

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Basic Principles of Plasma

Plasma state is the mixture of ionized gases which have a roughly zero net electrical charge. Plasma phase which is showed in phase of matter (Figure 2.1) has the highest energy. "Ionized" is molecules which at least one electron is removed and then, they may new ion and neutral species. The free charges make the plasma electrically conductive so that they can couple strongly to electromagnetic fields. For history of plasma, in 1879, Sir William Crookes firstly discovered the fourth state of matter and afterward, in 1928, Irving Langmuir called "plasma".

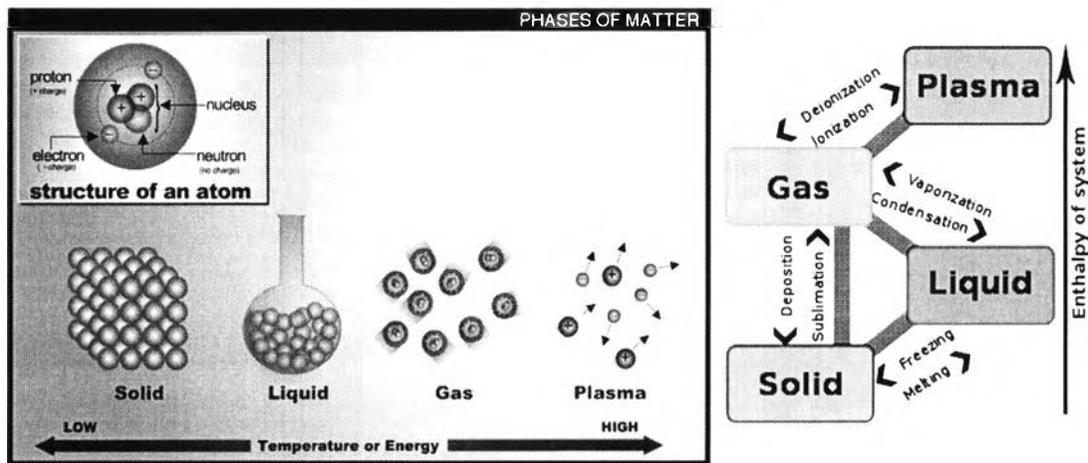


Figure 2.1 Phase of matter consists of solid, liquid, gas, and the fourth state named "plasma" (<http://www.en.wikipedia.org>).

Normally, plasma always occurs in nature. For example, lightning and auroras borealis are the most common natural plasma. (Fridman and Kennedy, 2004). Nevertheless, plasmas can be generated in a laboratory to study for improvement in many industries. They are commonly generated and sustained using electrical energy and are named "discharges". Figure 2.2 shows a schematic of a simple discharge. It consists of a voltage source to drive the current through a low-pressure gas between two parallel electrodes. Afterward, the gas "breaks down"

and forms plasma, usually weakly ionized which is a small fraction of the neutral gas density (Lieberman and Lichtenberg, 2005).

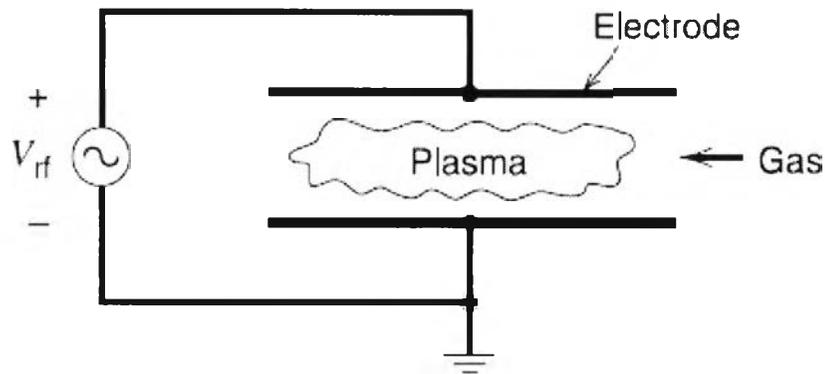


Figure 2.2 Schematic view of a discharge.

Generally, gaseous plasma consists of negative and positive charge as well as neutral gas (atoms or molecules). Firstly, the positively charged particles are mostly cations. Secondly, the negative charge can be both electrons and anions. Last but not least, the neutral species may be the mixtures between free radical species and stable neutral gases. Plasma possesses two significant properties (Eliasson and Kogieschatz, 1991).

1) *Quasi-neutral property*

The total negative charges have to equal to the total positive charges like neutral species owing to low degree of ionization.

2) *Interaction with electromagnetic fields*

Plasma can interact with an applied electromagnetic field due to they consist of ions.

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 called “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.

2.1.1 Generation of Plasma

At this time, researchers use many ways for generating charge to produce plasmas, such as, collisions between cosmic rays and gases in atmospheric layers. However, in the present study, an intensive external electric field is applied for metal electrodes to reduce their “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 get free from the surface and move corresponding to direction of the electric field despite its less kinetic energy to overcome the potential barriers. This phenomenon is known as “tunnel effect”. And then, the plasma is firstly 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.

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.

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 *et al.*, 2002). The formation of plasma has to use condition that is high sufficiently pressure. An example of this plasma is arc discharge.

The second type is “non-thermal plasma” or “non-equilibrium plasma”, which is non-thermodynamically 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, gliding arc discharge, glow discharge, corona discharge, and dielectric-barrier discharge, where the latter will be 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	$A^* + B_2 \longrightarrow AB + B$

2.1.1.1 Thermal Plasma

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. For important point of this, a condition for the happening thermal plasma is a sufficiently high 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.

For example, the advantage of thermal plasma technology is the one of alternative waste management solutions. Owing to it generates the very high temperatures, changing the state of wastes to destroy hazards. This technique is also highly flexible and easy to control, with a low effect on environment. In addition, it enables to the production of a valuable vitrified slag that may be used in construction and other applications.

With thermal plasma treatment forming the core of the process, the scientists try also to develop pre- and post-treatment processes to minimize the extent of any secondary effluent streams.

2.1.1.2 Non-Thermal Plasma

Non-thermal plasma or “cold plasma”, in contrast, is not in thermodynamic equilibrium. Typically, electrons in this method have very much higher temperature than the heavy ions and neutral species particles. Its applications depend chiefly on the reactivity of ions or radicals generated in the plasma for gas phase or surface reaction (Kroschwitz *et al.*, 1998). To illustrate removal hazardous materials in waste water, surface improvement and synthesis chemicals. This technique includes radio frequency, microwave, glow, gliding arc, dielectric-barrier, and corona discharges.

Non-thermal plasmas can be divided into many groups depending on their generation mechanism, their used pressure range, or the electrode geometry. In Figure 2.3, the discharges are grouped according to their temporal behavior, pressure range, and appearance.

The most eminent characteristics of six non-thermal discharges are listed as follows (Eliasson and Kogieschatz, 1991).

- 1) Glow discharge
- 2) Microwave discharge
- 3) Radio frequency discharge
- 4) Gliding arc discharge
- 5) Dielectric barrier discharge
- 6) Corona discharge

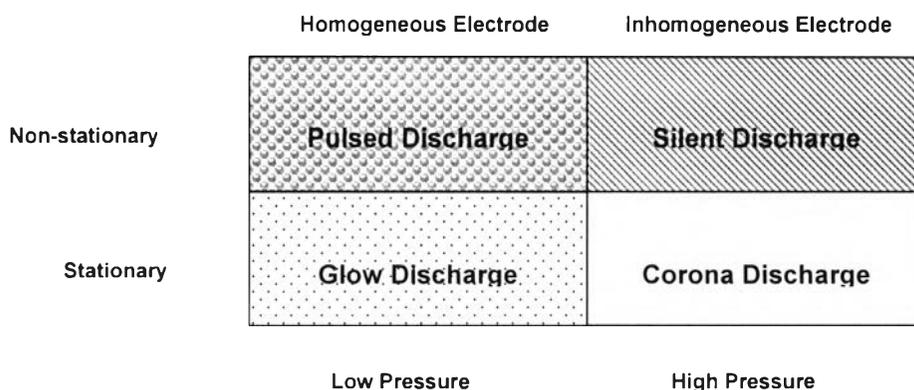


Figure 2.3 The various types of discharge classified according to temporal behavior, pressure, and geometric electrode (Eliasson and Kogieschatz, 1991).

1) Glow discharge: The glow discharge is stationary, weakly ionized, non-equilibrium and low-pressure discharge (about 0.1–10 torr), usually generated between cathode and anode. The discharge can be produced by applying a voltage to electrodes in a gas. Positive charges will be occurred and driven toward the cathode. Immediately, negative charges will be driven toward the anode and then, the charges will collide with themselves. Desired product(s) is/are produced. The glow discharge is the self-sustained continuous DC discharge having a cold cathode, which emits electrons as a result of secondary emission mostly induced by positive ions. Importance outstanding features of a glow discharge are large positive space charge and strong electric field. The thickness of the cathode surface is inversely proportional to gas density and pressure. The distance between electrodes is sufficiently large, Quasi-neutral plasma with a low electric field, the so-called positive column, is formed between the cathode and anode layers. (Fridman and Kennedy, 2004).

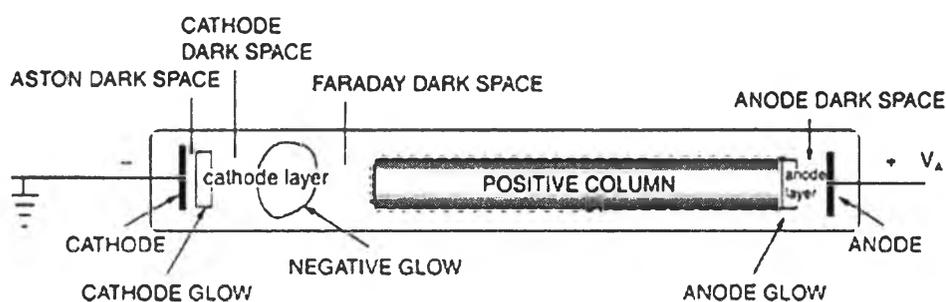


Figure 2.4 General structure of a glow discharge (Fridman and Kennedy, 2004).

Glow discharge is popular because it uses low voltage and current needed to run it. Its applications are used as laboratory tool for chemical investigation, and the neon tubes used for outdoor advertising and the fluorescent tubes. However, the too low pressure and the resulting low mass flow, the glow discharge has not been used for industrial production of chemicals.

2) Microwave discharge: The plasma is occurred by microwave that has frequency range of 300 MHz to 10 GHz in a dielectric tube and plasma column. This machine can be operated over a large frequency and pressure range and

produce large-volume non-equilibrium plasmas that result in plasma homogeneity. Hence, plasma columns can be scaled up to 4-m length. The most applications are similar glow discharge used in elemental analysis and plasma display or plasma television. For important advantages, it is easy to operate and possible for imposing a gas flow to make these discharges attractive also for plasma chemical investigations.

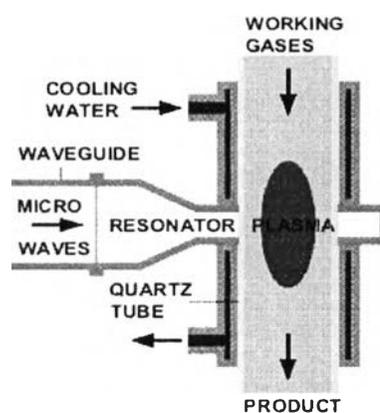


Figure 2.5 Schematic drawing of Microwave discharge.

3) Radio Frequency discharge: The radio frequency (RF) discharges are generated for optical emission spectroscopy in laboratory and plasma chemical researches. They can be divided into two types that are capacitive coupling and inductive coupling according to the method of coupling the RF power with the load. Figure 2.6 shows their structures consisting of an RF generator, a matching network, and an antenna of capacitive coupling (Liu *et al.*, 2008). Condition of RF discharges is low pressure (10–200 Torr), but are used also at atmospheric pressure and frequency higher than 10 MHz (Raizer *et al.*, 1995). Low-pressure RF discharges can be used in many industries such as steel, automotive, and agricultural industries. In addition, they can be used for etching purposes in semiconductor manufacturing. If the collision frequency is higher than the frequency of the applied field, the discharge will be similar to a DC discharge. This implies that non-equilibrium can be confirmed at low pressures, whereas thermal plasmas are generated at about atmospheric pressure.

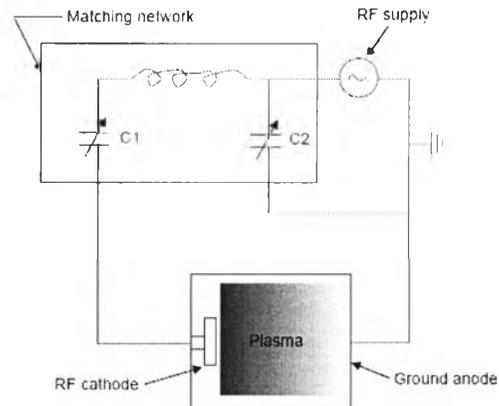


Figure 2.6 Schematic diagram of a capacitively-coupled plasma (CCP) plasma source with an equivalent electrical circuit.

4) Gliding arc discharge: The gliding arc discharge has least two diverging knife-shape electrode. These electrodes are immersed in a fast flow of feed gas. A high voltage and relatively low current discharge are generated across the fast gas flow between the electrodes (Fridman, 1999). During the gliding arc evolution, Phase of plasma will be divided into three parts following to Figure 2.7.

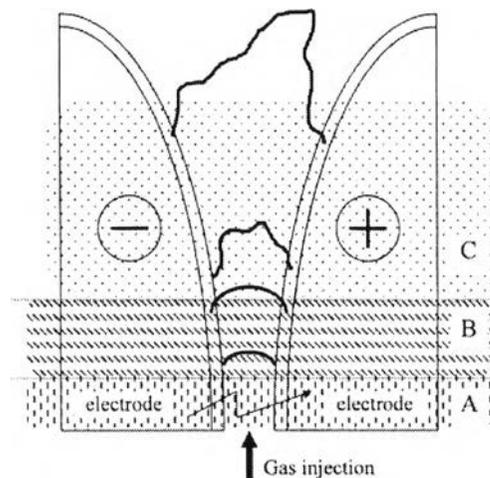


Figure 2.7 Phases of gliding arc evolution: (A) initial gas break-down; (B) equilibrium heating phase; (C) non-equilibrium reaction phase.

In part A: The initial break-down, Gas is injected into the system and then, the high voltage generator supplies the necessary electric field to

break down the gas between the electrodes. The discharge starts at the shortest distance (1–2 mm) between the two electrodes (Fridman *et al.*, 1999).

The equilibrium stage (B) happens after generation of a stable plasma. The velocity of gas flow about 10 m/s and the length of the arc column increase together with voltage (Fridman *et al.*, 1999).

In the last state (C), when the length of the gliding arc surpasses its critical value, heat losses from the plasma column begin to exceed the energy supplied by the source; therefore, the plasma in the state of thermodynamic equilibrium disappears. As a result, the discharge plasma cools rapidly to the gas temperature (about $T_0 = 2000$ K) while the plasma conductivity is maintained by a high value of the electron temperature $T_e = 1$ eV (about 11,000 K). After the decay of the non-equilibrium discharge, there is new breakdown at the shortest distance between electrodes and the cycle repeats (Fridman *et al.*, 1999).

5) Dielectric Barrier Discharge: Dielectric-barrier discharges (DBD) are operated in the atmospheric pressure range. The feature of DBD is dielectric layers that help the generated microdischarges, which are weakly ionized plasmas with properties resembling those of transient high pressure glow discharges, in gas to reach the electrode surfaces. Dielectric barrier may use glass, quartz, ceramics, plastic films, silicon rubber, and Teflon plates. The advantages of the dielectric barrier are limitation the amount of charge and energy deposited in an individual microdischarge, prevention formation of sparks and distribution the microdischarges evenly over the entire electrode surface.

The low charge mobility on the dielectric not only contributes to this self-arresting of filaments and limits the sideways region, but also the gap voltage is diminished, thereby allowing parallel filaments to easily form closeness to one another. From this reason, the space between parallel electrodes uniformly covers by discharge filaments, each roughly 0.1 mm in diameter and lasting only about 10 ns. In addition, high voltage and low frequency operation are likely to expand the microdischarges, while low voltage and high frequency operation are liable to ignite the old microdischarge channels every half period again.

For the mechanism of generated discharges in DBD (Figure 2.8.1-2.8.4), the voltage is applied across the gas exceeds for breakdown and the generation of narrow discharge filaments initiates the conduction of electrons toward the more positive electrode (Figure 2.8.1). When the charge collects on the dielectric layer, the voltage drop across the filament decreases below the sustaining level of discharges, these things make discharge extinguish (Figure 2.8.4) (Rainer *et. al.*, 2008).

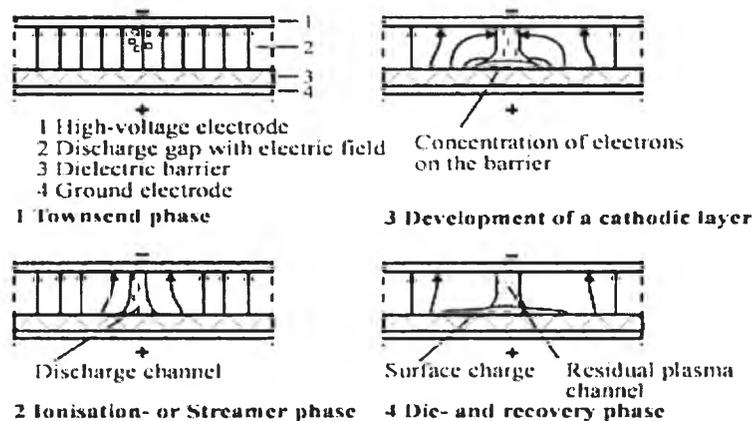


Figure 2.8.1- 2.8.4 The mechanism of generated discharges (Rainer *et. al.*, 2008).

Due to residual plasma channels on the dielectric reduce electric fields where microdischarges have already occurred, when the given voltage is increased, the additional microdischarges will begin at new locations and then, when the voltage is inverted, the next microdischarges will easily form at old microdischarge locations. The characteristic of DBD which the charges accumulate on dielectric is called memory effect (Rainer *et. al.*, 2008).

When sinusoidal voltage is applied (t_1) instead of DC electricity, inducing of an occurred electric field will simultaneously generate microdischarges cover the whole dielectric layer (t_2). Next, the microdischarges extinguish which resulting voltage between electrode and dielectric approximates to zero. At the same time, in the gas gap, residual plasma channels are still in part and their conductivity decreases continuously. These channels result to ignite new microdischarges easily, if the applied voltage is reversed. At t_3 , memory effect results to the voltage across the gas gap, and then, the new inverse microdischarges are occurred through residual channels of previous microdischarges (Rainer *et. al.*, 2008).

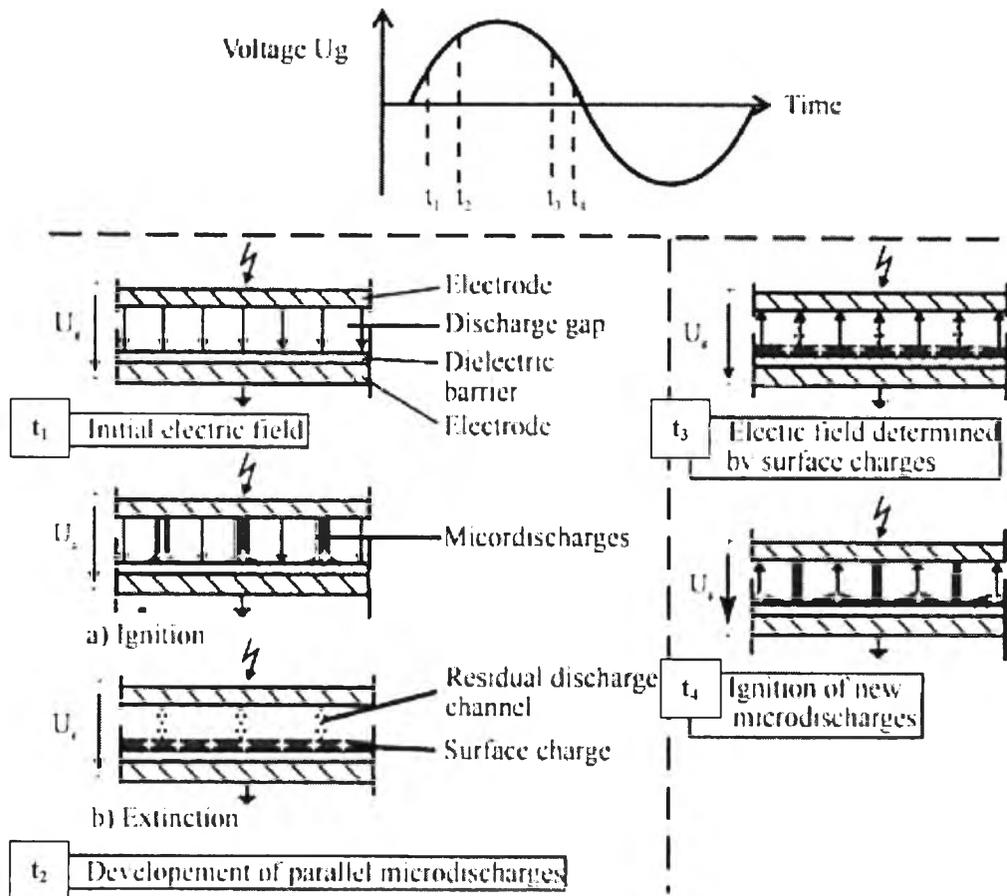


Figure 2.9 The mechanism of generated discharges by applying sinusoidal voltage in DBD (Rainer *et. al.*, 2008).

The DBD which combines between non-equilibrium and quasi-continuous behavior is used in ozone industries for ozone generation. To this end, experimental DBD studies have explored different ratio of gas mixtures, optimization of applied voltage and frequency and surface geometries. Related work has focused on maximizing the ultraviolet radiation from excimer molecules produced in DBD. 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 dynamic interactions between filaments, as well as the chemical and electronic interactions within filaments, have proven interesting. The schematic for dielectric barrier discharge reactor is shown in Figure 2.10.

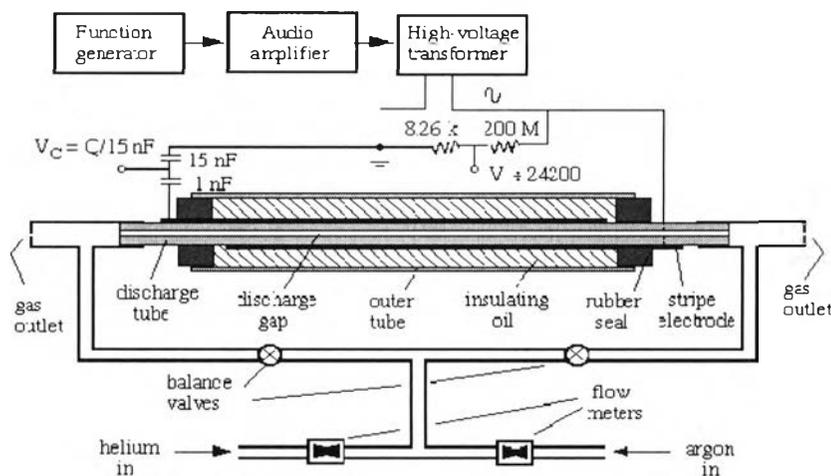


Figure 2.10 Schematic for dielectric barrier discharge reactor.

DBD plasmas are normally operated in one of the parallel-plate (Figure 2.11) or cylindrical (Figure 2.12) configurations. The parallel-plate configuration is used to surface treat fast-moving webs and films, and the annular volume of the cylindrical configuration is used to treat airflows for ozone production. At least one electrode of these geometries is covered with an insulating dielectric.

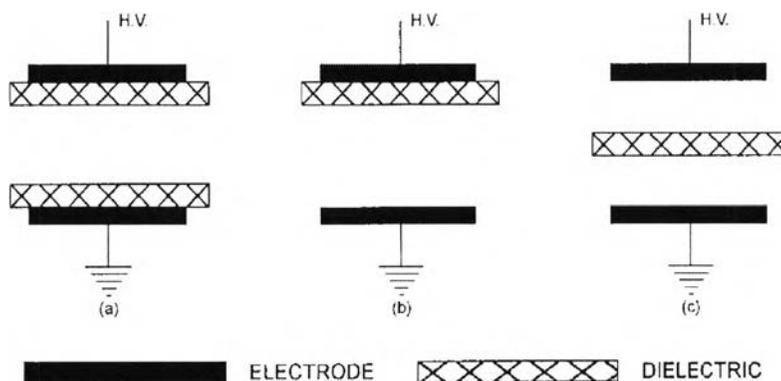


Figure 2.11 Schematic diagrams of parallel-plate DBD plasma source configurations.

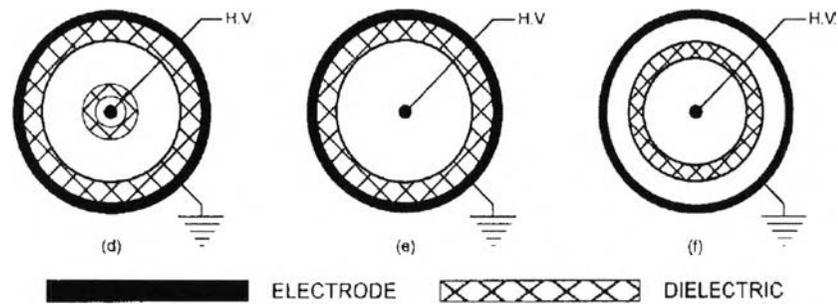


Figure 2.12 Schematic diagrams of cylindrical DBD plasma source configurations.

6) Corona Discharge: One type of discharge can operate at both extremely low and high pressure. This type of discharge is generally constructed with inhomogeneous electrode geometries; e.g. a pointed electrode and a plane electrode (or pin and plate), as shown in Figure 2.13. The discharge generated by this kind of electrode is called corona discharge.

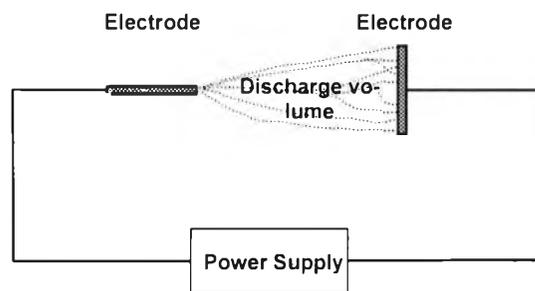


Figure 2.13 The corona discharge generated by inhomogeneous electrodes.

6.1) Positive Corona

Corona discharges exist in several forms, depending on the polarity of the field and the electrode geometrical configurations. 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 2.14. Unlike Hermstein's 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 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 *et. al.*, 1991).

6.2) 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 move 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 finally break down. In this sense, the corona discharge can be considered a partial breakdown.

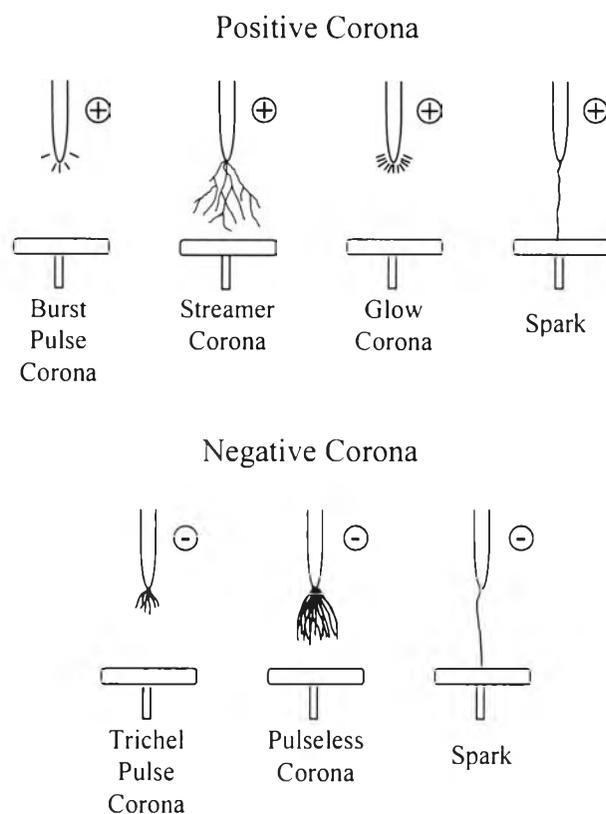


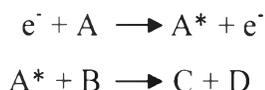
Figure 2.14 Schematic of various forms of corona discharge depending upon applied voltage at constant electrode geometrical configuration (Chang *et. al.*, 1991).

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.

2.1.2 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 also be applied to ions. For example, the reaction schematic is demonstrated below (McQuarrie and Rock, 1987).



where A, B are reactant.

C, D are product.

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 take place at a 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.

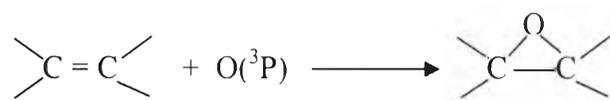
2.2 Applications of Non-Thermal Plasma

The non-thermal plasma has been widely used in many industrial applications. The first use of chemical synthesis via silent discharge is ozone generation by Siemen. Ozone can be used for decomposing compounds in wastewater (Horvath, 1980). Under selective experimental 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 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 (Patiño *et al.*, 1995; Suhr *et al.*, 1984; Suhr and Pfreundschuh, 1988; Tezuka and Yajima, 1996). 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 $O(^3P)$ (Patiño *et al.*, 1996; Patiño *et al.*, 1995; Suhr and Pfreundschuh, 1988; Suhr, 1983; Patiño *et al.*, 1999; Suga and Sekiguchi, 2005). The following reaction was 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 Suga and Sekiguchi's experiments.

There have been the extensive attempts 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 reaction time and shortening distance between the tip of the tube and the liquid surface, and the epoxide could be obtained with the highest yield (Suga and Sekiguchi, 2005).

Researchers used non-thermal plasma not only to synthesize chemical, treat waste water and develop process but also treat substance surface for surface properties improvement. In recent work, Kailu *et al.* (2009) synthesized carbon nanotube arrays from glow discharge-treated Ni/AAO membrane and found that the glow discharge treatment also improves the high dispersion of nickel-containing particles within AAO membrane, so the NiO nanoparticles are highly dispersed in carbon nanotubes.

2.2.1 The examples of combination between catalyst and plasma system

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 (Rainer *et al.*, 2008). 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 (Pietruszka and Heintze, 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; Pietruszka and Heintze, 2004). As reported by Heintze *et al.* (2004), they investigated the combined DBD and Ni/ α -Al₂O₃ 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 CO₂.

In additionally, equivalent of reactants have an effect on process efficiency. Kalra *et al.* (2004) studied production parameters including equivalent of hydrocarbon fuel and oxygen, efficiency of production synthesis gas and electric energy cost that had effects on synthesis gas production from hydrocarbon fuel by using gliding arc discharge. They reported that at higher equivalence ratio, methane flow was driving the arc there was a lower limit to this flow rate, electric energy cost is optimal between equivalence ratios 3.2 and 3.8 and the conversion was the best for equivalence ratio 3.0 to 3.6. Besides, Matin and Whitehead (2007) adapted mechanism of the reforming of methane with oxygen from high temperature in flame

to low temperature by using DBD. Moreover, they studied the conversion of methane, the production of hydrogen, methanol and C2 hydrocarbons as a function of the ration of the initial methane to oxygen concentrations and the plasma gas temperature. It is shown that these parameters play a vital role in determining the yields and selectivities for the reforming of methane with oxygen.

Another factor that involves in catalytic reaction is surface roughness. In 2011, Jolibois *et al.* studied effects of the rugosity due to glass beads on the characteristics of a surface DBD for generating ozone and nitrogen dioxide. They found that velocity of the electric wind is reduced about 1 m/s for discharges with an important surface roughness. Moreover, this velocity reduction increases gradually with the roughness size. However, the production of chemical species is rather due to the increase in exchange surface, is not correlated with the induced electric wind by the plasma.

Examples of using both non-thermal plasma and catalyst improve process efficiency. Tetsuji *et al.* (1996) studied nitric oxide decomposition in air by using non-thermal plasma processing and Cu-ZSM-5. Afterward, Tetsuji (2006) studied environment applications of atmospheric pressure non-thermal plasma including the high performance cleaning of combustion flue gas, the dioxin removal, the decomposition CFC, VOC and TCE, the sterilization in food and medicine industries, the surface modification, the water cleaning, and the gas reforming.

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 CH₄ 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 CH₄ to C2 hydrocarbons in a pulsed corona discharge with the following order: platinum > palladium > copper.

Miziolek *et al.* (1999) studied effect of halon 1301 and 1211 that could eliminate ozone and were hazardous wastes by using non-thermal plasma (NTP) for decomposition halon 1301 and 1211 and converting them to variety of commercial chemicals. They fed argon gas to plasma reactor that was set as AC 110 W and 4

kHz, and used GC/MS for analyzing exhaust gas. They found that NTP offered the possibility of not only destroying the halon stockpiles with high energy efficiency, but also of producing desired commercially variable chemicals.

Sutthiruangwong (1999) studied the conversion of methane for 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 CH₄ conversion than the catalytic system, and products mainly consisted of C₂ 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 C₂ 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 C₂H₄ conversion and CO₂ selectivity, which were in contrast with the effects of higher input frequency and feed flow rate. The commercial TiO₂ (Degussa P25), TiO₂, and 1%Pt/TiO₂ prepared by sol-gel method were used as photocatalysts. The presence of all studied photocatalysts increased the C₂H₄ and O₂ conversions, as well as CO₂ selectivity, in the following order: 1%Pt/TiO₂ > TiO₂ > Degussa P25. The synergistic effect of photocatalysts presented in the plasma reactor was resulted from the activation of TiO₂ by the UV light generated from the plasma.

2.2.2 The examples of catalysts that are used in Ethylene Epoxidation

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 ($\alpha\text{-Al}_2\text{O}_3$). Low-surface-area (LSA) $\alpha\text{-Al}_2\text{O}_3$, possessing the surface area less than $1\text{ m}^2/\text{g}$, 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 ($\text{C}_2\text{H}_4\text{Cl}_2$) and vinyl chloride ($\text{C}_2\text{H}_3\text{Cl}$), 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 and Chitwood, 1942; Campbell and Paffett, 1984; Tan *et al.*, 1986; Yeung *et al.*, 1998). The mechanism of chloride moderator is still in question that it has been attributed to geometric (Campbell and Paffett, 1984; Campbell and Koel, 1985; Campbell, 1986), electronic (Tan *et al.*, 1986; Lambert *et al.*, 2003), 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; Bhasin, 1990). 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; 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) α - 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 1wt.% 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) γ - Al_2O_3 , Au/ TiO_2 , and bimetallic Au-Ag/(HSA) γ - 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.

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/ α - Al_2O_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 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) γ -Al₂O₃ 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 favorable molecular oxygen sites.

As mentioned about the poorly dispersed silver on (LSA) α -Al₂O₃, 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 over well-dispersed Ag/SiO₂, Ag/ η -Al₂O₃, and Ag/TiO₂ in the presence and absence of C₂H₄Cl₂ (EDC) compared with those of poorly dispersed Ag/ α -Al₂O₃. 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/SiO₂, 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 SiO₂, respectively, compared with 23 % over 1 μ m Ag crystallites on α -Al₂O₃ in the absence of EDC and CO₂ at 523 K.

Due to well-dispersed silver over (HSA) α -Al₂O₃ support (approximately 78-104 m²/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).

TiO₂ 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 TiO₂ 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).

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) α -Al₂O₃, Ag/high-surface-area(HSA) γ -Al₂O₃, Au-Ag/(HSA) γ -Al₂O₃, and Au/TiO₂. The results showed that Ag/(LSA) α -Al₂O₃ 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) α -Al₂O₃ 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.

Suwannabart (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 O₂/C₂H₄ molar ratio of 1/1, a feed flow rate of 50 cm³/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/(low-surface-area) α -Al₂O₃ catalyst exhibiting comparative good epoxidation performance, the DBD system still provided the better performance

in terms of C_2H_4 conversion, C_2H_4O yield, and power consumption per C_2H_4O molecule produced.

In previous work, Permsin (2009) studied the effects of operational parameters for the DBD systems, including O_2/C_2H_4 molar ratio, applied voltage, and input frequency and compared efficiency of epoxidation of ethylene between a cylindrical dielectric barrier discharge (DBD) reactor and a parallel DBD reactor. Summarily, they found that the highest ethylene oxide yield was obtained using the cylindrical DBD reactor when an O_2/C_2H_4 molar ratio of 0.25:1 (1:4), an applied voltage of 15 kV, and an input frequency of 500 Hz were used. Under these optimum conditions, the ethylene oxide selectivity and the ethylene oxide yield were found to be 12.75 % and 2.41 %, respectively.

In addition, Suttikul *et al.* (2011) studied the combination of silver catalysts on two different supports (glass bead and alumina ball) in a low temperature dielectric barrier discharge (DBD) for the epoxidation of ethylene to ethylene oxide. In conclusion, silver supported on glass bead provided the highest ethylene oxide selectivity. The optimum Ag loading on the glass bead was found to be 20 wt.%, at which a maximum ethylene oxide selectivity of 30.56 % was obtained at the optimum applied voltage and input frequency of 19 kV and 500 Hz, respectively. Under these optimum conditions, the power consumption was found to be 12.81×10^{-18} W.s/molecule of ethylene oxide produced. Afterward, they studied ethylene epoxidation reaction for ethylene oxide production over silver catalysts loaded on two different supports (silica and alumina particles) in a low temperature AC dielectric barrier discharge (DBD) reactor. From the results, the presence of silver catalysts improved the ethylene oxide production performance. The silica support interestingly provided a higher ethylene oxide selectivity than the alumina support. The optimum Ag loading on the silica support was found to be 20 wt%, exhibiting the highest ethylene oxide selectivity of 30.6 %.

Moreover, Paosombat *et al.* (2012) studied the effects of ethylene (C_2H_4) feed position and O_2/C_2H_4 feed molar ratio on ethylene epoxidation in a parallel dielectric barrier discharge (DBD). The results showed that the ethylene feed position fraction of 0.5 and the feed molar ratio of O_2/C_2H_4 of 0.2:1 gave the highest EO selectivity of 34.3 % and the highest EO yield of 5.28 % with low power

consumptions of 2.11×10^{-16} Ws/molecule of ethylene converted and 6.34×10^{-16} Ws/molecule of EO produced when the DBD system was operated under the best conditions: an applied voltage of 19 kV, an input frequency of 500 Hz and a total feed flow rate of $50 \text{ cm}^3/\text{min}$.