



Cobaltous chloride as a hydrodenitrogenation catalyst  
by David Louis Whitcomb

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering  
Montana State University  
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Abstract:

The catalytic hydrodenitrogenation of a high nitrogen (0.191 wt %) and high sulfur (0.800 wt %) medium California gas oil was studied in a bench scale, packed bed, continuous, tubular reactor.

The primary objective of this research was to perform process development studies on the use of a 'cobaltous chloride alumina-silica catalyst for hydrodenitrogenation. Desulfurization was also studied.

The operating conditions studied were between 670 and 800°F, 800 and 1200 psig, liquid hourly space velocities from 0.25 and 2.0 hr<sup>-1</sup>, 2000 to 12,000 standard cubic feet hydrogen/bbl oil (SCF H<sub>2</sub>/bbl), catalyst compositions from zero to 9.0 percent cobalt, and chlorine-nitrogen ratios from zero to 15.0 atom/atom. Optimum catalyst- composition was 7.0 percent cobalt using Harshaw 1602-T alumina-silica support.

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In order to achieve the highest catalyst activity, the hot reactor system was purged with hydrogen to remove all traces of air and moisture. Some catalyst activation may also result from the treatment. At optimum reactor conditions, 91 percent conversion was realized.

Hydrogen consumption was determined by analyzing the effluent reactor gases. Consumption varied between 20 and 381 SCF H<sub>2</sub>/bbl for the range of operating conditions described above.

Sulfur removal followed the trend of nitrogen removal but at a lower level. Optimum sulfur removal was only 78 percent.

A comparison of cobaltous chloride with a commercial cobalt molybdate catalyst showed that the chloride was substantially better because it removed all but 190 ppm compared to 280 ppm "nitrogen in the product for the commercial catalyst.

An exploratory run made with a nickelous-cobaltous chloride catalyst showed that this catalyst also has a high denitrogenation activity.

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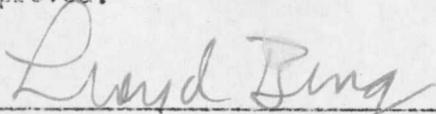
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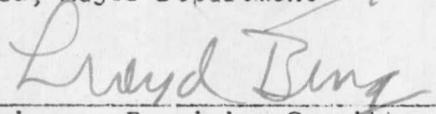
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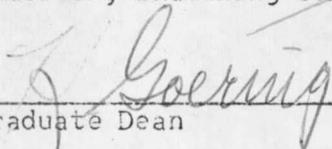
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## ABSTRACT

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## I. INTRODUCTION

Hydrotreating to remove nitrogen and sulfur impurities from various compounds found in petroleum is a well established refining process. It involves contacting a petroleum feed (or synthetic petroleum feed) with hydrogen in the presence of a catalyst. The method of contacting and the operating conditions vary according to the type of feed and the desired level of impurity removal.

Nitrogen removal has become important for several reasons. Nitrogen-containing compounds have been shown to be severe catalyst poisons in acid alkylation, polymerization, isomerization, catalytic cracking, and hydrocracking processes because of their polarity and basicity (1,2,3,4). It has also been found that nitrogen compounds are involved in gum formation, color instability, odor, and poor storage properties of fuels. Studies concerning nitrogen poisoning have revealed that the nitrogen concentrations in the feed stream must be very low in order for hydrocracking to be feasible (5).

Another study has shown that hydrotreating a catalytic cracking feedstock has lowered carbon production and improved selectivity in catalytic cracking operations. The feed treated had an average of 1.8 percent sulfur and 0.15 percent nitrogen, which pointed out the need to remove even small quantities of these impurities from the feedstocks (8).

Recent actions by some local governments to restrict the sulfur content of domestic fuels indicates that hydrotreating will become

even more important in future refining. Studies have indicated that the sulfur content of a large percentage of fuels consumed in the Atlantic Coast Megalopolis contain between 1 percent and 5 percent sulfur. Using an average of 2 percent sulfur, an estimated 3.7 million tons of sulfur dioxide would be emitted to the atmosphere if not recovered before the stocks are used as a fuel. A small percentage of this sulfur dioxide is converted to sulfur trioxide and subsequently to sulfuric acid in the combustion process (6).

Research on photochemical smog indicates that the initial reactants are hydrocarbons, particularly olefins and substituted aromatics, nitric oxide, and oxygen. It has been shown by chamber studies that straight automobile exhaust will provide sufficient quantities of these compounds that when subjected to photochemical reaction conditions will cause eye irritation (7). The source of the nitric oxide is not established but amounts varying from 15 to 200 ppm were measured indicating that a variation in fuel could possibly be a factor.

Nitrogen removal will become even more important due to the depletion of the known reserves of high quality nitrogen-free petroleum and the appearance of synthetic stocks which are derived from oil shales, Athabasca tar sands, and coal hydrogenation. For example, crude shale oil from the large beds of oil shale in Colorado contains approximately 2 percent nitrogen (9) and a typical Athabasca distillate contains 3.46 percent sulfur and 0.18 percent nitrogen (10).

These examples, then, point out the need for removing nitrogen impurities from refining feedstocks.

The methods available to remove nitrogen from petroleum stocks are varied and numerous. Many of the basic nitrogen compounds can be removed by extraction with a dilute solution of a strong mineral acid. More recently a process involving extraction with sodium aminoethoxide has been used successfully on a catalytic cycle oil containing 40 ppm nitrogen (4). Even though in both of these methods the nitrogen containing compounds can generally be recovered unchanged, the methods are very inefficient and almost always incomplete. In particular, the method employing the mineral acid scheme removes only the basic nitrogen compounds which usually comprise less than half the nitrogen compounds found in petroleum stocks (3,12).

Hydrotreating is a well defined and effective method of removing nitrogen from petroleum feedstocks. However, to obtain a satisfactory level of removal, severe conditions of pressure and temperature are required to denitrogenate medium to heavy gas oils. Flinn has reported that with heavy vacuum gas oils and residues, complete hydrodenitrogenation is not easily obtained even at 6000 psig (12). The catalysts most commonly used in hydrodesulfurization are also used to hydrodenitrogenate and consist of various combinations of nickel, tungsten, cobalt, and molybdenum impregnated on alumina or alumina-silica bases. Flinn

has reported using an active nickel-tungsten-alumina catalyst in experimental studies, and Brewer (13) has reported using nickel-molybdenum catalysts in commercial units. Kiovisky and others have noted the adverse effect of nitrogen compounds in petroleum fractions on the activity of a much-used cobalt molybdenum-alumina catalyst (5). (It is well established that cobalt, nickel, molybdate types of catalysts exhibit their activity only if they exist in a sulfided form. Falk (14) and Brewer have noted the conditions employed to sulfide the catalyst result in varying degrees of activity.)

To eliminate completely the undesirable characteristics of nitrogen-containing compounds in oils, the nitrogen must be completely removed. Concentrations of only a few parts per million can cause harmful effects. In general, nitrogen is harder than sulfur to remove from petroleum stocks and the presently used catalysts do not do an adequate job of removing the nitrogen from high nitrogen content oils even at extremely severe temperatures and pressures.

Nitrogen compounds present in petroleum and synthetic petroleum stocks have been studied quite extensively. The knowledge of their behavior in catalytic hydrogenation is essential to understanding why different reaction rates are observed in typical denitrogenation reactions (12). The nitrogen compounds present in petroleum, shale oil, and coal products are very similar in nature. They are generally

heterocyclic, with the nitrogen atom incorporated in either a five- or six-membered unsaturated ring. Some amines are also present. Nitrogen compounds present in petroleum can be classified as basic and non-basic. This classification is based upon the ability of the nitrogen compound to interact with a perchloric acid-acetic acid solution. About 25-35 percent of the nitrogen compounds occurring in petroleum are basic (12,14). The five-membered ring compounds are frequently non-basic with hexa-hydrocarbazole and indoline as notable exceptions, while the six-membered ring compounds are generally unsaturated and basic.

Hartung and Jewell (15) have identified indoles, carbazoles, phenazines, and nitriles in a hydrogenated, catalytically cracked furnace oil. Sauer and co-workers have estimated the concentration of carbazoles, indoles, pyrroles, pyridines, and quinoline in petroleum (3,15,16). Examples of these typical nitrogen-containing compounds are shown in Figure 1.

On the basis of spectral evidence and the weakly acidic nature of a specific fraction studied (3), small concentrations of the following classes of compounds could also be present: hydroxyindoles, hydroxycarbazoles, hydroxypyrroloindenes, and dihydropyrroloindenes. This fraction was also the most colored of those separated and analyzed. They undoubtedly contribute largely to the adverse color and odor of the













































































































































































































































