CHAPTER II
LITERATURE REVIEW

2.1 The Origins, Compositions and Properties of Natural Gas

Natural gas is a fossil fuel that contains a mixture of gaseous hydrocarbons, mainly methane (CH_4), with varying amounts of ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). Carbon dioxide, oxygen, nitrogen, and hydrogen sulphide are also often present (Victor *et al.*, 2006). Substantial quantities of the natural gas discovered are found to be present with either coal or oil. The formation of natural gas can be classified into two groups. The minor group derives from the microbial degradation of organic matter in shallow sedimentary rocks of no great age, and, like marsh gas, consists mainly of methane and carbon dioxide. The second group derives from deeper rocks of great age and is likely to have resulted from the chemical degradation of organic residues. Natural gas is "dry" when it is almost pure methane with the absence of the longer-chain hydrocarbons. It is considered "wet" when it contains other hydrocarbons in abundance. Those longer chain hydrocarbons can condense to form valuable light liquids (so-called natural gas liquids, or NGLs). "Sweet" gas possesses low levels of hydrogen sulphide compared to "sour" gas. Natural gas dissolved in oil reservoirs is called "associated" gas. When it occurs alone without contacting with oil, it is called "non-associated gas" (Rojey *et al.*, 1997; Wilkes, 1973).

Throughout the world, natural gas associated with sedimentary rocks varies in composition from mixtures of almost pure hydrocarbons to mixtures totally lacking in hydrocarbons, depending on the source of the gas. The proportion of gaseous hydrocarbons other than methane is extremely variable, but never more than 60%. In addition to methane, natural gas may contain other hydrocarbons, such as ethane, propane, butane and pentane, and heavier hydrocarbons in lower concentrations. C_3 and C_4 hydrocarbons are the main fractions in LPG (Liquefied Petroleum Gas). The heaviest fraction corresponding to hydrocarbons with five carbon atoms or more (C_{5+} fraction) is called natural gasoline. Hydrogen, helium, and argon are commonly present in small quantities. Traces of ammonia, mecury, arsenic, selenium and uranium are also found in natural gas. Apart from helium and argon, natural gas may also contain traces of other gases, e.g. krypton, neon, xenon, and radon (Rojey *et al.*, 1997).

Natural gas and methane have no odor unless sufficient hydrogen sulfide is present, or mercaptans are added. Hence, once leaks occur in the system and it is not possible to be detected by smelling. Careful maintenance, control, and operation of gas equipments are required for safety in its use. Natural gas is explosive in air in concentrations between 5.3 and 14%. In addition, natural gas has a low density, about 600 volumes of gas is equivalent to 1 volume of liquid. Importantly, natural gas produces much less atmospheric pollution than other hydrocarbon fuels (Vergara *et al.*, 1990).

2.2 End Uses of Natural Gas

The main use of natural gas is for heating in most western countries. Other major uses of natural gas are for producing electricity, chemical feedstock, and transportation.

Natural gas, as a result of its cleanliness upon combustion, its convenience, and flexibility in use, makes an ideal fuel for producing electricity. Both the economics and minimal impact on the environment attract natural gas to these stationary uses. Electricity itself can be used for power and heating, as well as for producing light. The conventional method in producing electricity with steam is to use gas or fossil fuels to heat water to produce steam which is used to drive a steam turbine and generator to produce electricity.

Natural gas is used as a fuel for some vehicles. Propane in liquid form at normal atmospheric temperatures has gained wider use than natural gas, although still of limited scope. Liquid natural gas needs to be kept at low temperatures. Transportation applications for natural gas are generally limited to vehicles used within limited or prescribed areas or routes, primarily where the gas is available within the vicinity of use. In addition to being a convenient and available fuel, pollution problems are minimized.

Natural gas, a primary source of methane, is used as a chemical feedstock. Methanol can be produced from methane. Other commercial applications for use of natural gas include production of hydrogen, which may also serve as a fuel and manufacture of ammonia. Fertilizers, plastics, and adhesives are produced from natural gas that has been reacted with steam (Vergara *et al.*, 1990).

2.3 The Nature of Plasma

Plasma is an ionized gas, which consists of charged particles (cations, anions, and electrons) and neutral gas particles (free radicals and stable neutral gases) moving freely in random direction. The degree of ionization can vary from 100% (fully ionized gases) to very low values (e.g. 10^{-4}-10^{-6}; partially ionized gases). Plasma is electrically neutral or quasi-neutral because the total density of negative charges is approximately equal to that of positive charges. Due to the high energy of plasma, it is often called a fourth state of matters, first identified by Sir William Crooked in 1879 (Roth, 1995), as compared to the energy levels of solids, liquids, and gases. As temperature increases, molecules become more energetic and transform in the sequence: solid, liquid, gas, and plasma (Fridman and Kennedy, 2004). Plasma traditionally is classified into two categories, equilibrium plasma and non-equilibrium plasma, based on the temperature of gas and electron (Eliasson and Kogelschatz, 1991; Fridman and Kennedy, 2004).

Equilibrium plasma is also called "thermal plasma". Plasma is in equilibrium when the temperature of the gas (T_0) is close to the temperature of electrons (T_e). High temperatures of typically 4,000-20,000 K are required to form this plasma type. So that the number of collisions of all particles increases to such an extent that the energy is equally distributed among all the particles. Typical examples of such plasmas are arcs and plasma torches. Thermal plasmas characterized by high temperatures are typically used for applications where heat is required, e.g. for cutting, welding, spraying, or as in analytical ICP (inductively coupled plasma) for the evaporation of materials (Fridman and Kennedy, 2004).

Non-equilibrium plasma is called "non-thermal" or "low temperature" plasma. This type of plasma exists when the temperature of the gas is much lower than the temperature of the electrons ($T_0 << T_e$). As an example, for plasma generated by glow discharges, the operating pressures are normally less than 1 kPa and the electrons have the temperatures of the order of 10^4 K with ions and neutral gas temperatures approaching room temperature. In the non-thermal plasmas, most electrical energy is supplied for the production of energetic electrons. This is in contrast to the thermal plasmas, which the energy is required for entirely heating the gas stream. Commonly, the non-thermal plasma are used for initiating the chemical reactions at much lower temperatures than those required for corresponding thermal reactions. The most important application of non-thermal plasma chemistry is the ozone synthesis for water purification under silent discharges. In addition, the first industrial plasmachemical process was the synthesis of nitric oxide in an AC arc at the end of the 19th century (Bogaerts *et al.*, 2002; Eliasson and Kogelschatz, 1991; Fridman *et al.*, 2005, Fridman and Kennedy, 2004, and Nasser, 1971).

2.4 Plasma Generation

In general, there are several methods for producing plasmas, e.g. combustion, flames, electrically heated furnaces, electric discharges (corona, spark, glow, arc, microwave discharge, plasma jets and radio frequency plasma), and shocks (electrically, magnetically and chemically driven) (Liu *et al.*, 1999). However, the use of an electric discharge is one of the most common methods to generate and maintain a gaseous plasma (Fridman and Kennedy, 2004). A simple discharge device consists of a voltage source that drives current through a gas between two parallel conducting plates or electrodes, as illustrated in Figure 2.1 (Liberman and Lichtenberg, 1994). When an externally intense electric field is applied across metal electrodes, the electrons liberated from the metal surface will immediately be accelerated to move corresponding to the direction of the electric field and then can collide with any neutral gaseous particles to form the ionized gases with an additional set of electrons. Accordingly, these electrons can further move and collide with other species. As a result, a large quantity of electrons including the excited atoms and molecules, ions and radicals can be formed in the bulk of the gases within a very short period of time after the application of electric field has been started. This progressive effect causes extensive breakdown of the gas, the current rises, and consequently the discharge is established. The active species generated by the collision between electrons and gaseous molecules can initiate the chemical reactions, leading to the production and destruction of the chemical species (McTaggart, 1967; Nasser, 1971).

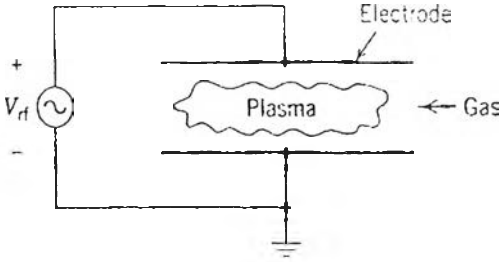


Figure 2.1 Schematic of a simple discharge device.
Ref.: Liberman and Lichtenberg, 1994

2.5 Types of Non-Thermal Plasma

Non-thermal plasma can be divided into several different types, according to their generation mechanisms, their pressure range, and the electrode geometry. The general features and applications of each non-thermal plasma type are briefly described here.

2.5.1 Radio Frequency Discharge

The radio frequency discharges (RF) can be generated both inductively and capacitively at a high frequency range (2-60 MHz) below atmospheric pressure, but at atmospheric pressure, it may become thermal plasma. The electrodes are normally kept outside the discharge volume, in contrast, the plasma is generated inside by an external induction coil/electrode wrapped around the annular system (Figure 2.2). This can help to completely avoid electrode erosion and contamination by the plasma with metal vapor. Since the wavelength of the electric field is much larger than the vessel dimensions, homogeneous plasma is formed. Low pressure RF discharges are widely applied 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; Eliasson and Kogelschatz, 1991).

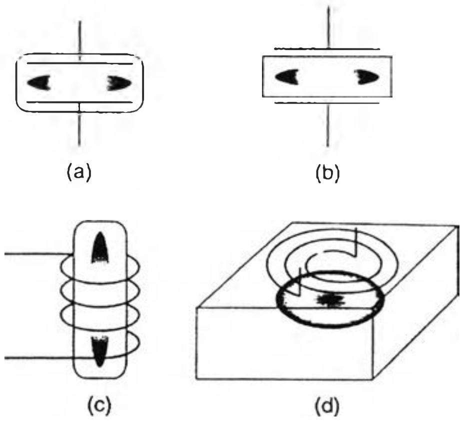


Figure 2.2 Common radio frequency discharge configurations.
Ref.: Fridman and Kennedy, 2004

2.5.2 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 (Figure 2.3). The pressure range of the system may vary from below 1 mbar to about atmospheric pressure. Due to the fact that at these wavelengths, only the light electrons can follow the oscillations of the electric field, the microwave discharges 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 begin possibly imposed with a gas flow (Eliasson and Kogelschatz, 1991; Fridman and Kennedy, 2004).

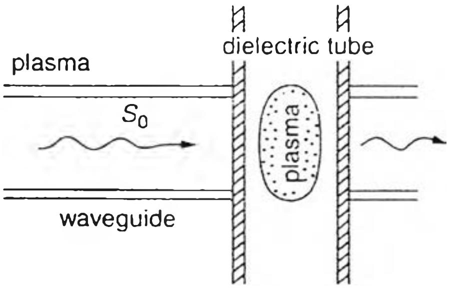
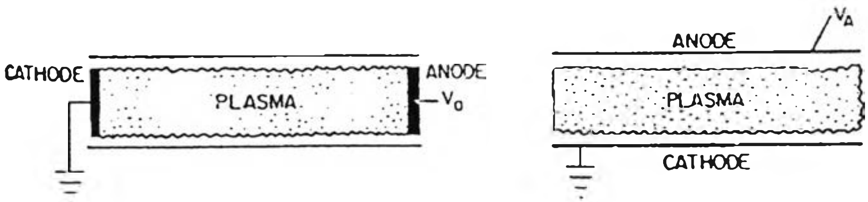


Figure 2.3 General schematic of microwave discharge in a wave guide.
Ref.: Fridman and Kennedy, 2004

2.5.3 Glow Discharge

Glow discharge is the stationary low pressure discharge, operated at the pressure lower than 10 mbar, and is usually established in a tube between two flat electrodes (Figure 2.4). A typical setup for producing a glow discharge needs only comparatively low electrical voltage across two metal electrodes and current to run. 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 suitable to use in any industrial applications of chemical productions. Examples of practical applications are neon tubes used for outdoor advertising and fluorescent lamps (Eliasson and Kogelschatz, 1991).



CLASSICAL DC ELECTRICAL DISCHARGE TUBE

PARALLEL PLATE PLASMA REACTOR

Figure 2.4 General schematic of glow discharge.
Ref.: Roth, 1995

2.5.4 Corona Discharge

The corona is a weakly luminous discharge, which usually appears at atmospheric pressure near sharp points, edges or thin wires where the electric field is sufficiently strong (Figure 2.5). The use of inhomogeneous electrode geometry is another way to stabilize discharge and to prevent a high current arc discharge at high pressure. In corona discharge, energies and densities of electrons can be roughly 5 eV and 10^{13} cm^{-3}, respectively. The behavior of this discharge type is not only different from that of the glow discharge but also depends significantly upon the type of electrodes used, either negative or positive types. Due to small active volume occurred only around the point, the corona discharge is not very well applicable for the industrial chemical reactions dealing with the large quantities of gases. Nevertheless, this discharge type has been extensively used in several commercial ways and is gaining attention for use in other applications such as electrostatic precipitator, electrophotography, static control in semiconductor manufacture, ionization instrumentation, control of acid gases from combustion sources, destruction of toxic compounds, and generation of ozone (Chang *et al.*, 1991; Eliasson and Kogelschatz, 1991; Fridman and Kennedy, 2004).

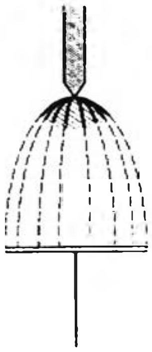


Figure 2.5 General schematic of corona discharge.
Ref.: McTaggart, 1967

2.5.5 Dielectric Barrier Discharge

Dielectric barrier discharge (DBD) 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 (Figure 2.6). Either one or both electrodes are covered with a dielectric material that is commonly made of glass. This glass dielectric uniformly 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. DBD has the excellent source of ideal electron energy in the range of 1-10 eV and the high electron density of 10^{14} cm^{-3}. Its unique benefit is to generate low excited atomic and molecular species, free radicals, and excimer with several electron volts. DBD is widely investigated for potential industrial applications in pollution control, e.g. ozone generators, excimer radiation sources, and free radical generation (Eliasson and Kogelschatz, 1991; Fridman and Kennedy, 2004; Xu, 2001).

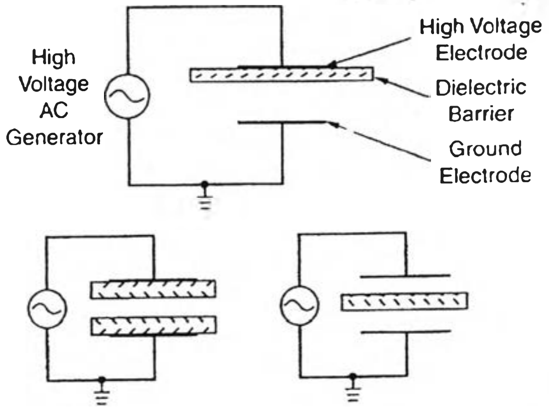


Figure 2.6 Common dielectric barrier discharge configurations.
Ref.: Fridman and Kennedy, 2004

2.6 Gliding Arc Discharge

2.6.1 General Features of the Gliding Arc

Gliding arc is a non-thermal plasma device that has at least two diverging knife-shaped electrodes. These electrodes are positioned in a laminar or turbulent gas. The high voltage is applied to the electrodes and provides the necessary electric field to break down any gas between the electrodes and the discharge. The gliding arc discharge is generated to form the plasma across the gas flow at the narrowest gap distance of the electrodes, then glides along the electrodes in the direction of gas flow and spreads until it disappeared. Another discharge forms immediately at the initial spot. The progress of this electric charge is depicted in Figure 2.7.

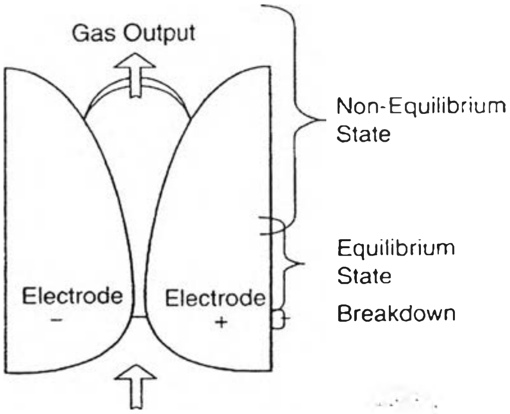


Figure 2.7 General schematic of gliding arc discharge.
Ref.: Fridman and Kennedy, 2004

Plasma generated by the gliding arc discharge has thermal or non-thermal properties, depending on system parameters, i.e. input power and flow rate. Along with completely thermal and completely non-thermal modes of the discharge, it is possible to define the transition regimes of the gliding arc. In this most interesting regime, the discharge starts as thermal, but during the space and time evolution becomes non-thermal. This powerful and energy-efficient transition discharge combines the benefits of equilibrium and non-equilibrium discharges in a single structure. It can provide plasma conditions typical for non-equilibrium cold plasmas but at elevated power levels.

2.6.2 Physical Phenomena of Gliding Arc

To provide a better understanding of the physical gliding arc phenomenon, the simplest case is considered, as depicted in Figure 2.8.

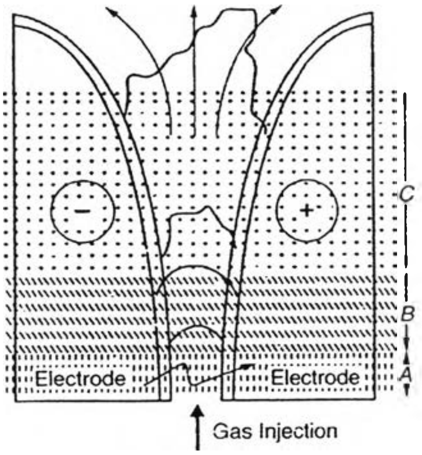


Figure 2.8 Phase of gliding arc phenomena: (A) reagent gas break down; (B) equilibrium heating phase; (C) non-equilibrium reaction phase.
Ref.: Fridman *et al.*, 1999

In region A, the initial break-down of the processed gas begins the cycle of the gliding arc evolution. The high voltage generator provides the necessary electric field to break down the gas between the electrodes and the discharge starts at the shortest distance between the two electrodes. Within a very short time of about 1 μs, a low-resistance plasma is formed and the voltage between the electrodes falls.

In region B, the equilibrium heating phase takes place after formation of a stable plasma channel. The electric discharge spreads along the electrodes with gas flow. The small equilibrium plasma volume is dragged by gas flow and the length of the arc increases together with the voltage. The quasi-equilibrium evolution is terminated when the arc length approaches the critical value. In this stage, the gas temperature does not drastically change ($T_e \approx T_0$). Physical parameters of the equilibrium phase of the gliding arc evolution are similar to those for the conventional atmospheric pressure arc discharges.

In region C, the non-equilibrium reaction phase begins when the length of the gliding arc exceeds its critical value. Heat losses from the arc begin to exceed the energy supplied and consequently it is not possible to sustain the plasma in the state of thermodynamic equilibrium. As a result, the discharge plasma rapidly cools while the plasma conductivity is maintained by a high value of the electron temperature. After decay of the non-equilibrium discharge, there is a new break down at the shortest distance between the electrodes and the cycle repeats. In general, up to 70 to 80% of the total gliding arc power can be dissipated into the plasma, leading to $T_e >> T_0$ in this phase. Furthermore, the non-equilibrium phase is favorable to occur the chemical reactions since the gliding arc has parameters similar to the glow discharge (Fridman *et al.*, 1999; Fridman and Kennedy, 2004).