CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Fundamentals of Plasma[1]

Plasma can be broadly defined as a state of matter in which a significant number of atoms and/or molecules are electrically charged or ionized (Kroschwitz *et al.*, 1998). It consists of positively charged particles, cation, and negatively charged particles, electron and anion, in neutral molecules, atoms, and radicals. Plasma possesses two important properties (Eliasson and Kogieschatz, 1991)

1) Quasi-neutral property

The total density of negative charge carriers must be equal to the total density of positive charge carriers.

2) Interaction with electromagnetic fields

Plasma can have some interactions with an applied electromagnetic field due to the fact that it consists of the charged particles.

When positive charges are fixed in a solid, but the electrons are free to move about, the system is called solid-state plasma. In liquid-state plasma, both positive and negative charges are fully mobile. Gaseous plasma, which is called now "plasma", is greatly different from gas in many aspects including pressure, distributions of charged-particles density in the entire plasma volume and temperature.

The energy required to generate plasma can be applied to the plasma by various methods. In industry, however, electrical energy is usually used for this purpose. A current is maintained in the discharge zone, whereby the majority of the charge transportation is affected by the highly mobile electrons, which are accelerated in the electron field. The electrons that liberate from a solid such as metal electrode is called electron emission. The reactant gases are collided by these

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[1] Most materials in this part are summarized from Kroschwitz *et al.*(1998), Eliasson and Kogieschatz (1991), and Sutthiruangwong (1999).

electrons and then the plasma is formed. Some important collision mechanisms, which occur in the gas are summarized in Table 1.

The combined steps of field emission process, collisions among these plasma species and the collisions between the species and the electrode surfaces are referred to as electric discharge phenomena.

Table 2.1 Collision mechanisms in the plasma (Sutthiruangwong, 1999)

Collision	
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	$e^- + AB \longrightarrow e^- + A + B$

Types of Plasma

The plasma produced by this discharged phenomenon can be classified into two types: thermal and non-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. An essential condition for the formation of thermal plasma is a sufficiently high working pressure. The large number of collision between particles leads to rapid redistribution of energy so that equilibrium is reached. An example of this plasma is arc discharge.

Nonthermal plasma or "cold plasma", in contrast, is far from thermodynamic equilibrium. Typically, electrons in this plasma have very much

higher temperature than the heavy ions and neutral species particles. Its uses are based chiefly on the reactivity of ions or radicals generated in the plasma for gas phase or surface reaction (Kroschwitz *et al.*, 1998). This group includes radio frequency, microwave, glow, dielectric-barrier, and corona discharge. The last one is used in this work.

When the pressure is increased in the case of glow discharge, the operating electric field is increased accordingly. Unfortunately, this makes the glow discharge becomes very unstable and usually turns into a high-current arc discharge, which is rarely controllable. The use of inhomogeneous electrode geometry, e.g., a pair of wire and plate metal electrodes oriented in a perpendicular direction to each other, is another method used for stabilizing the high–pressure discharge. The generated discharge is called corona and has become very inhomogeneous. The properties of discharges are shown in Figure 2.1.
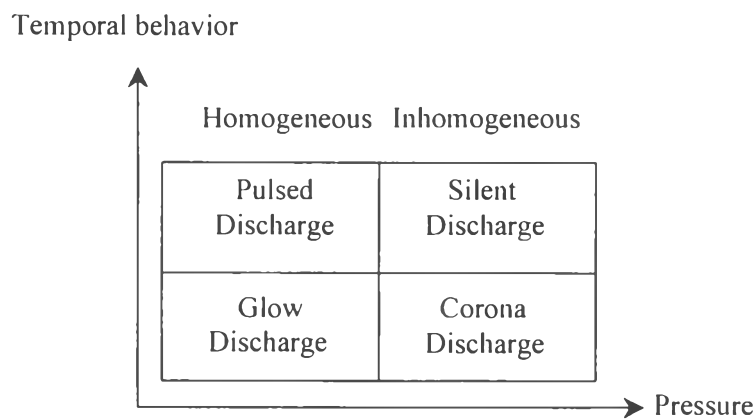
Temporal behavior

Figure 2.1 The forms of discharge according to their temporal behavior, pressure range and appearance (Eliasson and Kogeischatz, 1991)

The forms of corona discharge depend on the field polarity and the electrode geometry condition. For the wire and plate configuration, the discharge, which is produced from the positive wire electrode (positive corona), may appear as a tight sheath around the electrode or as a streamer moving away from the electrode. The discharge formed at the negative wire electrode may form rapidly moving glow or

active spots called tufts or beads. Chang *et al.* (1991) summarized the characteristics of streamer corona, which is illustrated in Table 2.2.

Table 2.2 Time and space scales for the streamer corona for the gap from 1 to 100 cm (Chang *et al.*, 1991)

Streamer rise time	1 ns
Streamer duration	1 μs
Repetition period	1 ns
Streamer diameter	20 μm
Electric field	$10^{-19} < E/N < 10^{-17}$ Vm^2
Ion temperature	10^3 K

2.2 Related Research in Plasma Applications

Li *et al.* (1996) studied the decomposition of dichloromethane by using a radio frequency plasma reactor. They found that using argon as a diluent gas shows higher decomposition efficiency than using nitrogen especially with the low oxygen content in the feed. It was explained that the ionization and excited energy of argon are lower than nitrogen, thus, the collision of excited argon species with dichloromethane is more effective.

Sano *et al.* (1997) studied the effect of oxygen on the acetaldehyde removal by using DC corona discharge. They found that the removal efficiency of acetaldehyde was greatly increased when oxygen was added because of the ozone formation. In the N_2-O_2 mixture, 1.7% of the O radicals produced reacted with acetaldehyde and the remaining reacted with oxygen to form ozone. The ozone formed according to

$$O + O_2 + M \longrightarrow O_3 + M \tag{2.1}$$

where M is a third collision partner: O_2, O_3, O, or N_2 (Eliasson and Kogelschatz, 1991).

Futamura *et al.* (1997) studied the effect of water on the organic compounds decomposition. They found that the decomposition of chlorinated hydrocarbons, trichloroethane and trichloroethylene, can be suppressed by water. It is due to the quenching of hot electrons. The energy transferred from electrons to chemicals are an important initial step for the chlorinated hydrocarbon degradation. In the case of non-chlorinated hydrocarbons, C_1-C_4 hydrocarbons, oxygen species produced from water can promote the decomposition of hydrocarbons at the lower electric field by inserting an O atom into the C-H bond.

In 1998, Sano *et al.* determined the effect of by-products on the 1,1,2-tricholo-1,2,2-trifluoroethane $C_2F_3Cl_3$ removal from N_2. They found that the dissociative electron attachment was the major pathway for the $C_2F_3Cl_3$ destruction and the by-products deposited at the anode as a layer of black particles. These particles changed into a transparent liquid when they contacted to room air. Even though one electron showed high performance for removing five molecules of $C_2F_3Cl_3$, the presence of non-deposited by-products of F-, and Cl-compounds significantly reduced the $C_2F_3Cl_3$ removal efficiency. In addition, with the optimum amount of water in the high concentration of $C_2F_3Cl_3$, the maximum removal efficiency was achieved due to the reduction of the Cl-by-products formation.

Shin *et al.* (2000) studied the destruction of phenol and methylene blue dye from water by pulseless corona discharge. They found that ozone showed a higher rate of chemicals removal even in a lower applied voltage. The main species involving in the oxidation, which were identified by using emission spectra, were OH radicals, ozone, OH ions, α atomic hydrogen, and β atomic hydrogen. It was further reported that aqueous electrons and OH radicals were dominant species in the pulseless corona discharge whereas H_2O_2 was the dominant species in the pulsed corona discharge.

NO_x are undesired products that are always present in utilizing nonthermal plasma technologies. Futamura *et al.* (2000) investigated the behavior of the NO_x formation and decomposition by a ferroelectric packed reactor. Their study indicated that N_2O can be produced in pure N_2 and its concentration increased when 2% oxygen was added and tended to be saturated with a higher oxygen content. Oxygen did not only suppress the formation of NO and NO_2 but also retard the decomposition

of NO and N_2O at lower Specific Energy Density (SEDs). At higher SEDs, the NO formation was promoted by the direct reaction between oxygen molecules and N atoms. They also studied the effect of Hazardous Air Pollutants (HAPs) on the NO_x formation. The results showed that methane, ethylene, and benzene did not affect the NO_x concentration. On the contrary, dichloromethane (CH_2Cl_2), trichloroethylene (C_2HCl_3), tetrachloromethane (CCl_4), and bromomethane (CH_3Br), enhanced the NOx formation, especially at higher SEDs.

Mok *et al.* (2000) investigated the effect of feed gas composition on the removal of NO_x. They found that increasing the oxygen content caused greater the removal of NO although oxygen can promote the NO formation. In addition, adding water into the feed decreased the rate of oxidizing NO because hydroxyl radicals, which are produced from water, reacted with ozone to form less active species.

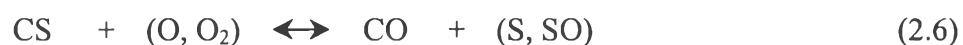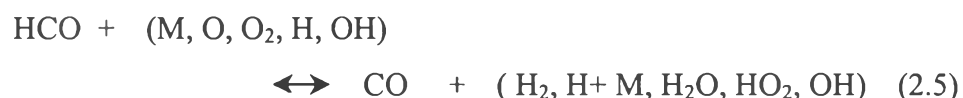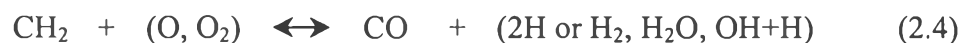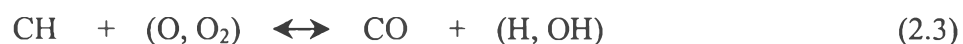$$OH^{\bullet} + O_3 \longrightarrow HO_2 + O_2 \qquad (2.2)$$

Even though oxygen is an important oxidizing agent, its concentration also affects the chemical decomposition efficiency as reported by Chang and Yu (2001). The authors investigated the effect of oxygen on the hexafluoroethane (C_2F_6) conversion efficiency by using dielectric barrier discharge (DBD). It was found that the conversion efficiency of C_2F_6 was reduced when the oxygen concentration of the feed was further increased from 10 to 20 %vol. They suggested that, in the presence of high oxygen concentration, electrons would waste their energy to overdose oxygen content instead of transferring energy for C_2F_6 destruction.
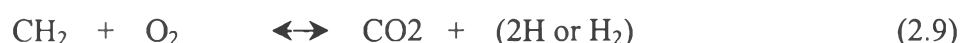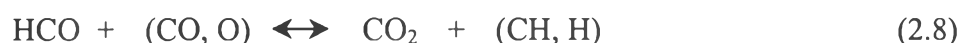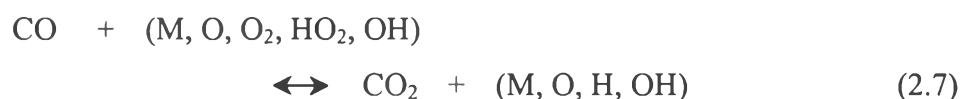
Tsai *et al.* (2001) studied the product distribution of methanethiol (CH_3SH) decomposition in a RF plasma reactor. In the absence of oxygen, over 83.7 % of the total sulfur input was converted to carbon disulfide (CS_2) at 60 W. When oxygen was added, the main product of sulfur was shifted to SO_2 due to the thermodynamic stability. Oxygen also played an important role for inhibiting dihydrogen sulfide (H_2S), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) formation. The mole fraction of methane, ethylene, and acetylene was rapidly decreased as the O_2/CH_3SH ratio increased from 0 to 3, and did not change when the O_2/CH_3SH ratio was further increased to 4.5. At the higher O_2/CH_3SH ratio and input power, CO can be

converted to CO_2 by reacting with O, OH, O_2, HCO, and H_2O. The mechanism of the formation and decomposition of CO and CO_2 are illustrated below.

CO formation and decomposition

$$CH + (O, O_2) \longleftrightarrow CO + (H, OH) \qquad (2.3)$$

$$CH_2 + (O, O_2) \longleftrightarrow CO + (2H \text{ or } H_2, H_2O, OH+H) \qquad (2.4)$$

$$HCO + (M, O, O_2, H, OH)$$
$$\longleftrightarrow CO + (H_2, H+ M, H_2O, HO_2, OH) \qquad (2.5)$$

$$CS + (O, O_2) \longleftrightarrow CO + (S, SO) \qquad (2.6)$$

CO_2 formation

$$CO + (M, O, O_2, HO_2, OH)$$
$$\longleftrightarrow CO_2 + (M, O, H, OH) \qquad (2.7)$$

$$HCO + (CO, O) \longleftrightarrow CO_2 + (CH, H) \qquad (2.8)$$

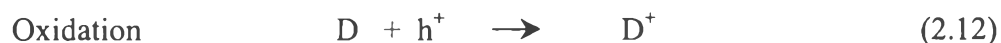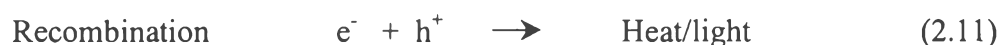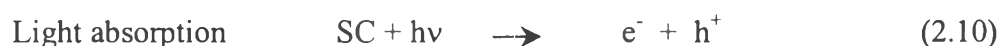$$CH_2 + O_2 \longleftrightarrow CO2 + (2H \text{ or } H_2) \qquad (2.9)$$

Although the nonthermal plasma technology shows high performance for the removal of VOCs, a major disadvantage of this technique is the formation of some unexpected toxic products such as NOx, phosgene, etc.

Huang *et al.* (2001) investigated the effect of adding hydrogen and oxygen on the CCl_4 decomposition in nitrogen. They found that the CCl_4 removal efficiency was higher with 2% of hydrogen in the feed and it was lower with oxygen instead of hydrogen. The effect of coating $Ca(OH)_2$ on the ground electrode was also investigated. It was found that $Ca(OH)_2$ did not only improve the CCl_4 destruction but also prevent the formation of ClCN in pure N_2, HCl in H_2/N_2 and $COCl_2$ in O_2/N_2, not to mention its ability to capture the produced NO_x to form $Ca(NO_3)_2$.

2.3 Fundamentals of Photocatalysis[2]

Photocatalysis consists of the combination of photochemistry and catalysis and implies that light and catalyst are necessary to accelerate a chemical transformation. When a catalyst, which normally is a semiconductor (SC) such as TiO_2, absorbs light or exciting photons, most often in the ultraviolet spectral range,

electrons from the filled valence band will move to the vacant conductance band, which is a higher energy level, and then positive holes will also form. The difference of either energy level is called energy band gab (E_{bg}) and corresponds to the wavelength of the absorbed light. The electron-hole pairs can recombine either[2] directly or indirectly by radiative and nonradiative processes. If the charges are localized by trapping at surface state, their mean lifetime can be long enough to allow their transfer to adsorb electron donors or acceptors. Provided the resulting intermediates are transformed before back electron transfer occurs, a photocatalytic redox reaction is produced. Overall reaction steps are shown below.

Light absorption	$SC + h\nu$	$\longrightarrow$	$e^- + h^+$	(2.10)
Recombination	$e^- + h^+$	$\longrightarrow$	Heat/light	(2.11)
Oxidation	$D + h^+$	$\longrightarrow$	D^+	(2.12)
Reduction	$A + e^-$	$\longrightarrow$	A^-	(2.13)

In the absence of water vapor, the photocatalytic oxidation of organic is seriously retarded, and total mineralization to CO_2 does not occur. Water is a major source of hydroxyl groups as the primary oxidant, which is generated by dissociative adsorption. Furthermore, hydroxyl groups can diminish the effect of recombination of electrons and holes that causes the reduction of catalysis activity. A mechanism involving hydroxyl ions as photohole traps is illustrated below (Peral *et al.*, 1997).

TiO_2	$+$	$h\nu$	$\longleftrightarrow$	$h^+ + e^-$	$\longleftrightarrow$	$h^+\!\!-\!\!e^-$	(2.14)
$HO\text{-}$	$+$	h^+	$\longrightarrow$	$HO^{\bullet}$			(2.15)
O_{2ads}	$+$	e^-	$\longrightarrow$	O^-_{2ads}			(2.16)
$HO^{\bullet}$	$+$	O^-_{2ads}	$\longrightarrow$	$HO_2^{\bullet} + O^-_{ads}$			(2.17)
$HO_2^{\bullet}$	$+$	e^-	$\longrightarrow$	$HO_2^- + O^-_{ads}$			(2.18)
HO_2^-	$+$	h^+	$\longrightarrow$	$HO_2^{\bullet}$ (hole-trap)			(2.19)

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[2] Most materials in this part is summarized from Herrmanns (1999),Peral *et al.* (1997), and Satterfild(1999).

Catalyst Properties

Titanium dioxide or titania is commonly used in the photocatalysis process because it is the best photocatalytic performance with maximum quantum yield, defined as the ratio of the reaction rate in molecules per second to the efficient photonic flux in photons per second. In addition, it is also a non-toxic and inexpensive material. To activate this catalyst, it is necessary to irradiate with ultraviolet light of a wavelength shorter than about 380 nm due to its relatively large band gap of 3.2 eV. The mechanism of photcatalytic process over TiO_2 is shown below (Herrmanns, 1999).
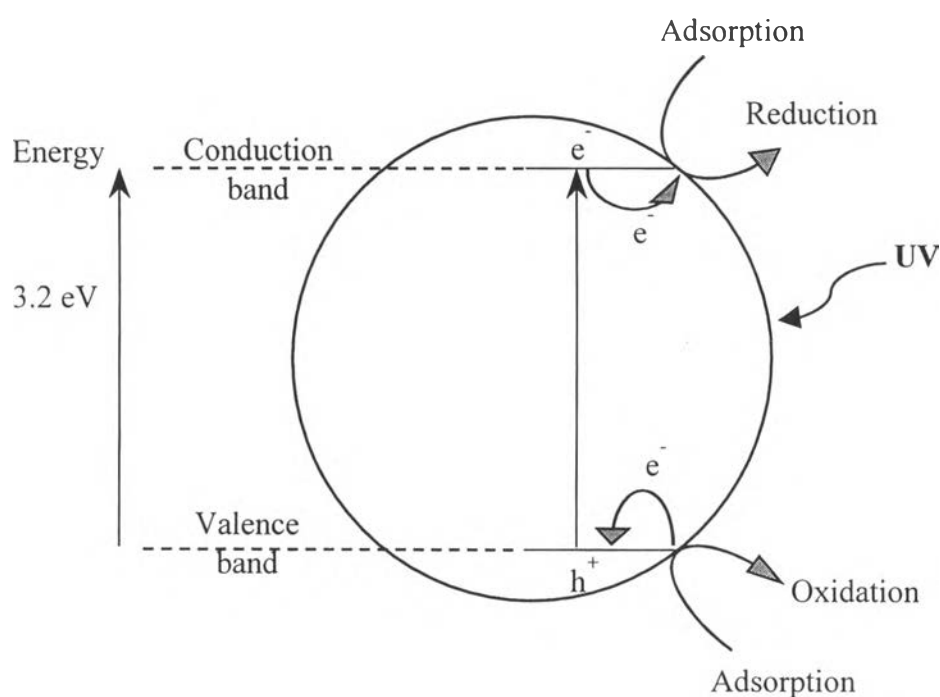

Figure 2.2 A schematic diagram of photocatalytic process over TiO_2

There are three crystalline forms of titania in nature: anatase, rutile, and brookite. Anatase and rutile are produced commercially whereas heating amorphous titanium dioxide produces brookite. Rutile is the thermally stable form at all temperature, but conversion of anatase to rutile is so slow that it may be unimportant in most catalyst reactions. Anatase is the preferred form used as a catalyst and catalyst support. Furthermore, anatase typically has a higher surface area than rutile,

which may account at least in part for its preference here and in other applications (Satterfield, 1991).

2.3 Related Research in Photocatalysis Applications

Obuchi *et al.* (1999) studied the photocatalytic decomposition of acetaldehyde over TiO_2/SiO_2 and $Pt-TiO_2/SiO_2$. They found that the unplatinized catalyst gave a conversion of acetaldehyde and a yield of CO_2 about 10 % less than the platinum loaded one. That is because platinum may help increasing the adsorption of the reactant, which was confirmed by calculation based on Langmuir-Hinshelwood. Platinum did not only enhance the rate of the reaction, but also help complete the catalyst regeneration at the lower temperature. Moreover, the FT-IR results showed the band of carbonic acid, suggesting the existence of acetic acid and/or formic acid as an intermediate adsorbed on the catalyst.

Pichat *et al.* (2000) investigated the efficiency of a photoreactor, which consisted of the TiO_2-coated fiber glass mesh around a UV-lamp. Carbon monoxide, n-octane and pyridene were chosen as reactants. They found that the rate of three pollutants removal, at the concentration range of 50-2000 ppmv in dry air and flow rate between 25 – 50 l/hr, are in range 5-10 μmol per Wh consumed by the UV-lamp. In addition, the concentration of these pollutants was not significantly affected by the air purifier when UV-lamp power is in the range 50-100 W. They concluded that the UV-lamp with an electrical power of 10 kW is required to eliminate a pollutant at concentration about 25 ppmv in the air flow rate of 100 m3/hr. Furthermore, they studied the effect of ozone in oxygen on the decomposition of n-octane. In the ozone-free oxygen, n-octane can be almost completely removed whereas its mineralization was low. Adding ozone in the system was able to enhance the mineralization of n-octane since ozone can directly react with alkene as an intermediate product and produce very oxidizing species viz O^{o-} and OH^o.

Using UV-light to activate TiO_2 may not be suitable in large-scale applications. Modification of TiO_2 to be activated by sunlight is, therefore, of great interest. Even though doping transition metals such as Cr, Co, Fe, or Mn on TiO_2 in

order to operate photocatalysts under visible light illumination is successful, activity of these catalysts tend to decrease due to the recombination of electrons and holes occurring easily (Nakamura *et al.*, 2000).

Nakamura *et al.* (2000) examined the photocatalytic activity of plasma-treated TiO_2 and raw TiO_2 powder for eliminating NO. It was found that the NO removal by both photocalysts increased with decreasing wavelength, and the reaction took place above 450 nm in the case of plasma-treated TiO_2 catalyst. They explained that the appearance of visible light absorption might be due to the change in the electronic state of TiO_2 caused by the reduction. The oxygen vacancies were formed in the crystal lactic of TiO_2 by the plasma treatment, maintaining the anatase structure. Furthermore, the oxygen vacancy state between the valence and conductance bands were newly formed and then react with O_2 or O-species to produce reactive oxygen species such as O^- and atomic oxygen.