CHAPTER III

EXPERIMENTS AND ANALYSIS TECHNIQUES

3.1 Experimental Apparatus

In this study, a two liter Series 4520 Bench Top reactor is used for the hydrogenation (HDG) of benzene. The system is designed and constructed in order to withstand a maximum operating temperature of 350°C and a maximum operating pressure of 1900 psig. The bomb material is made of T316 standless steel. A schematic diagram of the system is shown in figure 3.1

Liquid feed and catalyst are placed in the batch reactor and gas feed (hydrogen) is fed through valve 1 and valve 3 (gas inlet valve) into the top of the reactor. The gas inlet valve is connected to a dip tube which extends to a point near the bottom of the bomb cylinder. Inlet gas pressure is measured by a pressure guage, usually 0-2000 psi with a T316 stainless steel Bourdon tube, which is mounted on the bomb head using attachment fitting. Hydrogen pressure is controlled by a pressure regulator of the hydrogen cylinder.

There is a safety rapture disc attached to the bomb head which will rupture and release the bomb pressure before it reaches a dangerous level. This reactor is equipped with a Parr magnetic drive to provide an internal agitator for vigorous mixing and gas dispersion. A stiring shaft with two 6-blade turbine type impellers which are adjustable vertically on the shaft is used in

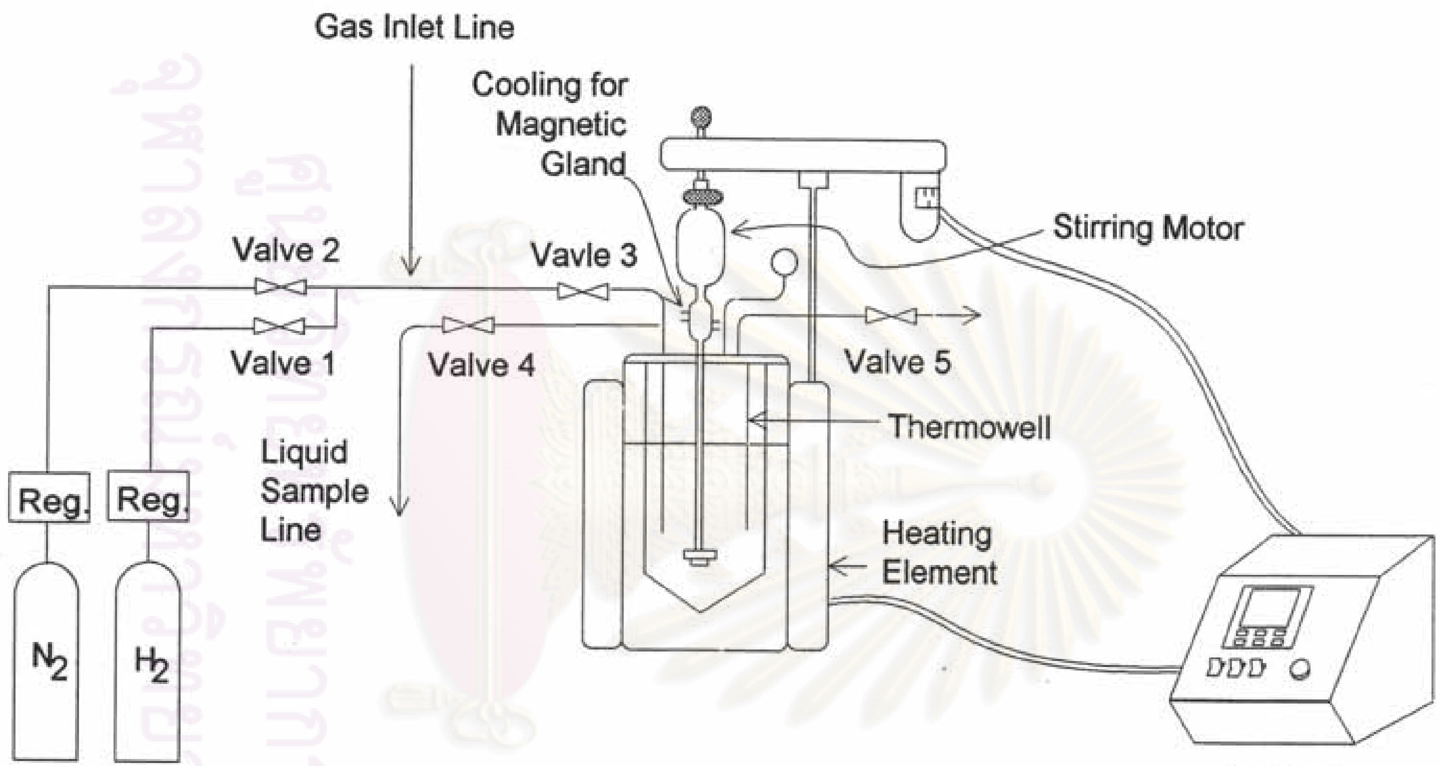


FIGURE 3.1 Schematic Diagram of the System.

this reactor. A water cooling channel is included to protect the magnets and seals, when working at elevated temperature.

The reactor is connected with a 4843 controller which is used to control the reactor temperature. A J type thermocouple in a 1/8 " diameter stainless steel sheath is inserted into the bomb head thermowell to measure the temperature inside the reactor during the reaction. The bomb is set in the heater where heat is generated for the reactor.

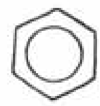
The liquids products are taken every 5 minutes during the first hour of the reaction and every 10 minutes after that by withdrawing from the sampling valve, which is attached to the same fitting as the gas inlet valve and connected to the same dip tube. After each experiment, each liquid sample are labeled and kept for analyses.

3.2 Experimental Procedures

The catalyst used in this study is Raney nickel from Fluka Chemic. Benzene (Cario Erba) and hydrogen (TIG) are employed as reactants for hydrogenation. N-hexane (J.T. Baker) used as liquid carrier which has a good solubility for benzene and nitrogen compounds. Benzene and n-hexane are free form thiophene (< 0.0001%). Nitrogen compounds used in these experiments are pyridine, quinoline, butylamine, pyrrole, indole, carbazole, pyrrolidine, and pyrazine.

Properties of the chemicals used in these experiments are given in Table 3.1 to 3.10, respectively.

TABLE 3.1 Properties of Benzene*

Formula	C_6H_6
Structure	
Chemical Name	Benzene
Physical Properties	
Molecular Weight	78.11
Form	liquid
Color	colorless
Melting Point (°C)	85.5
Boiling Point (°C)	80.1
Specific Gravity	0.879
Solubility	soluble in alcohol, ether, acetone
Purity	> 99%
Supplier	Cairo Erba

* From Encyclopedia of Chemical Engineering

TABLE 3.2 properties of n-hexane*

Formula	C_6H_{14}
Structure	$CH_3CH_2CH_2CH_2CH_2CH_3$
Chemical name	n-hexane
Physical properties	
Molecular weight	86.17
Form	liquid
Color	colorless
Melting point (°C)	-94
Boiling point (°C)	69
Specific gravity	0.659
Solubility	soluble in alcohol, ether, benzene
Purity	> 99%
Supplier	J.T. Baker Inc.

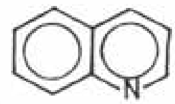
* From Encyclopedia of Chemical Engineering

TABLE 3.3 Properties of Pyridine*

Formula	C_5H_5N
Structure	
Chemical name	Pyridine
Physical properties	
Molecular weight	79.10
Form	liquid
Color	colorless
Melting point (°C)	-42
Boiling point (°C)	115-116
Specific gravity	0.982
Solubility	soluble in alcohol ether, benzene
Purity	> 99.5%
Supplier	MERCK

* From Encyclopedia of Chemical Engineering

TABLE 3.4 Properties of Quinoline*

Formula	C_9H_7N
Structure	
Chemical name	Quinoline
Physical properties	
Molecular weight	129.15
Form	liquid
Color	brown-black
Melting point (°C)	-15
Boiling point (°C)	108-110
Specific gravity	1.094
Solubility	soluble in alcohol, ether
Purity	>99%
Supplier	Fluka.

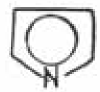
* From Encyclopedia of Chemical Engineering and supplier

TABLE 3.5 Properties of Butylamine*

Formula	$C_4H_{11}N$
Structure	$CH_3(CH_2)_3NH_2$
Chemical name	butylamine
Physical properties	
molecular weight	73.14
Form	liquid
Color	colorless
Melting point (°C)	62-65
Boiling point (°C)	0.722
Solubility	soluble in alcohol, ether, benzene
purity	> 98%
Supplier	Fluka.

* From Encyclopedia of Chemical Engineering

TABLE 3.6 Properties of Pyrrole*

Formula	C_4H_5N
Structure	
Chemical name	pyrrole
Physical properties	
Molecular weight	67.09
Form	liquid
Color	yellow-brown
Melting point (°C)	
Boiling point (°C)	129-131
Specific gravity	0.966
Solubility	soluble in alcohol, ether,benzene
Purity	>96%
Supplier	Fluka.

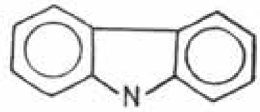
* From Encyclopedia of Chemical Engineering

TABLE 3.7 Properties of Indole*

Formula	C_8H_7N
Structure	
Chemical name	indole
Physical properties	
molecular weight	117.14
Form	solid
Color	colorless
Melting point (°C)	52
Boiling point (°C)	253-4
Specific gravity	-
Solubility	soluble in alcohol, ether, acetone, benzene, methanol
Purity	> 99%
Supplier	Fluka.

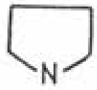
* From Encyclopedia of Chemical Engineering

TABLE 3.8 Properties of Carbazole*

Formula	$C_{12}H_9N$
Structure	
Chemical name	phenylenelimine or dibenzopyrrole
Physical properties	
Molecular weight	167.21
Form	solid
Color	white
Melting point (°C)	240-243
Boiling point (°C)	354.8
specific gravity	-
Solubility	slightly soluble in alcohol, ether
Purity	> 98%
Supplier	Fluka

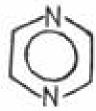
* From Encyclopedia of Chemical Engineering

TABLE 3.9 Properties of Pyrrolidine*

Formula	C_4H_9N
Structure	
Chemical name	Tetrahydropyrrole
Physical properties	
Molecular weight	71.12
Form	liquid
Color	colorless
Melting point (°C)	-
Boiling point (°C)	86-88
specific gravity	0.860
Solubility	soluble in alcohol, ether
Purity	> 99 %
Supplier	Fluka

* From Encyclopedia of Chemical Engineering

TABLE 3.10 Properties of Pyrazine*

Formula	$C_4H_2N_2$
Structure	
Chemical name	Pyrazine
Physical properties	
Molecular weight	80.09
Form	solid
Color	colorless
Melting point (°C)	50-53
Boiling point (°C)	113
specific gravity	0.881
Solubility	soluble in alcohol, ether
Purity	> 98 %
Supplier	Fluka

* From Encyclopedia of Chemical Engineering

The catalyst is weighted by water substitution technique. A picnometer is filled with water, and then balance the total weight. The catalyst is added into the picnometer, assume that water which overflow is less and can be ignored, a weight increase from an initial total weight is the weight of the catalyst. This catalyst suspended in water, thus before each experiment the water must be removed. This catalyst and approximately 300 cm^3 feed solution are placed in a batch reactor. The reactor is then connected to gas feed line, gas vent line and a water cooling channel at the top of the reactant. Before each run, the system is checked for leaks by gradually pressurising the system with nitrogen gas. The pressure test is conducted at a pressure higher than the reactor operating pressure 100 (0.69 MPa) psig. A pressure drop of 10 (68.95 kPa) psig. in one hour is the maximum acceptable leak.

3.3 Analysis Techniques

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

A Perkin Elmer model 8700 Gas Chromatograph equiped with Gl Sciences capillary column Model OV-1 is used to determine the amount of hexane, benzene, and their hydrogenated products in the liquid samples. Approximatelly 0.5 microliter of liquid sample is injected into the Gas Chromatograph. The sample is vaporized at a high temperature and mixed with a carrier gas. Part of the gas mixture is split 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 desorbed gas is added to the make up gas to increase the gas flow rate. 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 an Epson FX 850 dot matrix printer. The operating conditions of the gas chromatograph are summerized in Table 3.11

Qualitative analysis : The compounds are identified by comparing the retention times of the unknown peaks with the retention times of standard compounds. Table 3.12 shows the retention times of standard compounds suspected to be in the samples. The standard retention times are measured in the laboratory using the same gas chromatograph and operating conditions.

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

Table 3.11 Column conditions

Initial	Temperature	30 °C
Final	Time	10 minutes
Injector	Temperature	170 °C
Detector	Temperature	170 °C

Table 3.12 Retention Times

Compounds	Retention Time (min.)
n-Hexane	5.75
Benzene	7.55
cyclohexane	7.80