

## **CHAPTER II**

### **LITERATURE SURVEY**

The basic principles about the plasmas and the electric discharge environment, particularly in parts that deal with the chemical reaction of methane, are described within this chapter. Beginning with some basic knowledge about the chemical properties of the methane molecule, few aspects about the plasmas will then be introduced to eventually describe how the plasma can be generated for activating methane molecules in order to initiate the direct methane conversion. Along with these, some practical studies on the direct methane conversion process under the different types of the electric discharges will be mentioned so as to be the evidence on the advances of the work in this field. Finally, the aspects of the corona discharge reactor saved for the purpose of generating those plasmas for the present work will be discussed in details. It is necessary to point out that the present knowledge and insights about the electrical discharge environment and its plasma chemistry are very complicated and so much of those information will not be presented in here. Some literature (Nasser, 1971) is, however, recommended as good descriptive sources whenever the higher levels of the knowledge on the subjects of the plasmas are necessary.

#### **2.1 Physical and Chemical Properties of Methane**

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 different 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 deposits are now located in very remote areas which makes this resource somewhat expensive to transport.

The fact that methane is very flammable when presents in the oxygen atmosphere makes some people confused that methane is one of the very reactive molecules. Indeed, methane is a 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 those other common gases, respectively.

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

Gas	Ionization Energy (eV)	Gas	Ionization Energy (eV)
CH <sub>4</sub>	12.5	O <sub>2</sub>	12.2
H <sub>2</sub>	15.6	CO	14.1
N <sub>2</sub>	15.51	CO <sub>2</sub>	14.4
Li	5.39	Na	5.138
K	4.339	Cu	7.7

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

Based upon these data, although the ionization potential of the methane molecule is in the same order of magnitude with those of other

common gases, its bond energy between C-H is markedly high compared to other covalent bonds.

In almost all 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 has been traditionally applied for reaction with methane. At present, the oxidation of methane with oxygen is one of the most well known radical reactions which thermally converts the methane molecule into a wide range of products depending upon the reaction conditions used but, thermodynamically, this application favors for the production of CO<sub>2</sub>, CO and H<sub>2</sub>O (Poonphanapricha, 1997).

## **2.2 Gaseous Plasmas for Activating Methane Molecules**

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

### 2.2.1 Fundamental Properties of Plasmas

In its simplest definition, gaseous plasma is a mixture of the negatively and positively charged particles in an otherwise neutral gas. The positively charged particles are, in all cases, the cations but negatively charged particles can be either the electrons or the anions. The neutral species may be the mixture of free radical species with stable neutral gases. Two important properties are known to be possessed by the plasma.

#### (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

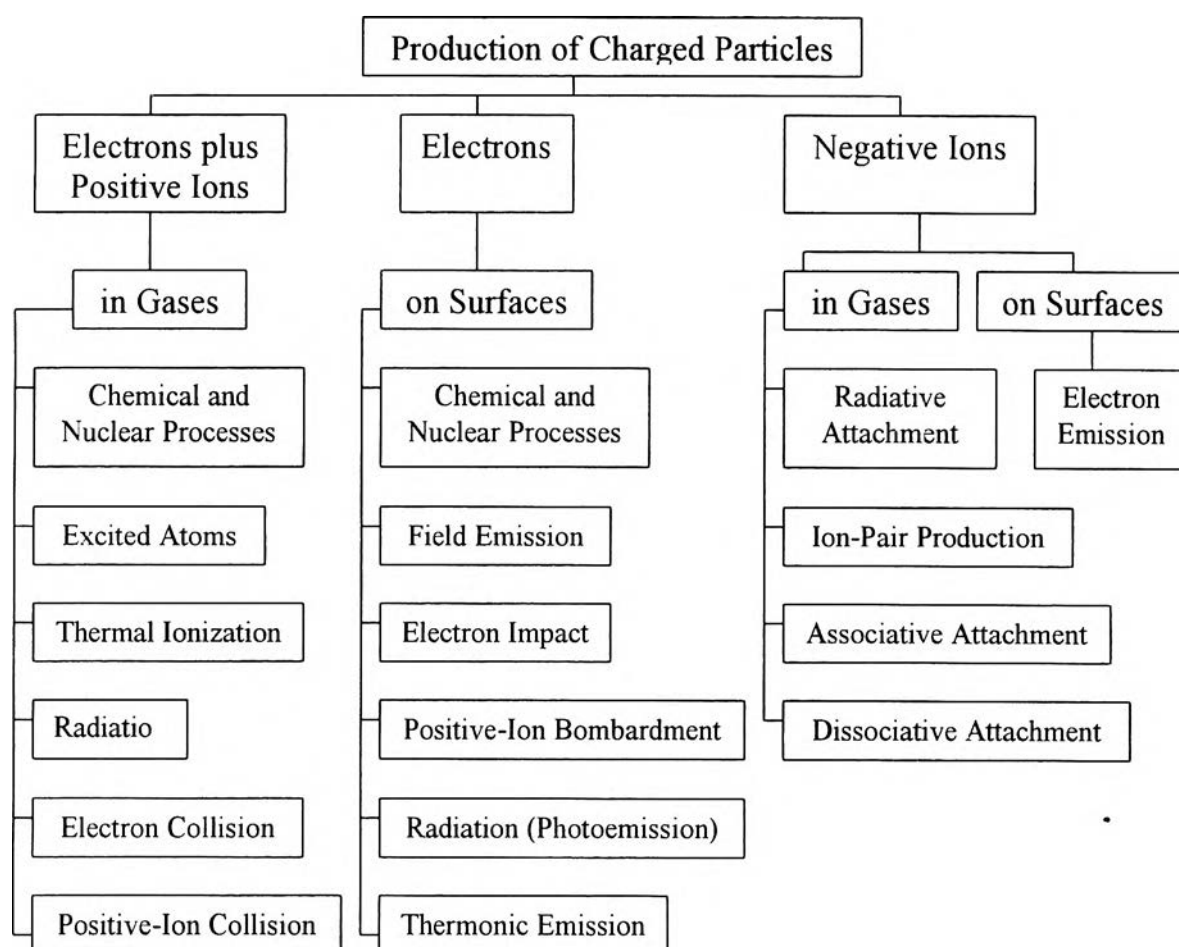
The plasma can have some interactions upon the applying of an electromagnetic field due to fact that they consist of charged particles. In general, plasma can occur in all states (Nasser, 1971). The plasma in solid is called solid-state plasma while the plasmas generated in the liquid and gaseous states don't have any specific names. From this point, only the gaseous plasmas (i.e., shortly called as "plasmas") will be discussed along with the chemical reaction.

Unlike gases, plasmas differ greatly in many aspects according to which they are usually classified. These aspects include the pressure, the distributions of charged-particle density in the entire plasma volume and temperature.

### 2.2.2 Generation of Plasmas

There are several means of generating charged particles to produce plasmas. The collisions between the cosmic rays and the gases in atmospheric layers can, for example, cause the electrons in those gaseous molecules liberated out and thus produce the charged species. This process of liberating electrons from gas particles with the creation of positive ion charge is termed ionization. On the other hand, the process of liberating electrons from a solid is called electron emission. Both of these processes are of equal importance for the generation of the plasmas. The electrons and charged particles produced in the gaseous boundaries may be induced by the electromagnetic waves to collide with the solid surfaces to emit other electrons. These electrons, in turn, can collide with other gaseous particles to cause ionization. Various common ways of creating the charged particles can be classified schematically as shown in Figure 2.1 (Nasser, 1971). From Figure 2.1, the formation of negative ions can take place when free electrons are available and attach themselves to neutral atoms or molecules, negative

ions are then formed. Gases with one or two electrons filling the outer shell of the atom form a charged negative ion. These gases, such as oxygen are usually known as “electronegative” gases. However, the electrons do not attach only to single atoms but they can also attach to the molecules of two (or more) atoms, such as  $O_2$  and thus form the negative charged particles as well. There are several ways for producing the ions and electrons. Each type of generation has each mechanism to release the ions and electrons such as negative ions which can be occurred in gases by the radiative attachment or surface of metal by electron emitting when electrons are activated.



**Figure 2.1** Alternative methods of charged particles generation (Nasser, 1971)

In the present study, the plasma was first generated by the collisions between the neutral molecules (e.g., methane) and the electrons emitted from the surface of metal electrodes. This process of plasma generation is commonly known as the “field” emission process. In this type of process, an externally intense electric field is applied across the metal electrodes to cause the reduction in its “potential barrier” and thus the energy that each electron requires for leaving the metal surface. A most interesting phenomena that occurs on the metal surface under the applying of an extremely high electric field is that many electrons can leak from the surface despite its less kinetic energy to overcome the potential barriers. This phenomena is known as “ tunnel effect”

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, all of these electrons can further move and collide with other species. As a result, a large quantity of electrons and plasma 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. Various numbers of collision mechanisms can be occurred simultaneously in the gaseous space for which many of those can initiate the chemical reactions leading to the production and destruction of the chemical species. Some important collision mechanisms occurred in the gases are typically shown in Table 2.3.

The combined steps of the field emission process among these plasma species and the collisions between the species and the electrode surfaces are referred to as “electric discharges” phenomena and they are applied as the basis for the plasma generation technique used in this present study.

**Table 2.3** Collision mechanisms in the gases (Nasser, 1971)

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

The plasma produced by this discharge phenomenon can be divided into two types. The first type is “thermal plasma”, which is characterized by high gas temperature and an approximately equal gas and electron temperature. This type of plasma can also be referred to as plasma in equilibrium. Typical examples of such plasma are those produced in the arcs and plasma torches. The second type of plasma is termed “low-temperature” or “non-thermal” (cold-) or “non-equilibrium” plasma. Low gas temperature and high electron temperature characterize this type of plasma. In other words, the non-equilibrium plasma consists of the electrons, which have much higher energy than the neutral gas particles. 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).

The first implementation of the electric discharges generation technique as a tool for activating the chemical reaction can be tracked back to Siemens’s experiments with the “silent discharge” presently known as

dielectric-barrier discharge for ozone generation (Siemens, 1857). Even though the larger installations of such ozone generating systems for the drinking water treatment plants were settled in many countries since the early of this century, some extensive studies on the plasma application for ozone production have still been continued to the last decades (Morinaga and Suzuki, 1962; Eliasson, 1987 and Nomoto *et al.*, 1995)

At present, the process dealing with the plasma chemistry of electric discharges may be classified into two types, namely, the volume chemistry process; e.g., the ozone production in the so-called dielectric-barrier discharge, and the surface chemistry process; e.g., etching, deposition, or surface modification. The important application of methane plasma in volume chemistry process is the use of ionized methane as the ion source of the mass spectrometers. The only application of methane plasma in the industrial surface chemistry process is the preparation of diamond coatings and ceramic materials (Nasser, 1971).

Only the non-equilibrium, volume chemistry plasma in the space filled with electric discharge will be treated in connection with the present study.

### **2.3 Types of Non- Equilibrium Plasmas**

When the potential difference is applied across the plasma, the electric field will exert itself 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 in the time available between collisions. Their collision partners take up the energy they lose through the collisions. If the pressure is small enough or the field is high enough, the electrons and some of the 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 again called a non-thermal or non-equilibrium plasma and can be classified into several types depending upon their generation mechanisms, their pressure range and the electrode geometry (Eliasson *et al.*, 1987).

### 2.3.1 Radio Frequency Discharge

These high frequency discharges are used extensively to produce plasmas 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 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. RF discharges work very well at low pressure, but are also used at atmospheric pressure in which a thermal plasma can sometimes occur (Nasser, 1971).

### 2.3.2 Microwave Discharge

Another type of high frequency discharge that can be practiced presently is the microwave discharge, 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.

### 2.3.3 Glow Discharge

This is the stationary low-pressure discharge usually occurring between flat electrodes encapsulated in a tube. The typical pressure involved is normally will below 10 mbar and, therefore, needs only comparatively low electrical potential difference (i.e., voltage) and current to run. Due to its low pressure and the resulting low mass flow, the discharge type only finds its best

application in the manufacture of fluorescent and neon tubes and is not suited to the industrial production of chemicals (Nasser, 1971).

#### 2.3.4 Corona Discharge

When the pressure is increased during 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 method 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.

#### 2.3.5 Dielectric Barrier Discharge

This type of electric discharge is defined by the discharge generated within the gas- filled gap 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. A dielectric layer that is commonly made of glass covers either one or both electrodes. Many previous works referred to this kind of discharge as the silent electric discharge in which it has long been known to use in many studies on the plasma chemical reactions (Thayachotpaiboon, 1996).

## 2.4 Related Research Work

Numerous studies of methane conversion using microwave plasma have been reported. Zerger *et al.* (1992) investigated the combined effects of microwave plasma and several types of heterogeneous catalysts on the oxidation of methane and oxygen at low pressures (3-500 torr). The microwave frequency of 2.45 GHz was used to generate the free-radical species, which resulted in the subsequent reactions over the catalysts that were placed downstream from the plasma zone. They found that, with the constant  $\text{CH}_4/\text{O}_2$  of about 2.22, the activation of microwave plasmas could lead to the formation of various gas-phase radicals, which then recombined over the catalyst surfaces. Many kinds of products could be obtained including ethane, ethylene,  $\text{C}_3$  compounds, formaldehyde and methanol. The influence of the different catalysts was also reported. Typical catalysts used for thermal activation of methane such as Li/MgO and related systems were not very active or selective in plasma reactions. The methane conversion ranging from 4-55 % could be obtained for different catalysts. Ethane was the primary product with the highest selectivity of 73 % while the ethylene was found to be the secondary product with the highest selectivity of 27 %. The Pt catalysts could promote the total oxidation pathway to  $\text{CO}_2$  as has been found with methane catalysts promoted thermally. While the  $\text{MoO}_3$  was observed to be effective in maximizing the ratio of ethane to ethylene, the highest  $\text{C}_3$  compounds were found with the Pt catalysts. They concluded from their work that the major reaction pathway for the formation of ethane and ethylene were due to the coupling of two similar radicals; i.e.,  $\text{CH}_3^\cdot$  and  $\text{CH}_2^\cdot$ , respectively.

Huang *et al.* (1994) focused on several designs of the microwave plasmas reactors for the oxidation of methane to produce methanol. With their specially designed reactors, they had proposed new techniques to control the generation of free radicals. Without the introduction of any catalysts into the

reaction systems, one of the most interesting conclusions was that the methane dimerization products ( $C_2$  hydrocarbons) could be eliminated by introducing  $CH_4$  downstream from the plasma zone to react with the plasma generated from the  $O_2$ . However, the highest selectivity obtained was only about 4.4 %. The attempt of varying the power and the  $CH_4/O_2$  ratio to increase the methane conversion (from 2.7-97 %) mostly produced carbon oxides from the reactions. Furthermore, the reactions had to be carried out under vacuum conditions (15-101 torr).

Lui *et al.* in 1996 revealed that when methane and oxygen were premixed and then passed through the AC electric field at atmospheric pressure, 5-10 % methane conversion and 7 - 9 % methanol selectivity could be achieved. The mixture of 76 % methane and 24 % oxygen at 68 °C were used with the reaction residence time of about 12.5 s. The results concluded that the oxygen conversion could be increased almost linearly with the increasing voltage ranging from 5-8 kV. In addition, no reactions were observed when only oxygen was passed through the reactor and mixed immediately with methane. A conclusion from that point was that the methane active species, rather than oxygen species, participated directly in the reaction.

Bhatnagar *et al.* (1993) made the extensive analysis on the effect of several parameters including the voltage, residence time, methane to oxygen feed ratio and the individual partial pressure on the change reaction behaviors, i.e., the change in methane conversion and product selectivity. Several conclusions were established including the decrease of methane conversion (i.e., from 4.07 to 1.73 %) and the degree of deep oxidation reactions (i.e.,  $CO_2$  selectivity falling from 57.71 to 48.62 %) with the increasing  $CH_4/O_2$  feed ratio (i.e., from 3 to 20) under 9 kV and total flow rate of 500 cc/min. This degree of deep oxidation reaction, however, increased only slightly with the increasing residence time and it was found to be nearly independent with the increasing voltages. With the methane/oxygen feed ratio of 3 and total flow

rate of 500 cc/min, the highest methane conversion (5.72 %) and methanol selectivity (17.76 %) could be obtained at the highest operating voltage of 18 kV. Although methane conversion higher than 5.72 % could be obtained by decreasing the methane/oxygen feed ratio but the selectivity of the desired products was dramatically low since most of the methane was converted into the carbon oxides products. The chemical pathways leading to the formation of each product were also been studied. From the results, a parallel pathway was found to be existed between the production of methanol and ethane. The pathways leading to the carbon monoxide might also be paralleled to the first two paths. The successively undesired pathways leading to the formation of carbon oxides from alcohol and ethane could also be observed. Upon the increasing voltage, it was found that the decomposition of large molecules like ethane could be occurred while this increased the methanol selectivity. Some preliminary kinetic studies had also been subjected to investigate in this work.

Thanyachotpaiboon (1996) studied the oxidative coupling of methane using the dielectric barrier discharge reactor at ambient temperature to determine the effects of voltage, residence time and third bodies on methane conversion and product selectivities. It was found that the methane conversion initially increased with increasing voltage and residence time above the breakdown voltage, and product selectivities were essentially independent of the voltage. Methane conversion also increased when helium and ethane presented in the feed stream.

Poonphanapricha (1997) studied the effect of ethane and propane that were introduced as pure reactant and also with methane in the system. The products that occurred in the system were C<sub>1</sub> to C<sub>4</sub> hydrocarbons. It was discovered that methane conversion increased with increasing the voltage or residence time. It was concluded that hydrogen abstraction was the most common initiate reaction that occurred in the system resulting in ethane, ethylene and propylene as the main products in the pure methane, ethane and

propane system, respectively. Under the presence of ethane or propane with methane in the system, ethane enhance methane conversion but in contrast, propane acted likes an inhibitor for methane reaction instead.

A previous work of Lui *et al.*(1997) on the application of the corona discharge with the oxidative coupling of methane was carried out by using an irreducible metal oxide, i.e., Sr/La<sub>2</sub>O<sub>3</sub>, as the catalyst coupled with the wire-plane electrode configuration for the production of either negative or positive electric discharges. In all cases, the inlet gaseous components were consisted of the mixture of methane and oxygen. From the results, the great enhancement in both the methane conversion and C<sub>2</sub> selectivity could be observed when the electric discharges and catalysts were present simultaneously into the reactions. They also found a saturation condition of the discharge current beyond that point, increases in the voltage caused nearly unchanged methane conversion.

Moreover, Lui *et al.* (1996) conducted a study of the gas discharge promoted catalytic conversion of methane to higher hydrocarbons using various metal oxide and zeolite catalysts was investigated over a wide range of temperature (373-973 K). It was demonstrated that the polarized OH group in the metal oxide catalysts (including NaOH treated Y zeolite) played an important role in gas discharge. The gas discharge effect resulted in a significant methane conversion and a high C<sub>2</sub> yield at such temperatures relatively low that no intrinsic catalytic activity was found in the absence of gas discharge. The lower the temperature, the greater the gas discharge effect was obtained. Especially, for NaOH treated Y zeolite, the lowest temperature (373 K) gas discharge effect was found with a very high methane conversion. Because of no C<sub>2</sub> activity in the absence of gas discharge, the gas discharge totally modified the catalyst activity. Most ethylene is easily adsorbed at the acidic sites in the Y zeolite due to the basicity of this selective product, and then they are oxidized to CO<sub>x</sub>.

Lui *et al.* (1996) continuously studied the Plasma Promoted Catalysis (PPC) and Catalyst Enhanced Plasma (CEP) that are two-fold of interaction of cold plasma and catalyst. The results showed that for low temperatures (as low as 100°C), methane conversion to C<sub>2</sub> hydrocarbons was achieved by using the PPC/CEP over NaOH treated Y zeolites. The results also demonstrated that the combination of corona discharge (cold plasma) and catalyst (PPC/CEP) exhibited a saturation current, after which the methane conversion and C<sub>2</sub> yield changed slightly. It was found that increasing oxygen partial pressure in the feed could increase methane conversion but decrease the C<sub>2</sub> selectivity and yield. Increasing residence time also decreased the C<sub>2</sub> yield. Moreover, the shape-selectivity and metal ion effects were not significant for methane conversion to higher hydrocarbons by PPC/CEP over zeolites.

The oxidative coupling of methane was studied via AC and DC corona discharges (Lui *et al.*, 1996). The results were shown that the selectivity of products, ethane and ethylene, were affected by electrode polarity, frequency, and oxygen partial pressure in the feed. Higher C<sub>2</sub> yields were obtained with the AC corona. The methane conversion could be improved to over 50% by increasing the residence time, but the C<sub>2</sub> selectivity decreased. A reaction mechanism including the oxidative dehydrogenation (OXD) of ethane to ethylene was presented to explain the experimental results. It was indicated that application of AC and/or DC gas discharge techniques could be employed for improving the economics of OCM processes.

In 1985, a study was conducted by Fraser and coworkers to investigate the decomposition of methane in an AC electric discharge at atmospheric pressure and 60 Hz. The AC electric discharge was operated capacity using a pyrex condenser with silver coating electrodes. A high voltage AC power supply with transformer was employed to generate the AC discharge. Methane destruction efficiency reached 67% at a feed methane concentration of 120

ppm. Higher inlet oxygen concentrations in the nitrogen stream were shown to increase the production of CO<sub>2</sub>.

Liu *et al.* (1998) investigated the production of acetylene via plasma catalytic conversion of methane over NaY zeolite. Hydrogen was produced as by-product. This investigation studied a methane/hydrogen feed with oxygen as an additive and helium as a diluent. The CH<sub>4</sub>/H<sub>2</sub>/O<sub>2</sub> system was found to be more selective for the production of C<sub>2</sub> hydrocarbons, compare to the CH<sub>4</sub>/O<sub>2</sub>, CH<sub>4</sub>/H<sub>2</sub>O and CH<sub>4</sub>/CO<sub>2</sub> systems. A high hydrogen feed concentration was more favorable for acetylene formation. The selectivity and yield of C<sub>2</sub>hydrocarbons were related to the hydrogen feed rate, gas temperature, concentration of oxygen, and flow rate. The highest yield of C<sub>2</sub> hydrocarbons (32%) was obtained at the lowest flow rate used (10 cm<sup>3</sup>/s: residence time~2.3 s).

Liu *et al.* (1998) investigated the interaction between the plasma and heterogeneous catalysts. Temperature programmed CO<sub>2</sub> desorption, a two-step plasma catalytic methane conversion (PCMC), and temperature programmed oxidation of carbonaceous species were carried out. The experiment demonstrated that NaOH treated Y, NaY and NaX zeolites could stabilize sustained streamer corona discharges at low temperature leading to better and longer lived PCMC. The experiments also confirmed that the basicity, polarity and reactivity of zeolite may be increased by plasma leading to improved behavior for PCMC. TPO of carbonaceous deposits showed that NaX, NaY, NaA and 5A zeolites generated less coke and it was oxidized below about 650 K while NaZSM-5 generates significantly more coke which could be oxidized at higher temperatures. A two- step PCMC in which methane is adsorbed without plasma and then the plasma is generated with co-reactants but without methane in the gas phase showed that active plasma species interacting with the catalyst surface are necessary for the selective production of higher hydrocarbons.