CHAPTER III
EXPERIMENTAL SECTION

The purpose of this work was to determine feasibility of the chemical reaction of methane and carbon dioxide in an electric discharge environment and to study the effects of carbon dioxide to methane ratio ,residence time and applied voltage on the methane conversion.

3.1 Experimental Setup

The schematic diagram of the entire reaction system used throughout this study is illustrated in Figure 3.1. The system can be categorized into three sections namely, the reactants make-up section, the reaction section and the sample collecting and analysis section.

3.1.1 The reactants make-up section

All reactant gases used in this work were supplied in gas cylinders by Thai Industrial Gases Public Co., Ltd. The specification of these gases is listed in Table 3.1. All of the reactants were used without any further purification. The flow rates of the gases fed into the reactor were controlled by a set of mass flow controllers and transducers supplied by SIERRA® Instrument, Inc. The error of the apparatus was reported to be less than 1%. The pressure read out at the discharge end of all pressure regulators connected to the gas
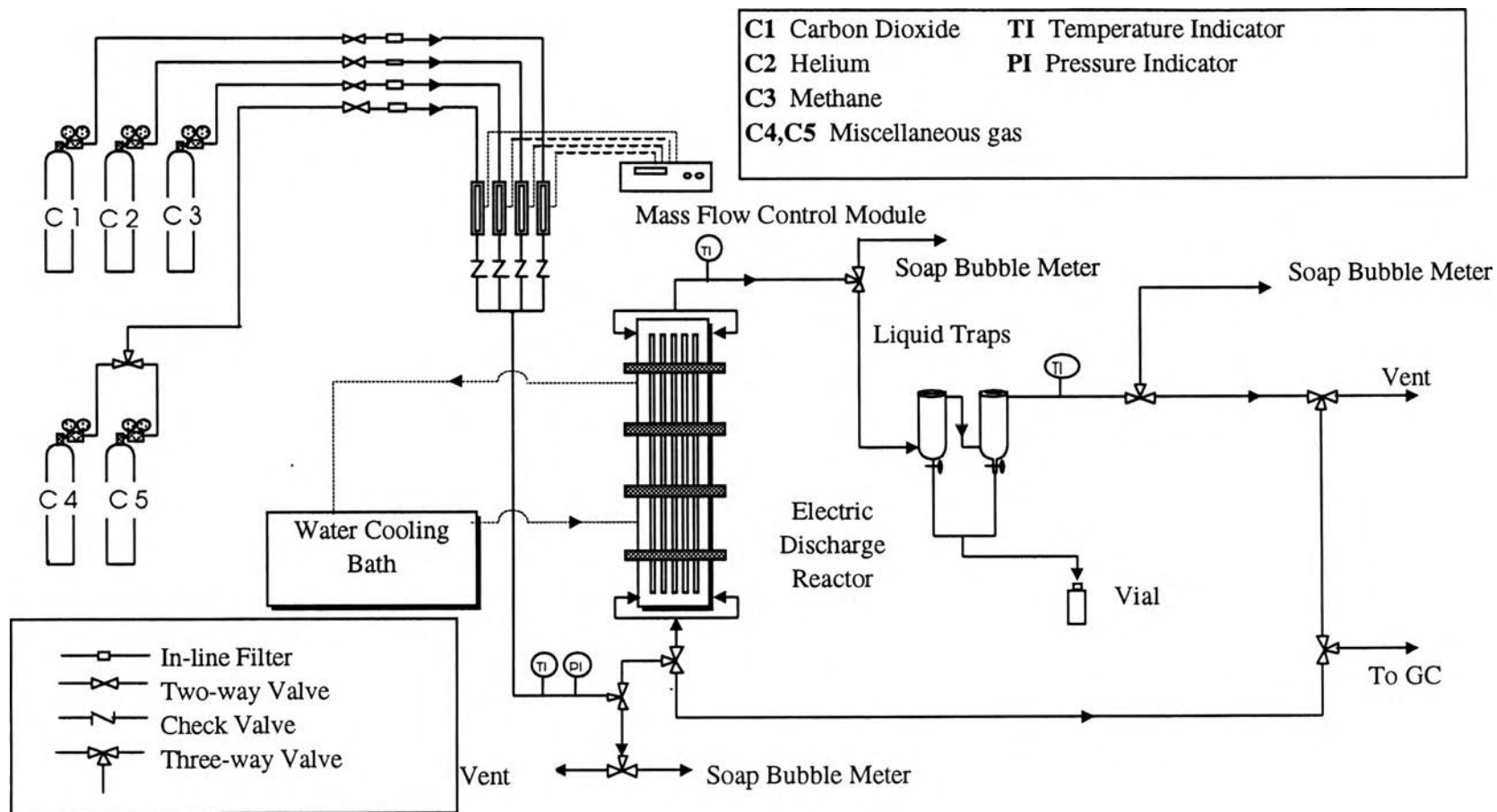
Figure 3.1 The schematic diagram of experimental equipment.

cylinders was maintained in the range of 20-30 psi. The 0.7 μm in-line filters were placed upstream of all the mass flow transducers in order to trap any

Table 3.1 Specification of the gases used in this experiment

Gas	Purity (%)
Methane	99.999
Carbon dioxide	99.999
Helium	99.999

foreign particles, which would be responsible for the improper function of the transducers. The Check valves supplied by Swagelok® were also placed downstream of all transducers to prevent any back flows. A pressure gauge was placed downstream of the mass flow control module just prior to the inlet zone of the reactor to monitor the total pressure of the gaseous stream. Since all the experiments were conducted at atmospheric pressure, the gauge had to read a zero. Also, this gauge was to ensure that the pressure in the overall system was not too high to cause leakage around the reactor.

3.1.2 Reaction Section

This section consisted of a DBD reactor and other accessories including a water cooling bath and a power supply unit.

3.1.2.1 DBD Reactor The configuration of the DBD reactor is depicted in Figure 3.2. Descriptively, this reactor was composed of two metal electrodes made of aluminum plates. One side of the aluminum plate was covered by a dielectric barrier which was made of glass. The thickness of this glass plate was about 0.3 cm. A Teflon spacer was then placed between the dielectric and the other aluminum plate to allow the space for the gas flow through the discharge zone. The active reaction volume for the electric discharges environment was 216 cm^3. This volume was defined by the
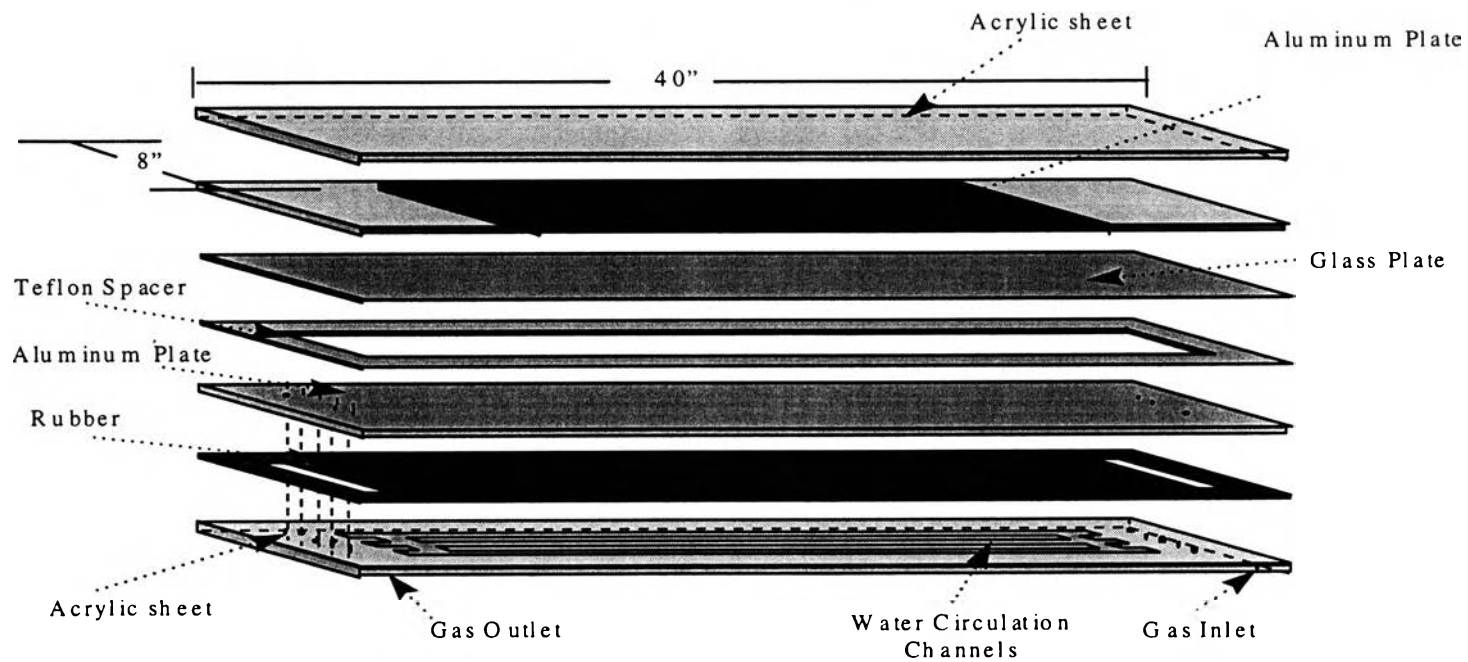
Figure 3.2 Configuration of DBD reactor.

thickness of the Teflon spacer and the projected area in which each aluminum plate could see each other. The other side of the aluminum plate, i.e., the one that was not covered by the glass plate, was subjected to cooling water to absorb the heat produced from the reaction zone. The cooling water temperature of 18°C was controlled in all the runs.

3.1.2.2 Power Supply System The schematic diagram of the power supply unit in series is illustrated in Figure 3.3. The domestic AC input of 220 V and 50 Hz was supplied through a variable transformer which was used for varying the voltage from 0 to 110 V. Thereafter, the output of this transformer was transmitted to the secondary high voltage (HVAC) transformer having a power multiplying factor of 125. The final output obtained from the HVAC transformer was then sent to the reactor for the generation of electric discharges. A voltmeter was connected to both input electrodes of HVAC transformer to measure the exact voltage supplied to it.

3.1.3 Sample collecting and analysis section.

The volumetric flow rates of the gaseous streams at both the inlet and outlet of the reactor were calibrated by using a soap bubble meter. During each run, the change in volumetric flow rate was extremely very small and then the flow rate was assumed to be constant. Two liquid traps were placed at the reactor outlet followed by connection of the gas line to a Gas Chromatography apparatus. Both liquid traps were maintained at the temperature ranging from -20 to -10°C to cool and collect any liquid products that might be produced from the reactions. No any liquid products could, however, be observed in any run when it reached a steady state.

The complete analysis of the gaseous products stream flowing out from the reactor was carried out using a Perkin-Elmer "Autosystem" Gas Chromatography (GC) apparatus with a thermal conductivity detector (TCD)
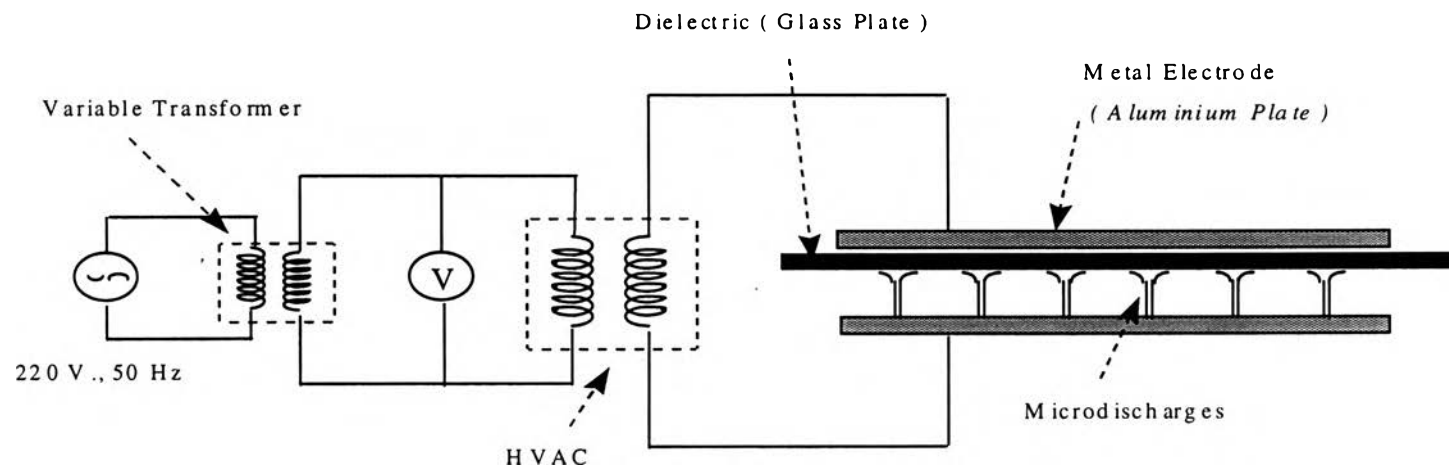
Figure 3.3 Power supply diagram.

and flame ionization detector (FID). After the stream had passed through the cold traps, it directly passed through a sampling loop, which was located within the GC valve. The body of this valve was inside the GC oven so that the temperature of the gaseous samples could be controlled. The 10-port valve with "precut and backflush" application was used in the present study, in which two GC packed columns were utilized simultaneously.

The first 30 ft x 1/8" HayeSep DB column allowed the separation of carbon monoxide, methane, carbon dioxide, acetylene, ethylene, water and ethane before being passed into the TCD detector. The second 5 ft x 1/8" HayeSep T column was used for the separation of air, formaldehyde, water and methanol.

The quantitative analysis of the percent volume of all the gaseous components in the product streams was carried out by correlating their concentrations to their component peak responses (i.e., peak area or height) derived from the GC chromatograms. The assumptions and calculation procedures are given in Appendix A.

Each cycle of GC analysis required about 15 minutes to complete before the next injection could be started. This GC application yielded a very good separation of N_2, CH_4, C_2H_2, C_2H_4, C_2H_6, CO, CO_2 and CH_3OH from the other components. The GC conditions used for the present study were summarized as follows:

Injector Type   : Automatic sampling valve (programmable)

Injector Temperature : 110^oC

Oven Temperature Program : 120^oC

Detector Type   : Thermal Conductivity Detector (TCD)

            Flame Ionization Detector (FID)

Detector Temperature : 160^oC

Carrier Gas   : He (99.999%)

Carrier Gas Flow Rate　　　: 30 ml/min

3.2 Experimental Procedure

3.2.1 Influence of carbon dioxide - methane ratio on the reaction

The mixture of CO_2 and CH_4 with the CO_2:CH_4 ratio of 1:1 at the composition of 80% helium and space time of 4 minutes was continuously fed into the reactor until no other gases peaks were shown on the GC chromatogram and the value of its peaks were constant. The voltage of 5,500 V was then applied to the reactor until a steady-state condition was reached. Then, all the necessary data were collected and analyzed. Afterwards, the power supply was stopped and the reactor system was purged with helium until no peak was observed on the GC chromatograms, and then another set of conditions was established. The voltage was varied according to the following values : 6,600 and 7,700 V. After a steady-state condition was attained for each voltage, all the required data were again collected. Before changing the voltage to any next values, the reactor system had to be purged with helium first until no peaks of other gases could be detected on the GC chromatograms. Thereafter, all of the experimental procedures above were followed again with different CO_2:CH_4 ratios of 0:1, 1:2 and 2:1 and at the space time of 6 minutes.

3.2.2 Influence of helium on the reaction

The mixture of CO_2 and CH_4 the ratio of 1:1 with the helium composition of 50 % and space time of 4 minutes was continuously fed into the reactor until no other peaks appeared on the GC chromatograms and the value of both peaks area were constant. The voltage at 5,500 V was then

applied to the reactor. When a steady state condition was attained, all the data were collected and analyzed. With the constant space time of 4 minutes, the voltage was varied according to the following values; 6,600 and 7,700V. At each voltage, after GC analysis of the outlet gas composition was completed, the reactor system was purged with helium until no any peaks of gases were observed on the GC chromatogram. After that, a next voltage could be applied. After completing all voltages, the space time was then changed to 6 and 8 minutes and the experiments were repeated.

With a constant CO_2: CH_4 ratio of 1:1, the helium concentration was varied from 20 % to 80% helium concentration.. All experiments were the same as above.