CHAPTER III

LITERATURE REVIEW

Gas purification involves the removal of vapor-phase impurities from a gas stream. Many methods for gas purification have been proposed, and the primary operation falls into one of the following three categories; 1) absorption into a liquid, 2) adsorption on a porous solid, 3) chemical conversion to another compound. In fact many research works to improve these processes are still going on.

Gas discharge technology is one promising method of achieving ultrahigh purification. Application of gas discharge processes with high - energy electrons has existed for over a hundred years, dating to the first electrostatic precipitator of Lodge (Oglesby and Nichols, 1978) and ozonizer of Simens (Horvath, 1980). The electrostatic precipitator (ESP) is a device - utilizing corona discharge for removing particulate pollutants in the form of either a solid (dust or fumes) or a liquid (mist) from a gas using the electrostatic force. One may realize that the corona-discharge reactor for the gaseous pollutant remover used in this work has the same working principle as ESP. Most information on ESP however focuses on the removal of particulate matter, whereas the reactor proposed in this work, utilizing low - energy electrons in gas discharge to induce electron attachment reaction, aims at separating gaseous impurities from a gas stream. Application of the electron attachment (a reaction of low energy electrons and gas molecules to produce negative ions), first proposed by Tamon et al. (1989), is still innovative for gas separation processes nowadays.

Many publications on electron attachment and other reactions of electron with many kinds of gas molecules have appeared but most of them involve only the reaction kinetics (Moruzzi and Phelps, 1966, Caledonia, 1975 and Massey, 1976). In fact basic information on gas purification using electron attachment and

the proposed use of the selectivity of electron to remove the electronegative gaseous molecules are still scarce.

Applications of gas discharge technology conducted to date are reviewed as follows.

Castle, Inculet, and Burgess (1969) discussed briefly about surface oxidation of discharge electrodes used in a wire - tube electrostatic precipitator. The rate of ozone generation in the precipitator with both stainless steel and copper wires was clarified. The reaction rate of ozone depended on the intensity of electron flux through the gas. The concentration of ozone generated was a linear function of current but decreased as the gas temperature increased.

Dorsey and Davidson (1994) reported an assessment of the contribution of contaminated wires and plates to ozone production in electrostatic air cleaners. It was found that runaway ozone generation due to contamination of electrode surfaces was a limiting factor in the long-term (7 weeks) effectiveness of electrostatic air cleaners. The corona discharge degraded to streamers after only two weeks, causing increased ozone levels. Wire contamination alone can increase ozone generation. These findings have serious implications for the safe operation of electrostatic air cleaners.

Chemical Vapor Decomposition (CVD) occurring on a discharge wire of an electrostatic air cleaner causes the corona current to decrease more than 95% at the same voltage (after 180 hrs operation). This phenomenon was shown by Jan H. Davidson et al. (1998). Neither current drop nor deposition occurred when operated with clean or dry air (after 2 days).

Several types of DC energized point - electrode reactors have been developed and tested for gas chemistry applications. Although designed with different purposes in mind, the configurations could be put to other uses.

Castle, Kanter, Lee, and Kline (1984) tested a narrow - gap, multipoint-to-plane geometry device in which the gas passed through a corona discharge at high velocity (approximately 100 m/s). The upper multipoint electrode (cathode) was separated from the lower flat electrode (anode) by acrylic spacers that electrically isolated the electrodes and allowed visual observation of the corona. The narrow gap spacing ensured that the inter - electrode space was filled with corona induced plasma. However, the lateral spacing of the pins allowed major fractions of the gas flow to bypass the corona zones. A DC current was applied to the multipoint pins through current limiting resistors.

An experimental investigation has been conducted by Chang, Jen - Shih et al. (1988) to obtain electrode surface temperature profiles of cylindrical hollow electrodes under corona discharges. The result show that a slight temperature increases (about 5 Kelvin within the 10 W input for discharge power level) occurs near the edge of the cylindrical hollow electrodes. Thus, the corona discharge still can be categorized as a cold discharge region.

The pulsed electron technology has also been shown to be capable of generating ozone and active radicals and decomposing several unwanted gases as well as aerosol particles.

Higashi, Sugaya, and Ueki (1985) and Weiss (1985) conducted the reduction of CO_2 the in exhaust gas from a diesel engine vehicle. It was shown that CO_2 concentration in a N_2 - CO_2 or even pure CO_2 gas could be reduced by DC and pulsed corona discharges, respectively. Further experiments for soot elimination and NO_x and SO_x reduction in a diesel-engine exhaust by a

combination of discharge plasma and oil dynamics have been investigated by Higashi, Uchida, Suzuki, and Fujii (1991, 1992).

Chang (1989) and Chakrabarti et al. (1995) found that the removal of NO_x, SO_x, and aerosol particles could be achieved when NH_3 or H_2O was introduced into a pulsed streamer corona reactor. The pulsed electrons have been shown to cause reactions between oxidizing radicals such as OH, O, and O_3 on the one hand and NO_x and SO_x on the other hand at the concentrations found in flue gases to form several acidic aerosol particles with NH_3 or H_2O injections.

Recent experimental study done by Helfritch (1993) led to the conclusion that H_2S decomposition to hydrogen and sulfur could be directly achieved electronically. A wire - in - tube pulsed corona reactor was energized by short voltage spikes to decompose small concentrations of H_2S contained in nitrogen. Some parameters including the reactor geometry, H_2S concentration, corona power, and the nature of the products were investigated.

Mizuno, Clements, and Davis (1986) compared the performance of the pulsed streamer corona, DC corona, and electron - beam processes. It was found that a pulsed streamer corona discharge produced the radicals instead of a high-energy electron beam. A positive pulsed streamer corona discharge in a non-uniform electrode geometry showed better energy efficiency and higher removal performance than a DC corona discharge. Based on the delivered power, the pulsed streamer corona process removed more than 90% of SO_2 with at least two times better power efficiency than the energetic electron-beam process.

Masuda, Sato, and Seki (1984) developed a high - efficiency ozonizer using traveling wave pulse voltage. The test results relating to the pulse-induced ozone generation showed a great enhancing effect on the speed of reactions by positive pulse corona producing streamers bridging across the entire electrode gap. It was believed that the ozone generated in a corona discharge was a two step process:

generation of oxygen free radicals by ionic processes and generation of ozone by free radical reactions. It was found that the ozone generation processes were substantially reduced by increasing the gas temperature, while the ozone loss processes were significantly enhanced by increasing the gas temperature. It was therefore recommended to operate an ozonizer in lower temperature conditions.

High-voltage pulser was used in a pulse-induced plasma chemical processing unit (PPCP unit). This pulser comprised a synchronous rotary spark gap that produced a very sharp negative pulse voltage. High electron energies could be achieved by both units since higher electric fields were allowed in surface-corona and pulse - corona systems than in direct-current systems because of the breakdown limits of the discharge.

Eliasson, Hirth, and Kogelschatz (1987) applied a dielectric-barrier discharge for ozone generation from oxygen. The resulting efficiency of the generation was reported. A value of 1200 g/kWh was the theoretical ozone generation efficiency calculated by thermochemical theory. He also estimated the maximum ozone generation efficiency of 400 g/kWh for pure oxygen by analyzing a Boltzmann equation. The actual ozone generation efficiency was approximately 200 g/kWh for pure oxygen, which was very low compared to the theoretical values. It was because the discharge energy was consumed not only in producing the ozone but was also dissipated in heating the test gas and the electrodes of the ozonizer. Also some of the ozone produced was destroyed by the heat.

After the work of Eliasson et al., there has been attempt to improve the ozone generation efficiency. Ito, Ehara, Sakai, and Miyata (1990) reported that the efficiency in the silent discharge showed a rise of 3-6% by the radiation of ultra-violet ray from the discharge in nitrogen gas. Later, Hattori, Ito, Ehara, and Miyata (1992) reported the superposition effect of two types of discharge in the same discharge space, silent and surface discharges, on ozone generation. Their ozonizer

had two power sources with a variable-phase shifter. A 22-30% increase in the efficiency was observed in their ozonizer.

Yamamoto et al.(1996) demonstrated a new concept -single-stage, catalysis-assisted packed-bed plasma technology, to decompose CCl_4, one of the ozone-depleting substances. The objective of the concept was twofold: to enhance the decomposition efficiency catalytically, and to selectively reduce the by-products. Either $BaTiO_3$ or $SrTiO_3$ pellets were packed in the ferroelectric packed - bed reactor employing an AC power supply. The configuration employed a unique one-stage catalysis/plasma process in which the $BaTiO_3$ pellets were coated or impregnated by active catalysts such as Co, Cu, Cr, Ni, and V. Enhancement of the CCl_4 destruction and the conversion of by-product CO to CO_2 were demonstrated using Ni catalyst in the one-stage plasma reactor.

The effect of carbon dioxide reaction has been studied

Tadaaki Shimizu et al. (1995) investigated decomposition of NH_3 to N_2 over limestone, the effect of coexisting gases, CO_2 and H_2O, on catalytic decomposition of NH_3 over limestone. In the absence of CO_2 and H_2O, NH_3 was decomposed to N_2. From a NH_3 - CO_2 mixture, $(NH_2)_2CO$ was formed through NH_3 decomposition over both calcined limestone and CO_2. However, from the NH_3 - CO_2 - H_2O mixture, $(NH_2)_2CO$ was not formed.

Ryoji Noyori et al. (1995) investigated homogeneous hydrogenation of carbon dioxide which is used in industry instead because effect of CO_2 is perceived to be less reactive and its efficient catalytic conversion has remained elusive because CO_2 is highly oxidized, thermodynamically stable compound, its utilization requires reaction with certain high energy substances or electro reductive processes. Catalytic hydrogenation is one of the most promising approaches to CO_2 fixation. Recent research has shown that high catalytic

efficiency, yields, and rates of reaction can be obtained from CO_2 with optimum conditions and catalysts.

The so - called non - thermal plasma including corona discharge has been widely studied

A non - thermal plasma chemical process with an AC powered ferroelectric packed - bed reactor was again tested by Zhang, Yamamoto, and Bundy (1996). In this work, the targeted gases to be decomposed were ammonia and odorous compounds gathered from animal houses. The plasma reactor packed with $BaTiO_3$ pellets produced high energy free electrons and radicals, which in turn, decomposed the targeted compounds. Four important parameters affecting the reactor performance were investigated: gas residence time, power voltage, power frequency and initial ammonia concentration.

Tamon, Sano, and Okazaki (1989) proposed a novel method of gas separation based on electron attachment. Two kinds of separation devices using either photocathode or glow discharge as electron source were constructed. They reported high efficiency for the removal from nitrogen of SF_6 at very low concentrations. Recently, Tamon et al. (1995) used two types of corona discharge reactors; deposition-type and sweep-out-type reactors, to remove from nitrogen dilute sulfur compounds, dilute iodine and oxygen. They also discussed the purification mechanism and presented simulation models for predicting the removal efficiency. Subsequently, Tamon, Sano, and Okazaki (1996) investigated the influence of coexisting oxygen and water vapor on the removal of six sulfur compounds from nitrogen. They discovered that the presence of oxygen and water vapor increased the removal efficiency.

Sano et al. (1996) used a new type of corona-discharge reactor, the wetted-wall reactor, and the conventional deposition-type reactor to remove iodine and methyl iodide from nitrogen. The removal mechanism of I_2 and CH_3I in the reactor was also discussed.

Kittisak Larpsuriyakul et al. (1996) and Wiwut Tanthapanichakoon et al. (1998) reported experimental results regarding the influence of the structure of the corona-discharge reactor on the removal of dilute gases. The effects of the reactor structure, namely the cathode diameter, the anode shape, and the number of cathodes, were investigated. The results revealed that the thicker the cathode diameter, the higher the removal efficiency. In contrast, the smaller the reactor diameter among three equivolume reactors, the higher the removal efficiency. As for the number of cathodes in a single reactor vessel, the single-cathode reactor always exhibited higher removal efficiency than the 5-cathode one.

Paisarn Khongphasarnkaln (1998) investigated the application of electron attachment to the removal of dilute gaseous pollutants using a corona-discharge deposition-type reactor. It has been found that the presence of O_2 enhanced the removal efficiency of each impurity gas. The enhancement was experimentally shown to be attributable to the ozone reaction in the removal of $(CH_3)_3N$ from O_2-N_2 mixed gas. Water vapor also enhanced the removal efficiency of $(CH_3)_3N$ and CH_3CHO. Furthermore, The high selectivity of electron attachment to electro negative gas molecules was utilized in the simultaneous removal of dilute $(CH_3)_3N$-CH_3CHO, NH_3-CH_3CHO, SO_2-$(CH_3)_3N$, SO_2-CH_3CHO, NO_2-CH_3CHO and CO_2 - CH_3CHO from the air in the single reactor. Compared to single impurity removal, it has been shown that the presence of SO_2 enhanced the removal efficiency but retarded that of CH_3CHO in the single reactor. Some reaction by-products generated could be avoided by using two independently operated reactors in series. In the case of coexisting of NO_2, it was noted that the lower the inlet NO_2 concentration, the lower the discharge current that still yielded beneficial effect. At

higher discharge currents, the retarding effect of CO_2 on CH_3CHO removal was obviously significant.

Han S. Uhm (1999) investigated the influence of the chamber temperature on the properties of the corona discharge system. It was found that the critical voltage V_c required for the corona discharge breakdown was inversely proportional to the chamber temperature T. The electrical energy w_c required for corona discharge breakdown was inversely proportional to the square of the chamber temperature T. Thus, the electrical energy consumption for the corona discharge system decreased significantly as the temperature increased. The plasma generation by corona discharge in a hot chamber was much more efficient than that in a cold chamber.

Wiwut Tanthapanichakoon et al. (2001) investigated the common gas species emitted during cremation. Even ultra - low concentrations of some organic compounds can still cause malodor. They summarized past and recent experimental results on the removal of sulfur compounds, nitrogen compounds and organics compounds, which indicated that the presence of oxygen and/or water vapor in N_2 gas contribute to an increase in the removal efficiency in the removal efficiency in many cases. Conversely, temperature elevation negatively affected the removal of SO_2.

Sano et al. (2001) applied a reactor using DC corona discharge of negative polarity to remove sulfur dioxide from oxygen - nitrogen mixture in the presence or absence of water vapor for temperatures ranging from room temperature to 350°C. It was observed that increasing the reactor temperature cause a decrease in the removal efficiency. Mixing water vapor with the process gas resulted in an increase of the removal efficiency. The effect of the presence of water vapor on improving the removal efficiency was significant under low temperature conditions, while it was relatively moderate under high temperature conditions.

Masaaki Okubo et al (2001). Investigated the removal of acetaldehyde (CH_3CHO) and ammonia (NH_3), which is another odor component of cigarette smoke. In the experiment, the ac barrier-type plasma reactor was used. In the experimental, more than 90% of acetaldehyde removal efficiency was obtain under dry air and N_2 environment. For NH_3 removal, almost 100% removal efficiency was obtained with minimum reaction byproduct under dry air environment.

Wiwut Tanthapanichakoon et al. (2003) investigated a corona discharge reactor is employed to remove acetaldehyde (CH_3CHO) from N_2 and air from room temperature up to 300°C. The more dilute the inlet concentration, the higher the removal efficiency. The presence of either oxygen or water vapor always enhances the removal of acetaldehyde from N_2.

Wiwut Tanthapanichakoon et al. (2003) investigated the individual and combined effect of O_2 and H_2O vapor on the separate and simultaneous removal of styrene and NH_3 from N_2 at elevated temperatures via corona discharge reaction. The presence of O_2 in N_2 always enhances the removal of styrene and / or NH_3 from N_2. The presence of H_2O in N_2 generally enhances the removal of styrene and / or NH_3 but its presence retards of NH_3 when H_2O concentration is too high or the temperature is 300°C. The combined effect of O_2 and H_2O is found to substantially retard the removal of styrene and / or NH_3 compared to the sole effect of coexisting O_2.