

CHAPTER I

INTRODUCTION

The principal objective of petroleum refining is gasoline. The quality of straight-run gasoline from fractional distillation tower is not suitable because it is too low in octane (30-50 clear octane) to meet quality requirements for motor gasoline (Kirk-Othmer, 1982). The demand of today's automobiles for high octane gasolines has stimulated the use of catalytic reforming to improve gasoline octane number. The fundamental purpose of catalytic reforming is to convert gasoline of unacceptable octane number into high octane number components without significantly changing the molecular weight.

Gasolines compose of four main hydrocarbon types, i.e. paraffins, olefins, naphthenes and aromatics. Normal paraffins have the lowest octane numbers of the family of hydrocarbons, while the isomerized or branched paraffins have much higher octane ratings. It is well known that the octane number scale has been defined by ascribing a zero rating to n-heptane which is particularly prone to knocking, and a rating of 100 to isooctane (2,2,4-trimethylpentane), one of the more highly branched octanes. Generally, monoolefins will have higher octane numbers than the corresponding paraffins. Naphthenes or cycloparaffins have octane numbers which are quite high and aromatics have exceptionally high octane numbers which are mainly higher than 100.

The octane number of gasoline may be increased by addition of alkyl lead compounds such as tetraethyllead and tetramethyllead. The compound causes undesired 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 (Satterfield, 1980). In catalytic reforming, main products are aromatic compounds (BTX : benzene, toluene and xylenes) which are suitable components to blend with straight-run gasoline to increase octane number due to their high octane numbers (benzene = 100, toluene = 120 and xylenes = 117).

There are four major reactions that take place during reforming; (1) dehydrogenation of naphthenes to aromatics, (2) dehydrocyclization of paraffins to aromatics, (3) isomerization of paraffins to isoparaffins and isomerization of C₅-ring naphthenes to C₆-ring naphthenes and (4) hydrocracking of hydrocarbons to lower molecular weight hydrocarbons. The most important reactions are the formation of aromatics from naphthenes and paraffins. In reforming processes, cycloparaffins, such as cyclohexane, methylcyclohexane and dimethylcyclohexanes, are converted to benzene by dehydrogenation or by dehydrogenation and dealkylation. Straight-chain paraffins such as hexane are converted to benzene by cyclodehydrogenation (dehydrocyclization) (Kirk-Othmer, 1978). Hydrocracking of high molecular weight paraffins into lower molecular weight paraffins is also one of the most significant reactions (Kobe et al., 1958).

Dehydrogenation is a main chemical reaction in catalytic reforming, and hydrogen gas is consequently produced in large quantities. Hydrogen is recycled

through the reactors where reforming process takes place to provide the atmosphere necessary for the chemical reactions and also prevents the carbon from being deposited on the catalyst, thus extending its operating life. An excess of hydrogen above whatever is consumed in the process is produced, and as a result, catalytic reforming processes are unique in that they are the only petroleum refinery processes to produce hydrogen as a by-product.

Catalytic reformer feeds are saturated materials. In the majority of cases the feed may be a straight-run naphtha but other low octane naphthas (e.g., coker naphtha) can also be processed after treatment to remove olefins and other contaminants. Hydrocarbon naphtha that contains substantial quantities of naphthenes is also a suitable feed. The yield of gasoline of a given octane number and at given operating conditions depends on hydrocarbon types in the feedstream. For example, high-naphthene stocks, which readily give aromatic gasolines, are the easiest to reform and give the highest gasoline yields. Paraffinic stocks, however, which depend on the more difficult isomerization, dehydrocyclization and hydrocracking reactions, require more severe conditions and give lower gasoline yields than the naphthenic stocks. The end point of the feed is usually limited to approximately 190°C (375°F) (Speight, 1991).

Catalytic reforming is usually carried out by feeding a naphtha (after pretreating with hydrogen if necessary) and hydrogen mixture to a furnace where the mixture is heated to the desired temperature, 450-520°C (840-965°F), and then the mixture is passed through fixed-bed catalytic reactors at hydrogen pressures of 100-1000 psi. Normally two (or more than one) reactors

are used in series, and reheaters are located between adjoining reactors to compensate for the endothermic reactions taking place.

Hundreds of patents have been issued on catalyst compositions. All commercially used catalysts contain platinum, either alone or in a combination with another metal. In monometallic forms platinum content is typically 0.35 to 0.6 wt%. Bimetallic catalyst with rhenium usually contains approximately 0.3 wt% platinum and 0.3 wt% rhenium. The minimum content is set by an excessive rate of coking and is also affected by the nature of the feedstock. Diolefins, for example, cause more rapid coking which can be counteracted by a higher platinum content. For maximum utilization of a very expensive material, the platinum is spread out in as finely divided form as possible. A large fraction of the total platinum atoms present are on the surface. The support is an alumina, in γ or η form, which may have been acidified by the incorporating into the structure of approximately 1% chloride or fluoride during catalyst preparation. The use of chloroplatinic acid for impregnation leads to the natural incorporation of chloride into alumina during preparation. Acidity is gradually lost during reaction and may be restored by adding small amounts of an organic chloride or fluoride to the feedstock. Presumably this compound decomposes to release a halogen acid, which is adsorbed by alumina (Satterfield, 1980).

All these catalysts are gradually poisoned by sulfur compounds in the feed that, being predominantly in the divalent state, adsorb on and coordinate with metal sites. Platinum monometallic catalysts may be operated satisfactorily with sulfur levels in the feedstock up to the range of 10 to 50 ppm, depending partly on platinum

loading on the catalyst and frequency of regeneration that is practicable. If sulfur compounds are completely removed from the feedstock while reaction is continued, at least some of the sulfur, which adsorbs on the catalyst, will slowly be hydrogenated to hydrogen sulfide and desorbs. Platinum-rhenium/alumina catalysts are more sensitive to sulfur. A level not exceeding the order of 1 ppm in the feedstock is typically required. This will usually necessitate prior hydrodesulfurization of the feed.

However, these bimetallic catalysts maintain their activity at lower hydrogen pressures over long periods of time. Lower hydrogen pressure also allows an increased degree of dehydrocyclization of paraffins to aromatics to occur and a higher yield of C₅+ product and of hydrogen. Bimetallic catalysts are also typically 3 to 4 times more active than all-platinum catalyst.

In this research, the effects of sulfur compounds on catalytic reforming of n-hexane are studied over commercial platinum-rhenium/ γ -alumina catalyst. The catalyst is utilized in a fixed-bed reactor operated under a low pressure of hydrogen. Sulfur compounds used in this study are carbon disulfide (CS₂), methyl disulfide ((CH₃)₂S₂), methyl sulfide ((CH₃)₂S), ethyl sulfide ((C₂H₅)₂S) and thiophene (C₄H₄S). The experiments are conducted by adding these compounds directly to the feedstock prior to each experiment. The results are compared with the results from the experiments using only n-hexane feed (reference experiment). The products are characterized by gas chromatographic techniques to investigate the effects of the sulfur compounds on each reaction in catalytic reforming of n-hexane.

Furthermore, the sulfur compounds are chosen to compare the effects of type and structure on catalytic

reforming of n-hexane, on the following factors:

- 1) The effect of structure is compared between ethyl sulfide (straight chain) and thiophene (cyclic).
- 2) The effect of number of sulfur atom is compared between methyl sulfide (1 sulfur atom) and methyl disulfide (2 sulfur atoms).
- 3) The effect of number of carbon atom is compared between methyl sulfide (2 carbon atoms) and ethyl sulfide (4 carbon atoms) and also compared between carbon disulfide (1 carbon atom) and methyl disulfide (2 carbon atoms).