CHAPTER I

INTRODUCTION

The developments of automobile have led to an increasing requirement for high-octane fuels with the advent of low lead and lead-free gasolines. The octane number which is the measurement of a fuel's antiknock properties may be improved by addition of alkyl lead compounds such as blending of tetraethyllead and tetramethyllead to the gasoline. Alkyl lead compounds causes undesire build-up of nonvolatile lead which deposits in the engine cylinders. Then it is necessary to add ethylene dichloride and ethylene dibromide to form volatile lead oxyhalides which are emitted in the exhaust. Latest antipollution standards promulgate a reduction or a total elimination of the additives and thus make it necessary to increase the octane number of the hydrocarbon base. Straight-run distillation of crude oil within temperature range set does not produce gasoline required in either quantity or quality.

Catalytic reforming is conducted in the presence of hydrogen gas over hydrogenation-dehydrogenation catalysts that may be supported on an acidified alumina. It usually carries out by feeding a mixture of naphtha and hydrogen to the furnace where the mixtures are heated to the desired temperature, and then passed through fixed-bed catalytic reactors under hydrogen pressure. The catalyst is the classic example of dual functionality. It is necessary that both metallic sites (for example, platinum) and acidic sites be present on the catalyst surface (Saterfield, 1980). Hydrogen reaction such as hydrogenation-dehydrogenation, dehydrocyclization and hydrocracking takes place on metallic sites, but cracking, isomerization, and olefin polymerization take place on acidic sites (Speight, 1991).

The purpose of catalytic reforming is to convert gasoline of unacceptable octane number into high octane number components without significantly changing the molecular weight. For a given molecular weight, branched paraffins have much higher octane numbers than liner (normal) paraffins, and the octane number of paraffins increases markedly with decreasing carbon number.

Catalytic reforming is also the principle source of aromatic chemicals (BTX: benzene, toluene, and xylenes). It is utilized on a major scale in petroleum refining. Aromatic compounds (BTX) have the highest octane numbers (100, 120, 117, respectively) therefore they are suitable components to blend with straight-run gasoline for improvement and they are also much in demand as feedstocks for many chemical manufactures.

The feeds of catalytic reformer are saturated materials. The majority of the feed may be a straight-run naphtha, but other by-product low-octane naphthas (for example, coker naphtha) can be processed after treatment to remove olefins and other contaminants. Catalytic reforming has several reactions contribute to increase in octane number but the greatest importance reactions are the formation of aromatics from naphthenes and paraffins. The aromatics can be increased greatly by reactions in catalytic reforming as dehydrogenation, isomerization and cyclization. The yield of gasoline depends on operating conitions and the hydrocarbon types in the feed. For example, high-naphthene stocks, are the easiest to reform and give the highest gasoline yields. Paraffinic stocks, are more difficult isomerization, dehydrocyclization and hydrocracking reactions and require more severe conditions and give lower gasoline yields than the naphthenic stocks.

However, naphtha from various crude sources contains carbon, hydrogen and small quantities of impurities such as sulfur, oxygen, nitrogen and various metals. These elements are usually part of complex organic compounds. Metals, hydrogen sulfide, ammonia, organic nitrogen and sulfur compounds will deactivate the catalyst (Gary and Handwert, 1984).

In this study, the effects of nitrogen compounds on catalytic reforming are investigated. Organonitrogen compounds are present in smaller concentrations in crude oil than sulfur compounds. The weight ratio nitrogen/sulfur varies from about 1:2 in some high nitrogen crudes to 1:5 to 1:10 in other crudes. A high nitrogen may contain 0.9 weight% nitrogen, but in many crude oils the nitrogen content is in the vicinity of 0.1 weight%. Nitrogen compounds are neutral or basic. The nitrogen bases are of aromatic and nonaromatic type. Many of them are derivatives of pyridine, quinoline and isoquinoline. The neutral nitrogen compounds might be derivatives of pyrrole, indole and carbazole. Pyrrole and quinoline have an unfavorable effect on gum content and color of the oil. Some of the nitrogen compounds are catalyst poisons. Nitrogen compounds may impart an unpleasant odor or reddish color to the crude distillates (Kalichevsky and Kobe, 1956).

Organic nitrogen compounds are converted into ammonia under reforming conditions, and this neutralizes acid sites on the catalyst and thus represses the activity for isomerization, hydrocracking, and dehydrocyclization reactions.

Accordingly, this research is conducted on the effects of nitrogen compounds on catalytic reforming of n-hexane. The catalyst used is the commercial Pt-Re/alumina catalyst and utilized in a continuous fixed-bed reactor. The nitrogen compounds used in this study are pyridine, quinoline, 2,6-dimethylpyridine, 1,2,3,4-tetrahydroquinoline, and pyrrole. The results are compared with the results from the experiments conducted by adding these compounds directly to the feed stock prior to each experiment, on the following factors.

1. The effects of the number of ring of nitrogen compounds are compared between: Pyridine and Quinoline.

2. The effects of the stearic hindrance of structure of nitrogen compounds are compared between: Pyridine and 2,6-Dimethylpyridine.

3. The effects of the ring saturation of nitrogen compounds are compared between: Quinoline and 1,2,3,4-Tetrahydroquinoline.

4. The effects of the basicity of nitrogen compounds are compared between: Pyridine and Pyrrole.

The conversion of n-hexane, hydrocracking reaction, isomerization reaction and aromatization reaction are investigated over an effects of nitrogen compound impurities.