MODELING AND SIMULATION OF PERVAPORATION MEMBRANE REACTOR

A DISSERTATION

Submitted in partial fulfilment 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 Project entitled, **"MODELING AND SIMULATION OF PERVAPORATION MEMBRANE REACTOR"**, in partial fulfillment of the requirement for the award of the degree of **Master of Technology** in **Chemical Engineering** with specialization in "**Computer aided process plant design**", and submitted in the **Department of Chemical Engineering, Indian Institute of Technology Roorkee**, Roorkee. This is an authentic record of my own work carried out during the period from June 2007 to june 2008, under the esteemed guidance of **Dr. V. K. Agarwal**, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee.

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

Date: June, 2008.

Place: IIT Roorkee.

YKSingh

(Vimlesh Kumar singh)

CERTIFICATE

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

26.6.08

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ABSTRACT:

Membrane reactor is a chemical reactor integrated with a membrane as a separator. In case of condensation reactions esterification reactions are best suited, because most of these are reversible endothermic reactions and the conversion is very slow. So there is a potential to enhance the reactant conversion into product. In this thesis we considered three systems over which I did work on "Modeling and Simulation of Pervaporation Membrane Reactor" From thermodnamic point of view the conversion of esterification reaction is limited by the equilibrium value. In order to increase conversion this process is carried out in membrane reactor. The reactor in this case is continuous stirred tank reactor integrated with membrane. With an idea to keep some assumptions, the mathematical model appears to have an unmatched concerns for analysis and simulation process.

In this work, a steady state model for isothermal condition has been developed which incorporates ordinary differential equations along with boundary conditions for state variables and appropriate parameters. The model equations are solved with Polymath (RKF045). The experimental operating data are available in literature were selected for testing the model predictions and to ascertain the correctness of proposed model.

The influence of several important operating variables on the esterification pervaporation reactor performance has been analyzed. Pervaporation and reaction rate are both increased with the operating temperature. Decreasing the initial molar reactant ratio of isopropanol with acetic acid, the ester rate formation increases significantly. When the S/Vo ratio increases higher ester conversions are obtained. Finally the effect of catalyst concentration has been considered showing that the final water content decreases with increasing catalyst concentration. From the results it can be concluded the right choice of these parameters has a great influence on the performance of the esterification pervaporation reactor. The results obtained with the model are in best agreement with the experimental values.

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NOMENCLATURE

A : Acid

B : Base

C_A : Concentration of acetic acid in reactor ($kmol/m^3$)

C_{A0} : Initial concentration of acetic acid in reactor ($kmol/m^3$)

C_B : Concentration of n-butanol in reactor ($kmol/m^3$)

C_C : Concentration of catalyst in reactor ($kmol/m^3$)

C_R : Concentration of n-butyl acetate in reactor ($kmol/m^3$)

C_H : Concentration of water in reactor ($kmol/m^3$)

E_a : forward activation energy (kJ/mol)

E_b : backward activation energy (KJ/mol)

F : Molar permeate flux (mol min^{-1} m^{-2})

i : component

IPA : isopropanol

J_H : Water flux through membrane ($kmol/m^2min$)

K_0 : frequencyfactor L/(mol.min)

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 ($kmol/m^3min$)

R : general rate constants (kJ/mol/K)

S : Area of membrane (m^2)

t : Reaction time (min)

T : temperature

V : Volume of reaction mixture (m^3)

X_A : Conversion of acids

X_B : Conversion of n-amyl alcohol

CHAPTER 1

INTRODUCTION

The use of membranes in the chemical industry has received considerable attention during the last decades. Since membranes permit selective permeation of one component from a mixture, the conversion of thermodynamically limited reactions can be enhanced through removing one or more product species from the reacting mixture. There are many Separation processes such as distillation, absorption, adsorption etc. among which pervaporation is one of the best way of energy saving process. The hybrid pervaporation require up to 70% less energy than the distillation process.

A class of industrially relevant equilibrium reactions is esterification reactions in which water is one of the products. 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.

$$R_1COOH + R_2OH \rightleftharpoons R_1COOR_2 + H_2O$$

The equilibrium-limited systems where the water is a byproduct by removing the water the reaction move in forward direction hence the ester conversion is increases. 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.

There are three types of pervaporation membrane rector:

(i) Batch pervaporation membrane reactor

(ii) Continuous membrane rector

(iii) Hybrid membrane rector

In hybrid pervaporation membrane rector the distillation column is integrated with the membrane system i.e. the two separate unit are combined and formed a single unit called hybrid pervaporation membrane rector.

1.1 Pervaporation membrane reactor:

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.

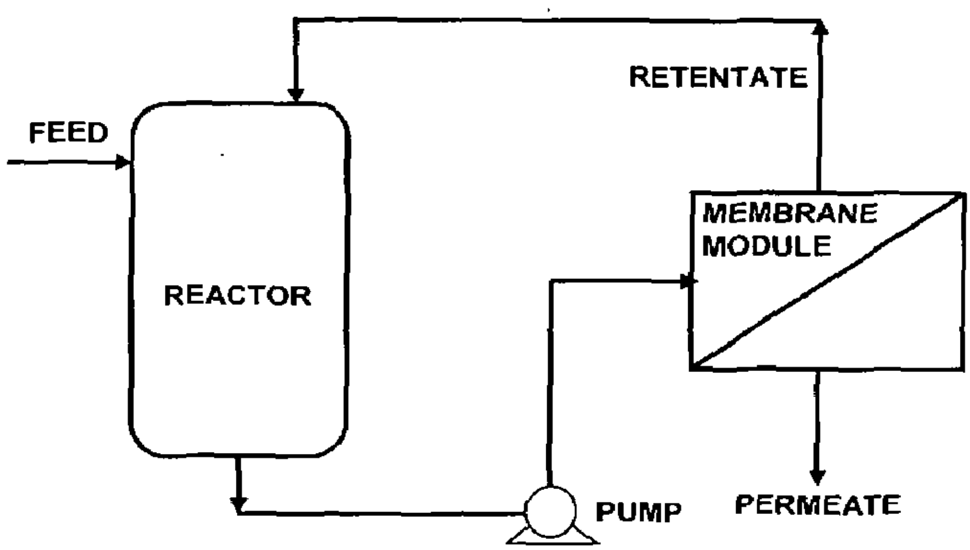

Fig 1.1 pervaporation membrane reactor

1.2 Pervaporation principle:

The word Pervaporation is a contraction of two words permeation and evaporation. In the Pervaporation one or more products (usually water) in a reaction liquid mixture contacting on one side of the membrane permeate preferentially through the membrane and the permeated steam is removed as a vapor from the other side of the membrane as a result the forward reaction can be enhanced. This process is different from the other membrane process in that there is a phase change as the solute permeates across the membrane. Thus both heat and mass transfer are important aspects in the performance of membrane reactor.

1.3 Industrial Applications of membrane reactor:

Established industrial applications of pervaporation include:

- 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.

Other products separated or purified by pervaporation include:

Alcohols	**Ketones**
Methanol	Acetone
Ethanol	Butanone
Propanol (both isomers)	Methyl isobutyl ketone (MIBK)
Butanol (all isomers)	**Amines**
Pentanol (all isomers)	Triethylamine
Cyclohexanol	Pyridine
Benzyl alcohol	Aniline
Aromatics	**Aliphatics**
Benzene	Chlorinated hydrocarbons (various)
Toluene	Dichloro methane
Phenol	Perchloroethylene
Ester	**Ethers**
Methyl acetate	Methyl tert-butyl ether (MTBE)
Ethyl acetate	Ethyl tert-butyl ether (ETBE)
Butyl acetate	Di-isopropyl ether (DIPE)
Organic Acid	Tetrahydro furan (THF)

1.4 Membranes:

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. The inorganic membranes like silica are mostly used where high temperature are required, it can work at 100^0C over 80 hr.

1.5 Transport through membrane:

The stream leaving the membrane module at the feed-side is called the retentate. Pervaporation comprises a number of consecutive steps. The membrane selectively adsorbs one or more of the components, which diffuse through the membrane and evaporate at the permeate side. The permeate stream is removed by applying either a vacuum pump. There are five different steps are considered, which are crucial for the overall performance of the separation process. These are

(1) Mass transfer from the bulk of the feed to the feed-membrane interface;

(2) Partitioning of the penetrants between the feed and the membrane, the selective layer of the membrane is usually at the feed side of the membrane.

(3) Diffusion inside the membrane,

(4) Desorption at the membrane-permeate interface and

(5) Mass transfer from the permeate-membrane interface.

The overall driving force for Pervaporation is the difference in partial vapor pressure between the feed and the permeate side of the membrane. Parallel to the mass transfer of steps 1 and 3, also heat is required for the evaporation process.

OBJECTIVE OF THESIS:

The aim of this thesis to model and simulate the membrane reactor for esterification reaction on the basis parameters temperature, initial molar ratio of reactants, catalyst concentration and ratio of membrane area over reaction volume etc. The main objective are summarized as follows:

- To develop the mathematical model of a pervaporation membrane reactor for the esterification of "Levulinic acid with n amyl alcohol, acetic acid with isopropanol and lactic acid with methanol".
- To simulate above model equations using polymath (RKF045) program.
- To validate the simulation results with available experimental values.

CHAPTER 2

LITERATURE REVIEW

The present chapter provide a *brief discussion of* the past work on **"pervaporation membrane reactor"**. Many number of research work has been done till date, But here we will take some important litratures over this. **Bagnell et.al.(1993)** Nafion tubes that function both as a reaction catalyst and a pervaporation membrane have been used to increase the yield in the esterification of acetic acid with methanol and n-butanol by selectively removing products, mainly water, from the reaction mixture. The experiments were performed at room temperature in a batchwise reactor using acidic protons in Nafion pellets and the Nafion membrane as the reaction catalyst. In some experiments the acidic protons in the membrane were partially or fully exchanged with caesium ions, which increased the intrinsic selectivity of the membrane for water but lowered its permeability. In the methanol reaction, the yield of methyl acetate was increased from the usual equilibrium value of 73% to a maximum of 77%. In the n-butanol reaction, the yield of n-butyl acetate increased from 70% to a maximum of 95%. The effect of the membrane's catalytic activity on its permselectivity was investigated. The catalytically active membranes showed significantly higher permselectivities for water at the same or higher flux, compared to when no reaction was taking place within the membrane phase.

Zhu et. al.(1996) *The esterification reaction* between acetic acid and ethanol was studied in a continuous flow pervaporation membrane reactor utilizing a polymeric/ceramic composite membrane. For a range of experimental conditions reactor conversions were observed which are higher than the corresponding calculated equilibrium values. This is due to the ability of the membrane to remove water, a product of the reaction. A theoretical model has been developed which gives a reasonable fit of the experimental results.

Zhu et. al.(1997)

A composite catalytic membrane with a cross linked PVA dense active layer coated on a porous ceramic plate support was prepared 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.

Lipnizki et.al.(1998) Pervaporation is one of the developing membrane technologies that can be used for various industrial applications but for a predefined task, the optimal process design is unlikely to consist solely of pervaporation. Often the optimised solution becomes a hybrid process combining pervaporation with one or more other separation technologies. A distinction will be made between hybrid and integrated processes. Hybrid processes are important and consequently need to be considered in process design. This paper focuses on pervaporation based hybrid processes that have been realised on an industrial scale. Both present and future prospects of applying these process combinations will be reviewed. The emphasis of this paper is, therefore, on pervaporation combined with distillation and with chemical reactors. The economic potential of these hybrid processes is evaluated, for various applications, by cost comparisons between the pervaporation-based hybrid processes and alternative separation processes.

Domingues et.al.(1999) This work is centred on the coupling of a pervaporation module to a discontinuous esterification reactor using a commercial GFT membrane and analysing 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 pmameters of the esteritication and the applicability of pervaporation to esterification by determining the membrane permeability and its selectivity under the conditions of 80°C and a surface area of 170 cm^2.

The results showed a flux of 0.54 kg/m2h, 96% selectivity in water and 99% conversion. A theoretical model was developed that satisfactorily agrees with the obtained experimental results, Thus allowing the prediction of the conversion variation with the pervaporation time.

Qureshi et. al.(2000) Acetone butanol ethanol (ABE) were produced in an integrated fermentation-product recovery system using Clostridium acetobutylicum (C. acetobutylicum) and a silicalite silicone composite membrane. Cells of C. acetobutylicum were removed from the cell culture using a 500,000 molecular weight cut-off ultrafiltration membrane and returned to the fed-batch fermentor. The ABE was removed from the ultrafiltration permeate using a silicalite–silicone composite pervaporation membrane.The silicalite silicone composite membrane (306 mthick) wasmade in our laboratory and characterized for flux and selectivities using model acetone ethanol butanol solution. Flux of the silicalite–silicone composite membrane was constant during pervaporation of fermentation broth at the same concentration of ABE. Acetone butanol selectivity was also not affected by the fermentation broth, indicating that the membrane was not fouled by the ABE fermentation broth. The silicalite–silicone composite membrane was exposed to fermentation broth for 120 h. Acetic acid and ethanol did not diffuse through the silicalite–silicone composite membrane at lowconcentrations.

Wang et.al. (2001) The presentwork is proposed to evaluate the potential of using pervaporation process to separatewater–acetic acid mixtures. A composite membrane of polyacrylic acid (PAA) dip-coated asymmetric poly (4-methyl-1-pentene) (TPX) membrane was prepared. To improve the interface peeling of the PAA/TPX composite membrane, the TPX membranes were surface-modified with residual air plasma in a tubular-type reactor. The surface properties of the plasma pretreated TPX membrane was characterized by atomic force microscopy (AFM) and water contact angle meter. The PAA/TPX composite membrane with plasma pretreatment effectively prevents the interface peeling.The effects of feed concentration, substrate membrane structure, plasma treatment conditions and compositions of coating solution on the pervaporation performances were investigated.

Optimal results were obtained with the PAA/TPX composite membrane prepared from the PAA/ethylene glycol (EG)/aluminum nitrate = 1/2/0.05 coating solution at the 5W/30 s plasma treatment condition. The water concentration of the permeate approach to 100 wt.% and a 960 g/m2 h permeation rate with a 3 wt.% feed acetic acid concentration at 25 °C was obtained.

Lim et.al.(2002) 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 ine4cient 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 dificulties have motivated e8orts for the development of other coupled reactive/separation processes. Pervaporation membrane reactors (PVMR), in particular, are receiving increased attention as a potentially competitive alternative to reactive distillation.In this paper, we present a model that we 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 and analyze the factors that affect and optimize their performance.

Koszorz et. al.(2003) This paper presents a study of enzymatic esterification of oleic-acid and i-amyl alcohol. The product of this reaction, i-amyl-oleate, is widely used as a bio-lubricant. During the esterifieation reaction, water is produced as a by-product, which has a disadvantageous effect on the reaction rate and enzyme activity. To enhance the effectiveness of the process, water should be removed. One of the most promising techniques for realizing this goal is pervaporation, which can be integrated on-line with the reaction system. Such integration can be realized in the form of a membrane reactor as was studied in this work. An immobilised lipase enzyme,Novozym 435 (Novo Nordisk, Denmark), which was taken as a catalyst in the experiments, proved to be very sensitive for the presence of water and alcohol in the reaction mixture.

Below a certain level of water concentration, enzymatic catalyst activity is very low. From the other side, high initial concentrations of alcohol deactivate the catalyst. Both of these influences were taken into consideration and introduced into the mathematical model of an integrated esterification-pervaporation process. Computer calculations performed with the use of this model showed that there exists a range of pervaporation process parameters which prohibits the reaction from proceeding.

Park et.al (2004) 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 is described. 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.

Bengtson et.al.(2004) To form membranes with catalytic effectiveness in hydrogenation nano-sized palladium clusters were incorporated in polymeric membranes made from poly(ether-*b*-amide) (PEBA) mainly by a solution-casting method. Several configurations of the Pd in the membrane were tested to optimise the catalytic activity: homogeneously distributed in PEBA, homogeneously distributed in PEBA /poly(vinylpyrrolidone) (PVP) blend, homogeneously distributed in PEBA/PVP blend with silica filler, two-layer configuration, and surface coated PEBA-membranes. The membranes were characterised by SEM, XRD and pervaporation flux density. The catalytic activity was tested in the pervaporative membrane reactor by hydrodechlorination of chlorophenol and chlorobenzene in diluted aqueous solution saturated by hydrogen at 30 °C. The produced hydrochloric acid is proportional to the reaction and detected exclusively in the feed. The decrease of the feed-pH was used to monitor the reaction progress of chlorophenol hydrodehalogenation online.

Alternatively, the hydrodehalogenation of chlorobenzene was traced by head space gas chromatography. An essential improvement of the homogeneous PEBA-membranes resulted in blending with PVP and adding silica filler. The calculated activity per gram of Pd in the hydrodechlorination of 4-chlorophenol increased about four times and an about two times higher conversion was detected, both at an even lower Pd content. The two-layered membranes at similar overall Pd content demonstrated about two times higher activity and conversion per time to related membranes with homogeneously partitioned Pd-nanoclusters. Surface coated membranes with a porous Pd-layer interconnected to the PEBA-membrane showed only at high Pd content a performance related to simple homogeneous membranes.

Peters et.al.(2005) Pervaporation is a promising option to enhance conversion of reversible condensation reactions, generating water as a by-product. In this work, composite catalytic membranes for pervaporation-assisted esterification processes are prepared. Catalytic zeolite H-USY layers have been deposited on silica membranes by dip-coating using TEOS and Ludox AS-40 as binder material. Membrane pre-treatment and the addition of binder to the dip-coat suspension appear to be crucial in the process. Tuning of catalytic layer thickness is possible by varying the number of dip-coat steps. This procedure avoids failure of the coating due to the high stresses, which can occur in thicker coatings during firing. In the pervaporation-assisted esterification reaction the H-USY coated catalytic pervaporation membrane was able to couple catalytic activity and water removal. The catalytic activity is comparable to the activity of the bulk zeolite catalyst. The collected permeate consists mainly of water and the loss of acid, alcohol and ester through the membrane is negligible. The performance of the membrane reactor is mainly limited by reaction kinetics and can be improved by using a more active catalyst.

Wichmann et.al(2005) A novel integrated process of enzymatic synthesis of sugar fatty acid esters from renewable sources was proposed for the system oleic acid/ a methyl glucoside focussing on the application of different membrane techniques. The operational parameters were studied and optimized carrying out the reaction in an enzymatic membrane reactor (EMR) where the catalyst remained retained by means of ultrafiltration.

A pervaporation unit coupled to the EMR was applied for by-product removal (water). A proper product separation and isolation was achieved applying combined techniques including filtration, evaporation, extraction and alternatively stepwise elution chromatography or dialysis.

Huifang et.al.(2006) A bulk mass transfer coefficient (BMTC) equation was derived from the mechanism of mass transfer in surface liquid membrane in this study, which was based on the analysis of biosorption process, conservation of mass in sludge granule and the unification of the dimension. A biosorption experiment was carried out in which anoxic sludge from an anoxic baffled reactor for printing and dyeing wastewater treatment was used to adsorb Acid Red GR dye. The results showed that there was a linear regression curve between ln [qe/(qe_q)] (qe and q were the amount adsorbed at equilibrium and at time t, respectively.) and time t. There was also a good agreement between the adsorbate amount measured and that predicted by the equation of BMTC. The BMTC of Acid Red GR dye adsorbed by anoxic sludge was 6.816 kg m-3 min-1. Experimental results indicated that the BMTC determined by a simple adsorptive experiment using this equation was credible. It could be a feasible and effective way to determine BMTC of activated sludge for biosorption performance.

Ulbricht (2006 This feature article provides a comprehensive overview on the development of polymeric membranes having advanced or novel functions in the various membrane separation processes for liquid and gaseous mixtures (gas separation, reverse osmosis, pervaporation, nanofiltration, ultrafiltration, microfiltration) and in other important applications of membranes such as biomaterials, catalysis (including fuel cell systems) or lab-on-chip technologies. Important approaches toward this aim include novel processing technologies of polymers for membranes, The synthesis of novel polymers with well-defined structure as 'designed' membrane materials, advanced surface functionalizations of membranes, the use of templates for creating 'tailored' barrier or surface structures for membranes and the preparation of composite membranes for the synergistic combination of different functions by different (mainly polymeric) materials. Self-assembly of macromolecular structures is one important concept in all of the routes outlined above.

These rather diverse approaches are systematically organized and explained by using many examples from the literature and with a particular emphasis on the research of the author's group(s). The structures and functions of these advanced polymer membranes are evaluated with respect to improved or novel performance, and the potential implications of those developments for the future of membrane technology are discussed.

Wasewar (2007) The pervaporation reactor is, specifically, 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 systems with those of conventional processes, it can be said that pervaporation reactor will play an important role in the chemical industry for new installations as well as for rehabilitation of existing plants.

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. 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 highly acidic catalyst The modified/improved model for pervaporation reactor for benzyl alcohol acetylation is presented. The parametric sensitivity is studied for the performance of pervaporation reactor. The use of pervaporation coupled to the esterification reaction increases the conversion considerably. 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. The present model can be extended for the other esterification reactions in pervaporation reactors.

Nikunj P et. al. (2007) Modeling of an esterification reaction in a batch pervaporation membrane reactor (PVMR), and an analysis of the PVMR performance under different reaction conditions for different membrane characteristics are presented. Esterification of ethyl alcohol with acetic acid was considered as the model reaction. The PVMR performance for this reaction could be represented by a 2-step series model. The PVMR performance was similar to that of the batch reactor when both the reactors were in the kinetic regime. However, the performance of the PVMR was superior to that of the batch reactor when both were in the intermediate/equilibrium regime of the reaction.

In these regions, the PVMR performance was influenced /limited by the membrane flux and selectivity. The analysis showed that the membrane flux affected the PVMR performance in the intermediate region and the membrane selectivity affected the performance in the equilibrium regime. Further, the limitations introduced by a low-flux membrane could be overcome by appropriate selection of the membrane area and that due to poor selectivity could be compensated to a certain extent by adjusting the feed ratio.

2.1 EXPERIMENTAL STUDIES ON MEMBRANE REACTOR:

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

Qinglin Liu.et.al (2001) Discussed the separation characteristics of the cross linked polyvinyl alcohol (PVA) membranes (prepared in their laboratory).They studied the performance of this membrane by pervaporation separation of the liquid mixtures of both water/acetic acid and water/acetic acid/n-butanol/butyl acetate. The permeation fluxes of water and acetic acid as a function of compositions were presented. The esterification of acetic acid with n-butanol catalyzed by $Zr(SO_4)_4H_20$ was carried out at a temperature range of 60-90°C. A kinetic model equation was developed for the esterification, then it was taken as a model reaction to study the coupling of pervaporation with esterification. Experiments were conducted to investigate the effects of several operating parameters, such as reaction temperature, initial molar ratio of acetic acid to *n*-butanol, ratio of the membrane area to the reacting mixture volume and catalyst concentration, on the coupling process, and the permeation flux expressions of water and acetic acid were presented.

$$J_W = P_W C_W \exp(S_{w,B}C_B + S_{W,E}C_E) \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2.1)$$

$$J_A = \frac{P_A C_W + m}{\exp(S_{A,B}C_B + S_{A,E}C_E)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2.2)$$

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

$$F = \frac{J_w \times S / V}{dC_E / dt} \qquad \text{.....................................(2.3)}$$

- If $F = 1$, the rate of water removal is equal to the water production rate, indicating that the conversion of the reaction could attain 100 %
- $F<1$, the rate of water removal is less than the water production rate, indicating that the conversion could be enhanced a little over the equilibrium conversion, and it is controlled by the water removal;
- $F>1$, the rate of water removal is larger than the water production rate, indicating that the conversion could attain 100%, and it is limited by the water production rate. And also variation of F with reaction time at different temperatures.

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

Table 2.1:

Author	System	Operating Conditions	Results and discussion	Remarks
Wijers J et. al. (2001)	Hydrodynamics in mic ane reactor for	Polymeric membrane Temp. 200^0C Viscosity, μ= 5-25 mpa	The horizontal configuration showed an increase in water flux up to 50% compared to a simulation in which natural conversion is omitted. The dimensionless heat and mass transfer coefficient Nu and Sh are also 4 times higher.	Flux measurements have been performed experimentally at different superficial velocity, temperatures and fluid compositions, showing that hydrodynamics is determined by forced and natural convection simultaneously.
Tsotsis T at. el. (2004)	Hybrid pervaporation membrane reactor	T=70^oC in presence of SPC 112-H^+(ion exchange resin) catalyst.	The pervaporation step though a membrane with adsorption in the permeate side .The equilibrium relations in reversible reactions, particularly for dilute reacting systems .slow reaction, non volatile product, or imperfect membranes.	The model integrate the pervaporation steps.The reactor model performs adequately in describing the experimental data.

Table 2.2:

Tsotsis T at. el. (2004)	Hybrid pervaporation membrane reactor	$T=70^{o}C$ in presence of SPC 112-H^{+}(ion exchange resin) catalyst.	The pervaporation step though a membrane with adsorption in the permeate side .The equilibrium relations in reversible reactions, particularly for dilute reacting systems .slow reaction, non volatile product, or imperfect membranes.	The model integrate the pervaporation steps.The reactor model performs adequately in describing the experimental data.
Keurentjes et. al. (2005)	Zeolite -coated ceramic pervaporation membranes, pervaporation esterification coupling and reactor Evaluation	Temp. $75^{0}C$ Catalyst Y-type Zeolite ceramic hollow fiber silica membranes with Zeolite coating.	A reactor evaluation proved that the outlet convection 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.

Table 2.3 :

Nakanec T et. al. (2005)	Pervaporation dehydration to the lipase calalyzed esterification of fructose / glucose with palmitic acid in 2 methyl-2 butanol	T= 40^0C, 54mM fructose and 54mM palmitic acid in 220mL of 2-methyl-2 butano Zeolite NaA membrane.	There is the formation of diester hence its formation reaction is very slow so catalyst requirement is essential.	It was possible to decrease the ratio of diester in the reaction produced by decreasing the ratio of fatty acid to sugar in the substrate solution.
Gmehling et. al. (2006)	Esterification of acitic acid with isopropanol coupled with pervaporation kinetics and pervaporation studies.	T= 329.15 to 353.85K for the esterification reaction and from 332.15 and 350.90K for the hydrolysis reaction polymeric membrane.	A kinetic expression was obtained by fitting simultaneously the kinetic result 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 parameters. The permeate concentration found to increase.	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 can be used to remove the selectivity the water.

Table 2.4:

Hakim E.A. et. al (2006)	Modeling and simulation of butanol separation from aqueous solutions using pervaporation.	$T=33^0C$, concentration 8-50 gm/l pressure 1 KPa Organophili membrane which is permeable to the butanol.	It was found that the butanol removal increases by increasing the feed concentration., the butanol concentration decreases linearly with time.	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.
Samuel heng et. al. (2006)	An alumina capillary membrane was used for ozone feed distribution.It has outer diameter of 2.5 mm and a nominal pore size of 0.6 μm. Its length is 120 mm.	The support was wash , sonicated and rinsed to remove dirt and contaminants and air calcined at T= 823K To burn away adsorbed organics.	Three ZSM-5 zeolite membranes of 3,6 and 12μm thicknesses were prepared. The Si / Al ratio of the ZSM -5 membranes is between 12 and 30 . The single gas permeation experiments showed that, all three ZSM-5 membranes treated by ozone are relatively free of defect and have excellent permeation properties.	This work demonstrated the use of inorganic membranes for water and waste water treatments. A 30 times higher TOC reduction was observed when a porous alumina capillary membrane was used to produced a fine cascade of 100 μm-sized ozone bubbles instead of

CHAPTER 3

MODELING AND SIMULATION OF MEMBRANE REACTOR FOR ESTERIFICATION REACTIONS

3.1 MATHEMATICAL MODEL DEVELOPMENT:

Modeling of any process is nothing but the set of mathematical equations which represents to actual system. Material and energy balances for systems at un-steady state operation are considered first, and then some of the various rate expressions for simultaneous mass and heat transfer are presented. Due to some logical assumptions we are only concern about the mass balances, because we assume the temperature change during the process is negligible hence we can neglect the energy balance equations.

3.1.1 ASSUMPTIONS:

- The reaction volume is constant.
- The temperature change during the reaction is negligible.
- Concentration change during the permeation is neglected.
- The membrane is unreactive during operation.
- The transport resistance is in the dense polymer layer.
- The resistance in the inorganic support structure on the permeate side is negligible.
- C_A and T at exit and outlet stream are same as the reactor.
- Inside the reactor, reactants takes negligible time in coming down from CA_0 *to* CA.
- There is a uniform mixing inside the reactor.

3.1.2 MASS BALANCE EQUATIONS:

Consider the Acid base (Esterification) reaction

$$A + B \rightleftharpoons R + H \quad \text{..............................(3.1)}$$

Acid Alcohol Ester Water

Now we apply the conservation of mass equation within the control volume for component i.

$$\begin{pmatrix}\text{Rate of accumulation of mass of}\\ \text{component i in control volume}\end{pmatrix} = \begin{pmatrix}\text{Rate of mass of component i}\\ \text{into the control volume}\end{pmatrix} - \begin{pmatrix}\text{Rate of mass of component i}\\ \text{into the control volume}\end{pmatrix} + \begin{pmatrix}\text{mass of component i}\\ \text{generated}\end{pmatrix} - \begin{pmatrix}\text{mass of component i}\\ \text{consumed}\end{pmatrix} - \begin{pmatrix}\text{Rate of mass of compoment i}\\ \text{transported through membrane}\end{pmatrix}$$

$$V\frac{dC_i}{dt} = (K_1C_AC_B)V - (K_2C_RC_H)V - S * J_i \quad \text{....................(3.2)}$$

Dividing by volume V we get

$$\frac{dC_i}{dt} = (K_1C_AC_B - K_2C_RC_H) - \frac{S}{V} * J_i \quad \text{............................(3.3)}$$

Where i is the general component may be any of the Acid (A), alcohol (B) Ester R and water(H)

k_1 *is forward rate constant,* k_2 *is backward rate constant*

C_i are the concentrations, V is the reaction volume (control volume)

S is the membrane area, J_i is the water flux.

After simplification we can write in differential forms as follows

$$\frac{dC_i}{dt} = \pm(k_1C_AC_B - k_2C_RC_H) - \frac{S}{V}J_i \quad \text{.........................(3.4)}$$

Where i is the component NO.

$$\frac{dC_A}{dt} = -(K_1C_AC_B - K_2C_RC_H) - \frac{S}{V}J_A \quad \text{.........................(3.5)}$$

$$\frac{dC_B}{dt} = -(K_1C_AC_B - K_2C_RC_H) - \frac{S}{V}J_B \quad \text{..............................(3.6)}$$

$$\frac{dC_R}{dt}=(K_1C_AC_B-K_2C_RC_H)-\frac{S}{V}J_R \qquad \text{.................. (3.7)}$$

$$\frac{dC_H}{dt}=(K_1C_AC_B-K_2C_RC_H)-\frac{S}{V}J_H \qquad \text{.....................(3.8)}$$

where, S is the membrane area, V is the volume of reaction mixture, and j is the water flow across the membrane. 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.

$$J_H = K_{PV}C_H \qquad \text{..(3.9)}$$

$$J_H = K_{PV1}-K_{PV2}{C_H}^2 \qquad \text{...(3.10)}$$

$$J_H = K_{V1}{C_H}^{K_{PV2}} \qquad \text{.......................................(3.11)}$$

Since the rate equation is given by

$$r_H = k_1C_AC_B - k_2C_RC_H \qquad \text{...................................(3.12)}$$

It was found experimentally that the concentration of isopropyl acetate, isopropanol and acetic acid in permeate were negligible as compared to water. Hence the material balance for the isopropyl acetate, isopropanol and acetic acid can be written as:

$$\frac{dC_R}{dt}=-\frac{dC_A}{dt}=-\frac{dC_B}{dt}(k_1C_AC_B-k_2C_RC_H) \qquad \text{........................(3.13)}$$

The equation (2.9) represents the homogeneous esterification reaction rate equation without catalyst. Since the esterification reactions are very slow. So magnify the reaction rate we use the catalyst. The effect of catalyst should be in the rate equation; hence the reaction can be written as

$$A+B+C \square \quad R+H+C$$

$$-\frac{dC_A}{dt}=K_1C_AC_BC_C-K_2C_RC_HC_C \qquad \text{......................(3.14)}$$

$$\text{or } -\frac{dC_A}{dt}=K_1C_C\left(C_AC_B-\frac{C_RC_H}{K}\right) \qquad \text{........................(3.15)}$$

where $K=\frac{k_1}{k_2}$

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 as.

$$-\frac{dC_A}{dt} = K_{obs}\left(C_A C_B - \frac{C_R C_R}{K}\right) \qquad \text{..............................(3.16)}$$

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

$$\frac{dC_H}{dt} = K_{obs}\left(C_A C_B - \frac{C_R C_R}{K}\right) - \frac{S}{V} J_H \qquad \text{............................(3.17)}$$

The conversions of acid and base can be written as

$$X_A = 1 - \frac{C_A}{C_{A0}} \qquad \text{...................................(3.18)}$$

$$X_B = 1 - \frac{C_B}{C_{B0}} \qquad \text{... ....(3.19)}$$

3.3 Simulation of Modeling Equations:

Simulation is nothing but the best and acceptable solution of a set of mathematical equations. The model equations are differential equations and there are solve by using a suitable numerical method. An optimized time step was considered for the solution.

The values and range of the various parameters used for simulations are given. On the basis of above modeling equations written above, the equations are non linear differential equation, which form an initial value problem .So these equations can be solved by polymath (RKF 045) method. The profiles of different reactants and products are presented and corresponding data table is also obtained. Now these data table is kept in EXCEL and plot the corresponding results with respect to time. Now the experimental data is also plotted w. r. t. time hence we can see the deviation of model with experimental values.

3.3.1 Conversion of ODEs into single variable systems:

The equations from (3.5) to (3.8) can be solved in polymath (RKF045) only if these are in one variable system. Hence we convert those equations into a single variable systems by writing different concentration and flux equations.

We assume that A is the limiting reagent therefore.

$$C_A = C_{A0} - C_{A0}X_A \quad ; \qquad J_A = K_{pv}C_A$$

$$C_B = C_{B0} - C_{A0}X_A \quad ; \qquad J_B = K_{pv}C_B$$

$$C_R = C_{R0} + C_{A0}X_A \quad ; \qquad J_R = K_{pv}C_R \qquad \text{...........} \ (3.20)$$

$$C_H = C_{H0} + C_{A0}X_A \quad ; \qquad J_H = K_{pv}C_H$$

The other conversion equations are as follows

$$C_B = C_{B0} - C_{AO} + C_A \ \& \ \ C_B = C_{A0} + C_{R0} - C_A$$

$$C_R = C_{A0} + C_{R0} - C_A \ \& \ \ C_R = C_{B0} + C_{R0} - C_B \qquad \text{................}(3.21)$$

$$C_H = C_{A0} + C_{H0} - C_A \ \& \ \ C_H = C_{H0} - C_{R0} + C_R$$

Where C_{A0} C_{B0} C_{R0} and C_{H0} are the initial values of concentrations which are known

Using equations (3.20) & (3.21) in equations (3.5 to (3.8) we get single variable ODEs.

$$\frac{dC_A}{dt} = -K_1C_A\left(C_{B0} - C_{A0}X_A\right) + K_2\left(C_{A0} + C_{R0} - C_A\right) * \left(C_{A0} + C_{H0} - C_A\right) - \frac{S}{V} * K_{PV}C_A$$

or this can be written as.

$$\frac{dC_A}{dt} = -K_1C_A\left(C_{B0} - C_{A0}X_A\right) + K_2\left(C_{A0} + C_{R0} - C_A\right)$$

$$* \left(C_{A0} + C_{H0} - C_A\right) - \frac{S}{V} * K_{PV}C_A \qquad \text{....................}(3.22)$$

$$\frac{dC_B}{dt} = -K_1C_AC_B + K_2\left(C_{B0} + C_{R0} - C_B\right) * \left(C_{B0} + C_{H0} - C_B\right) - \frac{S}{V} * K_{PV}C_B \text{.......}(3.23)$$

$$\frac{dC_R}{dt} = K_1C_AC_B - K_2C_R\left(C_{H0} - C_{R0} + C_R\right) - \frac{S}{V} * K_{PV}C_R \qquad \text{.....................}(3.24)$$

$$\frac{dC_H}{dt} = K_1 C_A C_B - K_2 C_R C_H - \frac{S}{V} * K_{PV} C_H \qquad \text{..............................(3.25)}$$

Now equation (3.22) can be written in mole fraction conversion X_A form as follows

$$\frac{dC_A}{dt} = -K_1 \left(C_{A0} - C_{A0} X_A\right) * \left(C_{B0} - C_{A0} X_A\right) + K_2 \left(C_{R0} + C_{A0} X_A\right) * \left(C_{H0} + C_{A0} X_A\right) - \frac{S}{V} * K_{PV} C_A$$

$$\frac{dC_A}{dt} = -K_1 \left(C_{A0} - C_{A0} X_A\right) * \left(C_{B0} - C_{A0} X_A\right) + K_2 \left(C_{R0} + C_{A0} X_A\right) * \left(C_{H0} + C_{A0} X_A\right) - \frac{S}{V} * K_{PV} \left(C_{A0} - C_{A0} X_A\right)$$

$$\begin{aligned}\frac{dx_A}{dt} = {} & K_1 \left(C_{A0} - C_{A0} X_A\right) * \left(C_{B0} - C_{A0} X_A\right) - K_2 \left(C_{R0} + C_{A0} X_A\right) \\ & * \left(C_{H0} + C_{A0} X_A\right) + \frac{S}{V} * K_{PV} \left(C_{A0} - C_{A0} X_A\right)\end{aligned} \qquad \text{..................(3.26)}$$

Equation (3.26) is for acid A similarly we can write the conversion in terms of mole fraction for X_B,X_R and X_H respectively.

3.4 Concluding Remarks:

The model equations for pervaporation esterification reaction were developed based on the mass balance, reaction kinetics and pervaporation data for the esterification reactions using water flux is liner relation with concentration.These set of model equations are used commonly in all three systems.The performance of pervaporation reactor was analyzed by studying effect of various parameters such as temperature, catalyst concentration, initial reactant ratio, ratio of membrane area over reaction volume and flux.

ESTERIFICATION OF LEVULINIC ACID WITH N-AMYL ALCOHOL

The esterification of levulinic acid ($CH_3COCH_2CH_2COOH$) with *n*-amyl alcohol ($C_5H_{11}OH$) can be represented schematically by:

$$A + B \square \quad E + W \qquad \text{.........................(4.1)}$$

Where; A is levulinic acid, B is *n*-amyl alcohol, R is *n*-amyl levulinate and W is water Assuming a constant reaction volume, the rate of water formation is given by:

$$r_W = k_1 C_A C_B - k_2 C_E C_W \qquad \text{...............................(4.2)}$$

k_1 and k_2 are the forward and backward reaction rate constants, respectively.

The equilibrium constant, K, is given by:

$$k_{eq} = \frac{[C_E][C_W]}{[C_A][C_B]} = \frac{K_1}{K_2} \qquad \text{.................................(4.3)}$$

The mass balance for water in a batch reactor with water removal through the pervaporation membrane is equal to:

$$r_W V = Aj_W + \frac{d}{dt}(VC_W) \qquad \text{............................(4.4)}$$

In which: V: reaction volume (L);S: membrane surface area (m2);J_W: water flux through the membrane kg/(m^2.min).

During the reaction in combination with pervaporation, the reaction volume is assumed to be constant. By substituting Eqn (4.2) into Eqn (4.4) we obtain:

$$\frac{dC_W}{dt} = k_1 C_A C_B - k_2 C_E C_W - \frac{S}{V} J_W \qquad \text{........................(4.5)}$$

For the other components a similar relation holds. From previous work [Verkerk et al., 2001} it is clear that the silica pervaporation membrane removes water with high selectivity.

This means that the flux of the other components through the membrane is negligible. Furthermore, the water flux depends linearly on the driving force for water, because water has a linear adsorption isotherm on silica. The driving force for water is given by the difference between the equilibrium vapor pressure of water at the feed side, $p_{w,*}$ and the pressure of water at the permeate side, p_W^P. Because the permeate pressure in the experiments was always smaller than 100 Pa, the driving force for water can be described using the equilibrium vapor pressure of water in the reaction mixture. The equilibrium vapor pressure for water can be expressed as equation

$$P_W * = \gamma_W x_W P_W^0 \qquad \text{.......................................(4.6)}$$

in which:

γ_W : activity coefficient of water in the retentate

x_w: mole fraction of water in the retentate (mol/mol)

. P_W^0 : vapor pressure of pure water (Pa).

The flux for water, J_W, is equal to

$$J_W = B(P_W * - P_W^P) \qquad \text{...(4.7)}$$

in which B denotes the mobility constant.

4.1 SYSTEM DESCRIPTION:

In this section we consider the pervaporation assisted esterification of levulinic acid and n amyl alcohol in the presence of high temperature resistance silica membrane. The influence of several process variables, such as process temperature, initial molar ratio of levulinic acid over n-amyl alcohol, ratio of effective membrane area over the volume of reacting mixture and catalyst content, flux on the esterification have been discussed.

Table 4.1 Values and range of various parameters used for this system:

Parameter	Notations and unit	Value/ Range
Initial mole ratio of livulinic acid and n amyl alcohol	$R0=C_{A0}/C_{B0}$	1-3
Ratio of membrane area to Reaction volume	S/V m^2/m^3	0-30
Equilibrium constant	$Keq=K_1/K_2$	1-5
Temperature	T (K)	300-450
Reaction time	t (hr) t(min)	800 48000
Frequency factor	K_0 lit/(mol.min)	36000
Activation energies	E_a, E_b joul/mol	60000 63080

4.2 Determination of kinetic parameters:

The reaction rate constants k_1 , k_2 are calculated from Arrhenius law:

$$k_1 = k_0 e^{\left(\frac{-E_a}{RT}\right)} \quad \text{and} \quad k_2 = k_0 \, e^{\left(\frac{-E_b}{RT}\right)}$$

$$k_1 = 36000 * \exp\left(\frac{-60000}{RT}\right) \text{ and } k_2 = 36000 * \exp\left(\frac{-63080}{RT}\right)$$

Where R=8.314 KJ/mol is universal gas constant

T is the reaction temperature in K

Table 4.2 Data for the forward rate constant:

T K	k1(expt) lr/(mol.min)	1000/T k-1	k1(model) lr/(mol.min)	lnk1	lnk1(expt)
328	9.5E-06	3.048780488	1.002E-05	-11.511	-11.561
348	4.2E-05	2.873563218	3.548E-05	-10.246	-10.068
373	0.00017	2.680965147	0.0001424	-8.857	-8.698
398	0.00057	2.512562814	0.0004802	-7.641	-7.466
408	0.00058	2.450980392	0.000749	-7.197	-7.444

Source: A.W. Verkerk, et al Tech University Eindhoven (2003); Proefschrift– ISBN 90-386-2944-3

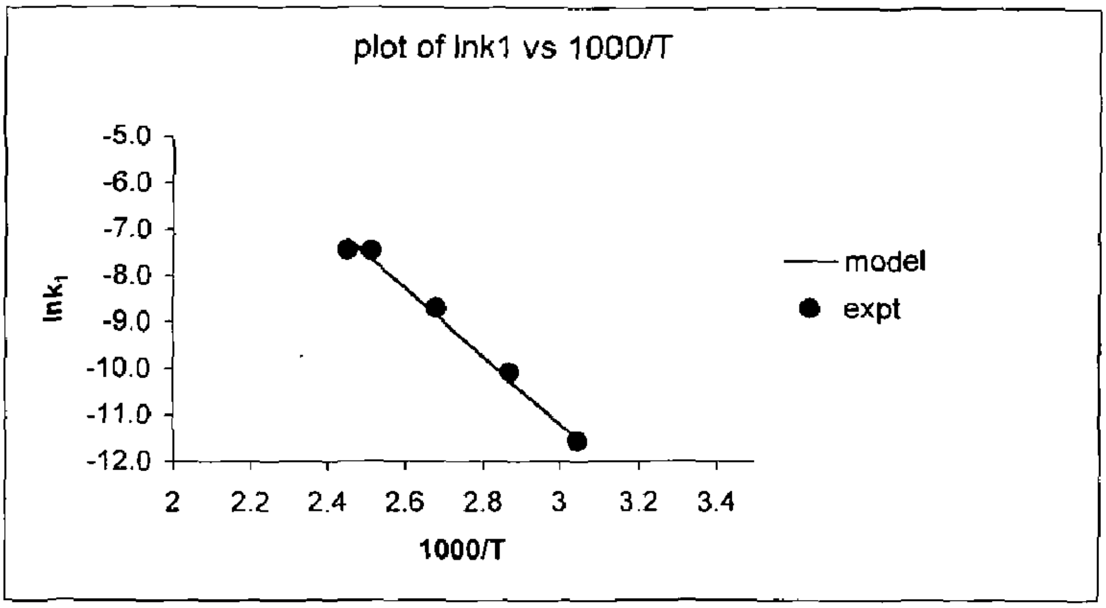

Fig 4.1 Arrhenius plot for the forward rate constant, k_1

4.3 Results and discussion:

In Figure 4.2 the concentration profiles are given for the esterification at a reaction temperature of 348 K. From the initial slope, the forward reaction rate constant, k_1, has been calculated. The forward reaction rate constant has been determined for each temperature using an initial equimolar mixture of 3.92 mol/L for all experiments. In Figure 4.1 the Arrhenius plot for the forward reaction rate constant is given.

From this plot, the Arrhenius parameters, activation energy, *Ea*, and the frequency factor, k_0, have been calculated according to Arrhenius law ; $\ln k_1 = \ln k_0 - \frac{E_a}{RT}$

From Figure 4.1 an activation energy of 60 kJ/mol and a frequency factor 36·103L /(mol.min) are obtained. These values are in good agreement with previous studies [Lehmus et al., 1999; Lee et al., 2002]. Table 4.3 gives the equilibrium constant, *K*, determined at various temperatures. Initially, an equimolar ratio of the reactants has been used. The equilibrium constants are calculated from the acid content when the reaction is in equilibrium. It can be seen that with increasing temperature, the equilibrium conversion also increases.

Table 4.3 Esterification equilibrium constants at different temperatures

Temperature(K)	Keq
328	2.3
348	2.9
373	3.4
398	4.1
408	4.9

Source: A.W. Verkerk, et al Tech *University Eindhoven (2003) Proefschrift– ISBN 90-386-2944-3*

4.3.1 Model validation:

In this section before going to the validation we solve the set of differential equations by Polymath (RKF045) and get the concentration profiles. These simulation results were compared with available experimental data of Lee et al.(2002) for the conditions of temperature, T=348K, CA0= CB0 =3.92 mol/lit. The model results of concentrations of acid, base, ester and water were compared with experimental results and are shown in the following figures 4.2 and 4.3 respectively. From figure 4.2 and 4.3 it is clear that the model fits the experimental values accurately. From equation (4.1) it is clear that if water is removed faster than reaction moves in forward direction rapidly (Le chatelier principle). In figure 4.3 with pervaporation there is more removal of water takes place and hence ester formation is increases in case of pervaporation.

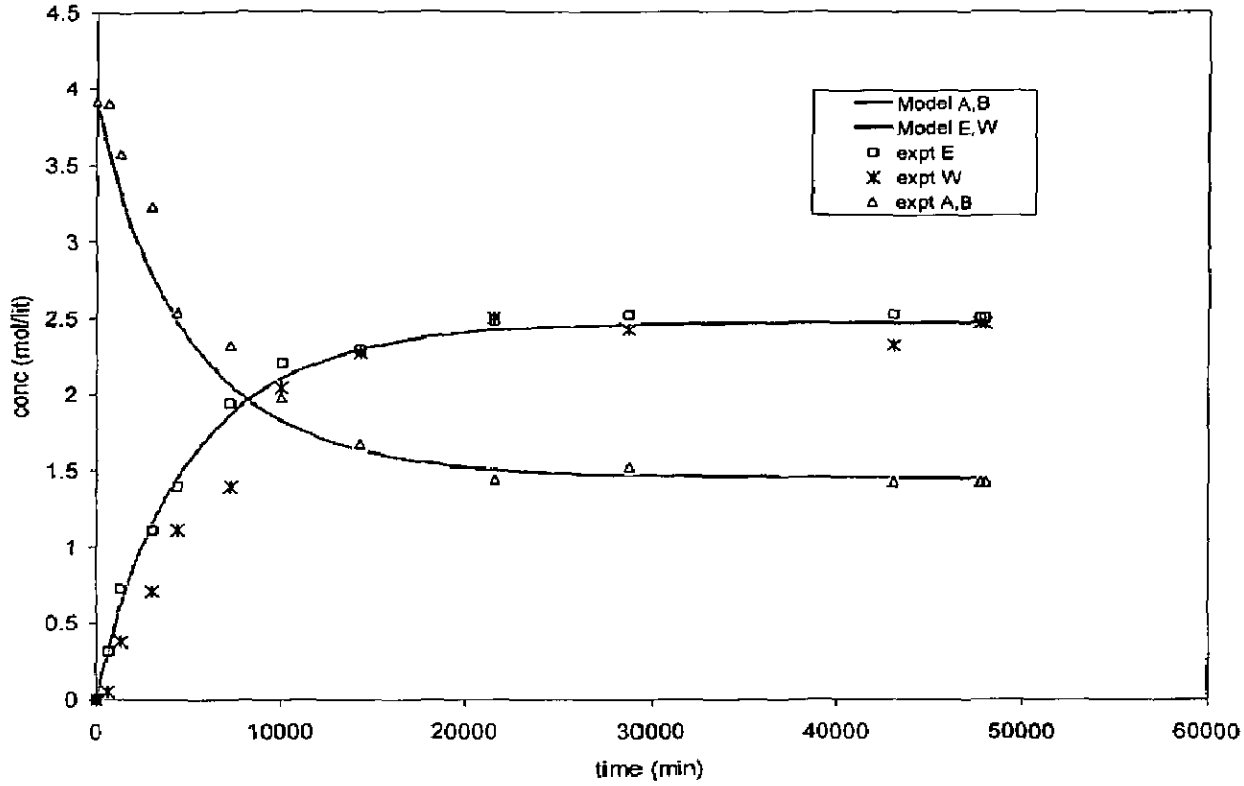

Figure 4.2 Concentration profiles for the esterification of levulinic acid with *n*-amyl alcohol at 348 K. without pervaporation.

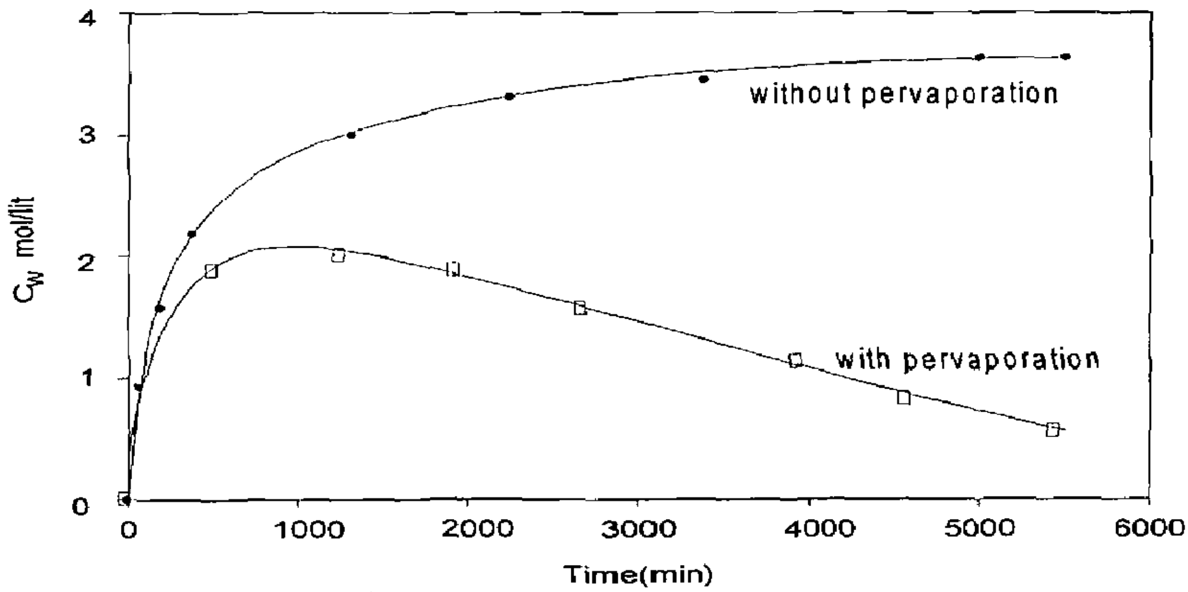

Fig 4.3 Water concentration profile compared with experimental points for esterification with and without pervaporation; T=408K, $C_{B0}/C_{A0}=1$

4.3.2 Effect of Water 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 of membrane used, 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. From the following figure it is seen that flux at higher temperature is high as compared to lower temperature. It was clearly observed that there were slight increased in the conversion as we increased the flux; this was because of the reaction limitations.

Table 4.4 Experimental Data for the water flux

Pw(atm) at T=348K	Jw(kg/(m2.hr))	Pw(atm) at T=408K	Jw kg/(m^2.min)
0.066	0.039	0.514	0.219
0.096	0.052	0.605	0.258
0.110	0.065	0.660	0.297
		0.779	0.396
		0.840	0.448

Source: Arjan W. Verkerk et al(2003) technical university Eindhoven,Proefschrift. ISBN 90-386-2944-3

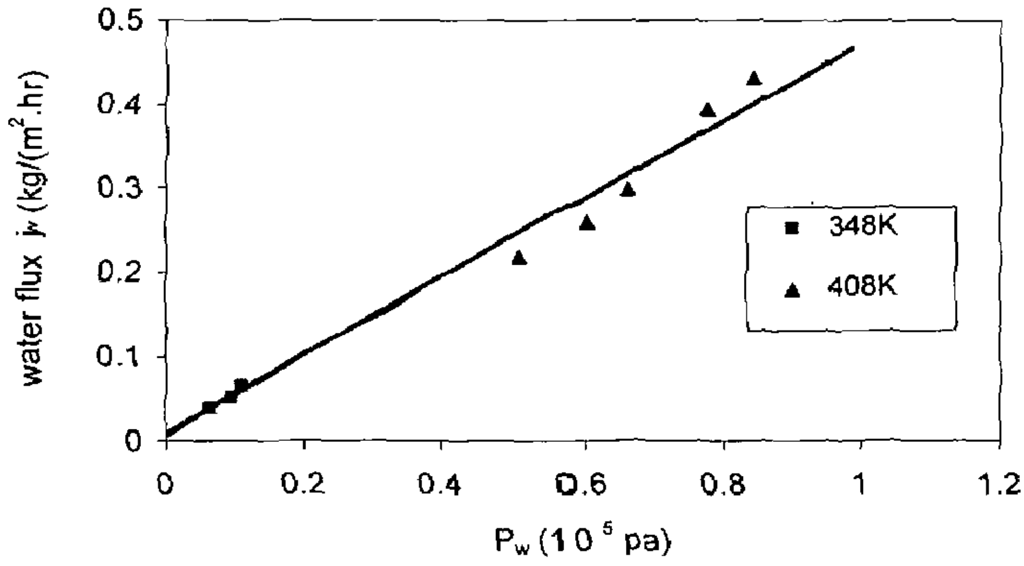

Figure 4.4.The water flux as a function of the driving force for water obtained during the pervaporation-assisted esterification

4.3.3 Esterification with and without pervaporation:

Figure 4.5a shows the concentration profile of the ester as a function of time for the reaction with and without pervaporation at 348 K. Without pervaporation, equilibrium is reached after approximately 500 h. In the case of reaction combined with pervaporation also the concentration of water as a function of time is given. Initially, the membrane cannot remove all the water formed. After 50 h, more water is removed by the membrane than is formed by the reaction. From this time onwards, the backward reaction decreases because the water concentration decreases. As a result, an increase in ester concentration is observed as compared to the equilibrium reaction. The model predicts that even a conversion of 100% is possible. Figure 4.5b shows that the conversion of n-amyl levulinate with and without pervaporation at 408K.

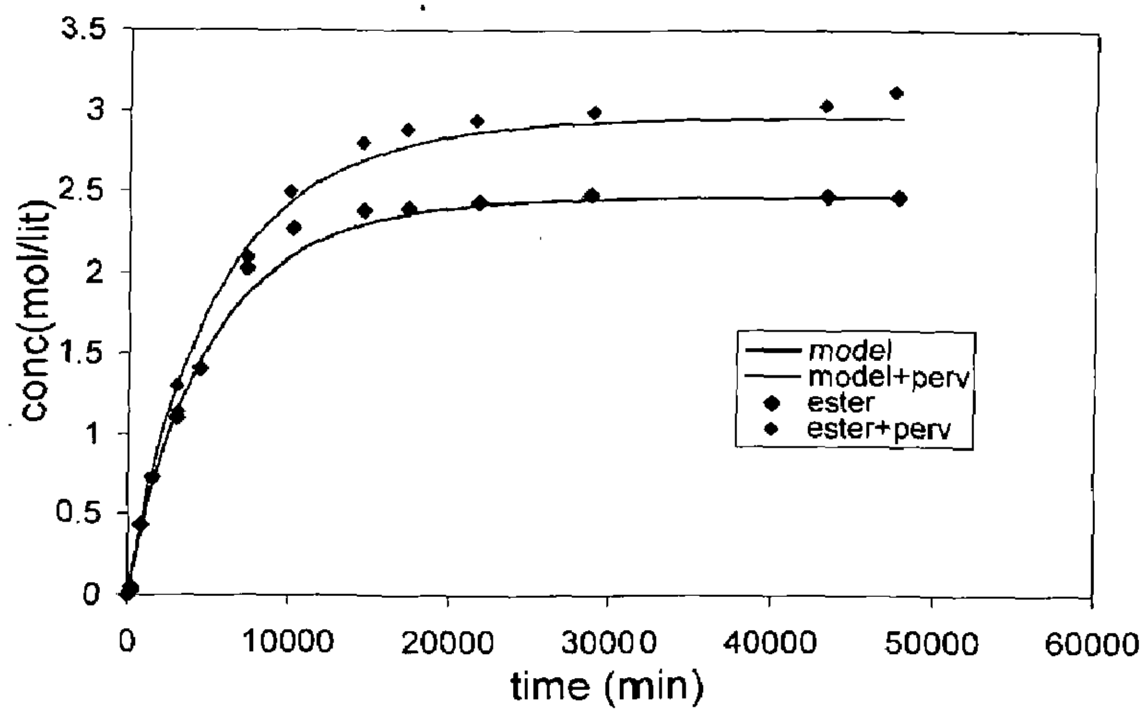

Figure 4.5 a. The conversion of *n*-amyl levulinate with and without pervaporation (PV) at T=348K, S/V 8 m^{-1} .

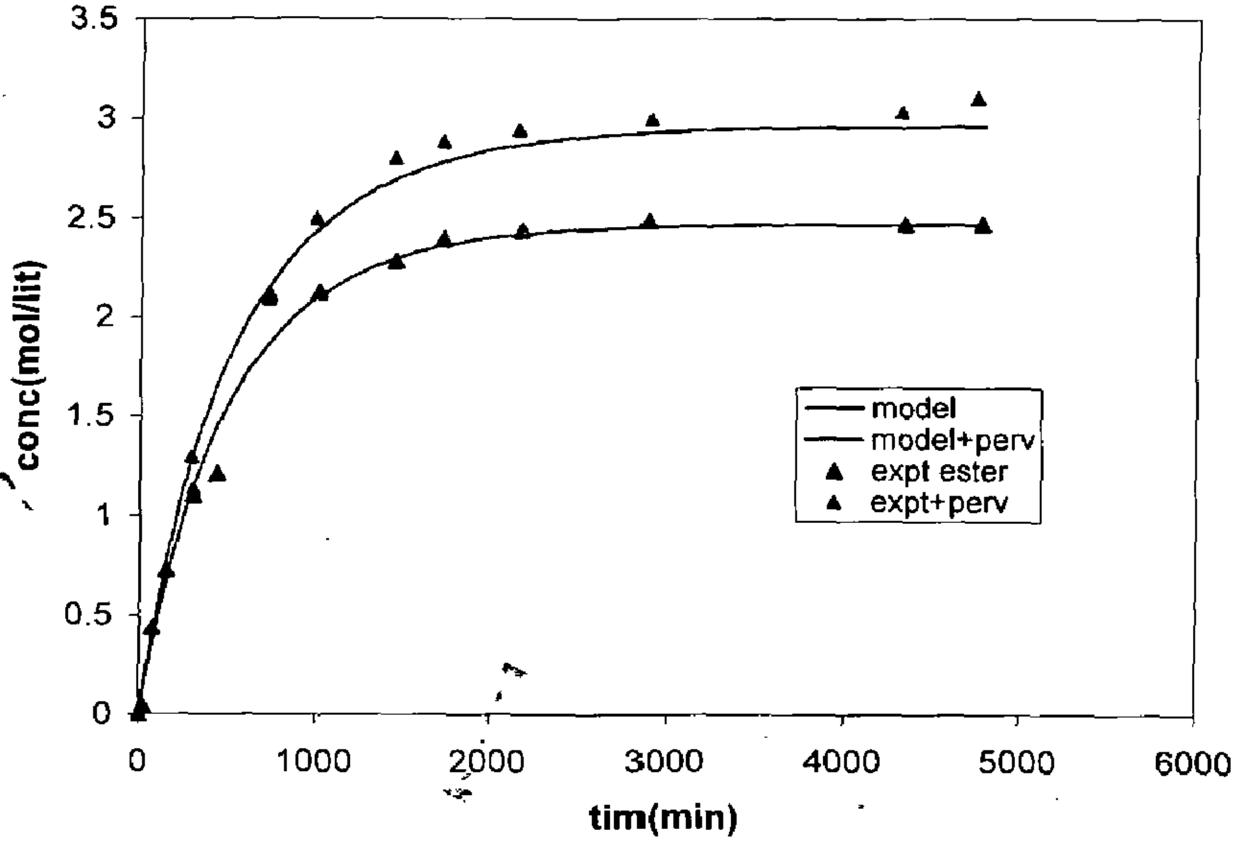

Figure 4.5 b The conversion of n-amyl levulinate with and without pervaporation (PV) at T= 408 K.S/V=8 m^{-1}

4.3.4 Effect of Temperature on Conversion:

Comparing Figures4.5a and 4.5b it can be seen that the reaction at 408 K is much faster than the reaction at 348 K. The conversion towards the ester with and without pervaporation and the water concentration are modeled reasonably well for both temperatures.The concentration profiles as a function of time are described using a value for k_1 which is obtained from the initial slope of the concentration profile and the water flux presented in Figure 4.4. At 408 K the reaction without pervaporation reaches equilibrium after 40 h, according to the model calculations an equilibrium conversion of 70 % is obtained. In the case of reaction combined with pervaporation a monotonous increase in the concentration of the ester is observed, and after 80 h a conversion of about 98 % is obtained.

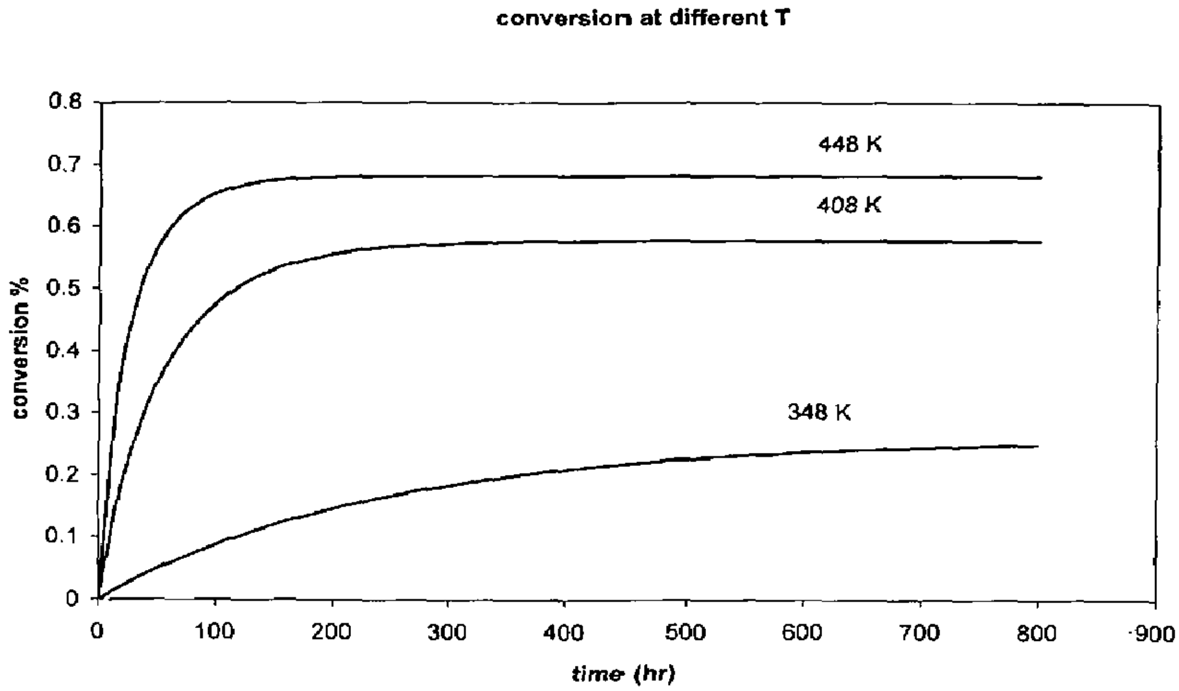

Figure 4.6 conversion of levulinic acid and *n*-amyl alcohol for the esterification at three different temperatures without pervaporation.

For this type of reactions there is a strong influence of the temperature, because the equilibrium constant is relatively low. To illustrate this, the hybrid process is modeled at an even higher temperature. In Figure 4.6 a comparison is made between the conversion at 348 K, 408 K and 448 K. The results for the conversion at 448 K are calculated for a system where the values of k_1, K and J_W are extrapolated from the data at lower temperatures. In above figure it is seen that a conversion of 70% is achieved in 200hr at 448K, instead of 400 hr at 408 K.

4.3.5 Influence of Initial Molar Ratio:

In esterification reactions the water formation is a big problem. The main purpose of the pervaporation membrane is to remove the water formed during the reaction, so that the equilibrium conversion can be exceeded (Lee Chatelier principle). A general introduction on membranes is given with emphasis on separation performance and the integration with reactions. Furthermore, from figure it is seen that the water concentration is increases with respect to R_0 keeping S/V constant 8 m^{-1} and hence the ester conversion is lower at higher R_0.

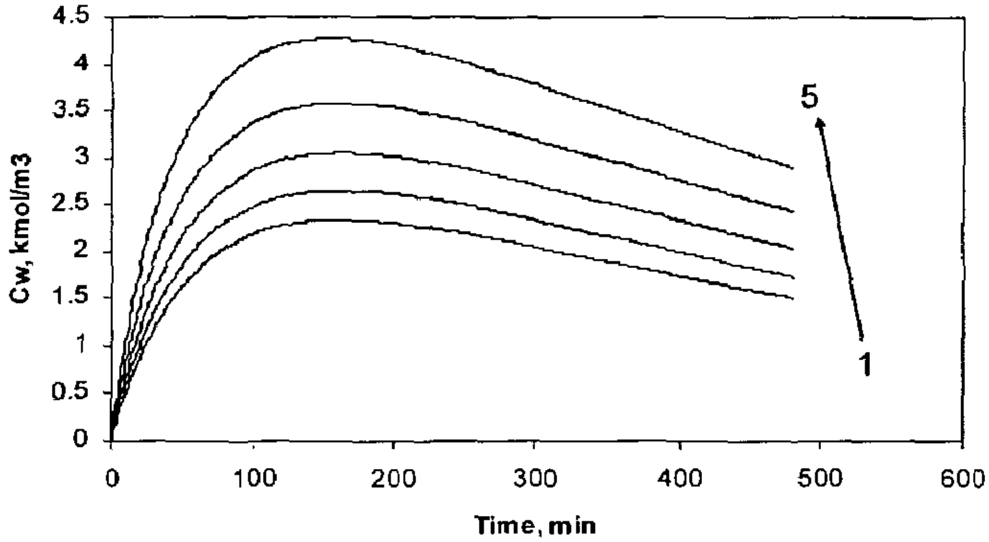

Figure 4.7 Effect of change in initial molar reactant on water concentration.
R_o for curve 1= 1; 2= 1.2; 3=1.5; 1.6; 4= 2; 5= 2.5
(T=408K; C_C=0.0295 kmol/m3; S/V=8 m^{-1})

4.3.6 Influence of Ratio of (S/V):

The equilibrium shift of the esterification reaction is depend on the amount of water in the reaction mixture, as we increase the ratio area of membrane with reaction volume, 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 n amyl alcohol and water content in reaction mixture were presented

In Figure 4.6 the S/V ratio was varied from 0 to 30 m^{-1} for 408K S/V=0 meace it is without pervaporation in this case it is seen that maximum water concentration hence minimum ester formation. Therefore on increasing S/V ratio water concentration is decreases with ester conversion is increases at the reactant molar ratio of Ro=1.5 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.

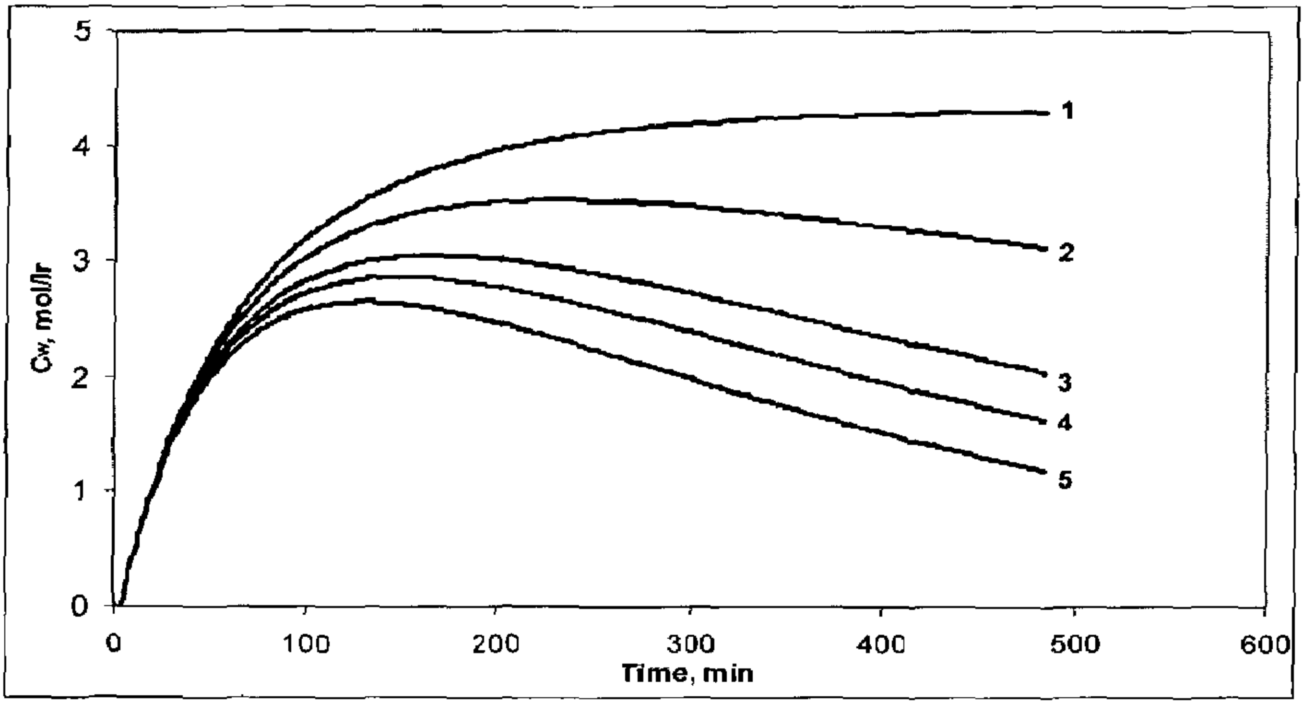

Figure 4.8: Effect of change in S/V ratio on water concentration.
S/V ratio for curve 1= 0 m^{-1}, 2= 5 m^{-1}, 3= 15 m^{-1}, 4= 25 m^{-1}, 5= 30 m^{-1}
(T=408K; C_C=0.0298 kmol/m^3; Ro=1.5)

4.4 Concluding Remarks:

The mathematical model results were compared with experimental values by (Lehmus et al.,1999; Lee et al., 2002) are best agreement.The effect of various parameters like Temperature, R_0, S/V ratio etc. on the conversion of ester are studied and it is found that the conversion of Levulinic acid were inhanced as compared to conventional reactor

By removing the water produced in the reaction using the supported silica pervaporation membrane, a conversion of 100% towards the ester is possible. A theoretical model describes the reaction kinetics for the hybrid process reasonably well using the separately determined reaction kinetics. The reaction at a temperature of 408 K is about 14 times faster than the reaction at a temperature of 348 K, which is mainly determined by the ratio of the forward reaction rate constants at the two temperatures.

Esterification of Acetic acid with Isopropanol

5.1 SYSTEM DESCRIPTION:

In this chapter we consider the pervaporation assisted esterification of Acetic acid with isopropanol in the presence of membrane PERVAP® 2201. The influence of several process variables, such as process temperature, initial molar ratio of acetic acid and isopropanol the ratio of effective membrane area over the volume of reacting mixture catalyst content, and flux on the esterification have been discussed.

Table 5.1 Value and range of the various parameters used in Modeling

Parameter	**Notations and unit**	**Value/ Range**
Initial molar ratio of isopropanol and acetic acid	$R_0=C_{B0}/ C_{A0}$	1-2
Initial molar ratio of water to isopropyl acetate	$R'_0=C_w/C_{iPrOAc}$	1.5-3.5
Ratio of membrane area to Reaction volume	S/V m^2/m^3	0-90
Equilibrium constant	$Keq=K_1/K_2$	1-5
Temperature	T (K)	320-450
Reaction time	t (min)	6000
Frequency factor	K_0 lit/(mol.min)	36000
Activation energies	E_a, E_b joul/mol	64590 73630

5.2 · Determination of Kinetic Parameters:

In this section the results of the reaction kinetics for the heterogeneously catalyzed synthesis and hydrolysis of isopropyl acetate are presented. Different kinetic models have been used to describe the esterification reaction catalyzed by ion exchange resins. The pseudo-homogeneous model assumes complete swelling of the polymeric catalyst in contact with polar solvents, leading to an easy access of the reactants to the active sites. This model has successfully been used for the description of esterification and transesterification reactions catalyzed by ion-exchange resins. An Arrhenius equation for temperature dependence for the forward and backward reaction was used:

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

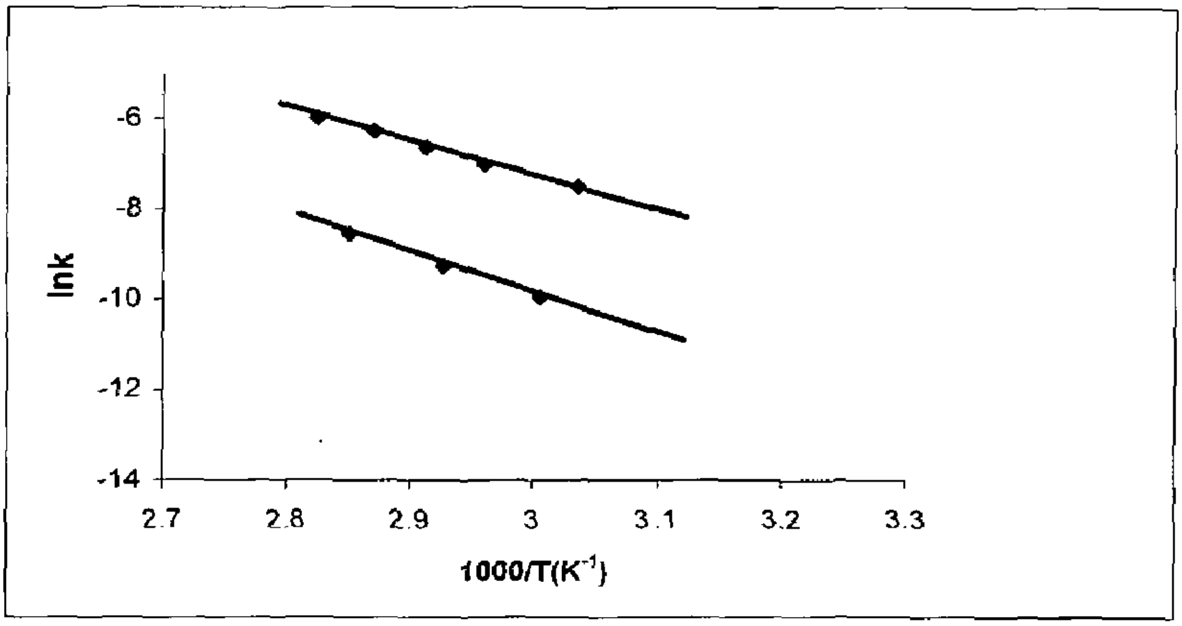

Fig 5.1 Arrhenius plot for the isopropyl acetate synthesis (K_1) and its hydrolysis (K_2). The lines represent the results of the model and points shows experimental values.

Kinetic measurements were performed in a temperature range from 329.15 to 353.85K for the esterification reaction and from 332.15 and 350.90K for the hydrolysis reaction. Typical results are shown in Fig.5.1. It can be seen that the reaction rate increases with increasing reaction temperature. Activation energies of 64.59 and 73.63 kJ/mol for the model were obtained for the esterification and hydrolysis reactions, respectively.

5.3. Results and discussion:

5.3.1. Model Validation:

Before going to the simulation we need the model validation first. In this situation we compared the simulation results with available experimental data of Maria et al (2006) for the condition of T= 348K, catalyst concentration C_C= 6 wait % the ratio of effective membrane area over volume of reaction mixture S/V = 30 m^{-1} initial molar ratio of isopropanol to acetic acid is 1.5 The model results of conversion of acetic acid and water concentration is shown in the following figure 5.2 and 5.3 respectively. It shows that the proposed model results were in excellent agreement with the available experimental results. Slightly over-predictions were observed for the time range of 200 to 300 min for conversion of isopropanol with respect to time.

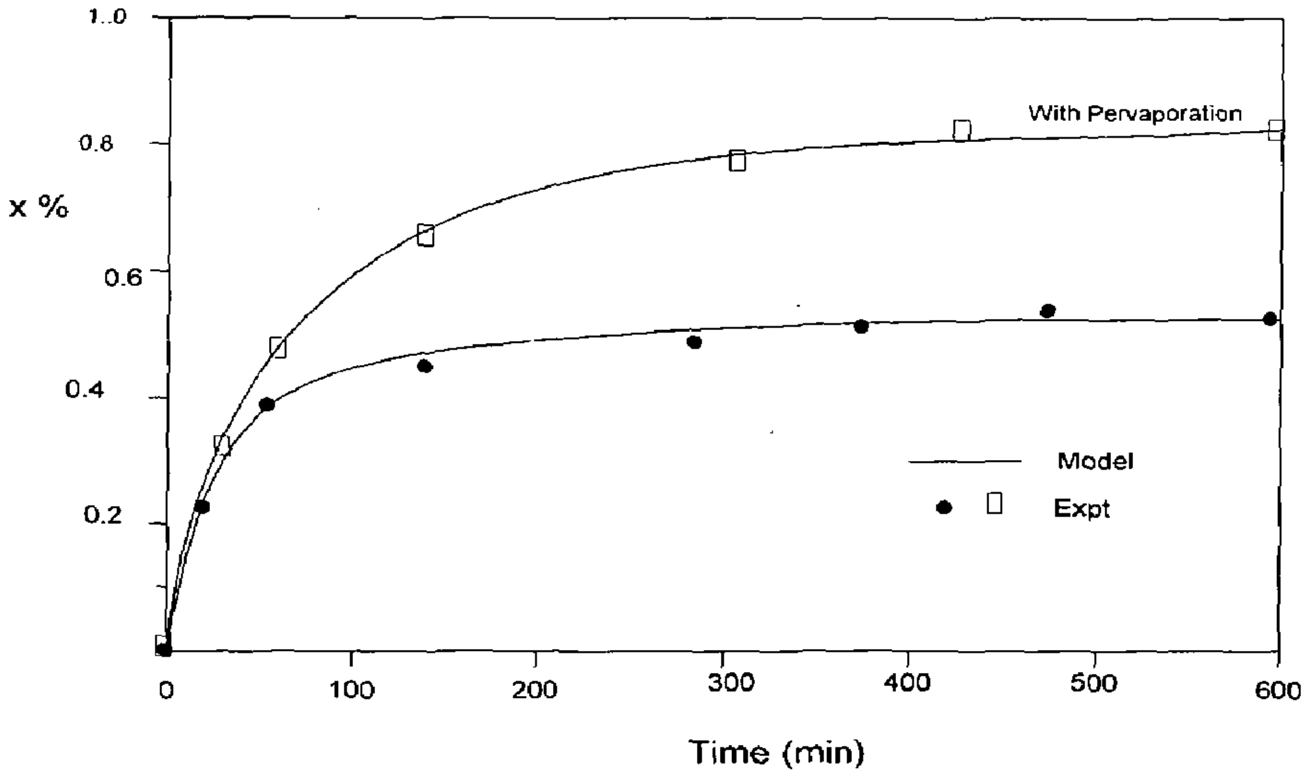

Fig 5.2 Conversion of isopropyl acetate with and without pervaporation at T= 348K, Catalyst =6 wait % and C_{B0}/C_{A0} =1.5

5.3.2 Effect of water concentration:

The water profile in the reacting mixture for the pervaporation-supported process shows that at the beginning the water content increases continuously until a maximum is reached. After this maximum, the water content decrease continuously and tends to go to zero. This means, that at the beginning of the process, the water production is faster than its removal by pervaporation due to the low water content. As the reaction proceeds, the water concentration increases continuously until a maximum is reached in which its removal by permeation rate is equal to its production by esterification. After the water content has reached the maximum value, the water removal by pervaporation from the reaction mixture is faster than its formation rate by esterification. As a consequence, the water concentration in the reactor decreases continuously. Due to the continuous water removal from the reaction mixture, the conversion obtained with the esterification pervaporation reactor is distinctly higher than the maximum equilibrium conversion, which can be achieved with a conventional CSTR reactor without pervaporation unit. Conversions higher than 90% can easily be achieved by combination with a pervaporation unit..

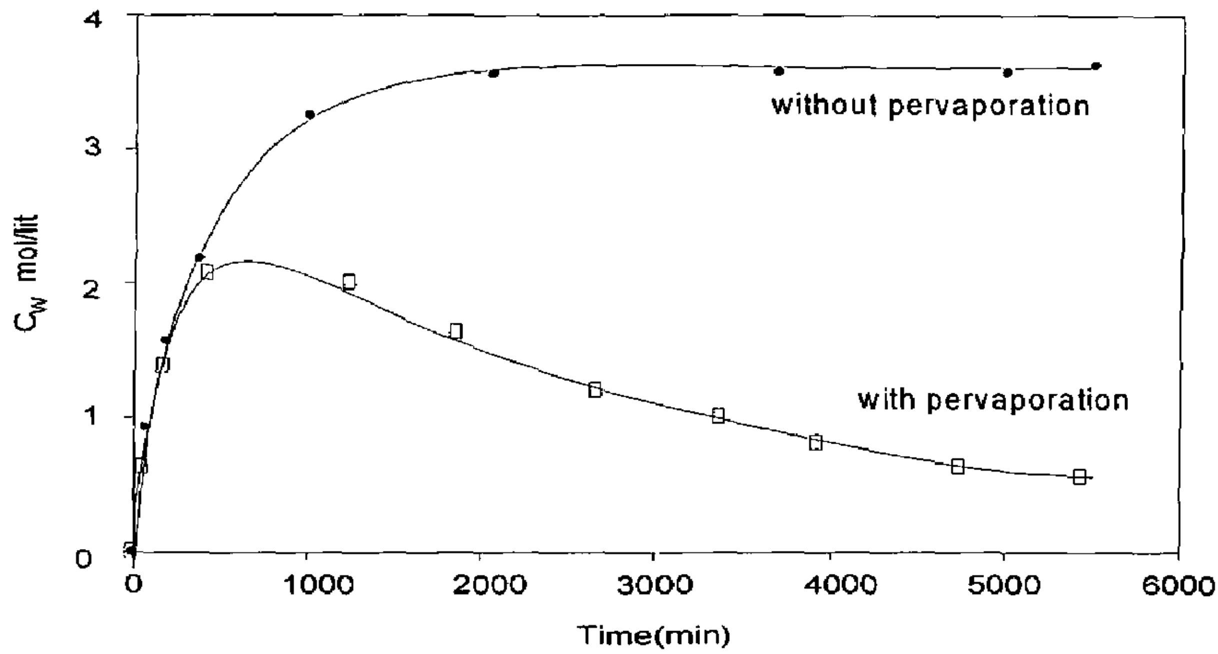

Fig 5.3 water concentration in the reaction mixture for esterification both with and without pervaporation at T=348K,C_C=6 wait %, C_{B0}/C_{A0}=1.5, S/V = 30 m^{-1}.

5.3.3. Effect of feed composition:

The water feed composition was varied between 2 and 20 wt.%. The composition range for the other components in the feed solution was as follows: isopropanol 30–50 wt.%, isopropyl acetate 21–51 wt.% and acetic acid 2–20 wt.%. In Fig. 5.4, the experimental water permeate flux is plotted as function of water weight fraction in the feed at different operating temperatures. For each operating temperature the flux increased with water feed composition due to a higher swelling of the membrane. The flux of the other organic components also increased with the water content in the mixture, probably caused by the coupled transport with water. In the composition range investigated in this work, the water flux was always much higher than the fluxes of the other components and close to the values of the total permeate flux.

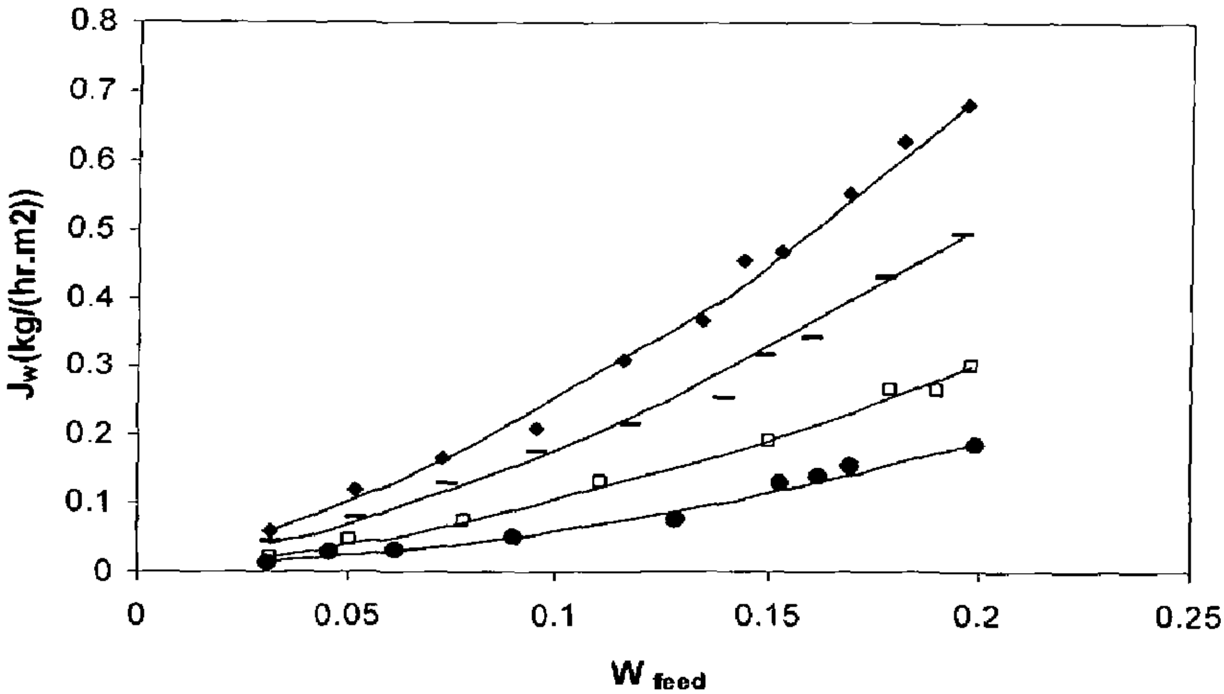

Fig 5.4 Water permeate flux vs. water weight fraction in the feed at different feed temperatures 321.15 K; (•) 331.15 K; (□) 341.15 K; (-) 348.15 K (■). The solid lines represent the results of the models.

5.3.4. Effect of temperature:

The operating temperature has a direct influence on the permeation and reaction rate. From the previous kinetic and pervaporation studies. It can be concluded that with increasing temperature both, the permeation rate through the membrane and the water production rate by esterification increase. In Fig. 5.5 the simulation results obtained at different operating temperatures are presented. From this figure it can be concluded that the maximum water content is reached faster at higher temperatures showing that the effect of the operating temperature on the water production is stronger than on the water permeation rate. After this maximum, the decreasing in water concentration in the reacting medium is faster at higher temperatures due to the higher permeability of the membrane with temperature. A similar temperature dependence has been described by other authors in the study of esterification pervaporation supported processes.

The membrane used in our work, PERVAP® 2201 shows a maximum long term temperature of 100 °C. By temperatures above 100 °C the membrane will be damaged, which sets a limit on the vapor pressure that can be used to drive the pervaporation. There is a good agreement between experimental data and the values calculated with the model proposed in this work can be observed, as shown in Fig. 5.5 and 5.6. Therefore this model was used to study the influence of the different operating parameters temperature, catalyst concentration, reactant ratio, and ratio of membrane area over reaction volume and initial molar ratio.

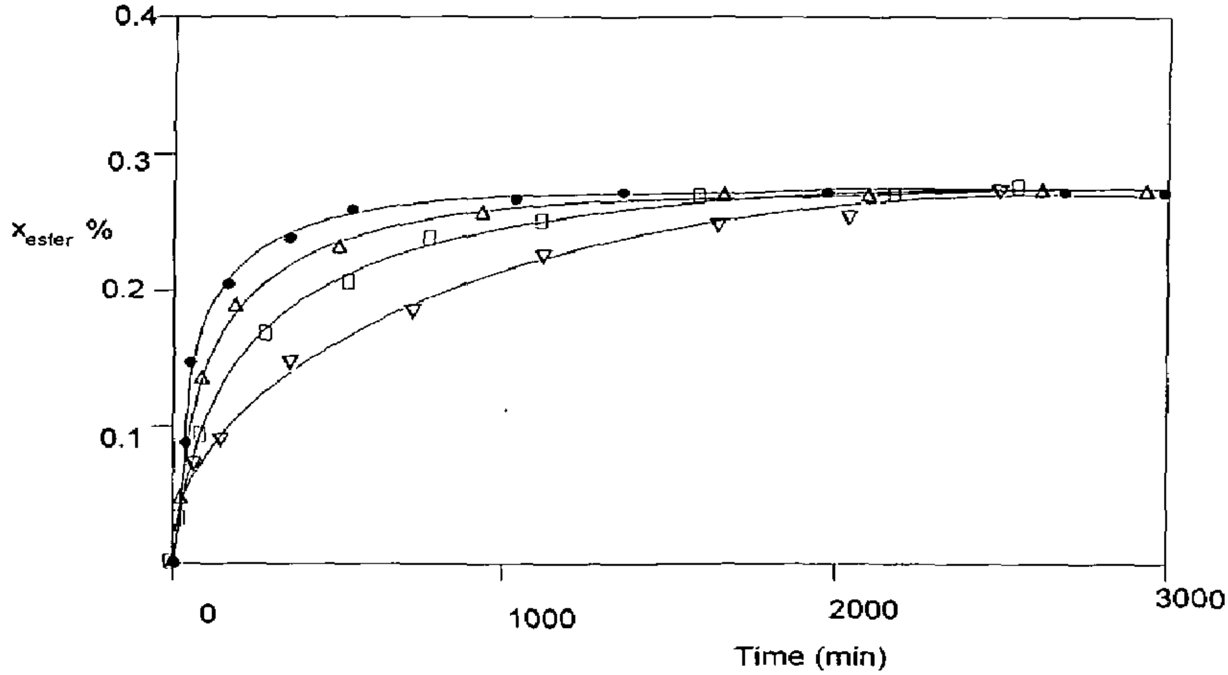

Fig 5.5 Isopropyl acetate mole fraction vs. time at different temperatures for the esterification reaction (catalyst = 6 wt.%, C_{B0}/C_{A0}= 2): (▽) 329.15 K; (□) 337.65 K; (Δ) 343.15 K; (•)353.85K.

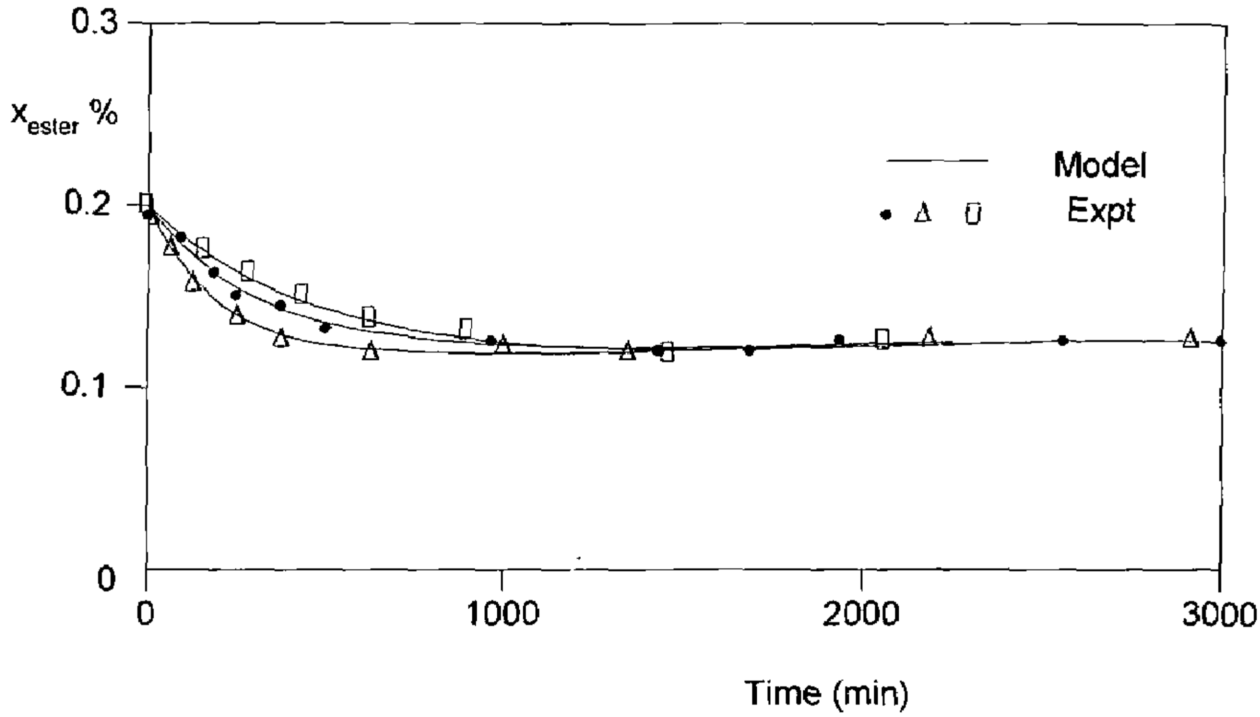

Fig 5.6 for the hydrolysis reaction (catalyst = 6 wt.%, C_{B0}/C_{A0} = 2.5) (◦)332.65K; (•)341.40K;(Δ) The continuous lines represent the results of the model.

5.3.5 Effect of initial molar reactant ratio:

The initial molar ratio of isopropanol to acetic acid C_{B0}/C_{A0} was varied from 1 to 2 for the esterification reaction. For the hydrolysis reaction the initial molar ratio of water to isopropyl acetate (C_W/C_{iPrOAc}) was varied from 1.5 to3.5.Different experiments were carried out in the esterification pervaporation reactor at different initial reactant molar ratios, C_{B0}/C_{A0}. In Figs. 5.7, 5.8 and 5.9 the experimental results are matched with the simulation results are presented. For a better comparison of the different performances only the simulation results are plotted in Fig. 5.9. When the C_{B0}/C_{A0} ratio increases the value of the maximum water content decrease, but the time was found to be nearly the same in the range of C_{B0}/C_{A0} studied.

In this work the lower values of the maximum water content are due to the dilution effect by increasing the initial molar reactant ratio. The same behavior has been described in the literature for the study of the coupling effect of esterification with pervaporation. In conventional reactors higher equilibrium conversions are obtained by increasing the initial molar reactant ratio, but the limited reactant will never react completely.

In Fig. 5.8 simulation results are plotted for the case that water is already present at the beginning of the reaction for a conventional reactor and for pervaporation coupled reactor. An initial water content of 10 wt.% was used for the simulation. In a conventional reactor, the equilibrium conversion decreases when water is present at the beginning of the process. When a pervaporation unit is used, the effect is less drastic. By increasing the water concentration in the pervaporation coupled reactor, the permeation rate through the membrane increases and consequently the water content in the reactor will decrease rapidly.

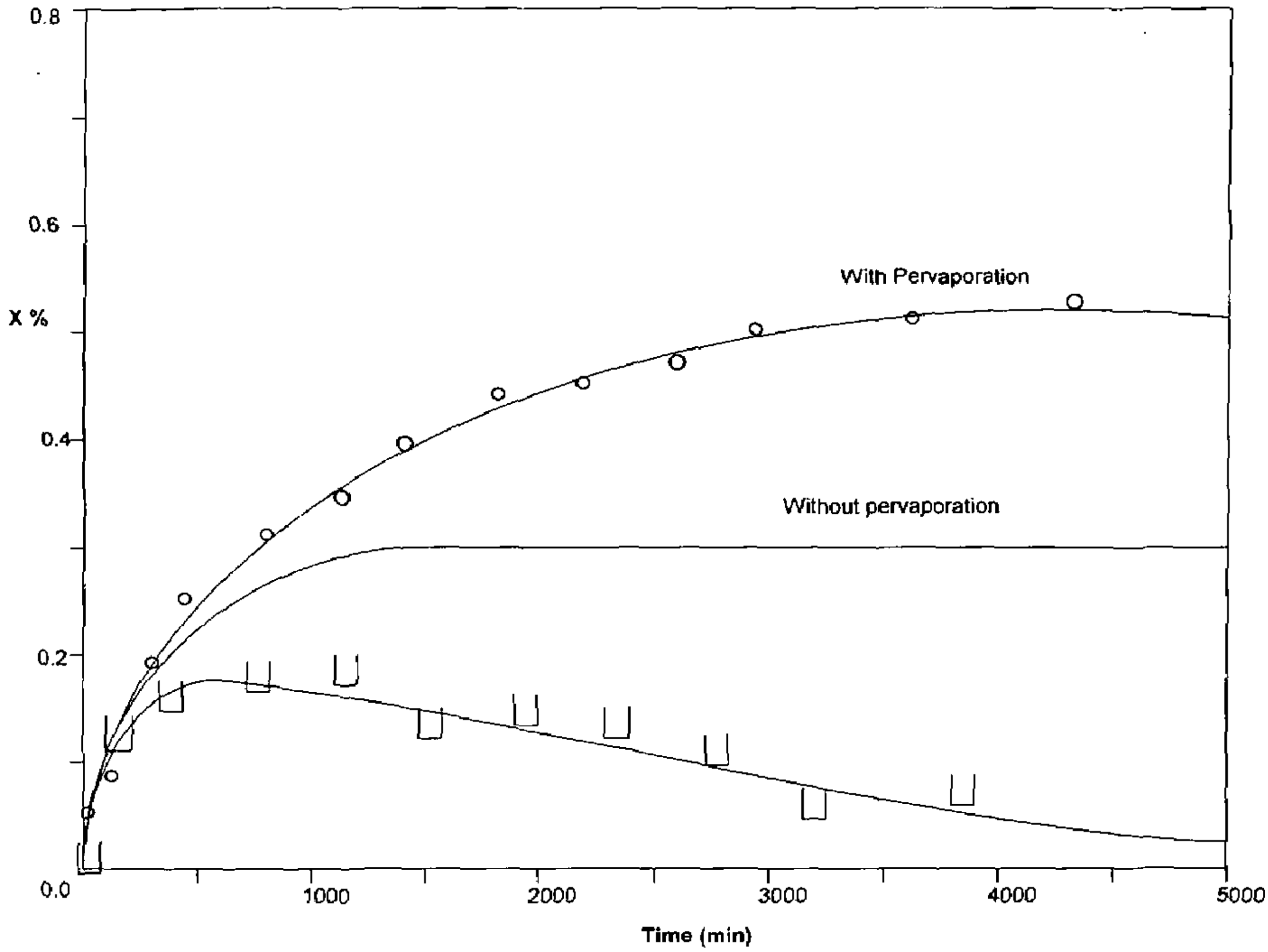

Fig 5.7 Variation of the mole fraction of isopropanol acetate (∘) and water(•) at C_{IPA}/C_{HOAc}=2.0;T $_{reaction}$ = 337K; Tperv=334K;A/V_0 = 30m-1;catalyst=6 wt%; The horizontal line represent corresponds to the esterification without pervapaporation.

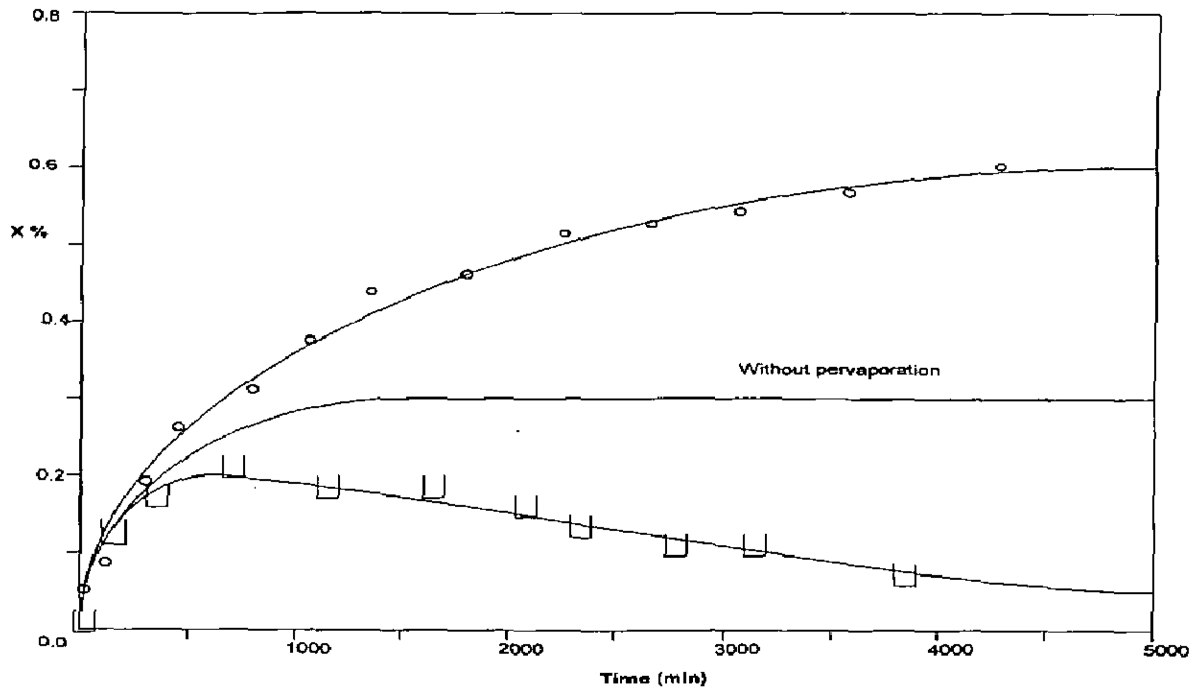

Fig 5.8 Variation of the mole fraction of isopropanol acetate (○) and water (•) at C_{B0}/C_{A0}=1.5;T $_{reaction}$ = 337K; Tperv =334K;S/V_0 = 30m^{-1};catalyst=6 wt%; The horizontal line represent corresponds to the esterification without pervapaporation

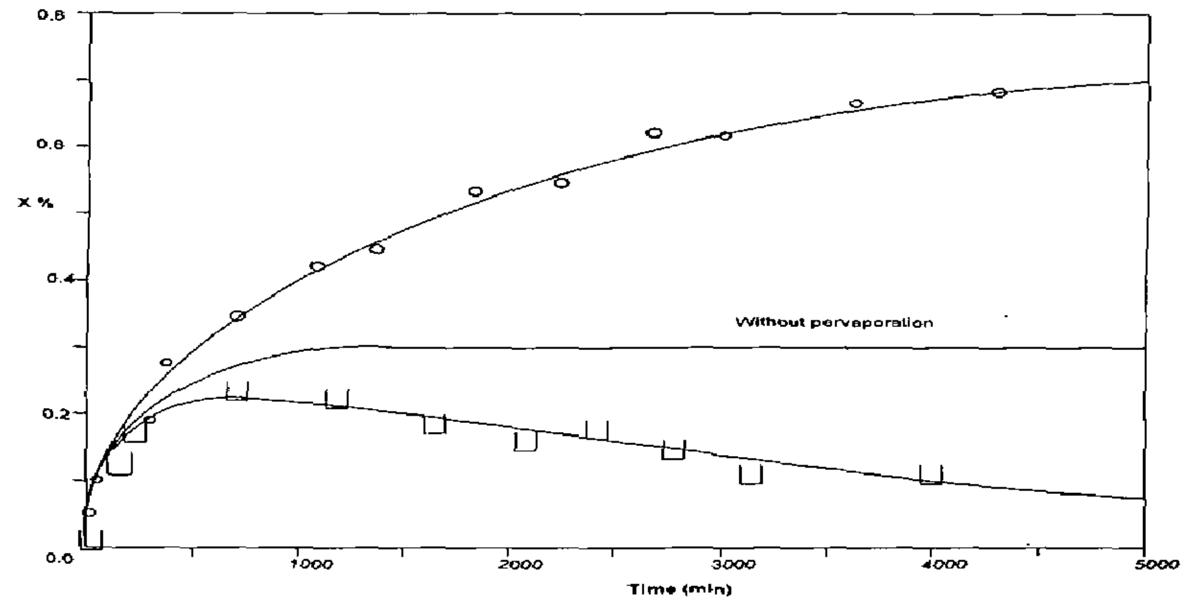

Fig 5.9 Variation of the mole fraction of isopropanol acetate (○) and water (•) at C_{B0}/C_{A0}= 1 T $_{reaction}$ = 337K; Tperv=334K;S/V_0 = 30m-1;catalyst = 6 wt%; The horizontal line represent corresponds to the esterification without pervapaporation.

5.3.6 Effect of the membrane area to initial solution volume ratio (S/V_0)

In a esterification–pervaporation reactor a low permeability of the membrane can be compensated by using larger membrane areas. In Fig. 5.10 the simulation results obtained for the performance of a esterification–pervaporation reactor at different S/V_0 ratio are presented. With increasing S/V_0 ratio higher isopropyl acetate compositions in the reactor are obtained. The maximum water concentration is reached faster at higher S/V_0 values, but the maximum value decreases with the S/V_0 ratio. Increasing the membrane area per unit of reaction volume, water will be extracted faster and obviously, the water concentration in the reactor will decrease faster.

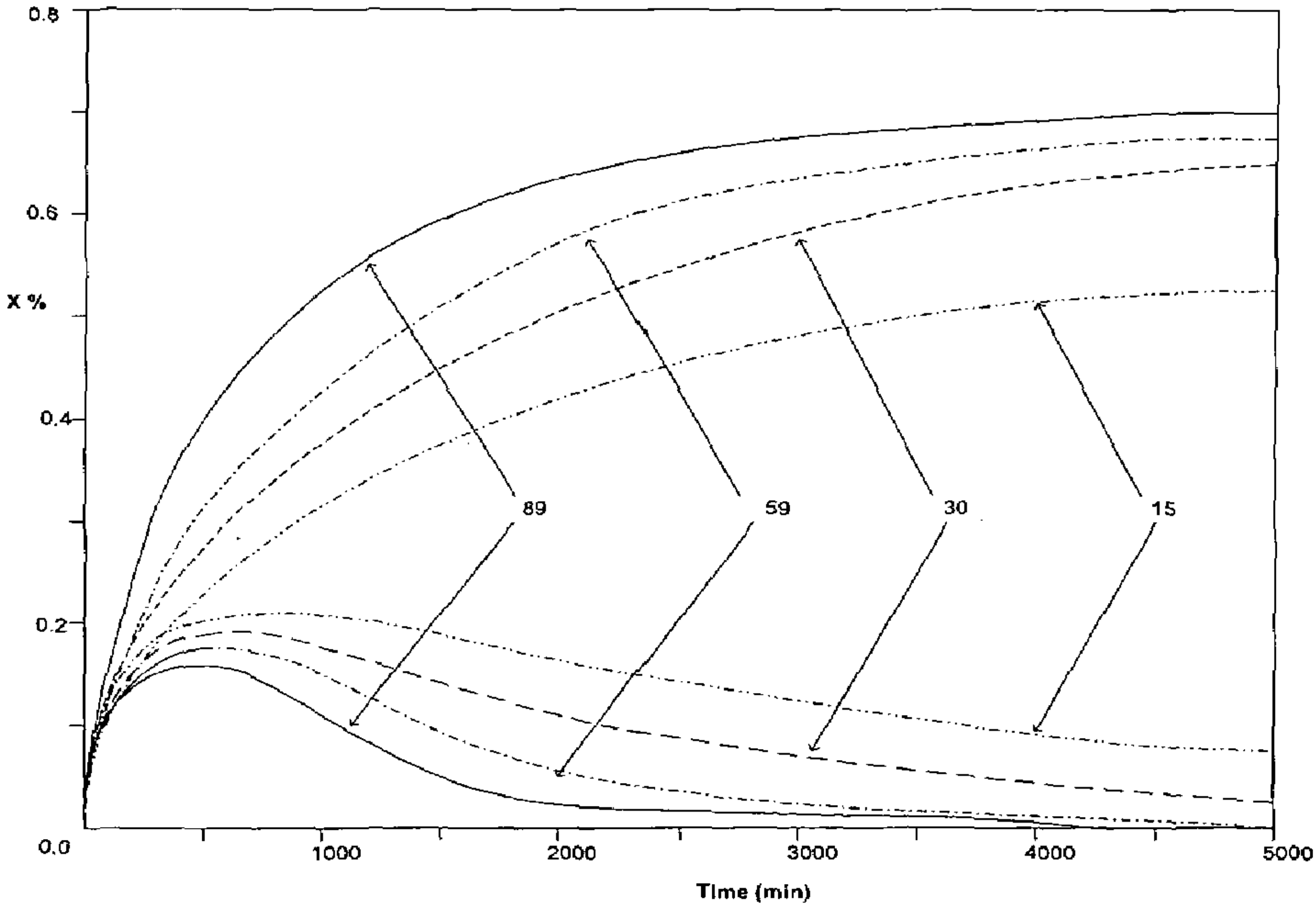

Fig 5.10 Effect of the ratio S/V_0 on the performance of the esterification pervaporation reactor T=343.15K; catalyst = 6 wait %; C_{B0}/C_{A0}=1.5

A zero value of this ratio corresponds to a conventional reactor without pervaporation unit. At a certain time, with increasing S/V_0 ratio higher conversions are achieved. From Fig. 5.10 it can be concluded that no huge improvements can be obtained using a S/V_0 ratio of $89m^{-1}$.The selection of the ratio of the membrane area and the reaction volume will normally be determined from an economical point of view.

5.3.7 Effect of amount of catalyst:

The catalyst concentration was varied between 2 and 13 wt.% for the esterification reaction and from 3.5 to 10 wt.% for the hydrolysis reaction. As expected, an increase of the catalyst amount leads to an increase of the reaction rate and hence the conversion. Consequently the equilibrium is reached faster with increasing catalyst concentration Fig. 5.13 shows a linear relationship between the initial reaction rate, expressed as moles per minute, and the amount of catalyst employed.

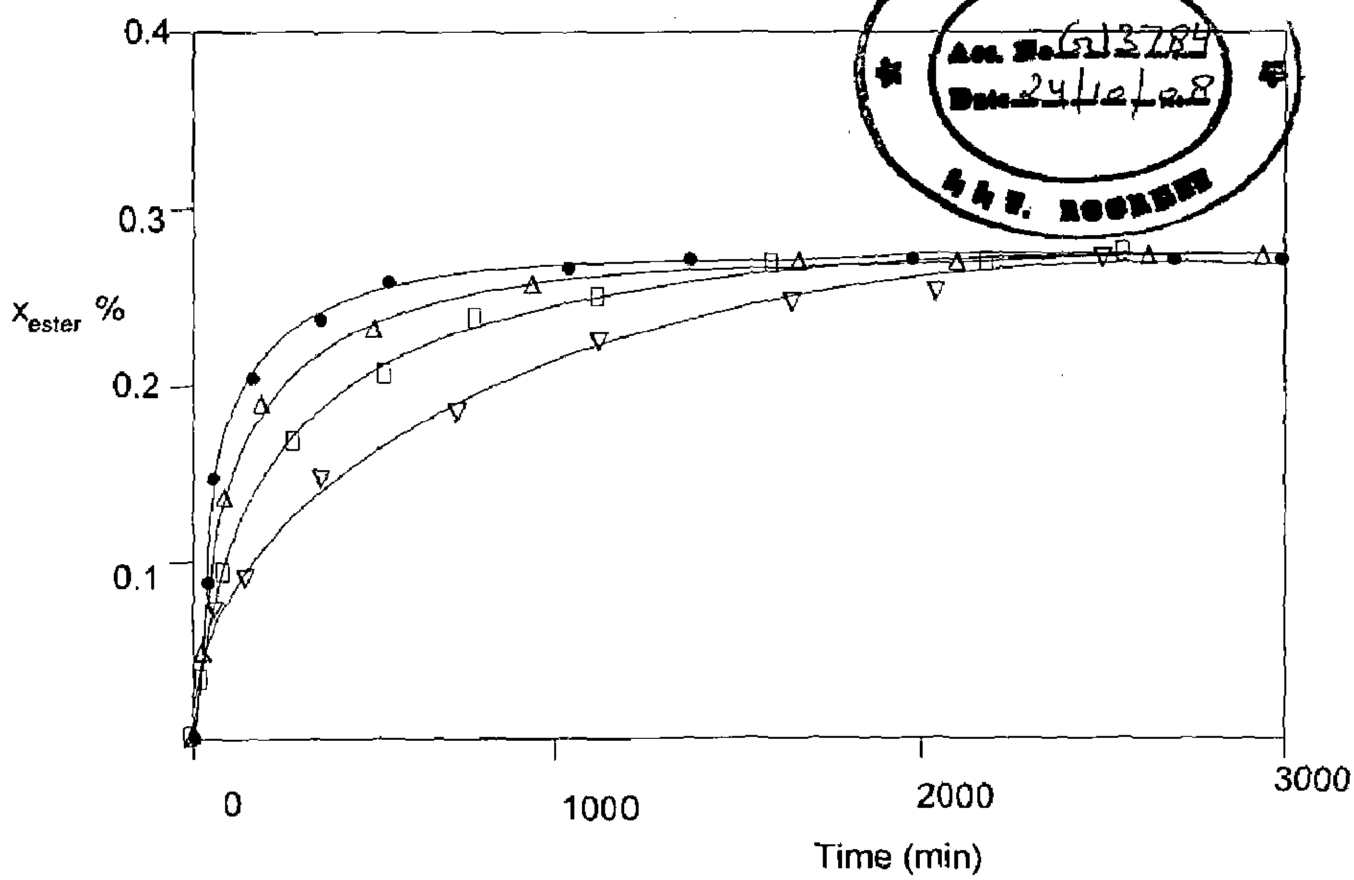

Fig 5.11 Isopropyl acetate mole fraction vs time at different catalyst loading for the esterification reaction T = 348.40 K,CB0/CA0=2; (∇) 2 wait %;(□) 6 wait %; (Δ) 10 wait %;(•) 13 wait %.

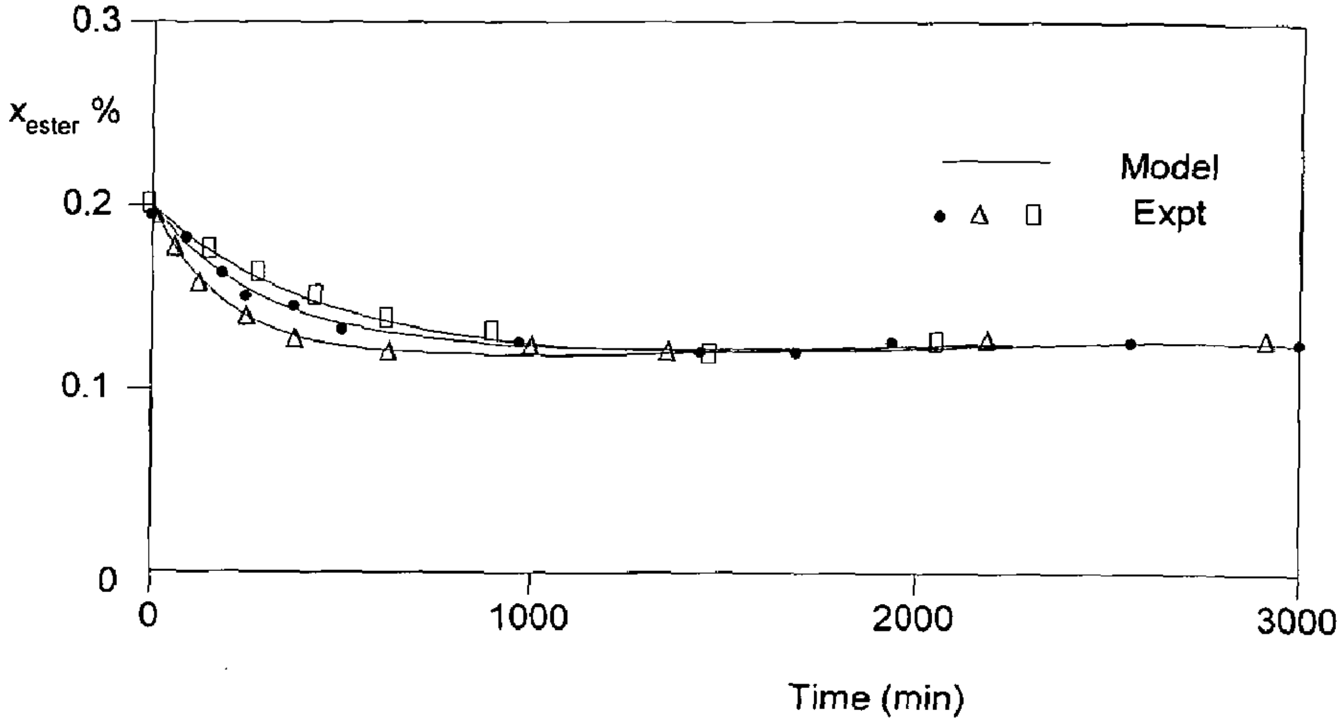

Fig 5.12 Isopropyl hydrolysis at different catalyst loading at T= 350.90K, CB0/CA0=2.5 (□) 3.5 wait %;(•) 6.0 wait %;(□)10 wait %; The continuous line represent the model.

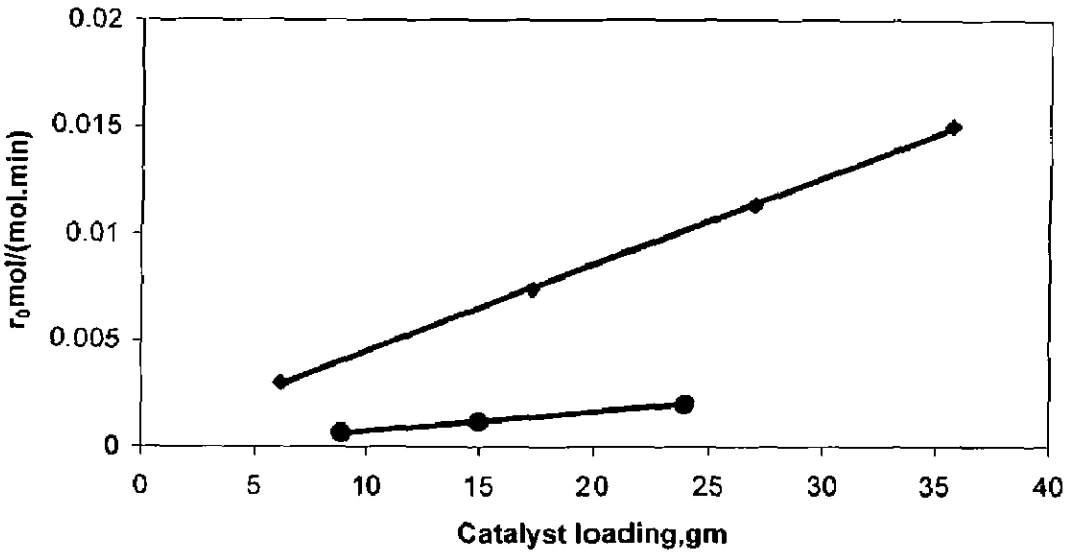

Fig. 5.13 Initial reaction rate vs. catalyst loading for the synthesis of isopropyl acetate (■) and its hydrolysis (•). The lines represent the results of the model.

5.4 Concluding Remarks:

The esterification of acetic acid with isopropanol combined with a pervaporation unit has been studied. The 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 used. The permeate flux was found to increase with the water content in the feed and the temperature.The experimental conversions achieved in the hybrid process were in all cases distinctly higher than the equilibrium limited conversion reached in a conventional reactor.

The influence of several important operating variables on the esterification pervaporation reactor performance has been analyzed. Pervaporation and reaction rate are both increased with the operating temperature. Decreasing the initial molar reactant ratio the ester rate formation increases significantly. When the S/Vo ratio increases higher ester conversions are obtained. Finally the effect of catalyst concentration has been considered showing that the final water content decreases with increasing catalyst concentration. From the results it can be concluded the right choice of these parameters has a great influence on the performance of the esterification pervaporation reactor.

The results obtained with the model are in good agreement with the experimental results obtained.

CHAPTER 6

ESTERIFICATION OF LACTIC ACID WITH METHANOL

The esterification of an aqueous solution of lactic acid with methanol is a reversible reaction. As excess of water amount is present in the reaction mixture, the conversion is greatly restricted by the chemical reaction equilibrium limitations. In this study the esterification kinetics of lactic acid with methanol both in the absence and presence of an ion exchange resin as a heterogeneous acid catalyst.

The esterification of aqueous lactic acid solution with methanol and its reverse reaction catalyzed by acidic cation exchange resins in a batch system was studied by Choi et al. The inhibiting effects of water and methanol on the resins were evaluated. The experimental data were correlated by a kinetic model that the inhibition by methanol and water was included. The reaction rate constants and the adsorption coefficients were determined from the experiments. The internal mass transfer was negligible since the resin size did not affect the reaction rate.

The reaction rate by sulfuric acid was larger than that by acidic resin at the initial period but the conversion of the reaction using sulfuric acid was smaller as reaction time increased. The sulfuric acid is less expensive than the resin, but the resins can be recycled several times, and they also offer various advantages over homogeneous catalyst. As the concentration of acidic resins and the reaction temperature were increased the reaction rate increased too. The activation energy of esterification E_{af} was calculated as 48.975 kJ/mol and the value of its reverse reaction E_{ab} was calculated as 44.605 kJ/mol. The value of adsorption coefficient of methanol obtained from the esterification reaction data is 273.5 g/mol and the reaction rate constant of esterification is calculated as 3.201 g/(mol min).

6.1 SYSTEM DESCRIPTION:

In this section we consider the pervaporation assisted esterification of Lactic acid with methanol in the presence of ion-exchange resin Lewatit SPC-112 H^{+}-catalyst. The influence of several process variables, such as process temperature, initial molar ratio of levulinic acid over n-amyl alcohol and ratio of 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 various parameters used for this system

Parameter	Notations and unit	Value/ Range
Initial mole ratio of livulinic acid and n amyl alcohol	$R0=CB_0/C_{A0}$	1-2.5
Ratio of membrane area to Reaction volume	S/V m^2/m^3	0-30
Equilibrium constant	$Keq=K_1/K_2$	1-5
Temperature	T (K)	300-450
Reaction time	t (min)	600
Frequency factor	K_0 lit/(mol.min)	36000
Activation energies	E_a, E_b joul/mol	60000 63080

6.2 Determination of kinetic parameters:

The reaction rate constants k_1, k_2 are calculated from Arrhenius law:

$$k_1 = k_0 e^{\left(\frac{-E_a}{RT}\right)} \quad \text{and} \quad k_2 = k_0 \, e^{\left(\frac{-E_b}{RT}\right)}$$

$$k_1 = 16175 * \exp\left(\frac{-48975}{RT}\right) \text{ and } k_2 = 16175 * \exp\left(\frac{-48975}{RT}\right)$$

Where R= 8.314 KJ/mol is universal gas constant

T is the reaction temperature in K

Table 6.2 Experimental values of reaction rate constants:

Temperature T (^{0}C)	**Forward rate constant K_1(lit/mol.min)*10^{-6}**	**Backward rate constant K_2 (mol.min)*10^{-6}**	**Equilibrium Constant Keq**
40	108.5	23.08	4.7
50	134.2	43.29	3.1
60	160.5	64.20	2.5
70	185.6	93.11	1.9

Source: Serap Akbelen ozen "Natural and applied sciences of Middle east technical University", 2004

With the help of Arrhenius equation we model the plot between lnk vs time and compare the model with experimental values which is given in above table .it is seen that my model result is fitted accurately with experimental values of Choi et al(2001).

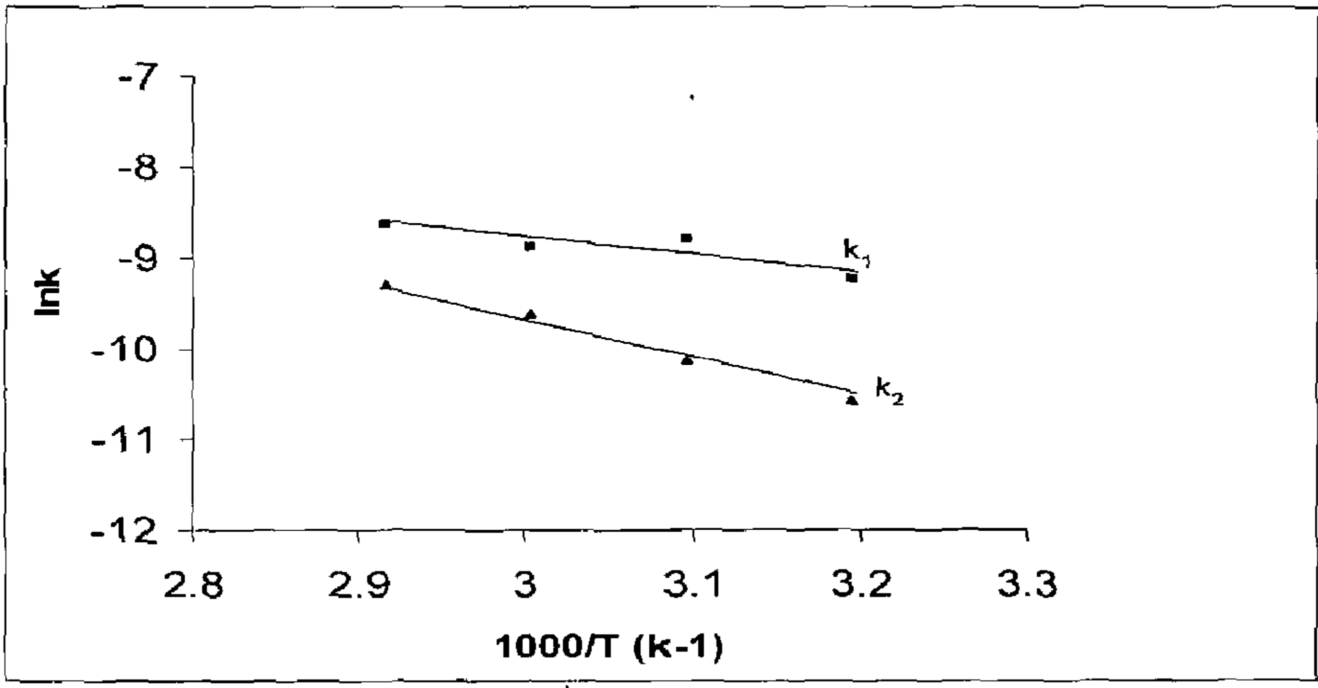

Fig 6.1 Arrehinius model for forward and backward rate constant; the points represents the experimental values taken by Choi et al (2001).

6.3 RESULTS AND DISCUSSION:

6.3.1 Model validation:

Before going to any simulation study,there is need of model validation. In this point of view the simulation results were compared with available experimental data of Choi at el(2001).For the condition of temperature, T=70^{0}C ,catalyst concentration C_C= 1 wt % the ratio of effective membrane area over reaction volume S/V= 20m^{-1}, initial molar ratio of methanol to lactic acid= 1:1.the model results of conversion of lactic acid and water concentration in the reaction is compared with experimental results and are shown in following figure 6.2 and 6.3 respectively.

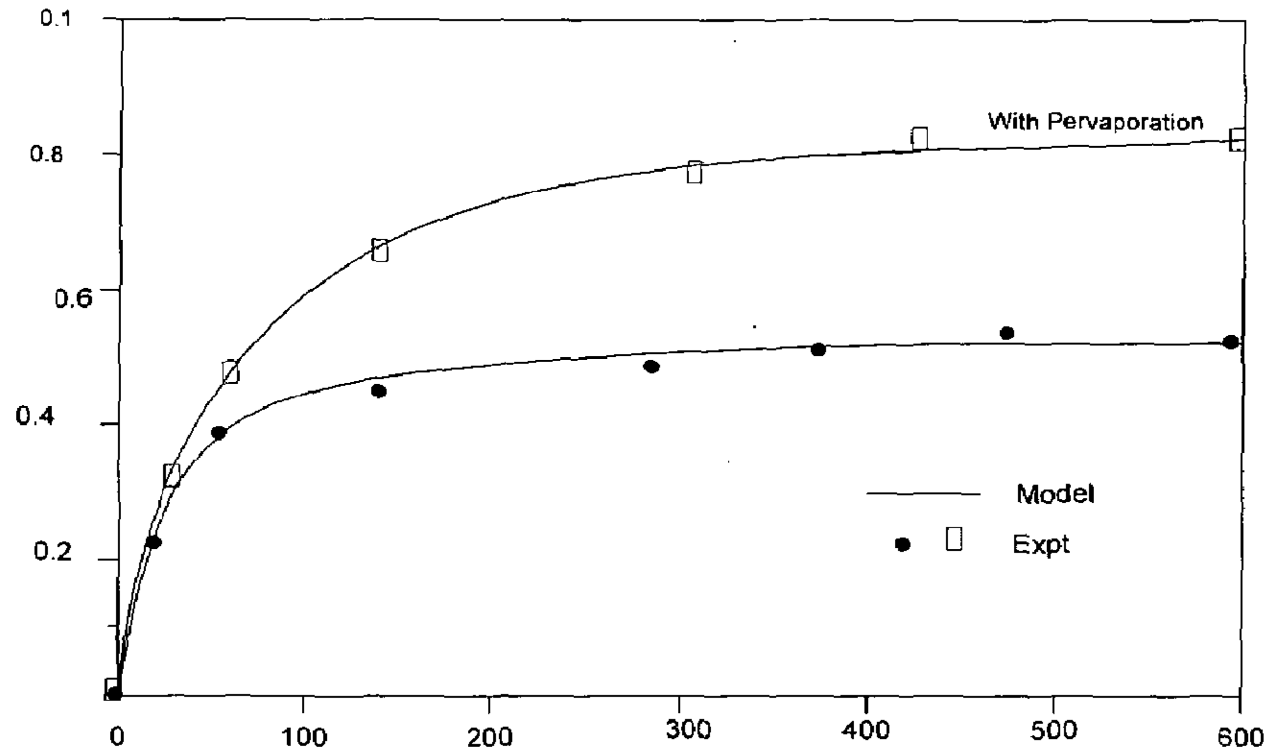

Fig 6.2 Lactic acid conversion with and without pervaporation; T=70°C, C_{B0}/C_{A0}=1, C_C=1 wt % SPC 112 H^+ catalyst

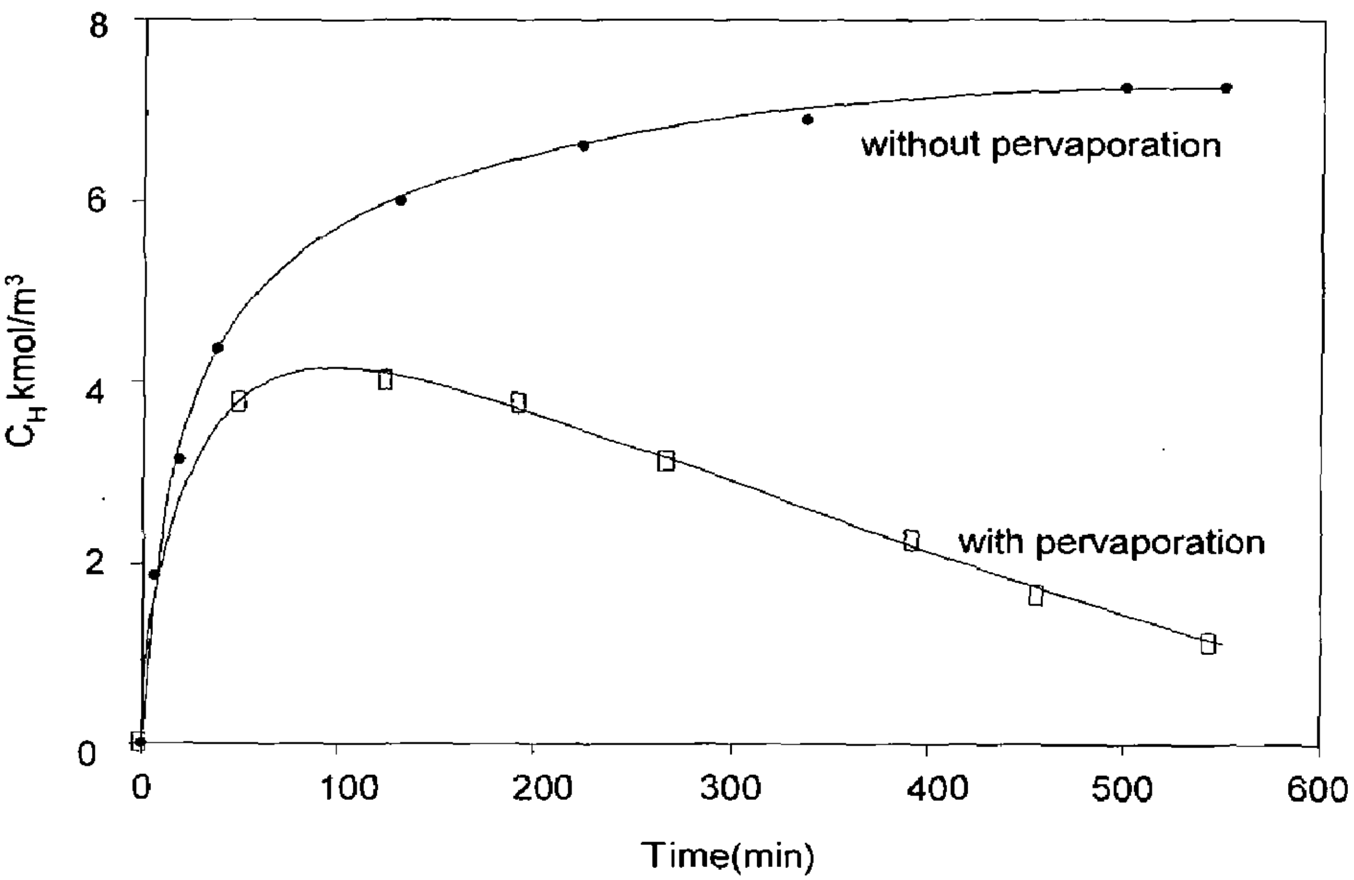

Fig 6.3 Water concentration profile compared with experimental points for esterification with and without pervaporation; $T=70^oC$,$C_C=1$ wt % $C_{B0}/C_{A0}=1$

6.3.2 Effect of Temperature on ester conversion:

Inefficient sampling due to methanol vaporization was observed above 70 °C, for the tested reaction temperatures between 40 °C and 85 °C. Therefore, 70 °C was chosen as the maximum working temperature for the lactic acid esterification. The effect of temperature on the esterification reaction of lactic acid and methanol in the presence of catalyst SPC 112 H^+ (Ion exchange resign) is shown in following figure 6.4.

As it can be seen from the figures, increasing temperature increases the conversion. At 40 °C the reaction reaches equilibrium at nearly 0.25 conversion whereas at 70 °C, the reaction reaches equilibrium at nearly 0.45 conversion. In addition to the obtained molar conversions, product distribution curves, as molar concentrations, with respect to the reaction time were obtained. The species concentrations at the temperatures 40 °C, 70 °C in the absence catalyst runs are shown in Figure 6.5.

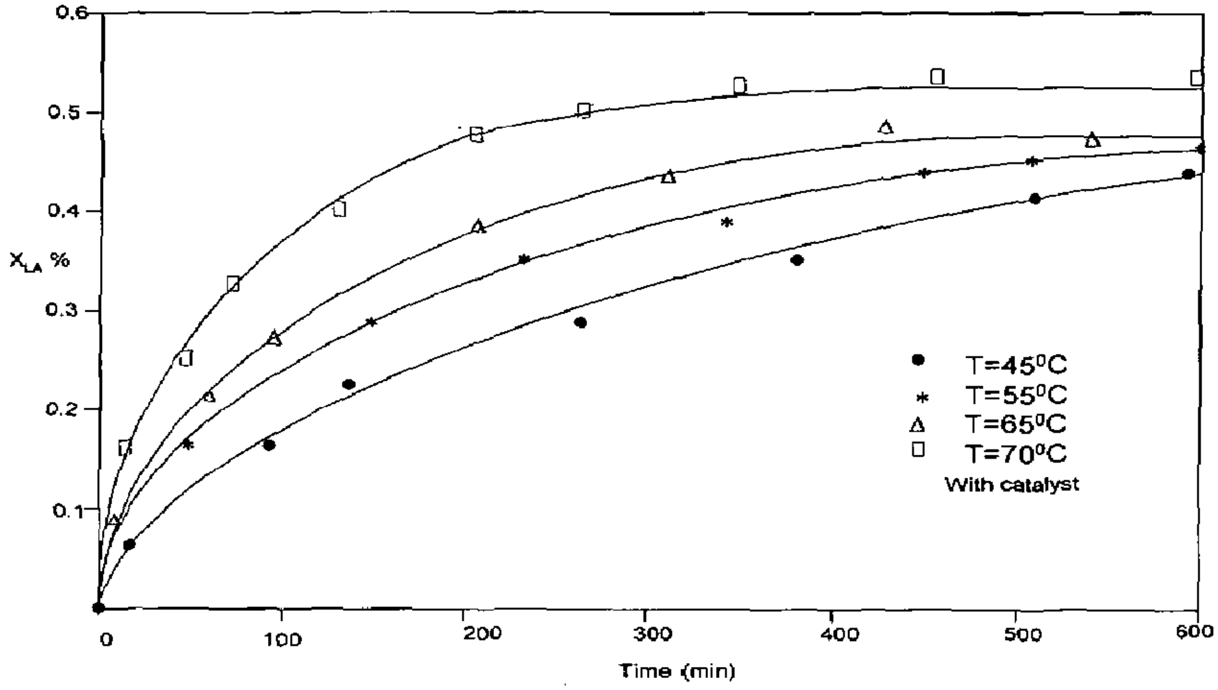

Fig 6.4 Effect of temperature on the esterification of lactic acid with methanol (C_{B0}/C_{A0}=1) in presence of catalyst C_C= 1 wt % SPC 112 H^+

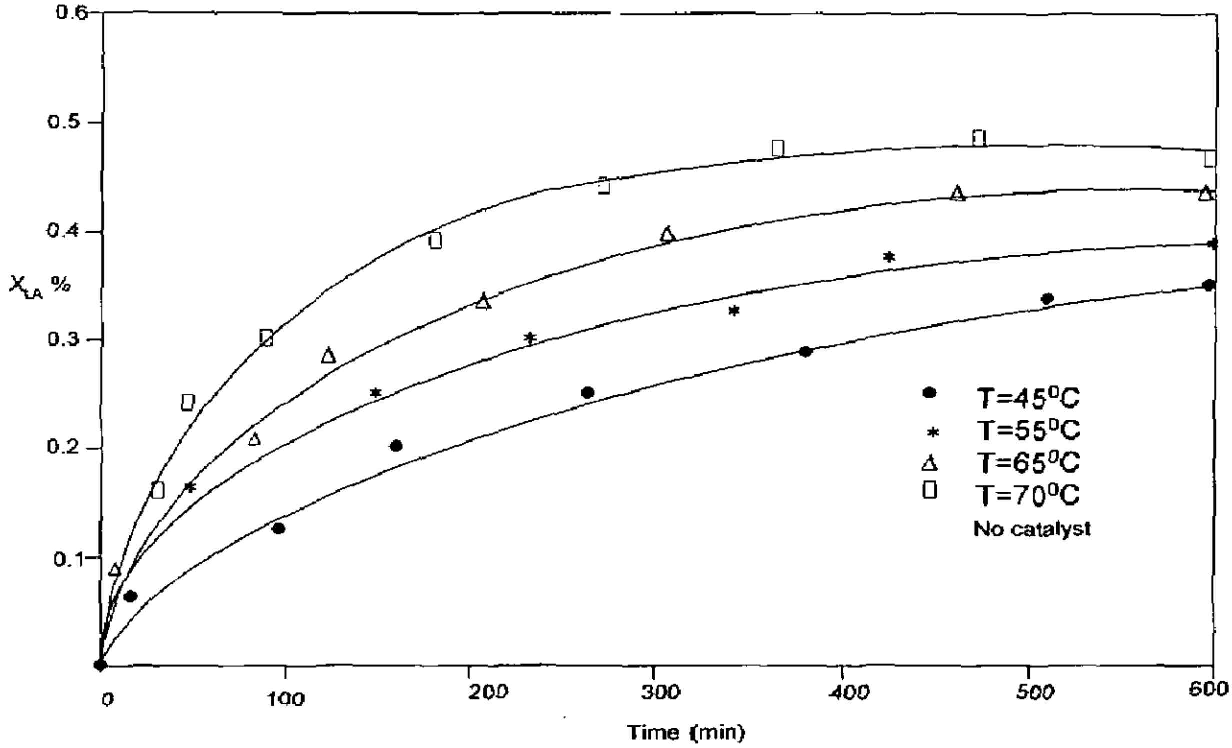

Fig 6.5 Effect of temperature on the esterification of lactic acid with methanol (C_{B0}/C_{A0}=1) in absence of catalyst.

6.3.3 Effect of Catalyst:

In order to see the effect of catalyst in the reaction rate methyl alcohol to lactic acid molar ratio was kept at 1:1. The catalyst had an acceleration effect on the reaction rate and therefore the reaction reaches equilibrium in a shorter time as it can be seen from the runs that are shown in Figure 6.3. In addition, the conversions also shifted up. In addition to the obtained molar conversions, product distribution curves, as molar concentrations, with respect to the reaction time were obtained. Temperature 40 °C, 70 °C with catalyst Lewatit SPC 112 H^+ runs are shown in Figure 6.4. The properties possessed by ion-exchange resins have resulted in the development of many procedures and processes for use in both research and industry. Many industrially important reactions involving acid or bases as catalysts can also be carried out using cation exchange or anion-exchange resins since standard ion-exchange resins are insoluble acids or bases. Catalysis with solid ion-exchange resins has the following advantages over the use of homogeneous catalysts like sulfuric acid.

1. The catalyst can be readily removed from the reaction product by decantation or simple filtration.
2. Continuous operations in columns are possible.
3. The purity of the products is higher since side reactions can be completely eliminated or are less significant.
4. It is possible to isolate the reaction intermediates.
5. Ion exchange resins can differentiate between small and large molecules.
6. Environmentally safe operability.
7. No corrosion.
8. A higher local concentration of H+/OH- ions.

For liquid phase esterification reactions use of ion-exchange resin as solid catalysts increases with regard to their advantageous properties. In comparison with the conventional homogeneous catalysts, esterification of lactic acid with methanol

6.3.4 Influence of ratio of effective membrane area to the reaction volume (S/V):

The equilibrium shift of the esterification reaction is depend on the amount of water in the reaction mixture, as we increase the ratio area of membrane with reaction volume, 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 methanol and water content in reaction mixture were presented in Figure 6.6. The S/V ratio was varied from 0 to 25 m^{-1} for 70^{O}C temperature, 1 wt % catalyst concentration and reactant ratio of Ro=1.0. 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.

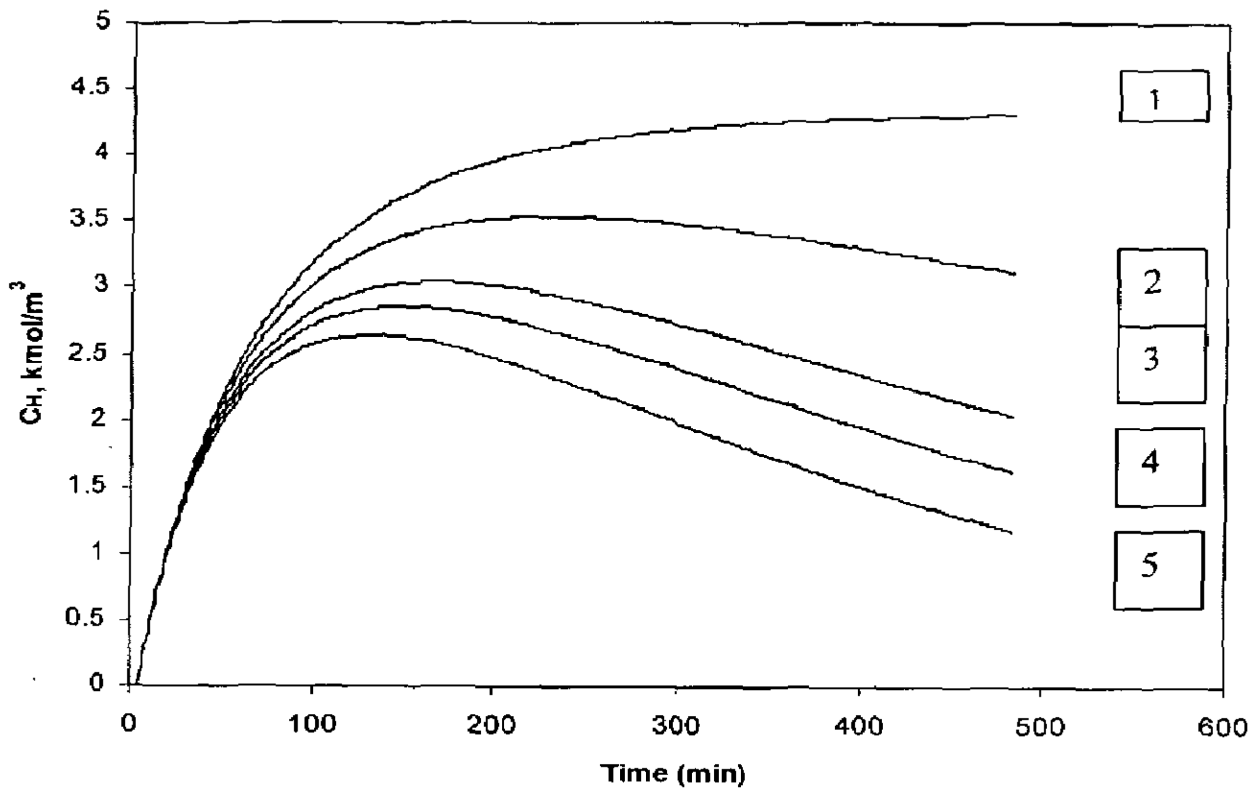

Fig 6.6 Effect of change of S/V on concentration of water (1)= 0m^{-1}1, (2) = 5m^{-1}, (3)= 10 m^{-1},(4)= 20 m^{-1} ,(4)=25 m^{-1},T= 70°C,C_C= 1 wt %

6.3.5 Influence of Initial molar ratio:

The effect of initial moalr reactant ratio of methanol with lactic acid 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_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 one reactant to the alcohol leads to a 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 alcohol to acid when operating with pervaporation may be the optimum performance conditions.

6.3.6 Influence of water 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 of membrane used, 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. From the following figure it is seen that flux at higher temperature is high as compared to lower temperature. It was clearly observed that there were slight increased in the conversion as we increased the flux; this was because of the reaction limitations.

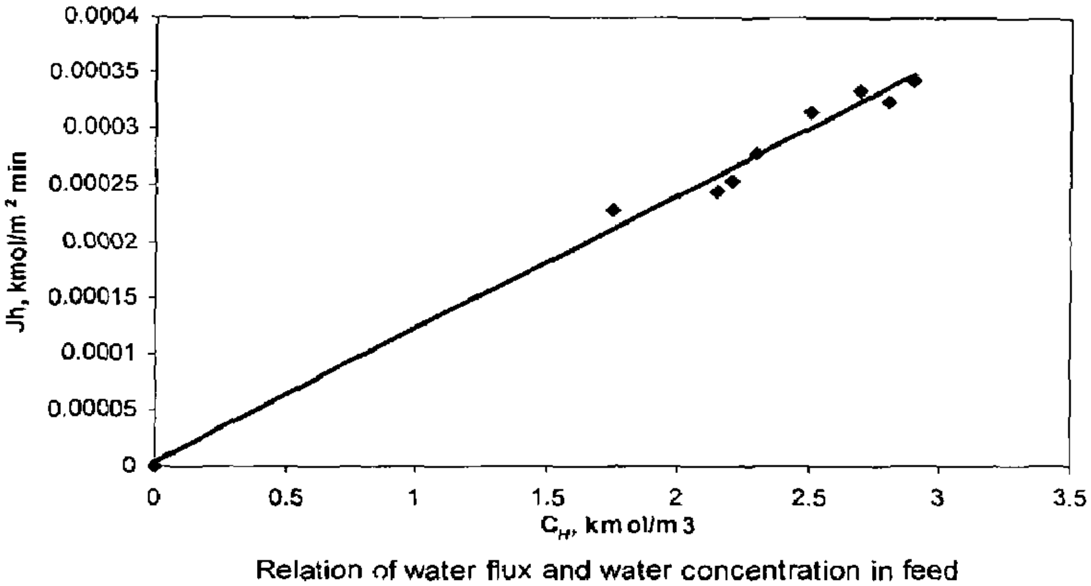

Figure 6.7 : Calculated curve compared to experimental points for water concentration in the reacting mixture for esterification both with and without pervaporation. (T=70 °C; C_C1 wt %; C_{B0}/C_{A0}=1.0)

6.4 Conclding Remarks:

The esterification of lactic acid with methanol combined with a pervaporation unit has been studied. In this work the model gives a good representation of the reaction rate for the Methyl lactate system with only four adjustable parameters Temperature, catalyst concentration, ratio of reactants, ratio of membrane area over reaction volume and water flux. The permeate flux was found to increase with the water content in the feed and the temperature. The results obtained with the model are in good agreement with the experimental results by Choi et al (2001).

The hydrolysis of Lactic Acid reaction and equilibrium constant decreases with increasing temperature due to exothermic reaction .The effect of temperature on conversion was studied in the range of 40-70 ^{0}C.It was seen that the ester conversion increases with temperature.

CHAPTER 7

CONCLUSION AND RECOMMENDATIONS

7.1 CONCLUSION:

- A mathematical model for a pervaporation membrane reactor with three different systems (i) Esterification of Levulinic acid with n amyl alcohol (ii) Acetic acid with Isopropanol (iii) Lactic acid with methanol were studied.
- Mathematical model consists of set of coupled Ordinary Differential Equations which constitutes initial value problem and these differential equations solved by using Polymath (RKF045) for the prediction of performance of model.
- The variation of conversion of acid, base, ester and water with different parameters like temperature, initial reactant ratio, catalyst concentration, membrane area over reaction volume are predicted by simulation results.
- The concentration, mole fraction and flux profiles of reactants and products are compared with experimental data. In all above systems we found that these profiles has best agreement with experimental values. Hence these results shows that our model is excellent for the pervaporation membrane reactor.
- Conversion of reactants was enhanced in pervaporation membrane reactor as compared to conventional reactor with better performance.

7.2 RECOMMENDATIONS:

- In esterification reactions the excess amount of water is present in the reaction mixture, the recovery of lactic acid from its dilute aqueous solutions is a major problem. the conversion is greatly restricted by the chemical reaction equilibrium limitations.
- Since the esterification of an alcohol and an organic acid involves a reversible equilibrium these reactions usually do not go to completion. Conversions approaching 100% can often be achieved by removing one of the products formed, either the ester or the water.
- The modeling is very sensitive with the kinetic parameters k_1, k_2 hence care should be taken in evaluation of these parameters.
- 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.
- Catalytic esterification of alcohols and acid in the vapor phase has received attention because the conversions obtained are generally higher than in the corresponding liquid phase reactions. Therefore the most effective method for the preparation of lactate esters of lower alcohols is passing vapors of the alcohol through the lactic acid previously heated to a temperature above the boiling point of the alcohol.
- There is a potential to studies the techno economic feasibility on Pervaporation membrane reactor. A stand- alone process based upon silica membranes is more expensive than the hybrid process as more membrane area is needed, but it is still 30% cheaper than the conventional process.

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