THEORETICAL STUDY ON THE PRODUCTION OF ISOPROPYL ACETATE IN MEMBRANE REACTOR

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Computer Aided Process Plant Design)

By

KESHAV DIXIT

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE - 247 667 (INDIA)
JUNE, 2008

CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the dissertation entitled, **"THEORETICAL STUDY ON THE PRODUCTION OF ISOPROPYL ACETATE IN MEMBRANE REACTOR"** in partial fulfillment of the requirement for the award of the degree of Master Of Technology in Chemical Engineering with specialization in **"COMPUTER AIDED PROCESS PLANT DESIGN"**, and submitted in the **Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee**. This is an authentic record of my own work carried out during the period of July 2007 to June 2008, under the esteemed guidance of **Dr. (Mrs.) Shashi**, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee.

The matter presented in this dissertation has not been submitted by me for the award of any other degree of this or any other Institute.

Date: June, 2008|23
Place: IIT Roorkee

Keshav Dixit
(Keshav Dixit)

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Shashi
Dr. (Mrs.) Shashi
Assistant Professor,
Department of Chemical Engineering,
Indian Institute of Technology,
Roorkee-247667

ACKNOWLEDGEMENT

I am greatly indebted to my guide **Dr. Shashi Kumar**, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, for her kind support and guidance during the entire the course of this work. Her co-operation and in depth knowledge have made my work possible.

My special thanks are due to **Dr. Surendra Kumar**, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, whose valuable knowledge helped me in understanding the phenomena during this work.

I would like to thank **Dr. Shrichand**, Head of Department, and Chairman, DRC, Department of Chemical Engineering, Indian Institute of Technology Roorkee, for providing various facilities during the course of this work.

I would like to thank Mr. Rahman Jee, Mangeram Jee, tripta Mem for their kind co-operation.

I would like to thank Aditya, Mohit, Zafar Sir and all of my friends for their suggestions and help in completion of this work.

Last but not least, it is all owed to the blessing of my parents and God that I have come up with this work in the due time.

Keshav Dixit

(Keshav Dixit)

ABSTRACT

In the field of chemical engineering, separation and purification of physical and chemical mixtures has been one of the major concerns. From the beginning of industrial development, large scale separations involving distillation, adsorption, filtration etc. have been introduced as unit operation processes. For all reversible reactions it is difficult to attain high conversion due to equilibrium limitation. Presently membrane reactors are used to overcome the equilibrium restrictions for liquid phase reversible reactions.

Membrane reactor is a chemical reactor in which membrane is uses as a separator. Membrane reactor is uses in a number of processes like dehydrogenation, hydrogenation, dehydration, reforming and waste water treatment. Membrane is a semi permeable barrier used to partially separate the components in reacting mixture. Esterification is one of the most important chemical processes. From thermodynamic point of view the conversion of esterification reaction is limited by the equilibrium value. To increase the equilibrium conversion of this reaction we use membrane reactor. Reactor used in this case is tubular. Isopropanol and Amberlyst 15 heated to reaction temperature and acetic acid heated separately and sends to tube side o the reactor. The sweep gas is feed in shell side. In order to study the performance of a reactor, it is essential to understand the complex process occurring in the membrane reactor. Thus it is desirable to develop a mathematical model for esterification reaction in a membrane reactor.

In the present work a steady state model for isothermal conditions has been developed which incorporates eight ODE's with appropriate constitutive relationships. The model equations are solved by ODE 45 solver in MATLAB 7.5. The experimental operating data are available in literature were selected for the validation of the model. The results are found to be in good agreement. The effect of operating parameters is studied.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

D_i	Diffusion coefficient	cm^2/min
F_i	Molar flow rate of species i	mol/min
j_i	Flux of component i	$mol/cm^2/min$
k^o	Pre exponential Arrhenius factor	mol/gm/min
k_1	Forward reaction rate constant	$cm^3/mol/min$
k_2	Backward reaction rate constant	$cm^3/mol/min$
k_e	Forward reaction rate constant	mol/gm/min
k_h	Backward reaction rate constant	mol/gm/min
L	Membrane length	cm
M	Mole ratio of isopropanol and acetic acid	-
m_{cat}	Mass of catalyst	gm
R	Gas constant	J/mol/K
r_1	Inner radius of membrane tube	cm
r_2	Outer radius of membrane tube	cm
r_i	Reaction rate of species i	$mol/cm^3/min$
r_i'	Reaction rate of species i	mol/gm/min
S	Membrane area	cm^2
T	Absolute temperature	K
w	Weight fraction	-
X	Conversion	-
x_i	Mole fraction of species	-
Δz	Control volume length	cm

Greek letters

γ	activity coefficient
v	stoichiometric coefficient
δ	rate ratio
τ	plasticizing coefficient

Subscript letters

A	acetic acid
B	isopropanol
E	isopropyl acetate
e	esterification reaction
f	feed side
feed	feed side
h	hydrolysis reaction
i, j	components
o	inlet conditions
s	shell side
t	tube side
W	water

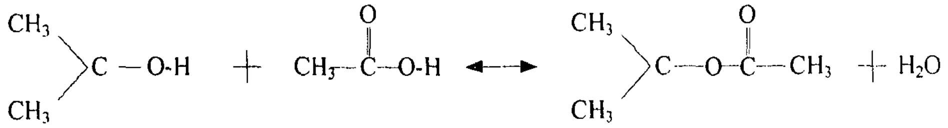
CHAPTER 1

INTRODUCTION

Membranes have gained an important place in chemical industries and are used in a broad range of applications. The key property of a membrane is to control the permeation rate of a chemical species through the membrane. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other components.

Since membrane permit selective permeation of one component from a mixture, the conversion of thermodynamically limited reactions can be enhanced through removing one or more product species from the reacting mixture. There are many equilibrium-limited systems where the applications of this concept would be beneficial, including dehydrogenations, synthesis of gas production and esterification. In this we focus on esterification coupling. Industrially widely applied esterification reactions are conveniently catalyzed using mineral acids. Esters have various applications, ranging from plasticizers, surface active agents, flavor and perfume materials, to solvent for the production of various chemicals. One of the main disadvantages of esterification reactions is that it has a low conversion. A simplified reaction equation is given by:

$$RCOOH + ROH \leftrightarrow RCOOR + H_2O$$



There are two methods to improve the conversion of equilibrium reactions. In the first approach, a large excess of one of the starting reactants is used. However, this result in a relatively inefficient use of reactor space and efficient separation is required after reaction products. For esterification reaction water is most appropriate component that can be removed. There are a number of ways to remove the water. Reactive distillation is an appropriate technique for removal of water (fig 1.1). However, for these systems the formation of an azeotrope is a potential drawback, which limits the selectivity. The main purpose of pervaporation membrane is to remove the water from the reaction mixture in acid with ethanol, and the equilibrium conversion was exceeded by removing water by pervaporation.

The replacement of the more common separations operations with membrane separations has the potential to save large amount of energy. This replacement require the production of high mass-transfer flux, defect-free, long life membrane on a large scale and the fabrication of the membrane into compact, economical modules of high surface area per unit volume.

1.1 DEFINITION OF MEMBRANE:

A membrane is a very thin envelope that surrounds and protects a cell. It controls the exchange between the cell and exterior environment. The membrane allows the passage of certain substances and prevents the passage of others. A membrane is a device that selectively permits the separation of one or more materials from a liquid. The first is the use of a membrane to remove a product from a reaction limited by chemical equilibrium, thus allowing higher conversions than would be possible in a conventional fixed bed catalytic reactor. Third is the use of the membrane to control how the reactants contact.

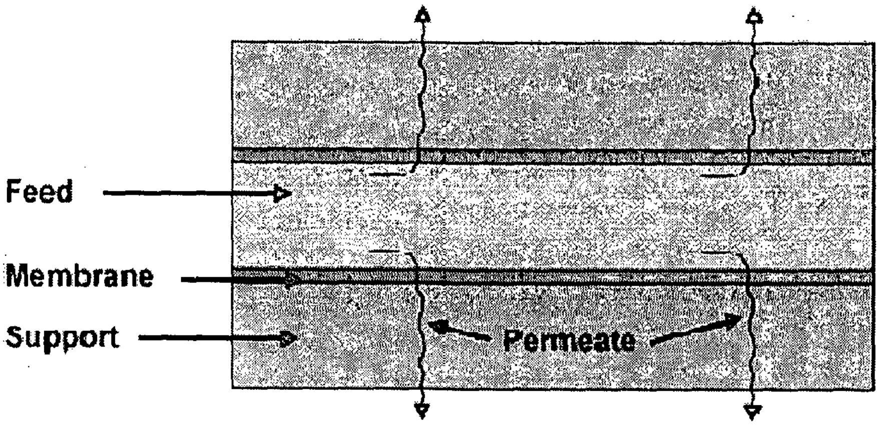


Fig 1.5 Membrane

In *Membrane Separation* [21]:

1. The two products are usually miscible.
2. The separating agent is semipermiable barrier.
3. A sharp separation is difficult to achieve.

Membrane separation is an emerging unit operation. Important progress is still being made in the development of efficient membrane materials and the packaging. Applications covering wider ranges of temperature and types of membranes materials are being found. Membrane separation processes have found wide application in such diverse industries as the beverage, chemicals, dairy, electronic, environmental, food, medical, paper, petrochemical, petroleum, pharmaceutical, and textile industries. Often compared to other separation equipment, membrane separators are more compact, less capital intensive and more easily operated, controlled and maintained.

Membrane is used as an active participant in a chemical transformation for increasing the reaction rate, selectivity and yield. The membrane does not only play the role as a separator but also as part of the reactor. Many catalytic processes of industrial importance (classically using fixed, fluidized or trickle bed reactors) involve the combination of high temperature and chemically harsh environments, two factors that strongly favor inorganic membranes. Mesoporous inorganic membranes have been used in large-scale gas diffusion process for uranium isotope separation.

Although much information about the mesoporous inorganic membranes used in the gas diffusion plants is still classified, mesoporous ceramic membranes, especially those made by the sol-gel method, have recently found many commercial applications. More importantly, decade has seen substantial progress in microporous and dense inorganic membranes. According to the IUPAC definition, microporous inorganic membranes are referred to those porous membranes with a pore diameter smaller than 2 nm. Microporous inorganic membranes include amorphous and crystalline (zeolite) ceramic membranes. The practically useful crystalline microporous membranes are of polycrystalline structure, consisting of many crystallites packed together without crystallite (grain) boundary gap in ideal case. Dense inorganic membranes are referred to those membranes made of a polycrystalline ceramic or metal, which allows certain gas materials to permeate through its crystal lattice.

Microporous inorganic membrane are always prepared as a thin film supported on porous inorganic support, which provide mechanical support but offers minimum mass transfer resistance. The permeate flux decreases dramatically during filtration process caused by the adsorption of solutes on outer membrane and inner pore surface, blocking of pores by rejected solutes or formation of a thick cake layer of precipitated solutes on top of the membrane. These would reduce productivity, and potentially shorten membrane life. Minimization of membrane fouling is essential to make the membrane process economical. A detailed understanding of causes of flux decline and their relative contribution are essential for minimizing fouling. For example, if adsorption is the main cause of fouling, then improvement of mass transfer by altering hydrodynamics is of little benefit.

To understand the mechanisms of flux decline, we used the resistance in series model and experimental methods to measure each of the fouling resistance. The fouling resistance is dependent on operation such as transmembrane pressure and cross flow velocity, as well as conditions of the solution such as concentration and size distribution of colloids, characteristics of membrane such as pore size, chemical nature, etc..

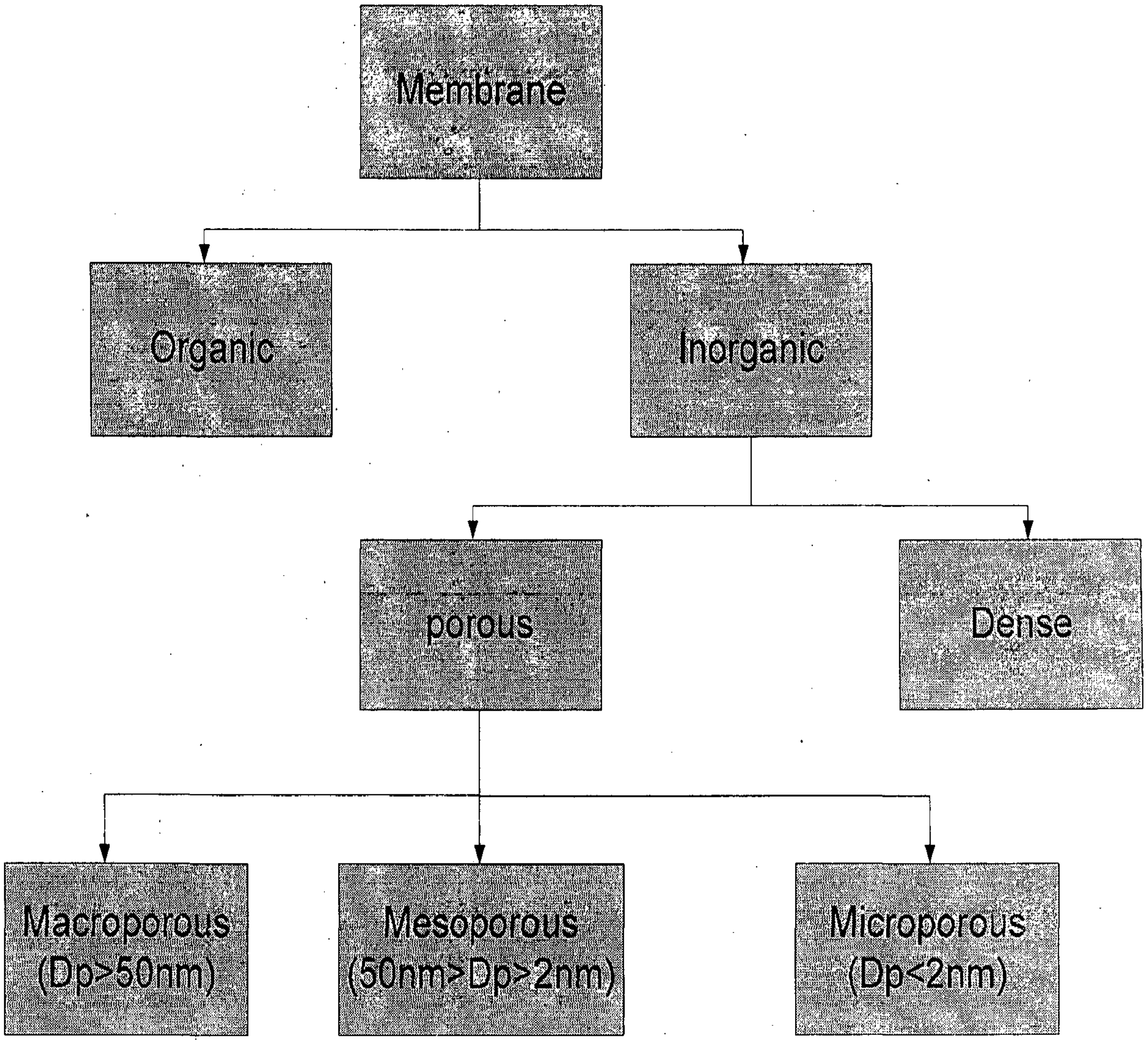
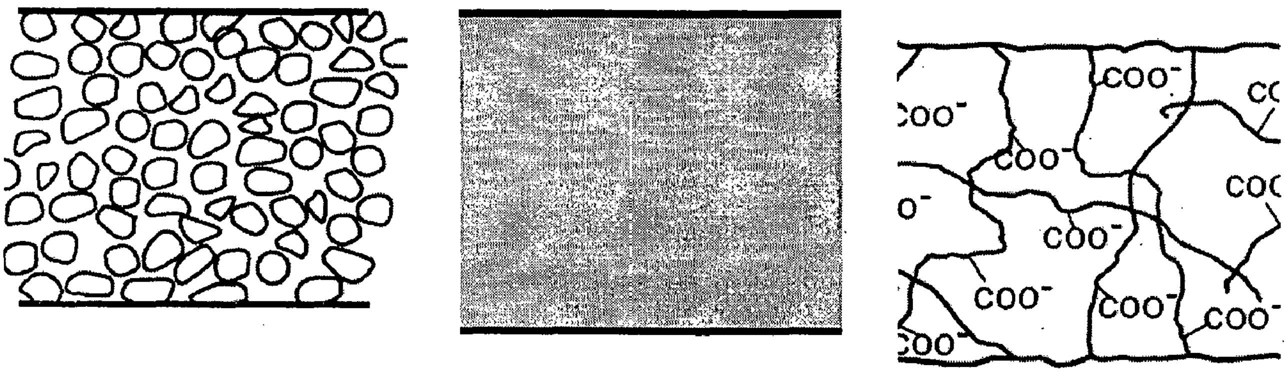


Fig 1.6 Classifications of membranes

1.2 TYPES OF MEMBRANE:

A membrane is nothing more than a discrete, thin interface that moderates that permeation of chemical species in contact with it. A whole normal filter meets this definition of a membrane, but by, convention, the term filter is usually limited to structures that separate particulate suspensions larger than 1 to 10μm.

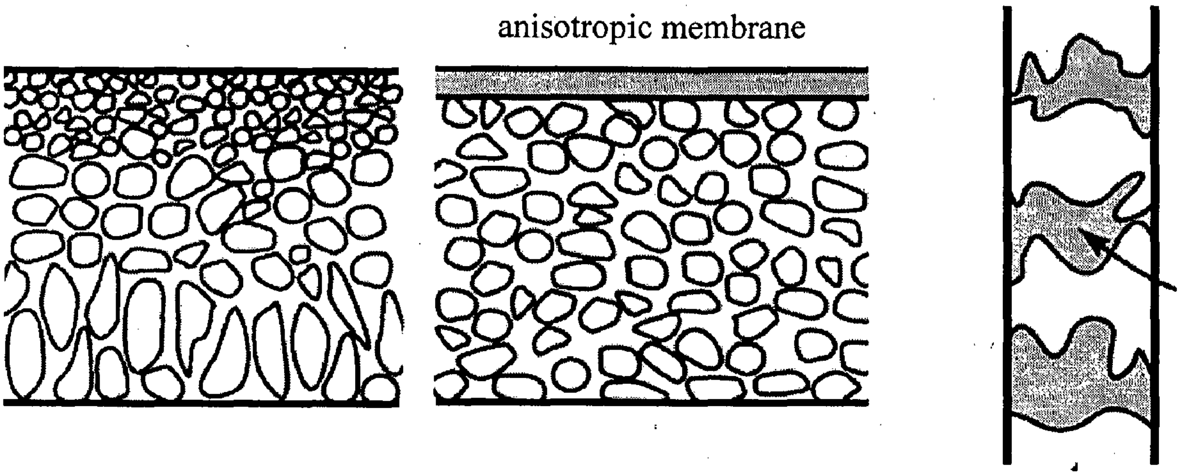
Symmetrical Membranes:


Isotropic microporous membrane

Nonporous dense membrane

Electrically charged membrane

Anisotropic Membranes:


Anisotropic membrane

Thin-film composite anisotropic membrane

Supported liquid

Fig 1.7 Schematic diagrams of the principal types of membranes

1.2.1 Organic Membranes:

Hydrogen-selective membranes include organic membranes, generally of the organic polymer type in the form of hollow fibers, and dense metallic membranes, mainly constituted by palladium and at least one other metal, which from a hydrogen-permeable alloy. Organic membranes are unstable especially in the presence of traces of aromatics, olefins and hydrogen sulphide. They degrade chemically, lose their properties at temperatures of more than 90-120^{0}C and require a high feed pressure, generally in the range 5-9 MPa. Metallic membranes require high temperature operations, generally of the order of 400-500^{0}C., and the hydrogen flux through such dense membrane remains low to very low. Further, such membranes are particularly sensitive to the effects of molecules such as carbon monoxide CO, carbon dioxide CO_2, hydrogen sulphide H_2S, or olefins, which inhibit, poison the membranes or dissolve in the metal (forming metal sulphide and carbides), limiting the flux of hydrogen through the membrane. Further, the hydrogen permeability of said organic and metallic membranes, which are dense materials, remains low.

1.2.2 Isotropic Membranes:

1.2.2.1 Microporous Membranes:

A microporous membrane is very similar in structure and function to a conventional filter. It has a rigid, highly voided structure with randomly distributed, interconnected pores. However, these pores differ from those in a conventional filter by being extremely small, on the order of 0.01 to 10 μm in diameter. All particles larger than the largest pores are completely rejected by the membranes. Particles smaller than the largest pores, but larger than smallest pores are partially rejected, according to the pore size distribution of the membrane. Particles much smaller than the smallest pores will pass through the membrane. Thus separation of solutes by microporous membrane is mainly a function of molecular size and pore size distribution. In general, only molecule that differs considerably in size can be separated effectively by microporous membrane, for example, in ultrafiltration and microfiltration.

1.2.2.2 Nonporous, Dense Membranes:

Nonporous, dense membrane consists of a dense film through which permeates are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material. Thus nonporous, dense membrane can separate permeants of similar size if their concentration in the membrane material (that is their solubility) differs significantly. Most gas separation, pervaporation, and reverse osmosis membranes use dense membrane to perform the separation. Usually these membranes have an isotropic structure to improve the flux.

1.2.2.3 Electrically Charged Membranes:

Electrically charged membrane can be dense or micro porous, but are most commonly very finely micro porous, with pore walls carrying fixed positively or negatively charged ions. A membrane with fixed positively charged ions is referred to as an anion-exchange membrane because it blinds anions in the surrounding fluid. Similarly, a membrane containing fixed negatively charged ions is called cation-exchange membrane. Separation with charged membranes is achieved mainly by exclusion of ions of the same charge as the fixed ions of the membrane structure, and to a much extent by the pore size. The separation is affected by the charge and the concentration of the ions in solution. For example, monovalent ions are excluded less effectively than divalent ions, in solutions of higher ionic strength, selectivity decreases. Electrically charged membranes are used for processing electrolyte solutions in electro dialysis.

1.2.3 Anisotropic Membranes:

The transport rate of a species through a membrane is inversely proportional to the membrane thickness. High transport rates are desirable in membrane separation processes for economic reasons; therefore, the membrane should be as thin as possible. Conventional film fabrication technology limits manufacture of mechanically strong defect-free film to about 20 μm thickness. The development of novel separation techniques to produce anisotropic membrane structures was one of the breakthroughs of the membrane technology during the past 30 years. Anisotropic membranes consist of an extremely thin surface layer supported on a much thicker, porous substructure. The surface layer and its substructure may be formed in single operation or separately. In composite membranes, the layers are made from different polymers. The separation properties and permeation rates of the membrane are determined exclusively by the surface layer; the substructure functions as a mechanical supports. The advantages of the higher fluxes provided by the anisotropic membranes are so great that almost all commercial processes use such membrane.

1.2.4 Ceramic, Metal and Liquid Membranes:

Membrane materials are organic polymers and, infect, the vast majority of membranes used commercially are polymer-based. However, in recent years, and interest in membranes formed from less conventional materials has increased. Ceramic membranes, a special class of microporous membranes, are being used in ultrafiltration and microfiltration applications for which solvent resistance and thermal stability are required. Dense metal membranes, particularly palladium membranes, are being considered for the separation of hydrogen from the gas mixtures, and supported liquid films are being developed for carrier-facilitated transport processes.

1.2.5 Zeolite Membranes:

A zeolite membrane is a porous layer that can separate mixtures by adsorption and diffusion differences, and in some cases, by molecular sieving Zeolite are inorganic crystalline structures with uniform, molecular-sized pores, and high mechanical, and chemical stability. These properties give zeolite membranes advantages over many polymeric membranes. Now more than 12 zeolite structures have been prepared as membranes. Zeolite membranes are most often polycrystalline layers deposited on tubular or discshaped porous supports. Significant work has been done to reduce the inter crystalline defects, improve crystal orientation and reduce the thickness of zeolite layers. Both gas separations and pervaporation using zeolite membranes have reported, with most studies focusing on membrane preparation and performance.

The materials of membrane construction can be classified as either dense or porous. Dense materials include palladium membranes that are semipermiable to hydrogen, and solid oxide electrolyte dense membranes such as modified zirconias and perovskites, which have reasonably high oxygen permeation rates at high temperatures. Porous inorganic membranes can be divided into Macroporous ($d_p>50$nm), mesoporous ($50>d_p>2$ nm) and microporous ($d_p>2$ nm). Macroporous materials, such as alumina membranes, provide no separative function, but may be used to support layers of smaller pore size to from composite membranes, or in applications where a well-controlled reactive interface is required.

Mesoporous materials for membranes have generally had pore sizes in the 4-5 nm range, so that permeation is governed by Knudsen diffusion. Typical materials are vycor glass, and composite membranes. Microporous membranes offer the potential for molecular sieving affects, with very high separation factors, and materials such carbon molecular sieves, porous silica and zeolite have been studied. The most active areas of development for membrane materials are currently synthesis of supported thin films such as supported Pd films on porous alumina or on porous stainless steel, and supported zeolite films.

1.3 MEMBRANE MATERIALS [21]:

All industrial membranes processes are made from natural or synthetic polymers. Natural polymers include wool, rubber, and cellulose. A wide variety of synthetic polymers has bee developed and commercialized since 1930. Synthetic polymers are produced by polymerization of a monomer by condensation or addition or by the copolymerization of two different monomers. The resulting polymer is categorized as having [21]:

1. A long linear chain such as linear polyethylene.
2. A branched chain, such as polybutadiene.
3. A three dimensional, highly cross-linked structure, such as phenol formaldehyde.
4. A moderately cross-linked structure, such as butyl rubber.

The linear polymeric chain softens with increase in temperature, is often soluble in organic solvents, and are referred as thermoplastic polymers. At other extreme, highly cross-linked polymers do not soften appreciably, are almost insoluble in most of organic solvents, and are referred to as thermosetting polymers. At low temperature, typically below 100^0C, idealized polymers can be classified as glassy or crystalline. If the temperature of a glassy polymer is increased, a point called glass transition temperature. T_g may be reached where the polymer become rubbery. If the temperature of crystalline material is increased, a point called melting temperature T_m, is reached where the polymer is melted, however thermosetting plastic never melts. Most polymers have both amorphous and crystalline regions, that is, a certain degree of crystallinity that varies from 5 to 90%, making it possible for some polymers to have both a T_g and a T_m. Membranes made of glassy polymers can operate below or above T_g; membranes of crystalline polymers must operate below T_m. Cellulose is the most readily available organic raw material in the world. The repeat unit of identical to cellulose triacetate groups are replaced by H. typically the number of repeat units (degree of polymerization) in cellulose is 1,000 to 1,500 whereas that in cellulose triacetate is around 300. Partially acetylated products are cellulose acetate and cellulose diacetate, with blends of two or three of the acetates being common. The triacetate is highly crystalline, of uniformly high quality hydrophobic.

Different Polymers Used As Membranes Materials:

Polyisoprene (natural rubber) is obtained from at least 200 different plants, with many of the rubber-producing countries being located in the Far East. Compared to the other polymers Polyisoprene has very low glass-transition temperature. Natural rubber has a degree of polymerization of from about 3,000 to 4,000 and is hard and rigid when cold, but soft easily deformed, and sticky when hot. Depending on the temperature, it slowly crystallizes. To increases the strength, elasticity and stability of rubber, it is vulcanized with sulfur, a process that introduces cross-link, but still allow unrestricted local motion of the polymer chain.

Aromatic polyamides are high-melting crystalline polymers that have better long-term thermal stability and higher resistance to solvents than do aliphatic polyamides, such as nylon. Some aromatic polyamides are easily fabricated into fiber, films, and sheets. Polyamides are characterized by the presence of aromatic rings and heterocyclic rings containing nitrogen attached oxygen. Polyimide is tough, amorphous polymers with high resistance to heat and excellent wear resistance. They can be fabricated into a wide variety of forms, including fibers, sheets, and films.

Polystyrene is a linear, highly pure polymer of about 1,000 units of the structure. Above a relatively low T_g, which depends on molecular weight, polystyrene becomes a viscous liquid that is easily fabricated by extrusion or injection molding. Like many other polymers, polystyrene can be annealed (heated and then cooled slowly) to convert it to a crystalline polymer with a melting point of 240^0C. Styrene monomer can be copolymerized with a number of other organic monomers, including acrylonitrile and butadiene from ABS copolymers.

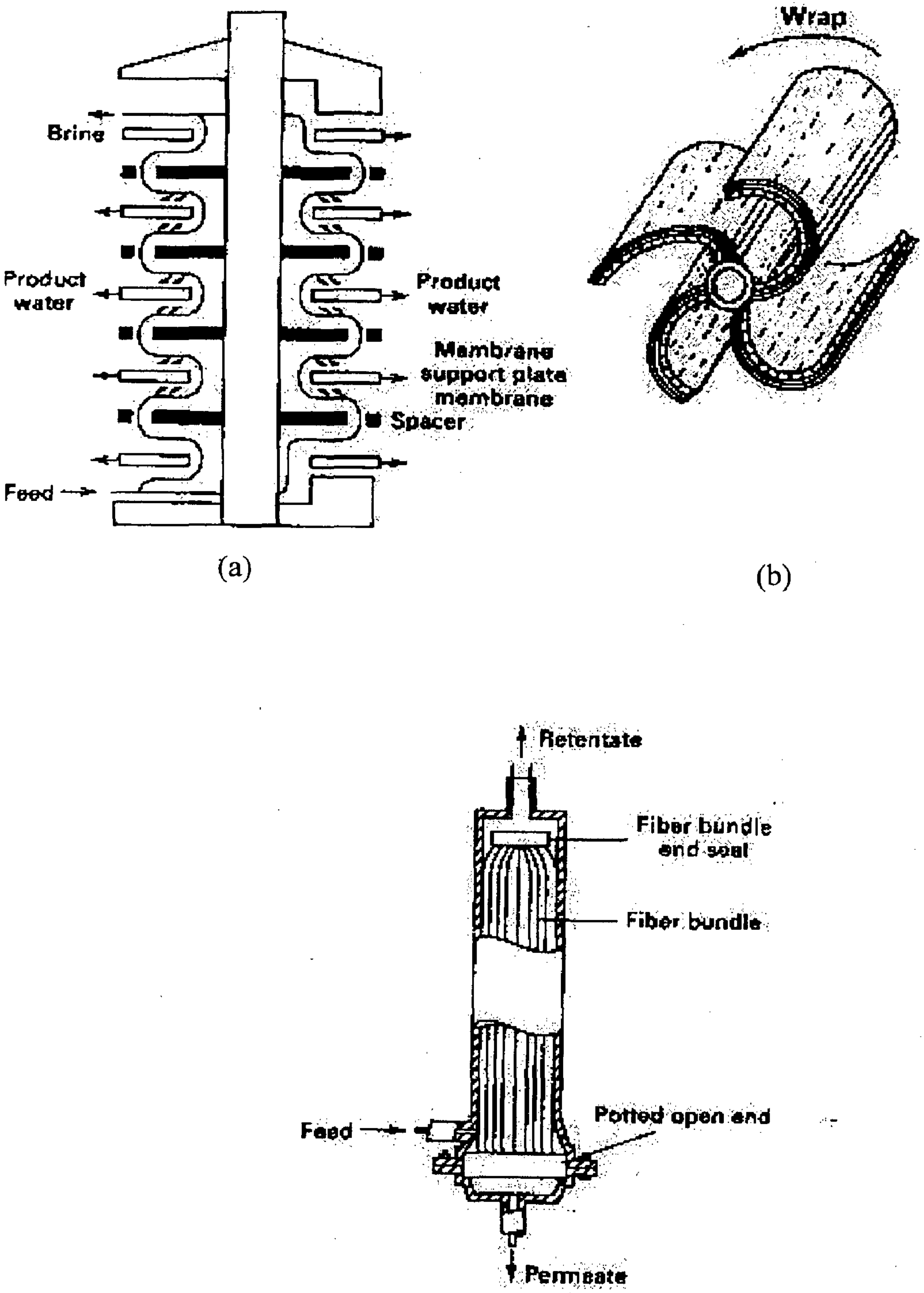
Polysulfones are relatively new synthetic polymers, first introduced in 1966. It contains the SO_2 group, which gives the polymers high strength. Polysulfones are easily spun into hollow fibers. Polytetrafluroethylene is a straight-chain, highly crystalline lymer with a very high degree of polymerization of the order of 100,000, which gives it considerable strength. It possesses exceptional thermal stability and can be formed into sheets, films, and tubing.

To be effective for separating a mixture of chemical components, a polymer membrane must possess high permeance and a high permeance ratio for the two species being separated by the membrane. The permeance for given species diffusing through a membrane of given thickness is analogues to a mass transfer coefficient. i.e. The flow rate of that species per unit cross-sectional area of membrane per unit driving force (concentration, partial pressure, etc.) the molar transmembrane flux of species is

$$N_i = (\frac{P_{Mi}}{l_M})(driving\ force) = \overline{P_{Mi}}(driving\ force) \qquad (1)$$

Where $\overline{P_{Mi}}$ is the permeance, which is defined as the ratio of P_{Mi}, the permeability, to l_M the membrane thickness. Polymer membrane can be dense or microporous. For dense amorphous membranes, no pores of microscopic dimensions are present, and diffusing species must dissolve into the polymer and then diffuse through the polymer between the segments of the macromolecular chains. A microporous membrane contains interconnected pores that are small (on the order of 0.005-20 μm), but large in comparison to the size of small molecules. The pores are formed by a variety of proprietary techniques. Such techniques are especially valuable for producing symmetric, microporous, crystalline membranes. Permeability for microporous is high, but selectivity is low for small molecules.

1.4 MEMBRANE MODULES:



(a) (b)

(c)

Fig 1.8 Common membrane module: (a) plate and frame, (b) four-leaf spiral wound, (c) hollow fiber [21]

1.5 MODULE FLOW PATTERN:

Perfect mixing was assumed on both sides of the membrane. Three other idealized flow patterns shown in Fig 1.9, have received considerable attention, all assume no mixing and are comparable to the idealized flow patterns used to design heat exchangers. These patterns are (b) countercurrent flow (c) cocurrent flow, and (d) crossflow. The flow pattern can significantly affect the degree of separation and the membrane area.

For flow patterns (b) to (d), fluid on the feed or retentate side of the membrane flows along and parallel to the upstream surface of the membrane. For countercurrent and cocurrent flow, permeate fluid at a given location on the downstream side of the membrane consists of fluid that has just passed through the membrane at the location plus the permeate fluid to that location. For the crossflow case, there is no flow of permeate fluid along the membrane surface. The permeate fluid that has just passed through the membrane at a given location is the only fluid there. For given module geometry, it is not always obvious which idealized flow pattern to assume.

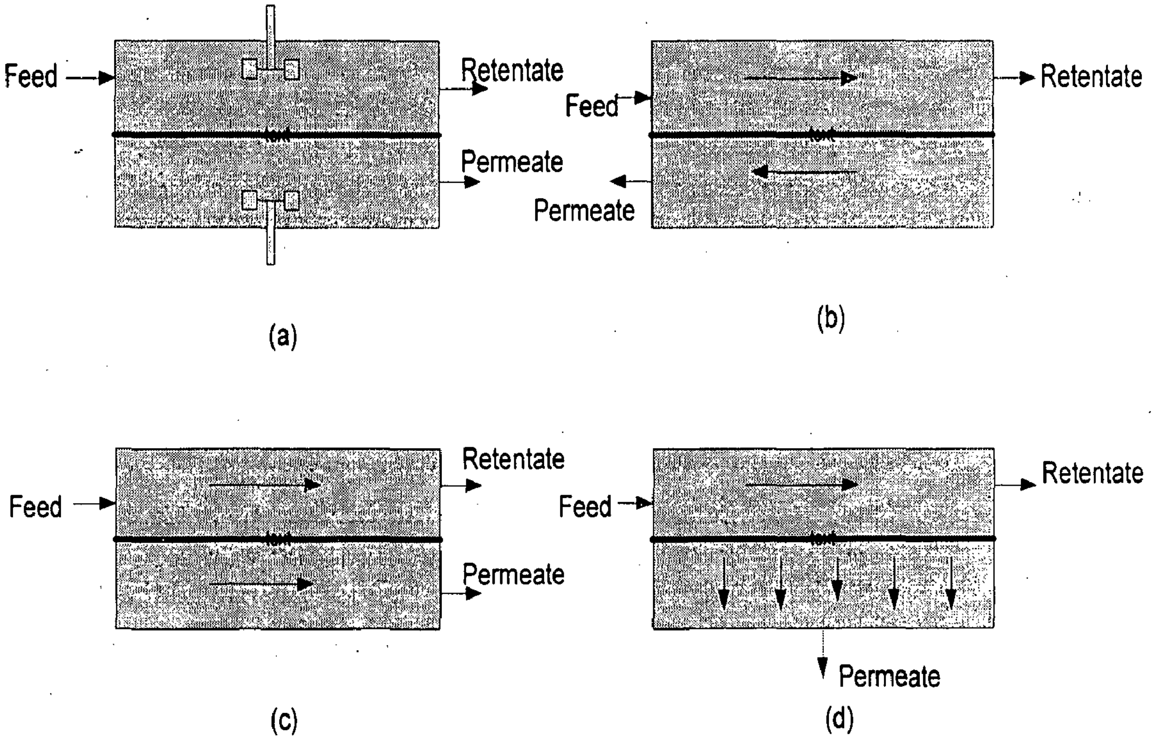


Fig 1.9 Idealized flow patterns in membrane modules: (a) perfect mixing; (b) countercurrent flow; (c) cocurrent flow; (d) crossflow.

Table 1.1 Characteristics of membranes used in different membrane separation processes, process driving forces and applications of such processes

Process	**Membrane types and pore radius**	**Membrane material**	**Process diving force**	**Applications**
Microfiltration	Symmetric microporous, 0.1-10 microns	Cellulose nitrate or acetate, Polyvinylidene difluoride (PVDF), Polyamides, Polysulfone, PTFE, Metal Oxides etc.	Hydro-static pressure difference at approx. 10-500 kp	Sterile filtration, Clarification
Ultrafiltration	Asymmetric microporous, 1-10 nm	Polysulfone, Polypropylene, Nylon 6, PTFE, PVC, Acrylic Copolymer	Hydrostatic pressure difference at approx. 0.1-1.0 Mpa	Separation of macromolecular solutions
Reverse Osmosis	Asymmetric skin-type, 0.5-1.5 nm	Polymers, Cellulosic acetate, Aromatic Polyamide	Hydrostatic pressure difference at approx. 2-10 Mpa	Separation of salts and microsolutes from solutions
Electrodialysis	Cation and anion exchange membrane	Sulfonated cross-linked polystyrene	Electrical potential gradient	Desalting of ionic solutions
Gas Separation	Asymmetric homogeneous polymer	Polymers & copolymers	Hydrostatic pressure and concentration gradients	Separation of gas mixtures
Pervaporation	Asymmetric homogenous polymer (A non-porous membrane)	Polyacrylonitrile, Polymers	Vapour pressure gradient	Separation of azeotropic mixtures
Nanofiltration	Thin-film membranes	Cellulosic Acetate and Aromatic Polyamide	9.3-15.9 bar	Removal of hardness and desalting

1.6 INDUSTRIAL APPLICATION OF MEMBRANE TECHNOLOGY:

Membrane technologies have seen a significant growth and increase in application in the last two decades. Membrane systems are now available in several different forms and sizes, each uniquely fitting a particular need and application. Membrane separation process have found a wide range of application in industries like the beverage, chemicals, dairy, electronic, environmental, food, medical, paper, petrochemical petroleum, pharmaceutical, and textile industries.

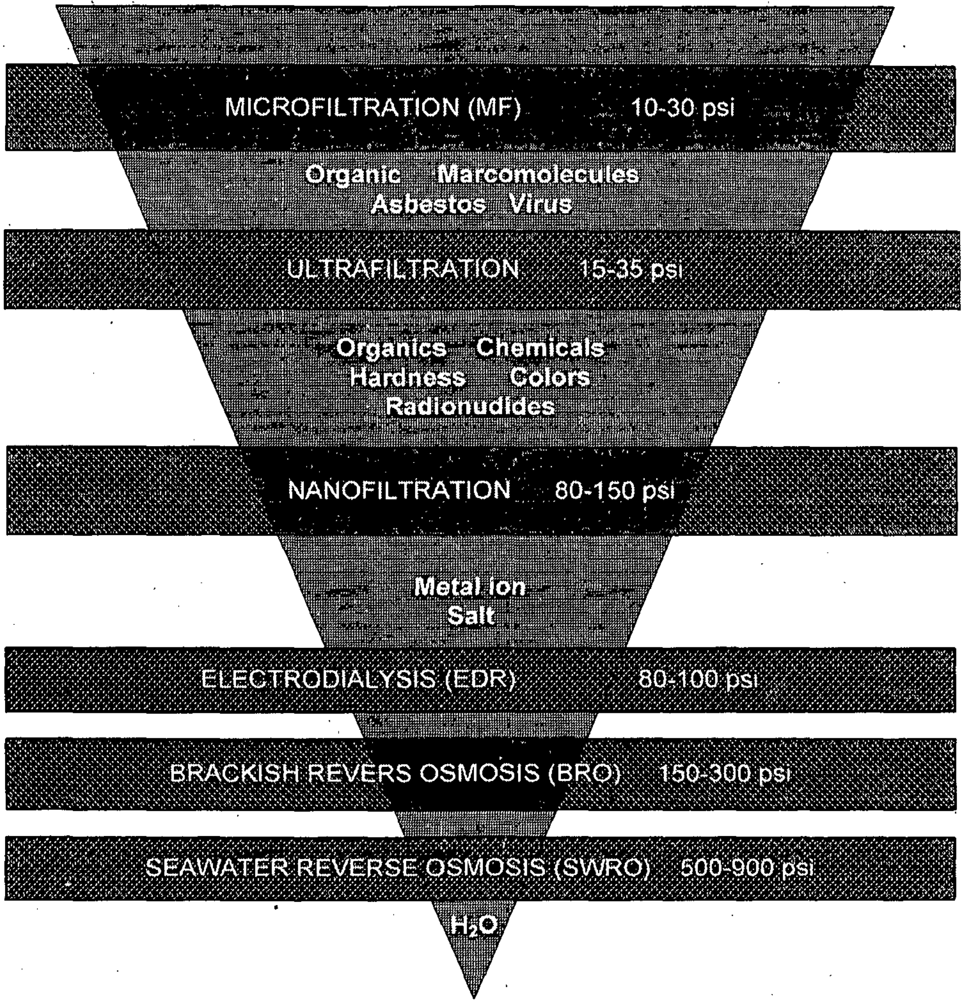


Fig 1.10 Classification of separation processes

1.6.1 Emerging Membrane Technologies:

Membrane based solvent extraction devices, recently developed appear to eliminate high capital, operating and maintenance costs of centrifugal devices and additionally provide very high volumetric transfer rates. Systems have been designed by using microporous membranes (hydrophobic or hydrophilic) for non-dispersive solvent extraction.

Hollow-fiber-contained-liquid-membranes (HFCLM) have been used for gas separation through a nonporous polymeric membrane. Microporous polypropylene hollow fibers have been used as the membrane material. Gas separations such as N_2-CO_2, CH_4-CO_2, SO_2-CO_2-N_2 and others have been studied by HFCLM technique.

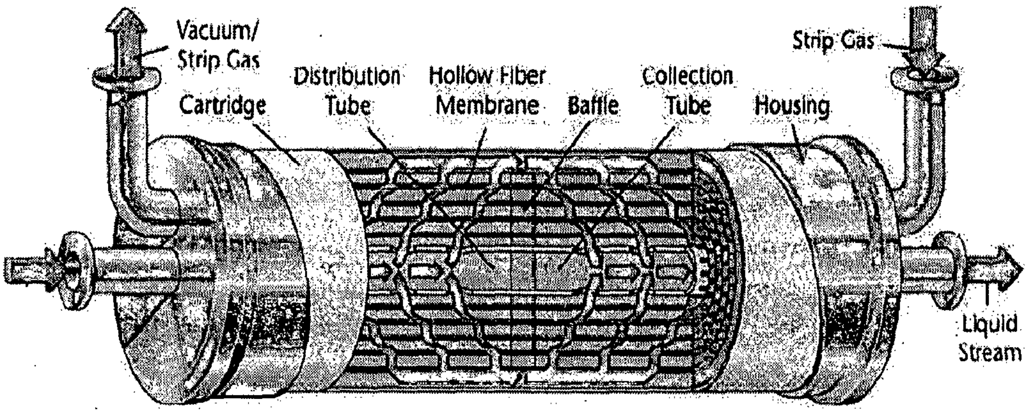


Fig 1.11 Hollow-fiber membrane system [9]

1.6.2 The Oil and Petrochemical Industry:

- Reducing the cost of hydrogen separation and recovery associated with oil refining and other processes.
- Reducing petroleum production costs by capturing reusable by-products.

1.6.3 Fossil Fuel Energy Producers:

- Lowering the cost and improving the efficiency of coal gasification.
- Economically recovering CO_2 and other by-products of fossil fuel combustion to help reduce greenhouse gas emissions.
- Capturing iron oxides and other undesirable fossil fuel combustion by-products found in stack emissions.

1.6.4 Natural Gas Energy Producers:

- Increasing natural gas reserves by removing excess carbon dioxide, nitrogen, and moisture from natural gas wells.

1.6.5 The Pulp and Paper Manufacturing Industry:

- Recovering fiber normally lost in the effluent.
- Recovering valuable chemicals for reuse and reducing the amount of chemicals released to the environment.
- Combining the uses above to convert a traditional paper factory to an almost self-contained process by separating chemicals and wastes from process water and recycling these valuable chemicals and now-clean water back into the processing stream.

1.6.6 Biotech and Pharmaceutical:

The biotech and pharmaceutical industries use membrane separation technology for a variety of purpose, including laboratory purification, as well as separation and concentration during both pre-filtration and sterilization. For the ever growing biotech industry, UF and NF are used to purify and concentrate antibiotics. To control water purify, RO and UF are utilized to remove suspended material, iron manganese, alkalinity, dissolved solids and other contaminants. Similarly, membrane filtration is used to purify water for injection, a vital component in most injectable drugs. Spiral-wound membrane systems are also used to purify water for kidney dialysis, which is then used to remove impurities from a patient's blood.

1.6.7 Water Cleanup/Purification Applications:

Producing potable and process grade water for industry and municipalities from surface and water, brackish water, sea water, brine water etc., using an inorganic reverse osmosis (RO) membrane with a very long lifetime. Inorganic RO membranes are resistant to chlorine and other disinfectants and can withstand steam treatments making them less vulnerable to bio-fouling.

1.6.8 Mining:

The mining industry produces large quantities of process water laden with acid and dissolved metals. Typically accumulated in ponds, this process water poses potential ground water pollution problems and is neutralized with large quantities of lime, However, the implementation of NF and thin-film UF membrane elements has enabled the mining industry to recover both economically valuable metals and reusable water from the acid-mixture, leading to an increase in lime neutralization efficiency and a corresponding decrease in costs related to lime purchase and sludge disposal.

1.7 APPLICATIONS IN DAILY LIFE:

Many industries are utilizing various technologies to minimize fresh water purchase and wastewater disposal. Few technologies, however, achieve the greater objectives of economically extracting valuables from the waste stream and improving product quality and/or process efficiencies. These are the challenges that membrane technology undertakes. Membrane systems for multiple industries that routinely separate and concentrate acid, dye, glycol, ink, lignin, lubricant, metal, oil, protein, PVA, solvent, sugar, starch, titanium dioxide, water and other valuables from product and waste streams. Similarly, membrane systems that reduce BOD, COD and TDS pollutants prior to open water discharge, and other that concentrate radioactive and toxic contaminants for economic disposal.

Car Washes: Excess minerals cause spotting on freshly washed cars. RO is used to produce spot-free rinse water.

Municipal: Advantages such as reduced feed water requirements longer equipment life, and reduced chemical usage all make membrane technology ideal for municipalities. Membrane elements remove various impurities from the source water, including metal ions, organic materials and other contaminants. The revolutionary purification process greatly improves quality by reducing salts, and disinfection by-products. The result is pure; crystal clear drinking exceeds EPA regulations.

Power: Membrane technology is used in the power generation industry to produce high-purity water for boilers and gas turbine injection. RO is employed in high and low-pressure boiler applications to remove free chlorine, silica, hardness, TDS, CO_2 and other contaminants. With a smaller footprint for space efficiency and the elimination of harsh chemicals, RO/EDI systems are fast becoming the new standard for pure-water performance.

Restaurants: RO purified water improves the taste of drinking water, ice, and other beverages, eliminates scaling of steam tables, and provides spot-free rinse water.

Water Vending: Both water vending machines and bottling plants use RO to produce safe, healthy, good-tasting water.

Marine: Oceangoing boats and yachts purify seawater with RO to produce drinking water.

Dialysis: Hospitals, dialysis clinics and in-home dialysis machines require high quality dialysis water. RO is widely used to produce the required quality water.

Laboratories: High purity water is used for sample preparation, rinsing glassware, and other lab uses.

In most applications where energy savings will be realized due to the efficiency and performance of our membranes compared to other membranes or compared to competing separation processes that do not use membranes.

1.8 ADVANTAGES AND DISADVANTAGES OF MEMBRANE SEPARATION [14]:

1.8.1 Advantages:

- Enhances reaction rates.
- increases reaction conversion.
- Enhances reaction selectivity.
- Reduces reaction severity.
- Increase catalyst life.
- Improve product life.
- Reduces capital investment.
- Complex instrumentation is not required.
- Low energy requirement.
- Good stability under wide range of operating conditions.
- Moderate cost to performance ratio.
- Environmental compatibility.

1.8.2 Disadvantages:

- Relatively new technology.
- Limited applications windows.
- Require extensive experimental development.
- Requires complex modeling.
- An extensive design effort requires.
- Increased operational complexity.
- Increased scale-up risks.
- Membranes are expensive.

1.9 PERVAPORATION MEMBRANE REACTOR (PVMR):

1.9.1 PVMR

Pervaporation membrane reactor as one type of the membrane reactor combines chemical reaction and separation by pervaporation in a single unit.

1.9.2 Pervaporation:

The pervaporation is a contraction of two words permeation and evaporation. In the pervaporation one or more products in a reaction liquid mixture contacting on one side of the membrane permeate preferentially through the membrane and the permeated steam is removed as a vapor from the other side of the membrane. As a result the forward reaction can be enhanced. Pervaporation resort to application of vacuum to the permeate side of the membrane. Vary high pressure ratio is achieved, so the minor component can be almost completely removed without excessive pressure difference across the membrane This process is different from the other membrane process in that there is a phase change as the solute permeates across the membrane. The best performing industrial membranes permeate water in preference to other component.

In general membrane is a perm selective barrier or interface between two phases. This is schematically illustrated in fig 1.15. The feed is typically at atmospheric pressure and the permeate at high vacuum. As the solute permeates across the membrane there is a phase change from liquid to vapor phase. Phase 1 is the feed phase or upstream side, while phase 2 is referred to as the permeate stream or downstream side. Separation is achieved because the membrane has the ability to transport one type of species from the mixture more readily than other species. This transport may occur through various transport mechanism. The driving force for mass transfer is the pressure gradient, electrical potential, concentration, temperature or chemical potential. In the case of pervaporation, phase 1 in fig 1.15 is a liquid phase and phase 2 is a vapor phase. The stream leaving the membrane module at the feed side is called the retentate. In the field of pervaporation two main applications is commercialized, one is dehydration of alcohols and other solvents, and second is removal of small amount of organic compounds from contaminated water [7]. Figure 1.14 shows a typical pervaporation system.

There are two ways in which pervaporation can be used to enhance reaction rates [24]:

1.9.3 Offline Pervaporation:

It is the simplest procedure and can be very effective. In this case, alcohol/water azeotrope from the top of the column is collected in a tank during the latter part of the batch. This tank contents are continuously dehydrated by pervaporation and resulting dry alcohol stored in a second tank.

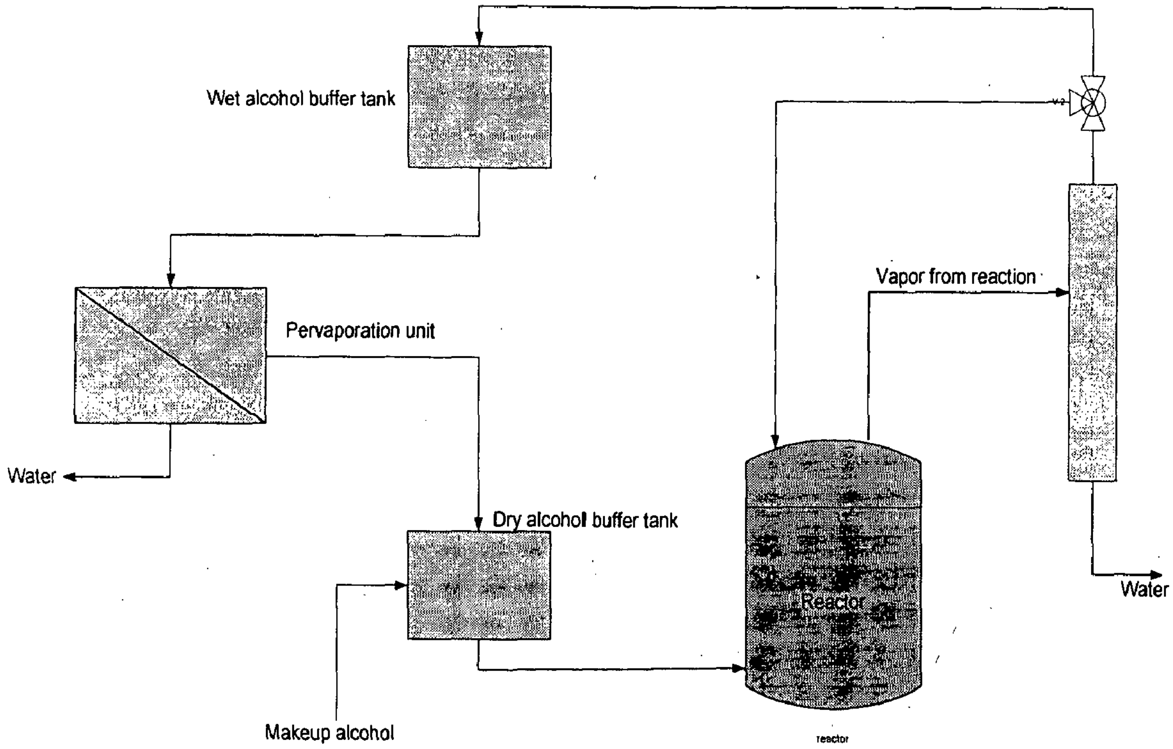


Fig 1.12 Offline pervaporation

1.9.4 Online Pervaporation:

It replace distillation column altogether. The reaction mixture continuously pumped through the pervaporation unit at a high rate. In general online pervaporation gives the most benefits, providing that the membrane is able to handle the reaction mixture.

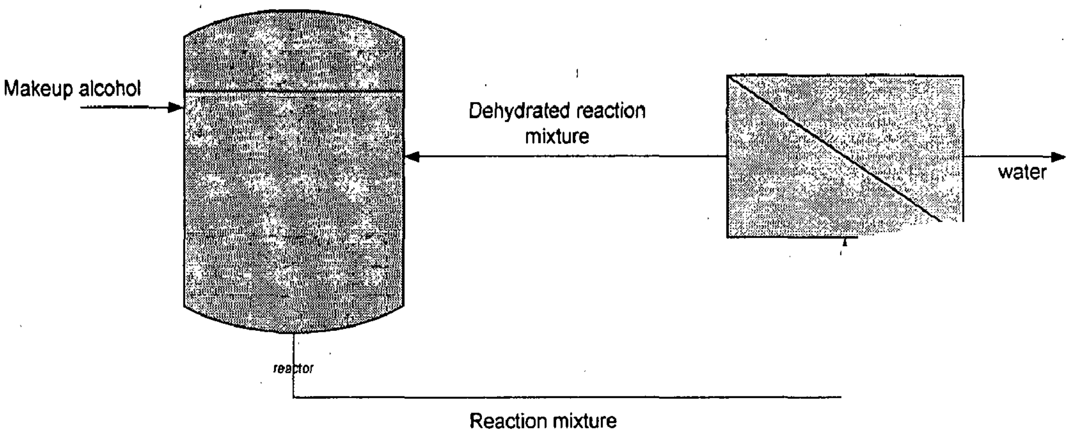


Fig 1.13 Online pervaporation

1.9.5 Membrane:

The membranes used in pervaporation processes are classified according to the nature of the separation being performed. *Hydrophilic membranes* are used to remove water from organic solutions. These types of membranes are typical made of polymers with glass transition temperatures above room temperatures. Polyvinyl alcohol is an example of a hydrophilic membrane material. *Organophilic membranes* are used to recover organics from solutions. These membranes are typically made up of elastomer materials (polymers with glass transition temperatures below room temperature): The flexible nature of these polymers makes them ideal for allowing organic to pass through. Examples include nitrile, butadiene rubber, and styrene butadiene rubber.

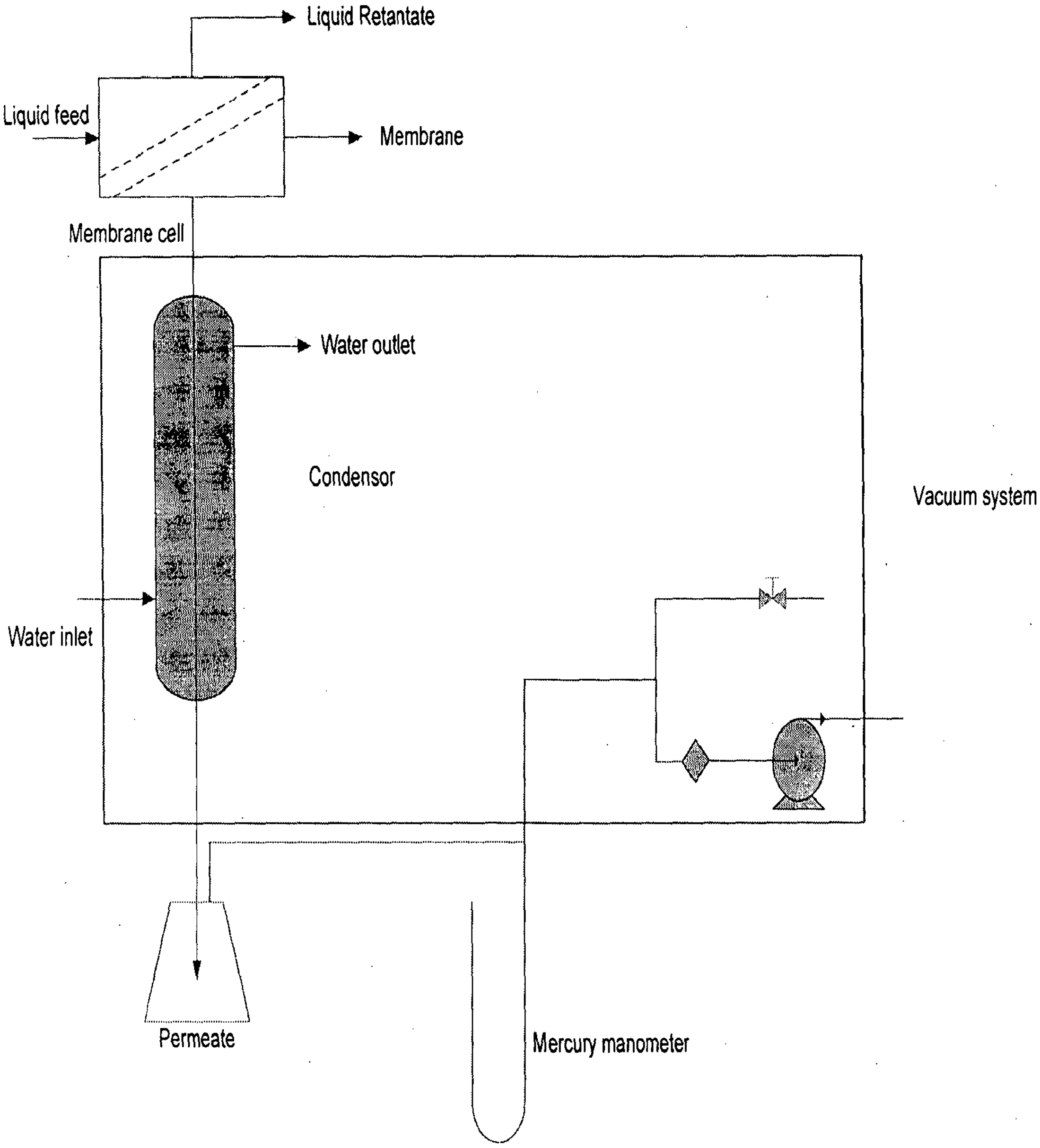


Fig 1.14 Simplified pervaporation process

Advantages of this process over other separation techniques are given below:

- Effective and economic separation of mixtures of substances with small difference in boiling point and azeotropic mixtures.
- Modular membrane design.
- No entrainers for separation of azeotropic mixtures.
- Reduced capital costs compared to conventional systems.
- Low energy consumption.
- No entrainer required no contamination.
- Permeate must be volatile at operating conditions.

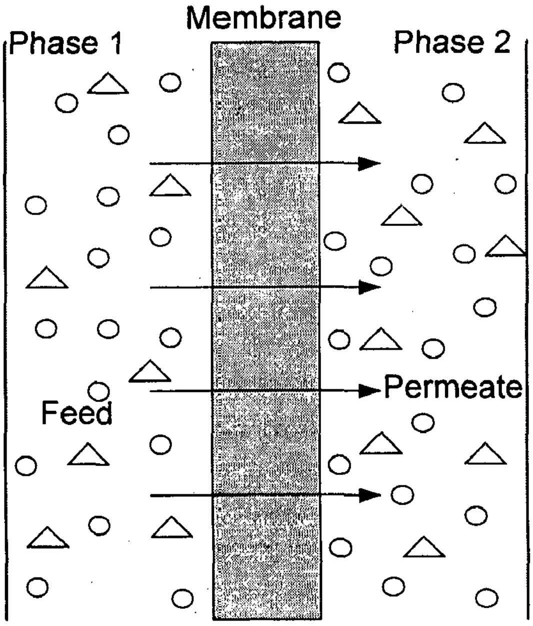


Fig 1.15 Schematic representation a membrane process

1.9.6 Pervaporation Characteristics:

1.9.6.1 Molecular Flux:

Molecular flux is the amount of a component permeated per unit area per unit time for a given membrane.

$$j_i = Q_i / At \qquad (2)$$

Where,

J_i = Flux of component "i" (moles/hr.cm^2)

Q_i = Moles of component "i" permeated in time "t"

A = Effective membrane surface area (cm^2).

1.9.6.2 Permselectivity:

The performance of a given membrane can be expressed in terms of a parameter called Permselectivity.

$$\alpha = \frac{\left(\frac{X_i^p}{X_j^p}\right)}{\left(\frac{X_i^f}{X_j^f}\right)} \qquad (3)$$

1.9.6.3 Permeability Coefficient:

The molecular flux for pervaporation across a membrane can be related to the Permeability coefficient by:

$$j_i = -P_i \Delta P / L \qquad (4)$$

$$\Delta P = P_1 - P_2 \tag{5}$$

$$P_1 = P_1^o X_{f,i},\ P_2 = PY_{p,i} \tag{6}$$

$$\Delta P = (P_1^o X_{f,i} - PY_{p,i}) \tag{7}$$

$$j_i = -P_i(P_1^o X_{f,i} - PY_{p,i}) / L \tag{8}$$

$$P_i = -j_i L / (P_1^o X_{f,i} - PY_{p,i}) \tag{9}$$

P_i = Permeability coefficient of component “i”.
γ_i = Activity coefficient of component “i” in the mixture.
ΔP = Change in partial pressure of pure component “i” across the membrane.
P_{io} = Saturation pressure of pure component i at feed temperature.
X_{ri} = Mole fraction of component i in liquid feed.
$Y_{p,i}$ = Mole fraction of component i in permeate.
J_i = Flux of component i.
L = Membrane Thickness.
K = Permeability constant.

CHAPTER 2

LITERATURE REVIEW

The review of literature on assigned dissertation topic is the pinnacle of every dissertation work as our dissertation topic is related to dynamic modeling of membrane reactor, which in turn is referred to as a chemical reactor with membrane as a separator, enormous literature is available on its various aspects. In this chapter we will discuss briefly different literature available on membrane reactor process. Many papers have been published on the development on membrane reactor and its process by different authors. In this chapter a brief description of their work is presented. These papers give information about the process description available in this literature.

This chapter also present models developed by different research workers for the analysis of the performance of the equipment. This chapter is divided into two sections; the first section includes research papers related to experimental work. The second section is the most important section. It deals with various research papers where mathematical modeling and simulation of membrane reactors are carried out and studied.

2.1 EXPERIMENTAL STUDIES ON MEMBRANE REACTOR:

There are number of research workers who have worked on the membrane reactor at laboratory scale and studied various aspects experimentally. In this section we give brief description of their work.

Maria Teresa Sanz et.al. (2006) studied the pervaporation of the polymeric membrane PERVAP2001 using Amberlyst 15 strongly acidic ion-exchange resin catalyst for esterification of acetic acid with isopropanol. They developed pseudo homogeneous model for rate equation.

$$r = \frac{1}{m_{cat} v_i} \frac{dn_i}{dt} = k_e a_A a_B - k_h a_E a_W \qquad (1)$$

And the kinetic parameters are given as

$$k_i = k_i^{o} \exp\left(-\frac{E_{A,i}}{RT} \right) \qquad (2)$$

And the permeation fluxes of quaternary mixture are given\

$$j_w = D'_{w,0} \exp\left(-\frac{E_w}{RT} \right) \left[\exp\left(\tau_{w,w} w_{w,feed} \right) - 1 \right] \qquad (3)$$

$$j_i = D'_{i,0} \exp\left(-\frac{E_i}{RT} \right) \exp\left(\tau_{W,i} w_w, feed \right) \left[\exp\left(\tau_{i,i} w_{w,feed} \right) - 1 \right] \qquad (4)$$

They found that permeation flux was increasing with the water content in the feel and the temperature. They showed that membrane shows the high selectivity towards water they concluded that membrane PERVAP2201 can be used to remove water selectivity formed during esterification reaction to obtained higher conversions.

T.A Peters et.al. (2005) discussed about the preparation of zeolite-coated pervaporation membranes for the integration of reaction and separation. Composite catalytic activities membranes for pervaporation-assisted esterification process are prepared. Catalytic zeolites H-USY layers have been deposited on silica membranes by dip-coating using TEOS and ludox AS-40 as binder material. They observed that tuning of catalytic layer thickness is possible by varying the number of dip-coat steps.

Jalal J. Jafar et.al. (2002) discussed the effectiveness of a tubular NaA membrane, prepared on a carbon/zirconium support, membrane was tasted for the removal of water from water/isopropanol and water/ethanol mixtures, in both pervaporation and vapour permeation modes and shown to give high selectivity. The esterification of lactic acid with ethanol to give ethyl lactate was studied in a batch reactor, without catalyst and with p-toluene sulphonic acid as catalyst. A series of experiments were taken with no loss of membrane performance. Use of a zeolite a vapor permeation membrane to remove water generated by the reaction gave substantially enhanced yields of product.

Maria Pilar et.al. (2002) discussed the use of a catalytically active zeolite membrane to displace equilibrium by selective water permeation during ethanol esterification. They compared effectiveness of the AZMR with FBR, ZMR (zeolite membrane reactor) three reactors were loaded with same amount of catalyst, FBR with the H-ZSM-5 catalyst packed as powder inside an impervious tube, in Zeolite membrane reactor (ZMR), with the H-ZSM-5 catalyst packed as powder inside a tubular Na-ZSM-5 membrane. In AZMR, where there was no catalyst other than the H-ZSM-5 membrane itself. The results show that under same conditions H-ZSM-5 membrane gives higher conversion than FBR, ZMR, and also shown that for equilibrium feed mixture the membrane had sufficient catalytic activity to carry out the esterification of ethanol with acetic acid, and at the same time was selective for water permeation. As a consequence, the reaction and separation functions could be coupled very efficiently, and the conversion obtained at the same feed rate and catalyzed loading was greater than in conventional fixed bed reactors or in reactors where the zeolite membrane was kept separated from the catalyst. In the latter case, the products formed on the catalyst must desorb, diffuse to the membrane surface and transport to the opposite side. Obviously this introduces a supplementary transport resistance compared to the case where reaction and separation are carried out without the presence of catalytic material other than the membrane itself.

Qinglin Liu et.al (2001) discussed the separation characteristic of the cross linked polyvinyl alcohol (PVA) membranes They studied the performance of this membrane by pervaporation separation of the liquid mixtures of water/acetic acid and water/acetic acid/n-butanol/butyl acetate. The permeation fluxes of water and acetic acid as a function of compositions were presented. The esterification of acetic acid with n-butanol catalyzed by $Zr(SO_4)H_2O$ was carried out at a temperature range of 60-90^0 C. A kinetic model equation was developed for esterification, and then it was taken as a model reaction to study the coupling of pervaporation with esterification. Experiments were conducted to investigate the effects of several operating parameters, such as reaction temperature, initial molar ratio of acetic acid to n-butanol, ratio of the membrane area to the Reacting mixture volume and catalyst concentration, on the coupling process, and the permeation flux expressions of water and acetic acid were presented.

$$J_w = P_w C_w \exp\left(S_{w,B} C_B + S_{w,E} C_E\right) \tag{1}$$

$$J_A = \frac{P_A C_w + m}{\exp\left(S_{A,B} C_B + S_{A,E} C_E\right)} \tag{2}$$

The ratio of the rate of water removal to water production was presented as an important factor and they defined it as coupling factor F

$$F = \frac{j_w \frac{S}{V}}{\frac{dC_E}{dt}} \tag{3}$$

- If F=1, the rate of water removal is equal to the water production rate, indicating that the conversion of the reaction could attain 100%
- F>1, the rate of water removal is less than the water production rate, indicating that the conversion could be enhanced a little over the equilibrium conversion, and it is controlled by the water removal.
- F>1, the rate of water removal is greater than the water production rate, indicating that the conversion could attain 100%, and it is limited by water production rate.

And also variation of F with reaction time at different temperatures, different molar ratios of acetic acid to n-butanol, different ratios of the membrane area to reacting mixture volume and different catalyst concentrations were studied. They concluded from the experiments that water content in the mixture increased during the reaction and then decreased when it reached to the maximum amplitude, it increased and F was less than 1, and after water content reached to the maximum amplitude, it decreased and F was larger than 1. S/V had a different effect on F from the other cases in that F increased earlier and than decreased with the increase of S/V. the catalyst and the catalyst concentration had a different influence in water content in liquid mixture from R_0 and S/V. the increase of temperature or catalyzed content resulted in water content increase earlier and then decreases later, while the decrease of R_0 or S/V resulted in the water content increase.

Qinglin Liu et.al. (1999) discussed preparation of $H_3PW_{12}O_{40}$/polyvinyl alcohol (PVA) catalytic membrane on porous ceramic plates. SEM (scanning electron microscopy) and XPS (X-ray photoelectron spectrometry) were used to characterize the membrane nature. The separative and catalytic properties of the membrane were tested by the Esterification of acetic acid with n-butanol it was found that different ways of cross linking played an obvious role in the membranes performance. Catalytic membranes with $H_3PW_{12}O_{40}$ entrapped in PVA were prepared. The cross linking method played a larger part in the performance of the membrane, and the membranes prepared with catalytic active layer cross linked by GA was proved to possess both good separative characteristics and good catalytic. The membrane thus prepared was characterized by SEM and XPS in order to investigate its nature further. It is indicated that the membrane before and after 120 h reaction had a similar surface morphology and nearly same absorption intensity.

Y.Zhu et.al (1998) discussed the esterification reaction between acetic acid and ethanol was studied in a continue flow pervaporation membrane reactor utilizing a polymeric ceramic composite membrane. For a range of experimental conditions reactor conversions were observed which are higher than the corresponding calculated equilibrium values. This is due to the ability of the membrane to remove water, a product of the reaction. A theoretical model has been developed which gives a reasonable fit of the experimental results.

Yushan Zhu et.al. (1996) studied the esterification of n-butyl alcohol an acetic acid in a PVA composite catalytic membrane cross linked with glutaraldehyde on a process ceramic plate. They prepared composite catalytic membrane cross linked PVA dense active layer coated on porous ceramic plate support and also prepared PAA (polyacrylic acid). Pervaporation experiments were carried out in batch reactor coupled with a membrane unit and liquid feed led to the reactor at atmospheric pressure and other side (permeate) a reduced pressure of not 5mm Hg were used. They studied for different temperatures the variation of permeation flux and selectivity for different PVA, PAA membranes and they observed for both flux is increasing and selectivity is decreasing with temperature and flux, selectivity in PVA or higher than PAA. They also studied the variation of conversion as a function of time with pervaporation and without pervaporation and they showed $X_{pv} > .95$, $X <.65$. For different temperatures they plotted conversion vs. time and they obtained high conversion at high temperature, and also observed the increase of temperature not only accelerates the esterification but also the pervaporation. Finally they studied the influence of initial molar reactant ratio (acetic acid/n-butyl alcohol) and catalyst concentration on reaction coupling.

Z.Gao et.al. (1996) prepared different composite hydrophilic membrane consisting of KA, NaA, CaA and NaX zeolites and polyvinyl alcohol polymer. The pervaporation and separation characteristics of different alcohol-water systems through these membranes were investigated at temperature ranging from 20 to 50^0C. distinct improvement on molecular transport and molecular sieving effect of the zeolites have been observed. Pervaporation-aided catalytic esterification of acetic acid with ethanol and salicylic acid with methanol have been carried out in a membrane reactor, leading to a considerable increase in conversion and a reduction in reaction time as result of continuous removal of water through the membrane. Acetone-water separation by pervaporation on a KA and CaA-filled polyvinyl alcohol membrane has been studied as well, which gives even better separation results than of the ethanol-water system. Application of the zeolite-filled pervaporation membrane to the methanol-acetone condensation reaction also promotes the reaction.

2.2 MATHEMATICAL MODELING STUDIES:

Mathematical modeling is an invaluable tool for the analysis and simulation of a complicated chemical process. A number of attempts have been made to develop the mathematical model of membrane reactor. A few of them are briefly discussed in this section.

Byoung-Gi Park et.al. (2004) described a new concept of a hybrid pervaporation membrane reactor system, which integrates the pervaporation step through a membrane with adsorption in the permeate side. Reaction experiments with the acetic acid-ethanol esterification reaction catalyzed by sulfuric acid have been carried out. They observed that PVMR-absorbent system shows significantly improved over the PVMR in the absence of the absorbent. They concluded that coupling pervaporation with absorption provides potential synergies in overcoming the equilibrium limitations in reversible reactions, dilute reacting systems, slow reactions, nonvolatile products, or imperfect membranes; they also validated the model utilizing the experimental data available in the literature.

In developing the model equations for the PVMR Lim et.al. have made the following assumptions:

- The reactor behaves as an ideal PFR.
- Membrane is completely uncreative.
- The main transport resistance is in the dense polymeric layer.
- Transport resistance in the inorganic support structure on the permeate side, and concentration polarization on the tube side are considered negligible.

Based on above assumptions the equations describing the PVMR are

Tube side:

$$\frac{dF_{ir}}{dV} = \nu_i k\left[\gamma_A \gamma_B X_A X_B - \gamma_E \gamma_W X_E X_W / K_{eq}\right] - \alpha_m \lambda_i U_i \left[\gamma_i X_i P_{is} - \varphi_i \psi_i P\right] \tag{1}$$

At $V = 0, F_{ir} = F_{AR}\left(\theta_i - \frac{\nu_i}{\nu_A} f_o\right)$

Shell side:

$$\frac{dF_{ir}}{dV} = \lambda_i U^o{}_i \alpha_m \left[\gamma_i X_i P_{is} - \varphi_i \psi_i P\right] \tag{2}$$

At V=0, $F_{ip}=0$

Suttichai Assbumrungrat et.al. (2003) discussed the synthesis of methyl acetate from methanol and acetic acid in pervaporation membrane reactors (PVMRs). Three modes of PVMR operations, i.e. semi batch, plug flow and continuous stirred tank were modeled using kinetic parameters of the reaction over Amberlyst-15 and permeation parameters for a polyvinyl alcohol (PVA membrane). Both of the reaction and permeation rates are expressed in terms of activities. The PVA membrane shows high separation factors for HOAc and MeOAc but very low for MeOH. The simulation results of SB-PVMR mode show quite good agreement with the experiments results. This studied focused on comparing PVMR performances between two modes of continuous flow operation for various dimensionless parameters. Such as Damkohler number (D_a), the rate ratio (δ), the feed composition and the membrane selectivity. They observed that flow characteristic within the reactors arisen from different operation modes affects the reactor performance through its influences on the reaction and permeation rate along the reactor. There are only some ranges of operating conditions where CS-PVMR is superior to PF-PVMR.

The assumptions taken for developing the mathematical model for pervaporation membrane reactors are:

- The reactors behaved ideally.

- Isothermally.
- Negligible pressure drop
- Negligible heat and mass transfer resistances aside from permeation process.
- No coupling effect of mixtures on the permeability.

The set of equations for different operating conditions is given as

$$\frac{dN_i}{dt} = v_i W k_i \frac{a_{HOAC}a_{MeOH} - a_{MeOAC}a_{H_2o} / K_e}{\left(a_{HOAC} + a_{MeOH} + a_{MeOAC}a_{H_2o}\right)^2} - AP_i a_i \tag{1}$$

$$\frac{dF_i}{dv} = v_i D_a \frac{a_{HOAC}a_{MeOH} - a_{MeOAC}a_{H_2o} / K_e}{\left(a_{HOAC} + a_{MeOH} + a_{MeOAC}a_{H_2o}\right)^2} - \frac{D_a \delta a_i}{\alpha_i} \tag{2}$$

$$\frac{dQ_i}{dv} = \frac{D_a \delta a_i}{\alpha_i} \tag{3}$$

$$\overline{F_{i,o}} - \overline{F_i} + v_i D_a \frac{a_{HOAC}a_{MeOH} - a_{MeOAC}a_{H_2o} / K_e}{\left(a_{HOAC} + a_{MeOH} + a_{MeOAC}a_{H_2o}\right)^2} - \frac{D_a \delta_i}{\alpha_i} = 0 \tag{4}$$

The rate expression is given as:

$$r = \frac{K_1\left(a_{HOAC}a_{MeOH} - a_{MeOAC}a_{H_2O} / K_e\right)}{\left(a_{HOAC} + a_{MeOH} + a_{MeOAC} + a_{H_2O}\right)^2}; with \tag{5}$$

$$a_i' = \frac{K_i a_i}{M_i}, K_1 = 8.497 \times 10^9 \exp\left(\frac{-60470}{r_g}\right)$$

$$K_e = 7.211 \times 10^{-2} \exp\left(\frac{3260}{R_g T}\right)$$

And $K_{HOAC} = 3.15, K_{MeOH} = 5.64, K_{MeAC} = 4.15, K_{H_2O} = 5.24$

The activity (a_i) can be calculated using the UNIFAC method.

Rates of pervaporation of species/through the membrane can be expressed as

$Q_i = AP_{iai}$

(Assuming that partial pressure of all species in the permeate side was low)

The relationship between the permeability coefficient and operating temperature can be correlated by the Arrhenius equation.

$$P_i = P_{i,o} \exp\left(\frac{-E_a}{R_g T}\right) \tag{7}$$

T.A.Peters et.al (2003) discussed about pervaporation membrane reactors and stated those are ideal candidates to enhance conversion in reversible reactions generating water as a by product. This equilibrium displacement can be enhanced through close integration of reaction and separation by way of catalytic membranes they developed catalytic hollow fiber pervaporation membrane for the close integration and separation. They also focused on the development of water selective hollow fiber silica membranes, the heterogeneous catalysis of esterification reaction and on the modeling of the pervaporation coupled esterification process in a catalytic membrane reactor. The esterification reaction between acetic acid and butanol has been taken as a model reaction, for which a parametric model study was carried out to provide a fundamental understanding of the catalytic membrane reactor behavior. They observed that catalytic membranes consist of a support coated with a water selective layer and on top of that a porous catalytic layer. Internal mass transfer limitations at thicker catalytic layer and deficiency of catalyst at thin catalytic layer lead to an optimum catalytic layer thickness. They stated that at this optimum catalytic layer thickness, the performance of catalytic membrane reactor exceeds the performance of inert membrane reactor due to the close integration of reaction and separation. The exact value of this optimum is a function of reaction kinetics and the membrane permeability. Subsequently, they developed mathematical model to provide design rule for catalytic hollow fiber membranes for condensation reactions. From the solution of the model they observed equilibrium displacement can be enhanced through integration of reaction and separation depending on the catalytic layer thickness. An optimum catalytic layer thickness is found to be 100 um under prevailing conditions. The exact position of this optimum is a function of the reaction rate constant and permeability of the membrane used.

The assumptions taken for developing the mathematical model are:

- The membrane reactor consists of tubular catalytic hollow fibers mounted in a module, which is single passed with no recirculation of reactants.
- The fluid flow and the chemical reaction take place in the shell side of the reactor module.
- The diffusion in the solid is neglected compared to that in the liquid filled pores in the layer.
- The reaction is to be first order in the reacting species, both for the forward and the backward reaction.
- The membrane is not permeable to the other components.

Model equations for the liquid membrane reactor

Mass balances and liquid membrane:

$$\frac{d(FC_i)}{dz} = 2\pi r_{cat} N_f D_{ej} \left(\frac{\partial C_i}{\partial r}\right)_{r_{cat}} + R_{bj}\varepsilon_m \pi r_m^{\ 2} \quad with\ D_{e,j} = \frac{\varepsilon_{cat}}{\zeta_{cat}} D_i \qquad (1),(2)$$

Catalytic layer

$$\frac{\partial C_i}{\partial r^2} + \frac{1}{r}\frac{\partial C_i}{\partial r} + \frac{\varepsilon_{cat} R_{cat,i}}{D_{e,j}} = 0 \quad with \qquad (3)$$

$$R_{cat,i} = k_r \frac{(1-\varepsilon_{cat})\rho_{cat}}{\varepsilon_{cat}} \left(C_A C_B - \frac{C_E C_w}{K}\right) \qquad (4)$$

Boundary conditions:

Membrane catalytic layer

$$P_i\left[\left(\gamma_i x_i p_i\right)-\left(y_i p_p\right)\right]=D_{e,j}\left(\frac{\partial C}{\partial r}\right)_{rmam} \tag{5}$$

Catalytic layer-bulk interface

$$D_{e,j}\left(\frac{\partial C}{\partial r}\right)_{r_{cat}}=k_{F,j}\left(C_{b,j}-C_{mem,j}\right) \tag{6}$$

Mass transfer polarization layer

$$Sh=\frac{k_{F,j}d_h}{D_i}=3.66+1.2\left(1-\varepsilon_m\right)^{-4} \tag{7}$$

The model was solved in MATLAB using Runge-kutta in the axial direction coupled with finite element method for the mass transfer and reaction in the catalytic layer.

Seong Y.lim et.al (2002) modeled a pervaporation membrane reactor (PVMR) for esterification reaction of acetic acid ethanol using a composite polymeric membrane reactor. The key difference between the other models and this model is they considered thermodynamic non idealities involved during the reactive and transport process. They analyzed three different class of reactors namely, CSTR, PER for which membrane and reactor are coupled and also separated.

The following assumptions are made for development of PERVMR

- The reactor behaves an ideal PFR.
- The main resistance is in dense polymeric layer.

- Transport resistance in the inorganic support structure on the permeate side, and concentration polarization on the tube side are considered negligible.

Based on above assumptions they modeled a **PFMR**

Tube side:

$$\frac{dF_{ir}}{dV} = v_i k\left[\gamma_1\gamma_2 X_1 X_2 - \gamma_3\gamma_4 X_3 X_4 / K_{eq}\right] - \alpha_m \lambda_i U_i\left[\gamma_i X_i P_{is} - \varphi_i \psi_i P\right] \qquad (1)$$

At $V = 0, F_{ir} = F_{AR}\left(\theta_i - \frac{v_i}{v_A} f_o\right)$

Where i= A, B, E, W.

Shell side:

$$\frac{dF_{ir}}{dV} = \lambda_i U^o{}_i \alpha_m\left[\gamma_i X_i P_{is} - \varphi_i \psi_i P\right] \qquad (2)$$

At V=0, F_{ip}=0

Where i= A, B, E, W.

Continuously stirred pervaporation membrane reactor (CSPVMR)

Reactor side:

$$F_{ir} - F_{iro} = v_i V_R k\left[\gamma_1\gamma_2 X_1 X_2 - \gamma_3\gamma_4 X_3 X_4 / K_{eq}\right] - U_i \int_0^{Am} \lambda_i\left[\gamma_i X_i P_{is} - \varphi_i \psi_i P\right] dA \qquad (3)$$

$$F_{iro} = F_{AR}{}^O\left(\theta_i - \frac{v_i}{v_A} f_0\right) \qquad (4)$$

Membrane shell side:

$$\frac{dF_{ip}}{dA} = \lambda_i U^o{}_i \left[\gamma_i X_i P_{is} - \varphi_i \psi_i P\right] \tag{5}$$

At A=0, $F_{ip}=0$

Where i= A, B, E, W.

Batch pervaporation membrane reactor (BPVMR)

Reactor side:

$$F_{ir} - F_{iro} = v_i V_R k\left[y_1 \gamma_2 X_1 X_2 - \gamma_3 \gamma_4 X_3 X_4 / K_{eq}\right] - U_i \int_0^{Am} \lambda_i \left[\gamma_i X_i P_{is} - \varphi_i \psi_i P\right] dA \tag{6}$$

At t=0, $N_{ir} = N_{AR}{}^O \left(\theta_i - \frac{v_i}{v_A} f_0\right)$

Shell side:

$$\frac{dF_{ip}}{dA} = \lambda_i U^o{}_i \left[\gamma_i X_i P_{is} - \varphi_i \psi_i P\right] \tag{7}$$

At A=0, $F_{ip}=0$

Where i= A, B, E, W.

Each equation is converted into dimensionless from and they observed dimensionless groups and they compared the reactor with that group.

Li Xuehui et.al. (2001) discussed a basic kinetic model of an esterification process coupled by pervaporation and a new method for measuring the model parameter had been established. Various effects on the shift of chemical equilibrium of esterification were taken into consideration in this kinetic model. The simulation results of this model coincided well with the experimental results.

R.Krupiczka et.al. (1999) discussed the hybrid process of the esterification of acetic acid with ethanol, coupled with pervaporation, and a simple, three parameter model describing the concentration profiles in the process was built. This work suggests that the activity based model is a better method for predicting concentration profiles than the concentrations profiles than the concentration model especially in the range of higher component concentration in which the thermodynamic constant calculated on the basis of concentrations are not true constants.

The experiments were performed using a wide range of initial molar ratios C_{et}/C_a (1:1; 2:1; 3:1, 5:1) with hydrophilic membrane PERVAP 1005 GET and ethanol-acetic acid as the reaction mixture. Appropriate activities were calculated using the UNIFAC group contribution method.

The assumptions used in model development are:

- Isothermal operation.
- Only water process through membrane.
- The reaction of acetic acid with ethanol displays first order kinetics, and is given as

$$r = k_f C_{cat}\left(a_{et}a_a - \frac{a_w a_e}{K^{(a)}}\right) \tag{1}$$

Where a_{et}, a_a, a_w and a_e are the appropriate activities and C_{cat}, K_f, $K^{(a)}$ are the catalyst concentration, the forward reaction rate constant and the equilibrium constant, respectively, and can be evaluated by using the activities:

$$K^{(a)} = \frac{a_w a_e}{a_{et}a_a} \tag{2}$$

- The molar rate of removal of water from the reaction mixture by pervaporation was assumed as the product of the permeability coefficient and concentration in the liquid:

$$n_w = AP_w c_w \tag{3}$$

Where A is area of membrane.

Model equations of the of the process

Total water balance (Only water process through membrane).

$$\frac{dM}{dr} = -n_w M_w \tag{4}$$

Water concentration profile in reactor side

$$\frac{dc_w}{d\tau} = \frac{AP_w c_w}{M}\left(c_w M_w - 1\right) + k_f C_{cat}\left(a_{et} a_a - \frac{a_w a_e}{K^{(a)}}\right) \tag{5}$$

Concentration profile of acid

$$\frac{dc_k}{d\tau} = \frac{M_w AP_w c_w}{M} c_k + k_f C_{cat}\left(a_{et} a_a - \frac{a_w a_e}{K^{(a)}}\right). \tag{6}$$

Xianshe Feng et.al (1996) discussed the pervaporation-facilitated esterification and a parametric study was carried out to provide a fundamental understanding of the reactor behavior.

A batch reactor integrated with a pervaporation unit was selected as a model system. It was shown by simulation that conversions exceeding equilibrium limits can be achieved by using pervaporation to remove water from the reaction mixtures, and that complete conversion of one reactant is obtainable when the other is in excess. The membrane reactor tolerates the presence of water, which can be either in the reaction medium or as impurity of the reagent. There are upper and lower limits in the performance of reactor facilitation by pervaporation. Membrane permeability, membrane area and the volume of reaction mixtures to be treated are important operating parameters influencing the reactor behavior. Operating temperature influences reactor performance through its influences on reaction rate membrane permeability.

The assumptions taken for developing the mathematical model are:

- Isothermal operation and negligible change in catalyst concentration.
- The change of volume of reaction mixtures in the membrane reactor is given by

$$\frac{dV}{dt} = -\Sigma \frac{J_i M_i}{\rho_i} S \tag{1}$$

Where Mi and p are molar mass and density of the species I, respectively.

- The membrane permeates only water.

Material balance on any reactant or product species at any instant

$$\frac{d(C_i V)}{dt} = -r_i V - J_i S \tag{2}$$

Reaction rate is given by

$$r = K_1 C_A C_B - K_2 C_E C_W = k_1 \left(C_A C_B - \frac{C_E C_W}{K_C} \right) \tag{3}$$

Acid concentration profile is written as

$$\frac{dX}{dt} = k_1 C_o \left[\frac{(1-X)(\theta_B - X)}{v} - \frac{(\theta_E + X)Y}{K_e} \right] \tag{4}$$

$$\frac{dY}{dt} = \left(\frac{1}{v} \right) \left[\frac{dX}{dt} - Y \frac{dv}{dt} - \left(\frac{S}{V_O} \right) \frac{J_w}{C_o} \right] \tag{5}$$

The initial conditions are

$$At\ t = 0, X_O = 0, V_o = 1$$

For a special where membrane permeability is so large that water is removed from the reactor as fast as it is formed they solved analytically the above equations and given an expression as:

$$k_l C_o t = \frac{1}{\theta_B - 1} ln\left[\frac{\left(1 - X/\theta_B\right)^{1-\varepsilon\theta_B}}{\left(1-X\right)^{1-\varepsilon}}\right] \tag{6}$$

Where $\theta_B > 1$

$$k_1 C_o t = \frac{(1-\varepsilon)X}{1-X} + \varepsilon ln\frac{1}{1-X} \tag{7}$$

$$\theta = 1 \text{ and } \varepsilon = \frac{C_o M_w}{\rho_w}$$

This represents the best performance that can be achieved by membrane pervaporation to facilitate the reaction since no reversal of the reaction occurs.

They also gave an expression that if the membrane permeability is so small that the performance is hardly affected by the membrane.

$$X = \frac{1 - \exp(\psi t)}{2y\left[\frac{\exp(\psi t)}{\psi - \beta} + \frac{1}{\psi + \beta}\right]} \tag{8}$$

where

$$\alpha = k_1 C_O\left(\theta_B - \frac{\theta_E \theta_w}{K_e}\right) \tag{9}$$

$$\beta = k_1 C_O \left(1 + \theta_B + \frac{\theta_E + \theta_w}{K_e} \right) \tag{10}$$

$$\gamma = k_1 C_O \left(1 - \frac{1}{K_e} \right) \tag{11}$$

This represents another extreme case of a simpler batch reactor.

2.3 OBJECTIVE OF THESIS:

We planned following objective based on reviewed literature

- To develop a mathematical model of a membrane reactor.
- To solve the model equations using MATLAB by developing computer program.
- To validate the proposed model with the available data.
- To study the effect of operating and design parameters on its performance.

2.4 CONCLUDING REMARKS:

In this chapter we have seen that various literatures are available in the field of membrane reactor. Many researches have worked in the field of mathematical modeling and have developed models by taking different assumptions and also with different objectives. It can be evident by the reviewed literature that a good deal of information can be obtained from the review presented herein.

CHAPTER 3

DEVELOPMENT OF MODEL

3.1 INTRODUCTION:

In this chapter we study the development of mathematical model for the esterification reaction of isopropanol and acetic acid in a pervaporation membrane reactor (PVMR). We are considering tubular membrane reactor which consist of shell and tube side. Liquid feed isopropanol with Amberlyst 15 (catalyst) and acetic acid are heated separately. Both feed streams are passed in tube side of membrane reactor. In this model we are using PVA (PERVAP 2201) membrane [19]. Liquid molecules dissolve in the membrane and permeate through membrane in shell side. Permeate in shell side collected in vapor state. Sweep gas used is nitrogen, reason to use it as a sweep gas is that it is inert in nature.

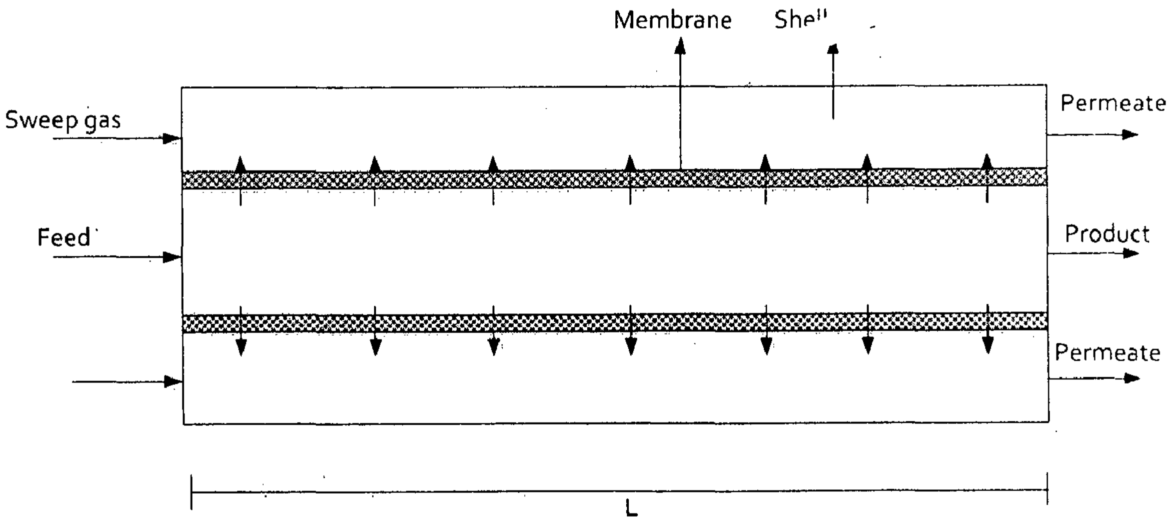


Fig 3.1 Membrane reactor

3.2 REACTION KINETICS:

Different kinetic models have been used to describe the esterification reaction catalyzed by ion exchange resins. The pseudo-homogeneous model assumes complete swelling of the polymeric catalyst in contact with polar solvents, leading to an easy access of the reactants to the active sites. This model has successfully been used for the description of esterification reactions catalyzed by ion-exchange resins [19].

The esterification of isopropyl alcohol and acetic acid can be representing schematically by:

$$\text{RCOOH} + \text{ROH} \leftrightarrow \text{RCOOR} + \text{H}_2\text{O} \tag{1}$$

$$(\text{CH}_3)_2\text{C-O-H} + \text{HO-OCCH}_3 \xleftrightarrow[k_h]{k_e} (\text{CH}_3)_2\text{-C-OOCCH}_3 + \text{H}_2\text{O} \tag{2}$$

Rate of reaction is given by:

$$r_i = \frac{1}{V}\frac{dn_i}{dt} = k_1 C_A C_B - k_2 C_E C_W \tag{3}$$

Arrhenius type temperature dependency for forward and backward reaction was used.

$$k_i = k_i^0 \exp\left(\frac{-E_{A,i}}{RT}\right) \tag{4}$$

3.3 ASSUMPTIONS:

The Mathematical model was developed by using following assumptions:

- Reactor was operated isothermally.
- Pressure was constant in both shell and tube side.
- Radial dispersion was negligible in both shell and tube side.

- Membrane was completely unreactive.
- The main transport resistance was in polymeric layer.
- Transport resistance in the inorganic support structure and concentration polarization effects on tube side was negligible.
- Fluid flow in both tube and shell side was plug flow.
- Purge gas was non reactive, so no reaction is consider in shell side.

3.4 MATERIAL BALANCES:

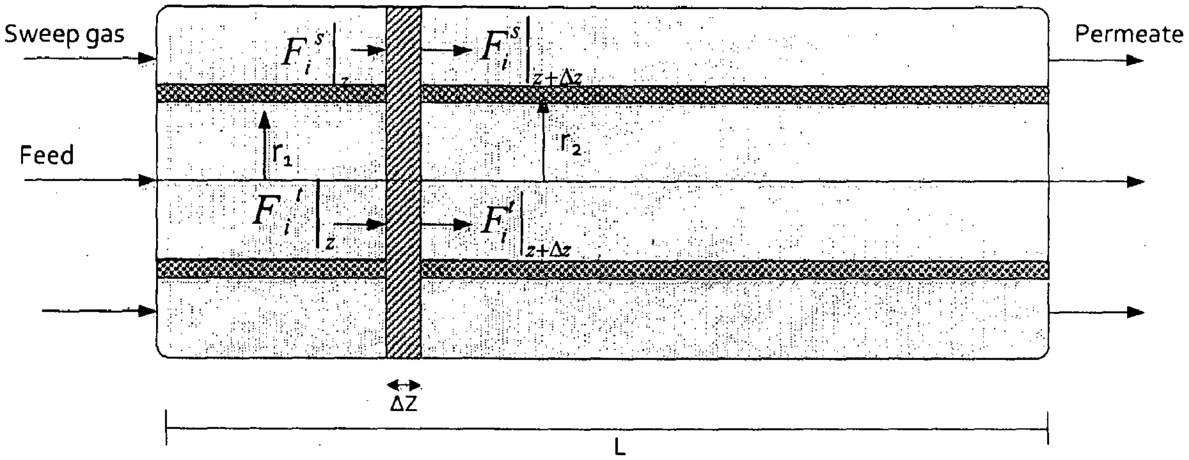


Fig 3.2 Control volume for mass balance in membrane reactor

We divided the length of reactor L into very small elemental length ΔZ as shown in the fig 3.2. We carry out the material balance around the control volume on both shell and tube side. Concentration and all other properties are constant in the control volume for all components.

In this section we comprise the material balance equations for transport through tube, shell and membrane. The model equations are given below:

Tube side balance:

$$\begin{pmatrix}\text{Molar flow of i}^{\text{th}}\text{ component}\\ \text{Into the control volume}\end{pmatrix} - \begin{pmatrix}\text{Molar flow of i}^{\text{th}}\text{ component}\\ \text{out of the control volume}\end{pmatrix} +$$

$$\begin{pmatrix}\text{Moles of i}^{\text{th}}\text{ component generated}\\ \text{or consumed by reaction}\end{pmatrix} - \begin{pmatrix}\text{Rate of moles of i}^{\text{th}}\text{ component}\\ \text{transported through the membrane}\end{pmatrix} = 0 \qquad (5)$$

$$F_i^t\Big|_z - F_i^t\Big|_{z+\Delta z} + (r_i')m_{cat} - j_i S = 0 \qquad (6)$$

$$S=2\pi r_1\Delta z \qquad (7)$$

Put value of S from equation (7) to equation (6) and than divide equation (6) by Δz, taking $\Delta z \rightarrow 0$, and than rearranging the terms

$$-\frac{dF_i^t}{dz} + \frac{(r_i')m_{cat}}{L} - 2\pi j_i r_1 = 0 \qquad (8)$$

Where i refers acetic acid, isopropanol, iso-propylacetate, water.

Shell side balance:

$$\begin{pmatrix}\text{Molar flow of i}^{\text{th}}\text{ component}\\ \text{Into the control volume}\end{pmatrix} - \begin{pmatrix}\text{Molar flow of i}^{\text{th}}\text{ component}\\ \text{out of the control volume}\end{pmatrix} +$$

$$\begin{pmatrix}\text{Rate of moles of i}^{\text{th}}\text{ component}\\ \text{transported through the membrane}\end{pmatrix} = 0 \qquad (9)$$

$$F_i^s\Big|_z - F_i^s\Big|_{z+\Delta z} - j_i S^s = 0 \qquad (10)$$

$$S^S = 2\pi r_2\Delta z \qquad (11)$$

Put value of S from equation (11) to equation (10) and than divide equation (10) by Δz, taking Δz→0, and than rearranging the terms

$$-\frac{dF_i^s}{dz}+2\pi j_i r_2=0 \tag{12}$$

Where i refers acetic acid, isopropanol, iso-propylacetate, water.

Total material balance equations for all components are given by:

Tube side balances:

Acetic acid

$$-\frac{dF_A'}{dz}+\frac{(r_A')m_{cat}}{L}-2\pi j_A r_1=0 \tag{13}$$

Isopropanol

$$-\frac{dF_B'}{dz}+\frac{(r_B')m_{cat}}{L}-2\pi j_B r_1=0 \tag{14}$$

Iso-propylacetate

$$-\frac{dF_E'}{dz}+\frac{(r_E')m_{cat}}{L}-2\pi j_E r_1=0 \tag{15}$$

Water

$$-\frac{dF_W'}{dz}+\frac{(r_W')m_{cat}}{L}-2\pi j_W r_1=0 \tag{16}$$

Shell side balance

Acetic acid

$$-\frac{dF_A^s}{dz} + 2\pi\, j_A r_2 = 0 \qquad (17)$$

Isopropanol

$$-\frac{dF_B^s}{dz} + 2\pi\, j_B r_2 = 0 \qquad (18)$$

Iso-propylacetate

$$-\frac{dF_E^s}{dz} + 2\pi\, j_E r_2 = 0 \qquad (19)$$

Water

$$-\frac{dF_W^s}{dz} + 2\pi\, j_W r_2 = 0 \qquad (20)$$

3.5 SET OF MATHEMATICAL EQUATIONS:

- Model include eight non linear differential equations (13-20) which form initial value problem with eight state variables ($F_A^t, F_B^t, F_E^t, F_W^t$) in tube side and ($F_A^s, F_B^s, F_E^s, F_W^s$) in shell side and z is the independent variable.

Boundary conditions:

The initial conditions of the reactor are listed below.

At z=0,

Tube side

$$F_A^t = F_{A,0}^t$$
$$F_B^t = F_{B,0}^t \quad (21)$$
$$F_E^t = 0$$
$$F_W^t = 0$$

Shell side

$$F_A^s = 0$$
$$F_B^s = 0 \quad (22)$$
$$F_E^s = 0$$
$$F_W^s = 0$$

3.6 PERMEATION THROUGH MEMBRANE:

The membrane used for esterification of acetic acid and isopropanol is commercially hydrophilic membrane PVA (PERVAP2201) [19] with maximum operating temperature is 100^0C. The transport through the membrane is a very complex phenomenon with interactions between the components and the components with the membrane. A number of authors supposed that water is the only permeating component through the membrane from the reaction mixture [5].

The most widely accepted transport model through the membrane is the solution/diffusion model. Based on this model, the permeation performance is determined by the solubility and diffusivity of each component through the membrane. The diffusion of the components permeating through the membrane can be assumed to occur according to Fick's first law for the components.

Permeation flux for above membrane is given below [19]

$$j_w = D'_{w,o} \exp\left(\frac{-E_w}{RT}\right)[\exp(\tau'_{w,w}\, w_{w,feed}) - 1] \tag{23}$$

$$j_i = D'_i \exp\left(\frac{-E_i}{RT}\right)\exp(\tau'_{w,i}\, w_{w,feed})[\exp(\tau'_{i,i}\, w_{i,feed}) - 1] \tag{24}$$

Where i refers acetic acid, isopropanol, iso-propylacetate, water.

3.7 CATALYST:

Catalyst used for the esterification reaction of isopropanol and acetic acid in the present work is Amberlyst 15. It is strongly acidic ion-exchange resin [19].

3.8 CONSTITUTIVE RELATIONSHIPS:

Constitutive relationships are given below [19]

Kinetic rate constants for forward and backward reactions are k_e and k_h respectively.

$$k_e = 1.02\times10^7 \exp\left(\frac{-64590}{RT}\right) \tag{25}$$

$$k_h = 1.9\times10^7 \exp\left(\frac{-73630}{RT}\right) \tag{26}$$

Permeation fluxes for all components through the membrane are given below [19]:

Water

$$j_w = 2\times10^6 \exp\left(\frac{-45800}{RT}\right)[\exp(6.5w_{w,feed})-1] \qquad (27)$$

Acetic acid

$$j_A = 2.8\times10^9 \exp\left(\frac{-56000}{RT}\right)\exp(12.3w_{w,feed})[\exp(.00038w_{A,feed})-1] \qquad (28)$$

Isopropanol

$$j_B = 8.1\times10^7 \exp\left(\frac{-47500}{RT}\right)\exp(10.1w_{w,feed})[\exp(.00033w_{B,feed})-1] \qquad (29)$$

Iso-propylacetate

$$j_E = 1.9\times10^9 \exp\left(\frac{-58500}{RT}\right)\exp(10.1w_{w,feed})[\exp(.00067w_{E,feed})-1] \qquad (30)$$

3.9 OPERATING PERAMETERS:

In this section standard operation conditions and parameters with boundary conditions are given below:

Table 3.1 Standard operating conditions

Operating conditions	Value	Units
Feed flow rate	0.000121	(Mol/min)
Temperature	348	K
Tube side pressure	1	atm
Shell side pressure	<1	atm
Feed ratio(isopropanol/acetic acid)	1	-

Table 3.2 Simulation parameters

Parameters	Value	Units
Inner radius of tube	0.35	cm
Outer radius of tube	0.5	cm
Length of reactor	25	cm
Thickness of membrane	5×10^{-3}	cm

Table 3.3 Physical properties

Properties	Value	units
Density of Acetic acid	1.05	gm/cc
Density of Isopropanol	0.760	gm/cc
Density of Iso-propylacetate	0.880	gm/cc
Density of Water	0.990	gm/cc
Molecular wt. of Acetic acid	60	-
Molecular wt. of Isopropanol	60	-
Molecular wt. of Iso-propylacetate	102	-
Molecular wt. of Water	18	-

3.10 CONCLUDING REMARKS:

In this chapter we derived model equation for the system of esterification reaction of acetic acid and isopropanol. To derive model we take simplify assumptions. Model contains set of eight non-linear ordinary differential equations, which form an initial value problem. These equations are solved by ODE solver of MATLAB 7.5. The physical properties and other simulation parameters are given in tabular form. In order to be brief it is not desirable to describe the computer program completely or give its listing in the thesis. However complete computer program may be obtained from the author or his guide on request.

CHAPTER 4

RESULT AND DISCUSSION

4.1 INTRODUCTION:

In this chapter results of the developed mathematical model for esterification reaction of acetic acid and isopropanol in tubular membrane reactor have been studied and discussed. Our proposed model predicts the change in flow rate of ester, flow rate of water in shell and tube side along with the length of the reactor and effect of operating parameters on the performance of membrane reactor. In this chapter numerically computed results are shown graphically.

The percentage yield of ester is calculated from the following formula:

$$\%\ \text{Yield of Ester} = \left(\frac{Ester_{retentate} + Ester_{permeate}}{AA_{feed}} \right) \times 100$$

4.2 VALIDATION OF MODEL:

For validation of above mathematical model, experimental data has been taken from the experimental work of Park and Tsotsis (2004). The variation in conversion with temperature in fixed bed is compared and is shown in table 4.1. These results show that the model is in good agreement with the experimental values within $\pm 3\%$ error. Hence, this results lead to validation of developed model.

Table 4.1 Comparison of conversion of model results with experimental results

Sl.No.	Temperature	%Conversion from experiment	%Conversion from model	% Error
1	312.67K	72.1	70.18	2.66
2	322.82K	72.1	70.30	2.50
3	332.96K	72.2	70.50	2.35
4	342.47K	72.4	70.80	2.20

4.3 EFFECT OF DIFFERENT PARAMETERS ON MEMBRANE REACTOR PERFORMANCE:

4.3.1 Effect of Initial Feed Ratio:

In the present work we have considered the three different feed ratios i.e. M=1, M=1.5, M=2 for the study. We saw in Fig 4.1-4.3 that as we increase feed ratio, conversion of acetic acid also increases. For M=1 conversion is 76.31%, M=1.5 conversion is 81.83% and M=2 conversion is 85.26%. As feed ratio increases, conversion increases because conversion is directly proportional to the concentration of feed components according to the rate equation. In Fig 4.4-4.6 we have seen that conversion for PVMR is always higher than the conversion of FBR. This is due to permeation of water through the membrane in PVMR, so concentration of products decreases i.e. rate of forward reaction increases. For M=1 conversion in FBR is 60.88% and in PVMR is 76.31%, for M=1.5 conversion in FBR is 72.30% and in PVMR is 81.83 and for M=2 conversion in FBR is 78.87% and in PVMR is 85.26%.

Mole fraction of ester and mole fraction of water decrease as feed ratio increases this is because of the dilution effect. In Fig 4.8-4.10 we have seen the effect of feed ratio on flow rate of water and other components in tube side and in Fig 4.11-4.13 we have seen the effect of feed ratio on the flow rate of water and other components in shell side.

From these figures it is clear that permeation of acetic acid (A.A.), isopropanol (IPA) and ester through the membrane is negligible as compared to water, so we can say that membrane is highly selective for water. Permeation of acetic acid, isopropanol, ester and water at M=1 and 343K temperature through membrane are 1.5×10^{-6} mol/min, 7.4×10^{-7} mol/min, 1.26×10^{-6} mol/min, 6.5×10^{-5} mol/min respectively.

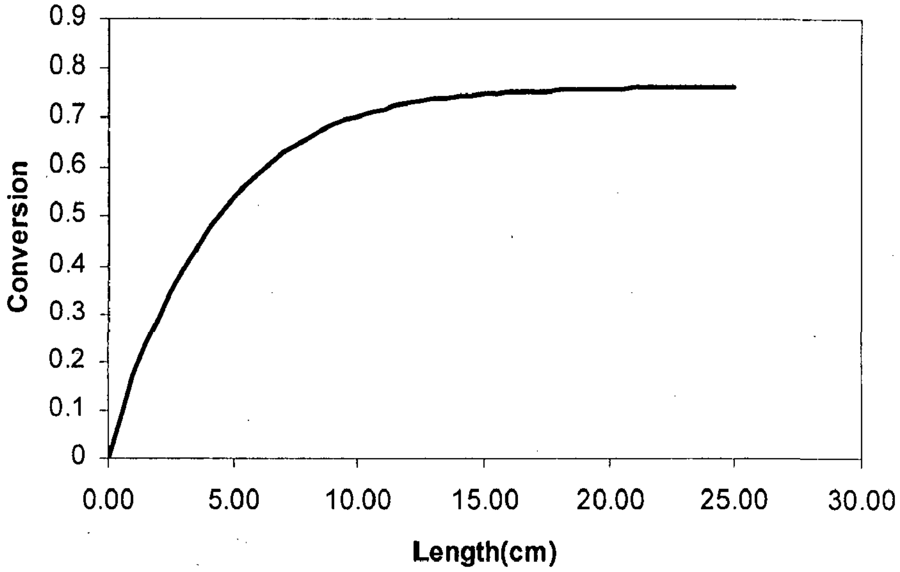


Fig 4.1 Conversion vs length at M=1 and temperature =343K

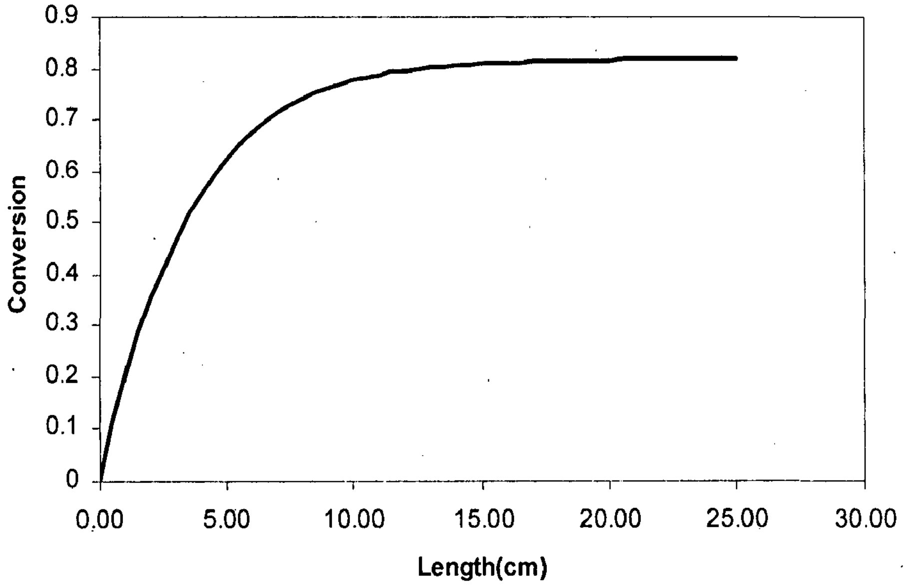


Fig 4.2 Conversion vs length at M=1.5 and temperature =343K

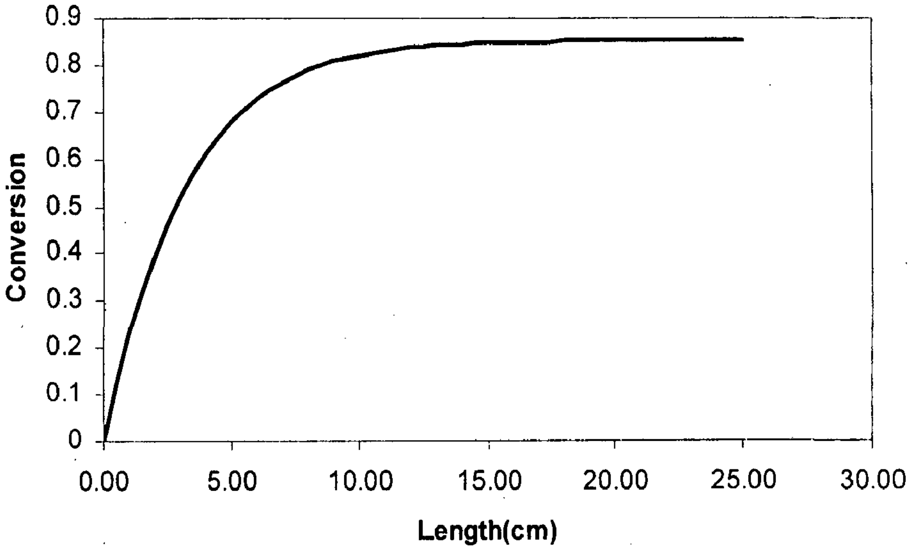


Fig 4.3 Conversion vs length at M=2 and temperature =343K

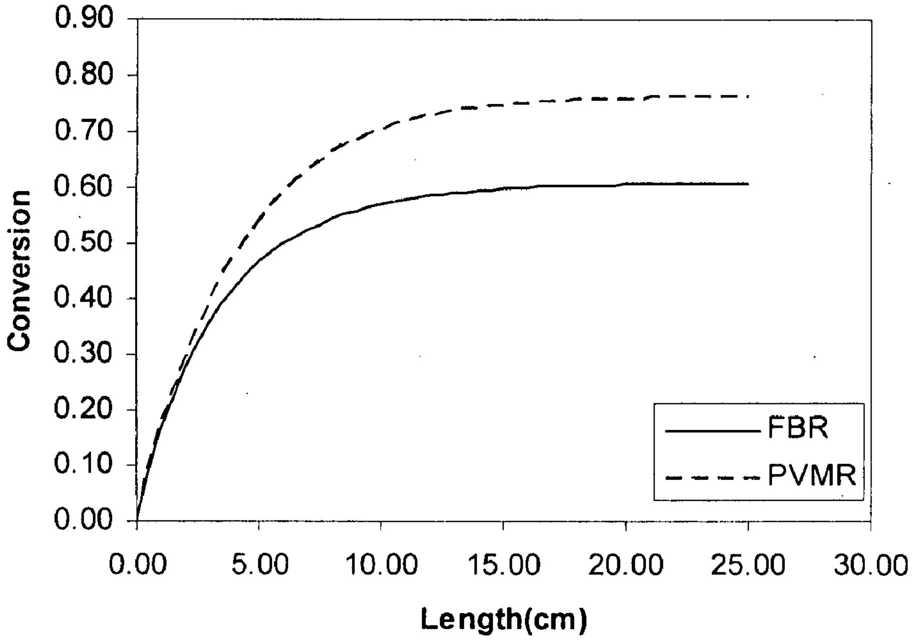


Fig 4.4 Conversion vs length at M=1 and temperature =343K

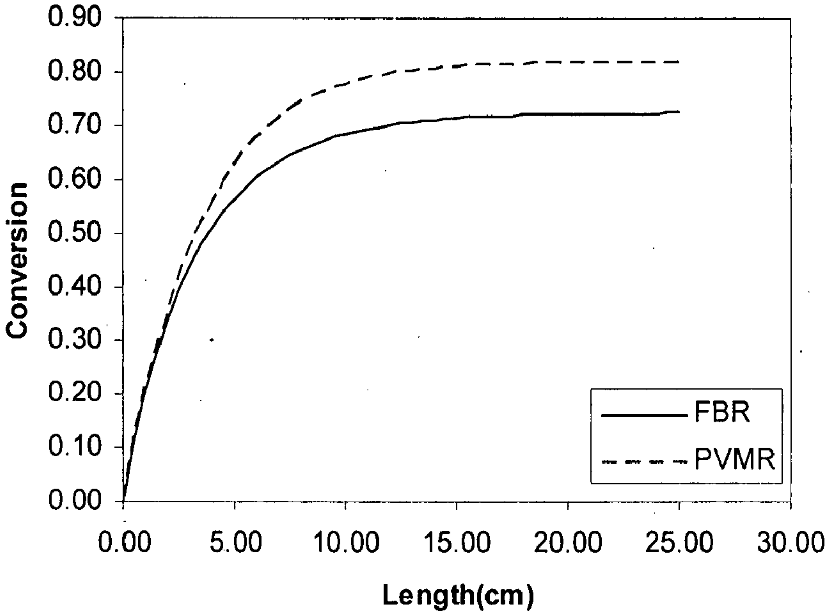


Fig 4.5 Conversion vs length at M=1.5 and temperature =343K

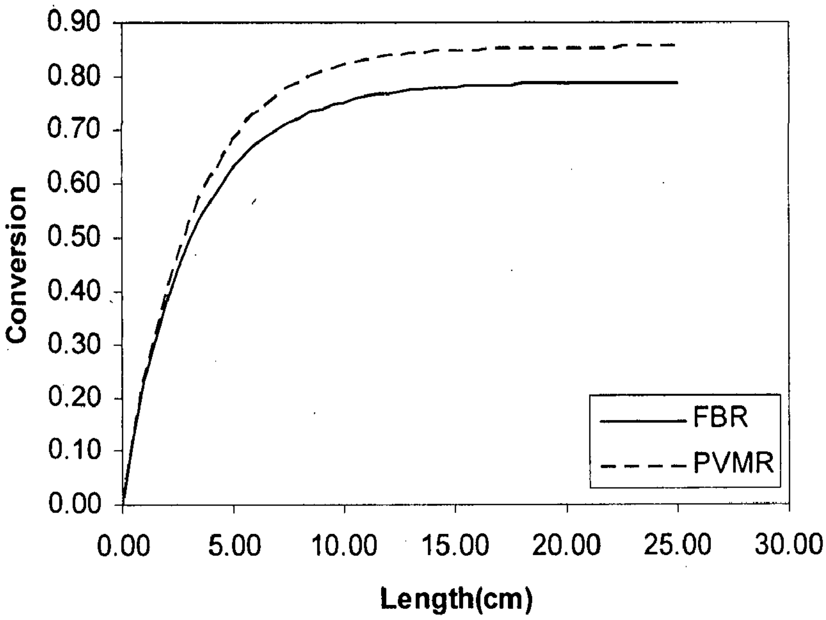


Fig 4.6 Conversion vs length at M=2 and temperature =343K

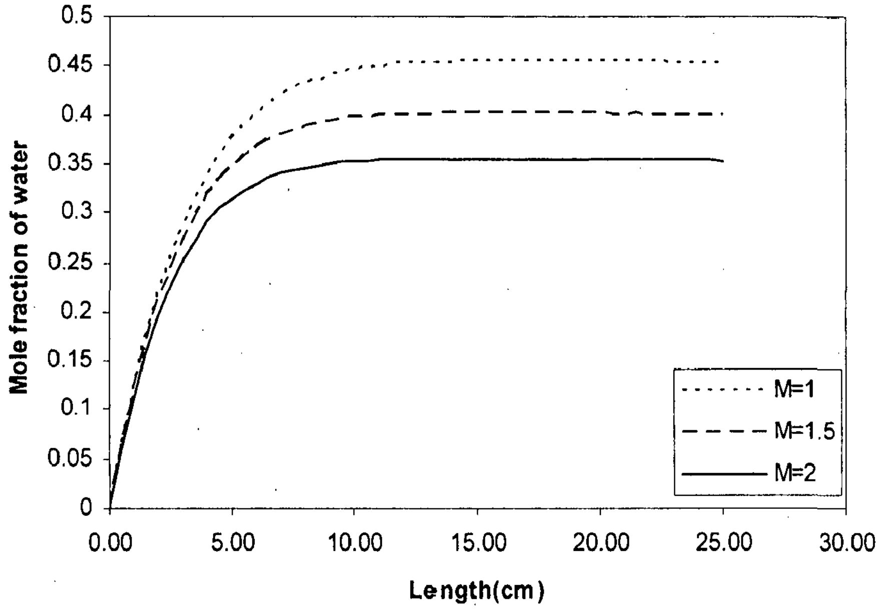


Fig 4.7 Mole fraction of water vs length at different values of M and temperature=348K

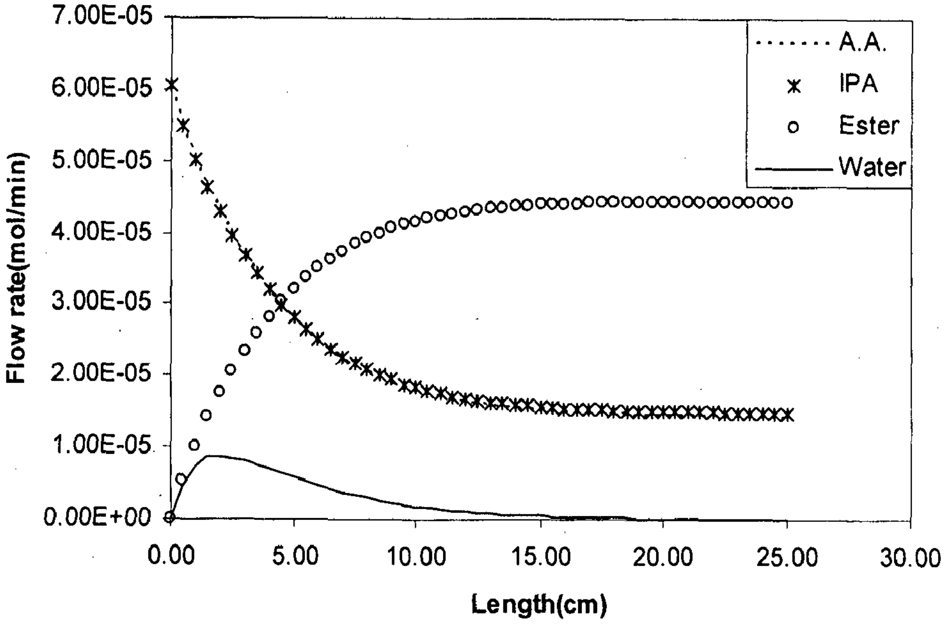


Fig 4.8 Flow rate in tube side of acetic acid, isopropanol, ester, water vs length at M=1 and temperature=343K

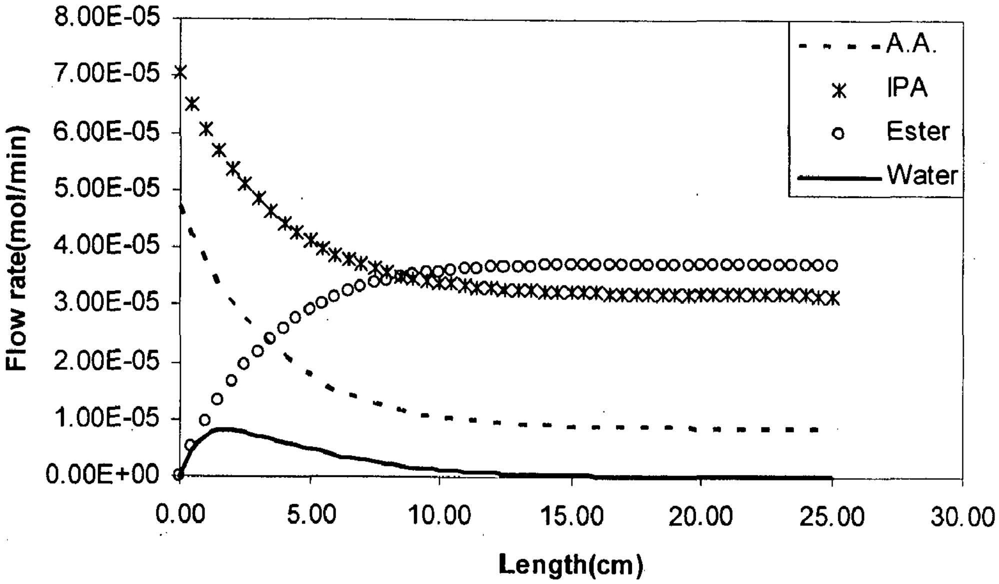


Fig 4.9 Flow rate in tube side of acetic acid, isopropanol, ester, water vs length at M=1.5 and temperature=343K

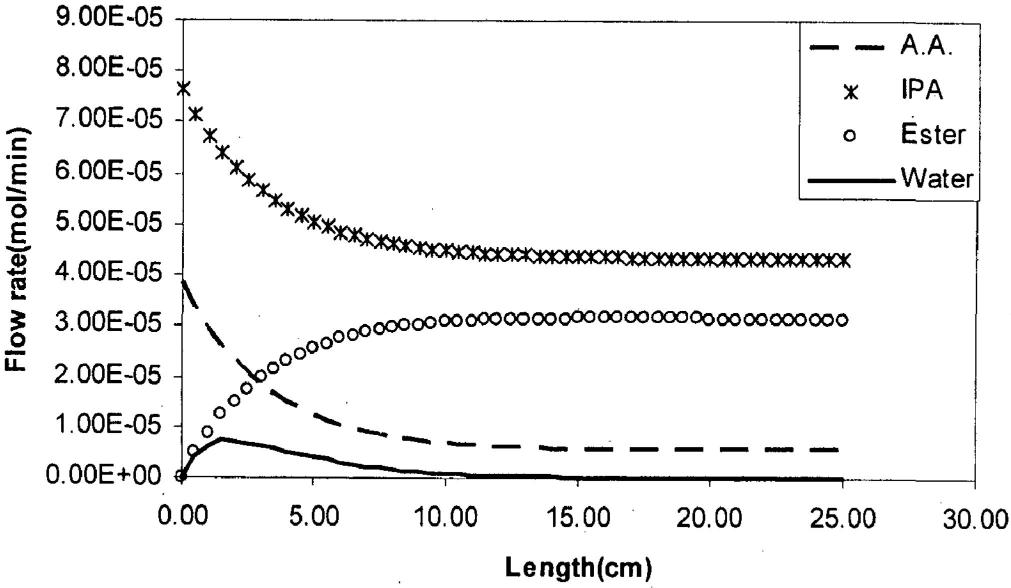


Fig 4.10 Flow rate in tube side of acetic acid, isopropanol, ester, water vs length at M=2 and temperature=343K

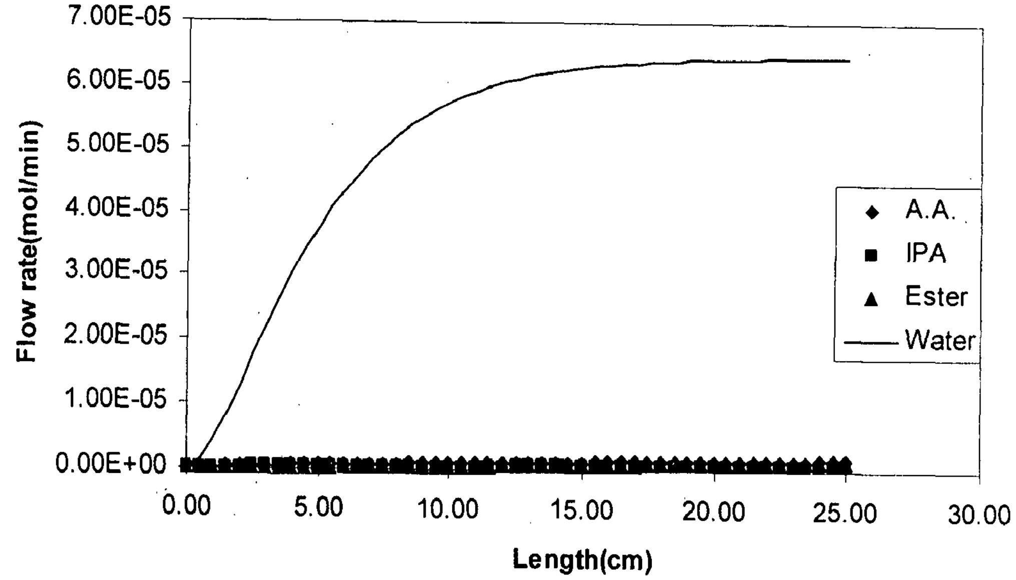


Fig 4.11 Flow rate in shell side of acetic acid, isopropanol, ester, water vs length at M=1 and temperature=343K

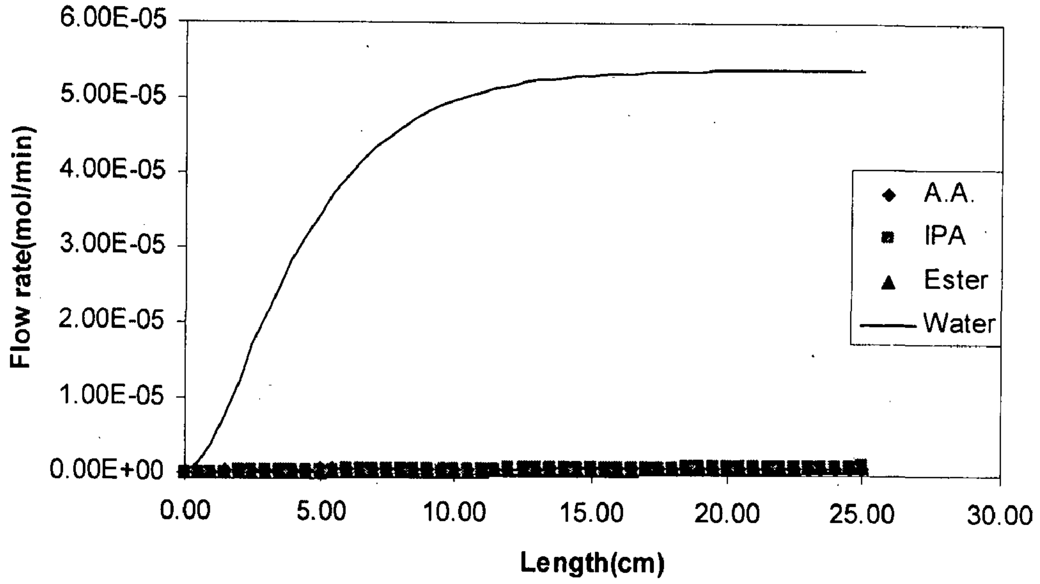


Fig 4.12 Flow rate in shell side of acetic acid, isopropanol, ester, water vs length at M=1.5 and temperature=343K

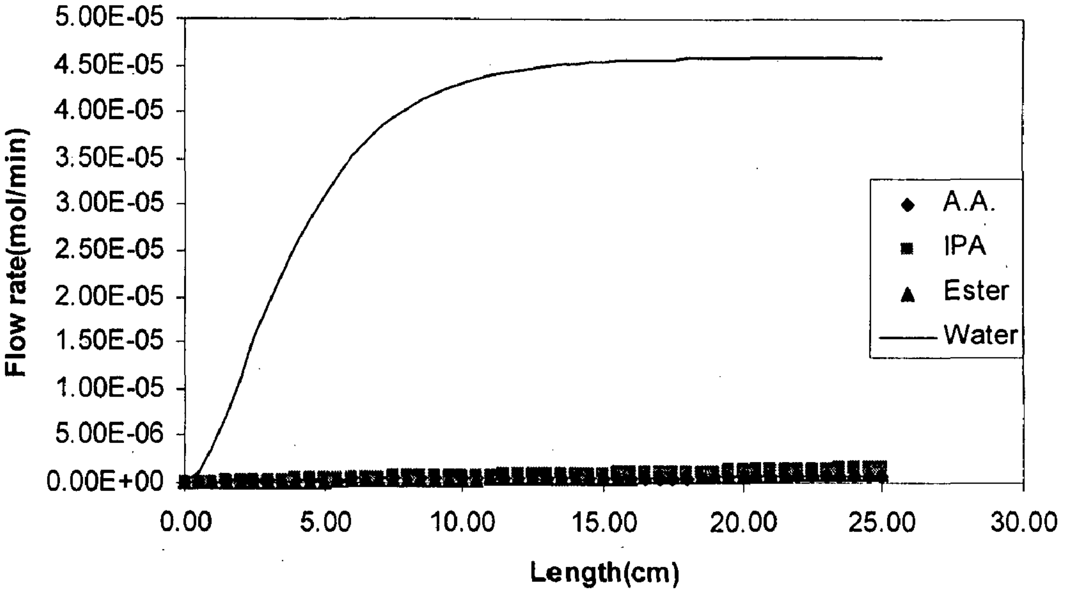


Fig 4.13 Flow rate in shell side of acetic acid, isopropanol, ester, water vs length at M=2 and temperature=343K

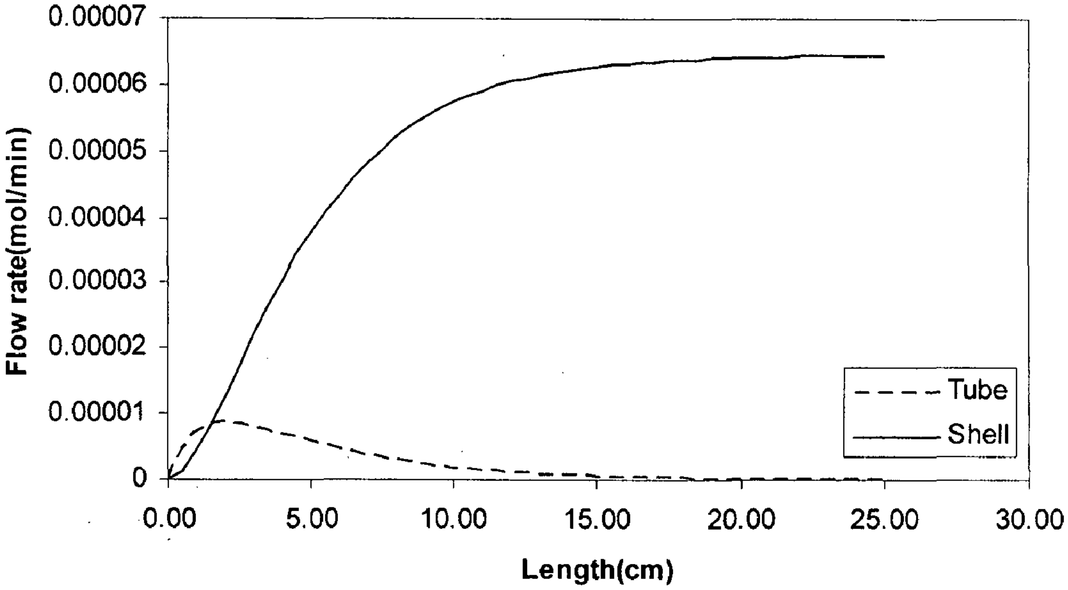


Fig 4.14 Flow rate of water at M=1 and temperature =343K

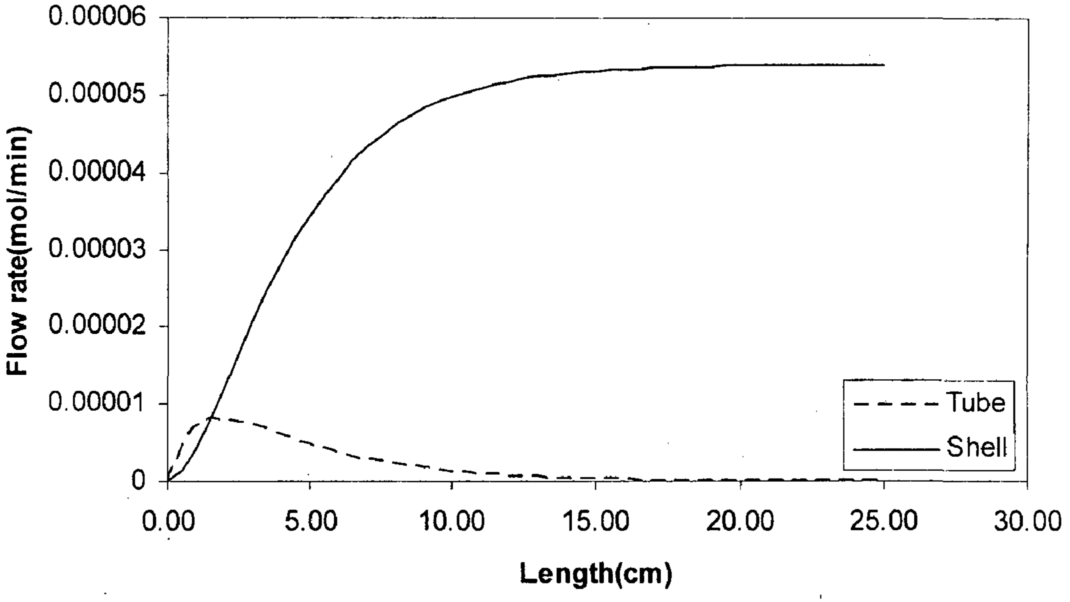


Fig 4.15 Flow rate of water at M=1.5 and temperature =343K

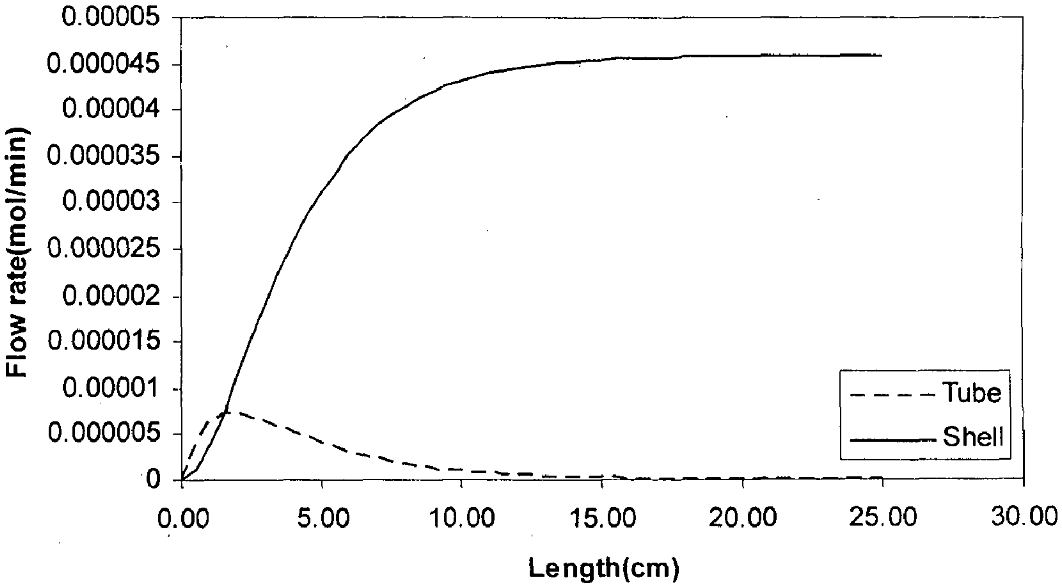


Fig 4.16 Flow rate of water at M=2 and temperature =343K

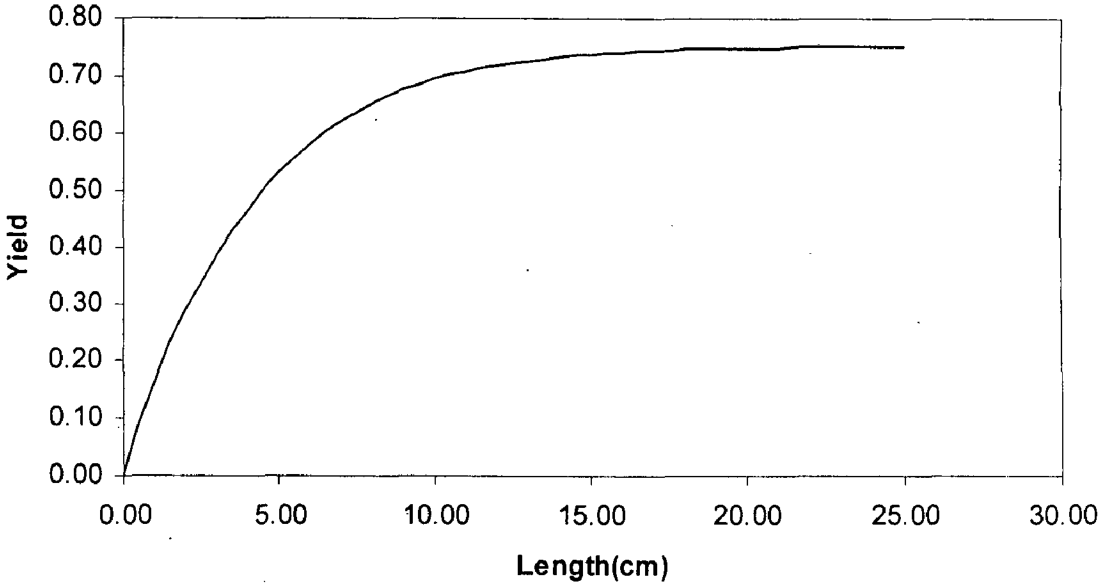


Fig 4.17 Yield of ester vs length at M=1 and temperature =343K

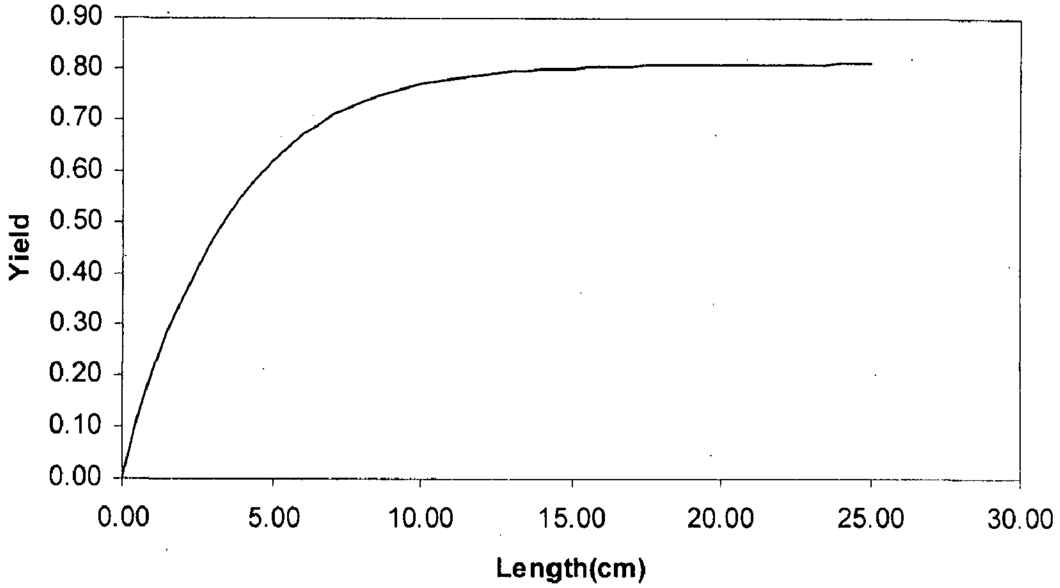


Fig 4.18 Yield of ester vs length at M=1.5 and temperature =343K

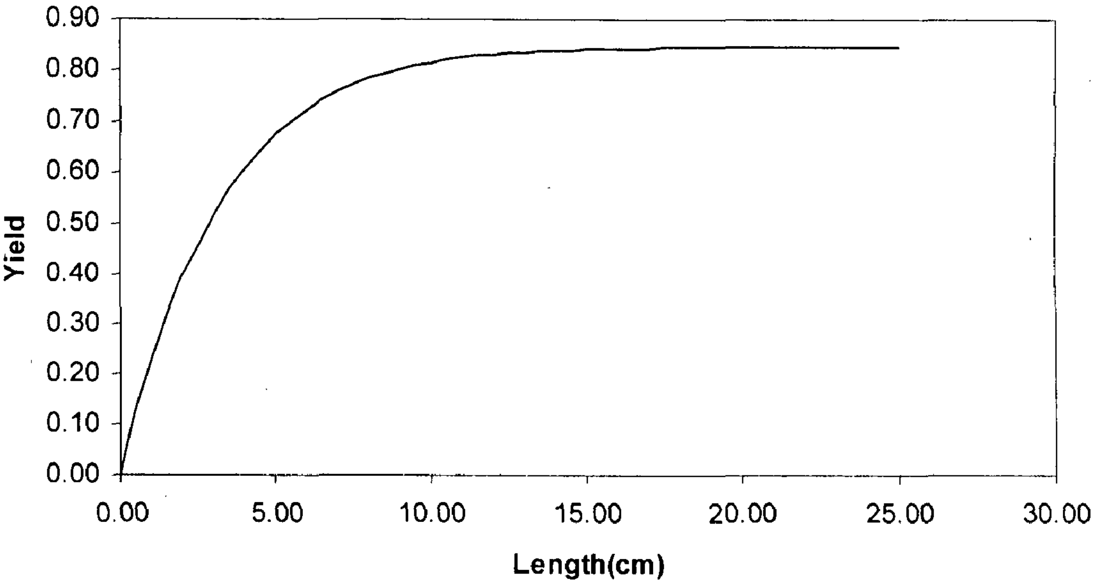


Fig 4.19 Yield of ester vs length at M=2 and temperature =343K

4.3.2 Effect of Temperature:

The Operating temperature has a significant effect on the performance of membrane reactor. Generally suitable temperature for esterification reaction of acetic acid and isopropanol is 343 K. In present work, we have studied the effect of three temperatures i.e. 340 K, 343 K and 348 K.

The Operating temperature has direct effect on the permeation rate and rate of reaction. The Operating temperature influences the driving force for mass transfer in pervaporation process. With increase in temperature, diffusion of permeating components also increases.

Heat of reaction for the esterification reaction of acetic acid and isopropanol is -5kJ/mol [1]. This is an indication of the equilibrium constant is not being a strong function of temperature. In general the equilibrium constant in most esterification reaction is weak function of temperature because of small values of heat of reaction. So we can say that temperature does not have significant effect on conversion. Fig 4.20 and 4.21 shows the variation in mole fraction of ester and isopropanol along with the length of reactor at different temperatures. From these figure it is clear that maximum contents of ester reaches faster at high temperature compare to lower temperature. This is due to high permeation flux through the membrane at high temperature.

Fig 4.22-4.24 shows the variation of flow rate of water in tube side and shell side along with the length of reactor. At T=340 K flow rate of water is 6.43×10^{-5} mol/min, T=343 K flow rate of water is 6.5×10^{-5} mol/min and T=348 K flow rate of water is 6.5×10^{-5}mol/min. which are nearly equal. But in case of high temperature, maximum content of water reaches faster than lower temperature. This shows that permeation flux of water through the membrane is high at high temperature, which is also clear from the permeation flux equation given by Sanz and Gembling (2006). Fig 4.25-4.27 show that equilibrium conversion reaches faster at higher temperature. This is also because of high permeation flux at high temperature, due to which water permeates at faster rate and hence the concentration of products decreases i.e. rate of forward reaction increases, so equilibrium conversion comes faster.

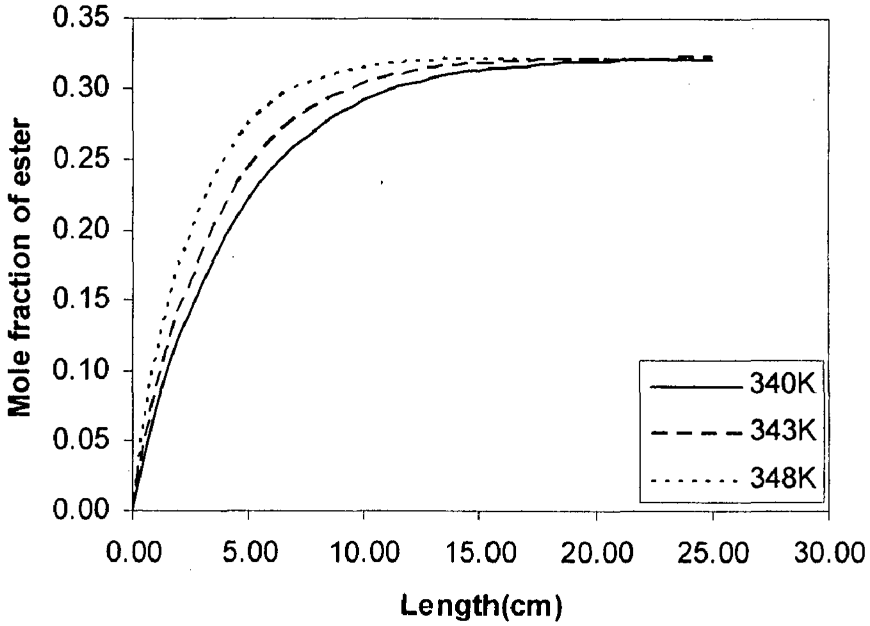


Fig 4.20 Mole fraction of ester vs length at different temperatures and M=1

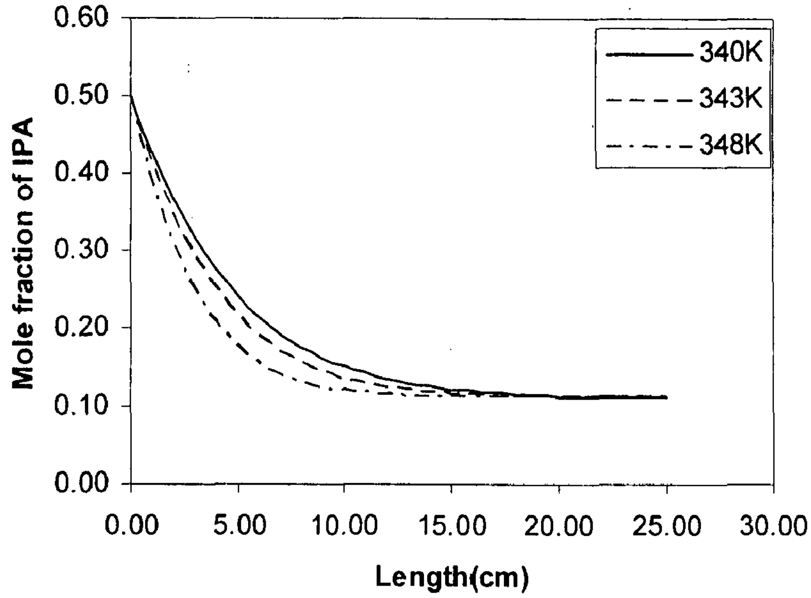


Fig 4.21 Mole fraction of isopropyl alcohol vs length at different temperature and M=1

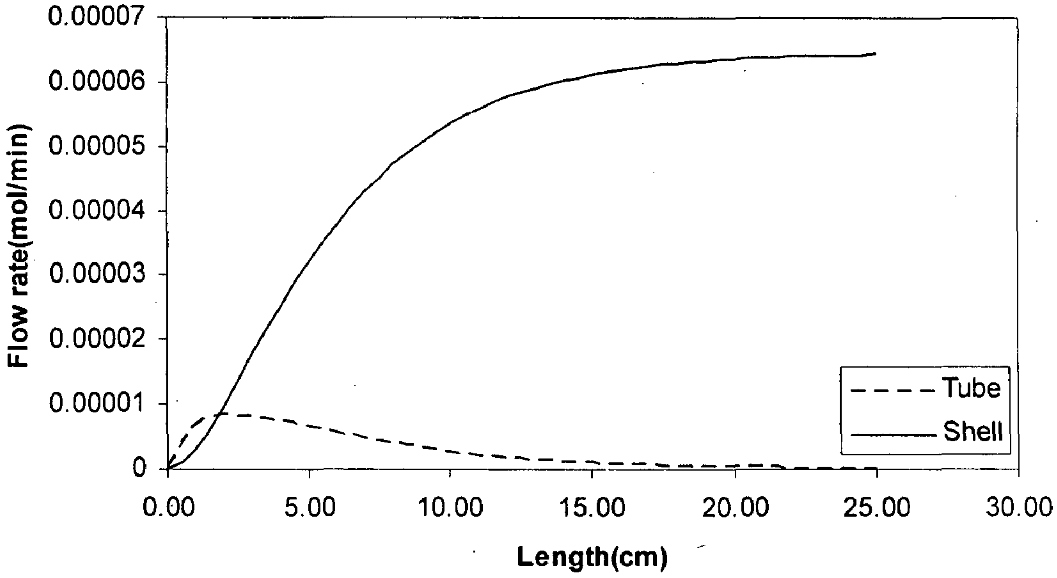


Fig 4.22 Flow rate of water at M=1 and temperature =340K

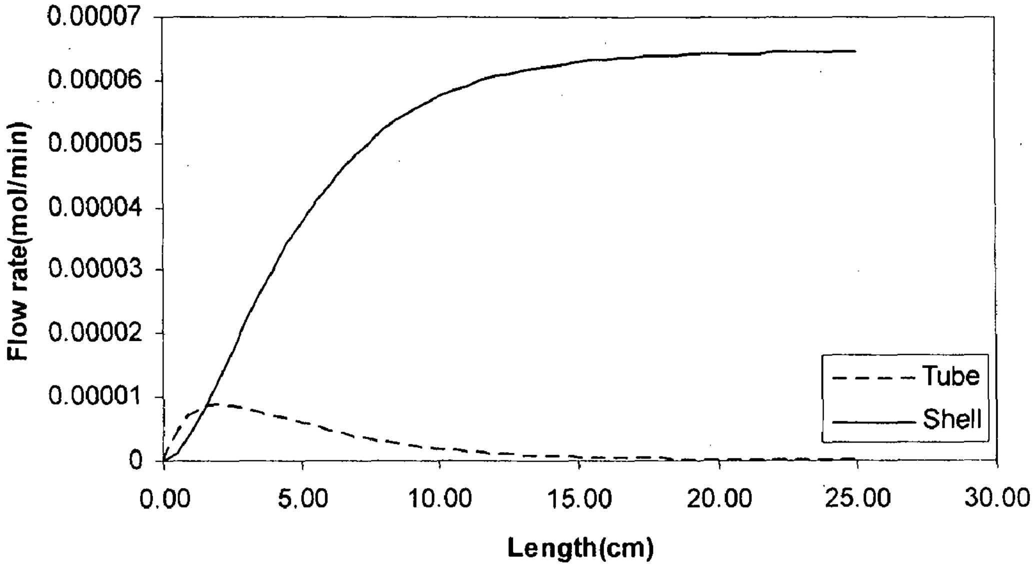


Fig 4.23 Flow rate of water at M=1 and temperature =343K

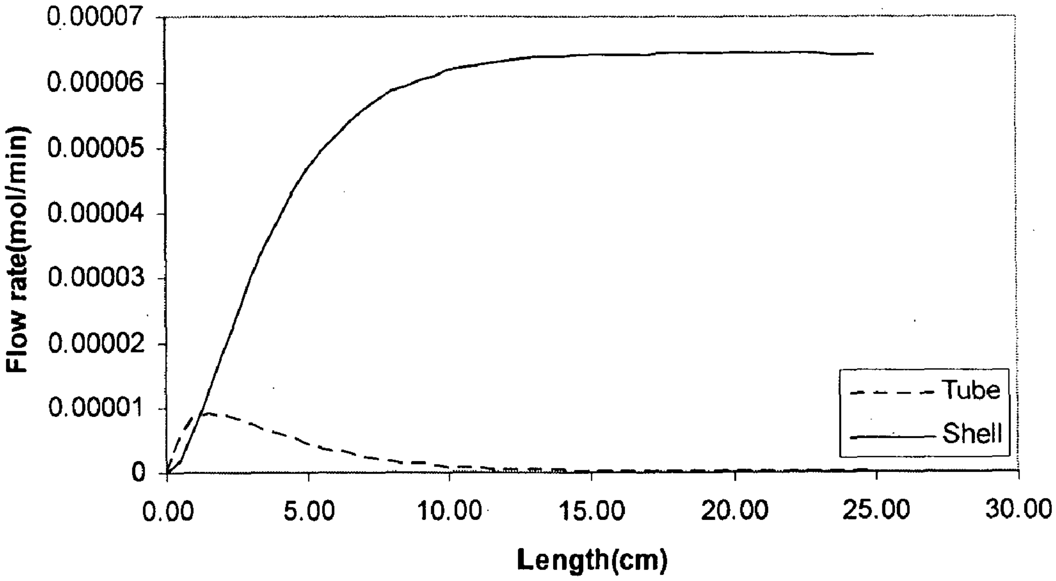


Fig 4.24 Flow rate of water at M=1 and temperature =348K

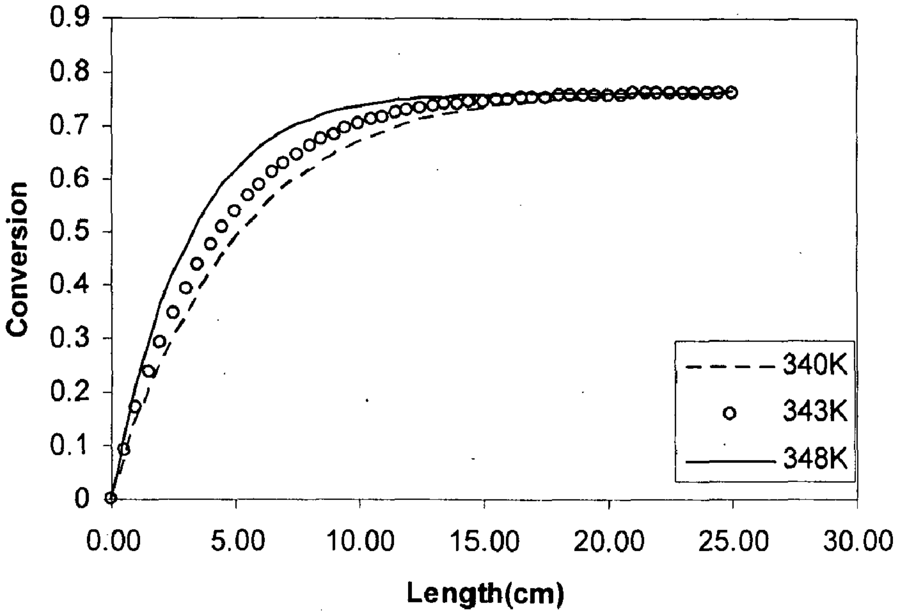


Fig 4.25 Conversion vs length at different temperature, M=1

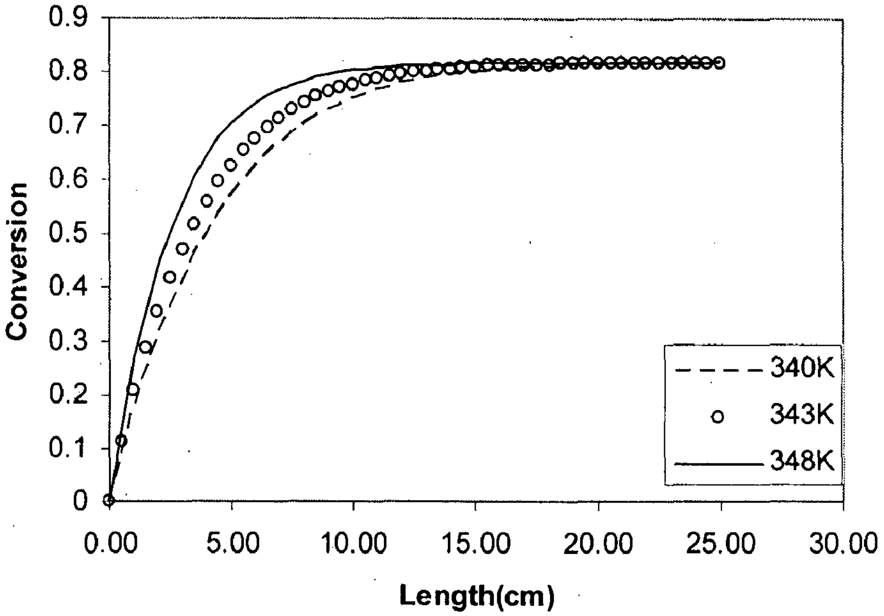


Fig 4.26 Conversion vs length at different temperature, M=1.5

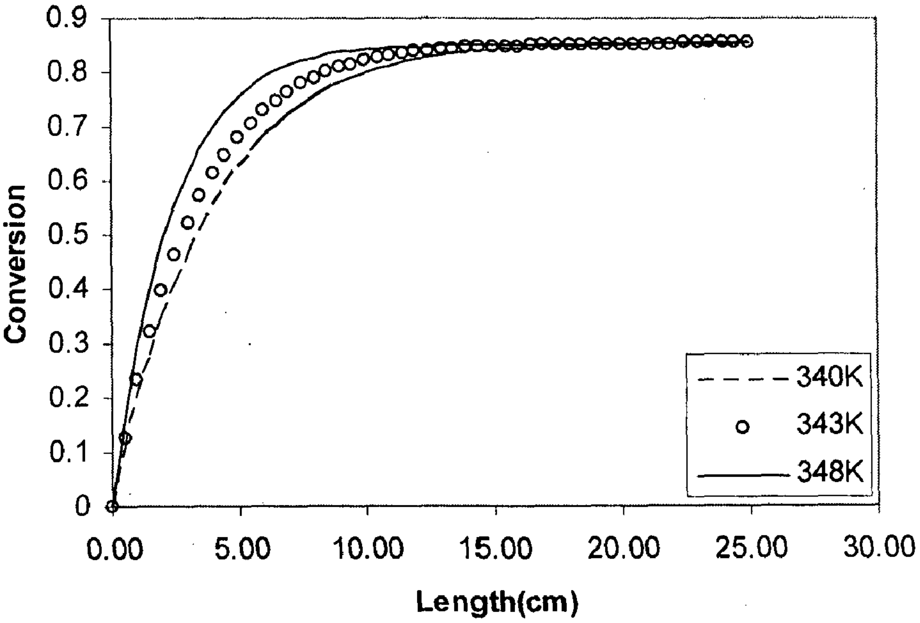
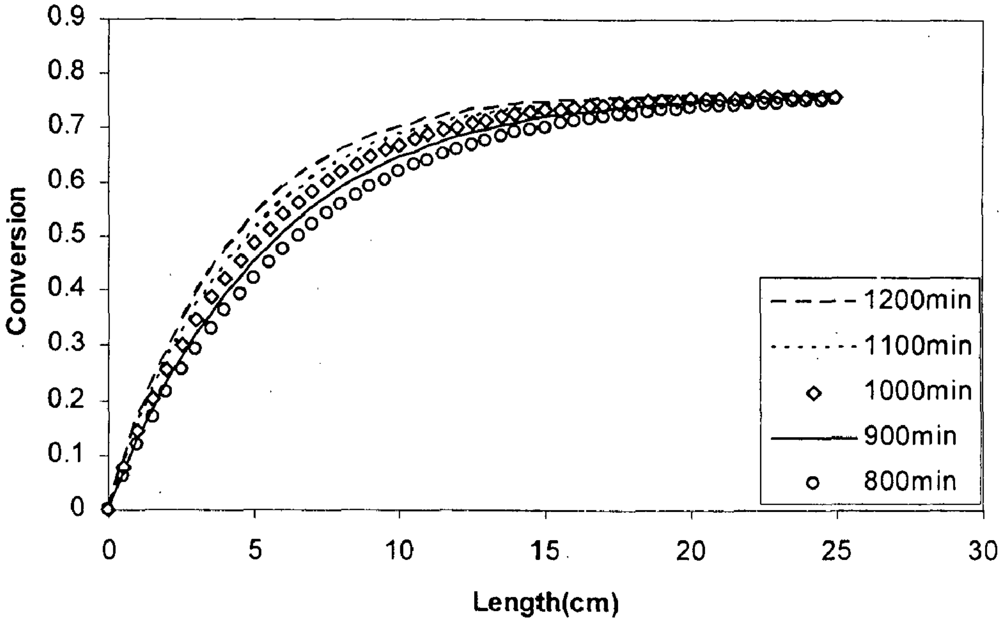


Fig 4.27 Conversion vs length at different temperature, M=2

4.3.3 Effect of Residence Time:

In this system, the volume of the reactor is kept constant, i.e. if we increases residence time flow rate decreases. Fig 4.28 shows the conversion vs length of reactor at different residence time. From this figure we saw that as we increase the residence time equilibrium conversion reached faster. This is because as we increase residence time flow rate decreases, hence reaction mixture getting more time to pass same volume of reactor.



'ig 4.28 Conversion vs length at different space time in min., M=1, T=343K

4.4 CONCLUDING REMARKS:

In this chapter all results regarding conversion of acetic acid, flow rate of acetic acid, isopropanol, ester and water, mole fraction of ester with the effect of temperature, initial feed ratio and residence time are presented graphically. From the results it is found that PVMR showing better performance compared to fixed bed reactor. In general results presented in this chapter show that PVMR can replace the FBR for esterification reaction.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

6.1 CONCLUSION:

A mathematical model for a membrane reactor with PVA membrane is developed for esterification reaction of acetic acid and isopropanol. Mathematical model consist eight ordinary differential equations. These differential equations solved by using ODE solver tool in MATLAB 7.5 for prediction of performance of the reactor. The variation of conversion of acetic acid, flow rate of components in shell and tube side of the membrane reactor and mole fraction of ester have been studied at various values of feed composition and temperature in membrane reactor (PVMR). The results have been compared with conventional fixed bed reactor (FBR).

On the basis of simulated results following conclusions have been drawn:

- Conversion of acetic acid is always higher than the FBR in PVMR.
- Conversion of acetic acid increases as feed ratio increases.
- Mole fraction of ester and water (Products) decreases as feed ratio increases.
- Permeation of acetic acid, isopropanol and ester through membrane is negligible as compare to water therefore PVA membrane is only selective for water.
- Permeation flux of water is high at high temperature.
- At high temperature, the system reaches equilibrium rapidly as compared to low temperature.
- There is negligible effect of temperature on equilibrium values of conversion.
- In order to achieve high conversion, the temperature should be 348 K and feed ratio of acetic acid and isopropanol should be greater than 1:1.

6.2 RECOMMENDATIONS:

- The correlations for permeance through membrane have been taken from literature. If these parameters evaluated experimentally in laboratory, it would have give better results.
- The correlations for kinetic data have been calculated theoretically. If these evaluated experimentally than it would give better results.
- The experimental results taken from the literature are sometimes quite different from those obtained at the industrial scale. It is therefore, recommended that the model must be tested for the data from industries. This will enhance the applicability of the developed model.

REFERENCE

[1] Ali, S.H., S.Q.Merchant (2006)
Kinetics of the esterification of acetic acid with 2-propanol: Impact of different acidic cation exchange resins on reaction mechanism.
Int. J. Chem. Kinet., 38,pp. 593-612

[2] Assabumrugrat, S., J.P.Panich, P.Praserthdam, J.Tagawa, S.Gofo (2003)
Theoretical study on the synthesis of methyl acetate from methanol and acetic acid in pervaporation membrane reactors, effect of continuous flw modes.
Chem. Eng. J., 95, pp. 57-65.

[3] Chemseddine, B., R.Audinos (1996)
Use of ion-exchange membranes in a reactor for esterification of oleic acid an methanol at room temperature.
J. Membr. Sci., 115, pp. 77-84

[4] Coronas, J., J.Santamaria (1999)
Catalytic reactors based on porous ceramic membrane.
Catal. Today, 51, pp. 377-389

[5] David, M.-O., R. Gref, T.Q. Nguyen, J. Neel (1991)
Pervaporation-esterification coupling part I. Basic kinetic model
Trans. IChemE, Part A, 69, pp.335-340

[6] David, M.-O., R. Gref, T.Q. Nguyen, J. Neel (1991)
Pervaporation-esterification coupling part II. Modeling of the influence of di operating parameters.
Trans. IChemE, Part A, 69, pp.341-346

[7] Feng, X., R.Y.M.Huang (1996)
Studies of membrane reactors for esterification facilitated by pervaporation.
Chem. Eng. Sci., 51, pp. 4673-4679

[8] Gao,Z., Y.Yue, W.Li (1996)
Application of zeolite-filled pervaporation membrane.
Zeolites, 16, pp.70-74

[9] http://www.lenntech.com/images/Boiler%20FE%20images/membrane.JPG

[10] Iglesia, O.D.L., R.Mallada, M.Menendez, J.Coronas (2007)
Continuous zeolites membrane reactor for esterification of ethanol and acetic acid.
Chem. Eng. J., 131, pp. 35-39

[11] Jafar, J.J., P. M. Budd, R. Hughes (2002)
Enhancement of esterification reaction yield using zeolites A vapor permeation membrane.
J. Membr. Sci., 199, pp. 117-123

[12] Keurentjes, J.T.F., G.H.R.Janssen, J.J.Gorissen (1994)
The esterification of tartaric acid with ethanol: kinetics and shifting the equilibrium by means of pervaporation.
Chem. Eng. Sci., 49, pp. 4681-4689

[13] Krupiczka, R., Z.Koszorz (1999)
Activity based model of the hybrid process of an esterification reaction coupled with pervaporation.
Separation and purification technology 16 pp. 55-59

[14] Kulprathipanja, S. (2001)
Reactive separation processes
Taylor & Francis, London

[15] Lim,S.Y., B.-G. Park, F. Hung, M. Sahimi, T.T. Tsotsis (2002)
Design issues of pervaporation membrane reactors for esterification.
Chem. Eng. Sci., 57, pp. 4933-4946

[16] Liu, Q.L., Z. Zhang, H.Chen (2001)
Study of coupling of esterification with pervaporation.
J. Membr. Sci., 182, pp. 173-181

[17] Park, B.-G., T.T. Tsotsis (2004)
Model and experiments with pervaporation membrane reactors integrated with an adsorbent system.
Chem. Eng. Prog., 43, pp. 1170-1180

[18] Peters, T.A., J.V. Twin, C.Houssen, M.A.G. Vortsman, N.E.Benes, Z.A.E.P.Vroon, A.Holmen, J.T.F.Keurentjes (2005)
Pervaporation of zeolite-coated pervaporation membranes for the integration of reaction and separation.
Catal Today, 104, pp.288-295

[19] Sanz, M.T. , J. Gmehling (2006)
Esterification of acetic acid with isopropanol coupled with pervaporation part I: Kinetics and pervaporation studies.
Chem. Eng. Technol, 123, pp.1-8.

[20] Sanz, M.T. , J. Gmehling (2006)
Esterification of acetic acid with isopropanol coupled with pervaporation part II: Study of pervaporation reactor.
Chem. Eng. Technol, 123, pp.9-14.

[21] Seader, J.D., E.J.Henley (1998)
Separation process principles, John Wiley & Sons.

[22] Shah, T.N., S.M.C.Ritchie (2005)
Esterification catalysis using functionalized membranes.
Appl. Catal. A, 296, pp. 12-20

[23] Tanaka, K., R.Yoshikawa, C.Ying, H.Kita, K.-I. Okamoto (2001)
Application of zeolite membranes to esterification reactions.
Catal Today, 67, pp.121-125

[24] Wynn, N. (2001)
Pervaporation comes on age.
Chem. Eng. Prog., 97, pp.66-72

[25] Xueuhi, L.,W. Lefu (2001)
Kinetic model of esterification by pervaporation.
J. Membr. Sci., 186 pp. 19-24

[26] Zhu, Y., R.G.Minet, T.T.Tsotsis (1996)
A continuous pervaporation membrane reactor for the study of esterification reactions using a composite polymeric/ceramic membrane.
Chem. Eng. Sci., 51, pp. 4013-4113