CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEWS

2.1 Plasma

Plasma is an ionized gas or refers as the fourth state of matter. "Ionized" means that at least one electron is not bound to an atom or molecule. The increase of temperature, molecules become more energetic and transform matter in the sequence of solid, liquid, gas and finally plasma. Plasma contains charge particles including positive particle, negative particles and radicals. For the positive particle, it mostly contains with cations. The negative particles are electrons or anions. Plasma can occur in nature or by manmade that provides several applications such as thermonuclear synthesis, electronics, lasers, fluorescent lamps, and etc. Plasma is widely used in 3 major features for applications in chemistry and related disciplines. The first feature is temperatures of a least some plasma components and energy density can significantly exceed in conventional chemical process. Another one, plasmas are able to produce very high concentration or energy and chemically active species. Moreover, plasma systems can essentially active species and keep bulk temperature as low as the room temperature (Fridman, 2008).

2.1.1 Plasma Generation

Plasma has wide ranges of electron temperature, pressure and electron density. In man-made plasma, electron temperature is possible to be from slight only above the room temperature to the interior temperature of stars or range of 1-20 Ev (Fridman, 2008). Generally, plasma can be generated by several methods such as combustion, flames, electrically heated furnaces and electric discharges (Liu *et al.*, 1999). For the mechanism, plasma will occur when a neutral gas is given sufficient energy from an electronic source to create new products and radicals. The source of free electrons is generally a high energy discharge. These collisions of electrons and gas molecules result in a net energy transfer to the molecules producing metastable fragments and energized ions (Hollahan *et al.*, 1974). In this process, the electrical field was input over metal electrodes resulting in reducing of potential barrier which numerous of electrons can overcome potential barrier and leak from the surface even though they have less kinetic energy. Plasma is firstly generated through the collision process between leak electrons and neutral gases following by the formation of ionized gases.

2.1.2 Plasma Classification

There are two main categories of plasma in chemical applications which are thermal and non-thermal plasma based on their energy level, temperature and electron density.

The first type is a thermal plasma or high temperature plasma which is characterized by both electrons and neutral species have the same temperature at a very high temperature in range of 5000–10,000 K. For man-made thermal plasma, it can be provided by applying high electrical power in the discharge (higher than 1 kW). Thus, the reactor temperature and energy consumption are very high, so the cooling of the electrodes is necessary to reduce their thermal erosion. (Holladay *et al.*, 2009).

The second type is non-thermal or non-equilibrium plasma which is characterized by unchanging in the neutral species temperature (room temperature) even though electrons temperature is very high in the range of 10,000–100,000K (1–10 eV). In this type, plasma does not play the important role for providing the energy to the system but it provides radicals and excited species to initiate and enhance chemical reactions. According to low temperature, the non-thermal plasma also has lower of the energy consumption which is one of non-thermal plasma advantages (T. Paulmier, 2005).

2.1.3 Generation of Non-Thermal Plasma

There are several types of non-thermal plasma those are categorized depending on generation, pressure input range and the electrode geometry. It normally consists of glow discharge, corona discharge, silent discharge or DBD, microwave discharge, radio frequency discharge and gliding arc discharge.

2.1.3.1 Glow Discharge

The glow discharge is a low-pressure discharge less than 10 mbar which is normally operated between flat electrodes. Electrons in the glow discharge are highly energetic. The excited neutral atoms and molecules, which are generated, are typical glow like in fluorescent tubes. Because of a very low pressure, it needs quite high electric field to divide the neutral gas. As the same reason, the glow discharge is not very suitable for chemical synthesis in the industry field.

2.1.3.2 Silent Discharge

The Silent or DBD discharge, it combines the large volume excitation of the glow discharge with high pressure characteristics of corona discharge. Its characteristic is a dielectric layer covers at least one electrode which is called dielectric-barrier discharges (DBD). Once the silent discharge is initiated at any location within the gap between electrodes, the charge accumulates on the dielectric to form an opposite electric field and interrupts the current flow in a few nanoseconds to generate microdischarges.

2.1.3.3 Microwave Discharge

The microwave discharge operates in the microwaves range (0.3-10 GHz) which is very high frequency. Normally, frequency is below 3 GHz. Accordingly, a very high frequency are operated so that light electrons can follow the oscillations of the electric field. Therefore, microwave discharge is far from local thermodynamic equilibrium and can be operated in a wide pressure range. Plasma will be provided by microwaves that produce electron with temperature from 4000 to 6000 K. This type has been studied for many applications such as purification of noble gases, the decontamination of radioactive wastes and steam plasma reforming.

2.1.3.4 Radio Frequency Discharge

The radio frequency discharge has been used in laboratory to provide plasma for optical emission spectroscopy and for plasma chemical investigations. The RF discharge operates at high frequencies at 2-60 MHz and very low pressure to achieve the non-equilibrium conditions. For RF discharge, electrodes will be kept at outside of discharge volume which will prevent electrode erosion and contamination for metal vapor (Petitpas *et al.*, 2007, Holladay *et al.*, 2009).

2.1.3.5 Corona Discharge

The corona discharge is self-sustained gas discharge that is generally operated in atmospheric pressure between metal electrodes. Common configurations are pointed electrode facing a plane, thin wire in cylinder or running parallel to a plane, or knife-edge shaped electrodes. The corona discharges improve the main disadvantage of the glow discharge for the industrial applications for its extremely low pressure.

The corona discharge appears as a filamentary discharge with radiating outward from the electrode. As it is easy to be established, so corona discharge has been used in numerous of applications.

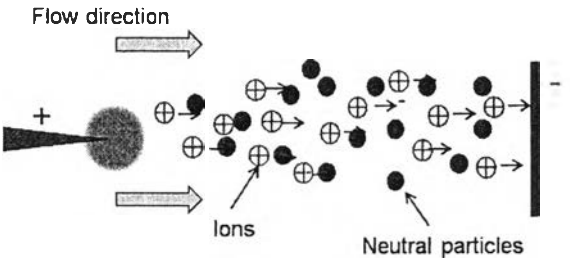


Figure 2.1 Schematic of corona discharge. (Tirumala *et al.*, 2012)

2.1.3.5.1 Positive Corona Discharges

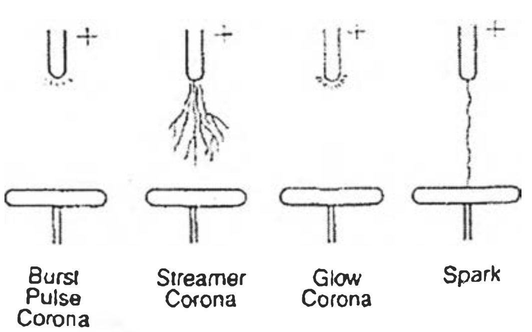


Figure 2.2 Schematic of positive corona discharges. (Chang, 1991)

The positive corona in the needle-plate electrode as showed in figure 2.2, when the input voltage increases, discharges start with burst pulse corona and proceed to the streamer corona, glow corona, and spark discharge. The corona that is generated at a positive wire electrode may appear as a tight sheath around the electrode or as a streamer moving away from the electrode.

2.1.3.5.2 Negative Corona Discharges

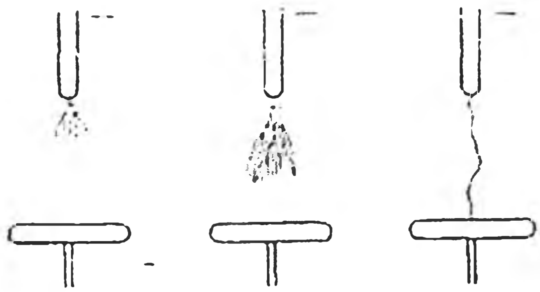


Figure 2.3 Schematic of negative corona discharges. (Chang, 1991)

The same geometry in negative corona, the initial form will be the trichel pulse corona, then its turn to pulseless corona and finally to spark discharge as the increasing of input voltage. The formation of negative glow normally requires clean and smooth electrodes. Comparison with the positive streamer corona, it is noisy and has higher the sparking potential.

In corona discharges, the small radius of point's curvature will lead to high needed fields for ionizing the neutral gases. Another factor which needs to control is input voltage. If input voltage is too high, the corona might bridge the gap as shown in figure 2.3. The characteristic of corona discharge is that generated plasma volume is smaller than the total discharge volume. Therefore, it tends to be not suitable for large quantities of large production scales (Chang, 1991, Holladay *et al.*, 2009).

2.1.3.6 Gliding Arc Discharge

The gliding arc discharge is typically generated in between at two diverging knife-shaped electrodes. It is operated at atmospheric pressure or higher. These electrodes are immersed in a fast flow of feed gas. A high voltage and relatively low current discharge are generated across the fast gas flow between the electrodes. The electric discharge forms at the closet point, spreads along the knife-edges of the electrodes, and ultimately disappears (Fridman *et al.*, 1999).

2.1.4 Use of Non-Thermal Plasma in Chemical Reaction

Accordingly, plasma is generated through the electron collision process that provides a mixture of charge particles. Therefore, chemical reactions in the plasma process are very complex. The basic reactions, which can be categorized into 3 types, are following this table;

Table 2.1 Basic reactions in the plasma process (Liu *et al.*, 1999)

Reaction	Mechanism
Electron molecular reactions.	
- Excitation	$e + A_2 \rightarrow A_2^* + e$
- Dissociation	
- Attachment	$e + A_2 \rightarrow 2A + e$
- Dissociation attachment	$e + A_2 \rightarrow A_2^-$
- Ionization	$e + A_2 \rightarrow A_2^- + A$
- Dissociation ionization	$e + A_2 \rightarrow A_2^+ + 2e$
- Recombination	$e + A_2 \rightarrow A^+ + A + 2e$
- Decomposition	$e + A_2^+ \rightarrow A_2$
	$e + AB \rightarrow A + B + e$
Decomposition	
- Penning dissociation	$M^* + A_2 \rightarrow 2A + M$
- Penning ionization	$M^* + A_2 \rightarrow A_2^+ + M + e$
- Ion recombination	$A^- + B^+ \rightarrow AB$
- Associative attachment	$A^- + A \rightarrow A_2 + e$
- Neutral recombination	$A + B + M \rightarrow AB + M$
- Synthesis	$A + B \rightarrow AB$
Heterogeneous reactions	
- Neutral recombination	$S\text{-}A + A \rightarrow S + A_2$
- Metastable de-excitation	$S + M^* \rightarrow S + M + hv$
- Neutral abstraction	$S\text{-}B + A \rightarrow S + AB$
- Sputtering	$S\text{-}B + M^* \rightarrow S + B + M$

Note:

- A and B refer to atom, A_2 and B_2 refer to molecule, M is a temporary collision partner and S is a solid surface site.
- There are any other reactions that aren't included in this table

According to plasma system overcomes many limitations of conventional techniques. Therefore, plasma systems have been used to examine the possible of several chemical processes, including a reforming of natural gas.

Rueangjitt *et al.* (2007) investigated the effect of feed components under the AC gliding arc system. The different feed system consisted of CH_4, CH_4/He, CH_4/C_2H_6/He, $CH_4/C_2H_6/C_3H_8$/He and $CH_4/C_2H_6/C_3H_8/CO_2$. The results showed that the presence of other gas components in natural gas was found to play an important role affecting the reaction performance. For H_2 and C_2 hydrocarbon yields were following order of these systems: $CH_4/C_2H_6/C_3H_8/CO_2$ > $CH_4/C_2H_6/C_3H_8$/He > CH_4/C_2H_6/He > CH_4/He > CH_4. The highest yields of H_2 and C_2 products were 35% and 42%, respectively at $CH_4/C_2H_6/C_3H_8/CO_2$ system.

Rueangjitt *et al.* (2008) also studied the effect of oxygen addition in feed under AC gliding arc system. The combined plasma reforming and partial oxidation of CO_2-containing natural gas, air gained over the pure oxygen in terms of reactant conversions, product selectivities, and specific energy consumption. The optimum conditions were found at HCs:O_2 feed molar ratio of 2/1 using air as an oxygen source, an applied voltage of 17.5 kV, and a frequency of 300 Hz.

Sreethawong *et al.* (2007) investigated the partial oxidation of methane with air for synthesis gas production via a multistage gliding arc discharge system. Several parameters were explored consisting of stage number, feed gas composition, feed flow rate, frequency, input voltage, and electrode gap distance for CH_4 and O_2 conversions and the product distribution. They found that the increase of stage number, voltage, and electrode gap distance gave higher CH_4 and O_2 conversions. The opposite results were found from CH_4/O_2 molar ratio, feed flow rate, and frequency.

Sekiguchi *et al.* (2003) studied the reforming of hydrocarbons for hydrogen production via a microwave discharge. The conversion of hexane and steam was affected by the plasma power. The conversion increased with increasing the plasma power and decreasing in O/C ratio. However, conversion of hexane was not sufficient only around 0.66.

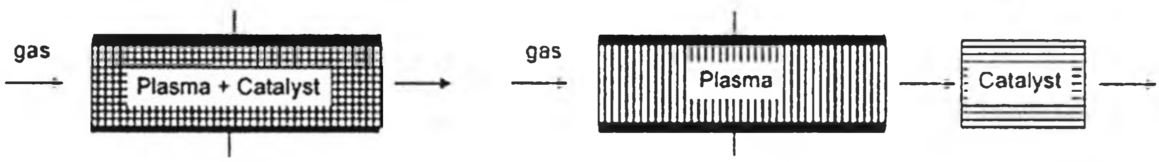
Aforementioned, the non-thermal plasma generates various species so that selectivity for desired products might not be efficiently achieved in plasma system. In order to increase selectivity, the combination of plasma and catalysts is an interesting solution.

2.1.5 The Incorporation of Plasma and Catalysts

The plasma catalysis technique has been developed to combine the advantages of the fast start up and variety of active species from the plasma technique and the high products' selectivity from the catalysts. The plasma catalysis technique can be classified into two types based on the catalyst position which are single-stage type or in-plasma catalysis and two-stage type or pre/post-plasma catalysis.

In single-stage type, the plasma and catalyst regions are either completely or partially overlap. Plasma discharges are ignited within the catalyst bed or on electrodes that are coated with catalysts. An overlap between plasma and catalyst makes a strong interaction which can affect their properties. For the effect of plasma on the catalyst, the catalyst directly contacts with the discharge and the active species are generally short-lived species such as excited-state atoms and molecules, reactive radicals, photons, and electrons. In addition, the plasma may prepare or modify the catalyst surface during the process by plasma-induced surface heating. For the effect of catalyst on plasma, catalyst also increases the lifetime of active species by the absorption process (Durme *et al.*, 2008).

In contrast with two-stage type, catalyst will be separated that plasma will be setup either upstream or downstream of the catalyst. For upstream-placed plasma, the plasma role is to provide reactive chemical species for being easier converted so that the catalyst is exposed only to species that exit from the plasma region or long-lived species. For downstream-placed plasma, the role of plasma is to convert the residual reactants and destroy the undesired byproducts generated from thermal catalysis (Chen *et al.*, 2008, Whitehead, 2010, Gallagher *et al.*, 2011).



(a) (b)

Figure 2.4 Schematic of (a) single-stage type and (b) two-stage type: pre-processing plasma.

Several articles examined the interaction or advantages of using the combination of plasma and catalyst.

Yu *et al.* (2011) investigated CO_2 reforming of propane over Ni/γ-Al_2O_3 catalyst under DBD plasma. The results showed that combined plasma and catalyst enhanced the conversion and selectivity of H_2 and CO by decreasing activation temperature of the catalyst. The effect of the temperature reaction showed that the conversion of CO_2 in the combination mode increased when the temperature was higher than 573 K. With this temperature, it isn't the temperature range of the propane reforming taking place, so this results confirmed that the activation temperature was reduced in the presence of plasma.Tu *et al.* (2012) also studied the effect of Ni/γ-Al_2O_3 catalyst in DBD reactor for dry reforming of CH_4 for synthesis gas production in the difference of catalyst-packed methods. The synergy of plasma and catalysis can be clearly observed that both the CH_4 conversion and H_2 yield are almost doubled.

Rueangjitt *et al.* (2009) studied the reforming of methane in AC micronized gliding arc discharge. The three systems had been tested to investigate the effect of catalysts which are plasma alone, plasma + unloaded catalyst, and combined plasma + Ni-loaded catalyst. The results showed that unloaded catalyst can improve methane conversion comparing with only plasma process. The highest conversion was found in the plasma with Ni-loaded catalyst system at around 50% of methane conversion. For the effect of catalyst on the selectivity, insignificant effect on product selectivity was found due to the short residence time in micro-reactor only in the range of 0.021–0.14 s.

Chavadej *et al.* (2007) investigated the combination of plasma and catalytic system for VOC removal in four-stage plasma-catalytic system. The experiment showed that the increase of input voltages enhanced benzene conversion and markedly increased the CO_2 selectivity. In contrast with frequency and flow rate, benzene conversion and the CO_2 selectivity decreased with increasing these parameters. There were also investigated the effect of catalyst which were commercial TiO_2, sol–gel TiO_2, and 1% Pt/sol–gel TiO_2. The results showed that in a presence of a small amount of TiO_2 either commercial or sol–gel could enhance the CO oxidation and leaded to a higher CO_2 selectivity. In addition, added Pt on sol–gel TiO_2 did not enhance the benzene conversion and the product selectivity resulting from the energy released from the plasma can lead to the oxidation and reduction reactions on the TiO_2 surface. For effect of number of stage, the operation at a higher stage is more affected to the product selectivity comparing with conversion.

2.1.6 Natural Gas Reforming

Natural gas is an important source of energy from fossil fuel. Normally, the composition of natural gas consists of hydrocarbon gases which are methane (70–90 %) and ethane (5–15 %) with varying lesser amounts of other heavier hydrocarbons (< 5 %), and other gases, such as nitrogen, carbon dioxide, hydrogen sulphide, and water vapor (Association, 2004). Methods which would be used to convert natural gas to synthesis gas are steam reforming of methane, partial oxidation of methane and carbon dioxide reforming of methane.

The first method is the steam reforming of methane (Eq. 1). Since steam reforming of methane is highly endothermic reaction, a huge amount of supplied energy is required. The reaction normally takes place at a very high temperature of 425-550 °C (Sreethawong, 2007).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^0_{298} = +206 \text{ kJ/mol} \qquad (1)$$

The partial oxidation of methane is also an attractively alternative way for converting methane to synthesis gas. This reaction is an exothermic reaction (Eq. 2); so it can reduce the energy demand for the methane reforming reaction (Anderson, 2005).

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + H_2 \qquad \Delta H^0_{298} = -36 \text{ kJ/mol} \qquad (2)$$

Carbon dioxide reforming of methane becomes more attractive because it not only lessons methane consumption but also uses of carbon dioxide (Tao, 2010). Eq. 3 shows that it could save half of the methane required to obtain the same amount of CO compared with either steam reforming or partial oxidation due to carbon source from CO_2. Therefore, CH_4-CO_2 reforming is directly beneficial for high CO_2-containing natural gases. However, CH_4-CO_2 reforming is also strongly endothermic reaction; it normally requires special methods to achieve a considerable reaction rate to meet industrial requirements.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^0_{298} = +247 \text{ kJ/mol} \qquad (3)$$

2.2 Objective and Scope

The objectives of this work were to determine the optimum conditions of the combination steam reforming of the CO_2-containing natural gas and partial oxidation in the corona discharge for synthesis gas production and to investigate the effect of Ni catalysts for synthesis gas production from the steam reforming of the CO_2-containing natural gas with partial oxidation in the corona discharge. The scope of this research will cover the following:

- The effects of voltage, frequency and flow rate will be investigated for partial oxidation of the CO_2-containing natural gas at hydrocarbons to oxygen feed molar ratio 2:1.
- The effect of steam will be investigated for combination partial oxidation and steam reforming at 5, 10, 15 and 20 mol% of steam.
- Under the optimum conditions, the effect of Ni catalysts on the synthesis gas production from the steam reforming of the CO_2-containing natural gas with partial oxidation will be investigated.