

CHAPTER I

INTRODUCTION



Cyclohexane is one of the most important chemicals in petrochemistry. It is used almost exclusively as a precursor for the production of cyclohexanol and cyclohexanone, these chemicals in turn are predominantly used as precursors of nylon 6 and nylon 66 with a small amount of cyclohexane being used as a solvent. Cyclohexane can be recovered directly from petroleum fractions, but it is practically produced from hydrogenation of benzene due to a very high degree of purity achieved.

Hydrogenation of benzene to cyclohexane is a strongly exothermic reaction. It can be carried out catalytically in the vapor or mixed liquid-vapor phase. The catalysts commonly used for this process are nickel and noble metals (rhodium, ruthenium, and platinum). Commercially, Raney nickel, nickel on supports such as alumina and kieselguhr, and platinum on alumina are cited.

Feedstocks, either petroleum or coal-derived liquids, usually contains impurities such as sulfur, nitrogen, oxygen, and metal compounds. A trace amount of these compounds can deactivate the catalysts used in various processes. These compounds can adsorb on active sites of catalyst surface, destroy the sites and cause a loss of catalyst activity. Previous studies showed that the catalysts used in the hydrogenation of benzene can

lose its activity due to sulfur poisoning. These sulfur compounds have unshared electron pairs which leads to a very strong chemisorption on the metal surface. Emmett, (1957) proposed that with 3 g of nickel catalyst used in benzene hydrogenation, the hydrogenation rate can be decreased to 50 % with the contamination of only 0.6 mg of thiophene.

Some investigations have suggested that the poisoning effect of sulfur depends on the nature of catalyst, the kind and amount of sulfur compounds and the experimental conditions of the experiment (Emmett, 1957; Marecot et al., 1992).

Other studies on effect of sulfur compounds on hydrogenation of benzene showed that the poisoning effect was irreversible and the time for total deactivation depends on the temperature, space velocity, initial sulfur concentration and metal particle size (Markos and Ilavasky, 1985).

Some researchers suggested that apart from sulfur compounds which were commonly blamed to be a poison for benzene hydrogenation, nitrogen compounds were also suspected to poison the catalysts used in this reaction. Pluynin and Leonenko (1976) proposed that nitrogen compounds irreversibly deactivated Raney nickel catalyst and the poisoning effect decreased when the number of N atom in the molecule of nitrogen compounds increased.

Some studies pointed out that nitrogen compounds were a stronger inhibitor of hydrogenation than sulfur compounds, since ammonia decreased the rate constant by a factor of 7 while hydrogen sulfide reduced the rate

constant by a factor of only 2.3.

In this project the role of nitrogen compounds on catalytic hydrogenation of benzene is studied over commercial Raney nickel catalyst. The primary purpose of this study is to find a suitable operating condition for hydrogenation of benzene in n-hexane solution. The experiment is conducted in a batch reactor system, operating temperatures are varied from 120 to 180°C at an increment of 30°C, and operating pressures are varied from 150 to 250 psig. at an increment of 50 psig.

The study on the effect of nitrogen compounds is conducted by adding these compounds directly to the feedstock prior to each experiment. The nitrogen compounds used in this study are pyridine, quinoline, butylamine, pyrrole, indole, carbazole, pyrrolidine, and pyrazine. The results are compared with the results from the experiments using undoctored benzene, on the following factors.

- (1) The effect of the basicity of nitrogen compounds.
- (2) The effect of the structure of nitrogen compounds: ring and chains.
- (3) The effect of ring saturation of nitrogen compounds and
- (4) The effect of the number of N. atom in nitrogen compounds.