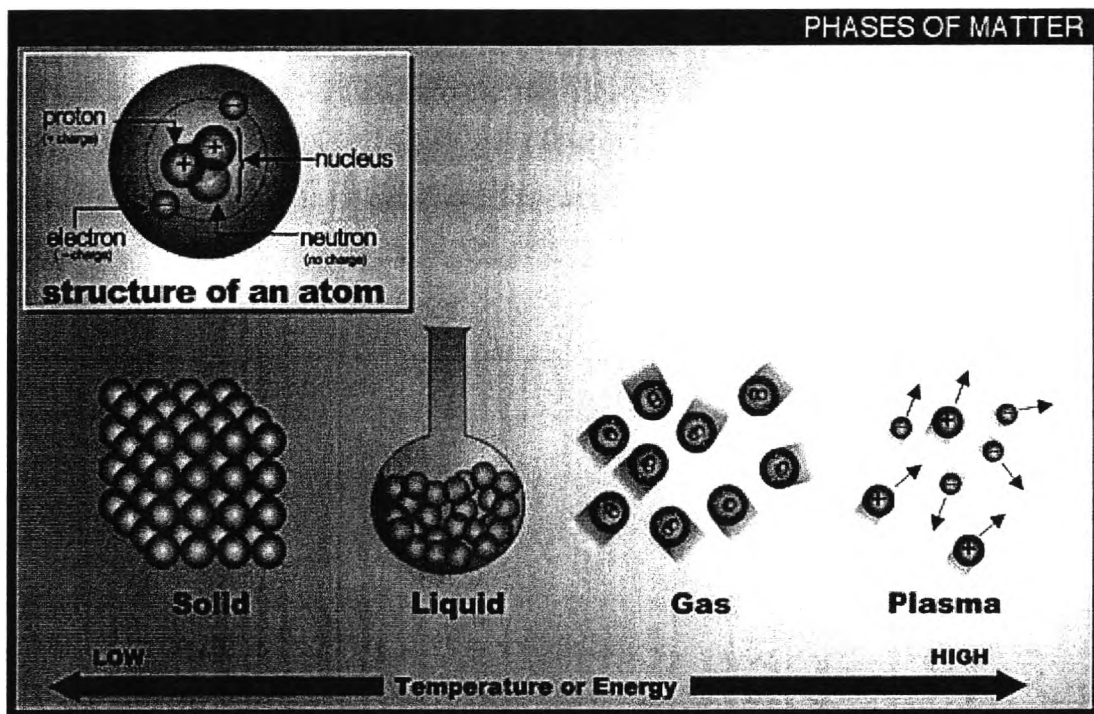


## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Basic Principles of Plasma

Regarding the principles of physics and chemistry, plasma is an ionized gas and is usually considered to be a distinct phase of matter, as showed in Figure 2.1. The term of “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.



**Figure 2.1** Phase of matter consists of solid, liquid, gas and the fourth state named “plasma” (<http://www.en.wikipedia.org>).

Since the gaseous plasma is an effective source of active species formation, including electrons, ions and radicals, a number of studies of chemical reactions using such plasma to initiate the reactions have been carried out extensively.

### 2.1.1 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 the following 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 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.

### 2.1.2 Types of Plasmas

There are several means of generating charged particles to generate 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 eventually reach 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 are that many electrons can leave the surface despite its less kinetic energy to overcome

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, as well as 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 electric field has been applied. Many active species can initiate the chemical reactions, leading to the production and destruction of the chemical species (Kruapong, 2000). The combined steps of the field emission process among these plasma species and the collision between the species and the electrode surfaces are referred to as “electric discharges” phenomena. Table 2.1 shows all possibilities of reactions occurs in the plasma environment.

**Table 2.1** Collision mechanisms in the plasma environment (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	$A^+ + B \rightarrow A + B^+$
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 temperatures of gas and electrons are approximately equal which are close to thermodynamic equilibrium (Fridman *et al.*, 1998). An example of such plasma is those produced in the arc discharge and plasma torches.

Thermal plasma or “hot plasma” is close to thermodynamic equilibrium. It has a uniform temperature for all particles and a very high temperature in the discharge region. An essential condition for the formation of thermal plasma is a sufficiently high working pressure. The large number of collision between particles leads to rapid redistribution of energy so that equilibrium is reached. An example of this plasma is arc discharge.

Thermal plasma technology offers a wide range of advantages over other waste management solutions due to the very high temperatures it generates, changing the state of wastes to destroy hazardous materials. It is also highly flexible and easy to control, with a low environmental impact of its own. In addition, it enables the production of a valuable vitrified slag that may be used in construction and other applications.

The second type is “non-thermal plasma” or “non-equilibrium plasma”, which is characterized by a low gas temperature and a high electron temperature. Typical energetic electrons may have energy ranging 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 is used in this study.

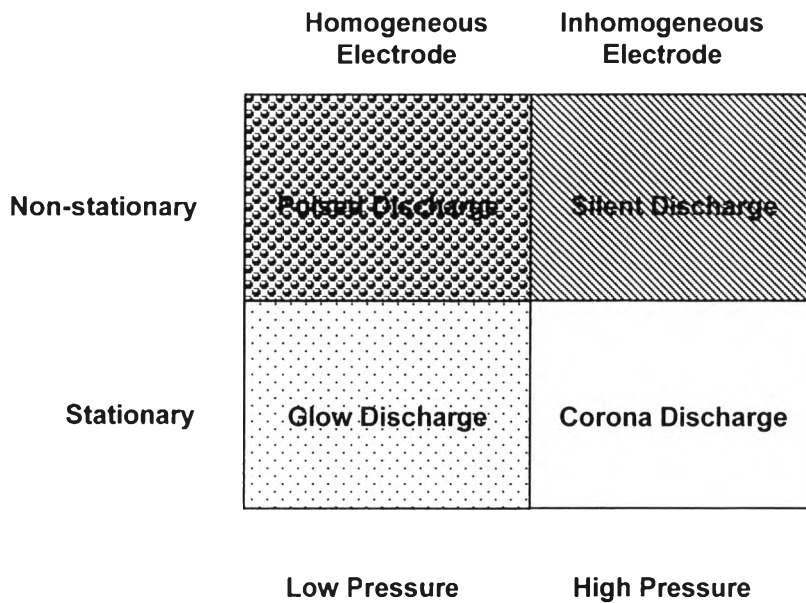
Non-thermal plasma or “cold plasma”, in contrast, is far from thermodynamic equilibrium. Typically, electrons in this plasma have very much higher temperatures than the heavy ions and neutral species particles. Its uses are based chiefly on the reactivity of ions or radicals generated in the plasma for gas phase or surface reaction (Kroschwitz *et al.*, 1998). This group includes radio frequency, microwave, glow, dielectric-barrier, and corona discharge.

### 2.1.3 Types of Non-Thermal Plasmas

It is customary to divide non-thermal plasmas into distinctive groups depending on the mechanisms used for their generation, their pressure range, or the electrode geometry. The most notable characteristics of six non-thermal discharges are listed as follows (Eliasson and Kogieschatz, 1991).

- 1) Glow discharge
- 2) Silent discharge
- 3) Radio Frequency discharge
- 4) Microwave discharge
- 5) Corona discharge
- 6) Dielectric barrier discharge

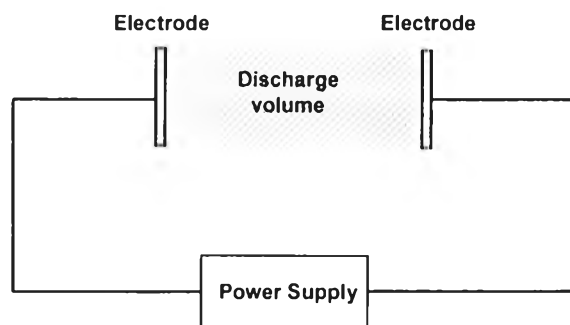
As shown in Figure 2.2, the discharges are grouped according to their temporal behavior, pressure range, and appearance.



**Figure 2.2** The various types of discharge classified according to temporal behavior, pressure, and geometric electrode (Eliasson and Kogieschatz, 1991).

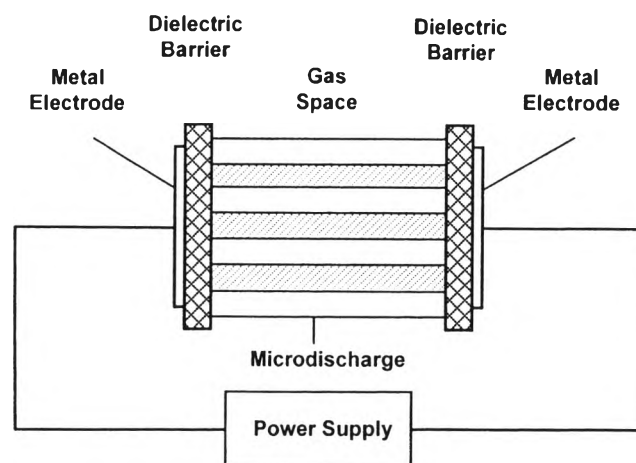
**1) Glow Discharge:** The glow discharge is a stationary and low-pressure discharge, usually generated between the flat electrodes (Figure 2.3). The glow can be produced by applying a potential difference between two electrodes in a gas. Since the pressure is typically lower than 10 mbar, the reduced 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.



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

2) **Silent Discharge:** The silent discharge is predetermined for applications in volume plasma chemistry. 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.

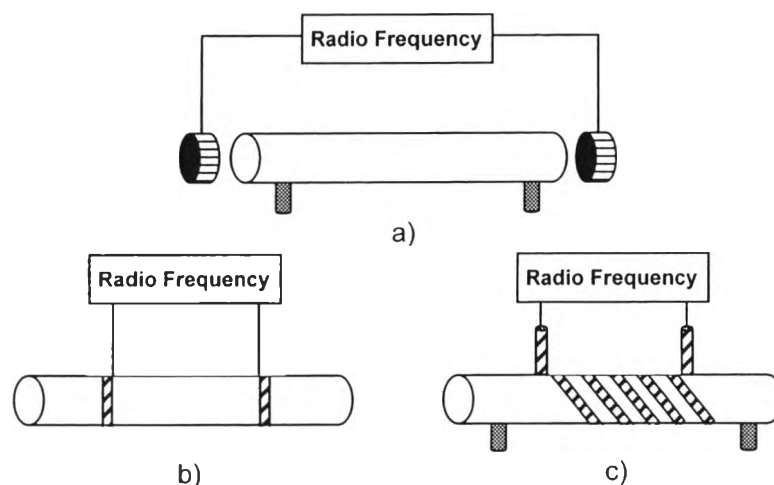


**Figure 2.4** The silent discharge-homogeneous electrode. (One or both electrodes is covered by a dielectric, and microdischarges are contained in the discharge gap).

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.

**3) Radio Frequency Discharge:** 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 vapour. 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 also used at atmospheric pressure. Low-pressure RF discharges for etching purposes have been 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 Figures 2.5(a) and 2.5(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.



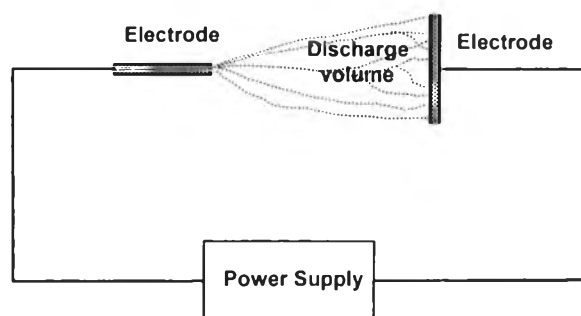
**Figure 2.5** Schematic of various types of radio frequency discharge: (a) and (b) contain capacitive coupling, normally used at low pressure, (c) use inductive coupling instead of capacitive coupling, which can be operated at pressure up to 1 bar.

**4) Microwave Discharge:** 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  $10^{15} \text{ cm}^{-3}$  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.

**5) Corona Discharge:** The main disadvantage of the glow discharge when it comes to industrial applications is its extremely low pressure. If the pressure increases, the electric field will increase 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 shown in Figure 2.6.



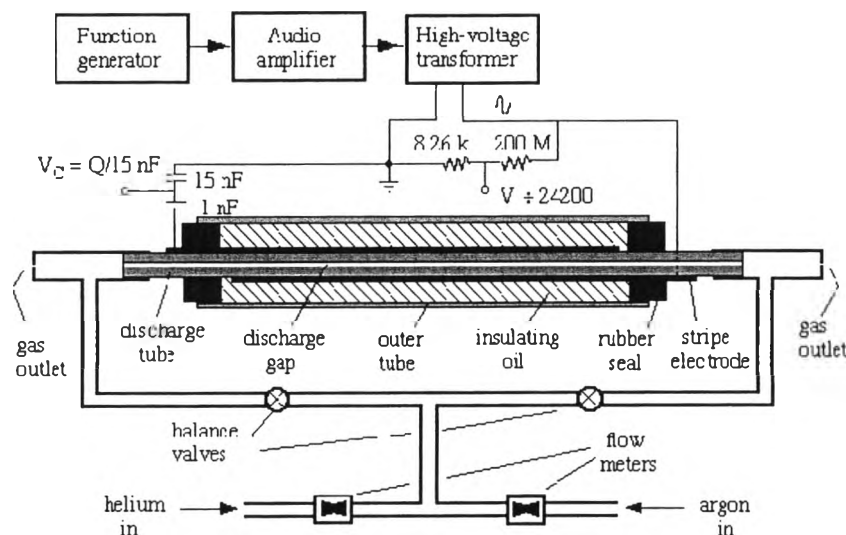
**Figure 2.6** The corona discharge-inhomogeneous electrodes.

## 2.2 Dielectric Barrier Discharge

Dielectric-barrier discharges (DBD) comprise a specific class of high-voltage, AC, and gaseous discharges that typically operate in the near-atmospheric pressure range. Their defining feature is the presence of dielectric layers that make it impossible for charges generated in the gas to reach the conducting electrode surfaces. With each half-cycle of the driving oscillation, the voltage applied across the gas exceeds that required for breakdown, and the formation of narrow discharge filaments initiates the conduction of electrons toward the more positive electrode. As charge accumulates on the dielectric layer at the end of filament, the voltage drop across the filament is reduced until it falls below the discharge-sustaining level, whereupon the discharge is extinguished. The low charge mobility on the dielectric not only contributes to this self-arresting of filaments but also limits the lateral region, over which the gap voltage is diminished, thereby allowing parallel filaments to form in close proximity to one another. Thus, the entire gas-filled space between parallel electrodes can become, on average, uniformly covered by transient discharge filaments, each roughly 0.1 mm in diameter and lasting only about 10 ns.

The DBD unique combination of non-equilibrium and quasi-continuous behaviour has provided the basis for a broad range of applications and fundamental studies. Its use in industrial ozone reactors has generated interest in optimizing conditions for specific chemical reactions. Several groups have modeled single-filament dynamics in order to account for many two- and three-body reactions involving electrons, ions, neutral atoms, and photons. These efforts have been moderately successful in explaining and predicting the chemical and radiative properties of various DBD systems. On another research front, it has been seen that the transverse spatial distribution of discharge filaments in 2D parallel-plate DBD can take the form of stable and large-scale patterns reminiscent of those associated with magnetic domains or Rayleigh-Bénard convection. These patterns have been modeled with some success using methods that apply generally to pattern formation in nonlinear dynamical systems. Thus, the dynamical interactions between filaments, as well as the chemical and electronic interactions within filaments, have proven

interesting. The schematic diagram for dielectric barrier discharge reactor is shown in Figure 2.7.



**Figure 2.7** Schematic for dielectric barrier discharge reactor.

### 2.3 Application of Non-Thermal Plasma in Chemical Synthesis

The non-thermal plasma is widely used in many industrial applications. The first use for chemical synthesis via silent discharge is ozone generation by Siemen (Horvath, 1980). Main areas of applications are the generation of reactive species, isomerizations, eliminations, cyclizations, condensations, and multi step reactions (Suhr, 1983). For the industrial production of epoxides, ethylene oxide, which is the most important epoxide in industrial processes, is made by conventional methods using catalysts. There are also some studies on plasma organic syntheses, such as oxidations of aromatic, liquid hydrocarbons, and olefins using oxygen plasma (Suhr *et al.*, 1984; Tezuka and Yajima, 1996; Suhr *et al.*, 1988; Patiño *et al.*, 1995). Furthermore, the product selectivity 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 proposed for the epoxidation of the carbon double bond:



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 the previous work of Suga and Sekiguchi (2005).

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).

## 2.4 Catalytic Plasma Processing

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 (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 combination of catalysis and non-thermal plasma 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 for a desired product than the catalysis technique (Heintze and Pietruszka, 2004).

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 Heintze and Pietruszka, 2004). As reported by Heintze and Pietruszka (2004), they investigated the combined DBD and Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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 product selectivity. At these temperatures, the plasma showed the dominant role. At the higher temperatures, however, the catalyst promoted the oxidation of CO to CO<sub>2</sub>.

Malik and Malik (1999) investigated combined system of cold plasma and a catalyst for VOC decomposition. They found that the addition of a suitable catalyst, particularly supported noble metal catalysts, such as platinum, palladium, rhodium, and ruthenium, could activate CH<sub>4</sub> at relatively low temperatures with faster rates and could further improve the efficiency, as well as the selectivity for the desired products. Noble metal electrodes showed the best results for the conversion of CH<sub>4</sub> to C<sub>2</sub> hydrocarbons in a pulsed corona discharge with the following order: platinum > palladium > copper.

Suttiruangwong (1999) studied the conversion of methane via partial oxidation of methane (POM) in a packed-bed reactor under AC corona discharge without and with Cu/ZnO catalyst. For reaction without catalyst, it was found that the non-catalytic system gave much higher CH<sub>4</sub> conversion than the catalytic system, and products mainly consisted of C<sub>2</sub> hydrocarbons. Methane conversion and product selectivity increased with decreasing total flow rate and increasing applied voltage. For reaction with catalyst, it gave the feasibility of methane conversion at

atmospheric conditions, but the amount of methanol produced was still 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 discharge without and with zeolite catalyst at ambient condition. For system with catalyst, the presence of Pt/KL zeolite enhanced the oxygen conversion and the selectivity for 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<sub>2</sub> hydrocarbons (ethylene and acetylene), increased with increasing applied voltage and decreasing either frequency or total flow rate.

Saktrakool (2003) developed a combined plasma and photocatalytic system for oxidation of ethylene as a model of VOC removal. Higher applied voltage and stage number of plasma reactors enhanced C<sub>2</sub>H<sub>4</sub> conversion and CO<sub>2</sub> selectivity, which were in contrast with the effects of higher input frequency and feed flow rate. The commercial TiO<sub>2</sub> (Degussa P25), TiO<sub>2</sub>, and 1%Pt/TiO<sub>2</sub> prepared by sol-gel method were used as photocatalysts. The presence of all studied photocatalysts increased the C<sub>2</sub>H<sub>4</sub> and O<sub>2</sub> conversions, as well as CO<sub>2</sub> selectivity, in the following order: 1%Pt/TiO<sub>2</sub> > TiO<sub>2</sub> > Degussa P25. The synergistic effect of photocatalysts presented in the plasma reactor was resulted from the activation of TiO<sub>2</sub> by the UV light generated from the plasma.

Tansuwan (2007) studied the epoxidation of ethylene in a low-temperature corona discharge system in the presence of different catalysts, including Ag/low-surface-area(LSA) $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, Ag/high-surface-area(HSA) $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Au-Ag/(HSA) $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Au/TiO<sub>2</sub>. The results showed that Ag/(LSA) $\alpha$ -Al<sub>2</sub>O<sub>3</sub> offered the highest selectivity for ethylene oxide, as well as the lowest selectivities for carbon monoxide and carbon dioxide. The selectivity for ethylene oxide increased with increasing applied voltage, but remained unchanged when frequency was varied within 300 to 500 Hz, and eventually decreased with the frequency over 500 Hz. The optimum Ag loading on (LSA) $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was found to be 12.5 wt.% with ethylene oxide selectivity of 12.98% at input voltage and frequency of 15 kV and 500 Hz, respectively.

Sreethawong *et al.* (2008) studied the epoxidation of ethylene in a dielectric barrier discharge (DBD) system to find the optimum operating conditions. The results showed the highest ethylene oxide yield of 5.62 % was obtained when an input frequency of 500 Hz and an applied voltage of 19 kV were used, with an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> molar ratio of 1/1, a feed flow rate of 50 cm<sup>3</sup>/min, and an electrode gap distance of 10 mm. When comparing with the corona discharge system with 0.2 wt.% Au-12.5 wt.% Ag/(LSA) $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst exhibiting comparative good epoxidation performance, the DBD system still provided the better performance in terms of C<sub>2</sub>H<sub>4</sub> conversion, C<sub>2</sub>H<sub>4</sub>O yield, and power consumption per C<sub>2</sub>H<sub>4</sub>O molecule produced.

Suttikul *et al.* (2011) studied the epoxidation reaction of ethylene using a DBD system in the absence and presence of both the Al<sub>2</sub>O<sub>3</sub>- and SiO<sub>2</sub>-supported Ag catalysts. The presence of Ag catalyst was found to enhance EO selectivity. Moreover, the Ag catalyst on the SiO<sub>2</sub> particles was experimentally found to be more effective than those on the Al<sub>2</sub>O<sub>3</sub> particles in catalyzing the ethylene epoxidation in terms of EO selectivity. The optimum Ag loading on the SiO<sub>2</sub> particles was found to be 20 wt.%, at which the maximum EO selectivity and the minimum H<sub>2</sub> and CO selectivities were obtained at the operating applied voltage and input frequency of 19 kV and 500 Hz, respectively. Under these optimum conditions, the power consumption was found to be  $15.26 \times 10^{-16}$  Ws per molecule of EO produced.

## 2.5 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 ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>). Low-surface-area (LSA)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, possessing the surface area less than 1 m<sup>2</sup>/g, was commercially widely used as silver catalyst support. Unfortunately, this support showed poor silver dispersion, which provided relatively low yield of ethylene oxide (Matar *et al.*, 1989). Interestingly, the 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 for ethylene oxide by 15-20%, but at the same time, decrease the rates of ethylene oxide and carbon dioxide formation (Law *et al.*, 1942; Campbell *et al.*, 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. Moreover, some previous research found that the alkali and transition metals, such as Cs and Cu, also provided the improvement of selectivity for ethylene oxide (Iwakura, 1985; and Bhasin, 1988). Recently, it was confirmed that copper-silver bimetallic catalysts could offer selectivity improvement compared with bare silver catalysts in the ethylene epoxidation (Jankowiak and Barteau, 2005).

The role of cesium was proposed that the presence of cesium could 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). At the same time, cesium could however promote the direct combustion. The mechanism was that cesium could provide the additional electron to silver lattice, transferring to adsorbed oxygen. Finally, the adsorbed oxygen possessed excess highly 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 cesium added, the selectivity for ethylene oxide is enhanced by the suppression of the rate of ethylene oxide oxidation, resulting in the decrease in the rate of direct combustion. It, however, has been investigated for adding cesium in high-surface-area(HSA)  $\alpha$ - $Al_2O_3$  that selectivity for 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 a previous work (Rojluechai *et al.*, 2006), the nominal 1 wt.% Au/ $TiO_2$  catalyst provided the highest selectivity for 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. However, ethylene conversion obtained from the following catalysts, Ag/(HSA) $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Au/TiO<sub>2</sub>, and bimetallic Au-Ag/(HSA) $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, 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.

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 wt.% bimetallic Ag-Au/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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 favourable in adsorption on Ag than atomic oxygen, which 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 oxidation (Kilty *et al.*, 1973). While other research group reported in the different way that the selectivity for ethylene oxide 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 for ethylene oxide decreased and rapidly dropped to zero, which was more rapidly dropped than Tories and Verikios' 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)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on the activity was investigated. It had been found that addition of small amount of Au can create the Au-Ag bimetallic catalyst, which enhanced the ethylene epoxidation, whereas at 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 to 0.63 wt.% at temperature range of 510-520 K. The ethylene conversion and selectivity for ethylene oxide were enhanced attributing to the existence of the bimetallic Au-Ag, which increased the new favourable molecular oxygen sites.

As mentioned about the poorly dispersed silver on (LSA)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 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.*, (1990) studied the activity and selectivity for ethylene oxide over well-dispersed Ag/SiO<sub>2</sub>, Ag/ $\eta$ -Al<sub>2</sub>O<sub>3</sub>, and Ag/TiO<sub>2</sub> in the presence and absence of C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub> (EDC) compared with those of poorly dispersed Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. In the presence of 0.5 ppm EDC, the well-dispersed catalyst exhibited the selectivity for ethylene oxide less than the poorly dispersed catalyst, except Ag/SiO<sub>2</sub>, 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<sub>2</sub>, respectively, compared with 23% over 1  $\mu$ m Ag crystallites on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in the absence of EDC and CO<sub>2</sub> at 523 K.

Due to well-dispersed silver over (HSA)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support (approximately 78-104 m<sup>2</sup>/g), it has also been used as support for ethylene epoxidation, but it was 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<sub>2</sub> also 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). However, it was reported that silver supported on TiO<sub>2</sub> 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.*, 1990; Yong *et al.*, 1991).