CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipments

3.1.1 Gases

2% O_2 in He purity of 99.9999%

H_2 purity of 99.99%

CH_4 purity of 99.99%

CO_2 purity of 99.99%

Air purity of 99.99%

3.1.2 Equipment

Six-port valve

Flow meter

Furnace

Quart reactor

Methanator

Thermocouple

Flame Ionization Detector (FID)

Computer

Mass flow controller

3.2 TPO Construction

TPO apparatus comprises five eminent equipments. They consist of furnace, methanator, mass flow controller, temperature controller and Flame Ionization Detector (FID). Considering the dimensions and the functions of them, they are different. The dimensions and duty of them can be purposed in this manner.

3.2.1 Quart reactor

The width, the height and the thickness of furnace are 4.5", 4.5" and 9.5" respectively. The oxidation of coke on catalyst occurs in quart reactor. For constant heating rate increasing is 13 K/min. Carbon dioxide becomes the product.

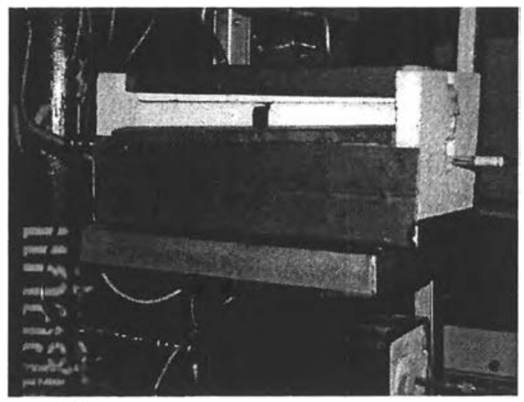


Figure 3.1 Quart reactor in furnace.

3.2.2 Methanator

The width, the height and the thickness of furnace are 3.5", 3.5" and 6" respectively. In this experiment, 0.5g of 15-wt% Nickel/gamma- alumina catalyst was used in methanator for methane conversion. The results of this experiment were affected by many parameters. In the influence of O_2, the TPO experiments carried out with 2% O_2 or less in the carrier gas, and methanator temperature should be below 430 °C. In the influence of temperature, the optimum temperature in methanator is 400 °C. In the influence of carrier gas flow rate, the sensitivity of Flame Ionization Detector (FID) increased with the flow rate linearly up to 65 cc/min and then it was leveled off at higher flow rates.

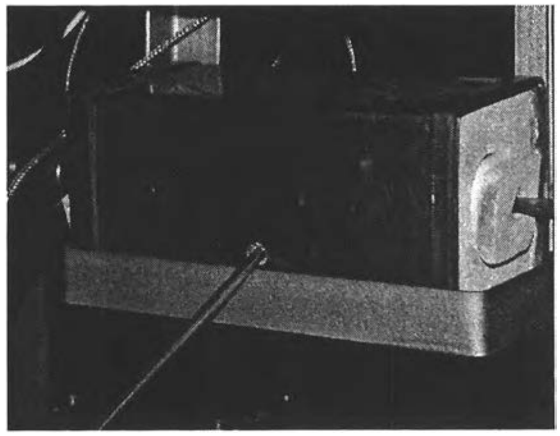


Figure 3.2 Methanator in furnace.

3.2.2.1 Catalyst Preparation

3.2.2.1.1 Imprenation Procedure (for γ alumina (γ Al_2O_3))

To weigh a support γ alumina (Al_2O_3) 10 gram. Then weigh $Ni(NO_3)_2$ -$6H_2O$ 7.432 gm after that dissolve Nickle Nitrate Hexa-hydrate($Ni(NO_3)_2$ -$6H_2O$) in water 2 ml. The impregnation solution(Nickle Nitrate) was added to the support in mortar drop by drop. To allow distribution of the fluid throughout the support bodies, by crushing. To leave 15% NiO/ γ Al_2O_3 at room temperature for 3 hours. To dry 15% NiO/ γ Al_2O_3 in oven at 80 °C for 6-8 hours. A 15% NiO/ γ Al_2O_3 was calcined in the flow of air, then, then the temperature was ramped to 500 °C in 2 hours and held for 4 hours. The 15% NiO/ γ Al_2O_3 was cooled in air. To reduce 15% NiO/ γ Al_2O_3 by flow of hydrogen. To store catalyst in descicator.

3.2.3 Flame Ionization Detector (FID)

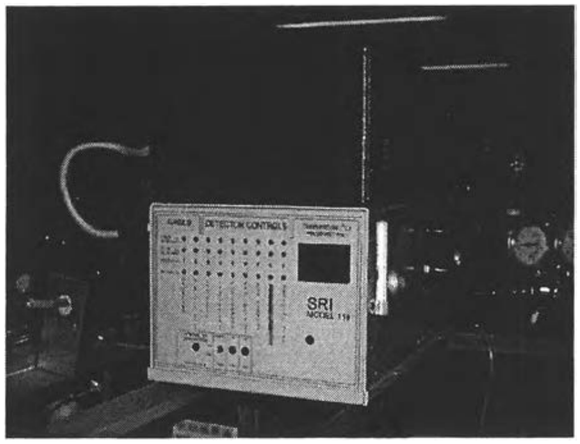


Figure 3.3 Flame Ionization Detector (FID).

Flame Ionization Detector (FID) is sesitive for CH_4. In another hand Thermal Conductivity Detector (TCD) is sensitive for CO_2. FID will give higher resolution, baseline stable and sensitivity than TCD.

3.2.3.1 Principle

Firstly, the effluent carrier gas was mixed with hydrogen, then pass through an stainless steel jet and ignited a diffusion flame at the jet's tip which ionized the analyze molecules. Secondly, positive and negative ions (as each sample component) were eluted into the flame. Thirdly, the negative ions were attracted by the electrostatic field and flew in the direction of the collector electrode. Finally, the negative ions was attracted by a collector electrode and transferred to the electrometer amplifier for analog signal production, in data system input.

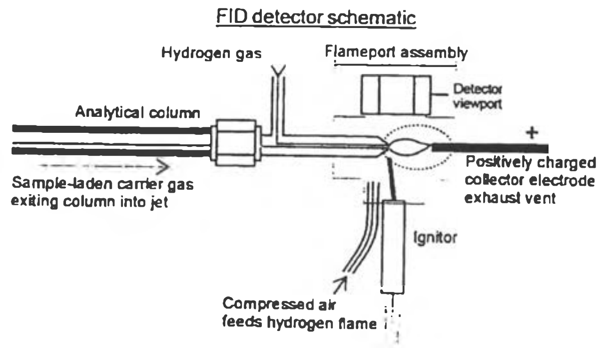
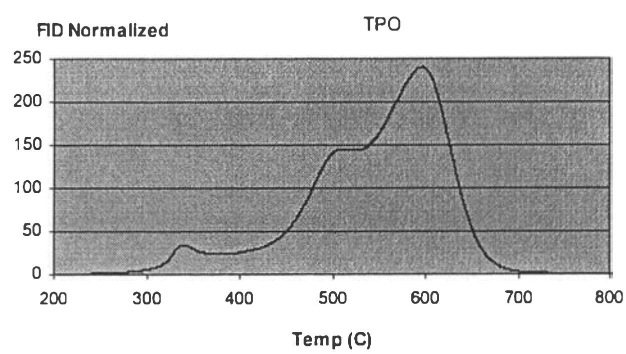
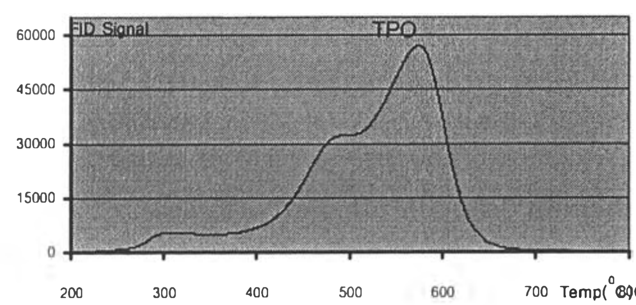


Figure 3.4 FID detector schematic.

3.2.3.2 Verification for the unit performance

Sample used : Co-Mo/SiO_2 catalyst (CH4@750^{0}C)





3.2.4 Temperature Controller

They are divided into 2 items.

TPO spectrum obtained from the Heterogeneous catalysis lab. of Okahama Amount of coke = 9.13 %	TPO spectrum obtained using the TPO unit constructed Amount of coke = 9.14 %

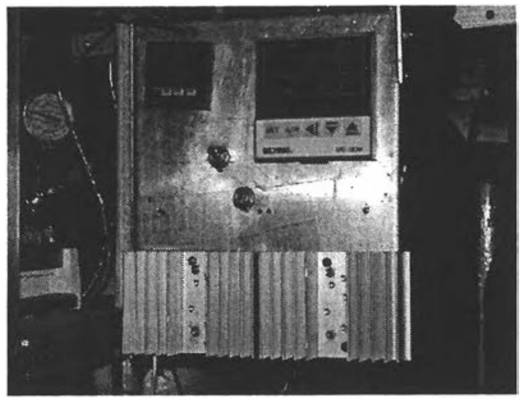


Figure 3.5 Temperature Controller.

The first (left) is temperature controller for furnace. The heating rate is 13 K/min, increases from 25 ^{0}C to 800 ^{0}C. The program can be set follows this.

The second (right) is temperature controller for methanator. This apparatus set constant temperature for 400 ^{0}C.

3.2.5 Mass Flow Controller

They are divided into 2 items.

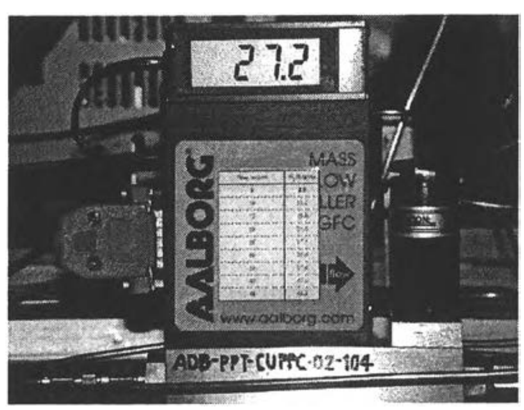


Figure 3.6 Mass Flow Controller.

The first is mass flow controller for 2%O_2/He. The mass flow rate is 40 cc/min.

The second is mass flow controller for H_2. The mass flow rate is 25 cc/min.

3.2.6 Control Panel

This panel supervises the gas valve system. The panel is composed of two ways valve for hydrogen (H_2), 2 three ways valves for carbon dioxide (CO_2) -

methane (CH_4) switch and 2%oxygen/He-He switch, 2 three ways valves for methanator-vent switch and FID-vent switch and six ports valve for methane or carbon dioxide calibration. This pictures shows thus.

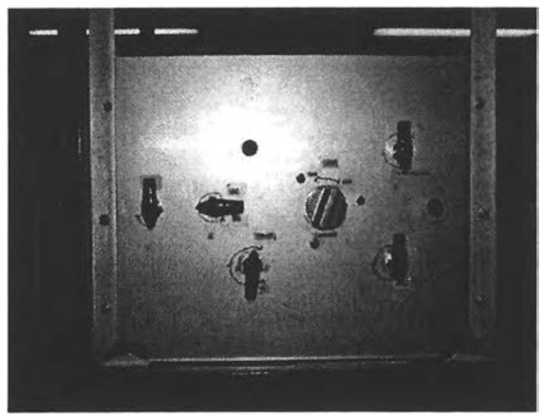


Figure 3.7 Control Panel.

3.3 TPO Construction Process

1. To outline of Temperature Programmed Oxidation as shown in Figure 3.3.1.
2. To construct Temperature Programmed Oxidation by following procedure.

- To construct the structure of TPO
- To fix the equipment in the right connection position as shown in Figure 3.3.1
- To connect pipeline for gas transfer, between apparatus.
- To test for gas leakage.

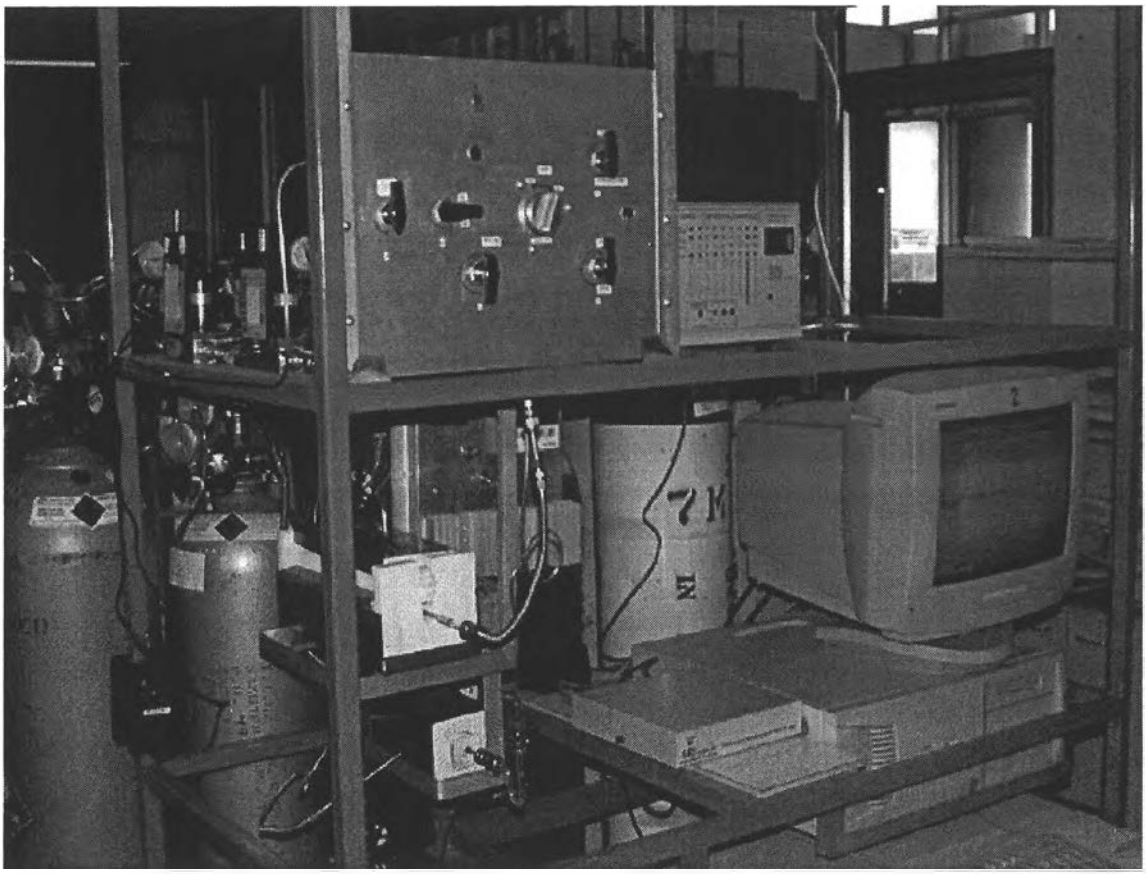


Figure 3.8 Complete Apparatus.

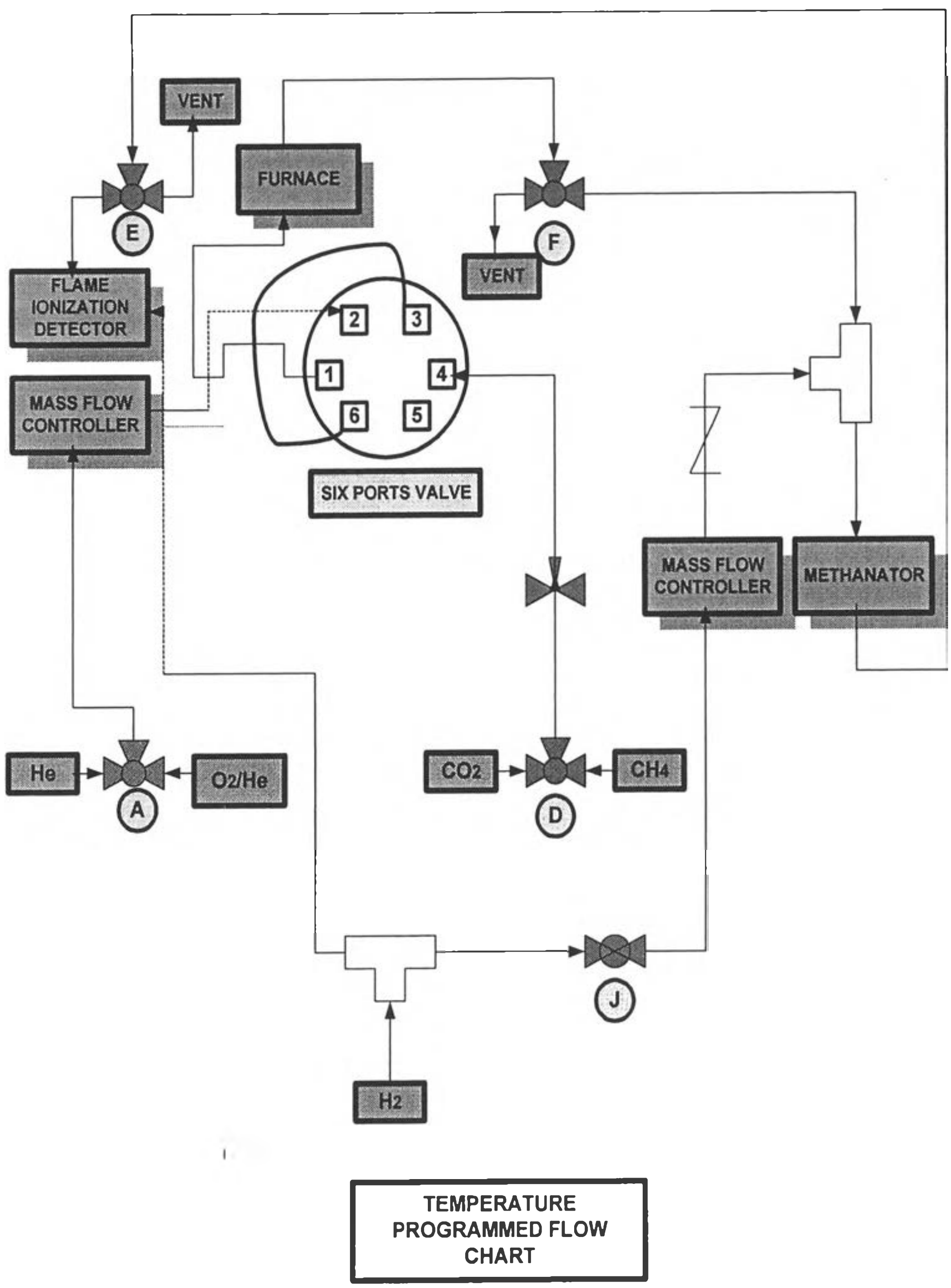


Figure 3.9 Temperature Programmed Oxidation Flow Chart

3.4 Temperature Programmed Oxidation Conditions

3.4.1 Calibration Conditions

3.4.1.1 Methane Calibration Methane will pass through three ways valve (D position), needle valve to six ports valve. In six ports valve, there is 2 step. The first step (loading), methane will fill in loop of six ports valve. The second step (injection), 2%O_2 in He is carrier gas for methane transferring. Methane and 2%O_2 in He transfer from furnace, three ways valve (F position), tee junction, methanator and three ways valve (E position) FID and computer.

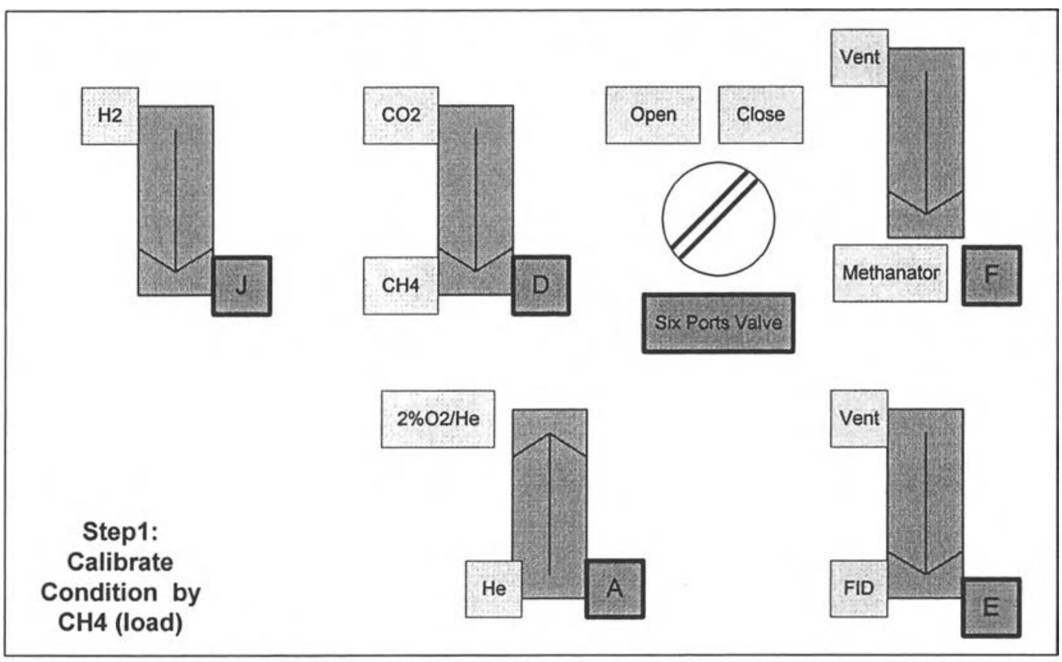


Figure 3.10 Methane calibrate condition (load).

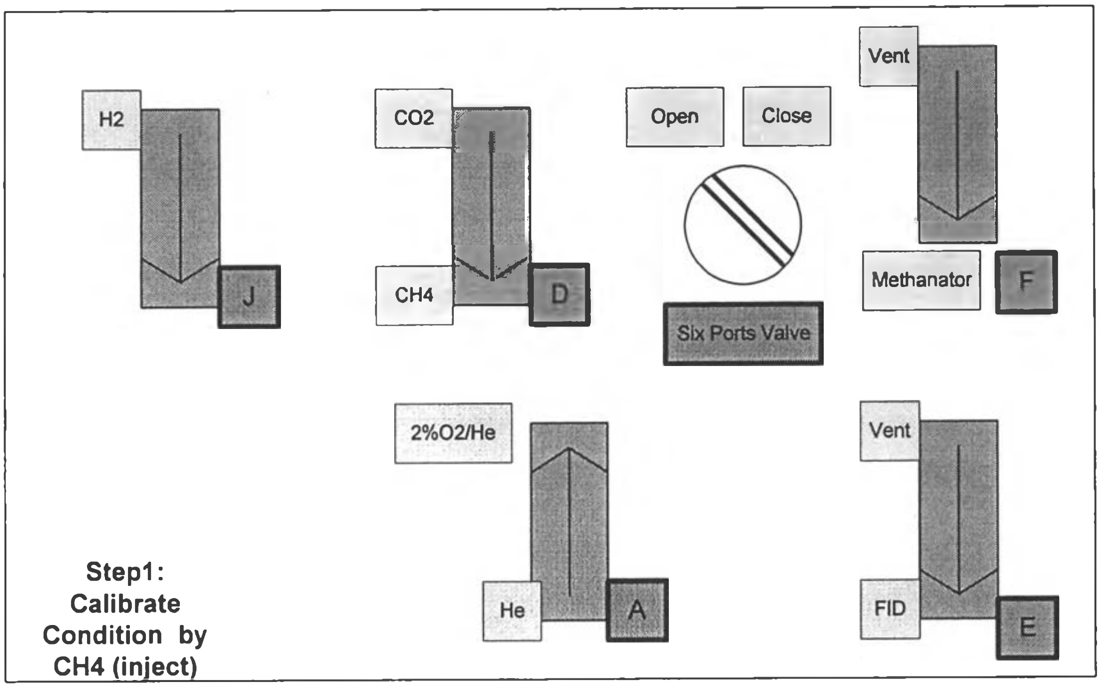


Figure 3.11 Methane calibrate condition (inject).

3.4.1.2 Carbon dioxide Calibration

The carbon dioxide calibration process likes methane calibration process.

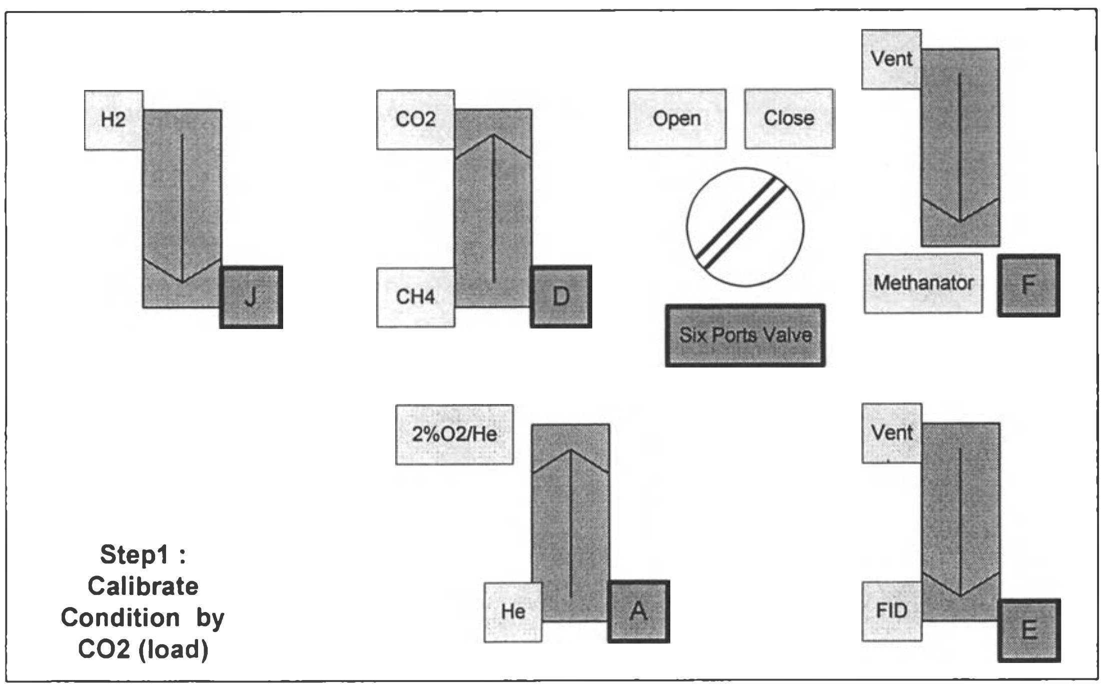


Figure 3.12 Carbon-dioxide calibrate condition (load).

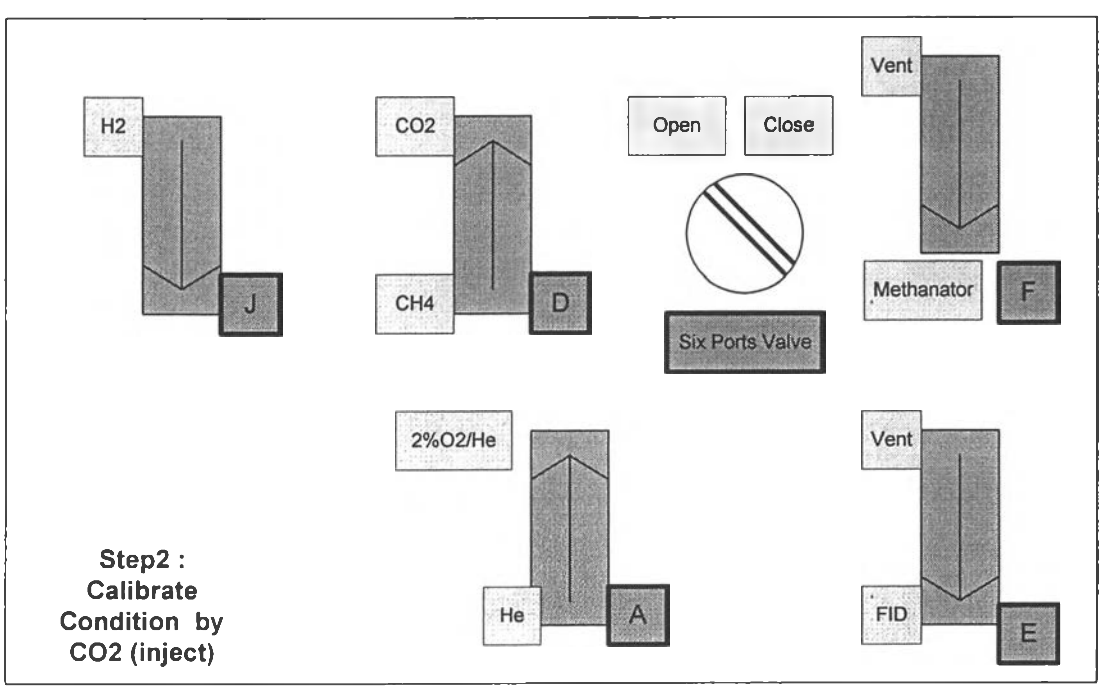


Figure 3.13 Carbon-dioxide calibrate condition (inject).

3.4.2 Measuring Conditions

3.4.2.1 2%O_2/He Measuring

The flow rate of 2%O_2/He can be measured by arrow adjusting as below picture. Gas direction is as same as the running process. There is different between 2 process at the arrow turned to vent in F position.

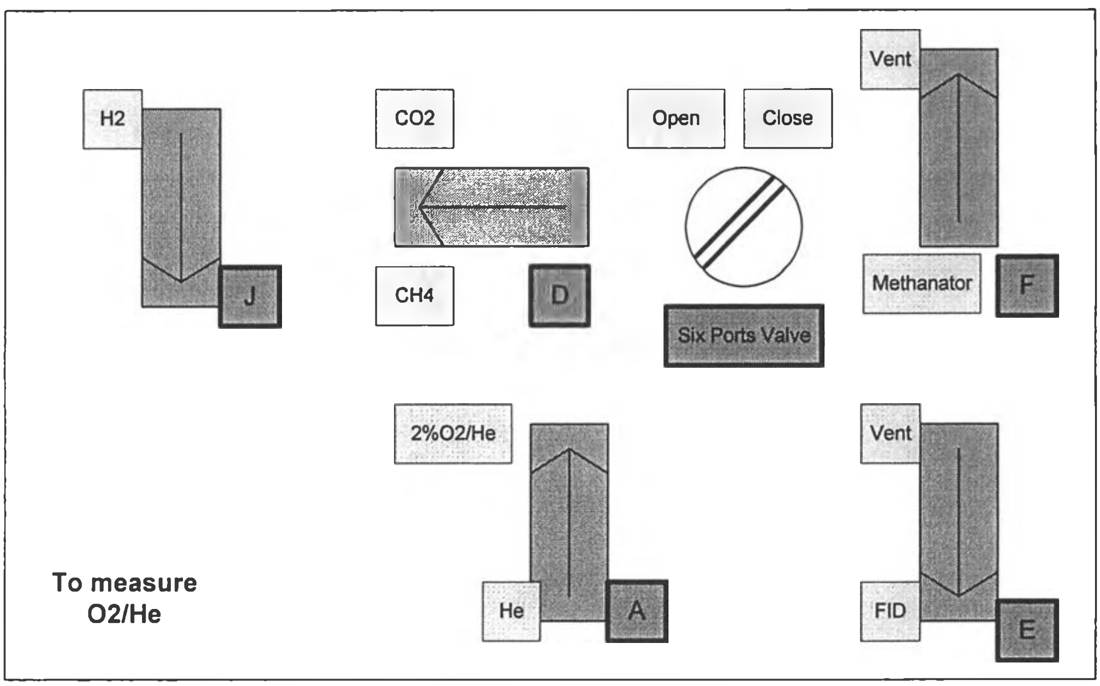


Figure 3.14 Oxygen/Helium measuring condition.

3.4.2.2 H_2 Measuring :

The flow rate of H_2 can be measured by arrow adjusting as below picture. Gas direction is as same as the running process. There is different between 2 process at arrow turned to vent in E position. Furthermore, a valve in A position is closed.

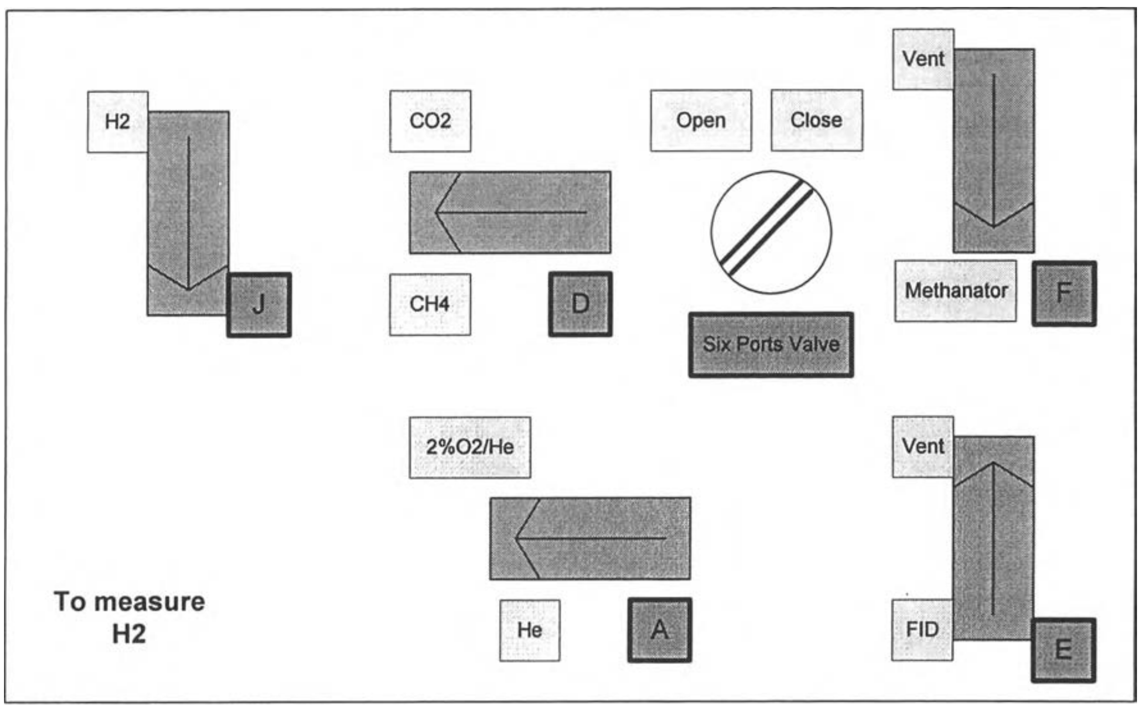
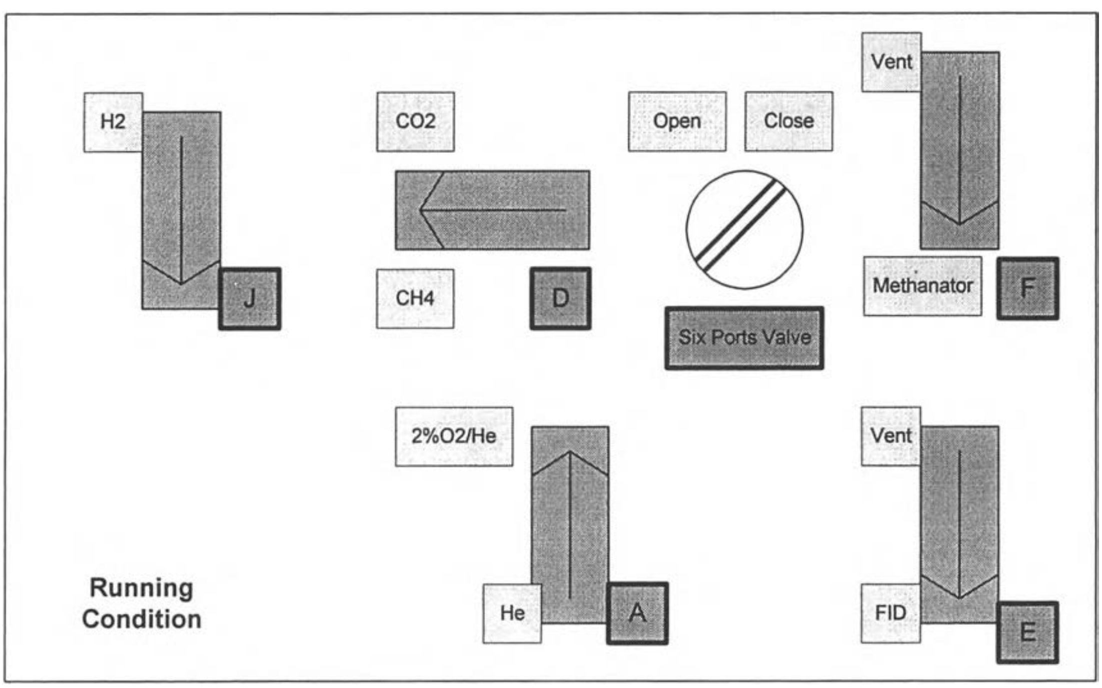


Figure 3.15 Hydrogen measuring condition.

3.4.3 Running Condition

This apparatus is appropriate to find amount of coke on catalyst. A process of an above picture can explain in detail by follow this. At the first, coke on catalyst is placed in a furnace which has constant temperature rate increasing(13^0C/min). An oxygen (O_2) (40 cm^3/min) that pass through mass flow controller and a six ports valve will react with carbon to give carbon dioxide (CO_2) in product. Carbon dioxide pass through three ways valve (F position) and tee junction to methanator. In methanator, hydrogen 25 cm^3/min) that pass through ball valve (J position), mass flow controller, check valve and tee junction, will react with carbon dioxide to give methane (CH_4) in product. Nickel on gamma alumina ($Ni/\gamma Al_2O_3$) is used as catalyst for carbon dioxide conversion. Methane will pass through three ways vale (E position) to flame ionization detector (FID) which detect methane information in an analog signal. An analog signal will be translated in digital signal by FID and then transfer to computer. PeakSimple is convenience program for Temperature



programmed Oxidation (TPO) running.

Figure 3.16 Running condition.

3.4.4 Cleaning Condition

Gas direction is as same as the running process. There is different between 2 process at arrow turned to He in A position.

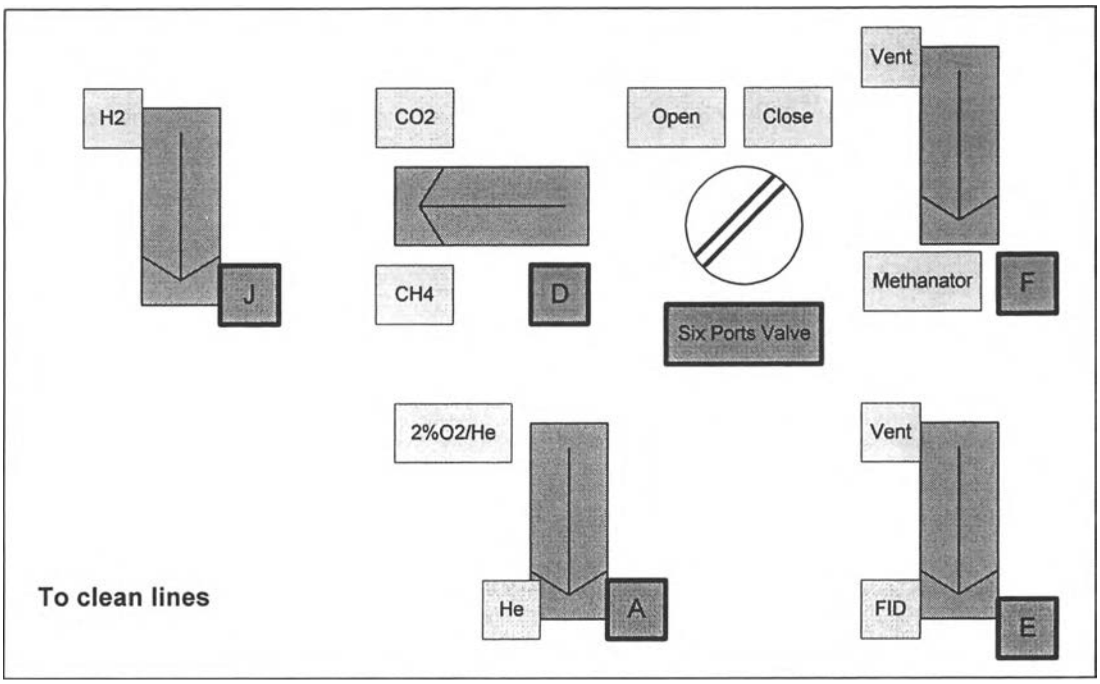


Figure 3.17 Cleaning condition.