



Hydrodenitrogenation of indole and quinoline with a nickelous chloride - gaseous hydrochloric acid catalyst system
by Thomas Joseph Buller

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

A supported NiCl_2 - gaseous HCl catalyst was used in the hydro-denitrogenation reactions of indole, a nonbasic compound, and quinoline, a basic compound. The reactions were carried out at a reactor temperature of 400°C ; a reactor pressure of 850 psig; space velocities of 4.0, 1.6, 1.0, and 0.7275 LHSV; a hydrogen rate of 500 SCF/bbl of liquid feed; a chloride to nitrogen content of eight to one; and using p-xylene as the carrier oil.

Nitrogen compositions were determined by a Kjeldahl analysis and a Mohr test was used to determine chloride contents. The amine forms of basic and nonbasic nitrogen compounds from indole and quinoline runs were isolated. These compounds were then identified using gas chromatography and mass spectrometry.

In this research, nitrogen was found easier to remove from the product oil of quinoline than indole at 4.0 LHSV. However, little difference, was' observed for lower -space velocities.

Different reaction mechanisms were proposed for the denitrogenation of indole and quinoline. It appeared that hydrochloride intermediates are present in the reaction sequences and that nitrogen leaves the reaction zone as ammonium chloride. Also, possible limiting steps in the reaction sequences were proposed.

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Signature Thomas J. Buller
Date September 3, 1973

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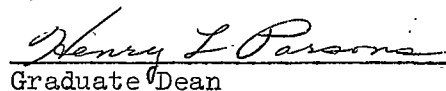
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Hydrodenitrogenation

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Hydrodenitrogenation

ABSTRACT

A supported NiCl_2 - gaseous HCl catalyst was used in the hydrodenitrogenation reactions of indole, a nonbasic compound, and quinoline, a basic compound. The reactions were carried out at a reactor temperature of 400°C ; a reactor pressure of 850 psig; space velocities of 4.0, 1.6, 1.0, and 0.7275 LHSV; a hydrogen rate of 500 SCF/bbl of liquid feed; a chloride to nitrogen content of eight to one; and using p-xylene as the carrier oil.

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I. INTRODUCTION

A. BACKGROUND

Indole and quinoline are heterocyclic nitrogen compounds which have been found in fossil fuel stocks. Indole, a nonbasic compound, has been isolated in petroleum crude oil (28) and in coal tar (3). Quinoline, a basic compound, has been identified in crude oil (24, 28), coal tar (3), and in hydrocracked shale oil (4, 7). The structure and other significant data on both these compounds as well as on other important nitrogen bases and nonbases are presented in Figure 1.

Nitrogen compounds are not desirable in fossil fuel stocks. There is now much evidence to suggest that the nitrogen in fuels is as important as the nitrogen in air in the formation of nitrogen oxides during combustion (10, 31). Nitrogen oxides in the presence of sunlight undergo a photochemical reaction with hydrocarbons to form smog. Also, in the petroleum industry, nitrogen is a poison for many catalysts. Its effect is most notably seen in catalytic reforming where nitrogen decreases the isomerization efficiency of dual-functional catalysts (2, 12, 15).

Today, with the United States experiencing a domestic shortage of production crude oil, different sources of energy must be found. One potential source is the Green River shale oil formation of Colorado, Utah and Wyoming. It contains an estimated one trillion barrels of oil. However, it also contains 2.4 percent nitrogen (7). Before this oil can be utilized, the nitrogen content must be reduced considerably.

Hydrodenitrogenation has been found to be the best way of removing nitrogen from petroleum stocks (12). In this destructive hydrogenation

BASIC COMPOUNDS

Pyridine



m.w. 79.10
m.p. -42 C
b.p. 116 C

Aniline



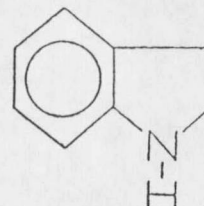
m.w. 93.13
m.p. -6 C
b.p. 184 C

Quinoline



m.w. 129.16
m.p. -16 C
b.p. 237 C

Indoline



m.w. 119.17
m.p.
b.p. 229 C

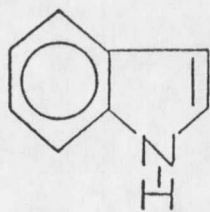
NONBASIC COMPOUNDS

Pyrrole



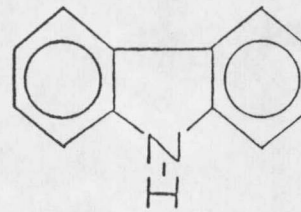
m.w. 67.09
m.p. -24 C
b.p. 131 C

Indole



m.w. 117.15
m.p. 52 C
b.p. 253 C

Carbazole



m.w. 167.21
m.p. 246 C
b.p. 355 C

FIGURE 1: Common Heterocyclic Nitrogen Compounds

process the most widely used catalysts are cobalt molybdate, nickel molybdate, and nickel tungsten sulfide. These catalyst systems generally denitrogenate nonbasic compounds easier than basic ones (12). Also, most nitrogen from these treatments ends up as ammonia. These systems are also better suited for desulfurization than denitrogenation.

This department, in hope of finding a better denitrogenation catalyst system, has been doing work on a nickelous chloride-gaseous hydrochloric acid catalyst system since 1966 (11,19,20). This work has primarily been aimed at determining the operating variables for maximum denitrogenation. However, work has also been done to determine the relative ease of denitrogenating a number of heterocyclic nitrogen compounds. This system has shown some unusual characteristics:

- 1) Basic compounds are generally easier to denitrogenate than nonbasic compounds.
- 2) There is a higher denitrogenation than desulfurization activity.
- 3) Hydrochloride intermediates are suspected in the reaction sequence.
- 4) Nitrogen appears to leave the reaction zone as ammonium chloride.

The work detailed in this report has been done to find a mechanism to account for these characteristics.

B. THEORY

In understanding the mechanism proposed in this report, "basicity"

