

CHAPTER III

METHODOLOGY

The presence of oxygen in the dielectric-barrier discharges (DBD) environment has been shown in most previous works to enhance the conversion of methane. However, the existence of oxygen also has a negative effect as it can destroy the desired products into the undesired carbon oxides. Therefore, only light hydrocarbons; methane, ethane and propane, were fed into an electric discharge reactor. The purpose of this work was to determine the effect of ethane and propane on methane conversion and to determine the rate of all reactions that occurred in the system.

3.1 Experimental Setup

The schematic diagram of the studied dielectric-barrier discharge system used throughout this study is illustrated in Figure 3.1. The system can be categorized into three sections i.e., the feed make-up section, the reaction section and the products section (or outlet section).

3.1.1 Feed 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%.

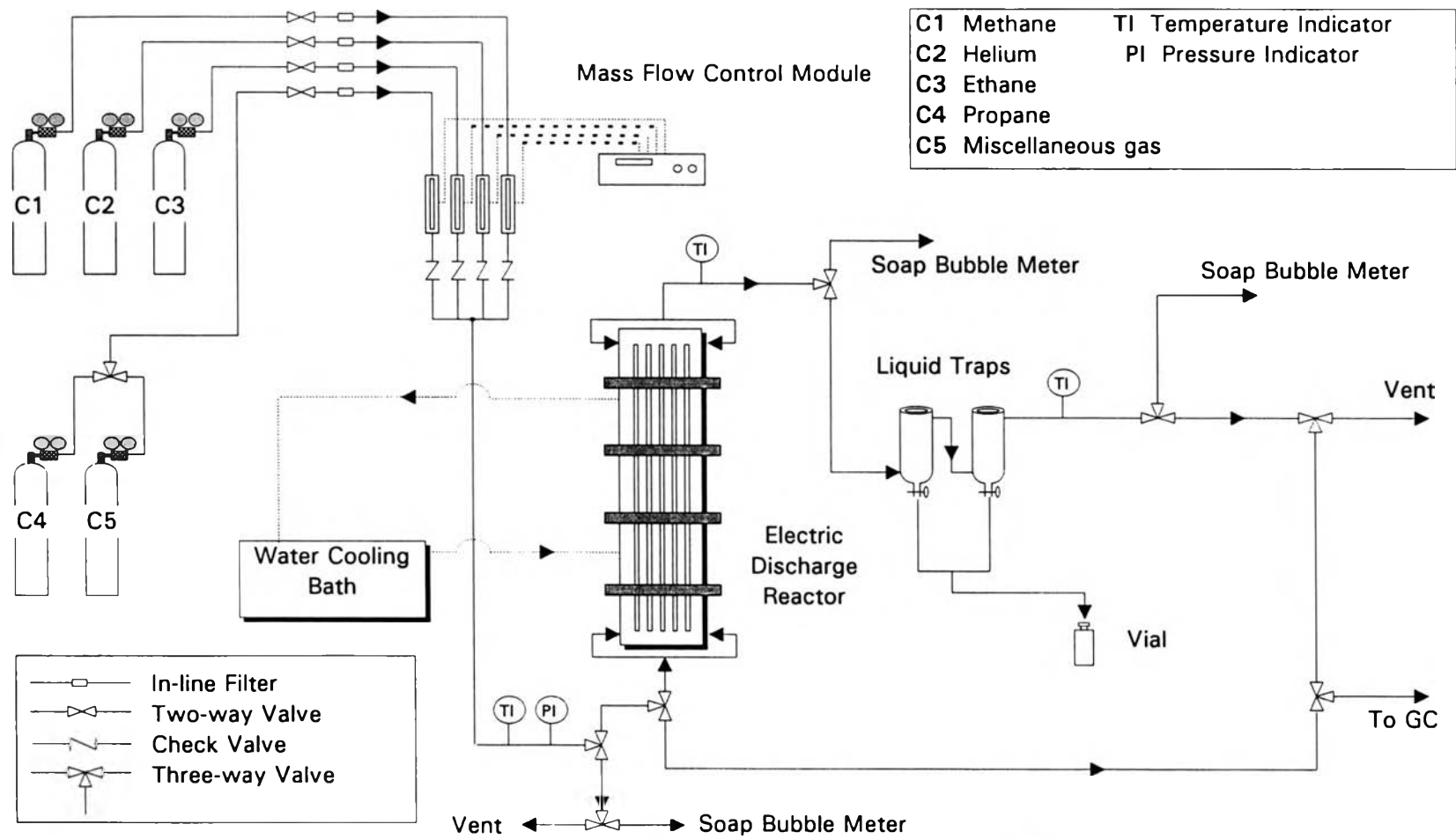


Figure 3.1 Flow diagram of the studied dielectric-barrier discharge (DBD) reactor.

Table 3.1 Specification of the gases used in the experiment

Gas	Purity (%)
Methane	99.0
Ethane	99.5
Propane	99.5
Butane	99.5
Ethylene (N ₂ balance)	5.26
Propylene (N ₂ balance)	0.51
Helium	99.999

The pressure read-out at the discharge end of all pressure regulators connected to the gas cylinders was maintained in the range of 20-30 psi. Check valves supplied by Swagelok[®] were also placed downstream of all transducers to prevent any back flows.

A pressure guage 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 guage had to read a zero. Also, this guage was to ensure that the pressure in the overall system was not too high, causing 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 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 231 cm³. This volume was defined by the 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. Two thermocouples (type K) were connected to both upstream and downstream positions of the reactor to measure any temperature changes due to the reactions. But, no significant temperature change (<5°C) could be observed during all the experiments.

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, 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.

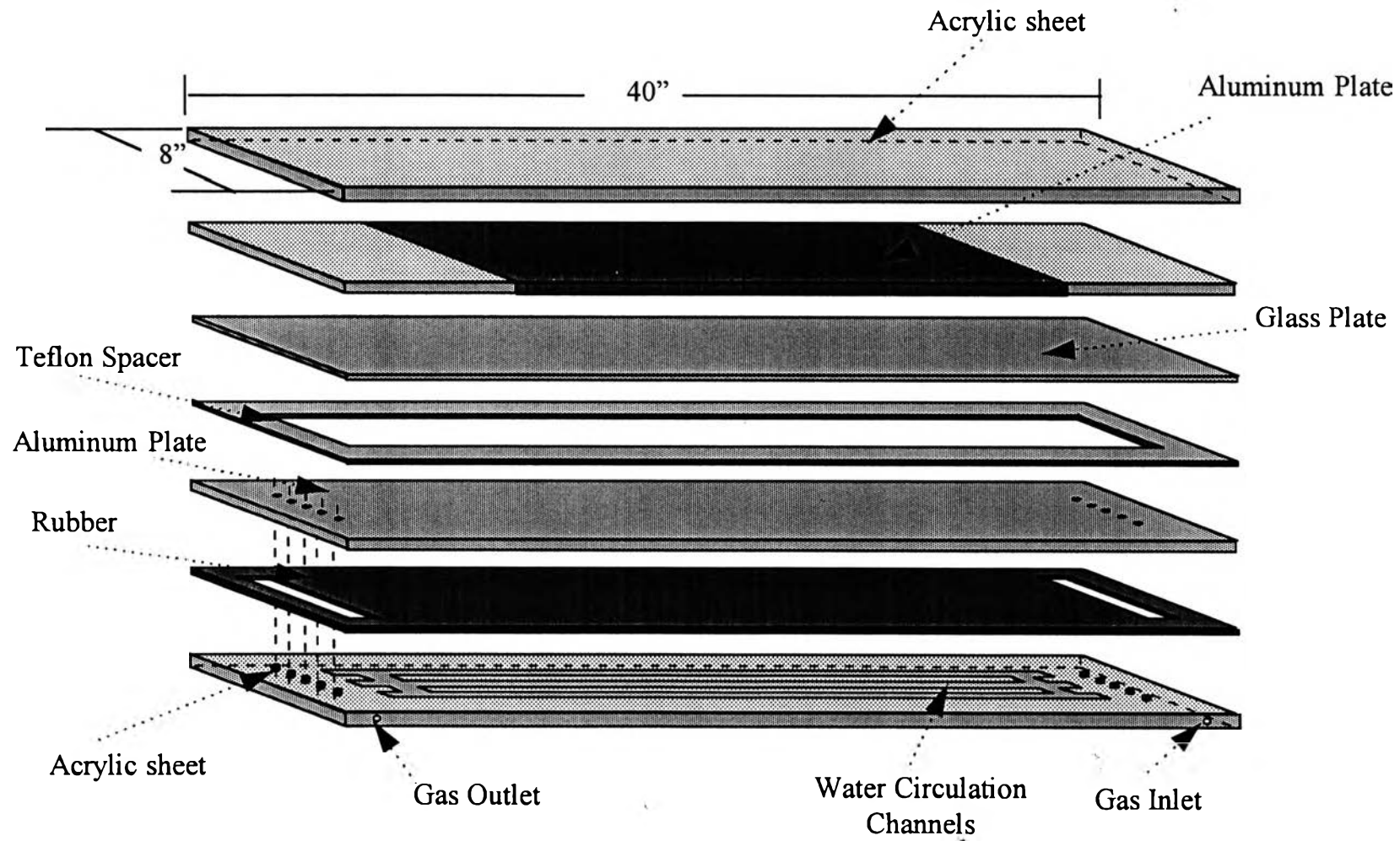


Figure 3.2 Reactor drawing.

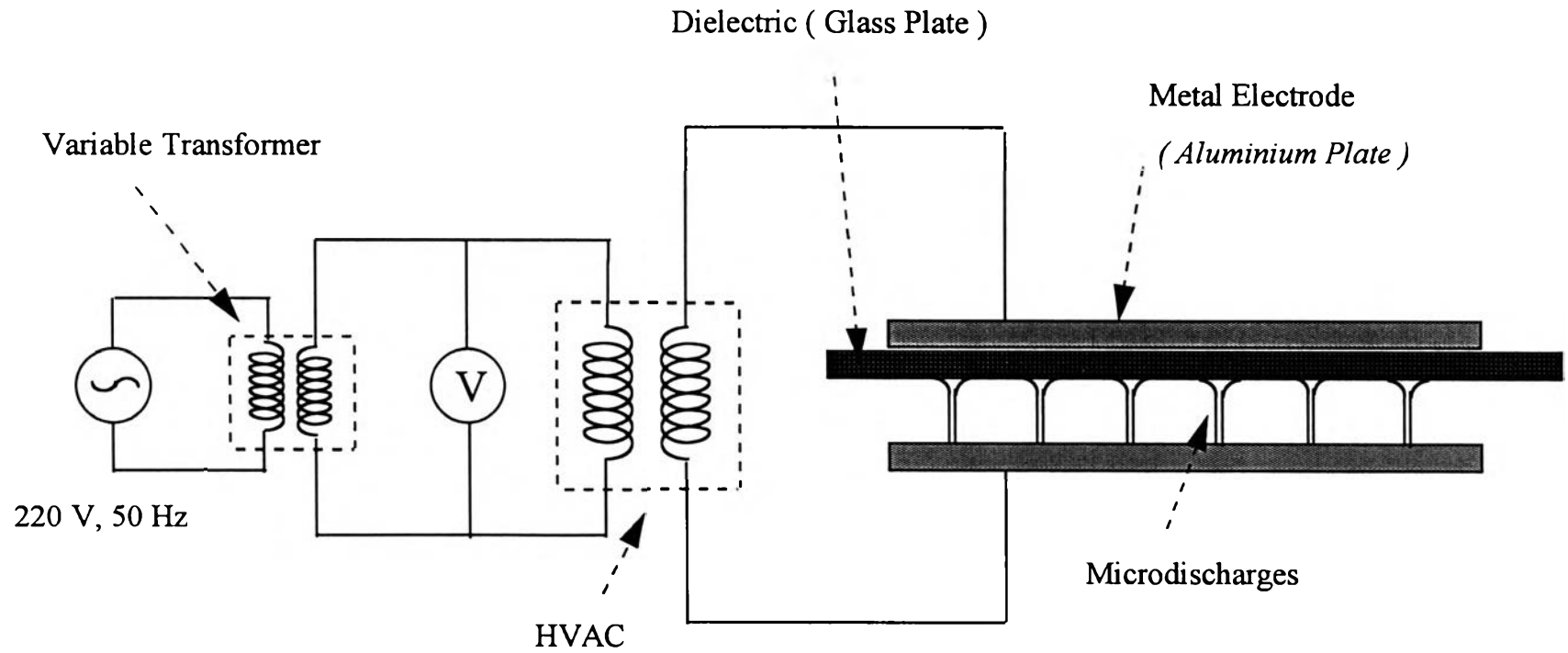


Figure 3.3 Schematic diagram of power supply unit.

3.1.3 Products Section (Outlet Section)

The volumetric flow rates of the gaseous streams at both the inlet and outlet of the reactor were measured 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 Chromatograph 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 done by using a Perkin-Elmer "Autosystem" Gas Chromatograph (GC) apparatus with a thermal conductivity detector (TCD). After the stream had passed through the cold traps, it directly flow pass 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. A 10-port valve with "precut and backflush" application was used in the present study in which GC packed columns were utilized. A $12' \times 1/8''$ Porapak-Q column allowed the separation of any traces of light hydrocarbon gases including O_2 and N_2 before being passed into the TCD detector.

The quantitative analysis of the volume percentage 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 10-15 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 , C_3H_6 , C_3H_8 and C_4H_{10} from the other components. The GC conditions used for the present study were summarized as follows:

Injector Type	: Automatic sampling valve (programmable)
Injector Temperature	: 160°C
Oven Temperature Program	: 100°C (5 min) then ramp up at 27°C/min to 140°C (hold 4-8 min)
Detector Type	: Thermal Conductivity Detector (TCD)
Detector Temperature	: 180°C
Carrier Gas	: He (99.999%)
Carrier Gas Flow Rate	: 20 ml/min

3.2 Experimental Procedure

3.2.1 Pure Methane System

Pure methane at the flow rate of 20 ml/min was continuously fed into the reactor until no other gases' peaks were observed on the GC chromatogram and the value of its peak was constant. The voltage of 5,625 V was 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 entire reactor system was purged with helium until no peak was observed on the GC chromatograms and then another set of conditions was established. The methane flow rate was varied according to the following values: 30, 40, 60 and 70 ml/min. At each of these flow rates, the same voltage of 5,625 V was applied until the data at the steady-state condition could be obtained. The voltage was then changed to 6,250 V and all of the above conditions were repeated.

With a constant flow rate of 40 ml/min of pure methane feed, the voltage was changed to 4,625 V and 5,125 V. After a steady-state condition was attained for each of these voltages, all the required data were taken and the system was purged between each condition.

3.2.2 Methane-Ethane System

The mixture of methane and ethane with a $\text{CH}_4/\text{C}_2\text{H}_6$ ratio of 9:1 and the total flow rate of 40 ml/min was continuously fed into the reactor until the values of both peak areas on the GC chromatogram were constant. The voltage of 5,625 V was then applied to the reactor. When a steady state condition was attained, all the data were collected and analyzed. At this constant voltage, the ratio of $\text{CH}_4/\text{C}_2\text{H}_6$ was varied according to the following values: 8:2, 7:3, 5:5, 3:7, 2:8 and 1:9. At each of these ratios, after GC analysis for the outlet gas composition was completed, the reactor system was purged with helium until no peak was observed on the GC chromatograms. After this point, the next ratio could be applied.

The mixture ratio which had the lowest methane composition but also had some conversion was chosen for varying a flow rate from 20 to 80 ml/min. At each of these flow rates, the same voltage of 5,625 V was applied. The procedure of each run was the same. Also, the mixture ratio which had the least ethane composition but also had some conversion was chosen for varying a flow rate from 20 to 80 ml/min as in the previous section.

3.2.3 Pure Ethane System

Pure ethane at the flow rate of 20 ml/min was continuously fed into the reactor until no other gases' peaks were shown on the GC chromatograms and the value of peak area was constant. The voltage of 5,625 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 entire reactor system was purged with helium until no peak was observed on the GC chromatograms. After this point, the next flow rate could be applied. The ethane flow rate was varied at the following values: 25 and 30 ml/min, with the same voltage of 5,625 V.

3.2.4 Methane-Propane System

The mixture of methane and propane with a $\text{CH}_4/\text{C}_3\text{H}_8$ ratio of 9:1 and the total flow rate of 40 ml/min 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 of 5,625 V was then applied to the reactor. When a steady state condition was attained, all the data were collected and analyzed. For the given voltage, the ratio of $\text{CH}_4/\text{C}_3\text{H}_8$ was varied according to the following values: 8:2, 7:3, 5:5, 3:7, 2:8 and 1:9. At each of these ratios, after GC analysis for the outlet gas composition was completed, the reactor system was purged with helium until no peak was observed on the GC chromatograms. After this point, the next ratio could be applied. Then the voltage was changed to 6,250 V and the experiments were repeated.

The mixture ratio which had the lowest methane composition but also had some conversion was chosen for varying a flow rate from 20 to 80 ml/min. At each of these flow rates, the same voltage of 5,625 V was applied. The procedure for each run was the same. Then, the mixture ratio which had the lowest propane but also had some conversion was chosen for varying a flow rate from 20 to 80 ml/min.

3.2.5 Pure Propane System

Pure propane at a flow rate of 20 ml/min was continuously fed into the reactor until no other gases' peaks were observed on the GC chromatograms

and the value of peak area was constant. The voltage of 5,625 V was 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 entire reactor system was purged with helium until no peak was observed on the GC chromatograms. After this point, the next flow rate could be applied. The propane flow rate was varied according to the following values: 25, 30, 35 and 40 ml/min, with the same voltage of 5,625 V. Then the voltage was changed to 6,250 V and the experiments were repeated.