MODELING OF PERVAPORATION REACTOR FOR ESTERIFICATION

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

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CANDIDATE'S DECLARATION

I, hereby, declare that the work which is being presented in the Dissertation entitled, **"MODELING OF PERVAPORATION REACTOR FOR ESTERIFICATION"**, 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 (IIT) Roorkee** , This is an authentic record of my own work carried out under the esteemed guidance of **Dr. V. K. Agarwal**, and **Dr. Kailas L. Wasewar.**

I have not submitted the matter, embodied in this dissertation for the award of any other degree of this or any other Institute/University.

Date:19,June, 2007.
Place: IIT Roorkee.

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CERTIFICATE

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

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ABSTRACT

In recent years pervaporation has emerged as an energy efficient and highly selective separation process for the separation of volatile products and for the dehydration of organic chemicals. Also the productivity and conversion rate can be significantly increased when reaction is coupled with pervaporation i.e. pervaporation reactor. The pervaporation reactor is, specially, the new technology for reaction and separation. It is rather difficult to predict the market potential of processes newly introduced on the market. However, In comparing investment costs, environmental aspects of pervaporation system with those of conventional processes, it can be said that pervaporation reactor will play an important role in the chemical industry for new installments as well as for rehabilitation of existing plants. Techno-economic studies are showing that pervaporation reactors have good market potential. The most common reaction system studied for the application of pervaporation is an esterification reaction between an alcohol and an acid in the presence of a catalyst. In this industrial reversible reaction, high conversion can get by adding a large excess of reactants. By placing a water selective pervaporation membrane in the esterification reactor; equilibrium can shift to the right thus reducing the excess reactants.

The model equations for pervaporation reaction were developed based on the reaction kinetics and pervaporation data for the esterification of acetic acid with *n*-butanol, lactic acid with ethanaol and acetic acid with ethanol. The available experimental data has been used for the modeling purpose. The influence of several process parameters, such as process temperature, initial mole ratio of acid over alcohol, the ratio of the effective membrane area over the volume of reacting mixture catalyst content, and flux, on the esterification have been discussed. The process parameters can be changed in order to attain the optimum values for the pervaporation-esterification coupling. The simulation results were compared with the experimental results and are in excellent agreement. Presented model can be used for every type of esterification reactions in pervaporation reactor.

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NOMENCLATURE

C_A : Concentration of acid in reactor (kmol/m^3)
C_{A0} : Initial concentration of acid in reactor (kmol/m^3)
C_B : Concentration of alcohol in reactor (kmol/m^3)
C_C : Concentration of catalyst in reactor (kmol/m^3) or (g/l)
C_R : Concentration of ester in reactor (kmol/m^3)
C_H : Concentration of water in reactor (kmol/m^3)
J_H : Water flux through membrane (kmol/m^2min)
J_A : Acid flux through membrane (kmol/m^2min)
J_B : Alcohol flux through membrane (kmol/m^2min)
J_A : Ester flux through membrane (kmol/m^2min)
k_1 : Forward reaction rate constant (m^3/kmol min)
k_2 : Backward reaction rate constant (m^3/kmol min)
k_{PV1} : Empirical constant in equation
k_{PV2} : Empirical constant in equation
k_{obs} : Observed kinetic constant (m^3/kmol min)
K : Equilibrium constant
r_H : Rate of formation of water by acetylation reaction (kmol/m^3min)
S : Area of membrane (m^2)
t : Reaction time (min)
V : Volume of reaction mixture (m^3)
i : Component number
X_i : Conversion of component i
X_A : Conversion of alcohol
X_A : Conversion of acid
E : Activation Energy (kJ/mol)
R : Gas constant (J/mol K)
T : Reaction Temperature (^{0}C)
R_0 : Initial molar ratio of reactants
S/V : Ratio of membrane area to reaction volume (m^{-1})

CHAPTER I

INTRODUCTION

The increased world-wide competitiveness in production has forced industry to improve current process designs. Consequently, the development of new process designs, and the reorganization of present process designs (with the possible integration of new technologies into them) is of growing importance to industry. Membrane technologies have recently emerged as an additional well-established mass transfer processes. Membranes have gained an important place in chemical technology and are used in broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane.

Membrane reactors have been investigated since the 1970s. The early investigations employed primarily polymeric membranes and enzymatic reactions. Later investigations show an abundance of petrochemical relevant systems and inorganic membranes. Whole cell fermentation-based chemical and biochemical productions as well as degradation of pollutants biologically or otherwise have also been studied in membrane reactors. Polymer membrane-based reactors have been blessed with some commercial success. The membrane inside the reactor (i.e. membrane reactor) has served a variety of functions. In some studies, the membrane has a single well-defined function. In others, the membrane allows two or more functions to be carried out. The variety of functions achievable via a membrane in a reactor is very broad. An understanding of the breadth of the roles capable of being performed by a membrane is likely to be quite useful in the future development of membrane reactors. This perspective can be developed by employing a variety of contexts including different membrane separation processes, different membranes, chemical/electrochemical reactions, enzymatic processes, fermentations, catalyst immobilization/segregation, catalytic membranes, integration of functions etc.

A membrane reactor has one or more of the functions such as : Separation of products from the reaction mixture; Separation of a reactant from a mixed stream for introduction into the reactor; Controlled addition of one reactant or two reactants; Non-dispersive phase contacting (with reaction at the phase interface or in the bulk phases); Segregation of a catalyst (and cofactor) in a reactor; Immobilization of a catalyst in (or on) a membrane; Membrane is the catalyst; Membrane is the reactor; Solid-electrolyte membrane supports the electrodes, conducts ions, and achieves the reactions on its surfaces; Transfer of heat; Immobilizing the liquid reaction medium.

In the last few years membrane operations have shown their potentialities in the rationalization of productions systems. Their intrinsic characteristics of efficiency, operational simplicity and flexibility, relatively high selectivity and permeability for the transport of specific components, low energy requirements, good stability under a wide spectrum of operating conditions, environment compatibility, easy control and scale up have been confirmed in a large variety of applications, and operations, as molecular separations, fractionations, concentrations, purifications, clarifications, emulsifications, crystallizations, etc. in both liquid and gas phases and in a wide spectrum of operating parameters, such as pH, T, P, etc.

The most common reaction system studied for the application of pervaporation reactor is an esterification reaction between an alcohol and an acid in the presence of a catalyst.

$$\underset{Acid}{R_1COOH} + \underset{Alcohol}{R_2OH} \overset{Cat}{\Longleftrightarrow} \underset{Ester}{R_1COOR_2} + H_2O \uparrow \tag{1.1}$$

Esterification reactions are typically limited by thermodynamic equilibrium, and face challenges with product purification. Commercially, they are carried out using either large excess of one of the reactants, or by removing through reactive distillation one of the products. The former is a relatively inefficient approach because it requires a large reactor volume. As a result reactive distillation, which favorably shifts equilibrium through the removal of one of the products, is becoming more common in plant-scale production. It is, however, an energy-demanding operation and is not recommended when dealing with temperature-sensitive chemicals or biocatalysts. The aforementioned difficulties have motivated efforts for the development of other coupled reactive/separation processes. Pervaporation reactors, in particular, are receiving increased attention as a potentially competitive alternative to reactive distillation. (Lim et al. 2002)

In this industrial reversible reaction, high conversion can get by adding a large excess of acid. By placing a water selective pervaporation membrane in the esterification reactor, equilibrium can shift to the right thus reducing the excess reactants. 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 pervaporation reactor tolerates the presence of water, which can be either in the reaction medium or as impurity of the reacting reagent. There are upper and lower limits in the performance of reactor facilitation by pervaporation. Membrane permeability, membrane area and the volume of the reaction mixtures to be treated are important operating parameters influencing the reactor behavior. Operating temperature influences reactor performance through its influences on reaction rate and membrane permeability. Both conversion and reaction rate can be enhanced by using pervaporation to remove water from the reactor simultaneously.

1.1 MEMBRANE REACTOR

There has been an engineering effort to combine reaction and separation into a single process unit so as to improve process performance. In recent years membrane technology has emerged as one of the viable unit operations in separation processes. The potential applications of membrane technology in reaction engineering are being recognized. Since separation membranes permit selective permeation of a component from a mixture, membrane reactors can help enhance the conversion of thermodynamically or kinetically limited reactions through controlled removal of one or more reactant or product species from the reaction mixture.

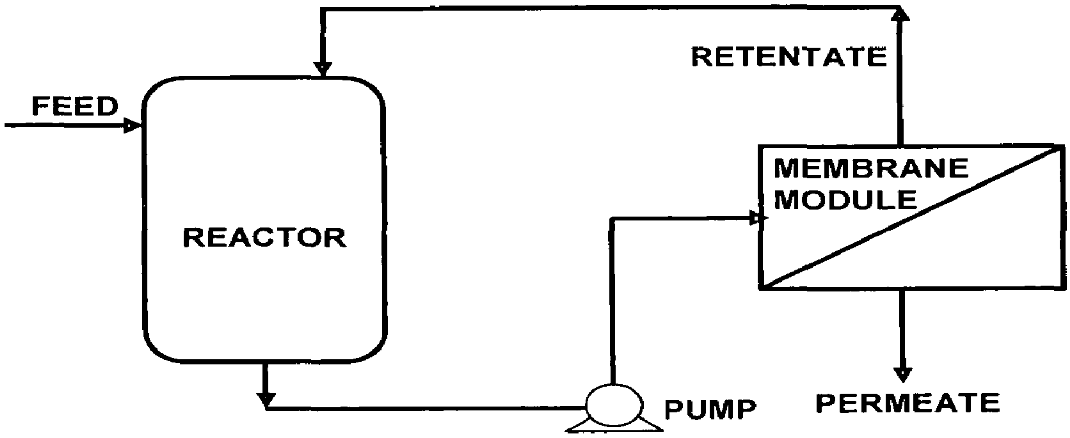

Figure 1.1 Typical diagram of membrane reactor.

There is currently a great deal of interest in the development and use of alternative non-conventional techniques that allow both the separation and purification of the compounds obtained during a process and the use of systems that combine the reaction and separation in a single process in order to increase the efficiency of the pervaporation reaction, as was theoretically described by Feng and Huang (1996). Among these techniques is that of the separation and purification of products through the use of selective membranes. A typical diagram for the membrane reactor has been given in the **Figure 1.** Details of the various functions and applications are available in the literature (Sirkar et al., 1999)

The nature of the membrane reactor is obviously influenced by the phase of the reaction medium exposed to the membrane and the desired phase of the permeated product stream. There are two categories for such cases; liquid reaction medium/liquid feed phase and gaseous reactions/gaseous feed phase. In the case of separation from liquid reaction mixture, reverse osmosis (Vasudevan et al., 1987), ultrafiltration (Cheryan and Mehaia, 1986; Closset et al., 1973), pervaporation (David et al., 1991; Strathmann and Gudernatsch, 1991), gas separation membranes (Sirkar, 1992; Twardowski and McGilvey, 1987), vacuum membrane distillation, electrodialysis (Strathmann, 1992), liquid membranes (Ricks et al., 1992) can be used. For separation from gaseous reaction mixture, liquid membranes (Ollis et al., 1972), Knudsen diffusion (Sun and Khang, 1988; Zaika et al., 1993; Wu and Liu, 1992), vapor permeation, gas permeation/molecular sieving (Willms et al., 1995; Dixon et al., 1994), etc. can be used. In the recent years pervaporation has emerged as an energy efficient and highly selective separation process for the separation of volatile products and for the dehydration of organic chemicals. Also the productivity and conversion rate can be significantly increased when reaction is coupled with pervaporation i.e. pervaporation reactor. (Wasewar, 2005)

1.2 PERVAPORATION TECHNOLOGY

1.2.1 History of Pervaporation

As early as 1906, L. Kahlenberg reported a qualitative study on the separation of a mixture of a hydrocarbon and an alcohol through a rubber membrane. In 1955, D. H. Hagerbaumer conducted the first quantitative investigation with a microporous Vycor glass membrane with a high-pressure drop across it, to allow for the separation of liquid-liquid mixtures.(1,99) Later in 1965 Binning et al., at American Oil, utilized this operation of separating a liquid-liquid mixture into a vapor mixture using a nonporous polymeric film. This research yielded a high degree of separation along with high permeation rates. The process did not come into commercial use until 1982 when Gesellchaft fur Trenntechnik mbH (GFT) of Germany installed a pervaporation plant to separate water from concentrated alcohol solutions. Since then, more than one hundred plants have been installed. Recently, Exxon has used pervaporation in its refineries to separate hydrocarbon mixtures containing aromatics and aliphatics. Another commercial use for pervaporation is the removal of methylene chloride from small waste streams.

1.2.2 Pervaporation Principle

Pervaporation involves the use of a liquid feed to produce a vapor permeate and a liquid retentate. In pervaporation, the separation of two or more components across a membrane is taken place by differing rates of diffusion through a thin polymer and an evaporative phase change comparable to a simple flash step. A concentrate and vapor pressure gradient is used to allow one component to preferentially permeate across the membrane. A vacuum applied to the permeate side is coupled with the immediate condensation of the permeate vapors. A schematic diagram for pervaporation is shown in **Figure 2.**

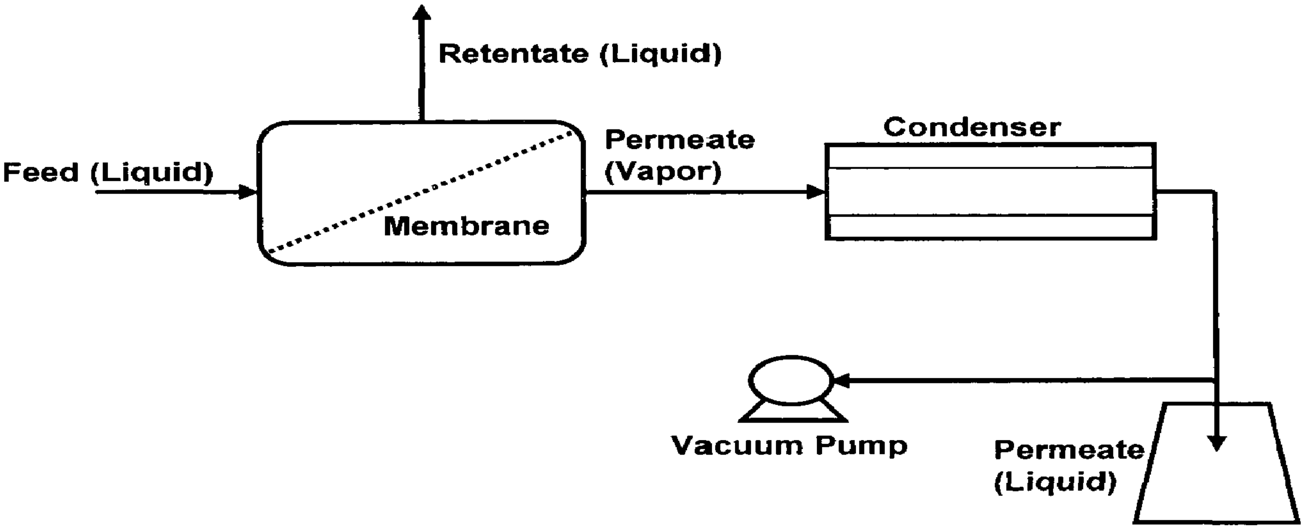

Figure 1.2 Schematic diagram of pervaporation process.

Liquid transport in pervaporation takes place to the thickness of the membrane by following steps:

1. Sorption of the permeate at the interface between the feed solution and membrane.
2. Diffusion across the membrane due to concentration gradient of individual permeant.
3. Desorption into vapor phase at the permeate side of membrane.

Pervaporation, in its simplest form, is an energy efficient combination of membrane permeation and evaporation. It's considered an attractive alternative to other separation methods for a variety of processes. For example, with the low temperatures and pressures involved in pervaporation, it often has cost and performance advantages for the separation of constant-boiling azeotropes dehydration of organic solvents and the removal of organics from aqueous streams. Additionally, pervaporation has emerged as a good choice for separation heat sensitive products. Characteristics of the pervaporation process include:

- Low energy consumption
- No entrainers for separation of azeotropic mixtures
- Permeate must be volatile at operating conditions
- Functions independent of vapor/liquid equilibrium
- Enables new chemical reaction routes in esterifications
- Effective and economic separation of mixtures of substances with small difference in boiling point and azeotropic mixtures
- Modular membrane design
- Reduced capital costs compared to conventional systems
- Simpler processing
- One step separation
- Cleaner end products
- Multi-purpose unit operation

1.2.3 Membranes for pervaporation

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.

1.3 ESTERIFICATION REACTIONS

There are many equilibrium-limited systems where the application of this concept would be beneficial, including dehydrogenations, synthesis gas production and esterifications. In this we focus on pervaporation-esterification coupling. Industrially widely applied esterification reactions are conveniently catalysed using mineral acids. A class of industrially relevant equilibrium reactions is esterification reactions in which water is one of the products. Esters have various applications, ranging from plasticizers, surface-active agents, flavor and perfume materials, to solvents for the production of various chemicals. One of the main disadvantages of esterification reactions is that they suffer from a low conversion. In addition to the low conversion, the presence of a possible azeotrope between reactants and products also makes an esterification process more difficult to operate. A simplified reaction equation is given by.

$$\underset{Acid}{R_1COOH} + \underset{Alcohol}{R_2OH} \overset{Cat}{\Longleftrightarrow} \underset{Ester}{R_1COOR_2} + H_2O \uparrow \tag{1.1}$$

In practice, there are two methods to improve the conversion of equilibrium reactions. In the first approach, a large excess of one of the starting reactant is used. However, this results in a relatively inefficient use of reactor space, and an efficient separation is required afterwards reaction products. For esterification reactions water is the most appropriate component that can be removed. There are a number of ways to remove one of the reaction products. Reactive distillation is an appropriate technique for the removal of water from alcohols **(see Figure 1.3)**. However, for these systems the formation of an azeotrope is a potential drawback, which limits the (process) selectivity. Furthermore, in the case of the production of temperature-sensitive products or for biocatalyst conversions, the application of distillation is not feasible as a result of temperature constraints. Membrane separations can be considered a viable alternative for a number of cases. For the removal of water from organic streams, pervaporation seems to be the appropriate membrane technique. The main purpose of the pervaporation membrane is to remove the water from the reaction mixture in order the increase the product yield.

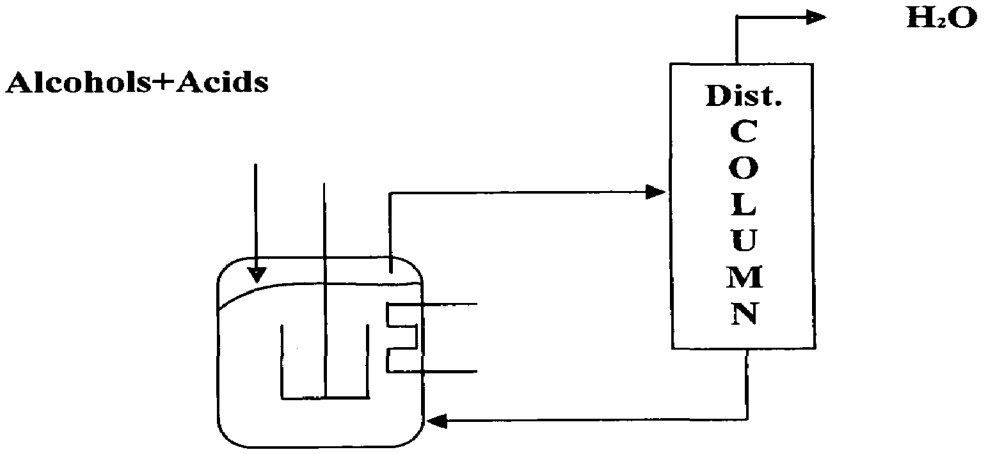

Figure 1.3 Conventional Process for the Production of Esters

1.4 ADVANTAGES AND DISADVANTAGES OF PERVAPORATION REACTOR

1.4.1 Advantages

Pervaporation separation technology offer advantages over existing mass transfer processes. Such advantages can comprise

- High selectivity and permeability for the transport of a specific components
- Increases reaction rate and conversion
- Low energy requirements
- Good stability under wide spectrum of operating conditions
- Moderate cost to performance ratio
- Environment compatibility
- Easy control and scale up have been confirmed in a large variety of applications

1.4.2 Disadvantages of pervaporation reactors

Pervaporation reactors have following disadvantages:

- Relatively new technology.
- Limited applications window.
- Extensive experimental development is required.
- Complex modeling requirement.
- Extensive design efforts.
- Increased operational complexity.
- Significant development costs.
- Increased scale-up risks.
- Certain solvents can quickly and permanently destroy the membrane.

1.5 TYPES OF PERVAPORATION PROCESSES

Various types of pervaporation separation processes have been developed for specific industrial applications. Some of the widely used processes are discussed hereunder:

1.5.1 Batch Pervaporation

Batch units are simple, flexible, and highly suited for smaller throughputs. The liquid feed from a batch tank is pumped through heat exchangers to recover the heat content from the product stream. It is then passed continuously through the membrane separation modules. The membrane modules are contained within vacuum chambers. The permeate is condensed and the retentate is returned back to the tank. With every pass, the retentate gradually becomes more and more concentrated. The process is repeated until the desired purification level is achieved.

1.5.2 Continuous Pervaporation

Continuous units are typically used in a manufacturing environment where larger throughputs are required. The feed is preheated and continuously passed through a series of membrane separation modules. Each module is housed in a vacuum chamber. The permeate from the modules is then condensed. A vacuum pump removes the incondensables from the system. To maintain a high removal efficiency of permeating components, the heat of vaporization is provided by the inter-stage heaters

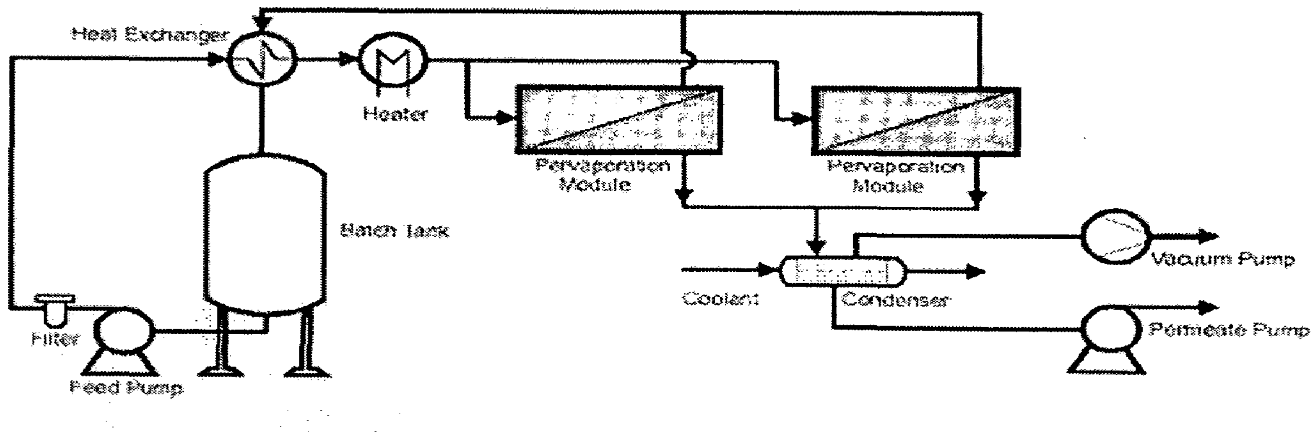

Fig.1.4.Continuous Pervaporation Unit

1.5.3 Hybrid Pervaporation

Hybrid units can be utilized in conjunction with conventional distillation columns. A portion of the overhead product from the column passes through the membrane modules. In doing so, the azeotrope is broken and a pure product is produced. The permeate is returned to the column. This process is used to debottleneck the overall dehydration process by achieving the desired level of separation.

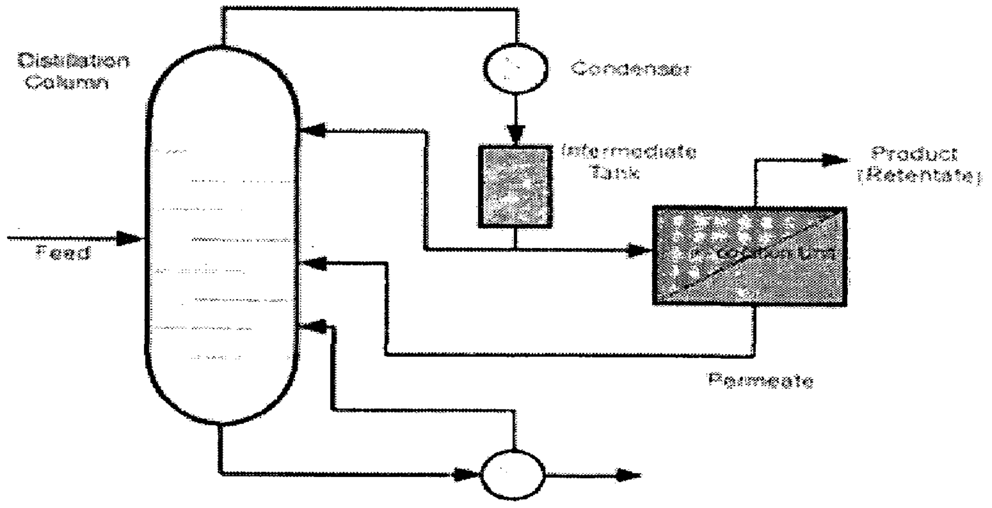

Fig. 1.5 Hybrid Pervaporation Unit

1.6 PERVAPORATION CHARACTERISTICS

1.6.1 Molecular Flux

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

$$J_i = Q_i / At \qquad (1)$$

Where, J_i = Flux of component "i" (moles/h cm^2)

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

A = Effective membrane surface area (cm^2)

1.6.2 Permselectivity

The separation factor or system selectivity is the ratio of mass fraction of a permeating component on the permeate side of the membrane, compared to the feed side.The performance of a given membrane can be expressed in terms of a parameter called permselectivity:

$$\alpha = (X_i^p / X^p{}_j)/(X^f{}_i / X^f{}_j) \qquad (2)$$

Where, X = Weight fraction, superscripts "p" and "f" denote "permeate" and "feed" respectively while "i" and "j" represent individual components. The extent to which a system is effective is indicated by its separation factor. The less volatile and more soluble a chemical is in water, the lower the separation factor is. For example, alcohols and aldehydes have low separation factors. High separation factor chemicals, such as aromatics and chlorinated compounds, have higher volatility and are less soluble in water. The higher the separation factor is for a chemical, the easier it is to separate out of solution with pervaporation.

1.6.3 Permeability Coefficient

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

$$J_i = P_i \Delta P / L \qquad (3)$$

$$or \qquad J_i = k \Delta P \qquad (4)$$

Where $\Delta P = P_1 - P_2$, $P_1 = P_1^0 X_{ri} \gamma_i$ and $P_2 = P \ Y_{pi}$ So by above equations

$$J_i = -P_i\left(P_1^0 X_{ri}\gamma_i - P\ Y_{pi}\right)/L \tag{5}$$

$$P_i = J_i L/\left(P_1^0 X_{ri}\gamma_i - P\ Y_{pi}\right) \tag{6}$$

Where, P_i = Permeability coefficient of component i '.

γ_i = Activity coefficient of component 'i ' in the mixter.

ΔP = Change in partial pressure of pure component 'i' across the membrane.

P_1^0 = Saturation pressure of pure component 'i' across the membrane.

X_{ri} = Mole fraction of component 'i' in the feed.

Y_{pi} = Mole fraction of component 'i' in the permeate.

J_i = Flux of component 'i'.

L = Membrane thikness.

$k = P_i / L$ = Permeability constant.

1.7 INDUSTRIAL APPLICATION OF PERVAPORATION

- Increases Reaction Yield In some chemical reactions, the product yield is limited by the formation of water. Continuous water removal from an equilibrium controlled reaction mixture by pervaporation unit will improve the reaction yield. An example is the process of formation of esters from acids and alcohols
- Separation of Azeotropic mixture in Chemical process Industries: Many commonly used solvents form azeotropes with water and distillation alone cannot separate them. Pervaporation membrane selectivity is not affected by azeotrope formation.
- Increases Distillation column efficiency for low Volatility feed: Distillation columns operating with low volatility differences of the feed components require a high reflux ratio. Pervaporation is independent of volatility differences. A hybrid peraporation unit attached to a distillation column will increase throughput and reduce operating costs.
- Solvent recovery in Pharmaceutical and chemical industries: In-house recovery of spent solvent is a difficult process for distillation as the solvents used form azeotropes with water. Pevaporation units minimize the disposal of used solvents and fresh solvent cost.

- Dehydration of Solvents Recovered from Activated Carbon Beds: Solvent vapors in effluent air from various industrial drying processes are often captured in activated carbon beds. These solvents are subsequently desorbed using steam. The recovered solvents with a high water content can be dehydrated using pervaporation.
- The treatment of wastewater contaminated with organics.
- Pollution control applications.
- Recovery of valuable organic compounds from process side streams
- Separation of 99.5% pure ethanol-water solutions
- Harvesting of organic substances from fermented broth.

1.8 TYPES OF MEMBRANE USED

A membrane is nothing more than a discrete, thin interface that moderates the 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 10 μm

1.8.1 Isotropic membranes

1.8.1.1 *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 membrane. Particles smaller than the largest pores, but larger than the 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 membranes 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.

1.8.1.2 *Nonporous, Dense membranes*

Nonporous, dense membranes consist of a dense film through which permeants 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 membranes 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 membranes to perform the separation. Usually these membranes have an isotropic structure to improve the flux.

1.8.1.3 *Electrically Charged Membranes*

Electrically charged membranes can be dense or micro porous, but are most commonly very finely micro porous, with the 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 binds 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 and, in solutions of higher ionic strength, selectivity decreases. Electrically charged membranes are used for processing electrolyte solutions in electro dialysis.

1.8.2 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 films to about 20 μm thickness. The development of novel separation techniques to produce anisotropic membrane structures was one of the major 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 a single operation or separately. In composite membranes, the layers are usually 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 membranes.

1.8.3 Ceramic, Metal and Liquid Membranes

The discussion so far implies that membrane materials are organic polymers and, infact, 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.

1.8.4 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. Zeolites are inorganic crystalline structures with uniform, molecular-sized pores, and high mechanical, thermal, and chemical stability. These properties give zeolite membranes advantages over many polymeric membranes. The first reported zeolite membranes were prepared by Suzuki [1987], and now more than 12 zeolite structures have been prepared as membranes. Zeolite membranes are most often polycrystalline layers deposited on tubular or disc-shaped 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 been reported, with most studies focusing on membrane preparation and performance.

1.9 PROPERTIES OF AN IDEAL MEMBRANE

A suitable membrane for membrane reactor should have high permeability and good separation selectivity, must be stable at reaction temperatures in the presence of reactive gases, and must be able to withstand a significant pressure drop. In general, for the same pressure drop, higher permeabilities are obtained with thinner membranes because the permeation rate is inversely proportional to thickness. However, the membrane must be thick enough to avoid formation of cracks and pinholes during its preparation and to prevent rupture from mechanical stresses that occur during its use. In fact, an optimal thickness exists because for very thick membranes the permeation rate of the products will be very small, and hence the conversion of the reactants will be low for equilibrium-limited reactions. On the other hand, for very thin membranes the permeation rate of the reactants will be very high, leading to a decrease in the conversion for equilibrium-limited reactions, unless the permeation rate of the products is high also to counter the effect.

1.10 DESCRIPTION OF THE PROBLEM

The most common reaction system studied for the application of pervaporation is an esterification reaction between an alcohol and an acid in the presence of a catalyst. In this industrial reversible reaction, high conversion can get by adding a large excess of acid. By placing a water selective pervaporation membrane in the esterification reactor; equilibrium can shift to the right thus reducing the excess reactants. Modeling of esterification of acetic acid with *n*-butanol, lactic acid with ethanaol and acetic acid with ethanol coupled pervaporation is studied in this paper. The available experimental data has been used for the modeling purpose. The influence of several process variables, such as process temperature, initial mole ratio of acetic acid over *n*-butanol, and the ratio of the effective membrane area over the volume of reacting mixture and catalyst content, flux on the esterification were discussed. Model results are in well comparison with available experimental results.

1.11 OBJECTIVE OF THE THESIS

Based on the reviewed literature following objectives have been planned

(i) To develop the mathematical model of a pervaporation reactor

(ii) To solve the model equation using numerical technique by developing computer program.

(iii) To validate the proposed model with available data.

(iv) To study the effect of operating and design parameters on the performance of reactor.

1.12 SYSTEM

Pervaporation reactor is a device in which the reaction and separation through membrane is carried out simultaneously in one unit. These kind of arrangement is particular important for reactions which are equilibrium limited. Out of many such reactions esterification is very important reaction industrially. Modeling of esterification of acetic acid with *n*-butanol, lactic acid with ethanaol and acetic acid with ethanol coupled pervaporation is studied in this paper. The available experimental data has been used for the modeling purpose. The influence of several process variables, such as process temperature, initial mole ratio of acetic acid over *n*-butanol, and the ratio of the effective membrane area over the volume of reacting mixture and catalyst content, flux on the esterification were discussed. Model results are in well comparison with available experimental results. Presented model can be used for the other esterification reactions in pervaporation reactor.

1.13 ORGANIZATION OF THESIS

Chapter I includes the introduction of thesis, brief introduction of membrane reactor, pervaporation reactor, its principle types, uses, advantages, disadvantages, description of membrane and objectives of thesis. Chapter II gives a brief literature review. Chapter III includes the model development. Chapte IV describes the solution technique and boundary conditions. Chapter V esterification of acetic acid with n-butanol. Chapter VI esterification of lactic acid with ethanol. Chapter VII esterification of acetic acid with ethanol. Chapter VIII gives results and discussion of results obtained from this model. Chapter IX gives concluding remarks and future recommendation.

CHAPTER II

LITERATURE REVIEW

The review of literature on assigned project topic is the pinnacle of every project work. As our project topic is related to modeling of pervaporation 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. The present chapter provides a brief discussion only on those aspects which are relevant to the objective of the dissertation work mentioned in chapter 1.

This chapter is divided into two parts: The first part includes the research papers regarding experimental work. The second part is most important part. It deals with various research papers where mathematical modeling of pervaporation reactor are carried out and studied. At the end of the chapter, some important papers discussed with their results, remarks and comparative study is presented in tabular form in a **Table 2.1**.

2.1 EXPERIMENTAL STUDIES ON PERVAPORATION REACTOR

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

Zhu et. al. (1996) studied the esterification reaction between acetic acid and ethanol in a continuous flow pervaporation membrane reactor utilizing a polymeric/ceramic membrane. For a range of experimental conditions reactor conversions were observed which are higher than the corresponding calculated equilibrium values. This is due to 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.

Polymeric membranes have found uses in gas and liquid separations. Polymers, like PVA, polyimide, and Nation have a high permselectivity to a number of chemical compounds. They are commonly used as membranes in industrial separations. A review paper on the use of polymeric membranes for gas separations has recently been published (Koros and Fleming, 1993) discussing materials selection, membrane formation, and trends in module and system design. Polymeric/inorganic composite type membranes have received increased attention in the last few years (Kita et al., 1987; Rezac and Koros, 1994, 1995). Such membranes are formed by the deposition of a thin dense polymeric film on an underlying inorganic (metal or ceramic) macroporous support. The inorganic layer support is believed to endow such membranes with a higher mechanical strength while maintaining the permselectivity of the dense polymeric film and increasing the overall permeance. An appropriate coating technique which deposits a crack-free polymeric film on the underlying inorganic porous support is important in the preparation of such composite membranes. A number of techniques have been investigated by various groups. A dip-coating method was introduced, for example, by Kita et al. (1987) and a "solution deposition technique" was studied by Koros and co-workers (Rezac and Koros, 1992). As is true with polymeric membranes, polymeric/inorganic composite membranes have mostly been studied for the separation of various organic compounds through pervaporation (PV) and vapor permeation (VP) processes. *(Zhu et. al. 1996)*

Zhu and Chen (1998) prepared a composite catalytic membrane with a crosslinked PVA dense active layer coated on a porous ceramic plate support using a novel method and evaluated with a pervaporation setup for the separation of several organic aqueous mixtures. Several key problems occurred during the preparation procedure are discussed. SEM (scanning electron microscopy), IR (infra-red) (ATR) (attenuated total refraction) and XPS (X-ray photoelectron spectrometry) were used to characterize the catalytic membrane natures. *N*-Butyl alcohol-acetic acid esterification was used as a model system for investigating into the coupling of reaction with pervaporation in a batch reactor. Different reaction parameters, temperatures, catalyst concentrations and initial reactant molar ratios were studied experimentally.

Gulik et. al. (2001) studied the hydrodynamics in a pervaporation membrane reactor for resin production. In this type of reactors it is important to reduce concentration and temperature polarization to obtain high water fluxes during operation. The influence of secondary flow on polarization, as induced by small density differences, is studied using Computational Fluid Dynamics in a model system. This model is operated in three parallel flow situations: horizontal, vertical opposed and vertical adding flow. Density-induced convection is found to be most elective in the horizontal situation increasing water fluxes up to 50%. Water fluxes were also determined experimentally using the horizontal setup. Influence of density-induced convection was observed experimentally.

Reaction conditions require elevated temperatures, typically above 200^{O}C. The mixtures are moderately viscous at these temperatures (μ = 5 - 25 mPa s). They have presented the occurring hydrodynamics in a model system of a membrane reactor for resin production. Flux measurements have been performed experimentally at different superficial velocities, temperatures and fluid compositions, showing that hydrodynamics is determined by forced and natural convection simultaneously.

CFD calculations were also performed on the model system. These calculations show that the hydrodynamics is indeed determined by forced and natural convection simultaneously. It was shown that natural convection is elective in reducing concentration polarization. Natural convection has been studied in three different configurations: horizontal, vertical adding and vertical opposing flow. The horizontal configuration showed an increase in water flux up to 50% compared to a simulation in which natural convection is omitted. The dimensionless heat and mass transfer coefficients (Nusselt number and Sherwood number) are also 4 times higher. (Gulik *et. al.* 2001)

Tanaka 2001 studied pervaporation-aided esterification of acetic acid with ethanol at 343 K using zeolite T membranes. Almost complete conversion was reached within 8 h when initial molar ratios of alcohol to acetic acid were 1.5 and 2. The reaction time courses were well described by a simple model based on the assumptions that the reaction obeyed second-order kinetics and the permeation flux of each component was proportional to its concentration. The influence of operating parameters on variation in conversion with reaction time was investigated by means of the simulation using the model.

The hybrid process of reaction with membrane separation has been increasingly attracting much attention. There have been a number of investigations done for hydrogen-permeable membrane reactors applied to reversible gas-phase reactions (Itoh, 1987; Umemiya, 1991). Some investigations have focused on water-permeable membrane reactors applied to liquid-phase reactions (David et al., 1991; Kita et al., 1987; Okamota et al., 1993, 1994; Yamamota, et al., 1995; Lipnizki et al., 1999). The esterification of oleic acid with ethanol could be improved by vapor permeation (VP) separations with asymmetric polyimide hollow fiber membrane (Okamota et al., 1994). Further improvement of the esterification was achieved by VP separation with zeolite NaA membrane because of its extremely high permeation flux (Lipnizki et al., 1999). However, the zeolite NaA membranes are unstable to acids and are not applied to the system where they directly contact with acids. Recently, we reported zeolite T membranes showed high pervaporation (PV) performance for water–organic liquid mixtures as well as good stability to acid solutions (Tagakiet et al., 1999) . In this study, PV separation with zeolite T membranes is applied to the esterification of acetic acid with ethanol.

Liu and Chen (2002) studied the modeling of esterification of acetic acid with *n*-butanol in the presence of Zr(SO4)2˙4H2O coupled pervaporation . The influence of several process variables, such as process temperature, initial mole ratio of acetic acid over *n*-butanol, the ratio of the effective membrane area over the volume of reacting mixture and catalyst content, on the esterification was discussed. The calculated results for the conversion of *n*-butanol to water and permeation flux were consistence with the experimental data. The permselectivity and water content can be roughly estimated by the model equations.

Benedict et. al. (2003) investigated the esterification of lactic acid and ethanol with and without pervaporation. Reactors coupled with membrane separation, such as pervaporation, can help enhance the conversion of reactants for thermodynamically or kinetically limited reactions via selective removal of one or more product species from the reaction mixture. An example of these reactions is esterification of carboxylic acids and alcohols. Esterification of lactic acid ($C_3H_6O_3$) and ethanol (C_2H_5OH) is studied in well-mixed reactors with/without a solid catalyst (Amberlyst XN-1010). Rate expressions for homogeneous and heterogeneous esterification are obtained from the experimental data using differential and integral methods. Experiments with a closed loop system of a "batch" catalytic reactor and a pervaporation unit reveal that fractional conversions of the two reactants and yield of ethyl lactate exceeding the corresponding maximum values in a reaction-only operation are obtained by stripping of the byproduct (water).

Two reactors with volumes of the reaction mixture of 2 and 5 L were employed in all experiments. The 2 L reactor contained four spinning baskets [diameter = 1.5 in., length = 2.5 in., 400 mesh stainless steel (SS) screen], each capable of holding up to 40 g of catalyst. The 5 L SS stirred contained solids reactor (SCSR) contained four spinning baskets (diameter = 1.5 in., length = 6.5 in., 400 mesh SS screen), each capable of holding up to 100 g of catalyst. Each reactor was heated with two resistance heaters clamped around the reactor. The process streams were well insulated with fiberglass insulation tape and foam pipe wrap. The pervaporation of water was accomplished by applying a vacuum on the permeate side of the pervaporation module by a 10^{-3} Torr vacuum pump. The permeate pressure was monitored by a 10^{-4} Torr vacuum transducer, which was connected to a digital vacuum indicator/controller. Permeate was condensed and collected in two 20 mL impingers at cryogenic temperatures with liquid nitrogen (-185 °C), with the permeate stream being well insulated between the pervaporation module and the impingers. During reaction-only (homogeneous or heterogeneous reaction) operation, the pervaporation module was bypassed. For conduct of the homogeneous reaction, the catalyst baskets were removed from the concentrated lactic acid (in water) is miscible in ethanol and hence suitable for esterification. The starting materials used in this study, therefore, were 88% (w/w; in water) lactic acid and anhydrous ethanol. Lactic acid and ethyl lactate (used as the product standard) were acquired from Aldrich Chemical, while ethanol was obtained from AAPER Chemical. Amberlyst XN-1010 (Rohm and Haas), a polymeric cation exchanger, was employed as the catalyst. Amberlyst XN-1010 is poly(styrenesulfonic acid) (PSSA) cross-linked with divinylbenzene. The key characteristics of the catalyst were density) 5.29 g/mL, surface area) 540 m2/g, particle size) 0.2-1.2 mm, and maximum operating temperature) 120 °C. (Benedict *et. al.* 2003)

Assabumrungrat et. al. (2003) studied the synthesis of methyl acetate (MeOAc) from methanol (MeOH) and acetic acid (HOAc) in pervaporation membrane reactors (PVMRs). Three modes of PVMR operation, i.e. semi-batch (SB-PVMR), plug flow (PF-PVMR) and continuous stirred tank (CS-PVMR) were modeled using the 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 experimental results. The study focused on comparing PVMR performances between two modes of continuous-flow operation for various dimensionless parameters, such as Damkohler number (*Da*), the rate ratio (δ), the feed composition and the membrane selectivity. Flow characteristic within the reactors arisen from different operation modes affects the reactor performance through its influences on the reaction and permeation rates along the reactor. There are only some ranges of operating conditions where CS-PVMR is superior to PF-PVMR.

Lauterbach and Kreis (2003) Pervaporation (PV) and vapour permeation (VP) are very suitable for the application to hybrid processes, such as the coupling with distillation or reaction. These hybrid membrane processes have gained much attention in recent years, because the membrane separation is very selective and not limited by the vapour-liquid equilibrium. Despite of all advantages hybrid membrane processes are not yet established in chemical industry due to a rather short lifetime of membranes and the lack of process know-how. Besides the promising progress in the development of reliable membrane materials detailed theoretical and experimental studies contribute to a better understanding of such hybrid processes. In this work the combination of batch reaction and pervaporation in loop configuration is investigated for the propyl-propionate-synthesis. Thereby it is about a heterogeneously catalysed esterification whose conversion is limited by the chemical equilibrium conversion. A multifunctional lab scale pervaporation and vapour permeation plant equipped with a flat membrane test cell is used to determine the separation characteristics of the hydrophilic, organic membrane. The influence of the decisive operational parameters on the transmembrane flux and the selectivity is investigated. The combination of batch reaction and pervaporation is investigated in a pilot scale membrane reactor. Via selective removal of the couple product water by from the reaction mixture and recycle of non-conversed reactants an almost entire conversion and high product purity can be achieved. The experimental data show a good agreement with simulation results accomplished with a sophisticated simulation tool. Parameters studies show the influence of the ratio of membrane area to the hold-up of the reaction mixture, the initial composition as well as the operational parameters on the batch time of this process.

Park and Tsotsis (2004) studied a new concept of a hybrid pervaporation membrane reactor (PVMR) system, which integrates the pervaporation step through a membrane with adsorption in the permeate side. Coupling pervaporation with adsorption provides potential synergies in overcoming the equilibrium limitations in reversible reactions, particularly for dilute reacting systems, slow reactions, nonvolatile products, or imperfect membranes. A model experimental system is selected, namely the esterification of acetic acid by ethanol, coupled through an asymmetric hydrophilic polymeric membrane to a water adsorbent system. The emphasis in this paper is also on utilizing the experimental data for validating a model, previously developed by our group, for the study of such reactors. The reactor model performs adequately in describing the experimental data.

Peters et al. (2005) developed a continuous composite catalytic pervaporation membrane reactor, as integration of reaction and separation which offers advantages in terms of process efficiency and compactness. They studied esterification of acetic acid and butanol in pervaporation reactor. Composite catalytic membranes was prepared by applying a zeolite coating on top of ceramic hollow fiber silica membranes .This approach allows independent optimization of the selective and catalytic properties.

The catalyst activity of the zeolite-coated pervaporation membrane was measured in the esterification reaction between acetic acid and butanol. The membrane was placed in a stainless steel module module using Kalrez O-rings. The effective membrane area used was 17 cm^2. The supply vessel was charged with a certain amount of acetic acid. Then, the system was heated to the reaction temperature (75 °C), after which the preheated equimolar amount of alcohol was added. The reaction temperature was maintained by means of a thermostatic water bath, in which the system was immersed. The liquid reaction mixture was recirculated through the membrane module, and the supply vessel by means of the pump at a liquid flow rate of 40 L / h. This liquid flow corresponded to a superficial velocity exceeding 2 m/s which was sufficiently high to eliminate polarization effects. On the permeate side a vacuum was maintained (10 mbar) by a cascade of a liquid nitrogen cold trap and a vacuum pump. After a short stabilization period (10 min), the flow toward the supply vessel was stopped, decreasing the reactor volume to 30 mL. Hence, the liquid was only flowing through the pump and the module containing the catalytic membrane (valves are in position 2). For kinetic measurements, samples were taken periodically and analyzed by a gas chromatograph, equipped with a flame ionization detector and a thermal conductivity detector. GC analysis confirmed that no byproducts were formed. The catalytic activity of the unsupported catalyst was evaluated in a batch reflux system (75 °C) in which the catalyst was dispersed in the bulk liquid. The reaction rate constants were evaluated from the measured time-dependent concentration curves by means of the differential method, using a nonlinear least-squares regression technique. (Peters et al. 2005)

Sakaki et. al. (2005) applied pervaporation dehydration to the lipase-catalyzed esterification of fructose/glucose with palmitic acid in 2-methyl-2-butanol with the intention of improving the reaction yield. The water content in the reaction mixture decreased to 0.03 wt% by means of pervaporation using a zeolite NaA membrane. With the aid of pervaporation dehydration, the total yield of fructose monopalmitate and dipalmitate reached 66% in the esterification started with 54 mM fructose and 108 mM palmitic acid. It was possible to decrease the ratio of diester in the reaction product by decreasing the ratio of fatty acid to sugar in the substrate solution.

They showed the influence of water concentration in the reaction mixture on the reaction yield and initial reaction rate in the enzymatic esterification. The reaction was carried out at 40 ^{0}C using 54 mM fructose and 108 mM palmitic acid. The lower water content in the reaction mixture led to the higher ester yield after equilibrium. The equilibrium constant for the production of fructose monopalmitate was calculated. The calculated values of equilibrium constant were in the range of 0.19 to 0.28, and the deviation is probably due to the nonlinearity between activity and concentration, and to the error in the calculation of sugar concentrations. Sugar concentrations after equilibrium were calculated from the initial sugar content and the yields of mono- and di-esters. The calculated sugar concentration may deviate somewhat from the real concentration in the reaction mixture because some of sugar remained undissolved in the solvent.The decrease of water concentration in the solvent led to the increase of the initial reaction rate in the range of 4.5 to 490 mM of water. The result means that the removal of water from the reaction mixture can shift the reaction equilibrium to enhance the production yield without any decrease of activity of *C.* They showed the time course of the esterification of fructose with palmitic acid in a lipasepacked column reactor accompanied with/without pervaporation. The reaction was carried out at 40 C using 54 mM fructose and 108 mM palmitic acid. The initial water concentration in the reaction mixture was about 90 mM (0.2 wt %). Without pervaporation dehydration the esterification reaction reached equilibrium after a 24 h reaction, and the concentrations of fructose mono- and dipalmitate were 8.6 and 0.44 mM, respectively. The total conversion of fructose to its mono- and di-palmitate was 17%. On the other hand, ester yield in the esterification accompanied with pervaporation dehydration continued to increase during the reaction, and the concentrations of fructose mono- and dipalmitate reached 28.2 mM and 7.1 mM, respectively, after a 56-h reaction. The total conversion of fructose to its mono- and di-palmitate was 66%. The water content in the reaction mixture could be decreased to 14 mM (0.03 wt %) by means of pervaporation dehydration using zeolite NaA membrane. In the esterification accompanied with pervaporation dehydration, the total conversion of fructose to its mono- and diesters reached 66% after a 56-h reaction at 40EC using 54 mM fructose and 108 mM palmitic acid. It was possible to decrease the ratio of diester to monoester in the product by decreasing the ratio of the fatty acid to sugar in the substrate solution. (Sakaki *et. al.* 2005)

***Chen-Yuan Tu et. al.* (2005) have** studied that preparation of hydrophilic poly (tetrafluoroethylene) (PTFE) membranes was performed by means of combined hydrogen plasma and ozone treatment and surface-initiating grafting polymerization. Acrylamide (AAm) and sodium 4-styrenesulfonate (NaSS) were used as monomers in grafting polymerization. Grafted PTFE membrane exhibited high hydrophilicity with a water contact angle of 38° and showed superior performance of pervaporation dehydration for various aqueous solutions of organic compounds. A high permeation flux of 422 g/m2 h and a high separation factor of 4491 were observed with PTFE-g-PSSA membrane in pervaporation dehydration of a 90 wt. % aqueous solution of isopropanol (IPA) at 65 °C. The PTFE-g-PSSA membrane also exhibits advantages of wide application scopes, low temperature-sensitivity, good membrane stability, and operation durability in pervaporation dehydration processes.

Commercially available PTFE membranes could be directly utilized in preparation of pervaporation dehydration membranes by means of surface-initiating grafting polymerization. The performance of pervaporation dehydration increased with increasing the surface hydrophilicity of the PTFE membranes. While applying in various organic solutions, the permeation fluxes decreased and the separation factors increased with increasing the molar volumes of the organic solvents in feeding solutions, as observed with the PTFE membranes in pervaporation dehydration of aqueous solutions of alcohols and dimethylformamide. In conclusion, the PTFE membranes developed in this work showed superior performances in pervaporation dehydration to other reported membranes.

Sanz and Gmehling Part-I (2006) have studied that Reaction–pervaporation hybrid processes can be an alternative to classical chemical processes to enhance the conversion of equilibrium-limited reactions such as esterification and trans-esterification. The esterification of acetic acid with isopropanol coupled with pervaporation was investigated. First, the synthesis and hydrolysis of isopropyl acetate have been studied using the commercial ion exchange resin Amberlyst 15. The influence of different operating parameters such as reaction temperature, initial molar reactant ratio and amount of catalyst was examined. Additionally, the performance of the commercial polymeric membrane PERVAP® 2201 has been studied. The influence of temperature and feed composition on the permeation characteristics of the membrane was analyzed, whereby preferential water permeation from the quaternary mixture involved in the esterification of acetic acid with isopropanol has been observed under the experimental conditions considered in this work.

The design of a pervaporation reactor requires information on reaction kinetics and pervaporation performance of the membrane.In this work, the heterogeneously catalyzed synthesis and hydrolysis of isopropyl acetate by Amberlyst 15 have been studied. A kinetic expression was obtained by fitting simultaneously the kinetic results of the esterification and the hydrolysis reactions. The pseudo-homogeneous model gives a good representation of the reaction rate for the isopropyl acetate system with only four adjustable parameters. In addition, the separation of the quaternary mixture by pervaporation using the commercial polymeric membrane PERVAP® 2201 has been investigated in this work. The permeate flux was found to increase with the water content in the feed and the temperature. The membrane showed a high selectivity towards water in the composition and temperature range studied.

El-Zanati *et. al.* (2006) have studied to separate butanol from an aqueous solution using pervaporation. A specially designed and manufactured cell was used to separate the butanol from butanol/water solutions of different butanol concentrations (6-8-11-16-20-50) g/l. A 250 cm3 butanol mixture at 33 ° C was used to feed the cell, while the pressure of permeation side was about ~ 0 bar. Results revealed that butanol concentration changes non-linearly during the first 3 h, and then proceeds linearly. The percentage of butanol removal increases with increasing feed concentration. The permeability of the used membrane was determined experimentally. A resistance in series model was used to simulate the pervaporation step. The butanol concentration in the feed during the pervaporation step was predicted by using the developed model. There is a fair agreement between butanol concentration in feeding tank of pervaporation cell both experimentally and predicted from the developed model.

A pervaporator modular cell was designed and manufactured at NRC workshops. It consists of one cell. The cell bodywas manufactured of stainless steel, all accessories made of chemical resistant materials, and the membrane support was made of yellow copper. The cell was 5 cm inner diameter, and it was 1.5 cm in height. The used membrane was imported from Sulzer Co., Perv. 2200. The feed flow velocity was adjusted in the range of high laminar flow at a Reynolds number of 926, to avoid the formation of dead zones or pockets and to prevent the formation of boundary layer in order to minimize the concentration polarization. The feeding velocity was ranged from 66 to 335 cm/min at the mentioned Re No. which also kept the consistency of laminar flow. The integrated experimental set-up, comprises of a feed tank which is heated by a water bath, the feed is pumped to a pervaporation cell using a feeding pump, such pump may be used for butanol solution recycling, the cell is provided with a condenser to condense the permeated butanol vapors. The system is attached to a vacuum pump to reduce the pressure at membrane permeate side. The chemicals and materials used in the experiments were: N2 gas; Butanol, authentic grade (Merck) and membrane of Sulzer Company, Germany.

In operating conditions: synthetic solutions of different butanol concentrations (5- 8-11-16-20-50) g/l were selected to study the effect of feed concentration. The feed solution of 250 cm^3 was heated to 33 ° C using a water bath of regulated temperature, the warm solution was then pumped to the cell pervaporation with flow rate of 500 ml/min. The cell was operated under vacuum (Pressure .1 kPa). Samples were collected every two hours from the feed tank at steady state condition and they were analyzed using Gas Chromatography showed the change of butanol concentration in the feed tank with time, for the initial butanol concentration of 16 g/l. From their results, it is clear, that the change of concentration can be divided into two stages: the first stage is a non-linear and it starts from zero time to approximately 3 h. This trend is repeated for all investigated cases (6-8-11-16-20-50) g/l. In this stage, the concentration decreased non-linearly with time. Then, the second stage starts from 3 h until the end of the pervaporation process, in which the concentration was changed linearly with time.

***Smitha et. al.* (2006)** worked on the pervaporation separation of 1,4-dioxane/water mixtures was carried out using cross linked blend membranes of chitosan (CS) and nylon 66 (NYL). These membranes were characterized by FTIR, TGA, XRD, and tensile strength to assess intermolecular interactions, thermal stability, crystallinity and mechanical strength, respectively. Sorption studies were carried out in pure liquids and binary mixtures of different compositions to evaluate polymer–liquid interactions. The effects of CS/NYL ratio, membrane thickness, feed concentration on the trans membrane permeation rate and separation factor were investigated. Optimum CS/NYL ratio was determined as 90/10 (w/w) for 4.3 wt.% feed water concentration at 40 °C Increasing barrier from 30 to 120 μm improved the separation factor from 767 to 1123 at the cost of flux, which lowered from 0.118 to 0.028 kg/m^2 h. The membrane performance was also investigated for the separation of various feed compositions of 1,4-dioxane–water mixtures and permeate pressures. The azeotrope formed at 82-wt. % dioxane was easily broken with a selectivity of 865 and water flux of 0.089 kg/m^2 h.

For experiment nylon 66 of molecular weight 25,000 was purchased from BDH Chemicals Ltd., Poole, England and chitosan having average molecular weight 500,000 were purchased from Chempol (India) Ltd, Nellore, India. The degree of deacetylation of chitosan as supplied by the vendor was 84%. Formic acid and sulfuric acid were purchased from Loba Chemie, Mumbai, India. Demineralized water (conductivity = 0.02 S/cm) used for the preparation of feed solutions was generated in the laboratory itself.

Experiments were carried out with an indigenously constructed pervaporation manifold operated at a vacuum as low as 0.05 mmHg in the permeate line. The test cell itself was made of glass and the membrane was generally supported by a sintered (stainless steel) disc. The volume of the liquid feed was approximately 100 ml and the membrane area about 20 cm^2. The permeate was alternatively collected in a cold trap after attaining the stabilization period of 24 h, in which it condensed totally. The experimental procedure is described in detail elsewhere (Sridhar, Susheela, Jayasimha Reddy, & Khan, 2001). The liquid thus recovered was weighed after allowing it to attain room temperature in a Sartorius electronic balance (accuracy: 10_4 g) to determine the flux and then analyzed by gas chromatography to evaluate separation factor. Tests were carried out at room temperature (30 ± 2 °C) and repeated twice using fresh feed solution to check for reproducibility. (Smitha *et. al.* 2006)

Benedict et. al. (2006) studied esterification of lactic acid ($C_3H_6O_3$) and succinic acid ($C_4H_6O_4$) with ethanol (C_2H_5OH) to generate ethyl lactate ($C_5H_{10}O_3$) and diethyl succinate ($C_8H_{14}O_4$), respectively, in well-mixed reactors with solid catalysts (Amberlyst XN-1010 and Nafion NR50) and two pervaporation membranes (GFT-1005 and T1-b) in this article. The results of catalyst compatibility and membrane stability studies are discussed. Experiments with a closed-loop system of a "batch"catalytic reactor and a pervaporation unit employing GFT-1005 reveal that for esterification of both lactic and succinic acids, fractional conversions of the two reactants exceeding the corresponding maximum values in a reaction-only operation and close to unity are obtained by stripping water, a reaction product. The kinetics of pervaporation is studied to obtain a working correlation for the flux of water in terms of temperature and water concentration on the feed side of the pervaporator. The efficacy of pervaporation-aided esterification is illustrated by attainment of near total utilization of the stoichiometrically limiting reactant within a reasonable time. Protocols for recovery of ethyl lactate and diethyl succinate from pervaporation retentate are discussed and simultaneous esterification of lactic and succinic acid, which is an attractive and novel concept, is proposed.

Sanz and Gmehling Part-II (2006) studied the esterification of acetic acid with isopropanol in a reactor combined with a pervaporation unit. The conversions achieved are distinctly higher than the equilibrium conversion. Kinetic and pervaporation parameters obtained in a previous study were used to describe the behavior of the hybrid process. The influence of different operating parameters such as reaction and pervaporation temperature, ratio of membrane area to initial reaction volume, initial molar reactant ratio and amount of catalyst on the process performance has been analyzed in this work.

Lauterbach and Kreis (2006) Pervaporation (PV) and vapour permeation (VP) are very suitable for the application to hybrid processes, such as the coupling with distillation or reaction. These hybrid membrane processes have gained much attention in recent years, because the membrane separation is very selective and not limited by the vapour-liquid equilibrium. Despite of all advantages hybrid membrane processes are not yet established in chemical industry due to a rather short lifetime of membranes and the lack of process knowhow. Besides the promising progress in the development of reliable membrane materials detailed theoretical and experimental studies contribute to a better understanding of such hybrid processes.

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.

Feng & Huang (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 the 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 reacting reagent. There are upper and lower limits in the performance of reactor facilitation by pervaporation. Membrane permeability, membrane area and the volume of the reaction mixtures to be treated are important operating parameters influencing the reactor behavior. Operating temperature influences reactor performance through its influences on reaction rate and membrane permeability.

The assumptions taken for developing the mathematical model are

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

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

Where M_i and . $_i$ 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

$$r = K_1 C_A C_B - K_2 C_E C_W = k_1 \left(C_A C_B - \frac{1}{K_C} C_E C_W \right) \tag{3}$$

Acid concentration profile is written as

$$\frac{dX}{dt} = k_1 C_0 \left[\frac{(1 - X)(\theta_B - X)}{v} - \frac{(\theta_E + X)Y}{K_e} \right] \tag{4}$$

$$\frac{dY}{dt} = \left(\frac{1}{v} \right) \left[\frac{dX}{dt} - Y \frac{dv}{dt} - \left(\frac{S}{V_O} \right) \frac{J_w}{C_0} \right] \tag{5}$$

The initial conditions are

At t=0, X_o=0, V_O = 1, and Y_O = .θ_w

For a special case where the 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

$$k_1C_0t = \frac{1}{\theta_B - 1} ln\left[\frac{(1 - X/\theta_B)^{1-\varepsilon\theta B}}{(1-X)^{1-\varepsilon}}\right] \tag{6}$$

(Where $\theta_B > 1$)

$$k_1C_0t = \frac{(1-\varepsilon)X}{1-X} + \varepsilon ln\frac{1}{1-X} \quad \text{(Where } \theta = 1 \tag{[7)}$$

Where $\varepsilon = C_O M_W / \rho_w$

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 given 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

$$\beta = k_1C_0\left(1 + \theta_B + \frac{\theta_E + \theta_W}{K_e}\right) \tag{9}$$

$$\gamma = k_1C_0\left(1 - \frac{1}{K_e}\right) \tag{10}$$

$$\psi = (\beta^2 - 4\alpha\gamma)^{\frac{1}{2}} \tag{11}$$

$$\alpha = k_1C_0\left(\theta_B - \frac{\theta_E\theta_W}{K_e}\right) \tag{12}$$

This represents another extreme case of a simple batch reactor (*Feng & Huang,* 1996)

Domingues *et al.* (1999) worked on the coupling of a pervaporation module to a discontinuous esterification reactor using a commercial GFT(PVA) membrane and analyzing its possible application on an industrial level. The reaction chosen for the pervaporation study was that of the esterification of benzyl alcohol with acetic acid. This study was used to determine the kinetic parameters of the esterification and the applicability of pervaporation to esterification by determining the membrane permeability and its selectivity under the conditions of 80 °C and a membrane surface area 170 cm^2. The results showed a flux of 0.54 kg/m^2 h, 96% selectivity in water and 99% conversion. A theoretical model was developed that satisfactorily agrees with the obtained experimental results, rims allowing the prediction of the conversion variation with the pervaporation time. For pervaporation model considering the esterification reaction, which can be schematically represented by:

$$A + B \Leftrightarrow R + H$$

Where A is acetic acid, B is benzyl alcohol, R is benzyl acetate and H is water, which is performed in a discontinuous reactor coupled to a pervaporation unit at a constant catalyst temperature and concentration.vThe rate of water formation is given by:

$$r_H = k_1 C_A C_B - k_2 C_R C_H \qquad (1)$$

Considering that the pervaporation module consists of a hydrophilic membrane through which water permeates preferentially, the water equilibrium in the reactor will be:

$$r_H V = SJ_H + \frac{d}{dt}(VC_H) \qquad (2)$$

Where J_H is the water flow across the membrane. The flow of a compound across a membrane depends mainly on the concentration of the compound in the mixture, and in a first approximation it may be considered that it varies linearly with the concentration in accordance with the expression:

$$J_H = K_{pH} C_H \qquad (3)$$

If, as is normal in pervaporation, the flow across the membrane is small, then the variation in the reaction volume will also be small and it may be considered that the volume remains constant throughout the reaction. Therefore, by substituting equations (1) and (3) in equation (2), the following is obtained:

$$\frac{dC_H}{dt} = (k_1C_AC_B - k_2C_RC_H) - \frac{S}{V}J_H \quad (4)$$

The flow for the other components in the reaction is given by:

$$J_i = k_{pi}C_i \quad (5)$$

Where i is A, B, R

Similarly, the concentrations of the other components in the reaction can be determined:

$$\frac{dC_i}{dt} = \pm\,(k_1C_AC_B - k_2C_RC_H) - \frac{S}{V}J_i \quad (6)$$

The concentration is related to the conversion acetic acid through the following equation:

$$C_i = \mathrm{Co} \pm \text{reaction - pervaporation}$$

In this way the concentration of the various components in the reactor can be calculated through the following equation:

$$C_i = \frac{C_{A0}\,(M_i - X_A)}{1 + \int \frac{S}{V}k_{pi}dt} \quad (7)$$

Where M is the stoichiometric relationship of the compounds, $M = C_{B0} / C_{A0}$ and $M_R = M_H = 0$. The simultaneous integration of equations (4) and (5), taking into account (7), allows the conversion/time ratio for the esterification with pervaporation to be obtained. Their experimental data had a good fit with a second order homogeneous kinetic model.

$$r = k_1\left(C_AC_B - \frac{C_RC_H}{K}\right) \quad (8)$$

For the analysis of the reaction kinetics in our case, the second order reversible model was assumed, taking int account the influence of the catalyst on the reaction rate.

The reaction rate for a homogeneous system with catalyst is:

$$\mathrm{A + B + C} \Leftrightarrow \mathrm{R + H + C}$$

$$-\left(\frac{dC_A}{dt}\right) = k_cC_AC_BC_C - k_{-c}C_RC_HC_C = k_1\,C_C\left(C_AC_B - \frac{C_RC_H}{K}\right) \quad (9)$$

Where k_c is the direct rate k_{-c} is the inverse rate, both with catalyst, and K^C is the equilibrium constant of the reaction with catalyst.

According to this model, the reaction also occurs without the catalyst being present and the rate of the reaction with catalyst is directly proportional to the catalyst concentration The overall rate of the disappearance of component A as K = K^C is:

$$-\left(\frac{dC_A}{dt}\right) = (k_1 + k_c C_C)\left(C_A C_B - \frac{C_R C_H}{K}\right) = K_{abs}\left(C_A C_B - \frac{C_R C_H}{K}\right) \qquad (10)$$

When the values for K_{abs} are known, the relationship between t and X_A can be calculated through equation (10).

The experiments were performed in the following manner. 140 grams of benzyl alcohol and 118 grams of acetic acid were weighed and then the catalyst was added to the acetic acid. They were heated separately to reaction temperature and mixed in the reactor. Samples were taken at 10 - 15 minute intervals. The experiments for determining the kinetics were performed at 60, 70 and 80 °C respectively and with different catalyst concentrations: 2.1, 4.1 and 11.0 mol/m^3, and without any catalyst. The molar ratio of the reagents was maintained constant and equal to 1.5 in excess acetic acid. The reaction was monitored by means of gas chromatography using a 2-metre Carbowax 20M column at an oven temperature of 160°C and injector and detector temperature of 200 °C. The experimental conditions for the pervaporation reaction are as follows: temperature 80 °C, catalyst concentration 4.1mol/m^3 and 1.5 in excess acetic acid, Membrane GFT Pervap 1005 this was a PVA polymer membrane as modified for organic acid resistance. The active polymer is supported on polyacrylonitrile layered onto cellulose material.

A theoretical model satisfactorily agrees with the obtained experimental results. But for higher reaction time (> 100 min) model over predicts the results and over prediction increase with increase in reaction time. In the pervaporation model simulation it is found that for a reaction time of 4 hours, the esterification without pervaporation is in equilibrium (49% acetic acid and 74% benzyl alcohol).When the membrane surface area is varied with the pervaporation module, a conversion greater then that at equilibrium was obtained in all cases.

Lim et. al. (2002) discussed the design issues of pervaporation reactors for esterification. Esterification reactions are typically limited by thermodynamic equilibrium, and face challenges with product purification. Commercially, they are carried out using either large excess of one of the reactants, or by removing through reactive distillation one of the products. The former is a relatively inefficient approach because it requires a large reactor volume. As a result reactive distillation, which favorably shifts equilibrium through the removal of one of the products, is becoming more common in plant-scale production. It is, however, an energy-demanding operation and is not recommended when dealing with temperature-sensitive chemicals or biocatalysts. The aforementioned difficulties have motivated efforts for the development of other coupled reactive/separation processes. Pervaporation reactors, in particular, are receiving increased attention as a potentially competitive alternative to reactive distillation.

They have presented a model that has developed to describe PVMR behavior. The simulation results of the model have been validated with experimentally observed pervaporation membrane reactor conversions. The model is used to describe a number of alternative PVMR configurations and analyze the factors that affect and optimize their performance. The model reaction that investigated is the esterification of acetic acid with ethanol to produce ethyl acetate and water, which can be expressed generally as:

$$A + B \Leftrightarrow E + W \qquad (1)$$

where A represents the acetic acid, B the ethanol, E the ethyl acetate, and W the water. The kinetics have been studied both in a PFR (Zhu et al., 1996), and in a batch reactor (Park, 2001), and shown to obey the following rate expression in terms of activities a_i :

$$r = k\left[a_A a_B - a_E a_W / K_{eq}\right] \qquad (2)$$

where r is the reaction rate, k the rate constant, and Keq the equilibrium constant. In the above expression the activities of the various chemical species i can be replaced by the activity coefficient, γ_i and the mole fractions X_i:

$$r = k\left[\gamma_1\gamma_2 X_1 X_2 - \gamma_3\gamma_4 X_3 X_4 / K_{eq}\right] \qquad (3)$$

To calculate the γ_i the UNIQUAC equation is utilized (Prausnitz et al., 1980). Further details on the use of this equation can be found in Zhu et al. (1996) and Park (2001).

A comprehensive analysis of the design characteristics of various PVMR configurations was prescribed. They have analyzed PVMR configuration for which the membrane and reactor units are separate, and systems for which both functions are coupled together in a single unit .They have also analyzed three different classes of reactors, namely, batch, CSTR and PFR. Important dimensionless groups were identified for each PVMR configuration and the behavior was analyzed in terms of these groups and compared with that of the other configurations. The basic reactor model was previously developed and validated experimentally by our group. The key difference of our model from other PVMR models is that it accounts for the thermodynamic non-idealities involved during the reactive and transport processes, and o8ers a unified means for accounting for these phenomena. (Lim *et. al.* 2002)

Wasewar **(2007)** has developed the modified model based on the available experimental data for the esterification of acetic acid and benzyl alcohol. The effect of membrane area and flux on the conversion of reactants was studied. The modified model has excellent results as compared to the previous model and in excellent agreement with experimental data. The modified model allows the evaluations of the reaction time necessary to achieve a given conversion. The model makes it possible to determine the membrane surface area / operating time ratio for a given conversion.

2.3 MOTIVATION FOR PRESENT WORK

It is evident from the aforementioned literature that the pervaporation reactor is augmently effective over the conventional separation units attached with a chemical reactor. Thus, it is axiomatic that the need to understand and quantify the process occurring in membrane reactor is aggrandized. Mathematical model appears an attractive tool for analysis and simulation of pervaporation reactor. This compels a chemical engineer for its modeling and simulation. It is obvious from the above literature review that large number of mathematical models has been developed for membrane reactor. These models include one dimensional model which may be used to obtain its behavior under steady and unsteady state operation. They are limited in their applications and differ from each other in terms of their complexities and the objectives of the studies carried out. In view of the above, studies on mathematical modeling of pervaporation reactor has been undertaken to achieve the objectives mentioned.

Table 2.1 For Literature Review

Author	System	Operating Conditions	Results	Remarks
Domingues et al. (1999)	Esterification Benzyl alcohol with acetic acid. Experimental Modeling	GFT (PVA) Membrane Temp.: 80 °C Membrane Surface Area 170 cm^2	Flux: 0.54 kg/m^2h Selectivity: 96% Conversion 99% The use of PV coupled to Esterification reaction increases conversion up to 100%	The Proposed Model has 6% error with respect to exp. Data up to 240 min. After 100% conversion & Dehydration, Flux reduces & permeability increases for other components.
Gulik G. J. S. et. al. (2001)	Hydrodynamics in a ceramic pervaporation membrane reactor for resin production	Polymeric membrane Temp. 200 ° C Viscosity μ = 5-25 mPas	The horizontal configuration showed an increase in water flux up to 50% compared to a simulation in which natural convection is omitted. The dimensionless heat and mass transfer coefficients Nu and Sh are also 4 times higher.	Flux measurements have been performed experimentally at different superficial velocities, temperatures and fluid compositions, showing that hydrodynamics is determined by forced and natural convection simultaneously.
Lim Y. *et. al.* (2002)	Design issues of pervaporation membrane reactors for esterification		In this paper they present a model that have developed to describe PVMR behavior. The simulation results of the model have been validated with experimentally observed pervaporation membrane reactor conversions. The model is used to describe a number of alternative PVMR configurations	The key difference of this model from other PVMR models is that it accounts for the thermodynamic non-idealities involved during the reactive and transport processes, and offers a unified means for accounting for these phenomena.

			and analyze the factors that afect and optimize their performance.	
Benedict J. Daniel *et. al.* (2003)	Esterification of Lactic Acid and Ethanol with/without Pervaporation	Temp. 75, 85, & 95°C Catalyst Amberlyst XN-1010 GFT-1005 Membrane	Pervaporation was promoted with increasing temperature. Reactors coupled with pervaporation, can help enhance the conversion of reactants for thermodynamically or kinetically limited reactions via selective removal of one or more product species from the reaction mixture.	Fractional conversions in excess of the equilibrium conversion attainable in a reactor without product separation were attained by selective removal of water from the reaction mixture by pervaporation
Peters A. *et al.* (2005)	Zeolite-Coated Ceramic Pervaporation Membranes; Pervaporation-Esterification Coupling and Reactor Evaluation	Temp. 75 °C Catalysts Y-type Zeolite Ceramic hollow fiber Silica membranes with Zeolite coating.	A reactor evaluation proved that the outlet conversion for the catalytic pervaporation-assisted esterification reaction exceeded the conversion of a conventional inert pervaporation membrane reactor, with the same loading of catalyst dispersed in the liquid bulk.	In the pervaporation-assisted esterification reaction, the catalytic membrane is able to couple catalytic activity and water removal.
Smitha B. et. al. (2006)	Dehydration of 1,4-dioxane by pervaporation using modified blend membranes of chitosan and nylon 66	Temp. 40 °C Crosslinked blend membranes of chitosan (CS) and nylon 66 (NYL)	Optimum CS/NYL ratio was determined as 90/10 (w/w) for 4.3 wt.% feed water concentration at 40 °C Increasing barrier from 30 to 120 μm improved the separation factor from 767 to 1123 at the cost of flux, which lowered from 0.118 to 0.028 kg/m^2 h. The azeotrope formed at 82-wt.% dioxane was easily broken with a selectivity of 865 and water flux of 0.089 kg/m^2 h.	Increasing water concentration in feed brought about enhanced membrane swelling and thereby improved flux at reduced selectivity due to plasticization effect. Varying thickness caused a considerable lowering of the flux with marginal improvement in selectivity. Higher permeate pressures resulted in a reduction in both the flux and selectivity.

Sakaki Keiji et. al. (2005)	Pervaporation dehydration to the lipase-catalyzed esterification of fructose/glucose with palmitic acid in 2-methyl-2-butanol	Temp. 40 °C 54 mM fructose and 54mM palmitic acid in 220 mL of 2-methyl-2-butano Zeolite NaA membrane	The water content in the reaction mixture decreased to 0.03 wt% by means of pervaporation using a zeolite NaA membrane. With the aid of pervaporation dehydration, the total yield of fructose monopalmitate and dipalmitate reached 66% in the esterification started with 54 mM fructose and 108 mM palmitic acid.	It was possible to decrease the ratio of diester in the reaction product by decreasing the ratio of fatty acid to sugar in the substrate solution
Sanz & Gmehling (2006)	Esterification of acetic acid with isopropanol coupled with pervaporation Kinetics and pervaporation studies.	329.15 to 353.85K for the esterification reaction and from 332.15 and 350.90K for the hydrolysis reaction Polymeric Membrane PERVAP® 2201	In this work, the heterogeneously catalyzed synthesis and hydrolysis of isopropyl acetate by Amberlyst 15 have been studied. A kinetic expression was obtained by fitting simultaneously the kinetic results of the esterification and the hydrolysis reactions. The pseudo-homogeneous model gives a good representation of the reaction rate for the isopropyl acetate system with only four adjustable parameters. The permeate flux was found to increase with the water content in the feed and the temperature.	The design of a pervaporation reactor requires information on reaction kinetics and pervaporation performance of the membrane. Based on these results it can be concluded that the membrane PERVAP® 2201can be used to remove selectively the water formed in the esterification reaction to obtain higher conversions by using membrane reactors.

El-Zanati E. *et. al.* (2006)	Modeling and simulation of butanol separation from aqueous solutions using pervaporation	A 250 cm3 Butanol mixture at Temp. 33 ° C Different Butanol concentrations (6-8-11-16-20-50) g/l. vacuum (Pressure~1 kPa) Organophili Membrane, which is permeable to the butanol	The permeation of the binary system was investigated, and it was found that the butanol removal increases by increasing the feed concentration. Also, the butanol concentration decreases linearly with time.	The permeability of the used membrane was determined experimentally. A resistance in series model was used to simulate the pervaporation step. The butanol concentration in the feed during the pervaporation step was predicted by using the developed model. There is a fair agreement between butanol concentration in feeding tank of pervaporation cell both experimentally and predicted from the developed model.

CHAPTER III

MODEL DEVELOPMENT

3.1 INTRODUCTION

In this chaptertion a mathematical model for esterification of acetic acid with *n*-butanol, lactic acid with ethanaol and acetic acid with ethanol in a pervaporation reactor have been developed. The available experimental data has been used for the modeling purpose. The influence of several process variables, such as process temperature, initial mole ratio of acetic acid over *n*-butanol, and the ratio of the effective membrane area over the volume of reacting mixture and catalyst content, flux on the esterification were discussed. Model results are in well comparison with available experimental results. Presented model can be used for the other esterification reactions in pervaporation reactor.

Besides, model requires kinetic equations for all the equations, catalyst parameters, and permeances of the species through the membrane so that solution of model equations may be obtained.

3.2 ASSUMPTIONS

The mathematical model was developed using the following assumptions

- The reactor was operated isothermally
- The reaction volume is constant.
- Concentration changes in the liquid mixture could be neglected due to small amount of permeation compared to the amount of the liquid mixture
- The membrane is completely un reactive
- The main transport resistance is in the dense polymeric layer.
- Transport resistance in the inorganic support structure on the permeate side, is considered negligible.

3.3 MASS BALANCE

This section comprises of the mass balance equations for transport through reactor to pervaporation module. The principle of conservation of mass for overall mass balance of ith component in control volume if given as

$$\left(\begin{array}{l}\text{rate of moles of i}^{th}\text{component}\\ \text{into the control volume}\end{array}\right) - \left(\begin{array}{l}\text{rate of moles of i}^{th}\text{component}\\ \text{out of the control volume}\end{array}\right) \pm \left(\begin{array}{l}\text{moles of i}^{th}\text{ component gene -}\\ \text{rated or consumed by reaction}\end{array}\right)$$
$$- \left(\begin{array}{l}\text{rate of moles i}^{th}\text{component transported}\\ \text{through the membrane}\end{array}\right) = \left(\begin{array}{l}\text{rate of accumulation of moles of}\\ \text{i}^{th}\text{component in controlvolume}\end{array}\right)$$

The principle of conservation of mass for semi batch reactor with pervaporation module of ith component in control volume in terms of molar concentration is given as

$$\left(\begin{array}{l}\text{rate of accumulation of moles of}\\ \text{i}^{th}\text{component in controlvolume}\end{array}\right) = \pm \left(\begin{array}{l}\text{moles of i}^{th}\text{ component gene -}\\ \text{rated or consumed by reaction}\end{array}\right)$$
$$- \left(\begin{array}{l}\text{rate of moles i}^{th}\text{component transported}\\ \text{through the membrane}\end{array}\right)$$

$$\frac{dC_i}{dt} = \pm\left(k_1 C_A C_B - k_2 C_R C_H\right) - \frac{S}{V} J_i \qquad (3.1)$$

Where i is A, B, R and H in equation (2) which is given below

3.4 THEORY AND MODELING

The general esterification reaction between an acid and an alcohol can be schematically represented by:

$$\begin{array}{ccccccc} A\,+ & & B & \Leftrightarrow & R & + & H \\ Acid & & Alcohol & & Ester & & Water \end{array} \qquad (3.2)$$

The system configuration is same as shown in **Figure 1.1**. The pervaporation reactor is in semi-batch mode as water is continuously removed from the reaction mixture using pervaporation.

The pervaporation module, which is water selective, hydrophilic membrane, was considered. Normally in pervaporation the flow across the membrane is small then the variation in the reaction volume will also be small and it can be neglected. Hence the component balance in pervaporation reactor can be:

$$\frac{dC_A}{dt} = -(k_1 C_A C_B - k_2 C_R C_H) - \frac{S}{V} J_A \qquad (3.3)$$

$$\frac{dC_B}{dt} = -(k_1 C_A C_B - k_2 C_R C_H) - \frac{S}{V} J_B \qquad (3.4)$$

$$\frac{dC_R}{dt} = (k_1 C_A C_B - k_2 C_R C_H) - \frac{S}{V} J_R \qquad (3.5)$$

$$\frac{dC_H}{dt} = (k_1 C_A C_B - k_2 C_R C_H) - \frac{S}{V} J_H \qquad (3.6)$$

Where, S is the membrane area, V is the volume of reaction mixture, and J_H is the water flow across the membrane. The relation between flux and feed water concentration may be linear polynomial or exponential. From experimental pervaporation data of flux and feed water concentration have been taken and plotted to get the relation between water flux (kmol/m^{2}min) and water concentration (kmol/m^3) in feed. The following relations may be developed:

$$J_H = k_{PV} C_H \qquad (3.7)$$

$$J_H = k_{PV1} C_H - k_{PV2} C_H{}^2 \qquad (3.8)$$

$$J_H = k_{pv1} C_H{}^{k_{pv2}} \qquad (3.9)$$

The rate of water formation by esterification reaction (2) can be written as:

$$r_H = k_1 C_A C_B - k_2 C_R C_H \qquad (3.10)$$

It was found experimentally that the concentration of ester, alcohol and acid in permeate were negligible as compared to water (Liu and Chen (2002)). Hence the material balance for the ester, acid, and alcohol can be:

$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = (k_1 C_A C_B - k_2 C_R C_H) \qquad (3.11)$$

The equation (7) represents the homogeneous esterification reaction rate equation without catalyst. The effect of catalyst should be in the rate equation; hence the reaction can be written as:

$$A + B + C \Leftrightarrow R + H + C \qquad (3.12)$$

$$\frac{-dC_A}{dt} = k_1 C_A C_B C_C - k_2 C_R C_H C_C \qquad (3.13)$$

$$\frac{-dC_A}{dt} = k_1 C_C \left(C_A C_B - \frac{C_R C_H}{K} \right) \tag{3.14}$$

The reaction also occurs without the catalyst and the rate of the reaction with catalyst is directly proportional to the catalyst concentration. Hence, the overall rate of disappearance of component A can be given by:

$$-\frac{dC_A}{dt} = k_{obs} \left(C_A C_B - \frac{C_R C_H}{K} \right) \tag{3.15}$$

The value of k_{obs} depends on the catalyst concentration and reaction temperature. Also the balance equation for water becomes,

$$\frac{dC_H}{dt} = k_{obs} \left(C_A C_B - \frac{C_R C_H}{K} \right) - \frac{S}{V} J_H \tag{3.16}$$

The conversion of component A (acid) and B (alcohol) can be given by:

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} \tag{3.17}$$

$$X_B = \frac{C_{B0} - C_B}{C_{B0}} \tag{3.18}$$

3.5 CONCLUDING REMARKS

In this chapter detailed derivation of model equations are presented. To derive model equations we have taken simplifying assumptions. Those assumptions also mentioned .Model consists of set of non-linear coupled ordinary differential equations from 3.3 to 3.16, which form an initial value problem (IVP). These equations are solved by Finite difference method and RKF method

SOLUTION OF MATHEMATICAL MODEL

4.1 INTRODUCTION

In order to predict the performance of the model, solutions of model equations are very essential. The developed mathematical model in chapter 3 consists of nonlinear ordinary differential equations. These equations constitutes initial value problem. So we can solve these equations by RKF method and Finite difference method

4.2 MATHEMATICAL MODEL

The general esterification reaction between an acid and an alcohol can be schematically represented by:

$$\underset{Acid}{A} + \underset{Alcohol}{B} \Leftrightarrow \underset{Ester}{R} + \underset{Water}{H} \qquad (4.1)$$

The component balance in pervaporation reactor can be:

$$\frac{dC_A}{dt} = -(k_1 C_A C_B - k_2 C_R C_H) - \frac{S}{V} J_A \qquad (4.2)$$

$$\frac{dC_B}{dt} = -(k_1 C_A C_B - k_2 C_R C_H) - \frac{S}{V} J_B \qquad (4.3)$$

$$\frac{dC_R}{dt} = (k_1 C_A C_B - k_2 C_R C_H) - \frac{S}{V} J_R \qquad (4.4)$$

$$\frac{dC_H}{dt} = (k_1 C_A C_B - k_2 C_R C_H) - \frac{S}{V} J_H \qquad (4.5)$$

The following relations may be developed between water flux and water concentration in pervaporation module.

$$J_H = k_{PV} C_H \qquad (4.6)$$

$$J_H = k_{PV1} C_H - k_{PV2} C_H^{\,2} \qquad (4.7)$$

$$J_H = k_{pv1} C_H^{\,k_{pv2}} \qquad (4.8)$$

The rate of water formation by esterification reaction (2) can be written as:

$$r_H = k_1 C_A C_B - k_2 C_R C_H \qquad (4.9)$$

It was found experimentally that the concentration of ester, alcohol and acid in permeate were negligible as compared to water (Liu and Chen (2002)). Hence the material balance for the ester, acid, and alcohol can be:

$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = (k_1 C_A C_B - k_2 C_R C_H) \qquad (4.10)$$

The equation (7) represents the homogeneous esterification reaction rate equation without catalyst. The effect of catalyst should be in the rate equation; hence the reaction can be written as:

$$A + B + C \Leftrightarrow R + H + C \qquad (4.11)$$

$$\frac{-dC_A}{dt} = k_1 C_A C_B C_C - k_2 C_R C_H C_C \qquad (4.12)$$

$$\frac{-dC_A}{dt} = k_1 C_C \left(C_A C_B - \frac{C_R C_H}{K} \right) \qquad (4.13)$$

The overall rate of disappearance of component A can be given by:

$$-\frac{dC_A}{dt} = k_{obs} \left(C_A C_B - \frac{C_R C_H}{K} \right) \qquad (4.14)$$

Also the balance equation for water becomes,

$$\frac{dC_H}{dt} = k_{obs} \left(C_A C_B - \frac{C_R C_H}{K} \right) - \frac{S}{V} J_H \qquad (4.15)$$

The conversion of component A (acid) and B (alcohol) can be given by:

$$X_A = \frac{C_{A0} - C_A}{C_{A0}} \qquad (4.16)$$

$$X_B = \frac{C_{B0} - C_B}{C_{B0}} \qquad (4.17)$$

4.3 METHODOLOGY

The model equations are non-linear coupled ordinary differential equations from equation 4.2 to 4.15 which constitutes initial value problem (IVP). We have been solved the above ODEs equations using RKF method in MATLAB and by Finite difference method in EXCEL also. For given boundary conditions and flow rates of feed and other parameters like process temperature, initial mole ratio of acid over alcohol, the ratio of the effective membrane area over the volume of reacting mixture, catalyst concentration, flux the equations are solved simultaneously. An optimized time step was considered for the solution. The values and range of the various parameters used for simulations are given in **Table 4.1**. Kinetic data and pervaporation data were taken from the available literature.

Table 4.1 Values and range of the various parameters used for simulation

Parameter	**Notation and Unit**	**Value/Range**
Initial mole ratio of acetic acid and n-butanol	$R_0 = C_{A0}/ C_{B0}$	1 – 2.5
Ratio of the effective membrane area over the volume of reacting mixture	S/V (m^2/m^3)	0 – 40
Equilibrium constant for temperature range * 50-90 °C	$K= k_1/k_2$	2 – 9
Observed kinetic constant for temperature range 50-90 °C	$k_{obs} = k_1C_C$ (m^3/kmol min)	0.000346-0.00306
Reaction time	t (min)	480
Catalyst concentration	C_C (kg/m^3)	0 – 100
Temperature	T (°C)	50-100

* The reaction rate constants for the esterification reaction are taken from the available literature:

$$k_1 = k_0 \exp\left(-\frac{E}{RT}\right) \text{ and } k_2 = k_0 \exp\left(-\frac{E}{RT}\right)$$

4.4 SELECTION OF TIME STEP FOR SIMULATION

The time step used in the simulation is important, as the model solution should be independent of the time steps. In view of this, first the sensitivity of model solution on time step was studied. **Figure 4.1** depicts the change in the conversion profile with respect to time for various time steps (0.05, 0.1, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, 4, 5, 7, 10 mins). It was observed that the end effect of change in time step was almost negligible and in the time range of 20 min to 120 min it was clearly differentiable. But for the time step less than 0.5 min, there were no change in the profile and also the final conversion and conversion after 60 min was not changed. (**Table 2**) Hence, time step of 0.5 min was used for further studies. This study is done from available experimental data from paper **Liu and Chen (2002)**

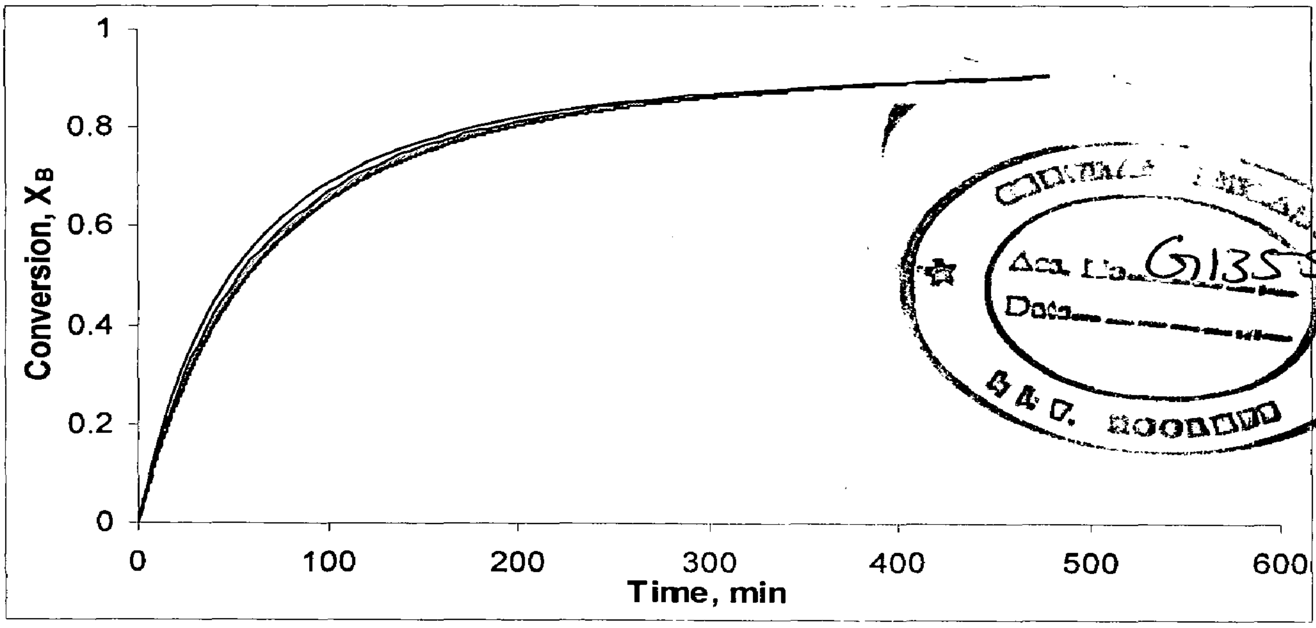

Figure 4.1 Change in conversion profile with respect to time for various time steps. (0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, 4, 7, 10 min) (T=80°C; C_C=0.0298 kmol/m^3; Ro=1.6; S/V=23 m^{-1})

Table 4.2 Time step sensitivity on conversion

Time Step (min)	Final Conversion (360 min)	Conversion (60 min)
0.05	0.9042	0.5013
0.10	0.9042	0.5014
0.25	0.9042	0.5018
0.50	0.9042	0.5020
0.75	0.9043	0.5052
1.00	0.9043	0.5109
1.25	0.9044	0.5116
1.50	0.9044	0.5123
1.75	0.9045	0.5106
2.00	0.9045	0.5136
4.00	0.9047	0.5193
5.00	0.9050	0.5222
7.00	0.9055	0.5287
10.00	0.9059	0.5374

Experimental conversion after 60 min. = 0.50

4.5 RELATION BETWEEN WATER FLUX AND WATER CONCENTRATION

4.5.1 For Esterification of Acetic acid with n-Butanol

The experimental pervaporation data of Liu and Chen (2002) of flux and feed water percentage have been taken and plotted to get the relation between water flux (kmol/m^{2}min) and water concentration (kmol/m^3) in feed. In actual, the relation between flux and feed water concentration is nonlinear and not constant throughout the reaction. Hence the following modified relation can be used.

$$J_H = k_{PV1} C_H - k_{PV2} C_H^{\ 2}$$

The following relation has been developed (**Figure 4.2**):

$$J_H = 0.0001 C_H - 0.000004 C_H^{\ 2} \tag{4.18}$$

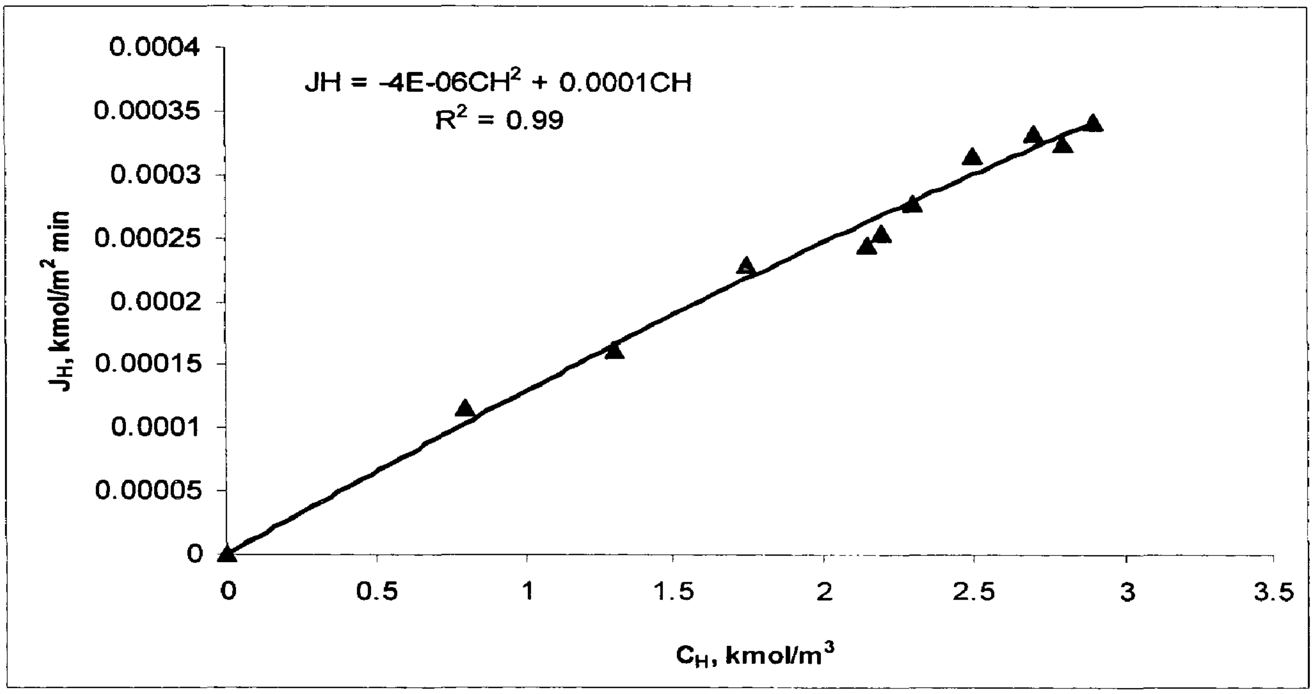

Figure 4.2 Relation of water flux and water concentration in feed based on the experimental data of Liu and Chen (2002)
(T=80°C; C_C=0.0298 kmol/m^3; Ro=1.6; S/V=23 m^{-1})

4.5.2 For Esterification of Lactic acid with Ethanol

The experimental pervaporation data of Benedict et al. (2003) of flux and feed water percentage have been taken and plotted to get the relation between water flux (kmol/m^{2}min) and water concentration (kmol/m^3) in feed. In actual, the relation between flux and feed water concentration is nonlinear and not constant throughout the reaction. Hence the following modified relation can be used.

$$J_H = k_{PVI}C_H - k_{PV2}C_H^{\ 2}$$

The following relation has been developed (**Figure 4.3**):

$$J_H = 0.0001C_H - 0.000004C_H^{\ 2} \tag{4.19}$$

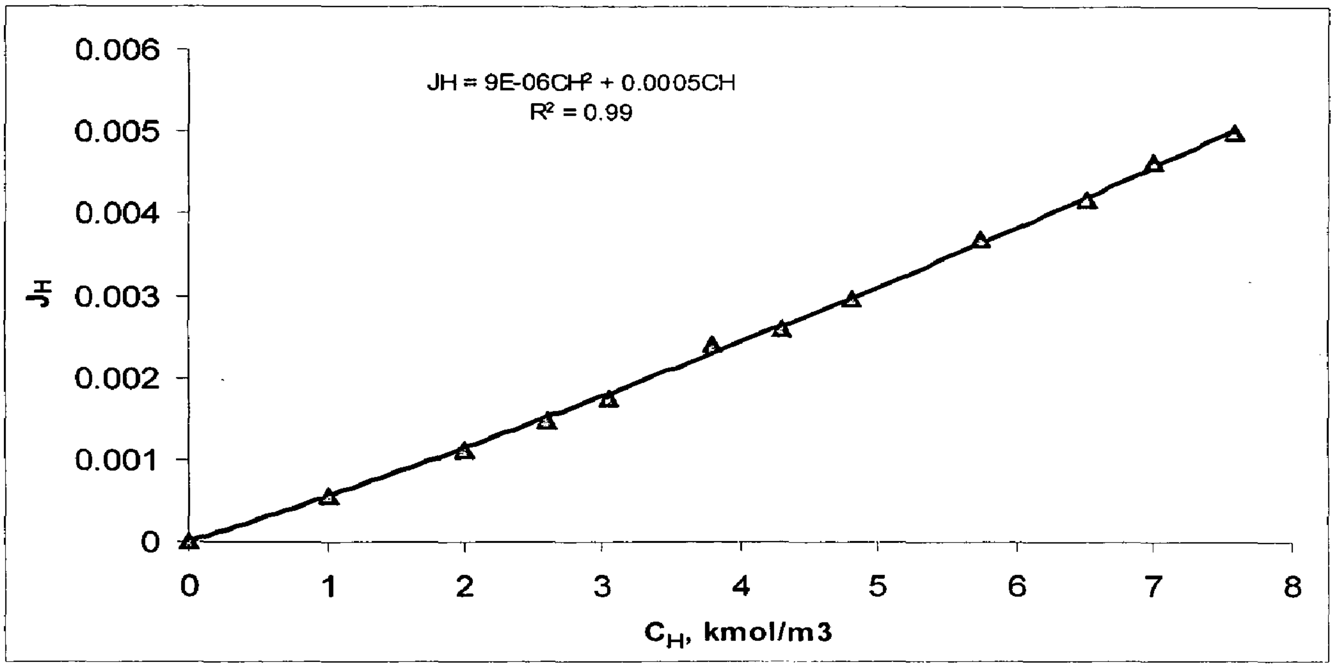

Figure 4.3 Relation of water flux and water concentration in feed based on the experimental data of Benedict et al (2003)
(T=95°C; Ro=1.2; C_C=31.4 g/l; S/V=20 m^{-1})

4.6. For Esterification of acetic acid with Ethanol

The experimental pervaporation data of Tanaka et al. (2001) of flux and feed water percentage have been taken and plotted to get the relation between water flux (kmol/m^2min) and water concentration (kmol/m^3) in feed. The relation between flux and feed water concentration is linear t constant throughout the reaction. Hence the following modified relation can be used.

$$J_H = k_{PV1}C_H$$

The following relation has been developed (**Figure 4.4**):

$$J_H = 0.004C_H \tag{4.20}$$

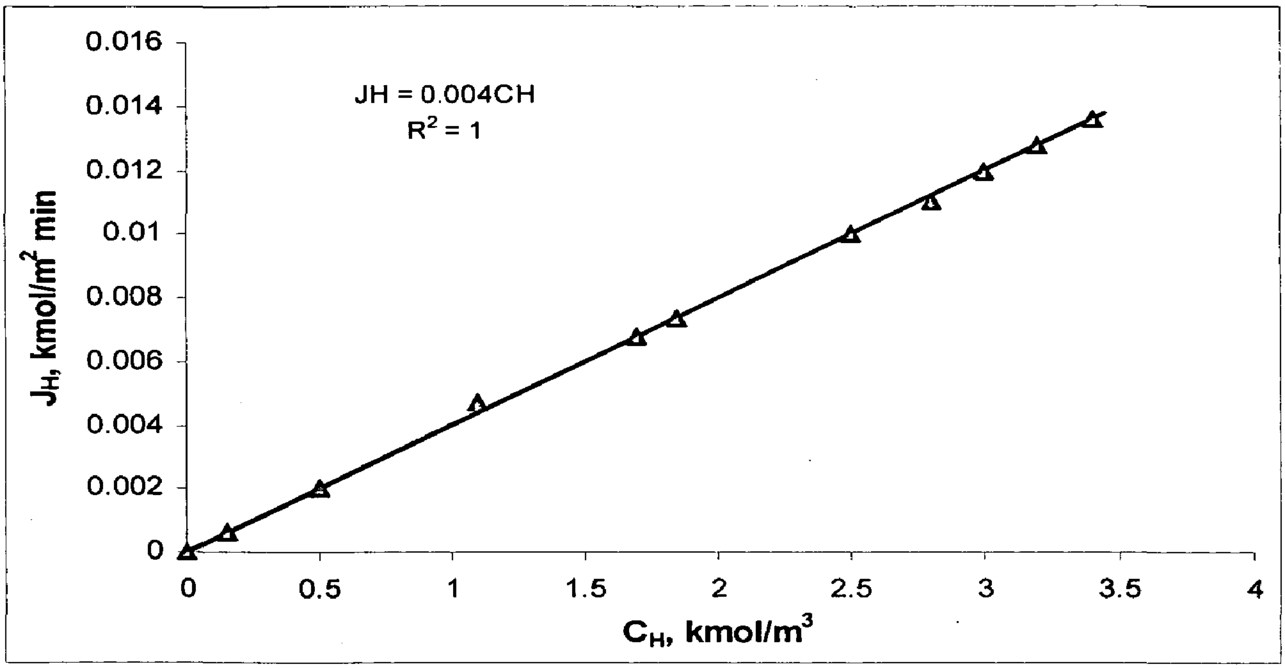

Figure 4.4 Relation of water flux and water concentration in feed based on the experimental data of Tanaka et al (2001)
(T=70°C; C_C=40 g/l; Ro=1.25; S/V=3.4 m^{-1})

4.5 CONCLUDING REMARKS

In this chapter detailed derivation of model equations are presented. To derive model we take simplifying assumptions. Those assumptions are also mentioned. Model consists of set of non-linear coupled ordinary differential equations, which form an initial value problem (IVP). These equations have been developed and solved to predict the model behavior using RKF method in MATLAB and by Finite difference method in EXCEL. The physical properties and simulation parameters are given abovein tabular form.

ESTERIFICATION OF ACETIC ACID WITH N-BUTANOL

5.1 SYSTEM CONFIGURATION

In this section, results of the developed mathematical model on pervaporation reactor have been studied and discussed for esterification of acetic acid with n-butanol in the presence of $Zr(SO_4)_2H_2O$. The influence of several process variables, such as process temperature, initial mole ratio of acetic acid over *n*-butanol, and the ratio of the effective membrane area over the volume of reacting mixture and catalyst content, flux on the esterification have been discussed.

Table 5.1 Values and range of the various parameters used for this system

Parameter	**Notation and Unit**	**Value/Range**
Initial mole ratio of acetic acid and n-butanol	$R_0 = C_{A0}/C_{B0}$	1 – 2.5
Ratio of the effective membrane area over the volume of reacting mixture	S/V (m^2/m^3)	0 – 40
Equilibrium constant for temperature range * 50-90 °C	$K = k_1/k_2$	9.010-7.099
Observed kinetic constant for temperature range 50-90 °C	$k_{obs} = k_1 C_C$ (m^3/kmol min)	0.000346-0.00306
Reaction time	t (min)	480
Catalyst concentration	C_C (kmol/m^3)	0.00282-0.0563
Temperature	T (°C)	50-90

* The reaction rate constants for the esterification reaction (8) are taken from the available literature (Liu and Chen,2002) :

$$k_1 = 4.531 \times 10^6 \exp\left(-\frac{53.13 \times 10^3}{RT}\right) \text{ and } k_2 = 4.376 \times 10^6 \exp\left(-\frac{58.94 \times 10^3}{RT}\right)$$

Our proposed model predicts the conversion of the reactant along the rection time of the reactor, and the effects of operating parameters on the performance of pervaporation reactor. The numerically computed results are shown graphically. The calculated results for the conversion of *n*-butanol to water concentration were consistence with the experimental data. The values and range of the various parameters used for simulations are given in **Table 5.1**.

5.2 RESULTS AND DISCUSSION

5.2.1 Model Validation

Before going for any simulation study, model validation is must. In view of this the simulation results were compared with available experimental data of Liu and Chen (2002) for the conditions of temperature, T = $80^{O}C$, catalyst concentration, C_C = 0.0298 kmol/m^3; the ratio of the effective membrane area over the volume of reacting mixture S/V = 23 m^{-1}; initial mole ratio of acetic acid and n-butanol is 1.6 and flux as per equation (6) in kmol/m^2min. The model results of conversion of butanol and water concentration in reaction mixture were compared with the experimental results and are shown in **Figure 5.1** and **Figure 5.2** respectively.

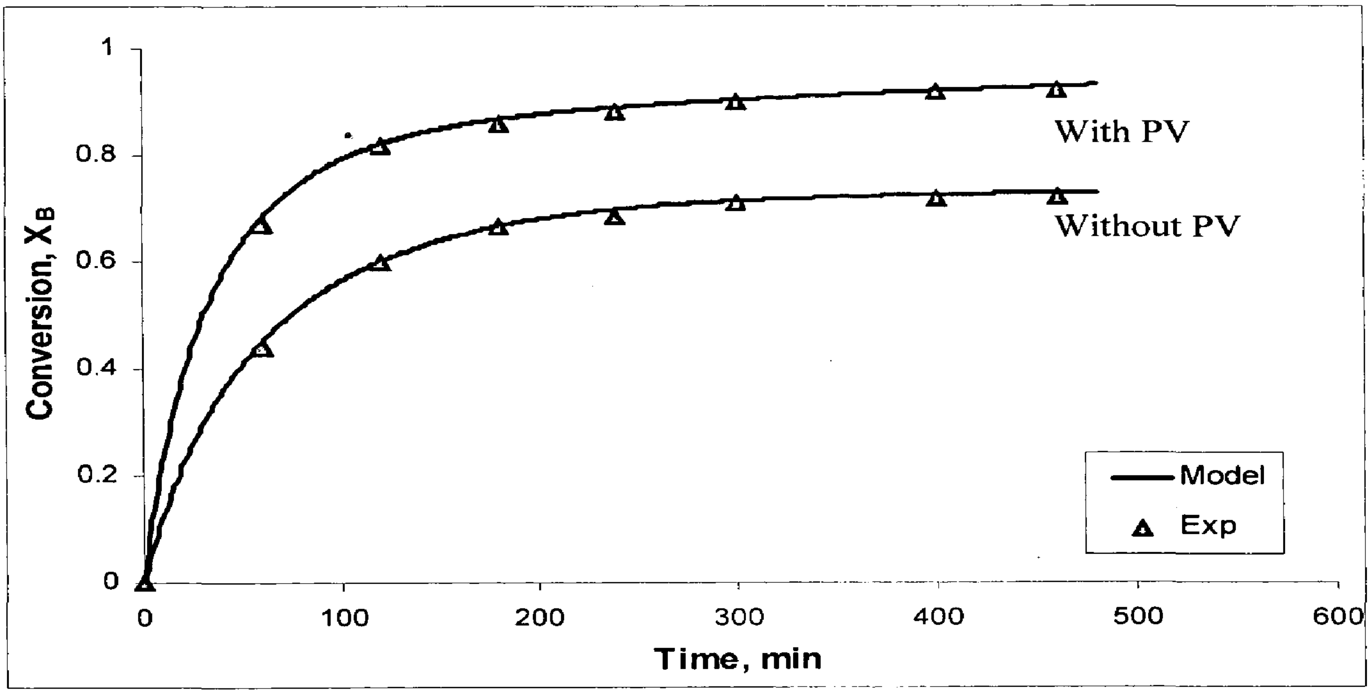

Figure 5.1 Calculated curves compared to experimental points for n-butanol conversion. both with and without pervaporation (T=80°C; C_C=0.0298 kmol/m^3; Ro=1.6; S/V=23 m^{-1})

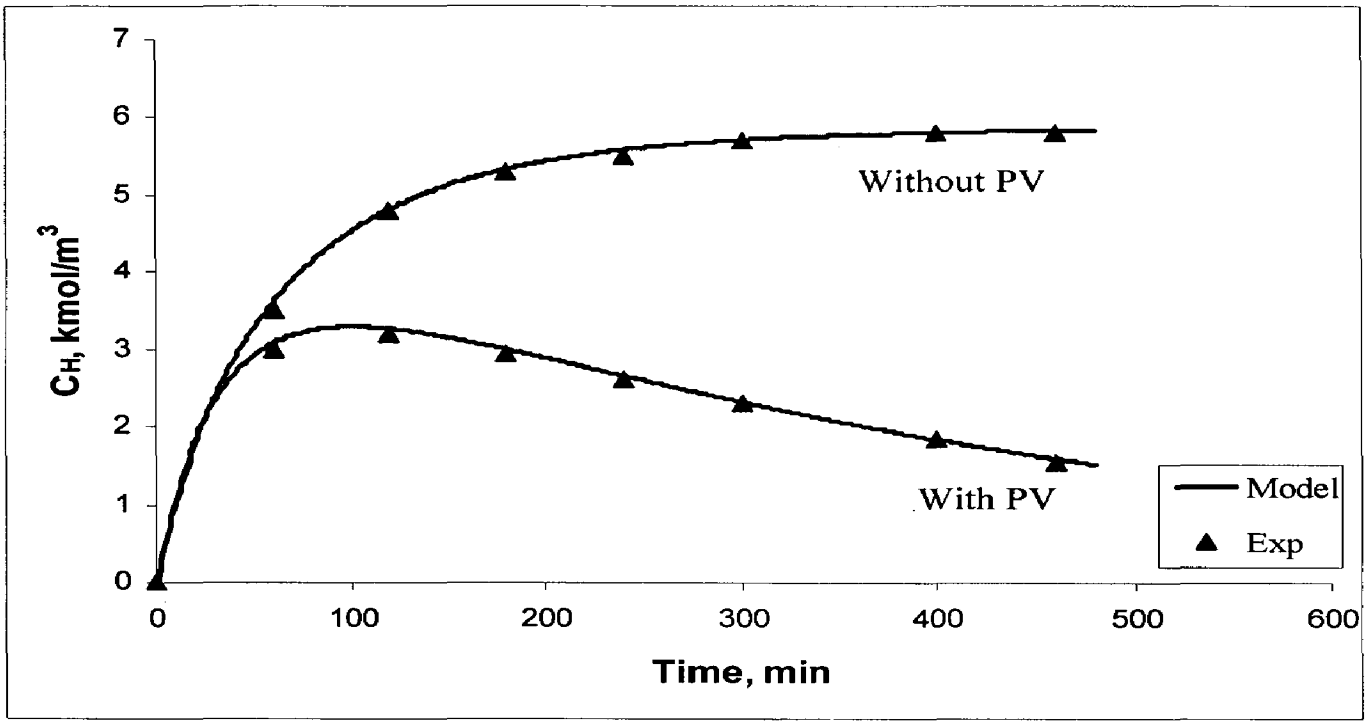

Figure 5.2 Calculated curves compared to experimental points for water concentration for esterification both with and without pervaporation. (T=80 °C; C_C=0.0298 kmol/m^3; Ro=1.6)

It shows that the proposed model results were in excellent agreement with the available experimental results. Slightly over-predictions were observed for conversion of butanol with respect to time due to the negligence of n-butanol permeating through the membrane by the model equations. It was indicated that PV enhanced the conversion for the PV-aided esterification than for the reaction without PV. The water content for the reaction without PV was higher than for the PV-aided reaction due to water removal by PV.

5.2.2 Effect of operating temperature

The simulation results for effect of reaction temperature on conversion of n-butanol and water content are shown in **Figure 5.3** and **Figure 5.4**. The temperature was varied from 50 to 90 ^{0}C for fixed value of catalyst concentration (C_C=0.0375 kmol/m^3), reactants ratio (Ro=1.6) and membrane area to reaction volume (S/V=23 m^{-1}). It can be observed form the **Figure 5.3** that the conversion increased with increase in temperature but the change in increased conversion is not significant at higher tempratire. For 80^{O}C and 90^{O}C temperatures, the conversion is almost same. So we can say that the optimum conversion temperature is 80^{O}C. An increase in temperature induced not only an acceleration of esterification but also acceleration in pervaporation.

Water production rate is higher in higher temperature than in a lower temperature (**Figure 5.4**) so the permeation parameter for water is also varied with the increase of temperature as a result water permeation flux was increased with increase in temperature. The reaction rate constants for the esterification are a function of process temperature, and were increased with the increase of the temperature. The accelerating of the reaction rate constant with the increase of the temperature for the forward reaction was faster than the backward process. So water production rate was higher in a higher temperature than in a lower temperature. Meanwhile, the permeation parameter for water is also varied with the temperature and was increased with the increase of the temperature. As a result, water permeation flux was increased with the increase of the process temperature.

5.2.3 Effect of ratio of effective membrane area to the reaction volume (S/V)

The equilibrium shift of the esterification reaction is depending on the amount of water in the reaction mixture, as we increase the ratio (area of membrane) the rate of water removal will be more and more conversion. Also the cost of membrane depends on the required membrane area. Hence the membrane area and conversion should optimize to get the optimum production cost, as the membrane area is small, time requires to achieve a particular conversion will be more, hence more operating cost. In case of high membrane area, operating cost will be low but capital cost will be more. In view of this, effect of ratio of effective membrane area over the volume of reacting mixture on the conversion of acetic acid was studied. The effect of the ratio of membrane area to reaction volume on the conversion of butanol and water content in reaction mixture were presented in **Figure 5.5** and **Figure 5.6.** The S/V was varied from 0 to 40 m^{-1} for 80^{O}C temperature, 0.0298 kmol/m^{3} catalyst concentration and reactant ratio of Ro=1.6. It was observed that the conversion achieved was a function of membrane surface area, conversion increases with increasing surface area. Time required to achieve a given duty of conversion was also varied with surface area of the membrane. Membrane area exerted no influence on reactive kinetics but caused the variation of the water removal rate. Water extraction rate was high for high surface area. As the water removal rate is high, the equilibrium will shift more towards right and higher conversion will be achieved.

5.2.4 Influence of catalyst concentration on reaction (C_C)

Catalyst concentration may be an alternative way to accelerate ester production. In view of this, the effect of catalyst concentration on the conversion of butanol was studied. The simulation results for conversion of n-butanol and water content variation in reaction mixture during pervaporation process over various catalyst concentrations were presented in **Figure 5.7** and **Figure 5.8**. The catalyst concentration was varied from 0.0141 kmol/m^3 to 0.0563 kmol/m^3 for fixed value of temperature (T = 80^{O}C), reactants ratio (Ro=1.6) and membrane area to reaction volume (S/V=23 m^{-1}). For catalyst concentration above 0.0298 kmol/m^3, the conversion of butanol is almost same. Hence the optimum catalyst concentration is 0.0298 kmol/m^3.

The conversion and water production rate is higher for higher C_C The effect of it is higher for a period at the beginning during the reaction than lower later. The variation of both forward and backward reaction rate occurred during the change of C_C The water production rate was higher (**Figure 5.8**) for a higher C_C since the forward reaction rate constant was higher than the backward one. Thus, the water contents in the reactor had higher maximum amplitude for a higher C_C during the reaction.

5.2.5 Influence of initial molar reactant ratio (acetic acid/n-butanol, Ro)

Figure 5.9 and **Figure 5.10** depict the effect of initial moalr reactant ratio on the butanol conversion and water in reaction volume. The reactant raio was varied from 1 to 2.5 for fixed values of the other parameters. The higher conversion was observed for higher ratios. Water production rate was decreased with the increase of R_O and caused the maximum amplitude in water content lower at a higher R_O. The water concentration in the reactor is lower for a higher R_O during the process. It is well known that a sufficient ratio of one reactant to the alcohol leads to a quasi-complete conversion of alcohol even without pervaporation. So this method would be carried out at the cost of separation difficulties. Decreasing the initial ratio of acid to alcohol when operating with pervaporation may be the optimum performance conditions.

5.2.6 Effect of Flux

In pervaporation process, to study the applicability for esterification process, the important parameter is the flux across the membrane. Flux depends on the type membrane used, the operating temperature, surface area of membrane, the reaction mixture and its composition. Membrane having higher flux requires less pervaporation membrane area and hence less production cost. The effect of flux on the performance of pervaporation reactor was studied by changing the flux to 1.5 times to 20 times of base value of flux. **Figure 5.11** and **Figure 5.12** show the effect of flux on the conversion and concentration of water in reaction mixture for the fixed volume. It was clearly observed that there were slight increased in the conversion as we increased the flux; this was because of the reaction limitations.

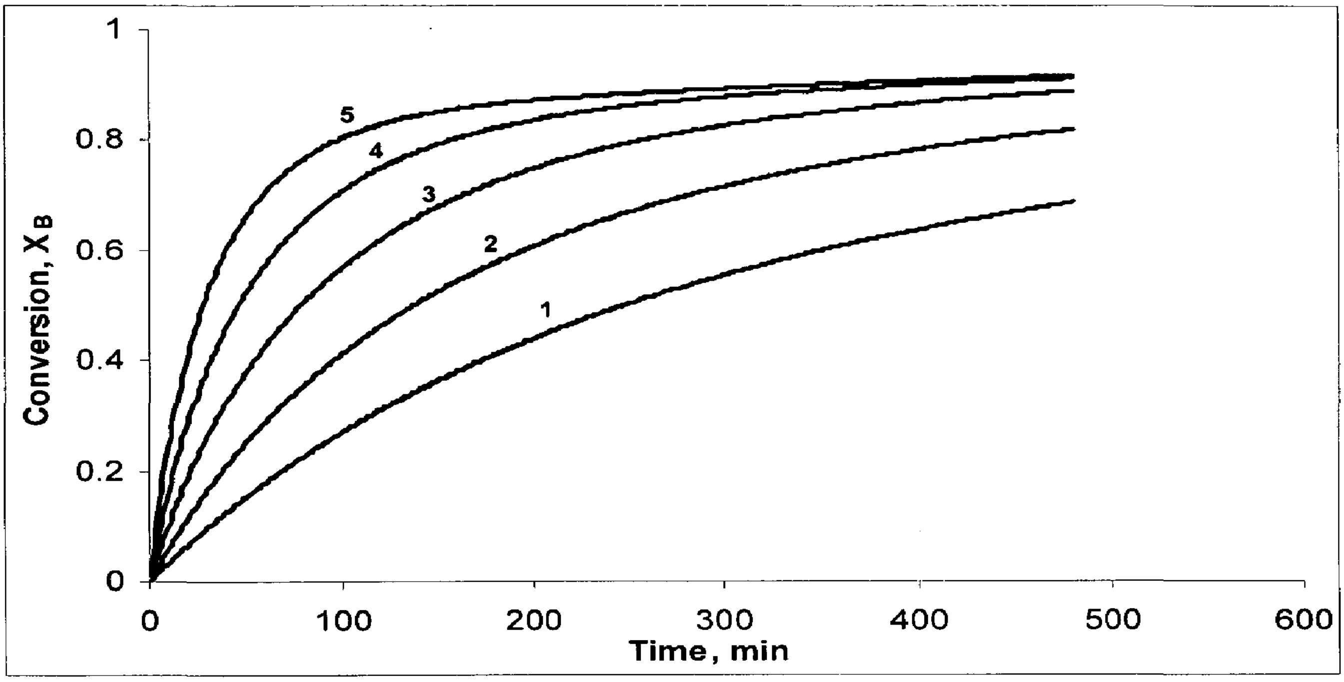

Figure 5.3 Effect of change in temperature on conversion of n-butanol. T for curve 1: 50 °C, 2: 60 °C, 4: 80 °C, 5: 90 °C ($Ro=1.6$; $C_C=0.0375$ kmol/m^3; $S/V=23$ m^{-1})

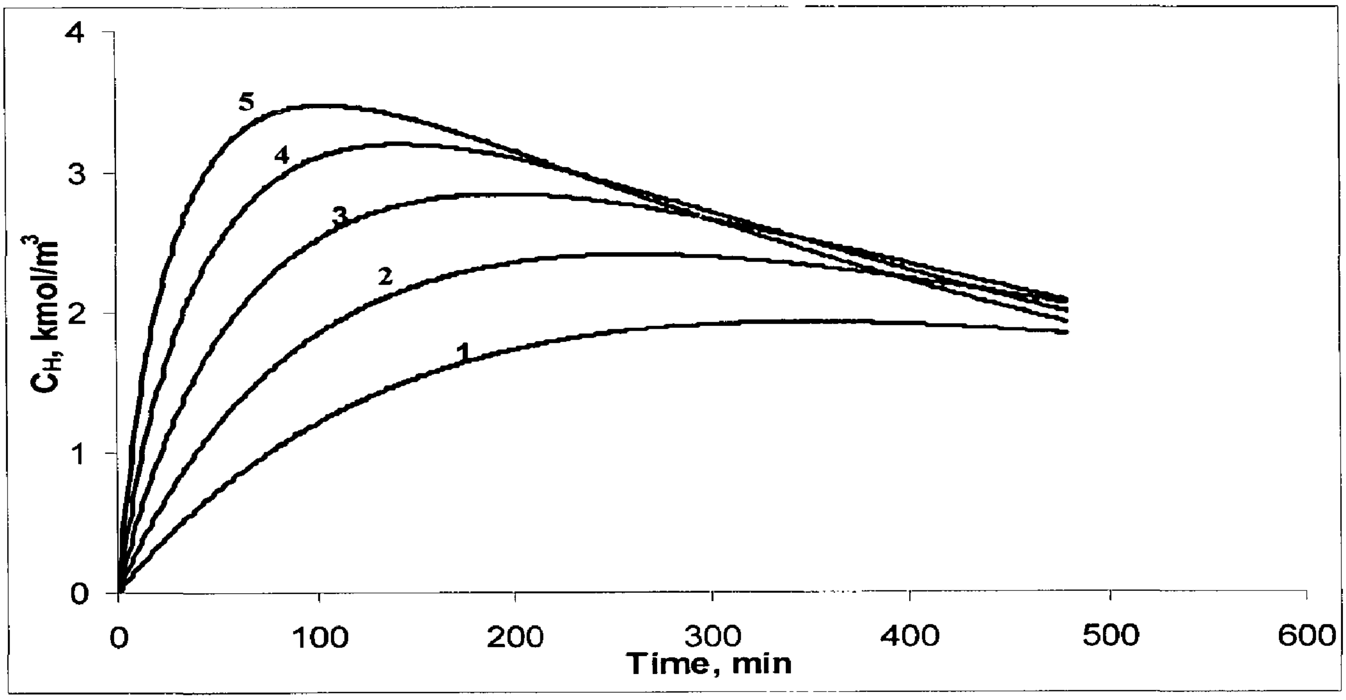

Figure 5.4 Effect of change in temperature on water concentration. Temperature for curve 1: 50 °C, 2: 60 °C, 4: 80 °C, 5: 90 °C ($Ro=1.6$; $C_C=0.0375$ kmol/m^3; $S/V=23$ m^{-1})

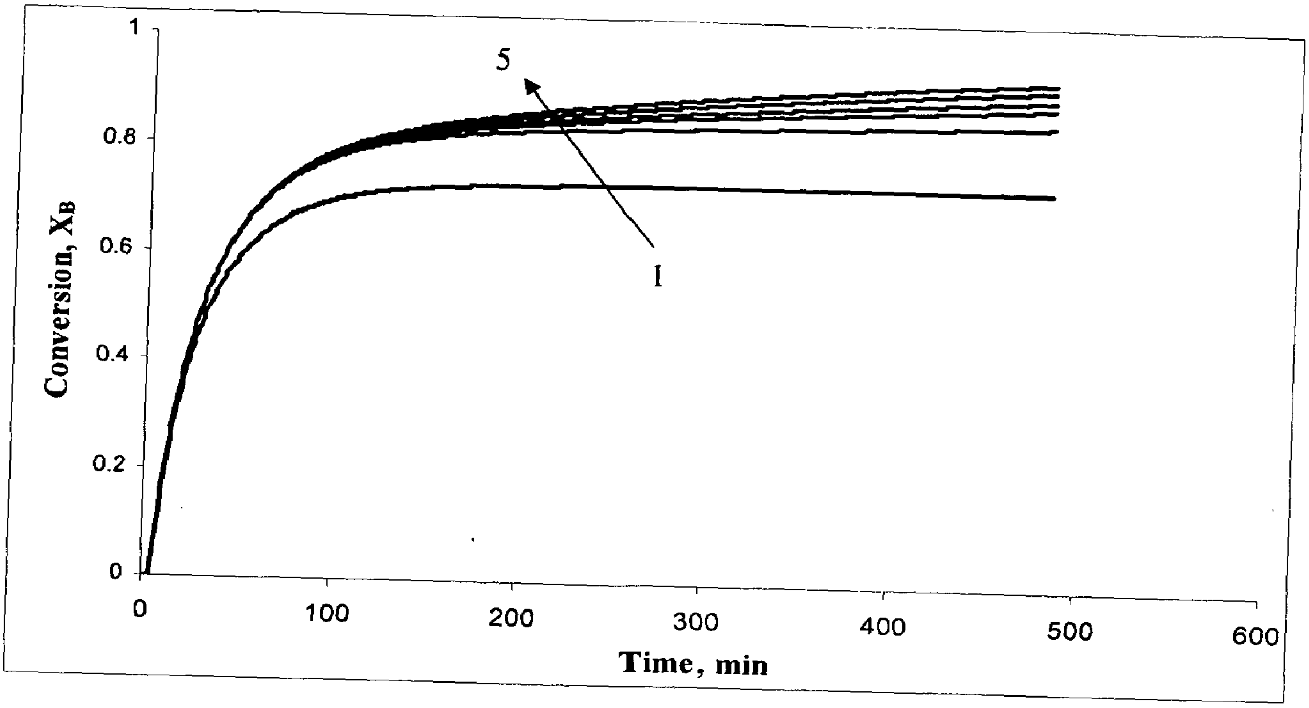

Figure 5.5 Effect of change in S/V on conversion of n-butanol. S/V ratio for curve 1: 0 m^{-1}, 2: 10 m^{-1}, 3: 23 m^{-1}, 4: 30 m^{-1}, 5: 40 m^{-1} (T=80°C; C_C=0.0298 $kmol/m^3$; Ro=1.6)

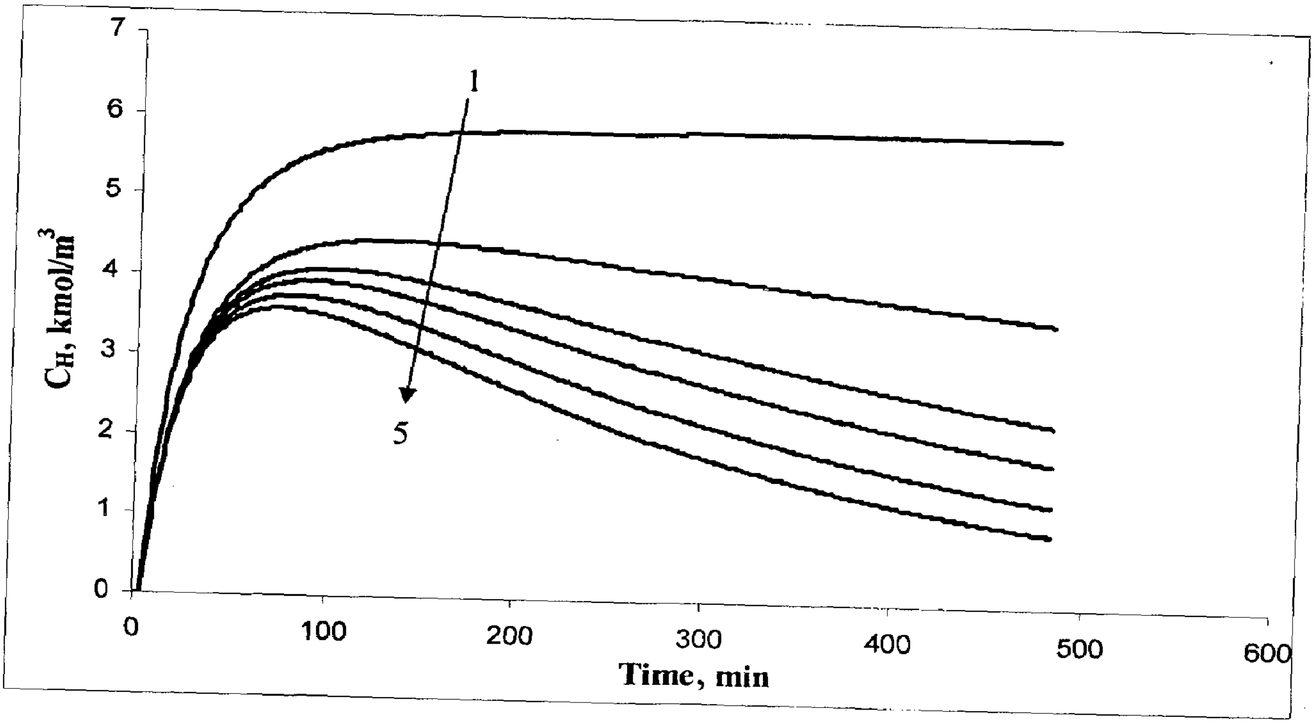

Figure 5.6 Effect of change in S/V ratio on water concentration. S/V ratio for curve 1: 0 m^{-1}, 2: 10 m^{-1}, 3: 23 m^{-1}, 4: 30 m^{-1}, 5: 40 m^{-1} (T=80°C; C_C=0.0298 $kmol/m^3$; Ro=1.6)

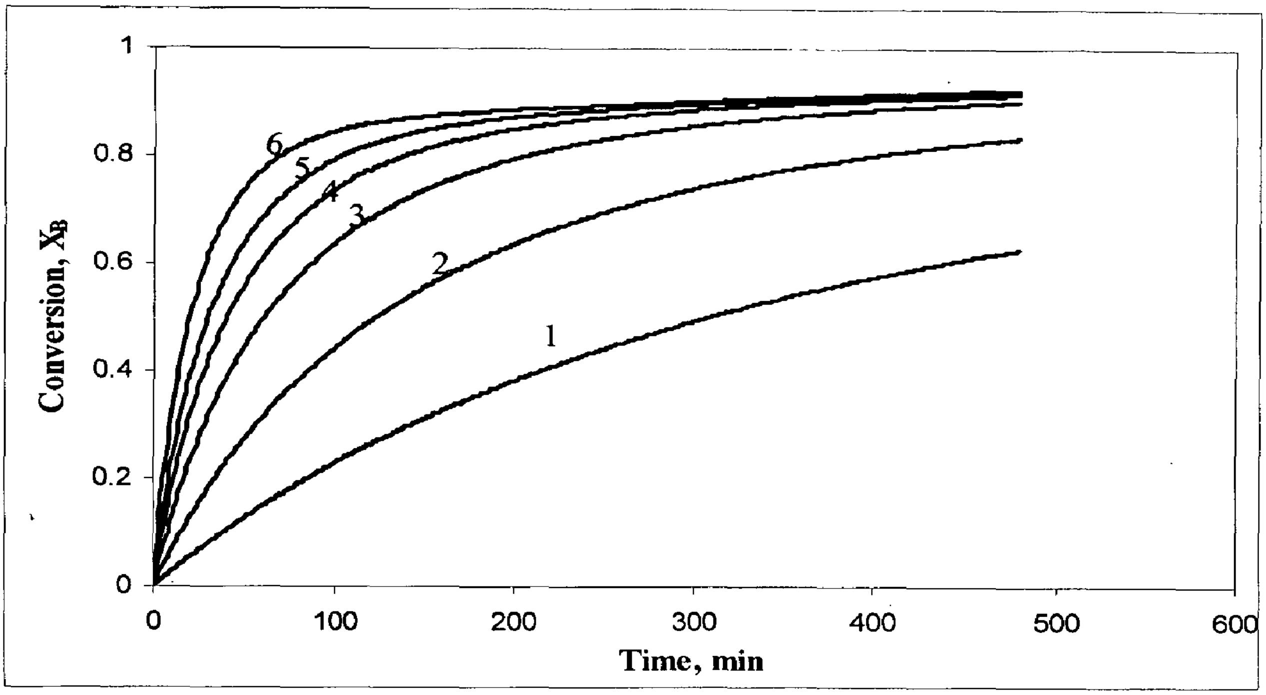

Figure 5.7 Effect of change in catalyst concentration on conversion of n-butanol. C_C for curve 1: 0.0028 kmol/m^3, 2: 0.0141 kmol/m^3, 3: 0.0298 kmol/m^3, 4: 0.0422 kmol/m^3, 5: 0.0563 kmol/m^3 (T=80°C; Ro=1.6; S/V=23 m^{-1})

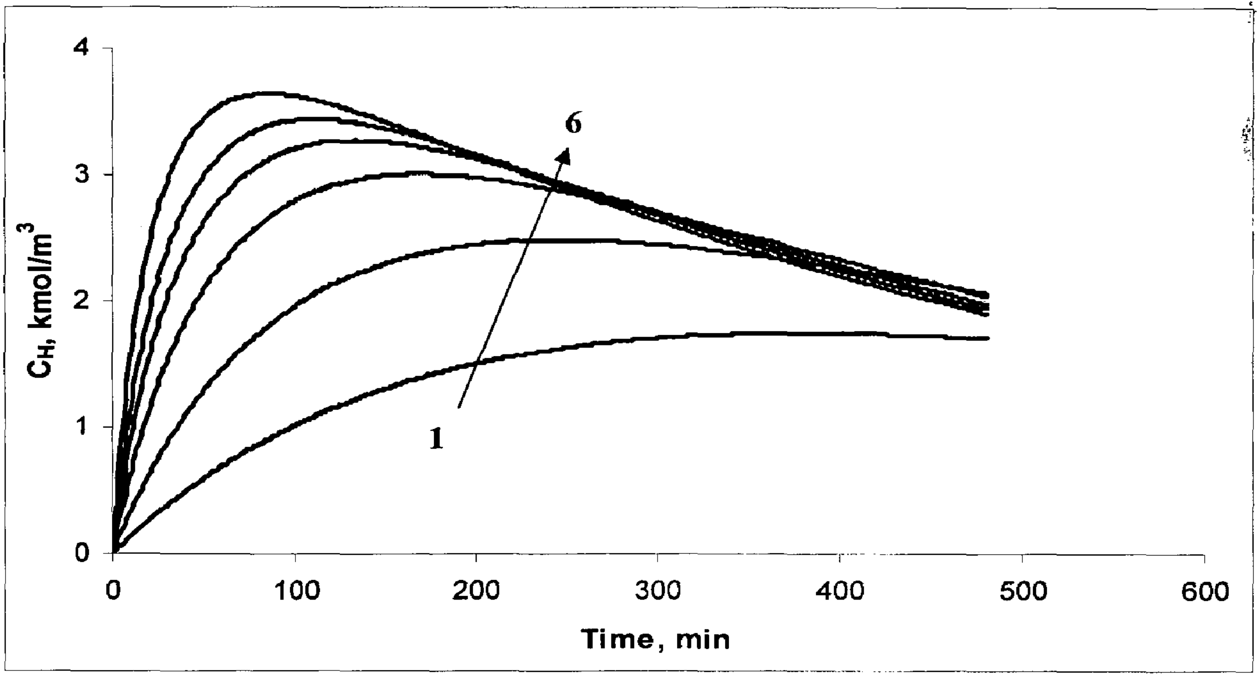

Figure 5.8 Effect of change in catalyst concentration on water concentration. C_C for curve 1: 0.0028 kmol/m^3, 2: 0.0141 kmol/m^3, 3: 0.0298 kmol/m^3, 4: 0.0422 kmol/m^3, 5: 0.0563 kmol/m^3 (T=80°C; Ro=1.6; S/V=23 m^{-1})

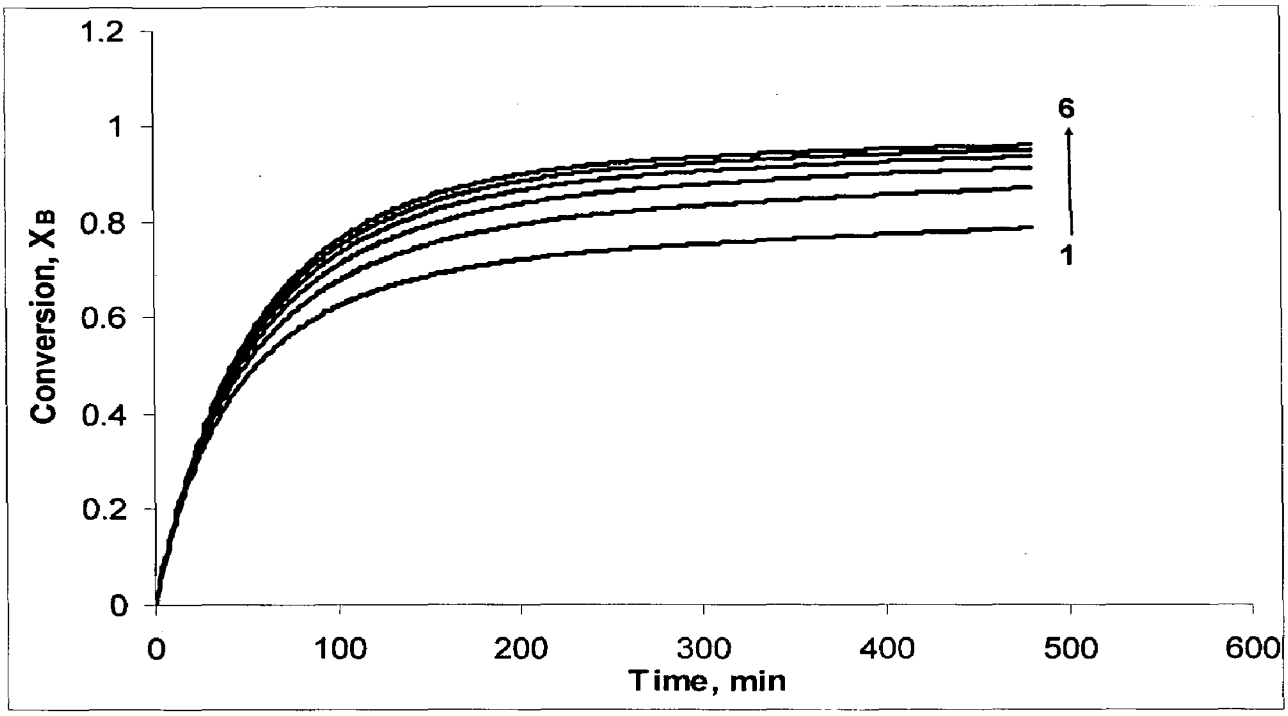

Figure 5.9 Effect of change in ratio of initial reactants on conversion of n-butanol. R_o for curve 1: 1, 2: 1.3, 3: 1.6, 4: 1.9, 5: 2.2, 6: 2.5 (T=80°C; C_C=0.0375 kmol/m3; S/V=23 m^{-1})

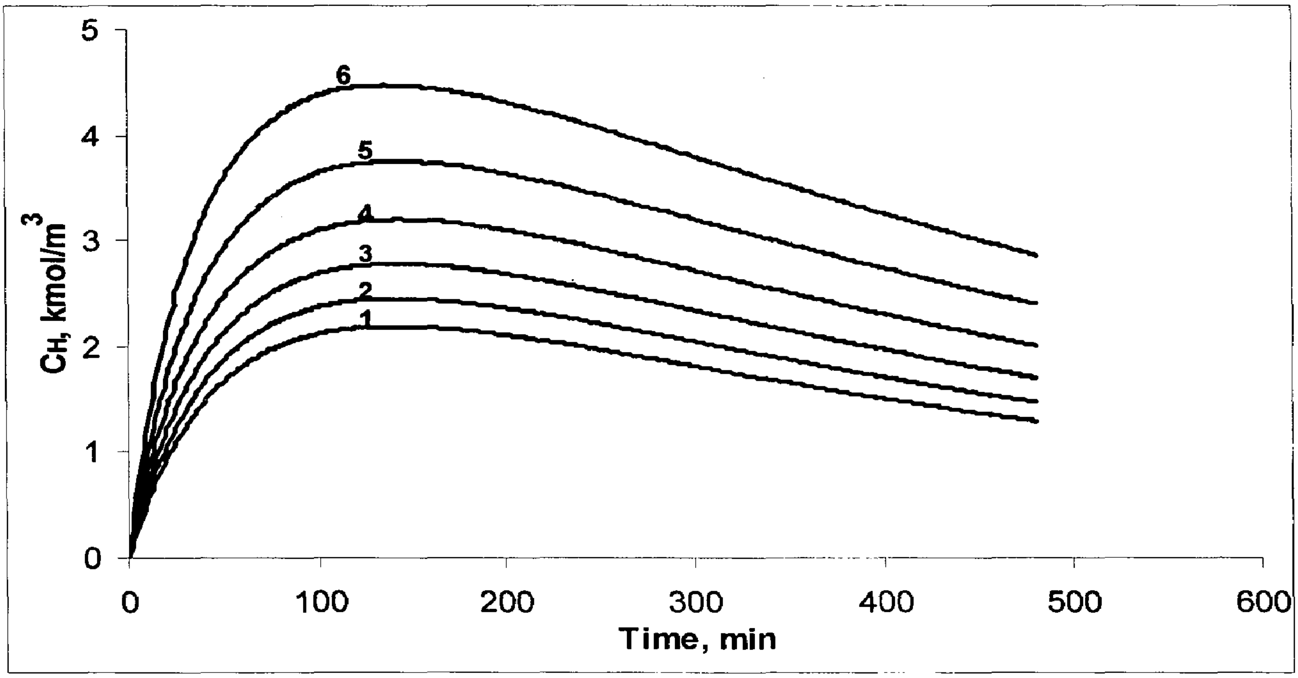

Figure 5.10 Effect of change in initial molar reactant on water concentration. R_o for curve 1: 1 , 2: 1.3, 3: 1.6, 4: 1.9, 5: 2.2, 6: 2.5 (T=80°C; C_C=0.0375 kmol/m3; S/V=23 m^{-1})

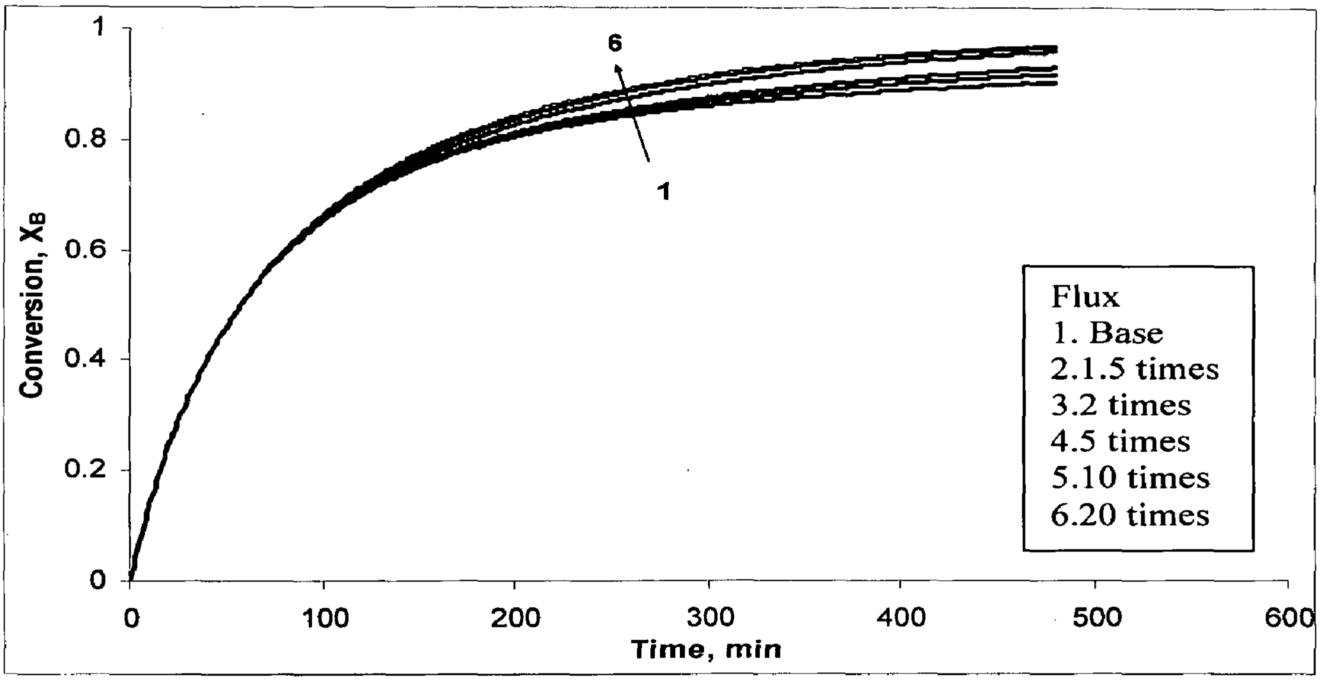

Figure 5.11 .Effect of change in flux on conversion of n-butanol with respect to time. Flux for curve 1: Base, 2: 1.5 times, 3: 2 times, 4: 5 times, 5: 10 times, 6: 20 times (T=80°C; C_C=0.0298 kmol/m^3; Ro=1.6)

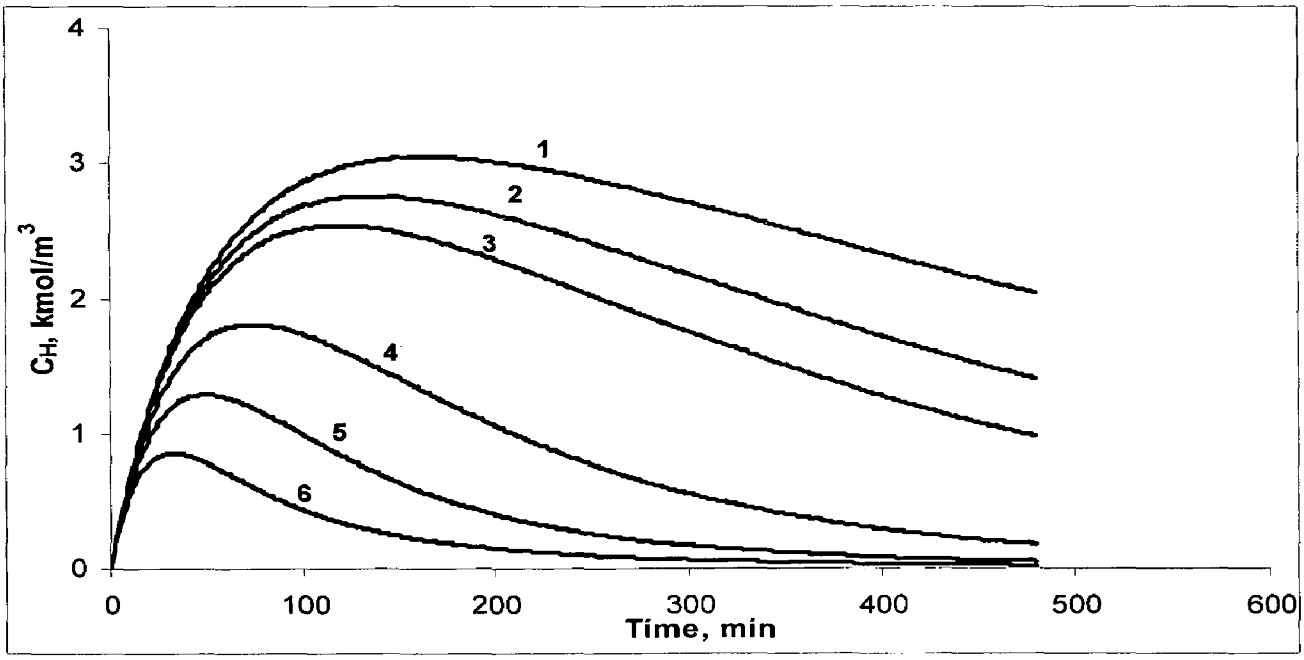

Figure 5.12.Effect of change in flux on water concentration with respect to time. Flux for curve 1: Base, 2: 1.5 times, 3: 2 times, 4: 5 times, 5: 10 times, 6: 20 times (T=80°C; C_C=0.0298 kmol/m^3; Ro=1.6)

5.3 CONCLUDING REMARKS

The model equations for pervaporation reaction were developed based on the reaction kinetics and pervaporation data for the esterification of acetic acid using n-butanol. The simulation results were compared with the experimental results and are in excellent agreement. The conversion of n-butanol was enhanced in pervaporation reactor as compared to conventional reactor. The performance of pervaporation reactor was analyzed by studying effect of various parameters such as temperature, catalyst concentration, reactant ratio, ratio of membrane area to reaction volume and flux on conversion of butanol and water removal.

ESTERIFICATION OF LACTIC ACID WITH ETHANOL

6.1 SYSTEM CONFIGURATION

In this section, results of the developed mathematical model on pervaporation reactor have been studied and discussed for esterification of lactic acid ($C_3H_6O_3$)with ethanol ((C_2H_5OH)in the presence of a solid catalyst Amberlyst XN-1010. The influence of several process variables, such as process temperature, initial mole ratio of lactic acid over ethanol, the ratio of the effective membrane area over the volume of reacting mixture catalyst content, and flux on the esterification have been discussed.

Table 6.1 Values and range of the various parameters used.

Parameter	**Notation and Unit**	**Value/Range**
Initial mole ratio of acetic acid and n-butanol	$R_0 = C_{B0}/ C_{A0}$	1 – 3
Ratio of the effective membrane area over the volume of reacting mixture	S/V (m^2/m^3)	0 – 30
Equilibrium constant for temperature range * 50-95 °C	$K= k_1/k_2$	2-4
Observed kinetic constant for temperature range 50-95 °C	$k_{obs} = k_1C_C$ (m^3/kmol min)	0.0003-0.004
Reaction time	t (min)	480
Catalyst concentration	C_C (g/l)	1-50
Temperature	T (°C)	50-95

* The reaction rate constants for the esterification reaction are taken from the available literature in Benedict et al (2003):

$$k_1 = k_0 \exp\left(-\frac{E}{RT}\right) \text{ and } k_2 = k_0 \exp\left(-\frac{E}{RT}\right)$$

Our proposed model predicts the conversion of the reactant along the rection time of the reactor, and the effects of operating parameters on the performance of pervaporation reactor. The numerically computed results are shown graphically. The calculated results for the conversion of lactic acid to water concentration were consistence with the experimental data. The values and range of the various parameters used for simulations are given in **Table 6.1**

6.2.1 RESULTS AND DISCUSSION

6.2.1 Model Validation

Before going for any simulation study, model validation is must. In view of this the simulation results were compared with available experimental data of Benedict et al (2003) for the conditions of temperature, T = 95^{O}C, catalyst concentration, C_C = 31.4 g/l the ratio of the effective membrane area over the volume of reacting mixture S/V = 20 m^{-1}; initial mole ratio of ethanol and lactic acid is 1.2 and flux as per equation (6) in kmol/m^2min. The model results of conversion of lactic acid and water concentration in reaction mixture were compared with the experimental results and are shown in **Figure 6.1** and **Figure 6.2** respectively.

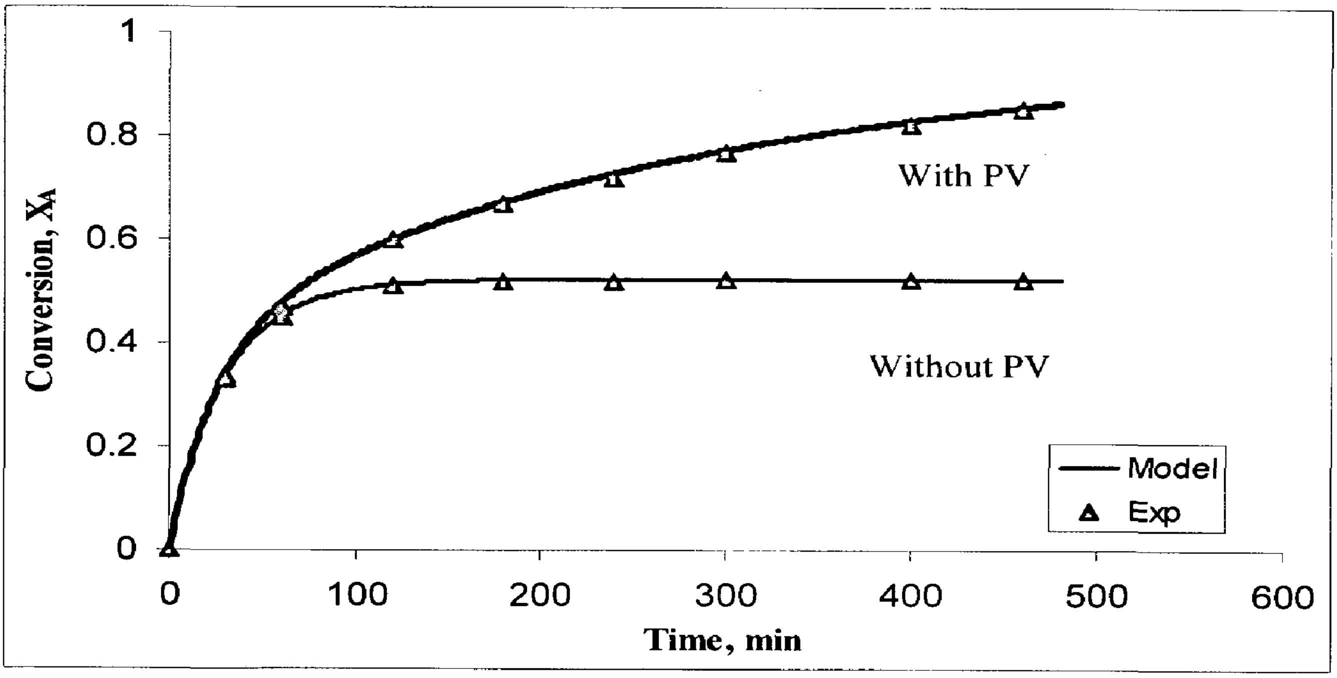

Figure 6.1 Calculated curves compared to experimental points for lectic acid conversion for esterification both with and without pervaporation. (T=95°C; Ro=1.2; C_C=31.4 g/l; S/V=20 m^{-1})

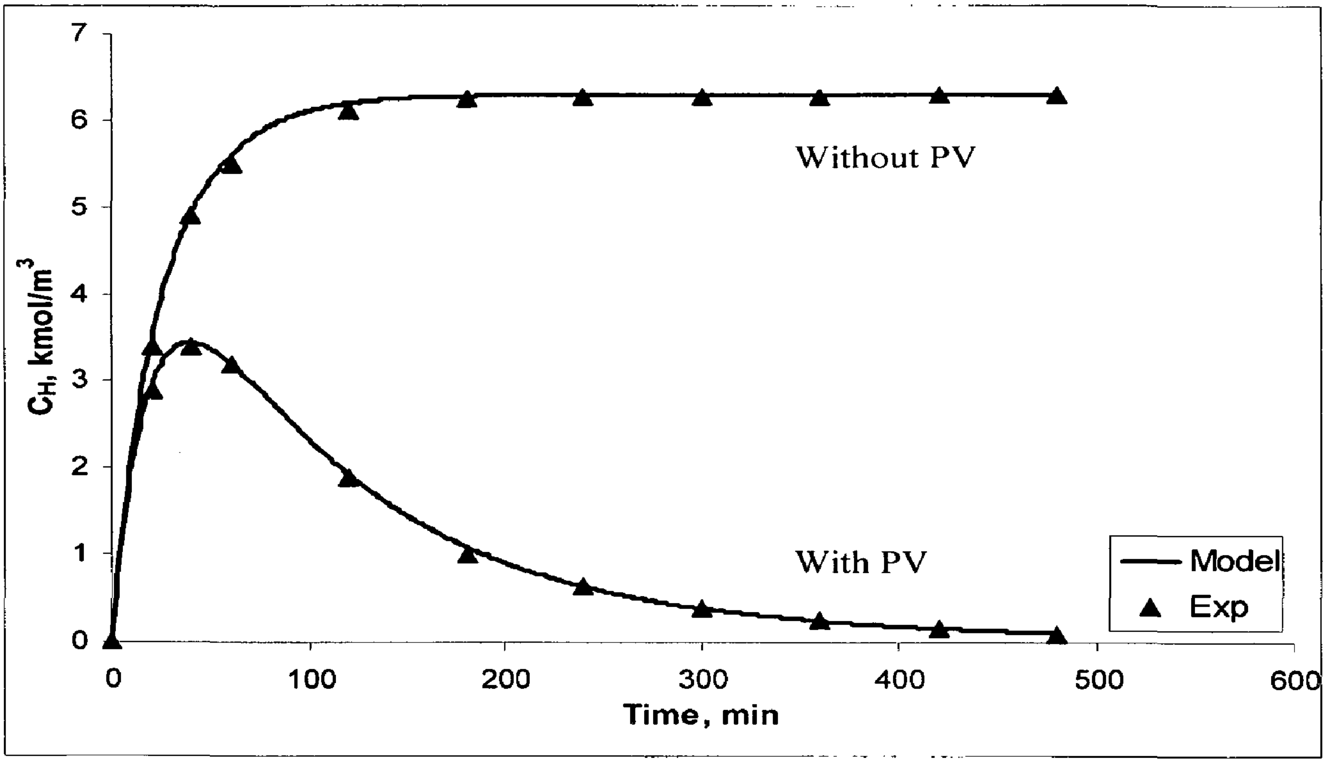

Figure 6.2 Calculated curves compared to experimental points for water concentration for esterification both with and without pervaporation. (T=95°C; Ro=1.2; C_C=31.4 g/l; S/V=20 m^{-1})

It shows that the proposed model results were in excellent agreement with the available experimental results. Slightly over-predictions were observed for conversion of lactic acid with respect to time due to the negligence of ethanol permeating through the membrane by the model equations. It was indicated that PV enhanced the conversion for the PV-aided esterification than for the reaction without PV. The water content for the reaction without PV was higher than for the PV-aided reaction due to water removal by PV.

6.2.2 Effect of operating temperature

The simulation results for effect of reaction temperature on conversion of lactic acid and water concentration are shown in **Figure 6.3** and **Figure 6.4**. The temperature was varied from 50 to 95 ^{0}C for fixed value of catalyst concentration (C_C=31 g/l), reactants ratio (Ro=1.2) and membrane area to reaction volume (S/V=20 m^{-1}). It can be observed form the **Figure 6.3** that the conversion increased with increase in temperature but the change in increased conversion is not significant at higher tempratire. For 80^{0}C and 95^{0}C temperatures, the conversion is almost same. So we can say that the optimum conversion temperature is 95^{O}C. An increase in temperature induced not only an acceleration of esterification but also acceleration in pervaporation.

Water production rate is higher in higher temperature than in a lower temperature (**Figure 6.4**) so the permeation parameter for water is also varied with the increase of temperature as a result water permeation flux was increased with increase in temperature. The reaction rate constants for the esterification are a function of process temperature, and were increased with the increase of the temperature. The accelerating of the reaction rate constant with the increase of the temperature for the forward reaction was faster than the backward process. So water production rate was higher in a higher temperature than in a lower temperature. Meanwhile, the permeation parameter for water is also varied with the temperature and was increased with the increase of the temperature. As a result, water permeation flux was increased with the increase of the process temperature.

6.2.3 Effect of ratio of effective membrane area to the reaction volume (S/V)

The equilibrium shift of the esterification reaction is depending on the amount of water in the reaction mixture, as we increase the ratio (area of membrane) the rate of water removal will be more and more conversion. Also the cost of membrane depends on the required membrane area. Hence the membrane area and conversion should optimize to get the optimum production cost, as the membrane area is small, time requires to achieve a particular conversion will be more, hence more operating cost. In case of high membrane area, operating cost will be low but capital cost will be more. In view of this, effect of ratio of effective membrane area over the volume of reacting mixture on the conversion of acetic acid was studied. The effect of the ratio of membrane area to reaction volume on the conversion of lactic acid and water content in reaction mixture were presented in **Figure 6.5** and **Figure 6.6.** The S/V was varied from 0 to 30 m^{-1} for 95^{O}C temperature, 31 g/l catalyst concentration and reactant ratio of Ro=1.3. It was observed that the conversion achieved was a function of membrane surface area, conversion increases with increasing surface area. Time required to achieve a given duty of conversion was also varied with surface area of the membrane. Membrane area exerted no influence on reactive kinetics but caused the variation of the water removal rate. Water extraction rate was high for high surface area. As the water removal rate is high, the equilibrium will shift more towards right and higher conversion will be achieved.

6.2.4 Influence of catalyst concentration on reaction (C_C)

Catalyst concentration may be an alternative way to accelerate ester production. In view of this, the effect of catalyst concentration on the conversion of lactic acid was studied. The simulation results for conversion of lactic acid and water content variation in reaction mixture during pervaporation process over various catalyst concentrations were presented in **Figure 6.7** and **Figure 6.8**. The catalyst concentration was varied from 1 g/l to 50 g/l for fixed value of temperature (T = 95°C), reactants ratio (Ro=1.3) and membrane area to reaction volume (S/V=23 m^{-1}). For catalyst concentration above 20 g/l, the conversion of butanol is almost same. Hence the optimum catalyst concentration is 20 g/l

The conversion and water production rate is higher for higher C_C The effect of it is higher for a period at the beginning during the reaction than lower later. The variation of both forward and backward reaction rate occurred during the change of C_C The water production rate was higher (**Figure 6.8**) for a higher C_C since the forward reaction rate constant was higher than the backward one. Thus, the water contents in the reactor had higher maximum amplitude for a higher C_C during the reaction.

6.2.5 Influence of initial molar reactant ratio (acetic acid/n-butanol, Ro)

Figure 6.9 and **Figure 6.10** depict the effect of initial moalr reactant ratio on the butanol conversion and water in reaction volume. The reactant ratio was varied from 1 to 3 for fixed values of the other parameters. The higher conversion was observed for higher ratios. Water production rate was decreased with the increase of R_O and caused the maximum amplitude in water content lower at a higher R_O. The water concentration in the reactor is lower for a higher R_O during the process. It is well known that a sufficient ratio of the alcohol to acid leads to a quasi-complete conversion of alcohol even without pervaporation. So this method would be carried out at the cost of separation difficulties. Decreasing the initial ratio of the alcohol to acid when operating with pervaporation may be the optimum performance conditions.

6.2.6 Effect of Flux

In pervaporation process, to study the applicability for esterification process, the important parameter is the flux across the membrane. Flux depends on the type membrane used, the operating temperature, surface area of membrane, the reaction mixture and its composition. Membrane having higher flux requires less pervaporation membrane area and hence less production cost. The effect of flux on the performance of pervaporation reactor was studied by changing the flux to 1.5 times to 20 times of base value of flux. **Figure 6.11** and **Figure 6.12** show the effect of flux on the conversion and concentration of water in reaction mixture for the fixed volume. It was clearly observed that there were slight increased in the conversion as we increased the flux; this was because of the reaction limitations.

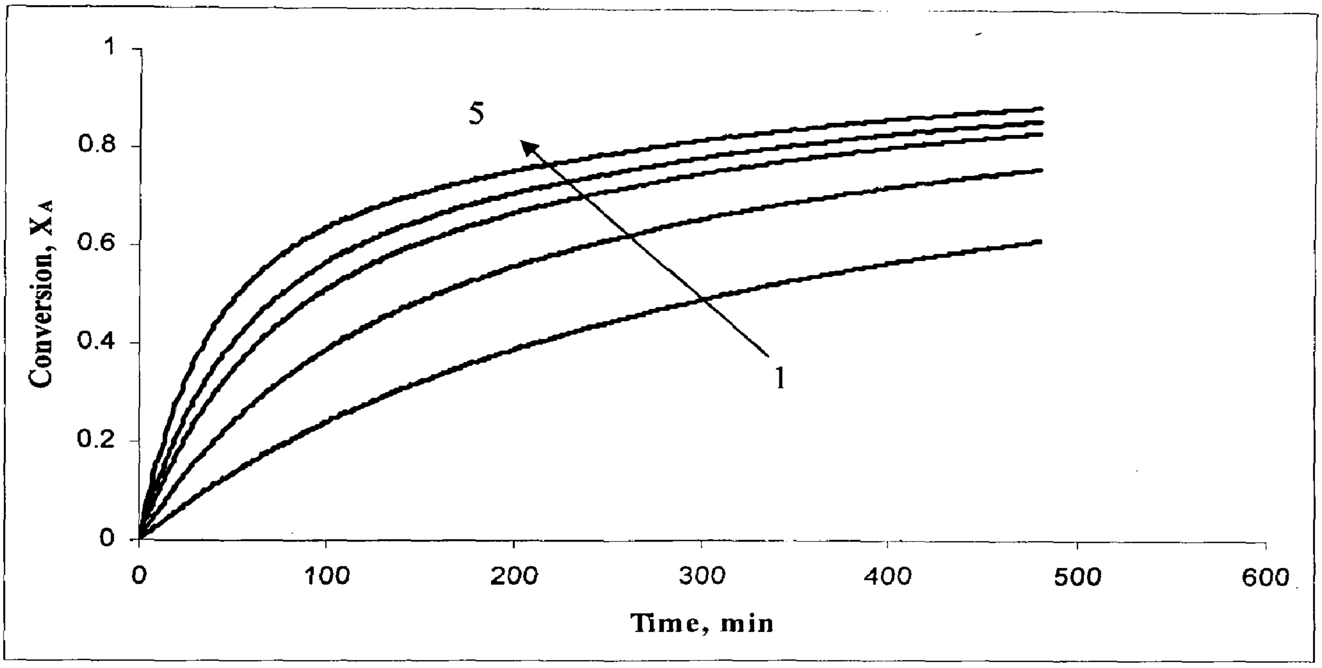

Figure 6.3 Effect of change in temperature on conversion of lactic acid.
T for curve 1: 50 °C, 2: 60 °C, 3: 75 °C, 4: 85 °C, 5: 95 °C
(Ro=1.2; C_C=31 g/l; S/V=20 m^{-1})

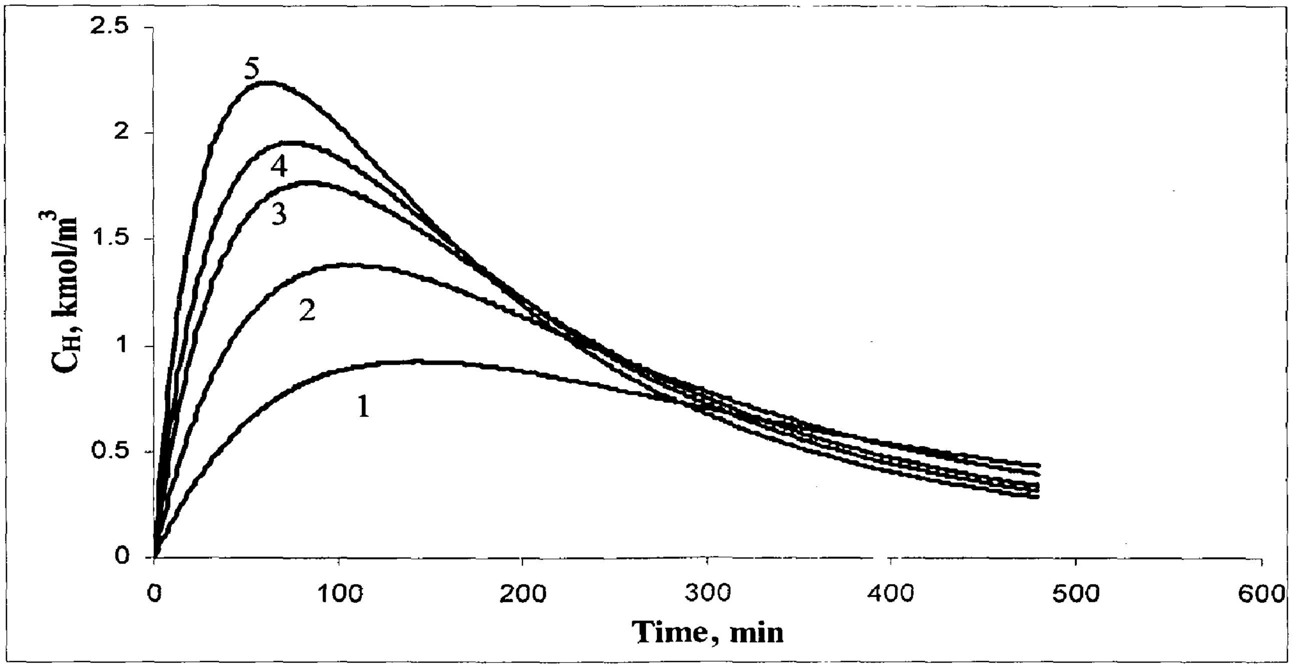

Figure 6.4 Effect of change in temperature on water concentration.
T for curve 1: 50 °C, 2: 60 °C, 3: 75 °C, 4: 85 °C, 5: 95 °C
(Ro=1.2; C_C=31 g/l; S/V=20 m^{-1})

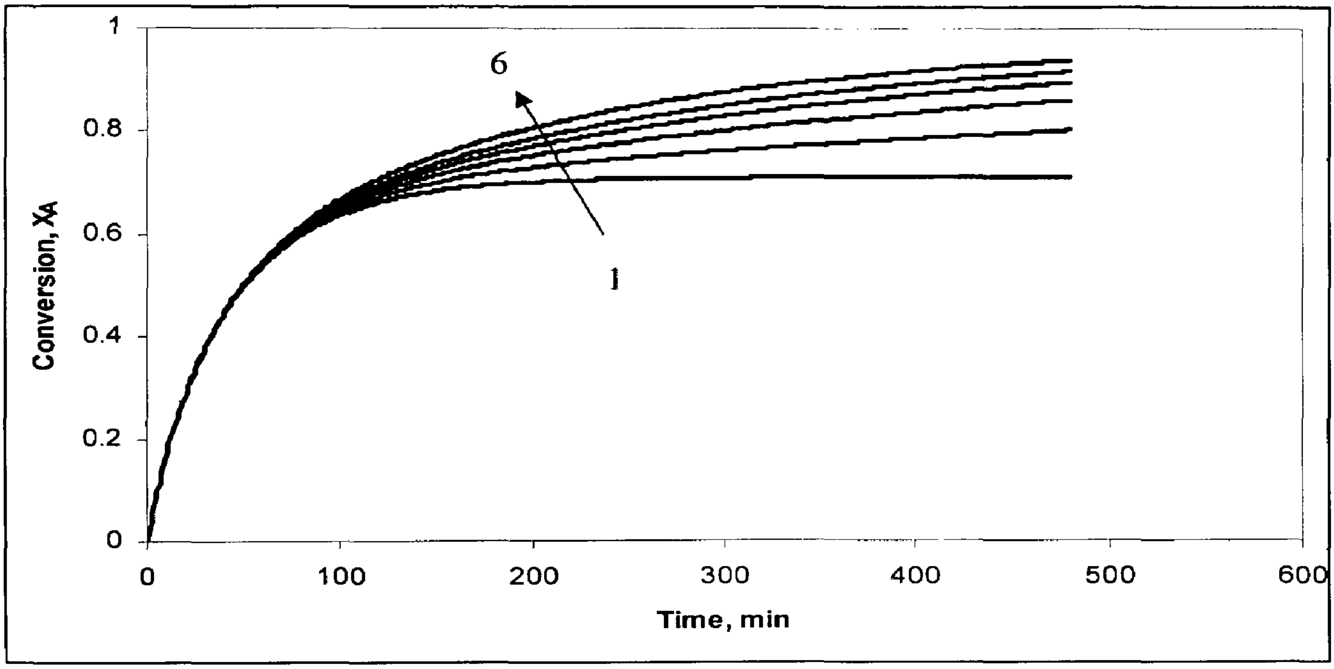

**Figure 6.5 Effect of change in S/V on conversion of lactic acid.
S/V ratio for curve 1: 0 m^{-1}, 2: 5 m^{-1}, 3: 10 m^{-1}, 4: 15 m^{-1}, 5: 20 m^{-1}, 6: 30 m^{-1}
(T=95°C; Ro=1.3; C_C=31 g/l)**

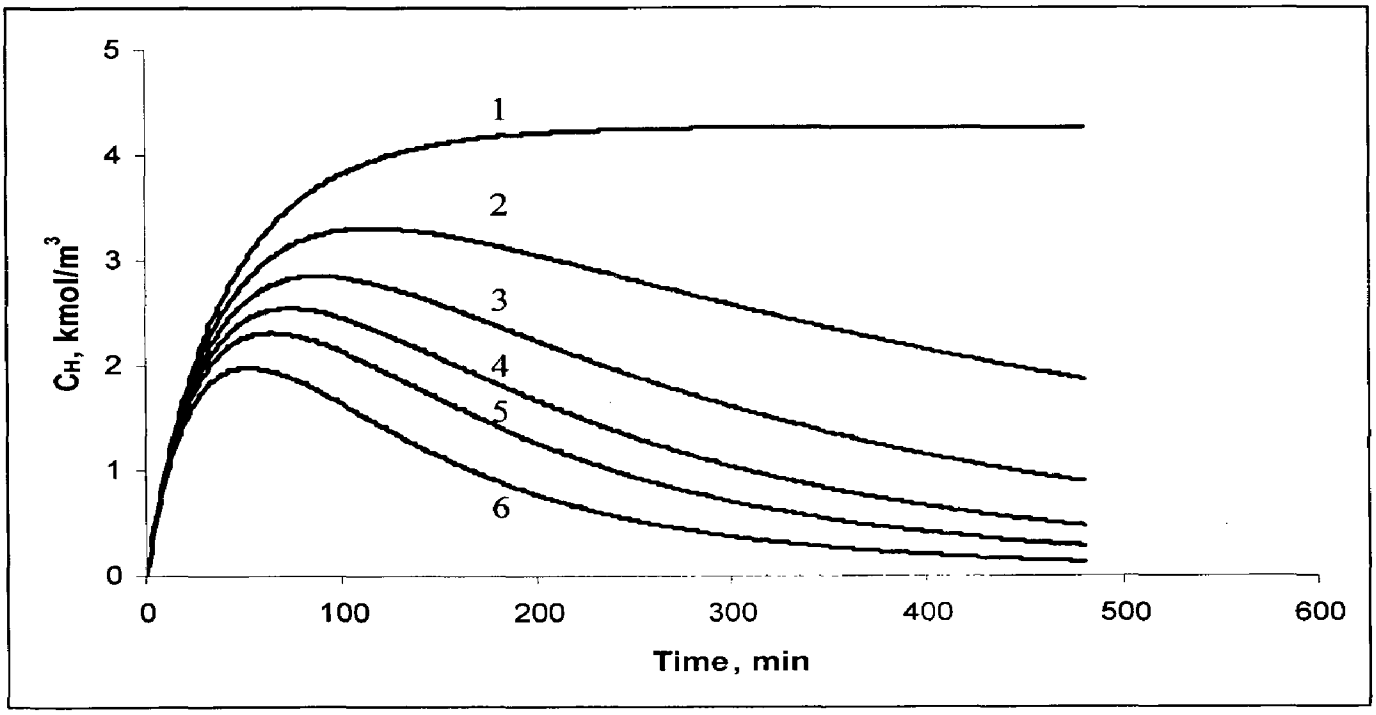

**Figure 6.6 Effect of change in S/V on concentration of water.
S/V ratio for curve 1: 0 m^{-1}, 2: 5 m^{-1}, 3: 10 m^{-1}, 4: 15 m^{-1}, 5: 20 m^{-1}, 6: 30 m^{-1}
(T=95°C; Ro=1.3; C_C=31 g/l)**

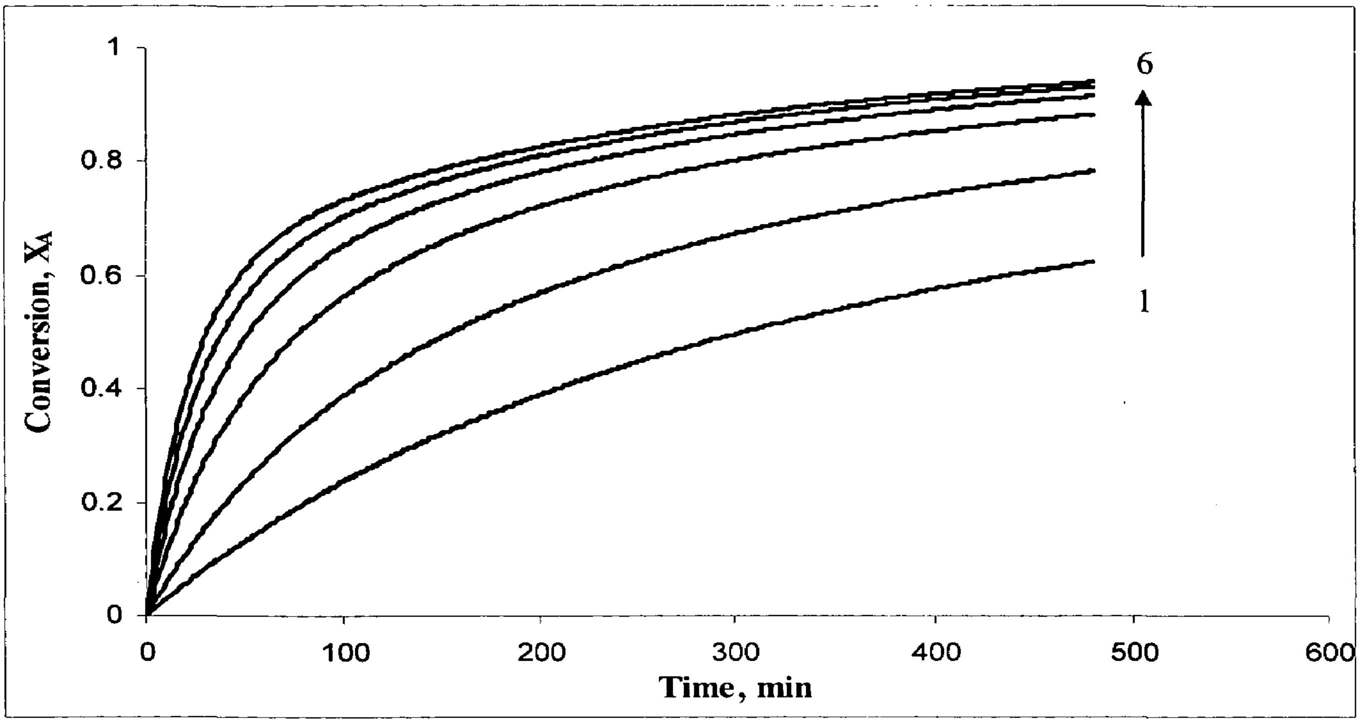

Figure 6.7 Effect of change in catalyst concentration on conversion of lactic acid. C_C for curve 1: 1 g/l, 2: 10 g/l, 3: 20 g/l, 4: 30 g/l, 5: 40 g/l, 6: 50 g/l (T=95°C; Ro=1.3; S/V=20 m^{-1})

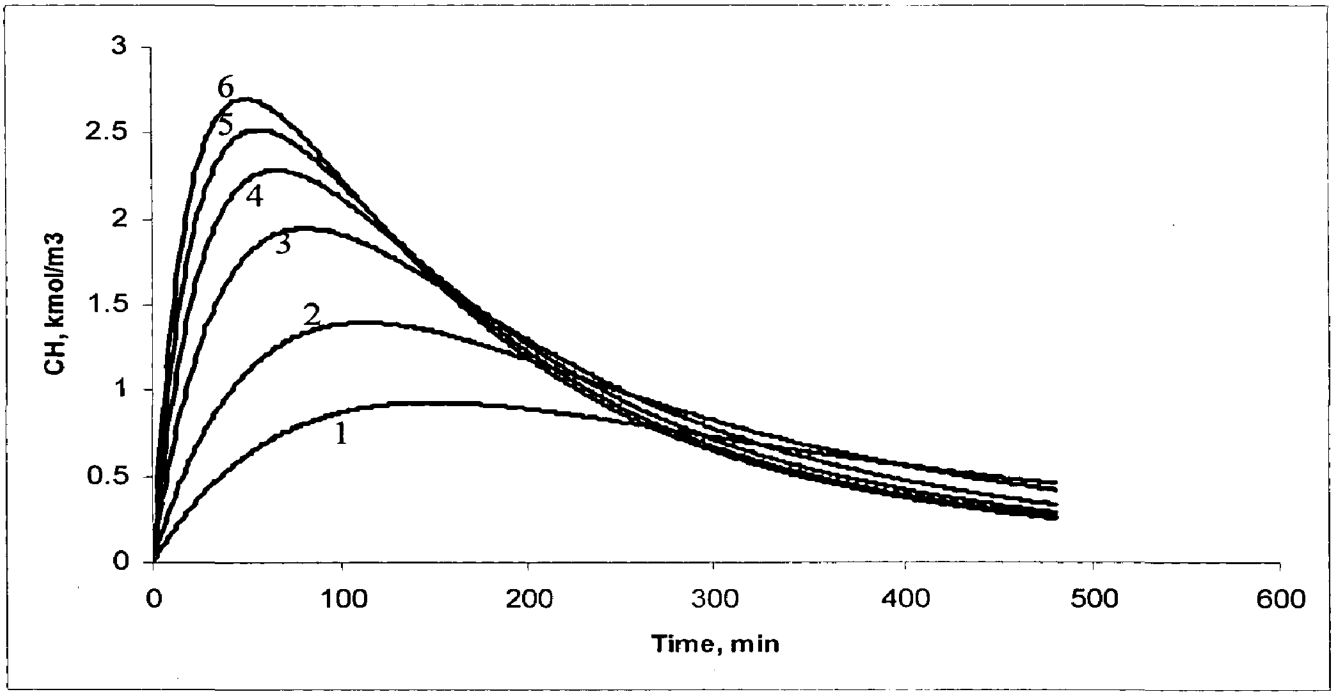

Figure 6.8 Effect of change in catalyst concentration on water concentration C_C for curve 1: 1 g/l, 2: 10 g/l, 3: 20 g/l, 4: 30 g/l, 5: 40 g/l, 6: 50 g/l (T=95°C; Ro=1.3; S/V=20 m^{-1})

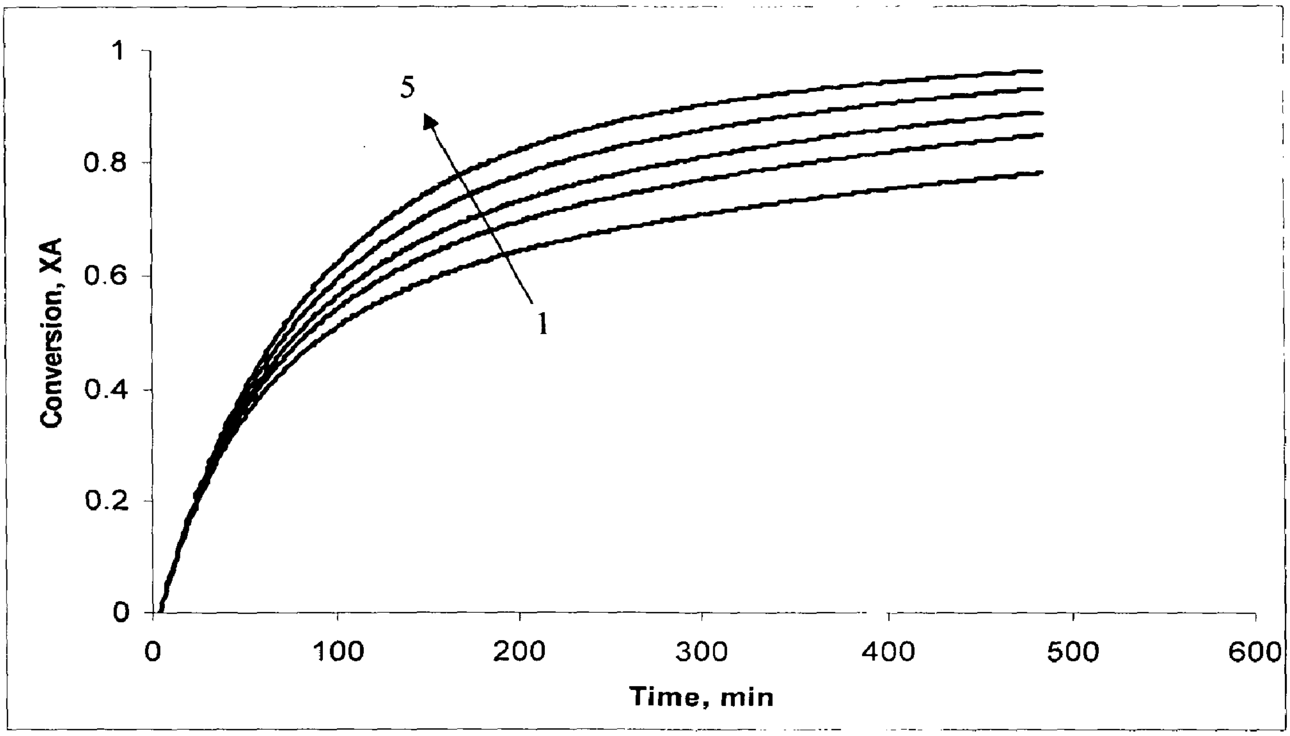

Figure 6.9 Effect of change in ratio of initial reactants on conversion of lactic acid R_o for curve 1: 1 , 2: 1.25, 3: 1.5, 4: 2, 5: 3 (T=95°C; C_C=20 g/l; S/V=15 m^{-1})

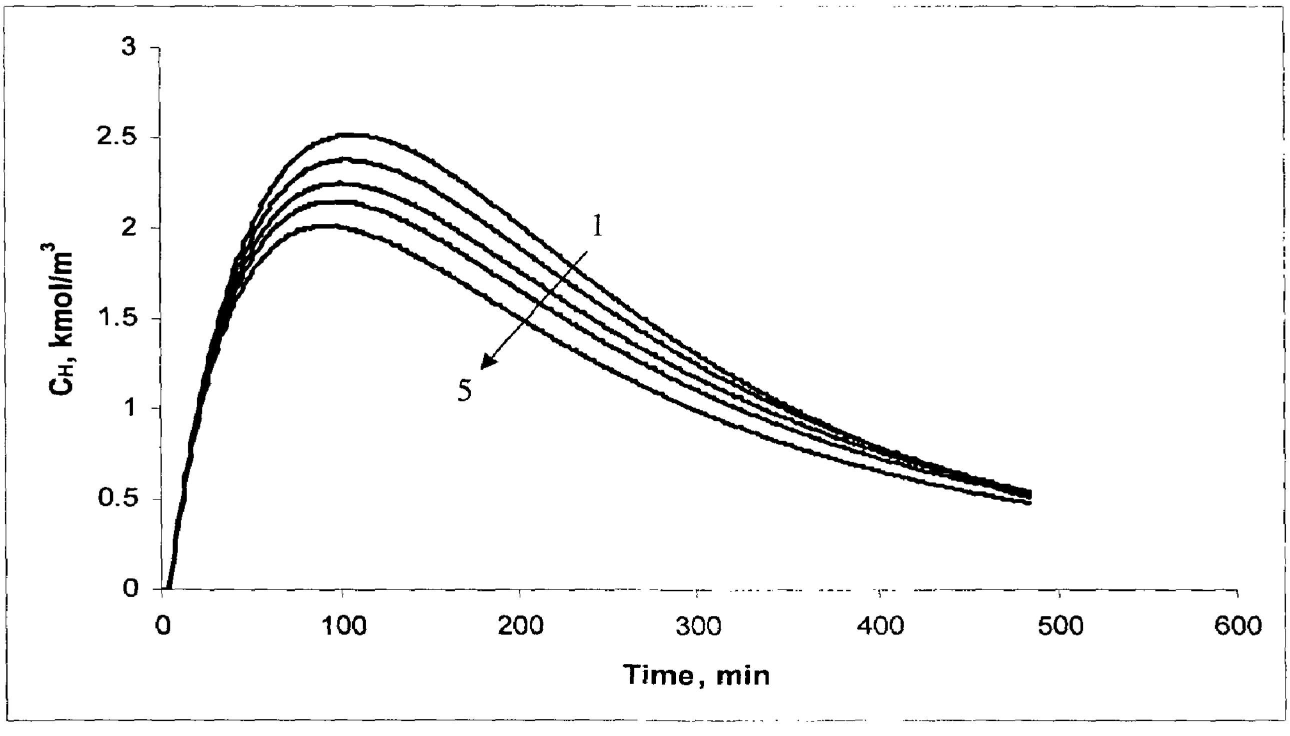

Figure 6.10 Effect of change in ratio of initial reactants on water concentration R_o for curve 1: 1 , 2: 1.25, 3: 1.5, 4: 2, 5: 3 (T=95°C; C_C=20 g/l; S/V=15 m^{-1})

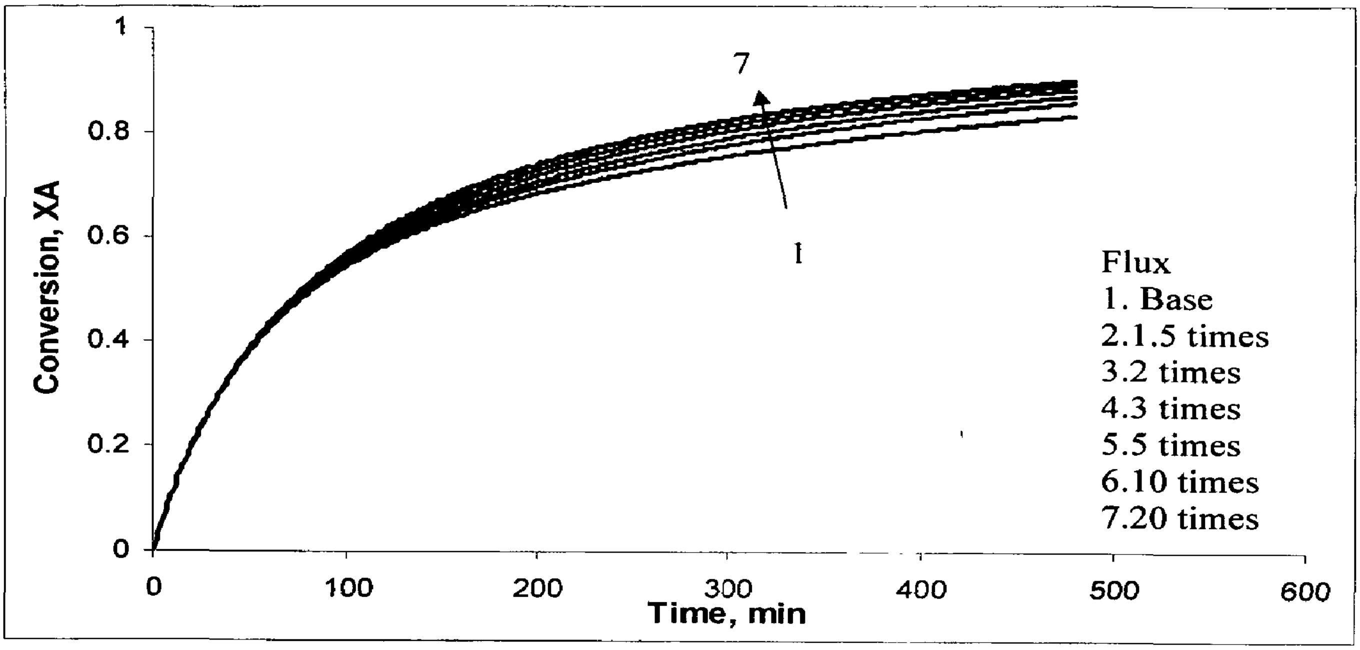

Figure 6.11 .Effect of change in flux on conversion of lactic acid with respect to time. Flux for curve 1: Base, 2: 1.5 times, 3: 2 times, 4: 3 times, 5: 5 times, 6: 10 times, 6: 20 times (T=95°C; Ro=1.2; C_C=20 g/l; S/V=15 m^{-1})

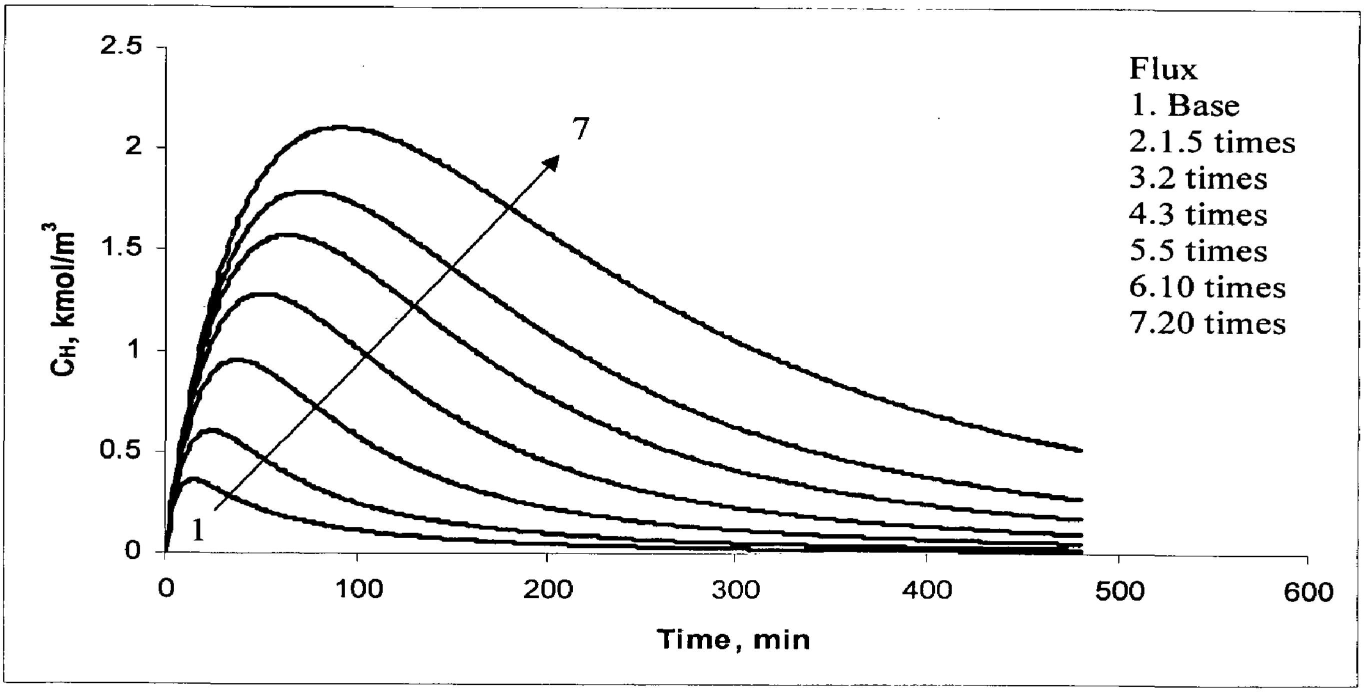

Figure 6.12 .Effect of change in flux on concentration of water with respect to time. Flux for curve 1: Base, 2: 1.5 times, 3: 2 times, 4: 3 times, 5: 5 times, 6: 10 times, 6: 20 times (T=95°C; Ro=1.2; C_C=20 g/l; S/V=15 m^{-1})

6.3 CONCLUDING REMARKS

The model equations for pervaporation reaction were developed based on the reaction kinetics and pervaporation data for the esterification lactic acid using n-ethanol. The simulation results were compared with the experimental results and are in excellent agreement. The conversion of lactic acid was enhanced in pervaporation reactor as compared to conventional reactor. The performance of pervaporation reactor was analyzed by studying effect of various parameters such as temperature, catalyst concentration, reactant ratio, ratio of membrane area to reaction volume and flux on conversion of lactic acid and water removal.

ESTERIFICATION OF ACETIC ACID WITH ETHANOL

7.1 SYSTEM CONFIGURATION

In this chapter, results of the developed mathematical model on pervaporation reactor have been studied and discussed for esterification of acetic acid with ethanol in the presence of cation exchange resin catalyst (Amberlyst 15, Organo). The influence of several process variables, such as initial mole ratio of acetic acid over ethanol, the ratio of the effective membrane area over the volume of reacting mixture catalyst content, and flux on the esterification have been discussed.

Table 7.1 Values and range of the various parameters used.

Parameter	**Notation and Unit**	**Value/Range**
Initial mole ratio of acetic acid and n-butanol	$R_O = C_{BO}/ C_{AO}$	1 – 2
Ratio of the effective membrane area over the volume of reacting mixture	S/V (m^2/m^3)	0 – 10
Equilibrium constant for temperature range * 50-70 ^OC	$K= k_1/k_2$	2-3
Observed kinetic constant for temperature range 50-95 ^OC	$k_{obs} = k_1C_C$ (m^3/kmol min)	0.0003-0.004
Reaction time	t (min)	480
Catalyst concentration	C_C (g/l)	1-150
Temperature	T (°C)	70

* The reaction rate constants for the esterification reaction are taken from the available literature in Tanaka et al (2001):

$$k_1 = k_0 \exp\left(-\frac{E}{RT}\right) \text{ and } k_2 = k_0 \exp\left(-\frac{E}{RT}\right)$$

The proposed model predicts the conversion of the reactant along the reaction time of the reactor, and the effects of operating parameters on the performance of pervaporation reactor. The numerically computed results are shown graphically. The calculated results for the conversion of acetic acid to water concentration were consistence with the experimental data. The values and range of the various parameters used for simulations are given in **Table 7.1**

7.2 RESULTS AND DISCUSSION

7.2.1 Model Validation

Before going for any simulation study, model validation is must. In view of this the simulation results were compared with available experimental data of Tanaka et al (2001) for the conditions of temperature, T = 70°C, catalyst concentration, C_C = 100 g/l the ratio of the effective membrane area over the volume of reacting mixture S/V = 3.4 m^{-1}; initial mole ratios of ethanol to acetic acid is 1.5 and flux as per equation (6) in $kmol/m^2min$. The model results of conversion of acetic acid and water concentration in reaction mixture were compared with the experimental results and are shown in **Figure 7.1** and **Figure 7.2** respectively.

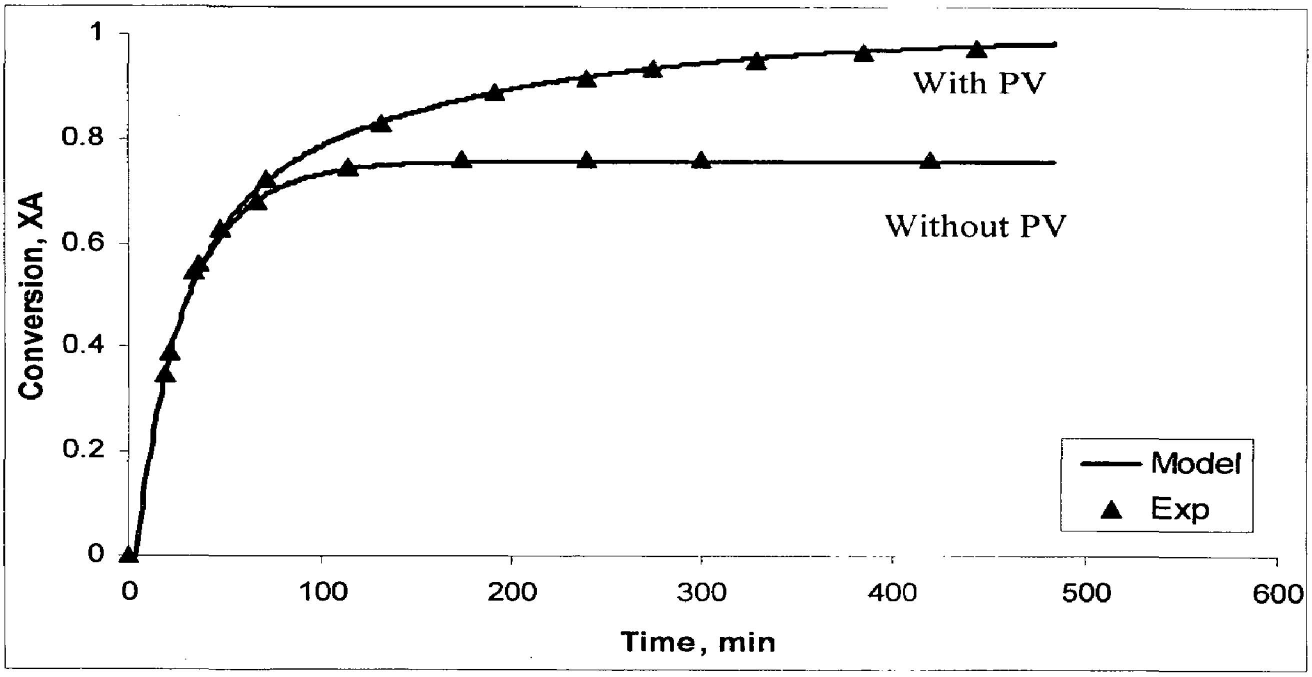

Figure 7.1 Calculated curves compared to experimental points for acetic acid conversion for esterification both with and without pervaporation. (T=70°C; Ro=1.5; C_C=100 g/l; S/V=3.4 m^{-1})

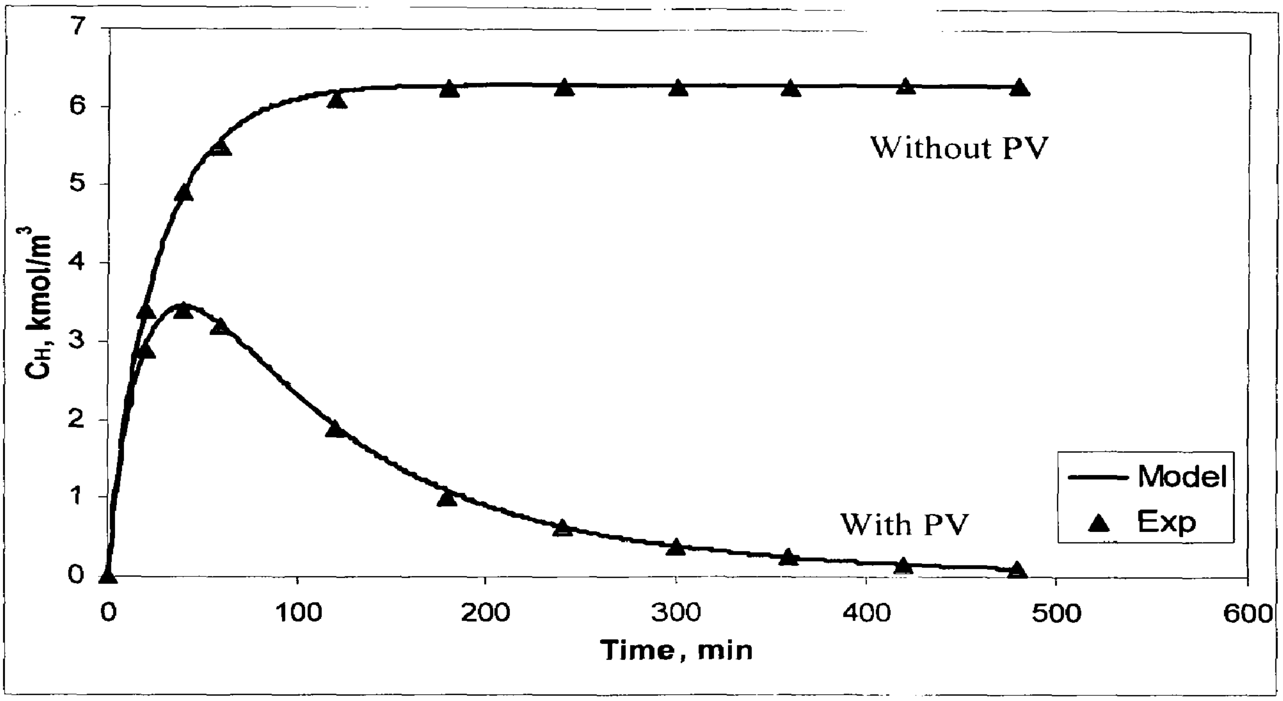

Figure 7.2 Calculated curves compared to experimental points for water concentration in the reacting mixture for esterification both with and without pervaporation. (T=70°C; Ro=1.5; C_C=100 g/l; S/V=3.4 m^{-1})

It shows that the proposed model results were in excellent agreement with the available experimental results. Slightly over-predictions were observed for conversion of acetic acid with respect to time due to the negligence of ethanol permeating through the membrane by the model equations. It was indicated that PV enhanced the conversion for the PV-aided esterification than for the reaction without PV. The water content for the reaction without PV was higher than for the PV-aided reaction due to water removal by PV.

7.2.2 Effect of ratio of effective membrane area to the reaction volume (S/V)

The equilibrium shift of the esterification reaction is depending on the amount of water in the reaction mixture, as we increase the ratio (area of membrane) the rate of water removal will be more and more conversion. Also the cost of membrane depends on the required membrane area. Hence the membrane area and conversion should optimize to get the optimum production cost, as the membrane area is small, time requires to achieve a particular conversion will be more, hence more operating cost. In case of high membrane area, operating cost will be low but capital cost will be more. In view of this, effect of ratio of effective membrane area over the volume of reacting mixture on the conversion of acetic acid was studied. The effect of the ratio of membrane area to reaction volume on the conversion of acetic acid and water content in reaction mixture were presented in **Figure 7.3** and **Figure 7.4.** The S/V was varied from 0 to 10 m^{-1} for 70 °C temperature, 40 g/l catalyst concentration and reactant ratio of Ro=1.25. It was observed that the conversion achieved was a function of membrane surface area, conversion increases with increasing surface area. Time required to achieve a given duty of conversion was also varied with surface area of the membrane. Membrane area exerted no influence on reactive kinetics but caused the variation of the water removal rate. Water extraction rate was high for high surface area. As the water removal rate is high, the equilibrium will shift more towards right and higher conversion will be achieved.

7.2.3 Influence of catalyst concentration on reaction (C_C)

Catalyst concentration may be an alternative way to accelerate ester production. In view of this, the effect of catalyst concentration on the conversion of acetic acid was studied. The simulation results for conversion of acetic acid and water content variation in reaction mixture during pervaporation process over various catalyst concentrations were presented in **Figure 7.5** and **Figure 7.6** The catalyst concentration was varied from 1 g/l to 150 g/l for fixed value of temperature (T = 70°C), reactants ratio (Ro=1.25) and membrane area to reaction volume (S/V=3.4 m^{-1}).

The conversion and water production rate is higher for higher C_C The effect of it is higher for a period at the beginning during the reaction than lower later. The variation of both forward and backward reaction rate occurred during the change of C_C The water production rate was higher (**Figure 7.6**) for a higher C_C since the forward reaction rate constant was higher than the backward one. Thus, the water contents in the reactor had higher maximum amplitude for a higher C_C during the reaction.

7.2.4 Influence of initial molar reactant ratio (Ro)

Figure 7.7 and **Figure 7.8** depict the effect of initial moalr reactant ratio on the acetic acid conversion and water in reaction volume. The reactant ratio was varied from 1 to 2 for fixed values of the other parameters. The higher conversion was observed for higher ratios. Water production rate was decreased with the increase of R_0 and caused the maximum amplitude in water content lower at a higher R_0. The water concentration in the reactor is lower for a higher R_0 during the process. It is well known that a sufficient ratio of the alcohol to acid leads to a quasi-complete conversion of alcohol even without pervaporation. So this method would be carried out at the cost of separation difficulties. Decreasing the initial ratio of the alcohol to acid when operating with pervaporation may be the optimum performance conditions.

7.2.5 Effect of Flux

In pervaporation process, to study the applicability for esterification process, the important parameter is the flux across the membrane. Flux depends on the type membrane used, the operating temperature, surface area of membrane, the reaction mixture and its composition. Membrane having higher flux requires less pervaporation membrane area and hence less production cost. The effect of flux on the performance of pervaporation reactor was studied by changing the flux to 1.5 times to 20 times of base value of flux. **Figure 7.9** and **Figure 7.10** show the effect of flux on the conversion and concentration of water in reaction mixture for the fixed volume. It was clearly observed that there were slight increased in the conversion as we increased the flux; this was because of the reaction limitations.

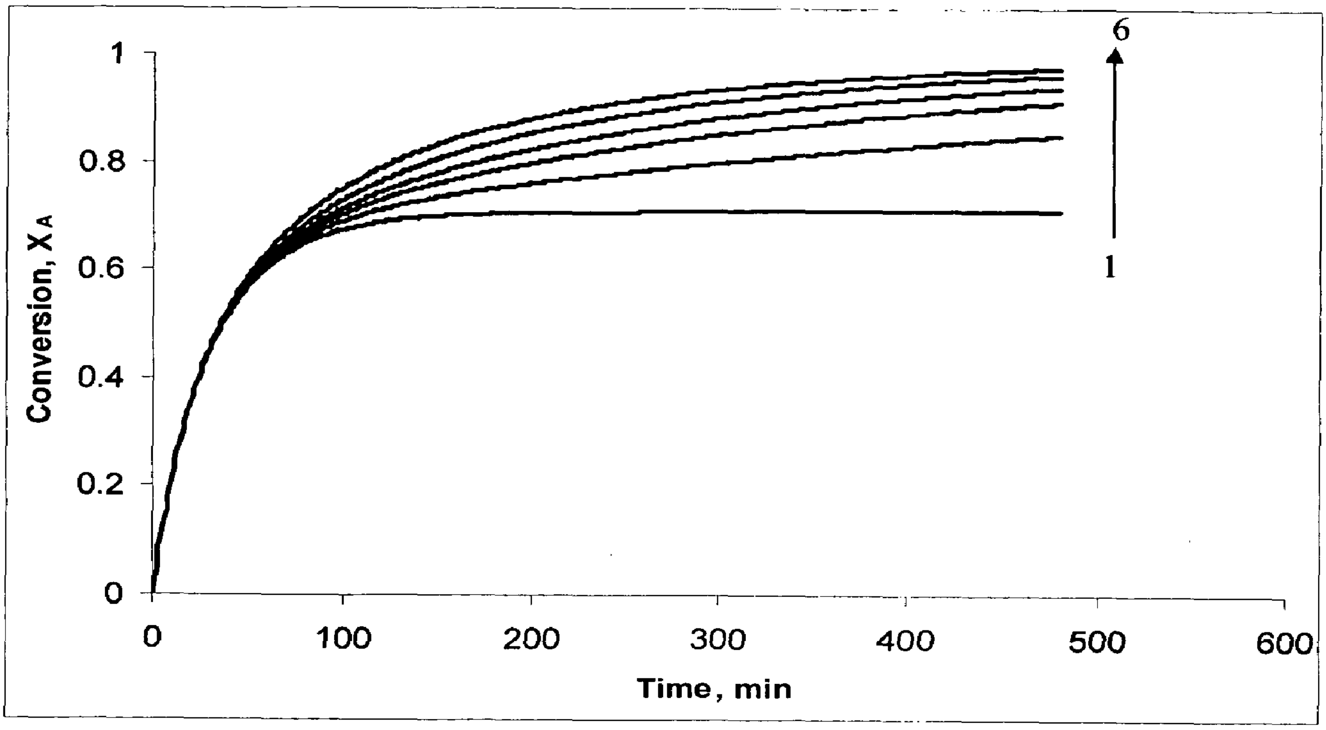

Figure 7.3 Effect of change in S/V on conversion of acetic acid
S/V ratio for curve 1: 0 m^{-1}, 2: 1 m^{-1}, 3: 2 m^{-1}, 4: 3 m^{-1}, 5: 5 m^{-1}, 6: 10 m^{-1}
(T=70°C; Ro=1.25; C_C=40 g/l)

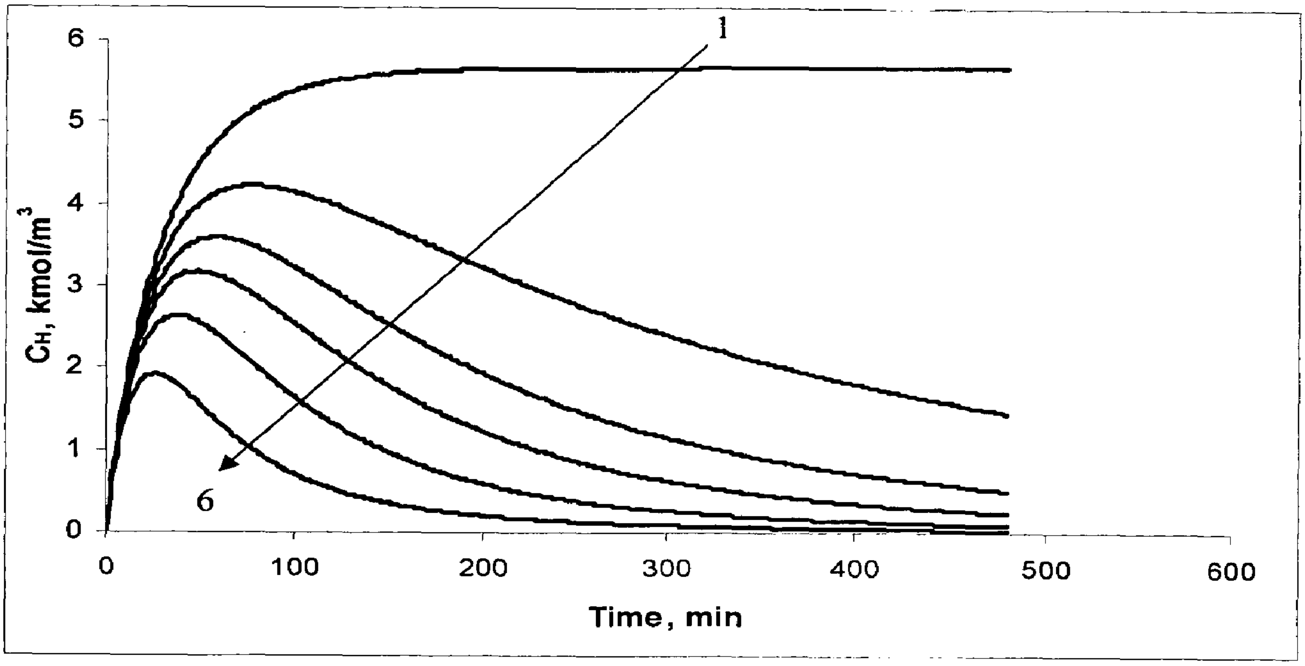

Figure 7.4 Effect of change in S/V on concentration of water
S/V ratio for curve 1: 0 m^{-1}, 2: 1 m^{-1}, 3: 2 m^{-1}, 4: 3 m^{-1}, 5: 5 m^{-1}, 6: 10 m^{-1}
(T=70°C; Ro=1.25; C_C=40 g/l)

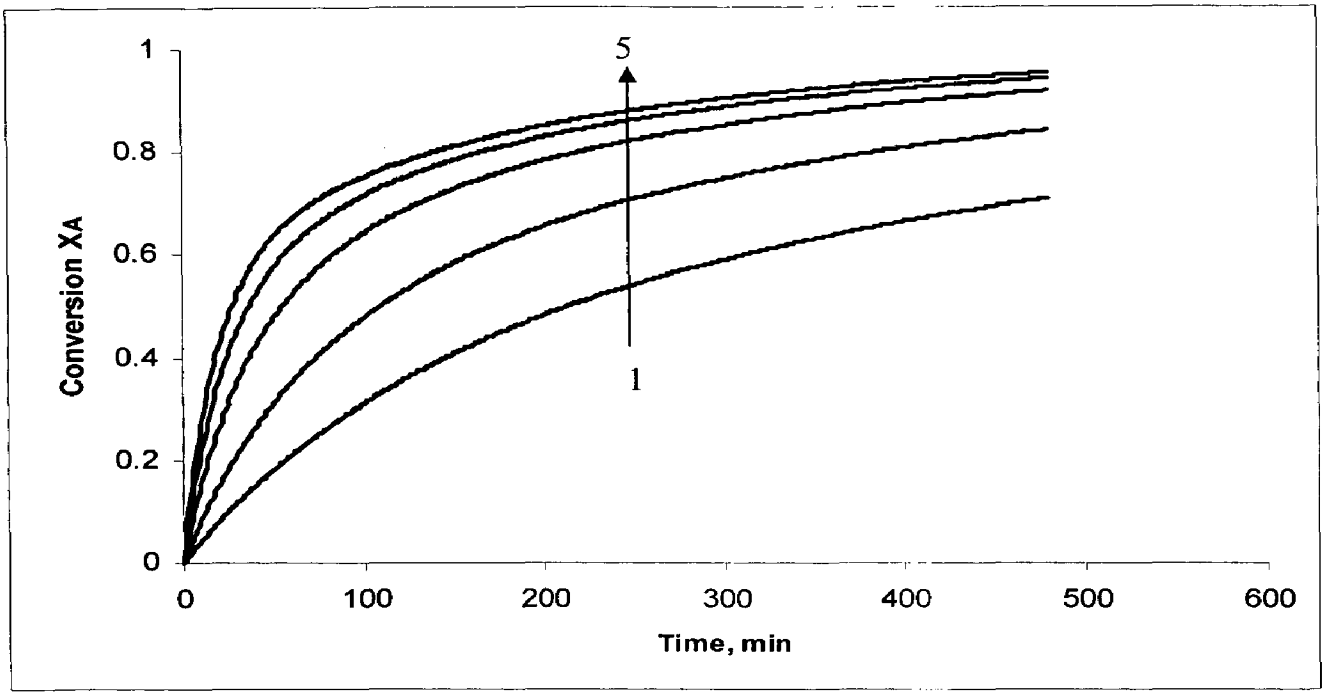

Figure 7.5 Effect of change in catalyst concentration on conversion of acetic acid. C_C for curve 1: 1 g/l, 2: 25 g/l, 3: 50 g/l, 4: 75 g/l, 5: 100 g/l (T=70°C; Ro=1.25; S/V=3.4 m^{-1})

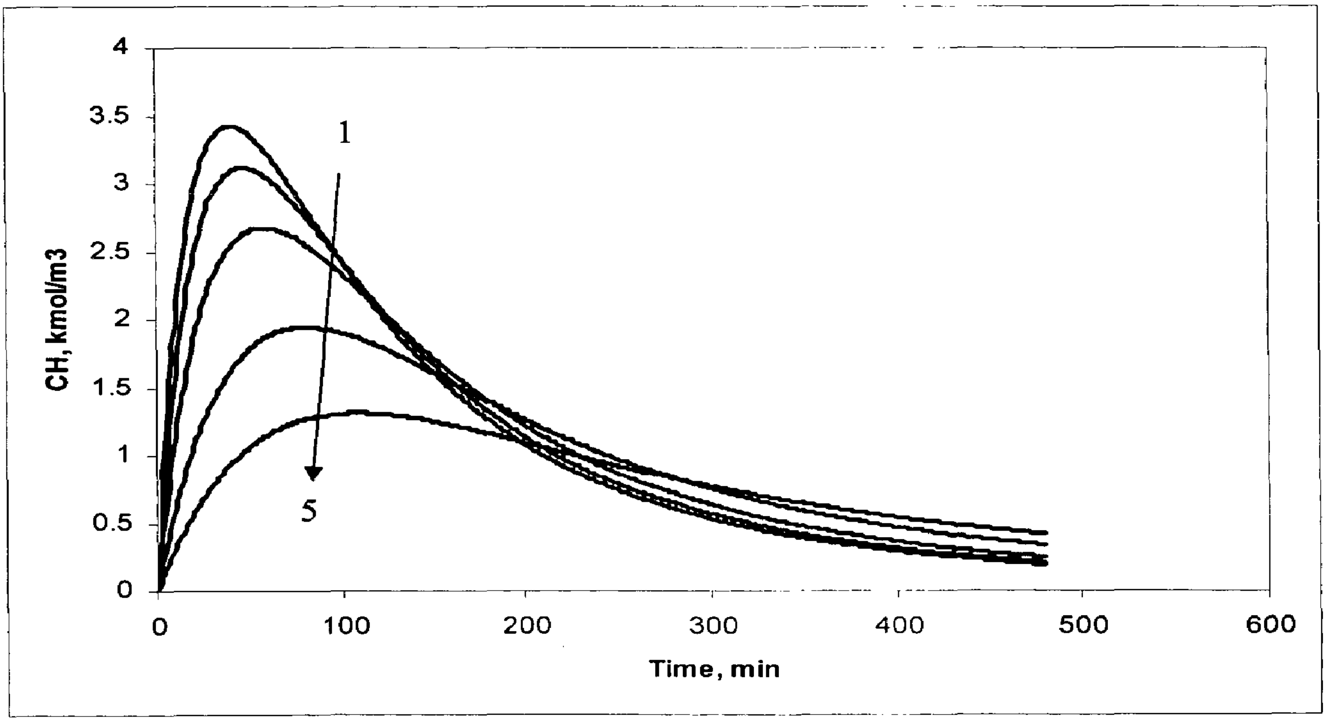

Figure 7.6 Effect of change in catalyst concentration on water concentration. C_C for curve 1: 1 g/l, 2: 25 g/l, 3: 50 g/l, 4: 75 g/l, 5: 100 g/l (T=70°C; Ro=1.25; S/V=3.4 m^{-1})

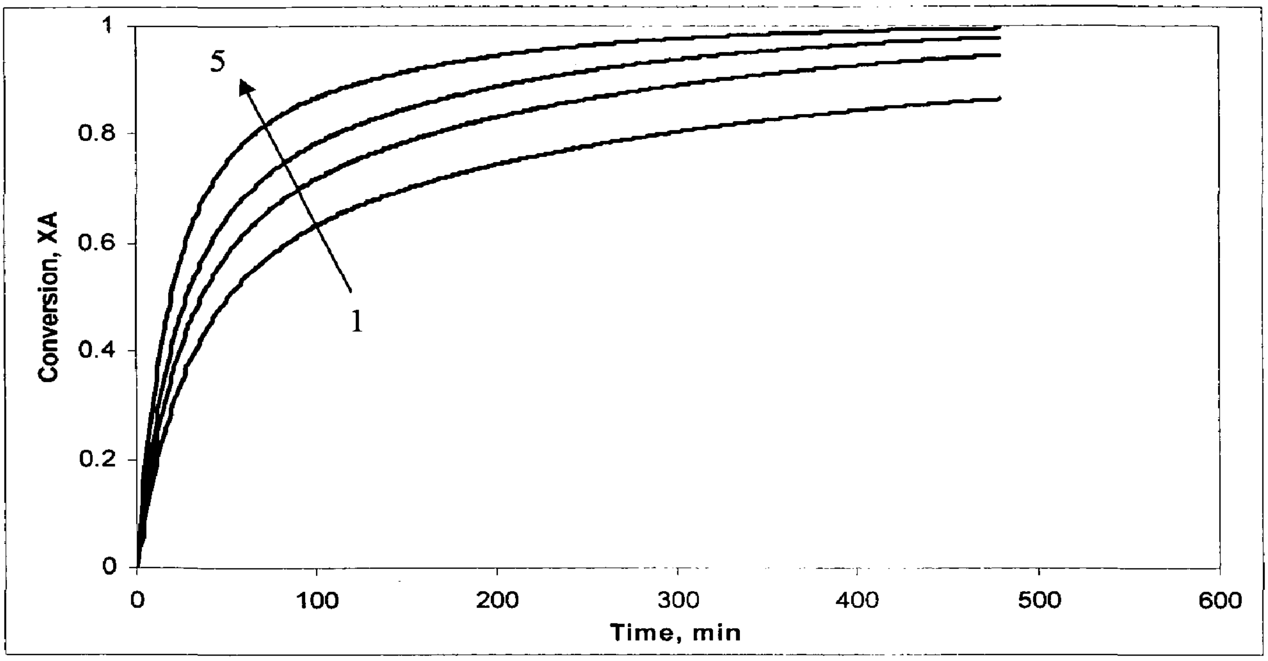

Figure 7.7 Effect of change in ratio of initial reactants on conversion of acetic acid
R_0 for curve 1: 1 , 2: 1.25, 3: 1.5, 4: 2
(T=70°C; C_C=40 g/l; S/V=3.4 m^{-1})

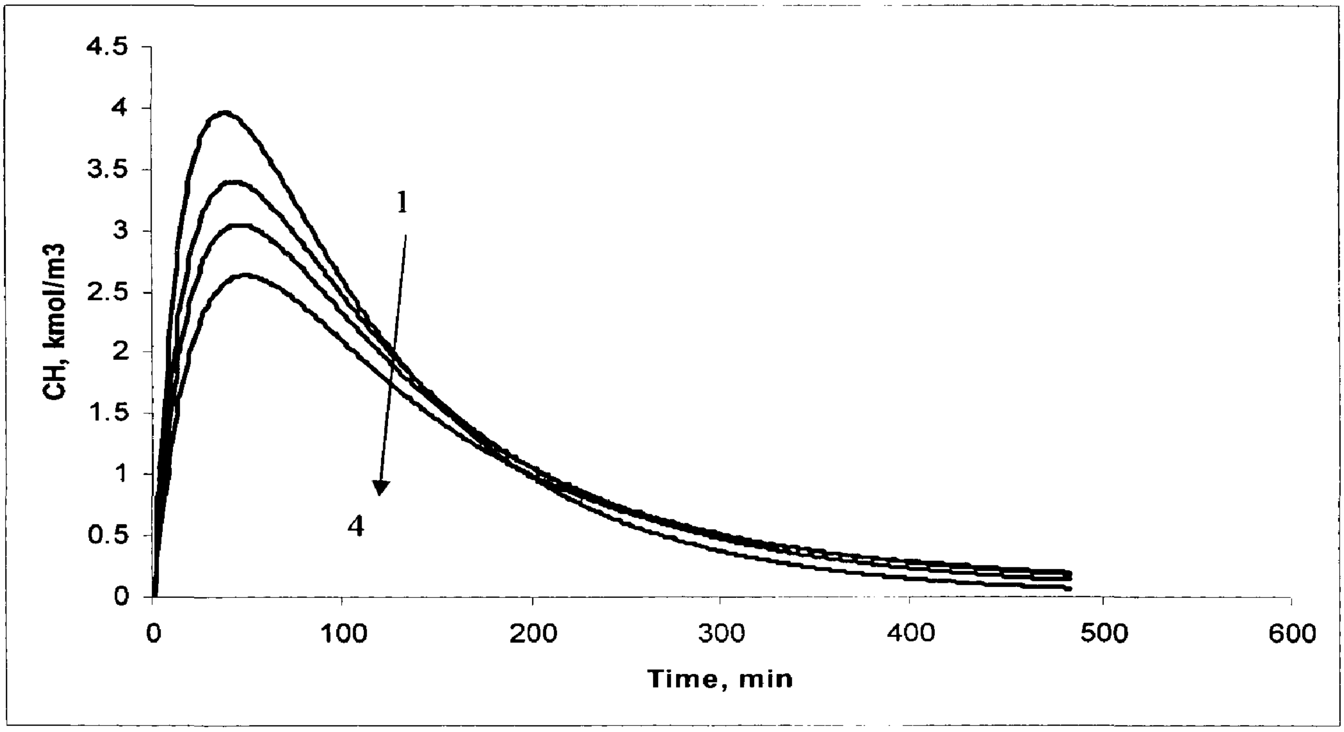

Figure 7.8 Effect of change in ratio of initial reactants on conversion of acetic acid
R_0 for curve 1: 1 , 2: 1.25, 3: 1.5, 4: 2
(T=70°C; C_C=40 g/l; S/V=3.4 m^{-1})

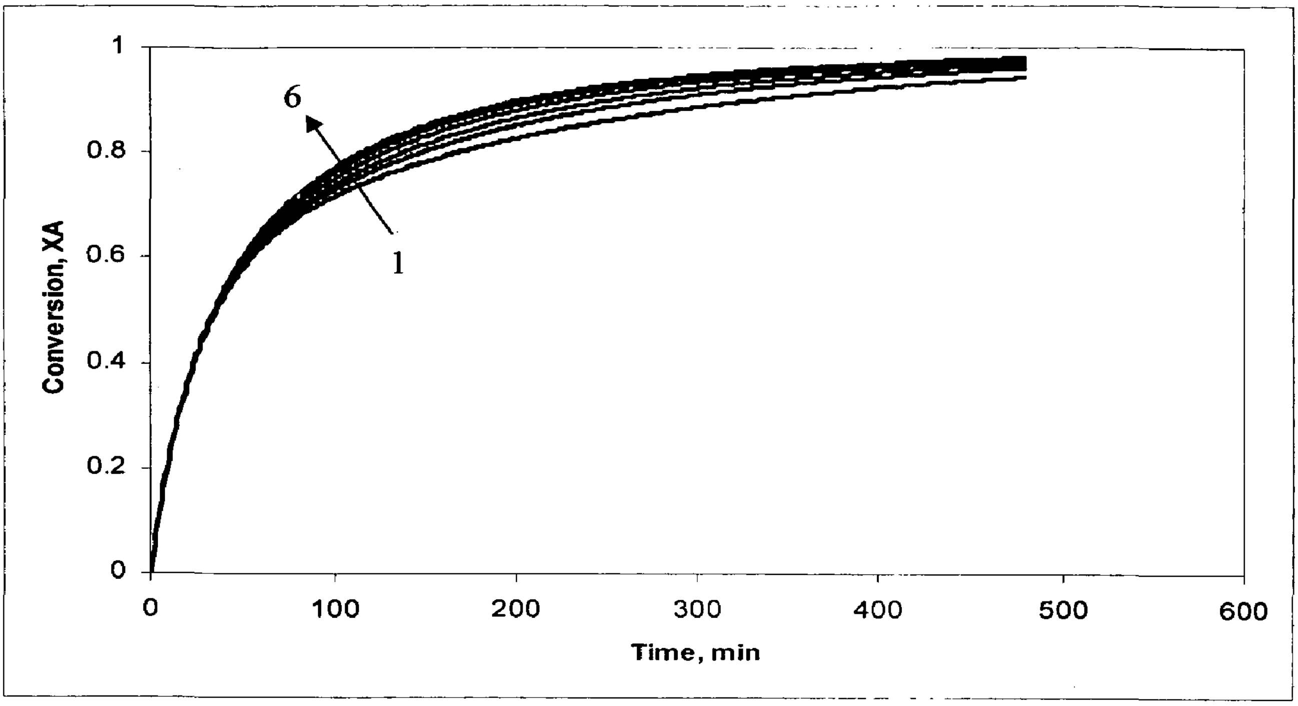

Figure 7.9 .Effect of change in flux on conversion of acetic acid with respect to time. Flux for curve 1: Base, 2: 1.5 times, 3: 2 times, 4: 3 times, 5: 5 times, 6: 10 times, 6: 20 times (T=70°C; C_C=40 g/l; Ro=1.25; S/V=3.4 m^{-1})

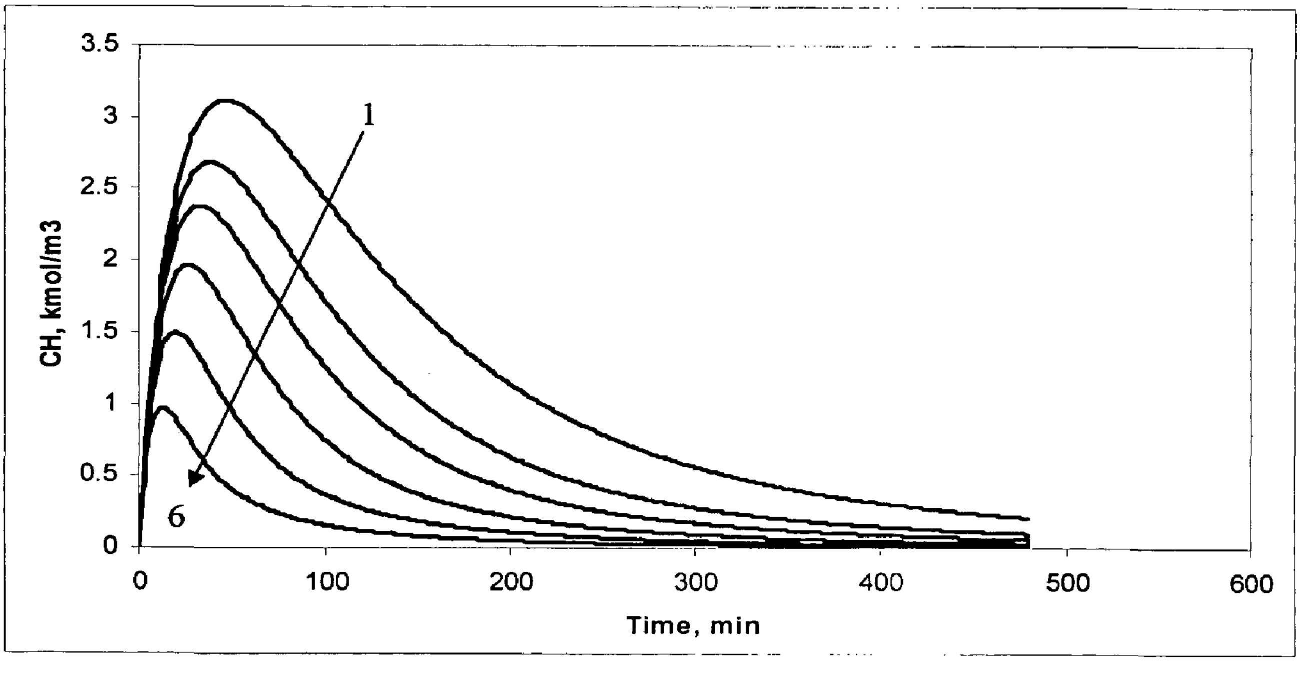

Figure 7.10 .Effect of change in flux on conversion of acetic acid with respect to time. Flux for curve 1: Base, 2: 1.5 times, 3: 2 times, 4: 3 times, 5: 5 times, 6: 10 times, 6: 20 times (T=70°C; C_C=40 g/l; Ro=1.25; S/V=3.4 m^{-1})

7.3 CONCLUDING REMARKS

The model equations for pervaporation reaction were developed based on the reaction kinetics and pervaporation data for the esterification lactic acid using n-ethanol. The simulation results were compared with the experimental results and are in excellent agreement. The conversion of acetic acid was enhanced in pervaporation reactor as compared to conventional reactor. The performance of pervaporation reactor was analyzed by studying effect of various parameters such as catalyst concentration, reactant ratio, ratio of membrane area to reaction volume and flux on conversion of lactic acid and water removal.

CONCLUSIONS AND RECOMMENDATIONS

8.1 CONCLUSIONS

- A mathematical model for pervaporation reactor is developed for esterification of acetic acid with n-butanol, lactic acid with ethanol and acetic acid with ethanol.
- Mathematical model consists of set of coupled Ordinary Differential Equations which constitutes initial value problem and these differential equations solved by using RKF method and Finite difference method for prediction of performance of model.
- The variation of conversion of reactant and concentration of water with operating conditions are studied and compared with available experimental data.
- The conversion of reactant was enhanced in pervaporation reactor as compared to conventional reactor. Pervaporation reactor has a good potential for enhancing conversion in reversible condensation reactions (especially esterification), generating water as a product
- The performance of pervaporation reactor was analyzed by studying effect of various parameters such as temperature, catalyst concentration, reactant ratio, ratio of membrane area to reaction volume and flux on conversion of rectants and water removal.
- The model presented can also be used for the other esterification reactions. The described model allows the evolution of the reaction time necessary to achieve a given conversion.

8.2 RECOMMENDATIONS FOR FUTURE WORK

- The process parameters of temperature, catalyst concentration, initial molar ratio of acid to alcohol, the ratio of the effective membrane area to the volume of reacting mixture, flux can be changed in order to attain the optimum values for the pervaporation-esterification coupling.

- Mathematical model equations are very sensitive to the kinetic parameters so kinetic parameters should be evaluated carefully

- The correlations for various constitutive properties for example permeance of the species through the membrane have been taken from the literature. If these parameters have been evaluated experimentally in the laboratory, it would have given better simulation results.

- The process parameters of temperature, catalyst concentration, initial molar ratio of acid to alcohol, the ratio of the effective membrane area to the volume of reacting mixture, flux can be changed in order to attain the optimum values for the pervaporation-esterification coupling.

- Techno-economic studies are showing that pervaporation reactors have good market potential. There are many examples where pervaporation reactors can reduce product costs by an important margin.

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3. **Shyambabu Patidar,** Kailas L. Wasewar, and V. K. Agarwal, Modeling and parametric sensitivity of pervaporation reactor for esterification of lactic acid with ethanol. *To be forwarded* **(2007)**

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