MODELING OF A MEMBRANE REACTOR FOR DEHYDROGENATION OF ETHYLBENZENE

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
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in
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ABSTRACT

Membrane reactor is a device in which the reaction and separation through membrane are carried out simultaneously in one unit. This kind of arrangement is particular important for reactions which are equilibrium limited out of many such reactions dehydrogenation is very important reaction industrially. The majority of chemical reactions do not reach complete conversion of the reactants, but in general, they reach an equilibrium conversion below 100%. The shift of conversion beyond its value at equilibrium at equilibrium can be achieved by continuous removal of the reaction products with membrane reaction products with membrane reactors. For the dehydrogenation reactions, since they are endothermic, the conversion favors high temperatures at the price of significant occurrence of side reactions, which reduce selectivity and lead to catalyst deactivation by cooking. By using a membrane reactor, the same conversion could be obtained at lower temperature thereby suppressing undesired reactions. The permeated reaction product can also be recovered in a rather pure form.

One such industrially important process is styrene production from ethylbenzene I dehydrogenation. The system proposed to study is dehydrogenation of ethylbenzene for production of styrene with its side reactions. The dehydrogenation of ethylbenzene to manufacture styrene is very important process industrially. as the reaction is reversible. The conversion is limited because of thermodynamic equilibrium due to continuous removal of product. The yield can be improved by carrying out reaction inside the membrane reactor. The reaction is carried out in a tube side packed with catalyst and in isothermal condition. Mathematical model is required which can predict the conversion and yields of reactants and products respectively.

Thus it is desirable to develop a mathematical model for manufacturing of styrene from EB in membrane reactor. The model equations are solved by using MATLAB ODE (Ordinary Differential Equations) solvers. The industrial operating data are available in literature are selected for testing the model predictions and to ascertain the correctness of the proposed model.

CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented in the dissertation entitled **"MODELLING OF A MEMBRANE REACTOR FOR DEHYDROGENATION OF ETHYLBENZENE"** in partial fulfillment of the requirement for the award of the degree **Master of Technology in Chemical Engineering with Specialization in Computer Aided Process Plant Design (CAPPD),** and submitted in the Department of Chemical Engineering of Indian Institute of Technology Roorkee, under the kind guidance of Dr. (Mrs.) Shashi, Assistant Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee.

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

Place: Roorkee
Date: 13 th June, 2007

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

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NOMENCLATURE

A	Cross-sectional area	m2
BEN	Benzene	
C_{pi}. c_p	Heat capacity of component i	KJ/mol.K
C_s	Inert purge ratio	
C_t	Feed dilution ratio of inert to reactant	
d	Membrane thickness	m
D	Diameter of reactor	m
D_i	Diffusion coefficient of component i	m^2/s
Da	Damkohler number	
D_j	Effective diffusivity for component j in the membrane	m^2/s
D_p	Diameter of catalyst	m
D_{ref}	Diffusion coefficient of reference component	m^2/s
EB	Ethylbenzene	
f_i	Reaction rate function for reaction i	(kPa)i
F_j	Molar flow rate of species i in reaction side	kmol s^{-1}
Fj	Molar flux of component i	kmol $m^{-2}s^{-1}$
$F_{i.o}$	Molar feed rate of species i	mol $^{S.1}$
H	Enthalpy of reaction	kJ/kmol
H_i	Henry's sorption constant of component i	mol/m3 pa
H_{ref}	Henry's sorption coefficient of reference component i	mol/m3
ko	Reaction constant at inlet conditions	mol $m^{-3}s^{-1}$
	Direct reaction rate constant	
K_E	Reaction equilibrium constant	
ki	Reaction rate constant, i = I, ...,6	molm^{-3}s^{-1}Pa
Ki	Effective Knudsen permeability	mol/m^2.s.Pa
Kp	Thermodynamic equilibrium constant	Pa
L	Reactor length	m
1	Length dimension	m

Mi	Molecular weight	g/mol
N'i	Molar flux in axial direction of shell side	mo^{1}/m^{2}.s
ni	Molar flow rate	kmol/s
Ni	Molar flux in axial direction of tube side, i=EB, ST, H_2, TOL……….	mol/m^{2}.s
P_f	Pressure in feed side	k Pa
P	Reaction pressure bar	
P'	Pressure of permeate side	Pa
P'i	Partial pressure in shell side	
P ei	Pecklet number	
P_f	Total feed pressure	Pa
Pi	Partial pressure in equilibrium with the concentration of component i inside the membrane	Pa
Pi	Permeability of species I	mol m^{-2}S^{-1} Pa^{-1}
Pi	Partial pressure in tube side, i=EB, ST, H_2,	Pa
Pi^F	Partial pressure of component i in the feed	Pa
PiP	Partial pressure of component i in the effluent permeate	Pa
PiR	Partial pressure of component i in the effluent retentate	Pa
P_p	Total permeate pressure	Pa
Ii p	Permeate side pressure	Pa
P_R	Total retentate pressure	Pa
P r	Pressure ratio	
Pr	Prandtl number	
P_{ref}	Reference pressure (feed flow)	Pa
Pt	Total pressure of system	Pa
PI	Total pressure in tube side	Pa
Ps	Total pressure in sweep side	Pa
q	Heat flux	kJ/m^{2}s
Q^F	Total feed volumetric flow rate	m^{3}/s
Q_{H2}	Hydrogen permeate rate	m^{3}/s
qi	Volume flux of species	ms^{-1}

Qi	Molar flow rate of species i in permeate side	mol s^{-1}
Q^P	Total permeate volumetric flow rate	m^3/s
Q^R	Total retentate volumetric flow rate	m^3/s
Q_{ref}	Reference volumetric flow rate (feed flow)	m^3/s
Qs	Flow rate of sweep gas into permeate side	m^3/s
R	Tube diameter	m
R	Radius of catalyst bed	m
r	Radial coordinate of catalyst bed	m
R	Ideal gas constant	Pa.m^3/mol K
r_1	Dimensionless n-butane reaction rate	
r_2	Dimensionless radial coordinate in vycor glass	
r_A	Dimensionless radial coordinate in catalyst bed	
r_{ext}	Radius of membrane	m
R_j	Inner radius of shell	m
r_j	Reaction rate of species i	mol/m^3s
rint,	Inner radius of membrane tube	m
Rj	Reaction rate of reaction	kmol/kg.s
Ro	Outer radius of tube	m
$r_{lot}.R_2$	Outer radius of membrane tube	m
ST	Styrene	
S	Membrane surface area	m^2
TOL	Toluene	
T	Absolute temperature	K
To	Initial temperature	K
Tin	Inlet temperature of feed	K
U	Overall heat transfer coefficient	W/m^2K
U_r	Rate of oxygen inside of catalyst bed	kmol$m^{-2}s^{-1}$
U_w	Local permeation rate of oxygen	kmol$m^{-2}s^{-1}$
v_z	Mixture linear velocity in shell side	m/s
V_z .	Mixture linear velocity in tube side	m/s
x	Dimensionless membrane spatial coordinate	

X_A	Reactor conversion of reactant	A
X_A	Thermodynamic equilibrium conversion of reactant based on feed conditions.	A,
Xi	Dimensionless species concentration in vycor glass	
Xj	molar fraction of component j in feed-side.	
Yi	Dimensionless species concentration in catalyst bed	
Yi	Dimensionless mole flow rate of species I	
Ys	Mole fraction of hydrogen in sweep gas	
z	Membrane spatial coordinate	m

Greek letter

αi	Selectivity of species i to cyclohexane	Pi / P_c
β	Permeability of O2	kmol/m.s.bar
Yi	Rate of reaction of species i	Kmol $m^{-3}s^{-1}$
γj	Dimensionless contact time for case j	
$\Gamma\varphi$	Effective exchange coefficient of ϕ	$kgm^{-1}s^{-1}$
λ	Membrane thickness	m
ε	Porosity of packed catalyst in reactor	
ε_b	Porosity of catalyst bed	
ε_p	Porosity of membrane	
A	Constant	
ε^R	Dimensionless total retentate volumetric flow rate	
Ψ^R	Dimensionless total pressure in the retentate	
ν	Kinematic viscosity.	m^2s^{-1}

INTRODUCTION

Membrane reactor is a device in which the reaction and separation through membrane are carried out simultaneously in one unit. This kind of arrangement is particular important for reactions which are equilibrium limited. out of many such reactions dehydrogenation is very important reaction industrially. The majority of chemical reactions do not reach complete conversion of the reactants, but, in general, They reach an equilibrium conversion below 100%. The shift of conversion beyond its value at equilibrium at equilibrium can be achieved by continuous removal of the reaction products with membrane reaction products with membrane reactors. For the dehydrogenation reactions, since they are endothermic, the conversion favors high temperatures at the price of significant occurrence of side reactions, which reduce selectivity and lead to catalyst deactivation by coking by using a membrane reactor, the same conversion could be obtained at lower temperature thereby suppressing undesired reactions. the permeated reaction product can also be recovered in a rather pure form. One such industrially important process is styrene production from ethylbenzene dehydrogenation. The system proposed to study is dehydrogenation of ethyl, benzene for production of styrene with its side reactions. The dehydrogenation of ethylbenzene to manufacture styrene is very important process industrially as the reaction is reversible the conversion is limited because of thermodynamic equilibrium due to continuous removal of product the yield can be improved by carrying out reaction inside the membrane reactor the reaction is carried out in a tube side packed with catalyst and in isothermal condition. Mathematical model is required which can predict the conversion and yields of reactants and products respectively.

1.1 Properties of an ideal membrane

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

1.2 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.]

1.3 Advantages

Membrane separation technologies offer advantages over existing mass transfer processes. such advantages are

a) high selectivity and permeability for the transport of a specific components "

b) low energy consumption

c) good stability under wide spectrum of operating conditions

d) moderate cost to performance ratio

e) environment compatibility

f) easy control and scale up have been confirmed in a large variety of applications

g) increased catalyst life

h) improved product quality

i) simplified separations

1.4 Disadvantages

a) relatively new technology

b) limited applications window

c) extensive experimental development is required

d) complex modeling requirement

e) extensive design efforts

f) increased operational complexity

g) significant development costs

h) increased scale-up risks

1.5 Membrane reactors for various applications:

The applications of membrane reactor with examples are mentioned in this section are as follows

(1) Dehydrogenation reactions:

Catalytic dehydrogenation of light alkenes, Dehydrogenation for other hydrocarbons such as ethybenzene, Ethanol dehydrogenation.

(2) Hydrogenation reactions:

Synthesis of methanol from carbon dioxide, Vitamin K from quinine and acetic anhydride, cis/trasn 2-butene 1,4 diol to cis/trans butaneddiol, Cyclopentadiene hydrogenation,.-methylstyrene to cumene etc.

(3) Oxidation reactions:-

The direction conversion of methane into ethylene and ethane by oxidative coupling with oxygen is the prime example of a reaction using membrane reactors to which solid oxide membranes have been applied, synthesis gas from methane, partial methane oxidation to methanol and formaldehyde.

(4) Pervaporation membrane reactor:

Production of ethyl and butyl acetate ethyl and n-butyl oleatte, diethyl tartrates, dimethyl urea, ethyl valerate, isopropyl ad propyl and methyl isobutyl ketone just to name a few.

(5) Water desalination:

Some of the largest plant in the world today for sea water desalination or gas separation are already based on membrane engineering. The Red Sea-Dead desalination project under discussion today is base, for example, totally on RO with a productivity of 27m3/s of permeate.

(6) Membrane based reactive separations for biological systems:

Protein hydrolysis and enzymatic reactions which require co-factor recycling, L-phenyl aniline synthesis from acetamidocinnamic acid using NADH (-nicotinamide adenine dinucleotde). The combination of conventional bioreactor with UF membrane has been utilized in a number of other important synthesis reactions, e.g. Growth hormone biosyntesis obtained by the bacteria E-Coli, Maltose hydrolysis, Clarification of fruit juice. Production of propionic and lactic acid by two different bacteria in membrane bioreactor.

(7) Environmental application of membrane bioreactor.

Membrane based bioreactor processes present an alternative, attractive solution to the problem of biomass separation from the waste to be treated since the membrane provide an effective barrier for microbes and other particles.

(8) Emerging applications:

Hydrogen production for integrated gasification combined cycle (IGCC), CO2 separation in IGCC, Water gas shift reaction in membrane reactor, Recover tritium from tritiated water from breeder-blanket fluids in fusion reactor systems.

1.6 Types of membrane

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

1.6.1 Isotropic Membranes

1.6.1.1 Microporous Membranes

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

1.6.1.2 Nonporous, Dense membranes

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

1.6.1.3 Electrically Charged Membranes

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

1.6.2 Anisotropic Membranes

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

1.6.3 Ceramic, Metal and Liquid Membranes

The discussion so far implies that membrane materials are organic polymers and, infact, the vast majority of membranes used commercially are polymerbased. However, in recent years, and interest in membranes formed form less conventional material has increased. Ceramic membranes, a special class of microporous membranes, are being used in ultrafiltration and microfiltration application for which solvent resistance and thermal stability are required. Dense metal membranes, particularly palladium membranes, are being considered for the separation of hydrogen from the gas mixtures, and supported liquid films are being developed for .carrier-facilitated transport process.

1.6.4 Zeolite membranes

A zeolite membrane is a porous layer that can separate mixtures by adsorption and diffusion differences, and, in some cases, by molecular sieving. Zeolities are inorganic crystalline structures with uniform, molecular-sized pores, and high mechanical, thermal, and chemical stability. These properties give zeolite membranes advantages over many polymeric membranes. The first reported zeolite membranes were prepared by Suzuki [1987], andnow more than 12 zeolite structures have been prepared as membranes. Zeolite membranes are most often polycrystalline layers deposited on tubular or discu-shaped porous supports. Significant work has been done to reduce the intercrystalline defects, improve crystal orientation and reduce the thickness of zeolite layers. Both gas separations and pervaporation using zeolite membrane have been reported, with most studies focusing on membrane preparation and performance.

1.7 Transport through membrane

The most important property of membranes is their ability to control the rate of permeation of different species. The two models used to describe the mechanism of permeation are illustrated in Figure 1.4. One is the solution -diffusion model, in which permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient. The permeants are separated because of the difference in Insolubilities of the materials in the membrane and the differences in the rates at which the material diffuse through the membrane. The other model is the pore-flow model, in which permeants are transported by the pressure-driven convective flow through tiny pores. Separation occurs because one of the permeates is excluded (filtered) from some of the pores in the membrane through which the permenants move. Both models were proposed in the nineteenth century, but the pore-flow model, because it was closer tonormal physical experience, was popular until the mid-1940s. However, during the 1940s, the solution diffusion model was used to explain transport of gases through films. The use of solution-diffusion model was relatively uncontroversial, but the transport mechanism in revere membranes was a hotly debated issue in the 1960s and early 1970s. By 1980, however, the proponents of solution -diffusion has carried the day; currently only a few die-hard pore-flow modelers use this approach to rationalize reverse osmosis.

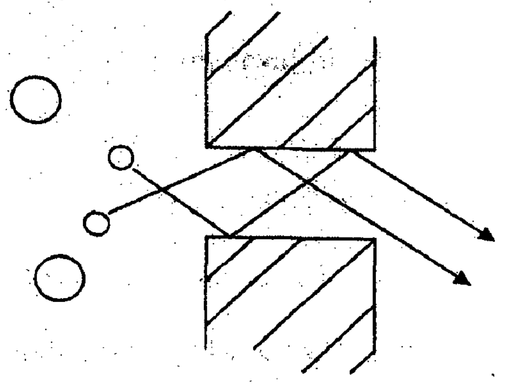

Fig 1.1(a) Microporous membranes separate
membranes separate
solubility and mobility of
permenats in the membrane material

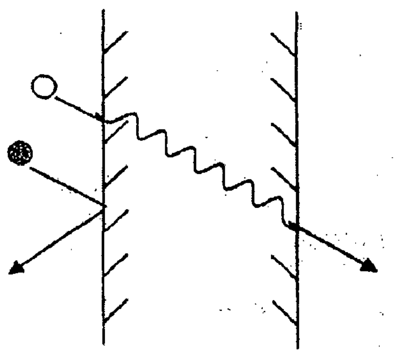

Fig1.1(b) Dense solution-diffusion
by molecular filtration because of
difference in the

Diffusion, the basis of the solution-diffusion model, is the process by which matter is transported from one part of the system to another by a concentration gradient. The individual molecules in the membrane medium are in constant random molecular motion, but in isotropic medium, individual molecules have no preferred direction of motion. Although the average displacement of an individual molecule from its starting point can be calculated, after a period of time nothing can be said about the direction in which any individual molecule will move. However, it a concentration gradient of permeate molecules are formed in the medium, simple statistics show that a net transport of matter will occur from the higher concentration to the lower concentration region. For example, when two adjacent volume elements with slightly different permeant concentrations are separated by an interface, then simply because of the difference in the number of molecules in each volume element, more molecules will move from the concentrated side to the less concentrated side of the interface than will move in the other direction. This concept was first recognized by Fick theoretically and experimentally in 1855. Fick formulated his results as the equation now called Fick's law of Diffusion, which states.

$$J_i = D_i \times (dC_i/dx) \qquad (1.1)$$

Transfer of component I or flux (g/cm2.s) and dC_i/dx is the concentration gradient of component i. The term D_i is called the diffusion coefficient (cm2/s) and is the measure of the mobility of the individual molecules. The minus sign shows that the direction of the diffusion is down the concentration gradient. Diffusion is an inherently slow process. In practical diffusion-controlled separation process, useful fluxes across the membrane are achieved by making the membranes very thin and creating large concentration gradients in the membrane.

Pressure-driven convective flow, the basis of the pore-flow model, is most commonly used to describe flow in capillary or porous medium. The basic equation covering this type of transport is Darcy's law, which can be written as

$$Ji = K' \times ci \times (dp/dx) \qquad (1.2)$$

Where dp/dx is the pressure gradient existing in the porous medium, ci is the concentration of component I in the medium and K' is a coefficient reflecting the nature of the medium. In general, convective-pressure-driven membrane fluxes are high compared with those obtained by simple diffusion.

The difference between the solution-diffusion and pore-flow mechanisms lies in the relative size and permeance of the pores. For membranes in which transport is best described by the solution-diffusion model and Fick's law, the free-volume elements (pores) in the membrane are the tiny spaces between the polymer chains caused by thermal motion of polymer molecules. These volume elements apper and disappear on about the same timescale as the motion of permeants traversing the membrane. On the other hand, for a membrane in which is best described by a pore-flow model and Darcy's law, the free-volume element (pores) are relatively large and fixed, do not fluctuate in position or volume on the time scale of permeant motion, and are connected to one another. The larger the individual free volume elements (pores), the more likely they are to be present long enough to produce pore-flow characteristics in the membrane. As a I rough rule of thumb, the transition between transient (solution-diffusion) and permanent (pore-flow) pores is in the range 5-10 A diameter.

- Ultrafiltration, microfiltration and microporous Knudsen-flow gas separation membranes are all clearly microporous, and transport occurs by pore flow.
- Reverse osmosis, pervaporations and polymeric gas separation membranes have a dense polymer layer with no visible pores, in which the separation occurs. These membranes show different transport rates for molecules as small as 2-5 A in diameter. The fluxes of permeants through these membranes are also much lower tan through the miroporous membranes. Transport is best described by solution diffusion model. The spaces between the polymer chains in these membranes are less than 5 A in diameter and so are within the normal range of thermal motion of the polymer chains that make up the membrane matrix permeate the membrane through free volume elements between the polymer chains that are transient on the timescale of the diffusion processes occurring.

1.7.1 Solution diffusion Model

The solution-diffusion model applies to reverse osmosis, pervaporation and gas permeation in polymer films. At first glance these process appear to be very different. Reverse osmosis uses a large pressure difference across the membrane to separate water from salt solutions. In pervaporation, the pressure difference across the membrane is small, and the process is driven by the vapor pressure of the permeate vapor. Gas permeation involves transport of gases down a pressure or concentration gradient. However, all three processes involve diffusion of molecules in dense polymer. The pressure, temperature, and composition of the fluids on either side of the membrane determine the concentration of the diffusion species at the membrane surface in equilibrium with the fluid. Once dissolved in the membrane, individual permeating molecules moves by the same random process of molecular diffusion no matter whether the membrane being used in reverse osmosis, pervaporation or gas separation. For example, cellulose acetate membranes were developed for desalination of water by reverse osmosis, but essentially identical membranes have been used in pervaporation to dehydrate alcohol and are widely used in gas permeation to separate carbon dioxide form natural gas.

1.7.1.1 Concentration and Pressure Gradients in Membranes:

The starting point for the mathematical description of diffusion in membranes is the proposition solidly based in thermodynamics, that the driving force of pressure, temperature concentration, and electrical potential are interrelated and that the overall force producing a component, I, is described by simple equation.

$$Ji = Li\ (dl.1i/dx) \qquad (1.3)$$

Where dl.1i/dx is the chemical potential gradient of component I ad Li is a coefficient of proportionality (not necessarily constant) linking this chemical potential driving force to flux.

Driving forces, such as gradients in concentration, pressure, temperature, and electric potential can be expressed as chemical potential gradients, and their effect on flux expressed by this equation. This approach is extremely useful, because many processes involve more than one driving force.

Chemical potential is written as (restricting to pressure ad concentration)

$$D\mu i = RT\ dln\ (\gamma_I\ ni) + Vi\ dp \qquad (1.4)$$

integrating the above equation for incompressible phases such as liquid and membrane, volume does not change with pressure. In this case

$$\mu i =1.\ \mu 0 + RT\ In\ (\gamma_I\ ni) + VI\ (P-P_{isat}) \qquad (1.5)$$

for compressible gases, volume changes with pressure, using ideal gas law and integrating the equation give.

$$\mu_I = \mu_I^0 + RT\ In\ (\gamma_I\ ni) + VI\ (P-P_{isat}) \qquad (1.6)$$

where l.1io is the chemical potential of pure I at a reference pressure, Pia Yi is the activity coefficient (mol/mol) linking molefraction (n_i) with activity vi is the molar volume of component i.

Where 0,1 represents feed, permeate side of the membrane(m) respectively.

1.7.1.2 Assumptions made in solution-diffusion model

Several assumptions must be made to define any permeation model

- The fluids on either side of the membran~ are in equilibrium with the membrane material at the interface.

This assumption means that the gradient in chemical potential from one side of 'the membrane to the other is continuous. Implicit in this assumption is that the rate of absorption and desorption at the membrane interface are much higher than the rate of diffusion through the membrane.

- The solution-diffusion model assumes that when pressure is applied across a dense. Membrane, the pressure throughout the membrane is constant at the highest value. This assumes, in effect, that solution diffusion membranes transmit pressure in the same way as liquids. From equation [3], assuming. i is constant

$$J_i = \frac{RTL_1}{n_1}\left(\frac{dn_1}{dx}\right) \qquad (1.7)$$

in above equation a more general term concentration is replaced as

$$C_i = m_i\, n_i \qquad (1.8)$$

then it becomes

$$J_i = \frac{RTL_1}{c_1}\left(\frac{dn_1}{dx}\right) \qquad (1.9)$$

this has the same form of Fick's law in which there term RTLj /Cj can be replaced by diffusion coefficient Di. Thus

$$Jj = -Di(dcj/dx) \qquad (1.10)$$

Integrating over the thickness of the membrane then gives

$$\mathrm{J} = \frac{D(c_{i0(m)} - c_{il(m)}}{l} \qquad (1.11)$$

1.8 Pervaporation .

A membrane may be defined as "an interphase separating two phases". Such membrane separations have been widely applied to a range of conventionally difficult separations. they potentially offer the advantages of ambient temperature operation, relatively low capital and running costs, and modular construction. pervaporation is one of these methods.

1.8.l.Process description

Two industrially important categories of separation problems are the separation of liquid mixtures, which form an azeotrope and/or where there are only small differences in boiling characteristics pervaporation is a membrane process, which shows promise for both of such separations.

Pervaporation is a separation process in which one or more components of a liquid mixture diffuse through a selective membrane, evaporate under low pressure on the downstream side and are removed by a vaccum pump or a chilled condenser. The process differs from other membrane process is that there is a phase change from liquid to vapor in the permeate.

Here the feed mixture is a liquid. The driving force in the membrane is achieved by lowering the activity of the activity of the permeate side. Components in the mixture permeate through the membrane and permeate side being held lower than the saturation vapor pressure. the driving force is controlled by a vacuum on the permeate side.

1.8.2. Process mechanism

Composite membranes are used for pervaporation with the dense layer in contact with the liquid and the porous supporting layer exposed to the vapor. The process can be described by a solution diffusional model that is in an ideal case there is equilibrium at the membrane interfaces and diffusional transport of components though the bulk of : membrane. The activity of a component on the feed side of the membrane is proportional to the composition of that component in the feed solution. The composition at the permeate phase interface depends on the partial pressure and saturation vapor pressure of the component. solvent composition within the melpbrane may vary considerably between the feed and permeate side interface in pervaporation. By lowering the pressure at the permeate side very low concentrations can be achieved while the solvent concentration on the feed side can be upto 90 percent. The modeling of material transport in pervaporation must take into account the concentration dependence of the diffusion coefficients.

The phase change occurs in the membrane and the heat of vaporization is supplied by the sensible heat of the liquid conducted through the thin dense layer. The decrease in temperature of the liquid as it passes through the thin dense layer. The decrease in temperature of the liquid as it passes through the separator lowers the rate of permeation and this usually limits the applications of pervaporation to removal of small amount of feed. typically 2-5 percent for one stage separation. if a greater removal is needed several stages are used in series with intermediate heaters.

The flux of each component is proportional to the concentration gradient and the diffusivity in the dense layer. However, the concentration gradient is often nonlinear because the membrane swells appreciably as it absorbs liquid, and the diffusion coefficient in the fully swollen polymer may be 10 to 100 times the value in the dense unswollen polymer. Furthermore, when the polymer is swollen mainly by absorption of one component, the diffusivity of other components is increased also. This interaction makes it difficult to develop correlations for membrane permeability and selectivity. However, in commercial applications of pervaporation, the liquid feed usually has a low concentration of the more permeable species, so the swelling of the membrane and the resulting nonlinear effects are not as pronounced as when testing pure liquids or solutions of high concentration.

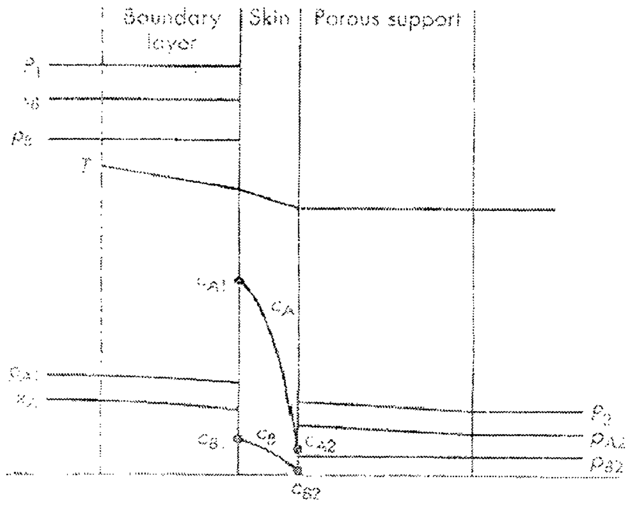

Fig. 1.2 Gradients in a pervaporation membrane

The gradients at steady state for a typical system are shown in previous figure. The feed is rich in B, but A is assumed to be much more soluble in the polymer, and there is a high concentration of A in the membrane at the uopstream side. The gradient of A is small near this boundary because of the high diffusivity, but diffusivity coefficient of A decreases as concentration of A decreases. The gradient of B has a similar shape, reflecting the change in diffusivity coefficient of B through the membrane. The concentrations of A & B are likely to be proportional to the downstream partial pressures of A & B, but Henry's law may not hold at the upstream side, where the membrane is highly is swollen by solvent

1.9 Polarisation phenomen ad membrane fouling

1.9.1 Polarisation

In order to achieve a particular separation via a membrane process the first step to develop a suitable membrane however during an actual separation e,g. a pressure driven process the membrane performance can change very much with time and often a typical flux-time behaviour may be observed the flux through membrane decrease with time this behaviour is shown schematically in figure 1.9. And is mainly due to concentration polarization and fouling. .

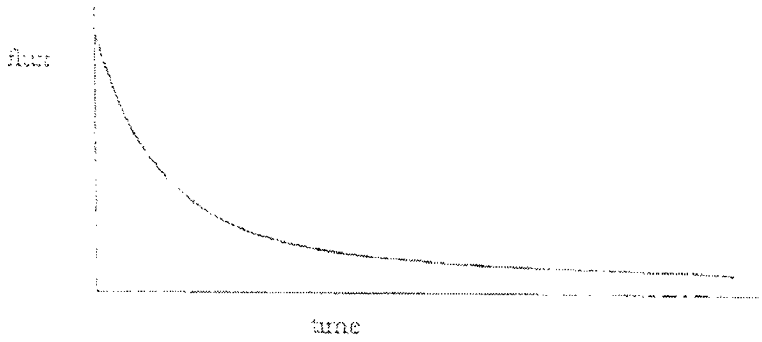

Figure 1.3 Flux behaviour as function of time

Flux decline can be caused by several factors which as concentration polarization adsorption Jellayer formation and pluging of the pores all these factors induce additional resistance on the feed side to the transport across the membrane the extent of these phenomena is strongly Dependent on the types of membrane process and feed solution employed fig. 1.10 provides a schematic representation of the various resistances that can arise. The various resistance depicted in fig contribute with a different extent to the total resistance Rtotal. In the ideal case only the membrane resistance Rm is involved. Because the membrane retains the solutes to a certain extent their will be an accumulation of retained molecules near the membrane surface. This results highly concentrated layer near the membrane and this layer exerts a resistance towards masstransfer i.e. a concentration polarization resistance Rcp. The concentration of the accumulated solute molecules may become so high that a gel layer can be formed which exerts the gel layer resistance RO. This mainly happens when the solution contains protein with porous membranes it is possible for some solutes to penetrate in to the membrane and block the pores, leading to the pore blocking resistance RP. Finally a resistance can arise due to adsorption phenomena i.e. the resistance Ra. Adsorption con take upon the membrane surface as well as with in the pores themselves. .

Flux decline has a negative influence on the economics of given membrane operation and for this reason measures must be taken to reduce its incidence however it is first necessary to distinguish between concentration polarization and fouling, although both not completely independent of each other since fouling can result form polarization phenomena.

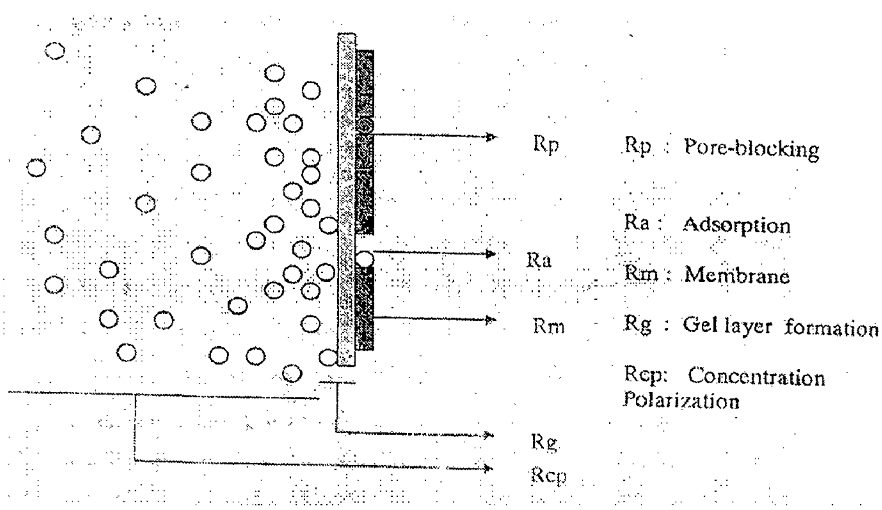

Fig. 1.4 Over view of various resistances towards mass transport across a membrane in Pressure driven process

1.9.2 Concentration polarization in diffusive membrane separations

There are many processes which are aimed to transport a specific component preferentially though a membrane, i.e. dialysis, diffusion dialysis, facilitated transport in supported and emulsion liquid membranes, pervaporation, membrane contactors. The transport in these processes are characterized by solution diffusion mechanism, i.e. the permeating component must dissolve in to the membrane from the feed side and will then diffuse through the membrane according to a driving force in these process it is frequently assumed that resistance to transport is completely determined by the membrane phase and boundary layer resistance are neglected, dependent on the hydrodynamics in the liquid feed and the resistance of the membrane for the specific permeating solute the resistance in the boundary may contribute to the overall resistance are even may be rate determining the concentration profiles for such a system is shown in the figure.

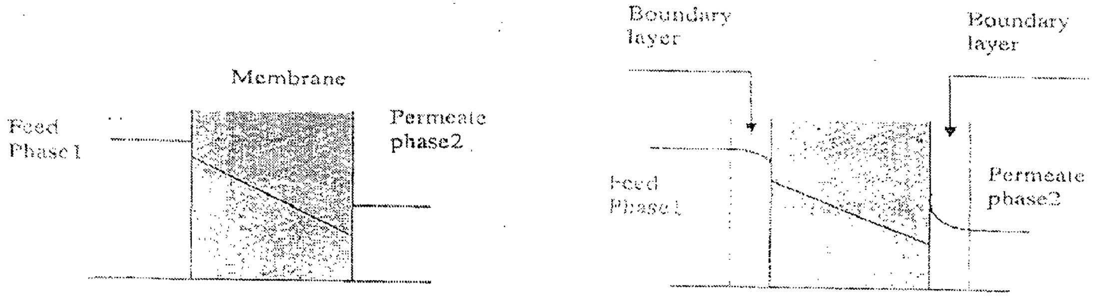

Fig 1.5 Concentration profiles for diffusive membrane

a) Without boundary layer resistance b) With boundary layer resistance

1.9.3 Membrane fouling

The performance of membrane operations is diminished by .polarization phenomena, although the extents to which these phenomena can occur differ considerably. Thus in micro filtration and ultra filtration the actual flux through the membrane can be only a fraction of the pure water flux whereas in pervaportion the effect is less severe. With all polarization phenomena (concentration, temperature polarization), the flux at a finite time is always less than the original value. When steady state conditions have been attained a further decrease in flux will not be observed, i.e., the flux will become constant a a function of time. Polarisation phenomena are reversible processes, but in practice a continuous decline in flux decline can often be observed. This is shown schematically in figure Such continuous flux decline is the result of membrane fouling, which may be define as the (ir) reversible deposition of retained particles, colloids, emulsions, suspensions, macromolecules, salts etc. on or in the membrane. This includes adsorption; pore blocking precipitation and cake formation.

Some extensive review articles have been written on fouling Fouling occurs mainly in micro filtration/ultrafiltration where porous membranes which are implicitly susceptible to fouling are used. In pervapourtion and gas separation with dense membranes, fouling is virtually absent.

1.9.4 Methods to reduce fouling:

Because of the complexity of the phenomenon, the methods for reducing fouling can only be described very generally. Each separation problem requires its own specific treatment, although several approaches can be distinguished.

1.9.4.1 Pretreatment of the feed solution

Pretreatment methods employed include: heat treatment, pH adjustment, addition of complexing agents (EDT A etc.) chlorination, adsorption onto active carbon, chemical clarification, pre-micro filtration and pre-ultrfiltration. Fouling reduction starts in developing a proper pretreatment method. Often, considerable time and effort is spent on membrane cleaning whereas pretreatment is often overlooked. Sometimes very simple measures can be taken, e.g. pH adjustment is very important with proteins. In this case, fouling is minimized at the pH value corresponding to the isoelectric point of th protein, i.e, at the point at which the protein is electrically neutral. In the pervaportion and gas separation, where fouling phenomena only playa minor role, pretreatment is important and often simple to accomplish. Thus, classical filtration or microfiltration methods can be used to prevent particles form entering the narrow fibers or channels on the feed side.

1.9.4.2 Membrane Properties

A change of membrane properties can reduce fouling. Thus fouling with porous membranes (micro filtration, ultrfiltration) is generally much more severe than with dense membranes (pervaportion, reverse osmosis). Furthermore, a narrow pore size distribution can reduce fouling (although this effect should not be overestimated).

The use of hydrophilic rather than hydrophobic membranes can also help reduce fouling. Generally proteins adsorb more strongly at hydrophobic surfaces (Negatively) charged membranes can also help, especially in the presence of (negatively) charged colloids in the feed. Another method is the pre-adsorbed of the membrane by a component which can be easily removed.

1.9.4.3 Module and process conditions:

Fouling phenomena diminish as concentration polarization decreases. Concentration polarization can be reduced by increasing the mass transfer coefficient (high flow velocities) and using lower flux membranes. Also the use of various kinds of turbulence promoters will reduce fouling, although fluidized bed systems and rotary module systems seem not .very feasible form a economical point view for large scale applications but they may attractive for small scale applications.

1.9.4.4 Cleaning

Although all the above methods reduce fouling to some extent cleaning methods will always be employed in practical. The frequency with which membranes need to be cleaned can be estimated from process optimization. Three cleaning methods can be distinguished: 1) Hydraulic cleaning 2) Mechanical cleaning 3) chemical and 4) electric cleaning.

1.9.4.4.1 Hydraulic cleaning

Hydraulic cleaning methods include back-flushing (only applicable to microfiltration and open ultrafiltration membranes), alternate pressuring and depressuring and by changing the flow direction at a given frequency.

The principle of back-flushing is depicted in figure. After a given period of time, the feed pressure is released and the direction of the permeate reversed from the permeate side to the feed side in order to remove the fouling layer within the membrane or at the membrane surface.

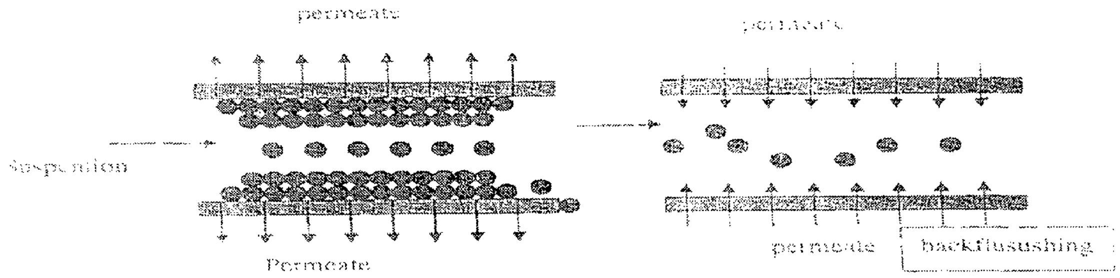

Fig: 1.6 The principle of back-flushing

1.9.4.4.2 Mechanical Cleaning:

Mechanical cleaning can only be applied in tubular systems using oversized sponge balls.

1.9.4.4.3 Chemical Cleaning:

Chemical cleaning is the most important method for reducing fouling, with a number of chemicals being used separately or in combination. The concentration of the chemical (e.g. active chlorine) and the cleaning time are also very important relative to the chemical resistance of the membrane. Although a complete list of the chemicals used cannot be given, some important (classes of) chemicals are;

- Acids (strong such as H_3PO_4, or weak such a critic acid)
- Alkali (NaOH) .
- Detergents (alkaline, nonionics)
- Enzymes (proteases, amylases, glucanases)
- Complexing agents (EDTA, polyacrylates, sodium hexametaphospate)

- Disinfectants (H202, and NaOCI)
- Steam and gas (ethylene oxide) sterilization

1.9.4.5 Electric cleaning:

Electric cleaning is a very special method of cleaning. By applying an electric field across a membrane charged particles molecules will migrate in the direction of the electric field. This method of removing particles or molecules from the interphase can be applied without interrupting the process and the electric field is applied at certain time intervals. A drawback of this method is the requirement to use electric conducting membranes and a special module arrangement with electrodes.

1.10 DESCRIPTION OF THE PROBLEM

The dehydrogenation of ethylbenzene to manufacture styrene is very important process industrially.As the reaction is reversible the conversion is limited because of thermodynamic equilibrium.Due to continuous removal of of product the yield can be improved by carrying out reaction inside a membrane reactor.The reaction is carried out in tube side packed with catalystand in isothermal condition.A mathematical model is required to predict the performance of membrane reactor with suitable assumptions.

LITERATURE REVIEW

The review of literature on assigned dissertation topic is the pinnacle of very dissertation work. As our dissertation topic is related to modeling of membrane reactor, which in turn is referred to as a chemical reactor with membrane as a separator, enormous literature is available on its various aspects. The present chapter provide a brief discussion of the literature only on those aspects which are relevant to the objective of the dissertation work mentioned in section 1.10 of Chapter 1.

This chapter is divided into three parts: The first part includes the research papers regarding the development of membrane reactor. The second part includes research papers related to experimental work. The third part is the most important part. In deals with various research papers where mathematical modeling and simulation of membrane reactors are carried out and studied.

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2.1 DEVELOPMENT OF MEMBRANE REACTOR

In this section all presented research papers outline the development in this emerging technological field.

Armor (1989) has studied the area of membrane catalysis, where metal membrane in the reactor acts as a catalyst as well as separator. Palladium and palladium alloy membrane reactors are compared ad discussed with regard to technology limitations and needs. Because of the limitation of palladium metal compositions, there I an emerging efforts in less costly but high hydrogen permeable metal membranes such as those composed of tantalum or niobium. An extended discussion on critical issues remaining for the successful commercial application of this technology is also given at the end.

Armor (1998) has worked on catalytic membrane reactor as applied to opportunities and applications within petroleum refineries. Since so many inorganic membranes take advantages of H_2 perm selectivity, and H_2 demand as increasing in a refinery, there is a number of interesting process applications being considered. By using Pd based membranes for dehydrogenation; oxyddehydrogenation and decomposition reactions H_2 production can be enhanced. Permselective H_2 membranes can be used for carrying out selective hydrogenations of organic substrates and coupled reactions. These membranes have been also considered for enhancing steam-reforming reactions for the production of bulk H_2, the water gas shift reaction and the conversion of natural gas to syngas and liquid fuels. Dense oxide membranes are also being developed for the selective oxidation of CH_4 to syngas. For many of these process the formation of carbon during steam reforming or dehydrogenation reactions will always be a huge hurdle towards any successful commercial application of Pd membranes to such processes, For all these purposes the critical issues that need to be resolved for the commercial use of catalytic membrane reactors have been discussed.

Caronas and Santamaria (199) have reviewed the developments and outstanding opportunities in the field of catalytic reactors based on porous ceramic membranes, both inert and catalytic. Rather than attempting a thorough review of the relevant literature, this work deals with some general concepts and then concentrates on a few selected examples that illustrate the application of membrane reactors. Authors at the end concluded that an important effort was still needed to develop methods of preparation and characterization, novel membrane materials and reactor configurations. Industrial applications are not foreseeable in the immediate future because of formidable practical problems involved in moving form laboratory to industrial scale in such a new technology.

Saracco et.al. (1999) have reviewed the most recent available literature in the field of membrane reactors. The authors have mentioned that since 1994, progress has been achieved in several areas (sol-gel deposition of defect free sol-gel derived membranes, reduction in thickness of Pd membranes, synthesis of zeolite membranes) whereas stagnation was noticed in some others (high temperature sealing of membranes into modules, scaling up of membrane reactor etc.) In their work, authors have suggested that despite the research efforts, industrial application does not seem to be round the corner. Authors also reviewed the special progress in the production of amorphous silica to layers, layers of zeolite ad a creeping improvement of dense metal membrane top layers.

Sirkar et al. (1999) have given overview which develops functional perspective of membranes in a variety of reaction processes. Various functions of the membrane in a reactor can be categorized according to the essential role of the membrane. They can be employed to introduce/separate/purify reactant(s) and products, to provide the surface for reactions, to provide the structure for the reaction medium or to retain specific catalysts. Within this context the membrane can be catalytic or non-catalytic, polumeric/inorganic and ionic/nonionic and have different physical/chemical structures geometries. The various possibilities of membrane inside reactor are discussed.

Dittmeyer et.al. (2001) have discussed two different membrane reactor concept which both rely on supported palladium, on one hand as a permselective membrane material, and on the other hand as based component of a membrane type hydrogenation catalyst. Dense palladium composite membranes can be used fopr hydrogen separation from packed bed catalyst in gas-phase hydrocarbon dehydrogenation reactions. Mesoporous membranes containing dispersed bimetallic Pd/X-clusters can be employed as so-called catalytic diffusers for liquids-phase hydrogenation. The principles of both concepts are introduced, recently obtained experimental data are evaluated in connection with literature results, and the perspectives of further developments are highlighted.

Julbe et.al. (2001) have reviewed and discussed the working concepts of membrane reactors. The main type of porous ceramic membranes, which have been developed for membrane reactor applications, are reported and discussed. Starting form a general basis here objective is to put recent developments and related synthesis methods. Authors finally conclude that may attractive developments are expected in the field of membrane science, based on the progress made in the field of catalyst optimization and new membrane synthesis methods.

Dixon (2003) has reviewed various aspects of recent research in catalytic inorganic membrane reactors. The author at the end concluded that progress towards commercialization of catalytic membrane reactors continue to be slow as from the industrial point of view. Many issues to be resolved before a case an be made for membrane reactors, including cost of membranes, their production in quantity and their reliability. On the research side, author has outlined that interest is strong with the trend in the number of publication on catalytic membrane reactors increasing steadily despite fluctuations form year to yer. Despite being the oldest area of application of catalytic membrane reactorsw, the removal of product hydrogen still gives rise to great deal of work, ad new reactions and new areas are being found. More detailed model are being developed which includes the use of two-dimensional reactor tube models, and concentration and temperature profiles.

2.2 EXPERIMENTAL STUDIES ON MEMBRAE 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 description of their work.

Itoh (1987) has carried out the first experiment for dehydrogenation of cyclohexane in laboratory scale palladium based membrane reactor. Palladium tube of 200 μm thickness, 17.0 mm OD and 140 mm long has been used. Inside the membrane tube cylindrical catalyst pellets (0.5 wt% Pt/Al_2O_3, 3.3 mm OD,3.6 mm high were uniformly packed. The conversion at the end of reaction inside packed bed palladium based membrane was 99.7% which is much higher as compared to the equilibrium conversion 18.7%.

Casanave et. al. (1995) have discussed dehydrogenation of iso-butane in membrane reactor using either mesoporous alumina membrane or microporous zeolite membrane. They observed that increase in the equilibrium conversion is because of two phenomena: a complete mixing of reactants products and sweep gas in case of mesoporous membrane and continuous separation of hydrogen in case of zeolite based microporous membrane. They also suggested that improvements in this area can be done by improving membrane catalyst and better reactor modeling.

Rezac et.al. (1995) have reported the increases of up to 1.5 times the traditional equilibrium limit for a membrane assisted reactor system with the dehydrogenation of n-butane as a model system. The use of thermally stable polymerceramic composite membranes to remove product hydrogen from the dehydrogenation reaction system has been evaluated as a function of the reaction temperature from 480 °C-540 °C. Under these conditions, the selectivity of the catalyst for the production of butanes was greater then 90% and was not markedly affected by the presence of membrane.

Sheintuch and Dessau (1996) have carried outdehydrogenation of iso-butane and propane in a membrane reactor made of a Pd/Ru (or PD/ag) tube packed with a supported Pt catalyst. A stream of nitrogen or its mixture with hydrogen was swept into the shell side. Significant gains in yield were achieved by separating the hydrogen through the selective Pd membrane: up to 76% butene at 500°C (compared with 32% in equilibrium) and 70% propene at 550°C (23% at equilibrium). The attained yields, however, were limited at low feed rates by suppressed catalyst activity in the absence of hydrogen. To avoid low activity and fast aging, hydrogen concentration should be kept at about 2% by adjusting the shell or tube side flow rates. Fast deactivation was observed with high ratios of shell to tube side flow rates. The degree of cracking and of isomerisation increases with conversion. Temperature should be kept below 500°C during butane dehydrogenation to avoid cracking and fast aging. Yields under high pressures (18 psi for isobutene and 100 psi for propane) were similar to those obtained under atmospheric conditions. Operation under pressure may be advantageous as high purity hydrogen can be produced. The yield dependence on feed rate and on hydrogen shell-side pressure were adequately described (at 500°C) by a simple model that incorporates a three-parameter rate expression, which accounts for the accelerating role of hydrogen pressure. The degree of cracking and isomerisation were adequately described by a single-parameter rate expression which assumes that the main and side reactions occur on the same sites. The model was optimized to determine the feed and shell flow rates which maximize the yield. The optimization suggests that, in the present design, the yield cannot be improved significantly beyond 90%, but almost complete conversion can be achieved when the reactor profile of hydrogen pressure is optimized.

Bernstein et.al. (1996) have considered a membrane reactor consisting of two recirculating flow systems connected via a membrane module. The reactor has been constructed and used to study the dehydrogenation of cyclohexane. The batch system has the advantages of easily varying the ratio of membrane area to reactor volume and sampling a very wide range of effective Damkohler numbers. With the batch reactor it was possible to experimentally confirm predictions that were based upon computer simulations but which were outside the range of experimental study for the conventional rectos used.

Weyten et.al. (1997) have considered direct dehydrogenation of propane to propene in tubulr H_2-selective silica membrane reactor. The membrane reactor was filled with chromia/alumina catalyst. The kinetics of catalyst was studied here. At 500 ^oC the deactivation of catalyst was slow. And propane yield is almost constant for 10 h operation. Under well-chosen conditions, the propene yield was at least twice as high as the value obtained at thermodynamic equilibrium in a conventional reactor. The theoretical concept of membrane reactor is already known. This paper shows experimentally that concept really works and combines the reactor experiment with the characteristics of the membrane and of the catalyst.

Seramm and Siedel-Morgenstern (1999) have studied the performance of a membrane reactor using two types of membranes experimentally. At first the mass transfer through a porous glass membrane was characterized. Then this membrane was modified with a thin palladium layer by an electroless plating technique. Reaction kinetics of the dehydrogenation of cyclohexanol Pd catalyst was determined in the slightly modified experimental setup. Higher conversions were found for the studied dehydrogenation reaction using the dense membranes as compared to the porous membrane. The application of a reactive sweep gas was found favorable compared to usage of an inert sweep gas.

Elnasaie et.al. (2001) have developed a procedure linking kinetic modeling of catalytic reactions to reactor modeling for different configurations [Proposed by --- (2000)]. It is applied to the catalytic dehydrogenation of methylbenzene to styrene to four configurations namely fixed bed with/without hydrogen selective membranes and bubbling fluidized bed with/without hydrogen selective membranes. The kinetic data for three in-house prepared catalysts were obtained form the laboratory scale experiments using pseudo-homogeneous models. They have concluded that rigorous, reliable reactor models integrated with reliable kinetic data and kinetic models are very powerful tools in the development of a process from the laboratory scale to the commercial scale. Thee models can help to save the expensive pilot plant stage or at least minimize its cost and maximize its utilization.

Keuler and Loenzen (2001) have investigated the dehydrogneation of 2-butanol to methyl ethyl ketone (MEK) in a membrane reactor. The membrane reactor consisted of a Pd-Ag film (2.2 μm thickness) deposited on the inside of an -α-alumina tube and packed with a 14.4% Cu on SiO_2 catalyst. The performance of membrane reactor with that of tubular reactor was carried out. The effects of the 2-butanol feed flow rate and the sweep gas to feed molar ratio on 2-butanol conversion were investigated. Selectivity towards MEK was found to be 96% for all conducted experiments.

Masuda et.al. (2003) have studied zeolite membrane reactor where ZSM-5 layer on cylindrical alumina filter was there. In their experimental study, they studied methanol to olefin conversion. The reaction was continued for 1h under the conditions of a methanol feed rate of 3.3 to 6.76×10^{-0} m^3-NTP min^{-1} a pressure drop form 0 to 13.3 Kpa. From experimental study they concluded that ZSM-5 was found to be useful for recovering inter-mediate species of reactions in series ad by adjusting the diffusion and chemical reaction rates of molecule within the ZSM-55 zeolite layer of the membranes, olefins at a high selectivity of about 80 to 90% could be recovered at 60-98% methanol conversion.

2.3 MATHEMATICAL MODELING

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

Mohan and Govind (1988) have studied fundamental understanding of the behavior of reactors with a permselective wall in terms of design parameters (reactor length, membrane thickness), operating variables (pressure ratio, feed flow rate,) physical properties and flow patterns. It is shown by simulation that equilibrium shift a be enhanced by recycling the unconverted reactants, and shifting feed location to separate products and to maintain high permeation rates to reduce back reaction.

Sun and Khang (1988) have demonstrated the possibility of achieving conversions above the original equilibrium conversion based on the feed conditions by combining the selective separation effect of a membrane and the catalytic function of transition metals. A catalytic membrane reactor consists of tubular Vycor glass membrane, which was impregnated with platinum catalyst in which model reaction of cyclohexane dehydrogenation was considered. The equilibrium shift was significant with high space-time. The performance was compared with that of conventional reactor and the membrane reactor was found to be superior.

The assumptions taken for developing the mathematical model are:

- Operation is isothermal.
- The interfacial mass-transfer resistance between the gas phase and the surface catalytic membranes is negligible.
- It is also assumed that the contents in the feed-side chamber and the permeate side chamber are well mixed.

The steady state equations for the system are given as follows:
In the catalytic membrane;

$$\frac{D_j}{RT}\frac{1}{r}\frac{d}{dr}\left[r\frac{dP_j}{dr}\right]+\sum_{i=1}^{m}v_{ij}k_i f_i(P)=0 \qquad (j=1,2...n) \qquad (2.1)$$

The boundary conditions are

$P_j = x_j P_f$, at $r=r_f$ (2.2)

$P_j = y_j P_p$, at $r=r_p$ (2.3)

In the feed side chamber (shell side);

$$Q_f^0 x_j^0 - Q_f x_j - 2L\frac{D_j}{RT}\left(r\frac{dP_j}{dr}\right)\Big|_{rf} = 0 \qquad (j = 1,2...n) \qquad (2.4)$$

In the permeate side chamber (tube side);

$$Q_f^0 y_j^0 - Q_f y_j - 2L\frac{D_j}{RT}\left(r\frac{dP_j}{dr}\right)\Big|_{rf} = 0 \qquad (j = 1,2...n) \qquad (2.5)$$

The following rate expression is used for the cyclohexane dehydrogenation:

$$r_1 = k\left(P_1 - \frac{P_2 P_3^2}{K_p}\right), kmol/(m^3 s) \qquad (2.6)$$

where, k and Kp are the reaction rate constant and the reaction equilibrium constant respectively. The equilibrium constant is calculated from Gibbs free-energy data;

$$K_p = 2.524x10^{26}\exp\left(\frac{-2.606x10^4}{T}\right), kPa^3 \qquad (2.7)$$

Wu and Liu (1992) have developed a mathematical model to evaluate the performance of a membrane reactor for the catalytic dehydrogenatin of ethylbenzene to styrene. The model previously discussed in the literature has been modified to include side reactions for estimating product selectivities. According to their analysis in selected case study an increase in styrene yield over the thermodynamiclimit is achieved by a hybrid system, i.e., a fixed bed reactor in conjunction with a membrane reactor. The proposed membrane reactor showed a different behavior in the generation of key side products, i.e. benzene and toluene.

Tayakout et.al. (1995) have established a catalytic membrane reactor modeling through mass balance equations in different control volumes. Two different strategies were followed to solve the parabolic differential system representing the mss balance. The orthogonal collocation methods in two spatial dimensions were used to solve the elliptic form of the equation corresponding to steady state. Finite difference method was used to solve the global dynamics system.

The following assumptions were taken into account to establish the model:

- The reactor is isothermal.

- The flow in each compartment is laminar with parabolic velocity profile and dispersion in axial and radial direction is considered.
- Transmembrane pressure is zero.

The dimensionless form of mass balance in different control volumes can be written as follows:

In the inner compartment:

$$\alpha^{(1)}\frac{\partial\Psi}{\partial t}+Pe^{(1)}\frac{\partial\Psi}{\partial\xi}-\frac{\partial^2\Psi}{\partial\xi^2}-\beta^{(1)}\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial\Psi}{\partial\rho}\right)=0 \qquad (2.8)$$

The interface and boundary conditions

For all ξ,ρ=0; $\frac{d\psi}{d\rho}=0$ (2.9)

For all ξ,ρ=0; $\frac{d\Psi}{d\rho}\Big|_{p=1}=\gamma^{(1)}\frac{d\Psi}{d\rho}\Big|_{p=0}$ (2.10)

In the membrane:

$$\alpha^{(2)}\frac{\partial\Psi}{\partial t}-\frac{1}{(a.\rho+r_{\text{int}})}\frac{\partial}{\partial\rho}\left((a.\rho+r_{\text{int}})\frac{\partial\Psi}{\partial\rho}\right)-\lambda\Phi^2R(\Psi)=0 \qquad (2.11)$$

The interface and boundary conditions

$\forall\xi,\rho=1;\quad \frac{d\Psi}{d\rho}\Big|_{p=1}=\gamma^{(1)}\frac{d\Psi}{d\rho}\Big|_{p=0}$ (2.12)

$\forall\xi,\rho=1;\quad \frac{d\Psi}{d\rho}\Big|_{p=1}=\gamma^{(2)}\frac{d\Psi}{d\rho}\Big|_{p=0}$ (2.13)

In the outer compartment,

$$\alpha^{(3)}\frac{\partial\Psi}{\partial t}+Pe^{(3)}F(\rho)\frac{\partial\Psi}{\partial\xi}-\frac{\partial^2\Psi}{\partial\xi^2}-\beta^{(3)}\frac{1}{(b\rho+r_{ext})}\frac{\partial}{\partial\rho}\left(b\rho+r_{ext})\frac{\partial\Psi}{\partial\rho}\right)=0 \qquad (2.14)$$

$\forall\xi,\rho=1;\quad \frac{d\Psi}{d\rho}\Big|_{p=1}=\gamma^{(2)}\frac{d\Psi}{d\rho}\Big|_{p=0}$ (2.15)

$\forall\xi,\rho=1;\quad \frac{d\Psi}{d\rho}=0$ (2.16)

$$\xi = 0 \qquad 0 < \rho < 1 \qquad 1 + \frac{1}{Pe^{(3)} F(\rho)} \frac{d\Psi}{d\xi} - \Psi = 0 \tag{2.17}$$

They solved these model equations using two method: orthogonal collocation method and finite difference method and they concluded that for a quick estimate form experimental data the collocation method should be selected. The finite difference method should be used when optimization problems associated to the system structure are to be solved.

Assabumrungrat and White (1996) have discussed performance of membrane reactor. The membrane chosen was a composite alumina packed with a catalyst and allowed low molecular gases to diffuse through it at a faster rate than gases with a high molecular weight. This allowed greater conversion to be achieved. Dehydrogenation of methyl-cyclohexane to toluene with production of hydrogen was considered. Data for the performance of the membrane have been estimated from previous experiments using single gases and membrane have been estimated from previous experiments using single gases and mechanisms considered were according to Knudsen and bulk flow. A standard kinetic model was also incorporated in the calculations. The correlations of maximum effective length of membrane reactors and maximum percentage conversion as function of feed velocity and membrane diameter demonstrated in this paper.

Assumptions taken for developing the model are as follows.

- The flow is steady state.
- The reaction is operated at isothermal conditions.
- The ideal gas law is used to determine gas properties.
- Pressure is constant in both shell and tube side.
- Axial diffusion is negligible.

Performing the material balance, a set of equation was obtained.

For flow in permeate side chamber (Shell Side):

$$Q_i\Big|_z - Q_i\Big|_{z+dz} + \frac{P}{RT}\pi D q_i dz = 0; \tag{2.18}$$

For flow in the packed bed chamber (tube side):

$$F_i\Big|_z - F\Big|_{z+dz} + \frac{\pi}{4}D^2\lambda_i r_t dz - \frac{P}{RT}\pi D q_i dz = 0 \tag{2.19}$$

Where subscript z and z+ dz represents the position of interest and i refers to each species.

λ_I is the stoichiometric coefficient of species i, namely 3 for hydrogen,2 for toluene and 1 for methyl-cyclohexane and subscripts t represents for toluene. The equations were further simplified and were solved using Runge-Kutta method.

Gobina and Hughes (1996) have carried out experimental and modeling study for catalytic dehydrogenation of n-butane. Use of nitrogen, carbon monoxide/nitrogen and oxygen/nitrogen sweep gases produced conversions up to 5 to 8 times and equilibrium hydrogen with O_2 or CO.

Model equations are formulated on the basis of following assumption.

- Conditions are isothermal.
- Temperature and Pressure gradients in catalyst pellet are neglected.
- Operation is steady-state.
- The pressure in the catalyst bed and Vycor glass is constant because of the low conversion of ethane.
- Radial changes of concentrations are included in the model.

The balance equations are developed as given below.

In the catalyst bed: For),$r_1<R_1$, where r_1 is the dimensionless radius and y_i represents the dimensionless concentration of species I, α and Pe_i represent a constant and as peclet number respectively.

$$\frac{\partial y_i}{\partial \xi} = \frac{\alpha}{Pe_i}\frac{1}{\partial r_1}\left[r_1\frac{\partial y_i}{\partial r_1}\right] + r_A \tag{2.20}$$

In the Vycor Glass, For 0<r2,1 and $r_2=(r-R_1)/(R_2-R_1)$

$$\beta \frac{\partial}{\partial r_2}\left[\frac{1}{\beta}\frac{\partial x_i}{\partial r_2}\right]=0 \tag{2.21}$$

where, $\beta = \dfrac{\Delta R}{(r_2 \Delta R + R_1)}$

In the shell (sweep gas) side:

$$\frac{dy_s}{d\xi} = (-1)^m d_1 \left[y_3^{1/2} - (P_r)^{1/2} y_s^{1/2}\right] \tag{2.22}$$

When an "oxidative extraction" reaction (i.e. air or CO as sweep gas) was used in the shell side instead of pure N_2, equation becomes:

$$\frac{dy_s}{d\xi} = (-1)^m d_1 \left[y_3^{1/2} - (P_r)^{1/2} y_s^{1/2}\right] - (-1)^m \gamma r_{H2} \tag{2.23}$$

where, $\xi = \dfrac{1}{L}$, and γ=0 for N_2 sweeep gas and 1 during extractive oxidation. r_{H2} is dimensionless rate of reaction of permeate hydrogen with oxygen for carbon monoxide and the other symbols are defined in the reaction.

Koukou et.al. (1996) have developed a mathematical model which predicts the effect of design parameters, operating variables and physical properties on the performance of a membrane reactor with a permselective wall. The model consists of full set of partial differential equations that described the conservation of mass, momentum of chemical species, coupled with chemical kinetics and appropriate boundary conditions for the physical problems. The solution involve method of finite volume technique. The model was applied to study the dehydrogenation of cyclohexane. It was concluded that gas separation and reactor performance are strongly influenced by dispersion effects only in the latter membrane reactor, while in both cases radial concentration profiles do not correspond to those obtained with plug flow. Therefore, simulations of this type problem should be based on complex dispersion models rather than the existing ideal plug flow ones.

Following assumptions are taken into account for development of mathematical model.

- Operation is steady state

- Operation is isothermal at atmospheric pressure.
- Sweep and feed gases are n co-current flow.

The mathematical analysis is based on the set of elliptic, partial differential equation that express the conservation of mass, momentum of chemical species for steady state, two-dimensional flow.

$$\frac{\partial \rho \varphi}{\partial t} + div(\rho \upsilon \varphi + \Gamma_{\varphi} grade \varphi) = S_{\varphi} \qquad (2.24)$$

The dependent variable φ may be: the mixture pressure P, the radial and axial velocity components v, w, the mass fractions of chemical component c_i and the mixture specific enthalpy h.

Dittmeyer et.al. (1997) have studied the catalytic dehydrogenation of ethylbenzene to styrene in a tubular palladium membrane reactor using a commercial styrene catalyst. A mathematical model of the reactor is presented which takes into account the different mss transport mechanism prevailing in the various layers of the membrane that is multi component in the stagnant gas film on both faces of the membrane, combined effective multicomponent diffusion, effective Knudsen diffusion and viscous flow in the macroporous support. Simulation calculations are carried out for industrially relevant operating and various process configurations.

The development of mathematical model relies on following assumptions.

- Flow of bulk gas phase on shell and tube side is plug flow type.
- The heat transfer resistance through the membrane is neglected i.e. the permeate gas phase and the retentate gas phase are assumed to be at the same temperature.
- Composite membrane is treated by accounting for upto three membrane layers, viz. that is the macro porous support layer, a micro porous skin layer and an impervious metal film coated either on the tube or on the shell side.

Mass Balance at the retentate side.

$$\frac{dn_i^R}{dz} = A^R \rho_B \sum_{j=1} \upsilon_{ij} r_j - 2\pi R_R J_j \Big|_{R_R} \tag{2.25}$$

Mass Balance on the permeate side:

$$\frac{dn_i^S}{dz} = 2\pi R_R J_i \Big|_{R_R} \tag{2.26}$$

Energy Balance under adiabatic conditions

$$\frac{dT}{dz} = \left[\sum_i -(\Delta H_{Rj}) r_j + (-\Delta H_{ox}) f H_2 \right] \frac{A_R \rho_B}{n_{tot} C\rho} \tag{2.27}$$

The pressure gradient dP/dz along the catalyst bed is calculated according to the Ergun equation and for the sweep gas side is determined using Hagen-Poiseuille equation. The above mentioned ODE both for axial and radial directions, are solved using following initial conditions:

$$n_i^k \Big|_{z=0} = n_i^{k,0}; T^k \Big|_{z=0} = T^{k,0}; i = 1..n; k = S, R$$

(2.28)

Equation are solved using generalized Newton Raphson Method.

Koukou et.al. (1997) have presented the development of mathematical model which simulates the performance of a non-isothermal packed-bed membrane reactor. The model takes into account the various heat exchanges taking place inside the reactor. In this study the developed mathematical model is applied to investigate the edothermic dehydrogenation of cyclohexane in a packed-bed membrane reactor, where a permsulective porous glass membrne is embodied.

Following assumptions are taken into account for development of mathematical model.

- Flow of mass on both side of the reactor is plug flow type.
- Operation is steady state.
- Flow of sweep and feed gas are in concurrent mode.
- Pressure is atmospheric pressure.
- The permeabilities of the component passing through the membrane are independent of temperature range studied.

The mathematical model developed in this study describes the balance of the relevant quantity expressed by the following partial differential equation.

$$\frac{\partial \rho\varphi}{\partial t} + div(\rho\upsilon\varphi + \Gamma_{\varphi} grad\varphi) = S_{\varphi} \qquad (2.29)$$

The dependent variable φ may be: the mixture pressure, P, the radial and axial velocity components v,w, the mass fractions of chemical component c and the mixture specific enthalpy h. Other terms have their usual meaning. In the solution procedure employed to sole the set of the conservation partial differential equatioins along with the proper boundary condition, the computational domain of interest is discretized into a number of finite control volumes (cells) and the differential equations for the various dependent variable. The equations were solved using mathematical package. Based on the result of the numerical simulation presented and analyzed in this study, it is concluded that heat effects taking place inside the reactor have to be taken into account, because possible omission of them will induce an overestimation in the predicted temperature and in calculated conversions.

Mon and Seung Bin Park (2000) have studied the effects of changing permeation rte, reaction rate and selectivity on the exit conversion of a membrane reactor and to provide a guideline in designing membrane in terms of selectivity and permeability. For both isothermal and non isothermal conditions the exit conversion is plotted as a function of Peclet number (Pe) and Damkohler number (Da). From this study it was fond that selective permeation is the controlling mechanism for midrange Pe. Increasing value of the sweeping gas flow rate increases the conversion. The model equations developed here consider steady state, isothermal operation; uniform flow in shell and tube side; membrane as inert to the reaction and pseudo-homogeneous model for catalyst bed.

The balance equations are written as follows:

Shell side:

$$\frac{dy_i^0}{d\xi} = \alpha_i \frac{1}{Pe}\left(\frac{y_i^0}{\sum y_i^0} - \frac{y_i}{\sum y_i^1}\right) + \upsilon_i Da\eta \qquad (2.30)$$

Boundary conditions are:

$$\xi = 0, y_i^0 = y_{i,0}^0 \tag{2.31}$$

Tube Side:

$$\frac{dy_i^1}{d\xi} = \alpha_i \frac{1}{Pe}\left[\frac{y_i^0}{\sum y_i^0} - \frac{y_i^1}{\sum y_i^1}\right] \tag{2.32}$$

Boundary condition:

$$\xi = 0, y_i^1 = y_{i,0}^1 \tag{2.33}$$

The two dimensionless numbers, Pe and Da are defined as follows:

$$\frac{1}{Pe} = \frac{2\pi R_i L p_c p_T^0}{F_{c,0}^0} \tag{2.34}$$

$$Da = \frac{\pi(R_0^2 - R_i^2) L\Psi k_0 P_T^0}{F_{c,0}^0} \tag{2.35}$$

Moustafa and Elnashaie (2000) have used rigorous heterogeneous model to study the performance of the membrane catalytic reactor for the dehydrogenation of ethylbenzene to styrene. The mathematical model I extended to simulate a novel hydrogen selective composite membrane for hydrogen separation. One side of the tyene while the other catalytic side is a hydrogenation section in which benzene is catalytically converted to cyclohexane. The continuous removal of hydrogen from the dehydrogenation section leads to the shift of equilibrium conversion in this section thus higher styrene yield is obtained.

Model equations rely on the following assumptions:

- The reaction mixture behaves as an ideal gas in both catalytic reaction sections.
- Both sections are operated at steady state.
- Radial variations in both beds are negligible.
- Axial diffusion of mass and heat transfer Is negligible.
- The catalytic effect of thin palladium membrane layer is neglected.

Model equation for the catalytic dehydrogenation section are as follows:

$$\frac{dX_i}{dL} = \frac{\eta_i \rho_B A_B R_i}{FF_{EB}} \tag{2.36}$$

$$\frac{dX_j}{dL} = \frac{\eta_i \rho_B A_B R_j}{FF_{H_2O}} \tag{2.37}$$

Model Equations for catalytic hydrogenation section is as follows:

$$\frac{dX_{BZ2}}{dL} = \frac{\eta \rho_{B2} A_{B2} (RR)}{FF_{BZ2}} \tag{2.38}$$

The Energy balance equations for two reactions are as follows:

$$\sum_{i=1}^{10} F_i C_{p_i} \frac{dT}{dL} = \sum_{j=1}^{6} (-\Delta H_j) \eta_j R_j \rho_B A_B + U(\pi N_t D)(T - T) \tag{2.39}$$

$$\sum_{i=1}^{3} F_i C_{p_i} \frac{dT'}{dL} + \frac{dQ_p}{dL} C_{pH_2} (T - T) = (-\Delta H') RR \eta \rho_{B2} A_{B2} - U(\pi N_t D)(T - T') \tag{2.40}$$

The dusty gas model equations are used for the catalyst particles in the dehydrogenation sections. The orthogonal collocation technique is used to solve the two point boundary value problems of the catalyst pellets for both reactor sections. The bulk phase differential equations are solved using subroutine DGEAR (IMSL) in which Runge-Kutta-Verner fifth and sixth order method is applied. Automatic step size is taken to ensure accuracy. The dat used to simulate the dehydrogenation section is taken from an industrial reactor at Polymer Corporation,Sario, Ont. Canada. The magnitude of increases in ethylbenzene conversion, styrene yield and selectivity are quite appreciable together wth te production of additional product, which is cyclohexane by the utilization of the permeated hydrogen through the membrane. The values of styrene yield reaches as high as 87%.

Hou et al. (2001) have proposed the model for membrane reactor taking into consideration radial and temperature profiles for each reactant. The model proposed here is applicable for a membrane reactor with a fixed bed of catalyst inside the membrane and with distribution of one of the reactants along the reactor through the membrane. Assumptions of isobaric condition, cylindrical symmetry, axial and radial components of gas velocity, diffusive and convective components of radial transport of mass and applicability of ideal gas are taken.

Mass balance yields-

$$\frac{\partial F}{\partial Z}=\frac{D_i\varepsilon_B}{R_G}\left(\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial(P_i/T)}{\partial r}\right)\right)+\frac{1}{r}\frac{\partial(u_r^{r)}}{\partial r}\frac{P_r}{P}+\rho_B\sum v_{ij}r_j \tag{2.41}$$

With boundary conditions as:

$$u_r=u_w\frac{r}{R} \tag{2.42}$$

Heat Balance yields –

$$\frac{\partial T}{\partial z}=\frac{1}{\sum R_iC_{p_i}}\left[\frac{\lambda_{er}}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)+\sum\frac{\partial(u_rT)}{\partial r}C_{p_i}\frac{P_i}{P}+\rho_B\sum r_j(-\Delta H_j)\right] \tag{2.43}$$

Following are the initial and boundary conditions:

At z = 0 F_o=F_{io} T=T_{in} (2.44)

At r = R Pi 0 except P_{02} = 1 T=T_R (2.45)

$$\left.\frac{\partial P_i}{dr}\right|_R=0\,except\,\beta\left.\frac{\partial P_{0_2}}{\partial r}\right|_r=u_w, \tag{2.46}$$

$$q=-\lambda_m\frac{\partial P}{\partial r}$$

The derivatives with respect to radius were approached by finite difference and the resulting sets of ordinary differential equation were solved by Runge-Kutta method.

The model predictions were validated with that of experiments and it was concluded that radial concentration profiles affect selectivity and yield attainable in the reactor.

Jayaraman et.al. (2001) have simulated annular reactor packed with matrices in which the catalysts/enzyme/microorganisms were immobilized. The results indicate tat the overall resistance and hence the conversion depends upon the Thiele modulus and another parameter. This parameter characterizes the ratios of the diffusion times and the ratios of length scales of the bulk liquid phase and the solid phase in the reactor shell. Analytical solutions have been obtained for linear reactors and a simplified semi-analytic method has been used for obtaining concentration profiles for nonlinear reactions. The following assumptions have been made in formulating design equations:

- The reactor is assumed to be of tubular geometry and steady state condition prevails in the reactor.
- The reactant movement through the tube side is by laminar convection in the axial direction and by diffusion in the radial direction.
- There is non convection in the membrane or shell.
- The reactor is assumed to be isothermal and the temperature gradients are neglected.
- The radial diffusion coefficients in the tube side, membrane bulk phase in the shell and through the pores of the matrices are constants and are independent of concentration.
- The matrices are assumed to be of spherical shape with a uniform radius throughout the bed.
- AS a representative example, reaction rate is assumed to follow Michaelis-Meten kinetics.

The model equations were solved using Newton-Raphson routine.

Sousa et.al. (200) have performed a theoretical study on a catalytic polymeric membrane reactor. The conversion enhancement over thermodynamic equilibrium is studied for the reaction A+B⇔ C+D. The model used, considers perfectly mixed flow and isothermal condition on both permeate and retentate sides. It is concluded here that the conversion of a reversible reaction can be significantly enhanced when the reactants' diffusion coefficients and/or sorption coefficient are higher than the products. The model equations were solved by the method of orthogonal collocation in finite elements.

The development of mathematical model relies on following assumptions:

- Steady state operation
- Perfectly mixed flow pattern on both retentate and permeate side
- Fickian transport across the membrane
- Isothermal operation
- Homogeneous catalyst distributions across the membrane.

Mass Balance in the membrane:

$$D_i H_i \frac{d^2 p_i}{dz^2} - \upsilon_i r = 0, i = A, B, C, D \quad (2.48)$$

The Boundary conditions:

$z=0; p_i=P_i^R$ (2.49)

$z=\delta; p=p_i^P$ (2.50)

Partial and total mass balance in the retentate chamber:

$$\frac{Q^F p_i^F}{RT} - \frac{Q^R p_i^R}{RT} + SD_i D_i \frac{dp_i}{dz}\Big|_{z=0} = 0 \qquad \text{i=A,B,C,D} \quad (2.51)$$

$$\frac{Q^F P^F}{RT} - \frac{Q^R P^R}{RT} + S\sum_i D_i H_i \frac{dp_i}{dz}\Big|_{z=0} = 0 \quad (2.52)$$

Partial and total mass balances in the permeate chamber:

$$\frac{Q^P p_i^P}{RT} + SD_i H_i \frac{dp_i}{dz}\Big|_{z=\delta} = 0 \quad (2.53)$$

$$\frac{Q^P p^P}{RT} + S\sum_i D_i H_i \frac{dp_i}{dz}\Big|_{z=\delta} = 0 \quad (2.54)$$

The model equations in this case are solved using orthogonal collocation in finite element method.

Sousa et.al. (2002) have considered the two reactions A ⇔ B and A ⇔ B+3C which describes the cyclohexane dehydrogenation.

The assumptions taken for developing the mathematical model are:

- Steady state operation.
- Isothermal conditions.
- Perfectly mixed flow on both permeate and retentate side.
- Fickian transport across the membrane was assumed.

Case I- For reaction A ⇔B

Mass balance in membrane and respective boundary condtions are:

$$\frac{d^2\Psi_i}{dx^2} - \upsilon_i \frac{\Phi_1^2}{\alpha_i \gamma_i}(\gamma_A \psi_A - \frac{\gamma_B \psi_B)}{K_e} = 0, \quad (2.55)$$

$$x = 0, \;\; \Psi_i = \Psi_i^R \quad (2.56)$$

$$x = 1, \quad \Psi_i = \Psi_i^P \tag{2.57}$$

Case II- For reaction: A ⇔ B+3C

Mass balance in the membrane and respective boundary conditions:

$$\frac{1}{e^{2\lambda\xi}}\frac{d^2\psi_i}{d\xi^2} = \upsilon_i \frac{\Phi_2^2}{\alpha_i}\left(\psi_A - \frac{\psi_B \psi_C^3}{K_p}\left(\frac{P_{ref}}{RT}\right)^3\right) = 0 \tag{2.58}$$

$$\Phi_2 = \lambda r'\left(\frac{k_d}{D_{ref}}\right)^{1/2} \tag{2.58}$$

$$\xi = \frac{In(\frac{r}{r'})}{\lambda}, \lambda = In\left(\frac{r'+\delta}{r'}\right) \tag{2.60}$$

These model equations are solved using adaptive wavelet based collocation method. They concluded that an adaptive wavelet based collocation method can treat this problem more accurate and efficient than any other conventional numerical method used.

Diakov V. and Arivind Varma (2003) have considered reaction involving methanol oxidative dehydrogenation to formaldehyde. The performance of the packed-bed membrane reactor (PBMR) was compared with that of the conventional fixed-bed reactor (FBR) over a wide range of operating conditions. An experimentally validated reactor model was used for this purpose.

The PBMR model:

The species mass balances for a steady-state plug-flow are given by:

$$\frac{d(vy_i)}{ds} = \left[\sum_{j=1}^{N_r} \rho_{ij}\right]\left[\frac{t_0}{C_T}\right] + qx_i; \qquad \text{I}=1, 2.....\text{N}_s \tag{2.61}$$

Where, y_i and x_i are the mole fraction of the component i inside the reactor and $s = \frac{z}{L}$ dimensionless coordinate along the length of the reactor.

For methanol partial oxidation, the rate expression is given by:

$$r_1(,c) = 0.0475.e^{-1760\left(\frac{1}{T}\frac{1}{485}\right)} xa^{0.5} \tag{2.62}$$

$$r_2(b,c) = \frac{2.91.e^{-8710\left(\frac{1}{T}-\frac{1}{485}\right)}.b.c}{\left[1+3.89e^{-5260\left(\frac{1}{T}-\frac{1}{485}\right)}c\right]^2} \tag{2.63}$$

It was found, both by simulations and experimental observation that relative reactor performance depends strongly on the operating conditions. Using formaldehyde yield as the basis for optimization, optimal reactor performances for a fixed catalyst mass were determined and compared. The results predicted higher optimal formaldehyde yield for the PBMR with oxygen fed via the membrane. The optimal reactor performance in this configuration is also less sensitive to variations in operating conditions and exhibits essentially 100% formaldehyde yield over a wide temperature range.

2.4 OBJECTIVE OF THESIS

On the basis of reviewed literature following objectives are made

i) To develope the mathematical model of a membrane reactor at steady state and isothermal condition .

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

iii) To validate the proposed model with available data.

iv) To study the effect of operating parameters on the performance of a membrane reactor.

CHAPTER III

MODEL DEVELOPMENT

3.0 INTRODUCTION

This chapter deals with development of mathematical model for manufacturing the styrene from ethylbenzene in a membrane reactor. We consider a tubular membrane reactor. The catalyst is packed on tube side. The feed is a mixture of ethylbenzene and steam and it is passed through tube, the steam as sweeping gas only in tube side passed through. The products like hydrogen and others are permeated by membrane to the shell. Vacuum is maintained in shell side. This model requires kinetic parameters, catalyst specifications and other physical properties pertaining to reaction components as well as separation carried out simultaneously in a membrane reactor so that solution of model equations my be obtained.

3.1 ASSUMPTIONS

- Operation is steady state.
- Gases behave ideally.
- Constant reactor wall temperature is maintained.
- Axial dispersion is negligible.
- Membrane is catalytically inactive.
- Flow of both sides of reactor is plug flow.
- Cocurrent flow of sweep & feed gas is maintained.
- The permeabilities of the components passing through the membrane are independent of temperature for the temperature range studied.
- Pressure drop is negligible inside reactor.

3.2 CHOICE OF CONTROL VOLUME

For developing model we divide the length of reactor L into small elemental length dz (as shown in Fig 3.1) and carry out the mass balance around dz both on tube & shell side of membrane reactor.

3.3 REACTIONS RATE EQUATIONS

Along with main reaction (ethylbenzene to styrene), many side reactions could possible occur. Depending on catalysts and operating conditions. All side reactions theoretically are reversible and can reach equilibria if an infinite contact time is given. The side reaction rates, however, are much slower than the main one. The reverse rates of the side reactions are negligible in this model. Carbon deposition and removal are excluded here because the resulting rate of change in the catalyst activity is much slower than those of dehydrogenation reactions. Reactions for minor side products, e.g., ethane, propane, and propylene, are ignored.

Main reaction:-

$$C_6H_5C_2H_5 \leftrightarrow C_6H_5C_2H_3 + H_2 \quad (3.1)$$

$$rate = k_1\left(P_{EB} - \frac{P_{ST}P_{H_2}}{K_P}\right) = k_1\left(P_{EB} - P_{EB,eq}\right) \quad (3.2)$$

$$K_P = \frac{P_{ST,eq}\,P_{H_2,eq}}{P_{EB,eq}} \quad (3.3)$$

Side reactions:-

$$C_6H_5C_2H_5 + H_2 \longrightarrow C_6H_5CH_3 + CH_4 \quad (3.4)$$

$$rate = K_2(P_{EB}P_{H2}) \quad (3.5)$$

$$C_6H_5C_2H_5 + H_2 \longrightarrow C_6H_6 + C_2H_4 \quad (3.6)$$

$$rate = K_3\,P_{EB} \quad (3.7)$$

$$1/2C_2H_4 + H_2O \longrightarrow CO + 2H_2 \quad (3.8)$$

$$rate = K_4\,(P_{H2O}P_{C2H4}) \quad (3.9)$$

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \quad (3.10)$$

$$rate = K_5\,(P_{H2O}P_{CH4}) \quad (3.11)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (3.12)$$

$$rate = K_6\,(P_t/T^B)\,(P_{H2O}P_{CO}) \quad (3.13)$$

The effective permeability is calculated according to Knudsen diffusion as follows:

$$K_i = \frac{2re_P}{3_r RTd}\left(8000R\frac{T}{\pi M_i}\right)^{1/2} \quad (3.14)$$

i = EB, ST, H_2, H_2O, TOL, BEN, CH_4, C_2H_4, CO, CO_2

Effective permeability is dependent on the pore size, porosity, and tortuosity of the membrane structure is addition to temperature and molecular weight.

3.4 MATERIAL BALANCE

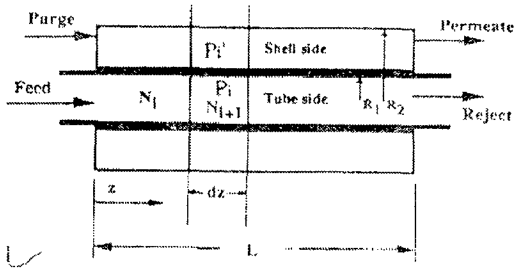

Fig. 3.1 Schematic of material balance in membrane reactor

A set of differential equations for each component can be derived through the shell material balance shown in Figure 3.1.

Tube side:-

$$\pi R_1{}^2 N_A \Big|_{z+\Delta z} - \pi R_1{}^2 N_A \Big|_z + 2\pi R_1 \Delta K_A (P_A - P_A') \quad (3.15)$$

$$(reaction\ rates)\pi R_1{}^2\ \Delta z = 0$$

$$\therefore \qquad \frac{dN_A}{dz} + \frac{2K_A}{R_1}(P_A - P_A') \pm reaction\ rates = 0 \quad (3.16)$$

The "±" sign in the equation is determined for each component as follows: "±" means that species are consumed in reactions, "-" means species are generated in reactions. Material balance for each component is described as follows:

$$\mathrm{EB}: \frac{\mathrm{dN_{EB}}}{\mathrm{dz}} + \frac{2K_{EB}}{R_1}(P_{EB} - P_{EB}') + k_1\left(P_{EB} - \frac{P_{ST}P_{H2}}{K_P}\right) +$$

$$\mathrm{k_2(P_{EB}P_{H2}) + k_3P_{EB} = 0} \quad (3.17)$$

$$\mathrm{ST}: \frac{dN_{ST}}{dz} + \frac{2K_{ST}}{R_1}(P_{ST} - P_{ST}') - k_1\left(P_{EB} - \frac{P_{ST}P_{H2}}{K_p}\right) = 0 \quad (3.18)$$

$$\mathrm{H_2}: \frac{dN_{H_2}}{dz} + \frac{2K_{H_2}}{R_1}(P_{H_2} - P_{H_2}') - k_1\left(P_{EB} - \frac{P_{ST}P_{H_2}}{K_P}\right) +$$

$$\mathrm{k_2(P_{EB}P_{H_2}) - 2k_4\ (P_{H_2O}P_{C_2H_4}) - 3k_5\ (P_{H_2O}P_{CH_4})}\ -$$

$$k_2 \frac{P_t}{T^6}\left(P_{H_2O}P_{CO}\right) = 0 \quad (3.19)$$

$$\text{H}_2\text{O}: \quad \frac{dN_{TOL}}{dz} + \frac{2K_{H_2O}}{R_1}(P_{H_2O} - P_{H_2O}') + k_4(P_{H_2O}P_{C_2H_2})$$

$$+ \; k_5(P_{H_2O}P_{CH_4}) + k_6\frac{P_t}{T^3}(P_{H_2O}P_{CO}) = 0 \tag{3.20}$$

$$\text{TOL}: \quad \frac{dN_{TOL}}{dz} + \frac{2K_{TOL}}{R_1}(P_{TOL} - P_{TOL}') - k_2(P_{EB}P_{H_2}) = 0 \tag{3.21}$$

$$\text{BEN}: \quad \frac{dN_{BEN}}{dz} + \frac{2K_{BEN}}{R_1}(P_{BEN} - P_{BEN}') - k_3P_{EB} = 0 \tag{3.22}$$

$$\text{CH}_4: \quad \frac{dN_{CH_4}}{dz} + \frac{2K_{CH_4}}{R_1}(P_{CH_4} - P_{CH_4}') - k_2(P_{EB}P_{H_2}) + k_5(P_{H_2O}P_{CH_4}) = 0 \tag{3.23}$$

$$\text{C}_2\text{H}_4: \quad \frac{dN_{C_2H_4}}{dz} + \frac{2K_{C_2H_4}}{R_1}(P_{C_2H_4} - P_{C_2H_4}') - k_3P_{EB} + \frac{1}{2}k_4(P_{H_2O}P_{C_2H_4}) = 0 \tag{3.24}$$

$$\text{CO}: \quad \frac{dN_{CO}}{dz} + \frac{2K_{CO}}{R_1}(P_{CO} - P_{CO}') - k_4(P_{H_2O}P_{C_2H_4}) - k_5(P_{H_2O}P_{C_2H_4}) + k_6\frac{P_t}{T^3}(P_{H_2O}P_{CO}) = 0 \tag{3.25}$$

$$\text{CO}_2: \quad \frac{dN_{CO_2}}{dz} + \frac{2K_{CO_2}}{R_1}(P_{CO_2} - P_{CO_2}') - k_6\frac{P_t}{T^3}(P_{H_2O}P_{CO}) = 0 \tag{3.26}$$

shell side

$$\pi(R_2^2 - R_1^2)N'_A\big|_{Z+\Delta Z} - \pi(R_2^2 - R_1^2)N'_A\big|_Z - 2\pi R_1\Delta z K_A(P_A - P_A') = 0 \tag{3.27}$$

$$\therefore \quad \frac{dN_A'}{dz} - \frac{2R_1K_A}{R_2^2 - R_1^2}(P_A - P_A') = 0 \tag{3.28}$$

Similarly, an equation for each component can be derived.

$$\frac{dN_i'}{dz} - \frac{2K_iR_1}{R_2^2 - R_1^2}(P_{i_2} - P_i') = 0 \qquad \text{i} = \text{EB, ST, H}_2, H_2O$$

TOL, BEN, CH_4, C_2H_4, CO and CO_2 (3.29)

$$\text{EB}: \quad \frac{dN'_{EB}}{dz} - \frac{2R_1K_{EB}}{R_2^2 - R_1^2}(P_{EB} - P'_{EB}) = 0 \tag{3.30}$$

$$\text{ST}: \quad \frac{dN'_{ST}}{dz} - \frac{2R_1K_{ST}}{R_2^2 - R_1^2}(P_{ST} - P'_{ST}) = 0 \tag{3.31}$$

$$H_2: \quad \frac{dN'_{H_2}}{dz} - \frac{2R_1K_{H_2}}{R_2^2 - R_1^2}(P_{H_2} - P'_{H_2}) = 0 \tag{3.32}$$

$$H_2O: \quad \frac{dN'_{H_2O}}{dz} - \frac{2R_1K_{H_2O}}{R_2^2 - R_1^2}(P_{H_2O} - P'_{H_2O}) = 0 \tag{3.33}$$

$$\text{TOL}: \quad \frac{dN'_{TOL}}{dz} - \frac{2R_1K_{TOL}}{R_2^2 - R_1^2}(P_{TOL} - P'_{TOL}) = 0 \tag{3.34}$$

$$\text{BEN}: \quad \frac{dN'_{BEN}}{dz} - \frac{2R_1K_{BEN}}{R_2^2 - R_1^2}(P_{BEN} - P'_{BEN}) = 0 \tag{3.35}$$

$$CH_4: \quad \frac{dN'_{CH_4}}{dz} - \frac{2R_1K_{CH_4}}{R_2^2 - R_1^2}(P_{CH_4} - P'_{CH_4}) = 0 \tag{3.36}$$

$$C_2H_4: \quad \frac{dN'_{C_2H_4}}{dz} - \frac{2R_1K_{C_2H_4}}{R_2^2 - R_1^2}(P_{C_2H_4} - P'_{C_2H_4}) = 0 \tag{3.37}$$

$$CO: \quad \frac{dN'_{CO}}{dz} - \frac{2R_1K_{CO}}{R_2^2 - R_1^2}(P_{CO} - P'_{CO}) = 0 \tag{3.38}$$

$$CO_2: \quad \frac{dN'_{CO_2}}{dz} - \frac{2R_1K_{CO_2}}{R_2^2 - R_1^2}(P_{CO_2} - P'_{CO_2}) = 0 \tag{3.39}$$

The relationship between total and partial pressures of each component can be expressed by the following equation:

tube side

$$P_i = (N/\Sigma N_i)P_t \qquad \text{i} = \text{EB, ST, H}_2, H_2O, TOL, \text{BEN, CH}_4, C_2H_4, CO, and\ \text{CO}_2 \tag{3.40}$$

shell side

$$P_i' = (N_i'/\Sigma N_i')P_8 \qquad \text{i} = \text{EB, ST, H}_2, H_2O, TOL, \text{BEN, CH}_4, C_2H_4, CO, and\ \text{CO}_2 \tag{3.41}$$

The Ergun equation has been used t calculate the pressure drop of the packed bed in the tube side. Annulus momentum balance has been performed t determine the pressure drop in the shell side (Bird et al., 1960) as follows:

$$-\frac{dP_t}{dz} = \frac{150\mu\upsilon_z}{D_p^2}\frac{(1-e)^2}{e^3} + \frac{1.75\rho\upsilon_z^2}{D_p}\left(\frac{1-e}{e^3}\right) \tag{3.42}$$

for tube side total pressure drop

where

$$\upsilon_2 = 0.0224\Sigma N_i(T/273) \tag{3.43}$$

$$\upsilon_2' = 0.0224\Sigma N_i'(T/273) \tag{3.44}$$

Density (ρ) *and* viscosity (μ) of the geseous mixture required by these equation are estimated by t correspenent tate and lucas mixing rule

BOUNDARY CONDITIONS:-

At Z= 0 : $N_{EB} = N_{EB,o}$ (3.45)

$N_{H2O} = N_{H2O,o}$ (3.46)

N_{ST}, N_{H2}, N_{TOL}, N_{BEN}, N_{CH4}, N_{C2H4}, N_{CO} & $N_{CO2} = 0$ for tube side (3.47)

$N_{H2O}' = N_{H2O,o}'$ (3.48)

N_{EB}', N_{ST}', N_{H2}', N_{TOL}', N_{BEN}', N_{CH4}', N_{C2H4}', N_{CO}' & $N_{CO2}' = 0$ for shell side (3.49)

At Z = L:

$P_t = P_{tl}$ (pressure at exit) for tube side (3.50)

$P_S = P_{Sl}$ (pressure at exit) for shell side (3.51)

Analysis of variables:-

Independent variable: z

State variables: N_{ST},N_{H2},N_{TOL} , N_{BEN} , N_{CH4} ,N_{C2H4} , N_{CO} , N_{CO2}, N_{EB},N_{H2O}, N_{EB}', N_{ST}', N_{H2}' , N_{TOL}', N_{BEN}', N_{CH4}', N_{C2H4}', N_{CO}', N_{CO2}', N_{H2O}', P_t & P_S.

Differential equations: 22

Boundary conditions: 22

SOLUTION OF MATHEMATICAL MODEL

4.0 INTRODUCTION

In order to predict the performance of the model, solution of model equations is very essential. The developed mathematical model in Chapter 3 consists of a set of nonlinear ordinary coupled differential equations. These equations constitute initial value problem. So we can use ODE solvers of MATLAB to solve these equations.

4.1 MATHEMATICAL MODEL

Model equations obtained by taking material balance of following components on tube side are as follows:

:

$$\text{EB}: \frac{\mathrm{dN_{EB}}}{\mathrm{dz}} + \frac{2K_{EB}}{R_1}(P_{EB} - P_{EB}') + k_1\left(P_{EB} - \frac{P_{ST}P_{H2}}{K_p}\right) +$$

$$\mathrm{k_2(P_{EB}P_{H2}) + k_3P_{EB} = 0} \qquad (4.1)$$

$$\text{ST}: \frac{dN_{ST}}{dz} + \frac{2K_{ST}}{R_1}(P_{ST} - P_{ST}') - k_1\left(P_{EB} - \frac{P_{ST}\,P_{H2}}{K_p}\right) = 0 \qquad (4.2)$$

$$\text{H}_2: \frac{dN_{H_2}}{dz} + \frac{2K_{H_2}}{R_1}(P_{H_2} - P_{H_2}') - k_1\left(P_{EB} - \frac{P_{ST}P_{H_2}}{K_p}\right) +$$
$$\mathrm{k_2(P_{EB}P_{H_2}) - 2k_4\,(P_{H_2O}P_{C_2H_4}) - 3k_5\,(P_{H_2O}P_{CH_4})} -$$

$$k_2\frac{P_t}{T^6}\left(P_{H_2o}P_{CO}\right) = 0 \qquad (4.3)$$

$$\text{H}_2\text{O}: \frac{dN_{TOL}}{dz} + \frac{2K_{H_2O}}{R_1}(P_{H_2O} - P_{H_2O}') + k_4(P_{H_2O}P_{C_2H_2}) \qquad (4.4)$$

$$k_5(P_{H_2O}P_{CH_4}) + k_6\frac{P_t}{T^3}(P_{H_2O}P_{CO}) = 0$$

$$\text{TOL}: \frac{dN_{TOL}}{dz} + \frac{2K_{TOL}}{R_1}(P_{TOL} - P_{TOL}') - k_2(P_{EB}P_{H_2}) = 0 \qquad (4.5)$$

$$\text{BEN}: \quad \frac{dN_{BEN}}{dz} + \frac{2K_{BEN}}{R_1}(P_{BEN} - P_{BEN}') - k_3 P_{EB} = 0 \qquad (4.6)$$

$$\text{CH}_4: \quad \frac{dN_{CH_4}}{dz} + \frac{2K_{CH_4}}{R_1}(P_{CH_4} - P_{CH_4}') - k_2(P_{EB}P_{H_2}) + k_5(P_{H_2O}P_{CH_4}) = 0 \qquad (4.7)$$

$$\text{C}_2\text{H}_4: \quad \frac{dN_{C_2H_4}}{dz} + \frac{2K_{C_2H_4}}{R_1}(P_{C_2H_4} - P_{C_2H_4}') - k_3 P_{EB} + \frac{1}{2}k_4(P_{H_2O}P_{C_2H_4}) = 0 \qquad (4.8)$$

$$\text{CO}: \quad \frac{dN_{CO}}{dz} + \frac{2K_{CO}}{R_1}(P_{CO} - P_{CO}') - k_4(P_{H_2O}P_{C_2H_4}) - k_5(P_{H_2O}P_{C_2H_4}) + k_6\frac{P_t}{T^3}(P_{H_2O}P_{CO}) = 0 \qquad (4.9)$$

$$\text{CO}_2: \quad \frac{dN_{CO_2}}{dz} + \frac{2K_{CO_2}}{R_1}(P_{CO_2} - P_{CO_2}') - k_6\frac{P_t}{T^3}(P_{H_2O}P_{CO}) = 0 \qquad (4.10)$$

Model equations obtained by taking material balance of following components on shell side are as follows:

$$\text{EB}: \quad \frac{dN'_{EB}}{dz} - \frac{2R_1K_{EB}}{R_2^2 - R_1^2}(P_{EB} - P'_{EB}) = 0 \qquad (4.11)$$

$$\text{ST}: \quad \frac{dN'_{ST}}{dz} - \frac{2R_1K_{ST}}{R_2^2 - R_1^2}(P_{ST} - P'_{ST}) = 0 \qquad (4.12)$$

$$\text{H}_2: \quad \frac{dN'_{H_2}}{dz} - \frac{2R_1K_{H_2}}{R_2^2 - R_1^2}(P_{H_2} - P'_{H_2}) = 0 \qquad (4.13)$$

$$\text{H}_2\text{O}: \quad \frac{dN'_{H_2O}}{dz} - \frac{2R_1K_{H_2O}}{R_2^2 - R_1^2}(P_{H_2O} - P'_{H_2O}) = 0 \qquad (4.14)$$

$$\text{TOL}: \quad \frac{dN'_{TOL}}{dz} - \frac{2R_1K_{TOL}}{R_2^2 - R_1^2}(P_{TOL} - P'_{TOL}) = 0 \qquad (4.15)$$

BEN : $$\frac{dN'_{BEN}}{dz}-\frac{2R_1K_{BEN}}{R_2^2-R_1^2}(P_{BEN}-P'_{BEN})=0 \tag{4.16}$$

CH4 : $$\frac{dN'_{CH_4}}{dz}-\frac{2R_1K_{CH_4}}{R_2^2-R_1^2}(P_{CH_4}-P'_{CH_4})=0 \tag{4.17}$$

C2H4 : $$\frac{dN'_{C_2H_4}}{dz}-\frac{2R_1K_{C_2H_4}}{R_2^2-R_1^2}(P_{C_2H_4}-P'_{C_2H_4})=0 \tag{4.18}$$

CO : $$\frac{dN'_{CO}}{dz}-\frac{2R_1K_{CO}}{R_2^2-R_1^2}(P_{CO}-P'_{CO})=0 \tag{4.19}$$

CO2 : $$\frac{dN'_{CO_2}}{dz}-\frac{2R_1K_{CO_2}}{R_2^2-R_1^2}(P_{CO_2}-P'_{CO_2})=0 \tag{4.20}$$

4.2 BOUNDARY CONDITIONS:-

At Z= 0 : $N_{EB} = N_{EB,O}$ (4.21)

$N_{H2O} = N_{H2O,O}$ (4.22)

N_{ST} , N_{H2} , N_{TOL}, N_{BEN} , N_{CH4} ,N_{C2H4} , N_{CO} & N_{CO2}= 0 for tube side (4.23)

$N_{H2O}' = N_{H2O,O}'$ (4.24)

N_{EB}', N_{ST}', N_{H2}' , N_{TOL}' , N_{BEN}', N_{CH4}', N_{C2H4}', N_{CO}' & N_{CO2}' = 0 for shell side (4.25)

At Z = L:

$P_t = P_{tl}$ (pressure at exit) for tube side (4.26)

$P_S = P_{Sl}$ (pressure at exit) for shell side (4.27)

4.3 OTHER PARAMETERS

Table No. 4.1 SIMULATION PARAMETERS

Parameters	Value
Tube diameter	0.634 cm
Shell diameter	1.574 cm
Membrane used	ceramic
Membrane Length	0.5 cm

Density of Catalyst	1500 kg/m^2
Pore Diameter (Membrane)	40 x 10^{-10} m
Membrane Thickness	5 μm
Tortuosity (Membrane)	2.95
Membrane Porosity	0.5
Catalyst size	2 mm
Packed bed porosity	0.6
Feed Flowrate of EB ($N_{EB,o}$)	0.0953 mol/m^2s
Feed flowrate of H_2O ($N_{H2O,o}$)	0.3812 mol/m^2s

Table No. 4.2 OPERATING CONDITIONS

Operating Condition	**Value**
Temperature	913 K
Total Pressure in tube side	1.2 atm
Total Pressure in shell side	0.9 atm
Steam to Ethylbenzene Ratio (Dilution Ratio)	4.0 mol/mol
No shell purge	0

4.4 Catalyst Specification:-

The kinetic expressions for the dehydrogenation of ethylbenzene to styrene on a 70 wt% F_2O_3:20 wt% K_2O:5 wt% Ce_2O:5 wt% Cr_2O_3 catalyst are given below.

Table 4.3: Kinetic parameters of the dehydrogenation of ethylbenzene cited from Industrial catalyst

Reaction Number	Reaction	Rate equation	A_i^*	E_i^{**}
1	$EB \leftrightarrow ST + H_2$	$R_1 = k_1\left(P_{EB} - \frac{P_{ST} P_{H_2}}{K_{EB}}\right)$	2.31 x 10^{-2}	90.89
2	$EB \rightarrow BZ + C_2H_4$	$R_2 = k_2 P_{EB}$	1.19 x 10^4	208.0
3	$EB + H_2 \rightarrow TOL + CH_4$	$R_3 = k_3 P_{EB} P_{H_2O}$	1.71 x 10^{-7}	91.52

4	$H_2O+1/2C_2H_4 \rightarrow CO+2H_2$	$R_4 = k_4P_{H_2O}P_{C_2H_4}^{O5}$	3.50 x 10^{-5}	104.0
5	$H_2O+CH_4 \rightarrow CO_2+3H_2$	$R_5 = k_5P_{H_2O}P_{C_2H_4}$	3.93 x 10^{-9}	65.72
6.	$H_2O+CO \rightarrow CO_2+H_2$	$R_6 =$ $k_6(P_T/T')P_{H_2O}P_{CO}$	1.61 x 10^{-3}	73.63

*A_1: pre-exponential factor for $k_i = A_i\exp(-E_i/R_gT)$

**E_1: activation energy of reaction [kJ/mol]

$K_{EB} = 10^5\exp(-\Delta F_0/R_gT). \Delta F_0 = a+bT+cT^2$,

$a = 12.7kJ/mol,$

$b = -0.1263kJ/(mol.K),$

$c = -2.194x10^{-9}kJ/(mol\,K^2)$

k_i: reaction i rate constant [mol/(kg.s.Pa”)], n = 1 for k_1 and k_2, n = 1.5 for k_4, n = 2 for k_3 and k_5, n = 3 for k_6

4.5 MATLAB ORDINARY DIFERENTIAL EQUATIONS SOLVERS

Equations of this models here in our case model equations are nonlinear-coupled ordinary differential equations, which constitutes initial value problem (IVP). In MATLAB this class of problem is solved using ‘ODE’ (Ordinary Differential Equations) solver.

Syntax : [z, N] = ODE15S(@membranereactor, zspan, No)

4.6 CONCULDING REMARKS

In this chapter solution technique and its suitability has been discussed. Boundary conditions and other physical properties are also mentioned. A program in MATLAB also has been developed to solve and predict model behavior.

RESULTS AND DISCUSSION

5.0 INTRODUCTION

In this chapter, results of the developed model have been represented and discussed. Our proposed model predicts the concentration profiles of components along the length of the reactor, conversion of reactions, yield of products, selectively of particular product and the effects of operating parameters on the performance of membrane reactor.

This percentage yield of the styrene is calculated from the following formula :

$$\% \text{ yield of ST} = \left(\frac{ST_{\mathrm{Retentate}} + ST_{Permeate}}{EB_{Feed}} \right) \qquad (5.1)$$

Same formula is applied for % yields of benzene and toluene.

This percentage selectivity of the styrene is decided from the formula given below

$$\% \text{ selectivity of ST} = \left(\frac{ST}{ST + BEN + TOL} \right) x100 \qquad (5.2)$$

5.1 VALIDATION OF MODEL

For validation of above mathematical model experimental data has been taken from Jeffrey C.S. Wu and Paul K.T. Liu (1992) for partial pressures of EB, ST & H_2 along length of reactor at temperature 913 K and Compared with model. This is shown in fig. 5.1, 5.2 & 5.3. The result shows that model is a good agreement with experimental values within ± 4% error. This result leads to the validation of model.

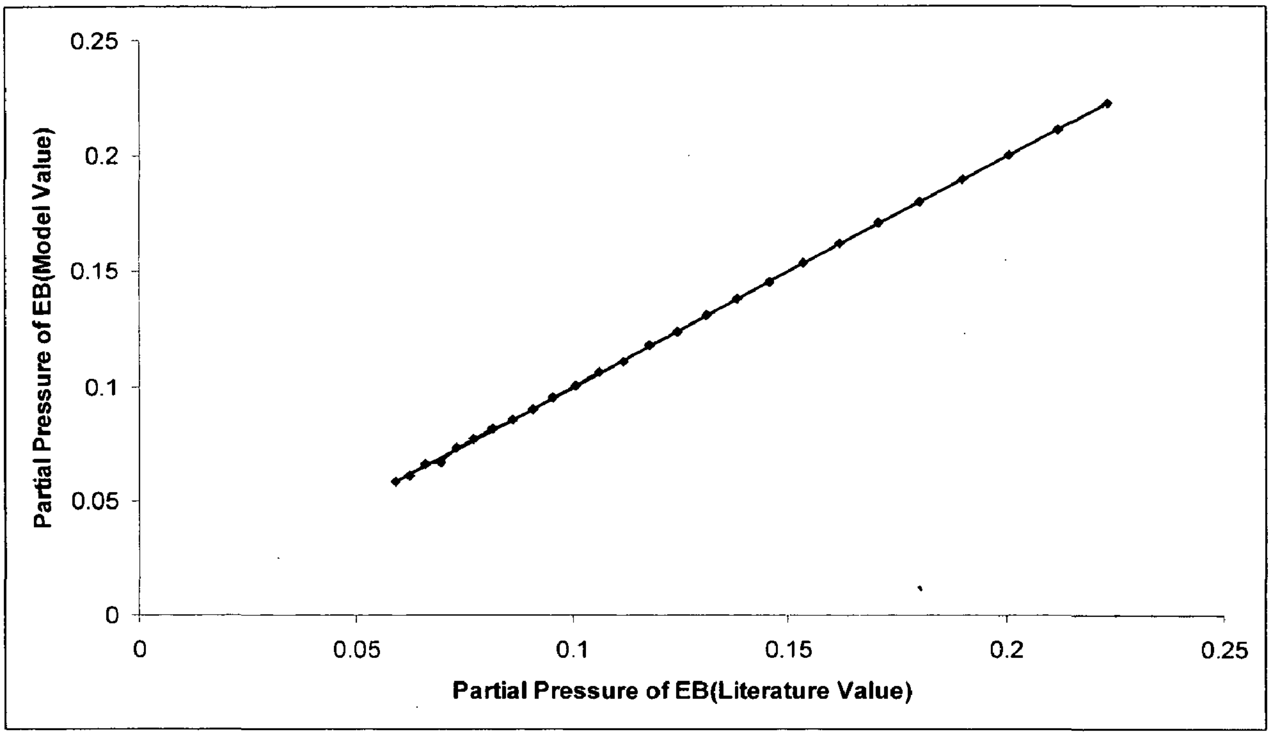

Fig. 5.1 Validation Plot of Tube Side EB Profile

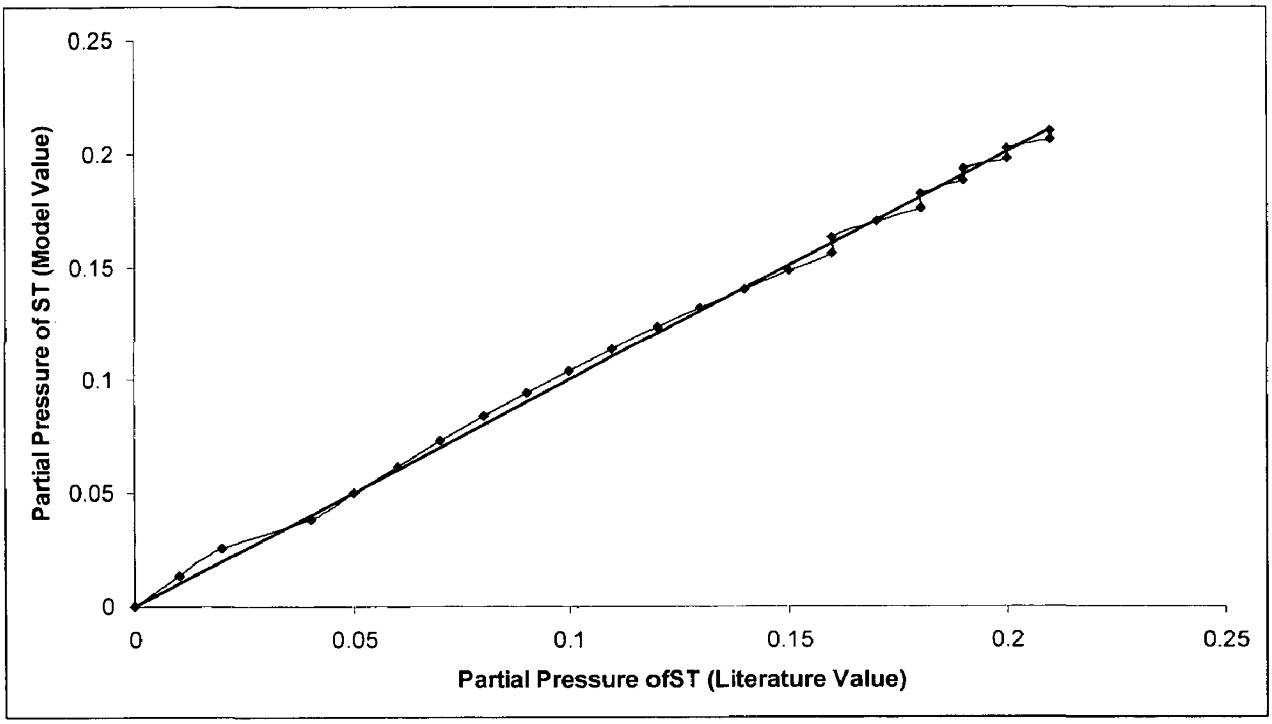

Fig.5.2 Validation Plot Tube Side ST Profiles

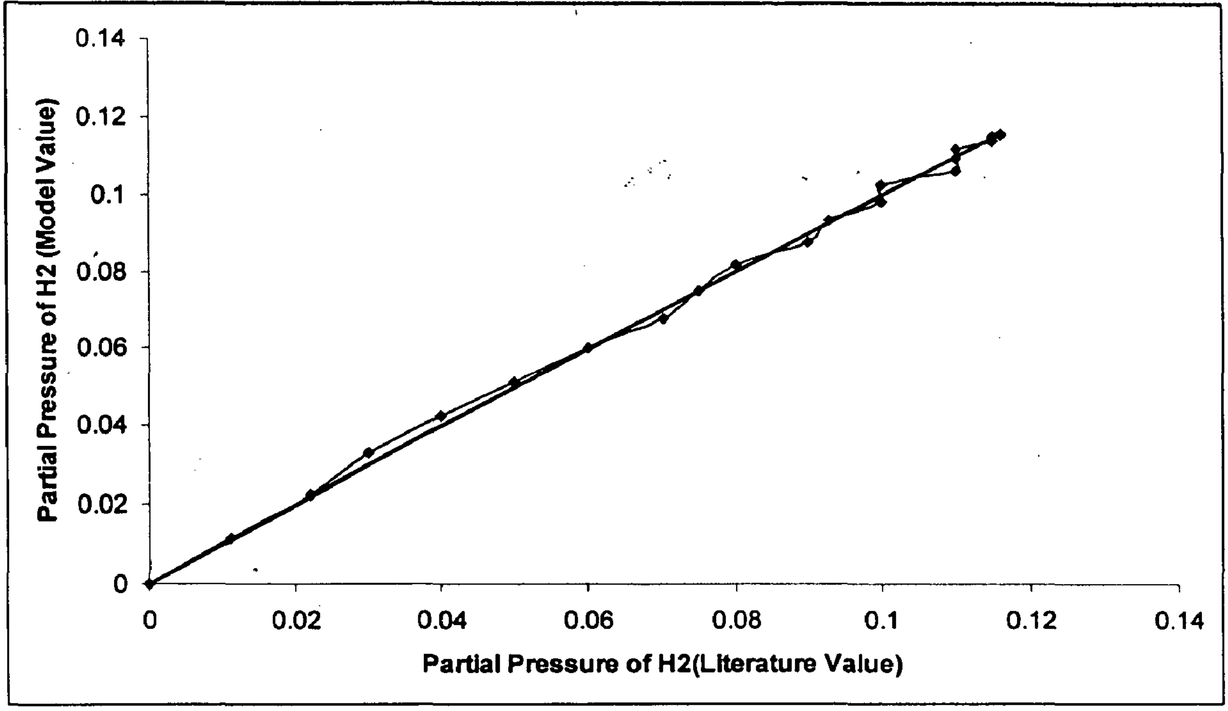

Fig.5.3 Validation Plot Tube Side H_2 Profiles

5.2 YIELD OF SIDE PRODUCTS

Toluene and benzene are the two key side products in ethyl benzene dehydrogenation. Benzene is generated from the scission of the ethylbenzene, and its rate is dependent on the partial pressure of ethyl benzene. Removing H_2 in the membrane reactor does not inhibit this side reaction. Toluene is generated by hydrogenolysis of the ethyl group m ethylbenezene molecules, and its rate is dependent of the partial pressure of H_2. This side reaction is inhibited by reducting the H_2 partial pressure in the membrane reactor.

5.3 EFFECT OF OPERATING CONDITIONS ON MEMBRANE REACTOR PERFORMANCE

Out of all operating conditions the effect of following operating parameters, which affect membrane reactor performance significantly are studied.

(i) Effect of operating temperature

(ii) Effect of Dilution Ratio (mole ratio of input steam to ethylbenzene fed to the reactor)

5.3.1 Effect of Operating Temperature

Operating temperature has very significant effect on membrane reactor's performance. Figure 5.6 to figure 5.8 show graphically variation in yields of styrene, benzene and toluene with temperature. The yield of styrene, benzene and toluene increases with increasing operating temperature. This is because of endothermic nature of the reactions.

5.3.2 Effect of Dilution Ratio

Dilution ratio is a mole ratio of input steam to ethylbenzene fed to the reactor. Dilution ratio is very much important in conventional reactor if the reaction is endothermic. In conventional reactor heat supplied by steam takes care of the change in the temperature due to endothermic reaction and hence thermodynamic equilibrium conversion is shifted. Figure 5.9 to figure 5.11 show graphically variation in yields of styrene, benzene and toluene with dilution ratio. The yield of styrene, benzene and toluene decreases with increasing dilution ratio.

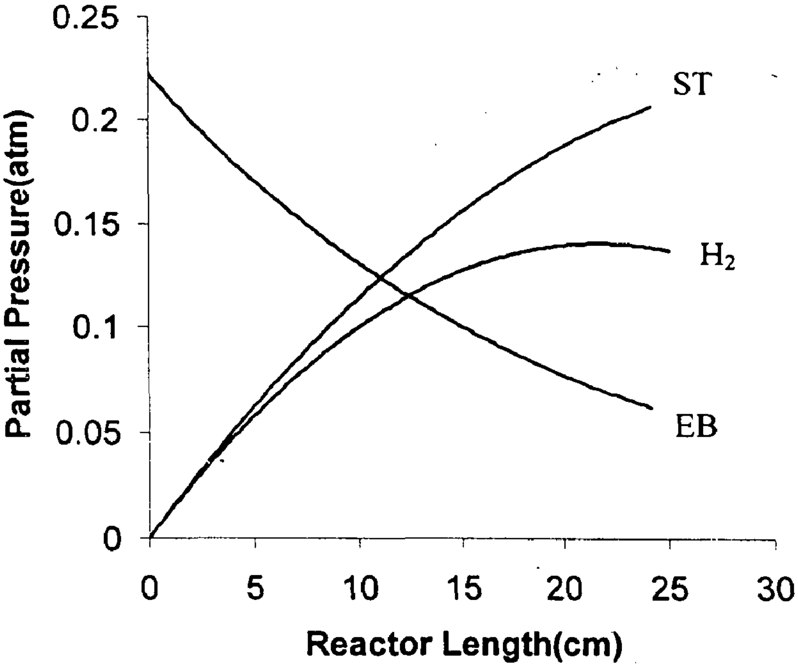

Fig.5.4 Tube Side Profiles Of Membrane Reactor

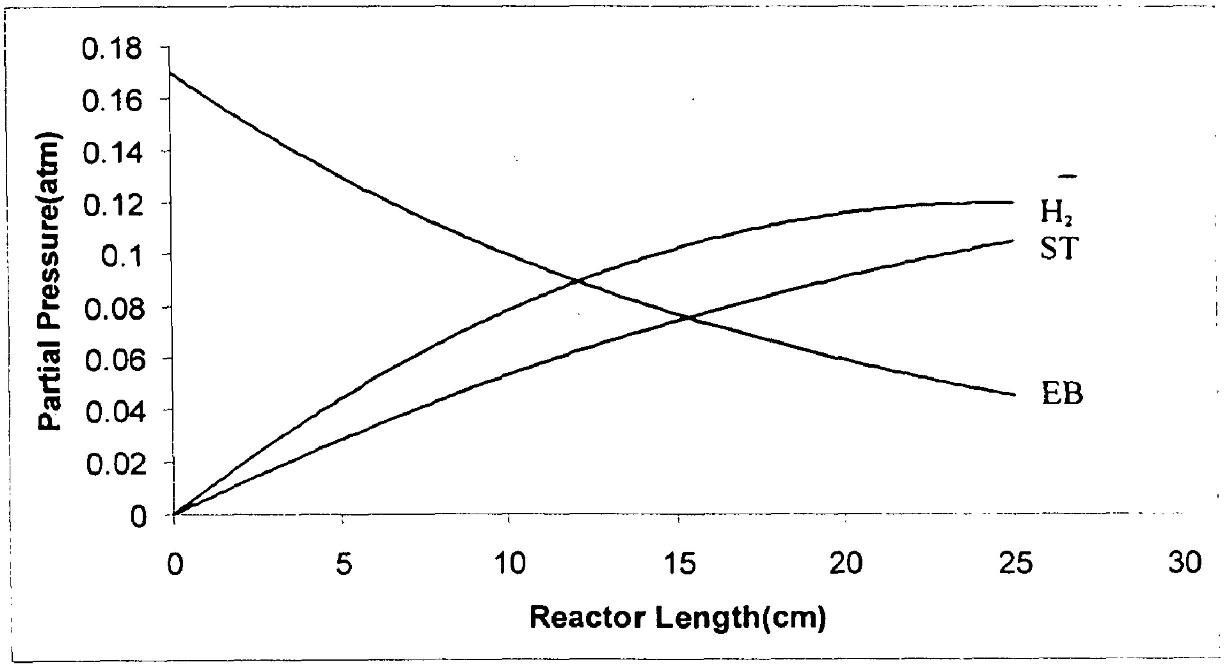

Fig. 5.5 Shell Side Profiles Of Membrane Reactor

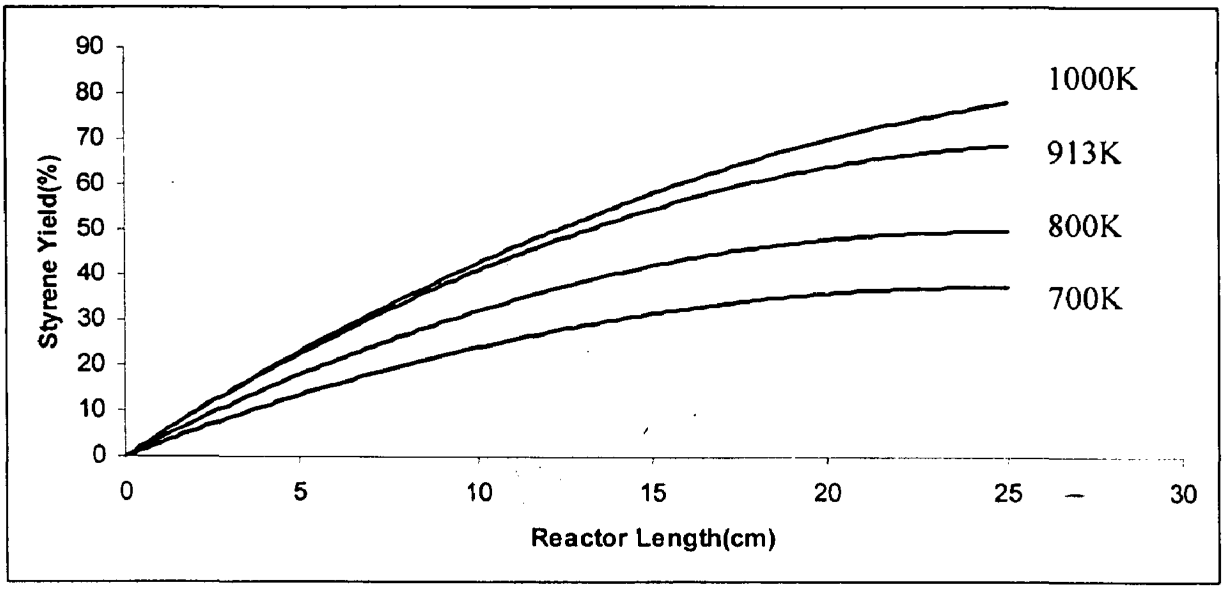

Fig.5.6 Effect Of Operating Temperature On Styrene Yield

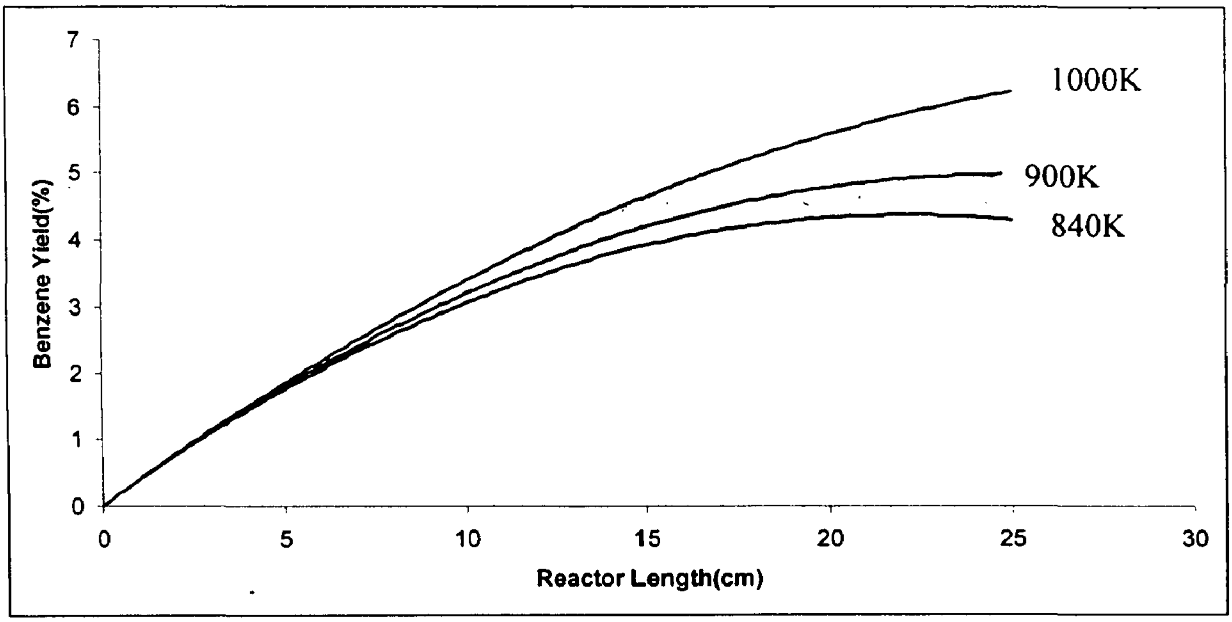

Fig.5.7 Effect of Operating Temperature on Benzene Yield

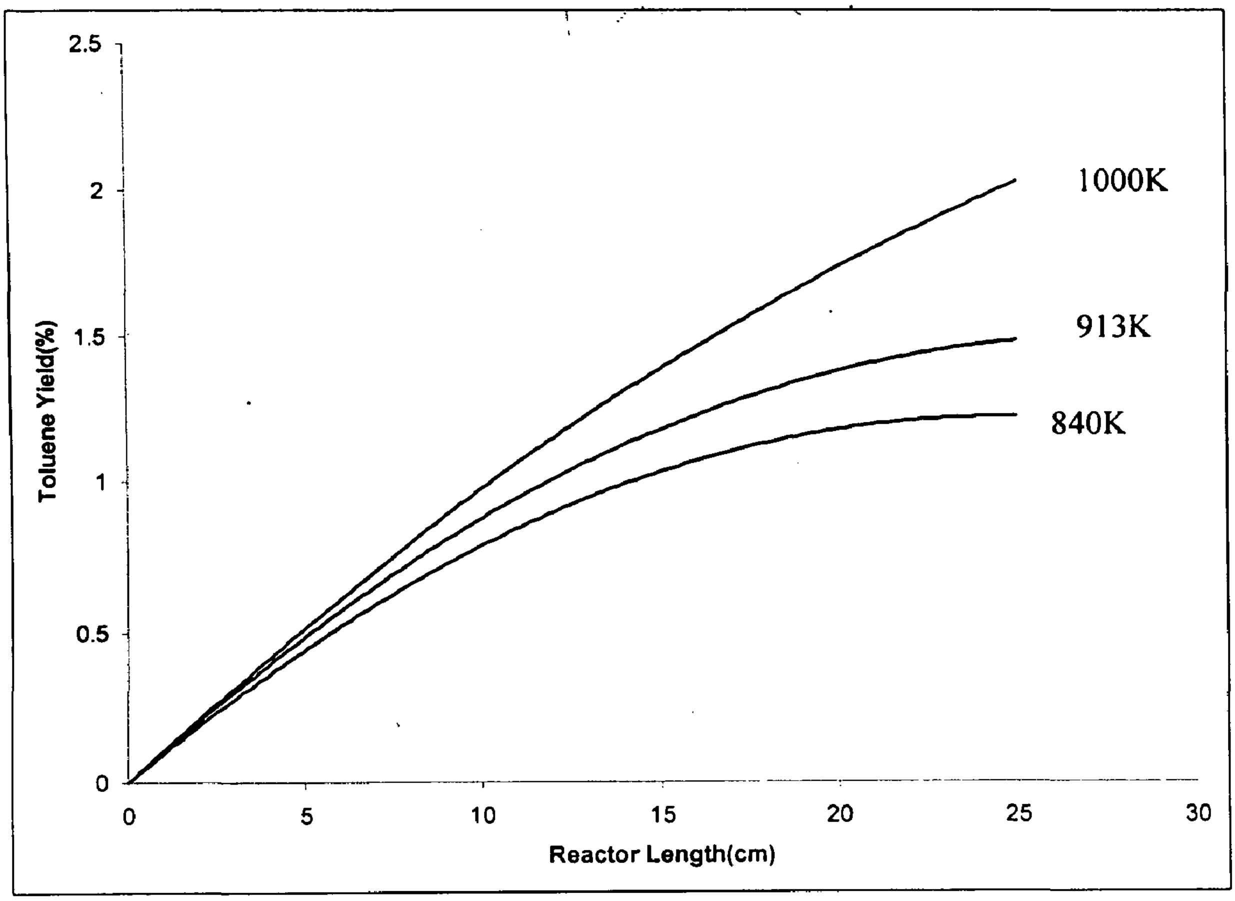

Fig.5.8 Effect of Operating Temperature on Toluene Yield

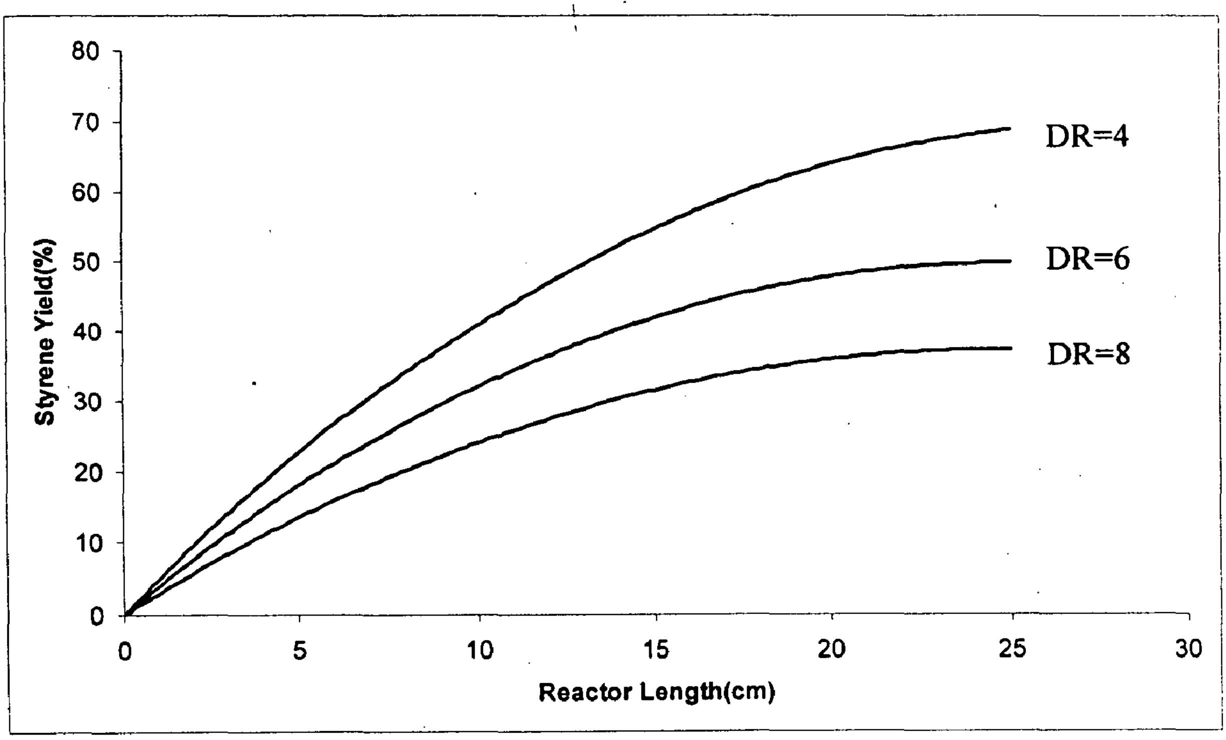

Fig.5.9 Effect Of Dilution Ratio On Styrene Yield

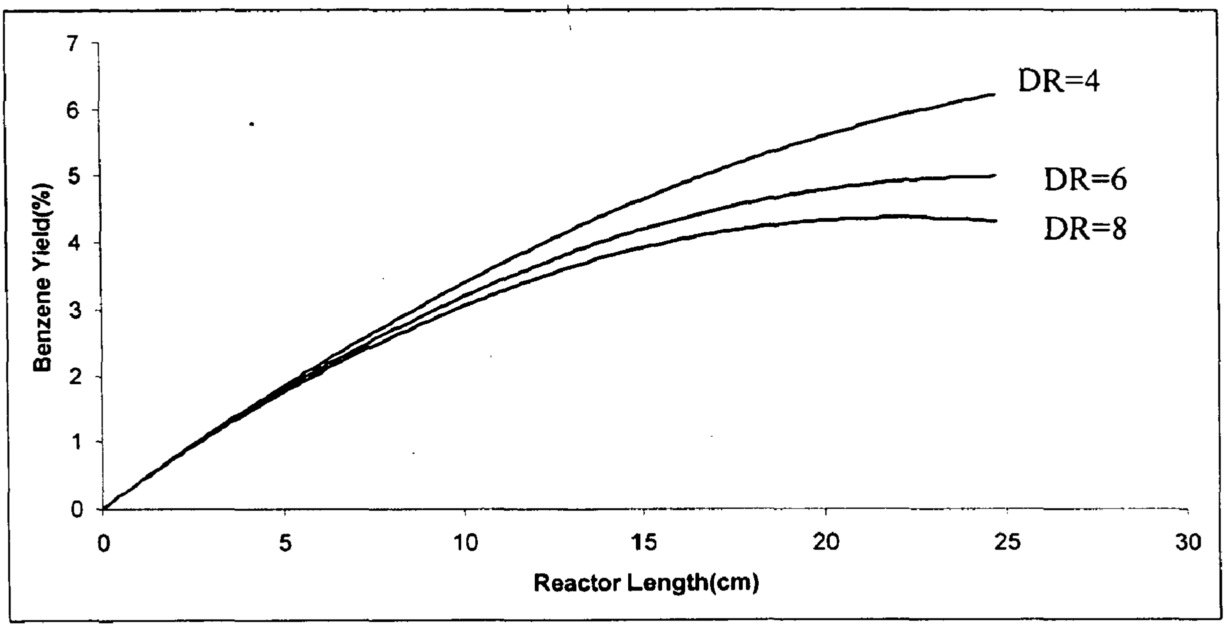

Fig.5.10 Effect of Dilution Ratio on Benzene Yield

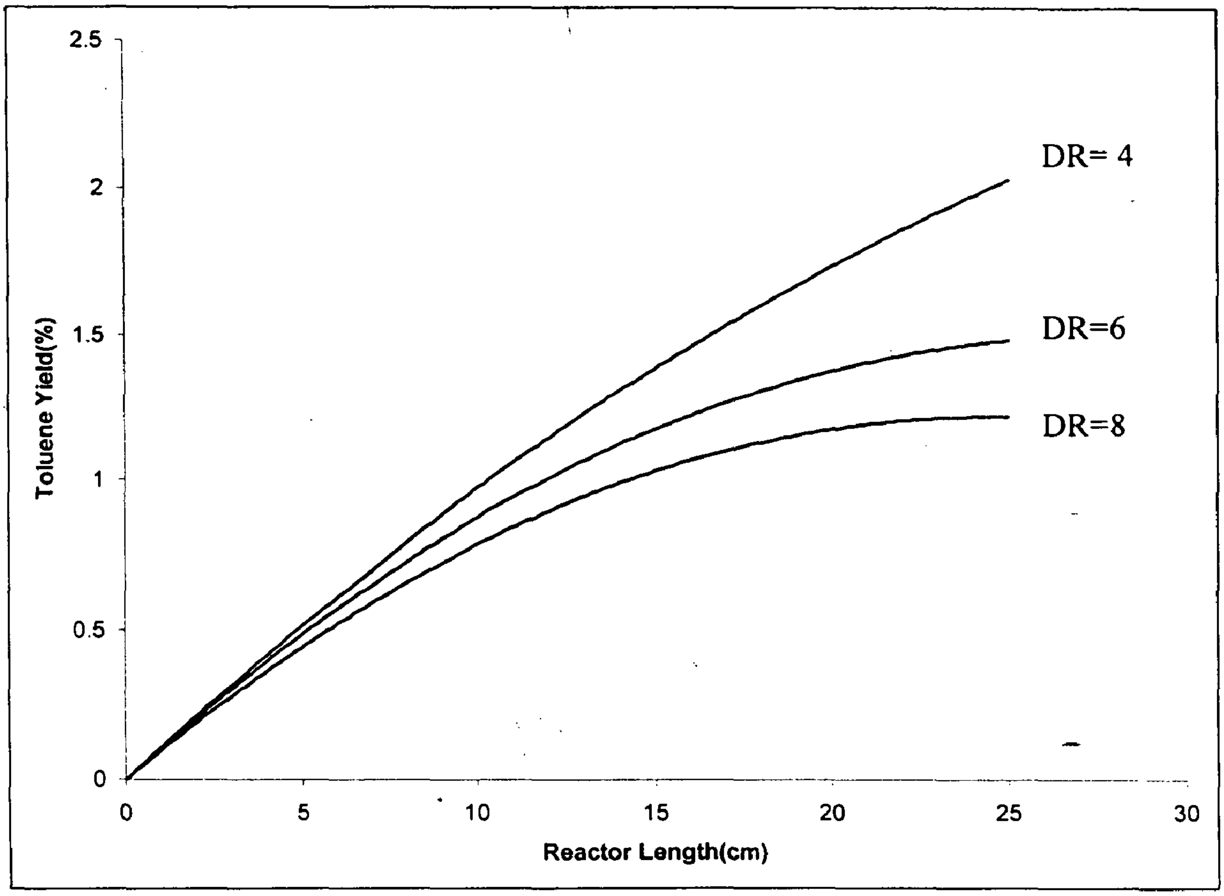

Fig.5.11 Effect of Dilution Ratio on Toluene Yield

5.4 CONCLUDING REMARK

In this chapter all results regarding the study of different parameters are represented graphically. Also to validate the model simulation parameters available from literature are used to solve model equations and further study has been carried out with different operating conditions. It was also found that all the results were in good agreement with the results obtained in literature.

CHAPTER VI

.CONCLUSIONS AND RECOMMENDATIONS

6.0 INTRODUCTION .

In this chapter we have discussed concluding remarks and recommendations briefly.

6.1 CONLUSIONS

- A mathematical model for membrane reactor with ceramic membrane is developed for styrene production from ethylbenzene.
- Mathematical model consists of a set of coupled ordinary differential equations, which constitutes initial value problem. Here the differential equations are stiff so MATLAB ODE suite is used to solve the differential equations for prediction of performance of the model.
- A steady state isothermal simulation has been carried out for detailed analysis of membrane reactor performance with different operating conditions.

6.2 RECOMMENDATIONS

- The kinetic parameters for accepted catalysts studied here are taken from sliterature recommended that these parameters may be chosen by conducting experiments in laboratory.
- Effective permeability in membrane is dependent on the pore size, porosity, and tortuosity of the membrane structure. It is recommended that these properties should be chosen properly.

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