CHAPTER II
LITERATURE SURVEY

The basic principles about the plasmas and the electric discharges environment, particularly in parts that deal with the chemical reaction of methane, are described within this chapter. Beginning with some basic knowledge about the chemical properties of the methane molecule, few aspects about the plasmas will then be introduced to eventually describe how the plasma can be generated for activating methane molecules in order to initiate the direct methane conversion. Along with these, some practical studies on the direct methane conversion process under the different types of the electric discharges will be mentioned so as to be the evidence on the advances of the work in this field. Finally, the aspects of the dielectric-barrier discharge reactor saved for the purpose of generating those plasmas for the present work will be discussed in details. It is necessary to point out that the present knowledge and insights about the electrical discharges environment and its plasma chemistry are very complicated and so much of those information will not be presented in here. Some literature (Nasser, 1971) is, however, recommended as good descriptive sources whenever the higher levels of the knowledge on the subjects of the plasmas are necessary.

2.1 Physical and Chemical Properties of Methane

Methane is commercially well-known as a very inexpensive and environmentally safe feedstock of fuel supplies. It is, in a chemical point of view, the smallest molecule in the entire hydrocarbon series, which consists of only one carbon atom surrounded by four hydrogen atoms. The most abundant and unique source of methane is the natural gas reserves, which are located in many different parts of the world. With its low molecular weight and non-

polar nature, the boiling point of methane is extremely low (-164°C) and can only be found in the gaseous state under ambient conditions. This property, coupled with the fact that many natural gas deposits are now located in very remote areas, which makes this resource somewhat expensive to transport.

The fact that methane is very flammable when presents in the oxygen atmosphere makes some people confused that methane is one of the very reactive molecules. Indeed, methane is a somewhat unreactive compound by its nature. Tables 2.1 and 2.2 compare the average bond energy of C-H bond inside the methane molecule and its first ionization potential with some of those other common gases, respectively.

Table 2.1 Average chemical bond energy of some covalent bonds (Perry, 1996)

Bond	Bond Energy(kJ/ mol)	Bond	Bond Energy(kJ/ mol)
C-H	463	H-H	436
C-C	344	O-H	463
C=C	615	O-O	142
C-O	350	O=O	539

Table 2.2 The first ionization potential of some common gases (Perry , 1996)

Gas	Ionization Energy (eV)	Gas	Ionization Energy (eV)
CH4	12.5	O2	12.2
H2	15.6	CO	14.1
N2	15.51	CO2	14.4
Li	5.39	Na	5.138
K	4.339	Cu	7.7

1 eV=1.6×10^{-19}J

Based upon these data, although the ionization potential of the methane molecule is in the same order of magnitude with those of other common gases, its bond energy between C-H is markedly high compared to other covalent bonds.

In almost all cases, methane can be made reactive only by using very reactive species such as radicals and so the radical chemistry is among the few effective techniques that has been traditionally applied for reaction with methane. At present, the oxidation of methane with oxygen is one of the most well known radical reaction which thermally converts the methane molecule into wide range of products depending upon the reaction conditions used but, thermodynamically, this application favors for the production of CO_2, CO and H_2O (Poonphatanapricha, 1997).

2.2 Gaseous Plasmas for Activating Methane Molecules

Since the gaseous plasma is an effective good source of active species formation including the electrons, ions and radicals, then a number of studies on the methane reactions using such plasma to initiate the reaction have been carried out intensively.

2.2.1 Fundamental Properties of Plasmas

In its simplest definition, gaseous plasma is a mixture of the negatively and positively charged particles in an otherwise neutral gas. The positively charged particles are, in all cases, the cations but negatively charged particles can be either the electrons or the anions. The neutral species may be the mixture of free radical species with stable neutral gases. Two important properties are known to be possessed by the plasma.

(1) Quasi-Neutral Property

The total density of negative charge carriers must be equal to the total density of positive charge carriers.

(2) Interaction with Electromagnetic Fields

The plasma can have some interactions upon the applying of an electromagnetic field due to fact that they consist of charged particles. In general, plasma can occur in all states (Nasser, 1971). The plasma in solid is called solid-state plasma while the plasmas generated in the liquid and gaseous states don't have any specific names. From this point, only the gaseous plasmas (i.e., shortly called as "plasmas") will be discussed along with the chemical reaction.

Unlike gases, plasmas differ greatly in many aspects according to which they are usually classified. These aspects include the pressure, the distributions of charged-particle density in the entire plasma volume and temperature.

2.2.2 Generation of Plasmas

There are several means of generating charged particles to produce plasmas. The collisions between the cosmic rays and the gases in atmospheric layers can, for example, cause the electrons in those gaseous molecules liberated out and thus produce the charged species. This process of liberating electrons from gas particles with the creation of positive ion charge is termed ionization. On the other hand, the process of liberating electrons from a solid is called electron emission. Both of these processes are of equal importance for the generation of the plasmas. The electrons and charged particles produced in the gaseous boundaries may be induced by the electromagnetic waves to collide with the solid surfaces to emit other electrons. These electrons, in turn, can collide with other gaseous particles to cause ionization. Various common ways of creating the charged particles can be classified schematically as shown in Figure 2.1(Nasser, 1971). From figure

2.1, the formation of negative ions can take place when free electrons are available and attach themselves to neutral atoms or molecules, negative ions are then formed. Gases with one or two electrons filling the outer shell of the atom form a charged negative ion. These gases, such as oxygen are usually known as "electronegative" gases. However, the electrons do not attach only to single atoms but they can also attach to the molecules of two (or more) atoms, such as O_2 and thus form the negative charged particles as well. There are several ways for producing the ions and electrons. Each type of generation has each mechanism to release the ions and electrons such as Negative ions can be occurred in gases by the radiative attaching or surface of metal by electron emitting when electrons are activated.
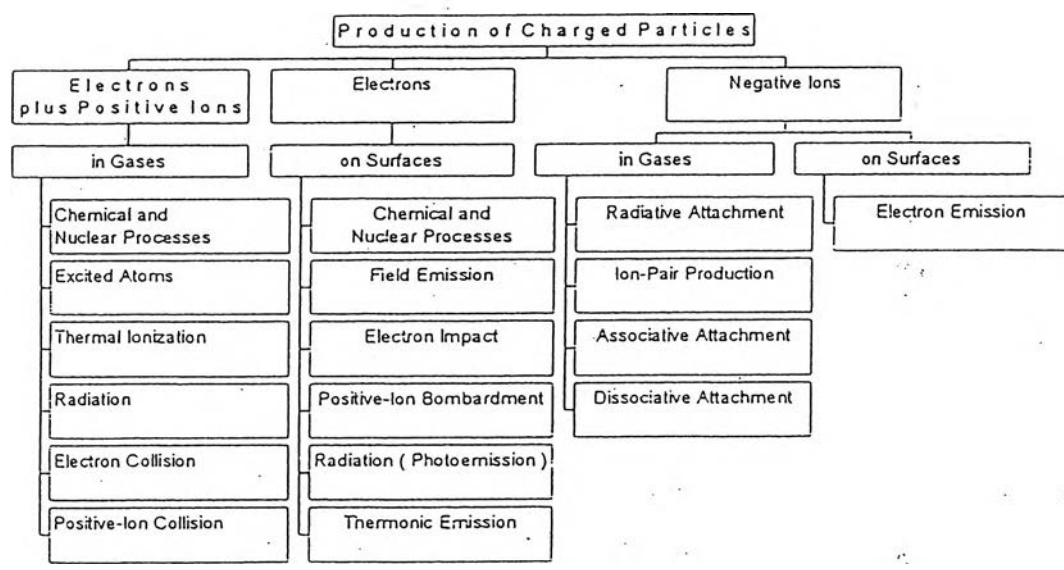
Production of Charged Particles			
Electrons plus Positive Ions	Electrons	Negative Ions	
in Gases	on Surfaces	in Gases	on Surfaces
Chemical and Nuclear Processes	Chemical and Nuclear Processes	Radiative Attachment	Electron Emission
Excited Atoms	Field Emission	Ion-Pair Production	
Thermal Ionization	Electron Impact	Associative Attachment	
Radiation	Positive-Ion Bombardment	Dissociative Attachment	
Electron Collision	Radiation (Photoemission)		
Positive-Ion Collision	Thermonic Emission		

Figure 2.1 Alternative methods of charged particles generation (Nasser, 1971)

In the present study, the plasma was first generated by the collisions between the neutral molecules (e.g., methane) and the electrons emitted from the surface of metal electrodes. This process of plasma generation is commonly known as the "field" emission process. In this type of process, an externally intense electric field is applied across the metal

electrodes to cause the reduction in its "potential barrier" and thus the energy that each electron requires for leaving the metal surface. A most interesting phenomena that occurs on the metal surface under the applying of an extremely high electric field is that many electrons can leak from the surface despite its less kinetic energy to overcome the potential barriers. This phenomena is known as " tunnel effect"

The electrons liberated from the metal surface will immediately be accelerated to move corresponding to the direction of the electric field and then can collide with any neutral gaseous particles in their vicinity to form the ionized gases with an additional set of electrons. Accordingly, all of these electrons can further move and collide with other species. As a result, a large quantity of electrons and plasma including the excited atoms and molecules, ions and radicals can be formed in the bulk of the gases within a very short period of time after the application of electric field has been started. Various numbers of collision mechanisms can be occurred simultaneously in the gaseous space for which many of those can initiate the chemical reactions leading to the production and destruction of the chemical species. Some important collision mechanisms occurred in the gases are typically shown in Table 2.3.

The combined steps of the field emission process among these plasma species and the collisions between the species and the electrode surfaces are referred to as "electric discharges" phenomena. The plasma produced by this discharge phenomenon can be divided into two types. The first type is "thermal plasma", which is characterized by high gas temperature and an approximately equal gas and electron temperature.

Table 2.3 Collision mechanisms in the gases (Nasser, 1971)

Collisions	
Elastic Collision	$e + A \longrightarrow e + A$
Excitation	$e + A \longrightarrow e + A^*$
Ionization	$e + A \longrightarrow 2e + A^+$
Attachment	$e + A \longrightarrow A^-$
Dissociative Attachment	$e + B_2 \longrightarrow B^- + B$
Recombination	$e + B_2^+ \longrightarrow B_2$
Detachment	$e + B_2^- \longrightarrow 2e + B_2$
Ion Recombination	$A^- + B^+ \longrightarrow AB$
Charge Transfer	$A^\pm + B \longrightarrow B^\pm + A$
Electronic Decomposition	$e + AB \longrightarrow A + B + e$
Atomic Decomposition	$A^* + B_2 \longrightarrow AB + B$

This type of plasma can also be referred to as plasma in equilibrium. Typical examples of such plasma are those produced in the arcs and plasma torches. The second type of plasma is termed "low-temperature" or "non-thermal" (cold-) or "non-equilibrium" plasma. This type of plasma is characterized by low gas temperature and high electron temperature. In other words, the non-equilibrium plasma consists of the electrons, which have much higher energy than the neutral gas particles. Those typical energetic electrons may have energy ranged from 1 to 10 eV. Which correspond to the temperature of about 10,000 to 100,000 K. (Rosacha et al., 1993)

The first implementation of the electric discharges generation technique as a tool for activating the chemical reaction can be tracked back to Siemens's experiments (Siemens, 1857) with the "silent discharge" (presently known as dielectric-barrier discharge) for the ozone generation in 1857. Even though the larger installations of such ozone generating systems for the

drinking water treatment plants were settled in many countries since the early of this century, some extensive studies on the plasma application for the ozone production have still been continued to the last decades. (Morinaga, 1961; Morinaga, 1962; Eliasson, 1987 and Nomoto, 1995)

At present, the process dealing with the plasma chemistry of electric discharges may be classified into two types, namely, the volume chemistry process; e.g., the ozone production in the so-called dielectric-barrier discharge, and the surface chemistry process; e.g., etching, deposition, or surface modification. The important application of methane plasma in volume chemistry process is the use of ionized methane as the ion source of the mass spectrometers. And the only application of methane plasma in the industrial surface chemistry process is the preparation of diamond coatings and ceramic materials (Nasser, 1971).

Only the non-equilibrium, volume chemistry plasma in the space filled with electric discharge will be treated in connection with the present study.

2.2 Types of Non- Equilibrium Plasmas

When the potential difference is applied across the plasma, the electric field will exert itself the charged particles and impart energy to them. The field does not directly influence the neutral species in the bulk of the plasma. The electrons, due to their light mass, are immediately accelerated to much higher velocities than those of heavier ions in the time available between collisions. The energy they lose through the collisions is taken up by their collision partners. If the pressure is small enough or the field is high enough, the electrons and some of the ions will, on average, have a kinetic energy, which is much higher than the energy corresponding to the random motion of the molecules. This plasma type is again called a non- thermal or non- equilibrium

plasma and can be classified into several types depending upon their generation mechanisms, their pressure range and the electrode geometry (Eliasson *et al.*, 1987)

2.3.1 Radio Frequency Discharge

These high frequency discharges are used extensively to produce plasmas for optical emission spectroscopy. The electrodes are normally kept outside the discharge volume whereas the plasma is generated inside by the induction technique. This can help avoid electrode erosion and contamination by the plasma. Since the wavelength of the electric field is much larger than the vessel dimensions, homogeneous plasma is formed. RF discharges work very well at low pressure, but are also used at atmospheric pressure in which a thermal plasma can sometimes occur (Nasser, 1971).

2.3.2 Microwave Discharge

Another type of high frequency discharge that can be practiced presently is the microwave discharge, induced by a microwave (0.3-10 GHz) radiation source that must be guided or directed into the gaseous vessel by using a wave guide structure or resonant cavity. As the dimensions of the cavities diminish when the frequency increases, the maximum microwave frequencies used for discharge applications are usually below 3 GHz.

2.3.3 Glow Discharge

This is the stationary low-pressure discharge usually occurring between flat electrodes encapsulated in a tube. The typical pressure involved is normally will below 10 mbar and, therefore, needs only comparatively low electrical potential difference (i.e.. voltage) and current to run. Due to its low pressure and the resulting low mass flow, the discharge type only finds its best

application in the manufacture of fluorescent and neon tubes and is not suited to the industrial production of chemicals (Nasser, 1971).

2.3.4 Corona Discharge

When the pressure is increased during of the glow discharge, the applied electric field will have to be increased accordingly. This, unfortunately, makes the glow discharge very unstable and usually turns into a high current arc discharge which is rarely controllable. The use of inhomogeneous electrode geometry; e.g., a pair of pointed and plane metal electrodes oriented in a perpendicular direction to each other, is another method used for stabilizing the high-pressure discharge. The discharge generated from this kind of electrode configuration is termed a corona discharge. The behavior of this type of discharge is not only different from that of the glow discharge but also depends significantly upon the type of electrodes used, either negative or positive types.

2.3.5 Dielectric- Barrier Discharge

This type of electric discharge is defined by the discharge generated within the gas- filled gap between a pair of metal electrodes of homogeneous geometry; e.g., the gap between two planar electrodes or in the annular space between two concentric cylinders. Either one or both electrodes are covered by a dielectric layer that is commonly made of glass. Many previous works referred to this kind of discharge as the silent electric discharge in which it has long been known to use in many studies on the plasma chemical reactions (Thayachotpaiboon *et al.*, 1996).

2.2 Related Research Work

Numerous studies of methane conversion using microwave plasma have been reported. Huang *et al.* (1994) reported methane dimerization to

ethane and ethylene via microwave plasma. Conversion of methane varied from 0 to 11% under low pressures ranging from 10 to 100 mmHg. The selectivities to ethylene and ethane were high, but excessive microwave power promoted carbon formation. They concluded that the energy efficiency of driving the methane dimerization reaction was only 2-8%.

Suib and Zerger (1993) included the use of catalysts to enhance the dimerization of methane in the microwave discharge. Products selectivities reached levels as high as 77% ethylene, 25% ethane, and 25% acetylene. Nickel and platinum catalysts were placed below the plasma zone, which provided reaction sites for radical combination. Reaction rates increased with the use of the catalysts but maximum conversion was observed without a catalyst. The operating pressures were quite low ranging from 10 to 50 Torr.

Another microwave plasma study on activating methane was carried out in the presence of air. The main objective was to convert methane into C_2 hydrocarbons and synthesis gas. The microwave power varied from 350 to 650 watts with a microwave frequency of 2.45 GHz. Pressure varied from 10 to 60 mbar. About 90 to 95% of oxygen was consumed in the discharge reactions. C_2 hydrocarbon yield of 22 % was achieved with 80% methane conversion and synthesis gas was also produced (Oumghar *et al.*, 1995)

In 1985, a study was conducted by Fraser and coworkers to investigate the decomposition of methane in an AC electric discharge at atmospheric pressure and 60 Hz. The AC electric discharge operated capacitively using a pyrex condenser with silver coating electrodes. A high voltage AC power supply with transformer was employed to generate the AC discharge. Methane destruction efficiency reached 67% at a feed methane concentration of 120 ppm. Higher inlet oxygen concentrations in the nitrogen stream were shown to increase the production of CO_2.

In 1986, Mallinson and Sliepecvich reported the first preliminary work with nonequilibrium discharges at the University of Oklahama. They

studied the partial oxidation of methane using an ozonolysis type reactor with applied AC voltage. Several experiments were conducted to develop an understanding of how the operating variables affecting the discharge reactions. Experiments showed that methane conversion increased with electrical frequency and that gas temperature and different types of waveforms had no major effect on the discharge reaction.

Bhatnager (1993) also studied the partial oxidation of methane using the ozonolysis discharge reactor. It was found that an increase in the methane/oxygen ratio decreased the methane conversion but the selectivity of methanol slightly increased. Alcohols and ethane were intermediates in the reactions. The formation of ethanol was found to be independent of the formation of ethane or methanol.

Lobban et al. (1996) investigated the oxidative coupling of methane using DC and AC corona discharges. Temperature programmed corona reaction experiments for DC positive and negative corona discharges showed that the rate of C_2 formation below 450 $^\circ$ C was very slow and the complete consumption of oxygen occurred at 875 $^\circ$ C. The positive corona produced higher C_2 yields greater than the negative corona. It was conducted that streamers of the positive corona were more favorable for OCM than the pulses of the negative corona. However, with no applied external heat the AC corona produced a maximum C_2 yield of 21%. Experiments were conducted with the AC corona to determine the effect of frequency, voltage, residence time, and oxygen partial pressure. They also suggested an OCM discharge mechanism.

A similar study to demonstrate the effects of a Sr/La_2O_3 catalyst on OCM in a DC corona discharge reactor was carried out by Lobban et al., (1997). They showed that the operating temperature of the corona discharge with Sr/La_2O_3 catalyst was much lower (<200 $^\circ$C) than the required temperature in the absence of a discharge. They found that an increase in the

oxygen partial pressure increased the methane conversion and the yield of C_2 products. The highest C_2 yield achieved was 11%.

Hill (1997) studied the oxidative coupling of methane using AC electric gas discharge. It was found that methane conversion increased with increasing oxygen partial pressure, voltage and gap width, but decreased with increasing flow rate and frequency. The condition in which the methane conversion increased caused the C_2 selectivity to decrease and so the C_2 yield remained essentially constant except at low methane conversions. Secondary reactions and CO formation also increased with increasing methane conversion. The CO selectivity remained high in all the experimental conditions but the CO_2 selectivity was usually constant and very low compared to the CO selectivity.

The methanol production is also enhanced by dilution of the source gas with a rare gas, such as Ar or He. The methanol production was increased about 2.5 times at the dilution ratio of 2.5 and gradually decreased as the dilution ratio further increased and the partial pressure of O_2 decreased (Mizuno et al., 1998).

A solid state pulse generator was developed to increase the frequency of pulse. A high voltage pulse of 1-2 μs rise time and 4-5 μs pulse width could be generated at frequency of 10 kHz. The pulse generator was used for the methanol synthesis. Methanol with concentration of up to 0.7 % was synthesized at 5 kHz pulse frequency and 6.7 s of gas residence time. when $CH_4 + O_2$ (96:4) mixture was used at room temperature (Mizuno et al., 1992).

The partial oxidation of methane to methanol with atmospheric oxygen was investigated experimentally and theoretically in a dielectric-barrier discharge (DBD). The predominant parameters of specific electric energy, oxygen content, flow rate, temperature and gas pressures were determined in both CH_4/O_2 and CH_4/air mixtures. Optimum methanol selectivity was found at an oxygen concentration of about 15% in both feed

gas mixtures. Low specific energy favored the selectivity towards methanol and suppressed the formation of carbon oxides. The experimental results indicated that high methanol selectivities could be obtained at high methane conversions. The highest methanol yield of 3% and the highest methanol selectivity of about 30% were achieved in CH_4/O_2 mixture. For the CH_4 / air mixture, as high as 2 % methanol yield was also obtained. In addition, other usefully products, like ethylene, propane and ethanol, were detected. Experiments and numerical simulations showed that the formation of H_2O and CO had a strong negative influence on methanol formation (Zhou et al. 1998).

Recently at the University of Oklahoma, methane conversion using methane / hydrogen feed with oxygen as an additive and helium as a diluent was systematically investigated (Liu et al., 1996). The $CH_4/H_2/O_2$ system was found to be more selective for the production of C_2 hydrocarbons compared to the CH_4/O_2, CH_4/H_2O, and CH_4/CO_2 systems. A higher hydrogen feed concentration was more favorable for acetylene formation. The selectivity and yield of C_2 hydrocarbons were related to the hydrogen feed rate, gas temperature, concentration of oxygen, and flow rate. The highest yield of C_2 hydrocarbons (32%) was obtained at the lowest flow rate used (10 cm^3/s, residence time ~ 2.3s).

Okumoto et al. (1998) studied direct methanol synthesis from CH_4 and O_2 by using pulsed discharge plasma in concentric-cylinder-type reactors. A combination of the pulse discharge and catalyst was tested and was proved to be effective in increasing both the production and selectivity of methanol. About 2 % of CH_4 could be converted into other hydrocarbons, and a methanol yield of around 0.5% and selectivity of 38% could be obtained when a catalyst of V_2O_5 + SiO_2 was combined with the pulsed discharge plasma.

Okazaki et al. (1998) developed a new technique for synthesizing methanol directly using ultra-short pulsed plasma inducing highly non-equilibrium chemical reactions at room temperature. The effects of methane

partial pressure and discharge parameters on the conversion efficiency and reaction selectivity were clarified. Relatively high values of 0.5% and 10% for methanol yield and selectivity were obtained, respectively. It was also reported that introduction of rare gases such as Ar and Kr could enhance the methanol yield.

Thanyachotpaiboon (1996) found that higher selectivity of C_3 and C_4 hydrocarbons could be obtained by the addition of ethane in feed by using AC electric discharge (dielectric barrier discharge reactor) in ambient condition.

Leethochawalit (1998) found that methane conversion increased remarkable with increases in CO_2: CH_4 ratio, voltage, helium concentration and space time by using AC electric discharge (dielectric barrier discharge reactor).

Sutthiruangwong (1999) performed experiment with catalyst and without catalyst and found that Non-catalytic system gave much higher methane conversion than the catalytic system and produced products mainly consisted of C_2 hydrocarbons.