CHAPTER III

EXPERIMENTS AND ANALYSIS TECHNIQUES

3.1 Experimental Apparatus

In this study, a fixed-bed flow reactor system is used for catalytic reforming of n-hexane. A schematic diagram of this system is shown in Figure 3.1. All parts are designed and constructed with stainless steel, i.e. tubes, fittings, and valves to withstand a maximum operating temperature of 500°C (932°F) and a maximum operating pressure of 500 psig (3.55 MPa). The stainless steel is also used to protect the system from corrosion.

Gas and liquid feed flow 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 a pressure regulator and pressure gauge 1, 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 which is located between by pass valve 18 and 20 upstream from the reactor. The mass flow meter is Allborg Instrument Model AFM 2600 having a capability to use for maximum pressure of 500 psig (3.55 MPa).

In the liquid section, each feed is filled in a burette (feed tank which shows liquid level) and is pumped through valve 2 and liquid filter into Eldex Precision Metering pump which has ability to generate high pressure at low flow rate. The feed pressure is monitored by pressure gauge 4. Safety line located before pressure gauge 4 is equipped with rupture disk,

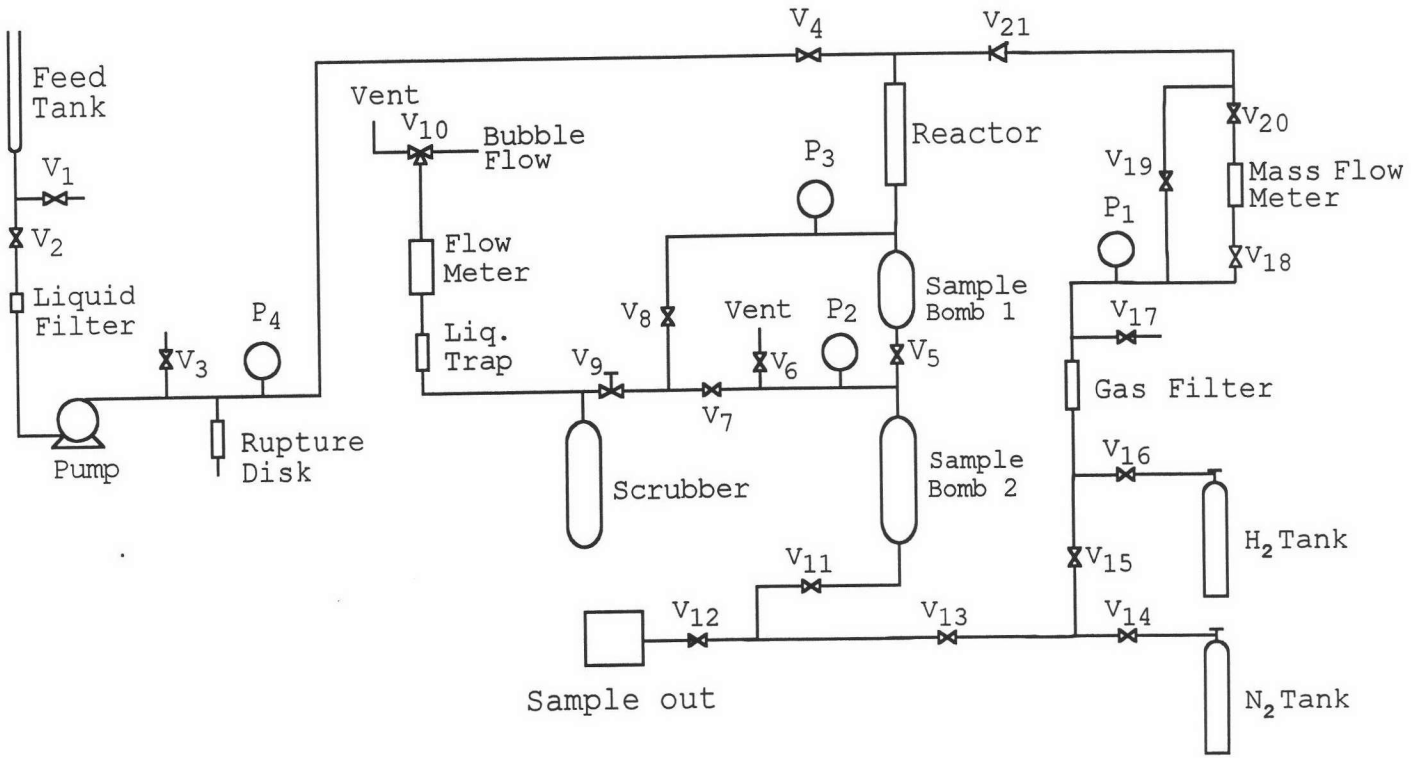

Figure 3.1 A Schematic Diagram of Reforming System

rated at 500 psig (3.55 MPa) to protect feed system from excessive pressure. Feed and hydrogen gas flow concurrently downward through the reactor which is packed in the middle part with 1.0 gram of Pt-Re/alumina catalyst supported by glass beads at the bottom of the reactor. The reactor consists of 19 inches (47.88 cm.) long, 0.5 inch (1.27 cm.) outside diameter, and 0.035 inch (0.089 cm.) thick, 316 stainless steel tube. A 1/2-inch Swagelok cross is connected to the top of the reactor. Two 1/2-inch to 1/4-inch reducers are connected to both sides of cross joined with liquid and gas lines, respectively. 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 by means of a 1/4-inch to 1/8-inch reducing union which is drilled for inserting the thermowell. A small thermocouple is inserted into the thermowell to measure the temperature of the catalyst bed during the reaction.

Two iron blocks, with grooves of reactor diameter running across their entire length are used as the heating blocks. This heating blocks are made to be fitted with heating bands which are placed around the assembled blocks. Two heating bands, rated at 800 watt and 220 volt are used to supply heat for the reactor. Brick is used as an insulator which is wrapped around the heating band to prevent heat loss (keep the reactor isothermal) and protect personnel from hot surface. Two thermocouple are placed outside the reactor wall, one for measurement of temperature at outside reactor wall and the other for the temperature controller. The bottom of the reactor is fitted with a 1/2-inch to 1/4-inch reducer to enable it to be connected to the sampling system.

Liquid and gas product flow through sample bomb 1 into the sample bomb 2 where they are separated. Pressure of the sampling system is monitored by pressure gauge 3 and 2, which are connected to sample bomb 1 and sample bomb 2, respectively. The outlet gas from the sample bomb flows into a scrubber which is filled with sodium hydroxide solution (60 vol% sodium hydroxide in water). The outlet gas flow rate is showed at a low pressure rotameter and is measured with a soap-film flow meter. A micrometering valve (valve 9) which is placed upstream from the scrubber is used to control the outlet gas flow rate. Liquid trap is used to prevent liquid and particle flowing into the gas measuring devices.

The liquid products are withdrawn every 6 hours during each experiment without interruption to the system by closing valve 5 and 7. Liquid product generated during sampling process is accumulated in sample bomb 1 while gaseous products flow through valve 8 into scrubber unit before venting to atmosphere. At sample bomb 2, there was both liquid and gaseous products which are withdrawn after 6 hours. Only gaseous products are vented to the outdoor scrubber unit through valve 6 while liquid products are collected into liquid sample box through valve 11 and 12. After finishing sampling process, the system is changed to the steady state by pressurizing sample bomb 2 with hydrogen gas approximately 100 psig (0.69 MPa) through valve 16, 15, 13 and 11, respectively before valve 11 and 8 are closed and valve 5 and 7 are slowly opened, respectively. After each experiment, liquid products are labelled and kept for analysis.

3.2 Experimental Procedures

The catalyst used in this study is R62 (Pt-Re/γ-alumina) commercial catalytic reforming catalyst which contained Pt 0.22 wt%, Re 0.44 wt% and Cl 1.0-1.1 wt%. The catalyst used is 1.0 gram and packed in the middle of the reactor. The catalyst is diluted with glass beads by 1:3 volume ratio. At the bottom of the reactor, glass beads are also used to support the catalyst. The reactor is mounted vertically and connected with gas and liquid feed lines. For leakage testing of the system, nitrogen gas is used by pressurizing the system to higher pressure than the operating pressure. Before study each experiment, the reactor is first gradually heated (5°C/3 min) to remove moisture and adsorbed gas on the catalyst surface at 200°C under a flow of nitrogen at 20 ml/3 sec for 1 hour. Then the reactor is pressurized with hydrogen and gradually heated (5°C/5 min) with flow rate of 10 ml/5.5 sec to the required temperature.

When the required temperature is reached (450°C) the temperature is hold for 1 hour. A run is started by pumping the liquid feedstock to the reactor at a flow rate of 5 ml/hr. After hydrogen and liquid feed rates are established, the first data from the pressure gauge and the temperature indicator is recorded. The first liquid product sample is collected after the first 12 hours and next samples are kept every 6 hours for analysis.

The compositions of liquid feedstock are n-hexane and 10 ppm chloride as dichloromethane. n-Hexane is a model compound for normal paraffin used for studying catalytic reforming reaction. The sulfur compounds used in this study are carbon disulfide, methyl disulfide, methyl sulfide, ethyl sulfide and

thiophene. The concentration of sulfur in each experiment is 10 ppm sulfur as sulfur compound.

Duration of each experiment is 144 hours. The feedstock is hexanes which containing 10 ppm chloride as dichloromethane to stabilize acid site of the catalyst. Each sulfur compound is added into the feedstock twice in each deactivated experiment at concentration of 10 ppm sulfur as sulfur compound. The first sulfur addition period is between the hours of 48 to 72. The second sulfur addition period is between the hours of 96 to 120. The compositions of feed in each experiment are shown in Table 3.1. Table 3.2 shows the experimental operating conditions.

Properties of n-hexane, dichloromethane, carbon disulfide, methyl disulfide, methyl sulfide, ethyl sulfide and thiophene are given in Tables 3.3 to 3.9, respectively.

Table 3.1 Composition of Feedstock

Feedstock : hexanes and 10 ppm chloride as dichloromethane (CH_2Cl_2)
Experiment
1 : Feedstock (preliminary run)*
2 : Feedstock (reference run)
3 : Feedstock (duplication of reference run)
4 : Feedstock (duplication of reference run)
5 : Feedstock and 10 ppm of sulfur as carbon disulfide
6 : Feedstock and 10 ppm of sulfur as methyl disulfide
7 : Feedstock and 10 ppm of sulfur as methyl sulfide
8 : Feedstock and 10 ppm of sulfur as ethyl sulfide
9 : Feedstock and 10 ppm of sulfur as thiophene

* Preliminary run is conducted to find a suitable operating condition for this study.

Table 3.2 Experimental Operating Conditions

Temperature	:	400 and 450°C for experiment 1
	:	450°C for experiment 2 to 9
Pressure	:	100 and 200 psig for experiment 1
	:	100 psig for experiment 2 to 9
Feed flow rate	:	5 ml/hour
H_2:H/C mole ratio	:	3:1, 6:1, and 9:1 for experiment 1
	:	6:1 for experiment 2 to 9
Duration of each experiment	:	144 hours
Sampling	:	every 6 hours
Catalyst	:	Pt-Re/γ-alumina (R62)
Catalyst weight	:	1.0 gram

Table 3.3 Properties of Hexanes*

Formula	C_6H_{14}
Structure	$CH_3CH_2CH_2CH_2CH_2CH_3$
Chemical name	Hexanes
Physical properties	
Molecular weight	86.18
Form	liquid
color	colorless
Melting point (°C)	-94
Boiling point (°C)	68.7
Specific gravity	0.663
Solubility	soluble in alcohol, ether, benzene
Purity	> 99%
Supplier	J.T. Baker Inc.

* From Encyclopedia of Chemical Engineering and supplier

Table 3.4 Properties of Dichloromethane*

Formula	CH_2Cl_2
Structure	CH_2Cl_2
Chemical name	Dichloromethane
Physical properties	
Molecular weight	84.93
Form	liquid
color	colorless
Melting point (°C)	-
Boiling point (°C)	40
Specific gravity	1.32
Solubility	Soluble in alcohol, ether, benzene
Purity	> 99.5%
Supplier	Fluka

* From Encyclopedia of Chemical Engineering and supplier

Table 3.5 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 (°C)	- 111.6
Boiling point (°C)	46
Specific gravity	1.26
Solubility	Soluble in ethanol, ether, benzene, chloroform, carbon tetrachloride
Purity	> 99.9%
Supplier	Merck

* From The Merck Index and supplier

Table 3.6 Properties of Methyl Disulfide*

Formula	$C_2H_6S_2$
Structure	CH_3SSCH_3
Chemical name	Methyl Disulfide
Physical properties	
Molecular weight	94.2
Form	liquid
color	colorless
Melting point (°C)	-
Boiling point (°C)	108-110
Specific gravity	1.06
Solubility	soluble in benzene
Purity	> 98%
Supplier	Fluka

* From supplier

Table 3.7 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 (°C)	- 83
Boiling point (°C)	36.37
Specific gravity	0.847
Solubility	soluble in alcohol, ether, insoluble in water
Purity	> 97%
Supplier	Fluka

* From The Merck Index and supplier

Table 3.8 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
Melting point (°C)	-
Boiling point (°C)	92
Specific gravity	0.835
Solubility	soluble in alcohol, ether, insoluble in water
Purity	> 98%
Supplier	Fluka

* From The Merck Index and supplier

Table 3.9 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

3.3 Analysis Techniques

After each experiment, liquid samples are analyzed every 6 hours for concentration of each compounds. A Shimadzu GC-8A Gas Chromatograph equipped with GL Science Capillary Column Model OV-1 is used to determine the amount of n-hexane and their reforming products in the liquid samples. Liquid sample is injected approximately 0.1 microliter with 1/8 split ratio. The sample is vaporized at a high temperature and mixed with a carrier gas. Compounds in the gas mixture are adsorped and desorped in the capillary column at different rates. Lighter compounds are adsorped and desorped faster than havier compounds.

Flame ionization detector is used to detect the signal which are converted to the chromatogram. The chromatogram are plotted and integrated. Then they are printed on the Chromatopac C-R6A printer. The operating conditions of the gas chromatograph are summarized in Table 3.10.

Qualitative analysis: The retention time of each unknown peaks are compared with the retention time of standard compounds. The retention time of standard compounds are shown in Table 3.11. The analysis results show that only the chromatogram of 2,3-dimethylbutane and 2-methylpentane have the same retention time.

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

Table 3.10 Operating Conditions for Gas Chromatographic Technique

Initial Temperature	35°C
Initial Time	8 min
Heating Rate	5°C/min
Final Temperature	150°C
Final Time	11 min
Injector Temperature	200°C
Detector Temperature	200°C
Hydrogen Flow Rate	47 cc/min
Air Flow Rate	500 cc/min
Sample Size	0.15 ml
Air Pressure	0.5 kg/cm^2
Hydrogen Pressure	0.6 kg/cm^2
Nitrogen Pressure	2.0 kg/cm^2
Range	10^2

Table 3.11 Retention Times of Standard Compounds

Compounds	Time (min)
n-Pentane	3.16
2,2-Dimethylbutane	3.49
2,3-Dimethylbutane and 2-Methylpentane	4.01
3-Methylpentane	4.31
n-Hexane	4.79
Methylcyclopentane	5.28
Benzene	6.02
Toluene	10.30
Ethylbenzene	15.47
Xylenes	16.17, 17.18
Propylbenzene	19.88