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CHAPTER II

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 solid, 3) chemical conversion to another compound (Kohl and Riesenfeld, 1979). In fact many research works to improve these processes are still going on.

Gas discharge technology is one promising method of achieving ultrahigh purification. Applications of gas discharge processes with high-energy electrons have 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 for removing particulate pollutants in the form of either a solid (dust or fumes) or a liquid (mist) from a gas using an 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 of 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. Applications of the so-called electron attachment (a reaction of low-energy electrons and gas molecules to produce negative ions), first proposed by Tamon et al. (1989), are still innovative for gas separation processes nowadays.

Although there are plenty of previous publications concerning electron attachment and other reactions of electron with gas molecules for many kinds of gases, most of them involve only the reaction kinetics (Moruzzi and Phelps, 1966, Caledonia, 1975 and Massay, 1976). Also the idea to utilize the selectivity of electron attachment for gas separation was not present in these articles. Hence, basic information of gas purification, particularly focusing on the removal efficiency of sample gases and the reactor structure, is needed in order to develop and construct an efficient reactor for the gaseous pollutant remover used in this work.

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

Penny and Hewitt (1953) and Penny and Craig (1960) conducted experiments to generate ozone and also observed the mechanism of electrode contamination caused by gas reactions in a corona device. Penny et al. reported that the mechanism for electrode contamination to increase ozone concentration was through an increase in corona current. Application of an electrical insulator to large (3.2-4.8 mm diameter) positive, wire electrodes caused high current, corona flares and reduced sparkover voltage. Deposition of dust on a discharge electrode caused similar effects.

White and Cole (1960), Lagarias (1960) and Peyrous and Lapeyre (1982) characterized in details the influences of air humidity, discharge polarity, radius of curvature of the discharge electrode, electrode material, temperature, and corona current on ozone generation in an electrostatic precipitator.

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

Dorsey and Davidson (1994) assessed the contributions of contaminated wires and plates to ozone production in electrostatic air cleaners. Short-term effect (7 days) in both filtered room air and particle-laden air were evaluated in a laboratory air cleaner operated in a wind tunnel. Long-term effects (7 weeks) were analyzed in a commercial air cleaner operated in room air. It was found that runaway ozone generation due to contamination of electrode surfaces was a limiting factor in the long-term 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.

Tamaki et al. (1979) reported the use of dc and ac coronas for the removal of NO from flue gas under several discharge conditions. However, the process was energy inefficient, and the performance was poor. The poor performance was probably due to the small ionization region of dc coronas (small active treatment volume), and the power efficiency was low because a large amount of energy was expended on ion migration, which does not contribute to the production of radicals.

Basic researches on electron beam process for removal of gaseous pollutants and on its performance were conducted by Masuda et al. (1978) and

Masuda, Hirano, and Akutsu (1981). They emphasized the development of electron beam $DeNO_x/DeSO_x$ process (E-beam $DeNO_x/DeSO_x$) and discovered that the $DeNO_x$ rate could be greatly enhanced by inserting a corona electrode system in the irradiation chamber and producing a negative corona at a field intensity above E = 2.3 kV/cm. However, in this case also the power consumption was too high to justify its use. It was because dc corona field produced transverse motion of negative ions (ionic current) to consume a high corona power.

The utilization of high-energy electron beams (400-800 keV) for the removal of various toxic pollutants, such as SO_x, NO_x, and Hg vapor, from stack gas (as an alternative to scrubbers) was under development by Kawamura et al. (1979, 1980, 1984, 1989) and Helfritch and Feldman (1985). In these processes, air pollutants reacted with the active radicals, and gaseous decomposition was possible by converting them to a solid particulate (e.g., Hg-vapor to HgO), to a liquid (such as SO_2 to SO_3 or H_2SO_4), or to a gas (NO to NO_2).

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 observations of the corona. The narrow gap spacing ensured that the interelectrode 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 was applied to the multipoint pins through current limiting resistors.

Another type of a multipoint-to-plane device was constructed by Yamamoto, Lawless, and Sparks (1988, 1989). This device was in the form of a narrow gap, triangle-shaped, dc corona discharge device. The design was intended to reduce the electrical sneakage (bypassing of the corona induced plasma) which was the major problem for the multipoint-to-plane geometry device. The volumetric filling factor of the corona induced plasma in this device was much higher than in the multipoint device.

More recently, Maezono (1988) and Maezono and Chang (1990) developed a corona torch to use the streamer corona and enlarge the active volume of the device. The plasma device consisted of two small diameter hollow electrodes. The gas flow enters the upstream cylindrical hollow electrode and exited at a downstream cylindrical hollow electrode. Therefore, all the reactive gas would pass through the active corona-induced plasma zone. High-speed gas flow near the exit of the electrode would cool the electrodes; hence, the chemical reactions and the stability of discharge was enhanced.

Similar device using capillary discharge tubes proposed by Palotiai and Chang (1988) consisted of a small diameter cylindrical tube with needle-type electrodes placed at the end of a cylindrical tube. A high voltage corona was applied to form streamer coronas or repeated spark discharges. The capillary walls confined the streamer and forced the gas to pass through the streamer region with minimal sneakage. Since the residential time requirement for chemical processings for this reactor was small, multiflow channel concepts should used for a larger gas flow rate application.

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 in exhaust gas from a diesel engine vehicle. It was shown that CO_2 concentration in a N_2-CO_2 or 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).

Control of hazardous emissions from incinerators is an important field. Control of heavy metals is a most critical issue. Urabe et al. (1986) have recently conducted an experiment at an incineration plant and have shown a very interesting result for the removal of Hg and HCl vapors, using dc and nanosecond pulsing energization. The reaction products formed fine particles from the gas phase reaction with ammonia, which was collected in a precipitator or fabric filters.

Masuda and Nakao (1986) reported that $DeNO_x$ was possible by both positive and negative pulsing and $DeSO_x$ only by positive pulsing. The reaction speed was greatly enhanced by raising the peak field intensity, increasing the pulse frequency, lowering gas temperature, and using sharp corona wires.

Subsequently, Civitano et al. (1987) and Dinelli, Civitano, and Rea (1990) studied the reactions occurring in both small pilot and full scale devices that introduced ammonia gas as the reduction reagent. They have also developed a preliminary model for the formation of pulsed corona streamers within which

the energetic electrons create the free radicals that are responsible for oxidation of the NO and SO_2 molecules. The pulsed electron process has been shown to operate over a wide range of concentration conditions.

Clements, Mizuno, Finney, and Davis (1989) have demonstrated that by superimposing a dc bias on the pulsed voltage, SO_2 removal efficiencies in excess of 99% may be achieved for humidified gas streams. Although NO_x removal efficiencies were not reported, the collection efficiency of high resistivity fly ash particles was significantly higher than with direct current alone.

By introducing NH_3 or H_2O into a pulsed streamer corona reactor, the removal of NO_x, SO_x, and aerosol particles can be achieved. The phenomenon has been investigated by Chang (1989) and Chakrabarti et al. (1995). The pulsed electrons have been shown to cause reactions between oxidizing radicals such as OH, O, and O_3 and NO_x and SO_x, at the concentrations found in flue gases to form several acid 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 hydrogen. Some parameters including the reactor geometry, H_2S concentration, corona power, and the nature of the products were investigated.

Comparison of the performance of the pulsed streamer corona, dc corona, and electron-beam processes has been made by Mizuno, Clements, and Davis (1986). 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 nonuniform electrode geometry showed better energy efficiency and removal performance than a dc corona discharge. 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 based on delivered power.

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 of 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 also 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.

Later, Masuda and Masuda et al. (1988) proposed two different types of an ozonizer. The first one used a planar or cylindrical alumina ceramic (92% purity) having a series of strip-like discharge electrodes attached to one of its surfaces and a film-like counter electrode embedded inside the ceramic. This ceramic-based ozonizer using high-frequency surface discharge was called the surface-induced plasma chemical processing unit (SPCP unit).

The second one was a pulse-induced plasma chemical processing unit (PPCP unit). High-voltage pulser used in this unit comprised a synchronous rotary spark gap which 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.

Applications of the pulse-induced plasma chemical process (PPCP) and the surface-induced plasma chemical process (SPCP) for the decomposition of NO_x and SO_x in flue gases were successfully carried out by Masuda and Wang (1990). In the plasma region, oxidizing radicals and high-density ozone generated significantly influenced the decomposition level of both processes.

At the same time, Masuda and Nakao (1990) combined PPCP $DeNO_x/DeSO_x$ with an electrostatic precipitator and with *E*-beam $DeNO_x/DeSO_x$ process and subsequently compared both systems with an independent PPCP process in order to gain an understanding of their fundamental characteristics and to secure an evaluation of their performances and cost effectiveness.

It was found that the removal of NO_x, and SO_2 by PPCP itself depended on negative or positive pulsing but positive pulsing should be used to reduce plant size. It was also reported that the combination of PPCP and *E*-beam $DeNO_x/DeSO_x$ did not significantly enhance the removal efficiency. For PPCP in electrostatic precipitation, NO could be removed in a dry precipitator whereas NO_2 removal was to be made in the wet one.

Besides $DeNO_x/DeSO_x$ processes, further applications of surface discharge induced plasma chemical process (SPCP) for destruction of various gaseous contaminants have been made recently by Masuda et al. (1993). Both the planar and cylindrical SPCP units proved their satisfactory performance for removal of CO, CFC, Hg vapor, isopropylalcohol, trichloroethylene, acetone, and other hazardous solvents.

Eliasson, Hirth, and Kogelschatz (1987) applied a dielectric-barrier discharge for ozone generation from oxygen. The resulting efficiency of generation was reported. The 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 ozone but also dissipated in heating the test gas and the electrodes of the ozonizer. Also the ozone produced was destroyed by the heat.

Similar dielectric barrier discharges with and without plasma photolysis have successfully been employed by Chang et al. (1991-1993) for removal of SO_2 and NO. Recent experiments utilizing ozone generated by dielectric barrier discharge has also been conducted by Chang and Tseng (1996) so that odor-causing gases, especially H_2S and NH_3, could be controlled.

After the work of Eliasson et al., there has been attempt to improve the ozone generation efficiency. Ito, Ehara, Sakai, and Miyata (1990) described that the efficiency in the silent discharge showed a rise of 3-6% by 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 discharge, 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.

Recently, the possibility of improvement in the ozone generation efficiency by the hybridization of the silent and surface discharge was shown by Nomoto (1989) and Nomoto et al. (1992, 1995). A hybrid discharge ozonizer with one power source was proposed to achieve higher efficiency of ozone generation. The ozonizer had two separated discharge spaces, where silent discharge and surface discharge occurred. The experiment was carried out at relatively low power level to avoid heating a test gas, because the experimental apparatus had no cooling system.

Mizuno (1986) originally developed a packed ferroelectric (high-dielectric ceramic) pellet layer used for an electrostatic precipitator. Basic performance of the ac energized ferroelectric packed-bed reactor was studied. The effect of the dielectric constant of the packed ferroelectric pellets on the particle collection efficiency was also investigated. In the operation to collect precharged particles, the particle penetration became minimum at a certain voltage V_{aco} and increased when the applied voltage exceeded V_{aco}. The value of V_{aco} became lower with the increase in the dielectric constant value. V_{aco} was always higher than the initiation voltage of partial discharge for all the pellets tested.

Later in 1988, Mizuno and Ito started to apply a packed bed reactor with ferroelectric $BaTiO_3$ pellets to decompose ammonia from dry air. The reactor employed the ac discharge generated inside a pellet layer held within the tube arrangement by two mesh electrodes. An intense electric field was formed around each dielectric pellet contact point, producing high energy free electrons as well as molecular ions throughout the cross section of the reactor.

Until 1992-1993, Mizuno et al. conducted experiments to reduce NO_x, SO_x, and CO_2 from combustion gases using an ferroelectric packed bed reactor.

NO_x and ozone generated in the deodorization process of air was also removed by connecting catalyzer layers to the pellet bed.

A laboratory-scale plasma reactor with a packed ferroelectric (high-dielectric-ceramic) pellet layer and a nanosecond pulsed corona reactor was constructed by Yamamoto et al. (1992). This study was the first attempt to develop baseline engineering data on the application of these plasma reactors to the destruction of various volatile organic compounds (VOC's) at ppm levels. The conversion rate of VOC's was found to be dependent on the electron energies in the reactor and may also be related to how strongly halogen species were bonded to the carbon.

The combined corona and catalyst technology was first developed by Mizuno, Chakrabarti, and Okazaki (1993). They reported a corona/catalyst arrangement, which consisted of a needle and a ground mesh electrode with 40-mm separation. Immediately after the corona section, the 20-mm thick catalyst layer consisting of Al_2O_3 pellets was held in place by the screen. Gas was exposed to the pulsed corona, immediately followed by the catalyst. This was considered a two-stage process.

Early in 1996, Yamamoto et al. 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.

A nonthermal 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, Yano, 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 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 removal of six sulfur compounds from nitrogen. They discovered that the precence of oxygen and water vapor increased the removal efficiency.

As a continuation, 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 mechnism of I_2 and CH_3I in the reactor was also discussed.

Recently Kittisak Larpsuriyakul et al. (1996) and Wiwut Tanthapanichakoon et al. (1996) reported experimental results regarding the influence of structure of 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 exhibits higher removal efficiency than the 5-cathode one.

A review paper by Chang, Lawless and Yamamoto (1991) described nearly all applications of corona discharge processes made to date. It shows that corona discharge processes emphasize either of the two aspects of the discharge: the ions produced or the energetic electrons producing the plasma. In an application using the ions, the corona typically occupies a small fraction of the total volume. However, a process using the electrons generally fills most of the volume with the plasma. For corona as an ion source, applications exist in electrostatic precipitation, electrophotography, static control in semiconductor manufacture, and atmospheric pressure ionization-mass spectrometry. For the corona-induced plasma reactor applications, control of NO_x, SO_x, and CO_x, toxic gases, volatile organic compounds, hazardous emissions, and ozone synthesis are among the applications being investigated. Furthermore, understanding of the reactions is ambiguous. Hence, reactive species in the plasma need to be identified and their dependence on electron energy must be clarified. They also reported that the mechanisms of ion- and plasma-induced aerosol particle formations and their growth rates are poorly understood and would bear further investigation.

A pipe equipped with a nozzle-plate electrode corona discharge system for NO_x removal has recently been employed by Ohkubo et al. (1994). The effect of additional gas composition on the corona discharge characteristics in the said pipe was investigated experimentally. The additional gas consisted of a mixture of N_2, O_2, NH_3 and a small amount of Ar or CO_2. The results showed that corona discharge characteristics are significantly influenced by the composition of the additional gas mixture.

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