CHAPTER II
LITERATURE REVIEW

2.1 Basic Principles of Plasma

In physics and chemistry, plasma is an ionized gas and is usually considered to be a distinct phase of matter, as depicted in Figure 2.1. "Ionized" means that at least one electron has been removed from a significant fraction of the molecules. The free charges make the plasma electrically conductive so that it couples strongly to electromagnetic fields. This fourth state of matter was first identified by Sir William Crookes in 1879 and dubbed "plasma" by Irving Langmuir in 1928 (http://www.en.wikipedia.org).
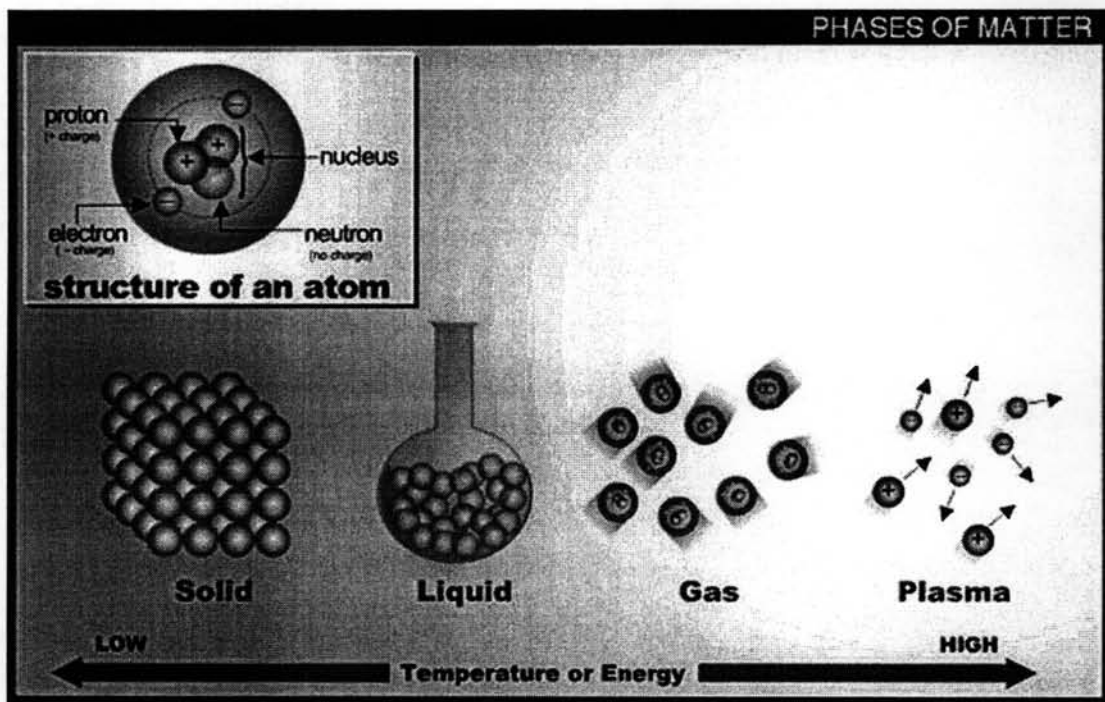

Figure 2.1 Phase of matter consists of solid, liquid, gas, and the forth state named "plasma".

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).

2.1.1 Quasi-neutral property

The total density of negative charge carriers must be equal to the total density of positive charge carriers due to low degree of ionization.

2.1.2 Interaction with electromagnetic fields

Plasma can have some interactions upon the applying of an electromagnetic field due to the 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 Generation of Plasma

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 phenomenon 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 2.1 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.

Plasma is divided into two types. The first type is "thermal plasma" or "equilibrium plasma". In this type, the temperature between gas and electron is approximately equal, which is close to thermodynamic thermal state (Harndumrongsak, 2002). An essential condition for the formation of this plasma is sufficiently high working pressure. An example of this plasma is arc discharge.

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). Examples of this plasma are radio frequency discharge, microwave discharge, glow discharge, dielectric-barrier discharge, and corona discharge, which the latter was used in this study.

Table 2.1 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	$A^\pm + B \longrightarrow A + B^\pm$
Electronic Decomposition	$e^- + AB \longrightarrow e^- + A + B$
Atomic Decomposition	$A^* + B_2 \longrightarrow AB + B$

2.3 Generation of Non-thermal Plasmas

It is customary to divide non-thermal plasmas into distinctive groups depending on the mechanism used for their generation, their pressure range, or the electrode geometry. In this section, we will briefly list the most notable characteristics of the following five non-thermal discharges (Eliasson and Kogieschatz, 1991);

    2.3.1 Glow discharge

    2.3.2 Silent discharge

    2.3.3 Radio Frequency discharge

    2.3.4 Microwave discharge

    2.3.5 Corona discharge

As shown in Figure 2.2, the discharges are grouped according to their temporal behaviour, pressure range, and appearance.
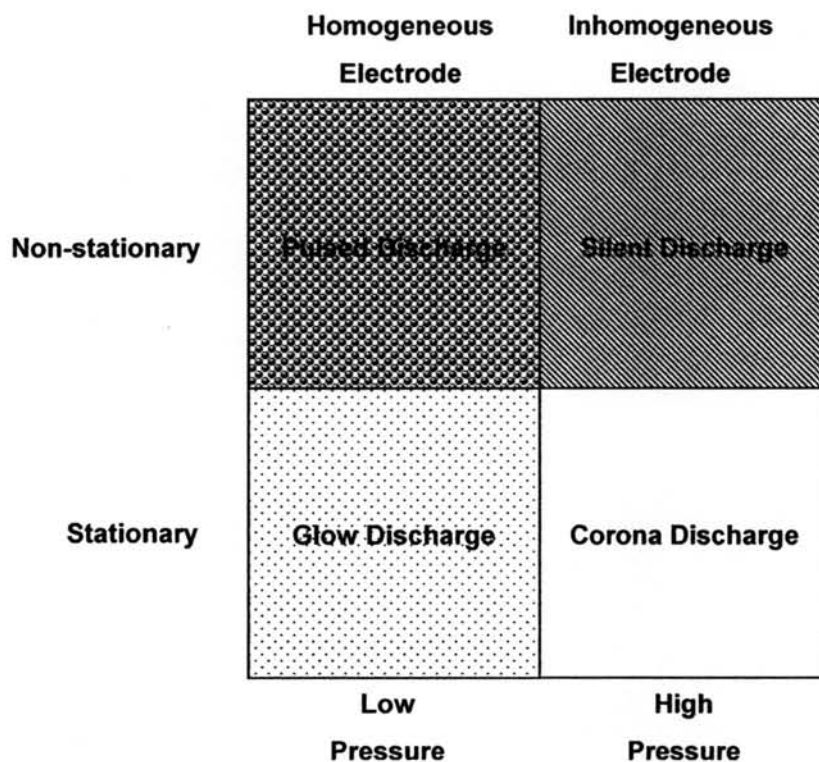
Figure 2.2 Various types of discharge classified according to temporal behaviour, pressure, and geometric electrode.
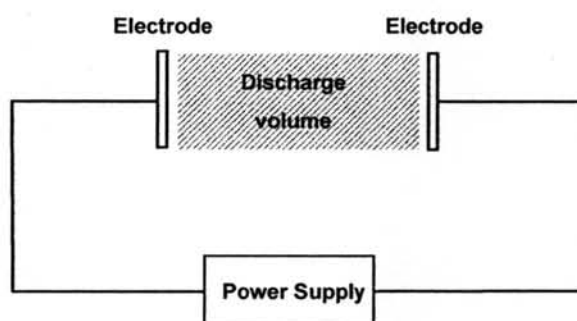

Figure 2.3 The glow discharge-homogeneous electrode can be operated at low pressure.

2.3.1 <u>Glow Discharge</u>: The glow discharge is a stationary and low-pressure discharge, usually generated between flat electrodes (Figure 2.3). The glow can be produced by applying a potential difference between two electrodes in a gas. Since

the pressure is typically smaller than 10 mbar, the reduced field or the electric field divided by the neutral gas density can therefore be quite high, which is a characteristic of non-thermal plasma.

One reason for the popularity of glow discharges is the comparatively low voltage and current needed to run them. It has become an important laboratory tool for plasma chemical investigations. There are some practical applications of glow discharge in light industry such as neon tubes (for outdoor advertising) and fluorescent tubes. However, the too low pressure and the resulting too low mass flow of the glow discharge have not been used for industrial production of chemicals.

2.3.2 <u>Silent Discharge</u>: The silent discharge is predetermined for applications in volume plasma chemistry. It has inherent advantages over the discharges, which have been treated until now. It combines the large volume excitation of the glow discharge with the high pressure of the corona discharge. The main elements of a silent discharge configuration are shown in Figure 2.4.
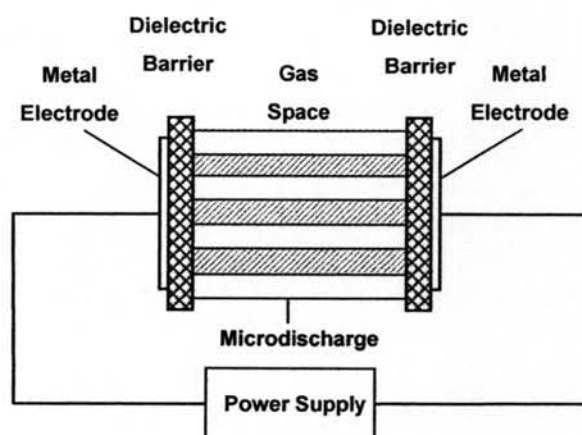

Figure 2.4 The silent discharge-homogeneous electrode. One or both electrode is covered by a dielectric, and microdischarges are contained in the discharge gap.

A characteristic of the silent discharge is that a dielectric layer covers at least one of the electrodes, sometimes both. For this reason, the silent discharge is also referred to as the "dielectric-barrier discharge (DBD)," or simply, "barrier

discharge." The dielectric is the key for the proper functioning of the discharge. Once ionization occurs at a location in the discharge gap, the transported charge accumulates on the dielectric. The dielectric serves two functions: (1) it limits the amount of charge transported by a single microdischarge and (2) distributes the microdischarges over the entire electrode area. The silent discharge is an excellent source of filaments containing energetic electrons. In most gases, the reduced field at breakdown corresponds to electron energies of about 1-10 eV. This is the ideal energy range for the excitation of atomic and molecular species and the breaking of chemical bonds.

2.3.3 <u>Radio Frequency Discharge</u>: The radio frequency (RF) discharges are used extensively in the laboratory to produce plasmas for optical emission spectroscopy and for plasmachemical investigations. The inductively coupled plasma (ICP) operating between 2-60 MHz is especially a widespread laboratory tool for spectroscopic analysis. Very common frequency used in the industrial applications is frequency of 13.56 MHz. One advantage of RF discharges is that the electrodes can be kept outside of the discharge volume, thus avoiding electrode erosion and contamination of the plasma with metal vapor. Since the wavelength of the electric field is much larger than the vessel dimensions, reasonably homogeneous plasmas can be generated. RF discharges work well at low pressure, but are used also at atmospheric pressure. Low-pressure RF discharges for etching purposes have found widespread applications in semiconductor manufacturing. As long as the collision frequency is higher than the frequency of the applied field, the discharge behaves very much like a dc discharge. This implies that non-thermal conditions can be expected at low pressures, whereas thermal plasmas are generated at about atmospheric pressure. Figure 2.5 shows three typical electrode configurations for RF discharges. While Figure 2.5 (a) and (b) use capacitive coupling and are mainly used at low pressure, the configuration shown in Figure 2.5 (c) uses inductive coupling by placing the discharge in the magnetic field of an induction coil. This arrangement is typical for RF torches and is used at pressures up to 1 bar.
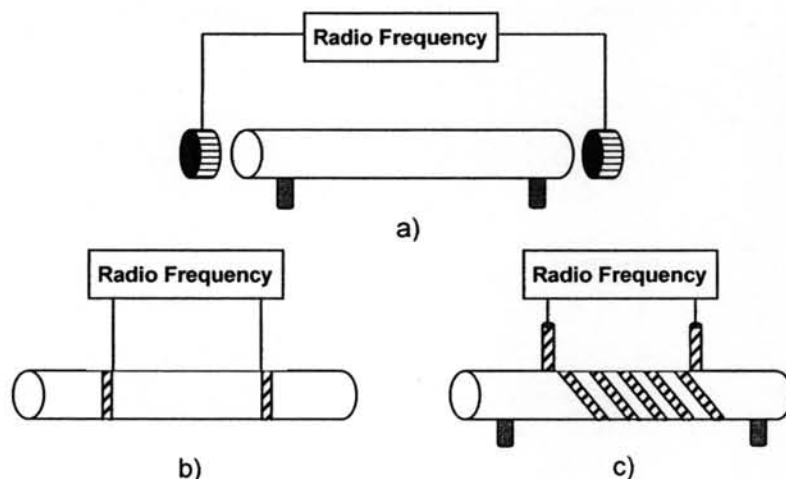
Figure 2.5 Schematic of various types of radio frequency discharge: (a) and (b) contain capacitive coupling, normally used at low pressure, (c) use inductive coupling instead of capacitive coupling, which can be operated at pressure up to 1 bar.

2.3.4 <u>Microwave Discharge</u>: In the microwave region (0.3-10 GHz), the wavelength of the electromagnetic field becomes comparable to the dimensions of the discharge vessel, which necessitates other coupling mechanisms. Most microwave-induced plasmas are produced in a waveguide 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. A very common frequency is 2.45 GHz, which is also used in microwave ovens.

Since at these frequencies only the light electrons can follow the oscillations of the electric field, microwave plasmas are normally far from local thermodynamic thermal state. They can be operated in a wide pressure range, starting from below 1 mbar to about atmospheric pressure. An interesting development is the use of microwaves to induce surface-wave-sustained discharges. They can be operated over a large frequency and pressure range and can produce large-volume non-thermal plasmas of reasonable homogeneity.

The plasma is contained in a dielectric tube of a few centimeters diameter and is sustained by an electromagnetic wave, which requires only the plasma column and the tube as its propagating media. Plasma columns of up to 4-m length have been thus produced. Due to the large pressure range, under which these discharges can be operated, electron densities between 10^8 and 10^{15}cm^{-3} have been reported. These surface wave plasmas have many similarities with the positive column of a glow discharge. Applications so far have been limited to elemental analysis and lasing media. The ease of operation and the possibility of imposing a gas flow and influencing plasma parameters make these discharges attractive also for plasmachemical investigations.

2.3.5 <u>Corona Discharge</u>: The main disadvantage of the glow discharge when it comes to industrial applications is its extremely low pressure. If one increases the pressure, one has to increase the field accordingly. At higher pressures and fields, one normally finds that the discharge becomes highly unstable and turns into a high-current arc discharge if the power supply provides enough current. One way of stabilizing the discharge at high pressure is the use of inhomogeneous electrode geometries; e.g., a pointed or a thin wire electrode and a plane electrode, as in Figure 2.6.
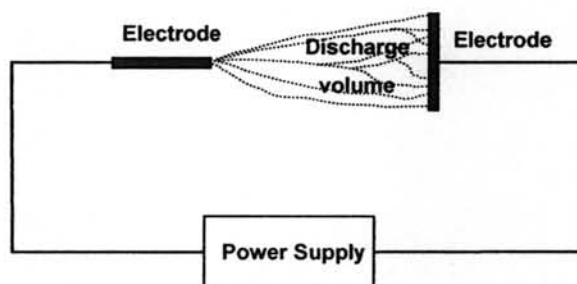
Figure 2.6 The corona discharge-inhomogeneous electrode can operate at high pressure.

Types of Corona Discharge:

Corona discharges exist in several forms, depending on the polarity of the field and the electrode geometrical configurations.

2.3.5.1 Positive Corona

For positive corona in the pin-plate electrode configuration, there is a corona inception voltage, which depends on the radius of the point and the gap spacing. Discharges start with burst pulse corona and when the voltage is increased, streamers are produced leading to the typical corona phenomenon named streamer corona, followed by glow corona. By increasing the voltage further, breakdown occurs and a spark bridges the gap, as depicted in Figure 2.7. Unlike Hermstein's the positive sheath (Hermstein, 1960) or Hermstein's glow, the positive streamer corona is a discharge confined to a narrow channel, which originates at the electrode. It produces an unsteady current (because the streamer is repetitive), is quite noisy, and is the direct precursor to a spark.

Positive Corona

| Burst Pulse | Streamer Corona | Glow Corona | Spark |

Negative Corona

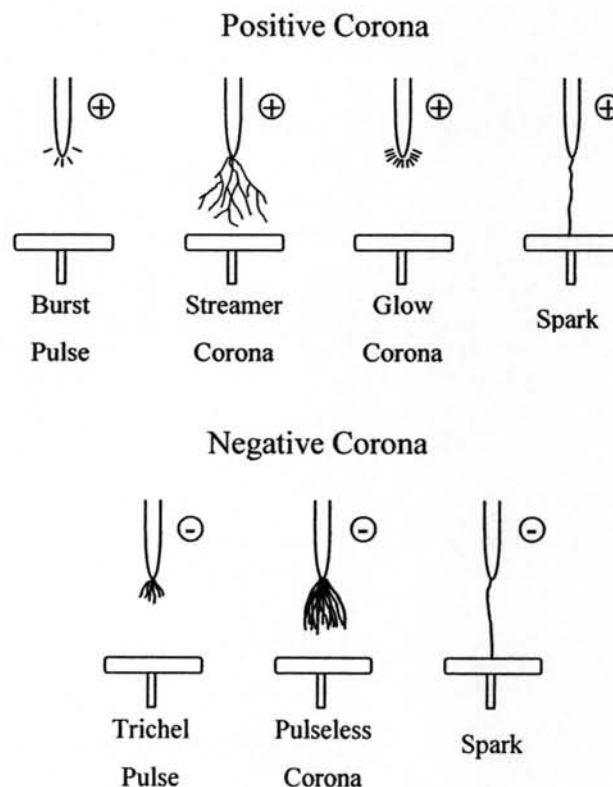| Trichel Pulse | Pulseless Corona | Spark |

Figure 2.7 Schematic of various forms of corona discharge depending upon applied voltage at constant electrode geometrical configuration (Chang, 1991).

Positive corona depends more on photoionization for its propagation. The positive streamer, for example, may advance at as much as one percent of the speed of light. In either case, the ultraviolet photon flux from ion-electron recombination is quite large (Chang, 1991).

2.3.5.2 Negative Corona

For negative corona in the same geometry, once voltage is increased, the so-called Trichel pulses are generated. Short current pulse or pulseless corona is observed with a frequency proportional to the applied voltage, and also depends on the radius of the point. As the voltage is increased further, a glow develops before complete breakdown occurs.

Negative corona generally propagates by impact ionization of the gas molecules, which is in slightly different manner from positive corona. Due to space-charge phenomena in the neighborhood of the point, the negative corona is less sensitive to the radius of curvature of the point than the positive corona. It is the small radius of curvature of the point that leads to the high fields necessary for ionizing the neutral molecules. The field drops rapidly as one moves away from the point toward the other electrode. It is very important that the applied voltage is not too high, otherwise the corona might bridge the gap, produce a spark, and eventually breakdown. In this sense, the corona discharge can be considered a partial breakdown.

The characteristic of corona discharge is that the generated-plasma volume excited is nearly smaller than the total discharge volume. This tends to be not suitable for large quantities of chemical species production. There are, however, applications where only very small concentrations of excited or charged species are needed. The outstanding example is electrostatic precipitators, which are operated at industrial scales for collecting the particulate emissions in the utility, steel, paper manufacturing, and cement and ore-processing industries.

2.4 The Initiation of Chemical Reactions in Non-Thermal Plasma

For initiation of chemical reactions in non-thermal plasma, the energy is very often transferred solely by the electrons. Firstly, the accelerated electrons are created by discharge mechanism. Secondly, such electrons collide with neutral gas and excite them to higher energy state. Finally, the excited gas molecules can either dissociate or initiate to the new chemical species because of their high energy level. The same can be also applied to ions. For example, the reaction schematic is demonstrated below (McQuarrie *et al.*, 1987).

$$e^- + A \longrightarrow A^* + e^-$$
$$A^* + B \longrightarrow C + D$$
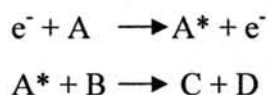
where   A and B are reactants.

C and D are products.

A* is the excited reactant marked by an asterisk (*).

Normally, this reaction $A + B \longrightarrow C + D$ may only take place at high temperatures, but in this case, the product C and D can be produced at the lower temperature induced by non-thermal plasma.

Besides transferring energy to gas molecules via fast electrons and ions, photon can also involve with initiating the new chemical species if it is energetic enough. The photon is taken place by emitting energy of excited molecules to lower state. The characteristics of electron and photon are quite different.

2.5 Application of Non-Thermal Plasma in Chemical Synthesis

The non-thermal plasma is widely used in many industrial applications. The first use of chemical synthesis via silent discharge is ozone generation by Siemen (Horvath, 1980). Under selective experiment conditions, organic plasma chemistry can be a valuable synthetic method. Main areas of applications are the generation of

reactive species, isomerizations, eliminations, cyclizations, condensations, and multistep reactions (Suhr, 1983).

For the industrial production of epoxides, ethylene oxide, which is the most important epoxides in industrial processes, is made by conventional methods using catalysts. There are also some studies on plasma organic syntheses such as oxidations of aromatic, liquids hydrocarbons, and olefins using oxygen plasma (Suhr *et al.*, 1984; Tezuka and Yajima, 1996; Suhr *et al.*, 1988; Patiño *et al.*, 1995). Furthermore, the selectivity of product formation is far superior to plasma oxidations in the gas phase, making these techniques attractive for preparative chemistry (Suhr *et al.*, 1984).

The previous studies on plasma oxidation at low pressure suggested that the most important species in the plasma partial oxidation was $O(^3P)$ (Suhr, 1983; Suhr *et al.*, 1988; Patiño *et al.*, 1995; Patiño *et al.*, 1996; Patiño *et al.*, 1999; and Suga and Sekiguchi, 2005). The following reaction was proposed for the epoxidation of the carbon double bond:

$$\text{>C=C<} + O(^3P) \longrightarrow \text{>C}\overset{O}{-}\text{C<}$$
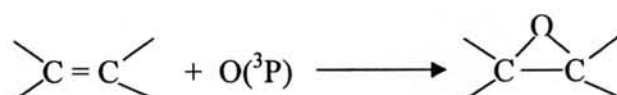
In addition, Jeong *et al.* (2000) reported that the concentration of $O(^3P)$ decreased significantly with increasing the distance between the tip and the tube in discharge reactor, which is in good accordance with Suga and Sekiguchi (2005)'s experiments.

In recent work, there is the extensive attempt to oxidize carbon double bond into epoxide by exposing a liquid 1-decene to atmospheric pressure glow plasma (APGP) where oxygen diluted with argon was used as a plasma gas. The results showed that the yields of all products (1,2-epoxydecane, 1-decanal, 1-nonanal, and 2-decanone) increased linearly with increasing the reaction time and shortening the tip of the tube and the liquid surface, and the highest yield of epoxide could be obtained by optimizing plasma reaction parameters (Suga and Sekiguchi, 2005).

2.6 Catalysts Used in Epoxidation of Ethylene

Ethylene can be catalytically converted into ethylene oxide with high selectivity over supported silver catalysts. The first commercial ethylene oxide production can be traced to Lefort's process in 1937 (Satterfield, 1991). Typically, a unique support for silver catalysts is alpha-alumina (α-Al_2O_3). Low surface area (LSA)α-Al_2O_3, possessing the surface area less than 1 m^2/g, was commercially widely used as silver catalyst support. Unfortunately, this support showed poor silver dispersion, which provided relatively low yield of ethylene epoxidation (Matar *et al.*, 1989).

Even though addition of few ppms of chloride to gaseous reactant as moderator in the form of chlorine-containing hydrocarbon species, such as dichloroethane ($C_2H_4Cl_2$) and vinyl chloride (C_2H_3Cl), has been reported to significantly increase the selectivity to ethylene oxide by 15-20%, but at the same time, the decreased rates of ethylene oxide and carbon dioxide formation were observed (Law *et al.*, 1942; Campbell *et at.*, 1984; Tan *et al.*, 1986; and Yeung *et al.*, 1998). The mechanism of chloride moderator is still in question that it has been attributed to geometric (Campbell *et al.*, 1984; Campbell *et al.*, 1985; and Campbell *et al.*, 1986), electronic (Tan *et al.*, 1986), or both effects.

Alkali and alkali earth, such as Cs and Re, also provided the improvement of ethylene oxide selectivity (Iwakura, 1985; and Bhasin, 1988). Rhenium added to a silver catalyst could enhance both the conversion of ethylene and the selectivity of ethylene oxide if a suitable quantity of rhenium is used (Jun *et al.*, 1992). The enhancement is because Re competed partly to trap electrons of silver with adsorbed oxygen, finally resulting in reduction of electron density of adsorbed oxygen. This electron-deficient oxygen tends to prefer electrophilic attack on ethylene to form ethylene oxide, leading eventually to improvement ethylene oxide selectivity.

The role of cesium was concluded that the presence of cesium can reduce the acidic sites on the support, resulting in suppressing the isomerization of ethylene oxide to acetaldehyde (Mao and Vannice, 1995; and Epling *et al.*, 1997). In the same time, cesium could also promote the direct combustion. The mechanism was that

cesium could provide the additional electron to silver lattice. The electron was further transferred to adsorbed oxygen. Finally, the adsorbed oxygen possessed excess electron density, benefiting the total oxidation of ethylene. Moreover, cesium addition could decrease the concentration of nucleophilic oxygen, which is responsible for carbon dioxide formation (Goncharova et al., 1995). Therefore, in the presence of optimum cesium added, the selectivity of ethylene oxide is enhanced by the suppression of the rate of ethylene oxide oxidation, exceeding the increase in the rate of direct combustion. It, however, has been investigated for adding cesium in high surface area (HSA)α-Al$_2$O$_3$ that selectivity of ethylene oxide was not enhanced, but the turnover frequency of ethylene oxidation, as well as the rates of ethylene oxide and acetaldehyde oxidation, were increased (Mao and Vannice, 1995).

In recent work, copper-silver bimetallic catalysts offered improved selectivities compared with bare silver catalysts in the ethylene epoxidation (Jankowiak and Barteau, 2005). In addition, it was also found that adding Cs and Cl provided more active and more selectivity for this reaction in their extended works.

With the roles of gold in ethylene epoxidation, there are relatively confused points of view for existing literatures as follows. The effects of alloying silver with gold on the oxygen adsorption properties of Ag over a set of 15% bimetallic Ag-Au/α-Al$_2$O$_3$ were studied (Kondaries and Verykios, 1996). The results showed that the presence of Au influenced the population and the activation energy of adsorbed oxygen species. Especially, when Au content increased, the molecular oxygen was more favorable in adsorption on Ag than atomic oxygen, which could be indicated by its lower activation energy of adsorption. Based on molecular oxygen theory, this adsorbed specie exhibited the vital role for ethylene oxide formation, whereas atomic oxygen was considered to be an unselective oxidant for partial oxygen (Kilty et al., 1973). While other research group reported in the different way that the selectivity of ethylene epoxidation was observed at constant value up to approximately 10 wt% Au content on the surface and decreased continuously at higher Au contents (Tories and Verikios, 1987). On the other hand, Geenen et al. (1982) reported that at the high Au loading, the selectivity to ethylene oxide decreased and rapidly dropped to zero, which was more rapidly dropped than Tories and Verikios (1987)' experiments. The

discrepancies might originate from the various alloying catalyst preparation techniques (Tories and Verikios, 1987). In a previous study (Rojluechai *et al.*, 2006), the effect of alloying Ag with Au supported on $(HSA)\alpha-Al_2O_3$ on the activity was investigated. It had been found that addition of small amount of Au can create the Au-Ag bimetallic, which enhances the ethylene epoxidation, whereas at the higher Au loading, the Au-Ag alloy can take place, leading to complete combustion. For this study, the optimum Ag to Au ratio was 13.18 wt% to 0.63 wt% at temperature range of 510-520 K. The ethylene conversion and selectivity of ethylene oxide were enhanced, attributing to the existence of the bimetallic Au-Ag, which increases the new favourable molecular oxygen sites.

As mentioned about the poorly dispersed silver on $(LSA)\alpha-Al_2O_3$, that is why many researchers attempt to determine other alternative supports to provide the better dispersed silver and to enhance the activity of the ethylene epoxidation. Seyedmonir *et al.*, (1989) studied the activity and selectivity for ethylene oxide formation over well-dispersed Ag/SiO_2, $Ag/\eta-Al_2O_3$, and Ag/TiO_2 in the presence and absence of $C_2H_4Cl_2$ (EDC) compared with those of poorly dispersed $Ag/\alpha-Al_2O_3$. In the presence of 0.5 ppm EDC, the well-dispersed catalyst exhibited the selectivity of ethylene oxide less than the poorly dispersed catalyst, except Ag/SiO_2, due to the presence of secondary oxidation reaction occurring on these reactive supports. In contrast, the ethylene oxide selectivities of 17 and 55% were obtained over 4.4 and 7.6 nm Ag crystallites on SiO_2, respectively, compared to 23% over 1 μm Ag crystallites on $\alpha-Al_2O_3$ in the absence of EDC and CO_2 at 523 K.

Focusing on well-dispersed silver over $(HSA)\alpha-Al_2O_3$ support (approximately 78-104 m^2/g), it has also been used as support for ethylene epoxidation, but it was found to be poor support for this reaction, and only complete oxidation was obtained. The absence of ethylene oxide was induced by this support containing a certain amount of acidity, leading to secondary oxidation of ethylene oxide, oxidation of ethylene, and isomerization of ethylene oxide to acetaldehyde (Mao and Vannice, 1995).

TiO_2 has some special properties, which are believed to enhance the catalytic activity of ethylene oxidation reaction. It has been known that titanium

dioxide exhibits a strong metal-support interaction effect with group VIII noble metals and possesses the ability for oxygen migration from reduced support particles onto the surfaces of the metallic particles of the catalysts, which, in turn, promotes oxidative reactions (Holgado *et al.*, 1998). It was reported that silver supported on TiO_2 showed zero ethylene oxide selectivity due to the isomerization of ethylene oxide to acetaldehyde on the support followed by the complete combustion (Seyedmonir *et al.*, 1989; Yong *et al.*, 1991).

In a previous work, the nominal 1% Au/TiO_2 catalysts provided the highest selectivity to ethylene oxide with relatively low ethylene conversion. Moreover, the catalytic activity of Au catalysts was found depending upon the size of Au particles and also catalyst preparation methods (Rojluechai *et al.*, 2006).

However, ethylene conversion obtained from these catalysts; (Ag/(HSA) α-Al_2O_3, Au/TiO_2, and bimetallic Au-Ag/(HSA) α-Al_2O_3), could not be detected at any temperature below 493 K. Even though the reaction temperature was raised up to 543 K, ethylene conversion was still low at 1-4%. Consequently, this limitation results in high energy consumption for catalyst activation at high temperature, which is a disadvantage for industrial application. The non-traditional catalysis technique is, therefore, expected to overcome this constraint. One of potential techniques is to combine the selective traditional catalysis and non-thermal plasma.

2.7 Catalytic Plasma Processing

In combination of catalysis and non-thermal plasma, this technique tends to offer a number of advantages over the conventional catalytic processes. One of them is low operational temperature close to room temperature at near or slightly higher than atmospheric pressure as described above. This implies comparatively lower energy consumption used for activating catalysts. Moreover, the catalytic problems at high temperature operation, i.e., catalyst deactivation, catalyst regeneration, and catalyst replacement, could be eliminated. However, they often provide less selectivity to a desired product than the catalysis technique (Pietruszka *et al.*, 2004).

The plasma properties can be influenced by catalysts in plasma zone. The catalysts can also change the reaction products due to the conductive surfaces, which lead to surface reaction. While the catalyst properties can also be influenced by plasma because it provides the heating of catalysts, resulting in desorbing of surface species (M. Kraus, 2001). The synergism between catalysts and plasma is achieved if this combination can improve reactant conversion or higher selectivity to the desired products as compared to the sole plasma or catalyst technique.

The gas temperature is the most important factor indicating the occurrence of the catalytic reaction. Moreover, at low temperature where the catalysts were not active, the plasma influence was observed. At the higher temperature, the catalysts became active. Thus, the catalytic plasma effect was still observed (Liu *et al.*, 1997; and Pietruszka *et al.*, 2004). As reported by Heintze *et al.*, (2004), they investigated the combined DBD and Ni/α-Al$_2$O$_3$ in the partial oxidation of methane. The results were reported that at lower temperatures, this combined catalyst-plasma had no influence on the conversion and products selectivity. At these temperatures (>300°C), the plasma showed the dominant role. At the higher temperatures, however, the catalyst promoted the oxidation of CO to CO$_2$.

Malik *et al.*, (1999) investigated combined system of cold plasma and a catalyst for VOC decomposition. They found that the addition of a suitable catalyst, particularly a supported noble metal catalysts, such as platinum, palladium, rhodium and ruthenium, could activate CH$_4$ at relatively low temperatures with faster rates and could further improve the efficiency, as well as the selectivity of the desired products. Noble metal electrodes gave the best results for the conversion of CH$_4$ to C$_2$ hydrocarbons in a pulsed corona discharge with the following order: platinum > palladium > copper.

Suttiruangwong (1999) studied the conversion of methane for partial oxidation of methane (POM) in the catalyst packed bed reactor under AC corona discharge with and without Cu/ZnO catalyst. For reaction without catalyst, it was found that the non-catalytic system gave much higher CH$_4$ conversion than the catalytic system, and products mainly consisted of C$_2$ hydrocarbons. Methane conversion and product selectivity increased with decreasing total flow rate and

increasing the applied voltage. For reaction with catalyst, it gave the feasibility of methane conversion at atmospheric conditions, but the amount of methanol produced was low. Synthesis gas was also found in the product stream.

Viriyasiripongkul (2000) investigated the oxidative coupling of methane to produce higher hydrocarbons by using AC electric discharges with and without zeolite catalyst at ambient condition. For system with catalyst, the presence of Pt/KL zeolite enhanced the oxygen conversion and the selectivity of ethylene. Moreover, hydrogen and carbon monoxide were the main products. For system without catalyst, it was found that methane, oxygen, and ethane conversions, as well as yields of C_2 hydrocarbons (ethylene and acetylene), increased with increasing the applied voltage and decreasing either frequency or total flow rate.

Saktrakool (2003) developed a combined plasma and photocatalytic system for oxidative removal of ethylene as a model of VOC. Higher applied higher voltage and stage number of plasma reactor enhanced C_2H_4 conversion and CO_2 selectivity, which were in contrast with the effects of higher applied frequency and feed flow rate. The commercial TiO_2 (Degussa P25), TiO_2, and $1\%Pt/TiO_2$ prepared by sol-gel method were used as photocatalysts. The presence of all studied photocatalysts increased the C_2H_4 and O_2 conversions, as well as CO_2 selectivity, in the following order: $1\%Pt/TiO_2 > TiO_2 >$ Degussa P25. The synergistic effect of photocatalysts presented in the plasma reactor is resulted from the activation of TiO_2 by the UV light generated from the plasma.