MODELING OF MEMBRANE REACTOR FOR METHANOL SYNTHESIS

A DISSERTATION

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

By

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CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented in the dissertation entitled **"MODELLING OF A MEMBRANE REACTOR FOR METHANOL SYNTHESIS"** 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: 15 th 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

Hydrogenation of carbondioxide into methanol is today considered as one of the promising methods to mitigate the greenhouse effect, caused by a substantial rise in CO_2 concentration in the atmosphere. Furthermore the methanol produced could be used as a fuel or basic material for producing various organic chemicals. From a thermodynamic point of view the yield of methanol synthesis is limited by the equilibrium. In order to increase the methanol yield, it is necessary to in situ removal of the condensable products (CH_3OH and H_2O) of the reaction. A membrane reactor satisfies this situation by selectively removing some reaction products from the reaction system.

In the present dissertation work, a steady state model for isothermal conditions has been developed which incorporates 10 differential equations along with 10 boundary conditions for state variables and appropriate constitutive relationships. The model equations are solved by using MATLAB ODE (Ordinary Differential Equations) solvers. Zeolite membranes with different values of the CH_3OH and H_2O permeances are considered in the membrane reactor modeling. The purpose of this study is to investigate the possibility to increase the CO_2 conversion into methanol in a membrane reactor with respect to traditional reactor. A comparison study is performed with the two types of zeolite membranes with respect to traditional reactor for CO_2 conversion, methanol selectivity and methanol yield. In the view of above simulation results it is concluded that the membrane reactor is showing better performance with respect to traditional reactor at any temperature.

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NOMENCLATURE

A_r	cross section area of reactor	m^2
D_i	Diffusion coefficient of component i	m^2/s
D_j	Diffusion coefficient of component j	m^2/s
D_{ref}	Diffusion coefficient of reference component	m^2/s
Da	Damkoehler number	
D	Diameter of reactor	m
F_i	Molar flow rate of species i in reaction side	$kmol\ s^{-1}$
$F_{i,o}$	Molar feed rate of species i	$mol\ s^{-1}$
F_i	Molar flux of component i	$kmol\ m^{-2}s^{-}$
Fi^r	Flow rate of component i in reaction side gas	$mol\ s^{-1}$
Fi^s	Flow rate of component i in shell side gas	$mol\ s^{-1}$
i	component	
j	Reaction	
J_i	Flux of species i through the membrane	$mol/(m^2.s)$
L	Reactor length	m
l	Length dimension	m
M_i	Molecular weight	g/mol
N_i	Molar flux of i in axial direction of tube side	$mol/(m^2.s)$
N'_I	Molar flux in axial direction of shell side	$mol/(m^2.s)$
P_i^F	Partial pressure of component i in the feed	Pa
P_i^P	Partial pressure of component i in the effluent permeate	Pa
P_i^R	Partial pressure of component i in the effluent retentate	Pa
P^F	Total feed pressure	Pa
P^P	Total permeate pressure	Pa
P^R	Total retentate pressure	Pa
P	Pressure in feed side	kPa
P'	Pressure of permeate side	kPa
P_{ei}	Pecklet number	

P_t	Total pressure in tube side	bar
P_s	Total pressure in sweep side	bar
P	Reaction pressure	bar
P_i	Permeability of species i	mol m^{-2} s^{-1} bar^{-1}
P_r	Prandtl number	
p_i	partial pressure in tube side	bar
p'_i	partial pressure in shell side	bar
p_H^r	partial pressure of hydrogen in reaction side	Pa
p_H^s	partial pressure of hydrogen in shell side	Pa
Q^F	Total feed volumetric flow rate	m^3/s
Q^P	Total permeate volumetric flow rate	m^3/s
Q^R	Total retentate volumetric flow rate	m^3/s
Q_i	Molar flux of species i in permeate side	$mol/(m^2.s)$
Q_{H2}	Hydrogen permeate rate	m^3/s
Q_s	Flow rate of sweep gas into permeate side	m^3/s
R, R_G	Ideal gas constant	$Pa.m^3/mol$ K
R_2	Outer radius of membrane tube	m
R_1	Inner radius of membrane tube	m
R_j	Reaction rate of reaction j	kmol/kg.s
R	Radius of catalyst bed	m
r_1	Dimensionless n-butane reaction rate	
r_2	Dimensionless radial coordinate in vycor glass	
r	Radial coordinate of catalyst bed	m
r_i	Reaction rate of species i	mol/m^3s
r_j	Reaction rate of species j	mol/Kg cat s
S	Membrane surface area	m^2
T	Absolute temperature	K
x	Dimensionless membrane spatial coordinate	
X	Reaction conversion	
x_i	Dimensionless species concentration in vycor glass	
y_s	Mole fraction of hydrogen in sweep gas	

y_i	Dimensionless species concentration in catalyst bed	
y_i	Dimensionless mole flow rate of species i	
z	Reactor abscissa	m

Greek letters

α_i	Dimensionless diffusion coefficient of component i	
α_H	Hydrogen permeation rate constant	mol m^{-1} s^{-1} $Pa^{-0.5}$
γ_i	Dimensionless sorption coefficient of component i	
δ	Membrane thickness	m
ν_i	Stoichiometric coefficient of component i	
λ_i	Stoichiometric coefficient	
γ_i	Rate of reaction of species i	Kmol $m^{-3}s^{-1}$
ξ	Dimensionless axial length	
α	$L^2 \varepsilon_1 / R_2$	
ε_1	Porosity of bed	
δ	P_d / A_g thickness	
γ	Constant value 0 or 1	
ν_{ij}	Stoichiometric coefficient of component in reaction j	
β	Permeability of O_2	kmol/m.s.bar
ρ_b	Density of catalyst bed	kg cat/m^3
ΔH_j	Reaction enthalpy of reaction j	kJ/mol

INTRODUCTION

One of the major global environmental problems facing mankind is the global warming of the atmosphere. The ever-increasing consumption of fossil fuels since the industrial revolution - some 250 years ago - has caused a marked increase in the global concentration of carbon dioxide. One possible approach to mitigate the emissions of carbon dioxide and methane to the atmosphere would be to recycle the carbon in a chemical process to form useful products such as methanol or dimethyl ether, for instance. Methanol has the advantage that it is liquid under normal conditions. It can be stored and transported as easily as gasoline, and can be used in conventional combustion engines without requiring any major adjustments. Methanol has twice the energy density of liquid hydrogen. Methanol synthesis can thus be looked upon as a way of converting hydrogen into an energy carder that can be more conveniently stored and transported. Methanol is a large scale product of chemical industry and it is a key material for producing various organic materials such as acetic acid, methylamine and formaldehyde. Methanol can also be used as a clean fuel in future - oriented energy systems such as power plants and methanol - fuelled automobiles.

The reactions that occur during the hydrogenation of CO_2 for the methanol synthesis are the following [Struis (1996)].

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H = -49.4 \text{ KJ/mol} \qquad (1.1)$$

$$CO_2 + H2 \leftrightarrow CO + H_2O \qquad \Delta H = 41.5 \text{ KJ/mol} \qquad (1.2)$$

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H = -90.9 \text{ KJ/mol} \qquad (1.3)$$

From above equations the CO_2 hydrogenation reaction (1.1) is a reversible reaction which is coupled with a water gas shift reaction (1.2), and by that with the synthesis reaction from CO and H_2 (1.3). In the reactions the first reaction is interested in the production of methanol and the reaction (1.2) is in competition with this for the conversion CO_2 into unwanted CO. The (1.1) and (1.3) reactions are exothermic reactions which are favored by the high pressures and the (1.2) reaction which is endothermic reaction favored by the high temperatures. The industrial operating conditions for the production of methanol are temperatures in 200-260 ^{0}C and at pressures of the order of 50-100 bar. The catalyst used for the synthesis is a mixture Cu-Zn oxides-based precipitated catalyst. The activity of the catalyst for the hydrogenation CO_2 was measured on several Cu based catalyst mixtures. This catalyst also showed the lowest reaction rate for the by-product CO, which is undesired because it comprises the overall efficiency of the process.

The synthesis of methanol overcomes the equilibrium restrictions on product yield by applying high pressures and by the recycling the unconverted reactants. So by the continuous removal of the products can increase the yield of methanol of the synthesis and reduce the recycling process and the operating pressure. Membrane reactors offer the facility of removing at least one of the products selectively from the reaction system, so equilibrium limited reactions can achieve higher conversions.

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.

Catalytic membranes and membrane reactors are the objectives of significant research efforts at academic and industrial levels. The development of catalytic membrane reactors (CMR) for high temperature applications became realistic only in the last few years with the development of high temperature resistant membranes. Due to the generally severe conditions of heterogeneous catalysis, most CMR 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.

A membrane reactor is a device that combines a membrane-based separation process with a chemical reaction step in one unit. The membranes as separating agent have been known for more than 100 years. But large scale applications have only appeared in the past 50 years as the replacement of the most common separation operation with membrane separation has the potential to save large amount of energy. Membranes are widely used with chemical and biochemical reactors. Sometimes these membranes as separating agent, are attached as separate unit with reactor, but usually are combined with the reactor, thereby known as membrane reactor.

Most chemical reactions are equilibrium reactions and employs a catalyst to enhance the kinetics. The compounds involved in the reactions are either liquid or gaseous. In the latter case the temperature is often higher. Furthermore, the conversion is carried out at a specific temperature at which is often higher than room temperature. The catalyst must be combined with the membrane system and various arrangements are possible. Figure (1.1) summarizes some membrane / catalyst combinations for tubular membranes.

The most simple and straightforward system is where the catalyst is located inside the bore of the tube figure 1.1(a). The advantage of this system is its simplicity in preparation and operation and in case of catalyst poisoning a new catalyst can easily be introduced. In the other two arrangements the catalyst is immobilized onto the membrane, either in the toplayer figure 1.1(b) or in the membrane wall figure 1.1(c). In the either case one of the products, not necessarily the required product, should permeate across the membrane which implies the necessity of permselective membranes under these specific conditions

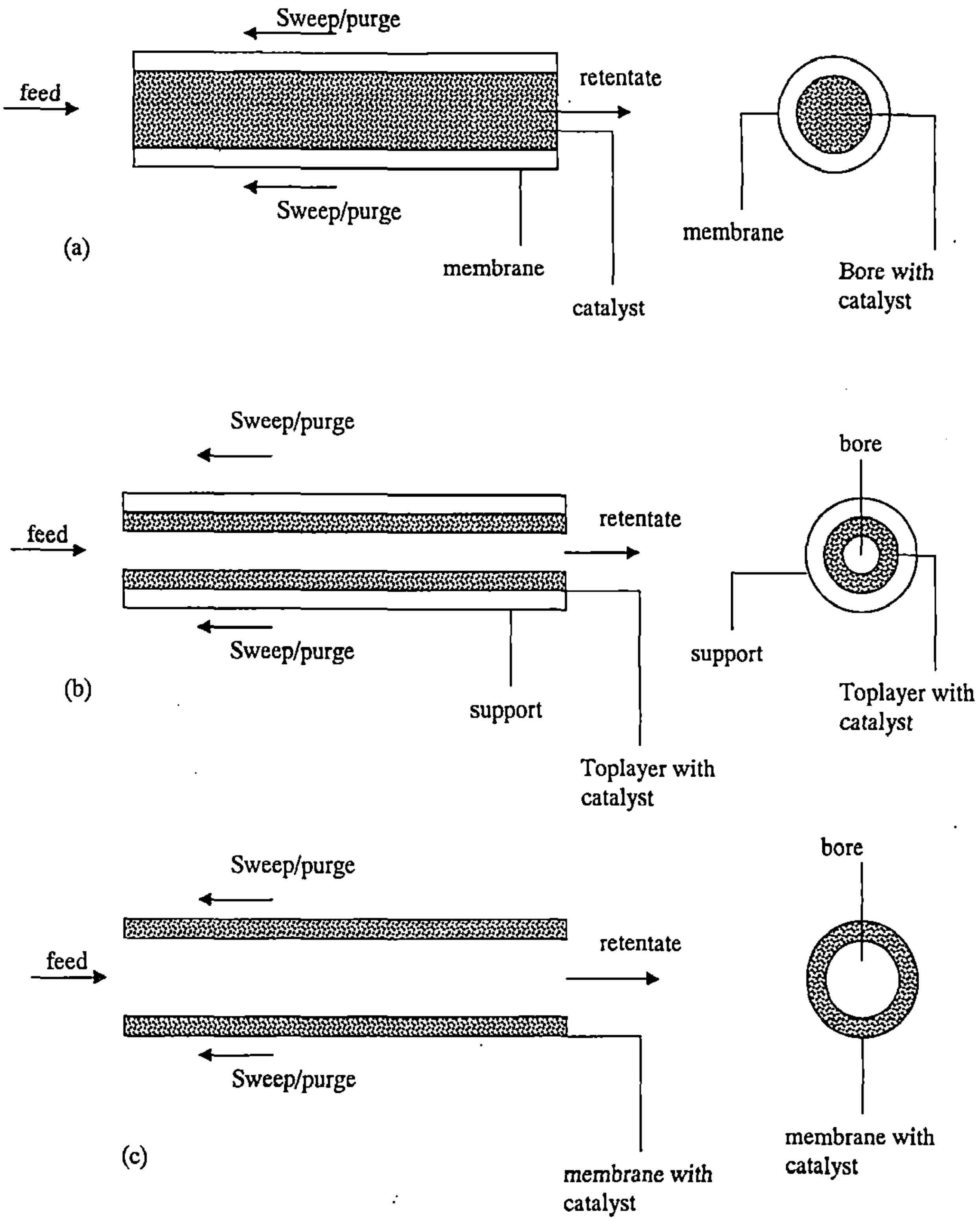

Figure 1.1 Schematic drawing of various membrane reactor concepts for a tubular configuration: (a) bore of the tube filled with catalyst, (b) top layer with catalyst, (c) membrane wall with catalyst

In a chemical reactor, the mixture consists of formed products after reaction and unreacted reactants. These components are partially separated by means of a semi permeable barrier called membrane. The components which move faster then other, pass through membrane. A general membrane separation process is shown in figure 1.2 (a) where mixture in a reactor is separated into two parts viz. permeate and retentate. Permeate is that part of mixture which passes through the membrane where as retentate is the part that doesn't pass through the membrane.

Various possibilities exist for such a combination. The most widely used concept is the selective removal of products from the reaction zone (figure. 1.2a), which is applied first of all to equilibrium limited reactions to increase the yield beyond the corresponding equilibrium value, or, generally speaking, to repress undesired secondary reactions of the products. In a different approach, only particular reactants are supplied selectively via a membrane to the reaction zone (figure. 1.2b), e.g. to establish an optimum concentration profile along the reactor. A third concept refers to a membrane that creates a well-defined reaction interface (or region) between two reactant streams (figure. 1.2c).The mass transport across a membrane can be permselective if only some components of a mixed stream permeate through the membrane (figure.1.2a and 1.2b) or non-permselective if all species permeate at comparable rates (figure. 1.2c).

Permselective transport is found first of all in dense membranes. It is governed by a solution-diffusion mechanism. Non-permselective transport normally occurs in macro- and mesoporous membranes. In the latter Knudsen diffusion is often the dominating transport mechanism. Microporous membranes represent a bit of both: permselective and non-permselective, the molecular transport is possible depending on the size of the permeating molecules in view of the pore size of the membrane (bottlenecks) as well as on the chemical nature of the permeating molecules and the membrane material. When the membrane reactor is used for carrying out a catalyzed reaction the questions arises whether the membrane itself has a catalytic function or not. If the membrane does not act as a catalyst we refer this as inert membrane catalytic reactor (IMCR figure 1.2d) ,if membrane acts as catalyst, we have catalytic membrane reactor (CMR,figure.1.2e & 1.2f). The CMR-case may be further subdivided into two categories, i.e. when the membrane acts as the sole catalyst (figure. 1.2e), and when a conventional catalyst is present in addition to the membrane (figure. 1.2f). [Dittmeyer *et. al.* (2001)].

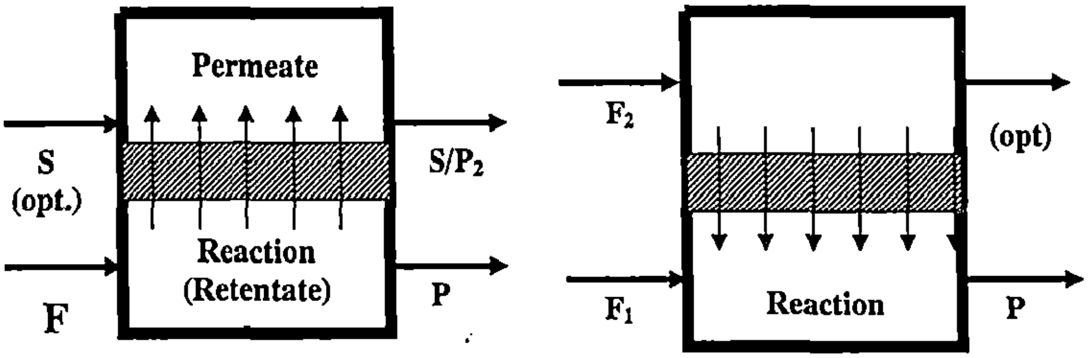

Figure 1.2a Removal of products **Figure 1.2b** Supply of reactants

Inert Membrane Catalytic Reactor (IMCR) Or Catalytic Membrane Reactor (CMR) (Membrane is Permselective)

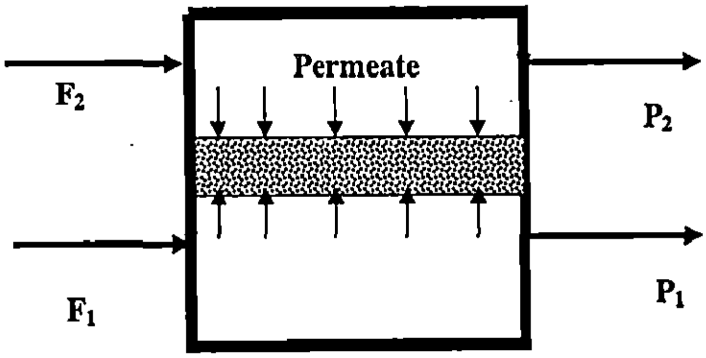

Figure 1.2c Reaction Interface

Catalytic Non-permselective Membrane Reactor

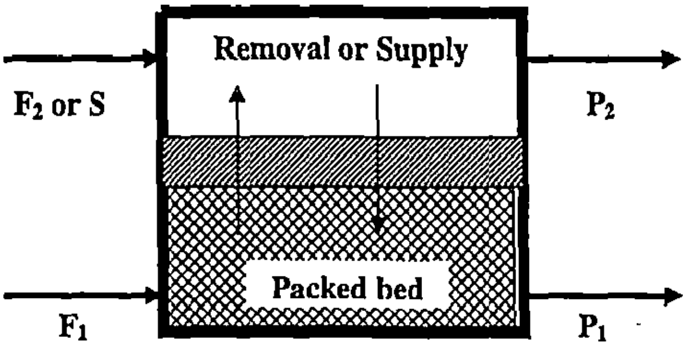

Figure 1.2d Packed Bed Catalytic Reactor (Inert Membrane)

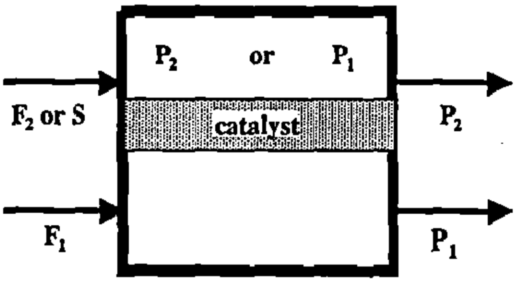

Figure 1.2e Catalytic Membrane Reactor

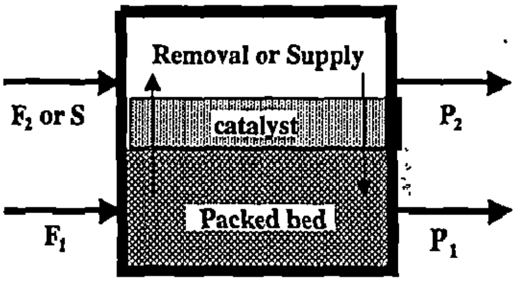

Figure 1.2f Packed Bed Catalytic Membrane Reactor

Catalytic membrane reactors can have the following advantages over conventional packed-bed reactors:

- An integration of reaction and separation into a single process reduces the separation costs and recycle requirements.
- An enhancement of thermodynamically limited or product-inhibited reactions results in higher conversions per pass.
- A controlled contact between incompatible reactants is possible to provide.
- The undesired side reactions may be eliminated. [Kulprathipanja (2001)]

1.1 USES OF MEMBRANE REACTOR

The uses of membrane reactor with examples are mentioned in this section as follows [Kulprathipanja (2001)]:

(1) Dehydrogenation reactions: -

- Catalytic dehydrogenation of light alkanes, Dehydrogenation of other hydrocarbons such as ethylbenzene, Etahnol dehydrogenation.

(2) Hydrogenation reactions: -

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

(3) Oxidation reactions: -

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

(4) Pervaporation membrane reactor: -

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

(5) Membrane based reactive separations for biological systems: -

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

(6) Environmental applications of membrane bioreactor: -

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

(7) Emerging applications: -

- Hydrogen production for integrated gasification combined cycle (IGCC), CO_2 separation in IGCC, Water gas shift reaction in membrane reactor, Recover tritium from tritiated water from breeder-blanket fluids in fusion reactor systems

The potential for membrane separative reactors or other means to improve the environmental and economic performance of some of the top 50 commodity chemicals in the U.S. chemical industry formed through partial oxidation or by dehydrogenation reactions was recently studied. The maximum energy saving was estimated to be 0.25 quadrillion BTU if every commodity chemical formed through either selective oxidation or dehydrogenation achieved maximum efficiency.

Maximum annual savings in feedstocks were estimated to be $ 1.4 billion. [Allen and Shonnard (2002)]

Reactions in catalytic membrane reactors			
Dehydrogenation	ethane	→	ethylene
	propane	→	propene
	cyclohexane	→	benzene
	cyclohexane	→	cyclohexene
	ethylbenzene	→	styrene
	butene	→	butadiene
	isopropylalcohol	→	acetone
hydrogenation	carbon dioxide	→	methanol
	propene	→	propane
	butane	→	butane
	ethylene	→	ethane
oxidation	carbon monoxide	→	carbon dioxide
	ethylene	→	ethylene oxide
	propylene	→	propylene oxide

1.2 ADVANTAGES AND DISADVANTAGES [Kulprathipanja (2001)]

1.2.1 Advantages

- Enhanced reaction rates.
- Increased reaction conversion.
- Enhanced reaction selectivity.
- Reduced reaction severity.
- Increased catalyst life.
- Simplified separations.
- Improved product quality.
- Heat integration benefits.
- Reduced equipment fouling/coking.
- Inherently safer unit.
- Reduced capital investment.
- Novel process configuration.
- Novel equipment designs.

1.2.2 Disadvantages

- Relatively new technology.
- Limited applications window.
- Extensive experimental development is required.
- Complex modeling requirement.
- Extensive design efforts.
- Increased operational complexity.
- Significant development costs.
- Increased scale-up risks.

1.3 MEMBRANES

Although it is difficulty to give an exact definition of a membrane, a general definition could be: a selective barrier between two phases, the term selective being inherent to a membrane or a membrane process. A membrane can be thick or thin, its structure can be homogeneous or heterogeneous, transport can be active or passive, passive transport can be driven by a pressure, concentration or a temperature difference. Michaels first brought up the idea of simultaneous reaction and separation with a membrane in 1968. It was thought that higher conversions could be obtained by using a membrane, as it would allow the selective permeation of one of the reaction products, leading to a shift in the product distribution of equilibrium reactions. At that time, polymeric membranes were developing quickly after the discovery of asymmetric membranes (membrane tubes with inner and outer surfaces having different pore sizes). However, polymers can withstand only mild chemical and thermal conditions. Since many biochemical reactions are operated at low temperatures and need only mild chemical conditions, most of the research work on catalytic membrane reactors was done with biochemical reactions. Lately, however, improved methods of manufacturing ceramic and metal membranes have been found. These methods can give thin (thickness of about 5 to 10 μm), defect-free, and permselective membranes, which are also chemically and thermally more stable as compared to the polymeric membranes. Therefore, the research on catalytic membrane reactors is now being done even for those chemical reactions, which require high temperatures and pressures. This has led to an increasing interest in the development of such membranes.

Two types of membranes, porous and nonporous (dense), have been used in catalytic membrane reactors. The nonporous metal membranes were the first ones to be used in catalytic membrane reactors. These membranes were made of Pd alloys, which adsorb hydrogen atoms and then transport them by diffusion, thus allowing selective permeation of hydrogen. Almost complete conversion of the reactants is possible with these membranes because they allow only one component to permeate. Nonporous oxide membranes have also been used. PbO membranes have been used for selectively permeating oxygen [Dittmeyer *et.al.* (2001)].

Porous membranes are glasses with small pores, composite ceramics, and zeolites. The new developments in ceramic membranes have given rise to many possibilities for catalytic membrane reactors. These membranes can be used at high temperatures. The separation factors of porous membranes are however much lower than those of Pd alloys, unless the pores are of molecular dimensions (for example zeolite membranes).

1.3.1 Nonporous Metallic Membranes

Many membrane separations and some catalytic membrane reactors to date have used Pd alloy membranes, which allow completely selective permeation of H_2. Details on several plants operating in the former Soviet Union capable of separating upto 2000 Nm^3h^{-1} of hydrogen, at a pressure of 3 MPa, from ammonia purge gas fed at 20MPa have been given. Some mobile plants for hydrogen generation (upto 25Nm^3h^{-1}) from the reaction between methanol and water vapors in packed-bed Pd-membrane reactors have been described. These membranes are Pd alloys since pure Pd undergoes a structural change from the α phase to the β phase as the temperature cycles, so that pure Pd becomes brittle. The only other metal membrane used until now in catalytic membrane reactors is silver, through which oxygen selectively permeates. Controlled addition of oxygen through a Ag membrane has been used to carry out oxidation of CH_3OH and C_2H_5OH and their mixtures to aldehydes. The yield of acetaldehyde from C_2H_5OH was 83% when oxygen diffused through the membrane, whereas it was only 56% when oxygen was premixed with C_2H_5OH. Silver membranes have been used to a much smaller extent than Pd alloy membranes [Mears (1976)].

Little progress has been made in large-scale catalytic membrane reactors with metal membranes because of cost, fabrication durability, and catalyst poisoning. Carbon and sulfur compounds can poison the membranes. Also, low permeabilities and metal sintering have posed big obstructions for the use of metal membranes.

1.3.2 Nonporous Oxide Membranes

Until now, nonporous oxide membranes have been used only for separating oxygen and hydrogen from gas-mixture streams. Therefore, their use is very limited.

Dense zirconia membranes, stabilized with oxides of magnesium, scandium or calcium, have a high permselectivity to oxygen and have been used in catalytic membrane reactors. Calcia-stabilized dense zirconia membranes have been used in the thermal decomposition of water to produce hydrogen, and in the steam reforming and shift reactions to produce hydrogen. A method for depositing a thin layer of silica within a porous Vycor glass tube by reacting SiH_4 on the tube side of the membrane with O_2 on the shell side has been developed. These membranes are highly selective to H_2 and are stable at 725 K.

1.3.3 Porous Ceramic Membranes

Ceramic membranes made of materials like alumina, ceria, titania, and zirconia are being manufactured lately. The main advantages of these membranes over polymeric membranes are greater fluxes and stability at high temperatures. For example, alumina membranes can be used at temperatures up to 1075 K without degradation of the pore structure. These membranes have porosities as high as 59 % and controlled, stable, and narrow pore size distributions. They are mechanically stable and can withstand pressure drops of 1.5 MPa. Further, they are resistant to corrosive chemicals. Catalytic materials that are deposited by impregnation can also be dispersed on ceramics and thus they can have high catalyst surface/volume ratios. The same materials used for ceramic membranes are also used as catalyst supports.

Ceramic membranes are often prepared by slip casting. Most of these membranes are made with layered or graded structure wherein a thin (few μm) permselective layer is deposited onto a thicker (several mm) macroporous layer. For example, a thin α-alumina layer with 4-nm diameter pores is deposited onto an α-alumina layer with 120 nm pores. The α-alumina layer acts as the separating membrane and the α-alumina serves as a high-temperature support. Such layered α-alumina membranes have been used in several separation applications and for research in membrane reactors. For example, in the dehydrogenation of ethylbenzene to styrene, the conversion was increased by 20-23% over the equilibrium conversion by using a packed-bed membrane reactor with a α-alumina membrane. Ceramic membranes have been modified also with MgO and SiO_2 to obtain better separation factors [Liu *et.al.* (1994)], [Coronas and Santamaria (1999)].

1.3.4 Porous Glass Membranes

Uniform, microporous Vycor glass membranes can be prepared with pores as small as 4 nm. These membranes are made by acid leaching one of the phases that form in Vycor glass. These glass membranes may be limited in their applications, however, because they are brittle. Moreover, when microporous glass is heated above 575 K for long periods, or to higher temperatures for shorter periods, it loses its microstructure. The development of composite ceramic membranes with pore diameters smaller than 4 nm may limit the use of glass membranes because of the various other advantages of ceramic membranes.

1.3.5 Zeolite Membranes

Although ceramic membranes have high fluxes and moderate separation factors, they are not used in high-purity separations which require very high selectivities to a single component in fluid streams. In such cases, zeolite membranes might be used because they can separate components in a fluid stream based on molecular sizes, yielding very high selectivities. Only a few cases of zeolite membranes have been reported. A patent by Suzuki reports on the preparation of many zeolite membranes. These are ultrathin layers (1 nm to 10 nm thick) prepared by forming a thin gel film by gentle sedimentation from a mixture. According to the patent, X, Y, ZSM-5, and silicalite-type zeolite membranes can be prepared in this manner. However, many zeolites have acidic properties which may not be useful for reaction systems. Although there are some articles on preparing zeolite membranes, these membranes are not available commercially [Suzuki (1987)].

1.4 PROPERTIES OF AN IDEAL MEMBRANE

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

1.5 MECHANISMS OF SEPARATION

The extent of separation of the various components in a fluid stream by a membrane depends on the transport mechanism under those operating conditions. The transport mechanism affects the fluxes of the components, which in turn affect the separating ability of the membrane. In nonporous metal membranes, only one separation mechanism called 'atomic diffusion' is present. This mechanism is discussed below. The use of these membranes to date has only been for the permeation of H_2 and O_2, which are required in many industrial reactions. However, in porous membranes, there exist four different mechanisms of separation, and these membranes can be used for a variety of compounds. Those four mechanisms are: Knudsen diffusion, surface diffusion, capillary condensation, and molecular sieving. These are discussed below.

1.5.1 Separation in Nonporous Membranes

Palladium alloys are the nonporous membranes used most often in catalytic membrane reactors. Hydrogen molecules adsorb and dissociate into atoms on the metal surface. These atoms then diffuse through the metal membrane because H atoms are soluble in Pd. At the other side, H atoms recombine and desorbs from the surface. Although other gases can dissociate on Pd, none have a significant solubility in Pd. Therefore, essentially infinite separation factors can be obtained when separating H_2 from other gases. The flux of hydrogen through the membrane is found to be proportional to the square root of the partial pressure of hydrogen.

Oxygen permeation through Ag membranes is similar to H_2 permeation through Pd alloy membranes. Apparently, oxygen atoms diffuse and the permeability into a vacuum is proportional to the square root of the partial pressure of oxygen. The permeability of oxygen is affected by the presence of other gases which adsorb on the Ag surface. The permeability of oxygen in Ag is much lower than that of hydrogen in Pd. Nonporous silica glass is also highly selective to H_2 and large separation factors can be obtained.

1.5.2 Separation in Porous Membranes

There are four mechanisms of separation in porous membranes, which are explained in the following subsections. More than one mechanism can be present at a time. The Knudsen mechanism gives relatively low separation factors compared to surface diffusion and capillary condensation. Molecular sieving can yield high separation factors. The separation factors for these mechanisms depend strongly on the pore size distribution, temperature, pressure, and the interactions between the gases being separated and the membrane surfaces. These mechanisms are described below.

1.5.2.1 Knudsen Diffusion

Under viscous flow (Poiseuille flow), the mean free path of fluid molecules is small in comparison with the pore diameter, and molecules undergo many more collisions with each other than with the walls of the membrane. The molecules in a mixture do not behave independently in viscous flow and no separation is possible. Therefore, viscous flow is not desirable in catalytic membrane reactors. As the pressure is lowered, the mean free path of the molecules becomes longer than the pore diameter. As a result, the molecules undergo more collisions with the pore walls than with each other, and the molecules flow through the pores independently of each other. This is Knudsen diffusion. In the Knudsen diffusion regime, an equimolar mixture of feed gas will have a separation factor equal to the square root of the ratio of the molecular weights of the gases when the permeate side is a vacuum. The separation factor will be lower if a pressure is maintained in the permeate side instead of a vacuum. The small pore sizes in ceramic membranes allow separation due to Knudsen diffusion. In composite membranes, the thin permselective layer can be in the Knudsen diffusion regime and can give all the separation, while the support layers are in the viscous regime. Separation in the Knudsen regime has the limitation that only the lighter component can be preferentially removed. When the molecular weights of the components do not differ by a significant amount, an economical separation by Knudsen diffusion is not possible. Most of the porous membranes used to date for gas-phase, catalytic membrane reactors have been operated at sufficiently low pressures that Knudsen diffusion predominates. Viscous flow can be present in porous membranes if the pressure or the pressure-drop is too high. But as mentioned before, viscous flow does not yield a separation.

1.5.2.2 Surface Diffusion

During diffusion through a membrane, a gas can chemisorb or physisorb on the pore walls and migrate along the surface. This is surface diffusion. It can occur in parallel with Knudsen diffusion. Surface diffusion increases the permeability of the more strongly adsorbed components in a diffusing mixture, while simultaneously reducing the permeability of the other diffusing components by decreasing the effective pore diameter. Therefore, this diffusion is very important for membranes with small pores. When surface diffusion occurs, the effect of selective adsorption of a component from a gas-mixture on the membrane surface must be taken into account. This can be done by assuming that the total flux of diffusion is the total of the fluxes due to surface diffusion by selective adsorption, and Knudsen diffusion. As the temperature increases, the gaseous species desorbs from the surface and Knudsen diffusion dominates at higher temperatures. For example, surface diffusion of cyclohexane during its dehydrogenation was found to lower the efficiency of separation of the product H_2. CO_2 was found to exhibit surface diffusion on a ceramic membrane.

1.5.2.3 Capillary Condensation

When one of the components in a gas mixture is a condensable vapor and if the pores of the membrane are small enough, then the condensate can block gas-phase diffusion through the pores. This condensate will evaporate on the low-partial-pressure side of the membrane.

The Kelvin equation represents thermodynamic equilibrium between gas and condensate in pores:

$$\frac{P}{P_s} = \exp\left(\frac{-2\gamma \cos\theta}{r_p \rho RT}\right)$$

where γ is the surface tension of the condensed fluid in the pore (J/m^2), P is vapor pressure in the gas phase (atm), P_s is the condensation vapor pressure in the bulk phase at the experimental temperature (atm), r_p is mean pore radius (m), θ is the contact angle between the condensed fluid and the pore wall, ρ is molar density of the condensed liquid (mol/m^3), T is temperature of fluid in the pore (K), and R is the universal gas constant (0.082 lit.atm/mol.K).

The Kelvin equation predicts that condensation can occur in small pores, although the partial pressure of the condensable vapor component in the gas mixture stream is below the normal equilibrium vapor pressure of that component. Because of capillary condensation, the pores can completely fill with the condensed liquid of that vapor component. For a narrow distribution of pore sizes, all the pores will be filled and the fluxes of the other components through the membrane will be quite small and limited by their solubility in the condensable component. Thus, extremely high separation factors are possible. As an example, separation factors as high as 460 were reported for H_2O/air separation, and 1000 for SO_2/H_2 separation, due to the condensation of H_2O and SO_2 respectively.

1.5.2.4 Molecular Sieve Separation

Most of the ceramic membranes and glass membranes used for separation have pores sizes, which are not small enough to separate the gas mixtures solely, based on their molecular sizes. Therefore, the separation factors with these membranes are low. However, some membranes have pores, which are of the size of the gas molecules. In these membranes, the smallest molecule has the greatest ability to diffuse through the pores whereas the other gas molecules are almost totally excluded. This yields very high separation factors. This mechanism is called molecular sieve separation. It has also been called shape selective or configurational diffusion. Zeolite membranes are good examples exhibiting this mechanism. Suzuki has presented examples of the selective separation that can be obtained with shape-selective zeolite membranes. He claims that zeolite membranes with pore sizes from 0.3 to 1.2 nm could be prepared so larger molecules could also diffuse through these materials [Mears (1976)], [(Suzuki (1987)].

1.6 OPERATING CHARACTERISTICS OF MEMBRANE REACTORS

Catalytic membrane reactors can be operated in various ways, depending on the contact of reactants (whether on one side or on both sides of the membrane), the type of flow of reactant and sweep gases (whether cocurrent or countercurrent), reactions on one side or both sides of the membrane, and the pressure drop across the membrane (whether equal or unequal pressures are present across the membrane).

1.6.1 Contact of Reactants

There are two ways of feeding reactants to the catalytic membrane reactor. One way is to feed both the reactants through the tube and no reactant on the shell side. The other way is to feed at least one reactant on the shell side and the others through the tube. These are discussed below.

1.6.1.1 Reactants on One Side

In the normal configuration of a membrane reactor, the reactants flow through the tube and only the sweep gases (usually inert) flow on the shell side. In such reactors, the purpose of the sweep gas is to sweep away the permeating products and to decrease their concentration on the shell side. This results in an increase in the permeation rates of the products. Although the conversion may increase due to the continuous removal of the products, there is the problem of mixing of the products with the sweep gas, which is usually an inert. This might create another problem of separating the products from the inert gas after it comes out from the membrane reactor. In such cases, the membrane reactor usually becomes uneconomical, unless the production rate or the conversion is high enough to counter the extra cost of separation equipment.

1.6.1.2 Reactants on Both Sides

Recently some catalytic-membrane reactors have been run with one reactant fed to the tube side of the membrane and a second reactant fed to the shell side. The studies show the advantages of this mode of operation. In traditional packed-bed reactors, the reactant concentration decreases monotonically from the entrance toward the exit of the reactor, provided no intermediate feed is supplied. Especially at the inlet, the selectivity is comparatively low for reactions such as partial hydrogenations or oxidations, which require low reactant concentrations. When a reactant is supplied through the membrane, the concentration of that reactant inside the reactor can be kept at a sufficiently low and constant level. This limits side reactions such as deeper hydrogenations or oxidations, and avoids the need to separate unconverted reactants. By simply keeping separated the bulk of two reactants, the undesired side reactions are avoided. Moreover, the separation of reactants allows better control of the reaction by varying the flow rates, concentrations, and pressures of the two reactants independently.

1.6.2 Type of Flow

There are two ways of flowing gases through a shell-and-tube reactor. When the direction of gases flowing on both the sides is the same, the flow is cocurrent. On the other hand, if the direction of the gases on both sides is opposite, the flow is countercurrent. Since the concentration difference across the membrane is the highest in a countercurrent flow, the usual preference for flow in membrane separation systems is countercurrent. However, the condition is not the same with reactive systems. In catalytic membrane reactors, the concentrations of reactants and products on each side of the membrane affect both the reaction and permeation rates. In such reactors, the purpose is not only to separate the required product but also to avoid permeation of reactants through the membrane, to maintain the required concentration of reactants for reaction inside the tube. Therefore, countercurrent flow may not be advantageous. When the reactants are fed on the tube-side of the reactor, two means are available to reduce the reactant permeation to the shell-side. The first method is back diffusion of the reactant from the shell-side to the tube-side. For this approach two conditions are necessary. First, the reactor has to be operated cocurrently. In this mode, the reactant concentration on the shell-side can exceed the feed side as one moves down the length of the reactor. This driving force makes reactants permeate from the shell-side into the tube. Secondly, the total pressure on each side of the membrane should be the same, so that the driving force for reactant permeation is reduced. The second approach is recycling of the unreacted feed. Recycling can work if the permeances of reactants lie in between the permeances of the products. In this manner, the unreacted feed is enriched in the reactants relative to one of the products. However, product accumulation in the recycled stream can limit the extent of conversion.

1.6.3 Simultaneous Reactions

In a catalytic membrane reactor, since the products permeate to the shell side of the membrane, it may prove advantageous if the products can be used for some other reaction on the shell side. In such a case, the permeating product gets continuously used in the reaction occurring on the shell side. This leads to increased permeation of the product, ultimately resulting in increased conversion in the tube. This approach has many advantages other than the one mentioned above. The hydrogen formed as product in one reaction is used as a reactant in the other. The reactants from the two reactions are not mixed. The heat of reaction from the exothermic hydrogenation reaction is transferred across the membrane to supply energy for the endothermic reaction [Dixon (2003)].

1.6.4 Pressure Drop Across the Membrane

Pressure drop across a membrane is the driving force for permeation of gases. In a catalytic membrane reactor, the permeating gases include the reactants and the products. The decision of maintaining a pressure drop across the membrane depends on the selectivity of the reactants over the products through the membrane. If the permselectivity of the membrane to the products is high, then maintaining a low pressure on the shell side will be advantageous. The low pressure increases the permeability of the products, leading to higher conversions. However, if the permselectivity of the products over the reactants is not high, then it is better to keep equal pressures across the membrane. This will reduce the loss of reactants and allow a modest amount of permeation of the products through the membrane. In most of the reactions carried out until now, the products have had high selectivity over the reactants, the majority of these reactions being dehydrogenations with hydrogen as the product. Therefore, in these cases, the reactor performance could be improved by keeping a lower pressure on the shell side as compared with that on the tube side [Hsieh (1989)].

1.7 DESCRIPTION OF THE PROBLEM

The hydrogenation of carbon dioxide to methanol is very important process industrially. As the reaction is reversible the conversion is limited because of thermodynamic equilibrium. Due to continuous removal of product the yield can be improved by carrying out reaction inside the membrane reactor. The reaction is carried out in a tube side packed with catalyst and in isothermal condition. Mathematical model is required which can predict the performance of membrane reactor and also can predict the conversion and yields of reactants and products respectively.

1.8 OBJECTIVES OF THESIS

Based on the reviewed literature following objectives have been planned

(i) To develop the mathematical model of a membrane reactor and to study the effect of operating and design parameters on its performance.

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

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

1.9 SYSTEM

Membrane reactor is a device in which the reaction and separation through membrane are carried out simultaneously in one unit. These kind of arrangement is particular important for reactions which are equilibrium limited. Out of many such reactions hydrogenation is very important reaction industrially. One such industrially important process is methanol synthesis from carbon dioxide hydrogenation. The system proposed to study is hydrogenation of carbon dioxide for methanol synthesis with its side reactions.

CHAPTER II

LITERATURE REVIEW

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

This chapter also presents the models developed by different research workers for the analysis of the performance of the extraction equipment. The present chapter provides a brief discussion of the literature on only those aspects which are relevant to the objectives of the dissertation work mentioned in section 1.8 of Chapter I.

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

2.1 DEVELOPMENT OF MEMBRANE REACTOR

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

Armor J.N. (1995) has studied the area of membrane catalysis, where metal membrane in the reactor acts as a catalyst as well as separator. Palladium and palladium alloy membrane reactors are compared and discussed with regard to technology limitations and needs. Because of the limitation of palladium metal compositions, there is an emerging effort in less costly but high hydrogen permeable metal membranes such as those composed of tantalum or niobium. An extended discussion on critical issues remaining for the successful commercial application of this technology is also given at the end.

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

Coronas J. and J. Santamaria (1999) have reviewed the developments and outstanding opportunities in the field of catalytic reactors based on porous ceramic membranes, both inert and catalytic. Rather than attempting a thorough review of the relevant literature, this work deals with some general concepts and then concentrates on a few selected examples that illustrate the application of membrane reactors. Authors at the end concluded that an important effort was still needed to develop methods of preparation and characterization, novel membrane materials and reactor configurations. Industrial applications are not foreseeable in the immediate future because of formidable practical problems involved in moving from laboratory to industrial scale in such a new technology.

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

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

Dittmeyer R. *et. al.* (2001) have discussed two different membrane reactor concepts which both rely on supported palladium, on one hand as a permselective 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/X – clusters can be employed as so-called catalytic diffusers for liquids-phase hydrogenation. The principles of both concepts are introduced, recently obtained experimental data are evaluated in connection with literature results, and the perspectives of further developments are highlighted.

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

Dixon A.G. (2003) 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.

2.2 EXPERIMENTAL STUDIES ON MEMBRANE REACTOR

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

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

Rezac M.E. *et. al.* (1995) have reported that increases of up to 1.5 times the traditional equilibrium limit for a membrane assisted reactor system with the dehydrogenation of n-butane as a model system. The use of thermally stable polymer-ceramic composite membranes to remove product hydrogen from the dehydrogenation reaction system has been evaluated as a function of the reaction temperature from 480^0C -540^0C. Under these conditions, the selectivity of the catalyst for the production of butanes was greater then 90% and was not markedly affected by the presence of membrane.

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

Struis R. P. W. J *et. al.* (1996) Methanol synthesis from CO_2 and H_2 is a promising chemical energy storage reaction for hydrogen. The methanol yield of the synthesis is limited by the thermodynamic equilibrium at the temperatures required by state-of-the-art catalysts. Substantial conversion improvements would be achieved by selective product separation from the catalyst bed of a synthesis reactor. A perfluorinated cation exchange material is evaluated for use as a vapour permeation membrane at temperatures up to 200°C. The permselectivities for methanol and water with respect to hydrogen depend on the counter ion in the polymer, and drop as a function of temperature. With respect to long term stability and performance, lithium is best suited as a counter ion, with permselectivities of 32 for water, and 5.6 for methanol, respectively. Permeability and permselectivity are found to increase with increasing partial pressures of both methanol and water vapours. The capability of the Li-Nafion membrane to separate products from a commercially available catalyst bed operating on CO_2 and H_2 at 200°C is demonstrated using a simple tubular membrane reactor module.

Casanave D. *et. al.* (1999) have discussed dehydrogenation of isobutane in a packed-bed zeolite membrane reactor using Pt-In catalyst. Enhanced dehydrogenation yields were obtained in the membrane reactor due to the separation of hydrogen from the reaction medium. Two sweeping modes were studied, namely the co-current and the countercurrent modes. Although the separation factor is higher in countercurrent than in co-current, the yield of reaction in these two sweeping modes is quite the same. The dehydrogenation reaction was limited by transport properties of the membrane in co-current mode while in countercurrent mode the limitation by kinetics was predominant. Reactor operation was described through theoretical modeling. A good agreement between the model and the experimental values was obtained with a co-current sweep gas. In countercurrent mode, the values predicted by the model for the yield of isobutene were slightly overestimated, due to hydrogen removal which induced catalyst local deactivation, or because the kinetic rate is inadequate when we are working far from the neighborhood of the equilibrium.

Ciavarella. P. ***et. al.*** **(2002)** have investigated isobutane dehydrogenation in a membrane reactor combining a bimetallic Pt-In/zeolite fixed-bed catalyst and a microporous MFI-alumina tubular membrane. The membrane reactor performance has been studied as a function of the feed and sweep flow rates and of the sweep (co- or counter-current sweep modes). Isobutene yields up to four times higher than that observed in a conventional reactor have been obtained. Depending on the conditions, it is shown that the performance of the membrane reactor is controlled either by the membrane or by the catalyst.

Luca Paturzo. ***et.al.*** **(2003)** have discussed the methane reforming with CO_2 seems to be a promising reaction system useful to reduce the greenhouse contribution of both gases into the atmosphere. On this basis, and considering the potentiality of this reaction system, the dry reforming reaction has been carried out in an Ru-based ceramic tubular membrane reactor, in which two Ru depositions have been performed using the co-condensation technique. Experimental results in terms of CH_4 and CO_2 conversion versus temperature during time are presented, as well as product selectivity and carbon deposition. These experiments have also been carried out using a traditional reactor. A comparison with literature data regarding dry reforming reaction is also provided. Experimental evidence points out a good catalyst activity for the methane dry reforming reaction, confirming the potentiality of a catalytic membrane applied to the reaction system.

Fausto Gallucci ***et. al.*** **(2004)** have studied zeolite membrane reactor. In their experimental study, they studied CO_2 hydrogenation into methanol. The reactor is placed in a temperature-controlled P.I.D. oven. Temperature is in the range between 200 and 263^{0}C. Reactants with purity percentage >99.995% are fed by means of mass-flow controllers driven by a computer software (furnished by Lira, Italy), used for all the experiments to keep the total feed flow rate at 800 ml/min, with ratios of H_2/CO_2 = 3 and 7. The reactor pressure was in the range between 20 and 24 bar. From experimental study they concluded that using a zeolite membrane reactor it is possible to obtain higher conversion of CO_2 and both higher methanol selectivity and methanol yield with respect to a traditional reactor (TR). From experimental study they concluded that the conversion of the main reaction in the membrane reactor increased by 22% against traditional fixed bed reactor, and the optimal non-uniform parameter of membrane permeation rate,$L_{1,opt}$, does exist.

Guangwen Chen *et. al.* (2004) have studied the methanol synthesis from CO_2 in a silicone rubber/ceramic composite membrane reactor. For their experiment they designed membrane reactor with a stainless steel shell is 200 millimeter (mm) long and the silicone rubber/ceramic membrane pipe has an outer diameter of 14 mm, while the length of the permeating membrane, l_1, is 150 and 50 mm, respectively. The reaction was carried out in the shell side. In the tube side, inert gas Ar was used as sweeping gas. The membrane reactor was placed in a thermostat and the feed enters the shell side via pre-heating coil. The reaction pressure was 0.3–1.6 Mpa, temperature was 200–230 ^{0}C. The feeding gas had a mole composition of 66.224% H_2, 25.552% CO_2 and 8.224% CH_4. From experimental study they concluded that the conversion of the main reaction in the membrane reactor increased by 22% against traditional fixed bed reactor, and the optimal non-uniform parameter of membrane permeation rate,$L_{1,opt}$, does exist.

2.3 MATHEMATICAL MODELING

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

Krishna Mohan and Rakesh Govind (1988) have studied fundamental understanding of the behavior of reactors with a permselective wall in terms of design parameters (reactor length, membrane thickness), operating variables (pressure ratio, feed flow rate), physical properties (rate constant, permeability of fast gas, equilibrium constant) and flow patterns (recycle, co-current, counter-current). Pure feed reacts on the high pressure side of the membrane, and the products formed are continuously removed to the lower pressure side so that thermodynamic equilibrium is never reached. It is shown by simulation that equilibrium shift can be enhanced by recycling the unconverted reactants, and shifting feed location to separate products and to maintain high permeation rates to reduce back reaction. It is also shown that the choice between co-current flow and counter-current flow depends on the system parameters.

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

The assumptions taken for developing the mathematical model are:

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

The steady state equations for the system are given as follows:

In the catalytic membrane;

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

The boundary conditions are

$$P_j = x_j P_f, \quad \text{at } r = r_f \qquad (2.2)$$

$$P_j = y_j P_p, \quad \text{at } r = r_p \qquad (2.3)$$

In the feed side chamber (shell side);

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

In the permeate side chamber (tube side);

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

The following rate expression is used for the cyclohexane dehydrogenation:

$$r_1 = k\left(P_1 - \frac{P_2P_3^{\,2}}{K_p}\right), \mathrm{kmol/(m^3s)} \tag{2.6}$$

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

$$K_p = 2.524\times10^{26}\exp\left(\frac{-2.606\times10^4}{T}\right), \mathrm{kPa}^3 \tag{2.7}$$

E. Gobina. ***et. al.*** **(1995)** have carried out an experimental and simulation study for the dehydrogenation of ethane to ethylene in a catalytic membrane reactor, with and without reaction on the permeate side. The membrane comprised a palladium-silver alloy deposited as a thin film on a Vycor glass support and palladium catalyst pellets were packed inside the membrane tube. Permeation data for the model were determined separately.

The assumptions made in the model development are

- Isothermal conditions prevail.
- Temperature and pressure gradients in the catalyst pellet may be neglected.
- Operation is steady state.
- The pressure in the catalyst bed and Vycor glass is constant because of the low conversion of ethane.
- Any change in pressure in the sweep gas due to hydrogen permeation may be neglected because of the small extent of permeation compared to the sweep flow rate.
- Axial dispersion is neglected but radial dispersion in both the catalytic bed and Vycor glass are accounted for.
- Radial changes of concentration are included in the model.

- Changes in flow rate along the reactor length are negligible due to the low conversions obtained.

In the catalyst bed: For $0<r_1<R_1$, where r_1 is the dimensionless radius and y_i represents the dimensionless concentration of species i, α and Pe_i represent a constant and a peclet number respectively.

$$\frac{\partial y_i}{\partial \xi}=\frac{\alpha}{Pe_i}\frac{1}{r_1}\frac{\partial}{\partial r_1}\left[r_1\frac{\partial y_i}{\partial r_1}\right]+r_A \qquad (2.8)$$

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

$$\beta\frac{\partial}{\partial r_2}\left[\frac{1}{\beta}\frac{\partial x_i}{\partial r_2}\right]=0 \qquad (2.9)$$

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

In the shell (sweep gas) side:

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

(2.10)

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

$$\frac{dy_s}{d\xi}=(-1)^m d_1\left[y_3^{1/2}-(P_r)^{1/2}y_s^{1/2}\right]-(-1)^m\gamma r_{H2} \qquad (2.11)$$

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

The differential equations for transport and reaction within the membrane module were solved using orthogonal collocation to give concentration profiles as a function of contact time, reactor length and radius. The simulation was validated with experimental data and was observed to correctly predict the increase in conversion with contact time for the range of experimental conditions investigated.

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

Assumptions taken for developing the model are as follows

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

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

For flow in permeate side chamber (Shell Side):

$$Q_i\big|_z - Q_i\big|_{z+dz} + \frac{P}{RT}\Pi\, D\, q_i\, dz = 0\ ; \qquad (2.12)$$

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

$$F_i\big|_z - F_i\big|_{z+dz} + \frac{\pi}{4}D^2\lambda_i r_i dz - \frac{P'}{RT}\pi D q_i dz = 0 \qquad (2.13)$$

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

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

Gobina E. and R. Hughes (1996) have carried out experimental and modeling study for catalytic dehydrogenation of n-butane. Use of nitrogen, carbon monoxide/nitrogen and oxygen/nitrogen sweep gases produced conversions up to 5 to 8 times the equilibrium conversion, the largest values occurring due to reaction coupling of the permeated hydrogen with O_2 or CO.

Model equations are formulated on the basis of following assumption

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

The balance equations are developed as given below:

In the catalyst bed: For $0<r_1<R_1$, where r_1 is the dimensionless radius and y_i represents the dimensionless concentration of species i, α and Pe_i represent a constant and a peclet number respectively.

$$\frac{\partial y_i}{\partial \xi} = \frac{\alpha}{Pe_i}\frac{1}{r_1}\frac{\partial}{\partial r_1}\left[r_1\frac{\partial y_i}{\partial r_1}\right] + r_A \qquad (2.14)$$

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

$$\beta\frac{\partial}{\partial r_2}\left[\frac{1}{\beta}\frac{\partial x_i}{\partial r_2}\right] = 0 \qquad (2.15)$$

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

In the shell (sweep gas) side:

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

(2.16)

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

$$\frac{dy_s}{d\xi} = (-1)^m d_1 \left[y_3^{1/2} - (P_r)^{1/2} y_s^{1/2} \right] - (-1)^m \gamma r_{H2} \qquad (2.17)$$

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

Jayaraman V.K. *et. al.* (2001) have simulated annular reactor packed with *matrices in which the catalysts/enzyme/microorganisms were immobilized.* The results indicate that the overall resistance and hence the conversion depends upon the Thiele modulus and another parameter. This parameter characterizes the ratios of the diffusion times and the ratios of length scales of the bulk liquid phase and the solid phase in the reactor shell. Analytical solutions have been obtained for linear 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 design equations:

- The reactor is assumed to be of tubular geometry and steady state condition prevails in the reactor.
- The reactant movement through the tube side is by laminar convection in the axial direction and by diffusion in the radial direction.
- There is no convection in the membrane or shell.
- The reactor is assumed to be isothermal and the temperature gradients are neglected.
- The radial diffusion coefficients in the tube side, membrane bulk phase in the shell and through the pores of the matrices are constants and are independent of concentration.
- The matrices are assumed to be of spherical shape with a uniform radius throughout the bed.
- As a representative example, reaction rate is assumed to follow Michaelis–Menten kinetics.

The model equations were solved using Newton-Raphson routine.

Guangwen Chen ***et. al.*** **(2004)** have studied the methanol synthesis from CO_2 in a silicone rubber/ceramic composite membrane reactor. The performance of the silicone rubber/ceramic composite membrane reactor was compared with that of the traditional fixed-bed reactor over a wide range of operating conditions. An experimentally validated reactor model was used for this purpose.

Several assumptions were made as follows:

- One dimensional plug flow in both shell and tube sides.
- The reactor is operated isothermally.
- The membrane tube diameter is far smaller than the tube length and much larger than the particle diameter, neglecting the axial mass and energy diffusion.
- The gas is ideal.
- The axial pressure drop on both sides of membrane is negligible.
- The radial concentration and temperature gradient between gas stream zone and catalyst, and inside the catalyst pellet as well are also negligible.

Shell side:

$$\frac{dF_i}{dl} = \rho S \sum_{j=1}^{m1} \upsilon_{i,j} r_j - \beta(l) N_i / l_1 \tag{2.18}$$

Tube side:

$$\frac{dQ_i}{dl} = \beta(l) N_i / l_1 \tag{2.19}$$

Where initial conditions: $l = 0$, $F_i = F_{i,0}$; $Q_i = Q_{i,0}$

Reaction rate

$$r_j = k_j + f_j\left(\overleftarrow{p}\right) \tag{2.20}$$

Permeation rate of component i

$$N_i = \frac{P_i}{l_m}\left(p_{h,i} - p_{l,i}\right) A_m \tag{2.21}$$

Based on CO_2, the main reaction conversion X_M to methanol and the side reaction conversion X_{CO} to CO were defined as follow,

$$X_M = \frac{F_M^{\bullet} + Q_M^{\bullet}}{x_{CO_2,0}} \tag{2.22}$$

$$X_{CO} = \frac{F_{CO}^{\bullet} + Q_{CO}^{\bullet}}{x_{CO_2,0}} \tag{2.23}$$

The fourth-order Runge–Kutta method was employed to simulate the process behaviors of the membrane reactor. The experimental results showed that the conversion of the main reaction in the membrane reactor increased by 22% against traditional fixed bed reactor, and the optimal non-uniform parameter of membrane permeation rate, $L_{1,\mathrm{opt}}$, does exist.

M.R. Rahimpour *et al.* (2004) investigates enhancement of CO conversion in a palladium–silver membrane reactor for methanol synthesis. A novel reactor configuration with perm-selective Pd–Ag (23 wt.% Ag) wall to hydrogen has been proposed. The reacting material is flowing through the tube side while synthesis gas is flowing through the shell side in co-current mode. The membrane reactor model is based on the following assumptions:

- Steady state conditions
- Plug flow is considered in reactor and shell side.
- The length of the reactor is not large enough to establish temperature and pressure gradients in it.
- Reaction rates developed by Graaf et al. were used to obtain the main reactions rates. The details of reaction rate expressions and the basis for using these rate expressions are explained.
- Gas mass transfer is neglected

The mass balance equations in terms of species molar flow rate are given in the following sections.

Reaction side

The mass balance equation for reaction side is

$$\frac{dF_i^r}{dx} = \rho_b A_r \sum_{j=1}^{3} \upsilon_{i,j} r_j - \alpha_H \left(\sqrt{p_H^r} - \sqrt{p_H^s} \right) \tag{2.24}$$

where i denotes H_2, CO, CO_2, CH_3OH and H_2O. A_r is cross section of tube reactor, F_i^r is flow rate of component i in reaction side, r_j is rate of jth reaction, x is axial coordinate, α_H is hydrogen permeation rate constant, ρ_b is density of bed and $\upsilon_{i,j}$ is stoichiometric coefficient of reactant *i* in reaction *j*. p_H^r and p_H^s are partial pressures of hydrogen in reaction

Shell side

The mass balance equation is written only for hydrogen in the shell side:

$$\frac{dF_i^s}{dx} = \alpha_H \left(\sqrt{p_H^r} - \sqrt{p_H^s} \right) \tag{2.25}$$

Where i denotes H_2

Boundary conditions for solving the equations

$$\alpha_H = \frac{2\Pi L\bar{P}}{\ln\left(\frac{R_0}{R_i}\right)} \quad \text{at } x = 0 \tag{2.26}$$

Hydrogen permeation in the palladium membrane is defined as

$$\alpha_H = \frac{2\Pi L\bar{P}}{\ln\left(\frac{R_0}{R_i}\right)} \tag{2.27}$$

where R_0 and R_i stand for outer and inner radius of Pd–Ag layer.

The resulting differential equations were solved by means of fourth-order Runge–Kutta method with the step size of 0.001 below which change in results was negligible. This choice worked out satisfactorily well in all runs. The results demonstrate that membrane reactor can raise carbon monoxide conversion beyond equilibrium value.

Jose M. Sousa. ***et. al.*** **(2004)** have presented a new numerical scheme using orthogonal collocation together with an independent variable (spatial coordinate) transformation, useful for solving the model equations associated to membrane reactors with catalytic membranes. This new scheme takes advantage of a noticeable feature of the concentration profile inside a catalytic membrane close to the membrane surfaces, this profile becomes steeper and steeper with the Thiele modulus.

Using traditional numerical methods for solving the model equations of a catalytic membrane reactor, namely finite differences with equispaced intervals or orthogonal collocation, for example, may lead to imprecise results. In order to illustrate the ability of this new numerical scheme for solving such equations, it is applied to the resolution of a case where an analytical solution is available (a generic A → B reaction carried out in a catalytic membrane with perfectly mixed flow pattern in both retentate and permeate sides). Then, the same numerical scheme is used for solving a model describing the cyclohexane dehydrogenation, A → B + 3C, carried out in a porous membrane with the same flow pattern as above and the results are compared with the ones obtained using an adaptive wavelet-based method. For these two models, solutions were also obtained using straight orthogonal collocation and finite differences with homogeneously distributed grid points for the sake of the comparison.

The results show that the new numerical approach is useful in dealing with this kind of problems, especially for high Thiele modulus values, showing high accuracy and demanding low computation time. Finally, this new scheme is applied to the resolution of a more complex model: a generic reaction 2A → B, carried out in a dense catalytic cylindrical membrane with plug–flow pattern for both retentate and permeate sides.

2.4 MOTIVATION FOR PRESENT WORK

It is evident from the aforementioned literature that the membrane reactors are augmently effective over the conventional separation units attached with a chemical reactor. Thus, it is axiomatic that the need to understand and quantify the process occurring in membrane reactor is aggrandized. Mathematical model appears an attractive tool for analysis and simulation of membrane reactor. This compels a chemical engineer for its modeling and simulation. It is obvious from the above literature review that large number of mathematical models has been developed for membrane reactor. These models include one dimensional or two dimensional models which may be used to obtain its behavior under steady and unsteady state operation. They are limited in their applications and differ from each other in terms of their complexities and the objectives of the studies carried out. In view of the above, studies on mathematical modeling of membrane reactors has been undertaken to achieve the objectives mentioned in section 1.8 of Chapter I.

2.5 CONCLUDING REMARKS

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

MODEL DEVELOPMENT

3.0 INTRODUCTION

In this section we concern over the development of mathematical model for manufacturing the methanol from hydrogenation of carbondioxide in a membrane reactor. We consider a tubular membrane reactor. The catalyst is packed on tube side. The feed is a mixture of carbondioxide and hydrogen and it is passed through tube, the inert gas Ar as sweeping gas, is also passed through shell as shown in figure 3.1. The products methanol, water and others permeated by membrane to the shell where it is swept by inert gas. Besides, model require kinetic equations for all the equations such as one main equation and two side reactions, catalyst parameters, and permeances of the species through the membrane so that solution of model equations may be obtained.

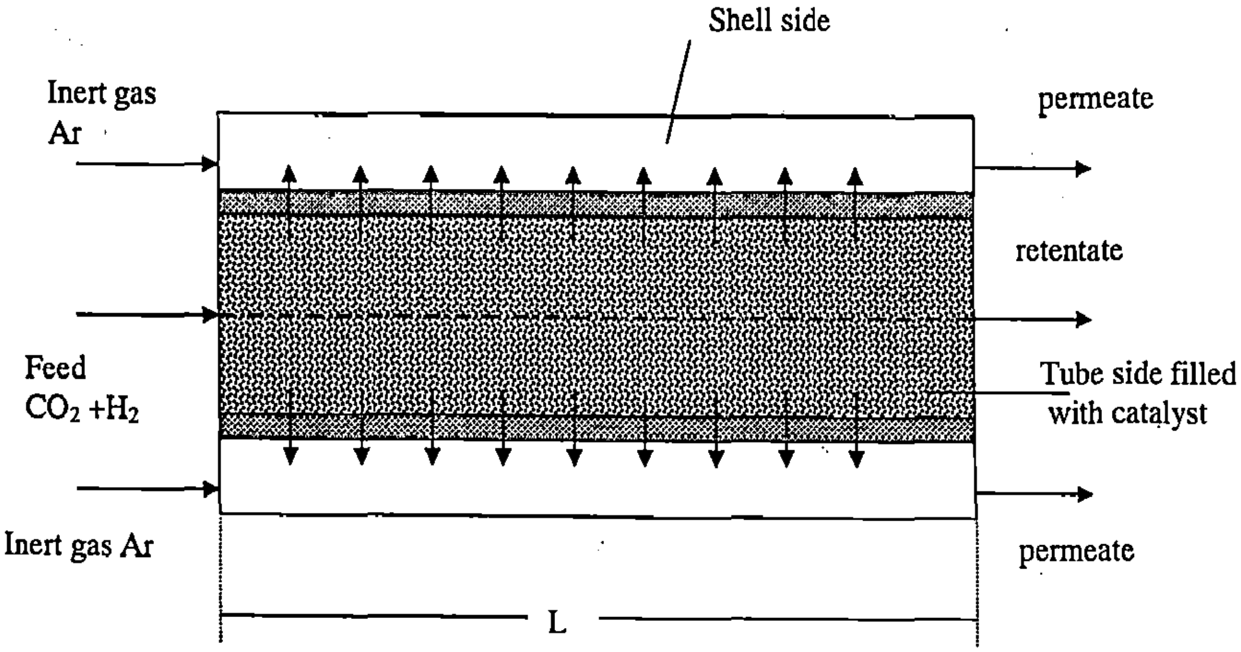

Figure 3.1 schematic diagram of membrane reactor

3.1 ASSUMPTIONS

The mathematical model is developed by using the following assumptions

- The reactor is operated isothermally and steady state.
- Fluid flow in both shell and tube side is plug flow.
- The permeation flux as a linear function of the species partial pressures
- Gas phase behaves ideally on both shell and tube side
- Isobaric conditions on reaction and permeation sides.
- Radial dispersion in tube and shell side is negligible.
- The radial concentration and temperature gradient between gas stream zone and catalyst, and inside the catalyst pellet as well are also negligible.

3.2 REACTION RATE EQUATIONS

The reaction rates for methanol synthesis from carbondioxide hydrogenation are given by the following equations, according to [Graaf (1988)], where partial pressure are used instead of partial fugacity because of the assumption of ideal gas behavior.

Main reaction:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \Delta H = -49.4\ KJ/mol \tag{3.1}$$

$$r_1 = \frac{k'_{ps,1}K_{CO_2}[p_{CO_2}p_{H_2}^{1.5} - p_{CH_3OH}\,p_{H_2O}/(p_{H_2}^{1.5}k_{p1})]}{(1+K_{CO}\,p_{CO}+K_{CO_2}\,p_{CO_2})[p_{H_2}^{0.5}+(K_{H_2O}/K_{H_2}^{0.5})p_{H_2O}]} \tag{3.2}$$

Side reactions

$$CO_2 + H2 \leftrightarrow CO + H_2O \qquad \Delta H = 41.5\ KJ/mol \tag{3.3}$$

$$r_2 = \frac{k'_{ps,2}K_{CO_2}[p_{CO_2}p_{H_2} - p_{H_2O}p_{CO}/(k_{p2})]}{(1+K_{CO}\,p_{CO}+K_{CO_2}\,p_{CO_2})[p_{H_2}^{0.5}+(K_{H_2O}/K_{H}^{0.5})p_{H_2O}]} \tag{3.4}$$

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad \Delta H = -90.9\ KJ/mol \tag{3.5}$$

$$r_3 = \frac{k'_{ps,3} K_{CO}[p_{CO} p_{H_2}^{1.5} - p_{CH_3OH} /(p_{H_2}^{0.5} k_{p3})]}{(1 + K_{CO} p_{CO} + K_{CO_2} p_{CO_2})[p_{H_2}^{0.5} + (K_{H_2O} / K_H^{0.5}) p_{H_2O}]} \tag{3.6}$$

The rate constants, adsorption equilibrium constants and reaction equilibrium constants are given in the literature [Graaf (1988)].

3.3 CHOICE OF CONTROL VOLUME

For developing model we divide the length of reactor L into small elemental length dz (as shown in Fig 3.1) and carry out the mass balance around dz both on shell side and tube side. The concentration of all the components present and other physical properties are assumed to be constant within the control volume chosen.

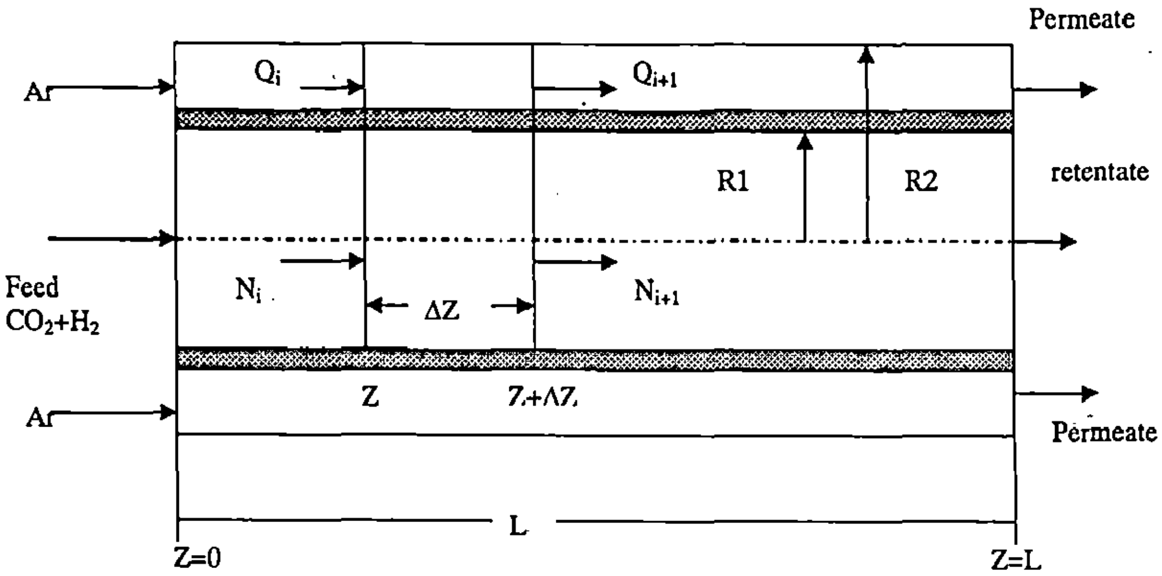

Figure 3.2 control volume of membrane reactor

3.4 MATERIAL BALANCE

The mass balance equations in terms of molar fluxes are derived around the control volume above and the final model is given by the following equations.

Tube side

rate $_{in}$ – rate $_{out}$ + rate of formation – transport rate through the membrane =0.

$$\pi R_1^2 N_i\big|_Z - \pi R_1^2 N_i\big|_{Z+\Delta Z} + \pi R_1^2 \sum_{j=1}^{3} \upsilon_{ij} r_j \rho_b \Delta Z - 2\pi R_1 \Delta z J_i = 0 \tag{3.7}$$

Divide the equation (1) by πr^2 . Z on both sides

$$\frac{N_i\big|_Z - N_i\big|_{Z+\Delta Z}}{\Delta Z} + \rho_b \sum_{j=1}^{3} \upsilon_{ij} r_j - \frac{2}{R_1} J_i = 0$$

$$\frac{dN_i}{dZ} = \rho_b \sum_{j=1}^{3} \upsilon_{ij} r_j - \frac{2}{R_1} J_i \tag{3.8}$$

Shell side

rate $_{in}$ – rate $_{out}$ + transport rate through the membrane =0.

$$\pi(R_2^2 - R_1^2) Q_i\big|_Z - \pi(R_2^2 - R_1^2) Q_i\big|_{Z+\Delta Z} + 2\pi R_1 \Delta z J_i = 0 \tag{3.9}$$

Divide the equation (3) by πr^2 . Z on both sides

$$\frac{dQ_i}{dZ} = \frac{2R_1}{\pi(R_2^2 - R_1^2)} J_i \tag{3.10}$$

where i= CO_2, H_2, CH_3OH, H_2O, CO

The flux of the species through the membrane is given by equation

$$J_i = P_i(p_i - p_i') \tag{3.11}$$

The total equations for the all the species are given by

Tube side:

$$CO_2: \quad \frac{dN_{CO_2}}{dZ} = -\frac{2}{R_1} P_{CO_2}(p_{CO_2} - p'_{CO_2}) + \rho_b(-r_1 - r_2) \tag{3.12}$$

$$H_2: \quad \frac{dN_{H_2}}{dZ} = -\frac{2}{R_1} P_{H_2}(p_{H_2} - p'_{H_2}) + \rho_b(-3r_1 - r_2 - 2r_3) \tag{3.13}$$

$$CH_3OH: \frac{dN_{CH_3OH}}{dZ} = -\frac{2}{R_1} P_{CH_3OH}(p_{CH_3OH} - p'_{CH_3OH}) + \rho_b(r_1 + r_3) \tag{3.14}$$

$$H_2O: \quad \frac{dN_{H_2O}}{dZ} = -\frac{2}{R_1} P_{H_2O}(p_{H_2O} - p'_{H_2O}) + \rho_b(r_1 + r_2) \tag{3.15}$$

$$CO: \quad \frac{dN_{CO}}{dZ} = -\frac{2}{R_1} P_{CO}(p_{CO} - p'_{CO}) + \rho_b(r_2 - r_3) \tag{3.16}$$

Shell side:

CO2: $$\frac{dQ_{CO_2}}{dZ} = \frac{2R_1}{(R_2^2 - R_1^2)} P_{CO_2}(p_{CO_2} - p'_{CO_2}) \qquad (3.17)$$

H2: $$\frac{dQ_{H_2}}{dZ} = \frac{2R_1}{(R_2^2 - R_1^2)} P_{H_2}(p_{H_2} - p'_{H_2}) \qquad (3.18)$$

CH3OH: $$\frac{dQ_{CH_3OH}}{dZ} = \frac{2R_1}{(R_2^2 - R_1^2)} P_{CH_3OH}(p_{CH_3OH} - p'_{CH_3OH}) \qquad (3.19)$$

H2O: $$\frac{dQ_{H_2O}}{dZ} = \frac{2R_1}{(R_2^2 - R_1^2)} P_{H_2O}(p_{H_2O} - p'_{H_2O}) \qquad (3.20)$$

CO: $$\frac{dQ_{CO}}{dZ} = \frac{2R_1}{(R_2^2 - R_1^2)} P_{CO}(p_{CO} - p'_{CO}) \qquad (3.21)$$

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

Tube side

$$p_i = \left(\frac{N_i}{\Sigma N_i}\right) P_t \qquad (3.22)$$

Where,

i = CO_2, H_2, CH_3OH, H_2O, CO

Shell side

$$p'_i = \left(\frac{Q_i}{\Sigma Q_i}\right) P_s \qquad (3.23)$$

Where,

i = CO_2, H_2, CH_3OH, H_2O, CO

3.5 MATHEMATICAL MODEL

The mathematical model comprises of set of mathematical equation, boundary conditions and constitutive relationships. These are presented sequentially in this section.

3.5.1 Set of Mathematical Equations

Model includes 10 differential equations presented by equations (3.12-3.16) and equations (3.17-3.21).In these equations z is independent variable and 10 state variables $N_{CO_2}, N_{H_2}, N_{CH_3OH}, N_{H_2O}, N_{CO}$ for tube side and

$Q_{CO_2}, Q_{H_2}, Q_{CH_3OH}, Q_{H_2O}, Q_{CO}$ for shell side.

3.5.2 Boundary conditions

The initial conditions of the reactor are listed as follows:

At z = 0,

Tube side:

$$N_{CO_2} = N_{CO_2,0} \tag{3.24}$$

$$N_{H_2} = N_{H_2,0} \tag{3.25}$$

$$N_{CH_3OH} = N_{H_2O} = N_{CO} = 0 \tag{3.26}$$

shell side:

$$Q_{CO_2} = Q_{H_2} = Q_{CH_3OH} = Q_{H_2O} = Q_{CO} = 0 \tag{3.27}$$

Thus, for 10 differential equations with one independent variable and 10 state variables there are 10 initial values given by equations (3.24) to (3.27).

3.5.3 Constitutive Relationships

Equations (3.2), (3.4), (3.6), represent the kinetic parameters for different chemical reactions.

3.6 CONCLUDING REMARKS

In this chapter detailed derivation of model equations are presented. To derive model we take simplifying assumptions. Those assumptions are also mentioned. Model consists of set of non-linear coupled ordinary differential equations, which form an initial value problem (IVP). These equations can be solved by ODE solvers of MATLAB.

CHAPTER IV

SOLUTION OF MATHEMATICAL MODEL

4.0 INTRODUCTION

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

4.1 MATHEMATICAL MODEL

Model equations developed in chapter 3 are summarized here in this section. The following model equations are obtained by taking material balance of components on tube side and on shell side:

Tube side

CO_2:
$$\frac{dN_{CO_2}}{dZ} = -\frac{2}{R_1} P_{CO_2}(p_{CO_2} - p'_{CO_2}) + \rho_b(-r_1 - r_2) \qquad (4.1)$$

H_2:
$$\frac{dN_{H_2}}{dZ} = -\frac{2}{R_1} P_{H_2}(p_{H_2} - p'_{H_2}) + \rho_b(-3r_1 - r_2 - 2r_3) \qquad (4.2)$$

CH_3OH:
$$\frac{dN_{CH_3OH}}{dZ} = -\frac{2}{R_1} P_{CH_3OH}(p_{CH_3OH} - p'_{CH_3OH}) + \rho_b(r_1 + r_3) \qquad (4.3)$$

H_2O: (4.4)

CO:
$$\frac{dN_{CO}}{dZ} = -\frac{2}{R_1} P_{CO}(p_{CO} - p'_{CO}) + \rho_b(r_2 - r_3) \qquad (4.5)$$

Shell side:

CO_2:
$$\frac{dQ_{CO_2}}{dZ} = \frac{2R_1}{(R_2^2 - R_1^2)} P_{CO_2}(p_{CO_2} - p'_{CO_2}) \qquad (4.6)$$

H_2:
$$\frac{dQ_{H_2}}{dZ} = \frac{2R_1}{(R_2^2 - R_1^2)} P_{H_2}(p_{H_2} - p'_{H_2}) \qquad (4.7)$$

CH_3OH:
$$\frac{dQ_{CH_3OH}}{dZ} = \frac{2R_1}{(R_2^2 - R_1^2)} P_{CH_3OH}(p_{CH_3OH} - p'_{CH_3OH}) \qquad (4.8)$$

$$\text{H}_2\text{O: } \frac{dQ_{H_2O}}{dZ} = \frac{2R_1}{(R_2^2 - R_1^2)} P_{H_2O}(p_{H_2O} - p'_{H_2O}) \tag{4.9}$$

$$\text{CO: } \frac{dQ_{CO}}{dZ} = \frac{2R_1}{(R_2^2 - R_1^2)} P_{CO}(p_{CO} - p'_{CO}) \tag{4.10}$$

with constitutive relationships as reaction kinetics as following

$$r_1 = \frac{k'_{ps,1} K_{CO_2}[p_{CO_2} p_{H_2}^{1.5} - p_{CH_3OH} p_{H_2O} /(p_{H_2}^{1.5} k_{p1})]}{(1 + K_{CO} p_{CO} + K_{CO_2} p_{CO_2})[p_{H_2}^{0.5} + (K_{H_2O} / K_{H_2}^{0.5}) p_{H_2O}]} \tag{4.11}$$

$$r_2 = \frac{k'_{ps,2} K_{CO_2}[p_{CO_2} p_{H_2} - p_{H_2O} p_{CO} /(k_{p2})]}{(1 + K_{CO} p_{CO} + K_{CO_2} p_{CO_2})[p_{H_2}^{0.5} + (K_{H_2O} / K_{H}^{0.5}) p_{H_2O}]} \tag{4.12}$$

$$r_3 = \frac{k'_{ps,3} K_{CO}[p_{CO} p_{H_2}^{1.5} - p_{CH_3OH} /(p_{H_2}^{0.5} k_{p3})]}{(1 + K_{CO} p_{CO} + K_{CO_2} p_{CO_2})[p_{H_2}^{0.5} + (K_{H_2O} / K_{H}^{0.5}) p_{H_2O}]} \tag{4.13}$$

The parameters used in the kinetic rate expressions are given in the following table.[27]

Table 4.1 kinetic and equilibrium constants

parameter	expression	units
$k'_{ps,1}$	(4.36+0.25) X 10^2 exp[(-65200+200) / RT]	(mol s $^{-1}$ bar $^{-1}$ Kg $^{-1}$)
$k'_{ps,2}$	(7.31+4.90) X 10^8 exp[(-123400+1600) / RT]	(mol s $^{-1}$ bar $^{-1/2}$ Kg $^{-1}$)
$k'_{ps,3}$	(2.69+0.14) X 10^7 exp[(-109900+200) / RT]	(mol s $^{-1}$ bar $^{-1}$ Kg $^{-1}$)
K_{CO_2}	(1.02+0.16) X 10^{-7} exp[(67400+600) / RT]	bar $^{-1}$
K_{CO}	(7.99+1.28) X 10^{-7} exp[(58100+600) / RT]	bar $^{-1}$
$k_{H_2O} / k_{H_2}^{0.5}$	(4.13+1.51) X 10^{-11} exp[(104500+1100) / RT]	bar $^{0.5}$
$\log_{10} k_{p,1}$	(3066 / T) – 14.650	----------
$\log_{10} k_{p,2}$	(-2073 / T) + 2.029	-----------
$\log_{10} k_{p,3}$	(5139 / T) – 12.621	-----------

4.2 OPERATING PARAMETERS

In this section the standard operating conditions and the simulation parameters with boundary conditions are given.

Table 4.2 standard operating conditions

Operating conditions	**value**	**unit**
Feed flow rate	400	cm^3 (STP) / min
Purge gas flow rate	1000	cm^3 (STP) / min
Temperature	503.16	K
Tube side total pressure	10	bar
Shell side total pressure	10	bar
H_2 / CO_2 ratio	3	----

Table 4.3 Simulation parameters

parameter	**value**	**unit**
Inner radius of the tube	0.67	cm
Inner radius of the shell	1	cm
Length of the reactor	20	cm
Density of catalyst	6779	Kg cat / m^3

Boundary conditions

In tube side

$$N_{CO_2} = 2.1091$$

$$N_{H_2} = 6.3273$$

$$N_{CH_3OH} = N_{H_2O} = N_{CO} = 0$$

Shell side

$$Q_{purge} = 3.1559$$

$$Q_{CO_2} = Q_{H_2} = Q_{CH_3OH} = Q_{H_2O} = Q_{CO} = 0$$

4.3 CATALYST SPECIFICATION

Methanol is conventionally produced from CO_2 hydrogenation over a commercial $Cu/ZnO/Al_2O_3$ catalyst. The catalyst consisting of CuO (65 wt %), ZnO (35 wt %), and Al_2O_3 (5 wt %) was used in the present study. The kinetic expressions are derived on basis of this catalyst only.

4.4 MEMBRANE SPECIFICATION

Zeolite membrane is a promising candidate for high performance membranes for industrial applications. In the present study we are considering two types of zeolite membranes. The first one is organophilic membrane silicalite, MFI-form without aluminum in which the organic species permeates faster than the water. The second one is hydrophilic membrane MOR / ZSM-5 / chabazite in which water permeate faster than the organic species. In the silicalite membrane (membrane A) the CH_3OH / H_2O selectivity of about 3 and in the MOR / ZSM-5 / chabazite (membrane B) the CH_3OH / H_2O selectivity of about 1 /3. The permeance of the other species are assumed ten fold lower with respect to CH_3OH and H_2O for both the cases in order to have an effective separation of the main products and an improved performance of the membrane reactors. The permeances of all species are taken from the literature [Piera (1998)] are given by the following table.

Table 4.4 species permeances

species	Permeances (mol / m^2 s bar)	
	Membrane A	Membrane B
CH_3OH	0.0287	0.0105
H_2O	0.0105	0.0287
H_2	0.00105	0.00105
CO_2	0.00105	0.00105
CO	0.00105	0.00105
purge gas	0.00105	0.00105

4.5 MATLAB ORDINARY DIFFERENTIAL EQUATIONS SOLVERS

Here in our case model equations are nonlinear-coupled ordinary differential equations, which constitutes initial value problem (IVP). In MATLAB this class of problem is solved using 'ode '(ordinary differential equations) solver. Here to solve our equations 'ode15s' is used.

Brief description of 'ode15s' solver:

ODE15S Solves stiff differential equations with variable order method. Syntax: [T, Y] = ODE15S (ODEFUN, TSPAN, Y0) with TSPAN = [T0 TFINAL] integrates the system o1f differential equations y' = f (t, y) from time T0 to TFINAL with initial conditions Y0. Function ODEFUN (T, Y) must return a column vector corresponding to f (t, y). Each row in the solution array Y corresponds to a time returned in the column vector T. To obtain solutions at specific times T0, T1...TFINAL (all increasing or all decreasing), use TSPAN = [T0 T1 ... TFINAL]. [T, Y] = ODE15S (ODEFUN, TSPAN, Y0, OPTIONS) solves as above with default integration properties replaced by values in OPTIONS, which is used generally for defining Relative Tolerance ('*RelTol*') and Absolute Tolerance ('*AbsTol*').

4.6 CONCLUDING REMARKS

In this chapter solution technique and its suitability has been discussed. Boundary conditions and other physical properties are also given in tabulated form. A program in MATLAB also has been developed to solve and predict model behavior. In order to be brief it is not desirable to describe the computer program completely or give its listing in the thesis. However complete computer program may be obtained from the author or his supervisor on request.

RESULTS AND DISCUSSION

5.1 INTRODUCTION

In this section, results of the developed mathematical model on membrane reactor have been studied and discussed. Our proposed model predicts the percentage conversion of the reactant along the length of the reactor, yield of products, selectivity of particular product and the effects of operating parameters on the performance of membrane reactor. The numerically computed results are shown graphically. The percentage conversion of carbondioxide is calculated from following formula:

$$\text{CO}_2 \text{ conversion } (\%) = \frac{CO_{2,in} - CO_{2.out}}{CO_{2,in}} X100 \qquad (5.1)$$

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

$$\text{CH}_3\text{OH yield } (\%) = \frac{CH_3OH_{out}}{CO_{2,in}} X100 \qquad (5.2)$$

The percentage selectivity of methanol is calculated by formula given below:

$$\text{CH}_3\text{OH selectivity } (\%) = \frac{CH_3OH_{out}}{CO_{2,in} - CO_{2.out}} X100 \qquad (5.3)$$

In particular, for membrane reactor both permeate and retentate flow rates are considered. In other words, for membrane reactor the compositions of outlet streams and the flow rates (retentate + permeate) have been used to calculate $CO_{2.out}$ and CH_3OH_{out}, while for traditional reactor only one outlet stream has been considered.

5.2 VALIDATION OF MODEL

For validation the above mathematical model equations are made applicable for fixed bed reactor by setting permeance through membrane equal to zero. The model equations are solved by the MATLAB ode solvers for the same operating conditions given by Fausto Galluci (2004).These results are compared with the experimental results by Fausto Galluci (2004) are given in form of a table shown below.

Table 5.1 Validation of modeling results with experimental results

	Modeling values	Experimental values	% Error
CO_2 conversion	5.21	5.00	+ 4.2
CH_3OH yield	2.6724	2.4	+ 11.35

It is clear from the above table that the model results are in good agreement with the experimental results. The results lead to validation of the mathematical model.

In the present study we are considering two types of zeolite membranes for the membrane reactors. The permeance properties of the two membranes are given in the chapter IV. The two membrane reactors are compared with respect to traditional reactor for CO_2 conversion, methanol selectivity and methanol yield at three different temperatures. The results are shown graphically below in the following figures.

5.3 CO_2 CONVERSION PROFILES

In this section we are considering the conversion of the reactant carbondioxide over three different temperature as 483 K, 503 K, 523 K and by keeping 10 bar pressure on reaction side and shell side. The conversion obtained in the two membrane reactors (MR-A, MR-B) are compared with the traditional reactor (TR). At all the temperatures the membrane reactors are giving higher conversions than the traditional reactor. The conversion difference between a membrane reactor and a traditional reactor is higher at low temperature because a higher methanol partial pressure on the reaction side allows a better permeation. Reaction (1)(methanol formation) is favored with respect to the reaction (2) (CO formation) by low temperatures. The methanol selective separation favours a higher production of methanol itself and, as a consequence, also a higher conversion is obtained.

CO_2 conversion of an MR-B (hydrophilic) is higher than that of an MR-A (organophilic) because the selective removal of water shifts both reactions (1) and (2). The conversion profiles are shown graphically below.

Table 5.2 CO_2 conversion at three different temperatures for the three reactors

Temperature	MR-A	MR-B	TR
483 K	21.6876	23.2916	12.5934
503 K	22.3404	24.6971	17.4196
523 K	24.6886	28.6707	18.8987

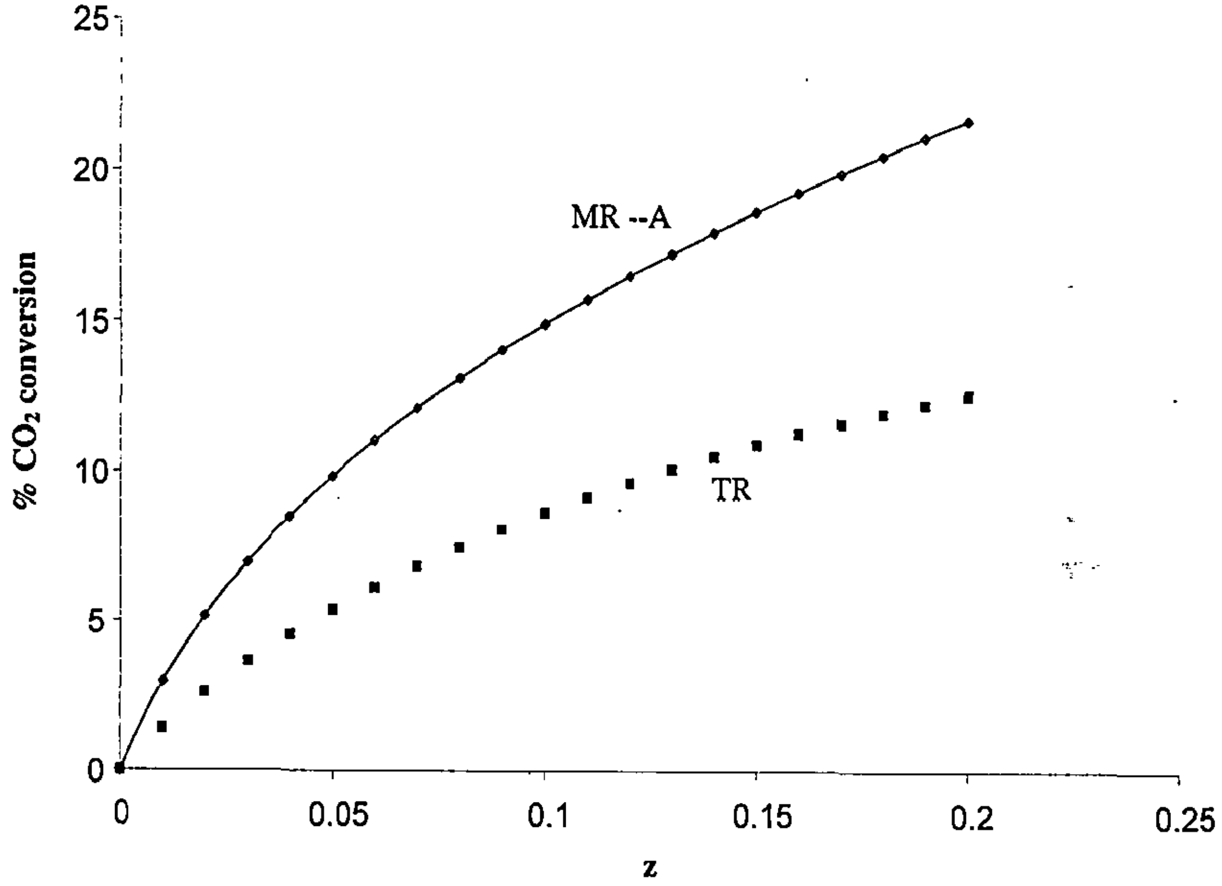

Figure 5.1 CO_2 conversion profiles for MR-A and TR at temperature 483 K and at pressure $P_t=P_s= 10$ bar

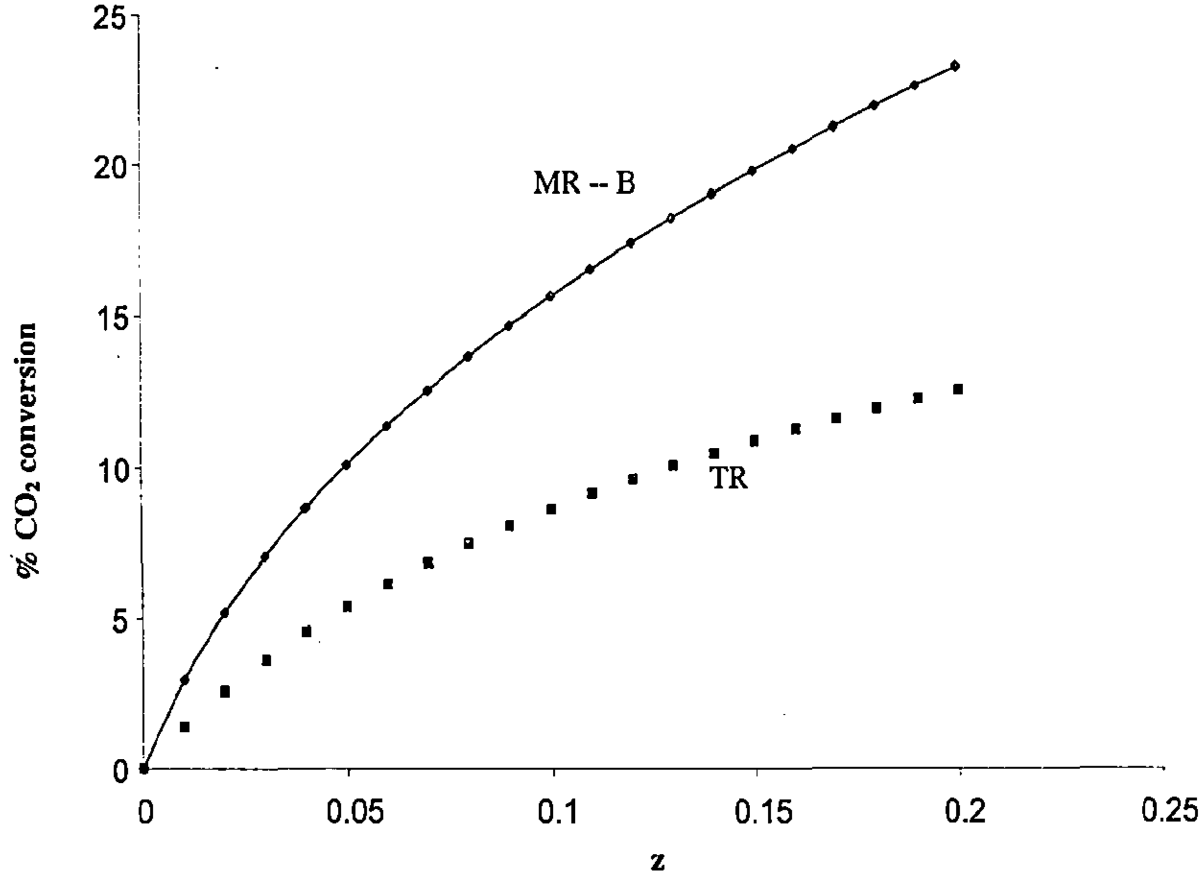

Figure 5.2 CO_2 conversion profiles for MR-B and TR at temperature 483 K and at pressure P_t=P_s= 10 bar

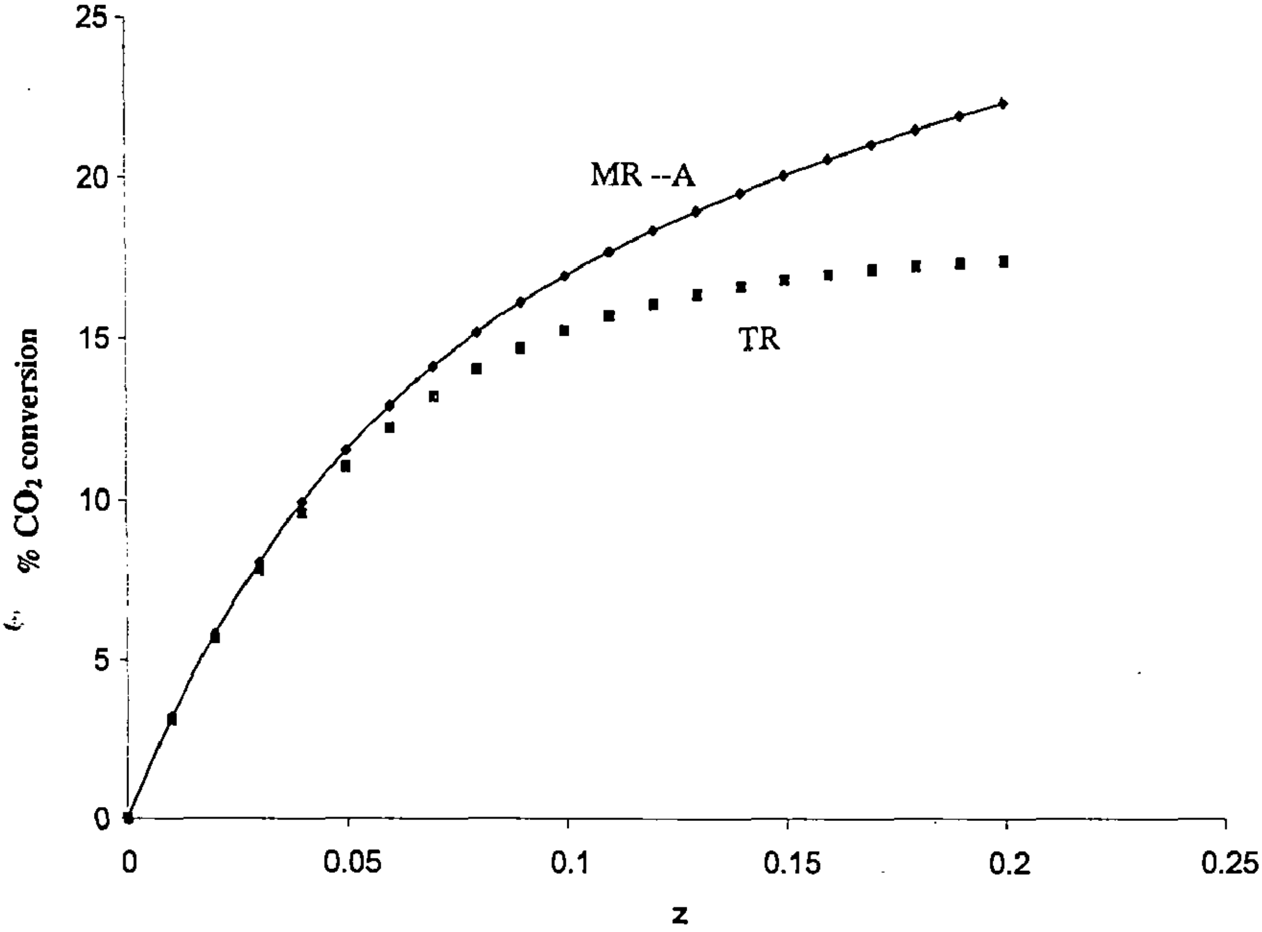

Figure 5.3 CO_2 conversion profiles for MR-A and TR at temperature 503 K and at pressure $P_t=P_s=$ 10 bar

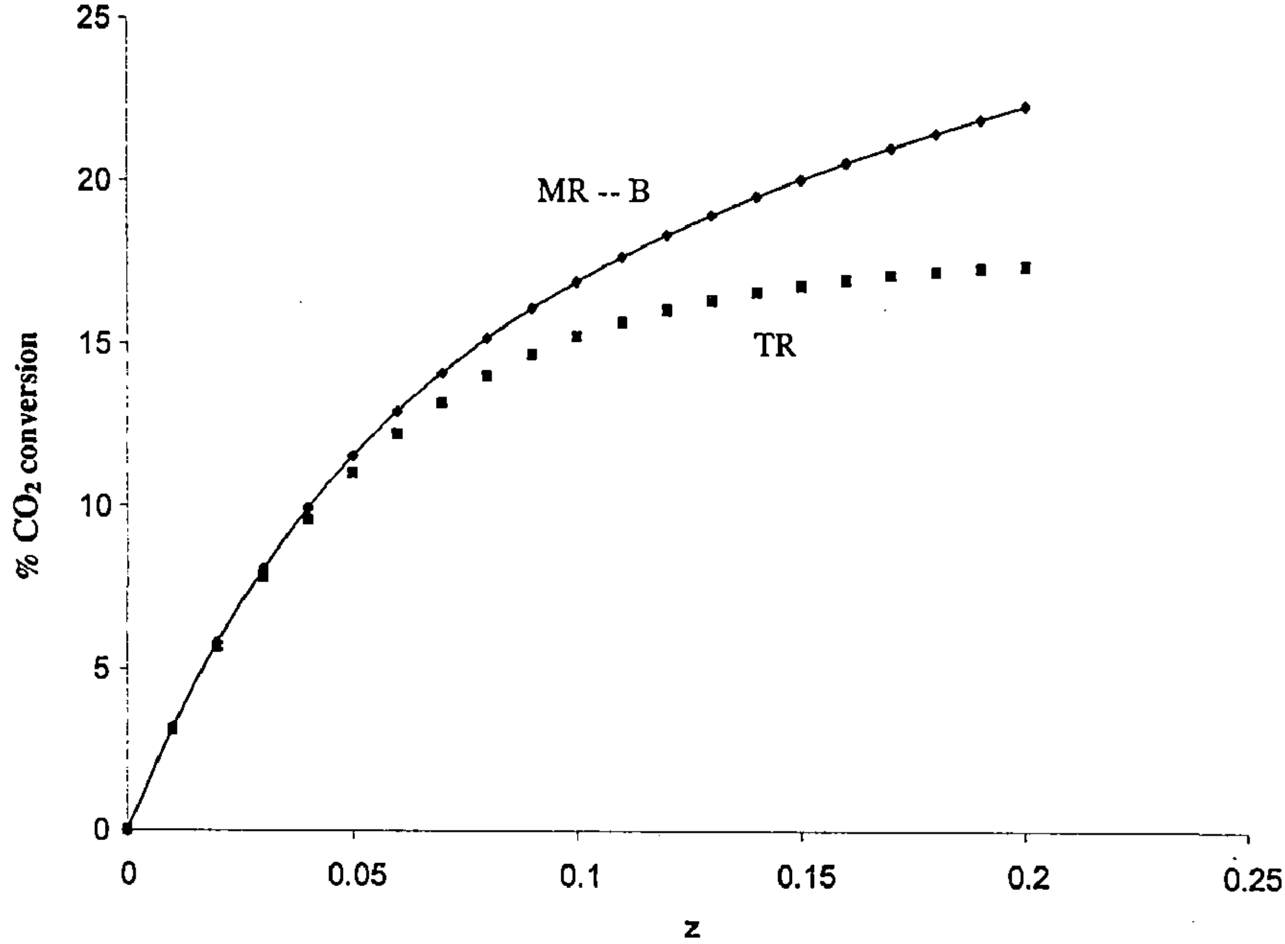

Figure 5.4 CO_2 conversion profiles for MR-B and TR at temperature 503 K and at pressure P_t=P_s= 10 bar

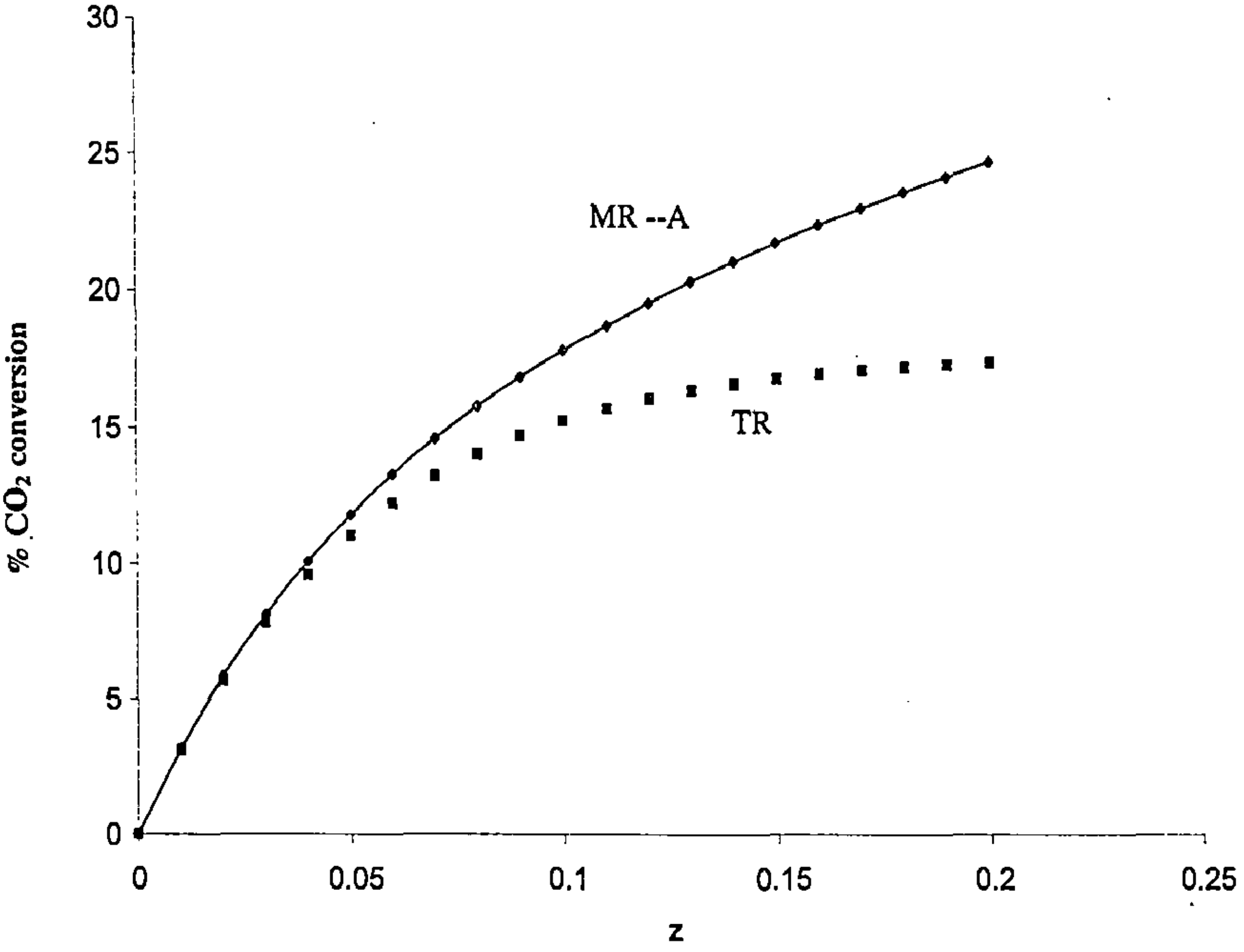

Figure 5.5 CO_2 conversion profiles for MR-A and TR at temperature 523 K and at pressure $P_t=P_s=$ 10 bar

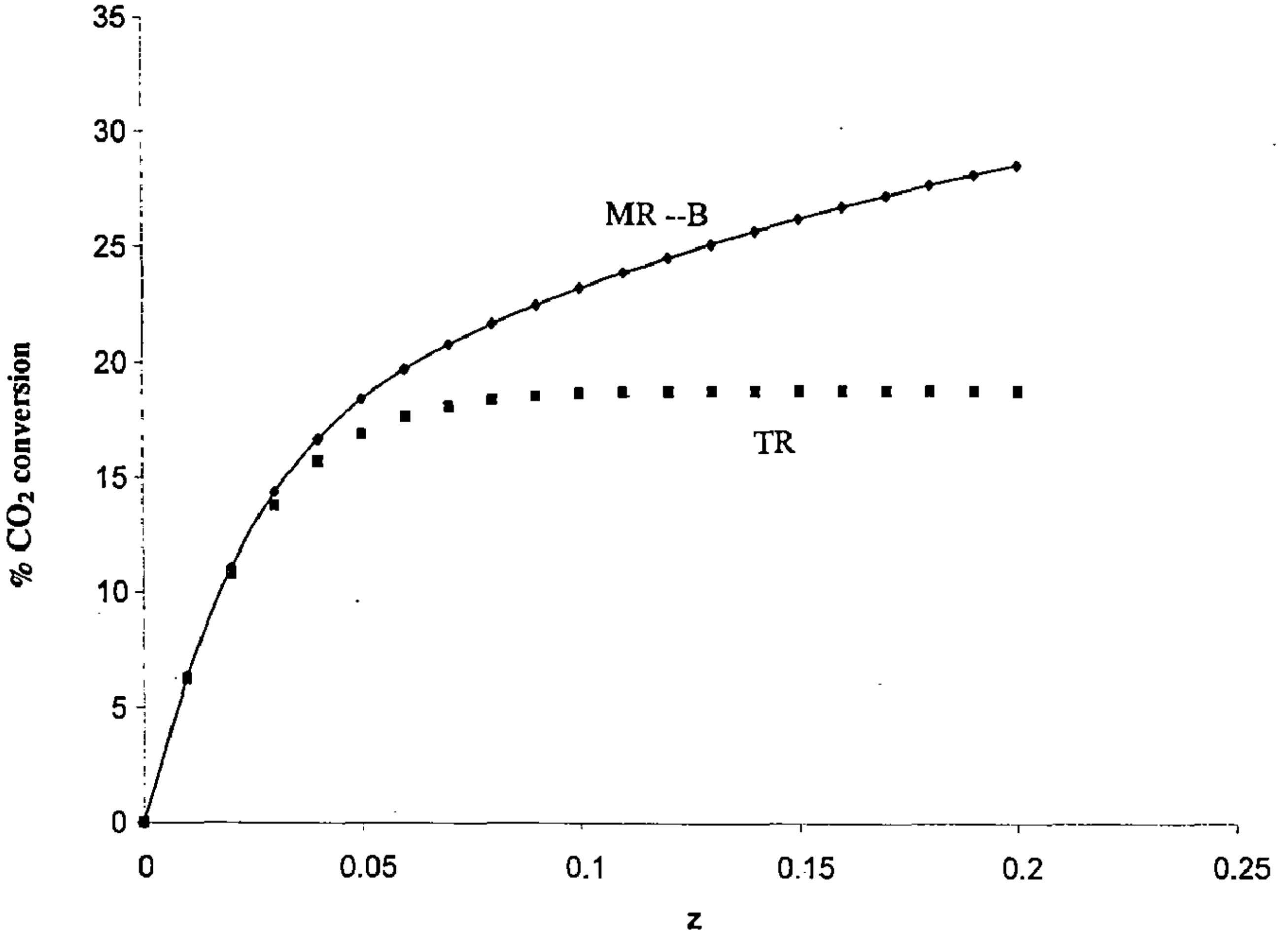

Figure 5.6 CO_2 conversion profiles for MR-B and TR at temperature 523 K and at pressure P_t=P_s= 10 bar

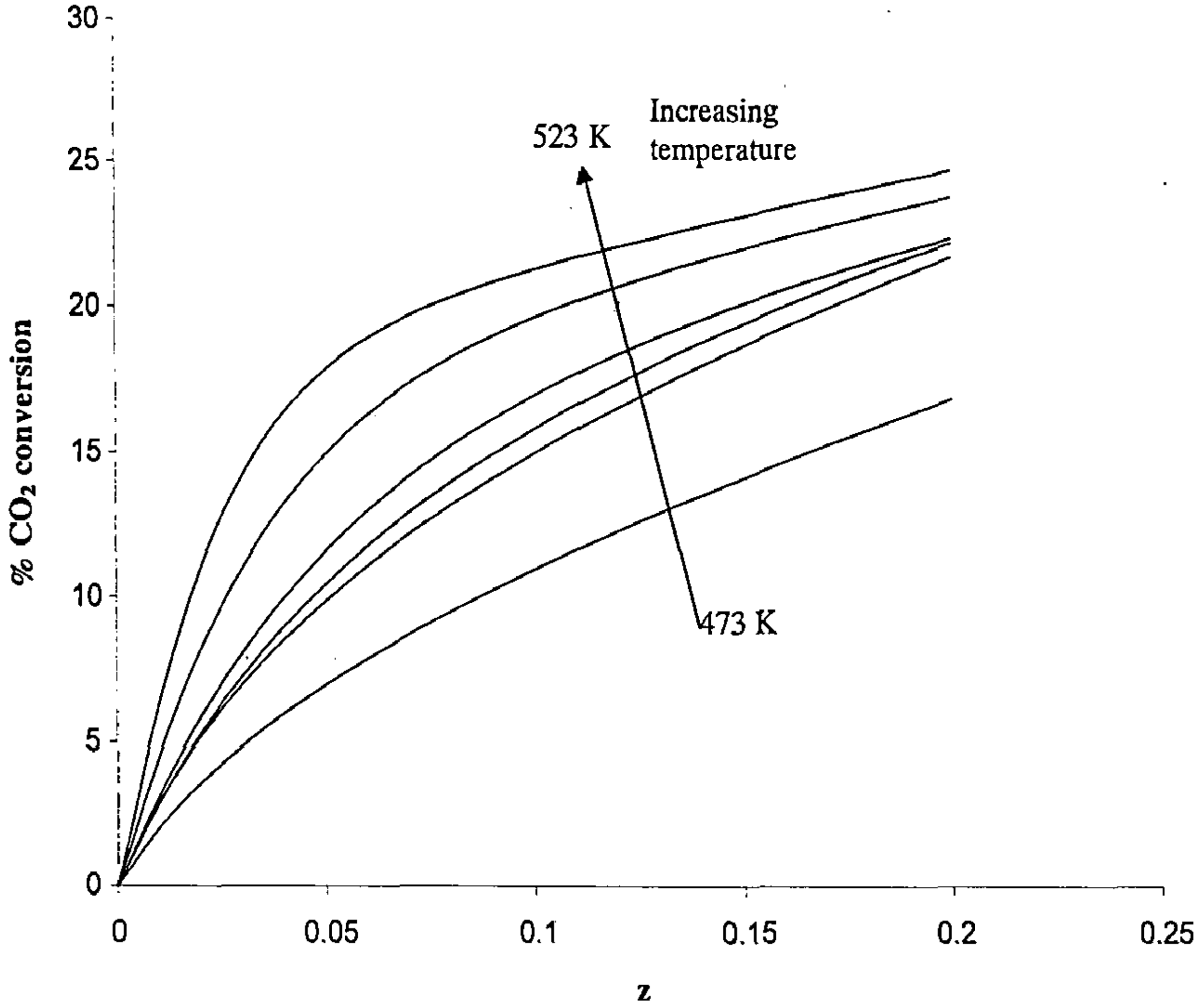

Figure 5.7 CO_2 conversion profiles for MR-A for different temperatures from 473 K to 523 K and at pressure P_t=P_s= 10 bar

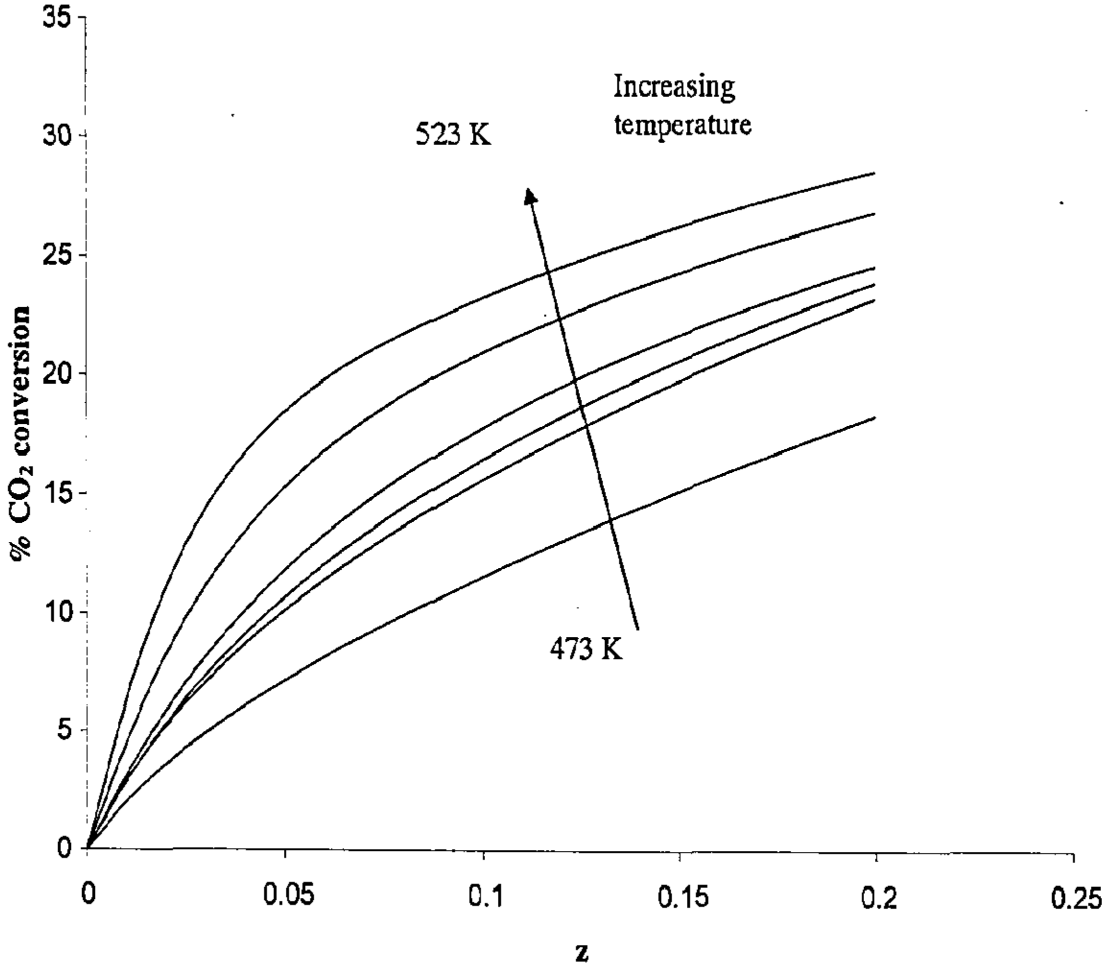

Figure 5.8 CO_2 conversion profiles for MR-B for different temperatures from 473 K to 523 K and at pressure P_t=P_s= 10 bar

5.4 METHANOL SELECTIVITY PROFILES

The axial profiles of methanol selectivity are reported in the following figures at three different temperatures and at the pressures 10 bar on both sides of the membrane. The membrane reactor performance for the methanol selectivity is compared with the traditional reactor. The MR-A has the highest selectivity, at any considered temperature, followed by the MR-B and TR. The use of MR shows some advantages from the selectivity point of view. With two competitive reactions (1) and (2), the selective separation of methanol increases the conversion and also the selectivity to the desired product. The selectivity values decreases rapidly with the temperature. The methanol/CO selectivity decreases when temperature increases due to the higher impact of the competitive reaction (2).

A minimum is present in the selectivity profile of the MR-A and MR-B it is due to the competitiveness between the reactions (1) and (2) and to their different rates. The selectivity decreases until a minimum because the higher CO production with respect to methanol, then it increases due to the methanol selective permeation.

Table 5.3 methanol selectivity at three different temperatures for the three reactors

Temperature	MR-A	MR-B	TR
483 K	68.1854	61.8245	57.9055
503 K	39.5139	34.2166	26.884
523 K	22.0633	15.7935	13.4564

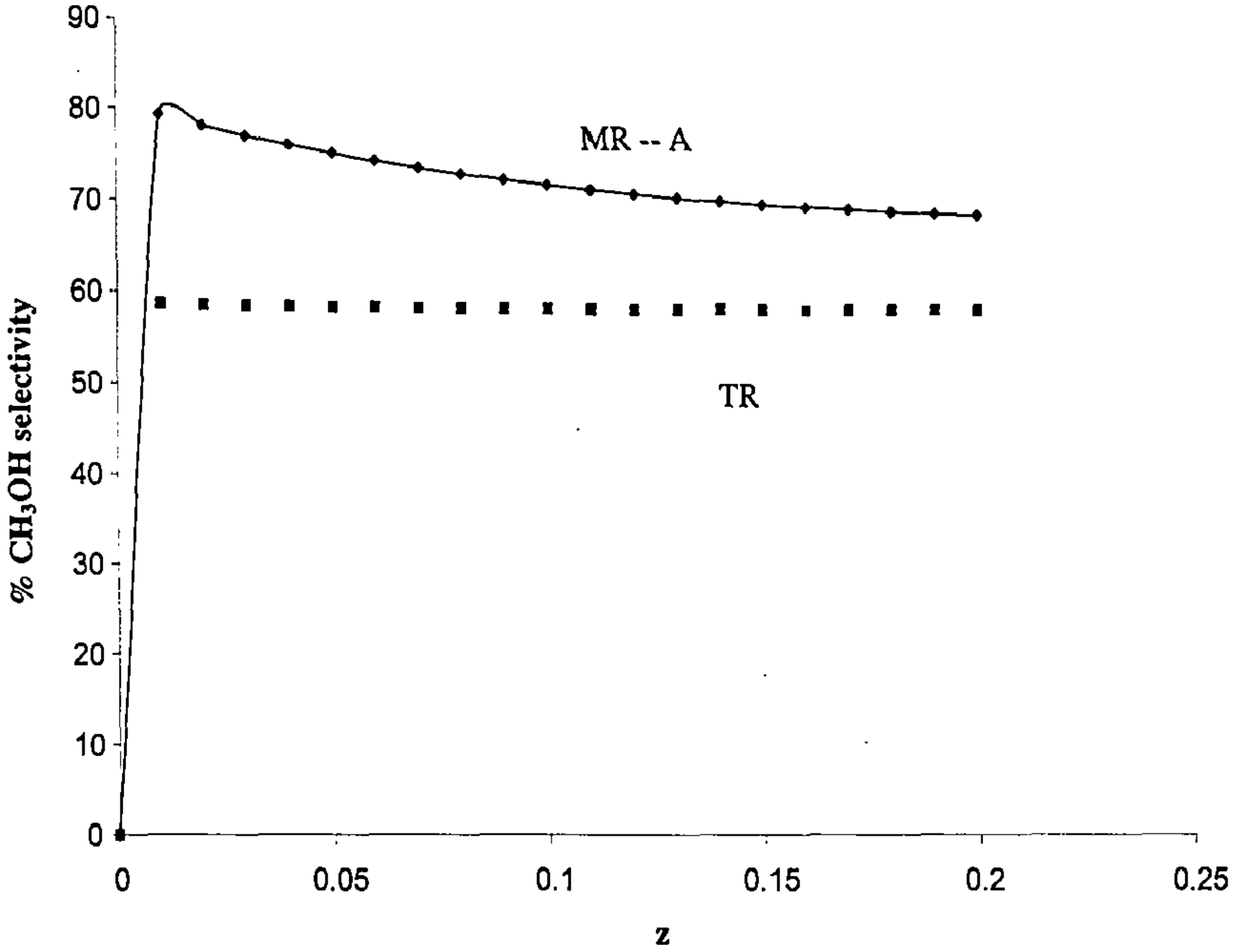

Figure 5.9 CH_3OH selectivity profiles for MR-A and TR at temperature 483 K and at pressure P_t=P_s= 10 bar

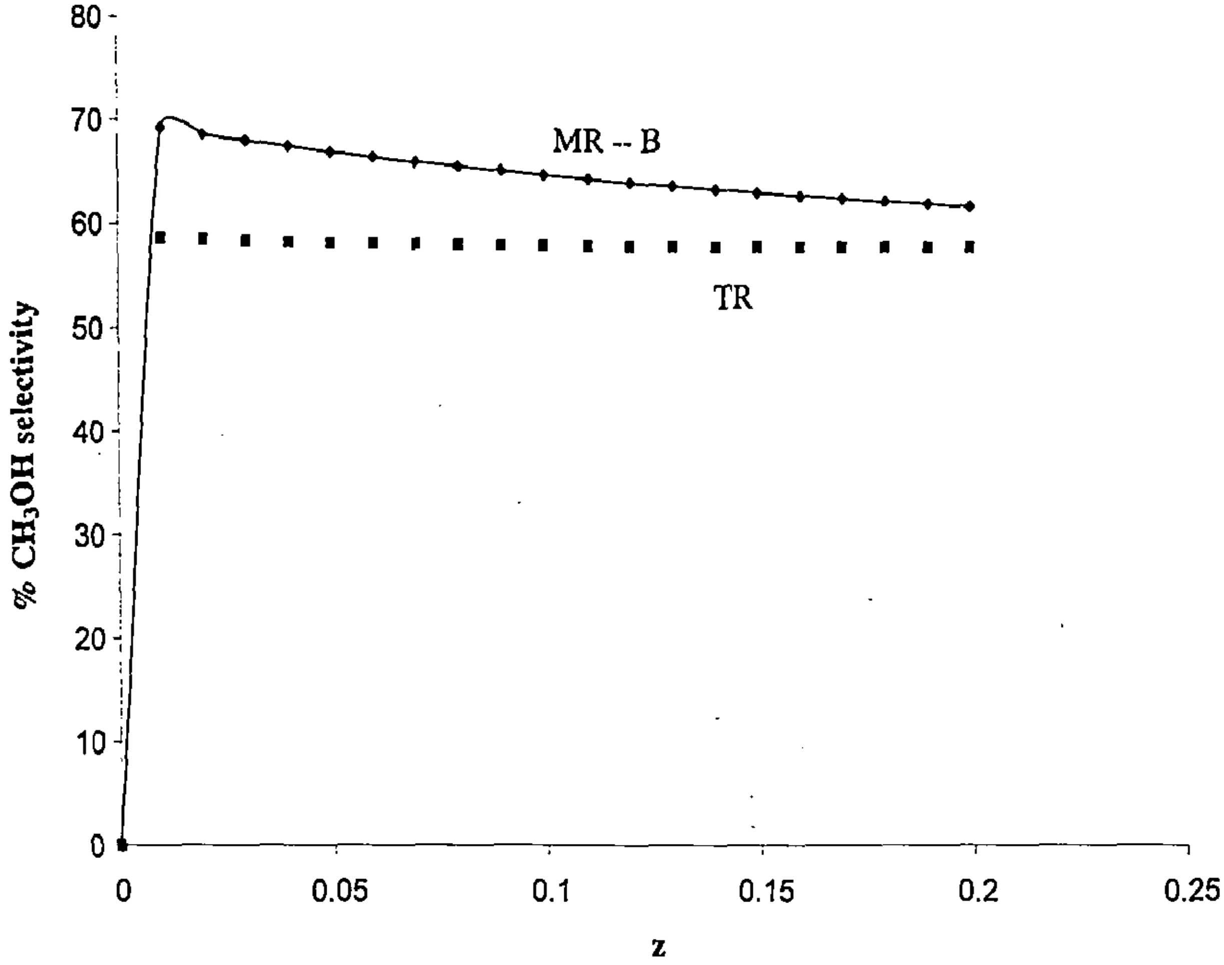

Figure 5.10 CH_3OH selectivity profiles for MR-B and TR at temperature 483 K and at pressure P_t=P_s= 10 bar

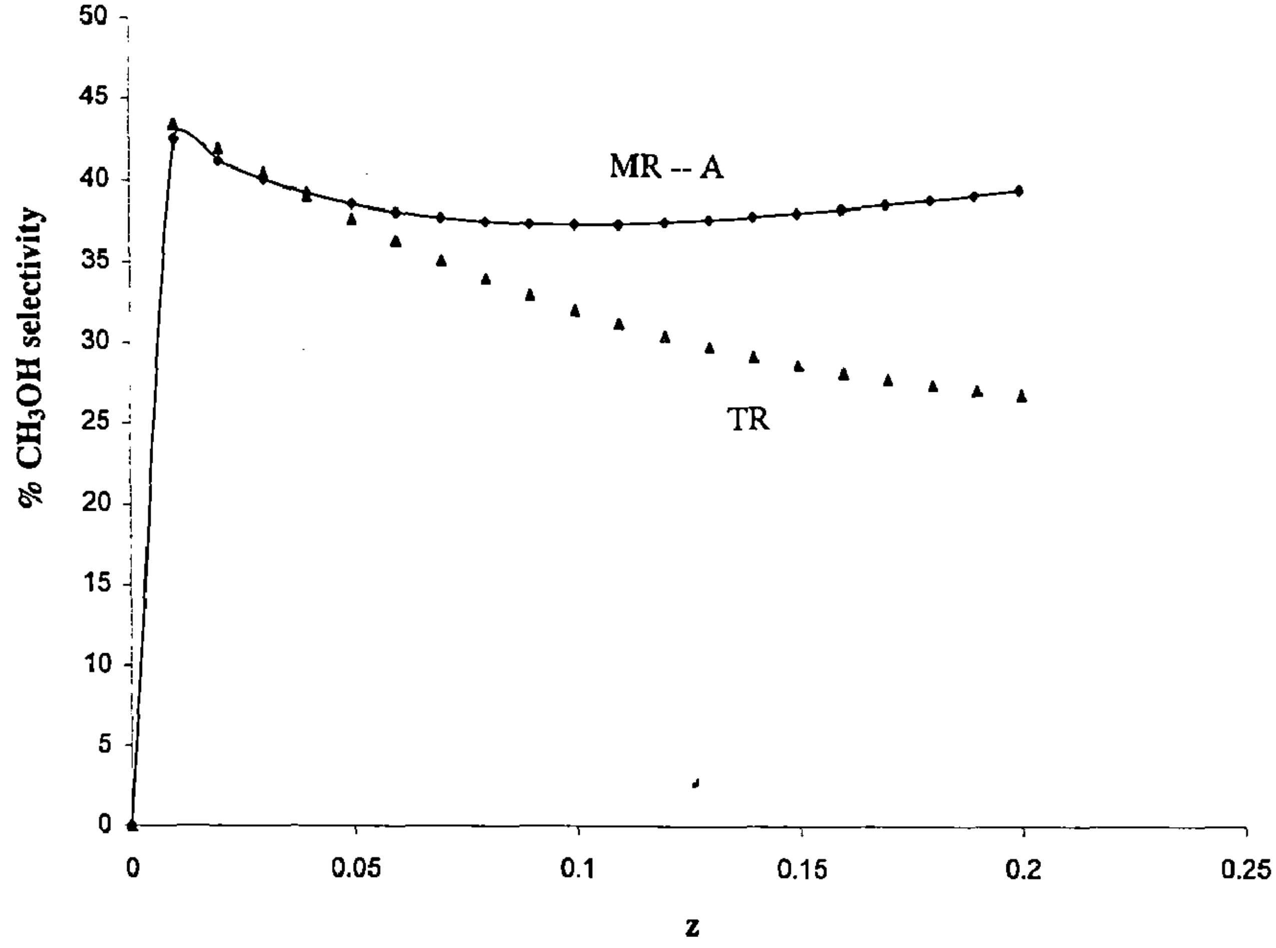

Figure 5.11 CH_3OH selectivity profiles for MR-A and TR at temperature 503 K and at pressure P_t=P_s= 10 bar

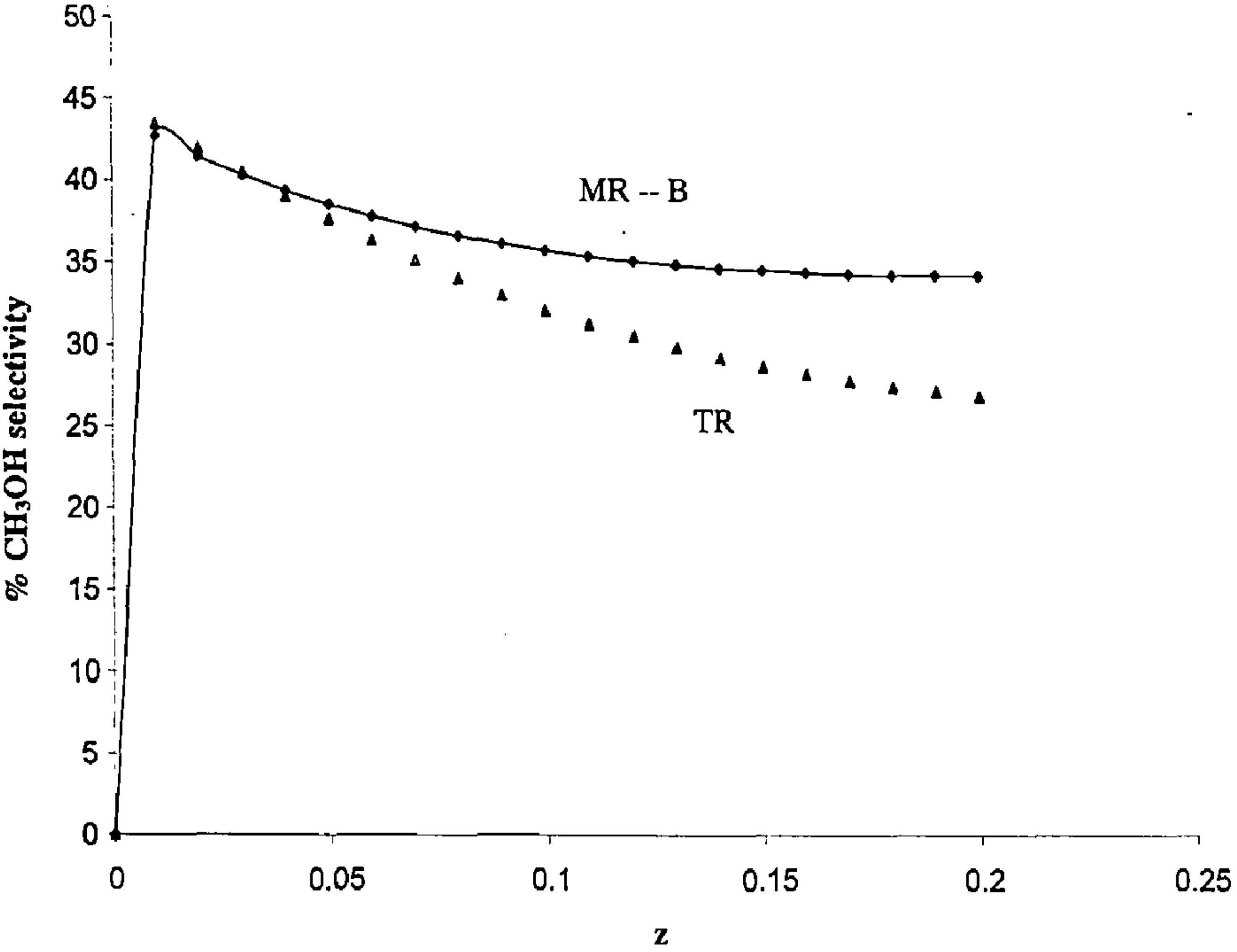

Figure 5.12 CH_3OH selectivity profiles for MR-B and TR at temperature 503 K and at pressure P_t=P_s= 10 bar

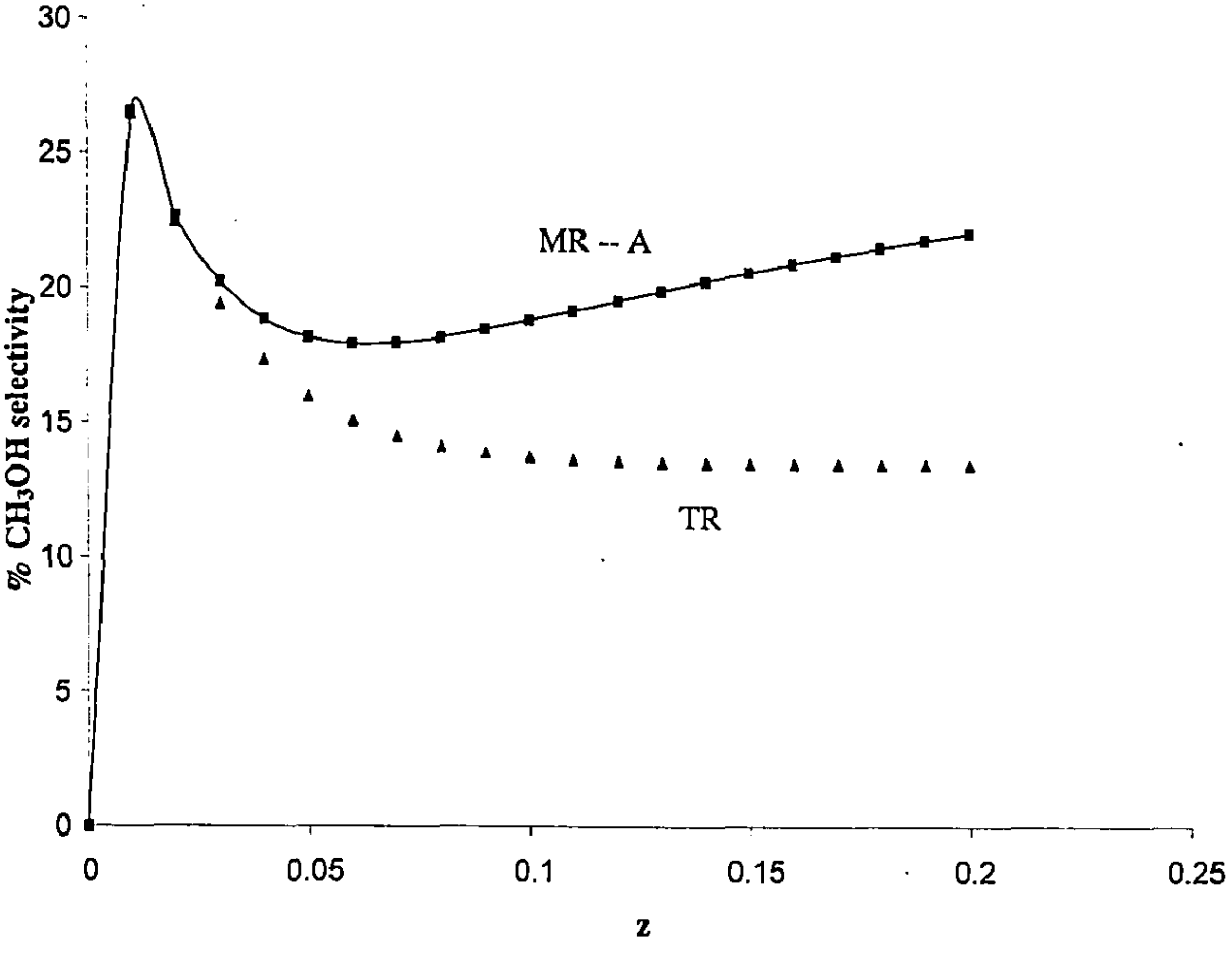

Figure 5.13 CH_3OH selectivity profiles for MR-A and TR at temperature 523 K and at pressure P_t=P_s= 10 bar

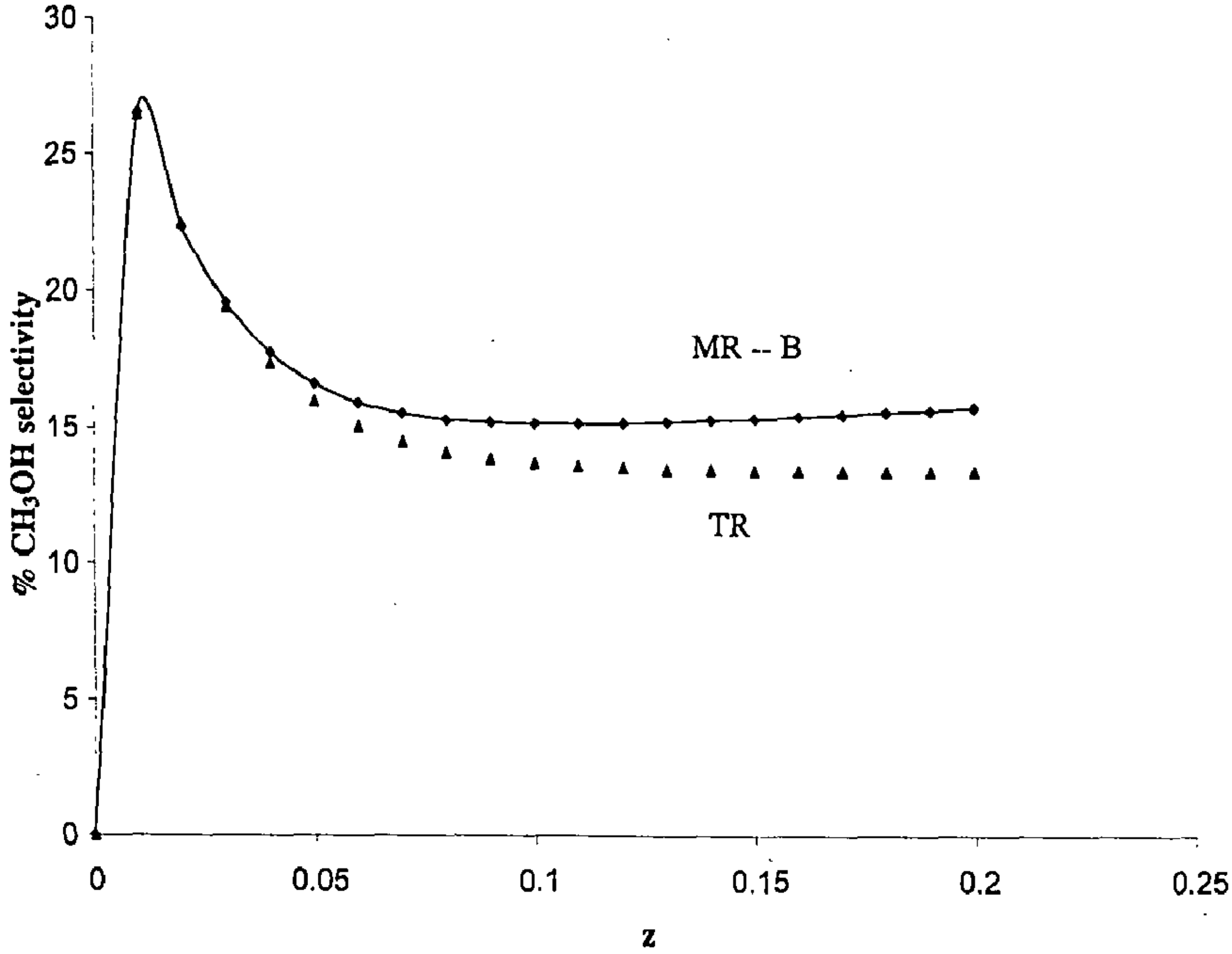

Figure 5.14 CH_3OH selectivity profiles for MR-B and TR at temperature 523 K and at pressure P_t=P_s= 10 bar

5.5 METHANOL YIELD PROFILES

The axial profiles of methanol yield are reported in the following figures at three different temperatures and at the pressures 10 bar on both sides of the membrane. The membrane reactor performance for the methanol yield is compared with the traditional reactor. It is interesting to have information on the methanol yield because the MR-B has a higher conversion but lower selectivity of the MR-A. The study shows that the methanol yield of MR-A is higher than that of MR-B, and the latest has a better yield than a TR. Also the yield shows that the major advantages are given at 483 K the lowest considered temperature. At this temperature the yield of MR-A is about 2.5 times higher than at 523 K.

Table 5.4 methanol yield at three different temperatures for the three reactors

Temperature	MR-A	MR-B	TR
483 K	14.7878	12.1766	7.2922
503 K	8.8276	8.4505	5.7673
523 K	5.4471	4.5281	2.5431

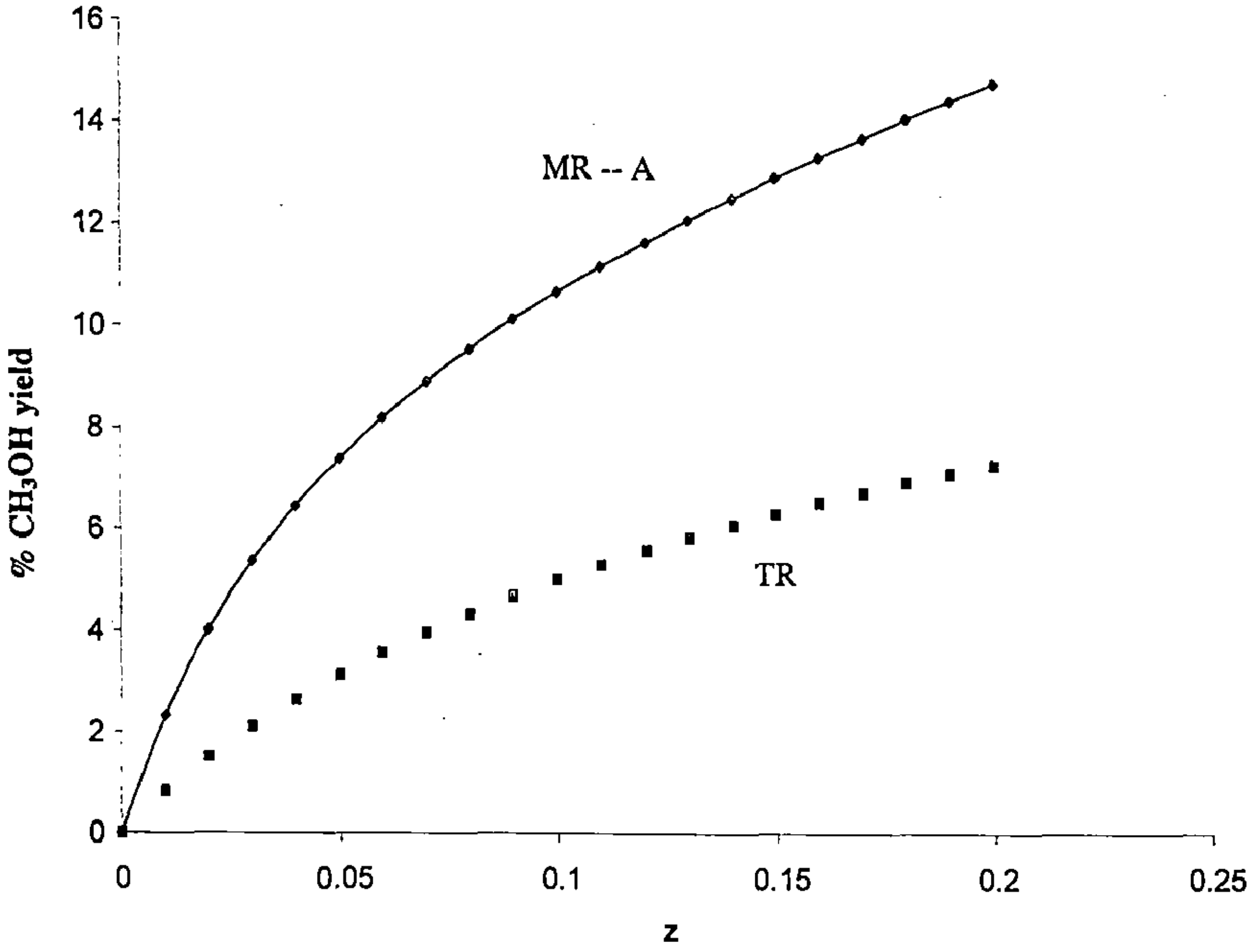

Figure 5.15 CH_3OH yield profiles for MR-A and TR at temperature 483 K and at pressure P_t=P_s= 10 bar

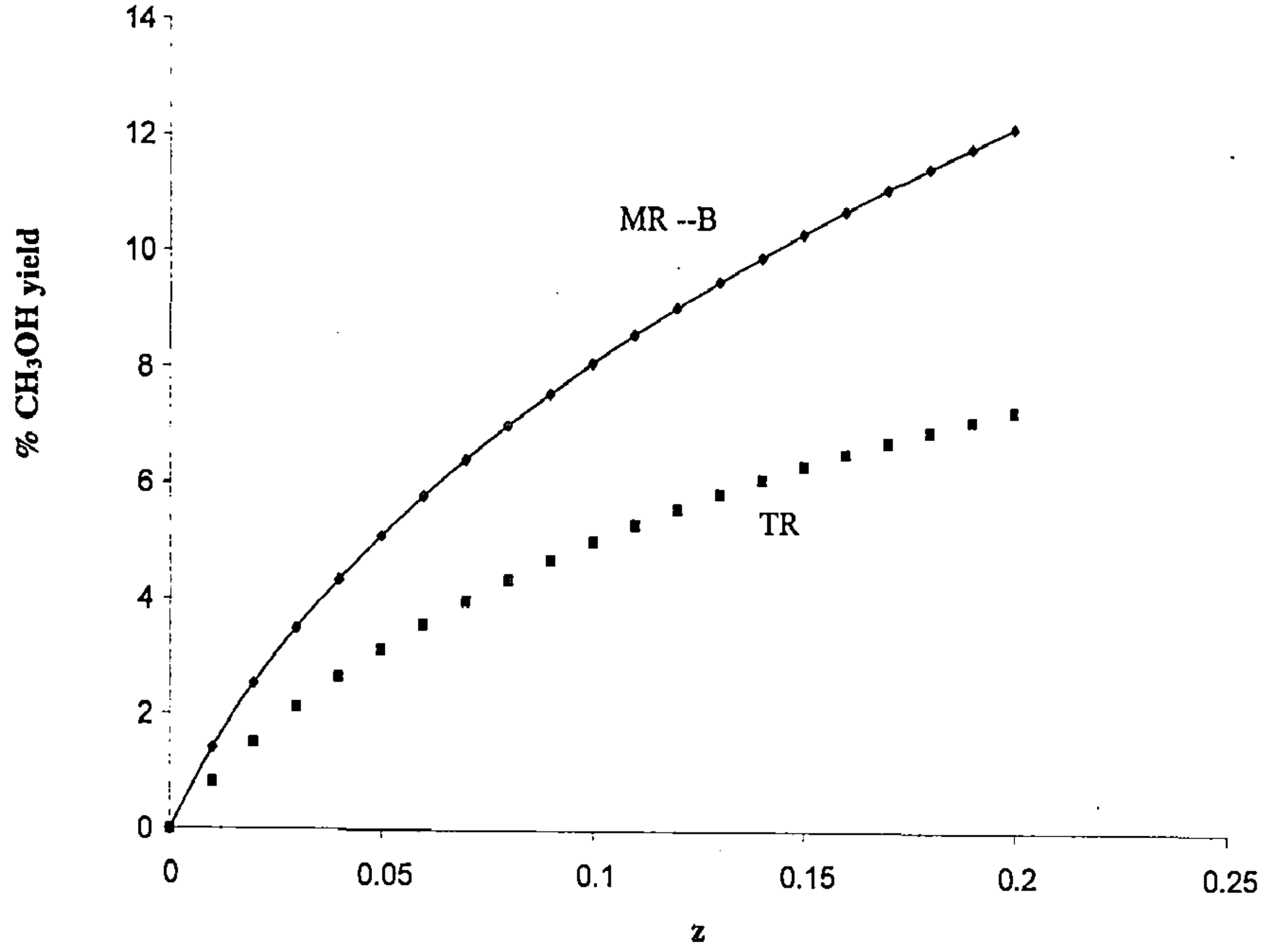

Figure 5.16 CH_3OH yield profiles for MR-B and TR at temperature 483 K and at pressure P_t=P_s= 10 bar

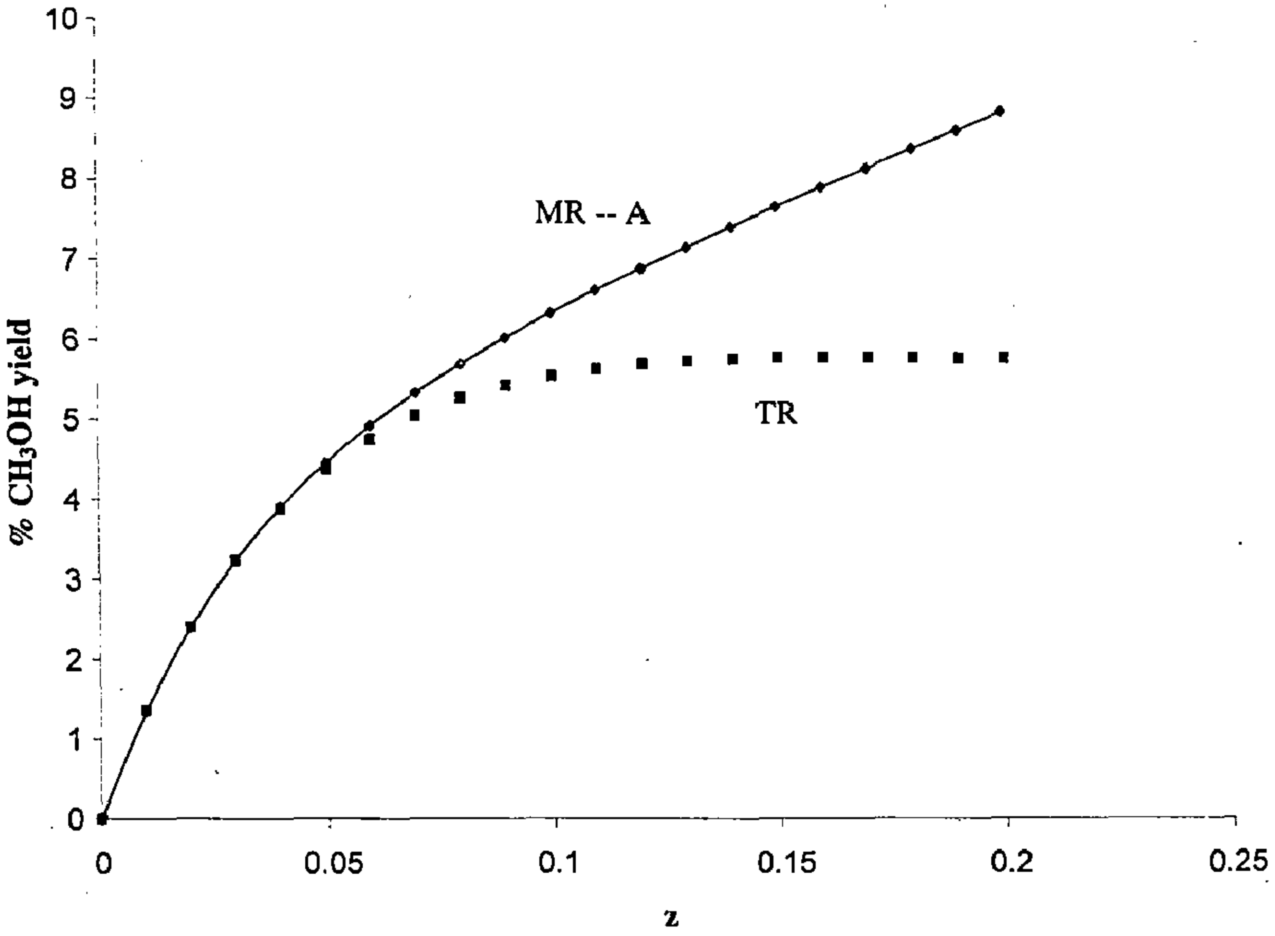

Figure 5.17 CH_3OH yield profiles for MR-A and TR at temperature 503 K and at pressure P_t=P_s= 10 bar

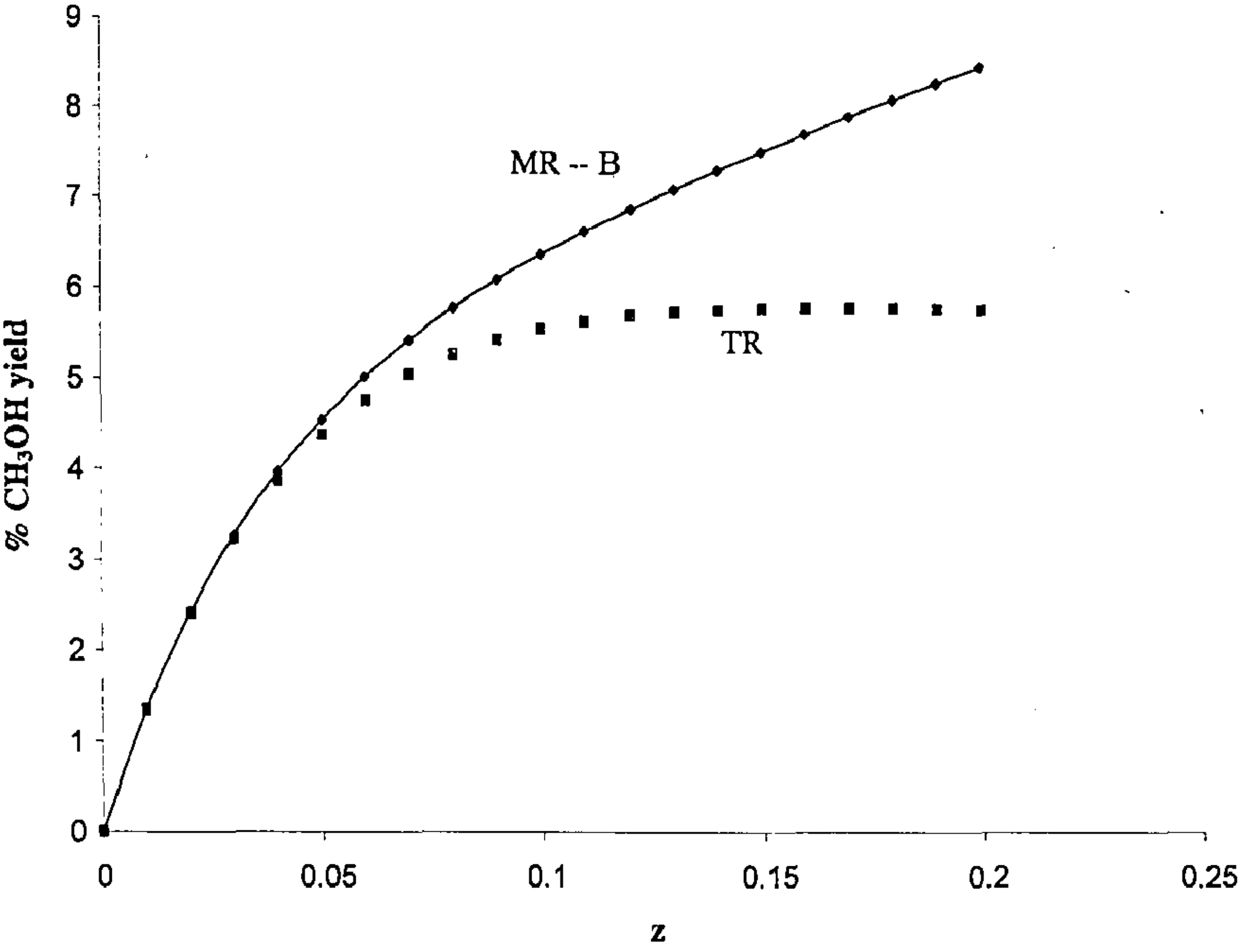

Figure 5.18 CH_3OH yield profiles for MR-B and TR at temperature 503 K and at pressure P_t=P_s= 10 bar

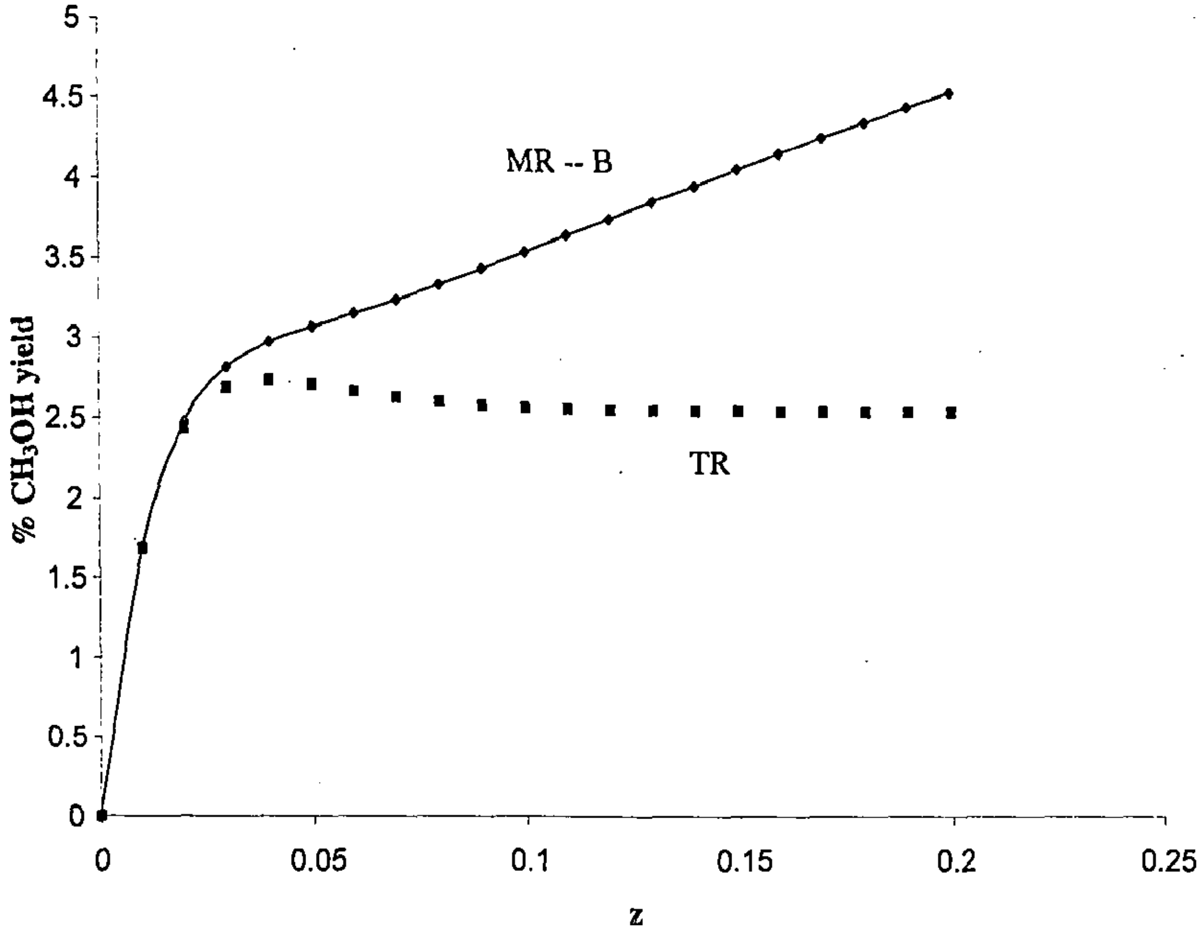

Figure 5.20 CH_3OH yield profiles for MR-B and TR at temperature 523 K and at pressure P_t=P_s= 10 bar

A comparision of the performance of all reactors is reported below in the following table for an oven temperature of 483 K and at a pressure of 10 bar.

Table 5.5 CO_2 conversion, methanol selectivity and yield of the outlet streams from MR-A, MR-B and TR at 483 K, 10 bar

	MR-A	MR-B	TR
CO_2 conversion	21.6876	23.2916	12.5934
CH_3OH selectivity	68.1854	61.8245	57.9055
CH_3OH yield	14.7878	12.1766	7.2922

5.6 CONCLUDING REMARKS

In this chapter all results regarding conversion of reactants, product selectivity and product yield are represented graphically. A comparative performance study of two zeolite membrane reactors with respect to traditional reactor is presented. It is found that the two membrane reactors are showing better performance at any temperature with the traditional reactor. In general the results presented in this chapter show that membrane reactor can replace the conventional fixed bed reactor used methanol synthesis.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.0 INTRODUCTION

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

6.1 CONCLUSIONS

- A mathematical model for membrane reactor with zeolite membrane is developed for methanol synthesis from carbon dioxide hydrogenation.
- Mathematical model consists of a set of coupled ordinary differential equations, which constitutes initial value problem. Here the differential equations are stiff so MATLAB ODE suite is used to solve the differential equations for prediction of performance of the model.
- In this study an organophilic (MR-A) and hydrophilic (MR-B) zeolite membranes are considered with modest permeances of permanent gases. Thus, conversion, selectivity and yield of two membrane reactors are studied and compared with those obtained in a TR.
- The MR-B reaches a higher conversion for all considered temperatures with respect to the MR-A. However, the MR-A selectivity is always higher than that of the MR-B due to better methanol permeation, thus, the MR-A is characterized by a higher yield when compared with the MR-B. Both membrane reactors have better performance of that of the TR.

6.2 RECOMMENDATIONS FOR FUTURE WORK

- Mathematical model equations are very sensitive to the kinetic parameters so kinetic parameters should be evaluated carefully
- The correlations for various constitutive properties for example permeance of the species through the membrane have been taken from the literature. If these parameters have been evaluated experimentally in the laboratory, it would have given better simulation results.

- The results obtained from the work in the laboratory are sometimes quite different from those obtained at the industrial scale. It is therefore, recommend that the model developed here must be tested for the data from industries. This will enhance the applicability of the model

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