

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Physicals 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 atmosphere makes some people confused that methane is one of the very reactive molecules. Indeed, methane is 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 bond (Perry *et al.*, 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 *et al.*, 1996)

Gas	Ionization energy (eV)	Gas	Ionization energy (eV)
CH <sub>4</sub>	12.5	O <sub>2</sub>	12.2
H <sub>2</sub>	15.6	CO	14.1
N <sub>2</sub>	15.51	CO <sub>2</sub>	14.4

$$1\text{eV} = 1.6 \times 10^{-19} \text{ J}$$

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 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 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<sub>2</sub>, CO and H<sub>2</sub>O (Poonphanapricha, 1997)

## 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 possesses two important properties (Eliasson and Kogieschatz, 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 1 shows 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	$e^- + A \longrightarrow e^- + A$
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	$A^+ + B \longrightarrow A + B^+$
Electronic Decomposition	$e^- + AB \longrightarrow e^- + A + B$
Atomic Decomposition	$A^* + B_2 \longrightarrow AB + B$

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.*, 1998). 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 to 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 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 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 the 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

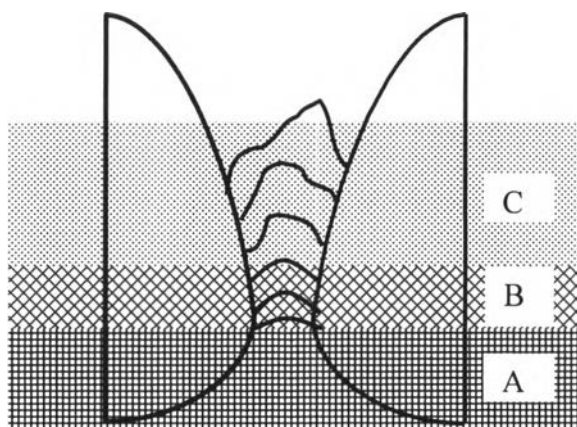
generated from this kind of electrode configuration is termed a corona discharge. The behavior of this type of discharge is not only different from that of the glow discharge but also depends significantly upon the type of electrodes used, either negative or positive types.

#### 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.*, 1996).

#### 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 closest 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 (Rusu *et al.*, 2003).



**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 and the discharge starts at the shortest distance between the two 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, Plasma is one of technology that has received increasing attention from many researchers especially using plasma for methane conversion. Therefore, numerous studies of methane conversion by



using plasma have been reported. Zerger *et al.* (1993) investigated the combined effects of microwave plasma and several types of heterogeneous catalysts on the oxidation of methane under the presence of oxygen at low pressures (3-500 torr). The microwave frequency of 2.45 GHz was used to generate free radical species over catalysts in plasma zone. They found that, with a constant  $\text{CH}_4/\text{O}_2$  ratio of about 2.22:1, the activation of plasmas could lead to the formation of various gas phase radicals including ethane, ethylene,  $\text{C}_3$  compound, formaldehyde and methanol. The influence of the different catalysts was also reported. Product selectivities reached level as high as 77%, 25% and 25% for ethylene, ethane and acetylene, respectively. Nickel and platinum catalysts were placed below the plasma zone, which provided reaction sites for radical combination. Reaction rates increased under the presence of the catalysts but the maximum conversion was observed without the catalyst.

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 of ethylene and ethane were high but excessive microwave power promoted carbon formation. They reported that the energy efficiency of driving the methane dimerization reaction was only 2-8%.

Another microwave plasma study on activating methane was carried out in the presence of air. The main objective was to convert methane into  $\text{C}_2$  hydrocarbon and synthesis gas. The microwave power was varied from 350 to 650 Watts with a microwave frequency of 2.45 GHz. The pressure was varied from 10 to 60 mbar. About 90 to 95% of oxygen was consumed in the discharge reactions.  $\text{C}_2$  hydrocarbon yield of 22% was achieved with 80% methane conversion and synthesis gas was also produced (Oumghar *et al.*, 1995)

Fraser *et al.* (1985) study the decomposition of methane in an AC electric discharge at atmospheric pressure and 60 GHz. The AC electric discharge operated using a pyrex condenser with silver coating electrode. A

high voltage AC power supply with transformer was employed to generate the AC discharge. Methane destructive 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 carbon dioxide.

In 1986, Mallinson and Sliepecvich reported the first preliminary work with nonequilibrium discharges at the University of Oklahoma. They studied the partial oxidation of methane using an ozonolysis type reactor with applied AC voltage. Experimental 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 and the selectivity of methanol slightly decreased. Alcohol and ethane were found to be independent of the formation of ethane or methanol.

Lobban *et al.* (1996) investigated the oxidative coupling of methane (OCM) using DC and AC corona discharges. Temperature programmed corona reaction experiments for DC positive and negative corona discharge showed that the rate of C<sub>2</sub> formation below 450°C was very slow and the complete consumption of oxygen occurred at 875°C. The positive corona produced higher C<sub>2</sub> yields greater than the negative corona. It was conducted that streamer of the positive corona were more favorable for OCM than the pulsed of negative corona. However, with no applied external heat the AC corona produced a maximum C<sub>2</sub> 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.

Methane conversion with hydrogen and oxygen as an additive and helium as a diluent was systematically investigated (Liu *et al.*, 1996). The CH<sub>4</sub>/H<sub>2</sub>/O<sub>2</sub> system was found to be more selective for the production of C<sub>2</sub> hydrocarbons compared to the CH<sub>4</sub>/O<sub>2</sub>, CH<sub>4</sub>/H<sub>2</sub>O, and CH<sub>4</sub>/CO<sub>2</sub> systems. A higher hydrogen feed concentration was more favorable for acetylene

formation. The selectivity and yield of C<sub>2</sub> hydrocarbons were related to the hydrogen feed rate, gas temperature, concentration of oxygen, and flow rate. The highest yield of C<sub>2</sub> hydrocarbons (32%) was obtained at the lowest flow rate used (10 cm<sup>3</sup>/s; residence time ~ 2.3 s).

Thayachotpaiboon (1996) studied pure methane conversion using a dielectric discharge plate reactor. The results were similar to the oxidative reaction system, such as 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 methanol 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<sub>3</sub> and C<sub>4</sub> hydrocarbons could be obtained by the addition of ethane in feed.

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<sub>2</sub> selectivity to decrease and so the C<sub>2</sub> yield remained essentially constant except at low methane conversions. Secondary reaction and carbon monoxide formation also increased with increasing methane conversion. The carbon monoxide selectivity remained high in all the experimental conditions but the carbon dioxide selectivity was usually constant and very low compared to the carbon monoxide selectivity.

Lobban *et al.* (1997) carried out the effect of a Sr/La<sub>2</sub>O<sub>3</sub> catalyst on OCM in DC corona discharge reactor. They showed that the operating temperature of the corona discharge with Sr/La<sub>2</sub>O<sub>3</sub> catalyst was much lower (<200°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<sub>2</sub> products. The highest C<sub>2</sub> yield achieved was 11%.

The partial oxidation of methane to methanol with atmospheric oxygen was investigated experimentally and theoretically in a dielectric-

barrier discharge (DBD) by Zhou *et al.*, (1998). The predominant parameters of specific electric energy, oxygen content, flow rate, temperature and gas pressures were determined in both CH<sub>4</sub>/O<sub>2</sub> and CH<sub>4</sub>/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 selectivity could be obtained at high methane conversion. In addition, other useful products, like ethylene, propane and ethanol were detected. Experiments and numerical simulations showed that the formation of water and carbon monoxide had a strong negative influence on methanol formation.

Leethochawalit (1998) reported that methane conversion increased with increases in CO<sub>2</sub>/CH<sub>4</sub> ratio, voltage, helium concentration, and space-time by using AC electric barrier discharge (DBD).

Okumoto *et al.* (1998) studied the direct methanol synthesis from methane and oxygen by using pulsed discharge plasma in a concentric-cylinder-type reactor. A combination of the pulse discharge and catalysts was tested and was proved to be effective in increasing both the production and selectivity of methanol. About 2 % of methane 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<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub> 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 determined. 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 methanol yield.

Lui *et al.* (1999) studied the methane conversion by using corona discharge and combining the plasma with the heterogeneous catalysts such as zeolite. It has been found that methane was converted mainly to acetylene over NaY zeolite in DC corona discharge. A higher selectivity was obtained from the direct conversion of methane to acetylene without using any catalysts.

Sutthiruangwong (1999) investigated methanol production from methane in a corona discharge reactor with and without catalyst and found that the non-catalytic system gave much higher methane conversion than the catalytic system and the products were mainly consisted of C<sub>2</sub> hydrocarbons.

Kruapong (2000) studied the partial oxidation of methane using an AC electric discharge reactor to produce synthesis gas. It was concluded that the presence of ethane in the feed containing methane and air enhanced the selectivity of hydrogen and ethylene. Nitrogen as diluent gas was more effective than He in methane conversion.

Larkin *et al.* (2001) studied the production of organic oxygenates in the partial oxidation of methane in a 3 stages silent electric discharge reactor. They stated that from stage one to stage three, the individual methane conversion increased from 21% to 30%, making the overall methane conversion 59%. The energy efficiency decreased by 19% from stage one to stage three. Organic oxygenate liquid production was enhanced while CO<sub>x</sub> production was minimized through the use of a high recycle ratio.

Supat *et al.* (2003) performed experiment of the production of synthesis gas from methane and air in a corona discharge over Pt/KL. The experimental results showed that methane and oxygen conversion increased with increasing input power but decreased with increasing CH<sub>4</sub>/O<sub>2</sub> feed, flow rate, and gap distance. The selectivity of ethane, produced from coupling of methane, changed opposite to methane conversion. With adding ethane in the feed gas, the methane conversion dropped significantly but oxygen conversion increased. The presence of Pt/KL had higher oxygen conversion but lower methane conversion than the absence of Pt/KL. In the presence of catalyst, carbon formation occurred markedly at the electrode surface.

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.