



Evaluation of nickel tungsten catalysts for hydrodesulfurization
by Delmar Roy Henderson

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

Three catalysts of various compositions of nickel and tungsten on a silica-alumina support were prepared and tested to determine their effectiveness as desulfurization catalysts on Mo. 2 Diesel fuel. Comparisons were made with the commercial Houdry-C catalyst.

It was found that the three prepared catalysts and the Houdry-C were not significantly different. That is, sulfur removal was the same for all catalysts. It was also found that the catalyst life was the same for the prepared catalyst DR-3 as it was for Houdry-C.

Operating conditions were also evaluated and it was found that increasing temperature while operating at a LHSV of 1.0 or less would be of no value. It was also found that increasing hydrogen flow beyond 5000 SCF/bbl did not increase sulfur removal.

Unless the feed stock were high in nitrogen (4) as well as sulfur, there appears to be no advantage in using a nickel tungsten catalyst over the commercial Houdry-C.

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CATALYSTS FOR HYDRODESULFURIZATION

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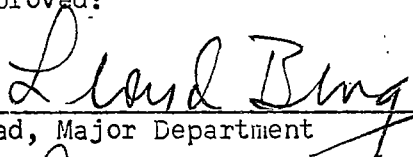
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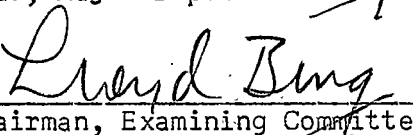
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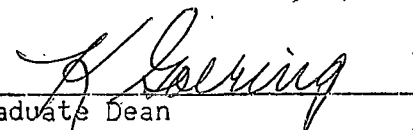
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ABSTRACT

Three catalysts of various compositions of nickel and tungsten on a silica-alumina support were prepared and tested to determine their effectiveness as desulfurization catalysts on No. 2 Diesel fuel. Comparisons were made with the commercial Houdry-C catalyst.

It was found that the three prepared catalysts and the Houdry-C were not significantly different. That is, sulfur removal was the same for all catalysts. It was also found that the catalyst life was the same for the prepared catalyst DR-3 as it was for Houdry-C.

Operating conditions were also evaluated and it was found that increasing temperature while operating at a LHSV of 1.0 or less would be of no value. It was also found that increasing hydrogen flow beyond 5000 SCF/bbl did not increase sulfur removal.

Unless the feed stock were high in nitrogen (4) as well as sulfur, there appears to be no advantage in using a nickel tungsten catalyst over the commercial Houdry-C.

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I INTRODUCTION

Hydrodesulfurization of diesel fuel and other fossil fuels has been of considerable interest to the refiner since the early 1950's. The purpose of desulfurizing was prompted initially by bad odors in the fuel (customer dissatisfaction) and corrosion problems associated with equipment that refined and burned the fuels. However, the reduction of sulfur in fossil fuels has gained interest more recently because of two added factors: a) shortage of elemental sulfur available resulting in inflationary prices of the sulfur, and b) the increasing emphasis on air pollution and resulting laws that are being legislated and/or enforced by state bodies. Legislation is limiting the amount of sulfur permissible in the burned fuels by setting controls on the amounts of sulfur dioxide allowable to be emitted to the atmosphere. By October 1, 1969 (2), the New York State Air Pollution Board has set limits on industries, residences, hospitals, and schools which allow 0.2 pounds of sulfur per million Btu gross heat content. This amounts to about 0.26 weight percent sulfur allowable in fuel oil.

Using hydrogen to treat refinery products is not new. During the early part of the century, I. G. Farbenindustrie (1) pioneered solid fuel hydrogenation, later the basis of Hitler's oil-from-coal program. Esso-Standard Oil Company had high pressure (3000 psig) hydrogenation and hydrocracking in operation at Baton Rouge, Louisiana and Bayway, New Jersey during the 1930's. Following World War II, (predominately in the early 1950's), hydro-treaters were installed to

pretreat the feed to reformers. Excess sulfur, nitrogen, and/or metals in catalytic reformer feed stock suppressed or poisoned the platinum catalyst. Also, the sulfur in the feedstock would form iron sulfide scale that not only plugged the reactors but caused severe metal loss. The hydrogen source for these pretreating units was obtained from the reforming by-products. A typical reformer reaction dehydrogenates cyclohexane to benzene and hydrogen. The hydrogen is normally burned or used in hydrogen processing units.

Other reasons that prompted refiners to turn to hydrogen treating was that the conventional treating processes didn't do the job. Processes such as Doctor treating and copper chloride sweetening only convert mercaptan sulfur to a non-odorous disulfide with the total sulfur content of the feed remaining the same. Improvements can be made by hydro-treating thermally cracked distillates (1) which are difficult to market because of poor color and stability. The hydrogen process will reduce sulfur, carbon residue, and improve the color, odor, phenol, and neutralization numbers. The diesel oils can be made from the catalytic cracked gas oils by hydro-treating. The product results in better cetane and bromine numbers, higher gravity, improved stability and color, as well as reduced sulfur content, olefin content, and carbon-to-hydrogen ratio.

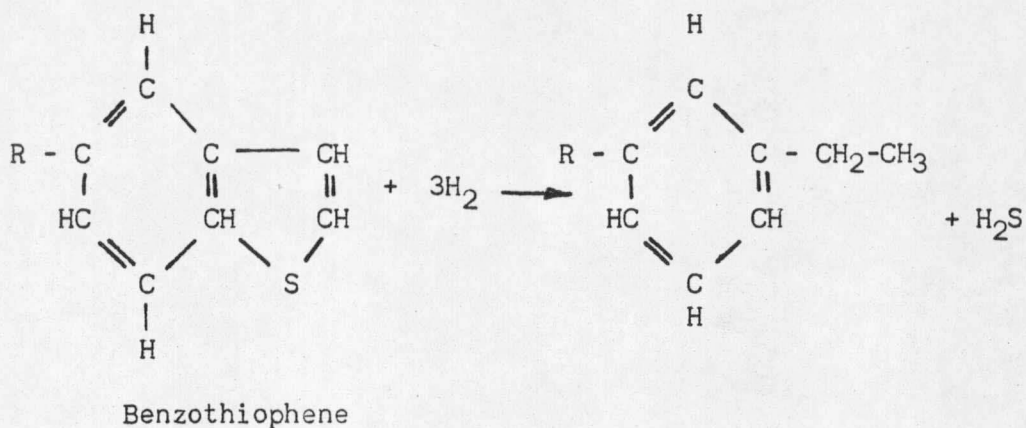
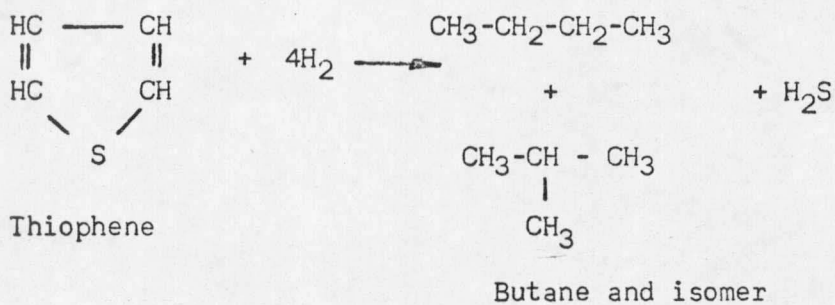
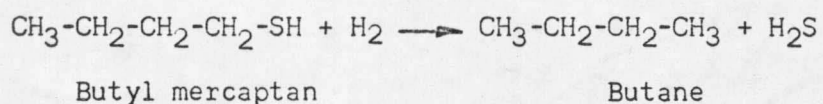
Not only diesel and middle distillates benefit from hydrotreating. Catalytic cracking also benefits by converting refractory sulfur com-

pounds and conjugated aromatics. Most of the cyclic sulfurs concentrate in the heavy gas oil. Refractory conjugated aromatics (multi-ring compounds) in heavy cycle oil crack to coke when the material is recycled in the reactor. A selective partial hydrogenation of these conjugated compounds reduces the refractoriness, resulting in less coke. Because the capacity of most catalytic cracking units is limited by the ability to burn coke from catalyst during regeneration, hydrogenation of heavy cycle oil allows several percent more catalytic gasoline yield at the maximum allowable coke rate.

II PROCESS REACTIONS

Not only desulfurization takes place during hydro-treating. Some of the other processing reactions are denitrification, deoxygenation, olefin and diolefin saturation, and hydrocracking. Typical reactions of these compounds are:

Desulfurization



Denitrification

