CHAPTER I
INTRODUCTION

1.1 General Introduction

Natural gas, of which methane is a major constituent, is an inexpensive and abundant resource. Conversion of methane to synthesis gas, which is a versatile feedstock of many chemical processes such as ammonia, methanol, and Fischer-Tropsch synthesis processes, can be achieved by partial oxidation, steam reforming, and carbon dioxide reforming. Several catalysts are active in these reactions but the main problem is a rapid deactivation of catalysts due to carbon deposition under the desired reaction conditions. Another drawback of these conventional synthesis gas productions is large external energy requirement due to their strongly endothermic reactions. Therefore, solving these problems to find ways to operate this process at milder reaction conditions is of great interest.

A non-equilibrium discharge is an effective tool to generate energetic electrons, which can initiate a series of plasma chemical processes such as ionization, dissociation, and excitation. Utilization of a non-equilibrium plasma as an initiation “catalyst” introduces no environmental problems, low cost, high selectivities, and energy-efficient synthesis in some cases. It is a volumetric process with high productivity, e.g. the interaction between accelerated charged particles and other chemical species takes place throughout the whole plasma volume to promote the reactions, that are not possible in surface catalysis technologies (Mutaf-Yardimci *et al.*, 1998). Plasma reactors are already being used to study different possible applications in control of toxic gases, volatile organic compounds, hazardous emissions, and for ozone synthesis (Eliasson *et al.*, 1987; Eliasson and Kogelschatz, 1991; Futamura *et al.*, 2001; and Huang *et al.*, 2001).

A low temperature plasma reactor is considered to be a promising technology to facilitate methane reforming reaction at lower temperatures and then reduce the conventional problems of synthesis gas production. It can be claimed that this project aims to utilize our natural gas more efficiently by converting methane into higher valuable products. Hence, the experimental results from this study will be directly benefit to the development of Thai petrochemical industry.

1.2 Objectives

1. To study the effects of feed gas composition, flow rate, gap width, and electrical discharge, i. e. input power, input low side voltage, and input frequency, on steam reforming with methane, partial oxidation of methane, and carbon dioxide reforming with methane under the corona discharge.
2. To study the effects of Pt/ZrO_2 and Pt/KL on synthesis gas production from methane under electric discharge.
3. To study combined carbon dioxide and steam reforming with methane and combined steam reforming and partial oxidation of methane to produce synthesis gas in low temperature plasma.

1.3 Scope of Work

There are three conventional reactions to produce synthesis gas from methane, i.e. steam reforming, carbon dioxide reforming, and partial oxidation. The drawbacks of these three reactions are high operating temperature and catalyst deactivation. The corona discharge could be an alternative novel approach to produce synthesis gas from methane since it can facilitate the reaction at a milder condition and probably reduce the cost of synthesis gas production in the industrial application. Therefore, these three main reactions to produce synthesis gas from methane have been studied under corona discharge instead of over thermal catalytic process.

Steam reforming with methane under electrical discharge has high tendency to produce carbon in the reactor. In the other word, synthesis gas cannot be produced by steam reforming with methane under corona discharge without carbon formation. The result of carbon dioxide reforming with methane in low temperature plasma is shown in Chapter II. The effects of CO_2/CH_4 feed mole ratio, input low side voltage, input frequency, flow rate, gap width, and waveform on methane and carbon dioxide conversions, current, and product distribution were investigated. To study partial oxidation of methane in an AC electric gas discharge, air was used as a source of oxygen to reduce operating cost as compared to pure oxygen. The effects of CH_4/O_2 ratio, residence time, input power, input frequency, adding ethane, waveform, and diluent gas on methane and oxygen conversions, specific energy consumption, and product selectivities are shown in Chapter III.

However synthesis gas can be produced from methane under corona discharge, methane conversion and synthesis gas selectivity are not as high as thermal catalytic system. To overcome the disadvantages of conventional catalytic process and non-equilibrium plasma process, the combination of catalyst and plasma could be an alternative way to improve synthesis gas production from methane. Chapter IV shows the result of synthesis gas production from reforming of methane with carbon dioxide in an AC electric discharge over Pt/ZrO_2. Pt/KL was introduced in the reactor to promote synthesis gas production from methane via partial oxidation of methane in air and carbon dioxide reforming under corona discharge. The results are shown in Chapter V. In both Chapter IV and V, electrical parameters were varied to investigate the effects of electrical parameters on methane reforming to synthesis gas with and without catalyst in the reactor.

Since water is a cheap reactant and easy to handle, it would be useful to develop synthesis gas production using steam as a co-reactant in a methane reforming process. Chapter VI shows the experimental results of a combined system of carbon dioxide reforming and steam reforming with methane in a corona discharge reactor. An experimental study of synthesis gas production from simultaneous steam reforming and partial oxidation of methane using as AC corona discharge is shown in Chapter VII. Besides reducing oxygen requirement in the system, the benefits of the combination of the two reforming reactions is a substantial improvement of thermal efficiency by transferring heat between the exothermic and endothermic reactions.

1.4 Chemicals Produced from Synthesis Gas

Synthesis gas, commonly abbreviated to Syngas, a mixture of hydrogen and carbon monoxide, is a versatile feedstock of several chemical processes as shown in Figure 1.1.

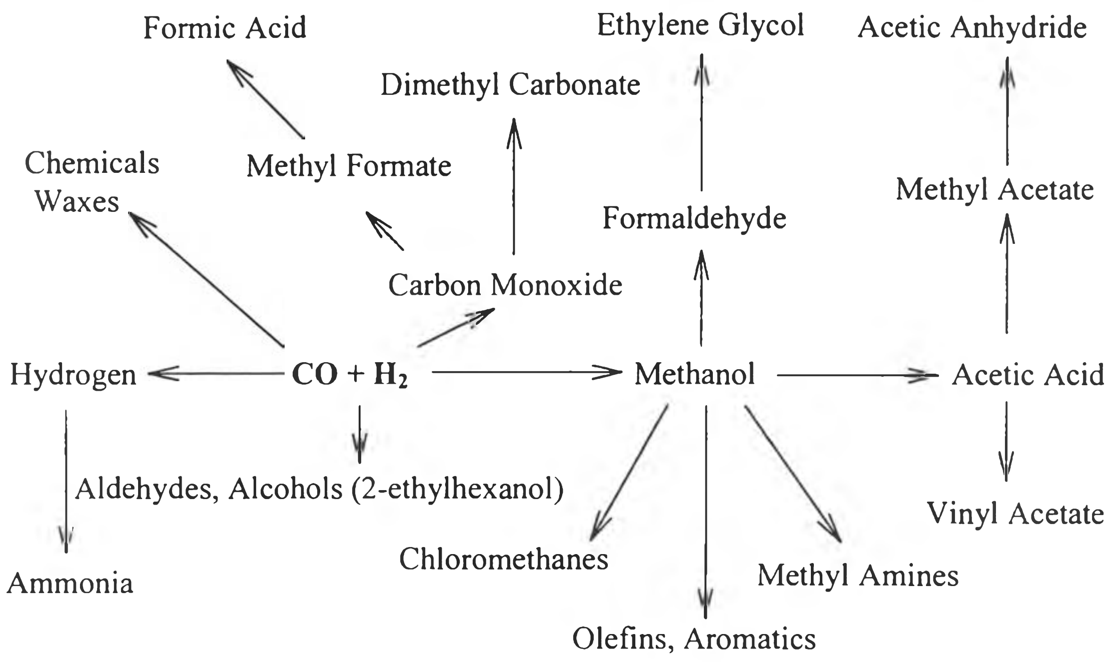


Figure 1.1 Chemicals from synthesis gas (Wender, 1996).

Almost all hydrogen, consumed in large quantities for the synthesis of ammonia by reaction with atmospheric nitrogen in the Haber process, is manufactured from syngas. The demand for hydrogen continues to grow in the increasing use of hydrogen to produce clean fuels and chemicals. The second largest use of syngas is for the production of methanol which is a precursor of other important chemicals such as formaldehyde, acetic acid, methyl chloride and methyl amines. In addition, methanol production has had a remarkable growth because its use as a raw material for methyl *t*-butyl ether (MTBE) that is used as octane enhancer in automotive fuels (Wender, 1996). The market of methanol for producing chemicals is only 24 million tons per year of methanol, which is far less than 10^7 million tons of natural gas reserves. For this reason, many industrial groups pay attention to produce methanol from remote natural gas as a transportation fuel or boiler fuel (Larkin, 2000). The Fischer-Tropsch synthesis remains the third largest consumer of syngas, mostly for transportation fuels but also as a growing feedstock source for the manufacture of chemicals, including polymers. The fourth largest use of syngas is the hydroformylation (oxo synthesis) in which large varieties of olefins react with syngas, in the presence of cobalt or rhodium catalysts, to form aldehydes and alcohols with one carbon more than the starting olefins. The wide applicability of this synthesis gas resulted in its steady growth in the synthesis of plasticizers, pharmaceuticals and hundreds of other chemicals. A direct application of syngas as fuel (and eventually also for chemicals) that promises to increase is its use for Integrated Gasification Combined Cycle (IGCC) units of the generation of electricity (and also chemicals). Methanol may play a part as a peaking fuel in IGCC. If excess syngas is available for IGCC units, its conversion to methanol may be the best road to take, for methanol is a convenient storage fuel for peak use. In addition, methanol synthesis plants can be converted to the production of ammonia. Syngas is the principle source of carbon monoxide, which is used in an expanding list of so-called carbonylation reactions (Wender, 1996).

1.5 Synthesis Gas Production

Many processes can manufacture synthesis gas. There are three main reactions to produce synthesis gas from methane i.e. steam reforming, partial oxidation, and carbon dioxide reforming as shown in reaction 1.1-1.3, respectively.

$$CH_4 + H_2O_{(g)} \rightarrow CO + 3H_2 \qquad (1.1)$$

$$CH_4 + 1/2\,O_2 \rightarrow CO + 2H_2 \qquad (1.2)$$

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \qquad (1.3)$$

1.5.1 Steam Reforming

The most important route of syngas production, at the present time, is methane steam reforming steam, which affords CO/H_2 in a molar ratio of 1:3. This reforming reaction, which is endothermic, is thermodynamically favored by high temperatures and low pressure. Along with catalytic naphtha reforming, steam reforming is one of the most important processes to produce hydrogen. Steam reforming is desirable to operate at low H_2O/CH_4 ratios due to having lower energy consumption (Cancino, 2001). Typical problems of steam reforming are sulphur poison and carbon formation especially when natural gas with higher hydrocarbons is used as a feedstock. To reduce carbon formation, it is necessary to operate at higher H_2O/CH_4 ratios than stoichiometric requirements resulting in higher H_2/CO, in the range of 3.4-5.0, than required for many synthesis processes (Zhang *et al.*, 2001). Higher contents of sulphur in the feedstock need to be removed to avoid poison to the nickel based reforming catalysts (Cancino, 2001).

1.5.2 Partial Oxidation

Partial oxidation of methane is an attractive way to produce synthesis gas since the reaction of partial oxidation is exothermic. This process has the advantage of energy saving and lower carbon dioxide emissions as compared to the other processes. The ratio of H_2/CO obtained with this process is 2:1, which is ideal for the production of methanol and Fischer-Tropch synthesis. A great deal of research has been carried out on the reaction of methane with oxygen but total oxidation to carbon dioxide, undesirable product, must be minimized. Two alternative routes have been proposed to describe the reaction pathway of partial oxidation of methane. For the first route, the indirect scheme, total oxidation of methane with oxygen to produce carbon dioxide and water, followed by the reformation of unconverted methane with its first primary products, carbon dioxide and water. For the second route, the direct scheme, methane directly converts to synthesis gas without passing the formation of carbon dioxide and water (Elmasides *et al.*, 2001). The indirect scheme is easier to achieve than the direct scheme. Due to the limitation of thermodynamic equilibrium of the reforming reaction at low temperatures, a high temperature (>800 °C) is required to obtain high selectivities of hydrogen and carbon monoxide (Otsuka *et al.*, 1998). Several drawbacks of the partial oxidation are as followed:

(1) This process requires pure oxygen as feed. Therefore, an air separation unit is needed resulting in increasing the investment and operating cost (Cancino, 2001).

(2) When using non-catalytic partial oxidation of methane, the main problem is related with the methane combustion, causing high temperatures and soot deposition on the burner (Cancino, 2001).

(3) Even several catalysts are active for catalytic partial oxidation of methane, a rapid deactivation of catalyst is a big problem (Otsuka *et al.*, 1998).

1.5.3 Carbon Dioxide Reforming

Since carbon dioxide has a considerably low cost or even negative price gas and is one of the most important greenhouse gaseous, the use of carbon dioxide to react with methane to produce synthesis gas has been becoming interesting for both environmental and commercial reasons. Synthesis gas can be produced from carbon dioxide reforming with methane to yield a low H_2/CO ratio, i.e. 1 or less. The ratio H_2/CO of 1 is ideal for the manufacture of certain chemicals such as alcohols via oxo-alcohol synthesis, acetic acid, polycarbonates, etc. Moreover, the carbon dioxide reforming ideally suited to decrease the high H_2/CO ratio obtained with the steam reforming when both processes are used combined. Carbon dioxide reforming of methane also produces methane impurities at the reactor outlet as low as 0.05% wt. This is important especially for polycarbonate production from synthesis gas (Cancino, 2001). Since carbon dioxide reforming of methane is a highly endothermic reaction, it can be utilized to transfer and store energy from solar energy or electricity in the form of carbon monoxide and hydrogen (Zhou *et al.*, 1998). Moreover, the advantage of the carbon dioxide reforming over the partial oxidation is that carbon dioxide provides a source of clean oxygen, resulting in eliminating the need for costly separation plants (Stagg-Williams *et al.*, 2000). The obstacles preventing commercialization of carbon dioxide reforming are as follows:

(1) Deactivation of the catalyst due to carbon deposit (reactions 1.4 and 1.5). For example, At a moderate temperature, 923 K, Pt/ZrO_2

catalysts have been shown to be more stable than other catalysts. However, this catalyst is rapidly deactivated when operated at the temperature of 1,073 K to reach high conversions and CH_4/CO_2 ratio greater than 1 (Zhou *el al.*, 1998; and Stagg-Williams *el al.*, 2000).

$$CH_4 \rightarrow C + 2H_2 \qquad (1.4)$$

$$2CO \rightarrow C + CO_2 \qquad (1.5)$$

(2) At high temperatures used in the reactor, higher hydrocarbons present in the feed are thermally cracked to form carbon (Cancino, 2001).

1.6 Plasma Chemistry

1.6.1 Plasma Classification

Plasma is a gas that is partially ionized. In other word, plasma consists of neutral gas particles and charged particles, which follow the path of the electric field. They are considered to be quasi-neutral because the total density of positive charge carriers is roughly equal to the total density of negative charge carriers. Due to the high particle energy of plasmas, they can be considered as a fourth state of matter when compared to the particle energy of solids, liquids, and gases. At present, the process dealing with the plasma chemistry of electric discharges is classified into two types of the surface chemistry processes and the volume chemistry processes. Examples of the surface chemistry are etching, deposition, or surface modification. The ozone production in a dielectric-barrier discharge reactor would be an example of the volume chemistry processes. The important application of methane plasma in the volume chemistry process is the use of ionized methane as the ion source of the mass spectrometers. The preparation of diamond coatings and ceramic materials is the only application of methane plasma in the industrial surface chemistry process (Nasser, 1971; Eliasson and Kogelschatz, 1991; and Hill, 1997).

The plasma volume chemistry process can be created in an apparatus that consists of electrodes, possibly other surfaces, and a discharge volume in which discharges take place. Interaction between accelerated particles consisting of atoms, molecules, and radicals, and other chemical species occurs in this discharge volume. This interaction leads to the destruction of chemical species. The externally induced electric field acts upon the ions and electrons without directly affecting the neutral species (Eliasson and Kogelschatz, 1991).

Plasma is possible to be classified into two types, i. e. equilibrium plasma and non-equilibrium plasma, based on the temperature of gas and temperature of electron. Equilibrium plasmas are also called thermal plasmas. Plasma is in equilibrium when kinetic energies of the charge particles and neutral species are the same. In other word, equilibrium plasmas exist when the temperature of the gas equals the temperatures of the electrons. This can be accomplished when gas temperatures are greater than 6,000 K at atmospheric pressure. High temperatures increase the number of collisions of all particles to such an extent that the energy is equally distributed among all the particles. Typical examples of such plasma are those produced in the arcs and plasma torches (Eliasson and Kogelschatz, 1991; and Grill, 1994).

Non-equilibrium plasma is called "low-temperature" or "non-thermal" or "cold" plasmas. This type of plasma consists of electrons, which have a much higher kinetic energy than the ions and neutral species have. In other word, non-equilibrium plasmas exist when the temperature of the gas is much lower than the temperature of the electrons. For example, applying strong electric fields at reduced pressures can generate electron energies in the range of 1 to 10 eV, which corresponds to the temperature of about 10,000 to 100,000 K, while the remaining particles energies are a few hundredths eV. This non-equilibrium plasma can initiate chemical reactions at much lower temperatures than those required for corresponding thermal reactions (Eliasson and Kogelschatz. 1991; and Rosacha *et al.*, 1993).

1.6.2 Types of Non-equilibrium Plasma

Non-equilibrium plasma can be classified into several types depending on their generation mechanisms, their pressure range and the electrode geometry.

1.6.2.1 Radio Frequency Discharge

The radio frequency discharges (RF) is operated at high frequencies in the range of 2 to 60 MHz and can be operated below atmospheric pressure, but at atmospheric pressure it may become the thermal plasma. The electrodes are normally kept outside the discharge volume whereas the plasma is generated inside by an external induction coil/electrode wrapped around the annular system. This can help to completely avoid electrode erosion and contamination by the plasma. Since the wavelength of the electric field is much larger than the vessel dimensions, homogeneous plasma is formed. Low-pressure radio frequency discharges have found widespread applications in semiconductor manufacturing for etching purposes. Moreover it is used extensively to produce plasmas for optical emission spectroscopy and for plasma chemical investigations (Nasser, 1971; and Eliasson and Kogelschatz, 1991).

1.6.2.2 Microwave Discharge

Microwave discharge systems are operated at high frequencies induced by microwave. The wavelength of the electromagnetic field in the microwave region is 0.3-10 GHz. Most microwave-induced plasmas are produced in the waveguide structure or resonant cavity. The pressure range of the system may vary from below 1 mbar to about atmospheric pressure. Due to the fact that at these wavelength, only the light electrons can follow the oscillations of the electric field, the microwave discharge are far from local thermodynamic equilibrium. This type of plasmas is mostly used for elemental analysis. It also has a great potential to apply for plasma chemical application because of its easy operation and being possibly imposed with a gas flow (Eliasson and Kogelschatz, 1991).

1.6.2.3 Glow Discharge

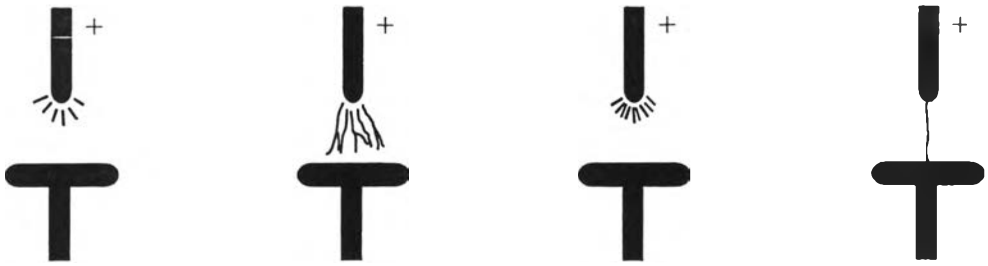
Glow discharge is the stationary low-pressure discharge, operated at the pressure lower than 10 mbar, and usually occuring between flat electrodes encapsulated in a tube. A typical setup for producing a glow discharge needs only comparatively low electrical potential difference (i.e. voltage) across two metal electrodes and current to run. The power can come from either AC or DC source. The electric field generated is generally about 10 V/cm. The electrons have energies between 0.5 to 2 eV corresponding to 5,000-20,000 K, and their densities fall within the range 10^8 to 10^{11} cm^{-3}. Due to the low pressure and the resulting low mass flows at which these systems have to be operated, it is not suited to any industrial applications of chemical productions. Examples of practical applications of glow discharge are neon tubes used for outdoor advertising and fluorescent tubes (Eliasson and Kogelschatz, 1991; and Larkin, 2000).

1.6.2.4 Dielectric-Barrier Discharge

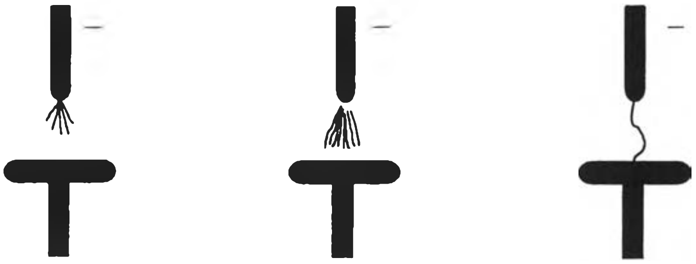
Dielectric-barrier discharge is also referred to "silent discharge". This type of electric discharge is generated within a uniform gas-filled space between a pair of metal electrodes of homogeneous geometry; e.g., the gap between two planar electrodes or in the annular space between two concentric cylinders. Either one or both electrodes are covered with a dielectric material that is commonly made of glass. This glass dielectric distributes the microdischarges across the entire electrode area and limits the duration of each microdischarge. The dielectric strength of the system depends on gap width, pressure, and composition of the gas. Dielectric-barrier discharge has electron energy in the range 1-10 eV and the electron density of 10^{14} cm^{-3}. The only commercial application of dielectric-barrier discharge is for the ozone generation. However, this type of discharge has been studied for destruction of toxic species (Eliasson *et al.*, 1987; Thayachotpaiboon *et al.*, 1996; and Eliasson and Kogelschatz, 1991).

1.6.2.5 Corona Discharge

When the pressure is increased during of the glow discharge, the applied electric field will have to be increased accordingly. Consequently the glow discharge is very unstable and usually turns into a high current arc discharge which is rarely controllable. The use of inhomogeneous electrode geometry is another way to stabilize discharge at high pressure for example needle-plate electrode and wire-plate electrode. The discharge generated from this kind of electrode configuration is turned a corona discharge. In corona discharge energies and densities can be around 5 eV and 10^{13} cm^{-3}, respectively.



Burst Pulse Corona Streamer Corona Glow Corona Spark



Trichel Pulse Corona Pulseless Corona Spark

Figure 1.2 Plasma environment with corona discharges (Chang *et al.*, 1991).

The corona discharge exists in many forms as shown in Figure 1.2, depending on the polarity of the field and the electrode geometrical configurations. There is an inception voltage that has to be reached before a corona discharge can take place. This inception voltage depends on the gap spacing and the radius of the point. For positive corona in the needle-plate electrode configuration, discharges start with burst pulse corona and proceed to the streamer corona, glow corona, and spark discharge with a steady increase in applied voltage. For a wire-pipe or wire-plate electrode configuration, corona generated at positive wire electrode appears either as a tight sheath around the electrode or as a streamer moving away from the electrode. For negative corona in the needle-plate electrode configuration, once inception voltage is reached, Trichel pulse corona is generated between the electrodes followed by pulseless corona and spark discharge as the applied voltage increases steadily. For a wire-pipe or wire-plate electrode configuration, corona discharged at negative electrodes may take the form of a general, rapidly moving glow or it may be concentrated into small active spots called "tufts" or "beads" (Eliasson and Kogelschartz, 1991; and Chang *et al.*, 1991).

1.6.3 Corona Discharge Application

Because corona is easy to establish, it has had wide application in a variety of processes such as electrostatic precipitators, electrophotographs, clean room ionizers for static control, and atmospheric pressure ionization sources (Chang *et al.*, 1991).

1.6.3.1 Electrostatic Precipitators

Electrostatic precipitators are used in building and home ventilation systems for control of particles in the indoor environment and widely used in industries for collecting particulate emissions in the utility, iron/steel, paper manufacturing, and cement and ore-processing industries. Electrostatic precipitators consist of round wire electrodes which are centered between flat collecting plates. The corona occupies only a small volume near the high voltage wire electrodes. Charging and movement of particles take place in interelectrode space which is filled with ions from the corona. When dust is carried by gas though the electrostatic precipitator, the ions from the corona charge individual dust particles. At the same time, the electric fields induce the particles toward the flat collecting plates. The industrial precipitator generates negative corona to avoid the formation of streamers and the lower sparking potential associated with them, while the indoor air cleaner has positive corona to reduce the production of ozone (Chang *et al.*, 1991).

1.6.3.2 Electrophotographys

This corona device is used as a surface charger in the electrophotographys and electrographic printers. The dimensions of the corona charger are small, usually a few centimeters in cross section. Since the operating voltage is proportional to the dimensions, the corona charging occurs at only a hundred volts. The photoconductive drum of a copier/printer must be given a uniform charge to exposure to the light image. The light leads to exposure discharge the surface, leaving patterns of charge on the drum which can attract oppositely charged toner particles. The toner is then transferred to the paper with the influence of a charger on the back side of the paper. The toner transfer is enhanced by an electric field which is produced by corona chargers (Chang *et al.*, 1991).

1.6.3.3 Clean Room Ionizers for Static Control

Controlling static charges in the handling of the wafers is important for the semiconductor chips manufacture because electrostatic attraction of particles in the air may enhance their deposition on the wafers leading to defects in subsequent operations. Corona is used to neutralize surface charges by deliberately introducing ions of one or both polarities near the ceilings of the clean rooms and allowing the air flow to carry them to the surfaces below (Chang *et al.*, 1991).

1.6.3.4 Atmospheric Pressure Ionization Sources

Atmospheric pressure ionization sources, a specialized gas analysis technique, have corona as the principle source of ions in a chain of ionization events. Atmospheric pressure ionization sources have two operating steps of the ionization at atmospheric pressure and the analysis in vacuum. For negative ions from corona, the extra electron is exchanged with more electronegative molecules until the most acidic molecules (highest electronegativity) become the final ions that reach the analysis section. With positive ions from corona, positive ions may capture electrons from less electronegative molecules, but the ion transfer is highly mediated by the presence of neutral molecules clustering around the positive core, particularly water molecules. The clustered molecules shield the core from direct charge exchanges and thus stabilize the ion (Chang *et al.*, 1991).