



CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURES

AND

ANALYSIS TECHNIQUES

3.1 Experimental Apparatus

A schematic diagram of this system is shown in Figure 3.1. The system used in this work is a three-phase system, called a trickle-bed reactor system. All parts were designed and constructed with stainless steel, i.e. tubes, fitting, and valves, to withstand a maximum operating pressure of 1600 psig (11.03 MPa) and to protect the system from corrosion.

Gas and liquid feeds flow concurrently from the upper part through the reactor. In the gas section, hydrogen gas is fed from the H_2 tank through a pressure regulator and pressure gauge, P_4 , which is used to control and measure hydrogen pressure, respectively. Before hydrogen gas flows into the reactor, its flow rate is measured by a mass flow meter, Alborg model AFM 2600, which is located upstream from the reactor. Liquid feed is pumped with Eldex precision metering pump to the reactor. The reactor is packed with 3 grams of NiMo/alumina catalyst supported with glass beads at the bottom of the reactor. The reactor has dimension : 43.2 cm (17 inches) long, 1.27 cm (0.5 inch) outside diameter, and

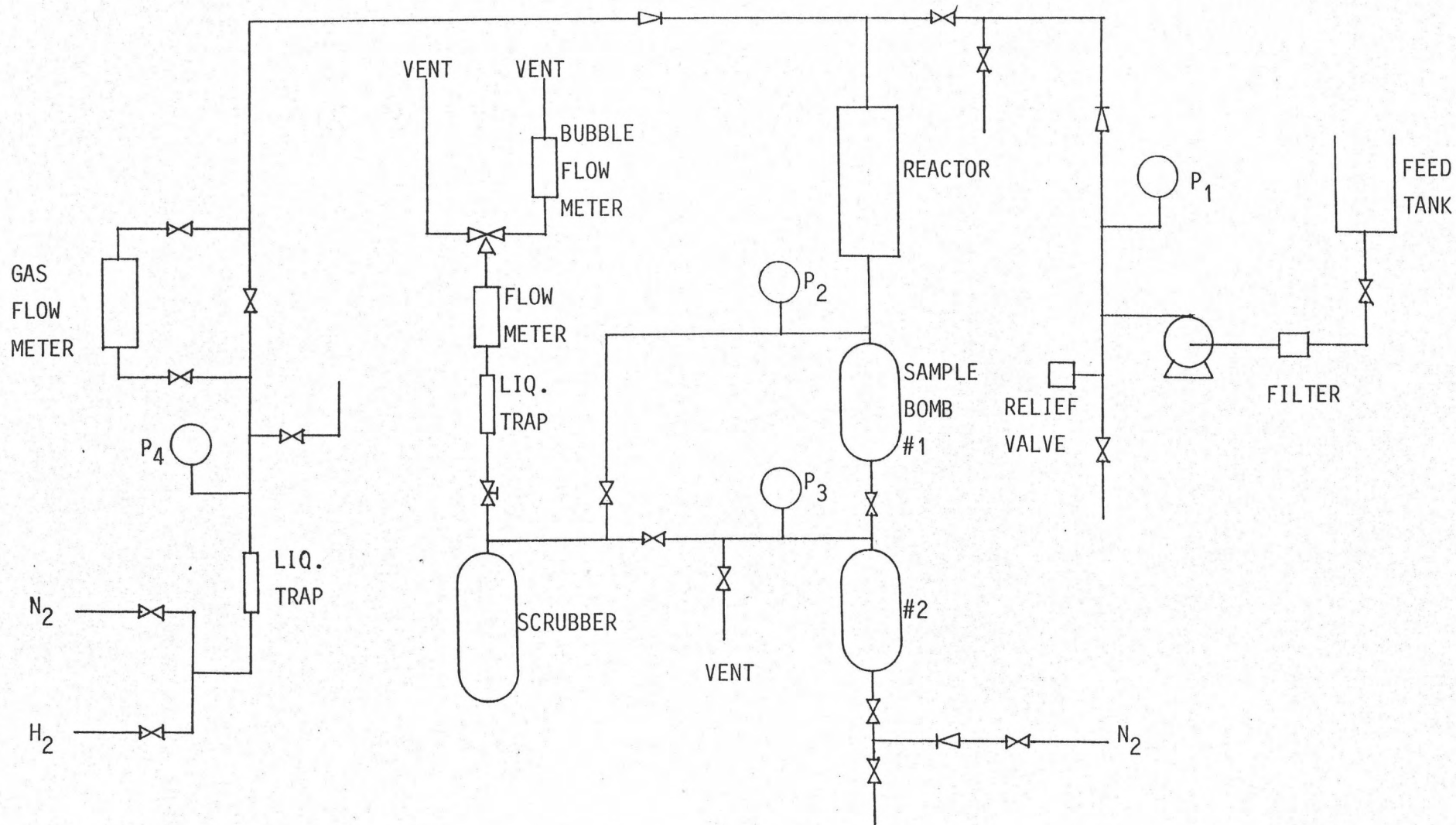


Figure 3.1 Schematic Diagram of the System

0.089 cm (0.035 inch) thick. It is made of 316 stainless steel tube. In the middle part of the reactor, two heating bands are placed to generate heat for the reactor and its temperature is measured by a thermocouple. Thermocouple is placed inside and outside of the reactor. The temperature of the reactor is controlled by a temperature controller which receives temperature signals from the thermocouple. Glass wool is used as an insulator which is wrapped around the heating band to prevent heat loss.

In the sample bomb #1 and #2, products of reaction and gas are separated. The outlet gas from the sample bomb flows into a scrubber which is filled with 30 vol% of ethanolamine solution. The outlet gas flow rate is showed at a low pressure meter and is measured with a soap-film flow meter. A micro-metering valve which is placed downstream from the scrubber is used to control the outlet gas flow rate.

Every 12 hours during experiment, the liquid products are collected. After each experiment, the catalyst in the reactor was collected for analysis.

3.2 Experimental Procedures

The catalyst used in this study was NiMo/alumina commercial hydrotreating catalyst supplied as 1/8 inch extrudates. The catalyst used was 3 grams and was packed in the middle of the reactor. At the bottom of reactor, glass beads were used to support the catalyst. The catalyst charged gave a packed bed of 2.5 inches in length.

The reactor is mounted vertically and connected with gas and liquid feed lines. For leakage testing of the system, nitrogen gas was used by pressurizing the system to higher pressure than the operating pressure. Before study each experiment, the reactor was first heated to remove moisture and adsorbed gas on the catalyst surface at 200 °C under a flow of nitrogen for 1.5 hours. Catalyst was converted to the sulfide form before each experiment.

When the required temperature was reached (300 °C) a run was started by pumping the liquid feedstock to the reactor at a flow rate of 10 cm³/hr. Then, pressurizing with hydrogen to 450 psig at a flow rate of 400 cm³/min. After hydrogen and liquid feed rates were established, the first data from the pressure gauge and the temperature indicator was recorded. The first liquid product sample was collected after the first 12 hours. Table 3.1 shows the experimental operating conditions.

The compositions of liquid feedstock were toluene, 1 wt% nitrogen as quinoline, 0.5 wt% carbon disulfide, and 5 wt% n-hexane as shown in Table 3.2. Toluene is used as a feed carrier and has a good solubility for these compounds. Quinoline is a good model compound for the 6-membered ring heterocyclic nitrogen compounds used for studying hydrodenitrogenation reaction (84). Carbon disulfide is used to produce hydrogen sulfide in the reaction for giving a sulfide-state of catalyst. Carbon disulfide is rapidly converted to H₂S and CH₄ (85). n-Hexane is used as an internal reference. Organometallic compounds used in were titanocene dichloride,

Table 3.1 Experimental Operating Conditions

Operating Conditions:

Temperature	: 200 - 300 °C for experiment 1
	: 300 °C for experiments 2 to 7
Pressure	: 450 psig
Feed flowrate	: 10 cm ³ /hour
Hydrogen flowrate:	400 cm ³ /minute
Time	: 120 hours
Sampling	: every 12 hours
Catalyst	: 1/8" Extrudate of NiMo/alumina
Catalyst weight	: 3 grams

Table 3.2 The Compositions of Feedstock

Feedstock: Toluene, 1 wt% Nitrogen as Quinoline, 0.5 wt% Carbon Disulfide, and 5 wt% n-Hexane

- Experiment 1 : Feedstock (preliminary run)
- Experiment 2 : Feedstock (reference run)
- Experiment 3 : Feedstock (duplication of reference run)
- Experiment 4 : Feedstock and 200 ppm of iron as ferrocene
- Experiment 5 : Feedstock and 200 ppm of iron (duplication run of experiment 4)
- Experiment 6 : Feedstock and 200 ppm of titanium as titanocene dichloride
- Experiment 7 : Feedstock and 200 ppm of mercury as diphenylmercury
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ferrocene, and diphenylmercury that they contain titanium, iron, and mercury, respectively. The concentration of metal in each experiment is 200 ppm.

Tables 3.3 to 3.7 are shown the properties of toluene, quinoline, titanocene dichloride, ferrocene, and diphenylmercury, respectively. Experiment 1 was conducted to find a suitable operating conditions for this reaction. For this study, the quinoline hydrodenitrogenation was conducted at 300 °C and 450 psig under the hydrogen pressure. In experiments 2 to 7, the concentration of metal used was 200 ppm of metal which was added directly to the liquid feedstock. The operating conditions were identical to the ones used in experiment 1 except the temperature which was 300 °C.

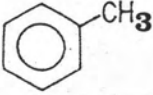
3.3 Analysis Techniques

In each experiment, two types of samples were collected: liquid product samples and catalyst samples. Catalyst samples were analysed for coke content, metal distribution, surface area, and pore volume whereas the liquid products were analysed for quality and quantity of each compound to monitor the distribution of nitrogen compounds.

3.3.1 Catalyst Characterization

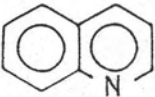
Catalyst samples were extracted with tetrahydrofuran (THF) in a Soxhlet extraction unit before they were analysed. The catalyst samples are dried and weighted at room temperature and placed in a furnace at 550 °C

Table 3.3 Properties of Toluene *

Formula	$C_6H_5CH_3$
Structure	
Chemical Name	Methylbenzene
Physical Properties	
Molecular Weight	92.13
Form	liquid
Color	colorless
Melting Point (°C)	-95
Boiling Point (°C)	110.8
Specific gravity	0.866
Solubility	Soluble in ether, alcohol Insoluble in water

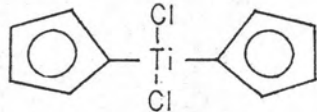
* From Chemical Engineering Handbook

Table 3.4 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)	-15
Boiling Point (°C)	237.1
Specific Gravity	1.095
Solubility	Soluble in alcohol, ether

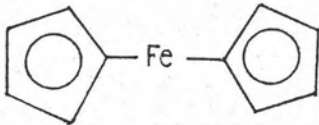
* From Chemical Engineering Handbook

Table 3.5 Properties of Titanocene dichloride *

Formula	$(C_5H_5)_2Cl_2Ti$
Structure	
Chemical Name	Bis(cyclopentadienyl) titanium dichloride, Dicyclopentadienyl titanium dichloride
Physical Properties	
Molecular Weight	249.00
Form	crystallide solid
Color	vivid red
Melting Point (°C)	289
Specific gravity	1.600
Solubility	Moderately soluble in toluene and in alcohol

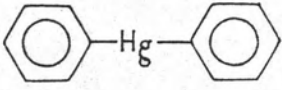
* From Encyclopedia of Chemical Technology

Table 3.6 Properties of Ferrocene *

Formula	$(C_5H_5)_2Fe$ or $C_{10}H_{10}Fe$
Structure	
Chemical Name	Bis(cyclopentadienyl)iron, Dicyclopentadienyliron
Physical Properties	
Molecular Weight	186.04
Form	crystalline solid
Color	orange
Melting Point (°C)	174-176
Boiling Point (°C)	249
Solubility	Soluble in alcohol, ether, toluene, and benzene

* From Chemical Engineering Handbook

Table 3.7 Properties of Diphenylmercury *

Formula	$(C_6H_5)_2Hg$ or $C_{12}H_{10}Hg$
Structure	
Chemical Name	Mercurydiphenyl
Physical Properties	
Molecular Weight	354.80
Form	crystallide
Color	white
Melting Point (°C)	121-124
Solubility	Moderately in toluene and in alcohol

* From Supplier (Fluka)

(1022 °F), 60 hours to burn off a carbonaceous material. The weight difference of catalyst after burning is defined as coke content on the catalyst. The amount of coke content is calculated as follows:

$$\text{Weight \% of coke content} = (W_1 - W_2)/W_1 \times 100$$

where

W_1 = weight of catalyst before burning

W_2 = weight of catalyst after burning

Metal distribution on a catalyst samples were analysed by Scanning Electronmicroscope, JEOL Model JSM-5400, equipped with an Energy Dispersive X-Ray Analyzer, LINK Model QX 2000. The metal distribution was analysed on a crosssectional area of the catalyst pellet at four locations from the edge to the center of the pellet, as shown in Figure 3.2.

An automatic physisorption instrument, ASAP 2000, and an automatic bench-top mercury intrusion porosimeter, PoreSizer 9320, are used to determine the surface area and the pore volume of the catalyst, respectively. Approximately 0.5 grams of the catalyst sample is used for the analysis of these properties. The operating conditions used in a physisorption instruments are shown in Table 3.8.

3.2.2 Liquid Product Characterization

A Perkin Elmer model 8700 gas chromatograph equipped with GL Science capillary column model OV-1 is used to analysed the quality and quantity of the liquid

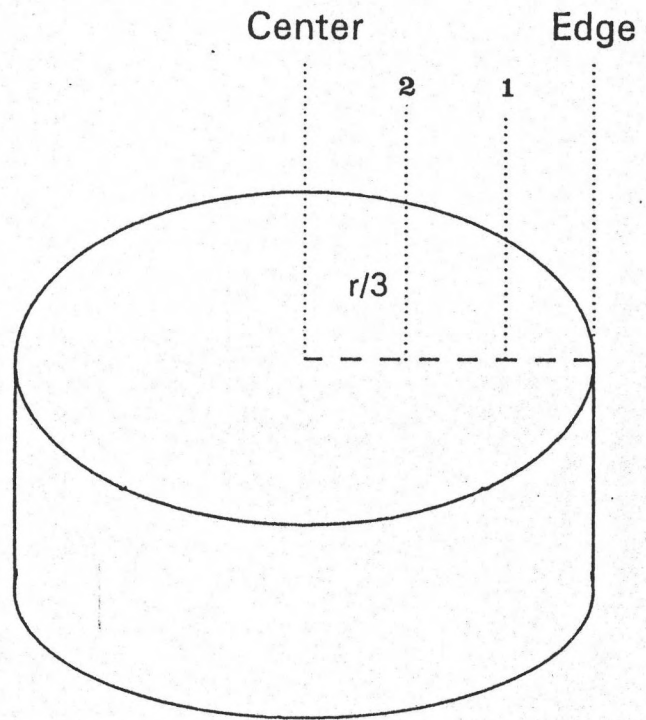


Figure 3.2 Cross-Section of Catalyst Pellet

Table 3.8 Operating Conditions for a Physisorption Instrument

Degas Conditions :

Temperature	250 °C
Time	3 hours
Vacuum Set	999 μmHg

Analysis Condition:

Vacuum Set	15 μmHg
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products: quinoline and their reaction intermediate products. The operating conditions of the gas chromatograph are shown in Table 3.9.

Qualitative analysis: The retention time of each unknown peaks are compared with the retention time of standard compounds. Retention time of standard compounds are shown in Table 3.10.

Quantitative analysis: The concentration of each compounds are calculated from the integrated areas shown in the chromatogram.

Table 3.9 Operating Conditions for Gas Chromatograph

Initial Temperature	45 °C
Initial Time	5 min
Heating Rate	6 °C/min
Final Temperature	160 °C
Final Time	10 min
Injector Temperature	225 °C
Detector Temperature	225 °C

Table 3.10 Retention Times of Standard Compounds

Compounds	Times (min)
n-Hexane	4.76
Toluene	8.84
Propylcyclohexane	14.91
Propylbenzene	15.37
Decahydroquinoline	21.91
5,6,7,8-Tetrahydroquinoline	23.68
Quinoline	23.99
1,2,3,4-Tetrahydroquinoline	26.73
