CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Basic Principles of Plasma

Plasma is normally referred to the forth state of the matter. As temperature increase, molecules become more energetic and transform in the sequence: solid, liquid, gas, and plasma. In the letter states, molecules in the gas dissociate to form a gas of atoms and then gas freely moving charge particle, electron, and positive ions. This stage first identified by Sir William Crookes in 1879 and named "plasma" by Irving Langmuir in 1928. This plasma stage is characterize by a mixture of electrons, ions, and neutral particles moving in random directions which is electrical neutral ($n_e \approx n_i$). (Fridman and Kennedy, 2004).

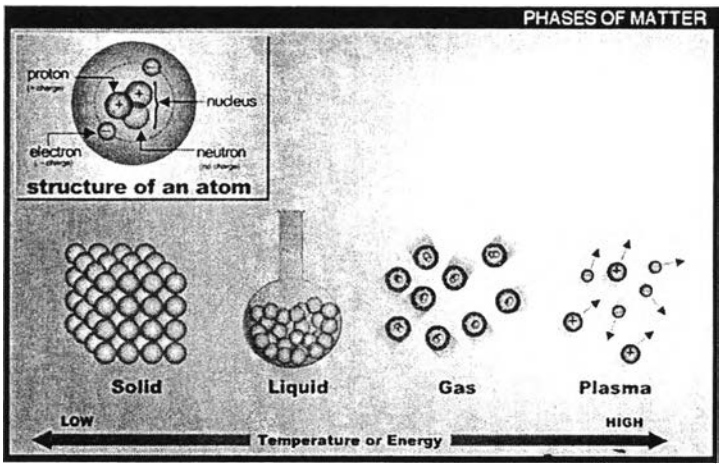


Figure 2.1 Phase of matter consists of solid, liquid, gas, and the forth state named "plasma".

Generally, plasma can occur in natural. For example, lightning and auroras borealis which are the most common natural plasma. (Fridman and Kennedy, 2004). However, plasmas can be generated in laboratory to study for improve in many industries. They are commonly generated and sustained using in electrical energy form and named them 'discharges'. Figure 2.2 shows the schematic of a simple discharge.

It is comprised of a voltage source to drive the current through a low-pressure gas between two parallel electrodes. Subsequently, the gas "breaks down" and forms plasma, usually weakly ionized which is a small fraction of the neutral gas density (Lieberman and Lichtenberg, 2005).

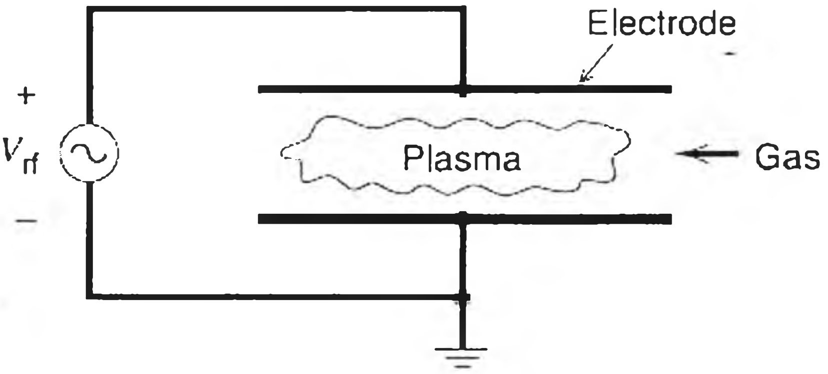


Figure 2.2 Schematic view of a discharge.

Gaseous plasma consists of negatively and positively charged particles in an otherwise neutral gas. The positively charged particles are mostly cations but the negative charge particles can be either electrons or anions. The neutral species may be the mixture of free radical species and stable neutral gases. Normally, plasma possesses two significant properties (Eliasson and Kogieschatz, 1991).

1) *Quasi-neutral property*

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

2) *Interaction with electromagnetic fields*

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

2.1.1 Generation of Plasma

There are several ways for generating charged particles to generate plasmas, for example, collisions between cosmic rays and gases in atmospheric layers. However, in the present study, an externally intense electric field is applied for metal electrodes in order to reduce 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 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.

The electrons liberated from the metal surface will immediately be accelerated to move corresponding to the direction of 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. Therefore, 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 the very short period of time after of electric field has been applied. Many active species can further initiate several 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 collision between the species and the electrode surfaces are referred to as "electric discharges" phenomena.

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	$A^* + B_2 \longrightarrow AB + B$

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). A crucial condition for the formation of this plasma type is sufficiently high working pressure. An example of this plasma is arc discharge.

The second type is “non-thermal plasma” or “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, gliding arc discharge, glow discharge, corona discharge, and dielectric-barrier discharge, where the latter will be used in this study.

2.1.2 Type of Plasma

2.1.2.1 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.

2.1.2.2 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.

2.1.2.2.1 Type of Non-thermal Plasmas

Non-thermal plasmas can be divided into distinctive groups depending on their mechanism used for their generation, 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) Corona discharge
6) Dielectric barrier discharge

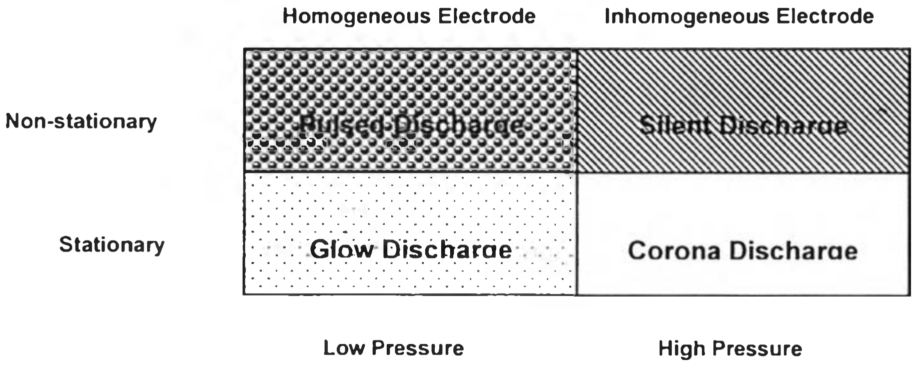


Figure 2.3 The various types of discharge classified according to temporal behavior, pressure, and geometric electrode (Eliasson and Kogeischatz, 1991).

1) Glow discharge

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).

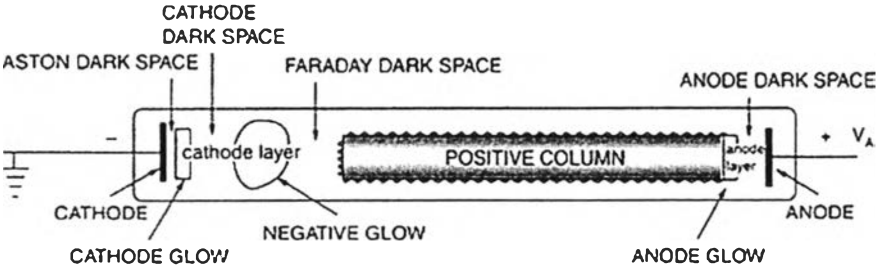


Figure 2.4 General structure of a glow discharge (Fridman and Kennedy, 2004).

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.

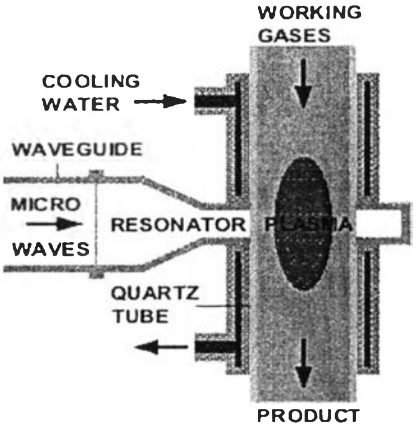


Figure 2.5 Schematic drawing of Microwave discharge.

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. 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.

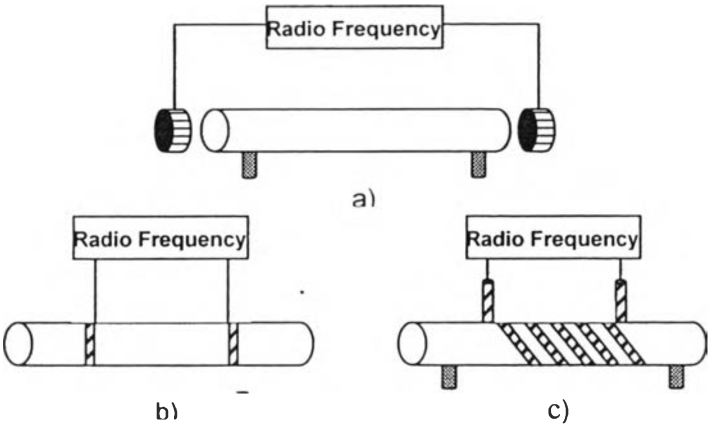


Figure 2.6 Schematic of various types of radio frequency discharge: (a) and (b) contain capacitive coupling, normally used at low pressure, (c) use inductive coupling instead of capacitive coupling, which can be operated at pressure up to 1 bar.

4) 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.

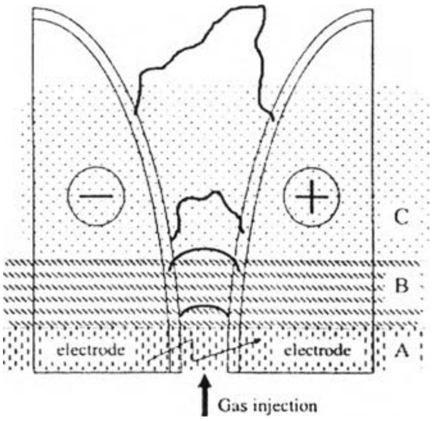


Figure 2.7 Phases of gliding arc evolution: (A) initial gas break-down; (B) equilibrium heating phase; (C) non-equilibrium reaction phase.

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) 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.

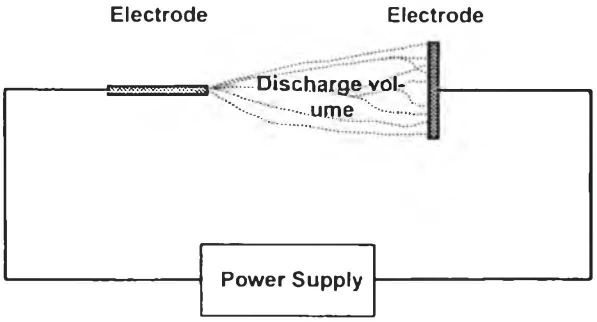


Figure 2.8 The corona discharge generated by inhomogeneous electrodes.

Types of Corona Discharge:

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

a) 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 2.14. 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, 1991).

b) 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.

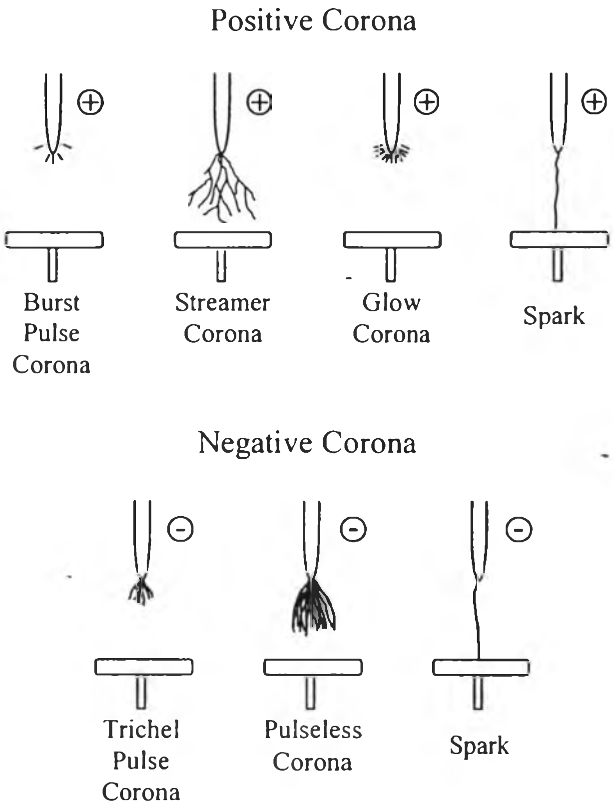


Figure 2.9 Schematic of various forms of corona discharge depending upon applied voltage at constant electrode geometrical configuration (Chang, 1991).

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.

6) 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 2.10.1-2.10.4), 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 2.10.1). 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 2.10.4) (Rainer *et. al.*, 2008).

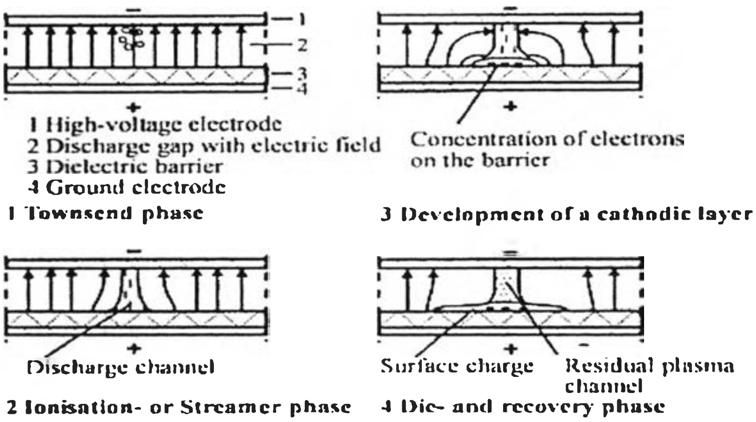


Figure 2.10 The mechanism of generated discharges. (Rainer *et. al.*, 2008).

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).

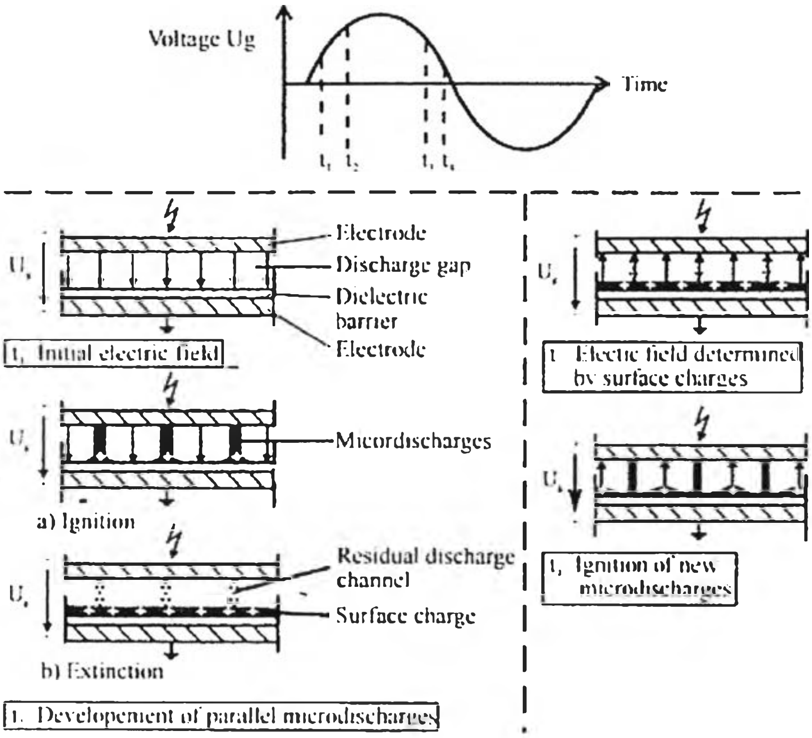


Figure 2.11 The mechanism of generated discharges by applying sinusoidal voltage in DBD. (Rainer *et. al.*, 2008).

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 2.12.

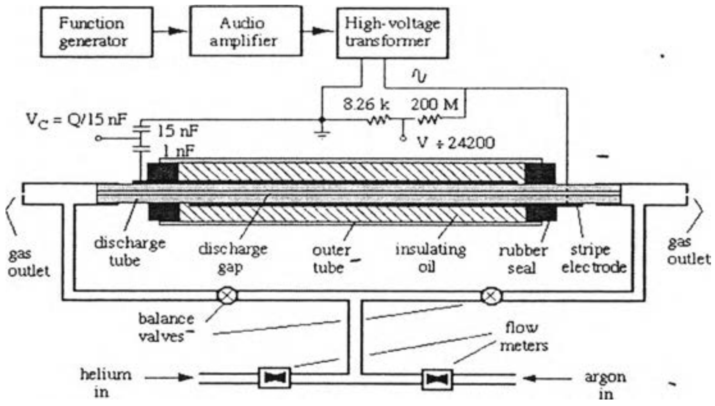


Figure 2.12 Schematic for dielectric barrier discharge reactor.

DBD plasmas are normally operated in one of the parallel-plate (Figure 2.13) or cylindrical (Figure 2.14) 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.

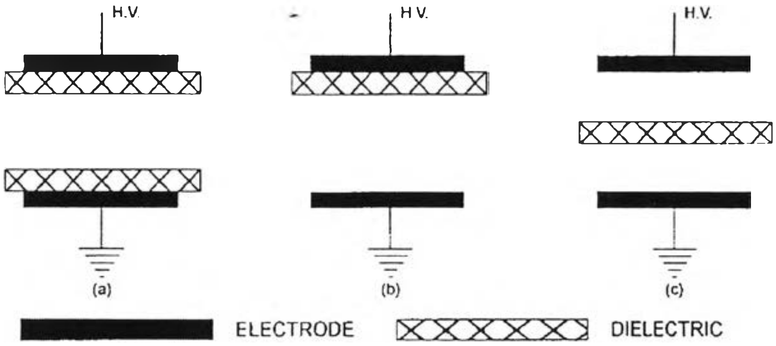


Figure 2.13 Schematic diagrams of parallel-plate DBD plasma source configurations.

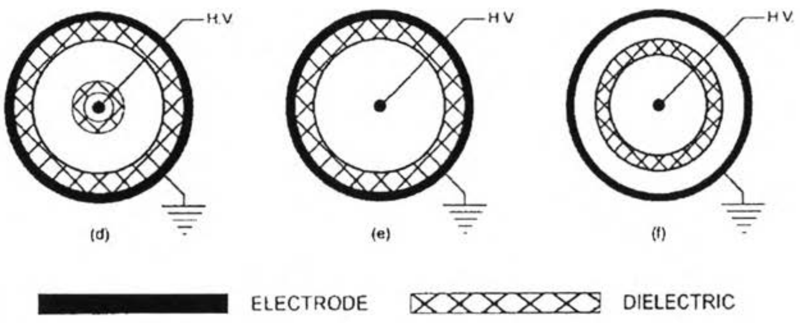


Figure 2.14 Schematic diagrams of cylindrical DBD plasma source configurations.

2.1.2.2.2 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 *et al.*, 1987).

$$e^- + A \longrightarrow A^* + e^-$$
$$A^* + B \longrightarrow C + D$$

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.

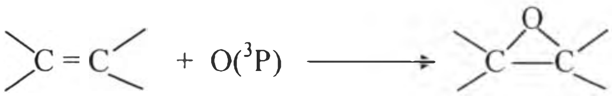
Besides transferring energy to gas molecules via fast electrons and ions, photon can also involve with initiating the new chemical species if it is energetic enough. The photon is taken place by emitting energy of excited molecules to lower state. The characteristics of electron and photon are quite 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 *et al.*, 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(^{3}P) (Patiño *et al.*, 1996; Patiño *et al.*, 1995; Suhr *et al.*, 1988; Suhr, 1983; Patiño *et al.*, 1999; and 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(^{3}P) 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.

From the previous work, Dulyalaksananon (2013) studied the ethylene epoxidation over two dielectrics rough surface glass plate in a low-temperature parallel dielectric barrier discharge (DBD). The result showed that the highest ethylene oxide activity occurred when operating at an applied voltage of 23 kV, an input frequency of 500 Hz, an O_2/C_2H_4 feed molar ratio of 0.2:1, and an ethylene feed position fraction of 0.5. Furthermore, the ethylene oxide selectivity which used two rough-surfaced glasses was higher than one smooth-surfaced glass about two times.

2.3 Combination between Plasma and Catalytic 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 (Pietruszka *et al.*, 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 Pietruszka *et al.*, 2004). As reported by Heintze *et al.* (2004), they investigated the combined DBD and $Ni/\alpha\text{-}Al_2O_3$ 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 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_2.

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_4 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_4 to C_2 hydrocarbons in a pulsed corona discharge with the following order: platinum > palladium > copper. In the same year, Suttiruangwong 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 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 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_2 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_2H_4 conversion and CO_2 selectivity, which were in contrast with the effects of higher input 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 was resulted from the activation of TiO_2 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)α-Al_2O_3, Ag/high-surface-area(HSA)γ-Al_2O_3, Au-Ag/(HSA)γ-Al_2O_3, and Au/TiO_2. The results showed that Ag/(LSA)α-Al_2O_3 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-Al_2O_3 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 O_2/C_2H_4 molar ratio of 1/1, a feed flow rate of 50 cm^3/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-Al_2O_3 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 *et al.* (2010) 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 $12.81\text{x}10^{-18}$ 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 cm^3/min.

2.4 Catalysts Used in Ethylene Epoxidation

Ethylene can be 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 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 thwe rates of ethylene oxide and carbon dioxide formation (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; and 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; 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)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, $Ag/(HSA)\gamma$-Al_2O_3, Au/TiO_2, and bimetallic Au-$Ag/(HSA)\gamma$-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-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 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-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 over well-dispersed Ag/SiO_2, Ag/η-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/α-Al_2O_3. 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_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 with 23% over 1 μm Ag crystallites on α-Al_2O_3 in the absence of EDC and CO_2 at 523 K.

Due to well-dispersed silver over (HSA) α-Al_2O_3 support (approximately 78-104 m^2/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_2 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_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 2013, Chongterdtoonskul *et al.* investigated the effect of second metals (Au, Ba, Pd, Sn and Cu) loaded on Ag forward to ethylene epoxdation, in comparison to Ag- and Au- loaded on the $SrTiO_3$. The result showed that selectivity decrease when second metal was added except Cu, after temperature reach to 548 K. selectivity decreased for all systems. Adding Cu can improve the catalytic performance by increasing Ag metallic fraction leading to reduce coke formation, moreover the difference between barrier for acetaldehyde and ethylene oxide increased when Cu was added due to Cu displayed highest differential bonding affinity toward the O and C atom of OMME. On the other hand, Au monocatalyst exhibited the lowest selectivity and then improved after adding Ag. In case of long term stability, adding Sn on Cu-Ag can remain the selectivity throughout 72 hour operation, meanwhile both yield and selectivity of momocatalyst Ag and bimetallic Cu-Ag sharply decreased after 20 operation time

2.5 Oxidants for Epoxidation Reaction

There are several oxidants for epoxidation reaction which provide different oxygen species leading to different epoxidation activity. Many researchers tried to study the effect of the oxygen sources on epoxidation activity, however it has inconsistent with the results

2.5.1 Air

The cheapest oxidant, is used only rarely without irradiation and without catalyst. Example of oxidations by air alone is he conversion of aldehydes into carboxylic acids (autoxidation) and the oxidation of acyloins to α-diketons (Milos, 1990).

2.5.2 Molecular Oxygen

The selective chemisorbed oxygen was a charged molecular species, O_2^-. Using infrared spectroscopy, they claimed to have indentified and adsorbed ethane peroxy species (CH_2-CH_2-O-O-Ag) by interaction of ethylene with molecular oxygen adsorbed on Ag. The ethylene peroxy complex decomposed at 383K and proposed to ethylene epoxide. Atomic oxygen was consider as an unselectivie oxidant.

In 1978, Cant and Hall demonstrated that molecular oxygen species was the oxidant and formed an intermediate with adsorb ethylene which was formed both ethylene oxide and CO_2. They used cis- or tran- 1,2-d_2-ethylene and they found 92% cis/trans equilibration in the ethylene epxidation. It can be concluded that addition of oxygen to the C=C bond of ethylene was not concerted and that some stage in the reaction co-ordinate there is free rotation about a C-C bond which is form during the reaction.

By temperature program desorption, the result shown that molecular oxygen can be removed from the surface of Ag (111) without any impact on the subsequent production of reaction with the atomically adsorbed oxygen. They offered that the valence stage of atomically adsorbed oxygen determine the reaction selectivity. The valence charge state, which determined by chloride promoters or subsurface oxygen atoms, a lower valence charge density on $O_{(a)}$ was made it better electrophile, favoring electrophilic attack on ethylene leading to selective oxidation. Meanwhile, higher density charge leaded to combustion (Grant *et al.*, 1985)

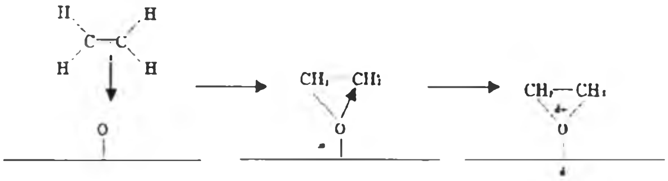


Figure 2.15 Selective oxidation by low density charge of $O_{(a)}$. (Couves *et al.*, 2004).

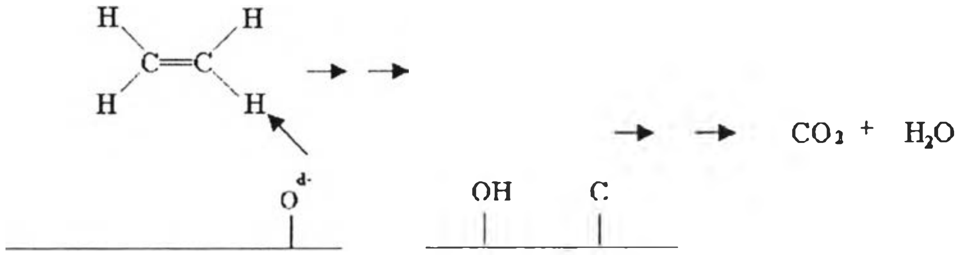


Figure 2.16 Combustion reaction by high density charge of $O_{(a)}$. (Couves *et al.*,2004)

2.5.3 Nitrous Oxide

Nitrous oxide was for the first time obtained more than 200 years ago (in 1793) by English scientific, Joseph Priestley. However, it for long time did not find practical application. Only 50 years later after discovery, because of the anesthesiological properties, it began to use in medicine.

In the period of the rapid development of rocket and space technology it was paid attention to the high energy characteristics of nitrous oxide, its ability to exhibit strong oxidizing properties and to decomposition in to nitrogen and oxygen in 2:1 ratio, which was close to the air composition. (Gaidei, 2009).

During the large decades, nitrous oxide has become the interesting reagents for selective oxidation. According to its light narcotic effect, this compound was used in medicine but it was not very toxic in chemistry. In addition, in the last two decades some special environmental restrictions were issue to prevent the emission of N_2O into the atmosphere due to this compound has been considered as ozone destruction and green house gas agent. Hence, it is a good way to reduce this emission gas by using it as feed stock to produce more valuable products. (Parmon *et al.*, 2005)

2.5.3.1 Gas Phase Catalytic Oxidation with N_2O

In the late 1970s-early 1980s, nitrous oxide has attracted a significant attention of researchers involved in finding for new way selective oxidation of methane to methanol at low conversion

Nitrous oxide was first particular used as an oxidant in relation to phenol problem. Nowadays, there are three steps in cumene technology: 1) alkylation of bezene to toluene 2) Oxidation of cumene to cumene hydroperoxide, and 3) decomposition of the latter to the phenol product and aceton as co-product. An ideal solution of the problem would be a direct oxidation of benzene to phenon with dioxygen as shown below.

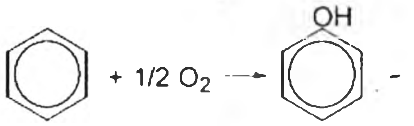


Figure 2.17 The directoxidation of benzene to phenol by dioxygen

However, many attempts accomplish this reaction were not successful. The interaction with O_2 in the presence of known catalyst leads to the destruction of aromatic ring and low phenol selectivity.

N_2O was first used for the oxidation of benzene by Iwamoto *et al.*, 1983. This reaction used vanadia catalyst providing better selectivity than using dioxygen. The selectivity exceeds about 70% at 550 °C. However, the selectivity proved to be too low for a commercial development.

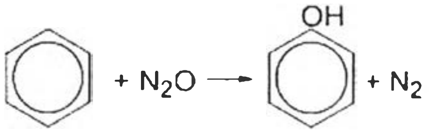


Figure 2.18 The directoxidation of benzene to phenol by N_2O

2.5.3.2 Liquid Phase Catalytic Oxidation with N_2O

The liquid phase oxidation of alkanes with nitrous oxide into carbonyl compounds can be applied to a variety of substrates including aliphatic, cyclic, heterocyclic alkenes and their derivatives. The epoxidation or carboxidation proceed non catalytic in temperature in range of 150 – 250 °C yielding ketones and aldehydes as the main products. Although the selectivity depends on structure of alkene and its composition, each type of alkene was shown to include substrates whose carboxidation proceeds selectively yielding to 90-99% of carbonyl compounds.

There some arguments between the effective of using molecularoxygen (O_2) and N_2O. Some shows that O_2 is more effective than N_2O, while others demonstrate that N_2O exhibits the higher selectivity than O_2

Yong and cant (1989) studied the effect of oxidant between nitrous oxide and oxygen for the conversion of ethylene to ethylene oxide over various catalysts (Ag sponge, Al/α-Al_2O_3, /α-Al_2O_3, and Al(Cs)/SiC). The experiment carried out in a conventional single pass flow system at ambient pressure and total flow rate in range 40-300 cm^3. In this experiment, it can be concluded that using oxygen as oxidant provide selectivity of ethylene epoxdation better than N_2O for all catalyst systems.

On the other hand, Tan and lambert claimed (1986) that N_2O decomposition is active on atomically clean Ag(111). The presence of preadsorbed O(a) enhance the rate of dissociative chemisorption. From TPD and TPR data, the result shown that O(a) deposited by N_2O is active in ethylene epoxidation. Thos O(a) species can identical with the resulting from he chemisorptions of O_2 itself. Moreover, using N_2O can lead directly to the formation of EO without the intervention of adventitiously produced gaseous oxygen.