CHAPTER III

EXPERIMENT AND ANALYSIS TECHNIQUES

3.1 Experimental Apparatus

In this study, a continuous fixed bed reactor is used for the reforming reaction of hexanes. The system is designed and constructed in order to withstand a maximum operating temperature of 500°C and a maximum operating pressure of 1600 psig (11.03 Pa). Stainless steel tubes, fitting, and valves are used to protect the system from corrosion. A general schematic diagram of the experimental set-up is shown in Figure 3.1. Details of the reactor system and experimental procedures are discribed elsewhere (Tanpichart, 1992 and Chantalaka, 1993). In this experiment, the reactor is the stainless steel tube (10.9 mm i.d., 485 mm long) 316 stainless steel tube place inside an electric furnace. 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 by means of a 1/4-inch to 1/8-inch reducing union that is drilled for inserting the thermowell. It's 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. A small amount of catalyst (1 g) is mixed with inert glass beads with an 1:3 volume prior to introduction into the reaction to improve temperature

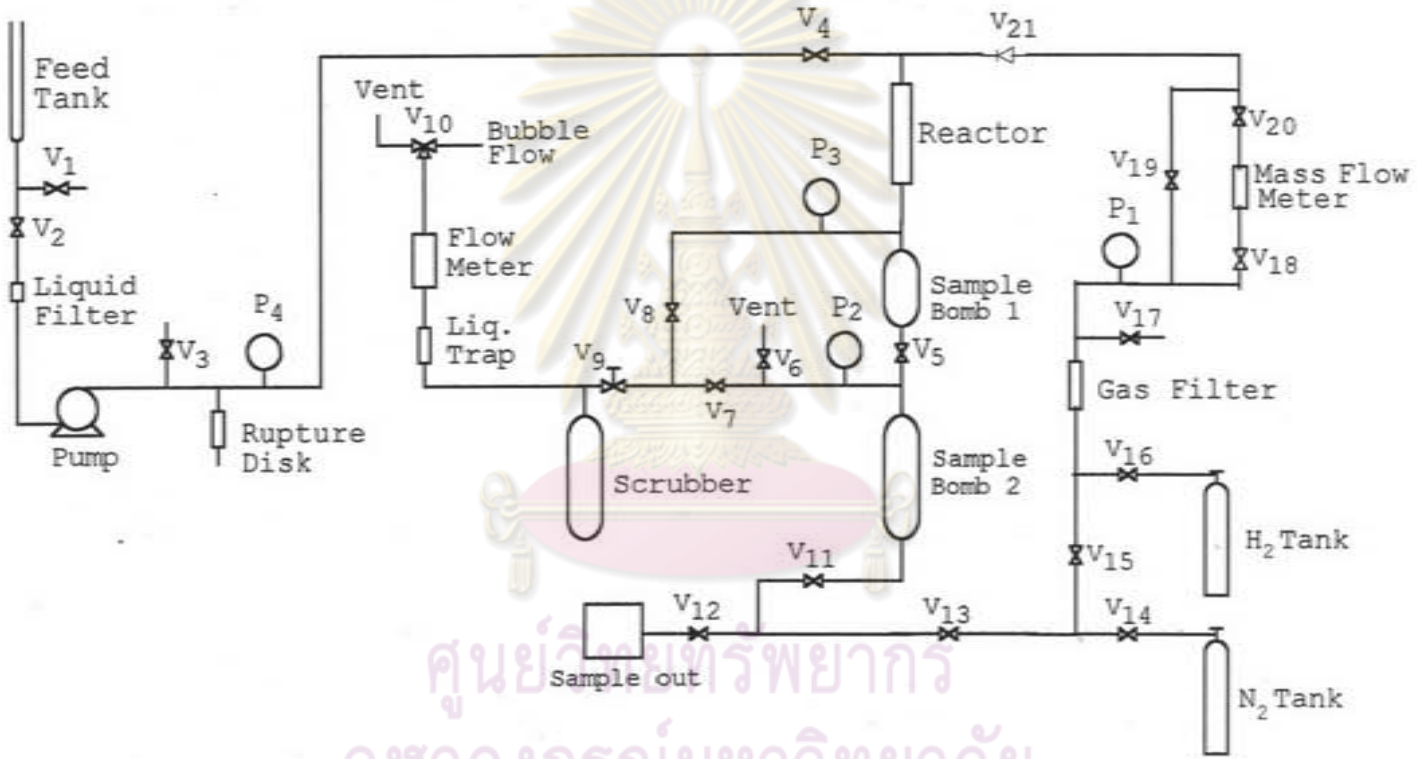


Figure 3.1 A Schematic Diagram of Reforming System

transfer through the catalyst bed. The catalyst bed is placed in the middle of the reactor that is filled in the bottom side which inert glass beads. Temperature is measured at the center of the catalyst bed by thermocouple.

The catalyst used in this study is Pt-Re/Al_2O_3. Hexanes (J.T. Baker) and hydrogen (TIG) are employed as reactants for reforming.

Nitrogen compounds used in these experiments are pyridine, 2,6-dimethylpyridine, 1,2,3,4-tetrahydroquino line, and pyrrole. Properties of the chemicals used in these experiments are given in Table 3.1 to 3.6, respectively.

3.2 Experimental Procedure

Gas and liquid feed flow in to the top of the reactor from two separated sections, called gas section and liquid section. In gas section, hydrogen pressure is controlled by the pressure regulator at the hydrogen cylinder. Hydrogen gas is fed through a mass flow meter to measure upstream hydrogen gas flow rate. In liquid section, hexanes are filled into the feed tank (burette that shows liquid level) and at a predetermined rate, is pumped with a help of calibrated Eldex precision metering pump that has ability to generate high pressure at low flow rate. The mixture was then flow concurrently through into the reactor.

Product oil and gas flow through sample bomb 1 into the sample bomb 2 where they are separated. The upstream pressure is considered as the reactor or system pressure. The gas flow rate is maintained by means of micrometering valve. The gas flow is monitored and controlled down steam from the micrometering valve by a

low pressure rotameter and a bubble flow meter, respectively.

During each experiment, liquid samples are taken every 6 hours during each experiment without interruption to the system. Liquid samples are labeled and kept for analyses but gas samples were not be kept. The liquid samples are analyzed for their composition by gas chromatographic analysis techniques.

TABLE 3.1 Properties of n-Hexane *

Formula	C_6H_{14}
Structure	$CH_3CH_2CH_2CH_2CH_2CH_3$
Chemical name	n-Hexane
Physicals properties	
Molecular weight (g/mole)	86.17
Form	liquid
Color	colorless
Melting point (^oC)	-94
Boiling point (^oC)	69
Specific gravity	0.659
Solubility	soluble in benzene, toluene
Purity	> 99%
Supplier	J.T. Baker Inc.

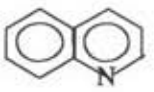
* From Encyclopedia of Chemical Engineering

TABLE 3.2 Properties of Pyridine *

Formula	C_5H_5N
Structure	
Chemical name	Pyridine
Physicals properties	
Molecular weight (g/mole)	79.10
Form	liquid
Color	colorless
Melting point (^{o}C)	-42
Boiling point (^{o}C)	115.2 $\pm$ 2.0
Specific gravity	0.982 $\pm$ 0.003
Solubility	soluble in hexanes benzene, toluene
Purity	> 99.5%
Supplier	Cairo Erba

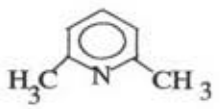
* From Encyclopedia of Chemical Engineering and Supplier

TABLE 3.3 Properties of Quinoline *

Formula	C_9H_7N
Structure	
Chemical name	Quinoline
Physicals properties	
Molecular weight (g/mole)	129.16
Form	liquid
Color	brown-black
Melting point (^{o}C)	-17 to -13
Boiling point (^{o}C)	108-110
Specific gravity	1.093
Solubility	soluble in hexanes benzene, toluene
Purity	> 97%
Supplier	Fluka

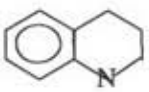
* From Encyclopedia of Chemical Engineering and supplier

TABLE 3.4 Properties of 2,6-Dimethylpyridine *

Formula	C_7H_9N
Structure	
Chemical name	2,6-Dimethylpyridine
Physicals properties	
Molecular weight (g/mole)	107.16
Form	liquid
Color	yellow
Melting point (^{o}C)	-
Boiling point (^{o}C)	142-145
Specific gravity	0.923
Solubility	soluble in hexanes benzene, toluene
Purity	> 98%
Supplier	Fluka

* From Encyclopedia of Chemical Engineering and Supplier

TABLE 3.5 Properties of 1,2,3,4-Tetrahydroquinoline*

Formula	$C_9H_{11}N$
Structure	
Chemical name	1,2,3,4-Tetrahydroquinoline
Physicals properties	
Molecular weight (g/mole)	133.20
Form	liquid
Color	colorless
Melting point (^{o}C)	9-14
Boiling point (^{o}C)	113-117
Specific gravity	1.057
Solubility	soluble in hexanes benzene, toluene
Purity	> 95%
Supplier	Fluka

* From Encyclopedia of Chemical Engineering and Supplier

TABLE 3.6 Properties of Pyrrole *

Formula	C_4H_5N
Structure	
Chemical name	Pyrrole
Physicals properties	
Molecular weight (g/mole)	67.09
Form	liquid
Color	colorless
Melting point (^{o}C)	-
Boiling point (^{o}C)	129-131
Specific gravity	0.966
Solubility	soluble in hexanes benzene, toluene
Purity	> 96%
Supplier	Fluka

* From Encyclopedia of Chemical Engineering and Supplier

3.3 Analysis Techniques

After each experiment, liquid samples are analyzed for concentration of each compound by using gas chromatographic analysis technique.

A Shimadzu model 8A Gas Chromatograph equipped with GL Sciences Capillary Column Model OV-1 is used to determine the amount of hexanes and their reforming products in the liquid samples. Approximately 0.1 microliter of liquid sample is injected into the Gas Chromatograph. The sample is vaporized at a high temperature of injection port and mixed with a carrier gas. Part of the gas mixture is splited and vented to the atmosphere, only a small portion of the gas mixture flows into the capillary column. Compounds in the gas mixture adsorb and desorb in the capillary column at different rates. Lighter compounds adsorb and desorb faster than heavier compounds. The gas mixture flows through a tip where the compounds are burned in a hydrogen flame. Flame ionization detector is used to detect the signal. The signals are plotted and integrated and are printed on a shimadzu C-R 3A chromatopac. The operating conditions of the gas chromatography are summarized in Table 3.7

Table 3.7 Operating Condition of the Gas Chromatography

Injector Temperature (°C)	30
Column Temperature (°C)	
- Initial Temperature	35
- Final Temperature	150
- Heat rate (°C/minute)	5
Initial Time (minutes)	8
Final Time (minutes)	10
Detector Temperature (°C)	200

Qualitative analysis: The compounds are identified by comparing the retention times of the unknown peaks with the retention time of standard compounds. The retention time of standard compounds suspected to be in the samples are shows in Table 3.8. They are measured in the laboratory using the same gas chromatography and operating condition.

Table 3.8 Retention Time of Compounds in Liquid Samples

Compounds	Retention Time (min.)
2,2-Dimetylbutane	3.52
*2,3-Dimetybutane and 2-Methylpentane	3.98
3-Methylpentane	4.21
n-Hexane	4.79
Methylcyclopentane	5.23
Benzene	6.0
Toluene	10.5
Ethylbenzene	15.5
**Mix-Xylene	16.3, 17.3
Propylbenzene	20.0

Remark:

* 2,3-Dimetybutane and 2-Methylpentane have a same retention time by the GC analysis technic.

** Mix-xylene (o-, m-, and p-xylene) have two retention times by the GC analysis technic.

Quantitative analysis: The results obtained from the gas chromatography are used to determine composition of the sample. The integrated areas shown on the chromatogram are used to calculate concentration of compounds in the solution.