ARTIFICIAL NEURAL NETWORKS APPLICATION IN COMBINED CARBON DIOXIDE REFORMING AND PARTIAL OXIDATION OF METHANE

RUZINAH ISHA

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Chemical)

Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia

OCTOBER 2005

This work is lovingly and respectfully in honour of my wonderful parents,
Isha Amat Ikram and Zaliha Moh,
as well as my beloved husband and lovely daughter,
Syed Izam Syed Mokhtar and Sharifah Nur Irdina Syed Izam Al-Yahya.

“Many of life’s experiences cultivate unforgettable lessons and rewards.”

ACKNOWLEDGEMENT

It is with great pleasure and pride that I wish to record my thanks to my advisor, Associate Prof. Dr. Nor Aishah Saidina Amin and my Co-advisor, Associate Prof. Dr Khairiyah Mohd Yususf for their constant and motivating guidance throughout the course of this work. I am indeed indebted to them for their inspiring and timely ideas and discussions without which this work would not have been a success.

I am grateful to all Chemical Reaction Engineering Group members Dr. Didi Dwi Anggoro, Faridahanim Shaari, Soon Ee Pheng, Chong Chee Ming, Tutuk Djoko Kusworo, Istadi, Kusmiyati, Terina, Sri Raj, Siti Kartina, Harjit, Tung Chun Yaw and Iradwiyanti for their invaluable supports, knowledge and friendship they have shared with me. I am also thankful to Kamarudin, Norzana, Rafiziana, Rafidah, Normaliza, Tan Yin Ling, Foo Chwan Yee, Siti Zubaidah and Norazian for their encouragement and for their constructive criticisms and timely help on various occasions. Special thanks to PTP-UTM scholarship and Malaysia researcher grant, IRPA vot 74005 for their financial support.

I am most indebted to my family especially to my parents, Isha Amat Ikram and Zaliha Moh for their constant support, love and encouragement throughout the course of my education. Finally, this note would go incomplete without a constructive support and understanding from my beloved husband, Syed Izam Syed Mokhtar.

ABSTRACT

A catalytic carbon dioxide reforming of methane with the effect of oxygen was carried out on 1 wt% of Rhodium (Rh) on Magnesium Oxide (MgO) and ZSM-5 catalysts. The effect of parameters on the methane conversion, synthesis gas selectivity and H_2/CO ratio were studied. Three main parameters: temperature, O_2/CH_4 ratio and catalyst weight in 100 ml/min total feed flow rate, have been identified as the major factors that control the process. The results indicated that Rh/MgO showed better catalyst reactivity and stability even though at temperature higher than 800°C. Thus, the optimization of the combined CORM and partial oxidation of methane over Rh/MgO catalyst was carried out. The optimization study was performed with the help of experimental design and two mathematical approaches: empirical polynomial and artificial neural network. Empirical polynomial models were employed to analyze the effect of parameters on the response factor and the correlation coefficient, r, was above 85%. However, the feed forward neural network correlation coefficient was more than 95%. The feed forward neural network modeling approach was found to be more efficient than the empirical model approach. The optimum condition for maximum methane conversion was obtained at 850°C with O_2/CH_4 ratio of 0.14 and 141 mg of catalyst resulting in 95% methane conversion. A maximum of 40% hydrogen selectivity was achieved at 909°C, 0.23 of O_2/CH_4 ratio and 309 mg catalyst. The maximum H_2/CO ratio of 1.6 was attained at 758°C, 0.19 of O_2/CH_4 and 360 mg catalyst. The utilization of neural network in predicting the reaction for other catalyst was also tested by introducing other reaction data in the network. The result showed a feed forward neural network was able to predict the output of the reaction even for different reaction or catalysts.

ABSTRAK

Kesan oksigen terhadap mangkin 1 % berat Rhodium di dalam Magnesium Oksida (MgO) dan ZSM-5 dikaji untuk proses pembentukan semula metana dengan menggunakan gas karbon dioksida (CORM). Kesan parameter terhadap penukaran metana, kepemilihan gas sintesis dan nisbah H_2/CO diselidiki. Tiga parameter utama: suhu, nisbah reaktan (O_2/CH_4) dan berat mangkin dalam 100 ml/min jumlah halaju suapan dikenalpasti sebagai faktor utama yang mengawal proses tersebut. Keputusan menunjukkan bahawa Rh/MgO mempunyai keaktifan dan kestabilan yang lebih baik walaupun pada suhu melebihi 800°C. Oleh itu, optimasi untuk kombinasi CORM dan oksidasi separa metana menggunakan mangkin Rh/MgO dijalankan. Proses optimasi dibuat dengan bantuan rekabentuk eksperimen dan dua pendekatan matematik: polinomial empirik dan rangkaian saraf buatan. Model polinomial empirik yang diterbitkan untuk menganalisa kesan parameter terhadap faktor keluaran dan pekali kolerasinya, r adalah melebihi 85%. Walau bagaimanapun, pekali kolerasi untuk suapan hadapan rangkaian saraf adalah melebihi 95%. Oleh itu, suapan hadapan rangkaian saraf adalah lebih efisen daripada model polinomial empirik. Penukaran metana tertinggi sebanyak 95% dihasilkan pada suhu 850°C dengan nisbah O_2/CH_4 sebanyak 0.14 dan 141 mg mangkin. Kepemilihan hydrogen secara maksima sebanyak 40% boleh dicapai pada suhu 909°C, nisbah O_2/CH_4 sebanyak 0.23 dan 309 mg mangkin. Nisbah maksima H_2/CO sebanyak 1.6 dihasilkan pada suhu 758°C dengan nisbah O_2/CH_4 sebanyak 0.19 dan 360 mg mangkin digunakan. Penggunaan suapan hadapan rangkaian saraf untuk meramal tindakbalas bermangkin yang lain juga dikaji untuk tindakbalas yang berbeza di dalam rangkaian yang sama. Keputusan menunjukkan suapan hadapan rangkaian saraf berupaya meramal tindakbalas walaupun untuk tindakbalas atau mangkin yang berlainan.

TABLE OF CONTENTS

2 **LITERATURE REVIEW**

3 **RESEARCH METHODOLOGY**

7 CONCLUSION AND RECOMMENDATIONS

LIST OF TABLES

TABLE NO. **TITLE** **PAGE**

LIST OF FIGURES

LIST OF SYMBOLS

ANOVA	-	Analysis of Variance
BET	-	Brunauer Emmett and Teller equation, m^2/g
Btu	-	British thermal unit
C1 Chemistry	-	Methane chemistry
C_2	-	Acetylene, ethylene and ethane hydrocarbons
C_2^+	-	Higher Hydrocarbons
COE	-	Crude oil equivalent
CORM	-	Carbon dioxide reforming of methane
d	-	Pore Diameter, nm
Det	-	Detector
DME	-	Dimethylether
EIA	-	United States Energy Information Administration
F	-	Total flow rate pass through catalyst, mL/min
F-T	-	Fischer-Tropsch synthesis
GC	-	Gas chromatography
GHG	-	Greenhouse gas
GHSV	-	Gas hourly space velocity
GTL	-	Gas to liquid
HHCs	-	Higher Hydrocarbons
LPG	-	Liquefied petroleum gas
MTG	-	Methanol to gasoline
n	-	Mole
NA	-	Nitrogen absorption
OCM	-	Oxidative coupling of methane
P	-	Partial pressure

POM	-	Partial oxidation of methane
ppm	-	Part per million
r	-	Correlation Coefficient
r	-	Heating rate, ° C/min
RMSE		Root Mean Square Error
RT	-	Retention time
RWGS	-	Reverse water gas shift reaction
S	-	Selectivity, %
SASOL	-	Suid-Afrikaans Sintetiese Olie
SMDS	-	Shell middle distillate synthesis
SRM	-	Steam reforming of methane
T	-	Temperature
t	-	Time
TCD	-	Thermal conductivity detector
TOS	-	Time on stream
TPR	-	Temperature-programmed reduction
W	-	Weight of catalyst, g
WGS	-	Water gas shift reaction
X	-	Conversion, %
XRD	-	X-ray diffraction
Y	-	Yield, %
ZSM-5	-	Zeolite Socony Mobil number 5
ΔG	-	Gibbs free energy
ΔH	-	Heat, or enthalpy
ΔS	-	Entropy

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 General Introduction

C1 chemistry refers to the utilization of single carbon-bearing molecules, such as carbon monoxide, synthesis gas (a mixture of carbon monoxide (CO) and hydrogen (H_2), carbon dioxide (CO_2), methane (CH_4), and methanol (CH_3OH), for the production of valuable chemicals, petrochemical intermediates, and ultra-clean transportation fuels. C1 chemistry could also be used to produce high-purity hydrogen or premium chemicals from synthesis gas or from methanol. The main resources of C1 molecules are natural gas, coal, biomass, and organic wastes.

Figure 1.1 exhibits the profile of natural gas reserves versus natural gas consumption from 1980-1999. It shows that the rate of natural gas discovery is higher than the rate of natural gas consumption. Thus, it is necessary to develop a conventional natural gas utilization technologies not only for combustion to supply energy requirement, but also to convert the natural gas to higher value added products for example the production of environment friendly dimethyl ether (DME) as liquid fuel and also for ammonia production.

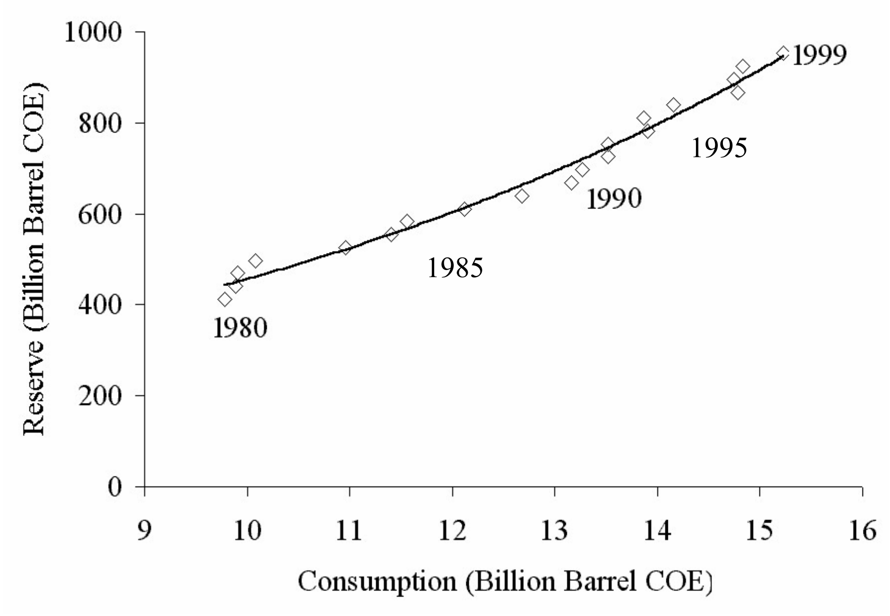

Figure 1.1 The world proven reserves of natural gas versus consumption from the year of 1980 to 1999 (United States Energy Information Administration, 2000). COE = Crude Oil Equilibrium

Most natural gas reserves in Malaysia are situated at remote areas. As shown in Table 1.1, Malaysia has about 85.8 trillion standard cubic feet of natural gas and ranks as the 11th world's largest natural gas reserve (Sarmidi *et al.*, 2001). It is reported that Malaysia still has many remote gas reserves waiting for exploitation. (Kementrian Tenaga, Komunikasi dan Multimedia Malaysia, 1999). Besides that, the numbers of global proven natural gas reserves have increased by a factor of four over the last 25 years (Bitter, 1997).

Table 1.1: **Gas reserves in Malaysia (Kementerian Tenaga, Komunikasi dan Multimedia Malaysia, 1999)**

Region	Trillion standard cu ft
Peninsular Malaysia (Duyung, Jerneh, etc.)	34.4
Sabah	43.7
Sarawak	7.7
Total	85.8

- 1 trillion = 1×10^{12}
- 1 cu ft = 0.028317 cu meter

In addition, CO_2 is released to the atmosphere when solid waste, fossil fuels (oil, natural gas and coal) and wood are burned. Furthermore, CO_2 and CH_4 are also found in biogas and flue gas. For example, in a well designed chamber, bio-decomposable materials in agricultures industries and waste water treatment process is decomposed to biogas and the gas mainly consisted of CH_4 and CO_2.

The main reason to utilize CO_2 is it can help to reduce the green house effect. Malaysia's greenhouse gas emissions totalled 144 million tonnes in term of CO_2 equivalent in 1994. Net emissions, after accounting for sinks of 68 million tonnes, amounted to 76 million tonnes CO_2 equivalent. On a per capita basis, net emissions amounted to 3.7 tonnes CO_2 equivalent. In terms of greenhouse gas, CO_2 accounted for 67.5% and nitrous oxide (N_2O) 0.1% of total CO_2 equivalent emissions. The fuel combustion energy sector accounted for 86.7% of the total CO_2 emissions and traditional biomass fuels accounted for 86.4% of the total N_2O emissions (Ministry of Science, Technology and Environment, 2000).

Synthesis gas is a very important petrochemical feedstock. It is the first step in a serial reaction to convert gas from hydrocarbons (e.g. natural gas, bio-gas etc.) into liquid form (e.g. gasoline, kerosene, diesel, petroleum wax etc) and higher value products (e.g. ammonia, alcohol etc). Synthesis gas can be produced via direct and indirect conversion. However, indirect conversion of natural gas to liquid fuels via synthesis gas is more efficient than scheme presently known for direct conversion

(Aasberg-Petersen *et al*., 2001). There are three types of process involved in indirect conversion of natural gas; Steam Reforming of Methane (SRM), Partial Oxidation of Methane (POM) and Carbon Dioxide Reforming of Methane (CORM) as shown Table 1.2.

Table 1.2: **Sources of synthesis gas and their applications (Ross *et al*., 1996; Bitter, 1997)**

	Reaction	$\Delta H_{R,298K}$ kJ/mol)	Applications	
CORM	$CH_4 + CO_2 \Rightarrow 2CO + 2H_2$	+247	Oxoalcohols, Polycarbonates, Formaldehyde	(1.1)
POM	$CH_4 + \frac{1}{2}O_2 \Rightarrow CO + 2H_2$	-36	Methanol synthesis, Fischer-tropsch Synthesis	(1.2)
SRM	$CH_4 + H_2O \Rightarrow CO + 3H_2$	+206	H_2 production, Ammonia Synthesis	(1.3)

Therefore, efficient and cheaper large scale process plant is required to accommodate the future use of synthesis gas. Although catalysis is only one of the several key factors for these developments, it plays an important role for advanced reactor designs, feedstock flexibility, and control of carbon formation. Thus, the catalysis of reforming reactions has long been a field of research in order to get industrial economical process output and applicable catalysis.

Today, the route to liquid, higher value products from gas is through conversion via synthesis gas (synthesis gas) as shown in Figure 1.2. The main gas-to-liquids GTL interest now is in Fischer–Tropsch (F–T) synthesis of hydrocarbons. While synthesis gas for GTL can be produced from any carbon-based feedstock such as hydrocarbons, coal, petroleum coke and biomass, the lowest cost routes to synthesis gas so far are based on natural gas. Thus, the focus for GTL has been largely on associated gas, so-called stranded or remotely located gas reserves, and larger gas reserves that are not currently being economically exploited.

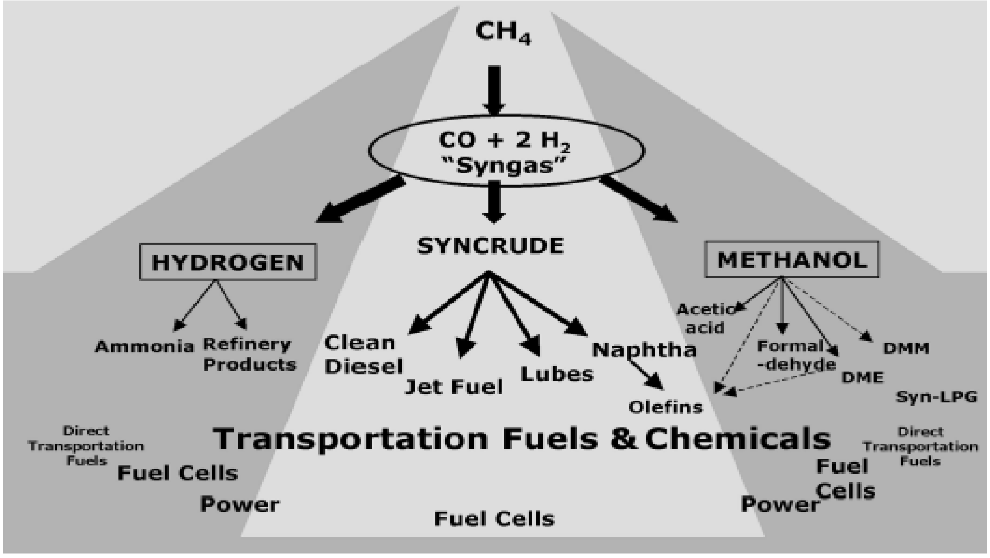

Figure 1.2 General application of synthesis gas (syngas) to higher value added product. (Fleisch *et al.*, 2002)

1.2 Research Background and Problem Statement

CORM is an interesting route of synthesis gas production. It is the most favourable due to its lower cost process compared to other catalytic reforming of methane processes due to the lower feedstock requirements (Ross *et al.*, 1996). Thus, many researchers have been involved in investigating to produce synthesis gas via catalytic CORM. The major obstacle preventing the commercialization of CORM is catalyst deactivation due to coking or sintering. Therefore, many researchers modify on catalysts by loading the support with metal in order to reduce the catalyst deactivation. Not only that, combination reaction of methane reforming reaction such as SRM and POM or POM and CORM is energically favourable when combining endothermic and exothermic reaction and produces a controllable H_2/CO ratio.

The most common catalyst support used for reforming reaction is γ-Al_2O_3. There are limited literatures about the usage of ZSM-5 and MgO catalyst in reforming reaction. ZSM-5 is a mixture of SiO_2 and Al_2O_3. It has a unique pore structure and high surface area material. However, MgO is an orthogonal crystal structure with Mg and O elements and has a small surface area. Most of the Group VIII metals such as Fe, Ni, Ru, Rh and Pt are more catalytically active towards reforming reaction. However, Rh not only exhibits high activity and stability, but also has a high resistance to the coke formation on the catalyst surface (Mark and Meier, 1997). Chen *et al.*(1997)illustrated that Rh is the best promoter among other nobel for the $Ni_{0.03}$ $Mg_{0.97}O$. Wang and Au (1997) suggested that high metal surface material is potentially to have a higher degree of metal dispersion. In addition, Chin (2002) found that Rh metal loaded catalyst shows excellent reactivity and stability compared to Ni catalysts on ZSM-5 support. Furthermore, the Rh metal loaded on MgO support exhibits extraordinary catalyst reactivity and stability (Wang and Ruckenstein, 2000). Thus, the capability of Rh metal loaded on ZSM-5 and MgO support in CORM and combination reaction of CORM and POM are very interesting field to investigate.

The development of mathematical model that represent the process can be used to study the process or reaction behaviour. Nevertheless, traditional method of developing the mathematical model via kinetics study is cumbersome. A new application on modelling such as empirical model and artificial neural networks model development can be employed. Empirical model developed via experimental design techniques in order to interpret experimental data. Artificial neural network is a new non-linear statistical technique inspired by models developed for explanation of human brain activity. Even though, detailed mechanistic models are used much more often than empirical models or artificial neural network for interpretation of catalytic processes, experimental design and mathematical modelling techniques are the mathematical tools normally used to optimize a process because they allow the gathering of maximum process information with reduced number of experiments (Larentis *et al., 2001)*.

The hypotheses of this research are:

1. combination reaction of CORM and POM shows better reactivity than CORM reaction itself.
2. neural networks model approach gives smaller error than empirical model and be able to predict the process output although with limited data.

1.3 Research Objectives

Computer technology such as experimental design and artificial neural network can be used to reduce time spent and experimental cost in research. Thus, the objectives of this research are:

1. to study the reactivity of Rh supported catalysts in CORM and combined CORM and POM reaction.
2. to develop model based on experimental design and artificial neural network
3. to apply neural network in predicting the catalyst performance in different reaction even with limited data available.

1.4 Scope of Study

The research focuses on modelling via different approaches in catalytic CORM in order to optimize the process conditions. The catalyst is prepared via wetness incipient impregnation. Rhodium (Rh) metal is used on ZSM-5 and MgO supports. Catalyst testing is carried out in fixed bed 9.1 mm inner diameter and 30 cm long vertical quartz tube reactor. The effect of temperature, catalyst weight in 100 ml/min of total flow rate and ratio of O_2/CH_4 are studied. 16 experiments are carried out according to the arrangement set by the design of experiment. Three operating parameters are evaluated to reach the optimization point of methane conversion, hydrogen selectivity and H_2/CO ratio. The product of the combined CORM and POM is analyzed by TCD gas chromatography.

Two mathematical models approach are developed to represent the process and predict the methane conversion, hydrogen selectivity and H_2/CO ratio for best catalyst reactivity. The second order polynomial empirical model is developed via STATISTICA v.6 software using Response Surface Methodology. The normalized variables are employed to compare the relative importance of the model. A feed forward neural network is developed as well in which neural networks toolbox from Matlab V.6.1 is used to model and simulate the process. A network with one input layer, one or more hidden layers and an output layer consisting of nodes that interconnect the layers is composed. Both models are compared and analyzed via ANOVA.

The CORM and POM reaction data with different catalysts application are used to test the ability of neural network to predict a few reactions in a network. A feed forward neural networks is developed. Three different networks are constructed namely; retraining NN, data combination NN and stacked NN. Neural network toolbox from Matlab V 6.1 is used to model and simulate the process. These three networks are compared and analyzed via ANOVA.

Besides employment of Design of Experiments, attempt to utilize Genetic Algorithm (GA) on reforming of methane process for modelling and optimization purposes should be done. There is an interest to apply Genetic Algorithms which is well suited in the field of combinatorial catalysis to discover optimal catalyst compositions within a limited number of experiments (Rodemerck *et al.,* 2004). In addition, a hybrid process modelling and optimization of Neural Network and Genetic Algorithms may become appropriate in modelling process. (Nandi *et. al.*, 2003).

Many researchers usually neglect the thermal and pressure effects in the process while simulating the process. Thus, simulation work should consider isothermal and non-isothermal operation in order to analyze the role of heat management in the process. In addition, pressure drop should be considered to picture the real reforming process.

For an economically viable and environmentally benign process, utilisation of methane and carbon dioxide from biomass degradation plant or incineration plant can be used as a reactant even though Natuna Oil Field has a special composition of natural gas composition in the world in which 70% and 30% of the composition are carbon dioxide and methane respectively. However, H_2SO_4 in natural gas is still available even though in small amount. Thus, separation H_2SO_4 is required. So, an integrated process from biomass degradation or incineration plant implementing a system that recycle the unreacted reactant is also necessary to provide an effective and efficient process. Therefore, more studies need to be done before scaling it up to pilot scale process.

REFERENCES

Aasberg-Peterson, K., Bak Hansen, J. -H., Christensen, T. S., Dybkjaer, I., Seier Christensen, P., Stub Nielsen, C., Winter Madsen, S. E. L. and Rostrup-Nielsen, J. R. (2001). Technologies for Large-scale Gas Conversion. *Applied Catalysis A: General*. (221): 379 – 387.

Abella, L. C. and Gallardo, S. M. (2001). Catalysis in the Natural Gas Industry in the Philippines: CH_4-CO_2 Reforming. *Proceeding of Regional Symposium of Chemical Engineering 2001*. PD7-1.

Ahmad R.S., Amin N.A.S., Noor Syawal, Tutuk D.K. (2003). Modelling of Partial Oxidation of Methane Using Response Surface Methodology. *Proceeding SNTPK V. Universitas Indonesia, Jakarta*

Alberty, R.A., and C.A. Gehrig. (1984). Standard Chemical Thermodynamic Properties of Alkane Isomer Groups. *Journal of Physical Chemistry Reference Data (*13):1173-1197.

Alberty, R.A. (1985). Standard Chemical Thermodynamic Properties of Alkylbenzene Isomer Groups. *Journal of Physical Chemistry Reference Data* (14):177-192.

Alberty, R.A., and C.A. Gehrig. (1985). Standard Chemical Thermodynamic Properties of Alkene Isomer Groups. *Journal of Physical Chemistry Reference Data* (14):803-821.

Anthony J. Hayter; (1995) *Probability and Statistics For Engineers and Scientists*, 2nd edition, USA, Duxbury Thompson Learning, : 535-590, 194-604, 657-663

Amin N.A.S, Anggoro D.D. (2004). Optimization of Direct Conversion of Methane to Liquid Fuels Over Cu Loaded W/ZSM-5 Catalyst. *Fuel*. (83): 487-494

Basile A, Paturzo L, Lagana. (2001a). The Partial Oxidation of Methane to syngas in a Paladium Membrane Reactor: Simulation and Experimental Studies. *Catalysis Today* (67): 55-64

Baughman D.R., Liu. Y.A. (1995) . *Neural Network in Bioprocessing and Chemical Engineering*. California. Academic Press Inc.

Bethke K.A., Kung H.H., (1997). Supported Ag Catalysts for Lean Reduction of NO with C_3H_6. *Journal of Catalysis* (172): 93-102

Bhat R.N, Sachtler W.M.H., (1997). Potential of Zeolite Supported Rhodium Catalysts For the CO_2 Reforming of CH_4. *Applied Catalysis A: General* (150): 279-296

Bitter, J. H. (1997). *Platinum Based Bifunctional Catalysts for Carbon Dioxide Reforming of Methane – Activity, Stability and Mechanism.* University of Twente: PhD Thesis.

Bouwmeester H.J.M., (2003). Dense Ceramic Membranes for Methane Conversion. *Catalysis Today –Online Journal*

Chen D, Lodeng R, Anungskas A. Alsvik O, Holmen A, (2001). Deactivation During Carbon Dioxide Reforming of Methane Over Ni Catalyst: Microkinetic Analysis. *Chemical Engineering Science.* (56): 1371-1379

Choudhary, V. R., Uphade, B. S. and Mamman, A. S. (1998), Simultaneous Steam and CO2 Reforming of Methane to Syngas over NiO/MgO/SA-5205 in Presence and Absence of Oxygen. *Applied Catalysis A: General*. (168): 33 – 46.

Choudhary, V. R. and Mamman, A. S. (2000). Energy Efficient Conversion of Methane to Syngas over NiO-MgO Solid Solution. *Applied Energy*. (66): 161 –175

Chin H. K. (2002). *Carbon Dioxide Reforming of Methane: the Effect of metal, Support, Temperature and Reactant Ratio.* Universiti Teknologi Malaysia. Master Thesis

Chiyoda Coporation. (2003). *Chiyoda Awarded FEED for Commercial DME Plant*. Japan. News Realease

Dey G. Mitra A, Banerjee R, Maiti B.R., (2001) Enchanced Production of Amilase by Optimisation of Nutrional Constituents Using Response Surface Methodology. *Biochemical Engineering Journal.* (7): 227-231

Dias J.A.C, Assaf J.M., (2004). Authothermal Reforming of Methane over Ni/γ-Al_2O_3 Catalysts: the enchancement effect of small quantities of Nobel Metals. *Journal of Power Source-Online Journal*

Erdöhelyi, A., Cserényi, J., Papp, E. and Solymosi, F. (1994). Catalytic Reaction of Methane with Carbon Dioxide over Supported Palladium. *Applied Catalysis A: General*. (108): 205 – 219

Fleisch T.H., Sills R.A., Briscoe M.D. (2002). Emergence of The Gas –to-Liquids Industry a Review of Global GTL Developments. *Journal of Natural Gas Chemistry* (11): 1-14

Grachia-Ochoa F. Castro E.G.(2001). Estimation of Oxygen Mass Transfer Coefficient in Stirred Tank Reactors Using Artificial Neural Networks. *Enzyme and Microbial Technology* (28): 560-569

Gurvich, L.V., V.S. Iorish, V.S. Yungman, and O.V. Dorofeeva. (1995). Thermodynamic Properties as a Function of Temperature. *CRC Handbook of Chemistry and* Physics. 75th Edition. Boca Raton: CRC Press: Chapter 5: 61-84.

Habibie S. (1998). Utilization of Natuna CO_2 and The EID Membrano River Project. *Environment, Inovation and Development of Energy Intensive Industries (EID) Membrano River Project*, (1) no 4 January: 1-2

Huang K., Zhan X., Chen F. Q., Lu D. W., (2003). Catalyst Design for Methane Oxidative Coupling by Using Artificial Neural Network and Hybrid Genetic Algorithm. *Chemical Engineering Scioence*

Ioannides T, Verykios X.E. (1998). Development of a novel Heat-Integrated Wal Reactor for Partial Oxidation of Methane to Synthesis Gas. *Catalysis Today* (46): 71-81

Ito M, Tagawa T. Goto S. (1999) Suppresion of Carbonaceous Depositions on Nickel Catalyst for the Carbon Dioxide Reforming of Methane. *Applied Catalysis A: General.* (177): 15-23

Jose M.R, Roura E., Contreras E. (2004). Biosynthesis of Ethyl Butyrate Using Immobolized Lipase: a Satistical Approach. *Process BioChemistry*

Kapur G.S. Sastry M.I.S., Jaiswal A.K. Sarpal A.S. (2004). Establishing Structure-Property Corelations and Classification of Base Oils Using Statistical Techniques and Artificial Neural Networks. *Analytica Chimica Acta* (506): 57-69

Khairiyah M.Y., Ani I. Lim J.S.(2003). Pore Size Determination of Asymemetric Membrane Using Neural Network. *International Conference on Chemical and Bioprocess Engineering, Kota Kinabalu.* August 27-29, 2003, 755-760

Kementerian Tenaga, Komunikasi dan Multimedia Malaysia. (1999). *National Energy Balance Malaysia 1980-1998 and Quarter 1 & 2*. Kuala Lumpur: Kementerian Tenaga, Komunikasi dan Multimedia Malaysia.

Lanouette R., Thibault J., Valade J.L., (1999). Process Modelling With Neural Network Using Small Experimental Dataset. *Computer and Chemical Engineering*. (23): 1167-1176

Larentis A.L. Salim V.M.M, Resende N.S. Pinto J.C. (2001). Modeling and Optimization of Combined Carbon Dioxide Reforming and Partial Oxidation of Natural Gas. *Applied CatalystA: General* (215): 211-224

Lemonidou, A. A., Goula M. A., and Vasalos, I. A. (1998). Carbon Dioxide Reforming of Methane Over 5 Wt. % Nickel Calcium Aluminate Catalysts –Effect of Preparation Method. *Catalysis Today*. (46). 175 – 183

Liguras, D.K., Kondarides, D.I., Verykios, X.E., (2003). Production of Hydrogen for Fuel Cells by Steam Reforming of Ethanol Over Supported Noble Metal Catalysts. *Applied Catalysis B: Environmental*. (1344). 1-10

Ma, L., Trimm, D.L. (1996). Alternative catalyst Bed Configurations for the Autothermic Conversion of Methane to Hydrogen. *Applied Catalysis* (*A* 138): 265-273

Malinova, T, Guo, Z.X, (2004). Artificial Neural Network Modelling of Hydrogen Storage properties of Mg-Based Alloys. *Material Science and Engineering (*A365): 219-227

Marengo, E., Gianotti, V., Angioi, S., Gennaro, M.C., (2004). Optimization by Experimental Design and Artificial Neural Network of the ion-interaction Reversed-phase Liquid Chromatographic Separation of Twenty Cosmetic Preservatives. *Journal of Chromatography A* (1029): 57-65

Matsuo, Y., Yoshinaga, Y., SEkine, Y., Tomishige, K., Fujimoto, K., (2000). Autothermal CO_2 Reforming of Methane over NiO-MgO Solid Solution Catalysts Under Pressurized Condition; Effect of Fluidized Bed Reactor and Its Promoting Mechanism. *Catalyst Today.* (63(2-4)): 439-445.

Ministry of Science, Technology and Environment. (2000). *Malaysia Initial National Communication – submitted to the United Nations Framework Convention on Climate Change*. Kuala Lumpur: Ministry of Science, Technology and Environment

Mo L, Fei J. Huang C, Zheng X. (2003) REfoming of Methane with Oxygen and Carbon Dioxide to Produce Syngas Over a Novel $Pt/CoAl_2O_4/Al_2O_3$ catalyst. *Journal of Molecular Catalysis A: Chemical* (193): 177-184

Molga E.J. (2003) Neural Network Approach to Support Modelling of Chemical Reactors: Problems, Resolutions, Criteria of Application. *Chemical Engineering Processing.* (42): 675-695

Morris A.J., Montague G.A, Willis M.J. (1994). Artificial Neural Networks: Studies in Process Modelling and Control. *Trans I. Chemical Engineering* (72A): 3-19

Muralidhar R.V. Chirumamica R.R, Marchant R, Nigam P. (2001). Respose Surface Approach for the Comparison of Lipase Production by Candida Cylindracea Using 2 Different Carbon Sources. *Biochemical Engineering Journal.* (9): 17-23

Nakamura, J., Aikawa, K., Sato, K. and Uchijima, T. (1994). The Role of Support in Methane Reforming with CO2 over Rhodium Catalysts. *Studies in Surface Science and Catalysis. (*90). 495 – 500

Nandi S. Badhe Y. Lonari J., Sridevi U. Rao B.S. Tambe S.S, Kulkarni B.D. (2003). Hybrid Process Modeling and Optimization Strategies Integrating Neural Network/ Support Vector Regression and Genetic Algorithms: Study of Benzene Isopropylation on Hbeta Catalyst. *Chemical Enginnering Journal (*97): 115-129

Nascimento C.A.O, Guidici R. Guardani R. (2000). Neural Network Based Approach For Optimisation for Industrial Chemical Process. *Computer and Chemical Engineering*. (24).: 2303-2314

O'Connor A.M., Ross J.R.H., (1998). The Effect of O_2 Addition on the Carbon Dioxide Reforming of Methane Over Pt/ZrO_2 Catalysts. *Catalysis Today.* (46): 203-210

Parego. C., and Peratello. S., (1999). Experimental methods in catalytic kinetics. *Catalysis Today.* 52(2-3): 133 – 145.

Parisi D.R., Laborde M.A., (2001) Modeling Steady State Heterogeneous Gas-Solid Reactor Using Feed Forward Neural Networks. *Computer and Chemical Engineering.* (25): 1241-1250.

Peng L., Xu X, Mu H., Hoy C.E., Jens A.N. (2002). Production of Structured Phospholipids by Lipase-Catalyzed Acidolysis: Optimization Using Response Surface Methodologhy. *Enzyme and Microbial Technology* (31): 523-532

Prabhu A.K., Oyama S.T., (2000a). Highly Hydrogen Selective Ceramic membranes: Application To the Transformation of Greenhouse Gases. *Journal of Membrane Science* (176): 233-248

Prado. C., Garrido J., Periago J.F., (2004). Urinary Benzene Determination by SPME/GC-MS: A Study of Variables by Fractional Factorial Design and Response Surface Methodology. *Journal of Chromatography. (Online Press)*

Portugal U.L., Santos A.C.S.F, Damyanova S., Marques C.M.P., Bueno J.M.C. (2002). CO_2 Reforming of CH_4 over Rh-Containing Catalysts. *Journal of Molecular Catalysis A: Chemical* (184): 311-322

Psichogios D, Ungar L. (1992). A hydrid Neural Network- First Principle Approach to Process Modelling. *American Institute of Chemical Engineers Journal.* (38): 1499-1511

Richardson J.T., Garrait M, Hung J.K. (2003). Carbon Dioxide Reforming with Rh and Pt-Rh Catalysts Dispersed on Ceramic foam Supports. *Applied Catalysis A: General*

Rodemerck U., Baerns M., Holena M., Wolf D. (2004). Application of Genetic Algorithm and a Neural Network for the Discovery and Optimization of New Solid Catalytic Materials. *Applied Surface Science.* (223): 168-174

Ross, J. R. H., Keulen A. N. J., Hegarty M. E. S. and Seshan K. (1996). The Catalytic Conversion of Natural Gas to Useful Products. *Catalysis Today.* (30):193 – 199

Ross, J. R. H. and O' Connor, A. M. (1998). "The Effect of O2 Addition on the Carbon Dioxide Reforming of Methane over Pt/ZrO2 Catalysts." *Catalysis Today. (*46). 203 – 210.

Rostrup-Nielsen, J. R., Anderson, J. R. and Boudart, M. (1984). *Catalysis Science and Technology*, vol.(5). New York: Springer.

Rostrup-Nielsen, J. R. (1993). Production of Synthesis Gas. *Catalysis Today*, (18(4)): 305 – 324.

Rostrup-Nielsen, J. R. (2000). New Aspects of Syngas Production and Use. *Catalysis Today*,(63(2-4)): 159 – 164

Ruckenstein, E. and Hu, Y. H. (1998). Combination of CO2 Reforming and Partial Oxidation of Methane over NiO/MgO Solid Solution Catalysts. *Industrial Engineering Chemistry Research*. (37):. 1744 – 1747

Ruckenstein, E. and Wang H. Y. (2000a). Carbon Dioxide Reforming of Methane to Synthesis Gas over Supported Cobalt Catalysts. *Applied Catalysis A: General.(*204(2)): 257 – 263

Ruckenstein, E. and Wang H. Y. (2000b). Carbon Dioxide Reforming of Methane to Synthesis Gas over Supported Rhodium Catalysts: the Effect of Support. *Applied Catalysis A: General*. (204(2)): 143 – 152

Sarmidi, M. R., Aziz, R., Hussain, M. A., Daud, W. R. W. (2001). Overview of Petrochemical Based Industries in Malaysia. *ASEAN Journal of Chemical Engineering*, 1(1):7 – 16.

Serra J.M., Corma A., Chica A., Argente E., Botti V. (2002). Can Artificial Neural Networks Help The Experimention In Catalysis. *Catalysis* Today (81): 393-403

Serra J.M., Corma A., Argente E., Valero S., Botti V.(2003). Neural Network for Modelling of Kinetic Reaction Data Applicable to Catalyst Scale Up and Process Control and Optimisation in a Frame of Combinatorial Catalysis. *Applied Catalysis A: General* (254): 133-145

Shao Z, Dong H. Xiong G., Cong Y. Yang W, (2000). Performance of a Mixed-Conducting Ceramic Membrane Reactor With High Oxygen Permeability for Methane Conversion. *Journal of Membrane Science.* (183): 181-192

Shell Malaysia, (2001). *Fisher-Tropsch Gas To Liquid Report.* Kuala Lumpur Shell Malaysia

Shene C, Diez C, Bravo S. (1999). Neural Network For the Prediction of the State of Zymomonas Mobilis CP4 Batch Fermentation. *Computer and Chemical Engineering.* (23): 1097-1108

Smith, J.M., H.C. Van Ness, and M.M. Abbott. (1996). *Introduction to Chemical Engineering Thermodynamics*. Fifth Edition. New York: The McGraw-Hill Companies: 559-604.

Souza M.M.V.M, Schmal M. (2003). Combination of Carbon Dioxide Reforming and Partial Oxidation of Methane over Suported Platinum Catalysts. *Applied Catalysis A: General* . (255): 83-92

Stagg-William, S. M. (1999). *Novel Catalytic Materials for Carbon Dioxide Reforming of Methane Under Severely Deactivating Conditions*. University of Oklahoma: PhD Dissertation.

Sridhar D.V. Seagrave R.C. Bartlett E.B.(1996). Process Modeling Using Stacked Neural Networks. *American Institute of Chemical Engineers Journal.* (42): 2529-2539

Sullivan J.A, Cunningham J. (1998). Selective Catalytic Reduction of NO with C_2H_4 over Cu/ZSM-5: Influences of oxygen Partial Pressure and Incorporated Rhodia. *Applied Catalysis B: Environmental* (15): 275-289

Tang S. -B., Qiu F. -L. and Lu S. -J. (1995). Effect of Supports on the Carbon Deposition of Nickel Catalysts for Methane Reforming with CO_2." *Catalysis Today*. (24): 253 – 255.

Thomas D.M. (1997). Design and Analysis of Industrial Experiments. *Chemical Engineering.* (6): 168-182

Uchijima, T., Nakamura, J., Sato, K., Aikawa, K., Kubushiro, K. and Kunimori, K. (1994). Production of Synthesis Gas by Partial Oxidation of Methane and Reforming of Methane with Carbon Dioxide. In: Paul, J. and Pradier, C. -M.(1st Eds.). *Carbon Dioxide Chemistry: Environmental Issue*. London: Athenaeum Press: 325 – 327.

United States Energy Information Administration. (2000). *World Energy Consumption*. New York: United States Energy Information Administration

Varnalis A.I. JG. Brennan, MacDougall D.B. Gilmour S.G. (2004). Optimisation of High Temperature Puffing of Patato Cubes Using Response Surface Methodology. *Journal of Food Engineering*. (61): 153-163

Vosloo, A. C. (2001). Fischer-Tropsch: A Futuristic View. *Fuel Processing Technology.* (71): 149 – 155

Wang, H. Y. and Au, C. T. (1997). Carbon Dioxide Reforming of Methane to Syngas Over SiO2-supported Rhodium Catalysts. *Applied Catalysis A: General.*(155). 239 – 252

Wolpert D.H., (1992). Stacked Generalization. *Neural Networks Vol* (5): 241-259

Xu. G, Shi K., Goa Y., Xu H., Wei Y., (1999). Studies of Reforming Natural Gas With Carbon Dioxide to Produce Synthesis Gas X. The Role of CeO and MgO Promoters. *Journal of Molecular Catalysis A: Chemical* (147): 47-54

Yin C, Rosendahl L, Luo Z, (2003). Method To Improve Prediction Performance of ANN Models. *Simulation Modeling Practice and Theory (*11):. 211-222

Zhang, C. -L., Liu, Z. -Q., Wu, T. -H., Yang, H. –M., Jiang, Y. -Z. and Peng, S. -Y.(1996). Complete Reduction of Carbon Dioxide to Carbon and Indirect Conversion to O2 using Cation-excess Magnetite. *Materials Chemistry and Physics*. (44): 194 – 198

Zhang J,Martin E.b. Morris A.J. Kiparissides, (1997). Inferential Estimation of Polymer Quality Using Stacked Neural Networks. *Computers and Chemical Engineering* (21): 1025-1030