REACTANT DILUTION EFFECTS AND REACTION KINETICS OF METHANE DRY REFORMING IN DIELECTRIC BARRIER DISCHARGE REACTOR

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Particularly dedicated to my treasured parents, my beloved husband and sibling and
to the memories of my cherished grandparents who have left our family

Long live all in my memory!

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Do not judge me by my successes, judge me by how many times I fell down and got back up again. Nelson Mandela (May his soul rest in peace)

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ABSTRACT

Methane dry reforming (MDR) is a promising way for fuel production due to the mitigation of carbon dioxide (CO_2) and methane (CH_4) emissions, as well as tackling global warming. Recently, dielectric barrier discharge (DBD) has received much attention for greenhouse-gas conversion. This study is divided into two main parts. In the first part, the feasibility of the main reactions in MDR as well as the key reactions generating solid carbon was investigated. A carbon-free MDR is practically possible by increasing the temperature higher than 1173 K at the atmospheric pressure, yielding a considerable amount of syngas with hydrogen to carbon monoxide ratio of unity ($H_2/CO=1$) suitable for downstream Fischer–Tropsch synthesis. A thermodynamic analysis was also performed for oxidative MDR to identify the condition for syngas production with no carbon deposition, with the minimum loss of syngas and a higher reactant conversion at a lower temperature. In the second part of the work, extensive laboratory and modeling studies were conducted to identify the effects of influential parameters (discharge power, CO_2/CH_4 ratio, gap spacing, and reactant flow rate) on DBD MDR in terms of reactant conversion, product distribution, discharge characteristics (including the reduced electric field, breakdown voltage, dielectric and gas capacitances, electron density, electron energy distribution function and mean electron energy) and energy efficiency. In the present study, CO_2/CH_4 ratio of 1, the flow rate of 50 ml/min, discharge gap of 1 mm, discharge power of 30 W and frequency of 10 kHz have been justified to present acceptable values of reactant conversion and yields of CO and H_2 as well as to maintain the H_2/CO ratio of close to unity (suitable for liquid fuel production) while maximizing the energy efficiency, conversion ability and production ability of H_2 and CO. Reactant dilution with coplasmagen gas, argon (Ar), facilitates the plasma generation due to their low breakdown voltage. Therefore, the effects of the diluent gas (Ar) on DBD MDR in terms of reactant conversion, product selectivity, discharge characteristics and energy efficiency were investigated. The results revealed that higher Ar dilution factor led to the greater performance and a further restriction of carbon deposition. To benchmark our model forecasts, we also presented an overview of reported conversions and energy efficiencies in literature, to show the potential for an enhancement in comparison with the state-of-the-art. However, adding Ar is not an economical approach to improve the efficiency of non-catalytic DBD MDR, due to increased energy consumption. Furthermore, a global kinetics model for Ar diluted DBD CH_4/CO_2 was proposed, and the kinetics behaviour was compared to the one for helium (He) diluted DBD MDR reported in the literature.

ABSTRAK

Pembentukan semula metana kering (MDR) adalah cara yang berpotensi untuk pengeluaran bahan api disebabkan oleh pengurangan karbon dioksida (CO_2) dan pengeluaran metana (CH_4), serta dapat menangani isu pemanasan global. Pada masa ini, pembuangan halangan dielektrik (DBD) telah menerima banyak perhatian sebagai kaedah penukaran gas rumah hijau. Pada bahagian pertama, kebolehupayaan tindak balas MDR serta tindak balas utama penjanaan karbon pepejal dikaji. MDR bebas karbon berkemungkinan boleh terhasil dengan meningkatkan suhu yang lebih tinggi daripada 1173 K pada tekanan atmosfera bagi menghasilkan sejumlah besar syngas dengan nisbah hidrogen kepada karbon monoksida ($H_2/CO=1$) yang sesuai untuk sintesis hiliran *Fischer-Tropsch*. Analisis termodinamik dilakukan untuk MDR oksidatif bagi mengenalpasti keperluan pengeluaran syngas tanpa pemendapan karbon dengan jumlah minimum kehilangan syngas dan penukaran bahan tindak balas lebih tinggi pada suhu yang lebih rendah, Seterusnya dalam bahagian kedua, melalui kajian makmal dan pemodelan yang menyeluruh, kesan daripada parameter utama (kuasa pelepasan, nisbah dan kadar aliran bahan tindak balas CO_2/CH_4 , jarak gas) pada DBD MDR dari segi penukaran bahan tindak balas, pengagihan produk, ciri-ciri pelepasan (termasuk pengurangan medan elektrik, pengirangan voltan, kepadatan elektron, fungsi pengagihan tenaga elektron dan purata tenaga elektron) dan kecekapan tenaga dikaji. Dalam kajian ini mendapati nisbah CO_2/CH_4 kepada 1, dengan kadar aliran 50 ml/min, jarak pengeluaran 1 mm, kuasa pelepasan 30 W dan frekuensi pada 10 kHz memberikan nilai pertukaran bahan kajian dan penghasilan CO dan H_2 yang boleh diterima di mana nisbah H_2/CO menghampiri penyatuan (sesuai untuk penghasilan cecair minyak) dengan memaksimumkan kecekapan tenaga, keupayaan penukaran dan penghasilan H_2 and CO. Bahan tindak balas pencairan dengan gas koplasmagen, argon (Ar), memudahkan penghasilan plasma akibat voltan pecahan rendah. Oleh itu, kesan gas pencair (Ar) pada DBD MDR dari segi penukaran bahan tindak balas, pemilihan produk, ciri-ciri pelepasan dan kecekapan tenaga telah dkaji. Keputusan menunjukkan bahawa lebih tinggi faktor pencairan Ar membawa kepada peningkatan prestasi dan lanjutan pada sekatan pemendapan karbon. Sebagai penandaaras model ramalan, tinjauan dari laporan ilmiah mengenai penukaran dan kecekapan tenaga bagi menunjukkan peningkatan potensi berbanding tahap pencapaian dibentang. Walau bagaimanapun, menambah Ar bukan satu pendekatan ekonomi untuk meningkatkan kecekapan bukan pemangkin DBD MDR kerana ia meningkatkan penggunaan tenaga. Oleh yang demikian, model kinetik global untuk DBD dicairkan Ar, CH_4/CO_2 adalah dicadangkan dan perbandingan tingkah laku kinetik dengan DBD MDR dicairkan helium (He) berdasarkan kajian lepas yang dilaporkan.

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LIST OF ABBREVIATIONS

AC	— Alternative current
APG	— Atmospheric pressure glow
APGD	— Atmospheric pressure glow discharge
APPJ	— Atmospheric pressure plasma jet
bpd	— Barrel per day
CCP	— Capacitively coupled plasma
DBD	— Dielectric barrier discharge
DC	— Direct current
DME	— Dimethyl ether
EEDF	— Electron energy distribution function
EOR	— Enhanced oil recovery
FID	— Flame ionization detector
FTIR	— Fourier transmission infra-red
FTS	— Fischer-Tropsch synthesis
GAD	— Gliding arc discharge
GC	— Gas chromatography
GHG	— Greenhouse gas
GTL	— Gas-to-liquid
ICP	— Inductively coupled plasma
LFG	— Landfill gas
MDR	— Methane dry reforming
NG	— Natural gas
OCM	— Oxidative coupling of methane
PTFE	— Poly tetra fluoro ethylene
RF	— Radio Frequency
RWGS	— Reverse water-gas shift reaction

SEI — Specific energy input
SPARG — Sulfur-passivated reforming
SRK — Soave-Redlich-Kwong
TCD — Thermal conductivity detector
Td — Townsend (unit of electric field)
VOC — Volatile organic compounds
WGS — Water gas shift

LIST OF SYMBOLS

a — Acceleration term

a_{ik} — Number of atoms of the k^{th} element present in each molecule of species i

A, B — Stand for atoms in Chapters 2 and 5, B is concentration of Ar and carbonaceous species in Chapter 6.

A_2, B_2 — Stands for molecules in Chapter 2

A_k — Total mass of k^{th} element in the feed

C_d — Dielectric capacitance (F)

C_{eff} — Effective capacitance (F)

C_g — Gas capacitance (F)

C_t — Total capacitance (F)

d — Distance between the electrodes (mm)

D_e — Diffusion coefficient

e — Electron charge (Coulomb)

E — Activation energy (J/mol)

E_e — Average bulk electric field (V/m)

E/N_X — Average reduced electric field (Td)

f — Frequency (Hz)

$f_i^{\circ g}$ — Standard-state fugacity of pure component i in the gas phase

$f_i^{\circ s}$ — Standard-state fugacity of pure component i in the solid phase

$\hat{f}_i^g$ — Fugacity of species i in gas system

$\hat{f}_i^s$ — Fugacity of species i in the solid phase

$\Delta G_{fC}^{\circ S}$ — Standard Gibbs energy of formation for solid graphite carbon (kJ/mol)

$\Delta G_{fi}^{\circ g}$ — Standard Gibbs free energy of formation for species i in the gas phase (kJ/mol)

ΔG_r° — Free energy change of reaction (kJ/mol)

$\overline{G_C^S}$ — Partial molar Gibbs free energy of carbon in a solid state (kJ/mol)

$\overline{G_C^g}$ — Partial molar Gibbs free energy of carbon in a gas state (kJ/mol)

$\overline{G_\iota^g}$ — Partial molar Gibbs free energy of species i in a gas phase (kJ/mol)

$\overline{G_\iota^s}$ — Partial molar Gibbs free energy of species i in a solid phase (kJ/mol)

$G_{(T,P)}^{t}$ — Total Gibbs free energy of two phase (kJ)

$G_{(T,P)}^{tg}$ — Total Gibbs free energy in gas phase (kJ)

$G_{(T,P)}^{ts}$ — Total Gibbs free energy in solid phase (kJ)

$G_C^{\circ s}$ — Standard Gibbs free energy of pure solid carbon (kJ/mol)

$G_{i,e}^{\circ g}$ — Standard Gibbs free energy of elements i in a gas phase (kJ/mol)

$G_i^{\circ g}$ — Standard Gibbs free energy of species i in a gas phase (kJ/mol)

$G_i^{\circ s}$ — Standard Gibbs free energy of species i in a solid phase (kJ/mol)

$\overline{\mathrm{I}}_g$ — Average discharge current (mA)

$\mathrm{I_P}$ — Peak current (mA)

$\mathrm{J_{collision}}$ — Collision term corresponding to the changes in electron energy distribution

$\mathrm{I_{pk\text{-}pk}}$ — Peak to peak current (mA)

$\mathrm{k_b}$ — Boltzmann constant

K — Reaction rate constant in Chapters 5 and 6, heat conductivity in appendix D

l — Length of reactor (cm)

$\mathrm{k_0}$ — Pre-exponential constant in Arrhenius equation

$\mathrm{k_{dissociation}^{X}}$ — Reaction rate constant for dissociation of X species

m, n — Indices for reaction rate based on general power law model

$\mathrm{m_e}$ — Mass of electron (kg)

$\mathrm{M_e}$ — Molar mass of electron (g/mol)

$\mathrm{M_w}$ — Molecular weight (g/mol)

$\mathrm{M^*}$ — Excited species such as $\mathrm{He^*}$, $\mathrm{Ar^*}$, $\mathrm{N_2^*}$ and $\mathrm{N^*}$

N — Number of species in a reaction system

$\mathrm{n_e}$ — Electron density (1/m^3)

$\mathrm{n_i}$ — Moles of species i (mol)

$\mathrm{n_C}$ — Moles of carbon (mol)

$\mathrm{N_X}$ — Gas density (1/m^3)

P — Pressure of the reaction system (atm)

P_i — Product in chapter 6 (P1, P2,…)

P° — Standard-state pressure (1 atm)

$\mathrm{P_{ave}}$ — Average electrical power (W)

$\mathrm{P_{dis}}$ — Discharge power (W)

$\mathrm{P_{input}}$ — Input power (W)

$\mathrm{P_{instant}}$ — Instantaneous input power (W)

$\mathrm{Q_d}$ — Discharged charges per half cycle (nC)

$\mathrm{Q_{pk\text{-}pk}}$ — Peak-peak charges per half cycle (nC)

$\mathrm{Q_t}$ — Total charges (nC)

r — Reaction rate

$\mathrm{r_i}$ — Radius of the high voltage electrode (mm)

$\mathrm{r_o}$ — Radius of the outer electrode (mm)

R — Molar gas constant (kJ/mole.K) in Chapter 4 and radical concentration in Chapter 6

$\mathrm{R^{X}_{dissociation}}$ — Reaction rate for dissociation of species X (m^3/s)

S — Solid surface sites in Chapters 2 and 4, reaction step in Chapter 6 (S1, S2…)

T — Temperature of the reaction system (K)

$\mathrm{T_e}$ — Temperature of electron (eV)

$\mathrm{T_g}$ — Gas temperature (K)

$\mathrm{TE_0}$ — Threshold energy of electron-molecule impact (eV)

$\mathrm{TE_1}$ — Threshold energy of molecule/atom-molecule/atom impact (eV)

$\mathrm{T_{HV}}$ — High voltage electrode temperature (K)

$\mathrm{T_w}$ — Wall temperature of the DBD reactor

v — Electron drift velocity (m/s)

V_B — Breakdown voltage (kV)

$\mathrm{V_C}$ — Instantaneous voltage across the capacitor (V)

V_g — Discharge voltage (kV)

V_{Min} — Minimum voltage (kV)

$\mathrm{V_{pk}}$ — Peak voltage (kV)

$\mathrm{V_{pk\text{-}pk}}$ — Peak to peak voltage (kV)

x — Reactant (CO_2/CH_4) conversion (%)

X — Concentration of CH_4/CO_2 in Chapter 2 and 6 at time t

X_0 — Initial concentration of CH_4/CO_2 in Chapter 2 and 6

y_i — Mole fraction of species i in a gas phase

Greek symbols

α — First Townsend ionization coefficient

β — Energy cost

ε — Mean electron energy (eV) in Chapter 5, efficiency of the reactant conversion in the plasma zone in appendix D

ΔT_g — Average increase in gas temperature (K)

Φ — Shift phase between current and voltage (Radian)

$\hat{\phi}_i$ — Fugacity coefficient of species i

γ_i — Stoichiometric coefficient of species i

λ_k — Lagrange multiplier

η — Electron attachment coefficient

μ_e — Electron drift mobility (m^2/V.s)

μ_C^S — Chemical potential of carbon in a solid phase

μ_C^g — Chemical potential of carbon in a gas phase

μ_i^S — Chemical potential of species i in a solid phase

μ_i^g — Chemical potential of species i in a gas phase

ρ_{gas} — Gas density (kg/m^3)

τ — Residence time (s)

ω — Angular velocity (Radian/s)

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CHAPTER 1

INTRODUCTION

1.1 Natural Gas the Most Available Basic Fossil-Fuel

Natural gas (NG) is an abundant, inexpensive and clean fuel. It has been formed during millions of years, under the earth's ground within the rocks surfaces or shelves. The principal components of NG are CH_4 and CO_2. The composition of the substances in NG is different and related to the type of the reservoir rocks and the type of the organic material. There are approximately 5,000 trillion cubic feet NG reservoirs equal to roughly 47% of the world's petroleum (Mooday, 1998). It is also mentioned that there are large resources of methane hydrates isolated in the vast regions of the subarctic tundra and under the seas where the continental shelves exist. These kinds of hydrocarbon resources will finally be exploited, although it will be more difficult to utilize them due to exhausting procedures such as drilling and extraction (Olah *et al.*, 2006).

Figure 1.1 depicts the geographical regions of world proven natural gas reserves, of which substantial extents are reported in Middle Eastern and Eurasian countries.

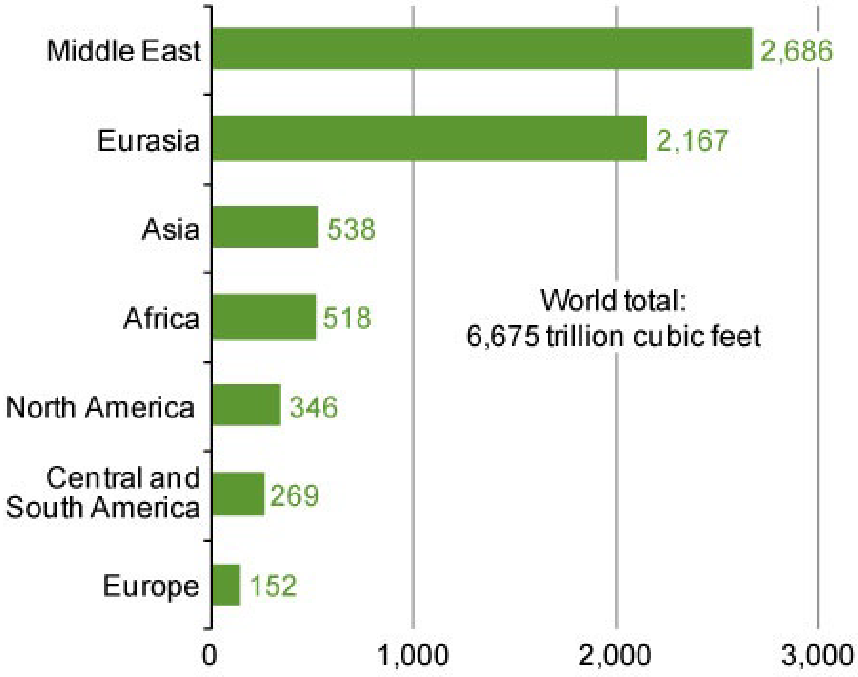

Figure 1.1 World NG reserves by geographic region, January 2011 (Vera J., 2011)

In spite of availability and low-cost of methane, the hazardous specification of natural gas is the reason for being economically unfeasible to transport over far distances. For more descriptions, it needs to be compressed and pumped through the long pipe lines, which is expensive and rarely practical. Furthermore, methane has hazardous physical properties to make it difficult to handle. It remains in the gas form; even in very high pressure is impossible to be liquefied. However, the significant attention of researchers to natural gas is attributed to search for the substituents to replace petroleum-based resources and for producing energy with low carbon emissions. Such an attention led to the deep and serious research, especially among developed countries (Klemm *et al.*, 2005; Klemm *et al.*, 2006; Simkovic, 2008). Furthermore, independent scarcity of oil in the near future is stimulating the governments to devote the research for a substituent that can compensate the shortcoming of oil-based fuels. In comparison, natural gas reserves are not as valuable as the petroleum reservoirs. Due to this fact, there is no sufficient care of natural gas associated with petroleum reservoirs. While the highly precise petroleum is carefully under-exploited, the natural gas coupled with petroleum reservoirs is volatilized into the environment or burnt inside the flares. Providentially, this situation is increasingly changing to attract more attention to maintain the natural gas resources due to the enhanced demand of the market to hydrogen production. Among the common fossil-fuels, natural gas is the most proper for hydrogen production. It is worth noting that natural gas is a clean and environmentally friendly fossil-fuel while emitting low amounts of carbon to the atmosphere. Therefore, natural gas is largely distributed to homes for household consumption such as cooking and central heating. Moreover, natural gas has been utilizing in gas-fired power plants in order to generate electricity.

Methane is released from various natural and human-influenced resources. It has a capacity over 20 times greater than CO_2 to absorb and maintain the heat in the atmosphere. Landfills, coal mining, agricultural activities, waste water treatment and combustion systems are common examples of human-influenced sources. Since methane is the principal components of natural gas, it is very promising and efficient to utilize methane as a feedstock for production of highly valuable chemicals and clean fuels. In the case of CO_2, the flue gases of fossil-fuel based power plants, cement and steel factories produce a large amount of CO_2 and need significantly to be controlled. Carbon dioxide is used in flash drying, welding, brewing, enhanced oil recovery (EOR) and carbonated beverages. Moreover, it has been employed as chemical feedstock, inert gas, and as a supercritical fluid for solvent extraction. The major CO_2 sources are (Chapel *et al.*, 1999):

1- CO_2 wells
2- Natural gas sweetening
3- Natural sources
4- Syngas production
5- Flue gases
6- Fossil fuel-fired power plants
7- Cement plants
8- Industrial furnaces
9- Lime kiln exhausts
10- Engine exhausts

The CO_2 released by the petrochemical plants can be recovered and utilized in the other industries. However, the amount of CO_2 produced by petrochemical industries is much higher than its consumption. According to aforementioned, since the most utilized feedstock for syngas production is currently CH_4, it plays a key role in the world's energy infra-structure. Moreover, CH_4 as a major contributor to the man-made greenhouse effect has attracted much attention since it can be converted into higher hydrocarbons and easily transportable liquids, such as methanol (CH_3OH), di-methyl ether (DME) and formaldehyde (HCHO). It is expected that methane will become increasingly important in the production of energy and chemicals during this century (Brown and Parkyns, 1991; Roth, 1994).

1.2 Background of Syngas Production

Syngas (synthesis gas), a versatile energy source, is the product of gasification or reforming of a carbon containing fuel such as coal, oil, natural gas, heavy residual fuel oil, gas oils, and biomass. Steam reforming of methane, the most preferred processes among the syngas production methods, contributes to 50% of global processes of hydrogen production. Nowadays, this figure touches 90% in the U.S. In this process, the reaction of natural gas (methane) with vaporized water in the presence of a metallic catalyst under high pressure and temperature generates syngas. During the past decades, heavier hydrocarbons up to naphtha have been employed as feedstock for syngas production over developed and selective catalysts (Olah *et al.*, 2006).

Although the formation of syngas from oil has been well-established for a long time, is not permanent since it is not supposed to meet the market demand in the long term, due to deficiency of oil reservoirs. In fact, the feedstock for syngas production is related to available resources in different countries and the downstream application. For instance, in the USA, coal was used as a conventional feedstock to generate syngas in 1940s (Mooday, 1998). At that time, natural gas due to being an inexpensive and efficient primary fuel source was introduced to the market and utilized in many plants such as methanol production units all over the world. In contrast to natural gas, the world's coal reservoirs are extensive and accessible at a lower price. However, the syngas produced by coal contained a larger quantity of CO_2 compared to its counterpart produced by natural gas due to coal's deficiency in hydrogen. Additionally, a great quantity of energy is required for removing or sequestering the produced CO_2, causing a large increase in the process cost (Neiva and Gama, 2010).

According to one estimation (Yamamura *et al.*, 1982), the investment for a methane-based syngas unit is almost three times lower than that for a coal-based syngas plant. Therefore, the syngas with low H_2/CO ratio could not be appropriate when using as a feedstock in most of chemicals plants such as methanol production, and gradually, avoided by the chemical industries of this field. Hence, natural gas is the most favorable fossil-fuel for syngas production due to the production of cheapest syngas and highest hydrogen to carbon monoxide ratio, which reduces the formation of carbon dioxide as a by-product (Parmon *et al.*, 1998).

The term syngas is derived from its usage as an intermediate for generation of synthetic natural gas and creating ammonia or methanol (Olsbye *et al.*, 1997). The potential of syngas conversion into valuable chemicals provides an attractive substituent to petroleum-based fuels and organic products. It is employed as a suitable feedstock for producing various kinds of products such as a transport fuel and electricity. The energy density of syngas is about 50% of that of natural gas. As syngas mostly comprises of H_2, CO, CH_4 and CO_2, it has some heating value and is well-suited for using as either heating gas or as a building-block feedstock for downstream applications such as fuel and chemical production (Saeidi *et al.*, 2014). The relative quantity of each species in the produced syngas depends on different parameters, such as type of feedstock, processing procedures and operation conditions. If syngas contains a large amount of nitrogen, this nitrogen should be removed. Since nitrogen and carbon monoxide have almost equal boiling points, which are -195.79 °C and -191.5 °C, respectively, post-treating of syngas by cryogenic processing in order to recover pure carbon monoxide would be very difficult. The carbon monoxide with the purity in the order of 99% is a proper feedstock for using in industrial purposes. The process gas comprising of CO_2, H_2, CH_4 and N_2 can be further treated by a special purification method to separate H_2. Regardless of the end-use, the particle impurities should be removed from syngas in scrubbers or cyclones as a first step of gas purification. Afterward, the gas stream is directed to ultimate purification where CO and H_2 are separated. The production cost notably depends on the final separation technique. There are four main techniques for purification of the process gas:

1- Pressure swing adsorption (PSA)
2- Cryogenic purification
3- Salt solution absorption
4- Membrane separation

The pure H_2 and CO, then, can be mixed in an appropriate ratio for using in Fischer-Tropsch process or in the other desired chemical production. Considering the downstream application, the ultimate hydrogen to carbon monoxide ratio can be adjusted employing the water-gas shift reaction (Saeidi *et al.*, 2014). Different qualitative analyses are required to select the most suitable and economic syngas production process for an especial application. Different downstream applications need different process criterion. Therefore, determination of the key factors, evaluation of the reaction process method and final gas processing techniques in detail are of great importance. When designing a syngas plant, some of the key factors such as unit capacity, feedstock accessibility, hydrogen to carbon monoxide ratio, and product purity are necessary to be determined since they strongly affect the reaction process design and the selection of the syngas production method.

1.3 Problem Statement

There are different basic methane reforming reactions for syngas production depending on the downstream objectives. Methane can be converted to hydrogen by steam reforming, partial oxidation and dry reforming or distinct combinations of these reforming reactions. Currently, syngas is mainly produced by methane-based steam reforming process. However, there are some inevitable drawbacks associated with steam-reforming of methane:

1- The stoichiometric H_2/CO ratio in the produced syngas by methane steam reforming is 3, which is higher than the value required by some downstream applications such as FTS (Eliasson *et al.*, 2000; Li *et al.*, 2007; Zhu *et al.*, 2001).

2- Due to the endothermicity of the reaction of steam reforming of methane, a large amount of energy is needed, resulting in a costly and energy-intensive process. The amount of energy required by the reaction is generally supplied by burning the other fossil-fuels like methane or coal, which add greenhouse gases to the atmosphere.

3- The necessity to use a selective and efficient catalyst for steam reforming of methane lead to the great demand on the process management and on the reactant purification to avoid coke formation, sintering or poisoning of the catalytic materials, which are sometimes expensive and time-consuming. To minimize the carbon deposition on the catalyst, excess steam more than the stoichiometric value is added to the reaction system which itself leads to a higher operation cost.

4- Furthermore, a considerable amount of CO_2 (the greenhouse gas) is being produced in syngas and higher hydrocarbons production (Liu *et al.*, 2003).

Partial oxidation of methane produces a theoretical H_2/CO ratio of 2, suitable value for many downstream synthesis processes such as methanol production. Partial oxidation of methane into syngas is traditionally performed catalytically and noncatalytically. The catalytic process can be operated at the lower temperatures compared to non-catalytic counterpart, hence; it can be the most economical and efficient process for syngas production. However, the catalytic process is still under research on the laboratory scale, due to the instability function and short lifetime of the catalyst during the runs (Wu *et al.*, 2005). In contrast, the non-catalytic methane partial oxidation process has been industrialized. It can operate at temperature and pressure of around 1300 ˚C and 30-100 atm, respectively. Thus, supplying high pressure and temperature lead to an expensive operation cost.

As aforementioned, the conventional syngas (hydrogen) production techniques are expensive, not environmentally friendly due to a large quantity of CO_2 emissions and not very energy efficient. Hence, discovering and selecting a friendly environmentally syngas production route is considered necessary. In last decades, from the standpoint of simultaneous mitigation of two undesirable and less valuable greenhouse gases (GHG) emissions, CH_4 and CO_2, it has been of interest to employ methane dry reforming (MDR). The feasible utilization of CH_4 and CO_2 to higher value-added products such as higher hydrocarbons, syngas and liquid oxygenates are being investigated (Eliasson *et al.*, 2000; Istadi *et al.*, 2005; Olsbye *et al.*, 1997). Additionally, this process has the potential benefit of generating a H_2/CO ratio close to 1, a suitable ratio for production of oxygenates and long-chain hydrocarbons. Furthermore, it can be used in areas where water is not easily available (Olah *et al.*, 2006). It is worth noting that biogas containing a substantial amount of CO_2 without pre-separation of CO_2 can be widely employed as the feedstock.

There are two major challenges concerning catalytic MDR by which the commercialization of this process can be limited: the first one is associated with the high temperature (>700 ˚C) requirement in order to reach the acceptable yield of syngas and reactant conversion. Supplying such a high temperature to break the strong C-H bonds of CH_4 in this quite endothermic reaction calls for a high-energy cost. The second one is the deposition of intensive carbon, which clogs the pores and rapidly deactivates the metal phase of the catalyst, particularly the surface of the non-noble metal catalyst. Thus, MDR is still under research at the laboratory scale.

The aforementioned challenges and defects associated with the current conventional techniques of CH_4 reforming into syngas production have attracted the researcher’s interest in a substitute reforming methods with lower reaction temperature and pressure, more active catalyst and decreased process cost. However, in the initial steps of development for a new technology, further technological research would be necessary to accomplish before the technology could be commercialized or introduced to the market.

There have been some investigations on the application of different kinds of plasma to break various molecular bonds since the 19th century. A Norwegian-British company Gasplus developed an environmentally friendly breakthrough for production of hydrogen and a high-grade carbon black via methane decomposition. This technique which is called Kværner process established in Norway in the late 1980s and has been industrialized since 1992 (Bromberg *et al.*, 2001). In view of its advantages for on-board applications, eliminating CO_2 emissions and enhancing the energy efficiency are eminent. It can be also an advantageous step for representing the future’s electric cars for which only water vapour exists in the exhaust gas. Depending on the case of application, the plasma reactor can be fabricated in the scale ranging from a small device to a gas station or even an industrial plant.

Compliance with the request of exploiting syngas as a primary fuel would necessitate a large enhance in the syngas production capability. However, in view of the above, syngas production is expensive and introducing an efficient and cost-effective method as well as a smaller scale developed reactor design with higher performance compatible with the market demand seems to be a distinguished step in present fuel resources. It is interesting to note that in the majority of the published research, data regarding the production ability and energy efficiency of methane dry reforming (MDR) in dielectric barrier discharge (DBD) has not been reported. Therefore, calculations and comparison of the energy efficiency of the different plasma techniques in order to make the effective remedies for reduction of the gap between the experimental and industrial values seem necessary.

1.4 Hypothesis

One of the suggested approaches for the reactions to occur is generating abundant levels of free radicals, which in contact and collision to the other excited molecules or particles can produce a vast variety of products. It is proven that plasma technology can generate a huge amount of free radicals, which play an important role in oxidative and non-oxidative reactions. In fact, non-equilibrium plasma technology overcomes the disadvantages of the commercial and high-temperature methods because the major amount of the electrical energy is consumed for the formation of energetic electrons, which are responsible for breaking C-H bonds of methane instead of heating the gas (Olah *et al.*, 2006). The potential of plasma reforming for syngas (or H_2) formation from natural gas (methane) has revealed a promising perspective for either on-board vehicles or stationary industrial application. Therefore, the necessity for H_2 storage and transport piping which both are costly and hazardous can be eliminated. The plasma reformer has the significant advantages of rapid start-up, compactness, light weight and low device cost.

In MDR, a dilution gas being chemically inactive is often introduced to the reactant mixture. Note that in the case of plasma, if the diluent gas does not activate CO_2 and CH_4, it cannot be a proper choice. Ar and He can affect the plasma discharge due to their lower breakdown voltages in comparison with the reactants of CH_4 and CO_2, which lead to the increased ionization and dissociation processes. Indeed, according to the literature (Avtaeva *et al.*, 1997), rare gas atoms such as Ar and He can be excited to the metastable levels and ionized states, which are responsible for energy transfer in the plasma. The excitation and ionization process for the rare gas atoms (Ar and He) are listed as below (Avtaeva *et al.*, 1997):

$$Ar + e^- \rightarrow Ar^* + e^- \quad (1.1)$$

$$Ar \rightarrow Ar^+ + e^- \quad (1.2)$$

$$He + e^- \rightarrow He^* + e^- \quad (1.3)$$

$$He \rightarrow He^+ + e^- \quad (1.4)$$

In fact, addition of noble gases such as He or Ar causes a greater value for electron energy distribution function in the gas discharge state, resulting in more opportunities for inelastic impact of methane/carbon dioxide with the co-reactants and the other species (Pu *et al.*, 2006). Hence, it is supposed that the ionization of CH_4 and CO_2 molecules in the presence of noble gases would become higher; and dissociation of CH_4 and CO_2 is faster.

A large number of studies about kinetics models of catalytic methane steam reforming (MSR) and MDR on a different catalyst at laboratory scale have been reported in the literatures (Bebelis *et al.*, 2000; Xu and Froment, 1989). However, due to the difference between molecular and species interactions behavior in non-thermal plasma and thermal reactors, these kinetics models are not applicable and valid for MDR with CO_2 in non-thermal plasma reactors. In has been proven that reactions between free radicals govern the reaction mechanism in DBD plasma chemistry. In our work, CO_2 and CH_4 are introduced into the reactor with a dilution gas, which is itself a case under plasma. In this regard, presenting a kinetics model that can explain the behavior of MDR with CO_2 in the presence of a diluent in DBD reactor is considered to be useful.

1.5 Objectives of the Research

Considering the main problems regarding the traditional syngas production, the purpose of this investigation is to evaluate the feasibility of producing reasonable quantities of syngas by MDR using a DBD plasma reactor. The main objectives of this study focus on:

1- Performing thermodynamic analysis of possible reactions in CO_2 reforming of CH_4 in order to feasibility study of producing syngas, hydrocarbon, and methanol by MDR.

2- Investigating the effect of important parameters of CO_2/CH_4 ratio, residence time (by varying gap distance and flow rate), and discharge power on the conversion, product distribution and energy efficiency of the plasma performance.

3- Evaluating the electrical discharge characteristics (such as voltage and current waveforms, transferred charges and total capacitance) of CO_2/CH_4 reactant mixture diluted with Ar in DBD.

4- Determining the effects of Ar on reactant conversion, product distribution, energy efficiency and production ability in MDR using DBD-plasma reactor and comparing the results with that of conventional approach.

5- Deriving a global reaction kinetics model for Ar diluted MDR.

1.6 Scopes of Research

The scopes of this research are focused on the procedures and concepts resulting in more findings about MDR into syngas via a DBD plasma reactor:

1- Thermodynamic equilibrium analysis of possible reactions in MDR with CO_2 into syngas and hydrocarbons.

2- Set up a DBD-plasma rig consisting of the electrical discharge diagnostics, flow measurement instruments, plasma generator and gas product analysing to conduct experiments.

3- The appropriate values of the dominant process parameters such as CO_2/CH_4 ratio, discharge power and residence time (by varying gap distance and flow rate) in terms of the energy efficiency, carbon deposition and reaction performance are determined.

4- Effect of Ar introduced into the CO_2/CH_4 reactant mixture are investigated to understand more deeply the role of the diluent as energy transfer shuttles on the performance and energy efficiency of the blank DBD reactor.

5- The simplified kinetics model is derived considering the activated CH_4 and CO_2 species and generated fragments by the exerted discharge power, which is aimed to determine the practical behaviour of MDR diluted by different mole fractions of the Ar.

1.7 Expected Contribution

1- The equilibrium optimal condition for syngas production by MDR and oxidative MDR with negligible carbon deposition and water formation while the loss of syngas is minimal would be expected.

2- A bridge is supposed to be built between electrical discharge characteristics of pure/diluted MDR in DBD and their reaction performance in order to determine an operating condition leading to a higher reactant conversion and energy efficiency.

3- The kinetics model of Ar diluted CO_2/CH_4 mixture at two types of conditions: one in the lower Ar content (less than 50%) and another one in the higher Ar content (higher than 50%) is expected to be presented.

1.8 Organization of the Thesis

This thesis is organized into seven chapters as shown in Figure 1.2.

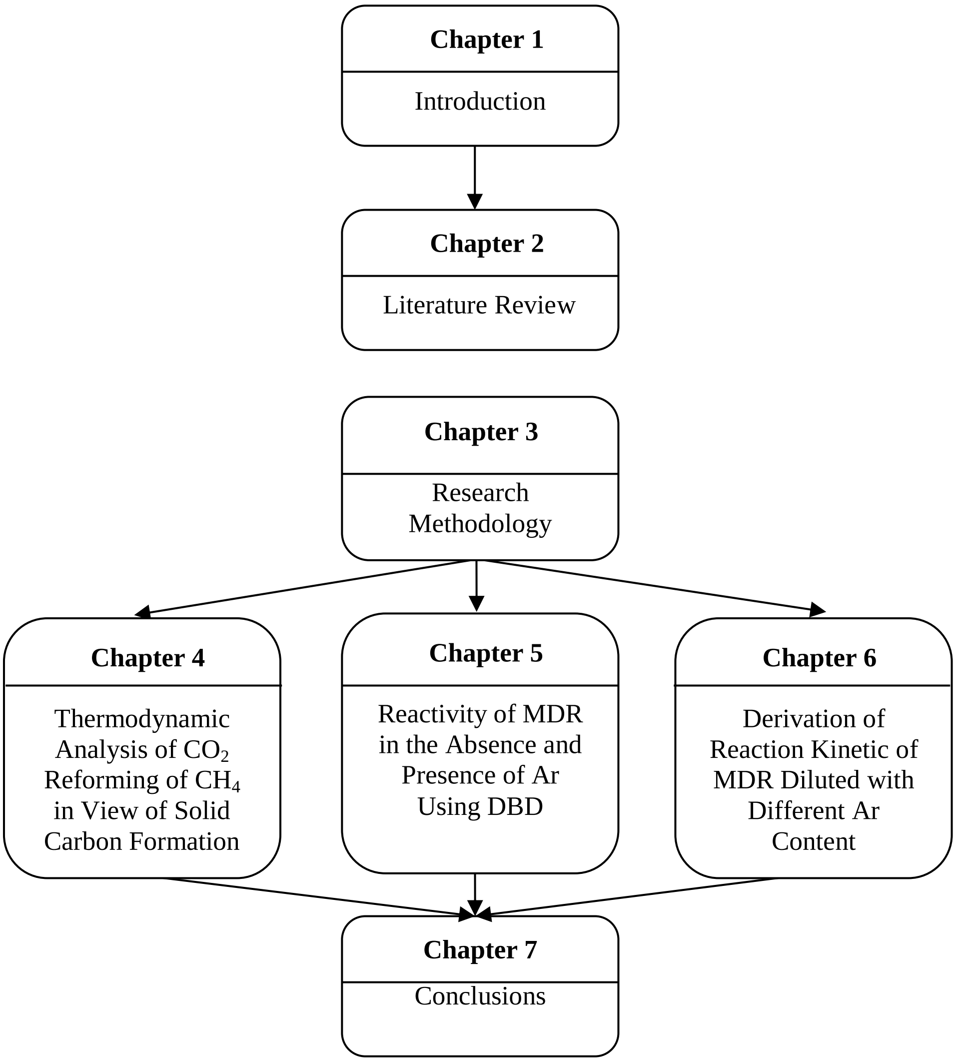

Figure 1.2 Organization of the thesis

Chapter 1 provides background of the research, problem statement, objectives and scopes of the study. Chapter 2 provides a review of related literature about the different types of hydrogen/syngas production along with their challenges. In addition, a variety of plasma reactors as new and promising alternatives for MDR and their advantages/disadvantages are discussed. The current research regarding the diluted CH_4 reforming and the reaction kinetics are also presented.

Chapter 3 provides the general description of research methodology for the thermodynamic analysis of MDR in view of carbon formation as well as the reaction kinetics for diluted MDR in detail. Chapter 4 investigates the thermodynamic analysis of MDR in view of carbon formation using Gibbs free energy minimization. Meanwhile, the experimental strategy for investigating the electrical discharge characteristics and the effect of dilution of CO_2 and CH_4 with Ar is presented in The optimal condition for syngas production from MDR and oxidative MDR with negligible carbon deposition and water production are addressed. Chapter 5 investigates the effect of important parameters of CO_2/CH_4 ratio, residence time and discharge power on reactant conversion, product distribution as well as energy efficiency of the plasma reactor. In this regard, the variation trends in reactant conversion and product distribution caused by introducing different amounts of CO_2 into the reactant mixture are reconciled by further discussion on the electrical discharge characteristics and the most important reactions involved in the plasma reaction system such as electron impact dissociation and excitation of CH_4 and CO_2.

In this section, the optimal operating condition of DBD plasma reactor is determined and then applied in studying the effect of diluent gas on the reactor performance. In this regard, the possible roles of diluted MDR with the various contents of the inert gas in terms of plasma discharge characteristics, reactant conversion, product distribution and energy efficiency of DBD reactor are discussed. Moreover, a comparison between the performance of diluted and undiluted DBD MDR with the earlier research is available in this study. The kinetics model for diluted MDR with Ar determined from Chapter 5 is presented in Chapter 6. Finally, Chapter 7 lists the contribution of the research and our recommendations for the future work.

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