

CHAPTER III

METHODOLOGY

The presence of oxygen in the dielectric-barrier discharges (DBD) environment has been shown in those previous works that it could enhance the conversion of methane. However, the existence of oxygen also contributes a great drawback effect as it can destroy the desired products into the undesired carbon oxides. Therefore, in almost all experimental cases of the present study, only pure methane would be fed into the electric discharges chamber so that its “real” reaction behavior at the steady-state conditions could be monitored without any influence from the other molecules. The purposes of this work were to determine the degree of activation of methane molecule and then what kind of product distributions would be obtained. The total flow rate was varied between 20-80 ml/min. while the voltage ranged from 3750 V - 10 kV was applied into the reactor.

In some experimental cases, the third-body molecules, i.e., helium and ethane, were also fed along with the methane in order to determine their influence on the methane conversion and the change in product distributions.

3.1 Experimental setup

The schematic diagram of the entire reaction system used throughout this study was illustrated in Figure 3.1. The system could be categorized into three parts, i.e., the reactant make-up section, the reaction section, the sample collecting and analysis section.

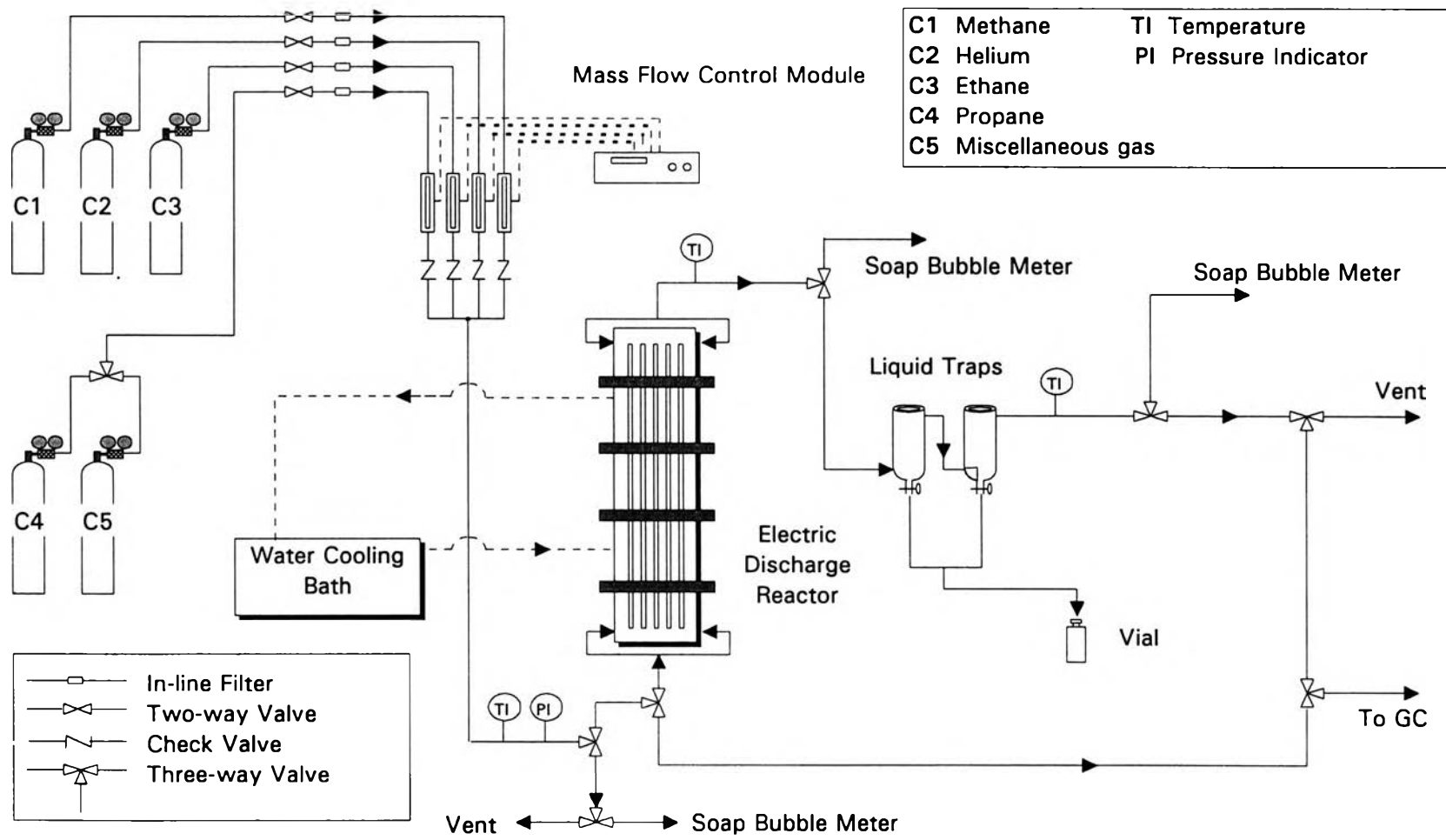


Figure 3.1 Equipment flow diagram.

3.1.1 The reactant make-up section

All the reactant gases used in this work were supplied in the gas cylinders by Thai Industrial Gases Public Co., Ltd. The specification of these gases was listed in Table 3.1.

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 balanced)	5.26
Propylene (N ₂ balanced)	0.51
Helium	99.999

All of these 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 control box and transducers supplied by SIERRA[®] Instrument, Inc. The error of this apparatus was reported to be less than 1 %.

The pressure read-out at the discharge end of all pressure regulators connected to the gas cylinders had to be maintained in the range of 20-30 psia to guarantee the reliable function of the transducers. The 0.7 μm in-line filters were placed upstream of all the mass flow transducers in order to trap any 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 pressure effects.

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 in the line of gaseous stream. Since all the experiments were conducted at atmospheric pressure, the gauge had to be read 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 The reaction section

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

3.1.2.1 The DBD reactor

The configuration of the reactor is depicted in Figure 3.2. Descriptively, this reactor 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 the cooling water to absorb the heat produced from the reaction zone. The cooling water temperature of 20 °C was controlled in all the runs. Two thermocouples (type K) were connected in both up- and downstream positions of the reactor to measure any temperature change due to the reactions. But, no significant temperature change (< 5 °C) could be observed during all the experiments.

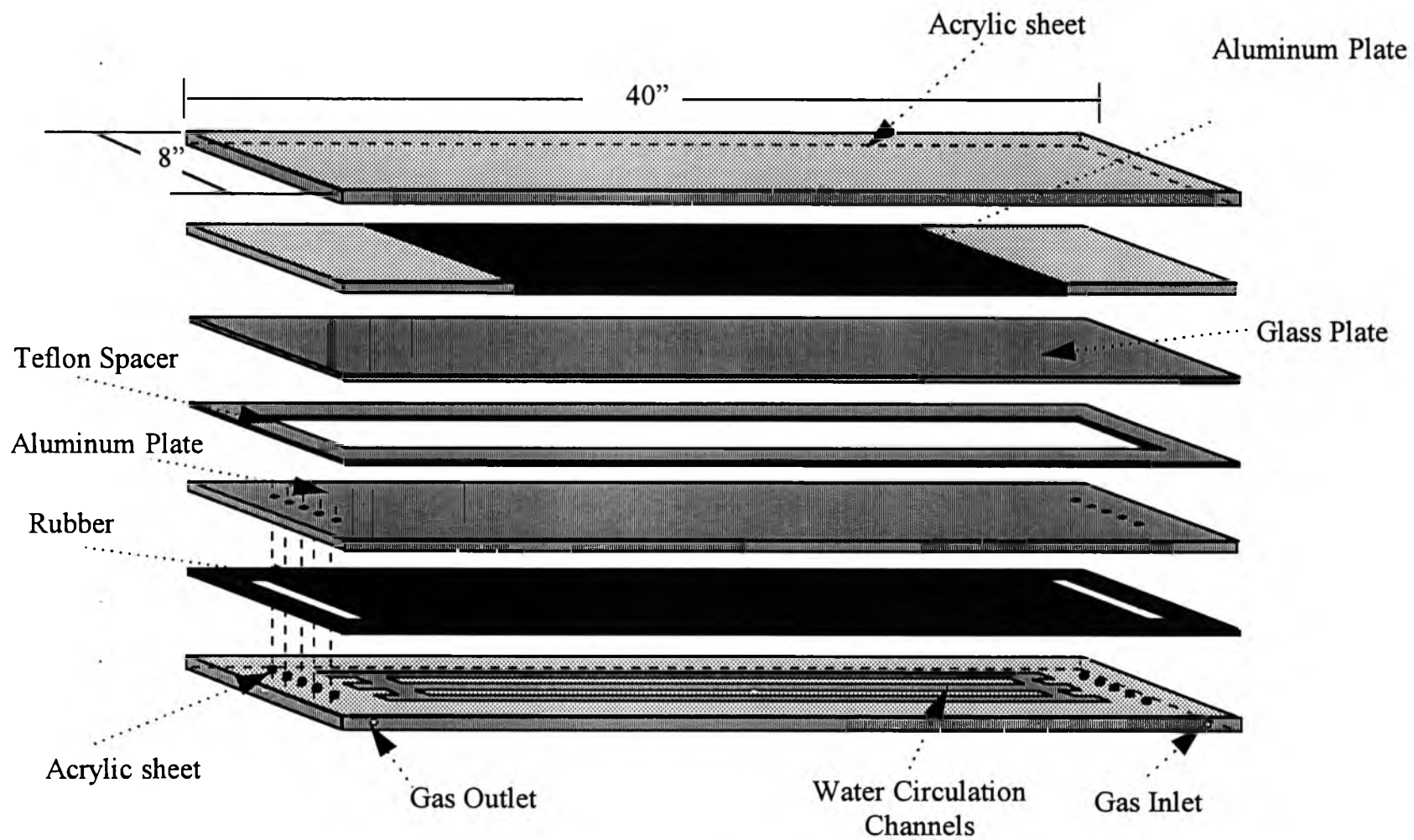


Figure 3.2 Reactor drawing.

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 the 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 both at 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 outlets followed the connection of the gas line to a Gas Chromatography apparatus. Both liquid traps were maintained at temperature ranged from -20 to -10 °C using cool ethanol to collect any liquid products that might be produced from the reactions. No any liquid products could, however, be observed in each run when it became steady-state.

The complete analysis of the gaseous product stream flowing out from the reactor was done by a Perkin-Elmer “Autosystem” Gas Chromatography (GC) apparatus with a thermal conductivity detector (TCD). After the stream had passed through the cold traps, it was directed to flow pass a sampling loop which was located within the GC valve. The body of this valve was locked

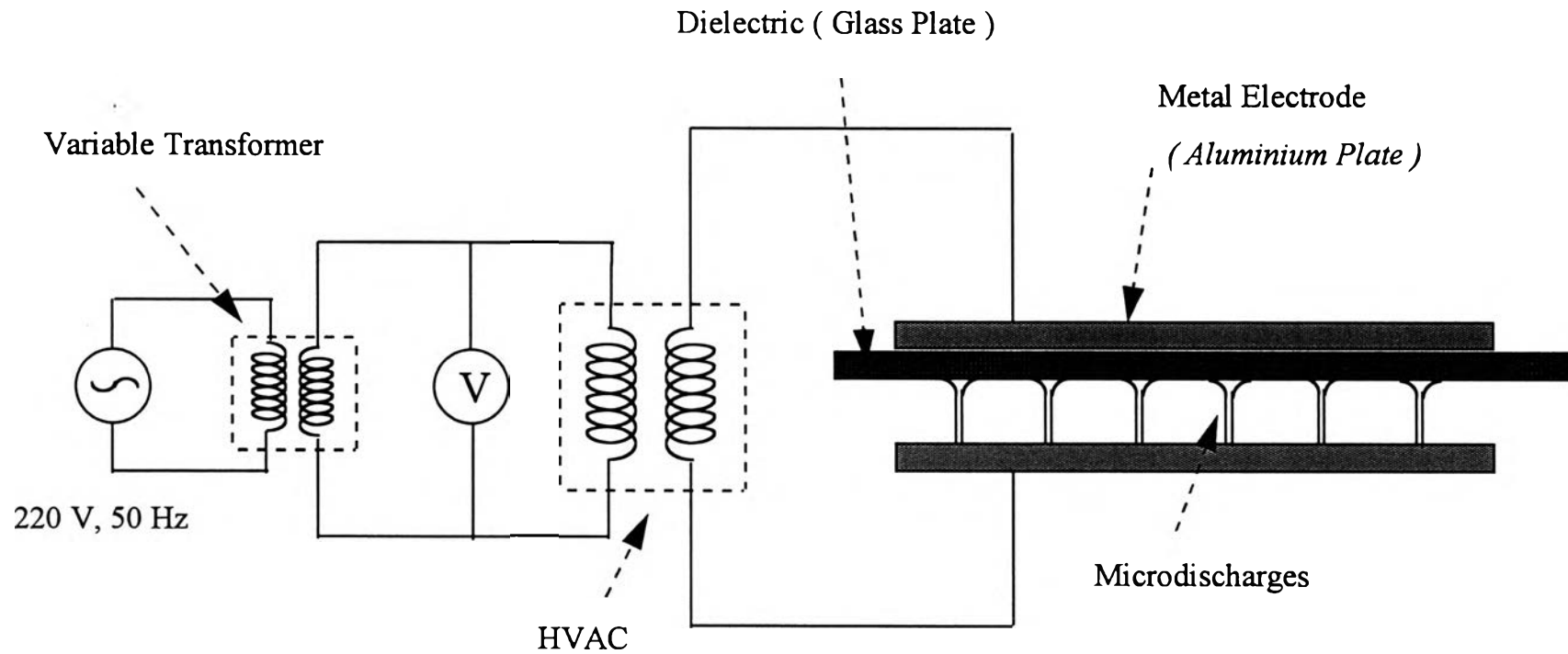


Figure 3.3 Schematic diagram of power supply unit.

inside the GC oven so that the temperature of the gaseous analysts could be controlled and then the precise quantitative analysis could be accomplished. The 10-port valve with “precut and backflush” application was applied in the present study in which two GC packed columns were utilized simultaneously.

The first 12' × 1/8" Porapak-Q column allowed the instant separation of any traces of light gases including the O₂, N₂ and CO from the remaining heavier gases (i.e., CH₄, CO₂, C₂-C₄ hydrocarbons). When those light components flew into this column, they would be eluted out very rapidly at about the same retention time (i.e., in the magnitude of few seconds). After that, they were sent in to a subsequent column, which was 6' × 1/8" Molecular Sieve 13X, where the sharp separation between each light component could be made.

The heavier gases, however, normally retained in the Porapak-Q column and then would be eluted out later at varying retention time. Therefore, after the lighter compounds flew out from Porapak-Q column into the MS13X column, the GC valve was automatically switched so that the remaining gases (i.e., heavier) were permitted to be separated only within Porapak-Q column before being passed directly into the TCD detector after their elution. Finally, when the separated light components flew out from the MS13X column, they would be directed to flow back into the Porapak-Q column again before passing out into the TCD detector.

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

Each cycle of GC analysis required about 24 min. to complete before a next injection could be started. This GC application yielded a very good separation of O₂, N₂, CO, CH₄, CO₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈ and C₄H₁₀ from the other components. The GC condition used for the present study was summarized as follows,

Injector Type: Automatic sampling valve (programmable)
Injector Temperature : 160 °C
Oven Temperature Program : 50 °C (4 min) then ramp up at 27 °C/min to 130 °C (0.0 min) followed by ramping down to 80 °C (8.50 min.) then ramp up again with 25 °C/min to 160 °C (5 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 procedures

3.2.1 Pure methane system

Part I Effect of voltage

Pure methane at the flow rate of 20 ml/min. was continuously fed into the reactor until no other gases' peaks showed on the GC chromatograms. The voltage of 3750 V was then applied to the reactor until a steady-state condition was reached. Thereafter, analysis of gas composition of the outlet stream was carried out. While keeping the flow rate constant, the voltage was increased according to the following values: 4500, 5000, 6250, 8750 and 10937 V. After a steady-state condition could be attained for each of these voltages, all the required data were taken before the voltage was raised to the new adjacent values. Afterwards, the power supply was stopped and the flow rate of pure methane was adjusted to 40 ml/min. The first voltage of 4500 V was then applied to the reactor before gaseous composition at the outlet stream was analyzed at the steady-state condition. While keeping the flow rate constant, the voltage was then increased according to the following values: 6250, 8750 and 10937 V. After a steady-state condition could be attained for each of these voltages, analysis of the gas composition at the outlet stream must be carried out before the next voltage could be applied.

Part II Effect of residence time

Pure methane with the flow rate of 20 ml/min was continuously fed into the reactor until no other gases' peaks were shown on the GC chromatograms. The voltage of 6250 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 pure methane until only its peak was shown on the GC chromatograms. The methane flow rate was varied according to the following values: 40 and 80 ml/min. At each of these flow rates, the same voltage of 6250 V was applied until the data at the steady-state condition could be gained. After GC analysis of the outlet gas composition was completed, the reactor system was purged with pure methane until only its peak was shown on the GC chromatograms. After this point, a next flow rate could be applied.

Part III Influence of different voltage rising approach

This experimental part was designed to determine the effect of different techniques of voltage rising on the methane conversion efficiency. In part I, the stepwise increase of the applied voltage was employed. But in this part, an increase of the applied voltage to any desired values was performed immediately.

Pure methane at the flow rate of 20 ml/min was continuously fed into the reactor until no peaks of other gases were shown on the GC chromatograms. The voltage at 4500 V was applied into the reactor until a steady-state condition was reached. After that, all the necessary data was collected and analyzed. Afterwards, the power supply was stopped and the reactor system was purged with pure methane until only the peak of methane was shown on the GC chromatograms. Then, pure methane at the flow rate of 20 ml/min was set and fed into the reactor again. In the next step, the voltage was increased according to the following values: 6250 and 7500 V. After a steady-state condition could be attained for each voltage, all the required data were collected. And, before changing the voltage to any next values, the

reactor system had to be purged with pure methane first until no peaks of other gases could be detected on the GC chromatograms. Additionally, the flow rate had to be set to 20 ml/min prior to the voltage change.

3.2.2 Influence of third-bodies on the methane reaction

Part IV Effect of helium on methane reaction

The mixture of CH₄ and He with CH₄/He ratio of 1:1 at the total flow rate of 20 ml/min was continuously fed into the reactor until no other peaks appeared on the GC chromatograms. The voltage of 3750 V was then applied to the reactor. When a steady state condition was reached, all the necessary data were collected and analyzed. While keeping the CH₄/He ratio constant, the voltage was then increased according to the following values: 5000 and 6250 V. After a steady state condition was attained for each of these voltages, all the required data were taken before a new adjacent voltage was applied. Thereafter, all of the experimental procedures above were followed again except for the change of CH₄/He ratio to 3:1.

Part V Effect of ethane on methane reaction

The mixture of C₂H₆ and CH₄ with C₂H₆/CH₄ ratio of 1:9 at the total flow rate of 20 ml/min was continuously fed into the reactor until no other peaks appeared on the GC chromatograms. The voltage at 4500 V was then applied to the reactor. When a steady state condition was attained, all the data were collected and analyzed. While keeping the C₂H₆/CH₄ ratio constant, the voltage was raised to 6250 V. and was left until a new steady state condition was attained. Afterwards, all the required data were collected before the power

supply was turned off. Finally, all of these experimental procedures were carried out again at the C_2H_6/CH_4 ratio to 1:4.

3.2.3 Reaction of ethane-helium and propane-helium systems

Part VI Effect of voltage

The mixture of C_2H_6 and He with C_2H_6/He ratio of 1:4 at the total flow rate of 20 ml/min was continuously fed into the reactor until no other peaks appeared on the GC chromatograms. The voltage at 5000 V was applied to the reactor. When a steady state condition was attained, all the data were collected and analyzed. The voltage was then increased to 6250 V before all the required data could be collected at the new steady state condition. After that, the power supply was shut off. Finally, all of these experimental procedures were carried out again by using C_3H_8 instead of C_2H_6 .