CHAPTER III

EXPERIMENTS AND ANALYSIS TECHNIQUES

3.1 Experimental Apparatus

The hydrodenitrogenation studies are carried out in a fixed-bed reactor employing a commercial $NiMo/Al_2O_3$ hydrotreating catalyst (3 wt% dry basis of Ni and 13 wt% dry basis of Mo). The entire system is constructed with stainless steel and allow safe operation at pressure up to approximately 1,600 psig (17 MPa). A simplified schematic of the experimental apparatus is shown in Figure 3.1.

Gas is fed from a high-pressure cylinder through a regulator which maintains reactor pressure at the desired level. Liquid feed is pumped into the reactor by a pump. Gas and liquid feed (described below) are passed over the reactor in concurrent downflow. The reactor in a vertical configuration is 48 cm (18.9 inch) length, 1.27 cm (0.5 inch) outside diameter, 0.089 cm (0.035 inch) thick of 316 stainless steel tube and contained 1 gram of catalyst. A single catalyst charge is used throughout an entire series of experiments reported here. The catalyst bed height is 1.3 cm, the remaining space at the bottom of the reactor is filled with 3-mm-diameter glass beads. The reactor is installed in a 10-cm-diameter block and heated by two heating bands. The temperature is measured by two thermocouples which are mounted axially in the reactor and placed outside of the reactor. The temperature of the reactor is controlled by a temperature controller which receives temperature signals from the thermocouple. Every effort is made to maintain the reactor isothermally. This necessitated the fabrication of an insulator surrounding the reactor which

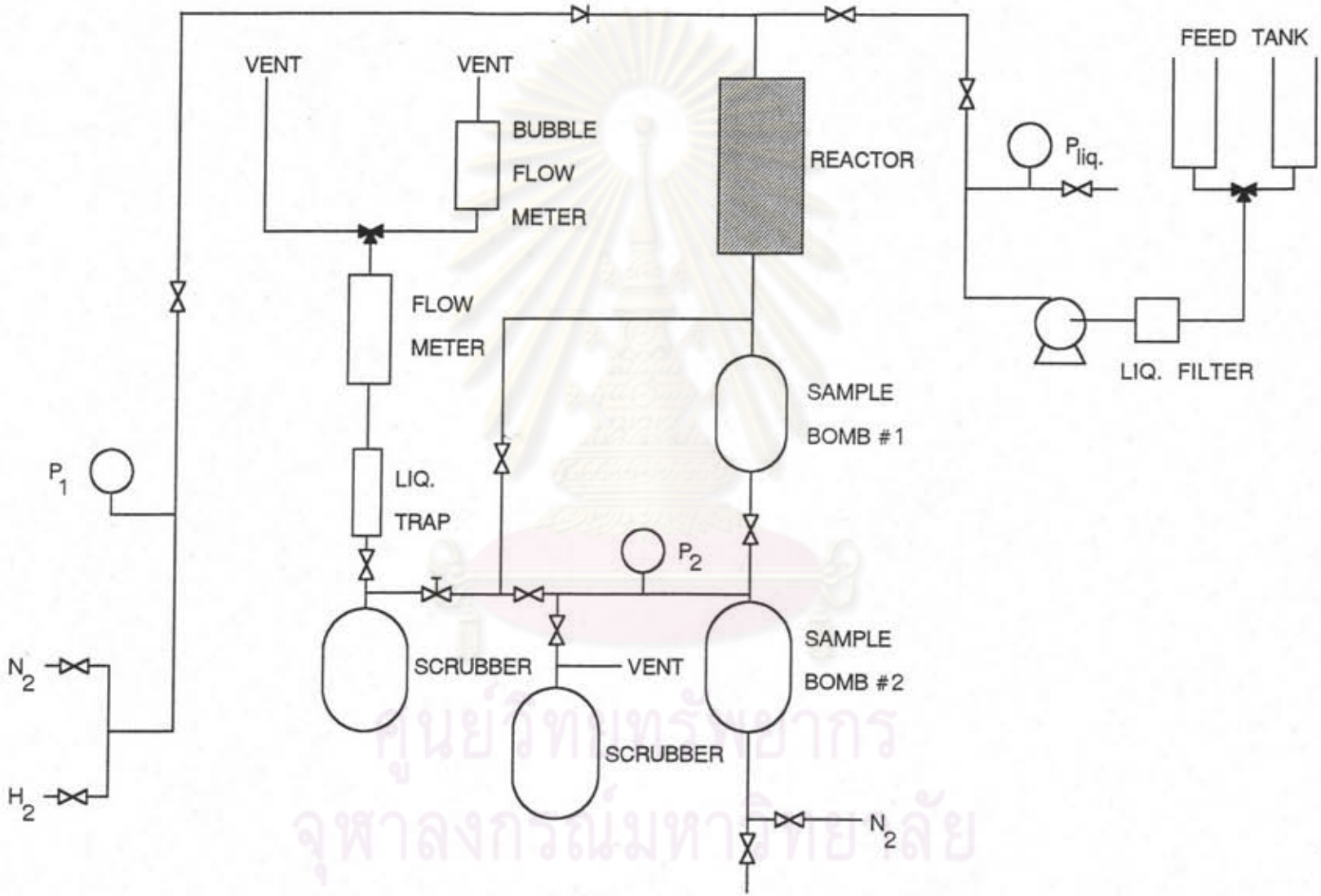

Figure 3.1 Simplified Schematic of Experimental Apparatus

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is made from insulation fire bricks. The liquid product is collected in sample bomb. The exhaust gas from the sample bomb flows into a scrubber which is filled with sodium hydroxide solution. Bubble flowmeter is used to measure exhaust gas flow rates. The unit is operated continuously but the liquid products are collected periodically from the reactor.

3.2 Experimental Procedures

The fresh catalyst is first heated under a flow of nitrogen at a rate of approximately 500 cm^3/min and 200 psig. Nitrogen is obtained from a high-pressure cylinder. The reactor temperature is raised from ambient to 200°C at a heating rate of 3°C/min and held at 200°C for 1 hour. It is considered that all the moisture and adsorbed gas on the catalyst surface are removed by this treatment. At the end of this period, the reactor is cooled to 150°C in a flow of nitrogen and then the catalyst is sulfided to maintain the catalyst in the sulfide form. If the catalyst is not sulfided before use, NiO may be reduced to metallic Ni by the reducing environment in the reactor, and this may then be difficult to convert to the sulfide. Metallic Ni may cause undesirable reactions and probably sinters more rapidly than a nickel sulfide (Satterfield, 1980).

In this study, sulfiding is accomplished with a mixture of 1 wt% C_2S/99 wt% hexanes flowing at 30 cm^3/hr. The temperature is increased at a rate of 5°C/min to a final temperature of 350°C which is maintained for 2.30 hours in the flow of hydrogen stream after the temperature is 150°C. The pressure of the system is 100 psig at a hydrogen flow rate of 500 cm^3/min. Hydrogen is obtained from a high-pressure cylinder.

After sulfidation, the reactor is cooled to a desired temperature at rate of 5°C/min with nitrogen stream. This is performed at a rate of nitrogen stream

approximately 500 cm^3/min and 200 psig for 1.30 hours. The gas is then switched to hydrogen stream at 400 cm^3/min and a liquid feed is allowed to flow into the reactor by a pump.

Properties of the chemicals used in these experiments are given in Table 3.1 to 3.8, respectively.

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Table 3.1 Properties of Toluene*

Formula	$C_6H_5CH_3$
Structure	
Chemical Name	Methylbenzene
Physical Properties	
Molecular Weight	92.14
Form	liquid
Color	colorless
Melting Point (^oC)	-95
Boiling Point (^oC)	68.7
Specific Gravity	0.87
Solubility	soluble in alcohol, ether insoluble in water
Purity	> 99.5%
Supplier	MERCK

* From Chemical Engineering Handbook and supplier

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Table 3.2 Properties of Quinoline*

Formula	C_9H_7N
Structure	
Chemical Name	Quinoline
Physical Properties	
Molecular Weight	129.16
Form	liquid
Color	brown-black
Melting Point (°C)	-17 to -13
Boiling Point (°C)	108 to 110
Specific Gravity	1.093
Solubility	soluble in alcohol, ether
Purity	> 97%
Supplier	Fluka

* From Chemical Engineering Handbook and supplier

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Table 3.3 Properties of Ethyl Sulfide*

Formula	$C_4H_{10}S$
Structure	$CH_3CH_2SCH_2CH_3$
Chemical Name	Ethyl Sulfide
Physical Properties	
Molecular Weight	90.19
Form	liquid
Color	colorless
Boiling Point (^oC)	92
Specific Gravity	0.835
Solubility	soluble in alcohol, ether insoluble in water
Purity	> 98%
Supplier	Fluka

* From The Merck Index and supplier

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Table 3.4 Properties of Thiophene*

Formula	C_4H_4S
Structure	
Chemical Name	Thiophene
Physical Properties	
Molecular Weight	84.14
Form	liquid
Color	colorless
Melting Point (°C)	-38.3
Boiling Point (°C)	82 to 84
Specific Gravity	1.063
Solubility	soluble with most organic solvents insoluble in water
Purity	> 98%
Supplier	Fluka

* From The Merck Index and supplier

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Table 3.5 Properties of Methyl Sulfide*

Formula	C_2H_6S
Structure	CH_3SCH_3
Chemical Name	Methyl Sulfide
Physical Properties	
Molecular Weight	62.13
Form	liquid
Color	colorless
Melting Point (^oC)	-83
Boiling Point (^oC)	36 to 37
Specific Gravity	0.847
Solubility	soluble in alcohol, ether insoluble in water
Purity	> 97%
Supplier	Fluka

* From The Merck Index and supplier

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Table 3.6 Properties of Methyl Disulfide*

Formula	$C_2H_6S_2$
Structure	CH_3SSCH_3
Chemical Name	Methyl Disulfide
Physical Properties	
Molecular Weight	94.20
Form	liquid
Color	colorless
Boiling Point (^oC)	108 to 110
Specific Gravity	1.060
Purity	> 98%
Supplier	Fluka

* From Supplier

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Table 3.7 Properties of Carbon Disulfide*

Formula	CS_2
Structure	CS_2
Chemical Name	Carbon Disulfide
Physical Properties	
Molecular Weight	76.14
Form	liquid
Color	colorless
Melting Point (^{o}C)	-111.6
Boiling Point (^{o}C)	46
Specific Gravity	1.26
Solubility	soluble in ethanol, ether, benzene, chloroform, carbon tetrachloride, oils
Purity	> 99.9%
Supplier	MERCK

* From The Merck Index and supplier

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Table 3.8 Properties of Benzene*

Formula	C_6H_6
Structure	
Chemical Name	Benzene
Physical Properties	
Molecular Weight	78.115
Form	liquid
Color	colorless
Boiling Point (^{o}C)	80.1
Specific Gravity	0.879 ± 0.002
Solubility	soluble in alcohol, ether, acetone
Purity	> 99.5%
Supplier	CARLO ERBA

* From Encyclopedia of Chemical Engineering and supplier

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3.3 Analysis Techniques

The liquid products are drawn periodically from the reactor and identified using gas chromatography. The gas chromatography is a Shimadzu GC-8A equipped with a flame ionization detector (FID). The column is a 50-m-long, 0.25-mm-i.d., 0.3 μm-film glass column packed with OV-1 Bonded. Peak areas are measured with a Chromatopac C-R3A integrator. The gas chromatographic operating conditions are summarized in Table 3.9.

Qualitative analysis: The retention time of each unknown peaks are compared with the retention time of commercially available compounds as standards. Molecular weight and retention time of standard compounds are shown in Table 3.10.

Quantitative analysis: The weight of each compounds are calculated from the integrated areas shown in the chromatogram using internal standardization. The advantages of internal standardization are that quantities injected need not be accurately measured and the detector response need not be known or remain constant since any change in response will not alter the area ratio (McNair and Bonelli, 1968). Internal standard which used in experiments is benzene since benzene is well resolved from other peaks, approximate concentration of unknown and structural similarity to unknown. Satterfield et al. (1978) used benzene as internal standard for investigating intermediate reactions in the catalytic hydrodenitrogenation of quinoline.

Table 3.9 Chromatographic Operating Conditions

Hydrogen Flow Rate	:	47 cm^3/min
Air Flow Rate	:	500 cm^3/min
Initial Temperature	:	60°C
Initial Time	:	19 min
Heating Rate	:	5°C/min
Final Temperature	:	110°C
Final Time	:	22 min
Injector Temperature	:	220°C
Detector Temperature	:	220°C
Sample Size	:	0.15 µl
Split Ratio	:	1/40.27
Air pressure	:	0.5 kg/cm^2
Hydrogen pressure	:	0.6 kg/cm^2
Nitrogen pressure	:	2.0 kg/cm^2
Range	:	10^2

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Table 3.10 Molecular Weight and Retention Time of Standard Compounds

Compounds	Molecular Weight	Retention Time (min)
Benzene	78.11	4.16
Toluene	92.14	7.45
Propylcyclohexane	126.24	16.69
Propylbenzene	120.20	18.09
Decahydroquinoline	139.24	32.27, 33.68
5,6,7,8-Tetrahydroquinoline	133.20	37.75*
Quinoline	129.16	38.80
o-Propylaniline	135.21	39.15
1,2,3,4-Tetrahydroquinoline	133.20	49.63

* From Sirisak, 1993

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The acronyms for the various compounds present are given in Table 3.11.

Table 3.11 Acronyms for Chemical Compounds

Acronym	Chemical Name
Q	Quinoline
PyTHQ	1,2,3,4-Tetrahydroquinoline
BzTHQ	5,6,7,8-Tetrahydroquinoline
DHQ	Decahydroquinoline
OPA	o-Propylaniline
PCH	Propylcyclohexane
PB	Propylbenzene
PCHA	Propylcyclohexylamine
DOPA	Dihydro o-Propylaniline

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