



Nickelous chloride-gaseous hydrochloric acid as a petroleum hydrodenitrogenation catalyst  
by Allan Reid Fedoruk

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  
© Copyright by Allan Reid Fedoruk (1973)

**Abstract:**

The hydrodenitrogenation of a variety of nitrogen-bearing compounds considered typical of those found in petroleum was carried out in a continuous flow system over a  $\text{NiCl}_2$ -gaseous  $\text{HCl}$  catalyst. The extent of denitrogenation of aniline, quinoline, pyridine, pyrrole, indole, and indoline was determined when reactor temperature was varied between  $450^\circ\text{C}$  and  $220^\circ\text{C}$  at a constant space velocity of 1.0 and when space velocity was varied between approximately .5 and 3.0 at a constant temperature of  $370^\circ\text{C}$  all at a hydrogen pressure of 875 psig. From these runs it was apparent that aniline was the easiest compound to remove, followed by pyridine and quinoline which were approximately equal, then pyrrole, and finally indole and indoline.

From this it appears that the more basic nitrogen compounds are more reactive, suggesting an interaction between the lone pair of electrons on nitrogen and the Lewis acid sites on the catalyst. In fact, adsorption of the nitrogen compound onto the catalyst may be the rate controlling step in the reaction; however, reactivity varies greatly with reactor temperature suggesting that the reaction mechanism changes with changing reactor conditions so that a C-N bond cracking step in the hydrogenated heterocyclic ring may also influence the reaction rate.

The  $\text{HCl}$  atmosphere in the reactor, maintained by adding methylene chloride to the feed, not only increased the acidity of the alumina catalyst, but also resulted in the nitrogen eventually leaving the reactor as  $\text{NH}_4\text{Cl}$  rather than  $\text{NH}_3$ , the form usually occurring in denitrogenation systems. The anticipated form of the active catalyst is as some  $\text{NiCl}_2$ ,  $\text{HCl}$  complex, possibly as the Friedel-Crafts acid  $\text{H}^+(\text{NiCl}_3)^-$ . After adsorption of the nitrogen onto the active catalyst sites, the reaction probably proceeds by the normal carbonium ion mechanism.

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at Montana State University, I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that any copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Signature

Olson Reid Jedounek

Date

February 14, 1973

NICKELOUS CHLORIDE-GASEOUS HYDROCHLORIC ACID AS A  
PETROLEUM HYDRODENITROGENATION CATALYST

by

ALLAN REID FEDORUK

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

of

MASTER OF SCIENCE


in

Chemical Engineering

Approved:

  
Head, Major Department

  
Chairman, Examining Committee

  
Graduate Dean

MONTANA STATE UNIVERSITY  
Bozeman, Montana

March, 1973

## ACKNOWLEDGEMENT

The author wishes to thank the staff of the Chemical Engineering Department of Montana State University for their assistance which led to the completion of this project. A special thanks goes to Dr. F. P. McCandless under whom this research was conducted and to Mr. J. Tillery and Mr. A. Huso for their help in equipment fabrication, maintenance and repair.

The author also wishes to acknowledge the Department of Chemical Engineering and The Petroleum Research Fund for the financial support given this project.

## TABLE OF CONTENTS

	page
List of Tables . . . . .	vi
List of Figures . . . . .	vii
Abstract . . . . .	viii
I. Introduction . . . . .	1
II. Research Objectives . . . . .	4
III. Experimental Preparation . . . . .	5
A. Equipment . . . . .	5
B. Reaction Materials . . . . .	7
C. Catalyst Preparation . . . . .	10
D. Charging the Reactor . . . . .	11
E. Initial Operating Conditions . . . . .	12
F. Initial Experimental Runs . . . . .	12
G. Pure Component Runs . . . . .	16
H. Product Analysis . . . . .	16
IV. Results and Discussion . . . . .	19
A. Initial Experimental Runs . . . . .	19
1. Line Out Time . . . . .	19
2. Diffusion . . . . .	19
3. Nickel Content on Catalyst . . . . .	20

	page
B. Pure Component Runs . . . . .	.21
1. Liquid Hourly Space Velocity (LHSV) as a Variable . . . . .	.21
a. Empirical Rate Equation. . . . .	.21
b. Data Evaluation. . . . .	.23
2. Temperature as a Variable. . . . .	.26
a. General Catalyst Theory. . . . .	.26
b. Interpretation of Data . . . . .	.28
C. Reaction Intermediates . . . . .	.33
V. Summary and Conclusions. . . . .	.36
VI. Recommendations for Future Work . . . . .	.37
VII. Appendix . . . . .	.38
VIII. Bibliography. . . . .	.49

## LIST OF TABLES

	page
TABLE 1 : Differential Analysis of LHSV Data. . . . .	.25
TABLE 2 : pKa Values of Nitrogen Compounds. . . . .	.28
TABLE 3 : Properties of Commercial Catalyst . . . . .	.39

## LIST OF FIGURES

	page
FIGURE 1 : Schematic Flow Diagram of Reactor System. . . . .	6
FIGURE 2 : Detailed Diagram of the Reactor . . . . .	8
FIGURE 3 : Typical Nitrogen Compounds Found in Petroleum . . . . .	9
FIGURE 4 : Time Requirements for Catalyst Line-out . . . . .	13
FIGURE 5 : Optimum Hydrogen Flow Rate. . . . .	14
FIGURE 6 : Optimum Nickel Content of the Catalyst. . . . .	15
FIGURE 7 : Effect of Space Velocity on Nitrogen Removal. . . . .	17
FIGURE 8 : Effect of Reactor Temperature on Nitrogen Removal . . . . .	18
FIGURE 9 : Conventional Carbonium Ion Mechanism. . . . .	33
FIGURE 10: Possible Aniline-Halide Complex Structures. . . . .	34
FIGURE 11: Possible Indole Hydrodenitrogenation Mechanism. . . . .	35
FIGURE 12: Test for Zero Order Kinetics. . . . .	40
FIGURE 13: Test for First Order Kinetics . . . . .	41
FIGURE 14: Test for Second Order Kinetics. . . . .	42
FIGURE 15: Differential Analysis of Aniline LHSV Data. . . . .	43
FIGURE 16: Differential Analysis of Indole LHSV Data . . . . .	44
FIGURE 17: Differential Analysis of Indoline LHSV Data . . . . .	45
FIGURE 18: Differential Analysis of Quinoline LHSV Data. . . . .	46
FIGURE 19: Differential Analysis of Pyridine LHSV Data . . . . .	47
FIGURE 20: Differential Analysis of Pyrrole LHSV Data. . . . .	48



## ABSTRACT

The hydrodenitrogenation of a variety of nitrogen-bearing compounds considered typical of those found in petroleum was carried out in a continuous flow system over a  $\text{NiCl}_2$ -gaseous HCl catalyst. The extent of denitrogenation of aniline, quinoline, pyridine, pyrrole, indole, and indoline was determined when reactor temperature was varied between  $450^\circ\text{C}$  and  $220^\circ\text{C}$  at a constant space velocity of 1.0 and when space velocity was varied between approximately .5 and 3.0 at a constant temperature of  $370^\circ\text{C}$  all at a hydrogen pressure of 875 psig. From these runs it was apparent that aniline was the easiest compound to remove, followed by pyridine and quinoline which were approximately equal, then pyrrole, and finally indole and indoline.

From this it appears that the more basic nitrogen compounds are more reactive, suggesting an interaction between the lone pair of electrons on nitrogen and the Lewis acid sites on the catalyst. In fact, adsorption of the nitrogen compound onto the catalyst may be the rate controlling step in the reaction; however, reactivity varies greatly with reactor temperature suggesting that the reaction mechanism changes with changing reactor conditions so that a C-N bond cracking step in the hydrogenated heterocyclic ring may also influence the reaction rate.

The HCl atmosphere in the reactor, maintained by adding methylene chloride to the feed, not only increased the acidity of the alumina catalyst, but also resulted in the nitrogen eventually leaving the reactor

as  $\text{NH}_4\text{Cl}$  rather than  $\text{NH}_3$ , the form usually occurring in denitrogenation systems. The anticipated form of the active catalyst is as some  $\text{NiCl}_2$ ,  $\text{HCl}$  complex, possibly as the Friedel-Crafts acid  $\text{H}^+(\text{NiCl}_3)^-$ . After adsorption of the nitrogen onto the active catalyst sites, the reaction probably proceeds by the normal carbonium ion mechanism.

## I. INTRODUCTION

One of the common impurities found in petroleum and synthetic petroleum stocks is nitrogen. The nitrogen atom is generally incorporated into a five or six membered ring to form a heterocyclic compound with these compounds classed as either basic or non-basic depending on the ability of the compound to react with a perchloric acid-acetic acid solution. Five membered ring compounds are usually non-basic and comprise 25 to 35 percent of the nitrogen compounds found in petroleum (5) while six membered ring compounds are generally basic. The concentrations of nitrogen containing compounds such as carbazole, indole, pyrrole, pyridine, and quinoline in petroleum have been estimated by Sauer and coworkers (17). Indoles, carbazoles, phenazines, and nitriles have been identified by Hartung and Jewell (8) in a hydrogenated, catalytically cracked furnace oil, while Drushel and Sommers (4) have identified pyridines, quinolines, indoles, carbazoles, phenols, and hydroxy compounds in light, catalytic cycle oil:

Nitrogen compounds in petroleum adversely affect many of the important refining processes. They are believed to reduce the activity of cracking or hydrocracking catalysts because of their polarity and basicity (13). It is also suspected that nitrogen compounds are to a great extent involved in gum formation, color formation, odor, and poor storage properties of fuels. While in the past many of these problems could be avoided simply by using petroleum feedstocks with negligible amounts of nitrogen, the decrease in known high-quality

oil reserves has resulted in refiners going more and more towards the less desirable feedstocks, that is, those containing nitrogen impurities. A further incentive for the removal of nitrogen from petroleum arises from today's environmental crisis. With the photochemical reaction of sunlight on the hydrocarbons, nitrogen oxides, and substituted aromatics of combustion exhausts often resulting in smog, the need for clean fuels free of all contaminants is very important.

There are a number of methods presently available for removing nitrogen from petroleum feeds. A dilute solution of strong mineral acid will remove many of the basic nitrogen compounds; however, with the basic nitrogen compounds usually comprising less than half of the total nitrogen compounds (6), nitrogen removal is not complete. Hydrotreating is a more successful method of nitrogen removal; however, with medium and heavy gas oils rather extreme temperature and pressure conditions are required and with heavy vacuum gas oils and residues, pressures as high as 6000 psig may not yield satisfactory hydrodenitrogenation (6). The destructive hydrogenation of nitrogen compounds is the most selective denitrogenation process available and is usually carried out in conjunction with hydrodesulfurization of the petroleum feed. Generally the catalyst is a sulfided cobalt, a nickel molybdate, or a nickel tungsten sulfide supported on silica alumina(24); however, these are not always active enough to denitrogenate some of the heavier petroleum fractions.

To this effect, preliminary investigations were undertaken at Montana State University to try to develop a more active denitrogenation catalyst. McCandless found metal chlorides in general to be particularly active catalysts (11) while Whitcomb attempted to determine the optimum operating conditions for a cobaltous chloride-gaseous HCl catalyst system (24). McCandless investigated a nickelous chloride-gaseous HCl catalyst system (12) with the results of several aspects of this work being sufficiently unusual to warrant further investigation. Some differences noted between the nickelous chloride catalyst system and a conventional dual functional hydrotreating catalyst were:

- 1) The nitrogen containing product leaves the reaction zone as ammonium chloride.
- 2) The denitrogenation activity is higher than when either a nickel tungsten sulfide or cobalt molybdate catalyst is used.
- 3) Quinoline is more easily removed than indole, the opposite being true with the nickel tungsten sulfide catalyst.
- 4) Hydrochloride intermediates in the nitrogen compound to ammonium chloride reaction are suspected under certain reaction conditions.

It was on this basis that a more detailed study of hydrodenitrogenation using a nickelous chloride-gaseous HCl catalyst system was undertaken.

## II. RESEARCH OBJECTIVES

The over-all objective of this research work was to further investigate the nickelous chloride-gaseous HCl catalyst system towards determining the nature of the hydrogenation active sites and the "acid" cracking active sites of the catalyst and towards accounting for the previously mentioned differences between this system and other hydrodenitrogenation systems. Additionally, it was hoped that some of the intermediate components in the hydrodenitrogenation reaction could be isolated and identified so that a mechanism for the catalyst system could be postulated.

### III. EXPERIMENTAL PREPARATION

#### A. EQUIPMENT

Several exploratory runs using the  $\text{NiCl}_2$  catalyst system were made to become familiar with the apparatus. Initial indications were that equipment used on earlier studies would be satisfactory for this work; however, on beginning serious investigations, several problems arose which required the altering of the reactor system. With a major reaction product being ammonium chloride, below its sublimation temperature of  $340^\circ\text{C}$ , it collected as a solid at the reactor outlet. As there was already a constriction in this zone of the reactor, the accumulation of even a small amount of  $\text{NH}_4\text{Cl}$  caused the reactor to plug. (in previous studies, the nitrogen had left the reactor as  $\text{NH}_3$  gas so this situation was not present). Temporary control of this problem was achieved by putting a small heating unit around the constriction to maintain the temperature above  $340^\circ\text{C}$ ; however, it was eventually decided that the reactor should be modified to better accommodate the  $\text{NH}_4\text{Cl}$  accumulation. A schematic diagram of the over-all reactor system is shown in FIGURE 1.

The reactor itself was a 52 inch length of one inch schedule 80 stainless steel pipe with each end of the pipe threaded for appropriate inlet and outlet fittings. The upper 31 inches of the pipe was mounted inside a 6 inch diameter aluminum block. Around this block were wrapped three heating coils, each controlled by a separate variac. The variacs for the upper and lower coils were controlled manually, while the variac for the middle coil was controlled by a Wheelco Capacitrol on-off

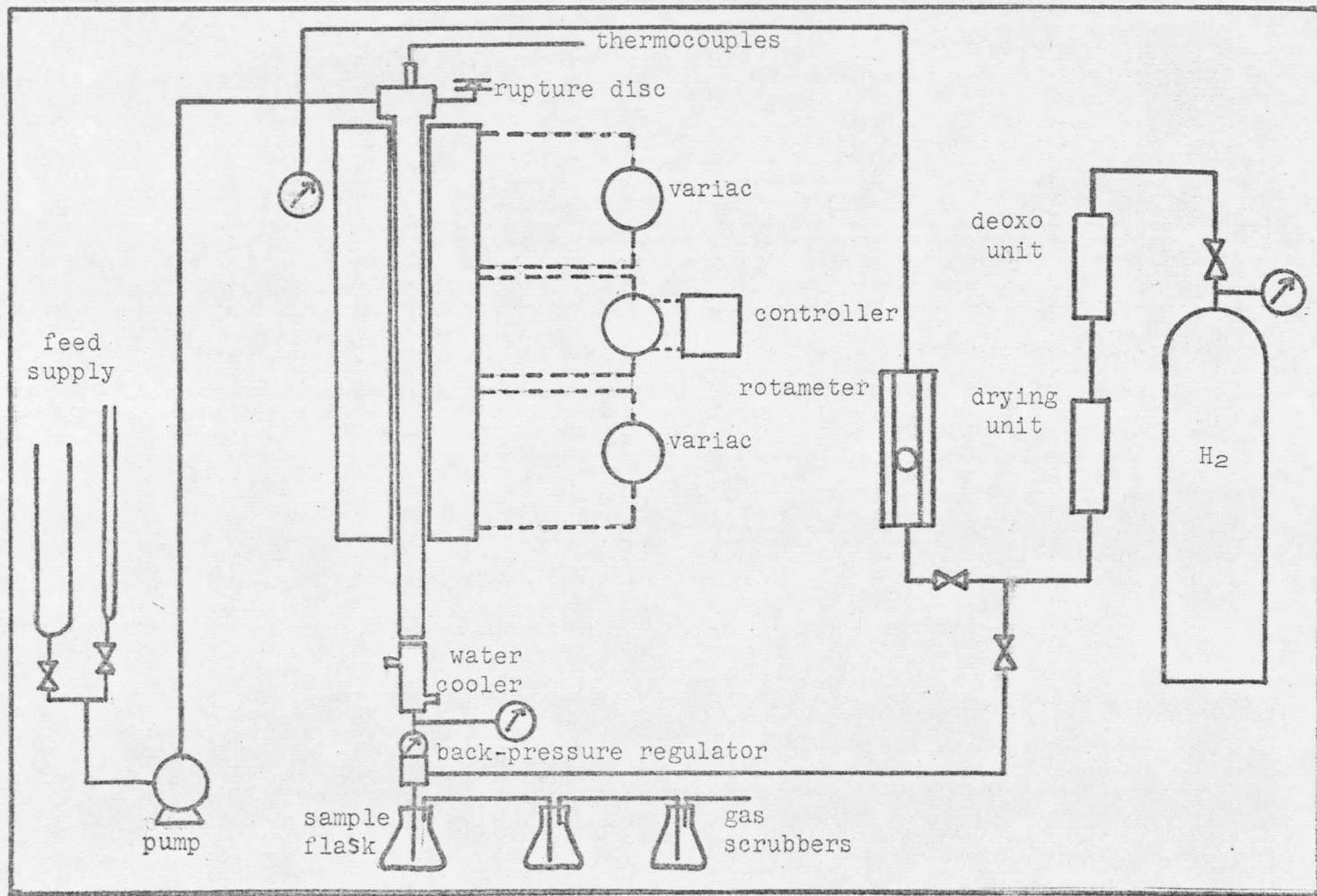


FIGURE 1: Schematic Diagram of Reactor System



controller using an iron-constantan thermocouple. This thermocouple plus three others were mounted in a stainless steel thermowell running axially through the catalyst bed. The heating section was then encased in a 12 inch diameter can packed with Zonelite insulation. The lower 21 inches of the pipe, which was not heated, served as a collecting section for the  $\text{NH}_4\text{Cl}$ . A detailed diagram of the reactor is presented in FIGURE 2:

At the top of the reactor were four stainless steel lines, one for hydrogen feed, one for petroleum feed, one to a pressure gauge, and one to a 2000 psig emergency rupture disc. Upon leaving the reactor, the petroleum passed through a water-cooled condenser after which the line divided, one going to a pressure gauge, the other through a Grove back pressure regulator to a sample bottle and effluent scrubbers. Other major equipment used was a Lapp diaphragm pump, an Englehard deoxo unit, a molecular sieve dehumidifier, a Brooks high-pressure gas rotameter, and a Leeds and Northrup indicating potentiometer.

#### B. REACTION MATERIALS

With the intent of this research being to study a variety of nitrogen compounds, it was decided to run those compounds shown in FIGURE 3 through the  $\text{NiCl}_2$ -gaseous HCl denitrogenation system, these compounds being considered both typical of those found in petroleum and readily available from commercial suppliers. As a carrier for the nitrogen

































































































