CHAPTER III

Experiments and Analysis Techniques

3.1 Experimental Apparatus

In this study, the experiments are carried out in a fixed-bed reactor. Schematic diagram of this system is shown in Figure 3.1. All parts are designed and constructed with stainless steel to withstand a maximum operating pressure of 1500 psig.

Gas and liquid are fed concurrently into the top of fixed-bed flow reactor from two separated sections, called gas section and liquid section. In the gas section, hydrogen gas is fed from the hydrogen tank through the a pressure regulator and pressure gauge 1 which are used to control and measure hydrogen pressure respectively. In the liquid section, liquid is fed from two separated burette (first burette for presulfiding catalyst, the other for feeded liquid hydrocarbon) and pumped through valve 4 and liquid filter into high pressure pump which has ability to generate high pressure at low flow rate. The feed pressure is measured by pressure gauge 2.

Gas and liquid feed flow through the reactor in concurrent down flow. The reactor is packed with 5.0 gram of catalyst in the middle part supported by glass beads at the bottom of the reactor. The reactor is made of 0.5 inch outside diameter, 18.9 inches long, 0.035 inch thick, 316 stainless steel tube. A 1/8 inch outside diameter, 316 stainless steel tube, with one end welded shut, is used as a thermowell. The thermowell is secured in the middle of the reactor. A small thermocouple is inserted into the thermowell to measure the temperature of the catalyst bed during the reaction.

The reactor is installed in two iron blocks and heated by two heating bands which are placed around the assembled blocks. Two heating bands, rated at 800 watts and 220 volts, are used to supply heat for the reactor. Brick is used as an insulator wrapped around the heating band to prevent heat loss and

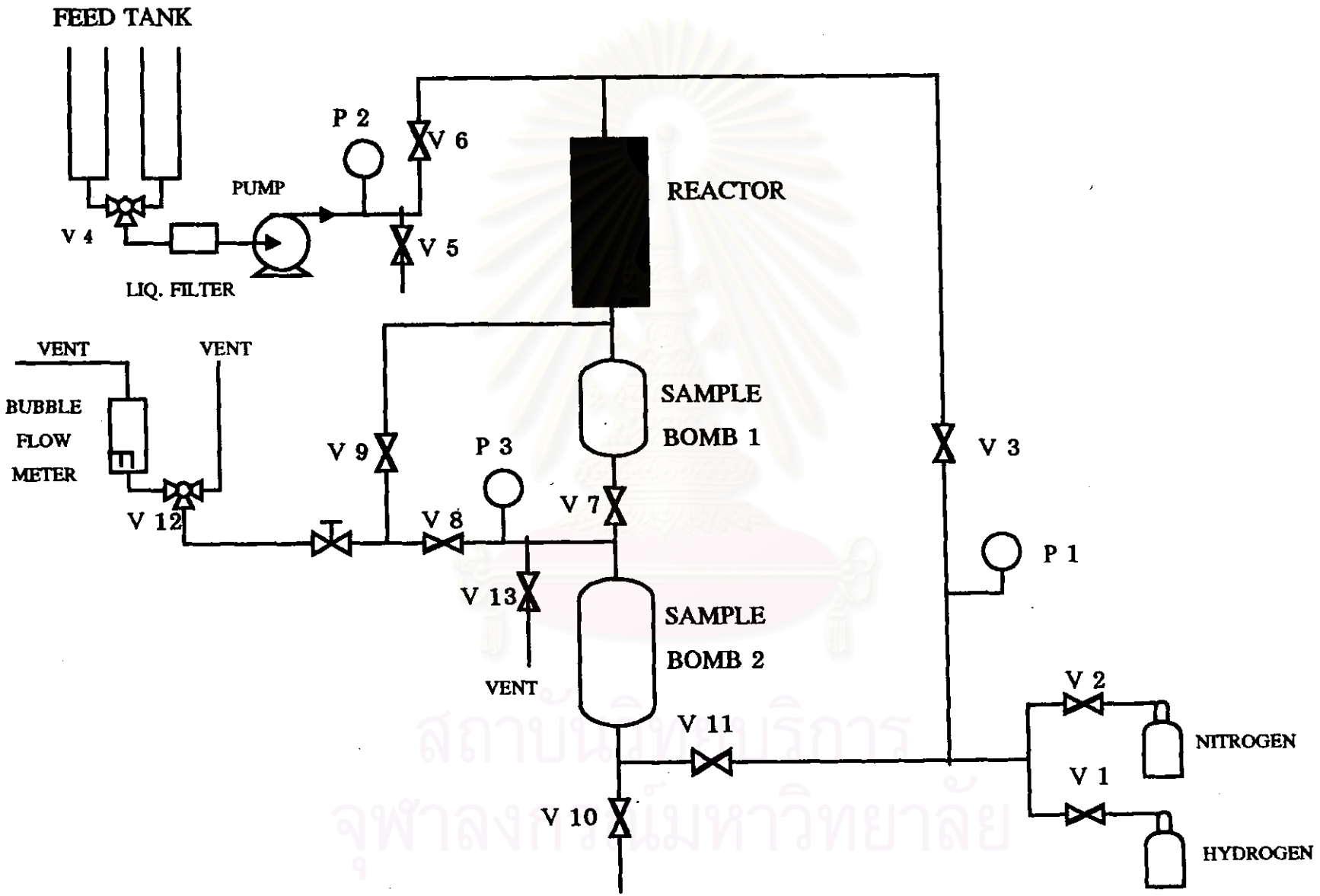

Figure 3.1 Simplified Schematic of Experimental Apparatus.

protect person from heat. Two thermocouple are placed outside the reactor wall, one for measurement of temperature at outside reactor wall and the other for the temperature controller.

Gas and liquid from the reactor flow through sample bomb 1 into sample bomb 2. Pressure gauge 3 is used to measure pressure in the sample bomb. At the sample bomb, gas and liquid are separated. The outlet gas from sample bomb goes through a micrometering valve which is used to control the outlet gas flow rate. The outlet gas flow rate is measured with a soap-film flow meter. Then gas flow passes the tank, which contains NaOH solution before it is released to the atmosphere.

The liquid products are withdrawn from the sample bomb 2 every 12 hours during the experiment without interruption to the system by closing valve 7, 8 and opening valve 10. Liquid product generated during withdrawing the sample is accumulated in the sample bomb 1 while gas flows through valve 9 and needle valve and vents to the atmosphere. After finishing sample withdrawal, the system is changed to the steady state by pressurerizing sample bomb 2 with hydrogen gas. The pressurizing is performed by closing valve 10, 3, and opening valve 11. Then close valve 9, 11 and open valves 3, 7, and 8. After each experiment, liquid products and catalysts are labeled and kept for analysis.

3.2 Experimental Procedure

Catalyst used in this study are $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$. The 5.0 grams of catalyst are packed in the middle part and supported by glass beads in the bottom of the reactor. The reactor is mounted vertically and connected with gas and liquid feed lines. After the reactor is packed, leakage is checked by nitrogen gas before starting the experimentation.

In first step of each experiment, the reactor is heated (5°C/3 min) to remove moisture and gas adsorbing on the catalyst surface at 150°C under a flow of nitrogen 300 ml/min and pressure at 200 psi for 1.5 hour. Then nitrogen gas is changed to hydrogen gas for presulfide catalyst. CS_2 is used for

presulfide catalyst. After sulfidation, the reactor is cooled up to a desired temperature. When the temperature is reached to the operating temperature, an operation is started by feeding the mixture of 10 ppm Hg, 100 ppm CS_2 in toluene (CS_2 is used to maintain the catalyst in the sulfide form) to the reactor at a flow rate 35 ml/hour, pressure 400 psig, hydrogen gas flow 30 ml/min.

Duration of each experiment is 60 hours and the sample is withdrawn from sample bomb every 12 hours. Then the samples and spent catalysts are digested to obtain the ionic form and reduce analytical interference before it is analzed by atomic absorption spectrometry.

3.3 Analytical Technique

3.3.1 Mercury measurement

Flow Injection Analysis Mercury Hydride system is a technique that provides the high sensitivity and is suitable for measurement mercury in water. The hydride technique involves in the reaction of acidified aqueous samples and a reducing agent such as sodium borohydride. The sodiumborohydride/acid reduction generates hydrides as shown in the following equations

$$NaBH_4 + 3H_2O + HCl \longrightarrow H_3BO_3 + NaCl + 8H$$

$$E^{m+} + H(excess) \longrightarrow Ehn + H_2(excess)$$

where E = the analyze of interest and m may or may not equal n

This reaction generates a volatile hydride which is transported to a quartz cell by means of an argon carrier gas. In the quartz cell, the hydrides are converted to gaseous metal atoms. This technique is applicable to the analysis of not only water but also other materials. For other materials, the sample must be digested and oxidized in order to ensure that the mercury in the sample is converted to the mercuric ion, and dissolved in aqueous media. The method of digestion used in this study is applied from ASTM D-3223 which is a standard method for determining of total mercury in water. In the procedure for digestion, 30 grams of liquid sample is contained in 250 ml flat round flask; 5 ml. of concentrated sulfuric acid and concentrated nitric acid are added and mixed after

each addition. Then 15 ml of potassium permanganate solution is added to a flask. The mixture is stirred vigorously for at least 15 min. and then 8 ml of potassium persulfate solution is added to the flask. The flask at the top is equipped with a reflux condenser and subsequently is heated in electric heating mantles at 95°C for approximately 2 hours. After that the flask is removed from the heater and cooled to ambient temperature. Then 6 ml of sodium chloride-hydroxylamine hydrochloride solution is added to the sample and shaken for a few seconds. The solution is transferred into 250 ml separating funnel and shaken virgously. After the water-phase separates from toluene-phase, the water-phase is added to a 100 ml volumetric flask. The solution in the funnel is still washed with 10 ml of deionized water. This water is also separated and added to the volumetric flask until the flask is filled up to the mark. Then the obtained aqueous solution is shaken and transferred to a sample bottle. The quantity of mercury containing in the digested solution is measured in the next step.

3.3.2 Catalyst characterization

Surface area and pore volume of the sample is measured by the BET method. A micromeritics model ASAP 2000 system consists of two parts: sample preparation or degassing and sample analysis. Approximate 0.4 grams of the catalyst is weighed and transferred into the sample preparation tube. The catalyst is heated and placed under vacuum to remove moisture and other contaminants. Temperature of degassing is carried out at 150°C and pressure is vacuumed until reaching 10 mmHg. After that, the sample tube might be allowed cool to ambient temperature and the catalyst is weighted and then the degassed sample is transferred from the degassed port to the analysis port. The sample information file is assign and then the sample is analyzed automatically at vacuum pressure of 15 mmHg. Liquid nitrogen is used as a coolant. The nitrogen gas is used as analysis gas.

Table 3.1 Properties of Toluene*

Formula	C_7H_8
Chemical Name	Toluene
Physical properties	
Molecular Weight	92.13
From	liquid
Colour	colourless
Boiling point (° C)	110.8
Melting Point (° C)	-95
Specific Gravity	0.866
Solubility	soluble in ether And alcohol
Purity	> 99%
Supplier	Merck

*From Encyclopedia of Chemical Engineering

Table 3.2 Properties of Mercuric chloride*

Formula	$HgCl_2$
Chemical Name	Mercuric chloride
Physical properties	
Molecular Weight	271.52
From	liquid
Colour	white
Boiling Point (° C)	302
Melting Point (° C)	277
Specific Gravity	5.44
Solubility	soluble water
Purity	> 99%
Supplier	Carlo Erba

*From Merck Index

Table 3.3 Properties of Diphenylmercury*

Formula	$C_{12}H_{10}Hg$
Chemical Name	Diphenylmercury
Physical properties	
Molecular Weight	354.8
From	solid
Colour	white
Boiling Point (° C)	-
Melting Point (° C)	121 - 124
Specific Gravity	2.32
Solubility	moderately soluble in toluene
Purity	> 97%
Supplier	Fluka

*From Supplier

Table 3.4 Properties of Nitric Acid*

Formula	HNO_3
Chemical Name	Nitric Acid
Physical properties	
Molecular Weight	63.02
From	liquid
Colour	colourless
Boiling Point (° C)	83
Melting Point (° C)	-41.59
Specific Gravity	1.502
Solubility	soluble in water
Purity	> 99%
Supplier	BDH

*From Merck Index

Table 3.5 Properties of Sulfuric Acid*

Formula	H_2SO_4
Chemical Name	Sulfuric Acid
Physical properties	
Molecular Weight	98.08
From	liquid
Colour	colourless
Boiling Point (° C)	~ 290
Melting Point (° C)	10
Specific Gravity	1.84
Solubility	soluble in water
Purity	> 99%
Supplier	Merck

*From Merck Index

Table 3.6 Properties of Potassium Permanganate*

Formula	$KmnO_4$
Chemical Name	Potassium Permanganate
Physical properties	
Molecular Weight	158.03
From	solid
Colour	dark purple
Boiling Point (° C)	-
Melting Point (° C)	-
Specific Gravity	2.71
Solubility	soluble water
Purity	> 99%
Supplier	Carlo Erba

*From Merck Index

Table 3.7 Properties of Potassium Persulfate*

Formula	K_2SO_8
Chemical Name	Potassium Per sulfate
Physical properties	
Molecular Weight	270.32
From	solid
Colour	white
Boiling Point (° C)	-
Melting Point (° C)	-
Specific Gravity	-
Solubility	soluble in water
Purity	> 99%
Supplier	Calro Erba

*From Merck Index

Table 3.8 Properties of Sodium Chloride*

Formula	$NaCl_2$
Chemical Name	Sodium Chloride
Physical properties	
Molecular Weight	58.54
From	solid
Colour	white
Boiling Point (° C)	804
Melting Point (° C)	-
Specific Gravity	2.17
Solubility	soluble in water
Purity	> 99%
Supplier	Carlo Erba

*From Merck Index

Table 3.9 Properties of Hydroxylamine-Hydrochloride*

Formula	$NH_2OH.HCl$
Chemical Name	Hydroxylamine-Hydrochloride
Physical properties	
Molecular Weight	69.49
From	solid
Colour	white
Boiling Point (° C)	58
Melting Point (° C)	33
Specific Gravity	1.20
Solubility	soluble in water and ether
Purity	> 99%
Supplier	Carlo Erba

*From Merck Index