MODELING AND SIMULATION OF CATALYTIC MEMBRANE REACTOR FOR DEHYDROGENATION OF CYCLOHEXANE

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
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in
CHEMICAL ENGINEERING
(With Specialization in Computer aided process plant design)

By

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CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented in the dissertation entitled "**MODELING AND SIMULATION OF CATALYTIC MEMBRANE REACTOR FOR DEHYDROGENATION OF CYCLOHEXANE**" 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 dissertation has not been submitted by me for the award of any other degree of this or any other Institute / University.

Place: Roorkee

Date: 8th June 2005.

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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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ABSTRACT

A simple mathematical model assuming isothermal operation and a plug flow pattern was developed to evaluate the performance of an FAU-type zeolite membrane reactor for use in the catalytic dehydrogenation of cyclohexane. The membrane reactor consisted of a catalyst bed and membrane, containing an impermeable region at the reactor inlet, followed by a permeable region. The impermeable region was required in order to achieve an equilibrium conversion before entering the permeable region, and the selective permeation of benzene and hydrogen was sufficient to shift the equilibrium. The results of the simulation for the membrane reactor were in good agreement with the experimental results. On the basis of the simulation, the zeolite membrane reactor was superior to the fixed bed reactor. The effect of co-feeding hydrogen with cyclohexane, to restrain coke formation on the catalyst due to the high hydrogen concentration in the feed side was clearly demonstrated. The rate of reaction and conversion along the length of the both the reactor configurations have been studied and concluded that the hybrid membrane reactor is superior to fixed bed reactor with the same operating conditions.

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Place: IIT Roorkee
Date: **Jaganmohan Rallapalli**

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NOMENCLATURE

A_c	Cross-sectional area of the catalyst bed	(m^2)
j_i	Flux of i^{th} component,	$(mol\ m^{-2}\ s^{-1})$
k	Reaction rate constant	$(mol\ m^{-3}\ Pa^{-1}\ s^{-1})$
K_B	Adsorption equilibrium constant of benzene	(Pa^{-1})
Kp	Equilibrium constant	(Pa^3)
l	Distance from the inlet of the reactor	(m)
L	Length of reactor	(m)
$N_{i,F}$	Molar flow rate of component *i* in the shell side	$(mol\ s^{-1})$
$N_{i,P}$	Molar flow rate of component *i* in the permeate side	$(mol\ s^{-1})$
p_i	Partial pressure of component *i* in the shell side	(Pa)
p_{CH}	Partial pressure of cyclohexane in shell side	(Pa)
p_H	Partial pressure of benzene in shell side	(Pa)
p_B	Partial pressure of hydrogen in shell side	(Pa)
P_F	Total pressure in shell side	(Pa)
P_P	Total pressure in tube side	(Pa)
Q_i	Permeance of component i	$(mol\ m^{-2}\ s^{-1}\ Pa^{-1})$
R	Outer radius of the porous support tube	(m)
r_C	Dehydrogenation rate of cyclohexane	$(mol\ m^{-3}\ s^{-1})$
R	Gas constant	$(m^3\ Pa\ mol^{-1}\ K^{-1})$
x_i	Mole fraction of component *i* in the feed side	(-)
$x_{i,0}$	Mole fraction of component *i* at the inlet of the feed side	(-)
$x_{i,l}$	Mole fraction of component *i* at the outlet of the feed side	(-)
$x_{CH,0}$	Mole fraction of cyclohexane at the inlet of the reactor	(-)
$x_{CH,l}$	Mole fraction of cyclohexane at the exit of the reactor	(-)
X_C	Conversion of cyclohexane	(-)
yi	Mole fraction of component *i* in the permeate side	(-)
$y_{i,0}$	Mole fraction of component *i* at the inlet of the tube side	(-)
$y_{i,l}$	Mole fraction of component *i* at the outlet of the tube side	(-)

Subscripts

Ar	Argon
B	Benzene
CH	Cyclohexane
H	Hydrogen
i	Component *i*
j	Component j

Greek letters

$\alpha_{i,j}^{perm}$	Perm selectivity of component *i* to component j	(-)
$\alpha_{i,j}$	Separation factor of component *i* to component j	(-)
Δp_i	Partial pressure gradient between shell and tube sides for i^{th} component	(Pa)
γ_i	Stoichiometric coefficient of i^{th} component	(-)

CHAPTER I

INTRODUCTION

In recent years, the demand for hydrogen keeps steadily increasing due to its wide industrial applications such as in ammonia and methanol productions, in hydrogenation of fats and oils as well as in hydro cracking and hydrodesulphurization processes, etc. Furthermore, with the development of fuel cell technology, hydrogen is also regarded as an important future energy source, which can provide more economic and environmental benefits than other fuels.

The reduction of CO_2 emissions is regarded as one of the requirements to reduce global warming, and exploiting alternative energy resources of petroleum. So study of procedures of reduced CO_2 emissions is an important topic for the sustainable development of the society. Many research groups are studying the technologies for development of clean energy systems; one major target is the Proton Exchange Membrane (PEM) fuel cell for power generation in high efficiency. Accordingly much attention has been focused on the storage and supply of hydrogen for the PEM system safely. One of the promising technologies to store and transport hydrogen is the utilization of dehydrogenation and hydrogenation of cyclic hydrocarbons, i.e. cyclohexane, methylcyclohexane, tetralin, and decalin.

One of the promising technologies to produce H_2 is dehydrogenation of cyclo-hydrocarbons such as Cyclohexane, Methylcyclohexane, Tetralin, and Decalin owing to no production of CO & CO_2 by the reaction. Additionally cyclic-hydrocarbons have relatively high H_2 content generally 6-8 wt. % as compared to straight chain hydrocarbons. So they burn more efficiently. In this regard the dehydrogenation of cyclohexane in a catalytic membrane reactor has drawn much attention and has been adopted as a promising process to produce H_2 and benzene. Basically this reaction is endothermic reversible reaction and so attainable conversion under ordinary condition is limited by the thermodynamics. The higher conversion can be achieved if one of the reaction products is selectively removed from the reactant system through a separation unit such as membrane. The membrane reactor provides most energy efficient separation of material at reaction temperature without consumption of energy.

The development of high temperature membranes to recover hydrogen is a topic of considerable scientific interest. Since coal gasification and several high-temperature industrial processes generate hydrogen as a byproduct, the recovery of hydrogen is of significant commercial importance. Many heterogeneous catalytic reactions can not achieve high conversion because of the limit imposed by the reaction equilibrium. For example, the dehydrogenation reaction of cyclohexane, catalyzed with platinum/alumina at 215 C in a conventional reactor, is limited to 33% conversion. If, however, hydrogen or one of reaction products is continuously removed from the reaction mixture through an inorganic membrane, the equilibrium is displaced towards the product side and the conversion is increased to nearly 80%. Since, this reaction is also favored by an increase in temperature; the temperature needed for desired conversion can be lowered. These principles can be applied to several other industrially significant reactions where the efficiency of the process depends on the effectiveness of removal of the one of the selective reaction products. Hence, the conversion of reactants can be enhanced dramatically if a method can be developed for recovering hydrogen at higher temperatures.

Great interest has recently been shown in the development of newer types of reactor configurations with a view to optimizing the yield of desired products and reducing the overall costs. Membrane based reactors have shown enormous potential in fulfilling these requirements. This is mainly because these reactors integrate the desirable properties of both synthetic membranes and catalysts. A large variety of catalytic reactions and bio reactions, viz. enzymatic reactions, microbial fermentations and plant and animal cell culture are routinely being conducted in annular reactors.

A membrane reactor is usually defined as a single apparatus that combines a reactor and a membrane separator. The membranes can be either organic in nature, i.e. polymer, or inorganic, with much of the recent focus being on inorganic membranes due to their ability to withstand higher temperatures and harsh chemical environments. Reviews concerning inorganic membranes and their application in membrane reactors, catalytic membrane reactors (either as inert membrane/packed bed systems or as catalytic membrane systems) involve selectively removing one reaction product component from the reaction environment thereby increasing the conversion in a thermodynamically limited reaction. Dehydrogenation reactions are the most common examples of this, with hydrogen or benzene is being selectively removed.

The introduction of catalytic membrane reactors for high temperature applications became realistic only in the recent years with the development of high temperature resistant membranes. Due to the generally severe conditions of heterogeneous catalysis, most catalytic membrane reactors applications use inorganic membranes which can be dense or porous, inert or catalytically active. The scientific literature on catalytic membrane reactors is significant today; however, practically no large-scale industrial applications have been reported so far because the relatively high price of membrane units. However, current and future advancements in the material engineering might significantly reverse this trend. The good H_2 selectivity and permeability of the last generation dense (Pd based) and almost dense SiO_2 membranes have been successfully exploited for a number of H_2 consuming or generating reactions; for some applications, the thermo-chemical instability of Pd membranes and the hydrothermal instability of silica remain the main problems to solve. Concerning O_2 generating or consuming reactions, the development of O_2 perm selective membranes with good fluxes in the range of 400–700 °C is still needed.

During the last 5 years, increasing concerns have been focused on carbon and Zeolite membranes, which can be prepared basically by carbonizing organic polymers as starting materials at high-temperatures, since it is expected that carbonized materials can be stable at high-temperatures and resist chemical attack. Its application, therefore, is expected to spread over not only high-temperature separations but also membrane reactors. Membrane reactors, in which a chemical equilibrium shift can be realized via selective product removal, have a possibility of playing an important role in establishing energy-efficient process in the future petrochemical and chemical industries. Especially, palladium membrane reactors have demonstrated their great performances for dehydrogenations, steam reforming reactions, etc., where only hydrogen is selectively separated from the reacting mixture, thereby realizing extremely high conversions over the equilibrium ones. However, it is often pointed out that palladium membranes have some problems in terms of cost and permeability when an industrial application of palladium membrane reactors is discussed. Such a condition will emphasize those other membrane materials alternative to palladium should be explored and developed. From this point of Membrane reactors have attracted considerable research interest over the past few years.

Zeolite membranes are of interest for a membrane reactor system because of their desirable thermal properties and high hydrogen permeability. Although palladium based membranes have an infinite selectivity for hydrogen permeation, which is suitable for dehydrogenation, they are poisoned by sulfur impurities in the feed side, deactivated by coking in dehydrogenation reactions, and eventually fail. Membrane operations in the last years have shown their potentialities in the rationalization of productions systems. Their intrinsic characteristics of efficiency, operational simplicity and flexibility, relatively high selectivity and permeability for the transport of specific components, low energy requirements, good stability under a wide spectrum of operating conditions, environment compatibility, easy control and scale up have been confirmed in a large variety of applications, and operations, as molecular separations, fractionations, concentrations, purifications, clarifications, emulsifications, crystallizations, etc. in both liquid and gas phases and in a wide spectrum of operating parameters, such as pH, *T*, *P*, etc.

For biological applications, synthetic membranes provide an ideal support to catalyst immobilization due to their wide available surface area per unit volume; enzymes are retained in the reaction side, do not pollute the products and can be continuously reused. The catalytic action of enzymes is extremely efficient, selective and highly stereo-specific if compared with chemical catalysts; moreover, immobilization procedures have been proven to enhance the enzyme stability. In addition, membrane bioreactors are particularly attractive in terms of eco-compatibility, because, they do not require additives, are able to operate at moderate temperature and pressure, reduce the formation of by-products. Potential applications have been at the origin of important developments in various technology sectors, mainly concerning: induction of micro-organisms to produce specific enzymes, techniques of enzymes purification, bioengineering techniques for enzyme immobilization, and design of efficient productive cycles.

1.2 Basic Principle of the membrane operation

The basic idea of a membrane reactor is to separate the reaction chamber into several compartments which interact by heat and mass transfer. This idea allows for many variations. Two common membrane reactor types are shown in Fig.1 (a) and Fig.1 (b). Another type of membrane reactor 'hybrid membrane reactor', which is a combination of impermeable region and membrane as shown in Fig. 1(c)A packed-bed membrane reactor is a type of catalytic membrane reactor which is a combination of a heterogeneous catalyst and a perm selective membrane. A membrane is a barrier in the form of a thin film or layer that can be selectively permeated by some components of a mixture. In the case a packed-bed membrane reactor, the membrane is in the form of a tube and is packed with catalyst. This allows both the reaction in the catalyst bed and the separation of the mixture components through the membrane to take place simultaneously. In the full length membrane reactor feed is introduced in tube side where the membrane is incorporated. One of the reactant products is selectively removed from the membrane by permeating the one component through that is the basic principle in enhancing the conversion by shifting the equilibrium in the forward side. In case of hybrid reactors, initial portion of the tubular region is fixed with the impermeable region and the next part is arranged with membrane of suitable type. In this case the reaction is carried out in the initial stages of the reactor, and then it permeates through the membrane. It has the advantage over the full length membrane reactor as it does not permeate the reactant components initially which is possible in later case.

1.3 Advantages of the membranes

Some significant advantageous properties of membrane reactors, compared to conventional reactors used in reaction engineering, are:

- Yield-enhancement of equilibrium limited reactions compared to conventional reactors.
- The reactor and the membrane can be divided into two individual compartments. For some reactions (e.g. oxidative dehydrogenation reaction) this aspect may be very important: by separating the stream and the oxidant, the extent of the side-reactions can be significantly decreased.

- By using a membrane, it is possible to control the interaction between two reactants
- The stoichiometry of the reaction can be easily maintained.
- The combination of the two processes (catalytic reactor and down-stream separation units) into one unit will reduce capital costs.
- The common tubular and disk shapes of the membranes are easy to maintain. The composite palladium ceramic membrane shows both a high single component permeability and selectivity which is an alternative to increase the reactor length or to reduce the reactant flow rate to achieve higher conversions in conventional reactors
- These membrane reactors have the greatest potential of catalytic inorganic membranes which can withstand high-temperature gas-phase reactions.
- Membranes present in the membrane reactors are permeable only to one or two components (selectivity of one component/other gases is infinite) so that separation also possible simultaneously with reaction
- These membrane reactors are used in the Hydrogenation and Dehydrogenation reactions where significant advantages are there. They are
    - No CO, CO2 or other by-products are produced, which is markedly different from other processes such as steam-reforming of methanol, liquefied natural gas (LNG), liquefied petroleum gas (LPG), and gasoline.
    - The dehydrogenation and hydrogenation of the cyclic hydrocarbons are reversible, and the reactants and products are recyclable. Therefore, this system would be more convenient than using metal hydrides (LiH, LiBH4, etc.).
    - The cyclic hydrocarbons have relatively high hydrogen contents (6–8 wt.%) and high boiling points (bp = 80–190^{0}C).
- The present infrastructures such as oil tankers and tank Lorries can be also used for the long-term storage and long-distance transportation of the liquid hydrocarbons. From these considerations, if the reversible processes are achieved under mild conditions for the dehydrogenation of cyclic

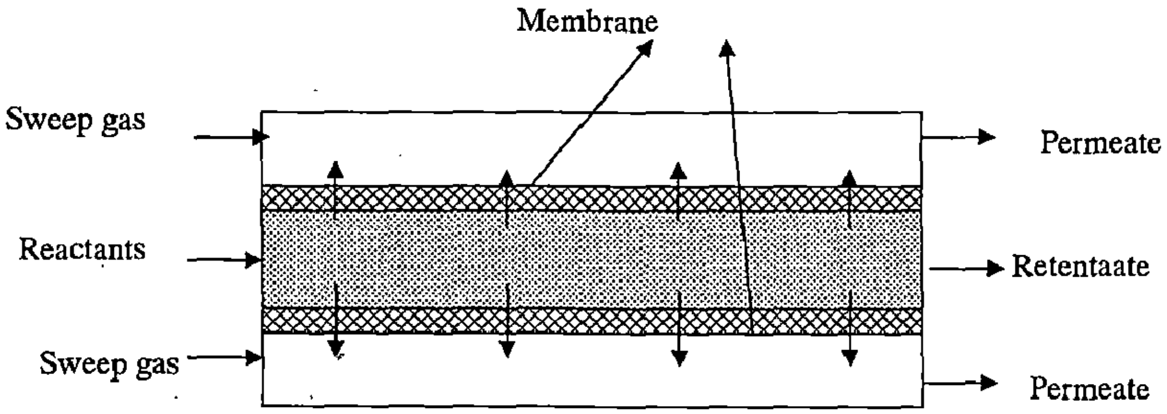

Fig. 1(a) Full length membrane reactor with reactants fed in tube side

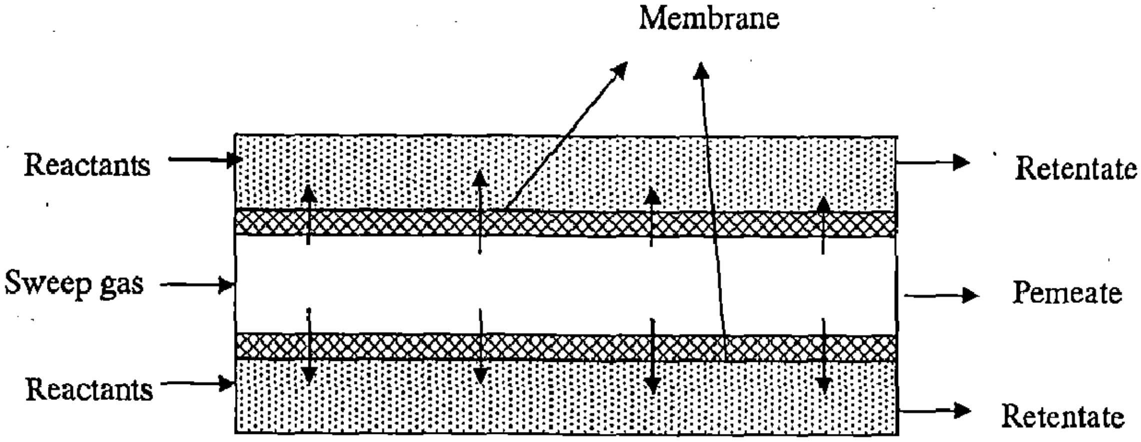

Fig. 1(b) Full length membrane reactor with reactants fed in tube side

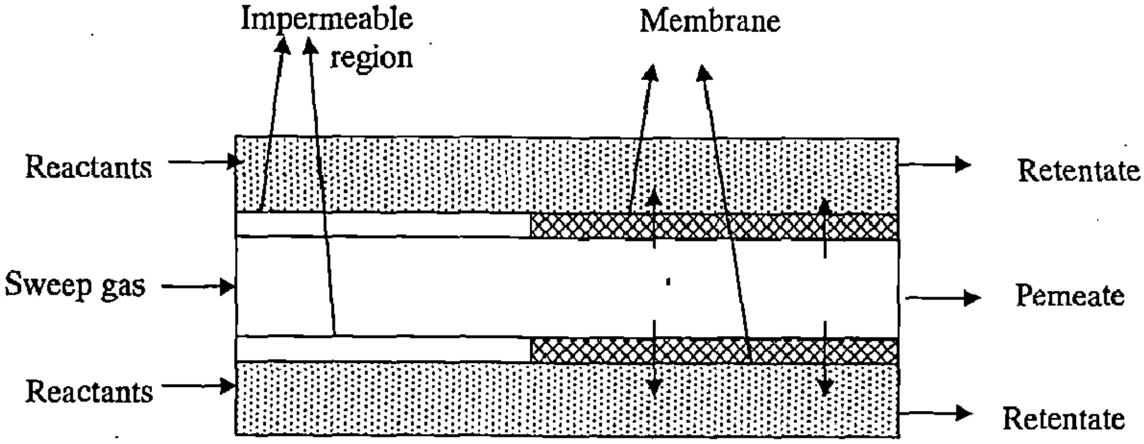

Fig. 1(c) Hybrid membrane reactor with reactants fed in tube side

  - hydrocarbon and the hydrogenation of aromatics, these hydrocarbons would be a hydrogen carrier.
- An integration of reaction and separation into a single process, thus reducing separation costs and recycle requirements.
- An enhancement of thermodynamically limited or product-inhibited reactions resulting in higher conversions per pass.
- A controlled contact of incompatible reactants.
- An elimination of undesired side reactions.

1.4 Drawbacks

- The common tubular and disk shapes of the membranes have low packing densities (low filtration area per unit volume)
- Due to selective transport of one or two components through the membrane there is a reduce in the volume efficiency of the reactor.
- The membrane technology is relatively new technology thorough knowledge is lacking.
- Membranes are very expensive and extensive experimental development which is required is not feasible in some cases.
- Reactor modeling is very complex and available data is inadequate.
- Extensive design efforts are suggested.
- Increased operational complexity.
- Significant development costs.
- Increased scale-up risks.
- The deactivation of membranes and choking of membranes are the possible obstacles in the processes.

1.5 Main characteristics of membrane reactors and membrane materials

Membrane reactors offer the possibility of overcoming the thermodynamic limitations of reversible chemical reactions. If at least one of the reaction products can selectively be removed from the reaction system, equilibrium- limited reactions can achieve higher conversions at lower temperatures. Low temperatures are preferred because at high temperatures both products and reactants may have the tendency to degrade leading to a loss of yield. High temperatures are also undesirable from a standpoint of energy consumption and waste production. In this way, both catalyst and membrane can be considered as a means to improve energy use efficiency, to minimize waste products and to reduce material and energy inventory at lower capital costs since separations can account for 70% of a chemical plant's cost .

The appropriate reactor design can improve yield or reaction selectivity, and this can also reduce downstream separation costs. After the pioneering work of Gryaznov (1986) on palladium-ruthenium alloys, the use of membranes to increase the conversion of engineering reversible reactions by separating gaseous products has been largely studied by a number of researchers. The results have been summarized in a number of recent reviews.A brief summary of different favorable reactions can occur efficiently in membrane reactors are given in Table 1.

1.6 Types of Membranes used

1.6.1 Palladium Membrane Reactors

The major tasks involved in the development of a thin-film palladium-ceramic composite membrane are (a) electrolyses plating of palladium on ceramic substrate, (b) characterization of palladium-ceramic composite membrane formed, measurement and evaluation of perm-selectivity of the composite membrane for hydrogen separation. Micro porous ceramic alumina membranes (alumina, 39 mm × 2 mm thickness, nominal pore size 150 nm and open porosity . 42% obtained from Velterop Ceramic Membrane Company of the Netherlands) were coated with a thin palladium film by electrolyses plating. Electrolyses plating is a three step process involving pretreatment of the substrate, sensitization and activation of the substrate surface, and electrolyses plating. The details of the plating procedures and formulations of the plating solutions are

Table 1 Membrane reactors studied with various reaction types

Reaction system	**Type**	**Membrane material**
Decomposition of H_2S	Porous	. - Al_2O_3
Decomposition of water	Porous	Fe_2O_3 + mol. Sieve
Decomposition of ammonia	Dense	Pd
Decomposition of CO_2	Porous	Ceramic
Dehydrogenation of cyclohexane to benzene	Dense	Y stab. ZrO_2
Dehydrogenation of ethylbezene to styrene	Porous	Al_2O_3 / Pd
Dehydrogenation of ethane to ethylene	Porous	Al_2O_3
Dehydrogenation of propane to propene	Porous	Al_2O_3 / silica
Dehydrogenation of propane to propylene	Porous	Al_2O_3
Dehydrogenation of isopropyl alcohol to acetone	Porous	Pd
Dehydrogenation of n-heptane to toluene + bezene	Dense	Pd / Rh
Dehydrogenation of isobutene	Dense	Silica
Dehydrogenation of n-butane	Porous	. - Al_2O_3
Hydrogenation of butanes	Porous	Pd / Sb
Hydrogenation of cyclohexene	Dense	Al_2O_3 – supp.RhS
Oxidative dehydrogenation of methanol	- - -	Al_2O_3 – supp.RhS
Oxidative dehydrogenation of propane	- - -	Al_2O_3
Oxidation of CO to CO_2	Porous	Al_2O_3
Oxidation of propene	- - -	MoO_3 on Au / YSZ / Ag
Oxidation of toluene	- - -	Al_2O_3
Steam reforming of methane	Dense	Pd-alloy
Partial oxidation of methane	Dense	Perovskite, Pd-alloy
Methane conversion into higher hydrocarbons	Dense	Pd-alloy

reported elsewhere. The palladium-ceramic membranes can be studied by taking SEM (scanning electron microscope) micrographs, EDX (energy-dispersive X-ray) analysis and measuring the thickness of the coated film by a weight-gain method.

The permeation of hydrogen through a palladium film is a complex process. The process begins with sorption of hydrogen molecules on the film surface and ends with hydrogen desorption from the ceramic substrate. It is believed that the hydrogen molecule dissociates into hydrogen atoms on one side of the film. The hydrogen atoms then diffuse through the film and re-associate on the other side. Since the reaction kinetics of formation of hydrogen atoms from molecules and the reverse reaction are assumed to be very fast, the permeation of the hydrogen atoms through the film is the rate limiting step. The permeability can be considered as product of solubility and diffusivity. The membranes have excellent mechanical strength and could withstand average pressures of 4 bars. The membranes have good mechanical strength and are capable of withstanding pressure difference of 4 bars at room temperature.

1.6.2 Zeolite Membrane Reactors

Selective permeation through zeolite membranes is mainly based on molecular sieving and selective adsorption. Thus, zeolite membranes, which have an excellent separation capability, are frequently utilized in membrane reactor systems. Most applications to date have concentrated on the synthesis of MTBE (methyl-*tert*-butyl ether) , esterification and dehydrogenation in MFI-type (ZSM-5 and silicalite) and A-type zeolite membrane reactors. In these applications, the selective removal of water or hydrogen, products in equilibrium-limited reactions, shifts the thermodynamic equilibrium and thus increases the conversion.

The FAU-type zeolite membrane can be synthesized by a hydrothermal process on the outer surface of a porous Al_2O_3 support tube (NOK, Japan, length = 250 mm, i.d. = 1.7 mm, o.d. = 2.1 mm, void fraction = 0.39, mean pore diameter is ca. 150 nm). For the implantation of seeds for nucleation, the outer surface of the support tube will be rubbed with NaY zeolite crystals (Tosoh, Si/Al = 2.8, crystal size = 0.5_m). For the membrane preparation, the initial composition is Al_2O_3:SiO_2:Na_2O:H_2O = 1:12.8:17:975 on a molar basis. The outer surface of the synthesized FAU-type zeolite membrane, except for the permeating portion (length = 26.5 mm), is sealed with a poly tetra fluorocarbon tube in order to make the membrane possible for operation up to 523 K.

1.6.3 Carbon Membrane Reactors

During the last 5 years, increasing concerns have been focused on carbon membranes, which can be prepared basically by carbonizing organic polymers as starting materials at high-temperatures, since it is expected that carbonized materials can be stable at high-temperatures and resist chemical attack. So far, four types of carbon membranes, i.e., sheet, capillary, hollow fiber and composite, have been prepared. From the standpoint of large-scale applications, capillaries, hollow fibers and tubular composites will be preferable because of their high packing density (membrane area per unit volume of vessel) whereas sheets (disks) are confined to treatment of fine chemicals, etc., and use in laboratory. Of the three types, hollow fibers would be the best in terms of high area/volume ratio and easier module assembly. Additional advantage is that the carbonization of original polymer fibers with several hundred micrometers in diameter can be carried out in a continuous process.

1.6.4 Ceramic Membrane Reactors

The ceramic membranes which are generally used in the industries are provided in multi-layered membranes which are tubular and will have an internal diameter of 6 mm, an external diameter of 10mm and total length of 10 cm. The thickest layer (thickness: 2 mm), composed of a mixture of alumina, zirconia and Titania with a pore size in the range of 4–5 μm is placed on the outer side of the membrane. The two subsequent layers (with the thickness of 20–30 and 5 μm, respectively and with pore size diameter in the range of 250–500 and 100–300 nm, respectively) are made of Titania and titania/zirconia. The top layer made of pure rutile Titania (thickness: 1–2 μm) and with pore size in the range of 5–6 nm was on the inner side of the ceramic membrane. Schematic cross-section of the membrane showing the four layers is provided elsewhere. The endings of all tested membranes (1.5 cm on each side) are coated with poly fluoroethlylenepropylene (PFEP) or with poly-perfluoroalkoxy (PPFA) in order to seal the ends and soften the surface on which the o-ring seals were placed.

In the present study, FAU-type zeolite tubular membrane is used for dehydrogenation of cyclohexane reaction. The catalyst is packed in shell side. The permeation of components is from shell to tube through membrane as shown Fig. 1. 1 wt. % Pt/Al_2O_3 type of catalyst is used. The effects of temperature, sweep gas flow rate, diluting medium and the diluting ratio on the conversion of cyclohexane have been studied. Two types of reactor configurations have been studied and compared. The expressions for permeance as a function of temperature have been developed for cyclohexane, benzene, and hydrogen by fitting the experimental data taken from B.H.Jeong et al. (2003) studies. The calculated values are found in good agreement with the experimental results.

1.7 Properties of the zeolite membranes

Zeolites are alumino-silicates with an open structure composed of a three dimensional network of SiO_4 and $A1O_4$ tetrahedral sharing all the corners with each other. A general formula for the chemical composition may be expressed as:

$$(M^+,0.5M^{2+})_m[Al_mSi_{x-m}O_{2x}].nH_2O$$

where M=extra frame work cation.

The exchange of silicon for aluminum in the framework results in a net negative charge which must be compensated by extra framework cations. In general, these may be any alkali, alkaline-earth or rare earth cation as well as organic cations such as the tetra-methyl ammonium ion. Water molecules are located in the channels and cavities, as are the neutralizing cations. Zeolites may be classified in various ways on the basis of structural differences, one of them being based on the size of the pore openings. Depending on the structure, the size of the pores is in the range 3 to 8 A. The apertures are bounded by oxygen atoms of connected tetrahedral. In general, these rings involve 6, 8, 10 or 12 oxygen atoms. However, other factors are involved in determining the final pore size. For example, the location, size and coordination of the extra framework cations. The latter is a well known parameter in the case of zeolite A, in which the channel aperture size can be tailored by using different sized extra framework cations.

The interconnected regular three dimensional networks of micro pores at a molecular scale and the extra framework cation content, are the key factors determining the physical and chemical properties of zeolites. The size of the pores gives the zeolites molecular sieving properties, i.e. if the molecule is larger than the pore size, it will not enter the structure. The shape of the pore may also influence the adsorption capability. The extra framework cations are in many cases exchangeable, which allows for the introduction of acid sites bonded to the non-saturated oxygen atoms.

Three different zeolite structures are: the faujasite [FAU] group zeolites (see Figure 1), zeolite A [LTA] (see Figure 2) and ZSM-5 [MFI]. All of them have found important applications and are therefore synthesized in an industrial scale. Zeolite X and Y are the synthetic analogues to the natural faujasite. The difference between these two zeolites is the Si/Al ratio which is *1-1.5* and *1.5-3* in zeolite X and Y, respectively. The channel system has equidimensional channels intersecting in a perpendicular fashion. The free aperture diameter for the channels is 8 A in NaY. Zeolite A has a Si/Al ratio of 1. The three dimensional channel systems have, like in FAU-type zeolites, equidimensional channels intersecting perpendicular to each other. The free aperture diameter for the channels is 4 A in zeolite NaA. ZSM-5 has a three dimensional pore system consisting of sinusoidal channels (5. 1x5.5 A) and intersecting straight channels (5.3x5.6 A). ZSM-5 can be synthesized with a wide variety of Si/Al ratios, mainly in the range 5-100 [5].

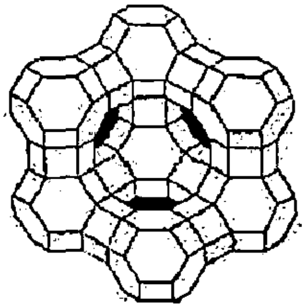

Fig 2. The framework structure of Fauiasite

1.7.1 Potential applications of zeolites

The unique properties of zeolites make them attractive in a variety of industrial applications. The potential acid sites, the high specific surface and the well defined pore dimension are features suitable for a selective catalyst material. For example, zeolite Y is an active component in catalytic cracking catalysts. Due to the molecular sieving ability, zeolites are used in various separation processes such as water removal from gases. However, the batch processes utilized requires regeneration of the sorption material. Since the beginning of the 80's, the development of zeolite membranes has attracted the attention of many research groups.

A zeolite membrane has the advantage that it can potentially sieve out molecules in a continuous process. For example, hydrophilic zeolite membranes derived from NaA were commercialized for alcohol dehydration and solvent dewatering. Various zeolites with different pore size and aluminum content such as Faujasite type structures, A-type structures and Ferrierite type structures were investigated in membrane applications. However, most literature concerning this field deals with MFI-type structures. Molecular sieve membranes also have a great potential as a component in membrane reactors. A membrane reactor can be used to combine reaction and separation in a continuous process. The selectivity of a reaction can be improved by selectively removing one of the products from the reaction mixture or by the controlled addition of a reactant through the membrane. Removing one of the products in equilibrium limited reaction can increase the conversion. For example, Van de Graaf et al increased the catalyzed conversion of propene into ethene, cis-2- butene and trans-2-butene by selectively removing trans-2-butene using a. silicalite-1 membrane. A catalytically active membrane allows the combination of catalyzed reactions and separation of products.

1.7.2 Faujasite type Zeolite membranes

In membrane applications, a high flux of the permeating species increases the efficiency. A thin membrane offers less resistance and is therefore desirable. In general , continuous and template free faujasite type films with a minimum thickness of 150 nm are prepared utilizing the seed film method. Surface seeding has previously been utilized in the synthesis of faujasite type films on inorganic membranes; however the continuous films are several microns thick. The method facilitates to allow for the preparation of truly thin films of faujasite. Thus, the developed film preparation procedure is of interest for the synthesis of highly efficient membranes. Furthermore, no calcinations of the as-synthesized films is required since the synthesis is carried out in the absence of organic templates. Seeded alumina wafers were hydro thermally treated in a zeolite precursor solution in order to obtain dense zeolite films. The template molecules present in the as-synthesized seed crystals were ion-exchanged with ammonium ions in order to obtain template free films. SEM images are used to study the morphology and thickness of the films. An aluminosilicate gel is rapidly precipitated during hydrothermal treatment of the film synthesis solution, leaving an almost clear solution in the upper part of the synthesis mixture. The film growth in the clear solution as well as in the lower part of the synthesis vessel can be investigated.

1.7.3 Permeation Mechanisms

Earlier researchers described transport through porous membranes as adsorption on the external surface, transport into the pores, inter-crystalline diffusion, transport out of the pores, and desorption. The operating conditions and the molecule determine which step rate is determining. Previous studies indicate that interfacial effects can be neglected for our conditions. Thus, only intercrystalline transport will be taken into account, and equilibrium adsorption will be assumed at the interfaces

Different mechanisms contribute to the selectivity of the zeolite membranes. In zeolite pores, adsorption and diffusion play a major role for some molecules, whereas for others molecular sieve effects dominate. Diffusion also takes place through the inter-crystalline regions, where the pores may be can be larger than the zeolite pores, and these are referred to as non-zeolite pores. Depending on the sizes of non-zeolite pores and diffusing molecules, other transport mechanisms such as molecular, Knudsen, and surface diffusion or viscous flow may occur. Pore blocking by adsorption and capillary condensation can be beneficial for restricting the permeation of few molecules specifically reactants. The permeation of hydrocarbons through the FAU-type zeolite membrane proceeds via the following five steps:

1. Adsorption on the external surface.
2. Transport from the external surface into the pores.
3. Diffusion between vacant sites.
4. Transport out of the pores to the external surface.

5. Desorption from the external surface.

The flux of component i through membrane can be written as

$$j_i = Q_i \Delta p_i \tag{1}$$

Where Q_i is permeance of component i which depends upon the membrane characteristics and the temperature. For FAU-type zeolite membrane, the permeances of cyclohexane, benzene, and H_2 are mentioned in Table. 1 at different temperatures.

CHAPTER II

LITERATURE REVIEW

To evaluate the performance of a membrane reactor, a number of modeling studies have been conducted. Most of the models are concerned with equilibrium-limited reactions since these systems have been mostly studied experimentally. The dehydrogenation of cyclohexane has been extensively studied as a model reaction in various membrane reactors. The reaction is as follows

$$C_6H_{12} \xrightleftharpoons{423-500k} C_6H_6 + 3H_2, \qquad .\,H = 206.2\ \text{kJ/mol} \tag{2}$$

This chapter presents the models developed by the different researchers for the performance of the Membrane Reactors and for the different reaction mechanisms with possible modeling and experimental conclusion to assist further research in the novel technology. This chapter briefly gives the brief discussion on the literature on only the aspects of membrane reactors used for different reaction systems and for their modeling work only.

Drioli E. et.al. discussed the coupling of reaction and separation in the membrane reactor and it has been demonstrated to be an interesting way to enhance the performance of several reactions. In particular, by-products can be separated, side-reactions can be avoided and higher yields and conversions can be achieved. This means that the same conversions of traditional reactors can be obtained at more mild conditions (e.g. lower temperatures and pressures) with consequent energy saving and, thus, environmental benefits. Low temperatures are preferred because they increase the life-time of the catalyst (it can be used for much longer time before it has to be regenerated) and reduce the tendency of both products and reactants to degrade (to avoid undesired side-reactions), which might lead to a loss of yield. Membrane reactors, then, seem to constitute a possible means for reducing waste production. In their work the potential role of high temperature membrane reactors in clean productions is presented and discussed. They emphasized in a membrane reactor one or more products can be continuously removed from the reaction zone, reagents can be supplied stoichiometrically, by-products can be separated, and side-reactions can be avoided

From all the case studies reported, they concluded that membrane reactors can find positive applications in clean productions. The membrane reactors can be operated at lower temperatures than the traditional devices (that means energy savings, a reduced tendency of reactants and products to decompose, and a longer catalyst life-time). They allow reaching higher conversions (up to 100%) and yields, to use more efficiently raw materials and to reduce load on downstream separations. Improvements in the synthesis of defect-free and homogeneous membrane layers, in the sealing of membranes into modules, longer term data of membrane reactor operations and costs reduction are at the basis of their introduction at industrial levels.

Dittmeyer R. *et. al.* have discussed two different membrane reactor concepts which both rely on supported palladium, on one hand as a perm selective membrane material, and on the other hand as base component of a membrane type hydrogenation catalyst. Dense palladium composite membranes can be used for hydrogen separation from packed bed catalyst in gas-phase hydrocarbon dehydrogenation reactions. Mesoporous membranes containing dispersed bimetallic Pd 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

Itoh et.al experimentally and theoretically studied dehydrogenation of cyclohexane reaction using a microporous Vycor glass membrane reactor and a palladium membrane reactor. Cyclohexane in the feed side was diluted with an inert gas and a sweep gas was introduced to the permeate side. A mathematical model assuming plug flow and isothermal conditions was developed. An increase in the flow rate of the sweep gas led to a decrease in the concentration of hydrogen in the permeate side. This resulted in an increase in the driving force for diffusion through the membrane, thus increasing the conversion. As the flow rate in the feed side decreased, the residence time in the reactor increased, and consequently the conversion increased. It should be noted that excellent agreement between the model and the experimental data was reported

Dixon A.G has reviewed various aspects of recent research in catalytic inorganic membrane reactors. The author at the end concludes that progress towards commercialization of catalytic membrane reactors continues to be slow as from the industrial point of view. Many issues to be resolved before a case can 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 from year to year. Despite being the oldest area of application of catalytic membrane reactors, the removal of product hydrogen still gives rise to great deal of work, and new reactions and new areas are being found. More detailed models are being developed which includes the use of two-dimensional reactor tube models, and concentration and temperature profiles.

Zeng et al. performed the oxidative coupling of methane by using perovskite-type oxides highly permeable to oxygen. One membrane surface was exposed to an O_2–N_2 mixture stream and another to CH_4–He mixture stream. At temperatures higher than 850^0 C and with a feed ratio He–CH_4 of 40–90^0C selectivity was higher (of the order of 70–90%) for the considered reaction than the traditional systems. The same reaction was studied by Omata et al. (reported in Falconer et al.) who used a PdO catalyst supported by MgO, which was deposited on a ceramic membrane. The formation of C_2 hydrocarbons was carried out near 1000 K by feeding air to the tube side and methane to the shell side. The catalyst was on the shell side. They reported three advantagesof this arrangement:

1. Air could be used instead of oxygen as a reactant without introducing large amounts of nitrogen into the exit stream. Neither nitrogen nor oxygen was detected in the gas phase in the methane stream.

2. The rate of C_2 formation per unit surface area was higher with respect to traditional systems.

3. The selectivity increased significantly: selectivities greater than 90% were measured in the membrane reactor, while for a supported catalyst selectivities were as low as 50%.

Kokugan et.al. fed pure cyclohexane directly into the feed side of membrane reactors. The conversions in the membrane reactors were evaluated using the pseudo equilibrium model, derived from the Gibb's free energy change for the reaction and the equilibrium constant. The predicted conversions using the pseudo equilibrium model were also in good agreement with the experimental data. A pseudo-homogeneous model was recently used to describe the transport mechanism through a catalyst bed. Radial diffusion and/or axial diffusion were considered to account for the concentration gradient in the radial direction, due to the selective permeation of hydrogen through the membrane. They defined the optimal configurations for various conditions for a given reactor geometry. The catalytic dehydrogenation of cyclohexane in an FAU-type zeolite membrane reactor was examined and an increase in conversion in the membrane reactor, exceeding the equilibrium value, was achieved, as the result of the simultaneous removal of benzene and hydrogen. The permeation properties of benzene and cyclohexane through an FAU-type zeolite membrane have been reported in detail. The contribution of the permeation properties of benzene and hydrogen to the conversion, however, is not still clear. The co-feeding hydrogen with cyclohexane to the feed side can also be tolerated in this system.

Bruce E.Koel et.al used a quasi empirical valence bond QVB scheme E.A. Carter, Chem. Phys. Letters 169 (1990) 218 for calculating the heats of formation of adsorbed species on surfaces to provide reliable estimates of the relative stabilities of several of the surface intermediates and adsorbate-surface bond strengths that are important in the selective dehydrogenation of cyclohexane to benzene over Pt surfaces. They estimated heats of adsorption and formation for adsorbed cyclohexyl c-C_6H_{11}, a cycloallylic intermediate c-C_6H_9, cyclohexadiene c-C_6H_8 , cyclohexadienyl c-C_6H_7, phenyl c-C_6H_5, and benzyne c-C_6H_4 on Pt surfaces. Estimates of these needed formation energies are then combined with the experimentally measured adsorption energies of cyclohexane $c\text{-}C_6H_{12}$, cyclohexene $c\text{-}C_6H_{10}$, and benzene C_6H_6 , to provide heats of reaction and an equilibrium thermodynamic description of a selective dehydrogenation mechanism that involves the step-wise, sequential removal of one H atom at a time from cyclohexane to form benzene. In addition, several further decomposition products of benzene are considered as precursors to undesirable carbon-forming reactions. In agreement with experimental observations, a cycloallylic species $c\text{-}C_6H_9$ is shown to be an important stable intermediate in cyclohexane dehydrogenation that could also be involved in the catalytic rate-limiting step. Carbon–Carbon bond cleavage and other possible surface Reaction pathways are not considered herein. Addition of measured or estimated values for the activation barriers involved in the reaction on Pt can now give a fairly complete description of the energetic of this prototypical hydrocarbon conversion reaction on Pt surfaces.

Okubo et.al. have studied the dehydrogenation of cyclohexane in a membrane reactor operated at 470 K. A thin alumina membrane was supported on the inner surface of an alumina hollow fiber. The overall conversions achieved in this membrane reactor (22 to 60%) were higher than that achieved in a conventional packed bed reactor (less than 20%). Conversion levels were further increased when additional catalyst was employed upstream from the membrane (i.e. the reactor was converted to a hybrid reactor consisting of a packed bed segment followed by a membrane reactor segment). The purpose of the experiments described in this paper was to explore the question of optimization of the relative lengths of the packed bed and the membrane segments of a hybrid membrane reactor. However, the results were not as originally anticipated. They found that a hybrid membrane reactor is not necessarily a better choice than the pure membrane reactor. Our interpretation of the results indicates that for reactions involving an increase in the number of moles of gaseous species, it is possible to increase the conversion achieved in a membrane reactor without necessarily having the high perm selectivity necessary to achieve good separation of the constituents of the reaction mixture. The enhancement in the conversion arises in large measure as a consequence of dilution of the reacting mixture by the sweep gas.

Jeong et.al reported on the synthesis of a NaY-type zeolite membrane on a porous Al_2O_3 support tube using a hydrothermal synthesis. The separation properties of the resulting membrane for binary mixtures of benzene and cyclohexane were investigated, and a separation factor of 107 was found at 373 K. The high separation factor can be attributed to the selective adsorption of benzene and the blocking of cyclohexane by benzene, adsorbed in the pores. Therefore, benzene selective FAU-type zeolite membranes would be expected to be useful for the dehydrogenation of cyclohexane in a membrane reactor. To my knowledge, it may be the first contribution of a zeolite membrane for this purpose. In the present study, a benzene selective FAU-type zeolite membrane was synthesized on a porous Al_2O_3support tube by hydrothermal synthesis. The catalytic dehydrogenation of cyclohexane was investigated in the membrane reactor packed with Pt/ Al_2O_3catalyst particles. The effects of temperature, sweep flow rate and cyclohexane feed rate on the conversion of cyclohexane were investigated. An FAU-type zeolite membrane was formed on a porous Al_2O_3support tube, for use in the selective separation of benzene and hydrogen from cyclohexane. The membrane was used for the catalytic dehydrogenation of cyclohexane in a membrane reactor packed with a Pt/ Al_2O_3 catalyst. The reaction was carried out in the temperature range of 423–523K over a 1.0 wt. % Pt/ Al_2O_3 catalyst prepared by means of an impregnation method. The activity of the catalyst was evaluated in a conventional packed bed and no significant deactivation was found after at least 3 days of use. The conversion of cyclohexane in the membrane reactor increased beyond the thermodynamic equilibrium value due to the simultaneous removal of hydrogen and benzene from the reaction site. The conversion of cyclohexane increased with increasing sweep flow rate, which can be attributed to the fact that the rapid removal of products leads to a high turnover rate. In addition, a decrease in the feed rate of cyclohexane led to a higher cyclohexane conversion. When the sweep flow rate was maintained at 100 cm^3 (STP) min-1 and the cyclohexane feed rate was maintained at 1.1 mol h^{-1}, the conversion of cyclohexane in the FAU-type zeolite membrane reactor reached 72.1% at 473 K, compared to the calculated equilibrium value, 32.2%.

Nubuko kariya et.al has accomplished Highly efficient production of hydrogen without CO_2 emission is achieved in the dehydrogenation of cyclic hydrocarbons under a non-steady spray pulse operation over supported Pt and Pt-M (M = Re, Rh,Pd) catalysts. Cyclohexane, methylcyclohexane, tetralin and decalin were efficiently dehydrogenated by the Pt-containing catalysts supported on thin active carbon cloth (CFF-1500S) sheets and alumite (anodized aluminum) plates. Production rate of hydrogen under the spray pulse mode is higher than the conventional batch-type liquid phase reaction and the steady state gas phase reaction in the flow system.The highest rate, 3800 m.mol g^{-1} Pt min^{-1}, was obtained in the dehydrogenation of cyclohexane over alumite heated at 375^0 C and cyclohexane feed of 190 $mmolmin^{-1}$ with 3.5 mmol pulse at 1.0 s interval. Bimetallic Pt-Rh/CFF-1500S catalyst showed a higher activity than monometallic Pt/CFF-1500S. Production rate of hydrogen is greatly dependent on the rate of reactant feed, the reaction temperature, and the support. Retardation by products adsorbed on the catalysts was negligible under the spray-pulse operation. Highly efficient production of hydrogen from cyclic hydrocarbons (cyclohexane, methylcyclohexane, and decalin) was achieved by a spray pulse operation with no CH4, CO_2, and other by-products.

The optimum temperature and the texture of catalyst support (surface area, heat conduction, etc. Slight retardation of the dehydrogenation reaction by the product adsorbed on the catalysts under the spray-pulse operations may be profitable for practical use, because the mixture of unreacted reactant and product can be used in a recycling loop without separation. Bimetallic Pt-Rh/CFF-1500S catalyst showed higher activities than monometallic Pt/CFF-1500S in the dehydrogenation of cyclohexane, probably due to the electronic effect of Rh metals to Pt and the synergistic effect of high C–H bond cleavage ability of Rh and high hydrogen recombination ability of Pt. Further studies of mechanism of dehydrogenation under pulse-splay operation, durability of catalyst and formation of coke, consideration about the detailed thermal balance of total system, and development of catalyst and reactor to improve the reaction rate are under progress. State of the wet–dry conditions is achieved by tuning of the reaction conditions such as reaction temperature, rate of reactant feeding, and catalyst supports. The rates of reactant feed and rates of hydrogen production greatly depend on the nature of the reactant (boiling point, hydrogen contents, etc.), the reaction

Cui.T et.al. has fabricated novel microreactors on silicon in order to dehydrogenate cyclohexane to benzene. There were 12 reactor chips on one single silicon wafer. The microreactor consisted of three chips, which are reaction chamber, separation membrane and reactor cap. The whole dimension of the reactor is 20 mm long, 14 mm wide and 3 mm high. As for reaction chamber, 80 microchannels 50 mm wide, 400 mm deep and 8 mm long have been etched. We use silicon h110i wafers to obtain high-aspect-ratio microstructures. Twenty nanometer Ti is sputtered and oxidized as the adhesion layer and catalyst carrier. Twenty nanometer Pt is sputtered as the catalyst. For the separation membrane, it is 6 mm by 8 mm, with 80 folded rectangular 4 mm thick Pd foil structures 50 mm wide, 200 mm high and 6 mm long anchored on silicon. This utilizes the combination of silicon h110i wet etching and dry etching together. These folded Pd microstructures contribute to increase the separation area of hydrogen. The reactor cap for inlet and outlet gas pipes is made of PDMS, which is a kind of relatively new material for MEMS applications. Finally, the reaction chamber, separation membrane and reactor cap have been bonded using Polyimide with very good contact strength between chips. The microreactors have been tested using a GC with a conversion value of 18.4%.

They designed, fabricated and tested the prototype microreactors for dehydrogenation of cyclohexane to benzene with good inherent selectivity and reaction control. The prototype microreactors have been designed, fabricated and tested. Relatively large area membrane with multi high-aspect-ratio folded microstructures has been fabricated using silicon wet and dry etching. Multi long high aspect- ratio microchannels have been etched for chemical reaction channels. PDMS and polyimide bonding with very stable chemical stability has been used for this chemical reaction device. The unique aspects of this research on microreactor for dehydrogenation of cyclohexane to benzene are as follows.

(1) The three-layer microreactor design is a very effective way to realize high efficiency for thermal reaction and gas separation.

(2) Ti oxidation using NaOH and H_2O_2 has been realized, which is a simple and very effective way to get the catalyst carrier compared to anodic oxidation. It is expected to achieve the higher efficiency on reaction and separation if the experimental setup is

improved in the future. And the micro manufacturing technologies in this paper are suitable for the fabrication of any other kinds of microreaction systems and wholly new MEMS devices.

Okuhara et.al. investigated the effect of Ru dispersion and residual Cl of Ru/ Al_2O_3 on the catalytic activity and selectivity of cyclohexane. They found that the dispersion and the residual Cl were the crucial factors controlling both activity and selectivity. They found that chlorine remains on the support affecting both acidity and the selectivity of the catalyst. The aim of this study was to find a better modification for the bi-functional catalyst (Pt/ Al_2O_3) to improve its activity for hydro conversion of cyclohexane. Their study has been directed to investigate:

1. The effect of adding a second metal, Ir, Rh, Re or U, on the catalytic activity of Pt/ Al_2O_3 catalyst.

2. The rôle of chlorination and fluorination on the catalytic activities of the catalysts. The dispersion of the metals with catalysts under study was determined using a pulsed technique of hydrogen chemisorptions, based on 1:1 stoichiometry (H/M)

3. Most of the catalysts under study enhance cyclohexane dehydrogenation up to 3508C beyond which the activity may not improve via further increase of temperature or even decline. This may be attributed to the stronger adsorption of the produced benzene molecules, thus retarding further cyclohexane adsorption and reaction.

4. Combination of Ir, Rh or Re with Pt enhances the catalytic activity, whereas U inhibits this activity.

5. Halogenation of the monometallic or bimetallic catalysts with chlorine or fluorine enhances the catalytic activity except for the catalysts containing Ir(F), PtIr(Cl), PtRh(Cl) and PtRh(F).

6. The optimum concentration of halogen for enhancing cyclohexane dehydrogenation is 3% by weight, which may be attributed to the increasing hydrogen spillover and improving the metal dispersion in the support.

Bryden K.J et.al have investigated and inferred that Palladium-based membranes are of technological interest as they possess very high perm selectivity for hydrogen. Diffusion through the palladium is often the rate-limiting step in hydrogen separation. The flux through these membranes can be increased by tailoring a microstructure that allows for higher hydrogen diffusivity. Nanostructured palladium has much higher hydrogen diffusivity than conventional palladium due to its large volume fraction of grain boundaries, thus providing greater hydrogen fluxes and better performance. By doping palladium with another element, enhanced stability against grain growth, suppression of the α-to-β phase transition that causes membrane cracking, and improved poisoning resistance can be achieved.

They have produced nanostructured Pd-based alloy membranes by pulsed electro deposition. This unique method of making nanostructured materials allows for the flexible tailoring of the elemental composition and microstructure of metal thin films. By controlling precursor concentrations, additives, pH, temperature, current density and pulse times, nucleation of new crystals can be favored over growth of existing crystals, resulting in films with ultra fine grain size. They have synthesized palladium--an iron film that is stable against grain growth to 400°C and does not experiences the α-to-β phase transition. The palladium-iron nanoalloys are also found to exhibit significantly improved surface properties compared to conventional materials. They do not require activation, and they recover readily from hydrogen sulfide poisoning. Besides hydrogen separation, these nanoalloy films are successfully applied in membrane-assisted hydrogenation and dehydrogenation reactions

Terry et.al conducted experiments to characterize US Filter ceramic membranes used in the catalytic dehydrogenation of cyclohexane to benzene. The reaction yield was studied as a function of membrane pore size for 50, 100, 200, and 2000 Å membranes. The effect on reaction yield, membrane permeability, and membrane selectivity of altering pore size by addition of successive thin film layers (silica oxide particles in an iron(III) supported solution) to the membrane surfaces was the primary focus of the study. The membranes were also characterized with a no reactive He/N_2 separation to determine the effect of successive thin film layers on the extent of Knudsen diffusion as the transport mechanism. This characterization demonstrated that Knudsen behavior could be obtained in a large pore diameter membrane by adding thin film layers to the surface. Reaction experiments showed a 300% increase in yield from that which was obtained in an impermeable reactor under similar conditions

$$\frac{d\left(\xi^R\psi^R\right)}{d\lambda}-\tau\alpha_i\gamma_i\left(\frac{d\psi_i}{d\rho}\right)_{\rho=0,\lambda}=0$$

$$\psi^R\frac{d\left(\xi^R\right)}{d\lambda}-\tau\sum\alpha_i\gamma_i\left(\frac{d\psi_i}{d\rho}\right)_{\rho=0,\lambda}=0$$

Most significantly, the coated membranes operating in the Knudsen regime rendered a higher reaction yield than the uncoated 50 Å membrane, whose transport mechanism was also Knudsen dominated. These phenomena can be explained by favorable surface effects between the thin film material and the reaction species. Thus, it was concluded, that a thin film (added to the surface membrane), which operates in the Knudsen regime and creates favorable surface effects to enhance membrane selectivity, can shift reaction equilibrium to a higher product yield than a membrane which only exhibits Knudsen diffusion.

Itoh.N & **Haraya** developed a carbon membrane reactor as one of the applications of carbon membranes was newly developed and examined using dehydrogenation of cyclohexane as a test reaction. Permeation of hydrogen, argon, cyclohexane and benzene through carbon membranes showed the so-called molecular-sieving like diffusion behavior. The performance of the carbon membrane reactor for the dehydrogenation was found to exceed that of a normal reactor, i.e., equilibrium conversion. When plug flow, no mixing diffusion, isobaric and isothermal conditions are assumed, changes of flow rate for each component along the axial direction of the carbon membrane reactor can be described by simultaneous ordinary differential equations as

Reaction side

$dU_C/dL = -Da \,.\, f_r - T_C(m_C - \beta n_C)$

$dU_B/dL = -Da \,.\, f_r - T_B(m_B - \beta n_B)$

$dU_H/dL = -3Da \,.\, f_r - T_H(m_H - \beta n_H)$

$dU_I/dL = -T_I(m_I - \beta n_I)$

Permeation side

$dV_C/dL = -T_C(m_C - \beta n_C)$

$V_B = 1 - U_C - U_B - V_C$

$V_H = 3(1 - U_C - V_C) - U_H$

$V_I = \alpha - U_I$

Initial conditions

at $L = 0 : U_C = 1; U_I = \alpha$;

$U_B = U_H = V_C = V_B = V_H = V_I = 0$

$f_r = (K_p m_C / P_r^3 - m_B m_H^3)/(m_H^3 + k_B k_P m_C / p_r^2)$

$T_i = Q_i A P_r / u_C^0$

$D_a = k_r P_r V_r / u_C^0$

$\alpha = u_I^0 / u_C^0; \beta = P_s / P_r$

In this study, the rate constant, *k*r

and the Next, the conversions calculated using the permeation rates measured in the binary-mode are compared with those in the single mode. The latter is found to be always higher than the former. The difference became larger with decreasing pressure on the separation side. This is because the reducing pressure gives a raise in the permeation flux and therewith cyclohexane, an undesired permeate, also moves from the reaction to the separation side. Clearly, such cyclohexane permeation results in a loss in the conversion. The performance of the carbon membrane reactor for the dehydrogenation was fairly good compared with that of a normal reactor, i.e., equilibrium conversion. The mathematical model derived on the assumption of ideal flow could explain the experimental data within a limited range of the reaction condition. Beyond the range, however, the data deviated significantly from the predictions. As the major reasons, it was pointed out that a radial concentration polarization of hydrogen depressed the conversion, and any change in the activity of the catalyst occurred under a less hydrogen atmosphere.

Byeong-Heon Jeong, 2004 et.al. has developed a simple mathematical model assuming isothermal operation and a plug flow pattern to evaluate the performance of an FAU-type zeolite membrane reactor for use in the catalytic dehydrogenation of cyclohexane. The membrane reactor consisted of a catalyst bed and membrane, containing an impermeable region at the reactor inlet, followed by a permeable region. The impermeable region was required in order to achieve an equilibrium conversion before entering the permeable region, and the selective permeation of benzene and hydrogen was sufficient to shift the equilibrium. The results of the simulation for the membrane reactor were in good agreement with the experimental results. On the basis of the simulation, the zeolite membrane reactor was superior to the Knudsen membrane reactor. The effect of co-feeding hydrogen with cyclohexane, to restrain coke formation on the catalyst due to the high hydrogen concentration in the feed side was clearly demonstrated. The effect of permeance and the separation factor on the conversion was evaluated, and as a result, the permeance was more important in terms of increasing the conversion than the separation factor. A simple mathematical model was developed to evaluate the performance of an FAU-type zeolite membrane reactor for the catalytic dehydrogenation of cyclohexane under the following assumptions:

(1) Isothermal conditions;
(2) Plug flow in both the feed and permeate sides;
(3) No axial or radial diffusion;
(4) Permeation through the membrane is proportional to the difference in partial pressures between the feed and permeate sides;
(5) Dehydrogenation reactions take place only on the catalysts packed in the feed side.

The mass balance equations for component *i* in the feed side and the permeate side in the membrane reactor are given as follows:

Feed side (catalyst bed):

$$\frac{dN_{i,F}}{dl} = \upsilon_i r_C S_R - 2\pi r Q_i (P_F x_i - P_P y_i)$$

Permeate side:

$$\frac{dN_{i,p}}{dl} = 2\pi r Q_i (P_F x_i - P_P y_i)$$

Where *Ni* is the molar flow rate of component *i*. *l* is the distance from the inlet of the reactor. . $_i$ is the stoichiometric coefficient of component *i*. r_C is the dehydrogenation rate of cyclohexane. S_R is the cross-sectional area of catalyst bed. *r* is the outer radius of the porous support tube. Q_i is the permeance of component *i*. P_F and P_P are the total feed and permeate pressures. x_i and y_i are the mole fractions of component *i* in the feed and permeate sides, respectively. The following reaction rate equation of cyclohexane, r_C was used

$$r_C = \frac{-k(KppC/p_H^3 - p_B)}{1 + (K_B K_p p_C/p_H^3)}$$

where *k*, K_B, and *K*p are, respectively, the reaction rate constant, the adsorption equilibrium constant for benzene, and the reaction equilibrium constant. p_i is the partial pressure component *i*.

sabita roy et.al identified electrolysis plating to deposit a thin metal film on microporous substrate. Electrolysis plating is the controlled autocatalytic deposition of a continuous film on the surface of a substrate by the interaction of a metal salt and a chemical reducing agent. This method can be used to make thin films of metals, alloys and composites on both conducting and no conducting surfaces. The primary objective of this project was to prepare and characterize a hydrogen permselective palladium-ceramic composite membrane for high temperature gas separations and catalytic membrane reactors. Electrolysis plating method was used to deposit a thin palladium film on microporous ceramic substrate. The objective of this paper is to discuss the preparation and characterization of a thin-film palladium-ceramic composite membrane for selective separation of hydrogen at elevated temperatures and pressures. In this study, they also presented a model to describe the hydrogen transport through the palladium-ceramic composite membrane in a co current flow configuration.

The process begins with sorption of hydrogen molecules on the film surface and ends with hydrogen desorption from the ceramic substrate. It is believed that the hydrogen molecule dissociates into hydrogen atoms on one side of the film. The hydrogen atoms then diffuse through the film and re-associate on the other

$$\mathrm{J_a}=\frac{Q_a}{h}\left[(px_a)^n-(py_a)^n\right]$$

The rates of permeation of the permeable components per unit membrane area are given by:

$$\frac{\mathrm{d(Vy_a)}}{\mathrm{dS}}=\left(\frac{Q_a}{h}\right)\left[(px_a)^n-(px_a)^n\right]$$

$$\frac{\mathrm{d(Vy_b)}}{\mathrm{dS}}=\left(\frac{Q_b}{h}\right)\left[(px_b)^n-(px_b)^n\right]$$

The above equations along with the material balance Equations are solved subject to initial conditions:

At $\mathrm{S}=0, \mathrm{L}=\mathrm{L_f}$; $\mathrm{x_a}=\mathrm{x_{af}}$; $\mathrm{x_i}=\mathrm{x_{if}}$ and
$\mathrm{V}=\mathrm{V_f}$; $\mathrm{ya}=\mathrm{y_{af}}$; $\mathrm{y_I}=\mathrm{y_{if}}$

Tayakout M. *et.al* 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 mass 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 an 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 follows:

In the inner compartment:

$$\cdot^{(1)}\frac{\partial\cdot}{\partial t}+\mathrm{Pe}^{(1)}\frac{\partial\cdot}{\partial,}-\frac{\partial^{2}\cdot}{\partial\cdot^{2}}-\cdot^{(1)}\frac{1}{\cdot}\frac{\partial}{\partial\cdot}\left(\cdot\frac{\partial\cdot}{\partial\cdot}\right)=0$$

The interface and boundary conditions

$$\forall\xi, . = 0; \quad \frac{d\Psi}{d\rho} = 0$$

$$\forall\xi, \rho = 0; \quad \left.\frac{d.}{d.}\right|_{.=1} = .^{(1)}\left.\frac{d.}{d.}\right|_{.=0}$$

In the membrane:

$$.^{(2)}\frac{\partial .}{\partial t} - \frac{1}{(a.. + r_{int})}\frac{\partial}{\partial .}\left((a.. + r_{int})\frac{\partial .}{\partial .}\right) - ..\ {}^{2}R(.\ ) = 0$$

The interface and boundary conditions

$$\forall. , . = 1; \quad \left.\frac{d.}{d.}\right|_{.=1} = .^{(1)}\left.\frac{d.}{d.}\right|_{.=0}$$

$$\forall\xi, . = 1; \quad \left.\frac{d.}{d.}\right|_{.=1} = .^{(2)}\left.\frac{d.}{d.}\right|_{.=0}$$

In the outer compartment,

$$.^{(3)}\frac{\partial .}{\partial t} + Pe^{(3)}F(.\ )\frac{\partial .}{\partial .} - \frac{\partial^2 .}{\partial .^2} - .^{(3)}\frac{1}{(b. + r_{ext})}\frac{\partial}{\partial .}\left((b. + r_{ext})\frac{\partial .}{\partial .}\right) = 0$$

$$\forall. , \qquad . = 1; \qquad \left.\frac{d.}{d.}\right|_{.=1} = .^{(2)}\left.\frac{d.}{d.}\right|_{.=0}$$

$$\forall. , \qquad . = 1; \qquad \frac{d.}{d.} = 0$$

$$. = 0 \qquad 0 < . < 1 \qquad 1 + \frac{1}{Pe^{(3)}F(.\ )}\frac{d.}{d.} - . = 0$$

They solved these model equations using two methods: orthogonal collocation method and finite difference method and they concluded that for a quick estimate from experimental data the collocation method should be selected. The finite difference hydrogen molecule dissociates into hydrogen atoms on one side of the film. The hydrogen atoms then diffuse through the film and re-associate on the other

$$\mathrm{J_a} = \frac{Q_a}{h}\left[(px_a)^n - (py_a)^n\right]$$

The rates of permeation of the permeable components per unit membrane area are given by:

$$\frac{\mathrm{d(Vy_a)}}{\mathrm{dS}} = \left(\frac{Q_a}{h}\right)\left[(px_a)^n - (px_a)^n\right]$$

$$\frac{\mathrm{d(Vy_b)}}{\mathrm{dS}} = \left(\frac{Q_b}{h}\right)\left[(px_b)^n - (px_b)^n\right]$$

The above equations along with the material balance Equations are solved subject to initial conditions:

At $\mathrm{S = 0, L = L_f \;; x_a = x_{af} \;; x_i = x_{if}}$ and

$\mathrm{V = V_f \;; ya = y_{af} \;; y_l = y_{if}}$

Tayakout M. *et.a*l 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 mass 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:

$$.^{(1)}\frac{\partial .}{\partial \mathrm{t}} + \mathrm{Pe}^{(1)}\frac{\partial .}{\partial .} - \frac{\partial^2 .}{\partial .^2} - .^{(1)}\frac{1}{.}\frac{\partial}{\partial .}\left(.\frac{\partial .}{\partial .}\right) = 0$$

The interface and boundary conditions

$$\forall \xi, . = 0; \quad \frac{d\Psi}{d\rho} = 0$$

$$\forall \xi, \rho = 0; \quad \left.\frac{d.}{d.}\right|_{.=1} = .^{(1)}\left.\frac{d.}{d.}\right|_{.=0}$$

In the membrane:

$$.^{(2)}\frac{\partial .}{\partial t} - \frac{1}{(a.. + r_{int})}\frac{\partial}{\partial .}\left((a.. + r_{int})\frac{\partial .}{\partial .}\right) - ..\,^{2}R(.\ ) = 0$$

The interface and boundary conditions

$$\forall . , . = 1; \quad \left.\frac{d.}{d.}\right|_{.=1} = .^{(1)}\left.\frac{d.}{d.}\right|_{.=0}$$

$$\forall \xi, . = 1; \quad \left.\frac{d.}{d.}\right|_{.=1} = .^{(2)}\left.\frac{d.}{d.}\right|_{.=0}$$

In the outer compartment,

$$.^{(3)}\frac{\partial .}{\partial t} + Pe^{(3)}F(.\ )\frac{\partial .}{\partial .} - \frac{\partial^{2} .}{\partial .^{2}} - .^{(3)}\frac{1}{(b. + r_{ext})}\frac{\partial}{\partial .}\left((b. + r_{ext})\frac{\partial .}{\partial .}\right) = 0$$

$$\forall . , \quad . = 1; \quad \left.\frac{d.}{d.}\right|_{.=1} = .^{(2)}\left.\frac{d.}{d.}\right|_{.=0}$$

$$\forall . , \quad . = 1; \quad \frac{d.}{d.} = 0$$

$$. = 0 \quad 0 < . < 1 \quad 1 + \frac{1}{Pe^{(3)}F(.)}\frac{d.}{d.} - . = 0$$

They solved these model equations using two methods: orthogonal collocation method and finite difference method and they concluded that for a quick estimate from experimental data the collocation method should be selected. The finite difference

$$\rho = 0(\forall\lambda); \psi_i = \psi_i^R(\lambda) and$$
$$\rho = 1(\forall\lambda); \psi_i = \psi_i^P(\lambda)$$

Jayaraman V.K et al. have developed An annular reactor packed with matrices in which the catalysts/enzyme/microorganisms are immobilized and the results indicate that the overall resistance and hence the conversion depend upon the Thiele modulus and another parameter, *a*. 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 can be obtained for linear reactions and a simplified semi-analytic method has been used for obtaining concentration profiles for nonlinear reactions. The following assumptions have been made in formulating the design equations:

1. The reactor is assumed to be of tubular geometry and steady state prevails in the reactor.
2. The reactant movement through the tube side is by laminar convection in the axial direction and by diffusion in the radial direction.
3. There is no convection in the membrane or shell.
4. The reactor is assumed to be isothermal and the temperature gradients are neglected.
5. 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.
6. The matrices are assumed to be of spherical shape with a uniform radius throughout the bed.
7. As a representative example, reaction rate is assumed to follow Michaelis–Menten kinetics.

With these assumptions the balance equations for the different regions can be written as follows.

Tube side:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(rD_1\frac{\partial c_1}{\partial r}\right) = V_0\left(1-\frac{r^2}{a^2}\right)\frac{\partial c_1}{\partial z}$$

Membrane:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(rD_2\frac{\partial c_2}{\partial r}\right)=0$$

Shell side bulk phase:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(rD_{3b}\frac{\partial c_{3b}}{\partial r}\right)=\frac{3(1-\varepsilon)}{y_s}D_{3s}\left(\frac{\partial c_{3s}}{\partial y}\right)_{y=y_s}$$

Shell side solid phase:

$$\frac{1}{y^2}\frac{\partial}{\partial y}\left(y^2D_{3s}\frac{\partial c_{3s}}{\partial y}\right)=\frac{V_{\max}C_{3s}}{k_m=C_{3s}}$$

The appropriate boundary conditions are

$$c_1(0,0)=c_0;\left(\frac{\partial c_1}{dr}\right)_{r=0}=0$$

$$D_1\left(\frac{\partial c_1}{dr}\right)=D_2\left(\frac{\partial c_2}{dr}\right)\quad \text{at } r=a$$

$C_2/C_1=k_1$

$$D_2\left(\frac{\partial c_2}{dr}\right)=D_{3b}\left(\frac{\partial c_{3b}}{dr}\right)\text{ at } r=b$$

$$D_{3b}\left(\frac{\partial c_{3b}}{dr}\right)=0\quad \text{at } r=d$$

$$\left(\frac{\partial c_{3s}}{dy}\right)_{y=0}=0$$

$$\rho = 0(\forall \lambda); \psi_i = \psi_i^R(\lambda) and$$
$$\rho = 1(\forall \lambda); \psi_i = \psi_i^P(\lambda)$$

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5. 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.
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With these assumptions the balance equations for the different regions can be written as follows.

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Membrane:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(rD_2 \frac{\partial c_2}{\partial r} \right) = 0$$

Shell side bulk phase:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(rD_{3b} \frac{\partial c_{3b}}{\partial r} \right) = \frac{3(1-\varepsilon)}{y_s} D_{3s} \left(\frac{\partial c_{3s}}{\partial y} \right)_{y=y_s}$$

Shell side solid phase:

$$\frac{1}{y^2}\frac{\partial}{\partial y}\left(y^2 D_{3s} \frac{\partial c_{3s}}{\partial y} \right) = \frac{V_{\max} C_{3s}}{k_m = C_{3s}}$$

The appropriate boundary conditions are

$$c_1(0,0) = c_0; \left(\frac{\partial c_1}{dr} \right)_{r=0} = 0$$

$$D_1 \left(\frac{\partial c_1}{dr} \right) = D_2 \left(\frac{\partial c_2}{dr} \right) \quad \text{at } r = a$$

$C_2/C_1=k_1$

$$D_2 \left(\frac{\partial c_2}{dr} \right) = D_{3b} \left(\frac{\partial c_{3b}}{dr} \right) \quad \text{at } r = b$$

$$D_{3b} \left(\frac{\partial c_{3b}}{dr} \right) = 0 \quad \text{at } r = d$$

$$\left(\frac{\partial c_{3s}}{dy} \right)_{y=0} = 0$$

2.2 Objective of the study

On the basis of the above literature review, we have aimed the following objectives.

1. To develop the simple mathematical model for a zeolite membrane reactor,
2. To solve the mathematical model by using MATLAB 6.5 software,
3. To validate the model with the available experimental results in the literature,
4. To study the effect of various parameters on the performance of the reactor.

CHAPTER III

MODEL DEVELOPMENT

3.0 MODEL DEVELOPMENT

The dehydrogenation of cyclohexane has been extensively studied as a model reaction in various membrane reactors.

$$C_6H_{12} \xrightleftharpoons{Pt/Al_2O_3} C_6H_6 + 3H_2 \qquad \Delta H = 206.2kj/mol \qquad (2)$$

A pseudo-homogeneous model was recently used to describe the transport mechanism through a catalyst bed.

A simple mathematical model was developed to evaluate the performance of an FAU-type zeolite membrane reactor for the catalytic dehydrogenation of cyclohexane under the following assumptions:

(1) Isothermal conditions;

(2) Plug flow in both the feed and permeate sides;

(3) No axial or radial diffusion;

(4) Permeation through the membrane is proportional to the difference in partial pressures between the feed and permeate sides;

(5) Dehydrogenation reactions take place only on the catalysts packed in the feed side.

The simulated membrane reactor was composed of quartz glass tube (i.d. = 10 mm, o.d. = 13 mm) containing an FAU-type zeolite membrane, which was fixed coaxially in the tubular reactor, as illustrated in Fig. 1. Almost half of the catalyst was packed in the area upstream from the permeation portion. The cyclohexane was diluted with argon and fed to the catalyst bed in the feed side of the membrane. Pure argon was also introduced to the permeate side of the membrane as a sweep gas. The total pressure in both the feed and permeate sides was maintained at 101.3 kPa. The model parameters for simulation are summarized in Table 1.

The mass balance equations for component *i* in the feed side and the permeate side in the membrane reactor are given as follows:

Feed side (catalyst bed):

$$\frac{dN_{i,F}}{dl} = \gamma_i r_c A_c - (2\pi r_2).Q_i\left(P_F x_i - P_P y_i\right) \tag{3}$$

Permeate side:

$$\frac{dN_{i,P}}{dl} = (2\pi r_1).Q_i\left(P_F x_i - P_P y_i\right) \tag{4}$$

where N_i is the molar flow rate of component *i*. *l* is the distance from the inlet of the reactor. γ_i is the stoichiometric coefficient of component *i*. r_C is the dehydrogenation rate of cyclohexane. Ac is the cross-sectional area of catalyst bed. *r* is the outer radius of the porous support tube. Q_i is the permeance of component *i*. P_F and P_P are the total feed and permeate pressures. x_i and y_i are the mole fractions of component *i*.in the feed and permeate sides, respectively.

The following reaction rate equation of cyclohexane, r_C,is used

$$r_C = \frac{-k(K_p p_{CH}/p_H^3 - p_B)}{1 + (K_B K_p p_{CH}/p_H^3)} \tag{5}$$

where *k*, *K*B, and *K*p are, respectively, the reaction rate constant, the adsorption equilibrium constant for benzene, and the reaction equilibrium constant. *pi* is the partial pressure of component *i*.

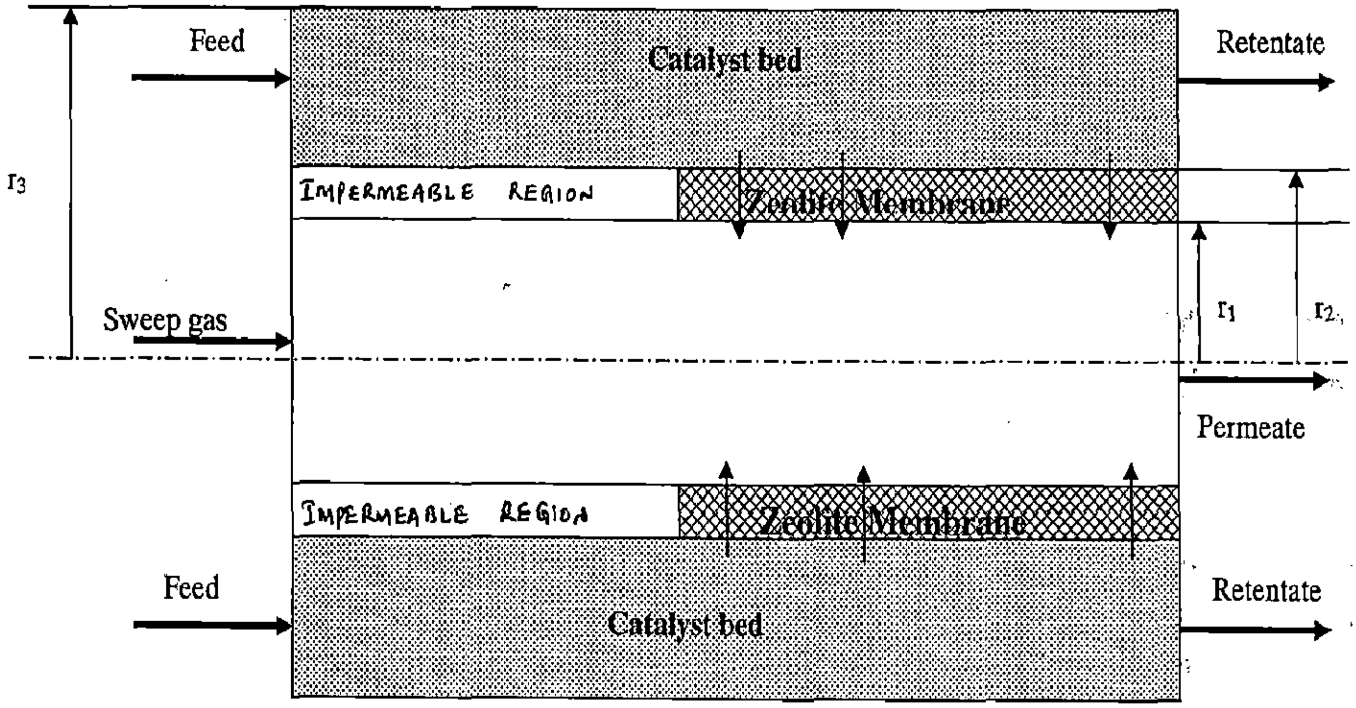

Fig. 3 Schematic diagram of a zeolite membrane reactor (hybrid type) used for simulation and discussion

Table 2 Operating conditions for simulation of both Membrane and Fixed bed reactors

Name	**Parameter Specification/Value**
Reactor	
Length (L)(m)	6×10^{-2}
Inner radius(m)	5×10^{-3}
Membrane packing	
Membrane type	FAU-type hybrid zeolite membrane
Length(m)	2.7×10^{-2}
Inner radius(m)	1.0×10^{-3}
Outer radius(m)	1.3×10^{-3}
Catalyst	1.0wt.%Pt/Al_2O_3
Cross-sectional area of the bed, feed side(A_c)(m^2)	7.5×10^{-5}
Cross-sectional area of the bed, tube side (A_c)(m^2)	2.0×10^{-6}
Molar flow rate	
Feed flow rate, feed side(mol s^{-1})	9.0434×10^{-6}
sweep flow rate, tube side(mol s^{-1})	4.5217×10^{-5}
Composition	
Mole fraction of cyclohexane, feed side	0.1
Mole fraction of diluent(Argon),feed side	0.9
Mole fraction of diluent(Argon), tube side	1.0(pure)
Total pressure	
P_F, feed side(pa)	1.013×10^{5}
P_P, tube side(pa)	1.013×10^{5}
Permeance[B.H.Jeong et al.2003]	
Q_A(Argon)(mol $m^{-2}s^{-1}pa^{-1}$)	1.0×10^{-10}

The literature values for K_B and K_p could be successfully utilized in these simulations. The activation energy of 32 kJ mol. 1 was similar to that reported by Itoh et al. [19]. As a result, the reaction rate constant, *k*, was obtained as follows:

$$k = 0.44 \exp(-3850/T) \qquad (\text{mol m}^{-3}\ \text{Pa}^{-1}\ \text{s}^{-1}). \qquad (4)$$

$$K_B = (2.03 \times 10^{-10}) \exp(6.270/T) \qquad (\text{Pa}^{-1}). \qquad (5)$$

$$K_p = (4.89 \times 10^{35}) \exp(3.190/T) \qquad (\text{Pa}^{3}). \qquad (6)$$

The model equations were numerically solved by the MATLAB 6.5 using the above parameters. The conversion of cyclohexane, X_C, was calculated from the ratio of the molar fractions of cyclohexane at the outlets of the feed and the permeate sides to those for cyclohexane at the inlets of both sides as follows:

$$X_C = 1 - \frac{\left(u_{x,1} \times x_{C,1} + u_{y,1} \times y_{C,1}\right)}{\left(u_{x,0} \times x_{C,0} + u_{y,0} \times y_{C,0}\right)} \qquad (7)$$

where $u_{x,0}$ and $u_{x,1}$ are the gas flow rates at the inlet and the outlet of the feed side, respectively. $u_{y,0}$ and $u_{y,1}$ are the gas flow rates at the inlet and the outlet of the permeate side, respectively.

CHAPTER IV

SIMULATION RESULTS AND DISCUSSIONS

4.0 RESULTS AND DISCUSSION

4.1 *Model Validation*

The model equations derived for both hybrid membrane reactor and fixed bed reactor, have been solved at operation conditions of experimental studies carried out by B.H. Jeong et al 2003. The experimental results for fixed bed and for hybrid type of reactor along with simulated results from model for fixed bed and membrane reactor have been shown in figures Fig. 4.to Fig. 5 The model results for fixed bed and hybrid membrane reactor are found in good agreement with the experimental results. The percentage of deviation in calculated results are shown in the Table 3. The model equations are solved in the temperature range of 423K to 498K and the percentage conversion is plotted against temperature in Fig. 4. The experimental values are taken from B.H Jeong et al. 2003 at temperatures 423 K, 448 K, 473 K, and 498K are compared with the calculated results obtained in the temperature range(423--498K). The percentage deviation of calculated values from the experimental values is less than % and is visualized in the Fig. 4. Additionally, the conversion in case of fixed bed reactor from our studies is compared with Experimental studies by B.H Jeong et al 2003. The calculated results of the conversion of cyclohexane using fixed bed reactor are in good agreement with the experimental values investigated at temperatures 423 K, 448 K, 473 K, and 498K. This is clearly shown in Fig. 4. Table 3 gives the percentage deviation of conversion for calculated results from the experimental results. These results lead to the validation of the model equations.

4.2 The study of the changes of the mole fraction of cyclohexane

Fig. 16 and Fig. 7 shows the changes in mole fraction of cyclohexane in the feed side as a function of distance from the reactor inlet at temperatures 423K and 498K respectively. The simulations are performed at 423, 448, 473, and 498K using the zeolite membrane reactor. The length of the impermeable region is 0.0335m from the inlet of the feed side. For the simulations of the impermeable region (i.e., a packed bed reactor segment), the reaction term in the model equation is only considered by substituting Q_i in the permeation term with 0. Meanwhile, both reaction and permeation terms are taken into account for the simulations of the permeable region (i.e., a membrane reactor segment). The mole fraction of cyclohexane decreases and is close to the equilibrium value at the end of impermeable region. A further decrease in cyclohexane concentration occurs in the permeable region, mainly due to the reaction resulting from a shift in the equilibrium. This shift of equilibrium is favored by the removal of the one of the products selectively by permeating through the membrane in the membrane reactor segment. Consequently, the magnitude of the conversions at the end of the membrane reactor was much higher than the equilibrium values. Fig. 8 enlightens the effect of temperature on mole fraction change in the reactor set up. The mole fraction of cyclohexane decreases at the outlet of the reactor in shell side as temperature increases and it reaches almost 0 i.e. completely disappeared from the reaction mixture. It also gives the optimal length of the impermeable region up to which the impervious material can be incorporated. In this case it is approximately 0.035 m.

5.3 Conversion of cyclohexane along the length of the both reactor configurations

The dehydrogenation reaction has been considered in shell and permeation in tube in case of hybrid membrane reactor, tubular type reactor with catalyst bed which acts as a fixed bed reactor. The conversion of cyclohexane is evaluated along the length in both cases viz. hybrid membrane reactor and fixed bed reactor setups. Fig. 9 and Fig. 10 show the variation in conversion along the length for hybrid membrane reactor at 473K and 498K respectively. These figures clearly indicate that the conversion increases rapidly upto 0.001 m after that it increases very slowly and almost constant up to 0.03m. Beyond 0.03 m length of the reactor, the conversion again increases rapidly and it reaches 74% at 473 K and 91% at 498 K. This is attributed to the fact that the there is no loss of reactant i.e. Cyclohexane at the initial stages. But the increase of conversion is not visible beyond 0.01 m till 0.03 m due to the lack of permeance of one of the products

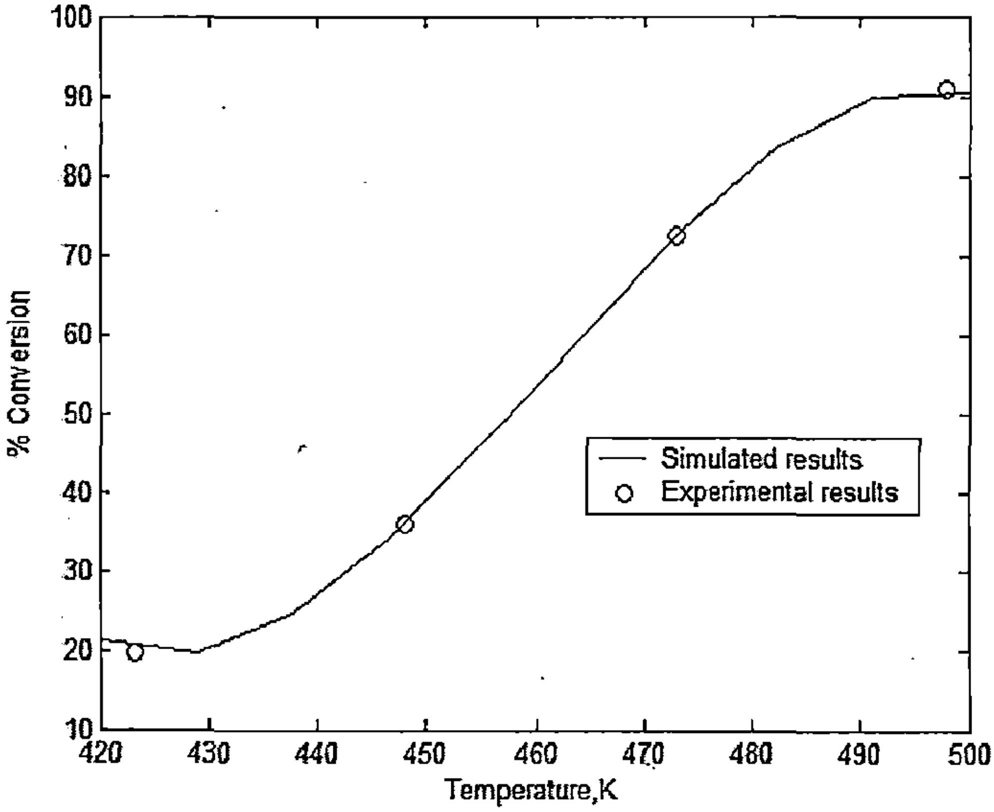

Fig. 4 Comparison of calculated % conversion of cyclohexane with the experimental value for hybrid membrane reactor.

Table 3 The deviation of calculated % conversion of hybrid membrane reactor from the experimental conversion (B.H.Jeong et al.2003) at different temperatures

Temperature K	**%Conversion (calculated)**	**% Conversion (experimental)**	**Deviation**	**Error**
423	19.764	19.625	-0.7083%	Less than -1%
448	35.863	35.900	+0.1031%	Less than +1%
473	72.648	72.845	+0.2838%	Less than +1%
498	90.810	91.052	+0.2658%	Less than +1%

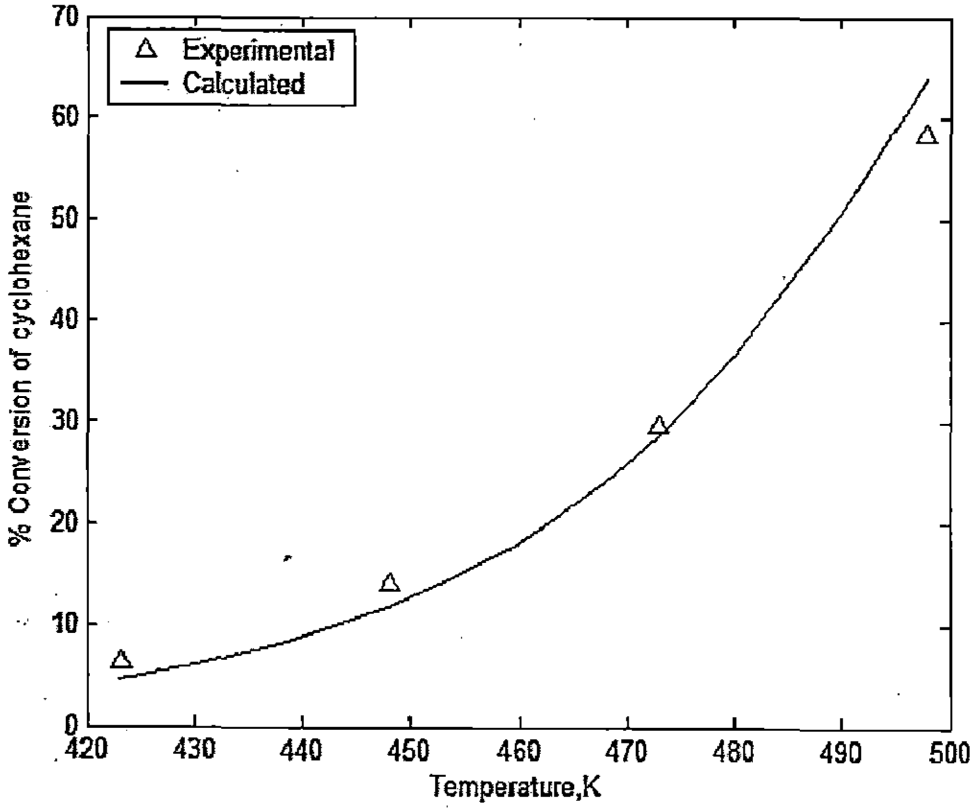

Fig. 5 Comparison of calculated % conversion of cyclohexane with the experimental value for fixed bed reactor

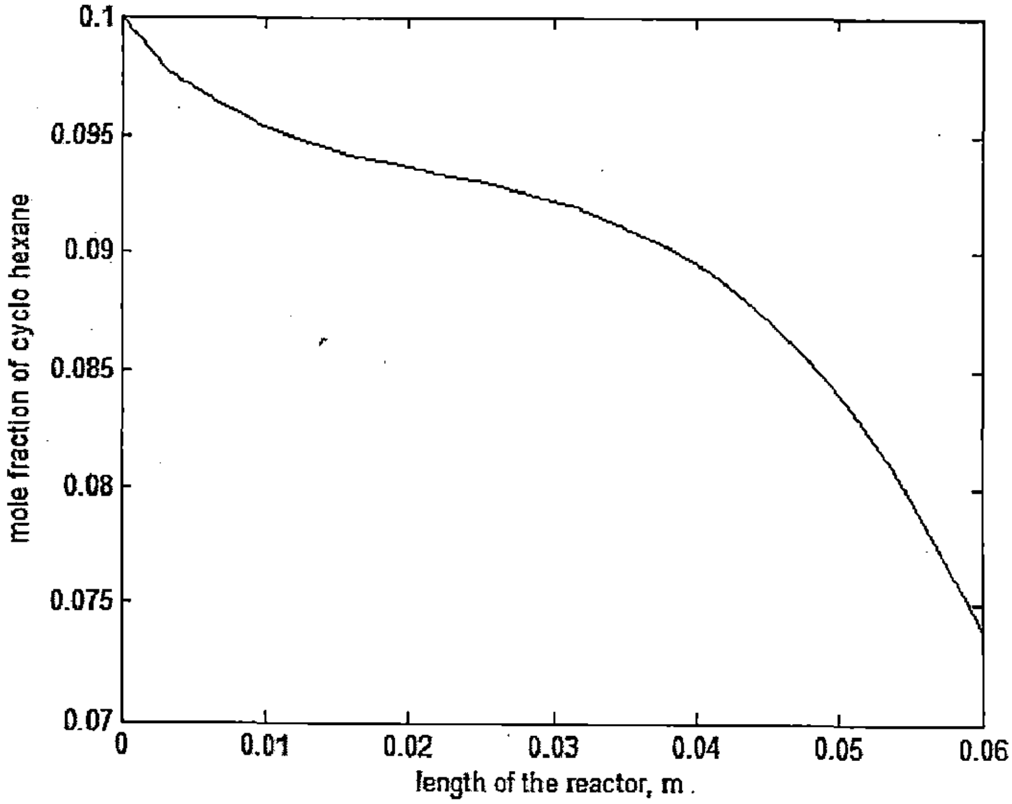

Fig. 6 The change of mole fraction of cyclohexane on shell side along the length of the membrane reactor at 423K

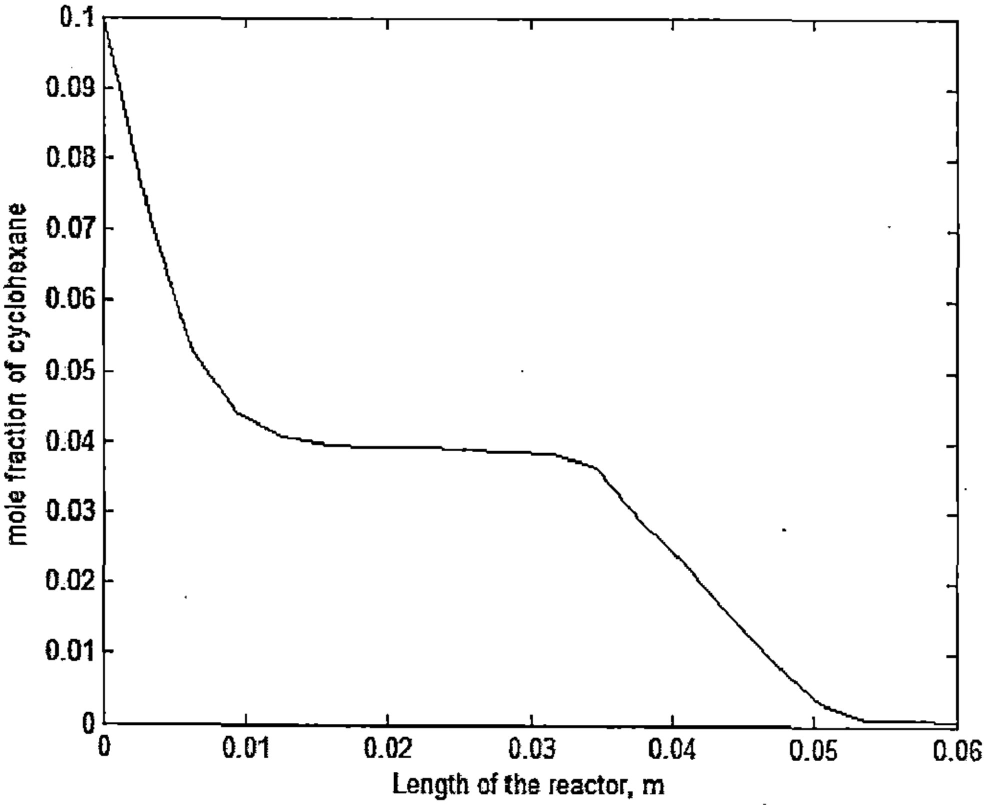

Fig. 7 The change of mole fraction of cyclohexane in shell along the length of the membrane reactor at 498K

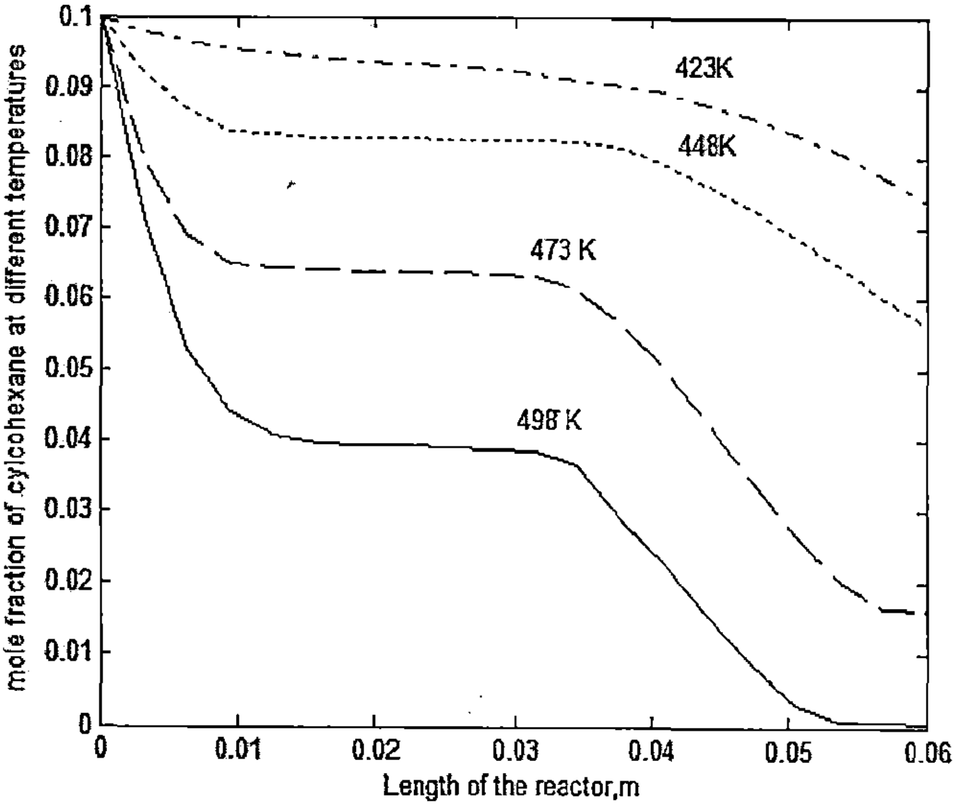

Fig. 8 The study of changes of mole fractions of cyclohexane in shell side along the length of the membrane reactor at different temperatures

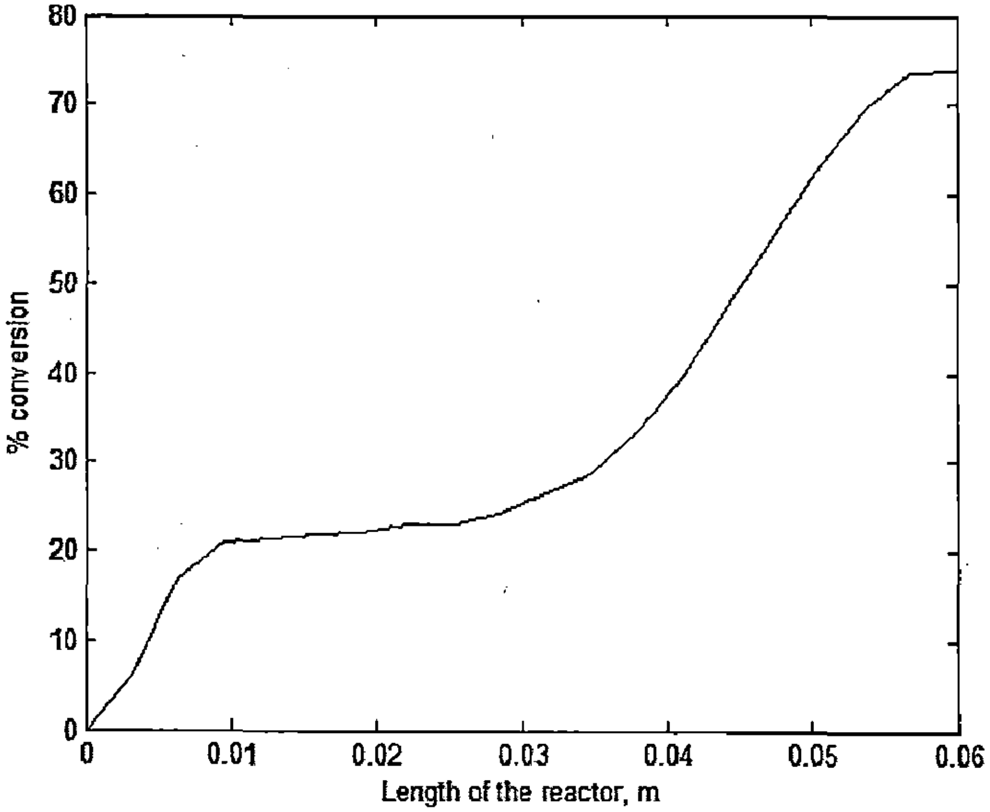

Fig. 9 Percentage conversion along the length of the hybrid membrane reactor at 473K

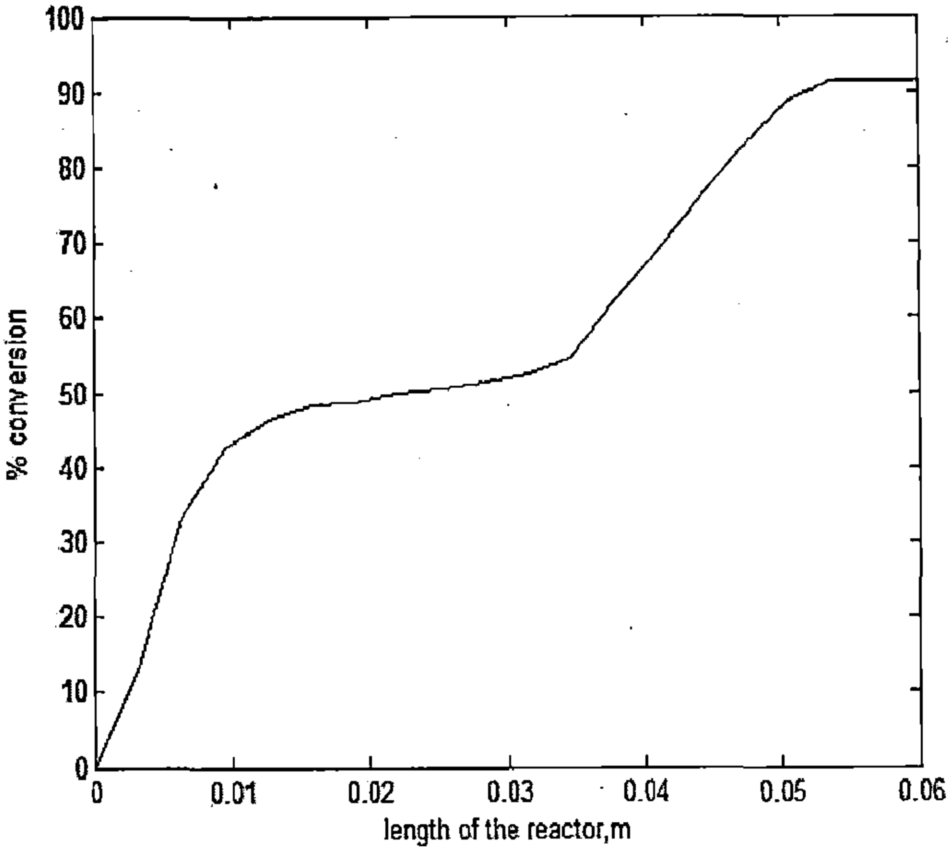

Fig. 10 Percentage conversion along the length of the hybrid membrane reactor at 498 K

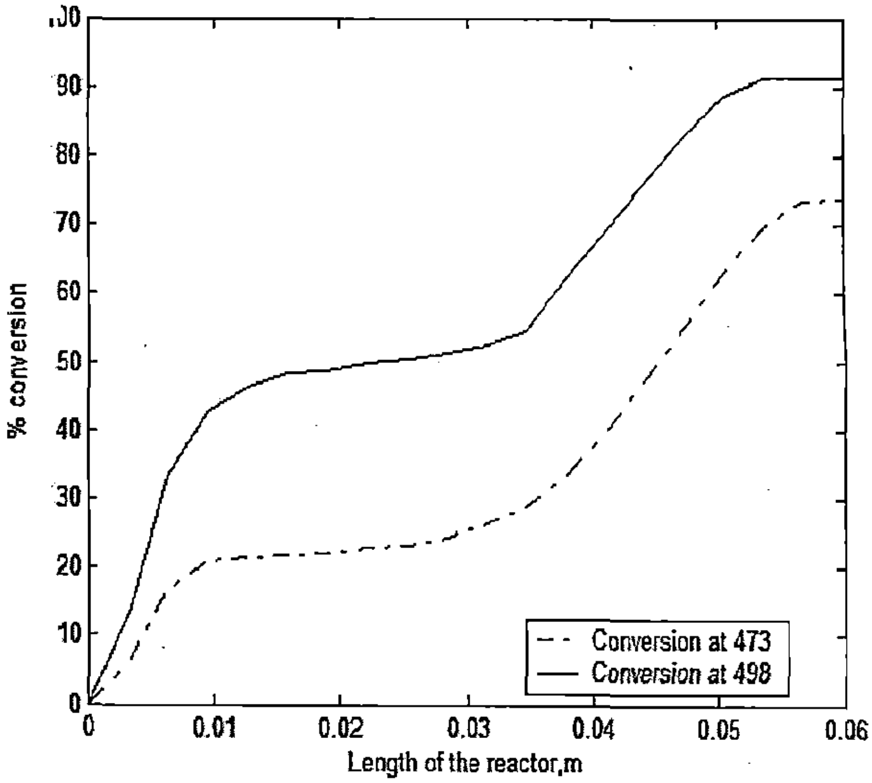

Fig. 11 Comparison of conversion along the length of the hybrid membrane reactor at 473 K and 498 K

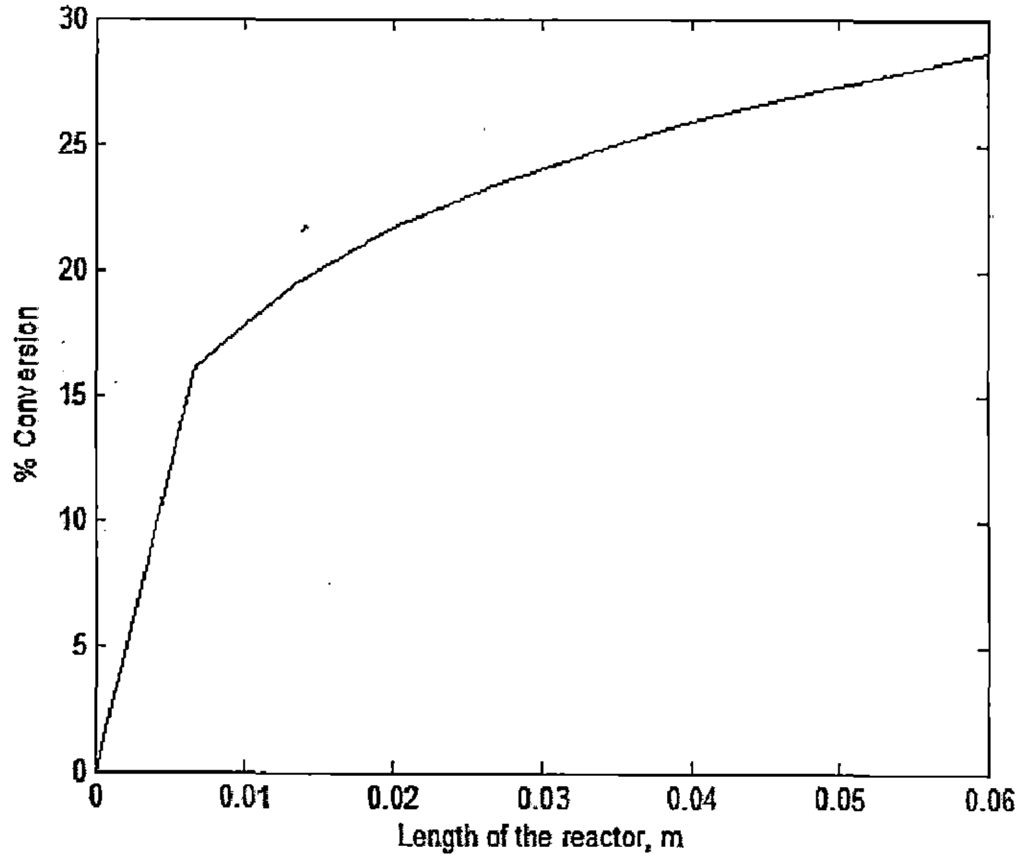

Fig. 12 Percentage conversion of the reaction along the length of the fixed bed reactor at 473 K

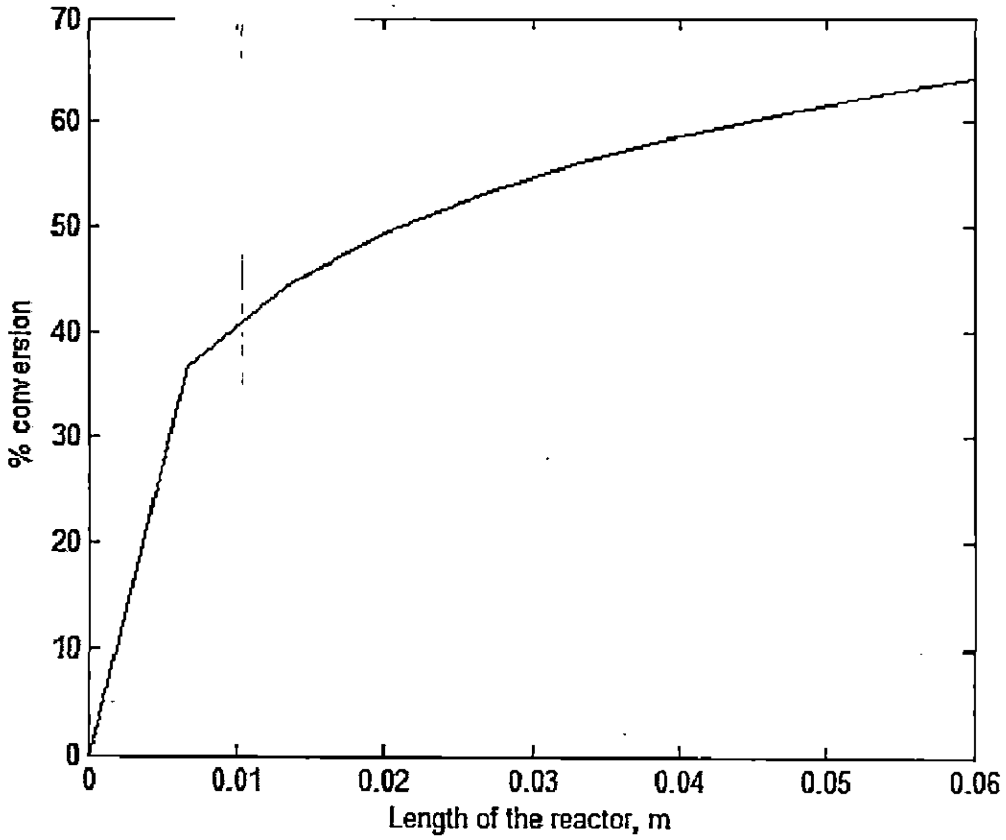

Fig. 13 Percentage conversion of the cyclohexane along the length of the fixed bed reactor at 498 K

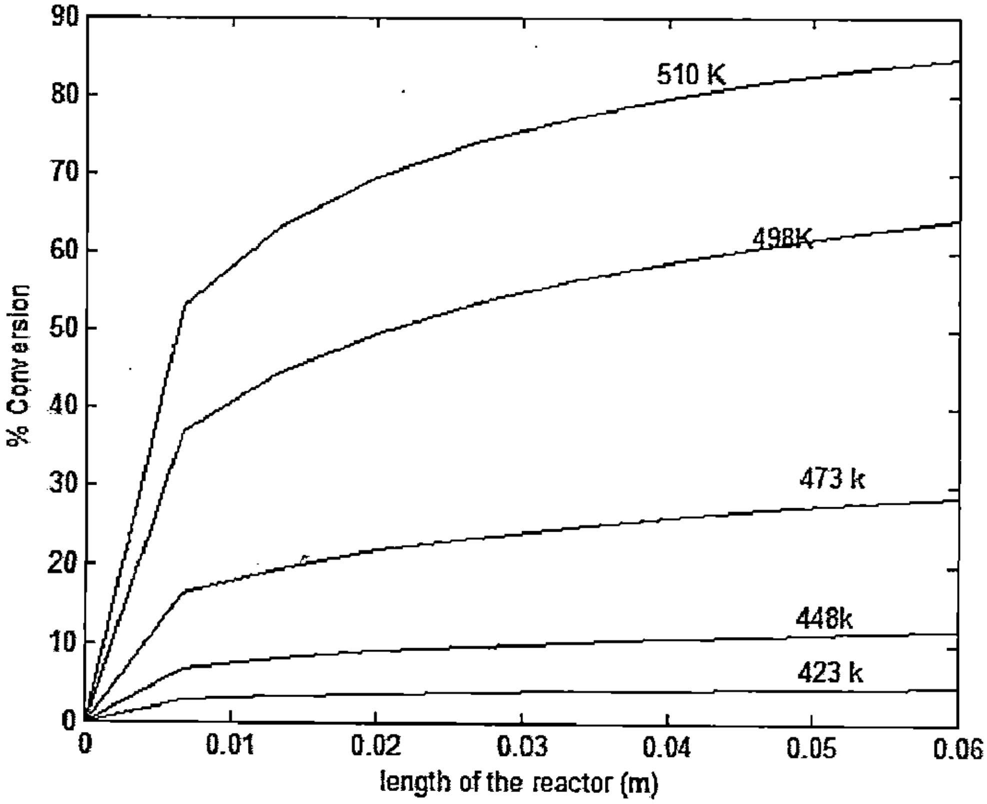

Fig. 14 Comparison of conversions along the length of the fixed bed reactor at different temperatures

through the impermeable region upto 0.03 m. Because this lack of removal of one of the products will limit the conversion thermodynamically. But beyond 0.03 m, zeolite membrane will permeate the benzene at high rate and hydrogen at some what lower rate than that of benzene through it so that equilibrium of the reaction will automatically shifted to right, giving high conversion of cyclohexane into the products. This effect is clearly depicted in the figures Fig. 9, Fig. 10. Fig. 11 compares the conversion of cyclohexane along the length of the membrane reactor at 473 K and 498 K. This graph enlightens the fact that the percentage conversion increases with increase of temperature. This is due to the fact that as the dehydrogenation of cyclohexane is an endothermic reaction, gives high yield at higher temperatures.

The conversion of the dehydrogenation reaction is now evaluated using the fixed bed reactor. Fig. 12 and Fig. 13 visualize the percentage conversion as a function of length of the reactor at particular temperatures 473 K and 498 K. These figures show the increase of conversion rapidly at the initial stages of the fixed bed reactor and then it increase very gradually. This is explained by the thermodynamic equilibrium concept, which favors the backward reaction once the equilibrium is attained and the hydrogen and benzene are consumed again to give the initial reactant cyclohexane. This way the conversion changes along the length of the reactor. Fig. 14 enlightens the effect of temperature on the conversion of the reaction along the length of the fixed bed reactor. It is clearly explained graphically that the increase of temperature increases the conversion, marginally at lower temperature domains i.e. 400K to 450 K and significantly at higher temperature domains i.e. 450K to 500K. This fact is supported by the Le Chatlier principle which says that high temperatures favor forward reactions in case of endothermic reactions like dehydrogenation of cyclohexane. Fig. 14 also indicates that longer lengths of the fixed bed reactors will not benefit by more conversion than the shorter length reactors of 0.01 to 0.02 m (in this case). But at higher temperatures, lengthy reactors will give high conversion than the shorter ones.

4.4 Comparison of hybrid membrane reactor with fixed bed reactor

The model equations are solved for fixed bed at operations mentioned in Table 2.

It is evident from the figure Fig. 15 that percentage conversion using hybrid reactor is higher than that of fixed bed at all temperatures. The percentage increase in conversion is more at higher temperatures. This is due to the fact that in the hybrid membrane reactor, one of the reaction products produced is permeated through the membrane there by shifting the thermodynamic equilibrium forward. The conversion in case of fixed bed limited by the thermodynamic equilibrium, and rate of backward reaction and forward reaction rate will be balanced to give a maximum of 32 % conversion at 473 K where as 75% (approximately) is achieved in case of hybrid membrane reactor. This is clearly seen in the Fig. 16 the rate of reaction as function of temperature in the reactor. The increase in reaction rate is not only enough to produce high conversions; the increase in the permeance rate of the permeable components with increase of temperature has also significant effect on the enhancement of the conversion. Fig. 17 clearly indicates the advantage and necessity of the removal of one of the reaction products from the reaction zone in order to shift the equilibrium forward. In this figure, the conversion is almost same upto 0.03 m approximately i.e. in the impermeable region. But beyond that length, the membrane effect dominates the equilibrium effect and yields high conversion. Almost 40% of the conversion increased beyond the impermeable region. That is, this much of the conversion advantage is possible with the membrane reactor to the fixed bed reactor. With this, it is concluded that hybrid membrane reactors will yield higher conversion than that of fixed bed reactors of same specifications and at the same operating conditions.

4.5 Effect of co-feeding hydrogen with cyclohexane

When the dehydrogenation is performed in the membrane reactor with hydrogen selective membranes, coking on the catalyst, due to the lack of hydrogen, gradually decreases the conversion. In the FAU-type zeolite membrane reactor, on the other hand,

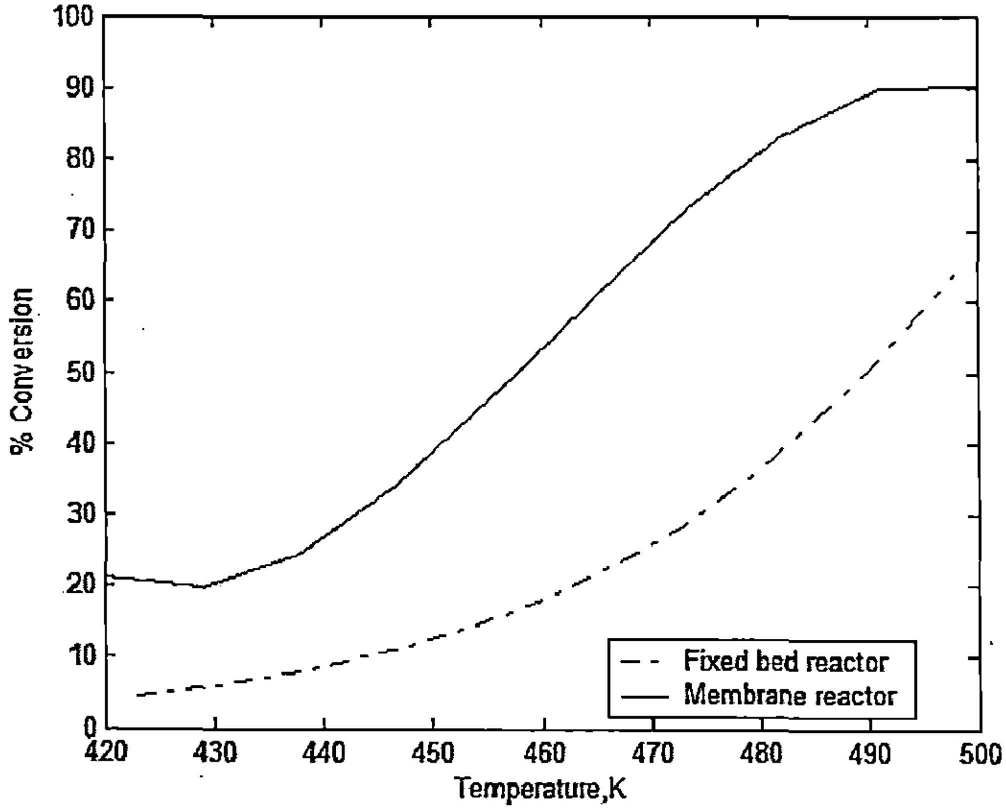

Fig. 15 Comparison of calculated % conversion of cyclohexane for both hybrid membrane reactor and fixed bed reactor.

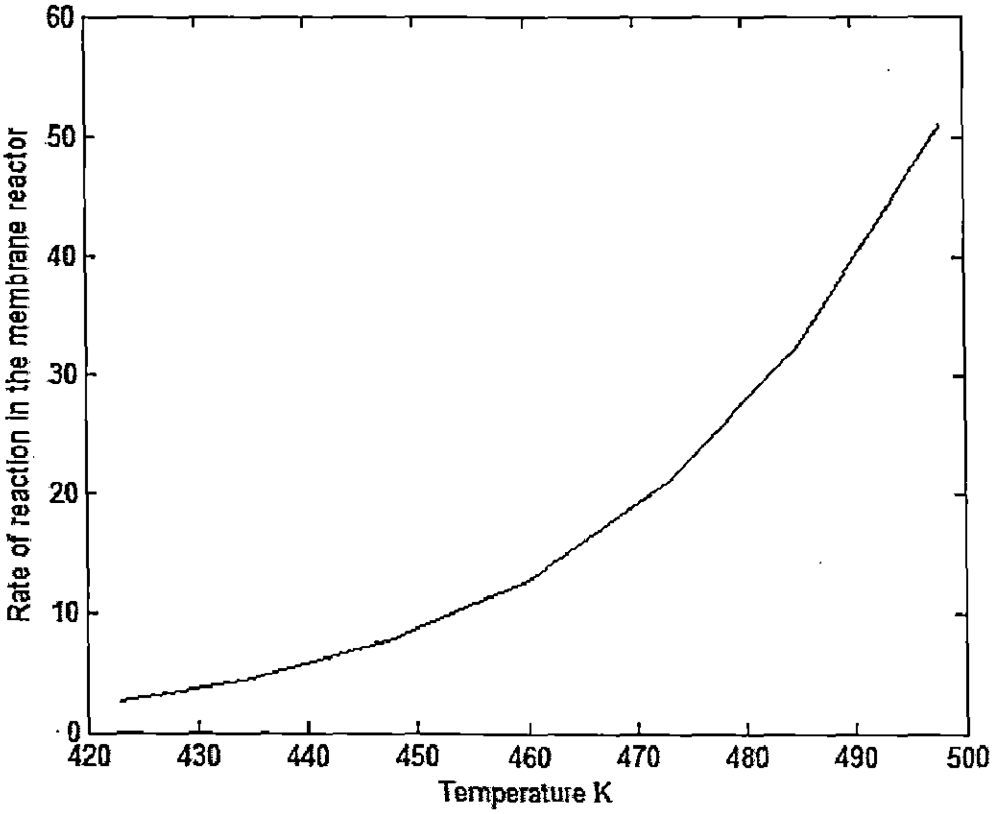

Fig.16 The rate of dehydrogenation reaction as a function of temperature

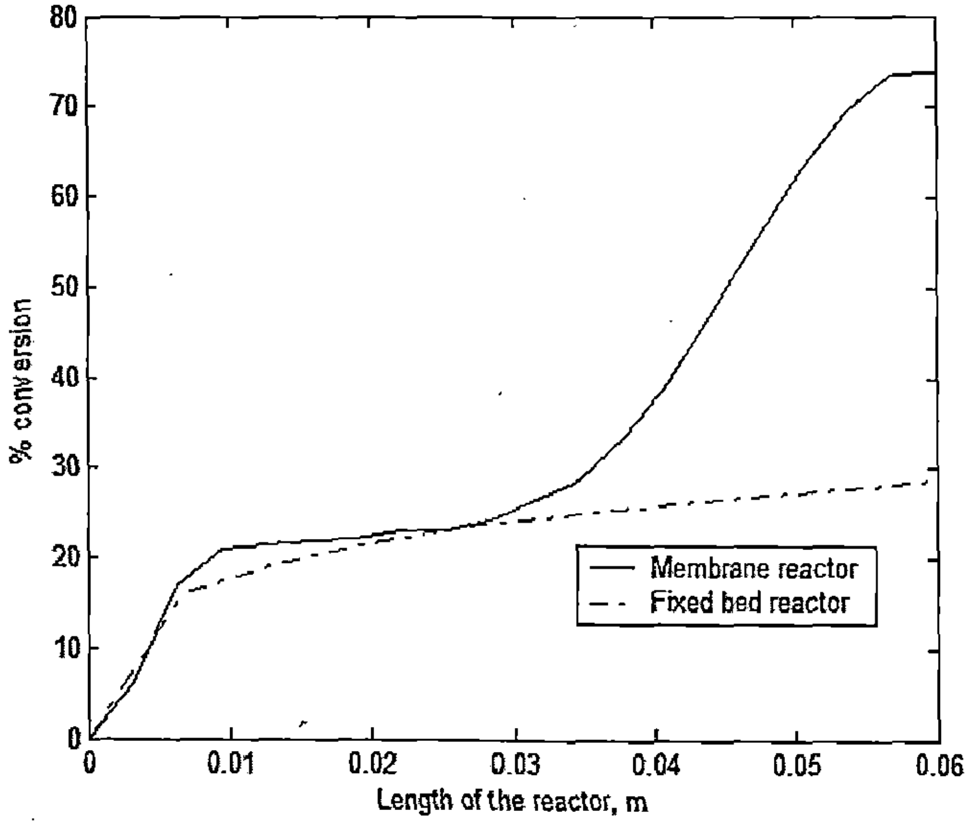

Fig. 17 Comparison of conversion of membrane reactor with fixed bed reactor along the length of the reactor at 473K

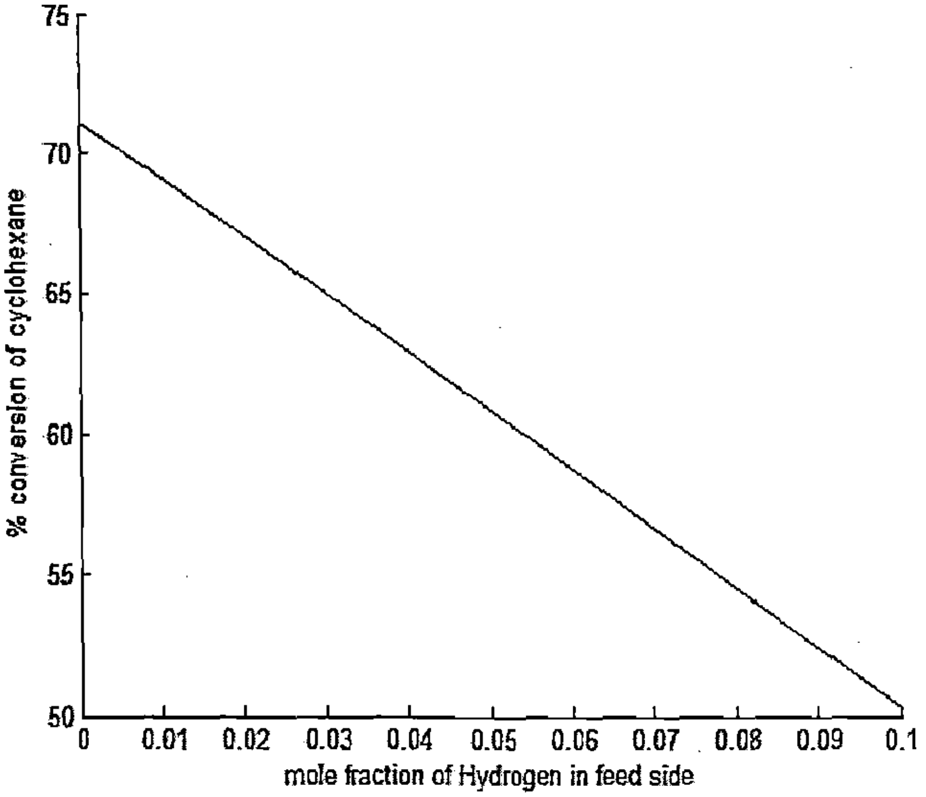

Fig. 18 Effect of hydrogeñ composition in reaction mixture on conversion at 498 K

the co-feeding of hydrogen with cyclohexane to the reaction side is possible. Fig. 18 shows the influence of mole fraction of hydrogen at the inlet of the feed side on the conversion at 473 K. The mole fraction of cyclohexane at the inlet of the feed side is maintained at 0.1. The conversion decreases with increasing mole fraction of hydrogen at the inlet. The co-feeding hydrogen with cyclohexane into the zeolite membrane reactor permits the hydrogen concentration on the reaction side to be maintained, thus inhibiting the extent of coking. But the presence of the hydrogen in the mixture favors the backward reaction and conversion decreases. This is clearly shown in the Fig.18. This may be the most useful feature of the zeolite membrane reactor, compared to a membrane reactor containing a hydrogen selective porous ceramic membrane.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The catalytic dehydrogenation of cyclohexane in an FAU-type zeolite membrane reactor was simulated using a simple mathematical model, which was developed under the assumptions of isothermal operation and a plug flow pattern. Using the same operating conditions and reactor dimensions, fixed bed reactor was also modeled, simulated and compared its performance with hybrid type membrane reactor. The changes in the mole fraction of cyclohexane along the length of the reactor were clearly shown. The effects of temperature and the co-feeding of hydrogen along with cyclohexane on the conversion along the length and at different temperatures were clearly explained. The conversion in the zeolite membrane reactor was much higher than the equilibrium conversion, and good agreement was found between the calculated values and the experimental ones. Based on the simulation results, the zeolite membrane reactor showed a better performance than the conventional fixed bed reactor. Finally, the effect of temperature on conversion was clearly explained and investigated the effect as a function of reactor length. The increase in conversion in the zeolite membrane reactor was mainly dependent on the permeance, diluting medium, and temperature than the separation factor.

5.2 Recommendations

1. Mathematical equations are very sensitive to kinetic parameters so kinetic parameters should be evaluated carefully,
2. The values for various constitutive properties for example. Permeance of the components through membrane has been taken from literature. If these values are evaluated experimentally in the laboratory, it would have given better simulation,
3. The results obtained from the work in the laboratory are sometimes quiet different from those obtained at industrial scale. It is, therefore, recommended

the model developed here is must be tested with the data from the industrials. It will enhance the applicability of the model.

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