CHAPTER II
LITERATURE REVIEW

The basic principles about the plasmas and the electric discharge environment are mainly described within this chapter. Beginning with some basic knowledge about natural gas, the chemical properties of the methane molecule, and the fundamental knowledge about the plasmas are then introduced to eventually describe how the plasma can be generated for activating various molecules in natural gas, especially methane, to form different products. Moreover, some experimental studies on the direct methane conversion process under different types of electric discharges are summarized so as to be the evidence on the advances of the work in this field. Finally, the aspects of the gliding arc discharge reactor, as well as the reforming and partial oxidation of methane, are explained in subsequent sections.

2.1 Natural Gas

Natural gas is a gaseous fossil fuel, which is composed of hydrocarbon gases, 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. Natural gas exists in nature under pressure in rock reservoirs in the earth's crust, either in conjunction with heavier hydrocarbons and water (called associated gas) or by itself (called non-associated gas). It is produced from the reservoir similarly to or in conjunction with crude oil (Dawe, 2000). Before natural gas can be used as a fuel, it must undergo extensive processing to remove almost all materials other than methane. The by-products of the processing include ethane, propane, butanes, pentanes, higher molecular weight hydrocarbons, elemental sulfur, and sometimes helium and nitrogen.

The major difficulty in the use of natural gas is transportation and storage because of its low density. Normally, natural gas can be stored in storage tanks or underground, in old gas wells. And, it can be transported by pipe line, truck, or ship.

Natural gas can be used for electricity generation, as feedstock for hydrogen production, as fuel for vehicles, for residence domestic use, such as cooking, for heating/cooling, for fertilizer production, in aviation, and others.

2.2 Physical and Chemical Properties of Methane

The methane is commercially well-known as a very inexpensive and environmentally safe feedstock of fuel supplies. It is, in a chemical point of view, the smallest molecule in the entire hydrocarbon series, which consists of only one carbon atom surrounded by four hydrogen atoms. The most abundant and unique source of methane is the natural gas reserves, which are located in many parts of the world. With its low molecular weight and non-polar nature, the boiling point of methane is extremely low (-164 °C) and can only be found in the gaseous state under ambient conditions. This property, coupled with the fact that many natural gas reserves are now located in very remote areas, makes this resource somewhat expensive to transport.

The fact that methane is very flammable when existing in the oxygen-containing atmosphere makes some people confused that methane is one of very reactive molecules. Indeed, methane is somewhat unreactive compound by its nature. Tables 2.1 and 2.2 compare the average bond energy of C-H bond inside the methane molecule and its first ionization potential with some of other common gases, respectively. Based upon these data, although the ionization potential of the methane molecule is in the same order of magnitude with that of other common gases, its bond energy between C-H is markedly high as compared to other covalent bonds.

In the most cases, methane can be made reactive only by using very reactive species, such as radicals, and so the radical chemistry is among the few effective techniques that have been traditionally applied for reactions with methane. The oxidation of methane with oxygen is a well-known radical reaction, which thermally converts methane molecule into a wide range of products, depending upon the reaction conditions used, but thermodynamically, this application is favorable for the production of CO_2, CO, and H_2O (Poonphatanapricha, 1997).

Table 2.1 Average chemical bond energy of some covalent bonds (Perry *et al.*, 1996)

Bond	Bond energy (kJ/mol)	Bond	Bond energy (kJ/mol)
C-H	463	H-H	436
C-C	344	O-H	463
C=C	615	O-O	142
C-O	350	O=O	539

Table 2.2 The first ionization potential of some common gases (Perry *et al.*, 1996)

Gas	Ionization Potential (eV)	Gas	Ionization Potential (eV)
CH_4	12.5	O_2	12.2
H_2	15.6	CO	14.1
N_2	15.51	CO_2	14.4

$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$

2.3 Gaseous Plasmas for Activating Methane Molecules

Since the gaseous plasma is an effective source of active species formation, including electrons, ions and radicals, a number of studies of the methane reaction using such plasma to initiate the reaction have been carried out extensively.

2.3.1 Fundamental Properties of Plasma

In its simplest definition, gaseous plasma consists of negatively and positively charged particles in an otherwise neutral gas. The positively charged particles are mostly cations, but the negatively charged particles can be either electrons or anions. The neutral species may be the mixture of free radical species with stable neutral gases. Plasma possesses the following two important properties (Eliasson and Kogieschatz, 1991).

1) Quasi-neutral property

The total density of negative charge carriers must be equal to the total density of positive charge carriers.

2) Interaction with electromagnetic fields

Plasma can have some interactions with an applied electromagnetic field due to the fact that it consists of charged particles.

Normally, plasma can occur in all states (Nasser, 1971). Plasma in solid is called solid-state plasma, while plasma generated in the liquid and gaseous states does not have any specific names. Only gaseous plasma is shortly called as "plasma". There are many differences between plasmas and gases. Their differences include pressure, distributions of charged-particle density in the entire plasma volume, and temperature.

2.3.2 Generation of Plasmas

There are several means of generating charged particles to produce plasmas, e.g. collisions between cosmic rays and gases in atmospheric layers. However, in the present research, an externally intense electric field is applied across metal electrodes to cause the reduction in its "potential barrier" and eventually reach the energy that each electron requires for leaving the metal surface. The most interesting phenomena on the metal surface under an extremely high electric field are that many electrons can leave the surface despite its less kinetic energy to overcome the potential barriers. This phenomenon is known as "tunnel effect". Afterward, the plasma is first generated by the collisions between the electrons emitted from the surface of metal electrodes and the neutral molecules. This process of plasma generation is normally known as the "field" emission process.

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 in their vicinity 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, as well as excited atoms and molecules, ions, and radicals, can be formed in the bulk of the gases within a very short period of time after applying electric field has been started. Many active species can initiate the chemical reactions, leading to the production and destruction of the chemical species (Kruapong, 2000). The combined steps of the field emission process among these plasma species and the collision between the

species and the electrode surfaces are referred to as "electric discharges" phenomena. Table 2.3 shows some important collision mechanisms.

Table 2.3 Collision mechanisms in the plasma (Nasser, 1971)

Collision	Reaction
Elastic Collision	$e^- + A \rightarrow e^- + A$
Excitation	$e^- + A \rightarrow e^- + A^*$
Ionization	$e^- + A \rightarrow 2e^- + A^+$
Attachment	$e^- + A \rightarrow A^-$
Dissociative Attachment	$e^- + B_2 \rightarrow B^- + B$
Recombination	$e^- + B_2^+ \rightarrow B_2$
Detachment	$e^- + B_2^- \rightarrow 2e^- + B_2$
Ion Recombination	$A^- + B^+ \rightarrow AB$
Charge Transfer	$A^\pm + B \rightarrow A + B^\pm$
Electronic Decomposition	$e^- + AB \rightarrow e^- + A + B$
Atomic Decomposition	$A^* + B_2 \rightarrow AB + B$

Plasma can be classified into two types:

1) Thermal Plasma or Equilibrium Plasma

In this kind of plasma, the temperatures of the bulk gas and electrons are approximately equal, which is close to thermodynamic equilibrium (Fridman *et al.*, 1999). An essential condition for the formation of the plasma is sufficiently high working pressure. Examples of such plasma are those produced in arc discharge and plasma torches.

2) Non-Thermal Plasma or Non-Equilibrium Plasma

This type of plasma is characterized by a low bulk gas temperature and high electron temperature. Those typical energetic electrons may have energy ranging from 1 to 10 eV, which corresponds to the temperature of about 10,000 to 100,000 K (Rosacha *et al.*, 1993). This plasma is divided into several types, depending on their generation mechanism, their pressure range, and the electrode geometry (Eliasson *et al.*, 1987).

2.4 Types of Non-Equilibrium Plasmas

When the potential difference is applied across the electrodes to generate plasma, the electric field will exert an influence on the charged particles and impart energy to them. The field does not directly influence the neutral species in the bulk of the plasma. The electrons, due to their light mass, are immediately accelerated to much higher velocities than those of heavier ions during the time available between collisions. Their collision partner takes up the energy that they lose through the collisions. If the pressure is small enough or the field strength is high enough, the electrons and some of ions will, on average, have a kinetic energy, which is much higher than the energy corresponding to the random motion of the molecules. This plasma type is called a non-thermal or non-equilibrium plasma and can be classified into several categories, as follows:

2.4.1 Glow Discharge

This is the stationary low-pressure discharge usually occurring between flat electrodes encapsulated in a tube. The typical pressure involved is normally below 10 mbar, and therefore, the discharge needs only comparatively low electrical potential difference (i.e. voltage) and low current to operate. Due to its low pressure and the resulting low mass flow, this discharge type is mostly used for the application in the manufacture of fluorescent and neon tubes, but is not appropriate to the industrial production of chemicals (Nasser, 1971).

2.4.2 Corona Discharge

When the pressure is increased during the generation of the glow discharge, the applied electric field will have to be increased accordingly. This, unfortunately, makes the glow discharge very unstable and usually turns into a high current arc discharge, which is rarely controllable. The use of inhomogeneous electrode geometry, e.g. a pair of pointed and plane metal electrodes oriented in a perpendicular direction to each other, is another way used for stabilizing the high pressure discharge. The discharge generated from this kind of electrode configuration is termed a corona discharge. The behavior of this type of discharge 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.

2.4.3 Radio Frequency Discharge (RF Discharge)

This high frequency discharge is used extensively to produce plasma for optical emission spectroscopy. The electrodes are normally kept outside the discharge volume whereas the plasma is generated inside by the induction technique. This can help to avoid the contamination by the plasma and the corrosion of electrode. The homogeneous plasma can be generated when the wavelength of the electric field is much larger than the vessel dimensions. Radio frequency discharge works very well at low temperatures, and it is also used at atmospheric pressure, at which thermal plasma can sometimes occur.

2.4.4 Microwave Discharge

Another type of high frequency discharge that can be practiced presently is the microwave discharge, which is induced by a microwave (0.3–10 GHz) radiation source that must be guided or directed into the gaseous vessel by using a wave guide structure or resonant cavity. As the dimensions of the cavities diminish when the frequency increases, the maximum microwave frequencies used for discharge applications are usually below 3 GHz. The typical frequency is 2.45 GHz. Microwave discharge is another attractive method for plasma chemical investigation because of the ease of operation and the possibility of imposing a gas flow to influence plasma parameters.

2.4.5 Dielectric Barrier Discharge

This type of electric discharge is defined by the discharge generated within the gas-filled gap between a pair with metal electrodes of homogeneous geometry, e.g. the gap between two planar electrodes or in the annular space between two concentric cylinders. A dielectric layer that is commonly made of glass covers either one or both electrodes. Many previous works referred this kind of discharge to the silent electric discharge, in which it has long been known to use in many studies for the plasma chemical reactions (Thanyachotpaiboon et al., 1998).

2.4.6 Gliding Arc Discharge

The gliding arc discharge is cold plasma, which is normally generated in between at least two diverging knife-shaped electrodes. 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. Another discharge immediately reforms at the initial spot. Figure 2.1 is considered to be the simplest case for a better physical understanding of the gliding arc phenomenon (Fridman *et al.*, 1999).
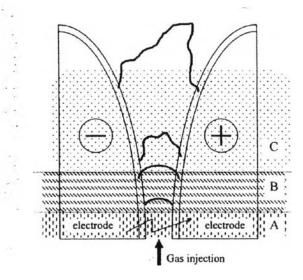

Figure 2.1 Phase of gliding arc phenomena: (A) reagent gas break-down; (B) equilibrium heating phase, and (C) non-equilibrium reaction phase.

The reagent gas break-down (A) 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.

The equilibrium heating phase (B) takes place after the formation of stable plasma channel. The electric discharge spreads along the electrodes, where the velocity of the gas flow and the gliding arc are very close.

The non-equilibrium reaction phase (C) begins losing heat from the plasma, where the heat loss exceeds the energy supplied by the source, and it is therefore not possible to sustain the plasma in the state of thermodynamic equilibrium. As a result, the discharge plasma rapidly cools to the gas temperature. After the decay of the non-

equilibrium discharge, there a new break-down occurred at the shortest distance between the electrodes, and the cycle repeats (Fridman *et al.*, 1999).

2.5 Related Research Works

In recent years, the plasma technology has become very interesting to be used for reforming methane to produce synthesis gas and higher hydrocarbons, in replacing catalytic reforming processes, which generally encounter many problems. The role of catalysts in the reforming process is to create radical species for enhancing the reaction. The role of plasma would be then to provide the energy and to create free radicals needed for methane reforming. The sole non-thermal plasma and the combined catalytic and non-thermal plasma systems for hydrocarbon reforming to produce hydrogen, as well as for other reactions, have also been demonstrated in several research works.

In 2001, Zhang *et al.* studied the conversion of methane with carbon dioxide to produce synthesis gas (syngas) and higher hydrocarbons over quartz fleece, zeolite NaX, zeolite HY, and zeolite NaY catalysts promoted by dielectric barrier discharge at low temperature and ambient pressure. The experimental results showed that methane conversion decreased in the following order: fleece (without catalyst) > NaY > HY > NaX. The highest CO_2 conversion of 40 % was reached when using zeolite NaY as the catalyst. The CO_2 conversion decreased in the following order: NaY > fleece > NaX > HY. Compared to the results from fleece, zeolite NaY was the most promising catalyst for producing synthesis gas and liquid hydrocarbons (C_5+). In the studied power range (100–500 W), syngas was the main product, and it increased significantly with increasing input power. The ratio of H_2/CO increased sharply when the ratio of CH_4 to CO_2 increased. When the flow rate increased, the yield of syngas decreased. One year later, Jiang *et al.* (2002) reported the methane conversion to higher hydrocarbons in the presence of carbon dioxide using a dielectric barrier discharge reactor with and without zeolite A. In the presence of zeolite A, no plasma-polymerized carbon film was produced, leading to a better production of light hydrocarbons (C_2-C_4).

Krawczyk and Młotek (2001) studied the gliding arc discharge combined with catalysts for nitrous oxide conversion in oxygen-containing gases. The results showed that nitrous oxide in a mixture with oxygen or air was not only decomposed to oxygen and nitrogen, but was also oxidized to nitric oxide. The overall conversions of nitrous oxide, as well as the degree of N_2O oxidation to NO, were studied as a function of its initial concentration, flow rate, and discharge power. The overall N_2O conversion and degree of oxidation to NO decreased with increasing flow rate and initial N_2O concentration, but they increased with increasing discharge power. The degree of N_2O oxidation to NO varied within 20–37 %. The overall conversion and degree of N_2O oxidation increased when granular dielectric materials (TiO_2, SiO_2 (quartz glass), and γ-Al_2O_3) were introduced into the reaction zone. The energy efficiency and overall conversion of N_2O were still further increased due to catalytic effects of a number of metal oxides (CuO, NiO, MnO_2, Fe_2O_3, Co_3O_4, and ZrO_2) deposited on γ-Al_2O_3. The activity of the oxide catalysts within the active power range of 300–360 W decreased in the following order: $CuO > Fe_2O_3 > NiO > MnO_2 > Co_3O_4 > ZrO_2$. It was concluded that the combined plasma-catalytic processing may be an efficient way for the reduction of N_2O emissions.

Rusu and Cormier (2003) investigated the methane reforming with steam using a gliding arc discharge reactor. The experiments clearly demonstrated the ability of gliding arc to accelerate chemical reactions at low temperatures. The experimental results indicated that a higher methane content and a lower total flow rate yielded a better selectivity, but the methane conversion was quite low (15–20 %) because of the only small fraction (10–15 %) of inlet gas passing through the discharge zone. In the same year, Supat *et al.* (2003) studied the synthesis gas production from simultaneous steam reforming and partial oxidation of methane using an AC corona discharge system. The benefits of the combination of the two reactions reduced the pure oxygen requirement in the system and increased the thermal efficiency by transferring heat between the exothermic and endothermic reactions. It was found that the coupling of methane increased with increasing CH_4/O_2 ratio, but the oxidation of methane to carbon dioxide and water was more favorable at higher oxygen concentrations. Adding water vapor in the feed stream greatly enhanced the conversions of methane and oxygen in an oxygen-lean system

but reduced the conversion of methane in the oxygen-rich system. Furthermore, the energy consumption for methane conversion could be substantially reduced by adding water vapor. The product distribution was strongly influenced by the feed gas concentration rather than the input power and applied frequency.

Kado *et al.* (2003) studied the conversion of methane to acetylene or syngas using non-equilibrium pulsed discharge under ambient temperature and atmospheric pressure. It was found that an increase in current led to a proportional increase in the pulse frequency. In the region of a relatively low methane conversion, the methane conversion increased in proportion to the pulsed frequency. However, the rising slope decreased with the increase in methane conversion due to a decrease in the probability of collision between a methane molecule and an electron. The methane conversion increased under the condition of the existence of rare gas, like argon or helium, because the pulsed frequency in the presence of inert gas becomes higher than that without any other kinds of coexisting gas under the condition of the same supplied energy. By using either carbon dioxide or steam, the reforming of methane produced syngas, as well as acetylene. The addition of oxygen gas also promoted the reaction to yield syngas, as well as acetylene, while suppressing the carbon dioxide formation. The use of oxygen was the most effective way in suppressing the carbon deposition by converting CH_x into carbon monoxide.

Zhang *et al.* (2004) studied the oxidative dehydrogenation of ethane under pulse corona plasma over various catalysts using carbon dioxide as oxidant. The experiments showed that the rare earth metal oxide catalysts, such as $La_2O_3/\gamma\text{-}Al_2O_3$ and $CeO_2/\gamma\text{-}Al_2O_3$, enhanced the conversion of ethane and the yields of ethylene and acetylene. The optimum Ce content for the oxidative dehydrogenation of ethane under pulse corona plasma was 10 %. The conversion of ethane increased with increasing concentration of carbon dioxide in the feed over $CeO_2/\gamma\text{-}Al_2O_3$. The total yields of ethylene and acetylene reached maximum values when the CO_2 content in the feed was 50 %.

Sekine *et al.* (2004) investigated the steam reforming of methane, propane, hexane, cyclohexane, methanol, and ethanol using non-equilibrium pulsed discharge under the conditions of atmospheric pressure and low temperature without the use of catalyst. In each case, the steam reforming proceeded efficiently and selectively, and

hydrogen was formed as a main product. Carbon deposition and wax formation were inhibited when the steam/carbon molar ratio was 1. The conversion of methane and the formation of hydrogen increased with increasing pulse discharge frequency, while the selectivity for products other than hydrogen was independent of pulse discharge frequency. The waveforms of current and voltage were not influenced dramatically by changing pulse discharge frequency. The changes in electrode distance and flow rate affected hydrogen formation but not the other products.

Chavadej *et al.* (2005) studied the effects of electrical parameters of a corona discharge reactor on the partial oxidation of methane in air and on the carbon dioxide reforming of methane in the presence and absence of Pt-loaded KL zeolite. For the partial oxidation of methane, it was found that the reactant conversion increased with decreasing applied frequency and increased with increasing input low-side voltage both in the presence and absence of Pt/KL except that the oxygen conversion was 100 % in the presence of Pt/KL. For the carbon dioxide reforming of methane, the applied frequency and input low-side voltage affected only the reactant conversions with no significant effect on reaction pathways both in the presence and absence of Pt/KL.

Chavadej *et al.* (2007) used the same system to study the removal of gaseous volatile organic compound (VOC). The results showed that an increase in either applied voltage or stage number of plasma reactors enhanced both benzene conversion and CO_2 selectivity, which was in contrast with the effects of frequency and feed flow rate. Commercial TiO_2 (Degussa P25), sol-gel TiO_2, and 1 % Pt/sol-gel TiO_2 were used as catalysts in this study. The presence of all studied catalysts hardly affected the benzene conversion, but markedly increased the CO_2 selectivity. The synergistic effect of catalysts in the plasma reactor system reasonably resulted from the activation of TiO_2 by the energy generated from the plasma, leading to the enhancement of the CO oxidation.

Chavadej *et al.* (2007) investigated a combined plasma and catalytic process for ethylene removal by using a multistage corona discharge system in the absence and presence of Pt/TiO_2. The effects of commercial TiO_2, sol-gel TiO_2, and 1 % Pt/sol-gel TiO_2 loaded on glass wool used as catalysts packed in the plasma reactors were studied. For the plasma system without a catalyst, it was found that both the

ethylene conversion and CO_2 selectivity increased with increasing applied voltage and stage number of plasma reactors, but decreased with increasing frequency and feed flow rate. In the presence of all studied catalysts in the plasma system, an increase in both C_2H_4 and O_2 conversions was obtained. The CO_2 selectivity increased in the presence of the catalysts in the following order: 1 % Pt/sol-gel TiO_2 > sol-gel TiO_2 = commercial TiO_2. When the TiO_2 was present in the plasma reactor system, it enhanced the ethylene oxidation reaction because its reducible property provides both the reaction sites and oxygen for the reaction. The presence of 1 % Pt on the sol-gel TiO_2 was found experimentally to promote the CO oxidation, leading to a higher CO_2 selectivity.

Nair *et al.* (2007) investigated plasma-assisted methane conversion in gas phase by partial oxidation at low energy density (80–200 kJ/mol CH_4) and low reactor temperature (130–140 °C). Although non-thermal plasma has the inherent advantage for initiating reactions, a disadvantage is the unfavorable selectivity for the desired product. The investigation was focused on identifying the plasma-initiated chemical reaction pathways by combining experiments and kinetic modeling. Sensitivity analysis indicated reaction intermediates, leading to the formation of oxygenates from an alternative oxidation pathway at the investigated temperatures (T < 200 °C). The selectivity for synthesis gas could be increased by partial oxidation at higher CH_4/O_2 ratios. Combined partial oxidation and steam reforming was also investigated in order to increase H_2 concentration. Isotopes were used in order to identify reaction pathways for the case of steam reforming experiments. However, the experiments at lower energy density indicated negligible steam conversion. At lower temperatures, the input plasma energy was primarily used for both CH_4 and O_2 conversions.

Zou *et al.* (2007) studied a hydrogen production from the partial oxidation of dimethyl ether (DME) using corona discharge plasma performed at ambient conditions. The partial oxidation could help to avoid the undesired carbon deposit formed from the decomposition of DME, and a stable operation was obtained. The carbon deposit was completely avoided when the O_2/DME ratio was 1.05. The partial oxidation could also greatly improve the conversion rate and energy efficiency. The optimal O_2/DME ratio was 1.38, at which the rate of H_2 production

was 1.33 times higher, and the energy efficiency was 1.72 times higher than that of DME decomposition. The higher O_2/DME ratio resulted in the complete oxidation and reduced the rate of H_2 production. The AC plasma was found to be more efficient than the DC plasma, and the optimum frequency was 2 kHz.

Kim *et al.* (2007) applied a plasma-catalytic system for the conversion of methane to C_2, C_3, or higher hydrocarbons in a dielectric barrier discharge (DBD) reactor at atmospheric pressure. The methane conversion increased with an increase in Pt loading on γ-Al_2O_3. The highest C_2H_6 selectivity was 50.3 % when 3 wt.% Pt/γ-Al_2O_3 catalyst was calcined at 573 K. the methane conversion increased with an increase in the catalyst weight in DBD reactor. The major products were C_2H_6 and C_3H_8, which were independent of catalyst weight.

Indarto *et al.* (2007) investigated the effects of total gas flow rate and addition of auxiliary gases (N_2, O_2, air, and water) on the CO_2 conversion process. The experimental results indicated that the conversion of CO_2 reached 18 % at the total gas flow rate of 0.8 L/min and produced CO and O_2 as the main gaseous products. Among the auxiliary gases, only N_2 gave a positive effect on the CO_2 conversion, and the power efficiency of 95 % and total gas flow rate of 2 L/min increased about three times as compared to the pure CO_2 process.

Sreethawong *et al.* (2007) investigated the partial oxidation of methane with air for synthesis gas production by using a multistage gliding arc discharge system. The results showed that increasing stage number of plasma reactors, voltage, and electrode gap distance enhanced both CH_4 and O_2 conversions, which were in contrast to the effects of increasing CH_4/O_2 molar ratio, feed flow rate, and frequency. The optimum conditions were found at a CH_4/O_2 feed molar ratio of 3/1, a feed flow rate of 150 cm^3/min, and a frequency of 300 Hz for the maximum CH_4 and O_2 conversions, high synthesis gas selectivity, and very low energy consumption. The energy consumption of the gliding arc system was found to be very low about 2.45×10^{-18}–2.96×10^{-18} Ws (15.3–18.5 eV)/molecule of methane converted as compared to 3.36×10^{-18} Ws (21 eV)/molecule of methane converted obtained from the corona discharge system with pin and plate electrodes.

Rueangjitt *et al.* (2007) studied the reforming of simulated natural gas via the non-thermal plasma process with the focus on the production of hydrogen and

higher hydrocarbons. The plasma reactor was operated with different feed compositions: pure 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 effects of all gaseous hydrocarbons and CO_2 present in the natural gas were investigated. The results showed that the addition of gas components to the feed strongly influenced the reaction performance and plasma stability. By comparisons among all the studied feed systems, both hydrogen and C_2 yields were found to depend on the feed gas composition in the following order: $CH_4/C_2H_6/C_3H_8/CO_2 > CH_4/C_2H_6/C_3H_8/He > CH_4/C_2H_6/He > CH_4/He >$ pure CH_4. The $CH_4/C_2H_6/C_3H_8/CO_2$ feed system provided the maximum yield of hydrogen and C_2 products (35 and 42 %, respectively) and also required the lowest input energy for producing hydrogen in the range of 3.58×10^{-18}–4.14×10^{-18} Ws (22.35–25.82 eV) per molecule of produced hydrogen.

Rueangjitt *et al.* (2008) continued to further investigate the effects of operational parameters, i.e. applied voltage and input frequency, as well as the effect of oxygen addition, on the reaction performance and discharge stability in the reforming of the simulated natural gas containing a $CH_4:C_2H_6:C_3H_8:CO_2$ molar ratio of 70:5:5:20. The results revealed a marked increase in both CH_4 conversion and product yield with increasing applied voltage and decreasing input frequency. At higher applied voltage and at lower frequency, the selectivities for H_2, CO, and all hydrocarbon products, except C_2H_2, were observed to be enhanced. The use of oxygen was found to provide a great enhancement of the plasma reforming of the simulated natural gas. For the combined plasma and partial oxidation in the reforming of CO_2-containing natural gas, air was found to be superior to pure oxygen in terms of reactant conversions, product selectivities, and specific energy consumption. The optimum conditions were found to be a hydrocarbons-to-oxygen 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, in providing the highest CH_4 conversion and synthesis gas selectivity, as well as extremely low specific energy consumption. The energy consumption was as low as 2.73×10^{-18} Ws (17.02 eV) per molecule of converted reactant and 2.49×10^{-18} Ws (16.60 eV) per molecule of produced hydrogen.

Rueangjitt *et al.* (2009) also continued to further investigate the effect of stage number of AC gliding arc discharge reactors on the process performance of the combined reforming and partial oxidation of simulated CO_2-containing natural gas having a $CH_4:C_2H_6:C_3H_8:CO_2$ molar ratio of 70:5:5:20. For the experiments with partial oxidation, either pure oxygen or air was used as the oxygen source with a fixed hydrocarbon-to-oxygen molar ratio of 2/1. Without partial oxidation at a constant feed flow rate, all conversions of hydrocarbons, except CO_2, greatly increased with increasing number of stages from 1 to 3; but beyond 3 stages, the reactant conversions remained almost unchanged. However, for a constant residence time, only C_3H_8 conversion gradually increased, whereas the conversions of the other reactants remained almost unchanged. The addition of oxygen was found to significantly enhance the process performance of natural gas reforming. The utilization of air as an oxygen source showed a superior process performance to pure oxygen in terms of reactant conversion and desired product selectivity. The optimum energy consumptions of 12.05×10^{24} eV per mole of reactants converted and 9.65×10^{24} eV per mole of hydrogen produced were obtained using air as an oxygen source and 3 stages of plasma reactors at a constant residence time of 4.38 s.