CHAPTER II
LITERATURE SURVEY

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 surrounded by four hydrogen atoms. The most abundant and unique source of methane is the natural gas reserves. Which are located in many 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 containing atmospheric makes some people confused that methane is one of the very reactive molecules. Indeed, methane is somewhat unreactive compound by its nature. Table 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 bond (Perry *et al.*, 1997)

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 *et al.*, 1997)

Gas	Ionization energy (eV)	Gas	Ionization energy (eV)
CH_4	12.5	O_2	12.2
H_2	15.6	CO	14.1
N_2	15.51	CO_2	14.4

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 bond.

In the most 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 reforming of methane with carbon dioxide is one of the most well-known radical reactions which thermally converts the methane molecule into a wide range of products depending upon the reaction conditions used.

2.2 Gaseous Plasmas for Activating Methane Molecules

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

2.2.1 Fundamental Properties of Plasma

In its simplest definition, gaseous plasma consists of negatively and positively charged particles in an otherwise neutral gas. The positively charged particles are mostly cations but the negatively charged particles can be either electrons or anions. The neutral species may be the mixture of free radical species with stable neutral gases. Plasma processes two important properties (Eliasson and Kogelschatz, 1991).

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

Plasma can have some interactions upon the applying of an electromagnetic field due to fact that they consist of charged particles.

Normally, plasma can occur in all states (Nasser, 1971). Plasma in solid is called solid-state plasma while plasma generated in the liquid and gaseous states does not have any specific names. Only gaseous plasma is shortly called as "plasma". There are many differences between plasmas and gases. Their differences include pressure, 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, e.g., collisions between cosmic rays and gases in atmospheric layers. However, in the present study, an externally intense electric field is applied across metal electrodes to cause the reduction in its "potential barrier" and thus the energy that each electron requires for leaving the metal surface. The most interesting phenomena on the metal surface under 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 phenomenon is known as "tunnel effect ". And then the plasma is first generated by the collisions between the electrons emitted from the surface of metal electrodes and the neutral molecules. This process of plasma generation is normally known as the "field" emission process.

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, these electrons can further move and collide with other species. As a result, a large quantity of electrons 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. Many active species can initiate the chemical reactions leading to the production and destruction of the chemical species (Kruapong, 2000) Table 2.3 show some important collision mechanisms.

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.

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

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

Plasma is divided into two types. The first type is "thermal plasma" or "equilibrium plasma". In this type, the temperature between gas and electron are approximately equal which is close to thermodynamic equilibrium (Fridman *et al.*, 1999). An essential condition for the formation of this plasma is sufficiently high working pressure. An example of such plasma is those produced in the arc discharge and plasma torches.

The second type is "non-thermal plasma" or "non-equilibrium plasma", which is characterized by low gas temperature and high electron temperature. Those typical energetic electrons may have energy ranged from 1 to 10 eV, which corresponds to the temperature of about 10,000 to 100,000 K (Rosacha *et* *al.*, 1993). This plasma can be classified into several types depending upon their generation mechanism, their pressure range and the electrode geometry (Eliasson *et al.*, 1987).

2.3 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 too much higher velocities than those of heavier ions are in the time available between collisions. Their collision partner takes up the energy they lose through the collisions. If the pressure is small enough or the field is high enough, the electron and some of 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 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.

2.3.1 Radio Frequency Discharge

These high frequency discharge are use 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 to avoid the contamination by the plasma. Since the wavelength of the electric field is much larger than the vessel dimensions, homogeneous plasma is formed. Radio frequency discharge works very well at low temperatures and it is 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 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. 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. A dielectric layer that is commonly made of glass covers either one or both electrodes. 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.*, 1998).

2.3.6 Gliding Arc Discharge

The gliding arc discharge is a cold plasma technique, which has at least two diverging knives shaped electrode. These electrodes are immersed in a fast flow of feed gas. A high voltage and relatively low current discharge is generated across the fast gas flow between the electrodes. The electric discharge forms at the closet point, spread along the knife-edges of the electrodes and disappears. Another discharges immediately reforms at the initial spot. Figure 2.1 is considered to be the simplest case for a better physical understanding of the gliding arc phenomenon (Fridman *et al.*, 1999).

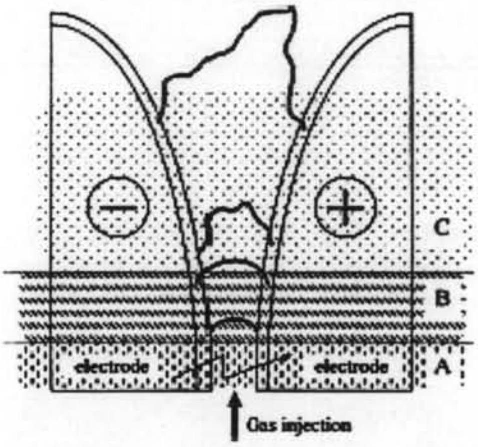

Figure 2.1 Phase of gliding arc phenomena: (A) reagent gas break down; (B) equilibrium heating phase; (C) non-equilibrium reaction phase.

The reagent gas break down (A) of the processed gas begins the cycle of the gliding arc evolution. The high voltage generator provides the necessary electric field to break down the gas between the electrodes.

The equilibrium-heating phase (B) takes place after formation of stable plasma channel. The electric discharge spread along the electrodes, which the velocity of the gas flow and the gliding arc are very close.

The non-equilibrium reaction phase (C) begins heat loss from the plasma to exceed the energy supplied by the source and it is not possible to sustain the plasma in the state of thermodynamic equilibrium. As a result, the discharge plasma rapidly cools to the gas temperature. After the decay of the non-equilibrium discharge, there is new break-down at the shortest distance between the electrodes and the cycle repeats (Fridman *et al.*, 1999).

2.4 Related Research Works

In recent years, the plasma technology could be very interesting to reform methane for synthesis gas and higher hydrocarbons production then the problems encountered in the catalytic reformers. The role of catalysers in the reforming process is to create radical species enhancing the reaction. The role of plasma would be then to provide the energy and to create free radicals needed for fuel reforming. The catalytic effect of non-thermal plasma to produce hydrogen has already been demonstrated in several papers. Thayachotpaiboon *et al.* (1998) studied pure methane conversion using a dielectric barrier discharge plate reactor. The results shown that increasing the voltage or the residence time led to increasing methane conversion and product selectivity. When methane was diluted with helium, a significant rise in methane conversion was obtained. It was concluded that helium was not only a diluent but also could make methane more active. In addition, it was found that higher selectivities of C_3 and C_4 hydrocarbons could be obtained by the addition of ethane in feed.

Methane conversion to higher hydrocarbons in the presence of carbon dioxide using a dielectric-barrier discharge at ambient conditions was investigated (Leethochawalit, 1998). Helium was also added in the feed at different concentrations. It was found that methane conversion increased remarkably with increases in CO_2/CH_4 ratio, voltage, helium concentration and space time. The C_2 products selectivities decreased but the carbon monoxide and hydrogen selectivities increased when voltage, helium concentration and space time were increased. Small amounts of methanol were produced while most reaction products were ethane, ethylene, acetylene, carbon monoxide and hydrogen.

Kogelschatz *et al.* (1999) studied low temperature conversion of two greenhouse gases CO_2 and CH_4 to synthesis gas in a high power dielectric-barrier discharge. It was found that the concentrations of all higher hydrocarbon products decreased with increasing CO_2 content in feed. In contrast, water production increased with rising CO_2. CO formation increased with the CO_2 content in the feed up to 80% and then decreased sharply. The synthesis gas amount increased almost linearly with the specific input energy and very high conversion rates were obtained for high specific input energies. In 2001, Zhang *et al.* studied the conversion of methane with carbon dioxide to produce synthesis gas and higher hydrocarbons over quartz fleece, zeolite NaX, zeolite HY, and zeolite NaY catalysts promoted by dielectric-barrier discharges at low temperature and ambient pressure. Experimental results showed that methane conversion decreases in the order fleece (without catalyst) > NaY > HY > NaX. The highest CO_2 conversion reached 40% when using zeolite NaY as the catalyst. CO_2 conversion decreases in the order NaY > fleece > NaX > HY. Compared to the results from fleece, zeolite NaY is the most promising catalyst for producing synthesis gas and liquid hydrocarbons (C_5+). In the range tested (100-500 W), syngas is the main product and increases significantly with increasing input power. The ratio of H_2/CO increased sharply when the ratio of CH_4 to CO_2 increased. When the flow rate increased, the yield of syngas decreased. One year later, Jiang *et al.* reported methane conversion to higher hydrocarbons in the presence of carbon dioxide via dielectric-barrier discharge reactor with and without zeolite A. In the presence of zeolite A, no plasma polymerized carbon film was produced that leads to a better production of light hydrocarbons (C_2-C_4).

Another results in methane reforming with carbon dioxide in dielectric-barrier discharge reactor were reported by Zhang *et al.* (2003). It was found that the product contains gaseous hydrocarbons, syngas and oxygenates. The oxygenates produced includes acetic acid, propionic acid, methanol and ethanol. The selectivities of acetic acid, propionic acid, methanol and ethanol were 5.2%, 1.0%, 0.3% and 1.8%, respectively, at the methane feed concentration of 66.8 vol.%.

Sutthiruangwong (1999) investigated methanol production from methane in a corona discharge reactor with and without catalyst and found that the non-catalytic gave much higher methane conversion than the catalytic system and the products were mainly consisted of C_2 hydrocarbons.

Kado *et al.* (2003) studied conversion of methane to acetylene or syngas using non-equilibrium pulsed discharge under the conditions of ambient temperature and atmospheric pressure. It was found that increasing the fixed current value led to a proportional increase in the pulse frequency. In the region of a relatively low methane conversion, methane conversion increased in proportion to the pulsed frequency. However, the rising slope decreased with the increase in methane conversion due to decrease in the probability of collision between a methane molecule and an electron. Methane conversion increased under the condition of the existence of rare gas like argon or helium, because the pulsed frequency in the presence of rare gas become higher than that with any other kind of coexisting gas under the condition of the same supplied energy. Using a mixture of methane and carbon dioxide or steam caused the reforming of methane to produce syngas as well as acetylene. Oxygen gas also promoted the reaction and gave syngas as well as acetylene while suppressing the carbon dioxide formation. The addition of oxygen was most effective in suppressing the carbon deposition by the converting CH_x into carbon monoxide.

Rusu and Cormier (2003) dedicated the study of methane steam reforming using a gliding arc discharge reactor. The experiments clearly demonstrated the ability of gliding arc to accelerate chemical reaction at low temperatures and with very low energetic costs. The experimental results indicate as a higher methane content and a lower total flow rate yielded better selectivity but methane conversion value was quite low (15-20%) because of the only small fraction (10-15%) of inlet gas passing through the discharge zone.

Supat *et al.* (2003) studied synthesis gas production from simultaneous steam reforming and partial oxidation of methane using an ac corona discharge. The benefits of the combination of the two reactions reduced the pure oxygen requirement in the system and increased the thermal efficiency by transferring heat between the exothermic and endothermic reactions. It was found that the coupling of methane increased with increasing CH_4/O_2 ratio but the oxidation of methane to carbon dioxide and water was more favorable at higher oxygen concentrations. Adding water vapor in the feed steam greatly enhanced the conversions of methane and oxygen in an oxygen-lean system but reduced the conversion of methane in the oxygen-rich system. Moreover, the energy consumption for methane conversion could be substantially reduced by adding water vapor. The product distribution was strongly influenced by the feed gas concentrations rather than the input power and applied frequency.

Li *et al.* (2004) studied carbon dioxide reforming of methane using DC corona discharge plasma reaction. The conversions of methane and carbon dioxide increased with increasing the discharge power and decreased with increasing the flow rate. The conversions of reactants via positive corona were generally higher than that via negative corona. They reported that the H_2/CO ratio increased with increasing CH_4/CO_2 ratio in the feed. Besides syngas and water, other product including various hydrocarbons and oxygenates were detected. There were visible coke mainly depositing on the cathode when the CH_4/CO_2 ratio was higher than 2/1. They proposed that the coke mainly formed via methane decomposition during the reaction.

Sekine *et al.* (2004) investigated steam reforming of methane, propane, hexane, cyclohexane, methanol, and ethanol using a nonequilibrium pulsed discharge under the conditions of atmospheric pressure and low temperature without the use of catalyst. In each case, steam reforming proceeded efficiently and selectively and hydrogen was formed as a main product. Carbon deposition and wax formation were prevented under the condition of molar steam/carbon ratio was 1. The conversion of methane and formation of hydrogen increased with increasing in pulse discharge frequency, while selectivity to products other than hydrogen was independent of pulse discharge frequency. The waveforms of current and voltage were not influenced dramatically by changes of pulse discharge frequency. The results of changing electrode distance and flow rate affecting hydrogen formation but not the other products.

Thakonpatthanakun (2004) studied partial oxidation of methane in a multi-stage gliding arc reactor. The results shown that increasing stage number, residence time, applied voltage or gap distance enhanced both methane and oxygen conversion in contrast with the negative effects of CH_4/O_2 feed molar ratio, total feed flow rate and frequency. The optimum condition was found at a CH_4/O_2 feed molar ratio of 3/1, a feed flow rate of 150 cm^3/min and frequency of 300 Hz for the maximum CH_4 and O_2 conversion and high synthesis gas selectivity. The energy consumption of the gliding arc system was found to be very low about 15.3-18.5 eV/molecule of methane converted as compared to 21 eV/molecule of methane converted obtained from the corona discharge system with pin and plate electrodes.

Zhang *et al.* (2004) studied the oxidative dehydrogenation of ethane under pulse corona plasma over various catalysts using carbon dioxide as oxidant. The experiment has confirmed that the rare earth metal oxides catalyst such as $La_2O_3/\gamma\text{-}Al_2O_3$ and $CeO_2/\gamma\text{-}Al_2O_3$ enhance conversion of ethane and the yield of ethylene and acetylene. The optimum Ce content for the oxidative dehydrogenation of ethane under pulse corona plasma is 10%. Conversion of ethane increased with increasing the concentration of carbon dioxide in the feed over $CeO_2/\gamma\text{-}Al_2O_3$. The total yield of ethylene and acetylene had maximum value at the CO_2 content in the feed was 50%.

Chavadej *et al.* (2005) studied the effects of electrical parameters of a corona discharge reactor on the partial oxidation of methane in air and on carbon dioxide reforming with methane in the presence and absence of Pt loaded KL zeolite. For the partial oxidation, it was found that the reactant conversion increased with decreasing applied frequency and increased with input low side voltage both in the presence and absence of Pt/KL except that the oxygen conversion was 100% in the presence of Pt/KL. For the carbon dioxide reforming with methane, applied frequency and input low side voltage affected only the reactant conversions with no significant effect on reaction pathways both in the presence and absence of Pt/KL.