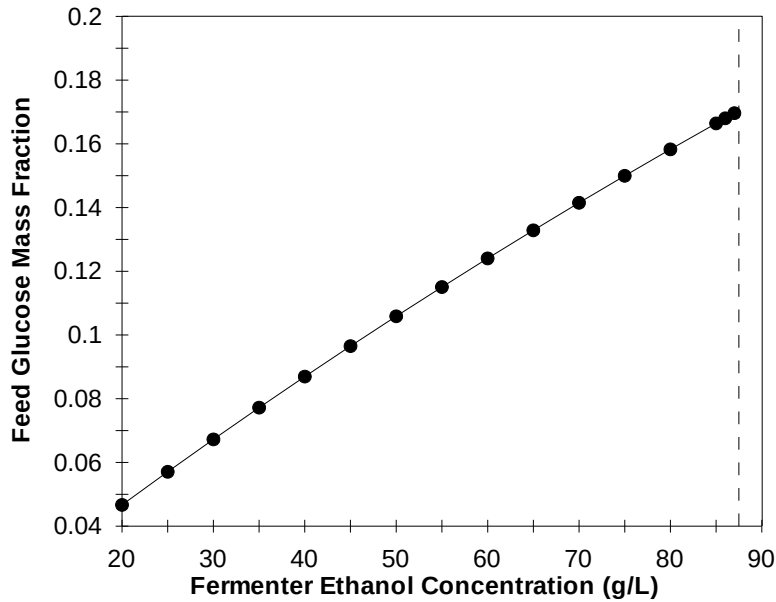


Figure 3.2. The dependence of glucose concentration in the feed on the ethanol concentration leaving the fermenter for a cell concentration of 100 g/L, a residual glucose concentration of 2.8 g/L and a production rate of 100 million L/y.

Lastly, it is clear that when the fermentation broth is contacted with a high temperature heat transfer surface such as a reboiler, considerable fouling may occur. To alleviate this problem, steam could be directly injected into the bottom of the distillation columns used in ethanol recovery. However, since the reboilers represent a relatively small capital cost, this alternative is expected to give almost identical results to the ones that are presented. The condensed steam would be removed as water at the bottom of the column.

3.3.2. Energy Considerations

If ethanol is to be a truly successful biofuel that will be both renewable in the long term and help to alleviate environmental problems such as global warming, then the energy consumption of the production process must be minimized. Furthermore, the economics of ethanol production are directly influenced by energy consumption in the form of steam and electricity. Figure 3.3 shows the variation of the total energy consumption as a function of the ethanol concentration leaving the fermenter. To provide a convenient basis of comparison, the energy consumption is normalized with respect to the ethanol production rate. This figure clearly shows that processes I, II and III are quite similar in their energy utilization while processes IV, V and VI provide a definite improvement with respect to the energy requirement. Furthermore, it is clear that process VI presents the best case from an energy point of view followed by

processes V and IV. The advantages of these processes are further intensified at lower ethanol concentrations since the energy requirement increases drastically for ethanol concentrations below approximately 50 g/L. Additionally, it can be seen on Figure 3.3 that processes I, II and III become very inefficient at low concentrations and the energy consumption even begins to approach the heat of combustion, which is approximately 29 800 kJ/kg for pure ethanol [18].

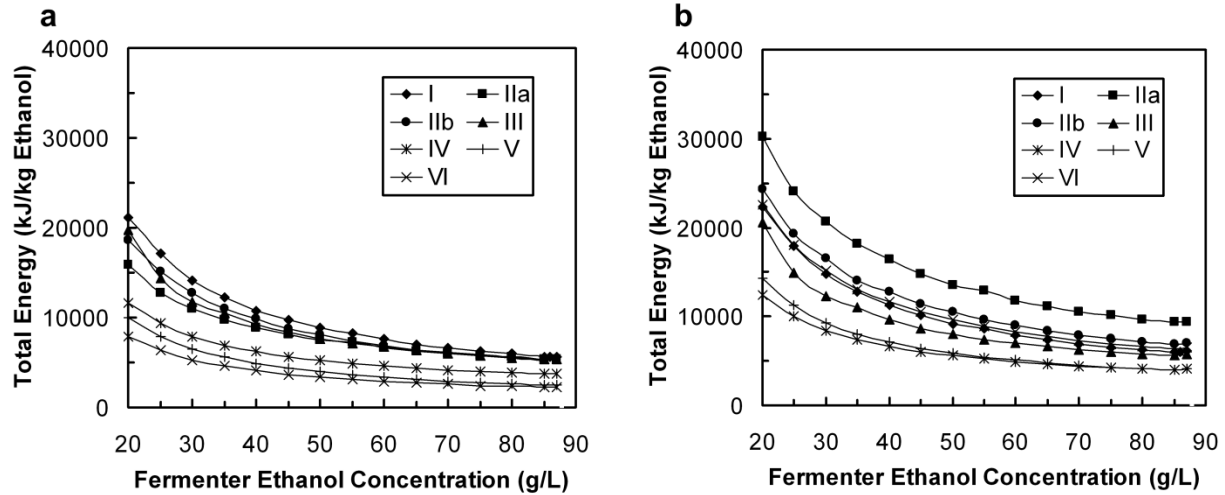


Figure 3.3. The variation of the total energy consumption for the alternative ethanol production processes with the ethanol concentration leaving the fermenter (a, electrical and heat energy are used equivalently; b, total energy is expressed in heat equivalent units with the efficiency of conversion to electrical energy being 35 %).

Since the distribution of the total energy between steam and electricity is also important, especially for economic reasons, Figure 3.4 shows this distribution for all the presented processing options for an ethanol concentration of 80 g/L. From this figure, it is clear that the processes requiring vapour compression require a proportionally higher amount of electricity rather than steam while the distillation options require mainly steam.

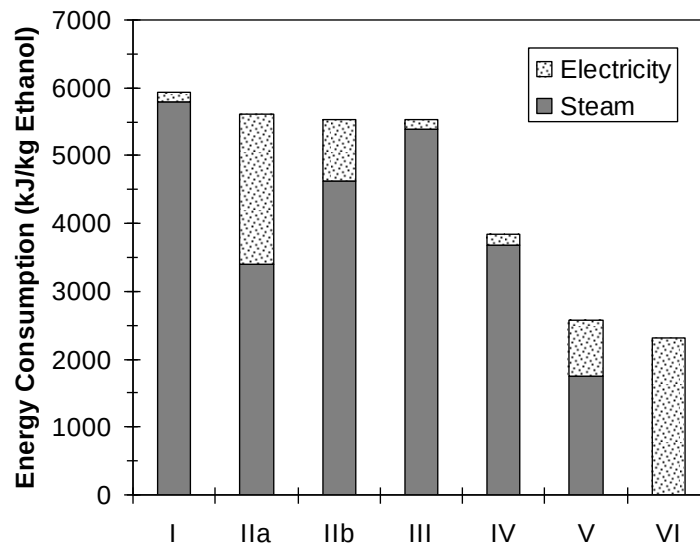


Figure 3.4. Breakdown of the total energy requirements between steam and electricity for the presented processing options at an ethanol concentration of 80 g/L.

3.3.3. Economic Considerations

An alternative ethanol production process must undoubtedly be economically competitive to be implemented on an industrial scale. Thus, it is insufficient to simply present a comparison based on energy consumption. That is, the capital and operating costs must also be included in the comparison.

Figure 3.5 shows the capital costs for all the processes at ethanol concentrations of 40 g/L and 80 g/L. Evidently, processes I, III and IV have relatively similar and relatively low capital costs while process V has an intermediate capital cost, and processes II and VI require relatively high capital investments. This implies that processes I, III, IV and possibly V present the best cases on a capital investment basis and processes II and VI likely require excessive capital to be competitive.

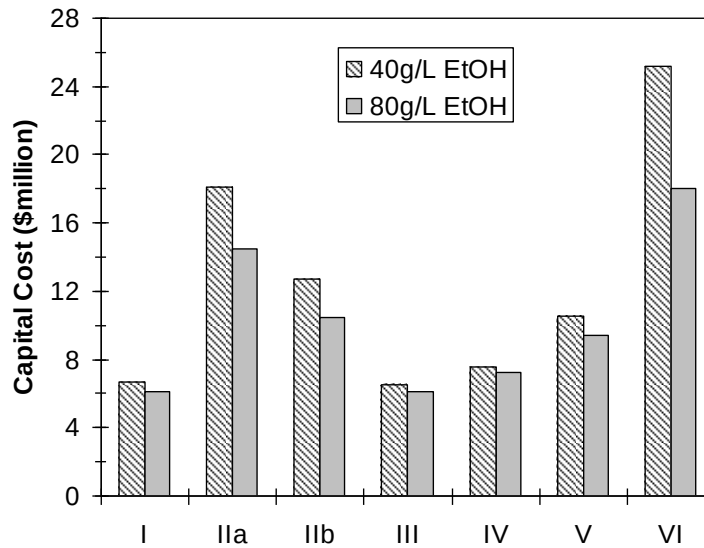


Figure 3.5. Capital equipment costs for all presented processing options at ethanol concentrations in the fermenter of 40 g/L and 80 g/L.

Figure 3.6 shows the breakdown of the capital cost between the fermentation system, distillation system and other equipment for the various schemes at an ethanol concentration of 80 g/L. The other costs mentioned in Figure 3.6 include compressors, pumps, heat exchangers, the absorber and centrifuge. Since the various recovery schemes significantly differ with respect to this type of equipment, it is to be expected that these may be quite variable and high in some cases. As expected, the cost of the fermentation system is constant for all processes since it is directly proportional to the fermenter volume. On the other hand, the costs of the distillation system and other equipment are relatively variable. It is apparent that the systems that employ compressors for vapour recompression heating have relatively high capital costs. It is also clear that these additional costs are not completely balanced by a proportional cost reduction in the distillation system.

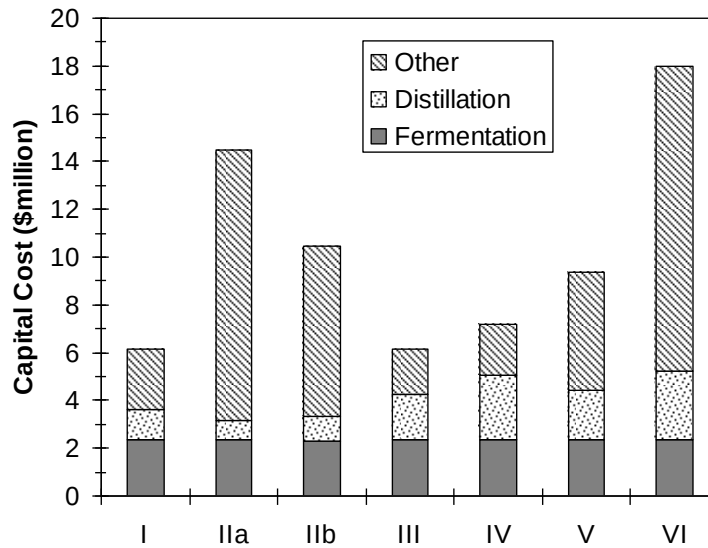


Figure 3.6. Breakdown of the capital cost between various plant sections for all the processing alternatives at an ethanol concentration of 80 g/L.

The utility costs represent another important factor contributing to the overall economic feasibility of a process. Figure 3.7 displays the utility costs for all the alternatives at ethanol concentrations of 40 g/L and 80 g/L. It is apparent that options IV and V result in the lowest utility costs, while options I, III and VI require intermediate utility costs and option II results in the highest utility costs.

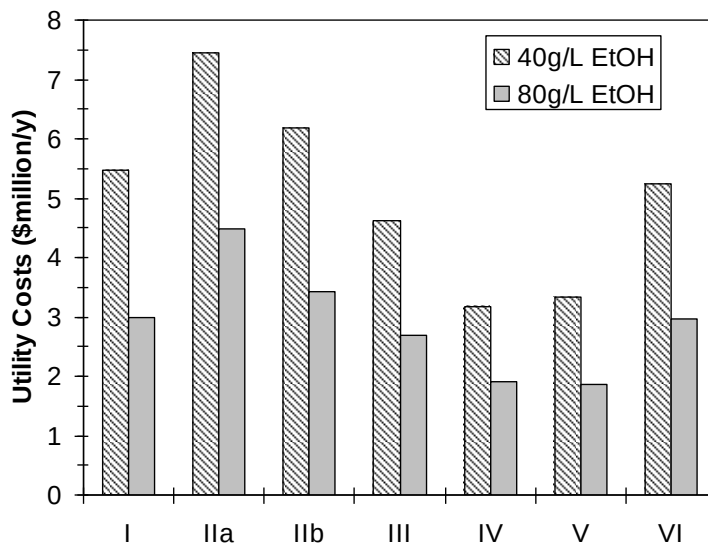


Figure 3.7. Utility costs for all presented processing options at ethanol concentrations of 40 g/L and 80 g/L.

Finally, the overall economic feasibility of an ethanol production process depends on both the capital investment and the operating cost and can be represented in terms of a production cost. As discussed earlier, the production cost in this case does not include the cost of the raw material since it is identical for all alternatives. The production cost for the alternative processing schemes is presented as a function of the ethanol concentration in Figure 3.8. From this figure, it is clear that processes II and VI are not economical, as shown by their relatively high production costs for all ethanol concentrations. Conversely, processes I, III and V give similar production costs for relatively high ethanol concentrations (greater than approximately 60 g/L) and show distinctive differences for lower ethanol concentrations. Furthermore, alternative IV is shown to yield the lowest ethanol production cost for all presented ethanol concentrations.

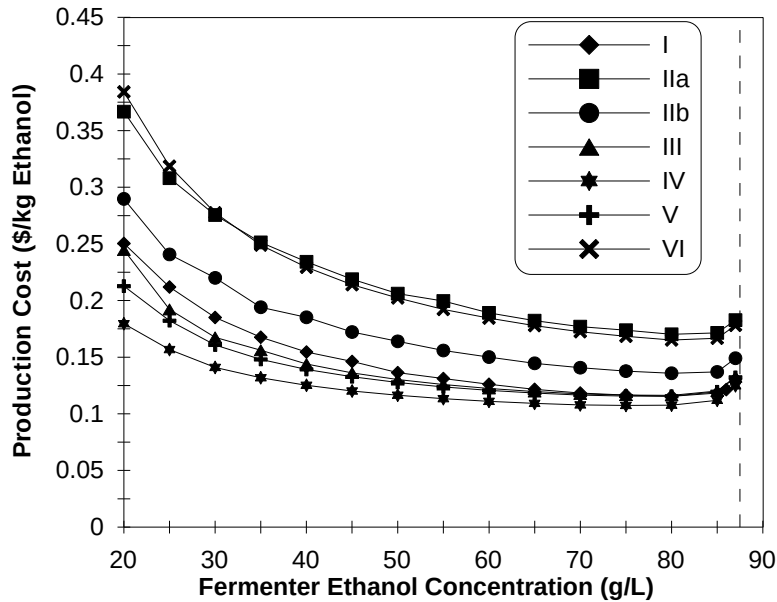


Figure 3.8. The variation of the ethanol production cost for the alternative ethanol production processes with the ethanol concentration leaving the fermenter.

3.3.4. Rankings

From the above discussion regarding both the energy consumption and economic feasibility of the six processing options, it is possible to rank them based on their energy efficiency and economic feasibility. Quantitatively, this ranking can be shown by plotting the energy consumption against the ethanol production cost, as shown in Figure 3.9. It is of course the objective to minimize both the energy consumption and the production cost. Thus, points closer to the origin of Figure 3.9 are preferable.

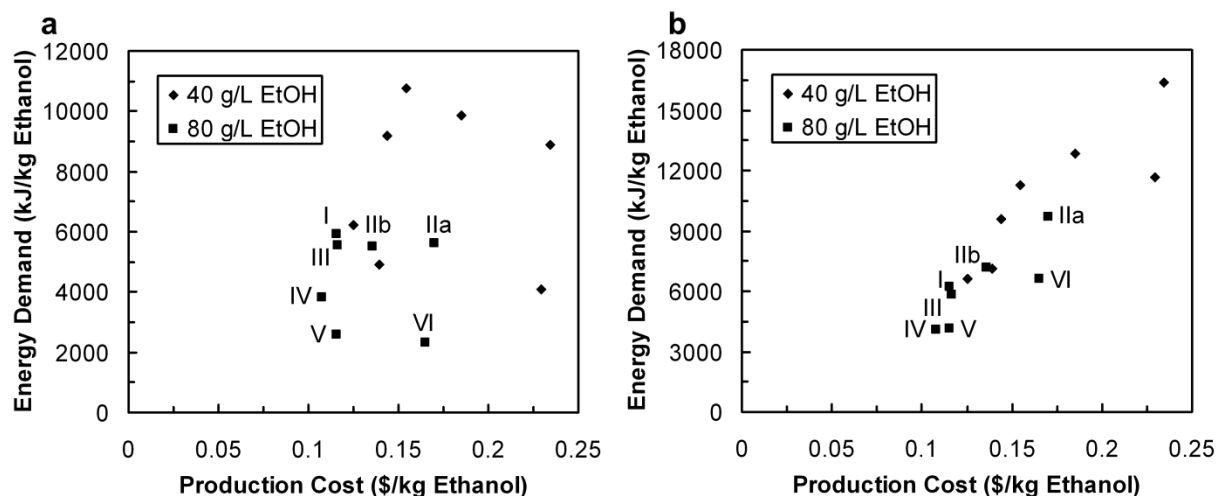


Figure 3.9. The normalized total energy consumption as a function of the normalized production cost for all processes at fermenter ethanol concentrations of 40 and 80 g/L, indicating economic and energy rankings (a, electrical and heat energy are used equivalently; b, total energy is expressed in heat equivalent units with the efficiency of conversion to electrical energy being 35 %).

From Figure 3.9, it is clear that options IV and V represent the best alternatives from both an economic and energy point of view. However, it is clear that option IV provides a slight economic advantage and option V is more energy efficient. Furthermore, it is shown that the other options suffer serious drawbacks from an economic viewpoint (VI), from an energy viewpoint (I, III) or from both (II).

3.3.5. Other Costs

As stated earlier, certain costs including the cost of raw materials, ethanol dehydration, pre-treatment and auxiliary solids recovery were not considered in the comparison to permit some generalization of the results and for simplicity. Ethanol dehydration is commonly accomplished through pressure swing adsorption. Pre-treatment and solids recovery costs vary depending on the raw materials used. Raw material costs can be highly variable. Some feedstock costs are presented in Table 3.4 to highlight the degree of variability [19].

Table 3.4. Selected Feedstock Costs [19]

	Cost (\$/L Ethanol)
U.S. Wet Milling Corn	0.106
U.S. Dry Milling Corn	0.140
U.S. Sugar Cane	0.391
U.S. Sugar Beets	0.417
Brazil Sugar Cane	0.079
E.U. Sugar Beets	0.256

3.4. Conclusions

A number of conclusions can be drawn from the above comparisons. It can be concluded that the two-column distillation option represents the most economical and, therefore, likely the most feasible option from the alternatives considered. Conversely, considerable energy savings can be realized if a vapour recompression system is integrated with the distillation column. Further energy savings are possible if a flash fermentation system is integrated with a vacuum distillation system that is heat integrated with a vapour recompression heat recovery system. However, this option is very expensive from an invested capital point of view and is therefore not feasible.

Furthermore, it has been shown that both two-column distillation and distillation with vapour recompression provide substantial energy savings over the other ethanol recovery schemes. This conclusion agrees well with the results of Larsson and Zacchi.⁹ It has also been shown that flash fermentation, while being somewhat competitive from an energy standpoint is not competitive economically. Lastly, the above analysis provides targets in terms of energy efficiency and economics that novel ethanol recovery schemes should match if they are to be competitive. This is particularly important for the development of new systems and was one of the main objectives of this study. Of course, since only limited flowsheets were used in the comparisons, these targets are only representative of the scope of the flowsheets presented.

3.5. Acknowledgement

The authors would like to acknowledge the Natural Science and Engineering Research Council of Canada for its financial support.

3.6. Nomenclature

C_m	Monod constant
C_{OL}	Operating labour cost (\$/y)
COM	Cost of Manufacturing (\$/y)
C_{UT}	Utility cost (\$/y)
DMC	Direct Manufacturing Costs
E	Ethanol concentration (g/L)
E_{max}	Maximum ethanol concentration (g/L)
E_X	Efficiency of cell production
FCI	Fixed Capital Investment (\$)
FMC	Fixed Manufacturing Costs
GE	General Expenses
r_E	Specific ethanol production rate (g Ethanol/g Cells.h)
$r_{E,max}$	Maximum ethanol production rate (L/h)
r_S	Specific substrate consumption rate (g glucose/g cells.h)
r_X	Specific cell production rate (g cells/g cells.h)
S	Substrate concentration (g/L)
Y	Specific ethanol yield

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SECTION II. MEMBRANE DEPHLEGMATION: A NOVEL HYBRID SEPARATION SYSTEM

INTRODUCTION TO MEMBRANE DEPHLEGMATION

4.1. Introduction and Objectives

Section I of this dissertation provided an overview of the ethanol production process and highlighted some key inefficiencies in the ethanol recovery process. Depending on the feedstock and specific process used, the separation processes can consume more than 50 % of the total process energy. This not only reduces the value of ethanol as an energy carrier but also decreases the economic viability of ethanol production. Clearly, there is a need for a more efficient ethanol recovery processes. This chapter introduces a new hybrid distillation-pervaporation separation process for enhanced ethanol recovery, dubbed “Membrane Dephlegmation”. Fundamental aspects of closely related separation processes are briefly reviewed. This information is then combined to explain the basic idea behind Membrane Dephlegmation. Finally, an overview of the research methodology used to analyze the system in Chapters 5 through 7 is presented.

4.2. Review of Pertinent Ethanol-Water Separation Methods

4.2.1. Distillation and Dephlegmation

Distillation exploits differences in relative volatility to effect separation of a mixture of chemical components. In continuous processes, vapour and liquid phases contact each other countercurrently in a column, with the vapour flowing upwards and the liquid flowing down through the action of gravity. Continuous contacting of the two phases allows the more volatile components to accumulate in the vapour phase, while the less volatile components migrate to the liquid phase. The liquid leaving the bottom of the column is partially vaporized in a reboiler to generate the vapour stream traveling upwards through the column and a bottoms product. The vapour stream leaving the top of the column is either partially or completely condensed. A portion of the condensate is returned to the column (reflux) to generate the liquid stream traveling down the column. The product stream leaving the top of the system is referred to as the distillate. The reflux ratio is defined as the ratio of the reflux flow rate over the distillate flow rate. A schematic representation of a conventional distillation column is shown in Figure 4.1.

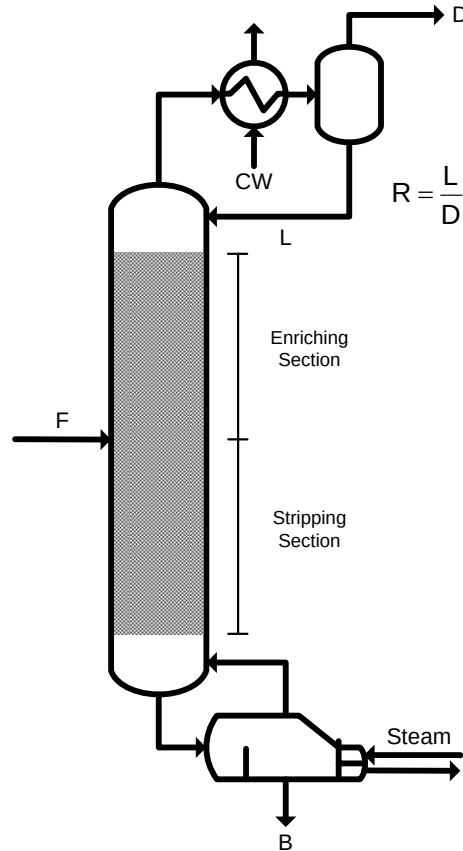


Figure 4.1. Schematic representation of a typical distillation column (F, Feed; B, Bottoms; D, Distillate; L, Reflux; R, Reflux Ratio; CW, Cooling Water).

The feed stream may enter the column as a liquid, vapour or two-phase system. Regardless, the section above the feed is usually referred to as the enriching section, while the lower section is referred to as the stripping section. Typically distillation columns either contain trays or packing to facilitate contacting of the two phases. However, wetted-wall columns, in which the liquid flows down the wall of a tube, are often used in experimental studies to determine heat and mass transfer rates. Although most columns operate under nearly adiabatic conditions, it is also possible to add or remove heat along the column's length to impact separation efficiency.

Dephlegmation is a process in which a vapour mixture flowing upwards is partially condensed on a vertical surface. The condensate then flows downwards due to gravity, inducing countercurrent contacting [1]. Similar to the enriching section of a distillation column, this contacting favours the condensation of less volatile components and the evaporation of more volatile species. However, unlike the enriching section of a distillation column, the

dephlegmation process is inherently non-adiabatic. The non-adiabatic nature of the process modifies heat and mass transfer rates, making it possible to alter column efficiency. Further, although it is technically possible, dephlegmation processes typically do not have an external reflux.

4.2.2. Pervaporation and Vapour Permeation

Pervaporation is a process in which a liquid feed stream is contacted with a selective membrane. Separation is achieved due to preferential sorption on and permeation through the membrane of one or more components. The components must be desorbed on the permeate side of the membrane. Vapour permeation is analogous to pervaporation, except the feed stream in contact with the membrane is in the vapour instead of the liquid phase. In either case, a driving force must be maintained by decreasing the partial pressure on the permeate side to facilitate transport across the membrane. Although this can be achieved using a simple vacuum pump or a sweep gas, the most economical alternative is usually to employ low temperature condensation coupled with a vacuum pump to purge permanent gases.

A number of organic, inorganic and composite membranes have been investigated for ethanol-water separation. These include both hydrophobic (ethanol permeating) and hydrophilic (water permeating) membranes. Generally, hydrophilic membranes have been more successful, due to their higher separation factors. Many hydrophilic organic membranes are available. However, polyimide membranes are commonly regarded as the best polymeric membranes for ethanol dehydration [2]. In fact, polyimide membranes have been commercialized specifically for this purpose [3]. Inorganic membranes generally provide higher flux and selectivity albeit at an increased production cost. Again, many different inorganic materials have been investigated for ethanol dehydration. However, NaA zeolite membranes have been particularly successful and are commercially available specifically for this purpose [4,5].

4.2.4. Hybrid Systems

In the conventional ethanol separation process, a distillation column is used to increase the concentration of the vapour stream leaving the beer column to near the azeotrope. The distillate is then dehydrated to produce anhydrous ethanol. Traditionally, pervaporation and vapour permeation have been applied only to dehydrate this stream. However, a number of

investigations have attempted to integrate the distillation and pervaporation/vapour permeation processes directly to synthesize more efficient hybrid processes.

Generally, two types of hybrid processes have been investigated. Several studies have attempted to optimize pervaporation system designs when it is used as the dehydration stage following distillation. Other studies have integrated the pervaporation process directly with other separation processes, using complex recycle streams and energy integration. Lipnizki et al. [6], presented a review of hybrid pervaporation processes. Included in their paper was a discussion of different approaches for integrating pervaporation with distillation in the ethanol production process. Frolkova and Raeva [7] provided a comprehensive review of methods available for ethanol dehydration. Their discussion also included a hybrid pervaporation-distillation process for breaking the ethanol-water azeotrope. Szitkai et al. [8] attempted to optimize the performance of a hybrid distillation-pervaporation process for ethanol separation. Their study employed a Mixed-Integer Nonlinear Programming (MINLP) approach to minimize the total annual cost.

Vane [9] reviewed various approaches to integrate pervaporation into the recovery of products from biomass fermentation. Ethanol production was one of the main topics covered. The review also presented several original processes employing both hydrophobic and hydrophilic membranes in conjunction with distillation to improve process efficiency. More recently, this group has proposed an innovative process, which combines distillation and vapour permeation to improve process energy efficiency [10-12]. Several variations were proposed but the general idea was to exploit the selective nature of the vapour permeation membrane together with vapour compression to improve separation performance and reduce energy load.

Del Pozo Gomez et al. [13,14] proposed a novel pervaporation process, in which both vapour and liquid streams are fed to a pervaporation module. The vapour and liquid phases are separated by a conductive wall and only the liquid is exposed to the membrane surface. As the liquid permeates through the membrane, heat is lost. Conventionally, this would cause a temperature drop, decreasing the permeation flux along the length of the module. However, in the proposed process, the heat lost due to permeation is supplied by partial condensation of the vapour stream. In a similar process, Fontalvo et al. [15,16] suggested a process in which a two-phase vapour-liquid mixture is contacted directly with a membrane surface. Again, the goal was that condensation of the vapour should provide energy to augment the pervaporation process.

Further, the presence of the two-phase mixture increased turbulence at the membrane surface and thereby decreased concentration polarization effects.

4.2.5. Membrane Dephlegmation

In this dissertation, a new hybrid distillation-pervaporation process is proposed. A detailed analysis of the separation process is presented in subsequent chapters, but this section introduces the basic idea behind the process. The next subsections in this chapter provide an overview of the experimental and theoretical investigations carried out to explore process performance.

The envisioned process is applicable to enriching the vapour stream leaving the beer column. However, it is intended that the process will also reduce overall energy demand by decreasing the recycle load on the steam stripping column. A schematic representation of the proposed process is shown in Figure 4.2. The proposed process uses a vertically-oriented pervaporation membrane. The experimental studies presented in this work employed a tubular hydrophilic NaA zeolite membrane but conceivable other membranes could be used. The vapour stream enters at the bottom and flows upward through the membrane module. As in a conventional distillation process, the vapour leaving the top of the module is condensed and partially refluxed to the membrane. The liquid reflux is allowed to flow downward on the membrane surface, facilitating two critical phenomena. First, the vapour and liquid streams are in countercurrent contact, thereby allowing enrichment of volatile components in the vapour stream (distillation). Secondly, the liquid exposed to the membrane undergoes partial dehydration due to the selective pervaporation of water through the hydrophilic membrane. The selective removal of water from the liquid stream changes both the material and energy balances in the system and therefore has a complex impact on the interaction of the vapour and liquid phases. Chapters 5 and 6 present a detailed discussion surrounding the impact that pervaporation has on the distillation process and vice versa.

Clearly, the proposed process is a hybrid distillation-pervaporation process. However, since pervaporation removes energy as well as mass from the system, the process is also similar to dephlegmation. That is, the pervaporation process drives partial condensation and thus, generates an internal reflux. Due to these similarities, the process has been named “Membrane Dephlegmation”.

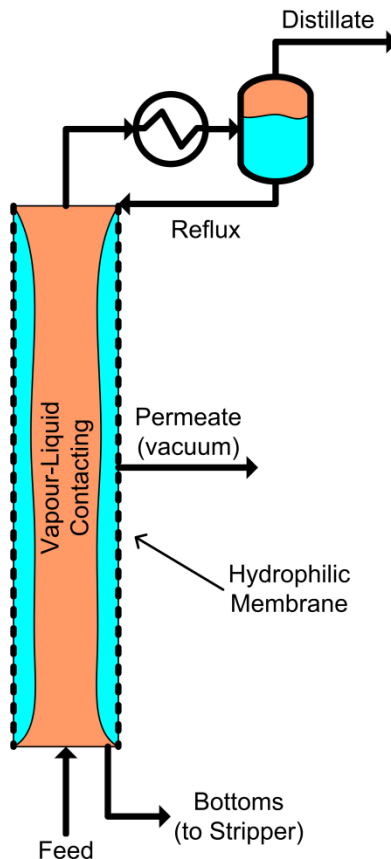


Figure 4.2. Schematic representation of the Membrane Dephlegmation process.

4.3. Research Methodology

In this dissertation, Membrane Dephlegmation has been studied to characterize performance and explore its potential for improving ethanol production efficiency. Both numerical and experimental investigations were performed. Detailed numerical analyses of the process are presented in Chapters 5 and 6. Chapter 7 provides a detailed summary of the completed experimental studies.

Chapter 5 provides a detailed overview of the Membrane Dephlegmation process. Simultaneously, important features of wetted-wall distillation are discussed. A simple design model is derived for both Membrane Dephlegmation and wetted-wall distillation to facilitate the discussion and explain the physical phenomena occurring in the systems. Exploratory simulations are performed for a variety of operating conditions to investigate system performance. Composition, temperature and velocity profiles are presented and used to explain the impact of operating parameters on efficiency and compare Membrane Dephlegmation with distillation.

In Chapter 6, the design model is used to carry out a detailed parametric study for the Membrane Dephlegmation process. The impact of critical operating parameters including feed flow rate, feed concentration, permeate pressure and reflux ratio on separation efficiency is investigated. Additionally, an analysis using McCabe-Thiele plots is presented to compare Membrane Dephlegmation to conventional distillation. The system's effect on the energy efficiency of the overall ethanol recovery process is also discussed.

A pilot-scale experimental system has been constructed to test performance and explore physical limitations. A detailed description of the pilot-scale system is provided in Chapter 7. Experimental data from this system are used to determine important model parameters and validate model predictions. Deviations of the model predictions from the experimental data are explained in terms of physical limitations in the experimental system and assumptions included in the model's derivation. Important physical limitations, including long-term membrane stability and flooding, are also investigated.

4.4. References

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A NEW HYBRID MEMBRANE SEPARATION PROCESS FOR ENHANCED ETHANOL RECOVERY: PROCESS DESCRIPTION AND NUMERICAL STUDIES

Jan B. Haelssig, André Y. Tremblay and Jules Thibault

Abstract

Ethanol is a biofuel that is produced through the fermentation of sugars derived from biomass. However, its usefulness as a fuel is partly limited by the energy intensive nature of the ethanol separation process. The ethanol recovery process is inefficient due to the dilute nature of the fermentation product and the presence of the ethanol-water azeotrope. This investigation presented a new hybrid separation process for energy efficient ethanol recovery. The new process is a hybrid of distillation and pervaporation. However, as opposed to most other hybrid processes, the distillation and pervaporation processes are combined in a single unit. An overview of the proposed system was provided and differences to the conventional separation process were highlighted. A mathematical model was derived to explain the transport phenomena occurring in the hybrid process. The model was then used to compare the process to distillation. It was shown that the hybrid process is capable of breaking the ethanol-water azeotrope. It was also demonstrated that the pervaporation process, which is associated with both material and energy transfer, induces partial condensation of the vapour and thereby effects the efficiency of vapour-liquid contacting. Simulations were presented to show the impact of reflux ratio and pervaporation flux on the performance of the process.

***This paper will be submitted to:** Chemical Engineering Science

5.1. Introduction

Ethanol is a biofuel that can be produced through the fermentation of saccharides found in biomass. However, the utility of ethanol as a biofuel is limited due to the energy intensive nature of its production process. Ethanol separation from water is a particularly energy intensive part of the production process, usually accounting for more than half of the total process energy requirement. Further, only low water content ethanol can be blended with gasoline and used in conventional gasoline burning engines. The requirement to produce anhydrous ethanol complicates the production process because ethanol and water form an azeotrope, making it impossible to recover pure ethanol through simple distillation. A special dehydration process is therefore required to recover anhydrous ethanol. The most commonly used methods for ethanol dehydration are currently extractive distillation, pressure swing adsorption of water on molecular sieves and pervaporation/vapour permeation of water through hydrophilic membranes [1].

In the conventional ethanol separation process, the fermentation mixture is first passed through a beer column. This column essentially behaves as a steam stripping column and produces a vapour stream having an ethanol composition between 30 and 60 % by mass (although this can vary). The bottoms stream leaving the beer column is composed mainly of water, with some residual solids. The vapour stream leaving the beer column usually enters another column, which operates as the enriching section of a distillation column. The bottoms product leaving the enriching column can go to a separate stripping column or be returned to the beer column. The distillate leaving the enriching column is normally near the azeotropic composition (approximately 90 % ethanol by mass). This distillate stream then undergoes dehydration to produce an anhydrous ethanol product [1,2].

Dephlegmation is a process in which a vapour, flowing upwards along a solid surface, is partially condensed. Liquid condensate is then allowed to flow in a countercurrent fashion to the vapour through the action of gravity. Similar to distillation, countercurrent contacting leads to the accumulation of the more volatile species in the vapour and the less volatile species in the liquid [3]. If this process is augmented with an external reflux, it becomes non-adiabatic distillation. A number of studies have shown the potential thermodynamic benefits of adding or removing varying quantities of heat from stages in a distillation column [4-8]. The addition or removal of heat modifies the temperature and composition profiles, which allows for the

minimization of the entropy production rate, thereby improving the thermodynamic efficiency of the column.

The ultimate goal of an ongoing set of studies is to synthesize a more efficient hybrid separation system to replace the enriching column and dehydration section of the ethanol recovery process. The proposed system is a hybrid of pervaporation, distillation and dephlegmation processes. In this study, an overview of the proposed system is provided along with a comparison to the conventional separation process. A mathematical model is then developed to describe the process and explain the transport phenomena governing its performance. Model results are then used to compare the system's theoretical performance to the wetted-wall distillation process. The geometry used to study the process is that of a commercially available NaA zeolite membrane. A literature model is used to describe transport through the membrane.

5.2. Process Description

To put the description of the proposed separation process into perspective, an overview of the conventional ethanol recovery process is first presented. Figure 5.1 presents a schematic overview of the conventional separation process. In reality, the feedstock pretreatment and fermentation steps of the ethanol production process are usually quite complicated. However, these are not the focus of this study and are therefore not discussed. The fermentation step produces a stream that usually contains at most 10 % ethanol by mass, if conventional substrates are used and at most 5 % ethanol by mass if cellulosic biomass is used. The fermentation broth then undergoes a separation step to remove insoluble solids. After solids separation, the dilute mixture is usually sent to a steam stripping column (beer column). The steam stripping column can operate with a reboiler or direct steam injection. In either case, ethanol is stripped from the feed stream to generate a vapour phase distillate stream that usually contains between 30 and 60 % ethanol by mass. The concentration of this distillate stream depends on the design of the beer column as well as the feed composition. The vapour stream exiting the beer column is then normally sent to a rectifying column, which increases the ethanol concentration to near the ethanol-water azeotrope. The concentration of the distillate stream leaving the rectifying column varies depending on the design of the column (i.e. reflux ratio and number of stages), but cannot exceed the composition of the ethanol-water azeotrope (~ 95.6 % by mass). Commonly the distillate concentration is between 90 and 94 % ethanol by mass. Normally, this distillate stream

then goes to a dehydration system (commonly Pressure Swing Adsorption, Pervaporation or Vapour Permeation), which produces anhydrous ethanol. The bottoms leaving the rectifying column is either recycled to the beer column or sent to a separate side stripping column to maintain a high ethanol recovery.

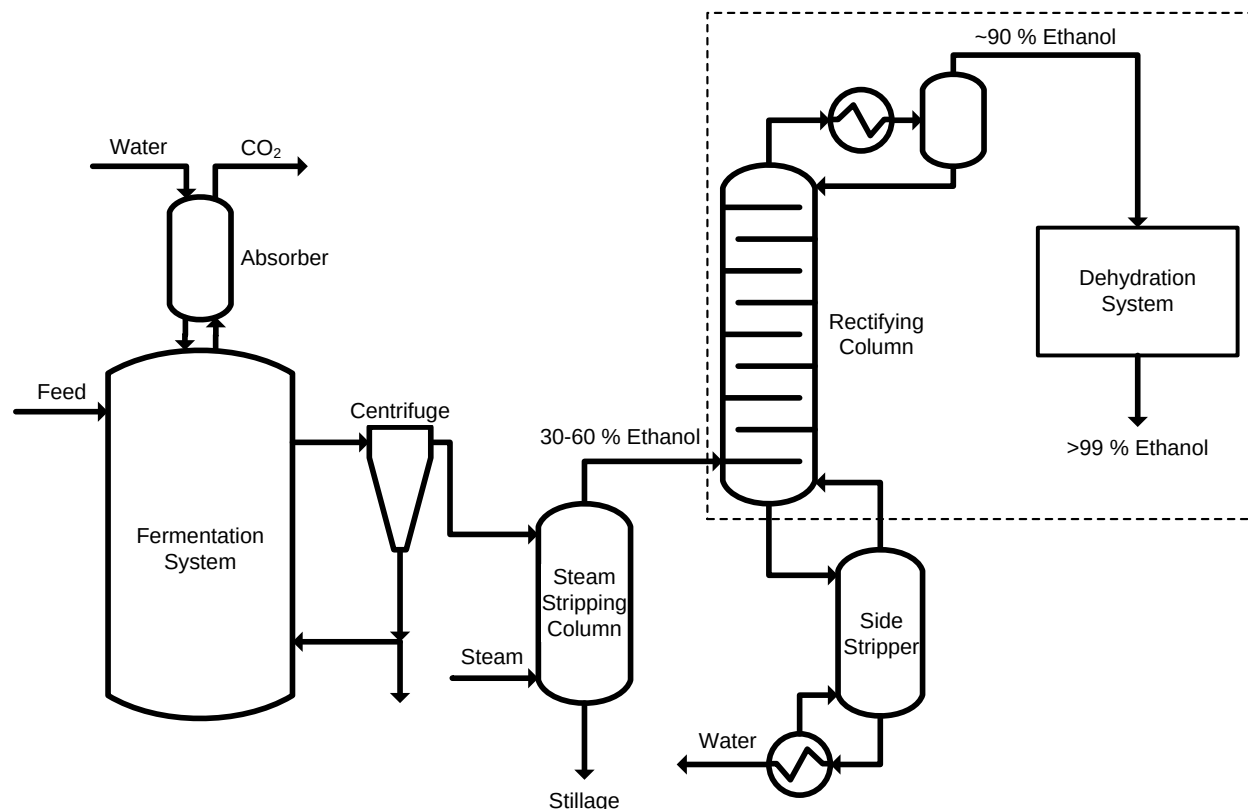


Figure 5.1. Overview of the conventional ethanol recovery process.

This study proposes a new hybrid pervaporation-distillation process. These types of hybrid processes have been the subject of a large number of investigations. To provide some background, a brief summary of the most relevant studies is provided here. Generally, two types of hybrid processes have been investigated. Several studies have attempted to generate optimal designs for using pervaporation as the dehydration stage following distillation. Other studies have integrated the pervaporation process directly with other separation processes, using complex recycle streams and energy integration. Lipnizki et al. [9] presented a review of hybrid pervaporation processes. Included in their paper is a discussion of different approaches to integrate pervaporation with distillation in the ethanol production process. Frolkova and Raeva [10] provided a comprehensive review of methods available for ethanol dehydration. Their discussion also included a hybrid pervaporation-distillation process for breaking the ethanol-

water azeotrope. Szitkai et al. [11] attempted to optimize the performance of a hybrid distillation-pervaporation process for ethanol separation. Their study employed a Mixed-Integer Nonlinear Programming (MINLP) approach to minimize the total annual cost.

Vane [12] reviewed various approaches to integrate pervaporation into the recovery of products from biomass fermentation. Ethanol production was one of the main topics covered. The review also presented several original processes employing both hydrophobic and hydrophilic membranes in conjunction with distillation to improve process efficiency. More recently, this group proposed an innovative process, which combines distillation and vapour permeation to improve process energy efficiency [13-15]. Several variations were proposed but the general idea was to exploit the selective nature of the vapour permeation membrane together with vapour compression to improve separation performance and reduce energy load.

Del Pozo Gomez et al. [16,17] proposed a novel pervaporation process, in which both vapour and liquid streams were fed to a modified pervaporation module. The vapour and liquid phases were separated by a conductive wall and only the liquid was exposed to the membrane surface. As the liquid permeates through the membrane, heat is lost. Conventionally, this would cause a temperature drop, decreasing the permeation flux. However, in the proposed process, the heat lost due to permeation is supplied by the partial condensation of the vapour stream. In a similar process, Fontalvo et al. [18,19] suggested that a two-phase vapour-liquid mixture be contacted directly with a membrane surface. Again, the goal was that condensation of the vapour should provide energy to augment the pervaporation process. Further, the presence of both phases increased turbulence at the membrane surface, thereby decreasing concentration polarization effects.

In this investigation, a hybrid membrane separation system is proposed to replace the rectifying column and dehydration system in the ethanol recovery process. A schematic representation of the proposed separation system is shown in Figure 5.2. A magnified view of this process is shown in Figure 5.3. In the new process, the vapour stream leaving the beer column enters the bottom of a vertically-oriented membrane unit and flows upwards through the module. As in a rectifying column, the vapour is partially condensed and refluxed to the system at the top of the membrane unit. The liquid reflux flows down the surface of the membrane through the action of gravity. This leads to countercurrent contacting of the vapour and liquid phases, allowing enrichment of the volatile components in the vapour phase. A vacuum pressure

is maintained on the permeate side of the membrane to maintain a driving force for the selective pervaporation of water. The pervaporation process is associated with a heat loss, since the permeating species must be vaporized. Thus, an energy flux also drives the partial condensation of the vapour phase. Clearly, the process includes aspects of distillation, dephlegmation and pervaporation. For this reason, the process will be referred to as Membrane Dephlegmation from here onward.

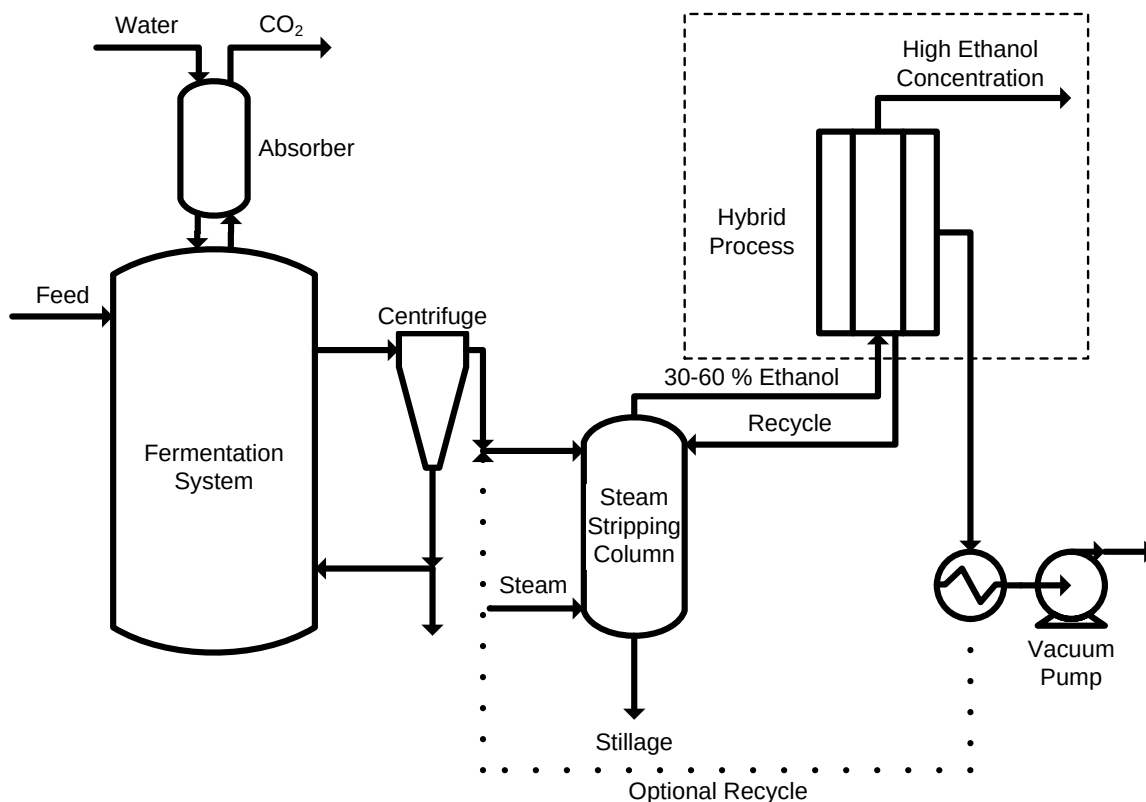


Figure 5.2. Overview of the ethanol separation process with the proposed hybrid separation process enclosed by the dashed box.

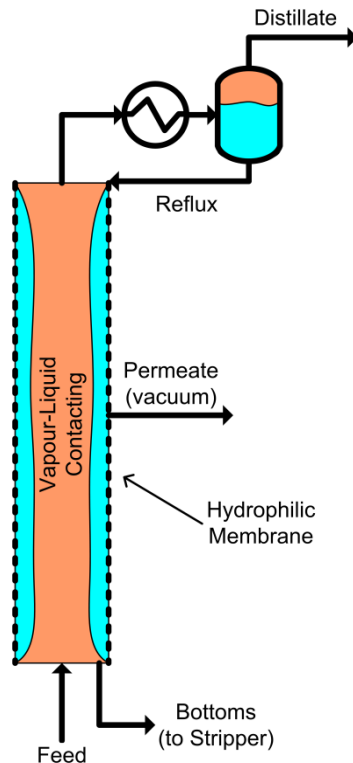


Figure 5.3. Details of the proposed hybrid process.

It is anticipated that the Membrane Dephlegmation process will be capable of producing a concentrated ethanol stream above the azeotropic composition. Further, it is expected that the pervaporation process will serve to improve the efficiency of the distillation process. Also, as shown in Figure 5.3, the liquid stream is dehydrated as it flows downward along the membrane. This implies that the bottoms stream leaving the unit should have a higher ethanol concentration than in a typical rectifying process. The higher bottoms ethanol concentration may lead to a decreased energy load in the stripping column, due to the lower water load. In many ways, Membrane Dephlegmation is very similar to the hybrid distillation-pervaporation processes described earlier. However, the major difference is that, in Membrane Dephlegmation, the pervaporation and distillation processes are actually carried out in the same unit. A description of the transport phenomena occurring in the Membrane Dephlegmation process is presented in the following section. This description is then used to derive a mathematical model to describe the process. A model is also derived to describe the conventional wetted-wall distillation process. These models are then used to compare the performance of Membrane Dephlegmation and distillation.

5.3. Mathematical Formalism

The Membrane Dephlegmation process could be carried out using various membrane geometries. The process could also employ a variety of hydrophilic membrane materials. However, NaA zeolite membranes are commercially available and are known to exhibit a particularly high water flux and selectivity [20,21]. Thus, this investigation employs the pervaporation model of Sommer and Melin [20] to describe the pervaporation process. Further, tubular NaA membranes with the selective layer inside the tubes are commercially available [22]. Thus, the mathematical model presented in this section is derived assuming a tubular geometry, with the selective layer on the inside of the tubes.

To supplement the discussion, an overview of the transport phenomena taking place in the non-adiabatic wetted-wall distillation process is shown in Figure 5.4. Further, an overview of the transport phenomena occurring in the Membrane Dephlegmation process is shown in Figure 5.5.

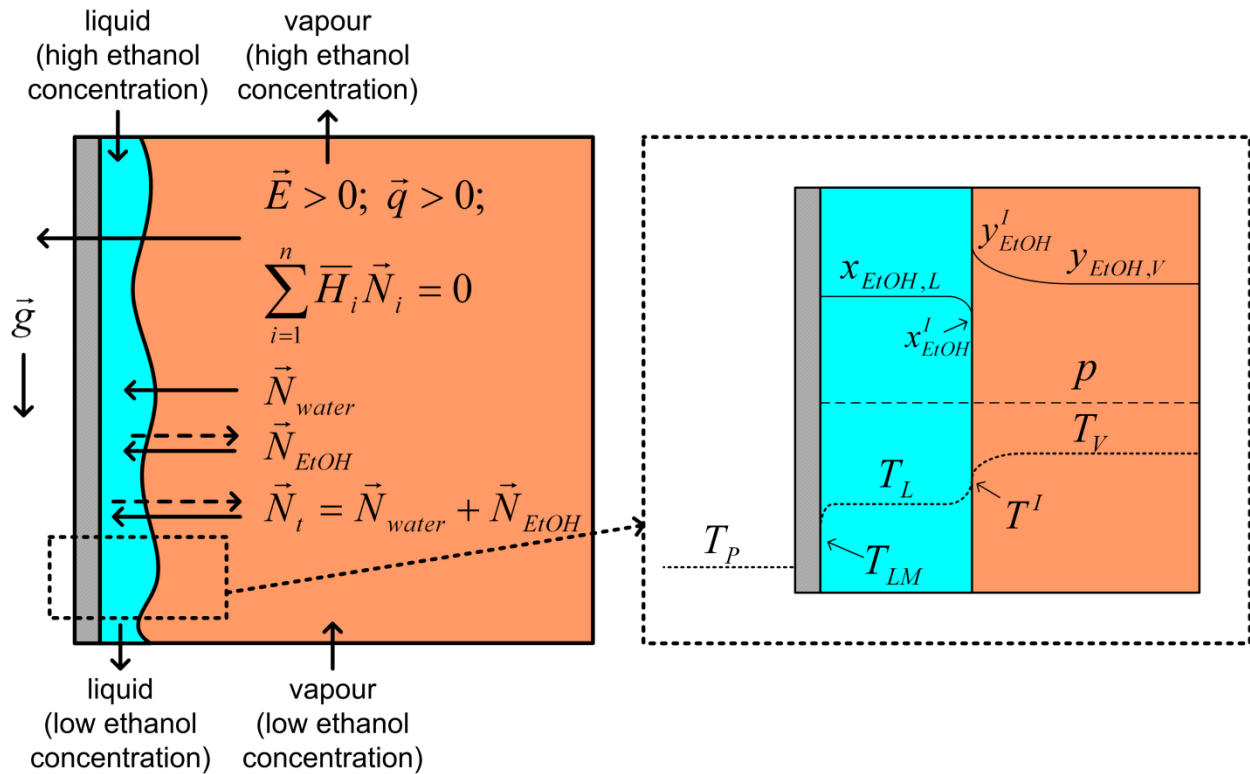


Figure 5.4. Overview of the transport processes involved in non-adiabatic wetted-wall distillation.

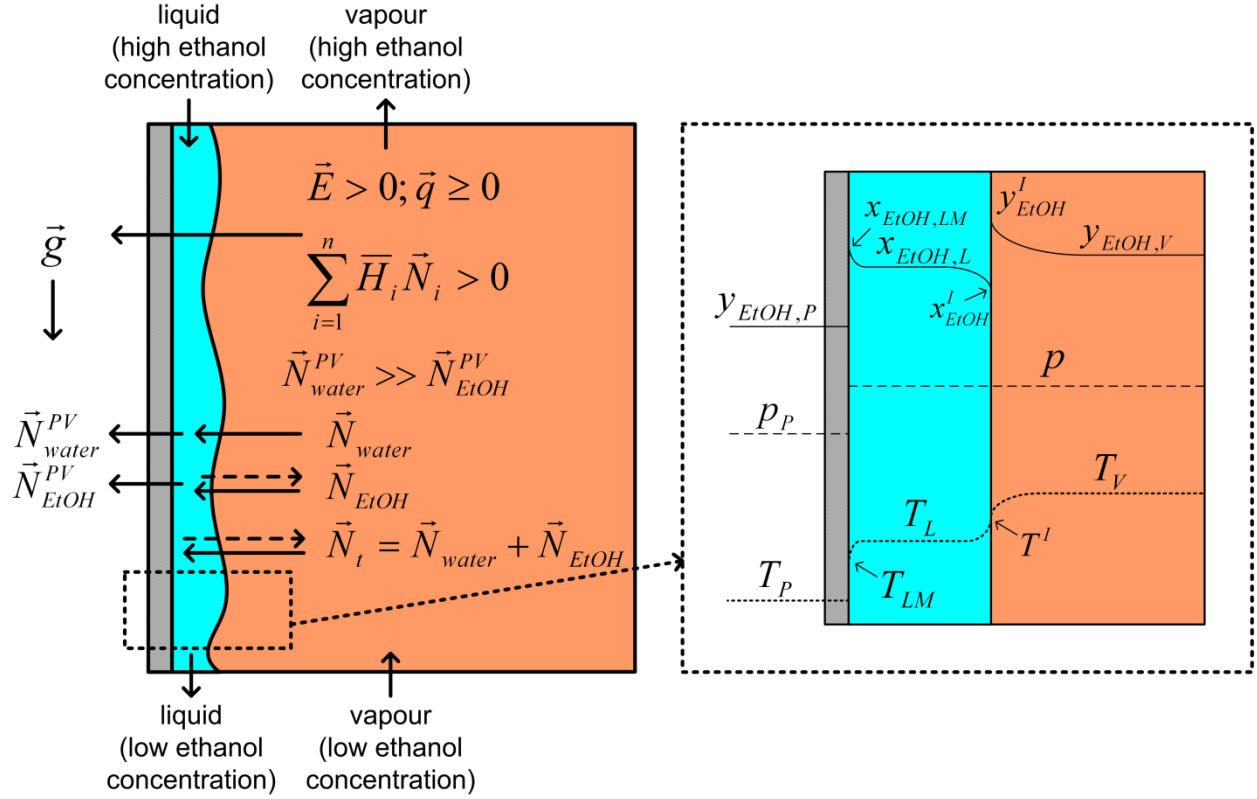


Figure 5.5. Overview of the transport processes involved in Membrane Dephlegmation.

The geometry of the system considered in this investigation is shown in Figure 5.6. The geometry corresponds to a tubular membrane with the selective layer supported on the inside of the tubes. The support is assumed to have a relatively open pore structure and therefore, its contribution to pressure drop on the permeate side is neglected. It is assumed that the liquid forms a smooth, evenly distributed film on the membrane surface. This is a reasonable assumption due to the good wetting characteristics of these membranes. The area available for vapour flow is equal to the cross sectional area minus the area required for countercurrent liquid flow. The membrane tubes are oriented vertically with gravity acting downward.

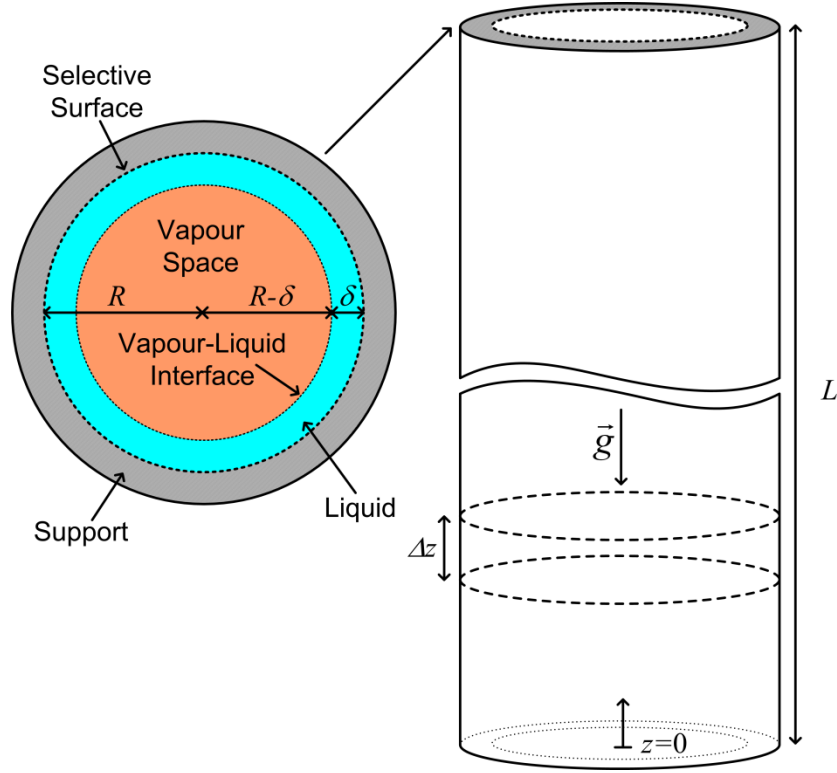


Figure 5.6. Schematic representation of the proposed membrane column.

5.3.1. Conservation Equations

A one-dimensional steady-state model was derived to describe the Membrane Dephlegmation process. The reference coordinate system, as shown in Figure 5.6, is oriented from the bottom upwards. The molar flux across the vapour-liquid interface is positive when the species moves from the vapour to the liquid phase (i.e. condensation). The pervaporation flux is unidirectional through the membrane from the liquid phase to the permeate side.

A summary of the one-dimensional material and energy conservation equations is presented in Table 5.1. The vapour phase momentum equation was not solved since hydrodynamic information is inherently included in the heat and mass transfer correlations presented in the following sections. However, the liquid phase velocity profile is required to determine the liquid film thickness and interface velocity (for use in heat and mass transfer correlations). Although not strictly true in this case, due to the countercurrent flow of the vapour phase, the Nusselt assumptions were used to derive the liquid phase velocity profile [23]. Previous computational studies have shown that, for the conditions presented in this investigation, deviation from these assumptions is minimal [24,25]. To derive the liquid phase

velocity profile, it is assumed that liquid flow is laminar, fully developed and not influenced by the shear effect caused by the vapour flow. Using these assumptions, the viscous shear force induced by the membrane wall is balanced by buoyancy and gravity forces and the momentum equation reduces to,

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{du_L}{dr} \right) = \frac{(\rho_L - \rho_V)g}{\mu_L} \quad (1)$$

This equation can be integrated assuming the shear force caused by the vapour phase is negligible (i.e. $\frac{du_L}{dr} = 0$ at $r = R - \delta$) and applying the no slip boundary condition at the membrane surface (i.e. $u_L = 0$ at $r = R$). Upon integration, the following equation is obtained to describe the liquid velocity profile,

$$u_L = \frac{(\rho_L - \rho_V)g}{2\mu_L} \left(\frac{r^2 - R^2}{2} + (R - \delta)^2 \ln \left(\frac{R}{r} \right) \right) \quad (2)$$

The interface velocity is obtained by substituting the interface position ($r = R - \delta$) into the velocity profile equation.

$$u^I = \frac{(\rho_L - \rho_V)g}{2\mu_L} \left(\frac{(R - \delta)^2 - R^2}{2} + (R - \delta)^2 \ln \left(\frac{R}{(R - \delta)} \right) \right) \quad (3)$$

Another important parameter is the liquid film thickness, since it determines the area of the vapour-liquid interface as well as the cross-sectional area available for vapour flow. The liquid mass flow rate can be calculated by solving the material balance equations. Further, by definition, the liquid mass flow rate is related to the velocity profile through the following expression.

$$\dot{m}_L = - \int_{R-\delta}^R \int_0^{2\pi} \rho_L u_L r d\theta dr \quad (4)$$

Integrating this equation yields,

$$\dot{m}_L = - \frac{\pi \rho_L (\rho_L - \rho_V) g}{\mu_L} \left[\frac{2R\delta(R - \delta)^2 - R^2(R - \delta)^2 - \delta^2(R - \delta)^2}{2} \ln \left(\frac{R}{(R - \delta)} \right) + \frac{\delta^2 R^2 - \delta^2 (R - \delta)^2}{4} + \frac{R^4 - (R - \delta)^4}{8} - \frac{R\delta(R - \delta)^2 - R^3\delta}{2} \right] \quad (5)$$

Given the liquid mass flow rate (determined from the material balance), this nonlinear equation can be solved iteratively for the film thickness.

The vapour phase component balance equations are identical for the wetted-wall distillation and Membrane Dephlegmation processes, and only include interphase component fluxes to or from the liquid phase. Similarly, both processes have the same vapour phase energy balance equation, with contributions from conduction and material transfer through the vapour-liquid interface. The component and energy balance equations for the vapour are identical for both processes because the vapour is only exposed to the liquid interface and not directly to the membrane, as shown in Figures 5.4 and 5.5. Conversely, the liquid phase component and energy balance equations are different, since the Membrane Dephlegmation process includes contributions from the pervaporation flux in addition to the vapour-liquid interface flux. In Membrane Dephlegmation, pervaporation contributes to the selective removal of water from the liquid phase. Further, pervaporation results in the loss of energy related to latent heat of vaporization required to evaporate the water permeating through the membrane. Of course, both the changes in the energy and component balances lead to changes in the fluxes across the vapour-liquid interface and therefore also impact the vapour phase indirectly. Equations describing the transport of species across the vapour-liquid interface are presented in the next section.

Table 5.1. Summary of Material and Energy Balance Equations (for C components)

Wetted-Wall Distillation	Membrane Dephlegmation
<u>C vapour component balances:</u>	
$\frac{dv_i}{dz} = -2\pi(R - \delta)N_i$	
<u>C liquid component balances:</u>	
$\frac{dl_i}{dz} = -2\pi(R - \delta)N_i$	$\frac{dl_i}{dz} = -2\pi(R - \delta)N_i + 2\pi R N_i^{PV}$
<u>1 vapour energy balance:</u>	
$\frac{dVH_V}{dz} = -2\pi(R - \delta)E_V$	
$E_V = h_V^*(T_V - T^I) + \sum N_i \bar{H}_{i,V}(T_V)$	
<u>1 liquid energy balance:</u>	
$\frac{dLH_L}{dz} = -2\pi(R - \delta)E_L + 2\pi R E_{LM}$	
$E_L = h_L^*(T^I - T_L) + \sum N_i \bar{H}_{i,L}(T_L)$	
$E_{LM} = h_{LM}^*(T_L - T_{LM})$	$E_{LM} = h_{LM}^*(T_L - T_{LM}) + \sum N_i^{PV} \bar{H}_{i,L}(T_L)$

5.3.2. Vapour-Liquid Interface Conditions

5.3.2.1. Jump Conditions for Interphase Heat and Mass Transfer

Jump conditions are required to describe the transport of material and energy across the vapour-liquid interface. Table 5.2 summarizes the material and energy balances at the vapour-liquid interface. The jump conditions for the vapour-liquid interface are identical for distillation and Membrane Dephlegmation. Energy transported through the interface to or from the vapour phase must be balanced by energy transported to or from the liquid phase. Similarly, material transport must be balanced through the vapour-liquid interface. Both the energy and material balance equations are comprised of diffusive and convective terms [26]. It is apparent that the convective portion in the energy balance equation is directly related to the latent heat of vaporization/condensation. This implies that energy and material transport across the interface are in tightly coupled processes.

Table 5.2. Summary of Vapour-Liquid Interface Heat and Mass Transfer Jump Conditions (for C components)

<u>1 interphase energy balance:</u>	
$E_v = E_L$ $h_v^*(T_v - T^I) + \sum N_i \bar{H}_{i,v}(T_v) = h_L^*(T^I - T_L) + \sum N_i \bar{H}_{i,L}(T_L)$	
<u>C-1 vapour side interphase component balances:</u>	
$N_i = K_v^*(y_{i,v} - y_i^I) + y_{i,v} \sum N_i$	
<u>C-1 liquid side interphase component balances:</u>	
$N_i = K_L^*(x_i^I - x_{i,L}) + x_{i,L} \sum N_i$	

The equations presented in Table 5.2 cannot fully describe the interphase heat and mass transfer processes because there are more unknown quantities than there are equations. Thus, some supplementary conditions are necessary to relate the interface compositions and temperature to each other. The next section describes the supplementary conditions required to fully describe the vapour-liquid interphase heat and mass transfer processes.

5.3.2.2. Supplementary Conditions

To compute the material and energy fluxes crossing the vapour-liquid interface, auxiliary expressions are required to supplement the component and energy balance equations presented in Table 5.2. Specifically, expressions are required to relate the interface compositions and

temperature. Conventionally, it is assumed that vapour-liquid equilibrium (VLE) conditions exist, under the system pressure, at the interface. The vapour-liquid equilibrium condition implies that the temperature, pressure and chemical potential of each species must be identical in both phases at the interface [27]. The chemical potential does not provide a convenient means to correlate vapour-liquid equilibrium data. It is usually more practical to express the equilibrium condition by defining a distribution coefficient (K-value), which depends on the vapour and liquid phase fugacity coefficients.

$$K_i = \frac{y_i^I}{x_i^I} = \frac{\bar{\phi}_{i,L}}{\bar{\phi}_{i,V}} \quad (6)$$

where y_i^I and x_i^I are the vapour and liquid phase mole fractions of species i , respectively. $\bar{\phi}_{i,L}$ and $\bar{\phi}_{i,V}$ are the liquid phase and vapour phase fugacity coefficients. In general, the liquid phase fugacity coefficient is given by,

$$\bar{\phi}_{i,L} = \frac{\gamma_i}{p} p_i^{sat} \phi_i^{sat} \exp\left(-\frac{V_{i,L}(p - p_i^{sat})}{RT}\right) \quad (7)$$

where the exponential term is commonly referred to as the Poynting factor. At relatively low pressures (i.e. when the ideal gas law is applicable), the Poynting factor and ϕ_i^{sat} approach unity. Further, $\bar{\phi}_{i,V}$ can be calculated using a variety of Equations of State; however, at low pressures it is approximately equal to unity. Thus, in this study (since all simulations were carried out at the standard pressure of 101325 Pa), the K-value was calculated using,

$$K_i = \frac{\gamma_i p_i^{sat}}{p} \quad (8)$$

where γ_i is the activity coefficient and p_i^{sat} is the saturation vapour pressure. In this study, the activity coefficient was calculated using the Wilson activity model and the vapour pressure was calculated using the extended Antoine equation. As shown in Table 5.3, once calculated, the K-value can be used to relate the interface mole fractions in the vapour and liquid phase. Further, as shown in Table 5.3, the interface mole fractions in each phase must sum to unity.

Table 5.3. Summary of Auxiliary Conditions at the Vapour-Liquid Interface (for C components)

C vapour-liquid equilibrium relations:

$$K_i x_i^I - y_i^I = 0$$

2 interface mole fraction summation equations:

$$\sum_{i=1}^C x_i^I - 1 = 0, \sum_{i=1}^C y_i^I - 1 = 0$$

5.3.3. Membrane-Liquid Interface Conditions

In the Membrane Dephlegmation process, additional equations are required to describe the transport of material and energy through the membrane. Further, conductive energy losses are also possible in the non-adiabatic wetted-wall distillation process. Thus, an energy balance is also required at the membrane-liquid interface in the distillation process. Table 5.4 provides a summary of the equations used to describe heat and mass transfer across the pervaporation membrane in this investigation. In the distillation process, the energy balance does not include coupling terms, since there is no material flux across the solid surface. Conversely, the energy balance for the Membrane Dephlegmation is coupled to the mass transfer process due to the heat loss associated with pervaporation.

As indicated in Table 5.4, mass transfer relations are not required at the liquid-solid interface for the wetted-wall distillation process. Conversely, for the Membrane Dephlegmation process, it is necessary to write material flux equations for both the liquid and membrane side of the interface. The material flux expression on the liquid side of the membrane has an analogous form to the equation written for the liquid side at the vapour-liquid interface [26]. Transport through zeolite membranes is often described using a solution-diffusion or adsorption-diffusion model. In this study, the model proposed by Sommer and Melin [20], which is based on a solution-diffusion mechanism, was used to describe transport across the membrane. This model is also summarized in Table 5.4. Since the NaA zeolite membranes are asymmetric, it is assumed that the permeate stream entering the porous support is unmixed. Thus, as shown in Table 5.4, the mole fractions on the permeate side can be related directly to the local pervaporation fluxes. Lastly, the mole fractions at the membrane-liquid interface and in the permeate must sum to unity.

Table 5.4. Summary of Membrane-Liquid Interface Heat and Mass Transfer Jump Conditions
(for C components)

Wetted-Wall Distillation	Membrane Dephlegmation
1 interphase energy balance:	
$E_{LM} = E_M$	
$h_{LM}^*(T_L - T_{LM}) = h_M^*(T_{LM} - T_P)$	$h_{LM}^*(T_L - T_{LM}) + \sum N_i^{PV} \bar{H}_{i,L}(T_L) =$ $h_M^*(T_{LM} - T_P) + \sum N_i^{PV} \bar{H}_{i,V}(T_P)$
C-1 liquid side interphase component balances:	
Not Required	$N_i^{PV} = K_{LM}^*(x_{i,L} - x_{i,LM}) + x_{i,L} \sum N_i^{PV}$
C membrane flux expressions:	
	$N_i^{PV} = Q_i(\gamma_i x_{i,LM} p_i^{sat} - y_{i,P} p_P)$
	$Q_i = Q_i^{ref} \left[\frac{E_i}{R} \left(\frac{1}{353.15} - \frac{1}{T_{LM}} \right) \right]$
Not Required	$Q_E^{ref} = 4.221 \times 10^{-13} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$
	$Q_W^{ref} = 1.744 \times 10^{-9} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$
	$E_E = 25.7 \frac{\text{kJ}}{\text{kmol}}, E_W = 17.0 \frac{\text{kJ}}{\text{kmol}}$
C-1 membrane flux to permeate mole fraction relations:	
Not Required	$y_{i,P} = \frac{N_i^{PV}}{\sum N_i^{PV}}$
2 membrane interface mole fraction summation equations:	
Not Required	$\sum_{i=1}^C x_{i,LM} - 1 = 0, \sum_{i=1}^C y_{i,P} - 1 = 0$

5.3.4. Heat and Mass Transfer Coefficients

The equations shown in Tables 5.1 through 5.4 fully describe the wetted-wall distillation and Membrane Dephlegmation processes. However, since the momentum equations are not solved for the vapour phase and only a one-dimensional model is presented, it is not possible to directly determine the thickness of the boundary layers for temperature and composition. Therefore, it is not possible to directly estimate the heat and mass transfer rates across the vapour-liquid and membrane-liquid interfaces. Instead, empirical correlations must be employed

to calculate heat and mass transfer coefficients and thereby fully define the heat and mass transfer processes. These correlations inherently incorporate hydrodynamic effects.

A summary of the correlations used to estimate heat and mass transfer coefficients in the liquid and vapour phase is presented in Table 5.5. For the vapour phase, the flows investigated in this study were laminar ($Re < 2000$). It is known that, under hydrodynamically and thermally fully developed conditions for laminar flow in a pipe, the Nusselt number is approximately constant [28]. For a constant wall temperature, the Nusselt number is equal to 3.66. In the present case, the vapour flows through a pipe that is wetted with a moving liquid film. It is implied that the wall temperature, in this case, actually refers to the interface temperature. Clearly, the temperature profile and interface temperature change along the length of the membrane. However, it is assumed that the temperature and concentration profiles change relatively slowly along the length of the membrane. Thus, a constant vapour phase Nusselt number of 3.66 is assumed and used in the simulations. For mass transfer calculations, the Sherwood number is calculated using the Chilton-Colburn analogy. As shown in Table 5.5, film theory was used to correct the heat and mass transfer coefficients for high flux conditions (see [26] for a detailed discussion on this topic).

In the liquid phase, heat transfer coefficients must be estimated at both the vapour-liquid and membrane-liquid interfaces. Further, although the distillation process only requires a mass transfer coefficient at the vapour-liquid interface, both vapour-liquid and liquid-solid mass transfer coefficients are required in the Membrane Dephlegmation process. At the vapour-liquid interface, the heat and mass transfer correlations are derived by assuming diffusion in a smooth laminar falling film [23]. Conventionally, this is known as Penetration Theory for diffusion in a falling film. Although, these assumptions may not be strictly true, it has been shown that under the relatively low liquid flow rates encountered in the processes described here, Penetration Theory provides a good estimate of the heat and mass transfer rates [25]. Further, some of these assumptions have already been used to derive the liquid phase velocity profile and to determine the liquid film thickness.

At the membrane-liquid interface, the liquid phase heat and mass transfer coefficients are derived assuming diffusion to/from a solid surface into a laminar falling film (see [29] for a full derivation). As in the vapour phase, all liquid phase heat and mass transfer coefficients are corrected for high flux conditions using film theory [26]. Lastly, the external heat transfer

coefficient, which accounts for heat losses to the surroundings, is assumed to be zero in this investigation. That is, wetted-wall distillation simulations are adiabatic.

Table 5.5. Summary of Vapour and Liquid Phase Heat and Mass Transfer Coefficients

Vapour Phase Heat Transfer Coefficient:

$$\text{Nu}_V = \frac{h_V(D-2\delta)}{k_V} = 3.66$$

$$\text{Re}_{V,rel} = \frac{\rho(\bar{u}_V + u^I)(D-2\delta)}{\mu_V}, \text{Pr}_V = \frac{C_{p,V}\mu_V}{M_V k_V}, h_V^* = h_V \frac{\Psi}{(e^\Psi - 1)}, \Psi = \frac{\sum N_i C_{p,i,V}}{h_V}$$

Vapour Phase Mass Transfer Coefficient:

$$\text{Sh}_V = \frac{K_V(D-2\delta)}{D_{AB,V}} = 3.66$$

$$\text{Re}_{V,rel} = \frac{\rho(\bar{u}_V + u^I)(D-2\delta)}{\mu_V}, \text{Sc}_V = \frac{\mu_V}{\rho_V D_{AB,V}}, K_V^* = K_V \frac{\Phi}{(e^\Phi - 1)}, \Phi = \frac{\sum N_i}{c_t K_V}$$

Liquid Phase Heat Transfer Coefficient (Vapour-Liquid Interface):

$$\text{Nu}_L = \frac{h_L \delta}{k_L} = 2\delta \sqrt{\frac{u^I}{\alpha_L \pi \Delta z}}$$

$$\alpha_L = \frac{k_L M}{\rho_L C_{p,L}}, h_L^* = h_L \frac{\Psi}{(e^\Psi - 1)}, \Psi = \frac{\sum N_i C_{p,i,L}}{h_L}$$

Liquid Phase Mass Transfer Coefficient (Vapour-Liquid Interface):

$$\text{Sh}_L = \frac{K_L \delta}{D_{AB,L}} = 2\delta \sqrt{\frac{u^I}{D_{AB,L} \pi \Delta z}}$$

$$K_L^* = K_L \frac{\Phi}{(e^\Phi - 1)}, \Phi = \frac{\sum N_i}{c_t K_L}$$

Liquid Phase Heat Transfer Coefficient (Liquid-Solid Interface):

$$\text{Nu}_{LM} = \frac{h_{LM} \delta}{k_L} = \frac{\delta^{4/3}}{1.8574726} \left(\frac{\rho_L g}{\mu_L \alpha_L \Delta z} \right)^{1/3}$$

$$\alpha_L = \frac{k_L M}{\rho_L C_{p,L}}, h_{LM}^* = h_{LM} \frac{\Psi}{(e^\Psi - 1)}, \Psi = \frac{\sum N_i^{PV} C_{p,i}}{h_{LM}}$$

Liquid Phase Mass Transfer Coefficient (Liquid-Solid Interface):

$$\text{Sh}_{LM} = \frac{K_{LM} \delta}{D_{AB,L}} = \frac{\delta^{4/3}}{1.8574726} \left(\frac{\rho_L g}{\mu_L D_{AB,L} \Delta z} \right)^{1/3}$$

$$K_{LM}^* = K_{LM} \frac{\Phi}{(e^\Phi - 1)}, \Phi = \frac{\sum N_i^{PV}}{c_t K_{LM}}$$

External Heat Transfer Coefficient:

$$h_M^* = 0$$

5.4. Numerical details

5.4.1. Physical Property Estimation

Temperature and composition dependent properties for the ethanol-water system were used in all simulations. The liquid phase viscosity, thermal conductivity and diffusion coefficient were calculated using the Neural Network models developed by Haelssig et al. [30]. The vapour phase viscosity, thermal conductivity and diffusion coefficient were calculated using the Reichenberg, Wassiljewa and Fuller methods, respectively [31]. Pure component viscosity and thermal conductivity were estimated using temperature dependent polynomial relationships [32]. The latent heat of vaporization was calculated from the expressions provided in [33]. The vapour pressure for both species was determined using the extended Antoine equation [33]. The Wilson model was used to estimate the activity coefficients for the ethanol-water system [34]. The liquid phase densities (and molar volume) of ethanol and water were calculated using the expressions provided in [33]. The excess volume for mixing was estimated using the Wilson equation [27]. The ideal gas law was applied to estimate the vapour phase density (and molar volume). The heat capacities in the vapour and liquid phase were calculated using temperature dependent polynomial relationships [32].

The liquid and vapour phase enthalpies were calculated using the temperature dependent heat capacities. For the vapour phase, the partial molar enthalpy for each component was determined from,

$$\bar{H}_{i,V} = H_{i,ref} + \int_{T_{ref}}^T C_{p,i}^{ig} dT \quad (9)$$

The reference enthalpy, $H_{i,ref}$, was referenced to 298.15 K. The mixture enthalpy was calculated as a mole weighted average of the partial molar enthalpies.

$$H_V = \sum_{i=1}^C y_{i,V} \bar{H}_{i,V} + H^R \quad (10)$$

The residual enthalpy, H^R , is 0 under the ideal gas assumption. In the liquid phase, the partial molar enthalpy for each component was calculated using,

$$\bar{H}_{i,L} = H_{i,ref} + \int_{T_{ref}}^T C_{p,i}^{ig} dT - \Delta H_i^{vap}(T) \quad (12)$$

Again, the mixture enthalpy was calculated as a mole weighted average of the partial molar enthalpies,

$$H_L = \sum_{i=1}^C x_{i,L} \bar{H}_{iL} + H^E \quad (13)$$

The excess enthalpy was calculated using the Wilson activity model [27].

5.4.2. Solution Methodology

The differential material and energy balance equations presented in Table 5.1 were discretized using a finite difference approximation. The column was divided into N segments. In the calculations, the number of segments was increased until a grid independent solution was obtained. The discretized material and energy balance equations were combined with the interface conditions presented in Tables 5.2 through 5.4. The heat and mass transfer coefficients were estimated using the correlations presented in Table 5.5. When combined, the material and energy balance equations and interface conditions form a system of $(5C+4)N$ or $(8C+4)N$ nonlinear equations for the wetted-wall distillation and Membrane Dephlegmation cases, respectively. The nonlinear equations form a block tri-diagonal system, which must be solved iteratively. In this study, an in-house simulator was programmed in the Java programming language, to solve the system of equations. The simulator employed a block tri-diagonal version of the Thomas algorithm, combined with a modified Newton's method to converge on the solution.

5.5. Results and discussion

A primary objective of this study was to analyze the performance of the Membrane Dephlegmation process. Further, the efficiency of Membrane Dephlegmation should be compared to wetted-wall distillation. Specifically, it is desired to determine how pervaporation impacts the vapour-liquid contacting process and how distillation affects the pervaporation process. To this end, the mathematical model presented in the previous sections was used to carry out several simulations under a variety of operating conditions. For comparison, the wetted-wall distillation process was also simulated at similar conditions. The geometry considered in this investigation is shown in Figure 5.6. An internal diameter of 6 mm and a length of 2.4 m were used in the simulations presented. It is recognized that it would be difficult to produce a 2.4 m long membrane tube commercially. However, it is known that 1.2 m long membrane tubes are commercially available [22]. Thus, it was assumed that these membranes could be placed in series to increase the length without significantly affecting flow behaviour. In

fact, an experimental system using two such membranes is currently under investigation. The external heat transfer coefficient was assumed to be 0 for the simulation cases considered in this investigation. Thus, the wetted-wall distillation results are equivalent to adiabatic distillation. However, the Membrane Dephlegmation process remains non-adiabatic due to the energy loss associated with pervaporation.

To analyze system performance, composition, temperature and velocity profiles for four different sets of operating conditions are presented in this section. Clearly the composition profiles are critically important, since a separation system is being investigated. However, as mentioned earlier, the heat and mass transfer processes are tightly coupled at both the vapour-liquid and membrane-liquid interfaces. Therefore, the temperature profiles also have a direct impact on the separation efficiency. Further, the velocity profiles impact heat and mass transfer rates, since the system hydrodynamics effect the heat and mass transfer coefficients. The presented simulation results include one wetted-wall distillation case and three Membrane Dephlegmation cases. For Membrane Dephlegmation, results are presented for two different permeate pressures and reflux ratios. The permeate pressure affects the driving force for pervaporation and therefore impacts the transmembrane flux. Of course, the membrane flux impacts the liquid concentration and, through the vapour-liquid interface, also the vapour phase composition. The reflux ratio governs the liquid flow rate and concentration. A higher reflux ratio will inherently lead to a higher average liquid phase concentration of volatile components (ethanol), which will in turn also favour the accumulation of these components in the vapour phase. However, there is a cost associated with higher reflux ratios. Higher reflux ratios lead to a lower overall ethanol recovery in the distillate, since more ethanol is entrained in the liquid phase leaving the column. This liquid stream must be recycled, putting a higher energy load on the stripping column.

Figure 5.7 shows the composition profiles for the four simulation cases presented in this investigation. The location of the ethanol-water azeotrope is also indicated on the figure. The location of the azeotrope is important since conventional distillation will never reach a higher ethanol concentration than the azeotropic point. Figure 5.7a shows the composition profile for the wetted-wall distillation case. It is confirmed that the azeotropic composition is not reached in this case. Further, it is shown that the vapour phase ethanol concentration is always higher than the liquid phase concentration. This is expected, since the higher relative volatility of ethanol

favours its movement to the vapour phase. Figures 5.7b through 5.7d show the composition profiles for the Membrane Dephlegmation cases. Figure 5.7b illustrates a case with the same reflux ratio used in the distillation simulation but combined with a very low permeate pressure. The low permeate pressure leads to a high pervaporation flux and thereby causes dehydration of the liquid phase. The increased ethanol concentration in the liquid phase also increases the vapour phase concentration. Further, it is demonstrated that pervaporation of the liquid phase also causes dehydration of the vapour phase above the azeotropic concentration. Figure 5.7c shows a Membrane dephlegmation case with the same reflux ratio and an intermediate permeate pressure. The higher permeate pressure leads to a lower pervaporation flux and thus, a lower ethanol concentration leaving the top of the column. However, as expected, a higher ethanol concentration is achieved than in the distillation case. Figure 5.7d shows Membrane Dephlegmation results for a low permeate pressure and a lower reflux ratio than the other cases. The lower reflux ratio leads to a lower average ethanol concentration in the liquid phase. The lower liquid phase concentration also leads to a lower vapour phase concentration, as compared with the case presented in Figure 5.7b. However, the concentration leaving the top of the column still reaches a concentration near the azeotrope, showing the definite impact of pervaporation.

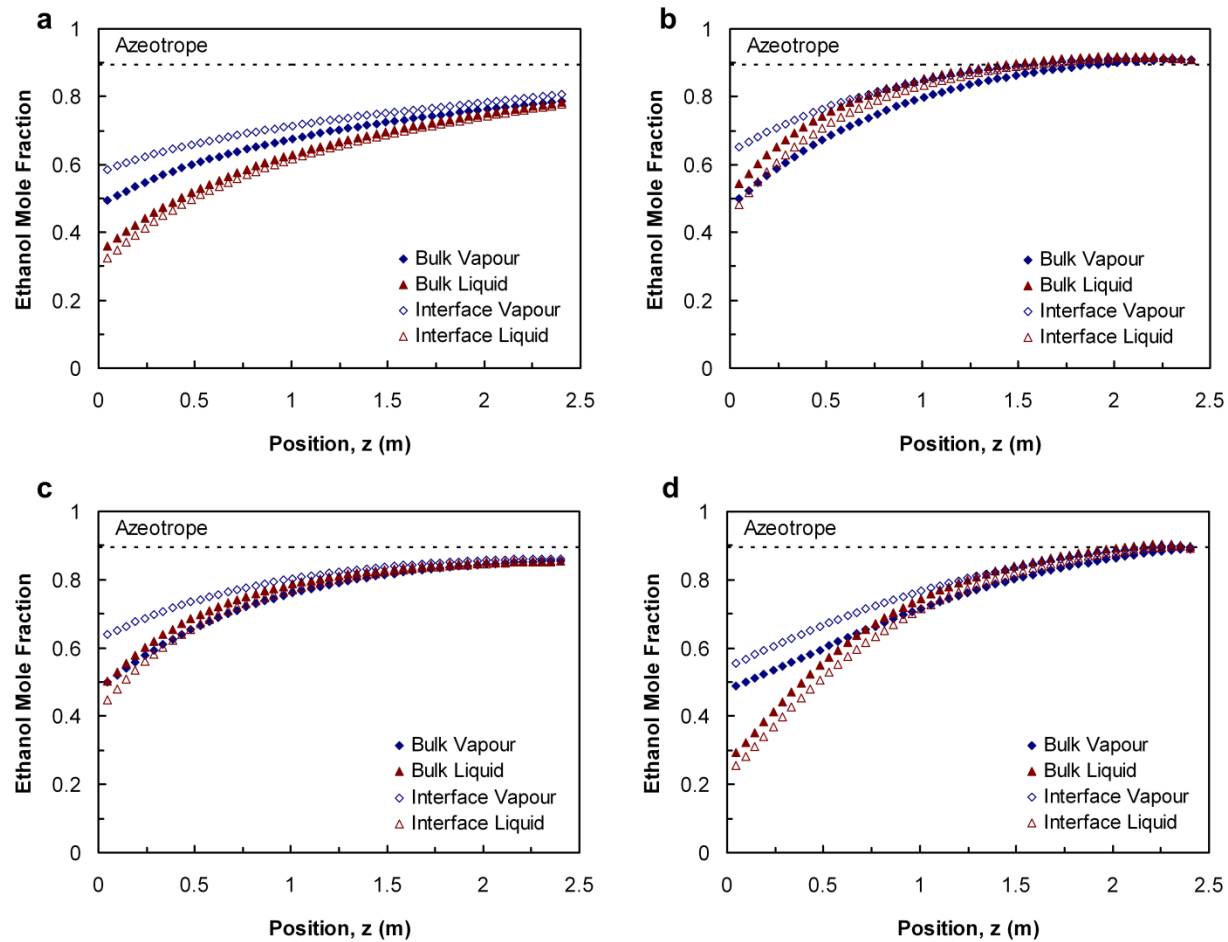


Figure 5.7. Composition profiles for: a) distillation, reflux ratio of 2.5; b) permeate pressure of 5333 Pa, reflux ratio of 2.5; c) permeate pressure of 12000 Pa, reflux ratio of 2.5; d) permeate pressure of 5333 Pa, reflux ratio of 0.25 (for all cases: feed velocity of 3 m/s, feed ethanol mole fraction of 0.476 (70 % ethanol by mass), liquid feed temperature of 313 K, vapour feed temperature of 383 K).

Figure 5.8 shows the temperature profiles for the same simulation cases presented in Figure 5.7. It is apparent from the vapour and liquid temperature profiles that the vapour and liquid were introduced into the column in superheated and subcooled states, respectively. In each case, the liquid quickly increases in temperature to near the interface temperature. The fast increase in liquid temperature is the direct result of a high condensation flux at the top of the column. As shown in Figure 5.9, the high condensation flux is accompanied by a rapid increase in the liquid phase velocity (decrease of the vapour phase velocity) at the top of the column. As shown in Figure 5.8, a longer distance is required for the superheated vapour to approach the

interface temperature. This is a direct result of the relatively low thermal conductivity of the vapour phase.

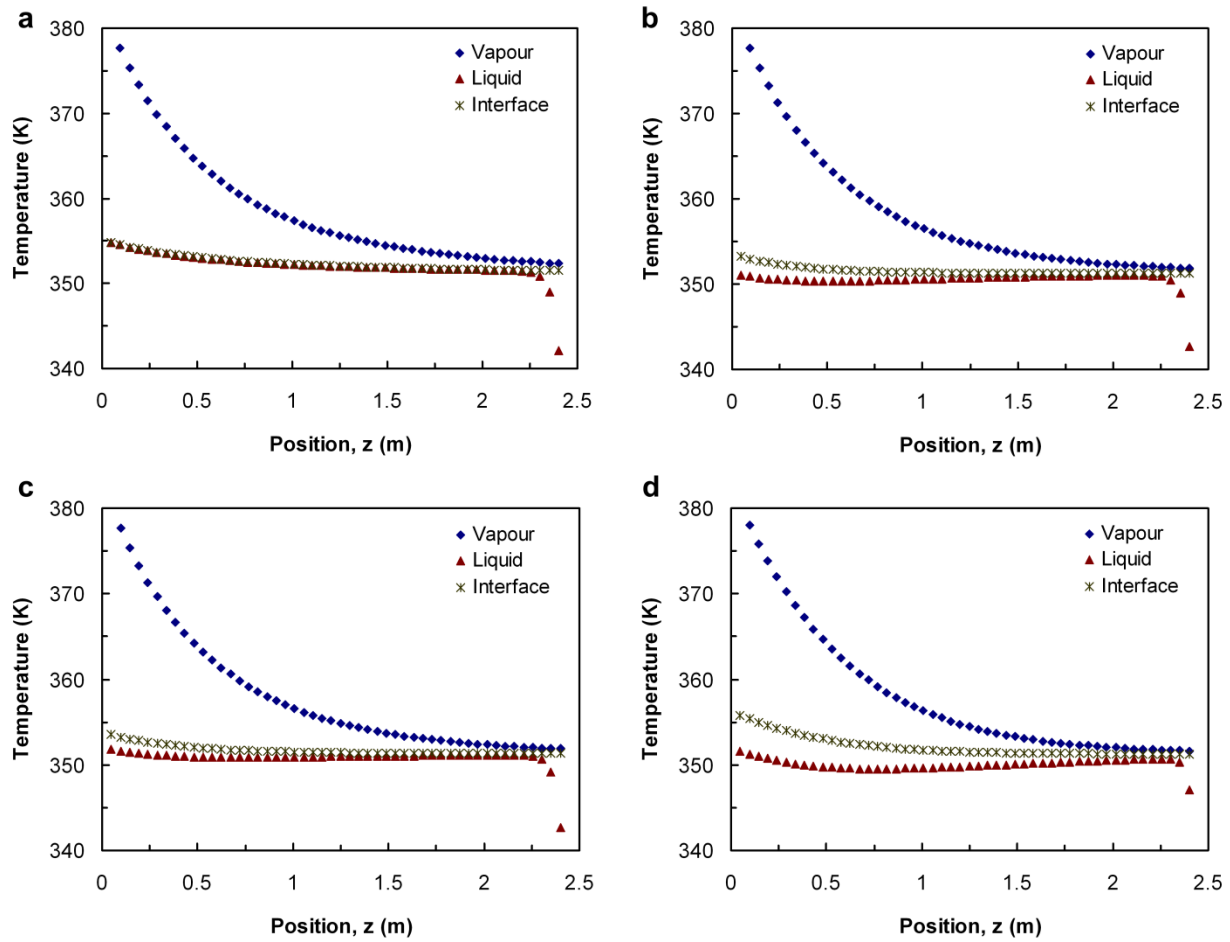


Figure 5.8. Temperature profiles for: a) distillation, reflux ratio of 2.5; b) permeate pressure of 5333 Pa, reflux ratio of 2.5; c) permeate pressure of 12000 Pa, reflux ratio of 2.5; d) permeate pressure of 5333 Pa, reflux ratio of 0.25 (for all cases: feed velocity of 3 m/s, feed ethanol mole fraction of 0.476 (70 % ethanol by mass), liquid feed temperature of 313.15, vapour feed temperature of 383.15 K).

It is also important to note the impact of the pervaporation flux and reflux ratio on the temperature and velocity profiles. As shown in Figure 5.8a, once the liquid phase approaches the interface temperature, it follows a similar trend. Conversely, as indicated in Figures 5.8b through 5.8d, the presence of a pervaporation flux leads to local liquid subcooling. The amount of subcooling in the liquid phase is related to the liquid flow rate as well as the magnitude of the pervaporation flux. As shown in Figure 5.8d, a lower reflux ratio leads to a higher degree of liquid subcooling. In this case, two primary causes are responsible for the lower liquid

temperature. First, as shown in Figure 5.9, a lower reflux ratio leads to a lower liquid flow rate. A lower liquid flow rate implies that the liquid film is more susceptible to temperature changes. The second reason is that, as shown in Figure 5.7d, the average liquid phase ethanol concentration is lower when a lower reflux ratio is specified. The lower ethanol concentration leads to a higher driving force for water pervaporation, causing an increased water and energy flux across the membrane. The interface temperature is primarily governed by vapour-liquid equilibrium conditions. For lower concentrations, the interface temperature tends to change with composition. However, as the concentration approaches the azeotrope, the interface temperature approaches a nearly constant value.

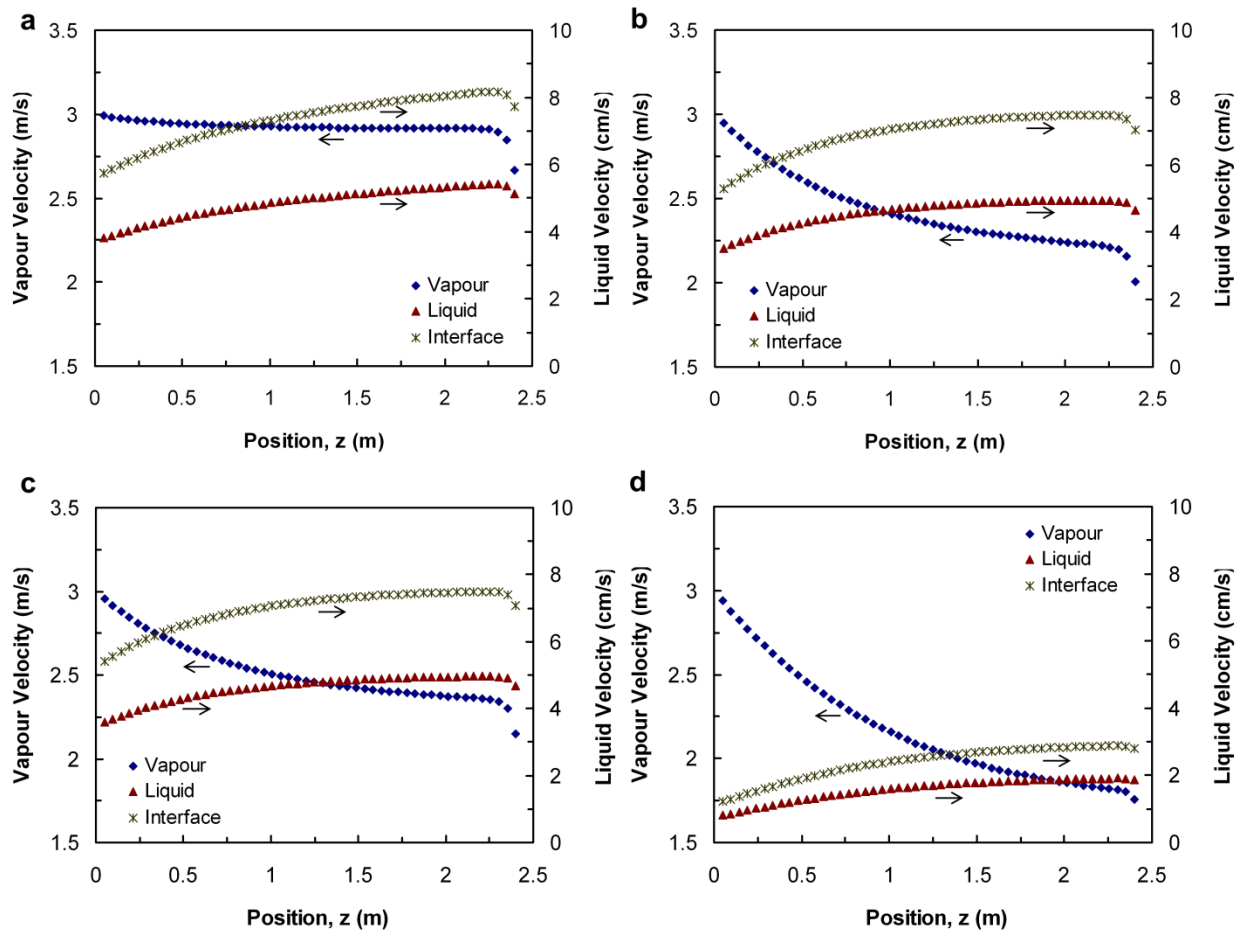


Figure 5.9. Velocity profiles for: a) distillation, reflux ratio of 2.5; b) permeate pressure of 5333 Pa, reflux ratio of 2.5; c) permeate pressure of 12000 Pa, reflux ratio of 2.5; d) permeate pressure of 5333 Pa, reflux ratio of 0.25 (for all cases: feed velocity of 3 m/s, feed ethanol mole fraction of 0.476 (70 % ethanol by mass), liquid feed temperature of 313.15, vapour feed temperature of 383.15 K).

5.6. Conclusions

Ethanol is a biofuel, conventionally produced through the fermentation of biomass-derived sugars. However, the energy intensive nature of the ethanol production process limits the usefulness of ethanol as a renewable fuel. The separation processes used to recover anhydrous ethanol from the fermentation broth are particularly energy intensive, usually accounting for more than 50 % of the total process energy demand. The recovery of ethanol is difficult for two main reasons. First, the fermentation process is limited to ethanol concentration of at most 10 % by mass when conventional substrates are employed. If cellulosic substrates are used, genetically modified micro-organisms must be employed to ferment the sugars. These micro-organisms are even more sensitive to ethanol inhibition, leading to final ethanol concentrations of at most 5 %. The second problem is that ethanol and water form an azeotrope at a concentration of approximately 95.6 % ethanol by mass. Special separation techniques are therefore required to break this azeotrope and produce anhydrous ethanol.

This investigation presented a new hybrid separation for efficient ethanol recovery, dubbed Membrane Dephlegmation. The proposed process is a hybrid of distillation and pervaporation. An overview of the proposed system was provided and qualitatively compared to the conventional separation process. A detailed mathematical model was then derived to explain the transport phenomena occurring in the hybrid process. The model was used to compare the Membrane Dephlegmation process to conventional distillation. The hybrid process was shown to be capable of breaking the ethanol-water azeotrope. Further, it was demonstrated that the pervaporation process, which is associated with both material and energy transfer, indirectly affects heat and mass transfer across the vapour-liquid interface. It is possible to adjust the influence of pervaporation on the process by adjusting the permeate pressure. The reflux ratio was also shown to impact the performance of the Membrane Dephlegmation process. In conventional distillation, higher reflux ratios lead to higher ethanol concentrations in the liquid phase, which favours the accumulation of ethanol in the vapour phase. However, in the Membrane Dephlegmation process, the reflux rate affects both vapour liquid contacting and the pervaporation flux.

5.8. Acknowledgement

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

5.9. Nomenclature

C	number of chemical species
C_p	heat capacity, kJ/kmol.K
c_t	total molar concentration, kmol/m ³
D	diameter, m
D_{AB}	Fick diffusion coefficient, m ² /s
E	interphase energy flux, kJ/m ² .s or activation energy, kJ/kmol
g	gravitational acceleration, 9.81 m/s ²
H	enthalpy, kJ/kmol
$\bar{H}$	partial molar enthalpy, kJ/kmol
ΔH^{vap}	latent heat of vaporization, kJ/kmol
h^*	corrected heat transfer coefficient, kJ/m ² .s.K
h	heat transfer coefficient, kJ/m ² .s.K
K^*	corrected mass transfer coefficient, kmol/m ² .s
K	mass transfer coefficient, kmol/m ² .s or distribution coefficient
k	thermal conductivity, kJ/m.s.K
L	total liquid molar flow rate, kmol/s or length, m
l	liquid component molar flow rate, kmol/s
M	molar mass, kg/kmol
$\dot{m}$	mass flow rate, kg/s
N	interphase molar flux, kmol/m ² .s or number of segments
Nu	Nusselt number
Pr	Prandtl number
p	pressure, Pa
Q	membrane permeability, kg/m ² .h.bar

R	internal tube radius, m or universal gas constant, 8.314 J/mol.K
Re	Reynolds number
r	radial coordinate
Sc	Schmidt number
Sh	Sherwood number
T	temperature, K
u	velocity, m/s
V	total vapour molar flow rate, kmol/s or molar volume, m ³ /kmol
v	vapour component molar flow rate, kmol/s
x	liquid phase mole fraction
y	vapour phase mole fraction
z	axial coordinate
Δz	differential element

Greek letters

α	thermal diffusivity, m ² /s
δ	liquid film thickness, m
$\bar{\phi}$	fugacity coefficient
θ	angular coordinate
γ	activity coefficient
Φ	film theory energy correction factor
Ψ	film theory mass correction factor
μ	viscosity, Pa.s
ρ	density, kg/m ³

Subscripts

E	ethanol
i	species i
L	liquid phase
LM	liquid-membrane interface
M	membrane (solid surface)
P	permeate (or external temperature)

<i>ref</i>	at reference conditions
<i>rel</i>	relative
<i>V</i>	vapour phase
<i>W</i>	water

Superscripts

<i>E</i>	excess
<i>I</i>	interface
<i>ig</i>	ideal gas
<i>PV</i>	pervaporation
<i>R</i>	residual
<i>ref</i>	at reference conditions
<i>sat</i>	saturation conditions
<i>vap</i>	vaporization

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NUMERICAL INVESTIGATION OF MEMBRANE DEPHLEGMATION: A HYBRID PERVAPORATION- DISTILLATION PROCESS FOR ETHANOL RECOVERY

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Abstract

Ethanol is a renewable fuel that could help alleviate the dependence of the transportation sector on fossil fuels to supply energy. Ethanol can be produced through the fermentation of sugars obtained from a variety of biomass. However, the energy intensive nature of the ethanol separation process limits the usefulness of ethanol as a biofuel. Membrane Dephlegmation is a hybrid pervaporation-distillation process that could help improve the efficiency of ethanol recovery. As opposed to most other hybrid pervaporation-distillation processes, Membrane Dephlegmation combines both processes in a single unit. In this investigation, a mathematical model of the Membrane Dephlegmation process was used to carry out a parametric study for important operating conditions and geometric variables. The impacts of feed flow rate, feed concentration, permeate pressure, reflux ratio, membrane length and membrane diameter on separation efficiency was studied. McCabe-Thiele plots were used to compare the performance of Membrane Dephlegmation to conventional distillation. Membrane Dephlegmation was shown to be more efficient than distillation, yielding ethanol concentrations above the ethanol-water azeotrope for similar operating conditions.

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6.1. Introduction

Worldwide demand for energy is increasing rapidly, at least partly driven by dramatic growth in developing countries. This growth has sparked concerns over the finite availability of fossil fuels and the impact of their combustion on climate change. Consequently, renewable fuels and sustainable energy systems have received increased attention and are expected to become critically important to support future global economic growth. Interest in liquid biofuels, such as ethanol, has been particularly high because these fuels fit into established infrastructure for the transportation sector. In fact, ethanol has been blended with gasoline and used in conventional internal combustion engines for many years.

Ethanol is produced through the anaerobic fermentation of sugars, which can be obtained from a variety of biomass. Commonly, saccharine or starchy (ex. corn or sugar cane) biomass is used as the sugar source. However, it is now widely accepted that low-value, cellulosic biomass or waste residues should be used to avoid competition for food and generate a better alternative fuel. To minimize external energy inputs, the ethanol production process should be as energy efficient as possible. Ethanol recovery from the fermentation product stream is known to be a particularly energy intensive process, accounting for a large portion of the total process energy demand. The ethanol separation process is energy intensive for two primary reasons. For conventional types of biomass, the fermentation process is limited to final ethanol concentrations of approximately 10 % by mass, due to the inhibitory effect of ethanol on the micro-organisms. Cellulosic processes employ genetically modified micro-organism to ferment the sugars obtained from the biomass. Since these micro-organisms are more susceptible to ethanol inhibition, the fermentation product contains even less ethanol. The recovery of ethanol from such a dilute solution leads to a high energy consumption. Further, ethanol and water form an azeotrope at approximately 95.6 % ethanol by mass. Thus, distillation becomes inefficient at high concentrations and a special dehydration process is required to break the azeotrope.

In a previous paper, a new hybrid membrane separation process was proposed for ethanol recovery [1]. This process can be used for ethanol separation, for any upstream process configuration. The process, which has been named Membrane Dephlegmation, combines distillation and pervaporation. However, as opposed to most other hybrid processes the distillation and pervaporation processes are carried out together within a single unit. A mathematical model was derived and used to carry out preliminary numerical investigations into

the performance of the process. In this investigation, the mathematical model is used to carry out a parametric study for the system. To provide relevant background information, pertinent aspects of the conventional ethanol separation and Membrane Dephlegmation processes are reviewed. To investigate the potential benefits of Membrane Dephlegmation, simulation results are presented to study the impact of critical operating parameters including feed flow rate, feed concentration, permeate pressure and reflux ratio. The effect of membrane geometry is also studied. Additionally, an analysis using McCabe-Thiele plots is presented to compare the process to conventional distillation. Due to their prevalence in distillation design, these plots provide a convenient basis for comparison and emphasize the advantages of Membrane Dephlegmation. Lastly, the potential benefits of Membrane Dephlegmation on the energy efficiency of the overall ethanol recovery process are qualitatively discussed.

6.2. Process Overview

An overview of the conventional ethanol recovery process is presented in Figure 6.1. Feedstock pretreatment and fermentation processes are usually quite complicated and depend on the type of biomass used as the feedstock. The fermentation step produces a stream that usually contains at most 10 % ethanol by mass, if conventional substrates (starchy or saccharine biomass) are used. Conversely, if cellulosic biomass is used, recombinant micro-organisms are required in the fermentation process. These micro-organisms generally have a lower ethanol tolerance and are usually limited to an ethanol concentration of 5 % by mass. The fermentation broth then undergoes a separation step to remove insoluble solids.

After solids separation, the dilute mixture, which contains primarily ethanol and water, is usually sent to a steam stripping column (beer column). The steam stripping column can operate with a reboiler or direct steam injection. In either case, ethanol is stripped from the feed stream to generate a vapour phase distillate stream that normally contains between 30 and 60 % ethanol by mass. The distillate concentration primarily depends on the design of the column and the feed concentration. The bottoms product leaving the beer column is mainly water, with some residual dissolved solids.

Conventionally, the vapour stream exiting the beer column enters the bottom of a rectifying column. The rectifying column increases the ethanol concentration to near the ethanol-water azeotrope. Commonly the distillate concentration is between 90 and 94 % ethanol by mass. To produce anhydrous ethanol, the distillate must undergo a dehydration process. Currently,

extractive distillation, pressure swing adsorption and vapour permeation/pervaporation are the most commonly employed separation processes [2]. The bottoms product leaving the rectifying column contains a significant portion of the ethanol and must be recycled. The ethanol can either be recovered in a separate stripping column or recycled to the beer column.

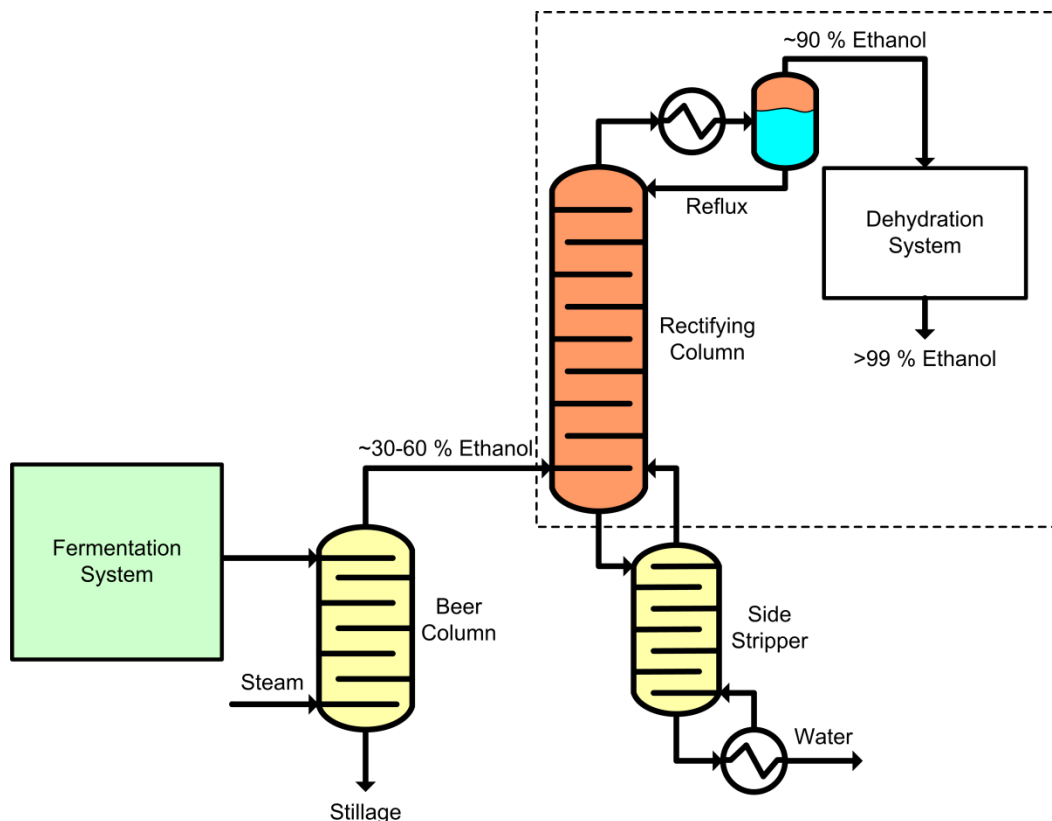


Figure 6.1. Overview of the conventional ethanol recovery process.

This paper investigates a hybrid distillation-pervaporation process. The primary goal is to replace the rectifying and dehydration sections in the ethanol recovery process with a single unit. Hybrid distillation-pervaporation processes have been the subject of a large number of studies. Only a brief overview of relevant processes is provided here. Lipnizki et al. [3] presented a review of hybrid pervaporation processes. Included in their paper was a discussion of different approaches for integrating pervaporation and distillation in the ethanol production process. Szitkai et al. [4] presented an optimization study for a hybrid distillation-pervaporation process for ethanol separation. A Mixed-Integer Nonlinear Programming (MINLP) approach was employed to minimize the total annual cost.

Recently, several processes have been proposed to directly integrate distillation and pervaporation. Del Pozo Gomez et al. [5,6] proposed an efficient pervaporation process that can

be easily combined with distillation. The pervaporation module is specifically designed for heat integration between vapour and liquid streams. Both vapour and liquid streams were fed to a modified pervaporation module. Inside the module, the vapour and liquid streams were separated by a conductive wall and only the liquid is exposed to the membrane surface. Normally, pervaporation results in a liquid temperature drop due to the heat loss associated with permeation and evaporation of water through the membrane. However, their process supplied the heat lost due to pervaporation by partial condensation of the vapour stream. Fontalvo et al. [7,8] also proposed a process in which a two-phase vapour-liquid mixture was contacted directly with a membrane surface. Partial condensation of the vapour again provided energy to drive the pervaporation process. Additionally, it was suggested that the presence of the vapour phase increased turbulence in the module, decreasing the effect concentration and temperature polarization.

Several hybrid distillation-pervaporation processes have also been proposed specifically for ethanol-water separation. Vane [9] provided an overview of some processes that integrate pervaporation directly into the ethanol production process. Vane et al. [10] proposed an innovative, hybrid distillation-vapour permeation process to improve the energy efficiency of the ethanol separation process. The process uses a hydrophilic vapour permeation membrane following the stripping column to efficiently produce ethanol at high concentrations. The process was validated experimentally using a pilot-scale separation system [11]. The energy requirements of the investigated process were determined to be significantly lower than required for conventional separation processes.

Membrane Dephlegmation is a hybrid pervaporation-distillation process. A schematic representation of the ethanol separation process, incorporating the Membrane Dephlegmation system, is shown in Figure 6.2. As shown in Figure 6.2, the ultimate goal is to replace the rectifying column and dehydration system with a single unit. In the proposed process, the vapour stream leaving the beer column enters the bottom of a vertically-oriented membrane unit and flows upwards through the module. As in a rectifying column, the vapour is partially condensed and refluxed to the system at the top of the membrane unit. The liquid reflux flows down the surface of the membrane through the action of gravity. This leads to countercurrent contacting of the vapour and liquid phases, allowing enrichment of the volatile components in the vapour phase. A vacuum pressure is maintained on the permeate side of the membrane to maintain a

driving force for the selective pervaporation of water. Since permeating species must be vaporized, the pervaporation process is associated with a heat loss. Thus, an energy flux also drives the partial condensation of the vapour phase. The pervaporation flux can be tailored to modify vapour-liquid contacting and condensation through adjustment of the permeate pressure. The process has been named Membrane Dephlegmation since it includes aspects of pervaporation, dephlegmation (refluxed condensation) and distillation.

In a previous numerical study it was shown that Membrane Dephlegmation is capable of producing a distillate above the azeotropic composition [1]. In this investigation, a detailed numerical analysis of the impact of important operating parameters on the ethanol recovery performance is presented. Critical parameters, including flow rate, feed concentration, permeate pressure, reflux ratio and membrane geometry, are studied to determine their impact on separation efficiency. The performance of the system is also compared to distillation using McCabe-Thiele plots.

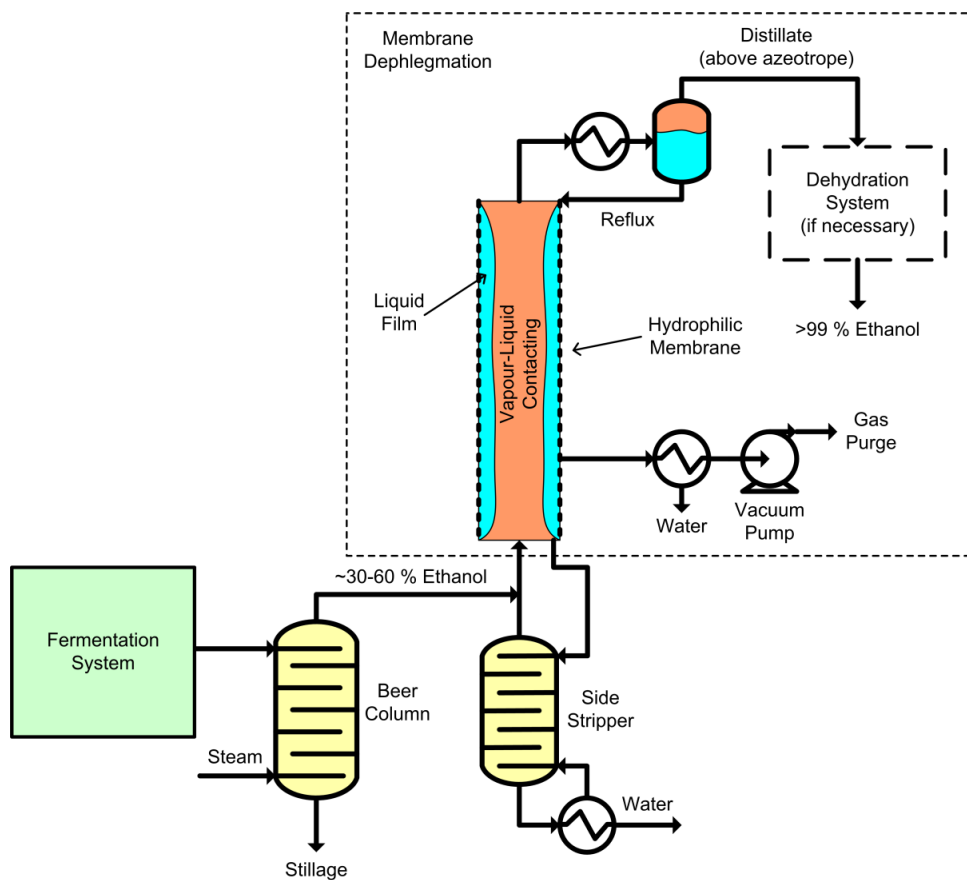


Figure 6.2. Overview of an ethanol-water separation process incorporating Membrane Dephlegmation.

6.3. Numerical Methodology

6.3.1. Modeling

A mathematical model to describe the Membrane Dephlegmation and wetted-wall distillation processes was previously presented [1]. Therefore, only a brief summary of the model equations and solution methods is presented in this section. The Membrane Dephlegmation process could be carried out using various membrane geometries. The process could also employ a variety of hydrophilic membrane materials. However, NaA zeolite membranes are commercially available and are known to exhibit a particularly high water flux and selectivity [12,13]. Thus, in this investigation, the pervaporation model of Sommer and Melin [12] is used to describe the pervaporation process. Further, tubular NaA membranes with the selective layer inside the tubes are used in the simulations since these membranes are commercially available and provide a convenient geometry for the process [13,14]. Therefore, the mathematical model presented in this section is derived for a tubular membrane geometry, with the selective layer on the inside of the tubes. This provides a convenient geometry since it is relatively compact and allows good liquid distribution. An overview of the transport processes involved in the Membrane Dephlegmation process is presented in Figure 6.3. Figure 6.3 also shows a schematic representation of the tubular membrane geometry used in this investigation.

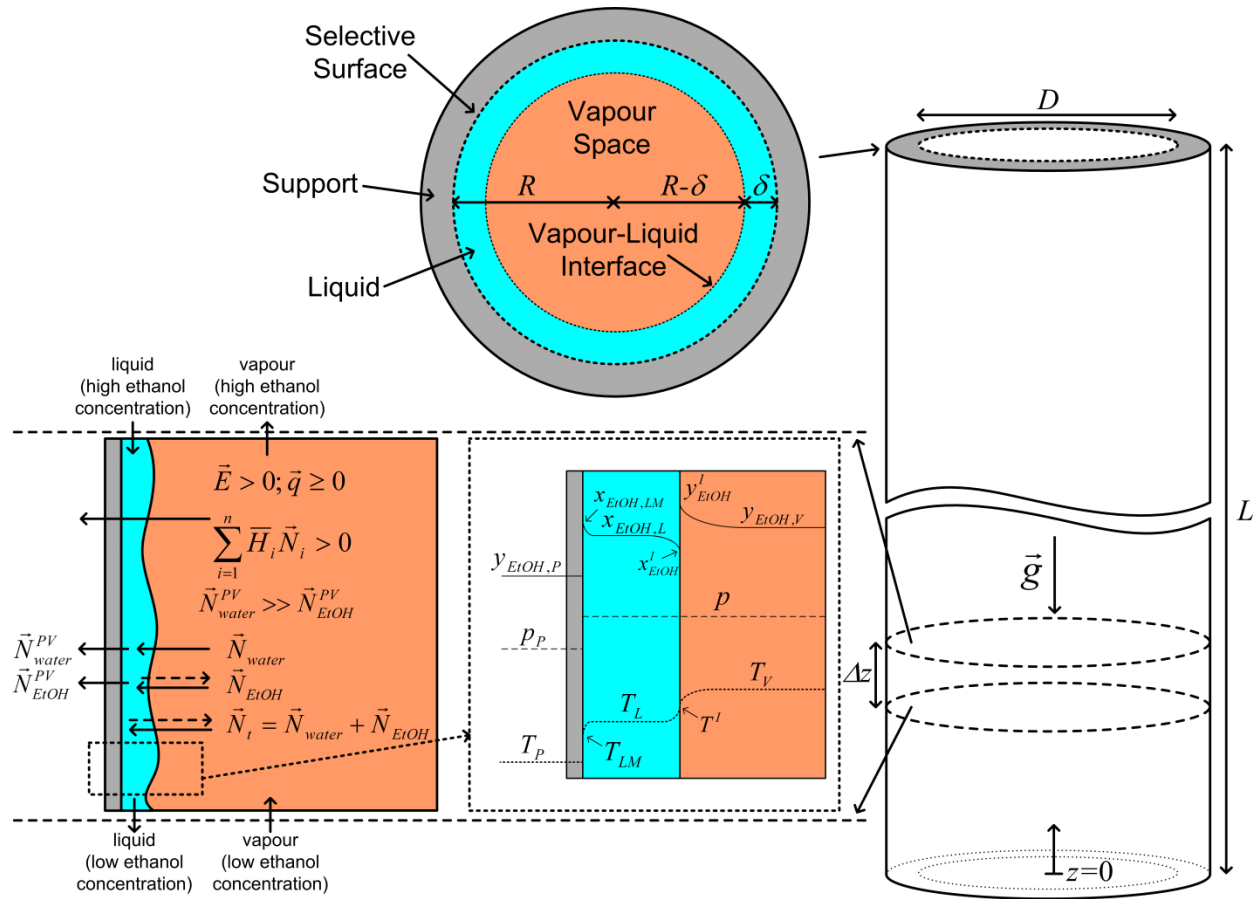


Figure 6.3. Overview of transport processes and schematic representation of the investigated geometry.

The steady state transport model employed in this investigation to describe both the Membrane Dephlegmation and wetted-wall distillation processes solves one-dimensional material and energy balances for both the liquid and vapour phase. A summary of the material and energy balance equations is provided in Table 6.1. The vapour phase is only exposed to the liquid phase, as shown in Figure 6.3. Thus, the vapour component balances only include component sources due to material transfer across the vapour-liquid interface. Conversely, the liquid is exposed to both the vapour-liquid and membrane-liquid interfaces. Therefore, the liquid component balances include sources due to material transport through the vapour-liquid interface and through the membrane by pervaporation. Similarly, the vapour phase energy balance only includes a source term to account for conductive and convective (i.e. energy transfer associated with the latent heat of condensation/evaporation) energy transport across the vapour-liquid interface. The liquid phase energy balance accounts for both conductive and convective energy transfer across the vapour-liquid and membrane-liquid interface.

Table 6.1. Summary of Material and Energy Conservation Equations (for C components)**C vapour component balances:**

$$\frac{dv_i}{dz} = -2\pi(R - \delta)N_i$$

C liquid component balances:

$$\frac{dl_i}{dz} = -2\pi(R - \delta)N_i + 2\pi R N_i^{PV}$$

1 vapour energy balance:

$$\frac{dVH_V}{dz} = -2\pi(R - \delta)E_V$$

1 liquid energy balance:

$$\frac{dLH_L}{dz} = -2\pi(R - \delta)E_L + 2\pi R E_{LM}$$

Interface material and energy balances are required to calculate the source terms in the material and energy conservation equations presented in Table 6.1. Table 6.2 provides a summary of the component and energy balances at the vapour-liquid interface. A single energy balance is required. Conversely, component balances are required on both the liquid and vapour side. To solve the interphase flux expressions, some auxiliary conditions are also required to relate component mole fractions and temperature at the interface. It is commonly assumed that vapour-liquid equilibrium prevails at the interface [15]. Under this assumption, interface mole fractions and temperature can be related using a distribution coefficient (or K -value), as shown in Table 6.2 [16]. Under the ideal gas assumption, the distribution coefficient may be determined using the following expression.

$$K_i = \frac{\gamma_i P_i^{sat}}{p} \quad (1)$$

Of course, the mole fractions in each phase must also sum to unity by definition. The combination of these expressions fully defines transport across the vapour-liquid interface.

Table 6.2. Summary of Conditions at the Vapour-Liquid Interface (for C components)

1 energy balance at the vapour-liquid interface:

$$E_V = h_V^*(T_V - T^I) + \sum N_i \bar{H}_{i,V}(T_V) = E_L = h_L^*(T^I - T_L) + \sum N_i \bar{H}_{i,L}(T_L)$$

C -1 vapour side component balances at the vapour-liquid interface:

$$N_i = K_V^*(y_{i,V} - y_i^I) + y_{i,V} \sum N_i$$

C -1 liquid side component balances at the vapour-liquid interface:

$$N_i = K_L^*(x_i^I - x_{i,L}) + x_{i,L} \sum N_i$$

C vapour-liquid equilibrium relations:

$$K_i x_i^I - y_i^I = 0$$

2 interface mole fraction summation equations:

$$\sum_{i=1}^C x_i^I - 1 = 0, \sum_{i=1}^C y_i^I - 1 = 0$$

Expressions are also required to characterize material and energy transport across the membrane-liquid interface. Table 6.3 summarizes the equations required to calculate transport through the membrane-liquid interface. The energy balance includes both conductive and convective components. If the model is used to simulate wetted-wall distillation, the pervaporation flux is removed and the convective term disappears. Further, the equations required to determine the pervaporation flux are not used when simulating wetted-wall distillation. For the Membrane Dephlegmation process, a component balance is required on the liquid side of the membrane-liquid interface to account for mass transfer through the liquid boundary layer. Flux expressions are required to determine the pervaporation flux across the membrane. In this study, the model proposed by Somer and Melin [12] was used to estimate water and ethanol flux through the NaA zeolite membrane. As shown in Table 6.3, this model is based on a solution-diffusion mechanism. It should be noted that the ethanol permeability is much smaller than the water permeability and therefore, the contribution of the ethanol flux was negligible in the current study. Finally, as shown in Table 6.3, an expression is required to relate the pervaporation flux to the permeate concentration and again mole fractions must sum to unity.

Table 6.3. Summary of Conditions at the Membrane-Liquid Interface (for C components)

1 interphase energy balance at the membrane-liquid interface:

$$E_{LM} = h_{LM}^* (T_L - T_{LM}) + \sum N_i^{PV} \bar{H}_{i,L}(T_L) = E_M = h_M^* (T_{LM} - T_P) + \sum N_i^{PV} \bar{H}_{i,V}(T_P)$$

C -1 liquid side component balances at the membrane-liquid interface:

$$N_i^{PV} = K_{LM}^* (x_{i,L} - x_{i,LM}) + x_{i,L} \sum N_i^{PV}$$

C membrane flux expressions:

$$N_i^{PV} = Q_i (\gamma_i x_{i,LM} p_i^{sat} - y_{i,P} p_P)$$

$$Q_i = Q_i^{ref} \left[\frac{E_i}{R} \left(\frac{1}{353.15} - \frac{1}{T_{LM}} \right) \right]$$

$$Q_E^{ref} = 4.221 \times 10^{-13} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}, \quad Q_W^{ref} = 1.744 \times 10^{-9} \frac{\text{kmol}}{\text{m}^2 \cdot \text{s} \cdot \text{Pa}}$$

$$E_E = 25.7 \frac{\text{kJ}}{\text{kmol}}, \quad E_W = 17.0 \frac{\text{kJ}}{\text{kmol}}$$

C -1 membrane flux to permeate mole fraction relations:

$$y_{i,P} = \frac{N_i^{PV}}{\sum N_i^{PV}}$$

2 membrane interface mole fraction summation equations:

$$\sum_{i=1}^C x_{i,LM} - 1 = 0, \quad \sum_{i=1}^C y_{i,P} - 1 = 0$$

Several heat and mass transfer coefficients are required to solve the equations presented in Tables 6.1 through 6.3. An in-depth discussion of the expressions used to estimate these parameters was presented previously [1]. As a summary, laminar flow was assumed in the vapour phase and the heat and mass transfer coefficient were determined based on expressions for laminar flow in a tube. The liquid phase velocity profile and film thickness were calculated analytically, assuming a smooth laminar liquid film and negligible interaction with the vapour phase (Nusselt assumptions). This allowed the expressions of the liquid phase heat and mass transfer coefficients to be determined analytically. The heat and mass transfer coefficients were corrected for high flux conditions using film theory [15]. The model also includes an external heat transfer coefficient (h_M^*) to account for external heat losses from the membrane system. In this study, it was assumed that there were no external conductive heat losses (i.e. $h_M^* = 0$). It is realized that perfect insulation is impossible to achieve but it is expected that the impact of external conductive losses would be small.

6.3.2. Numerical Details

Temperature and composition dependent properties for the ethanol-water system were used in all simulations. The liquid phase viscosity, thermal conductivity and diffusion coefficient were calculated using the Neural Network models developed by Haelssig et al. [17]. The vapour phase viscosity, thermal conductivity and diffusion coefficient were calculated using the Reichenberg, Wassiljewa and Fuller methods, respectively [18]. Pure component viscosity and thermal conductivity were estimated using temperature dependent polynomial relationships [19]. The latent heat of vaporization was calculated from the temperature dependent expressions provided in [20]. The vapour pressure for both species was determined using the extended Antoine equation [20]. The Wilson activity model was used to calculate the activity coefficients for the ethanol-water system [21]. The liquid phase densities (molar volume) of ethanol and water were calculated using the expressions provided in [20]. The excess volume for mixing was estimated using the Wilson equation [16]. The ideal gas law was applied to estimate the vapour phase density (and molar volume). The heat capacities in the vapour and liquid phase were calculated using temperature dependent polynomial relationships [19]. The liquid and vapour phase enthalpies were calculated through integration of the temperature dependent heat capacities (see [1] for details). In the vapour phase, the residual enthalpy was assumed to be 0 (under the ideal gas assumption). In the liquid phase, the excess enthalpy was calculated using the Wilson activity model.

The conservation equations presented in Table 6.1 were discretized using a finite difference approximation. The column was divided into N segments and the number of segments was increased until a grid independent solution was obtained. The discretized conservation equations form a system of nonlinear algebraic equations, which were combined with the interface conditions presented in Tables 6.2 and 6.3 to form a large block tri-diagonal system of nonlinear equations. When combined with the heat and mass transfer correlations and physical properties discussed earlier, the equations can be solved for all unknowns. In the case of wetted-wall distillation, a system of $(5C+4)N$ equations is formed. Conversely, a system of $(8C+4)N$ equations must be solved for the Membrane Dephlegmation process. The block tri-diagonal system of nonlinear equations must be solved iteratively. In this study, an in-house code, programmed in the Java programming language was employed to solve the equations. The

simulator used a block tri-diagonal version of the Thomas algorithm, combined with a modified Newton's method to converge on the solution.

6.3.3. Parametric Study

For this investigation, simulations were performed for a wide variety of operating conditions and tube geometries. It must be noted that, commercial membranes are available at lengths of 1.2 m, with a tube diameter of 0.006 m [14]. To increase the length of the tube it is assumed that the membranes could be placed in series. In fact an experimental system using these membranes in series is currently under investigation.

A summary of the operating conditions and geometries investigated in this study is provided in Table 6.4. In all cases considered, the external heat transfer coefficient (h_M^*) was assumed to be 0. The vapour entered the membrane column under superheated conditions, at a temperature of 383 K. Meanwhile, the liquid was refluxed to the column in the subcooled state, at 313 K. Results of the parametric study are presented in the following sections.

Table 6.4. Summary of Investigated Operating Conditions and Geometries

Feed Velocity (m/s)	1, 3, 5, 7
Feed Ethanol Mass Fraction	0.5, 0.7, 0.9
Permeate Pressure (Pa)	0, 5300, 12000, 18700
External Reflux Ratio	0.25, 0.5, 1, 2.5, 5, 10
Length (m)	1.2, 2.4, 3.6
Diameter (m)	0.006, 0.008, 0.012

6.4. Results and discussion

6.4.1. Operating Lines for Membrane Dephlegmation

Operating line plots are used extensively in the analysis of chemical separation processes. In the design of binary distillation columns, McCabe-Thiele plots are particularly convenient (see [22] for a full discussion). For binary distillation, these plots are usually made with respect to the more volatile species (ethanol in this case). On the plots, the vapour phase concentration is plotted as a function of the liquid phase concentration. Vapour-liquid equilibrium data are plotted, since the driving force for separation in distillation processes is proportional to the difference between the equilibrium curve and the operating line. In a typical staged distillation column, the operating line is obtained by performing a mass balance and represents a plot of the vapour concentration entering each tray and the liquid concentration exiting the same tray. If

equilibrium is reached on the tray, the exiting vapour and liquid concentrations correspond to a point on the equilibrium line. In packed and wetted-wall distillation columns mass is exchanged throughout the length of the column. Thus, the operating line simply represents the profile of the bulk liquid and vapour phase concentrations along the length of the column.

Membrane Dephlegmation is similar to distillation, since it involves continuous vapour-liquid contacting. Thus, the liquid and vapour concentrations at each column position drive the separation process. However, as opposed to distillation, the composition of the liquid phase is altered due to the selective permeation of water through the pervaporation membrane. Since pervaporation changes the liquid phase concentration and is associated with an energy flux, vapour-liquid mass transfer is also affected. Regardless, similar to wetted-wall distillation, vapour and liquid phase concentrations are available along the length of the Membrane Dephlegmation column. Thus, the performance of distillation and Membrane Dephlegmation can be compared using plots of their operating lines.

Figure 6.4 shows plots of the operating lines for both wetted-wall distillation and Membrane Dephlegmation, for one set of operating conditions. As in conventional McCabe-Thiele plots, the vapour-liquid equilibrium line for the ethanol-water system and the 45 degree line are also shown on the figure. It is important to note that only enriching lines are plotted, since the columns have a vapour feed and no reboilers. If a distillation column is operated with an infinite reflux ratio (i.e. no distillate leaves the system), the operating line will follow the 45 degree line. This represents the maximum separation achievable in the column. Practically, a column cannot be operated with an infinite reflux ratio. Therefore, the operating line for distillation must always fall between the 45 degree line and the equilibrium line. That is, if the plot is made with respect to the more volatile component, the vapour phase concentration must always be greater than the liquid phase concentration. This is demonstrated in Figure 6.4 for the wetted-wall distillation operating line. As opposed to distillation, Membrane Dephlegmation incorporates the selective removal of water from the liquid phase at the membrane-liquid interface. Dehydration of the liquid phase leads to higher liquid phase ethanol concentrations and, as shown on Figure 6.4, the operating line can fall below the 45 degree line. Since the liquid phase ethanol concentration is higher, there is a higher driving force for ethanol to transfer to the vapour phase. Further, it is apparent that Membrane Dephlegmation is not limited to the

azeotropic composition. Differences in the operating lines for distillation and Membrane Dephlegmation are most easily explained using composition and flux profiles.

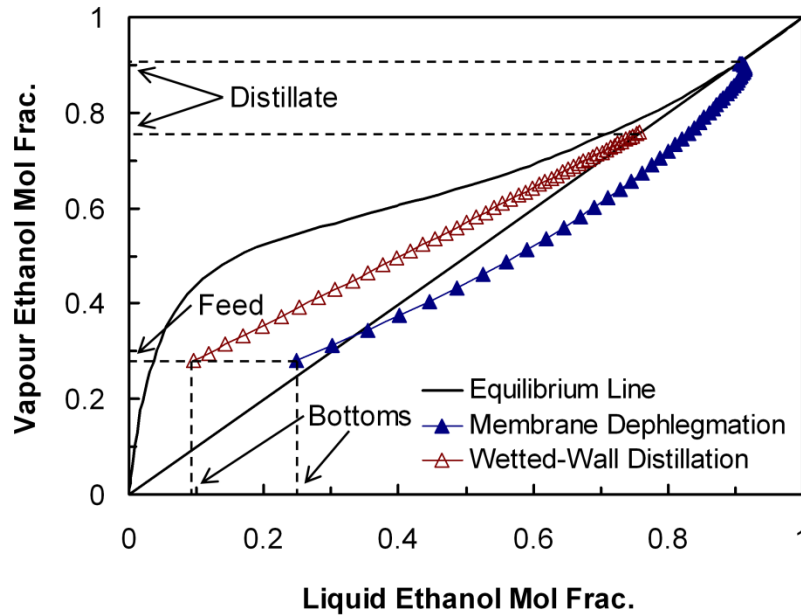


Figure 6.4. Representative examples of operating lines for wetted-wall distillation and Membrane Dephlegmation (feed ethanol mole fraction, 0.2811 (0.5 by mass); feed velocity, 3 m/s; reflux ratio, 2.5; permeate pressure, 5300 Pa; length, 2.4 m; tube diameter, 0.006 m).

Figure 6.5 shows composition and flux profiles for the distillation and Membrane Dephlegmation cases presented in Figure 6.4. From Figure 6.5c, it is apparent that the distillation process is driven only by heat and mass transfer through the vapour-liquid interface. As expected, the vapour phase concentration always remains above the liquid phase concentration. Figure 6.5c shows that the magnitudes of the ethanol and water fluxes crossing the vapour-liquid interface are nearly equal, with ethanol evaporating and water condensing. The similar molar flux magnitudes result from the nearly equal molar latent heats of vaporization for ethanol and water. The nearly equal magnitudes of the interphase fluxes also result in a nearly linear operating line, as shown in Figure 6.4. Near the top end of the column, there is a jump in the condensation flux due to the subcooled nature of the liquid reflux.

From the composition profiles for Membrane Dephlegmation, Figure 6.5a, it is clear that dehydration of the liquid phase leads to a higher liquid phase ethanol concentration. In fact, as was also indicated by the operating line, the liquid phase ethanol concentration becomes higher than the vapour phase concentration. From the flux plot, Figure 6.5b, it is clear that the flux of

water through the membrane leads to an increased water condensation flux. In distillation, the water condensation flux only supplies the energy required for ethanol evaporation. Conversely, in Membrane Dephlegmation, the water condensation flux must supply the energy required for ethanol evaporation and water permeation. Comparing the flux and composition profiles, it is also apparent that pervaporation of water leads to a higher initial driving force for ethanol evaporation. This results in a more rapid increase in the vapour phase ethanol concentration and a higher ethanol evaporation flux, for Membrane Dephlegmation than for distillation. Since the operating line plots inherently contain information about both composition and flux profiles, they are used extensively in the following sections to discuss the impact of various operating conditions on system performance.

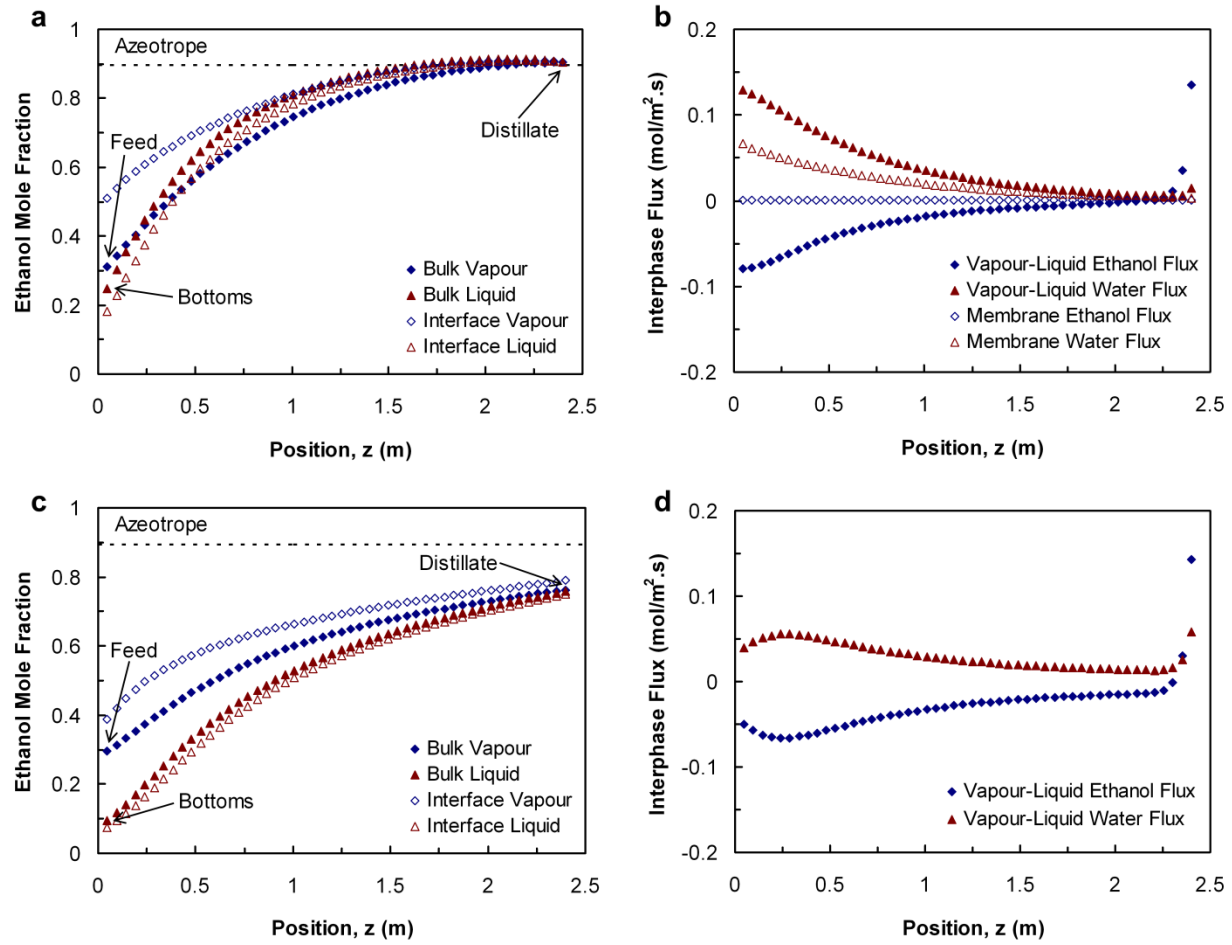


Figure 6.5. a) Composition profiles for Membrane Dephlegmation; b) Flux profiles for Membrane Dephlegmation; c) Composition profiles for wetted-wall distillation; d) Flux profiles for wetted-wall distillation (feed ethanol mole fraction, 0.2811 (0.5 by mass); feed velocity, 3 m/s; reflux ratio, 2.5; permeate pressure, 5300 Pa; length, 2.4 m; tube diameter, 0.006 m; vapour-liquid flux is positive for condensation and negative for evaporation).

6.4.2. Impact of Feed Velocity

The impact of feed velocity and reflux ratio on distillate concentration for Membrane Dephlegmation and distillation are shown in Figure 6.6. Clearly, lower feed velocities lead to longer vapour-liquid contact times and therefore more accumulation of ethanol in the vapour phase. For distillation, as expected, the distillate concentration never reaches the azeotrope. Further, Membrane Dephlegmation always outperforms distillation. However, concentrations above the azeotrope are not reached at all velocities. At very high feed velocities, a large quantity of water enters the system. As shown in Figure 6.7, the higher average concentration leads to a

higher water flux through the membrane. However, at very high velocities, the membrane area is not sufficient to offset the increased water load.

In wetted-wall distillation, the reflux ratio has a greater impact on separation performance at lower velocities. This is expected because lower velocities lead to larger contact times and therefore, more mass transfer. However, an opposing trend is observed for the Membrane Dephlegmation cases. For very low velocities, the impact of the reflux ratio becomes negligible. Conversely, at high velocities, the effect of the reflux ratio becomes more pronounced. This results from the complex interactions between vapour-liquid contacting and pervaporation occurring in the Membrane Dephlegmation system. At low velocities, the concentration quickly rises above the azeotrope. Above the azeotrope, the shape of the equilibrium line does not favour the preferential movement of ethanol to the vapour phase. Therefore, distillation effects become small. Since the reflux ratio primarily impacts the efficiency of the distillation process, the effect of reflux ratio on Membrane Dephlegmation at low velocities is small.

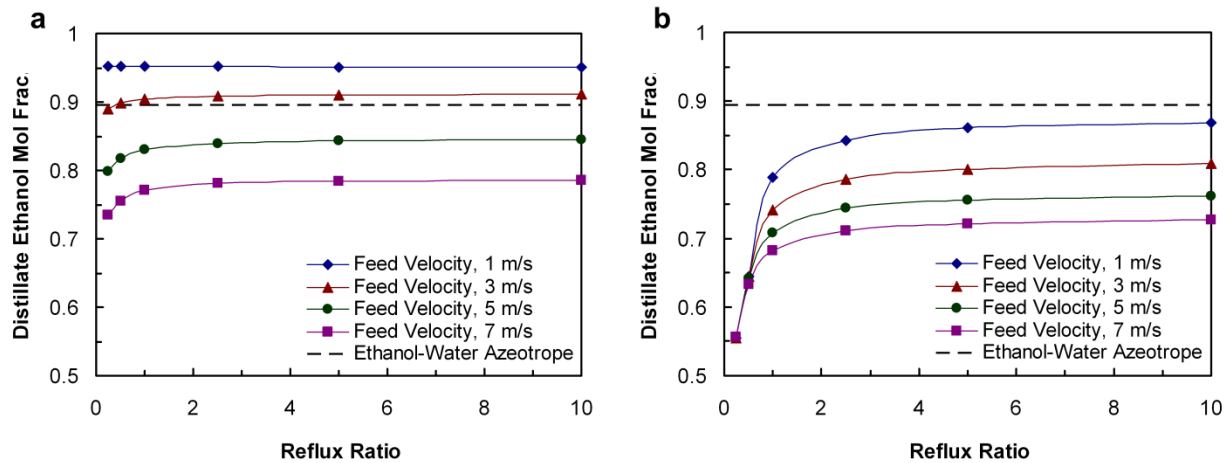


Figure 6.6. Effect of reflux ratio and feed velocity on distillate concentration for a) Membrane Dephlegmation and b) wetted-wall distillation (feed ethanol mole fraction, 0.4771 (0.7 by mass); permeate pressure, 5300 Pa; length, 2.4 m; tube diameter, 0.006 m).

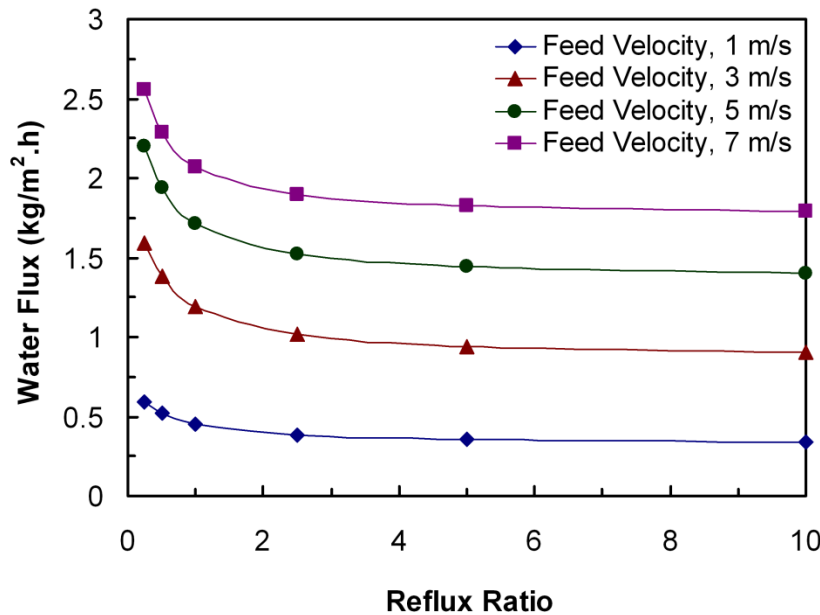


Figure 6.7. Effect of the reflux ratio and feed velocity on pervaporation water flux (feed ethanol mole fraction, 0.4771 (0.7 by mass); permeate pressure, 5300 Pa; length, 2.4 m; tube diameter, 0.006 m).

Figure 6.8 shows the impact of the feed velocity and reflux ratio on the operating lines for Membrane Dephlegmation and distillation. For distillation, the slope of the operating line is usually controlled by the reflux ratio. This is confirmed in Figure 6.8a, where both distillation cases have similar slopes. At lower concentrations, the slopes of the operating lines for Membrane Dephlegmation are also similar. This is likely because the effect of distillation is more pronounced at lower concentrations. However, at higher concentrations, the operating lines for Membrane Dephlegmation in Figure 6.8a diverge. For a lower feed velocity, a higher distillate concentration is achieved. Again, the higher distillate concentration achieved at lower feed velocities results from the increased effect of the membrane. That is, at lower velocities, less water enters the system and proportionally, pervaporation has a larger impact on the final concentration. Figure 6.8b shows that changing the reflux ratio leads to changes in the slope of the operating line. For distillation, the change in the slope also leads to a lower distillate concentration. However, although the slope of the operating line for Membrane Dephlegmation is also altered by the reflux ratio, the distillate concentration is relatively unaffected. In the case presented, the impact of reflux ratio on the distillate concentration is small because the

concentration rises to near the azeotrope very quickly. Once near the azeotrope, the effect of distillation becomes small and the two cases are governed primarily by pervaporation.

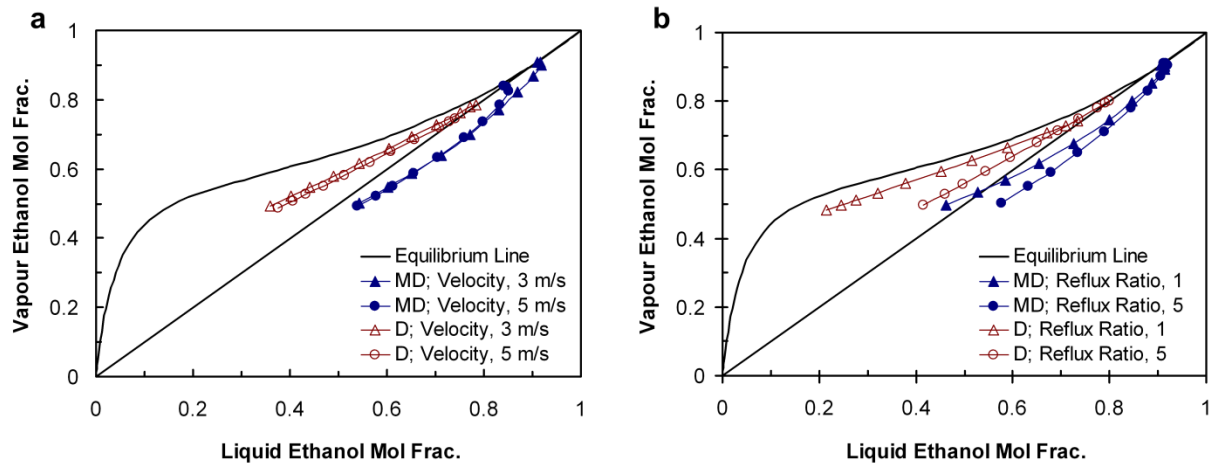


Figure 6.8. Operating line plots showing the effect of a) feed velocity (reflux ratio of 2.5) and b) reflux ratio (feed velocity of 3 m/s) on performance (feed ethanol mole fraction, 0.4771 (0.7 by mass); permeate pressure, 5300 Pa; length, 2.4 m; tube diameter, 0.006 m; MD refers to Membrane Dephlegmation; D refers to Distillation).

6.4.3. Impact of Permeate Pressure

Permeate pressure affects the driving force for pervaporation, such that lower permeate pressures lead to a higher pervaporation flux. The effect of permeate pressure on distillation cannot be studied, since distillation is not associated with a pervaporation flux. However, for Membrane Dephlegmation, permeate pressure is a critical operating variable that determines the level of separation achieved. Figure 6.9 shows the impact of permeate pressure on distillate concentration, pervaporation water flux and the operating lines. The inverse proportionality between permeate pressure and pervaporation flux is obvious from Figure 6.9b. Further, Figure 6.9a shows that the higher water fluxes resulting from lower permeate pressures lead to higher ethanol concentrations in the distillate.

Operating lines for two different permeate pressures are shown in Figure 6.9c. The shape of the curves is similar, since the reflux ratio is the same in both cases. Clearly the increased pervaporation flux, associated with the lower permeate pressure, moves the operating line further away from the equilibrium line. This leads to improved mass transfer between the vapour and liquid phases at lower concentrations and eventually to a higher distillate concentration.

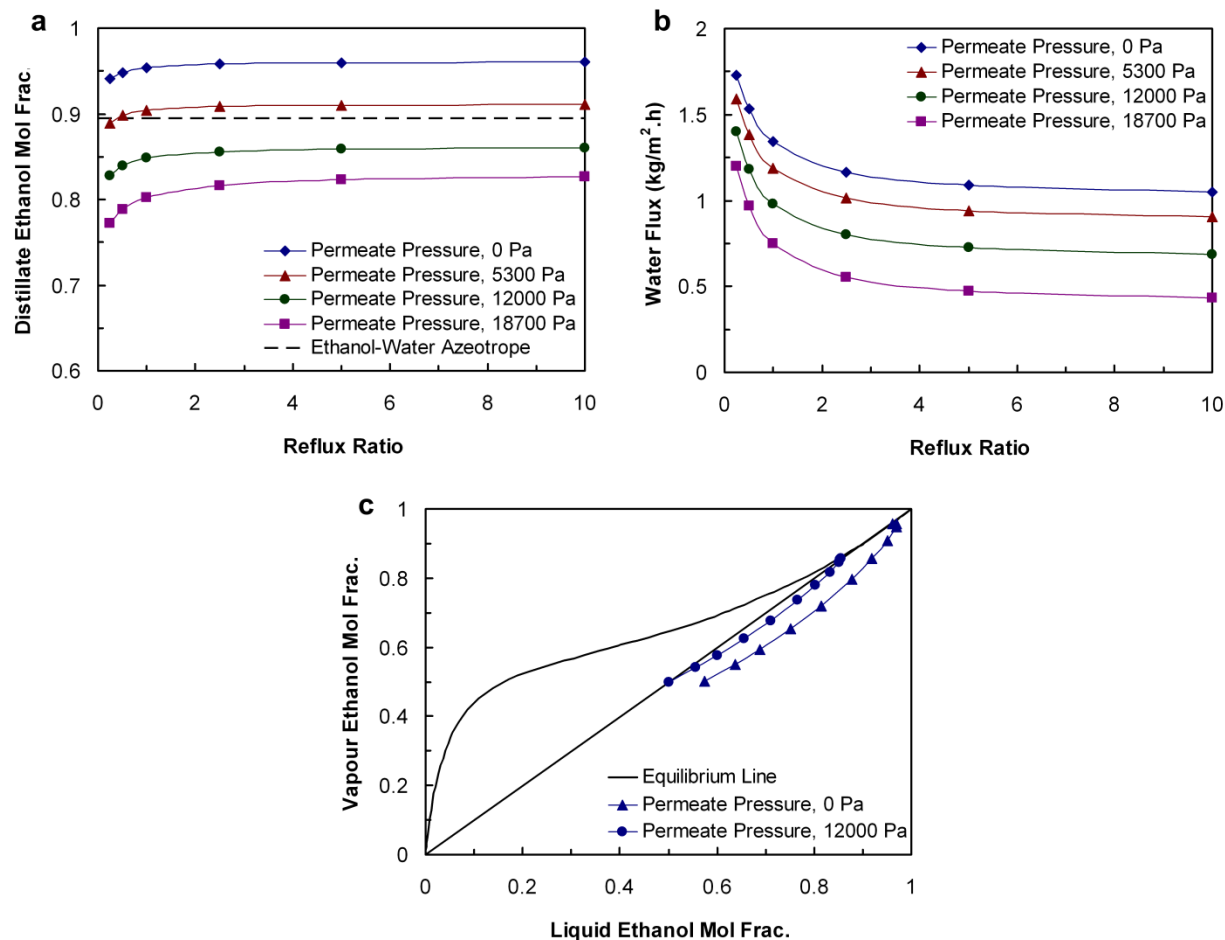


Figure 6.9. Effect of reflux ratio and permeate pressure on a) distillate concentration, b) pervaporation water flux and c) effect of permeate pressure on operating lines for a reflux ratio of 2.5 (feed ethanol mole fraction, 0.4771 (0.7 by mass); feed velocity, 3 m/s; length, 2.4 m; tube diameter, 0.006 m).

6.4.4 Impact of Feed Composition

The impact of feed composition and reflux ratio on distillate concentration for Membrane Dephlegmation and wetted-wall distillation are shown in Figure 6.10. The effect of the feed composition on the pervaporation water flux and the operating lines is also presented. The effect of the feed concentration on the distillate concentration is highly nonlinear for both the Membrane Dephlegmation and distillation cases. This is a direct consequence of the nonlinearity of the vapour-liquid equilibrium curve. At low ethanol concentrations, vapour-liquid equilibrium strongly favours the movement of ethanol to the vapour phase. Conversely, the distribution of ethanol and water between vapour and liquid phases approaches unity at higher ethanol

concentrations. It implies that, at very low feed concentrations, ethanol moves to the vapour phase very quickly and differences between the distillate concentrations at high reflux ratios are relatively small.

The relatively high efficiency of ethanol transport across the vapour-liquid interface in Membrane Dephlegmation at low ethanol concentrations can be easily seen in Figure 6.10d. From the operating lines for Membrane Dephlegmation, it is apparent that efficient vapour-liquid contacting combined with a very high water flux, at low ethanol concentrations, leads to a rapid increase in the ethanol concentration. In fact, for the cases presented, the ethanol concentration for the case with the lower feed concentration reaches the feed concentration of the other case over the first few centimetres of the column. After this point, the operating lines become essentially identical leading to a very small difference in the distillate concentration.

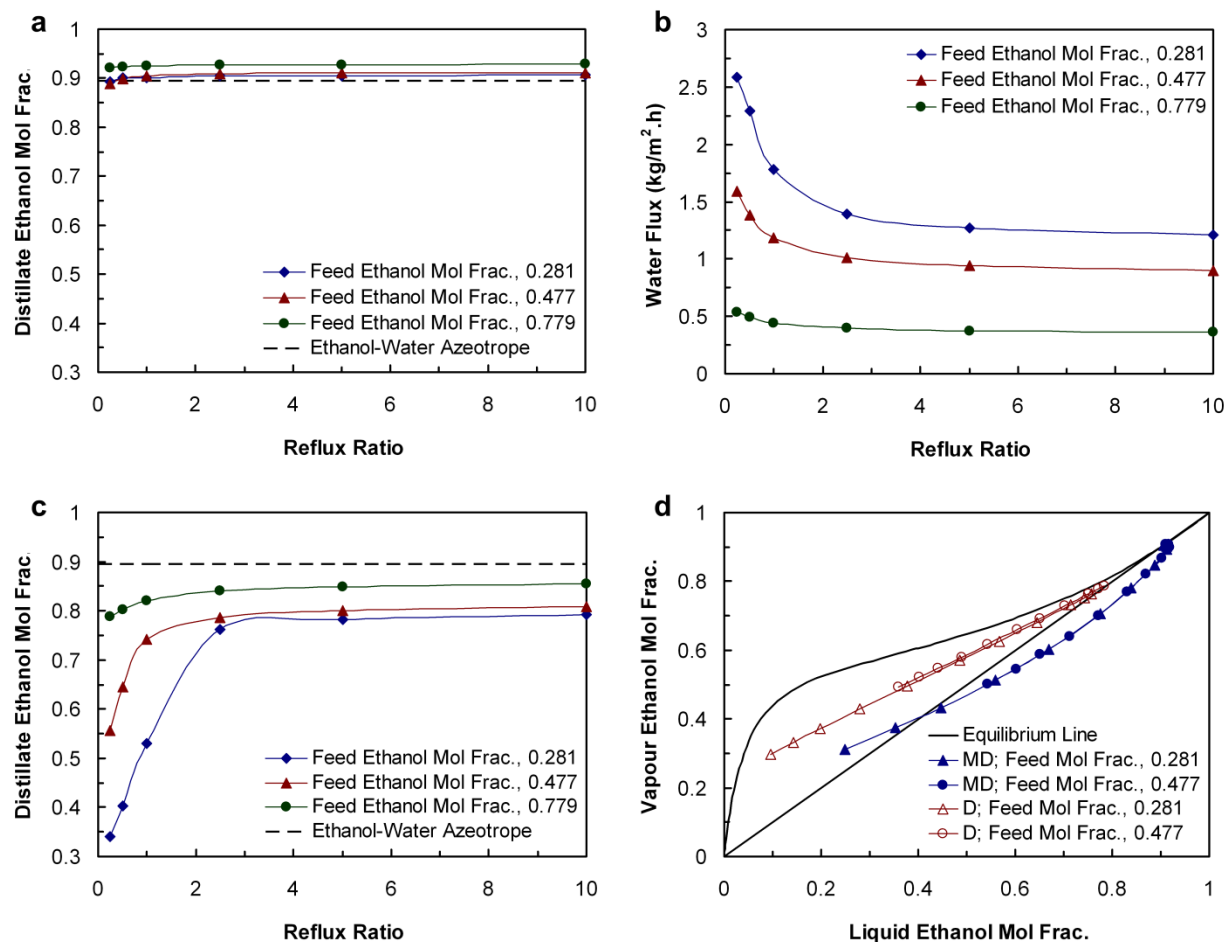


Figure 6.10. Effect of reflux ratio and feed concentration on a) distillate concentration for Membrane Dephlegmation, b) pervaporation water flux, c) distillate concentration for wetted-wall distillation and d) operating lines at two feed concentrations and a reflux ratio of 2.5 (feed velocity, 3 m/s; permeate pressure, 5300 Pa; length, 2.4 m; tube diameter, 0.006 m; MD refers to Membrane Dephlegmation; D refers to Distillation).

6.4.5. Impact of Geometry

Geometry plays an important role in Membrane Dephlegmation, since it determines both the area of the vapour-liquid interface and the membrane area. In this investigation, a tubular membrane geometry was used to study the Membrane Dephlegmation process. Since a cylindrical geometry was employed, both the length and diameter can be adjusted. Figure 6.11 shows the impact of tube length and diameter on the distillate concentration for Membrane Dephlegmation and wetted-wall distillation. The impact of tube length and diameter on the respective operating lines is shown in Figure 6.12.

The available membrane area and the area of the vapour-liquid interface increase proportionally to the tube length. Thus, as expected, the distillate concentration increases proportionally to the tube length. The impact of the increased membrane area available for larger tube lengths is apparent from the operating lines shown on Figure 6.12a. Specifically for the Membrane Dephlegmation case, the larger membrane area allows more water to permeate and thus, a higher distillate concentration is achieved.

The impact of the diameter is more complex than the effect of length. The diameter affects both the surface area and the cross-sectional area. The results in Figures 6.11 and 6.12 are presented for a fixed velocity. Increasing the diameter therefore leads to an increase in the flow rate that is proportional to the diameter squared. However, the surface area is only increased in direct proportion to the diameter. Thus, the effective surface area relative to the flow entering the column decreases when the diameter is increased. This effect is demonstrated on Figure 6.12b, which shows that the operating line is much shorter for higher diameters. Figure 6.12b also shows that the efficiency of vapour-liquid contacting, in particular, is negatively affected by an increase in the diameter. The inefficiency of vapour-liquid contacting is indicated by the short length operating line for distillation with larger tube diameters.

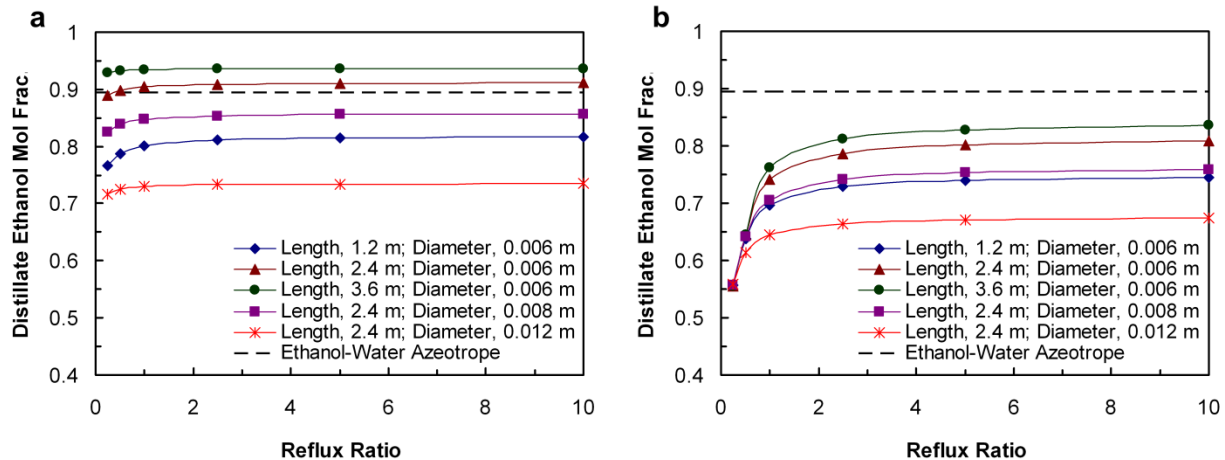


Figure 6.11. Effect of reflux ratio and geometry on distillate concentration for a) Membrane Dephlegmation and b) wetted-wall distillation (feed velocity, 3 m/s; permeate pressure, 5300 Pa; feed ethanol mole fraction, 0.4771 (0.7 by mass)).

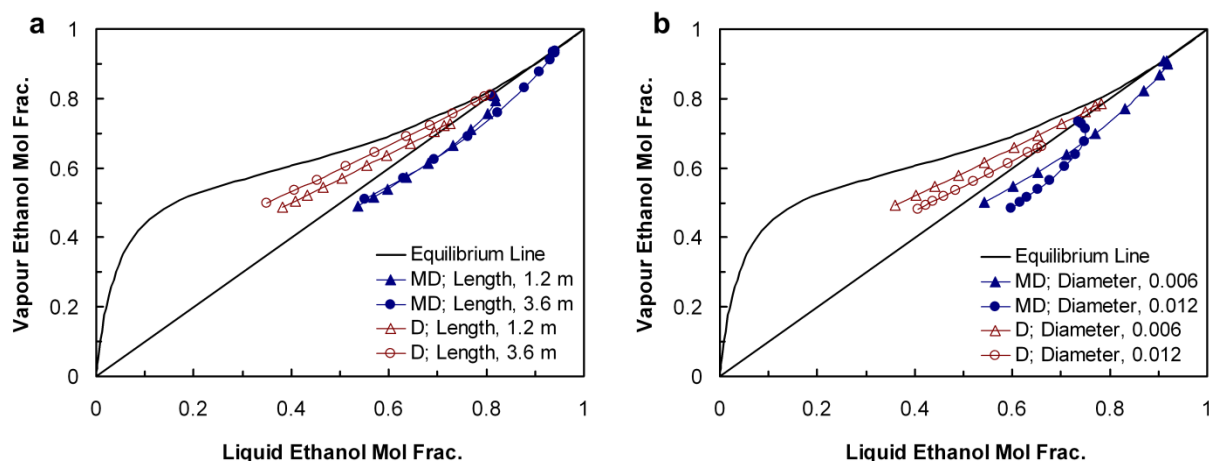


Figure 6.12. Operating line plots showing the effect of a) length (tube diameter of 0.006 m) and b) diameter (length of 2.4 m) on performance (feed velocity, 3 m/s; permeate pressure, 5300 Pa; feed ethanol mole fraction, 0.4771 (0.7 by mass); reflux ratio, 2.5; MD refers to Membrane Dephlegmation; D refers to Distillation).

6.4.6. General Discussion

The previous sections discussed the impacts of pertinent operating conditions on the performance of the Membrane Dephlegmation process. This section focuses on important technical limitations and provides a qualitative analysis of the system's effect on the overall energy efficiency of ethanol recovery. In the parametric study, a wide range of ethanol feed concentrations were investigated. However, it is known that NaA zeolite membranes become unstable when operated in pervaporation mode at high water concentrations [23]. It may therefore not be possible to use these types of membranes to process feeds with high water content. However, zeolite T membranes have shown better long-term stability for pervaporation under high water concentrations and may therefore be a suitable alternative [24].

Several membrane geometries were analyzed in this study. Currently, tubular membranes with a length of 1.2 m and a diameter of 6 mm are commercially available [14]. Due to the relatively low flooding velocities encountered in small diameter tubes, this configuration may not be optimal. To study physical limitations, experimental investigations of Membrane Dephlegmation using these membranes are underway.

As discussed in the previous section, the Membrane Dephlegmation process provides improved performance over distillation. In particular, it was demonstrated that the Membrane Dephlegmation process can achieve a higher distillate concentration than distillation for the same

reflux ratio. This effect is particularly pronounced when intermediate feed concentrations (30 to 80 % by mass) are used. Since the same separation can be achieved using a lower reflux ratio, less energy demand is placed on the steam stripping column. Further, the higher relative distillate concentration means that, if a dehydration system is required, it would be smaller. A full economic and energy analysis for an ethanol recovery process using Membrane Dephlegmation is ongoing.

6.5. Conclusions

Worldwide energy demand is increasing rapidly in most sectors. Ethanol is a renewable fuel that could help alleviate the transportation sector's dependence on fossil fuels. Ethanol is a biofuel, produced through the fermentation of sugars obtained from a variety of biomass. However, the energy intensive nature of the ethanol production process limits the usefulness of ethanol as a biofuel. Ethanol separation from the fermentation stream is a particularly energy intensive process, made difficult by the dilute nature of the fermentation products and the presence of the ethanol-water azeotrope. The Membrane Dephlegmation process proposed in this work is a hybrid pervaporation-distillation process for ethanol recovery, carried out in a single unit. A vapour stream is passed vertically through a pervaporation module. The exiting vapour is condensed and partially refluxed to the system, leading to simultaneous countercurrent vapour-liquid contacting and pervaporation.

In this investigation, a mathematical model of the Membrane Dephlegmation process was used to perform a parametric study for important operating conditions and geometric variables. Specifically, the impact of feed flow rate, feed concentration, permeate pressure, reflux ratio, membrane length and membrane diameter on separation efficiency was studied. McCabe-Thiele plots were used to compare the performance of Membrane Dephlegmation to conventional distillation. It was shown that the water flux through the membrane leads to dehydration of the liquid phase, thereby shifting the operating line below the 45 degree line. Further, dehydration of the liquid phase leads to a higher driving force for ethanol transport to the vapour phase, which leads to better separation performance.

6.6. Acknowledgement

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

6.7. Nomenclature

C	number of chemical species
D	diameter, m
E	interphase energy flux, $\text{kJ/m}^2\cdot\text{s}$ or activation energy, kJ/kmol
g	gravitational acceleration, 9.81 m/s^2
H	enthalpy, kJ/kmol
$\bar{H}$	partial molar enthalpy, kJ/kmol
h^*	corrected heat transfer coefficient, $\text{kJ/m}^2\cdot\text{s}\cdot\text{K}$
h	heat transfer coefficient, $\text{kJ/m}^2\cdot\text{s}\cdot\text{K}$
K^*	corrected mass transfer coefficient, $\text{kmol/m}^2\cdot\text{s}$
K	mass transfer coefficient, $\text{kmol/m}^2\cdot\text{s}$ or distribution coefficient
L	total liquid molar flow rate, kmol/s or length, m
l	liquid component molar flow rate, kmol/s
N	interphase molar flux, $\text{kmol/m}^2\cdot\text{s}$ or number of segments
p	pressure, Pa
Q	membrane permeability, $\text{kg/m}^2\cdot\text{h}\cdot\text{bar}$
R	internal tube radius, m or universal gas constant, $8.314 \text{ J/mol}\cdot\text{K}$
T	temperature, K
V	total vapour molar flow rate, kmol/s or molar volume, m^3/kmol
v	vapour component molar flow rate, kmol/s
x	liquid phase mole fraction
y	vapour phase mole fraction
z	axial coordinate
Δz	differential element

Greek letters

δ	liquid film thickness, m
γ	activity coefficient

Subscripts

E	ethanol
-----	---------

<i>i</i>	species <i>i</i>
<i>L</i>	liquid phase
<i>LM</i>	liquid-membrane interface
<i>M</i>	membrane (solid surface)
<i>P</i>	permeate (or external temperature)
<i>ref</i>	at reference conditions
<i>V</i>	vapour phase
<i>W</i>	water

Superscripts

<i>I</i>	interface
<i>PV</i>	pervaporation
<i>ref</i>	at reference conditions
<i>sat</i>	saturation conditions

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MEMBRANE DEPHLEGMATION: A HYBRID MEMBRANE SEPARATION PROCESS FOR EFFICIENT ETHANOL RECOVERY

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Abstract

Ethanol is a renewable biofuel produced through the fermentation of sugars obtained from biomass. However, the usefulness of ethanol as a fuel is partly limited by the energy intensive nature of the separation processes employed in its production. A hybrid pervaporation-distillation separation process was developed for the efficient separation of ethanol from water. An experimental system was constructed to investigate process performance. The system employed vertically-oriented, commercially available, tubular NaA zeolite membranes. This configuration allowed both the dephlegmation and pervaporation processes to be carried out within the same unit. The process was simulated using a model that included coupled heat and mass transfer across the vapour-liquid interface as well as permeation through the pervaporation membrane. Experiments were performed at a variety of feed concentrations, feed flow rates, reflux ratios and permeate pressures. The hybrid process produced ethanol at concentrations well above the ethanol-water azeotrope and yielded improved performance compared to distillation for the same operating conditions. The experimental results were used to validate the simulations and to study the impact of important model parameters. The model predicted the experimental results very well, despite requiring only one fitting parameter. The hybrid process appears to be very efficient for ethanol-water separation and the validated design model will allow detailed process optimization to be performed in the future.

***This paper will be submitted to:** Journal of Membrane Science

7.1. Introduction

Now more than ever, the world is faced with a growing energy shortage. As the demand for energy increases, concerns about the finite availability of fossil fuels and the impact of their combustion on climate change have sparked interest in cleaner energy sources and biofuels. Ethanol is a biofuel produced through the anaerobic fermentation of biomass-derived sugars. However, the energy intensive nature of its production process is a major factor limiting the usefulness of ethanol as a biofuel. The separation processes currently employed to recover ethanol from the fermentation stream are particularly inefficient, usually accounting for more than half of the total process energy demand. There are two primary reasons for the inefficiency of the ethanol separation processes. First, the fermentation product stream is relatively dilute, containing at most 10 % ethanol when conventional substrates are used in the fermentation and at most 5 % ethanol when cellulosic substrates are employed. Secondly, ethanol and water form an azeotrope at approximately 95.6 % ethanol by mass. Since only low water content ethanol can be blended with gasoline and used in gasoline burning engines, special techniques are required to break the azeotrope. The most commonly used methods for ethanol dehydration are currently extractive distillation, pressure swing adsorption of water on molecular sieves and pervaporation/vapour permeation of water through hydrophilic membranes [1].

In the conventional ethanol separation process, ethanol is recovered using several distillation steps combined with a dehydration process. Normally, the fermentation mixture is first passed through a beer column. This column acts as a steam stripping column to produce a vapour phase distillate stream having an ethanol concentration between 30 and 60 % by mass. The final concentration of the distillate depends on the column design and composition of the feed stream. The bottoms product leaving the beer column is essentially water, with some residual solids. The vapour stream leaving the beer column usually enters another column, which operates as the enriching section of a distillation column. The distillate leaving the enriching column is normally near the azeotropic composition (typically between 90 and 94 % ethanol by mass). This distillate stream then undergoes dehydration to produce an anhydrous ethanol product. The bottoms product can go to a separate stripping column or be returned to the beer column [1,2].

The benefits of hybrid pervaporation/vapour permeation-distillation are well established [3]. In recent years, several innovative processes have been proposed to integrate distillation and pervaporation. Del Pozo Gomez et al. [4,5] proposed a pervaporation process that can be easily coupled to distillation. In the proposed process, both vapour and liquid streams were fed to a modified pervaporation module. The vapour and liquid streams were separated by a conductive wall and only the liquid was exposed to the membrane surface. Normally, pervaporation of the liquid would result in a temperature drop. However, in their process, the heat lost due to pervaporation is supplied by partial condensation of the vapour stream. Similarly, Fontalvo et al. [6,7] suggested a process in which a two-phase vapour-liquid mixture was contacted directly with a membrane surface. Again, partial condensation of the vapour provided energy to drive the pervaporation process. Further, the presence of the vapour phase increased turbulence in the module, decreasing the effect concentration polarization.

Several hybrid distillation-pervaporation processes have also been proposed specifically for ethanol-water separation. An overview of some techniques to integrate pervaporation into the ethanol production process was provided by Vane [8]. Vane et al. [9] proposed an innovative, hybrid distillation-vapour permeation process to improve the energy efficiency of the ethanol separation process. Their approach was then validated experimentally using a pilot-scale separation system [10]. The energy requirements of the investigated process were determined to be significantly lower than for the conventional separation process.

The commercial availability of NaA zeolite pervaporation membranes presents enormous opportunities for energy savings in dehydration processes. Commercial applications of zeolite membranes have been reviewed by several authors [11,12]. Compared to polymeric alternatives, these membranes have both relatively high water fluxes and separation factors. Since the surface area requirement for a membrane system is inversely proportional to the flux, a higher flux implies that fewer membranes will be required to achieve the same separation. Conversely, higher separation factors lead to lower operating costs, since less permeate must be recycled to maintain a high overall recovery. Further, these types of membranes share the typical characteristics of other membrane systems, allowing them to be easily integrated into hybrid processes.

In recent years, NaA zeolite membranes have been the subject of numerous studies. Since the main topic of the current study involves an application of these membranes and not

membrane making, only a brief overview of some relevant literature is presented here. Large-scale vapour permeation systems for ethanol dehydration using NaA zeolite membranes have existed for over a decade [13]. Sommer and Melin [14,15] investigated the performance of several commercial inorganic membranes for the dehydration of organic solvents. Generally, NaA zeolite membranes were shown to possess excellent flux and selectivity towards water. The tubular membranes employed in their study and used in previous large scale systems had the zeolite layer deposited on the outside of the tubes. However, Pera-Titus et al. [16,17] developed a technique to efficiently deposit the thin zeolite layer on the inside of tubular membranes. Tubular membranes with the selective zeolite layer inside the tubes are now commercially available and have shown the same excellent separation performance [18,19].

Of course, NaA zeolite membranes are not the only hydrophilic zeolite membranes that have been investigated for the dehydration of organic solvents. It is known that NaA type membranes are susceptible to degradation under acidic conditions [20,21]. Further, it has been shown that NaA zeolite membranes break down during pervaporation under very high water concentrations [22]. This phenomenon is generally not observed during vapour permeation. For these reasons, several authors have developed T and MER-type zeolite membranes which do not degrade as easily [23-26]. These membranes also tend to provide a very high water flux and selectivity. Despite the known limitations of NaA type membranes, the ethanol recovery system discussed in this investigation employs this type membrane.

In a previous paper, a new hybrid membrane separation process for efficient ethanol recovery, dubbed Membrane Dephlegmation, was proposed [27]. This process, which is intended to replace the enriching column and dehydration system in the ethanol separation process, couples both the distillation and pervaporation within the same unit. In the previous study, it was shown numerically, that the proposed system was capable of breaking the ethanol-water azeotrope. Further, it was determined that pervaporation enhanced the effectiveness of the distillation process. It was also determined that the presence of a vapour phase in the module effectively supplied the energy required for pervaporation process.

When considering an internally coupled hybrid distillation-pervaporation process, an immediate comparison that comes to mind is the application of Membrane Distillation. In membrane distillation, aqueous solutions are normally contacted with a hydrophobic membrane. Due to its hydrophobic nature, the membrane acts as a physical barrier that prevents the liquid

from moving to the permeate side. Separation is achieved due to the partial evaporation and migration of volatile species to the permeate side. Normally, the membrane itself has little effect on the selectivity of the process. Instead, as in distillation, the performance of the process is predominantly controlled by the vapour-liquid equilibrium of the mixture. For azeotropic mixtures, this usually means the same purity restrictions encountered in distillation. Conversely, Membrane Dephlegmation employs pervaporation membranes, which are not restricted by vapour-liquid equilibrium. Vapour-liquid contacting is used to supply heat to assist the pervaporation process and differences in relative volatility create a distillation effect, which increases the overall efficiency of the process.

To validate the previously presented theoretical predictions and to analyze physical limitations in a real process, a pilot-scale experimental system has been constructed. The pilot-scale system employs commercially available NaA zeolite membranes [19]. In this investigation, details of the experimental system are provided. Concurrently, an overview of the Membrane Dephlegmation process is presented. Subsequently, a brief overview of the mathematical model used to describe Membrane Dephlegmation and wetted-wall distillation is provided. Experimental data from the pilot-scale system are then used to determine unknown parameters required in the model and the model is validated. Results are presented to show the impact of critical operating parameters on system performance. Finally, physical limitations of the system are discussed and future improvements are suggested.

7.2. Materials and Methods

7.2.1. Membranes and Modules

In Membrane Dephlegmation, distillation and pervaporation are carried out in a single unit. This can be achieved using a vertically-oriented pervaporation membrane, with countercurrent vapour-liquid contacting on its surface. In this case, vapour is introduced into the bottom of the membrane and allowed to flow upwards. The vapour leaving the top of the membrane is condensed and partially refluxed to the system. The liquid reflux flows downward along the membrane, due to gravity, producing countercurrent contacting. It was previously proposed that tubular NaA zeolite membranes with the selective layer inside the membrane tubes provide a convenient configuration for this process [27].

Commercial NaA zeolite membranes were obtained from the Fraunhofer Institut für Keramische Technologien und Systeme (IKTS) [19]. A schematic representation of the membranes and modules is provided in Figure 7.1. Pertinent membrane characteristics are provided in Table 7.1. In these membranes, the selective NaA zeolite layer is deposited on the inside of four channel tubular alumina supports. The ends of the membrane are dipped in glass to provide sealing. During operation the tubular membranes were placed into stainless steel modules. The modules were sealed using EPDM o-rings, seated on the glass dipped area of the membrane tubes and against the stainless steel module. The vapour feed entered the tube side of the membranes from the bottom and the refluxed liquid entered at the top. A vacuum was applied to the shell side of the modules to provide a driving force for the pervaporation process.

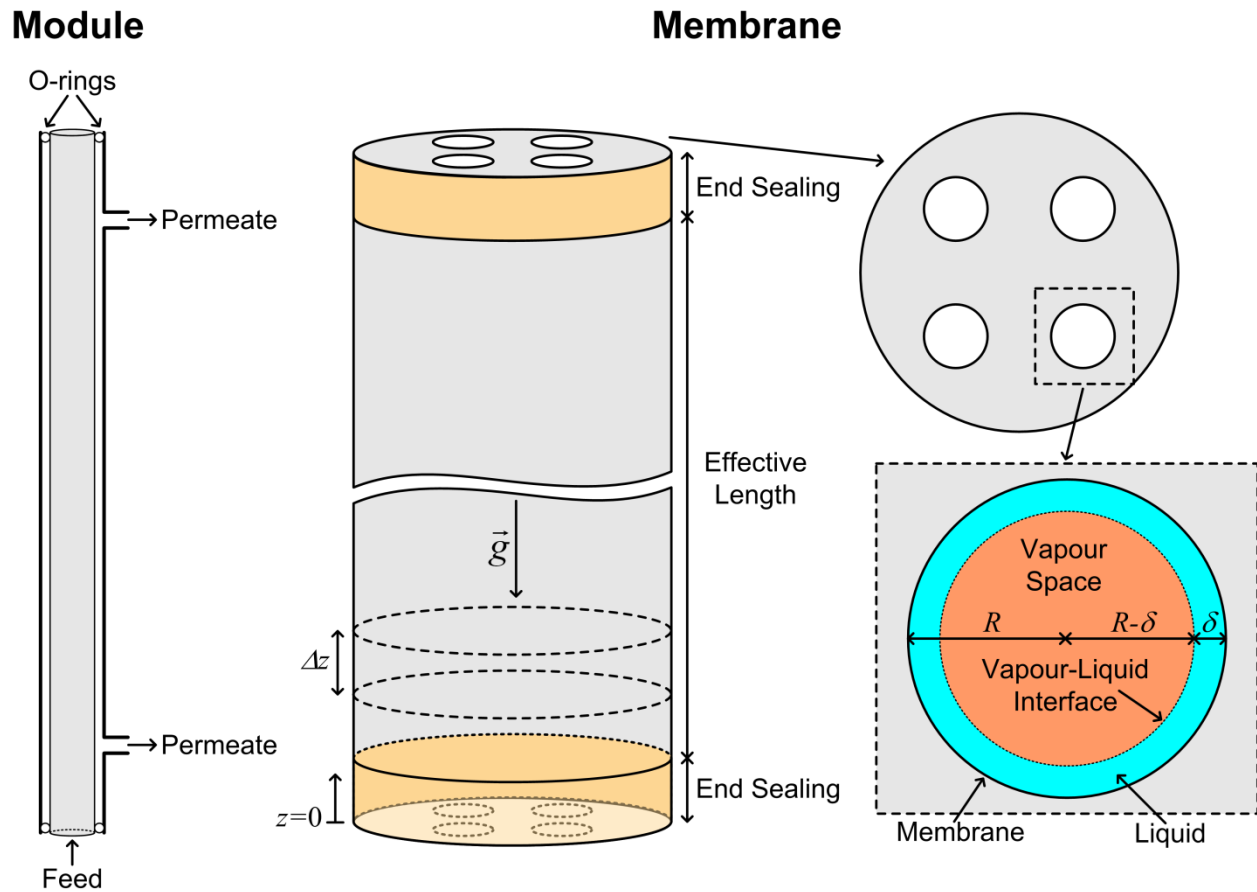


Figure 7.1. Illustration of the module and four channel NaA zeolite membranes.

Table 7.1. Characteristics of the NaA Zeolite Membranes

Membrane Tube Diameter (mm)	20.5
Number of Channels	4
Channel Diameter (mm)	6
Effective Length (m)	1.2
Filtration Area (m²/membrane)	0.089
Cross-Sectional Flow Area (m²)	0.0001131
Number of Membranes in System	2
Support Mean Pore Size (μm)	approx. 4
Zeolite Layer Thickness (μm)	approx. 15
Zeolite Pore Size (nm)	0.41

7.2.2. Pilot-Scale System

A schematic representation of the Membrane Dephlegmation system used in this study is shown in Figure 7.2. Ethanol-water solutions were prepared at specified concentrations and placed in the feed container (A). A constant feed flow rate was maintained using a gear pump (B) and the feed flow rate was monitored by tracking the change in the mass of the feed container over time using a balance (A). For faster monitoring response, a turbine flow meter was also placed on the feed line. The feed was totally vaporized on the tube side of a shell and tube heat exchanger (C) and its temperature was adjusted using a heating tape on the feed pipe. The vapour feed entered the bottom of the membrane column (D) and was allowed to flow vertically upwards. Temperature and pressure were monitored at both the ends of the membrane modules but not between the two membrane modules. The vapour leaving the top of the membrane column was fully condensed on the tube side of a shell and tube heat exchanger (I). To maintain the system at atmospheric pressure, this heat exchanger was left open to the atmosphere. Chilled water at approximately 5°C was used as the coolant. The condensate was collected in a reflux line, in which a constant liquid inventory was maintained. Another gear pump (J) was used to provide reflux to the column and to pump distillate out of the system. The distillate was collected and its flow rate was determined by tracking the change in the mass of the distillate container over time using a balance (K). The reflux ratio was adjusted using parallel valves and flow meters on the reflux and distillate lines. The reflux was returned to the top of the column and its return temperature was monitored. The condensate leaving the bottom of the column was collected and its flow rate was determined using a balance (E).

To maintain a driving force for pervaporation, a vacuum was applied to the shell side of the membranes. Condensable vapours (mainly water) were recovered using a shell and tube heat exchanger (F) cooled with chilled water at approximately 5°C. The condensate was collected in a vacuum tank (H). For concentration measurements, permeate samples were taken using a sample port located directly on the vacuum line (G). The permeate flow rate was not directly monitored and was instead determined by mass balance. Incondensable gases were purged from the system using a dry running scroll pump. The vacuum pressure was controlled using a bleed valve located directly before the vacuum pump.

During operation, temperatures and flow rates were monitored to control the process and to determine when steady state conditions were reached. Further, distillate and bottoms samples were taken to ensure a steady concentration. Ethanol concentration of the samples was determined using density measurements made on an Anton Paar DMA 4500 M density meter. This density meter allows determination of the ethanol concentration to within 0.03 % by volume.

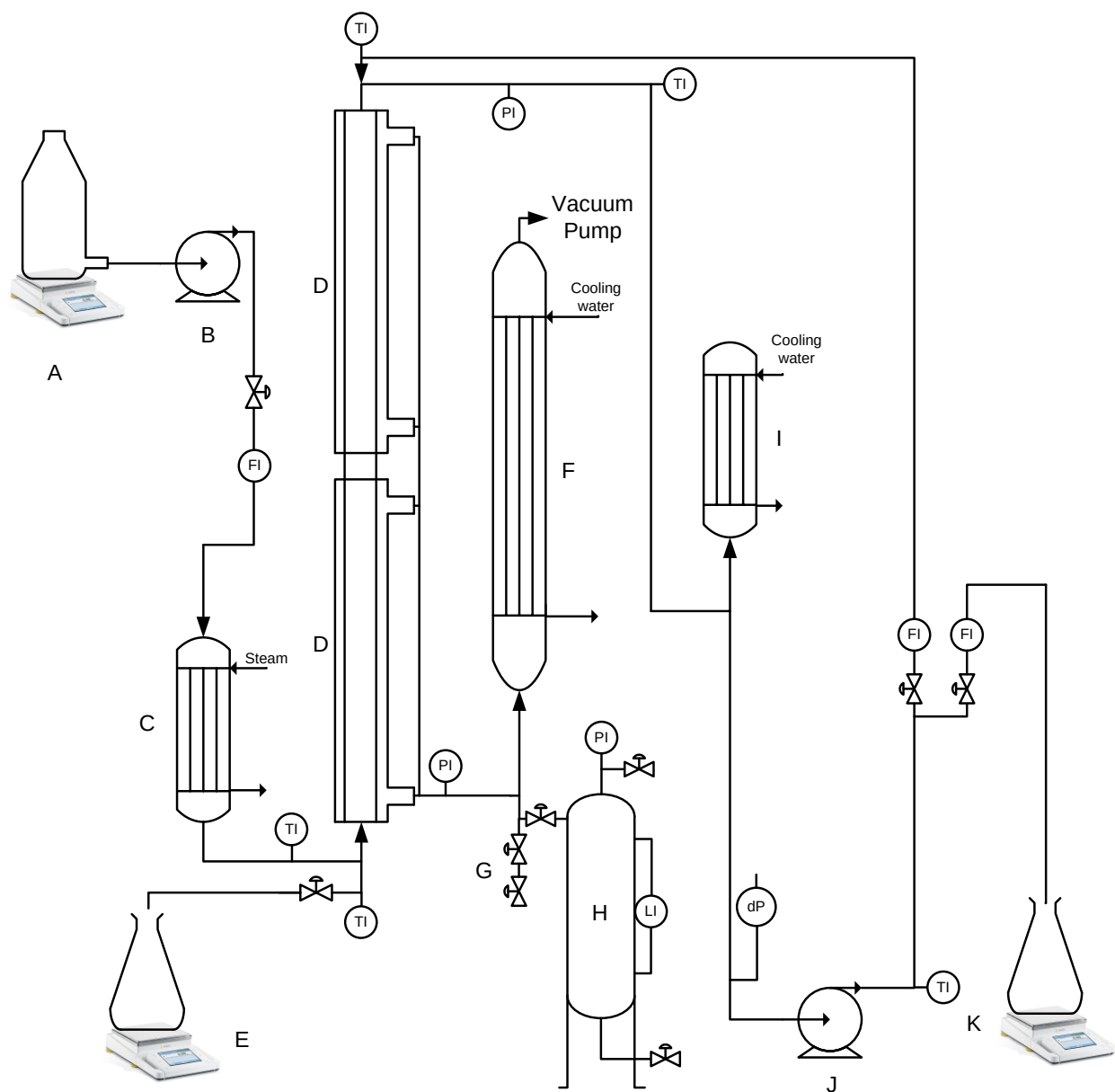


Figure 7.2. Schematic representation of the pilot-scale experimental system (letter descriptors for equipment are explained in the text).

7.2.3. Experimental Runs

To study the impact of pertinent operating variables on system performance, experimental runs were carried out at a variety of feed flow rates, feed concentrations, permeate pressures and reflux ratios. Altogether, over 100 experimental data points were obtained. Depending on the operating conditions, it usually took the system between 2 and 4 hours to reach steady state conditions. A summary of the ranges of the operating variables investigated in this

study is provided in Table 7.2. Additionally, several experiments were performed without applying a vacuum to the shell side of the membrane. Without a pervaporation flux, the system behaves as a wetted-wall distillation column. The wetted-wall distillation experiments were performed to confirm the validity of assumptions made in the mathematical model about vapour-liquid contacting efficiency. An overview of the mathematical model is presented in the following section.

Table 7.2. Summary of the Ranges of Experimental Conditions Tested

Feed Velocity (m/s)	1.1 to 12
Feed Ethanol Mass Fraction	0.1 to 0.9
Permeate Pressure (Pa)	5300 to 18700
External Reflux Ratio	0 to infinity

7.3. Mathematical Formalism

7.3.1. System Modeling

A mathematical model to describe the Membrane Dephlegmation and wetted-wall distillation processes was previously derived [27]. Only the main equations and pertinent aspects related to the present investigation are reviewed in this section. A summary of the equations solved in the model is provided in Table 7.3. The model solves the one-dimensional steady state material and energy balance equations for the liquid and vapour phases. Interface jump conditions are applied at the vapour-liquid and liquid-membrane interfaces, to couple the conservation equations. Heat and mass transfer through the vapour-liquid interface are inherently coupled in both distillation and Membrane Dephlegmation due to the energy associated with material crossing the interface. Further, material and energy transport through the membrane by pervaporation are also coupled since water must evaporate as it permeates through the membrane.

Since the liquid flows down the surface of the membrane, the vapour phase is only exposed to the liquid phase and not to the membrane. Thus, the vapour component balances only include component sources due to material transfer across the vapour-liquid interface. Conversely, the liquid is exposed to both the vapour-liquid and membrane-liquid interfaces. Therefore, the liquid component balances include sources due to material transport through the vapour-liquid interface and through the membrane by pervaporation. Similarly, the vapour phase energy balance only includes a source term to account for conductive and convective (i.e. energy

transfer associated with the latent heat of condensation/evaporation) energy transport across the vapour-liquid interface. The liquid phase energy balance accounts for both conductive and convective energy transfer across the vapour-liquid and membrane-liquid interfaces.

Interface material and energy balances are required to calculate the source terms in the material and energy conservation equations. A summary of the component and energy balances at the vapour-liquid interface is also provided in Table 7.3. Only a single energy balance is required for the vapour-liquid interface. Conversely, component balances are required on both the liquid and vapour side of the interface. To solve the interphase flux expression, some auxiliary conditions are required to relate component mole fractions and temperature at the interface. Vapour-liquid equilibrium conditions are assumed to prevail at the interface and a distribution coefficient (K-value) is used to relate interface mole fractions. Of course the mole fractions in each phase must also sum to unity by definition.

Expressions are also required to determine material and energy fluxes across the membrane-liquid interface. As shown in Table 7.3, the energy balance includes both conductive and convective components. In the wetted-wall distillation model, the pervaporation flux is not present and the convective term disappears. Further, the equations required to determine the pervaporation flux are not used when simulating wetted-wall distillation. For the Membrane Dephlegmation process, a component balance is required on the liquid side of the membrane-liquid interface to account for mass transfer through the liquid side boundary layer. The permeate concentration is related to the pervaporation flux by assuming a locally unmixed permeate. Again, the mole fractions on both sides of the membrane must sum to unity.

As shown in Table 7.3, flux expressions are required to characterize the transport of water and ethanol through the membrane. Transport through zeolite membranes is usually described using solution-diffusion or adsorption-diffusion models. Sommer and Melin [14] investigated the dehydration performance of commercial NaA zeolite membranes for several organic solvents. A simple model based on the solution-diffusion model was presented in their study for ethanol dehydration. More complex expressions are available based on the Maxwell-Stefan equations [28,29]. Further, it has been proposed that the permeation equations should be divided into expressions to describe transport through intracrystalline and intercrystalline pores [29,30]. However, it has been shown that water flux usually only depends on its driving force (pseudo-Fickian process) [31]. Thus, a simple solution-diffusion model is usually adequate to

characterize water transport. Conversely, ethanol transport is usually a coupled process, depending on both its own concentration gradient and the water flux. However, the separation factor of NaA zeolite membranes is known to be very high and therefore, the ethanol flux is expected to contribute very little to the overall performance of the system. Further, the ethanol concentration in the permeate stream in all the experiments was less than 1 % by mass. Thus, for simplicity, the solution-diffusion model presented by Sommer and Melin [14] is used to describe both the ethanol and water transport processes. The water and ethanol flux are calculated from,

$$N_i^{PV} = Q_i (\gamma_i x_{i,LM} P_i^{sat} - y_{i,P} P_P) \quad (1)$$

Where the permeability is calculated from the following temperature dependent Arrhenius-type expression,

$$Q_i = Q_i^{ref} \left[\frac{E_i}{R} \left(\frac{1}{353.15} - \frac{1}{T_{LM}} \right) \right] \quad (2)$$

It is possible to treat the permeability coefficient at the reference conditions (Q_i^{ref}) and the activation energy (E_i) as model fitting parameters. The reference permeability coefficients determined by Sommer and Melin [14] were 1.744×10^{-9} kmol/m².s.Pa (11.31 kg/m².h.bar) and 4.221×10^{-13} kmol/m².s.Pa (0.007 kg/m².h.bar) for water and ethanol, respectively. The fitted activation energies were 17.0 kJ/kmol and 25.7 kJ/kmol for water and ethanol, respectively. The membranes used by Sommer and Melin [14] were not produced by the same manufacturer as the membranes employed here. However, as shown later, the previously proposed parameters fit the experimental permeation data very well. Therefore, the parameters were not re-fitted for the current study.

Table 7.3. Summary of Membrane Dephlegmation and Distillation Model Equations (for C components)

<u>C vapour component balances:</u>	$\frac{dv_i}{dz} = -2\pi(R - \delta)N_i$
<u>C liquid component balances:</u>	$\frac{dl_i}{dz} = -2\pi(R - \delta)N_i + 2\pi RN_i^{PV}$
<u>1 vapour energy balance:</u>	$\frac{dVH_V}{dz} = -2\pi(R - \delta)E_V$
<u>1 liquid energy balance:</u>	$\frac{dLH_L}{dz} = -2\pi(R - \delta)E_L + 2\pi RE_{LM}$
<u>1 energy balance at the vapour-liquid interface:</u>	$E_V = h_V^*(T_V - T^I) + \sum N_i \bar{H}_{i,V}(T_V) = E_L = h_L^*(T^I - T_L) + \sum N_i \bar{H}_{i,L}(T_L)$
<u>C -1 vapour side component balances at the vapour-liquid interface:</u>	$N_i = K_V^*(y_{i,V} - y_i^I) + y_{i,V} \sum N_i$
<u>C -1 liquid side component balances at the vapour-liquid interface:</u>	$N_i = K_L^*(x_i^I - x_{i,L}) + x_{i,L} \sum N_i$
<u>C vapour-liquid equilibrium relations:</u>	$K_i x_i^I - y_i^I = 0$
<u>2 interface mole fraction summation equations:</u>	$\sum_{i=1}^C x_i^I - 1 = 0, \sum_{i=1}^C y_i^I - 1 = 0$
<u>1 interphase energy balance at the membrane-liquid interface:</u>	$E_{LM} = h_{LM}^*(T_L - T_{LM}) + \sum N_i^{PV} \bar{H}_{i,L}(T_L) = E_M = h_M^*(T_{LM} - T_P) + \sum N_i^{PV} \bar{H}_{i,V}(T_P)$
<u>C -1 liquid side component balances at the membrane-liquid interface:</u>	$N_i^{PV} = K_{LM}^*(x_{i,L} - x_{i,LM}) + x_{i,L} \sum N_i^{PV}$
<u>C membrane flux expressions:</u>	See Description in Text (Equations 1 and 2)
<u>C -1 membrane flux to permeate mole fraction relations:</u>	$y_{i,P} = \frac{N_i^{PV}}{\sum N_i^{PV}}$
<u>2 membrane interface mole fraction summation equations:</u>	$\sum_{i=1}^C x_{i,LM} - 1 = 0, \sum_{i=1}^C y_{i,P} - 1 = 0$

7.3.2. Numerical Details

The model requires estimation of several interphase heat and mass transfer coefficients. An in-depth discussion of the expressions used to estimate these parameters was previously presented [27]. In summary, laminar flow was assumed in the vapour phase and the heat and mass transfer coefficients were determined based on the expressions for laminar flow in a tube. The liquid phase velocity profile and film thickness were calculated analytically, assuming flow of a smooth laminar liquid film (Nusselt assumptions). This implies that both the velocity profile and film thickness depend on the liquid flow rate. Since the liquid flow rate varies along the length of the membrane module, the liquid velocity and film thickness also vary. Once the liquid velocity profile and film thickness had been calculated, expressions for the liquid phase heat and mass transfer coefficients could be determined analytically. It is important to note that, under some conditions, the liquid film could completely disappear from the membrane surface due to evaporation to form vapour and/or pervaporation through the membrane. Under the conditions investigated in the present study, complete disappearance of the film from the membrane surface was not observed. If the liquid film were to disappear from a section of the membrane, the exposed membrane section would behave as a vapour permeation unit and it would be necessary to incorporate an additional membrane flux model into the simulation to account for this change.

Physical and transport properties were determined using temperature and composition dependent correlations for the ethanol-water system. The liquid phase viscosity, thermal conductivity and diffusion coefficient were calculated using the Neural Network models developed by Haelssig et al. [32]. The vapour phase viscosity, thermal conductivity and diffusion coefficient were calculated using the Reichenberg, Wassiljewa and Fuller methods, respectively [33]. Pure component viscosity and thermal conductivity were estimated using temperature dependent polynomial relationships [34]. The latent heat of vaporization was calculated from the temperature dependent expressions provided in [35]. The vapour pressure for both species was determined using the extended Antoine equation [35]. The Wilson activity model was used to calculate the activity coefficients for the ethanol-water system [36]. The liquid phase densities (and molar volume) of ethanol and water were calculated using the expressions provided in [35]. The excess volume of mixing was estimated using the Wilson equation [37]. The ideal gas law was applied to estimate the vapour phase density (and molar volume). The heat capacities were calculated using temperature dependent polynomial relationships [34]. The liquid and vapour

phase enthalpies were calculated through integration of the temperature dependent heat capacities (see [27] for details). In the vapour phase, the residual enthalpy was assumed to be 0 (under the ideal gas assumption). In the liquid phase, the excess enthalpy was calculated using the Wilson activity model.

The conservation equations presented in the previous section were discretized using a finite difference approximation. The column was divided into N segments. In the calculations, the number of segments was increased until a grid independent solution was obtained. The discretized conservation equations form a system of nonlinear algebraic equations. These equations were combined with the interphase material and energy balances to form a large block tri-diagonal system of nonlinear equations. When combined with the heat and mass transfer correlations and physical properties, the equations can be solved for all unknowns. In the case of wetted-wall distillation, a system of $(5C+4)N$ equations is formed. Conversely, a system of $(8C+4)N$ equations must be solved for the Membrane Dephlegmation process. The system of nonlinear equations was solved using an in-house simulator, programmed in the Java programming language. The simulator combined a block tri-diagonal version of the Thomas algorithm with a modified Newton's method to iteratively converge on the solution.

7.4. Results and Discussion

7.4.1. Model Validation

As mentioned earlier, it was necessary to characterize external heat losses from the membrane modules by determining the external heat transfer coefficient. Further, initially it was not clear whether the literature values of the permeation parameters presented earlier were applicable to the membranes investigated in this study. Although there are many coupled effects in the overall process, the external heat transfer coefficient has a particularly high effect on the bottoms and distillate flow rates. The effect on the bottoms flow rate is particularly pronounced because the external heat losses determine the amount of condensate formed in addition to any external reflux. Thus, the external heat transfer coefficient was determined by minimizing the deviation between the predicted bottoms flow rate and the experimental bottoms flow rate. Upon minimizing this deviation, the external heat transfer coefficient was determined to be approximately $10 \text{ W/m}^2\text{K}$. Figure 7.3 shows a parity plot comparing the predicted and experimental bottoms flow rates for this final fitted value. It is shown that model predictions

agree very well with the experimental data for both Membrane Dephlegmation and wetted-wall distillation. This validates the assumption, that a constant external heat transfer coefficient can adequately describe external heat losses. It is likely that a constant external heat transfer coefficient is sufficient because heat losses from the system are relatively low compared to other heat effects.

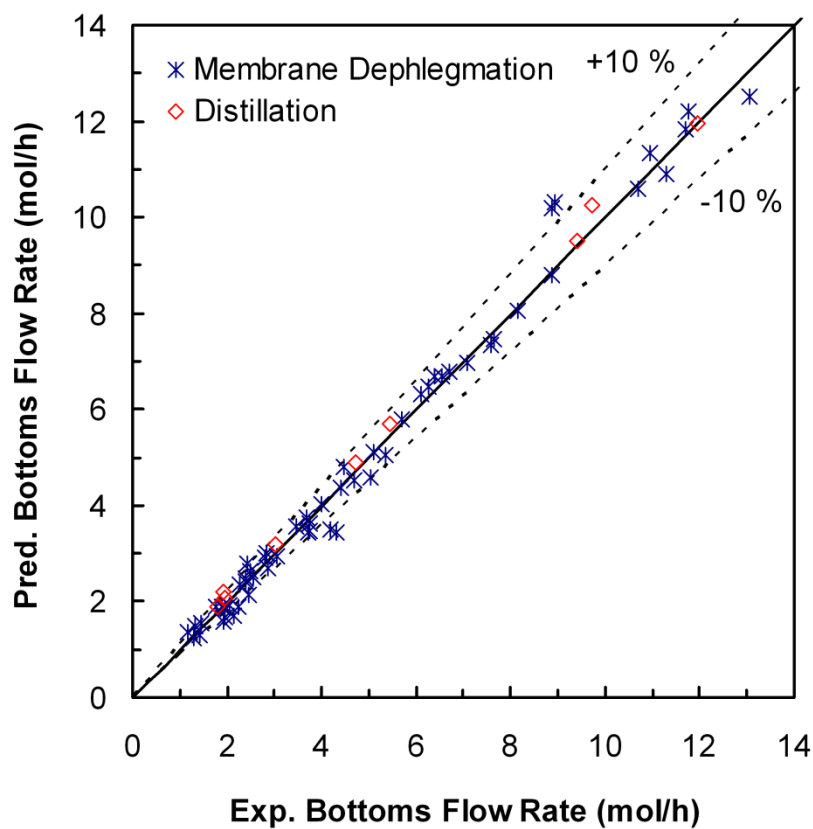


Figure 7.3. Parity plot comparing predicted and experimental bottoms flow rate (range of operating conditions shown in Table 7.2).

Once the external heat transfer coefficient was calculated, it was necessary to determine whether the permeation parameters provided by Sommer and Melin [14] could be applied to the membranes employed in this investigation. The water flux through the membrane is of primary importance in the current study. Thus, it was important to establish that the water permeation flux was adequately predicted using the literature parameters. Figure 7.4 shows a parity plot comparing predicted and experimental values of the water flux through the membrane. Clearly the model predictions of the water flux are very similar to the experimental values. Although it may be possible to fit the permeation parameters to the data to achieve slightly better agreement,

the impact would be negligible. Thus, the previously published parameters were used in all of the simulations.

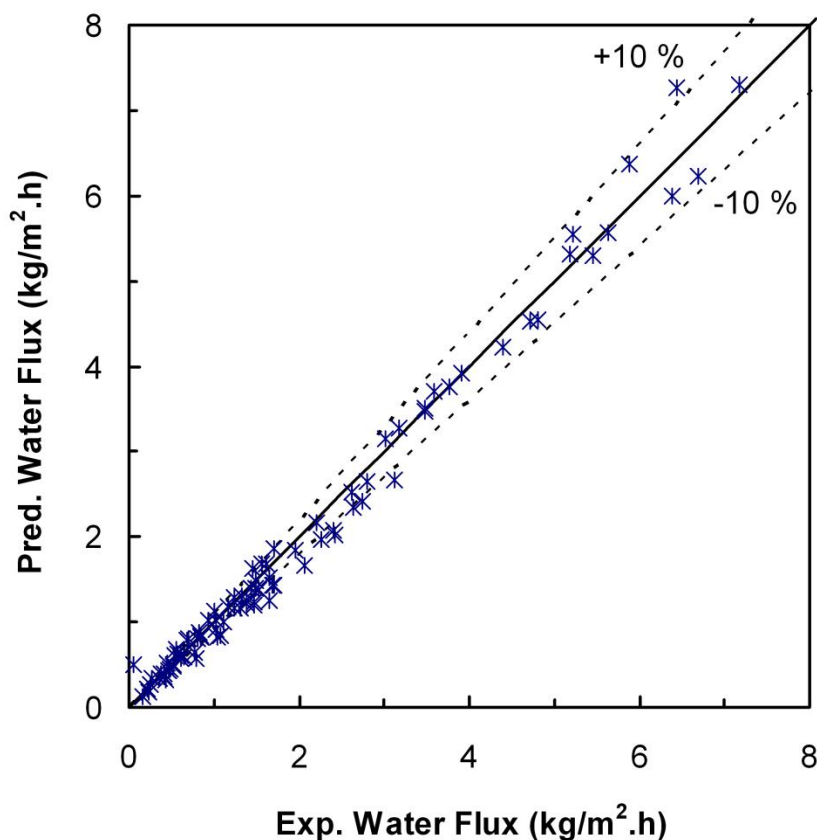


Figure 7.4. Parity plot comparing predicted and experimental pervaporation water flux (range of operating conditions shown in Table 7.2).

Once the external heat transfer coefficient was determined and it was established that the permeation parameters could predict the water flux, it was necessary to verify that the model could predict the separation performance of the system. Two critically important separation characteristics are the distillate concentration and the ethanol recovery in the distillate. The importance of the distillate concentration is obvious, since this is the desired product stream. Conversely, the importance of the ethanol recovery in the distillate is not immediately apparent. The ethanol recovery actually combines two important parameters, the bottoms flow rate and composition. The bottoms flow rate and composition are important because in an overall separation process, this stream would be recycled to a steam stripping column. Thus, a lower ethanol recovery in the distillate implies that more ethanol is returned to the stripping column. It follows that a lower ethanol recovery in the distillate leads to a higher energy demand on the

stripping column. Conversely, a higher ethanol recovery in the distillate yields a more efficient process. Figure 7.5 shows a parity plots comparing predicted and experimental values of the distillate concentration and ethanol recovery in the distillate. From Figure 7.5a it is clear that the model predicts the distillate concentration very well for both wetted-wall distillation and Membrane Dephlegmation. Figure 7.5b indicates that the model also predicts the ethanol recovery quite well. However, these predictions are not quite as good as the ones for distillate concentration. The larger deviation in predictions of the ethanol recovery results from the fact that this parameter includes both variability in the distillate flow rate and composition. Regardless, good agreement is observed and the model is considered to be validated.

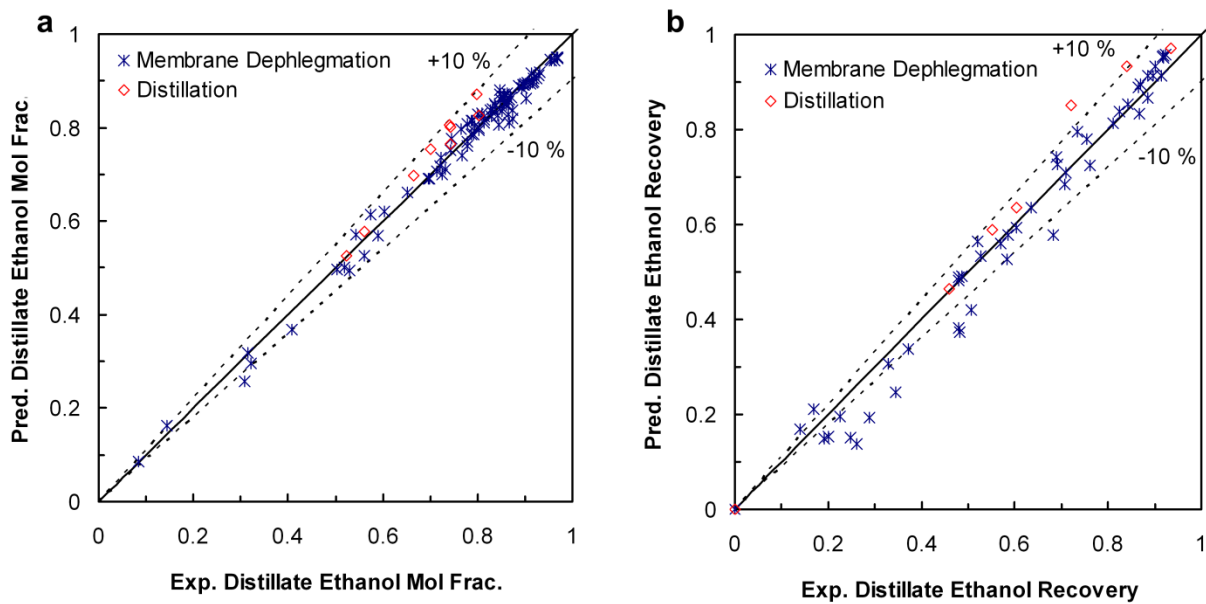


Figure 7.5. Parity plots comparing predicted and experimental: a) distillate concentration and b) ethanol recovery in the distillate (range of operating conditions shown in Table 7.2).

7.4.2. Impact of Operating Conditions on Performance

Experiments were carried out to study the impact of pertinent operating variables on system performance. Experimental runs were carried out at a variety of feed flow rates, feed concentrations, permeate pressures and reflux ratios. This section discusses the effect of these parameters on the separation efficiency of the system. For comparison, results from wetted-wall distillation experiments are also presented. Figure 7.6 shows the impact of permeate pressure and reflux ratio on the distillate concentration and water flux through the membrane. Figure 7.6c shows the variation of the distillate concentration with reflux ratio for wetted-wall distillation.

The ethanol-water azeotrope is also shown on the plots. As expected, the distillate in the wetted-wall distillation case does not reach the ethanol-water azeotrope, even when infinite reflux ratio is approached. In Membrane Dephlegmation, a lower permeate pressure leads to a higher water flux through the membrane because the driving force is increased. As shown in Figure 7.6a, the higher water flux leads to dehydration of the retentate stream and it is possible to break the azeotrope. It is also observed, as discussed in the previous section, that the model predictions of the distillate concentration and water flux are very good approximations of the experimental data. Figure 7.6a also shows the predicted distillate concentration under zero permeate pressure conditions. This represents the maximum possible separation that the experimental system would be able to achieve for the specified feed velocity and concentration. It is shown that, at the highest reflux ratio, the distillate concentration reaches approximately 99 % ethanol by mass. Lastly, it is observed that increasing the reflux ratio improves that separation performance of the system. This is expected since the distillation process becomes more efficient for higher reflux ratios. However, higher reflux ratios lead to higher bottoms flow rates. Since the bottoms stream must be recycled to the steam stripping column in a complete ethanol recovery process, a higher bottoms flow rate would increase the energy demand for this column. Clearly, an optimal reflux ratio exists, that would minimize the load on the stripping column and maximize the performance of the Membrane Dephlegmation system.

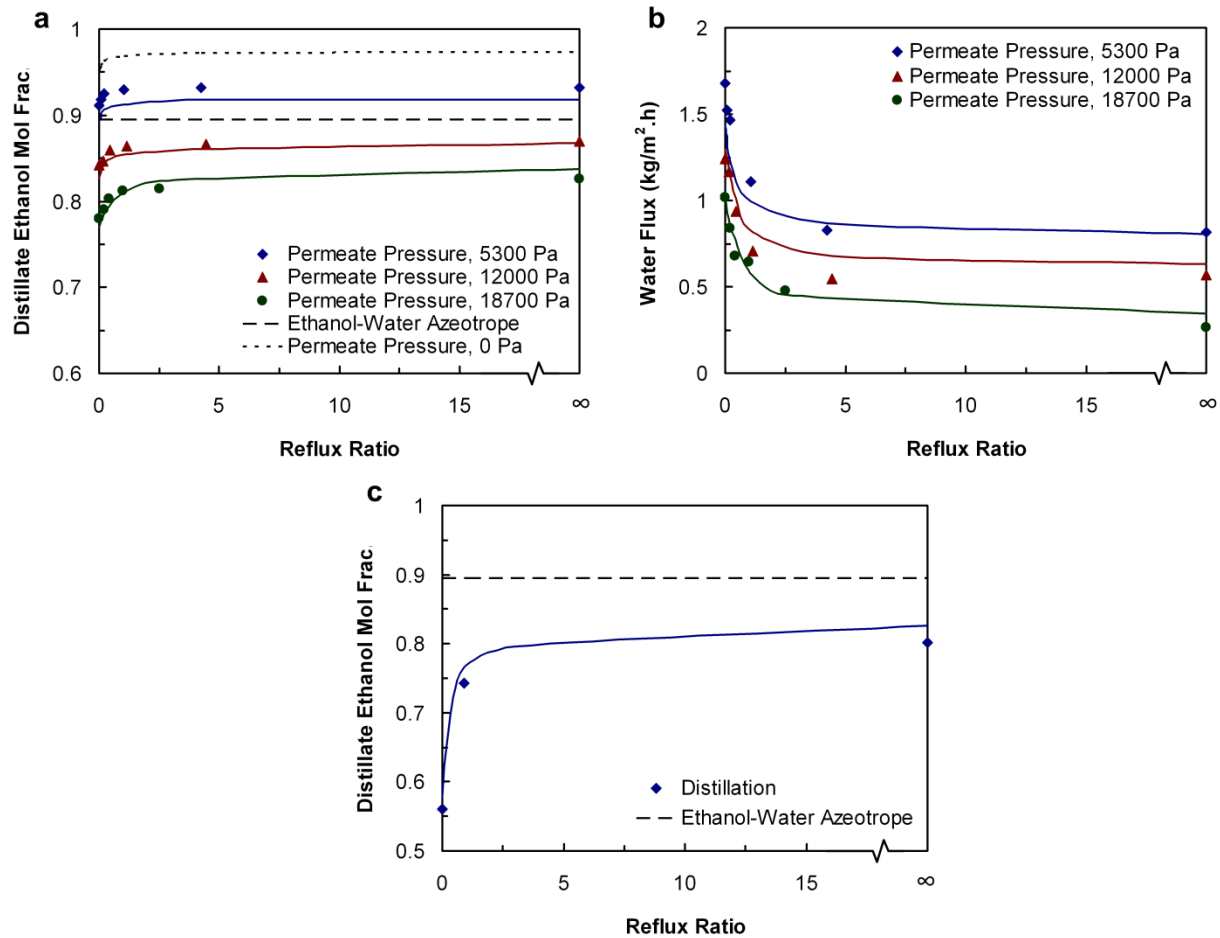


Figure 7.6. Impact of permeate pressure and reflux ratio on a) distillate concentration; b) pervaporation water flux for Membrane Dephlegmation and impact of reflux ratio on c) distillate concentration for wetted-wall distillation (feed velocity of 2.98 m/s; feed ethanol mass fraction of 0.7).

The variation of the distillate ethanol concentration and water flux with feed velocity and reflux ratio is shown in Figure 7.7. Increasing the feed velocity increases the water flux and decreases the final distillate concentration. On first glance, the direct impact of feed velocity is not clear. A higher feed velocity is associated with a higher mass flow rate. An increased mass flow rate, at a fixed feed composition, implies an increased water load on the system. It follows that more water must be removed through the membrane to reach the same final distillate concentration. Although, as shown on Figure 7.7b, a higher water flux is achieved under higher feed velocities, the higher flux does not completely offset the increased water load. Higher velocities are also associated with shorter contact times. As a result, there is less time for heat

and mass transfer across the vapour-liquid and membrane-liquid interfaces. As expected, the decreased contact time also leads to lower final distillate ethanol concentration.

As in the previous results, increasing reflux ratios lead to higher distillate concentrations. However, the effect of the reflux ratio is smaller at lower velocities. Higher reflux ratios lead to more efficient vapour-liquid contacting. However, vapour-liquid contacting is already quite efficient at very low velocities due to the increased contacting time. Therefore, the relative impact of a changing reflux ratio is less pronounced. Further, vapour-liquid equilibrium favours ethanol movement to the vapour phase more at low concentrations. Since low velocities lead to a higher final ethanol concentration, more of the column operates at high concentrations. Thus, distillation effects, which are strongly influenced by the reflux ratio, are less evident. From Figure 7.7a it is also apparent that the model predicts a larger impact of the reflux ratio on system performance at very high velocities than is observed experimentally. It is likely that at very high velocities, the liquid film begins to become influenced by vapour shear effects. These effects could lead to instability in the liquid film and could lead to lower vapour-liquid contacting performance. Such effects are not included in the model and therefore, some deviation from the experimental results at very high velocities is to be expected.

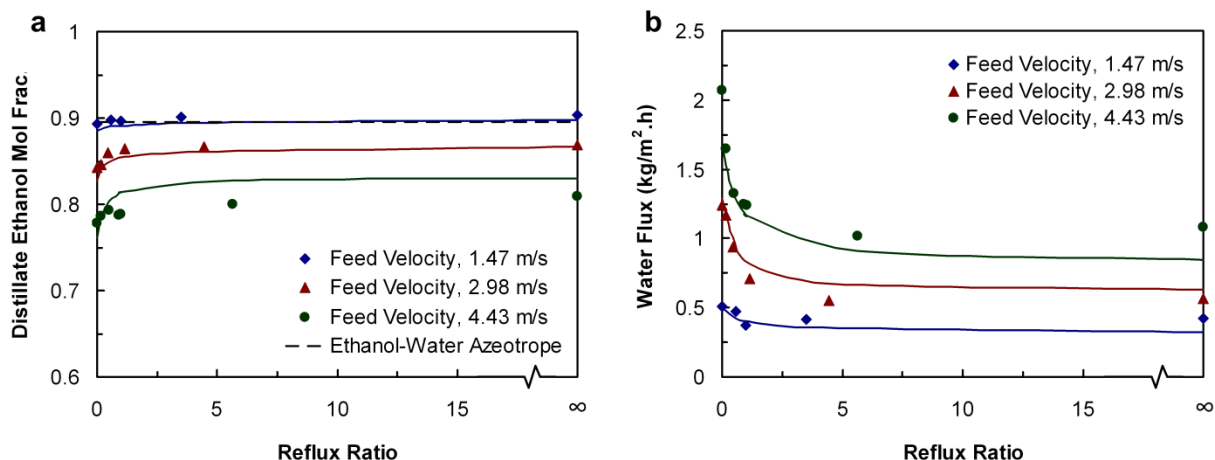


Figure 7.7. Impact of feed flow rate and reflux ratio on a) distillate concentration and b) pervaporation water flux (permeate pressure of 12000 Pa; feed ethanol mass fraction of 0.7).

Figure 7.8 shows the dependence of the distillate concentration and trans-membrane water flux on the feed concentration and velocity. For this data, no external reflux was returned to the column. However, due to external heat losses and heat losses associated with pervaporation, a liquid film builds on the membrane due to condensation. The formation of this

liquid film leads to an internal reflux. From Figure 7.8 it is apparent that, at low velocities, the effect of feed concentration on distillate concentration and water flux is minimal. A low feed velocity implies that the water load on the system is relatively small, regardless of the feed concentration. It follows that much of the water in the feed can be quickly removed by the membrane and the concentration increases rapidly, not far from the entrance. Once a high concentration is achieved, the flux through the membrane remains relatively low, due to the lower water driving force, and the concentration changes very slowly. Thus, the distillate concentration is relatively independent of the feed concentration at low velocities since most of the membrane is exposed to a retentate at very high concentrations.

At higher feed velocities, the effect of the feed concentration becomes more important. Figure 7.8 shows that at very high velocities, the distillate concentration approaches the feed concentration. This is expected for two reasons. First, a high velocity leads to very low contact times and therefore only limited vapour-liquid mass transfer. Secondly, at high feed rates, the water loading on the system is very high relative to the dehydration capacity of the membranes. Thus, even though the flux through the membranes is quite high, the total quantity of water in the feed stream and thereby the concentration of the retentate are only sparingly affected by the pervaporation flux.

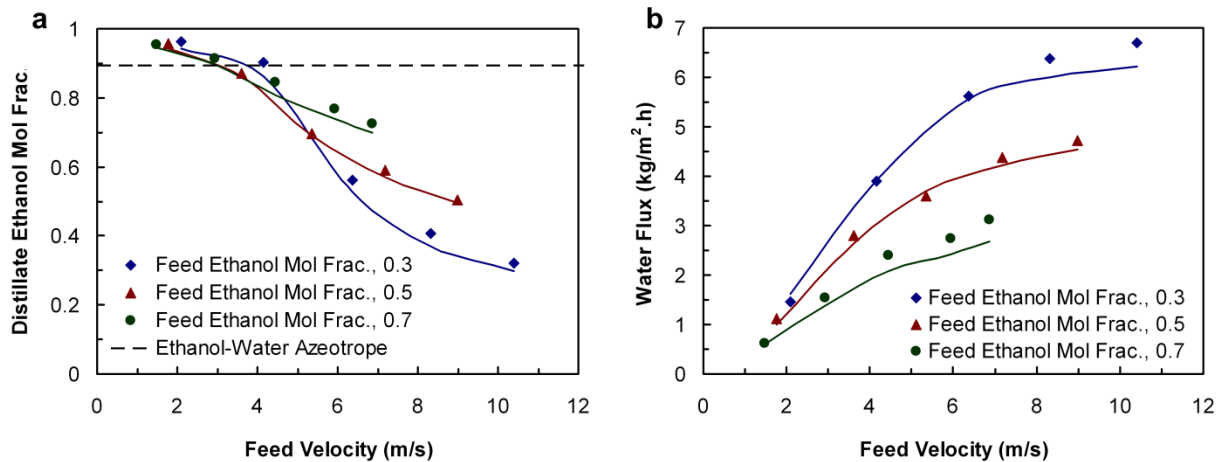


Figure 7.8. Impact of feed concentration and feed velocity on a) distillate concentration and b) pervaporation water flux (permeate pressure of 5300 Pa; no external reflux).

7.4.3. General Discussion

The previous sections presented a validation of the mathematical model used to describe Membrane Dephlegmation and discussed the impact of important operating conditions on system

performance. This section highlights some other features that must be considered in system design and discusses some important limitations.

As discussed earlier, the membranes used in this investigation had a relatively small channel diameter of approximately 6 mm. At such small diameters, under countercurrent flow, the possibility of flooding or liquid entrainment in the vapour is a concern. In fact, the flooding velocity for countercurrent flow of water and air in a 7 mm tube varies between approximately 3 and 6 m/s, depending on the liquid flow rate [38,39]. In the system used in this study, the flooding velocity was approached under some circumstances. In operating the system it was important to avoid entrainment of the liquid film in the vapour. If higher velocities are desired to increase vapour-liquid mass transfer, it may be necessary to use larger diameter membranes. However, larger diameter membranes with a reasonably high length to diameter ratio are not currently commercially available. Further, increasing tube diameter has the negative effect of decreasing the surface area to volume ratio.

The instability of NaA zeolite membranes at high water concentrations and under acidic conditions was briefly discussed in the introduction section. Acidic conditions were not encountered in the course of the experiments performed for this study. However, several experiments were performed at high water concentrations. It was observed that the membranes were generally stable for several months when feed concentrations of above approximately 70 % ethanol by mass were employed. At higher water concentrations, membrane performance degraded over time. Membrane degradation was proportional to the concentration of water in the feed. Degradation of membrane performance was not a gradual phenomenon. Instead, the membranes first provided good separation performance for some time but then failed rapidly after prolonged exposure to high water concentrations. To prevent failure of the membranes, most of the experimental runs were therefore performed at feed concentration greater than 70 % ethanol by mass. Since it may be beneficial to use feeds with water content higher than 30 % in the Membrane Dephlegmation process, it is suggested to investigate membranes that show better stability at higher water concentrations. Zeolite T membranes have been shown to have good ethanol-water separation characteristics and appear to have better long-term stability at higher water concentrations [23-26]. It is therefore suggested to use these types of membranes, if higher water content feeds are desired. It should, however, not be necessary to go below 70 % ethanol, since the beer column is capable of achieving this concentration.

7.5. Conclusions

Ethanol is a biofuel that could help alleviate the dependence of the transportation sector on fossil fuels. Ethanol is produced through the anaerobic fermentation of sugars obtained from biomass. However, ethanol separation from the fermentation stream is an energy intensive process, made difficult by the dilute nature of the fermentation product and the presence of the ethanol-water azeotrope. This investigation presented an experimental study of a new hybrid distillation-pervaporation separation process for ethanol recovery, named Membrane Dephlegmation. To test performance, a pilot-scale experimental system was constructed. The pilot-scale system employed vertically-oriented commercial NaA zeolite membranes. The membranes were exposed to a vapour phase feed and a liquid phase reflux, facilitating both countercurrent vapour-liquid contacting and pervaporation.

The system was used to obtain experimental results at a variety of feed velocities, feed concentrations, permeate pressures and reflux ratios. Further, wetted-wall distillation experiments were carried out by operating the system without a pervaporation flux. The experimental results were used to validate a previously presented mathematical model and to determine key model parameters. It was determined that Membrane Dephlegmation could break the ethanol-water azeotrope and that ethanol concentrations greater than 99 % by mass are achievable. The effects of pertinent operating conditions on system performance were discussed in detail. The possibility of flooding at very high vapour velocities was also discussed. Finally, membrane stability under long-term operation was examined. It was determined that the type of membranes used in this investigation should not be exposed to ethanol feed concentrations below 70 % ethanol by mass.

7.6. Acknowledgement

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

7.7. Nomenclature

C	number of chemical species
D	diameter, m
E	interphase energy flux, $\text{kJ/m}^2\cdot\text{s}$ or activation energy, kJ/kmol
g	gravitational acceleration, 9.81 m/s^2

H	enthalpy, kJ/kmol
$\bar{H}$	partial molar enthalpy, kJ/kmol
h^*	corrected heat transfer coefficient, kJ/m ² .s.K
h	heat transfer coefficient, kJ/m ² .s.K
K^*	corrected mass transfer coefficient, kmol/m ² .s
K	mass transfer coefficient, kmol/m ² .s or distribution coefficient
L	total liquid molar flow rate, kmol/s or length, m
l	liquid component molar flow rate, kmol/s
N	interphase molar flux, kmol/m ² .s or number of segments
p	pressure, Pa
Q	membrane permeability, kg/m ² .h.bar
R	internal tube radius, m or universal gas constant, 8.314 J/mol.K
T	temperature, K
V	total vapour molar flow rate, kmol/s or molar volume, m ³ /kmol
v	vapour component molar flow rate, kmol/s
x	liquid phase mole fraction
y	vapour phase mole fraction
z	axial coordinate
Δz	differential element

Greek letters

δ	liquid film thickness, m
γ	activity coefficient

Subscripts

E	ethanol
i	species i
L	liquid phase
LM	liquid-membrane interface
M	membrane (solid surface)
P	permeate (or external temperature)
ref	at reference conditions

V vapour phase

W water

Superscripts

I interface

PV pervaporation

ref at reference conditions

sat saturation conditions

7.8. References

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SECTION III. SUPPORTING COMPUTATIONAL INVESTIGATIONS

OVERVIEW OF AUXILIARY COMPUTATIONAL STUDIES

Section II of this dissertation presents three computational studies that were carried out to support the experiments and simulations presented in Section II. The computational studies were divided into three journal papers, which have been published. This chapter provides a summary of the computational studies and explains the research methodology employed to implement them.

In Chapters 9 and 10, Multiphase Computational Fluid Dynamics (CFD) is used to study hydrodynamics and heat and mass transfer for countercurrent vapour-liquid flow in narrow channels. As discussed in Section II, Membrane Dephlegmation relies on efficient countercurrent vapour-liquid contacting in small tubes. Chapter 9 presents an investigation that focuses on the hydrodynamics of vapour-liquid flow in a narrow channel. Countercurrent vapour-liquid flow inherently involves the movement of a free surface. The Volume-Of-Fluid (VOF) method was used to track interface dynamics. The effects of important parameters on the flow patterns were studied. The impact of the liquid Reynolds number, ethanol concentration, contact angle and pressure drop on the velocity profiles, film smoothness and liquid holdup were investigated.

In Chapter 10, a new computational methodology for the Direct Numerical Simulation (DNS) of coupled interphase heat and mass transfer is proposed. The proposed method uses the Volume-Of-Fluid (VOF) method to track vapour-liquid interface dynamics and solves the fully coupled species and energy equations to directly estimate heat and mass transfer rates. The proposed technique is broadly applicable to many industrially important applications, where coupled interphase heat and mass transfer occurs, including distillation. The model was validated using the ethanol-water system for the cases of wetted-wall vapour-liquid contacting and vapour flow over a smooth, stationary liquid. Wetted-wall contacting was of particular interest, since this is the type of contacting occurring in the systems studied in Section II. Good agreement was observed between empirical correlations, experimental data and numerical predictions for vapour and liquid phase mass transfer coefficients. The study provided useful information about the hydrodynamics expected to be present in Membrane Dephlegmation. Further, the study provided

validation of the heat and mass transfer correlations used in the one-dimensional Membrane Dephlegmation model presented in Section II.

In Chapter 11, neural network models are used to correlate data for important transport properties for the ethanol-water system. Specifically, a three-layer feed-forward neural network with six neurons in the hidden layer is used to model viscosity, thermal conductivity, surface tension and the Fick diffusion coefficient. The models were tested for accuracy by comparing predictions to external experimental data. The results showed that the neural network models provided highly accurate predictions of the transport properties. Since all the models retain the same simple matrix structure, their integration into computer codes is straightforward and non-repetitive. The neural network models were used in the prediction of transport properties in Chapters 9 and 10 as well as all the simulations carried out in Section II.

PARAMETRIC STUDY FOR COUNTERCURRENT VAPOUR-LIQUID FREE-SURFACE FLOW IN A NARROW CHANNEL

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Abstract

In this investigation, the effects of some important parameters on the flow patterns in a narrow vertical channel for countercurrent vapour-liquid flow of an ethanol-water system were studied. The parameters included the liquid Reynolds number, ethanol concentration, contact angle and pressure drop. The vapour phase velocity profile was significantly influenced by the pressure drop through the channel. The ethanol concentration and liquid Reynolds number were found to have a significant impact on the liquid holdup (average film thickness) as well as the velocity profiles in the liquid and vapour phases. In the ranges studied, the contact angle and pressure drop were found to have a negligible effect on the liquid holdup.

***This paper has been published:** J.B. Haelssig, S.Gh. Etemad, A.Y. Tremblay, J. Thibault, Parametric study for countercurrent vapour-liquid free-surface flow in a narrow channel, Canadian Journal of Chemical Engineering DOI: 10.1002/cjce.20409 (2010).

9.1. Introduction

Many of the most widely used chemical engineering separation techniques depend on efficient vapour-liquid and/or gas-liquid contacting. In absorption or stripping, gases and liquids are brought into intimate contact to facilitate mass transfer of chemical species to or from the liquid phase. Conversely, the distillation process is characterized by simultaneous heat and mass transfer between an evaporating liquid and a condensing vapour, which allows accumulation of volatile species in the vapour phase. Dephlegmation or diabatic distillation is a process in which a vapour, flowing upwards, is partially condensed. Liquid condensate is then allowed to flow in a counter-current fashion to the vapour through the action of gravity, which leads to accumulation of the volatile species in the vapour [1]. It is clear that hydrodynamics play a critical role in these processes. In fact, heat and mass transfer efficiencies are directly linked to the fluid dynamics in these systems, since the flow patterns are largely responsible for determining the interfacial area available for heat and mass transfer.

Computational Fluid Dynamics (CFD) facilitates the analysis of system hydrodynamics through the solution of the continuity and momentum conservation equations. The ability to predict velocity, pressure, temperature and concentration profiles makes CFD an indispensable tool for process design. Many studies have been carried out to determine the effects of geometry and various operating conditions on momentum, heat and mass transfer. Hydrodynamic behaviour in structured packing has been a particularly active area for research [2-9]. Heat and mass transfer effects have also been included in the analysis of fluid flow on structured packing [10]. Other studies have been carried out to study single or multi-component evaporation and condensation [11-14].

In the preliminary design stage of a vapour-liquid separation device, similar to a dephlegmator, it is useful to carry out CFD simulations to study vapour and liquid flow patterns under typical operating conditions. Further, it is convenient to neglect heat and mass transfer effects in the preliminary design stage, since these significantly complicate the simulations. Dephlegmation is commonly carried out in rectangular channels or tubular geometry. The channel or tube surfaces are not necessarily smooth and may indeed be rough to promote heat and mass transfer. The present investigation aims to determine the effect of various operating parameters on the fluid dynamics of counter-current vapour-liquid flow in a narrow vertical channel. The effects of heat and mass transfer are neglected and a simple geometry is used to

allow the simplified study of the impacts of other important parameters. The physical properties of an ethanol-water system are used and the effect that a change in composition has on the system is studied. Further, the effects of varying liquid flow rates and pressure drops through the channel on the flow behaviour are investigated.

9.2. Numerical Methodology

9.2.1. Governing Equations

The commercial CFD code, FLUENT, was used to simulate the fluid dynamics of the two-phase ethanol-water system [15]. For free-surface flows, FLUENT provides a Volume-Of-Fluid (VOF) model which tracks the interface on a fixed Eulerian mesh by solving a continuity equation for the volume fraction of one of the phases. In this case, the vapour phase was specified as the primary phase and thus the volume fraction of the liquid phase was solved. It follows that a computational cell is filled with liquid when the volume fraction is unity, filled with vapour when the volume fraction is zero and partially filled with liquid when the volume fraction is between zero and one. To determine the actual location of the vapour-liquid interface, an interpolation scheme must be implemented. In this case, the interface location was reconstructed using a Piecewise Linear Interface Calculation (PLIC), which assumes a piecewise linear interface. The continuity equation for the volume fraction of the liquid phase takes the following form.

$$\frac{\partial}{\partial t}(\alpha_L \rho_L) + \nabla \cdot (\alpha_L \rho_L \vec{u}_L) = 0 \quad (1)$$

Where α_L , ρ_L , and $\vec{u}_L$ are the liquid volume fraction, liquid density and velocity, respectively. In accordance with the one-fluid formulation for two-phase flow, the VOF model solves a single momentum throughout the computational domain. The momentum equation is,

$$\frac{\partial}{\partial t}(\rho \vec{u}) + \nabla \cdot (\rho \vec{u} \vec{u}) = -\nabla p + \nabla \cdot [\mu (\nabla \vec{u} + \nabla \vec{u}^T)] + \rho \vec{g} + \vec{F} \quad (2)$$

Where the density and viscosity are volume-averaged according to $\rho = \alpha_L \rho_L + (1 - \alpha_L) \rho_V$ and $\mu = \alpha_L \mu_L + (1 - \alpha_L) \mu_V$. For thin film flow, the effect of surface tension can be significant. FLUENT includes the effect of surface tension as a body force in the momentum equation according to the method proposed by Brackbill et al. [16]. According to this method, the surface tension force is calculated by the following equation.

$$\vec{F} = \sigma \frac{\rho \kappa \nabla \alpha_L}{0.5(\rho_L + \rho_V)} \quad (3)$$

Where σ , ρ , ρ_L , ρ_V and κ are the surface tension, mixture density, liquid density, vapour density and curvature, respectively. The curvature is a function of the unit normal vector according to the following equation.

$$\kappa = \nabla \cdot \vec{n} \quad (4)$$

Where the unit normal vector is defined by $\vec{n} = \frac{\nabla \alpha_L}{|\nabla \alpha_L|}$. At computational cells adjacent to the wall, the unit normal vector is adjusted using the contact angle (θ) according to the following equation.

$$\vec{n} = \vec{n}_w \cos \theta + \vec{t}_w \sin \theta \quad (5)$$

Where $\vec{n}_w$ and $\vec{t}_w$ are unit vectors normal and tangential to the wall, respectively.

9.2.2. Simplified Analytical Solution

For comparison purposes, it is possible to derive a simplified analytical solution to the steady-state countercurrent vapour-liquid flow problem described above. For the liquid phase it is possible to assume that the flow is laminar and that the vapour-liquid interface is smooth. Further, it is possible to neglect inertia effects. Under these assumptions, the momentum equations for the liquid phase reduce to,

$$\frac{d^2 u_L}{dy^2} = \frac{(\rho_L - \rho_V)g}{\mu_L} \quad (6)$$

Similarly, the vapour phase momentum equations may be simplified by neglecting inertia effects and assuming that the pressure difference is the main driving force for flow. Under these assumptions, the momentum equations for the vapour phase reduce to,

$$\frac{d^2 u_V}{dy^2} = -\frac{\Delta P}{\mu_V L} \quad (7)$$

The liquid phase equation can be integrated by applying the no slip boundary condition at the wall (i.e. at $y=0$, $u_L=0$) and a no slip boundary condition at the interface (i.e. at $y=\delta$, $u_L = u_V = u_{\text{int}}$). After integration, the liquid phase velocity profile is given by,

$$u_L = \frac{(\rho_L - \rho_V)g}{2\mu_L}(y^2 - \delta y) + \frac{u_{\text{int}}}{\delta} y \quad (8)$$

Similarly, the vapour phase momentum equation can be integrated by applying a no slip boundary condition at the interface (i.e. at $y = \delta$, $u_L = u_V = u_{\text{int}}$) and the usual condition of zero normal velocity gradient at the symmetry plane (i.e. at $y = \frac{W}{2}$, $\frac{du_V}{dy} = 0$). Thus, the vapour phase velocity profile is given by,

$$u_V = \frac{\Delta P}{2\mu_V L}(\delta^2 - y^2 + Wy - W\delta) + u_{\text{int}} \quad (9)$$

Two unknowns remain in the velocity profile equations, the film thickness and the interface velocity. It is possible to solve for these unknowns by enforcing two further restrictions. First, the shear stress must be continuous across the interface (i.e. at $y = \delta$, $\mu_V \frac{du_V}{dy} = \mu_L \frac{du_L}{dy}$).

Substituting this condition into the equations for the velocity profiles gives,

$$F_1 = \frac{(\rho_L - \rho_V)g}{2}\delta + \frac{u_{\text{int}}\mu_L}{\delta} + \frac{\Delta P}{L}\left(\delta - \frac{W}{2}\right) = 0 \quad (10)$$

Secondly, the mass flow rate of the liquid film is known and is related to the liquid velocity through,

$$\dot{m} = -\int_0^\delta \rho_L u_L dy = \text{const}$$

Thus, enforcing the mass flow rate restriction leads to,

$$F_2 = -\frac{\rho_L(\rho_L - \rho_V)g}{12\mu_L}\delta^3 + \frac{\rho_L u_{\text{int}}}{2}\delta + \dot{m} = 0 \quad (11)$$

Equations 10 and 11 form a system of coupled nonlinear equations that can be solved iteratively for the film thickness and interface velocity using Newton's method.

9.2.3. Geometry and Solution Methodology

The geometry used in this investigation, shown schematically in Figure 9.1, consisted of a narrow channel having a width of 6 mm and a length of 200 mm. Liquid was introduced at a constant velocity through a 1 mm opening between two walls at the top of the channel. To facilitate introduction of vapour into the system, the static pressures were specified at the top and bottom of the channel. The vapour entered at the bottom of the channel, through a space having a

width of 6 mm minus twice the liquid film thickness. The vapour exited at the top through a 3 mm gap. A two-dimensional model was used to represent the geometry and due to the presence of symmetry, only half of the domain was modelled.

A pressure based, unsteady, laminar, explicit VOF formulation was used. Pressure-velocity coupling was achieved using the Pressure-Implicit with Splitting Operators (PISO) scheme. Spatial discretization of the continuity and momentum equations was carried out using the Pressure Staggering Option (PRESTO!) and a First-Order Upwind Scheme, respectively. The time step was automatically adjusted to match a specified Courant number. A global Courant number of 0.5 was determined to provide adequate solution stability and accuracy when combined with the computational grid. The vapour and liquid phases were set as the primary and secondary phases, respectively. Constant physical properties and a constant surface tension were specified. As mentioned above, liquid entered at a constant velocity and a pressure inlet and pressure outlet were specified for the vapour. The no-slip boundary condition, with a specified contact angle, was used at the wall. Unsteady simulations were carried out until the system reached a pseudo steady-state. The pseudo steady-state was reached when there was negligible change or periodic behaviour in the velocity profile at the channel midsection, the film thickness at the channel midsection and the average velocity at the vapour outlet.

Grid refinement studies were carried out for one of the cases in the parametric study. As shown in Figure 9.2, a grid consisting of 7380 quadrilateral cells provided grid independent solutions with respect to the film thickness and velocity profile at the channel midsection. This grid also provided converged solutions with respect to the average velocity leaving the channel (not shown on Figure 9.2).

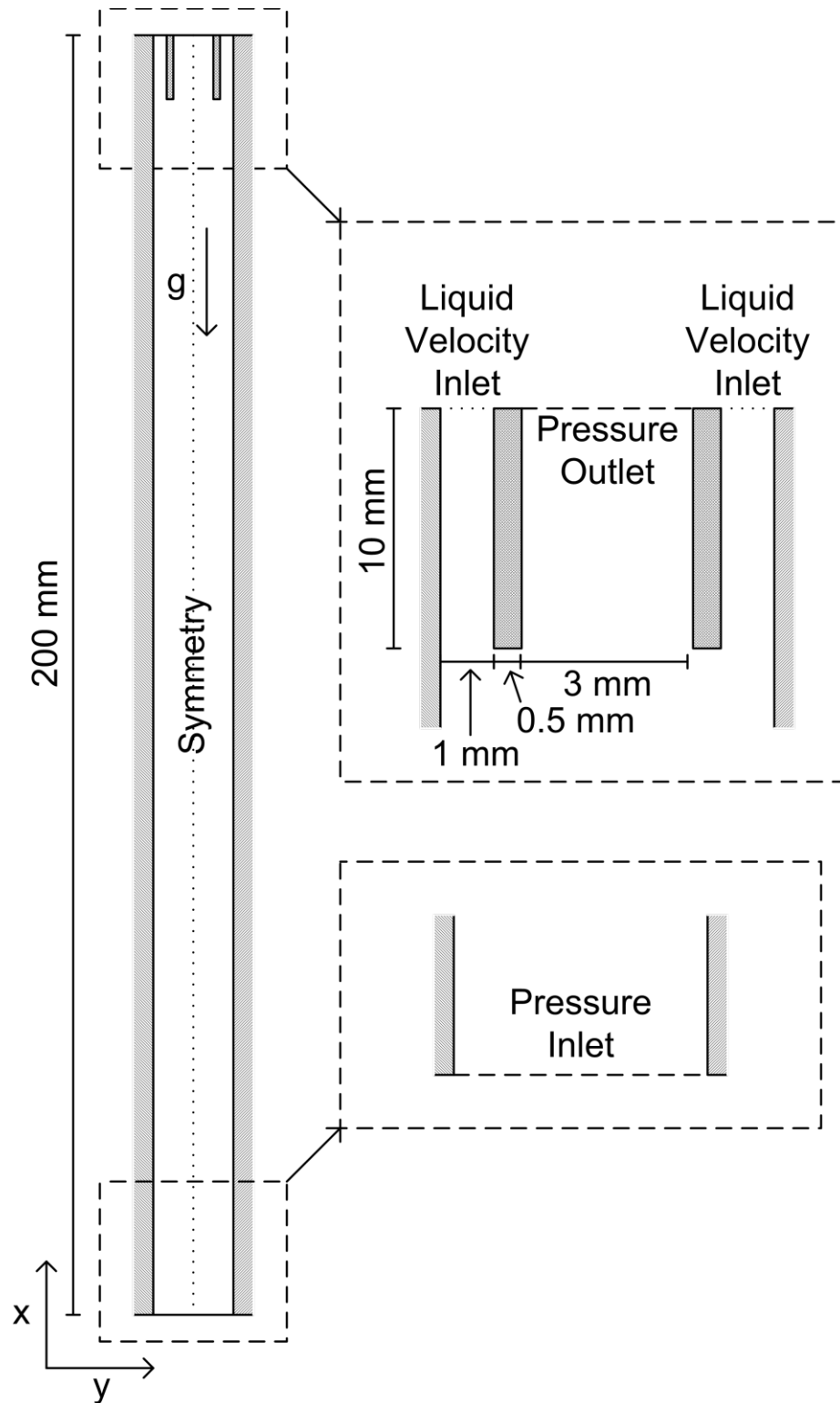


Figure 9.1. Schematic representation of the domain geometry.

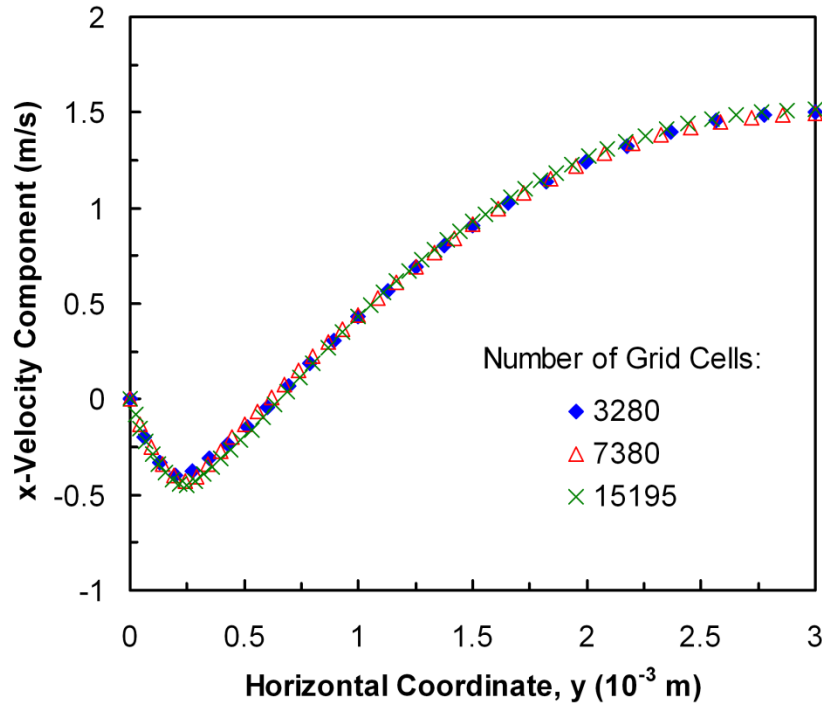


Figure 9.2. Velocity profiles at channel midsection ($x = 100$ mm) for three levels of grid refinement (Re_L of 500; ΔP of 4 Pa; Ethanol Mole Fraction of 0.85).

9.2.4. Parametric Study

The physical properties of an ethanol-water system depend on temperature and composition. Without the inclusion of heat and mass transfer effects in the current model, it is not possible to determine the exact temperature and composition profiles that would exist in the system being studied. However, as a preliminary approximation it is possible to assume that, in this small channel section, the bulk vapour and liquid will have the same composition. Further, it is possible to assume that the bulk liquid and bulk vapour will be at the bubble point and dew point temperatures, respectively. These assumptions are obviously not strictly true but are made so that composition effects may be investigated in a simplified fashion. Table 9.1 shows the physical properties used in this investigation. The liquid viscosity and surface tension were calculated using the neural network models provided by Haelssig et al. [17]. The vapour viscosity was estimated by the Reichenberg method as presented by Poling et al. [18]. The liquid density, vapour density, bubble point temperature and dew point temperature were estimated using the Wilson-Virial model in Aspen HYSYS 2006 [19].

Table 9.1. Summary of Physical Properties*

Ethanol Mole Fraction	Liquid Temperature (K)	Vapour Temperature (K)	Liquid Density (kg/m ³)	Vapour Density (kg/m ³)	Liquid Viscosity (10 ⁻³ Pa.s)	Vapour Viscosity (10 ⁻⁵ Pa.s)	Surface Tension (mN/m)
0.00	373.15	373.15	947.89	0.5890	0.3033	1.2100	59.25
0.10	359.66	370.48	926.34	0.6856	0.4811	1.1848	30.02
0.30	354.69	364.48	873.37	0.8847	0.6284	1.1376	23.20
0.50	352.89	357.50	826.76	1.0935	0.6151	1.0945	21.05
0.70	351.70	352.27	786.80	1.3041	0.5629	1.0626	19.69
0.85	351.24	351.26	760.21	1.4538	0.5215	1.0495	18.82
1.00	351.32	351.32	735.56	1.5995	0.4829	1.0401	18.00

*The vapour temperature was used to estimate vapour properties and the liquid temperature was used to estimate liquid properties and surface tension

A parametric study was carried out to determine the impact of several pertinent parameters on the flow behaviour in the channel. Table 9.2 summarizes the parameters and parameter ranges that were included in the study. The liquid Reynolds number was adjusted by varying the liquid mass flow rate. As shown in the table, the effects of mixture composition, liquid Reynolds number, contact angle and pressure difference between the top and bottom of the channel were included.

Table 9.2. Summary of the Ranges of the Variables used in the Parametric Study

Parameter	Range
Ethanol Mole Fraction	0.0, 0.1, 0.3, 0.5, 0.7, 0.85, 1.0
Liquid Reynolds Number	30 to 1000
Contact Angle (°)	30, 60
Pressure Drop (Pa)	0 to 6

9.3. Results and Discussion

9.3.1. Comparison with the Simplified Analytical Solution

9.3.1.1. Channel midsection velocity profiles

It is possible to compare the numerical results, calculated using the VOF method, with the results obtained from the simplified analytical solution described above. Of course, it is only

reasonable to compare these two results under fully developed steady-state flow conditions. It is reasonable to assume that fully developed flow will have been reached at the channel midsection ($x = 100$ mm), due to the relatively high length to width ratio of the channel. Thus, one approach is to compare the numerically predicted velocity profiles at the channel midsection with the analytical solution for the velocity profiles.

Figure 9.3 shows a comparison of analytical and numerical solutions for velocity profiles at channel midsection ($x = 100$ mm) for three simulation cases. From Figure 9.3 it is clear that the numerical predictions agree well with the analytical solution. Further, it is shown that for lower liquid flow rates, the numerical predictions are closer to the analytical solution than for higher liquid flow rates. The larger discrepancy between the numerical and analytical velocity profiles at higher liquid flow rates is likely due to the presence of surface waves.

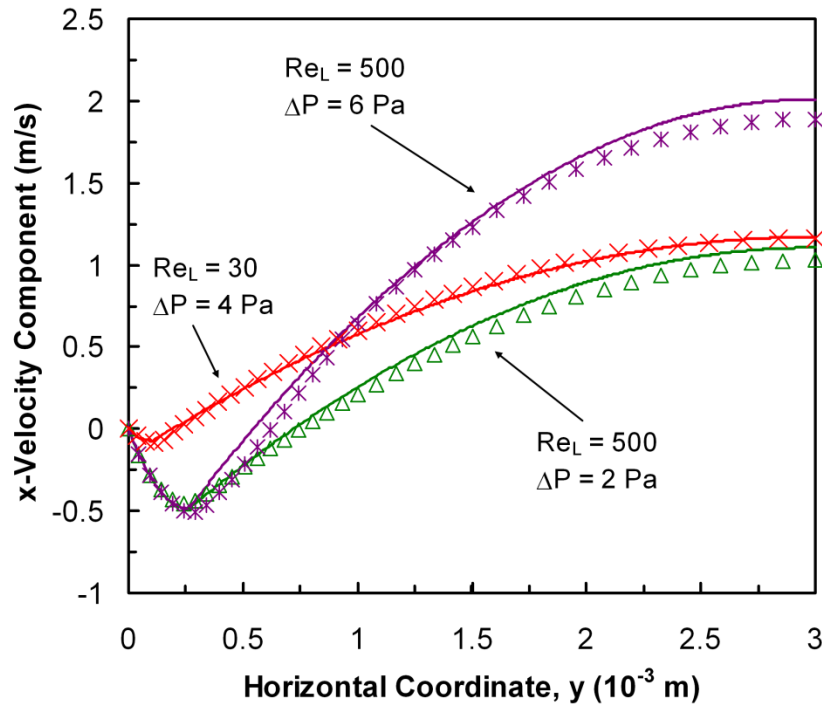


Figure 9.3. Comparison between analytical and numerical solutions for velocity profiles at channel midsection ($x = 100$ mm) for three simulation cases (Lines are analytical solution; Symbols are numerical solution; Ethanol Mole Fraction of 0.85).

9.3.1.2. Vapour phase friction factor

The vapour phase friction factor is related to the vapour phase pressure loss for flow through the channel. The friction factor can be calculated from both the numerical and analytical solutions and can be defined as,

$$f = \frac{2\mu_v}{\rho u_{ave,V,rel}^2} \frac{\partial u_v}{\partial n} \quad (12)$$

In this case the friction factor is based on the average vapour phase velocity relative to the interface velocity. By defining the friction factor based on the relative vapour velocity it is possible to compare the results not only to the analytical solution but also to the normal value for flow between moving parallel plates (which is $24/Re$, where Re is based on the vapour velocity relative to the velocity of the interface).

Figure 9.4 shows the variation of the vapour phase friction factor as a function of vapour phase Reynolds number for the numerical predictions, analytical solution and flow between moving parallel plates. It is important to note that the friction factor was again calculated at the channel midsection. From Figure 9.4 it is clear that the friction factor predicted from the simplified analytical solution is almost identical to the case of flow between moving parallel plates. Further, it is apparent that the numerical predictions of the friction factor are also very similar to the analytical solution. The similarity can again be attributed to the relatively smooth vapour-liquid interface.

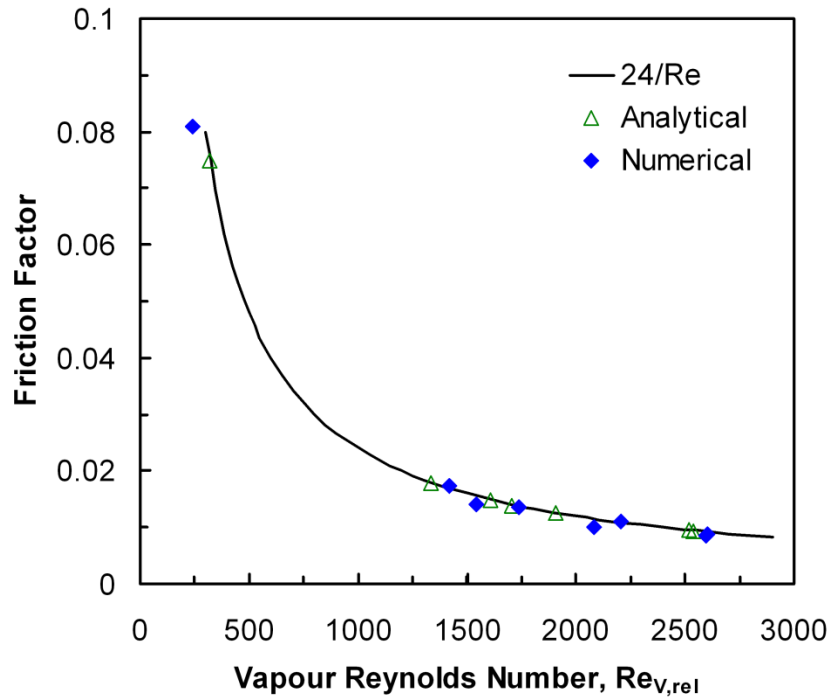


Figure 9.4. Vapour phase friction factor as a function of vapour phase Reynolds number for numerical predictions, analytical solution and flow between moving parallel plates.

9.3.2. Parametric Study Results

As mentioned in the previous section, the impact of certain key parameters on the fluid flow behaviour in the vertical channel was investigated. Specifically, the flow pattern and liquid film behaviour were monitored. To show the impact of the investigated parameters on the flow behaviour, the velocity profile at the channel midsection ($x = 100$ mm) was monitored. Furthermore, the liquid holdup, which is defined as the volume of liquid in the channel divided by the total volume of the channel, was calculated. The volume of liquid in the channel can be calculated from the liquid phase fraction according to $V_L = \int_V \alpha_L dV$. The liquid holdup provides a measure of the average liquid film thickness. The Weber number was also calculated and used in the analysis. For this investigation, the Weber number (We) and liquid Reynolds number (Re_L) were defined in the following way.

$$We = \frac{\rho_L u_{ave,L}^2 \delta_{ave}}{\sigma} \quad (13)$$

$$\text{Re}_L = \frac{4\Gamma}{\mu_L} \quad (14)$$

Where $u_{ave,L}$ is the average liquid velocity, δ_{ave} is the average film thickness and Γ is the liquid mass flow rate per unit channel width. The Weber number is, by definition, the ratio of a fluid's inertia to its surface tension. Thus, when the Weber number is much greater than unity, inertial forces dominate. Conversely, surface tension forces are dominant when the Weber number is lower than unity.

The results are summarized in Figures 9.5 through 9.10. It is important to note that for the two contact angles investigated, a negligible change in the steady-state results was observed. The negligible impact of contact angle is a direct result of the wall being completely wetted at steady state, for the conditions used in this study. As a result, the only observed impact of the contact angle in this study was during the initial wetting of the wall. As expected, the higher contact angle simulations predicted an initially thicker advancing liquid film. Figure 9.5 shows the effect of the pressure difference through the channel on the velocity profile. As expected, the vapour phase velocity increases with increasing pressure difference. Further, it is shown that the pressure drop had a negligible impact on the liquid film thickness and liquid velocity profiles. This is a direct result of the relatively low shear stress exerted by the vapour on the liquid under the pressure differences included in this investigation.

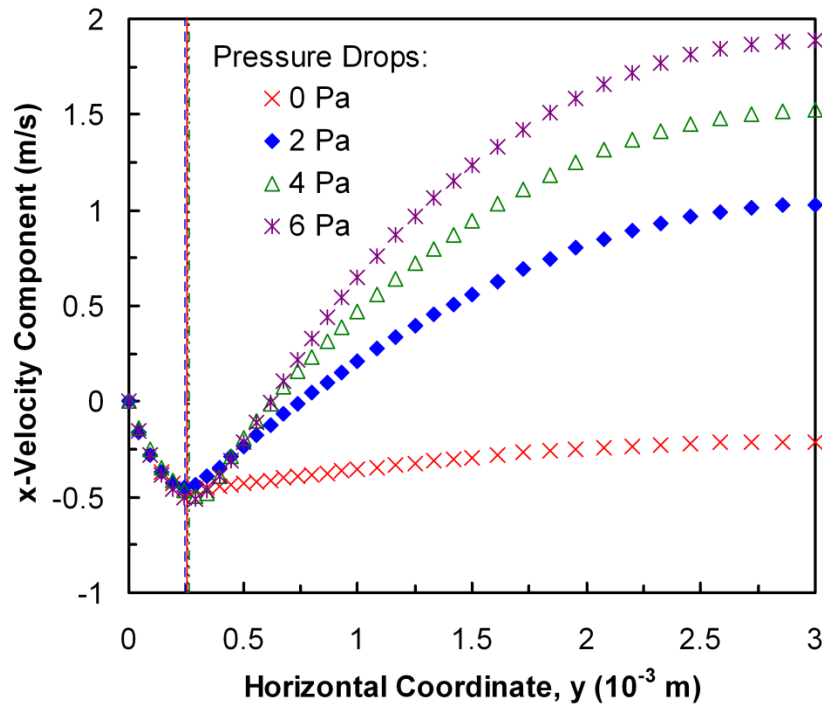


Figure 9.5. Velocity profiles at channel midsection ($x = 100$ mm) for four pressure drops (Re_L of 500; Ethanol Mole Fraction of 0.85).

The impact of the liquid Reynolds number on the velocity profile is shown in Figure 9.6. As expected, higher liquid flow rates lead to thicker liquid films as well as lower minimum vapour velocities. It is also important to note that with increasing liquid Reynolds numbers, the velocity gradient normal to the interface in the vapour phase becomes more pronounced. Thus, a higher shear stress is exerted by the vapour on the liquid by increasing the liquid Reynolds number, for the same pressure difference. Since the vapour flow rates were approximately the same for all cases, it is reasonable that thicker liquid films will lead to higher maximum vapour velocities (since less cross-sectional area is available for vapour flow). However, since the minimum vapour velocity is also lower for thicker films, the increase in the maximum vapour velocity is not as much as would be achieved by simply decreasing the cross-sectional area available for vapour flow.

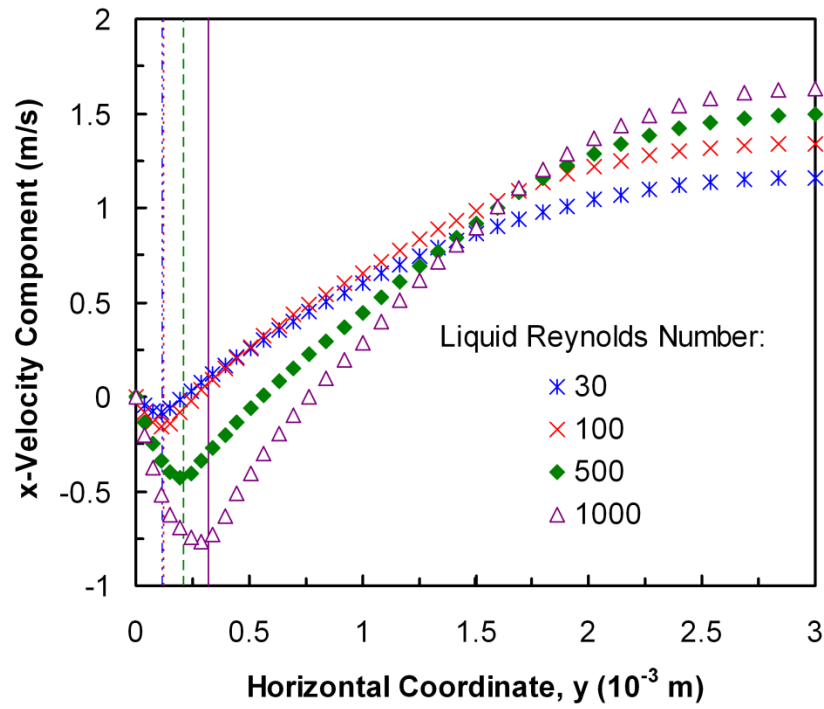


Figure 9.6. Velocity profiles at channel midsection ($x = 100$ mm) for four liquid Reynolds numbers (ΔP of 4 Pa; Ethanol Mole Fraction of 0.85).

The effect of the ethanol concentration on the velocity profile is shown in Figure 9.7. It is shown that the ethanol concentration impacts the flow pattern and film thickness. It is further demonstrated that the greatest impact occurs at ethanol mole fractions less than 0.5. This is likely due to the greater decrease in the surface tension at low ethanol concentrations.

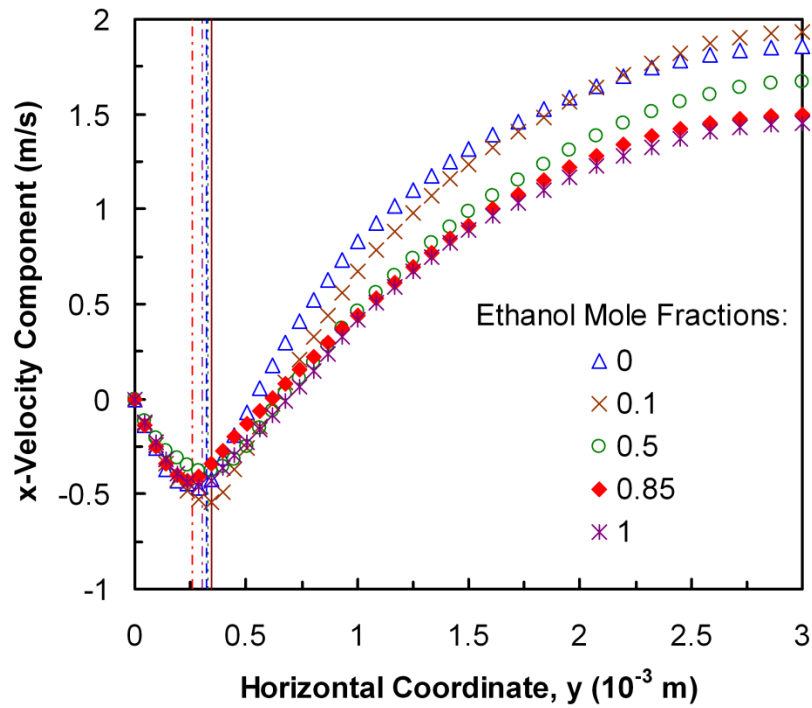


Figure 9.7. Velocity profiles at channel midsection ($x = 100$ mm) for five ethanol mole fractions (Re_L of 500; ΔP of 4 Pa).

Figure 9.8 shows the variation of the liquid holdup with liquid Reynolds number for three ethanol concentrations. As expected, the liquid holdup increases with the liquid Reynolds number. However, the increase is nonlinear, with a sharp increase at low Reynolds numbers and a more linear increase at higher Reynolds numbers.

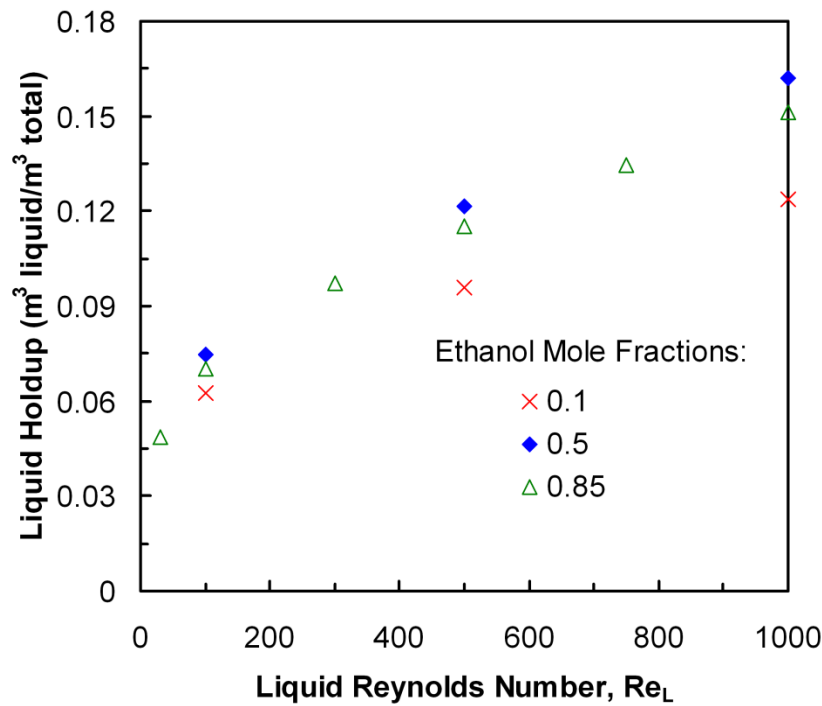


Figure 9.8. Variation of liquid holdup with liquid Reynolds number for three ethanol mole fractions (ΔP of 4 Pa).

The variation of the Weber number with ethanol concentration, for three different Reynolds numbers, is shown on Figure 9.9. It is illustrated that, for a constant Reynolds number, the ethanol concentration has a significant impact on the relative importance of the surface tension force. However, surface tension is not the only factor responsible for the variation of the Weber number with composition. The other physical properties also play an important role. Surface tension changes monotonically between pure water and pure ethanol, however, the change in the Weber number is not monotonic. Thus, the other physical properties must necessarily also affect this system.

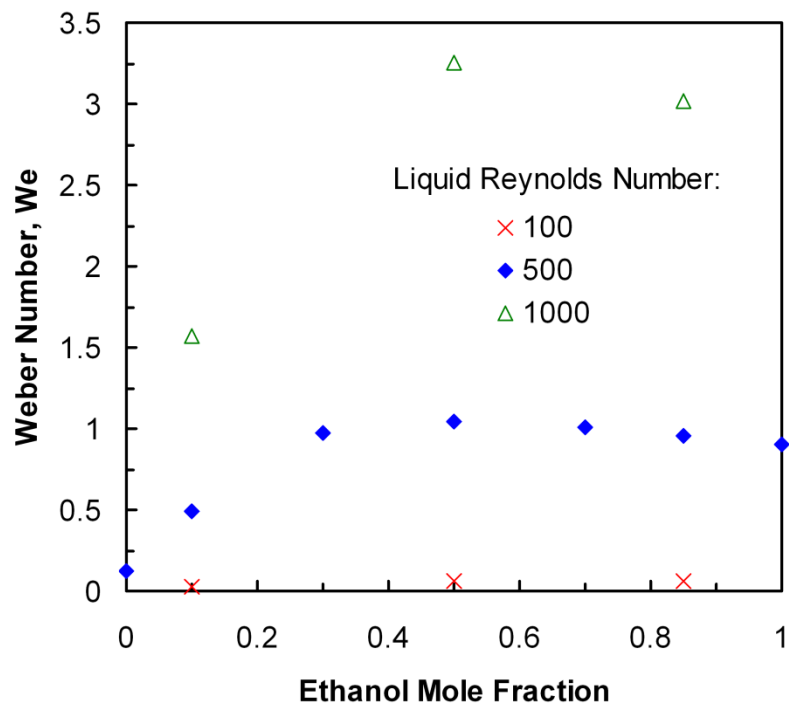


Figure 9.9. Variation of Weber number with ethanol mole fraction for three liquid Reynolds numbers (ΔP of 4 Pa).

Figure 9.10 shows the impact of the Weber number on the liquid holdup, for Reynolds numbers of 100, 500 and 1000. It is shown that, for a constant Reynolds number, the increase in the liquid holdup with Weber number is nearly linear. Furthermore, there is a significant increase in the liquid holdup with increasing Weber number, even when Reynolds number remains constant.

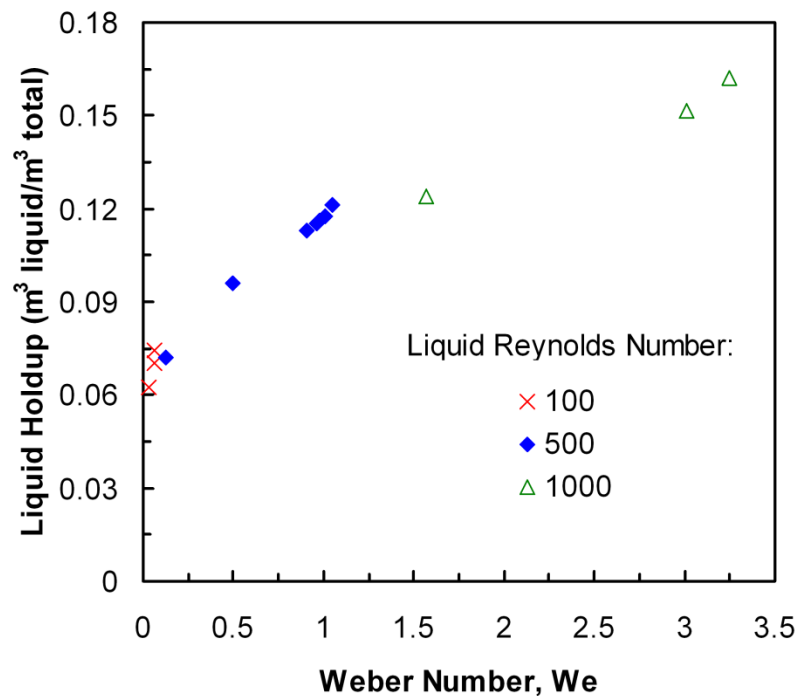


Figure 9.10. Variation of liquid holdup with Weber number for three liquid Reynolds numbers (ΔP of 4 Pa).

9.4. Conclusions

In the preliminary design of vapour-liquid separation devices, it is important to study the fluid flow behaviour to identify physical limitations and predict optimal performance. In this investigation, a simple geometry consisting of a narrow vertical channel with a width of 6 mm and a height of 200 mm was used to investigate the impact of certain key parameters on the flow patterns during countercurrent vapour-liquid flow for an ethanol-water system. The parameters included the liquid Reynolds number, ethanol concentration, contact angle and pressure drop. In this preliminary study, heat and mass transfer effects were neglected. In the ranges studied, the contact angle and pressure drop were found to have a negligible effect on the liquid holdup. However, as expected, the vapour phase velocity profile was greatly influenced by the pressure difference through the channel. The ethanol concentration and liquid Reynolds number were found to have a significant impact on the liquid holdup (average film thickness) and velocity profiles. In the future, the current model will be extended to account for heat and mass transfer effects. The model will then be used for the design and optimization of a vapour-liquid contacting device to be used in energy efficient ethanol recovery.

9.5. Acknowledgment

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

9.6. Nomenclature

f	friction factor, $\frac{2\mu_V}{\rho u_{ave,V,rel}^2} \frac{\partial u_V}{\partial n}$
F	nonlinear equations
$\vec{F}$	volumetric body forces, N/m ³ .s
$\vec{g}$	gravitational acceleration, 9.81 m/s ²
L	length, m
$\dot{m}$	liquid mass flow rate, kg/s
n	direction normal to the interface
$\vec{n}$	interface unit normal vector
$\vec{n}_w$	wall unit normal vector
p	pressure, Pa
Re_L	liquid phase Reynolds number, $\frac{4\Gamma}{\mu_L}$
$Re_{V,rel}$	vapour phase Reynolds number relative to the interface, $\frac{\rho(u_{ave,V} - u_{int})(W - 2\delta)^2}{\mu_V}$
t	time, s
$\vec{t}_w$	wall unit tangential vector
$\vec{u}$	velocity, m/s
W	distance between parallel plates (channel width), m
We	Weber number, $\frac{\rho_L u_{ave,L}^2 \delta_{ave}}{\sigma}$
x	vertical coordinate, m
y	horizontal coordinate, m

Greek letters

α	volume fraction, m ³ phase/m ³
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δ	liquid film thickness, m
Γ	liquid mass flow rate per unit wetted width, kg/m.s
μ	viscosity, Pa.s
κ	curvature
θ	contact angle, degrees
ρ	density, kg/m ³
σ	surface tension, N/m

Subscripts

<i>ave</i>	average
<i>int</i>	interface
<i>L</i>	liquid phase
<i>rel</i>	relative to the interface velocity
<i>V</i>	vapour phase
<i>W</i>	wall

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DIRECT NUMERICAL SIMULATION OF INTERPHASE HEAT AND MASS TRANSFER IN MULTICOMPONENT VAPOUR-LIQUID FLOWS

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Abstract

A Volume-of-Fluid methodology for direct numerical simulation of interface dynamics and simultaneous interphase heat and mass transfer in systems with multiple chemical species is presented. This approach is broadly applicable to many industrially important applications, where coupled interphase heat and mass transfer occurs, including distillation. Volume-of-Fluid interface tracking allows investigation of systems with arbitrarily complex interface dynamics. Further, the present method incorporates the full interface species and energy jump conditions for vapour-liquid interphase heat and mass transfer, thus, making it applicable to systems with multiple phase changing species. The model was validated using the ethanol-water system for the cases of wetted-wall vapour-liquid contacting and vapour flow over a smooth, stationary liquid. Good agreement was observed between empirical correlations, experimental data and numerical predictions for vapour and liquid phase mass transfer coefficients. Direct numerical simulation of interphase heat and mass transfer offers the clear advantage of providing detailed information about local heat and mass transfer rates. This local information can be used to develop accurate

heat and mass transfer models that may be integrated into large scale process simulation tools and used for equipment design and optimization.

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10.1. Introduction

Simultaneous interfacial heat and mass transfer occurs frequently in a wide variety of industrial applications. For example, many of the most widely used chemical separation techniques depend on efficient vapour-liquid and/or gas-liquid contacting. In absorption and stripping, gases and liquids are brought into intimate contact to facilitate mass transfer of chemical species to or from the liquid phase. Conversely, distillation is characterized by simultaneous heat and mass transfer between an evaporating liquid and a condensing vapour, which allows accumulation of volatile species in the vapour phase. Clearly, fluid dynamics also play a critical role in these processes. In fact, heat and mass transfer efficiencies are directly linked to fluid flow patterns, through the interfacial area and heat and mass transfer coefficients.

Through solution of the continuity, momentum, energy and species equations, Computational Fluid Dynamics (CFD) enables the prediction of velocity, pressure, temperature and concentration profiles in very complex systems. Further, CFD facilitates the analysis of phenomena occurring at temporal and/or spatial scales that are difficult to investigate experimentally. The ability to study complex systems and aid in understanding fundamental phenomena makes CFD an indispensable tool for engineers and scientists. However, despite immense progress in CFD techniques, multiphase flows remain a challenging topic with no unified modeling approach.

In general, continuum models for multiphase flow can be grouped into two categories, multi-fluid and one-fluid models. In multi-fluid models, which are based on the interpenetrating-continua assumption, interface dynamics are not directly resolved. Instead, every point in the solution domain is occupied by different proportions of each phase and separate conservation equations must be solved. It follows that closure laws must be specified for interface momentum, energy and mass transfer. It is the accurate specification of these closure laws, which are usually

empirical, that leads to inaccuracies in multi-fluid models. However, since interface dynamics are not explicitly resolved, multi-fluid models can be used to simulate multiphase flows on relatively coarse grids. This characteristic has made multi-fluid models the only multiphase modelling approach suitable for most applications of industrial significance.

Conversely, one-fluid models provide a Direct Numerical Simulation (DNS) of interface dynamics, but not necessarily of turbulence, and therefore closure laws are generally not required. In turbulent flows, turbulence must still be modeled through the Reynolds-Averaged Navier-Stokes (RANS) or Large Eddy Simulation (LES) approaches or by resolving the Kolmogorov scales (DNS of turbulence). In one-fluid models, a single set of conservation equations is solved and the interface is tracked by solving an auxiliary equation. Obviously, directly tracking interface dynamics has the advantages of avoiding empirical closure laws in the transport equations and providing a detailed description of interfacial physics. However, there is a high computational cost associated with interface tracking and an even higher cost when combined with DNS of turbulence. This cost has limited the applicability of the one-fluid approach to relatively small scale investigations.

In chemical separation processes, CFD analysis is particularly promising for the improvement of vapour-liquid and gas-liquid contacting systems. CFD has recently been used in many studies to investigate fluid behaviour as well as heat and mass transfer during flow over structured packing, with the intention of developing more efficient vapour-liquid and gas-liquid contacting devices. A diverse set of multiphase models was used in these studies.

Liu et al. [1] employed a pseudo-single-liquid phase model to study mass transfer in a commercial scale packed distillation column. Their model, which aimed to represent the two-phase flow through single-phase flow equations with appropriate auxiliary source terms, provided good global correlation with experimental data. Raynal et al. [2] studied liquid holdup and pressure drop in structured packing. Their method consisted of three-dimensional single-phase flow simulations to determine dry pressure drop, two-dimensional interface tracking simulations using the Volume-Of-Fluid (VOF) method and finally, the combination of the resulting data to estimate pressure drop through the packing. Klöcker et al. [3] and Egorov et al. [4] used a combination of CFD and rate-based simulations to investigate reactive separation processes. The CFD simulations were used as virtual experiments to derive hydrodynamic and mass transfer correlations.

Yuan et al. [5] applied a two-fluid model to analyze flow in a packed column with novel structured internals. Empirical models were employed to account for interfacial drag. Iliuta et al. [6,7] used two-zone, two-fluid, one dimensional models to investigate flow behaviour in columns containing random and structured packing. The slit model was used to derive closure terms for the conservation equations. Yin et al. [8] used a two-fluid model to investigate mass transfer in a randomly packed distillation column. Energy transport was not included in the model, thus, neglecting the coupling between interphase heat and mass transfer. Empirical relationships were employed for interfacial drag, area and the interphase mass transfer coefficients. Haghshenas et al. [9] applied a similar model to study hydrodynamic behaviour and mass transfer in structured packing. Khosravi Nikou et al. [10] used a two-fluid model to study hydrodynamics, heat and mass transfer in structured packing. Again, empirical relationships were utilized for interfacial drag, area and the interphase heat and mass transfer coefficients.

One-fluid models, specifically the VOF model, have also received considerable attention in the analysis of structured packing. Szulczewska et al. [11] employed a two-dimensional VOF model to study countercurrent gas-liquid flow on a flat and a corrugated plate, with the corrugated plate representing a typical structured packing. Using a similar model, Gu et al. [12] studied countercurrent gas-liquid flow on flat and corrugated inclined plates. Valluri et al. [13] also studied film flow over a corrugated surface and compared the CFD results with experimental data. Hoffmann et al. [14] and Xu et al. [15] used a three-dimensional VOF model to investigate countercurrent gas-liquid flow over an inclined plate. Similarly, Ataki and Bart [16] carried out three-dimensional simulations of gas-liquid flow over a single structured packing element. With the intention of improving hydrodynamic performance, Luo et al. [17] used three-dimensional VOF simulations to study the impact of channel opening angle on structured packing efficiency. It should be noted that, due to the relatively high computational cost, these studies have been limited to relatively simple geometries. Further, these studies have only focused on fluid dynamics, neglecting interphase heat and mass transfer effects. A notable exception is the study of Chen et al. [18]. Although the study of Chen et al. neglects heat transfer, empirical models for interphase mass transfer are coupled with a three-dimensional VOF model to investigate mass transfer efficiency in a representative unit of structured packing. In another recent study, Haroun et al. [19] used a VOF model for direct simulation of reactive

absorption. Heat effects were not included in this investigation but mass transfer efficiency was successfully predicted without the need for empirical expressions.

From the above discussion, it is clear that most CFD studies of gas-liquid and vapour-liquid contacting have focused exclusively on fluid dynamic behaviour. In cases where mass and/or heat transfer have been considered, empirical models were usually employed to predict interphase transport. When multi-fluid models are applied, the use of auxiliary relationships in terms of closure laws is compulsory. However, in one-fluid models, interface dynamics are an integral part of the solution. Thus, when combined with energy and species conservation equations and appropriate interface jump conditions, it is possible to resolve interface heat and mass transfer efficiencies without the need for empiricism. That is, instead of resorting to empirical relationships to predict heat and mass transfer coefficients, direct simulation of interphase heat and mass transfer is carried out and these coefficients become an integral part of the solution.

Direct simulation of interphase heat and mass transfer is not a new concept. In fact, many studies have focused on the simultaneous heat and mass transfer occurring during a variety of phase change processes. These processes inherently involve flows where a free-surface exists between these two phases. Further, they are characterized by coupled interfacial heat and mass transfer. Despite previous research efforts, the accurate description of simultaneous interfacial heat and mass transfer in two-phase flows having a free-surface remains a very challenging problem. This challenge is directly linked to the complex coupled phenomena taking place at the interface.

The interface present in free-surface flows is inherently dynamic with potentially complex topologies. The dynamic and arbitrary nature of these interfaces makes their study particularly challenging. Various techniques have been used to model free-surface flows. Generally, formulations based on fixed or moving grids are possible. Moving grid methods may be purely Lagrangian (i.e. the grid moves with the fluids) or more commonly, a combination of Eulerian and Lagrangian methods (these are often referred to as Arbitrary Eulerian-Lagrangian or ALE methods). The main advantage of these methods is that the grid is usually aligned with the interface in such a way that it is directly resolved and the application of boundary conditions is relatively simple (see, for example [38-40]). Fixed grid formulations may be purely Eulerian or a Lagrangian framework may be used to track the location of the interface. For fixed grids, the

most commonly employed approaches include the Volume-Of-Fluid (VOF), Front Tracking (FT), Level Set (LS) and Phase Field (PF) methods [41]. Each of these approaches has its own advantages and disadvantages and most have been comprehensively reviewed [41-48]. Numerous extensions to these methods have also been proposed to include interfacial heat and mass transfer effects.

Juric and Tryggvason [20] developed a two-dimensional Front Tracking model with phase change. This model was then applied to study film boiling, showing good agreement with experimental results.

The Level Set method has received considerable attention for simulation of phase change processes. Gibou et al. [21] coupled a Ghost Fluid technique, to impose the interface jump conditions, with the Level Set method. This method was then validated for two-dimensional film boiling. A similar coupled Ghost Fluid and Level Set method was proposed by Tanguy et al. [22], except that their method also implemented a species jump condition. Their method was evaluated based on the evaporation of water droplets in air. Son and Dhir [24] have also developed a two-dimensional axisymmetric Level Set simulation of film boiling. Luo et al. [23] used a Level Set method to study two- and three-dimensional film boiling. Yang and Mao [25] as well as Wang et al. [26] used a Level Set method to study interfacial mass transfer. Heat transfer effects were neglected in these studies.

The Volume-Of-Fluid method originally developed by Hirt and Nichols [49] has been the most widely used approach to simulate free-surface flows. Consequently, it has also received a considerable amount of attention in the study of phase change phenomena. Welch and Wilson [27] developed a VOF method with phase change and applied it to simulate two-dimensional film boiling. Wohak and Beer [28] used a VOF simulation based on heat transfer to predict liquid evaporation rates. Davidson and Rudman [29] presented a VOF based method for the calculation of heat and mass transfer across arbitrary interfaces. Harvie and Fletcher [30,31] developed a model for the simulation of droplets impacting on hot surfaces. Simulations of droplet impacts were shown to correlate well with experimental results. The evaporation of droplets on hot surfaces was also studied using VOF methodology by Nikolopoulos et al. [32] and Strotos et al. [33]. Both of these studies used a VOF method with adaptive mesh refinement in the vicinity of the interface to improve numerical accuracy and computational efficiency. However, the study by Nikolopoulos et al. [32] used a kinetic theory approximation to estimate

the evaporation rate while the study by Strotos et al. [33] employed a simplified form of Fick's law.

Evaporation of methanol as well as ethanol/isooctane mixtures in an inclined channel has been studied by Banerjee [34,36] within a VOF framework. In both cases, the evaporation rate was calculated based on a simplified form of Fick's law. Similarly, Banerjee and Isaac [35] studied the evaporation of gasoline in an inclined channel using a VOF formulation. Schlottke and Weigand [37] employed a VOF method to simulate simultaneous heat and mass transfer during droplet evaporation in three dimensions. In this study, evaporation rates were calculated based on Fick's law. Good agreement was observed between numerical results and empirical correlations.

Based on the preceding discussion, it is clear that CFD analysis has tremendous potential to aid in the design and improvement of vapour-liquid and gas-liquid contacting equipment. Multi-fluid models are currently the only viable alternative for simulating large scale systems. However, suitable closure laws are required for accurate simulation. One-fluid models may be used for direct simulation of interface dynamics as well as heat and mass transfer but their range of applicability is limited by computational cost. A reasonable approach would be to apply direct simulation to cases where computational costs are not too high. Further, direct simulation can be applied to simplified or representative geometries to derive closure laws for multi-fluid models. This second application is akin to carrying out direct numerical simulation of turbulence to develop closure laws.

Although there are clearly alternative options, the VOF model provides a convenient basis for the simulation of free-surface flows with interphase heat and mass transfer. Further, vapour-liquid contacting in systems with multiple chemical species has many important industrial applications. Thus, the present study proposes a mathematical formulation for simultaneous interfacial multicomponent heat and mass transfer within a VOF framework for free-surface vapour-liquid flow. The formulation incorporates the full material and energy interface jump conditions and is therefore applicable to systems with multiple condensable chemical species. Detailed descriptions are provided for the incorporation of the interface jump conditions for heat and mass transfer into the VOF formulation. The partial differential equations are solved using a Finite Volume Methodology (FVM) and simulation results are presented for vapour-liquid contacting in a narrow two-dimensional channel for the ethanol-water system.

Although the results are presented for the ethanol-water system in two dimensions, the mathematical formulation is easily extensible to three dimensions and systems with more than two chemical species.

10.2. Mathematical Formalism

10.2.1. Volume-Of-Fluid (VOF) interface tracking

The current study uses VOF methodology to investigate coupled interfacial multicomponent heat and mass transfer in free-surface vapour-liquid flow. The details surrounding the VOF method have been reviewed by several authors [41-46]. Thus, only a general description of pertinent aspects is presented in this section.

The VOF formulation for two-phase flow does not explicitly track the interface. Instead, a conservation equation is solved for the volume fraction of one of the phases. The conservation equation, written for the liquid phase in a vapour-liquid system is,

$$\frac{\partial}{\partial t}(\alpha_L \rho_L) + \nabla \cdot (\alpha_L \rho_L \vec{u}) = S_L \quad (1)$$

where α_L is the volume fraction of the liquid phase and S_L is any mass source for the liquid phase. The liquid volume fraction is defined such that a computational cell is filled with liquid when α_L is unity, filled with vapour when α_L is zero and partially filled with liquid when α_L is between zero and one. In a vapour-liquid system only one volume fraction equation must be solved since the volume fraction of the vapour is simply calculated as $1 - \alpha_L$.

Clearly, solution of the volume fraction conservation equation only provides a diffuse approximation of the interface location. To estimate the actual location of the interface within a computational cell, the interface must be captured or reconstructed. One of the most widely used approaches for interface reconstruction, known as Piecewise Linear Interface Calculation (PLIC), assumes a piecewise linear interface. It is further assumed that the interface is normal to the gradient of the volume fraction. In this study, a method similar to that presented by Gueyffier et al. [50] and Rider and Kothe [44] is used to reconstruct the PLIC interface. Accurate interface reconstruction is vital to solution accuracy, since the reconstructed interface is used to calculate fluid propagation through the solution domain and establishes the interfacial area available for heat and mass transfer.

10.2.2. Momentum equations

In accordance with the one-fluid formulation of interfacial flow, a single set of momentum equations can be written to describe momentum transport in both phases.

$$\frac{\partial}{\partial t}(\rho \vec{u}) + \nabla \cdot (\rho \vec{u} \vec{u}) = -\nabla p + \nabla \cdot \mu (\nabla \vec{u} + (\nabla \vec{u})^T) + \rho \vec{g} + \vec{F} \quad (2)$$

where $\vec{u}$ represents the shared velocity field, p is the pressure and $\rho \vec{g}$ is the gravitational force. The density and viscosity are volume averaged according to, $\rho = \alpha_L \rho_L + (1 - \alpha_L) \rho_V$ and $\mu = \alpha_L \mu_L + (1 - \alpha_L) \mu_V$. $\vec{F}$ can include any other volumetric forces. In this case, $\vec{F}$ includes forces due to surface tension. Employing the Continuum Surface Force (CSF) model proposed by Brackbill et al. [51], the surface tension force can be expressed in the following way.

$$\vec{F} = \sigma \frac{\rho \kappa \nabla \alpha_L}{0.5(\rho_L + \rho_V)} \quad (3)$$

where σ , ρ , ρ_L , ρ_V and κ are the surface tension, mixture density, liquid density, vapour density and curvature, respectively. The curvature is determined from the unit normal vector according to $\kappa = \nabla \cdot \vec{n}$, where the unit normal vector is $\vec{n} = \frac{\nabla \alpha_L}{|\nabla \alpha_L|}$ (which points from the vapour to the liquid phase). In the presence of solid boundaries, the unit normal vector near the boundary is adjusted using the contact angle (θ). In this case, the unit normal vector in cells adjacent to the wall is $\vec{n} = \vec{n}_w \cos \theta + \vec{t}_w \sin \theta$, where $\vec{n}_w$ and $\vec{t}_w$ are unit vectors normal and tangential to the wall, respectively.

10.2.3. Energy equation

The one-fluid form of the energy equation, neglecting pressure and viscous dissipation, can be written in enthalpy form as,

$$\frac{\partial}{\partial t}(\rho h) + \nabla \cdot (\rho h \vec{u}) = \nabla \cdot (k \nabla T - \sum h_i \vec{j}_i) + S_E \quad (4a)$$

where h is the mass-averaged enthalpy,

$$h = \frac{\alpha_L \rho_L h_L + (1 - \alpha_L) \rho_V h_V}{\alpha_L \rho_L + (1 - \alpha_L) \rho_V} \quad (4b)$$

and T is the shared temperature field. The thermal conductivity is volume averaged according to $k = \alpha_L k_L + (1 - \alpha_L) k_V$. The enthalpy depends on the temperature, species mass fractions and heat capacity according to (for a system with C chemical species),

$$h_L = \sum_{i=1}^C \omega_{i,L} h_{i,L} \quad \text{and} \quad h_{i,L} = \int_{T_0}^T c_{p,i,L} dT \quad (5a)$$

$$h_V = \sum_{i=1}^C \omega_{i,V} h_{i,V} \quad \text{and} \quad h_{i,V} = \int_{T_0}^T c_{p,i,V} dT \quad (5b)$$

The second term on the right side of the energy balance, $\nabla \cdot (-\sum h_i \vec{j}_i)$, accounts for energy transfer due to species diffusion. The source term, S_E , accounts for any heat transfer related to the movement of mass across the interface (i.e. phase change). Details surrounding the calculation of this source term are presented in subsequent sections.

10.2.4. Species equations

In this study, a phase-averaged form of the species equations was employed. Thus, in a system with C chemical components, it is necessary to solve $C-1$ species equations for each phase. The phase-averaged species equation, written for an arbitrary phase q , is,

$$\frac{\partial}{\partial t} (\alpha_q \rho_q \omega_{i,q}) + \nabla \cdot (\alpha_q \rho_q \vec{u} \omega_{i,q}) = -\nabla \cdot \alpha_q \vec{j}_{i,q} + \alpha_q S_{i,q} \quad (6)$$

where $\omega_{i,q}$ is the mass fraction of component i in phase q , $S_{i,q}$ is the source of species i in phase q due to interfacial mass transfer and $\vec{j}_{i,q}$ is the diffusion flux of component i in phase q . Assuming that Fick's law applies (i.e. a binary or a dilute system) and neglecting the effect of thermal diffusion (Soret effect), the diffusion flux can be written as,

$$\vec{j}_{i,q} = -\rho_q D_{iM,q} \nabla \omega_{i,q} \quad (7)$$

where $D_{iM,q}$ is the diffusion coefficient of species i in the mixture of phase q . For a binary vapour-liquid system, one species equation must be solved in each phase. These two equations, written for component 1, are,

$$\frac{\partial}{\partial t} (\alpha_L \rho_L \omega_{1,L}) + \nabla \cdot (\alpha_L \rho_L \vec{u} \omega_{1,L}) = \nabla \cdot (\alpha_L \rho_L D_{12,L} \nabla \omega_{1,L}) + \alpha_L S_{1,L} \quad (8a)$$

$$\frac{\partial}{\partial t} (\alpha_V \rho_V \omega_{1,V}) + \nabla \cdot (\alpha_V \rho_V \vec{u} \omega_{1,V}) = \nabla \cdot (\alpha_V \rho_V D_{12,V} \nabla \omega_{1,V}) + \alpha_V S_{1,V} \quad (8b)$$

From these expressions, it is clear that although component 1 in the vapour phase is the same chemical species as component 1 in the liquid phase, no innate coupling between these two components is included in these equations. Coupling is achieved by incorporating suitable interface jump conditions, in the form of volumetric source terms, into the solution of the species and energy equations. The interface jump conditions and their transformations into volumetric sources are described in the following sections.

10.2.5. Interface jump conditions

In general, coupling between interphase heat and mass transfer is very strong in vapour-liquid systems. Thus, it is best to implement a model able to handle the general case of tightly coupled interphase heat and mass transfer. To this end, it is necessary to include appropriate jump conditions to ensure conservation of mass and energy across the interface. In general, the energy and species jump conditions can be written as (where $C-1$ species jump conditions exist for each phase),

$$\sum_{i=1}^C \Delta H_{vap,i} \dot{m}_i - (k_V \nabla T_V - k_L \nabla T_L) \cdot \vec{n} = 0 \quad (9a)$$

$$\dot{m}_i + \vec{j}_{i,L} \cdot \vec{n} - \omega_{i,L}^I \sum_{i=1}^C \dot{m}_i = 0 \quad (9b)$$

$$\dot{m}_i + \vec{j}_{i,V} \cdot \vec{n} - \omega_{i,V}^I \sum_{i=1}^C \dot{m}_i = 0 \quad (9c)$$

Thus, it is apparent that the interfacial heat flux depends on the interfacial mass flux and vice versa. It is important to note that the energy jump condition neglects viscous terms, kinetic energy changes as well as energy contributions resulting from non-ideal mixing of chemical species. $\Delta H_{vap,i}$ is the latent heat of vaporization of component i , $\dot{m}_i$ is defined as the mass flux of species i from the vapour to the liquid phase (i.e. $\dot{m}_i$ is positive when species i is condensing and negative when species i is evaporating), $\omega_{i,L}^I$ is the mass fraction adjacent to the interface of species i in the liquid phase and $\omega_{i,V}^I$ is the mass fraction adjacent to the interface of species i in the vapour phase. For a binary vapour-liquid system, the jump conditions can be simplified to take the following form.

$$\dot{m}_1 + \frac{\Delta H_{vap,2} \dot{m}_2}{\Delta H_{vap,1}} - \frac{(k_V \nabla T_V - k_L \nabla T_L) \cdot \vec{n}}{\Delta H_{vap,1}} = 0 \quad (10a)$$

$$\dot{m}_1 + \rho_L D_{12,L} \nabla \omega_{1,L} \cdot \vec{n} - \omega_{1,L}^I (\dot{m}_1 + \dot{m}_2) = 0 \quad (10b)$$

$$\dot{m}_1 + \rho_V D_{12,V} \nabla \omega_{1,V} \cdot \vec{n} - \omega_{1,V}^I (\dot{m}_1 + \dot{m}_2) = 0 \quad (10c)$$

These expressions provide a suitable basis for simulations involving simultaneous interfacial heat and mass transfer. However, incorporation of these conditions into the previously described conservation equations requires transformation into volumetric energy, species and mass source terms, which must be included in interfacial cells. Numerical details surrounding this transformation are provided in a subsequent section.

10.2.6. Supplementary interface conditions

The interface jump conditions described in the previous sections are not sufficient to close the coupled heat and mass transfer problem. This results from the fact that in addition to the shared temperature field and species mass fraction fields in the vapour and liquid phases, it is possible to specify an interfacial temperature as well as interfacial species mass fractions in each phase. This implies that there are a further $2(C-1)$ (two phases and C chemical species in each phase with the sum of the mass fractions in each phase summing to unity) unknown mass fractions and one unknown interface temperature. To close the problem, it is possible to assume that vapour-liquid equilibrium (VLE) conditions exist, under the system pressure, at the interface. Vapour-liquid equilibrium exists when the temperature, pressure and chemical potential of each species are identical in all phases [52]. However, the chemical potential does not provide a convenient means for correlation of vapour-liquid equilibrium data. Instead, it is more convenient to express the equilibrium condition by defining a K-value according to vapour and liquid phase fugacity coefficients.

$$K_i = \frac{y_i}{x_i} = \frac{\bar{\phi}_{i,L}}{\bar{\phi}_{i,V}} \quad (11)$$

where y_i and x_i are the vapour and liquid phase mole fractions of species i , respectively. $\bar{\phi}_{i,L}$ and $\bar{\phi}_{i,V}$ are the liquid phase and vapour phase fugacity coefficients. In general, the liquid phase fugacity coefficient is given by,

$$\bar{\phi}_{i,L} = \frac{\gamma_i}{p} p_i^{sat} \phi_i^{sat} \exp \left(- \frac{V_{i,L} (p - p_i^{sat})}{RT} \right) \quad (12)$$

where the exponential term is commonly referred to as the Poynting factor. At relatively low pressures (i.e. when the ideal gas law is applicable), the Poynting factor and ϕ_i^{sat} approach unity. Further, $\bar{\phi}_{i,V}$ can be calculated using a variety of Equations of State; however, at low pressures it is approximately equal to unity. Thus, as was done in this study (since all simulations were carried out at the standard pressure of 101325 Pa), it is often possible to calculate the K-value using,

$$K_i = \frac{\gamma_i p_i^{sat}}{p} \quad (13)$$

where γ_i is the experimentally correlated activity coefficient and p_i^{sat} is the saturation vapour pressure. Together with the conservation equations and interface jump conditions, the VLE relations provide all the information required to solve the coupled heat and mass transfer problem.

10.3. Numerical Details

10.3.1. Enforcement of the interface conditions

As previously discussed, it is necessary to impose appropriate interface jump and thermodynamic conditions to describe simultaneous interfacial heat and mass transfer. This section provides details surrounding the incorporation of the interface jump and thermodynamic conditions into the numerical model. The previously described transport equations were discretized using Finite Volume Methodology on structured two-dimensional Cartesian grids. The vapour-liquid interface was reconstructed using a PLIC algorithm [44,50]. The temperature and mass fraction gradients in the interface jump conditions depend not only on the cell values but also on the interface conditions. Thus, these gradients should be calculated based on the interface values and interface location, based on PLIC reconstruction. Further, the interface temperature and mass fractions are restricted by the VLE condition. It is apparent that the interface jump conditions and thermodynamic relations represent a set of $3C+1$ coupled nonlinear equations that must be solved simultaneously for the unknowns. The following discussion describes this set of equations and focuses on their solution. To facilitate the discussion, the arbitrary PLIC interface location shown in Figure 10.1 is used as a reference.

Given the reconstructed interface shown in Figure 10.1, it is possible to discretize the species jump conditions for a binary system in the following way.

$$F_1 = \dot{m}_1 - \omega_{1,V}^I (\dot{m}_1 + \dot{m}_2) + \rho_V D_{12,V} \left[\left(\frac{\omega_{1,V}|_{i+1,j} - \omega_{1,V}^I}{x_{i+1,j} - x_A} \right) n_x + \left(\frac{\omega_{1,V}|_{i,j-1} - \omega_{1,V}^I}{y_{i,j-1} - y_B} \right) n_y \right] = 0 \quad (14)$$

$$F_2 = \dot{m}_1 - \omega_{1,L}^I (\dot{m}_1 + \dot{m}_2) + \rho_L D_{12,L} \left[\left(\frac{\omega_{1,L}|_{i-1,j} - \omega_{1,L}^I}{x_{i-1,j} - x_A} \right) n_x + \left(\frac{\omega_{1,L}|_{i,j+1} - \omega_{1,L}^I}{y_{i,j+1} - y_B} \right) n_y \right] = 0 \quad (15)$$

The one-fluid approximation for the conductive heat flux across the interface is,

$$(k_V \nabla T_V - k_L \nabla T_L) \cdot \vec{n} \approx k \nabla T \cdot \vec{n} \quad (16)$$

Thus, the energy jump condition becomes,

$$F_3 = \dot{m}_1 + \frac{\Delta H_{vap,2} \dot{m}_2}{\Delta H_{vap,1}} - \frac{k}{\Delta H_{vap,1}} \left[\left(\frac{T_{i+1,j} - T_{i-1,j}}{2\Delta x_{i,j}} \right) n_x + \left(\frac{T_{i,j+1} - T_{i,j-1}}{2\Delta y_{i,j}} \right) n_y \right] = 0 \quad (17)$$

As pointed out earlier, the unit normal vector is arbitrarily chosen to point from the vapour to the liquid phase and the mass fluxes ($\dot{m}_i$) are positive when mass is transferred from the vapour to the liquid phase. The thermodynamic relations can be written in the following way (note that in general the K-values depend on temperature, pressure and species mole fractions).

$$F_4 = x_1^I K_1 - y_1^I = \left(\frac{\omega_{1,L}^I / M_1}{\omega_{1,L}^I / M_1 + \omega_{2,L}^I / M_2} \right) K_1 - \left(\frac{\omega_{1,V}^I / M_1}{\omega_{1,V}^I / M_1 + \omega_{2,V}^I / M_2} \right) = 0 \quad (18)$$

$$F_5 = x_2^I K_2 - y_2^I = \left(\frac{\omega_{2,L}^I / M_2}{\omega_{1,L}^I / M_1 + \omega_{2,L}^I / M_2} \right) K_2 - \left(\frac{\omega_{2,V}^I / M_2}{\omega_{1,V}^I / M_1 + \omega_{2,V}^I / M_2} \right) = 0 \quad (19)$$

$$F_6 = \omega_{1,V}^I + \omega_{2,V}^I - 1 = 0 \quad (20)$$

$$F_7 = \omega_{1,L}^I + \omega_{2,L}^I - 1 = 0 \quad (21)$$

For a binary system, the interface jump conditions and thermodynamic relations comprise a system of 7 coupled nonlinear equations (F_1 to F_7) that must be solved to determine the following vector of unknowns.

$$X = (\dot{m}_1, \dot{m}_2, \omega_{1,L}^I, \omega_{2,L}^I, \omega_{1,V}^I, \omega_{2,V}^I, T^I) \quad (22)$$

In the present study, Newton's method was employed to converge on the solution iteratively.

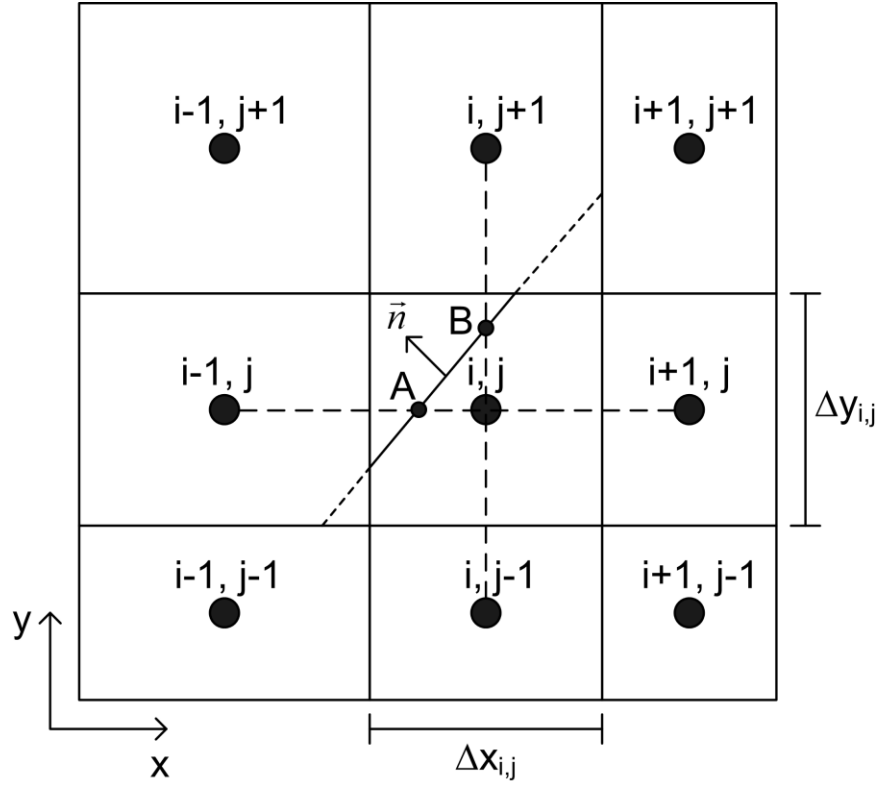


Figure 10.1. Arbitrary PLIC interface on a structured Cartesian grid.

Once the species mass fluxes crossing the interface have been determined it is necessary to include appropriate volumetric sources in the conservation equations. The volumetric sources are calculated in the following way.

10.3.1.1. Volumetric species sources

In a binary system, species equations are solved in each phase for component 1. The volumetric sources for component 1 are,

$$S_{1,L} = \dot{m}_1 \frac{A}{V\alpha_L} \quad (23a)$$

$$S_{1,V} = -\dot{m}_1 \frac{A}{V\alpha_v} \quad (23b)$$

where V is the volume of the interfacial cell and A is the interfacial area as calculated from the PLIC interface. It is important to determine the interfacial area from the PLIC interface instead of using the often employed global relationship $\frac{A}{V} = |\nabla \alpha_L|$. The global relationship does not

accurately represent the interfacial area locally and therefore yields incorrect estimates of interface heat and mass sources.

10.3.1.2. Volumetric energy source

The energy source is calculated from the species mass fluxes and latent heats according to,

$$S_E = (\Delta H_{vap,1} \dot{m}_1 + \Delta H_{vap,2} \dot{m}_2) \frac{A}{V} \quad (24)$$

10.3.1.3. Volumetric mass sources

The total mass sources in each phase are related to the species mass fluxes according to,

$$S_L = (\dot{m}_1 + \dot{m}_2) \frac{A}{V} \quad (25a)$$

$$S_V = -(\dot{m}_1 + \dot{m}_2) \frac{A}{V} \quad (25b)$$

10.3.2. Physical properties

Temperature and composition dependent properties for the ethanol-water system were used in the simulations. The liquid phase viscosity, thermal conductivity and diffusion coefficient were calculated using the Neural Network models developed by Haelssig et al. [53]. The vapour phase viscosity, thermal conductivity and diffusion coefficient were calculated using the Reichenberg, Wassiljewa and Fuller methods, respectively [54]. The heat capacities in the vapour and liquid phase were calculated from polynomial relationships [56]. The latent heat of vaporization was calculated from the expressions provided in [55]. The vapour pressure was determined from an extended Antoine equation [55]. The Wilson model was used to estimate the activity coefficients for the ethanol-water system [57]. The liquid phase densities of ethanol and water were assumed to be constant at 735 kg/m³ and 950 kg/m³, respectively, with ideal mixing. The ideal gas law was applied to estimate the vapour phase density. Further, the surface tension and contact angle were assumed to be constant at 0.05 N/m and 30 degrees, respectively.

10.3.3. Solution methodology

The transient conservation equations were solved according to FVM using the CFD code FLUENT 6.3.26 [58]. FLUENT includes a VOF model with PLIC reconstruction and it is also capable of solving the presented energy and species equations. Further, it includes the volumetric

surface tension force. The FLUENT PLIC variables are not all accessible and thus, an external PLIC algorithm was implemented to approximate the interfacial area and interface location. The interface jump conditions were discretized using the PLIC interface, combined with the thermodynamic relations to form a system of nonlinear equations and solved for the relevant unknowns, in accordance with the algorithm presented earlier. Once calculated, the source terms, along with the temperature and composition dependent properties, were incorporated into the CFD code using User Defined Functions (UDF). Pressure-velocity coupling was achieved using the Pressure-Implicit with Splitting Operators (PISO) scheme. Spatial discretization of the continuity and volume fraction equations was carried out using the Pressure Staggering Option (PRESTO!) and the Geo-Reconstruct algorithm, respectively. The momentum, energy and species equations were discretized using a Second-Order Upwind Scheme. Explicit temporal discretization was employed. Since an explicit approach was used for time integration, the Courant-Friedrichs-Levy (CFL) condition must be obeyed to ensure solution stability. In the current study, adaptive time stepping was employed, with the time step being adjusted to maintain a CFL number ($\frac{u_{\max} \cdot \Delta t}{\Delta x}$) of 0.25.

10.4. Results and Discussion

Two validation cases are now presented to confirm the current model's ability to predict mass transfer performance during vapour-liquid contacting. The focus is on mass transfer performance since this is the primary objective for vapour-liquid contacting devices.

10.4.1. Case 1: Countercurrent wetted-wall contacting

Wetted-wall columns are used extensively to study heat and mass transfer during vapour-liquid contacting. Data from these systems are usually relatively easy to interpret due to the simple geometry. Generally, experimental results from wetted-wall studies are correlated using empirical relationships. In this study, wetted-wall contacting simulations were carried out for a short two-dimensional channel and compared to several empirical correlations and some literature data.

10.4.1.1. Geometry

The simple geometry used to carry out wetted-wall contacting simulations is shown in Figure 10.2. The geometry consists of a two-dimensional channel having a width of 6 mm and a

length of 30 mm. Since the channel is symmetrical, a solution of only half of the domain was required. Liquid was introduced at the top of the channel at a constant velocity, temperature and composition and flowed downward along an impermeable, adiabatic wall through the action of gravity. The no slip boundary condition was used for the velocity at the wall. The liquid temperature was adjusted to be close to but slightly below the bubble point temperature. Vapour was introduced at the bottom of the channel and flowed countercurrent to the liquid, exiting at the top of the channel. The vapour entered with a constant temperature and composition, with the temperature being adjusted to be slightly above the dew point temperature. The bubble and dew point temperatures are defined in the usual way. That is, the bubble point temperature is the temperature at which vapour bubbles begin to form when a liquid mixture with a constant composition is slowly heated at constant pressure. Conversely, the dew point temperature is the temperature at which liquid droplets begin to form when a vapour mixture with a constant composition is slowly cooled at constant pressure.

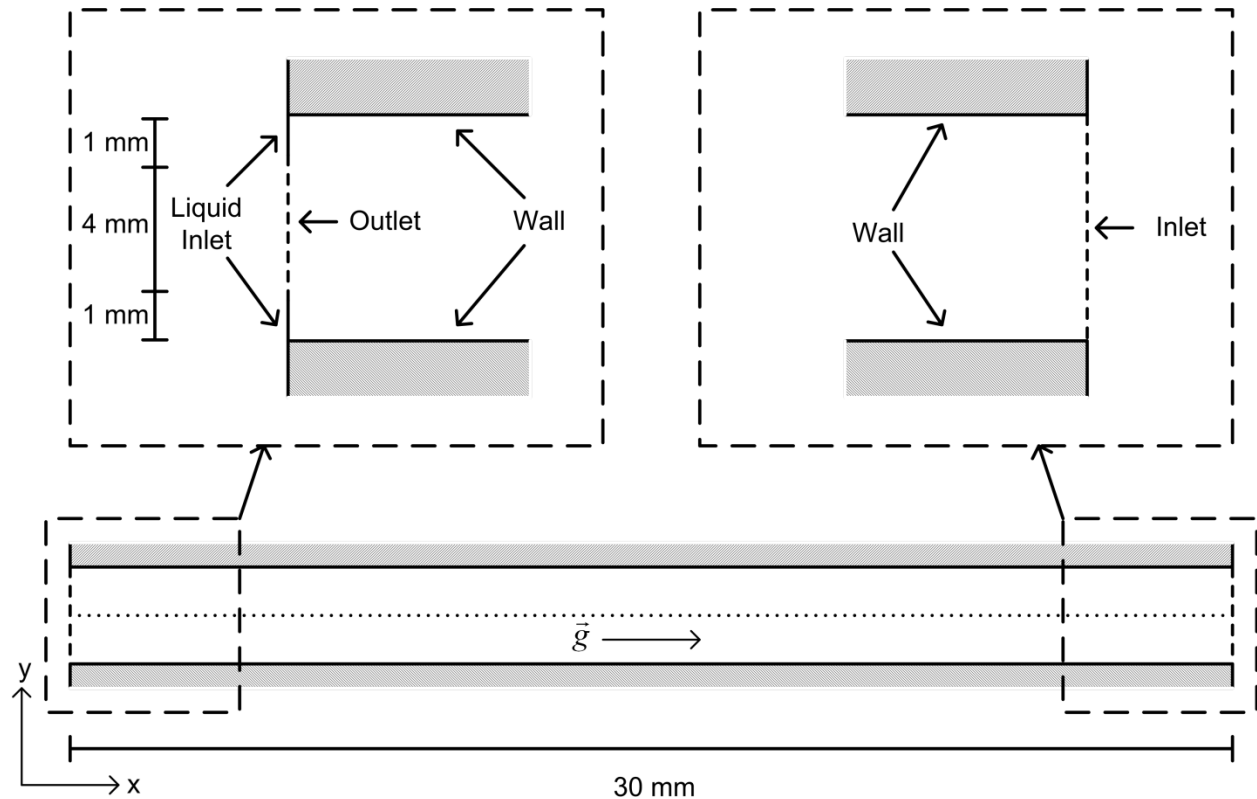


Figure 10.2. Short two-dimensional channel geometry used for wetted-wall contacting simulations (note that the gravitational direction is shown from left to right, in the positive x direction).

10.4.1.2. Computational methodology

Accurate numerical solutions to partial differential equations rely on discretization on a computational grid with sufficiently high resolution. In the current study, simulations were carried out using a structured two-dimensional Cartesian grid. Three structured computational grids were used to determine grid convergence. The three grids consisted of 40×200 , 60×300 and 90×450 cells, respectively. For one of the simulation cases, the grid consisting of 90×450 cells provided a pseudo steady-state solution in which the outlet velocity, composition and temperature profiles were less than 1 % different from the solution calculated on the 60×300 grid. Thus, the 90×450 grid was used in all simulation runs.

From the grid refinement studies, it became apparent that the highest grid resolution was required to resolve the concentration boundary layers, with a particularly high resolution required in the liquid phase. This is reasonable due to the relatively high density of the liquid phase. However, even coarse grids, in which the liquid concentration boundary layer was not adequately resolved, provided relatively good estimates of outlet composition. This indicates a relatively small mass transfer resistance in the liquid phase for the wetted-wall system, which is in agreement with the literature [59].

To compare the results with empirical correlations and literature data, steady-state values are required. In this study, transient simulations were carried out until reaching a pseudo steady-state. As mentioned earlier, adaptive time stepping was employed to obey the CFL condition. For the simulation cases investigated in this study, this condition resulted in time steps between 0.000005 and 0.00002 seconds. The pseudo steady-state was defined as the time when negligible changes were observed in the outlet velocity, composition and temperature profiles. The pseudo steady-state was typically achieved within two liquid residence times. As a result, simulations lasted for 0.1 to 1 seconds of real flow time. To speed up the simulations, they were carried out in parallel with distribution over 8 to 24 processors on a Sun Fire Cluster. The geometry shown in Figure 2 has a length of 3 cm. To reduce the impact of end effects, the middle 1 cm was used in the calculation of average mass transfer coefficients.

The initial conditions were specified in the following way. Initially, the channel was filled only with stagnant vapour near the dew point temperature with a constant composition. The initial vapour temperature and composition were equal to those defined at the vapour inlet

boundary. Starting at $t=0$, liquid and vapour were introduced into the channel according to the boundary conditions defined earlier.

10.4.1.3. Mass transfer coefficients

Some preliminary discussion on the calculation of mass transfer coefficients is required prior to comparing the numerical results with experimental data and empirical correlations. In general, mass transfer coefficients are correlated as zero-flux coefficients where, for example for the vapour phase,

$$K_{V,local} = \frac{-D_{12,V} \nabla \omega_{1,V} \cdot \vec{n}}{(\omega_{1,V}^I - \bar{\omega}_{1,V})} \quad (26)$$

where $(\omega_{1,V}^I - \bar{\omega}_{1,V})$ is the difference between the interface ethanol mass fraction and bulk ethanol mass fraction. It is apparent that the zero-flux mass transfer coefficient depends on the diffusion flux, not the overall flux. The average mass transfer coefficient can be calculated from,

$$K_V = \frac{1}{L} \int_0^L K_{V,local} dx \quad (27)$$

Analogous expressions are applicable for liquid phase mass transfer coefficients. Further, mass transfer data are often correlated based on the dimensionless Sherwood number. The vapour phase Sherwood number, as defined on the basis of the hydraulic diameter is,

$$Sh_{D_h,V} = \frac{K_V D_h}{D_{12,V}} \quad (28)$$

It is important to note that for the liquid phase, the characteristic length is the film thickness instead of the hydraulic diameter.

10.4.1.4. Fluid dynamics

For the wetted-wall contacting simulations, the liquid phase ethanol mass fractions were between 0.05 and 0.3 and vapour phase ethanol mass fractions were between 0.1 and 0.7. Further, both the liquid and vapour phase flow rates were varied to investigate the effect of flow conditions on heat and mass transfer. As a results, the ranges of the pertinent dimensionless groups were $1300 < Re_{D_h,V} < 3800$, $0.71 < Sc_V < 0.75$, $180 < Re_L < 1317$ and $150 < Sc_L < 385$. In the range of liquid flow rates studied, the falling film does not form a smooth interface. Instead, the falling film flows downward, under the influence of gravity, with surface waves building at

the interface. The shape and size of the surface waves are not only influenced by liquid flow rate but also by surface tension forces, vapour flow and heat and mass transfer.

Inclusion of the surface tension force in free-surface simulations is known to be problematic due to the occurrence of parasitic currents. Parasitic currents are high local velocities in the vicinity of the interface caused primarily by inaccuracies in evaluating the curvature term, which is used to calculate the surface tension force. Since parasitic currents can have a detrimental effect on the accuracy of a free-surface simulation, their impact on the present study merits further discussion. Although it is difficult to quantify the impact of parasitic currents in the current simulations, some general discussion is possible. To minimize the impact of parasitic currents, the curvature term has been evaluated on a regular Cartesian grid using a nine-point stencil. However, it is important to realize that the use of a Cartesian grid with a nine-point stencil will not completely eliminate parasitic currents and that these parasitic currents could lead to increased mixing in the vicinity of the interface, thereby leading to fictitiously high mass transfer rates (especially in the liquid phase). Thus, it is important to obtain some estimate of the intensity of these parasitic currents. To estimate the impact of parasitic currents on the present simulations, the maximum liquid velocity was compared to the theoretical maximum velocity of a freely falling laminar liquid film (see, for example [60]). It was determined that the maximum liquid velocity in the simulation cases was never more than 25 % higher than this theoretical maximum. Thus, the impact of parasitic currents on the present simulations is likely not very large. One likely explanation for this relatively small impact is that the current study investigates flow over a flat surface and thus curvature of the interface was never very high. Parasitic currents would probably be much more important if the present method were applied to cases with more inherent curvature (for example, heat and mass transfer in bubbles, droplets, jets, flow over wavy surfaces etc.).

Figures 10.3 and 10.4 show the shape of the vapour-liquid interface for one of the simulation cases. Also shown on these figures are the composition, temperature and velocity profiles as well as contour plots for composition and temperature. Note that the orientation of the geometry is the same as the one shown in Figure 10.2, with the gravity vector directed from left to right and only half of the symmetric geometry being shown. It is apparent that the wavy interface causes some fluid circulation, particularly in the vapour phase, and distortion of the

velocity profiles. The local mixing in the vapour phase leads to some local variation of the heat and mass transfer rates.

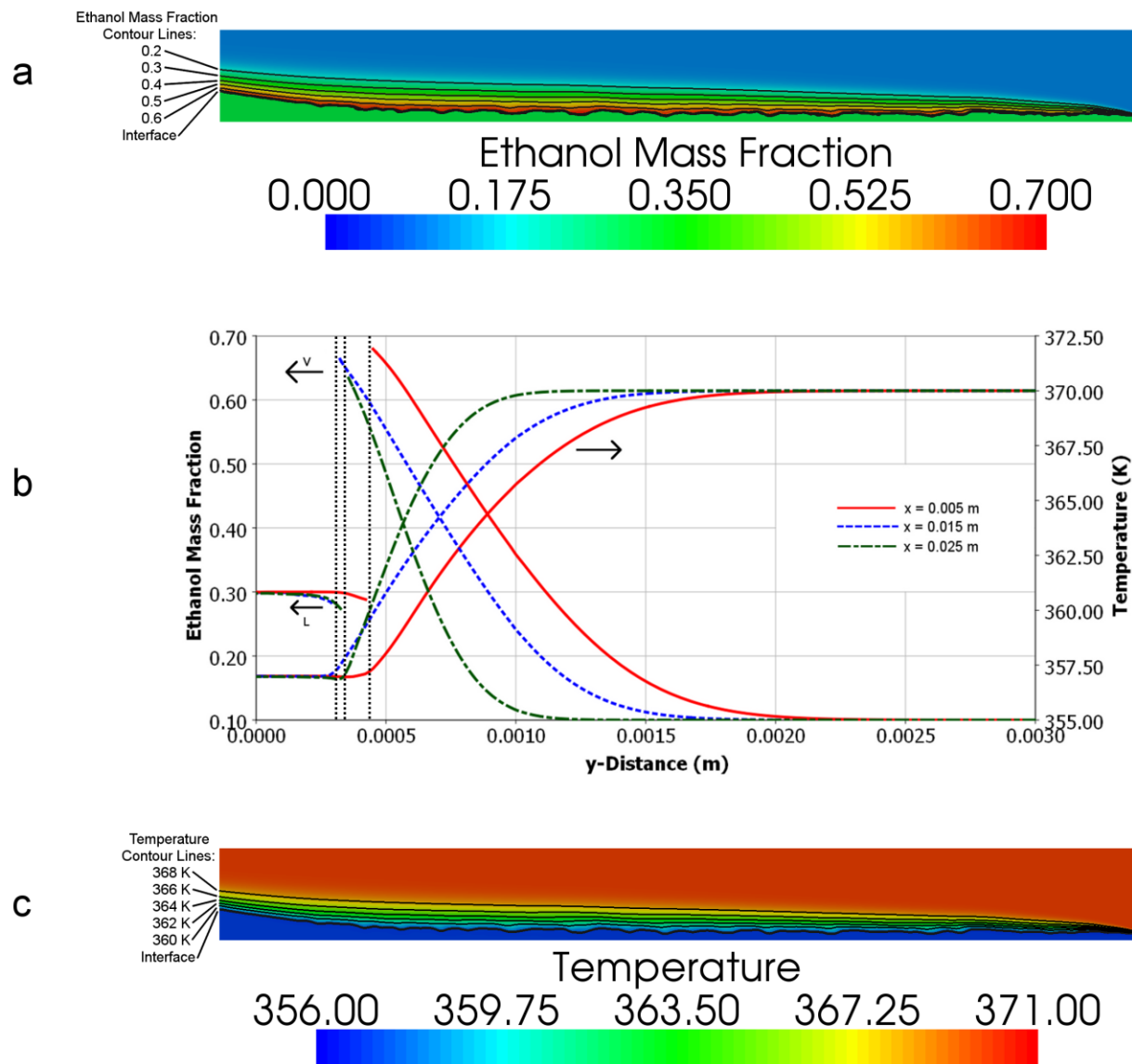


Figure 10.3. a) Contour plot for ethanol mass fraction. b) Ethanol mass fraction and temperature profiles at three distances along the length of the channel (the vertical dotted lines show the location of the interface). c) Contour plot for temperature.

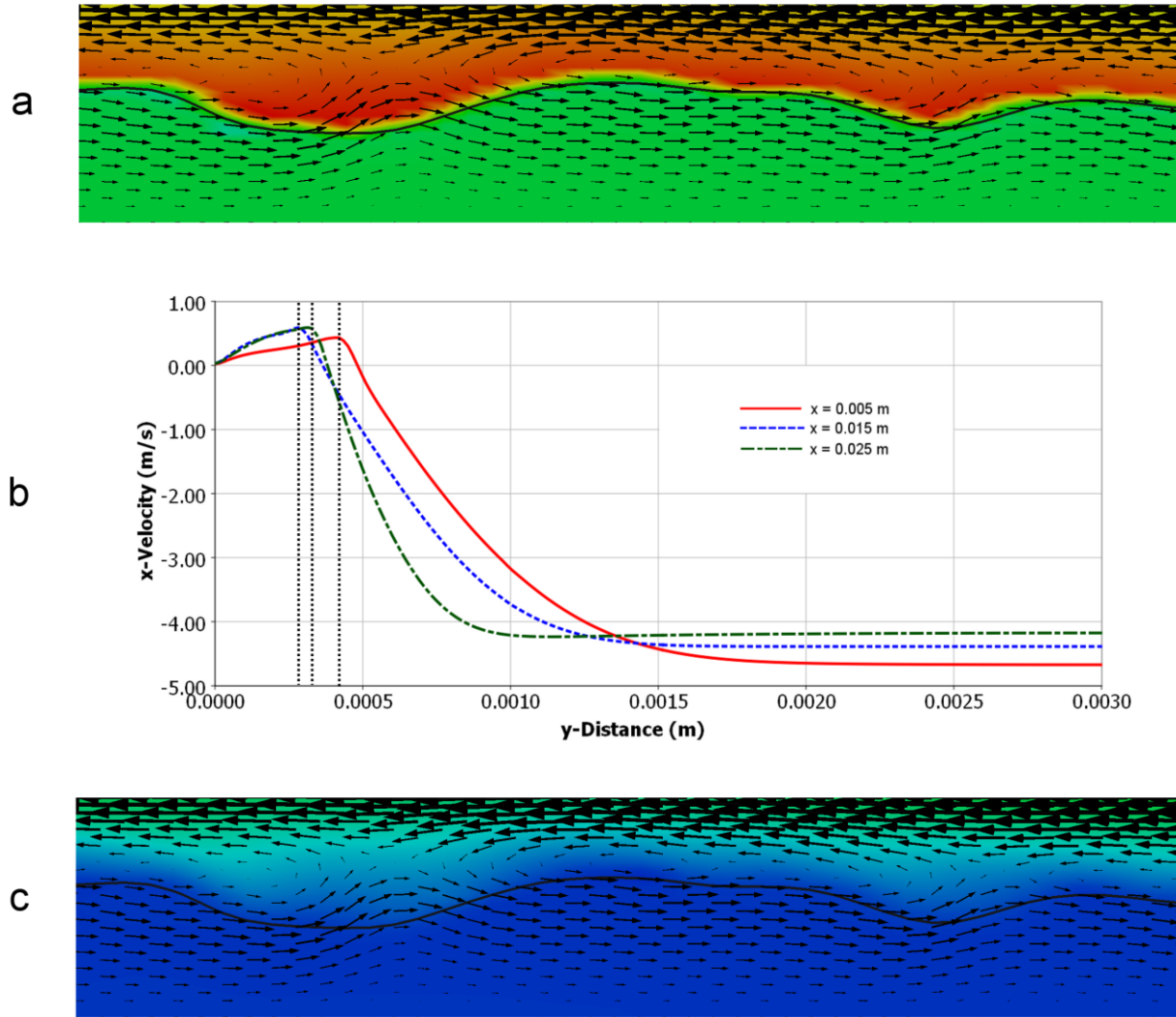


Figure 10.4. a) Magnified view of the vapour-liquid interface showing ethanol mass fraction contours and velocity vectors. b) Velocity profiles at three distances along the length of the channel (the vertical dotted lines show the location of the interface). c) Magnified view of the vapour-liquid interface showing temperature contours and velocity vectors.

As previously discussed, vapour-liquid equilibrium conditions were enforced at the interface. As expected, the existence of vapour-liquid equilibrium causes a discontinuity in the composition profile at the interface. Further, due to its higher relative volatility with respect to water, the ethanol composition profiles show minimum and maximum values at the interface in the liquid and vapour phase, respectively. Of course, this discontinuity also indicates a net movement of ethanol from the liquid to the vapour phase.

10.4.1.5. Liquid phase mass transfer

The liquid phase mass transfer coefficient can be compared to Penetration Theory for diffusion in a laminar falling film. For a smooth laminar falling film, Penetration Theory predicts the Sherwood number to be given by (see, for example [60]),

$$Sh_L = 2\delta \sqrt{\frac{u^I}{D_{12,L}\pi L}} \quad (29)$$

where u^I is the interface velocity, δ is the film thickness and L is the wall length.

It is clear that the results predicted from Penetration Theory will be different from the simulation results due to the wavy nature of the interface at higher Reynolds numbers and the impact of interaction with the vapour phase. However, the same general trend should be observed. Figure 10.5 shows the comparison of the simulation results with Penetration Theory predictions. The x-axis in Figure 10.5 is essentially a transformation of the right side of equation 29, neglecting constant values, except that the Reynolds number is expressed in terms of the average liquid velocity instead of the interface velocity. Two data sets are included in Figure 10.5. The first data set, shown on Figure 10.5 as solid diamonds, represents simulation cases in which the liquid flow rate was varied. As expected, the numerical predictions show a similar trend when compared with Penetration Theory. Further, numerical predictions for the Sherwood number are higher. This is reasonable, since surface waves increase liquid mixing and thereby the mass transfer rate. The second data set, shown on Figure 10.5 as open triangles, represents simulation cases in which vapour flow rate and composition were varied. Since Penetration Theory does not account for variation of vapour phase conditions, it is reasonable to expect that there will be very little correlation between the simulations and Penetration Theory for this data set. This lack of correlation is confirmed by the large range of deviations from Penetration Theory shown on Figure 10.5 for the second data set. The presence of this large range of deviations is directly linked to vapour-liquid interaction effects, which are not included in Penetration Theory. Specifically, in the range studied, higher vapour flow rates tended to suppress liquid surface waves, leading to closer agreement with Penetration Theory. Conversely, for similar liquid flow rates and lower vapour velocities, a larger discrepancy was observed.

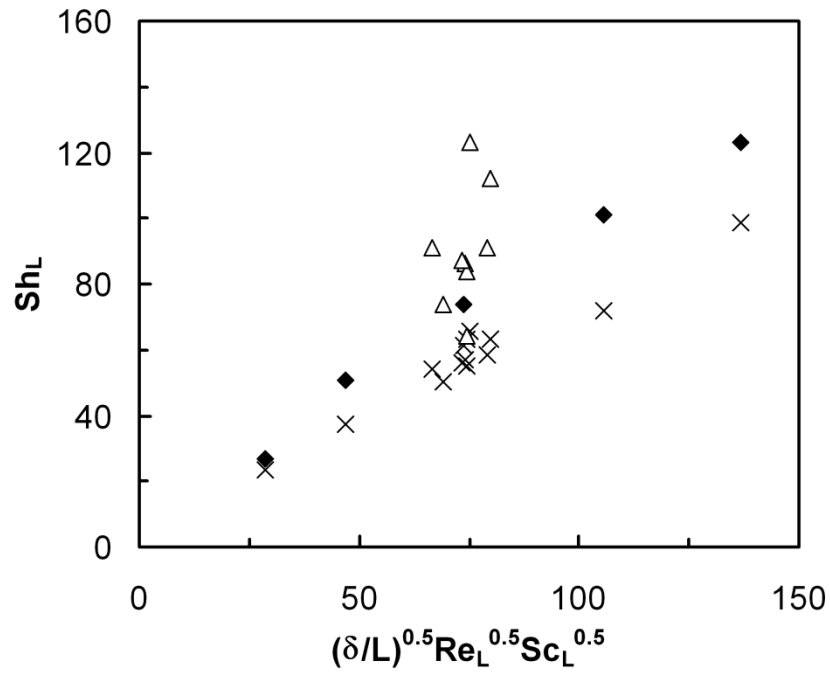


Figure 10.5. Comparison of liquid phase Sherwood number with predictions from Penetration Theory for: $\blacklozenge$, simulations with $2658 < Re_{D_h,V} < 3034$, $0.26 < \omega_{ethanol,L} < 0.3$ and $0.1 < \omega_{ethanol,V} < 0.7$; $\triangle$, simulations with $1301 < Re_{D_h,V} < 3482$, $0.05 < \omega_{ethanol,L} < 0.6$ and $0.1 < \omega_{ethanol,V} < 0.7$; $\times$, Penetration Theory predictions.

10.4.1.6. Vapour phase mass transfer

In wetted-wall contacting, the vapour phase mass transfer resistance is usually rate controlling, making its prediction especially important. For the ethanol-water and methanol-water systems, Ito and Asano [59] studied wetted-wall contacting in a square channel with one wetted wall. Although this is not the same as the geometry used in the simulations, the results for vapour phase mass transfer may still be compared on the basis of dimensional analysis. Figure 10.6 shows a comparison between the experimental data of Ito and Asano [59] and the simulation results. Clearly there is a relatively large scatter in the experimental data, making the comparison difficult. The scatter is likely due to a large range of operating conditions and experimental variability. Further, it is known that even very small non-adiabatic effects, which are often difficult to control in experiments, can have a large impact on mass transfer rates. However, the simulated predictions lie within the range of experimental data. Additionally, some scatter is also observed in the simulation results, due to the impact of varying operating

conditions. This type of scatter often leads to difficulties in trying to develop accurate empirical mass transfer correlations, since it is difficult to capture all the interacting effects. This emphasizes the convenience of employing a predictive model, such as the one proposed in this investigation, to provide estimates of mass transfer efficiencies for various conditions.

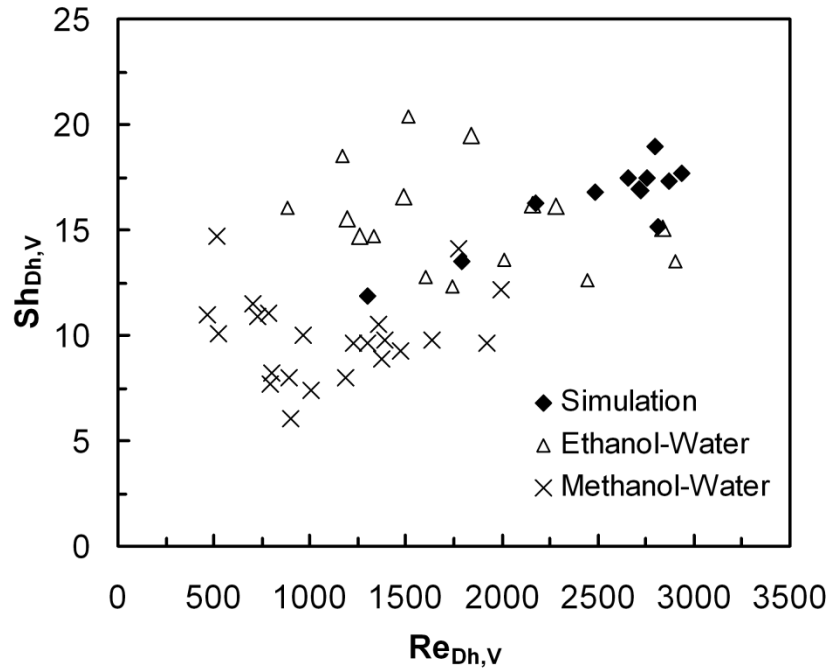


Figure 10.6. Comparison between experimental results, adapted from [59], and numerical predictions for vapour phase Sherwood number (simulation results for: $1300 < Re_{Dh,V} < 2936$, $0.71 < Sc_V < 0.75$, $180 < Re_L < 1317$ and $150 < Sc_L < 385$).

In addition to the experimental data presented in Figure 10.6, a vast array of empirical correlations for vapour phase mass transfer in wetted-wall contacting also exists in the literature, some of which are shown in Table 10.1. These correlations were developed using a variety of chemical systems, for specific ranges of dimensionless groups. All the correlations have a similar form given by the following equation.

$$Sh_{Dh,V} = A Re_{Dh,V}^B Sc_V^C Re_L^D \quad (30)$$

Table 10.1 also presents the mean and maximum deviations of the simulation results from the empirical mass transfer correlations. Clearly the range of deviations is quite broad. The large range of deviations is partly due to the limited ranges covered by some of the correlations, some of which do not cover the entire range of simulation results. Overall, given geometrical

differences and the difference in chemical species, agreement between the empirical correlations with larger ranges of applicability and the simulation results is reasonable. A parity plot for simulated and empirical Sherwood number, for the three correlations showing the best agreement, is shown in Figure 10.7. Two of the most commonly cited correlations for vapour-liquid mass transfer, correlations 1 and 9, provided good agreement with the simulation results.

Table 10.1. Deviation of Simulated Vapour Phase Mass Transfer in Wetted-Wall Contacting from Empirical Correlations (simulations for: $2490 < Re_{D_h,V} < 3482$, $2500 < Re_{D_h,V,rel} < 3801$,

$0.71 < Sc_V < 0.75$, $180 < Re_L < 1317$ and $150 < Sc_L < 385$)

Coefficients	Ranges	Mean Deviation (%)	Maximum Deviation (%)	Ref.
1. $A = 0.023$, $B = 0.83$, $C = 0.44$	$2000 < Re_{D_h,V} < 27000$ $Re_L \approx 1000$	17.76	30.93	[61]
2. $A = 0.0318$, $B = 0.79$, $C = 0.5$	$2000 < Re_{D_h,V} < 27000$ $Re_L \approx 1000$	19.26	32.58	[62]
3. $A = 0.0065$, $B = 0.83$, $D = 0.15$	$2000 < Re_{D_h,V} < 17000$ $25 < Re_L < 1200$	36.50	54.01	[63]
4. $A = 0.0387$, $B = 0.66$, $C = 0.5$, $D = 0.115$	$115 < Re_{D_h,V} < 350$ $4 < Re_L < 32$	30.03	46.25	[64]
5. $A = 0.0093$, $B = 0.68$, $D = 0.34$	$3000 < Re_{D_h,V} < 10000$ $195 < Re_L < 800$	10.37	16.89	[65]
6. $A = 0.00283$, $B = 1.0$, $C = 0.5$, $D = 0.08$	$2400 < Re_{D_h,V} < 9100$ $110 < Re_L < 480$	49.57	68.56	[66]
7. $A = 0.00814$, $B = 0.83$, $C = 0.44$, $D = 0.15$	$2000 < Re_{D_h,V} < 20000$ $Re_L < 1200$	24.89	41.46	[67]
8. $A = 0.0328$, $B = 0.77$, $C = 0.33^*$	$3000 < Re_{D_h,V,rel} < 30000$ $Re_L < 300$	19.65	33.42	[68]
9. $A = 0.0338$, $B = 0.8$, $C = 0.33^*$		9.36	21.36	[69]

*Based on $Re_{D_h,V,rel}$ instead of $Re_{D_h,V}$.

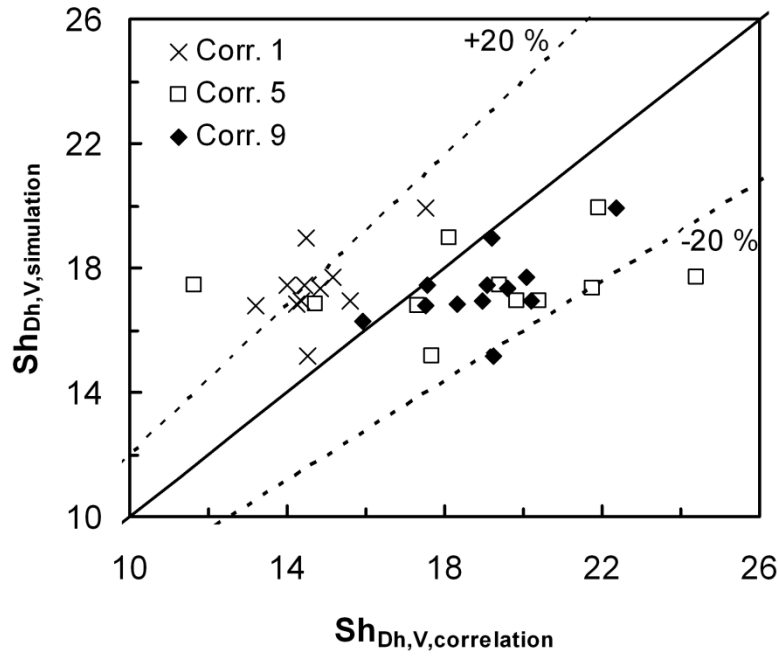


Figure 10.7. Parity plot for the three correlations showing the best agreement with the simulated vapour phase mass transfer results (simulations for: $2490 < Re_{D_h,V} < 3482$, $2500 < Re_{D_h,V,rel} < 3801$, $0.71 < Sc_V < 0.75$, $180 < Re_L < 1317$ and $150 < Sc_L < 385$).

10.4.2. Case 2: Contacting in a short horizontal channel

Analysis of the preceding wetted-wall contacting case is not trivial due to the complex interacting effects between fluid dynamics, heat and mass transfer. To reduce the number of interacting effects, another validation case is presented. This case consists of vapour flowing horizontally over a smooth, stationary liquid. This is of course analogous to heat transfer in a horizontal channel with a constant wall temperature.

10.4.2.1. Geometry

The geometry used to investigate vapour flow over a smooth, stationary liquid is shown in Figure 10.8. The dimensions of the channel are the same as those used for the wetted-wall case. Vapour was introduced at one end of the channel and exited at the opposite end. The vapour entered with a constant temperature and composition, with the temperature being adjusted to be slightly above the dew point. The liquid level was maintained by three walls, simulating a stationary pool of liquid in two dimensions. The upper boundary shown in Figure

The diagram illustrates a microfluidic device layout. At the top, two inlet/outlet regions are shown in cross-section. The left region features a 'Wall' on the left, a 'Liquid level' indicated by a dashed line, and an 'Outlet' on the right. The right region features a 'Wall' on the left, a 'Liquid level' indicated by a dashed line, and an 'Inlet' on the right. Both regions show a 'Free Stream' above the liquid level. Vertical dimensions of 2 mm and 1 mm are indicated for the left inlet/outlet region. A vertical arrow labeled δz_1 points downwards from the top regions to the central channel. The central channel is a long, narrow rectangular region with a total length of 30 mm, as indicated by a horizontal dimension line at the bottom. A coordinate system with x and y axes is shown at the bottom left corner.

10.4.2.2. Computational methodology

The initial conditions were specified in the following way. Initially, the lower part of the domain was filled with stagnant liquid, as shown in Figure 10.8. The remainder of the channel was filled with stagnant vapour at the dew point temperature with a constant composition. The initial vapour temperature and composition were equal to those defined at the inlet boundary.

10.4.2.3. Vapour phase mass transfer

Two mass transfer correlations for laminar mass transfer in a channel are given in Table 10.2. Both expressions shown in Table 10.2 are originally heat transfer correlations that may be applied to mass transfer by analogy.

Table 10.2. Correlations for Laminar Mass Transfer in a Channel

Correlation	Reference
1. $Sh_{D_h,V} = 7.54 + \frac{0.03(Re_{D_h,V} Sc D_h/L)}{1 + 0.016(Re_{D_h,V} Sc D_h/L)^{2/3}}$	Adapted from heat transfer [67]
2. $Sh_{D_h,V} = 1.85(Re_{D_h,V} Sc D_h/L)^{1/3}$	Adapted from heat transfer [55]

Figure 10.9 shows the comparison between simulated predictions of the vapour phase Sherwood number and predictions from the correlations in Table 10.2. Clearly there is a good agreement between the simulation results and the correlations. The average deviations from correlations 1 and 2 are 3.99 % and 9.01 %, respectively. The small amounts of scatter in the data shown in Figure 10.9 are likely due to small variations in flow rates and material properties. The good agreement between the empirical correlations and model predictions inspires confidence in the model's ability to accurately predict mass transfer performance. Thus, the model may be generally applied to estimate heat and mass transfer performance in vapour-liquid flow.

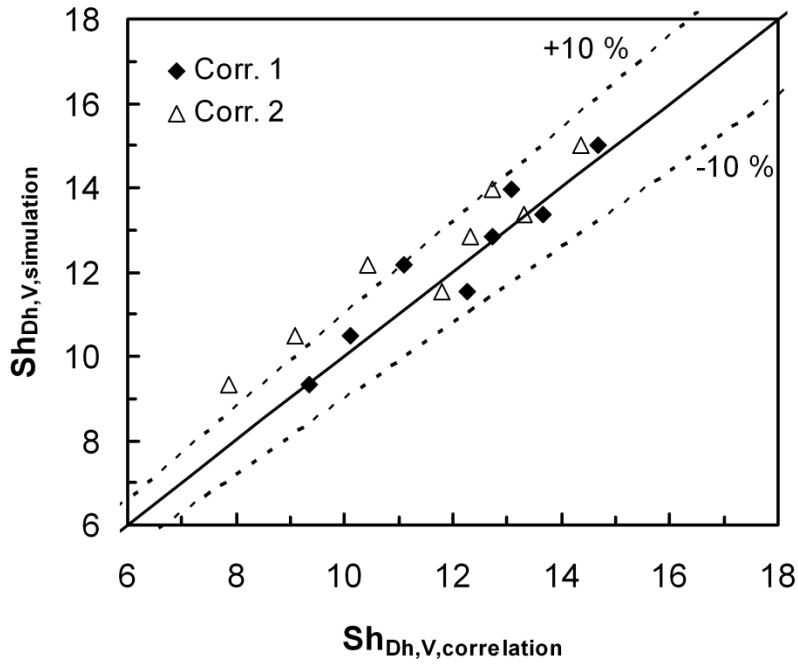


Figure 10.9. Parity plot comparing simulated values of vapour phase Sherwood number to predictions from Correlation 1 and Correlation 2 for: $438 < Re_{Dh,V} < 2381$ and $0.66 < Sc_V < 0.75$

10.5. Conclusions

Simultaneous interphase heat and mass transfer is critical in many industrial applications. Coupled interfacial heat and mass transfer in systems with multiple condensable components is particularly important in chemical separation processes. However, the scenario with multiple phase changing species also presents great modeling challenges due to the strongly coupled nature of heat, mass and momentum transport. This investigation presented an original VOF surface tracking method, which can be applied to direct simulation of interface dynamics and coupled interphase heat and mass transfer. The method is novel since it incorporates the full interface species and energy jump conditions, making it applicable to systems with multiple phase changing species. Simulation results were presented for vapour-liquid contacting in a narrow two-dimensional channel for the binary ethanol-water system. However, the mathematical formulation is generally applicable to all types of free-surface flows, including, films, sprays, bubbles, droplets etc. Applicability is mainly limited by the required computational resources. The approach is also easily extensible to three dimensions and systems with multiple

chemical species, using standard VOF methods and multi-species transport models. The extensions to three dimensions and multiple chemical species will be demonstrated in a future study.

Two simulation cases were presented for model validation. The first case compared experimental data and empirical correlations with simulation results for mass transfer during wetted-wall contacting in a narrow channel. Generally, good agreement was observed between correlations and simulation results for both liquid and vapour phase mass transfer. The second case, which was intended to provide a more detailed validation for the direct simulation of vapour phase mass transfer, investigated vapour flow over a smooth, stationary liquid. Again, good agreement was observed between numerical predictions and literature correlations. Agreement with experimental results and the fundamental theoretical nature of the model inspire confidence in its ability to provide accurate estimates of interface dynamics and heat and mass transfer performance.

The advantage of direct numerical simulation of interface dynamics and interphase heat and mass transfer is clearly the prospect of obtaining a priori predictions of the local heat and mass transfer coefficients. This local information can be used to develop accurate heat and mass transfer models that may be integrated into large scale process simulation tools and used for equipment design and optimization. Thus, this approach has the potential to save both time and money, by limiting the need for costly exploratory experiments. However, the availability of computational resources continues to be a key limitation, especially for three-dimensional simulations.

10.6. Acknowledgment

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

10.7. Nomenclature

A	interfacial area, m^2
c_p	specific heat, J/kg.K
C	number of chemical species
D_h	hydraulic diameter (for a channel: $2(W - 2\delta)$), m

D_{iM}	diffusivity of species i in mixture, m ² /s
D_{12}	diffusivity of species 1 in species 2, m ² /s
F	nonlinear equations
$\vec{F}$	volumetric body forces, N/m ³ .s
$\vec{g}$	gravitational acceleration, 9.81 m/s ²
h	enthalpy, J/kg
ΔH_{vap}	latent heat of vaporization, J/kg
$\vec{j}$	species mass diffusion flux, kg/m ² .s
k	thermal conductivity, W/m.K
K	K-value or mass transfer coefficient, m ² /s
L	length, m
$\dot{m}_i$	total interface mass flux of species i, kg i/m ² .s
M	molar mass, kg/kmol
$\vec{n}$	interface unit normal vector
$\vec{n}_w$	wall unit normal vector
p	pressure, Pa
R	universal gas constant, 8.314 J/mol.K
$Re_{D_h,V}$	vapour phase Reynolds number, $\frac{\rho_V D_h u_{ave,V}}{\mu_V}$
$Re_{D_h,V,rel}$	Reynolds number based on relative velocity, $\frac{\rho_V D_h (u_{ave,V} - u^I)}{\mu_V}$
Re_L	liquid phase Reynolds number, $\frac{4\Gamma}{\mu_L}$
S	volumetric source term in conservation equation
Sc	Schmidt number, $\frac{\mu}{\rho D_{12}}$
$Sh_{D_h,V}$	vapour phase Sherwood number, $\frac{K_V D_h}{D_{12,V}}$

Sh_L	liquid phase Sherwood number, $\frac{K_L \delta}{D_{12,L}}$
t	time, s
$\vec{t}_w$	wall unit tangential vector
T	temperature, K
$\vec{u}$	velocity, m/s
V	molar volume, m ³ /kmol or cell volume, m ³
W	channel width (distance between plates), m
x	liquid phase mole fraction or position, m
X	vector of unknowns
y	vapour phase mole fraction or position, m

Greek letters

α	volume fraction, m ³ phase/m ³
δ	liquid film thickness, m
$\bar{\phi}$	fugacity coefficient
γ	activity coefficient
Γ	liquid mass flow rate per unit wetted width, kg/m.s
μ	viscosity, Pa.s
κ	curvature
θ	contact angle, degrees
ρ	density, kg/m ³
σ	surface tension, N/m
ω	mass fraction
$\bar{\omega}$	bulk mass fraction

Subscripts

<i>ave</i>	average
<i>A</i>	point A
<i>B</i>	point B
D_h	hydraulic diameter
<i>E</i>	energy equation

<i>i</i>	species <i>i</i>
<i>L</i>	liquid phase
<i>max</i>	maximum
<i>q</i>	phase <i>q</i>
<i>rel</i>	relative
<i>V</i>	vapour phase
<i>W</i>	wall
<i>1</i>	species 1
<i>2</i>	species 2

Superscripts

<i>I</i>	interface
<i>sat</i>	saturation conditions

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CORRELATION OF TRANSPORT PROPERTIES FOR THE ETHANOL-WATER SYSTEM USING NEURAL NETWORKS

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Abstract

Process design and simulation rely heavily on the accuracy and availability of transport property correlations. General models that combine the properties of pure components often lack the necessary accuracy. In this investigation, neural networks were used to model some important transport properties for the ethanol-water binary system. Specifically, a three-layer feed-forward neural network with six neurons in the hidden layer was used to model viscosity, thermal conductivity, surface tension and the Fick diffusion coefficient based on an array of experimental data. These neural network models were then compared to some conventional models that are commonly used to predict the aforementioned transport properties. The results showed that the neural network models were able to represent the experimental data very well for the system studied. One advantage in using neural network models to represent these properties is their ability to predict complex and interrelated behaviours without a priori information about the underlying model structure. Further, since all the models retain the same simple matrix structure, their integration into computer codes becomes straightforward and non-repetitive.

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11.1. Introduction

The availability of suitable correlations for physical and transport properties is vital to the accurate modeling and simulation of many chemical separation and reaction systems. The

ethanol-water system has received considerable attention in the past due to its prevalence in the food and beverage industry. More recently, ethanol has become an important biofuel due to its increased use in gasoline mixtures. Bio-ethanol is usually produced through the fermentation of sugars derived from various biomass sources. The fermentation process is usually limited to ethanol concentrations below approximately 10 wt% for conventional substrates or 5 wt% for cellulosic substrates. This relatively dilute concentration as well as the presence of an ethanol-water azeotrope makes separation relatively energy intensive. To improve process performance it is critical to have accurate process models for existing and novel unit operations. The availability of accurate physical and transport property correlations allows the improved modeling and simulation of these unit operations in view of designing better separation processes.

Most correlations used to predict physical and transport properties of mixtures are based on some general equations that make use of the properties of individual components of the mixture. Although these equations provide, in many cases, a relatively good estimation of a given property, they are often not accurate enough to be used in process design. It is highly preferable to resort to experimental data of the actual mixtures being studied. To be used efficiently in process modeling, the experimental data must be encapsulated in a prediction model. Neural networks, which have been successfully applied to model a variety of systems, can be used advantageously. Neural networks have the advantage of being able to predict complex and interrelated behaviors without a priori information about the underlying model structure or theoretical considerations. Neural networks are in some ways analogous to the human brain. Specifically, much like learning in the human brain is based on the strength of synaptic connections between neurons, artificial neural networks exploit matrices of numerical coefficients (or weights) to store information [1].

This work presents the application of various commonly used transport property correlations to the ethanol-water system. Neural network models are then presented for each of these transport properties and the results are compared to experimental data and general predictive models. Finally, the suitability of the neural network models is discussed in terms of their fit and ease of integration into transport simulations.

11.2. Theory

11.2.1. Common Transport Property Correlations

Many correlations have been proposed for the prediction of mixture transport properties. Some of these are based on some theoretical considerations while others are purely empirical. Further, many of these correlations are only suitable for certain groups of chemicals (i.e. polar or non-polar mixtures) or for certain conditions (i.e. low pressure, dilute mixtures etc.) and may yield poor results if extrapolated to other systems. Table 11.1 presents a summary of the correlations that were compared to the neural network models presented in this paper. Pure component properties and pure component property correlations were taken from Perry and Green [2] and Yaws [3]. For details on the calculation procedure for these models see the original references and Appendix 11.A.

11.2.2. Application of Neural Networks for Data Correlation

A simple three-layer feed-forward neural network with 6 neurons in the hidden layer, including the bias, was used to correlate the data in this investigation [1]. The effect of the number of neurons in the network on the model error was studied. It was determined that neural networks with 6 neurons provided good results for all the modeled properties. Further, only two inputs (mole fraction and temperature) and one output (the desired transport property) were considered. In this scheme, the outputs of neurons are computed by calculating the weighted sum of the scaled inputs and passing the sum through a transfer function. A simple sigmoid function was used as the transfer function. The neural network is able to “learn” by adjusting the weights that interconnect the layers of neurons. It is therefore apparent that finding an appropriate neural network model consists of finding the optimal values of the weights. A quasi-Newton method has been used as the learning algorithm in this investigation [13]. A schematic representation of the neural network used in this investigation is given in Figure 11.1.

Given the optimal weights and specific inputs, calculation of the output is carried out using the algorithm shown in Figure 11.2.

Table 11.1. Summary of Physical and Transport Property Correlations for a Binary Mixture

Model	Comments
Viscosity	
Arithmetic, Geometric and Harmonic Means	Simple means with no parameters
Grunberg and Nissan [4]	$\ln \mu_m = x_1 \ln \mu_1 + x_2 \ln \mu_2 + x_1 x_2 G_{12}$
Teja and Rice [5,6]	$\ln(\mu_m \varepsilon_m) = x_1 \ln(\mu \varepsilon)_1 + x_2 \ln(\mu \varepsilon)_2$
Neural Model*	6 hidden neurons
Diffusion Coefficient**	
Simple [7]	$D_{12} = [x_2 D_{12}^0 + x_1 D_{21}^0] \alpha$
Vignes [8]	$D_{12} = [(D_{12}^0)^{x_2} (D_{21}^0)^{x_1}] \alpha$
Sanchez and Clifton [9]	$D_{12} = [x_2 D_{12}^0 + x_1 D_{21}^0] [1 - m + m \alpha]$
Neural Model*	6 hidden neurons
Thermal Conductivity	
Arithmetic, Geometric and Harmonic Means	Simple means with no parameters
Baroncini et al. [10]	$k_m = \left[x_1^2 A_1 + x_2^2 A_2 + 2.2 \left(\frac{A_1^3}{A_2} \right) x_1 x_2 \right] \frac{(1 - T_{rm})^{0.38}}{T_{rm}^{1/6}}$
Li [11]	$k_m = \phi_1^2 k_1 + \phi_2^2 k_2 + 2 \phi_1 \phi_2 k_{12}$
Filippov [7]	$k_m = w_1 k_1 + w_2 k_2 - G_{12} w_1 w_2 (k_2 - k_1)$
Jamieson [7]	$k_m = w_1 k_1 + w_2 k_2 - G_{12} (k_2 - k_1) [1 - (w_2)^{1/2}] w_2$
Neural Model*	6 hidden neurons
Surface Tension	
Arithmetic, Geometric and Harmonic Means	Simple means with no parameters
Meissner and Michaels [12]	$\sigma_m = \sigma_w \left(1 - (0.411) \log \left(1 + \frac{x_o}{a} \right) \right)$
Tamura [7]	$\sigma_m = (\psi_w^\sigma \sigma_w^{1/4} + \psi_o^\sigma \sigma_o^{1/4})$
Neural Model*	6 hidden neurons

*Details in text

** α is a thermodynamic factor (calculated using the Wilson equation)

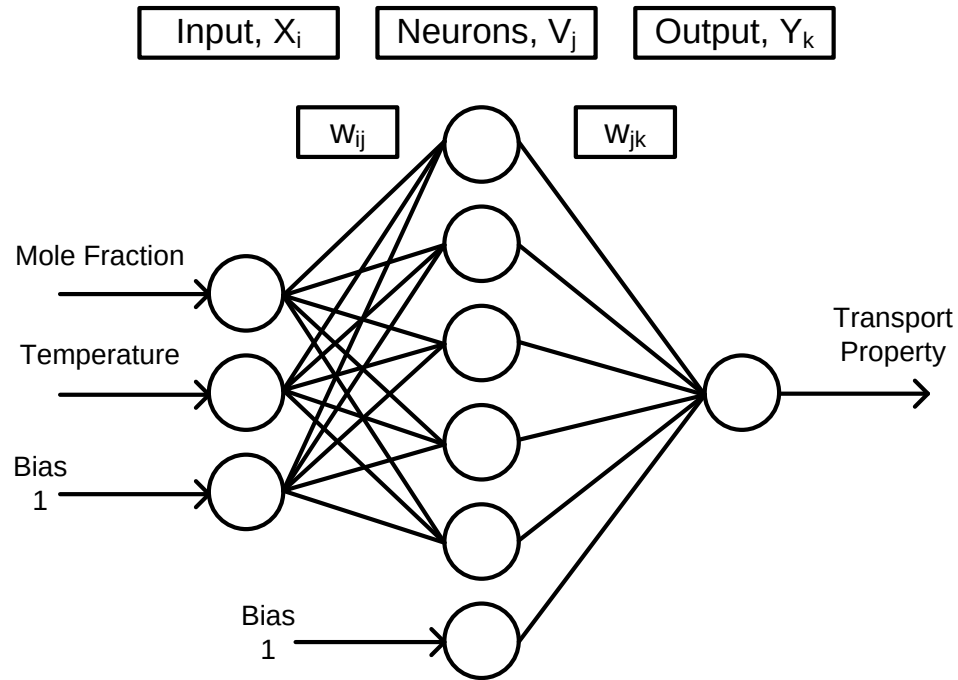


Figure 11.1. Schematic representation of the three-layer feed-forward neural network applied in the investigation.

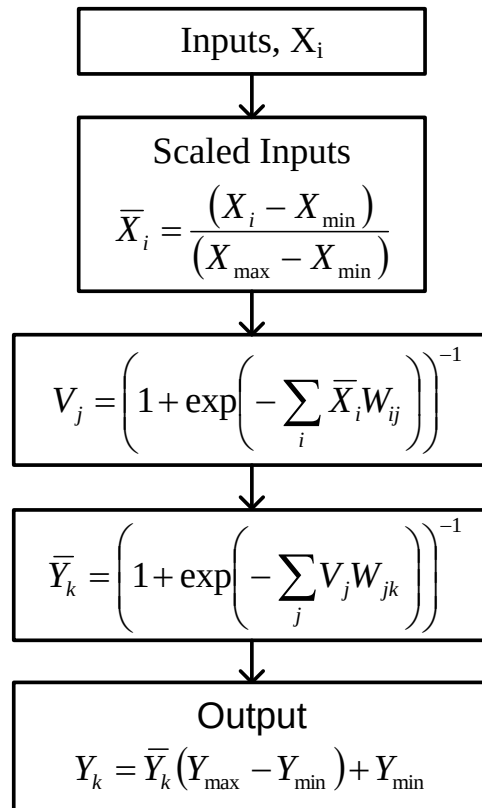


Figure 11.2. Algorithm for neural network model calculations.

11.2.3. Data Analysis and Model Comparison

The fit of the models was observed visually through the use of parity plots and analyzed numerically using the Root Mean Square Relative Error (RMSRE) and the standard deviation in the SRE (σ_{SRE}). These quantities are defined by the following expressions.

$$\text{RMSRE} = \sqrt{\frac{1}{N} \sum_{i=1}^N \left(\frac{y_{\text{exp},i} - y_{\text{pred},i}}{y_{\text{exp},i}} \right)^2} \quad (1)$$

$$\sigma_{\text{SRE}} = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (\text{SRE}_i - \text{MSRE})^2} \quad (2)$$

Where the Square Relative Error (SRE_i) is defined by $\text{SRE}_i = \left[(y_{\text{exp},i} - y_{\text{pred},i}) / y_{\text{exp},i} \right]^2$ and the Mean Square Relative Error (MSRE) is defined by $\text{MSRE} = 1/N \sum_{i=1}^N \text{SRE}_i$. In this case, N represents the number of data points and $y_{\text{exp},i}$ and $y_{\text{pred},i}$ are the experimental and predicted values of the dependent variable. The RMSRE gives a normalized measure of the total error in the model predictions compared to the experimental data. Conversely, the standard deviation in the SRE, referred from here on simply as the standard deviation, provides an indication of the variance or scatter in the SRE.

11.3. Results and Discussion

11.3.1. Neural Network Models

As mentioned above, the neural network models are characterized by their respective weights. Tables 11.2a through 11.2d summarize the neural network models for viscosity, diffusion coefficient, thermal conductivity and surface tension. A Microsoft Excel tool which can calculate all the above mentioned properties using the neural network models is available from the author's website [14].

Table 11.2a. Neural Network Parameters for the Viscosity Model (Viscosity in 10^{-3} Pa.s;
Temperature in K)

Inputs Min.	Inputs Max.	Outputs Min.	Outputs Max.		
0.00	1.00	0.00	4.50		
280.00	355.00				
		W_{ij}	W_{jk}		
0.9342	-6.2555	-12.7280	-12.0150	-13.4020	-972.22
1.3839	-0.9846	-11.0640	-11.0570	-11.0790	-3369.70
5.1499	-6.9750	-0.0910	-0.1052	-0.0750	-5324.40
					2574.60
					2744.40
					969.51

Table 11.2b. Neural Network Parameters for the Fick Diffusion Coefficient Model (Diffusion
Coefficient in 10^{-9} m²/s; Temperature in K)

Inputs Min.	Inputs Max.	Outputs Min.	Outputs Max.		
0.00	1.00	0.00	3.00		
290.00	360.00				
		W_{ij}	W_{jk}		
-4.8137	-1.8079	1.9589	49.0380	4.7693	-463.23
0.3345	-1.9540	2.1088	-5.8926	-0.3177	-3433.20
0.8076	6.0251	-5.4164	10.9790	-0.7729	-1483.80
					-1770.40
					-473.19
					5671.10

Table 11.2c. Neural Network Parameters for the Thermal Conductivity Model (Thermal Conductivity in W/m.K; Temperature in K)

Inputs Min.	Inputs Max.	Outputs Min.	Outputs Max.		
0.00	1.00	0.00	0.80		
210.00	355.00				
		W_{ij}	W_{jk}		
-2.4383	-60.0060	2.3775	15.1980	7.4064	-131.23
-1.5992	112.5300	1.5077	8.8539	-1.0240	812.33
0.0746	341.2400	-0.0044	23.2710	8.2459	-138.93
					787.64
					-2278.80
					815.97

Table 11.2d. Neural Network Parameters for the Surface Tension Model (Surface Tension in mN/m; Temperature in K)

Inputs Min.	Inputs Max.	Outputs Min.	Outputs Max.		
0.00	1.00	10.00	80.00		
260.00	380.00				
		W_{ij}	W_{jk}		
0.1349	5.3025	5.2870	26.0510	88.4330	-338.61
0.2038	-4.2618	-4.4744	2.6117	1.2819	-3503.90
-4.4053	8.2230	7.2465	-1.6034	7.3417	1087.10
					-1.91
					-2736.00
					5158.10

11.3.2. Viscosity

As stated in Table 11.1, the viscosity was modeled using simple means and the single adjustable parameter models of Grunberg and Nissan [4] and Teja and Rice [5,6]. The adjustable parameters were determined to be 3.435 and 1.399 for the Grunberg and Nissan and Teja and Rice correlations, respectively. These parameters were determined by minimizing the RMSRE for all the experimental datasets in order to compare the predictions of these models under the same conditions as for neural networks. The arithmetic, geometric and harmonic means did not provide very good estimates of the mixture viscosity. Figure 11.3 shows the parity plots for the

Grunberg and Nissan, Teja and Rice and neural network models. It is shown and further emphasized on Figure 11.4, for three representative datasets, that the neural network model provides a much better fit to the experimental data. It can also be seen in Figure 11.4 that the Grunberg and Nissan and Teja and Rice models are not capable of predicting the nonsymmetrical nature of the viscosity's variation with composition. It is also shown that these models over predict the viscosity at higher temperatures and under predict the viscosity at lower temperatures. Thus, their performance could probably be improved by including a correction for the adjustable parameter's variation with temperature.

Numerically, the fit of the models to the experimental data can be expressed in terms of the RMSRE and standard deviation. These results are shown in Table 11.3. It is clear from the values presented in this table that the neural network model provides a superior fit for all the datasets studied in this investigation.

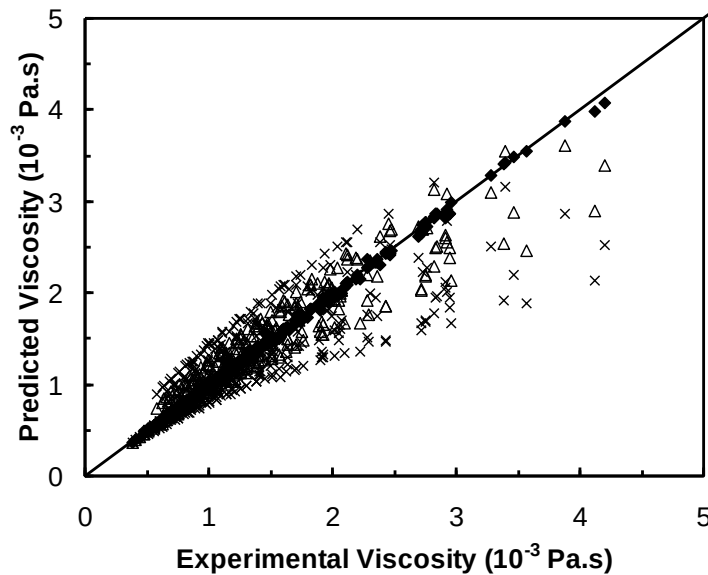


Figure 11.3. Parity plot comparing experimental and predicted viscosity for: $\blacklozenge$, neural network model; $\times$, Grunberg and Nissan model; $\triangle$, Teja and Rice model.

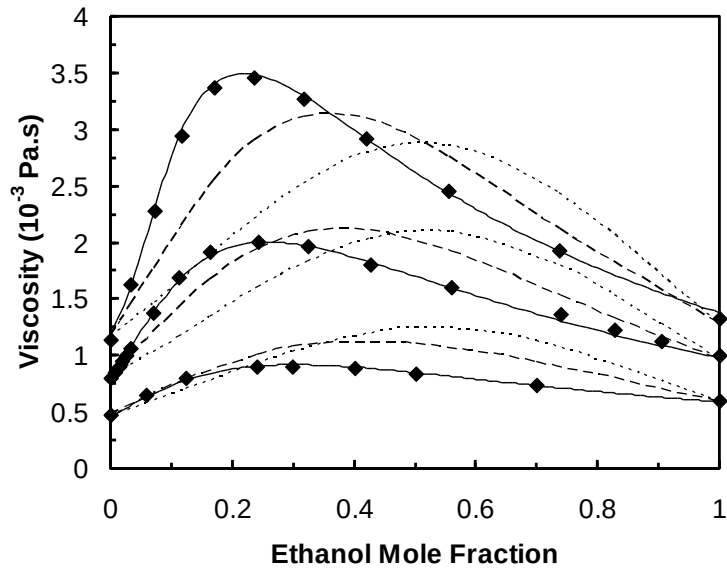


Figure 11.4. Plot comparing viscosity predictions by: —, neural network model; - - -, Grunberg and Nissan model; - · -, Teja and Rice model for three experimental datasets (◆, top curves: $T = 288.16$ K [15]; middle curves: $T = 303.1$ K [16]; bottom curves: $T = 333.15$ K [17]).

Table 11.3. Evaluation of the Best Three Models for Prediction of the Viscosity for Each Experimental Dataset

Data Sources	Number of Data Points	Correlation	RMSRE	σ_{SRE}
Bingham et al. [17]	97	Grunberg and Nissan [4]	0.2536	0.0912
		Teja and Rice [5,6]	0.1624	0.0332
		Neural Model	0.0200	0.0006
Kikuchi and Oikawa [15]	88	Grunberg and Nissan [4]	0.2338	0.0594
		Teja and Rice [5,6]	0.1330	0.0208
		Neural Model	0.0146	0.0004
Dizechi and Marschall [16]	80	Grunberg and Nissan [4]	0.2221	0.0586
		Teja and Rice [5,6]	0.1219	0.0211
		Neural Model	0.0190	0.0008
Traube [18]	65	Grunberg and Nissan [4]	0.2351	0.0600
		Teja and Rice [5,6]	0.1303	0.0196
		Neural Model	0.0274	0.0006
All Data	330	Grunberg and Nissan [4]	0.2373	0.0698
		Teja and Rice [5,6]	0.1393	0.0248
		Neural Model	0.0202	0.0006

11.3.2.1. Model Validation and Generalization

The neural network models were validated in two ways. First, the neural network models were used to generate plots of the transport property throughout the entire composition and temperature range. These curves were then assessed visually for smoothness and consistency. The smoothness and consistency can also be seen in the Microsoft Excel tool provided on the author's website [14]. Secondly, external datasets that were not included in the learning process were used to analyze model performance. For viscosity, the data of Belda et al. [19] were used to validate the model. This dataset included 84 data points. The RMSRE and the standard deviation were calculated to be 0.0453 and 0.0032, respectively. A parity plot for this dataset is given in Figure 11.5 to show model performance visually. It is apparent from the plot, the RMSRE and the standard deviation that the model fits this external dataset quite well. The viscosity model can thus be considered to be at least applicable to the entire concentration range for temperatures between 10 and 75 °C (i.e. the range of the data included in the learning set).

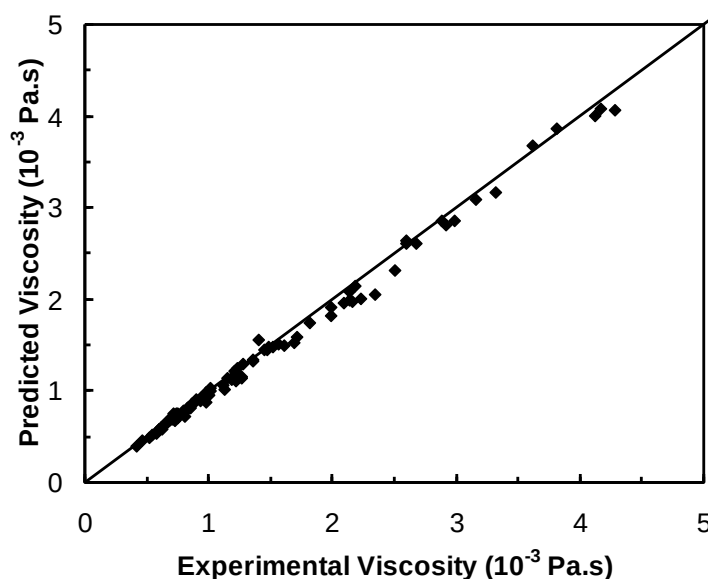


Figure 11.5. Parity plot showing the performance of neural network model for viscosity for the external dataset of Belda et al. [19].

11.3.3. Diffusion Coefficient

The prediction of the diffusion coefficient warrants some additional theoretical discussions to discern between the Maxwell-Stefan and the Fick diffusion coefficient. The difference in these diffusion coefficients arises from the difference in the relations used to

represent diffusion. For a complete discussion on this topic refer to, for example, Taylor and Krishna [20]. For the discussion presented here, it is sufficient to realize that the Fick and Maxwell-Stefan diffusion coefficient are related through a thermodynamic factor that approaches unity at infinite dilution (i.e. at infinite dilution the Maxwell-Stefan and Fick diffusion coefficients are equivalent). This explains the presence of the thermodynamic factor in the correlations for prediction of the Fick diffusion coefficient listed in Table 10.1.

$$D = \mathbf{D}\alpha \quad (3)$$

D is the Fick diffusion coefficient, $\mathbf{D}$ is the Maxwell-Stefan diffusion coefficient and α is a thermodynamic factor defined by the following equation (binary mixture).

$$\alpha = 1 + x_1 \frac{\partial \ln \gamma_1}{\partial x_1} \quad (4)$$

In this equation, x is the mole fraction and γ is the activity coefficient. It is clear that prediction of the thermodynamic factor will depend on the selected thermodynamic model. Taylor and Krishna [20] provide equations for the calculation of the thermodynamic factor for several thermodynamic models. In this investigation, the Wilson equation was chosen to estimate the thermodynamic factor for the ethanol-water system. Furthermore, the infinite dilution coefficients were estimated from the experimental data. The adjustable parameter for the model of Sanchez and Clifton [9] was determined to be 0.826 by minimizing the RMSRE for all datasets.

Figure 11.6 shows the parity plots for all the models for the prediction of the diffusion coefficient presented in Table 11.1. It is clear from this figure that the model of Vignes [8] and the simple model provide the worst fits for the data. This point is further emphasized upon observation of the predictions given for the dataset presented in Figure 11.7. It is however not clear from the parity plot whether the model of Sanchez and Clifton or the neural network model provides a better fit. From Figure 11.7, it appears as though the neural network model provides a better fit but this plot only shows a single dataset.

Numerically, the fit of the models to the experimental data, expressed in terms of the RMSRE and its standard deviation, is shown in Table 11.4. It is clear from the values presented in the table that the neural network model provides a better fit for all the data sets. However, it must be emphasized that the model of Sanchez and Clifton also provides a good fit for the data.

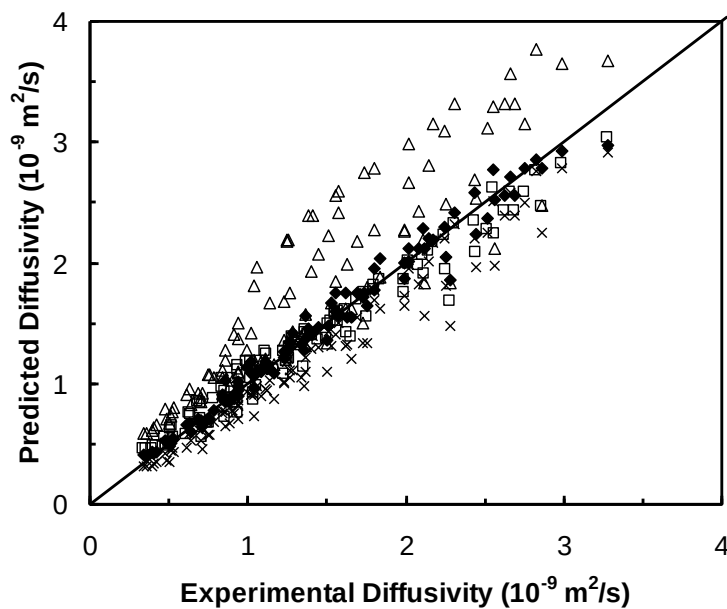


Figure 11.6. Parity plot comparing experimental and predicted diffusivity for: $\blacklozenge$, neural network model; $\times$, simple model; $\triangle$, Vignes model; $\square$, Sanchez and Clifton model.

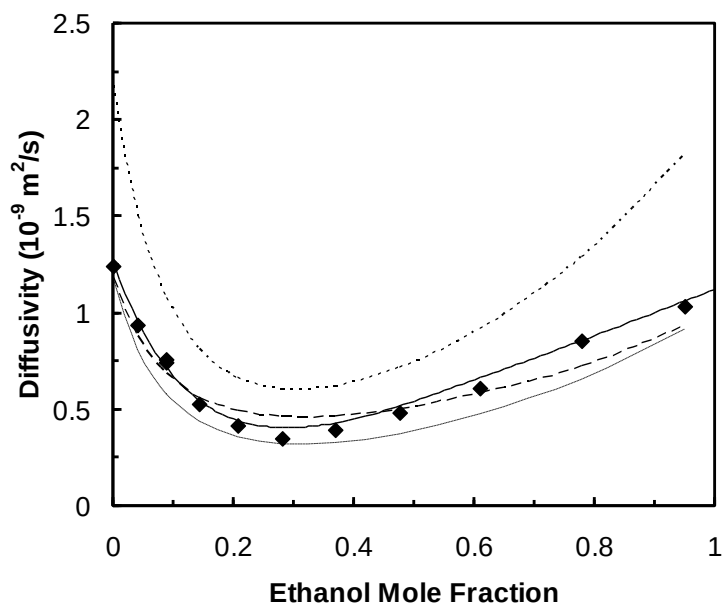


Figure 11.7. Plot comparing diffusivity predictions by: —, neural network model; ···, Vignes model; ---, simple model; - · -, Sanchez and Clifton model for an experimental dataset ($\blacklozenge$, Kircher [21] at 298.15 K).

Table 11.4. Evaluation of Four Models for Prediction of the Diffusion Coefficient for Each Experimental Dataset

Data Sources	Number of Data Points	Correlation	RMSRE	σ_{SRE}
Tyn and Calus [22]	29	Simple [7]	0.1286	0.0176
		Vignes [8]	0.2770	0.0787
		Sanchez and Clifton [9]	0.0755	0.0095
		Neural	0.0816	0.0106
Kircher [21]	24	Simple [7]	0.1652	0.0177
		Vignes [8]	0.4259	0.1871
		Sanchez and Clifton [9]	0.1245	0.0211
		Neural	0.0661	0.0053
Pratt and Wakeham [23]	49	Simple [7]	0.1576	0.0321
		Vignes [8]	0.4431	0.1981
		Sanchez and Clifton [9]	0.1443	0.0280
		Neural	0.0683	0.0091
All Data	102	Simple [7]	0.1518	0.0253
		Vignes [8]	0.3985	0.1675
		Sanchez and Clifton [9]	0.1236	0.0222
		Neural	0.0718	0.0087

11.3.3.1. Model Validation and Generalization

The neural network model for diffusion coefficient was again assessed visually for smoothness and consistency. Further, the data of Hammond and Stokes [24], Galand et al. [25] and Harris et al. [26] were used to validate the model. These datasets included 74 data points. The RMSRE and the standard deviation were calculated to be 0.0770 and 0.0085, respectively. A parity plot for these datasets is given in Figure 11.8 to show the model performance visually. Again, it is apparent that the model fits these external datasets quite well. The diffusivity model can thus be considered to be at least applicable to the entire concentration range for temperatures between 25 and 85 °C (i.e. the range of the data included in the learning set).

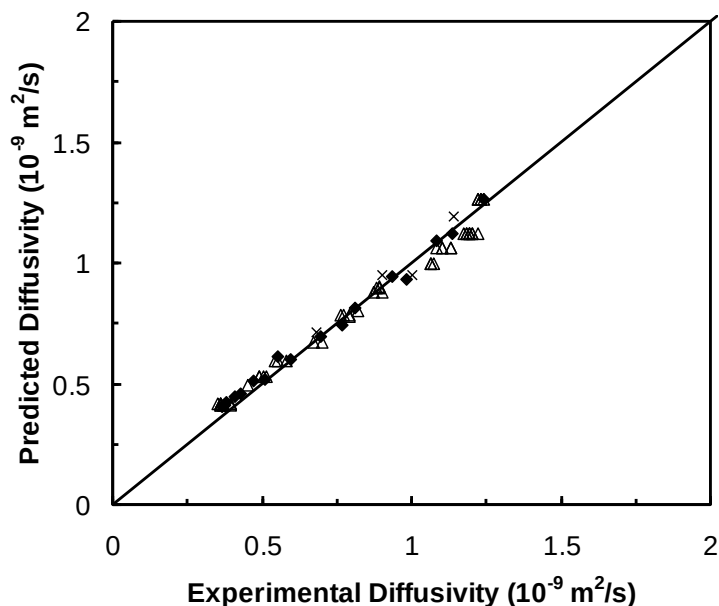


Figure 11.8. Parity plot showing the performance of neural network model for diffusion coefficient for the external datasets of: ◆, Hammond and Stokes [24]; ×, Galand et al. [25]; △, Harris et al. [26].

11.3.4. Thermal Conductivity

Five experimental datasets were taken from the literature to evaluate the models for thermal conductivity [27-31]. Figure 11.9 shows a plot of four of these datasets at a temperature of 293.15 K. As shown on this figure, the data of Filippov [27] does not appear to agree with the other data. This dataset was therefore not used in evaluation and comparison of the thermal conductivity models.

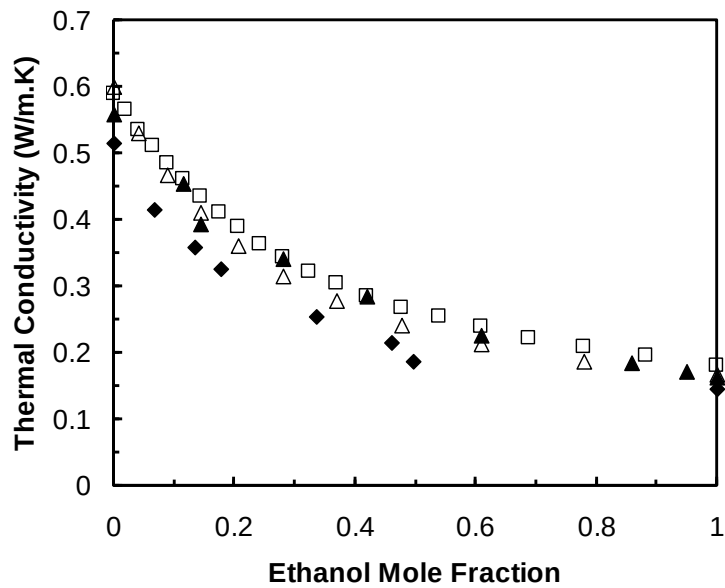


Figure 11.9. Plot showing the thermal conductivity data from: $\blacklozenge$, Filippov [27]; $\blacktriangle$, Tsederberg [30]; $\triangle$, Riedel [29]; $\square$, Bates et al. [28] at 293.15 K.

For thermal conductivity, the models of Filippov and Jamieson (see [7]), along with the neural network model, gave the best fit for the experimental data. The adjustable parameters were determined to be -0.507 and -0.849 for the Filippov and Jamieson models, respectively. These parameters were determined by minimizing the RMSRE for all presented datasets. As shown in Figure 11.10, the Filippov, Jamieson and neural network models all provided similar results in predicting the thermal conductivity. Figure 11.11 shows the predictions of the neural network, Filippov and Jamieson models for one dataset. However, this is somewhat deceptive since different models gave better results than others for some of the datasets.

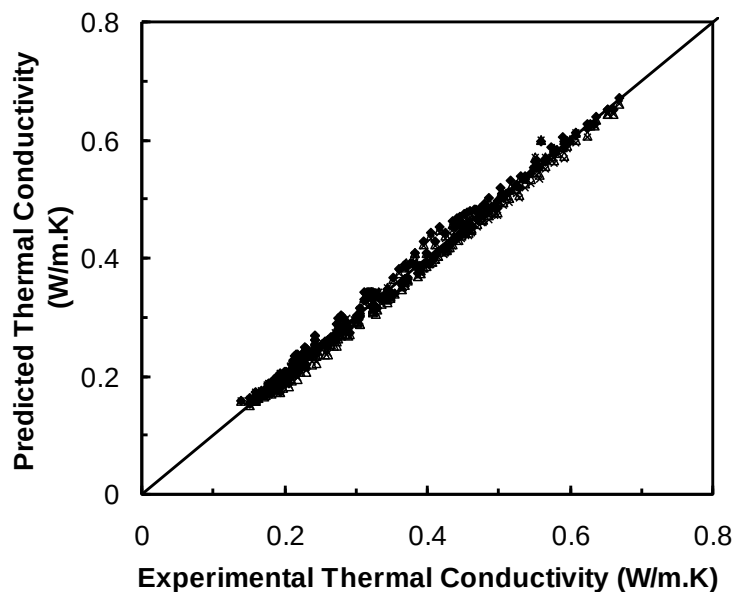


Figure 11.10. Parity plot comparing experimental and predicted thermal conductivity for: $\blacklozenge$, neural network model; $\times$, Jamieson model; $\triangle$, Filippov model.

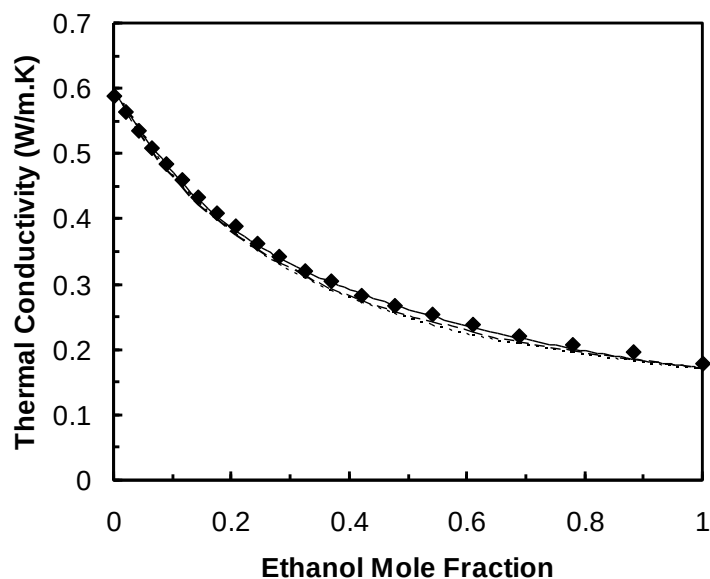


Figure 11.11. Plot comparing thermal conductivity predictions by: —, neural network model; - - -, Filippov model; - · -, Jamieson model for an experimental dataset ($\blacklozenge$, Bates et al. [28] at 293.15 K).

The numerical comparison of the fit of the models to the experimental data, expressed in terms of the RMSRE and standard deviation, is shown in Table 11.5. It is shown that the best three models give very similar results when they are compared for the entire dataset, however, some differences can be seen when looking at datasets from individual authors.

Table 11.5. Evaluation of the Best Three Models for Prediction of the Thermal Conductivity for Each Experimental Dataset

Data Sources	Number of Data Points	Correlation	RMSRE	σ_{SRE}
Riedel [28]	68	Filippov [7]	0.0315	0.0008
		Jamieson [7]	0.0382	0.0014
Bates et al. [29]	126	Neural Model	0.0530	0.0037
		Filippov [7]	0.0399	0.0030
		Jamieson [7]	0.0388	0.0027
Tsederberg [30]	51	Neural Model	0.0284	0.0028
		Filippov [7]	0.0397	0.0019
		Jamieson [7]	0.0370	0.0015
Assael et al. [31]	36	Neural Model	0.0411	0.0023
		Filippov [7]	0.0393	0.0013
		Jamieson [7]	0.0436	0.0015
		Neural Model	0.0574	0.0028
All Data	281	Filippov [7]	0.0357	0.0021
		Jamieson [7]	0.0367	0.0020
		Neural Model	0.0396	0.0027

11.3.4.1. Model Validation and Generalization

The neural network model for thermal conductivity was again assessed visually for smoothness and consistency. Further, the data of Qun-Fang et al. [32] were used to validate the model. This dataset included 7 data points. The RMSRE and the standard deviation were calculated to be 0.0619 and 0.0041, respectively. A parity plot for this dataset is given in Figure 11.12 to show model performance visually. It is apparent that the model fits this external datasets quite well. The thermal conductivity model can thus be considered to be at least applicable to the entire concentration range for temperatures between -40 and 80°C (i.e. the range of the data included in the learning set).

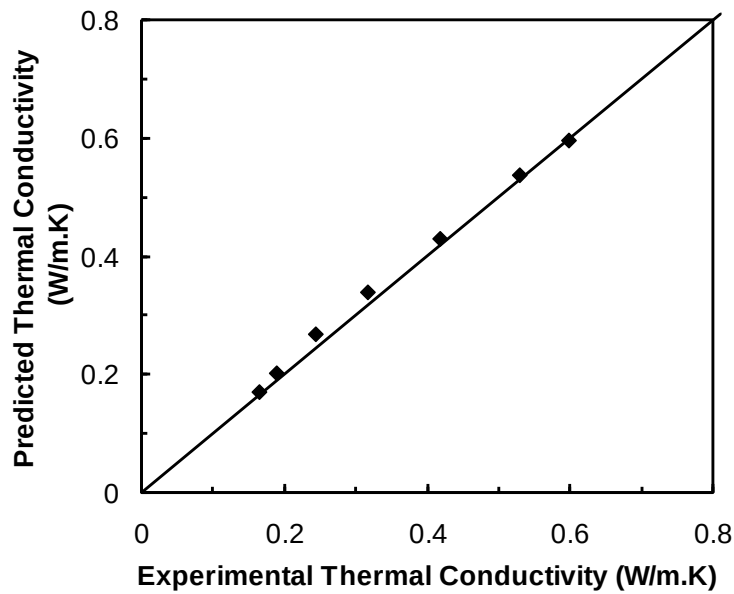


Figure 11.12. Parity plot showing the performance of neural network model for thermal conductivity for the external dataset of Qun-Fang et al. [32].

11.3.5. Surface Tension

For surface tension, the harmonic mean and the model of Tamura (see [7]), along with the neural network model, gave the best fit for the experimental data. Figure 11.13 shows the parity plots for these three models. It is shown that the harmonic mean does not provide a very good fit for the experimental data. Conversely, the model of Tamura provides a relatively good fit for the data but there appear to be some systematic deviations. The neural network model appears to provide a very good fit for the entire dataset. This point is further emphasized upon examination of a single representative dataset in Figure 11.14. The model of Tamura under predicts the data at low ethanol concentrations and over predicts it at higher concentrations while the neural network model provides a good fit across the entire composition range.

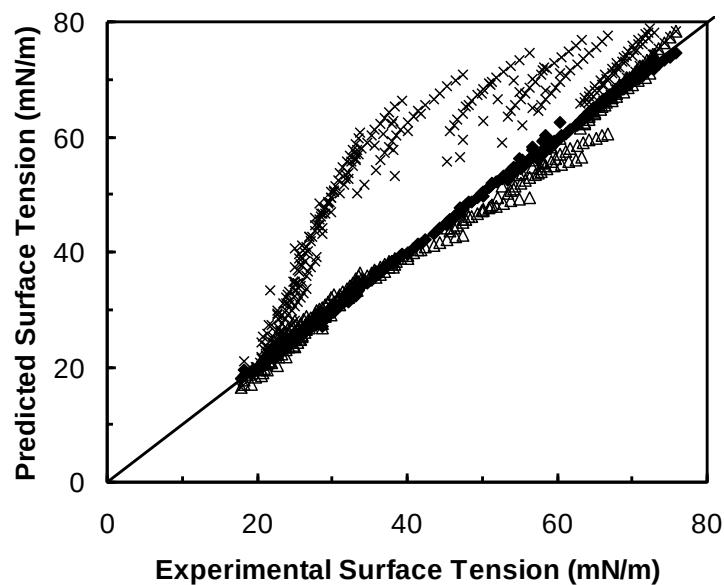


Figure 11.13. Parity plot comparing experimental and predicted surface tension for: $\blacklozenge$, neural network model; $\times$, Harmonic mean; $\triangle$, Tamura model.

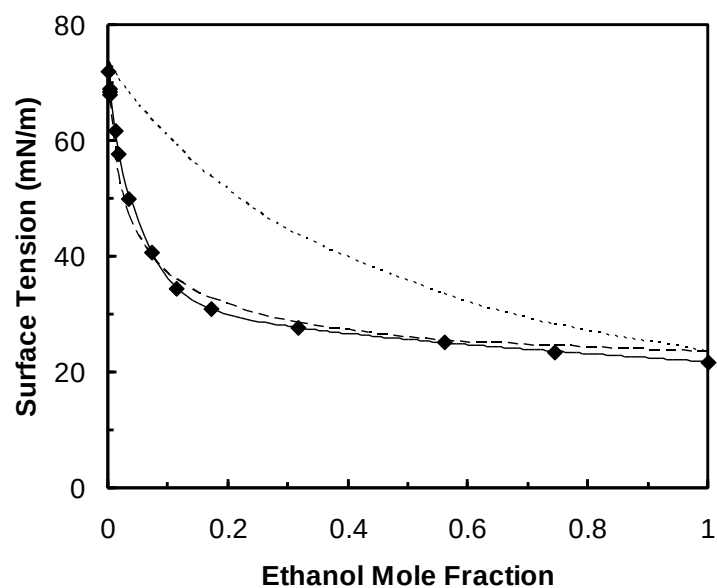


Figure 11.14. Plot comparing surface tension predictions by: —, neural network model; - - -, Harmonic mean; . . ., Tamura model for an experimental dataset ($\blacklozenge$, Teitelbaum et al. [33] at 298.15 K).

The numerical comparison of the fit of the models to the experimental data, expressed in terms of the RMSRE and standard deviation, is shown in Table 11.6. These values further illustrate the above discussion and confirm that indeed the best fit is provided by the neural network model.

Table 11.6. Evaluation of the Best Three Models for Prediction of the Surface Tension for Each Experimental Dataset

Data Sources	Number of Data Points	Correlation	RMSRE	σ_{SRE}
Bonnell et al. [34]	42	Harmonic	0.4104	0.1515
		Tamura [7]	0.0434	0.0027
Valentiner and Hohls [35]	40	Neural Model	0.0176	0.0005
		Harmonic	0.4668	0.1821
	200	Tamura [7]	0.0349	0.0011
		Neural Model	0.0159	0.0003
Teitelbaum et al. [33]	14	Harmonic	0.3886	0.1881
		Tamura [7]	0.0492	0.0031
Kalbassi and Biddulph [36]	14	Neural Model	0.0093	0.0002
		Harmonic	0.4129	0.1622
	296	Tamura [7]	0.0357	0.0018
		Neural Model	0.0371	0.0021
All Data	296	Harmonic	0.4043	0.1803
		Tamura [7]	0.0461	0.0028
		Neural Model	0.0142	0.0005

11.3.5.1. Model Validation and Generalization

Again, the neural network model for surface tension was assessed visually. Further, the data of Vazquez et al. [37] were used to validate the model. This dataset included 98 data points. The RMSRE and the standard deviation were calculated to be 0.0222 and 0.0006, respectively. A parity plot for this datasets is given in Figure 11.15 to illustrate model performance visually. From the RMSRE, standard deviation and parity plot it is apparent that the model fits this external dataset quite well. The surface tension model can thus be considered to be at least applicable to the entire concentration range for temperatures between -10 and 80°C (i.e. the range of the data included in the learning set).

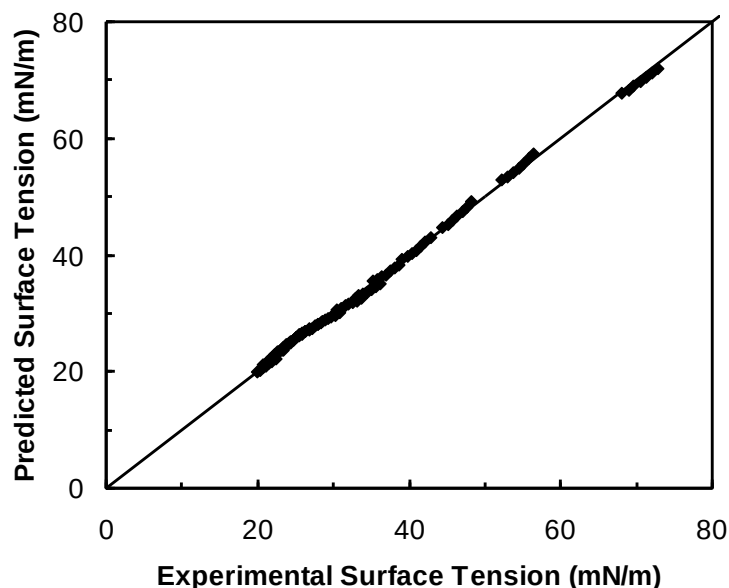


Figure 11.15. Parity plot showing the performance of neural network model for surface tension for the external dataset of Vazquez et al. [37].

11.3.6. General Discussion

From the results and discussions presented above for viscosity, diffusivity, thermal conductivity and surface tension, it is clear that certain properties are more easily predicted than others. Empirical or theoretically based correlations are suitable for cases where the property changes monotonously throughout the entire composition range, as in the case of thermal conductivity and surface tension. However, it is clear that more complicated models are required for properties that display more complex non-ideality such as viscosity and the diffusion coefficient. The neural network models were quite suitable for predicting both the simple and complex behaviors. This inherent flexibility is a direct result of the neural network's ability to adapt to the underlying behavior expressed by the data without rigorously specifying the structure of the model. The neural network's flexibility was demonstrated by using a single neural structure to model four transport properties of the ethanol-water system with an excellent accuracy. A major advantage of using neural network models is therefore the elimination of the need to search for more complicated models when non-ideality is encountered.

11.4. Conclusions

A three-layer feed-forward neural network with six hidden neurons has been used to model the viscosity, thermal conductivity, surface tension and the Fick diffusion coefficient for the ethanol-water binary system. To illustrate the capability of these neural network models to model the presented data, they have been compared to some conventional models that are commonly used to predict the transport properties. The results showed that the neural network models were able to represent the experimental data very well for the system studied. The advantage in using neural network models lies in their ability to predict complex and interrelated behaviors without a priori information about the model structure. Additionally, due to their consistent simple matrix structure, these models can be easily integrated into computer codes in a straightforward and non-repetitive manner. The four transport property models, derived in this investigation, can be used with confidence in simulation and process design.

11.5. Acknowledgment

Financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

11.6. Nomenclature

A	Coefficient in the Baroncini Correlation
a	Coefficient in the Meissner and Michaels Correlation
D	Fick Diffusion Coefficient
D^0	Diffusion Coefficient at Infinite Dilution
D	Maxwell-Stefan Diffusion Coefficient
G	Fitting Constant
k	Thermal Conductivity
N	Number of Data Points
RMSRE	Root Mean Square Relative Error
T_r	Relative Temperature
V	Neurons
W	Neural Network Weights
w	Mass Fraction
X	Neural Network Inputs

x	Mole Fraction
Y	Neural Network Outputs
α	Thermodynamic Factor in the Diffusivity Correlations
ε	Parameter in the Teja and Rice Correlation or Difference between Experimental and Predicted Values
ϕ	Coefficient in the Li Correlation
γ	Activity Coefficient
μ	Viscosity
σ	Surface Tension
σ_{SRE}	Standard Deviation in the Square Relative Error
ψ	Coefficient in the Tamura Correlation

Appendix 11.A: Additional Information for Models

11.A.1. Viscosity

11.A.1.1. Arithmetic Mean

$$\mu_m = x_1\mu_1 + x_2\mu_2$$

11.A.1.2. Geometric Mean

$$\ln \mu_m = x_1 \ln \mu_1 + x_2 \ln \mu_2$$

11.A.1.3. Harmonic Mean

$$\mu_m = \frac{1}{x_1/\mu_1 + x_2/\mu_2}$$

11.A.1.4. Grunberg and Nissan

$$\ln \mu_m = x_1 \ln \mu_1 + x_2 \ln \mu_2 + x_1 x_2 G_{12}$$

11.A.1.5. Teja and Rice

$$\ln(\mu_m \varepsilon_m) = x_1 \ln(\mu \varepsilon)_1 + x_2 \ln(\mu \varepsilon)_2$$

$$\varepsilon = \frac{V_C^{2/3}}{(T_C M)^{1/2}}$$

$$V_{Cm} = x_1^2 V_{C1} + x_2^2 V_{C2} + 2x_1 x_2 V_{C12}$$

$$T_{Cm} = \frac{x_1^2 T_{C1} V_{C1} + x_2^2 T_{C2} V_{C2} + 2x_1 x_2 T_{C12} V_{C12}}{V_{Cm}}$$

$$M_m = x_1 M_1 + x_2 M_2$$

$$V_{C12} = \frac{(V_{C1}^{1/3} + V_{C2}^{1/3})^3}{8}$$

$$T_{C12} V_{C12} = \psi_{12} (T_{C1} T_{C2} V_{C1} V_{C2})^{1/2}$$

Note: For a given T, the pure component viscosities must be evaluated at $T[T_{C1}/T_{Cm}]$ for component 1 and $T[T_{C2}/T_{Cm}]$ for component 2.

11.A.2. Diffusion Coefficient

11.A.2.1. Simple

$$D_{12} = [x_2 D_{12}^0 + x_1 D_{21}^0] \alpha$$

11.A.2.2. Vignes

$$D_{12} = [(D_{12}^0)^{x_2} + (D_{21}^0)^{x_1}] \alpha$$

11.A.2.3. Sanchez and Clifton

$$D_{12} = [x_2 D_{12}^0 + x_1 D_{21}^0] [1 - m + m\alpha]$$

(α is a thermodynamic factor defined by the specific thermodynamic model)

Thermodynamic Factor

$$\alpha = 1 + x_1 (Q_{11} - Q_{12})$$

$$Q_{11} = -\frac{2}{S_1} + \frac{x_1}{S_1^2} + \frac{x_2 \Lambda_{21}^2}{S_2^2}$$

$$Q_{12} = -\frac{\Lambda_{12}}{S_1} - \frac{\Lambda_{21}}{S_2} + \frac{x_1 \Lambda_{12}}{S_1^2} + \frac{x_2 \Lambda_{21}}{S_2^2}$$

$$S_1 = x_1 + x_2 \Lambda_{12}$$

$$S_2 = x_2 + x_1 \Lambda_{21}$$

$$\Lambda_{12} = \frac{V_{2,L}}{V_{1,L}} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right)$$

$$\Lambda_{21} = \frac{V_{1,L}}{V_{2,L}} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT}\right)$$

$$\lambda_{12} - \lambda_{11} = 325.0757 \frac{\text{cal}}{\text{mol}}$$

$$\lambda_{21} - \lambda_{22} = 953.2792 \frac{\text{cal}}{\text{mol}}$$

11.A.3. Thermal Conductivity

11.A.3.1. Arithmetic Mean

$$k_m = x_1 k_1 + x_2 k_2$$

11.A.3.2. Geometric Mean

$$\ln k_m = x_1 \ln k_1 + x_2 \ln k_2$$

11.A.3.3. Harmonic Mean

$$k_m = \frac{1}{x_1/k_1 + x_2/k_2}$$

11.A.3.4. Filippov

$$k_m = w_1 k_1 + w_2 k_2 - G_{12} w_1 w_2 (k_2 - k_1)$$

$$k_2 \geq k_1$$

11.A.3.5. Jamieson

$$k_m = w_1 k_1 + w_2 k_2 - G_{12} (k_2 - k_1) \left[1 - (w_2)^{1/2}\right] w_2$$

$$k_2 \geq k_1$$

11.A.3.6. Baroncini

$$k_m = \left[x_1^2 A_1 + x_2^2 A_2 + 2.2 \left(\frac{A_1^3}{A_2} \right) x_1 x_2 \right] \frac{(1 - T_{rm})^{0.38}}{T_{rm}^{1/6}}$$

$$A_2 \geq A_1$$

$$T_{rm} = \frac{T}{T_{Cm}}$$

$$T_{Cm} = x_1 T_{C1} + x_2 T_{C2}$$

$$k_i = \frac{A_i (1 - T_{ri})^{0.38}}{T_{ri}^{1/6}} \rightarrow A_i = \frac{k_i T_{ri}^{1/6}}{(1 - T_{ri})^{0.38}}$$

11.A.3.7. Li

$$k_m = \phi_1^2 k_1 + \phi_2^2 k_2 + 2\phi_1 \phi_2 k_{12}$$

$$k_{12} = 2(k_1^{-1} + k_2^{-1})^{-1}$$

$$\phi_i = \frac{x_i V_i}{\sum_j x_j V_j}$$

11.A.4. Surface Tension

11.A.4.1. Arithmetic Mean

$$\sigma_m = x_1 \sigma_1 + x_2 \sigma_2$$

11.A.4.2. Geometric Mean

$$\ln \sigma_m = x_1 \ln \sigma_1 + x_2 \ln \sigma_2$$

11.A.4.3. Harmonic Mean

$$\sigma_m = \frac{1}{x_1/\sigma_1 + x_2/\sigma_2}$$

11.A.4.4. Meissner and Michaels

$$\sigma_m = \sigma_w \left(1 - (0.411) \log \left(1 + \frac{x_o}{a} \right) \right)$$

$$a = 26 \times 10^4 (\text{ethanol})$$

11.A.4.5. Tamura

$$B = \log \left(\frac{\psi_w}{\psi_o} \right) = \log \left(\frac{x_w V_w}{x_o V_o} \right)$$

$$W = 0.441 \frac{q}{T} \left(\frac{\sigma_o V_o^{2/3}}{q} - \sigma_w V_w^{2/3} \right)$$

$$q = 2(\# \text{carbons})$$

$$C = B + W$$

$$\frac{\psi_w^q}{\psi_o} = 10^C$$

$$\psi_o + \psi_w = 1$$

$$\sigma_m = (\psi_w^\sigma \sigma_w^{1/4} + \psi_o^\sigma \sigma_o^{1/4})^4$$

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CONCLUSIONS

Worldwide demand for energy is increasing rapidly, at least partly driven by dramatic growth in developing countries. This growth has sparked concerns over the finite availability of fossil fuels and the impact of their combustion on climate change. Consequently, renewable fuels and sustainable energy systems have received increased attention and are expected to become critically important to support future global economic growth. Interest in liquid biofuels, such as ethanol, has been particularly high because these fuels fit into established infrastructure for the transportation sector. In fact, ethanol has been blended with gasoline and used in conventional internal combustion engines for many years.

Ethanol is a renewable fuel produced through the anaerobic fermentation of biomass-derived sugars. However, the energy intensive nature of its production process is a major factor limiting the usefulness of ethanol as a biofuel. The separation processes currently employed to recover ethanol from the fermentation stream are particularly inefficient, usually accounting for more than 50 % of the total process energy demand. Two primary factors are responsible for the inefficiency of the ethanol separation processes. First, the fermentation product is relatively dilute, containing at most 10 % ethanol when conventional substrates are used in the fermentation and at most 5 % ethanol when cellulosic substrates are employed. Secondly, ethanol and water form an azeotrope at approximately 95.6 % ethanol by mass. Since only low water content ethanol can be blended with gasoline and used in gasoline burning engines, special techniques are required to break the azeotrope. The most commonly used methods for ethanol dehydration are currently extractive distillation, pressure swing adsorption of water on molecular sieves and pervaporation/vapour permeation of water through hydrophilic membranes.

In the conventional ethanol separation process, ethanol is recovered using several distillation steps combined with a dehydration process. Normally, the fermentation mixture is first passed through a beer column. This column acts as a steam stripping column to produce a vapour phase distillate stream having an ethanol concentration between 30 and 60 % by mass. The final concentration of the distillate depends on the column design and the composition of the

feed stream. The bottoms product leaving the beer column is essentially water, with some residual solids. The vapour stream leaving the beer column usually enters another column, which operates as the enriching section of a distillation column. The distillate leaving the enriching column is normally near the azeotropic composition (typically between 90 and 94 % ethanol by mass). This distillate stream then undergoes dehydration to produce an anhydrous ethanol product. The bottoms product from the enriching column can go to a separate stripping column or be returned to the beer column.

In this dissertation, a new hybrid pervaporation-distillation separation system, named Membrane Dephlegmation, was investigated for use in efficient ethanol recovery. The ultimate goal was to synthesize a more efficient separation system to replace the enriching column and dehydration section of the ethanol recovery process. The process was investigated using both numerical and experimental techniques. Details of the individual studies were presented in journal paper format in the preceding chapters. To summarize the most important findings, the following sections highlight the major contributions made in the publications presented in this dissertation. More research efforts are necessary to determine whether Membrane Dephlegmation is competitive with conventional ethanol separation processes. Further, it has not been established whether the Membrane Dephlegmation process could be applied to other chemical systems. A list of recommendations for future research efforts is therefore also provided below.

12.1. Major Contributions

This section provides a brief summary of the major contributions included in each of the journal papers presented in this dissertation. The contributions are divided into the chapters in which they were presented.

Chapter 3: In this paper, six alternative ethanol recovery processes were investigated. Process simulations were performed to estimate energy efficiency and cost. Weaknesses and potential processing improvements were highlighted in the conventional process. Further, economic and energy targets were established. These economic and energy targets provide a convenient baseline to which other ethanol separation processes should be compared. It was shown that distillation using two heat integrated columns operating at different pressures provided a good compromise between economics and energy efficiency.

Chapter 5: In this paper, an overview of the Membrane Dephlegmation concept was presented. In Membrane Dephlegmation, as opposed to most other hybrid distillation-pervaporation processes, the distillation and pervaporation processes are carried out in a single unit. A mathematical model was derived to explain the transport phenomena occurring in the process. Simulations were carried out to compare Membrane Dephlegmation with distillation. It was determined that Membrane Dephlegmation provided improved performance over distillation and that the process was capable of breaking the ethanol-water azeotrope.

Chapter 6: In this study, the effect of important operating conditions and geometric variables on Membrane Dephlegmation performance was investigated. Investigated parameter included the feed flow rate, feed concentration, permeate pressure, reflux ratio, membrane length and membrane diameter. McCabe-Thiele plots were used to compare the operating lines of Membrane Dephlegmation to conventional distillation. It was shown that the pervaporation of water in Membrane Dephlegmation shifts the operating line below the 45 degree line, leading to greater separation efficiency compared to distillation.

Chapter 7: In this paper, Membrane Dephlegmation was studied using a pilot-scale experimental system. The system used commercially available NaA zeolite pervaporation membranes. Experiments were performed at a variety of feed concentrations, feed flow rates, reflux ratios and permeate pressures. The system was also operated as a wetted-wall distillation to characterize vapour-liquid contacting performance. The experimental results were used to validate the mathematical model and to determine important model parameters. Long-term membrane stability was also studied.

Chapter 9: In this study, the effects of operating parameters and physical properties on countercurrent vapour-liquid flow in a narrow channel were investigated using multiphase CFD. The Volume-Of-Fluid method was used to track the movement of the vapour-liquid interface. A simple analytical flow model was also derived and compared to the CFD results. It was shown that the analytical model compared well with CFD predictions at low velocities.

Chapter 10: In this paper, a method was developed to track vapour-liquid interface dynamics and directly estimate interphase heat and mass transfer rates in systems with multiple chemical species. Due to the industrial importance of multicomponent vapour-liquid flows, this method has wide reaching implications. The Volume-of-Fluid method was used for interface tracking. To estimate coupled heat and mass transfer rates, the full interface species and energy jump conditions were incorporated into the method. The model was validated using the ethanol-water system for two cases. Good agreement was observed between empirical correlations, experimental data and numerical predictions for vapour and liquid phase mass transfer coefficients. Direct numerical simulation of interphase heat and mass transfer offers the clear advantage of providing detailed information about local heat and mass transfer rates, without the need for experiments. Thus, simulations can be carried out for a representative geometry and the results can be used to develop heat and mass transfer models that may be integrated into large scale process simulation tools and used for equipment design and optimization.

Chapter 11: In this paper, neural network models were developed to correlate data for important transport properties for the ethanol-water system. Specifically, models were developed to estimate viscosity, thermal conductivity, surface tension and the Fick diffusion coefficient. The neural network models were shown to provide highly accurate predictions of the transport properties. These models were incorporated into the simulations presented in Section II and Chapters 9 and 10.

12.2. Future Work

Membrane Dephlegmation appears to be a promising separation technology for improving the efficiency of distillation processes and breaking azeotropes. However, more research efforts are necessary to determine whether Membrane Dephlegmation is competitive with conventional ethanol separation processes. Further, its applicability to other chemical separations has not yet been established. The computational method presented in Chapter 10 could theoretically be used to predict heat and mass transfer in all types of multicomponent vapour-liquid flows. However, the method has so far only been tested for two geometries for the ethanol-water system. A list of recommendations for future research efforts is provided below.

The recommendations are divided into sections focusing on Membrane Dephlegmation and the direct simulation of interphase heat and mass transfer.

Membrane Dephlegmation:

1. A technical and economic analysis should be performed for an ethanol recovery process employing Membrane Dephlegmation, to ascertain the industrial feasibility of such a process. The results should be compared to the baseline targets established in Chapter 3.
2. The Membrane Dephlegmation process is not limited to ethanol separation. The process could be applied to other organic-water or organic-organic systems. In fact, the process is not even limited to systems with azeotropes. Of course, suitable pervaporation membranes are required. Other applications of Membrane Dephlegmation should be investigated.
3. In the studies presented in Section II of this dissertation, Membrane Dephlegmation was used in place of the enriching section of a distillation column. However, it may also be possible to use a similar process in place of the stripping section. Such a process would be applicable to systems where vapour-liquid equilibrium unfavourable at low concentrations. Of course, the membranes employed in such a process would be exposed to vapour coming directly from the reboiler and would therefore need to be stable at high temperatures.

Direct Numerical Simulation of Heat and Mass Transfer:

1. The computational method developed in Chapter 10 has only been tested for two two-dimensional cases for the ethanol-water system. Since the formulation is not limited to binary systems, the method should be applied to investigate phase change in true multicomponent system. Further, the proposed framework is not limited to two-dimensional simulations. The performance of the method to estimate heat and mass transfer rates in three-dimensional geometries should therefore be assessed.
2. The Volume-Of-Fluid method is one of the most commonly employed interface tracking techniques. However, other methods, including level set, compressive interface capturing and phase field methods are available. These methods are beneficial in the simulation of some types of free surface flows. The method developed in Chapter 10 to estimate heat and mass transfer rates does not necessarily need to be coupled with the Volume-Of-Fluid method to track interface motion. In fact, only estimates of the interface location

and local interfacial area are necessary. All of the aforementioned interface tracking techniques permit estimation of the interface location and interfacial area. Approaches should therefore be developed to integrate the method from Chapter 10 into other interface tracking frameworks.