CHAPTER III

EXPERIMENTAL

3.1 Materials and Equipment

Equipment

1. Gas Chromatograph 7890 (FID detector)
2. Surface Area Analyzer (TF, Sorptomatic 1990)
3. TPDRO (Thermo Finnigan 1100)

Chemicals

- Palladium (II) nitrate dihydrate ($Pd(NO_3)_2.2H_2O$)
- Nikel(II) Chloride hexahydrate ($NiCl_2.6H_2O$)
- Manganese (II) acetate tetrahydrate ($C_4H_6MnO_4.4H_2O$)
- Alumina ($\alpha-Al_2O_3$)

Solvent

- n-hexane 95%, AR
- 1-hexene 97%, AR
- 1-hexyne 97%, AR
- n-heptane 95%, AR

Gas

- Hydrogen (99.99% purity)
- Nitrogen (99.99% purity)
- Helium (99.995% purity)
- Air Zero (99.99% purity)

3.2 Experiment Procedure

3.2.1 Preparation of α-Al₂O₃ Supported Pd and Ni Monometallic Catalysts

The supported alumina (α-Al₂O₃) was calcined at 1000 °C for 3 hours with heating rate 10 °C/min. The low loaded 0.3wt% of Pd/Al₂O₃ catalyst was prepared by impregnating palladium (II) nitrate dehydrate aqueous solution on alumina. Similarly as prepared Pd catalyst, the 0.3wt%, 1wt%, 1.5wt%, 2wt%, and 3wt% of Ni/Al₂O₃ catalysts were prepared by depositing nickel (II) chloride hexahydrate aqueous solution on alumina. After impregnation, the catalysts were dried at 110 °C overnight and subsequently calcined at 500 °C for 3 hours with heating rate 10 °C/min.

3.2.2 Preparation of Pd-Ni and Ni-Mn Bimetallic Catalysts

The Pd-Ni bimetallic catalysts at various Ni loading were prepared by impregnating nickel (II) chloride hexahydrate aqueous solution on 0.3%Pd/Al₂O₃ monometallic catalyst, according to Pd/Ni molar ratio 2.0, 1.5, 1.0, and 0.5 respectively. The Ni-Mn bimetallic catalysts at various Mn molar ratios were prepared by impregnating manganese (II) acetate tetrahydrate on 0.3%Ni/Al₂O₃ according to Ni/Mn molar ratio 2.0, 1.5, 1.0, and 0.5. After impregnation, the catalysts were dried at 110 °C overnight and subsequently calcined at 500 °C for 3 hours with heating rate 10 °C/min.

3.2.3 Catalyst Characterization

3.2.3.1 Brunauer-Emmett-Teller Method (BET)

The catalysts were measured by BET surface area analyzer (TF, Sorptomatic 1990). Brunauer-Emmett-Teller surface area analyzer will analyze textual properties of the supports and the catalysts (surface area, total pore volume, and average pore diameter)

3.2.3.2 Temperature Programmed Reduction (TPR)

Temperature programmed reduction will be employed for evaluating the number and quantity of the reducible species present in the prepared catalyst and the temperature, at which the reduction itself takes place as a function of

temperature. The 0.5 g of catalysts was treated with N_2 (10 ml/min) at 300 °C (10 °C /min) and hold for 1 hour. Subsequently, TPR analysis were carry out under 5% H_2 in N_2 (10 ml/min) started at 35 °C to 900 °C (10 °C /min) and hold for 30 min.

3.2.3.3 *H₂-chemisorption*

The catalyst samples were reduced at 350 °C and pretreated in N_2 (10 ml/min) at 300 °C (10 °C/min) and hold for 1 hour. Subsequently, pulse chemisorptions were analyzed with 5% H_2 in N_2 waited 5 min between pulses. The hydrogen was detected by thermal conductivity detector which the hydrogen-signals were lower as hydrogen was chemisorbed on the catalyst sample. Hydrogen pulse introduction was repeated until the signal area was constant, indicating surface saturation.

3.2.4 Feed/Product Characterization

Gas chromatograph 7890 is used for analyze compounds that can be vaporized without decomposition using FID or TCD as detector. In this role, retention times or volumes are used for qualitative identification, and peak heights or peak are as provide quantitative information. For qualitative purposes, GC is much more limited than most of the spectroscopic methods. Gas Chromatograms are widely used to establish the purity of organic compounds. The appearance of additional peaks reveals any contaminants present, and the areas under these peaks provide estimates of the extent of contamination. Such areas are only estimates because different components may have widely differing detector response factors. Gas chromatographic techniques are also useful for evaluating the effectiveness of purification procedures.
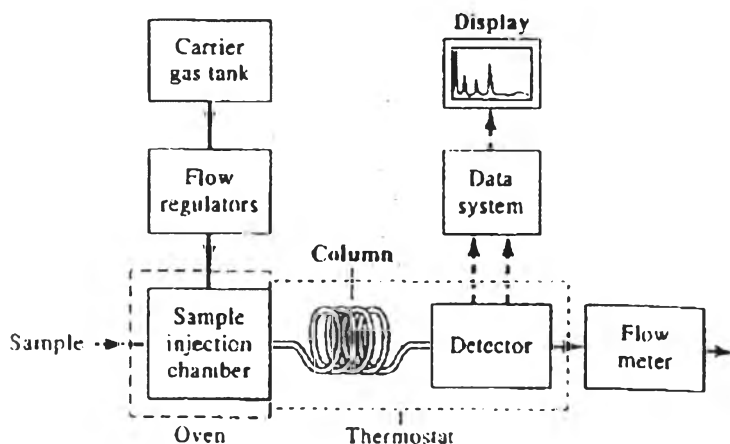
Figure 3.1 Block diagram of a typical gas chromatograph (Skoog et al., 2007).

3.2.5 Reaction Testing

The 0.5 g of catalyst was treated with H_2 gas flow in the reactor at 350 °C for 1 hour. Then 1-hexyne mixed with n-heptane was filled into the sample reservoir. Liquid in the system was circulated by peristaltic pump with constant H_2 pressure (100 ml/min) 1.5 bar and constant temperature at 40 °C. Then, liquid mixture was passed through the fixed bed reactor. The liquid sample was taken every half hour and analyzed for its components by gas chromatography.
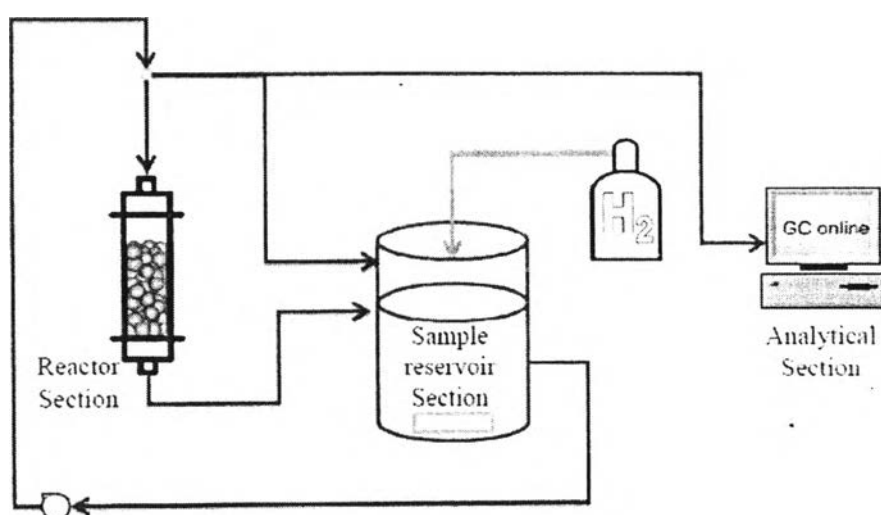

Figure 3.2 The process flow diagram of 1-hexyne selective hydrogenation reaction.

3.2.6 GC Analytical Section

The GC conditions and specification are summarized as follows:

Injector type:	Split 100:1
Injection temperature:	200 °C
Oven temperature:	Isothermal at 100 °C
Detectors:	Flame ionization detector (FID)
GC columns:	GS-GASPRO 30 m × 0.32 mm×0.5 mm
Carrier gas:	High purity Helium (99.995%)
	High purity Nitrogen (99.99%)
Carrier gas flow rate:	5 ml/min

3.2.7 Reaction Performance Evaluation

In this reaction, the conversion and selectivity were calculated to obtain conversion and selectivity.

The conversion of 1-Hexyne can be written as follows

$$1\text{-Hexyne conversion } (\%1\text{-Hexyne}_{conv}) = \frac{(\text{moles of } 1\text{-Hy}_{initial} - \text{moles of } 1\text{-Hy}_{final}) \times 100}{\text{moles of } 1\text{-Hy}_{initial}}$$

The selectivity of 1-Hexene and n-Hexane can be written as followed

$$1\text{-Hexene selectivity } (\%1\text{-Hexene}_{sel}) = \frac{(\text{moles of } 1\text{-He}_{final} - \text{moles of } 1\text{-He}_{initial}) \times 100}{\text{moles of } 1\text{-hexyne converted}}$$

$$\text{n-Hexane selectivity } (\%n\text{-Hexane}_{sel}) = \frac{(\text{moles of } 1\text{-Ha}_{final} - \text{moles of } 1\text{-Ha}_{initial}) \times 100}{\text{moles of } 1\text{-hexyne converted}}$$

$$1\text{-Hexene yield } (\%1\text{-Hene}_{yield}) = \frac{(\%\text{conversion} \times \%\text{selectivity})}{100}$$

Above all, the conversion, selectivity, and yield result of each compound will be discussed in next chapter.