



Catalytic hydrodenitrogenation in the presence of chlorides
by Frank Philip McCandless

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Montana State University
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Abstract:

The hydrodenitrogenation of a heavy California gas oil containing 0.515 percent nitrogen and 0.858 percent sulfur has been studied using a catalyst system consisting of alumina supported NiCl₂ and HCl. The catalysts were made by impregnating a commercial alumina catalyst with aqueous solutions of the metal chlorides followed by drying at 230°C.

The nitrogen left the reaction zone combined in NH₄Cl.

The study was carried out in a fixed bed, tubular flow, integral reactor. The range of operating conditions was: Temperature 572 to 832°F., Pressure 200 to 1200 psig, LHSV 1/8 to 2 cc oil/hr/cc catalyst, catalyst compositions 0 to 17.7 percent nickel and Cl to N ratios of 0 to 18.8 atom/atom. A hydrogen rate of 5000 SCF/bbl of oil was used for all tests. Methylene chloride, ethylene dichloride and gaseous HCl were investigated as a means of supplying HCl to the reaction zone. The chlorides decomposed to form HCl in the preheating section of the reactor.

At 800°F., 1000 psig, LHSV=1/2 and Cl/N=9.4, the nitrogen removal increased from 73.5 percent with no nickel on the alumina pellets to 92.5 percent with 4.2 percent nickel on the support. Increasing the nickel content above 4.2 percent to 17.7 percent increased the nitrogen removal to 94.2 percent. At 800°F., 1000 psig, LHSV=1/2 using a catalyst containing 6.1 percent nickel, the nitrogen removal was increased from 66 percent to 93 percent by increasing the Cl/N ratio in the reactor from 0 to 18.8. However, at a Cl/N=9.4 conversion was about 90 percent. At 1000 psig, LHSV=1/2 and a Cl/N ratio of 9.4, the nitrogen removal was increased from 54.5 to 92.5 percent by increasing the temperature from 572°F. to 832°F. Increasing reactor pressure from 200 to 1200 psig increased nitrogen removal from 62 to 93.5 percent at 800°F., LHSV=1/2 and Cl/N=9.4. At 800°F., 1000 psig, Cl/N=9.4, the reaction appeared to be 2nd order as shown by a plot of the concentration of nitrogen in the product as a function of space velocity.

At lower temperatures and pressures the mode of nitrogen removal was different. Under these conditions the nitrogen that was removed from the feed was combined in a heavy, viscous material that was insoluble in the product oil. This material was probably the hydrochloride of intermediate nitrogen bases formed in the reactor.

Sulfur removal followed the trend of nitrogen removal only at a lower level, At the optimum denitrogenation conditions sulfur removal was only 80,percent.

The catalyst system appeared to have considerable hydrocracking activity as shown by ASTM distillations of the product.

CoCl₂ also showed a high denitrogenation activity while MnCl₂ and SrCl₂ were inactive.

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ABSTRACT

The hydrodenitrogenation of a heavy California gas oil containing 0.315 percent nitrogen and 0.858 percent sulfur has been studied using a catalyst system consisting of alumina supported NiCl_2 and HCl . The catalysts were made by impregnating a commercial alumina catalyst with aqueous solutions of the metal chlorides followed by drying at 230°C . The nitrogen left the reaction zone combined in NH_4Cl .

The study was carried out in a fixed bed, tubular flow, integral reactor. The range of operating conditions was: Temperature 572 to 832°F ., Pressure 200 to 1200 psig, LHSV $1/8$ to 2 cc oil/hr/cc catalyst, catalyst compositions 0 to 17.7 percent nickel and Cl to N ratios of 0 to 18.8 atom/atom. A hydrogen rate of 5000 SCF/bbl of oil was used for all tests. Methylene chloride, ethylene dichloride and gaseous HCl were investigated as a means of supplying HCl to the reaction zone. The chlorides decomposed to form HCl in the preheating section of the reactor.

At 800°F ., 1000 psig, LHSV= $1/2$ and $\text{Cl}/\text{N}=9.4$, the nitrogen removal increased from 73.5 percent with no nickel on the alumina pellets to 92.5 percent with 4.2 percent nickel on the support. Increasing the nickel content above 4.2 percent to 17.7 percent increased the nitrogen removal to 94.2 percent. At 800°F ., 1000 psig, LHSV= $1/2$ using a catalyst containing 6.1 percent nickel, the nitrogen removal was increased from 66 percent to 93 percent by increasing the Cl/N ratio in the reactor from 0 to 18.8 . However, at a $\text{Cl}/\text{N}=9.4$ conversion was about 90 percent. At 1000 psig, LHSV= $1/2$ and a Cl/N ratio of 9.4 , the nitrogen removal was increased from 54.5 to 92.5 percent by increasing the temperature from 572°F . to 832°F .. Increasing reactor pressure from 200 to 1200 psig increased nitrogen removal from 62 to 93.5 percent at 800°F ., LHSV= $1/2$ and $\text{Cl}/\text{N}=9.4$. At 800°F ., 1000 psig, $\text{Cl}/\text{N}=9.4$, the reaction appeared to be 2nd order as shown by a plot of the concentration of nitrogen in the product as a function of space velocity.

At lower temperatures and pressures the mode of nitrogen removal was different. Under these conditions the nitrogen that was removed from the feed was combined in a heavy, viscous material that was insoluble in the product oil. This material was probably the hydrochloride of intermediate nitrogen bases formed in the reactor.

Sulfur removal followed the trend of nitrogen removal only at a lower level. At the optimum denitrogenation conditions sulfur removal was only 80 percent.

The catalyst system appeared to have considerable hydrocracking activity as shown by ASTM distillations of the product.

CoCl_2 also showed a high denitrogenation activity while MnCl_2 and SrCl_2 were inactive.

I. INTRODUCTION

A. Background

The removal of nitrogen from petroleum oils is a very important operation in petroleum refining because many of the difficulties of processing and of preparing acceptable products can be traced directly to the nitrogen containing compounds present in the oil. Nitrogen removal will become even more important in the future because of the depletion of high quality nitrogen free crude oils and with the use of shale oils which contain a very high percentage of nitrogen compounds.

In the problems of processing, nitrogen compounds are severe catalyst poisons and hence feed streams to most catalytic processes must be essentially free from nitrogen compounds if optimum conversion of the feed stocks is to be obtained. The nitrogen compounds being basic in character react or otherwise interact with acid functions of the catalysts to reduce activity. For example, nitrogen containing compounds have been shown to be severe poisons for acid alkylation, polymerization, isomerization, catalytic cracking and hydrocracking catalysts. (14,20,22) This poisoning can best be illustrated by a specific example such as the data reported by Jacobson which shows the effect that nitrogen compounds have on the hydrocracking of a light cycle oil in the presence of a cobalt sulfide catalyst. (14)

These data are shown in the table below:

TABLE I

Example of Nitrogen Poisoning

<u>Nitrogen content of feed stream</u>	<u>Time conversion can be maintained at 60% per pass before raising reactor temperature to 715° F.</u>
0.1 PPM	4,000 hours
1.5 PPM	2,500
100 PPM	<100

Obviously a very low concentration of nitrogen in the feed stream is required if the hydrocracking process is to be feasible. There are many similar studies reported in the literature which show the adverse effect that nitrogen compounds have on catalytic activity.

In petroleum products, nitrogen compounds adversely affect product color, stability⁽²⁸⁾, odor, and some nitrogen compounds have been shown to suppress detonation and tetraethyl lead response⁽¹⁵⁾. Nitrogen compounds are also involved in the formation of gums^(16,28) and sludges in petroleum products.

Obviously then, there is adequate justification for the treating of many feed stocks and products for nitrogen removal.

B. Methods of Denitrogenation

Many of the basic nitrogen compounds can be removed from petroleum oils by extraction with a dilute solution of a strong mineral acid⁽¹⁸⁾. However, this is a very inefficient method and complete denitrogenation is not possible since, in general, less than half of the nitrogen

compounds found in petroleum oils are basic^(23,24). Also, in extraction process the whole nitrogen containing molecule is removed. In the heavier oils this can amount to a large loss in product since, even though the nitrogen content of the oil may be less than 1%, the nitrogen compound content may run as high as 10 to 20 percent by weight (15).

Adsorption methods can also be used to remove nitrogen compounds from oils and in this case the removal is nearly complete⁽²⁶⁾. However, this method still has the disadvantage of having a high loss in raw materials since, again, the whole nitrogen containing molecule is removed. Because of the limitations of the physical methods mentioned above, hydrogenation has become a popular method of denitrogenating petroleum oils. It has the advantage that it is selective because it removes only the nitrogen atom from the heterocyclic molecule and the remaining product is a usable hydrocarbon. It also has a processing advantage because the hydrodenitrogenation process is continuous while adsorption requires a cyclic operation.

Hydrogenation is a very effective method for removing the nitrogen from light petroleum oils, however, extreme conditions of temperature and pressure are required to denitrogenate heavy gas oils using present catalysts.^(10,14) For example, Flinn and co-workers showed that a heavy naphtha containing only 240 PPM nitrogen can be easily freed of nitrogen by hydrogenation in the presence of an active nickel tungsten

sulfide catalyst at 300 psig, 600°F. and a 4.0 LHSV (liquid hourly space velocity cc oil/hr/cc catalyst). However, if the feed is a deasphalted residuum containing 2800 PPM nitrogen the product from hydrodenitrogenation at 6000 psig, 740°F., and a 0.5 LHSV still contained 250 PPM nitrogen.⁽¹⁰⁾ This level of nitrogen is still too high for the feed to most catalytic operations.

A more active catalyst would significantly reduce the temperature and pressure needed for hydrodenitrogenation and permit the optimum use of heavy oils which contain a high level of nitrogen. For this reason a catalyst has been sought which is more active than the commercial hydrodenitrogenation catalysts presently available.

C. Types of Nitrogen Compounds in Petroleum

Nitrogen compounds present in petroleum have been studied extensively since the importance of these compounds toward catalytic behavior has been recognized.^(1,3,10,18,23,24,26) The amount of nitrogen present in petroleum varies widely with crude source. Perhaps the extremes of American crudes can be shown by comparison of Ponca City (Oklahoma) and Wilmington (California) crudes.⁽³⁾ The amount of nitrogen present in these crudes is shown below in Table 2 together with the composition of another California oil to show that nitrogen content varies considerably within a given district.

