

SIMULATION STUDY ON THE CARBON DIOXIDE REFORMING OF  
METHANE USING HYDROGEN PERMSELECTIVE MEMBRANE REACTOR

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To my beloved parents  
for your patience and understanding.

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## ABSTRACT

Carbon dioxide reforming of methane to syngas with  $H_2/CO$  ratio of unity has received much attention in current catalytic research. However, the water formation and intensive energy requirement has limited its applicability for appropriate industrial practice. Accordingly, combined  $CH_4$  reforming with  $CO_2$  and  $O_2$  (CORM-POM) and the utilization of permreactor system have been introduced to overcome these problems. In this study, the model application of hydrogen permselective membrane reactor to promote equilibrium shifts of  $CH_4-CO_2$  reforming processes was investigated. The thermodynamic equilibrium analysis indicated that the CORM process performance was in correspondence with temperature, but the  $H_2/CO$  product ratio below unity was observed. Nevertheless, the addition of  $O_2$  in CORM process to improve the  $CH_4$  conversion and the  $H_2$  yield as well as to obtain  $H_2/CO$  ratio of unity is theoretical feasible at selected temperatures and  $CH_4:CO_2:O_2$  feed ratios. Extended studies have been conducted to investigate the permreactor system application in promoting CORM reaction enhancements. The dynamic equilibrium results suggested that the reaction enhancements were influence strongly by the amount of hydrogen removal and the temperature is an important factor in determining the potential enhancement margins as the reaction-separation system operated at 900K exerts the most significant reaction enhancements. Besides, the  $H_2/CO$  product ratio was improved close to unity for CORM reaction, while for combined CORM-POM the ratio was maintained at 1.0-1.2 with the utilization of permreactor system. In addition, the space velocity is an important factor to control the kinetic-transport behaviors in permreactor systems while the maximum attainable conversion and product yield levels were considerably determined by the sweep factor. The findings from dynamic equilibrium approach were confirmed by the kinetic-transport modeling results as the data obtained were well-match with the dynamic equilibrium approach. In short, the dynamic equilibrium technique can be useful diagnostic and optimization tool for membrane catalysis applications.

## ABSTRAK

Pembentukan semula metana menggunakan karbon dioksida untuk menghasilkan singas dengan nisbah  $H_2/CO$  yang sama telah menarik perhatian para penyelidik kini. Tetapi, pembentukan air dan keperluan tenaga yang intensif telah melimitkan aplikasinya dalam pasaran industri. Sehubungan ini, kombinasi proses pembentukan semula  $CH_4$  dengan  $CO_2$  dan  $O_2$  (CORM-POM) serta penggunaan sistem permreaktor telah diperkenalkan untuk mengatasi masalah-masalah tersebut. Dalam kajian ini, model penggunaan membran reaktor permselektif hidrogen sebagai pendorong kepada pemindahan keseimbangan dalam proses pembentukan semula  $CH_4-CO_2$  telah dikaji dari segi permodelan. Analisis keseimbangan termodinamik menunjukkan bahawa prestasi proses CORM dipengaruhi oleh suhu, tetapi nisbah produk  $H_2/CO$  didapati sentiasa kurang daripada satu. Akan tetapi, penambahan  $O_2$  ke dalam proses CORM untuk meningkatkan penukaran  $CH_4$  dan penghasilan  $H_2$  serta memperolehi nisbah  $H_2/CO$  yang sama boleh dicapai pada suhu dan nisbah suapan  $CH_4:CO_2:O_2$  yang tertentu. Penyelidikan lanjut telah dijalankan untuk mengkaji penggunaan sistem permreaktor untuk meningkatkan tindakbalas dalam proses CORM. Keputusan keseimbangan dinamik menunjukkan bahawa peningkatan tindakbalas dipengaruhi oleh kuantiti hidrogen yang dikeluarkan dan suhu memainkan peranan yang penting dalam menentukan margin keupayaan peningkatan memandangkan sistem tindakbalas-pemisahan pada 900K memberikan peningkatan tindakbalas yang paling ketara. Selain itu, nisbah produk  $H_2/CO$  dapat diperbaiki sehingga menghampiri satu dalam proses CORM, manakala nisbah tersebut dikekalkan pada 1.0-1.2 dalam kombinasi proses CORM-POM dengan menggunakan sistem permreaktor. Di samping itu, kelajuan ruang merupakan faktor yang penting dalam mengawal tabiat kinetik-pengangkutan dalam sistem permreaktor, manakala pencapaian maksima penukaran serta penghasilan produk adalah dipengaruhi oleh faktor sapu. Keputusan daripada kaedah keseimbangan dinamik dapat disahkan dengan keputusan daripada permodelan kinetik-pengangkutan memandangkan data-data yang diperolehi adalah dalam persetujuan dengan kaedah keseimbangan dinamik. Pendek kata, teknik keseimbangan dinamik boleh dijadikan suatu kaedah diagnostik serta pengoptimalan yang berguna dalam aplikasi membran pemangkinan.

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## LIST OF SYMBOLS

$A$	-	Membrane area
$A_i$	-	Chemical formulas
$A_k$	-	Total number of atomic masses of element $k$
$a_{ik}$	-	The number of atoms of element $k$ present in each molecule of chemical species $i$
$C$	-	Atom carbon
$C_1$	-	Hydrocarbons that content one carbon atom
$C_2$	-	Hydrocarbons that content two carbon atoms
$CH_x$	-	Methyl radical
$D_M$	-	Hydrogen permeability coefficient
$D_0$	-	Pre-exponential term of permeability constant
$\Delta E$	-	Activation energy for diffusion of hydrogen
$F$	-	Reaction flow rate
$F_i$	-	Molar flow rate of component $i$
$F_{\text{Sweep Gas}}$	-	Sweep gas flow rate
$F_{H_2}^t$	-	Hydrogen Molar flow rate in the tube side
$F_{H_2}^s$	-	Hydrogen molar flow rate in the shell side
$f_i$	-	Reactant conversions or product yields
$G^t$	-	Total Gibbs free energy
$\Delta G_f^0$	-	Standard Gibbs energy change
$H$	-	Atom hydrogen
$H_{2, \text{Permeate}}$	-	Amount of hydrogen in permeate zone
$H_{2, \text{Retentate}}$	-	Amount of hydrogen in retentate (reaction) zone
$\Delta H^{\circ}_{298}$	-	Standard heat of formation

$I$	-	Sweep factor
$J_{H_2}$	-	Hydrogen permeation
$K_j$	-	Equilibrium constant for reaction $j$
$k$	-	Kinetic rate constant
$L$	-	The total length of the reactor tube
$n$	-	Total mole in reaction zone
$n$	-	Constant power of the pressure
$n_i$	-	Final mole of species $i$
$n_{i0}$	-	Initial mole of species $i$
$O$	-	Atom oxygen
$P$	-	Pressure
$\Delta P_{H_2}$	-	Hydrogen partial pressure difference at the upstream and downstream of membrane surface
$P_{H_2,Reaction}$	-	Hydrogen partial pressure on reaction side
$P_{H_2,Permeation}$	-	Hydrogen partial pressure on permeation side
$P^\circ$	-	Standard pressure
$P_{Permeation}$	-	Total pressure permeation zone
$P_{Reaction}$	-	Total pressure reaction zone
$R$	-	Universal gas constant
$R_1$	-	The radius of the membrane reactor
$r_i$	-	Net reaction rate of the component $i$
$T$	-	Temperature
$v$	-	Volume
$V_{Reaction}$	-	Reaction flow rate
$W$	-	Catalyst weight
$X_i$	-	Reactant conversion of species $i$
$Y_i$	-	Product yield of species $i$
$y_{H_2,Reaction}$	-	Hydrogen mole fraction in reaction zone
$y_i$	-	Mole fraction of species $i$
$Z$	-	The dimensionless length of the reactor
$\rho$	-	Catalyst bulk density

$v_i$	-	Stoichiometric coefficients
$\sigma$	-	The porosity of the catalyst bed
$\mu_i$	-	Chemical potential
$\varepsilon_j$	-	Equilibrium coordinates of reaction $j$
$\lambda_k$	-	Lagrange multipliers for element $k$
$\delta_M$	-	Membrane thickness
$\eta$	-	Effectiveness Factor

## LIST OF ABBREVIATIONS

ADP	-	Average Deviation Percentage
AME	-	Algebraic Multi-Equation Equilibrium
ATR	-	Autothermal Reforming of Methane
BCM	-	Billion Cubic Meters
CMR	-	Catalytic Membrane Reactor
CNG	-	Crude Natural Gas
CORM	-	Carbon Dioxide Reforming of Methane
CPO	-	Catalytic Partial Oxidation of Methane
DM	-	Dense Membrane Reactor
DME	-	Dimethyl Ether
EE/FSU	-	Eastern Europe/Former Soviet Union
Eq.	-	Equilibrium
ER	-	Equilibrium Reaction
F-T	-	Fischer-Tropsch synthesis
GHSV	-	Gas Hourly Space Velocity
IMR	-	Inert Membrane Reactor
ktoe	-	Kilo tones of oil equivalent
LNG	-	Liquefied Natural Gas
LM	-	Lagrange's Undetermined Multiplier
MeOH	-	Methanol
MTG	-	Methane to Gasoline
PM	-	Porous Membrane Reactor
POM	-	Partial Oxidation of Methane
RWGS	-	Reverse Water Gas Shift
SEP	-	Membrane Separation
SRM	-	Steam Reforming of Methane

TCHP	-	Thermo Chemical Heat Pipe
WGS	-	Water Gas Shift

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## CHAPTER 1

### INTRODUCTION

#### 1.1 General Introduction

Natural gas is a mixture of light hydrocarbons and non-hydrocarbon gases which exists in gaseous state in a separate reservoir inside the earth's crust and is found near or with accumulation of crude oil. This combustible gas contains between 70 to 98% of methane, with higher hydrocarbons (ethane to hexane or short carbon chain paraffin) present in a quantity of up to maximum 16%, while diluents (nitrogen and carbon dioxide) can account to a maximum of 15% (Ross *et al.*, 1996). The precise composition, however, depends on the particular source and nature of the gas. For example, at Natuna Island, Indonesia, vast natural gas reservoirs consist of only 28 mol% of methane and 71 mol% of carbon dioxide (Suhartanto *et al.*, 2001). The principal component of natural gas is methane (CH<sub>4</sub>). This gas is colorless, flammable and odorless. It is formed when plants decay and where there is very little air. Methane is released to the atmosphere via raising livestock, coal mining, drilling of oil and natural gas, rice cultivation and garbage sitting in landfills. This gas stays in the air for only ten years, but it traps twenty times more heat than carbon dioxide.

As mentioned previously, some natural gas reserves are found to contain a high portion of carbon dioxide, such as that found from Natuna Island has been proven to consist of 71% of carbon dioxide and only 28% of methane (Suhartanto *et al.*, 2001). Carbon dioxide is the most prominent greenhouse gas. It is emitted to the

atmosphere as human exhale, burning of fossil fuels for energy, and deforestation activities. Since the Industry Revolution, the concentration of carbon dioxide has been reported to increase exponentially and this causes the global climate to change (Behr, 1998). This global issue has attracted much attention and efforts have been carried out to reduce the emission of greenhouse gases to the air. Generally, this carbon dioxide content in natural gas does not have any significant industrial applications and are released to the atmosphere. Nonetheless, the carbon dioxide is well-known as the major greenhouse gas which contributes to greenhouse effect. Therefore, utilization of carbon dioxide together with methane from natural gas has become an important topic in the current research field. Apart from the cheap and plentiful carbonaceous materials, this process is also beneficial to the environment, whereby it can reduce the global warming issues.

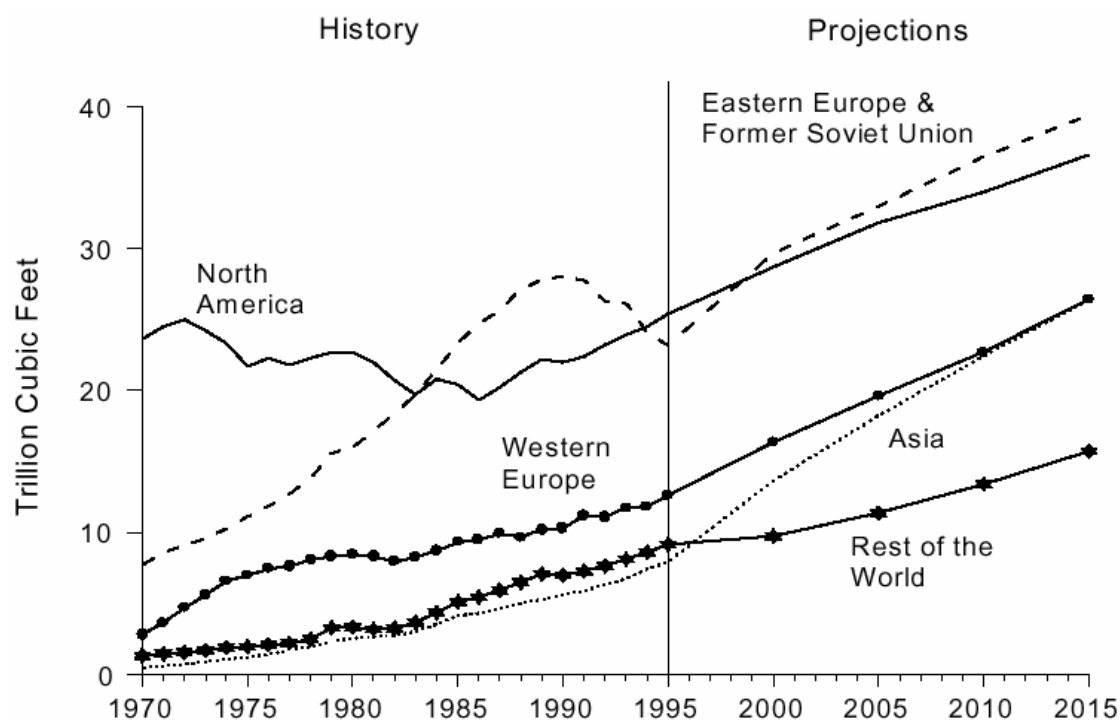
From the economic viewpoint,  $\text{CO}_2$  and  $\text{CH}_4$  are relatively inexpensive due to their natural abundance, extreme thermodynamic stability and extremely low reactivity. Hence, conversion of these two molecules to other chemicals with higher commercial value is of great concern. In this regard, many methods have been introduced in order to reduce the emission of these greenhouse gases to the atmosphere (Seshan and Lercher, 1994; Paul and Pradier, 1994). One of these alternatives is to utilize these greenhouse gases in chemical processes, such as the utilization of  $\text{CO}_2$  and  $\text{CH}_4$  for the production of synthesis gas (syngas).

Syngas (a mixture of hydrogen and carbon monoxides) is a building block in the chemical and petrochemical industries such as for the production of ammonia, methanol, phosgene, acetic acid, oxo-alcohols, and higher hydrocarbons. In some cases, either hydrogen or carbon monoxide is required and this can be acquired from the syngas. For example, the biggest consumer of syngas is for ammonia synthesis, which requires only hydrogen while carbon monoxide is used in the production of paints, plastics, pesticides and insecticides with hydrogen as only a by-product. Thus, the production of synthesis gas from methane and carbon dioxide, also known as Carbon Dioxide Reforming of Methane (CORM) has received strong interests in the past decades and still is an important topic of the current research.

## 1.2 Research Background

### 1.2.1 Methane Utilizations

Natural gas consumption in 2020 is projected to total 162 trillion cubic feet, nearly double the 1999 total of 84 trillion cubic feet (Figure 1.1). The growth of natural gas consumption in developing countries is expected to be significantly greater than in the rest of the world (Energy Information Administration, 2002). The natural gas reserves in Malaysia are estimated around 75 trillion cubic feet or 1.4% of the world natural gas reserves in January 1, 2002, which ranks 14th in the world's largest natural gas reserve list (Energy Information Administration, 2002).



**Figure 1.1** World natural gas consumption, 1970-2015 (Energy Information Administration, 2002)

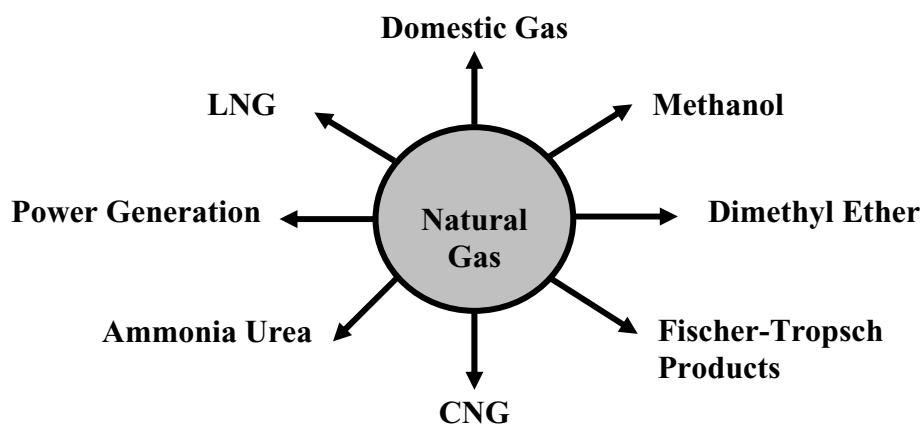
Malaysia has three main sources of natural gas which are all located in South China Sea: from offshore Sarawak, offshore Peninsular Malaysia and offshore Sabah. Malaysia possesses 2,430 BCM of proven natural gas reserves in 1999. Its production has been increasing steadily over decade, reaching 32,942 ktoe in 1999, double from 1989. Malaysia accounted for approximately 17 % of world's total LNG exports in 1999, third after Indonesia (26 %) and Algeria (19 %) (Asia Pacific

Energy Research Centre, 2002). Table 1.1 shows a summary of natural gas utilization across sectors in Malaysia.

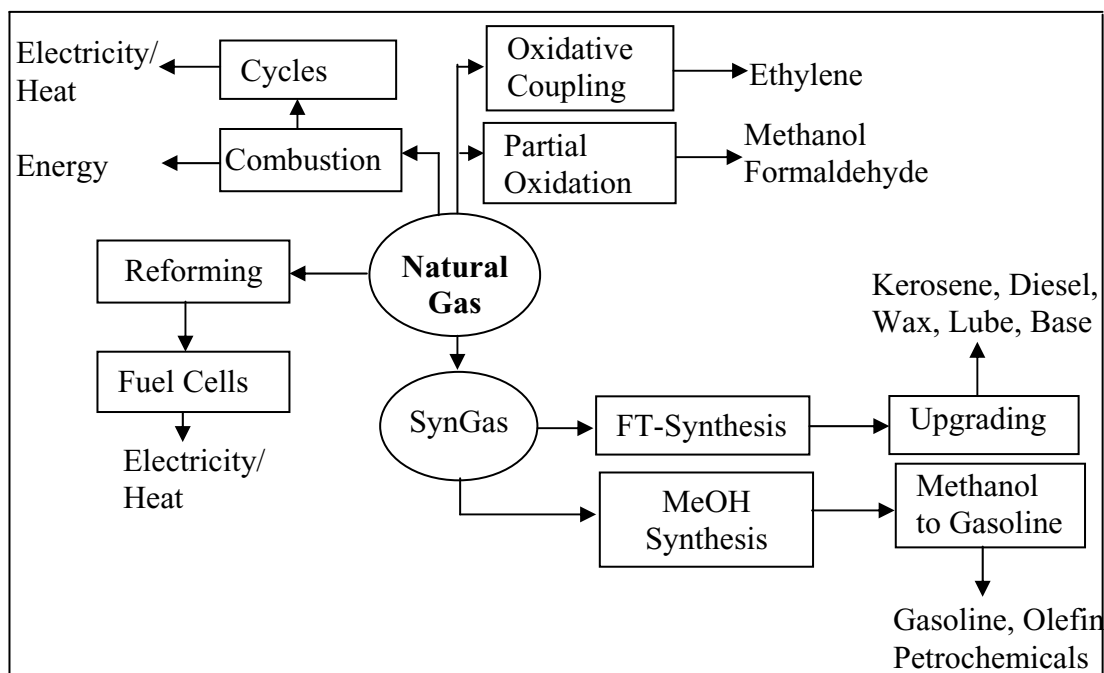
**Table 1.1** : Natural gas consumption in Malaysia in 1999, ktoe

Sector	Consumption (ktoe)	Percentage
Electricity	10,138	61.1 %
Industry Sector	1,701	10.3 %
Residential and Commercial	12	0.1 %
Transport Sector	0	0.0 %
Non-energy (Fertilizer and Petrochemical Feedstock)	1,005	6.1 %
Other	3,727	22.5 %
<b>Total Consumption</b>	<b>16,583</b>	<b>100 %</b>

Currently, the main usage of natural gas is in non-catalytic combustion for heating purposes, while the significant usage in the petrochemical industry is for the production of hydrogen through steam reforming process. According to Ross *et al.* (1996), the routes of methane utilization for the production of useful chemicals can be classified into two categories: direct and indirect. The direct route involved one-step process in which the methane is reacted directly with oxidizing agent to produce the desired product such as C<sub>2</sub> hydrocarbon, formaldehyde, acetic acid, and so on. The indirect route, on the other hand, is a two-step process whereby methane is first converted into synthesis gas, in which the synthesis gas is then further converted into the desired product such as ammonia, methanol, oxo-alcohol, and so on. Figures 1.2 and 1.3 show the general methane utilization option.



**Figure 1.2** Natural gas utilization options



**Figure 1.3** Routes of natural gas utilization (Widodo and Yuswan, 2000)

### 1.2.2 Carbon Dioxide Utilizations

Carbon dioxide is usually considered an undesired material in the waste stream and is a major component of stack gas. Energy conversion processes, which burn fossil fuels such as coal and natural gas and produce electricity and industrial process heat, are responsible for a large proportion of carbon dioxide emissions in industrialized nations. Carbon dioxide gas is an important carbonaceous resource that is found in gas phase or carbonates form. The amount of carbon dioxide consisted in atmosphere is around 0.034 volume percent (v/v %). The estimated total amount of carbon exists as carbon dioxide gas in atmosphere is  $720 \times 10^9$  tones (Behr, 1988). The amount of carbon in atmosphere is always varies because it depends strongly on the natural cyclic and human's activities. Since the Industry Revolution, the concentration of carbon dioxide has been reported to increase exponentially and this causes the global climate to change. According to Behr (1988), the concentration of carbon dioxide in atmosphere has increased from 250 ppm before Industry Revolution to 315 ppm (year 1958) and 340 ppm (year 1984). This global issue has attracted many attentions from delegates from all around the

world and efforts have been carried out to reduce the emission of greenhouse gases to the air.

Carbon dioxide is a non-toxic solid material at temperature of  $-78.9^{\circ}\text{C}$ , and releases  $645\text{kJ/kg}$  of energy when heated from  $-78.9^{\circ}\text{C}$  to  $0.0^{\circ}\text{C}$  (Aresta and Forti, 1986). Besides, carbon dioxide is also a stable chemical up to  $1200^{\circ}\text{C}$ . These characteristics have made carbon dioxide an important chemical for application in the chemical industry. The important utilizations of carbon dioxide include: as refrigerant agent (40%); carbonate drinks (20%); oil recovery enhancement (5-10%); and production of others chemicals. Moreover, carbon dioxide gas also can be used as raw materials for the production of other organic chemicals (Paul, 1994) as follow:

- (a) Hydrogenation of carbon dioxide to methanol.
- (b) Production of urea and its derivatives.
- (c) Formation of organic carbonate cyclic.
- (d) Production of salicylic acid and its derivatives (Aspirin).

### **1.2.3 Combination of Methane and Carbon Dioxide Utilizations**

Many natural gas reserves contain large amounts of carbon dioxide, in addition to  $\text{CH}_4$  and other lower alkanes. There are many natural gas reserves in Southeast Asia, Eastern Europe and North Sea that contain large amount of carbon dioxide (25-75%). For example, at Natuna Island, Indonesia a vast natural gas reservoir with the composition of which is shown in Table 1.2 (estimated total gas volume of 222 trillion cubic feet) lies beneath the sea (Suhartanto *et al.*, 2001). The heating value is too low to be utilized feasibly unless carbon dioxide is removed and this resource is wasted since transportation or separation of carbon dioxide is too expensive. Thus, it would be highly desirable to utilize such low-valued natural gas without emission of carbon dioxide.

**Table 1.2** : Dry composition of Natuna natural gas field (Suhartanto *et al.*, 2001)

Component	(mol %)
Carbon Dioxide (CO <sub>2</sub> )	71.0
Methane (CH <sub>4</sub> ) + C <sub>2+</sub> Hydrocarbons	28.0
H <sub>2</sub> S	0.5
N <sub>2</sub>	0.5

In recent years, considerable attention was paid to global warming due to the greenhouse effect. The reduction and utilization of carbon dioxide and methane (most important greenhouse gases) are therefore becoming increasingly important. Therefore, catalytic reforming of methane with carbon dioxide, which are two of the most abundant carbon-containing materials, into synthesis gas has been proposed as one of the most promising technologies for utilization of these two major greenhouse gases. As a result, carbon dioxide reforming of methane to synthesis gas (Edwards and Maitra, 1995; Ross *et al.*, 1996; Matsuo *et al.*, 2000; Ruckenstein and Wang, 2000; Seok *et al.*, 2002) has received renewed interests from the perspectives of utilization enhancement of natural gas and exploitation of the carbon resources inherently contained in cheap CO<sub>2</sub> and CH<sub>4</sub> into valuable products.

The CORM process is of special interest since it produces synthesis gas with low H<sub>2</sub>/CO ratio. The low H<sub>2</sub>/CO ratio synthesis gas can be preferentially used for production of liquid hydrocarbons in the Fischer-Tropsch synthesis network (Ross *et al.*, 1996; Wilhelm *et al.*, 2001). This reaction has also very important environmental implications because both methane and carbon dioxide are greenhouse gases which may be converted into valuable feedstock. In addition, this process has potential thermochemical heat-pipe applications (Fraenkel *et al.*, 1986; Levy *et al.*, 1993) in the recovery, storage and transmission of solar and other renewable energy resources by using the large amount of heat of reaction produced from this reversible reaction system.

### 1.2.4 Synthesis Gas

Synthesis gas, which is a mixture of  $H_2$  and  $CO$  with different ratios, is an important petrochemical feedstock. Synthesis gas is well known as an important intermediate in petrochemical industries for converting hydrocarbon resources into useful chemicals such as methanol, dimethyl ether, ammonia and so on. In principle, synthesis gas can be generated from any hydrocarbon feedstock. This is reflected in industrial practice, which includes large-scale syngas production from a wide variety of materials such as natural gas, naphtha, residual oil, petroleum coke and coal (Wilhelm *et al.*, 2001). The syngas cycle closed is illustrated in Figure 1.4 (Rostrup-Nielsen, 2002).

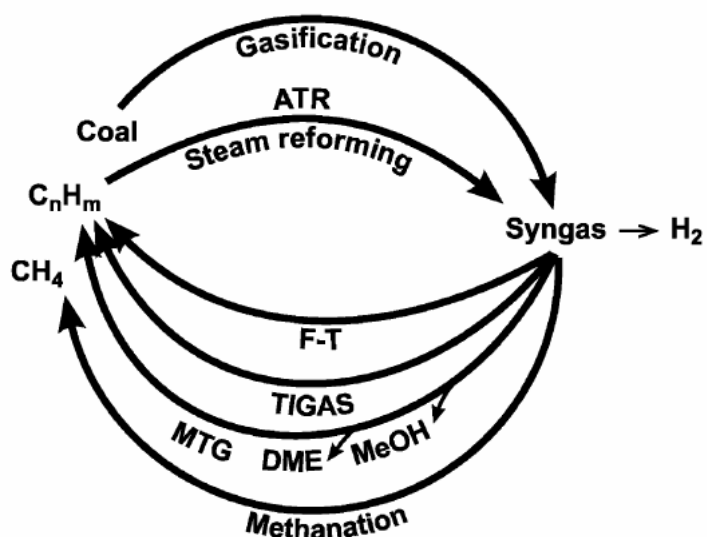


Figure 1.4 The syngas cycle

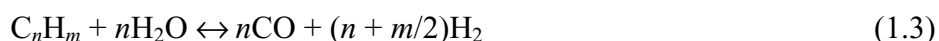
#### 1.2.4.1 Syngas Productions

The conversion of hydrocarbons to hydrogen and synthesis gas will play an important role in the 21st century ranging from large gas to liquid plants and hydrogen plants for refineries to small units providing hydrogen for fuel cells. Another trend is the conversion of natural gas into transportation fuels such as methanol, DME, synthetic gasoline, and diesel. The synthesis gas can be obtained



from reforming of natural gas with either steam or carbon dioxide, or partial oxidation (Tsang, *et al.*, 1995; Ross *et al.*, 1996; Sung, 1997; Aasberg-Petersen *et al.*, 2001; Wilhelm *et al.*, 2001; Joensen and Rostrup-Nielsen, 2002):

**1) Steam Reforming of Methane (SRM):**



**2) Partial Oxidation of Methane (POM)**



**3) Autothermal Reforming of Methane (ATR)**



**4) Carbon Dioxide Reforming of Methane (CORM)**



**Table 1.3 :** Composition, use and reaction of syngas (Gallardo and Abella, 2000)

H <sub>2</sub> /CO Ratio	Application	Reaction
>3	Hydrogen, Ammonia	Steam Reforming
3	Methanol	Steam Reforming
2	Alkanes, Fischer-Tropsch Synthesis	Partial Oxidation
1	Oxoalcohols, Polycarbonates, Formaldehyde, Pure CO	Carbon Dioxide Reforming

**a) Steam Reforming of Methane**

Steam reforming is the current dominant commercial method and most widely used process in the production of syngas from methane. This process is also well known as wet reforming of methane process due to the presence of steam in the

reaction. The important pathways of steam reforming reactions are as shown in Equations (1.1)-(1.3) (Sung, 1997). Equation (1.1) represents the endothermic steam reforming reaction where synthesis gas with 3:1 H<sub>2</sub>/CO ratio is produced. Equation (1.2) shows the exothermic water gas shift reaction, which produced CO<sub>2</sub> and H<sub>2</sub>. Meanwhile, Equation (1.3) indicates the steam reforming of higher hydrocarbons, which are present in small quantities in natural gas. In recent years, steam reforming technology has shown much progress, resulting in cheaper plants due to better materials for reformer tubes, better control of carbon limits, and more effective catalysts and process concepts with high feedstock flexibility (Rostrup-Nielsen and Alstrup, 1999; Rostrup-Nielsen, 2000).

### **b) Partial Oxidation of Methane**

The predominant commercial technology for syngas generation has been, and continues to be, steam reforming of methane, in which methane and steam are catalytically and endothermically converted to hydrogen and carbon monoxide. An alternative approach to this is partial oxidation, the exothermic reaction of methane and oxygen to produce synthesis gas. Partial oxidation of methane process may represent the ideal solution for many of chemicals production, especially for Fischer-Tropsch synthesis. This “dream reaction” has the right ratio of H<sub>2</sub>/CO = 2 and a very low heat of reaction comparable to that of the CORM and SRM. Partial oxidation reactions may be carried out either by catalytic partial oxidation or by non-catalytic partial oxidation.

The non-catalytic partial oxidation needs high temperature to ensure complete conversion of methane and to reduce soot formation. Some soot is normally formed and is removed in a separate scrubber system downstream of the partial oxidation reactor. The thermal processes typically resulted in a product gas with H<sub>2</sub>:CO = 1.7-1.8. Catalytic partial oxidation has been a subject to intensified research efforts in recent years. In catalytic partial oxidation reaction, the process is initiated catalytically (flameless) as opposed to ATR and POM. It has been shown that under extremely short residence times, in the order of milliseconds, methane may be partially oxidized forming H<sub>2</sub> and CO as the main products (Bodke *et al.*, 1998; Basini *et al.*, 2001).

### c) Autothermal Reforming of Methane

Autothermal reforming of methane is a process that combines partial oxidation reaction with catalytic steam reforming reaction in one reactor. The process is called “autothermal” because the endothermic reforming reactions proceed with the assistance of the internal combustion (or oxidation) of methane. Autothermal reforming of methane process has been used for industrial synthesis gas production since the late 1950s. However, new developments have been made in the 1990s, including operation at low steam to carbon ratios and development of new burner designs ensuring safe operation and high on-stream factors (Aasberg-Petersen *et al.*, 2001). For large scale Fischer-Tropsch units, ATR appears to be fulfilling the requirements of H<sub>2</sub>/CO ratio close to two (Rostrup-Nielsen, 2000).

### d) Carbon Dioxide Reforming of Methane

Carbon dioxide reforming of methane was investigated by Fischer and Tropsch in 1928 and has been practiced for decades. The major difference between CORM from other syngas production reactions is the introduction of carbon dioxide as oxidant rather than steam and oxygen. At the same time, CORM reactions allowed the production of syngas with lower H<sub>2</sub>/CO ratios (closed to unity) compared to other reactions. It may be argued that CO<sub>2</sub>-reforming of methane would be better than steam reforming to meet the required syngas compositions. However, CO<sub>2</sub>-reforming (or “stoichiometric reforming”) is rarely feasible due to the cost of CO<sub>2</sub> available. In addition, the economic pressure (20-40 bar) applied in the syngas plant resulted in non-complete conversion of methane due to pressure and thermodynamics factors (Rostrup-Nielsen, 2000).

**Table 1.4 :** Comparison of syngas generation technologies (Wilhelm, 2001)

<b>Technology</b>	<b>Advantages</b>	<b>Disadvantages</b>
SRM	<ul style="list-style-type: none"> <li>• Most extensive industrial experience</li> <li>• Oxygen not required</li> <li>• Lowest process temperature requirement</li> <li>• Best H<sub>2</sub>/CO ratio for hydrogen applications</li> </ul>	<ul style="list-style-type: none"> <li>• H<sub>2</sub>/CO ratio often higher than required when CO is to be produced</li> <li>• Highest air emissions</li> </ul>
ATR	<ul style="list-style-type: none"> <li>• Natural H<sub>2</sub>/CO ratio often is favorable</li> <li>• Lower process temperature requirement than POM</li> <li>• Syngas methane content can be tailored .</li> </ul>	<ul style="list-style-type: none"> <li>• Limited commercial experience</li> <li>• Usually requires oxygen</li> </ul>

by adjusting reformer outlet temperature

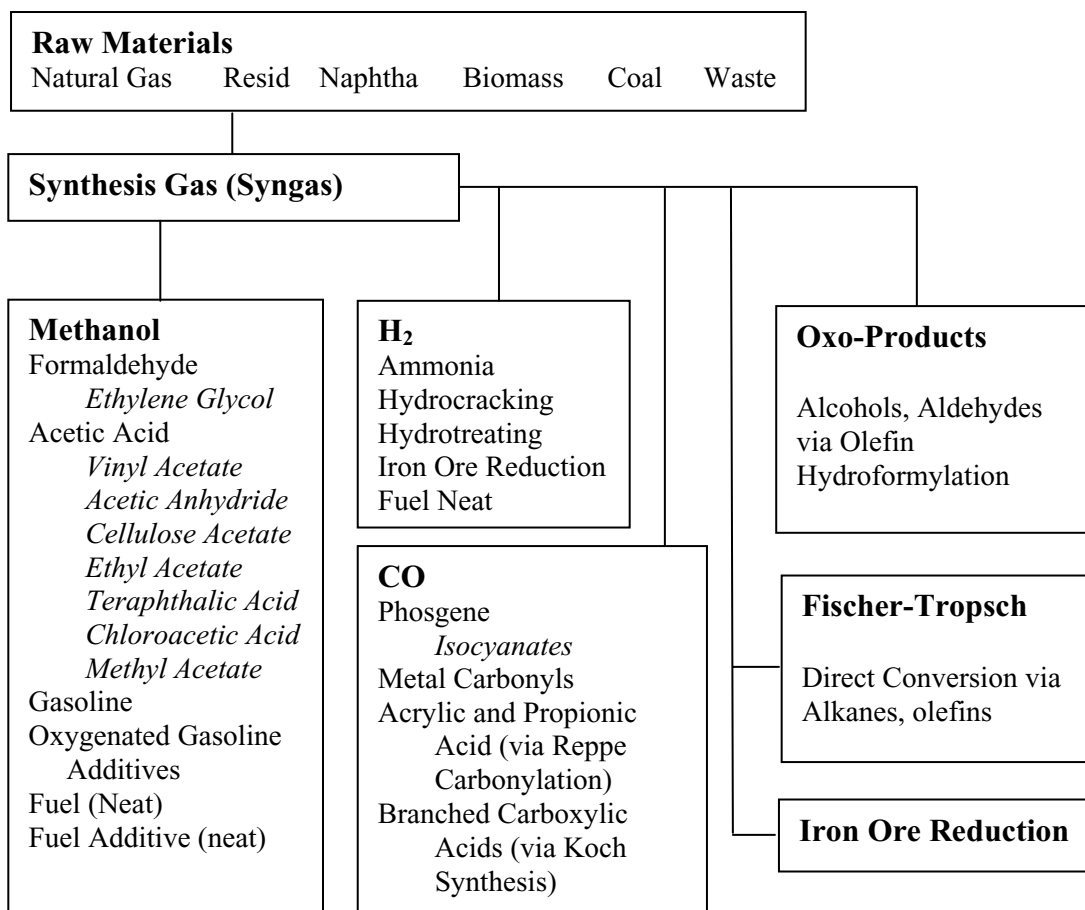
POX	<ul style="list-style-type: none"> <li>• Feedstock desulfurization not required</li> <li>• Absence of catalyst permits carbon formation and, therefore, operation without steam, significantly lowering syngas CO<sub>2</sub> content</li> <li>• Low methane slip</li> <li>• Low natural H<sub>2</sub>/CO ratio is an advantage for applications requiring ratio &lt; 2.0</li> </ul>	<ul style="list-style-type: none"> <li>• Low natural H<sub>2</sub>/CO ratio is a disadvantage for applications requiring ratio &gt; 2.0</li> <li>• Very high process operating temperatures</li> <li>• Usually requires oxygen</li> <li>• Syngas methane content is inherently low and not easily modified to meet downstream processing requirement</li> </ul>
CORM	<ul style="list-style-type: none"> <li>• Utilization of cheaper and plentiful carbonaceous sources.</li> <li>• H<sub>2</sub>/CO ratio more appropriate for Fischer-Tropsch synthesis</li> <li>• Provides an interesting route to utilize the CO<sub>2</sub>-rich gas field</li> </ul>	<ul style="list-style-type: none"> <li>• Limited commercial experience</li> <li>• Very high process operating temperatures</li> <li>• Greater amount of carbon are fed, catalyst coking become more severe</li> </ul>

#### 1.2.4.2 Syngas Utilizations

The oil crisis in 1973 has demonstrated the danger and disadvantages of human on relying too firmly on a single raw material. Nevertheless, the feedstock diversification for the petrochemical industry around the world is still limited after 30 years from the oil crisis. Currently, 86% of all petrochemicals are derived from oil, while only 9% from natural gas and 5% from coal have been reported (Wittcoff, 1996). Thus, the feedstock diversification for petrochemical industry has become increasingly critical, indicating the depletion of global fossil reserves and enduring future supply shortage.

Among the most successful integration of new raw materials and development of new processes, which can deliver the same petrochemical products as efficiently as established pathways has been the production of synthesis gas or syngas (Tsang, 1995). Syngas is an important intermediate for converting an array of hydrocarbon resources such as natural gas into valuable chemicals. Furthermore, syngas and its pure constituents are precursors for a myriad of chemicals including methanol, ammonia, aldehydes and alcohols from hydroformylation, alkanes and olefins from Fischer-Tropsch synthesis (Tsang, 1995; Verykios, 2002; Ross *et al.*, 1996; Froment, 2000). Substantial progress has been made to develop processes

which directly transform syngas into end-use products (e.g. acetic acid, ethylene glycol), circumventing methanol production as an intermediate step (Ross *et al.*, 1996). Thus, syngas consumption and production is expected to continue to grow in the near future. Figure 1.5 shows the overall schematic of the syngas utilizations (Raybold, 2000).



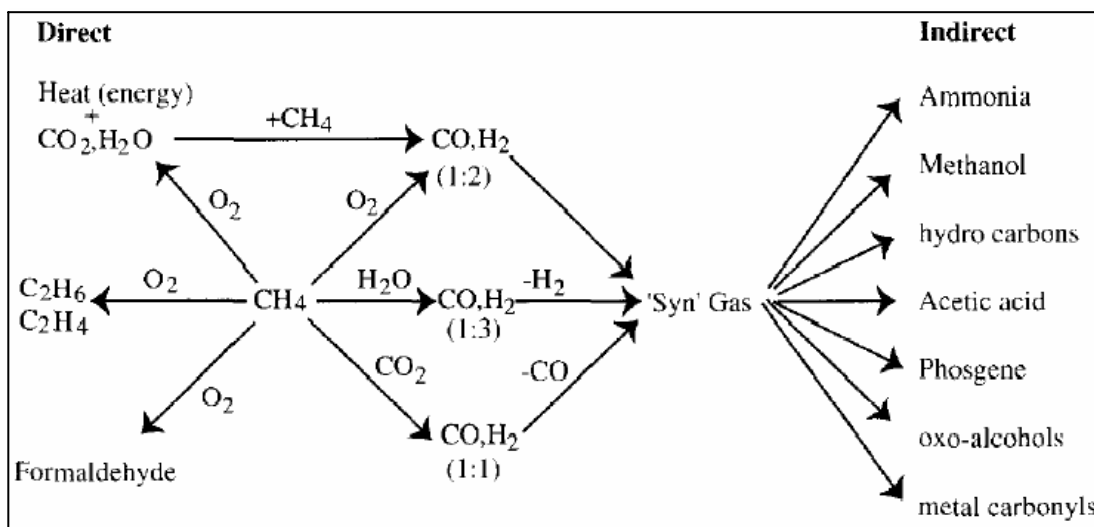
**Figure 1.5** Current sources and utilizations of synthesis gas

## 1.2.5 Carbon Dioxide Reforming of Methane

### 1.2.5.1 The Chemistry of CORM Process

Currently, the main usage of natural gas is in (non-catalytic) combustion for heating purposes, while the only significant consumption in the petrochemical industry is for the production of hydrogen through steam reforming. Ross *et al.*

(1996) have summarized various chemicals which can be produced from natural gas together with the reaction pathways involved in these conversions, as shown in Figure 1.6. However, only 20% of carbon dioxide is utilized in materials for the production of other organic chemicals (Aresta and Forti, 1986; Paul, 1994).



**Figure 1.6** Various direct and indirect routes for the production of natural gas (Ross *et al.*, 1996)

Since methane and carbon dioxide are well-known as most plentiful and cheapest carbonaceous material, utilization of these two molecules has received much attention from research studies. The development of new routes for effective utilization of methane and carbon dioxide is of great interest in the chemistry field. Even though research into the CORM reaction has commenced since 1920s, it has recently attracted renewed interest. Initially, this renewed interest was caused by a belief that the reaction offered a potential method of reducing the concentration of CO<sub>2</sub> emitted to the atmosphere and also introduced a new plentiful carbonaceous resource for the petrochemical industries feedstock. This reaction has an advantage in the production of synthesis gas as well as in the elimination of greenhouse gases. Besides, the CH<sub>4</sub> reforming by CO<sub>2</sub> possess a special characteristic from an industrial perspective due to its capability in producing synthesis gas at low hydrogen to carbon monoxide ratio, which can be preferentially used for Fischer-Tropsch synthesis. Furthermore, both CH<sub>4</sub> and CO<sub>2</sub> are the cheapest reactants and most abundant carbon-containing materials. Therefore, it is not surprise that this reaction is gaining

more and more attention in the catalytic field research nowadays (Wang and Lu, 1998; Seok *et al.*, 2001; Kim *et al.*, 2002; Li *et al.*, 2004).

Although noble metals have been employed successfully as catalysts in this reaction in terms of activity and selectivity, cost and limited availability of these metals, however, deterred their widespread applications in the industrial field. A possible substitute for these noble metals is nickel, which is relatively inexpensive and has been known to yield high activities in this gas forming reaction. However, studies have indicated that nickel tend to deactivate more rapidly than noble metals. Therefore, researchers are constantly trying to modify nickel catalyst in order to improve its performance while at the same time, seeking discovery of new high performance catalysts. Meanwhile, a literature review on the catalysis of CORM process shows that Group VIII metals are effective catalysts for this reaction after which they are distributed in reduced form on suitable supports (Wang and Ruckenstein, 2000; Wang and Lu, 1996; Froment, 2000; Seung *et al.*, 2002). In the latter case, emphasis should be on developing catalysts that are capable of carbon-free operation under practical reaction conditions. To date, alumina and magnesia or combinations thereof are the most promising substances among the various supports that had been studied (Seok *et al.*, 2002; Zhang *et al.*, 2002).

Analysis on the reaction mechanism indicates that the most effective catalysts for this CORM process are those of metal-support combinations, which actively dissociate  $\text{CH}_4$  into  $\text{CH}_x$  residues including carbon, whilst at the same time, activate  $\text{CO}_2$  to generate CO and an adsorbed O species on the catalyst surface. The O produced is then consumed in the conversion of  $\text{CH}_x$  and C to CO. However, there still exists a major problem from the application of these metal-support catalysts in this process, which is the net of carbon formation. This occurs when the dissociation of  $\text{CH}_4$  and the activation of  $\text{CO}_2$  steps are out of balance. Considering the current status of catalyst development and the likely future large-scale applications of CORM process, efforts to optimize both the catalysts performance and reactor design are undoubtedly to become a significant study in the future works.

### 1.2.5.2 Current and Potential Applications

The CORM process has to date had no significant commercial application by itself. However, there is now increasing interest in  $C_1$ -chemistry to produce chemicals reactions for the thermochemical storage and transmission of renewable energy sources such as solar energy. Hence, this process is likely to become an increasingly important industrial reaction in the future. This catalytic carbon dioxide reforming of methane into synthesis gas which utilizes those abundant materials is gaining more and more attention nowadays following the great advantages as follow (Edwards and Maitra, 1995; Hung, 1996; Seung *et al.*, 2002; Verykios, 2002):

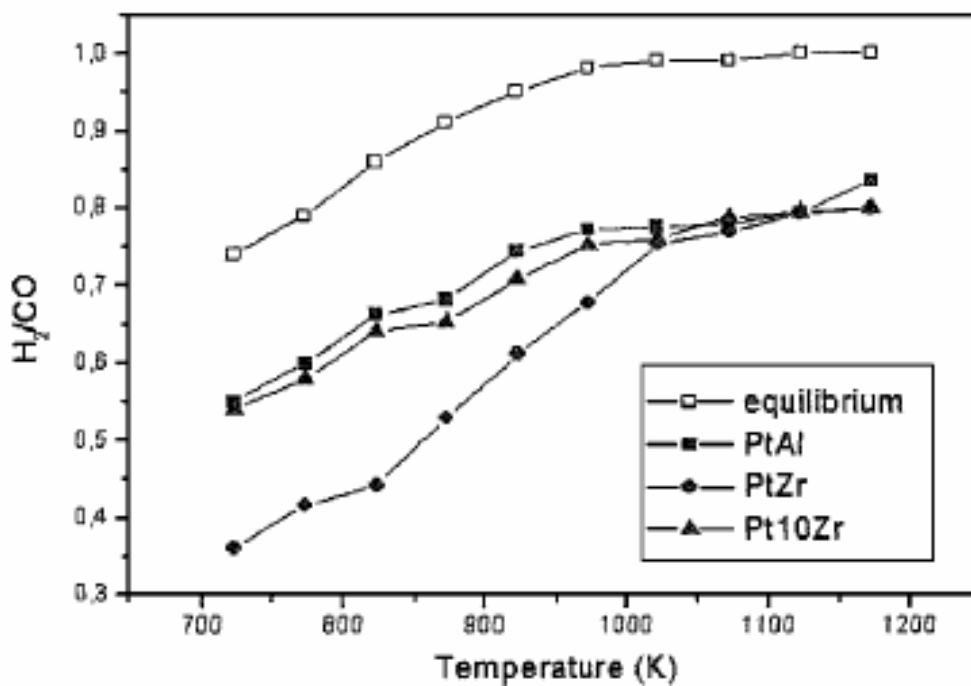
- 1) From the environmental point of view, this reaction plays a vital role whereby it consumes both methane and carbon dioxide, thus reducing the risk of global warming. These natural gases, which are well known as potential “greenhouse gases” and acting as important carbonaceous sources, can be converted into valuable feedstock instead of being emitted to the atmosphere and consequently causing the global warming issue.
- 2) This reaction is capable in producing a product mixture with low ratio of  $H_2/CO$  (1:1). This ratio is desirable for direct use as feedstock for the production of many useful chemicals, such as Fisher-Tropsch process.
- 3) This endothermic and reversible reaction is applied in the chemical energy transmission systems, in which a power source is used to drive the endothermic reaction while the product gases are transported to consumers at remote areas, where the methanation reaction can be performed.
- 4) There are immense natural gas reserves in Eastern Europe, the North Sea, Southeast Asia, and other places that contain large amounts of  $CO_2$ . The heating value of these natural gas resources is very low that transportation and utilization are unfeasible unless the  $CO_2$  is removed. The CORM process can convert those untapped resources to syngas for subsequent production of transportable energy liquids.
- 5) This process can directly convert landfill gas, which commonly consists of equal amount of  $CH_4$  and  $CO_2$ , to valuable syngas.



During the last several years, there has been increasing concern about the need to develop an energy conversion and utilization strategies, which can reduce the emission of CO<sub>2</sub> to the atmosphere. The CORM process has since attracted much attention since it involves the consumption of CO<sub>2</sub> in the production of synthesis gas and this CO<sub>2</sub> could in principle be derived from a source, which would otherwise be emitted directly to the atmosphere. The synthesis gas produced from this process is long known as an important feedstock for the production of chemicals and fuels. Another latest usage for this process is in the case of solar-based energy storage and transmission applications (Seung *et al.*, 2002; Edwards and Maitra, 1995; Verykios, 2002).

#### **1.2.5.3 Process Limitations**

The uniqueness of the CORM process is the applicability to utilize methane and carbon dioxide to produce syngas with H<sub>2</sub>/CO unity ratio which is favorable for both economic and environment benefits. However, although intensive efforts have been focused on CORM, this process still has not reached commercialization level due to the following limitations: (1) It is an intensively endothermic reaction which required extremely high operating temperature (>700K) that consumes much energy (Halliche *et al.*, 1996; Lemonidou and Vasalos, 2002; Wilhelm *et al.*, 2001); and (2) The unavoidable water formation as undesirable side product which indirectly reduced the syngas selectivity and the final H<sub>2</sub>/CO product ratio (Bradford and Vannice, 1996; Wang and Ruckenstein, 2000). Thus, these problems must first be overcome before it is applicable for commercialization purpose.



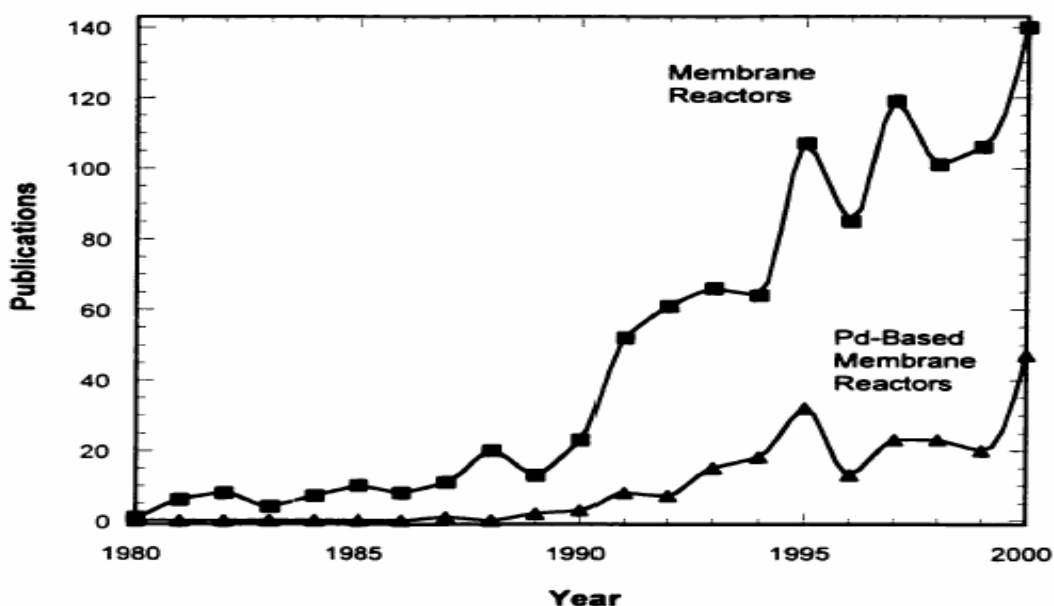
**Figure 1.7** Experimental laboratory and equilibrium results on the  $H_2/CO$  product ratio of  $CO_2/CH_4$  reforming as a function of temperature (Souza *et al.*, 2001)

In the meantime, the growing interest in recent study on CORM in order to overcome these problems are: (1) the addition of oxygen (also well-known as combined carbon dioxide reforming and partial oxidation of methane (combined CORM-POM)) to improve the methane conversion and syngas ratio (O'Connor and Ross, 1998; Larentis *et al.*, 2001; Tomishige *et al.*, 2004); and (2) introduction of permreactor system to overcome thermodynamic limitation and suppress undesirable side reactions (Prabhu *et al.*, 1999; Onstot *et al.*, 2001; Ferreira-Aparicio *et al.*, 2002). The past decade has experienced growing interest in these developments and intensive studies are still necessary to obtain more relevant results for future commercialization purpose.

### 1.2.6 Membrane Catalysis

A membrane reactor is a unit where chemical reaction and separation process take place simultaneously. Membrane catalysis refers to the application of membrane reactor in catalysis systems. The driving forces behind the interest in

membrane catalysis continue to be the use of membranes to catalyze reactions and also to carry out important separations. For the last 10 years, there is increasing number of publications on research on membrane reactor. This shows that membrane reactor is starting to gain more essential role in the research field. In terms of membrane catalysis, membranes are generally activated with catalysts in a reaction system (Winston and Sirkar, 1992) by: a) Impregnating porous films with catalysts solutions; b) Entrapping the catalyst with the membrane; c) Dispersing or adsorbing a catalytic species throughout the membrane matrix; d) Depositing a normally heterogeneous catalyst on the exterior and/ or interior surface of a membrane; and e) Covalently attaching a normally soluble catalyst to the pore wall surface of membrane.



**Figure 1.8** Number of annual membrane reactor and Pd-based membrane reactor publications over the past 20 years (Raybold, 2000)

Table 1.5 summarizes the current status of a variety of membrane materials potentially useful for membrane catalysis. The relative permselectivity features are shown with some indication of the crucial limitations to the application of these membrane devices. The final column of Table 1.5 summarizes the commercial availability of the membrane themselves. This last column does not refer to the status of their uses as a membrane reactor but simply to the availability of the membrane so that others can evaluate it in membrane reactor configurations.

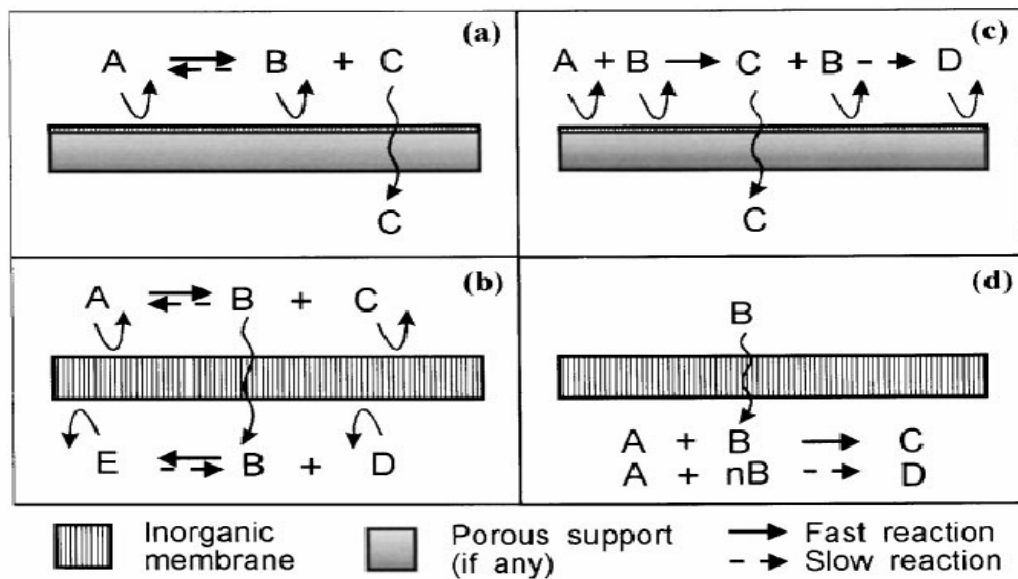
**Table 1.5** : Types of material for membrane reactors (Armor, 1995)

Type	Permselective	Limitation	Status
• Polymer	Yes	Temperature	Commercial
• Zeolite in Polymer	No	Temperature	Development
• Permselective metal	Yes	Brittle, Cost, etc.	Commercial
• Solid inorganic oxide	Yes	Need lower Temp	Development
• Porous oxide	No	Thermal stability	Commercial
• Thin coating on any above	Yes/No	Thickness, durability	Fundamental Research

### 1.2.6.1 Advantages of Membrane Catalysis

Three major areas of applications of membrane reactors are listed as follow (Saracco *et al.*, 1999):

- 1) *Yield-enhancement of equilibrium-limited reactions*: a reaction product is selectively permeating through the membrane, thereby enhancing the per-pass conversion compared to conventional fixed-bed reactors; coupling of reactions at opposite membrane sides has also been envisaged in this context (Figure 1.9b).
- 2) *Selectivity enhancement*: accomplished by selective permeation (Fig. 1.9c) or controlled addition (Fig. 1.9d) of a reactant through the membrane.
- 3) *New emerging application opportunities*: a number of potential applications (membrane reactor with separate feed of reactants, catalytic filters and traps, slurry membrane reactor, etc.) are investigated recently, which do not require membrane permselectivity to gases and therefore appear to be closer to industrial success.



**Figure 1.9** Prevalent application opportunities of inorganic membrane reactors

Basically, membrane reactors offer more advantages over conventional fixed bed reactors. These advantages include higher energy efficiency, lower capital and operating cost, and ease of scale up. Promising benefits that are not readily realized with conventional reactor geometries (Winston and Sirkar, 1992) include:

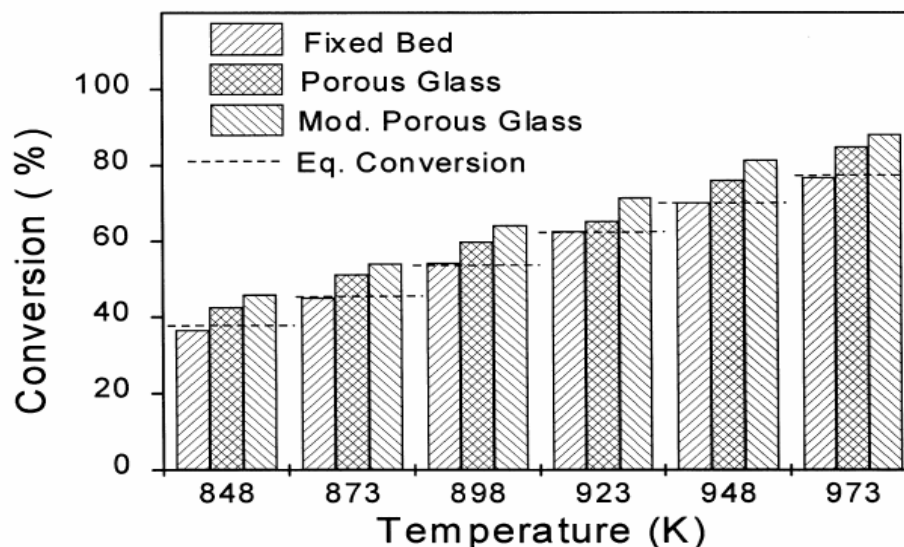
- a) Efficient multiphase contacting.
- b) Elimination of diffusional resistance in rapid reaction
- c) Integration of separation and purification steps with catalyst reaction.
- d) Integration of heat exchange with catalytic reaction.
- e) Displacement of unfavorable equilibria limitation.
- f) Controlled contact of incompatible coreactant.
- g) Elimination of undesirable side reaction.
- h) Amelioration of catalyst poisoning.
- i) Control of reaction pathway in complex network.

A permselective membrane reactor is used to remove product from the reaction zone as it forms. This can be beneficial to an equilibrium-limited process (e.g. CORM process) by allowing higher one-pass reactor conversions to be achieved, and decreasing reaction temperature in endothermic reaction, as well as by simplifying downstream recovery and purification steps (Kikuchi, 1995). Based on this concept, many works have been reported on hydrogen-permselective reactors for

the production of high purity hydrogen (Armor, 1995; Kikuchi, 1995; Galuszka *et al.*, 1998). The interest in application of high-temperature (ceramic) membrane reactors is still growing. Methane reforming reactions are reversible and thus, the conversion is limited by thermodynamic equilibrium. A shift in attention can be noticed from improving of equilibrium limited reactions via membrane separation of one of the products, towards selectivity increase and dosing of reactants via membranes. Attempts to improve permselectivity have been undertaken for all types of the membranes applicable in high-temperature reactors. Several major advantages of membrane reactor application in the CORM process will be discussed in the following section.

#### **1.2.6.2 Reactant Conversion Enhancement**

CORM process is well known as a high endothermic reversible reaction. This high endothermic reaction needs high operating temperature in order to achieve commercial acceptable conversion of reactants. The conversion of methane in CORM process in the conventional fixed-bed mode of operation is limited by the reversibility of the reforming reaction (Prabhu and Oyama, 2000). For such reversible reactions, preferential removal of one or more of the products during reaction will cause a shift in equilibrium, thereby overcoming the thermodynamic limitations. Figure 1.10 indicates that the conversion of methane in porous glass and modified porous glass membrane reactor is higher compared to conventional fixed-bed reactor. For the application of membrane reactor in CORM process, hydrogen will be continuously removed from the reaction system, which will disturb the equilibrium state of reaction. As pointed out by Le Chatelier's principle, the removal of product from a system at equilibrium will shift the reaction to the right hand side and consequently, more reactants are converted to products. In other words, the removal of hydrogen from the reaction system will lead to an increase in the reactant conversions.



**Figure 1.10** Comparison of methane conversion in three different reactor configurations (Prabhu and Oyama, 2000)

### 1.2.6.3 Product Yield Enhancement

The most common application of membrane reactors lies in the circumvention of a chemical equilibrium so as to achieve higher per-pass conversions by selective permeation, through the membrane, of at least one of the reaction products (Fig. 1.9a). The major potential candidates for such application of inorganic membrane reactors are in the dehydrogenations process. Since dehydrogenation reactions are mostly endothermic, conversion is favored at high temperatures at the price of significant occurrence of side reactions, which reduce selectivity and lead to catalyst deactivation by coking. By using a membrane reactor, equal conversions could be obtained at lower temperatures, thereby suppressing undesired reactions. Furthermore, since dehydrogenations imply an increase of the overall number of gas molecules of the system, they can be forced to high conversions by reducing the operating pressure, which entails comparatively high reactor volume. Moreover, the permeated reaction product can be recovered in a quite pure form. However, if the membrane is not permselective enough, the conversion increment remains limited by the permeability of the reactants, which also affects the purity of the product.

With regard to catalysis, the opportunity still exists in using a membrane to enhance certain reactions by disturbing the equilibrium product selectivity, thus shifting the steady-state concentration of reactants and products away from an otherwise unfavorable equilibrium over working catalyst. With permselective inorganic membrane, one can also generate pure, permeated gas having some potential by-product value. Referring to Le Chatelier's principle again, by removing the product from a system at equilibrium, the reaction is shifted to the right hand side and consequently leads to more product formation. Thus, the yield of hydrogen will be improved and at the same time increasing the conversion of the reactants.

#### **1.2.6.4 Product Selectivity Enhancement**

The improvement of reaction selectivity is another application of membrane reactors which most of the researchers are focusing to nowadays. A permselective membrane refers to a membrane that could allow permeation of an intermediate product while rejecting either reactants or other undesired products (Fig 1.9c). In the case of CORM process, the major problem is the reduction of hydrogen selectivity caused by the RWGS reaction. By continuous removal of hydrogen along the reaction, the selectivity of hydrogen will increase due to the suppression of the RWGS reaction.

Another method to increase the reaction selectivity is by controlling the addition of a reactant along the reactor. This can be done through either oxygen or hydrogen permselective membrane, which is known to be able to drive certain partial oxidations or hydrogenations to achieve higher product selectivities. This is applicable in CORM process by controlling the addition of carbon dioxide along the reactor into the reaction system. The major advantage of this application is the reduction of RWGS reaction since the concentration of carbon dioxide is very low in the system. At the same time, this also helps to increase the selectivity of the desirable products ( $H_2$  and  $CO$ ) in the CORM process.



### 1.2.6.5 New Emerging Application Opportunities

Another potential application of membrane reactor is the controlling of reactant(s) introduction into the reaction system when the reactants need to be supplied into the system separately. In this reactor, different reactants are fed separately at the two sides of a catalytically active membrane. Since the reaction rate is higher than the transport rate inside the membrane, the reaction takes place in a small zone or a plane. Changing the reactant concentrations outside the membrane will result in shifting the position of the reaction plane to a new location where transport rates to the reaction plane are again matched by the reaction stoichiometry (Saracco *et al.*, 1999). According to Prabhu *et al.* (1999), this application of membrane reactor system in high temperature process (e.g. CORM process) also helps to reduce hot spots in the catalyst bed and avoid undesirable side reactions.

## 1.3 Problem Statements

Despite the great advantages offered by these developments, there are still many areas of uncertainty and these problems need to be solved before this application can be proceed commercially. Many researchers are still competing to search for solutions to overcome several significant problems as stated below:

1. The CH<sub>4</sub>-CO<sub>2</sub> reforming reactions are highly endothermic that possess very high energy consumption. The current catalyst is not able to achieve conversion over 80% unless in extreme temperature conditions (> 800° C).
2. The combined carbon dioxide reforming and partial oxidation of methane is in early research stage and the understanding of the effects of operation parameters (CH<sub>4</sub>:CO<sub>2</sub>:O<sub>2</sub> contents and temperatures) are still uncertain.
3. Permreactor system exhibits very promising potential in promoting greater reaction enhancements. However, the study on CH<sub>4</sub>-CO<sub>2</sub> reforming is still lacking in literature. Additionally, the design of permreactor system received less attention as many researches have only investigated the appropriateness of the catalyst for permreactor operations.

## 1.4 Hypotheses

A membrane reactor is a unit where chemical reaction and separation process take place simultaneously. For the last 10 years, there is increasing number of publications on research regarding membrane reactor development, especially for high endothermic and reversible reactions. This is because application of membrane reactor for equilibrium-limited reaction such as CORM process has been proven to be able to enhance the reactants conversion and product selectivity. According to Le Chatelier's principle, preferential removal of one or more products from the reaction zone at equilibrium will shift the reaction to the right hand side and consequently, more reactants are converted to products. In addition, this removal of desirable products from reaction zone also helps in products selectivity and yield enhancement. Besides, products removal from reaction zone is able to suppress occurrence of side reactions. Following this, few hypotheses have been outlined in this research, which include:

1. Additional of oxygen into CORM process can increase the methane conversion and improve the syngas ratio.
2. Application of hydrogen permselective membrane reactor can further improve the conversions and syngas yields by suppressing the effect of water formation and other side reactions
3. Alteration of sweep factor offers the possibility to achieve same conversion and yield values from conventional reactor at lower temperature using permreactor system.

## 1.5 Objectives

In recent years, there are increasing interests in the development of membrane reactor system for reversible and high endothermic reactions. In order to overcome the problems as listed in the previous problem statements, considerable research efforts in the application of permreactor systems in thermodynamic equilibrium limited processes have been carried out in the past few years and very promising

results have been claimed through these works. This is because with proper permreactor design, the reactant conversions and product yields can be enhanced and achieved higher reaction performance. Nonetheless, reports on permreactor applications for CORM process is still lacking in literature, whereas research in permreactor application for combined CORM-POM process is a novel approach. Consequently, the main purpose of the present study is to conduct simulation study to analyze the CORM and combined CORM-POM reactions using hydrogen permreactor system. The objectives of this research are:

1. To investigate the effects of oxygen addition in CORM process using thermodynamic equilibrium approach.
2. To study the dynamic equilibrium compositions of CORM and combined CORM-POM with hydrogen permselective membrane reactor.
3. To examine the influences of permreactor parameters (permselective area, sweep factor and space velocity) on the CORM reaction enhancements based on dynamic equilibrium approach and reaction kinetic modeling.

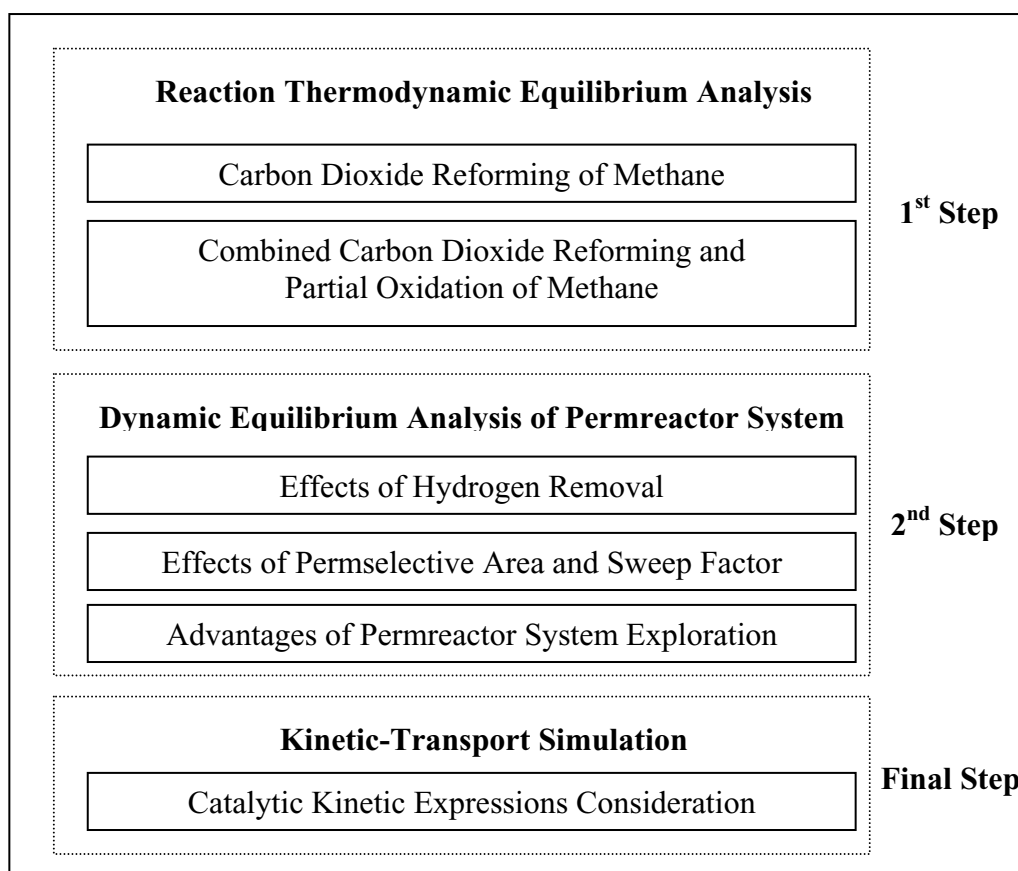
## **1.6 Scope of the Study**

Generally, this study is divided into three parts. The initial part is to conduct a thermodynamic equilibrium analysis on CORM and combined CORM-POM reactions. Due to the complexity of the multi-reaction network, the Gibbs free energy minimization method using Lagrange's undetermined multiplier is used. The applicability of this approach will be determined throughout this part. The effects of reactant feed ratios and operating temperatures on CORM and the effects of oxygen addition on combined CORM-POM have been studied from the point of reaction equilibrium compositions. Consequently, the appropriate conditions for the reaction systems to maximize hydrogen production and to obtain syngas with CO to H<sub>2</sub> ratio unity will be determined and will be used as basic for the second part of this work.

The next part focuses on the dynamic equilibrium analysis of the CORM and combined CORM-POM reactions using permreactor system. The Palladium-based

membrane reactor has been selected and the simulation studies are conducted using Mathcad Professional software. The effectiveness of hydrogen permselective membrane reactor is investigated by studying the effect of hydrogen removal on the reaction enhancements. The membrane permselective area, reaction flow and sweep factor are widely recognized as the key factors of permreactor parameters on hydrogen removal and their effectiveness are examined by examining the effects on conversion and yield enhancements,  $H_2/CO$  ratio variations, and suppression of water formation.

Finally, kinetic-transport simulations are conducted in order to explore the relevant thermodynamic and kinetic barriers of CORM and CORM-POM in permreactor system. The reaction kinetics to describe the catalytic reaction displacement for both reforming reactions is extracted from literatures, which were conducted under the similar conditions with the present work.



**Figure 1.11** Flowchart of scopes of research

## 1.7 Thesis Organization

The following chapters will focus on the simulation analysis of CORM and combined CORM-POM in Palladium-based permreactor systems. Chapter 2 will discuss the simulation approaches used throughout this work. The basic assumptions and simulation details on model derivations will be described in this chapter.

Chapter 3 explores the thermodynamic equilibrium compositions of CORM and combined CORM-POM reactions based on Lagrange's undetermined multiplier approach. The applicability of this approach will be confirmed based on the comparison with algebraic multi-reaction equilibrium method. The effects of feed ratio as a function of temperatures are examined to determine the optimal conditions that provide superior conversions, yields and  $H_2/CO$  ratio.

Chapter 4 presents the dynamic equilibrium investigation on CORM and combined CORM-POM process in permreactor system. The overall effectiveness of hydrogen permselective membrane reactor for the reaction systems will be examined and discussed in details. The reaction conditions are based on the findings from Chapter 3 while the permreactor parameters will be studied, which include permselective area, reaction flow and sweep factor.

In Chapter 5, mathematical model with the consideration of reaction kinetic developed for both reactions in permreactor system will be elaborated. The non-equilibrium simulation results will be compared with the thermodynamic equilibrium compositions of conventional reactor as well as dynamic equilibrium data.

Finally, Chapter 6 will summarize the primary conclusions of the present work, based on the results and findings obtained throughout the previous chapters. From this summary, important topic will be identified for future investigation in the research field.

equilibrium shifts, which will be a useful tool to propose the proper permreactor parameters for laboratory experimental studies, which consequently lead to time and cost saving.

3. Performing the dynamic equilibrium analysis on CH<sub>4</sub>-CO<sub>2</sub> reforming processes with porous membrane reactor. The hydrogen permselective dense membranes are widely recognized as expensive materials and the cost of permreactor fabrication will be very costly although significant reaction improvements have been proven through the present work. Thus, it is worthwhile to investigate the porous membrane reactor in reaction enhancements since the cost of porous membranes are much cheaper compared to dense membrane.
4. The simulation data obtained need to be verified by conducting laboratory experiment tests under real reaction-separation condition. The influence of permreactor parameters on the hydrogen removal from a mix stream containing the entire components involved in CORM process needs to be analyzed. Finally, it is important to study the effect of space velocity on the catalytic reactivity as it is recognized as an important factor in CORM reaction-separation process.

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