



## CHAPTER II

### CARBON DIOXIDE REFORMING WITH METHANE IN LOW TEMPERATURE PLASMAS

#### 2.1 Abstract

There are increasing concerns about the emissions of greenhouse gases, especially carbon dioxide and methane to the atmosphere. A number of research work has been done in methane catalytic reforming with carbon dioxide to reduce atmospheric emissions and to produce synthesis gas (carbon monoxide and hydrogen). Unfortunately methane catalytic reforming with carbon dioxide has several drawbacks including coke formation and high temperature operation. In this work, a low temperature plasma reactor was used to facilitate this reaction in the absence of catalysts and at ambient conditions. The reactor consisted of wire and plate electrodes in a quartz tube that was operated with carbon dioxide to methane feed mole ratios of 0.5-3, input low side voltages of 32-72 V, input frequencies of 300 – 800 Hz, flowrates of 50-125 sccm, and a gap widths between the two electrodes of 0.6-1.5 cm. It was found that the methane and carbon dioxide conversions both increased with increasing voltage, gap width, and carbon dioxide to methane feed mole ratio but decreased with increasing frequency, and flowrate. Carbon dioxide conversion is always lower than methane conversion. The  $H_2/CO$  ratio depends on only on the  $CH_4/CO_2$  ratio.

#### 2.2 Introduction

With increasing population and rapid technology development, it is possible that we have begun to encounter the alteration of the climate. Greenhouse gases, which include carbon dioxide, methane, ozone, halocarbons and nitrous oxide, mainly come from the combustion of fossil fuels (coal, oil, and natural gas) for power generation and transportation. One of the more useful reactions for reducing the concentration of methane and carbon dioxide, major greenhouse gases and the main component in natural gas, especially in Asia which has high carbon dioxide

content, is carbon dioxide reforming with methane (reaction 2.1) for production of synthesis gas (carbon monoxide and hydrogen) at a lower H<sub>2</sub>/CO ratio compared to steam reforming of methane (reaction 2.2), which is the conventional process for synthesis gas production.



The carbon dioxide reforming with methane reaction is highly endothermic. It can be utilized to transfer and store energy (e.g. Solar energy or electricity) in the form of carbon monoxide and hydrogen. Although the conversion of carbon dioxide and methane to syngas has potential applications in industry and also has environmental advantages, it has only occasionally been practically commercialized. A major problem is the deactivation of the catalyst due to carbon deposition (reactions 2.3 and 2.4) at the desired reaction conditions.



So far, no effective commercial catalyst exists which can operate without carbon formation [1]. Another drawback of catalytic carbon dioxide reforming with methane is the high process temperature required of more than 800 °C. Therefore, solving these problems to find ways to operate this process at milder reaction conditions is of great interest.

In this work, a low temperature plasma reactor was used to facilitate this reaction at lower temperatures. This has been shown to be possible in other methane conversion studies without carbon dioxide, such as helping in the catalytic conversion of methane over Sr/La<sub>2</sub>O<sub>3</sub> [2].

A plasma is a quasineutral gas consisting of charged and neutral gas molecules with a collective behavior in which the charged molecules follow the path of the electric field. It is in equilibrium when the kinetic energy of the charged

particles and neutral species are the same. The non-thermal, also called cold, plasma, and its non-equilibrium properties, high electron temperature and low bulk gas temperature, provide the capability for initiating chemical reactions at low temperature and with lower energy input.

Corona discharge and dielectric barrier discharge (DBD) techniques are two of the commonly used methods for producing non-equilibrium plasmas at atmospheric pressure [3], [4], [5]. Because the corona is particularly easy to establish, it has had wide application in a variety of processes such as electrostatic precipitation, electro-photography and also synthesis of chemicals [3]. The electron energy, which corresponds to the electron temperature, is restricted to less than 6 eV in the corona discharge [6]. These relatively low-energy electrons have insufficient energy to ionize methane, which has an ionization potential greater than 12 eV [7], but high enough to dissociate CH<sub>4</sub> and CO<sub>2</sub> molecules with dissociation energies of 4.5 and 5.5 eV, respectively (reactions 2.5 and 2.6) [1].



The utilization of non-equilibrium plasma techniques for carbon dioxide reforming with methane has been studied in the dielectric barrier discharge. The combination of solid state catalysts with a dielectric-barrier discharge was studied for carbon dioxide reforming of methane. It is shown that the use of a catalytic coating in the discharge can have a promoting effect on the plasma chemistry and the use of the ceramic foams improved the temperature and lowered the undesired temperature increase [4]. The dielectric barrier discharge has also been used to investigate the effect of a non-equilibrium discharge on the production of synthesis gas from two major greenhouse gases carbon dioxide and methane. A pronounced synergistic effect caused by free radical reactions was observed using these two gases simultaneously with a minimum required specific energy of 40 eV/molecule for the production of syngas and the highest energy efficiency (electric energy converted to chemical energy in the syngas) reached so far was about 7%[1]. The

effect of a third body (helium) was also investigated in for he DBD for carbon dioxide reforming [8].

### 2.3 Experimental

The flow rate of feed gases, methane and carbon dioxide, were controlled by a set of mass flow controllers supplied by SIERRA Instrument, Inc. The feed gases were introduced downward through the reactor and analyzed on-line by a Perkin-Elmer gas chromatograph, with thermal conductivity (TCD) and flame ionization (FID) detectors. The exhaust gas from the reactor was introduced into a condenser cooled by a mixture of dry ice and acetone that was used to remove the condensable products. All experiments were carried out at atmosphere pressure. The power supply unit consisted of an AC power supply for converting domestic AC power 220 V, 50 Hz, using a function generator for varying the frequency in the range of 300 to 800 Hz with a sinusoidal waveform. A few experiments used a square waveform. The output was then transmitted to a high voltage alternating current (HVAC) transformer. The HVAC could step up the low side voltage to the high side voltage by nominal factor of 125 at 60 Hz. This factor may not be constant with changes in frequency due to changes in power factor because of the capacitive nature of the reactor system. The electrodes were connected to the HVAC by stainless steel rods. The discharge occurred in a quartz tube with an i.d. of 8 mm between two stainless steel electrodes. The upper wire electrode is centered axially within the reactor tube, while the lower electrode is a circular plate with eight holes to allow gas to pass through the reactor and is positioned perpendicular to the reactor axis. An Omega K-type thermocouple was attached to the outside wall of the reactor at a central point between the two electrodes for monitoring the reaction temperature. Measurement of the gas temperature of the corona is complicated by the discharge, which can occur between the wire tip and the thermocouple. Therefore, the thermocouple was placed only after collecting all data. The gas discharge is usually initiated at room temperature and the gas is self-heated by the plasma. All the experiments were operated at atmospheric pressure.

For this system, the conversions are defined as:

Conversion of methane = (moles of CH<sub>4</sub> consumed/moles of CH<sub>4</sub> introduced) x 100 %

Conversion of carbon dioxide = (moles of CO<sub>2</sub> consumed/moles of CO<sub>2</sub> introduced) x 100 %

H<sub>2</sub>/CO mole ratio = moles of H<sub>2</sub> produced/moles of CO produced

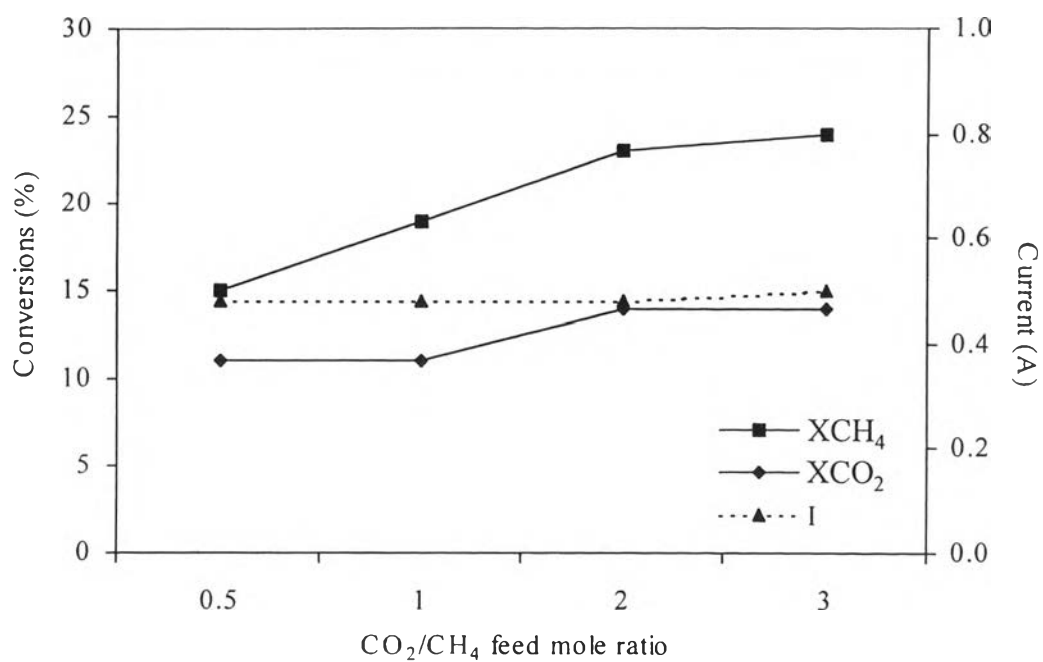
CO/C<sub>2</sub> mole ratio = moles of CO produced/moles of ethane, ethylene and acetylene produced

In some cases, at lower methane conversions, the product material balances could be below 50%, however in most cases, analytical improvements usually would allow a product balance to the 80-90% range. Water was not quantified.

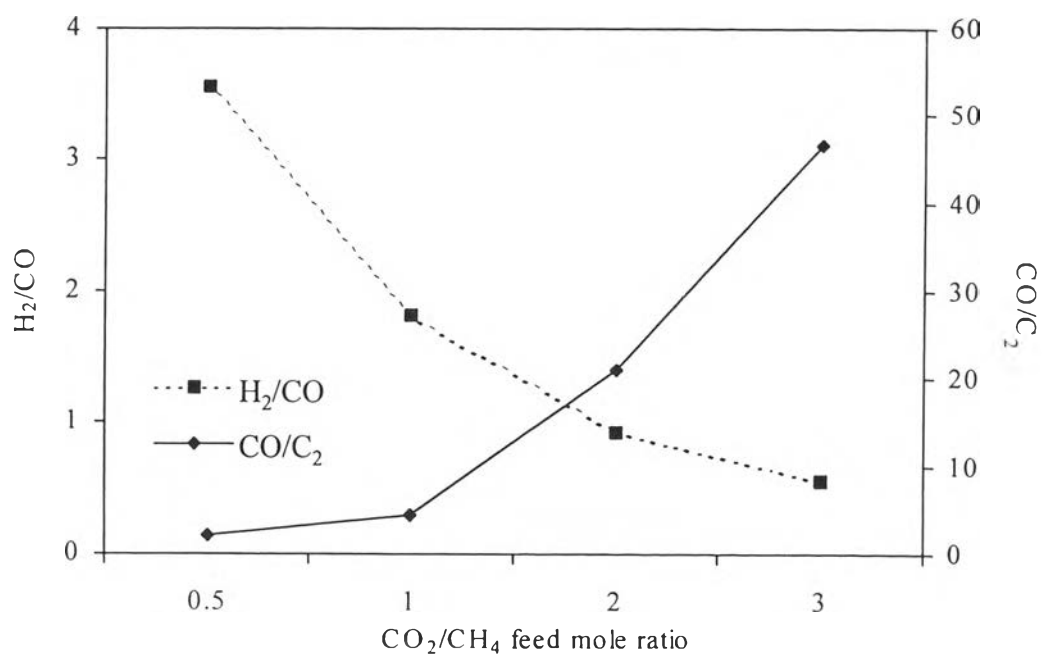
## 2.4 Results and Discussion

A base “standard” experiment in this study has a feed mixture of carbon dioxide and methane at a 3:1 ratio flowing at 50 sccm through a quartz tube with an inner diameter of 8 mm. This non-stoichiometric ratio was chosen to minimize carbon formation. The gas gap between the electrodes was set at 1.2 cm. This results in a residence time of 0.72 seconds. The applied voltage was a sinusoidal wave fixed at 48 volt of low side voltage with a frequency set at 700 Hz.

Figure 2.1 shows the effect of varying the CO<sub>2</sub>/CH<sub>4</sub> feed mole ratio. The CO<sub>2</sub>/CH<sub>4</sub> ratio was varied from 0.5 to 3 and has no significant effect on carbon dioxide conversion. The methane conversion increases from 15 to 24 percent. The C<sub>2</sub> production rapidly decreases while carbon monoxide rapidly increases which makes the CO/C<sub>2</sub> ratio increase from about 1 to 23. The hydrogen production slightly decreases which makes the H<sub>2</sub>/CO mole ratio in the product gas decrease from 3.6 to 0.6. The current is constant at about 0.48 A.



(a)



(b)

**Figure 2.1** Effect of  $\text{CO}_2/\text{CH}_4$  feed mole ratio (a) conversions and current (b)  $\text{H}_2/\text{CO}$  and  $\text{CO}/\text{C}_2$ ; overall flowrate, 50 sccm; input low side voltage, 48 V; input frequency, 700 Hz; gap width, 1.2 cm.

The dissociative attachment of carbon dioxide (reaction 2.6), which occurs within the range of electron energies of this corona discharge, can produce both carbon monoxide and negatively charged oxygen species ( $O^-$ ), resulting in increasing carbon monoxide. This  $O^-$  can combine into molecule oxygen (reaction 2.7) or abstract hydrogen from the methane molecule to form the methyl radicals in the corona discharge (reaction 2.8), resulting in increasing methane conversion with increasing carbon dioxide content.



Subsequently, methyl radicals can combine to form  $C_2$  hydrocarbon. The carbon dioxide conversion slowly increases with increasing  $CO_2/CH_4$  ratio, even though dissociative attachment increases with increasing carbon dioxide content in the feed because carbon dioxide may also be “re” formed, resulting in lower net carbon dioxide conversion. Oxygen molecules, which can be produced from reaction 2.7, were not found in our experiments because oxygen easily forms negative ions either by direct attachment or dissociative attachment and were consumed in the reaction.  $O^-$  increases with increasing carbon dioxide content probably increases the rate of oxidation of methane and  $C_2$  products to produce carbon monoxide and carbon dioxide as suggested by the increasing  $CO/C_2$  ratio. Carbon formation occurs more easily in the reactor with high methane content conditions because there is not sufficient  $O^-$  to react with the carbon. The  $H_2/CO$  ratio is strongly dependent on the  $CO_2/CH_4$  ratio. Thus, the  $H_2/CO$  ratio can be adjusted into the desirable ratio for industrial processes (e.g. lower  $H_2/CO$  ratios of about 1 for producing acetic acid, and about 2 for methanol synthesis).

To investigate the effect of applied voltage on the system, the applied voltage was varied from 48 to 72 volts of low side voltage. The results are shown in Figure 2.2. The methane and carbon dioxide conversions increase with increasing applied voltage. The  $H_2/CO$  mole ratio increases from 0.3 at just above the breakdown voltage and then becomes constant at about 0.56 with increasing voltage. The  $CO/C_2$

also decreases and is relatively constant at higher voltages. The current increases with increasing voltage.

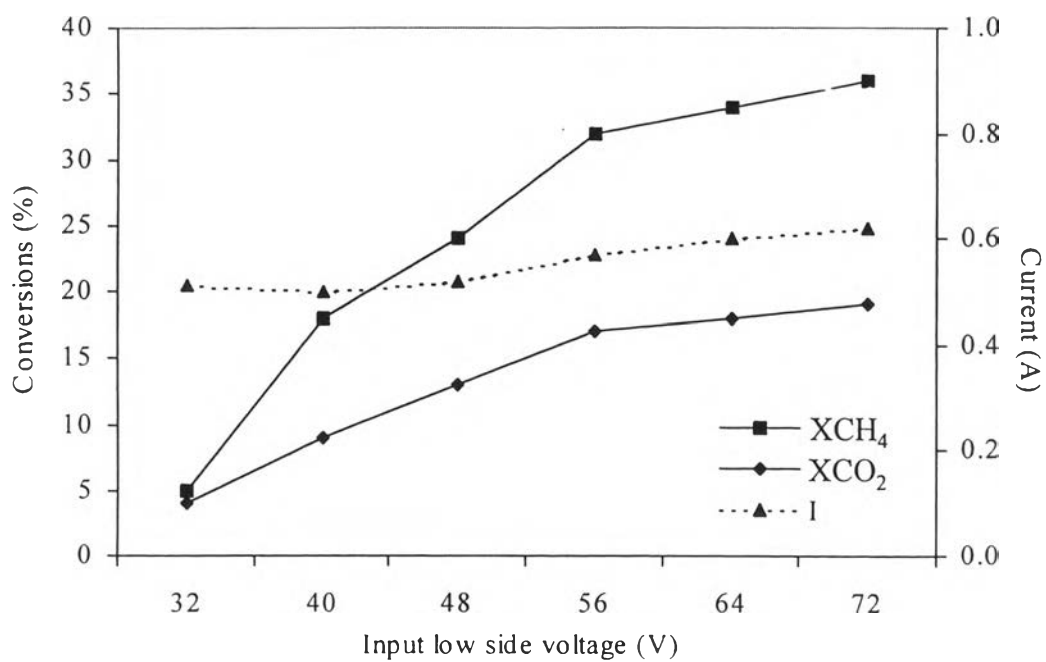
In contrast to increases in the applied voltage, methane and carbon dioxide conversions decrease with increasing frequency, as shown in Figure 2.3, using an input low side voltage of 60 V. Current also decreases with increasing frequency. The frequency has no strong effect on the H<sub>2</sub>/CO mole ratio. As the ac discharge is applied, each electrode performs alternatively as anode or cathode. The alternating behavior has proven effective in eliminating contaminant accumulation on the electrodes, which shows that the system behavior is significantly different with ac discharges than with dc [5]. The capacitive nature of the reactor creates a phase lag between the voltage and current waveforms and this increases with higher frequency, thus reducing the power factor and power input at constant applied voltage.

The methane and carbon dioxide conversions change in the same way with the current, which indicates more available electrons are in the system to initiate the reactions. Unfortunately, the conversion cannot reach 100% by increasing voltage and decreasing frequency because the discharge becomes unstable due to carbon formation on both electrodes as well as the quartz tube wall (reaction 2.9).

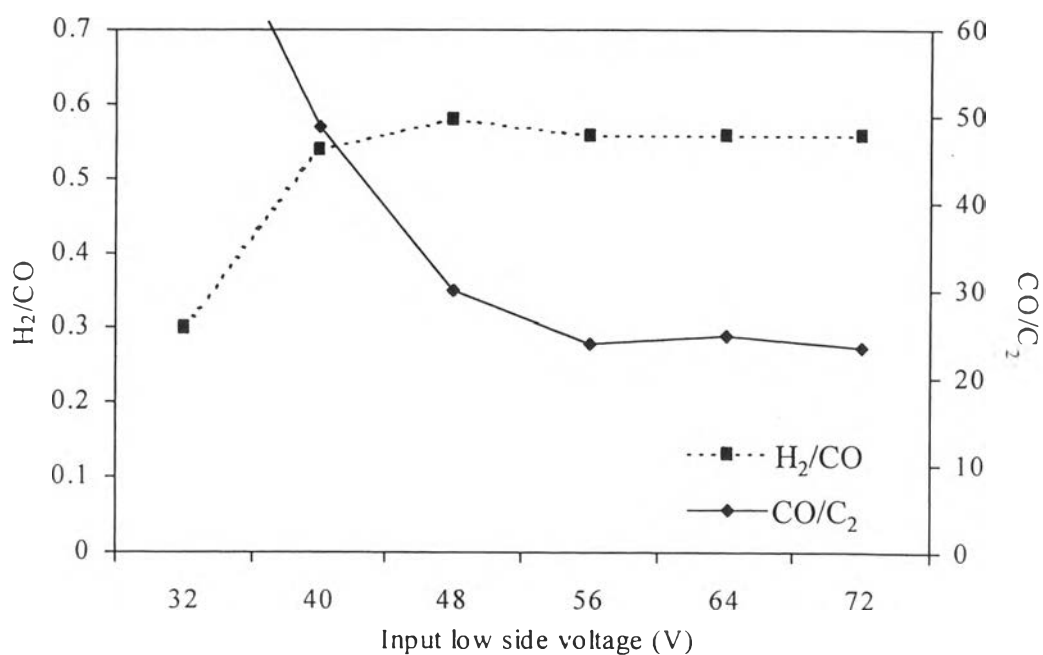


That the carbon atoms from methane and carbon dioxide favor formation of carbon monoxide more than C<sub>2</sub> hydrocarbons at low current implies that carbon monoxide formation is easier than the coupling of methane. At high current, carbon monoxide can react further to form carbon leading to decreasing carbon monoxide and the CO/C<sub>2</sub> but increasing carbon formation. The hydrogen atoms (or OH) tend to form H<sub>2</sub>O more than hydrogen, so hydrogen decreases at high voltage and low frequency. With increasing H<sub>2</sub>O formation, the oxygen atoms in the system are not sufficient to inhibit carbon formation. The hydrogen and carbon monoxide decrease at the same rate with increasing current so the H<sub>2</sub>/CO is almost constant.



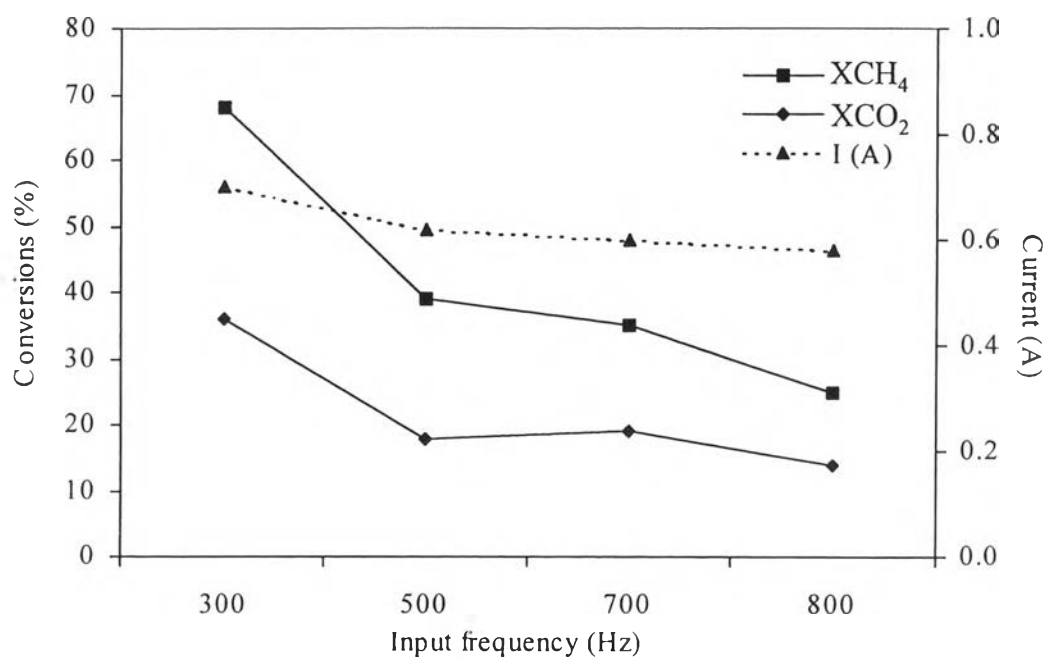


(a)

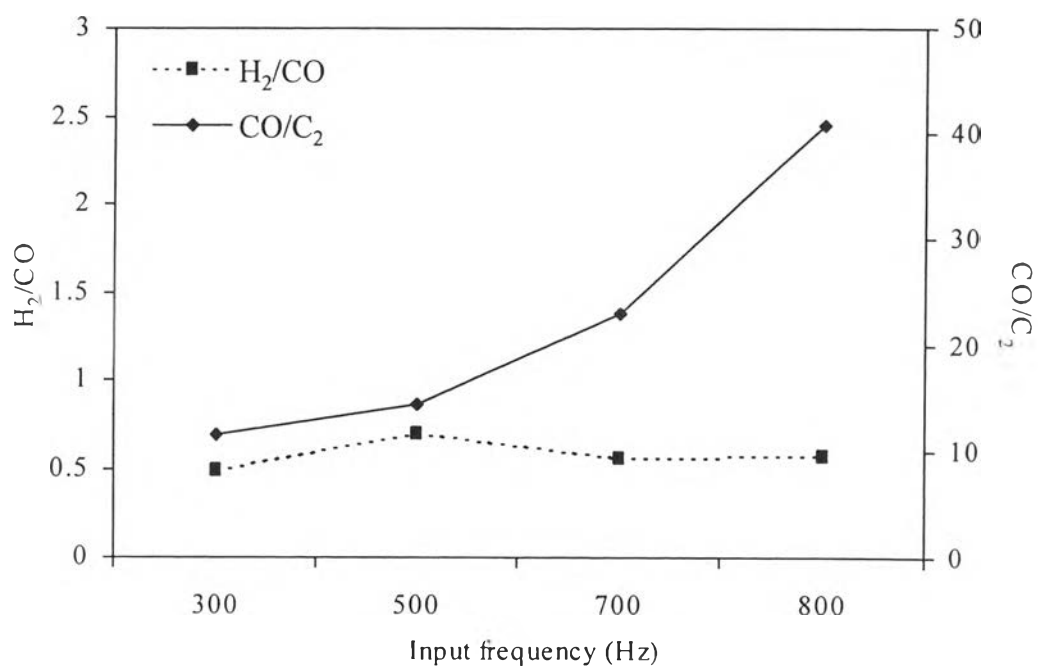


(b)

Figure 2.2 Effect of input voltage (a) conversions and current (b) H<sub>2</sub>/CO and CO/C<sub>2</sub>; overall flowrate, 50 sccm; input frequency, 700 Hz; gap width, 1.2 cm; CO<sub>2</sub>/CH<sub>4</sub> feed mole ratio, 3.

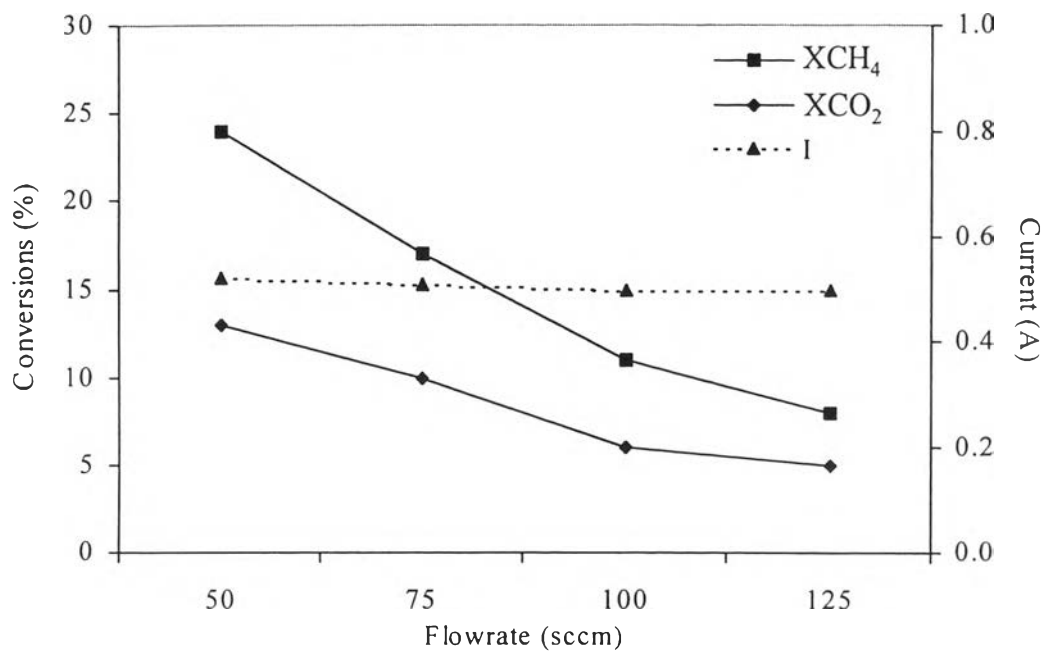


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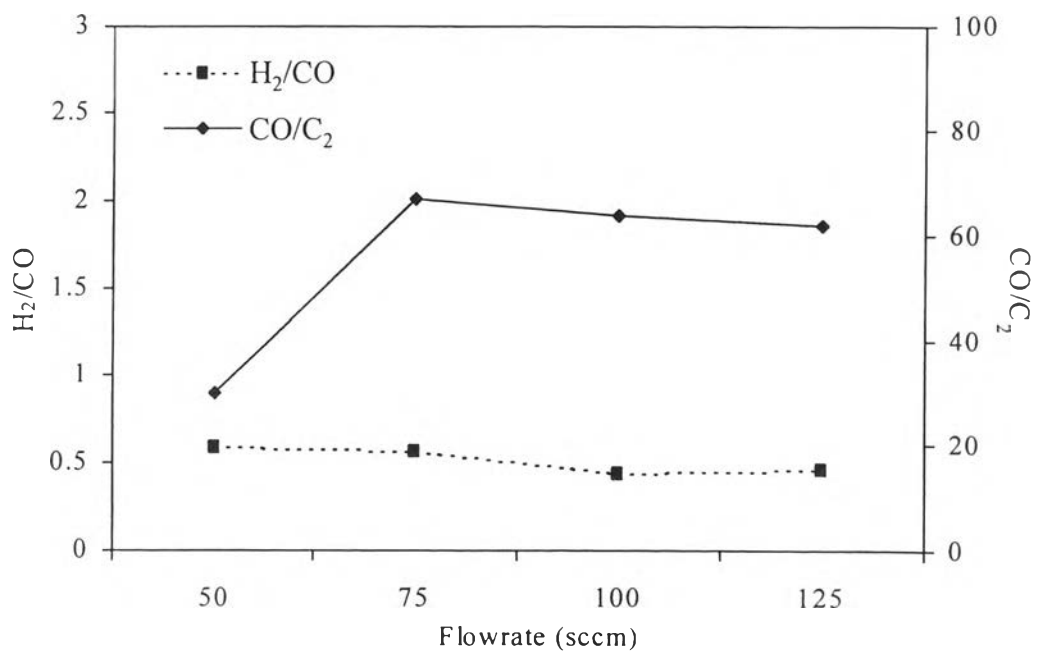


(b)

**Figure 2.3** Effect of input frequency (a) conversions and current (b)  $H_2/CO$  and  $CO/C_2$ ; overall flowrate, 50 sccm; gap width, 1.2 cm; input low side voltage, 60 V;  $CO_2/CH_4$  feed mole ratio, 3.



(a)



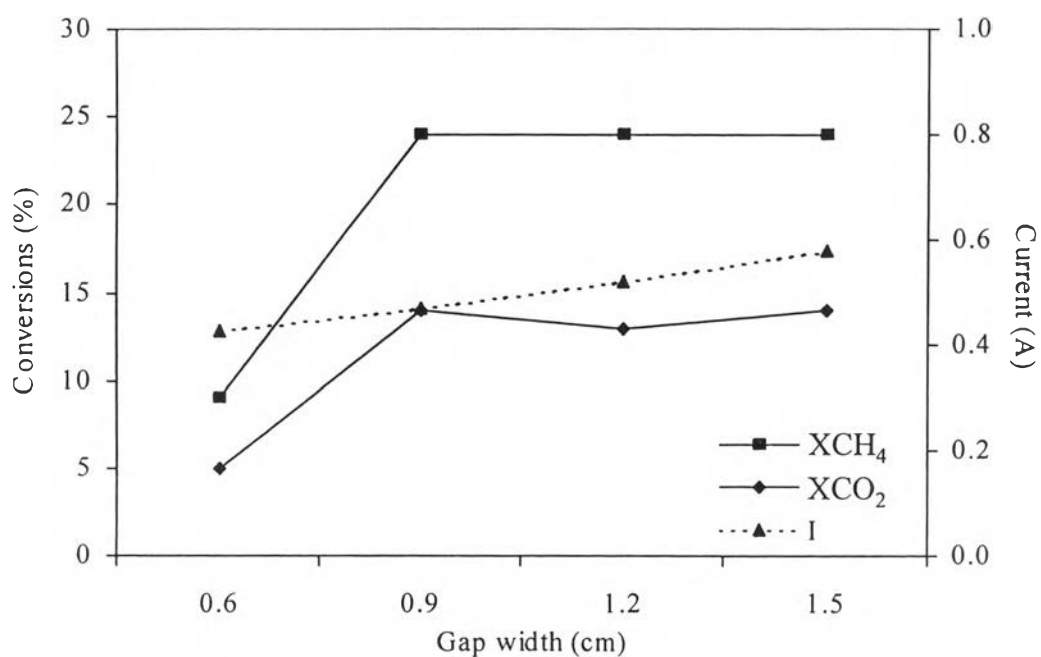
(b)

**Figure 2.4** Effect of flowrate (a) conversions and current (b)  $H_2/CO$  and  $CO/C_2$ ; gap width, 1.2 cm; input lowside voltage, 48 V; input frequency, 700 Hz;  $CO_2/CH_4$  feed mole ratio, 3.

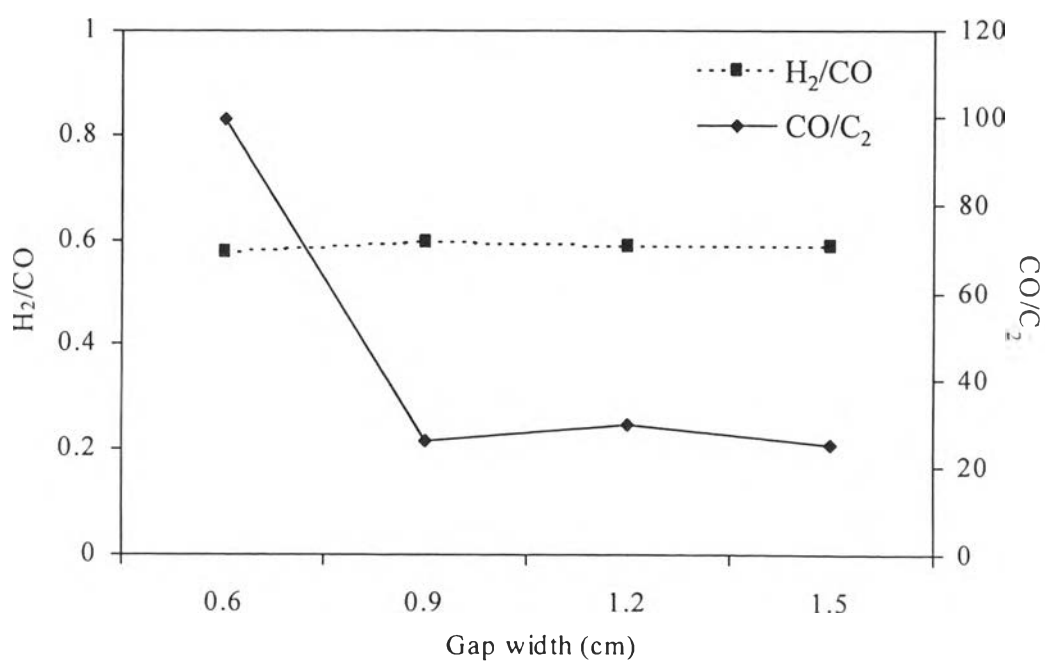
The flow rate was varied from 50 - 125 sccm, which corresponds to residence times of 0.29 to 0.72 seconds. Figure 2.4 shows that the methane and carbon dioxide conversions decrease with increasing flow rates as expected due to decreased residence times. The current remains fairly constant at 0.5 A over most of the flow rate range. Paschens Law predicts that the power and current remain constant with increases in the flow rate as are observed here. The flowrate has no strong influence on the  $H_2/CO$  and  $CO/C_2$  ratios.

Figure 2.5 shows the effect of gap width, varied between 0.6 and 1.5 cm, which corresponds to residence times of 0.36-0.91 seconds at the constant flowrate of 50 sccm. The methane and carbon dioxide conversion appear to increase with increasing gap width and then start to level off at the gap width of 0.9 cm. As the gap width is increased, the  $H_2/CO$  ratio is nearly constant. The two main effects of increased gap width are increased residence times and decreased electric field strength ( $E/\text{gap width}$ ). Larger gap widths also allow electrons to travel further distances between the electrodes, increasing the chance for inelastic collisions and subsequent reactions. As mentioned earlier, the current remains constant with increases in the flow rate. However the current slightly increases with increasing gap width because of the effect of the electric field strength. At increased gap width, higher current and power are required to maintain the same voltage. At small gap widths, the effect of residence time overcomes the effect of the electric field strength and gives lower conversions. At the larger gap width, the conversions are nearly constant because of the compensation of residence time and electric field strength effects.

For all experiments the temperature is proportional to the current. These experiments operate at room temperature (feed temperature) without an external heat source or insulation. The carbon dioxide reforming with methane (reaction 2.1) is a strongly endothermic reaction. The increase of temperature comes from the discharge itself (energy release from the discharge). The heat release from the reaction would be expected to lower the temperature.

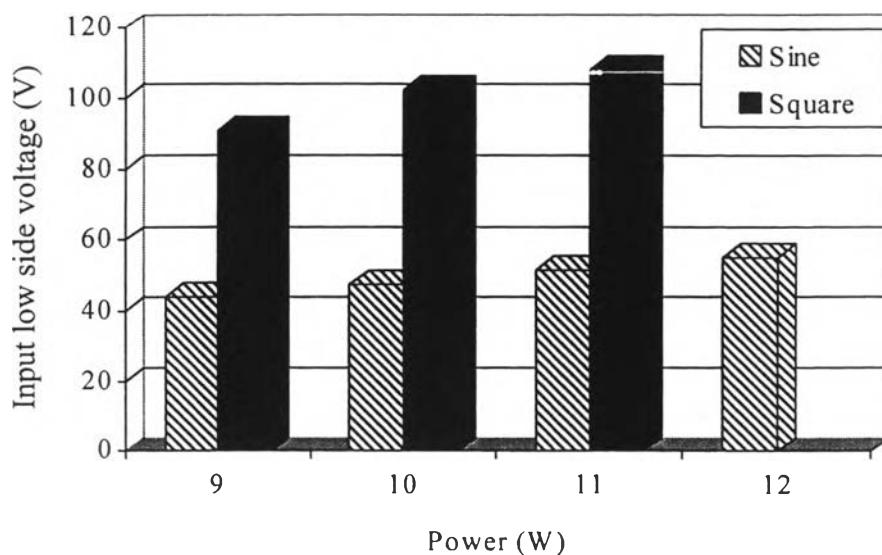


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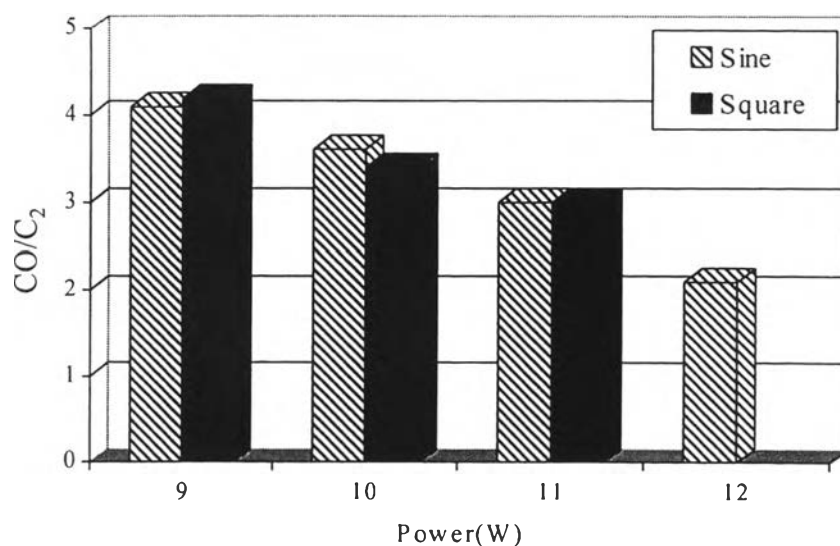


(b)

**Figure 2.5** Effect of gap width (a) conversions and current (b) H<sub>2</sub>/CO and CO/C<sub>2</sub>; overall flowrate, 50 sccm; input low side voltage, 48 V; input frequency, 700 Hz; CO<sub>2</sub>/CH<sub>4</sub> feed mole ratio, 3.



(a)



(b)

**Figure 2.6** Effect of waveform: (a) Input low side voltage vs. Power (b) CO/C<sub>2</sub> vs. Power; overall flowrate, 100 sccm; input frequency, 700 Hz; gap width, 1.0 cm; CO<sub>2</sub>/CH<sub>4</sub> feed mole ratio, 3.

The comparison between the effect of using a square waveform also has been briefly examined at a gap width of 1 cm, a flowrate of 100 sccm (residence time of 0.23 seconds), and a carbon dioxide to methane feed mole ratio of 3. The results

show, in Figure 2.6, that to obtain the same power, the voltage has to be higher in the case of the square wave compared to the sine wave because the power factor is lower. The discharge becomes stable at the same power of 9 W. Data at 12 W using the square wave could not be obtained because of the limitation of the transformer. The current, methane conversion, carbon dioxide conversion, and product distribution are nearly the same at the same power with the different waveform.

The limitation for improving the capacity and efficiency of carbon dioxide reforming with methane by using corona discharge is carbon formation. The discharge becomes unstable due to carbon formation at high current and high methane content in the feed. Preliminary results suggest that the “carbon free” operating region can be expanded by using the square wave, which has to be studied further to optimize the capacity and efficiency.

## 2.5 Conclusions

1. For all of the experiments, the CO<sub>2</sub> conversion is always lower than the CH<sub>4</sub> conversion because the dissociation energy of CO<sub>2</sub> (5.5 eV) is higher than the dissociation energy of methane (4.5 eV) and CO<sub>2</sub> can be produced from reverse reaction of CO<sub>2</sub> dissociative reaction.

2. The major product is syngas (hydrogen and carbon monoxide), with small amounts of acetylene. Very small amounts of ethane, ethylene and methanol were found in some conditions.

3. The hydrogen to carbon monoxide mole ratio was not sensitive to applied voltage, frequency, gap width or flowrate. The only parameter that strongly effects the hydrogen to carbon monoxide ratio is methane to carbon dioxide ratio.

4. The waveform does not effect the conversions and product distribution, but is attractive for study because of a larger operating region without carbon formation.

## 2.6 Acknowledgements

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## 2.7 References

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