

CHAPTER II

BACKGROUND

The basic principles about the plasmas and the electric discharges environment, particularly in parts that deal with the chemical reactions of methane, are described within this chapter. Beginning with some basic knowledge about the chemical properties of the methane molecule, aspects about the plasmas will then be introduced to eventually describe how the plasma can be generated for activating the 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. Finally, the aspects of the dielectric-barrier discharge reactor for the purpose of generating the plasmas for the present work will be discussed in detail. 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 given by Nassar (1971) is, however, recommended as a good descriptive source whenever higher levels of knowledge on the subject of plasmas are necessary.

2.1 Physical and Chemical Properties of Methane

Methane is commercially well-known as a very inexpensive and an 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 and reservoir conditions. This property, coupled with the fact that many natural gas deposits are now located in very remote areas, makes this resource somewhat expensive to transport.

The fact that methane is very flammable under the presence of oxygen makes some people confuse 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 show the average bond energy of C-H bond inside the methane molecule and its first ionization potential in compared with some of those other common gases.

Table 2.1 Average chemical bond energy of some covalent bonds (Organic Chemistry book)

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 (Physical Chemistry book)

Gas	Ionization Energy (eV)*	Gas	Ionization Energy (eV)
CH ₄	12.5	O ₂	12.2
H ₂	15.6	CO	14.1
N ₂	15.51	CO ₂	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 methane molecule is in the same order of magnitude as 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 which is one of the few effective techniques that have 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 formation of CO₂, CO and H₂O.

2.2 Gaseous Plasmas for Activating Methane Molecules

Since the gaseous plasma is another good source of active species including electrons, ions and radicals, some research on methane reactions using such plasmas to initiate the reaction can be summarized as follows.

2.2.1 Fundamental Properties of Plasma

In its simplest definition, gaseous plasma is a mixture of the negatively and positively charged species in an otherwise neutral gas. The positively charged particles are, in all cases, the cations but the negatively charged particles can be either electrons or anions. The neutral species may be a 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 interactions upon the application of an electromagnetic field due to the fact that they consist of charged particles. In general, plasmas can occur in all states. The plasma in the solid is called solid-state plasma while the plasmas generated in the liquid and gaseous states do not have any specific names(Nasser, 1971). From this point, only the gaseous plasmas (i.e., shortly called as “plasmas”) will be discussed along with the chemical reactions. 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 Plasma

There are several means of generating charged particles to produce the plasma. The collisions between cosmic rays and gases in atmospheric layers can, for example, cause the electrons in those gaseous molecules to be liberated and thus produce charged species. This process of liberating an electron from a gas particle with the creation of positive charge is termed *ionization*. On the other hand, the process of liberating an electron from solids is called *electron emission*. Both of these processes are of equal importance for the generation of the plasmas. The electrons and charged species produced in the gaseous phase may be induced by electromagnetic waves to collide with the solid surfaces to emit other electrons. These electrons, in turn, can collide with other gaseous species to cause ionization. Various common methods of creating the charged species can be classified as schematically shown in Figure 2.1.

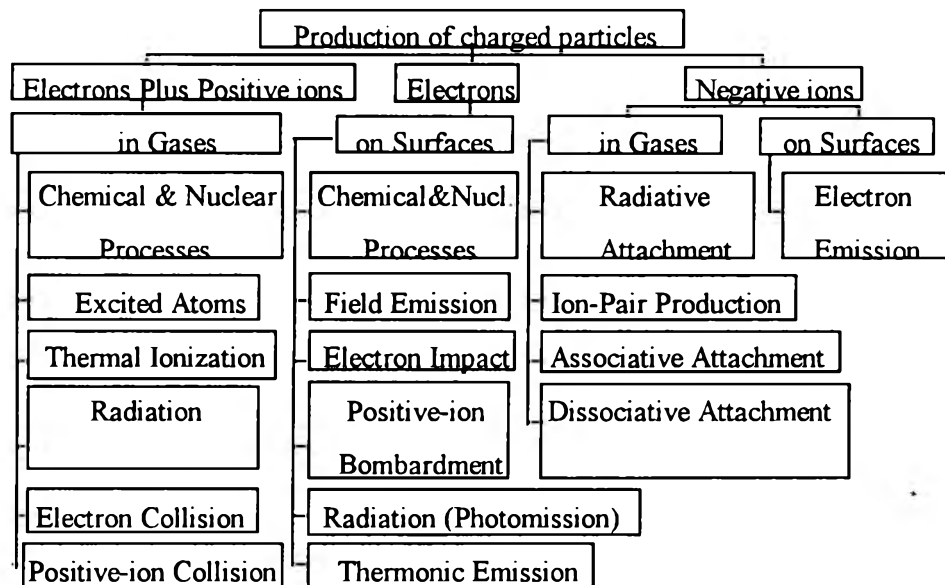


Figure 2.1 Alternative methods of charged particles generation. (Nasser, 1971)

From Figure 2.1, it can be seen that the formation of negative ions can take place when free electrons are available and attach themselves to neutral atoms or molecules. Gases with one or two electrons deficient in their outer shell tend to easily attach one electron, thereby filling the outer shell of the atom and forming a charged negative ion. These gases, such as oxygen, are usually known as “electronegative” gases. However, the electrons do not attach only to atoms but they can also attach to the molecules of two (or more) atoms, such as O_2 and thus form negative charged species as well.

In the present study, the plasma was first generated by collisions between neutral molecules (e.g., methane) and the electrons emitted from the surface of the metal electrode. This process of plasma generation is commonly known as the “field” emission process and is also shown in Figure 2.1. 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 eventually the electrons can leave the metal surface. A most interesting phenomena that occurs on the metal surface under the application of an extremely high electric field is that many electrons can leak from the surface despite of less kinetic

energy to overcome the potential barrier. 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 the vicinity to form the ionized gases with an additional set of electrons. Accordingly, all of these electrons can move further and collide with other species. As a result, a large quantity of electrons and plasma including 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 the electric field has been started. Various collision mechanisms can occur simultaneously in the gaseous space leading to the production and destruction of the chemical species. Some important collision mechanisms occurring in the gases are shown in Table 2.3.

Table 2.3 Collision mechanisms of gases in electric field (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	$A^+ + B \longrightarrow B^+ + A$
Electronic Decomposition	$e + AB \longrightarrow A + B + e$
Atomic Decomposition	$A^* + B_2 \longrightarrow AB + B$

Collisions 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 plasma generation technique used in this present study.

The plasma produced by this discharge phenomena can be divided into two types. The first type is a “thermal plasma”, which is characterized by a high gas temperature and an approximately equal electron temperature. This type of plasma can also be referred to as plasma in equilibrium. Typical examples of such plasmas are those produced in the arcs and plasma torches. The second type of plasma is termed a “low-temperature” or “non-thermal” (cold-) or “non-equilibrium” plasma. This type of plasma is characterized by low gas temperatures and high electron temperatures. In other words, the non-equilibrium plasma consists of the electrons which have much higher energy than the neutral gas species. Those typical energetic electrons may have energy ranged from 1 to 10 eV which will correspond to temperatures of about 10,000 to 100,000 K (Rosacha et al., 1993).

The first implementation of the electric discharge generation technique as a tool for activating chemical reactions can be tracked back to Siemen’s experiments (Siemens, 1857) with the “silent discharge” (presently known as dielectric-barrier discharge) for ozone generation in 1857. Even though large installations of such ozone generating systems for drinking water treatment plants have been used in many countries since the early of this century, some extensive studies on plasma application for ozone production have continued to recent decades (Morinaga, 1961; Morinaga, 1962; Eliasson, 1987; Nomoto, 1995).

At present, the processes dealing with 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. In addition, the only application of methane plasma in the industrial surface chemistry process is the preparation of diamond coating and ceramic materials. (Nasser, 1971)

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

2.3 Type of Non-Equilibrium Plasma

When the potential difference is applied across the plasma, the electric field will provide energy to the charged species. The neutral species in the bulk of plasma are not directly influenced by the field. The electrons, due to their light mass, are immediately accelerated to extremely high velocities than those heavier ions in the time available between collisions. The energy they lose through the collisions is taken up by their collision partners. If the pressure is small enough or the electrical field is high enough, the electrons and 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 “non-thermal” or “non-equilibrium” plasma and can be classified into several types depending upon their generation mechanisms, their pressure ranges and the electrode geometry (Eliasson, 1991).

2.3.1 Radio Frequency (RF) Discharge

These high frequency discharges are 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 prevent electron 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 discharge works very well at low pressure, but is also used at atmospheric pressure in which thermal plasma can sometimes occur. (Nasser, 1971)

Gogolides et al. (1995) conducted a study on RF plasma in methane. They focused their interest on the application of RF plasma for the deposition of the diamond-like carbon films. Even though, no results could be exactly related to the study of the direct methane upgrading process, their published paper showed another good qualitative and quantitative discussion on the subject of methane plasma.

2.3.2 Microwave Discharge

This is another type of high frequency discharge that can be practiced presently. The microwave discharge induced by a microwave (0.3-10 GHz) radiation source must be guided or directed into gaseous vessel by using a wave guide structure or “resonant cavity”. As the dimensions of cavities diminish when the frequency increases, the maximum microwave frequencies used for discharge applications are usually below 3 GHz. Some experimental work in the area of direct methane conversion under the influence of the microwave discharge was conducted by Zerger et al. (1992) and Huang et al. (1994).

Zerger et al. (1992) investigated the combined effects of microwave plasma and several types of heterogeneous catalysts on the oxidation of methane under the presence of oxygen at low pressures (3-500 torr). The microwave frequency of 2.45 GHz was used to generate free-radical species which resulted in subsequent reactions over catalysts that were placed downstream from the plasma zone. They found that, with a constant CH_4/O_2 ratio of about 2.22:1, the activation of microwave plasmas could lead to the

formation of various gas-phase radicals including ethane, ethylene, C₃ 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 ranged from 4-55% for different catalysts. Ethane was the primary product with the highest selectivity of 73% while ethylene was found to be the secondary product with the highest selectivity of 27%. Pt catalysts could promote the total oxidation pathway to CO₂ as has been found with methane catalysts promoted thermally. While MoO₃ was observed to be effective in maximizing the ratio of ethane to ethylene, the highest amount of C₃ compounds was found with the Pt catalysts. They concluded from their work that the major reaction pathway for the formation of ethane and ethylene was due to the coupling of two similar radicals i.e., CH₃* and CH₂*, respectively.

In the latter work conducted by Huang et al. (1994), they focused on several designs of the microwave plasmas reactors for the oxidation of methane to produce methanol. With their specially designed reactors, they 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 methane dimerization products (C₂ hydrocarbons) could be eliminated by introducing CH₄ downstream from the plasma zone to react with the plasma generated from the O₂. The highest selectivity obtained was about 4.4%. The attempt of varying the power and the CH₄/O₂ 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).

2.3.3 Glow Discharge

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

2.3.4 Corona Discharge

When the pressure is increased in case of the glow discharge, the operating 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 an 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. Due to a small active volume occurring only around the pointed electrode, the corona discharge is not very applicable for the industrial chemical reactions dealing with large quantities of gases. However, the principles of this discharge type are used in electrostatic precipitators. (Nasser, 1971)

Previous work of Lui et al. (1995) 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/La₂O₃, 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 consisted of a mixture of methane and oxygen. From the results, great enhancement in both the methane conversion and C₂ selectivity could be observed when the electric discharges and catalysts were present simultaneously in the system. They also found a saturation condition of the discharge current beyond an increase in the voltage which 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 temperatures (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 C₂ 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 has been achieved with a very high methane conversion. That is because of no C₂ activity in the absence of gas discharge, the gas discharge totally modifies the catalytic activity of this catalyst. 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_x.

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 the low temperature (as low as 100°C) methane conversion to C₂ hydrocarbons was achieved by using the PPC/CEP over NaOH treated 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 C₂ yield changed slightly. It was found that increasing oxygen partial pressure in the feed could increase methane conversion but decrease the C₂ selectivity and yield. Increasing residence time also decreased the C₂ 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 to products, ethane and ethylene, was affected by electrode polarity, frequency, and oxygen partial pressure in the feed. Higher C₂ yields were obtained with the AC corona. The methane conversion could be improved to over 50% by increasing the residence time, but the C₂ selectivity decreased. A reaction mechanism including the oxidative dehydrogenation (OXD) of ethane to ethylene was presented to explain the experimental results that can be indicates that application of AC and/or DC gas discharge techniques can be employed for improving the economics of OCM processes.

2.3.5 Dielectric-Barrier Discharge (DBD)

This type of the electric discharges 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 annular space between two concentric cylinders. Either one or both electrodes are covered by the dielectric layer which is commonly made of glass. Many previous works referred to this kind of discharge as the “silent electric discharge” in which its use has been known in many studies on plasma chemical reactions (Nasser, 1971).

The dielectric is the key for proper functioning of the discharge in which it can enable the system to be operated under the atmospheric pressure and a high pressure range. With this dielectric and the usual application of alternating high voltages (50 or 60 Hz power frequency to several kHz), substantial quantities of plasma are created by a large number of the so-called “micro-discharges” in the gas, which are statistically spread in space and time over the entire electrode area. Once, ionization takes place at a location in between the discharge gap, the transported charge moves and accumulates on the surface of the dielectric creating the opposite field to the applied electric field which acts across the gap. After a few nanoseconds, the magnitude of this opposite field will counterbalance the external applied field and the small current or, in other words, the flow of energetic electrons within the micro-discharges across the gap is interrupted. Throughout the course of applying the sinusoidal high voltage, the formation of the micro-discharges will be started again and again once a high enough field is reached in the gap during successive cycles. As a summary, the dielectric serves two functions. The first function is to limit the amount of charges transported by a single micro-discharge and thereby to minimize the chance of arc formation. The other task is to distribute the micro-discharges over the entire electrode area to maximize the chance for every gaseous species to meet the energetic electrons and, hence, be converted into other species. (Nasser, 1971)

Apart from the only present commercial utilization of this DBD principle for the generation of ozone, some recent works on the dielectric-barrier discharge applications for the destruction of the toxic species, such as NO_x , SO_x from the flue gases, H_2S , NH_3 and volatile organic compounds were also the subject of studies (Rosacha et al., 1993; Penetrante et al., 1995; Li et al., 1995; Chang et al., 1996). Their mutual purpose was to monitor the feasibility of using this type of plasma reaction for treating and controlling air

pollution. Though no commercially-promising results have come up from those works, those studies of dielectric-barrier-discharges chemical reactions show an encouraging number of interests attempting to apply the DBD to chemical reaction processes.

Some recent studies of the partial oxidation of methane to methanol under the dielectric-barrier discharge environment are reviewed here. The work of Mallinson et al. in 1987 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. For the mixture of 76% methane and 24% oxygen at 68°C and the reaction residence time of about 12.5 sec, the oxygen conversion could be increased almost linearly with increasing voltage ranged 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 can be drawn that the methane active species participate directly in the reaction.

Bhatnagar et al. (1995) carried out an experimental work to determine the effect of several parameters including the voltage, residence time, methane to oxygen feed ratio and partial pressure on the reaction behaviors i.e., methane conversion and product selectivity. It was concluded that methane conversion decreased significantly and the degree of deep oxidation reactions (CO₂ selectivity) also decreased slightly as an increase in the CH₄/O₂ feed ratio when the system was operated at 9 kV and the total flow rate of 500 cc/min. For the CH₄/O₂ feed ratio of 3 and the total flow rate of 500 cc/min, the system gave the highest values of methane conversion (5.72%) and methanol selectivity (17.76%) 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 decreased since most of the methane was converted

into carbon oxide products. A parallel pathway was found to exist between the production of methanol and ethane. The pathways leading to carbon monoxide might also be paralleled to the first two paths. The undesired pathways leading to the formation of carbon oxides from alcohol and ethane were also observed. It was pointed out that the decomposition of large molecules like ethane resulted in an increase in the methanol selectivity. Preliminary kinetic studies were also presented in this work.

Shepelev et al. (1993) made an attempt to determine the effect of ethane on the methane oxidation reaction. In this work, a small dielectric-barrier discharge (silent electric discharge) reactor with an active plasma zone of 1.6 ml was used. Similar results to the aforementioned work were reported. For example, an increase in voltage led to an increase in carbon oxides selectivity. The oxygen conversion dropped significantly with an increase in the reaction mixture flow rate. As methanol selectivity rose with a decrease in the residence time, it was concluded that this desired product could be further oxidized to carbon oxides at lower flow rates. The formation of ethylene and formaldehyde was also detected in this experimental work. When only ethane and oxygen were simultaneously fed into the reactor, the oxygen consumption was also found to be increased at higher voltages. A dramatic rise in both acetaldehyde and ethylene selectivities was obtained as the voltage was decreased. It was found that a lower selectivity of carbon oxides along with a higher selectivity of ethylene and higher hydrocarbon products could be achieved when the oxygen concentration was lowered for a given inlet flow rate and voltage

Thanyachotpaiboon (1996) studied pure methane conversion using a dielectric-barrier discharge plate-reactor with an active plasma zone of about 231 ml. The results were similar to the oxidative reaction system, such as increasing the voltage or the residence time led to increasing methane

conversion and product selectivities. When methane was diluted with helium, a significant rise in methane conversion was obtained. It was concluded that helium was not only a diluent but also could make methane to be more active. In this work, all products were hydrocarbons and ethane had the highest product selectivity. It was found that, when ethane or propane was introduced with methane into the reactor, the selectivities of C_3^+ hydrocarbon products increased significantly.

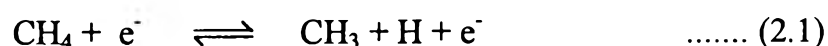
2.4 Kinetics of Reactions

In this part, many mechanisms for the reactions were suggested. The molecules of reactants were activated and converted to excited molecules before becoming stable products. The excited molecules could be in the form of ionized molecules or free radicals. For this study, all reactions were assumed to be free-radical reactions. Because of the mechanisms that include many reversible reactions, it seems to be very complicated to project the exact rate expressions. Overall rate of reactions were determined instead by using only changes in the moles of reactants to calculate the values of all kinetic constants as described clearly in this part.

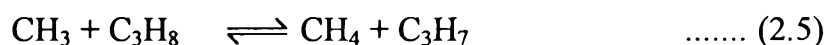
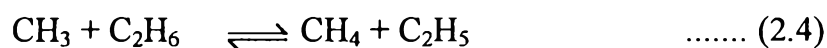
2.4.1 Mechanisms of chemical reactions

2.4.1.1 *Initiation of the Discharge Reaction*

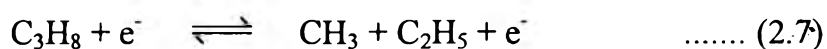
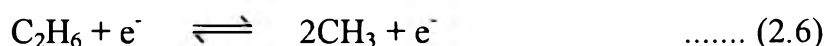
Methane will be activated by discharges to form methyl radicals that can be further activated to CH_2 radical and so on. Ethane and propane can be activated like methane to form ethyl radicals and propyl radicals, etc.



Not only discharges but free radicals can activate stable species by hydrogen abstraction reactions. Methyl radicals can react directly with ethane and propane to form ethyl radical and propyl radical, respectively.



Besides this, discharges can attack ethane or propane molecules to crack into smaller hydrocarbon radicals in decomposition reactions.

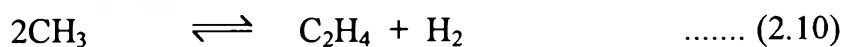
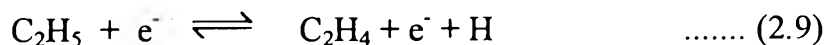
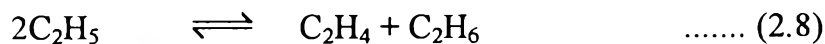


2.4.1.2 Formation of Products

Methyl radicals react themselves to form ethane and propane by the reverse reactions 2.6 and 2.7. With a large quantity hydrogen radicals in the environment, the reverse reactions 2.1, 2.2 and 2.3 will occur as terminations. In addition, they can be produced together with other products by hydrogen-transfer disproportionation such as in reaction 2.8. For other products, free radicals of reactants react further as follows:

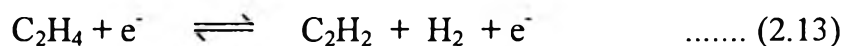
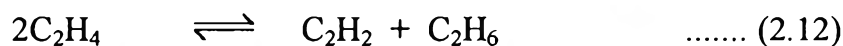
Ethylene Formation:

There are four possibilities of reactions to produce ethylene from both ethane and methane. Three of them are coupling reactions and the rest, reaction 2.9, is dehydrogenation reaction.



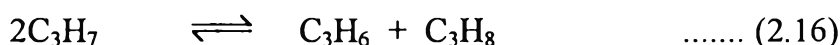
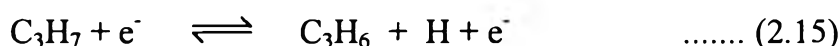
Acetylene Formation:

Acetylene is possibly occurred from ethylene by coupling reaction and dehydrogenation reaction.



Propylene Formation:

There will be three chemical reactions to produce propylene, two coupling reactions and one dehydrogenation reaction (reaction 2.15).



Reaction 2.14 can occur to produce propylene with reaction 2.15 in less H_2 rich environment and to produce propane via reaction 2.3 if there are many H_2 molecules in the system.

Butane Formation:

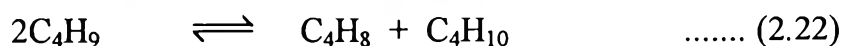
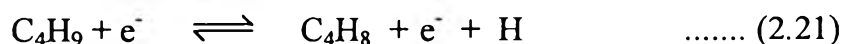
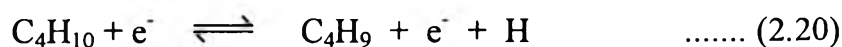
There will be three coupling reactions that possibly occur to form butane.



With the previous discussion, it seems that reaction 2.19 may be better to produce butane in a system with high H_2 concentration.

Butene Formation :

If the discharge of the system is high enough to produce butane, it could be activated by H transfer to butyl radicals that will further react to form butene as shown in reactions 2.20, 2.21 and 2.22.



If the conditions of the system are not sufficient to produce butane, butene might be produced from C_2H_4 radicals as shown in reactions 2.23 and 2.19 in a system with low H_2 concentration.



Moreover, butene can be produced following reaction 2.24 with a coupling reaction of CH_2 radical and propylene.

It can be observed at this point that alkane products are mostly occurred by hydrogenation and coupling reactions while alkene and alkyne products are possibly occurred via both dehydrogenation and coupling reactions. The reactions that can be occurred will depend on a condition of the system. For hydrogenation reaction, it prefers high H_2 rich environment that opposites to dehydrogenation reaction. If a conversion of reactants are too low, the chance of coupling reactions of the same type of radicals is hard to occur.

2.4.2 Determination of Reaction Rates

Overall reaction models were developed for which they explained the reaction behavior for the systems studied. As mentioned before, data for calculating rates of product production were not sufficient, a power law model was chosen to express the reaction rates in terms of the reactants.

2.4.2.1 *Differential Analysis*

Because most of the experiments had reactant conversions below 10%, a differential mode of analysis was chosen. The form of the rate expression for two gas mixture system is given below:

$$R_{CH_4} = \left(-\frac{dP_{CH_4}}{dt} \right) = k_1 P_{CH_4}^{a_1} P_B^{b_1} \quad \text{..... (2.25)}$$

$$R_B = \left(-\frac{dP_B}{dt} \right) = k_2 P_{CH_4}^{a_2} P_B^{b_2} \quad \text{..... (2.26)}$$

where P_{CH_4} = partial pressure of methane in feed

- P_B = partial pressure of ethane or propane in feed
 k_i = rate constant, min^{-1}
 a_i, b_i = orders of methane and ethane or propane, respectively
 t = residence time

The partial pressures of the reactants used were averaged values between inlet and outlet partial pressure of each reactant. Using the solver in the Excel program, the parameters k_i , a_i and b_i were obtained.

2.4.2.2 Plug Flow Model

Since the volume of the reactor was large, the residence times for all experiments were quite high to be considered a differential reactor. Thus the assumption of differential conditions may not be valid in some systems that have conversion more than 10%. Due to this, it was better to apply a plug flow model for the reaction system.

In this case also the conversion rate of reactants were represented by power law equations (equations 2.25, 2.26). In the experiments carried out, the partial pressure of methane in the feed was very high. Since the fractional conversion of methane was below 10% for most of the experiments, the partial pressure of methane remained essentially constant during the course of the reaction. Thus the term corresponding to the partial pressure of methane can be lumped with the rate constant to obtain an apparent rate constant. Equation 2.26 becomes

$$\left(-\frac{dP_B}{dt}\right) = k_2' P_B^{b_2} \quad \text{..... (2.27)}$$

where $k_2' = \text{apparent rate constant, min}^{-1}$
 $= k_2 P_{\text{CH}_4}^{a_2}$

Integrating the above equation, we have

$$P_B = [k_2' (1-b_2) t + P_{B_i}^{(1-b_2)}]^{1/(1-b_2)} \quad \text{..... (2.28)}$$

where P_{B_i} = initial partial pressure of ethane or propane in feed

Solver on the Excel program was used to find the parameters, k_2' and b_2 . The data points used for the regression included the varying residence time experiments and varying ratio experiments.

Equation 2.25 can be written as

$$\begin{aligned} \left(-\frac{dP_{\text{CH}_4}}{dt}\right) &= k_1' P_{\text{B}}^{b_1} \\ &= k_1' [-k_2'(1-b_2)t + P_{\text{Bi}}^{(1-b_2)}]^{b_1/(1-b_2)} \end{aligned} \quad \text{..... (2.29)}$$

where $k_1' =$ apparent rate constant, min^{-1}
 $= k_1 P_{\text{CH}_4}^{a_1}$

Integrating the above equation we get

$$P_{\text{CH}_4} = \frac{k_1'}{k_2'(b_1+1-b_2)} ([-k_2'(1-b_2)t + P_{\text{Bi}}^{(1-b_2)}]^{1+b_1/(1-b_2)} - P_{\text{Bi}}^{(b_1+1-b_2)}) + P_{\text{CH}_4i} \quad \text{..... (2.30)}$$

where $P_{\text{CH}_4i} =$ initial partial pressure of methane in feed

The parameters k_1' and b_2 are obtained from regression.

To estimated the exponents for the partial pressure of methane, it was decided to do some experiments in which ethane or propane was present in large amounts in the feed in order to maintain a nearly constant ethane or propane partial pressure. The equations 2.25 and 2.26, in terms of apparent rate constants, are shown below

$$\left(-\frac{dP_{\text{CH}_4}}{d\tau}\right) = k_1'' P_{\text{CH}_4}^{a_1} \quad \text{..... (2.31)}$$

$$\left(-\frac{dP_{\text{B}}}{d\tau}\right) = k_2'' P_{\text{CH}_4}^{a_2} \quad \text{..... (2.32)}$$

where $k_1'' =$ apparent rate constant, min^{-1}
 $= k_1 P_{\text{B}}^{b_1}$

$k_2'' =$ apparent rate constant, min^{-1}
 $= k_2 P_{\text{B}}^{b_2}$

The procedure to determine the parameters was similar to the one followed in the previous case.

To estimate the rate constants k_1 and k_2 we again used the data in which the concentration of methane is high in the feed and is nearly constant during

the reaction. After assuming partial pressure of methane to be constant and integrating the equation 2.26, we get

$$P_B = [k_2' P_{CH_4}^{a_2} (1-b_2) \tau + P_{Bi}^{(1-b_2)}]^{1/(1-b_2)} \quad \text{..... (2.33)}$$

where k_2' = apparent rate constant, min^{-1}

After substituting the values of a_2 and b_2 , the above equation was regressed to obtain the value of k_2 . Substituting 2.33 into 2.25 and integrating, we get an expression for partial pressure of methane. The value of k_1 can be estimated from the regression analysis.